DESIGN AND SYNTHESIS OF ORGANIC MATERIALS FOR OPTOELECTRONICS

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The design and synthesis of new π-conjugated organic semiconductors are currently at the forefront of research in order to realize stable and efficient organic electronic devices. Linear polycyclic aromatic hydrocarbons are π-conjugated organic systems widely studied for electronic applications. Pentacenes, for example, are a current choice in Organic Field Effect Transistors (OFETs). But practical applications of this class of compounds have been limited by their air (O₂) and light sensitivity and poor solubility in most common organic compounds.

Structural modification increases the stability, improve the solubility, and improve the thin film packing and mobility over the parent hydrocarbon. The electronic, physical, and photophysical properties of pentacenes, can be easily modified by changing the substitution pattern on the main aromatic skeleton.

A comparative study of suitably functionalized, highly soluble tetraceno[2,3-b]thiophenes (3.1-3.3) and pentacenes (3.4-3.6) that show higher photoxidative stability than that of unfunctionalized corresponding acenes is reported. The absorption and emission of 3.1-3.3 ($A_{max} = 624-656$ nm, $\lambda_{max} = 634-672$ nm, $\Phi_F \approx 10\%$) and 3.4-3.6 ($A_{max} = 672-704$ nm, $\lambda_{max} = 682-718$ nm, $\Phi_F \approx 10\%$) were found to be systematically red-shifted by the substitution in the order of the tert-butylethynyl < triisopropylsilylethynyl < phenylethynyl groups. The oxidation potentials of these compounds were similar ($E_{1/2} \approx 0.70$ V), except for 3.4, which showed lower oxidation potential ($E_{1/2} \approx 0.63$ V).

Stability and emission in the solid state are important features of organic compounds to be used as Organic Light Emitting Diodes (OLEDs). The substantial emission of compounds in solution usually becomes weak in the solid state due to both intermolecular energy and electron transfer. Compounds containing an aromatic fumaronitrile core have attracted significant attention as candidates in electroluminescent devices because of their strong emissions in the solid state. Changing the substituents on fumaronitrile core helps to change the emission properties in the solid state. These
compounds have higher propensity to form Fluorescent Organic Nanoparticles in appropriate inferior/superior solvent mixtures.

Compounds 5.1 and 5.2 show negative solvatochromic absorption behavior, but show both positive and negative solvatochromic behavior in the fluorescence spectra. In a water/THF mixture, 5.1 as well as 5.2 aggregate into 50-150 nm nanoparticles. The emission of nanoparticles of the new types of fluorescent organic nanoparticles 5.1 and 5.2 is much higher than that of either 5.1 or 5.2 in solution.

The emission spectra and morphologies of 5.3, 5.4, and 5.5 are affected by the water/THF ratio. At a high water/THF ratio (7:1), nanorods (1-3 µm × 80 nm) of 5.4 and nanofibers (0.8-1.5 µm × 100 nm) of 5.5 are observed. Nanoparticles of 5.3 retain a spherical structure. The chemical effects of the electron-donating or electron-withdrawing groups at the para positions are believed to play a major role in the formation of such nanostructures.
This dissertation is dedicated to my late parents

&

my teachers
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CHAPTER 1. OPTOELECTRONICS: APPLICATIONS OF ORGANIC MATERIALS

1.1 Introduction

Optoelectronics is usually considered as a sub-field of photonics. This studies about the application of electronic devices that source, detect, and control light. Though light is often considered as visible light, in this context, light includes invisible forms of electromagnetic radiation such as γ-rays, X-rays, ultraviolet and infrared. Optoelectronics is based on the quantum mechanical effects of light on semiconducting materials under the influence of electric fields.

Optoelectronic devices can be defined as optical to electrical or electrical to optical instruments or transducers that use such devices in their applications. Usually electro optics is erroneously used as a synonym for optoelectronics but it is a much wider branch of physics that covered all interactions between light and electric fields.

1.2 Optoelectronic Devices

Optoelectronic devices can be divided mainly into two groups: (i) organic light emitting diodes (OLEDs); and (ii) organic field effect transistors (OFETs) or organic thin film transistors (OTFTs). Organic materials having good fluorescence quantum yields are useful for OLEDs. On the other hand molecules having suitable molecular packing to enhance charge mobility from one to another are useful for OTFTs. They also find applications in other electronic device, such as photovoltaic solar energy collectors and p- or n-type semiconductors in p-n hetero-junctions. Organic semiconductors have advantages
over their inorganic counterparts since they have structural flexibility, low temperature solution processing, and low cost.\textsuperscript{8}

1.2.1 Organic Light Emitting Diodes

OLEDs have attracted considerable attention given their great potential applications in flat panel displays and other display devices. Significant progress has been achieved in the development of full color OLED based displays.\textsuperscript{9,10} The basic principle of an OLED is simple. When a layer of emitting material is placed between an anode and a cathode, light is emitted due to the recombination of holes and electrons.\textsuperscript{7} A schematic diagram of OLED is illustrated in the Figure 1.1, showing the structure and operation of OLED. Numerous modifications and changes must be effected in order for OLEDs to become practical.

![Figure 1.1. Structure and operation of OLED](image)

Many organic compounds have been used successfully in OLEDs. The major problem with such compounds is low fluorescence quantum yield in the solid state due to aggregation.\textsuperscript{11,12}
Representative molecules and their derivatives that have been used in OLEDs with various degrees of success are represent in Figure 1.2. Abbreviations are stated in APPENDIX A.

![Structures of some compounds used in OLEDs.](image)

**Figure 1.2.** Structures of some compounds used in OLEDs.\textsuperscript{13}

### 1.2.2. Organic Field Effect Transistors

OFETs based on organic polymers, oligomers, and monomers are an alternative to traditional inorganic Si, Ge, and GaAs-based semiconductors.\textsuperscript{14-16} Though the relatively low charge carrier mobility ($\mu$) of organic semiconductors along with a too low switching speed ($I_{on}/I_{off}$) have become issues in their practical application\textsuperscript{4}, their processing advantages and structural flexibility make them competitive in several existing thin film transistor applications such as in active matrix flat panel displays and electronic papers. Such devices are normally prepared on glass or plastic substrates. Depending on the nature of the organic material to be
deposited as the active material, two main techniques are used: i. thermal vacuum evaporation ii. spin coating. There are two common types of device configurations used in OTFTs, (i) top-contact and (ii) bottom-contact configurations (Figure 1.3).

**Figure 1.3.** OTFT device configuration: (a) Top-contact device (b) Bottom-contact device.\(^{17}\)

In top contact devices, the source and drain electrodes are placed onto the organic semiconducting layer. Whereas, the semiconducting layer is deposited onto the source and drain electrodes in bottom-contact devices. The bottom contact device configuration is the most convenient platform for the fabrication of solution-processed semiconductor devices. The top contact device configuration typically yields higher performance devices, both because of improved organic film formation on the obstruction free dielectric surface and due to the superior contact between the source and drain electrodes and the organic semiconductor.

The important device parameters are charge mobility \((\mu)\), current modulation \((I_{on}/I_{off})\) and threshold voltage \((V_T)\). In the case of p-type semiconductors (the majority of carriers are holes), if the gate electrode is biased positively with respect to the source electrode, they operate in the depletion mode. Thus, the channel region is depleted of carriers producing a
high channel resistance. This is called the off state. On the other hand, if the gate is negatively biased with respect to the source, it operates in an accumulation mode and this results in a low channel resistance. This is called the on state. The ratio of the currents in the on state and off state is called the current modulation and referred as $I_{on}/I_{off}$. This ratio should be $10^6$ or above for the proper operation of TFTs. Electrode polarity is reversed for n-type semiconductors. Charge carrier mobility ($\mu$) is a quantity relating the drift velocity of charges to the applied electric field across a material and the charge mobility essentially gauges how easily charge carriers can move through the semiconductor. An acceptable $\mu$ value is $1 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ or above. The drift velocity ($v_d$) is the average velocity that a particle attains due to an electric field and the threshold voltage ($V_T$) is the maximum voltage to turn on the transistors. This voltage should be low (~ 15 V) so that it takes lower voltage to charge and discharge the display’s pixels (thereby turning on and off).

The most widely used organic compounds in semiconductors are pentacenes, oligothiophenes, and polythiophenes. The highest field effect mobility known so far for an organic molecule is of pentacene ($2.4 \text{ cm}^2\text{V}^{-1}$; on/off ratio greater than $10^6$ at 15 V of operating voltage). This value is more than the industrial bench mark of $1 \text{ cm}^2\text{V}^{-1}$, set by an amorphous hydrogenated silicon based field effect transistors. The plot (Figure 1.4) shows the maximum charge carrier mobility values for a particular class of compounds as reported in the literature.

Present research has concentrated on pentacenes and their derivatives with the aim of improve the efficiency of OFETs because of its excellent charge carrier ability. Alkyl substituted ethynylated pentacene derivatives have shown enhanced $\pi$-stacking abilities as
well as increased stability over unsubstituted analogs. Figure 1.5 illustrates several potential organic materials for OFETs.

![Figure 1.4. The best performance of OFETs of different classes of compounds as an active layer vs time.](image1)

![Figure 1.5. Representative molecules for OFETs.](image2)
1.2.3. Photovoltaic Devices

A delocalized \( \pi \)-system in a molecule that absorbs light can create photogenerated charge carriers, and transport these charge carriers. Vacuum evaporation and solution processing techniques are widely used for the preparation of thin films for solar cells.\(^8\) Phthalocyanine and perylene are commonly used for the application of organic solar cells.\(^23\) Though, many organic compounds have been used in photovoltaic cells, usage of pentacenes is not common. Recently, pentacene has been used in a device in conjunction with \( C_{60} \). Pentacene is the donor and \( C_{60} \) the acceptor.\(^24\) A heterojunction with an electron acceptor promotes the dissociation of excitons and allows broader coverage of the solar spectrum by compensating for the special region where the absorption of pentacene is low. Figure 1.6 shows examples of organic semiconductors used in solar cells.

