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**DESIGN, SYNTHESIS AND APPLICATIONS OF NOVEL
SOLUBLE *N*-HETEROACENES**

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Design, Synthesis and Applications of Novel Soluble *N*-heteroacenes

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Abstract

N-heteroacenes with the *CH* groups in the backbone of acenes replaced by *N* atoms are expected to own charming semiconducting properties and potential practical applications in organic electronics. The electron-deficient *N*-heteroacenes can be used as acceptor moieties in D-A molecules or *n*-type semiconductors depending on the application requirements. Although the researchers in all over the world are devoted to developing commercially available organic electronics, the study of organic memories, photovoltaics (OPVs) and field-effect transistors (OFETs) can still not stride out laboratory conditions, and the ultimate organic materials, which can satisfy all requirements for practical applications in the three types of devices are in high desire. Inspired by this gap, this dissertation focuses on design and synthesis of novel soluble *N*-heteroacenes and investigation of their applications in organic memories, OPVs and OFETs. For organic memories, the molecules have been designed based on two assumptions about multiple electron “traps” or multiple electrons intermolecular charge transfer, and accordingly, different electron-deficient *N*-heteroacene units are combined together to induce multiple electron “traps” or strong electron-deficient *N*-heteroacenes are utilized to accept multiple electrons. The memory devices have been fabricated and the corresponding switching behaviors, the ON/OFF ratios, the endurance and retention performance have been evaluated. Molecular calculation has been carried out to study the structure-property relationship. In summary, an efficient molecular designing strategy to approach rewritable, multilevel organic memory materials has been developed. For OPVs, the D- π -A structure molecules are designed with large conjugated *N*-heteroacene as acceptor moiety and linked to widely investigated donor units by π -bridges. The large conjugation of *N*-heteroacenes is expected to induce broad absorption and facilitate charge

carriers' transport. The typical BHJ architecture OPV devices have been fabricated and the corresponding PCE, V_{oc} , J_{sc} , and FF are investigated. Morphology analysis of the organic films has been carried out to study the effect of molecular stacking on the device performance. In summary the as-designed molecule has showed PCE up to ~2%, which is expected to own better performance after structure modification. For OFETs, large conjugated *N*-heteroacenes with deep LUMO level lower than -4.0 eV has been designed. The single-crystal OFET devices have been fabricated and the corresponding transfer and output curves, V_{TH} , ON/OFF ratios and field-effect mobility are investigated. Theoretical calculation has been conducted to study the ideal mobility of molecules and structure-property relationship. In summary a new family of *N*-heteroacenes have been developed for air-stable, high performance *n*-type OFETs.

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Scheme Captions

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Abbreviations

D-A	Donor-Acceptor
OLED	Organic Light-emitting Diodes
ORM	Organic Resistance Memory
OPV	Organic Photovoltaic
OFET	Organic Field-effect Transistor
HR MS	High Resolution Mass Spectroscopy
ESI	Electrospray Ionization
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization-Time of Flight
NMR	Nuclear Magnetic Resonance Spectroscopy
XRD	X-ray Diffraction
UV-vis	Ultraviolet-visible
TEM	Transmission Electron Microscopy
SAED	Selected-Area Electron Diffraction
AFM	Atomic Force Microscopy
Si	Silicon

Al	Aluminum
Ca	Calcium
Pt	Platinum
Au	Gold
ITO	Indium Tin Oxide
2D	Two Dimensional
3D	Three Dimensional
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

Chapter 1

Introduction

1.1 Background & Motivation

1.1.1 Charming Properties of *N*-heteroacenes

Since the discovery of conductive polymers in 1977 by Heeger, A. J. Shirakawa, H. and MacDiarmid, A. G., the development of organic π -conjugated materials have attracted a lot of attention, and large progress have been achieved in the exploration of their unique optical and electrical properties.¹ To date, millions of π -conjugated materials, including both polymers and small molecules, have been developed. Organic small molecules have 1) well-defined molecular structures, which make them be able to keep good batch to batch repeat; 2) easily controlled energy levels, which are favor for the demonstration of structure-property relationship; and 3) more accurate calculation-experiment matching, contributing to better investigation of intrinsic semiconducting mechanism. Thus, developing novel π -conjugated small molecules are crucial for both fundamental study and practical applications.

The π -conjugated materials can be classified as either a *p*-type (electron-rich systems, often play as donors), in which hole charge carriers are dominant, or *n*-type (electron-deficient systems, often act as acceptors), in which electron charge carriers are dominant. Acenes, a large family of π -conjugated small molecules, have proved to be excellent *p*-type semiconducting materials in organic electronics. When the *CH* groups in acenes' backbone are replaced by *N* atoms, or *NH* units, *N*-heteroacenes, the analogues of acenes, are generated and the intrinsic molecular structures have been changed, and special semiconducting

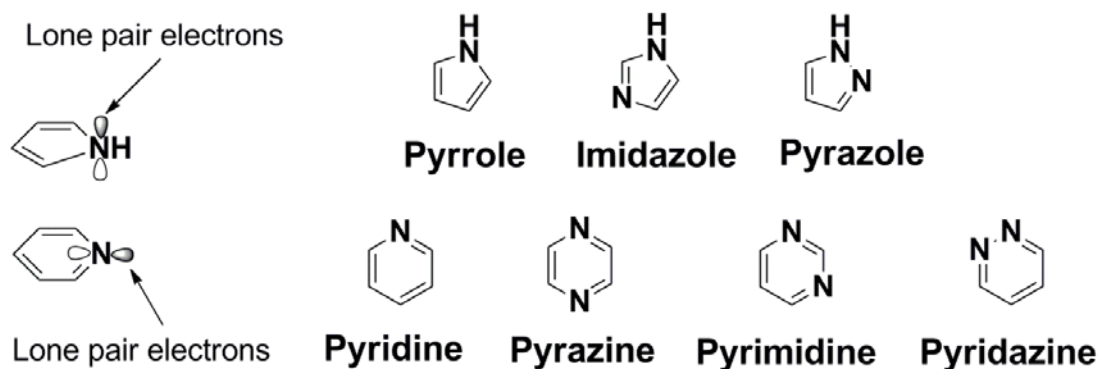


Figure 1.1.1 a) Different distribution of the lone pair electrons of *N* or *NH* in *N*-heteroacenes.

b) Several families of representative *N*-heteroacenes.

properties are expected. All *N* atoms in the backbone of *N*-heteroacenes adopt sp^2 hybridization, while the distribution of lone pair electrons is different, which depends on the molecular structure. As shown in Figure 1.1.1 a), for the *N* atom in pyrrole, the lone pair electrons are located at *p* orbital and participate in the formation of the large π bond. In this situation, the electron-donating conjugation effect of *N* atom is stronger than the electron-withdrawing inductive effect, thus, it is an electron-rich system. While in the situation of pyridine or pyrazine, the lone pair electrons are located at sp^2 hybridized orbital and do not generate any bonds. Because of the stronger electron negativity of *N* atoms, they are electron-deficient systems.² Therefore, *N*-heteroacenes can act as different roles such as electron donors or acceptors based on their intrinsic *N* characteristics. Figure 1.1.1 b) shows the structure of some typical *N*-heteroacenes. Pyrrole, pyridine or pyrazine, own $(4n + 2) \pi$ electrons, which is in consistent with the Huckel's rule, hence they are aromatic systems. When the *N* atoms in pyrazine are reduced to *NH*, the lone pair electrons are located at *p* orbital, and there are $(4n) \pi$ electrons. Theoretical calculation based on this type of molecules has been carried out, and the results indicate that they are also aromatic but with lower aromaticity level compared to their parent compounds.^{3,4} The broad structural diversity of *N*-

heteroacenes can be achieved by varying the intrinsic characteristics, the number and position of *N* atoms, besides of other common molecular modification strategies. As the structure changed, the semiconducting properties of *N*-heteroacenes can be tuned accordingly. In addition, *N*-heteroacenes are more stable than their counterpart acenes because they are more resistive to oxygen. All the advantages of *N*-heteroacenes such as multiple applications in building up molecules, different aromaticity, high structure diversity and good environmental stability make them good candidates in the applications of organic electronics and promising semiconducting performance are expected.

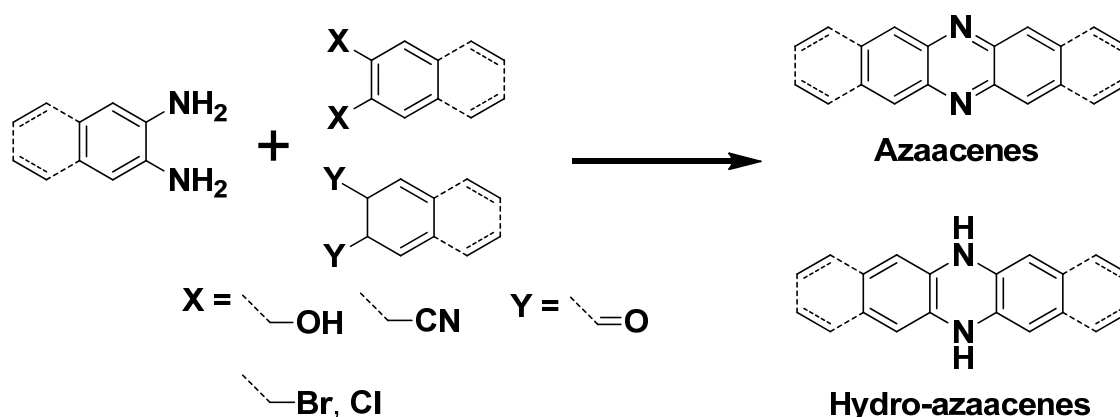


Figure 1.1.2 Representative synthetic route for *N*-heteroacenes.

Currently, most of the *N*-heteroacenes applied in organic electronics are linearly fused systems. To approach them, people usually utilize conventional substitution reaction between *ortho*-diamine based acenes and *ortho*-diketone, *ortho*-dihydroxy, *ortho*-dicyano, or *ortho*-dihalo substituted acenes. As shown in Figure 1.1.2, when *ortho*-diamine based acenes react with *ortho*-diketone, in certain situations azaacenes can be directly obtained. However, if the target products are highly electron-deficient, only hydro-azaacenes can be separated. The reaction between *ortho*-diamine based acenes and *ortho*-dihydroxy, *ortho*-dicyano, or *ortho*-dihalo substituted acenes generally produce hydro-azaacenes. Further oxidation of

hydro-azaacenes possibly gives their corresponding azaacenes. With these preparation strategies, a series of *N*-heteroacenes from low to high conjugation, i.e. anthracene to heptacene analogues have been successfully developed.

1.1.2 Applications of *N*-heteroacenes

Organic electronics have been predicted to be the next generation of electronics. Compared with the conventional *Si*-based inorganic electronics, organic electronics are cheaper with lower fabrication cost, more flexible and easier to process. In addition, there are various materials which can be specialized for certain requirements through molecular designing strategies. All the advantages make organic electronics popular and scientists all over the world are devoted themselves into this area. Among all the organic electronics, organic memories, OLEDs, OPVs and OFETs are closely connected to people's daily life. OLEDs have been well developed and commercialized in practical application, however, the development for organic memories, OPVs and OFETs still stays in laboratory research. A key factor which limits their development is that there are few of ultimate organic materials that have potential practical application in the three types of devices. Inspired by this gap and considering the charming advantages of *N*-heteroacenes, this dissertation will focus on design and synthesis of novel soluble *N*-heteroacenes and the investigation of their applications in organic memories, OPVs and OFETs.

1.1.2.1 Applications in Organic Memories

The novel organic memories should combine the advantages of the three leading memory technologies of today, which are expected to own the non-volatile ability of flash memory, the high switching speed of dynamic random access memory (DRAM), the high data storage

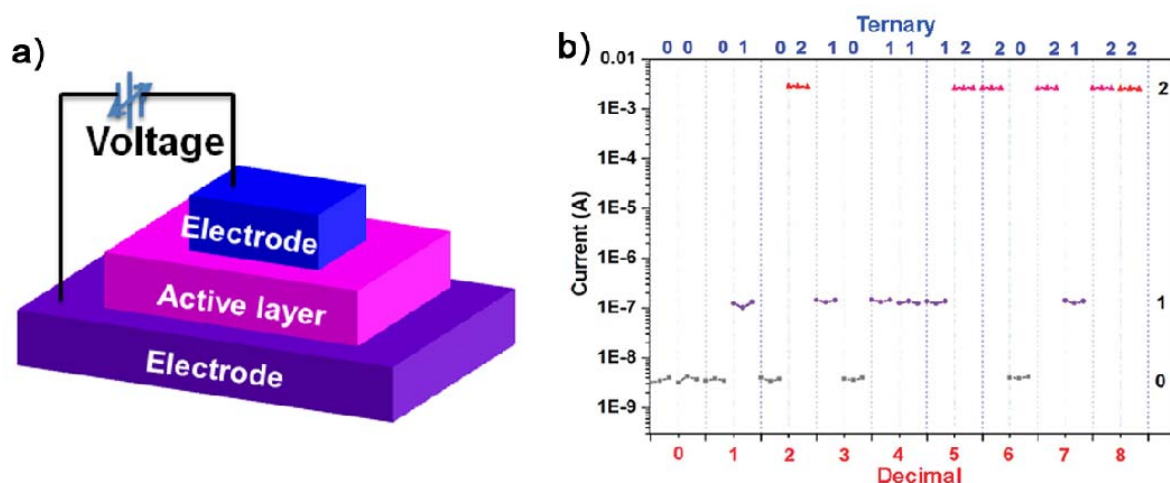


Figure 1.1.3 a) Schematic graph of a typical ORM device. b) Data storage performance of a ternary ORM device (reproduced based on literature).^{6,8}

density and high cycling endurance of hard-disk drives (HDDs). ORMs are promising candidates satisfying all the requirements.⁵ Figure 1.1.3 a) shows the schematic structure of a typical ORM device, which has a simple metal-insulator-metal (MIM) sandwich structure with the organic active layer clamped between two metal electrodes.⁶ When applied an appropriate voltage, the device can be switched to high or low resistance levels, corresponding to different memory states.⁷ Current-voltage (I - V) curves are generally used to characterize the switching behaviors. The basic parameters to evaluate the performance of ORMs include 1) the ON/OFF ratios (ratios of different resistance states), which should be ≥ 10 for less misreading; 2) cycling endurance, the higher of endurance the more reliable of memories, for practical application the memories should be capable to be repeatedly switched for more than 10^{12} cycles; 3) retention time, an ideal memory should be able to be retentive for more than 100 years. Remarkably numbers of organic materials have been investigated and most of them display two-state memory behaviors. Encouragingly, multilevel memory materials have been presented in recent advance of ORMs. Figure 1.1.3 b) shows a class of

typical data storage performance of a ternary states ORM.⁸ Obviously the data storage capacity of ternary device is increased exponentially from 2^n to 3^n compared with two states ORMs, which can realize high density data storage (HDDS) in a more convenient way. However, most of the reported multilevel ORM materials only show typical write-once-read-many-times (WORM) performance or their memory behaviors have to be induced by various excitation sources,⁸⁻¹¹ which has become a limitation for their practical application. Novel multilevel, rewritable, enduring and easily controllable ORM materials are in high desire.

Various mechanisms have been proposed to explain the memory behaviors of organic materials, e.g. filamentary effect of active metal electrodes, induce of negative differential resistance region (NDR), filling of electron “traps” and intermolecular charge transfer.¹²⁻¹⁴ As reported from previous researchers, the most efficient way to develop multilevel memory materials is to introduce different electron-deficient units in D-A molecules, which could play as multiple electron “traps”. The step-by-step filling of electron “traps” will induce the gradual changes of resistance in ORMs, which realizes the multilevel switching behavior. Another possibility to achieve multilevel memory is utilizing multiple electrons intermolecular charge transfer. As illustrated above, certain *N*-heteroacenes are electron-deficient systems and different electron deficient units can be obtained by tuning the position and number of *N* atoms. Thus, *N*-heteroacenes have great potential to be used as building blocks for multilevel ORM materials.

1.1.2.2 Applications in Organic Photovoltaics

OPVs, which can generate current directly from sunlight, are promising solutions to address more and more serious global power crisis. It is believed that the first observation of

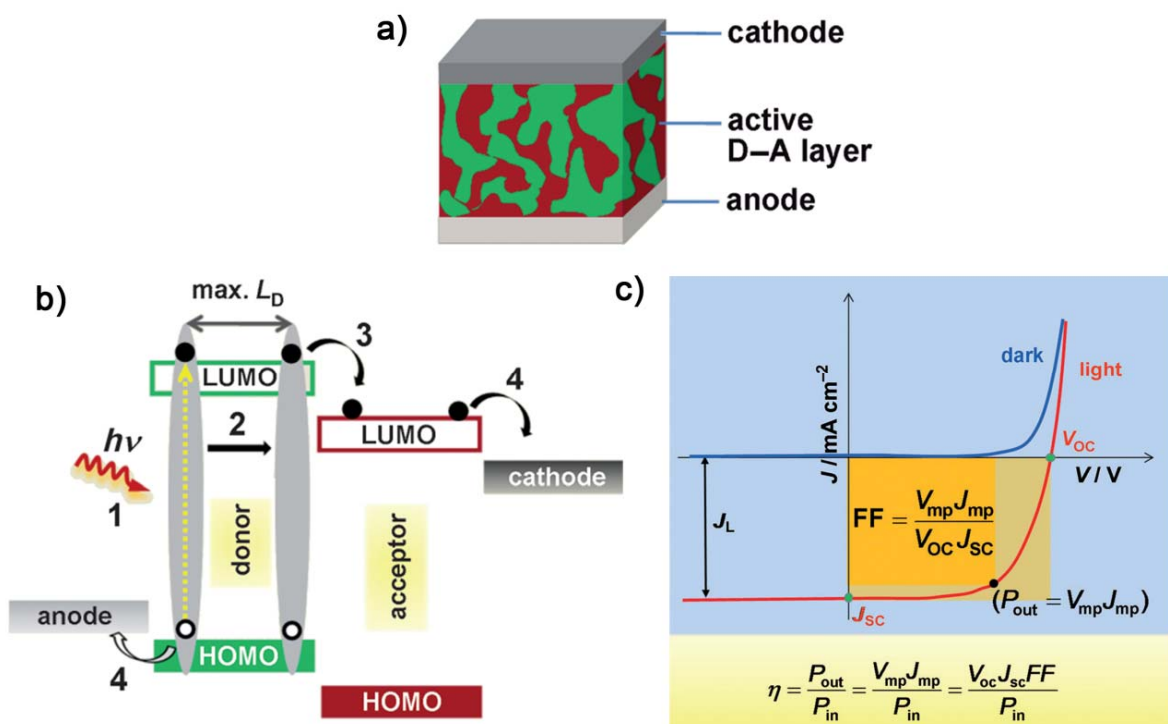


Figure 1.1.4 a) Schematic graph of a typical BHJ architecture OPV device. b) Fundamental steps of photocurrent generation. c) J - V characteristics of a typical OPV device. V_{mp} and J_{mp} are voltage and current, respectively, at which the power output of a device reaches its maximum. J_L is the photocurrent (reproduced based on literature).¹⁵

photocurrent emergence can be traced back to 1839 by Becquerel, A. E.^{15,16} This phenomenon has ever since been known as the photovoltaic effect and opened a new window of clean and renewable energy generation. Since the landmark discovery of phase separation phenomena of organic blended films in 1995, the bulk heterojunction (BHJ) based architecture has become a standard solution-processed OPV device structure.^{17,18} Figure 1.1.4 a) shows the typical schematic graph of a BHJ architecture OPV device, with active layer clamped between two electrodes, which is similar to the MIM memory device. Figure 1.1.4 b) shows the basic fundamental steps of how the photocurrent can be generated: 1) exciton (electron-hole pair bound by Coulomb interactions) generated by photoexcitation; 2) exciton

diffused to the D-A interface of blended films; 3) charge separation of excitons at the D-A interface of blended films; 4) free charge carriers transport and collection at the external electrodes. The direct characterization of OPVs can be illustrated by current-voltage (J - V) curves. Figure 1.1.4 c) depicts a representative J - V curve of an OPV device when measured under dark or light illumination conditions. The key evaluation parameter of OPVs is power conversion efficiency (PCE), which is determined by the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF). The bottom equation in Figure 1.1.4 c) illustrates the calculation of PCE, which can be defined as the result of division from V_{oc} , J_{sc} , and FF to the input power. The ratio between the efficient photos generating charge carriers and the incident photos at certain wavelength can be defined as external quantum efficiency (EQE). It is organic small molecules that firstly came to people's view in the search for new OPV materials, to date, remarkable improvements in PCE have been achieved from about 1% to over 10%.¹⁹ However, these results are still far away from the theoretical calculated PCE (20–24%).^{20,21} Clearly, there is still a long way to develop ultimate OPV materials with higher performance. Typical active layer in BHJ devices is comprised of a p -type semiconductor (donor) and an n -type semiconductor (acceptor). Fullerene and its derivatives are widely employed as acceptors due to their good stability and low LUMO levels.²²⁻²⁵ Compared with the well-developed acceptors, donor materials are largely behind of development, although they play an important role in the charge carriers' generation and transport. D-A type small molecules are now being systematically studied as donors for OPV application,^{26,27} and certain N -heteroacenes have been incorporated to induce broader absorption in visible and near-infrared region, which can contribute to better harvest of sunlight.^{28,29} This dissertation is interested in introducing larger conjugated N -heteroacenes as acceptor moieties in D-A molecules to increase the whole conjugation of molecules. Broad

absorption and good charge carriers' transport are proposed and high OPV performance of the as-designed molecules is expected.

1.1.2.3 Applications in Organic Field-effect Transistors

OFETs are crucial building blocks for numbers of electronic circuits. Basically a typical OFET device is composed by a gate insulator layer, an organic active layer, and three terminals (gate, drain and source, respectively).³⁰ When applying a voltage to the drain and source terminals, the drain-source current (I_{DS}) is generated and flow via the organic active layer. When a potential is applied to the gate and source terminals (V_{GS}), the I_{DS} can be adjusted exponentially as V_{GS} is below threshold voltage (V_{TH}). Many factors such as the device configuration, the materials used for terminals and insulator layer, and the molecular structure and intermolecular arrangements within organic active layer, etc. can influence the device performance of OFETs. Figure 1.1.5 a)–d) shows the typical device architectures of OFETs: a) Bottom Gate/Bottom Contact, b) Bottom Gate/Top Contact, c) Top Gate/Top Contact, and d) Top Gate/Bottom Contact. Generally, better performance can be achieved when the devices are fabricated with architecture b) or d), because of the better contact between electrodes and active layer. The parameters used to evaluate the performance of OFETs are field-effect mobility (μ , the drift velocity of charge carriers under electric field), ON/OFF ratio (the current ratio between on-state and off-state), and threshold voltage (V_{TH} , the minimum gate voltage that is required to turn on the transistor).³¹ The general characterization of OFET performance can be easily illustrated by transfer and output curves. Figure 1.1.5 e) shows a representative output curve of an OFET device, which contain two distinct regimes: linear and saturation. The field-effect mobility of materials can

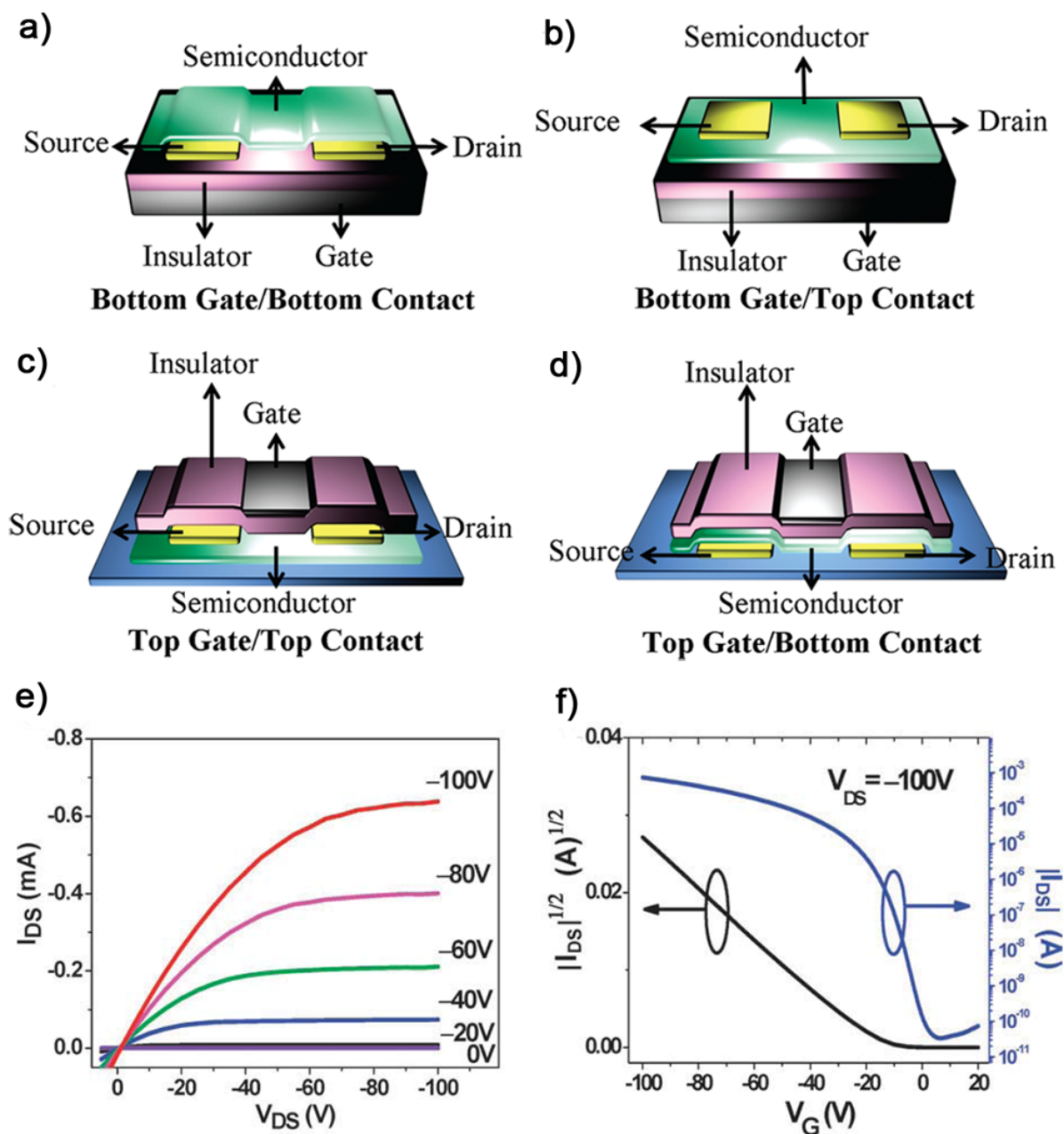


Figure 1.1.5 a) Bottom gate/bottom contact device. b) Bottom gate/top contact device. c) Top gate/top contact device. d) Top gate/bottom contact device. e) Output characteristics and f) transfer curves of a pentacene-based Bottom Gate/Top Contact OFET device (reproduced based on literature).^{31,32}

be extracted from the transfer curves (Figure 1.1.5 f)).³² Since the first report of OFET

utilizing polythiophene as active layer in 1986, which achieved large modulation of I_{DS} , the searching for new high performance OFET materials has made large progress,³³ and the performance of OFETs has been improved immensely over the past decades. In contrast to the conventional amorphous *Si*-based transistors, OFETs have reached comparable field-effect mobility up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, the poor operational stability of OFETs limits their practical application when the devices are exposed to ambient conditions, because oxygen, moisture or light can act as performance degrading exponents. Such challenge is particularly true for electron-transporting (*n*-type) OFETs. Actually, to date, few of *n*-type materials are reported to own high electron mobility up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ambient conditions with good stability. To develop air-stable *n*-type high mobility materials the molecules should be highly electron-deficient systems, and the LUMO levels should be lower than -4.0 eV. Large *N*-heteroacenes with more *N* atoms doped in backbone can satisfy the requirements and they are potential candidates to be developed as air-stable *n*-type materials.

1.2 Hypothesis

- Different electron-deficient *N*-heteroacene units can be utilized to induce multiple electron “traps”, and the strong electron-deficient *N*-heteroacene moieties can generate multiple electrons intermolecular charge transfer in D-A molecules. The as-prepared molecules, which are designed based on these rules, have the potential to be developed as good performance multilevel ORM materials.

By verifying the structure, position and number of *N* atoms in *N*-heteroacenes, different electron-deficient units can be achieved, which can be used as acceptor moieties in D-A molecules. The various electron-deficient *N*-heteroacene units can play as multiple electron

“traps” to induce multilevel memory behavior. Compared with other reported multilevel memory materials, whose electron “traps” are induced by dispersed electron-withdrawing groups, the acceptor moiety formed by *N*-heteroacene units can be conjugated together. On the other hand, D-A molecules with strong electron-deficient *N*-heteroacenes as acceptors can possibly accept multiple electrons to generate multiple electrons intermolecular charge transfer. Considering the charming semiconducting properties of conjugated *N*-heteroacenes in organic electronics, good multilevel memory performance is expected for materials designed in these strategies.

- Large conjugated *N*-heteroacenes can be used as acceptor moiety to build up D- π -A molecules for high performance OPV application.

As pushing up the length of *N*-heteroacenes, their conjugation will be increased as well. The D- π -A molecules with this type of *N*-heteroacenes as acceptor moieties are feasible due to their broad absorption in visible region, which contributes to better sunlight harvesting and charge carriers generation. In addition, with the increase of conjugation, the π - π interaction between adjacent molecules will be enhanced, which is favored for the facilitation of charge carrier transport. Thus the molecules designed in this strategy are expected to own high OPV performance.

- Large conjugated *N*-heteroacenes with more *N* atoms doped in backbone are expected to own lower LUMO levels and applied as high performance air-stable *n*-type OFET materials.

As the conjugation of *N*-heteroacenes is increased, the optical band gap of the molecules become narrower, which will further lower the LUMO level in certain extents. Besides, by

increasing the conjugation, more N atoms can be introduced into the backbone of molecules, and the whole molecule can be developed as a highly electron-deficient system with dramatically decreased LUMO levels. With the two aspects, the N -heteroacenes with LUMO levels lower than -4.0 eV can be probably achieved as air-stable n -type OFET materials with good performance.

1.3 Objectives

- The first objective of this dissertation is to design and synthesize a series of D-A molecules with conjugated N -heteroacenes as acceptor moieties, which can be applied as multilevel rewritable ORM materials with high ON/OFF ratio, good endurance and retention performance.

The key point of this objective is the acceptor engineering through combining different electron-deficient N -heteroacene units or synthesizing strong electron-deficient N -heteroacenes as acceptor moieties in D-A molecules. Suitable side chains will be connected to the molecules to ensure that they can be processed by a solution-processing method. The molecules will be characterized with common physical and chemical strategies. Typical MIM ORMs will be fabricated based on the novel molecules to investigate their memory performance. Molecular calculation will be utilized to study the switching mechanism in order to investigate the structure-property relationship, and we expect to find out efficient molecular designing strategies for developing multilevel rewritable ORM materials with high ON/OFF ratio, good endurance and retention performance.

- The second objective of this dissertation is to design and synthesize D- π -A molecules with large conjugated *N*-heteroacenes as acceptor moieties which can be used as high performance OPV materials.

Large *N*-heteroacenes that would have more than three rings fused together to make large conjugated acceptor moiety will be developed. Side chains engineering will be carried out to ensure that the molecules have good solubility for solution process. The molecules will be characterized with common physical and chemical strategies. Typical BHJ OPVs based on the novel molecules will be fabricated and their OPV performance will be investigated. Both molecular simulation and morphology analysis will be used to investigate the structure-property relationship, and efficient molecular designing strategies for developing high performance OPV materials with large conjugated *N*-heteroacenes as acceptors are expected.

- The third objective of this dissertation is to design and synthesize large conjugated highly electron-deficient *N*-heteroacenes which can be applied as air-stable *n*-type OFET materials.

Long and linearly-fused large conjugated electron-deficient *N*-heteroacenes with LUMO levels lower than -4.0 eV will be designed and synthesized. Certain side chains will be attached onto the molecules to ensure they have good solubility in solution and orderly stacking in solid states. The molecules will be characterized with common physical and chemical strategies. Single crystal OFETs will be fabricated and the corresponding device performance will be evaluated. Theoretical calculation will be carried out to study the structure-property relationship, and a new family of air-stable, good performance *n*-type OFET materials is expected.

1.4 Scope

In this dissertation, the D-A and D- π -A molecules will be synthesized with originally designed *N*-heteroacene acceptor moieties and widely investigated donor units. The large conjugated electron-deficient *N*-heteroacenes will incorporate more *N* atoms in the backbone of oligoacenes. All the synthesis will start from commercially available reagents and solvents, and the target molecules will be prepared through multiple-step organic reaction.

Physical and chemical characterization will be carried out after the synthesis of molecules. HR MS, including ESI and MALDI-TOF will be used to characterize the molecular formula and molecular weight of novel molecules. NMR will be applied to determine the molecular structure. UV-vis absorption spectroscopy will be utilized to analyze the optical properties of molecules, cyclic voltammetry (CV) analysis and electron ionization energy analysis will be used to study the electrochemical properties. X-ray crystallographic analysis will be used to study the molecular stacking behavior in crystals. Powder XRD patterns will be used for analysis of molecular stacking in micro crystals. TEM and SAED will be conducted to investigate the packing orientation of molecules in micro crystals. AFM will be used to study the morphology of films. Out-of-plane XRD pattern will be carried out to investigate the crystallinity of thin films. Molecular simulation and theoretical calculation will be carried out to compute the electron distribution of molecules in frontier orbits and help to explain the mechanisms of experimental results.

All the devices will be fabricated with solution processing method and standard characterization strategies. MIM architecture ORM devices will be fabricated, and the corresponding *I-V* curves, ON/OFF ratio, endurance and retention performance will be

evaluated. BHJ architecture OPV devices with ITO/anode buffer layer/active layer/cathode structure will be fabricated, the corresponding J - V and EQE curves, PCE, J_{sc} , V_{oc} and FF will be evaluated. Bottom Gate/Top Contact architecture OFET devices will be fabricated, and the corresponding transfer and output characteristics, field-effect mobility, ON/OFF ratio, V_{TH} and environmental stability will be evaluated.

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Chapter 2

N-heteroacenes for Organic Memories

2.1 Literature Review

Polymer materials have been widely investigated in ORMs, while few of them displayed multilevel memory behavior.¹⁻¹⁰ A breakthrough was achieved by Li's group, who reported the protonic acid doped polymer **1** (Figure 2.1.1 a)) and the corresponding memory properties.¹¹ In their contribution, polyazomethine was synthesized firstly and the as-prepared polymer was doped by *p*-toluenesulfonic acid (TsOH). Pt was used as top and bottom electrodes to avoid filamentary effect in their ORM devices, which showed multilevel memory behavior by controlling the "RESET" voltage (shown in Figure 2.1.1 b)) with reasonable ON/OFF ratio between neighboring states (> 10) if the devices were only "SET" to three states. The devices can be switched for more than 10^3 cycles between each state with narrow distribution of resistance, showing charming endurance performance with good uniformity. However, with the resistance of devices decreasing, the retention time decreased accordingly. The authors believed that the protonic acid doping of a poly(schiff base) was an energetically unfavorable process, which explained the bad retention performance of the doped polymer. The multilevel memory behavior was proposed to be induced by electric-field induced doping/dedoping effect. Later, Zhang's group developed a polyoxometalate (POM) based inorganic-organic hybrid polymer **2** (Figure 2.1.1 a)) with multilevel memory behavior.¹² ORM devices were fabricated with Pt as top electrode and ITO as bottom electrode, similar to **1**, the multiple resistance states were achieved by controlling the "RESET" voltage. The device can only be switched between the three states for less than 20

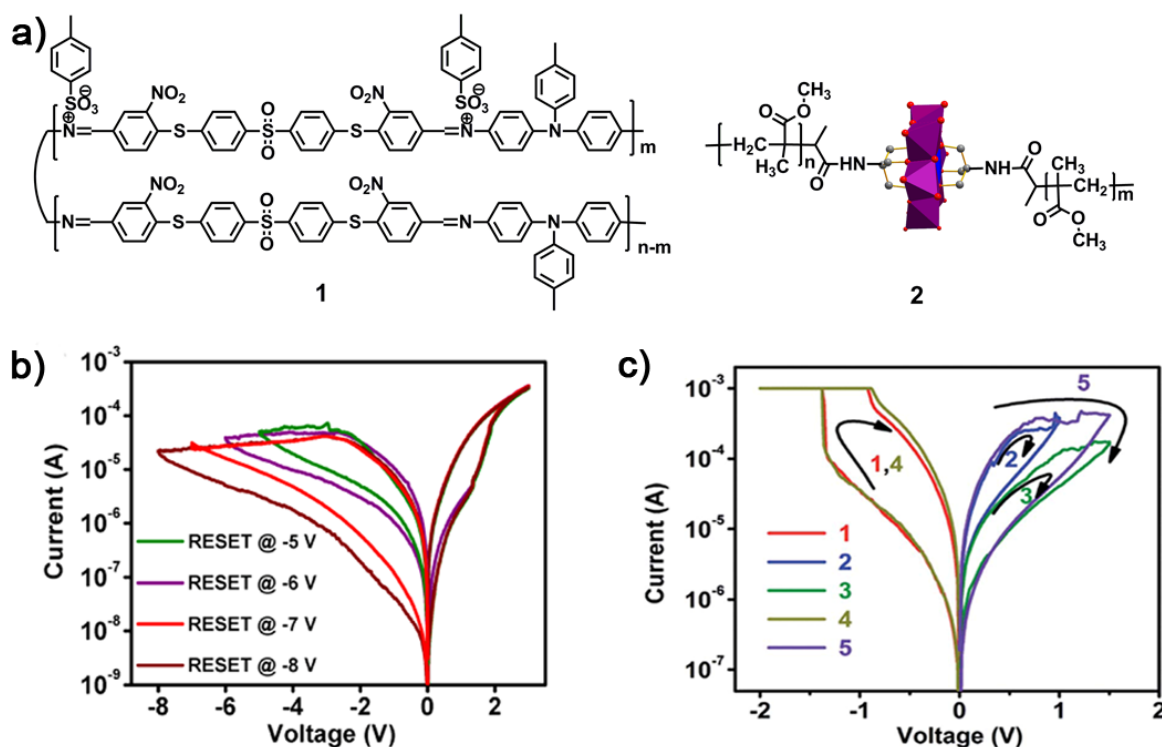


Figure 2.1.1 a) Molecular structure of representative multilevel ORM polymers. b) I - V curves for **1**. c) I - V curves for **2** (reproduced based on literature).^{11,12}

cycles with ON/OFF ratio at ~ 5 , although each state can be retentive for more than 10^4 seconds. The authors believed that the multiple redox process in **POM** induced by various electronic fields was responsible to the different resistance levels, which changes the charge carrier density.

As the investigation of polymers, organic small molecules have been studied for application in ORMs as well, and most of them displayed two-state memory behaviors.¹³⁻¹⁵ In 2010, Lu's group and Gu's team collaborated together to present the first multilevel memory behaviors of a series of small molecules (**1–4** in Figure 2.1.2), the ORM devices with Al as top electrode and ITO as bottom electrode showed three distinct resistance states with ON/OFF ratio larger than 10^2 , which was high enough for practical application. Different from

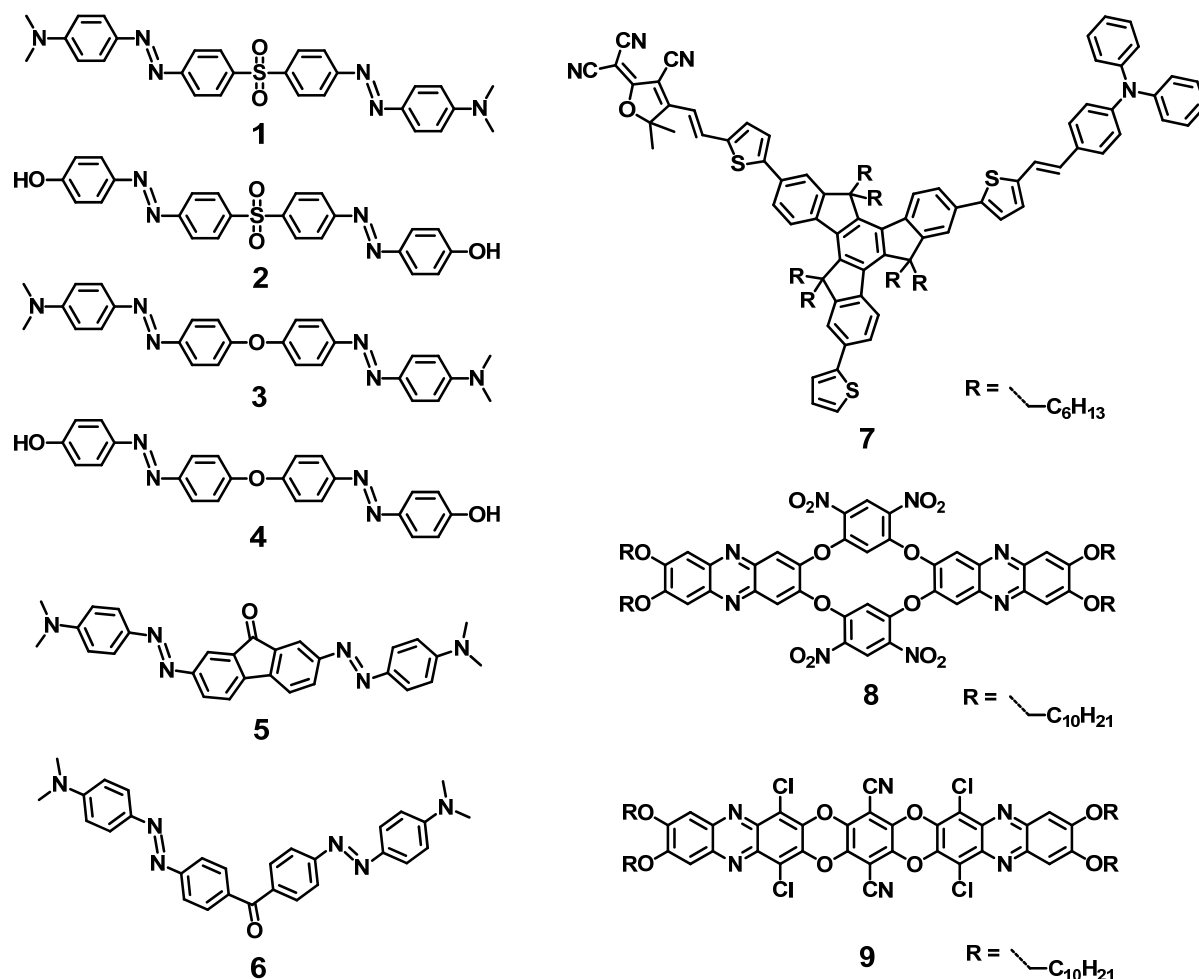


Figure 2.1.2 Molecular structures of representative multilevel ORM small molecules.

multilevel polymers, the resistances of molecules **1–4** were tuned step-by-step in set process, with typically write-once-read-many-times (WORM) characteristics.¹⁶ All the three resistance states were well retentive. Later in 2012 continued with this work, Lu's group designed two small molecules (**5–6** in Figure 2.1.2) with different planarity of donor units. However, the difference of ORMs between **1–4** and **5–6** only displayed in ON/OFF ratio.¹⁷ Rewritable multilevel small molecule (**7** in Figure 2.1.2) was reported by Song's group,¹⁸ which had a typical D- π -A structure with triphenylamine (TPA) as a donor and 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) as an acceptor. The

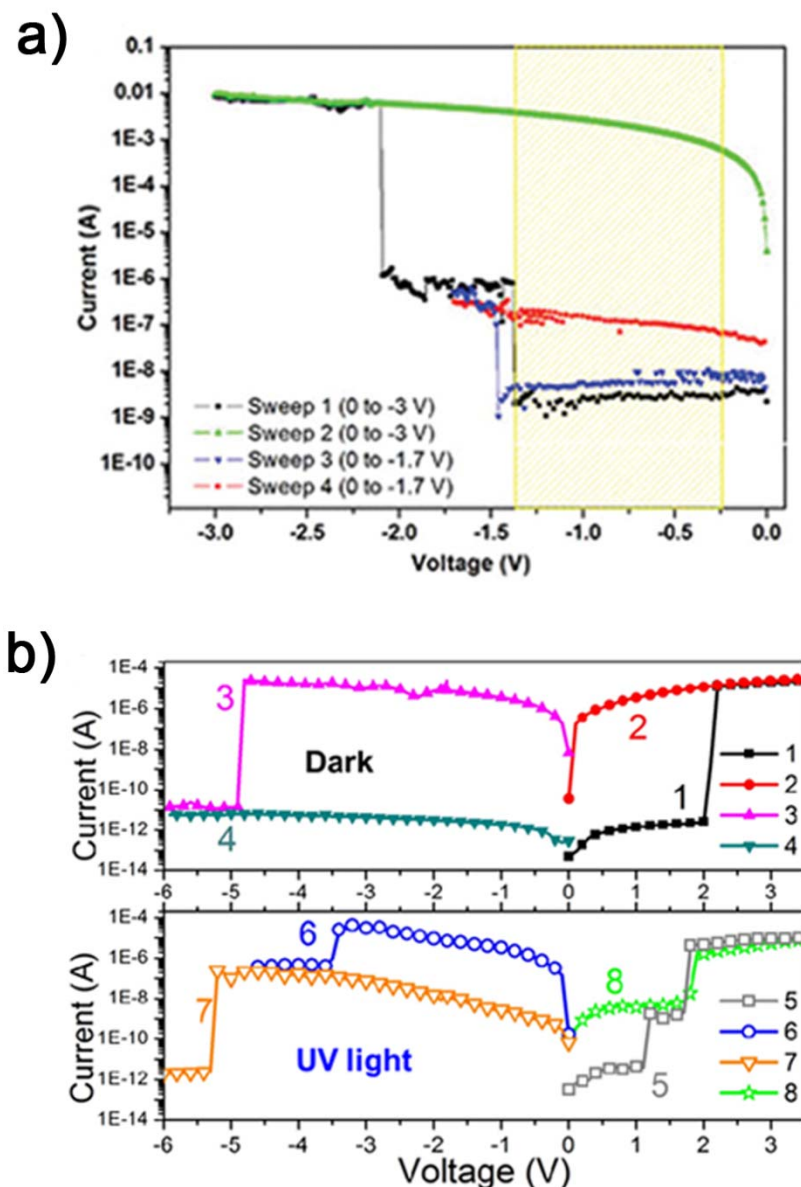


Figure 2.1.2 a) Representative I - V curves of a ternary WORM type ORM. b) I - V curves of ORM based on molecule 7 (reproduced based on literature).^{16,18}

memory devices utilized Al as top electrode and ITO as bottom electrode. Interestingly, in dark conditions, the devices only showed two-state memory behavior, but under UV light, three states memory behavior could be observed. The device could be “SET” or “RESET” to different resistance states by controlling the “SET” and “RESET” voltage step-by-step with

charming ON/OFF ratio ($> 10^2$). Although the three states were well retentive, the authors did not investigate the endurance performance of the devices. Large π conjugated *N*-heteroacenes had also been investigated (**8–9** in Figure 2.1.2).^{19,20} The molecules had multiple electron-withdrawing groups (pyrazine and nitro groups in **8**, pyrazine and cyano groups in **9**). The devices architecture and memory behavior based on the two molecules were similar with **1–4**, which were ternary and WORM type. All the authors believed that the different electron withdrawing groups in these molecules played as multiple electron “traps”, which could be filled at different “SET” voltage inducing the multilevel memory behavior. However, the rewritable ability and endurance performance were key limits for their practical application. Developing multilevel, rewritable, endurable and well retentive memory materials are still challenging and in urgent demand.

