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**NANYANG
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UNIVERSITY**

SINGAPORE

**POLYAROMATIC HYDROCARBONS FOR ANOLYTE
APPLICATIONS IN LITHIUM BASED SECONDARY
BATTERIES**

ANDREY V. LUNCHEV

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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APPLICATIONS IN LITHIUM BASED SECONDARY
BATTERIES**

ANDREY V. LUNCHEV

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

04.12.2018

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Date

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Andrey V. Lunchev

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from paper published in the following peer-reviewed journals where I was a first author.

Chapter 5 is published as Lunchev, A.V., Tan, K.S., Grimsdale, A.C., Yazami, R., “Electrical and electrochemical properties of lithium solvated electron solutions derived from 1,3,5-triphenylbenzenes”, *New J. Chem.*, **42**, pp. 15678-15683 (2018). DOI 10.1039/C8NJ03362E

The contributions of the co-authors are as follows:

- Prof A. C. Grimsdale and Prof. R. Yazami provided the initial project direction and edited the manuscript drafts.
- K.S. Tan and I prepared the manuscript drafts.
- I co-designed the study with Prof A. C. Grimsdale, K.S. Tan and Prof. R. Yazami and performed the laboratory work at the School of Materials Science and Engineering and The School of Chemical and Biomedical Engineering. K.S. Tan and I also analyzed the data.
- I performed synthesis of the materials.

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- Prof A. C. Grimsdale and Prof. R. Yazami provided the initial project direction and edited the manuscript drafts.
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- Z. Liu and H. Su performed quantum chemical modeling.

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- Prof A. C. Grimsdale provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Prof A. C. Grimsdale and performed the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- Dr S. Morris and Dr. Rakesh Ganguly performed X-Ray diffraction experiments and analyzed the data.
- Assoc. Prof. H. Sun and X. Chen performed quantum yield measurements.
- V. C. Hendrata and A. Jaggi performed synthesis of some materials.

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Abstract

A possible way to overcome some limitations of Li-ionic batteries, including slow rate of charge and discharge, high cost, and safety issues, is to use liquid based electrodes due to their fast ion transport, high solubility of active components, and complete elimination of such solid based electrode drawbacks as metal dendrite formation.

While some types of non-solid based cathodes (air or catholytes like iodide/triiodide system) have already been investigated, utilization of liquid based anodes (anolytes) is a relatively new concept. One promising approach for a liquid based anode uses solvated electron solutions (SES) formed by the reaction between polycyclic aromatic hydrocarbons (PAH) and alkali metals in organic solvents. This concept has been successfully demonstrated with biphenyl and naphthalene as the PAH. Considering that it should be possible to optimize the ability of PAHs to form Li SES that are suitable for anolyte applications by varying their size and substituents or heteroatoms in the aromatic rings, this thesis represents a systematic study on formation, electrical and electrochemical properties of Li SES based on a number of polyaromatic systems: p-terphenyl, anthracene, 1,3,5-triphenylbenzene and its derivatives, triphenylene, hexaphenylbenzene and hexa-peri-hexabenzacoronene derivatives, and isomeric phenyl- and bipyridines.

The maximum achieved Li:PAH ratio for p-terphenyl is 2.4:1 and for anthracene is 2:1. The ratios of Li:PAH = 2:1 for both the molecules were achieved in more concentrated Li SES prepared from suspensions of these PAHs in THF. A Li:PAH ratio of 4:1 can be achieved for 1,3,5-triphenylbenzene. However, the aromatic system degrades when the ratio is above 2:1. Electron donating groups in 1,3,5-triphenylbenzene framework have a negative effect on Li SES formation due to destabilization of the resulting anion. A Li:PAH ratio of 4:1 was achieved for triphenylene in a dilute solution, but could not be obtained with higher concentrations of the PAH. Although hexaphenylbenzene does not react with lithium, it was shown that a hexa-peri-hexabenzacoronene derivative can react with 6 mole equivalents of lithium or potassium. For the isomeric phenylpyridines, the achieved Li:PAH ratio is 2:1 except for 4-phenylpyridine, which forms a precipitate when the Li:PAH ratio is larger than 1:1. For all the Li SES based on bipyridines and biphenyl in HMPA, the Li:PAH ratios are lower than 2:1.

Among the PAH solutions of ~0.1 M concentration, p-terphenyl, triphenylene, and anthracene based Li SES demonstrate the highest conductivity, which is higher than the value for Li SES based on naphthalene of the same concentration. For p-terphenyl and anthracene, conductivity significantly increases upon the increase of PAH concentration. The conductivity of Li SES prepared from suspensions of these materials in THF is the highest among Li SES studied in this project and comparable to the maximum achieved for naphthalene and biphenyl. In the case of 1,3,5-triphenylbenzene derivatives, it was found that incorporation of alkyl chains significantly increase the solubility of PAH, but makes negative effect on conductivity. The majority of tested Li SES demonstrate decrease in conductivity upon temperature increase, which is similar to metals and ammonia based Li SES. However, some of the studied Li SES with high concentration of Li and those prepared in HMPA demonstrate the opposite behavior.

The values of OCP (E) vs Li^+/Li for studied Li SES in THF lie in the range of 0.6 – 0.9 V. The lowest value of OCP was obtained for 1,3,5-triphenylbenzene (0.47V), while Li SES in HMPA generally demonstrate high values (>1.2V). Based on the E(T) data, ΔS and ΔH were calculated. It was shown that for p-terphenyl and anthracene the correlation between ΔS and Li:PAH ratio (x) is quasi linear (tested for $x > 0.5$). In general, ΔS increases with the increase of x for all the studied Li SES. The lowest values of ΔS were obtained for phenylpyridines while the highest values are reached for Li SES in HMPA. The calculated ΔS values for various Li SES are much higher than those for solid state electrodes used in LIB. The $\Delta H(x)$ exhibits more complex correlation than $\Delta S(x)$. For the case of p-terphenyl, the results of quantum chemical modelling demonstrate the feasibility of formation of dimeric structures, which can be related to this more complex behaviour.

The obtained results allowed to clarify the correlations between structures of PAH and properties of the resulting Li SES, and demonstrate the potential feasibility of using the Li SES based on some of the studied materials such as p-terphenyl, anthracene, triphenylene, 1,3,5-triphenylbenzene and 3-phenylpyridine as anolytes in secondary batteries.

During the course of the project, a new approach for synthesis of 5,7-diazapentacene derivatives and precursors was developed. The structure and electronic properties of these novel materials were characterized. These compounds may find potential applications in both Li SES and OFET.

Lay Summary

Currently lithium-ion batteries (LIBs) are a dominant source of energy for portable devices and electric vehicles due to their light weight and high amount of energy per volume they can store. However, LIBs have several limitations, which turn out to be especially critical in electric vehicle applications. The first one is a relatively slow rate of charge and discharge, meaning it takes a long time to charge an electric vehicle (from 6 to 8 hours for complete recharge). Moreover, fabrication of conventional LIBs requires rather expensive materials. A possible option to overcome these limitations is to use a new concept of battery by utilizing a solid electrolyte and liquid based electrodes instead of the conventional approach where solid electrodes are separated by a liquid electrolyte. In any battery, electric current flows from negatively charged anode to positively charged cathode through an external circuit. While some types of non-solid based cathodes have already been investigated, and solid state electrolytes are well known, utilization of liquid based anodes (anolytes) is a relatively new concept. One possible anolyte can be made of solvated electron solutions (SES), which are formed upon reaction between a specific type of organic materials called polyaromatic hydrocarbons (PAH) and lithium metal in an appropriate organic solvent. This concept has been successfully demonstrated with biphenyl and naphthalene which are the simplest PAH.

Considering that it should be possible to tune properties of the SES that are suitable for anolyte applications by using different types of PAH, this thesis represents a systematic study of SES made from different PAH in terms of their applicability in batteries.

In this study, SES were examined based on three parameters that define applicability of a material in batteries.

First, the chemical reactivity of the selected materials with lithium was studied. It was found that a larger PAH does not necessarily react with a larger amount of lithium, as was initially hypothesized. It was also shown that the chemical structure plays a key role in determining the reactivity of a PAH.

Electrical conductivity, an important characteristics of materials for batteries that shows how well the material transmits an electrical current was also studied for various SES. It was shown that some solutions demonstrate high values of conductivity, which are close

to those for biphenyl and naphthalene, while others exhibit low values. Also, it was shown that concentration of PAH in a solution significantly affects the conductivity. Based on these results, correlations between PAH structure and electrical conductivity were clarified. Electrochemical properties that define the material applicability in batteries were studied in electrochemical cell. Based on these experiments, some fundamental properties of Li SES were identified.

The obtained results allowed clarification of the correlations between structures of PAH and properties of the resulting SES, and demonstrate the potential feasibility of using SES based on some of the studied materials in rechargeable batteries.

During the course of the project, a new approach for synthesis of novel PAH that can find application in SES and organic transistors was developed. The structure and electronic properties of these novel materials were characterized.

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Figure A.8. ^{13}C NMR spectra of **81a**.

Figure A.9. HRMS spectra of **81a**.

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Figure A.11. ^{13}C NMR spectra of **81b**.

Figure A.12. HRMS spectra of **81b**.

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Figure A.21. HRMS spectra of **81e**.

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Figure A.26. ^{13}C NMR spectra of **94b**.

Figure A.27. HR MS spectra of **94b**.

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Figure A.29. ^{13}C NMR spectra of **94c**.

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Figure A.32. ^{13}C NMR spectra of **80a**.

Figure A.33. HR MS spectra of **80a**.

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Figure A.35. ^{13}C NMR spectra of **80b**.

Figure A.36. HR MS spectra of **80b**.

Figure A.37. ^1H NMR spectra of **93b**.

Figure A.38. ^{13}C NMR spectra of **93b**.

Figure A.39. HR MS spectra of **93b**.

Abbreviations

+M	Positive mesomeric effect
−M	Negative mesomeric effect
Ac	Acyl
CN	Cyano
CV	Cyclic Voltammetry
DCE	1,2-dichloroethane
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DEC	Diethyl carbonate
DFT	Density Functional Theory
DMAP	4-Dimethylaminopyridine
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DOD	Depth of discharge
dppf	1,1' -Ferrocenediyl-bis(diphenylphosphine)
dppp	1,3-Bis(diphenylphosphino)propane
D _{th}	Theoretical energy density
E	Open circuit voltage (potential)
E_g^{CV}	Bandgap value from CV
E_g^{opt}	Optical bandgap
EC	Ethylene carbonate
ESI	Electrospray ionization
ESR	Electron spin resonance
Et	Ethyl
Et ₂ O	Diethyl ether
EtOAc	Ethyl acetate
eV	Electron volt

Fc	Ferrocene
FET	Field effect transistor
FWHM	Full width at half maximum
GC	Gas chromatography
HBC	Hexa-peri-hexabenzocoronene
Hex	n-Hexyl
HMPA	Hexamethylphosphoramide
HOMO	Highest occupied molecular orbital
HPB	Hexaphenylbenzene
HPLC	High-performance liquid chromatography
HRMS	High-Resolution Mass Spectrometry
Hz	Herz
iPr	Isopropyl
J	Dipole–dipole coupling constant (NMR).
LED	Light emitting diode
LIB	Lithium-ion battery
M	Molarity (moles per liter)
m	Mass
MALDI	Matrix Assisted Laser Desorption/Ionization
Me	Methyl
MS	Mass spectrometry
N	Normality (mole equivalents per liter)
NBS	N-bromosuccinimide
nBu	n-Buthyl
NMR	Nuclear Magnetic Resonance
NO ₂	Nitro
OCP	Open circuit potential
OCV	Open circuit voltage
OFET	Organic field effect transistors
OLED	Organic light-emitting diode
OMe	Methoxy

PAH	Polyaromatic hydrocarbon
PEEK	Polyetheretherketone
Ph	Phenyl
PIFA	[Bis(trifluoroacetoxy)iodo]benzene
PL	Photoluminescence
PTFE	Polytetrafluoroethylene
R	Substituent
RFB	Redox flow battery
S	Siemens (unit of conductivity)
SCXRD	Single Crystal X-Ray Diffraction
SES	Solvated electron solutions
T	Temperature
Tg	Triglyme
TOF	Time of Flight
tBu	tertiary-butyl
Tf	Trifluoromethylsulfonyl
TCE	1,1,2,2-Tetrachloroethane
THF	Tetrahydrofuran
TIPS	Triisopropylsilylethynyl
TLC	Thin layer chromatography
TMEDA	Tetramethylethylenediamine
TMS	Tetramethylsilane
Ts	p-Toluenesulfonyl
UV-Vis	Ultraviolet-Visible
V	Volt
z	Charge
Å	Angstrom
δ	Chemical shift
ΔE_{Li}^B	Theoretical binding energy of Li to PAH
Δ	Heating of reaction mixture
ΔG	Gibbs free energy change

ΔH	Enthalpy change
ΔS	Entropy change
ϵ	Molar absorptivity
λ_{max}	Wavelength of maximum absorbance
λ_{onset}	Onset of a peak in UV-Vis spectra
σ	Electrical conductivity
Φ	Quantum yield

Chapter 1

Introduction

This chapter first introduces the problems related to lithium-ion batteries in applications that require fast charge and discharge rate along with high levels of safety. It introduces a novel concept of secondary (rechargeable) batteries using liquid based electrodes (anolytes and catholytes) that can overcome the issues related to conventional ones, followed by discussion of lithium solvated electron solutions (Li SES) used as anolytes in these new types of batteries. The section 1.2 represents hypothesis related to properties of Li SES. Section 1.3 discusses the objectives of the thesis and section 1.4 represents the strategy to reach these objectives. Section 1.5 provides the thesis overview, and section 1.6 summarizes findings and outcomes.

1.1. Problem statement

Currently lithium-ion batteries (LIBs) are a dominant source of energy for portable devices and electric vehicles due to their light weight, high energy and power density (**Figure 1.1**), low or even no memory effect, and low self-discharge effect [1-4]. A combination of these properties has made LIBs the most convenient energy source among other types of commercially available rechargeable (secondary) batteries. However, LIBs have several limitations, which turn out to be especially critical in electric vehicle applications. The first one is a relatively slow rate of charge and discharge, which is controlled by the diffusion of the active species within solid electrodes [5]. As a result, it takes a long time to charge an electric vehicle (from 6 to 8 hours for complete recharge). Fast charging is disadvantageous due to formation of lithium metal dendrites, which is a serious safety issue [6]. Besides slow charging and safety concerns, fabrication of conventional LIBs requires rather expensive materials, such as cobalt salts.

Using liquid based electrodes instead of solid ones in LIBs should overcome these issues due to fast ion transport and high solubility of active species. These features of liquid based electrodes should allow a high energy density to be achieved and completely eliminate such problems as metal dendrite formation.

Figure 1.1. Specific energy density versus volumetric energy density for different types of batteries.

Today there has been only a little work done on liquid based anodes and cathodes (anolytes and catholytes) compared to solid-state ones, although this area is becoming more extensively investigated [7]. An example of a system utilizing these electrodes is a redox flow battery (RFB) [8, 9]. In this type of battery, pumps transfer a liquid based cathode and anode from external tanks, so they circulate through the cell. These batteries have several advantages, including scalable capacity, no limit to the depth of discharge, and no limit to the cycle life. However, since currently known RFBs, such as the Vanadium Redox Flow Battery (**Figure 1.2**, left), do not utilize alkali metals, these energy sources have very low volumetric and specific energy density comparing to LIBs (**Figure 1.1**), which makes them not suitable for electric vehicle and portable device applications.

A semi-solid rechargeable Li flow cell (**Figure 1.2**, middle) is an attempt to combine the advantages of LIB and RFB [10]. This battery utilizes suspensions consisting of solid electrode materials, electrolyte, and conducting carbon additives (**Figure 1.2**, right). Since this cell employs lithium-based salts (like LiCoO_2 , LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$) instead of metallic Li, these liquid electrodes require significant amounts of carbon-based additives to improve conductivity [11], which decreases energy density of these batteries. Another point is that the flowing electrode materials contain both solid and liquid phases; as a result, there is always a risk of clogging during the operation. Additionally, these flow cells also need pumps to operate, which require an additional energy source.

Figure 1.2. Schematic diagram of vanadium redox battery (left); schematic diagram of semi-solid flow cell (middle); semi-solid suspension of LiCoO_2 for the semi-solid flow cell (right).

A possible way to combine the advantages and overcome the disadvantages of both LIBs and the discussed flow cells is to utilize liquid based electrodes. Although solid-free cathodes have already been used in lithium based batteries (e.g. lithium-air battery [12] or triiodide/iodide redox couple aqueous catholyte [13, 14]), a liquid based anode (anolyte), however, is a relatively new and promising concept.

An ideal lithium based anolyte should have the following properties. Firstly, it should have high volumetric and gravimetric energy storage capacity. It means that the anolyte should contain as much lithium as possible. Secondly, this liquid based anode should have high electronic and ionic conductivity. The electrode should also have a low working voltage ($< 1 \text{ V vs Li}^+/\text{Li}$), demonstrate electrochemical reversibility, and possess fast electrode kinetics over a wide temperature range.

One possible anolyte is based on a solvated electron solution (SES), which is formed upon reaction between a polyaromatic hydrocarbon (PAH) and an alkali metal in an appropriate organic solvent.

Although the concept of a liquid PAH based Li SES anolyte has been successfully demonstrated with biphenyl [15] and naphthalene [16], which are the simplest PAHs, no systematic studies on more complex polyaromatic systems have been performed.

1.2. Hypothesis

Polyaromatic hydrocarbons (PAH) are organic compounds composed of multiple aromatic rings. A variety of PAHs has been extensively investigated as potential candidates for use in a wide range of electronic applications, including solid-state electrode materials in charge storage devices [17-19]. Some PAHs, such as hexa-peri-hexabenzocoronene, are discotic liquid crystals, which tend to form extended columns with high charge carrier mobility along these columns. These compounds may accept a number of positive or negative charges, so the charges delocalize over conjugated polyaromatic system.

It is hypothesized that introduction of substituents with particular electronic effects or incorporation of heteroatoms into the aromatic system would make it feasible to tune PAHs' ability to accept electrons giving stable polyanions. Enlarging PAHs' aromatic system should increase the amount of alkali metal atoms per PAH in SES, giving the solutions with higher energy density. Enlarging the aromatic system should also make positive influence on charge transport characteristics due to π -stacking effect, which should lead to improvement of SES electrochemical properties.

Thus, it should be possible to optimize ability of PAHs to form SES that are suitable for liquid anode applications by varying their size and substituents or heteroatoms in the aromatic rings.

1.3. Objectives and Scope

Although it has been recently shown that Li SES based on the simplest PAHs, such as biphenyl and naphthalene, have properties that are potentially suitable for use as liquid anodes, much more work needs to be done to determine the optimal properties of PAHs for this application. Thus, the objective of this work is to find fundamental relations between intrinsic characteristics of PAHs, such as aromatic system size and electronic structure, and properties of the resulting Li SES.

1.4. Strategy

In order to understand these fundamental relations, chemical and physical properties of PAH based SES should be analyzed, which include:

- Compatibility of PAHs with alkali metals and solvents used for SES formation (including PAH solubility, stability, and rate of SES formation)
- Charge transport characteristics of SES
- Electrochemical parameters of corresponding SES, including those related to thermodynamics and kinetics of the SES reduction and oxidation processes

Since the variety of possible PAHs is very wide, it is impossible to perform completely systematic studies of all the compounds that are potentially suitable for SES formation. Thus, one should focus on some types of PAHs first in order to understand general relations between their structure and properties. Considering the positive results for naphthalene and biphenyl, these structures should be starting points for enlarging the aromatic system and introducing substituents. The main routes of the structures modification are shown in **Figure 1.3**.

Figure 1.3. The main ways of PAH structure modification: enlarging aromatic system, doping with heteroatoms, substituents incorporation.

Therefore, compounds with 3 and 4 aromatic rings should be tested first. The effect of substituents incorporation and/or heteroatom doping can also be revealed during studies based on these structures.

The next step should be an investigation of SES' properties involving more complex aromatic structures. Since solubility of these compounds may decrease, incorporation of

alkyl substituents may be required in order to facilitate solubility.

The results from testing of these materials combined with theoretical studies would make it possible to select an array of PAHs for further investigation in order to design PAHs that are the most suitable for SES based liquid electrode applications.

1.5. Dissertation Overview

The thesis addresses fundamental relations between intrinsic characteristics of PAHs, such as aromatic system size and electronic structure, and properties of the resulting Li SES.

Chapter 1 provides a rationale for the research and outlines the goals and scope. The problem that addressed by the thesis is described in section 1.2. The objectives are stated in section 1.3. The strategy to reach the objectives is discussed in section 1.4.

Chapter 2 reviews the literature concerning the preparation, characterization and properties of Li SES.

Chapter 3 discusses the principles underlying the experimental methods used for characterization of Li SES and PAH.

Chapter 4 represents the results on the electrical and electrochemical properties of Li SES based on p-terphenyl and anthracene. Since p-terphenyl can be considered as a molecule of biphenyl with one additional benzene ring connected via a C-C bond, and anthracene is naphthalene with one additional fused benzene ring, these molecule are the next step after the previously reported studies on biphenyl and naphthalene.

Chapter 5 elaborates the results on Li SES prepared from 1,3,5-triphenylbenzene and its derivatives. The influence of substituents on Li SES properties is also discussed.

Chapter 6 is dedicated to electrical and electrochemical properties of triphenylene based

Li SES.

Chapter 7 represents the results on hexaphenylbenzene and hexa-peri-hexabenzocoronene as sources for Li SES.

Chapter 8 discusses the electrical and electrochemical properties of Li SES derived from heteroaromatic structures: phenylpyridines and bipyridines. The effect of a different solvent, HMPA (hexamethylphosphoramide), on Li SES formation and properties is also shown in this chapter.

Chapter 9 represents the results on synthesis and properties of a novel class of polyheteroaromatic materials: derivatives of 5,7-diazapentacene (quinolino[3,2-b]acridine), which can find applications both in Li SES and OFET.

Chapter 10 summarizes and discusses the results obtained in previous chapters in context of hypothesis, objectives, and strategy. It also discusses questions remained unaddressed in terms of this thesis and possible directions in further studies.

Appendix provides details on synthetic procedures and characterization of the synthesized compounds. The data on novel 5,7-diazapentacene, including ^1H NMR, ^{13}C NMR and high resolution mass spectra, is represented in the second part of the appendix.

1.6. Findings and Outcomes

This research led to several novel outcomes by:

1. Establishing a correlation between structures of PAH and Li:PAH ratio that can be achieved in resulting Li SES.
2. Deriving electrical, electrochemical and thermodynamical parameters of studied Li SES.
3. Finding a correlation between structures of PAH and the corresponding Li SESs'

electrical and electrochemical properties.

4. Establishing novel synthetic procedures to 5,7-diazapentacene derivatives and precursors.
5. Correlating the structure of novel 5,7-diazapentacene derivatives and precursors and their electronic properties.

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Chapter 2

Literature Review

This chapter covers the major preceding aspects related to lithium based solvated electron solutions (SES) related to the present work. It starts with the general characteristics and considerations regarding these materials, including the explanation of the term “solvated electron” and the feasibility of their application in rechargeable batteries. The following section 2.2 covers the aspects of SES formation, namely the influence of solvent, alkali metal, and polyaromatic hydrocarbon’s structure. This section also demonstrates the variety of PAH based SES currently known. The section 2.3 describes the characterization techniques applicable for Li SES: ESR, NMR, UV-Vis and FTIR spectroscopy. Theoretical First Principle calculations are also discussed in this section. Electrical properties (conductivity) are covered in the section 2.4, and the section 2.5 is dedicated to electrochemical properties, including half- and full cell experiments.

2.1. Introduction to solvated electron solutions

In 1807, Sir Humphry Davy observed formation of a blue colored product during the reaction between potassium and gaseous ammonia [1]. Later it was found that other alkali metals also form deep colored solutions upon dissolution in liquid ammonia. This color may vary from blue to bronze depending on concentration, although some solutions may appear to be greenish [2]. Only Group I and Group II elements (excluding beryllium and magnesium, which are only partially soluble) are able to give such solutions in ammonia [3]. Amines behave the same way as ammonia [4]. Appearance of the intensive color is attributed to formation of solvated electrons upon the metals dissolution. The term “solvated electron” refers to the presence of free electrons in the solution, which are not bound to any particular atom or molecule, but occupy vacant space between the molecules in such a solution [5].

It is possible to obtain these free electron solutions in aqueous media by means of ionizing radiation [6]. However, these solutions are very unstable, in contrast with those obtained using ammonia or some other compounds.

In 1980s Sammels proposed a concept of ammonia based Li SES as a potential liquid electrode which could be used instead of metallic lithium [7]. While ammonia based Li SES have almost all the discussed advantages of liquid electrodes, unfortunately, they have very serious safety issues due to evaporation producing gaseous ammonia during the discharge, which leads to pressure build-up inside the cell.

Conjugated aromatic compounds with low-energy antibonding orbitals may act as acceptors of alkali metal electrons. Addition of alkali metals to solutions of compounds like naphthalene or biphenyl in appropriate solvents leads to formation of deeply colored liquids [4, 8]. In this type of solution, the conjugated hydrocarbon accepts an electron from an alkali metal giving an ion radical, while the alkali metal cation is solvated by means of the solvent used. Since generally the term “solvation” means formation of a single liquid

phase with weak non-covalent interactions, these systems may also be considered as solvated electron solutions [9].

In contrast to ammonia, PAHs are solids and need to be dissolved in an appropriate solvent prior to SES preparation. These solutions are more promising for liquid anode application than ones involving liquid ammonia, as they do not require cooling or excessive pressure to remain liquid.

In this part of the thesis, the main aspects of PAH based SES formation are discussed first (section 2.2). Since this thesis is focused on Li based SES, information on SES prepared with other alkali metals in section 2.2 is provided for more detailed understating of these principles. In section 2.3 the approaches to Li SES characterization are discussed, and section 2.4 is related to charge transport properties of Li SES.

2.2. Preparation of conjugated aromatic compounds based SES

Alkali metals react with conjugated aromatic compounds giving corresponding radical ion - cation pair according to the equation below. (A represents aromatic compound, M represents alkali metal). In these reactions, electrons occupy low-energy antibonding orbitals of the aromatic compounds [10].

Reaction with additional equivalent of metal may give a dianion, which is usually diamagnetic:

Some conjugated aromatic substances can form polyanions:

Some unstable radical ions tend to couple giving dimeric dianions, or even to decompose:

Since both alkali metals and SES are highly reactive species, preparation of SES requires absence of oxygen, water and solvent impurities. In the case of operations with lithium metal, the presence of nitrogen is also undesirable due to lithium nitride formation [11].

Since SES formation is a heterogeneous process, which occurs at the phase boundary between solid and liquid, adequate contact between these phases must be established. For large scale preparation, alkali metal powder is an optimal choice [12]. Good stirring is also important in this process.

The reaction goes smoothly experiencing no issues as long as the equilibrium defined by eq. 1-3 is favorable for products formation, and these products are stable under certain conditions.

For conjugated aromatic compounds with fused rings, reactivity increases in the order: benzene < biphenyl < naphthalene < anthracene, which is similar to the electron affinities of these substances [13-16].

The situation with alkali metals is more complex. If one considers just the ionization potential and heat of sublimation, which decrease in the order $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$, then the reducing power would increase from Li to Cs. However, the solvent effect also has significant influence on the reaction. Since dissociation of ionic compounds in most organic solvents is negligible due to strong electrostatic interaction between ionic pairs, the solvation of ionic pairs plays an important role. In poor solvating solvents the reduction ability should increase from Li to Cs. On the other hand, in strongly solvating solvents this order is reversed due to increase of solvation as cation size decreases. If the reaction product is a solid, its lattice energy should also be considered [17].

The following order describes solvating ability of organic solvents for alkali metal cations [18]: diethyl ether < 1,4-dioxane < 2-MeTHF < tetrahydropyran < THF < dimethoxyethane (DME, glyme (1)) < diglyme (2) < triglyme (3) < tetraglyme (4). From this order one can realize the influence of steric (diethyl ether < 2-MeTHF < THF) and chelating effects (THF < glyme < triglyme). Moreover, ion pairs may interact with solvents in different ways [19, 20]. Solvent may intervene in between the ions separating them from each other and yielding a loose ion pair. Conversely, ions lack this kind of interaction in tight ion pairs. A temperature decrease facilitates solvation processes. Since the electron transfer process

from an alkali metal to a conjugated system has very low activation energy, SES can be prepared between room temperature and the freezing point of the employed solvent.

Figure 2.1. Substances with high solvating ability for alkali metal cations.

Generally, ideal conditions for SES formation are difficult to predict. The following parameters play critical role: solvent, temperature, time, as well as the conjugated aromatic compounds and alkali metals chemical and electronic properties [17].

Benzene, the simplest conjugated aromatic system, is the most resistant compound towards radical ion formation. Nevertheless, potassium in DME at $-80\text{ }^{\circ}\text{C}$ leads to formation of this ion radical, which was detected by electron spin resonance (ESR) spectroscopy [21, 22]. The use of ESR in radical ion characterization will be discussed in section 2.3. According to ESR studies, Rb and Cs in DME or THF also give a benzene ion radical following eq. 1 [23]. Despite benzene not reacting with Li and Na in these solvents, it is possible to detect the corresponding radical ion using Na-K alloy in THF:DME mixture (2 : 1 by volume) at $-83\text{ }^{\circ}\text{C}$, with only 0.1% conversion of benzene at equilibrium [24].

Alkyl substituents destabilize benzene based radical ions prepared using Na-K alloy in DME-THF at $-100\text{ }^{\circ}\text{C}$ with the following order: $\text{Me} < \text{Et} < {}^i\text{Pr} < {}^t\text{Bu}$ [25]. Increasing number of these groups also leads to decrease of stability. In contrast, electron withdrawing groups (CN and NO_2) and organometallic substituents demonstrating hyper conjugation effect (Me_3Si and Me_3Ge) stabilize benzene radical ion [26].

Crown ethers such as 18-crown-6 (**5**), dicyclohexyl-18-crown-6 (**6**) and [2.2.2] cryptand (**7**) (**Figure 2.1**), owing to their excellent solvation ability, facilitate radical-ion formation in reactions between potassium and benzene, toluene and mesitylene [27, 28]. The

formation of radical anions is also feasible with Rb and Cs using 18-crown-6 and [2.2.2] cryptand [27, 29]. Sodium does not react under these conditions.

By contrast to benzene, biphenyl, the simplest PAH with a single bond between aromatic moieties, reacts with both lithium and sodium in THF at room temperature. Li may form adducts with biphenyl with ratios higher than 2:1. For example, a 0.5 M THF solution of biphenyl dissolves 2.5 equivalents of Li per PAH [30]. By contrast with Li, the reaction with Na is reversible and only ~30 mol% of Na can be dissolved [31]. Addition of Et₂O shifts the equilibrium leading to precipitation of the metal. Although a formation of crystalline product occurs in concentrated solutions at -78 °C, attempts to separate it from THF result in decomposition with loss of Na [32]. Biphenyl reacts more completely with Na upon increasing solvating ability of a solvent. Thus, sodium completely reacts with biphenyl in DME giving sodium biphenylide, and in triglyme (**3**, Tg) it is possible to isolate blue crystals of the compound Na(biphenyl)*2Tg, which is an example of a compound with solvent-separated ion pairs [33]. Similar products with Rb and K can also be isolated in the solid state [20]. Potassium in DME first reacts with biphenyl forming a blue solution of paramagnetic K(biphenyl), which after some time turns into a red-brown solution of diamagnetic K₂(biphenyl) [12]. This compound is a strong base, which reacts with DME showing 90% conversion in 4 hours. Both Li and K based SES demonstrate similar behavior in THF solutions [19].

Naphthalene reacts with lithium in THF giving first a greenish solution of the monoadduct, which then turns to deep purple upon reaction with an additional equivalent of Li. This solution slowly decomposes at room temperature, but is stable at -80 °C [34]. Sodium gives only traces of the corresponding radical ion (~10⁻³ % at 20 °C) in Et₂O [35], whereas in DME and THF the conversion to the 1:1 adduct is quantitative [36]. However, increasing the concentration of this Na adduct by solvent evaporation leads to decomposition into the metal and naphthalene [37]. Potassium gives corresponding product with naphthalene in Et₂O only with 13% conversion [22], however, in THF it completely converts to a green solution of potassium naphthalenide. Further reaction with potassium as per eq. 2 gives the corresponding dianion, which, in contrast to the dilithium compound, is stable in THF [38].

However, dilithium naphthalenide can be stabilized with tetramethylethylenediamine (TMEDA) in hexane, giving crystals of the composition $[\text{C}_{10}\text{H}_8][\text{Li}^*\text{TMEDA}]_2$ [39]. This ligand also allows one to obtain the corresponding adduct of Li with anthracene (**8**), which crystallizes from a benzene-hexane mixture as $[\text{C}_{14}\text{H}_{10}][\text{Li}^*\text{TMEDA}]_2$ [40].

Although one can prepare monosodium anthracenide in THF solution [41], reactions between lithium and PAHs with more than two fused aromatic rings, including anthracene (**8**) [42], phenanthrene (**9a**) [43], benz(a)anthracene (**10**) [44], 9,10-diphenylphenanthrene (**9b**) [43], naphthacene (**11**) [42], pentacene (**12**) [45] and perylene (**13**) [42] (**Figure 2.2**) often lead to dianion formation. Moreover, reactions between an equimolar ratio of Li and these conjugated PAHs tend to give the corresponding dianion in 50% conversion due to the large value of equilibrium constant defined by eq. 2. However, both radical ions and dianions of perylene (**13**) [46] and corannulene (**14**) [1] are known (**Figure 2.2**).

Figure 2.2. PAHs reduced to radical ions or dianions.

Although hydrocarbons like biphenylene (**15**) [47], heptalene (**16**) [48], and 16-annulene (**17**) [6] (**Figure 2.3**) may give stable radical ions, formation of dianions as per eq. 2 with antiaromatic $4n$ π -conjugated systems is more favorable. Dilithium dianions of cyclooctatetraene (**18**) [2], pentalene (**19**) [3], 16-annulene (**17**) [6], 1,9-dimethyldibenzo[b,f]pentalene (**20**) [49], azulene (**21**) [42], heptalene (**16**) [8], octalene (**22**) [50], pyrene (**23**) [42], bis(cyclohepta)[cd,gh]pentalene (**24**) [9],

bis(cyclohepta)[cd,gh]heptalene (**25**) [9], 15,16-dimethyl-15,16-dihydropyrene (**26**) [42], and acepleyadilene (**27**) [4] are known (**Figure 2.3**). Some compounds give tetraanions as per equation 3 upon reaction with lithium, for example, 1,2,3,4-tetraphenyl-1,3-butadiene (**28**) [10], 5,5-dimethyl-1,2,3,4-tetraphenyl-5-silacyclopentadiene (**29**) [11], octalene (**22**) [50], 9,9'-bianthranyl (**30**) [12], and acepleyadilene (**27**) [4] (**Figure 2.4**).

Figure 2.3. Compounds with $4n$ π -electron systems giving adducts with alkali metals.

Figure 2.4. PAHs reduced to tetraanions with lithium.

Radical ions formed in reactions between alkali metals and polyaromatic hydrocarbons with bridged double or triple bond (trans-stilbene (**31**) [51], tetraphenylethylene (**32**) [52], tolane (**33**) [51] (**Figure 2.5**) in THF are unstable. These adducts decompose to starting compound and corresponding dianion over time. Tolane ion radicals tend to transform into dimeric dianions [53]. Nevertheless, it is possible to obtain stable solutions of tetraphenylethylene and tolane radical ions in hexamethylphosphoramide (HMPA) [53, 54]. This is attributed to the exceptionally powerful solvation properties of HMPA, which, for example, leads to virtually complete dissociation of ionic pairs between alkali metals and anthracene radical ion according to conductivity studies [55]. Since disproportionation process involves ion pairs, it does not occur when these pairs are fully dissociated.

Figure 2.5. PAHs with bridged multiple bond.

Fluorene (**34**) reacts with Li in THF, as well as with other alkali metals, giving radical ion at $-70\text{ }^{\circ}\text{C}$. However, at higher temperatures this radical ion decomposes, giving the corresponding anion (**Figure 2.6**) [56]. Radical anions derived from 2,3-benzofluorene and 4,5-methylenepheneanthrene show similar behavior. The rate of decomposition is very sensitive to substituents at the 2-position of fluorene, which is, according to molecular orbital calculations, the position of the highest unpaired spin density. The first-order reaction rate constant measured at $25\text{ }^{\circ}\text{C}$ decreases in the order: $\text{OMe} > \text{CN} > \text{Me} > \text{H} > \text{NO}_2$. Thus, electron donating groups at the fluorene 2-position destabilize the radical ion, and electron withdrawing groups demonstrate a stabilizing effect, which follows a Hammett-type relationship. A possible explanation of the CN groups unusual behavior is related to interactions between an alkali metal and a CN group, significantly changing the group's electronic effect and the reaction rate. The reaction of 2-halofluorenes (where

halogen is F, Cl, or Br) with Li leads to C-X bond fission, giving non-substituted fluorene, which reacts with an excess of lithium in the usual way [57, 58].

Figure 2.6. Formation and decomposition of fluorene radical ion.

The electron deficient pyridine molecule, which is one of the simplest heterocyclic aromatic compounds, accepts electrons much more easily than benzene. Pyridine undergoes dimerization upon reaction with lithium, giving the 4,4'-bipyridyl (**43**) radical ion [13]. Ion radicals of quinoline (**35**), isoquinoline (**36**), acridine (**37**), and 9,10-diazaphenanthrene (**38**) (**Figure 2.7**) also dimerize giving dianions in THF solutions. However, the corresponding radical ions except that for pyridine can be detected in HMPA [59]. One can attribute this effect to complete dissociation of ionic pairs in this solvent, thereby suppressing association of ionic couples.

2,4,6-Triphenylpyridine (**39**) [14] and 2,5-diphenylbenzofuran (**40**) [15] give dilithium dianions upon reaction with metallic lithium. For 2,2'-bipyridyl (**41**), a structure with two bonded heterocyclic rings, both the radical anion and dianion are known [16]. Radical ions derived from reactions between alkali metals and conjugated aromatic compounds with 2,2'-bipyridyl structural pattern (4,4'-dimethyl-2,2'-bipyridyl (**42**), 1,10-phenanthroline (**44**), 4,7-dimethyl-1,10-phenanthroline (**45**)) are also known (**Figure 2.7**) [60].

Figure 2.7. Heterocyclic compounds giving adducts with alkali metals.

2.3. Characterization of conjugated aromatic compounds based SES

Common methods for characterization of solutions obtained in reactions between alkali metals and mixtures of organic solvents and conjugated organic compounds are ESR (Electron Spin Resonance), NMR (Nuclear Magnetic Resonance) and UV-Vis (Ultraviolet-Visible) spectroscopy.

ESR spectroscopy is a technique which allows detection of unpaired electrons due to their paramagnetic properties and, thus, ability to show electron spin resonance. For paramagnetic compounds, the method provides detailed information on electronic structure, position of unpaired electron, properties of chemical bonds, as well as on interactions between molecules. Since ESR is a very useful method to demonstrate formation of radical ions and to study their properties, spectral data for a large variety of conjugated aromatic compound adducts with alkali metals has been reported [17, 30, 61-64].

For example, ESR is a very useful for investigating behavior of an unpaired electron in lithium naphthalenide at different temperatures in ethereal solvents [65]. The unpaired electron interacts with the molecule of naphthalene giving a 25 line spectrum. Each line in

this spectrum is additionally split into 4 lines due to interaction with lithium magnetic moment. The spectrum of lithium naphthalenide in diethyl ether has 25 lines, while at -70 °C it becomes divided into groups of 4 lines (**Figure 2.8**).