**Figure 1.6.** Examples of organic semiconductors used in solar cells.
1.3. Objective and Scope of the Project

Recently, organic materials have emerged as potential candidates in the optoelectronic field competing with their inorganic counterparts. As has been illustrated briefly above, organic materials can be employed as semiconductors or luminescent materials. The objective of this project is two-fold: the synthesis and study the photophysical properties of i. organic semiconductors ii. organic luminescent materials including Fluorescent Organic Nanoparticles (FONs).

Though many organic semiconductors appear in the present literature, and pentacene and its derivatives dominate the OFET field, the pentacenes are not perfect. Many laboratories are trying to reach the optimum position in the organic conductor field by minimizing drawbacks such as instability and insolvency. We have synthesized a new class of pentacene derivatives by substituting two methoxy groups and two ethynyl groups with different substituents on the main aromatic skeleton. These show interesting photophysical, and electrochemical properties.

The past decade has seen great progress in the synthesis of luminescent materials for OLEDs because luminescent materials are the primary substances for OLEDs. Fluorophores emitting long wavelength light are usually polar and are highly emissive in solution but weakly emissive in the solid state because of the aggregation due to either attractive dipole-dipole interactions or effective intermolecular π-stacking.

We have designed and synthesized two classes of luminescent materials with a diphenylfumaronitrile core. The presence of polar and relatively bulky cyano groups in J-aggregates and this enhances the emission in the solid state. Substituting carbazole derivatives on the diphenylfumaronitrile core enhances the emission quantum yield in the
solid state. Similarly, substituting phenylacetylene with electron donating and electron withdrawing groups at the para position of the phenylacetylene moiety tunes the emission color while increasing the emission quantum yield in the solid state.

The next important application is to make FONs using diphenylfumaronitrile based compounds. We reported diphenylfumaronitrile based FONs for the first time in the history of FONs and one of our compounds shows highest emission quantum yields among reported compounds to date. We suggest that these nanoparticles will be good candidates in nanosized optoelectronic devices.

1.4. References


CHAPTER 2. TETRACENO[2,3-b]THIOPHENES AND PENTACENES: HISTORY AND NATURE

2.1. Introduction

Two thirds of all known organic compounds have aromatic structures.¹ Aromatic nuclei are the basic building blocks of carbon nanotubes and acenes.² Acenes are polycyclic aromatic hydrocarbons (PAHs) which have attracted continuous attention as organic π-conjugated materials for optoelectronic applications.³ Benzene or benzol, was first discovered in 1825⁴, and benzothiophene are the smallest members of pentacene and tetraceno[2,3-b]thiophene families respectively. The small members of these families such as benzene, naphthalene, benzothiophene can be extracted from coal tar.

![Known structures of acenes (left) and acene[2,3-b]thiophenes (right).](image)

**Figure 2.1.** Known structures of acenes (left) and acene[2,3-b]thiophenes (right).
Higher homologs, however, can only be achieved from synthesis. A list of acenes which have synthesized to date is given in Figure 2.1.

Pentacenes to heptacenes and anthra[2,3-b]thiophenes to tetraceno[2,3-b]thiophenes are unstable under air (O₂) and light.⁵,⁶ Hence, special conditions must be employed if they are being used in devices. Among the acenes, pentacene (Chart 1.1), tetraceno[2,3-b]thiophene (Chart 1.1) and their derivatives have attracted the greatest attention as viable candidates for the charge transport layer in OFETs.⁷-¹¹ But the practicality of this has been limited by several factors such as insolubility, instability, and herringbone packing in the solid state.⁵

Minimization of above factors has been achieved by the functionalization of the acene backbone at different positions.⁵,¹²-¹⁵ These days much research is being carried out to functionalize the acene backbone under different criteria.

**2.2. General Synthetic Approaches to Pentacenes and Tetraceno[2,3-b]thiophenes**

Several syntheses have been reported to make angular condensed aromatic hydrocarbons but there is no good general method for making linear PAHs. Pentacene was first synthesized in 1930s starting from m-xylophenone¹⁶-¹⁸ and tetraceno[2,3-b]thiophene was synthesized in 2006 starting from 2-(trimethylsilylmethyl)-3-(trimethylammonium)thiophene iodide.⁶
Erich Clar, the originator of modern PAHs chemistry was born in Czech-Sudetenland. He moved to Scotland in 1946 and served as a professor in University of Glasgow from 1953 to 1972 and died in 1987. During his research career, he attempted to synthesize many possible acenes including pentacenes. In September 24th 1987, he was awarded the first “Polycyclic Aromatic Hydrocarbon Research Award” at the 11th International Symposium on PAHs because of the importance of PAHs especially pentacene in the various fields including optoelectronics.\textsuperscript{19,20}

\textbf{Figure 2.2.} A photograph of Erich Clar taken from the web site of University of Glasgow.\textsuperscript{21}

After that several approaches, including dehydrogenation, deoxygenation or both, have been introduced for the synthesis of pentacene analogs.

\textit{Scheme 2.1} First synthesis of pentacene
Clar attempted to synthesize pentacene starting from \textit{m}-xylophenone and obtained 4,6-dibenzoyl-1,3-dimethylbenzene. It was subsequently heated with copper to convert to dihydropentacene, and this was then passed through a copper catalyst at 300°-400°C to convert it into pentacene (Scheme 2.1).\textsuperscript{16-18} Today pentacenequinone is synthesized utilizing an efficient four-fold aldol condensation between 1,4-cyclohehenedione and 1,2-dibensaldehyde (Scheme 2.2).\textsuperscript{22} Another alternative path to pentacenequinone is the Cava reaction\textsuperscript{23,24} which converts \(\alpha,\alpha,\alpha',\alpha'\)-tetrabromo-o-xylenes to \(o\)-quinodimethanes. Then \(o\)-quinodimethane in situ react with terminal quinones producing internal quinones (Scheme 2.3).\textsuperscript{25}
Synthesis of tetraceno[2,3-b]thiophenes is a benchmark for the synthesis of pentacene derivatives because it is the first heteroatomic pentacene. Bao and co-workers introduced this heteroatomic pentacene starting from 2-(trimethylsilylmethyl)-3-(trimethylammonium)thiophene iodide and this was treated with 1,4-anthroquinone in the presence of tetrabutylammonium fluoride to produce tetraceno[2,3-b]thiophene-5,12-dione.6

2.3. Reactivity of Pentacene and Tetraceno[2,3-b]thiophene

Linear acenes possess many unsolved problems such as less persistent and more reactive with increase in the number of rings.19,20,26-32 Anthracene can be protonated and undergoes Diels-Alder reactions at the central ring.33 Tetracene and pentacene tend to react via 1,4-cycloadditions. While the aromaticity increases from the end to the center ring the size of the coefficient of HOMO increases simultaneously.33 For example, pentacene and anthracene participate in the Diels-Alder reaction with acetylene at the central ring and the activation energies (E_a) for these reactions are 24.0 and 29.4 Kcal/mol respectively. The E_a for reactions at the rings at the end of pentacene skeleton is 32.7 Kcal/mol.33 Computational calculations also have been carried out to prove the reactivity of acenes toward nucleophilic and electrophilic addition as well as the Diels-Alder reaction with molecular oxygen. Further, the reactivity of acenes with water and hydrochloric acid (HCl) increases from benzene to pentacene. The activation energy (E_a) for the addition of singlet oxygen to acenes is similar to that of the reaction with HCl.34,35 However, both singlet and triplet oxygen react with acenes and a most reactive central ring enables them to form endo-peroxides which block the conjugation, across the central ring under operating conditions.
2.4. Solid State Properties of PAHs

PAHs are planer or near planer molecules with minimal conformational flexibility. These molecules pack more tightly than other twisted molecules in the solid state.\textsuperscript{36,37} PAHs all pack according to the herringbone motif, in which the edge of the one molecule is oriented towards the face of the next molecule having minimal $\pi$-stacking in their crystal structure (Figure 2.3).\textsuperscript{38,39}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{herringbone_structure.png}
\caption{Herringbone structure of pentacene, adapted from reference 38.}
\end{figure}

Pentacene shows any number of polymorphs.\textsuperscript{39} This polymorphic nature complicates device studies since band structure calculations reveal considerable electronic differences among polymorphic forms.\textsuperscript{39,40} These issues have urged other detailed investigations of film formation during the vapor deposition of pentacene. Well prepared and high quality OFET’s made from pentacene and tetraceno[2,3-\textit{b}]thiophene show mobilities around 1.5 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} and 0.31 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} respectively.\textsuperscript{6,41} Hence, the packing motif of the acenes and the deposition method highly affects the charge transport mobility of a semiconductor. That will determine an OFETs’ performance.

Pentacene is a $p$-type semiconductor. Hence, the charge carriers are preferably holes. Under operation, pentacene is going from the neutral state to the radical cation and \textit{vise versa}. The
energy required for this reorganization is small. So, hole transport through pentacene film is
effective as compared to other hole carriers.

2.5. References

1854.
9482.


(21) http://www.chem.gla.ac.uk/dept/history/clar.htm.


CHAPTER 3. DESIGN AND SYNTHESIS OF FUNCTIONALIZED PENTACENES AND TETRACENO[2,3-\(b\)]THIOPHENES

3.1. Background

Due to their high reactivity especially at the central ring, herringbone packing in the solid state and low solubility, practical applications of acenes have been limited.\(^1,^2\) Introduction of different substituents to the aromatic skeleton is one method that potentially overcomes such problems.\(^3-^6\) This approach was first introduced in 1942\(^7,^8\) (Scheme 3.1) and exposed a way to synthesize many pentacene derivatives. Focus on optimizing orbital overlap in the solid state to achieve higher mobility can be managed by improving the order in films. This effort mainly depends on the substrate modification, rather than pentacene modification.

Scheme 3.1 First reported functionalized pentacene

![Scheme 3.1](attachment:image.png)

This type of modification paves the way to achieve higher solubility, improve stability, and suitable \(\pi\)-stacking.\(^9\) These factors simplify the purification and processing, increase the charge transport mobility and the device lifetime.\(^9,^10\)

Organic electronics represent a rapidly developing field because of their low-cost of production, mechanical flexibility and large area coverage. These can not be achieved easily with silicon technologies. Compared with inorganic candidates for optoelectronics, organic materials have unique advantages; for example: subtle modification of the physical skeleton improves the physical, mechanical, electronic properties, the thin film packing and the
mobility over the parent hydrocarbon.\textsuperscript{11,12} Anthony et. al. showed that the solid state packing of pentacene could be improved by substitution with various trialkylsilylethynyl functionalities at the 6 and 13 positions.\textsuperscript{9,13} Improved packing results in enhanced intermolecular orbital overlap which is a prerequisite for better OFET device performance.\textsuperscript{14-16} The relatively small short of the use of pentacene as an active material in OFETs, combined with its instability, is said to be the reason for the rather small pool of pentacene derivatives.

