Self-assembled networks of conjugated oligomers

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NANYANG
TECHNOLOGICAL
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**SELF-ASSEMBLED NETWORKS OF CONJUGATED
OLIGOMERS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2013

**SELF-ASSEMBLED NETWORKS OF CONJUGATED
OLIGOMERS**

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Abstract

2D self-assembly of non-covalently bonded structures offers an attractive way to prepare processable functional organic macromolecular materials and offers a lot of prospective ways for making progress in nanoscience and advancing nanotechnology. Non-covalent interactions for example hydrogen bonding and metal ion co-ordination offer stability, and more importantly flexibility to the resulting networks. In this thesis work, novel, non-covalently bonded 2D supramolecular structures (trigonal and linear conjugated molecules facilitated via hydrogen bonding interactions and metal-ion co-ordination) have been studied. As a part of ongoing efforts into the development of self-assembled functional materials, this thesis work reports on the synthesis and characterization of conjugated oligomers bearing various functional groups, and some initial studies on their self-assembly using scanning tunneling microscopy (STM) and optical spectroscopy.

Various 2D supramolecular networks of trigonal oligophenylenes were observed by STM at the liquid-graphite interface. Depending on whether the solvent used was either alkylated (*n*-tetradecane, phenyl-octane) or non-alkylated (tetrahydro-naphthalene), different types of networks were achieved. These periodic networks were either open networks (hexagonal arrangement with a central cavity) or close-packed structures. In the open network observed using tetrahydronaphthalene as the STM solvent the central cavity is occupied by several solvent molecules. Furthermore, in most cases it was observed that these arrangements were chiral, with left and right handed domains in the same sample. It was found that the nature of the solvent and time greatly influenced the self-assembly process as shown by both STM and photophysical studies on these molecules.

Synthesis and self-assembly of linear and trigonal terpyridines (tpys) and 2D self-assembled networks of trigonal tpys with linear tpys through zinc metal ion (Zn(II)) co-ordination are also reported. The resulting Zn(II) co-ordination networks were characterized by means of X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering (SAXS), BET, and other photophysical and electrochemical methods. These metallo-supramolecular Zn(II) networks revealed the influence of the metal ion on the thermal, optical and electrical properties of the synthesized metallo-supramolecular assemblies. Moreover, these networks have shown high luminescence with a long fluorescence life time and good thermal stabilities.

Non-covalent interactions for instance hydrogen bonding and metal-ligand co-ordination can direct the intermolecular energy transfer process by the self-assembly of donor and acceptor molecules. Looking forward for the possibilities of these self-assembled networks for light harvesting applications, efficient intermolecular energy transfer was observed in the self-assembled network of trigonal amine molecules and linear PDI molecules. These new donor (**D**) and acceptor (**A**), **D-A** couples may serve as models for light harvesting systems.

Apart from that, the monolayer patterns of these kinds of 2D networks could be used as a template to build hierarchical nanostructures. These hierarchical nanostructures may be tested in electronic devices and as templates for formation of hybrid organic-inorganic nanomaterials in future.

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Chapter 1 Introduction and literature review

1.1 Motivation

The field of supramolecular electronics has progressed rapidly in recent years.¹⁻⁴ Supramolecular electronics with an appropriate device length in the range 5-100 nm is one of the most promising “bottom-up” techniques in nanoelectronics using π -conjugated molecules. Supramolecular π -conjugated ‘oligomers’ have attracted much attention in the last few decades due to the reversibility of the non-covalent interactions (Hydrogen bonding, Coordination bonding, Hydrophobic interactions, Electrostatic, and van der Waals interactions). Defined chemical structures and physical properties of oligomers ease better control over their supramolecular structures.

Self-assembly of organic molecules by reversible non-covalent interactions such as hydrogen bonding is a very fascinating area of research⁵⁻⁷ with many applications in bottom up techniques for macromolecular device fabrication⁸ and templates to introduce guest into the voids inside the supramolecular networks.⁹ Development and understanding of research of 2D supramolecular structures has attracted a lot of attention in the last decade.¹⁰⁻¹⁴ Among the advantages of non-covalent assembly by hydrogen bonding is its simplicity, in which multi-component supramolecular architectures can be obtained from small components in solution in a single step under mild conditions and it gives directionality to the macromolecular structure. 2D hydrogen bonded self-assembled structures of trigonal molecules are very exciting as these structures have more hydrogen bonding motifs for making extended hydrogen bonding networks which can be used in various optoelectronic devices. Abbel and co-workers synthesized supramolecular structures of π -conjugated

oligomers.⁵ Small oligomers such as oligofluorene, oligo(phe-nylenevinylene) and perylenebisimide were self-assembled by hydrogen bonding interactions towards generating white light. This is a promising material for white light emitting diodes.

Figure 1.1 Structures of three π -conjugated oligomers with blue, green and red emission.⁵ Reprinted from Ref. [5] with permission from the American Chemical Society.

To build artificial hierarchical nanostructure, such as those existing in nature, by synthetic routes is still a challenge for researchers. There is much literature on mono-component 2D self-assembled networks as discussed earlier but very few on multicomponent self-assembled networks. It is not easy to build multicomponent hierarchical networks of small oligomers.

In a study by Balandina et. al., one, two and three component self-assembled networks have been observed at the phenyloctane/Au interface which were stabilized by non-covalent interactions.¹⁵ Recently a three component hierarchical 2D self-assembled network was observed at the liquid/solid interface.¹⁶ This hierarchical self-assembly is the best example of careful selection of the template for host-guest based recognition directed self-assembly. Here, firstly isophthalic acid was directed to self-assemble on a coronene molecular template, using hydrogen bonding interactions. Then, alkoxyated dehydrobenzo annulene (DBA) acted as host for this hetromolecular cluster, to form a well ordered three component 2D crystal. Using a similar approach, a four component self-assembled network has been visualized at the liquid/graphite interface.¹⁷ Firstly, a DBA derivative (bisDBA-C10) with decyl chains was chosen as a host network. Upon addition of a mixture of COR and ISA, to the host network (DBA derivative (bisDBA-C10) with decyl chains) a “Kagomé” network is formed. This network is characterized by hexagonal and triangular voids. The hexagonal voids are filled with COR/ISA hetero-clusters. Triangular voids are occupied with triphenylene as guest molecules, resulting in four-component host–guest architecture. Another interesting example on molecular recognition based study, a four component self-assembled network is observed¹⁸ on phenyloctane/HOPG interface in which 1D patterned monolayer acts as template for higher order self-assembly. Hence in achieving hierarchical self-assembly, the key point to note is that the template should be the most stable self-assembled network, so that it could be possible to build other complex structures even of lower stability over it.

Self-assembly rapidly and easily generates large and complex supramolecular networks from easily available building blocks with maximum efficiency. Besides, due to the thermodynamically driven self-correcting ability, self-assembly shows great potential for the

synthesis of supramolecules. Another efficient non-covalent interaction is the metal-ligand co-ordination, which is highly directional. As compared to networks achieved through hydrogen bonding self-assembly, metal-ligand co-ordination allows the construction of highly directional and robust self-assembled supramolecular architectures. Defects formed during the synthesis of conventional covalently bound molecular macromolecules are difficult or impossible to remove. Self-assembled materials held together by non-covalent linkages are potentially self-healing due to their dynamic nature. Burattini and co-workers had reported² a novel supramolecular polymer system possessing self-healing properties that exploits non-covalent cross-linking of polymer chains through π - π stacking interactions involving the intercalation of pyrenyl end groups into polyimide chain folds.

The optoelectronic properties of organic molecules and their supramolecular networks can be tuned by synthetic design. Supramolecular self-assembly has the ability to control the electronic properties of an organic compound by providing an opportunity for much variation in synthetic design. Here not only the properties of individual molecules, but also those of supramolecules (ensembles of individual molecules) can be controlled. Functionalization with flexible functional groups facilitates solubility in organic solvents. This makes their ease in solution processing at room temperature, which is helpful in fabrication of less expensive, flexible (able to bend into many shapes) and novel electronic devices for example, Organic Light Emitting Diodes (OLEDs), Organic Photovoltaics (OPVs), Organic Field Effect Transistor (OFETs) and others.

Transition metal-complexes of π -conjugated terpyridines have a lot of prospective to be used as novel functional materials in electronic and optoelectronic devices. Complexes of heavy transition metal ions, for example, Pt^{2+} , Ru^{2+} , Os^{2+} , and Ir^{2+} , have been explored

thoroughly.¹⁹ In the direction towards the progress in new metal-ligand supramolecular networks, filled electron shells metal-ions have achieved a lot of importance.²⁰ The low cost and toxicity of Zinc(II) ions, made Zn metal-ion co-ordination polymers, highly promising. This prior work inspired the use of Zn^{2+} as a template to assemble organic units into polymer networks through co-ordination to chelating terpyridyl units in this research work.

Scheme 1.1 Supramolecular self-assembled polymers by metal complexation.²⁰ Adapted from Ref. [20].

Self-assembled monolayers (SAMs) on surfaces can be either covalently bonded chemisorbed networks or non-covalently bonded physisorbed networks of molecules. Chemisorbed self-assembled monolayers are more important for device application point of view as they are more stable than their physisorbed counterparts²¹. Self-assembly of small oligomers has been widely used for surface modification. Surface properties of substrates can be modified by SAMs of organic molecules covalently bonded to surfaces. Hence SAMs are used to modify the work function of electrodes in organic electronic devices by minimizing the energy barrier for charge carrier injection or extraction.²² Theoretical work on SAM of conjugated oligomers have been reviewed in detail by Heimel et. al.²³ In this work interface energetics in SAMs of 4'-nitro- and 4'-fluoro-4-mercaptobiphenyls on Au(111) has been investigated. Lowering of the hole-injection barrier from the electrode into a subsequently deposited organic semiconductor for both SAMs has been observed.

SAMs of π -conjugated oligomers on conducting surfaces are very crucial for many electronic device applications such as OLEDs, OPVs, OFETs and etc. The electronic properties of surfaces can be modified by molecular SAMs on conducting surfaces for a variety of applications, including molecular and organic electronics. In organic electronic devices interface between organic molecules and electrodes can be modified by SAMs. For example electron injection has been enhanced by inserting a methoxy terminated SAM and a polymer-based insulating nanolayer between Ag cathode and the MEH-PPV layer in organic electronic devices and hence the turn-on voltage is significantly reduced.²⁴

In organic FETs, SAMs are used to control the surface carrier density. A new technique has been developed²⁵ to control the charge density in the channel by using organosilane monolayers SAMs on SiO₂ gate insulators. It was observed that in the transistor channel, SAMs with fluorine and amino groups can accumulate holes and electrons, respectively. These properties depend on the well organization of electric dipoles of the SAMs molecules, and a weak charge transfer between active layer of organic films and SAMs. A new type of molecular self-assembly followed by the growth of organosilane SAMs at the surface of organic semiconductors has been reported.²⁶ An increase of the surface conductivity of organic materials is observed. For organosilane molecules with a large dipole moment, SAM induced surface conductivity of organic molecular crystals approaches 10^{-5} S per square, which is comparable to the highest conductivity realized in OFETs at ultra-high densities of charge carriers. SAM functionalized organic surfaces are fully accessible to the environment which makes them very attractive for sensing applications.

Some important points have been focused for building reliable organic optoelectronic devices using SAMs.²⁷ In order to reduce the Schottky barrier and facilitate charge transfer, the

molecule with an electrical dipole typically from 5 to 15 debye should be preferred for SAM. For a stable self-assembled layer on the substrate the polarizability of the molecules involved in the self-assembly process should be matched to the polarizability of the organic semiconductor molecule.

SAMs of organic molecules have also been used as alternative gate dielectric materials in OTFTS.²⁸ These are seen to have excellent insulating properties and large capacitance values, which are the main properties of gate dielectric material. Not only that but a non-linear IV behavior, similar to a semiconductor junction, of mesopyridyl pophyrin self-assembled monolayers on gold is observed. A potential application of SAM for memory devices has also been proposed.²⁹

To study the interface engineering between self-assembled monolayer and metal electrode it is important to understand the underline science behind it for better device performance. Hence lots of studies on SAMs (either covalently or non-covalently bonded to the substrate) are in progress. These studies have established a very important role of SAMs for application in molecular electronics. However, self-assembled organic molecules weakly bonded to the substrate are not applied to the organic electronic devices yet. Even for covalently bonded typical alkane-thiol SAMs, the basic properties, especially the chemical state of the adsorbed molecules, are not well understood at the moment. Furthermore, the relationship between the molecular structure and local functions (electrical-conduction, etc.) is not clear. But the future solution could be a acombination of physisorbed noncovalent networks with chemisorbed SAMs, which can offer a wide design flexibility of organic electronic devices.³⁰

Most commonly the organic molecules are tested as SAMs by scanning probe microscopic (SPM) techniques such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). AFM is in principle the more versatile technique and ultrahigh vacuum (UHV) studies have demonstrated atomic resolution on surfaces³¹ and more recently an ability to distinguish between different surface atoms.³² However, without significant advances in force sensor technology³³ the prospect for routine molecular (not to mention sub-molecular) imaging is poor. STM is one of the most powerful tools to observe the self-assemble patterns of the organic molecules on conducting surfaces such as HOPG, Au, Ag, and Cu etc. as discussed in detail in chapter 3. STM is a technique used to study surface properties of materials upto atomic level. STM works on the principle of quantum tunneling. When a sharp conducting tip is brought very near (less than 10 Å) to the conducting flat surface, a bias applied between the two can allow electrons to tunnel through and a tunneling current is detected.³⁴ The resulting tunneling current depends on the applied voltage, tip position, and the local density of states (LDOS) of the sample. Structural and electronic information is acquired by monitoring the current as the tip's position scans across the substrate. Therefore, molecular self-assemblies on the conducting substrates can be visualized with atomic or even sub-atomic resolution. The tunneling current depends on the on the sign and polarity between tip and sample. It can occur either from the tip to the unoccupied states of the sample or from the occupied states of the samples into the tip. Following figure 1.2 shows the basic working principle of STM.

Figure 1.2 Basic principle of the Scanning Tunneling Microscope.

STM has its own limitations in scanning a surface of interest. First difficulty starts from the sample preparation (As discussed in detail in chapter 3). And the next challenge comes with the requirement of atomically flat, clean and conducting substrates for STM imaging. In STM imaging, it is important to decide between an ambient or UHV approach. As STM studies can be performed in both ambient and UHV conditions. Ambient STM studies can typically be performed at liquid/solid interface. This approach works well for a wide range of soluble molecular systems but imaging is often unstable and physical (dust and other pollutants in the air) and chemical (chemical reactivity) contamination and artifacts can be problematic.³⁵ The alternative UHV approach offers more stable tunneling conditions, together with an atomically clean substrate lattice that provides an in-situ reference for structure analysis. But this approach, however, is not suitable to systems with ultra-low vapour pressures or which decompose or denature at elevated preparation temperatures.

Another constraint in STM imaging at liquid/solid interface is of selection of the solvents for imaging of the organic molecules, which can increase the tunneling currents. Some of the most common solvents utilized are 1,2,4-trichlorobenzene (TCB), heptanoic acid, 1-phenyloctane, n-tetradecane and 1-octanol, with relative dielectric constants near 2.5. STM imaging can be in principle performed in almost any solvent, as long as faradaic and capacitive currents are minimized. This can be achieved by insulating the STM tip through the use of coatings or by using low-dielectric media, to allow working in the picoampere regime.³⁶

Although with the help of scanning probe microscopes (SPMs) such as STM it is possible to achieve a high vertical resolution ($\leq 1 \text{ \AA}$) and a high lateral resolution ($\leq 10 \text{ \AA}$) there still remain many challenges in imaging. In obtaining the atomic resolution with the STM the stability of the tip and the sample is highly desirable. Therefore it is also important to avoid mixing of electronic energy levels of organic molecules and conducting substrate which can lead to resolution loss. The surface imperfections of highly ordered pyrolytic graphite (HOPG), can lead to artifacts in STM imaging. Despite its flat surface, STM images of HOPG occasionally exhibit disordered and partially ordered features of different shapes, which occurs at the surface steps and grain boundaries.³⁷ Therefore in experiments with biological and organic molecules adsorbed on graphite, it is necessary to distinguish between the features of defective graphite and those of adsorbed molecules. In contrast to this, in a more recent study, honeycomb porous and linear non-porous 2D architectures of DBA molecules were formed on graphite and Au(111) using van der Waals interactions.³⁸ During the transformation of the honeycomb porous network to a linear non-porous on Au (111) a defective structure was formed while this transformation was more accurate in the case of HOPG substrate. The reason behind this “defective” structure has been suggested to be the

kinetic trapping of the solute molecules on the gold surface. Hence it can be concluded that “artifacts” or “defects” in the self-assembled structures can vary with the imaging conditions (UHV or ambient), tunneling currents (as high tunneling currents can destroy the organic samples), nature of the substrate, solvent and solute.

1.2 Objectives

Hence this research work aims to develop two dimensional (2D) self-assembled networks of conjugated oligomers through non-covalent interactions for instance hydrogen bonding and metal-ligand co-ordination. The key components in forming the 2D networks are the branching units with trigonal cores, and the linear units. The units at the termini of the branching units are designed to be able to form directional, specific non-covalent bonds to the corresponding units to create the networks. A two dimensional graphite-like network is produced by combination of branching and linear units. Here suitable core materials for 2D systems include triphenylbenzenes. The first step is to prepare branched and linear units and test their self-assembly by non-covalent interactions between the end groups. Here metal-ligand, acid-base, and electrostatic interactions between cations and anions or specific hydrogen bonds, are to be used as binding forces. The self-assembly of conjugated oligomers with hydrogen bonding motifs at terminal position is to be studied by STM. The π unit in the zinc co-ordinated supramolecular networks is either a p-type or an n-type linear monomer. P-type linear monomer is chosen because it is linear and is a good electron donor. The long alkoxy groups are introduced onto tpy molecules to enhance the solubility. Following the rapid and efficient method³⁹ used by Xue et al., metal co-ordinated supramolecules are produced. On the other hand, the n-type linear monomer chosen is 2,1,3-benzothiadiazole (good electron acceptor) and with the R-groups in the 5- and 6- positions, the solubility of the

supramolecules is enhanced. Electronic and the optoelectronic properties of all of these 2D self-assembled supramolecular networks as well as their metal complexes are to be examined. Finally, depending upon the electronic and optoelectronic properties of these 2D self-assembled supramolecular networks they may be used for light harvesting applications.

1.3 Materials and methods

All of these new organic molecules (as shown in figure 1.3 and figure 1.4) were synthesized (synthetic details are given in chapter 2) and fully characterized (chapter 2, chapter 3 and chapter 4). Their structures were verified by Nuclear Magnetic Resonance (NMR) spectroscopy, Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF) mass spectroscopy, Elemental Analysis and High Resolution Electrospray⁺-Time-Of-Flight mass spectra (HR ES⁺-TOF MS). Thermal behavior of these synthesized molecules was analyzed using techniques, such as, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Their electrochemical properties were evaluated by Cyclic Voltammetry (CV). 2D self-assembled network by hydrogen bonding were studied by means of techniques such as Scanning Tunneling Microscopy (STM). 2D self-assembled network by co-ordination bonding were studied by the techniques such as X-ray photoluminescence spectroscopy or small angle X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques. The photophysics of the materials was studied by UV-Vis absorption spectroscopy, photoluminescent spectroscopy and femtosecond time-resolved photoluminescence dynamics. Figure 1.3 and figure 1.4 shows the structure of various trigonal and linear oligomers (with hydrogen and co-ordination bonding sites at the terminal positions) for making 2D self-assembled networks through hydrogen bonding and zinc metal-ion co-ordination.

Figure 1.3 Structures of synthesized trigonal oligomers with hydrogen bonding and co-ordination bonding sites at terminal positions.

Figure 1.4 Structures of synthesized linear oligomers with hydrogen bonding and co-ordination bonding sites at terminal positions.