Figure 2.8. Experimentally obtained ESR spectra of lithium naphthalenide in diethyl ether at 26 °C (top) and -70 °C (bottom) [65].

ESR is useful to study the electronic structure of ion radicals, which makes significant influence on their chemical properties, especially in case of heteroaromatic compounds. Based on ESR study of substituted pyridines, it was shown that mesomeric structures with negative charge localized on nitrogen and unpaired electron localized at the 2-, 4-, and 6-positions of the pyridine ring (**46a-c**) make significant contribution to the radical ion electronic structure (**Figure 2.9**) [66]. Hyperfine splittings data has also allowed some conclusions to be made concerning 2,2'-bipyridyl (**41**) [67] and 4,4'-bipyridyl (**43**) [68] ion radicals' electronic structures. This data shows that mesomeric structures where the negative charge is located in one ring on nitrogen atom and an unpaired electron is distributed in the π -system of the other (**47** and **48**) make the most significant contribution to the overall structure (**Figure 2.9**). Generally, detailed ESR spectral data is available for a wide range of heterocyclic radical ions [66].

Figure 2.9. Mesomeric structures of pyridine (**46a-c**), 2,2'-bipyridyl (**47**), and 4,4'-bipyridyl (**48**) radical ions formed upon reduction with alkali metals.

NMR can also provide useful information for determining SES properties. Since NMR signals are broadened in presence of radical ions, this broadening in some cases allows assigning ESR spectrum [69]. A significant advantage of NMR comparing to ESR is possibility to measure weak interactions between a solvent and dissolved species.

Solutions of lithium in mixtures of THF and biphenyl, naphthalene, phenanthrene (**9a**), anthracene (**8**) or trans-stilbene (**31**) have been the objects of ^7Li NMR studies [70]. In that report, the authors demonstrate a relation between ^7Li NMR chemical shift and concentration of corresponding radical ion. Values of ^7Li NMR chemical shifts for biphenyl and trans-stilbene increase upon increasing the concentration, showing linear variation. By contrast, this relation is not linear for naphthalene (**Figure 2.10a**). Additional measurements in presence of LiCl show linear relation between ^7Li NMR chemical shift and radical ion concentration (**Figure 2.10b**). A possible explanation of this effect is that Li naphthalenide exists as a tight ion pair with no Li^+ exchange between naphthalene/solvent sites. The authors assumed that Li^+ in these ion pairs is indistinguishable from Li^+ from LiCl. Thus, Li exchange takes place between Li in solution and the ionic pairs, but not among the ion pairs, which makes the relation linear. Based on chemical shifts data, the authors of this report have also shown that radical ions of anthracene and biphenyl in THF solutions exist as loose ion pairs, whereas the adduct with trans-stilbene is a solvent-separated ion pair.

Figure 2.10. Relationships between the ${}^7\text{Li}$ NMR shift and the radical anion concentration for Li-naphthalenide in THF. a) Non-linear relationship b) Linear relationship in presence of LiCl [70].

Although NMR measurements on radical ions may be difficult to interpret due to broadened signals and a wide range of chemical shifts, some dianions formed in reactions between PAHs and alkali metals have been characterized by ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR [4, 6, 8, 30].

Since SESs have very deep color, demonstrating strong absorption in the visible part of the electromagnetic spectrum, UV-Vis (Ultraviolet-visible) spectroscopy is useful for determining formation or decomposition of radical ions. In literature, one can find UV-Vis spectral data for a wide range of radical ion solutions [30, 61, 63]. This method is also useful for kinetics studies involving radical ions [58].

FTIR (Fourier transform infrared) spectroscopy can be helpful in study of ion radicals and dianions formation mechanism upon alkali metal dissolution. Yazami and Tan used FTIR technique to investigate processes that occur upon reactions of varying quantities of lithium with solutions of biphenyl [71] and naphthalene [72] in THF. They found that the reactions of PAH with 0 – 1 equivalents of Li lead only to formation of corresponding ion radicals, which then react with additional quantities of lithium giving the dianions.

Theoretical First Principle calculations can provide useful information on interactions between lithium and PAH, as well as interactions of molecules in Li SES [73]. Binding

energies between lithium and a number of PAH were studied at the B3LYP/6-31G*//HF/6-31G* level of calculation. It was shown that Li atoms bind to interstitial and edge sites of the molecules demonstrating significantly negative binding energies (-211.0 kJ/mol for anthracene, -146.2 kJ/mol for phenanthrene, and -142.8 kJ/mol for pyrene). It was also found that the planar aromatic structure of these molecules becomes distorted upon interaction with metallic lithium leading to stronger interaction between the aromatic core and the atoms of lithium and lowering the HOMO level, which directly related to the discharge process.

Figure 2.11. Optimized geometries of 2Li-doped anthracene (left) and phenanthrene (right) systems [72].

Such First Principle calculations were also employed to study interactions between lithium and linear annulated PAH, such as anthracene and tetracene [74]. It was shown that the calculated binding energy of lithium is highly dependent on the size of the PAH and the position of the metal atoms towards the PAH molecule. It was also shown that the binding energy increases upon the absorption of the second atom of lithium. Additionally, natural bond orbital charge analysis showed that the neutral atoms of lithium acquire fractional positive charge upon the interaction with the PAH molecules. The authors also demonstrated a good correlation between the extent of charge transfer, deformation and binding energies.

2.4. Electrical properties of Li SES

Electrical conductivity of a material, σ , is a quantitative value that justifies the ability to conduct electrical current. This characteristic is inverse to the resistance. Electrical conductivity values demonstrate different relation with temperature in metals, semiconductors and electrolyte solutions due to different mechanisms of charge transfer in these media [75]. In metals, where charge transport occurs due to mobility of the outer-shell electrons, electrical conductivity decreases upon increase of temperature. The explanation of this effect is increased vibrational motions of the fixed positive ions at higher temperatures, which leads to an increased rate of collisions between moving electrons and stationary metal cations. For semiconductors, whose charge carriers consists of both holes and electrons, electrical conductivity generally increases with temperature increase. The reason is formation of more electron-hole pairs upon absorption of more thermal energy. The reason for electrical conductivity in electrolyte solutions is mobility of both positive and negative charge carriers. For these solutions, the conductivity depends on concentration of charge carriers and typically increases with temperature, which is related to an increased charge carriers' mobility.

Solutions of lithium in ammonia do not behave like standard electrolytes. Although at lower concentrations of the metal these solutions behave like an ideal electrolyte, at higher concentrations they demonstrate exceptionally high effective electron mobility compared to standard electrolytes. A distance between cavities that contain electrons in alkali metal ammonia solutions decreases with increase of concentration, so at some concentration electrical current can propagate through the media as a flux of electrons moving through the cavities [76].

Both **Figures 2.12** and **2.13** demonstrate that solutions of Li in liquid ammonia exhibit metallic behavior above certain concentrations [77]. Red box in both the figures shows the temperature range where ammonia is liquid. **Figure 2.12** shows that for concentrations of Li below 20 mol% conductivity increases with temperature, and for 20 mol% temperature

increase does not influence conductivity. For concentration of Li above 20 mol % (**Figure 2.13**) conductivity decreases with temperature, which is similar to solid metals.

Figure 2.12. Conductivity data of ammonia-based Li SES for various concentrations of lithium (in mol %) [77].

Figure 2.13. Conductivity data of ammonia-based Li SES for various concentrations of lithium (in mol %) [77].

Adducts of alkali metals with conjugated polyaromatic hydrocarbons in ethereal solvents demonstrate similar temperature – conductivity correlations; thus, these solutions can be also classified as SES. Recently Tan and Yazami [71, 72] studied conductivity of biphenyl and naphthalene based Li SES with PAH concentration above 0.4 M and Li:PAH ratios = 0.5, 1, 1.5, 2. They showed that conductivity of these solutions decreases with temperature increase. **Figure 2.14** demonstrates this relation for naphthalene.

Figure 2.14. Conductivity versus temperature profiles for $\text{Li}_x\text{N}(\text{THF})_{10.4}$ (N = naphthalene, $x = 0.5, 1.0, 1.5, 2.0$) [72].

However, at low concentrations (10^{-4} mol), solutions of lithium mono and diadducts with PAHs, such as anthracene (**8**), naphthacene (**11**), and pentacene (**12**), as well as lithium monoadducts with biphenyl, 1,1':4',1''-terphenyl (p-terphenyl, **49**), and 1,1':4',1'':4'',1'''-quaterphenyl (**50**) (**Figure 2.15**) in THF and 2-MeTHF demonstrate increase of conductivity with temperature increase [78].

Figure 2.15. Structures of 1,1':4',1''-terphenyl (**49**) and 1,1':4',1'':4'',1'''-quaterphenyl (**50**).

This fact can be rationalized by considering the properties of ammonia SES. The concentration of solvated electrons in these PAH based solutions is not enough to establish sufficient electron transfer between ion pairs. As a result, relation between conductivity and temperature for PAH based Li SES is similar to electrolytes at low concentrations. However, relations between conductivity and temperature for more concentrated solutions of these PAHs (**8**, **11**, **12**, **49**, **50**) have not been performed yet.

Figure 2.16. Relations between conductivity and Li:PAH:THF ratio: a) for biphenyl (shown as β); b) for naphthalene (shown as N) [71, 72].

Conductivity of PAH based Li SES significantly depends not only on the concentration of the corresponding Li – PAH adduct, but also correlates with the PAH : Li ratio. For both naphthalene and biphenyl, conductivity measured at 25 °C in THF solutions initially increases with increasing the amount of lithium per PAH. Above a certain ratio the conductivity decreases as shown in **Figure 2.16**. This effect is valid for a wide range of Li SES concentrations (from 0.45 M up to maximum solubility of certain PAH in THF). For biphenyl maximum conductivity is 12.0 mS/cm in 1.22 M solution with Li : PAH = 1.2 : 1 (overall molecular ratio is $\text{Li}_{1.2}(\text{biphenyl})(\text{THF})_{8.2}$). For naphthalene this value is 12.4 mS/cm in 1.47 M solution with Li : PAH = 0.5 : 1 (overall molecular ratio is $\text{Li}_{0.5}(\text{biphenyl})(\text{THF})_{6.2}$). Thus, biphenyl based Li SES requires more lithium to achieve the highest value of conductivity comparing to naphthalene. Conductivity of metallic lithium is 1.047×10^8 mS/cm [79], which is $\sim 10^7$ times higher than maximum conductivity of both naphthalene and biphenyl based Li SES.

2.5. Electrochemical properties

In order to understand the feasibility of PAH based Li SES applications in batteries, some studies of their electrochemical properties were performed. It was shown that Li SES made of naphthalene or biphenyl with PAH:Li ratio of 1:1, demonstrate open circuit potentials (OCP, also referred as open circuit voltage, OCV) of 0.65 V and 0.68 V respectively in a Li/Ceramics/Li SES half-cell configuration [71, 72]. Since the half-cell experiments were performed in this project as well, the theoretical and experimental considerations related to this topic are discussed in Chapter 3. Based on the correlation between OCP and temperature, which shows quasi-linear behavior (**Figure 2.17**), the entropy (ΔS) and enthalpy (ΔH) values were calculated from the values of the slope and the intercept of the corresponding plot, respectively. For $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$, $\Delta S = -290 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta H = -149 \text{ kJ mol}^{-1}$. The ΔS absolute value is larger than those for solid state electrodes in Li-batteries, which are Li_xC_6 ($+80 < \Delta S < -20 \text{ J K}^{-1} \text{ mol}^{-1}$, $0 < x < 1$) [80] and Li_xCoO_2 ($+20 < \Delta S < -60 \text{ J K}^{-1} \text{ mol}^{-1}$, $0.55 < x < 0.95$) [81]. This is probably related to the liquid state of the Li SES that provides more configurational (mixing) entropy to the system, comparing to the solid-state materials.

Figure 2.17. Quasi-linear correlation between OCP and temperature for Li/Ceramics/ $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$ half-cell [72].

Regarding the ΔH for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$, its absolute value is higher than the range of values of the anodic Li_xC_6 ($-55 < \Delta H < -10 \text{ kJ mol}^{-1}$) but is in the range for the cathodic Li_xCoO_2 ($-413 < \Delta H < -382 \text{ kJ mol}^{-1}$). This is related to the fact that the OCP value for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$ (0.65 V vs. Li) lies in between of those for Li_xC_6 ($< 0.2 \text{ V}$) and Li_xCoO_2 ($> 3.6 \text{ V}$).

These values of entropy and enthalpy change were also determined for $\text{Li}_{1.0}(\text{Biphenyl})(\text{THF})_{10.4}$ [82]. The $\Delta S = -467 \text{ J K}^{-1} \text{ mol}^{-1}$, which is higher than the value of $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$, and significantly higher than the values for the solid state materials due to same reasons as for naphthalene based Li SES. The value of enthalpy change (ΔH), which is -208 kJ mol^{-1} , is also higher than the one of naphthalene based Li SES. The values of ΔS and ΔH for the tested naphthalene and biphenyl bases Li SES half-cells are shown in the **Table 2.1**.

Table 2.1. Entropy and enthalpy changes for Li / ceramics /Li SES half-cells.

Half-cell (Li SES / Li)	$\Delta S (\text{ J K}^{-1} \text{ mol}^{-1})$	$\Delta H (\text{ kJ mol}^{-1})$
$\text{Li}_{0.5}(\text{Biphenyl})(\text{THF})_{10.4}$	-420	-197
$\text{Li}_{1.0}(\text{Biphenyl})(\text{THF})_{10.4}$	-467	-208
$\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$	-290	-159

Also, the discharge of a full cell based on Li SES containing iodine in methanol as a cathode was studied (configuration: (-)Ni/1M $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$, 0.5 M LiI, THF/Ceramics membrane/0.1 M I_2 , 0.5 M LiI, methanol/Ni(+)) [72]. The OCV vs depth of discharge (DOD) plot consists of two parts: a flat plateau at 2.6V until 60% DOD, and a slope at above 60% DOD ending at 1.9 V (**Figure 2.18**).

It was shown that in the discharged Li SES/ I_2 cell, both Li SES and iodine can be electrochemically recovered, demonstrating the reversibility of the reactions that occur in the cell [83].

Figure 2.18. OCV vs depth of discharge (DOD) for the Li SES/I₂ full cell configuration

The OCV studies on more complex compounds, such as cyclopentadienones **51a,b** (Figure 2.19), were performed earlier in our group [84]. Since these compounds tend to accept electrons upon the reaction with lithium giving the corresponding anions **52** with aromatic 4n+2 π -systems, they should also be considered as Li SES.

Figure 2.19. Structure of the studied cyclopentadienone derivatives **51a,b** and their dianions [84].

These compounds readily react with 0.5 equivalent of lithium in 0.2 M THF solution giving Li SES with the values of conductivity 935 $\mu\text{S}/\text{cm}$ for **51a** and 673 $\mu\text{S}/\text{cm}$ for **51b**. Both **51a** and **51b** based Li SES have OCV vs Li of 1.59 V for the composition: 0.2M PAH, 0.5 M LiI in THF, 0.5 mole equivalents of Li. This value is lower than the OCV of the blank 0.5 M LiI solution (2.18 V), which indicates the formation of Li SES.

2.6. This project in context of literature

As seen from this chapter, the reactions of lithium and a large variety of PAH with different structure and substituents have been studied. The resulting Li SES were characterized using ESR, NMR, FTIR and UV-Vis techniques. Some correlations between structure and properties of these materials have been established. However, there is only a couple of publications related to electrical and electrochemical properties of these materials. Although there were some studies on conductivity of PAH based Li SES at low concentrations, the first systematic studies that reveal correlation between conductivity, concentration and Li:PAH ratio for Li SES based on naphthalene and biphenyl, which are the simplest PAH, were performed and published only recently [71, 72]. Considering that the usage of Li SES based on PAH as anolytes in rechargeable batteries is a relatively new concept proposed by Yazami in 2010 [85], the electrochemical properties of the PAH based Li SES have not been studied yet in detail, except in the pioneering works of Yazami and Tan on naphthalene and biphenyl based Li SES. Cyclopentadienones are the only more complex systems studied [84]. Thus, the systematic studies on correlation of electrical and electrochemical properties of Li SES and PAHs structure is a novel research direction, with only a few publications known.

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Chapter 3

Experimental Methodology

The beginning of this chapter gives the rationale for choosing the methods used in the present work. Then, the basic principles of the used methods for characterization of organic molecules, including Nuclear Magnetic Resonance, Mass Spectrometry, Optical Spectroscopy and Electrochemical methods, are discussed. Following the approach to synthesis of Li SES, the electrical and electrochemical methods for characterization of these solutions are described, namely conductivity and half-cell experiments.

3.1. Chapter outline

The project consists of the following parts: synthesis of PAHs, characterization of the synthesized PAHs, preparation of PAH based Li SES, and characterization of Li SES by means of conductivity studies and electrochemical half-cell experiments to determine thermodynamical parameters of the Li SES. This chapter describes the experimental techniques and characterization methods used in this project.

Synthetic procedures are described in Appendix 1. Chemicals for synthesis of PAHs and preparation of Li SES were obtained from Sigma-Aldrich and TCI Chemicals and used as received unless otherwise specified in Appendix 1. Anhydrous solvents were purchased from Sigma-Aldrich and used as received. Air sensitive reactions were performed under an inert atmosphere of nitrogen using Schlenk technique [1]. Standard organic chemistry techniques were used for purification of organic materials such as recrystallization, distillation, and column chromatography [2].

In order to characterize synthesized materials and byproducts, standard techniques for characterization of organic materials were used, such as MALDI TOF MS, HRMS, and ^1H and ^{13}C NMR. The combination of these methods allows clear and unequivocal identification of the organic materials' chemical structure. This spectral data is shown together with the synthetic procedures in Appendix 1. Since some of the synthesized conjugated aromatic molecules demonstrate very characteristic optical properties, UV-Vis and photoluminescence spectroscopy were also used for characterization. These optical spectroscopy techniques, as well as cyclic voltammetry, were used to define electronic properties of the synthesized molecules, such as band gap, HOMO and LUMO energy levels.

The principles of Nuclear Magnetic Resonance (NMR) spectroscopy, a basic technique for determining the structure of organic compounds, are described in Section 3.2.1. Section 3.2.2 is dedicated to the principles of mass spectrometry techniques used in the project: Matrix Assisted Laser Desorption/Ionization-Time of Flight-Mass Spectrometry (MALDI-

TOF MS) and High Resolution Mass Spectrometry (HRMS). Section 3.2.4 covers optical spectroscopy methods (UV-Vis and photoluminescent spectroscopy, as well as the determination of quantum yield). The electrochemical technique (Cyclic voltammetry) used in this project is described in Section 3.2.3. Li SES preparation is discussed in Section 3.3. Conductivity and conductivity versus temperature measurements on Li SESs are discussed in Section 3.7. Section 3.8 describes the electrochemical half-cell setup that allows one to determine the open circuit potentials and the thermodynamic parameters of the studied Li SESs.

3.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is a non-destructive analytical technique, which is used for determining chemical structure, as well as purity and content of the sample [3]. In general, NMR is a phenomenon in which certain types of nuclei, depending on their spin properties, absorb and radiate electromagnetic radiation in magnetic field. The most important parameters for interpretation of NMR data are chemical shift, peak splitting pattern, and integration value (mostly for ^1H NMR), which demonstrates the relative intensity of signals.

Chemical shift (δ) is a relative resonant frequency, which can be defined by equation:

$$\delta = (\nu - \nu_s) / \nu_0$$

Where $(\nu - \nu_s)$ – frequency difference between the detected signal and the reference, and ν_0 is the central resonant frequency for the nucleus in the applied magnetic field. In this equation, the chemical shift is a ratio of Hz to MHz, which gives a dimensionless value $1/10^6$, or ppm (parts per million). Although tetramethylsilane (TMS) is a common reference for proton and carbon NMR spectroscopy, whose chemical shift is defined as zero ($\nu - \nu_s = 0$), common solvents with known shifts can also be applied as additional internal calibration markers.

Since the effective magnetic field experienced by the nuclei depends on the degree of electron shielding around it, the chemical shift is related to the chemical environment which surrounds the nuclei. The value of the chemical shift thus depends upon the nature

of neighboring atoms, including their electronic structure. Thus, substituents in organic molecules significantly influence the values of chemical shifts, as shown in **Figure 3.1** for ^1H NMR data. Electron withdrawing groups decrease the electron density located on adjacent atoms, resulting in higher resonant frequencies of the nuclei and, thus, higher values of the chemical shift. Factors related to sample preparation can also influence chemical shift values, such as temperature, concentration, solvent, and paramagnetic impurities.

Figure 3.1. Ranges of chemical shifts (δ , ppm) for ^1H in compounds with different substituents [4].

In NMR spectra, a value of chemical shift is displayed on the horizontal (x) axis, and the vertical axis represents the intensity of signals. Since relaxation times of different ^1H nuclei are generally similar, the integral ratio of different peaks is directly proportional to the relative quantities of different protons present. Since different carbon nuclei generally have very different relaxation times, and longer relaxing nuclei give signals with lower intensity, this consideration is not usually applicable for ^{13}C spectral data.

Spin-spin coupling (also known as J-coupling) is an effect of a peak splitting into two or more lines due to influence of adjacent nuclei on the effective magnetic field of the detected one. In first order ^1H spectra, where the difference in chemical shift is much larger than the

coupling constant (measured in absolute frequency, Hertz), the total number of lines in the peak is $N+1$, where N is the number of neighboring protons of a different nature in the molecule. Thus, a single line peak in ^1H NMR spectra means no adjacent protons of different nature, two lines indicate the system with one neighboring nucleus, etc. A good illustration of this relation is the ^1H NMR spectra of chloroethane (**Figure 3.2**), where the protons in the methylene fragment, which have three neighboring protons of different nature, appear as a quartet of four lines, and protons in the methyl group appear as a triplet of three lines. The ratio of the intensities of the signals within the multiplets are determined by the binomial distribution (1:1 for a doublet, 1:2:1 for a triplet and so on).

Figure 3.2. ^1H NMR spectra of chloroethane [5].

For the reported studies on PAH, ^1H and ^{13}C NMR were used for identifying their structure and purity. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer operating at 400 MHz. Chloroform- d (CDCl_3), Dichloromethane- d_2 (CD_2Cl_2) and Dimethylsulfoxide- d_6 ($\text{DMSO}-D_6$) were used as solvents, and tetramethylsilane (TMS) as internal standard. Samples were prepared by dissolution of 8.0 – 12.0 mg of the compound in ~ 0.4 ml of the corresponding solvent. Bruker TopSpin 4.0 software was used to process the NMR spectra.

3.3. Mass Spectrometry Techniques: Matrix Assisted Laser Desorption/Ionization-Time of Flight-Mass Spectrometry (MALDI TOF MS) and High-Resolution Mass Spectrometry (HRMS)

Mass spectrometry (MS) is an analytical technique, which allows determination of the quantity and type of chemical species present. Mass spectra is a plot of mass-to-charge ratio versus the intensity of the peak [6].

The equipment for obtaining MS data generally consists of three main units: sample introduction system with ionization source, charged species transfer and separation system, and a detector.

Among different MS techniques, MALDI-TOF MS allows analysis of high molecular weight compounds, which tend to decompose under conventional techniques [7]. This method is also convenient and reliable for analysis of PAHs [8].

Figure 3.3. MALDI TOF MS working principle [9].

MALDI TOF MS operation procedure is shown in **Figure 3.3**. Firstly, irradiation of laser power on a sample film composed of a uniform mixture of matrix and analyzing material results in energy transfer from the matrix to the sample molecules, giving differently charged ions on the sample slide. A voltage gap between ground and the sample slide accelerates the ions towards the ground. Then the ions start moving towards the detector without any external driving force. Ions with smaller mass to charge ratio move faster, and the time of ion flight is indicative of different m/z [9].

For some of the PAH described in the report, mass spectra were measured on a MALDI Shimadzu AXIMA spectrometer using α -cyano-4-hydroxycinnamic acid as a matrix.

High-resolution mass spectrometry (HRMS) is a standard method to confirm chemical composition of material by means of the exact mass determination [10]. In this technique, electrospray ionization (ESI) is a convenient way to generate charged species, which are produced by injection of a fine aerosol containing the analyte into the first vacuum stage of the spectrometer through a capillary bearing a potential difference about 3 kV [11]. This is a mild ionization technique leading to very little fragmentation, which is very useful when M^+ is the ion of interest, as it is for the exact mass determination.

In this project, the accurate mass analyses were run at the Chemistry Department, National University of Singapore, using a micrOTOF-Q II (Bruker) mass spectrometer in ESI mode on a double focusing magnetic sector mass spectrometer at a mass resolution of 40 000 (FWHM using a hybrid linear ion trap/orbitrap tandem mass spectrometer).

3.4. Studies on optical properties: UV-Vis Absorption spectroscopy (Abs), Fluorescence spectroscopy (FL), Quantum yield measurements

A molecule can absorb a photon of a certain energy which leads to a transition into an excited state. When a molecule absorbs electromagnetic radiation in the visible (400-600nm) or in the ultraviolet (200-400nm) region, it causes an electronic transition within its structure. This energy leads to transfer of electrons from their ground state orbitals to excited state orbitals or antibonding orbitals having higher energy levels. In general, there

are three types of ground state orbitals to be involved: σ (bonding) and π (bonding) molecular orbitals, as well as n (non-bonding) atomic orbital [12]. Additionally, there are two types of antibonding orbitals that can be involved in the transition: σ^* and π^* orbitals (since the n electrons do not form bonds, there is no n^* antibonding orbital).

The following transitions can occur when an electron at a bonding orbital is transferred to an antibonding orbital due to excitation: σ to σ^* , n to σ^* , n to π^* and π to π^* (**Figure 3.4**).

Figure 3.4. The energy level diagram showing the absorption of different amounts of energy.

Both σ to σ^* and n to σ^* transitions require a relatively significant amount of energy and occur in the far ultraviolet (UV) region or less often in the 180-240 nm region. As a result, molecules or parts of molecules consisting solely of σ bonds do not demonstrate absorption in the near UV or visible region. The transitions of the n to π^* and π to π^* type in molecules having unsaturated groups occur at longer wavelengths as they require less energy. Although the π to π^* transitions demonstrate the absorption of fairly low intensity when occurring in isolated fragments of a molecule, conjugation of unsaturated groups of the molecule has a significant effect on the absorption spectrum. The maximum of absorption shifts to a longer wavelength and the intensity often increases.

Although the absorption bands observed in the UV and visible regions are often not specific enough to allow identification of an unknown sample, this information can be used to

confirm the structure deduced from its NMR or infrared spectrum or by other methods. When molecules are exposed to a radiation of a certain wavelength that energy matches an electronic transition within the molecule, some of this radiation will be absorbed. The spectrometer records the degree of absorption at each wavelength. Since the absorbance of a sample is proportional to the amount of molecules along the spectrometer light beam, it is important to correct the absorbance value considering this and other factors in order to be able to compare the absorption of different materials. This corrected value is called “molar absorptivity” and is defined by the following equation:

$$\varepsilon = A / (c l)$$

where A is absorbance, c is the sample concentration in moles/liter, and l is the length of light path through the sample in cm.

The absorbance (A) is related to percentage transmittance T by the equation:

$$A = \log \left(\frac{I_0}{I} \right) = \log \left(\frac{100}{T} \right) = \varepsilon cl$$

Where, I_0 is the intensity of the incident radiation and I is the intensity of the transmitted radiation. The ratio I/I_0 is called transmittance, which is also expressed as % transmittance. In the spectrophotometer, a sample is illuminated with the beam of monochromatic light and the I/I_0 ratio is measured.

Figure 3.5. A schematic diagram of a spectrophotometer [13].

Figure 3.5 demonstrates main components of a spectrophotometer. A beam of light passes through a monochromator, so monochromatic radiation is generated, which then passes through the sample and intensity of this light is detected. In the present work, UV-Vis absorption spectra were recorded using a Shimadzu UV-2700 Spectrometer.

When a molecule has absorbed a photon, which results in the transition to the excited state, a rapid relaxation from the higher vibrational level to the lowest one occurs via non-radiative dissipation of the energy to the environment due to intermolecular collisions. When the molecule reaches the lowest energy level of the lowest excited state, the molecule can return to the one of the vibrational levels of its ground state by means of light emission known as fluorescence (**Figure 3.6**) [14].

Figure 3.6. The mechanism of fluorescence.

The phenomena of fluorescence has some characteristic features. First, the emission wavelength is usually independent from the excitation wavelength due to the fast internal conversion. Second, there is the mirror image rule, which is related to the fact that the vibration levels of the excited states resemble those of the ground state. In emission spectra, the peaks are usually broadened due to equilibrium in solution state and fast relaxation. The third feature is the wavelength gap between the emission and the absorption peak, known as the Stokes Shift (**Figure 3.7**). This red-shift of the emission peak has several reasons, such as excited-state reactions, solvent orientation effects, formation of complexes, etc.

Figure 3.7. An example of the mirror reflection between the absorption and the emission spectra [15].

A machine that detects and quantifies fluorescence, known as a spectrofluorimeter, has the same components as a spectrophotometer. However there are two major differences, such as the second monochromator placed before the detector, and the position of the detector at 90° to the incident light beam in order to avoid interference of the transmitted excitation light. In this work, a Cary Eclipse Fluorescence Spectrophotometer was used.

An important characteristic of fluorescence is quantum yield, which defines the efficiency of the photon emission process. The quantum yield (Φ) is a ratio of the number of the emitted photons to the number of the photons being absorbed. In this project, the absolute quantum yields were determined by the group of associate Professor Sun Handong at the School of Physical and Mathematical Sciences, NTU, using Quantum Efficiency Measurement System QE-2000 (Otsuka Electronics Co., Ltd) employing the integrated sphere technique [16]. The given Φ values for solutions in chloroform are average values of three independent measurements.

UV Visible absorption spectroscopy is a very useful technique to determine a band gap of an organic semiconductor. Since an electron in a molecule is transferred from lower energy orbital (highest occupied molecular orbital, HOMO) to higher energy orbital (LUMO)

upon absorption of a photon having quantified energy, it is possible to determine a bandgap energy of the molecule $E_g^{opt} = E(LUMO) - E(HOMO)$ using the following equation [17-19]:

$$E_g^{opt} = \frac{hc}{\lambda_{onset}} = \frac{1242}{\lambda_{onset} (nm)}$$

In this equation, h is Planck's constant, c is the speed of light, and λ_{onset} is the onset of a peak at the longest absorption wavelength.

3.5. Cyclic voltammetry

Cyclic voltammetry is an electrochemical technique which is used to investigate oxidation and reduction processes for materials under different values of electrical potentials [20]. In this method, the current change is detected as the voltage sweep goes through a three electrode (working, counter, and reference) circuit immersed into the sample solution containing an auxiliary electrolyte. **Figure 3.8** demonstrates a typical loop for a reversible electrochemical process with only one electrochemically active component present.

Figure 3.8. A typical cyclic voltammogram [21].

The oxidation process at the anode occurs during the forward sweep (from V_1 to V_2), and the reduction on the cathode occurs during the reversed sweep. There are three criteria of

a reversible electrochemical process, based on a voltammogram:

- 1) The voltage gap between the reduction and the reduction current peaks is only dependent on the number of electrons involved in the process:

$$\Delta E = E_p^a - E_p^c = \frac{59}{n} \text{ mV}$$

- 2) The intensities of the anode and cathode current peaks are comparable or equal:

$$\frac{i_p^a}{i_p^c} = 1$$

- 3) The peak voltage value is independent on the scan rate, while the peak current is proportional to the square root of the scan rate, as per Randles-Sevcik equation:

$$i_p = (2.69 * 10^5) n^{3/2} S D^{1/2} \nu^{1/2} C_A^*$$

In this equation, n is the number of electrons transferred in the reduction, S is the working electrode surface area (cm^2), D is the diffusion coefficient, ν is the sweep rate, and C_A^* is the molar concentration of the material A in the bulk solution.

For irreversible electrochemical reactions, usually the higher voltage is required at a slower scanning rate in order to drive the reaction, which is related to the drifting speed of the active species and the change of diffusion with the thickness.

Cyclic voltammetry is a very useful technique which can be utilized for various applications. The technique can be used to obtain qualitative information on electrochemical processes under various conditions, such as reversibility of the electrochemical reaction and the presence of intermediates in oxidation and reduction reactions. In quantitative analysis, it can be used to determine the formal reduction potential, the electron stoichiometry of the system, and the diffusion coefficient of an analyte.

Cyclic voltammetry is also a very useful technique to estimate energy band diagrams for

organic semiconductors [22-24]. For these materials, HOMO represents the energy required to extract an electron from the molecule, which is an oxidation process, and LUMO represents the energy needed to add an electron to the molecule, which is a reduction process. These processes can be defined using cyclic voltammetry by measuring corresponding reduction E_{red} and oxidation E_{ox} potentials [19]. In order to calculate the HOMO and LUMO energy levels of the analyte, the known value for ferrocene is used, whose HOMO level is commonly considered to be -4.8 eV [25]. For the case when ferrocene is used as pseudo-reference for cyclic voltammetry experiment, the HOMO and LUMO levels can be determined using the following equations [26]:

$$E(\text{HOMO}) = -(E_{\text{ox}}^{\text{onset}}(\text{vs. Fc/Fc}^+) + 4.80)$$
$$E(\text{LUMO}) = -(E_{\text{red}}^{\text{onset}}(\text{vs. Fc/Fc}^+) + 4.80)$$

In this work, cyclic voltammetry experiments were performed using a CHI 604E Electrochemical Analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm²) was used as working electrode, platinum wires were used as counter electrode and reference electrode, respectively. nBu₄NPF₆ (0.1 M) was used as supporting electrolyte. Potential was recorded in an anhydrous DCM solution and the scanning rate was 50 mV/s. Fc⁺/Fc (HOMO = -4.8 eV) was used as an external standard.

3.6. Li SES preparation

Since operations with lithium require an inert atmosphere and anhydrous conditions, all the experiments with Li SES were carried out in an inert atmosphere of argon inside a glovebox (Model EQ-VGB-4, MTI). A defined amount of lithium foil was added to a mixture of PAH and anhydrous THF (supplied by Sigma Aldrich: anhydrous, inhibitor-free, >99.9%; stored over 4Å molecular sieves for 3 days prior to use), then stirred using a glass magnetic stirrer in a sealed glass bottle at room temperature until all the lithium has dissolved, which usually took from 24 to 72 hours.

3.7. Conductivity and conductivity versus temperature measurements

The conductivity (σ) refers to the ability of a solution to conduct an electrical current with no relations to geometrical factors and is measured in Siemens per centimeter (S/cm). This property of a solution remains constant at a fixed temperature and composition. For the case of a simple two-electrode cell having an uniform cross-section (A), where the electrodes are separated by a distance (l), the conductivity is given as [27]:

$$\sigma = G \frac{l}{A}$$

where G is the solution conductance.

Ohm's law demonstrates the following correlation between electrical current (I) that passes through the solution, the potential difference across (ΔV) the electrodes, and resistance (R):

$$\Delta V = IR$$

Since $R = \frac{1}{G}$, the conductance can be obtained as $G = \frac{1}{R}$.

Although two electrode technique is the simplest experiment to determine conductivity, it is unable to mitigate the possible contamination or damage of the electrode surface due to deposits formation, which leads to the increase of contact resistance [9]. A reliable way to eliminate these issues is a four electrode technique, which utilizes reference voltage to compensate any contamination or damage of the electrodes [28].

In this project, a Cond 3310 meter equipped with TetraCon 325 Standard conductivity cell probe (measurement range 1 μ S/cm to 2 S/cm) utilizing four-electrode measuring principle was used for conductivity studies [29]. Measurements were performed by immersion of the probe in the solution. Prior to measurements, the meter was calibrated with standard 0.01 M KCl solution. **Figure 3.9** demonstrates the schematic diagram of the probe.

Figure 3.9: The schematic diagram of TetraCon 325 probe. 1- pair of voltage electrodes; 2 - pair of current electrodes, 3 - Temperature sensor, 4 – Shaft, 5 - Connection Head (Adapted from Ref [29] with permission from Xylem Analytics, Inc.).

In order to perform conductivity versus temperature measurements, Li SES was placed in a sealed tube with attached TetraCon 325 probe. After the cell was assembled (**Figure 3.10**), it was taken out of the glove box and immersed into ice/water mixture. The readings were taken after removing the cooling bath and gradually warming up the cell to the ambient conditions. The uncertainty in the temperature measurement is ± 0.1 °C, and the uncertainty in the conductivity values is ± 1 μ S.

Figure 3.10. Conductivity vs temperature experiment setup.

3.8. Test Cell Design and setup

A prototype of the cell Li SES // air was patented in 2010 [30]. The schematic diagram of the cell is shown in the **Figure 3.11**.

Figure 3.11. Schematic diagram of the Li SES // air prototype model. (Adapted from Ref: [30] with permission from Prof Rachid Yazami).

The H-shaped cell consists of two glass tubes with the solid electrolyte ceramic membrane fixed in between the tubes using an epoxy glue to prevent leakage. The membrane is Li-ion conducting LTAP produced by Ohara Inc. The glass tubes are equipped with hermetic Teflon caps and stainless steel wires connecting the inner and the outer sides of the glass tubes. The epoxy glue is applied at the top of the caps to prevent the air entering the cells via the grooves between the caps and the stainless steel wires. The stainless steel wires are connected to the metal grids, which serve as current collectors. The glass tubes are filled with liquid based electrodes (anolyte and catholyte) and sealed with the caps to make the air-tight system. If the air is used as a cathode material, the catholyte side is unscrewed allowing oxygen to enter the system. **Table 3.1** demonstrates the electrochemical reactions

that occur upon discharge of the cell.

Table 3.1. Characteristics of Li SES//air battery with oxygen as cathode (left) and water (right).

Cell structure	Li SES (Anode)// Li-conducting ceramic membrane //Oxygen (Cathode)	Li SES (Anode)// Li-conducting ceramic membrane //Water (Cathode)
Anode	$\text{Li}_x(\text{PAH}) \rightarrow x\text{Li} + \text{PAH} + x\text{e}^-$	$\text{Li}_x(\text{PAH}) \rightarrow x\text{Li} + \text{PAH} + x\text{e}^-$
Cathode	$x\text{Li}^+ + x\text{e}^- + (x/2) \text{O}_2 \rightarrow (x/2) \text{Li}_2\text{O}_2$	$x\text{Li}^+ + x\text{e}^- + x\text{H}_2\text{O} \rightarrow x\text{LiOH} + (x/2)\text{H}_2$
Overall reaction	$\text{Li}_x(\text{PAH}) + (x/2) \text{O}_2 \rightarrow (x/2) \text{Li}_2\text{O}_2 + \text{PAH}$	$\text{Li}_x(\text{PAH}) + x\text{H}_2\text{O} \rightarrow x\text{LiOH} + (x/2)\text{H}_2 + \text{PAH}$

However, this prototype cell has very significant limitations:

- 1) The epoxy glue can react with Li SES leading to the sample contamination
- 2) Since epoxy glue is very difficult to remove when it is hardened and it is used to put the parts of the cell together, it is a very complex task to disassemble the cell without breaking it.
- 3) PTFE (Teflon) reacts with Li SES [31]
- 4) Since commercially available PTFE (Teflon) sheets and rods are often found to be porous [32], the material may allow air to enter the cell over time.

Considering all the disadvantages of the prototype cell, an upgraded cell configuration was used in this project [33, 34], whose schematic diagram is shown in **Figure 3.12**.