Bao et. al. recently showed that tetraceno[2,3-\textit{b}]thiophene, an asymmetric sulfur containing acene, exhibited field effect mobility as high as 0.47 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} with a decent on-off ratio ($>10^3$ at room temperature).\textsuperscript{17} This compound seems quite interesting given that its OFET device performance is comparable to that of pentacene. However, tetraceno[2,3-\textit{b}]thiophene also suffers from instability and decomposes within 60 minutes in solution. We anticipated that its properties and performance could be improved by suitable substitution.

Since the first appearance of functionalized pentacene in 1942, different types of functionalized pentacenes were introduced with various expectations (Chart 3.1).\textsuperscript{4,7,8,18,19} But no functionalized tetraceno[2,3-\textit{b}]thiophenes have been previously reported.
**Chart 3.1.** Selected functionalized pentacenes reported in the literature.
3.2. Chemical Modification of Pentacene and Tetraceno[2,3-b]thiophenes

Our goals were two fold: to understand the effect of substituents on the properties of the tetraceno[2,3-b]thiophenes and to compare properties with analogous pentacenes.

Chart 3.2. Target compounds$^{20}$ and parent hydrocarbons

Compounds 3.1-3.3 (Chart 3.2) are functionalized at the 6,11 and 5,12 positions with methoxy and alkylethynyl and phenylethynyl groups, respectively, while 3.4-3.6 (Chart 3.2) is substituted at the 5,14 and 6,13 positions with similar functionalities. Methoxy groups and ethynyl branches are expected to improve the solubility of target compounds. Furthermore, ethynyl spacer groups will push the bulky ends away from the aromatic skeleton and allow close contact among acene cores.

3.3. General Description for the Synthesis

Compounds 3.1-3.6 were synthesized from 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione (3.9), which was first methylated using dimethyl sulfate in the presence of anhydrous
potassium carbonate (Scheme 3.2).\textsuperscript{21-23} Double aldol condensation of the product (2,3-dihydro-9,10-dimethoxy-1,4-anthracenedione, \textbf{3.10}) with one equivalent of 2,3-thiophenedicarboxaldehyde or 1,2-benzenedicarbaldehyde, produced 5,11-dimethoxy-5,12-tetracenequinone[2,3-\textit{b}]thiophene (\textbf{3.11a}) and 5,14-dimethoxy-6,13-pentacenequinone (\textbf{3.12a}) respectively, which were finally converted into \textbf{3.1-3.6} following known synthetic procedures.\textsuperscript{23-25}

\textit{Scheme 3.2} Synthetic scheme for compounds \textbf{3.1-3.6}

Reagents and conditions. (a) anhydrous K$_2$CO$_3$, Me$_2$SO$_4$, acetone, dioxane, rt, 30 min, 55 °C, 12 hrs. (b) 5% KOH, tetrahydrofuran (THF), reflux, 12 hrs. (c) R$\equiv$C$\equiv$Li, rt, 12 hrs, then 10% HCl, SnCl$_2$, rt, 24 hrs.
Our initial attempt was to perform methylation after the aldol of condensation between 3.9 and either 2,3-thiophenedicarboxaldehyde or 1,2-benzenedicarboxaldehyde. But reactions of the aldol products (6,11-dihydroxy-5,12-tetracenequinone[2,3-b]thiophene, 3.13a and 7,12-dihydroxy-6,13-pentacenequinone, 3.13b) with dimethyl sulfate resulted in an inseparable isomeric mixture of the methylated products (3.11a, 3.11b and 3.12a, 3.12b) (Scheme 3.3). This is because 3.13a as well as 3.13b undergoes tautomerization under the reaction conditions employed (anhydrous K₂CO₃, Me₂SO₄). However, an optimized reaction condition (Scheme 3.2) was used to accomplish the methylation of 3.9 in the first step, which afforded 3.10 in a good yield. The aldol type condensation of 3.10 with 2,3-thiophenedicarboxaldehyde or 1,2-benzenedicarbaldehyde yielded only 3.11a and 3.12a respectively.

Scheme 3.3 Isomeric mixture of methylated products
Reagents and conditions. (a) 5% KOH, EtOH, reflux, 12 hrs. (b) Anhydrous K$_2$CO$_3$, Me$_2$SO$_4$, acetone, dioxane, 55 ºC, 36 hrs.

### 3.4. Photophysical Properties

The tetraceno[2,3-\textit{b}]thiophene derivatives (3.1-3.3) are deep blue while the new pentacene derivatives (3.4-3.6) are blue-green. Each is quite soluble in common organic solvents and thus easily processible. Figure 3.1 shows the absorption and fluorescence spectra of 3.1-3.6 recorded in dichloromethane. The $\pi$ - $\pi^*$ band is highly sensitive to the substituents and showed significant bathochromic shifts compared to that of the corresponding unfunctionalized acenes. For example, the absorption maxima of 3.1 (624 nm) and 3.4 (672 nm) are more than 90 nm red shifted than those of 3.7 (532 nm)$^{17}$ and 3.8 (578 nm),
respectively. This huge red-shift in absorption can be attributed to the $\pi$-conjugation extending ethynyl group as well as the electron donating methoxy group. The latter is known to cause a red shift of about 25 nm in the absorption of several compounds.\textsuperscript{23,26} Interestingly, the absorption maxima are also sensitive to the peripheral substituents attached to the ethynyl group. In the order of the $t$-butyl<tri-iso-propylsilyl<phenyl groups, the compounds in both series showed an increment of about 15 nm in absorption maxima.

**Figure 3.1.** Normalized absorption and Fluorescence spectra of 3.1-3.6 recorded in dichloromethane.

Absorption maxima ($A_{\text{max}}$), extinction coefficients ($\varepsilon$), emission maxima ($\lambda_{\text{max}}$), and fluorescence quantum yields ($\Phi_F$) of 3.1-3.6 recorded in dichloromethane are presented in Table 3.1.
Table 3.1 Photophysical properties of 3.1-3.6 recorded in dichloromethane

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A_{\text{max}}$ (nm)/$\varepsilon$(M$^{-1}$cm$^{-1}$)</th>
<th>$A_{\text{max}}$ (nm)$^a$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\Phi_F$</th>
<th>$E_{1/2}$ (V)$^b$</th>
<th>Optical EG (eV)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>624 (10100)</td>
<td>633</td>
<td>634</td>
<td>0.08</td>
<td>0.69</td>
<td>1.86</td>
</tr>
<tr>
<td>3.2</td>
<td>639 (13300)</td>
<td>646</td>
<td>648</td>
<td>0.09</td>
<td>0.71</td>
<td>1.83</td>
</tr>
<tr>
<td>3.3</td>
<td>656 (13400)</td>
<td>674</td>
<td>672</td>
<td>0.11</td>
<td>0.69</td>
<td>1.72</td>
</tr>
<tr>
<td>3.4</td>
<td>672 (10300)</td>
<td>679</td>
<td>682</td>
<td>0.09</td>
<td>0.63</td>
<td>1.70</td>
</tr>
<tr>
<td>3.5</td>
<td>686 (14200)</td>
<td>691</td>
<td>712</td>
<td>0.12</td>
<td>0.70</td>
<td>1.69</td>
</tr>
<tr>
<td>3.6</td>
<td>704 (13500)</td>
<td>725</td>
<td>718</td>
<td>0.11</td>
<td>0.70</td>
<td>1.58</td>
</tr>
</tbody>
</table>

$^a$Recorded in thin film. $^b$E$_{1/2}$ values against the ferrocene/ferrocenium redox system (-4.8 V). $^c$Performed in a 0.1 M solution of Bu$_4$NPF$_6$ in DCM using a Pt electrode, and a Ag/AgCl reference electrode. $^c$Optical band gap (E$_G$) determined from the onset of the thin film absorption peak.

The tetraceno[2,3-\(b\)]thiophenes especially show very small Stokes shifts (~9-16 nm).

Compounds 3.1-3.3 are weakly fluorescent ($\Phi_F \sim 10\%$), similar to 3.8 and other linear hydrocarbon acenes. The $\Phi_F$ values of 3.1-3.6 were found to be similar (~ 10%) in various solvents such as dichloromethane, tetrahydrofuran, and toluene (Table 3.2).
Table 3.2 Fluorescent quantum yields of 3.1-3.6 in different solvents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Φf</th>
<th>Toluene</th>
<th>DCM</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>0.14</td>
<td>0.08</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>0.10</td>
<td>0.11</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>0.10</td>
<td>0.09</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.13</td>
<td>0.12</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>0.11</td>
<td>0.11</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

The absorptions of 3.1-3.6 were also recorded in thin films, which were made by casting 2-3 drops of concentrated dichloromethane solutions of the compounds on a quartz plates and evaporating the solvent. The thin film absorption (Figure 3.2) of 3.1-3.6 were expectedly red shifted and broadened from those recorded in solution, apparently due to the strong electronic interactions in the film. The thin films of these compounds were stable under laboratory conditions, at least for three weeks.

Figure 3.2. Thin-film absorption spectra of 3.1-3.6 on quartz.

3.5. Electrochemical Properties

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of 3.1-3.6. The CV graphs were obtained with a scan rate of 100 mV/s and with the compounds in
0.1 M tetrabutylammonium phosphorushexafluoride (Bu₄NPF₆) in anhydrous dichloromethane. The oxidation potentials of tetraceno[2,3-b]thiophenes (3.1-3.3, E₁/₂ ~ 0.70 V) were found to be similar to that of pentacene (E₁/₂ ~ 0.70 V) and its derivatives (3.5 and 3.6), indicating that the electrochemical HOMO levels of these compounds are similar (Table 3.1 and Figure 3.3). Interestingly 3.4 showed a lower E₁/₂ value (0.63 V) and also turned out to be the most unstable to light (vide infra). The optical band gaps estimated either in solution or the solid states are higher for 3.1-3.3 (1.86 eV – 1.72 eV in solid) than for 3.4-3.6 (1.70 eV – 1.58 eV in solid). This indicates that the LUMO levels of tetraceno[2,3-b]thiophenes are higher than those of pentacenes, since their HOMO levels are similar. Furthermore, there is also a distinct trend of decreasing optical band gap going from 3.1 to 3.3 or from 3.4 to 3.6. Thus, the LUMO levels of both series are similarly and considerably affected by the substitution pattern.

