Fused-Molecular Systems for Organic Light Emitting Diodes

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FUSED-MOLECULAR SYSTEMS FOR ORGANIC LIGHT EMITTING DIODES

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Avinash Jami

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FUSED-MOLECULAR SYSTEMS FOR ORGANIC LIGHT EMITTING DIODES

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Organic light emitting diodes (OLEDs) are electronic devices made by sandwitching organic light emissive materials between two electrodes. When voltage is applied across the two conductors, a bright light is generated. The color of the emitting light depends on the band gap of the semiconducting material. The work described here focuses on designing and synthesizing narrow band gap molecular systems derived from fused-arene derivatives for producing organic blue light emitting diodes.

Three molecular systems derived from anthracene, pyrene, and carbazole, were designed and synthesized. Two molecular systems of anthracen-9-ylmethyl anthracene-9-carboxylate and pyren-1-ylmethyl 4-bromobenzoate were synthesized through Steglich esterification reaction and the third, pyren-1-ylmethyl 4-(9-hexyl-6-{4-[(pyren-1-ylmethoxy) carbonyl] phenyl}-9H-carbazol-3-yl) benzoate was synthesized by Grignard metathesis followed by Kumada coupling reaction. Structural characterizations were performed using $^1$H, $^{13}$C NMR and FTIR analysis. Photophysical properties of these systems were studied in chloroform ($\text{CHCl}_3$) solution using UV-visible and Fluorescence spectroscopies. The absorption and fluorescence emission spectra revealed the potential applicability of these three systems as blue and blue-green emitters for OLEDs. The future work of this project will focus on utilizing these three molecular systems to fabricate OLED devices.
CHAPTER 1
INTRODUCTION

1.1 Overview:

Organic light emitting diodes (OLEDs) are light emitting diodes in which the emissive layer (EML) between the two electrodes is made of organic compounds. OLEDs can be used in commercial applications like displays and lighting. An organic green-light emitting diode with some significant characteristics was first reported by Tang and VanSlyke in 1987 at Eastman Kodak using small molecules like aromatic diamine (4,4’-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline)\(^1\) and 8-hydroxyquinoline aluminum (Alq\(_3\)).\(^1\) It was a double-layer structure of organic thin films fabricated by vapour deposition. Effective injection of charge (electrons and holes) resulted from a high work function, low sheet resistant and optically transparent ITO (indium-tin-oxide) anode and a low work function alloy Mg:Ag cathode, respectively. Unique characteristics of this first prepared OLED included high electroluminescent emission efficiency, low voltage drive, quick response and ease of fabrication. Organic molecules and polymers exhibiting electroluminescence in blue, green and red spectral regions have been developed subsequently. Remarkable research following the discovery of OLEDs in organic and conjugated polymer thin films\(^2,3\) has lead to an immense literature on them\(^2,4\). The EML works on the principle of electroluminescence, i.e emitting light in response to passage of electric current through it.

Kido, et al., produced the first white OLED in 1993.\(^6\) They included red, green and blue light emitting materials together in their device to produce white light. In 2011, HoonSeo, et al., demonstrated hybrid organic white-light emitting diodes using N,N\(^1\)-
dicarbazolyl-3,5-benzene and 4,7-diphenyl-1,10-phenanthroline\textsuperscript{6}. In 1992, Grem, \textit{et al.}, first reported a blue OLED containing poly (p-phenylene) (PPP).\textsuperscript{7} Lee, \textit{et al.}, synthesized a series of blue fluorescent emitters based on a t-butylated bis (diarylaminoaryl) anthracene series.\textsuperscript{8} Through steric hinderance which reduces self-quenching properties, t-butyl groups, prevent molecular aggregation between blue emitters\textsuperscript{8}. In 2012, Chen, \textit{et al.}, produced three anthracene derivatives with carbazole moieties as side groups, 2-tert-butyl-9,10-bis[4-(9-carbazolyl)phenyl]anthracene, 2-tert-butyl-9,10-bis{4-[3,6-di-tert-butyl-(9-carbazolyl)]phenyl}anthracene and 2-tert-butyl-9,10-bis{4’-[3,6-di-tert-butyl-(9-carbazolyl)]biphenyl-4-yl}anthracene, to use in blue OLEDs\textsuperscript{9}. Tang and Vanslyke in 1987 demonstrated the first bright green-light emission using aluminum tris (8-hydroxyquinolinate) (Alq\textsubscript{3}) thin film organic layers\textsuperscript{1}. A highly efficient non-doped green OLED was reported by Ku, \textit{et al.}, by incorporating 9,9-diarylfluorene terminated 2,1,3-benzothiadiazole (DFBTA).\textsuperscript{10} This device exhibited remarkable characteristics, including a luminescence of 12.9 cd/A and an 81\% solid state photoluminescence quantum yield\textsuperscript{10}. 
1.2 Research goal:

The goal of my research thesis is to develop synthetic procedures to make small molecular systems based on fused aromatic molecules for OLED applications. In this thesis, I focus on the synthetic methods, characterization, and photophysical properties of three systems that are derived from anthracene, pyrene and carbazole. System 1 is an anthracene based molecular system prepared from an esterification (DCC coupling) reaction between 9-anthracenemethanol and 9-anthracenecarboxylic acid. System 2 is a pyrene based molecular system prepared in a similar manner as System 1 utilizing a DCC coupling reaction between 4-bromobenzoic acid and 1-pyrenemethanol. System 3 is derived from carbazole and pyrene derivatives prepared by Grignard metathesis followed by a Kumada coupling reaction between System 2 and 3,6 dibromo 9-hexyl carbazole. Photophysical properties of these three systems will also be discussed to evaluate their optoelectronic properties in solution. Future work will focus on utilizing these three molecular systems to evaluate potential applicability for OLEDs.
CHAPTER 2

BACKGROUND

2.1 Basic principle of an Organic light-emitting diode (OLED):

An organic light-emitting diode (OLED) is an electric device that emits bright light when electric current is applied (electroluminescence). A typical organic light emitting diode is made of series of organic layers sandwiched between two electrodes, a cathode and an anode, one of which will be transparent. In general, a high work function, low sheet resistance and optically transparent ITO (indium-tin-oxide) anode and a low work function metal cathode such as Ca, Mg, Al or their alloys Mg:Ag, Li:Al are used as electrodes. The layers between the two electrodes include an electron transport layer (ETL), an emissive layer (EML) and a hole transport layer (HTL).

![Diagram](image)

**Figure 2.1:** Basic construction of double heterostructure OLED (Eugene Polikarpov and Mark E. Thompson, 2011).^5
2.2 Organic light emitting diodes operation:

The operation principle of an OLED is analogous to that of inorganic LED. In detail, it can be divided into four processes\(^5\) that are necessary for device operation:

1) **Charge injection:** A low work function metallic cathode and a transparent indium-tin-oxide (ITO) anode are used to inject electrons and holes respectively. When a voltage is applied, both electrons and holes are injected from the cathode and anode to the electron transporting layer (ETL) and the hole transporting layer (HTL) respectively.

2) **Charge transport:** These charges travel across their respective layers and enter into the emissive layer (EL) “active” region. Charge transport efficiency can be enhanced by selecting organic electron transporting (ETL) and hole transporting (HTL) layers with high LUMO or low HOMO levels, respectively.

3) **Charge recombination and**

4) **Light emission:** These charges combine with each other, electrons reacting with holes to form excitons, which decay radiatively to give out light by the process of spontaneous emission. Both the electrons and holes are odd electron species with half-integer spin. Depending on how the spins of two such particles are combined, an exciton formed by the recombination can be either in a singlet state or a triplet state.\(^{15,16}\) The probability of formation of the singlet and triplet states is approximately 25\% and 75\%, respectively.\(^{14,15}\) In fluorescent OLEDs only singlet excitons are responsible for useful light emission, whereas in phosphorescent OLEDs, both triplet and singlet excitons are responsible for the useful light emission.
Figure 2.2: OLED operation mechanism (Svetlana V. Eliseeva and Jean-Claude G. Bunzil, 2011).\textsuperscript{3}

2.3 Device structures:

Design of the device structure, along with selection of molecules with suitable electronic and optical properties, plays an important role in efficient device operation. Possible layer sequences and energy level diagrams of different device structures include:

a. Single layer

b. Two-layer or single heterostructure device

c. Double heterostructure and

d. Multilayer structure.
Both the frontier orbitals, HOMO (highest occupied molecular orbital or valence band) and LUMO (lowest unoccupied molecular orbital or conduction band) play an important role in OLED devices. The energy difference between the HOMO and LUMO levels is known as the HOMO-LUMO gap, and it limits the color of the emitted light. The different colors emitted from an OLED depends on a type of organic molecule used in the emissive layer, and the intensity or brightness depends on the amount of current generated.

2.4 Classification of OLEDs:

OLEDs are fabricated either by using small molecules or polymers\textsuperscript{28,29}.

1) Examples of small molecule-based devices (SM-OLED) include tris (8-hydroxyquinolinato) aluminum (Alq$_3$), BCP (4,7-diphenyl-1,10 phenenthroline), Diamine (4,4’-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline), perylene,
anthracene, stilbene and PTCDA (3,4,9,10-perylentetracarboxylic dianhyride) etc.