Figure 3.12. The schematic diagram of the test cell used in this project [33, 34].

This cell has a similar configuration to the one shown in **Figure 3.11**. The caps are made of a material that is resistant to Li SES (polyetheretherketone, PEEK) and connected to the tubes with screw threads. O-rings made of fluorinated rubber provide sealing between the cap and the tube, and between the steel wire and the cap. The membrane holder is made of PEEK, as well as the parts that connect the membrane with the tubes by means of the screw thread. The aluminum screw sleeve tightens the membrane holder and the tube connectors together. Since all the parts are connected via screw threads, there is no difficulty in assembling and disassembling the cell. Current collectors are made of nickel mesh spot-welded onto nickel wire. No platinum was used in this setup due to possibility of Pt-Li alloy formation upon reaction between Li SES and platinum leading to permanent damage of the electrodes.

Figure 3.13. Cell used for OCV measurements.

The cell shown in **Figure 3.12** and **Figure 3.13** was used for half-cell OCV measurements. In this case, one of the Ni meshes is wrapped with Li foil and immersed in an electrolyte solution of LiPF_6 (1 M) in EC:DEC (1:1 by volume). This cell is schematically describe as follows:

Since metallic lithium has lower value of electrode potential than Li SES, the metal becomes an anode in this cell. This cell allows to measure standard electrode potentials of various Li SES versus lithium metal. Also, the half-cell experiments performed at different temperatures allow to determine thermodynamic parameters of the half-cell.

The half-cell has the following reversible electrochemical reaction, which is in thermodynamic equilibrium (δ , which is much lower than x , denotes a small portion of lithium involved in the process):

In the half-cell, OCV is a function of composition (x), pressure (P), and temperature (T). Since the pressure has no meaningful changes, $E(x,P,T)$ turns into $E(x,T)$ in the half-cell experiments.

The half-cell free energy is related to $E(x,T)$ via the following equation:

$$\Delta G(x,T) = -nFE(x,T)$$

Where n is the number of charge carried by the ion exchanged in the half-cell (n is 1 for Li^+) and F is a Faraday constant (96485 C mol^{-1}). Thus, the free energy can be derived from $E(x,T)$. Moreover, ΔG is related to the enthalpy ΔH and entropy ΔS according to the following equation:

$$\Delta G(x,T) = \Delta H(x) - T \Delta S(x)$$

Combining these equations and obtaining the derivative of $E(T)$ function, we can define molar $\Delta H(x)$ and molar $\Delta S(x)$ for Li_xPAH in a half-cell at a particular value of x with the following formulas [35]:

$$\Delta S(x,T) = F \left(\frac{\partial E(x,T)}{\partial T} \right) \bigg|_x$$

$$\Delta H(x,T) = -F \left(E(x,T) - T \frac{\partial E(x,T)}{\partial T} \right) \bigg|_x$$

In these equations, $\left(\frac{\partial E(x,T)}{\partial T} \right) \bigg|_x$ is a slope of the $E(T)$ plot for the fixed composition x , thus, the intercept of this plot is $-\Delta H/F$. Thus, the OCV measurements performed at different temperatures using this half-cell allow to determine thermodynamic parameters of corresponding Li SES having various compositions in charge/discharge reactions. This method was previously used to identify ΔS and ΔH of solid-state electrodes in Li-ion batteries (Li_xC_6 [36] and Li_xCoO_2 [37]).

In this project, OCV vs temperature experiments were performed using the following procedure: the half-cell was assembled in a glove box, then placed into a climate chamber. The half-cell was cooled down to 10°C , then the OCV was recorded upon heating the half-cell up to 25°C in the climate chamber. The temperature was detected using a thermocouple connected to the Li SES part of the half-cell. The uncertainty in the

temperature measurement is ± 0.1 °C, and the uncertainty in the voltage values is ± 1 mV.

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Chapter 4*

p-Terphenyl and Anthracene based Li SES

This chapter discusses the studies on Li SES derived from p-terphenyl and anthracene. p-Terphenyl is a molecule of biphenyl with one additional benzene ring connected via a C-C bond, and anthracene is naphthalene with one additional fused benzene ring. The chapter begins with conductivity studies. This section shows that the maximum achieved conductivity for diluted solutions is for Li:PAH ratio equal to 1:1. The maximum Li:PAH ratios reached in the experiments are 2.4:1 for p-terphenyl and 2:1 for anthracene. The Li SES prepared from suspensions of these PAH in THF give solutions with much higher concentrations and many times higher conductivity. Open circuit potential versus temperature experiments in a half-cell allowed the ΔS and ΔH values of the corresponding Li SES at different Li:PAH ratio to be derived. The values of ΔS demonstrate quasi linear increase with the ratio increase, while ΔH demonstrates more complex correlation. The change of ΔH trend for Li:p-terphenyl ratio >2 , as well as the maximum achieved ratio of 2.4 suggests the formation of adducts with two molecules of p-terphenyl. This concept is supported by our model based on the First Principle calculations. The more concentrated Li SESs prepared from suspensions demonstrate deviations from the values for the diluted solutions due to more significant intermolecular interactions.

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4.1. Introduction

Considering the preliminary results on biphenyl and naphthalene, it was decided to continue the studies on p-terphenyl (**49**), that has one more benzene ring connected by C-C bond than biphenyl, and anthracene (**8**), that has one more fused benzene ring than naphthalene (Figure 4.1).

Figure 4.1. Chemical structures of biphenyl, naphthalene, p-terphenyl (**49**) and anthracene (**8**).

4.2. Preparation of Li SES based on p-Terphenyl and anthracene

Li SES were prepared by dissolving lithium metal in THF solutions of **49** and **8** in THF. Since these materials have limited solubility in THF, the studies were initiated with 0.1 M solutions, having the formulas of $\text{Li}_x(\text{PAH})(\text{THF})_{12.3}$. Lithium metal was added to a THF solution of corresponding PAH in a glove box under the atmosphere of argon and then stirred in a sealed bottle for 24h. The reaction gives dark solutions whose color varies from green when the Li:PAH molar ratio is below 1.5:1 to dark orange when the ratio is 2:1 or above. The maximum achieved Li:**49** molar ratio is 2.4:1 and the highest Li:**8** ratio is 2:1. Larger amounts of lithium do not react with the solutions. It was also found that Li SES can be prepared from suspensions of corresponding PAH in THF, meaning that Li SES of a certain concentration can be prepared even if PAH solubility is limited. Li SES with the composition $\text{Li}_x(\text{PAH})(\text{THF})_{12.3}$, which corresponds to ~ 1 M solutions (not considering volume expansion), were successfully prepared using suspensions of **8** or **49** in THF.

4.3. Conductivity (σ) of p-terphenyl and anthracene based Li SES

Among the 0.1 M solutions of p-Terphenyl (**49**) based Li SES, $\text{Li}_{1.0}(\textbf{49})(\text{THF})_{123}$ demonstrates the highest conductivity, and $\text{Li}_{2.4}(\textbf{49})(\text{THF})_{123}$ exhibits the minimum. The value of $\text{Li}_{0.5}(\textbf{49})(\text{THF})_{123}$ stays in between of those for $\text{Li}_{2.3}(\textbf{49})(\text{THF})_{123}$ and $\text{Li}_{2.4}(\textbf{49})(\text{THF})_{123}$ (**Figure 4.2**). All the p-terphenyl based Li SES demonstrate quasi-linear decrease of conductivity upon the increase of temperature, which is similar to metals, as well as Li SES based on ammonia [1] and other polyaromatic hydrocarbons (PAH), such as naphthalene, biphenyl, and corannulene. The most significant decrease in conductivity upon the temperature increase is observed for $x = 1.0$ and 1.5 , while the slope is much less steep for the higher values of n . The values of conductivity at 22 °C are shown in **Table 4.1**.

Figure 4.2. The conductivity versus temperature graphs for $\text{Li}_x(\textbf{49})(\text{THF})_{123}$, $x = 0.5, 1.0, 1.5, 2.0, 2.3, 2.4$.

The Li SES of higher concentrations (~ 1 M) with the general formulae $\text{Li}_{1.0}(\textbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{2.0}(\textbf{49})(\text{THF})_{12.3}$ were prepared from suspensions of **49** in THF. We found that the conductivity values at 22 °C (**Table 4.1**) increase more than twelve times for

$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ and more than five times for $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ compared to SES with a ten times lower concentration of $\sim 0.1 \text{ M}$ ($\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ respectively). As shown in **Figure 4.3**, $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ has higher conductivity than $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$. Surprisingly, unlike $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ which showed a metal-like linear decrease of the conductivity within an increase of temperature, $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ demonstrates an insignificant increase of conductivity within the temperature increase. The measured values of conductivity consist of both ionic and metallic conductivity: $\sigma = \sigma_I + \sigma_M$. The metallic conductivity increases with the increase of T , while the ionic conductivity decreases:

$$\left. \frac{\partial \sigma_I}{\partial T} \right|_x > 0; \left. \frac{\partial \sigma_M}{\partial T} \right|_x < 0$$

Thus, $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ has a higher contribution of the ionic type of conductivity than the metallic one most probably due to the high amount of Li^+ present.

Figure 4.3. The conductivity versus temperature graphs for $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$.

Table 4.1. The conductivity ($\mu\text{S}/\text{cm}$) values at 22 °C for the compositions $\text{Li}_x(\mathbf{49})(\text{THF})_n$ tested.

Li SES	σ ($\mu\text{S}/\text{cm}$) at 295 K	σ (T, range 280 – 295 K) ($\mu\text{S}/\text{cm}$) =
$\text{Li}_{0.5}(\mathbf{49})(\text{THF})_{123}$	103	$-4.94T + 1564$
$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{123}$	636	$-20.2T + 6594$
$\text{Li}_{1.5}(\mathbf{49})(\text{THF})_{123}$	460	$-20.0T + 6339$
$\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{123}$	288	$-4.89T + 1728$
$\text{Li}_{2.3}(\mathbf{49})(\text{THF})_{123}$	188	$-2.86T + 1061$
$\text{Li}_{2.4}(\mathbf{49})(\text{THF})_{123}$	54	$-1.36T + 468$
$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$	8140	$-88.9T + 34175$
$\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$	1614	$+6.93T - 425$

Anthracene (**8**) based Li SES with the formula $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$ demonstrate an increase of conductivity with the increase of Li:**8** ratio reaching the maximum at the ratio of 1:1. Then it drops with the lowest value being measured for the 2:1 ratio (**Figure 4.4**). Remarkably, the conductivity values for $\text{Li}_{0.5}(\mathbf{8})(\text{THF})_{123}$ and $\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{123}$ are close to each other, as well as the values for $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{123}$ and $\text{Li}_{1.5}(\mathbf{8})(\text{THF})_{123}$. All the solutions demonstrate the negative quasi-linear trend of $\sigma(T)$, similar to Li SES based on p-terphenyl of the same concentration.

Figure 4.4. The conductivity versus temperature graphs for $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$, $x = 0.5, 1.0, 1.5, 2.0$.

The Li SES prepared from suspension of anthracene (**8**) in THF having the formulae of $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ (~1 M solution, not considering volume expansion) demonstrate much higher conductivity comparing to the diluted solutions, which is close to the value obtained for naphthalene (~12.4 mS/cm for $\text{Li}_{0.5}(\text{Naphthalene})(\text{THF})_{6.2}$) and more than sixteen times higher than the ten times less concentrated $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ (**Figure 4.5**). The conductivity values for $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ are ~1 mS/cm higher than those for p-terphenyl based $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$. However, the value for $\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{12.3}$ is about ten times lower comparing to $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$. Unlike $\sigma(T)$ trend for p-terphenyl based $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$, the values of conductivity decrease upon temperature increase for both $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ and $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$, although the value of the slope for the last one is very low meaning that $\sigma_I \sim \sigma_M$. The values of conductivity at 22 °C (295 K), as well as linear approximations of $\sigma(T)$, are shown in **Table 4.2**.

Table 4.2. The conductivity ($\mu\text{S}/\text{cm}$) values at 22 °C (295 K) for the compositions $\text{Li}_x(\mathbf{49})(\text{THF})_n$ tested.

Formula	σ ($\mu\text{S}/\text{cm}$)	σ (T), ($\mu\text{S}/\text{cm}$) =
$\text{Li}_{0.5}(\mathbf{8})(\text{THF})_{123}$	219	$-4.84T + 1644.0$
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{123}$	547	$-11.25T + 3839.8$
$\text{Li}_{1.5}(\mathbf{8})(\text{THF})_{123}$	528	$-10.41T + 3594.1$
$\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{123}$	223	$-3.84T + 1354.1$
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$	8980	$-78.2T + 3207$
$\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{12.3}$	754	$-0.02T + 759.6$

Figure 4.5. The conductivity versus temperature graphs for $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ and $\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{12.3}$.

4.4. Open-circuit potentials, entropy and enthalpy

4.4.1. p-Terphenyl

The E vs T profiles of p-terphenyl based $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ ($x = 0.5, 1.0, 2.0, 2.3, 2.4$) in Li/Ceramics/Li SES half-cell configurations (described in Chapter 3) [2] are shown in **Figure 4.6**. The OCP values are versus Li/Li^+ . The formula $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ corresponds to 0.1M solution of PAH in THF.

Table 4.3 shows open circuit potential E values vs Li/Li^+ at 295.15K (22°C) for the Li SES tested, as well as the linear fit E(T) equations in the range 12 – 22°C (285 – 295 K). Among the studied $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$, the highest value of E is for $x = 0.5$, then it gradually decreases to the lowest value for $x = 2.4$. For all these Li SES, E linearly decreases with the increase of temperature. All the E values are below 1 V.

Table 4.3. Open-circuit potential (E) values at 22 °C and linear fit E(T) equations of $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$, $x(\text{Li}) = 0.5, 1.0, 2.0, 2.3, 2.4$.

x in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$	E (mV) vs Li^+/Li at 295 K	E (T, range 285 – 295 K) =
0.5	780.4	$-1.74T + 1293.1$
1	770.8	$-2.10T + 1389.2$
2	729.8	$-2.74T + 1539.1$
2.3	659.8	$-2.92T + 1522.5$
2.4	584.2	$-3.03T + 1478.7$

Figure 4.6. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$, $x(\text{Li}) = 0.5, 1.0, 2.0, 2.3, 2.4$.

Figure 4.7 shows the correlation between E at 22 °C and $z = x(\text{Li})/x(\text{Li})_{\text{max}}$; where $x(\text{Li})_{\text{max}} = 2.4$. Considering the following equation ($v = 1$ for Li^+ , and $F = 96485 \text{ C mol}^{-1}$), that demonstrates the correlation between z and E:

$$E(z) = E^\circ + k \frac{RT}{vF} \ln \left(\frac{1-z}{z} \right)$$

the values of potential E° and the coefficient k , which shows the deviation of the studied solutions from the ideal solution, can be obtained via fitting the data to the equation. The calculated values are: $E^\circ = 0.76 \text{ V}$, and $k = 1.1$. The coefficient k represents deviation from the ideal solution. Since the studied Li SES are quite dilute, the deviation of the coefficient from 1 is insignificant.

Figure 4.7. Correlation between E at 295 K and $z = x(\text{Li})/x(\text{Li})_{\text{max}}$.

The entropy (ΔS) and enthalpy change (ΔH) of a corresponding Li SES formation can be assessed using the following thermodynamics equations [3] (note that one electron is transferred from lithium metal, F is a Faraday constant):

$$\Delta S = F \frac{\partial E}{\partial T}$$

$$\Delta H = -F \left(E - T \frac{\partial E}{\partial T} \right)$$

Thus, the entropy changes were derived from the slopes of the corresponding linear fits, and the enthalpy changes from the intercepts. The resulting values of the entropy and the enthalpy changes of the half-cell reactions are shown in the **Table 4.4**.

As seen from the **Table 4.4**, both the absolute values of the entropy and the enthalpy change increase upon the increase of n . The correlation between the entropy and the enthalpy versus the amount of lithium (x) in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ demonstrates a linear trend (**Figure 4.8**) until the maximum Li:PAH ratio 2.4 for ΔS , but only until 2 for ΔH . As x increases above 2, the value of ΔH becomes smaller, which is discussed below.

Table 4.4. ΔS and ΔH values of the $\text{Li}_x(\mathbf{49})(\text{THF})_{123}/\text{Li}$ half-cells, $x = 0.5, 1.0, 2.0, 2.3, 2.4$.

x in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$	ΔS ($\text{J K}^{-1}\text{mol}^{-1}$)	ΔH (kJ mol^{-1})
0.5	-167.8	-124.8
1	-202.6	-134.0
2	-264.4	-148.5
2.3	-281.7	-146.9
2.4	-292.4	-142.7

Figure 4.8. Correlations between the entropy change (left), the enthalpy change (right) and $x(\text{Li})$ in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$.

The obtained composition-dependence of ΔS and ΔH for $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ is completely different from the results on the intercalation of lithium to graphite [4]. In the case of graphite, an exponential decrease of ΔS from $60 \text{ J mol}^{-1} \text{ K}^{-1}$ (for $\text{Li}_{0.01}\text{C}_6$) to $-16 \text{ J mol}^{-1} \text{ K}^{-1}$ (for $\text{Li}_{0.46}\text{C}_6$) occurs first, then a significant increase of entropy change is observed around the $\text{Li}_{0.5}\text{C}_6$ composition, which is related to a phase transition, then ΔS slowly decreases upon the $\text{Li}:\text{C}$ ratio increase (**Figure 4.9**). The ΔH values first rise from -56 kJ mol^{-1} to -15 kJ mol^{-1} , and then, after an insignificant decrease in between $\text{Li}_{0.2}\text{C}_6$ and $\text{Li}_{0.5}\text{C}_6$, a phase transition occurs leading to the increase to -8 kJ mol^{-1} . After reaching this value, the enthalpy change slowly decreases as the amount of lithium increases.

Figure 4.9. Correlations between the entropy change, the enthalpy change and $x(\text{Li})$ in solid-state Li_xC_6 [4].

Since $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ is a solution, which means its molecules have more degrees of freedom compared to the solid Li_xC_6 , the values of the entropy change are significantly higher for $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ (Table 4.4). In contrast to Li_xC_6 , where the intercalation process occurs between two solid materials (lithium metal and graphite) giving a solid Li_xC_6 , the formation of Li SES is a process where solid Li metal transfers into a liquid phase, meaning the whole system becomes much more disordered, so entropy values are negative for all $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$, as seen from the linear fit equation. Considering relatively low concentration of the studied solutions (123 molecules of THF per molecule of PAH, which is ~ 0.1 M solution of PAH in THF), the interactions between the molecules are much lower than in the solid Li_xC_6 , which prevents phase transition effects, thus, no drastic decrease or increase of ΔS is observed in particular parts of the graph. Also, since the increase of x in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ does not lead to a change in molecules' position against each other in the solution like it happens in the solid (crystal structure changes, changes in interactions between graphite layers, Li – Li interactions, etc.), the linear correlation between the composition and the entropy looks reasonable for $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$.

This fundamental difference between the liquid and the solid states also makes an impact on the enthalpy change (**Figure 4.8**). Much higher ΔH for $\text{Li}_x(\mathbf{49})(\text{THF})_{12.3}$ is probably related to a contribution from both charge transfer from Li to PAH giving Li^+ and the cation solvation by THF molecules, while it was shown that lithium atoms are essentially neutral when intercalated into graphite [5]. The correlation between ΔH and $x(\text{Li})$ is not quasi-linear, showing an increase of enthalpy when $x(\text{Li}) > 2$, which is probably related to conformational changes in the PAH molecule and effects related to lithium ion interactions. However, the correlation is quasi-linear when $0.5 < x(\text{Li}) < 2$.

We also recorded E versus T profiles for more concentrated p-terphenyl based Li SES, as are $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$, which are shown at the **Figure 4.10**. The values of E at 22 °C, as well as E(T) linear approximation equations, and ΔS and ΔH derived from E(T) are shown in **Table 4.5**.

Figure 4.10. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_x(\mathbf{49})(\text{THF})_{12.3}$, $x(\text{Li}) = 1.0$ and 2.0 .

Table 4.5. Open-circuit potentials at 22°C, E(T) equations, ΔS and ΔH of the $\text{Li}_x(\mathbf{49})(\text{THF})_{12.3}/\text{Li}$ half-cells, $x = 1.0$ and 2.0 .

Composition	OCV (E, mV) at 295 K	E (T, range 285 – 295 °C) =	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ mol ⁻¹)
$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$	758.2	$-1.35T + 1158.3$	-130.3	-111.8
$\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$	658.7	$-3.25T + 1621.0$	-313.6	-156.4

As can be concluded from the **Table 4**, the increase of concentration leads to the change of ΔS and ΔH values. The values of both ΔS and ΔH for $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ are lower than those for $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{123}$, however, these values for $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ are higher than the ones for more diluted $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{123}$. This deviation should be related to higher intermolecular interactions in the more concentrated solutions comparing to the diluted ones.

4.4.2. Anthracene

The E vs T profiles of anthracene based $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$ ($x = 0.5, 1.0, 2.0$) in Li/Ceramics/LiSES half-cell configurations (described in Chapter 3) [2], as well as the E vs T profile for ten times more concentrated $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$, are shown in **Figure 4.11**. The OCP values are versus Li/Li^+ .

Figure 4.11. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$, $x(\text{Li}) = 0.5, 1.0, 2.0, 2.3, 2.4$.

Table 4.6. Open-circuit potentials at 22 °C, $E(T)$ equations, ΔS and ΔH of the $\text{Li}_x(\mathbf{8})(\text{THF})_{123}/\text{Li}$ half-cells ($x = 0.5, 1.0, 2.0$) and $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$.

Formula	E at 22 °C (295 K), mV	$E(T)$ (mV)=
$\text{Li}_{0.5}(\mathbf{8})(\text{THF})_{123}$	941.5	$-1.31T+1329$
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{123}$	908.0	$-1.41T+1324$
$\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{123}$	903.2	$-1.75T+1423$
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$	888.1	$-1.37T+1293$

Table 4.6 shows open circuit potential E values vs Li/Li^+ at 295.15K (22 °C) for the Li SES tested, as well as the linear fit $E(T)$ equations in the range 12 – 22°C (285 – 295 K). Among the studied $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$, the highest value of E is for $x = 0.5$, then it decreases to the lowest value for $x = 2.0$. The concentrated $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$ has even lower value. For all these Li SES, E linearly decreases with the increase in temperature. All the $E(T)$ values are in between 880 and 960 mV.

Table 4.7. ΔS and ΔH of anthracene based Li SES tested in the half cell.

Formula	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ mol ⁻¹)*
Li _{0.5} (8)(THF) ₁₂₃	-126.4	-128.3
Li _{1.0} (8)(THF) ₁₂₃	-138.9	-128.6
Li _{2.0} (8)(THF) ₁₂₃	-172.7	-138.1
Li _{1.0} (8)(THF) _{12.3}	-126.4	-123.1

Figure 4.12. Correlations between the entropy change (left), the enthalpy change (right) and $x(\text{Li})$ in $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$.

The values of ΔS and ΔH calculated in the same manner as for Li SES based on **49** are shown in **Table 4.7**. The absolute values of ΔS demonstrate quasi-linear increase with the increase of $x(\text{Li})$, which is similar to **49** (**Figure 4.12**, left). The $\Delta H(x)$ demonstrates a more complex correlation having similar values for $x = 0.5$ and 1.0 , and a significant increase in the absolute value for $x = 2.0$ (**Figure 4.12**, right).

4.5. Modeling of interactions between lithium and p-terphenyl¹

For better understanding of the structure property relations in terms of p-terphenyl based Li SES, the modeling of these systems based on theoretical First Principle calculations was

¹ This part of thesis was performed in collaboration with Liu Zhihao and Assoc. Prof. Su Haibin. Since the modeling on anthracene was performed solely by Assoc. Prof. Su Haibin's group, it is not discussed in this thesis.

performed in collaboration with Assoc. Prof. Su Haibin's group. Although elaborating the model that would reflect the properties of these Li SES in the most precise way is still under development, this section describes the initial results.

Standard DFT calculations at uM06 theory level where the Van Der Waals force was taken into consideration have been performed with Gaussian 09 software package. In the calculation, the 6-31g (d,p) basis set in combination with uM06 were used to optimize the geometries of the binding structures and calculate the energies of all molecules. Various binding structures between lithium atoms and p-terphenyl molecules were considered and optimized and their energy profiles were obtained. The most stable binding structure with lowest energy was selected to model the interaction between lithium atoms and p-terphenyl molecules.

The maximum achieved Li:**49** ratio of 2.4 in the experiments, which is close to 2.5, suggests the formation of a layered dimer with the formula of $\text{Li}_{5.0}(\text{49})_2$, where lithium is placed in between of the p-terphenyl molecules. The dimer formation is also possible for Li:PAH ratio of 1:2 (0.5 Li per PAH). The calculations support this idea, showing that the dimer structures $\text{Li}_y(\text{49})_2$ demonstrate lower average binding energy per Lithium atom ΔE_{Li}^B compared with the binding structures where lithium atoms only interacts with one molecule of **49**. The geometrical structures of the binding complexes of lithium with one or two molecules of **49** and the corresponding binding energies are illustrated in **Figure 4.13**. For structures with one PAH molecule having Li:PAH ratios of 1:1 and 2:1, the side benzene rings are out of the plane of the middle benzene ring. Also, the σ -bonds bent a little bit due to the interaction with lithium atoms while this bending disappears at the dimer structures due to the interaction between two molecules of **49**. Surprisingly, lithium atoms tend to fill the space between the molecules of p-terphenyl first, only the fifth atom of lithium appears outside of this area. This could be related to the fact that the influence of solvent on Li – PAH interaction was not considered in this model, thus, the interaction with two molecules of p-terphenyl is more favorable in terms of energy comparing to only one molecule. However, the influence of solvent can make a very significant impact on the geometry of Li – PAH ionic pairs, as well as the energy of the system due to solvation of the lithium

ion, thus, we will be necessary to consider this factor in future models in order to make them more accurate.

a)

$$\text{Li}(\mathbf{49}): \Delta E_{\text{Li}}^B = -0.637 \text{ eV}$$

$$\text{Li}_2(\mathbf{49}): \Delta E_{\text{Li}}^B = -0.993 \text{ eV}$$

b)

$$\text{Li}(\mathbf{49})_2: \Delta E_{\text{Li}}^B = -1.401 \text{ eV}$$

$$\text{Li}_2(\mathbf{49})_2: \Delta E_{\text{Li}}^B = -1.623 \text{ eV}$$

$$\text{Li}_4(\mathbf{49})_2: \Delta E_{\text{Li}}^B = -1.774 \text{ eV}$$

$$\text{Li}_5(\mathbf{49})_2: \Delta E_{\text{Li}}^B = -1.623 \text{ eV}$$

Figure 4.13. Calculated structures of $\text{Li}_x(\mathbf{49})$ and $\text{Li}_x(\mathbf{49})_2$. a): geometrical structures with one p-terphenyl (**49**) molecule when Li:PAH ratio is 1:1 and 2:1; b): geometrical structures with 2 p-terphenyl molecules forming burger-like structures. The average interaction (binding) energies ΔE_{Li}^B are shown below the structures.

Table 4.8. Calculated average binding energy (eV) for $\text{Li}_x(\mathbf{49})_2$.

x in $\text{Li}_x(\mathbf{49})_2$	Average binding energy (ΔE_{Li}^B , eV)
1	-1.401
2	-1.623
4	-1.744
5	-1.502

The average binding energies ΔE_{Li}^B per lithium atom for the dimers obtained from these calculations are shown in **Table 6**. The table shows that the highest value of ΔE_{Li}^B is for $\text{Li}_4(\mathbf{49})_2$, while the lowest is for $\text{Li}_1(\mathbf{49})_2$. Since the binding energy represents the energy that the system produces upon interaction with a certain amount of lithium, it should correlate with the enthalpy change: $\Delta E_{Li}^B \sim \Delta H$ [6]. **Figure 4.14** shows the comparison of calculated ΔE_{Li}^B (in kJ per mol) and experimental values of $\Delta H(x)$. This comparison demonstrates that $\Delta E_{Li}^B(x)$ and $\Delta H(x)$ have similar trend. Both the values decrease from $x = 0.5$ to $x = 2.0$, then the increase is observed. The value for $x = 2.5$ is lower than the value for $x = 0.5$. Since the experimental maximum of x is 2.4, not 2.5, it is expected that the difference between the values of ΔH when $x = 2$ and 2.5 is not as significant as this difference for ΔE_{Li}^B . Also, the values for ΔH and ΔE_{Li}^B are of the same order (in kJ/mol), with the maximum difference for $x = 2$ (~ 20 kJ/mol) and the minimum for 2.5 (~ 2 kJ/mol).

Figure 4.14. Experimental values of Enthalpy (ΔH) and calculated values of Binding energy ΔE_{Li}^B vs $x(Li)$.

4.6. Conclusions

Among tested $Li_x(49)(THF)_{12,3}$, the Li SES with $x = 1$ demonstrates the highest conductivity. For $x > 1$, the conductivity of Li SES gradually decreases until $x = 2.4$ (the lowest value). 2.4 is the highest achieved Li : PAH ratio for p-Terphenyl (49). Anthracene based Li SES demonstrates the highest conductivity for Li:8 ratio of 1:1. The maximum Li:8 ratio achieved is 2:1. All these Li SES demonstrate metal-like linear decrease of the conductivity with the increase of temperature.

Li SES can be prepared from suspensions of p-terphenyl or anthracene in THF, giving Li SES with many times higher conductivity than the more diluted solutions (8.1 mS/cm for $Li_{1.0}(49)(THF)_{12,3}$, 1.6 mS/cm for $Li_{1.0}(49)(THF)_{12,3}$, and 9.0 mS/cm for $Li_{1.0}(49)(THF)_{12,3}$ at 22 °C,). However, the conductivity value of $Li_{2.0}(8)(THF)_{12,3}$ is significantly lower (754 μ S/cm at 295 K). Although $Li_{1.0}(49)(THF)_{12,3}$ demonstrates linear decrease with temperature increase, $Li_{2.0}(49)(THF)_{12,3}$ shows a slight increase in conductivity with the increase of temperature due to the higher contribution of ionic conductivity. The

conductivity of $\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{12.3}$ has insignificant changes upon temperature increase due to the same reasons.

The OCP values for Li SES based on **49** and **8** decrease upon the increase of Li:PAH ratio. Li SES based on **8** exhibit higher values of OCP vs Li^+/Li comparing to **49**.

The calculated ΔS values for various $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$ and $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ are much higher than those for Li_xC_6 (**Table 4.9**), which is related to more degrees of freedom in a liquid than in a solid state. The ΔH values are much higher as well, which is probably related to a charge transfer and solvation of lithium ion upon Li SES formation.

In general, ΔS for Li SES based on **8** exhibits lower values than those based on **49**, which is similar to the situation with biphenyl and naphthalene, with the lower values of ΔS for the last one. It could be related to the fact that benzene rings in the aromatic systems with the rings connected by ordinary bonds (biphenyl and p-terphenyl **49**) can rotate along the axis of the ordinary bonds. Thus, these systems have more degrees of freedom comparing to rigid systems with fused benzene rings (naphthalene and anthracene **8**), resulting in higher absolute values of entropy.

The ΔS demonstrates linear increase of the absolute value upon the increase of x in $\text{Li}_x(\mathbf{49})(\text{THF})_{123}$ and $\text{Li}_x(\mathbf{8})(\text{THF})_{123}$. This behaviour, which is completely different from solid state Li_xC_6 , should be attributed to a fundamental difference between a liquid and a solid phases in terms of their thermodynamic properties. Since the interaction between the active species in the solution is much lower than in the solid, the phase transition effects are less likely and the intermolecular interactions have less significant influence on the system properties. The $\Delta H(x)$ is more complex for both **8** and **49** than $\Delta S(x)$.

Table 4.9. Entropy and enthalpy changes for various Li SES/Li for comparison against $\text{Li}_x\text{CoO}_2/\text{Li}$ [7] and $\text{Li}_x\text{C}_6/\text{Li}$ [4] half-cells.

Type of half-cell	ΔS ($\text{J K}^{-1}\text{mol}^{-1}$)	ΔH (kJ mol^{-1})
$\text{Li}_{0.5}(\text{Biphenyl})(\text{THF})_{24.7}$	-420	-196
$\text{Li}_{1.0}(\text{Biphenyl})(\text{THF})_{24.7}$	-467	-208
$\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{24.7}$	-290	-159
$\text{Li}_{0.5}(\mathbf{49})(\text{THF})_{123}$	-168	-125
$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{123}$	-203	-134
$\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{123}$	-264	-149
$\text{Li}_{2.3}(\mathbf{49})(\text{THF})_{123}$	-282	-147
$\text{Li}_{2.4}(\mathbf{49})(\text{THF})_{123}$	-292	-143
$\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$	-130	-112
$\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$	-314	-156
$\text{Li}_{0.5}(\mathbf{8})(\text{THF})_{123}$	-126	-128
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{123}$	-139	-129
$\text{Li}_{2.0}(\mathbf{8})(\text{THF})_{123}$	-173	-138
$\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$	-126	-123
$\text{Li}_x\text{CoO}_2/\text{Li}$, $0.5 < x < 1$	$-70 < \Delta S < 20$	$-413 < \Delta H < -382$
$\text{Li}_x\text{C}_6/\text{Li}$, $0 < x < 1$	$-18 < \Delta S < +62$	$-20 < \Delta H < -10$

In case of more concentrated solutions, as are $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$, $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$, the deviation of the ΔS and ΔH values is observed comparing to those for the diluted solutions. This effect might be attributed to more significant intermolecular interactions in the more concentrated solutions.

The initial results on modeling of interactions between lithium and molecules of p-terphenyl (**49**) demonstrate feasibility of dimeric structures formation. The calculated average binding energies demonstrate correlation with the values of enthalpy change obtained from the half-cell experiments.

These results suggest that Li SESs based on **8** and **49** may be suitable for use as anolytes

in liquid-based refuelable batteries.

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Chapter 5*

Li SES based on 1,3,5-triphenylbenzene and its derivatives

This chapter is dedicated to Li SES based on 1,3,5-triphenylbenzene. First, a rationale is given for studies on this PAH and its derivatives having various substituents. Then the synthesis of molecules having 1,3,5-triphenylbenzene framework is discussed, followed by studies on conductivity of the corresponding Li SES. This chapter also discusses half-cell experiments on these Li SES, and thermodynamical parameters based on the experimental results. The chapter finishes with discussion of the obtained results, comparison with Li SESs studied previously, and feasibility of application of 1,3,5-triphenylbenzene based Li SES in secondary batteries.

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5.1. Introduction

After performing the studies on anthracene and p-terphenyl based Li SES, it was decided to continue the investigations with 1,3,5-triphenylbenzene (**51a**, **Figure 4.1**) and its derivatives. These molecules can be classified as biphenyl derivatives with two additional phenyl rings at positions 3 and 5 of the same ring. Since this molecule has four benzene rings, it should uptake 4 atoms of Li per molecule, which is more than for biphenyl (maximum 2.5 mole equivalents of Li per PAH in 0.5 M solution) and naphthalene (<2.5 mole equivalents of lithium per molecule). Substituents with different electronic effects attached to the 4-position of each side ring may influence not only the electronic properties of these rings, but also of the central ring due to mesomeric (+M or –M) and inductive (I) effects of certain groups. Mesomeric effect means the influence of particular substituents on an electronic structure of conjugated system due to interaction between p-orbitals [1]. Inductive effect occurs due to polarization of bonds in a molecule influenced by certain functional groups. Thus, 1,3,5-triphenylbenzene is also a good structure for the study of substituent influences on Li SES properties.

In general, substituents may affect the stability of the radical ion formed during the reaction between Li and 1,3,5-triphenylbenzene derivatives in different ways. Substituents with +M effect like OMe and F in **51d-e** (**Figure 5.1**) may destabilize the radical ion due to increased electron density in the π -system. However, electron pairs of oxygen in OMe group may stabilize the Li cation and facilitate charge separation processes. By contrast, electron-withdrawing groups with –M effect in **51e-f** should stabilize the radical ion due to delocalization of the additional electron among the electronegative heteroatoms. Although incorporation of electronegative groups may lead to decrease of solubility in solvents with relatively low polarity, such as THF and diethyl ether, compounds with alkyl chains usually have higher solubility in these solvents. Substituents should also be compatible with lithium. Thus, moieties that react with lithium, like ester, hydroxy, and amino groups should not be considered. Among halogenated compounds, only Ar-F bond is tolerant to metallic lithium. Based on these considerations, structures **51a-f** were chosen for the study of substituent effects on 1,3,5-triphenylbenzene based Li SES formation and properties.

R = H (1,3,5-triphenylbenzene, **51a**),
OMe (**51b**), ⁿBu (**51c**), F (**51d**), CN (**51e**), NO₂ (**51f**)

Figure 5.1. 1,3,5-triphenylbenzene derivatives selected for Li SES studies.

5.2. Synthesis of 1,3,5-triphenylbenzene and its derivatives

There are well established approaches to the synthesis of 1,3,5-triphenylbenzene and its derivatives. The first is based on a Suzuki reaction (**Figure 5.2**), where 1,3,5-tribromobenzene reacts with the corresponding boronic acid (**52**) in presence of base (K₂CO₃ or Na₂CO₃ are standard reagents) and an appropriate palladium based catalyst in toluene, 1,4-dioxane or DMF at elevated temperature. Although different types of catalysts have been used for this reaction, Pd(PPh₃) is the standard one. This reaction goes smoothly and gives products with high yields, typically above 80%. Suzuki cross-coupling is an effective way to synthesize 1,3,5-triphenylbenzene [2] and a large variety of its derivatives (**Figure 5.2**), including those with methyl [3] (**51g**) and vinyl [4] (**51h**) substituents, electron donating (**51b**, **51i**, **51j**) [5-7] and electron withdrawing groups (**51e**, **51k**, **51l**) [8-10], as well as ones with silicon containing moieties (**51m**) [11].

Figure 5.2. Synthesis of 1,3,5-triphenylbenzene derivatives via Suzuki cross-coupling using 1,3,5-tribromobenzene.

Another approach related to Suzuki cross-coupling is a reaction between benzene-1,3,5-triyltriboronic acid or its pinacol triester (**53**) and corresponding halogenides (**54**) (**Figure 5.3**) [3, 12, 13]. $\text{Pd(PPh}_3)_4$ is a standard catalyst for this reaction, although Pd(dppf)Cl_2 or Pa(OAc)_2 as a source of Pd(0) can also be used. The reaction can be mediated by either K_2CO_3 or CsF as a base. Standard solvents for this reaction are DMF, 1,4-dioxane or DME. Although this method can afford products that contain different types of substituents [3, 12], including those with polyaromatic fragments [12, 14], its application is quite limited compared to that shown in **Figure 5.2**. The reaction yields vary from mediocre to good (35 – 80%).

Figure 5.3. Synthesis of 1,3,5-triphenylbenzene derivatives via Suzuki cross-coupling using benzene-1,3,5-triyltriboronic acid or its pinacol ether.

Despite both these approaches based on Suzuki reaction being reliable methods, that allow a variety of products with different types of substituents to be made, they have some

disadvantages. Firstly, the corresponding boronic acids (**52** and **53**) are often not commercially available materials, thus one needs to synthesize them prior to synthesis of the compounds **51a-f** via Suzuki reaction protocols. Secondly, palladium based compounds, which are standard catalysts for these type of reactions, are quite expensive. Additionally, for both the reactions excessive amounts of either boronic acid (**52** for the reaction shown in the **Figure 4.2**) or halogenide (**54** for **Figure 5.3** reaction) are required in order to obtain good yields of the product.