Figure 3.3. Cyclic voltammograms of 3.1-3.6.
The photooxidative stability of 3.1-3.6 was studied by monitoring changes in the absorption spectrum of air saturated solutions under ambient light (Figure 3.4). Compounds 3.5 and 3.6 were relatively stable; while compounds with the tert-butylethynyl function (3.1 and 3.4) were quite unstable. The long wavelength absorptions of 3.1 and 3.4 decayed to almost zero within 5 and 10 hrs, respectively. On the other hand, there was comparatively little change (less than 20%) in the absorption of 3.5 and 3.6 even after 10 hrs of ambient light illumination. The corresponding tetraceno[2,3-b]thiophene derivatives (3.2 and 3.3) showed intermediate stability with their absorption diminishing almost 80% in 10 hrs. Substitution seems to increase the photooxidative stability of these compounds, especially in the pentacene series, because 3.7 and 3.8 are not stable and disappear in less than one hour under ambient light.17

![Figure 3.4](image)

**Figure 3.4.** Photo-oxidative stability of 3.1-3.6 monitored through decrease in their absorption in toluene solution upon exposure to ambient light.

It is noted that 3.1-3.6 are more photostable than their unsubstituted analogs, i.e., 3.7 and 3.8. The π-electrons being delocalized through the ethynyl group may be the reason for the higher photostability of 3.1-3.6.
The formation of endoperoxide across the most reactive central ring is the reason for the light instability of linear acenes. The enhanced photo-stability of 3.2, 3.3, 3.5, and 3.6 compared to that of 3.7 and 3.8 may also be related to the bulkiness of the substituent at the central ring and the presence of the methoxy group, which may hinder the approach of O₂.

3.6. Preparation and Characterization

3.6.1. General

All chemicals and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. Reactions of moisture and air sensitive compounds were carried out in a dry-box. ¹H and ¹³C NMR spectra were recorded using a Bruker 300MHz spectrometer with tetramethylsilane (TMS) as the internal standard and chemical shifts relative to TMS at 0.0 ppm are reported in parts per million (PPM) for ¹H NMR on the δ scale. UV-visible absorption spectra were recorded using a Shimadzu UV-vis spectrometer. Fluorescence spectra were recorded using a Spex-Fluorolog fluorimeter. Thin layer chromatography was performed on MERCK Silica Gel 60 thick layer plates. Column chromatography was performed on Sorbent Technologies brand silica gel (40-63 um, Standard grade). High Resolution Mass analyses were performed at University of Illinois SCS Mass Spectrometry Laboratory.

3.6.2. Synthesis

2,3-Dihydro-9,10-dimethoxy-1,4-anthracenedione (3.10). Compound 3.10 was prepared by a modified methylation method. Compound 3.9 (2.5 g, 10.3 mmol) was added to a 500 ml oven dried round-bottom flask equipped with a stir bar and acetone (200 ml) and dioxane
(100 ml) added. During stirring dimethyl sulfate (28 ml, 169 mmol) and anhydrous potassium carbonate (15 g, 118.2 mmol) were also added. The entire mixture was stirred under argon at room temperature for about 30 minutes and then refluxed for 12 hours. The optimal formation of 3.10 was monitored using GC-MS. The reaction mixture was allowed to cool and filtered. The filtrate was concentrated and was subjected to next step without further purification.

6,11-Dimethoxy-5,12-tetracenequinone|2,3-b|thiophene (3.11a). Thiophene-2,3-carboxaldehyde (1 eq. of 3.10 as estimated from the GC/MS profile) and THF (100 ml) were added to the concentrated solution of 3.10 and the mixture stirred several minutes until all solids dissolved. Ethanolic KOH (5%, 5.75 ml) was then added. The mixture was refluxed for overnight, following which it was cooled and poured into ice cold water bath. The product precipitated, was filtered and dried. The brown crude solid product was purified by column chromatography using dichloromethane as solvent. Evaporation of the solvent yielded pure 3.11a in the form of orange yellow solid (yield 20 %). ¹H NMR (300 MHz, CDCl₃) δ = 8.84 (s, 1H), 8.75 (s, 1H), 8.45 (m, 2H), 7.77 (m, 3H), 7.60 (d, 1H), 4.18 (s, 6H); ¹³C NMR (300 MHz, CDCl₃) δ = 183.06, 182.71, 156.00, 155.96, 144.53, 143.08, 132.88, 132.03, 131.45, 130.71, 129.91, 125.02, 124.83, 122.79, 122.04, 121.30, 121.27, 63.20; HRMS m/z [M]+ calcd for C₂₂H₁₄O₄S 374.0613, found 374.0614.

5,14-Dimethoxy-6,13-pentacenequinone (3.12a). Compound 3.10 was caused to react with 1,2-bezenedicarbaldehyde to obtain 3.12a following the same procedure employed for 3.11a. Pure 3.12a was isolated as yellow solid (yield 21 %). ¹H NMR (300 MHz, CDCl₃) δ = 8.84 (s,
3H, 8.44 (m, 2H), 8.12 (m, 2H), 7.79 (m, 2H), 7.70 (m, 2H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ = 182.98, 156.04, 135.16, 132.37, 131.42, 129.93, 129.91, 129.06, 128.74, 124.83, 121.68, 63.28; HRMS $m/z$ [M]$^+$ calcd for C$_{24}$H$_{16}$O$_4$ 368.1048, found 368.1049.

**General procedure for the synthesis of 3.1-3.6.** Compounds 3.1-3.6 were synthesized starting from either 3.11a or 3.12a following a general method. The synthesis of 3.1 is detailed as an example. An oven dried 100 ml round-bottom flask equipped with a stir bar was clamped in a dry box. tert-Butylacetylene (0.13 ml, 1.06 mmol) was added to the flask and dissolved in dry dichloromethane (10 ml). To this stirring solution was added drop wise n-BuLi (0.44 ml of 2.5 M solution in hexane). The mixture was stirred for about 30 minutes at room temperature. In a separate flask a solution of 3.11a (0.1 gm, 0.27 mmol) in dry dichloromethane (5 ml) was prepared, and was slowly added to the lithiated tert-butylacetylene solution. The whole mixture was allowed to stir at room temperature overnight. Then it was taken out of the dry box and was quenched with 10% HCl (1 ml). To this was added SnCl$_2$ in 10% HCl (1 ml) and the mixture was stirred at room temperature under dark and argon for 24 hours. The progress of the reaction was monitored by thin layer chromatography (TLC). After the reaction was complete, the solution was dried with anhydrous Na$_2$SO$_4$ and the filtrate evaporated to obtain crude 3.1. The product was purified in dark by column chromatography over silica gel using a mixture of hexane and dichloromethane (1:1) as the eluent.

**5,12-Bis(tert-butylethynyl)-6,11-dimethoxytetraceno[2,3-b]thiophene (3.1).** Yield: 34 %. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 9.31 (s, 1H), 9.26 (s, 1H), 8.30 (m, 2H), 7.53 (d, 1H), 7.42
5,12-Bis(tri-iso-propylsilylethynyl)-6,11-dimethoxytetraceno[2,3-b]thiophene (3.2). It was prepared by the reaction between tri-iso-propylsilylacetylene and 3.11a and purified by column using a mixture of hexane and dichloromethane (2:3) as the eluent. Yield: 41%; $^1$H NMR (300 MHz, CDCl3) δ = 9.53 (s, 1H), 9.47 (s, 1H), 8.32 (m, 2H), 7.54 (d, 1H), 7.45 (m, 2H), 7.38 (d, 1H), 4.10 (s, 6H), 1.33 (s, 42H); $^{13}$C NMR (300 MHz, CDCl3) δ = 149.55, 140.40, 140.02, 131.68, 130.19, 125.77, 125.72, 125.16, 125.07, 124.76, 124.68, 123.68, 123.09, 121.89, 120.48, 115.62, 114.30, 107.34, 106.63, 106.33, 94.73, 63.78, 18.94, 18.44, 11.61, 11.02; HRMS m/z [M + H]$^+$ calcd for C$_{44}$H$_{57}$O$_2$Si$_2$S 705.3617, found 705.3621.

5,12-Bis(phenylethynyl)-6,11-dimethoxytetraceno[2,3-b]thiophene (3.3) was prepared by the reaction between phenylacetylene and 3.11a and purified by column using a mixture of hexane and dichloromethane (9:1) as the eluent. Yield : 35%; $^1$H NMR (300 MHz, CDCl3) δ = 9.59 (s, 1H), 9.45 (s, 1H), 8.41 (m, 2H), 7.85 (m, 4H), 7.91 (d, 1H), 7.72 (d, 1H), 7.62-7.45 (m, 8H), 4.21 (s, 6H); $^{13}$C NMR (300 MHz, CDCl3) δ = 149.05, 141.00, 140.05, 131.54, 131.50, 130.99, 130.88, 130.33, 128.76, 128.64, 125.98, 125.93, 125.39, 125.30, 124.78, 124.69, 124.49, 124.41, 123.88, 123.03, 121.39, 120.07, 115.32, 114.04, 103.41, 103.02, 91.48, 63.73 ; HRMS m/z [M]$^+$ calcd for C$_{38}$H$_{24}$O$_2$S 544.1497, found 544.1509.
6,13-Bis(tert-butylethynyl)-5,14-dimethoxypentacene (3.4) was prepared by the reaction of tert-butylacetylene and 3.12a and purified by column chromatography using a mixture of hexane and dichloromethane (1:1) as the eluent. Yield: 40%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 9.40 (s, 2H), 8.26 (m, 2H), 7.95 (m, 2H), 7.39 (m, 4H), 4.10 (s, 6H), 1.66 (s, 18H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ = 132.19, 131.37, 128.76, 126.47, 125.73, 125.55, 124.91, 123.08, 115.11, 113.00, 80.84, 63.66, 31.34, 29.42; HRMS m/z [M]$^+$ calcd for C$_{36}$H$_{34}$O$_2$ 498.2559, found 498.2553.

