Carbazole, Fluorene and Perylene Based Materials for Potential Applications in Organic Light Emitting Diodes-Syntheses and Characterization

by

Madiha Irfan

Department of Chemistry
Quaid-i-Azam University
Islamabad
2015
Carbazole, Fluorene and Perylene Based Materials for Potential Applications in Organic Light Emitting Diodes—Syntheses and Characterization

A dissertation submitted to the Department of Chemistry, Quaid-i-Azam University, Islamabad, in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Organic Chemistry

by

Madiha Irfan

Department of Chemistry
Quaid-i-Azam University
Islamabad
2015
DECLARATION

This is to certify that this dissertation titled "Carbazole, Fluorene and Perylene Based Materials for Potential Applications in Organic Light Emitting Diodes – Synthesis and Characterization" submitted by Ms. Madiha Irfan is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, as satisfying the partial requirement for the degree of Doctor of Philosophy in Organic Chemistry.

External Examiner-I:

Dr. Khalid Masud
Principal Scientist
N.L.P., P.O. Box No.1356
Nilore, Islamabad

External Examiner-II:

Dr. Muhammad Arshad
Principal Scientist, Chemistry Division
Directorate of Science, PINSTECH
Nilore, Islamabad

Supervisor:

Prof. Dr. Aamer Saeed Bhatti
Department of Chemistry
Quaid-i-Azam University
Islamabad

Head of Section:

Prof. Dr. Shahid Hameed
Department of Chemistry
Quaid-i-Azam University
Islamabad

Chairman:

Prof. Dr. M. Siddiq
Department of Chemistry
Quaid-i-Azam University
Islamabad
# Table of Contents

<table>
<thead>
<tr>
<th>Acknowledgments</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>II-IV</td>
</tr>
<tr>
<td>List of Abbreviations</td>
<td>V</td>
</tr>
<tr>
<td>Abstract</td>
<td>VI-VII</td>
</tr>
</tbody>
</table>

## Chapter-1 Introduction

1.1 Organic electronics                                                         01
1.2 Organic light-emitting diodes (OLEDs)                                        02
1.3 History of OLEDs                                                             03
1.4 Working principle and structure of OLEDs                                     04-07
1.5 Merits and demerits of OLEDs                                                 07-08
1.6 Applications                                                                 08
1.6.1 Display Applications                                                       08-11
1.6.2 Solid-state lighting                                                       11-12
1.7 Materials for OLEDs                                                          13-16
1.7.1 Emitting materials                                                         16-19
1.7.2 Small molecules                                                            19
1.8 Carbazole-based materials                                                    20-23
1.9 Use of polypyridine in OLEDs                                                 23-24
1.20 Fluorene-based materials                                                   24-27
1.21 Perylene-based materials                                                    27-28
1.2.1.1 Commonly-used precursors of perylene                                    28-31
1.2.2 Plan and objective of work                                                 32-39

## Chapter-2 Results and discussion

2.1 Synthesis, characterization and studies of carbazole                         40-44
2.1.1 Thermal properties                                                         44-46
2.1.2 Photophysical properties                                                   46-48
2.1.3 Electrochemical properties                                                 48-50
2.2 Synthesis, characterization and studies of bis-                              50-53
carbazole pyridine copolymers

2.2.1 Thermal properties 53-54
2.2.2 Photophysical properties 55-56
2.2.3 Electrochemical properties 56-58

2.3 Synthesis, characterization and studies of carbazole/fluorene small molecular materials 58-70

2.3.1 Thermal properties 70-73
2.3.2 Photophysical properties 73-76
2.3.3 Electrochemical properties 76-78

2.4 Synthesis, characterization and studies of Perylene derivatives 78-81

2.4.1 Thermal properties 82-83
2.4.2 Photophysical properties 83-84
2.4.3 Electrochemical properties 84-86

Chapter-3 Experimental

3.1 Chemicals and reagents 87
3.2 Purification of solvents 87-88
3.3 Instruments used 88-89
3.4 Chromatographic techniques 89
3.4.1 Thin layer chromatography (TLC) 89
3.4.2 Column chromatography 89
3.5 General procedure for synthesis of N-alkylcarbazoles 89-90
3.5.1 N-Butylcarbazole 90
3.5.2 N-Octylcarbazole 90
3.6 General procedure for the synthesis of 3,6-diacetyl-N-alkylcarbazole 90
3.6.1 3,6-Diacetyl-N-butylcarbazole 90-91
3.6.2 3,6-Diacetyl-N-octylcarbazole 91
3.7 General procedure for polymer synthesis 91
3.7.1 Poly[3,6-N-butylcarbazole-4-phenylpyridine-2,5-diyl] (P1a) 91-92
3.7.2  Poly[3,6-N-butylcarbazole-4-(3-nitrophenylpyridine)]-2,5-diyl (P1b) 92
3.7.3  Poly[3,6-N-butylcarbazole-4-(3-hydroxyphenylpyridine)]-2,5-diyl (P1c) 92
3.7.4  Poly[3,6-N-butylcarbazole-4-(3-bromophenylpyridine)]-2,5-diyl (P1d) 93
3.7.5  Poly[3,6-N-octylcarbazole-4-phenylpyridine-2,5-diyl] (P2a) 93
3.7.6  Poly[3,6-N-octylcarbazole-4-(3-nitrophenylpyridine)]-2,5-diyl (P2b) 93
3.7.7  Poly[3,6-N-octylcarbazole-4-(3-hydroxyphenylpyridine)]-2,5-diyl (P3c) 94
3.7.8  Poly[3,6-N-octylcarbazole-4-(3-bromophenylpyridine)]-2,5-diyl (P3d) 94
3.7.9  3,3’-Bi(9-octylcarbazole) 94
3.7.10 6,6’-Diacetyl-N-octyl-3,3’-biscarbazole 95
3.7.11 General procedure for the synthesis of polymers 95
3.7.12 Poly[6,6’-{3,3’-N-octylbiscarbazole-4-phenylpyridine}]-2,5-diyl (P3a) 95-96
3.7.13 Poly[6,6’-{3,3’-N-octylbiscarbazole-4-(3-bromophenylpyridine})]-2,5-diyl (P3b) 96
3.7.14 Poly[6,6’-{3,3’-N-octylbiscarbazole-4-(3-nitrophenylpyridine})]-2,5-diyl (P3c) 96
3.7.15 Poly[6,6’-{3,3’-N-octylbiscarbazole-4-(3-hydroxyphenylpyridine})]-2,5-diyl (P3d) 97
3.7.16 3,6-Dibromo-N-octyl carbazole 97
3.7.17 3-Bromo-9-octylcarbazole 97
3.7.18 2,7-Dibromo-9,9-dioctyl-9H-fluorene 98
3.7.19 2-Bromo-9,9-dioctyl-9H-fluorene 98
3.7.20 General procedure for synthesis of boronic acid 99
3.15.1  9-Octyl-9H-carbazol-3,6-di-yl-boronic acid  99
3.15.2  9-Octylcarbazole-3-boronic acid  99
3.15.3  9,9-Dioctyl-9H-fluoren-2,7-diylboronic acid  100
3.15.4  9,9-Dioctyl-9H-fluoren-2-ylboronic acid  100
3.16    9-(7-Bromo-9,9-dioctylfluoren-2-yl)-9H-carbazole  100
3.17    9-(6-Bromo-9-octyl-9H-carbazol-3-yl)-9H-carbazole  101
3.18    General procedure for Pd-catalyzed Suzuki coupling  101
3.18.1  9-(7-(6-(7-(9H-Carbazol-9-yl))-9,9-dioctyl-9H-fluoren-2-yl)-9-octyl-9H-carbazol-3-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9H-carbazole  102
3.18.2  9-(6-(6-(6-(9H-Carbazol-9-yl))-9-octyl-9H-carbazol-3-yl)-9-octyl-9H-carbazol-3-yl)-9-octyl-9H-carbazol-3-yl)-9H-carbazole  102
3.18.3  9-(9-Octyl-6-(9-octyl-9H-carbazol-3-yl)-9H-carbazol-3-yl)-9H-carbazole  103
3.18.4  9-(9,9-Dioctyl-7-(9-octyl-9H-carbazol-3-yl)-9H-fluoren-2-yl)-9H-carbazole  104
3.18.5  9-(7-(7-(9H-Carbazol-9-yl))-9,9-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9H-carbazole  104
3.18.6  9-(9,9'-Dioctyl-7-(9,9'-dioctyl-9H-fluorene-2-yl)-9H-fluorene-2-yl)-9H-carbazole  105
3.18.7  2,7(6-(9-Octyl-9H-carbazolyl)3-yl)9,9'-dioctyl-9H-fluorene  106
3.19    General procedure for synthesis of N,N-disubstituted-aryl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide  106
3.19.1  N,N-Di-p-tolyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide  107
3.19.2  N,N-Di-2-methoxyphenyl-1,6,7,12-tetrachloro-
3.19.3 N,N-Di-2-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide  
3.19.4 N,N-Di-3-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide  
3.19.5 N,N-Di-4-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide  
3.20 General procedure for synthesis of N,N-disubstituted-aryl-1,6,7,12-tetra(substituted phenoxy)-3,4,9,10-perylenedicarboximide  
3.20.1 N,N-Di-p-tolyl-1,6,7,12-tetraphenoxy-3,4,9,10-perylenedicarboximide  
3.20.2 N,N-Di-p-tolyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximide  
3.20.3 N,N-Di-2-methoxyphenyl-1,6,7,12-tetra(2,5-dimethoxyphenoxy)-3,4,9,10-perylenedicarboximide  
3.20.4 N,N-Di-2-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximide  
3.20.5 N,N-Di-3-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximide  
3.20.6 N,N-Di-4-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximide  

Conclusions  
References
Acknowledgments

All praises and glory be to ALLAH SUBHANA’O TAALA, the only creator who helped and guided me in all fields of life. All respects for HOLY PROPHET HAZRAT MUHAMMAD (P.B.U.H) whose life is an ideal pattern of success for us.

I feel great pleasure and privileges to express my profound sense of gratitude and earnest appreciations for my worthy supervisor Prof. Dr. Aamer Saeed, Department of Chemistry, Quaid-i-Azam University, Islamabad, for enthusiastic encouragement and astonishing suggestions.

I am also thankful to Prof. Dr. Kevin, D. Belfield for his support and guidance during my stay at University of Central Florida under the Pak-USAID joint project, i.e., No. 4-279/PAK-US/HEC/2010/917.

I am grateful to Prof. Dr. Amin Badshah, Chairman, Department of Chemistry, Quaid-i-Azam University, Islamabad for providing me all necessary research facilities.

I cordially thank to Prof. Dr. Shahid Hameed, Head of Organic Chemistry Section, Department of Chemistry, Quaid-i-Azam University, Islamabad, and all teachers of Organic Chemistry Section especially Prof. Dr. Nasim Hassan Rama, Prof. Dr. Aurangzeb Hassan, Dr. Muhammad Farman who taught in such a way that enabled me to tackle all sorts of problem during the research work.

I am indebted to Higher Education Commission (HEC) of Pakistan for scholarship.

Many thanks to staff members of this department, especially Mr. Mahmood, Mr. Sharif Chohan, Mr. Shams, Mr. Ali Zaman, Mr. Shabbir, Mr. Iliyas, Mr. Matloob, Mr. Rana Tahir, Mr. Haneef, Mr. Tasleem, Mr. Saqib, Mr. Mustafa, Mr. Irfan Sabir, Mr. Tayyab, Mr. Rashid, Mr. Liaqat, Mr. Shahid Naeem, Mr. Aamir for their all-time devotion.

I also owe recognition to my lab fellows: Dr. Zaman Ashraf, Dr. Amara Mumtaz, Dr. Naeem Abbas, Dr. Hummera Rafique, Ms. Aliya Ibrar, Mr. Parvaiz Ali, Ms. Mobeen Arif, Ms. Asma Khurshid, Ms. Sidra Jamal, Ms. Uzma Ilyas, Mr. Jamal ul din, Mr. Shamsul Mahmood, Ms. Iram Batoold, Ms. Madiha Kazmi, Ms. Noor-ul-Ain for their help at crucial time of my research work and all my seniors and juniors for their encouragement.

Special thanks are reserved for my sister-like friend Shumaila Bukhari, for her prayers and support. I am also thankful to my dearest friends Asma Maqbool and Rida-e-Zenab for their succor. Many thanks to Ms. Sabahat Jaleel for her cooperation.

Finally, I would like to thank my parents for their support, love and everything they dedicated me and, last but not least, to all my family members and those who prayed for my success.

Madiha Irfan
List of Figures

Figure 1.1 (a) First OLED-based KODAK camera (b) Organic RFID tag by Poly IC
Figure 1.2: Multifunctional organic semiconducting materials (a) CuPc (b) DCMT
Figure 1.3: Representation of optical excitation and photoluminescence
Figure 1.4: Single-layer OLED setup
Figure 1.5: Multi-layer OLED setup
Figure 1.6: Structure of PEDOT:PSS a common hole-injection material
Figure 1.7: Energy level diagram of a single layer OLED device architecture
Figure 1.8: Various OLED display applications (a, b) Samsung recent OLED-based smart flexible cell phone (c) Galaxy S5 mobile phone by Samsung (d) Tablet by Samsung
Figure 1.9: (a) OLED display by SONY (b) LG first 55” TV (c) First curved OLED TV by SONY
Figure 1.10: FOLED (a) Prototype display by Samsung (b) Bus stop with FOLED lightening
Figure 1.11: OLED-based fabric
Figure 1.12: Lightening panel based on OLED (a) by Philips (b) (c) by Novaled
Figure 1.13: Hole-transporting materials in OLED devices
Figure 1.14: Hole-transporting STARBURST materials
Figure 1.15: Typical examples for ETL materials
Figure 1.16: Chemical structure of PPV and its soluble derivatives
Figure 1.17: PPV derivatives with electron withdrawing groups
Figure 1.18: Commonly-used polymers: PT and PPP
Figure 1.19: Small molecular emitting materials
Figure 1.20: Polymers employing bicarbazole moiety
Figure 1.21: Bicarbazole polymers by heck coupling
Figure 1.22: Green phosphorescent emitter polymer
Figure 1.23: Starburst oligocarbazole
Figure 1.24: Synthetic scheme to oligocarbazole
Figure 1.25: Poly-fluorene, a ladder-type polymer
Figure 1.26: Suzuki-coupled synthesized polyfluorenes (poly-2,7-fluorene derivatives)
Figure 1.27:  Green-emitting polyfluorenes
Figure 1.28:  Oligofluorene containing triphenylamine moiety
Figure 1.29:  Carbazole-fluorene dendrimers
Figure 1.30:  Fluorene-TPE polymer
Figure 1.31:  Fluorene/carbazole and fluorene/thiophene oligomers
Figure 1.32:  General perylene imide structure
Figure 1.33:  Commonly-used precursors of perylene
Figure 1.34:  Red-emitting perylene derivatives
Figure 1.35:  Perylene-PPV polymer
Figure 1.36:  Light-harvesting perylene-based material
Figure 1.37:  Regioisomeric synthesized perylene derivatives
Figure 2.1:  Mass fragmentation pattern of 3,6-diacetyl-N-butyl carbazole
Figure 2.2:  Crystal structure of 3,6-diacetyl-N-octyl carbazole
Figure 2.3:  $^1$H-NMR spectrum of polymer P1a
Figure 2.4:  TG thermogram of P1a
Figure 2.5:  Combined TG curves of P, P2
Figure 2.6:  DSC thermogram of P2a
Figure 2.7:  UV/Vis spectra of P1, P2 in CHCl$_3$ (10$^{-5}$ M)
Figure 2.8:  Photoluminescence spectra of P1 and P2 in CHCl$_3$ solution (10$^{-5}$M)
Figure 2.9:  Cyclic voltammograms of P1 and P2 in DMSO (1 mM) at glassy carbon working electrode, TBAP (0.1 M) supporting electrolyte, Ag/AgCl, platinum wire as reference and auxiliary electrode respectively, 100 mV/s scan rate
Figure 2.10:  Energy band diagram of P1, P2 with respect to ITO
Figure 2.11:  TG plots of the polymers P3
Figure 2.12:  DSC thermogram of P3a
Figure 2.13:  UV/Vis absorption and emission spectra of P3 in CHCl$_3$ 10$^{-5}$M
Figure 2.14:  Cyclic voltammograms of P3a, P3b, P3c and P3d (1 mM each) recorded at glassy carbon electrode in their DMSO solution containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte employing potential scan rate of 50 mV s$^{-1}$
Figure 2.15: Energy band diagram of polymers P3a-d with respect to ITO-PEDOT
Figure 2.16: Isotope pattern of derivative 9 in APCI-MS
Figure 2.17: (a) APCI-MS of bromo-fluorene derivative (10)  (b) Isotope pattern
Figure 2.18: $^1$H-NMR spectrum of CFT
Figure 2.19: $^1$HNMR spectrum of CCT
Figure 2.20: (a) APCI-MS of CCT (b) Expansion of APCI-MS
Figure 2.21: (a) APCI-MS of CCF (b) Expansion of APCI-MS
Figure 2.22: MALDI-TOF-MS of CFD
Figure 2.23: $^1$H-NMR spectrum of CFM
Figure 2.24: (a) APCI-MS of CFM (b) Expansion of APCI-MS
Figure 2.25: (a) TG curves of CFT (b) CCF
Figure 2.26: (a) TG curves of CFC (b) CCT
Figure 2.27: DSC thermogram of CFT
Figure 2.28: XRD of CFT
Figure 2.29: Absorption spectra of carbazole/fluorene dyes in CHCl$_3$ $10^{-5}$ M
Figure 2.30: Emission spectra of carbazole/fluorene dyes in CHCl$_3$ $10^{-5}$ M
Figure 2.31: CV curves of C/F dyes (1 mM each) recorded at platinum electrode in DCM solution containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte at potential scan rate of 50 mV s$^{-1}$
Figure 2.32: Energy band diagram of carbazole/fluorene dyes with respect to ITO-NPB
Figure 2.33: $^1$H-NMR spectrum of compound 11
Figure 2.34: $^1$H-NMR spectrum of POM
Figure 2.35: TG curves of PDIs
Figure 2.36: DSC thermogram of P4N
Figure 2.37: (a) Absorption spectra of PDIs in CHCl$_3$ $10^{-5}$ (b) Emission spectra of PDIs in CHCl$_3$ $10^{-5}$ M
Figure 2.38: CV curves of PDIs (1 mM each) recorded at glassy carbon working electrode, platinum wire (counter), sat. Ag/AgCl (reference) in their DMSO solution containing 0.1M (TBAP) as a supporting electrolyte employing potential scan rate of 50 mV s$^{-1}$
Figure 2.39: Energy band diagram of PDIs with respect to ITO-NPB
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>EIL</td>
<td>Electron-injection layer</td>
</tr>
<tr>
<td>Eg</td>
<td>Energy gap</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron-transport layer</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>HIL</td>
<td>Hole-injection layer</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole-transport layer</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IP</td>
<td>Ionization potential</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
</tr>
<tr>
<td>PDI</td>
<td>Perylenediimide</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>RFID</td>
<td>Radiofrequency identification tag</td>
</tr>
<tr>
<td>SSL</td>
<td>Solid state lightening</td>
</tr>
<tr>
<td>TBAB</td>
<td>Tetrabutylammonium bromide</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin-layer chromatography</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Abstract