Another common approach to synthesis of substituted 1,3,5-triphenylbenzenes is condensation of acetophenones mediated by SiCl_4 [15] or SOCl_2 in absolute ethanol [16] (**Figure 5.4**). This reaction gives high yields of products, and is applicable for synthesis of 1,3,5-triphenylbenzenes with substituents of different nature. A significant advantage of this reaction is the availability of various starting substituted acetophenones (**55**), as well as other reagents, which gives an easy access to a variety of substituted 1,3,5-triphenylbenzenes required for the studies on substituents influence on the Li SES properties. A disadvantage of this method is that it utilizes highly reactive chemicals (SOCl_2 or SiCl_4). Additionally, aggressive compounds, like HCl , form during the reaction. It means that this method is not applicable for synthesis of 1,3,5-triphenylbenzenes with substituents that are sensitive to acidic media, such as ester groups. However, since lithium can also destroy these groups during preparation of corresponding SES, compounds with these groups would not be considered in terms of the project anyway.

Figure 5.4. Synthesis of 1,3,5-triphenylbenzene derivatives by acetophenones condensation.

Considering the pros and cons of the described methods for 1,3,5-triphenylbenzene derivatives preparation, it was decided to obtain the corresponding compounds via the acetophenone condensation procedure (**Figure 5.4**). A modification of the procedure described by Elmorsy et al. that involves SiCl_4 was used for synthesis of **51a-e** [15]. The employed procedure is described in Appendix 1 (Synthetic Procedures). Since the reaction gave relatively low yields of the products under reported conditions (stirring for 6 hours at ambient temperature), the procedure was modified by carrying out the reaction at 40 °C for 20 hours instead. The products **51a-d** were obtained in 60 – 83% yields. The structure and purity of the products was defined using ^1H and ^{13}C NMR.

Since the attempts to obtain the compound with nitro groups **51f** using SiCl_4 were not successful, SOCl_2 was used according to a literature procedure [17], which afforded the product in 65% yield. Unfortunately, the product does not dissolve in standard solvents for NMR (CDCl_3 , DMSO-D_6 , acetonitrile- D_3), so the MALDI TOF MS technique was used for the compound characterization.

In order to obtain the compound with cyano groups (**51e**), the following strategy was applied (**Figure 5.5**). First the compound **51n** was obtained via condensation of p-iodoacetophenone in EtOH- SiCl_4 mixture [18] in 60% yield. Then this compound was reacted with copper (I) cyanide in anhydrous DMF at reflux according to a literature method [19], giving the target material **51e** in 70% yield. ^1H and ^{13}C NMR spectra for the compounds **51n** and **51e** match those described in literature.

Figure 5.5. Synthesis of **51e**.

5.3. Preparation of Li SES and their conductivity

Since THF is a common solvent for PAH based SES preparation, it was decided to use it in these studies. A standard way to prepare SES is addition of lithium metal to a solution of PAH. Thus, the first step was to determine solubility of **51a-f** in THF at the ambient conditions. These results are shown in the **Table 5.1**.

Table 5.1. Solubility of **51a-f** in THF at 25 °C.

Material	Unit	51c	51b	51a	51d	51e	51f
Solubility	mg/ml	>1680	330	165	64	<11	~0
	mol/l	>3.5	0.83	0.54	0.18	<0.03	~0

These results on solubility show that the compound **51c** with n-butyl chains has the highest solubility. The compound gives viscous liquids upon mixing with THF with significant increase of volume, so the exact solubility limit was not defined. **51b**, the compound with methoxy groups, dissolves in THF better than unsubstituted 1,3,5-triphenylbenzene **51a**. **51d** has much lower solubility in THF comparing to **51a-c**. The compound with electron withdrawing CN groups **51e** has very limited solubility, and **51f** is insoluble in the most common solvents, while being slightly soluble only in DMF. Despite the materials **51d-f** having very limited solubility, dissolved traces of them might react with Li, and, if the resulting species are soluble in THF, the reaction would go further due to equilibrium shifting between solid and dissolved PAH. However, all attempts to obtain Li SES with **51d-e** by trying to dissolve Li in suspensions of these compounds in THF were not successful.

Li SESs were prepared according to the procedure described in Chapter 3. Since both lithium and corresponding adducts with conjugated systems are very sensitive to oxygen and moisture, the operations were performed under an argon atmosphere in a glovebox. Upon addition of Li (Li:PAH ratio 1:1) to 0.5 M THF solutions of **51a-c** (the formulas of the resulting Li SES are $\text{Li}_x(\text{PAH})(\text{THF})_{24.7}$) it was found that the **51a** solution turned dark blue within 5 min, and within 24 hours the whole amount of Li was completely dissolved.

Although the reaction between Li and the solution of **51b** is slower (dark blue solution starts to form after 15 – 20 minutes), there was no evidence of undissolved lithium after 24 hours. The color of the **51c** solution remained unchanged for the first 30 minutes, but it had turned dark blue after 24 hours. However, approximately 88% of Li remained unreacted, so the actual Li:PAH ratio in this solution is 0.125 : 1. Conductivity values for the resulting solutions are shown in **Table 5.2**. Among the tested materials, the unsubstituted 1,3,5-triphenylbenzene (**51a**) based solution has the highest conductivity. A solution with **51b**, the compound with n-butyl chains, demonstrates less than half that value, and the solution based on **51c**, which reacted only with ~12% of the lithium, demonstrates negligible conductivity comparing with **51a-b**. Thus, **51c** was not be considered for further experiments.

A possible explanation for the behavior of **51c** is related to the electronic properties of this material. Methoxy groups in this compound enrich its π -system electron density, which leads to destabilization of the corresponding radical anion.

Table 5.2. Conductivity readings for Li SES prepared with **51a-c** at 22 °C.

Material	51a	51b	51c
σ ($\mu\text{S}/\text{cm}$)	1550	4.7	663

5.4. Conductivity versus Li:PAH ratio and versus temperature.

Further, conductivity experiments were performed involving 0.5M THF solutions of **51a,c** with higher Li:PAH ratio. These results are shown in the **Table 5.3**. Conductivity increases for both **51a,c** upon Li:PAH mole ratio increase from 1 to 2, then starts decreasing when Li:PAH ratio is higher then 2. The conductivity values for Li:PAH = 4 is even lower than for Li:PAH = 1. For the compound **51c**, the conductivity is always more than twice less than for **51a**, and much lower than for naphthalene and biphenyl in similar conditions. This effect may be related to the insulating properties of alkyl chains, which hinders electron transfer between ionic pairs.

Table 5.3. Conductivity readings (in mS/cm) for Li SES prepared using **51a,c** with different Li mole ratio at 22 °C.

x(Li)	1	2	3	4
51a	1.55	1.87	1.37	1.13
51c	0.66	0.73	0.60	0.51

Most probably, the reason of this conductivity trend is chemical decomposition of 1,3,5-triphenylbenzene framework upon interaction with a certain amount of lithium. This effect is related to Li Pearson hardness, which means that the metal preferably interacts with large charge density centers, especially with σ -bonds. Thus, excess of Li leads to σ -bonds scission with fragmentation of the inner arene core, forming C-Li covalent bonds. This process leads to decrease in amount of free electrons and charged species, negatively affecting the conductivity. Contrary to Li, complexes of Na and K with 1,3,5-triphenylbenzene (**51a**) are stable in solution, and have been isolated [20].

Figure 5.6. ^1H NMR spectra of pure **51a** (bottom), the crude product derived from $\text{Li}_{2.0}(\mathbf{51a})$ ($(\text{THF})_{24.7}$ upon quenching with iodine (middle) and the crude product derived from $\text{Li}_{4.0}(\mathbf{51a})$ ($(\text{THF})_{24.7}$ upon quenching with iodine (top) (solvent: CDCl_3). The peak related to the **51a** middle ring is at 7.79ppm.

The products from attempts to recover the starting **51a** from the solutions with 2 and 4 equivalents of lithium per molecule of **51a** by means of quenching the solutions with iodine (equimolar to the amounts of lithium) give support to this argument (the procedure is described in Appendix 1). It was found that **51a** can be recovered from $\text{Li}_{2.0}(\textbf{51a})(\text{THF})_{24.7}$ solutions using iodine in THF. Although some products of TPB decomposition are present in the resulting mixture, the amount of **51a** present in the crude product was 38% by weight (defined by NMR, **Figure 5.6**), and, after recrystallization from ethanol, **51a** was recovered in 50% yield based on to the amount used for the Li SES preparation. On the other hand, the amount of **51a** present in the crude product derived from $\text{Li}_{4.0}(\textbf{51a})(\text{THF})_{24.7}$ was only 2 wt % (defined by NMR)., the rest is a complex mixture of decomposition products and oligomers, as seen in the NMR spectra of the crude product. The comparison between ^1H NMR spectra of pure **51a**, the crude product derived from $\text{Li}_{2.0}(\textbf{51a})(\text{THF})_{24.7}$ and the one derived from $\text{Li}_{4.0}(\textbf{51a})(\text{THF})_{24.7}$ upon quenching with iodine are shown at in the Figure 4. These results are in agreement with the observations reported previously, where a derivative of **51a** was treated with excessive amounts of lithium metal, which led to destruction of the 1,3,5-triphenylbenzene framework [20]. HPLC and GC/MS analysis of the hydrolyzed reaction mixture showed various products, including terphenyls, biphenyls, styrene and oligomers formed due to polymerization of the fragments.

Figure 5.7. The conductivity vs. temperature correlation for $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$ (black), $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ (red), $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ (green), $\text{Li}_{4.0}(\mathbf{51c})(\text{THF})_{24.7}$ (blue).

Figure 5.7 demonstrates correlation between temperature and conductivity for solutions of **51a** and **51c** containing 2 and 4 equivalents of Li per PAH. All the conductivity vs temperature plots show a negative slope (conductivity decreases with temperature); the same trend as is seen for metals and Li SES based on naphthalene and biphenyl. However, this correlation is not completely linear, unlike the plots seen for metals and Li SES based on naphthalene and biphenyl. These three Li SES samples, with the highest and the lowest conductivities for TPB, and the highest conductivity for **51c** were then selected for open-circuit potentials (E) vs temperature (T) study.

5.5. Open-circuit potentials (E) vs temperature (T) profiles of Compound **51**-based Li SES

As seen from **Figure 5.8**, the OCV for $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ in Li/Ceramics/Li SES half-cell configuration (described in Chapter 3) is much lower than for the two other solutions,

which is also a result of TPB aromatic core decomposition. The OCV value obtained for $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ vs. Li is the lowest among all Li SES studied so far.

From **Figure 5.8**, the slopes of $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$, $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ and $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ are -4.32 mV K^{-1} , -2.64 mV K^{-1} and -1.00 mV K^{-1} respectively. From the thermodynamics equations, described in Chapter 3, the enthalpy changes and the entropy changes of the half-cell reactions were computed and are presented in **Table 5.4**.

Figure 5.8. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$ (red), $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ (blue) and $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ (black) in Li/Ceramics/Li SES half-cell configurations.

Table 5.5 compares the entropy changes of the half-cell reactions of 1,3,5-triphenylbenzene based Li SES and those Li SES prepared using naphthalene and biphenyl, against the solid oxide-based LIB cathode material, Li_xC_6 and Li_xCoO_2 . As can be seen the changes in entropy (ΔS) are greater for the Li SES than for the standard anodes used in

LIBs, which can be attributed to their being in a liquid as opposed to a solid state, which allows for more degrees of freedom. The ΔS for the 1,3,5-triphenylbenzene based systems are of the same order as the values for biphenyl or naphthalene, however, the value for $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ is much lower, which could be related to the side reaction happening upon the Li SES formation.

Table 5.4. ΔH and ΔS of the $\text{Li}_x(\mathbf{51a})(\text{THF})_{24.7}/\text{Li}$ half-cells for $x = 1$ and 2 and $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}/\text{Li}$ half-cell.

Sample	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
$\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$	-190	-417
$\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$	-74	-96
$\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$	-142	-255

Table 5.5. Entropy changes ΔS for Li SES/Li; ΔS for comparison against $\text{Li}_x\text{CoO}_2/\text{Li}$ half-cell where $0 < x < 1$. Data for $\text{Li}_x\text{CoO}_2/\text{Li}$ is obtained from ref [12] and for Li_xC_6/Li from ref [13].

Type of half-cell	ΔS (J K ⁻¹ mol ⁻¹)
$\text{Li}_{0.5}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-420
$\text{Li}_{1.0}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-467
$\text{Li}_{1.0}N(\text{THF})_{24.7}$ (Naphthalene-based)	-290
$\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$	-417
$\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$	-96
$\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$	-255
$\text{Li}_x\text{CoO}_2/\text{Li}$	$-70 < \Delta S < 20$
Li_xC_6/Li	$-20 < \Delta S < +62$

5.6 Conclusions

The suspensions of substituted 1,3,5-triphenylbenzenes **51d**, **51e** and **52f** ($R = \text{F}$, NO_2 , CN) in THF do not react with metallic lithium due to the very low solubility of these compounds in THF. The reaction rate of **51b** ($R = \text{OMe}$) and Li is low due to its higher electron density at the aromatic core compared to the unsubstituted 1,3,5-triphenylbenzene **51a**. Thus, PAH with high electron density at the aromatic system are not the best candidates for Li SES>

The conductivity of $\text{Li}_x(\mathbf{51a})(\text{THF})_{24.7}$ and $\text{Li}_x(\mathbf{51c})(\text{THF})_{24.7}$ increases with increased number of added Li atoms until $x = 2$ and then decreases after $x = 2$, which is related to the decomposition of the TPB molecules when $x > 2$.

Conductivity values of Li SES based on **51a** are higher of those with **51c**. This effect is due to insulating properties of alkyl chains that hinder charge propagation between the molecules. Thus, although alkyl chains significantly increase solubility of PAH, they tend to make negative impact on solubility.

Conductivity vs. temperature correlation for $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$, $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ and $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ has a negative trend, which is similar to metals and the SESs based on naphthalene and biphenyl. However, unlike for metals and naphthalene or biphenyl based Li SES, this relation is not completely linear.

The calculated ΔS for $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$, $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ and $\text{Li}_{4.0}(\mathbf{51c})(\text{THF})_{24.7}$ are mostly configurational (mixing) entropy for each of their respective solution systems.

Calculated ΔS for $\text{Li}_{2.0}(\mathbf{51a})(\text{THF})_{24.7}$, $\text{Li}_{2.0}(\mathbf{51c})(\text{THF})_{24.7}$ and $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ are high, probably because the LiSES is in a liquid phase which gives its molecules more degrees of freedom than are found in solid electrode materials.

These results suggest that Li SESs based on **51a** with 2 lithium atoms per TPB molecule may be suitable for use as anolytes in liquid-based refuelable batteries. However, the observed fact that **51a** does not favorably interact with more lithium than biphenyl and naphthalene suggests m-linked benzene rings do not enhance the ability to bind with more lithium.

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Chapter 6*

Triphenylene based Li SES

This chapter is dedicated to Li SES based on triphenylene, which is an aromatic system with four fused rings. It was found that Li SES made from triphenylene has much higher electric conductivity comparing to naphthalene based Li SES of the same concentration. From the studies of open circuit voltage versus temperature for the Li SES derived from triphenylene, the values of entropy and enthalpy change in the half-cell were calculated. Based on quantum chemical modeling of lithium-triphenylene interactions, it was shown that the unusually high values of conductivity could be related to the formation of conductive complex.

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6.1. Introduction

After performing the studies on aromatic systems that contain three (p-terphenyl) and four (1,3,5-triphenylbenzene) aromatic rings connected via ordinary σ bonds, and the system with three fused aromatic rings (anthracene), the next step is to consider a system with four fused aromatic rings, namely, triphenylene (**56**, **Figure 6.1**). As in the previous chapter, the studies started with conductivity measurements. After that, the Li SES with the highest conductivity and the highest Li:PAH ratio were tested in half-cell experiments.

Figure 6.1. Structures of naphthalene, anthracene and triphenylene.

6.2. Conductivity of triphenylene based Li SES

The conductivity vs. temperature correlation for $\text{Li}_x(\textbf{56})(\text{THF})_{123}$ solutions ($x = 0.5; 1.0; 2.0; 3.0; 4.0$) and naphthalene based $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$ is shown in **Figure 6.2**. Although the conductivity of $\text{Li}_{1.0}(\textbf{56})(\text{THF})_{123}$ is lower than that of $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$, the conductivities of all the other solutions are significantly higher. The highest value of conductivity is observed for $\text{Li}_{2.0}(\textbf{56})(\text{THF})_{123}$. This value at 22 °C (295 K) is 17 times higher than for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{123}$ (**Table 6.2**). The conductivity of triphenylene based Li SES starts decreasing upon further increase of Li:**56** ratio, however, the conductivity of $\text{Li}_{4.0}(\textbf{56})(\text{THF})_{123}$ at 22 °C is still 9.7 times higher than for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{123}$. This significant difference in conductivity between naphthalene and **56** based Li SES may be related to more interactions between triphenylene-Li ion pairs due to triphenylene's π -stacking properties. All the $\sigma(T)$ profiles demonstrate a quasi-linear correlation, which is similar to metals, as well as to ammonia and PAH based Li SES.

Figure 6.2. The conductivity vs. temperature correlation for $\text{Li}_x(\mathbf{56})(\text{THF})_{123}$ ($x = 0.5; 1.0; 2.0; 3.0; 4.0$) and $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$, N = naphthalene.

Table 6.1. The conductivity (σ , $\mu\text{S/cm}$) values at 295 K (22 °C) and the equations of quasi-linear $\sigma(T)$ for the studied Li SES.

Li SES	σ ($\mu\text{S/cm}$) at 295 K	$\sigma(T)$ ($\mu\text{S/cm}$) =
$\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$	34.2	$-3.02T+920$
$\text{Li}_{0.5}(\mathbf{56})(\text{THF})_{123}$	17.6	$-0.78T+248$
$\text{Li}_{1.0}(\mathbf{56})(\text{THF})_{123}$	62.2	$-6.06T+1848$
$\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$	579	$-12.07T+4133$
$\text{Li}_{3.0}(\mathbf{56})(\text{THF})_{123}$	344	$-7.52T+2590$
$\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$	331	$-8.32T+2954$

Among the studied Li SES based on **56**, the conductivity first increases upon the increase of Li:**56** ratio reaching the peak at 2:1, then decreases (**Figure 6.3**). This pattern is very

similar to dilute naphthalene and biphenyl based solutions with the formula of $\text{Li}_x(\text{PAH})(\text{THF})_{25}$.

Figure 6.3. Conductivity versus Li:**56** ratio profile.

6.3. Open-circuit potentials (E) vs temperature (T)

Based on the conductivity results, the two solutions with the highest conductivity and the highest Li:PAH ratio were chosen for open-circuit potential (E) vs temperature (T) study. The E vs T profiles of $\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ in Li/Ceramics/Li SES half-cell configurations are shown in **Figure 6.4**. The enthalpy changes (**Table 4.2**) and the entropy changes of the half-cell were calculated using the equations discussed in Section 3.8.

Figure 6.4. The OCP (E) vs T profiles of $\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ in Li/Ceramics/Li SES half-cell configurations.

Table 6.2. Open-circuit potentials at 22 °C, linear fits of $E(T)$ profiles, ΔS and ΔH of the $\text{Li}_n(\mathbf{56})(\text{THF})_{123}/\text{Li}$ half-cells, $n = 2.0$ and 4.0 .

Li SES	E at 295 K (mV)	$E(T)$ (mv) =	ΔS (J/(mol*K))	ΔH (kJ/mol)
$\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$	747.2	$-2.48T+1478$	-239.3	-142.7
$\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$	678.8	$-3.25T+1636$	-313.6	-157.9

Table 6.3 compares the entropy changes of the half-cell reactions of **56** based Li SES and those Li SES prepared using naphthalene and biphenyl, against the solidoxide-based LIB cathode material LiCoO_2 and the anode material Li_xC_6 . As can be seen the changes in entropy (ΔS) are much greater for the Li SES than for the standard electrode materials used in LIBs, which can be attributed to their being in a liquid as opposed to a solid state, which allows for more degrees of freedom. The ΔS for the triphenylene based Li SES are lower

than the values for biphenyl, however, the entropy change value for $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ is higher than the one for $\text{Li}_{1.0}\text{N}(\text{THF})_{24.7}$.

Table 6.3. Entropy changes for various Li SES/Li compared with $\text{Li}_n\text{CoO}_2/\text{Li}[1]$ and $\text{Li}_n\text{C}_6/\text{Li}$ [2] half-cells ($0 < n < 1$).

Type of half-cell	ΔS ($\text{JK}^{-1}\text{mol}^{-1}$)
$\text{Li}_{0.5}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-420
$\text{Li}_{1.0}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-467
$\text{Li}_{1.0}\text{N}(\text{THF})_{24.7}$ (Naphthalene-based)	-290
$\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$	-239
$\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$	-316
$\text{Li}_n\text{CoO}_2/\text{Li}$	$-70 < \Delta S < 20$
$\text{Li}_n\text{C}_6/\text{Li}$	$-18 < \Delta S < +62$

6.4. Modeling of intermolecular interactions in triphenylene based Li SES²

To better understand the properties of triphenylene based Li SES and interactions between lithium and the PAH, the structures of triphenylene – lithium adducts with Li: $\mathbf{56}$ ratios of 2:1 and 4:1 were modeled in collaboration with Prof. Su Haibin's group. Since the possible reason of unusually high conductivity of $\mathbf{56}$ based Li SES comparing to naphthalene is conductive complex formation due to Li-triphenylene-stacking, the modeling of corresponding dimeric structures with the formula $\text{Li}_{2x}(\mathbf{56})_2$ was performed. Geometries of the corresponding adducts are shown in **Figure 6.5**. The interaction with lithium leads to significant distortion of the planar aromatic structure of triphenylene. The increase of Li:PAH ratio leads to even more significant distortion. However, this effect is much less for the dimeric structures. When lithium interacts with two molecules of triphenylene, it tends to occupy the space in between the molecules first. Lithium does not interact with the central ring of triphenylene, and the maximum number of lithiums in between the molecules is three.

² The modeling was performed in collaboration with Liu Zhihao and Assoc. Prof. Su Haibin

Table 6.4. Calculated average binding energies ΔE_{Li}^B for $Li_x(\mathbf{56})_1$ and dimeric $Li_{2x}(\mathbf{56})_2$ ($x = 2$ and 4).

	ΔH (kJ/mol) experimental	ΔE_{Li}^B , eV	ΔE_{Li}^B , kJ mol	ΔE_{Li}^B (Dimer), eV	ΔE_{Li}^B (Dimer), kJ
$Li_2(\mathbf{56})$	-142.7	-0.67	-64.6	-1.41	-136.1
$Li_4(\mathbf{56})$	-157.9	-0.94	-90.7	-1.24	-119.6

The average binding energies ΔE_{Li}^B per lithium atom for $Li_x(\mathbf{56})$ and the dimers $Li_{2x}(\mathbf{56})_2$ obtained from these calculations are shown in **Table 6.4**. Since the binding energy represents the energy that the system produces upon interaction with a certain amount of lithium, it correlates with the enthalpy change: $\Delta E_{Li}^B \sim \Delta H$ [3]. As seen from the **Table 6.4**, the values of ΔE_{Li}^B for $Li_x(\mathbf{56})_1$ are significantly lower than the values of ΔH . However, the ΔE_{Li}^B is much larger for the dimeric structures. The value for $Li_2(\mathbf{56})_2$ is very close to the experimental value of ΔH . Nevertheless, ΔE_{Li}^B of $Li_8(\mathbf{56})_2$ is a bit lower than the value for $Li_4(\mathbf{56})_2$, which is different from ΔH and ΔE_{Li}^B correlation for $Li_x(\mathbf{56})$ (both the values increase upon the Li: $\mathbf{56}$ ratio increase). This result can explain the fact that $Li_{4.0}(\mathbf{56})(THF)_{123}$ has lower conductivity than $Li_{2.0}(\mathbf{56})(THF)_{123}$, meaning that the formation of the $Li_8(\mathbf{56})_2$ conductive complex is less thermodynamically favorable compared to $Li_2(\mathbf{56})_4$.

Figure 6.5. Structures of $\text{Li}_2(\mathbf{56})_1$ (top left), $\text{Li}_4(\mathbf{56})_1$ (top right), $\text{Li}_4(\mathbf{56})_2$ (bottom left), $\text{Li}_8(\mathbf{56})_2$ (bottom right).

6.5. Attempts to synthesize a triphenylene derivative of higher solubility³

Considering the results on diluted Li SES prepared from **56**, attempts to prepare Li SESs of higher concentrations from suspensions of **56** in THF were performed the same manner as it was done for anthracene and p-terphenyl. However, these attempts were not successful due to formation of precipitate on the surface of lithium that prevents the reaction from proceeding further. Thus, in order to obtain **56** based Li SES of higher concentrations, the material should have higher solubility, which can be achieved by incorporation of aliphatic substituents into the molecule.

The most convenient route to substituted triphenylenes is oxidation of corresponding 1,2-dialkoxybenzenes by means of iron (III) chloride (**Figure 6.6**) or some other strong oxidizing agents [4].

³ These experiments were performed with help of final year project students Chia Wei En and Ho Guan Yang Clarence

Figure 6.6. Synthesis of **56a**.

Although **56a** and its derivatives with longer chains can be easily synthesized from commercially available materials using this method, the compound **56a** should not be considered as a potential source of Li SES due to the effect of alkoxy groups that destabilizes corresponding PAH ions in Li SES. This negative effect of electron donating groups was shown in Chapter 5 using methoxy substituted 1,3,5-triphenylbenzene as an Li SES source. However, it was decided to try using this approach to obtain **56b** by means of oxidation of **58**, which was synthesized from 1,2-dichlorobenzene by means of Kumada coupling [5] (**Figure 4.7**).

Figure 6.7. Attempts to synthesis of **56b**.

However, the attempts to obtain **56b** by oxidation of **58** using various oxidants were unsuccessful. A complex mixture of oligomers was obtained instead.

Another performed attempt was a nickel mediated cross coupling of 1,2-dibromobenzene **59** [6], which was synthesized from **58** [7] (**Figure 6.8**). However, this attempt was unsuccessful as well since **59** does not react under these conditions.

Figure 6.8. An attempt to synthesize **56b** by means of Nickel mediated coupling.

Since the oxidation of **58** leads to a complex mixture of oligomers, another possible approach to synthesize triphenylene **56c** is to oxidize o-terphenyl derivative **60**, which was prepared from **59** by means of Suzuki coupling [8] (**Figure 6.9**). However, in contrast to unsubstituted o-terphenyl [8], this reaction also led to a complex mixture of oligomers when FeCl_3 or DDQ were used as oxidants. Nevertheless, it is known that photochemical oxidation of o-terphenyl is a convenient way of triphenylene synthesis [9]. Although it requires specialized equipment, such as quartz glassware and UV radiation source, which was not available during the course of the project, it should be used in future for attempted synthesis of **56c**, if access to such equipment can be obtained.

Figure 6.9. An attempt to synthesis of **56c**.

Some other ways that could lead to the structures **56b,c** with high probability of success are reactions involving aryne intermediates [10], 9-stannofluorenes [11] or diaryliodonium salts [12]. Although it seems feasible to synthesize **56b** from a highly substituted o-terphenyl derivative using DDQ as an oxidant [8], the synthesis of this o-terphenyl derivative is a complex synthetic task, which in case of success would lead to very small quantities of the final product, which would not be enough for detailed Li SES studies.

6.6. Conclusions

Among tested $\text{Li}_n(\mathbf{56})(\text{THF})_{123}$, the Li SES with $n = 2$ demonstrates the highest conductivity, which is almost ten times higher of the naphthalene based Li SES (Li:Naphthalene ratio = 1:1) of the same concentration in THF. For $n > 2$, the conductivity of Li SES gradually decreases until $n = 4$, however, these values are still higher of the one for naphthalene. All Li SES tested demonstrate quasi-linear decrease of conductivity with temperature increase, similar to metals and Li SES based on ammonia, naphthalene and biphenyl.

The values of ΔS and ΔH for $\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ were calculated based on OCP vs T correlation. The ΔS values are lower of those for biphenyl suggesting the molecules in triphenylene based Li SES have less degrees of freedom. However, the ΔS for $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ is higher than that for naphthalene based Li SES. The ΔS values for both $\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\mathbf{56})(\text{THF})_{123}$ are higher than the values for solid state electrodes due to more degrees of freedom in a solution compared to a solid.

Based on the modeling of interactions between Li and triphenylene, binding energies of lithium to one and two molecules of triphenylene were obtained (Li: $\mathbf{56}$ ratio = 2 and 4) by Assoc. Prof. Su Haibin and Liu Zhihao. Based on these results, one can conclude that the unusually high conductivity of triphenylene based Li SES could be related to a conductive complex formation.

However, unlike p-terphenyl and anthracene, the suspension of $\mathbf{56}$ in THF does not dissolve lithium completely due to precipitate formation at the surface of lithium. The attempts to synthesize $\mathbf{56}$ with alkyl chains, which would have higher solubility in THF, by means of oxidation and nickel mediated coupling were unsuccessful. However, some other methods mentioned in the section 4.4 of this chapter may lead to successful synthesis of $\mathbf{56}$ with alkyl chains incorporated into its structure.

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Chapter 7

Hexaphenylbenzene (HPB) and Hexa-peri-hexabenzocoronene (HBC) as sources for Li SES

This chapter discusses the results of testing hexaphenylbenzene (HPB), hexa-peri-hexabenzocoronene (HBC) and their derivatives as Li SES sources. The first section provides a rationale for choosing these materials, followed by synthesis of HPB, HBC and their derivatives. Then the chapter represents preparation of corresponding SES, showing that only a suspension of the HBC derivative bearing hexyl chains reacts with lithium and potassium in THF, while mixtures containing other HPB and unsubstituted HBC do not react. Conductivity versus temperature experiments, which are discussed in the last section, demonstrate a complex behavior for Li SES based on the HBC with hexyl chains, and quasi-linear decrease of conductivity with temperature increase for K SES. However, the conductivity values for both Li and K SES exhibit significantly lower values compared to Li SES of the same concentration based on other PAH.

7.1. Introduction

In order to investigate the influence of PAH with large amount of benzene rings on resulting Li SES performance, the properties of hexaphenylbenzene derivative with alkyl substituents were studied (**61**, **Figure 7.1**). This compound can be considered as 1,3,5-triphenylbenzene with three additional benzene rings attached to the central one. Since unsubstituted hexaphenylbenzene (**61a**) has quite limited solubility in THF, it was decided to perform the studies on **61b**. The role of the hexyl chains in **61b** is to increase the solubility.

Figure 7.1. Structures of biphenyl, 1,3,5-triphenylbenzene (**51a**), hexaphenylbenzene (**61a**) and hexaphenylbenzene with six attached hexyl chains (**61b**) to improve solubility.

Hexa-peri-hexabenzocoronene **62a** is another object of study in this chapter, which can be considered as triphenylene with several additional fused rings. This material is easily available via oxidation of hexaphenylbenzenes **61a,b**. Considering the very low solubility

of **62a** in organic solvents, the HBC having hexyl chains (**62b**) attached to improve solubility was the object of study as well.

Figure 7.2. Structures of naphthalene, triphenylene (**56**), and hexa-peri-hexabenzocoronenes (**62a,b**).

7.2. Synthesis of hexaphenylbenzene derivative with high solubility

Two main approaches to synthesis of hexaphenylbenzene and its derivatives are shown in **Figure 7.3**. The first approach, which is shown as Method I, involves trimerization of diphenylacetylene [1]. The most common catalyst for this process is $Co_2(CO)_8$, although some other inorganic and organometallic compounds can also be quite effective [2, 3]. This reaction leads to formation of the product **61c**. The trimerization of **57** with unequal substituents gives a statistical mixture of isomeric products.

Another process (Method II) is Diels-Alder reaction between a diphenylacetylene (**63**) and a tetraphenylcyclopentadiene (**51**), followed by elimination of CO and aromatization of the middle ring [4, 5]. Typically, the reaction requires heating in a high boiling point solvent like diphenyl ether. In contrast with Method I, this reaction allows one to obtain a

single product with various substituents in the molecule (**61d**). If some of the substituents among the groups of R, R' or R'' are unequal, the reaction leads to formation of statistical mixtures.

Figure 7.3. Approaches to synthesis of substituted hexaphenylbenzenes (**61**).

Although Method II is effective for synthesis of hexaphenylbenzenes with various substituents in one molecule, Method I requires only one reactant, thus, it is more convenient for preparation of **61b**, which has only one type of substituent (R = n-hexyl). Thus, in order to obtain **61b**, one needs to synthesize 1,2-bis(4-hexylphenyl)ethyne (**63a**) first.

Although dibromotolane **64** (**Figure 7.4**) gives products with long alkyl chains under Kumada cross-coupling conditions [6, 7], unfortunately, attempts to obtain the tolane with n-hexyl moieties (**63a**) via the reaction between dibromotolane **64** and n-hexylmagnesium

bromide mediated by $\text{PdCl}_2(\text{dppf})$ or $\text{NiCl}_2(\text{dppp})$ were not successful. Thus, it was decided to use an alternative approach described by Ito et al. [8], which is based on the fact that dibromostilbene **66** participates in Kumada coupling more readily than the corresponding tolane. Based on this method, firstly 4,4'-dibromostilbene (**66**) was obtained from **65** via a McMurry reaction [9] in 76% yield. Then this compound was introduced into reaction with hexylmagnesium bromide in THF catalyzed by $\text{NiCl}_2(\text{dppp})$, which allowed us to afford the product (**67**) in 82% yield. After successive reactions of bromination (95% yield of **68**) and double HBr elimination (56% yield), 4,4'-di-n-hexyltolane (**63a**) was successfully obtained.

Figure 7.4. Synthesis of **60**. Here and further Hex = n-hexyl ($n\text{-C}_6\text{H}_{13}$).

Unfortunately, this four-step process gave **63a** in a low overall yield of 33%. In order to obtain the amount of **63a** that is sufficient for further experiments, an alternative approach shown in **Figure 7.5** was implemented. This approach is based on a tandem reaction, which involves Sonogashira cross-coupling with trimethylsilylacetylene, followed by cleavage of the TMS group and an additional Sonogashira coupling [10]. This approach produced **63a** in 42% yield. Despite the overall yield is not much higher than for the route discussed above, it significantly decreases the number of steps.

Figure 7.5. Optimized procedure for synthesis of **63a**.

Finally, trimerization of **63a** mediated by $\text{Co}_2(\text{CO})_8$ in 1,4-dioxane gave **61b** in 93% yield (**Figure 7.6**).

Figure 7.6. Synthesis of hexaphenylbenzene derivative **56**.

7.3. Synthesis of hexa-peri-hexabenzocoronene and its derivative.

A standard procedure to synthesize **62a** was employed [11, 12] (**Figure 7.7**). First, condensation of **69** and **70** in presence of base [13] gave **51a** in 80% yield. Then, Diels-Alder reaction between **51a** and diphenylacetylene followed by elimination of CO gave **61a** in 89% yield, which was oxidized using iron (III) chloride to produce **62a** in 80% yield.

Figure 7.7. Synthesis of **62a**.

62b was synthesized in the same manner as **62a**, by oxidation of **61b** using iron (III) chloride (**Figure 7.8**).

Figure 7.8. Synthesis of **62b**.

7.4. Synthesis of Li SES based on HPB.

The next step after the synthesis of compound **62b** is formation of Li SES based on this material. Although the compound has very high solubility in THF, which is of the same

order as for 1,3,5-triphenylbenzene with *n*-butyl chains (**51c**) due to the effect of alkyl chains, the solutions of **62b** in THF do not react with lithium. A possible explanation of this behavior, which is very unusual for PAHs, is related to its structure. Owing to steric interactions of neighboring benzene rings, the stable conformation of this molecule has side rings rotated out of the central ring plane. In crystals, this molecule has a propeller-like conformation with a 65° angle between the substituent benzene rings and the plane of the central ring (**Figure 7.9**) [14], while in gas phase these rings are perpendicular to the central one with $\pm 10^\circ$ oscillations [15]. Since π -conjugation between two aromatic rings requires them to be in the same plane, this molecule should be considered as a group of separate benzene rings connected with the central one by ordinary σ -bonds, with no π -conjugation between the rings. Thus, these benzene rings in hexaphenylbenzene should have similar properties to benzene, which does not react with lithium. As a result, hexaphenylbenzene and its derivatives should not be considered as potential candidates for Li SES.

Figure 7.9. Structure of non-substituted hexaphenylbenzene in crystals (hydrogen atoms omitted for clarity) [14].

7.5. Synthesis and electric conductivity of Li SES based on HBC

A suspension of unsubstituted hexa-peri-hexabenzocoronene **62a** in THF does not react with metallic lithium. This can be explained by the extremely low solubility of this material and its high crystal lattice energy. However, a suspension of **62b** in THF reacted with six mole equivalents of lithium giving a Li SES of a composition $\text{Li}_{6.0}(\text{62b})(\text{THF})_{123}$ (equal to ~ 0.1 M solution of PAH). The conductivity of this solution demonstrates a complex correlation with temperature, generally exhibiting a positive trend, as seen from **Figure 7.10** and **Table 7.1**. It was also found that SES can be formed using potassium instead of

lithium. In this case, the K SES of composition $K_{6.0}(\mathbf{62b})(\text{THF})_{123}$ demonstrates a negative trend of conductivity versus temperature. This difference in behavior between Li and K SES can be related to the degradation of HBC aromatic core which happens in presence of lithium, but not in presence of potassium, which is similar to 1,3,5-triphenylbenzene [16]. However, both Li SES and K SES demonstrate very low values of conductivity (**Table 7.1**), which is significantly lower than Li SES of the same concentration based on other PAH studied (anthracene, p-terphenyl, triphenylene). This effect could be related to the influence of alkyl groups that prevent charge propagation. As was previously shown for 1,3,5-triphenylbenzene in Chapter 5, alkyl chains increase the solubility, but decrease the conductivity. A similar effect is observed for **62b**, which has more and longer alkyl chains than **51c**.

Figure 7.10. The conductivity versus temperature graphs for $\text{Li}_{6.0}(\mathbf{62b})(\text{THF})_{123}$ and $\text{K}_{6.0}(\mathbf{62b})(\text{THF})_{123}$.

Table 7.1. The conductivity ($\mu\text{S}/\text{cm}$) values at 22°C for the compositions for $\text{Li}_{6,0}(\mathbf{62b})(\text{THF})_{123}$ and $\text{K}_{6,0}(\mathbf{62b})(\text{THF})_{123}$.

Composition	Conductivity at 295 K (22°C) ($\mu\text{S}/\text{cm}$)	Linear approximation, $\sigma(T)$ ($\mu\text{S}/\text{cm}$) =
$\text{Li}_{6,0}(\mathbf{62b})(\text{THF})_{123}$	30	$0.64T - 157.4$
$\text{K}_{6,0}(\mathbf{62b})(\text{THF})_{123}$	21	$-0.32T + 115.8$

7.6. Conclusions

Hexaphenylbenzene **61b** solution in THF does not react with lithium. This effect is due to its molecular structure with no conjugation between the benzene rings. A suspension of unsubstituted hexa-peri-hexabenzocoronene in THF does not react with lithium as well owing to its extremely low solubility in THF and its high crystal lattice energy. However, a THF suspension of hexa-peri-hexabenzocoronene with n-hexyl substituents **62b** reacts with lithium giving the corresponding Li SES. The obtained Li SES of the formula $\text{Li}_{6,0}(\mathbf{62b})(\text{THF})_{123}$ exhibits complex correlation between its conductivity and temperature, showing a positive trend. However, $\text{K}_{6,0}(\mathbf{62b})(\text{THF})_{123}$, produced by dissolving potassium in a **62b**-THF mixture, demonstrates negative trend in terms of conductivity versus temperature, which is similar to metals, ammonia based Li SES, as well as the majority of Li SES discussed in this thesis. Nevertheless, the conductivity values of these **62b** based solutions are significantly lower than those derived from p-terphenyl (**49**), anthracene (**8**), and trihenylene (**56**) with the same concentration. A significant contribution to this observation is related to the effect of alkyl chains that hinder charge propagation in the media. Thus, although these groups increase the solubility of the larger PAH, they make a serious negative impact on the conductivity of resulting Li SES. As a general result, one can see that the increase in the size of PAH does not necessarily lead to better properties of the resulting Li SES comparing to more simple ones.