1.4 Scope and overview of the thesis

Ordered 2D self-assembled networks through non-covalent interactions of conjugated oligomers have great potential to be used in many electronic devices such as Organic Light Emitting Diodes (OLEDs), Organic Photovoltaics (OPVs), and Organic Field Effect Transistors (OFETs). This is because, such ordered structures have a potential to incorporate some secondary species like organic or inorganic nano particles in a periodic fashion to form composites and combine the excellent electronic properties of inorganic materials with the

processability of organic materials. The formation of ordered assemblies of the inorganic and organic components can be expected to optimize the performance of such composites. The formation of such ordered structures requires ordered 2D organic macrostructures. Although, covalently bonded 2D structures were very well studied in the past, they turned out to be insoluble gels due to the extensive cross-linking within them. Non-covalent self-assembly such as hydrogen bonding and metal co-ordination (as studied in this thesis work), suggests an attractive way to prepare processable functional organic macromolecular materials. Self-assembled non-covalent networks are different from their covalent counterparts, because it is easy to form large self-assembled networks through non-covalent interactions of small organic molecules. Reversibility is the most important property of this kind of self-assembly, which gives the ability for self-correction of defects formed during the assembly process. More importantly, metal-ligand co-ordinated self-assembled networks which are held together by non-covalent metal co-ordination linkages are both as robust as covalent networks and also potentially self-healing due to their dynamic nature. Thus, in this thesis, new hydrogen bonding and Zn(II)-co-ordinated supramolecular 2D networks were prepared. Extended 2D networks were achieved through disassembling of the formed Zn(II)-co-ordinated networks and then re-assembling by inserting the linear bis(tpy) linkers (p-type or n-type). These new 2D Zn(II)-co-ordinated networks were studied for their self-assembly and other important photophysical properties. They were also further examined for their possible suitability in light harvesting applications.

Chapter 2 describes the detailed synthesis and characterization of new trigonal molecules for 2D self-assembly. Although both tri-iodo and tri-bromo molecules were taken as the basic unit for forming trigonal molecules for hydrogen bonding or metal-ion co-ordination, most of

the molecules were successfully synthesized only from a trigonal tri-iodo molecule. The reason being that an iodide is more reactive than a bromide. For molecules for metal-ion coordination, the structures beginning with a central triphenylbenzene unit, extending conjugation through the p-type linker units and end with 2,2':6,2''-terpyridines units in the three arms are mainly discussed. P-type linker was taken with or without long alkoxy chains. Long alkoxy chains attached on the p-type linker in these cores are to enhance the solubility of these core molecules for 2D self-assembly through metal-ligand co-ordination.

Self-assembly studied through Scanning Tunneling Microscopy (STM) of star-shaped trigonal 1,3,5-Tris-(1,1-biphenyl-4-yl)-benzene (TBB) derivatives substituted by different functional groups on the terminal positions of the three arms of the molecule: I (**1a**), Br (**1b**), COOCH₃ (**2a**), COOH (**2b**), NH₂ (**3**), and CN (**4**) is reported in chapter 3. A comparative study on the self-assembly of 1,3,5-tris(4-iodophenyl)benzene (**1a**) and 1,3,5-tris(4-bromophenyl)benzene (**1b**) at the liquid/solid interface showed that (**1a**) self-assembles to form a regular hexagonal array on Highly Oriented Pyrolytic Graphite (HOPG) whereas (**1b**) was not observed to self-assemble under the same conditions. This was attributed to the greater ability of the heavier iodine atom to form a strong intermolecular halogen-hydrogen bond in liquid compared to the lighter bromine. When deposited from 1-phenyloctane as the solvent, the triester TBB **2a** first formed a chiral open network which was not observed to evolve with time. In turn, when deposited from tetrahydronaphthalene, TBB **2a** also formed a chiral open network but with different lattice parameters as compared to Phase I and with solvent molecules co-adsorbed inside the nanopores. In tetrahydronaphthalene, the initial nanoporous structure of TBB **2a** progressively evolved into a chiral close-packed row-like structure where molecules were associated two-by-two in a head-to-tail fashion to form pairs.

Finally, when deposited from 1-phenyloctane, the tricyano TBB **4** only formed short-range ordering with an open honeycomb structure and a close-packed row-like structure.

Metallo-supramolecular networks have received a lot of interest in the past, not only for the higher strength of this non-covalent interaction in comparison to other non-covalent interactions (such as hydrogen-bonding) but also for the self-healing ability of these networks due to their dynamic nature. The p-type organic molecules are defined as the organic molecules that are electron rich and thus strong in electron donating, whereas, n-type organic molecules are defined as the organic molecules that are electron poor and thus strong in electron accepting. The n-type linker units, dialkoxybenzothiadiazole is likely to be a good electron acceptor. So both type of p-type and n-type linker units were used in forming extended 2D self-assembled networks through metal-ligand co-ordination. Chapter 4 describes the synthesis and self-assembly of linear and star-shaped trigonal terpyridines (tpys) and two component extended self-assembled 2D networks of trigonal tpys with linear tpys through zinc metal ion Zn(II) co-ordination. The resulting Zn(II) co-ordination networks were characterized by means of X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering (SAXS), BET, and other photophysical and electrochemical methods. Small angle XRD results showed a short range order in these 2D self-assembled networks. These metallo-supramolecular Zn(II) networks revealed the influence of the metal ion on the thermal, optical and electrical properties of the synthesized metallo-supramolecular assemblies. The porosity and the surface area of the 2D Zn(II)-co-ordinated self-assembled networks were investigated by sorption analysis using nitrogen. It was observed that these networks are nonporous due to their highly interpenetrating nature. These networks have shown high luminescence with long fluorescence life times and good thermal stabilities.

In chapter 5, the efficient intermolecular energy transfer between a new donor-acceptor couple, with 1,3,5-tris[4-amino(1,1-biphenyl-4-yl)]-benzene (TBB, **3**) as the donor (**D**) and a linear carboxylate derivative, PMI-monoacid (**21**) as acceptor (**A**) is reported. It was observed that this energy transfer occurs via a Förster resonance energy transfer (FRET) pathway by a nonradiative long range dipole-dipole coupling of the donor and acceptor molecules both in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) solutions. Förster radius (R_0) equal to 3.4 nm (taking into account the random dipole orientations of the donor and acceptor molecules) and the quantum yield of the donor TBB (**3**) equal to 0.53 in THF solution for TBB (**3**)-PMI-monoacid (**21**) (**D-A** couple **A**) was calculated. A slightly smaller value for the Förster radius was observed in DMSO solution where the quantum yield of the donor was comparatively lower but the spectral overlap integral was higher for couple **A**. Intermolecular energy transfer was also observed between TBB (**3**) as the donor (**D**) and PDI-diacid (**20**) as the acceptor. Förster radius for TBB (**3**)-PDI-diacid (**20**) (**D-A** couple **B**) was calculated to be 3.1 nm in THF and 2.8 nm in DMSO solution. Intermolecular energy transfer efficiencies of 95% and 86% was calculated from steady state and time resolved measurements respectively for the couple **A** in THF solution and 85% in DMSO solution from steady state measurement. For couples **B**, comparatively much smaller values of energy transfer efficiencies were calculated from steady state measurements. The difference in these values is discussed in detail. These new **D-A** couples are capable of serving as models for light harvesting systems.

Chapter 2 Synthesis of new trigonal molecules with non-covalent bonding units at the terminal positions

2.1 Introduction

Studies of supramolecular sciences have become one of the major areas of scientific interest. It is connecting scientists from all areas of sciences, including chemists, physicists, and biologists. A supramolecule has many subunits, each designed to perform a specific task. Therefore, while a supramolecule is still in some ways a single molecule, it is engineered to function like a large complex system. The possibility of ordering of π -conjugated systems at these different length scales has produced the area of supramolecular electronics.⁴⁰

Figure 2.1 Diagram illustrating difference in the dimensions between molecular electronics and plastic electronics.⁴¹ Adapted from Ref. [41].

Supramolecular electronics has bridged the gap between molecular electronics (Angstrom dimensions), and plastic electronics (dimensions in the micrometer range) as it lies somewhere between molecular electronics and the plastic electronics in dimensions. The

concept of molecular electronics, i.e. a single molecule device, has been put forward in a review⁴² by Joachim et al. They call this ‘mono-molecule’ electronics, wherein, single molecules integrate the basic device functions. By contrast, plastic electronics is a well established field of scientific and technological interest dealing with bulk materials, and differing from conventional electronics only in the nature of the materials (i.e organic instead of inorganic semiconductors).

Large supramolecular structures can easily be synthesized with the self-assembly of small π -conjugated molecules and have lot of potential for optoelectronic device applications. Supramolecular assemblies of π -conjugated systems are reviewed⁴³ by E.W. Meijer. Due importance is given to both the synthesis of new molecules and to the device fabrication and they are interrelated in the sense that they are complementary to each other. Yuan et al. have synthesized⁴⁴ a number of linear and trigonal π -conjugated tpys using single, double, and triple bonds and these rigid structures displayed blue emission in solution. Solubility of these robust structures was improved by attaching fluorene and truxene units. Absorption wavelength (λ_{max}) is red shifted for tpy derivatives with double and triple bond linkages compared to those with single-bond linkages probably due to the increase in the conjugation. In comparison with 4'-phenyl-tpy, the molar absorption coefficient (ϵ_{max}) of these structures was increased by $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. These novel complexes, with good energy transfer efficiencies, are very promising candidates for light-harvesting applications.

Solubility is a very important factor for synthesizing a material for nano-device applications. Barada et al. synthesized⁴⁵ a series of c3-symmetric π -conjugated compounds. They reported a 20-70% increase in fluorescence quantum yields by incorporation of o-carborane clusters into extended trimeric π -conjugated systems. Incorporation of carboranes makes them thermally stable and as well as water soluble.

Supramolecular assemblies can be formed by non-covalent interactions for example, hydrogen-bonding, co-ordination bonding, hydrophobic interactions, electrostatic, and van der Waals forces. Supramolecular assemblies of conjugated polymers formed by different noncovalent interactions have been reviewed⁴⁶ by Leclere et al. The natures of the interactions between the π -conjugated small molecules for supramolecular organization and their morphology emerging upon aggregation have been discussed. The emission and the charge transport properties have been investigated. Hence, it can be concluded that structures of the polymer and supramolecular organization have a great influence on these properties.

Many studies have examined the organization of hydrogen bonding to stabilize binary molecular structures. Hydrogen bonding offers the stability, precision and more importantly the flexibility of nanostructures. Donor and acceptor systems can be formed together by supramolecular assembly as it is easier than depositing two different layers on the substrate for device applications and at the same time it can significantly reduce the size of the device. For instance, a hydrogen-bonded triad (**D-A-D**) has been studied as a possible material for solar cell applications.⁴¹

Figure 2.2 Chemical structure of a self-assembled hydrogen-bonded supramolecular network.⁴¹ Adapted from Ref. [41].

The term “metallo-supramolecular chemistry” emerged in the beginning of 90s to illustrate supramolecular co-ordination driven chemistry. This sub-field of supramolecular chemistry had progressed by investigating the metal-directed self-assembly of a number of ligands and then extended to vast structures. Co-ordination driven self-assembly techniques, based on the electron-poor square-planar Pt^{2+} complexes (made up of pyridyl donors) had opened a lot of possibilities for the metal-ligand self-assembly in past. After then, a vast collection of research papers on 2D and 3D supramolecular self-assemblies via directional co-ordination bonding approach have been published. A lot of work in this field has been done on co-ordination driven self-assembly of metallo-supramolecules by Stang’s group.^{19,47–58}

Terpyridine is one of the most appropriate ligands for the creating supramolecular self-assembled networks via metal-ligand co-ordination. It gives comparatively stable, and at the same time, well directional metal-ion bonding. Supramolecular chemistry of terpyridine metal complexes have been reviewed.¹ A new metallo-supramolecular polymer with a 2,6-bis(19-methylbenzimidazolyl)pyridine ligand has been synthesized. It was self-assembled with Zn^{2+} ions, which gave, a material with interesting optical properties.⁵⁹ Different transition metal complexes (e.g. Ir^{3+} , Rh^{3+} , Os^{2+} , Ru^{2+} and others) had emerged with remarkable properties when complexed with pyridine ligands. The research in the field of co-

ordination networks of Ru^{2+} complexes progressed because of their robust structure and simplicity in the synthesis.⁶⁰ Recently Yuan et al. reported⁶¹ a series of metallomacromolecules, based on thiophene-functionalized bisterpyridine- Ru^{2+} with truxene moieties. At the same time, research on d10 transition metal ions also progressed rapidly. Vellis et al. have synthesized⁶² a series of soluble terpyridine ligands. Complexation of these ligands with Zn^{2+} and Ru^{2+} makes them highly applicable compounds for optoelectronics. Even though metal-directed self-assembly provided evidence to be an influential means to construct large supramolecular structures, the ultimate purpose has constantly been the ordered self-assembly of different organic units with distinct functions.

Figure 2.3 Chemical structures and space-filling models of (A)“small” supramolecular rectangle, (B)“large” supramolecular rectangle, and (C) supramolecular square.⁵² Reprinted from Ref. [52] with permission from the American chemical Society.

Therefore, as a first step to achieve ordered networks, this thesis work reports on the synthesis and characterization of both the hydrogen bonding and co-ordination bonding molecules for making ordered 2D self-assembled networks. The basic unit for synthesizing these molecules is 1,3,5-tri-(p-iodophenyl)-benzene. Extension of this basic unit by linear molecules bearing hydrogen bonding motifs (such as amine, carboxylic acid, and uracil) and co-ordination bonding motifs (terpyridine), through single bond or triple bonds (which can

give extended structures without losing conjugation) provides the hydrogen bonding and coordination bonding molecules for 2D self-assembly. The purpose of introducing long alkoxy chains in molecule **14** is to enhance the solubility of the core molecule **16** for 2D self-assembled networks.

2.2 Synthesis of molecules for 2D hydrogen bonding networks

The synthetic procedure to TBBs **1-4** is presented in scheme 2.1. The key intermediate in the synthesis 1,3,5-tri-(p-iodophenyl)-benzene **1a** was synthesized in 80% yield by cyclotrimerisation of 4-iodoacetophenone according to a literature procedure.⁶³ Suzuki coupling of **1a** with commercially available boronates gave compounds **2a**, **3**, and **4** in moderate (40-62%) yields. Hydrolysis of the ester **2a** produced the triacid **2b** in 86% yield.⁶⁴

Scheme 2.1 Synthetic route to TBBs **1-4**. The triacid TBB **2b** is obtained by hydrolysis of TBB **2a**.

The synthesis of core molecule **5** is outlined in scheme 2.2. Molecule **5** was synthesized via palladium-catalyzed Sonogashira cross-coupling reactions as reported in literature.⁶⁵ Firstly 1,3,5-tri-(p-iodophenyl)-benzene **1a** was coupled with trimethylsilylacetylene (TMSA) to

afford **5a**, followed by cleavage of the TMS protecting group by addition of a 1M aqueous solution of K_2CO_3 .

Scheme 2.2 Synthetic route to core molecule **5a** and **5b**. **5b** is obtained by deprotection of TMSA group from **5a**.

Molecule **8**, bearing three uracil recognition sites, was synthesized as shown in scheme 2.3. In the first step 1-hexyluracil (**6**) was synthesized by reaction of uracil with 1-bromo hexane in the presence of K_2CO_3 and DMSO. Subsequent deprotonation of **6** with LDA and addition of I_2 afforded the C_6 -iodinated derivative **7**. And finally, **8** was prepared by Sonogashira cross-coupling reaction between 1,3,5-tris-(4-ethynyl-phenyl)-benzene (**5b**) with **7** in the presence of CuI and $[Pd(PPh_3)_4]$, as a light-brown powder, which was purified by repeated precipitation cycles and characterized by 1H and ^{13}C NMR spectroscopy in DMSO- d_6 . Molecule **8** proved to be barely soluble in most organic solvents, probably due to extended homomolecular double H-bonding interactions between the peripheral uracil moieties in solution. As a result, visualization of self-assembly of **8** at liquid/solid interface was not achieved by STM techniques.

Scheme 2.3 Synthetic route to iodo uracil molecule **7** and trigonal molecule **8** with uracil unit at terminal position.

Linear (1D) arrays through complementary triple H-bonds between uracil and melamine units have been reported.⁶⁶ Uracil units at the terminal positions were introduced to trigonal core **5b** to be engineered to form a 2D self-assembled network with linear or trigonal melamine units at the terminal positions. Due to the time limitations and the solubility problems mentioned above this work could not be finished but will be carried forward by future students.

2.3 Co-ordination bonding molecules and their Synthesis

Figure 2.4 shows the structure of trigonal core tpy molecules for making 2D self-assembled networks through zinc metal-ion co-ordination.

Figure 2.4 Chemical structures of new molecules for 2D metal ion co-ordinate supramolecular networks.

Details of synthetic procedures for synthesis of **14**, **15** and **16** (including the synthesis of their intermediates) according to scheme 2.4 - 2.9 and the characterization data (including ^1H NMR, ^{13}C NMR, MALDI-TOF mass spectra, Elemental Analysis and HRMS) are described in detail in the Experimental Section.

Figure 2.5 shows the structure of other linear molecules prepared by co-workers in my group which can be used to form the extended 2D self-assembled networks via zinc metal ion co-ordination in combination with trigonal-tpy molecules. Molecule **17** (a p-type molecule) and **18** (an n-type molecule) were synthesized by Dr. Lim Zheng Bang. The molecule **19**

containing a strong absorbing and emitting PDI unit has been made by Dr. Sung Ju Cho for combination with units such as **16**. It could possibly be complexed by metal-ligand co-ordination with **14** or **16** for light harvesting applications, but time did not permit synthesis of networks containing it.

Figure 2.5 Chemical structures of linear molecules for 2D zinc metal-ion co-ordinate supramolecular networks.

2.3.1 Synthesis of core, terpyridyl and linker monomers

Boronation of **1a** through Suzuki coupling reaction gave the key intermediate core molecule **9** in a moderate yield. Synthesis scheme of trigonal core **9** is outlined in scheme 2.4.

Scheme 2.4 Synthetic route to trigonal molecule **9**.

In the first step towards the synthesis of p-type linker monomer **13**, 2,5-dibromobenzene-1,4-diol (2,5-dibromohydroquinone) was dialkylated to form 1,4-dibromo-2,5-bis(dodecyloxy)benzene **12** as outlined in scheme 2.5. This reaction involved the nucleophilic substitution of bromide by phenoxide anions generated using base.⁶⁷

Scheme 2.5 Synthetic route to 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**).

4'-(4-Bromophenyl)-2,2':6'2''-terpyridine **10** was synthesized through the reaction of 4-bromobenzaldehyde and 2-acetylpyridine. The enolate of 2-acetylpyridine was produced by KOH under mild conditions, followed by an aldol condensation and a Michael addition. The

intermediate, soluble diketone, was then permitted to form the central pyridine ring with an aqueous ammonia nitrogen source.⁶⁸ Finally by boronation through a Miyaura reaction **10** was converted to 4'-(4-pinacolatoboronphenyl)-2,2':6',2''-terpyridine **11**.

P-type linker monomer **13**, was synthesized through the Suzuki-coupling reaction of 1,4-dibromo-2,5-bis(dodecyloxy)benzene **12** with boronated tpy molecule **11** in a moderate yield of 53%. Synthesis of terpyridyl monomer **13** is outlined in scheme 2.6. This molecule was synthesized according to the procedure previously described in our group and the structure of this molecule was confirmed by ¹H NMR and ¹³C NMR.

Scheme 2.6 Synthesis of p-type monomer **13**.

2.3.2 Synthesis of new 2D core molecule **14** for co-ordination bonding

In the next step towards synthesis of molecule **14**, molecule **11** and **12** were Suzuki-coupled to yield **13**. The final step involved in the preparation of the new 2D p-type core for 2D self-assembly is outlined in scheme 2.7, with compounds **9**, and **13** as the coupling units. In the presence of Pd (0) catalyst, compound **13** was Suzuki-coupled with triborane **9** to produce compound **14** as an off white solid. The structure of this novel trigonal-tpy molecule **14** was confirmed by ^1H NMR and ^{13}C NMR and its molecular weight was confirmed by high resolution mass spectrometry (HRMS). 2D self-assembled networks from molecule **14** were made through zinc metal ion co-ordination. The details (synthesis and characterization) of these will be discussed in chapter 4.

Scheme 2.7 Synthesis scheme of 2D supramolecule **14**.

2.3.3 Synthesis of new 2D core molecule **15** for co-ordination bonding

Novel molecule **15** was designed for its possible formation of a metal organic framework via zinc metal ion co-ordination and was synthesized in good yield through coupling of tribromo compound **1b** with imidazole (as shown in scheme 2.8). The structure of this novel trigonal imidazole molecule **15** was confirmed by ^1H NMR, ^{13}C NMR and the molecular weight was confirmed by HRMS.

Scheme 2.8 Synthesis scheme of molecule **15**.

2.3.4 Synthesis of new 2D core molecule **16** for co-ordination bonding

Compound **16** was synthesized according to a previously reported procedure⁶⁹ via Suzuki-coupling of tri-bromo molecule **1b** with tpy boronate **11** (as shown in scheme 2.9). The solubility of **16** was found to be not very good. It is soluble in only high polarity solvents like DMSO and DMF and slightly soluble in THF and chloroform. The purpose of removing long alkoxy (as in molecule **14**) chain is to increase the porosity of the networks made through zinc metal-ion co-ordination.