2) Examples of polymer-based devices (P-OLED) include derivatives of poly(p-phenylene-vinylene (PPV), polyphenylene, poly(alkylthiophene) and poly(9,9-dialkyl fluorine), etc.

Examples for Small molecule OLEDs (SM-OLEDs):

[Chemical structures of Alq³, BCP (Bathocuproine), and Diamine]
Examples for Polymer-based OLEDs (P-OLEDs):

Poly(p-phenylene vinylene) - PPV

Polyphenylene
Electrical conductivity of these organic molecules is due to the delocalization of loosely bound π-electrons, which is the result of conjugation over some or all of the molecule. SM-OLEDs can be fabricated using vacuum deposition under ultrahigh vacuum conditions whereas P-OLEDs can be applied using spin-coating or even ink-jet printing techniques.

### 2.5 Background of OLEDs:

**A) Table 1:** Comparison of inorganic LEDs vs OLEDs – Advantages, disadvantages, efficiency and fabrication.

<table>
<thead>
<tr>
<th></th>
<th>LED (Light emitting diode)</th>
<th>OLED (Organic light emitting diode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>General description</td>
<td>Heavy, rigid</td>
<td>Thin, flat, lighter and more flexible</td>
</tr>
<tr>
<td>Active layer</td>
<td>Inorganic</td>
<td>Organic</td>
</tr>
<tr>
<td>Backlight</td>
<td>Needs backlight</td>
<td>Doesn’t need backlight</td>
</tr>
<tr>
<td>Power consumption</td>
<td>Consumes more power</td>
<td>Consumes less power</td>
</tr>
<tr>
<td>Parameter</td>
<td>Low contrast ratio</td>
<td>High contrast ratio</td>
</tr>
<tr>
<td>----------------------------</td>
<td>--------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Contrast ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viewing angle</td>
<td>Narrow</td>
<td>Wide</td>
</tr>
<tr>
<td>Moisture</td>
<td>Resistant</td>
<td>Sensitive</td>
</tr>
<tr>
<td>Lifetime</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Response time</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td>Processing temperature</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Color accuracy</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Cost</td>
<td>Low cost</td>
<td>Expensive</td>
</tr>
<tr>
<td>Outdoor performance</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>

**B) Applications of OLEDs:**

a. Solid-state lighting: OLEDs can be used in household lighting, automobiles, etc.

b. Display technologies: OLED is the new technology that is being applied to flat panel displays like TV’s and smartphones etc.

**C) OLED Characterization parameters:**

a. **Luminescence efficiency**: External and internal quantum efficiencies.

i. **External quantum efficiency** ($\eta_{EQE}$): It is the ratio of photons and electrons moving out and into the device, respectively. It quantifies conversion efficiency of electrical energy into optical energy. It can also be defined as the product of the internal quantum efficiency and light extraction efficiency.

ii. **Internal quantum efficiency** ($\eta_{IQE}$): It is the ratio of internally generated photons to the electrons moving into the device. In fluorescent OLEDs, only
singlets result in the emission of useful radiation, placing a theoretical limit on
the internal quantum efficiency (the percentage of excitons formed that result in
emission of a photon) of 25%\textsuperscript{11}. However, phosphorescent OLEDs generate light
from both triplet and singlet excitons, allowing the internal quantum efficiency
of such devices to reach nearly 100%\textsuperscript{12}. In general, conjugated polymers have
rod-like rigid structures. These rod-like rigid polymers are susceptible to
aggregation, leading to fluorescence quenching which results in lower quantum
efficiency.

\textbf{iii. Light extraction efficiency:} It is the ratio of amount of light (fraction of
photons) generated in the device to the amount of light (fraction of photons) that
escapes into free space from the device.

\textbf{b. Voltage drive:} A certain minimum voltage must be reached to overcome the barriers
to injecting charges into the organic materials. The lower the voltage required, the
higher the efficiency of the OLED.

\textbf{D) Effects of increases in conjugation:} An increase in the conjugation of the organic
materials used in the OLEDs leads to the emission of longer wavelength visible light,
moving from blue to red. Conjugation increases the energy of the HOMO (\(\pi\)) and
decreases the energy of the LUMO (\(\pi^*\)), so less energy is required for an electronic
transition (\(\pi \rightarrow \pi^*\)) in a conjugated system than in a non-conjugated system. In the
presence of more conjugated double bonds in a compound, less energy is required for
the electronic transitions, therefore the longer the wavelength at which the electronic
transition occurs. The \(\lambda_{\text{max}}\) increases as the number of conjugated double bonds
increases. $\lambda_{\text{max}}$ is the wavelength in the absorbance spectrum at which the absorption of light is the maximum.