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Chapter 8*

Li SES derived from phenylpyridines and bipyridines

This chapter discusses the electrical and electrochemical properties of Li SES based on heterocyclic materials, namely, phenylpyridines and bipyridines, which are the simplest polyheteroaromatic systems with two rings connected via ordinary bond. The chapter starts with preparation of Li SES based on phenylpyridines and studies on their electrical conductivity, followed by open circuit potential measurements in a half cell. The modeling of geometry and electronic structure of lithium-phenylpyridine adducts was performed for better understanding of interactions between lithium and these heteroaromatic systems. Since bipyridines tend to form insoluble adducts with lithium in THF, HMPA was used to prepare corresponding Li SES. The electrical conductivity and open circuit voltage experiments were performed involving these solutions. To better understand the effect of HMPA on the properties of Li SES, these experiments were also performed using Li SES based on biphenyl using HMPA as a solvent.

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8.1. Introduction

After performing the studies on polyaromatic hydrocarbons of various sizes to assess the effects of size in their ability to form Li SES and the properties of the Li SES formed, the second important question to be addressed is the influence of heteroatoms incorporated into the aromatic structure. Among all the heteroatoms, the incorporation of electronegative nitrogen atoms is of particular interest, since they should stabilize the corresponding negatively charged species formed upon the reaction with lithium. Thus, the materials discussed in this chapter first are the simplest polyaromatic heterocyclic structures, which are 2-, 3-, and 4-phenylpyridines (**71**, **72**, and **73** respectively, **Figure 8.1**). In the context of strategy (Chapter 1), these molecules can be considered as biphenyl with one CH group substituted by nitrogen at the 2, 3, or 4 position. To investigate the influence of nitrogen doping in more detail, the second part of the chapter discusses isomeric bipyridines **41**, **74**, and **43** that contain two atoms of nitrogen (**Figure 8.1**).

Figure 8.1. Structures of 2-phenylpyridine (**71**), 3-phenylpyridine (**72**), 4-phenylpyridine (**73**), 2,2'-bipyridine (**41**), 3,3'-bipyridine (**74**), 4,4'-bipyridine (**43**).

8.2. Li SES based on phenylpyridines

8.2.1. Conductivity

The conductivity (σ) vs T profiles for $\text{Li}_{1.0}(\mathbf{71})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$, $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ and $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$ are shown in **Figure 8.2**. **71** with a Li:PAH ratio of 1:1 and 2:1 demonstrate the lowest conductivity, while the conductivity of $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ is higher than the one with Li:PAH = 1.0. The

conductivity values are much higher for $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ and even higher for $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$. Among the studied series, the highest value of σ (1.45 mS/cm) was recorded for $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$. The conductivity measurements on $\text{Li}_{2.0}(\mathbf{73})(\text{THF})_{10.4}$ could not be performed, since a very viscous suspension formed upon the reaction with lithium which prevented the metal from further reaction. The Li SES demonstrate metal-type decrease of conductivity with increasing temperature, however, $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ exhibits slight increase of its conductivity with the temperature increase. Moreover, $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ has a more complex σ -T profile than the other tested PAH, as shown in **Figure 8.3**. First, the conductivity decreased with the temperature increase reaching a limit at 283 K (152 $\mu\text{S}/\text{cm}$), followed by an increase in conductivity, which indicates a phase transition at the limit point. Since the conductivity of Li SES is a very complex phenomenon related to such factors as the negative charge density distribution in the molecule, the position of the metal ion(s) towards the molecule, the charge distribution between the metal atom and the molecule, the ions – solvent interactions, and interactions between these ion pairs, it is not easy to find a clear correlation between the conductivities of these solutions and some particular parameters of these phenylpyridine-Li ion pairs, which have not yet been investigated in detail.

The significantly lower conductivity of Li SES based on **71** could be related to chemical reactions that occur upon interactions between lithium and **71**. When quenched by alcohols, a significant evolution of gas is observed, which is the evidence for the formation and hydrolysis of LiH and, possibly, aryllithium compounds. Li SES based on 3- (**72**) and 4-phenylpyridine (**73**) do not demonstrate this effect. When the Li SES with Li:**71** ratio of 2:1 is quenched by iodine solution in THF, formation of a complex mixture of products is detected by ^1H NMR and MALDI TOF MS, although the starting 2-phenylpyridine (**71**) is still present in the mixture. The chemical transformations of 2-phenylpyridine upon interaction with lithium leading to formation of oligomers and LiH offers an explanation for the complex conductivity vs temperature behavior of **71** based Li SES, as well as low conductivity values.

The values of conductivity at 22 °C (295 K) are shown in **Table 8.1**. As can be seen, all the values for phenylpyridines are lower than the ones for biphenyl and naphthalene based Li SES. This phenomena is probably related to the fact that the negative charges of the solvated electrons in biphenyl are delocalized around the whole π -system of the molecule, while in all the studied phenylpyridines these additional electrons are predominantly localized at the more electronegative nitrogen atom [1]. This localization of the charge density leads to lower probability of electrical current propagation between the molecules upon the interaction, thus, lower conductivities of phenylpyridines based Li SES compared to those of biphenyl and naphthalene are observed.

Figure 8.2. The conductivity versus temperature graphs for $\text{Li}_{1.0}(\mathbf{71})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$, $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ and $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$.

Figure 8.3. The conductivity versus temperature graph $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$.

Table 8.1. Conductivity values at 22 °C of the Li SES based on 2-, 3- and 4-phenylpyridines studied compared to the values for biphenyl and naphthalene based Li SES [2, 3] of the same concentration. Right column demonstrates the linear fit equation for $\sigma(T)$ for studied phenylpyridine based Li SES, as well as for naphthalene and biphenyl based Li SES [2, 3].

Li SES	Conductivity (mS/cm) at 295 K	$\sigma(T)$ ($\mu\text{S/cm}$) =
$\text{Li}_{1.0}(\mathbf{71})(\text{THF})_{10.4}$	0.10	$-0.58T+270$
$\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$	0.16	$+0.28T+75$
$\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$	1.12	$-9.99T+4070$
$\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$	0.90	$-0.63T+820$
$\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$	1.45	$-14.6T+5762$
$\text{Li}_{1.0}(\text{Biphenyl})(\text{THF})_{10.4}$	11.5	$-94.1T+13500$
$\text{Li}_{2.0}(\text{Biphenyl})(\text{THF})_{10.4}$	7.8	$-67.6T+9200$
$\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$	8.8	$-87.6T+10700$
$\text{Li}_{2.0}(\text{Naphthalene})(\text{THF})_{10.4}$	5.4	$-60.9T+6.80$

8.2.2. Open-circuit potentials (E) vs temperature (T) profiles

Considering the results for conductivity, the three Li SES with the highest values of σ were chosen for the open-circuit potentials (E) vs temperature (T) investigations, namely $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$, $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$. Additionally, $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ was studied as well due to its unusual behavior in terms of conductivity. The E vs T profiles of the corresponding Li SES in Li/Ceramics/Li SES half-cell configurations are shown in **Figure 8.4**.

Figure 8.4. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_{1.0}(\mathbf{71})(\text{THF})_{10.4}$, $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$, $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$, and $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$.

Figure 8.5. Open-circuit potential (E) vs temperature (T) profile for $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ in the range 282 – 298 K.

The $E(T)$ values for $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$ and $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$ are very close to each other, while the values for $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ are twice lower. For $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$, the $E(T)$ demonstrates first a positive slope (**Figure 8.5**), and then the slope changes its sign at 285 K (614mV), which is evidence for a phase transition, as is also observed in σ vs T experiment (**Figure 8.3**). The values of entropy and enthalpy change in the half cell were calculated using the equations discussed in Section 3.8 [4].

The values of ΔS and ΔH of $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$ and $\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$ (**Table 8.2**) are very close to each other, which is probably due to structural similarities of these isomeric molecules. Remarkably, these molecules demonstrate very close values of some other thermodynamical parameters, such as the enthalpy of vaporization and sublimation [5]. The ΔS and ΔH values of $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ are much lower comparing to the previous two, which could be related to changes in both the structure of the molecule and the charge density distribution upon the addition of the second electron, as well as the interactions with lithium ions. The difference in ΔH between $\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$ and $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$ could be related to a change in structure of **72** upon the addition of one more electron to

the aromatic system. Remarkably, the ΔS and ΔH values for $\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$ are closer to those with 1:1 PAH:Li ratio rather than to $\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$.

Table 8.2. Open-circuit potentials at 22°C, linear fits, ΔS and ΔH of the half-cells with Li SES based on **71**, **72**, and **73**.

Li SES	E at 295 K (22 °C) (mV)	E(T) (mV) =	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ mol ⁻¹)
$\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$	872	-1.12T+1220	-108.1	-116.0
$\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$	634	-0.61T+814	-58.9	-39.2
$\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$	873	-1.17T+1202	-112.9	-117.7
$\text{Li}_{2.0}(\mathbf{71})(\text{THF})_{10.4}$	603	-1.15T+942	-111.0	-90.9

Table 8.3 compares the obtained ΔS values for the phenylpyridines based Li SES with the other known values for naphthalene and biphenyl based Li SES, as well as with the standard materials used in Li-ion batteries.

Table 8.3. Entropy changes ΔS of various Li SES/Li, as well as solid-state $\text{Li}_x\text{CoO}_2/\text{Li}$ [6] and $\text{Li}_x\text{C}_6/\text{Li}$ [7] half-cells.

Li SES	ΔS (J K ⁻¹ mol ⁻¹)
$\text{Li}_{0.5}(\text{Biphenyl})(\text{THF})_{10.4}$	-420
$\text{Li}_{1.0}(\text{Biphenyl})(\text{THF})_{10.4}$	-467
$\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{10.4}$	-290
$\text{Li}_{1.0}(\mathbf{72})(\text{THF})_{10.4}$	-108.1
$\text{Li}_{2.0}(\mathbf{72})(\text{THF})_{10.4}$	-58.9
$\text{Li}_{1.0}(\mathbf{73})(\text{THF})_{10.4}$	-112.9
$\text{Li}_x\text{CoO}_2/\text{Li}$, $0 < x < 1$	$-70 < \Delta S < 20$
$\text{Li}_x\text{C}_6/\text{Li}$, $0 < x < 1$	$-20 < \Delta S < +62$

These values for the phenylpyridines are significantly lower, which is probably related to the charge density localization in the corresponding PAH anions at the nitrogen atom [1], and, consequently, the localization of the lithium counter ions leading to less degrees of

freedom. However, these values are generally still higher than those of the solid materials due to more degrees of freedom in a liquid as compared to a solid.

8.2.3. Modeling⁴

The localization of lithium atoms close to the nitrogen atoms in phenylpyridines is clearly observed based on modeling of the studied systems (**Figure 8.6**). The geometrical structures of aromatic cores become significantly distorted. The HOMO of the system indicates that the 2s electron of lithium is dominantly localized near the nitrogen with higher electron density at the site.

Figure 8.6. Geometry, HOMO and LUMO structures of Li₁(71), Li₂(71), Li₁(72), Li₂(72), Li₁(73), Li₂(73).

⁴ This part of thesis was performed in collaboration with Liu Zhihao and Assoc. Prof. Su Haibin.

When the second lithium atom is added, it occupies the space above the center of the other (benzene) ring of the molecule. As seen from these pictures, the electron at LUMO is dominantly localized near the atom of lithium, which suggests that the mechanism of charge propagation is mostly related to electron transfer between atoms of lithium in Li SES. As seen from the HOMO and LUMO structures of $\text{Li}_2(\mathbf{73})$, the charge density of both the orbitals is significantly localized at the atoms of lithium indicating that the 2s electron of the lithium will not be transferred to the molecule. This supports the unstable character of this adduct and the fact that preparation of the corresponding Li SES was unsuccessful.

8.3. Li SES based on bipyridines

8.3.1. Effect of solvent on Li SES formation

Solutions of **43** and **73** (synthesized according to literature procedure [8], see Appendix) in THF react with lithium forming insoluble black precipitates (**Figure 8.7**). A THF solutions with various amounts of lithium can only be obtained in case of **41**. These solutions exhibit very low values of electric conductivity (**Table 8.4**), which could be related to partial formation of a precipitate.

Table 8.4. Electric conductivity of $\text{Li}_x(\mathbf{43})(\text{THF})_{10.4}$ at 295 K (22 °C).

x in $\text{Li}_x(\mathbf{43})(\text{THF})_{10.4}$	0.5	1.0	1.5	2.0
Conductivity (σ , $\mu\text{S}/\text{cm}$)	6.3	11.4	26.8	38.9

The precipitate formation is related to the difference in donor properties of THF and bipyridines. The molecules having sp^2 nitrogen in their structure demonstrate better solvating properties to metal cations than those with oxygen [9]. Thus, in case of the reaction between lithium and THF solutions of bipyridines, the resulting cation of lithium tends to interact more with nitrogens of bipyridines rather than with the atoms of oxygen in THF. Considering that bipyridines have two atoms of nitrogen, the precipitate formed in the reaction is a mixture of oligomers where an atom of lithium is positioned in between a couple of bipyridine molecules. A way to overcome the formation of insoluble oligomers

is using a solvent with stronger solvating properties, which is also inert to lithium metal. Taking into account these considerations, it was decided to use hexamethylphosphoramide (HMPA, **Figure 8.7**) [10], which has previously been used to prepare Li SES [11-13]. The corresponding Li SES based on **41** and **43** were successfully prepared using HMPA (supplied by Sigma-Aldrich: absolute, over molecular sieves, H₂O < 0.03%) as a solvent.

Figure 8.7. Chemical structure of HMPA (left); a mixture of **43** and lithium in THF (middle); a mixture of **41** and lithium in HMPA (right).

8.3.2. Li SES based on 2,2'-phenylpyridine in HMPA: conductivity and half-cell experiments.

For the Li SES prepared from 2,2'-bipyridine (**41**) in HMPA with the formula of Li_x(**41**)(HMPA)_{10.4} ($x = 0.5, 1.0, 1.5, 2.0$), the conductivity first increases from $x = 0.5$ reaching the maximum at $x = 1.5$. The Li SES with $x = 2.0$ demonstrates the values close to the one with $x = 0.5$. The conductivity versus temperature demonstrates negative trend for $x = 0.5$ and 1.0 , and positive trend for $x = 1.5$ and 2.0 (**Figure 8.8**). The values of conductivity at 22 °C (295 K) and linear approximation equations are shown in **Table 8.5**.

Figure 8.8. The conductivity versus temperature graphs for $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$, $x = 0.5, 1.0, 1.5, 2.0$.

Table 8.5. The values of conductivity at 22 °C and linear fit equations for studied $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$.

x in $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$	Conductivity ($\mu\text{S/cm}$) at 295 K	$\sigma(T)$ ($\mu\text{S/cm}$) =
0.5	563	$-2.24T + 1228$
1.0	709	$-0.71T + 917$
1.5	769	$3.57T - 285$
2.0	589	$1.85T + 39.8$

The E vs T profiles of the corresponding Li SES in Li/Ceramics/LiSES half-cell configurations are shown in **Figure 8.9**. The $E(T)$ values for $\text{Li}_x(\mathbf{41})(\text{THF})_{10.4}$ exhibit decrease with the increase of Li: $\mathbf{41}$ ratio. A significant decrease of $E(T)$ was observed for $\text{Li}_{1.5}(\mathbf{41})(\text{THF})_{10.4}$ above 297 K. The obtained OCP values for Li SES based on $\mathbf{41}$ in HMPA are higher comparing to $\text{Li}_{0.5}(\mathbf{41})(\text{THF})_{10.4}$. However, all these values are significantly above 1 V vs Li^+/Li , and much higher than for Li SES discussed previously,

resulting in significantly lower potential between these Li SES made in HMPA and cathode materials, and, hence, does not make these materials suitable for applications as anolytes. The values of ΔS and ΔH for $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$ in the half cell (**Table 8.6**) were calculated using the equations discussed in Section 3.8. These values for $\text{Li}_{0.5}(\mathbf{41})(\text{HMPA})_{10.4}$ are close to those obtained for Li SESs based on biphenyl in THF, and much higher when $x > 0.5$. The values of ΔS and ΔH are much lower for $\text{Li}_{0.5}(\mathbf{41})(\text{THF})_{10.4}$. This can be related to more significant dissociation of $\mathbf{41}$ -Li ion pairs due to higher solvation properties of HMPA comparing to THF, leading to more degrees of freedom of the system (higher ΔS) and production of more energy owing to solvation (higher ΔH).

Figure 8.9. The open circuit potential versus temperature graphs for the half-cells $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}/\text{Li}$ and $\text{Li}_{0.5}(\mathbf{41})(\text{THF})_{10.4}/\text{Li}$ half cells.

Table 8.6. Open-circuit potentials at 295K (22°C), linear fits, ΔS and ΔH of the LiSES/Li half-cells with $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$ ($x = 0.5, 1.0, 1.5, 2.0$) and $\text{Li}_{0.5}(\mathbf{41})(\text{THF})_{10.4}$.

x in $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$	E at 295 K (22 °C) (mV)	E(T) (mV)=	ΔS (J/(mol*K))	ΔH (kJ/mol)
0.5	1789	-4.16T+3015	-401.4	-290.4
1.0	1690	-5.20T+3234	-501.7	-311.6
1.5	1350	-5.14T+2856	495.9	-275.5
2.0	1358	-6.00T+3128	-578.9	-302.0
$\text{Li}_{0.5}(\mathbf{41})(\text{THF})_{10.4}$	1171	-1.11T+1498	-107.1	-144.5

8.3.3. Li SES based on 4,4'-phenylpyridine and biphenyl in HMPA: conductivity and half-cell experiments.

For Li SES prepared from 4,4'-bipyridine (**43**) in HMPA having the formula of $\text{Li}_x(\mathbf{43})(\text{HMPA})_{10.4}$, the maximum achieved Li:**43** ratio is 1.75:1. Larger amounts of lithium do not dissolve in the solution of **43** in HMPA. As seen from the **Figure 8.10**, $\text{Li}_{1.0}(\mathbf{43})(\text{HMPA})_{10.4}$ exhibits higher conductivity (1221 $\mu\text{S}/\text{cm}$ at 295 K) than $\text{Li}_{1.75}(\mathbf{43})(\text{HMPA})_{10.4}$ (1180 $\mu\text{S}/\text{cm}$ at 295 K). Both demonstrate quasi linear $\sigma(T)$ correlation between 281 K and 295 K with positive trend ($\sigma(T) = 6.44T - 727$ for Li:**43** = 1:1, and $7.72T - 1056$ for 1.75:1), showing that the contribution of ionic conductivity is higher than the metallic one.

Figure 8.10. The conductivity versus temperature graphs for $\text{Li}_x(\mathbf{43})(\text{HMPA})_{10.4}$, $x = 1.0$ and 1.75.

The E vs T profile of $\text{Li}_{1.75}(\mathbf{43})(\text{HMPA})_{10.4}$ in Li/Ceramics/LiSES half-cell configurations demonstrates complex correlation with a drop in voltage when the temperature is higher than 294K (**Figure 8.4**). Similar to $\text{Li}_x(\mathbf{41})(\text{HMPA})_{10.4}$, the obtained value of OCV for $\text{Li}_{1.75}(\mathbf{43})(\text{HMPA})_{10.4}$ (1.66 V at 22 °C) is significantly above 1 V vs Li^+/Li , which makes these materials unsuitable for applications as anolytes.

Figure 8.11. The open circuit potential versus temperature graphs for the half-cell $\text{Li}_{1.0}(\mathbf{43})(\text{HMPA})_{10.4}/\text{Li}$.

For better understanding of the HMPA influence on Li SES properties, it was decided to perform conductivity and half-cell OCP studies on biphenyl based Li SES using HMPA as a solvent. The maximum achieved Li:Biphenyl ratio was 0.75:1. Larger amounts of lithium do not react with the solution. The conductivity versus temperature and OCP versus temperature plots for the obtained Li SES of the formula $\text{Li}_{0.75}(\text{Biphenyl})(\text{HMPA})_{10.4}$ are shown at the **Figure 8.12**.

Figure 8.12. Conductivity versus temperature (left) and OCP versus temperature (right) profiles for $\text{Li}_{0.75}(\text{Biphenyl})(\text{HMPA})_{10.4}$.

Table 8.7. The values of conductivity at 22 °C, $\sigma(T)$ linear fit equation, open-circuit potential at 295 K (22 °C), $E(T)$ linear fit equation, calculated values of ΔS and ΔH for $\text{Li}_{0.75}(\text{Biphenyl})(\text{HMPA})_{10.4}$.

Parameter	Value
Conductivity (mS/cm) at 295K (22 °C)	2.08
$\sigma(T)$ (mS/cm) =	$-0.0006T + 2.26$
E at 295K (22°C) (mV)	1226
$E(T)$ (mV) =	$-13.3T + 5164$
ΔS (J/(mol*K))	-1283
ΔH (kJ/mol)	-498

The conductivity value of $\text{Li}_{0.75}(\text{Biphenyl})(\text{HMPA})_{10.4}$ is lower comparing to biphenyl based Li SES of same composition made in THF. The conductivity demonstrate insignificant change with temperature, which means that the contribution of the ionic and the metallic conductivity are almost equal.

The OCP demonstrates values that are higher than 1 V in the studied range of temperature and significantly change upon changing temperature (Figure 8.12, right). The obtained values of ΔS and ΔH shown in **Table 8.7**. Remarkably, the obtained value of ΔS is the highest among all the Li SES studied in this or previous works. This unusual value can be a result of more significant ion pairs dissociation in HMPA comparing to THF that provides more degrees of freedom to the system.

8.3.4. HMPA as a solvent for Li SES

As seen from the experiments discussed in sections 8.3.2 and 8.3.3, HMPA makes it possible to prepare Li SES based on 2,2'-bipyridine (**41**) and 4,4'-bipyridine (**43**) due to better solvating properties of this solvent. However, the OCP values for the Li SES prepared in HMPA are higher than 1 V vs Li^+/Li and significantly higher than the values for Li SES in THF, which means that Li SES in HMPA are not applicable as anolytes in secondary batteries due to much lower potential between these Li SES made in HMPA and

cathode materials comparing to other Li SES made in THF. However, these Li SES could find an application as catholytes. The fact that the maximum Biphenyl:Li ratio obtained in HMPA is 0.75:1, which is significantly lower than the one obtained in THF, means that THF is a better solvent used to prepare PAH based Li SES than HMPA. Nevertheless, more studies on various Li SES prepared in HMPA should be done in order to understand the effect of this solvent in detail.

8.4. Conclusions

The Li SES based on 3- (**72**) and 4-phenylpyridines (**73**) demonstrate much higher electrical conductivity values than those of 2-phenylpyridine (**71**). Among the studied materials, the largest conductivity was achieved in $\text{Li}_{1.0}(\textbf{73})(\text{THF})_{10.4}$. However, all these Li SES exhibit much lower conductivity values than naphthalene and biphenyl based Li SES, what is probably related to the localization of the negative charge density dominantly on the more electronegative atom of nitrogen leading to less probability of electric current propagation upon the interaction between the molecules.

The ΔS and ΔH values of the studied Li SES with Li:PAH ratio of 1:1 are very close. This result could be related to structural similarities between the studied molecules. These values of ΔS are much lower than those for naphthalene and biphenyl probably due to the localization of the charge density in the heterocyclic systems resulting in less degrees of freedom. However, these values are higher than those for solid-state materials Li_xC_6 and Li_xCoO_2 due to more degrees of freedom in a liquid compared to a solid. The Li SES based on 2-phenylpyridine (**71**) demonstrates a phase transition around 284 K that was detected by the change of trend in both conductivity and OCP vs T.

Our modeling of the corresponding Li-phenylpyridines adducts on their geometrical structures and molecular orbitals demonstrates significant distortion of the aromatic structure and localization of the lithium atom close to the nitrogen atom. However, when the second atom of lithium is added, it stays above the center of benzene ring. The electronic structure of the HOMO show that the electronic density is significantly higher

near the nitrogen atom, suggesting the localization of the 2s electron of lithium atom. The structures of HOMO and LUMO of Li₂(**73**) supports the instability character of the corresponding Li SES.

Although biphenyl **41** and **73** do not form Li SES in THF, it is possible to prepare them in HMPA due to better solvating characteristics of this solvent. The Li SES based on **41** and **43** demonstrate complex correlations of conductivity and OCP versus composition and temperature. These Li SES exhibit the OCP being higher than 1 V versus Li⁺/Li and much higher than other Li SES made in THF, resulting in significantly lower potential between these Li SES made in HMPA and cathode materials, which prevents using them as anolytes in secondary batteries, although they might be considered in catholyte applications. Taking into account the maximum Li:Biphenyl ratio of 0.75:1 in corresponding Li SES made in HMPA, which is significantly lower than the ratio achieved for biphenyl in THF, and the OCP of biphenyl based Li SES made in HMPA being above 1V versus Li⁺/Li, THF can be considered as a better solvent than HMPA for the applications of Li SES as anolytes.

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Chapter 9*

Larger polyheteroaromatic systems: synthesis and electronic properties of 5,7-diazapentacene derivatives

The first part of the chapter discusses the synthesis of 5,7-diazapentacene derivatives – a novel class of materials that can find applications not only in Li SES, but also as materials for organic field effect transistors OFET). Starting with synthesis of precursors, the approaches to synthesis of these polyheteroaromatic molecules are represented, in particular, Friedländer reaction followed by dehydrogenation, acid or water elimination, and oxidation. A successful approach that involves a reaction with an arylodonium salt is discussed at the end of the synthetic part. The characterization part includes the results on Single Crystal X-Ray Diffraction (SCXRD), Cyclic Voltammetry (CV), UV Visible and Photoluminescence spectroscopy. Based on the CV and UV Vis results, the electronic properties of the novel 5,7-diazapentacene derivatives were defined. Changes in UV Vis absorption and photoluminescence spectra of the synthesized materials and their precursors upon exposure to acids are also discussed in this chapter.

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9.1 Introduction

Acenes are polyaromatic hydrocarbons having linearly fused benzene rings. The simplest representatives of acenes are naphthalene and anthracene. While feasibility of naphthalene based Li SES applications in secondary batteries was investigated before, anthracene is discussed in Chapter 4 of this thesis. The higher acenes [1] are one of the most heavily investigated classes of organic semiconductors, in part because of the exceptionally high ($>10 \text{ cm}^2/\text{Vs}$) charge carrier mobilities measured in single crystals of acenes such as pentacene (**75**) and rubrene (**76**, **Figure 9.1**). [2] Charge carrier mobilities above $1 \text{ cm}^2/\text{Vs}$ have also been measured in field effect transistors (FETs) using thin films of solution processable pentacene derivatives such as TIPS-pentacene (**77**). [3, 4] While these acenes are p-type materials, the incorporation of nitrogen atoms into the aromatic core of acenes such as pentacene increases their electron affinity and lowers the frontier molecular orbital energies, making them better electron acceptors and transporters. As a result **78**, a tetraazapentacene analogue of TIPS-pentacene is an n-type semiconductor. [5] Thus, pyrazinacenes such as **78** which contain pyrazine rings have become widely studied materials due to their potential application as n-type semiconductors in OFETs and other organic electronic devices, [1, 6] and there exist well developed procedures for their synthesis. [7, 8] Due to the electronic properties of nitrogen doped acenes, the Li SES based on these materials can also find a potential application as anolytes in secondary batteries.

Figure 9.1. Structures of previously known acenes and tetrazaacenes and of the new diazapentacenes.

However, some nitrogen doped acenes, which could be important for elucidating structure-property relations such as 5,7-diazapentacene (quinolino[3,2-b]acridine) (**79**), have never been synthesized, and, thus, studied. The only reported attempt to synthesize **79** was unsuccessful. [9] The authors obtained a mixture of products with secondary amino groups instead of the target molecule with pyridine rings. Thus, the aim of this chapter is to propose a route to synthesis of a novel class of nitrogen doped acenes – derivatives of 5,7-diazapentacene (**80**) and to study the electronic properties of these materials, in order to assess the feasibility of using them in OFET and, in Li SES as anolytes for secondary batteries.

9.2. Synthesis of novel 5,7-diazapentacene derivatives

9.2.1. Synthesis of precursors and attempts to obtain 5,7-diazapentacene framework via dehydrogenation

In order to obtain the diazapentacene framework, it was decided to utilize an approach based on a double Friedländer condensation [10, 11] between one molecule of diaminodiketone **82** and two molecules of cyclohexanone **83** giving a derivative of pyrido[3,2-g]quinoline **81** (Figure 9.2) followed by oxidation to produce the desired diazapentacene **80**. It was anticipated that alkyl chains in the 12 and 14 position of the diazapentacene framework **80** would stabilize the target molecule as well as improve its solubility, thus, it was decided to attach hexyl chains onto the framework.

Figure 9.2. An approach to synthesis of 5,7-diazapentacene framework by means of Friedlander reaction followed by dehydrogenation.

A new approach was implemented to synthesize the compound **82**. First, nitration of m-dibromobenzene (**10**) gave 1,5-dibromo-2,4-dinitrobenzene (**85**) [12], which was then subjected to Sonogashira coupling [13] with 1-heptyne in THF using $\text{Pd}(\text{PPh}_3)_4$ as catalyst and Et_3N as a base. The reaction was complete within 8 hours at room temperature, giving the product **86** in 78% yield, but did not give the compound **86** if performed at higher temperatures. If the reaction mixture was kept for longer than 8 hours, the yield started to decrease gradually. Tandem reduction of nitro groups and hydrolysis of triple bonds of **86** using hydrated SnCl_2 [14, 15] gave **82** in 60% overall yield, which is good for a four step process. A reported procedure for synthesis of monoaminophenones that utilizes tin in acidic conditions [16] failed to give the desired product, although the starting material was completely consumed. Given the good yields and mild conditions, the proposed procedure that involves SnCl_2 is a convenient way to prepare **82**. Although it has not yet been tested if this is a general reaction there seems to be no reason why it should not work equally well to produce other similar molecules.

Figure 9.3. Synthesis of **82**.

For the synthesis of the pentacene precursors **81**, the screening of conditions for the Friedlander reactions was conducted (**Figure 9.4**) including acid, base and Lewis acid catalyzed conditions as shown in **Table 9.2** to investigate the extent of reactions for each type. It was discovered that the desired reaction does not take place in basic conditions nor when Lewis acids were used, with the starting material being recovered and no indication of **81a** having been formed. The reaction in acidic conditions in refluxing AcOH was successful, but the yield of 12% obtained was not satisfactory. It was observed that lowering the temperature was effective in producing **81a** in 45% yield with a conversion

rate of 98.4%. When using ethanolic HCl as a catalyst, we found the reaction had a much higher yield of 73% and took less time than in case of acetic acid and so these conditions were selected as the initial conditions for all future Friedländer reactions.

Figure 9.4. Synthesis of **81a**.

Table 9.1. Conditions screening for the reaction between **82** and cyclohexanone.

Entry	Reagents	Amount of catalyst	Conditions	Yield
1	Bi(OTf) ₃ , EtOH	20 mol %	75 °C, 48h	-
2	FeCl ₃ , EtOH	20 mol %	75 °C, 24h	-
3	LiOH, MeCN	50 mol %	75 °C, 24h	-
4	KOH, EtOH	50 mol %	75 °C, 48h	-
5	TsOH·H ₂ O	2.1 eq	80 °C, 2h	-
6	AcOH	Solvent	110 °C, 48h	12%
7	AcOH	Solvent	85 °C, 60h	45%
8	HCl, EtOH	2 eq	75 °C, 20h	73%

To test that these optimized conditions were generally applicable a variety of pyrido[3,2-*g*]quinolone derivatives **81b–e** were synthesized using these conditions (**Table 9.2**). Remarkably, 1,3-cyclohexanedione gave only the product of monoaddition even when a significant excess of the reactant was used, while acetophenone did not react.

Table 9.2. Reaction of various ketones with **82** under optimized conditions.

Reactant	Product	Time	Yield
81b	16h	60%
81c	48h	51%
81d	24h	32%
81e	48h	49%

It was then attempted to obtain the corresponding pentacene derivatives **80** by means of dehydrogenation of **81a** and **81b** using Pd/C. Unfortunately, these materials were not produced upon attempting the reaction at different temperatures, i.e. 200 °C and 170 °C and utilizing different solvents (p-cymene, nitrobenzene, diphenyl ether). The complex mixture of oligomers formed in the reaction may be evidence for the desired products having low stability under the reaction conditions.

All the synthesized compounds were characterized by means of ^1H and ^{13}C NMR (Appendix). Additionally, the accurate masses of new materials **82** and **81a-e** was determined using HR MS (Appendix).

9.2.2. Synthesis of 5,7-diazapentacene framework via HX elimination

Considering the unsuccessful attempts of **81a** and **81b** dehydrogenation, it was decided to examine an alternative approach, which involves Friedländer reaction followed by elimination of HX (X = Br, OAc, OMe or OH) shown in **Figure 9.5**. The additional benzene rings in the structure of **87** should provide an additional stabilization to the 5,7-diazapentacene framework.

Figure 9.5. Approach to synthesis of diazapentacene that involves the elimination of HX.

The material with X = Br (**89a**) was synthesized from α -tetralone (**90**) by bromination with N-bromosuccinimide (NBS) [17]. **89b** and **89c** were synthesized as shown in **Figure 9.6** [18]. α -tetralone was first reduced with sodium borohydride. Protection of hydroxy group followed by oxidation using KMnO_4 gave **89b**. **89c** was obtained by hydrolysis of the ester **89b**.

Figure 9.6. Synthesis of **89b** and **89c**.

However, it was found that **89a** is unstable and spontaneously decomposes even when storing in a fridge at $+6^\circ\text{C}$ giving α -naphthol and HBr . Although **89b** and **89c** are stable at room temperature, they decompose under Friedländer reaction conditions giving α -naphthol with no evidence of condensation with **82**.

Figure 9.7. Decomposition of **89a-c**.

9.2.3. Synthesis via oxidation

Because of the unsuccessful dehydrogenation of **81a, b**, we decided upon incorporation of additional benzene rings, as represented by the structure **93**, to stabilize the 5,7-diazapentacene (2) framework. It was expected to synthesize **93** by oxidation of **94**, which could be obtained by a Friedländer reaction between **82** and **95** (Figure 9.8).

Figure 9.8. Synthetic strategy for making **93**.

Since additional methoxy groups facilitate the oxidation reaction represented in **Figure 9.8**, it was decided to synthesize derivatives of **94** having various number of methoxy groups attached to the side benzene rings. The compounds **95b,c** (**Figure 9.9**) required for synthesis of these derivatives of **94** were prepared by means of Friedel-Crafts reaction between 1,2-dimethoxybenzene and corresponding phenylacetic acid chlorides [19, 20].

Figure 9.9. Synthesis of **95b,c**.

It was found that **82** and **95a–c** did not react under the conditions used to make **81a–e**. Instead, we found that **95a–c** reacted with **82** under solvent free conditions using p-toluenesulfonic acid (TsOH) as a catalyst at 105 °C giving **94a–c** in good to moderate yields (**Figure 9.10**). It was found that among **94a–c** only **94b** could be converted to the desired product **93b** using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ /[bis(trifluoroacetoxy)iodo]benzene (PIFA) as oxidant [21], though the yield was only 28%. **94a** did not react in these conditions, while **94c** gave

a complex mixture of oligomeric products. Other oxidants tested such as DDQ and FeCl_3 did not convert **94a–c** to the desired products.

All the synthesized compounds were characterized by ^1H and ^{13}C NMR (Appendix 1). Additionally, the accurate mass of new materials **94a–c** and **93b** was determined using HR MS (Appendix 1).

Figure 9.10. Synthesis of **18b**.

9.2.4. Synthesis involving iodonium salts.

It was found that the diaminodiketone **82** reacts with diphenyliodonium triflate [22] in the presence of catalytic amounts of copper (I) iodide in 1,2-dichloroethane at 70°C , to give the 5,7-diazapentacene **6a** in 30% yield (**Figure 9.11**).

Figure 9.11. Synthesis of 5,7-diazapentacene **80a**.

The derivative of 5,7-diazapentacene **80b** bearing phenyl groups was synthesized employing the strategy shown in **Figure 9.12**. First, 1,5-dimethyl-2,4-dinitrobenzene (**96**)

was obtained by means of nitration. Then **96** was oxidized using CrO_3 [23] followed by Friedel-Crafts reaction between the acid **97** chloride and benzene in 1,1,2,2-tetrachloroethylene [24] to give **98** in 61% yield. The reduction of **98** by hydrogen at atmospheric pressure in presence of Pd/C gives diaminodiketone **99** in 86% yield. The reaction of **99** with two equivalents of diphenyliodonium triflate leads to the 5,7-diazapentacene **80b** in 55% yield.

All the synthesized compounds were characterized by ^1H and ^{13}C NMR (Appendix 1). Additionally, the accurate masses of the novel 5,7-diazapentacenes **80a,b** was determined using HR MS (Appendix 1).

Figure 9.12. Synthesis of **80b**.

9.3. Single crystal X-Ray diffraction results⁵

To investigate the packing of the molecules, single crystals of **81a**, **81b** and **80a** were grown and subjected to single crystal X-ray diffraction (SCXRD) analysis. SCXRD was performed on **81a** on a Bruker D8 Quest with a Photon II detector using Mo K_α of wavelength 0.71073 Å and a multilayer mirror monochromator at 100 K. The frames were integrated using Bruker SAINT software package, absorption corrections were applied

⁵ The SCXRD experiments and data processing were performed by Samuel Alexander Morris (NTU MSE) and Rakesh Ganguly (NTU SPMS CBC).

using the program SADABS. SHELXT and SHELXL were used for structural solution and refinement respectively.

The final refinement yielded a $R_1 = 6.05\%$, a $wR_2 = 17.08\%$ and a *goodness-of-fit* factor of 1.018. The final structure was solved in the monoclinic space group $P2_1/c$ with the unit cell $a = 16.6840(7) \text{ \AA}$, $b = 9.5024(6) \text{ \AA}$, $c = 18.4451(8) \text{ \AA}$, $\beta = 113.6951(16)^\circ$ and $V = 2677.7(2) \text{ \AA}^3$ (CCDC 1583758).

The refined structure is made up of single units (**Figure 9.13**, left) that display π - π stacking through the aromatic backbone with a π - π stacking distance of $3.68 \text{ \AA}$ (Figure 6 right), each neighbouring stack alternates between two orientations at 90° to each other. This π - π stacking distance is appreciably greater than the values of $3.43 \text{ \AA}$ reported for TIPS-pentacene [3], or of 3.30 - $3.35 \text{ \AA}$ reported for TIPS-1-aza-pentacene derivatives [25]. This is due to the less planar nature of **81a** resulting from the nonaromatic rings, thus, it is anticipated that fully aromatised 5,7-diazapentacenes would pack more closely.

Figure 9.13. A single monomer unit of **81a** (left) and the π - π stacking of the monomer units that are separated by $3.68 \text{ \AA}$ (right). Black, blue and pink spheres represent carbon and nitrogen and hydrogen respectively.