Scheme 2.9 Synthesis scheme of 2D supramolecule **16**.

2.4 Characterization of molecules for novel 2D self-assembled networks

2.4.1 Photophysical properties

Room temperature UV–visible absorption and photoluminescence (PL) spectra of TBBs **2a**, **2b**, **3**, **4** and **8** recorded in tetrahydrofuran (THF) and in the solid state are presented in figure 2.6 and figure 2.7. The UV–Vis absorption maxima in THF solution of trigonal oligomers

TBB **2a**, TBB **2b**, TBB **4**, and TBB **8** were observed at 299, 291, 294 and 335 nm respectively, which are due to the π - π^* transition of the aromatic rings, while the maxima of the photoluminescence spectrum were observed at 354, 353, 362 and 402 nm respectively. The thin solid film fluorescence spectra of the TBBs **2a**, **2b** and **4** were significantly red-shifted by 45, 44 and 65 nm relative to their corresponding monomeric spectra obtained from the dilute solutions. The experimental red shift and broadening of the PL spectra of **2a**, **2b**, **4** and **8** in solid state support the formation of intermolecular hydrogen bonds.^{70,71} A red shift of 26 nm was observed for **8**, probably due to the extended homomolecular double H-bonding interactions formed between the peripheral uracil moieties in solution.

Figure 2.6 UV-visible absorption spectra (blue lines) and normalized fluorescence spectra of **2a**, **2b**, **4** and **8** in dilute (1×10^{-6} M) Tetrahydrofuran (THF) solutions (red lines) and in the solid state (black lines).

However, the emission of TBB **3** in solid film is almost identical with that of the dilute solution, except for some broadening which confirms the negligible intermolecular interactions of **3** in solid films. To further confirm this behavior low temperature photoluminescence measurements in solid thin films were performed. From figure 2.7, it is clear that no major shift in the photoluminescence peak was observed with increasing temperature, which should be due to the very small radius and large binding energy of Frenkel excitons in the organic molecules. However, the full width at half-maximum (FWHM) in photoluminescence spectra of TBB **3** in the solid state became broadened by 0.189 eV upon increasing the temperature from 10 to 300 K.

Figure 2.7 UV-Vis absorption spectra (blue lines) and normalized fluorescence spectra of TBB **3** in dilute (1×10^{-6} M) THF solutions (red lines) and in thin solid film (black lines) b) Temperature dependent PL spectra from 10 K (black lines) to 300 K (pink line) of TBB **3**.

In summary, the temperature dependence of PL in the solid state was measured for the TBB **3**. It was observed that full width at half-maximum becomes narrower upon decreasing the temperature from 300 K to 10 K, showing the aggregation of molecules with decreasing temperature. A red shift in PL could indicate that either the molecules are self-assembling themselves with the hydrogen bonding motif at the terminal position or through stacking interactions (π - π).^{71,72} Although a significant red shift in emission was not observed for TBB **3**. This may be due to the fact that this low temperature PL measurement was performed in solid thin films not in solution. The photophysical properties of **14**, together with its self-assembled networks are discussed in chapter 4.

2.4.2 Thermal behavior of the novel trigonal molecules

The hydrogen bonding molecules described above are thermally very stable and hence can be self-assembled through ultra-high vacuum (UHV) deposition conditions. The molecules for metal-ion co-ordination are also very stable up to 300 °C, and hence are good candidates for formation of self-assembled networks. The Thermogravimetric Analysis (TGA) plots and corresponding Differential Scanning Calorimetry (DSC) plots of 2D conjugated cores **3**, **8**, **14** and **15** are shown in the experimental section. T_{5d} and T_g of **3**, **8**, **14** and **15** are listed in table 2.1.

Table 2.1 5% weight loss temperature (T_{5d}) and glass transition temperature (T_g) of 2D conjugated cores **3**, **8**, **14** and **15**.

Molecules	T_{5d} ($^{\circ}\text{C}$) ^a	T_g ($^{\circ}\text{C}$) ^b
3	150	110
8	374	— ^d
14	310	115
15	306	134

^a T_{5d} = 5% weight loss temperature; ^b T_g = glass transition temperature; ^drelevant data is not found.

2.4.3 Electrochemical properties of new trigonal molecules

The electrochemical behaviour of 2D conjugated cores **3**, **8** and **14** was investigated by Cyclic Voltammetry. The oxidation onset potentials ($E_{\text{onset,ox}}$) of **3**, **8** and **14** are 1.37 V, 1.53 and 1.47 V versus Ag/Ag^+ , respectively. The calculated HOMO values (eV) of **3**, **8** and **14** are thus -5.77, -5.93, and -5.87, respectively. The reduction onset potentials ($E_{\text{onset,red}}$) of **3**, **8** and **14** are -0.76 V, -0.69 and -0.73 V versus Ag/Ag^+ , respectively, corresponding to calculated LUMO values (eV) for **3**, **8** and **14** of -3.64, -3.71 and -3.67, respectively. The electrochemical bandgaps ($E_{\text{g,ele}}$) of **3**, **8** and **14** are thus 2.13, 2.22 and 2.20 eV, respectively, which are not very close to their $E_{\text{g,opt}}$ (3.27 eV, 3.39 and 3.19 eV, respectively).

The optical bandgap was measured using the absorption edge of the UV/Vis spectra using the equation: $E_g = hc/\lambda$ wavelength are in good agreement with the electrochemical band gap measured for trigonal oligomers bearing the similar structures.^{73,74} The electrochemical band gap was calculated by the onset values. These were estimated by taking the intersection point between the baseline and the tangent line drawn to the rising portion of the current.

The error in optical and electrochemical band gap is approximately $> 1\text{ eV}$ which is quite high than the literature reported values (0.3 eV).⁷⁵ Basically the electrochemical bandgap is believed to be larger than the optical band gap and the reason behind this is that the optical band gap is created by excitation of electrons from HOMO to LUMO. The difference, between reduction potential and oxidation potential of the species, is called the electrochemical band gap. Electrochemical reduction requires higher energy than LUMO and again for oxidation the energy should be lower than HOMO, these extra energy requirements for redox make the electrochemical band gap higher in value than optical band gap. But in our case the optical band gap is higher than the electrochemical band gap. The band-gap values derived from CV should be construed to have many interfering factors, such as those arise from physical & surface status of electrodes. The redox potentials could be different in different media and critically depend on the quality of electrode surface, pre-adsorbed gases, status of electrolyte (deaerated or not). And another reason for this difference could be, due to the inaccuracy when extrapolating data from the CV and UV-vis absorption plots. The plots are shown in figure A12, A25 and A34 in experimental section and the data are listed in table 2.2.

Table 2.2 Redox properties of 2D conjugated cores **3**, **8** and **14**.

Molecules	CV					
	E _{onset,ox} (V)	E _{onset,red} (V)	E _{HOMO} (eV) ^a	E _{LUMO} (eV) ^b	E _{g,ele} (eV) ^c	E _{g,opt} (eV) ^d
3	1.37	-0.76	-5.77	-3.64	2.13	3.27
8	1.53	-0.69	-5.93	-3.71	2.22	3.39
14	1.47	-0.73	-5.87	-3.67	2.20	3.19

^aE_{HOMO} = -(E_{onset,ox} + 4.4) eV; ^bE_{LUMO} = -(E_{onset,red} + 4.4) eV; ^cE_{g,ele} = E_{LUMO} - E_{HOMO}; ^dE_{g,opt} [cf. Table 2.2].

2.5 Conclusion

In conclusion, novel cores for 2D supramolecules (with terminal hydrogen bonding and co-ordination motif) with and without long alkyl chain were successfully synthesized. Most of these trigonal symmetric molecules are soluble in common solvents and displayed blue emission in solution or in solid state. 2D Self-assembly of hydrogen bonding molecules is described in chapter 3. The molecules for co-ordination bonding molecules are thermally stable up to 300 °C and hence are good candidates for metal-ligand co-ordinated self-assembly process as in order to form stable 2D self-assembled networks which will be further discussed in chapter 4.

Chapter 3 Self-assembled 2D supramolecular networks studied by STM

3.1 Introduction

A full control over charge injection as well as charge transport at the organic-organic and organic-inorganic interfaces is very important for device applications. Therefore, the self-assembly of organic molecules at the surfaces of interest is critical. This is only possible with a greater control of the interaction between adsorbed molecules and electrically conducting surfaces. Among the most considered conducting surfaces for STM imaging, Highly Oriented Pyrolytic Graphite (HOPG) has achieved much attention because of its layered nature and ease of preparation. Au(111), Ag(111), Ag(110), and Cu(111) are other important conducting surfaces widely used for STM imaging under UHV conditions. Mica, Si/SiO_x and quartz (used for STM and AFM imaging), are insulating surfaces, have been used for STM imaging by making them conducting with the application of a thin layer of conducting metals such as Pt and Au.

Apart from inert and conducting nature of the surface, another important criterion for selecting a particular surface is its ease of preparation together with that it must be atomically flat. With this regard HOPG is one of the best surfaces of interest, as a freshly cleaved and atomically flat HOPG surface can be achieved just by peeling off a thin layer of it from a number of layers.

Another essential factor for good quality STM imaging is sample preparation. A continuous film with intermolecular π -overlap is beneficial to increase the charge-carrier mobility. Instead, if the charges reside in local potential minima, or traps, they will be trapped and

relatively high voltages will be needed to dislodge them. Such traps can be due to oxidizable or reducible chemical impurities, grain boundaries, inhomogeneities at the dielectric interface, or crystallographic defects, resulting in low mobility. Despite the possibility to obtain well-ordered two-dimensional monolayer on graphite^{13,76,77} as studied with STM, and the ability to vacuum evaporate these oligomers to gain crystalline films; it is a challenge to increase control over the mesoscopic order of such oligomers into larger domains by less expensive means.

It is possible to observe self-assembled networks at either a liquid/solid interface or an air/solid interface. For the self-assembly process from solution, a detailed understanding of the solute-solvent interaction is desirable in order to eventually understand and to control the results, as molecules possess different structures in different solvents and the concentration of the solvents is also very important for the self-assembly process⁷, which is an important finding of the Marcus group. At the same time substrate temperature also plays a significant role in self-assembly process. Recently Fichou's group showed a temperature dependent 2D supramolecular self-assembly at liquid/solid interface using STM techniques in which hexakis(n-dodecyl)-peri-hexabenzocoronene (HBC-C12) was observed on Au(111).⁷⁸ It was claimed that the packing density of 2D self-assembled networks of HBC-C12 could be tuned accurately by regulating the substrate temperature as shown in figure 3.1. This factor is very important for future application of such assemblies in devices.

Figure 3.1 STM image of HBC- C12. (A) Metastable α -phase at 20 $^{\circ}\text{C}$ (B) β -network at 25 $^{\circ}\text{C}$ (C) γ -network at 35 $^{\circ}\text{C}$ (D) δ -network at 50 $^{\circ}\text{C}$.⁷⁸ Reprinted from Ref. [78] with permission from the American Chemical Society.

Intermolecular interactions and adsorbate–substrate interactions, contribute significantly in the formation of 2D patterns on the surfaces. The nature of the surface, in combination with the temperature, determines the strength of the interaction of the adsorbate with the surface. This concept has been best presented in a review⁴ by De Feyter and De Schryver which mainly deals with hydrogen bonded, supramolecular architectures. 2D self-assemblies of thiophene-fluorenone conjugated oligomers were observed on HOPG surface. These studies dealt with the influence of the molecular structure of fluorenone-thiophene based materials⁷⁹ on their self-organization properties. Multi-component systems are highly important in optoelectronic devices. For example, in solar cells the active layer consists of electron-donor and electron-acceptor components, while in LEDs, the emissive wavelength can be tuned by dopants in a multi-component fashion. In all these devices, the organization of the different components will largely determine the macroscopic properties. 2D self-assembly of two component system has been reported¹³ and this finding demonstrates an approach to precisely grow 2D stoichiometric composite materials at the molecular scale, and to controllably fabricate ordered and homogeneous 2D structures with nanometer dimensions. Three component miniaturized H-bonded architectures of supramolecular assemblies have

reported⁶⁶ by Pallas et al. This self assembly on the Ag(111) surface mediated by triple H-bonding interactions has been studied by STM as shown in the following figure 3.2.

Figure 3.2 Chemical structures of the molecular components formed via directional H-bonding units and STM images of multi-component sub-monolayers of molecules on Ag(111) surfaces.⁶⁶ Reprinted from Ref. [66] with permission from the Wiley-VCH.

In a very informative review,⁸⁰ self-assemblies of functional nanostructures on solid surfaces has been reviewed. The importance and dependence of STM techniques to visualize the monolayer patterns of self-assembled molecules on conducting surfaces has been focused. The geometry of such monolayer patterns is tremendously significant for their application in electronic devices. Porous self-assembled monolayer patterns of organic molecules are always essential for development of many useful applications. One of them could be as a host for the synthesis of inorganic nanoparticles inside the ordered network. The progress towards the design and usefulness of self-assembled networks on surfaces, in

one of the important studies, has been highlighted as a current advance in supramolecular surface sciences.⁸¹

The most studied interactions in supramolecular chemistry are hydrogen bonding interactions and metal–ligand co-ordination interactions. Weaker interactions between molecules, for example, van der Waals interactions and electrostatic interactions are not very conventional. These interactions have a potential of a decisive role in the formation of self-assembled patterns at surfaces. Self-assembly of polar molecule is also governed by the electrostatic interactions between them. The development of honeycomb networks of subphthalocyanine molecules at a Ag(111) surface is shown in figure 3.3. This is a representative example of electrostatic interactions where adsorbed molecules are well separated by maximum of three lattice spaces. Hence, the self-assembly of molecules at surfaces depends on more than one factor. The molecule–molecule and molecule–substrate interactions, together with the polarizability of the molecules and substrate, governs the precise development of these patterns.⁸²

Figure 3.3 Honeycomb network of the subphthalocyanine molecules ($14 \times 14 \text{ nm}^2$).⁸¹ Reprinted from Ref. [81] with permission from the Wiley-VCH.

Work on 2D self-assemblies of benzene-1,3,5-triyl-tribenzoic acid (BTA) has been reported⁸³ by Mario Ruben et al. The motivating point here is that a void of size 2.95 nm in the BTA network has been found as shown in figure 3.4. One could synthesize an inorganic nanoparticle inside this void to make supramolecular organic-inorganic nanocomposite materials.

Figure 3.4 STM picture of the honeycomb pattern at high-resolution. (b) Proposed structure (c) Chemical structure of 4,4,4'-Benzene-1,3,5-triyl-tribenzoic Acid.⁸³ Reprinted from Ref. [83] with permission from the American Chemical Society.

3.2 Self-assembled networks of TBBs by STM

Self-assembly of organic molecules by reversible non-covalent interactions such as hydrogen bonding is a very fascinating area of research^{4,11} with many applications in a bottom-up technique for fabrication of macromolecular devices^{3,40} and of templates for introducing guests into the voids inside the supramolecular network.¹⁰ Development and understanding of research of 2D supramolecular structures has attracted a lot of attention in the last decade.⁸¹ Among the advantages of non-covalent assembly by hydrogen bonding is its simplicity, in which multi-component supramolecular architectures can be obtained from small components in solution in a single step under mild conditions and it gives

directionality to the macromolecular structure. 2D hydrogen bonded self-assembled structure of trigonal molecules are very exciting as these structures possess multiple hydrogen bonding motifs for creating an extended hydrogen bonding network. Trigonal halogenated oligomers such as **1a** and **1b** are potential basic building blocks for the synthesis of many star shape organic molecules with hydrogen bonding motifs in this thesis work. So as a first step towards understanding such self-assembled structures, it is crucial to understand the self-assembly of these core molecules themselves on conducting surfaces like Au(111), Cu(111), Ag(111), Ag(110), graphite(001) and on other conducting surfaces of importance. HOPG(0001) is a substrate with a layered surface which interacts weakly with adsorbed molecules by van der Waals interactions. So it is an ideal substrate to study the self-assembly by intermolecular interactions. By contrast other substrates like Ag(111) allow stronger interactions with the adsorbed molecules i.e. electrostatic and charge transfer interactions. For this reason these different substrates give rise to different self-assembled patterns of the adsorbed molecules.^{12,84,85}

Formation of 2D supramolecular networks by non-covalent interactions on surfaces by self-assembly process is currently a much studied area of research,^{11,81} as it has scientific interest and potential nanotechnological advantages.^{3,40} To understand the mechanism behind the formation of such networks is very complicated as it depends not only on the nature of the solute, nature of the solvent, and method of assembly (UHV deposition or at liquid/solid interface) but also on the interactions between solvent and solute molecules, between solute molecules and also on solute-surface interactions.⁸⁶ Self-assembly at liquid/solid interface is largely governed by the interaction of solute molecules with the solvent. The dependence of self-assembly on choice of solvent(s) cannot be ignored as depending on the nature of the solvent used during self-assembly, one may see different patterns in the self-assembled

networks⁷. Even a change in the concentration of a (co-)solvent can alter the self-assembled network structure. Control of these patterns has great significance for potential use of these assembled molecules in various applications.

A careful selection of organic solvent for self-assembly at liquid/solid interface is thus critical. The criteria of selection of a solvent for STM studies are first the (usually low) vapor pressure of the solvent. Secondly it should be an electrochemically inert and preferably non-polar solvent. The third and the most important aspect is that the organic molecule must be soluble in the solvent. And last but not least is that it should have minimal interaction with the substrate so that one only visualizes the pattern of the molecules of interest. The choice of solvent may also introduce chirality into the self-assembled network.

Many 2D chiral self-assembled networks have been observed by STM in the past few years.^{86–89} Chiral self-assembled networks can be achieved for both chiral and achiral molecules depending on either the solvent used for self-assembly or on the surface at which the self-assembled monolayer forms. Formation of chiral 2D self-assembled structure by an achiral molecule can have a great importance for its future applications, as chirality can significantly influence (or even completely alter) the electronic properties of a molecule at a surface.⁹⁰

In this thesis work self-assembly of trigonal molecules **1a**, **1b**, **2a**, **2b**, **3**, and **4** using three different solvents *n*-tetradecane, tetrahydronaphthalene and 1-phenyloctane was reported. The chemical structure of these solvent molecules is shown in figure 3.5. An open network structure of molecules of trigonal oligomer **2a** is observed for both solvents (tetrahydronaphthalene and 1-phenyloctane), although it differs in the geometrical arrangement of the molecules around a central cavity of different size. Co-adsorption of

solvent molecules inside these cavities was observed with tetrahydronaphthalene. Since this open network structure is not stable with time so a closed packed structure in tetrahydronaphthalene becomes observable after formation of the open network structure.

Figure 3.5 Chemical structures of solvent molecules for STM a) *n*-tetradecane b) tetrahydronaphthalene c) 1-phenyloctane.

3.2.1 Trigonal oligomer **1a** in *n*-tetradecane

Upon deposition of the molecules of **1a** on graphite, STM images reveal that the molecules self-assemble into large hexagonal 2D structures as shown in figure 3.6. As shown in the high resolution STM images (figure 3.6 (b) and figure 3.6 (c)) the molecules form a chiral hexagonal network. The lattice parameter is 4.3 nm. The molecules form hexagons composed of six molecules. The molecules appear as a yellow equilateral triangle with a 1.7 nm side length in the STM images. The center of the hexagon is empty. This chiral arrangement is similar to the ordering of triangular molecules like melamine on Au(111).⁹¹ The two enantiomeric domains of this chiral structure are presented in the STM images figure 3.6 (b) and figure 3.6 (c).

These STM images of the molecule show short arms terminated by iodine atoms. The head-to-tail arrangement is quite unusual, as the molecules are far apart from each other (i.e. not close-packed) but the triangular molecular shape is clearly visible. Although the heavy atom,

iodine is not more visible than the other atoms, the molecules seem quite stable on the surface. The hexagonal pattern is clearly visible at room temperature. Such a hexagonal mesh is typically formed by molecules with three fold bonding sites. Here the interactions responsible for such kind of self-assembly are intermolecular hydrogen-halogen bond interactions, i.e. a weak hydrogen bonding interaction between iodine and a nearby hydrogen atom of the neighboring molecule.