Π-conjugated molecules are integral components of organic light-emitting diodes (OLEDs) responsible for light creation via absorption and emission, charge transportation and recombination. The present thesis focuses on the syntheses, characterization and studies of conjugated polymeric and small molecules for potential applications in OLEDs and multifunctional materials addressing the carbazole, fluorene and perylene. Carbazole-based materials are thoroughly studied electro- and photoluminescent stuff with excellent stability; these are common in the field of organic electronics due to their hole-transporting properties. Thus, some new carbazole-based polymers were synthesized in good yields by a cost-effective, modified Chichibabin reaction. The methodology involved the alkylation of carbazolic nitrogen, followed by Friedel-Crafts acetylation at 3,6 positions to afford the monomer. Polymerization entailed reaction with suitably-substituted benzaldehydes using ammonium acetate in refluxing acetic acid leading to creation of pyridine ring in situ, thus, comprising both hole- and electron-transporting moieties in the unit. Different alkyl chains were attached to investigate the effect of chain length on thermal properties. Similarly, the influence of electron-donating and electron-withdrawing substituents on the optical properties was also studied. Polymers exhibit good thermal stability, good solubility with blue emission. A second series of polymers having octyl chain and 3,3′-biscarbazolyl moiety was synthesized using the same methodology, exploiting better thermal properties of biscarbazole unit. The resulting polymers possess improved thermal stability, blue emission with solution processability providing the potential use as charge-transporting as well as light-emitting materials in OLEDs.

In addition to the polymeric materials, different small molecular entities employing carbazole/fluorene core were also synthesized by Suzuki cross coupling in good yields. Fluorene was preferred due to its excellent morphological stability and blue light emission. A variation of the core nucleus from fluorene to carbazole was a key point to study its effect on thermal, optical and electrochemical properties. All molecular substances exhibited high thermal stability and blue emission.

Perylene is a well-known n-type stable material. Different small molecular frameworks having the substitution on imide part and the bay position of the perylene
nucleus were also synthesized. The synthetic strategy aimed at the imidization with suitable anilines followed by nucleophilic substitution with phenols. The resulting objects are amorphous in nature, possess good solution processability and electron-transporting properties due to their decreased LUMO level with good emissive properties ranging from yellow to orange depending on the substituents, thereby indicating their potential use in OLEDs as either electron-transporting or emissive layers. All the synthesized compounds were characterized by spectroscopic techniques like FTIR, $^1$H-NMR, $^{13}$C-NMR, mass spectrometry and the elemental analyses.
1.1 Organic electronics

After the discovery of electroluminescence in silicon carbide in 1907,\(^1\) much attention was paid to the inorganic substances until Pope et al discovered that organic materials can also possess the electroluminescence.\(^2\) The organic electronics field emerged in late 1970’s with the development of first organic thin film transistor (OTFTs), \textit{i.e.}, an electro-optical device.\(^3\) With the gradual development and discovery of different classes of organic stuff, electronic devices using the organic entities as active layers were developed. Organic materials are being employed in optoelectronic devices such as organic light-emitting diodes (OLEDs), organic field effect transistor (OFETs)\(^4\), organic photovoltaic (OPVs)\(^5\), xerography,\(^6\) renewable energy sources, organic solar cells,\(^7\) biosensors\(^8\) and, most importantly, radio frequency identification (RFIDs) tags that will replace the traditional bar codes.\(^9\) The major reasons of these to be as active layers is that organic compounds are soluble in a number of solvents that make them solution processable and cost effective; secondly, the mechanical strength and structural flexibility render their use effective for large panels.\(^10\) Figure 1.1 represents some of the commercial products utilizing organic semiconducting materials.

![Figure 1.1](image1)

(a) First OLED based KODAK camera (b) Organic RFID tag by Poly IC

The organic semiconducting stuff can be employed as either light emissive or charge transporting layer. Several electronic devices were developed utilizing either one or a couple of properties of organic semiconducting materials, e.g., copper phthalocyanine (CuPc) was used in photovoltaic cells both as light-harvesting and charge transporting material.\(^11\) Tris(8-hydroxyquinolinato)aluminum (Alq3) used as light-emitting and
charge-transporting material in OLEDs\textsuperscript{12}, \(3',4'\)-dibutyl-5,5\textsuperscript{''}-bis(dicyanomethylene)-5,5\textsuperscript{''}-dihydro-2,2\textsuperscript{'}:5\textsuperscript{'}:2\textsuperscript{''}-terthiophene (DCMT) has been used as a charge-transporting material in field-effect transistors (FET).\textsuperscript{13} The structures of CuPc and DCMT are shown in Fig. 1.2. Organic electronics is a multidisciplinary field. With the combined contributions of chemists, material scientists and physicists since the last couple of decades, the commercialization of organic electronic devices led to OLEDs, OFETs, OPVs and solar cells.\textsuperscript{14-18} The first organic electronic product introduced in the consumer market in 2002 by Philips was OLED-based display panel. In 2004 Kodak launched the Kodak Easy Share LS633 digital zoom camera featured a full color active matrix OLED display\textsuperscript{19} and this commercialization is increasing to date. The US marketing research institute, IDTechEx, concluded in 2006 that the global market for organic and printed electronics will grow from its current 1.18 billion US dollars to more than 40 times, i.e., to a volume of 48.18 billion US dollars, within the next 10 years.\textsuperscript{20}

![Figure 1.2: Multifunctional organic semiconducting materials (a) CuPc (b) DCMT](image)

1.2 Organic light-emitting diodes (OLEDs)

An organic light-emitting diode (OLED), as the name indicates, is an optoelectronic device whose emissive electroluminescent layer is composed of a film of organic semiconducting material deposited between two electrodes. The development of organic light-emitting diodes (OLEDs) has been the subject of intense research heading for the fabrication of large-area multicolor and full color flat panel displays.\textsuperscript{21} On changing the mode of excitation, different kinds of luminescence can be observed. Optical excitation of a matter results in transfer of an electron from the highest occupied
molecular orbital (HOMO, $S_0$) to the lowest unoccupied molecular orbital (LUMO, $S_1$). The excited electron rapidly relaxes to the vibrational ground state with emission of light. Due to energy loss in the excited state, the wavelength of the emitted light is longer than the absorption wavelength. The principle of photoluminescence (PL) is shown in the Jablonski diagram (Fig 1.3).

![Jablonski Diagram](image)

**Figure 1.3:** Representation of optical excitation and photoluminescence (Jablonski diagram)

Generation of light under the effect of applied voltage is called electroluminescence (EL). Under the influence of electric field, electrons and holes injected from their respective electrodes to active organic material, recombines to form excited state and radiative decay of electron-hole pair is produced by this process. Electroluminescence results in non-thermal generation of light. The energy of emitted photon is equal to the difference between valence and conduction band.  

1.3 **History of OLEDs**

Bernanose and co-workers in 1950 first demonstrated electroluminescence in organic materials by applying a high voltage alternating-current (AC) field to crystalline thin films of acridine orange and quinacrine. In 1960, electroluminescent cells were developed by using doped anthracene. Electroluminescence in single crystal of anthracene was first reported in 1960s by Pope *et al.* However, the fabricated device needed a high drive voltage of 400 V to obtain blue emission resulting from anthracene. In order to reduce the operating voltage, vacuum-deposited anthracene thin films was used by Vincett *et al* in 1982 that led to a significant reduction of drive voltage (upto 12V).
McNeill et al and Bolto et al first reported high conductivity (1 S/cm) in iodine-doped oxidized polypyrrole in 1963.\textsuperscript{28} In 1977 Shirakawa et al reported high conductivity in iodine-doped polyacetylene and received Nobel Prize in chemistry.\textsuperscript{29}

The first attempt to develop a polymer LED by using doped-film of polyvinylcarbazole was made by Partridge in early 1980.\textsuperscript{30} The first double layer OLED was invented at Kodak by Tang and Slyke in 1987 by using thin films of 1,1-bis-4-[di(p-tolyl)amino]phenylcyclohexane (TAPC) as a hole-transporting material and tris(8-quinolino)aluminum (Alq3) as a green OLED emitting material sandwiched between transparent indium-tin oxide (ITO), serving as anode and Mg/Ag alloy working as cathode, was reported to exhibit a luminance of over 1000 cd/m\textsuperscript{2} at a drive voltage of ca. 10 V.\textsuperscript{31,12} Subsequently, this concept was adopted for use with polymers by Burroughess et al and Friend et al in 1990 when they developed first polymer light-emitting diode (PLED) using thin film of poly(p-phenylene vinylene) (PPV) by spin-coating.\textsuperscript{32,33} After that extensive research has been carried out to understand and develop PLEDs. Baldo et al in 1998, used the phosphorescent metal complexes as emissive materials for OLEDs which in turn improved the efficiency of device very much.\textsuperscript{34} Fukuda et al reported emission from polyfluorenes which provide more advanced polymer-based devices.\textsuperscript{35} Now-a-days, these kinds of polymers possess the most promising features for commercial applications. Devices fabricated from these polymers have lifetimes of more than 10,000 hours at 200 cd/m\textsuperscript{2} with device efficiencies in excess of 20 lm/W, that is, comparable to inorganic LEDs based on III-V semiconductors in terms of brightness and efficiencies.\textsuperscript{36, 37}

1.4 Working principle and structure of OLEDs

A typical OLED is composed of a substrate, an emissive layer, conducting layers and anode and cathode terminals. The layers are made of organic molecules that conduct electricity. The first most basic OLEDs consisted of a single organic emissive layer that is sandwiched between two metal electrodes. Indium-tin-oxide (ITO) is the most widely-used anodic material, which is either coated on substrate or commercially available ITO-coated substrate used. ITO has certain characteristics as universal choice anode. First, it is transparent (>90\%) which is pre-requisite for anode to perceive light. Moreover, it possesses high work function, good adhesion to organic layers and wide band gap. ITO
must be cleaned prior to use to meet the HOMO level of organic stuff. A suitable cathode material must be electropositive enough with low work function to ensure efficient electron injection into the organic semiconductor with high current density. K, Ca, Li, etc. metals can be used for this purpose but due to their high reactivity, these can be easily degraded, affecting the lifetime of device. By using the metal alloys Al/Li, Mg/Ag, LiF/Al etc. this problem can be solved. This is the simplest single-layered structure of an OLED with poor device efficiency. The performance of an OLED is determined by the number of charge carriers that are injected and the number of holes and electrons that actually recombine under emission of light. Efficiency of single layer device was low because electrons and holes have different mobilities and as a result charge seems to be close to one electrode resulting in non-radiative loss of energy. A typical single-layer OLED setup is shown in Fig. 1.4.

![Figure 1.4: Single-layer OLED setup](image)

In order to improve device efficiency, the multi-layer OLED architecture was introduced which is shown in Fig. 1.5. Additional hole (HTL) and electron-transport layers (ETL) are introduced in order to balance the different charge carrier mobilities. By varying transport properties and thickness of these supporting layers, the recombination zone can be shifted towards the emission layer. Due to low work function of ITO compared with HTL, there is need to introduce hole injection layer in-between anode HTL to ensure maximum hole injection at interface. Introduction of HIL and EIL helps to reduce the barrier for charge injection. For this purpose, use of poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT/PSS) is very common (Fig. 1.6).
As hole and electron leakage is common at interphase of layers, hole-blocking layer (HBL) and electron-blocking layer (EBL) were added in order to lock up charges in active layer. The advantages concerning a multi-layer device setup are the possibility to adapt the HOMO and LUMO levels of the used materials. A good overlap of the corresponding energy levels is essential to obtain a maximum carrier injection into different layers.\textsuperscript{46}

\begin{center}
\includegraphics{figure1.5.png}
\end{center}

**Figure 1.5:** Multi-layer OLED setup

Upon application of voltage to the electrodes of an OLED device, electrons from the cathode and holes from the anode are injected into the organic semiconductor. Due to electric field between the two electrodes, the positive and negative charge carriers move through the organic layer. As soon as they recombine in the emitting material, light is generated and difference of energy between ground and excited states decides the emission color. The energy level diagram of a single layer organic LED is shown in Fig. 1.7. The elementary steps involved in working of OLED are: i) charge injection ii) charge transportation iii) charge recombination iv) radiative decay of exciton.

\begin{center}
\includegraphics{figure1.6.png}
\end{center}

**Figure 1.6:** Structure of PEDOT:PSS a common hole injection material
In order to maximize device efficiency, significant efforts were made during last two decades through the designing and synthesis of new materials and device engineering.\textsuperscript{47-50} and device engineering.\textsuperscript{51-53}

1.5 Merits and demerits of OLEDs

OLEDs encompass many advantages when compared with other display technologies and commercialization of OLEDs is growing tremendously.