When viewed down the z -axis this creates a zig-zag pattern of interlinking ‘layers’ of the aromatic backbones with the interlayer region made up of the extended C_6H_{13} chains interacting through van der Waals forces (**Figure 9.14**).

Figure 9.14. A structural view down the z-axis showing the alternating stacks of the monomeric unit of **81a** alternated at 90 ° to each other (shown left as red and blue lines) and how those zig-zag units connect through the extension of their C₆H₁₃ units (right). Black, blue and pink spheres represent carbon and nitrogen and hydrogen respectively.

Single-crystal X-ray crystallography was also performed on **81b**. The crystals were grown from ethanol. A Bruker SMART APEX-II was used with a Mo K α wavelength 0.71073 Å and a graphite monochromator at room temperature. The frames were integrated using Bruker SAINT software package, absorption corrections were applied using the program SADABS and the space group assigned using the program XPREP. SHELXT and SHELXL were used for structural solution and refinement respectively. The final refinement yielded a $R_1 = 6.23\%$, a $wR_2 = 13.91\%$ and a *goodness-of-fit* factor of 1.046. The final structure was solved in the triclinic space group *P*-1 with the unit cell $a = 8.8518(19)$ Å, $b = 12.613(3)$ Å, $c = 14.689(3)$ Å, $\alpha = 89.365(2)^\circ$, $\beta = 86.918(2)^\circ$, $\gamma = 74.577(2)^\circ$ and $V = 1578.6(6)$ Å³ (CCDC 1583759).

The final structure seen in the X-ray structure is in fact a dimer of the initially targeted compound (**Figure 9.15**). The structure of **81b** remains intact apart from a dimerization reaction across the central ring, this yields an X-shaped molecule (**Figure 9.15**), whose long C₆H₁₃ groups extend out and interact with each other to cause stacking of the dimerised units along the y-axis.

Figure 9.15. The X-shaped dimer of **81b**. Left shows one dimer molecule where the C_6H_{13} groups that normally extend out from the para position from each nitrogen have been omitted for clarity. Right shows the connection between each monomeric unit to form the X-shaped dimer. It should be noted that each $C_{40}H_{44}N_2$ half of the dimer connects through the central ring at 180° to each other such that each monomeric units' C_6H_{13} groups extend in opposite directions. Black, blue and pink spheres represent carbon, nitrogen and hydrogen respectively.

For both newly synthesised and recrystallized **81b**, the proton shifts in the NMR spectrum are observed for the protons on the central ring in the aromatic region, rather than at ca. $\delta 4.5$ as would be expected for the bridgehead protons in the dimer, and no ions corresponding to the dimer are seen in the mass spectra. Since both the NMR and mass spectra are consistent with the monomeric rather than dimeric structure, one can tentatively conclude that a dimerization has occurred during the X-ray measurements, either during handling of the crystal or upon X-ray irradiation. **81b** appears to be stable in the solid as no change in the NMR spectrum was seen in crystals that been left exposed to light for several weeks. We also found that the irradiation of **81b** in solution with 325 nm laser light for 5 hours did not lead to any detectable dimerization.

The Single Crystal XRD data obtained from crystals grown from the solution of **80a** in 1,2-dichlorobenzene also suggests the formation of dimer (**Figures 9.16, 9.17 and 9.18**). SCXRD was carried out on a BRUKER D8 Quest system using a microfocus Mo source with a multilayer mirror along with a Photon II CPADs detector. The collection was carried

out at 100 K. The data was processed using the BRUKER SAINT software package and absorption corrections applied using the program SADABS. The data was refined using an anisotropic full-matrix least squares refinement on F^2 , yielding a $R_1 = 6.44\%$, $wR_2 = 13.64\%$ and a *goodness-of-fit* of 0.938. The dimer of compound **80a** (CCDC 1852346) crystallizes into the monoclinic space group C2/c with a unit cell of $a = 23.823(3) \text{ \AA}$, $b = 10.0672(15) \text{ \AA}$, $c = 23.365(4) \text{ \AA}$, $\beta = 110.107(5)^\circ$ and $V = 5262.1(14) \text{ \AA}^3$. A colorless plate-like specimen of $C_{32}H_{39}N_2O_{1.50}$, approximate dimensions 0.021 mm x 0.176 mm x 0.188 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Figure 9.16. A truncated single dimer molecule of compound **6a** where the C_6H_{13} tails have been removed for clarity. The tails would attach to the opposite ring carbon from each nitrogen. Hydrogen bonds can be observed as dashed lines; it is these favorable hydrogen bonds which may encourage the nitrogen atoms to remain on the same face during dimerization. Carbon, oxygen, nitrogen and hydrogen are shown as black, red, blue and pink spheres respectively. Hydrogens attached to the carbon backbone have been removed for clarity. The same coloring scheme is followed throughout all following images.

SCXRD shows the dimer of compound **80a** stacks parallel to the b -axis (**Figures 9.16** and **9.17**). The four nitrogen atoms hydrogen bond with two symmetry-equivalent waters of crystallization, which in turn hydrogen bond to a second water of crystallization. This is

different to the dimer of **81b**, which does not crystallize with any water in the structure. It is clear that with water in the crystal, the favorable formation of hydrogen bonds encourage the direction of the pyridine groups to face the same way, unlike in the dimer of **81b**, where they face in opposite directions within the dimer. The dimerization of **80a** prohibits π - π interactions between neighboring molecules, instead, neighboring molecules predominantly interact through van de Waals forces from the long extending C_6H_{13} units as can be seen in **Figure 9.18**.

Figure 9.17. This shows how the x-shaped dimers interconnect in the a-c plane. The long C_6H_{13} chains extend to interact with each other through van de Waals forces. A single unit of the dimer has been highlighted in yellow. The image shows a 2x2x2 supercell of compound **80a** viewed down the b-axis where the unit cell is shown as blue dashed lines.

Figure 9.18. A ‘side-on’ view of how the dimer stacks parallel to the b-axis. The relationship between the waters of crystallization and the nitrogen from the pyridine rings are also clearly shown.

Although it was not investigated in detail whether the dimerization of **80a** happens during XRD measurements or during the crystal growth, the absence of any signals from the dimer in the NMR or MS, and the formation of dimer during XRD experiment in the case of **81b** suggests that dimerization happens during the exposure to X-Ray radiation.

Attempts to produce good quality single crystals of **93b** and **80b** suitable for SCXRD analysis have to date proven unsuccessful. This could be due to the low solubility of these materials in organic solvents.

9.4. Optical properties.

Since azaacenes have been reported to show strong absorption and fluorescence [26, 27] the absorption and emission properties of the new materials were studied. Among **81a-e**, it was decided to focus on **81a** and more complex conjugated systems **81b** and **81e**. All these molecules showed strong absorption in the UV and/or violet and strong green or yellow fluorescence, suggesting they may have potential for use as emissive materials, e.g. in LEDs. The absorption and emission maxima, as well as quantum yield (Φ), for **81a,b,e**, **94a-c** and **93b** in chloroform solution (5×10^{-5} M) are tabulated in **Table 9.3**.

Figure 9.19 shows the UV Vis absorption and PL emission spectra of **81a,b** and **81e**. The peaks of **81b** in the visible part of the spectra are shifted to longer wavelengths comparing to **81a**, as would be expected given the longer conjugation length in **81b** due to the extra benzene rings. The absorption peaks for **81b** also demonstrate higher intensity than the peaks for **81a**. In the UV part of the spectra, **81b** shows several peaks (324nm, 311nm, 298nm, 290nm, 266nm) which are significantly red-shifted comparing to the single broad peak for **81a** at 265nm. The photoluminescence spectra also display a similar red shift between **81a** and **81b**. Thus, the additional benzene ring enlarges the aromatic system, which leads to the red shift of the **81b** spectra compared to **81a**.

Figure 9.19. UV Vis (left) and photoluminescence (right) spectra of **81a** (black), **81b** (red) and **81e** (blue) in solution (5×10^{-5} M in chloroform).

The absorption spectra of **81e**, whose structure is isoelectronic to septacene, demonstrates four absorption peaks with the maximum intensity at 400 nm (**Figure 9.19**). The emission spectra has three distinctive peaks with the maximum intensity at 460 nm, which corresponds to a Stokes shift of 60 nm. Since the aromatic system of **81e** is even larger than that of **81b**, an even larger red shift compared to **81a** is observed.

Table 9.3. Optical properties of **81a,b,e**, **94a-c**, and **93b** in chloroform solution.

	λ_{max} (abs) (nm)	λ_{onset} (nm)	λ_{max} (em) (nm)	Stokes Shift (nm)	ϵ (L M ⁻¹ cm ⁻¹)	Φ
81a	370	415	438	45	16380	0.42
81b	407	419	456	49	28600	0.10
81e	400	464	460	60	7620	0.30
94a	382	405	463	81	24480	0.08
94b	398	430	467	37	20200	0.17
94c	403	437	467	30	19300	0.23
93b	462	542	579	37	31120	0.27

Since the nitrogen atoms in **81a,b** are weakly basic the effects of acid upon the absorption and emission spectra of these compounds were studied. Addition of 1 equivalent of trifluoroacetic acid to a solution of **81a** in chloroform led to a significant red shift in both UV-Vis and fluorescence spectra, and change of the peaks pattern as well (**Figure 9.20**). This significant change in both UV-Vis and PL spectra is related to the protonation of a nitrogen, which leads to changes in the molecules' electronic structure. Further addition of the acid has not led to any further change in the spectra.

Figure 9.20. UV Vis (left) and photoluminescence (right) spectra of **81a** (black), a mixture of **81a** with 1 equivalent of CF₃COOH (red), a mixture of **81a** with 2 equivalents of CF₃COOH (red) (5×10⁻⁵ M in chloroform).

For compound **81b**, addition of 1 eq. CF_3COOH leads to significant changes in both the UV-Vis and photoluminescence spectra, but the value of the absorption maximum is not changed significantly (**Figure 9.21**). Addition of one more equivalent of CF_3COOH leads to decreased intensity of the peak at 408 nm and an increase of the peak at 421 nm. In the emission spectra, two distinct peaks become visible upon addition of 2 equivalents of CF_3COOH .

Figure 9.21. UV Vis (left) and photoluminescence (right) spectra of **81b** (black), a mixture of **81b** with 1 equivalent of CF_3COOH (red), a mixture of **81b** with 2 equivalents of CF_3COOH (red) (5×10^{-5} M in chloroform).

Compounds **94a-c** demonstrate similar patterns in both UV-Vis and PL spectra but with lower absorption in UV part of the spectra for **94b**.

The colour of the solutions containing **94a-c** significantly changes upon addition of 10 equivalents of acid, as shown in **Figure 9.22**. No change in either UV Vis or PL spectra was observed upon addition of 1 and 2 eq of CF_3COOH to a solution of **94a** in chloroform (**Figure 9.23**). However, 10 eq of CF_3COOH leads to the appearance of a broad peak in UV Vis spectra with a maximum at 396 nm and a shift of the maximum to 502 nm in PL spectra.

Figure 9.22. The solutions of **94a** (left), **94b** (middle) and **94c** (right) in chloroform before (left picture) and after the addition of trifluoroacetic acid (right picture).

By contrast as shown in **Figures 9.24** and **9.25**, the spectra of **94b** and **94c** change upon addition of 1 eq. of CF_3COOH . The peak at 397nm starts to disappear and the peak at 449nm becomes more intense upon increase of the concentration of the acid. Unlike for **94a**, fluorescence quenching is observed for **94b** and **94c** upon addition of acid.

Thus, the protonation of the compounds **94b** and **94c** occurs more easily than for **94a**. This is explained by the electron density and thus the basicity, of the aromatic system in **94b** and **94c** being increased by the electron donating methoxy substituents in these molecules. This enrichment of the aromatic core electron density also explains the red shift in spectra with increasing number of methoxy groups from **94a** to **94c**.

Figure 9.23. UV Vis (left) and photoluminescence (right) spectra of **94a**, and mixtures of **94a** with 1 equivalent, 2 equivalents, and 10 equivalents of CF_3COOH (5×10^{-5} M in chloroform).

Figure 9.24. UV Vis (left) and photoluminescence (Right) spectra of **94b**, and mixtures of **94b** with 1 equivalent, 2 equivalents, and with 10 equivalents of CF_3COOH (5×10^{-5} M in chloroform).

Figure 9.25. UV Vis (left) and photoluminescence (right) spectra of **94c**, and mixtures of **94c** with 1 equivalent, 2 equivalents, and 10 equivalents of CF_3COOH (5×10^{-5} M in chloroform).

Considering the changes that occur in the UV-Vis spectra of **94a-c** upon the addition of acid are quite similar to the ones observed for **81a,b** (the intensity of one peak decreases, and the intensity of another gradually increases), and the presence of only one isosbestic point in the spectra (333nm for **94a**, 414nm for **94b**, and 412nm for **94c**), we again conclude that only one nitrogen is protonated in this range of acid concentrations.

Figure 9.26. UV Vis (above left) and photoluminescence above (right) spectra of **93b**, and mixtures of **93b** with 1 equivalent, 2 equivalents, and 10 equivalents of CF_3COOH (5×10^{-5} M in chloroform). Solutions of **93b** in CHCl_3 before (bottom left) and after (bottom right) addition of 10 equivalents of CF_3COOH .

Compound **93b** displays (**Figure 9.26**) two peaks in UV absorption spectrum at 435 and 462 nm and two peaks in the photoluminescence spectrum, at 540 and 581 nm (Stokes shift is 117nm). The onset of absorption is at 542 nm, which corresponds to an optical bandgap of 2.3 eV. Since the aromatic system of **93b** is larger than that of **94a-c**, a larger red shift is observed. A significant change in the absorption spectra is observed upon addition of trifluoroacetic acid. Upon addition of 10 eq. of trifluoroacetic acid, the mixture demonstrates a broad absorption with the maximum intensity at 516 nm which shows as a change in colour from red to purple (**Figure 9.26** inset), which is similar to the colour change seen with indicators such as litmus. Again it can be concluded from the pattern of the change in UV-Vis spectra upon the acid addition, that as for all the previously mentioned compounds only one nitrogen protonates upon addition of the acid in the studied

range of concentrations. Quenching of fluorescence is observed upon addition of the acid, as was also seen for **94b** and **94c**.

This extreme change in optical properties suggests that compounds based on the diazapentacene framework may have potential for use in sensors. Unlike tetrazapentacenes whose solutions have been shown to undergo colour charges upon addition of anions such as fluoride due to a charge transfer process [28], no change in absorption or emission spectra were observed upon adding fluoride or cyanide anions to solutions of **93b**. This is because the lower number of nitrogen atoms in the diazapentacenes make them less able to accept an electron through charge transfer.

The optical absorption spectra of **80a** and **80b** are shown in **Figure 9.27**. Both the spectra exhibit very similar pattern, with a slight red shift of the signals of **80b**. Both the compounds exhibit no fluorescence. The values of λ_{max} and λ_{onset} are shown in **Table 9.4**.

Figure 9.27. UV Vis absorption spectra of **80a,b**.

Table 9.4. Optical properties of **80a,b**.

	80a	80b
λ_{max} (nm)	429, 551	430, 558
λ_{onset} (nm)	674	687

9.5. Electrochemical properties and electronic structure of 5,7-diazapentacene derivatives and their precursors.

As shown in **Figure 9.28**, both **81a** and **81b** demonstrate two reversible reductive and oxidative peaks in CV using $\text{FcCp}_2/\text{FcCp}_2^+$ as internal standard from which their HOMO and LUMO energy levels were calculated using the equations shown in Chapter 3, section 3.5. **81a** and **81b** show very similar oxidation potentials of 0.9 and 0.8 V corresponding to HOMO energies of -5.7 and -5.6 eV respectively, and identical reduction potentials of -1.3 V corresponding to a LUMO energy value of -3.5 eV. **81e** demonstrates similar CV profile to **81a,b**. As also shown in **Figure 9.28**, the compound **93b** demonstrates a lower oxidation potential than **81a,b** of 0.4 V, but an identical reduction potential of -1.3 V (versus Fc/Fc^+) corresponding to HOMO and LUMO energies of -5.2 and -3.5 eV, and a smaller bandgap (E_g^{CV}) of 1.7 eV compare with 2.2 and 2.1 eV for **81a** and **81b** respectively. This is to be expected given the more extended π -system in **93b** compared with **81a,b**. For all three compounds the optical bandgaps E_g^{opt} calculated from UV Vis spectra using the equation discussed in Chapter 3, section 3.4 were larger by 0.6-0.9 eV

Figure 9.28. CV plots for **81a,b** (left), and **81e, 93b** (right).

80a and **80b** show oxidation potentials of 0.4 and 0.6 V corresponding to HOMO energies of -5.2 and -5.4 eV respectively (**Figure 9.29**). The values of reduction potentials are -1.3 V and -1.4 V corresponding to a LUMO energy value of -3.5 eV and -3.6 eV respectively. Thus, based on the results from CV, the compound **6a** has a band gap of 1.7 eV and **6b** of

1.8 eV. The E_g^{opt} and E_g^{CV} of **80a** are similar to **93b**, however E_g^{CV} of **80b** was found to be insignificantly larger.

Figure 9.29. CV plots for **80a,b**.

The electrochemical data and calculated frontier orbital energies and bandgaps for these molecules are tabulated in **Table 9.5**. These compare with reported values for pentacene of -5.00 and -3.20 eV [29], and -5.40 and -3.40 eV for an inseparable mixture of 1,8- and 1,11-diazapentacenes [25]. It is also reported in patent literature that a 5,12-diazapentacene has calculated HOMO and LUMO energy levels 0.54 eV and -0.41 eV respectively lower than those of pentacene corresponding to values of -5.54 and -3.20 eV [30]. The new azaacenes **80a,b** demonstrate similar values of HOMO and LUMO to the mixture of 1,8- and 1,11-diazapentacenes. These experimental and theoretical results confirm that introduction of nitrogen ‘dopant’ atoms into pentacene lowers the frontier orbital energies.

While solution cast thin films of **93b** and **80a** appear to be of good quality, attempts to obtain charge carrier mobilities from FETs based on them have to date proved unsuccessful. This could be related to the effect of hexyl chains that loosen the crystal package. The works on fabricating FET from **80b** are ongoing.

Table 9.5. Electrochemical data and electronic properties of compounds **81a,b,e**, **93b**, **80a,b**.

	E_{onset}^{ox} (V) vs Fc/Fc ⁺	E_{onset}^{red} (V) vs Fc/Fc ⁺	HOMO level (eV)	LUMO level (eV)	E_g^{CV} (eV)	E_g^{opt} (eV)
81a	0.9	-1.3	-5.7	-3.5	2.2	3.0
81b	0.8	-1.3	-5.6	-3.5	2.1	3.0
81e	0.8	-1.3	-5.6	-3.5	2.1	2.7
93b	0.4	-1.3	-5.2	-3.5	1.7	2.3
80a	0.4	-1.3	-5.2	-3.5	1.7	1.8
80b	0.6	-1.4	-5.4	-3.4	2.0	1.8

9.6. Conclusions

A convenient and general 4 step procedure for synthesis of various derivatives of pyrido[3,2-g]quinoline including an octahydro- (**81a**), a tetrahydro-dibenzo-5,7-diazapentacene (**81b**), and a number of 2,3,7,8-tetraphenylpyrido[3,2-g]quinolones (**94a-c**) via Friedlander condensation has been developed.

Although the attempts in converting these molecules to fully aromatized 5,7-diazapentacene by means of dehydrogenation were not successful, a tetrabenzo-5,7-diazapentacene **93b** was synthesized by employing a double Friedlander reaction followed by oxidation. Nevertheless, a procedure for synthesis of novel 5,7-diazapentacene derivatives **80a,b** has been established employing a double condensation of diaminodiketones with diphenyliodonium triflate. These newly synthesized materials were characterized using ¹H and ¹³C NMR, HR MS, Cyclic voltammetry, UV Vis and PL spectroscopy. For the compounds **80a**, **81a,b**, single crystal X-Ray diffraction was used to define the structure. It was found that the compounds **80a** and **81b** undergo dimerization in crystals upon the exposure to X-Rays.

Electrochemical measurements and UV Vis spectroscopy results show that the effect of the nitrogen atoms is to lower the HOMO and LUMO energies of our new materials compared

to pentacene. The materials show strong absorbance in the UV and violet regions of the spectrum, and strong fluorescence, suggesting they may have potential as emissive materials. It was also found that the solutions of some of the compounds show significantly altered UV Vis absorption and photoluminescence spectra upon exposure to acids, which suggests they may have applications in sensing for acids. The measured optical and electrical properties of the 5,7-diazapentacene derivatives and precursors suggest that suitably functionalized 5,7-diazapentacenes may be suitable for application in organic electronic devices. The amounts of the diazapentacenes obtained were too small for Li SES investigations. While there is no reason to believe they could not form such solutions, this will require preparation of larger quantities of the materials to test experimentally.

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Chapter 10

Conclusions and Future Work

This chapter summarizes the outcomes obtained in terms of correlations between chemical structure of the studied PAHs and properties of the resulting Li SES. According to the objectives and the strategy stated in Chapter 1, the obtained results are summarized and discussed in terms of PAH reactivity with lithium metal and maximum Li:PAH ratio achieved (Section 10.1.1), electric conductivity of Li SES (Section 10.1.2), as well as parameters related to half cells containing the studied Li SES (section 10.1.3), such as open circuit voltage, enthalpy change and entropy change. Section 10.2 represents the outcomes in context of the initial hypothesis. Section 10.3.1 discusses questions remained unaddressed in terms of already studied Li SES and possible directions in further studies on Li SES. Section 10.3.2 discusses the perspectives in studies of the novel 5,7-diazapentacenes and possible ways to implement the developed synthetic route to produce a variety of novel azaacenes, including larger representatives of this class.

10.1. Summary of results and discussion

10.1.1. PAH structure, reactivity of PAH with lithium and maximum Li:PAH ratio in Li SES

In order to investigate the correlations between the structure of PAH and the properties of corresponding Li SES, a number of PAH were studied according to the strategy discussed in Chapter 1, section 1.3. Based on the results previously obtained for the simplest PAH, which are naphthalene and biphenyl [1, 2], it was decided to investigate the changes in properties of Li SES upon incorporation of more benzene rings into these PAHs' structures. Thus, the study has started with p-terphenyl, where an additional benzene ring is connected via single bond to *para*-position of biphenyl molecule, and anthracene, which can be considered as naphthalene with one additional fused benzene ring. When Li SES were prepared using these molecules, it was found that the maximum Li:PAH ratio for p-terphenyl (**49**) is 2.4:1 and for anthracene (**8**) is 2:1. The ratios of Li:PAH = 2:1 for both **49** and **8** were achieved in more concentrated Li SES prepared from suspensions of these PAHs in THF. Since it is known that the maximum achieved Li:PAH ratio for biphenyl is 2.5:1, and the ratio of 2:1 can be reached with naphthalene, it was found that the addition of one more benzene ring producing ribbon-type aromatic systems does not lead to an increase in Li:PAH ratio. Thus, it was decided not to consider larger linear polyaromatic systems, such as tetracene (**11**), quaterphenyl (**50**) or pentacene (**12**). A Li:PAH ratio of 4:1 can be achieved for 1,3,5-triphenylbenzene (**51a**), a system with three benzene rings connected to the central one via σ -bonds. However, the aromatic system degrades when the ratio is above 2:1. Some of 1,3,5-triphenylbenzene derivatives with electron withdrawing groups do not react with lithium even in THF suspensions due to very limited solubility. The ratio of 4:1 was also achieved for triphenylene (**56**), a structure having four fused ring with one in the middle. However, this ratio was not achieved at higher concentrations of **56**. Hexaphenylbenzene **61b** does not react with lithium since there is no conjugation between its benzene rings due to steric effects. It was shown that hexa-peri-heabenzocoronene derivative **62b** can react with 6 mole equivalents of lithium or potassium, however, the maximum Li:PAH ratio was not identified.

For polyheteroaromatic structures, namely, isomeric phenylpyridines, the achieved Li:PAH ratio is 2:1 except for 4-phenylpyridine, which forms precipitate when Li:PAH ratio is larger than 1:1. For all the Li SES based on bipyridines and biphenyl in HMPA, the Li:PAH ratios are lower than 2:1.

These results show that the increase in number of rings does not necessarily lead to the increase of Li:PAH ratio. It was found that the Li:PAH ratio can be increased upon addition of benzene rings, either fused or connected via single bonds, giving structures that have a benzene ring in the center. Ribbon-type aromatic structures having either fused rings or connected by single bonds, do not lead to the increase in Li:PAH ratio upon addition of more rings. Steric effects that prevent conjugation between benzene rings prevent the formation of Li SES. PAH having electron donating groups (like methoxy group in **51b**) do not tend to form Li SES due to instability of the charged species formed. It was also shown that the achieved Li:PAH ratio is dependent on PAH concentration and the nature of the solvent.

10.1.2. PAH structure and electric conductivity of Li SES

The electric conductivity at 22 °C (295 K) of the Li SES studied is tabulated in **Table 10.1**. Among the PAH solutions of ~0.1 M concentration having the formula of $\text{Li}_x(\text{PAH})(\text{THF})_{123}$, p-terphenyl based $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{123}$, triphenylene based $\text{Li}_{2.0}(\mathbf{56})(\text{THF})_{123}$, and anthracene based $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{123}$ demonstrate the highest conductivity. These values are below 1 mS/cm. Remarkably, Li SES based on naphthalene of the same concentration shows very low value of conductivity. For both **8** and **49** conductivity significantly increases upon the increase of PAH concentration. The conductivity of $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$, prepared from suspensions of **49** and **8** in THF, is the highest among Li SES studied in this project. The conductivity values for these solutions are close to the maximum achieved for naphthalene and biphenyl, which are 12.0 mS/cm for $\text{Li}_{1.2}(\text{Biphenyl})(\text{THF})_{8.2}$ and 12.4 mS/cm for $\text{Li}_{0.5}(\text{Naphthalene})(\text{THF})_{6.2}$ [1, 2].

In general, the conductivity rises upon increase of PAH concentration within the studied range of PAH:THF ratios, which is related to the increase of charge carriers in a solution.

Table 10.1. Electrical conductivity (σ) and $\sigma(T)$ linear fit equations for the studied Li SES.

Li SES	σ ($\mu\text{S}/\text{cm}$) at 295K	σ (T) ($\mu\text{S}/\text{cm}$) =
Li _{0.5} (49)(THF) ₁₂₃	103	-4.94T + 1564
Li _{1.0} (49)(THF) ₁₂₃	636	-20.2T + 6594
Li _{1.5} (49)(THF) ₁₂₃	460	-20.0T + 6339
Li _{2.0} (49)(THF) ₁₂₃	288	-4.89T + 1728
Li _{2.3} (49)(THF) ₁₂₃	188	-2.86T + 1061
Li _{2.4} (49)(THF) ₁₂₃	54	-1.36T + 468
Li _{1.0} (49)(THF) _{12.3}	8140	-88.9T + 34175
Li _{2.0} (49)(THF) _{12.3}	1614	+6.93T - 425
Li _{0.5} (8)(THF) ₁₂₃	219	-4.84T + 1644.0
Li _{1.0} (8)(THF) ₁₂₃	547	-11.25T + 3839.8
Li _{1.5} (8)(THF) ₁₂₃	528	-10.41T + 3594.1
Li _{2.0} (8)(THF) ₁₂₃	223	-3.84T + 1354.1
Li _{1.0} (8)(THF) _{12.3}	8980	-78.2T + 3207
Li _{2.0} (8)(THF) _{12.3}	754	-0.02T + 759.6
Li _{2.0} (51a)(THF) _{24.7}	1873	-16.6T+6761
Li _{4.0} (51a)(THF) _{24.7}	1126	-5.63T+2789
Li _{2.0} (51c)(THF) _{24.7}	722	-4.87T + 2159
Li _{4.0} (51c)(THF) _{24.7}	502	-1.96T+1080
Li _{0.5} (56)(THF) ₁₂₃	17.6	-0.78T+248
Li _{1.0} (56)(THF) ₁₂₃	62.2	-6.06T+1848
Li _{2.0} (56)(THF) ₁₂₃	579	-12.07T+4133
Li _{3.0} (56)(THF) ₁₂₃	344	-7.52T+2590
Li _{4.0} (56)(THF) ₁₂₃	331	-8.32T+2954
Li _{6.0} (62b)(THF) ₁₂₃	30	0.64T – 157.4
K _{6.0} (62b)(THF) ₁₂₃	21	-0.32T + 115.8
Li _{1.0} (71)(THF) _{10.4}	100	-0.58T+270
Li _{2.0} (71)(THF) _{10.4}	158	+0.28T+75
Li _{1.0} (72)(THF) _{10.4}	1119	-9.99T+4070
Li _{2.0} (72)(THF) _{10.4}	897	-0.63T+820
Li _{1.0} (73)(THF) _{10.4}	1445	-14.6T+5762
Li _{0.5} (41)(HMPA) _{10.4}	563	-2.24T + 1228
Li _{1.0} (41)(HMPA) _{10.4}	709	-0.71T + 917
Li _{1.5} (41)(HMPA) _{10.4}	769	3.57T – 285
Li _{2.0} (41)(HMPA) _{10.4}	589	1.85T + 39.8
Li _{1.0} (43)(HMPA) _{10.4}	1221	6.44T – 727
Li _{1.75} (43)(HMPA) _{10.4}	1180	7.72T – 1056
Li _{0.75} (Biphenyl)(HMPA) _{10.4}	2080	0.06T + 2260
Li _{1.0} (Naphthalene)(THF) ₁₂₃	34	-3.02T+920

For the studied molecules, the conductivity first reaches the peak with the Li:PAH ratio of 1:1, except for **51a,c** and **56**, where the ratio of 2:1 exhibits the maximum conductivity. Then, conductivity decreases upon further increase of the ratio.

The effect of substituents was also studied in this project. Although alkyl chains increase solubility of higher PAH, they lead to decrease in conductivity compared to unsubstituted PAH due to their insulating effect. The low values of conductivity for Li and K SES based on larger PAH **62b** can be related to this effect as well. The fact that these Li and K SES demonstrate low values of conductivity does not support the initial hypothesis that conductivity of SES should increase upon the increase of PAH size.

The majority of tested Li SES demonstrate decrease in conductivity upon temperature increase, which is similar to metals and ammonia [3] based Li SES (**Table 10.1**). However, some of the studied Li SES demonstrate the opposite behavior. The measured values of conductivity have a contribution of metallic conductivity, which decreases with the temperature increase, and ionic, which increases when temperature rises. Thus, some of the Li SES with higher concentration of Li ions demonstrate positive trend of conductivity versus temperature. The Li SESs with HMPA as a solvent generally demonstrate positive trend due to more significant dissociation of PAH-Li ion pairs.

10.1.3. PAH structure and electrochemical properties of Li SES

During the experiments in a half cell (configuration: Li/Ceramics electrolyte (Ohara, Japan)/Li SES), open circuit potentials (OCP, E), E(T), ΔS and ΔH for the studied Li SES were defined. This data is shown in **Table 10.2**.

In general, the values of OCP vs Li^+/Li for studied Li SES in THF lie in the range of 0.6 – 0.9 V. The lowest value of OCP was obtained for 1,3,5-triphenylbenzene based $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ (0.47 V). The Li SES in HMPA generally demonstrate high values of OCP (>1.2 V), with the highest value for $\text{Li}_{0.5}(\mathbf{41})(\text{HMPA})_{10.4}$ (~1.8 V). Although these solutions in HMPA are not suitable for anode applications, they may find an application as

catholytes.

For all the studied Li SES, OCP decreases with temperature increase. Based on the $E(T)$ data, ΔS and ΔH were calculated. It was shown that for **49** and **8** the correlation between ΔS and x in $\text{Li}_x(\text{PAH})(\text{THF})_n$ ($x \geq 0.5$) is quasi linear. Considering that ΔS increases with the increase of Li:PAH ratio for all the studied Li SES, this correlation seems to be general. This behaviour, which is completely different from solid state Li_xC_6 and Li_xCoO_2 , should be attributed to a fundamental difference between a liquid and a solid phases in terms of their thermodynamic properties. Since the interaction between the active species in the solution is much lower than in the solid, the phase transition effects are less likely and the intermolecular interactions have less significant influence on the system properties.

The $\Delta H(x)$ exhibits more complex correlation than $\Delta S(x)$. For the case of **49**, the initial results on modeling of interactions between lithium and the PAH demonstrate feasibility of dimeric structures formation, which could be related to more complex behaviour of $\Delta H(x)$. The calculated average binding energies demonstrate correlation with the values of ΔH obtained from the half-cell experiments.

The lowest values of ΔS were obtained for phenylpyridines **71-73** (Chapter 8). This can be related to the fact that lithium in these ion pairs is localized close to the electronegative atom of nitrogen, leading to less degrees of freedom in the system.

The highest values of ΔS are reached for Li SES in HMPA, with the absolute maximum for the biphenyl-based $\text{Li}_{0.75}(\text{Biphenyl})(\text{HMPA})_{10.4}$ ($\Delta S = -1283 \text{ J K}^{-1}\text{mol}^{-1}$), which is related to more significant dissociation of PAH-Li ionic pairs, leading to more degrees of freedom in the system.

In general, the calculated ΔS values for various Li SES are much higher than those for Li_xC_6 and Li_xCoO_2 (shown in Chapter 4, **Table 4.9**; Li_xC_6 ($0 < x < 1$): $-18 < \Delta S < +62 \text{ J}/(\text{mol K})$, $-20 < \Delta H < -10 \text{ kJ/mol}$ [4]; Li_xCoO_2 ($0.5 < x < 1$): $-70 < \Delta S < 20 \text{ J}/(\text{mol K})$, $-413 < \Delta H < -382 \text{ kJ/mol}$ [5]), which is related to more degrees of freedom in a liquid then in a solid state. The ΔH values are much higher comparing to the solid state anode material, which

is probably related to a charge transfer and solvation of lithium ion upon Li SES formation. In general, ΔS for Li SES based on the molecules with fused rings exhibit lower values than for those based on the molecules with benzene rings connected via single bond. It could be related to the fact that benzene rings in the aromatic systems with the rings connected by ordinary bonds (biphenyl, p-terphenyl **49**, 1,3,5-triphenylbenzene **51a**) can rotate along the axis of the ordinary bonds. Thus, these systems have more degrees of freedom comparing to rigid systems with fused benzene rings (naphthalene, anthracene **8**, triphenylene **56**), resulting in higher absolute values of entropy.

Table 10.2. Open-circuit potentials at 295K (22 °C), E(T) linear fit equations, ΔS and ΔH of the studied Li SES/Li half-cells.

Li SES	E (mV) vs Li ⁺ /Li at 295K	E (T) (mV) =	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ mol ⁻¹)
Li _{0.5} (49)(THF) ₁₂₃	780.4	-1.74T + 1293.1	-167.8	-124.8
Li _{1.0} (49)(THF) ₁₂₃	770.8	-2.10T + 1389.2	-202.6	-134.0
Li _{2.0} (49)(THF) ₁₂₃	729.8	-2.74T + 1539.1	-264.4	-148.5
Li _{2.3} (49)(THF) ₁₂₃	659.8	-2.92T + 1522.5	-281.7	-146.9
Li _{2.4} (49)(THF) ₁₂₃	584.2	-3.03 + 1478.7	-292.4	-142.7
Li _{1.0} (49)(THF) _{12.3}	758.2	-1.35T + 1158.3	-130.3	-111.8
Li _{2.0} (49)(THF) _{12.3}	658.7	-3.25T + 1621.0	-313.6	-156.4
Li _{0.5} (8)(THF) ₁₂₃	941.5	-1.31T+1329	-126.4	-128.3
Li _{1.0} (8)(THF) ₁₂₃	908.0	-1.41T+1324	-138.9	-128.6
Li _{2.0} (8)(THF) ₁₂₃	903.2	-1.75T+1423	-172.7	-138.1
Li _{1.0} (8)(THF) _{12.3}	888.1	-1.37T+1293	-126.4	-123.1
Li _{2.0} (51a)(THF) _{24.7}	699.5	-4.32T+1972	-190.0	-417
Li _{4.0} (51a)(THF) _{24.7}	474.1	-1.00T+770	-74.0	-96
Li _{2.0} (51c)(THF) _{24.7}	678.8	-2.64T+1468	-142.0	-255
Li _{2.0} (56)(THF) ₁₂₃	747.2	-2.48T+1478	-239.3	-142.7
Li _{4.0} (56)(THF) ₁₂₃	678.8	-3.25T+1636	-313.6	-157.9
Li _{1.0} (72)(THF) _{10.4}	872	-1.12T+1220	-108.1	-116.0
Li _{2.0} (72)(THF) _{10.4}	634	-0.61T+814	-58.9	-39.2
Li _{1.0} (73)(THF) _{10.4}	873	-1.17T+1202	-112.9	-117.7
Li _{2.0} (71)(THF) _{10.4}	603	-1.15T+942	-111.0	-90.9
Li _{0.5} (41)(HMPA) _{10.4}	1789	-4.16T+3015	-401.4	-290.4
Li _{1.0} (41)(HMPA) _{10.4}	1690	-5.20T+3234	-501.7	-311.6
Li _{1.5} (41)(HMPA) _{10.4}	1350	-5.14T+2856	495.9	-275.5
Li _{2.0} (41)(HMPA) _{10.4}	1358	-6.00T+3128	-578.9	-302.0
Li _{0.5} (41)(THF) _{10.4}	1171	-1.11T+1498	-107.1	-144.5
Li _{0.75} (Biphenyl)(HMPA) _{10.4}	1226	-13.3T + 5164	-1283	-498

The concentration of Li SES affects the values of OCP, ΔS and ΔH . For example, in case of more concentrated solutions, as are $\text{Li}_{1.0}(\mathbf{49})(\text{THF})_{12.3}$, $\text{Li}_{2.0}(\mathbf{49})(\text{THF})_{12.3}$ and $\text{Li}_{1.0}(\mathbf{8})(\text{THF})_{12.3}$, the deviation of the OCP, ΔS and ΔH values is observed comparing to those for the diluted solutions. OCP tends to decrease with concentration of Li SES increase. This effect might be attributed to more significant intermolecular interactions in the more concentrated solutions.

Table 10.3 represents the maximum achieved Li:PAH ratio, E vs Li^+/Li for the Li SES with the maximum ratio, E vs LiCoO_2 ($E(\text{LiCoO}_2 \text{ vs } \text{Li}^+/\text{Li}) = 4.2\text{V}$ [6]), and calculated theoretical energy density (D_{th}) for the studied Li SES. The theoretical energy density was calculated using the following equation [7]:

$$D_{th} = E_c C_{th} = E_c \frac{nF}{3.6M_r}$$

In this equation, E_c is a potential of Li SES vs LiCoO_2 , C_{th} is the theoretical gravimetric capacity, n is a number of electrons transferred from Li SES to LiCoO_2 , F is Faraday constant, M_r is a molecular weight of PAH, and 3.6 is a coefficient to convert the units of C_{th} from C/g into mAh/kg.

Table 10.3. Maximum achieved Li:PAH ratio, E vs Li^+/Li at the maximum ratio, E vs LiCoO_2 , and calculated theoretical energy density (D_{th}) for the studied Li SES. *Maximum Li:PAH ratio for the reported OCP vs Li^+/Li in a half cell [1, 2].