Figure 3.6 STM image of 1, 3, 5-tris(4-iodophenyl)benzene **1a** on HOPG at room temperature in *n*-tetradecane. (a) $60 \times 57 \text{ nm}^2$, (b) $22 \times 16 \text{ nm}^2$ (c) $25 \times 19 \text{ nm}^2$. Tunneling parameters: $V_s = +0.8 \text{ V}$, $I_t = 8 \text{ pA}$. (d) Scheme of the two chiral orientations of the molecular structure.

Recently 2D self-assembly of 1,3,5-tris (4'-bromophenyl) (**1b**) has been reported.^{12,84,85} The disordered covalent network on Cu(111), Ag(110) and Ag(111)⁸⁴, an ordered covalent network on Au(111)⁸⁵ and a non-covalent assembly on graphite(001)¹² under ultra-high vacuum (UHV) deposition conditions has been studied by STM. Under UHV conditions on

graphite(001), (**1b**) self-assembled to form a chain of dimers with long range order but no sub-molecular resolution was achieved. The chain of dimers has been observed to collapse completely upon annealing. This was attributed to the inferior stability of this non-covalent network which was supposed to be initially stabilized by weak Br...H-C hydrogen bonds. In this thesis work self-assembly of **1a** and **1b** on HOPG in solution at room temperature, as a comparative study of the effect of the two halo groups (iodo and bromo) on the self-assembly of the trigonal molecules was studied. Self-assembly of **1a** and **1b** at the liquid/solid interface, was compared with the previously reported self-assembly of **1b** under UHV conditions.¹²

Although **1a** molecules showed a non-covalent network on graphite (001) under UHV conditions, as reported by Gutzer et al., no self-assembly of **1b** at liquid/HOPG interface at room temperature was observed. The self-assembled network of **1b** under UHV was attributed to the weak Br...H-C hydrogen bond interaction but it may be possible that at room temperature this bond is not as strong as the I...H-C bond, forming an ordered network of **1b** on HOPG.

Halogen-hydrogen bond interaction is a type of hydrogen bonding interaction for self-assembly which has not been extensively discussed in literature. This may be because this is not as strong an interaction as other hydrogen bonding interactions.⁹² The relative strength of halogen-hydrogen bonding plays a considerable role, in the self-assembly process. This bond strength increases with the size of the halogen so is stronger with iodine (the largest size halogen) than with bromine. Theoretically calculated strength⁹³ of this bond is 4 kJ/mol with a H...I distance of 3.007 Å, while H...Br distance is 2.987 Å with bond energy is smaller by 15%. In this study on self-assembly of **1a** and **1b**, it was observed that the iodide **1a** self-

assembled in a hexagonal fashion whereas the bromide **1b** showed no self-assembly at liquid/solid interface on HOPG at room temperature. This was attributed to the weaker H...Br interaction being unable to produce a periodic pattern of **1b** molecules on HOPG at room temperature.

3.2.2 Trigonal oligomer **2a** in 1-phenyl octane

A novel supramolecular network for oligomer **2a** was observed in phenyloctane/graphite interface which shown a chiral open network structure. Long range ordering in the self-assembled network of trigonal molecules of **2a** was observed immediately after the deposition. Large area defect free domain up to a size of $30 \times 30 \text{ nm}^2$ was achieved as shown in figure 3.7. Triangular shapes of the molecules of ester **2a** were well resolved with the tunneling parameter of $I_t = 15 \text{ pA}$, $V_s = 0.6 \text{ V}$. High resolution image of the open network structure is shown in figure 3.7 (b), where a submolecular resolution was achieved. Not only the perfect triangular shapes of the molecules but also the orbital structures of the molecules were observed in an area of $12 \times 12 \text{ nm}^2$, with the tunneling parameters of $I = 10 \text{ pA}$, $V_s = 0.9 \text{ V}$. A proposed model of the open network structure is shown in figure 3.7 (c), with two chiral orientations of the molecular structures (Right handed and Left handed domains). The unit cell has lattice parameters $a = 2.8 \text{ nm}$, $b = 2.5 \text{ nm}$, $\alpha = 84^\circ$. Each unit cell is containing two molecules of trigonal oligomer **2a** with an opposite orientation (one oriented up and one oriented down). This open structure was completely empty with a cavity of size $2.8 \times 1.5 \text{ nm}^2$. The chiral network formation of an achiral ester molecule **2a** was probably caused by the breaking of symmetry by molecular adsorption at the surface⁹⁴, giving rise to displaced geometry of the molecular structure. Furthermore, a refined analysis of figure 3.7, evidences two types of molecules having either a bright (white molecules peaking down) or dark (grey

molecules peaking up) STM contrast shown in the superimposed model. This is a typical signature of molecules being adsorbed on different crystallographic sites of the HOPG surface.

Figure 3.7 STM image of trigonal oligomer **2a** on HOPG at room temperature in 1-phenyloctane. (a) $30 \times 30 \text{ nm}^2$, tunneling parameters: $V_s = +0.6 \text{ V}$, $I_t = 15 \text{ pA}$. (b) $12 \times 12 \text{ nm}^2$, tunneling parameters: $V_s = +0.9 \text{ V}$, $I_t = 10 \text{ pA}$. (c) Proposed model of the two chiral orientations. Reproduced from Ref. [64] with permission from the Royal Society of Chemistry.

3.2.3 Trigonal oligomer **2a** in tetrahydronaphthalene

A two dimensional nanoporous network of molecules of trigonal oligomer **2a** with nanocavities capable of containing tetrahydronaphthalene solvent molecules was observed on HOPG (figure 3.8). A long range ordering of the honey-comb structure was obtained after the deposition of molecules of trigonal oligomer **2a** on the HOPG surface. Large domains with open honey-comb structure up to $30 \times 30 \text{ nm}^2$ were observed as shown in figure 3.8 (a). This network was less stable in comparison with the row-like structure of trigonal oligomer **2a**. High resolution STM image $20 \times 18 \text{ nm}^2$ of this open network was achieved as shown in figure 3.8 (b). The triangular shape of the ester molecules was resolved. In STM image, figure 3.8 (b), it was observed that the cavities of the honey comb structure were not completely empty.⁹⁵ This co-adsorption of solvent molecule was observed for tetrahydronaphthalene, but not for 1-phenyloctane, presumably due to the different shapes of the solvent molecules. This open honey-comb supramolecular networks were observed with different chiralities. A proposed model of the two chiral networks is shown in figure 3.8 (c). The STM images shown in figure 3.8 (a) and figure 3.8 (b) showed the left and right chiralities respectively.

Figure 3.8 STM image of trigonal oligomer **2a** on HOPG at room temperature in tetrahydronaphthalene. (a) $30 \times 30 \text{ nm}^2$, tunneling parameters: $V_s = +1.1 \text{ V}$, $I_t = 8 \text{ pA}$. (b) $20 \times 18 \text{ nm}^2$, tunneling parameters: $V_s = +1.2 \text{ V}$, $I_t = 8 \text{ pA}$. (c) Proposed model of the two chiral orientations of the molecular structure. Reproduced from Ref. [64] with permission from the Royal Society of Chemistry.

Long range ordering of supra molecular networks of trigonal oligomer **2a** was achieved by depositing a drop of molecules of **2a** in tetrahydronaphthalene solvent on HOPG surface. As shown in figure 3.9 (a), a large domain up to an area of $30 \times 30 \text{ nm}^2$ was imaged with STM with a tunneling parameter of $I_t = 20 \text{ pA}$, $V_s = 0.9 \text{ V}$. Highly dense molecules on the HOPG surface which formed a defect free close-packed supramolecular network was imaged with

STM. Figure 3.9 (c) shows a proposed model of the molecular structure with unit cell dimensions $3.3 \times 2.2 \text{ nm}^2$ as observed from STM imaging. During the STM imaging, tetrahydronaphthalene molecules were observed in some of the STM images. The appearance of the tetrahydronaphthalene molecules was believed to play a role in the formation of the row like supramolecular networks of molecules of trigonal oligomer **2a**. In this closed pack row like structure pairing of trigonal molecules of ester (one pointing up and one pointing down) was observed. This row like structure with paired molecules is similar to the structure of a liquid crystal as reported in literature.⁹⁶ The distances between two adjacent rows of molecules were measured as 1.58 nm and 1.68 nm (as shown in proposed model in figure 3.9 (c)).

Figure 3.9 STM image of trigonal oligomer **2a** on HOPG at room temperature in tetrahydronaphthalene. (a) $30 \times 30 \text{ nm}^2$, tunneling parameters: $V_s = +1.0 \text{ V}$, $I_t = 20 \text{ pA}$. (b) $15 \times 15 \text{ nm}^2$, tunneling parameters: $V_s = +0.9 \text{ V}$, $I_t = 20 \text{ pA}$. (c) Proposed row like model of the molecular structure. Reproduced from Ref. [64] with permission from the Royal Society of Chemistry.

3.2.4 Chirality in self-assembled networks of TBBs

It is very interesting to note that the self-assembled networks of all these TBB molecules (**1a**, **2a**) are chiral. The TBB molecules (**1a**, **2a**) being highly symmetrical, with no chiral or prochiral element. The chirality in the 2D arrangement of these molecules arises from symmetry breaking induced by adsorption on the surface.⁹⁴ Hence a sudden change in the symmetry of trigonal oligomer by molecular adsorption is responsible for the formation of chiral networks of achiral molecules at surface. Furthermore, a refined analysis of fig. 3.7 (a) evidences two types of molecules having either a bright molecules peaking down or dark molecules are peaking up in STM contrast. This is a typical signature of molecules being adsorbed on different crystallographic sites of the HOPG surface. Note that chiral 2D supramolecular networks have already been observed either from achiral, prochiral or chiral molecules.⁸⁶⁻⁸⁹

3.2.5 Trigonal oligomer 4 in 1-phenyloctane

Trigonal oligomer **4** was observed to self-assemble in 1-phenyloctane with short range ordering. On the same sample, both open honey-comb structure and close packed row like structure co-existed as shown in figure 3.10 (a), $30 \times 30 \text{ nm}^2$ with tunneling parameters : $V_s = +0.6 \text{ V}$, $I_t = 15 \text{ pA}$. This may be attributed to the instability of this honeycomb structure as compared to other open structures of ester **2a**. A more clearly visible close packed structure can be seen in figure 3.10(b), $12 \times 12 \text{ nm}^2$, tunneling parameters: $V_s = +0.9 \text{ V}$, $I_t = 10 \text{ pA}$. Figure 3.10 (c) shows a proposed model of the molecular structure of cyano oligomer **4** with unit cell dimensions $1.9 \times 2.1 \text{ nm}^2$.

Figure 3.10 STM image of trigonal oligomer **4** on HOPG at room temperature in 1-phenyloctane. (a) $50 \times 50 \text{ nm}^2$, tunneling parameters: $V_s = x \text{ V}$, $I_t = 20 \text{ pA}$. (b) $12 \times 12 \text{ nm}^2$, tunneling parameters: $V_s = x \text{ V}$, $I_t = 15 \text{ pA}$. (c) Proposed model of the molecular structure with unit cell dimensions $1.9 \times 2.1 \text{ nm}^2$. Reproduced from Ref. [64] with permission from the Royal Society of Chemistry.

3.2.6 Self-assembly of carboxylic acid **2b** and amine **3**

During the course of this work self-assembly of carboxylic acid oligomer **2b** was reported at heptanoic acid/graphite interface.⁹⁷ Three polymorphic structures were identified with weaker C-H...O hydrogen bonds between the carboxylic acid groups giving displaced geometry in the structures. This is unlike its smaller counterparts with one and two phenyl ring shorter arms respectively, such as trimesic acid (TMA) and 1,3,5-benzene-tribenzoic acid (BTA) which were observed to self-assemble under ultrahigh vacuum (UHV) deposition^{9,83} and at liquid/solid interface^{97,98} as reported in the literature. Self-assembly of TMA and BTA produced polymorphic structures but a much stronger O-H...O hydrogen bond was observed to stabilize these structures.

Although displaced geometrical chiral structures for trimer **2a** has been observed as described in this chapter, however, the self-assembly of carboxylic acid oligomer **2b** has been not observed so far, with phenyloctane and tetrahydronaphthalene as STM solvents. This might be due to poor solubility of this oligomer **2b** in the above mentioned solvents. Similarly amine **3** was also not been observed to self-assemble in the above mentioned solvents. It is anticipated that self-assembly behavior of these oligomers with STM at liquid/solid interface will be observed by using appropriate solvents in future, as the role of solvent is very critical in obtaining self-assembled nanostructures. Further investigations are in process to achieve this.

3.3 Conclusion

A periodic hexagonal pattern of molecules of an iodo-substituted trigonal oligophenylene **1a** on HOPG under liquid/solid interface was observed, while the corresponding bromide **1b** did not show any self-assembly under the same scanning conditions. This was attributed to the greater strength of the H...I hydrogen bonding interaction to the H...Br interaction. This illustrates that minor variations in strengths of interactions might have profound effects upon the abilities of materials to assemble which has a considerable importance in the design and production of supramolecular assemblies for possible functional nanomaterials. A periodic pattern of molecules of a trigonal oligomer **2a** and trigonal oligomer **4** on HOPG at room temperature was observed with different phases. Depending on whether the solvent used was either alkylated (phenyl-octane) or non-alkylated (tetrahydronaphthalene), different types of networks were obtained. These networks were either open networks or close-packed. Molecular and even sub-molecular resolution was achieved, thus allowed refined interpretation. In the open network observed using tetrahydronaphthalene as the STM solvent the central cavity was occupied by several solvent molecules. This kind of network could act as a matrix for composites made by incorporating some guest molecules of appropriate size inside the nanocavities in the future to form a multi-component host-guest system. Furthermore, in most cases, it was observed that these arrangements were chiral, with left and right handed domains in the same sample. Finally, trigonal oligomers **2b** and **3** were not observed to self-assemble with the solvents tetrahydronaphthalene and 1-phenyloctane.

Chapter 4 2D self-assembled networks by Zinc(II) metal ion co-ordination

4.1 Introduction

Co-ordination driven self-assembly, gives a better control over the rational design of one- (1D), two-(2D) and three-dimensional (3D) supramolecular networks by taking advantage of the predictable nature of the metal-ligand co-ordination and ability of ligands to program directionality. Thus, this strategy of metal-ligand co-ordination represents an alternative method for “bottom-up” technique in nanoelectronics by establishing a synthetic approach for designing molecules of required dimensions of few nanometers. For instance, a wide range of 1D, 2D and 3D systems by co-ordination bonding has been widely explored in past years.^{25,26,99–101}

Hence, these supramolecular co-ordination networks have found a lot of prospective to be utilized for different nanotechnological applications. For example, supramolecular co-ordination networks formed by Fe metal ions have been reported⁹⁹ with the excellent magnetic properties. Ruthenium(II) co-ordination complexes with terpyridine ligands have been reported¹⁰² to be used in the building of polymer wires on gold. Zinc metal ion complexes are very well known for their optoelectronic properties^{20,103–106} and are potential candidates for many optoelectronic devices. In another application, non-linear optical properties of zinc metal ion co-ordination networks have been reported¹⁰⁷ very recently.

Although there is a vast library of hydrogen bonding molecules which can be observed on surface by STM techniques on conducting surface as described in chapter 3, there are only

a few co-ordination networks which have been visualized on conducting surfaces.^{48,108–111} For example template directed self-assembly of co-ordination networks has been observed at surfaces by STM techniques.¹⁰⁹ For example adsorption of Co(II) complexes on HOPG surface have produced an ordered network with inter-digitation of the pyridinen moieties as shown in figure 4.1.

Figure 4.1 Adsorption of Co(II) complexes on HOPG surface produced an ordered network with inter-digitation of the pyridinen moieties. Reprinted from Ref. [109] with permission from the Wiley-VCH.

STM study on the self-assembly of co-ordination complexes of Pt^{2+} has been reported by Stang and co-workers.¹¹⁰ The monolayers were studied both on two conducting substrates HOPG and Au(111) to examine the effect of substrate on the structure of the matallacycle and it has been observed that the molecules self-assemble into well ordered 2D patterns on the surface of both substrates. A detailed overview of such 2D self-assembled networks by co-ordination bonding was given in a review paper by Ciesielski et.al.¹⁴

Terpyridines were proposed as building blocks for supramolecular chemistry decades ago.^{112,113} Still there is lot of prospective for development in the supramolecular chemistry

of terpyridines and a lot of research work has been going on in this field to date.^{20,100,114–120}

Transition metal-complexes of π -conjugated bis- and tris(terpyridine) have high prospective to be used as new functional materials in electronic and optoelectronic devices. Heavy transition metal ions, such as Pt^{2+} , Ru^{2+} , Os^{2+} , and Ir^{2+} have been explored thoroughly in past.^{28, 86, 90} In particular, electron-poor square-planar divalent Pt^{2+} and Pd^{2+} ions have been widely used in conjunction with electron-rich nitrogen containing moieties in the self-assembly process.^{15,91} Metal ions with filled electron shells have recently achieved much importance as models for the advancement of new metallopolymers. The low cost and nontoxicity of Zn^{2+} ions has made them a promising candidate for making highly developed co-ordination networks. The other advantage of using Zn^{2+} ions for co-ordination is that metal to ligand charge transfer (MLCT) processes do not occur in such systems, because of the full d10 electron configuration of the Zn^{2+} ions. Hence there is only the possibility of intraligand (IL) charge transfer in these systems. And high PL quantum yields and EL performance has been reported¹²³ in the last decade using such systems.

This research work mainly focuses on the 2D metallo-supramolecular networks of Zn^{2+} ions with terpyridine ligands. To create metallo-supramolecular networks and extended polymer networks, monomers with self-assembling end-groups are mandatory. In the previous work in this field, the focus has been on linear and tetrahedral Zn^{2+} terpyridine networks with respect to their prospective use as novel two photon absorbing materials.¹⁰⁷ From a thorough examination of their photophysical properties together with their structural characterization, it has been concluded that by changing conjugated backbone on the terpyridine units it is possible to modify of the optoelectronic properties of these networks¹⁰¹. Strong emission in the solid state indicates that these materials correspond to

the capable candidates with respect to their potential applications in optoelectronic devices such as OLEDs. Hence it was anticipated that the Zn^{2+} based materials can, in general, be solution processed by the attachment of more solublizing groups to π -conjugated terpyridines. These complexes could be very promising candidate for solar cell applications. In extension of this work, the present investigations aim the design of zinc metal co-ordinated 2D networks made up of trigonal and linear π -conjugated terpyridines with respect to their possibility in the field of optoelectronic device applications. Various bis(terpyridine) derivatives were used in the synthesis of self-assembled supramolecular 2D networks by Zn^{2+} metal-ion co-ordination with tpy ligands. Photophysical properties with respect to their device applications along with their thermal, and electrochemical properties, as well as ordering in their self-assembled networks, is discussed.

4.2 Formation of 2D Zn(II) co-ordinated self-assembled networks

2D Zn(II)–co-ordinated self-assembled networks **N1** was obtained by refluxing its 2D monomers **14** with zinc acetate ($\text{Zn}(\text{OAc})_2$) at the stoichiometric ratio of 1:1.5, in NMP solutions followed by anion exchange using an excess of NH_4PF_6 . Although 2D monomer **14** is soluble in common organic solvents (e.g. ether, DCM, CHCl_3 , THF etc.), but its 2D networks **N1-3** are not only insoluble in those common organic solvents but also in highly polar aprotic solvents (e.g. DMSO, DMF, NMP, acetonitrile etc.) at room temperature. This behavior is believed to be caused by the highly crosslinked or interpenetrated structure of the 2D networks. Therefore, all the unwanted byproducts (including any unreacted starting material **14**) can be washed away by using ether to get the final networks **N1-3** in solid form.

Formation of new 2D Zn(II)-co-ordinated self-assembled supramolecular network **N1** from trigonal tpy molecule **14** is shown in scheme 4.1 and of new 2D Zn(II)-co-ordinated self-assembled extended (by linear terpyridene molecules) supramolecular networks **N2** and **N3** of trigonal-tpy molecule **14** is shown in scheme 4.2.

Scheme 4.1 Synthesis of one component 2D Zn(II)-co-ordinated self-assembled supramolecular network **N1**.

Extended networks **N2** and **N3** were formed using the p-type or n-type conjugated tpy linker units **17** and **18** shown in scheme 4.2. 2,5-bisdodecyloxy-p-phenylene was employed as the p-type linker (**17**) in **N3**, due to it being linear and electron rich so that it is a good electron donor. In the other extended network **N2**, 2,1,3-benzothiadiazole (benzo[c][1,2,5]thiadiazole) was used as the n-type linker (**18**) as it is known to be a good electron acceptor.¹⁰¹

The same insoluble behavior was found for the 2D extended networks **N2** and **N3**. Networks **N2** and **N3** were obtained by refluxing 2D network **N1** with zinc acetate Zn(OAc)_2 at the stoichiometric ratio of 1:1.5 in NMP solution to break the network,

followed by inserting the linear bis(tpy) monomers **17** and **18** in between the 2D molecules, respectively, to form the 2D extended networks **N2** and **N3** after anion exchange using an excess of NH_4PF_6 . After forming networks **N2** and **N3**, any residual 2D starting monomer (**14**) and the linear bis(tpy) monomers (**17** and **18**) were washed away with ether.