Advantages

OLEDs are luminous themselves, thus no back light is required. Efficiency of OLEDs is better than that of other display technologies.

Since variety of organic materials can be used as emitter with benefit of tuning their properties, so broad range of visible spectrum can be produced from blue to red and color- tuning can easily be maintained.

OLEDs have lower cost than other display technologies due to the solution-processed fabrication, such as inkjet printing and screen printing, are possible for polymer OLEDs.

OLEDs are lightweight because these are very thin devices with a layer thickness, measuring only \( \approx 100\text{nm} \).

OLEDs can be easily fabricated on plastic substrates owing to thinness and close relationship of organic materials to plastic paving the way for flexible electronics.

OLEDs have fast response time, \textit{i.e.}, less than 1\( \mu \text{s} \) because organic molecules have short radiative lifetime.
They require less power because no polarizers are required because of their self-luminance.

OLEDs have high brightness and high resolution because OLED pixel can directly emit light. (White OLEDs can be as bright as 150, 000 cd/m^2).

Direct emission of light with receiving of same amount of light cause OLED to have wide viewing angle (lambertian emission) and viewing angle is as high as 160 degrees.

**Disadvantages**

As organic materials are very sensitive to oxygen and water molecules, OLEDs are highly susceptible to degradation by oxygen and moisture which in turn can degrade the device very fast. So, the main disadvantage of an OLED is the lifetime. However, by proper encapsulation and using suitable materials lifetimes exceeding 60,000 hours have been reported.

Devices based on small molecule have low glass transition temperature T_g (<70°C), so the operating temperature cannot exceed the glass transition temperature.

Low mobility of charges due to amorphous nature of the organic molecules is also a serious problem.

1.6 **Applications**

Enormous commercialization of OLEDs, due to their potentially-beneficial characteristics in contrast to conventional LEDs, is making head. OLEDs have found their way in two major fields, i.e., display and lightening applications and are booming since their launch in market. Moreover, the development of flexible OLEDs (FOLEDs) has opened door to change the concept of electronic applications, from lighting to displays and even for fabrics.

1.6.1 **Display Applications**

The ease of access to all three basic colors for OLEDs makes it possible to design full color displays. Work on both active matrix (AM) and passive matrix (PM) OLEDs display is flourishing equally. The OLEDs are being used in small electronic applications including mobile phone displays, MP3 player, digital cameras, digital watches, car radios, etc. Recently, OLED-based tablet has entered the market. Since the development of first OLED-based mobile phone, numerous modifications have been incorporated for better results. Currently, Samsung is dominating in the market for commercializing OLED
small displays. Samsung has launched its Galaxy S5 Active with 5.1” HD AMOLED display. According to Display Search, Samsung has sold more than 67 million 4” OLED displays in 2010. Recently, Samsung has launched the world first flexible OLED smartphone named Galaxy Round, at SK Telecom in South Korea, with a 5.7” display (Fig. 1.8 a-d). This technology helps to read the words even from side by the help of curved-screen.

![Figure 1.8: Various OLED display applications (a, b) Samsung recent OLED-based smart flexible-cell phone (c) Galaxy S5 mobile phone by Samsung (d) Tablet by Samsung](image)

OLEDs also benefited the large displays as well like computer screens, laptops, television, etc. The large displays based on OLED, have amazingly beautiful screens, with vivid color production at nearly any viewing angle. Many companies such as Sony, LG Display and Samsung are working on large OLED display panels. In 2007, SONY produced the very first commercial OLED TV having 11” screen. During the year 2008 SONY introduced 27-inch high-definition display having 3-mm thickness, with power consumption of 45W and a one-million-to-one contrast ratio. Lately, LG has launched the world first OLED 55” TV. More recently, LG at a London event has launched the world’s first 4K curved OLED TV that will be available commercially in October 2014 which can set the future direction of OLED display market. The production of large
screen displays needed the solution processing. However there exists strong competition for large screen display, notably plasma.\textsuperscript{59} Figure 1.9 represents the OLED-based large display devices.

Due to flexibility present in organic material, flexible (FOLEDs) can be developed. UDC has introduced a rollable OLED with full-color and full-action\textsuperscript{60} in February 2006, featuring a metal foil substrate and a multilayer thin film as encapsulation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.9.png}
\caption{(a) OLED display by SONY (b) LG first 55” TV (c) First curved OLED TV by SONY}
\end{figure}

FOLED has ample applications from rollable TV screens to product wrappers to clothing. Next generation flexible or transparent OLED devices were presented in consumer electronics show. These types of displays are expected to expand the OLED applications in consumer markets in the near future. Figure 1.10 represents some of the notable FOLEDs applications.
Moreover, wearable electronics has been attracting much attention of late. OLED-based wearables has advantage over LED fabric as they need additional textile diffusional layer for covering and also OLED-based fabrics are aesthetically more pleasant. Recently K. Kim et al have reported the high-performance OLED on soft fabric first time for wearable display (Fig. 1.11).62

1.6.2 Solid-state lighting

Due to enormously increasing energy crisis, the alternative energy resources are attracting attention along with construction of electronic devices with low energy usage. Traditional light sources include incandescent bulbs and fluorescent lamps but with the drawbacks that incandescent bulbs dissipate heat which in turn decreases the efficiency, while fluorescent lamps are toxic due to incorporation of mercury. The conversion of electricity into light by the use of semiconductors refers to the solid-state lighting (SSL). OLEDs are also potentially useful for energy-efficient and inexpensive solid-state lighting. For lighting applications, OLEDs have high light quality, close to that of sunlight. SSL differs fundamentally in terms of system architecture, materials, controls, drivers, and photometric properties.63 Being flat, OLEDs have
privilege to cover large area without additional elements for light distribution and can adapt to any location, also they are non-toxic, cost-effective due to easy processing, less energy and requiring low operating voltage and giving complete control over color. In comparison to the current energy-saving light bulbs, OLEDs encompass the potential to be more efficient. In contrast to display application, lighting needs a high luminance. A luminance of $>5 \times 10^3$ cd/m$^2$ for lighting versus $\sim 10^2$ cd/m$^2$ for display. U.S. Department of Energy (DOE) has set a goal for OLED lighting up to 125 lm/W with an illuminance of 10,000 lm/m in 2015.$^{64}$ For such applications, structure with both hole and electron transporter is required. Reineke et al reported this type of structure with efficiency greater than incandescent bulbs and fluorescent lamps.$^{65}$ Such materials have critical issue of their lifetime being thermally-unstable. OLEDs also found applications in photocopiers, laser printing, sign boards, traffic signals,$^{66}$ etc.

For residential lighting, that consumes 23% of energy according to US department of energy. OLED-based lightening sources will work. Especially after the introduction of white OLED by Kido et al,$^{67}$ several attempts were made to increase the efficiency. WOLEDs with the efficiency of over 120 lm/W were reported by Reineke et al.$^{65}$ Due to high external quantum and power efficiencies of OLEDs for monochromatic emission of light, white light can be easily obtained by combining them in a single device. Many industrial companies working on production of OLED lightening sources and many lighting products based on OLED have been introduced by them with appealing designs. Some notable firms include the Philips, Osram, Konica Minolta, GE, Novaled, LG Chem, etc. (Fig. 1.12).

Thus, commercially wide spreading OLEDs will consume less energy, it will be amazing for several reasons (delaying global warming, conservation of fossil fuels, decreasing the trade imbalance, etc.). Ultimately, OLEDs are great for our economy and environment.
1.7 Materials for OLEDs

Two types of entities can be used for OLED applications, i.e., polymers and small molecular substances along with popularity of using organic metal complexes and dendronized structure. Organic materials are usually in the form of amorphous films in OLEDs where transportation of carriers is executed by hopping mechanism through the molecules/polymer segments from site to site because interaction of organics was carried out through van der Waals interaction which are very weak. Materials used in OLEDs possess certain characteristics. They are chemically, thermally and electrochemically stable and their light emission matches with suitable color coordinates of the CIE-system (Commission International de L’ Eclairage). Moreover, the efficient transportation of charge carriers is also an important prerequisite for OLED stuff.

Additionally, good film forming properties of these substances are also needed due to the fact that life-time of device becomes shorter by the crystallization of the thin films that results in suppression of charge carrier mobilities. For good film formation, small molecules having bulky side groups are more appropriate. Because crystallization is prevented due to presence of bulky substituents which leads to the formation of molecular glasses and thin films can be prepared easily from these materials by vacuum deposition.

For cathodic and anodic materials, metals are used as described previously. The important components of OLEDs are charge-transporting and emitting entities. Materials used as HTL have to exhibit HOMO levels in the order of -5.3 eV in order to meet the level of anode or HIL. Various hole-transporting materials have been developed but
most-commonly used are triarylamine and carbazole derivatives such as \(N,N'-\text{diphenyl-N,N'-bis(1-naphthyl)-(1,1''-biphenyl)-4,4'-diamine}\) (NPD), \(4,4',N,N'-\text{dicarbazol-biphenyl}\) (CBP), \(N,N'-\text{bis(3-methylphenyl)-N,N'-diphenylbenzidine}\) (TPD), \(\text{tris(4-carbazoyl-9-ylphenyl)amine}\) (TCTA) and \(4,4',4''-\text{tris(diphenyl amino)triphenylamines}\) (TDATAs). The structures are given in Fig. 1.13.

![Structures of NPD, TPD, CBP, TCTA, and TDATAs](image1.jpg)

**Figure 1.13:** Hole-transporting materials in OLED devices

The evolution of starburst molecules as HTL/HIL has increased the efficiency of OLED device along with the structural features that inhibits the crystallization. Recently, Kim *et al* have reported the starburst molecules, *i.e.*, PDA-TPE and TPA-TPE, working as hole-transporter and emitter with effective charge-transporting properties (Fig. 1.14).\(^7\)}
Figure 1.14: Hole-transporting STARBURST materials

Spiro-linked molecules also showed stable characteristics in terms of thermal behavior e.g., 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene (Spiro-TAD) with a $T_g$ of 133°C and can also be employed as electron-blocking layer.\(^76,77\)

Materials used for electron transport are often metal complexes like Alq3 and BAlQ.\(^56\) Alq\(_3\) is the most widely utilized stuff still today due to its high stability and also being green emitter. Other ETMs include molecules containing electron poor molecules with electron-withdrawing moieties such as 1,3,4-oxadiazole (OXD)\(^78\), triazole, triazine, pyridine, etc. 2-(Biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) was used as an ETM and showed excellent electron transport.\(^79\) 4,7-Diphenyl-[1,10]phenanthroline (BPhen),\(^80\) 2,2',2''-(1,3,5-phenylene)tris(1-phenyl-1H-benzimidazole) (TPBI),\(^81,82\) 3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole (TAZ)\(^83,84\) were also employed as electron-transporting materials. Structures of some common electron-transporting substances are given in Fig. 1.15.
1.7.1 Emitting materials

After the discovery of first green-emitting polymer based on fluorescent poly(p-phenylenevinylene) PPV as emitter in a single layer device, tremendous work has started to enhance the properties. PPV being insoluble, is difficult to process. A few years later its derivatives were developed employing solubilizing chains, *i.e.*, soluble PPV derivatives like poly(2-methoxy-5-(2’-ethyl)hexyloxy-\(p\)-phenylenevinylene) (MEH-PPV) and poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-\(p\)-phenylenevinylene] (OC1C10-PPV) (Fig. 1.16), along with improved electronic properties as the introduction of different alkoxy substituents showed the emission in red region. This turned out to be the most beneficial result that the emitted color of the polymeric materials can also be influenced by the side chain substitution pattern, which in turn was helpful to tune the properties by carrying out structural modifications. This concept was used later on a wider scale and is in practice currently.
PPV-based polymers have served as a model polymer and a subject of great interest. Polythiophene (PT) and its derivatives provided a new series of materials from red to blue light emission. The fact that injection of electrons in conjugated polymers is more difficult than hole injection is well-studied. The problem can be solved by a number of ways, i.e., by using the low work function metals for cathode. But as majority of such metals can be degraded easily under environmental conditions, this strategy is not advantageous as it affects the stability of device, e.g., for increasing the efficiency calcium can be used in place of aluminum but calcium is vulnerable to atmospheric degradation. The other strategy involves the improvement in the electron-accepting properties, i.e., electron affinity of semiconducting material and this idea was first used by researchers at Cambridge Display Technology (CDT) in 1993 by the use of an electron-withdrawing group. Cyano group was selected for attachment to vinylene bonds of MEH-PPV derivatives. Knoevenagal polycondesation of appropriate monomers leads to the dialkoxy-substituted PPVs, i.e., poly[5-(2-(ethylhexyloxy)-2-methoxycyanoterephthalyliden] (MEH-CN-PPV) and cyano-polyphenylene vinylene (CN-PPV) as depicted in Fig. 1.17. CN-PPV is a bright red fluorescent material having an internal efficiency of 0.2% for single layer device.
Poly (3-hexylthiophene) (P3HT) is a well-known red emitter due to its high charge carrier mobility.\textsuperscript{93, 94} High energy gap materials between HOMO and LUMO level are required for blue light emission. Polymers based on PPV can be designed for blue emitting electroluminescent materials by modifying the structure, \textit{i.e.}, by interrupting the conjugation of main chain but this tactic results in broadening of emission spectrum due to emission from the longest conjugated part. Poly(para-phenylene) PPP was used as a blue light-emitting material in PLEDs pioneerly by Jing \textit{et al} and Koch \textit{et al}\textsuperscript{95, 96} but, like PPV, solubility issue of PPP hinders its processability. To resolve this problem, suitable alkyl, aryl or alkoxy groups were introduced onto the PPP backbone by several research groups which increases its solubility in common organic solvents and hence processability. Heeger \textit{et al} reported the synthesis of monoalkoxy substituted PPPs, \textit{i.e.}, poly[2-(2' -ethylhexyloxy)-1,4-phenylene] (EHO-PPP), poly(2-decyloxy-1,4-phenylene) (DO-PPP) and poly[2-(6' -cyano-6'-methyl-heptyloxy)-1,4-phenylene] (CN-PPP), which are soluble in common organic solvents.\textsuperscript{97} Structures of alkylated polythiophene (PT) and PPP are given in Fig. 1.18.

Besides the conjugated homopolymers, many new conjugated copolymers were also synthesized, \textit{i.e.}, fluorene-carbazole, fluorene-thiophene copolymers, etc. in order to adjust the band gap and tuning the properties of materials. A variety of blue fluorescent
polymers have been designed and synthesized so as to enhance the color purity, brightness and efficiency but the development of highly efficient pure blue light-emitting polymers is still challenging to date.

1.7.2 Small molecules

Small molecules have advantage of being purified easily when compared with polymers. Since the discovery of emission from small molecules, different classes of molecular materials have been synthesized. Some notable small molecular emitters for OLEDs include: Alq₃, coumarin, rubrene, conjugated small molecules as well as some metal chelates, such as zinc and beryllium, copper and barium chelates (Fig. 1.19).⁹⁸ Highly efficient fluorescent red OLEDs were demonstrated by using rubrene and coumarin in the device as dopants, with current efficiency reached 6.4 cd/A and 9.0 cd/A at 100 mA/cm² respectively.⁹⁹ The development of green fluorescent OLEDs employing small molecules as dopants has achieved internal quantum efficiency of nearly 10% with CIE coordinates of (0.24, 0.62).¹⁰⁰

Moreover, three dimensional molecular structure of small molecules as designed by introduction of some substituents which not only increased the processability but also reduced the crystallization, i.e., a common problem to small molecular material that shorten device lifetime.