2.2 D-A Molecules with Different *N*-heteroacene Units as Acceptor Moiety

2.2.1 Molecular Design

Considering different *N*-heteroacene units own various electron-withdrawing abilities, it might be feasible to fuse multiple *N*-heteroacene units, an imidazole and a pyrazine into one molecule to play as a single acceptor moiety. Such design might generate multiple electron “traps”. Moreover, **TPA** can be selected as donor unit in memory materials because it has the strong ability to stabilize charge separated state. To ensure the devices can be fabricated through solution processing method, side chains are required to attach on the backbone of molecules to help increase the solubility of the as-designed compounds in common organic solvents. Triisopropylsilyl (**TIPS**) has been widely proven to be a perfect substituted group, because the bulk spherical configuration with diameter at ~ 7 Å can lower the π - π interaction

of molecules in solution, which enhances their solubility efficiently. Besides that, attaching **TIPS** to molecules can facilitate the 2D stacking of molecules in solid states so as to increase π -overlap between adjacent molecules.²¹ With these considerations, we propose a novel D-A molecule 4-(diphenylamino)phenyl-4,11-bis((triisopropylsilyl)ethynyl)-1*H*-imidazo[4,5-*b*]phenazine (**TPA-BIP**), which has **TPA** as a donor unit and 4,11-bis((triisopropylsilyl)ethynyl)-1*H*-imidazo[4,5-*b*]phenazine (**BIP**) as acceptor moiety with two electron “traps”.

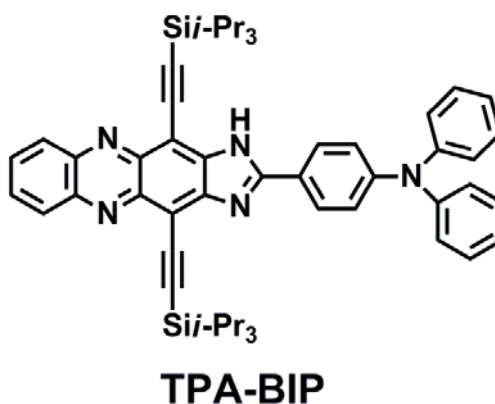


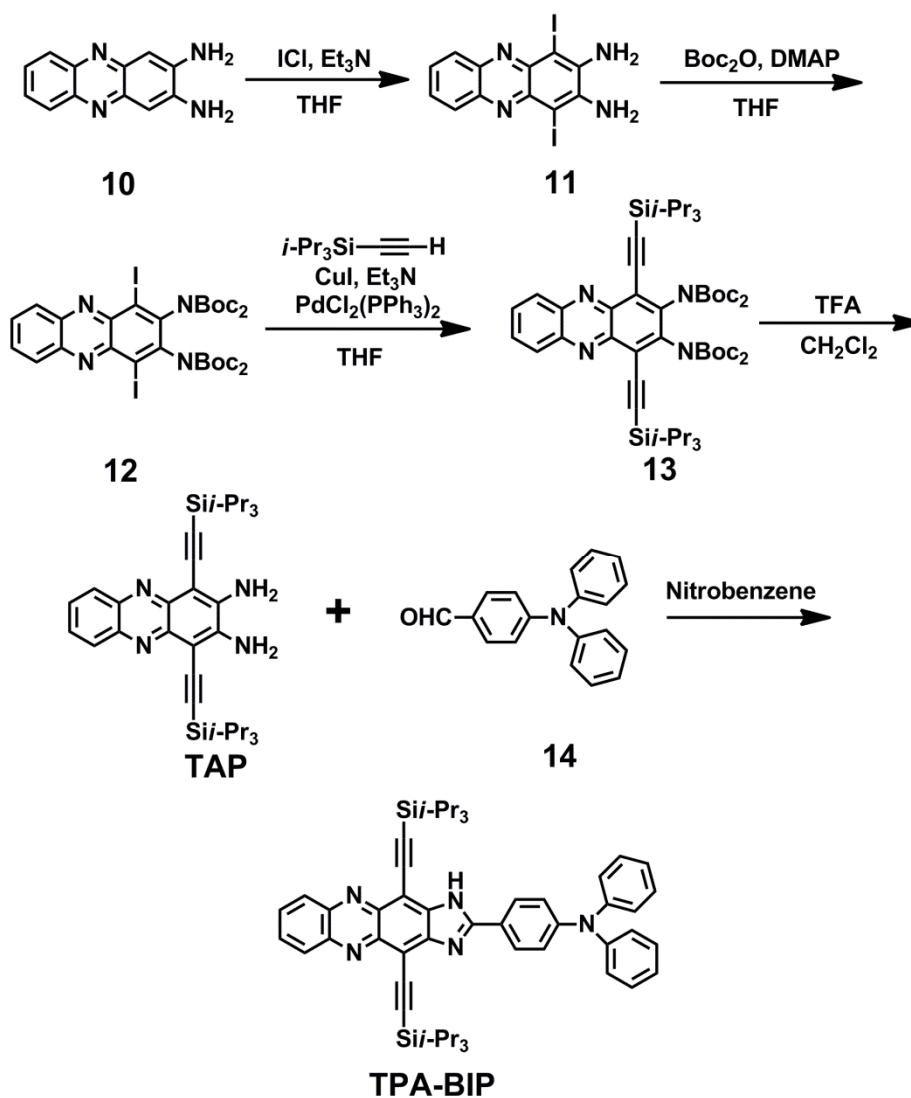
Figure 2.2.1.1 Molecular structure of **TPA-BIP**.

2.2.2 Synthesis of TPA-BIP

The synthetic route for **TPA-BIP** is illustrated in Scheme 2.2.2.1.

Synthesis of TAP

The intermediate diamine 1,4-bis((triisopropylsilyl)ethynyl)-2,3-diaminophenazine (**TAP**) was synthesized according to a literature reported procedure.²² The commercially available 2,3-diaminophenazine was treated with iodine monochloride in anhydrous tetrahydrofuran (THF) under N₂ atmosphere to produce 1,4-iodine substituted compound **11**. The two amino

Scheme 2.2.2.1 Synthetic route for **TPA-BIP**.

groups of **11** were protected by tert-butoxycarbonyl (Boc) to give compound **12**. Sonogashira coupling between **12** and **TIPS** acetylene produced compound **13**, which was deprotected by trifluoroacetic acid (TFA) to generate **TAP** as golden yellow solid in yield of ~19%.

Synthesis of TPA-BIP

In a 100 ml round bottom flask, **TAP** (550.27 mg, 0.96 mmol) and commercially available 4-(diphenylamino)benzaldehyde **14** (283.62 mg, 1.04 mmol) were well dissolved in nitrobenzene (10 mL). The system was heated at 180 °C for 48 hours. After that, the system

was cooled down to room temperature and nitrobenzene was removed by reduced pressure distillation method. The solid residue was obtained as crude product and further purified by flash column chromatography with ethyl acetate (EtOAc) and hexane (EtOAc: hexane = 1: 20) over silica gel, the pure **TPA-BIP** (140 mg) was afforded as dark red powder in yield of 17%.

2.2.3 Molecular Characterization

The novel **TPA-BIP** had been characterized by HR MS, NMR and X-ray crystallographic analysis.

2.2.3.1 HR MS Analysis

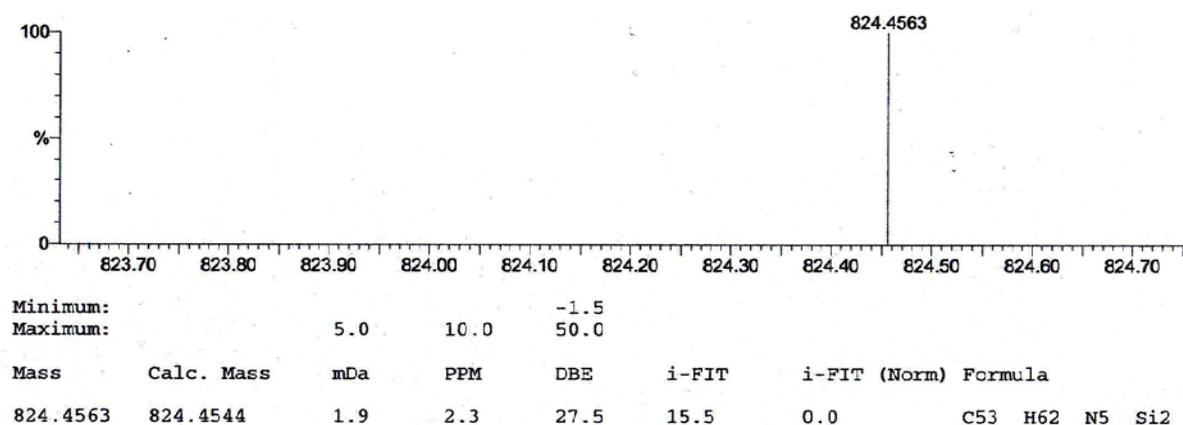


Figure 2.2.3.1.1 HR MS (ESI) spectra of **TPA-BIP**.

The HR MS (ESI) spectra of **TPA-BIP** were recorded on a Waters Q-ToF premier™ mass spectrometer.

The chemical formula of **TPA-BIP** is C₅₃H₆₁N₅Si₂. As shown in Figure 2.2.3.1.1, the calculated m/z value of $[M+1]^+$ for **TPA-BIP** is 824.4544, and the actual m/z value of that found in spectra is 824.4563, which is well consistent with the calculated result.

2.2.3.2 NMR Analysis

^1H NMR and ^{13}C NMR spectra of **TPA-BIP** were recorded on a Bruker 300-MHz spectrometer.

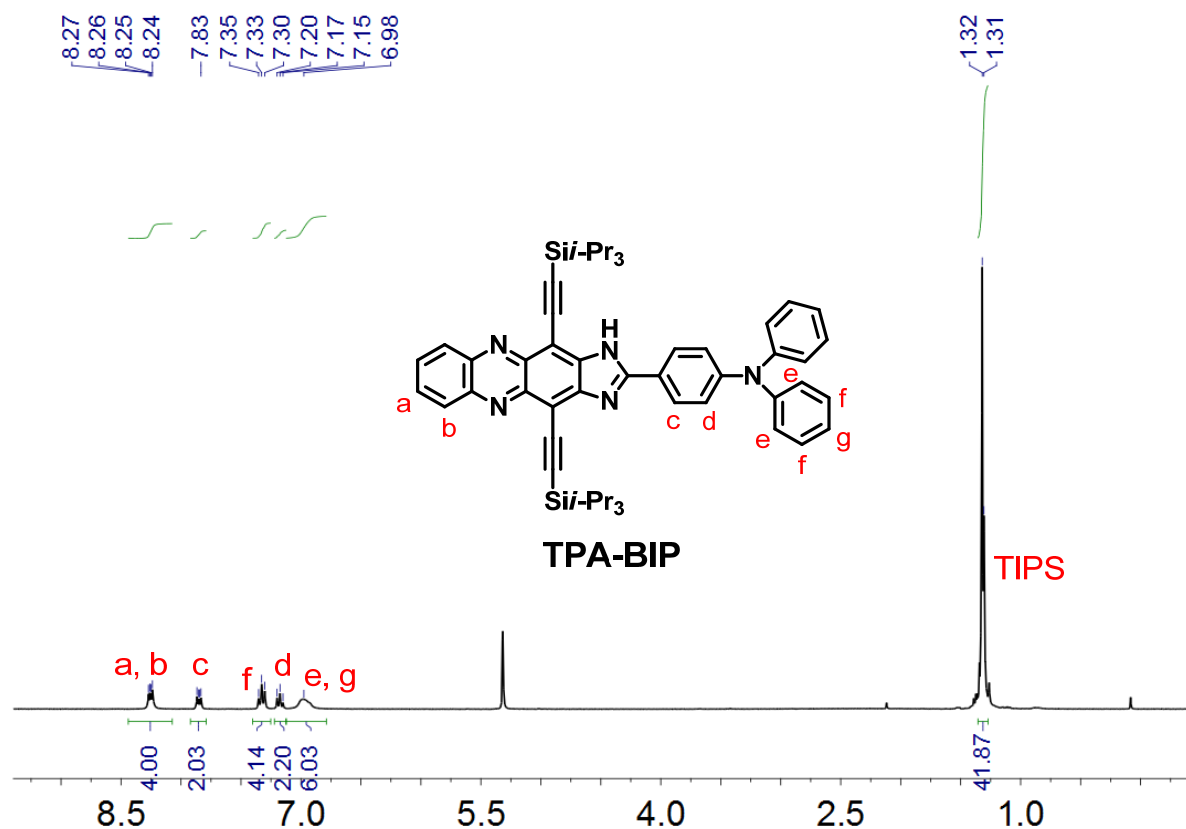


Figure 2.2.3.2.1 ^1H NMR spectra of **TPA-BIP** in CD_2Cl_2 .

The ^1H NMR spectra were collected in CD_2Cl_2 . As shown in Figure 2.2.3.2.1, the protons can be indexed as ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{H}} = 1.21\sim 1.42$ (42H), $6.90\sim 7.13$ (4H), $7.02\sim 7.25$ (2H), $7.17\sim 7.39$ (6H), $7.66\sim 7.87$ (2H), $8.11\sim 8.35$ (4H), which are well corresponding to the molecular structure.

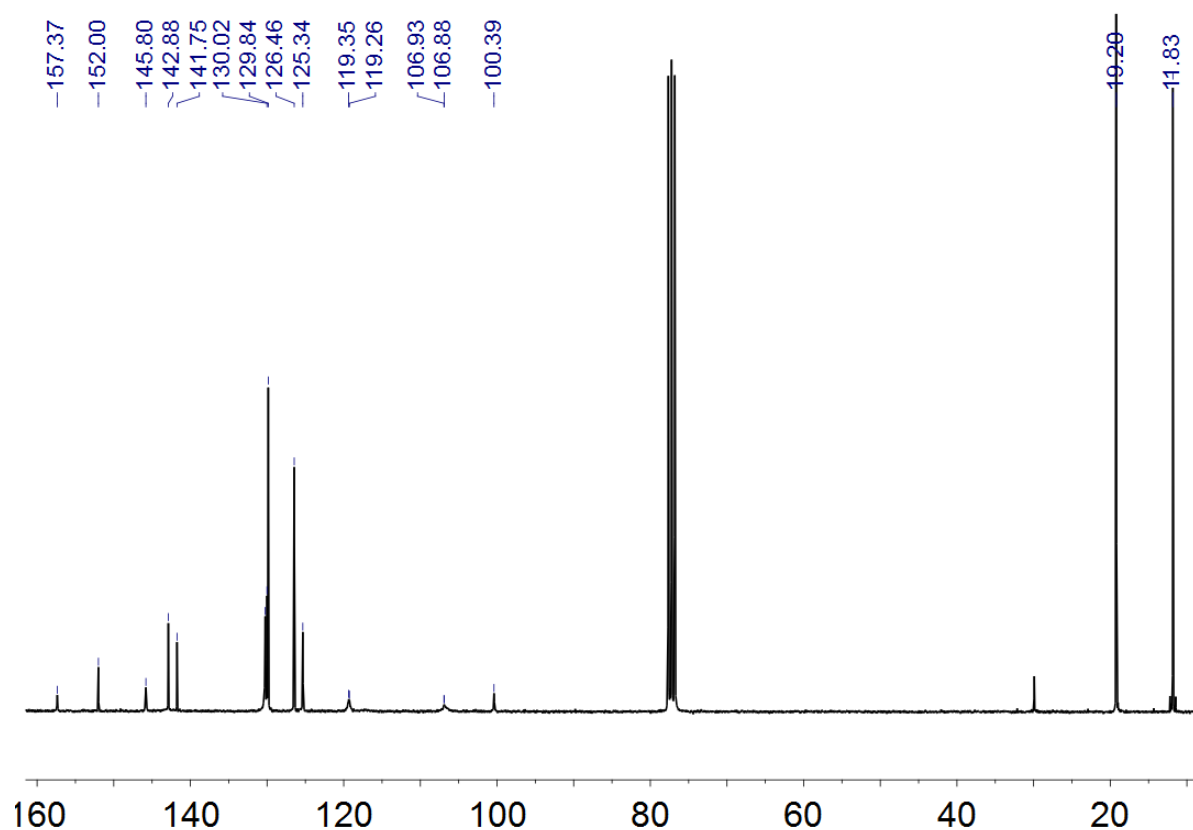


Figure 2.2.3.2.2 ^{13}C NMR spectra of **TPA-BIP** in CDCl_3 .

The ^{13}C NMR spectra of **TPA-BIP** were collected in CDCl_3 . As shown in Figure 2.2.3.2.2, the carbon atoms can be indexed as ^{13}C NMR (75 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 157.37, 152.00, 145.80, 142.88, 141.75, 130.02, 129.84, 126.46, 125.34, 119.35, 119.26, 106.93, 106.88, 100.39, 19.20, 11.83$. The carbons located at 11.83 and 19.20 are corresponded to **TIPS** group, and only 14 carbons can be observed in range of 100–160 ppm, which is 3 carbons less than theoretical value. Maybe certain carbons of **TPA-BIP** have no signals in ^{13}C NMR spectra in our experimental conditions.

2.2.3.3 Crystal Analysis

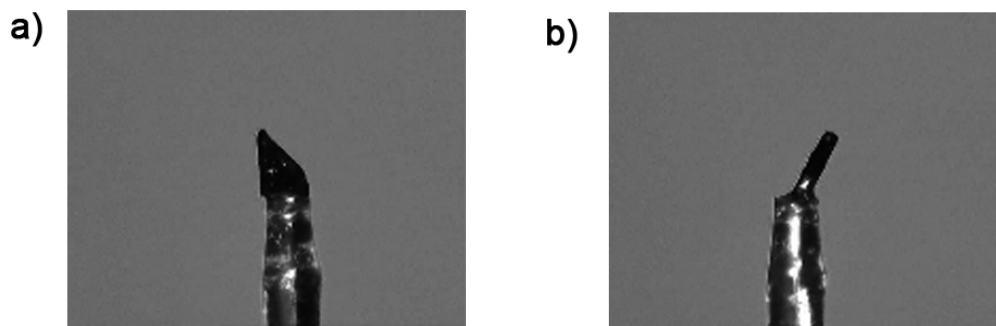


Figure 2.2.3.3.1 Images of a) top view & b) side view of **TPA-BIP** crystals.

Sheet-like single crystals of **TPA-BIP** were obtained in CH_2Cl_2 solution through slowly evaporation method. Figure 2.2.3.3.1 shows the top and side view of the crystals. Single-crystal XRD data was collected on a SuperNova CCD diffractometer at 293 K, which used graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The direct method was used to resolve the molecular structure, which was refined by full-matrix least-squares cycles in SHELX-97. The anisotropic thermal parameters were utilized to refine all of the non-hydrogen atoms. The hydrogen atoms were located at geometrically calculated positions and were not refined, which were omitted for illustration convenience.

As shown in Figure 2.2.3.3.2 a) & b), it is clear that **TPA** has a twisted conformation from both top and side view, which probably induces a bit of twist in **BIP** moiety. Demonstrated from Figure 2.2.3.3.2 c), **TPA-BIP** adopts offset 2D face-to-face stacking between neighboring molecules, but because of the twisted conformation of **TPA**, the molecules can not stack perfectly in parallel. The intermolecular distance between adjacent molecules is $3.3 \text{ \AA}$ and $3.4 \text{ \AA}$, respectively, which is shorter than that of van der Waals bond, indicating the existence of strong π - π interactions. Both the 2D face-to-face stacking and strong π - π

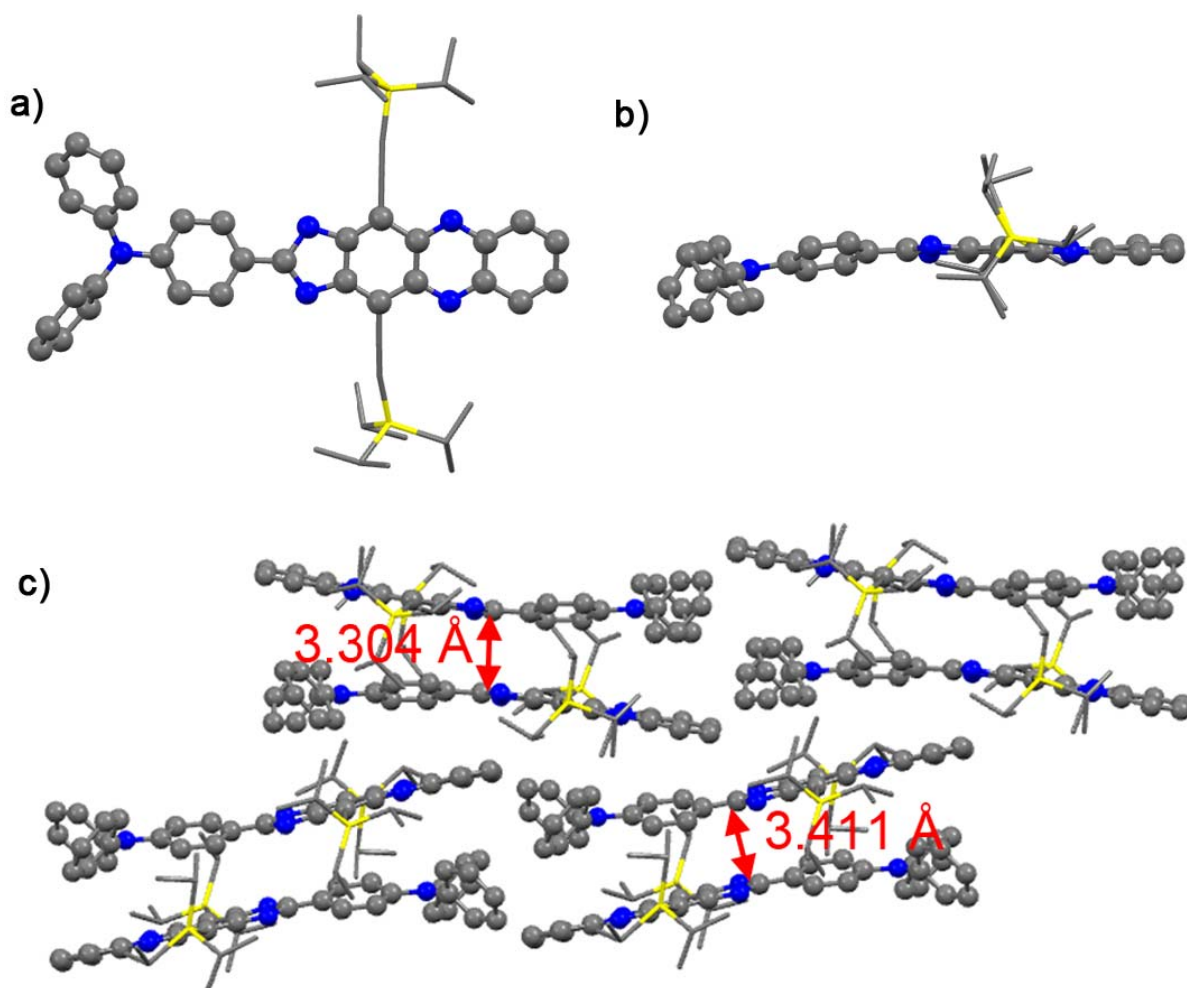


Figure 2.2.3.3.2 a) Top view and b) side view of **TPA-BIP** crystal structure. c) Molecular stacking of **TPA-BIP**.

interactions can contribute to the orderly arrangement of **TPA-BIP** in solid state, which is probable to facilitate charge carriers' transport.

2.2.3.4 Optical Properties of **TPA-BIP**

The optical properties of **TPA-BIP** were investigated through UV-vis absorption spectra, which were recorded on a Shimadzu UV-2501 spectrophotometer. Figure 2.2.3.4.1 shows the normalized UV-vis absorption spectra of **TPA-BIP** in CH₃CN (red line) and in film (blue

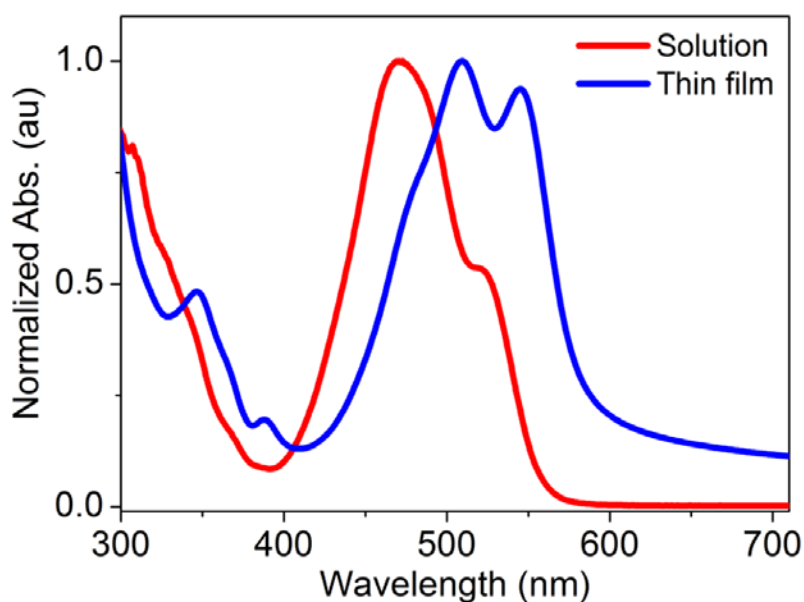


Figure 2.2.3.4.1 Normalized UV-vis absorption spectra of **TPA-BIP** in CH_3CN (red line) and in film (blue line).

line). **TPA-BIP** exhibits a broad absorption band in visible region with the maximum absorption wavelength (λ_{max}) at 467 nm in CH_3CN . The optical band gap (E_g) is determined to be 2.17 eV from the onset absorption wavelength (λ_{onset}) at 572 nm, based on the equation $E_g = hc/\lambda_{\text{onset}}$, where h is the Planck constant ($6.63 \times 10^{-34} \text{ m}^2\text{kg/s}$), c is the speed of light ($3 \times 10^8 \text{ m/s}$). The λ_{max} at 467 nm is largely red-shifted to 509 nm when **TPA-BIP** going from solution to film, and a new absorption band with λ_{max} at 545 nm appears. The λ_{onset} at 572 nm is largely red-shifted to 593 nm in film as well. All the red shifts of λ_{max} and λ_{onset} together with the appearance of new absorption band suggest the stronger molecular interaction of **TPA-BIP** in solid state.

2.2.3.5 Electrochemical Properties of TPA-BIP

The electrochemical properties of **TPA-BIP** were investigated through cyclic voltammetric (CV) curves, which were recorded on a CHI 604E Electrochemical Analyzer. Glassy carbon

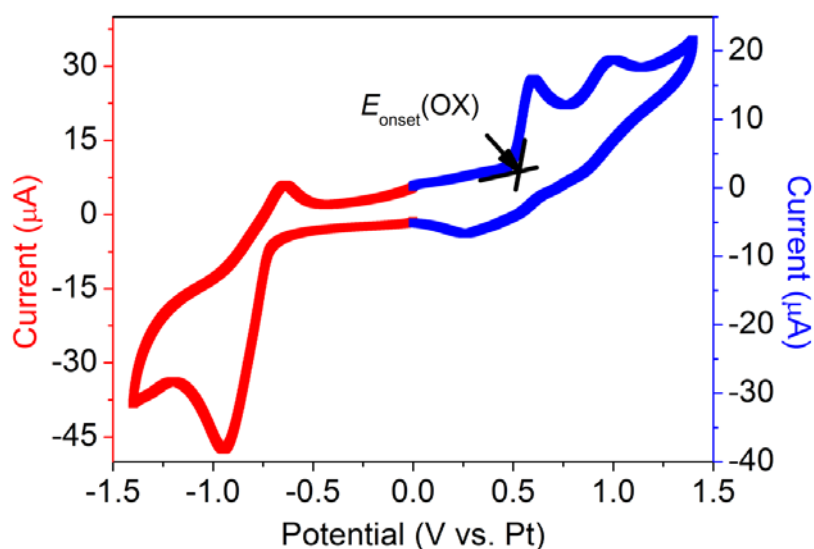


Figure 2.2.3.5.1 Cyclic voltammetric (CV) curves of **TPA-BIP** in anhydrous CH₃CN.

used as counter and reference electrodes, respectively. FeCp₂⁺/FeCp₂ was used as an external standard. The potentials were recorded in anhydrous CH₃CN solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte at a scanning rate of 50 mV s⁻¹. As shown in Figure 2.2.3.5.1, **TPA-BIP** has two irreversible oxidative peaks and a couple of less reversible reductive peaks. The onset of the first oxidative potential ($E_{\text{onset}}(\text{OX})$) is 0.28 V versus FeCp₂⁺/FeCp₂, which determines the HOMO level of **TPA-BIP** to be -5.08 eV, based on the equation: $E_{\text{HOMO}} = -(4.80 + E_{\text{onset}}(\text{OX}))$ eV, where E_{HOMO} is the HOMO level of molecule, $E_{\text{onset}}(\text{OX})$ is the onset of oxidative potential versus FeCp₂⁺/FeCp₂. While the LUMO level of **TPA-BIP** is calculated to be -2.91 eV from the difference between the HOMO level and E_g .^{17,23}

2.2.4 Memory Device Fabrication Based on TPA-BIP

The memory devices based on **TPA-BIP** were fabricated with metal/insulator/metal sandwich architecture with ITO and Pt as bottom and top electrodes, respectively. ITO glass

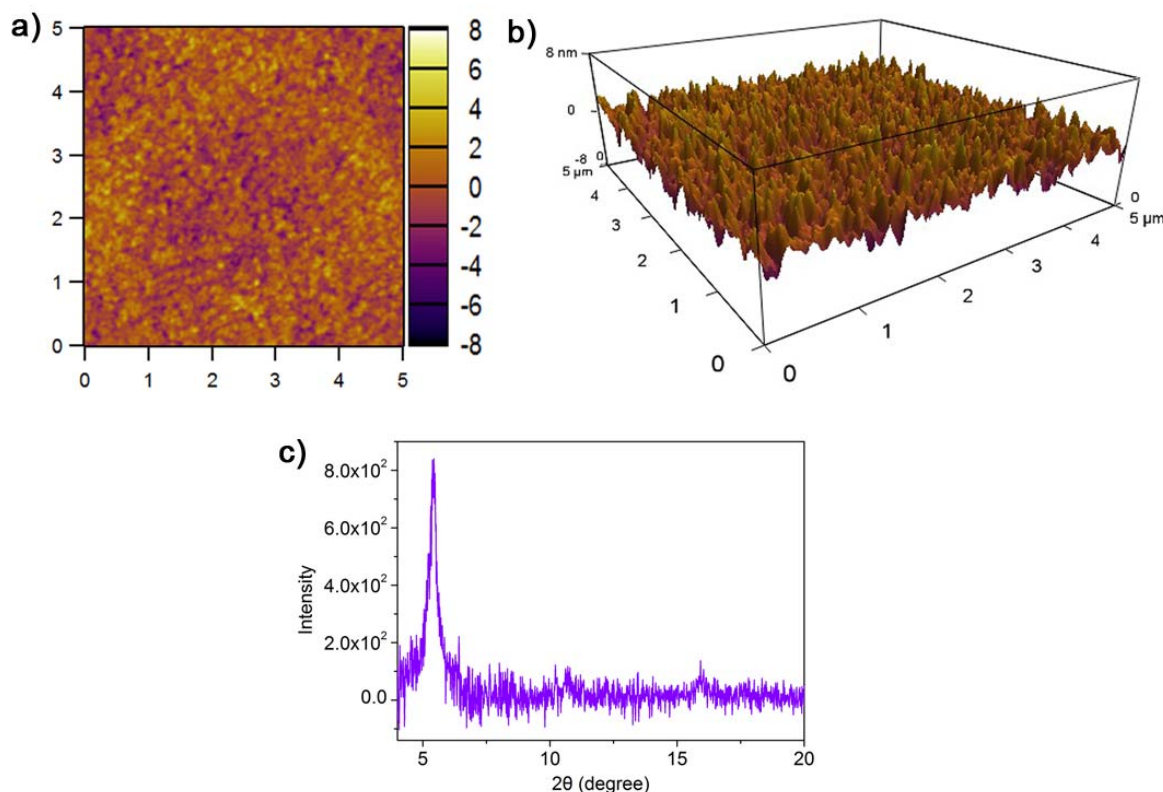


Figure 2.2.4.1 a) AFM images of a $5\ \mu\text{m} \times 5\ \mu\text{m}$ **TPA-BIP** film. b) Corresponding 3D AFM images. c) XRD patterns of the corresponding film.

substrates were cleaned by ultrasonic in ethanol, acetone and isopropanol, respectively, and dried under flowing N_2 . **TPA-BIP** was spin-coated onto pre-cleaned ITO glass substrates in a solution of cyclohexanone (10 mg/mL) and dried at $120\ ^\circ\text{C}$ on a hotplate. The thickness of **TPA-BIP** film was measured to be $\sim 120\ \text{nm}$ by an Alpha-Step IQ Surface Profiler. To avoid filamentary effect,^{24,25} Pt was sputter-coated on the top of organic layer through a shadow mask with diameter at $100\ \mu\text{m}$. Tapping-mode AFM (Asylum Research Cypher S) was carried out to investigate the morphology and microstructure of **TPA-BIP** film. Figure 2.2.4.1 a) shows the AFM height image of a $5\ \mu\text{m} \times 5\ \mu\text{m}$ **TPA-BIP** film. The film is crystalline with clear grain boundaries. The root-mean-square roughness (RMS) of **TPA-BIP**

film is 1.298 nm. Figure 2.2.4.1 b) shows the corresponding 3D AFM height image. The film rolls up and down within the range of -10 to 10 nm, suggesting the film is well continuous. The XRD patterns of the corresponding film was recorded on D8/max2500 with Cu Ka source ($\kappa = 1.541 \text{ \AA}$). As shown in Figure 2.2.4.1 c), a diffracton peak at 5.4° can be observed with intensity $\sim 8 \times 10^2$, corresponding to the AFM images.

2.2.5 Memory Characteristics of TPA-BIP

The memory characteristics of the ITO/**TPA-BIP**/Pt devices were demonstrated by current-voltage (I - V) curves, which were measured in ambient conditions using Keithley 4200 semiconductor characterization system in the voltage sweeping model. As shown in Figure 2.2.5.1 a), in the low sweeping voltage of “Sweep 1”, the ITO/**TPA-BIP**/Pt device retains at high resistance state (HRs). An instantaneously increase of current can be observed when the voltage reaches threshold voltage (V_{TH}), as a result, the new low resistance state (LRs) is achieved. The transform of the device from HRs to LRs can define the process as a “SET” action. After removing power supply or applying a dual sweep “Sweep 2” the device can maintain the LRs. Thus, the ITO/**TPA-BIP**/Pt device is a typical non-volatile memory. In the following negative sweep “Sweep 3”, the recovery of device from LRs to HRs can be observed, and the process is served as “RESET” action. In the dual negative sweep “Sweep 4” the device maintains the HRs. Based on the I - V curves illustrated above, the ITO/**TPA-BIP**/Pt device can be regarded as a two-state rewritable non-volatile memory. The ON/OFF ratio of the device is achieved to be 10^3 when read at 0.2 V, indicating the device will have much less misreading possibility in practical applications.

The endurance performance of ITO/**TPA-BIP**/Pt devices was investigated by the typical

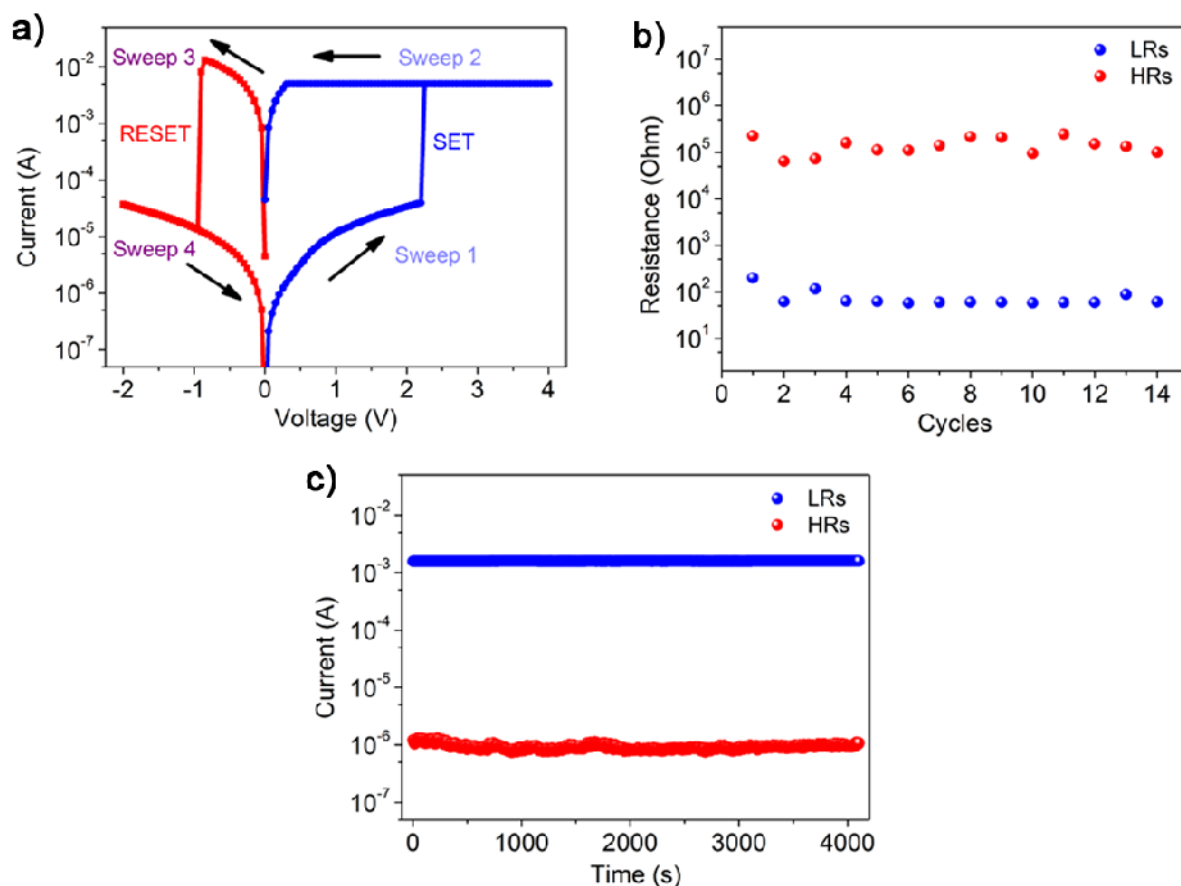


Figure 2.2.5.1 a) I - V curves of ITO/TPA-BIP/Pt device. b) Resistance distribution of 14 cycles. c) Retention performance of ITO/TPA-BIP/Pt device.

“SET”-“RESET” cyclic switching operations. Generally, the devices were able to be repeatedly switched between HRs and LR for more than 14 cycles. Figure 2.2.5.1 b) shows the corresponding resistances distribution of 14 cycles when the device is read at 0.2 V. The average ON/OFF ratio of the resistance magnitude between the HRs and the LR is about 10^3 , which is corresponding to that deduced from I - V curves. The resistances of HRs and LR are well distributed in a narrow range. The average V_{TH} of “SET” or “RESET” processes for the 14 cycles is 2.60 V or -1.45 V, respectively. The orderly stacking of TPA-BIP molecules in film possibly contributes to the good endurance performance.

The retention performance of the device was evaluated by applying a reading voltage of -0.2 V to either LR or HR in ambient conditions. As shown in Figure 2.2.5.1 c), there is no obvious current degradation for each state can be observed in 4000 s during the test. Based on the retention evaluation, **TPA-BIP** has the potential to be used as a kind of stable memory material.

2.2.6 Mechanism Discussion

Molecular calculation was conducted using the density functional theory (DFT) calculations (B3LYP/6-31G*) in *Gaussian 09* to describe the switching mechanism and the generated charge carriers' migration process of ITO/**TPA-BIP**/Pt devices.^{26,27} As shown in Figure 2.2.6.1, the LUMO coefficient of **TPA-BIP** is mainly located at the **BIP** moiety, while the HOMO coefficient is distributed on the whole molecule. The difference between the HOMO level of **TPA-BIP** and the working function of ITO (-4.8 eV) is 0.12 eV, which determines the holes injection energy barrier. However, the electrons injection energy barrier is established to be 2.74 eV based on the difference between the LUMO level of **TPA-BIP** and the working function of Pt (-5.6 eV). Therefore, holes injection is dominated for the charge carriers' migration.

One possibility to inducing the memory behavior of **TPA-BIP** is the filling of electron "traps". Electrostatic potential (ESP) calculation of **TPA-BIP** was carried out with same calculation method. As shown in Figure 2.2.6.2, the surface of **TPA-BIP** has continuous positive ESP (in blue) with certain negative regions (in red), corresponding to imidazole and pyrazine units, respectively, which serve as electron "traps" to block the mobility of charge carriers. It is because of the electron "traps" and the energy barrier between molecules and

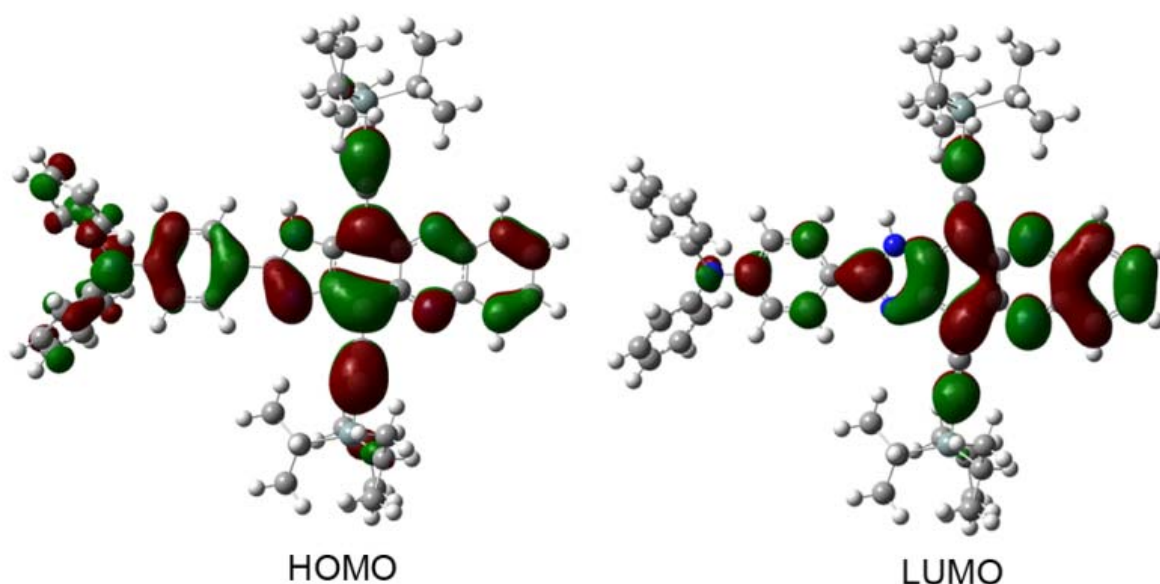


Figure 2.2.6.1 Electron density distribution of HOMO & LUMO levels of **TPA-BIP**.

electrodes that the conductivity of ITO/**TPA-BIP**/Pt devices is low in HRs. As the voltage approaches to threshold value, the electrons “traps” will be filled so that electrons can exceed the energy barrier. In this situation charge separation occurs and free charge carriers are generated. As a result, the devices are set to LR and the molecular surface of **TPA-BIP** becomes continuous positive. It is noteworthy that the multiple electron “traps” can be possibly filled in same time, thus the devices display only two-state memory behavior. The corresponding non-volatile memory behaviour may come from the few release of charge carriers.^{28,29} This mechanism has been well illustrated in azo-benzene based D-A molecules by Lu’s group. Intermolecular charge transfer can also possibly induce the memory behavior of **TPA-BIP**. Charge transfer complexes can be formed as charge carriers, in which situation electrons migrates from the HOMO level of one molecule to the LUMO level of another molecule. The as formed charge transfer complex can be stable without the existence of electronic field, leading to non-volatile memory behavior.⁸ Kang’s group has used this type of mechanism to explain the memory behavior for polyimide based D-A polymers.

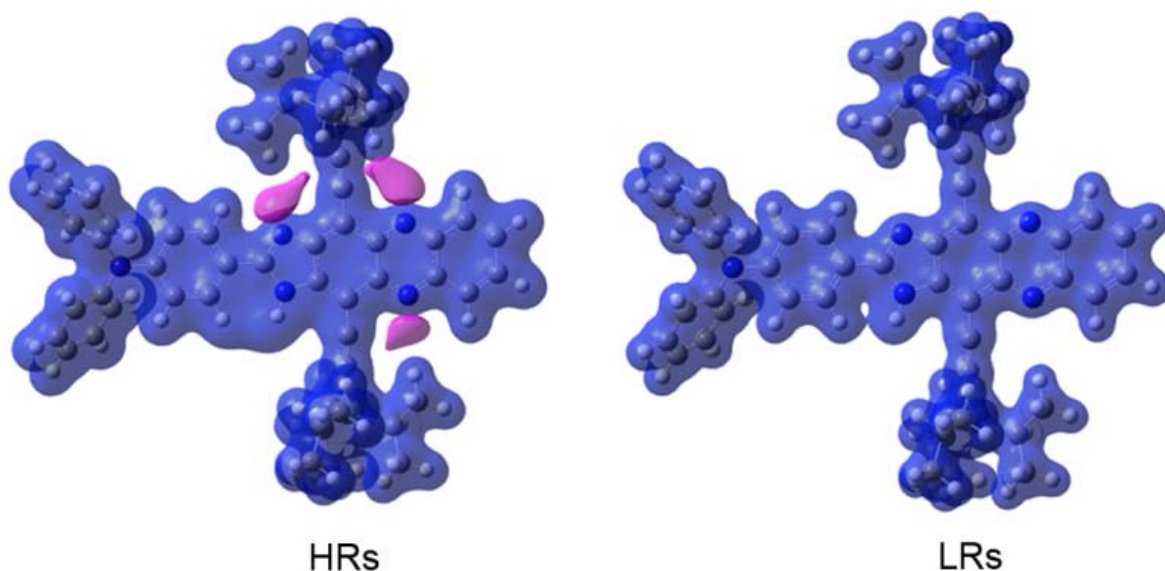


Figure 2.2.6.2 Electrostatic potential (ESP) calculation of **TPA-BIP** in HRs & LRs.