The concept of reversible self-assembly was demonstrated in these networks which confirmed the concept for formation of the networks. By adding more metal ions into the 2D network **N1**, co-ordination complexes can be dissociated again in favour of an open form with each zinc ion only attached to one tpy unit and its other co-ordination sites presumably saturated by solvent molecules. Disassembly of **N1** was followed by re-self-assembly to form extended 2D networks **N2** and **N3**. 2D network **N1** was only partially soluble in the NMP solution at 105 °C and the color of solution was light brown at that moment, after adding 1.5 equivalents of $\text{Zn}(\text{OAc})_2$ in NMP, the insoluble solid gradually dissolved in the solution and the colour of solution gradually changed to light yellow before adding the linear bis(tpy) linkers. All these novel 2D Zn(II)–co-ordinated self-assembled networks **N1-3** were obtained in moderate yields (> 50%).

Scheme 4.2 Synthesis of 2D Zn(II)-co-ordinated self-assembled two component extended supramolecular networks **N2** and **N3**.

4.3 Characterization of new 2D self-assembled networks

These novel Zn(II) co-ordinated 2D networks (**N1-3**) were characterized completely by photophysical measurements and their properties were compared with the starting material (**14**). These metal complexes were also characterized by other techniques such as X-ray photoelectron spectroscopy (XPS) confirming the presence of zinc metal ions in these networks, and small angle X-ray scattering (SAXS) measurements, which showed a short range ordering in these networks. Porosity and surface area measurements were performed using the BET technique, although it was found that these networks were nonporous which is believed to be due to the highly interpenetrating nature of the networks and space filling by long alkyl chains.

4.3.1 Photophysical properties of 2D self-assembled networks **N1-3**

Photophysical properties of 2D self-assembled networks **N1-3** are in agreement with the observations for the terpyridine ligands and their Zn(II) complexes discussed previously.¹⁰¹ Figure 4.2 (a) and (b) shows the appearance of self-assembled networks with naked eyes and under UV lamp respectively. The presence of Zn(II) ions in the molecular structure of the synthesized co-ordination networks **N1-3** is clearly indicated by the observed red shifts in the recorded emission spectra.

Figure 4.2 Solid appearance and (b) solid fluorescence of 2D networks **N1-3**.

Furthermore, the emission spectra of the discussed systems (**N1-3** compared to **14**) were measured in solid state at room temperature. Molecules **14**, **17** and **18** were emissive and the resulting Zn(II) co-ordination networks **N1-3** were emissive too. The solid state optical properties of the networks can be adjusted by inserting different types of linkers into the extended networks. This aspect might be explained by the fact that the synthesized metallo-supramolecular networks tend to aggregate mainly due to the conjugated and rigid structure of the spacers (**17** and **18**) and core **14**. Figure 4.3 shows the emission spectra of core **14** (emission peak at 436 nm) compared to the Zn(II) co-ordination networks **N1-3** demonstrating the red shift of 82, 233, and 115 respectively. **N2** shows red fluorescence under a UV lamp, as shown in figure 4.2, in comparison to the networks **N1** and **N3** both of which show yellow fluorescence under a UV lamp. This again shows the effect of the inserted n-type linker **18** which has a lower band gap and acts as sole emissive unit to produce red fluorescence in network **N2**, whereas, network **N3** which has the p-type linker **17** shows similar emission to network **N1**. Hence it is apparent that after Zn^{2+} ion complexation with tpy ligands, the position of the emission peak changes significantly.

Figure 4.3 Solid state photoluminescence spectra of core molecules **14**, **17**, **18** and their 2D self-assembled networks **N1-3**.

Moreover, it was expected that the Zn(II) tpy connectivity will increase the electron delocalization on the conjugated and rigid spacers, which can be observed by red shift in the PL spectra of **N1-3**. This may be due to the fact that Zn(II) tpy connectivity will increase the electron delocalization on the conjugated rigid spacers. The reason behind the red shift in the emission spectrum is the increase in conjugation, which will increase the number of delocalized electrons in the system. Finally, the longer the value of conjugation length, the lower will be the energy gap between closest energy levels and the longer will be the absorption wavelength, and so the emission wavelength too.

4.3.2 Femtosecond time-resolved photoluminescence dynamics of **14** and its Networks **N1-3**

Fundamentally, fluorescence is a property of electronically excited states. Thus, fluorescence mechanisms can be better understood by time-resolved fluorescence spectroscopy. To obtain the dynamics of the PL spectra, the fluorescence lifetime of the **14** and its Zn^{2+} self-assembled networks **N1-3** was measured. The fluorescence decay behavior in the presence of Zn^{2+} is shown in figure 4.4, with the exponential fit results. Lifetime of trigonal molecule **14** was found to be 0.45 ns whereas the lifetimes of the zinc metal ion co-ordinate networks were 1.16 ns, 0.51 ns, and 1.68 ns for **N1**, **N2** and **N3** respectively as shown in figure 4.4.

Figure 4.4 Time-resolved fluorescence decay of **14** and its self-assembled networks **N1-3** in solid state.

An increase in the fluorescence lifetime of networks **N1-3** was observed after zinc metal ion co-ordination of trigonal and linear terpyridine moiety in **14**, **17** and **18**. Similar results were observed of networks **S1** (similar to **N1**), **S3** (similar to **N3**) and **S4** (similar to **N2**) made up of a tetragonal tpy molecule (having similar branching units to trigonal tpy molecule **14**). The synthesis of these was previously reported¹⁰¹ and the structures are shown in figure 4.5. The values of fluorescent life time were measured as 2.1 ns, 1.22 ns and 0.93 ns for **S1**, **S3** and **S4** respectively. The fluorescence decay profiles of **S1**, **S3** and **S4** are shown in figure 4.6.

Figure 4.5 Molecular structure of tetragonal molecule **2**. b) Formation of 3D Zn(II)-co-ordinated self-assembled supramolecular network **S1**. c) Formation of 3D Zn(II)-co-ordinated self-assembled supramolecular networks **S3** and **S4**.¹⁰¹ Adapted from Ref. [101].

Figure 4.6 Time-resolved fluorescence decay profile of 3D self-assembled networks **S1**, **S3** and **S4** in solid state.

These results further suggest that networks with similar units have same lifetime values. Enhancement in the lifetime after zinc metal ion co-ordination may be attributed to the increase in conjugation after metal complexation as observed with a red shift in the PL spectra too. These results also suggest a complete modification in the energy levels after zinc metal ion complexation. Networks **N2** and **S4** were formed by the n-type linker unit **18**, which has a lower band gap. Hence the fluorescence lifetime of these networks are also lower compared to the results obtained for **N1**, **S1**, **N3** and **S3** which were formed by the p-type linker units. These results will be explained in detail in future with the help of ongoing studies on energy level calculations of self-assembled networks.

4.3.3 Thermal behavior of 2D self-assembled networks **N1-3**

Thermogravimetric analysis (TGA) plots and Differential Scanning Calorimetry (DSC) plots of core molecule **14** and its 2D networks **N1-3** of core and its 2D networks **N1-3** are shown in the Experimental Section. T_{5d} , T_g and T_m of 2D networks **N1-3** are listed in table 4.1.

Table 4.1 5% weight loss temperature (T_{5d}), glass transition temperature (T_g) and melting temperature (T_m) of **14** and 2D networks **N1-3**.

Networks	T_{5d} (°C) ^a	T_g (°C) ^b	T_m (°C) ^c
14	310	115	— ^d
N1	374	— ^d	— ^d
N2	390	— ^d	— ^d
N3	386	— ^d	— ^d

^a T_{5d} = 5% weight loss temperature; ^b T_g = glass transition temperature; ^c T_m = melting temperature; ^drelevant data is not found.

According to table 4.1, 2D zinc metal ion co-ordinated self-assembled networks **N1-3** have slightly higher T_{5d} compared to their respective starting materials **14**. Besides that, **N1-3** are generally more thermally stable compared to **14** as more than 50% of materials of **N1-3** remain after heating to 900 °C. Thus, Zn(II)–co-ordination helped to improve the thermal stabilities of these Zn(II)–co-ordinated networks **N1-3**. But no phase transitions (T_g and T_m) were observed in the DSC measurements of **N1-3**. Also, these 2D Zn(II)–co-ordinated self-assembled networks **N1-3** are not crystalline as no significant exothermic peaks (T_c) were observed during the heating cycles in their DSC plots.

4.3.4 Small angle X-ray scattering of 2D self-assembled networks N1-3

SAXS patterns of **N1**, **N2** and **N3** in the solid state were compared. As can be seen from figure 4.7, **N1**, **N2** and **N3** have similar patterns, featuring peaks at scattering vector $q = 2.46 \text{ nm}^{-1}$, 2.09 nm^{-1} and 2.66 nm^{-1} . Thus, it appears possible that all three networks **N1**, **N2**, and **N3** exhibit a similar structural organization. These results also showed that probably these networks have short range ordering with repeating units of approximately 2.6 nm, 3.0 nm and 2.5 nm for networks **N1**, **N2** and **N3** respectively, which is in agreement with the values calculated using the Chem 3D program.

Figure 4.7 SAXS patterns of blank sample holder and 2D networks **N1-3**.

The proposed model of the π - π stacking interactions between such monolayer of these 2D ordered structures, is shown in figure 4.8. The typical distance (y_1 and y_2 as shown in figure 4.8(a) and (b)) between the pyridine substituted benzene interacted by face to face π - π stacking interactions has been calculated as 3.2 to 3.4 Å using Density Functional

Theory (DFT) calculations.¹²⁴ The distance x_1 and x_2 calculated from the small angle XRD measurements are 7.8 nm, 15 nm and 12.5 nm for networks **N1**, **N2** and **N3** respectively.

Figure 4.8 Representation of π - π stacking interaction between monolayers (a) for one component self-assembled network **N1**, (b) for two component self-assembled networks **N2** and **N3**.

The π - π stacking interactions between each monolayer of these 2D ordered structures have the potential to permit nanoparticles to be introduced into the vacant spaces inside the

networks. The π - π stacking interactions in these networks would give tubular structures which could contain a rod-shaped or sphere-shaped nanoparticle. Some catalyst particles for making carbon nanotubes could be introduced into 2D networks with particle separation of several nm or even tens of nm. If an array of such particles could be created inside such a network, which would act as the feed source for the nanotubes, it could be possible to create an ordered array of carbon nanotubes with intertube separation of several nm. Such arrays are currently unknown but would be of great interest to materials scientists as these arrays can play a critical role in advancing the “bottom up” technique for nanofabrication.

4.3.5 XPS studies on 2D self-assembled networks N1-3

XPS measurements were performed with monochromatic Al-K alpha radiation with a power of 200 W to confirm the existence of the zinc metal-ions and to achieve more data in favor of the proposed network structures. Characteristic electron binding energies of the elements had been calculated using this method. The intensity of the recorded peaks is associated with the concentration of the elements present. The recorded XPS spectrum showed binding energy peak of C1s and Zn 2p electrons of the terpyridine ligands. This has confirmed the presence of Zn metal ion in the network structures **N1**, **N2** and **N3**, while there is an absence of Zn 2p peaks in the starting material **14**.

XPS spectra of the zinc complexes on carbon tape substrates are shown in figure 4.9. Zn 2p and peaks were clearly observed at 1022, and 1045 eV for network **1**, 1030, and 1053 eV for network **2** and 1027, and 1050 eV for network **3** respectively in addition to the O1s, C1s, and F1s peaks (may be due to PF₆–counterions), indicating a successful complexation of the terpyridine units.

In addition a significant shift in the Zn 2p peaks was observed for networks **N1**, **N2** and **N3**, although the splitting of Zn 2p peak was same for all three networks (23 eV). This shift was probably due to the difference in binding of terpyridine unit of these networks with zinc metal ions. **N2** with electron acceptor unit **18** has the highest binding energy whereas **N3** with electron donating unit **17** has comparatively less binding energy and **N1** made up of molecule **14** has least binding energy. The difference in the binding energy of these networks was reflected by a significant shift in the XPS spectrum.

Figure 4.9 XPS spectra of **14** and its zinc metal ion complexes on a carbon tape. (a) Wide-scan spectra, (b) Zinc 2p region.

4.3.6 Porosity and surface area measurement of the 2D self-assembled networks

The porosity and the surface area of the 2D Zn(II)-co-ordinated self-assembled networks **N1-3** were investigated by sorption analysis using nitrogen. The results are shown in figure 4.10 and summarized in table 4.2.

Table 4.2 Nitrogen sorption analysis of 2D networks **N1-3**.

Networks	S_{BET} [m^2g^{-1}] ^a	S_{micro} (t_{plot}) ^b [m^2g^{-1}]	V_{micro} [cm^3g^{-1}] ^b	Pore Size _{ad} ^c (Å)	Pore Size _{de} ^d (Å)
N1	0.1526	*	*	*	*
N2	0.1512	16.3734	0.007337	*	*
N3	0.0379	0.1789	0.0089	*	*

^aSurface area calculated from the N_2 adsorption isotherm using the Brunauer–Emmett–Teller method ; ^bThe micropore surface area and micropore volume using t-plot method based on the Halsey thickness equation;

^cAdsorption average pore width (4V/A by BET); ^dDesorption average pore width (4V/A by BET);*relevant data is not found.

Figure 4.10 Nitrogen adsorption–desorption isotherms of 2D networks **N1-3** measured at 77.3 K

In comparison to the covalently bonded organic microporous networks based on tetraphenylmethane reported earlier,^{125–128} the surface areas of these networks are basically small ($< 2.1 \text{ m}^2\text{g}^{-1}$). All the values are well within the experimental error of the equipment. The negative dip for these networks is believed to be due to small sample size. These materials are thus believed to be highly interpenetrating networks, and hence no porosity was found in these 2D Zn(II)–co-ordinated self-assembled networks. Similar results were

reported¹⁰¹ for the 3D Zinc metal ion co-ordinated networks with similar tpy branching units previously mentioned in this thesis.

Acknowledgement is given to Dr. Abbie Trewin from University of Liverpool for her comments which assisted in evaluating the porosity and surface area results of networks **N1-3**. Dr. Trewin is currently attempting to develop a molecular model of these materials to understand their non-porosity.

4.3.7 TEM characterization of 2D self-assembled networks

TEM analysis was done in order to visualize the self-assembled zinc co-ordinated networks on the surfaces. A hexagonal kind of network was reported¹¹⁷ for metal-co-ordinated tpy molecules. But for the networks discussed in this thesis work, no ordered structure was found in the TEM images probably due to the insoluble nature of the networks, which made it impossible to obtain a very thin film on the copper grid substrate. To solve this problem electron energy loss spectroscopy (EELS) was performed in order to find out which parts contain Zn, but it was not possible to see the zinc peaks by this method probably due to the low concentration of zinc metal ions in these networks. TEM diffraction patterns showed the amorphous nature of that network **N1**. TEM images obtained for network **N1** on carbon-coated Cu grids are shown in figure 4.11. Sample preparation was done by casting a dilute ethanol solution (suspension of network **N1**) on carbon coated Cu grids.

Figure 4.11 TEM images of network **N1** on carbon coated Cu grids. TEM images with 50 nm and 20 nm scale bars obtained for the lower and higher resolution, respectively.

4.4 New metal-organic framework with trigonal imidazole (**15**)

Possibly due to the highly interpenetrating networks **N1-3** of **14**, as reported earlier for the similar kind of tetragonal molecules¹⁰¹ molecule **15** was synthesized, which has the similar structure like **14** but without long alkyl chains. It is possible to make nanoporous networks with non-covalent interaction of such kind of molecule with suitable metal ions. Metal-organic frameworks (MOFs) can be made by reacting metal ion or complex with suitable ligands, for example, zinc ions complexed with 2-methylimidazole produce ZIF-8 as reported earlier¹²⁹ (as shown in figure 4.12). Similarly, trigonal molecule **15** with imidazole at the terminal position might produce an extended MOF structure with bigger pore sizes. This work is currently in progress. Preliminary results suggest a MOF has been synthesized. Characterization of which is underway in the group of Prof. Huo Fengwei.

Figure 4.12 MOF made by reacting zinc metal ion with suitable ligands 2-methylimidazole to produce ZIF-8.¹²⁹ Reprinted from Ref. [129] with permission from the Nature Publishing Group.

Synthesis procedure of making MOF-15 is described in experimental section and a proposed model for its structure is shown in figure 4.13.

Figure 4.13 Proposed unit structure of MOF -**15** formed by zinc metal- ion co-ordination with trigonal imidazole molecule **15**.

Based on the preliminary XRD results, MOF-**15** is a crystalline material and TGA data showed that it is stable up to 350 °C. However, the sample was obtained in the form of polycrystals; hence its structure has not yet been resolved. Finally, based on the XRD results, it can be concluded that the MOF-**15** is a crystalline material. The appearance of strong peaks in the range of 5-10 degree in XRD pattern indicates the possibility of well-defined (microporous) structure, which has to be confirmed with single crystal X-ray measurements. TGA and XRD data are shown in figure 4.14 and figure 4.15 respectively.

Figure 4.14 TGA scan of MOF-15.

Figure 4.15 XRD plots (5° to 60°) of MOF-15.

4.5 Conclusion

Synthesis and characterization of various Zn(II) terpyridine self-assembled networks were described in this chapter. Their photophysical properties were studied in detail and compared to the constituent chelating mono-terpyridine ligands that exhibited good photoluminescence properties. The formation of the Zn(II) tpy connectivity was evidenced and discussed by means of various techniques. It was observed that the presence of the Zn(II) ions in the synthesized model complexes revealed interesting spectroscopic properties, in particular, enhanced fluorescence and fluorescence life time. Such Zn(II) systems are potentially interesting for the construction of optoelectronic devices. These Zn(II) supramolecular networks were investigated and compared to the uncomplexed ligands **14**, **17**, and **18** in order to understand the influence of the Zn(II) ions on the photophysical properties of the designed structures. The synthesized Zn(II) co-ordination polymers revealed marked red shifts in the emission spectra. Thus, from the experimental results it was concluded that the characteristics of the spacer (length and conjugation) are considerably influencing the photophysical properties of the Zn(II) co-ordination networks. Small angle X-ray scattering, results showed that probably these networks have short range ordering. X-ray photoelectron spectroscopy results showed the presence of zinc metal ions in the network. Thus, this research work on 2D self-assembled networks shows there are a lot of different opportunities and possibilities to be considered in order to develop various useful organic networks that can be studied and applied in organic electronic devices as in general, they are found to be more thermally stable as compared to their starting materials especially at very high temperature due to the effect of zinc metal ion co-ordination.

Chapter 5 2D self-assembled networks for light harvesting applications

5.1 Introduction

Nature has developed through evolution, progressively more efficient biological systems^{130, 131} for solar energy harvesting. The ultimate goal in research into light harvesting systems is to develop an efficient artificial light harvesting system to overcome our daily energy needs in an environmentally sustainable way. To design artificial light harvesting systems (as shown in figure 5.1) at least as efficient as the ones produced by nature, it is crucial to learn from natural light harvesting antennas.¹³⁰ Energy transfer has been observed in many model systems for different applications, starting from natural biological systems¹³¹ to synthetic molecules^{132–134} in the past. Studying energy transfer processes between organic molecules for light harvesting applications is a very well developed area^{132,135} of research. The organization of the donor (**D**) and acceptor (**A**) molecules are critical for such systems, because the efficiency of energy transfer from the donor to the acceptor depends on the geometry between the donor and acceptor molecules. The active layer in light harvesting systems for photovoltaic or other applications could be simply a blend of donor and acceptor molecules or it could be made up of covalently or non-covalently (either by hydrogen bonding or metal co-ordination) bonded donor and acceptor molecules. Resonance energy transfer (RET) from donor chromophores to acceptor fullerene molecules has been studied as a potential mechanism for charge separation in photovoltaic devices using an active layer of a donor-acceptor blend.^{136,137} Light harvesting complexes made up of covalent, semi-covalent and non-covalent bonds have been reviewed in detail in a recent paper.¹³⁵ For an organized geometry of donor-acceptor molecules, energy transfer could be both intramolecular^{137–139} in

which the donor and acceptor parts belong to the same molecule connected through a spacer via covalent interactions¹⁴⁰ or intermolecular^{134,141,142} in which the donor and acceptor are assembled via hydrogen bonding or by metal co-ordination.