Figure 1.19: Small molecular emitting materials
1.8 Carbazole-based materials

Carbazole and its derivatives have attracted extensive interest because of their biological activity.\textsuperscript{67} Carbazole molecules exhibit high thermal, morphological, photochemical and environmental stability due to their complete aromatic nature, explored as HTLs due to their excellent hole-transporting capacity and high-charge carrier mobility.\textsuperscript{101} It can easily be functionalized at its 3,6-, 2,7 or $N$-positions\textsuperscript{102,103} and can be linked covalently both as building blocks in the main chain\textsuperscript{104} and pending groups in the side chain into polymeric systems.\textsuperscript{105}

Carbazole has high electron density at 3,6 positions and substitution at these position provides 3,6-disubstituted derivatives. These give rise to synthesis of molecular materials, poly(carbazole-3,6-diyl) and copolymers.\textsuperscript{106}

N-substituted carbazoles can be dimerized by means of chemical oxidation and used to synthesize 3,3'-bicarbazole.\textsuperscript{107,108} 3,3'-Bicarbazolyl derivatives have evolved as luminescent materials, which can be employed as the blue light-emitting materials in OLEDs. The glass-forming tendency of these bis-carbazolyl derivatives is superior to that of corresponding carbazole derivatives. Furthermore, they have low ionization potential and show good hole injection and transport properties as compared to carbazole materials.\textsuperscript{109} The bicarbazylum radical cations are stabilized by the delocalization of the charge throughout the extended $\pi$-conjugation between the two nitrogen atoms, thus, preventing the poly-coupling reaction. Bicarbazolyl containing polymers have been synthesized by modified Ullmann coupling reaction with glass forming ability having an emission maxima in the region of wavelength 410-412 nm (Fig. 1.20 (a) Poly([3,3']bicarbazol-9,9'-diyl)-1,2-phenyleneoxygenhexamethyleneoxy-1,2-phenylene), (b) Poly([3,3']bicarbazol-9,9'-diyl)-(9-(2-ethylhexyl)-3,6-carbazolylene)).\textsuperscript{110}

![Figure 1.20: Polymers employing bicarbazole moiety](image_url)
Similarly, copolymers of 3,3’-bicarbazole with phenylene and thiophene have been synthesized by Heck-coupling possessing the blue and greenish-blue emitting properties, respectively, due to electron donating thiophene moiety. Structures of copolymers, i.e., copoly[6,6’-bis(9-(2-ethylhexyl)carbazole-3-yl)thieno-(2,5)thienylidenevinylene] (EHCzThThV) and copoly[6,6’-bis(9-(2 ethylhexyl)carbazole-3-yl)phenylenevinylene] (EHCzPhV) are given in Fig. 1.21.

![EHCzThThV and EHCzPhV](image)

**Figure 1.21:** Bicarbazole polymers by Heck coupling

Pandya *et al* reported the synthesis of oligomers with 9,9’-dioctyl-3,3’-bicarbazole and 2,5-diaryl-1,3,4-oxadiazole by Suzuki-coupling, that served as host for phosphorescent green emitters (Fig. 1.22). 

![Green phosphorescent emitter polymer](image)

**Figure 1.22:** Green phosphorescent emitter polymer

Although poly(N-substituted-3,6-carbazoles)s possess short conjugation length compared with poly(2,7-carbazoles) but p-doping induces attractive electrical properties to them. For example, for *N*-ethyl derivative, conductivity ranges from $10^{-3}$ to $10^{-4}$ S cm$^{-1}$, that was increased later up to 1 S cm$^{-1}$ by electroreductive copolymerization with 1,4-dibromobiphenyl that results in introduction of phenylene units into the main chain.
In the fields of organic chemistry and material sciences, \(\pi\)-conjugated small molecules possessing definite chemical structures have been widely investigated for the use in various organic electronic devices ranging from (OLED), solar cells, organic (OFET), to active materials for two decades, owing to their high thermal and chemical stabilities, excellent electronic and optical properties, fine film-forming characteristics and easy purification processes.\(^{115-118}\) Moreover, the advantages of oligomers include the tuning of their properties by varying the molecular design either by selecting the suitable side chain and terminal groups for good processing, by changing the end-capping groups, by inserting certain groups and by altering the conjugated cores, charge-transporting and emissive properties can be controlled. So, optoelectronic properties can be optimized by distinct molecular design along with the processing.\(^{119-121}\)

Carbazole moiety has been extensively utilized either as a main core/ substituent due to its distinctive photo, electrical, and chemical properties as hole-transport, light-emissive materials for OLED devices\(^{122}\), solar cells\(^{123}\), non-linear optic (NLO) stuff\(^{124}\), organic photoconductors\(^{125}\), and as host materials for phosphorescence applications.\(^{126}\) Carbazole-based materials are being employed as host materials in phosphorescent OLED devices, due to their high-triplet energy levels and low-oxidation potentials proving very prospective.\(^{127}\) The formation of stable radical cations and efficient hole-mobility of carbazole results in its proficient use in organic semiconductor devices. Furthermore, introduction of carbazole to organic molecules can give rise to enhanced thermal stability and glassy-state durability.\(^{128}\) The synthesis of starburst oligocarbazoles with central pyrene core was reported by Ren \textit{et al} with high thermal and electrochemical stability which in turn increases the lifetime of OLED device.\(^{129}\) Figure 1.23 represents the structure of one of the starburst oligocarbazoles, \textit{i.e.}, 1,3,6,8-tetrakis(9,9',9''-trioctyl-9\(H\),9\(H\),9''\(H\)-[3,3':6',3''-tercarbazol]-6-yl)pyrene.
Carbazole-based polymeric materials and small molecules have both been employed, but the molecular materials can serve as model systems for polymeric systems because of their well-defined structure, monodispersity and high purity which arises due to purification of small molecules, i.e., (by chromatography, recrystallization etc) in contrast to polymers.\textsuperscript{130} Gong \textit{et al} reported the synthesis of carbazole-only oligomers with improved properties for OLEDs.\textsuperscript{131}

Use of polypyridine in OLEDs

As described earlier, conjugated polymer with high electron affinity are required for OLEDs. High electron affinity can be achieved either by attaching electron-withdrawing group to polymer or by employing electron deficient rings like pyridine in the polymer backbone.\textsuperscript{132} Electron affinity of pyridine-based polymers is high in contrast to phenylene containing polymers. Furthermore, polypyridine has better electron-transport properties and shows more resistance against oxidation. Due to high electron affinity of pyridine-based polymers, the use of relatively stable metals as electrodes is possible, e.g., Al, Au
or doped-polyaniline. Pyridine-based conjugated polymers have proved to be promising candidates for light-emitting device, particularly in case of symmetrically-configured alternating current light-emitting devices. The use of polypyridine as electron-transporting layer is very much pronounced with improved performance of LED. These polymers are highly luminescent materials. Fluorescence-quenching was avoided upon incorporation of pyridine due to inter system crossing (ISC) effect of heavy atom. These polymers have the issue of stability due to their sensitivity to oxygen and humidity. To overcome this problem, investigation of the iridium(III) polypyridine complexes as active layers in optical oxygen sensors has been carried out.

1.20 Fluorene-based materials

Fluorene nuclei have attracted much attention as active optoelectronic material for many years in OLEDs, solar cells and OFETs. Fluorene derivatives are considered to be significant candidates for OLEDs due to their high fluorescence as the name indicates. The chemical stability arises in terms of their rigid planar biphenyl structure. They possess good solubility which makes them solution processable due to substitution of different groups at C-9 position along with high thermal stability, good film-forming properties, high quantum yield of photoluminescence (PL) and electroluminescence (EL) efficiencies and liquid crystalline properties. Many spiro-functionalized fluorene derivatives at the bridge position of fluorene (C-9) were also synthesized because of their active use as organic functional material, having a specific steric configuration and physical properties. The design and synthesis of fluorene-based stuff can be controlled to obtain the desired properties due to its synthetic versatility at aromatic 2,7 and C-9 positions. Scherf et al first described the so-called ladder-type polymers (LPPP) that are known today as 9,9′-dialkylated polyfluorenes (Fig. 1.25).

![Polyfluorene, a ladder-type polymer](image)

R1: methyl; R2: phenyl; R3: n-hexyl

**Figure 1.25:** Polyfluorene, a ladder-type polymer
Fluorene derivatives find use as blue-emitting materials in (OLEDs). Solubility and photoluminescent quantum yield of number of a fluorene based compounds are suitable to be utilized in OLEDs but the disadvantage that limits their use in OLEDs is the trouble to inject charges in these materials that can be improved by introducing different electron donor and acceptor substituents in the structure to alter the HOMO and LUMO energy levels. Well defined poly(2,7-flourene) have been prepared through palladium-catalyzed Suzuki-couplings which show strong blue emission (Fig. 1.26).

![Suzuki-coupled synthesized polyfluorenes](image)

**Figure 1.26:** Suzuki-coupled synthesized polyfluorenes (poly-2,7-fluorene derivatives)

PFs have poor spectral stability due to formation of aggregates in solid state that results in yellow emission and hinders the use of these materials as blue emitters in OLEDs and because of oxidation of fluorene on C-9 due to incomplete alkylation. Both of these problems can be resolved by purification and introduction of bulky substituents to fluorene core which result in increased Tg and reduced excimer formation. Recently, novel carbazole-fluorene-based copolymers were synthesized through Suzuki-coupling with improve spectral stability for blue OLEDs by using sterically-hindered pendants. Several highly-efficient red-emitting phosphorescent PLEDs have been reported that employ PFs as host material, with iridium or osmium complexes serving as phosphorescent dopants. Palladium-catalyzed Suzuki-coupling results in PFs-based hosts for green emitting phosphors (Fig. 1.27).

![Green emitting polyfluorenes](image)

**Figure 1.27:** Green emitting polyfluorenes
Fluorene derivatives do not have good hole-transport property,\textsuperscript{156, 157} however, it can be enhanced by incorporating triarylamine groups.\textsuperscript{158} Thus, for improving the hole-transporting properties of fluorene-based materials and developing new light-emitting materials, many research groups have focused to introduce triarylamine groups into the backbones of light emitting compounds.\textsuperscript{159}

Qing \textit{et al} report the synthesis, properties and crystal structure of fluorene containing triphenyl amine moieties (Fig. 1.28: 2,7-bis[4-(diphenylamino)phenyl]fluorene) in this context.\textsuperscript{160}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.28.png}
\caption{Oligofluorene-containing triphenylamine moiety}
\end{figure}

Small molecular fluorene-based materials have the advantage of purification to avoid aggregate formation. Dendrimers based on carbazole-fluorene were synthesized with improved hole-transporting properties for multilayer OLEDs applications with increased thermal stability owing to carbazole units at periphery (Fig. 1.29 (a) 9’,9”-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis-9’ H-9,3’,6’,9’ -tercarbazole (OFC-G2), (b) 9’9’ -(9,9’-spirobi[fluorene]-2,7-diyl)bis-9’H-9,3’,6’,9’ -tercarbazole (SBFC-G2).\textsuperscript{161}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.29.png}
\caption{Carbazole-fluorene dendrimers}
\end{figure}

Recently, the fluorene-based fluorophores have been reported, being end-capped by tetraphenylethene (TPE) groups with superb thermal stability as compared to fluorene-
only materials with strong fluorescence in solid state and are used for fabrication of blue OLED (Fig. 1.30).\(^{162}\)

![Diagram](image)

**Figure 1.30:** Fluorene-TPE polymer

Moreover, bifluorene core-based substances with electron-donating and accepting-moieties were synthesized by Grisonio *et al* in an attempt to tailor the properties by the use of suitable functional groups and end-capping materials (Fig. 1.31).\(^{163}\)

![Diagram](image)

**Figure 1.31:** Fluorene/carbazole and fluorene/thiophene oligomers

### 1.21 Perylene based materials

Perylene-3,4,9,10-tetracarboxydiimides (PDI) are the most attractive efficient molecular materials with fascinating properties. They are polycyclic aromatic nuclei with excellent photophysical properties. The general structure of perylene diimide is shown in Fig. 1.32.
Figure 1.32: General structure of perylene diimide

Owing to their excellent thermal and photo-stability, unique optoelectronic properties and high luminescence efficiency, perylenetetracarboxylic diimides (PDIs) have found their way in wide array of applications to the current research of academia and industry.\textsuperscript{164-166} These are attractive electron-accepting, n-type molecular semi-conducting materials and proved to be active functional compounds for organic electronic applications such as in OLEDs,\textsuperscript{167} solar cells,\textsuperscript{168} artificial light-harvesting complexes,\textsuperscript{169} OFETs,\textsuperscript{170} etc. PBIs encompass the advantages of synthetic simplicity, easy purification and better solubility. The PDI can be derivatized using its imide positions and bay region with a variety of substituents that are useful for tuning its properties upto desired level for a variety of applications.\textsuperscript{171-176} Various bay-functionalized PDIs with appealing properties have been synthesized subsequently.\textsuperscript{177}

Substitution at the imide positions could improve the solubility of PDIs with very negligible effect on optical properties of 3,4:9,10-perylenebis(dicarboximide)s while the packing behavior of PDIs in the solid state is also affected.\textsuperscript{178-185} More pronounced effect on optical and redox properties of these chromophores can be attained by direct substitution of the perylene nucleus at bay position along with other key benefits, such as, bay substitution minimizes the $\pi-\pi$ stacking by creating twist in the structure that results in improved solubility of the dye and also provides additional sites for the attachment of other chromophores besides the imido positions, which serves as building block for construction of complex systems.\textsuperscript{186} Consequently, the bay-functionalization approach is vital for controlling the chemical structures and physical properties of PDI dyes.
1.2.1.1 Commonly-used precursors of perylene

The most commonly-used precursors of perylene are shown in Fig. 1.33 including unsubstituted perylenebis anhydride (a), 1,7-dibromoperylenebis anhydride (b), 1,6,7,12-tetrabromoperylenebis anhydride (c), 1,6,7,12-tetrachloroperylenebis anhydride (d).

![Figure 1.33: Commonly-used precursors of perylene](image)

Bay-substituted perylene derivatives are very common due to very low solubility of unsubstituted perylene. Substitution at bay position results in twisted structure with limiting intermolecular interaction, thus increasing the solubility and providing variety of synthetic routes.\textsuperscript{187} Imidizat ion of perylene anhydride can be executed with aliphatic and aromatic amines by simple condensation with the difference in case of aromatic amines, high-boiling solvent, i.e., quinoline, molten imidazole is needed due to their low reactivity, while aliphatic amines can work well with other solvents even water.\textsuperscript{188, 189}

The substitution of halogen atoms (-Cl, -Br) at bay position by various nucleophiles can result in a variety of molecular designs. Perylene derivatives with electron-donating substituents at bay position show bathochromic shift as compared to unsubstituted PBIs, while substitution with electron-accepting groups leads to hypsochromic shift.\textsuperscript{190} Feng et al reported two novel perylene dyes by substitution at carbonyl group of perylene core.
with enhanced photophysical properties. Emission in the red region of spectrum provides basis for designing other PDIs (Fig. 1.34).\textsuperscript{191}

![Figure 1.34: Red-emitting perylene derivatives](image1)

Moreover, copolymers of perylene and oligo(p-phenylene ethynylene) moieties were synthesized by Hagihara–Sonogashira cross-coupling possessing efficient electron and energy-transporting properties due to their donor-acceptor system (Fig. 1.35).\textsuperscript{192}

![Figure 1.35: Perylene-PPV polymer](image2)

Dubey \textit{et al} established the synthetic route for mono and di bay-substituted functionalized pyrrolidinyl moiety to perylene core which can serve as synthons for attachment of bulky groups and, most importantly, possesses supplementary sites through which other chromophores can attach close to perylene core and can serve as building blocks for the
construction of complex light-harvesting arrays and artificial photosynthetic systems. Structures are given in Fig. 1.36 (a) DB-1,7-PDI-C$_{60}$, (b) N,N’-dioctyl-1-pyrroldinyl-6-[2-(hydroxymethyl)pyrroldinyl]perylene-3,4,9,10 tetracarboxy diimide.

**Figure 1.36:** Light-harvesting perylene-based material

Recently, synthesis and separation of 1,6 and 1,7 symmetric and asymmetric regioisomers of perylene bisimides were carried out efficiently to address the key problem in purification of regioisomers providing a route of designing systems for colorful dyes with enhanced properties (Fig. 1.37).

**Figure 1.37:** Regioisomeric synthesized perylene derivatives
1.2.2 Plan and objectives of work

A survey of literature indicates that carbazole, fluorene and perylene-based materials display a wide range of applications in organic electronics especially in light-emitting diodes (LEDs). The objective of current work was to synthesize polymeric and non-polymeric materials as potentially active for applications in OLEDs as emitter, hole and electron-transporting materials.