6,13-Bis(tri-iso-propylsilylethynyl)-5,14-dimethoxypentacene (3.5) was prepared by the reaction between tri-iso-propylsilylacetylene and 3.12a and purified by column using a mixture of hexane and dichloromethane (2:3) as the eluent. Yield: 47%; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 9.62 (s, 2H), 8.30 (m, 2H), 7.99 (m, 2H), 7.43 (m, 4H), 4.12 (s, 6H), 1.39 (s, 42H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ = 149.58, 132.49, 131.81, 128.56, 126.83, 126.11, 125.83, 125.30, 125.18, 123.15, 115.38, 107.61, 107.38, 63.73, 18.92, 12.31; HRMS m/z [M]$^+$ calcd for C$_{46}$H$_{58}$O$_2$Si$_2$ 698.3975, found 698.3984.

6,13-Bis(benzylethynyl)-5,14-dimethoxypentacene (3.6) was prepared by the reaction between phenylacetylene and 3.12a and purified by column using a mixture of hexane and dichloromethane (3:7) as the eluent. Yield: 38%; $^1$H NMR (300 MHz CDCl$_3$). $\delta$ = 9.56 (s, 2H), 8.35 (m, 2H), 8.10 (m, 2H), 7.92 (m, 4H), 7.57-7.28 (m, 10H), 4.23 (s, 6H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ = 149.59, 132.52, 131.54, 131.12, 128.79, 128.68, 128.49, 126.42, 126.20, 126.03, 125.80, 125.40, 124.55, 123.07, 115.06, 104.16, 91.92, 63.67; HRMS m/z [M]$^+$ calcd for C$_{40}$H$_{26}$O$_2$ 538.1933, found 538.1931.
3.7. Conclusions.

Tetraceno[2,3-b]thiophenes (3.1-3.3) and pentacenes (3.4-3.6) substituted with the methoxy, alkylethynyl and phenylethynyl groups were synthesized. The absorption and emission spectra of 3.1-3.3 ($A_{\text{max}} = 624 – 656 \text{ nm}, \lambda_{\text{max}} = 634 – 672 \text{ nm}, \Phi_F \sim 10\%$) and 3.4-3.6 ($A_{\text{max}} = 672 – 704 \text{ nm}, \lambda_{\text{max}} = 682 – 718 \text{ nm}, \Phi_F \sim 10\%$) were found to be systematically red shifted by the substitution in the order of the tert-butylethynyl<tri-iso-propylsilylethynyl<phenylethynyl groups. The oxidation potentials were similar ($E_{1/2} \sim 0.70 \text{ V}$), except for 3.4, which showed lower oxidation potential ($E_{1/2} \sim 0.63 \text{ V}$). Compounds 3.1-3.6 are quite soluble in common organic solvents and more stable than the unfunctionalized compounds. The derivatives containing the tert-butylethynyl functionality were relatively more unstable than the rest.

3.8. References


(26) The magnitude of this shift agrees with the empirical rules for absorption spectroscopy, each methoxy group inducing a red shift of ~25 nm.
CHAPTER 4. ORGANIC NANOPARTICLES: BRIEF HISTORY AND INSIDE

4.1. Introduction

If at least two dimensions of a particle are less than few hundred nanometers, it can be called a nanoparticle.1 (Though this is the generally accepted definition for a nanoparticle it can change from application to application). Though nanoparticles are considered an introduction of modern science, their history traces to 9th century Mesopotamia for they were first observed as the glittering effect of clay pots’ surface.2 The study of organic nanoparticles does not have a lengthy history and examples for organic nanoparticles are not common. But around 15 million organic compounds have been introduced by chemical laboratories so far and every year around one million more accumulate.3 Nanoparticles have numerous applications. They play an important role in the formulation of pigments and in the production of catalysts. They also serve as a transport media in medicine inside the body and can be used as an emissive material in optoelectronics such as nanosized OLEDs.4-7 Studying the scientific literature reveals that much has been reported about inorganic nanoparticles and their formation but little is known about the particles formed in organic systems. Organic nanoparticles appear in many forms. Some are naturally abundant and others are synthetically generated (Figure 4.1).
Several methods have been reported for the preparation of nanoparticles (Figure 4.2). In our research project, the reprecipitation method $^{4,8-11}$ was used because this is the most suitable and economical method for the preparation of nanoparticles given that the preparation of low cost materials is one of our targets.

**Figure 4.1.** Classification of organic nanoparticles.

**Figure 4.2.** Methods for the preparation of nanoparticles.
Reprecipitation methods are of two types: 1) change in solvent composition, 2) change in temperature or pressure. For many experiments, the solvent composition is changed for nanoparticle preparation because its simplest under laboratory conditions.

4.1.1. Reprecipitation Method

In the reprecipitation method the compound containing the chromophore is dissolved in a superior organic solvent and then an inferior solvent is added vigorously into the solution (Figure 4.3). The free molecules in the solution begin to aggregate following the addition of a certain quantity of the inferior solvent. Initially, spherically shaped particles are formed as the superior solvent is replaced by inferior solvent and dispersed in bulk inferior solvent. The reason for this spherical shape is because of the minimization of interfacial energies between chromophore compound and the inferior solvent. The reprecipitation method is also called the *Ouzo Effect*. The Ouzo effect enables one to create a dispersion of small droplets in a surrounding liquid phase without the use of surfactants or dispersing agents.

![Phase diagram for nanoparticle formation.](image)

**Figure 4.3.** Phase diagram for nanoparticle formation.
As the inferior solvent fraction increases, the molecules aggregate into larger structures. These may be spherical or non-spherical structures because of the competition between anisotropic growth and spherical aggregation with time (Figure 4.4).

**Figure 4.4.** FE-SEM images of DHBIA nanoparticles in the time course of (a) 15 min, (b) 30 min, and (c) 1 h.\textsuperscript{11}

### 4.1.2. Milling Process

Milling a coarse suspension is a simple and well understood process. Particle size depends on the impact and shear forces of the milling process. The milling process has several disadvantages such as the long processing time, discoloration, fractionation, and the generation of heat. This limits its usefulness.
4.1.3. Chemical Reactions

Nanoparticles can also be prepared under special reaction conditions. Surface controlling agents must be added during the formation of a precipitate for this to work. These interfere with the nucleation and particle growing to avoid agglomeration and to control particle size.

4.2. Fluorescent Organic Nanoparticles (FONs)

FONs are a special subset of organic nanoparticles. They hold higher potential for application because of the variability and flexibility in material synthesis and nanoparticle preparation.

Figure 4.5. Emission spectra of perylene microcrystals with different sizes. Taken from reference 15.
Figure 4.6. Structures of compounds used for FONs.\textsuperscript{8-11,17}

Systematic research in this field was initiated by a Japanese scientist Hachiro Nakanishi in 90’s.\textsuperscript{14-16} He used perylene and phthalocyanine in demonstrating the preparation procedures for FON’s and such particles exhibited size dependent fluorescent properties (Figure 4.5).\textsuperscript{15}

Subsequently different types of organic compounds have been introduced to
make FONs. Figure 4.6 shows representative molecules of which FONs with exciting photophysical properties are made.

FONs have attracted great research interest in many fields especially in organic electronics because of their special properties. These properties lie between the properties of bulk materials and those of molecule compounds. The electronic properties of organic nanoparticles basically differ from inorganic nanoparticles because of a weak van der Waals type or hydrogen bonding which holds the assembly together.

The striking feature of these FON’s is Aggregation Induced Enhanced Emission (AIEE). This feature is remarkable because in it intermolecular vibronic interactions reduce the radiative deactivation processes leading to the quenching of emission. This unusual fluorescence found in these nanoparticles is correlated with aggregation morphology and clearly explained by molecular exciton model.\textsuperscript{18-21} Aggregation strongly depends on the molecular geometry.

\textbf{4.2.1. Molecular Exciton Model}

When two molecules come to a close enough distance under photon flux, their transitions dipole moments will interact. This is called “Excitonic Coupling”. This coupling can be explained on the basis of Figure 4.7.

Due to the interaction of the dipole moments, the energy of individual molecules (E) splits into two new states such as $E_1$ and $E_2$. If the molecules are parallel to each other they start to repel and acquire a higher energy state. This causes stronger absorption and the net result is a blue shifted absorption with respect to the isolated chromophore. This parallel aggregation is
named as $H$-aggregation. Similarly, head-to-tail aggregation causes a red shifted absorption. and head-to-tail is named $J$-aggregation.$^7$

**Figure 4.7.** Band splitting of parallel vs anti-parallel aggregation.

The nature of the molecules such as the substituents, their twisted nature and polarity, and other factors play important roles in aggregation morphology. Changes of the fluorescence also have a direct correlation to the aggregation morphology. $H$-aggregation where molecules are assembled parallel to each other with strong intermolecular interaction induces a nonradiative deactivation process that quenches the fluorescence while $J$-aggregation enhances the fluorescence due to a lack of strong intermolecular interactions. The relationship between $J$-aggregation and enhanced emission has been observed in the
pseudoisocyanine dye shown (Figure 4.8) where it was explained by the twisted nature and relatively bulky groups block that force the face-to-face intermolecular interactions.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{pseudoisocyanine_dye.png}
\caption{Structure of pseudoisocyanine dye.}
\end{figure}

4.3. References


CHAPTER 5: FUMARONITRILE BASED FLUORESCENT ORGANIC NANOPARTICLES

5.1. Introduction

The objective of this part of the project is two fold: i. preparation of highly fluorescent organic nanoparticles ii. tuning the emission of the organic nanoparticle.

Diphenylfumaronitrile was utilized as the core because, in the *trans* form, it consists of anti-parallel dipoles (Figure 5.1). Thus, concentration related fluorescence quenching in the solid state should be considerably reduced due to dipole-dipole interactions.

Different groups were substituted at the *para* position of diphenylfumaronitrile core to alter the photophysical properties of our target compounds.