**E) Importance of fused aromatic systems as emissive materials**: Fused aromatic molecular systems often have high quantum yields. For fluorescence, it can be defined as the ratio of number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\# \text{ photons emitted}}{\# \text{ photons absorbed}}$$

$\pi$ - Conjugated molecular systems, because of their high stability and excellent charge carrier mobility, have drawn considerable interest in the field of organic electronics and may lead to practical applications$^{17}$. High charge carrier mobility results from their lower oxidation potential, high conjugation obtained by fused aromatic rings and high rigidity favoring improved $\pi$-$\pi$ overlap in the solid state leading to effective interchain and intrachain charge transport. Changes in molecular packing can also be induced by ring fusion, such as conversion from less promising herringbone packing to the preferred $\pi$-stacking.

Two pyrene based derivatives with thienyl and trifluoromethylphenyl functional groups, respectively, at the 1, 3, 6 and 8 positions were synthesized through Suzuki coupling reactions by H. J. Zhang, *et al.*$^{18}$ These molecules were characterized in terms of their crystal structures, electrochemical and optical properties and were used as active materials in Organic field-effect transistor (OFET) devices.
Anthracene (C\textsubscript{14}H\textsubscript{10}) is a crystalline solid with an energy band gap of ~ 3.9 eV, low melting point, and poor electrical conductivity\textsuperscript{19}. Research on single crystal organic molecules, which include tetracene, pentacene and rubrene molecular crystals is rare\textsuperscript{20-27}. Acenes having \( n \)-linked benzene rings (\( n=3 \): anthracene; \( n=4 \): tetracene; \( n=5 \) pentacene) facilitate intermolecular overlap of \( \pi \) systems because of their planar shapes enables efficient crystal packing and prolonged \( \pi \) systems.\textsuperscript{30}
CHAPTER 3

EXPERIMENTAL PROCEDURES:

3.1 Materials:

9-Anthracenemethanol, 9-anthracencarboxylic acid, 4-bromobenzoic acid, 1-
pyrenemethanol, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP),
dichloromethane (DCM), pyren-1-ylmethyl 4-bromobenzoate, 3,6-dibromo 9 hexyl
carbazole, tert-butyl magnesium chloride, anhydrous tetrahydrofuran,
bpis((diphenylphosphino)propane]nickel(II) chloride, hexane, chloroform, chloroform-D,
silica gel. All the materials were obtained from Sigma-Aldrich and were used without
any further purification.

3.2 Characterization:

$^1$H and $^{13}$C NMR spectra were recorded using a 500 MHz Jeol NMR
spectrometer. IR spectra were recorded using a Perkin Elmer Spectrum One FTIR.
Fluorescence spectra were recorded using a Perkin Elmer LS 55 spectrometer, and UV
spectra were recorded using a Perkin Elmer Lambda 35 spectrometer.
3.3 Procedure for the synthesis of anthracen-9-ylmethyl anthracene-9-carboxylate

– System (1):

To a 100 mL two-necked round-bottom flask, 9-anthracenemethanol (0.9 eq, 0.50 g, 2.4 mmol), 9-anthracenecarboxylicacid (1 eq, 0.59 g, 2.6 mmol), dicyclohexylcarbodiimide (1 eq, 0.49 g) and 4-dimethylaminopyridine (0.08 g) were added. The flask was degassed using argon for 15-30 minutes. Dichloromethane (DCM) (30 mL) was added to the reaction mixture by syringe through one of the septa forming a cloudy, bright-yellow colored solution, and it was stirred for 24 hours at room temperature. The solution flask was wrapped with aluminum foil the entire time to prevent exposure to light. No further change in the appearance of the solution was observed, even after 24 hours. The solution was transferred to a 100 mL one necked round-bottomed flask. Any solid left in the reaction flask was washed using a few mL of DCM into the original solution. Solvent was extracted from the solution using a Rotovap, leaving a yellow colored solid to the walls of the flask. A sufficient amount of DI water was added to the flask, and all the solid was scrapped into it. Now the solution was filtered using suction filtration for around one hour, yielding a yellow colored solid. The sample was dried under vaccum for 24 hrs. TLC was performed for the product using the two starting materials, 9-anthracenemethanol and 9-anthracenecarboxylic acid in DCM: Hexane solution (3:2). Samples were prepared for TLC by dissolving minute amounts in DCM that were spotted on a TLC plate. The TLC plate was then placed for a few minutes inside a jar having a few mL of DCM: Hexane solution. A UV-lamp was used to observe the spots on the TLC plate. The TLC experiment supported product
formation along with some leftover initial reactants. $^1$H and $^{13}$C NMR spectra were performed for the sample dissolved in deuterated chloroform. The NMR spectrum also showed the presence of some impurities along with the product, suggesting further purification was required. Further purification was done by column chromatography using a DCM: Hexane solution (3:2). Solvent was removed by rotovap for the fractions that showed the presence of the product the in TLC, yielding a yellow colored solid (49.14% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.58-8.62 (d, 2H), δ 8.54 (s, 1H), δ 8.5 (s, 1H), δ 8.2-8.24 (d, 2H), δ 7.96-8.02 (d, 2H), δ 7.92-7.96 (d, 2H), δ 7.46-7.54 (m, 4H), δ 7.32-7.44 (m, 4H), δ 6.7 (s, 2H).
3.4 Procedure for the synthesis of pyren-1-ylmethyl 4-bromobenzoate – System (2):