2.2.7 Summary

In summary, a novel D-A molecule **TPA-BIP** with *N*-heteroacenes as acceptor has been successfully synthesized and characterized. The ORM devices based on **TPA-BIP** exhibits two-state rewritable non-volatile memory behavior with high ON/OFF ratio up to 10^3 and good retention performance for each state. The results suggest that the D-A molecule with *N*-heteroacenes as acceptor moiety can be potentially applied as rewritable non-volatile memory materials. Although we have introduced multiple *N*-heteroacene units to act as multiple electron “traps”, multilevel memory behaviors can not be observed, which may be because that the different “traps” are filled at same time or the switching behavior is induced by intermolecular charge transfer.

2.3 D-A Molecules with Multiple Acceptor Moieties

2.3.1 Molecular Design

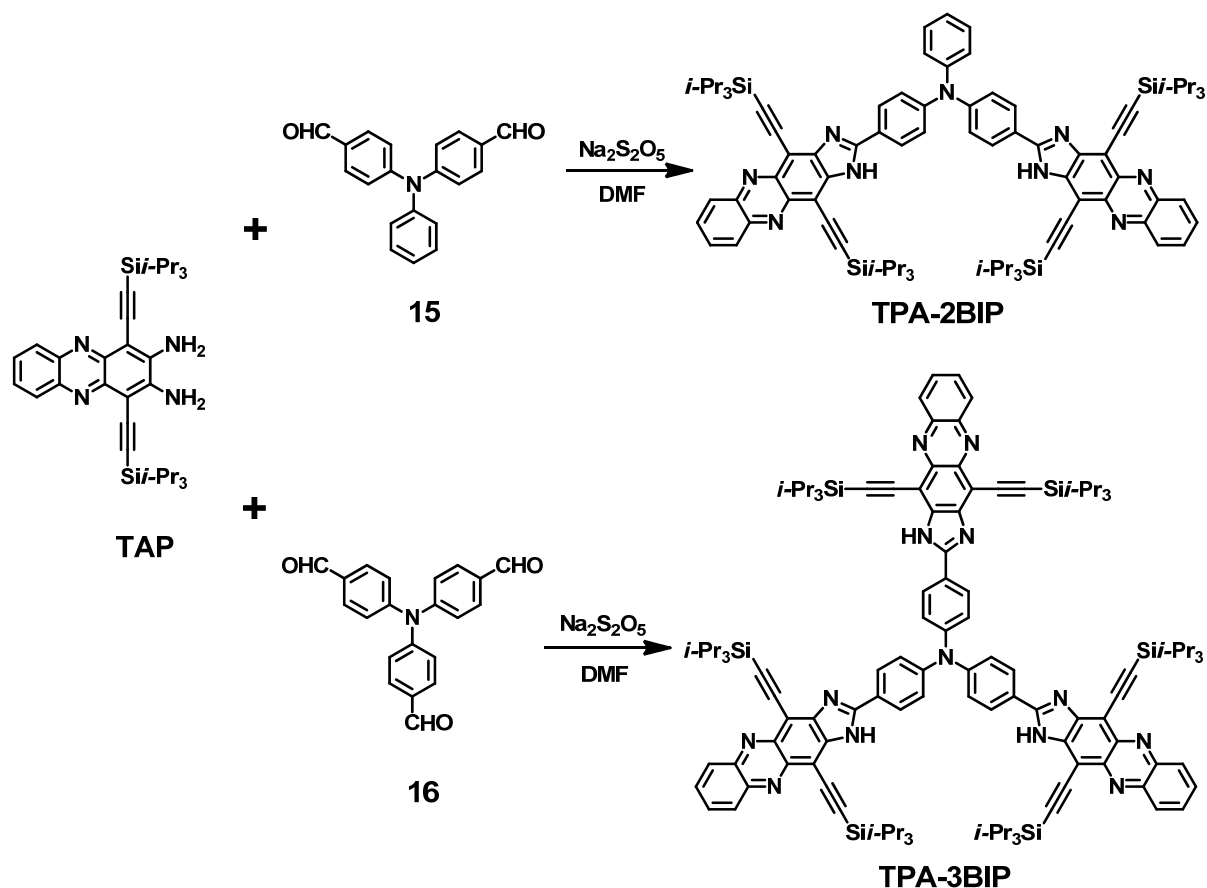
In the previous work, **BIP** has been demonstrated to be a useful acceptor moiety, which can be utilized to develop rewritable non-volatile memory materials. However, it fails that developing multilevel memories by introducing multiple electron “traps” with different *N*-heteroacene units. Considering these factors, increasing more acceptor moieties is proposed. In this part, we would like to investigate the possibility of obtaining multilevel memory materials through increasing more **BIP** units on a single **TPA**. Here, two molecules 4,4'-di(4,11-bis((triisopropylsilyl)ethynyl)-1*H*-imidazo[4,5-*b*]phenazin)triphenylamine (**TPA-2BIP**) containing a single **TPA** and two **BIP** moieties, and tris(4-(4,11-bis((triisopropylsilyl)ethynyl)-1*H*-imidazo[4,5-*b*]phenazin)phenyl)amine (**TPA-3BIP**) combining a single **TPA** and three **BIP** moieties are designed.

2.3.2 Synthesis of TPA-2BIP & TPA-3BIP

The synthesis of **TAP** has been illustrated in 2.2.2 Synthesis of TPA-BIP. 4,4'-diformyltriphenylamine **15** and tris(4-formylphenyl)amine **16** were synthesized from **TPA** and phosphorus oxychloride based on a literature reported procedure.³⁰ The synthetic route for **TPA-2BIP** and **TPA-3BIP** is illustrated in Scheme 2.3.2.1.

Synthesis of TPA-2BIP

In a round bottom flask, **TAP** (580 mg, 1.016 mmol), compound **15** (146 mg, 0.485 mmol) were well dissolved in *N,N*-dimethylformamide (DMF, 25 mL). Sodium metabisulfite (207 mg, 1.089 mmol) was added and the system was heated at 120 °C for 12 hours. The mixture



Scheme 2.3.2.1 Synthetic route for **TPA-2BIP** and **TPA-3BIP**.

was poured into iced water (100 mL) after it was cooled down to room temperature. After filtration, the solid residue was obtained as crude product, which was further purified by flash column chromatography with EtOAc and hexane (EtOAc: hexane = 1: 20) over silica gel, and finally the pure **TPA-2BIP** (97 mg) was obtained as dark red powder in yield of 6.9%.

Synthesis of **TPA-3BIP**

TPA-3BIP (73 mg) was prepared in same procedure illustrated above, with **TAP** (594 mg, 1.041 mmol), compound **16** (103 mg, 0.313 mmol) and sodium metabisulfite (216 mg, 1.139 mmol), as dark red powder in yield of 3.7%.

2.3.3 Molecular Characterization

The novel **TPA-2BIP** & **TPA-3BIP** have been characterized by HR MS and NMR.

2.3.3.1 HR MS Analysis

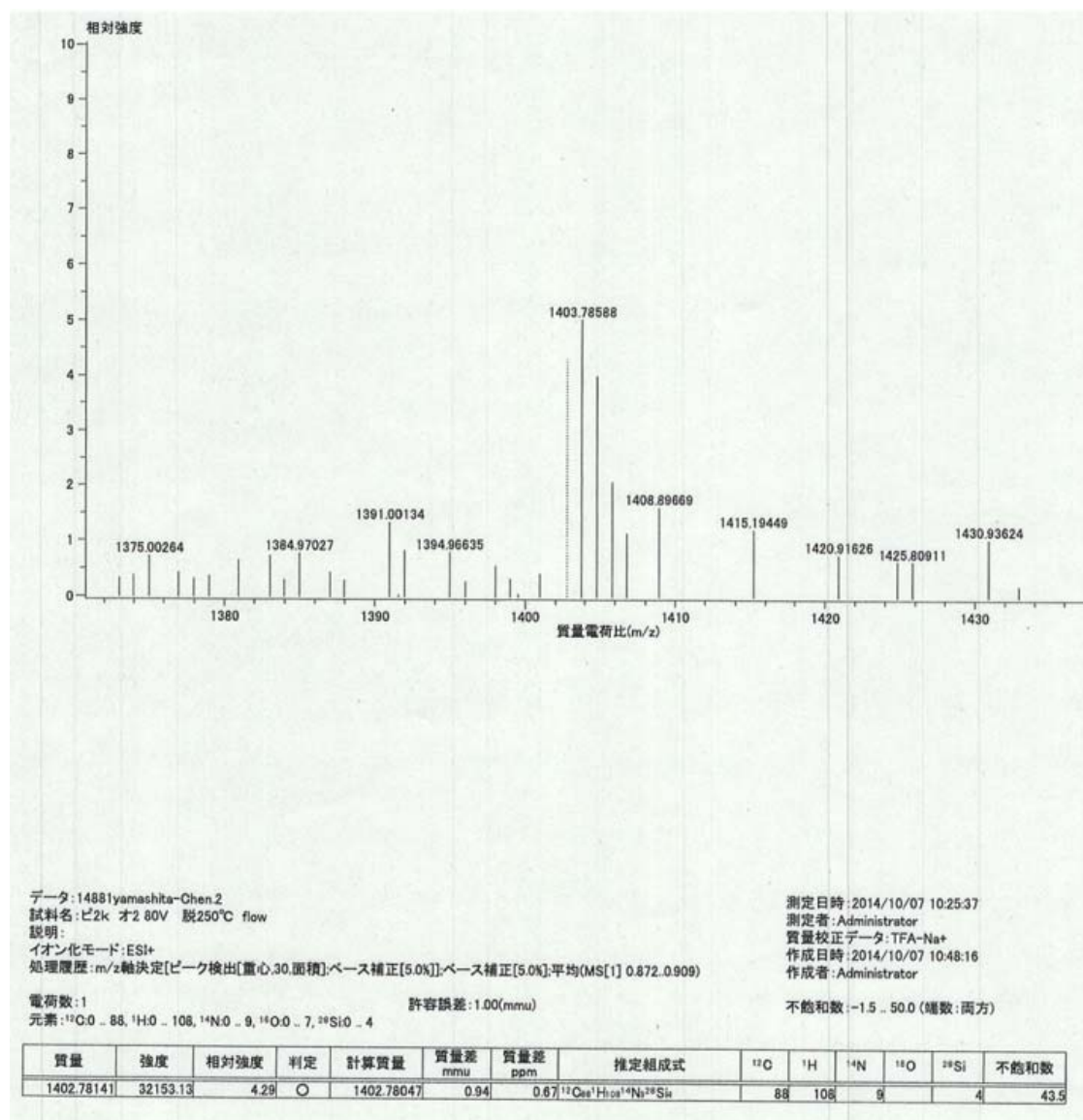


Figure 2.3.3.1.1 HR MS (ESI) spectra of **TPA-2BIP**.

The HR MS (ESI) spectra of **TPA-2BIP** were collected on a JEOL spiral TOF JMS-S3000 spectrometer.

The chemical formula of **TPA-2BIP** is $C_{88}H_{107}N_9Si_4$. As shown in Figure 2.3.3.1.1, the calculated m/z value of $[M+1]^+$ for **TPA-2BIP** is 1402.7727, and the actual m/z value of that found in spectra is 1402.7804, which is well consistent with the calculated result.

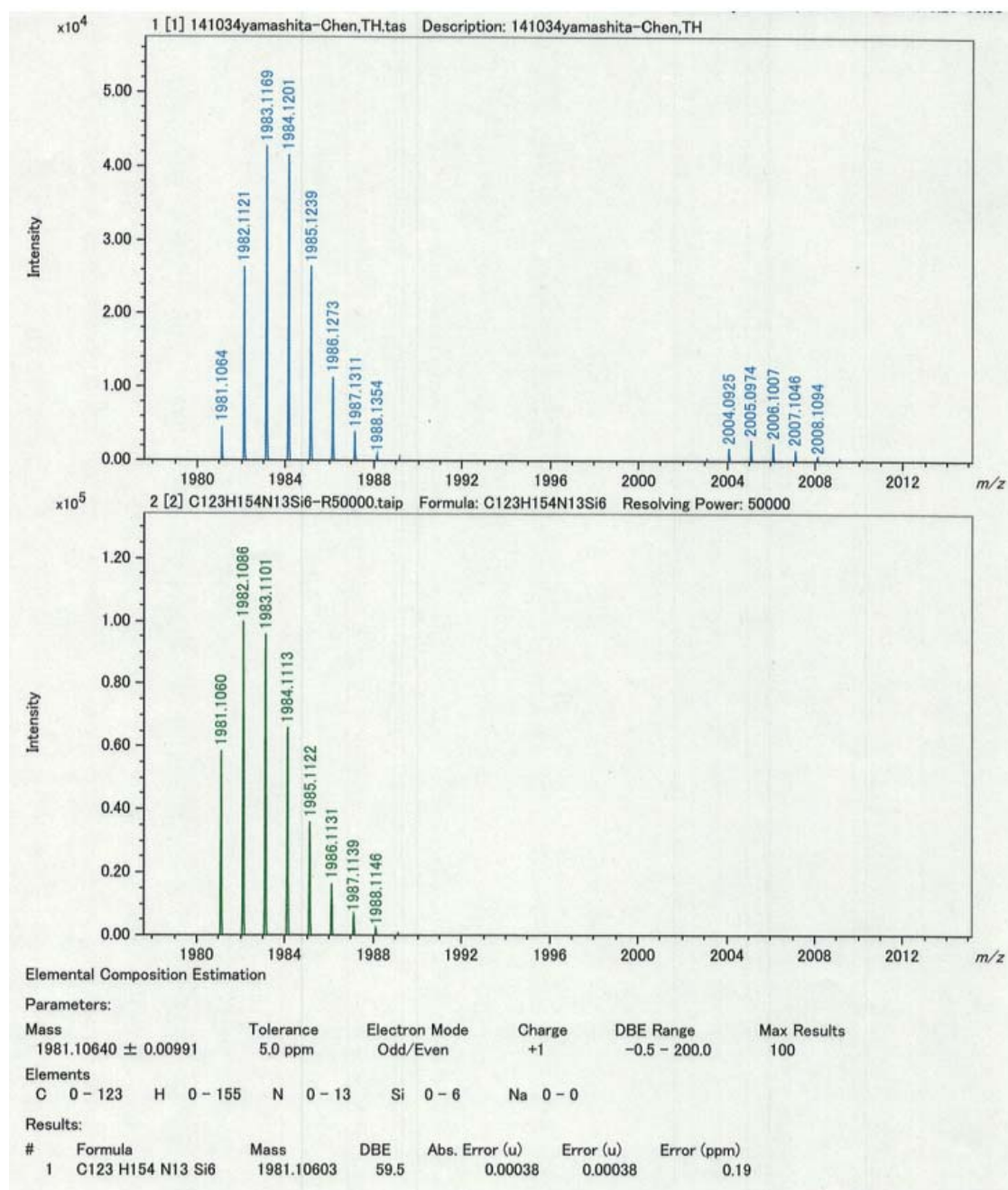


Figure 2.3.3.1.2 HR MS (MOLDI-TOF) spectra of **TPA-3BIP**.

The HR MS (MOLDI-TOF) spectra of **TPA-3BIP** were collected on the same machine with **TPA-2BIP**.

The chemical formula of **TPA-3BIP** is $C_{123}H_{154}N_{13}Si_6$. As shown in Figure 2.3.3.1.2, the calculated m/z value for **TPA-3BIP** is 1981.1021, and the actual m/z value found in spectra is 1981.1060, which is well consistent with the calculated result.

2.3.3.2 NMR Analysis

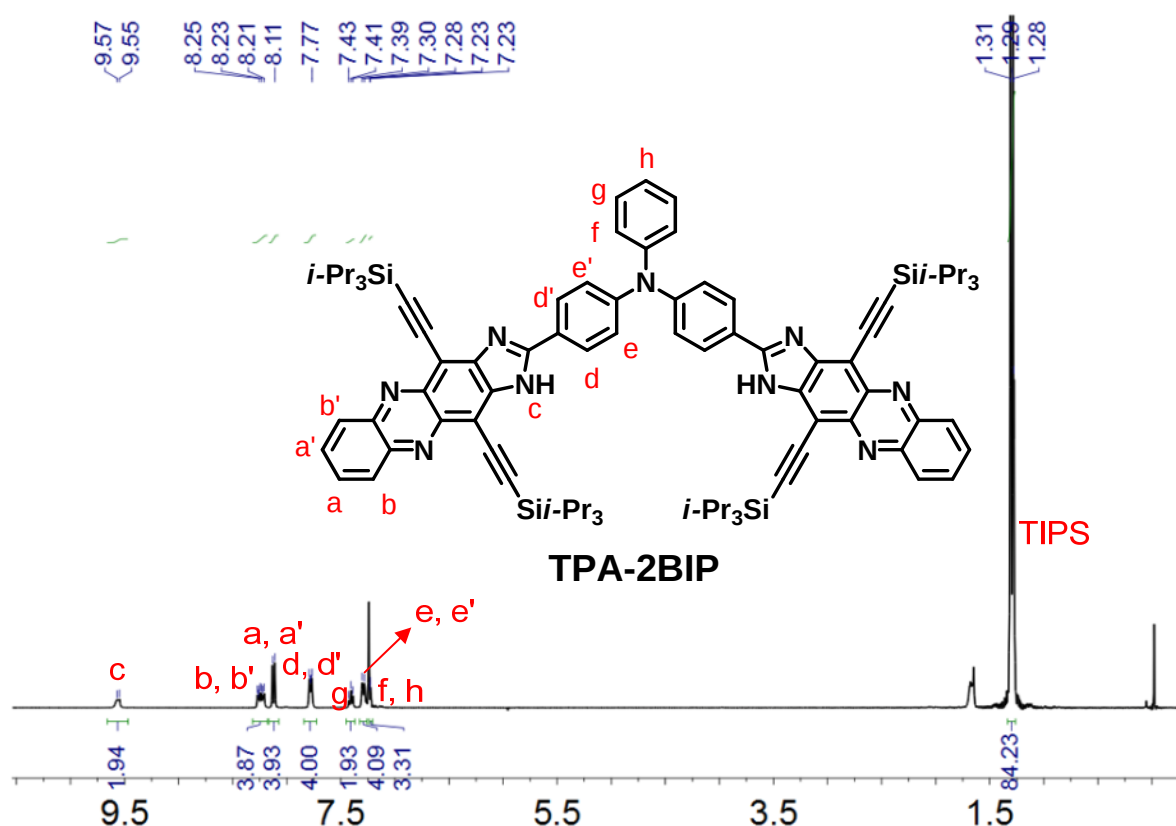


Figure 2.3.3.2.1 ^1H NMR spectra of **TPA-2BIP** in $CDCl_3$.

^1H NMR and ^{13}C NMR spectra of **TPA-2BIP** and **TPA-3BIP** were recorded on a Bruker 400-MHz spectrometer in $CDCl_3$.

Figure 2.3.3.2.1 shows the ^1H NMR spectra of **TPA-2BIP** in CDCl_3 , the protons can indexed as ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 1.28$ (42H), 1.32 (42H), 7.22~7.24 (3H), 7.27~7.31 (4H), 7.38~7.44 (2H), 7.75~7.80 (4H), 8.10~8.14 (4H), 8.20~8.28 (4H), 9.54~9.58 (2H), which are well consistent with its molecular structure.

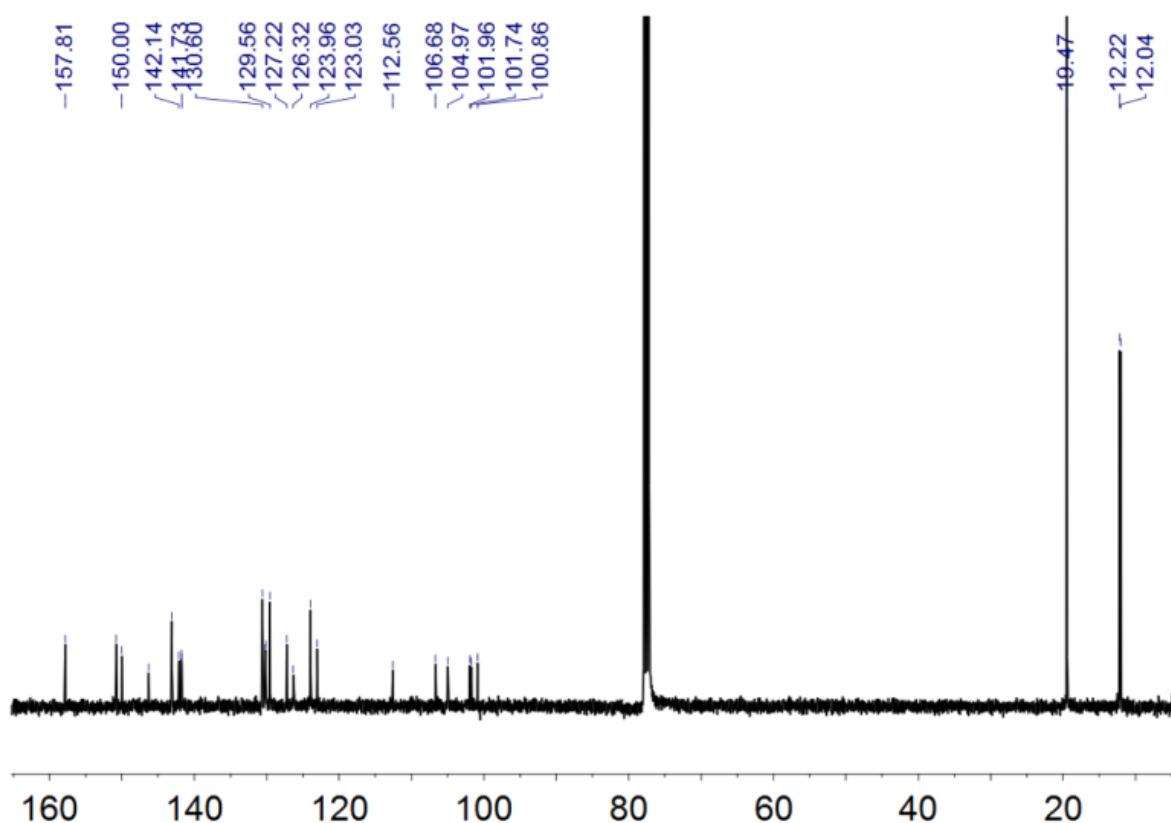


Figure 2.3.3.2.2 ^{13}C NMR spectra of **TPA-2BIP** in CDCl_3 .

Figure 2.3.3.2.2 shows the ^{13}C NMR spectra of **TPA-2BIP** in CDCl_3 . The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 157.81$, 150.76, 150.00, 146.31, 143.10, 142.14, 141.79, 141.73, 130.60, 130.22, 130.13, 129.56, 127.22, 126.32, 123.96, 123.03, 112.56, 106.68, 104.97, 101.96, 101.74, 100.86, 19.47, 12.22, 12.04. The carbons located at 12.04, 12.22 and 19.47 are corresponded to the two types of **TIPS** groups. There are only 22 carbons can be observed in range of 100–160 ppm, which is 5 carbons less than theoretical

value. Maybe certain carbons of **TPA-2BIP** have no signals in ^{13}C NMR spectra in our experimental conditions.

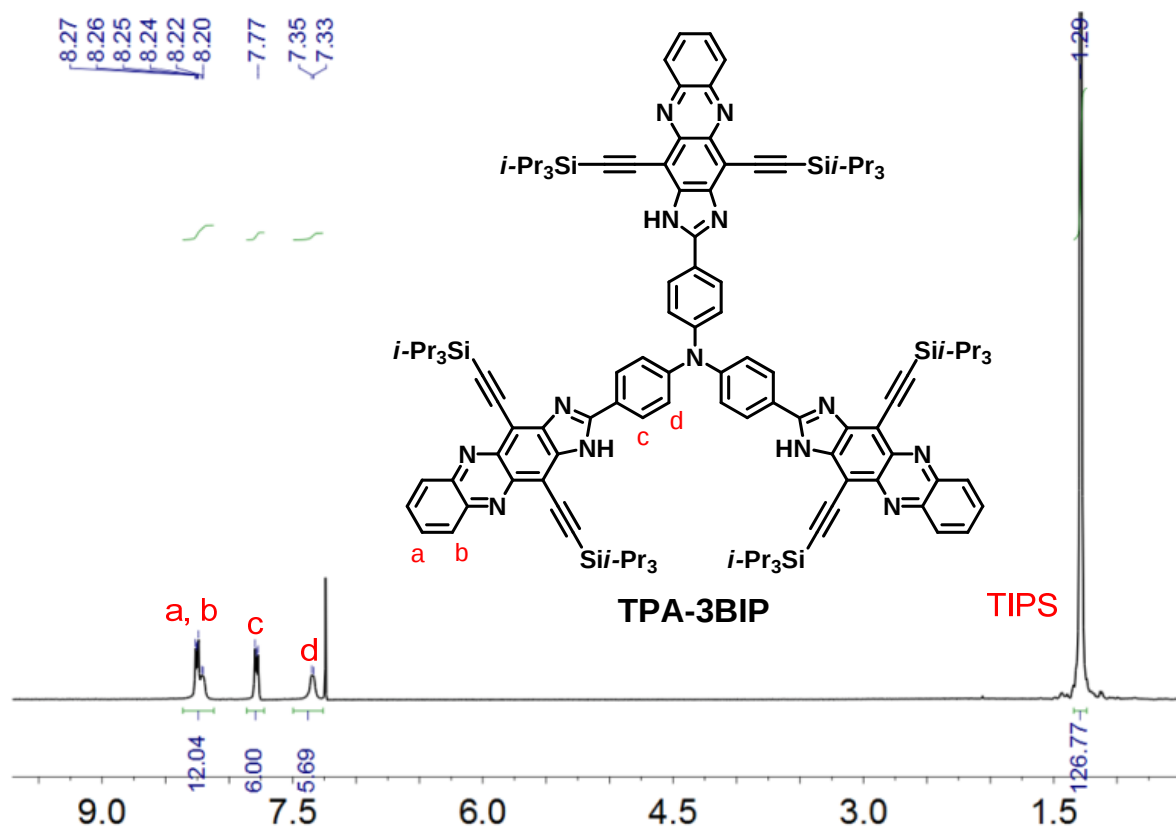


Figure 2.3.3.2.3 ^1H NMR spectra of **TPA-3BIP** in CDCl_3 .

Figure 2.3.3.2.3 shows the ^1H NMR spectra of **TPA-3BIP** in CDCl_3 , the protons can be indexed as ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 1.28\sim 1.30$ (126H), $7.34\sim 7.36$ (6H), $7.76\sim 7.81$ (6H), $8.18\sim 8.28$ (12H), which are well consistent with its molecular structure.

Figure 2.3.3.2.4 shows the ^{13}C NMR spectra of **TPA-3BIP** in CDCl_3 . The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 156.96, 149.25, 142.53, 141.30, 129.91, 129.71, 129.30, 124.76, 123.94, 105.56, 100.65, 18.84, 11.50$. The carbons located at 11.50 and 18.84 are corresponded to the **TIPS** group, only 11 carbons can be observed in range of

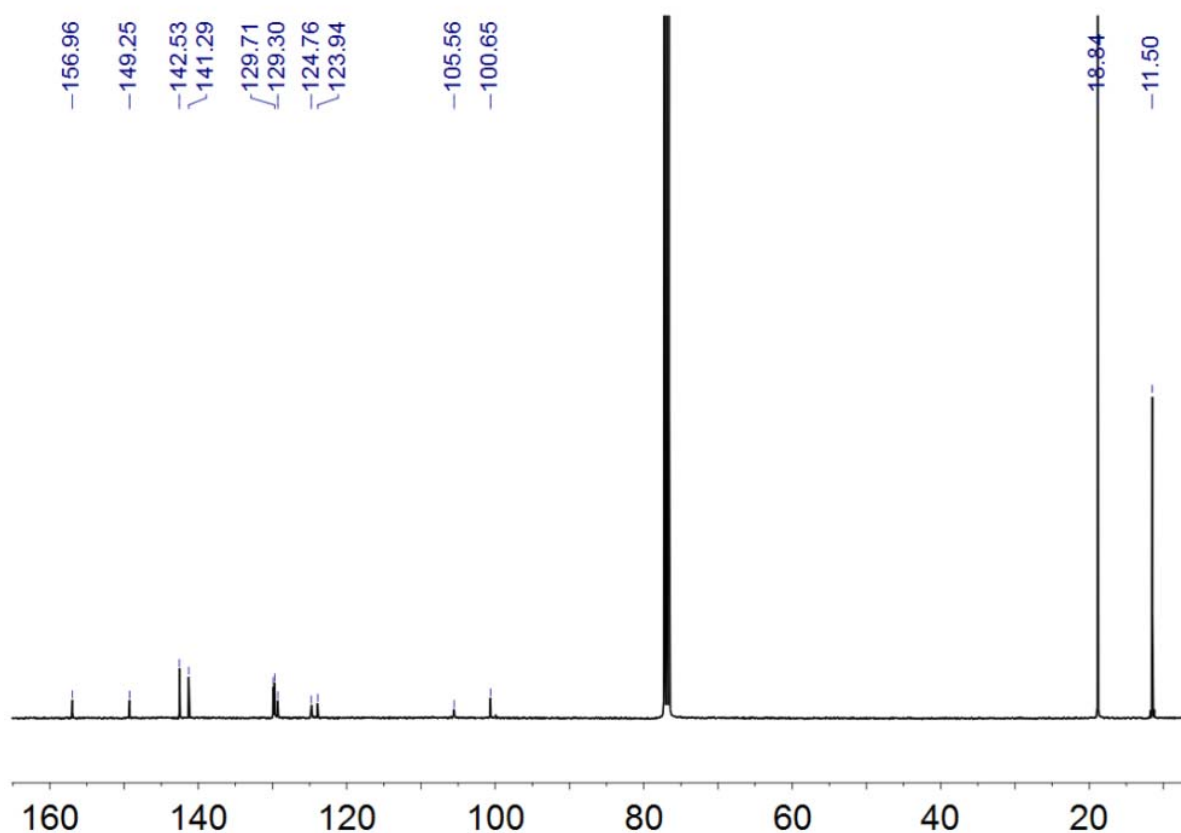


Figure 2.3.3.2.4 ^{13}C NMR spectra of **TPA-3BIP** in CDCl_3 .

100–160 ppm, which is 2 carbons less than theoretical value. Maybe certain carbons of **TPA-3BIP** have no signals in ^{13}C NMR spectra in our experimental conditions.

2.3.3.3 Optical Properties of **TPA-2BIP** & **TPA-3BIP**

The optical properties of **TPA-2BIP** and **TPA-3BIP** were investigated through UV-vis absorption spectra, which were recorded on a Shimadzu UV-2501 spectrophotometer. Figure 2.3.3.3.1 a) & b) show the normalized UV-vis absorption spectra of **TPA-2BIP** and **TPA-3BIP** in CH_2Cl_2 (red line) and in film (blue line). **TPA-2BIP** has a broad absorption band with the maximum absorption wavelength (λ_{max}) at 491 nm in CH_2Cl_2 . Similarly, **TPA-3BIP** also has a broad absorption band with λ_{max} at 481 nm in CH_2Cl_2 . The onset absorption

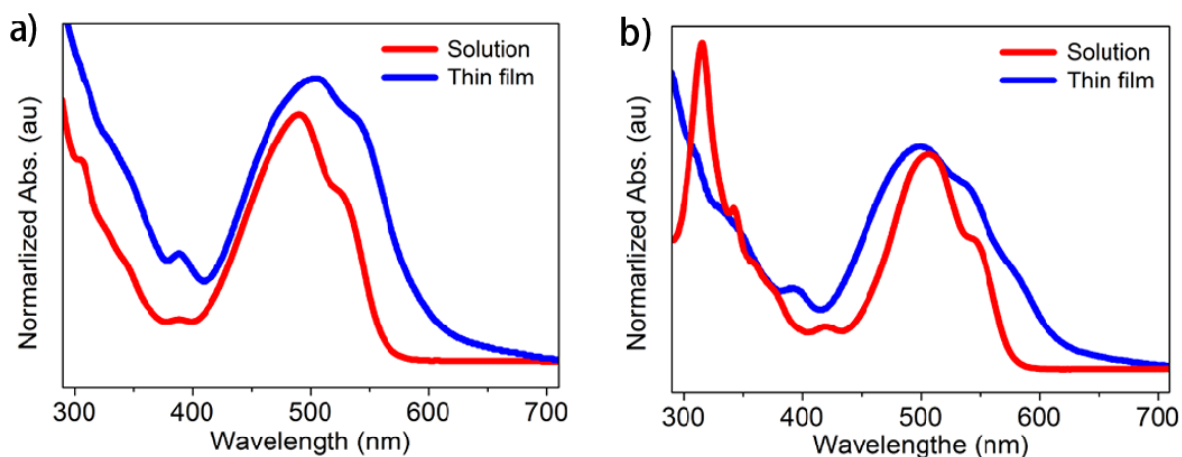


Figure 2.3.3.3.1 Normalized UV-vis absorption spectra of a) **TPA-2BIP** (red line: in solution, blue line: in film) & b) **TPA-3BIP** (red line: in solution, blue line: in film).

wavelength of **TPA-2BIP** (λ_{onset}) is 563 nm, and the optical band gap (E_g) is determined to be 2.20 eV through the same equation illustrated in **2.2.3.4 Optical Properties of TPA-BIP**. The E_g for **TPA-3BIP** is established to be 2.22 eV from the λ_{onset} at 558 nm. Compared with **TPA-2BIP**, both the λ_{max} and λ_{onset} of **TPA-3BIP** in solution are blue-shifted, suggesting that the energy gap of intramolecular electrons transition is enlarged as more acceptor moieties introduced in molecules. The λ_{onset} of **TPA-2BIP** is red-shifted to 601 nm in film, and that of **TPA-3BIP** is red-shifted to 617 nm, indicating that strong π - π stacking of molecules exists in solid state. The red-shift of **TPA-3BIP** in film is 16 nm larger than that of **TPA-2BIP**, suggesting that it may have stronger interaction between neighbouring molecules in solid state.

2.3.3.4 Electrochemical Properties of TPA-BIP & TPA-3BIP

The electrochemical properties of **TPA-2BIP** and **TPA-3BIP** were investigated through cyclic voltammetric (CV) curves, which were carried out in anhydrous CH_2Cl_2 with the same

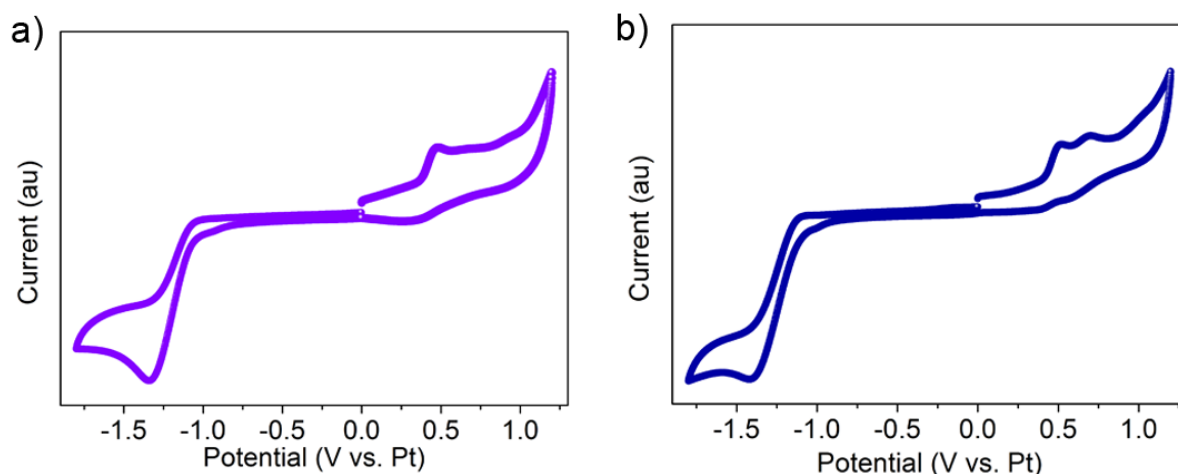


Figure 2.3.3.4.1 Cyclic voltammetric (CV) curves of a) **TPA-2BIP** & b) **TPA-3BIP** in anhydrous CH_2Cl_2 .

method of **TPA-BIP** illustrated in 2.2.3.5 Electrochemical Properties of TPA-BIP. As shown in Figure 2.3.3.4.1 a), **TPA-2BIP** displays one irreversible oxidative peak and one irreversible reductive peak. The onset of the oxidative potential ($E_{\text{onset}}(\text{OX})$) is 0.40 V versus $\text{FeCp}_2^+/\text{FeCp}_2$, and the HOMO level of **TPA-2BIP** is determined to be -4.94 eV, which is calculated with the equation illustrated in 2.2.3.5 Electrochemical Properties of TPA-BIP. The LUMO level is established to be -2.74 eV from the difference between HOMO level and E_g . **TPA-3BIP** (Figure 2.3.3.4.1 b)) also exhibits one irreversible reductive peak, however, there are two irreversible oxidative peaks can be observed. The potential versus $\text{FeCp}_2^+/\text{FeCp}_2$ of the first oxidative peak is 0.44 V, and with the same calculation method of **TPA-2BIP**, the HOMO and LUMO levels are determined to be -4.98 eV and -2.76 eV, respectively. Based on the CV curves and above analysis, there is no clear effect on the reductive behavior of molecules when more acceptor moieties are attached, and it can be further confirmed with the fact that **TPA-2BIP** and **TPA-3BIP** own close LUMO levels. Increasing the acceptor moieties might have minor influence on the oxidative properties of

molecule, because a minor up-shift of $E_{onset}(OX)$ of **TPA-3BIP** can be observed. Probably the increase of acceptor moieties can cause the dispersing of electrons distribution, which makes the electron-donating ability of donor unit weaker.

2.3.4 Memory Device Fabrication Based on TPA-2BIP & TPA-3BIP

The memory devices based on **TPA-2BIP** and **TPA-3BIP** were fabricated in the same procedure with **TPA-BIP** illustrated in 2.2.4 Memory Device Fabrication Based on TPA-BIP, the only difference was that the top electrode was changed from Pt to Au considering its higher working function. The thickness of **TPA-2BIP** and **TPA-3BIP** films was measured to be ~60 nm by an Alpha-Step IQ Surface Profiler.

The morphology and microstructure of **TPA-2BIP** and **TPA-3BIP** films were investigated by tapping-mode AFM (Park Systems Co.). Figure 2.3.4.1 a) and c) show the corresponding height images of AFM. The high crystalline of films with clear grain boundaries can be observed for both **TPA-2BIP** and **TPA-3BIP**, however, the film of **TPA-3BIP** has the smaller grain size than that of **TPA-2BIP**. The films for the two molecules are well smooth with the root-mean-square roughness (RMS) at 1.496 nm for **TPA-2BIP** and 1.127 nm for **TPA-3BIP**, respectively. The relatively smaller grain size and smoother surface of **TPA-3BIP** film suggests that the stacking of molecules in solid state has been changed as the acceptor moieties are increased to their backbone, which can possibly enhance the contact between electrodes and organic films. Figure 2.3.4.1 b) & d) show the corresponding 3D height images of AFM. The film of **TPA-2BIP** rolls up and down within the range of -4 to 8 nm, and that of **TPA-3BIP** is -4 to 4 nm, suggesting both the films are well continuous. The XRD patterns of the films of **TPA-2BIP** and **TPA-3BIP** were investigated in same method

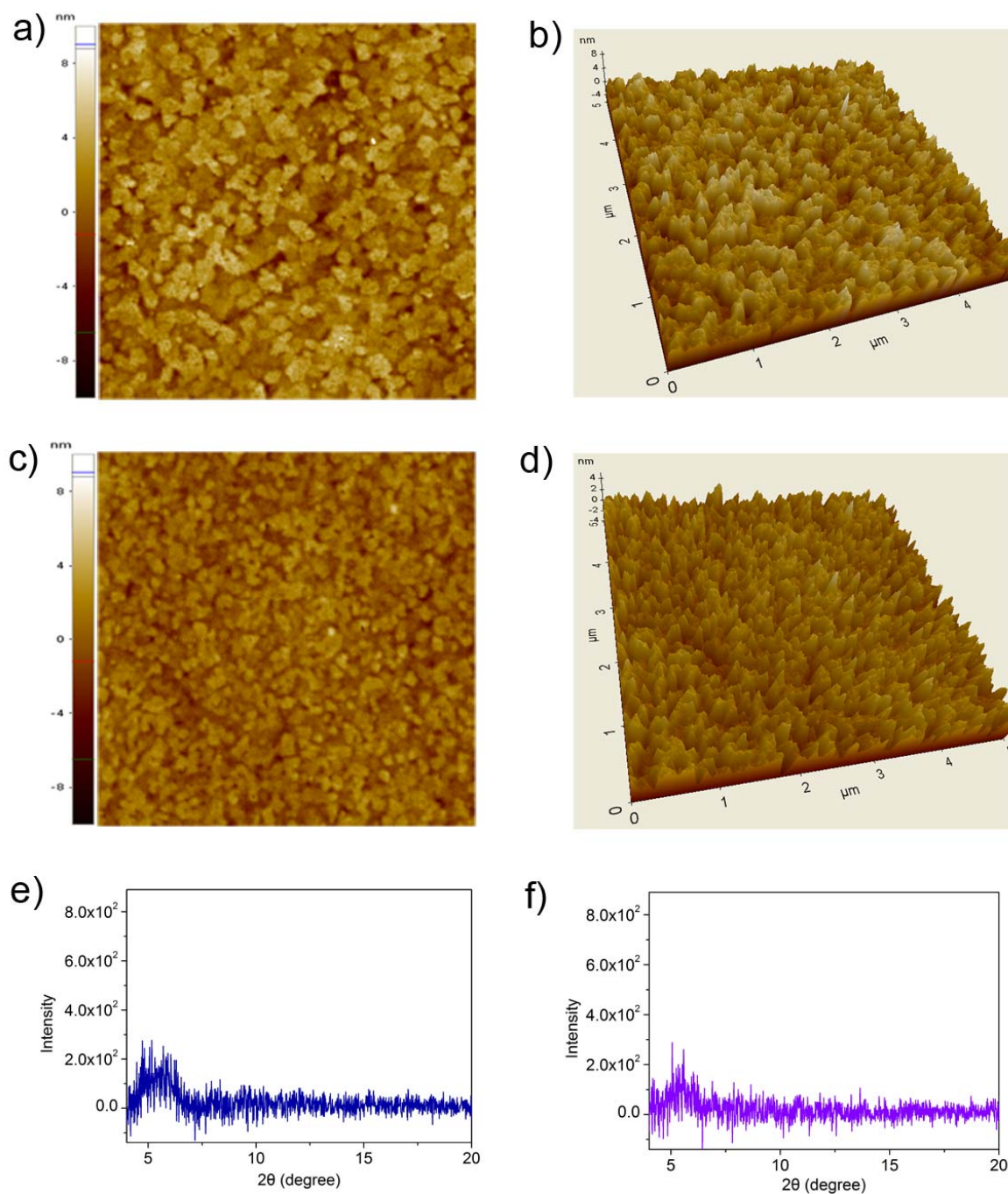


Figure 2.3.4.1 a) & c) AFM images of $5\ \mu\text{m} \times 5\ \mu\text{m}$ the films of **TPA-2BIP** & **TPA-3BIP**, respectively. b) & d) 3D AFM images of the corresponding films, respectively. e) & f) XRD patterns of the films of **TPA-2BIP** & **TPA-3BIP**, respectively.

with **TPA-BIP**. As shown in Figure 2.3.4.1 e) & f), however, there are only broad diffraction

peaks in range of 4° – 7° with low intensity that can be observed. The films might be too thin for XRD diffraction measurement.

2.3.5 Memory Characteristics of TPA-2BIP & TPA-3BIP

The memory properties of ITO/TPA-2BIP/Au and ITO/TPA-3BIP/Au devices were characterised by current-voltage (I - V) curves, which were performed under the same conditions with that of TPA-BIP illustrated in 2.2.5 Memory Characteristics of TPA-BIP. As shown in Figure 2.3.5.1 a) ITO/TPA-2BIP/Au device. The current of ITO/TPA-2BIP/Au device maintains in low magnitude range under low sweeping voltage in the first positive sweep, whose state can be defined as high resistance state (HRs). The current is abruptly increased to the magnitude of compliance (1 mA) at threshold voltage (V_{TH}), in which situation the device is switched to a low resistance state (LRs). The switching process can be defined as a “SET” action. After removing voltage supply or apply a dual positive sweep again the current can be maintain at LRs, suggesting that the ITO/TPA-2BIP/Au device is a non-volatile type memory. The device can be recovered to its initial HRs from LRs in the reverse sweep from 0 V to -2 V, and the recovery process is defined as a “RESET” action. As shown in Figure 2.3.5.1 b), ITO/TPA-3BIP/Au device has similar switching behaviors with ITO/TPA-2BIP/Au, but the current in HRs is ~ 10 times larger, indicating that ON/OFF ratio is ~ 10 times smaller. Based on the I - V curves of ITO/TPA-2BIP/Au and ITO/TPA-3BIP/Au devices and above analysis, there is little influence on the switching behavior by verifying the acceptor moieties, but that is possibly able to induce different conductivity in HRs, thus, result in different ON/OFF ratio. Combined with the UV-vis absorption spectra and height images of AFM, the more ordered molecular stacking in solid state and the better contact between electrodes and organic films can affect the conductivity of molecules to induce

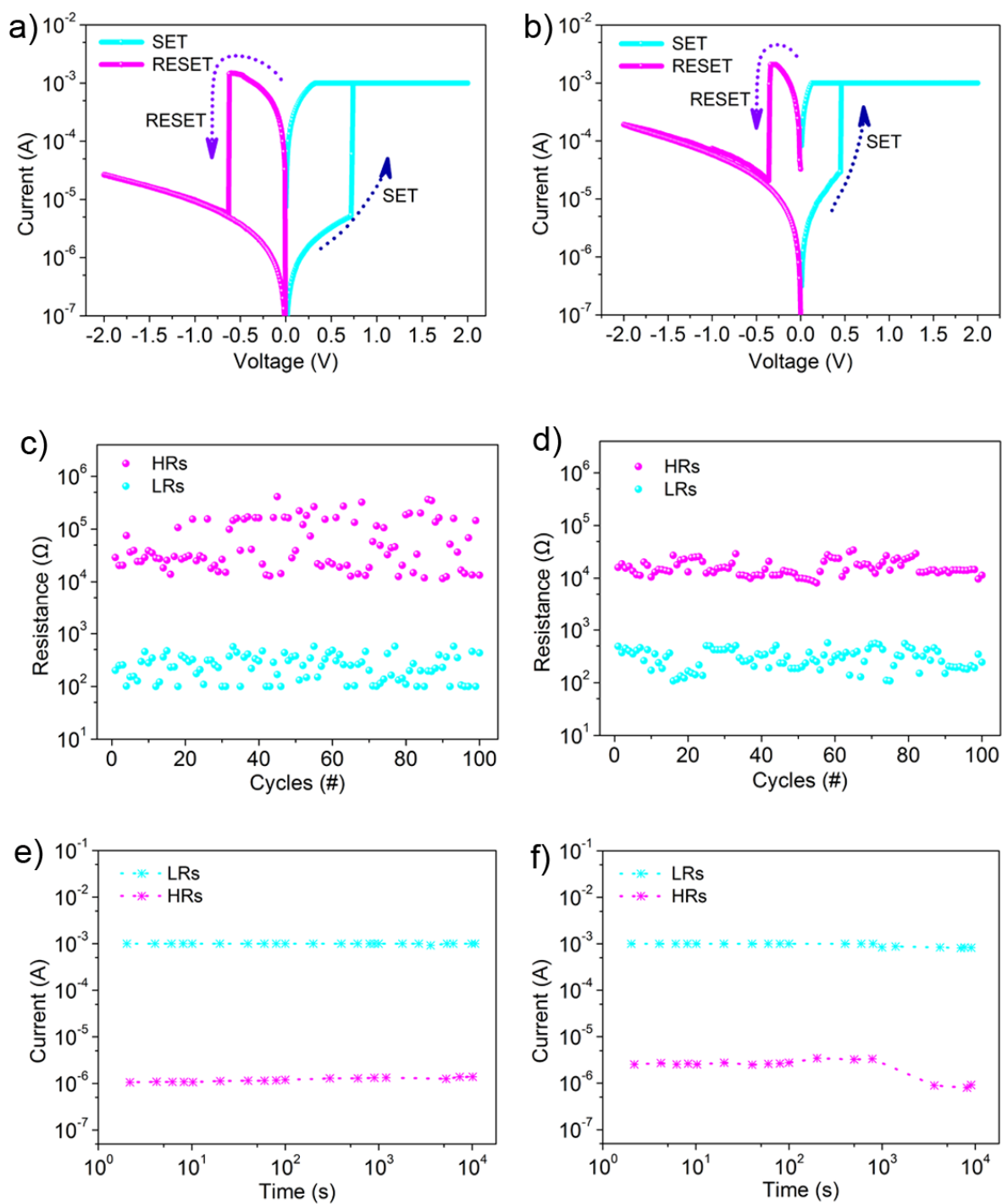


Figure 2.3.5.1 a) & b) I - V curves, c) & d) resistance distribution, e) & f) retention performance of the ITO/**TPA-2BIP** (or **TPA-3BIP**)/Au devices, respectively.

different ON/OFF ratio.