![Figure 5.1. Structure of diphenylfumaronitrile (S-substituent group).](image)

5.2. Highly Fluorescent Organic Nanoparticles

5.2.1. General Description of the Synthesis

Carbazole derivatives show high emission quantum yields in the solid state, and the compounds can easily be modified at the 3- and 6- positions to tune the optical properties.\(^1,2\)

Carbazole (5.6) was converted into 3,6-di-\textit{tert}-butyl-9\(H\)-carbazole (5.7) and
Scheme 5.1 Synthetic scheme for compounds 5.1-5.2

Reagents and conditions. (a) $t$-BuCl, ZnCl$_2$, nitromethane, 40-50 °C, 5 h (b) I$_2$ (1 equiv) in diethyl ether, NaOCH$_3$ (2.1 equiv), 30 min at -78 °C, 4 h at 0 °C, 3% aq HCl (c) Pd(OAc)$_2$ (3%), P($t$-Bu)$_3$ (9%), Cs$_2$CO$_3$ (4 equiv), 30 h at 110 °C.
4-bromophenylacetonitrile (5.8) was converted into bis(4-bromophenyl)fumaronitrile (5.9) in good yield following literature methods (Scheme 5.1). Following a modified literature procedure 1,2-dicyano-trans-1,2-bis-4-(carbazolyl)phenylethylene (5.1) and 1,2-dicyano-trans-1,2-bis-4-(3,6-di-t-butylcarbazolyl)phenylethylene (5.2) were synthesized (Scheme 5.1).

### 5.2.2. Photophysical Properties in Solid State and Solution

While compound 5.1 is red, compound 5.2 is yellow in the solid state. Both 5.1 and 5.2 are stable and can be dissolved in common organic solvents such as carbon tetrachloride (CCl₄), dichloromethane (DCM), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF).

A change in solvent from nonpolar CCl₄ to polar DMF causes a negative solvatochromic shift in the π-π* absorption band from 450 nm to 415 nm for 5.1 and from 470 nm to 440 nm for 5.2, Figure 5.2. It is known that solvatochromism depends on molecular structure and the nature of the chromophore, as well as the solvent.¹

![Figure 5.2](image_url)

**Figure 5.2.** Normalized absorption spectra of 5.1 and 5.2 in (a) carbon tetrachloride, (b) dichloromethane, (c) tetrahydrofuran, and (d) N,N-dimethylformamide.
Reichardt’s pyridinium N-phenoxide betaine dye and N-(o-phosphoniobenzylidene)-4-aminophenolate betaine dyes (see Appendix A) have been reported to show negative solvatochromic behavior. Generally in order for this to be observed, the dipole moment of the molecule in the ground state ($\mu_g$) is expected to be higher than that of the excited state ($\mu_e$). Consequently, the $\mu_g$ of 5.1 and 5.2 should be larger than $\mu_e$, because negative solvatochromic behavior was observed, Figure 5.2.

Interestingly, the emission spectra of 5.1 and 5.2 show both positive and negative solvatochromism with increasing solvent polarity, Figure 5.3. For example, the emission spectrum of 5.2 was observed with a peak around 580 nm in CCl$_4$. A broad and red shifted emission was observed with 5.2 with a peak around 680 nm in DCM. The emission spectrum of 5.2 was blue shifted to 520 nm in DMF.

**Figure 5.3.** Normalized fluorescence spectra of 5.1 and 5.2 recorded in (a) carbon tetrachloride, (b) dichloromethane, (c) tetrahydrofuran, and (d) N,N-dimethylformamide.

Although inverted solvatochromic behavior of the absorption of 4’-hydroxy-1-methylstilbazolium betaine (see Appendix A) has been reported no such inverted solvatochromism has been observed in fluorescence spectra. A solvent-induced change in
the electronic ground state structure results in various solvents. Accompanying structural changes of 5.1 and 5.2 in the excited states is intramolecular electron transfer between the carbazole chromophore and diphenylfumaronitrile core to give 5.1 and 5.2 as a charge separated state. The excitation spectra of 5.1 and 5.2 obtained at 600 nm show that the emission comes from different choromophores in CCl₄, DCM, and DMF (Figure 5.4).

![Excitation spectra of 5.1 and 5.2 recorded in (a) carbon tetrachloride, (b) dichloromethane, and (c) N,N-dimethylformamide.](image)

**Figure 5.4.** Excitation spectra of 5.1 and 5.2 recorded in (a) carbon tetrachloride, (b) dichloromethane, and (c) N,N-dimethylformamide.

The excitation spectra of 5.1 and 5.2 in CCl₄ are similar to their UV absorption spectra, indicating that the emission mainly comes from 5.1 and 5.2 in the singlet excited state (S₁). New absorption bands appear between 300 nm and 450 nm when 5.1 and 5.2 are dissolved in DCM. The 350 nm band became strong and the 450 nm band became weak when 5.1 and 5.2 were dissolved in DMF.

We submit that intramolecular electron transfer occurs in 5.1 and 5.2 and that this is facilitated by the polarity of the solvents. The quantum yields of emission of 5.1 and 5.2
decrease with increasing solvent polarity. In the highly polar DMF, the charge separation in **5.1** and **5.2** is almost complete. Therefore, the emission yield becomes very low.

**Table 5.1** Photophysical Properties of **5.1** and **5.2**.

<table>
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<tr>
<th>Compound</th>
<th>$A_{\text{max}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\Phi_{\text{em}}$</th>
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<tr>
<td>CCl₄</td>
<td>445</td>
<td>530</td>
<td>0.37</td>
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<tr>
<td>DCM</td>
<td>435</td>
<td>618</td>
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<td>THF</td>
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<td>608</td>
<td>0.02</td>
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<tr>
<td>DMF</td>
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<td>520</td>
<td>&lt; 0.01</td>
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<tr>
<td>Thin film</td>
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<td>608</td>
<td>0.72</td>
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<tr>
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<td>590</td>
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<th>$\lambda_{\text{max}}$</th>
<th>$\Phi_{\text{em}}$</th>
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<tbody>
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<td></td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
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<tr>
<td>DCM</td>
<td>457</td>
<td>670</td>
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<tr>
<td>THF</td>
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<td>638</td>
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<tr>
<td>DMF</td>
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<td>Thin film</td>
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<td>Nanoparticles</td>
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<td>0.81</td>
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</table>

The solution emission quantum yield was calculated using riboflavin (0.30 in ethanol) as a reference. Solid state quantum yields were measured using an integrating sphere.
The markedly enhanced solid state emission quantum yields of 5.1 and 5.2 were measured on a thin film using an integrating sphere, Table 5.1. Figure 5.5 shows the solid state emission of 5.1 and 5.2 under 366 nm UV light.

![Figure 5.5. Solid state emission of 5.1 and 5.2 under 366 nm UV light.](image)

Park and co-workers observed similar behavior for 1-cyano-trans-1,2-bis-(4’-methylbiphenyl)-ethylene (CN-MBE). In the case of CN-MBE, the polar, bulky cyano group minimizes parallel face to face interaction, which induces the \( H \)-type aggregation, and this minimizes the fluorescence in the solid state. Since \( J \)-type aggregation enhances the emission, 8,9 5.1 and 5.2 may form \( J \)-type aggregates in the solid state. 8,9

### 5.2.3. Preparation of Nanoparticles

Distilled water was rapidly injected into a THF solution of 5.1 or 5.2 while swirling. Nanoparticles began to form as the water fraction increases. Nanoparticles can be clearly observed under the light from the 366 nm UV lamp. Concentrations of chromophores in final solutions were \( 1 \times 10^{-5} \) molL\(^{-1} \).
5.2.4. SEM Images of Nanoparticles.

Scanning Electron Microscopy (SEM) images were recorded on a Hitachi S-2700 electron microscope at 15 kV. Samples for SEM were prepared by placing few drops of the FON (Fluorescent Organic Nanoparticle) solution onto a glass cover slip placed on an aluminum stub. The samples were allowed to dry in an oven (45°C) before viewing under the electron microscope. To enhance the contrast and quality of the SEM images, the prepared samples were sputter-coated with gold/palladium. Quartz PCI 7 imaging software was utilized to process the images and determine the size of the particles.

5.2.5. Properties of Nanoparticles

Nanoparticles of 5.1 and 5.2 were prepared following a literature method. The red shifted absorption of 5.1 and 5.2 in water/THF (9:1, with nanoparticles) compared to that in

![Figure 5.6](image)

**Figure 5.6.** Compound 5.1 and 5.2 with nanoparticles; water : THF (9 : 1), without nanoparticles; water : THF (1 :9).
water/THF (1:9, without nanoparticles) indicates J-type aggregation occurs with an increasing amount of water (Figure 5.6). The nanoparticle solutions were transparent and stable. No precipitation was observed on keeping 5.1 and 5.2 at room temperature for several months.

Figure 5.7. Scanning Electron Microscopy (SEM) images, (a), Fluorescence microscope images, (b), and Picture of nanoparticle solutions, (c) of 5.1 and 5.2.
The diameters of nanoparticles from 5.1 and 5.2 were in the range of 50-150 nm as determined by Scanning Electron Microscopy (SEM), Figure 5.7 (a). Fluorescence microscope images prove that the emission comes from the nanoparticles, Figure 5.7 (b). Strong emissions in a water/THF (9:1) mixture can be clearly seen, Figure 5.7 (c), with quantum yields of emission higher than those reported for CN-MBE (0.69)\textsuperscript{1} FONs. However, no clear particle size change was observed on making the particles in solvents differing in water/THF ratio.

### 5.2.6. Preparation and Characterization

**3,6-Di-tert-butyl-9H-carbazole (5.7) and bis(4-bromophenyl)fumaronitrile (5.9).**

Compounds 5.7 and 5.9 were synthesized according to literature methods.