To a 100 mL two-necked round bottom flask, 4-bromobenzoic acid (0.9 eq, 0.38 g, 1.9 mmol), 1-pyrenemethanol (1 eq, 0.5 g, 2.1 mmol), dicyclohexylcarbodiimide (1 eq, 0.44 g) and 4-dimethylaminopyridine (0.12 g) were added. The flask was degassed using argon for 15-30 minutes. Dichloromethane (30 mL) was added to the reaction mixture by syringe through one of the septa, forming a cloudy white-colored solution that was stirred for 24 hours at room temperature. The solution flask was wrapped with aluminum foil the entire time to prevent exposure to light. No change in the appearance of the solution was observed even after 24 hours. The solution was transferred to a 100mL one necked round-bottomed flask. Any solid left in the reaction flask was washed using a few mL of DCM into the original solution. The solvent was extracted from the solution using a Rotovap, leaving a white-colored solid on the walls of the flask. A sufficient amount of DI water was added to the flask and all the solid was scrapped into it. The solution was then filtered using suction filtration for around one hour, yielding a dry white-colored solid. The sample was then dried under vaccum for 24 hours. A TLC experiment was performed on the product using the two starting materials, 4-bromobenzoic acid and 1-pyrenemethanol in DCM: Hexane solution (3:2). Samples were prepared for TLC by dissolving minute amounts in DCM and spotted on a TLC plate. The TLC plate was then placed for a few minutes inside a jar having a few mL of DCM: Hexane solution. A UV-lamp was used to observe the spots on the TLC plate. The TLC results supported product formation along with some residue of 1-pyrenemethanol. $^1$H and $^{13}$C NMR spectra were recorded for the sample dissolved in deuterated chloroform. The NMR spectrum also showed the impurities such as 1-
pyrenemethanol and DCC along with the product, suggesting further purification was required. Further purification was done by column chromatography using a DCM: Hexane solution (3:2). Solvent was removed using a Rotovap for the fractions that showed the presence of product on the TLC plates, yielding a white-colored solid (71.05% Yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.36-8.38 (d, 1H), \(\delta\) 8.18-8.26 (m, 4H), \(\delta\) 8.02-8.16 (m, 4H), \(\delta\) 7.9-7.94 (d, 2H), \(\delta\) 7.52-7.56 (d, 2H), \(\delta\) 6.1 (s, 2H).
3.5 Procedure for the synthesis of pyren-1-ylmethyl 4-(9-hexyl-6-{4-[(pyren-1-ylmethoxy) carbonyl] phenyl}-9H-carbazol-3-yl) benzoate – System (3):