The endurance performance of ITO/**TPA-2BIP**/Au and ITO/**TPA-3BIP**/Au devices was investigated by cyclic switching through the typical “SET”-“RESET” operations. Generally, both **TPA-2BIP** and **TPA-3BIP** can be repeatedly switched between HRs and LRs for more than 100 cycles. Figure 2.3.5.1 c) & d) show the corresponding resistances distribution of each state when read at 0.1 V for 100 cycles. In LRs the resistances of both **TPA-2BIP** and **TPA-3BIP** have a narrow distribution in range of 10^2 – $5 \times 10^2 \Omega$. In HRs the resistances of **TPA-3BIP** can still maintain narrow distribution in the range of 10^4 – $5 \times 10^4 \Omega$, however, those of **TPA-2BIP** are distributed scattered in a wide range of 10^4 – $5 \times 10^5 \Omega$. The average ON/OFF ratio device between HRs and LRs for the 100 cycles of ITO/**TPA-2BIP**/Au is $\sim 4 \times 10^2$, and that of ITO/**TPA-3BIP**/Au device is $\sim 7 \times 10$, respectively. The ON/OFF ratio of both **TPA-2BIP** and **TPA-3BIP** is high enough for practical application. The average V_{TH} for ITO/**TPA-2BIP**/Au and ITO/**TPA-3BIP**/Au devices have very close value, which is 0.83 V and 0.84 V for “SET” process and -0.69 V and -0.66 V for “RESET” process, respectively. The close average V_{TH} is further corresponded to the fact that there is no significant effect on the switching behaviors by changing the number of acceptor moieties.

The retention performances of ITO/**TPA-2BIP**/Au and ITO/**TPA-3BIP**/Au devices were evaluated by applying a reading voltage of -0.1 V on both HRs and LRs in ambient conditions. Figure 2.3.5.1 e) & f) show the corresponding evaluation results, no obvious current decay can be observed for each state in 10^4 seconds during the test, indicating that both the two states of the two types of device are well retentive.

2.3.6 Mechanism Discussion

Molecular calculation of **TPA-2BIP** and **TPA-3BIP** was carried out in same method with

TPA-BIP illustrated in 2.2.6 Mechanism Discussion (TMS ((trimethylsilyl)ethynyl)) groups were used instead of **TIPS** for calculation convenience). Figure 2.3.6.1 a) shows the electron density distribution of **TPA-2BIP**, the HOMO coefficient is dispersed on **TPA** and one **BIP** moiety (A1), while the LUMO coefficient is mainly located on the other **BIP** moiety (A2). The HOMO and LUMO levels of **TPA-2BIP** display a typical D-A distribution, although the molecule owns an A-D-A structure. As shown in Figure 2.3.6.1 b), the HOMO coefficient of **TPA-3BIP** is dispersed on the whole molecule, including the **TPA** unit and the three **BIP** moieties, and the distribution of LUMO coefficient of **TPA-3BIP** is similar to **TPA-2BIP**. Based on the calculation results, there is probably only one acceptor moiety of **TPA-2BIP** and **TPA-3BIP** can act as the “real” acceptor, although both the two molecules have multiple acceptor moieties. The energy barrier is estimated to be 2.36 eV between the LUMO level of **TPA-2BIP** and the working function of Au (-5.1 eV), and that of **TPA-3BIP** is determined to be 2.34 eV, respectively. In another hand, the energy barrier is 0.14 eV between the HOMO level of **TPA-2BIP** and the working function of ITO (-4.8 eV), and that of **TPA-3BIP** is 0.18 eV, respectively. Thus, holes injection is dominated in charge carriers’ migration for the two types of devices.

The memory behaviors of ITO/**TPA-2BIP**/Au and ITO/**TPA-3BIP**/Au devices can be explained by electron “traps” mechanism. In HRs, the energy barriers and electron “traps” induced by acceptor moieties of both **TPA-2BIP** and **TPA-3BIP** can block the electrons injection and charge carriers migration. After the voltage is increased to V_{TH} the electron “traps” can be filled and the corresponding devices will be set to LR. As illustrated in previous section, only one acceptor moiety in **TPA-2BIP** or **TPA-3BIP** can act as “real” acceptor moiety, therefore, only one electron “traps” will be filled in switching process. As a

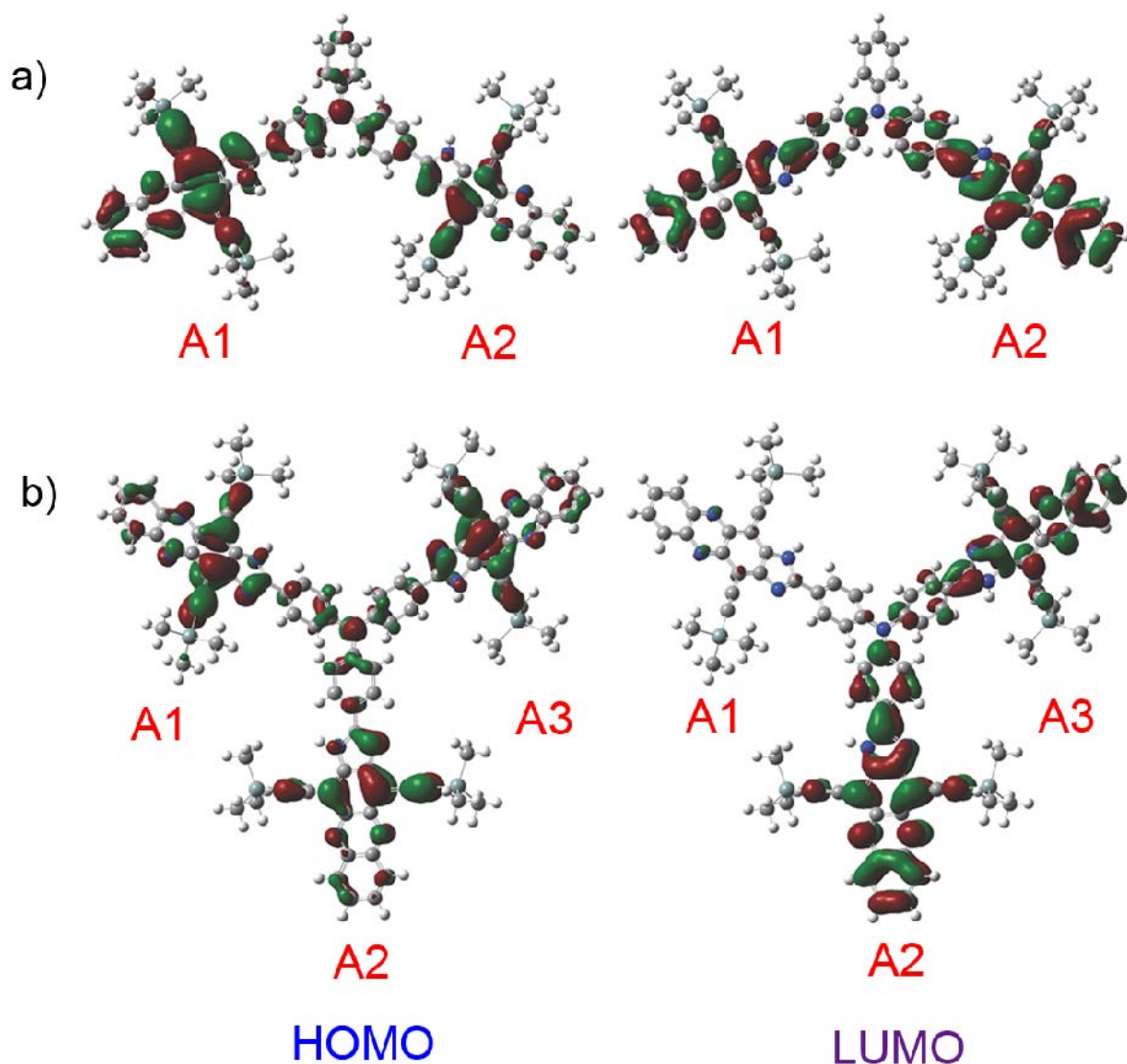


Figure 2.3.6.1 Electron density distribution of a) **TPA-2BIP** & b) **TPA-3BIP**.

result, similar memory behaviors can be observed in ITO/**TPA-2BIP**/Au and ITO/**TPA-3BIP**/Au devices. Intermolecular charge transfer occurring between HOMO and LUMO levels of the two molecules can also demonstrate the switching mechanism of the two types of devices, which can form charge transfer complex as charge carriers. The non-volatile memory performance were probably coming from the stabilized charge carriers, which are generated by filling of electron “traps” or intermolecular charge transfer.

2.3.7 Summary

Two D-A molecules **TPA-2BIP** and **TPA-3BIP** with a single **TPA** donor unit and various number of **BIP** acceptor moieties have been synthesized and characterized. Sandwich architecture memory devices have been fabricated with **TPA-2BIP** or **TPA-3BIP** as active layer. Similar switching behaviors are observed and the two molecules own close threshold voltage. The ON/OFF ratio of the two types of devices shows difference in magnitude of 10 times. The **TPA-3BIP** film has smaller grain size and is smoother than **TPA-2BIP** based on the morphology analysis of active layers, which can explain its low ON/OFF ratio. The similar switching process has been demonstrated to be induced by filling of electron “traps” or intermolecular charge transfer, which can occur between the HOMO level of donor unit and LUMO level of “real” acceptor moiety. In this part it is found that increasing acceptor moieties does not generally induce multilevel memory behaviors, and the morphology of active layer may can influence the ON/OFF ratio of devices.

2.4 D-A Molecules with Strong Electron-deficient *N*-heteroacene and Multiple Donors

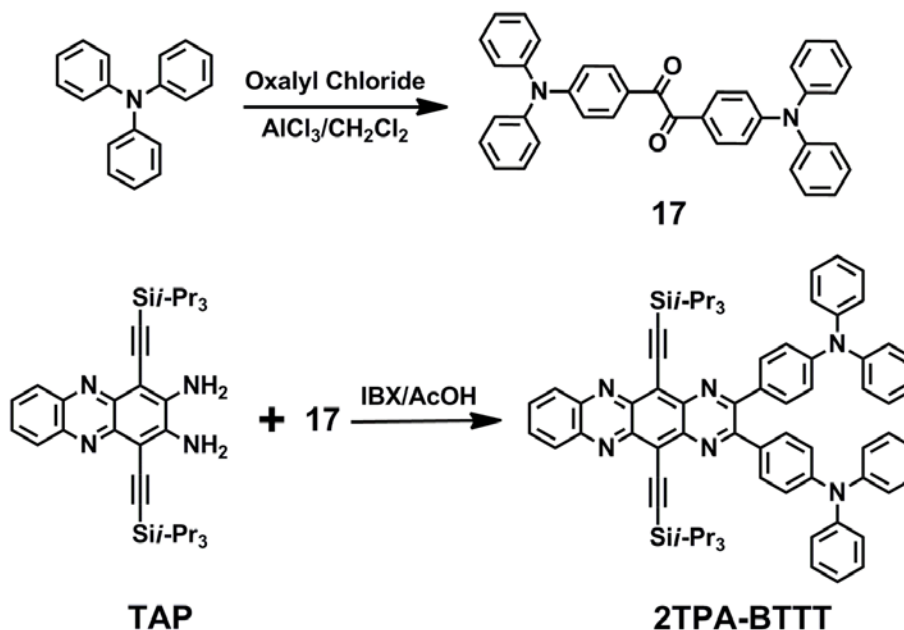
2.4.1 Molecular Design

Considering the acceptors engineering including incorporation of multiple electron “traps” through different *N*-heteroacene units and increasing the number of acceptor moieties does not generally induce multilevel memory behaviors, we would like to design molecules from another aspect. The rewritable memory behaviors in D-A molecules have also been proved to be induced by intermolecular charge transfer, in which situation the recombination of charge carriers can functionalize as “RESET” operation in switching process.⁸ An interesting issue is whether multiple electrons intermolecular charge transfer can occur so that various charge

carriers' generation can be obtained to adjust the resistance of certain materials, and besides of that the rewritable memory performance can be possibly realized through different charge carriers' recombination, thus, rewritable multilevel memory materials are expected. To achieve this concept, multiple donor units with strong electron-deficient acceptor in one molecule can be a solution. We propose a novel tetraazatetracene derivative 2,3-(4,4'-bis(*N,N*-diphenylamino)benzyl)-5,12-bis((triisopropylsilyl)ethynyl)-1,4,6,11-tetraazatetracene (**2TPA-BTTT**), which contains two **TPA** units as donors and 5,12-bis((triisopropylsilyl)ethynyl)-1,4,6,11-tetraazatetracene (**BTTT**) as an acceptor.

2.4.2 Synthesis of 2TPA-BTTT

The synthesis of **TAP** has been illustrated in [2.2.2 Synthesis of TPA-BIP](#). The synthetic route for **2TPA-BTTT** is illustrated in Scheme 2.4.2.1.



Scheme 2.4.2.1 Synthetic route for **2TPA-BTTT**.

Synthesis of 4,4'-bis(*N,N*-diphenylamino)benzil 17

In a round bottom flask, anhydrous aluminum chloride (1335 mg, 10 mmol) was suspended in anhydrous CH_2Cl_2 (50 mL), oxalyl chloride (646 mg, 5 mmol) was added in one portion, and **TPA** (2940 mg, 12 mmol) was added in several small portions. The system was heated to reflux for 6 hours. After that the system was cooled down to room temperature, quenched by pouring the solution into iced water. Hydrochloric acid (37%, 10 mL) was added to the mixed solution and stirred for 10 minutes. After that, the organic layer was collected, and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined organic phases were washed with water and brine, and dried over anhydrous Na_2SO_4 . The pure compound **17** (1710 mg) was obtained after flash column chromatography over silica gel with CH_2Cl_2 and hexane (CH_2Cl_2 : hexane = 1: 1) as yellow powder in yield of 65%.

Synthesis of **2TPA-BTTT**

In a round bottom flask, **TAP** (1215.3 mg, 2.12 mmol) and **17** (530.4 mg, 0.98 mmol) were dissolved in acetic acid (20 mL), and 2-iodoxybenzoic acid (**IBX**, 7.5 mg) was added in one portion. The system was heated to reflux for 48 hours under Argon atmosphere. After that the solution was cooled down to room temperature and poured into iced water. After filtration, the solid residue was obtained as crude product, which was further purified by flash column chromatography with EtOAc and hexane (EtOAc: hexane = 1: 20) over silica gel to afford pure **2TPA-BTTT** (137.0 mg) as dark blue powder in yield of 13%.

2.4.3 Molecular Characterization

2TPA-BTTT has been characterized with HR MS, NMR and X-ray crystallographic analysis.

2.4.3.1. HR MS Analysis

The HR MS (ESI) spectra of **17** and **2TPA-BTTT** were collected on a JEOL spiral TOF JMS-S3000 spectrometer.

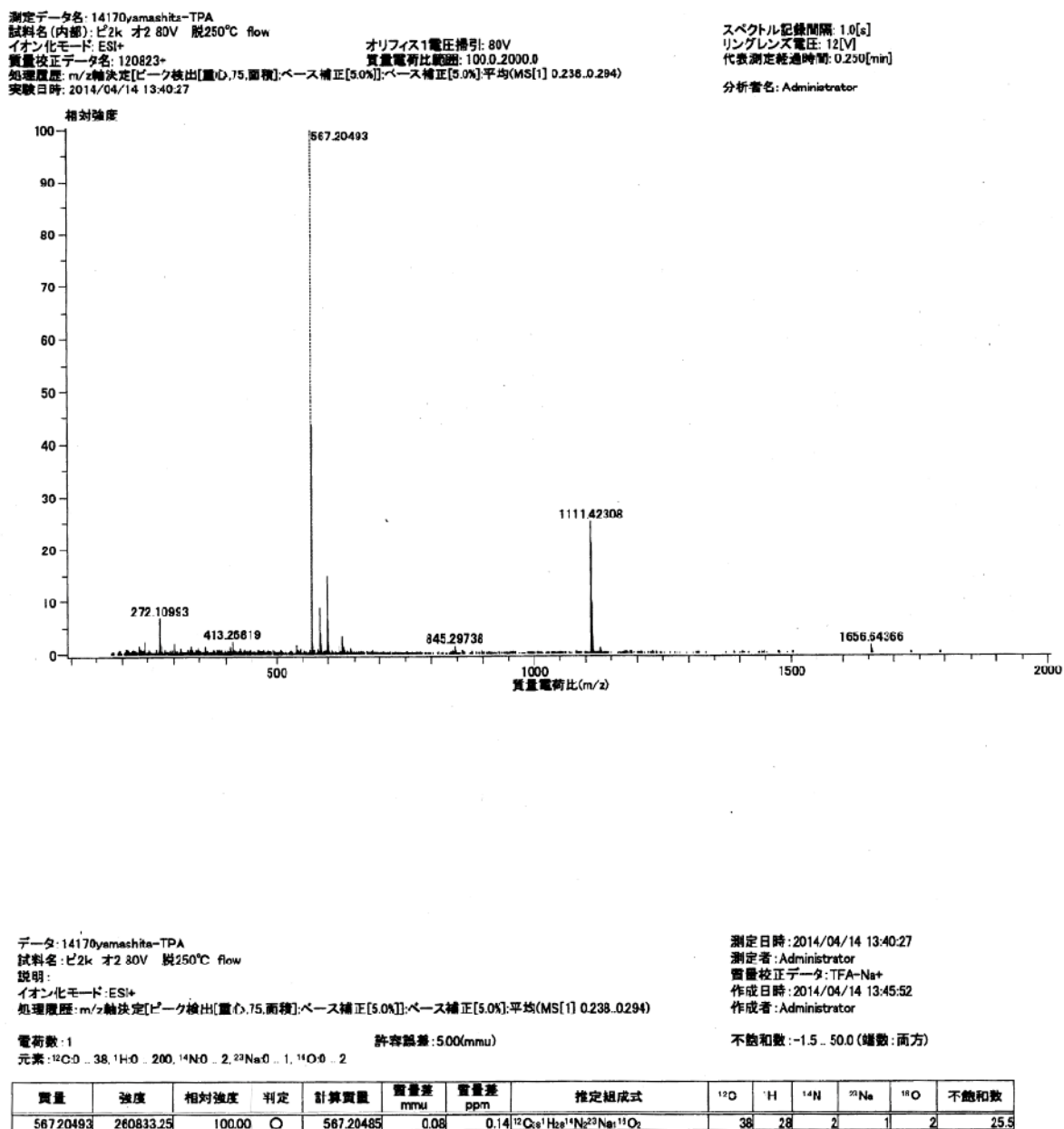


Figure 2.4.3.1.1 HR MS (ESI) spectra of **17**.

The chemical formula of **17** is $C_{38}H_{27}N_2O_2$. As shown in Figure 2.4.3.1.1, the calculated m/z value for $[M+Na]^+$ of **17** is 567.2049, and the actual m/z value found in spectra is 567.2049, which is well consistent with calculated result.

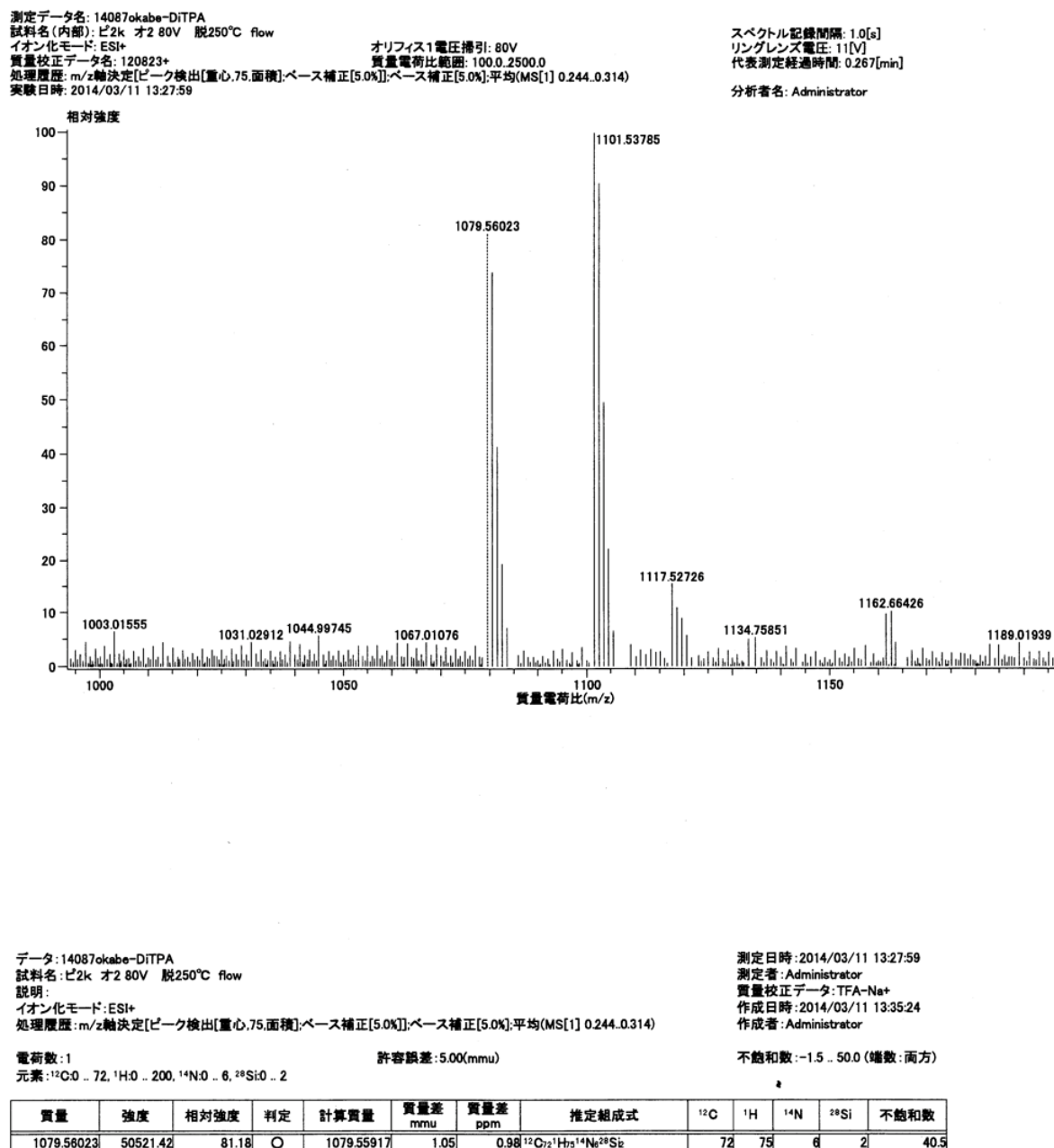


Figure 2.4.3.1.2 HR MS (ESI) spectra of **2TPA-BTTT**.

The chemical formula of **2TPA-BTTT** is $C_{72}H_{73}N_6Si_2$. As shown in Figure 2.4.3.1.2, the calculated m/z value for $[M+1]^+$ of **2TPA-BTTT** is 1079.5596, and the actual m/z value of that found in spectra is 1079.5602, which is well consistent with calculated result.

2.4.3.2 NMR Analysis

^1H NMR and ^{13}C NMR spectra of **17** were recorded on a Bruker 300-MHz spectrometer in $CDCl_3$.

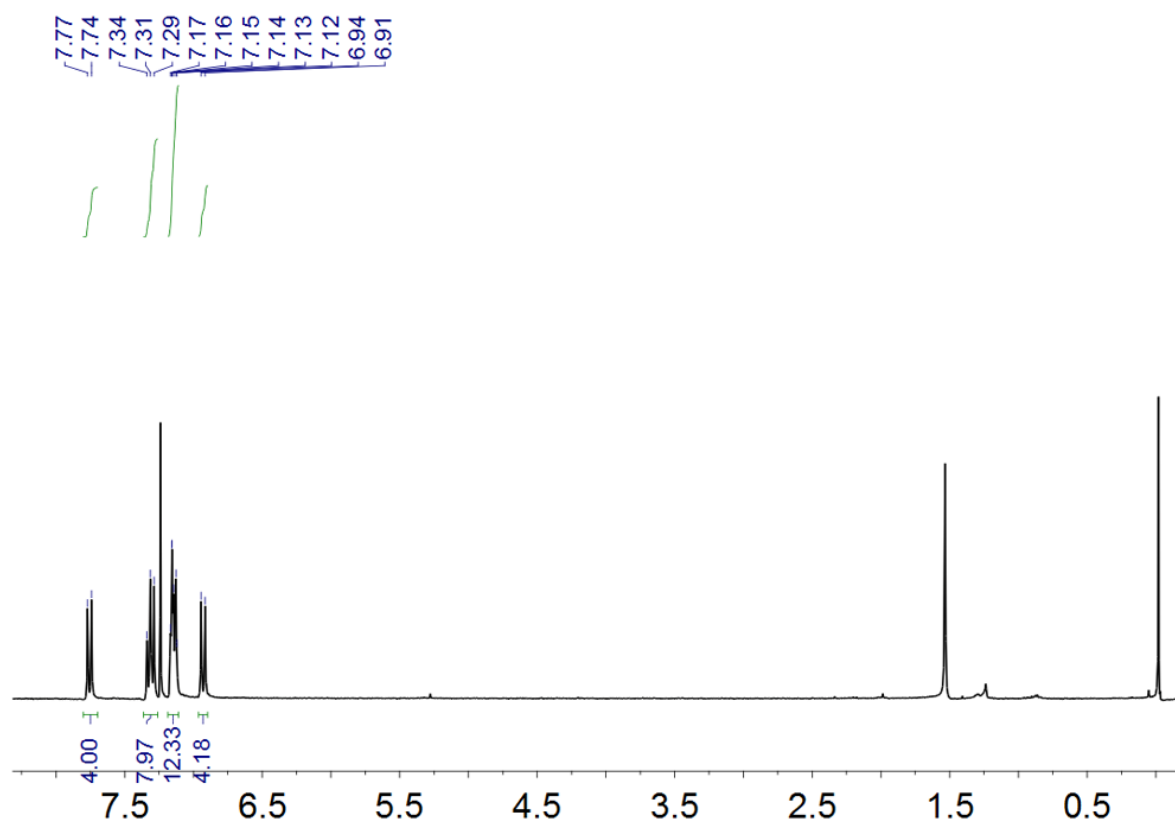


Figure 2.4.3.2.1 ^1H NMR spectra of **17** in $CDCl_3$.

Figure 2.4.3.2.1 shows the ^1H NMR spectra of **17** in $CDCl_3$, the protons can be indexed as ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ_H = 6.91~6.98 (4H), 7.11~7.20 (12H), 7.28~7.38 (8H), 7.73~7.81 (4H), which are well consistent with its molecular structure.

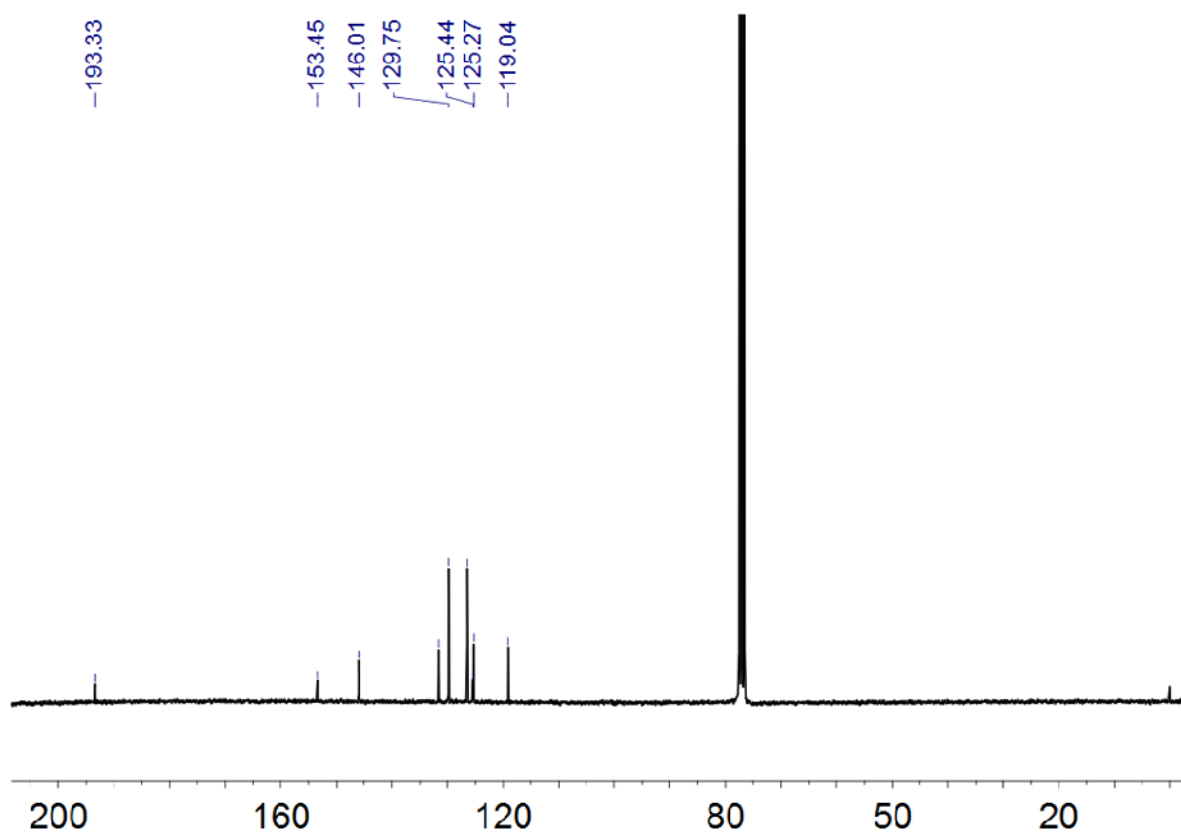


Figure 2.4.3.2.2 ^{13}C NMR spectra of **17** in CDCl_3 .

Figure 2.4.3.2.2 shows the ^{13}C NMR spectra of **17** in CDCl_3 . The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 193.33, 153.45, 146.01, 131.65, 129.75, 126.42, 125.44, 125.27, 119.04$. There are 9 carbons can be observed in the range of 100–200 ppm, which is well consistent with the theoretical value.

^1H NMR and ^{13}C NMR spectra of **2TPA-BTTT** were recorded on a JEOL JNM-AL 400-MHz spectrometer in CD_2Cl_2 .

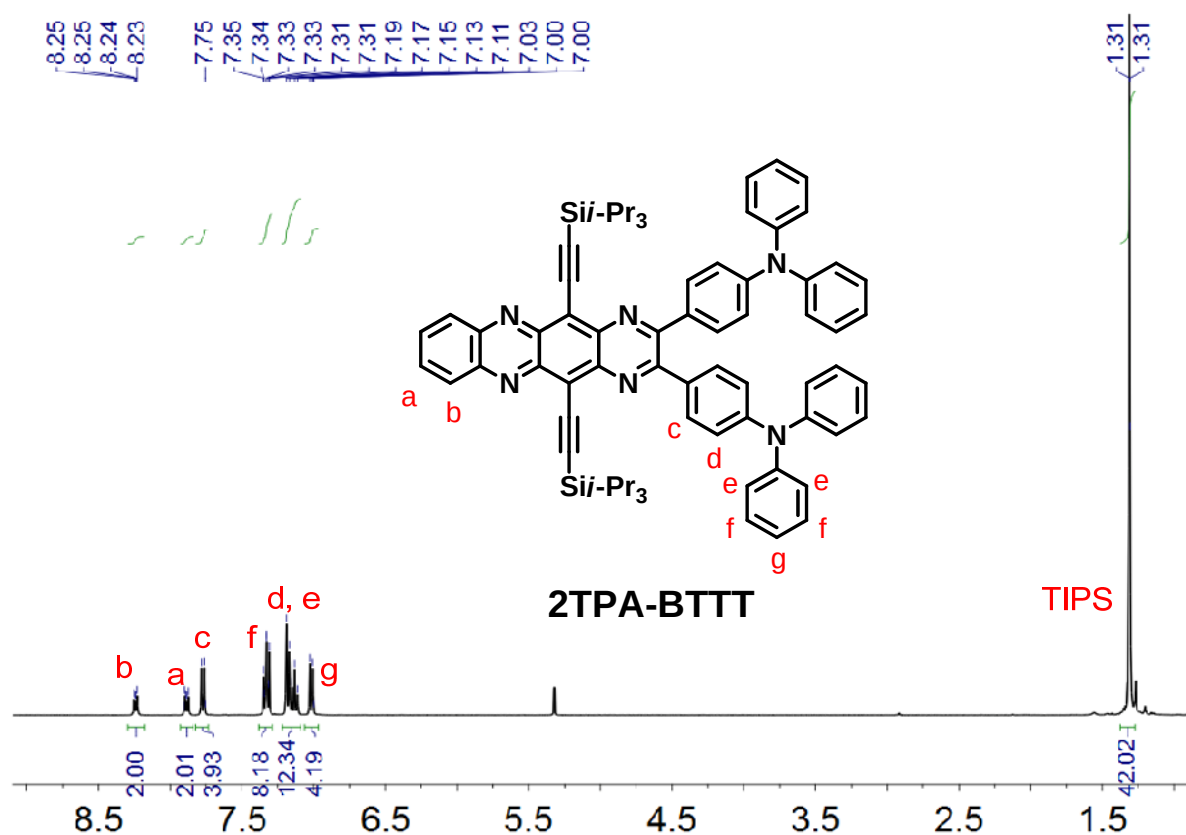


Figure 2.4.3.2.3 ^1H NMR spectra of **2TPA-BTTT** in CD_2Cl_2 .

Figure 2.4.3.2.3 shows the ^1H NMR spectra of **2TPA-BTTT** in CD_2Cl_2 , the protons can be indexed as ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{H}} = 1.28\sim 1.32$ (42H), $6.99\sim 7.04$ (4H), $7.10\sim 7.20$ (12H), $7.29\sim 7.36$ (8H), $7.74\sim 7.80$ (4H), $7.85\sim 7.92$ (2H), $8.20\sim 8.27$ (2H), which are well consistent with its molecular structure.

Figure 2.4.3.2.4 shows the ^{13}C NMR spectra of **2TPA-BTTT** in CD_2Cl_2 . The carbons can be indexed as ^{13}C NMR (101 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}} = 155.11, 150.33, 147.55, 145.09, 143.63, 142.08, 132.13, 132.01, 130.67, 129.98, 125.95, 124.50, 121.66, 121.46, 109.80, 102.87, 19.25, 12.23$. The carbons located at 12.23 and 19.25 are corresponded to **TIPS** group, There are 16 carbons can be observed in range of 100–160 ppm, which is well consistent with the theoretical value.

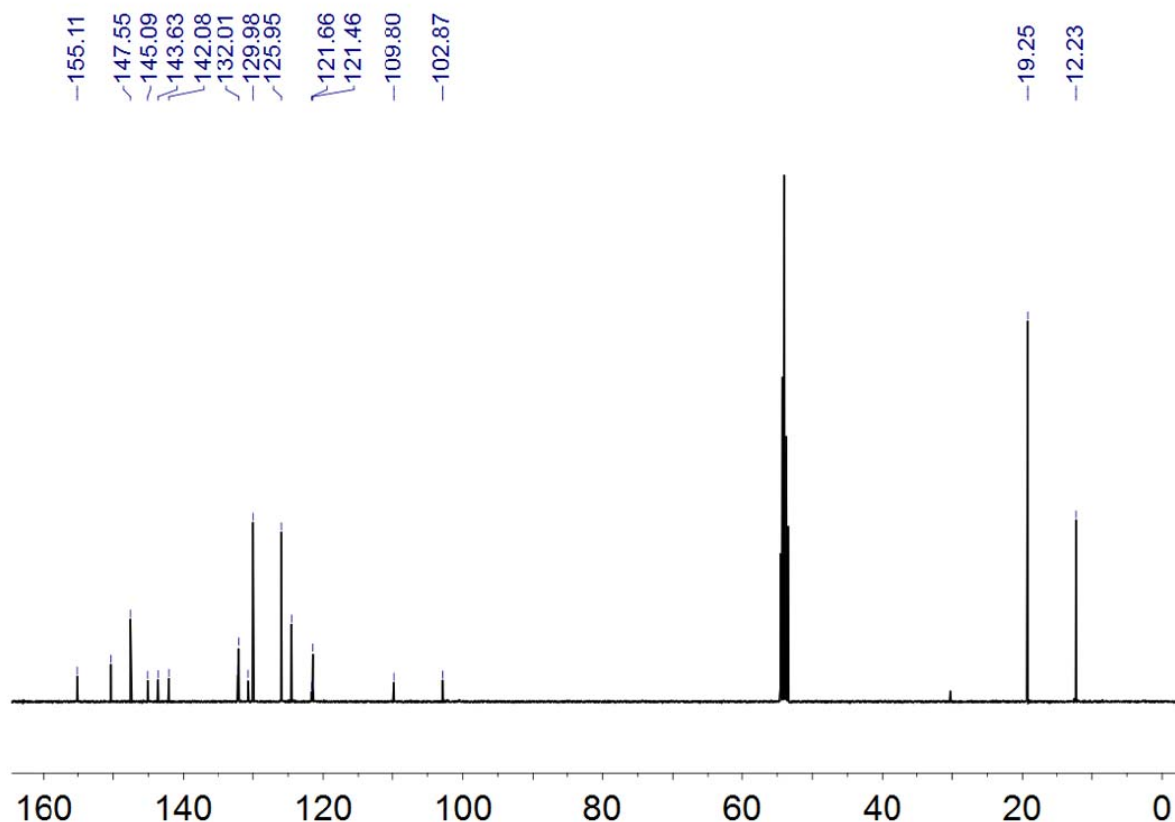


Figure 2.4.3.2.4 ^{13}C NMR spectra of **2TPA-BTTT** in CD_2Cl_2 .

2.4.3.3 Crystal Analysis

Needle-like single crystals of **2TPA-BTTT** were obtained through slowly diffusion of CH_3CN to its toluene solution. Single-crystal XRD data were collected at 90 K with a BRUKER-APEX II X-ray diffractometer, which used a large area CCD detector equipped with graphite monochromated Mo-K alpha radiation ($\lambda = 0.71069 \text{ \AA}$). The structures were solved and refined by SHELXL-97 program. The hydrogen atoms were located at geometrically calculated positions and were not refined, which were omitted for illustration convenience. The CCDC number for **2TPA-BTTT** is 1014927. Figure 2.4.3.3.1 a) & b) display the top and side view of **2TPA-BTTT** crystal structure. It is clear that **TPA** unit has a twisted conformation from both top and side view, which probably induces a bit of bending

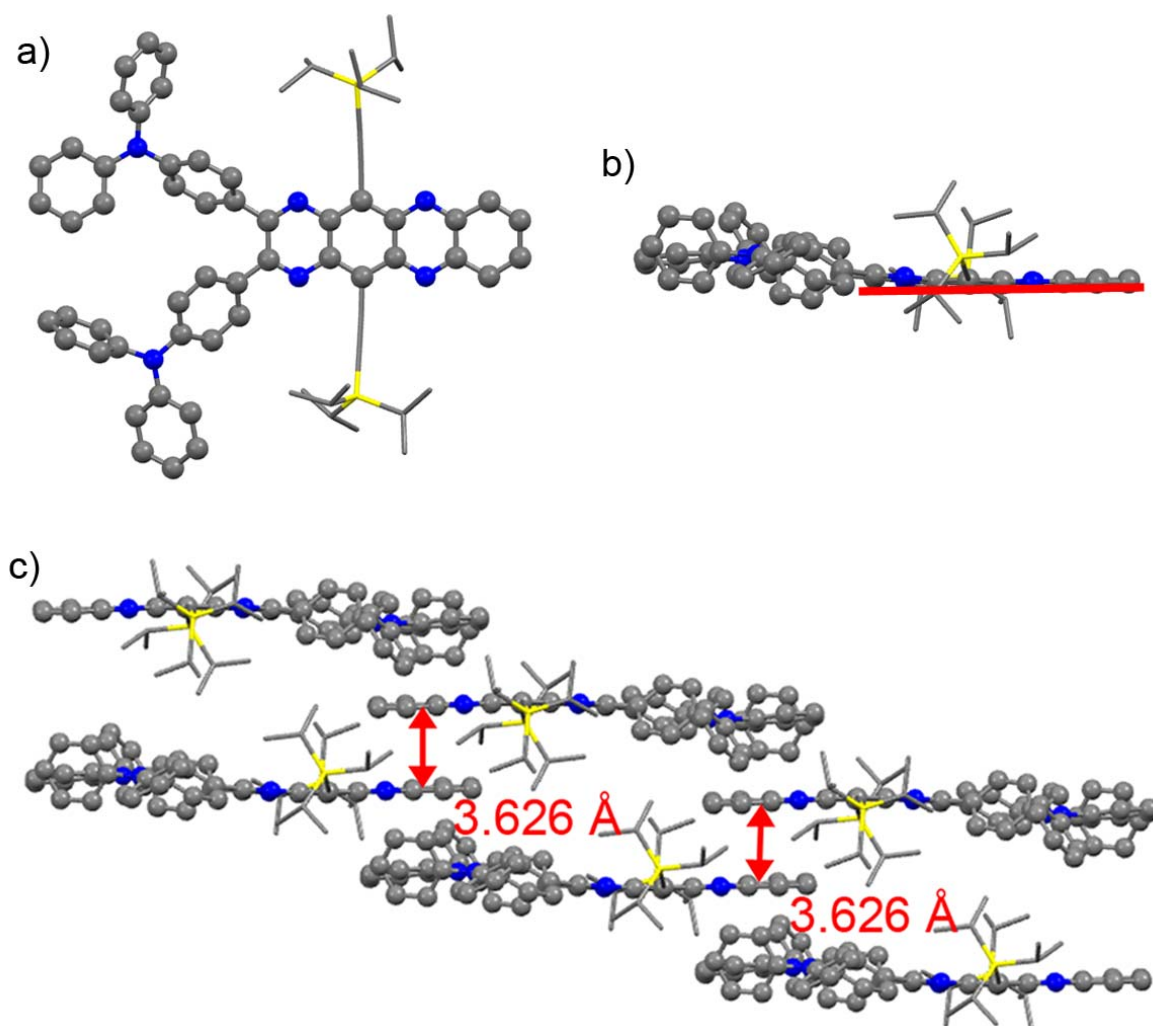


Figure 2.4.3.3.1 a) Top view & b) side view of the crystal structure of **2TPA-BTTT**. c)

Molecular stacking of **2TPA-BTTT**.

in **BTTT** moiety. As illustrated in Figure 2.4.3.3.1 c), 2D offset intersection face-to-face stacking mode is adopted between the neighboring molecules of **2TPA-BTTT** crystal. The interlayer distance between **BTTT** moieties is 3.626 Å, which is larger than that of common plane *N*-heteroacenes but shorter than van der Waals bond, indicating that there is strong π - π interactions between adjacent molecules.

2.4.3.4 Optical Properties of 2TPA-BTTT

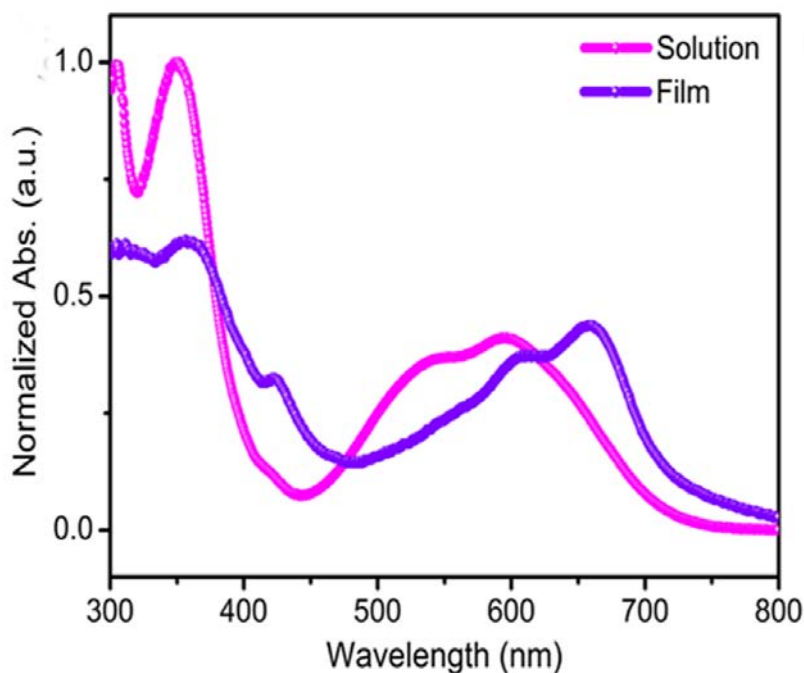


Figure 2.4.3.4.1 Normalized UV-vis absorption spectra of **2TPA-BTTT** (magenta line: in solution, violet line: in film).