Figure 5.1 Representation of structural association of light-harvesting networks of plants and green algae.¹³⁰ Reprinted from Ref. [130] with permission from the Nature Publishing Group.

Non-covalent interactions for instance hydrogen bonding can direct the intermolecular energy transfer process by the self-assembly of donor and acceptor molecules in solution as well as thin solid films. The electrostatic nature of hydrogen bonding could induce the transitional dipole moment in the donor and acceptor molecules which is the main criteria for resonance energy transfer. RET takes place when the donor and acceptor are coupled via long range dipole-dipole interactions. There are two mechanisms¹⁴³ (as shown in figure 5.2) by which energy transfer can take place in such situations. First the Förster dipole-dipole mechanism (FRET), i.e. through space, energy transfer favored by good spectral overlap and secondly the Dexter double electron-exchange mechanism, i.e., through bond, electron transfer promoted by orbital overlap. The applicability of mechanism of energy transfer for a given system is related to the proximity of the donor and acceptor molecules, typically this should be in the order of 10 nm for FRET. The primary conditions for FRET are that the donor must have multiple electronic transitions and long life time, whereas the acceptor must be able to quench the fluorescence of the donor. Perylenediimide chromophores (PDIs) are an important class of chromophores as they can act as acceptors for both covalently^{140,144–146} and noncovalently^{134,135,147–149} bonded systems for light harvesting applications and have been intensely studied.^{150,151}

Figure 5.2 Schematic representation of Förster and Dexter energy transfer processes. Adapted from Ref. [143].

PDIs have emerged as one of the best candidates as acceptors in **D-A** light harvesting systems because of their desirable photophysical and photochemical properties and high fluorescence quantum yields. For the systems studied in this work, complementary hydrogen bonding between the donor TBB (**3**) and a PDI-diacid (**20**) or a PMI-monoacid (**21**) produces a dipole-dipole interaction pair necessary for the efficient transfer of energy (figure 5.3). This motivated investigation of the mechanism of energy transfer from **3** to **20** and **21**. Efficient energy transfer does not only depend on the spectral overlap of the absorption spectra of the acceptor and the emission spectra of the donor but also on many other factors such as the relative orientation of transition dipoles of the donor and acceptor, distance between the donor and acceptor molecule, and also on the quantum yield of the donor, as energy cannot be transferred if it dissipates too rapidly. Combinations of PDIs and porphyrin are well known **D-A** systems¹⁴⁴ in which PDIs perform the role of a donor. Artificial light harvesting porphyrins^{144,152} and multiporphyrin^{153,154} antennas have been discussed in two excellent review articles. These multiporphyrin arrays are of different geometrical arrangements such

as ring-shaped, windmill-shaped, star-shaped and possessing a dendritic architecture and it has been observed that the efficiency for light harvesting applications depends on the geometry.

The aim to build a simple model for light harvesting by the self-assembly of donor and acceptor, is analogous to the strategy that nature adopts in natural photosynthetic systems in which proteins are organized by supramolecular hydrogen bonding interactions. DMSO and THF were selected as solvents to study the energy transfer process in these systems because of the poor solubility of these molecules in nonpolar solvents. A slight difference in the Förster radii and energy transfer efficiency values were observed in these solutions for both the **D-A** model systems. This may be attributed to the difference in nature of the hydrogen bond formation between the donor and acceptor molecules in different solutions. Such systems with complementary hydrogen bonding motifs are very exciting as they can give rise to intermolecular energy transfer by two component hydrogen bonding 2D self-assembly.

Figure 5.3 PDI diacid (**20**) and PMI-monoacid (**21**) and a representation of the molecular structure of the TBB-PMI supramolecular complex, held together via amine-carboxylate hydrogen bonding interactions.

5.2 Energy transfer between hydrogen bonding molecules

The energy transfer from TBB (**3**) as donor to two carboxylate based acceptor molecules; PDI diacid (**20**) and PMI-monoacid (**21**) has been investigated in this study. Noncovalent interaction between the donor and acceptor moiety is facilitated by hydrogen bonding motifs at the termini of TBB (**3**) donor and PDI and PMI acceptor molecules. The synthesis of the

two acceptor molecules, PDI-diacid (**20**) and PMI-monoacid (**21**) was done by Dr. Sung Ju Cho using procedure based on the literature.^{142,155}

The efficient intermolecular energy transfer between a new donor-acceptor couple, with 1,3,5-tris[4-amino(1,1-biphenyl-4-yl)]-benzene (TBB **3**) as the donor (**D**) and a linear carboxylate derivative, PMI-monoacid (**21**) as acceptor (couple **A**) is reported here. For TBB (**3**)-PDI-diacid (**20**) (**D-A** couple **B**), comparatively much smaller values of energy transfer efficiencies have been calculated from steady state measurements. The difference in these values is discussed further in this chapter. These new **D-A** couples are capable of serving as models for light harvesting systems.

5.2.1 Steady state UV-vis absorption and emission spectroscopy

To investigate the energy transfer process from the donor to the acceptor, the steady-state UV-vis absorption and emission spectra of the donor and the two acceptors, PDI-diacid (**20**) and PMI-monoacid (**21**) in DMSO and THF solutions was studied and the corresponding experimental results are shown in figure 5.4.

Figure 5.4 Spectral overlap of donor TBB (**3**) with PDI-diacid (**20**) and PMI-monoacid (**21**) in DMSO and THF (a) Absorption and emission spectra of TBB (**3**) and PMI-monoacid (**21**) in DMSO (b) Absorption and emission spectra of TBB (**3**) and PMI-monoacid (**21**) in THF (c) Absorption and emission spectra of TBB (**3**) with PDI-diacid (**20**) in DMSO (d) Absorption and emission spectra of TBB (**3**) with PDI-diacid (**20**) in THF.

The primary requirement for an efficient energy transfer process is a good spectral overlap between the emission of the donor and absorption of the acceptor, measured by the spectral overlap constant J . The values of the overlap integral J were calculated for the **D-A** couple **A** as $2.36 \times 10^{15} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$ and $1.94 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$ and for the couple **B**, as $1.46 \times 10^{15} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$ and $1.17 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$ in DMSO and THF solutions respectively.

FRET usually occurs over distances comparable to the dimensions of most organic molecules, i.e. between 10 to 100 Å and the Förster radius R_0 is given by the following Eq. 1.

$$R_0 = 9.78 \times 10^3 [n^{-4} \kappa^2 Q_D J(\lambda)]^{1/6} \text{ Å} \quad (1)$$

where n is the refractive index of the solution which is 1.45 and 1.40 for DMSO and THF solutions respectively, and κ^2 is the orientation dipole moment constant of the **D-A** couple. Q_D is the fluorescence quantum yield of the donor, which is calculated as 0.03 in DMSO solution and 0.53 in THF solution. Since, it is very hard to predict the orientation of the transitional dipole of the donor and acceptor molecules, the value of the orientation dipole moment constant has been taken to be 2/3 for calculation of the Förster radius (which is true for most organic **D-A** couple, that are not rigidly bound to each other by a spacer molecule) assuming that the donor and acceptor dipoles are randomly oriented.¹³² The Förster radius for **D-A** couple **A** has been calculated to be 3.4 nm in THF and 3.2 nm in DMSO solution using Eq. 1. Similarly the Förster radius for **D-A** couple **B** has been calculated to be 3.1 nm in THF and 2.8 nm in DMSO solution. The calculated values of the Förster radii for **D-A** couple **A** and **D-A** couple **B** are very similar in DMSO and THF solutions. These values are in agreement to those predicted on the basis of the nature of the solvent. It is obvious that solvent molecules play a critical role in the self-assembly via hydrogen bonding of the donor and acceptor molecules. As the polarity of the solvents affects the self-assembly of **D-A**, the value of the Förster radius is expected to be higher in a more polar solvent like DMSO in comparison to the less polar THF, and an increase in the theoretical distance between the donor and acceptor, as solvent molecules are expected to come in between the donor and acceptor molecules. It is expected that the solvent will participate in many two-dimensional self-assembly processes, in particular in cases where supramolecular interactions (for example, hydrogen bonding) can occur between the solvent molecules and the adsorbed

molecules.¹⁵⁶ Since donor and acceptor here have hydrogen bonding motifs and DMSO is a polar solvent. So it is possible that the solvent can make a non-covalent interaction with the donor or acceptor molecule before donor or acceptor molecules could interact themselves.

5.2.2 Quenching of fluorescence of the donor TBB (3) by PMI and PDI acceptors

To gain further insight into the energy transfer process, fluorescence quenching experiments of the donor in the presence of both the acceptors, i.e. PMI-monoacid (**21**) and PDI-diacid (**20**) respectively were performed. Although a donor to acceptor ratio of 1:4 was found to fully quench the fluorescence of the donor molecule for the **D-A** couple **A** in DMSO solution, both the carboxylated PDI and PMI derivatives induced a significant decrease in the emission intensity of the TBB (**3**) donor, at a donor to acceptor ratio of 1:4 for both the **D-A** couples, i.e. couple **A** and couple **B**, which suggests the occurrence of intermolecular energy transfer (figure 5.5). The energy transfer efficiency as calculated from the steady state fluorescence measurements is given by the equation (2) as,

$$\eta = 1 - \frac{F_{DA}}{F_D} \quad (2)$$

where F_{DA} is the fluorescence intensity of the donor in the presence of the acceptor and F_D is the fluorescence intensity of the donor in the absence of the acceptor. Hence the energy transfer efficiency as calculated from the steady state measurements were 85% and 95% for the **D-A** couple **A** and 39% and 41% for the couple **B** in THF and DMSO solutions respectively.

Figure 5.5 Emission spectra of a mixture of TBB (3) and PMI-monoacid (21) and PDI-diacid (20) in DMSO and THF at various concentrations of TBB (3) (a) Emission spectra of a mixture of TBB (3) and PMI-monoacid (21) in DMSO (b) Emission spectra of a mixture of TBB (3) and PMI-monoacid (21) in THF (c) Emission spectra of a mixture of TBB (3) and PDI-diacid (20) in DMSO (d) Emission spectra of a mixture of TBB (3) and PDI-diacid (20) in THF.

In this study, due to the good spectral overlap between the absorption spectra of the PMI-monoacid (21) and the emission spectra of TBB (3), the fluorescence of the donor was completely quenched by the acceptor at a D-A ratio of 1:4. Hence, this D-A pair was ideal for studying the energy transfer process instead of the TBB (3)-PDI-diacid (20), D-A couple

(couple **B**). In the later case the acceptor was not able to fully quench the emission of the donor. Also the quantitative analysis of energy transfer was difficult due to the significant overlap between the donor (**3**) and acceptor PDI-diacid (**20**) emissions. Herein the main focus was on the time resolved PL measurements of the TBB (**3**)-PMI-monoacid (**21**) (couple **A**) in THF solution.

5.2.3 Femtosecond time-resolved photoluminescence dynamics

Resonance energy transfer is used to study supramolecular systems when there is more than one acceptor molecule near a donor molecule (as in the case of the donor acceptor systems studied in this chapter). For such systems apart from steady state measurements, it is crucial to perform the time resolved measurements for accurate quantitative measurements. In order to obtain more insight into the energy transfer process and also to compare the energy transfer efficiency from steady state and time-resolved fluorescence emission measurements, femtosecond decay dynamics of the fluorescence emission has been investigated. Figure 5.6 (a) and 5.6 (b) show the time-resolved fluorescence decay curves of TBB (**3**)-PMI-monoacid (**21**) recorded at 425 nm and 579 nm, in order to monitor the lifetime change for the donor and acceptor. Life time of the donor was observed to decrease from 0.4866 ns to 0.0754 ns at a **D-A** ratio of 1:4. The decrease in the life time of the donor in the presence of the acceptor is a very common phenomenon in FRET.

A similar behavior has been observed in the donor and acceptor's lifetime as reported earlier. The decrease in the donor quantum dots (QDs) exciton lifetime was accompanied by an increase in the acceptor QDs exciton lifetime, which provides evidence for enhanced FRET between the QDs.¹⁵⁷ A similar observation in a hybrid nanocrystal quantum-dot¹⁵⁸ patterned p-i-n structure has been reported and a kinetic model was proposed for the non radiative

energy transfer, which was confirmed by transient measurements. Energy transfer efficiency in terms of the life time of the donor and acceptor was calculated to be 86%, which is smaller than the value calculated from steady state measurements for the **D-A** couple **A** using the following Eq. 3,

$$\eta = 1 - \frac{\tau_{DA}}{\tau_D} \quad (3)$$

where, τ_{DA} is the lifetime of the donor in the presence of the acceptor and τ_D is the life time of the donor in the absence of the acceptor. The low value for the energy transfer efficiency as calculated from the time resolved measurements in comparison to the steady state measurements can be attributed to the perturbation of the donor radiative rate by the acceptor molecules as described in the literature.¹⁵⁹

Figure 5.6 Time-resolved fluorescence decay of TBB (**3**)- PMI-monoacid (**21**) (a) recorded at 425 nm and (b) recorded at 579 nm.

5.2.4 Comparison of energy transfer efficiency for D-A couple A and B

The Förster radius for **D-A couple A** has been calculated to be 3.4 nm in THF and 3.2 nm in DMSO solution, while the Förster radius for **D-A couple B** has been calculated as 3.1 nm in THF and 2.8 nm in DMSO solution. This can be attributed to the lower value of quantum yield of the donor in DMSO solution although a larger spectral overlap of the donor emission and acceptor absorption has been observed in DMSO for both the couple **A** and couple **B**, because the Förster radius is directly proportional to the quantum yield of the donor. On the other hand, quantitative measurement of the energy transfer in both of these **D-A couple** was complicated due to major overlap between emission spectrum of the donor and acceptor molecules. Intermolecular energy transfer efficiencies of 95% and 86% have been calculated from both steady state measurements and time resolved measurements respectively for couple **A** in THF solution, while 85% transfer efficiency was obtained in DMSO solution from steady state measurements. However for couple **B** comparatively smaller values of energy transfer efficiencies, i.e. 39% and 41% have been calculated from steady state measurements in THF and DMSO solutions respectively. The geometry or orientation between the donor and acceptor molecules is very important for an efficient energy transfer. It is clearly evident from the above results that **D-A couple A** turns out to be a more efficient **D-A couple**, as from the quenching experiments relatively smaller values for the energy transfer efficiencies for the **D-A couple B** was obtained. It could also be possibly because the dipole–dipole interaction between TBB (**3**) and PDI-diacid (**20**) molecules was insufficient (because interaction dipoles of TBB **3** and PDI (**20**) might not be in the same plane to give a favorable interaction for energy transfer) to give an efficient intermolecular energy transfer. Hence interaction of the acceptor molecule **20** and **21** with donor molecule **3** plays a major role in the energy transfer process for these two systems under study and **D-A**

couple **A** turns out to be a more efficient **D-A** couple. A comparison between the energy transfer efficiency between **D-A** couples **A** and **B** from steady state and time-resolved measurements is summarized in table 5.1.

Table 5.1 Comparison of energy transfer efficiency between **D-A** couples **A** and **B**.

Solvent				Tetrahydrofuran (THF)	Dimethyl Sulfoxide (DMSO)
Quantum yield of donor (TBB (3))				0.53	0.03
Life time of donor (ns)				0.4866	Nil
D-A Couple	TBB (3) - PMI monoacid 21 (Couple A)	Life time of donor in the presence of acceptor (ns)		0.0754	Nil
		Spectral overlap integral (J) ($\text{M}^{-1} \text{cm}^{-1} \text{nm}^4$)		1.94×10^{14}	2.36×10^{15}
		Forster radii (R_0) (nm)		3.4	3.2
		Energy transfer efficiency	From Steady state measurements	95%	85%
			From Time resolved measurements	86%	Nil
	TBB (3) PDI diacid 20 (Couple B)	Spectral overlap integral (J) ($\text{M}^{-1} \text{cm}^{-1} \text{nm}^4$)		1.17×10^{14}	1.46×10^{15}
		Forster radii (R_0) (nm)		3.1	2.8
		Energy transfer efficiency	From Steady state measurements	39%	41%

5.3 Conclusion

Two novel donor-acceptor (**D-A**) couple consisting of 1,3,5-tris[4-amino(1,1-biphenyl-4-yl)]-benzene TBB (**3**) (**D**) and PDI and PMI derivatives with glycine substituents (**A**) have been studied as model systems for energy transfer processes and the intermolecular energy transfer between them have been observed. This energy transfer occurred without the involvement of a photon and is a result of a long range dipole-dipole interaction between the donor TBB (**3**) and the acceptor molecules (PDI and PMI). Very high intermolecular energy transfer efficiencies were obtained from both steady state measurements (the extent of quenching of the donor by the acceptor) and time resolved measurements (life time of the donor in the presence and absence of the acceptor) for TBB (**3**)-PMI-monoacid (**21**) (**D-A** couple **A**). In contrast, the magnitude of the energy transfer efficiencies for TBB (**3**)-PDI-diacid (**20**) (**D-A** couple **B**), were very small, which is apparent even from the quenching experiments. Hence the interactions of the acceptor molecules **20** and **21** with the donor **3** plays a major role during the energy transfer process in these two systems with the **D-A** couple **A** being more efficient than the **D-A** couple **B**. Such systems comprising of donor and acceptor molecules coupled by the self-assembly of complementary hydrogen bonds could be very useful for light harvesting applications.

Chapter 6 Conclusion and future work

6.1 Conclusion

2D self-assembled networks, formed by hydrogen bonding and metal-ligand co-ordination were studied in this thesis work and these networks showed distinct photophysical and thermal properties. The synthesis and characterization of two new types of trigonal cores for 2D organic self-assembled networks (hydrogen bonding units and metal ion co-ordination units) have been discussed in chapter 2. Most of these trigonal symmetric molecules were soluble in common solvents and they display blue emission in solution or in the solid state.

Periodic patterns of molecules of trigonal oligomers (with hydrogen bonding units at terminal position) on HOPG at room temperature were observed. Depending on whether the solvent used was either alkylated (phenyl-octane) or non-alkylated (tetrahydronaphthalene), different types of networks were obtained. These networks were either open networks or close-packed networks. Molecular and even sub-molecular resolution was achieved, thus allowed refined interpretation of the self-assembly process. In the open networks observed using tetrahydronaphthalene as the STM solvent the central cavity was occupied by several solvent molecules. Furthermore, in most cases it was observed that these arrangements are chiral, with left and right handed domains in the same sample. These kinds of network can act as matrices for nano composites made by incorporating some guest molecules of appropriate size inside the nanocavities in the future to form a multi-component host-guest system. Self-assembly of these trigonal molecules under UHV conditions will be further investigated in future.

Self-assembly of trigonal tpy molecule **14** through Zn(II) co-ordination to form new 2D supramolecular networks **N1** and extended networks **N2** and **N3** was discussed in chapter 4. The metal co-ordinated network **N1** can be disassembled by adding more metal ions and re-self-assembled to form extended 2D networks **N2** and **N3** after inserting linear bis(tpy) linkers (p-type **17** or n-type **18**). These were found to have only short range order and no porosity according to the small angle X-ray scattering and BET results respectively. Hence they are amorphous materials with highly interpenetrating networks. Modeling studies on these 2D Zn(II)-co-ordinated self-assembled networks **N1–3** is being done by Dr. Abbie Trewin from University of Liverpool to understand their non-porosity. Since these networks have shown high luminescence with a long fluorescence life time and good thermal stabilities they might be usefully tested in organic electronic devices such as OLEDs, although solubility could be an issue.

In chapter 5, model systems for light harvesting applications by intermolecular energy transfer were investigated. Two novel donor-acceptor (**D-A**) couples consisting of 1,3,5-tris[4-amino(1,1-biphenyl-4-yl)]-benzene TBB (**3**) (**D**) and PDI and PMI derivatives with a glycine substituent (**A**) were studied as model systems for energy transfer processes and the intermolecular energy transfer between them were observed. Very high intermolecular energy transfer efficiencies were obtained from both steady state measurements (the extent of quenching of the donor by the acceptor) and time resolved measurements (life time of the donor in the presence and absence of the acceptor) for TBB (**3**)-PMI-monoacid (**21**) (**D-A** couple **A**). In contrast, the magnitude of the energy transfer efficiencies for TBB (**3**)-PDI-diacid (**20**) (**D-A** couple **B**), were very small, which was apparent even from the quenching experiments. Hence the interactions between acceptor molecules and donor molecules were observed to play a major role during the energy transfer process in these two systems. This

work presented in this thesis has clearly shown that such systems comprising of donor and acceptor molecules coupled by the self-assembly of complementary hydrogen bonds could be very useful for light harvesting applications. This establishes the opportunity for further exciting research in this field. And the energy transfer phenomena between bis(terpyridine) Zinc(II) moieties (mainly between molecule **19** and **16** at current) are being further investigated by the research group of Prof. Sun Hangdong.