PAH	Max ratio	Li:PAH	E vs Li^+/Li (V) at max ratio	E vs LiCoO_2 (V)	D_{th} (Wh/kg)
C_6 (graphite)	1		0.1	4.1	1526
Naphthalene	1*		0.8	3.4	712
Biphenyl	1*		0.7	3.5	609
49	2.4		0.6	3.6	1007
8	2		0.9	3.3	994
51a	4		0.5	3.7	1296
51c	2		0.7	3.5	396
56	4		0.7	3.5	1646
72	2		0.6	3.6	1245
73	2		0.6	3.6	1245

The obtained values of theoretical energy density for the studied PAH are generally lower than the value for graphite. Nevertheless, the value for triphenylene (**56**) is larger. **51a**, **72** and **73** have the values close to graphite. The value for **51c** is one of the lowest showing that the incorporation of alkyl chains leads to decrease of theoretical energy density value. All the tabulated D_{th} values are calculated for PAH themselves, not their solutions, meaning that the energy density of Li SES, depending on the concentration, should be significantly lower. However, the Li SES of certain concentration should demonstrate higher energy density comparing to vanadium redox batteries having specific energy density of 5 – 20 Wh/kg [8]. Even taking into account these considerations, Li SES can be very useful in some other configurations of batteries, for example, as a transfer medium for lithium ions between a solid electrode and a solid electrolyte membrane.

10.2. Outcomes in context of hypothesis

As seen from section 10.2, this thesis represents the systematic studies on electrical and electrochemical properties of various Li SES. The structure - property correlations in terms of electrical conductivity were clarified. Based on half-cell experiments, electrochemical and thermodynamical parameters of the studied Li SES were defined, which allowed to make conclusions on correlations between these parameters and structure of corresponding PAH.

It was shown that introduction of substituents with particular electronic effects or incorporation of heteroatoms into the aromatic system makes it feasible to tune PAHs' ability to accept electrons and influences the properties of the resulting Li SES. This result proves the initial hypothesis. However, enlarging PAHs' aromatic system does not necessarily increase the amount of alkali metal atoms per PAH in Li SES. Also, it was shown that increasing the size of the aromatic system does not necessarily have positive influence on charge transport characteristics. The outcomes of the thesis demonstrate that the correlation between a structure of PAH and properties of resulting Li SES are more complex than it was initially hypothesized.

However, the obtained results in terms of formation, electrical and electrochemical properties of the studied Li SES demonstrate the potential feasibility of using the Li SES based on some of the tested materials, such as p-terphenyl (**49**), anthracene, triphenylene, 1,3,5-triphenylbenzene and 3-phenylpyridine, as anolytes in secondary batteries.

10.3. Future work

10.3.1 Further studies on Li SES

Although the thesis represents the detailed and systematic study on various Li SES, there are still some questions to address. Even though it was shown that in half cell experiments involving Li SES based on anthracene (**8**) and p-terphenyl (**49**), ΔS demonstrates quasi linear increase upon the increase of x , and ΔS increases upon the increase of Li:PAH ratio in all the studied Li SES, the $\Delta S(x)$ profiles for other PAHs should be investigated in more details in order to prove the generality of the observed quasi linear correlation. Additionally, all these experiments were performed when $x \geq 0.5$. In order to understand the behaviour of Li SES in more details, the half-cell thermodynamical parameters should be studied for $x < 0.5$ in $\text{Li}_x(\text{PAH})(\text{THF})_n$ as well.

As seen from Chapter 6 and **Tables 10.1-10.3**, triphenylene (**56**) demonstrates electrical and electrochemical properties that are the most promising for applications in Li SES based batteries. However, the attempts to obtain Li SES of concentrations higher than $\sim 0.1\text{M}$ were unsuccessful due to the formation of precipitate on the surface of lithium that prevented the metal from further reaction. A possible way to overcome this issue is to improve the solubility by incorporating alkyl chains into triphenylene framework. This can be done using the methods discussed in Chapter 6, section 6.4.

Although some attempts on investigating the influence of solvent on Li SES properties were performed while comparing THF and HMPA, the influence of some other solvents used for preparing Li SES should be studied, such as dimethoxyethane (**1**), diglyme (**2**) and DMSO. Since THF has a relatively low boiling point of 66°C , which may limit its

applications in Li SES, these three solvents, along with their good solvation properties, could find an application in the liquid based batteries.

In order to investigate structure – property relations in Li SES in more detail, some other polyaromatic systems should be examined, such as acenaphthylene (**100**), pyrene (**23**), o-terphenyl (**101**, of particular interest in terms of comparison with p-terphenyl **49**) and perylene **13**. Also, antiaromatic systems, such as cyclooctatetraene (**18**), octalene (**22**), biphenylene (**15**), fulvalene (**102**) and pentalene (**19**) are also interesting objects for studies on Li SES due to high ratio between the amount of Li that can react with these compounds and their relatively low molecular weight. However, the preliminary studies have shown that the solutions based on cyclooctatetraene with the composition $\text{Li}_{1.0}(\mathbf{18})(\text{THF})_{12.3}$ and $\text{Li}_{2.0}(\mathbf{18})(\text{THF})_{12.3}$ demonstrate extremely low values of electric conductivity (13.4 and 7.5 $\mu\text{S}/\text{cm}$ at 22 °C respectively).

Figure 10.1. Structures of acenaphthylene (**100**), pyrene (**23**), o-terphenyl (**101**), perylene (**13**), cyclooctatetraene (**18**), octalene (**22**), biphenylene (**15**), fulvalene (**102**), and pentalene (**19**).

As seen from the results on 1,3,5-triphenylbenzene and its derivatives, some correlations

between electronic effects of functional groups and properties of Li SESs were established. However, low solubility of some substituted 1,3,5-triphenylbenzenes with electron withdrawing groups (CN, NO₂, F) prevented the studies on Li SES made from these materials. Thus, in order to investigate the influence of these groups in detail, more simple molecules with higher solubility in THF could be studied, for example, a variety of naphthalenes and biphenyls bearing one or even a couple of cyano-, nitro-, or other electron withdrawing groups.

The obtained results will be used in further investigations related to fabrication and tests of prototype full cells based on Li SES studied. In order to improve characteristics of Li SES secondary batteries, such as energy density, some other configurations of these batteries will also be tested.

10.3.2. Further studies on azaacenes

As seen from the Chapter 9, convenient procedures for synthesis of various novel 5,7-diazapentacene derivatives and precursors have been established. The measured optical and electronic properties of the 5,7-diazapentacene derivatives suggest they may be suitable for application in organic electronic devices. However, while solution cast thin films of **80a** and **93b** appear to be of good quality, attempts to obtain charge carrier mobilities from FETs based on them have to date proved unsuccessful. For **93b**, it can be related to its amorphous nature, which is also suggested by our inability to grow good quality single crystals for X-ray analysis. The attempts to fabricate OFET based on **80a,b** using other techniques to produce thin films, such as vapour deposition, are ongoing. Additionally, these materials should be tested in terms of Li SES formation and properties of the resulting Li SES, once sufficient amounts have been obtained.

The developed procedure that involves iodonium salts should make it possible to synthesize a variety of azaacenes having different size and structure, which will eventually lead to better understanding of the properties of these novel materials. This could be done by incorporation of various substituents either into diaminodiketone **82** or into

phenyliodonium structure. By enlarging the aromatic system of these materials, it should be possible to synthesize larger heteroacenes. Although the preliminary attempts to obtain diazahexacene from **103** (synthesized from 3,6-dibromonaphthalene-2,7-diamine [9] via Sonogashira coupling followed by triple bond hydrolysis using p-toluenesulfonic acid [10]) led only to the product of monoaddition (**104**) in low yield, it is believed that it is possible to find optimum conditions to synthesize the desired diazahexacene. Additionally, **104** might be used as a starting material for preparing various diazaazapentacene derivatives via Friedländer condensation.

Figure 10.2. Reaction between **103** and diphenyliodonium triflate.

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APPENDIX

A.1 Synthetic procedures

General procedure for synthesis of 1,3,5-triphenylbenzene derivatives (51a-d). To a mixture of corresponding acetophenone and 100 ml of absolute ethanol, silicon tetrachloride (2.1 – 2.6 equivalents) was added in one portion at 0 °C under nitrogen. After the addition was completed and evolution of gaseous hydrogen chloride had finished, the reaction mixture was heated up to 40 °C and stirred for 20 hours at this temperature. Then the reaction mixture was poured into water mixed with ice. The resulting mixture was extracted twice with dichloromethane. The combined extracts were washed once with saturated NaCl solution, dried over anhydrous MgSO₄, and then concentrated. The crude product was purified either by recrystallization or by column chromatography.

1,3,5-triphenylbenzene (51a). 4.0 g (33.3 mmol) of acetophenone, and 11.9 g (8.0 ml, 70.2 mmol, 2.1 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 2.2 g (yield 63%) as pale yellow crystals. ¹H NMR (400MHz, CDCl₃): δ= 7.41 (m, 3H), 7.50 (m, 6H), 7.72 (d, 6H, J = 7.33Hz), 7.80 (s, 3H). ¹³C NMR (400MHz, CDCl₃): δ= 125.21, 127.39, 127.57, 128.88, 141.18, 142.38

4,4''-dimethoxy-5'-(4-methoxyphenyl)-1,1':3',1''-terphenyl (51b). 4.0 g (26.8 mmol) of 1-(4-methoxyphenyl)ethan-1-one, and 11.8 g (8.0 ml, 69.7 mmol, 2.6 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 2.6 g (yield 75%) as pale yellow crystals. ¹H NMR (400MHz, CDCl₃): δ= 3.87 (s, 9H, OCH₃), 7.01 (d, J = 8.59 Hz, 6H), 7.63 (d, J = 8.59 Hz, 6H), 7.66 (s, 3H). ¹³C NMR (400MHz, CDCl₃): δ= 55.39 (OCH₃), 114.27, 123.86, 128.37, 133.87, 141.85, 159.32.

4,4''-dibutyl-5'-(4-butylphenyl)-1,1':3',1''-terphenyl (51c). 4.0 g (22.8 mmol) of 1-(4-butylphenyl)ethan-1-one, and 8.9 g (6.0 ml, 52.3 mmol, 2.3 eq.) of silicon tetrachloride were used. Purified via column chromatography (hexane: dichloromethane 4:1). Obtained

3.1 g (yield 86%) as a pale yellow oil that turned into a waxy solid. ^1H NMR (400MHz, CDCl_3): δ = 0.96 (t, J = 7.33 Hz, 9H, CH_3), 1.41 (m, 6H, CH_2), 1.66 (m, 6H, CH_2), 2.68 (t, J = 7.58, 6H, Ar- CH_2), 7.29 (d, J = 8.34 Hz, 6H, Ar-H), 7.61 (d, J = 8.34 Hz, 6H, Ar-H), 7.74 (s, 3H, Ar-H). ^{13}C NMR (400MHz, CDCl_3): δ = 13.99, 22.44, 33.67, 35.34, 124.62, 127.18, 128.89, 138.64, 142.17, 142.29

4,4''-difluoro-5'-(4-fluorophenyl)-1,1':3',1''-terphenyl (51d). 6.1 g (44.1 mmol) of 1-(4-fluorophenyl)ethan-1-one, and 11.8 g (12.0 ml, 104.6 mmol, 2.4 eq.) of silicon tetrachloride were used. Purified via recrystallization from ethanol. Obtained 3.4 g (yield 63%) as pale yellow crystals. ^1H NMR (400MHz, CDCl_3): δ = 7.16 (m, 6H), 7.63 (m, 6H), 7.66 (m, 3H). ^{13}C NMR (400MHz, CDCl_3): δ = 115.78 (d, J = 21.96 Hz, F-C- CH), 124.85, 128.89 (d, J = 8.78 Hz, F-C-CH- CH), 137.01, 141.54, 161.46, 163.91 (d, J = 246.63 Hz, F-C).

4,4''-diiodo-5'-(4-iodophenyl)-1,1':3',1''-terphenyl (51n). 5.0 g (20.3 mmol) of 1-(4-iodophenyl)ethan-1-one, and 6.7 g (4.5 ml, 39.2 mmol, 1.9 eq.) of silicon tetrachloride were used. Purified via column chromatography (hexane: dichloromethane 4:1). Obtained 2.8 g (yield 60%) as yellow crystals. ^1H NMR (400MHz, CDCl_3): δ = 7.33 (d, J = 8.34 Hz, 6H), 7.60 (s, 3H). ^{13}C NMR (400MHz, CDCl_3): δ = 93.63, 124.93, 129.13, 138.03, 140.21, 141.61.

5'-(4-cyanophenyl)-[1,1':3',1''-terphenyl]-4,4''-dicyanitrile (51e). A mixture of 4,4''-diiodo-5'-(4-iodophenyl)-1,1':3',1''-terphenyl (**51n**, 5.5 g, 8.0 mmol), copper (I) cyanide (2.5 g, 27.6 mmol, 3.4 eq.) and DMF (45 ml, freshly distilled from CaH_2) was refluxed under nitrogen for 24 hours. Then the reaction mixture was cooled down to 90 °C, and 100 ml of water together with 15 ml of 1,2-ethylenediamine was added. The mixture was extracted with DCM, the extract was dried over anhydrous MgSO_4 and then concentrated. Flash column chromatography (DCM) afforded 1.93 g (5.1 mmol, yield 70%) of the product. ^1H NMR (400MHz, CDCl_3): δ = 7.74 – 7.84 (m, 12H + 3H). ^{13}C NMR (400MHz, CDCl_3): δ = 111.95 (C-CN), 118.56 (CN), 126.37, 128.00, 132.86, 141.28, 144.56

4,4''-dinitro-5'-(4-nitrophenyl)-1,1':3',1''-terphenyl (51f). To a mixture of 4-nitroacetophenone (10.0 g, 60.8 mmol), and 30 ml of anhydrous ethanol, thionyl chloride (8.0 ml, 113.0 mmol) was added under nitrogen at room temperature. The rate of addition was adjusted in order not to allow the reaction temperature to increase above 50 °C. 4-nitroacetophenone became completely dissolved when all the thionyl chloride had been added, and after ca. 10 minutes the formation of a yellow precipitate was observed. The mixture was stirred at reflux for 12 hours, then cooled down to room temperature, and the yellow precipitate was separated and washed successively with ethanol, deionized water, diethyl ether, and once again ethanol. Recrystallization twice from dichloromethane gave 5.8 g of the product (65%). MALDI TOF (%): 411.45 [M-NO] (46), 441.40 [M] (12), 465.05 [M+Na] (100).

Reaction of 51a based Li SES with water. Li SES prepared using 12 ml of anhydrous THF, **51a** (1.84 g, 6.0 mmol) and Li (0.17g, 24.0 mmol) was poured into iced water, giving a yellowish solid. The organic components were extracted with CH₂Cl₂, and the extract was dried over anhydrous MgSO₄. The solution was almost completely evaporated, then diluted with ethanol and left in fridge for recrystallization. The resulting crystals were collected by filtration and washed with ethanol. According to ¹H and ¹³C NMR, these crystals were recovered **51a**, which was obtained in 100 mg quantity (yield 5%).

Recovery of 1,3,5-triphenylbenzene (51a) from Li_{2.0}(51a)(THF)_{24.7} In a glovebox, lithium (103.9 mg, 2.0 equivalents, 14.97 mmol) was added to a mixture of triphenylbenzene (2.294 g, 7.49 mmol) and 15ml of anhydrous THF. The bottle was sealed and the mixture stirred overnight. Then, the cap was replaced with a rubber seal, the bottle removed from the glovebox and connected to an argon line. A solution of iodine (1.95g, 7.81 mmol) in THF (8 ml) was carefully added after cooling of the bottle with ice. After the solvent was evaporated, the mixture was redissolved in dichloromethane, washed with aqueous Na₂S₂O₃ solution, dried over MgSO₄, filtered, and evaporated. The resulting crude product was subject to NMR study (see Chapter 5). The crude product was recrystallized from ethanol, giving 1,3,5-triphenylbenzene (**1**) (1.15 g, 50% recovery).

The crude residue recovered from $\text{Li}_{4.0}(\mathbf{51a})(\text{THF})_{24.7}$ was obtained in the same manner using 4 equivalents of iodine (3.95 g, 15.8 mmol).

1,2-dihexylbenzene (58). To a mixture of magnesium (8.8 g, 0.037 mol) and anhydrous diethyl ether (140ml) a solution of n-hexylbromide (55g, 0.033 mol) in 30ml of anhydrous diethyl ether was added at $+10^{\circ}\text{C}$ under N_2 , then refluxed for 30 minutes. The resulting solution was filtered and added dropwise to a mixture of $\text{NiCl}_2(\text{dppp})$ (0.17g, 0.34 mmol), 1,2-dichlorobenzene (19.4g, 0.013 mol) and 120ml of anhydrous diethyl ether under nitrogen at $+5^{\circ}\text{C}$. The resulting mixture was warmed up to room temperature and stirred at reflux for 24 hours. After that, the mixture was quenched with 2N HCl and extracted with diethyl ether. The organic fraction was washed with water and aq. NaHCO_3 , then dried over MgSO_4 , filtered and evaporated. The crude product was purified by vacuum distillation ($100 - 120^{\circ}\text{C}$, 4.6 mmHg) giving 24.1 g of 1,2-dihexylbenzene (74% yield). : ^1H NMR (400MHz, CDCl_3): δ = 0.83 (t, J = 6.3 Hz, 6H), 1.20-1.71 (m, 16H), 2.53 (t, J = 7.7 Hz, 4H), 7.03- 7.19 (m, 4H) ; ^{13}C NMR (400MHz, CDCl_3): δ = 14.10, 22.67, 29.50, 31.33, 31.81, 32.72, 125.71, 129.10, 140.58

1,2-dibromo-4,5-dihexylbenzene (59). Bromine (9.5 ml, 0.185 mol) was added to a mixture of 1,2-dihexylbenzene (39.9 g, 0.16 mol) and iron (III) chloride (0.58 g, 3.58 mmol) in 250ml of chloroform at $+5^{\circ}\text{C}$, then stirred for 24 hours at room temperature. The mixture then washed with diluted solution of $\text{Na}_2\text{S}_2\text{O}_3$, water, dried over MgSO_4 , then evaporated. Flash column chromatography (hexane) yielded **59** as a colorless liquid (47.68g, 0.118mol, 74%). ^1H NMR (400MHz, CDCl_3): δ = 7.37 (s, 2H), 2.50 (t, J = 7.9 Hz, 4H), 1.56– 1.49 (m, 6H), 1.37–1.25 (m, 20H), 0.94–0.85 ppm (m, 10H).

4',5'-dihexyl-1,1':2',1''-terphenyl (60). A mixture of sodium carbonate (7.07 g, 66.7 mmol), 30 ml of distilled water, 1,2-dibromo-4,5-dihexylbenzene (**59**, 4.00 g, 9.90 mmol), phenylboronic acid (3.62 g, 29.7 mmol), $\text{Pd}(\text{PPh}_3)_4$ (49.5 mg, 0.43 mmol) and 50 ml of dimethoxyethane was refluxed for 24 hours. After refluxing, the mixture was cooled to room temperature and poured into 140 ml of 1M HCl. The resulting mixture was extracted with DCM. The organic fraction was washed with water and brine, then dried over

anhydrous MgSO_4 . The residue was purified by column chromatography on silica gel (hexane : ethyl acetate 19:1) giving **60** in 51% yield (2.02 g, 5.07 mmol). ^1H NMR (400MHz, CDCl_3): δ = 7.43 – 7.19 (m, 12H), 2.70 (m, J = 7.8 Hz, 6H, CH_2), 1.71 (m, 4H, CH_2), 1.30 – 1.54 (m, 12H, CH_2), 0.92 (t, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR (400MHz, CDCl_3): δ = 130.2, 129.3, 127.6, 126.1, 32.6, 31.9, 31.2, 29.5, 22.5, 14.0.

E-1,2-bis(4-bromophenyl)ethane (66). To a mixture of zinc powder (19.91 g, 304.5 mmol) and 250 of anhydrous THF titanium (IV) chloride (16.7 ml, 28.82 g, 151.9 mmol) was added at -10°C under nitrogen. Then a solution of 4-bromobenzaldehyde (**65**, 10.01 g, 54.1 mmol) in 200 ml of anhydrous THF was added to the mixture at $-5 - 0^\circ\text{C}$. The resulting mixture was refluxed for 6 hours, then cooled down to room temperature and quenched with 60 ml of saturated K_2CO_3 solution. The resulting mixture was filtered through silica, then mixed with 300 ml of water, and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous MgSO_4 , and partially evaporated until a white precipitate started to form. Then it was diluted with hexane (ca. twice volume), and the precipitate was collected by filtration, washed sequentially with hexane and methanol, then dried *in vacuo*. E-1,2-bis(4-bromophenyl)ethane was obtained in the amount of 6.93 g (yield 76%). ^1H -NMR (400MHz, CDCl_3): δ = 7.17 (s, 2H, $=\text{C}-\underline{\text{H}}$), 7.70 (m, 2H), 7.75 (m, 2H). ^{13}C -NMR (400MHz, CDCl_3): δ = 121.63 ($\underline{\text{C}}-\text{Br}$), 128.00, 128.13, 131.65, 135.90.

E-1,2-bis(4-hexylphenyl)ethane (67). To a mixture of E-1,2-bis(4-bromophenyl)ethane (4.10 g, 12.1 mmol), $\text{NiCl}_2(\text{dppp})$ (340 mg, 0.6 mmol), and 100 ml of anhydrous THF a 2M solution of hexylmagnesium bromide (19.0 ml, 38.0 mmol) was added under nitrogen. The resulting mixture was stirred at ambient temperature for 4 days. After quenching with ca. 5 ml of methanol, the mixture was evaporated and mixed with 150 ml of diethyl ether and 100 ml of 1.5M aq. HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 50ml). The combined organic extracts were dried over anhydrous MgSO_4 and concentrated. The crude product was purified using column chromatography (hexane : chloroform 10:1), yielding 3.47 g of the product (yield 82%). ^1H NMR (400MHz, CDCl_3): δ = 0.89 (t, J = 6.57Hz, 6H, $\underline{\text{CH}_3}-\text{CH}_2$), 1.32 (m, 12H), 1.62 (m, 4H, $\text{Ar}-\text{CH}_2-\underline{\text{CH}_2}$), 2.60 (t, J = 7.58Hz, 4H, $\text{Ar}-\underline{\text{CH}_2}$), 7.05 (s, 2H, $=\text{C}-\underline{\text{H}}$), 7.16 (d, J =

8.08, 2H), 7.42 (d, $J = 8.08$, 2H). ^{13}C NMR (400MHz, CDCl_3): $\delta = 14.11, 22.63, 29.01, 31.42, 31.76, 35.74, 126.32, 127.73, 128.72, 135.00, 142.42$.

1,2-dibromo-1,2-bis(4-hexylphenyl)ethane (68). To a solution of E-1,2-bis(4-hexylphenyl)ethane (3.20 g, 9.2 mmol) in 45 ml of chloroform a mixture of bromine (1.6 g, 9.7 mmol) and 10 ml of chloroform was added at ambient temperature. The mixture was stirred for 1 hour, then the solvent was evaporated, and the crude product was purified by flash column chromatography (hexane : chloroform 1:1), resulting in 4.41 g of the product (yield 95%). ^1H NMR (400MHz, CDCl_3): $\delta = 0.87$ (m, 6H, CH_3), 1.22 – 1.37 (m, 6H), 1.50 (m, 2H), 1.63 (m, 2H), 2.49 (t, $J = 7.83$ Hz, 2H, Ar- CH_2), 2.62 (t, $J = 8.08$ Hz, 2H, Ar- CH_2), 5.44 (s, 1H), 5.48 (s, 1H), 6.95 (d, $J = 8.34$, 2H), 7.06 (d, $J = 8.34$, 2H), 7.21 (d, $J = 8.08$, 2H), 7.40 (d, $J = 8.08$, 2H). ^{13}C NMR (400MHz, CDCl_3): $\delta = 14.10, 22.60, 28.82, 29.06, 31.07, 31.17, 31.65, 31.71, 35.53, 35.77, 56.52, 59.54, 127.73, 128.10, 128.44, 128.75, 135.12, 137.36, 143.42, 143.98$.

1,2-bis(4-hexylphenyl)ethyne (63a)

Method a

A mixture of 1,2-dibromo-1,2-bis(4-hexylphenyl)ethane (4.21 g, 8.3 mmol) and potassium *tert.*-butoxide (9.78 g, 87.2 mmol) in 60 ml of *tert.*-butanol was refluxed for 12 hours under nitrogen. The mixture was poured into a mixture of water and ice, then extracted with diethyl ether. The organic extract was washed with 2M HCl, water, then dried over anhydrous MgSO_4 , followed by concentration and purification by column chromatography (hexane), affording 1.60 g of the product (yield 56%).

Method b

To a mixture of 1-bromo-4-hexylbenzene (16.1 g, 66.8 mmol), copper (I) iodide (1.2 g, 6.4 mmol, 9.6 mol %), Tetrakis(triphenylphosphine) palladium(0) (4.6 g, 4.0 mmol, 6.0 mol%), and 160 ml of absolute toluene in 250 ml Schlenk flask 1,8-diazabicyclo[5.4.0]undec-7-ene (52 ml, 348 mmol, 5.2 eq.) was added under nitrogen. After purging the mixture with nitrogen for 20 minutes, trimethylsilylacetylene (4.8 ml, 33.7 mmol, 0.5 eq.) and deionized water (0.47 ml, 26.1 mmol, 39 mol%) were added successively. The flask was sealed with a glass stopper, and the mixture was stirred at 65 °C for 44 hours. After cooling down, the

reaction mixture was poured into a mixture of diethyl ether (200 ml) and 5% aqueous NH_4Cl solution. After separating the organic layer, the aqueous layer was extracted with diethyl ether (2 x 150 ml). The combined organic layers were successively washed with 10% aq. HCl (2 x 120 ml), brine (2 x 100 ml), and water (2 x 100 ml), then dried over anhydrous MgSO_4 . The solvent was evaporated, and the crude product purified by column chromatography (hexane), followed by recrystallization from hexane/dichloromethane. Obtained 4.9 g of 1,2-bis(4-hexylphenyl)ethyne (yield 42%).

NMR data for 1,2-bis(4-hexylphenyl)ethyne obtained via both methods is identical.

^1H NMR (400MHz, CDCl_3): δ = 0.90 (t, J = 6.82 Hz, 6H, CH_3), 1.27 – 1.39 (m, 12H), 1.62 (m, 4H, $\text{Ar-CH}_2\text{-CH}_2$), 2.62 (t, J = 7.58 Hz, 4H, Ar-CH_2), 7.16 (d, J = 8.34, 2H), 7.44 (d, J = 8.34, 2H). ^{13}C NMR (400MHz, CDCl_3): δ = 14.08, 22.60, 28.93, 31.23, 31.71, 35.91, 88.93 ($\text{-C}\equiv$), 120.61, 128.43, 131.45, 143.22.

Hexakis-[4-hexylphen-1-yl] benzene (61b). To a solution of 1,2-bis(4-hexylphenyl)ethyne (6.0 g, 17.3 mmol) in anhydrous 1,4-dioxane dicobalt octacarbonyl (360 mg, 1.1 mmol, 6 mol%) was added under nitrogen. The reaction mixture was stirred at reflux for 72 hours. After evaporation of the solvent, the crude product was purified by column chromatography (hexane : dichloromethane 10 : 1 $\rightarrow$ 8 : 1), affording 5.6 g of the product (yield 93%). ^1H NMR (400MHz, CDCl_3): δ = 0.85 (t, J = 6.82 Hz, 18H, CH_3), 1.07 – 1.30 (m, 36H), 1.38 (m, 12H, $\text{Ar-CH}_2\text{-CH}_2$), 2.33 (t, J = 7.58, 12H, Ar-CH_2), 6.60 (d, J = 8.08, 12H), 6.65 (d, J = 8.08, 12H). ^{13}C NMR (400MHz, CDCl_3): δ = 14.11, 22.63, 28.51, 31.15, 31.72, 35.34, 126.44, 131.39, 138.28 (C quat.), 139.02 (C quat.), 140.28 (C quat.). MALDI-TOF MS: m/z 1045.3 [M^+] (20%), 1068.5 [$\text{M}+\text{Na}$] (31%), 1084.5 [$\text{M}+\text{K}$] (23%).

General procedure for synthesis of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one derivatives (51a-b). To a mixture of 1,3-diphenylpropan-2-one (**69**, 2.30 g, 10.9 mmol) and corresponding 1,2-bisphenylethane-1,2-dione (**70**, 11.1mmol) in 45 ml of anhydrous EtOH, potassium hydroxide (0.38 g, 6.77 mmol) was added. The mixture was stirred at reflux for 2 h, then cooled down to -6 °C. The black precipitate was collected by filtration, washed successively with ethanol, water, and then again ethanol. Then the solid was dried in oven for 20 h at 65 °C.

2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (51a). Yield 83% (3.29 g, 8.8 mmol). ^1H NMR (400MHz, CD_2Cl_2): δ = 6.92 (d, J = 8.4 Hz, 4 H), 7.26–7.14 (m, 16 H). ^{13}C NMR (400MHz, CD_2Cl_2): 125.50, 127.52, 128.00, 128.02, 128.52, 129.31, 130.19, 131.03, 133.25, 154.83, 200.37. MALDI TOF MS: m/z 383.45 [$\text{M}-1$] (100%)

3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one (51b). Yield 78% (2.40 g, 8.3 mmol). ^1H NMR (400MHz, CD_2Cl_2): δ = 7.25–7.19 (m, 10 H), 6.84–6.70 (d, J = 8.4 Hz, 4 H), 3.747 (s, 6 H). ^{13}C NMR (400MHz, CD_2Cl_2): 55.23, 113.36, 124.89, 125.33, 127.26, 128.00, 130.21, 131.12, 131.52, 154.43, 159.97, 200.29. MALDI TOF MS: m/z 443.71 [$\text{M}-1$] (100%).

3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (hexaphenylbenzene, 61a). A mixture of **51a** (1.94 g, 5.1 mmol), diphenylacetylene (3.91 g, 21.9 mmol) and 10 g of benzophenone was refluxed for 2 h under nitrogen. The mixture was cooled down to room temperature and diluted with 2 ml of diphenyl ether and kept for 24 h. The formed precipitate was filtered, washed with toluene and dried in vacuo. Obtained 2.40 g (4.5 mmol, 89% yield) of **61a**. ^1H NMR (400MHz, CDCl_3): δ = 6.87 (m, 30H). ^{13}C NMR (400MHz, CDCl_3): δ = 140.61, 140.30, 131.42, 126.55, 125.16.

Hexa-peri-hexabenzocoronene (62a). A solution of iron (III) chloride (27.7 g, 171 mmol) in 50ml of nitroethane was added to a solution of **61a** (2.40 g, 4.46 mmol) in 600 ml of DCM at room temperature under nitrogen. The mixture was stirred at room temperature for 15 h, then 200 ml of methanol was added. The precipitate was filtered, washed with methanol, then refluxed in toluene for 16 h, filtered, washed with toluene, dried in vacuo. Obtained 1.88 g (3.60 mmol) of **62a** in 80% yield. MALDI TOF MS: m/z = 522.28.

3,3'-bipyridine (74). $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (14.2 g, 59.6 mmol) and triphenylphosphine (62.4 g, 238 mmol) were mixed in anhydrous DMF under nitrogen and stirred for 1 h at 50 °C. Then zinc powder (3.84 g, 58.7 mmol) was added at 50 °C and stirred for 1 h at this temperature. After this, 3-bromopyridine (5.8 ml, 60.1 mmol) was added and the mixture was stirred at

50 °C for 20 h. The reaction mixture was cooled down and poured into a mixture of concentrated ammonia solution (100 ml) and water (500 ml), then extracted with DCM. The DCM fraction was extracted with 2 N HCl. The aqueous layer was isolated and neutralized with NaOH, then extracted with DCM. The organic fraction was washed with brine, dried over MgSO₄ and evaporated giving 3,3'-bipyridine (4.70 g, 30.1 mmol) as colorless oil in 60% yield. The product solidified upon drying in desiccator over P₂O₅. ¹H NMR (400MHz, CDCl₃): δ = 8.83 (s, 2H), 8.65 (m, 2H), 7.87 (m, 2H), 7.40 (m, 2H). ¹³C NMR (400MHz, CDCl₃): δ = 149.25, 148.13, 134.33, 133.42, 123.69.

1,5-dibromo-2,4-dinitrobenzene (85). 1,3-Dibromobenzene (**84**, 7.0 g, 29.7 mmol) was slowly added to a stirring mixture of concentrated sulfuric acid (6.5 mL) and fuming nitric acid (6.5 mL), while being cooled in an ice bath. 1,3-dibromobenzene was added slowly so as to maintain a temperature of 10-20 °C. After the addition was complete, the temperature was maintained at 35 °C for 3 h. The reaction mixture was then poured onto crushed ice. The solid precipitate formed was collected by filtration, and washed several times with water. The solid was then dissolved in a mixture of absolute ethanol (90 mL) and acetone (20 mL), the solution filtered and cooled in the fridge overnight. The crystals collected were washed with cold ethanol to give **85** (6.73 g, 20.7 mmol) as a bright yellow solid with a yield of 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.47 (1H, s), 8.24 (1H, s). ¹³C NMR (100 MHz, CDCl₃) δ 119.86, 122.88, 141.39, 149.47.

1,5-di(hept-1-yn-1-yl)-2,4-dinitrobenzene (86). In a sealed flask, **85** (0.200 g, 0.61 mmol), Pd(PPh₃)₄ (0.036 g, 0.03 mmol) and CuI (0.012 g, 0.06 mmol) were added and purged with N₂ for 5 min. After which, degassed 1-heptyne (0.17 mL), THF (8 mL) and Et₃N (0.43 mL) were added. The mixture was then stirred at room temperature for 7h. The reaction mixture was then filtered through Celite, redissolved in diethyl ether, washed two times with NH₄Cl (10% aqueous solution), then dried over MgSO₄ and concentrated. Purification via column chromatography (Hexane: Et₂O = 9:1) gave **86** (0.172 g, 0.482 mmol) as a brown oil with a yield of 78%. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (1H, s, CH), 7.76 (1H, s, CH), 2.53 (4H, t, J = 7.07 Hz, ≡-CH₂), 1.67 (4H, m), 1.50-1.35 (8H, m), 0.94 (6H, t, J = 7.07Hz). ¹³C NMR (400 MHz, CDCl₃) δ 147.07 (C-NO₂), 141.03 (CH), 123.82 ((Ar)C≡), 121.52 (CH),

105.91 ($\equiv\text{C}-$), 74.94 ($(\equiv\text{C}-)$), 31.02 ($\equiv\text{CH}_2$), 27.72, 22.14, 20.06, 13.91 (CH_3). HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_4$ m/z 357.1814, found m/z 357.1813 (correct isotope distribution)

1,1'-(4,6-diamino-1,3-phenylene)bis(heptan-1-one) (82). A solution of **86** (3.75 g, 10.52 mmol) in 15 mL of EtOH was added to a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (25.2 g, 112 mmol) in EtOH (70 mL) and stirred at 70 °C for 4 h under nitrogen. The reaction mixture was quenched with 5% aq Na_2CO_3 (400 mL), mixed with 500 mL of EtOAc, and 50 g of Celite, and filtered. The organic layer was separated, dried over MgSO_4 , and then concentrated. Purification via column chromatography (hexane: EtOAc = 2:1) gave **82** as a yellow solid (2.1 g, 6.32 mmol, 60%). ^1H NMR (400 MHz, CDCl_3) δ 8.32 (1H, s, CH), 6.58 (4H, br. s, NH_2), 5.66 (1H, s, CH), 2.86 (4H, t, $J = 7.58$ Hz, $\text{C}(\text{O})-\text{CH}_2$), 1.73 (4H, m), 1.41-1.26 (12H, m), 0.91 (6H, t, $J = 7.07$ Hz, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 200.85 (CO), 154.63 ($\text{C}-\text{NH}_2$), 138.69 (CH), 110.51 ($\text{C}-\text{C}=\text{O}$), 98.65 (CH), 38.69 ($\text{CH}_2-\text{C}=\text{O}$), 31.73 (CH_2), 29.26 (CH_2), 25.65 (CH_2), 22.55 (CH_2), 14.04 (CH_3). HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_2$ m/z 333.2537, found m/z 333.2535 (correct isotope distribution).

12,14-dihexyl-1,2,3,4,8,9,10,11-octahydroquinolino[3,2-b]acridine (81a). **82** (0.503 g, 1.51 mmol), EtOH (10 mL) and 37% wt HCl (0.30 mL, 3.62 mmol) were added into a sealed flask and purged with N_2 for 5 min. Cyclohexanone (0.38 mL, 3.82 mmol) was added and the reaction was stirred at 75 °C for 20 h. The reaction mixture was cooled down to room temperature, then quenched with 5% aqueous NaOH solution. The organic layer was then extracted, washing several times with CH_2Cl_2 , the organic fraction was dried over MgSO_4 then filtered. Purification via flash chromatography (CH_2Cl_2 : EtOAc: Et_3N = 1:1:0.1) gave **7a** (0.497 g, 0.92 mmol) as a yellow solid with a yield of 73%. ^1H NMR (400 MHz, CDCl_3) δ 8.64 (1H, s, CH), 8.55 (1H, s, CH), 3.16 (8H, m), 2.98 (4H, t, $J = 5.81$, CH_2), 1.96 (8H, m), 1.71-1.65 (4H, m), 1.65-1.54 (4H, m), 1.43-1.34 (8H, m), 0.93 (6H, t, $J = 7.07$ Hz) ^{13}C NMR (100 MHz, CDCl_3) δ 161.01, 144.89, 144.73, 127.41, 124.69, 117.89, 35.07, 31.78, 30.19, 27.97, 23.24, 22.70, 14.05. HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{45}\text{N}_2$ m/z 457.3577, found m/z 457.3582 (correct isotope distribution).

7,9-dihexyl-5,6,10,11-tetrahydrobenzo[h]benzo[7,8]quinolino[3,2-b]acridine (81b). **82** (0.203 g, 0.61 mmol), EtOH (5 mL) and 37% wt HCl (0.18 mL, 2.00 mmol) were added into a sealed flask and purged with N₂ for 5 min. a-Tetralone (0.17 mL, 1.28 mmol) was added and the reaction was stirred at 75 °C for 20 h. The reaction mixture was cooled down to room temperature, then quenched with 5% aqueous NaOH solution. The mixture was then extracted with dichloromethane (DCM), the organic fraction was dried over MgSO₄, then filtered and evaporated. Recrystallization from EtOH gave **81b** as a yellow solid (0.176 g, 0.32 mmol, 52%). ¹H NMR (400 MHz, CDCl₃) δ = 8.96 (1H, s, CH), 8.70 (2H, d, J = 7.58 Hz, CH), 8.61 (1H, s, CH), 7.47 (2H, m, CH), 7.41 (2H, m, CH), 7.30 (2H, d, J = 7.33 Hz, CH), 3.27 (2H, m, CH₂), 3.19 (2H, t, J = 5.81), 3.04 (2H, m, CH₂), 1.78 (2H, m, CH₂), 1.60 (2H, m, CH₂), 1.46 – 1.34 (4H, m, CH₂), 0.94 (6H, t, J = 7.07 Hz). ¹³C NMR (100 MHz, CDCl₃) δ = 154.24, 145.87, 143.62, 139.59, 135.36, 129.75, 129.39, 127.63, 127.52, 127.29, 126.93, 125.57, 118.29, 31.84, 30.16, 30.01, 28.46, 28.29, 25.61, 22.74, 14.10. HRMS (ESI): [M + H]⁺ calcd for C₄₀H₄₅N₂ m/z 553.3577, found m/z 553.3579 (correct isotope distribution).