The synthesis of copolymers of carbazole and pyridine was planned to achieve the advantage of having both hole and electron-transporting moieties in the same unit as electron injection is more difficult than hole injection. Furthermore, the presence of electron acceptor moiety in the system helps to emit in the blue region. The study of effects of different chain-lengths and substitution with electron-donating and electron-accepting groups on the thermal and photophysical properties was also intended.

An additional series of polymers with increased carbazole content was designed in order to probe the thermal and charge-transporting behavior in comparison with the above-mentioned polymers. For this rationale, 3,3’-bicarbazolyl systems were used for polymerization due to better properties of bis-carbazole moiety as indicated by a scan of literature. Towards this end, syntheses were carried out by an economical and simple modified Chichibabin reaction. The generalized scheme specified below as:

**General synthetic route adopted for polymerization**
The plausible mechanism is given under:

**Proposed mechanism for pyridine ring formation**

The small molecular stuff is also utilized for OLEDs due to simplicity and ease of purification. The synthesis of different oligomeric compounds was planned by Suzuki cross-coupling with only carbazole content and also with fluorene-carbazole, by changing the content ratio of both moieties in order to study and compare the effect on properties. Fluorene was selected due to its emission in blue region of spectrum and its excellent stability. Earlier, fluorene/carbazole oligomers are known all-through C-C bond, however, we have end-capped all the materials through nitrogen of carbazole moiety. Synthesis was carried out by the given general route:
General synthetic route adopted for synthesis of molecular materials
Boronic acid + Bromo derivative $\rightarrow$ oligomeric product

**Boronic acid used**

**Used bromo derivatives**

The general mechanism of Suzuki coupling is shown below:

**General mechanism of Suzuki coupling**

The next target was synthesis of small compounds of perylene. Perylene is selected due to its efficient n-transport behavior and easy purification since purity and homogeneity are pre-requisites for good device performance. In order to tune the emission color differently, substituted anilines and phenols were employed and their properties were compared. The adopted scheme for the synthesis provided below:
The synthesized compounds along with codes, selection reason and expected properties are provided below giving the key hypotheses:

### List of synthesized compounds with codes, structures and expected properties

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Code</th>
<th>Structure</th>
<th>Selection reason</th>
<th>Expected effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1a</td>
<td><img src="image1" alt="Structure" /></td>
<td>Combination of carbazole (donating) and pyridine (accepting) scaffolds in the same unit for better charge-transporting behavior and to study and compare the effect of different substituents varying from donating to accepting on material properties especially optical and electrochemical</td>
<td>Simply D-A interaction balances the charge transportation</td>
</tr>
<tr>
<td>2</td>
<td>P1b</td>
<td><img src="image2" alt="Structure" /></td>
<td>Decreased LUMO level due to (-\text{NO}_2) group for easy electron injection</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>P1c</td>
<td><img src="image3" alt="Structure" /></td>
<td>Increased conjugation length due to donating (-\text{OH}) group</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><strong>P1d</strong></td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>High HOMO level with increased band gap because of -Br group</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><strong>P2a</strong></td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>Improved transporting behavior throughout series with enhanced solubility</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><strong>P2b</strong></td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>Switching the alkyl chain length for improved solubility and to observe its effect on other material properties</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td><strong>P2c</strong></td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>Decrease in absorption bandwidth with a more-decreased LUMO level due to octyl level due to octyl chain</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td><strong>P2d</strong></td>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>Enhanced emission wavelength due to combining effect of octyl and -OH groups</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td><strong>P3a</strong></td>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>Increased electron density with a high HOMO level</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td><strong>P3b</strong></td>
<td><img src="image7" alt="Chemical Structure" /></td>
<td>Increase of carbazolic content in polymer by using dimeric carbazole for better transporting properties, keeping same substituents to set a rationale</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Enhanced hole transportation due to increased donor content</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High HOMO level with low band gap</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P3c</td>
<td><img src="image1" alt="Diagram of P3c" /></td>
<td>Improved accepting properties due to -NO₂ group</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P3d</td>
<td><img src="image2" alt="Diagram of P3d" /></td>
<td>Lower HOMO level with increased red-shifted absorption and emission wavelengths</td>
<td></td>
</tr>
</tbody>
</table>

To study oligomeric c/f hybrids by varying ratios of carbazole/fluorene and carbazole-only dyes by changing the end-capping materials

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CFT</td>
<td><img src="image3" alt="Diagram of CFT" /></td>
<td>Effect of central carbazole moiety on conjugation by diend-capping</td>
</tr>
<tr>
<td></td>
<td>CCP</td>
<td><img src="image4" alt="Diagram of CCP" /></td>
<td>Terminal nitrogen-coupled carbazole-only dye relative to formerly-reported pentamer by coupling at 3,6 positions</td>
</tr>
<tr>
<td></td>
<td>CCT</td>
<td><img src="image5" alt="Diagram of CCT" /></td>
<td>Effect of shortening the carbazole content</td>
</tr>
<tr>
<td></td>
<td>CCF</td>
<td><img src="image6" alt="Diagram of CCF" /></td>
<td>Single-end capping to study effect of terminal alkylated carbazole</td>
</tr>
<tr>
<td>17</td>
<td>CFD</td>
<td>Outcome of increased fluorene content by incorporating central fluorene moiety</td>
<td>Better optical properties and electrochemical stability due to increased conjugation</td>
</tr>
<tr>
<td>18</td>
<td>CFM</td>
<td>Comparing monoanalog of CFD with other singly end-capped dyes</td>
<td>Improved optical and electrochemical properties due to more conjugation</td>
</tr>
<tr>
<td>19</td>
<td>CFC</td>
<td>Changing end-capping moiety with central fluorene unit</td>
<td>Lambda increases when compared with CCP owing to fluorene</td>
</tr>
<tr>
<td>20</td>
<td>PM</td>
<td>Effect of donor group at imide position</td>
<td>High HOMO value due to D-A-D interaction</td>
</tr>
<tr>
<td>21</td>
<td>POM</td>
<td>Effect of symmetrical molecule with similar donating groups on properties</td>
<td>Increased thermal stability due to symmetry, rigidity</td>
</tr>
<tr>
<td>22</td>
<td>PDM</td>
<td>Outcome of bulky substituents at bay and imide position</td>
<td>Increased red-shift of absorption and emission with peak broadening due to bulky substituents</td>
</tr>
<tr>
<td>23</td>
<td>P2N</td>
<td>Increased band gap with broadened peaks</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>P3N</td>
<td>Effect on materials’ properties by changing the position of accepting group at imide position considering the crowding and symmetry</td>
<td>High LUMO level as a result of D-A-A interaction</td>
</tr>
<tr>
<td>25</td>
<td>P4N</td>
<td>Better thermal stability due to planarity</td>
<td></td>
</tr>
</tbody>
</table>
2.1 Synthesis, characterization and studies of carbazole-pyridine copolymers

Towards the synthesis of polymers, first step involved the alkylation of carbazole. Carbazole was alkylated on the nitrogen atom by butyl/octyl alkyl halides in a diphasic system of benzene:water using the phase transfer catalyst by the reported method.\textsuperscript{195, 196} Products were obtained in excellent yield after recrystallization/column chromatography and characterized through IR and NMR with vanishing signal of N-H and appearing new signals of alkyl group in the aliphatic region. In the subsequent step, N-alkylated carbazoles were acetylated with acetyl chloride at 3,6-positions by Friedel-Craft acylation using aluminum chloride as a catalyst under anhydrous condition in good yield.\textsuperscript{197} 3,6-Diacetyl-N-alkyl carbazoles served as monomers for the synthesis of different polymers (Scheme 2.1).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{Scheme 2.1:} Synthesis of N-alkyl carbazole and corresponding monomers}
\end{tikzpicture}
\end{center}

The characterization of monomers involves FTIR, NMR and GC-MS. In FTIR distinguished absorption of C=O of acetyl appeared at 1705 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR indicated the appearance of characteristic peak for acetyl protons at δ 2.75 ppm as a singlet with the presence of two sets of doublets and a doublet of doublet in the aromatic region with the disappearance of multiplet. Similarly, in \textsuperscript{13}C-NMR, a peak at δ 198.1 ppm for (C=O) of acetyl group confirmed the acetylation.

GC-MS showed a molecular ion peak at m/z 363 (M\textsuperscript{+}) and 264 (100\%) due to loss of methyl group of acetyl and six alkyl groups from octyl chain.
3,6-Diacetyl–N-octyl carbazole was finally confirmed by single crystal X-ray crystallography (Fig 2.2). The crystal was grown by recrystallization in ethanol.

The polymers were synthesized from the corresponding monomers via modified Chichibabin reaction using ammonium acetate in glacial acetic acid by generating the pyridine ring in situ upon reflux in good yield as shown in (Scheme 2.2) and oligomeric fractions were separated by successive fractionation. Modified Chichibabin reaction entails the use of ammonium salt with glacial acetic acid that creates pyridine ring in situ with increased yield in contrast to original Chichibabin reaction that uses the
pyridine ring itself employing ammonia to generate substituted pyridines with low yield (almost 20%) and for some cases, yield was increased upto 30% by utilizing costly catalyst. In modified Chichibabin reaction, yield has been increased up to 20-30% than original under cheaper conditions avoiding the use of pyridine as reactant, so this reaction proves to be more efficient than the traditional Chichibabin reaction. The copolymers of carbazole-pyridine are novel class of polymers that were achieved by a cheaper method in contrast to previously used costly methods that involves the use of catalyst.

\[ \text{Scheme 2.2: Synthesis of polymers (P1, P2)} \]

The physical constants of synthesized polymers are given in Table 2.1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>m.p. (°C)</th>
<th>Rf</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1a</td>
<td>C₄H₉</td>
<td>H</td>
<td>138-140</td>
<td>0.35</td>
<td>44</td>
</tr>
<tr>
<td>P1b</td>
<td>C₄H₉</td>
<td>NO₂</td>
<td>158-160</td>
<td>0.45</td>
<td>49</td>
</tr>
<tr>
<td>P1c</td>
<td>C₄H₉</td>
<td>OH</td>
<td>151-153</td>
<td>0.27</td>
<td>40</td>
</tr>
<tr>
<td>P1d</td>
<td>C₄H₉</td>
<td>Br</td>
<td>99-102</td>
<td>0.45</td>
<td>66</td>
</tr>
<tr>
<td>P2a</td>
<td>C₈H₁₇</td>
<td>H</td>
<td>104</td>
<td>0.55</td>
<td>39</td>
</tr>
<tr>
<td>P2b</td>
<td>C₈H₁₇</td>
<td>NO₂</td>
<td>107-109</td>
<td>0.25</td>
<td>46</td>
</tr>
<tr>
<td>P2c</td>
<td>C₈H₁₇</td>
<td>OH</td>
<td>131-134</td>
<td>0.15</td>
<td>42</td>
</tr>
<tr>
<td>P2d</td>
<td>C₈H₁₇</td>
<td>Br</td>
<td>118</td>
<td>0.47</td>
<td>40</td>
</tr>
</tbody>
</table>

Where: dec= decomposition
The polymers were characterized through FTIR, $^1$H-NMR, $^{13}$C-NMR and elemental analysis while the molecular weights were determined by static laser light-scattering experiment.

FTIR possesses characteristic peak due to C=N stretching vibration in the range of 1644-1631 cm$^{-1}$ for all the polymers indicating the pyridine ring formation with removal of peak at 1715 cm$^{-1}$ while peaks at 3415 for OH and at 1523 cm$^{-1}$ for NO$_2$ group respectively.

In $^1$H-NMR, the disappearance of signals of acetyl protons at 2.75 ppm and presence of complex pattern of splitting with peak-broadening in the aromatic region indicated the polymerization. The $^1$H-NMR spectrum of one of the representative polymers presented in Fig. 2.3. In $^{13}$C-NMR, the peaks for aromatic carbons appeared in the range of $\delta$ 150.1-109.5 ppm.

**Figure 2.3:** $^1$H-NMR spectrum of polymer P1a

SLLS experiment was performed to calculate the weight-average molecular weight of polymers in THF solutions. For this purpose, different concentrations of polymer in THF were prepared and filtered through PTFE filter (0.2 $\mu$) to remove the dust particles completely. Sample tubes were pre-dried first by washing on acetone assembly, drying overnight in oven and eliminating the effect of light covering with aluminum foil. In the static laser light scattering (LLS) technique, the angular dependence of the excess absolute time-average scattered intensity, the so-called Raleigh ratio $R_{vv}(q)$ at a scattering angle $\theta$, is measured. The molecular weights of the polymers in a dilute solution at a concentration $C$ can then be obtained on the basis of following equation:
\[
\frac{K_c}{R_{\text{vv}}(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} \right) < R_g^2 > q + 2A_2C
\]

Where \( K = 4\pi^2 n^2 (\text{dn}/\text{dC})^2/N_{\lambda_0} \lambda_0^4 \) and \( q = (4\pi n/\lambda_0)\sin (\theta/2) \) with \( N_A, \text{dn}/\text{dC}, n \) and \( \lambda_0 \) being Avogadro's number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light in vacuo, respectively. \( M_w \) is the weight average molar mass; \( A_2 \) is the second virial coefficient and \( < R_g^2 > Z^{1/2} \) is the root-mean square Z-average radius of gyration of the polymer chain. dn/dC can be measured by plotting different prepared concentrations of polymeric solutions versus various voltages. The obtained values of \( x, y \) from graph, when inserted into the following formula, i.e., \( \text{dn}/\text{dC} = \text{dn}/\text{dv} \times \text{dv}/\text{dC} \) give dn/dC value while ‘n’ is the refractive index of used solvent and can be calculated or obtained from literature. By measuring \( R_{\text{vv}}(q) \) at a set of \( C \) and \( \theta \), \( M_w, < R_g > Z \) and \( A_2 \) can be determined from a conventional Zimm plot which incorporates \( q \) and \( C \) extrapolation on a single grid. There are experimental points at all grids except along the lower line (the \( \theta = 0 \) line) and the left-most line (the \( C = 0 \)). The values of \( M_w \) and \( < R_g > Z \) were calculated from the slopes of \([Kc/R_{\text{vv}}(q)]C \rightarrow 0 \) vs \( q^2 \) and \([Kc/R_{\text{vv}}(q)]q \rightarrow 0 \) vs \( C \) and the intercept of \([Kc/R_{\text{vv}}(q)]q \rightarrow 0, C \rightarrow 0 \), respectively. Polymers with butyl chain have the molecular weights in the range of 0.56-0.12 \( \times 10^5 \) (g/mol) while octyl chain polymers molecular weight lie in the range of 1.28-2.43 \( \times 10^5 \) (g/mol). The results indicate that molecular weights of octyl chain polymers are almost two fold higher than the polymers having the butyl chain. Moreover, polymers with bromo group (P1d, P2d) exhibit low molecular weight as compared to other groups while the polymers with NO2 group in second series show the highest MW probably due to dipolar interaction of nitro group.

The MW of polymers positioned in the range that their processing can be easily done with no hurdle compared to high MW polymers due to their high viscosity. The molecular weights are provided in Table 2.2.

**Table 2.2:** Molecular weights of polymers P1, P2

<table>
<thead>
<tr>
<th></th>
<th>P1a</th>
<th>P1b</th>
<th>P1c</th>
<th>P1d</th>
<th>P2a</th>
<th>P2b</th>
<th>P2c</th>
<th>P2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_w) ( \times 10^5 ) (g/mol)</td>
<td>0.57</td>
<td>0.56</td>
<td>0.75</td>
<td>0.12</td>
<td>1.28</td>
<td>2.43</td>
<td>1.73</td>
<td>1.29</td>
</tr>
</tbody>
</table>
2.1.1 Thermal properties
The thermal properties of the two series of polymers, P1 and P2, were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). For TG, the samples were heated (Perkin Elmer Thermal Analysis System 409) in the range of 25-800°C at a heating rate of 10°C/min and at a nitrogen gas rate of 80mL/min. Polymers P1 and P2 lost weight gradually during the early phase of the experiment. A thermogravimetric curve of P1a is shown in Fig. 2.4.