**1,2-Dicyano-trans-1,2-bis-(carbazolyl)phenylethylene (5.1).**

Compound 5.9 (300 mg, 0.77 mmol) and carbazole (283 mg, 1.69 mmol) were mixed with dry toluene (80 ml) in a round bottom flask containing a stir bar. Then Pd(OAc)\textsubscript{2} (3%), P(t-Bu)\textsubscript{3} 7% and Cs\textsubscript{2}CO\textsubscript{3} (990 mg, 3.04 mmol) were added and the mixture stirred under argon at 110°C for \(\approx 30\) hours. The reaction mixture was cooled to room temperature and filtered using gravity filtration. The solid mixture on the filter paper was washed with small amount of toluene and dichloromethane (The small quantity of 5.1 that dissolves on this filtration is unavoidable.). The solid mixture was dissolved in tetrahydrofuran and the filtrate collected. Removal of solvent under vacuum gives red powder (yield 19 %). \(\textsuperscript{1}H\) NMR (300 MHz, CDCl\textsubscript{3}) \(\delta = 8.17\) (m, 8H), 7.87 (d, 4H), 7.57 (d, 4H), 7.47 (t, 4H), 7.34 (t, 4H); \(\textsuperscript{13}C\) NMR
1,2-Dicyano-trans-1,2-bis-4(3,6-di-t-butylcarbazolyl)phenylethylene (5.2).

Compound 5.9 (300 mg, 0.77 mmol) and 3,6-di-t-butylcarbazole (473 mg, 1.69 mmol) were mixed with dry toluene (80 ml) in a round bottom flask containing a stir bar. Then, Pd(OAc)$_2$ (3%), P(t-Bu)$_3$ 7% and Cs$_2$CO$_3$ (990 mg, 3.04 mmol) were added and the mixture stirred under argon at 110°C for around 30 hours. The reaction mixture was cooled to room temperature and toluene was removed completely under vacuum. The solid mixture was completely dissolved in tetrahydrofuran and the unreacted Cs$_2$CO$_3$ removed under gravity filtration. While swirling, an excess amount of water was rapidly added to the tetrahydrofuran solution until yellow color colloid was formed. This colloid was filtered and dried under vacuum giving yellow solid (yield 52%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.18 (m, 8H), 7.83 (d, 4H), 7.53 (s, 8H), 1.49 (s, 36H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ = 141.51, 136.75, 128.65, 124.53, 122.26, 121.73, 107.32, 32.54, 29.45; HRMS $m/z$ [M]$^+$ calcd for C$_{56}$H$_{56}$N$_4$ 784.4505, found 784.4509.

5.3. Tuning the Emission of Fluorescent Organic Nanoparticles

5.3.1. General Description for the Synthesis

A diphenylfumaronitrile core was modified with various phenylacetylenes having para positioned electron donating and withdrawing groups in order to further understand the
Scheme 5.2 Synthetic scheme for compounds 5.3, 5.4, and 5.5.

Reagents and conditions. (a) PdCl$_2$(PPh$_3$)$_2$, PPh$_3$, CuI, Et$_3$N, stir 20 h at 70 °C, 2 h at rt.$^1$

Emission behavior of chemically like compounds; 1,2-Dicyano-trans-1,2-bis-4-(phenylacetylene)phenylethylene (5.3), 1,2-dicyano-trans-1,2-bis-4-(4-formylphenylacetylene)phenylethylene (5.4), and 1,2-dicyano-trans-1,2-bis-4-(4-methoxyphenylacetylene)phenylethylene (5.5) (Scheme 5.2).

5.3.2. Photophysical Properties in the Solid State and Solution

In the solid state 5.3 is greenish yellow, 5.4 is yellow, and 5.5 is yellowish orange. Thin films formed from 5.3, 5.4 and 5.5 on quartz are stable lasting for several months at room temperature. The bulky and polar cyano groups in the diphenylfumaronitrile core probably
restrict face-to-face intermolecular interactions, so \(J\)-aggregation in the solid state is likely the preferred arrangement.\(^2\) The acetylene spacer group facilitates electronic communication between adjacent phenyl rings via the triple bond regardless of its twist.\(^3\)

**Figure 5.8.** Solid state emission of \(5.3\), \(5.4\), and \(5.5\) under 366 nm UV lamp.

**Figure 5.9.** Normalized absorption spectra of \(5.3\), \(5.4\), and \(5.5\) in (a) carbon tetrachloride, (b) dichloromethane, and (c) \(N,N\)-dimethylformamide.
The enhanced emission of 5.3, 5.4, or 5.5 in the solid state (Figure 5.8 and Table 5.2) relative to that observed in solution confirms the J-aggregation.²,⁴

Each is highly soluble in common organic solvents and the normalized UV absorption spectra are shown in CCl₄, CH₂Cl₂ (DCM), and DMF, Figure 5.9. The π-π* absorption band of 5.3 is shifted to shorter wavelengths with increasing solvent polarity as is the absorption of 5.5. The π-π* absorption band of 5.4 however is shifted to longer wavelengths in DCM and shorter wavelengths in DMF.

![Normalized emission spectra of 5.3, 5.4, and 5.5 in (a) carbon tetrachloride (b) dichloromethane (c) N,N-dimethylformamide.](image)

**Figure 5.10.** Normalized emission spectra of 5.3, 5.4, and 5.5 in (a) carbon tetrachloride (b) dichloromethane (c) N,N-dimethylformamide.
Table 5.2 Photophysical Properties of 5.3, 5.4, and 5.5

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<td>521</td>
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<td>556</td>
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<td><strong>Compound 5.5</strong></td>
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<td>528</td>
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<td>620</td>
<td>0.13</td>
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<tr>
<td>Thin film</td>
<td>427</td>
<td>568</td>
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Quantum yields of fluorescence in solution were calculated with 9,10-diphenylanthracene (0.90 in cyclohexane) as a reference. Thin film quantum yields were measured using an integrating sphere.

This clearly indicates that the dipole moment of these compounds in the ground state ($\mu_g$) is greater than it is in the excited state ($\mu_e$) in highly polar solvents like DMF. The absorption of 5.5 is broader and red shifted, while that of 5.4 is narrow and blue shifted relative to that of 5.3.
The emission spectra of \textbf{5.3}, \textbf{5.4}, and \textbf{5.5} in CCl$_4$, DCM, and DMF are shown in Figure 5.10. The fluorescence of \textbf{5.5} undergoes an obvious red shift with increased solvent polarity and broadens, while a small red shift occurs with \textbf{5.3} and no changes at all are observed with \textbf{5.4}. The blue shift in the absorption maximum and red shift in the emission of \textbf{5.5} are attributed to the electron-donating groups on the phenylacetylene moiety. The ground state of \textbf{5.5} is stabilized when surrounded by polar solvent molecules, causing a blue shift in the absorption maximum.

When excited to its singlet state, \textbf{5.5} undergoes rapid intramolecular electron transfer giving a charge separated state and this causes broadening and a red shift in the emission. However, the dipole moment in \textbf{5.4} is much smaller because of the electron-withdrawing groups on the phenylacetylene moiety.

The polarity of the solvent has only a minor affect on the emission spectra of \textbf{5.4}. The structural changes of \textbf{5.4} in nonpolar and polar solvents must be relatively minor. So are the changes in the absorption spectra. Solvent polarity has serious affect on the emission quantum yield and lifetime. In polar solvents, the emission quantum yield becomes quite small and the lifetime short suggesting that the reorientation of the solvent dipole moment causes the excited state energy to be rapidly lost in polar solvents. However, in the case of \textbf{5.5}, the formation of the charge separated state is likely the main reason for the small quantum yield and short lifetime. The absorption spectra, quantum yields of emission, and lifetimes are summarized in Table 5.2.
5.3.3. Properties of Nanoparticles

Highly emissive nanoparticles of 5.3, 5.4, and 5.5 were prepared from water/THF mixtures using the reprecipitation method.\textsuperscript{2,6,7} In the cases of 5.3 and 5.4 nanoparticles were first to form from a THF solution when 75% water was added while with 5.5 only 63% water was required. Formation of nanoparticles is confirmed by the appearance of a broad UV absorption in the long-wavelength region due to Mie scattering.\textsuperscript{2,6} Figure 5.11 (a) shows the UV absorption changes of nanoparticles of 5.3, 5.4, and 5.5 formed as a result of the use of different water/THF ratios for the reprecipitation. The absorption peak at 401 nm resulting in the case of 5.5 when a solvent with an water/THF ratio of 1:7 is used, is red shifted to 438 nm when the solvent used for reprecipitation has an water/THF ratio of 6:2. When the water/THF ratio is 7:1 the peak shifts to 449 nm implying the formation of J-aggregates is caused by an increase in the water ratio. Similar phenomena were observed for 5.3. The aggregation of 5.4 is a more complex process. With 5.4, the absorption at 375 nm resulting from nanoparticles formed using a solvent with an water/THF ratio of 1:7 is blue shifted to 360 nm when the solvent used has an water/THF ratio of 6:2 and red shifted to 383 nm for a solvent from which nanoparticles are reprecipitated that has an water/THF ratio of 7:1. Scanning Electron Microscope (SEM) measurements show the particle size and morphology changes as a result of the use of solvents of different water/THF ratios. For example, spherical particles were observed when nanoparticles were formed from solvents with a 6:2 water/THF ratio for all three compounds, 5.3, 5.4, and 5.5. Larger spherical particles for 5.3 (~300 nm), nanorods for 5.4 (1-3 µm × 80 nm), and diamond shape nanorods for 5.5 (0.8-1.5 µm × 100 nm) were observed when the solvent used for
5.3

Absorbance

Intensity

Emission Intensity

5.4

Absorbance

Intensity

Emission Intensity
Figure 5.11. Absorption (a), Excitation (b), Emission (c) spectra of 5.3, 5.4, and 5.5 in different water/THF solutions. Black – (1:7), Red – (6:2), and Green – (7:1).

reprecipitation had a 7:1 water/THF ratio. We carefully carried out the experiments several times making the 6:2 and 7:1 water/THF ratio samples under the same conditions and similar results were observed. The water ratio used for reprecipitation as well as the substituents at the para position of phenylacetylenes are important factors for the formation of nanostructures of different morphology.

Emission spectra also show differences for 5.3, 5.4, and 5.5. The highest emission intensity results for each when a solvent of water/THF ratio of 6:2 is used for the reprecipitation. However, the emission is suddenly decreased if nanoparticles are prepared from a solvent
with a water/THF ratio of 7:1 (Figure 5.11). This must be related to morphology changes that result when particles are formed from a solvent that has a water/THF ratio of 7:1.