6.2 Future work

6.2.1 Supramolecular organic-inorganic composites

Composites of organic and inorganic materials are of great interest to be used as the active components in electronic devices such as solar cells.¹⁶⁰ This is because such composites or hybrid materials offer the chance to combine the excellent electronic properties of inorganic materials with the processability of organic materials. The internal organization of hybrid materials has a strong influence on the final performance of these devices.^{160,161} Blends of inorganic semiconductor nanoparticles with conjugated polymers have displayed promising performance in light emitting diodes and solar cells. In these blends, particles are randomly distributed throughout the material. The formation of ordered assemblies of the organic and inorganic components can be expected to optimize the performance of such composites.

In this thesis work, ordered 2D assemblies of conjugated oligomers were formed. The next step will be the formation of organic-inorganic composites which shall be taken further by future students. Two routes to such composite materials are possible. Firstly, organic networks could be made which contain free volumes within them into which nanoparticles might be introduced by blending. In this case, the nanoparticles might act as templates to

induce the self-assembly of organic units around them. Alternatively, the organic network might be used as nanoreactors, in which nanoparticles are synthesized within the vacant areas inside the network. Hence both proposed routes are expected to be investigated by future students. It is anticipated that the nanoparticles grown in the nanoreactors may have different size and shape from those obtained by conventional synthetic methods and so the properties (including device performance) of the composite materials from two routes might differ

A new possible application as photonic band gap materials¹⁶² has emerged with the hybrid materials made up of ordered organic-inorganic kind of networks. High refractive index contrast in such ordered hybrid networks, essential for photonics applications, has been achieved by synthesizing inorganic nanoparticles by the processes such as a sol-gel. Ordered 2D or 3D assemblies of inorganic particles in an organic matrix might also act as photonic crystals with potential application in a number of areas and are expected to be studied in future.

If suitably functionalized side chains are attached to the linear units (e.g. phenylene ethynylenes), then the cavities within the networks can be lined with groups such as amines, thiols or nitriles which bind to inorganic nanoparticles. The end groups chosen will depend upon the desired nanoparticles to be bound. The residual functional groups X (as shown in figure 6.1) could be used to self-assemble the cages to form higher-level assemblies. Enclosure of individual nanoparticles within the cages by using internal functional groups will produce new supramolecular composite nanomaterials. This kind of “inside” or endo-functionalization method, as mentioned by Stang, may have application in nano-sized electronic devices. Thus, the ability to control the self-assembly of the conjugated units by addition of various chemical composition of nanoparticles and by varying the nature, dimension and shapes of the organic units are expected to be studied by future students.

Figure 6.1 Representation of two component 2D Self-assembled macrocycles formed by desymtrization of trigonal core molecule **14**.

6.2.2 Molecular Modeling studies

The experimental data of STM on self-assembly of 2D hydrogen bonding networks which were discussed in chapter 3, can be explained by modeling studies of the molecular conformation and the adsorption on graphite using molecular mechanics (MM) and molecular dynamics (MD) simulations. The calculations using MM and MD can provide information about the lattice parameters and the adsorption energy. Similarly, the small angle XRD results for self-assembled networks by zinc metal ion co-ordination can be further discussed in depth with computational techniques such as normal mode analysis, molecular dynamics and Monte Carlo based simulations. These simulation studies are currently in progress with our collaborators.

6.2.3 Studies on non-linear optical properties and two photon absorption (TPA) properties of these networks

Linear tpy molecules and their self-assembled networks had shown two photon absorption (TPA) and non-linear optical (NLO) properties¹⁰⁷. In future, it is expected that these trigonal tpy molecules and their self-assembled networks are proficient candidates for measurements of these properties as TPA depends on the asymmetric structure and delocalized electron density and these trigonal tpy molecule and their self-assembled networks fulfill these basic requirements.

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Experimental Section

Most of the initial chemicals used in this thesis work were purchased from commercially available sources, e.g. Sigma Aldrich and Alfa Aesar. Synthesis of all compounds reported in this thesis work was done under N₂ atmosphere. Thin Layer Chromatography (TLC) was done on aluminum sheets pre-coated with silica gel or aluminium oxide. TLC plates were visualized with UV lamp. Purification of organic compounds was done using column chromatography on the silica gel 60 Geduran (Merck) or neutral aluminium oxide (Brockmann Grade I, 58 angstroms).

Nuclear Magnetic Resonance (NMR) spectra (¹H and ¹³C) were recorded on a Bruker Advance 400 spectrometer. Deuterated solvents such as chloroform (CDCl₃), DMSO-d₆, and CD₂Cl₂ were used for the NMR characterization. Chemical shifts in NMR spectra are specified by δ in units of ppm referenced to residual proton signals for above mentioned NMR solvents. Coupling constants (J) are stated in Hertz (Hz). Splitting patterns in NMR results are designated as, s for singlet; d for doublet; t for triplet; q for quartet; AB, pair of doublet which is mirror image to each other; m for multiplet; and br for broad.

Mass spectrum of all the synthesized molecules was recorded using a Shimadzu Axima Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF) mass spectrometer. High Resolution Electrospray⁺-Time-Of-Flight Mass Spectra (HR ES⁺-TOF MS) were done by Mr. Yang Yifan and Asst. Prof. So Cheuk Wai from School of Physical and Mathematical Sciences (Division of Chemistry & Biological Chemistry), Nanyang Technological University.

Thermogravimetric Analysis (TGA) was carried out on a TA TGA-Q500 with a dynamic heat rate of (10 °C/min) under N₂ atmosphere (50 mL/min) in the temperature range 25–800 °C. Differential Scanning Calorimetry (DSC) experiments were carried out on a TA DSC-Q10 with dynamic heating and cooling rate (5 °C/min) under N₂ atmosphere (50 ml/min) in the temperature range 0–300 °C, depending on the decomposition temperature of the sample used.

The electrochemical Cyclic Voltammetry (CV) was performed on a Solartron 1255B frequency response analyzer with a sweep rate 100 mV/s by a platinum working electrode. The counter electrode used was Au and the reference electrode used was Ag/Ag⁺. Electrolyte used in these electrochemical measurements was DCM containing 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆).

Small-angle X-ray scattering (SAXS) experiments were performed by an Anton Paar experimental setup which was outfitted with two laterally graded multilayer optics in a side-by-side fashion. Hence this arrangement had provided a highly focused parallel beam of monochromatic Cu K α radiation. The beam was operated at 40 kV and 50 mA. The X-ray exposure times for SAXS patterns were typically 4 hours. The sample-to-detector distance was 263.3 mm.

The porous properties of the networks were investigated by nitrogen adsorption at 77.3 K using ASAP Chemisorption Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation). Samples were degassed at 100 °C for 6 h under vacuum (10⁻⁵ bar) before analysis.

The XPS experiments were performed at a home-made UHV system with base pressure at 3 x 10⁻¹⁰ torr. The X-ray source was monochromatic Al-K alpha at power 200W (SPECS). The

photon energy used was 1486.3 eV. The electron analyzer was Omicron EA125 with the energy resolution better than 0.1 eV.

Basic UV-Vis absorption spectra were performed with a UV-Vis Shimadzu UV-2501PC spectrophotometer and corresponding PL spectra's were recorded with a Shimadzu RF-5301PC spectrofluorophotometer at MSE. Other photophysical measurements were carried out at School of Physical and Mathematical Sciences (SPMS) by Dr. He Tingchao and Dr. Liu Xinfeng in the groups of Prof. Sun Handong, and Prof. Sum Tze Chien respectively. UV-Vis absorption spectra for solutions were recorded on a Shimadzu UV-3101 PC spectrophotometer. For the measurements of photoluminescence (PL) emission spectra, a cw He-Cd laser emitting at 325 nm was used as the excitation source and the signals were dispersed by a 750 mm monochromator combined with suitable filters, and detected by a photomultiplier using the standard lock-in amplifier technique. The temperature dependent PL measurements were performed between 10 K and 300 K within a helium closed-cycle cryostat. Time-resolved photoluminescence (TRPL) measurements were carried out at room temperature by the time-correlated single photon counting (TCSPC) technique with a resolution of 10 ps (PicoQuant PicoHarp 300). The third harmonic of a titanium-sapphire laser (Chameleon, Coherent Inc.) at 325 nm (100 fs, 80 MHz) was used as the excitation source.

STM Characterization

This work was carried out at CNRS by Dr. Fabien Silly and Dr. Xiaonan Sun in the group of Prof. Denis Fichou. STM measurements at liquid/solid interface were carried out at room temperature. Solutions of the TBB compounds **1-4** were prepared either in *n*-tetradecane ($C_{14}H_{30}$, 99%, Aldrich), 1-phenyloctane (99%, Aldrich) and in tetrahydronaphthalene (99%, Aldrich). Because of the poor solubility of the TBB compounds under study here, all solutions were saturated. A droplet of this solution was then deposited on a freshly cleaved HOPG substrate. STM imaging was carried out using a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope at the liquid/solid interface. To acquire constant current images at room temperature mechanically etched Pt/Ir wires were used with a bias voltage applied to the sample. Obtained STM images were further developed and analyzed using the home made application FabViewer¹ and software WSXM 5.0.²

List of abbreviations

DCM = Dichloromethane (CH_2Cl_2)

DI water = Deionized H_2O

DMSO = Dimethyl sulfoxide

EA = Ethyl acetate

EtOH = Ethanol

MeOH = Methanol

NMP = N-Methyl-2-pyrrolidone

RBF = Round bottomed flask

RT = Room temperature

$\text{PdCl}_2(\text{dppf})$ = [1,1-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)

$\text{Pd}(\text{PPh}_3)_4$ = Tetrakis(triphenylphosphine)palladium

$(\text{Ph}_3\text{P})_2\text{PdCl}_2$ = Bis(triphenylphosphine)palladium(II) dichloride

THF = Tetrahydrofuran

Et_2O = Diethyl ether

Synthesis and characterization

Synthesis of 1, 3, 5-Tris(4-halophenyl)benzenes)

1,3,5-Tris(4-iodophenyl)benzene (**1a**), and 1,3,5-tris(4-bromophenyl)benzene (**1b**) were synthesized according to a modified literature procedure.³

Synthesis of 1, 3, 5-Tris(4-iodophenyl)benzene (**1a**)

A 100 mL round bottomed flask was charged with 4-iodoacetophenone (1.23 g, 5 mmol), silicon (IV) chloride (1.5 mL, 10 mmol) and anhydrous ethanol (25 mL). The synthesis was carried out at 50 °C for 18 h during which the progress of the reaction was monitored by TLC. The reaction solution turned brownish yellow with time. Extraction of the crude reaction mixture was done with CH₂Cl₂ and then the solvent was evaporated using rotary evaporator and the residue was purified by column chromatography on silica eluting with hexane, followed by recrystallization from ethanol to yield the desired product as pale yellow needles, (904 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ =7.80 (6 H s, d, J=8.4 Hz), 7.68 (3H, s), 7.40 (6H, d, J=8 Hz). This spectral data agreed with the results reported in the literature.³

Figure A1 ¹H NMR of compound **1a**.

Synthesis of 1, 3, 5-Tris (4-bromophenyl) benzene (**1b**)

To a stirred solution of 4-bromo acetophenone (19.9 g, 0.10 mol) in dry ethanol (100 mL) at 0 °C, Silicon (IV) chloride (12 mL, 0.11 mol) was added dropwise. The resulting reaction solution was stirred at 45 °C for 24 h and the crude product collected by filtration and washed with ethanol. Recrystallization from CH₂Cl₂-EtOH gave **1b** as white needles. (9.1 g, 50%).

¹H NMR (400 MHz, CDCl₃): 7.60 (6 Hs, dd, J = 8.4 Hz); 7.68 (3 Hs, s); 7.50 (6 Hs, dd, J = 8 Hz).

Figure A2 ¹H NMR of compound **1b**.

Synthetic procedure for the Suzuki-Miyaura cross-coupling reaction of TBBs

A mixture of aryl halide (1 equiv.), arylboronic acid pinacol ester (3.4 equiv.), Pd(PPh₃)₄ (10 mol%), K₂CO₃ solution (2M) in H₂O, and solvent THF was heated at 80 °C under N₂ atmosphere. Reaction was closely monitored by TLC till completion. THF was removed by rotary evaporator and the reaction mixture was extracted with CH₂Cl₂. The combined organic layers were washed with H₂O and brine, and then dried over MgSO₄. The solvent was evaporated, and the crude compound was purified by column chromatography to obtain the desired product.

Synthesis of 1,3,5-Tris[4-methoxy carbonyl(1,1-biphenyl-4-yl)]benzene (**2a**)

4-Methoxycarbonylphenylboronic acid pinacol ester (894 mg, 3.4 mmol), **1a** (684 mg, 1.0 mmol), and Pd(PPh₃)₄ (10 mol%, 120 mg) were added to a 100 mL two neck round bottomed flask, followed by addition of 35 mL THF and 20 mL K₂CO₃ (2M, aqueous) solution which was degassed for 30 min. The resulting reaction mixture was allowed to reflux under nitrogen for 24 h. The reaction mixture was extracted with CH₂Cl₂. The organic phase was eluted with EA-hexane through a silica column and dried to yield **2a** as light brown needles (300 mg, 42%). ¹H NMR (400 MHz, CDCl₃): δ=8.15 (d, 6H, J=8.0 Hz), 7.90 (s, 3H), 7.74-7.85 (m, 18H), 3.96 (s, 9H). This spectral data agreed with the results reported in the literature.⁴

Figure A3 ¹H NMR spectrum of TBB **2a** (400 MHz, CDCl₃).

Synthesis of 1,3,5-Tris[4-carboxy(1,1-biphenyl)-4-yl]benzene (**2b**)

To a suspension of **2a** (100 mg, 0.14 mmol) in 10 mL THF/MeOH (v:v=1:1), 2 mL concentrated NaOH solution was added and the mixture was stirred overnight. The pH value was adjusted to about two using concentrated HCl. The reaction mixture was first filtered and subsequently washed with water and finally dried under vacuum at 50 °C to give compound **2b** as a white solid (80 mg, 86%). ¹H NMR (400 MHz, DMSO-d₆): δ=8.04-8.06 (m, 15H), 7.89 (d, 12H, J=8Hz). MALDI TOF MS: m/z 669.70 (M⁺). Mw calcd. 666.72.

Figure A4 ¹H NMR spectrum of TBB **2b** (400 MHz, DMSO-d₆).

Figure A5 MALDI TOF Mass spectra of TBB **2b**.

Synthesis of 1,3,5-Tris[4-amino(1,1-biphenyl-4-yl)]benzene (**3**)

4-Aminophenylboronic acid pinacol ester (1.12 g, 5.15 mmol), **1a** (1.03 g, 1.50 mmol), and Pd(PPh₃)₄ (10 mol %, 120 mg) were added to a 100 mL two neck round bottom flask. And followed by addition of 35 mL THF and 20 mL K₂CO₃ (2M, aqueous) solution which was degassed for 30 min. Finally the resulting solution was allowed to reflux under nitrogen for 24 h. The extraction of the mixture was done with CH₂Cl₂. The organic phase was eluted with THF and hexane through a silica column and dried to yield a light yellow powder (540 mg, 62%). ¹H NMR (400 MHz, DMSO-d₆): δ=7.86 (s, 3H), 7.82 (d, 6H, J=8.0 Hz), 7.66 (d, 6H, J=8.0 Hz), 7.43 (d, 6H, J=8.0 Hz), 6.69 (d, 6H, J=8.0 Hz), 5.72 (s, 6 H), ¹³C NMR (100 MHz, DMSO-d₆): δ=148.9, 141.9, 140.5, 137.9, 127.9, 127.7, 127.5, 126.3, 124.0, 114.9. MALDI TOF MS: m/z 579.73 (M⁺). Mw calcd. 579.73. **Anal. Calcd.** C₄₂H₃₃N₃: C, 87.01; H, 5.74; N, 7.25. Found: C, 81.83; H, 7.56; N, 6.28.

Figure A6 ^1H NMR spectrum of TBB 3 (400 MHz, DMSO-d_6).

Figure A7 ¹³C NMR spectrum of TBB 3 (100 MHz, DMSO-d₆).

Figure A8 MALDI TOF Mass spectra of TBB 3.

Figure A9 HR ES⁺-TOF MS TBB 3.

Figure A10 Thermo gravimetric analysis (TGA) of TBB 3.

Figure A11 Differential Scanning Calorimetry (DSC) data of TBB 3.

Figure A12 Cyclic voltammograms of TBB 3 on a platinum electrode (wire) in 0.1 M Bu_4NPF_6 , DCM solution with a sweep rate of 100 mV/s.

Synthesis of 1,3,5-Tris[4-cyano(1,1-biphenyl-4-yl)]benzene (**4**)

4-Cyanophenylboronic acid pinacol ester (391 mg, 1.71 mmol), **1a** (342 mg, 0.50 mmol), and Pd(PPh₃)₄ (10 mol%, 60 mg) was added to a 100 mL two neck round bottom flask. And followed by addition of 35 mL THF and 20 mL mL K₂CO₃ (2M, aqueous) solution which was degassed for 30 min. Finally the resulting solution was allowed to reflux under nitrogen for 24 h. The mixture was extracted with CH₂Cl₂ and the organic layer was dried over MgSO₄. The organic phase was eluted with chloroform through a silica column and dried to yield a light brown powder (120 mg, 40%). ¹H NMR (400 MHz, CDCl₃): δ=7.90 (s, 3H), 7.85 (d, 6H, J=8.0 Hz), 7.74-7.77 (m, 18H). This spectral data agreed with the results reported in the literature⁵

Figure A13 ¹H NMR spectrum of TBB **4** (400 MHz, CDCl₃).

Synthesis of 1,3,5-Tris-(4-trimethylsilylethynyl-phenyl)-benzene(5a)

1a (480 mg, 0.70 mmol), triphenyl phosphine (18 mg, 0.07 mmol), copper(I) iodide (9 mg, 0.04 mmol) and palladium (II) acetate (11 mg, 0.05 mmol) were dissolved under inert atmosphere in triethylamine (50 mL). Trimethylsilylacetylene (0.3 mL, 2.2 mmol) was slowly added and the resulting solution was stirred for 24 hours at room temperature. Triethylamine was neutralized with dilute HCL. The mixture was extracted with CH₂Cl₂ and the organic layer was dried over MgSO₄. After evaporating the solvent, the crude product was purified by column chromatography (silica gel, 5% EA/hexane) to afford the product (300 mg, 79%) as yellow needle like crystals. **¹H NMR (400 MHz, CDCl₃):** δ = 7.74 (s, 3H), 7.63 (d, $3J(\text{H,H}) = 8.0$ Hz, 6H), 7.57 (d, $3J(\text{H,H}) = 8.0$ Hz, 6H), 0.27 (s, 27H); **¹³C NMR (100 MHz, CDCl₃):** δ = 142.7, 140.7, 132.5, 127.1, 125.0, 122.5, 104.8, 95.2, 0.0.

Figure A14 ¹H NMR spectrum of compound **5a** (400 MHz, CDCl₃).

Figure A15 ¹³C NMR spectrum of compound **5a** (100 MHz, CDCl₃).

Figure A16 MALDI TOF Mass spectra of compound **5a**.

Synthesis of 1,3,5-Tris-(4-ethynyl-phenyl)-benzene (**5b**)

5a (850 mg, 1.4 mmol) was dissolved in THF (20 mL) and methanol (80 mL). After adding potassium carbonate (1.2 g, 8.7 mmol), the resulting solution was allowed to stirred for approximately 5 h at room temperature. The mixture was extracted with CH_2Cl_2 . The organic phase was eluted with EA and hexane through a silica column and dried to yield **5b** as a light yellow solid (460 mg, 85%). ^1H NMR (400 MHz, CDCl_3): δ = 7.75 (s, 3H), 7.65 (d, $3J(\text{H},\text{H}) = 8.0$ Hz, 6H), 7.61 (d, $3J(\text{H},\text{H}) = 8.4$ Hz, 6H), 3.16 (s, 3H).

Figure A17 ^1H NMR spectrum of compound **5b** (400 MHz, CDCl_3).