![Figure 2.4: TG thermogramm of P1a](image)

The combined TG thermograms for polymers P1 and P2 are shown in Fig. 2.5.

![Figure 2.5: Combined TG curves of P1, P2](image)

The thermal analysis results indicate that polymers P1 and P2 have high $T_d$ and good thermal stability above 300°C, which is very attractive feature for fabricating the stable organic electroluminescent devices. The results of thermal analysis are given in Table 2.3.
Table 2.3: Thermal data for polymers, P1 and P2

<table>
<thead>
<tr>
<th></th>
<th>P1a</th>
<th>P1b</th>
<th>P1c</th>
<th>P1d</th>
<th>P2a</th>
<th>P2b</th>
<th>P2c</th>
<th>P2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d$ (°C) $^1$</td>
<td>380</td>
<td>300</td>
<td>265</td>
<td>300</td>
<td>376</td>
<td>295</td>
<td>400</td>
<td>295</td>
</tr>
<tr>
<td>$T_g$ (°C) $^2$</td>
<td>154</td>
<td>165</td>
<td>161</td>
<td>170</td>
<td>124</td>
<td>160</td>
<td>158</td>
<td>164</td>
</tr>
</tbody>
</table>

$^1$ Decomposition temperature determined by TG at heating rate of 10°C/min under N$_2$ atmosphere

$^2$ Glass transition temperature determined by DSC at heating rate of 10°C/min under N$_2$ atmosphere, 2nd run

For DSC, the samples were first heated to melting, cooled to the glassy state and reheated to determine the glass transition temperature ($T_g$). A representative DSC graph for P2a is shown in Fig. 2.6. $T_g$ is calculated from the second heating curve. Almost all the polymers manifest $T_g$ above 150°C as data are given in Table 2.3.

![DSC thermogram of P2a](image)

Figure 2.6: DSC thermogram of P2a

2.1.2 Photophysical Properties

The photophysical properties including absorption and emission spectral studies of the polymer were investigated as solutions in chloroform. Figure 2.7 shows the absorption spectra of the two series of polymers.
The solution of P1a exhibits an absorption maximum at 301 nm along with a shoulder peak at higher wavelength. Similarly, P1b, P1c and P1d have \( \lambda_{\text{max}} \) values of 282, 285 and 300 nm, respectively. Distinct shoulders are observed for all of the four polymers towards higher wavelengths. Similar spectra are obtained for polymers of series P2. The \( \lambda_{\text{max}} \) values are 291, 284, 291 and 289 nm for P2a, P2b, P2c and P2d, respectively, along with the distinct shoulders. The main peaks on the graphs are attributed to \( \pi \) to \( \pi^* \) transition and the shoulders correspond to \( n \) to \( \pi^* \) transitions in the respective materials. A comparison of the photophysical properties of the synthesized polymers may be made with structurally-related polymers previously synthesized by Zheng et al.\(^{199} \). The observed difference in the absorption spectra of both polymer series arises due to the lengths of alkyl chain. As the chain length increases, there is a strong decrease in bandwidth of absorption and emission bands.\(^{200} \) By comparing both series of polymers, the shifting in absorption maxim to an upper limit is observed by increasing chain length.\(^{201} \) Furthermore, polymers with similar groups in both series show almost similar absorption maxima but the apparent differences in going from one to other are due to the electron-donating and electron-withdrawing nature of the substituents. The additional absorption peak in the absorption spectrum of P1c is due to optical transition attributed to presence of auxochromic OH group which increases the conjugation length\(^{202} \) and becomes part of extended chromophore. This effect is absent in other polymers.
Table 2.4: Absorption and emission spectroscopic data of polymers, P1 and P2

<table>
<thead>
<tr>
<th></th>
<th>P1a</th>
<th>P1b</th>
<th>P1c</th>
<th>P1d</th>
<th>P2a</th>
<th>P2b</th>
<th>P2c</th>
<th>P2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max, abs}}$ (nm)</td>
<td>301</td>
<td>282</td>
<td>285</td>
<td>300</td>
<td>291</td>
<td>284</td>
<td>291</td>
<td>289</td>
</tr>
<tr>
<td>$\lambda_{\text{max, em}}$ (nm)</td>
<td>417</td>
<td>424</td>
<td>397 (491)</td>
<td>421</td>
<td>426</td>
<td>435</td>
<td>400 (524)</td>
<td>431</td>
</tr>
</tbody>
</table>

The Photoluminescence (PL) spectra of the polymer solutions of series P1 and P2 in CHCl₃ are shown in Fig. 2.8. Polymers P1a, P1b, P1c and P1d emit maximum at 417, 424, 397 (491) and 421 nm respectively whereas the polymers P2a, P2b, P2c and P2d emit maximum at 426, 435, 400 and 431 nm respectively. Polymers P1c and P2c having hydroxyl functionality show an extra emission band at 491 and 524 nm respectively. Polymers give a maximum emission peak centered ranged from 468 to 486 nm individually. These suggest that polymers solutions in CHCl₃ should emit blue-green light. The results of optical studies are given in table 2.4.

Figure 2.8: Photoluminescence spectra of polymers P1 and P2 in CHCl₃ solution 10⁻⁵M

2.1.3 Electrochemical Properties

The electrochemical behavior was determined through cyclic voltammetry on glassy carbon electrode using TBAP as supporting electrolyte (0.1 M) in DMSO with platinum counter and sat Ag/AgCl reference electrode with concentration of sample solution (1 mM). All the polymers of both series show almost identical behavior with irreversible oxidation peak and reversible reduction peak (Fig. 2.9). The oxidation peak arises due to electron-donor carbazole moiety while electron-deficient pyridine moiety causes the appearance of reduction peak. The anomalous behavior show by polymer (P2d) having a
reversible oxidation peak and partially reversible reduction peak suggested the high-lying HOMO level for this polymer. The HOMO values were calculated from the onset of oxidation potential using ferrocene as an internal standard (4.8 eV) and its values ranged for P1 series polymers from 5.32-5.47 eV with higher HOMO value for P1d polymer. For P2 series polymers, the HOMO value ranged from 5.27-5.38 eV. The similar trend for substitution pattern in both cases was observed. Moreover, as the position and substitution of nitrogen had pronounced effect on HOMO level, so polymers with octyl chain exhibited very close values matching to ITO that accounted for an easy hole injection. Thus, these polymers can act as a hole-transport layer for OLEDs.

The values of LUMO energy levels for these π-conjugated copolymers were estimated from the values of energy band gaps calculated from absorption threshold of UV-Visible spectrum and the values of HOMO energy levels. The values of LUMO levels also dropped considerably to 2.38-2.60 eV for P1 series and 2.29-2.52 eV for P2 series polymers.

**Figure 2.9:** Cyclic voltammograms of P1 and P2 in DMSO (1 mM) at glassy carbon working electrode, TBAP (0.1 M) supporting electrolyte, Ag/AgCl, platinum wire as reference and auxiliary electrode respectively, 100 mV/s scan rate

This trend appeared because of inclusion of electron deficient pyridine ring into polymer that reduces the electron injection barrier. So, inclusion of pyridine moiety has considerable effect on LUMO level. Thus, in conclusion polymers can serve as both electron and hole-transport layer in OLEDs. The energy level diagram of polymers with respect to ITO is shown in Fig.2.10 and data is provided in Table 2.5.
2.2 Synthesis, characterization and studies of bis-carbazole pyridine copolymers

Another series of carbazole-pyridine copolymers were synthesized employing the bicarbazolyl moiety in order to check the effect of increased carbazole content on the properties. For this purpose, oxidative dimerization of N-octyl carbazole was achieved using anhydrous ferric chloride in dry chloroform and product was obtained in high yield after recrystallization from ethanol. N-Octyl carbazole was selected for oxidative coupling due to the fact that octyl chain (although it decreases the glass transition temperature based on extra van der walls interactions as compared to butyl chain) but increases the solubility in a number of common organic solvents that is a pre-requisite of processing and thin-film formation. So, octyl chain was utilized throughout the synthesis. The N-octylated-dicarbazole was acetylated in the same manner as previously described at 6,6’ positions in good yield, after purification by recrystallization from ethanol, served as monomer (Scheme 2.3).
Scheme 2.3: Synthesis of N,N’-octyl-3,3’-biscarbazole and monomer

The characterization was performed by FTIR, NMR and elemental analysis. In FTIR, strong bands of alkyl stretching appear at 2981, 2858 cm\(^{-1}\) along with presence of strong C=O stretching at 1711 cm\(^{-1}\) that was absent in case of 3a. \(^1\)H-NMR indicated a characteristic peak at δ 2.65 ppm due to acetylenic protons along with the disappearance of multiplets from the aromatic region as in case of N-octyl-dicarbazole. Similarly, the presence of peak at δ 197.6 ppm for ketonic carbon in \(^{13}\)C-NMR, confirmed the synthesis of monomer while other aromatic carbons appeared in the range of 147.1-106.3 ppm and aliphatic carbons at their respective chemical shift values. Elemental analysis indicated the closeness between the calculated and found elemental compositions confirming the monomer synthesis.

Table 2.6: Physical constants of 3a and 3b

<table>
<thead>
<tr>
<th>Entry</th>
<th>m.p. (°C)</th>
<th>R(_f)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>75</td>
<td>0.38</td>
<td>72</td>
</tr>
<tr>
<td>3b</td>
<td>196</td>
<td>0.16</td>
<td>71</td>
</tr>
</tbody>
</table>

The monomer was polymerized by the same method as described above on increasing reaction time (Scheme 2.4). Polymers were obtained in good yield after fractionation in the identical manner and characterized through IR, NMR and elemental analysis while MW was determined by SLLS method.
Scheme 2.4: Synthesis of polymers (P3a-d)

FTIR results while demonstrating the formation of polymers by the disappearance of C=O stretching and the presence of strong C=N stretching in the range of 1654-1640 cm\(^{-1}\), indicated the generation of pyridine ring \textit{in situ}. \(^1\)H-NMR results confirmed the synthesis of polymers owing to the appearance of broad signals as multiplets in the aromatic region and the disappearance of signal due to acetyl protons at δ 2.65 ppm. Aromatic carbons appeared in the range of 144.8-106.2 ppm (\(^{13}\)C-NMR) with no ketonic carbon, confirming the polymer formation. Elemental analysis proves the synthesis with close agreement of results between the found and calculated compositions. Physical data of polymers are given in Table 2.7.

Table 2.7: Physical constants of P3 polymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>m.p. (°C)</th>
<th>R(_f)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3a</td>
<td>H</td>
<td>160-162</td>
<td>0.27</td>
<td>68</td>
</tr>
<tr>
<td>P3b</td>
<td>Br</td>
<td>233 with dec</td>
<td>0.25</td>
<td>60</td>
</tr>
<tr>
<td>P3c</td>
<td>NO(_2)</td>
<td>151 with dec</td>
<td>0.13</td>
<td>51</td>
</tr>
<tr>
<td>P3d</td>
<td>OH</td>
<td>191-193</td>
<td>0.12</td>
<td>56</td>
</tr>
</tbody>
</table>

MW of polymers lies in range of 1.36-1.59x10\(^5\) (g/mol) (Table 2.8) and again P3b polymer showed the similar trend in the series, \textit{i.e.}, being the lowest. The MW was indicative of good processability of polymeric solutions.
Table 2.8: MW of P3 series polymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Molecular weight (10^5 g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3a</td>
<td>H</td>
<td>1.36</td>
</tr>
<tr>
<td>P3b</td>
<td>Br</td>
<td>1.38</td>
</tr>
<tr>
<td>P3c</td>
<td>NO_2</td>
<td>1.61</td>
</tr>
<tr>
<td>P3d</td>
<td>OH</td>
<td>1.59</td>
</tr>
</tbody>
</table>

The synthesized polymers are soluble in common organic solvents like CHCl_3, DCM, DMF, DMSO, DMSO and acetone at room temperature. The solubility data of polymers are given in Table 2.9.

Table 2.9: Solubility data of polymers: P1, P2, P3

<table>
<thead>
<tr>
<th>Entry</th>
<th>CHCl_3</th>
<th>DCM</th>
<th>DMF</th>
<th>DMSO</th>
<th>Acetonitrile</th>
<th>Acetone</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1a</td>
<td>++</td>
<td>++</td>
<td>-+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P1b</td>
<td>++</td>
<td>++</td>
<td>-+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P1c</td>
<td>++</td>
<td>++</td>
<td>-+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P1d</td>
<td>++</td>
<td>++</td>
<td>-+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P2a</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P2b</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P2c</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P2d</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>P3a</td>
<td>++</td>
<td>++</td>
<td>-+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>P3b</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>P3c</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>P3d</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
</tr>
</tbody>
</table>

++: highly soluble at r. t.; +: soluble at r. t.; +*: partially soluble; 
+*: soluble on heating; -: insoluble

2.2.1 Thermal properties

Thermal properties of the polymers were determined by Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). The thermal decomposition temperatures of these pyridine-core-polymers were found to be above 300°C, demonstrating that these polymers are thermally stable which is essential for lifetime of devices made from these substances. The thermal stability of these materials is on account of attachment of
pyridine moiety at 3 and 6 positions of carbazole that makes it non-planar and increases the thermal stability.\textsuperscript{204} The results are depicted in Fig. 2.11.

**Figure 2.11:** TG plots of the polymers P3

For DSC, samples were first heated to melting and then cooled to glassy state and reheated to determine the glass transition temperature (T\textsubscript{g}). All the polymers exhibit high T\textsubscript{g} values. Figure 2.12 shows the DSC graph of P3\textsubscript{a}. The results of DSC indicate the stability of polymers which in turn gives the strength of mechanical properties of devices and high morphological stability of films which is a prerequisite for applications in OLEDs.