The investigation of optical properties of **2TPA-BTTT** was carried out on a Shimadzu UV-2501 spectrophotometer through UV-vis absorption spectra. Figure 2.4.3.4.1 shows the normalized UV-vis absorption spectra of **2TPA-BTTT** in CH_2Cl_2 (magenta line) and in film (violet line). **2TPA-BTTT** exhibits two absorption bands in CH_2Cl_2 with the maximum absorption wavelength (λ_{max}) at 548 nm and 594 nm in visible region, respectively. The onset absorption wavelength (λ_{onset}) of **2TPA-BTTT** in CH_2Cl_2 is 709 nm, which determines the optical band gap (E_g) to be 1.75 eV, based on the same equation illustrated in **2.2.3.4 Optical Properties of TPA-BIP**. The λ_{max} at 548 nm and 594 nm are red-shifted to 607 nm and 658 nm in film, respectively, suggesting the strong π - π interaction between adjacent molecules. The λ_{onset} has a minor red-shift from 709 nm to 721 nm in film as well, corresponding to the

stronger molecular interaction in solid state.

2.4.3.5 Electrochemical Properties of 2TPA-BTTT

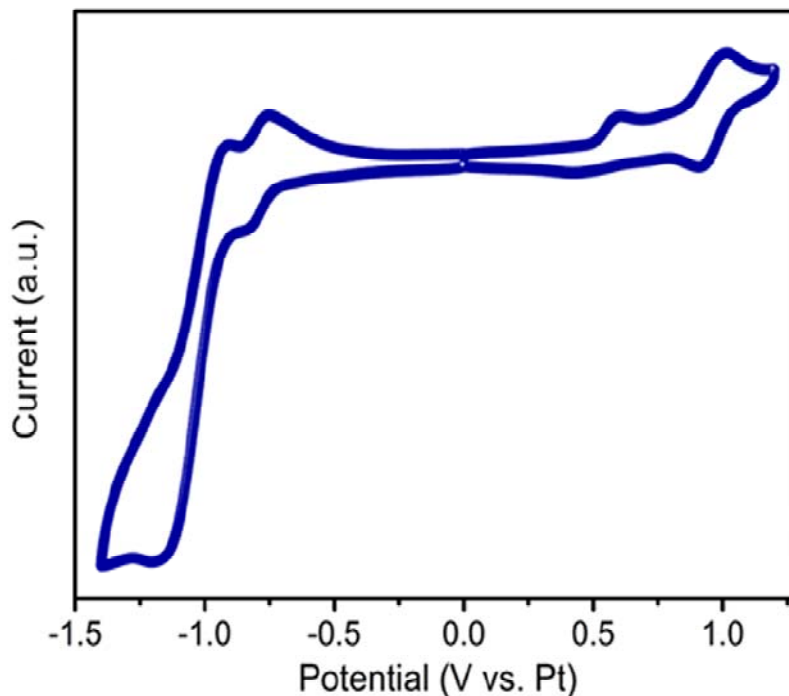


Figure 2.4.3.5.1 Cyclic voltammetric (CV) curves of **2TPA-BTTT** in anhydrous CH_2Cl_2 .

Cyclic voltammetric (CV) analysis of **2TPA-BTTT** was carried out in anhydrous CH_2Cl_2 to investigate its electrochemical property. The measurement conditions were same as that of **TPA-BIP** illustrated in 2.2.3.5 Electrochemical Properties of TPA-BIP. As shown in Figure 2.4.3.5.1, an irreversible oxidative peak and a reversible oxidative peak can be observed, and interestingly, **2TPA-BTTT** has a reversible reductive peak followed by a less reversible reductive peak. The onset potential of the first oxidative peak ($E_{\text{onset}}(\text{OX})$) versus $\text{FeCp}_2^+/\text{FeCp}_2$ is 0.30 eV, and the HOMO level of **2TPA-BTTT** can be determined to be -5.03 eV, utilizing the same calculation method illustrated in 2.2.3.5 Electrochemical Properties of TPA-BIP. The LUMO level is established to be -3.28 eV from the difference

between HOMO level and E_g . According to the CV curves analysis that various redox behaviors exist in **2TPA-BTTT**, multiple electrons injection can be induced between molecules when excited by voltage, and multilevel memory performance is expected.

2.4.4 Memory Device Fabrication Based on 2TPA-BTTT

The memory devices based on **2TPA-BTTT** were fabricated in the same procedure with **TPA-2BIP** & **TPA-3BIP** illustrated in 2.3.4 Memory Device Fabrication Based on TPA-2BIP & TPA-3BIP. The thickness of **2TPA-BTTT** film was measured to be ~ 70 nm by an Alpha-Step IQ Surface Profiler.

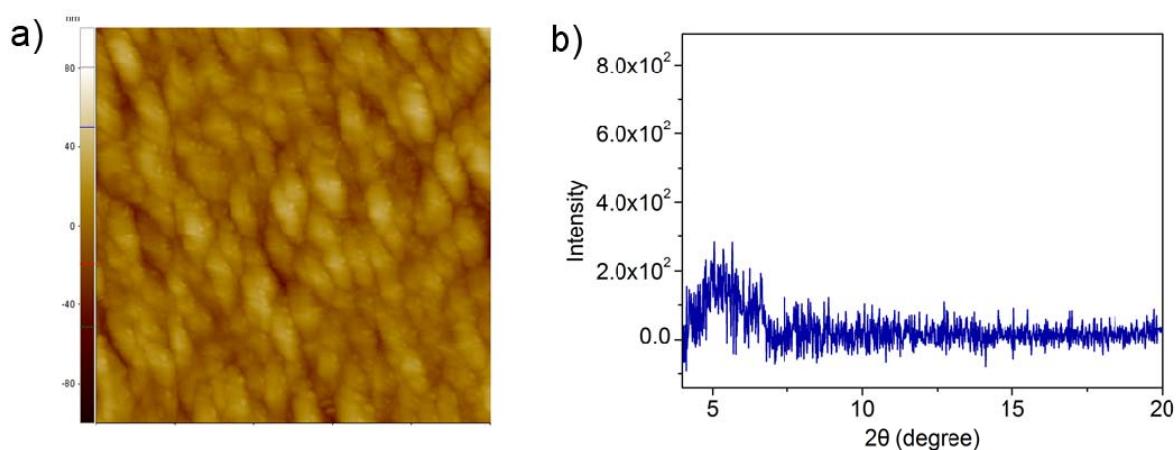


Figure 2.4.4.1 a) AFM image of a $5\ \mu\text{m} \times 5\ \mu\text{m}$ film of **2TPA-BTTT**. b) XRD patterns of the corresponding film.

Tapping-mode AFM (Park Systems Co.) was carried out to investigate the morphology and microstructure of **2TPA-BTTT** film. The height image of AFM (Figure 2.4.4.1 a)) shows that the film is high crystalline with clear grain boundaries. The root-mean-square roughness (RMS) of **2TPA-BTTT** film is 12.168 nm, suggesting the film is well continuous. The XRD patterns of the **2TPA-BTTT** film were investigated in same method with **TPA-BIP**. As

shown in Figure 2.4.4.1 b), however, only a broad diffraction peak in range of 4° – 7° with low intensity can be observed. The film might be too thin for XRD diffraction measurement.

2.4.5 Memory Characteristics of 2TPA-BTTT

The memory properties of ITO/2TPA-BTTT/Au devices were demonstrated by current-voltage (I - V) characteristics, which were measured under same conditions with that of TPA-BIP Illustrated in 2.2.5 Memory Characteristics of TPA-BIP. The I - V curves are shown in Figure 2.4.5.1 a). The current of ITO/2TPA-BTTT/Au device retains in low

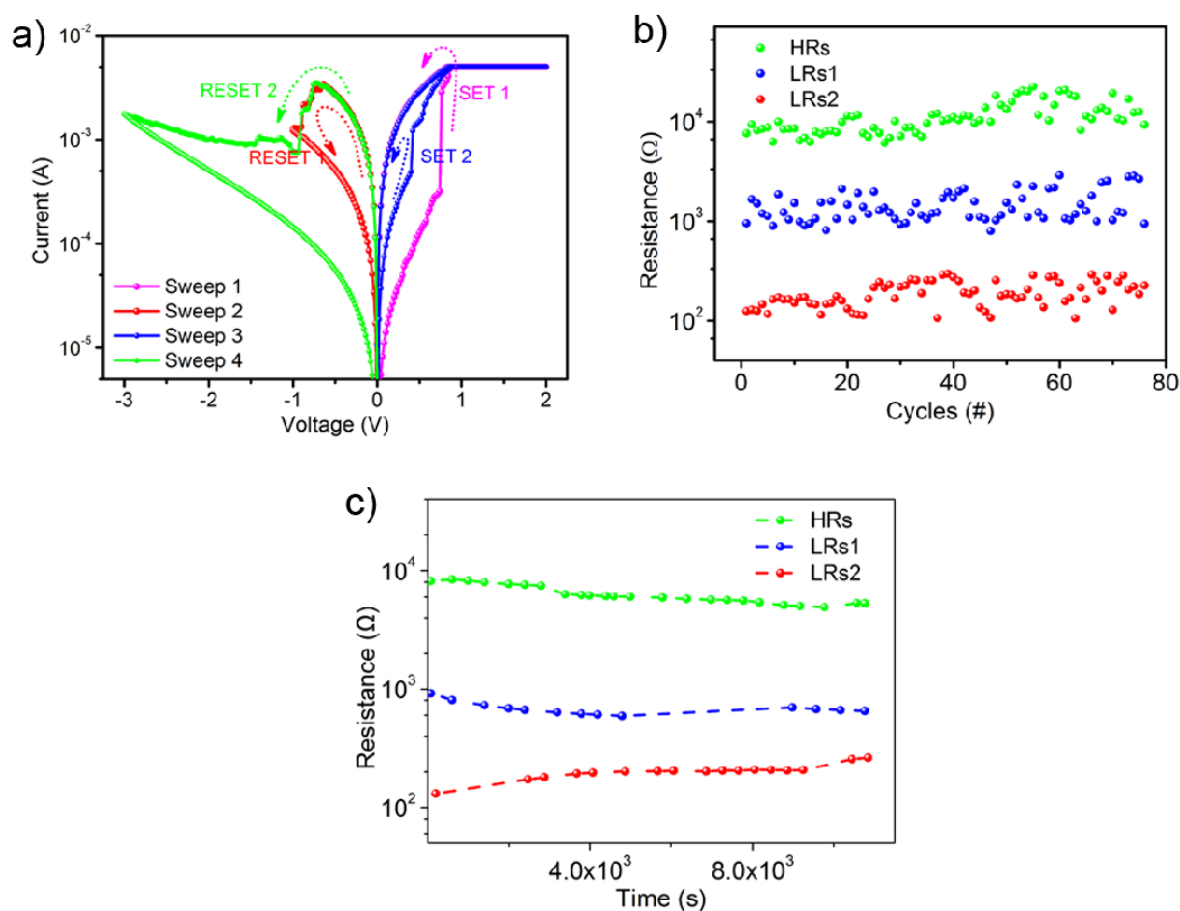


Figure 2.4.5.1 a) I - V curves, b) resistance distribution & c) retention performance of ITO/2TPA-BTTT/Au device.

magnitude range in the low sweeping voltage of “Sweep 1”, whose state can be defined as high resistance state (HRs). There is an abrupt increase of current when the sweeping voltage approaches the threshold voltage (V_{TH}), indicating the device is switched to low resistance state (LRs2). The switching process from HRs to LRs2 can be regarded as “SET 1” action. The LRs2 can be well maintained in the dual sweep or even after removal of the power supply, suggesting the ITO/2TPA-BTTT/Au device is a typical non-volatile memory. The current drops into an intermediate range in the reverse “Sweep 2” from 0 V to -1.0 V, in which state it can be defined as “LRs1”, and the process can be regarded as “RESET 1” action. The device can be further switched to LRs2 from LRs1 in another positive sweep (Sweep 3), in which situation the switching acts as “SET 2” process. The initial HRs can be totally recovered by a large reverse sweep (Sweep 4) from 0 V to -3 V, and the recovery of from LRs2 to HRs can act as “RESET 2” process. Basically, LRs2 can be generated either from HRs or LRs1 by “SET 1” or “SET 2” processes, and the “RESET 1” operation is able to induce the intermediate LRs1 from LRs2. Using a large reverse sweep by “RESET 2” process HRs can be easily obtained, hence the three distinct resistance states can be well transformed between each other through “SET 1”, “SET 2” or “RESET 1”, “RESET 2” operation. On the basis of above analysis, the ITO/2TPA-BTTT/Au device is a rewritable multilevel memory

The endurance performance of the ITO/2TPA-BTTT/Au devices were investigated with cyclic switching operations through the typical cycle of “SET 1”-“RESET 1”-“SET 2”-“RESET 2”. Generally, the device can be repeatedly switched among HRs, LRs1 and LRs2 for more than 70 cycles. Figure 2.4.5.1 3 b) shows the resistances distribution of the three states for 76 cycles when the device is read at 0.2 V in each state. The average ON/OFF ratio

between “LRs2” and “LRs1” or “LRs1” and “HRs” is ~ 8 . The average V_{TH} for LRs2 in “SET 1” or “SET 2” process is ~ 1 V, and that for LRs1 in “RESET 1” process is $\sim (-0.8)$ V. The recovery of initial HRs is a gradually changing process, thus the average V_{TH} for HRs in “RESET 2” process can not be clearly defined. The resistances of the three states distribute in a narrow magnitude range, suggesting that the multilevel memory behaviors are highly reproducible.

The retention performance of ITO/**2TPA-BTTT**/Au devices was evaluated by applying a reading voltage of -0.2 V to HRs, LRs1 or LRs2 in ambient conditions, respectively. As shown in Figure 2.4.5.1 3 b), there is no obvious current decay for each state can be observed in 10^4 seconds during the test, suggesting that the each memory state is well retentive.

2.4.6 Mechanism Discussion

Molecular calculation based on **2TPA-BTTT** was carried out in same method with **TPA-BIP** illustrated in 2.2.6 Mechanism Discussion to investigate the switching mechanism and charge carriers' migration. As shown in Figure 2.4.6.1 a), the HOMO and LUMO coefficients of **2TPA-BTTT** are distinctly located at **TPA** and **BTTT** moieties, respectively. The distinct distribution of energy levels and the good stacking of **2TPA-BTTT** molecules are favored for intermolecular charge transfer. Figure 2.4.6.1 b) shows the energy diagrams of ITO/**2TPA-BTTT**/Au device. The energy barrier between the HOMO of **2TPA-BTTT** and the working function of ITO (-4.8 eV) is determined to be 0.3 eV, however, that between the LUMO level and the working function of Au (-5.1 eV) is 1.72 eV. Thus, holes injection is dominated in charge carriers' migration. It is noteworthy that **2TPA-BTTT** has very close HOMO and HOMO-1 (-5.093 eV) levels based on calculation, so that in a single excitation

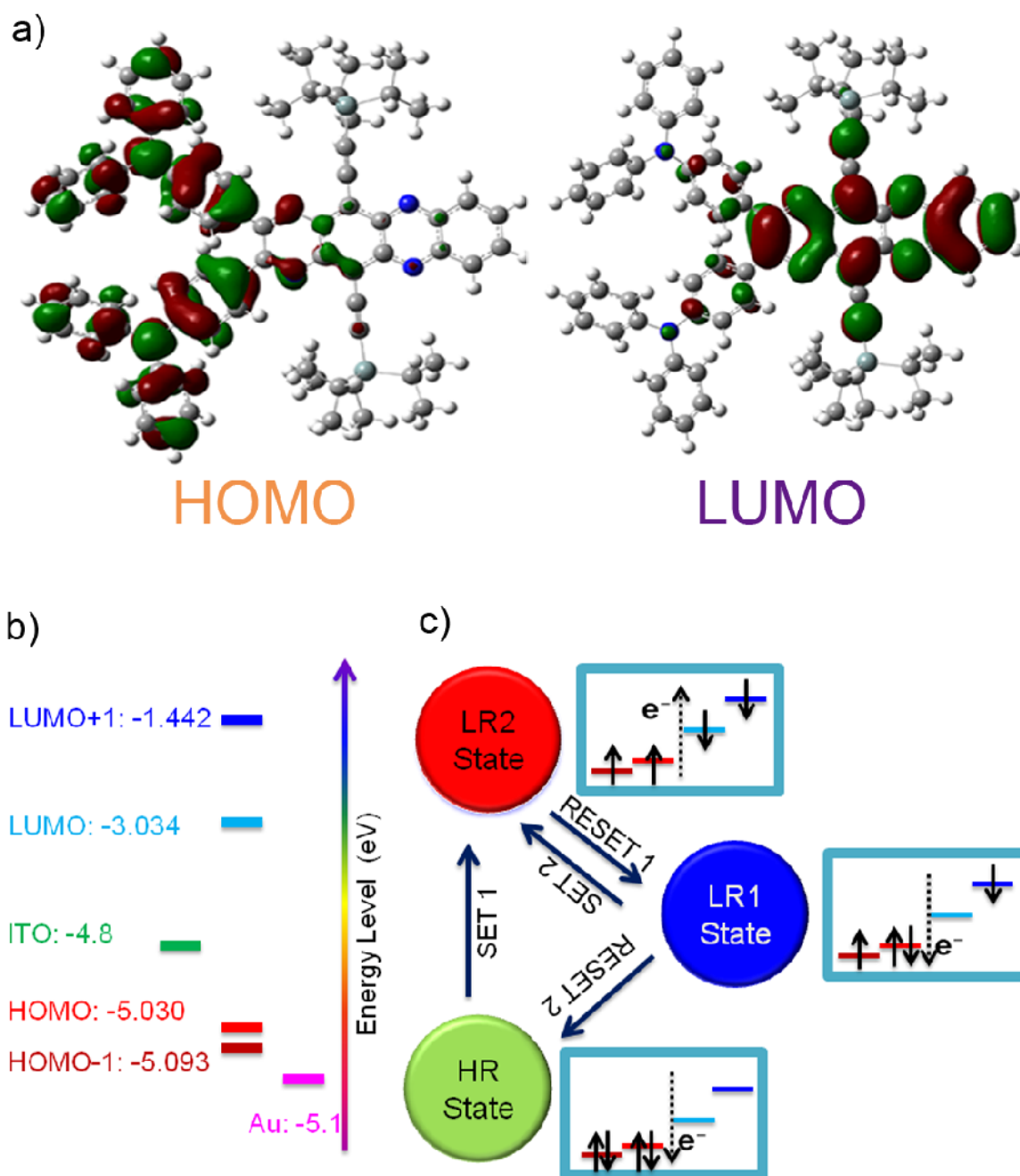


Figure 2.4.6.1 a) Electron density distribution of **2TPA-BTTT**. b) Energy diagrams of ITO/**2TPA-BTTT**/Au system. c) Proposed mechanisms for the multilevel memory behavior.

process double-electron injection might occur. As shown in Figure 2.4.6.1 c), in HRs the holes injection is possibly blocked by energy barriers between electrodes and organic films,

thus the current of device is under low magnitude range. Double-electron excitation from HOMO and HOMO-1 levels could occur in “SET 1” process as the voltage approaches to V_{TH} ,^{8,31} in which situation the device is set to LRs2. The charge transfer complexes can be formed in this process as main charge carriers, and it should be stable enough even without electronic field apply, which attributes the non-volatile property of ITO/**2TPA-BTTT**/Au device. The charge transfer complexes are possibly partially recombined in the reverse “RESET 1” process, and the device is reset to LRs1. Applying positive voltage to the intermediate LRs1 can further realize double-electron excitation again, and accordingly the LRs2 is achieved from LRs1. A larger reverse sweep can totally release the charge transfer complex, in which case the initial HRs is recovered.

2.4.7 Summary

In summary, a novel D-A molecule **2TPA-BTTT** combining two **TPA** donor units and one strong electron-deficient tetraazatetracene acceptor moiety has been designed and synthesized. The MIM architecture memory devices based on **2TPA-BTTT** display non-volatile rewritable multilevel memory behaviors with good endurance performance. The charming memory properties are probably generated by multiple electrons intermolecular charge transfer. This success suggests that incorporating multiple donors with strong electron-deficient acceptors is an efficient molecules designing strategy to develop novel rewritable multilevel memory materials.

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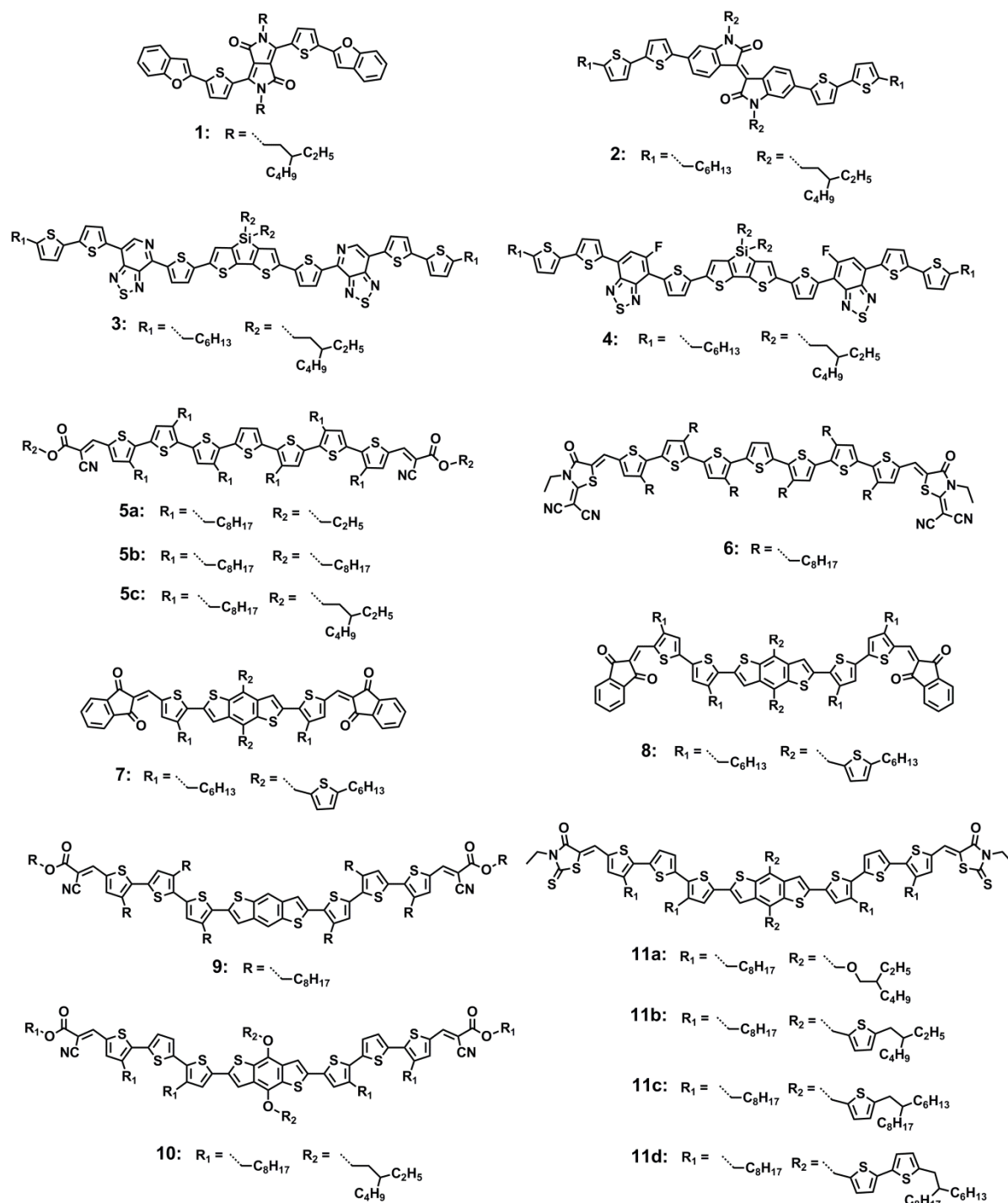
Chapter 3

N-heteroacenes for Organic Photovoltaics

3.1 Literature Review

There has been an intense of research interested in developing novel *p*-type organic small molecule semiconducting materials for application in bulk heterojunction (BHJ) architecture OPVs during the last decade, e.g. subphthalocyanine, merocyanine, squaraine, diketopyrrolopyrroles, borondipyrromethene, isoindigo, fused acenes, oligothiophenes, triphenylamine derivatives and so on.¹⁻⁶ In this part, some representative high performance small molecules featuring certain designing rules will be reviewed. The chemical structures of these molecules are shown in Figure 3.1.1.

The early small molecule based BHJ OPVs only showed PCEs in range of 1–3%, whose efficiency was limited by the low photocurrent density and fill factor.⁷ A remarkable breakthrough was achieved by Nguyen's group in 2009, who developed the small molecule **1** (Figure 3.1.1) with fused benzofuran (**BF**) as donor and diketopyrrolopyrrole (**DPP**) as acceptor, and thiophenes linked the donors and acceptor as a π -bridge.⁸ The whole molecule showed a typical D- π -A- π -D structure. The blended film of **1** with [6,6]-phenyl-C₇₁-butyric acid methyl ester (**PC₇₁BM**) showed very little phase separation in room temperature. Interestingly, after thermal annealing, enhanced phase separation of the film could be achieved and the optimized device showed a PCE up to 4.4% with a J_{sc} of 10 mA/cm², a V_{oc} of 0.9 V, and a FF of 0.48. Inspired by this success, developing novel *p*-type small molecules had been speed up. In 2010, Reynolds *et al.* reported the synthesis of the isoindigo-based

Figure 3.1.1 Molecular structures of some representative *p*-type small molecules.

oligoacenes **2** with two oligothiophenes in the end of molecules to play as donors and isoindigo centered in the middle for acceptor. Employing it as new electron donor and [6,6]-

phenyl-C₆₁-butyric acid methyl ester (**PC₆₁BM**) as an acceptor in blended film,⁹ the as-fabricated OPV device had a PCE up to 1.76% with a J_{sc} of 6.3 mA/cm², a V_{oc} of 0.74 V, and FF of 0.38. Soon after, the PCE could be further optimized to be 2.15% by using polydimethylsiloxane (**PDMS**) as a macromolecular additive.¹⁰

An important family of high performance small molecules **3–4** with D-A-D-A-D structure (Figure 3.1.1) were reported by Bazan and Heeger et al., among them dithieno(3,2-*b*; 2',3'-*d*)silole (**DTS**) was used as donor and located in the center. In the famous molecule **3** two strong electron withdrawing [1,2,5]thiadiazolo[3,4-*c*]pyridine (**PT**) groups were used as acceptors and the ending groups were two bithiophenes.¹¹ Strong and wide absorption of **3** in visible region was achieved and the molecule owned high hole mobility up to $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The OPV device with **3** and **PC₇₁BM** blended film as active layer showed a PCE up to 6.7%, which was the highest record at that time. It was noteworthy that after adding certain solvent additive such as 1,8-diiodooctane (**DIO**) for solution-processing, more excellent OPV performance could be received. The morphology analysis of the as-prepared film suggested that the addition of **DIO** could efficiently decrease the domain sizes. A systematic study on this family of small molecules had been conducted by Bazan's group. Deduced from their research, the OPV performance of these molecules could be significantly influenced by many factors such as the molecular shape, the bending angle of different unit, and the dipole moment of molecules.¹² Molecule **4** was developed by Gupta and Heeger et al., which used fluorinated 2,1,3-benzothiadiazole (**BT**) unit instead of **PT** as acceptor. The authors believed that the stronger acceptor moiety could lower the HOMO level of molecules and thus the V_{oc} of OPV devices would be increased.¹³ The optimized OPV devices based on **4** utilized an inverted device structure with polyethylenimine (80% ethoxylated) (**PEIE**) modified ZnO as

electron transporting layer, which showed excellent performance with a PCE up to 7.88% and a J_{sc} of 15.2 mA/cm², a V_{oc} of 0.77 V and a FF of 0.67. It was mentionable that high device stability was observed when the OPVs based on **4** were exposed to ambient conditions.

A family of oligothiophenes based compounds **5a–c**, **6** had been designed and synthesized by Chen and coworkers. For these molecules the single bond linked oligothiophenes were believed to act as donor moieties and the electron withdrawing groups of alkyl cyanoacetate were used as acceptors at the ending of molecules.¹⁴ Molecule **5b** owned a narrow band gap of 1.8 eV and exhibited the best OPV performance with a PCE up to 5.08%, and a J_{sc} of 10.7 mA/cm², a V_{oc} of 0.86 V, and a FF of 0.55.¹⁴ A remarkable advance had been achieved in recently when the alkyl cyanoacetate groups were changed to 2-(1,1-dicyanomethylene)rhodanine to produce compound **6**, which significantly decreased the optical band gap to 1.62 eV, mainly coming from the deeper LUMO level of -3.36 eV.¹⁵ The optimized PCE was up to 9.30% (certified at 8.995%) with a J_{sc} of 14.87 mA/cm², a V_{oc} of 0.91 V, and a FF of 0.69. The electron transport layer (ETL) materials played a key role for the enhancement of performance. When poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (**PFN**) was used as ETL material, the devices had higher and more reproducible performance and the average PCE was 9.03%. When LiF or ZnO was used as ETL, the average PCE was only 7.55%. The reduced energy barrier between the electrodes and organic films possibly resulted in the enhancement of devices, in which case the efficiency of charge carriers transport and collection could be improved accordingly.

Benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT**) based small molecules had also been investigated to be an important family of high performance OPV materials. Li's group developed a series of

BDT based small molecules **7–8** with indenedione (**ID**) as acceptor unit and ending groups. In these molecules a single thiophene or bithiophene was used as π -bridges, and the authors believed that the length of π -bridges could influence their OPV performance. Both **7** and **8** had broad absorption in visible region, and the absorption of **8** was significantly enhanced in comparison with that of **7**. The OPV devices based on **8** and **PC₇₁BM** blended film as active layer achieved the best performance with a PCE up to 6.75%, a J_{sc} of 11.05 mA/cm², a V_{oc} of 0.92 V, and a FF of 66.4%. Chen's group had also designed a series of **BDT** based molecules **9–10**, **11a–d**. Oligothiophenes were used as π -bridges to link the **BDT** units with various acceptor moieties, which were alkyl cyanoacetate and 3-ethylrhodanine groups, respectively.^{16–18} Different alkyl side chains were attached to the **BDT** units or acceptor moieties to investigate their influence on morphology and microstructure of films and OPV performance. Among these molecules, compound **11b** achieved the best OPV performance when using **PDMS** as solvent additive, with the optimized parameters of PCE up to 8.12%, a J_{sc} of 13.17 mA/cm², a V_{oc} of 0.93 V, and a FF of 0.66. The authors proposed that the narrower optical band gap and deeper HOMO levels of molecules could be accounting for their better device performance. In addition, the morphologies of organic films should also have certain influence on their OPV performance.

To summarize, the organic small molecules based OPVs have made great progress, and more exciting discoveries and achievement are expected in the very near future.

3.2 D- π -A Small Molecule with N-heteroacene as Acceptor

3.2.1 Molecular Design

BDT has been widely investigated as excellent donor unit for high performance OPV

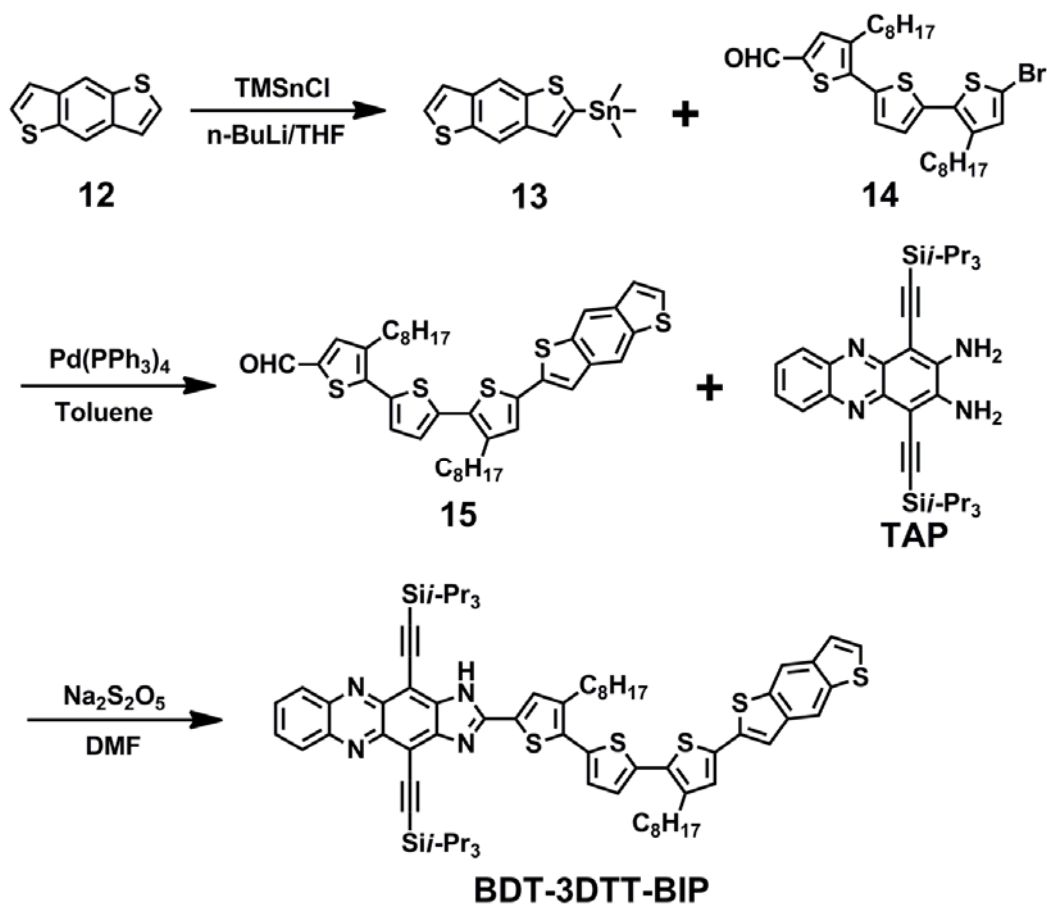
materials. In our previous study, **BIP** has been demonstrated to be a useful acceptor moiety with moderate electron withdrawing ability.^{19,20} The existence of electron-deficient imidazole and pyrazine units in **BIP** makes it be able to induce intramolecular charge transfer and wide absorbance in visible region, which benefits charge carrier's generation.²¹⁻²⁴ The relatively large conjugated backbone of **BIP** moiety can probably contribute to enhance the conjugation of whole molecule, and also facilitate the charge carrier's migration. When donor and acceptor are connected by a π -bridge, the absorption and conjugation are expected to be increased. In this work, we would like to connect **BIP** with **BDT** unit by a π -conjugated bridge 3,3''-dioctyl-2,2':5',2''-terthiophene (**3DTT**), to build up a D- π -A molecule **BDT-3DTT-BIP** and investigate its OPV performance.^{17,18,25-28}

3.2.2 Synthesis of BDT-3DTT-BIP

Scheme 3.2.2.1 shows the synthetic route for **BDT-3DTT-BIP**. The synthesis of **TAP** has been illustrated in 2.2.2 Synthesis of TPA-BIP. Compound **14** was prepared through a literature reported procedure.^{29,30}

Synthesis of compound 13

Compound **13** was synthesized by a modified procedure from literature.³¹ In a well-dried round bottom flask, **BDT** (207 mg, 1.08 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 15 mL) under Argon atmosphere. *n*-Butyllithium (0.75 mL, 1.2 mmol, 1.6 M in hexane) was added into the system after it was cooled down to -78 °C. The reaction was kept at -78 °C for 2 hours and trimethyltin chloride (427 mg, 2.14 mmol) was added in one portion. The system was slowly warmed up to room temperature and stirred overnight. After that, the reaction was quenched by addition of diethyl ether (50 mL), which was extracted with

Scheme 3.2.2.1 Synthetic route for **BDT-3DTT-BIP**.

Na_2CO_3 solution and water. The organic layer was collected and crude product could be obtained by evaporating solvents. The pure product was afforded as white powder (252 mg) by recrystallization of crude products from CH_3CN solution in yield of 65.9%.

Synthesis of compound 15

In a well-dried flask, compound **13** (167 mg, 0.47 mmol) and compound **14** (351 mg, 0.59 mmol) were dissolved in anhydrous toluene (20 mL) under Argon atmosphere. Tetrakis(triphenylphosphine)palladium(0) (59 mg, 0.05 mmol) was added as solid, and the resulting solution was heated to reflux for 12 hours. After that the system was cooled down to room temperature, and crude product was obtained by evaporating solvents. The pure

compound **15** was afforded as orange colour powder (137 mg) by flash column chromatography over silica gel with CH₂Cl₂ and hexane (CH₂Cl₂: hexane = 1: 4) in yield of 42.3%.

Synthesis of **BDT-3DTT-BIP**

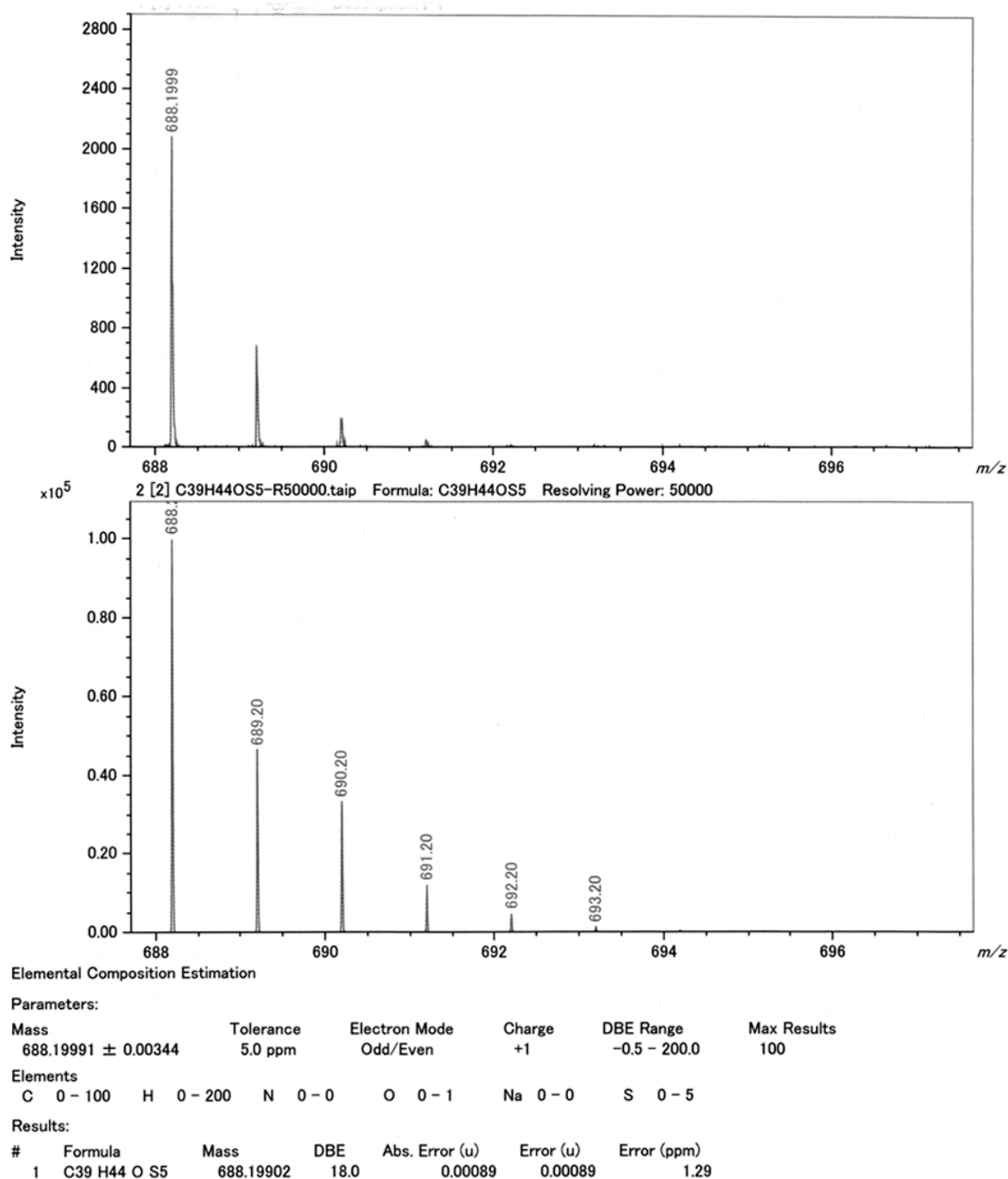
In a round bottom flask, **TAP** (159 mg, 0.28 mmol), compound **15** (165 mg, 0.24 mmol) were dissolved in *N,N*-dimethylmethanamide (DMF 25 mL). Sodium metabisulfite (61 mg, 0.32 mmol) was added and the system was heated to 120 °C for 12 hours. After cooled down to room temperature, the mixture was poured into ice water (100 mL) and filtered, the solid residue was obtained as crude product, and the pure **BDT-3DTT-BIP** was afforded as dark red powder (61 mg) by flash column chromatography over silica gel with CH₂Cl₂ and hexane (CH₂Cl₂: hexane = 1: 3) in a yield of 20.4%.

3.2.3 Molecular Characterization

The compound **13**, **15** and **BDT-3DTT-BIP** have been characterized by HR MS and NMR.

3.2.3.1 HR MS Analysis

The HR MS (MALDI-TOF) spectra of **15** and **BDT-3DTT-BIP** were recorded on a JEOL spiral TOF JMS-S3000 spectrometer.

Figure 3.2.3.1.1 HR MS (MALDI-TOF) spectra of **15**.

The chemical formula of **15** is C₃₉H₄₄OS₅. As shown in Figure 3.2.3.1.1, the calculated m/z value for **15** is 688.1996, and the actual m/z value found in spectra is 688.1990, which is well consistent with the calculated result.

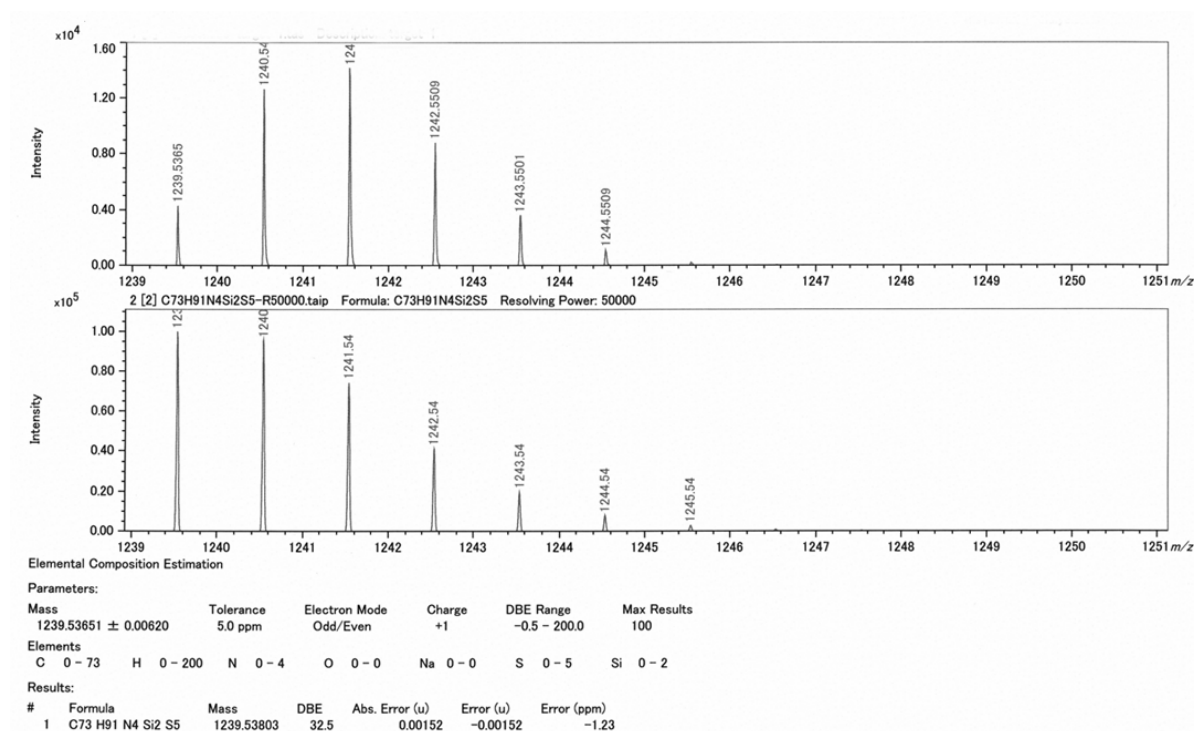


Figure 3.2.3.1.2 HR MS (MALDI-TOF) spectra of **BDT-3DTT-BIP**.

The chemical formula of **BDT-3DTT-BIP** is $C_{73}H_{90}N_4Si_2S_5$. As shown in Figure 3.2.3.1.2, the calculated m/z value for $[M+1]^+$ of **BDT-3DTT-BIP** is 1239.5308, and the actual m/z value for that found in spectra is 1239.5380, which is well consistent with the calculated result.

3.2.3.2 NMR Analysis

^1H NMR spectra of **13** was recorded on a JEOL JNM-AL300 spectrometer in CDCl_3 .

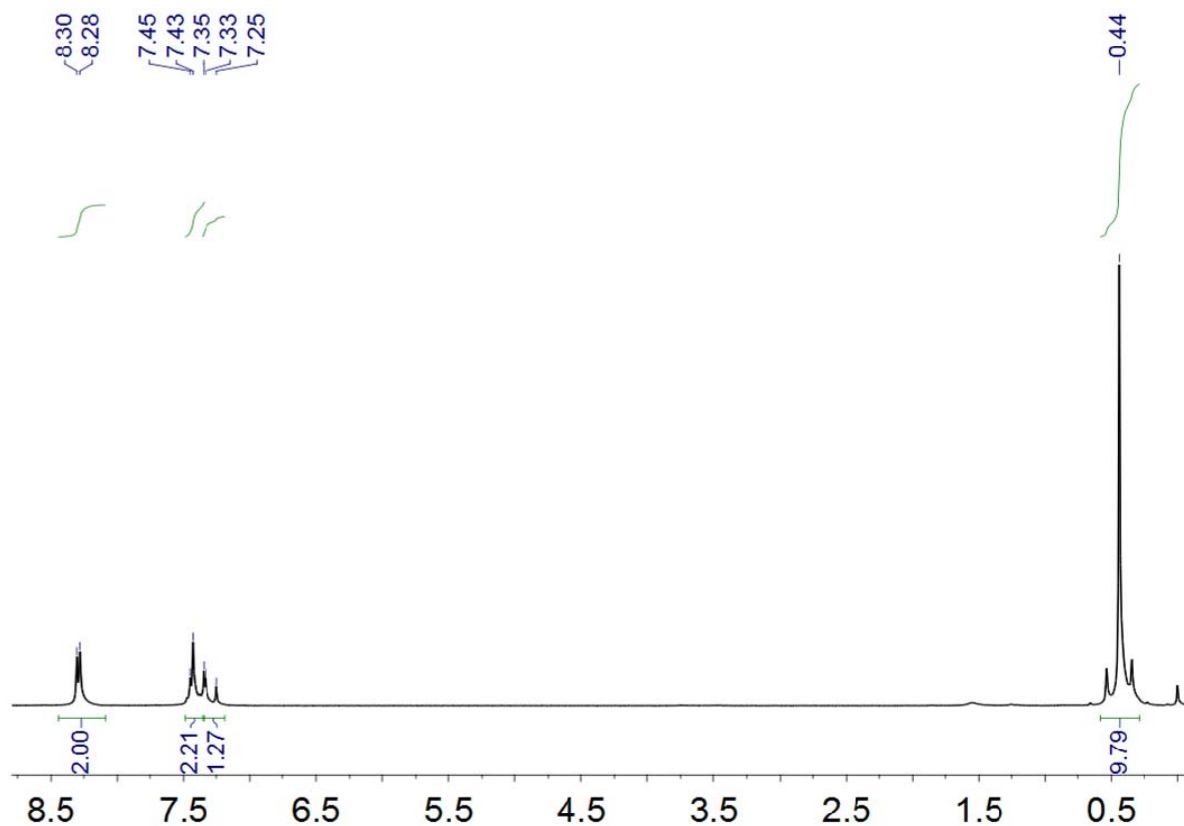


Figure 3.2.3.2.1 ^1H NMR spectra of **13** in CDCl_3 .