To a 250 mL two-necked round bottomed flask, 3, 6-dibromo-9-hexyl carbazole (1 eq, 500 mg, 1.222 mmol) was added. The flask was degassed using argon for 15-30 min. An argon environment and a water reflux were maintained throughout the experiment. Anhydrous THF (20 mL) was added to the reaction flask by syringe slowly through one of the septa forming a clear solution. Tert-butyl magnesium chloride (2.1 eq, 2.56 mL, 2.56 mmol) was added slowly in a dropwise manner to the round-bottomed flask by a syringe for one hour. The reaction was allowed to run for 2 hours with the flask partially immersed in an oil bath. The temperature of oil bath was raised and maintained at 80°C for 2 hrs after the temperature of oil bath reached 80°C. After 2 hours of reaction, the formation of clear yellow-colored solution was observed. Pyren-1-ylmethyl 4-bromobenzoate-System 2 (2 eq, 1.110g dissolved in 20 mL of anhydrous THF and degassed) was added to the warm reaction flask by syringe. When the flask reached room temperature (either naturally or cooled by ice), a first portion of Ni catalyst [1,3-bis(diphenylphosphino) propane]nickel(II) chloride (1/30 eq, 40 mg dissolved in 1 mL of anhydrous THF and degassed) was added by syringe to the reaction flask, forming a clear, dark copper red-colored solution. Then, the reaction was allowed to run for 30 min before the addition of a second portion of Ni catalyst (1/60 eq, 20 mg dissolved in 1 mL of anhydrous THF and degassed). No change in the appearance of the solution was observed. The reaction was allowed to run overnight. Then next day, formation of a clear, light copper-colored solution was observed, and the reaction was quenched by adding a few drops of methanol (5 mL) to the original solution. The solution was
transferred to a 100mL one necked round bottomed flask and the solvents were extracted from the solution using a Rotovap, leaving a very light brown-colored solid to the walls of the flask. A sufficient amount of DI water was added to the flask and the solid was scrapped into it. Now the solution was filtered using suction filtration for around one hour, yielding a dry light brown-colored solid. The sample was dried under vaccum for 24 hours. A TLC experiment was performed for the product using the two starting materials 3,6-dibromo-9-hexyl carbazole and pyren-1-ylmethyl 4-bromobenzoate-System 2 in a DCM:Hexane solution (1:3), which did not confirm the presence of the product, as there was no clear separation of the spots. $^1$H and $^{13}$C NMR were performed and they supported product formation by the coupling reaction (73% yield). $^1$H NMR 500 MHz, CDCL$_3$): $\delta$ 8.32-8.4 (d, 2H), $\delta$ 8-8.26 (m, 16H, 4H), $\delta$ 7.88-7.94 (d, 4H), $\delta$ 7.5-7.58 (m, 6H), $\delta$ 6.1 (s, 4H), $\delta$ 4.2-4.3 (t, 2H), $\delta$ 1.8-1.9 (m, 2H), $\delta$ 1.2-1.4 (m, 6H), $\delta$ 0.8-0.9 (t, 3H).
CHAPTER 4

RESULTS AND DISCUSSION


Scheme 1: Synthetic route for the preparation of System 1

Reaction mechanism:
As depicted in Scheme 1, System 1 was prepared by using the well known ‘Steglich esterification’ method, by reacting 9-anthracenemethanol with 9-anthracenecarboxylic acid in the presence of dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP) and dichloromethane (DCM) under an argon environment at room temperature to yield a yellowish solid crude product. In the reaction mechanism, DMAP acts as an acyl group transferring catalyst and strong nucleophile, DCC acts as a coupling reagent by activating carboxylic acid to further reaction, and DCM acts as a solvent. The product formed was further purified by column chromatography using a DCM: Hexane solution (3:2) to give a yellow powdered solid in 49.14% yield. The structure of the product was confirmed by $^1$H NMR and the presence of the carbonyl group is confirmed by $^{13}$C NMR and FTIR. In the $^1$H NMR, the peaks at $\delta$ 8.5 (s, 1H), $\delta$ 8.24-8.20 (d, 2H), $\delta$ 7.96-7.92 (d, 2H), and $\delta$ 7.44 -7.32 (m, 4H) confirm
the presence of the methoxy anthracene unit. The peaks at δ 8.8-8.4 (d, 2H), δ 8.62-8.58 (d, 2H), δ 8.54 (s, 1H) and δ 7.54-7.46 (m, 4H) confirm the presence of the carboxy anthracene unit. The peak at δ 6.7 (s) clearly indicates that the esterification was successful for the formation of the product. In the $^{13}$C NMR, the peak at δ 169.89 confirms the presence of carbonyl functional group. FTIR also supports the formation of the ester bond, with the peaks at 1704 cm$^{-1}$ and 1786 cm$^{-1}$ that correspond to the carbonyl stretching. The peak at 1195 cm$^{-1}$ correspond to the ester C-O stretching. The peak at 3052 cm$^{-1}$ correspond to aromatic C-H stretching. The peak at 1523 cm$^{-1}$ agrees with the expected aromatic C=C stretching. The peak at 2922 cm$^{-1}$ and 1446 cm$^{-1}$ corresponds to aliphatic C-H bond stretching.
4.2 Photophysical studies of System 1 in solution phase:

Figure 4.1: (a) UV-Vis absorption and (b) Fluorescence emission spectra (excited at 350 nm) of System 1.
The photophysical properties of System (1) were studied in chloroform (CHCl₃) solution. As shown in Figure 4.1(a), the absorption spectrum exhibits the typical spectral features of anthracene with four characteristic bands at 339, 353, 370 and 390 nm, which correspond to vibronic transitions of S₀-S₁. However, the photoluminescence emission spectrum of the compound as shown in the Figure 4.1(b), shows an unresolved broad peak with a peak maxima at 465 nm. This spectral behavior indicates that vibronic couplings of individual anthracene units are overlapped to give single broad peak. The emission spectrum was obtained by exciting at 350 nm. The emission wavelength is in the range of 399 to 599 nm, with a maximum emission at 465 nm that confirms that System 1 is a blue-light emitter as shown in the Figure 4.2.