**Figure 2.12:** DSC thermogram of P3\textsubscript{a}

Results of thermal analysis are given in Table 2.10.
Table 2.10: Thermal data of polymers P3

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3a</td>
<td>360</td>
<td>126</td>
</tr>
<tr>
<td>P3b</td>
<td>320</td>
<td>159</td>
</tr>
<tr>
<td>P3c</td>
<td>264</td>
<td>158</td>
</tr>
<tr>
<td>P3d</td>
<td>365</td>
<td>164</td>
</tr>
</tbody>
</table>

1 Decomposition temperature ($T_d$) measured at a heating rate of 10°C under nitrogen atmosphere

2 Glass transition temperature determined by DSC at a heating rate of 10°C under nitrogen atmosphere, 2nd run

2.2.2 Photophysical properties

The UV-Vis absorption spectra of all polymers were recorded in chloroform at room temperature as shown in Fig 2.13. The spectrum has broad absorption bands from 250-430 nm. The absorption spectra of all the polymers are identical in the region of 311-406 nm. The major absorption band in all the polymers originates from the $\pi-\pi^*$ transition of the biscarbazole moiety of conjugated polymer. The shoulder peak towards lower energy region derives from n-$\pi^*$ transition of lone pair of electrons of nitrogen atom. These polymers have a long tail band above 430 nm which may have arisen due to formation of charge-transfer conjugated complex by strong interaction of electron-deficient pyridine and electron-donating biscarbazole.\(^{199}\)

The fluorescence spectra of these polymers are recorded with the excitation wavelength corresponding to the maximum absorption wavelength of the polymers. The synthesized polymers possess D-A system with carbazole being donor and pyridine, acceptor unit. The polymer P3c exhibits the red-shifted absorption and emission profile as compared to other polymers revealing good acceptor properties owing to nitro group. The fluorescence spectra of polymers in CHCl$_3$ are illustrated in Fig 2.13b. The emission bands are sharp and narrow and display red shift compared to carbazole with considerable Stokes shift values. The PL spectral profiles of the polymers were found to be very similar. Photoluminescence spectra are located in blue region with emission maxima at 402, 406, 442, 435 nm. The results depict the blue light-emitting properties of the polymers in solution. The results are shown in Table 2.11.
Table 2.11: Absorption and emission data of polymers P3

<table>
<thead>
<tr>
<th>Entry</th>
<th>P3a</th>
<th>P3b</th>
<th>P3c</th>
<th>P3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max, abs}}$ (nm)</td>
<td>326, (389)</td>
<td>323, (400)</td>
<td>343, (411)</td>
<td>342, (409)</td>
</tr>
<tr>
<td>$\lambda_{\text{max, em}}$ (nm)</td>
<td>402</td>
<td>406</td>
<td>442</td>
<td>435</td>
</tr>
</tbody>
</table>

Figure 2.13: UV/Vis absorption and emission spectra of series P3 polymers in CHCl$_3$ 10$^{-5}$M

2.2.3 Electrochemical properties

In order to investigate the electrochemical properties of polymers P3a, P3b, P3c and P3d, cyclic voltammetry was employed and the cyclic voltammograms were recorded on glassy carbon electrode in the 1mM solution for each polymer containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte at a potential scan rate of 50 mV/s (Fig. 2.14). All the potentials were measured vs. Ag/AgCl as a reference electrode and for each measurement the ferrocence/ferrocenium (Fc) redox system was employed as an internal standard. During anodic scan, the onset of oxidation for P3a, P3b, P3c and P3d was found.
Figure 2.14. Cyclic voltammograms of P3a, P3b, P3c and P3d (1mM each) recorded at glassy carbon electrode in their DMSO solution containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte employing potential scan rate of 50 mV s⁻¹

Table 2.12: Electrochemical parameters of polymers P3a-d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Band gap (^a) (eV)</th>
<th>HOMO (^b) (eV)</th>
<th>LUMO (^c) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3a</td>
<td>2.851</td>
<td>-4.76</td>
<td>-1.909</td>
</tr>
<tr>
<td>P3b</td>
<td>2.684</td>
<td>-4.70</td>
<td>-2.016</td>
</tr>
<tr>
<td>P3c</td>
<td>2.793</td>
<td>-4.97</td>
<td>-2.177</td>
</tr>
<tr>
<td>P3d</td>
<td>2.639</td>
<td>-4.71</td>
<td>-2.071</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from the absorption threshold of UV-Visible absorption spectrum

\(^b\) HOMO was calculated employing ferrocence value of 4.8 eV below the vacuum level

\(^c\) Estimated from HOMO and band gap by using a relation: Band gap (E\(_{o-o}\)) = HOMO-LUMO

The copolymers show a quasi-reversible process. The HOMO energy levels of the copolymers P3a, P3b, P3c and P3d significantly decrease the energy barrier for the injection of holes in the emissive Alq\(_3\) (5.80 eV) from indium tin oxide (ITO) (4.80 eV). The values of LUMO energy levels for these \(\pi\)-conjugated copolymers were estimated from the values of energy band gaps calculated from absorption threshold of UV-Visible spectrum and the values of HOMO energy levels. The LUMO values dropped from -1.909 to -2.177 eV due to incorporation of electron-deficient pyridine ring into copolymer that reduces the electron injection barrier as related to structurally-similar copolymers reported by Guan et. al.\(^{205}\) The estimated values of HOMO and LUMO energy levels of copolymers P3a, P3b, P3c and P3d are gathered in Table 2.12. The
values of HOMO energy levels for these copolymers containing bicarbazole moieties depict that there may be a more feasible hole-injection contact as these values are relatively more close to the Fermi level of PEDOT (5.0 eV) as shown in Fig 2.15. The lower values of HOMO and LUMO of these P3a, P3b, P3c and P3d copolymers than the structurally-similar copolymers, reported in literature \(^{206, 111}\), are assigned to the extended \(\pi\)-conjugation in the copolymers in question. Moreover, all co-polymers have high band gap energy which accounts for their blue light emission. Based on the HUMO and LUMO level, these compounds may be good candidates as hole-transporting and electron-transporting materials for OLEDs.

**Figure 2.15:** Energy band diagram of polymers P3a-d with respect to ITO-PEDOT

### 2.3 Synthesis, characterization and studies of carbazole/fluorene small molecular materials

First step involves the alkylation of carbazole at nitrogen by reported method \(^{195, 196}\) and then subsequent di and mono brominations of \(N\)-octylcarbazole were carried out easily using 2.0 eq of \(\text{Br}_2\) in AcOH for di-bromo-\(N\)-octylcarbazole (1) and 1.0 eq of NBS/DMF for mono-bromo-\(N\)-octylcarbazole (3) \(^{207, 208}\). Brominating agent should be added in calculated amount to avoid poly-brominated product and also for bypassing bromination at alkyl chain, reaction must be carried out in dark. Both products were obtained in high yields after recrystallization (EtOH) and column chromatography (hexane). These were characterized by NMR and GC-MS. The \(^1\)H-NMR of 3,6-dibromocarbazole (1) possesses
three distinct signals in aromatic region (6H) with two doublets at δ 8.15 and 7.29 ppm and doublet of doublet at δ 7.56 ppm with disappearance of multiplet present in N-octylcarbazole. In GC-MS presence of M⁺ at m/z= 437 (100%) along with peaks 439, 435 (isotopic peaks for 2-Br atoms) confirms the structure. Similarly, in case of 3-bromo-N-octylcarbazole (3) two sets of multiplet appear along with two doublets in ¹H-NMR, while in GC-MS, M⁺ at m/z= 357 (100%) and 359 for one Br-atom prove the structure. The bromo-N-octylatedcarbazoles (1, 3) were converted to corresponding boronic acids by treating with n-BuLi (2.4, 1.2 eq for 1 and 3, respectively) to afford lithiation in dry THF (freshly-distilled) at -78°C, following the addition of tri-isopropyl boronate. Reaction was quenched with 2 M HCl that caused hydrolysis (Scheme 2.5). The boronic acids were obtained in 63, 61% yields, respectively. The reaction must be carried out in completely inert atmosphere and all apparatus should be oven-dried (03 hrs) to ensure complete removal of air and moisture. Boronic acids obtained were used without any further purification and characterization. Only their m.p. were matched with the reported ones. Corresponding boronic acids were prepared each time separately for coupling reaction.

**Scheme 2.5:** Synthetic route to N-octylcarbazole-di and mono boronic acids

Dialkylation of 2,7-dibromo and 2-bromofluorene at 9th position was executed by octyl bromide using pulverized KOH as a base to ensure maximum interaction in the presence of catalytic amount of KI in DMSO at room temperature. Products were obtained after purification by recrystallization (EtOH) and column chromatography (hexane) in good yields. Reaction should be effected in degassed DMSO under inert atmosphere to avoid formation of fluorenone due to oxidation. Both products were characterized through NMR and elemental analysis. Alkylation was proved by the presence of distinct
signals in the aliphatic region of both $^1$H and $^{13}$C-NMR. Elemental analysis revealed the calculated and found amounts for the atoms were in close agreement.

The transformation of dialkylation bromofluorenes (5, 7) to their corresponding boronic acids (6, 8) was conducted in a similar manner (Schemes 2.6 and 2.7, respectively) as described above for carbazoles under the same reaction conditions with 54 and 57% yields for 6 and 8, respectively. The only difference in both the syntheses is that boronic acid of alkylationated fluorene requires vigorous stirring otherwise gel would form.

**Scheme 2.6:** Synthesis of 9,9-dioctyl-9H-fluoren-2,7-diylboronic acid

The monoboronic acid (8) was not obtained by evaporation due to its very fine state; rather it was isolated by centrifugation for 1 hour at 1000 rpm. The synthesized boronic acids were in line with the reported melting points and used as such without further characterization and purification. They were freshly-synthesized for each experiment.

**Scheme 2.7:** Synthesis of 9,9-dioctyl-9H-fluoren-2-ylboronic acid

3,6-dibromo-9-octylcarbazole (1) was converted to 9-(6-bromo-9-octyl-9H-carbazol-3-yl)-9H-carbazole (9) as shown in Scheme 2.8 under Ulmann reaction conditions by treating with carbazole using CuI and 18-Crown-6, upon refluxing in o-dichloro benzene for four days under inert atmosphere. The reaction requires purging with nitrogen to ensure complete air removal for efficient coupling to occur. The product was isolated in 71% yield after being purified through column chromatography.
Scheme 2.8: Synthesis of bromo carbazolyl derivative (9)

The characterization of (9) is performed by NMR and APCI-MS techniques. In $^1$H-NMR, appearance of doublet of triplet at $\delta$ 7.29 ppm along with new signals in aromatic region, in contrast to prominent three signals in case of 3,6-dibromo-$N$-octylcarbazole (1), ensures the coupling of carbazole. Analogous to this, in $^{13}$C-NMR, a number of signals present in aromatic region confirm the coupling.

APCI-MS confirms the structure with peaks at 523.2 (M$^+$) and 525 for di-isotopic mass (Fig. 2.16).

Figure 2.16: Isotope pattern of derivative 9 in APCI-MS
In a similar manner, 2,7-dibromo-9,9’-dioctylfluorene (5) was also coupled to carbazole under same Ulmann coupling conditions (Scheme 2.9) to afford compound (10) in a 57% yield following purification by column chromatography.\textsuperscript{213}

\textbf{Scheme 2.9:} Synthesis of bromo-carbazolo fluorenyl derivative (10)

The characterization was effected by NMR and APCI-MS. The presence of three distinct sets of multiplets in \textsuperscript{1}H-NMR distinguished it from 2,7-dibromo-9,9’-dioctylfluorene. Also, in \textsuperscript{13}C-NMR, existence of a number of signals in aromatic region confirms the monoamination of dibrominated alkylfluorene with carbazole. In APCI-MS, appearance of characteristic isotopic pattern with peaks at 634 (M+) and 636 (M+2) proves the coupling as presented in Fig. 2.17.

\textbf{Figure 2.17:} (a) APCI-MS of bromo fluorene derivative (10) (b) Isotopic pattern of derivative (10)

The targeted compounds were achieved through Suzuki-cross coupling via Pd(0)-catalyzed reaction by the end-capping of synthesized bromo derivatives (9, 10) with the different synthesized boronic acid. A number of carbazole-fluorene dyes have been synthesized and compared on the basis of their properties.
Suzuki-coupling of 1.0 eq of carbazole diboronic acid (2) with 2.4 eq of compound (10) under standard reaction conditions using toluene:water (1:2) afforded the desired product in good yield (Scheme 2.10).214,208,162

Scheme 2.10: Synthesis of compound CFT

The product was characterized through FTIR, $^1$H-NMR, $^{13}$C-NMR, APCI-MS and elemental analysis. In IR, strong absorption at $\nu$ 3074, 2991, 2865 cm$^{-1}$ for sp$^2$ C-H stretch of aromatic ring and sp$^3$ C-H stretching vibration of alkyl chain indicated the coupling. Further it was confirmed by NMR analysis. In $^1$H-NMR, signals in aliphatic region for 85 protons, a triplet at $\delta$ 4.42 ppm due to protons present in the vicinity of nitrogen, i.e., N-CH$_2$ and complex pattern of signals appeared in aromatic region (mainly as multiplets). In $^{13}$C-NMR, signals arise for aromatic carbons in the range of 152.6-108.9 ppm and aliphatic carbons at their respective positions with most acidic methylene carbon of fluorene (9$^{th}$ carbon) at $\delta$ 55.7 ppm and N-CH$_2$ at $\delta$ 45.4 ppm. $^1$H-NMR spectrum of dye CFT is shown in Fig. 2.18.

Molecular structure was further confirmed through APCI-MS which exhibited a peak at 1387.9 (M+2H)$^+$. Elemental analysis ensured elemental composition to be in line with calculated one.
The other designed targeted compound was synthesized by SM coupling under similar reaction conditions consisting only of carbazole nucleus through coupling of bromo derivative (9) with carbazole diboronic acid (2) in 59% yield after purification (Scheme 2.11). The characterization was brought about by FTIR, NMR, APCI-MS and elemental analysis.

FTIR analysis indicates strong signals of sp\(^2\) C-H and sp\(^3\) C-H (stretching) at \(\nu\) 3077, 2972, 2849 cm\(^{-1}\). In \(^1\)H-NMR, new signals were present in aromatic region and, in aliphatic region, intense signals appeared for alkyl chain protons (51-H). In \(^{13}\)C-NMR, peaks for aromatic carbons were observed in the range of 145.9-109.0 ppm. APCI-MS gave a peak at 1164.8 [M+H]\(^+\) that prove the synthesis. Further confirmation was achieved through close consistency of found and calculated composition of atoms by means of elemental analysis.

The other targeted compound was obtained by coupling of (9) with carbazole monoboronic acid (4) via Suzuki coupling in the same manner in 61% yield (Scheme 2.12).
FTIR results again suggest the presence of alkyl chain by strong absorption at $\nu$ 2971 and 2859 cm$^{-1}$. The $^1$H-NMR spectrum of compound CCT is presented in Fig. 2.19. In $^1$H-NMR, occurrence of distinct sets of multiplets in aromatic region with appearance of signals (34-Hs) in aliphatic region confirms the coupling alongside $^{13}$C-NMR signals for aromatic carbons from $\delta$ 148.2-114.3 ppm.

APCI-MS contained a peak at 722.4 [M+H]$^+$ and a peak at 445.2 [M-octyl carbazole]$^+$ as shown in Fig. 2.20. This loss is feasible and more intense due to susceptibility of N-octylcarbazole for removal. Elemental analysis further confirmed the structure bearing close agreement between calculated and found elemental compositions.
The SM-coupling of carboxalonic monoboronic acid (4) with compound (10) was also conducted in good yield by the same method (Scheme 2.13).

Scheme 2.13: Synthesis of compound CCF

$^1$H-NMR reveals doublet of doublet at $\delta$ 7.97 ppm probably due to protons attached on fluorene close to methlenic carbon, with a number of multiplets in aromatic region. In $^{13}$C-NMR, signals of aromatic carbon present in the range of 151.2-108.2 ppm. Further confirmation of synthesized compound came through APCI-MS as presented in Fig. 2.21. APCI-MS demonstrated peaks at 833.5 [M+H]$^+$, 556.3 [M-N-octylcarbazole] and 385.1 [M-C$_{12}$H$_{26}$]. It is interesting to note that peak due to loss of alkyl group is more intense than carbazole-only material described previously. Elemental composition was also found close to the calculated one.
The next series of targeted compounds involved the Suzuki-coupling with the use of boronic acid of dialkylated fluorene (6 and 8). SM-coupling of fluorene-diboronic acid (6) with compound (10) yielded the product in 66% yield (Scheme 2.14) through increased reaction time that ensured maximum end-capping in contrast to the method applied by Grisorio et al in 2006 for bisfluorene end-capped at 2,7-positions by carbazolyl bromide via similar SM-coupling reaction.

Scheme 2.14: Synthesis of compound CFD

In FTIR, strong intense bands for alkyl and aryl groups indicated the coupling. $^1$H-NMR possesses a set of multiplets in aromatic region in the range of 8.21-7.30 ppm. In the same way, signals of aromatic carbons appear from 150.3-112.8 ppm in $^{13}$C-NMR.

Ultimate confirmation of structure was gained through MALDI-TOF that showed a peak at 1498.0 [M+2H]$^+$ (Fig. 2.22) and close uniformity in elemental composition between calculated and found values was noticed.
Fluorene-monoboronic acid (8) was Suzuki-coupled to compound (10) to form the singly end-capped material in good yield (Scheme 2.15).

\[
\text{C}_8\text{H}_{17} \text{C}_8\text{H}_{17} \text{N} \text{Br} \text{C}_8\text{H}_{17} \text{C}_8\text{H}_{17} \overset{\text{Pd}(\text{PPh}_3)_4/2\text{MK}_2\text{CO}_3}{\text{Toluene/ Reflux 48 hr}} \text{C}_8\text{H}_{17} \text{C}_8\text{H}_{17} \text{N} \text{B} \text{OH} \text{OH} (8) (10) (\text{CFM})
\]

**Scheme 2.15:** Synthesis of compound CFM

\(^1\text{H}-\text{NMR}\) of CFM is provided in Fig. 2.23. In \(^1\text{H}-\text{NMR}\), the most deshielded signal appears at \(\delta 8.20 \text{ ppm}\) as doublet probably owing to protons attached to fluorene core close to site of coupling and most shielded doublet of a doublet of doublet for (4-Hs) at \(\delta 7.34 \text{ ppm}\) (may be attributed to carbazolic moiety) along with many multiplet sets in the aromatic region. Aliphatic protons appear at their respective chemical shifts. Aromatic carbons appear in the range of 151.4-114.5 ppm in \(^{13}\text{C}-\text{NMR}\).
Molecular structure was further confirmed through APCI-MS that gave a peak at m/z 944.7 [M+H]+ while a peak at 556.3 with low intensity was found due to loss of 9,9-dioctyfluorene from molecular ion followed by detachment of carbazole moiety to render a peak at 338.3 (Fig. 2.24). Elemental analysis shows the calculated and found values were in close agreement.