Figure 3.2.3.2.1 shows the ^1H NMR spectra of **13** in CDCl_3 , the protons can be indexed as ^1H NMR (300 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 8.10\sim 8.43$ (2H), $7.37\sim 7.51$ (2H), $7.37\sim 7.28$ (1H), $0.26\sim 0.51$ (9H), which are well consistent with its molecular structure.

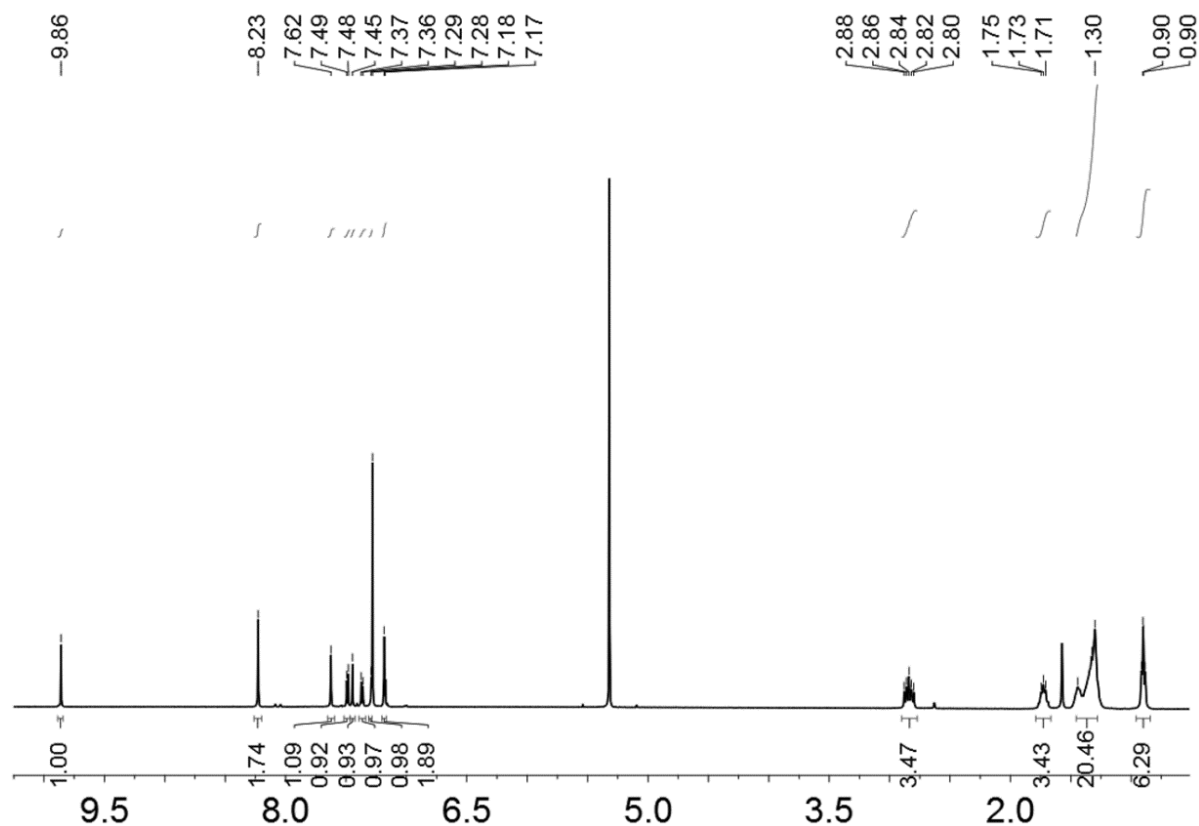


Figure 3.2.3.2.2 ^1H NMR spectra of **15** in CDCl_3 .

^1H NMR and ^{13}C NMR spectra of **15** were recorded on a JEOL JNM-ECX400 spectrometer in CDCl_3 .

Figure 3.2.3.2.2 shows the ^1H NMR spectra of **15** in CDCl_3 , the protons can be indexed as ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 9.80\sim 9.88$ (1H), $8.17\sim 8.25$ (2H), $7.56\sim 7.65$ (1H), $7.45\sim 7.50$ (1H), $7.41\sim 7.45$ (1H), $7.32\sim 7.38$ (1H) $7.26\sim 7.30$ (1H), $7.13\sim 7.19$ (2H), $2.74\sim 2.89$ (4H), $1.64\sim 1.77$ (4H), $1.28\sim 1.48$ (20H), $0.82\sim 0.94$ (6H), which are well consistent with its molecular structure.

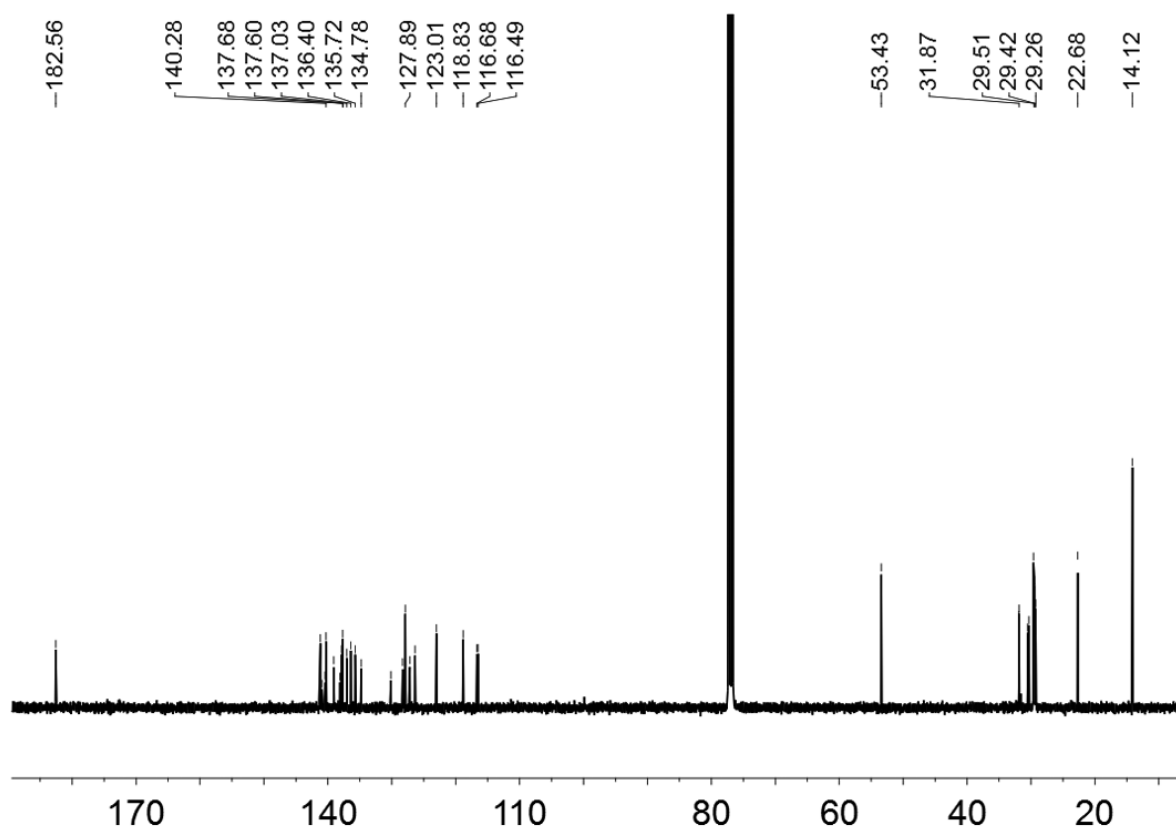


Figure 3.2.3.2.3 ^{13}C NMR spectra of **15** in CDCl_3 .

Figure 3.2.3.2.3 shows the ^{13}C NMR spectra of **15**. The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 182.56, 141.16, 140.92, 140.42, 140.28, 139.08, 138.10, 137.85, 137.68, 137.60, 137.03, 136.40, 135.72, 134.78, 130.14, 128.30, 127.89, 127.19, 126.37, 123.01, 118.83, 116.68, 116.49, 31.89, 31.87, 30.52, 30.33, 29.62, 29.51, 29.45, 29.42, 29.28, 29.26, 22.68, 14.12$. There are 35 carbons can be observed, which is well consistent with the theoretical value.

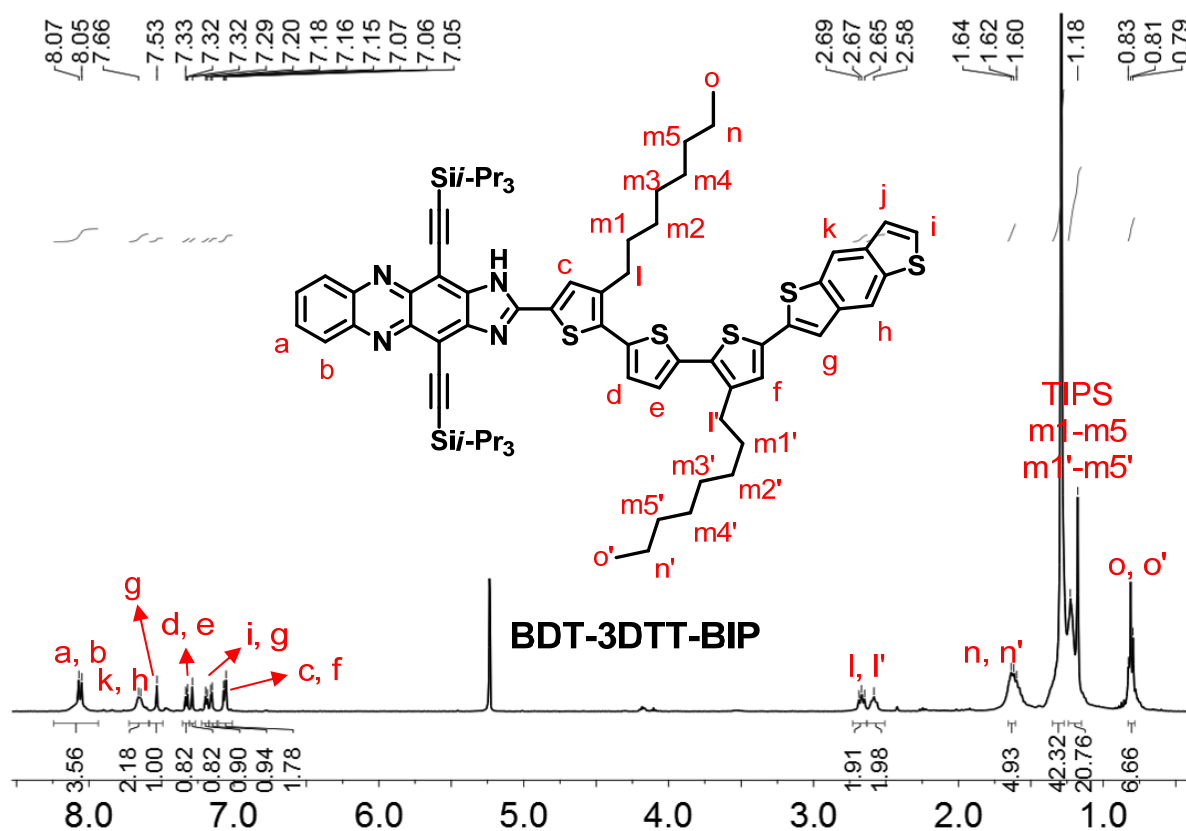


Figure 3.2.3.2.4 ^1H NMR spectra of **BDT-3D TT-BIP** in CD_2Cl_2 .

^1H NMR and ^{13}C NMR spectra of **BDT-3D TT-BIP** were recorded on a JEOL JNM-ECX400 spectrometer in CD_2Cl_2 .

Figure 3.2.3.2.4 shows the ^1H NMR spectra of **BDT-3D TT-BIP** in CD_2Cl_2 , the protons can be indexed as ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{H}} = 9.51\sim 9.92$ (1H), $8.05\sim 8.28$ (4H), $7.71\sim 7.82$ (2H), $7.61\sim 7.67$ (1H), $7.38\sim 7.43$ (1H), $7.34\sim 7.34$ (1H), $7.23\sim 7.29$ (2H), $7.15\sim 7.19$ (1H), $7.11\sim 7.15$ (1H), $2.69\sim 2.83$ (4H), $1.67\sim 1.78$ (4H), $1.23\sim 1.46$ (62H), $0.84\sim 0.93$ (6H), which are well consistent with its molecular structure.

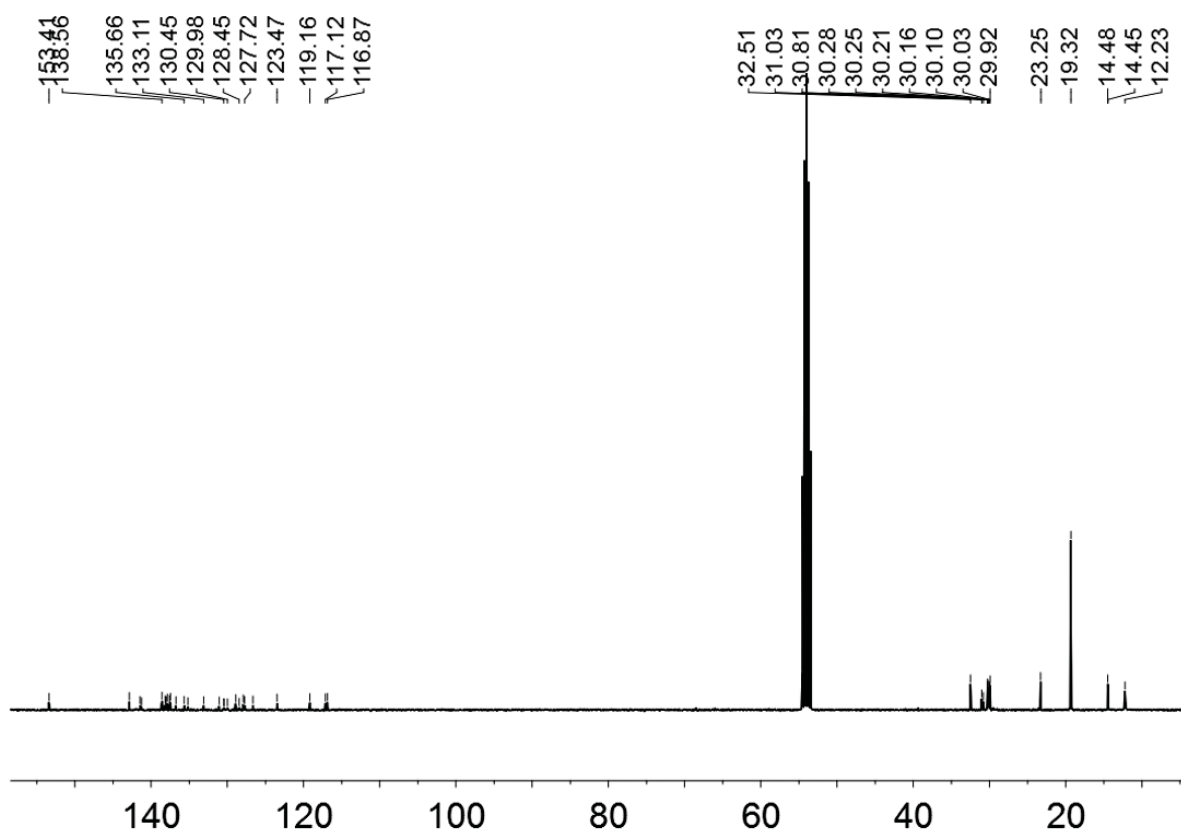


Figure 3.2.3.2.4 ^{13}C NMR spectra of **BDT-3DTT-BIP** in CD_2Cl_2 .

Figure 3.2.3.2.3 shows the ^{13}C NMR spectra of **BDT-3DTT-BIP** in CD_2Cl_2 . The carbons can be indexed as ^{13}C NMR (101 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}} = 153.41, 142.86, 141.44, 141.26, 138.56, 138.16, 138.07, 137.89, 137.62, 137.47, 136.75, 135.66, 135.17, 133.11, 131.08, 130.45, 129.96, 128.91, 128.45, 127.92, 127.72, 126.64, 123.47, 119.16, 117.12, 116.87, 32.51, 31.03, 30.81, 30.28, 30.25, 30.21, 30.16, 30.10, 30.03, 29.92, 23.29, 23.25, 19.32, 14.48, 14.45, 12.23$. There are only 26 carbons can be observed in range of 100–160 ppm, which is 5 carbons less than theoretical value. Maybe certain carbons of **BDT-3DTT-BIP** have no signals in ^{13}C NMR spectra in our experimental conditions.

3.2.3.3 Optical Properties of BDT-3DTT-BIP

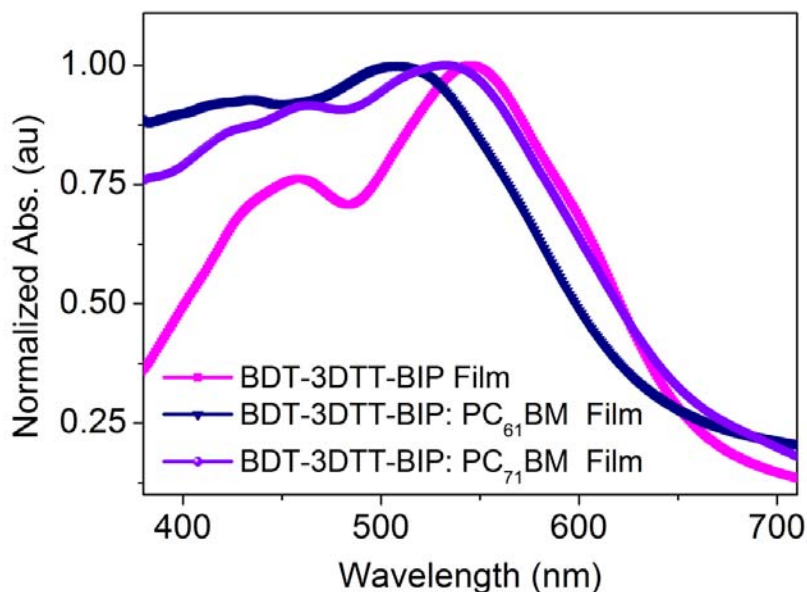


Figure 3.2.3.3.1 Normalized UV-vis absorption spectra of **BDT-3DTT-BIP** film (magenta), **BDT-3DTT-BIP/PC₆₁BM** blended film (navy) & **BDT-3DTT-BIP/PC₇₁BM** blended film (violet).

The optical properties of **BDT-3DTT-BIP** film and its blended films with **PC₆₁BM** or **PC₇₁BM** were investigated by UV-vis absorption spectra recorded on a JASCO UV/VIS/NIR Spectro-photometer V-670. The normalized absorption spectra are shown in Figure 3.2.3.3.1. **BDT-3DTT-BIP** film has two absorption bands in visible region, whose maximum absorption wavelength (λ_{max}) is at 458 nm and 547 nm, respectively. The onset absorption wavelength (λ_{onset}) is 665 nm, which determines the optical band gap (E_g) of 1.86 eV based on the equation illustrated in 2.2.3.4 Optical Properties of TPA-BIP. When blended with **PC₆₁BM** in 1:1 ratio, the λ_{max} at 547 nm is blue-shifted to 508 nm, meanwhile, the λ_{max} of **BDT-3DTT-BIP/PC₇₁BM** blended film in 1:1 ratio also has a blue-shift to 531 nm, which is still 23 nm red-shifted compared to the **BDT-3DTT-BIP/PC₆₁BM** blended film. Thus, the

BDT-3DTT-BIP/PC₇₁BM blended film has a minor wider absorption range and moderate miscibility. Both the two blended films cover a broad range of absorption in visible region from 400 nm to 642 nm, suggesting they might have the potential to obtain high J_{sc} in OPV devices.

3.2.3.4 Electrochemical Properties of BDT-3DTT-BIP

Table 3.2.3.4.1 Statistic ionization potentials of **BDT-3DTT-BIP**.

Samples	1	2	3	4	Average
IP (eV)	-5.37	-5.38	-5.32	-5.32	-5.35

Ionization potential (IP) was evaluated with atmospheric photoelectron spectroscopy (Riken Keiki, AC-3) to investigate the electrochemical properties of **BDT-3DTT-BIP**. Table 3.2.3.4.1 summarizes the statistic IPs, and the average IP is measured to be -5.35 eV, which establishes the HOMO level of **BDT-3DTT-BIP**. The LUMO level is determined to be -3.49 eV from the difference between HOMO level and E_g .

3.2.4 OPV Device Fabrication Based on BDT-3DTT-BIP

The OPV devices were fabricated with a typical BHJ architecture of ITO/anode buffer layer/donor:acceptor/Ca/Al through solution-processing method. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or molybdenum oxide (MoO₃) was adopted as anode buffer layer, and **PC₆₁BM** or **PC₇₁BM** was used as acceptor, respectively. The ITO glass substrates (20.0 mm × 20.0 mm, 15 Ω per square) were pre-cleaned by water Semico clean 56, water, and isopropanol under ultrasonic. After dried on a

hotplate at 120 °C the substrates were treated by UV/O₃ for 20 min, followed by spin-coating of PEDOT:PSS (Clevios P VP AI4083, 200 µL) or MoO₃ solution at 3000 rpm for 30 seconds. The as-prepared anode buffer layer was thermal annealed at 130 °C for 10 min in air. After that, the substrates were transferred to a N₂-filled glove box (O₂ and H₂O < 10 ppm). **BDT-3DTT-BIP/PC₆₁BM** or **BDT-3DTT-BIP/PC₇₁BM** (10 mg/mL, 100 µL) in CHCl₃ were spin-coated on the substrates at 1500 rpm for 30 s. Ca (10 nm) and Al (70 nm) were vapor deposited on the organic layer under high vacuum (1.0×10^{-4} Pa) through a shadow mask, which determined the active area to be 4.0 mm².

3.2.5 OPV Characteristics of BDT-3DTT-BIP

Table 3.2.5.1 ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM**/Ca/Al device parameters with different donor:acceptor ratios.

Donor:Acceptor ratios	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
1:3 (25%)	1.03	0.52	0.26	0.14	412.0	534.0
1:2 (33%)	1.32	0.56	0.22	0.17	479.6	370.3
2:3 (40%)	2.13	0.39	0.26	0.21	156.3	180.2
1:1.2 (45%)	2.63	0.61	0.28	0.45	83.5	284.2
1:1 (50%)	1.43	0.62	0.25	0.22	258.5	435.6
3:2 (60%)	0.54	0.59	0.19	0.06	2103	775.2
2:1 (67%)	0.37	0.71	0.16	0.043	5616	994.4
3:1 (75%)	0.12	0.76	0.16	0.014	16616	3393

The OPV performance of **BDT-3DTT-BIP** is demonstrated by current-voltage (J - V) curves, which were recorded on a Keithley 2611B SYSTEM Source Meter unit under AM 1.5G illumination at the intensity of 100 mW/cm² using a solar simulator (Bunko-keiki, CEP-2000RP). The external quantum efficiency (EQE) was measured under illumination of monochromatic light using the same system at the intensity of 1.25 mW/cm².

The optimized weight ratio of **BIP-3DTT-BDT** to **PC₆₁BM** or **PC₇₁BM** was 1: 1.2, the detailed parameters are summarized in Table 3.2.5.1.

Table 3.2.5.2 ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM** (1:1.2)/Ca/Al device parameters at different annealing temperature.

Annealing temperature (°C)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
non-annealing	2.63	0.61	0.28	0.45	83.5	284.2
85	2.49	0.57	0.28	0.39	103.5	271.3
100	1.32	0.65	0.21	0.18	668	398.9
120	0.53	0.20	0.25	0.03	390.0	358.2
140	0.29	0.58	0.17	0.03	3270	1173
150	0.13	0.50	0.17	0.01	5788	222.8

Thermal annealing has already been proved to be effective for controlling film morphology to facilitate charge carrier separation and transportation, while it did not work well to improve the performance of our devices.^{32,33} When the ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM**/Ca/Al device was thermal treated at 100 °C, the PCE was largely decreased

from 0.45% to 0.18%, the detailed parameters are summarized in Table 3.2.5.2. To further investigate the reason why thermal annealing decreased the PCE of devices, we measured the AFM images of **BDT-3DTT-BIP/PC₆₁BM** blended film in two conditions: without annealing and annealed at 100 °C. After annealing, increased domain size in film were observed, which could decrease the exciton dissociation at the donor:acceptor interfaces due to the reduced interface area. This phenomenon was consistent with the decreased J_{sc} of device after annealed at 100 °C.

Table 3.2.5.3 ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM** (1:1.2)/Ca/Al device parameters with different **DIO** concentration.

DIO concentration (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
0	2.63	0.61	0.28	0.45	83.5	284.2
0.1	3.18	0.58	0.28	0.51	103.8	233.6
0.2	2.06	0.47	0.31	0.30	72.4	306.9
0.5	4.42	0.57	0.36	0.90	37.2	273.1
1	-	-	-	-	-	-

1,8-diiodooctane (**DIO**) was added to the mixed donor:acceptor solutions and might enhance the crystallization of **BDT-3DTT-BIP**.³⁴ The PCE of ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM**/Ca/Al device with 0.5 % **DIO** addition by volume was double enhanced from 0.45% to 0.9% compared to the device without **DIO** addition, the detailed parameters are summarized in Table 3.2.5.3.

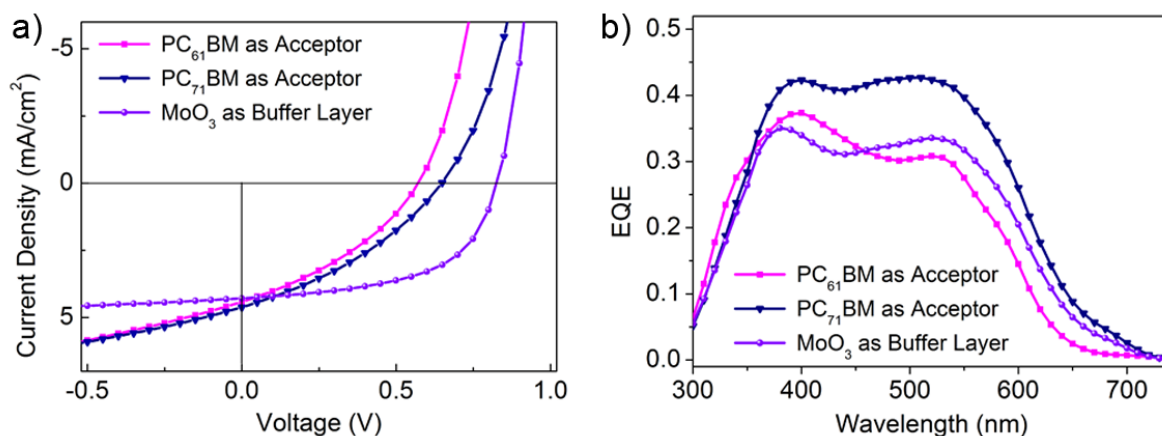


Figure 3.2.5.1 a) J - V curves and b) EQE plots of the ITO/PEDOT:PSS/BDT-3DTT-BIP:PC₆₁BM/Ca/Al device (square), ITO/PEDOT:PSS/BDT-3DTT-BIP:PC₇₁BM/Ca/Al device (triangle), and ITO/MoO₃/BDT-3DTT-BIP:PC₇₁BM/Ca/Al device (sphere).

The OPV devices were further optimized by using PC₇₁BM as acceptor and MoO₃ as anode buffer layer. The ITO/MoO₃/BDT-3DTT-BIP:PC₇₁BM/Ca/Al device displayed the ultimate performance with PCE up to 1.97%. Table 3.2.5.4 summarizes the optimal performance parameters of the ITO/PEDOT:PSS/BDT-3DTT-BIP:PC₆₁BM (or PC₇₁BM)/Ca/Al devices. Figure 3.2.5.1 a) shows the J - V curves of three types of optimized devices with different anode buffer layer or acceptors. The ITO/PEDOT:PSS/BDT-3DTT-BIP:PC₆₁BM/Ca/Al device with 0.5 % DIO addition by volume has an optimized PCE of 0.90% with a J_{sc} of 4.42 mA/cm^2 , a V_{oc} of 0.57 V, and a FF of 0.36, respectively. In the same optimized conditions, when the acceptor is replaced by PC₇₁BM, the J_{sc} , V_{oc} , and PCE have a minor increase, probably resulting from the improved absorption of PC₇₁BM in visible region, while the FF has little change. The device is further optimized by changing anode buffer layer from PEDOT:PSS to MoO₃, which shows a PCE of 1.97%, increased by 89.4%. Although the J_{sc} has a minor decrease, the V_{oc} is increased by 26%, which is probably from the more alignment of working function of MoO₃ (HOMO level in the range of -5.3 to -5.7 eV) with

the HOMO level of **BDT-3DTT-BIP**.³⁵ The FF also has a large increase by 60%. The enhancement is probably coming from the reduced chemical interaction between **BDT-3DTT-BIP** and anode buffer layer, because the N atoms in **BIP** can react with the acidic PEDOT:PSS, which thus decreases the OPV performance.³⁵⁻³⁷

The EQE plots of the as-fabricated devices were investigated and the corresponded plots are shown in Figure 3.2.5.1 b). ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM**/Ca/Al device has high conversion of absorption (EQE > 10%) from 309 nm to 611 nm, with two maximum EQE value at 396 nm (37%) and 521 nm (31%), respectively. As **PC₇₁BM** is used as acceptor, the range of high photon conversion (EQE > 10%) is expanded from 311 nm to 644 nm, which is 31 nm broader than the device with **PC₆₁BM** as acceptor. The larger photo conversion range is corresponded to the broader absorption of **BDT-3DTT-BIP/PC₇₁BM** blended film and the higher J_{sc} in $J-V$ curves of ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₇₁BM**/Ca/Al device. The maximum EQE values are increased to 42% at 399 nm and 43% at 508 nm, respectively. Keeping **PC₇₁BM** as acceptor, when the anode buffer layer is replaced with MoO₃, the EQE curves show similar tendency but with decreased EQE at 35% (384 nm) and 34% (522 nm), respectively. The higher EQE efficiency of ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₇₁BM**/Ca/Al device probably results from the existence of leakage current in the dark.

Table 3.2.5.4 Optimal performance parameters of the ITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM** (or **PC₇₁BM**)/Ca/Al devices.

Devices	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PC₆₁BM as acceptor ^a	0.61	2.63	0.28	0.45
PC₆₁BM as acceptor ^b	0.65	1.32	0.21	0.18
PC₆₁BM as acceptor ^c	0.57	4.42	0.36	0.90
PC₇₁BM as acceptor ^d	0.65	4.62	0.35	1.04
MoO ₃ as buffer layer ^e	0.82	4.29	0.56	1.97

^aITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM**/Ca/Al device without **DIO** addition and thermal annealing.

^bITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM** /Ca/Al device without **DIO** addition and annealed at 100 °C.

^cITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₆₁BM** /Ca/Al device with 0.5% **DIO** addition and without thermal annealing.

^dITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₇₁BM**//Ca/Al device with 0.5% **DIO** addition and without thermal annealing.

^eITO/PEDOT:PSS/**BDT-3DTT-BIP:PC₇₁BM**/Ca/Al device with 0.5% **DIO** addition and without thermal annealing.

3.2.6 Results Discussion

3.2.6.1 Molecular Calculation

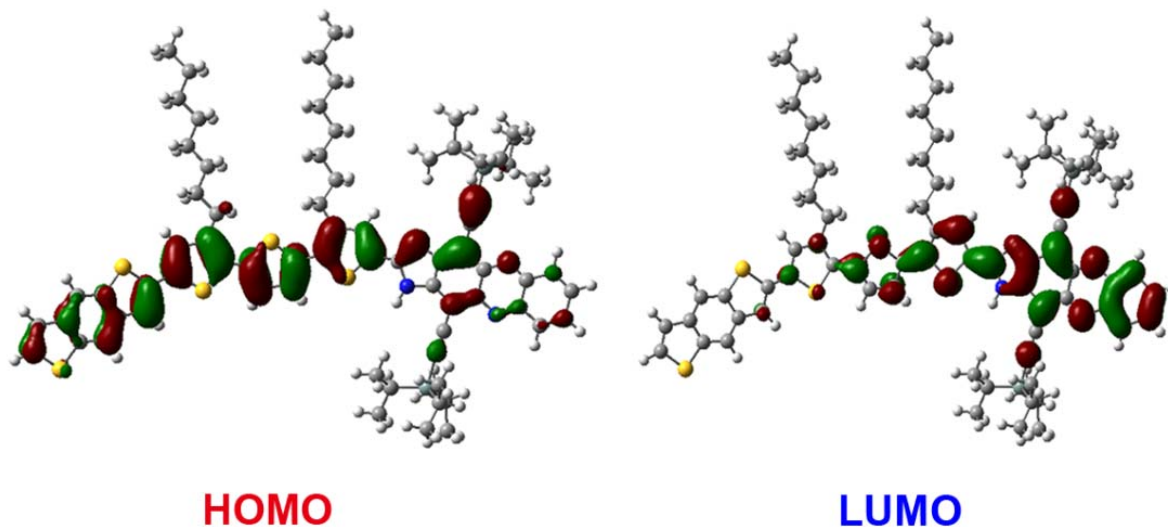


Figure 3.2.6.1.1 Electron density distribution of HOMO & LUMO levels of **BDT-3DTT-BIP**.

Molecular calculation was carried out to study the intrinsic molecular configuration and electron density distribution of **BDT-3DTT-BIP** in same method with **TPA-2BIP** & **TPA-3BIP** illustrated in 2.3.6 Mechanism Discussion.^{38,39} As shown in Figure 3.2.6.1.1, the optimized structure of **BDT-3DTT-BIP** shows a broad “V” shape conformation, and the two octyl chains are in the same side. The HOMO coefficient is distributed on the **BDT** and **3DTT** units, while LUMO coefficient is mainly located on the **BIP** moiety. The calculated molecular ground state dipole moment is 4.90 D, which is also consistent with the electron density distribution of HOMO and LUMO levels. The stronger intramolecular charge transfer can facilitate the charge separation at the donor:acceptor interfaces, thus improve the OPV performance.

3.2.6.2 Morphology Analysis

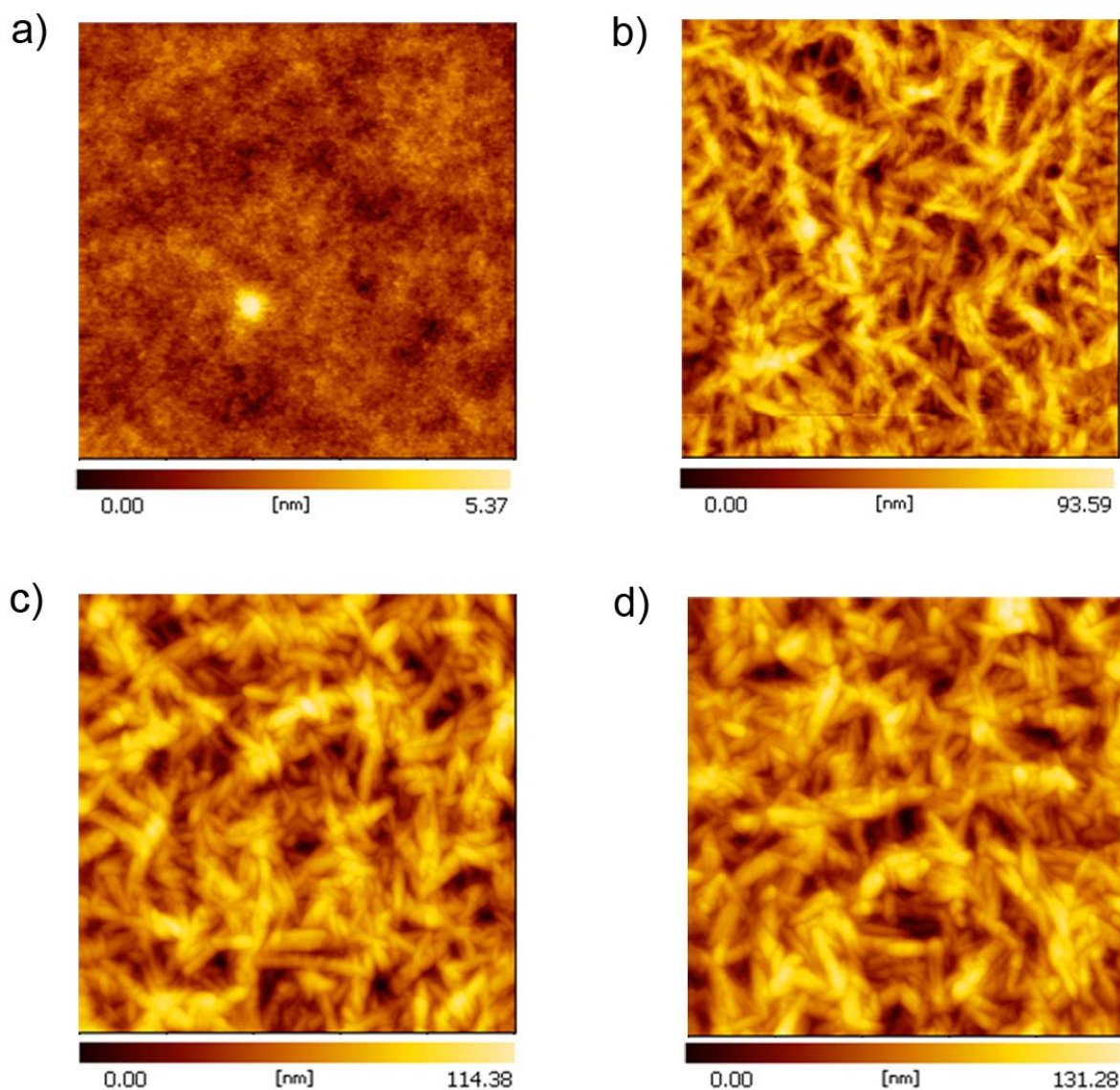


Figure 3.2.6.2.1 AFM images of a) **BDT-3DTT-BIP/PC₆₁BM** blended film without **DIO**, b) **BDT-3DTT-BIP/PC₆₁BM** blended film with **DIO**, c) **BDT-3DTT-BIP/PC₇₁BM** blended film with **DIO**, d) **BDT-3DTT-BIP/PC₇₁BM** blended film with **DIO** and MoO₃ buffer layer.

The morphology analysis of the corresponding films was investigated by SPA400, SPI3800N AFM (Seiko instruments Inc.) in tapping mode using silicon probes with a resonant

frequency of ~ 138 kHz and a force constant of 16 N m^{-1} . As shown in Figure 3.2.6.2.1 a), when **BDT-3DTT-BIP/PC₆₁BM** blended film spin-coated on ITO/PEDOT:PSS substrate without the addition of **DIO**, the film is smooth and well continuous with a small roughness (RMS = 0.48 nm). As **DIO** is added, the film shows a large increase of RMS from 0.48 nm to 15 nm (Figure 3.2.6.2.1 b)). The increased domain size and crystallinity of blended film can be observed and possibly enhance the charge carrier's transportation, thus contribute to the improved J_{sc} (from 2.63 to 4.42 mA/cm^2) and FF (from 28% to 36%). Meanwhile, the **BDT-3DTT-BIP/PC₇₁BM** blended films on ITO/PEDOT:PSS or ITO/MoO₃ substrate (Figure 3.2.6.2.1 c) & (d)) show similar morphologies with close roughness after adding **DIO** (RMS = 18.2 nm and RMS = 20.2 nm, respectively). The performance enhancement of ITO/MoO₃/**BDT-3DTT-BIP:PC₇₁BM**/Ca/Al device might have little relevance to the morphology.

3.2.6.3 XRD Patterns Analysis

The out-of-plane XRD patterns of the corresponding films was collected on a RINT-TTRIII/NM diffractometer equipped with a rotating anode (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). As shown in Figure 3.2.6.3.1, the **BDT-3DTT-BIP/PC₆₁BM** blended film shows no diffraction peak. After adding **DIO**, a diffraction peak at $2\theta = \text{ca. } 4.6^\circ$ can be observed, which is corresponding to the d_{100} spacing value (the distance between the planes of the major conjugated backbone separated by the longer alkyl chain (C₈H₁₇) of 19.3 $\text{\AA}$.⁴⁰ The obvious XRD peak suggests that highly organized assembly of **BDT-3DTT-BIP** molecules after adding the **DIO**. The **BDT-3DTT-BIP/PC₇₁BM** blended film shows similar diffraction peak position when **DIO** is added, but the peak is much sharper than **BDT-3DTT-BIP/PC₆₁BM** blended film, suggesting it has higher crystallinity.

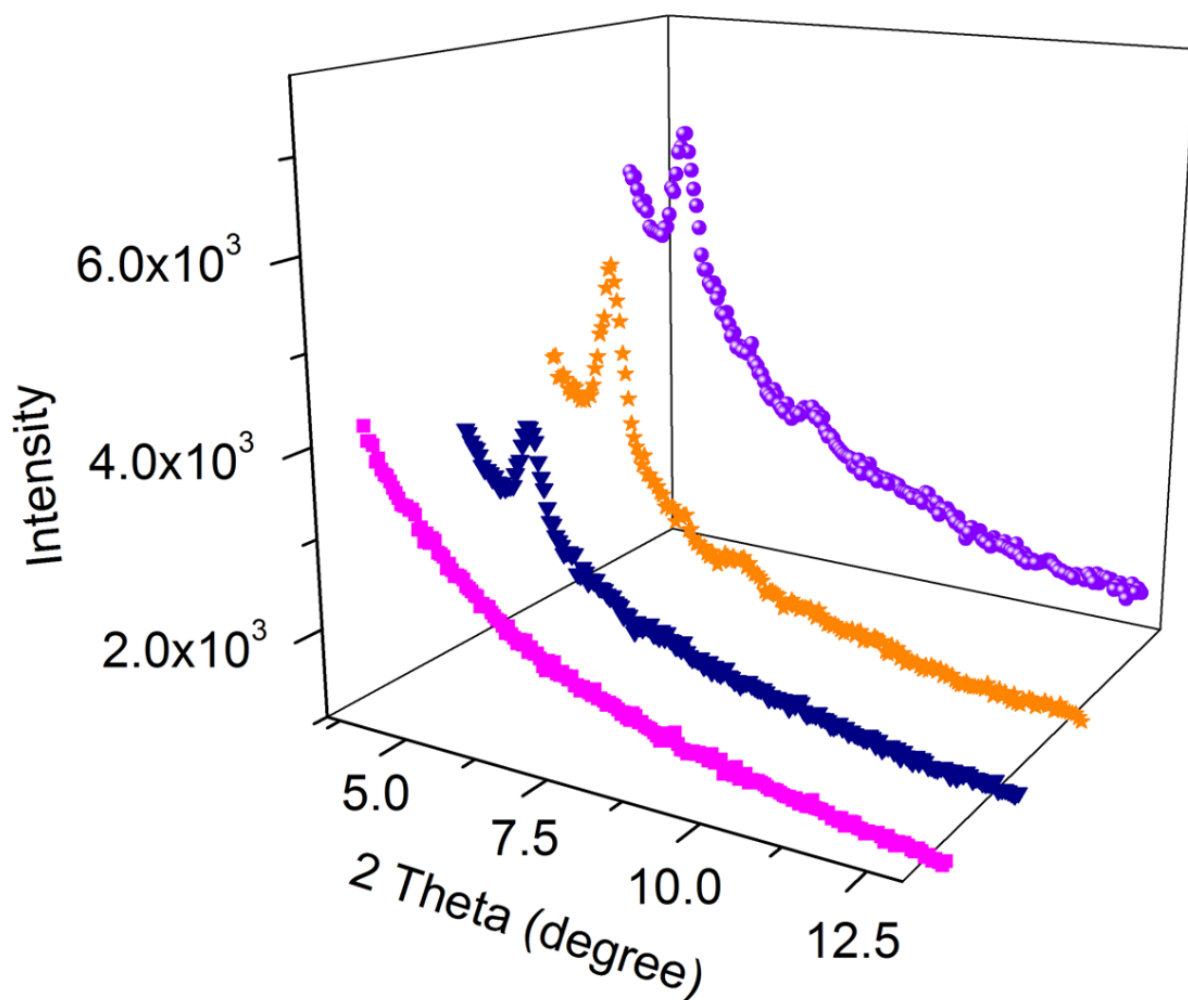


Figure 3.2.6.3.1 XRD patterns of corresponding films (magenta: **BDT-3DTT-BIP/PC₆₁BM** blended film without **DIO**, navy: **BDT-3DTT-BIP/PC₆₁BM** blended film with **DIO**, orange: **BDT-3DTT-BIP/PC₇₁BM** blended film with **DIO** on PEDOT:PSS, violet: **BDT-3DTT-BIP/PC₇₁BM** blended film with **DIO** on MoO₃).

When anode buffer layer (PEDOT:PSS) is changed to MoO₃, a peak in same position can be observed with a minor decreased sharpness. In previous study, people has already demonstrated that the donor molecules have stronger nucleation and crystallinity on PEDOT:PSS surface because of certain interactions, which explains the lower crystallinity of **BDT-3DTT-BIP/PC₇₁BM** blended film on MoO₃ surface.⁴¹ The enhanced PCE probably

mainly comes from the more aligned energy level and reduced chemical reaction between active layer and anode buffer layer.

Compared with the highest record in recent advances, there is a gap of efficiency for **BDT-3DTT-BIP** with PCE ~2%. From the analysis of AFM images (Figure 3.2.6.2.1), the surface of the active layer is in high roughness. The rough surface could induce bad contact between the electrodes and active layer, which was not favor for the transportation and collection of the separated charge carriers. This result corresponded to the increased intensity of (100) peak in Figure 3.2.6.3.1, which proved that the crystallinity of **BDT-3DTT-BIP** was enhanced after adding **DIO**. The above discussion might explain the relatively low J_{sc} and PCE of **BDT-3DTT-BIP** based OPV devices, which was mainly ascribed to the excessive crystalization of **BDT-3DTT-BIP**.