Figure 4.2: Blue light emission of System 1 under UV irradiation
4.3 Synthesis and Characterization of pyren-1-ylmethyl 4-bromobenzoate – System (2):

Scheme 2: Synthetic route for the preparation of System 2

Reaction mechanism:
As depicted in Scheme 2, System 2 was prepared by using the well known ‘Steglich esterification’ method, by reacting 4-bromobenzoic acid with 1-pyrenemethanol in the presence of dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP) and dichloromethane (DCM) under an argon environment at room temperature to yield a white solid crude product. In the reaction mechanism, DMAP acts as acyl group transferring catalyst and strong nucleophile, DCC acts as a coupling reagent by activating carboxylic acid to further reaction, and DCM acts as the solvent. The product formed was further purified by column chromatography using a DCM: Hexane solution (3:2) to give a pure white powdered solid in 71.05% yield. The structure of the product was confirmed by $^1$H NMR and the presence of a carbonyl group was confirmed by $^{13}$C NMR and FTIR. In the $^1$H NMR, the peaks at δ 8.36-8.38 (d, 1H), δ 8.18-8.26 (m, 4H) and δ 8.02-8.16 (m, 4H) confirm the presence of...
a pyrene unit. The peaks at δ 7.9-7.94 (d, 2H) and δ 7.52-7.56 (d, 2H) confirm the presence of the bromobenzene unit. The peak at δ 6.1 (s) clearly indicates that the esterification was successful for the formation of the product. In the $^{13}$C NMR, the peak at δ 165.95 confirms the presence of a carbonyl functional group. FTIR also supports the formation of the ester bond with the peak at 1721 cm$^{-1}$ that corresponds to carbonyl (C=O) stretching. The peak at 1273 cm$^{-1}$ correspond to the ester C-O stretching. The peak at 3043 cm$^{-1}$ corresponds to aromatic C-H stretching. The peaks at 1590 cm$^{-1}$ and 1484 cm$^{-1}$ agree with the expected aromatic C=C stretching. The peak at 1396 cm$^{-1}$ corresponds to aliphatic C-H bond stretching.
4.4 Photophysical examination of System 2 in solution phase:

Figure 4.3: (a) UV-Vis absorption and (b) Fluorescence emission spectra (excited at 345 nm) of System 2.
The photophysical properties of System (2) were studied in chloroform (CHCl₃) solution. As shown in the Figure 4.3(a), the absorption spectrum exhibits typical spectral features characteristic of pyrene, with two sets of peaks in the range of 260 to 360 nm. Two characteristic bands at 267 and 277 nm from one set, which correspond to S₀-S₂ vibronic transitions. Three characteristic bands are observed at 316, 329 and 346 nm from set two, which correspond to S₀-S₁ vibronic transitions. The photoluminescence emission spectrum of the System (2) as shown in the Figure 4.3(b), shows a maximum emission at 377 nm with two low energy shoulders at 396 and 416 nm. The emission spectrum was obtained by exciting at 345 nm, which corresponds to the 0-0 transition. The emission wavelength in the range of 360 to 450 nm confirms that System 2 is a blue-light emitter, as shown in Figure 4.4.

Figure 4.4: Blue light emission of System 2 under UV irradiation.

Scheme 3: Synthetic route for the preparation of System 3
Reaction mechanism:
As depicted in Scheme 3, System 3 was prepared by using the Kumada coupling method, by reacting pyren-1-ylmethyl 4-bromobenzoate with 3,6 dibromo 9 hexyl carbazole in the presence of tert-Butylmagnesium chloride, Ni catalyst [1,3-bis(diphenylphosphino) propane]nickel(II) chloride and anhydrous THF under an argon environment to yield a light brown colored solid crude product in 73% yield. The mechanism shows the sequence of steps (oxidative addition, transmetalation, trans/cis isomerization and reductive elimination respectively) undergone by the reactants to form the required product. The structure of the product was confirmed by $^1$H-NMR and the presence of carbonyl group was confirmed by $^{13}$C NMR and FTIR. In the $^1$H NMR, the peaks at $\delta$ 8.32-8.4 (d, 2H) and $\delta$ 8-8.26 (m, 16H) confirm the presence of two pyrene units. Peaks at $\delta$ 8-8.26 (m, 4H) and $\delta$ 7.88-7.94 (d, 4H) confirm the presence of two benzene units. The peak at $\delta$ 7.5-7.58 (m, 6H) confirms the presence of the carbazole unit. The peak at $\delta$ 6.1 (s, 4H) confirms the presence of methylene hydrogens from both the sides. Peaks at $\delta$ 4.2-4.3 (t, 2H), $\delta$ 1.8-1.9 (m, 2H), $\delta$ 1.2-1.4 (m, 6H) and $\delta$ 0.8-0.9 (t, 3H) confirm the presence of a hexyl chain. In the $^{13}$C NMR, the peak at $\delta$ 165.93 confirms the presence of the carbonyl functional group. The FTIR also supports the formation of the ester bond with peaks at 1719 cm$^{-1}$ that correspond to carbonyl stretching. The peak at 1590 cm$^{-1}$ and 1470 cm$^{-1}$ agrees with aromatic C=C stretching. The peak at 1396 cm$^{-1}$ corresponds to aliphatic C-H bond stretching. Peak at 1273 cm$^{-1}$ correspond to the ester C-O stretching.
4.6 Photophysical examination of System 3 in solution phase:

**Figure 4.5:** (a) UV-Vis absorption and (b) Fluorescence emission spectra (excited at 275 nm) of System 3.
The photophysical properties of System (3) were studied in chloroform solution. As shown in Figure 4.5(a), the absorption spectrum exhibits typical spectral features characteristic of pyrene, with two sets of peaks in the wavelength range of 260 to 360 nm. Two characteristic bands at 268 and 278 nm from one set, correspond to S₀-S₂ vibronic transitions. Three characteristic bands at 316, 330 and 346 nm from set two, correspond to S₀-S₁ vibronic transitions. Absorption peaks from carbazole were not clearly resolved since they were merged with the pyrene spectrum. The photoluminescence emission spectrum of System (3), as shown in Figure 4.5(b), shows a maximum emission at 377 nm, with two energy shoulders at 397 and 417 nm. Emission peaks from carbazole were not clearly resolved since they were merged with the pyrene spectrum. The emission spectrum was obtained by exciting at 275 nm. The emission wavelength in the range of 350 to 497 nm confirms that System (3) is a sky blue-light emitter, as shown in Figure 4.6.

Figure 4.6: Blue light emission of System 3 under UV irradiation
Figure 4.7: All the systems emitting different colors under UV irradiation.
CHAPTER 5

CONCLUSION

The main objective of this thesis was to synthesize fused molecular systems that can be efficiently used in the active layer of OLEDs.

In conclusion, three fused molecular systems, anthracen-9-ylmethyl anthracene-9-carboxylate (System (1) by Steglich esterification reaction), pyren-1-ylmethyl 4-bromobenzoate (System (2) by Steglich esterification reaction) and pyren-1-ylmethyl 4-(9-hexyl-6-{4-[pyren-1-ylmethoxy carbonyl] phenyl}-9H-carbazol-3-yl) benzoate (System (3) by Grignard metathesis followed by a Kumuda coupling reaction) based on anthracene, pyrene and carbazole, respectively, were synthesized and purified. System (1) showed absorbances of anthracene corresponding to $S_0$-$S_1$ vibronic transitions and a maximum emission from irradiation at 350 nm was observed at 465 nm in the wavelength range of 399 to 599 nm, which confirms the emission of blue light. System (2) showed absorbances of pyrene corresponding to $S_0$-$S_1$ and $S_0$-$S_2$ vibronic transitions, and a maximum emission from irradiation at 345 nm was observed at 377 nm and 396 nm in the wavelength range of 360 to 450 nm, which confirms the emission of blue light. System (3) showed absorbances of pyrene corresponding to $S_0$-$S_1$ and $S_0$-$S_2$ vibronic transitions, and a maximum emission from irradiation at 275nm was observed at 377 nm and 397 nm, which confirms the emission of sky blue light. Their structural properties were confirmed using $^1$H NMR, $^{13}$C NMR, FTIR spectroscopies. Their photophysical properties were studied using UV-visible and fluorescence
spectroscopies in solution. Future work will be focusing on utilizing these molecular systems in making OLEDs and testing their characteristics.
APPENDIX A: $^1$H and $^{13}$C NMR spectra of compounds

System 1

$^1$H NMR spectrum of System 1
$^{13}$C NMR of System 1
System 2

$^1$H NMR spectrum of System 2
$^{13}$C NMR spectrum of System 2
System 3
$^1$H NMR of System 3
$^1$H NMR of System 3 (Expanded)
$^{13}$C NMR of System 3
$^{13}$C NMR of System 3 (Expanded)
APPENDIX B: FTIR spectra of compounds

FTIR spectrum of System 1

FTIR spectrum of System 2
FTIR Spectrum of System 3
LITERATURE CITED