Structure/spectral relationships seem to be apparent even in the nanoparticle emissions of 5.3, 5.4, and 5.5. With 5.5 an electron-donating para methoxy group is attached, with 5.4 with an electron-withdrawing carboxaldehyde is attached, while there is no substituent at the para position in 5.3. Because the cyano of the diphenylfumaronitrile core is strongly electron-withdrawing, both 5.3 and 5.5 show obvious charge separated character in the excited states that is not observed with 5.4. The electronic characteristics also must cause the different aggregation patterns and different morphologies when solvents having the water/THF ratio of 7:1 are used. During the aggregation of 5.3, 5.4, or 5.5, single molecule properties change due to intermolecular interactions. The more the molecular aggregation, the more intermolecular interaction there are. We show the electronic band structure formed in the nanoparticle in Figure 5.12.

![Electronic band structure formed in the nanoparticle.](image)

**Figure 5.12.** Electronic band structure formed in the nanoparticle.
The emission of nanoparticles shows multieponential decay (Table 5.3), while the emission decay of the compounds in solution shows monoexponential decay (Table 5.2).

Size and shape have serious effects on the emission of the nanoparticles. Compounds, 5.3, 5.4, or 5.5 when formed from a solution with a water/THF ratio in the solvent of less than 6:2, exist as spherical particles. When the water/THF ratio of the solvent is increased to 7:1, a larger particle size or rod structure causes the emission of 5.3, 5.4, and 5.5 to be quenched (Figure 5.11).

### Table 5.3. Photophysical properties of 5.3, 5.4, and 5.5 in nanoparticle solution

<table>
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<tr>
<th>Water/THF ratio</th>
<th>$A_{\text{max}}$/nm</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\tau_{1,2}$/ns</th>
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<td></td>
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</tr>
<tr>
<td>1/7</td>
<td>384</td>
<td>515</td>
<td>&lt; 100 ps</td>
</tr>
<tr>
<td>6/2</td>
<td>390</td>
<td>501</td>
<td>2.27, 1.09</td>
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<tr>
<td>7/1</td>
<td>393</td>
<td>503</td>
<td>1.18, 0.29</td>
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<td><strong>Compound 5.4</strong></td>
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<tr>
<td>1/7</td>
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<tr>
<td>6/2</td>
<td>360</td>
<td>518</td>
<td>1.43, 5.21</td>
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<td>7/1</td>
<td>383</td>
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<td>3.77, 1.33</td>
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<td><strong>Compound 5.5</strong></td>
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<tr>
<td>1/7</td>
<td>401</td>
<td>601</td>
<td>&lt; 100 ps</td>
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<tr>
<td>6/2</td>
<td>438</td>
<td>536</td>
<td>0.81, 3.12</td>
</tr>
<tr>
<td>7/1</td>
<td>449</td>
<td>537</td>
<td>0.88, 3.05</td>
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Under a fluorescence microscope, that the emission comes from the nanoparticles can be clearly seen, Figure 5.13. The emission colors of the particles correlate with the emission spectra of the nanoparticle solutions.

Figure 5.13. SEM images of 5.3, 5.4, and 5.5 in (a) water/THF 6 : 2 (b) water/THF 7 : 1 (A). Widefield images of 5.3, 5.4, and 5.5 in water/THF 7 : 1 (B).
5.3.4. Preparation and Characterization

Synthesis of 1,2-dicyano-trans-1,2-bis-4-(phenylacetylene)phenylethylene (5.3)

Bis(4-bromophenyl)fumaronitrile (1g, 2.57 mmol), PdCl₂(PPh₃)₂ (60mg, 0.09 mmol), PPh₃ (20 mg, 0.08 mmol), and Cul (16 mg, 0.08 mmol) were mixed with triethylamine (60 ml) in 100 ml round bottom flask. This mixture was stirred under argon around 5 minutes and heated to 70° C. Phenylacetylene (0.60 ml, 5.47 mmol) was added drop-wise to the reaction mixture which was further stirred for ≈ 20 hours at 70° C. Then the resultant mixture was stirred 2 hours at room temperature. The reaction mixture was left undisturbed for several minutes so that the solid materials would separate from the liquid. This liquid portion was carefully removed, the solid materials collected and the resultant precipitate dried under lab conditions. This solid was dissolved in a large amount of THF and filtered. The filtrate was collected. A small amount of this filtrate was taken into a conical flask and distilled water was rapidly added. After the addition of a large amount of water, a colloidal solution appeared in the flask. This colloid was filtered under gravity filtration and dried under vacuum gives greenish yellow powder (52%). ¹H NMR (300 MHz, CDCl₃) δ = 7.87 (d, 4H), 7.69 (d, 4H), 7.58 (m, 4H), 7.40 (m, 6H); ¹³C NMR (300 MHz, CDCl₃) δ = 132.27, 131.81, 131.34, 128.93, 128.75, 128.47, 127.24, 124.55, 122.55, 116.44, 93.12, 88.31; HRMS m/z + calcd for C₃₂H₁₈N₂ 430.1470, found 430.1466.

Synthesis of 1,2-dicyano-trans-1,2-bis-4-(4-formylphenylacetylene)phenylethylene (5.4)

The procedure used for 5.3 was followed. 4-Ethynylbenzaldehyde (700 mg, 5.4 mmol) was used instead of phenylacetylene. Yellow powder (73%). ¹H NMR (300 MHz, CDCl₃) δ = 10.07 (s, 2H), 7.91 (m, 8H), 7.72 (d, 8H); ¹³C NMR (300 MHz, CDCl₃) δ = 191.25, 135.95,
132.50, 132.34, 131.91, 129.62, 128.86, 128.67, 126.44, 116.28, 91.92; HRMS m/z [M]^+ calcd for C_{34}H_{18}O_{2}N_{2} 486.1368, found 486.1370.

**Synthesis of 1,2-dicyano-trans-1,2-bis-4-(4-methoxyphenylacetylene) phenylethylene (5.5)**

The procedure used for 5.3 was followed. 4-Methoxyphenylacetylene (0.70 ml, 5.40 mmol) was used instead of phenylacetylene. Yellowish orange powder (29%). ^1^H NMR (300 MHz, CDCl₃) δ = 7.85 (d, 4H), 7.66 (d, 4H), 7.53 (d, 4H), 6.92 (d, 4H), 3.87 (s, 6H); ^1^C NMR (300 MHz, CDCl₃) δ = 160.21, 133.35, 133.31, 132.03, 129.40, 128.71, 127.11, 114.63, 114.49, 114.16, 93.34 55.34; HRMS m/z [M]^+ calcd for C_{34}H_{22}O_{2}N_{2} 490.1681, found 490.1680.

**5.4. Conclusions**

Carbazole based D-A compounds 5.1 and 5.2 were successfully synthesized. The compounds exhibit good stability and solubility in common organic solvents and aggregate to nanoparticles in water/THF. The formation of FONs of 5.1 and 5.2 with diameters of 50-150 nm in THF/water mixture was affected. A negative solvatochromism in the absorption spectra of 5.1 and 5.2 was observed. Both positive and negative solvatochromic behavior in the emission spectra suggest intramolecular electron transfer in 5.1 and 5.2.

The morphology of 5.3, 5.4, and 5.5 change depending on the water/THF ratio of the solvent from which they are reprecipitated. The compounds form nanoparticles from solvents with the appropriate water/THF mixtures (6:2), and this result in enhanced emission. However, when the water/THF ratio is increased to 7:1, the emission becomes weak and the
nanoparticles aggregate into a different morphological structures. Substitution of electron withdrawing and electron donating groups on the para position of the phenylacetylene moiety affect the emission in the solid state and nanoparticle solution. The emission spectra of 5.3 and 5.4 show no clear solvatochromic behavior but 5.5 displays a positive solvatochromism.

5.5. References

APPENDIX A

LIST OF ABBREVIATIONS:

FE-SEM  Field Emission Scanning Electron Microscopy
HTL    Hole Transport Layer
DCM    4-(dicyanomethylene)-2-methyl-6-[4-(dimethylaminostyryl)-4H-pyran]
BSA    bisstyrylanthracene
DCDDC  3-(dicyanomethylene)-5,5-dimethyl-1(4-dimethylamino-styryl)cyclohexene
PTCDA  3,4,9,10-perylene-tetracarboxylic-dianhydride
PCBM   [6,6]-phenyl C₆₁ butyric acid methyl ester
DH-5T   α,α'-dihexyl-quinquethiophene
DH-6T   4',3-dihexyl-2,2';5',2;5,2';5',2;5,2'-sexithiophene
DHBJAA N,N'-di[4-(2'-benzo[d]thiazolyl)-3-hydroxyphenyl]5-tert-butylishalophalamide
ABAN   7'-(dodecylamino)-methyl-2-acetamido-7-(benzofuran-2-yl)-1,8-naphthyridine
PDDP   1-phenyl-3-((dimethylamino)styryl)-5-((dimethylamino)phenyl)-2-pyrazoline
PPB    1,4-di[(E)-2-phenyl-1-propenyl]-benzene
DAP    1,3-diphenyl-5-(2-anthryl)-2-pyrazoline
DHIA   N,N'-di[3-hydroxy-4-(2’benzothiazole)phenyl]isophthalic amide
DHBIA  N,N'-di[3-hydroxy-4-(2’benzothiazole)phenyl]5-tert-butyl-isophthalic amide
Fc     Ferrocene
Fc⁺    Ferrocenium
Tert   Tertiary
NMR    Nuclear Magnetic Resonance
s (for NMR) Singlet
m (for NMR) Multiplet
d (for NMR) Doublet
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Figure B1. Structures of (a) pyridinium $N$-phenoxide betaine dye, (b) $N$-($o$-hosphoniobenzylidene)-4-aminophenolate betaine dye and (c) 4’-hydroxy-1-methylstilbazolium betaine.
Figure B2. Normalized emission spectra of 3.1-3.6 in different solvents at room temperature.
Figure B3. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.11a.
Figure B4. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.12a.
Figure B5. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.1.
Figure B6. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.2.
**Figure B7.** $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.3.
Figure B8. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.4.
Figure B9. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.5.
Figure B10. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 3.6.
Figure B11. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 5.1.
Figure B12. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 5.2.
Figure B13. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 5.3.
Figure B14. $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 5.4.
**Figure B15.** $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of 5.5.
Figure B16. $^1$H NMR of 3.11a (top) and 3.11b (bottom).