3.2.7 Summary

In summary, a novel D- π -A small molecule **BDT-3DTT-BIP** with an *N*-heteroacene as acceptor moiety has been synthesized and characterised. The standard BHJ structure OPV devices are investigated through solution-processing method with different acceptor materials and different anode buffer layers. The ultimate performance is achieved by using **PC₇₁BM** as acceptor and MoO₃ as anode buffer layer, the optimised PCE is 1.97%. AFM images and XRD patterns indicates the anode buffer layer has no obvious influence on film morphologies, and combining with the J - V curves and EQE plots, the more aligned working function of anode buffer layer and reduced chemical interactions between buffer layer and active layer play an important role to enhance the PCE of the devices.

3.3 References

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Chapter 4

N-heteroacenes for Organic Field-effect Transistors

4.1 Literature Review

There has been a lot of research on the investigation of novel *n*-type OFET materials. However, currently there are few of *n*-type materials that can achieve comparable field-effect mobilities in contrast to the well-developed *p*-type semiconductors. Another limitation of today's development of *n*-type materials is their poor operational stability in air conditions. Therefore, much attention has been attracted for developing novel air-stable high performance *n*-type materials. In this part, the representative *n*-type materials with electron mobilities up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions will be reviewed.

Naphthalene diimides (**NDIs**) and perylene tetracarboxylic diimides (**PDI**s) are famous well-investigated *n*-type materials with high electron mobilities and good air stability. The *n*-type OFETs based on **NDIs** were firstly reported in 1996 with electron mobility up to $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under vacuum. When the devices were exposed to air, 1–2 order of magnitude decrease of electron mobility was observed.¹ Figure 4.1.1 shows the molecular structures of the representative **NDIs** and **PDI**s derivatives with *n*-type performance, whose electron mobilities are up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and Table 4.1.1 summarizes their principal OFET performance parameters.

One of the most successful *n*-type **NDIs** derivatives was molecule **1**, whose hydrogen atoms at *NH* positions were substituted by alkyls or other groups. Shukla and coworkers reported the OFETs based on **1**. When the devices were measured under continuous stream Argon

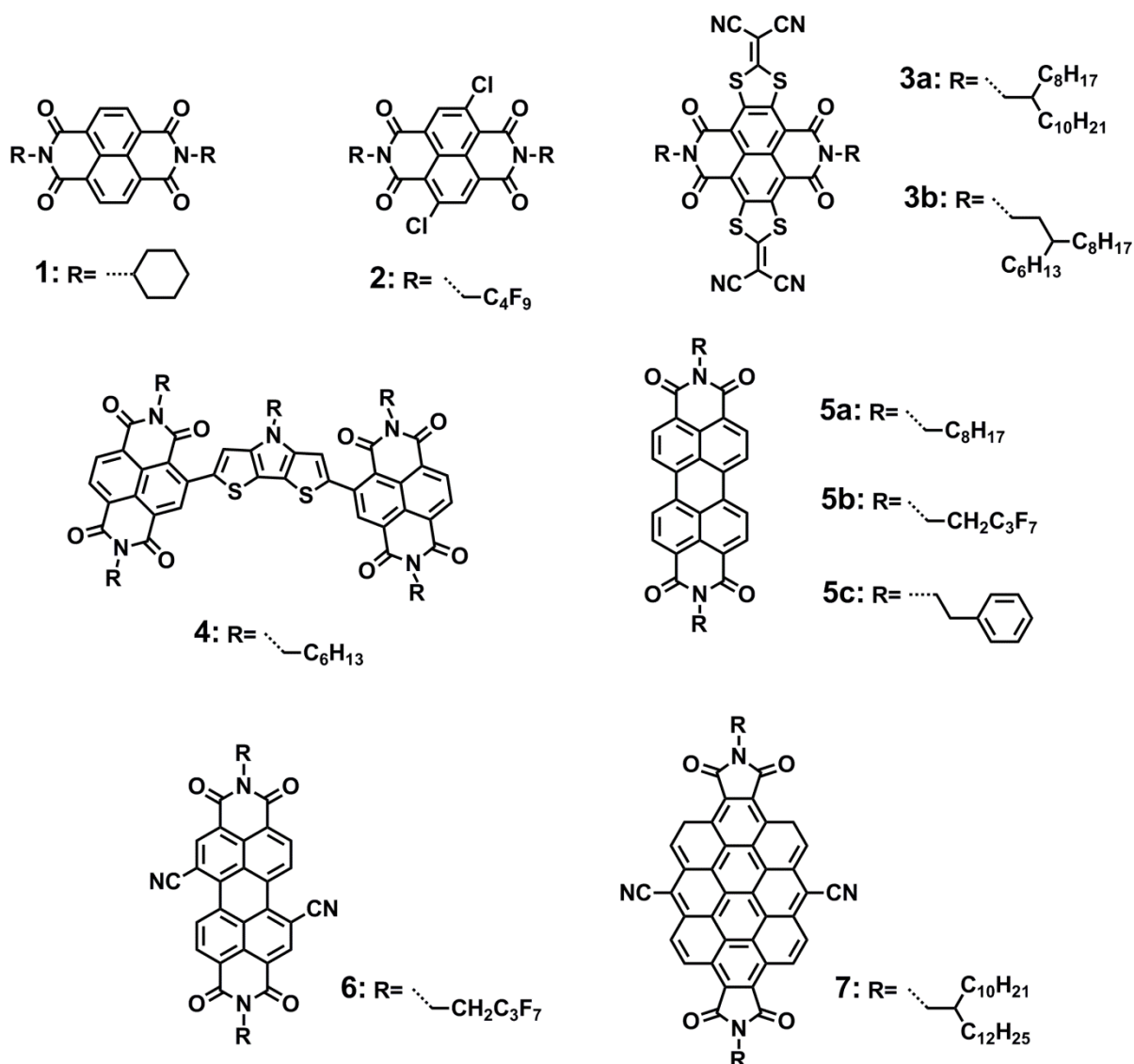


Figure 4.1.1 Molecular structures of the representative **NDIs** and **PDIs** derivatives.

atmosphere, high electron mobility up to $6.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an ON/OFF ratio of 6×10^8 were achieved. However, when the devices were tested under ambient conditions, the high electron mobility was significantly decreased to $0.41 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The authors believed that with the cyclohexyl groups substituted at *N* position high crystalline packing and good thin film morphology could be achieved in solid state of **1**, which contributed to the high *n*-channel performance.² Compound **2** with chlorine at the naphthalene core and fluorinated

Table 4.1.1 Summarized OFET performance parameters of the representative **NDIs** & **PDI**s derivatives. *Measured under ambient conditions.

Molecules	Fabrication process	Max mobility (cm ² V ⁻¹ s ⁻¹)	ON/OFF ratio	V _{TH} (V)
1	Evaporation	6.2	10 ⁸	58
2	Solution	4.26*	10 ⁶	18
3a	Spin coating	1.2	10 ⁸	-4.8 to 6.2
3b	Spin coating	3.5	10 ⁸	-2.5
4	Spin coating	1.5		13
5a	Evaporation	1.7	10 ⁷	10–15
5b	Nanowire	1.4		
5c	Evaporation	1.44	10 ⁵	14–29
		1.24*	10 ⁶	28–43
6	Solution	1.3		-8
	Crystal	6		
		3*		
	Crystal	5.1 (290K)		
		10.8(230K)		
7	Spin coating	1.0	10 ⁵	-15
		0.51*	10 ⁴	4–40

chains in sides was another successful *n*-type **NDIs** derivative. **2** showed excellent electron transporting properties in ambient conditions with mobility up to $4.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and ON/OFF ratio of 5×10^5 under bias stress.³ It was noteworthy that the high performance OFET devices were fabricated by an easily accessible solution shearing method. Core-expanded **NDIs** derivatives were also charming *n*-type materials with high electron mobilities and good stability. The expanded conjugation could enhance the neighboring molecular stacking, and the strong electron-deficient characteristics could lower the LUMO levels efficiently, which potentially contributed to high electron mobility and good environmental stability. Compound **3a**, which was processed by spin-coating method exhibited electron mobility up to $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an ON/OFF ratio of 10^8 .⁴ **3a** showed excellent air stability that it could even be annealed in ambient conditions. It was proposed that the low LUMO level (-4.3 eV) and close π - π stacking of **3a** accounted for the excellent air-stable *n*-type performance. Recently, a similar core-expanded **NDIs** derivative **3b** was synthesized and it showed excellent air-stable electron transporting property as well, whose mobility was up to $3.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a ON/OFF ratio of $\sim 10^8$.⁵ As **NDIs** was introduced to ambipolar semiconducting materials, high electron mobility could be still achieved. A typical ambipolar compound **4** was reported with two **NDIs** linked by an electron-rich donor unit in 2012, which owned electron mobility up to $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in N_2 and hole mobility of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶

PDIs were reported as *n*-type materials in the same year with **NDIs** in 1996 by Horowitz et al.⁷ Similarly, the alkyls substituted **PDIs** in *N* position were charming candidates for high performance *n*-channel OFETs. Compound **5a** could be easily synthesized by combining **PDIs** backbone and octyl chains. The highest electron mobility of optimized OFET devices with **5a**

as active layer was $1.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an ON/OFF ratio of 10^7 when tested under a partial pressure of H_2 (10^{-4} Torr).⁸ However, when the devices were measured in ambient conditions the electron mobility decreased to $0.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The electron mobility under air could be improved to $0.67 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ if the substrates were changed to polymethylmethacrylate (**PMMA**) and cyclic olefin copolymer (**COC**) coated Si/SiO₂.^{8,9} Another **PDI**s derivative **5b** with phenylethyls as side chains also displayed air-stable *n*-channel performance with an electron mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in thin film OFETs. The electron mobility was increased to $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ if **5b** was prepared as nanowires.¹⁰ **PDI**s could also be functionalized by fluorinated alkyls, in which situation **5c** was obtained. The OFETs based on **5c** showed electron mobility of $1.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under vacuum. It was noteworthy that the devices had little degradation when tested in air and the electron mobility could still maintain high value at $1.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹¹ Molecule **6** was a famous *n*-type semiconductor, and the two cyano groups attached to the backbone of **PDI** core could efficiently lower its LUMO level. Highly crystalline films of **6** were obtained on the triethoxy-1*H*,1*H*,2*H*,2*H*-tridecafluoron-octylsilane treated gate dielectrics. The OFET devices fabricated through solution-processing method achieved high electron mobility up to $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ambient conditions.¹² Furthermore, single-crystal OFETs based on **6** were also fabricated, and the electron mobility reached $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum. When the devices were measured in air, a minor decrease but still excellent electron mobility of $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was investigated.¹³ In another work, single-crystal OFETs of **6** with a vacuum-gap also showed high electron mobility of $5.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In this situation the *n*-channel performance was temperature-dependant and as the measurement temperature decreased from 290 K to 230 K, the electron mobility increased from $5.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $10.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Interestingly, the devices displayed a band-like electron transporting characteristics.¹⁴ Recently, large disc-like ovalene diimides **7** was designed for *n*-type OFETs.

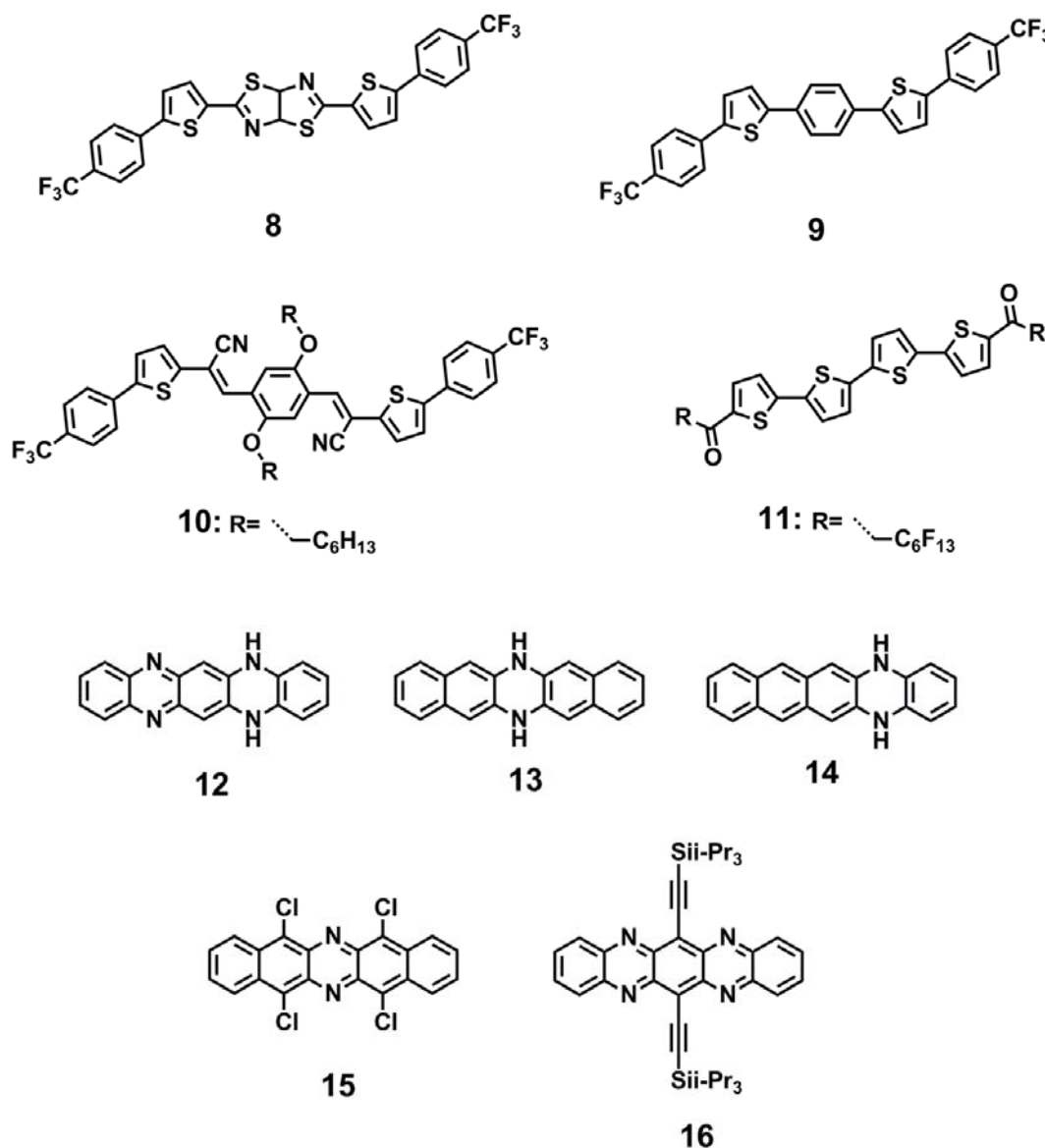


Figure 4.1.2 Molecular structures of the representative oligoacenes.

The electron mobilities of the as-fabricated devices reached $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum and $0.51 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in air, which were one of the best records for solution-processed *n*-channel OFETs.¹⁵

Oligoacenes are a large family of organic semiconducting materials for OFETs. Figure 4.1.2 shows the molecular structures of representative oligoacenes, and Table 4.1.2 summarizes the

corresponding OFETs parameters. Thiophene based oligoacenes are famous *p*-type semiconductors, while when certain electron-withdrawing groups are connected on their backbone they can be switched to *n*-type materials. Compound **8** had a simple structure with two electron-withdrawing trifluoromethyl groups at the ending of thiophenes. The OFETs based on **8** showed high electron mobility of $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on bare SiO_2 substrate, which could be further increased to $1.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the substrate was modified by trichloro(octadecyl)silane (**OTS**). However, the threshold voltage of the devices was in range of 63–67 V, making them power consuming.¹⁶ **9** was another trifluoromethyl group modified thiophene based *n*-type molecule. The thin film OFETs based on **9** exhibited electron mobility of $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and that of the corresponding single-crystal devices was up to $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum.¹⁷ As more electron-withdrawing groups such as cyano groups were introduced, compound **10** was designed and the enhanced molecular stacking and lower LUMO level was expected. High electron mobility of **10** up to $2.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with ON/OFF ratio of 10^7 were obtained for devices fabricated by evaporation method.¹⁸ Molecule **11** utilized long fluorinated hexyl chains as electron-withdrawing groups to lower the LUMO level of molecule. The electron mobility of OFETs based on **11** was up to $4.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on the polystyrene (**PS**) modified Si/SiO₂ substrate in N₂ atmosphere.¹⁹

N-heteroacenes have also been investigated as *n*-type semiconductors. Actually, the development of N-heteroacenes has a long history of more than 100 years. The earliest document referred N-heteroacene was 5,14-dihydro-5,7,12,14-tetraazapentacene **12**,²⁰ which was synthesized by Fischer and Hepp in 1890. Later, 6,13-dihydro-6,13-diazapentacene **13** was reported by Hinsberg in 1901.²¹ Although these N-heteroacenes was firstly reported in 19th century, their semiconducting properties had not been efficiently investigated for about

Table 4.1.2 Summarized OFET performance parameters of the representative oligoacenes.

*Measured under ambient conditions.

Molecules	Fabrication process	Max mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	ON/OFF ratio	V_{TH} (V)
8	Evaporation	1.2	10^7	63
9	Crystal	3.1		
10	Evaporation	2.14	10^7	34
11	Evaporation	4.6		
15	Crystal	3.39	10^4	
16	Evaporation	3.3		
		0.5*		

100 years. In 2003, Nuckolls' team reported the breakthrough discovery, in which **13** and **14** were demonstrated to be *p*-type organic semiconductors, although the hole mobility of their corresponding OFET devices only reached 5×10^{-5} and $6 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively.²² After that, similar semiconducting property of **12** was also investigated with the mobility of $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.²³ The initial findings of these compounds inspired researchers a lot and more compounds were designed and synthesized. A pentacene analogue compound **15** was reported with a pyrazine ring in the center of molecule. Single-crystal OFET devices based on **15** with graphite as electrodes exhibited high electron mobility up to $3.39 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in ambient conditions.²⁴ A soluble 6,13-bis(triisopropylsilyl)ethynylpentacene (**TIPS-PEN**) analogue **16** was developed by Miao's group, which showed charming *n*-type performance. The OFET devices based on **16** fabricated by thermal evaporation process showed high

electron mobility in range of 1.0–3.3 cm² V⁻¹ s⁻¹ under vacuum. When measured in air the electron mobility had around 1 order decrease.²⁵ These successes strongly encourage us and we believe more inspiring discoveries can be expected on the development of *N*-heteroacenes in the applications of OFETs.

4.2 Large *N*-heteroacenes for Air-stable *n*-type OFETs

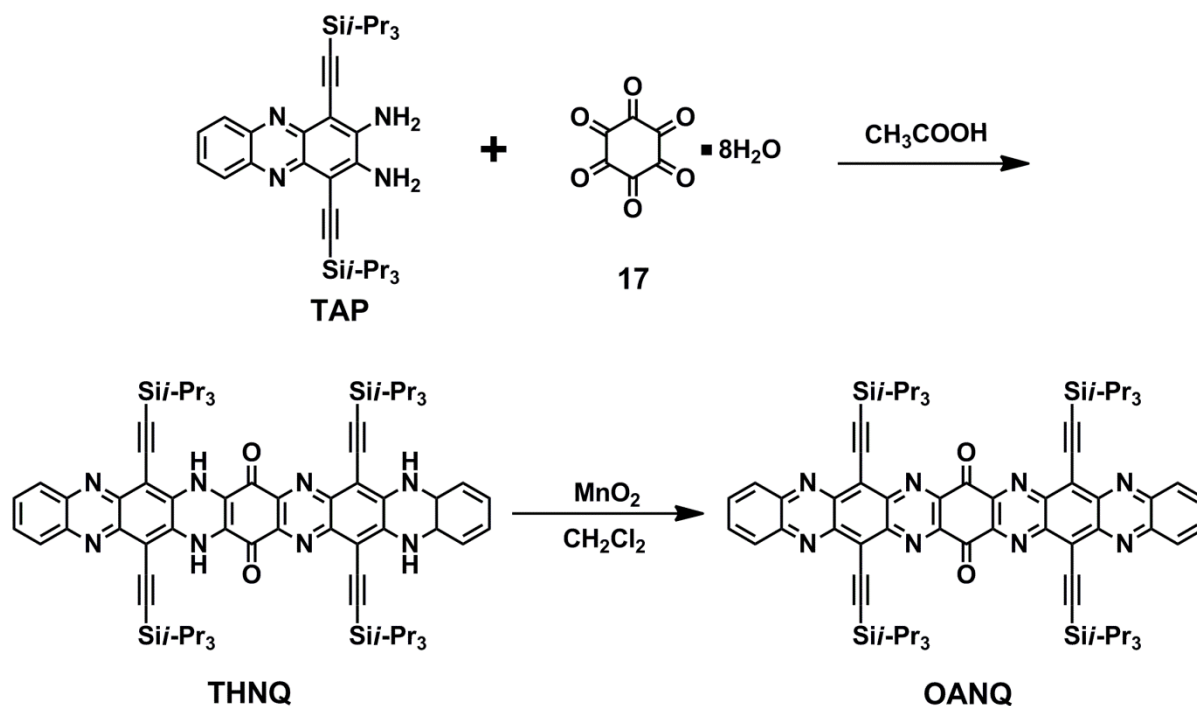
4.2.1 Molecular Design

As the length of *N*-heteroacenes increases, the molecules become more and more unstable, thus, it is very challenging to balance the conjugation and stability of large *N*-heteroacenes. In the study of the *C*-*C* bond in quinone structure, people have found that the bonds have different length, which indicates that quinone is not aromatic system like acenes. Thus, large conjugated *N*-heteroquinones should have moderate conjugation levels compared to the corresponding parent *N*-heteroacenes. In this part large linearly-fused *N*-heteroquinones owning relatively moderate conjugation level are proposed to break the deadlock of instability of large *N*-heteroacenes. The large π -conjugated backbone in *N*-heteroquinones can be constructed to induce strong π - π interaction and π -overlap between adjacent molecules, contributing to efficient electron transport. Moreover, more *N* atoms can be introduced to the as-prepared *N*-heteroquinones to lower the LUMO level to achieve air-stable electron transporting property. In addition, the moderate conjugation might be in favor of good stability when *N*-heteroquinones are exposed to ambient conditions. Considering all the advantages, we propose a large *N*-heteroquinone 6,10,17,21-tetra-((triisopropylsilyl)ethynyl)-5,7,9,11,16,18,20,22-octaazanonacene-8,19-dione (**OANQ**) with 8 *N* atoms doped in the backbone. The as-prepared **OANQ** is expected to own good electron-transporting ability and

good operational stability under air conditions.

It is noteworthy that the synthetic convenience of **OANQ** should be taken into consideration in molecule design. There has been intense of investigation on the reaction between *ortho*-diamine based acenes and hexaketocyclohexane octahydrate (**HKCO**). Generally, people get star-shape products, in which case all the carbonyl groups totally react with amino groups. In this research we plan to use **TAP** as the starting *ortho*-diamine based acenes, and we believe that because of the steric effect of **TIPS** substitutes, **TAP** might mainly attack **HKCO** from para-positions to produce a linear-fused *N*-heteroquinone.

4.2.2 Synthesis of OANQ



Scheme 4.2.2.1 Synthetic route for **OANQ**.

The synthesis of **TAP** has been illustrated in 2.2.2 Synthesis of TPA-BIP. The synthetic route for **OANQ** is illustrated in Scheme 4.2.2.1. Firstly, the intermediate 6,10,17,21-tetra-

((triisopropylsilyl)ethynyl)-5,9,18,22-tetrahydro-5,7,9,11,16,18,20,22-octaazanonacene-9,10-dione (**THNQ**) was obtained as main product, which strongly verified our hypothesis. The further oxidation of **THNQ** with MnO_2 in CH_2Cl_2 could give **OANQ** as dark green powder in 91.1% yield.

Synthesis of **THNQ**

In a round bottom flask, **TAP** (583.5 mg, 1.02 mmol) and **HKCO** (150.8 mg, 0.48 mmol) were dissolved in acetic acid (20 mL), and the system was heated to reflux under Argon atmosphere for 48 hours. After that, the system was cooled down to room temperature and the solution was poured into iced water. After filtration, the solid residue was obtained as crude product. The pure **THNQ** was afforded as dark blue powder (129.7 mg) by further purifying crude product by flash column chromatography over silica gel with ethyl acetate (EtOAc) and hexane (EtOAc: hexane = 1: 10) in yield of 21.7%.

Synthesis of **OANQ**

In a round bottom flask, **THNQ** (94 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (5 mL), excess of activated MnO_2 was added and the system was stirred for 2 hours at room temperature. After that MnO_2 was removed by filtering mixture through silica gel. The solvents were evaporated to get crude product, and the pure **OANQ** (82 mg) was obtained as dark green powder with further purification by flash column chromatography with CH_2Cl_2 and hexane (CH_2Cl_2 : hexane = 5: 1) in yield of 91.1 %.

4.2.3 Molecular Characterization

The compounds **THNQ** and **OANQ** have been characterised by HR MS, NMR and X-ray

crystallographic analysis.

4.2.3.1 HR MS Analysis

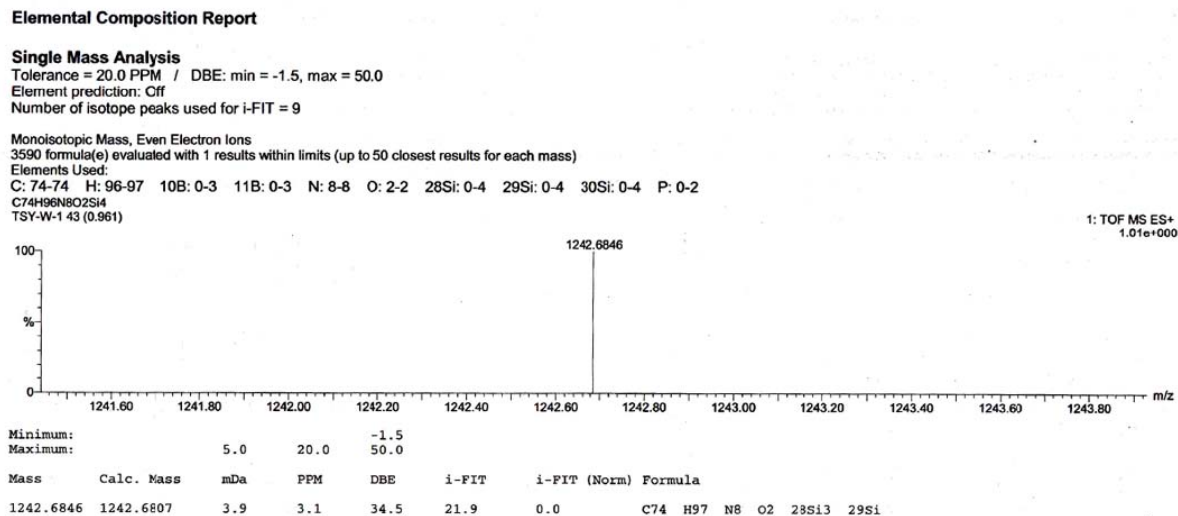


Figure 4.2.3.1.1 HR MS (ESI) spectra of **THNQ**.

HR MS (ESI) spectra of **THNQ** and **OANQ** were recorded on a Waters Q-ToF premierTM mass spectrometer.

The chemical formula of **THNQ** is C₇₄H₉₆O₂N₈Si₄. As shown in Figure 4.2.3.1.1, the calculated m/z value for $[M+1]^+$ of **THNQ** is 1242.3807, and the actual m/z value for that found in spectra is 1242.6846, which is well consistent with the calculated result.

The chemical formula of **OANQ** is C₇₄H₉₂O₂N₈Si₄. As shown in Figure 4.2.3.1.2, the calculated m/z value for $[M+1]^+$ of **OANQ** is 1238.6494, and the actual m/z value for that found in spectra is 1238.6563, which is well consistent with the calculated result.

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions

3749 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 74-74 H: 92-97 10B: 0-3 11B: 0-3 N: 8-8 O: 2-2 28Si: 0-4 29Si: 0-4 30Si: 0-4 P: 0-2

C74H96N8O2Si4

TSY-W-1 12 (0.277)

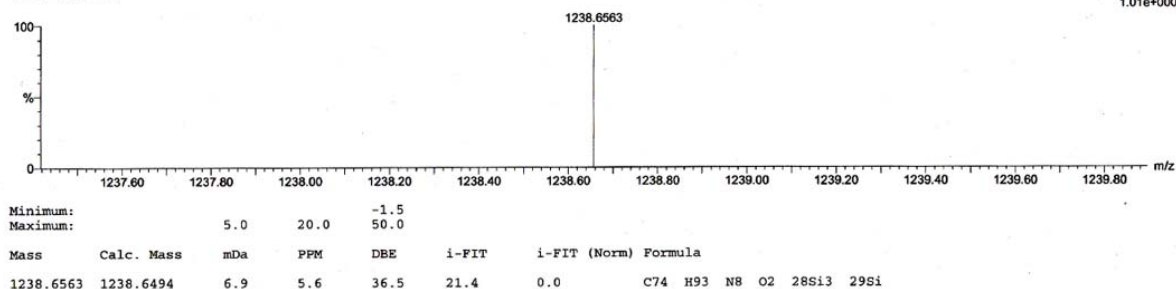
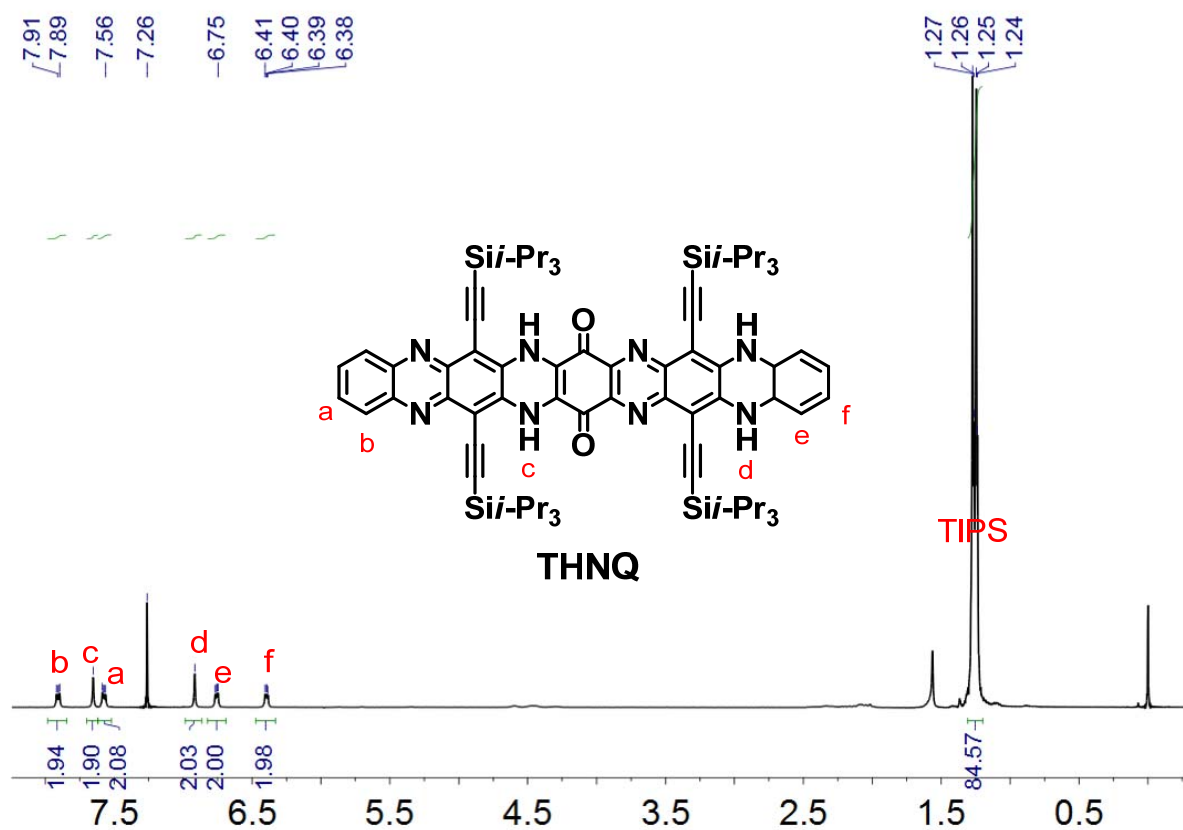
1: TOF MS ES+
1.01e+000

Figure 4.2.3.1.2 HR MS (ESI) spectra of OANQ.

4.2.3.2 NMR Analysis

Figure 4.2.3.2.1 ¹H NMR spectra of THNQ in CDCl₃.

^1H NMR and ^{13}C NMR spectra of **THNQ** and **OANQ** were recorded on a Bruker 400-MHz spectrometer in CDCl_3 .

Figure 4.2.3.2.1 shows the ^1H NMR spectra of **THNQ** in CDCl_3 , the protons can be indexed as ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 1.20\sim 1.30$ (84H), 6.35~6.45 (2H), 6.72~6.80 (2H), 6.88~6.96 (2H), 7.53~7.62 (2H), 7.63~7.69 (2H), 7.87~7.96 (2H), which are well consistent with its molecular structure. It is noteworthy that the hydrogen atoms attached on *N* atoms of pyrazine rings are located at 5, 9, 18 and 22 positions, indicating that this arrangement is a preferable stable structure for **THNQ**.

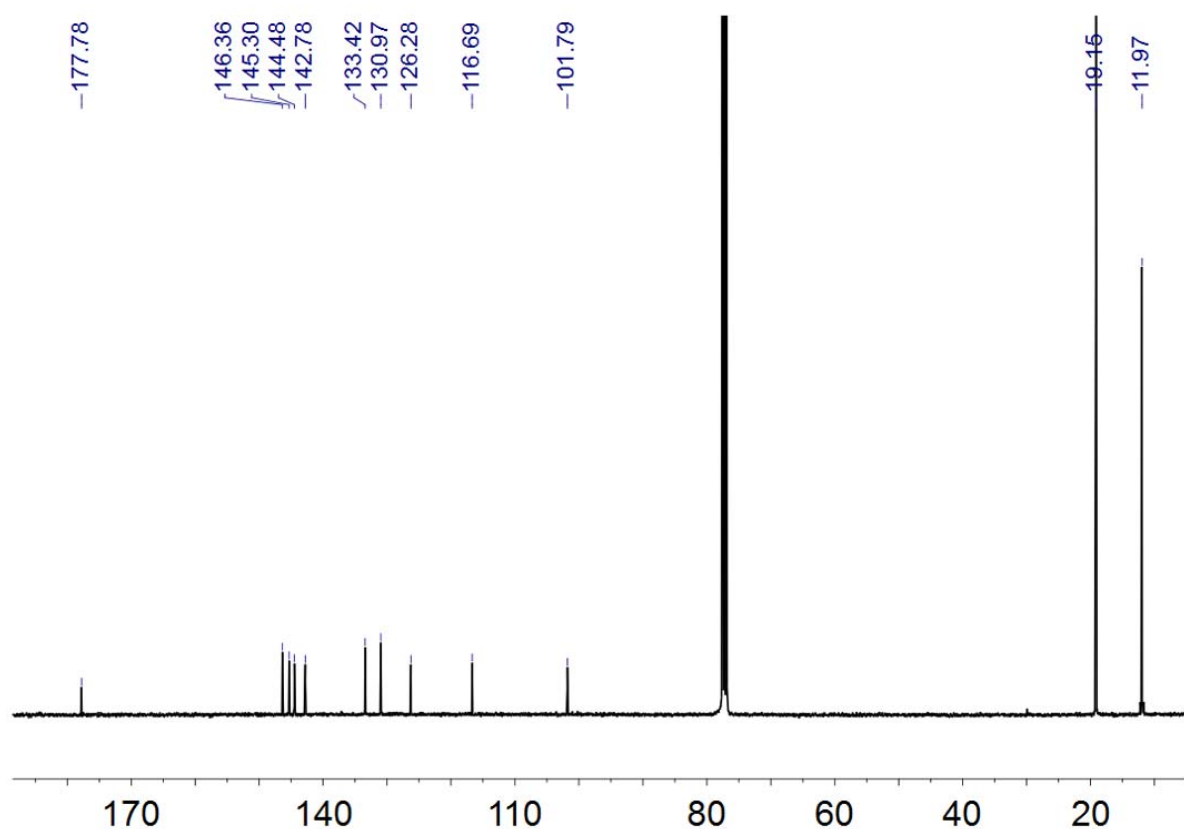


Figure 4.2.3.2.2 ^{13}C NMR spectra of **THNQ** in CDCl_3 .

Figure 4.2.3.2.2 shows the ^{13}C NMR spectra of **THNQ** in CDCl_3 . The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 173.13, 144.18, 144.14, 142.50, 141.36, 140.64, 138.43, 129.29, 129.17, 128.52, 125.69, 124.29, 114.29, 106.55, 106.34, 101.53, 99.12, 98.05, 97.76, 18.91, 11.49, 11.43$. There are 22 carbons can be observed, which are well consistent with the theoretical value.

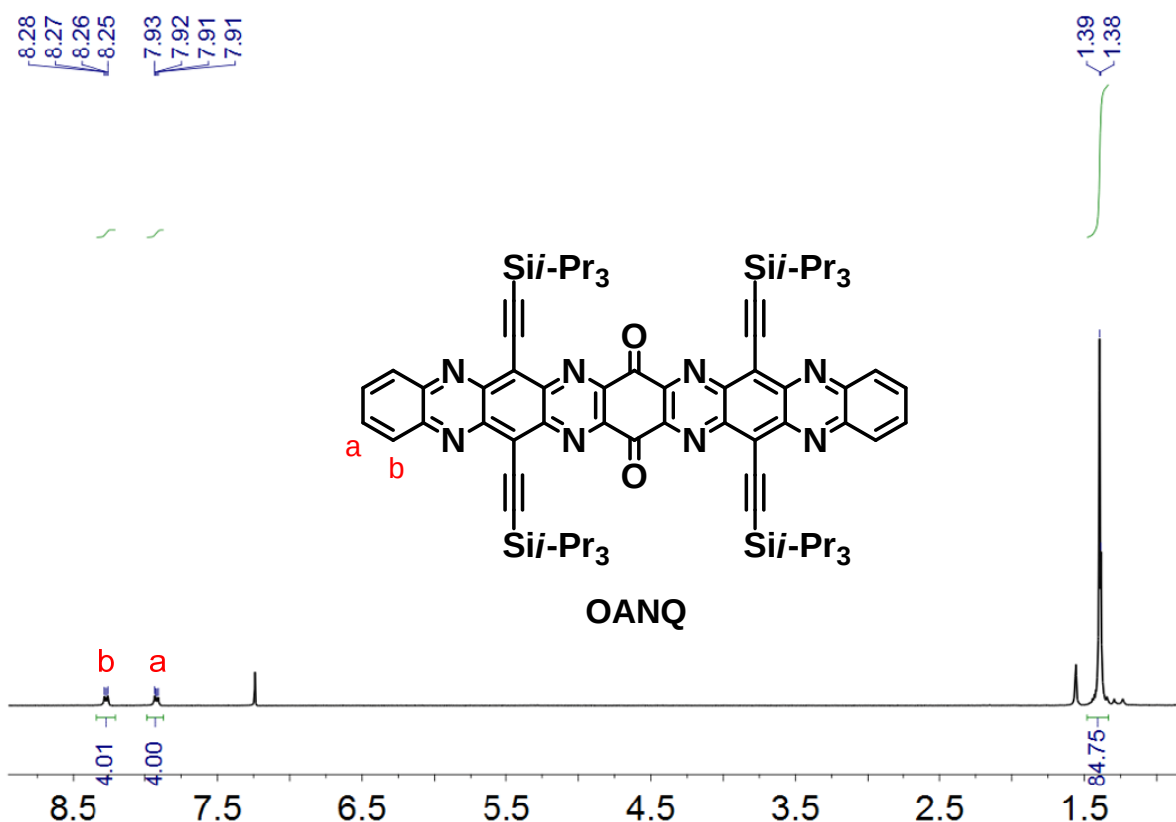


Figure 4.2.3.2.3 ^1H NMR spectra of **OANQ** in CDCl_3 .

Figure 4.2.3.2.3 shows the ^1H NMR spectra of **OANQ** in CDCl_3 , the protons can be indexed as ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta_{\text{H}} = 1.33\sim 1.46$ (84H), $7.87\sim 7.99$ (4H), $8.21\sim 8.33$ (4H), which are well consistent with its molecular structure.

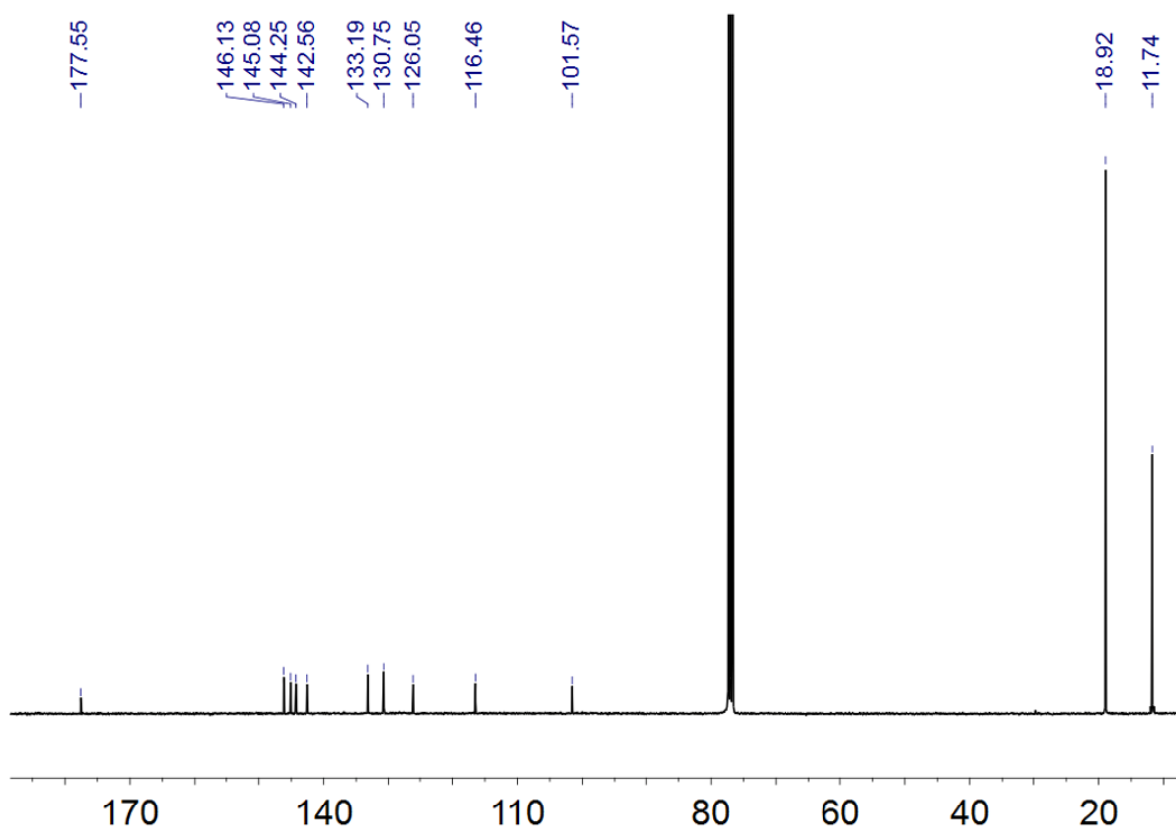


Figure 4.2.3.2.4 ^{13}C NMR spectra of **OANQ** in CDCl_3 .

Figure 4.2.3.2.4 shows the ^{13}C NMR spectra of **OANQ** in CDCl_3 . The carbons can be indexed as ^{13}C NMR (101 MHz, CDCl_3 , 298 K): $\delta_{\text{C}} = 177.55, 146.13, 145.08, 144.25, 142.56, 133.19, 130.75, 126.05, 116.46, 101.57, 18.92, 11.74$. There are 12 carbons can be observed, which are well consistent with the theoretical value.

4.2.3.3 Crystal Analysis

Plate-like single crystals of **THNQ** and **OANQ** were obtained through a vapor diffusion method, in which CH_3CN was slowly diffused into the toluene solution of compounds. The single crystal data was collected with the same method illustrated in [2.4.3.3 Crystal Analysis](#). The CCDC numbers for **THNQ** and **OANQ** are 1046845 and 1046846, respectively. Both

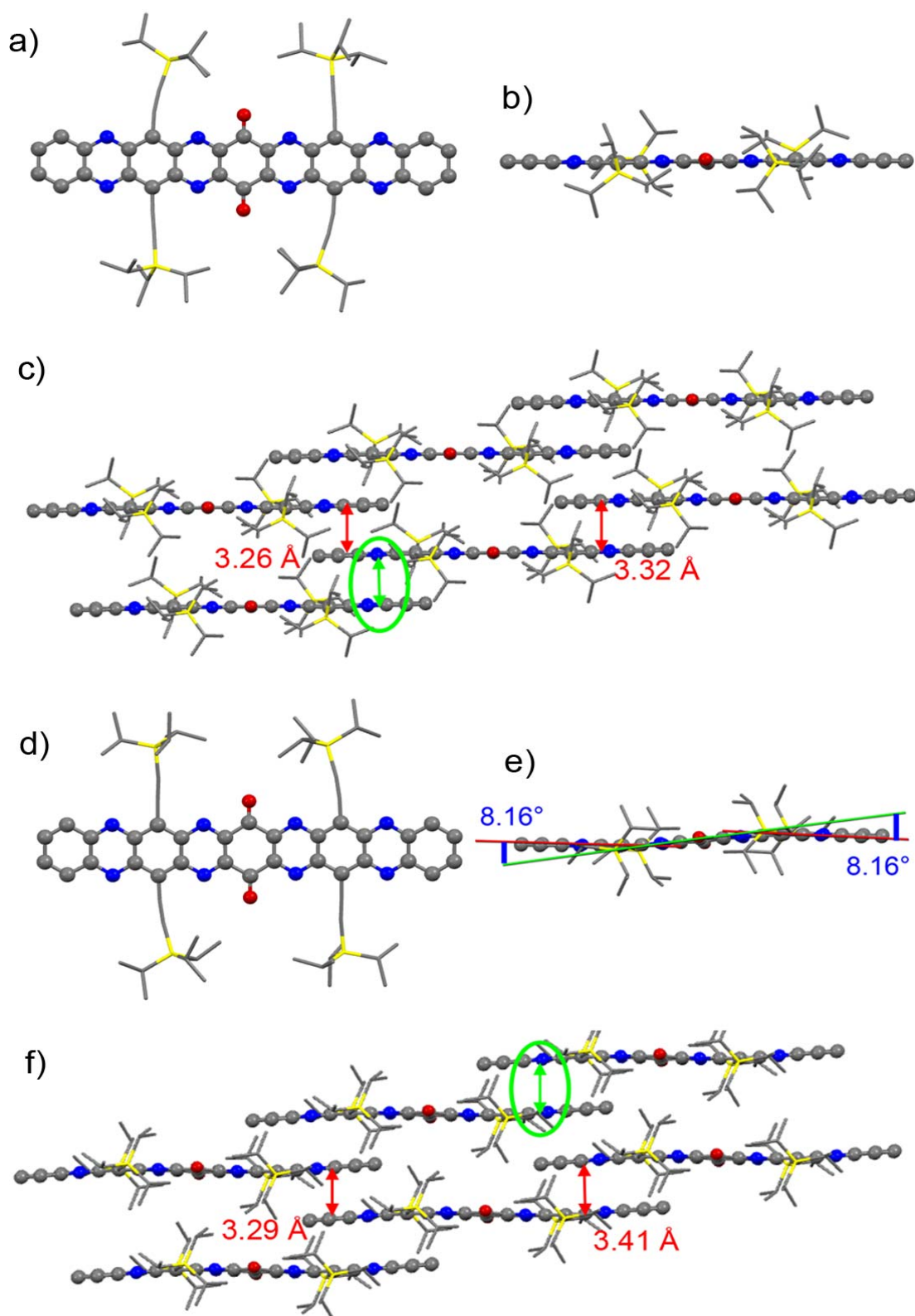


Figure 4.2.3.3.1 a) & d) Top view, b) & e) side view, c) & f) molecular stacking of **THNQ** & **OANQ** crystal structure, respectively.