1,1'-(4,6-dihexyl-2,8-dimethylpyrido[3,2-g]quinoline-3,7-diyl)bis(ethan-1-one) (81c). Obtained by reaction of **82** with acetylacetone employing the same procedure as for **81b** in 51% yield. ¹H NMR (400 MHz, CDCl₃) δ = 8.73 (1H, s, N-C=C(H)-C-N), 8.65 (1H, s, CH), 3.02 (4H, m, CH₂), 2.70 (3H, s, CH₃-CO), 2.65 (3H, s, CH₃-Ar), 1.77 (4H, m, CH₂), 1.53 (4H, m, CH₂), 1.28 – 1.43 (8H, m, CH₂), 0.91 (6H, t, J = 7.07 Hz, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ = 206.10 (CO), 155.27, 146.25, 143.10, 135.17, 128.24, 123.76, 120.10, 32.68, 31.59, 31.42, 30.21, 30.08, 24.19, 22.61, 13.99. HRMS (ESI): [M + H]⁺ calcd for C₃₀H₄₁N₂O₂ m/z 461.3163, found m/z 461.3166 (correct isotope distribution).

6-amino-7-hexanoyl-9-hexyl-3,4-dihydroacridin-1(2H)-one (81d). Obtained from reaction of **82** with 1,3-cyclohexedione employing the same procedure as for **81b** with 32% yield, recrystallized from hexane/EtOH. ¹H NMR (400 MHz, CDCl₃) δ = 8.70 (1H, s, N-C=C(H)-C-N), 7.01 (1H, s, CH), 6.42 (2H, br. s., NH₂), 3.46 (2H, m, CH₂), 3.16 (2H, t, J = 6.06 Hz, CH₂), 3.09 (2H, t, J = 7.33 Hz, CH₂), 2.75 (2H, t, J = 6.32 Hz, CH₂), 2.15 (2H, m, CH₂), 1.56 – 1.85 (6H, m, CH₂), 1.32 – 1.48 (10H, m, CH₂), 0.88 – 0.96 (6H, m, 2CH₃).

^{13}C NMR (100 MHz, CDCl_3) δ = 203.32, 199.27, 166.23, 156.13, 151.18, 151.10, 131.95, 121.89, 121.30, 118.51, 110.54, 41.09, 39.82, 35.34, 31.66, 31.63, 31.41, 30.07, 29.15, 28.94, 25.25, 22.66, 22.53, 21.09, 14.06, 13.99. HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{37}\text{N}_2\text{O}_2$ m/z 409.2850, found m/z 409.2861 (correct isotope distribution)

13,15-dihexylbenzo[4,5]furo[3,2-b]benzofuro[2',3':5,6]pyrido[3,2-g]quinoline (81e).

Obtained from reaction of 8 with benzofuranone employing the same procedure as for **81e** with 45% yield, purified using column chromatography (Hex:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ = 9.26 (1H, s, N-C=C(H)-C-N), 8.77 (1H, s, CH), 8.45 (2H, d, J = 7.58 Hz, CH), 7.65 (2H, t, J = 7.58 Hz, CH), 7.55 (2H, J = 8.08 Hz, CH), 7.47 (2H, m, CH), 3.48 (4H, t, J = 7.83 Hz, CH_2), 1.94 (4H, m, CH_2), 1.58 (4H, m, CH_2), 1.22 – 1.46 (8H, m, CH_2), 0.92 (6H, t, J = 6.82 Hz, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ = 160.05, 149.11, 145.77, 144.37, 131.52, 128.72, 126.34, 124.80, 123.43, 123.25, 122.90, 118.13, 112.06. HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{37}\text{N}_2\text{O}_2$ m/z 529.2850, found m/z 529.2862 (correct isotope distribution)

Attempted dehydrogenation of 81a and 81b. 81a: 12,14-dihexyl-1,2,3,4,8,9,10,11-octahydroquinolino[3,2-b]acridine (**81a**, 0.2 g, 0.439 mmol) and Pd/C (0.047 g, 0.439 mmol) were added to a flask, connected to a reflux condenser and bubble counter and were purged in N_2 for 5min. Ph_2O (5 mL) was added and the reaction mixture was heated at 200 $^\circ\text{C}$ for 24 h. The reaction mixture was quenched with CHCl_3 (30 mL), 10 % HCl (20 mL) and aq NaOH was added till the mixture was alkaline. The organic layer was extracted, washed with water and DCM several times. TLC only showed spots of Ph_2O and no trace of the desired product.

81b: **81b** (0.167 g, 0.366 mmol) and Pd/C (0.040 g, 0.376 mmol) were added to a flask, connected to a bubble counter and were purged in N_2 for 5min. Ph_2O (4.2 mL) was added and the reaction mixture was heated at 175 $^\circ\text{C}$ for 24h. The reaction mixture was filtered through celite, washed with DCM, and the filtrate evaporated. After which hexane was added, and left in the freezer for 1 h. Then, the mixture was filtered and a brown residue (0.030 g) was obtained. NMR showed it consisted of a complex mixture of oligomers.

4-bromo-3,4-dihydronaphthalen-1(2H)-one (89a). A mixture of NBS (4.0g, 22.4 mmol) and benzoyl peroxide (80mg, 0.3 mmol) was added to a refluxing mixture of α -tetralone (3.0g, 20.5 mmol) and chloroform (60ml). The mixture was refluxed for 4h, then cooled down to room temperature, filtered and evaporated. Column chromatography afforded 1.8 g (8.2 mmol, 40% yield) of the product, which completely decomposed to α -naphthol (confirmed by ^1H NMR) and HBr within 16 h while stored in a fridge at $+6^\circ\text{C}$.

4-hydroxy-3,4-dihydronaphthalen-1(2H)-one (89c). A mixture of 4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (**89b**, 0.60 g, 2.94 mmol), wet K_2CO_3 (0.46 g, 3.34 mmol) and methanol (40 ml) was stirred at room temperature for 0.5 h. The mixture was evaporated, diluted with water then was extracted with DCM. Flash chromatography (hexane: EtOAc = 4:1) afforded **6** in 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (1H, d), 7.59-7.37 (3H, m), 4.97-4.94 (1H, m), 4.10-2.02 (5H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 197.50, 145.38, 134.09, 131.16, 128.34, 127.14, 127.03, 77.35, 77.03, 76.72, 67.84, 60.43, 35.14, 32.09, 14.18.

4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (89b). A solution of 1,2,3,4-tetrahydronaphthalen-1-yl acetate (**92**, 1.50 g, 7.88 mmol) in acetone (35 ml) was added to aqueous MgSO_4 (2.26 g, 18.8 mmol). Afterwards, KMnO_4 (6.45 g, 40.8 mmol) was added over 1 hour and stirred further for 4 hours at room temperature. The mixture was filtered and the filtrate was treated with saturated solution of Na_2SO_3 . The mixture was filtered and extracted with DCM. The extract was washed with brine, then was dried over MgSO_4 . Purification was performed via flash column chromatography (hexane: EtOAc = 9:1) producing **89b** with a yield of 75%. ^1H NMR (400 MHz, CDCl_3) δ 8.06-8.03 (1H, m), 7.59-7.43 (3H, m), 6.12 (1H, m), 2.96-2.27 (4H, m), 2.11 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 196.81, 170.46, 140.70, 133.93, 132.01, 129.05, 128.35, 127.21, 77.35, 77.03, 76.71, 69.08, 34.38, 28.48, 21.22.

1,2,3,4-tetrahydronaphthalen-1-ol (91). Sodium borohydride (1.42g, 37.6 mmol) was slowly added at room temperature to a mixture of α -tetralone (**5**, 4.55 ml, 34.2 mmol) and

methanol (35 ml). The mixture then was stirred for 40 minutes. Then it was diluted with water (35 ml) and extracted with ethyl acetate. The organic layer was separated, washed with brine, dried and concentrated to give **91** (5.01g, 33.8mmol) in 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.41 (1H, m), 7.25-7.09 (3H, m), 4.78 (1H, m), 2.86-1.90 (7H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 138.83, 137.12, 129.02, 128.65, 127.59, 126.19, 77.35, 77.03, 76.71, 68.17, 32.29, 29.25, 18.80.

1,2,3,4-tetrahydronaphthalen-1-yl acetate (92). Triethylamine (3.40 ml, 24.4 mmol) and DMAP (0.26 g, 2.10 mmol) were added to a solution of 1,2,3,4-tetrahydronaphthalen-1-ol (**9**, 3.00 g, 20.3 mmol) in DCM (40 ml). Next, acetic anhydride was added to maintain the mixture at room temperature. The reaction was stirred for one hour at room temperature. Afterwards, sodium bicarbonate solution was added, followed by extraction with DCM. Purification using flash chromatography (hexane: EtOAc = 9:1) gave **92** (4.24 g, 22.2 mmol) with a yield of 91%. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.11 (4H, m), 6.00 (1H, t), 2.88-2.76 (2H, m), 2.10 (3H, s), 2.01-1.82 (4H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 170.79, 137.95, 134.58, 129.45, 129.09, 128.10, 126.08, 77.34, 77.03, 76.71, 70.00, 29.09, 28.98, 21.50, 18.81.

1-(3,4-dimethoxyphenyl)-2-phenylethan-1-one (95b). AlCl_3 (4.0 g, 30.0 mmol) was added to a mixture of 1,2-dimethoxybenzene (8.4 ml, 66.0 mmol), 2-phenylacetyl chloride (2.6 ml, 19.7 mmol) and DCM (20 ml) at 15°C . The mixture was stirred for 1h at room temperature, poured into a mixture of ice, water and concentrated HCl, then extracted with DCM. The organic fraction was washed with brine, dried over MgSO_4 , filtered and evaporated. Recrystallization from methanol afforded 4.0 g (15.8 mmol) of **95b** (80% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.66 (dd, $J_1 = 2.02\text{Hz}$, $J_2 = 8.34\text{Hz}$, 1H, CH), 7.56 (d, $J = 2.02\text{Hz}$, 1H, CH), 7.23 – 7.34 (m, 5H, $-\text{C}_6\text{H}_5$), 6.88 (d, $J = 8.34\text{Hz}$, 1H, CH), 4.24 (s, 2H, CH_2), 3.93 (s, 3H, OMe), 3.91 (s, 3H, OMe). ^{13}C NMR (100 MHz, CDCl_3) δ = 196.32, 153.34, 149.09, 135.08, 129.79, 129.32, 128.67, 126.81, 123.47, 110.71, 110.02, 56.07, 55.95, 45.22.

1,2-bis(3,4-dimethoxyphenyl)ethan-1-one (95c). Thionyl chloride (5.7 ml, 79 mmol) was refluxed with 2-(3,4-dimethoxyphenyl)acetic acid (8.3 g, 42 mmol) and 15 ml of DCM for 2h. After cooling down to room temperature, the excess of thionyl chloride and DCM were removed in vacuo. The resulting oil was redissolved in 80 ml of DCM, followed by the addition of 1,2-dimethoxybenzene (7.5 ml, 59 mmol) and AlCl₃ (7.9 g, 59 mmol). The mixture was refluxed for 2 h, then poured into a mixture of water (50 ml), ice and concentrated HCl (10 ml) and extracted with DCM. The organic fraction was washed with brine, dried over MgSO₄, filtered and evaporated. Recrystallization from ethanol afforded 10.3 g (33 mmol) of **95c** (77% yield). ¹H NMR (400 MHz, CDCl₃) δ = 7.66 (dd, J₁ = 2.02Hz, J₂ = 8.34Hz, 1H, CH), 7.56 (d, J = 2.02Hz, 1H, CH), 6.88 (d, J = 8.34Hz, 1H, CH), 6.81 (m, 3H), 4.18 (s, 2H, CH₂), 3.94 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.85 (s, 3H, OMe). ¹³C NMR (100 MHz, CDCl₃) δ = 196.49, 153.31, 149.05, 149.04, 147.95, 129.74, 127.47, 123.38, 121.41, 112.41, 111.34, 110.68, 109.97, 56.03, 55.92, 55.83, 44.74.

4,6-dihexyl-2,3,7,8-tetraphenylpyrido[3,2-g]quinoline (94a). The procedure is representative for synthesis of **94a-c**. A mixture of **82** (499 mg, 1.5 mmol), **95a** (648 mg, 3.3 mmol, 2.2 eq) and TsOH·H₂O (628 mg, 3.3 mmol, 2.2 mmol) was stirred at 105°C under nitrogen for 1 h. Cooled down to room temperature, quenched with aqueous ammonia, extracted with DCM, dried over MgSO₄, and then evaporated. Recrystallization from ethanol afforded 294 mg (0.45 mmol) of **94a** (30% yield). ¹H NMR (400 MHz, CDCl₃) δ = 9.13 (1H, s, N-C=C(H)-C-N), 8.88 (1H, s, CH), 7.39 – 7.44 (4H, m, Ph), 7.29 – 7.36 (4H, m, Ph), 7.19 – 7.25 (10H, m, Ph), 3.11 (4H, m, Ar-CH₂), 1.76 (4H, m, CH₂), 1.38 (4H, m, CH₂), 1.23 (8H, m, CH₂), 0.85 (6H, t, J = 6.82 Hz, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ = 160.93, 146.68, 146.18, 141.28, 138.99, 133.28, 130.59, 130.04, 129.84, 127.98, 127.68, 127.53, 127.07, 125.10, 120.45, 31.40, 31.10, 30.00, 29.92, 22.50, 13.97. HRMS (ESI): [M + H]⁺ calcd for C₄₈H₄₉N₂ m/z 653.3890, found m/z 653.3905 (correct isotope distribution).

2,8-bis(3,4-dimethoxyphenyl)-4,6-dihexyl-3,7-diphenylpyrido[3,2-g]quinoline (94b). The procedure for synthesis of **94a** was used. **94b** was obtained by recrystallization from

ethanol in 33% yield. ^1H NMR (400 MHz, CDCl_3) δ = 9.08 (1H, s, N-C=C(H)-C-N), 8.84 (1H, s, CH), 7.30 – 7.40 (6H, m, Ph), 7.22 – 7.26 (4H, m, Ph), 7.17 (2H, dd, J_1 = 8.34 Hz, J_2 = 2.02 Hz, 2H, CH), 6.85 (2H, d, J = 2.02 Hz), 6.80 (2H, d, J = 8.34 Hz, CH), 3.87 (6H, s, OCH₃), 3.63 (6H, s, OCH₃), 3.09 (4H, m, Ar-CH₂), 1.74 (4H, m, CH₂), 1.37 (4H, m, CH₂), 1.23 (8H, m, CH₂), 0.84 (6H, t, J = 6.82 Hz, CH₃). ^{13}C NMR (100 MHz, CDCl_3) δ = 159.96, 148.83, 147.73, 146.70, 146.26, 139.47, 133.82, 133.04, 130.58, 129.58, 128.20, 127.12, 124.92, 123.16, 120.38, 113.49, 110.48, 55.79, 55.60, 31.39, 31.08, 29.99, 29.90, 22.49, 13.96. HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{52}\text{H}_{57}\text{N}_2\text{O}_4$ m/z 773.4324, found m/z 773.4313 (correct isotope distribution).

2,3,7,8-tetrakis(3,4-dimethoxyphenyl)-4,6-dihexylpyrido[3,2-g]quinoline (94c). The procedure for synthesis of **94a** was used. **94c** was obtained in 63% yield after being purified using column chromatography (DCM : EtOAc 1:1). ^1H NMR (400 MHz, CDCl_3) δ = 9.06 (1H, s, N-C=C(H)-C-N), 8.82 (1H, s, CH), 7.12 (2H, dd, J_1 = 8.34 Hz, J_2 = 2.02 Hz, CH), 6.97 (2H, d, J = 2.02 Hz, CH), 6.88 (2H, d, J = 8.34 Hz), 6.76 – 6.83 (4H, m, 2CH), 6.72 (2H, m, CH), 3.93 (6H, s, OCH₃), 3.87 (6H, s, OCH₃), 3.75 (6H, s, OCH₃), 3.70 (6H, s, OCH₃), 3.13 (4H, m, Ar-CH₂), 1.78 (4H, m, CH₂), 1.42 (4H, m, CH₂), 1.26 (12H, m, CH₂), 0.86 (6H, t, J = 6.82 Hz, CH₃). ^{13}C NMR (100 MHz, CDCl_3) δ = 160.93, 146.68, 146.18, 141.28, 138.99, 133.28, 130.59, 130.04, 129.84, 127.98, 127.53, 127.07, 125.10, 120.45, 31.40, 31.10, 30.00, 29.92, 22.50, 13.97. HRMS (ESI): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{56}\text{H}_{65}\text{N}_2\text{O}_8$ m/z 893.4735, found m/z 893.4752 (correct isotope distribution).

20, 22 – dihexyl - 2, 3, 6, 7, 13, 14, 17, 18 octamethoxydibenzo [a,c] dibenzo [5, 6 : 7, 8]- quinolino [2, 3-i] acridine (93b). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.21 ml, 9.4 mmol, 9.1 eq of BF_3) was added to a mixture of **94b** (772 mg, 1.0 mmol), [Bis(trifluoroacetoxy)iodo]benzene (PIFA, 1871 mg, 4.4 mmol, 4.4 eq) and 8 ml of anhydrous DCM at +5°C under nitrogen. Then the mixture was stirred for 2 h at +15°C. After quenching with saturated aqueous Na_2CO_3 solution, the organic compounds were extracted with DCM. The organic fraction was dried with MgSO_4 and evaporated. Column chromatography (DCM : EtOAc : Et_3N = 9:1:0.2) afforded 214 mg of the product as a red solid (28% yield). ^1H NMR (400 MHz, CD_2Cl_2 + CF_3COOH) δ = 9.61 (1H, s, N-C=C(H)-C-N), 9.53 (1H, s, CH), 8.56 (2H, d, J = 7.58, CH),

8.41 (2H, d, $J = 8.08$), 8.34 (2H, s, CH), 8.00 (2H, s, CH), 7.94 (2H, m, CH), 7.83 (2H, m, CH), 4.25 (6H, s, OCH₃), 4.21 (4H, m, CH₂), 4.12 (6H, s, OCH₃), 2.17 (4H, m, CH₂), 1.68 (4H, m, CH₂), 1.34 – 1.48 (8H, m, CH₂), 0.92 (6H, t, $J = 7.07$ Hz, CH₃). ¹³C NMR (100 MHz, CD₂Cl₂ + CF₃COOH) $\delta = 159.15, 158.57, 152.16, 147.39, 136.71, 134.49, 131.61, 131.01, 130.61, 128.77, 127.47, 126.67, 126.39, 125.14, 125.11, 117.12, 109.72, 107.43, 106.31, 57.42, 57.18, 34.65, 33.58, 31.97, 30.37, 23.17, 14.27$. HRMS (ESI): [M + H]⁺ calcd for C₅₂H₅₃N₂O₄ m/z 769.4005, found m/z 769.4014 (correct isotope distribution)

1,5-dimethyl-2,4-dinitrobenzene (96). 25 g (22.4 ml, 0.13 mol) of 1,5-dimethyl-2,4-dinitrobenzene were dissolved in 60 ml of 98% H₂SO₄ at 15 °C. Then 12 ml of 70% HNO₃ was added within 1 h at a rate that the temperature did not exceed 15 °C. The reaction mixture was stirred for 1 h, poured onto the mixture of ice and water, the resulting precipitate was filtered and washed with water. The solid was recrystallized from methanol (100ml) two times to produce 16.5 g of the product (50% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.72 (1H, s), 7.38 (1H, s), 2.70 (6H, s). ¹³C NMR (400 MHz, CDCl₃) δ 146.74, 138.99, 137.30, 121.7

4,6-dinitroisophthalic acid (97). A solution of 1,5-dimethyl-2,4-dinitrobenzene (**96**, 15.7 g, 80 mmol) in 120 ml of 98% H₂SO₄ was added within 2 h to a mixture of chromium (VI) oxide (40.0 g, 400 mmol) and 140 ml of 98% H₂SO₄ in a rate that the temperature did not increase above 15 °C. The mixture was stirred with cooling until the temperature dropped to +5 °C, then it was stirred for 2 h at room temperature. The mixture was then poured onto ice and extracted with diethyl ether. The organic phase was collected, evaporated, dissolved in water, filtered, washed with dichloromethane (DCM), then extracted with diethyl ether. The drying of the solution over MgSO₄ followed by evaporation gives 12.4 g of the product (60% yield). ¹H NMR (400 MHz, DMSO-D₆) δ 8.75 (1H, s), 8.31 (1H, s). ¹³C NMR (400 MHz, DMSO-D₆) 163.80, 148.81, 131.80, 130.67, 120.24

(4,6-dinitro-1,3-phenylene)bis(phenylmethanone) (98). 12.3 g (48.0 mmol) of 4,6-dinitroisophthalic acid (**97**) were mixed with 43 ml of SOCl₂, then heated for reflux until

all the solid is dissolved, which took about 4 h. The excess of SOCl_2 was distilled off, after that 45 ml of 1,1,2,2-tetrachloroethane and 20 ml of benzene were added, followed by the addition of AlCl_3 (27.8 g, 208 mmol) at 0 °C within 40 min. The mixture was stirred overnight at room temperature, then poured into the mixture of methanol (100 ml), ice (100 g) and concentrated HCl (10 ml). The resulting mixture was partially evaporated, mixed with 150 ml of water, and then extracted with dichloromethane. The organic fraction was dried over MgSO_4 and evaporated. Column chromatography (Hex:EtOAc = 3:2) afforded 11.0 g of the product (61% yield). ^1H NMR (400 MHz, CDCl_3) δ 9.09 (1H, s), 7.76 (4H, m), 7.66 (2H, m), 7.59 (1H, s), 7.50 (4H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 190.49, 146.86, 141.15, 134.86, 134.55, 129.62, 129.41, 129.31, 129.20, 124.78, 121.28.

(4,6-diamino-1,3-phenylene)bis(phenylmethanone) (99). A mixture of **(98)**, 4,6-dinitro-1,3-phenylenebis(phenylmethanone) (11.0 g, 29.2 mmol), 2.85 g Pd/C (10% of Pd), 230 ml of dichloromethane, and 110 ml of methanol was stirred for 72 h under hydrogen (1 atm). The resulting mixture was filtered through the pad of Celite, evaporated, and purified using column chromatography (DCM:EtOAc = 9:1). Afforded 8.0 g of the product (86% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (1H, s), 7.47 (4H, m), 7.37 (2H, m), 7.30 (4H, m), 6.59 (4H, br. s), 5.81 (1H, s). ^{13}C NMR (400 MHz, CDCl_3) δ 197.11, 155.31, 146.46, 139.87, 130.49, 128.43, 127.90, 110.26, 98.45.

Diphenyliodonium triflate ([Ph₂I]OTf). Triflic acid (14.8 ml, 167.6 mmol) was added to a mixture of benzene (5.8 ml, 63.9 mmol), iodobenzene (6.3 ml, 57.0 mmol), 3-chloroperbenzoic acid (14.4 g, 64.8 mmol), and 220 ml of DCM at +15 °C (cooling with ice). The mixture was stirred for 50 minutes at room temperature, then evaporated, and 200 ml of diethyl ether was added. The mixture kept for 30 minutes in a fridge at -20 °C, the precipitate filtered, washed with diethyl ether and dried in vacuo. Obtained 20.5 g (47.7 mmol) of the product (white crystals, 84% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.25 (m, 4H), δ 7.67 (m, 2H), 7.53 (m, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 135.13, 132.03, 131.73, 116.44.

12,14-dihexylquinolino[3,2-b]acridine (80a). A mixture of 629 mg (1.9 mmol) of 1,1'-(4,6-diamino-1,3-phenylene)bis(heptan-1-one), 1.67 g (3.9 mmol) of diphenyliodonium triflate, 79 mg (0.4 mmol) of copper (I) iodide, and 20 ml of 1,2-dichloroethane was stirred at 70 °C for 12 h under nitrogen. The mixture was quenched with 3ml of concentrated aqueous ammonia and 10 ml of water, extracted with DCM. The organic phase was dried over MgSO₄, evaporated, then purified using column chromatography (DCM:EtOAc:Et₃N = 1:1:0.1) producing 255 mg (0.6 mmol, 30% yield) of the product as a black powder. ¹H NMR (400 MHz, CDCl₃) δ 9.31 (1H, s), 9.21 (1H, s), 8.14 (2H, d, J = 9.09 Hz), 8.08 (2H, d, J = 9.09 Hz), 7.67 (2H, m), 7.36 (2H, m), 3.72 (4H, t, J = 8.08 Hz), 1.89 (4H, m), 1.64 (4H, m), 1.47 – 1.34 (8H, m), 0.93 (6H, t, J = 7.07 Hz). ¹³C NMR (400 MHz, CDCl₃) δ 151.43, 148.06, 146.18, 130.78, 130.67, 128.32, 125.09, 124.58, 123.97, 123.53, 121.41, 31.78, 31.63, 30.23, 28.21, 22.66, 14.05. HRMS (ESI): [M + H]⁺ calcd for C₃₂H₃₇N₂ m/z 449.2951, found m/z 449.2955 (correct isotope distribution).

12,14-diphenylquinolino[3,2-b]acridine (80b). A mixture of 500 mg (1.6 mmol) of (4,6-diamino-1,3-phenylene)bis(phenylmethanone), 1.43 g (3.3 mmol) of diphenyliodonium triflate, 60 mg (0.4 mmol) of copper (I) iodide, and 15 ml of 1,2-dichloroethane was stirred at 70 °C for 12 h under nitrogen. The mixture was cooled down to room temperature, then 10 ml of THF and 2 ml of trimethylamine were added. The mixture was filtered, and the black precipitate was washed with THF, then dried in vacuo. Obtained 376 mg (0.9 mmol, 55% yield) of the product as a black powder. ¹H NMR (400 MHz, CD₂Cl₂ + CF₃COOD) δ 9.97 (1H, s), 9.10 (1H, br. s), 8.49 (2H, d, J = 3.03 Hz), 8.21 (2H, d, J = 8.84 Hz), 7.89 (2H, m), 7.78 (2H, m), 7.69 (4H, m), 7.53 (4H, m). ¹³C NMR (400 MHz, CD₂Cl₂ + CF₃COOD) δ 144.99, 143.62, 138.29, 131.86, 131.28, 130.57, 130.51, 129.18, 128.90, 119.76, 119.10, 116.26, 113.41, 110.57, 108.49. HRMS (ESI): [M + H]⁺ calcd for C₃₂H₂₀N₂ m/z 433.1699, found m/z 433.1695 (correct isotope distribution).

1-(8-amino-12-hexylbenzo[b]acridin-9-yl)heptan-1-one (104). A mixture of 1,1'-(3,6-diaminonaphthalene-2,7-diyl)bis(heptan-1-one) (**103**, 152 mg, 0.40 mmol), diphenyliodonium triflate (354 mg, 0.82 mmol) and copper (I) iodide (15 mg, 0.08 mmol) in 4 ml of DCE was stirred for 16 h at 70 °C. The mixture was cooled down to room

temperature, quenched with aqueous ammonia, extracted with DCM, dried over MgSO_4 , then evaporated. Column chromatography ($\text{DCM}:\text{EtOAc}:\text{Et}_3\text{N} = 1:1:0.1$) afforded 26.2 mg of **104** (15% yield) as a black powder. ^1H NMR (400 MHz, CDCl_3) δ 8.71 (s, 1H), 8.56 (s, 1H), 8.38 (s, 1H), 8.10 (m, 2H), 7.68 (m, 1H), 7.39 (m, 1H), 6.98 (s, 1H), 5.87 (br.s., 2H, NH_2), 3.63 (m, 2H), 3.17 (m, 2H), 1.92 – 1.76 (m, 4H), 1.67 – 1.09 (m, 12H), 0.93 (m, 6H). ^{13}C NMR (400 MHz, CDCl_3): δ 203.53 (C=O), 152.07, 150.72, 148.82, 146.97, 144.83, 136.38, 135.93, 130.67, 130.06, 126.71, 126.09, 125.13, 124.69, 124.40, 123.49, 122.18, 121.48, 105.90, 39.69, 31.71, 31.58, 30.02, 29.04, 27.93, 24.70, 22.61, 22.55, 14.07, 14.05.

Figure A.3. HR MS spectra of **86**. **Figure A.4.** ^1H NMR spectra of **82**.

Figure A.5. ¹³C NMR spectra of **82**.

Figure A.6. HR MS spectra of **82**.

Chemical structure: 1,1'-bis(cyclohexylidene)-2,2'-bipyridine

^{13}C NMR spectrum (CDCl₃) peaks (ppm):

- 161.032
- 144.977
- 144.770
- 127.439
- 126.668
- 124.702
- 117.902
- 77.319
- 77.083
- 76.883
- 35.057
- 31.791
- 30.202
- 29.202
- 27.890
- 26.600
- 23.247
- 22.709
- 14.060

Figure A.8. ^{13}C NMR spectra of **81a**.

Figure A.9. HRMS spectra of **81a**. Figure A.10. 1H NMR spectra of **81b**.

Figure A.11. ¹³C NMR spectra of **81b**.

Figure A.12. HRMS spectra of **81b**.

Figure A.13. ¹H NMR spectra of **81c**. Figure A.14. ¹³C NMR spectra of **81c**.

Figure A.15. HRMS spectra of **81c**.

Figure A.16. 1H NMR spectra of **81d**.

Figure A.17. ^{13}C NMR spectra of **81d**.

Figure A.18. HRMS spectra of **81d**.

Chemical structure: C1=CC=C2C(=C1)OC3=C(C2)C4=CC=CC=C4C5=CC=CC=C5C6=CC=CC=C6C7=CC=CC=C7C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10C11=CC=CC=C11C12=CC=CC=C12C13=CC=CC=C13C14=CC=CC=C14C15=CC=CC=C15C16=CC=CC=C16C17=CC=CC=C17C18=CC=CC=C18C19=CC=CC=C19C20=CC=CC=C20C21=CC=CC=C21C22=CC=CC=C22C23=CC=CC=C23C24=CC=CC=C24C25=CC=CC=C25C26=CC=CC=C26C27=CC=CC=C27C28=CC=CC=C28C29=CC=CC=C29C30=CC=CC=C30C31=CC=CC=C31C32=CC=CC=C32C33=CC=CC=C33C34=CC=CC=C34C35=CC=CC=C35C36=CC=CC=C36C37=CC=CC=C37C38=CC=CC=C38C39=CC=CC=C39C40=CC=CC=C40C41=CC=CC=C41C42=CC=CC=C42C43=CC=CC=C43C44=CC=CC=C44C45=CC=CC=C45C46=CC=CC=C46C47=CC=CC=C47C48=CC=CC=C48C49=CC=CC=C49C50=CC=CC=C50C51=CC=CC=C51C52=CC=CC=C52C53=CC=CC=C53C54=CC=CC=C54C55=CC=CC=C55C56=CC=CC=C56C57=CC=CC=C57C58=CC=CC=C58C59=CC=CC=C59C60=CC=CC=C60C61=CC=CC=C61C62=CC=CC=C62C63=CC=CC=C63C64=CC=CC=C64C65=CC=CC=C65C66=CC=CC=C66C67=CC=CC=C67C68=CC=CC=C68C69=CC=CC=C69C70=CC=CC=C70C71=CC=CC=C71C72=CC=CC=C72C73=CC=CC=C73C74=CC=CC=C74C75=CC=CC=C75C76=CC=CC=C76C77=CC=CC=C77C78=CC=CC=C78C79=CC=CC=C79C80=CC=CC=C80C81=CC=CC=C81C82=CC=CC=C82C83=CC=CC=C83C84=CC=CC=C84C85=CC=CC=C85C86=CC=CC=C86C87=CC=CC=C87C88=CC=CC=C88C89=CC=CC=C89C90=CC=CC=C90C91=CC=CC=C91C92=CC=CC=C92C93=CC=CC=C93C94=CC=CC=C94C95=CC=CC=C95C96=CC=CC=C96C97=CC=CC=C97C98=CC=CC=C98C99=CC=CC=C99C100=CC=CC=C100C101=CC=CC=C101C102=CC=CC=C102C103=CC=CC=C103C104=CC=CC=C104C105=CC=CC=C105C106=CC=CC=C106C107=CC=CC=C107C108=CC=CC=C108C109=CC=CC=C109C110=CC=CC=C110C111=CC=CC=C111C112=CC=CC=C112C113=CC=CC=C113C114=CC=CC=C114C115=CC=CC=C115C116=CC=CC=C116C117=CC=CC=C117C118=CC=CC=C118C119=CC=CC=C119C120=CC=CC=C120C121=CC=CC=C121C122=CC=CC=C122C123=CC=CC=C123C124=CC=CC=C124C125=CC=CC=C125C126=CC=CC=C126C127=CC=CC=C127C128=CC=CC=C128C129=CC=CC=C129C130=CC=CC=C130C131=CC=CC=C131C132=CC=CC=C132C133=CC=CC=C133C134=CC=CC=C134C135=CC=CC=C135C136=CC=CC=C136C137=CC=CC=C137C138=CC=CC=C138C139=CC=CC=C139C140=CC=CC=C140C141=CC=CC=C141C142=CC=CC=C142C143=CC=CC=C143C144=CC=CC=C144C145=CC=CC=C145C146=CC=CC=C146C147=CC=CC=C147C148=CC=CC=C148C149=CC=CC=C149C150=CC=CC=C150C151=CC=CC=C151C152=CC=CC=C152C153=CC=CC=C153C154=CC=CC=C154C155=CC=CC=C155C156=CC=CC=C156C157=CC=CC=C157C158=CC=CC=C158C159=CC=CC=C159C160=CC=CC=C160C161=CC=CC=C161C162=CC=CC=C162C163=CC=CC=C163C164=CC=CC=C164C165=CC=CC=C165C166=CC=CC=C166C167=CC=CC=C167C168=CC=CC=C168C169=CC=CC=C169C170=CC=CC=C170C171=CC=CC=C171C172=CC=CC=C172C173=CC=CC=C173C174=CC=CC=C174C175=CC=CC=C175C176=CC=CC=C176C177=CC=CC=C177C178=CC=CC=C178C179=CC=CC=C179C180=CC=CC=C180C181=CC=CC=C181C182=CC=CC=C182C183=CC=CC=C183C184=CC=CC=C184C185=CC=CC=C185C186=CC=CC=C186C187=CC=CC=C187C188=CC=CC=C188C189=CC=CC=C189C190=CC=CC=C190C191=CC=CC=C191C192=CC=CC=C192C193=CC=CC=C193C194=CC=CC=C194C195=CC=CC=C195C196=CC=CC=C196C197=CC=CC=C197C198=CC=CC=C198C199=CC=CC=C199C200=CC=CC=C200C201=CC=CC=C201C202=CC=CC=C202C203=CC=CC=C203C204=CC=CC=C204C205=CC=CC=C205C206=CC=CC=C206C207=CC=CC=C207C208=CC=CC=C208C209=CC=CC=C209C210=CC=CC=C210C211=CC=CC=C211C212=CC=CC=C212C213=CC=CC=C213C214=CC=CC=C214C215=CC=CC=C215C216=CC=CC=C216C217=CC=CC=C217C218=CC=CC=C218C219=CC=CC=C219C220=CC=CC=C220C221=CC=CC=C221C222=CC=CC=C222C223=CC=CC=C223C224=CC=CC=C224C225=CC=CC=C225C226=CC=CC=C226C227=CC=CC=C227C228=CC=CC=C228C229=CC=CC=C229C230=CC=CC=C230C231=CC=CC=C231C232=CC=CC=C232C233=CC=CC=C233C234=CC=CC=C234C235=CC=CC=C235C236=CC=CC=C236C237=CC=CC=C237C238=CC=CC=C238C239=CC=CC=C239C240=CC=CC=C240C241=CC=CC=C241C242=CC=CC=C242C243=CC=CC=C243C244=CC=CC=C244C245=CC=CC=C245C246=CC=CC=C246C247=CC=CC=C247C248=CC=CC=C248C249=CC=CC=C249C250=CC=CC=C250C251=CC=CC=C251C252=CC=CC=C252C253=CC=CC=C253C254=CC=CC=C254C255=CC=CC=C255C256=CC=CC=C256C257=CC=CC=C257C258=CC=CC=C258C259=CC=CC=C259C260=CC=CC=C260C261=CC=CC=C261C262=CC=CC=C262C263=CC=CC=C263C264=CC=CC=C264C265=CC=CC=C265C266=CC=CC=C266C267=CC=CC=C267C268=CC=CC=C268C269=CC=CC=C269C270=CC=CC=C270C271=CC=CC=C271C272=CC=CC=C272C273=CC=CC=C273C274=CC=CC=C274C275=CC=CC=C275C276=CC=CC=C276C277=CC=CC=C277C278=CC=CC=C278C279=CC=CC=C279C280=CC=CC=C280C281=CC=CC=C281C282=CC=CC=C282C283=CC=CC=C283C284=CC=CC=C284C285=CC=CC=C285C286=CC=CC=C286C287=CC=CC=C287C288=CC=CC=C288C289=CC=CC=C289C290=CC=CC=C290C291=CC=CC=C291C292=CC=CC=C292C293=CC=CC=C293C294=CC=CC=C294C295=CC=CC=C295C296=CC=CC=C296C297=CC=CC=C297C298=CC=CC=C298C299=CC=CC=C299C300=CC=CC=C300C301=CC=CC=C301C302=CC=CC=C302C303=CC=CC=C303C304=CC=CC=C304C305=CC=CC=C305C306=CC=CC=C306C307=CC=CC=C307C308=CC=CC=C308C309=CC=CC=C309C310=CC=CC=C310C311=CC=CC=C311C312=CC=CC=C312C313=CC=CC=C313C314=CC=CC=C314C315=CC=CC=C315C316=CC=CC=C316C317=CC=CC=C317C318=CC=CC=C318C319=CC=CC=C319C320=CC=CC=C320C321=CC=CC=C321C322=CC=CC=C322C323=CC=CC=C323C324=CC=CC=C324C325=CC=CC=C325C326=CC=CC=C326C327=CC=CC=C327C328=CC=CC=C328C329=CC=CC=C329C330=CC=CC=C330C331=CC=CC=C331C332=CC=CC=C332C333=CC=CC=C333C334=CC=CC=C334C335=CC=CC=C335C336=CC=CC=C336C337=CC=CC=C337C338=CC=

Figure A.20. ^{13}C NMR spectra of **81e**.

Figure A.21. HRMS spectra of **81e**. Figure A.22. 1H NMR spectra of **94a**.

Figure A.23. ¹³C NMR spectra of **94a**.

Figure A.24. HR MS spectra of **94a**.

Figure A.27. HR MS spectra of **94b**. Figure A.28. 1H NMR spectra of **94c**.

Figure A.29. ^{13}C NMR spectra of **94c**.

Figure A.30. HRMS spectra of **94c**.

Chemical structure of 1,1'-bis(6-phenylhex-1-en-1-yl)-2,2'-bipyridine is shown. The structure consists of two bipyridine units linked at their 2,2' positions, with a 6-phenylhex-1-en-1-yl group attached to the 1-position of each bipyridine unit. The chemical formula is $C_{30}H_{30}N_2$.

The ^{13}C NMR spectrum (CDCl₃) shows peaks at the following chemical shifts (ppm): 151.448, 148.009, 146.204, 130.754, 130.705, 128.381, 128.357, 124.670, 123.968, 123.529, 121.381, 77.318, 76.680, 31.778, 31.665, 30.223, 28.203, 22.664, and 14.044.

Figure A.32. ^{13}C NMR spectra of **80a**.

Figure A.33. HR MS spectra of 80a.

Figure A.34. 1H NMR spectra of 80b.

Figure A.35. ¹³C NMR spectra of **80b**.

Figure A.36. HR MS spectra of **80b**.

Figure A.37. ^1H NMR spectra of **93b**.

Figure A.38. ^{13}C NMR spectra of **93b**.

Figure A.39. HR MS spectra of **93b**.