Synthesis of 1-Hexyluracil (**6**)

To a suspension of uracil (2.8 g, 25 mmol) in DMSO (30 mL), dry K_2CO_3 (3.8 g, 27.5 mmol) was added, and the suspension was stirred for 20 min. 1-Bromohexane (3.5 mL, 25 mmol) was added and the resulting reaction solution was stirred for 20 h at 40 °C. The suspension was diluted with CHCl_3 , washed with 0.1 M HCl solution, and brine, and dried over MgSO_4 . The organic layer was concentrated and poured into cold hexane with vigorous stirring. The product, which was precipitated from the hexane solution was then filtered and finally washed with cold hexane to afford compound **6** (1.79 g, 35%) as a white solid. Spectral data agreed with the results reported in the literature.⁶

Figure A18 ^1H NMR spectrum of compound **6** (400 MHz, CDCl_3).

Synthesis of 1-Hexyl-6-iodouracil (7)

To a solution of **6** (1.7 g, 8.7 mmol), in 60 mL THF, LDA (24 mL of a 1.8 M solution, 43.5 mmol) was added dropwise, and then the resulting solution was stirred under N₂ atmosphere at -78 °C for approximately 1.5 h. After that I₂ (11 g, 43.5 mmol) was added and finally the resulting solution was stirred again for 2 h. The resulting solution was treated with acetic acid (1.2 mL) and further kept for warming up to room temperature. The mixture was extracted with CHCl₃. The organic phase was eluted with EA and hexane through a silica column and dried to yield **7** as a brown solid (2.02 g, 72%). Spectral data agreed with the results reported in the literature.⁶

Figure A19 ¹H NMR spectrum of compound **7** (400 MHz, CDCl₃).

Synthesis of 1,3,5-Tris[(1-hexylurac-6-yl)ethynyl]phenyl benzene (**8**)

A mixture of **7** (0.70 mmol, 252 mg) and dry THF/Et₃N (30 mL/10 mL) was degassed under N₂ atmosphere for 20 min. Bis(triphenylphosphine)palladium dichloride (4.2 mg, 3 mol%) and CuI (2.5 mg, 6 mol%) were added and the mixture stirred at 25 °C for 15 min. A solution of 1,3,5-triethynyltriphenylbenzene (0.20 mmol, 76 mg) in anhydrous THF (10 mL) was then added dropwise and mixture stirred at 45 °C overnight. Upon completion of the reaction, solvents were removed by rotary evaporator. The resulting solid purified by recrystallization from CHCl₃ and MeOH, to afford **8** (118 mg, 62%) as a pale yellow powder (120 mg, 62%).

¹H NMR (400 MHz, DMSO): δ 11.47 (s, 1H), 8.05 (d, J = 7.6 Hz, 3H), 7.74 (d, J = 8.3 Hz, 2H), 6.85 (s, 1H), 6.00 (d, J = 2.2 Hz, 1H), 4.00 – 3.94 (m, 2H), 1.69 (dd, J = 14.1, 6.9 Hz, 2H), 1.30 (d, J = 5.0 Hz, 6H), 0.84 (t, J = 7.0 Hz, 3H). **HR ES⁺-TOF MS:** calculated m/z : 961.4649 (M^+), found: m/z 961.4653 (M^+). **MALDI TOF MS:** m/z 961.16 (M^+). Mw calcd. 962.79. **Anal. Calcd.** C₆₀H₆₀N₆O₆: C, 74.98; H, 6.29; N, 8.74; O, 9.99. Found: C, 76.19; H, 5.12; N, 6.41.

Figure A20 ¹H NMR spectrum of compound **8** (400 MHz, DMSO-d₆).

Figure A21 MALDI TOF Mass spectra of compound **8**.

Figure A22 HR ES⁺-TOF MS of compound **8**.

Figure A23 Thermo gravimetric analysis (TGA) of TBB **8**.

Figure A24 Differential Scanning Calorimetry (DSC) data of TBB **3**.

Figure A25 Cyclic voltammograms of **8** on a platinum electrode (wire) in 0.1 M Bu₄NPF₆, DCM solution with a sweep rate of 100 mV/s.

Synthesis of Triboronate (9)

1a (684.09 mg, 1 mmol), bis(pinacolato)diborane (1.15 g, 4.5 mmol), potassium acetate (1.18 g, 12 mmol) and PdCl₂(dppf) (65.85 mg, 0.09 mmol) were dissolved in anhydrous DMSO (15 mL) and then the solution was degassed under N₂ atmosphere. The resulting solution was stirred at 80 °C for 12 h, cooled to RT, and then poured into ice water. The extraction of the resulting reaction solution was done with CHCl₃ and water. Finally the CHCl₃ layers were dried over anhydrous MgSO₄. The solvent was evaporated with rotary evaporator; the residue was washed with cold hexane. Then the product was purified by recrystallization from MeOH-THF to afford **9** as an off-white solid (350 mg, 51%). ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.82 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 1.37 (s, 12H).

Figure A26 ¹H NMR spectrum of compound **9** (400 MHz, CDCl₃).

Synthesis of 4'-(4-Bromophenyl)-2,2':6'2''-terpyridine (**10**)

To a solution of 4-bromobenzaldehyde (29.6 g, 160 mmol), 2-acetylpyridine (36 mL, 320 mmol) and EtOH (600 mL) was added in RBF. Aqueous ammonia (560 mL, 400 mmol) and potassium hydroxide (24.64 g, 440 mmol) were then added to the resulting solution. The resulting solution was then stirred for 5 h at 42 °C. Crude off white solid was achieved after filtration of the reaction solution. This was then washed with EtOH. Finally recrystallization of the crude product from MeOH-CHCl₃ (10:1) afforded **10** as a white solid (24.50 g, 40%).

¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, J = 4.0 Hz, 1H), 8.71 (s, 1H), 8.67 (d, J = 8 Hz, 1H), 7.91-7.87 (m, 1H), 7.78 (d, J = 8 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.39-7.35 (m, 1H).

Figure A27 ¹H NMR of compound **10** (400 MHz, CDCl₃).

Synthesis of 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine (**11**)

The mixture of **10** (12.90 mmol, 5 g), Pd(dppf)Cl₂ (282 mg, 0.39 mmol), potassium acetate (4.75 g, 48.40 mmol), and bis(pinacolato)diboron (5.0 g, 19.35 mmol) and was degassed under N₂ atmosphere in a RBF. Then dioxane (60 mL) was added through a syringe. The reaction mixture was then stirred at 80 °C for 24 h. After cooling down to RT, the dioxane was removed under reduced pressure. The solid was extracted with CH₂Cl₂. The CH₂Cl₂ layer was dried over MgSO₄ and then concentrated using a rotary evaporator. Finally recrystallization from MeOH–THF, **11** was obtained as a light purple solid (4.5 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.77 (s, 1H), 8.73 (d, *J* = 4.0 Hz, 1H), 8.68 (d, *J* = 8 Hz, 2H), 7.96–7.87 (m, 3H), 7.36 (t, *J* = 6Hz, 1 H), 1.37 (s, 6H).

Figure A28 ¹H NMR of compound **11** (400 MHz, CDCl₃).

Synthesis of 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**)

2,5-Dibromohydroquinone (4.00 g, 15.06 mmol) was dissolved in absolute EtOH (150 mL) containing sodium hydroxide (0.92 g, 23 mmol) at RT under N₂ atmosphere. The reaction solution was then heated up to 80 °C with constant stirring. The color of solution changed from colorless to reddish brown then dodecylbromide (7.2 mL, 30 mmol) was then added dropwise. After approximately 24 h stirring under N₂, the resulting reaction solution was cooled to RT. The precipitate was then filtered and washed with MeOH to give **12** as a white solid (5.00 g, 55%). ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 1H), 3.94 (t, *J* = 6 Hz, 2H), 1.83–1.76 (m, 2H), 1.51–1.44 (m, 2H), 1.33–1.23 (br, 16H), 0.88 (t, *J* = 6.0 Hz, 3H).

Figure A29 ¹H NMR of compound **12** (400 MHz, CDCl₃).

Synthesis of **13 a monoadduct of 4'-(4-Pinacolatoboronophenyl)-2,2':6',2''-terpyridine with 1,4-dibromo-2,5-bis(dodecyloxy)benzene**

11 (4.0 g, 9.20 mmol), **12** (10 g, 16 mmol), and Pd(PPh₃)₄ (638 mg, 0.55 mmol) were degassed using N₂ in a RBF. Degassed, THF (90 mL) and aqueous K₂CO₃ (2 M, 30 mL) and were then injected into the RBF. The reaction mixture was then stirred in the dark at 80 °C for 24 h. After completion of the reaction (monitoring with TLC), the reaction mixture was cooled to RT and THF was removed using a rotary evaporator. The reaction mixture was then extracted with CH₂Cl₂. Organic layer was dried over MgSO₄; solvent was removed by rotary evaporator. Finally the compound was purified by column chromatography on alumina eluting with 10% EA in hexane. The product **13** was obtained as a off-white solid (4 g, 53%).

¹H NMR (400 MHz, CDCl₃): δ 8.98 (s, 1H), 8.77 (t, *J* = 8.0 Hz, 2H), 8.03–7.94 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 6.0 Hz, 1H), 4.03 (t, *J* = 6.0 Hz, 1H), 3.900 (t, *J* = 6.0 Hz, 1H), 1.84 (t, *J* = 8 Hz, 1H), 1.71 (t, *J* = 8 Hz, 1H), 1.51 (t, *J* = 8 Hz, 1H), 1.26–1.19 (br, 16 H), 0.89–0.81 (m, 3 H).

Figure A30 ^1H NMR spectrum of compound **13** (400 MHz, CDCl_3).

Synthesis of **14**, a triadduct of **12** with Triboronate

9 (0.10 mmol, 68 mg), **13** (0.6 mmol, 500 mg) and $\text{Pd}(\text{PPh}_3)_4$ (0.010 mmol, 12 mg) were put into RBF and degassed using N_2 . Aqueous K_2CO_3 (2 M, 20 mL) and toluene (35 mL) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 90 °C for 72 h and monitored by TLC. The reaction mixture was cooled to RT and toluene was removed using a rotary evaporator. The resulting reaction solution was then extracted with CHCl_3 and dried over MgSO_4 . Solvent was removed with rotary evaporator and the pure compound was obtained by column chromatography on alumina eluting with 25% EA in hexane. **14** was obtained as an off-white solid (90 mg, 35%). ^1H NMR (400 MHz,

CD₂Cl₂): δ 8.85 (s, 1H), 8.73 (dd, $J = 11.4, 6.1$ Hz, 2H), 8.05 – 7.72 (m, 12H), 7.70 – 7.48 (m, 1H), 7.46 – 7.32 (m, 3H), 7.17 – 7.09 (m, 2H), 4.02 (d, $J = 5.8$ Hz, 2H), 1.75 (s, 2H), 1.42 (s, 2H), 1.24 (d, $J = 23.0$ Hz, 16H), 0.84 – 0.80 (m, 3H). **¹³C NMR (101 MHz, CD₂Cl₂):** δ 156.76, 156.64, 151.04, 149.77, 130.79, 130.69, 130.60, 128.38, 128.04, 127.45, 127.35, 124.47, 121.71, 119.10, 116.62, 116.46, 70.27, 54.00, 35.21, 32.49, 32.17, 30.23, 30.21, 29.93, 26.75, 25.82, 23.23, 14.45, 11.76. **HR ES⁺-TOF MS:** calculated m/z : 2562.6750 (M^+), found: m/z 2562.6750 (M^+).

Figure A31 ¹H NMR spectrum of compound **14** (400 MHz, CD₂Cl₂).

Figure A32 ^{13}C NMR spectrum of compound **14** (100 MHz, CD_2Cl_2).

Figure A33 HR ES⁺-TOF MS of compound **14**.

Figure A34 Cyclic voltammograms of **14** on a platinum electrode (wire) in 0.1 M Bu₄NPF₆, DCM solution with a sweep rate of 100 mV/s.

Synthesis of trigonal imidazole derivative **15**

Compound **1b** (0.51 g, 0.94 mmol), KOH (0.32 g, 5.64 mmol), imidazole (0.39 g, 5.64 mmol), and CuI (58 mg, 0.3 mmol) were added to DMSO (40 mL). The reaction mixture was heated to 160 °C and refluxed for 2 days. After completion of the reaction, the product was extracted using CH₂Cl₂ and brine. CH₂Cl₂ was evaporated with rotary evaporator and the product **15** was obtained as a light brown powder (250 mg, 53%). **¹H NMR (400 MHz, DMSO):** δ 8.38 (s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 8.02 (s, 1H), 7.87 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.15 (s, 1H). **¹³C NMR (101 MHz, DMSO):** δ 140.64, 138.38, 136.49, 135.59, 129.99, 128.70, 124.45, 120.58, 117.99, 39.50. **HR ES⁺-TOF MS:** calculated m/z : 505.2141 (M^+), found: m/z 505.2151 (M^+). **Anal. Calcd.** C₃₃H₂₄N₆: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.16; H, 5.20; N, 15.91.

Figure A35 ¹H NMR spectrum of compound **15** (400 MHz, DMSO-d₆).

Figure A36 ¹³C NMR spectrum of compound **15** (100 MHz, DMSO-d₆).

Figure A37 HR ES⁺-TOF MS compound **15**.

Figure A38 Thermo gravimetric analysis (TGA) of **15**.

Figure A39 Differential Scanning Calorimetry (DSC) data of **15**.

Synthesis of **16**

Compound **16** was prepared by Suzuki coupling reaction of tpy boronate with **1b**. In a two neck round bottom flask 1,3,5-tris-(4-bromophenyl)benzene (103 mg, 0.19 mmol), tpy boronate (320 mg, 0.76 mmol), [Pd(PPh₃)₄] (23 mg, 0.020 mmol) and 2 M aqueous K₂CO₃ (5.7 mL, 1.14 mmol) and THF (50 mL) were added under N₂ atmosphere. The product precipitated from the reaction mixture and was separated by filtration. The collected solid was further purified by washing with THF and water. Finally it was washed with Et₂O and compound **16** was afforded as a white solid (175 mg, 75%). ¹H NMR and ¹³C NMR spectral data agreed with the results reported in the literature.⁷

Figure A40 ¹H NMR spectrum of compound **16** (400 MHz, CDCl₃).

Figure A41 ¹³C NMR spectrum of **16** (100 MHz, CDCl₃).

Synthesis of Zn(II)-self-assembled network of **14** (**N1**)

To a solution of **14** (25 mg, 0.010 mmol) in NMP (10 mL), Zinc(II) acetate dihydrate (4.2 mg, 0.015 mmol) in NMP (2 mL) was added dropwise. The resulting solution was then stirred at 105 °C under N₂ atmosphere for 24 h. An excess of NH₄PF₆ was then added into the hot solution and stirring was continued for 30 min. The resulting reaction solution was added slowly into MeOH for precipitation. The precipitate was then filtered off and washed with MeOH. Precipitate was again dissolved in NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried under vacuum for 24 h to give **N1** as a yellow solid (27 mg, 74%).

Synthesis of Zn(II)-self-assembled network of **14** with **18** (**N2**)

N1 (15 mg, 0.005 mmol) in NMP (10 mL) was heated to 105 °C. Zinc(II) acetate dihydrate (2.18 mg, 0.008 mmol) in NMP (2 mL) was added dropwise into the resulting solution. The reaction mixture was stirred at 105 °C under N₂ for 1 h. **27** (9.63 mg, 0.0075 mmol, 1.5 times S1 moles) in NMP (10 mL) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N₂ for 24 h. An excess of NH₄PF₆ was then added into the hot reaction mixture and stirring was continued for 30 min. The resulting reaction solution was added slowly into MeOH for precipitation. The precipitate was then filtered off and washed with MeOH. Precipitate was again dissolved in NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried under vacuum for 24 h to give **N2** as a red solid (14 mg, 62%).

Synthesis of Zn(II)-self-assembled network of **14** with **17** (**N3**)

N1 (15 mg, 0.005 mmol) in NMP (10 mL) was heated to 105 °C. Zinc(II) acetate dihydrate (2.2 mg, 0.0075 mmol) in NMP (2 mL) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N₂ for 1 h. **26** (7.2 mg, 0.0075 mmol, 1.5 times S1 moles) in NMP (10 mL) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N₂ for 24 h. An excess of NH₄PF₆ was then added into the hot reaction mixture and stirring was continued for 30 min. The resulting reaction solution was added slowly into MeOH for precipitation. The precipitate was then filtered off and washed with MeOH. Precipitate was again dissolved in NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried under vacuum for 24 h to give **N3** as a yellow solid (12 gm, 55%).

Figure A42 TGA scans of 2D metal-ion co-ordinated self-assembled supramolecular networks **N1–3**.

Figure A43 DSC scans of 2D metal-ion co-ordinated self-assembled supramolecular networks **N1–3**.

Synthesis of imidazole MOF-15

Trigonal imidazole (26.67 mmol) and zinc nitrate hexahydrate (20 mmol) were loaded in a 5 mL vial containing 1 mL DMF. 100 μ L of DMF solution of nitric acid (1 drop of nitric acid in 1 mL DMF) was added to the above mixture to obtain a clear solution. The vial was capped and placed in an oven preheated to 120 °C for 20 h. After cooling to RT, the reaction solution was decanted and the solid product was washed several times with DMF, filtered, and dried in air before the characterization.

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Research Publications

Research papers published in peer-reviewed journals

1. Tingchao He, Zheng Bang Lim, Lin Ma, Hairong Li, [Deepa Rajwar](#), Yongjun Ying, Ziyun Di, Andrew C. Grimsdale, and Handong Sun, **“Large Two-photon Absorption of Terpyridine-based Quadrupolar Derivatives: Towards The Applications of Optical Limiting and Biological Imaging”** *Chem. Asian J.* 8, 2013, 564.
2. T. He, [D. Rajwar](#), L. Ma, Y. Wang, Z. B. Lim, A. C. Grimsdale, H. Sun, **“Wavelength dependence of optical nonlinearity of terpyridine-based Zn(II)-co-ordinated self-assembled polymers”** *Appl. Phys. Lett.* 101, 2012, 213302.
3. [Deepa Rajwar](#), Xiaonan Sun, Sung Ju Cho, Andrew C. Grimsdale, and Denis Fichou, **“Synthesis and 2D Self-assembly at the Liquid-solid Interface of End-substituted Star-shaped Oligophenylenes”** *CrystEngComm* 14, 2012, 5182.

Papers submitted/ in preparation

1. **“Efficient Intermolecular Energy Transfer Between a Novel Donor-Acceptor Couple: A Trigonal Molecule and a Perylene Chromophore”** submitted to *Phys. Chem. Chem. Phys.*
2. **“Novel 2D and 3D metallo-supramolecular networks with superior optical properties based on zinc metal ion co-ordination”** manuscript in preparation.

International Conferences and Workshops, Presentations and Participations

1. [Deepa Rajwar](#), Xiaonan Sun, Fabien Silly, Andrew Clive Grimsdale, Denis Fichou; STM studies on self-assembly of trigonal molecules, International Conference of Young Researchers on Advanced Materials (ICYRAM-2012) July 1-6, 2012, Matrix Building, Biopolis, Singapore.
2. 2nd International workshop on "Natural and Artificial Photosynthesis, Bioenergetics and Sustainability" June 11-14, 2012, Nanyang Executive Centre, NTU, Singapore.
3. [Deepa Rajwar](#), Andrew C. Grimsdale, Fabien Silly, Denis Fichou; Trigonal Conjugated Oligomers - Self-Assembly by Hydrogen bonding, International Conference on Materials for Advanced Technologies (ICMAT-2011) June 26 – July 1, 2011, Suntec, Singapore.
4. [Deepa Rajwar](#), Ritu Srivastava, M. N. Kamalasanan, Andrew Clive Grimsdale; Host-Guest Energy Transfer in DCM doped Zn(mq)₂, International Conference on Materials for Advanced Technologies (ICMAT-2009) 28 June - 3 July, 2009, Suntec, Singapore.

National Conferences and Workshops, Presentations and Participations

1. [Deepa Rajwar](#), Tingchao He, Handong Sun, Andrew Clive Grimsdale; Synthesis and Self-assembly Behavior of a Novel Trigonal Hydrogen Bonding Molecule, SINGAPORE, 5th MRS-S Conference on Advanced Materials, March 20 - 22, 2012 Nanyang Executive Centre, NTU, Singapore.
2. [Deepa Rajwar](#), Andrew Clive Grimsdale, Fabien Silly, Denis Fichou; Self-assembly of Trigonal Conjugated Oligomer, 4th MRS-S Conference on Advanced Materials, March 17 –19, 2010, IMRE Auditorium, Singapore.