THNQ and **OANQ** crystallized in triclinic space group (P-1) with one molecule in each unit cell. Figure 4.2.3.3.1 displays the molecular structures and stacking patterns. All hydrogen atoms and solvent molecules are omitted for clarification. From the top view of **THNQ** and **OANQ** structures (Figure 4.2.3.3.1 a) & d)) no obvious difference on molecular conformation can be observed. It is clear that **THNQ** owns a perfect plane conformation from side view (Figure 4.2.3.3.1 b)), while **OANQ** has a slight twist, in which situation one tetraazaacene unit bends up and the other one bends down relative to the quinone center (Figure 4.2.3.3.1 e)). The dihedral angle between the tetraazaacene units and quinone center is determined to be 8.16° . It is believed that such a twisted configuration can release the molecular strain generated from bulky substituents and the π - π interaction, which should be important to enhance the stability of molecular structure and the stacking between adjacent molecules. As shown in Figure 4.2.3.3.1 c) and f), a face-to-face 2D ‘bricklayer’ stacking of molecules can be observed for both **THNQ** and **OANQ**. The two types of molecules adopt unsymmetrical overlapping, however, the overlapping area for **OANQ** is a bit of larger (see cycle region), probably leading to a stronger π - π interaction between neighboring molecules. The interplanar distances between adjacent **THNQ** molecules are 3.26 Å and 3.32 Å, respectively, and that for **OANQ** are 3.29 Å and 3.41 Å. The enlarged intermolecular distance might be induced by the twisted configuration. All the interplanar distances for **THNQ** and **OANQ** are shorter than van der Waals bond, suggesting that there is strong π - π interaction between adjacent molecules. It has been demonstrated that 2D electron transport and large transfer integrals are favored from 2D face-to-face stacking and strong π - π interaction of molecules,²⁶ thus **OANQ** is expected to own good electron transporting properties in solid state.

4.2.3.4 Optical Properties of THNQ & OANQ

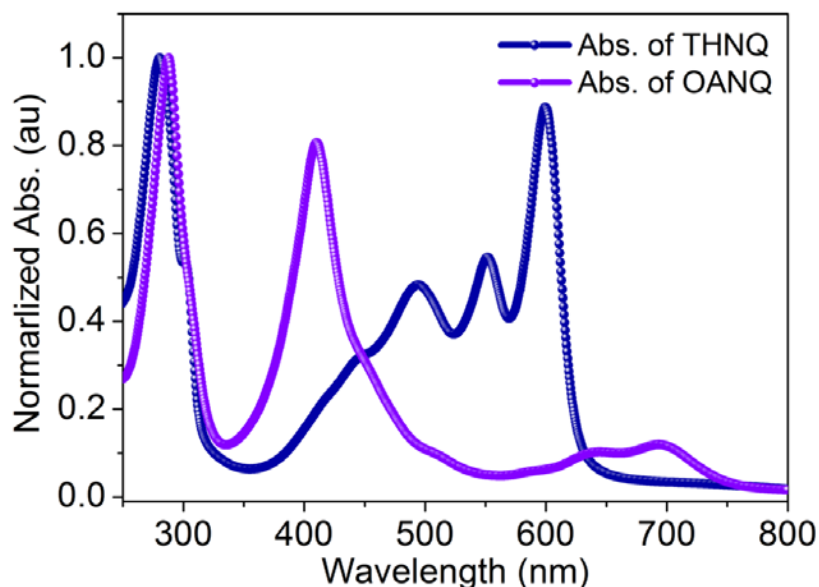


Figure 4.2.3.4.1 Normalized UV-vis absorption spectra of **THNQ** & **OANQ** in CH₂Cl₂.

The optical properties of **THNQ** and **OANQ** were investigated in CH₂Cl₂ through UV-vis absorption spectra, which were recorded on a Shimadzu UV-2501 spectrophotometer. As shown in Figure 4.2.3.4.1, **THNQ** (blue line) has three absorption bands with the maximum absorption wavelength (λ_{max}) at 494 nm, 551 nm, and 599 nm, respectively. **OANQ** (violet line) exhibits a strong absorption band with λ_{max} at 409 nm, and two relatively weak absorption bands with λ_{max} at 641 nm and 694 nm, respectively. The onset absorption wavelength (λ_{onset}) of **THNQ** is 632 nm, which determines the optical band gap (E_g) to be 1.96 eV based on the equation illustrated in 2.2.3.4 Optical Properties of TPA-BIP. Similarly, deduced from the λ_{onset} at 753 nm, the E_g of **OANQ** is established to be 1.65 eV. It is noteworthy that the λ_{onset} of **OANQ** is larger than **TIPS**-pentacene and its analogues, but smaller than hexacene and its *N*-substituted counterpart compounds, suggesting that **OANQ** owns relatively moderate conjugation level.^{25,27,28}

4.2.3.5 Electrochemical Properties of THNQ & OANQ

Table 4.2.3.5.1 Summarized energy levels for **THNQ** and **OANQ**. ^[a]Energy levels determined from experimental results. ^[b]Energy levels deduced from DFT calculations (B3LYP/6-31G*).

Molecule	HOMO ^[a] (eV)	LUMO ^[a] (eV)	Gap ^[a] (eV)	HOMO ^[b] (eV)	LUMO ^[b] (eV)	Gap ^[b] (eV)	λ_{onset} (nm)
THNQ	-5.04	-3.08	1.96	-4.96	-3.08	1.87	632
OANQ	-6.01	-4.32	1.65	-5.68	-3.92	1.75	753

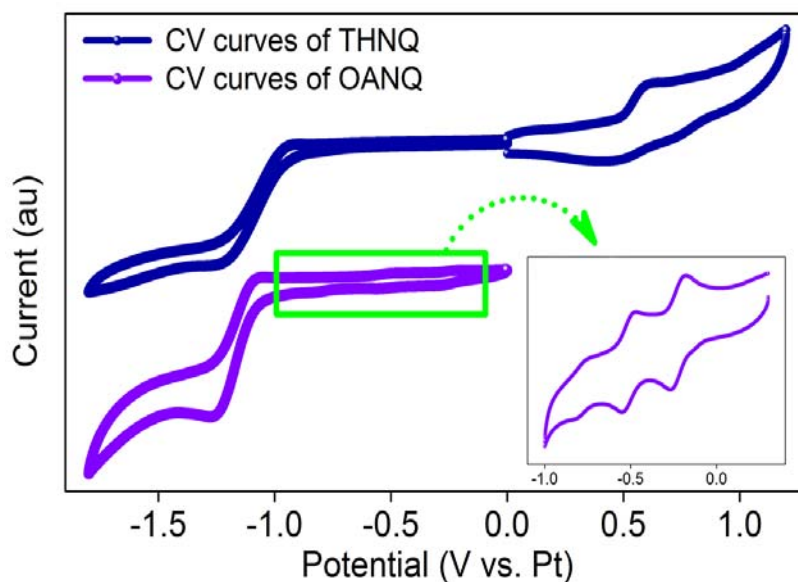


Figure 4.2.3.5.1 Cyclic voltammetric (CV) curves of **THNQ** & **OANQ** in anhydrous CH_2Cl_2 .

The electrochemical properties of **THNQ** and **OANQ** were investigated by cyclic voltammetric (CV) curves in anhydrous CH_2Cl_2 with the same method illustrated in **2.2.3.5 Electrochemical Properties of TPA-BIP**. As shown in Figure 4.2.3.5.1, **THNQ** has one irreversible oxidative peak and one irreversible reductive peak. **OANQ** does not display any oxidative peak, but three less reversible reductive peaks and one irreversible reductive peak

can be clearly observed. The onset oxidative potential ($E_{\text{onset}}(\text{OX})$) of **THNQ** is at 0.24 V versus $\text{FeCp}_2^+/\text{FeCp}_2$, which determines the HOMO level to be -5.04 eV based on the equation illustrated in **2.2.3.5 Electrochemical Properties of TPA-BIP**. The LUMO level is calculated to be -3.08 eV from the difference between HOMO level and E_g . The existence of hydro-pyrazine rings in **THNQ** strongly increases the HOMO level, which probably acts as electron-donating part in backbone. The half-wave potential of the first less reversible reductive peak of **OANQ** ($E_{1/2}(\text{RE})$) is at -0.48 V versus $\text{FeCp}_2^+/\text{FeCp}_2$, which estimates the LUMO level of **OANQ** to be -4.32 eV with the same method as **THNQ**. Accounting to the difference between the LUMO level and E_g , the HOMO level of **OANQ** is calculated to be -6.01 eV. Theoretical calculation has been carried out to investigate the HOMO and LUMO levels of **THNQ** and **OANQ**. Table 4.2.3.5.1 summarizes the experimental and calculated results. There is minor difference of E_g between the experimental and calculated results. The calculated HOMO and LUMO levels of **THNQ** are well consistent with the experimental results, while those of **OANQ** have ~0.4 eV difference.

4.2.4 OFET Device Fabrication Based on OANQ

Single-crystal OFET devices based on **OANQ** were fabricated to investigate its electron-transporting properties, considering that there are less defects and grain boundaries in crystals than in film, which can better demonstrate the intrinsic semiconducting properties of molecules. The heavily doped *n*-type Si wafers were used as substrates with a capacitance of $7.5 \text{ nF}\cdot\text{cm}^{-2}$, on which a layer of SiO_2 with the thickness of 500 nm was doped as dielectric layer. The substrates were pre-cleaned under ultrasonic with pure water, piranha solution ($\text{H}_2\text{SO}_4\text{: H}_2\text{O}_2 = 2\text{: 1}$), pure water and isopropanol successfully. In order to prevent any influence of moisture, after cleaning the substrates were dried at 90 °C for 0.5 hours in a

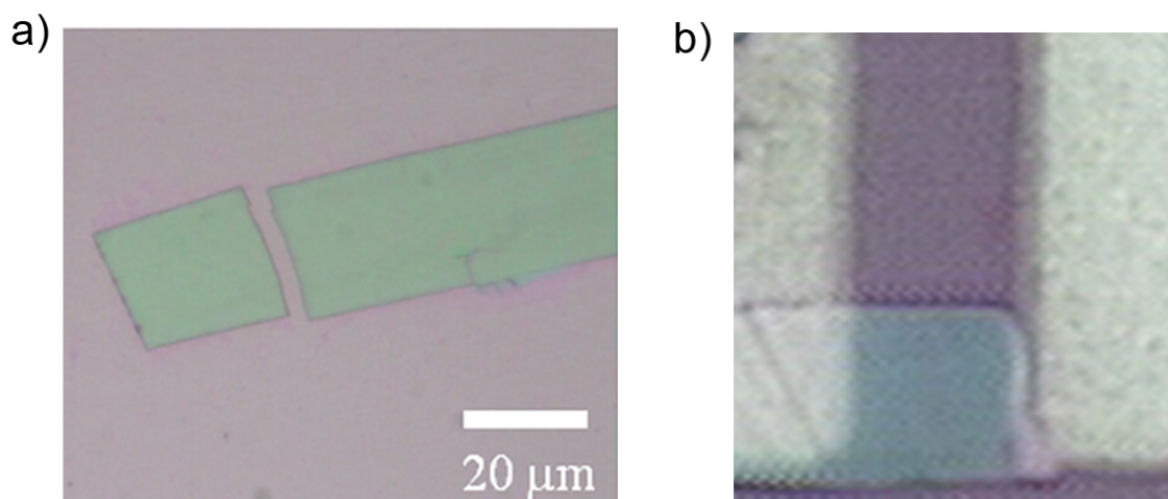


Figure 4.2.4.1 Representative photos of a) micrometer-sized crystal sheets & b) single-crystal OFET device.

vacuum oven. After cooled down, a little drop of trichloro(octadecyl)silane (**OTS**) was casted on the substrates, and the as-casted substrates were placed in a vacuum oven again and heated to 120 °C for 2 hours. The substrates were transferred to a N₂-filled glove box (O₂ and H₂O < 10 ppm) after cooled down to room temperature. Micrometer-sized crystal sheets of **OANQ** were prepared by a drop-casting method, by pouring the toluene/CH₃CN solution of **OANQ** (~1 mg/mL) over the **OTS**-modified substrates and evaporating solvents slowly at room temperature in the N₂-filled glove box. The crystal sheets showed width from several to hundreds of micrometers and thickness at several tens of nanometers, respectively (Figure 4.2.4.1a)). The single-crystal OFETs were fabricated with Bottom Gate/Top Contact architecture. Ag was thermal evaporated on the crystal sheets as drain and source terminals with a copper grid as shadow mask in a thickness of 60 nm, which was expected to align the working function (-4.2 eV) of terminals with the LUMO level of **OANQ** (-4.32 eV). Figure 4.2.4.1b) shows the photo of a representative single-crystal OFET device.

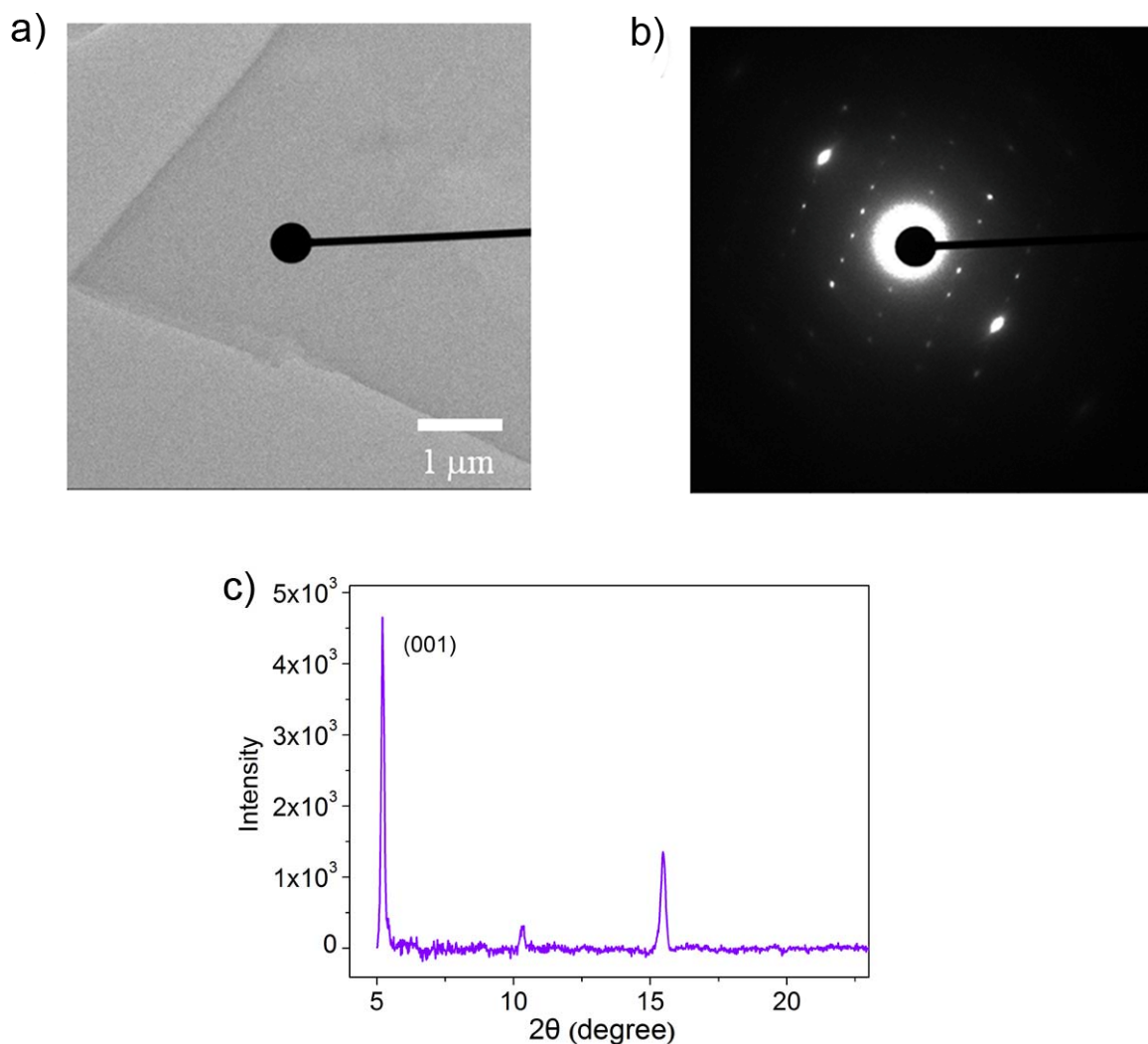


Figure 4.2.4.2 a) TEM, b) SEAD & c) XRD patterns of **OANQ** micrometer-sized crystal sheets.

The crystallinity of **OANQ** crystal sheets was investigated by TEM and SAED analysis. Figure 4.2.4.2 b) shows the representative SAED patterns of a crystal sheet grown on an amorphous carbon-coated TEM grid. Identical diffraction patterns can be observed at different spots of the crystal sheet, indicating that the as-prepared crystal sheet has high crystalline quality. The molecular orientation of the as-casted crystal sheets on substrates was investigated by powder XRD patterns, which was recorded on D8/max2500 with Cu Ka

source ($\kappa = 1.541 \text{ \AA}$). As shown in Figure 4.2.4.2 c), strong Bragg reflections with intensity up to $\sim 10^3$ – 10^4 can be observed at 5.20° , 10.35° and 15.50° , which are indexed as (001), (002) and (003), respectively. The sharp diffraction peak at 5.20° is corresponded to the d -space of 1.68 nm, suggesting that a nearly edge-on molecular orientation on the substrates was adopted in **OANQ** crystal sheets, in which the molecules possibly crystallize into 2D network with π - π interaction and van der Waals interaction as driving forces.

4.2.5 OFET Characteristics of OANQ

The OFET performance of the as-fabricated devices was demonstrated by current-voltage (I - V) curves, which were recorded on a Micromanipulator 6150 probe station by a Keithley 4200 SCS in a clean and shielded box at room temperature in air.

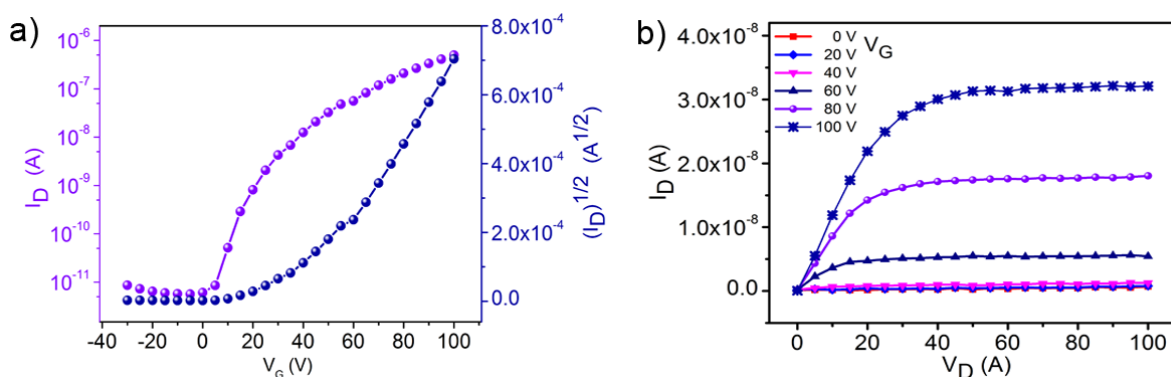


Figure 4.2.5.1 a) Transfer & b) output curves of typical single-crystal OFET device.

All the single-crystal OFET devices of **OANQ** exhibited typical n -type behaviors, and Figure 4.2.5.1 a) & b) show the representative transfer curves and output characteristics. The highest electron-transporting mobility (μ) is determined to be $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the devices display an ON/OFF ratio $\sim 10^5$, which is deduced from the transfer curves. The mobility (μ) is calculated in the saturation regime based on the following equation: $I_D = \mu C_i (W/2L)(V_G - V_T)^2$,

where I_D is the drain-source current, μ is the field-effect mobility, C_i is the gate dielectric capacitance, V_G is the gate voltage, V_T is the threshold voltage, W and L are the channel width and length, respectively. It was noteworthy that the devices exhibited excellent air-stability and there was no obvious mobility degradation observed even after one month storage in ambient conditions.

4.2.6 Results Discussion

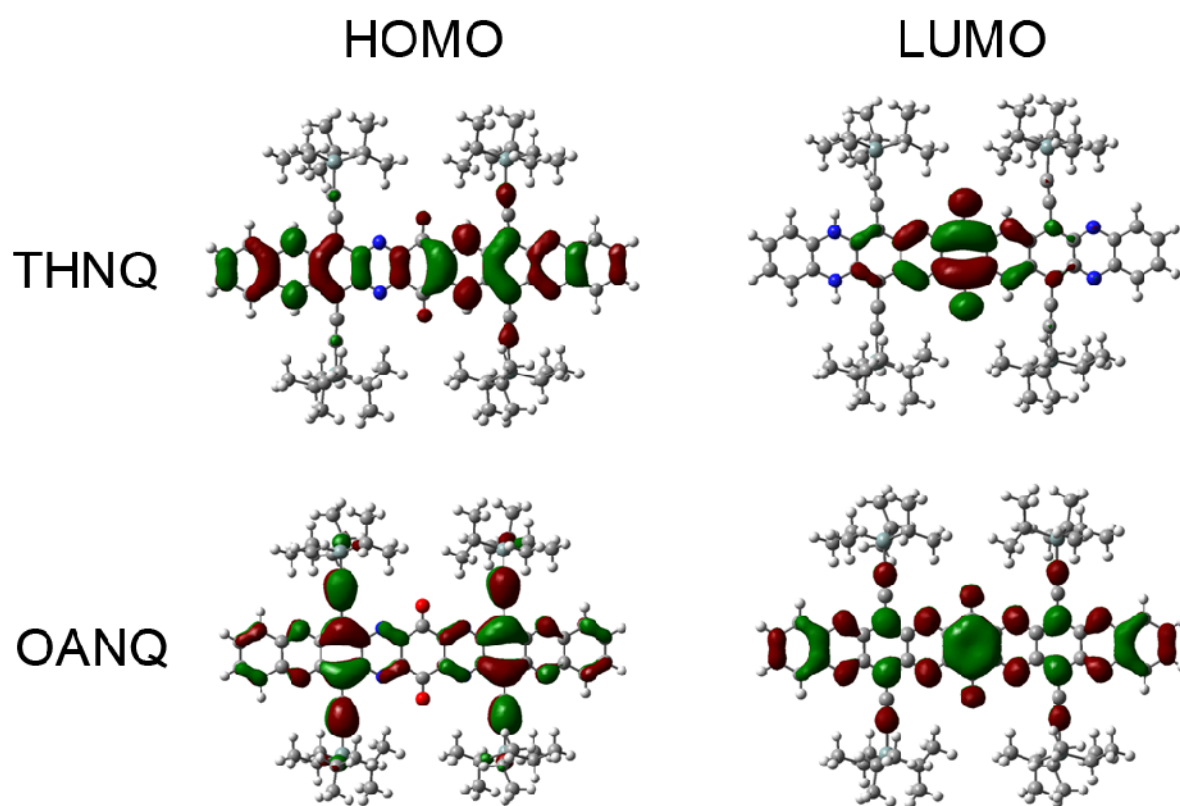


Figure 4.2.6.1 Electron density distribution of HOMO and LUMO levels of **THNQ** & **OANQ**.

Molecular calculation was conducted to investigate the electron density distributions of **THNQ** and **OANQ** with the same method illustrated in [2.2.6 Mechanism Discussion](#). As shown in Figure 4.2.6.1, the HOMO coefficient of **THNQ** is distributed on the whole

molecule, however, its LUMO coefficient owns low electron density and is mainly located at the quinone centre. In contrast, **OANQ** has low electron density in HOMO level and high electron density in HUMO level, which is well dispersed on the whole molecule. The well delocalized π electrons and particularly low LUMO level of **OANQ** suggest that it should own good air-stable *n*-type performance in OFETs.

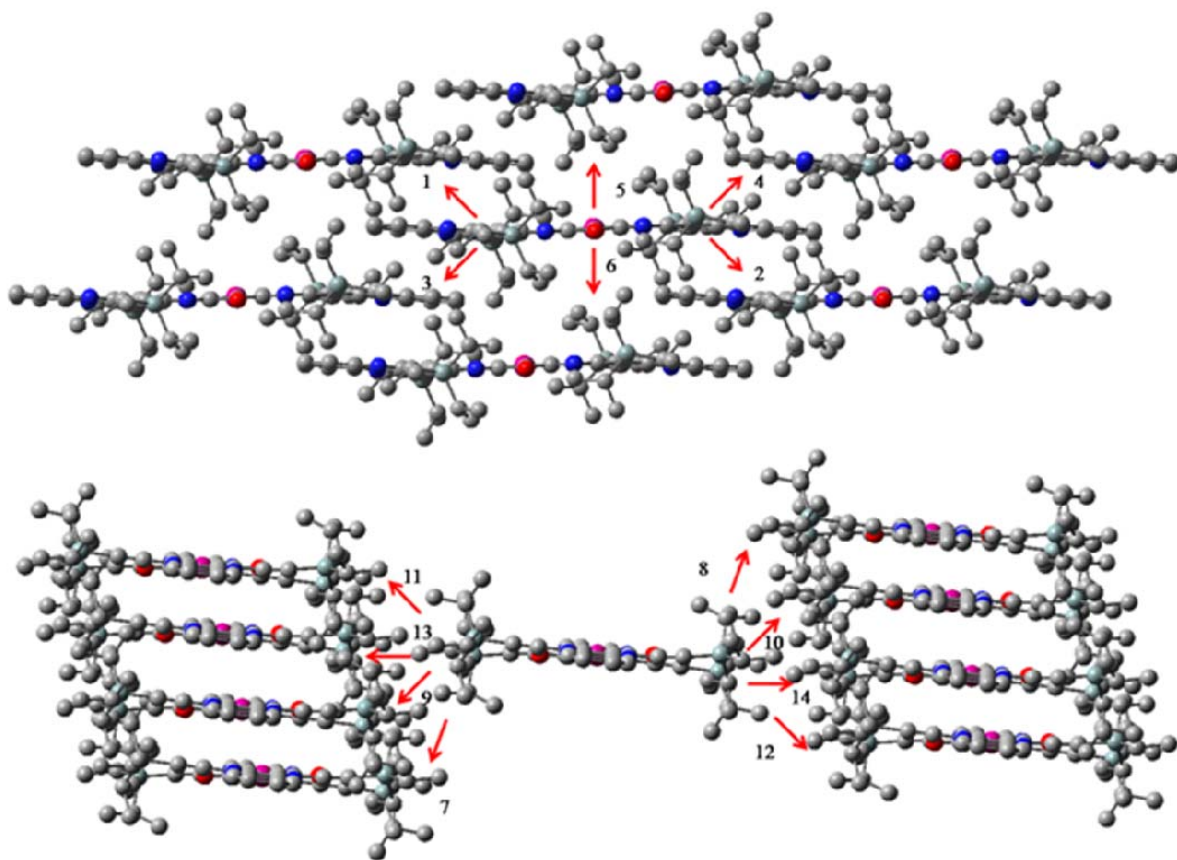


Figure 4.2.6.2 Hopping routes of **OANQ** in the crystals.

Theoretical calculation based on the Marcus electron transfer theory and incoherent Brownian motion model was carried out to understand the structure-property relationship of **OANQ**.²⁹⁻³¹ Based on its single crystal structure, the hole and electron mobilities of **OANQ** could be calculated. The calculation methodology had been described in Shuai's review.

The mobility can be described by Einstein equation:

$$\mu = \frac{e}{k_B T} D \quad (1)$$

Where the diffusion coefficient D is estimated as

$$D = \frac{1}{2d} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2d} \sum_i r_i^2 W_i P_i \quad (2)$$

r_i , W_i and P_i are the hopping distance, rate and probability ($P_i = W_i / \sum_i W_i$). And n is the dimension of the structure.

The hopping rate W can be described by Marcus theory in the following equation:

$$W = \frac{V^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (3)$$

Where V is the intermolecular electronic coupling term and λ is the reorganization energy.

The electronic coupling for the hole and electron can be obtained by using Prof. Shuai's code based on equation 4.

$$V = \frac{H_{12} - \frac{1}{2}(H_{11} + H_{22})S_{12}}{1 - S_{12}^2} \quad (4)$$

The H matrix elements are calculated by $H_{ij} = \langle \phi_i | H | \phi_j \rangle$, where ϕ_i and ϕ_j represent the LUMO levels for electron transport of isolated molecules in the dimer. H is the self-consistent Hamiltonian matrix of the dimer and S_{12} is the overlap integral.

Table 4.2.6.1 The electronic couplings (V) for all the hopping pathways of **OANQ**.

Pathway	Center-Center (Å)	V_h (meV)	V_e (meV)
1	14.40	-2.498	33.725
2	14.40	-2.503	33.727
3	17.65	8.698	15.315
4	17.65	8.697	15.317
5	7.76	-1.837	-1.538
6	7.76	-1.836	-1.539
7	18.93	0.32	0.32
8	18.93	0.321	0.321
9	19.05	0.955	0.282
10	19.05	0.955	0.282
11	22.60	-0.223	-0.001
12	22.60	-0.223	-0.001
13	18.49	-0.201	0
14	18.49	-0.202	0

There are 14 pathways for the intermolecular electronic couplings V (V_h for hole transfer and V_e for electron transfer), which are shown in Figure 4.2.6.2 and were calculated at DFT/PW91PW91/6-31G(d) level.^{32,33} Table 4.2.6.1 summarizes all the electronic coupling

values. The hole and electron reorganization energies of **OANQ** were calculated at the DFT/B3LYP/6-31G(d) level to be 0.1253 eV and 0.1102 eV.³⁴ The largest electron transfer integrals of **OANQ** were aligned in 1, 2 and 3, 4 directions (Figure 4.2.6.2), which achieved comparable results of 33.725 and 15.315 meV to the famous **PDI**s derivatives with calculated transfer integral of 50 meV.³⁵ The calculated hole and electron mobilities in room temperature were determined to be $0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which was well consistent with the experimental results.

4.2.7 Summary

In summary, a large π -conjugated N-heteroquinone **OANQ** containing 8 N atoms has been designed and synthesized. The moderate conjugation and the slight twisted conformation on the backbone of **OANQ** make it own good environmental stability. Combined with the particular low LUMO level and 2D π - π stacking, **OANQ** displays high and air-stable electron-transporting mobility up to $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the single-crystal OFET devices. Besides that, the as-prepared devices show good environmental stability in ambient laboratory conditions.

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Chapter 5

Conclusions & Future Work

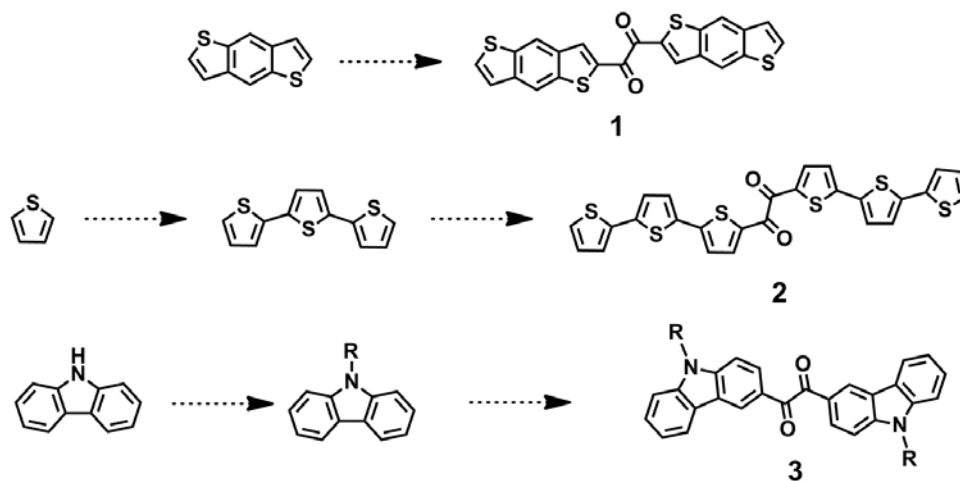
5.1 Conclusions

A series of D-A molecules with novel *N*-heteroacenes as acceptors have been designed and synthesized for ORMs application, based on two series of hypothesis: different *N*-heteroacene units can induce multiple electron “traps” and strong electron-deficient *N*-heteroacenes can be used as acceptors to induce multiple electrons intermolecular charge transfer. When imidazole and pyrazine are combined together as a single acceptor moiety, only two-state non-volatile memory behaviors can be observed. Probably the acceptor moiety acts as a single electron “trap” or the memory behaviors are induced by intermolecular charge transfer. Increasing the acceptor moieties shows no obvious influence on the switching process of molecules, although the morphology of films does affect the ON/OFF ratio. When strong electron-deficient *N*-heteroacene acceptor is combined with multiple donors, the molecule show multilevel, rewritable, non-volatile memory behaviors, which were possibly induced by multiple electrons intermolecular charge transfer. The success indicates an efficient molecule designing strategy to develop multilevel memory materials.

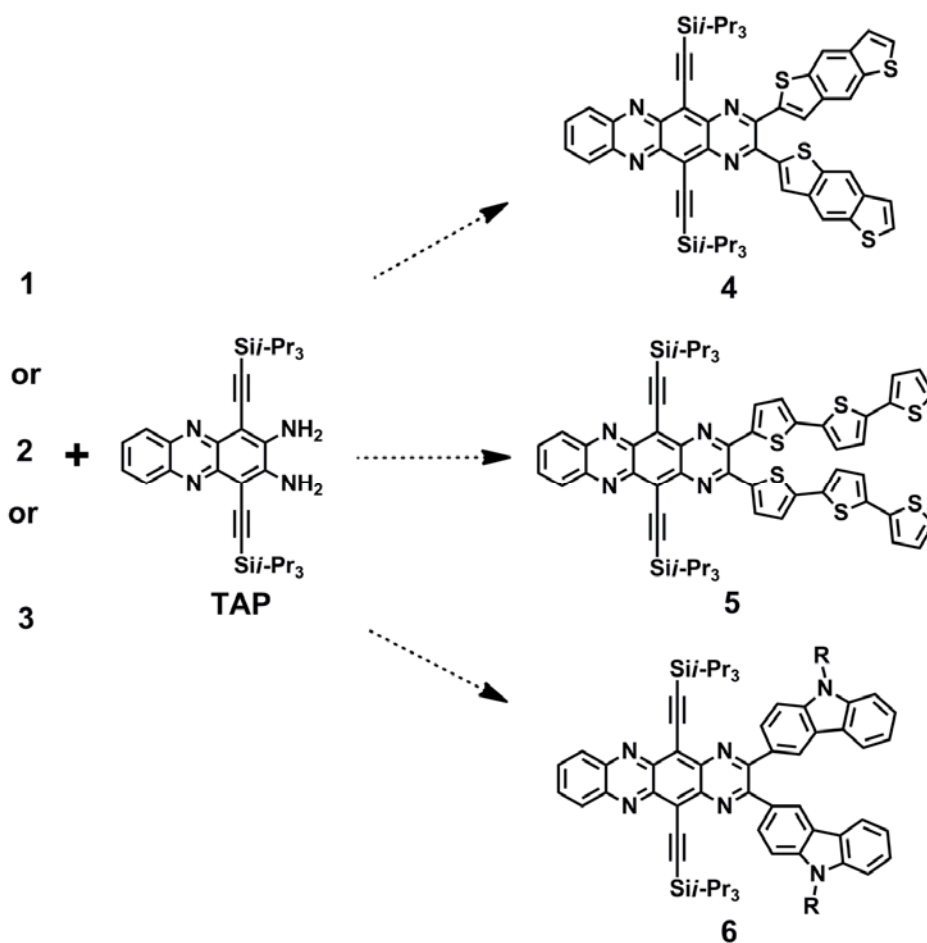
The novel D- π -A small molecule with a large *N*-heteroacene as acceptor moiety and widely explored benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT**) as a donor has been synthesized and characterised for OPVs. The molecule is expected to own high OPV performance resulting from the increased conjugation. The as-fabricated OPV device through solution-processing method shows a PCE of 1.97%. MoO₃ has been proved to be a useful anode buffer layer for

this type of materials and the enhanced performance probably comes from the more aligned energy level between the working function of MoO₃ and the HOMO level of molecule, and the reduced chemical interactions between MoO₃ and organic film. Although there is a gap between our results of PCE at 1.97% and the highest record in literature, it is believed that large *N*-heteroacenes have the potential to be applied as good acceptor moieties and after structure modification, better performance can probably be achieved.

The large π -conjugated *N*-heteroquinone has been designed and synthesized through convenient condensation reaction, which has 8 *N* atoms in its backbone with lineally fused structure. The existence of quinone centre makes the as-prepared *N*-heteroquinone own relatively moderate conjugation level, thus it has good stability. A particularly deep LUMO level lower than -4.0 eV is obtained by introducing more *N* atoms, which makes it have the potential to be applied as air-stable *n*-type materials. The single-crystal OFET devices based on the as-prepared *N*-heteroquinone show charming electron-transporting mobility up to 0.2 cm² V⁻¹ s⁻¹ when measured under ambient condition, and the devices can maintain the good performance for long period. Based on the theoretical calculation, there is large space to be filled for the OFET performance of this type of *N*-heteroquinone materials, although our initial results are out of the highest records. It is noteworthy that the excellent operational stability of our *N*-heteroquinone makes it shine among the other reported air-stable *n*-type materials. It is believed that more inspiring results can be achieved after molecular modification based on the as-designed *N*-heteroquinone, and the design of large π -conjugated *N*-heteroquinones is a promising way to develop novel air-stable *n*-type materials.

5.2 Future Work of *N*-heteroacenes for Organic Memories

Scheme 5.2.1 Synthetic route for the typical donor units.



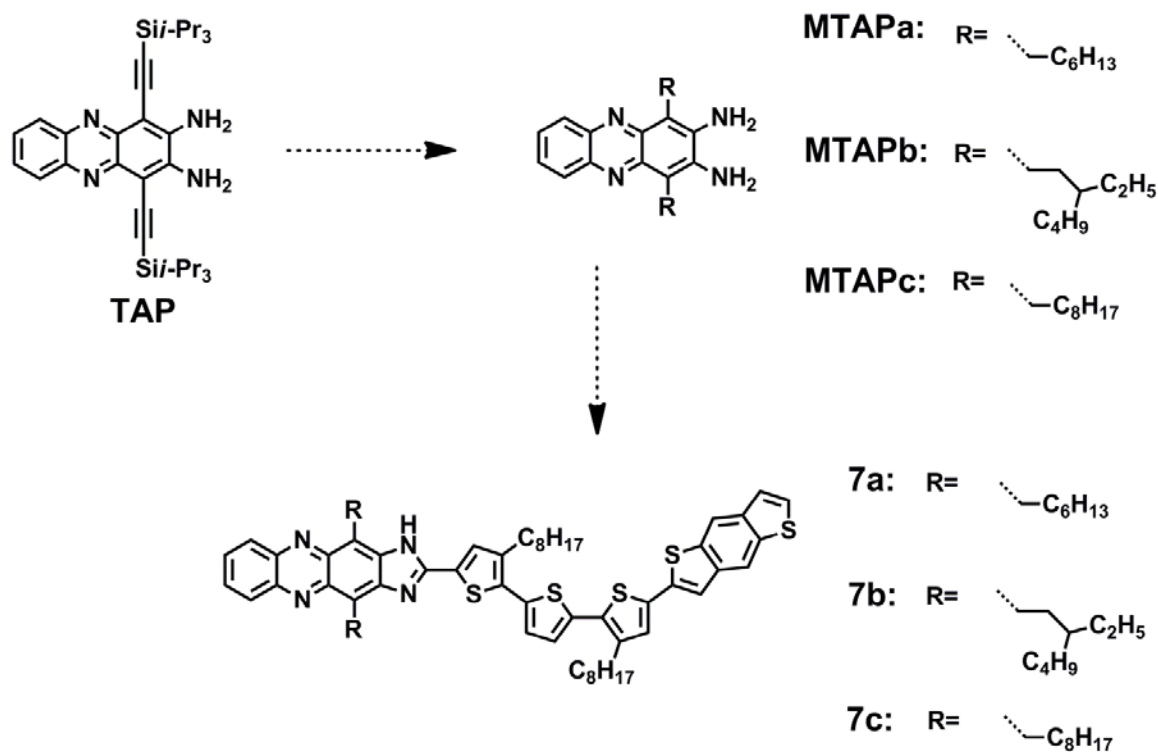
Scheme 5.2.2 Synthetic route for target D-A molecules.

We have found an efficient way to achieve rewritable, multilevel memory materials by combining strong electron-deficient *N*-heteroacenes and multiple triphenylamine (**TPA**) donor units. On the basis of these studies, we will further investigate the designing strategy and expand it to be available for more types of donor units. Thus, various typical donor units will be synthesized from **BDT**, thiophene or carbazole (shown in Scheme 5.2.1).

The typical donor units will be combined with the successful 5,12-bis((triisopropylsilyl)ethynyl)-1,4,6,11-tetraazatetracene (**BTtT**) acceptor moiety in similar procedure illustrated in **2.4.2 Synthesis of 2TPA-BTtT** (shown in Scheme 5.2.2). It is expected that the as-designed molecules will display similar rewritable and multilevel switching behaviors with that of **2TPA-BDTT**. Through comparing the memory properties of these molecules, one type of ultimate material with good endurance and easy to control will be potentially achieved.

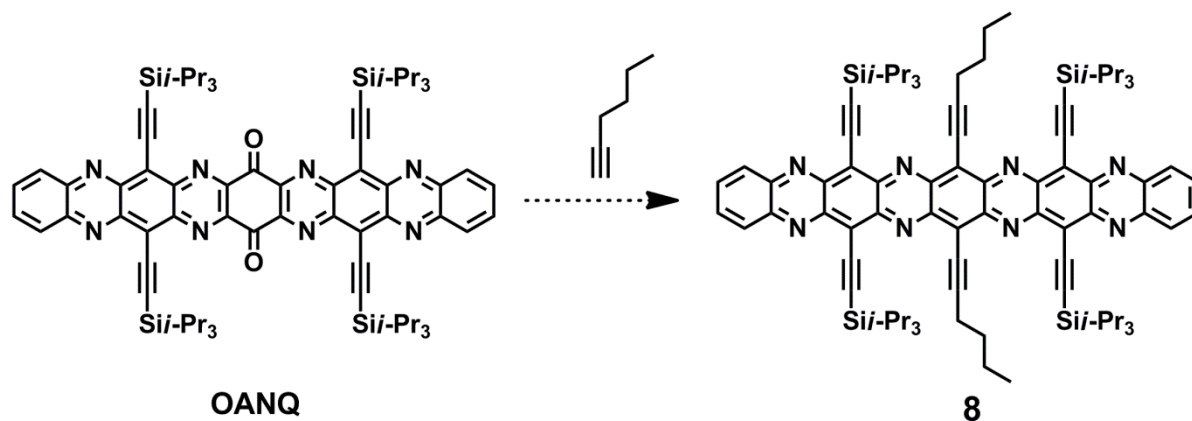
5.3 Future Work of *N*-heteroacens for Organic Photovoltaics

The morphology and crystallinity of molecules in solid states have proved to greatly affect the OPV performance. We have demonstrated that the D- π -A molecules with large *N*-heteroacens as acceptors can be utilized as donor materials for OPV application, although their initial performance is quite behind of the highest records. The molecular side chains have been reported to play an important role for determining the morphology and crystallinity of films, and the selection of suitable side chains is critical for developing high performance OPV materials. Considering these factors, various side chains will be introduced onto 4,11-bis((triisopropylsilyl)ethynyl)-1*H*-imidazo[4,5-*b*]phenazine (**BIP**) moiety, and novel D- π -A small molecules **7a–c** (shown in Scheme 5.3.1) are proposed. More inspiring

Scheme 5.3.1 Synthetic route for **7a–c**.

OPV performance based on these molecules is expected.

5.4 Future Work of *N*-heteoacenes for Organic Field-effect Transistors

Scheme 5.3.1 Synthetic route for **8**.

As the conjugation of **OANQ** is increased, a deeper LUMO level should be achieved, which is expected to enhance the *n*-type performance of molecules in ambient conditions. Thus, the possibility will be investigated by changing the carbonyl groups with alkyl chains, in which situation a nonacene analogue **8** is designed (shown in Scheme 5.3.1). To date there is no literature report about the semiconducting properties of large conjugated nonacenes because of their tough synthesis and instability. Hence, the properties investigation of **8** is challenging and significant for both fundamental study and practical application, and **8** is expected to own charming *n*-type performance in OFETs.

Appendixes

Publications during Ph. D. Candidate

1. **Wang, C.**[‡] Zhang, J.[‡] Long, G. Aratani, N. Yamada, H. Zhao, Y. & Zhang, Q. Synthesis, structure and air-stable *n*-type field-effect transistor behaviors of functionalized octaazanonacene-8,19-dione. *Angewandte Chemie-International Edition* **54**, 6292-6296, (2015)
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3. **Wang, C.** Wang, J. Li, P. Gao, J. Tan, S. Y. Xiong, W. Hu, B. Lee, P. S. Zhao, Y. & Zhang, Q. Synthesis, characterization, non-volatile memory device application of a novel *N*-substituted heteroacene. *Chemistry-An Asian Journal* **9**, 779-783, (2014)
4. **Wang, C.** Li, G. & Zhang, Q. A novel heteroacene 2-(2,3,4,5-tetrafluorophenyl)- 1*H*-imidazo[4,5-*b*]phenazine as a multi-response sensor for *F*⁻ detection. *Tetrahedron Letters* **54**, 2633-2636 (2013).
5. **Wang, C.**[‡] Okabe,[‡] T. Long, G. Kuzuhara, D. Zhao, Y. Aratani, N. Yamada, H. & Zhang, Q. A novel D- π -A small molecule with *N*-heteroacene as acceptor moiety for photovoltaic application. *Dyes and Pigments* **122**, 231-237 (2015)

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