To study the effect of higher carbazole content with fluorene, SM-coupling of fluorene diboronic acid (6) with (9) was accomplished and product was isolated in 68% yield (Scheme 2.16).
Scheme 2.16: Synthesis of compound CFC

$^1$H-NMR of CFC displays a number of signals in the aromatic region with two distinct sets of doublets for two protons at δ 7.94, at 7.78 ppm owing to the peripheral carbazolic moiety with the existence of aliphatic protons at their respective chemical shifts. In $^{13}$C-NMR, peaks emerge in the range of δ 151.2-108.6 ppm for aromatic carbons. APCI-MS peak at 1275.7 [M+H]$^+$ confirmed the synthesis gathering support from elemental analysis.

Physical data of all the dyes are provided in Table 2.13.

Table 2.13: Physical constants of the Suzuki-coupled dyes

<table>
<thead>
<tr>
<th>Entry</th>
<th>R$_f$</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFT</td>
<td>0.27</td>
<td>88</td>
<td>67</td>
<td>1385.9</td>
</tr>
<tr>
<td>CCP</td>
<td>0.21</td>
<td>91</td>
<td>59</td>
<td>1163.7</td>
</tr>
<tr>
<td>CCT</td>
<td>0.39</td>
<td>79</td>
<td>61</td>
<td>721.4</td>
</tr>
<tr>
<td>CCF</td>
<td>0.43</td>
<td>72</td>
<td>62</td>
<td>832.5</td>
</tr>
<tr>
<td>CFD</td>
<td>0.29</td>
<td>77</td>
<td>66</td>
<td>1496.1</td>
</tr>
<tr>
<td>CFM</td>
<td>0.48</td>
<td>69</td>
<td>64</td>
<td>943.7</td>
</tr>
<tr>
<td>CFC</td>
<td>0.24</td>
<td>66</td>
<td>68</td>
<td>1274.8</td>
</tr>
</tbody>
</table>

2.3.1 Thermal properties

The thermo gravimetry analysis was performed in the temperature range of 0-850°C under nitrogen atmosphere at a heating rate of 10°C/min. The synthesized compounds show good thermal stability with onset of decomposition temperature (T$_d$) in the range of 232-435°C (except CCT). The singly end-capped materials have T$_d$ low as compared to di end-capped material. This trend appears on account of symmetry and rigidity of these materials in contrast to singly-substituted material. The first stage of decomposition is probably loss of alkyl groups. The thermal decomposition temperature increases by
increasing carbazole moieties at periphery. A comparison of TG profile for di and mono end-capped material is given in Fig. 2.25.

![Figure 2.25: (a) TG curves of CFT (b) CCF](image)

The compound represented in (a) is di-end-capped material with \( T_d \) of 435°C. This compound splits in three stages. The second stage comes to an end at 665°C. It is apparent that the process of disintegration gets slower as temperature rises. The completion of degradation process (812°C) leaves 43% residue.

The compound depicted in (b) seems to degrade in a single step having \( T_d \) at 344°C, whereas \( T_f \) (the temperature at which 100% mass loss is observed) is found at 470°C. This indicates the resistance offered by the bonds of the compound in the early part of the pyrolysis. Near the last part of the decomposition, however, the bond-breaking process cannot withstand the soaring thermal energy. There is no residue at the end of this run.

![Figure 2.26: (a) TG curves of CFC (b) CCT](image)
CFC begins to degrade at 232°C and gives a mass loss of 88% for the first stage which terminates at 418°C. The second stage (final stage) comes to an end at 500 °C as the intermediate formed at the completion of first step exhibits no thermal stability. There is no residue. The compound exhibits one-step degradation (TG traces of CCT). It starts to decompose at 80°C and 100% mass loss manifests a temperature of 412°C (Fig. 2.26). The early decomposition reflects the easy bond-cleavage probably owing to incorporation of central dioctylated carbazole and moisture. Thermal behavior was determined by DSC in the range of 25-400°C upon a heating rate of 10°C/min under inert atmosphere. All compounds exhibited a clear endothermic melting peak during the first heating scan. Other minor phase transitions were also detected by DSC. Upon cooling, no crystallization peaks were observed. The DSC thermogram of CFT is reproduced in Fig. 2.27.

The first peak (endothermic in nature) at 68°C is believed to arise due to the melting of the compound. The exothermic peak at 350°C may be attributed to the change in phase of the substance. Apparently, compounds are supercooled liquids with semi-crystalline nature and negligible glass transition. XRD was also performed to check the nature and results were supportive to DSC with absence of crystallinity. XRD of CFT is provided in Fig 2.28. Almost all the dyes have similar DSC results. The results of thermal studies were indicative of the stability of dyes that were end-capped on both sides and also the
dyes incorporating the central fluorene unit are more stable than the dyes possessing central carbazole unit.

![Figure 2.28: XRD of CFT](image)

The data of thermal studies are provided in the Table 2.14

**Table 2.14:** Thermal data of carbazole/fluorene dyes

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T_d$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_{cr}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFT</td>
<td>435</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>CCP</td>
<td>419</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td>CCT</td>
<td>133</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td>CCT</td>
<td>344</td>
<td>58</td>
<td>-</td>
</tr>
<tr>
<td>CCF</td>
<td>433</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CFD</td>
<td>402</td>
<td>72</td>
<td>-</td>
</tr>
<tr>
<td>CFM</td>
<td>232</td>
<td>78</td>
<td>-</td>
</tr>
</tbody>
</table>

Where: $T_d$ = Decomposition temperature; $T_m$ = Melting temperature; $T_{cr}$ = Crystallization temperature

### 2.3.2 Photophysical properties

Figure 2.29 presents the absorption and emission spectra of synthesized compounds recorded in chloroform. **CFT** shows the maximum absorption at 349 nm for $\pi-\pi^*$ transition of conjugated backbone. The introduction of 3,6-linked carbazole did not significantly affect the decrease in absorption wavelength (blue shift) on account of
decrease in conjugation associated with the meta-linked carbazole. Furthermore, there is a small band at 292 nm related to $\pi-\pi^*$ transition of carbazole moiety while its monosubstituted analogue, CCF, exhibits hypsochromic shift at 334 nm signifying decreased conjugation in contrast to CFT. The maximum absorption, in case of CCP (carbazole-only material), is blue shifted to a value of 343 nm differing from CFT that incorporates fluorene moieties also. This blue shift indicates the decrease in conjugation length or no conjugation over long distance on account of meta-linked carbazole. For the singly end-capped carbazole-only material, i.e., CCT $\lambda_{\text{max}}$ appeared at 337 nm showing a decrease in absorption position as against doubly end-capped material, i.e., CCP. Absorption in case of CFC, was observed at 346 nm. In case of CFD, maximum absorption occurs at 350 nm owing to conjugated backbone. The red shift in absorption position was ascribed to increased fluorene content that caused the increase in conjugation length. The compound CFM (mono analogue of CFD) has $\lambda_{\text{max}}$ at 340 nm, blue shifted from CFD by 10 nm based on decreased fluorene content. The presence of small bands for these substances in the range of 267-293 nm was attributed to transitions from carbazole moiety. It is evident that UV/VIS spectra of all doubly end-capped materials were almost similar and same was the case with the singly end-capped stuff. However, the spectra of doubly and singly end-capped materials differ from each other on the basis of bathochromic shift resulting from large conjugation in case of disubstituted species. It is interesting to note that extent of this red shift is less in case of carbazole-only material due to minimization of conjugation while by increasing fluorene content, the shifts become larger. Also, by switching the central core from carbazole to fluorene, red shift enhances. The presence of alkyl groups did not cause significant effect on the optical properties. The results are depicted in Table 2.15.
Table 2.15: Optical data of dyes

<table>
<thead>
<tr>
<th>Entry</th>
<th>$\lambda_{\text{max}, \text{abs}}$ (nm)</th>
<th>$\lambda_{\text{max}, \text{em}}$ (nm)</th>
<th>Stoke shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFT</td>
<td>349, (292)</td>
<td>400</td>
<td>51</td>
</tr>
<tr>
<td>CCP</td>
<td>343, (297)</td>
<td>400</td>
<td>57</td>
</tr>
<tr>
<td>CCT</td>
<td>337, (290)</td>
<td>450, 550</td>
<td>113</td>
</tr>
<tr>
<td>CCF</td>
<td>334, (293)</td>
<td>452, 550</td>
<td>118</td>
</tr>
<tr>
<td>CFD</td>
<td>350, (292)</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td>CFM</td>
<td>340, (291)</td>
<td>402, 507</td>
<td>62</td>
</tr>
<tr>
<td>CFC</td>
<td>346, (295)</td>
<td>400</td>
<td>54</td>
</tr>
</tbody>
</table>

Synthesized dyes demonstrate the blue emission properties in solution with the maximum emission for all the compounds in the range of 400-452 nm. The di-substituted materials possess the sharp emission peak centered at 400 nm while the singly-substituted entities reveal broad emission peak that is more bathochromically shifted with Stoke shifts in the range of 120-110 nm and also a shoulder peak is present in these materials above 500 nm (Fig. 2.30). The broadened emission peaks and larger stoke shifts are signs of spectral instability of the singly end-capped stuff. The tail might be due to excimer formation that interrupts its use in devices. Contrarily the di end-capped materials have more localized emission peaks in the blue region. Also, it is important to note that stoke shift of di-substituted materials is low (in the range of 50-57 nm) as compared to mono-substituted...
counterparts probably on account of deviation from planarity. Moreover, the emission spectra of di-substituted material are like the absorption spectra and independent of fluorene content with no pronounced change on the alteration of central carbazole to fluorene nucleus. On the other hand, the mono-substituted stuff possesses the similar trend comparable to their absorption spectra with the exception of compound C FM having a sharp peak pattern. Results of optical studies indicate better properties for di-end-capped materials than singly end-capped material.

![Emission spectra of carbazole/fluorene dyes in CHCl₃ 10⁻⁵ M](image)

**Figure 2.30:** Emission spectra of carbazole/fluorene dyes in CHCl₃ 10⁻⁵ M

### 2.3.3 Electrochemical properties

The electrochemical properties of dyes were determined through cyclic voltammetry on platinum electrode in the 1mM solution for each dye containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte at a potential scan rate of 50 mV/s (Fig 2.31). All the potentials were measured vs. Ag/AgCl, as a reference electrode, and for each measurement the ferrocence/ferrocenium (Fc) redox system was employed as an internal standard. The HOMO, LUMO, band gap values of all the dyes are collected in Table 2.16.
Table 2.16: Electrochemical parameters of dyes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Band gap (^a) (eV)</th>
<th>HOMO (^b) (eV)</th>
<th>LUMO (^c) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFT</td>
<td>3.16</td>
<td>-5.86</td>
<td>-2.694</td>
</tr>
<tr>
<td>CCP</td>
<td>3.31</td>
<td>-6.12</td>
<td>-2.81</td>
</tr>
<tr>
<td>CCT</td>
<td>3.23</td>
<td>-5.93</td>
<td>-2.70</td>
</tr>
<tr>
<td>CCF</td>
<td>3.19</td>
<td>-5.38</td>
<td>-2.186</td>
</tr>
<tr>
<td>CFD</td>
<td>3.05</td>
<td>-5.50</td>
<td>-2.451</td>
</tr>
<tr>
<td>CFM</td>
<td>3.23</td>
<td>-5.72</td>
<td>-2.510</td>
</tr>
<tr>
<td>CFC</td>
<td>3.22</td>
<td>-5.43</td>
<td>-2.21</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from the absorption threshold of UV-Visible absorption spectrum.

\(^b\) HOMO was calculated employing ferrocene value of 4.8 eV below the vacuum level.

\(^c\) Estimated from HOMO and band gap by using a relation: Band gap (E\(_{o-o}\)) = HOMO - LUMO

Almost all the compounds show similar electrochemical behavior with no observed reduction peaks. The observable difference, in case of compound CCP (carbazole-only material), lies in the irreversible oxidation peak showing its electrochemical instability while, with the introduction of fluorene moiety, the oxidation peak becomes reversible suggesting that materials with fluorene content are stable hole-carriers. Cyclic voltammograms of carbazole/fluorene dyes are presented in Fig. 2.31.

![Cyclic voltammograms of C/F dyes](image)

**Figure 2.31:** Cyclic voltammograms of C/F dyes (1mM each) recorded at platinum electrode in DCM solution containing 0.1M tetra-n-butyl ammonium perchlorate (TBAP) as a supporting electrolyte employing potential scan rate of 50 mV s\(^{-1}\)
The values of HOMO level range from 5.38-6.12 eV with the highest value for compound CCF giving a hole-injection barrier of 0.38 eV with respect to ITO (5.0 eV) suggesting its use in OLEDs as hole-transporting material. Similarly, the dyes with fluorene content incorporated in them possess high-lying HOMO level for CFC, CFD, CFM while, unexpectedly, the carbazole-only species CCP, CCT hold low-lying HOMO and LUMO level with increased band gap consistent with their optical properties. Furthermore, CCP has HOMO value lower than CCT owing to enhancement in carbazole core which reduces the oxidation potential while, in case of CCT, presence of terminal high electron-donating nature of alkylated carbazole, makes oxidation favorable. The reason for such behavior of carbazole-only entities is that HOMO value for nitrogen-containing compounds depends on the position of nitrogen atom. Results of electrochemical studies reveal that the fluorene-containing stuff is electrochemically more stable than the corresponding carbazole-only substances and may be attractive candidate for hole-transportation in OLEDs.

![Energy band diagram of carbazole/fluorene dyes with respect to ITO-NPB](image)

**Figure 2.32:** Energy band diagram of carbazole/fluorene dyes with respect to ITO-NPB

### 2.4 Synthesis, characterization and studies of perylene derivatives

The synthesis of perylene derivative was conducted in a simple manner by condensation of tetrachloroperylene with differently-substituted anilines employing catalytic amounts of zinc acetate in quinoline with overnight reflux in good yield (Scheme 2.17). The obtained products were purified by simple washing with water and methanol.\(^{215,190}\) The reaction was also tried in water with discouraging yield. Use of catalyst, inert atmosphere and solvent increases the yield. These conditions would work best in case of electron-
withdrawing substituted-anilines with improved yield. So, this route was adopted for synthesis. The synthesized perylene precursors were soluble in limited number of solvents, especially those with NO₂ group were soluble only in DMSO.

![Scheme 2.17: Synthesis of substituted perylene bisimides (11-15)](image)

The course of imidization was clearly observed by FTIR results that indicated the appearance of characteristic band for imide functionialty at υ 1704 cm⁻¹ with disappearance of peaks for anhydride functionality at 1797, 1762 cm⁻¹ while the presence of bands at υ 2970-2833 cm⁻¹ and 1536-1527 cm⁻¹ were suggestive of imidized perylene (11-15) with methyl, methoxy and nitro-substituted anilines. Physical constants of perylene bisimides are given in Table 2.17.

**Table 2.17:** Physical constants of perylene bisimides

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>m.p. (°C)</th>
<th>R_f</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>4-CH₃</td>
<td>&gt;300</td>
<td>0.78</td>
<td>83</td>
</tr>
<tr>
<td>12</td>
<td>2-OCH₃</td>
<td>&gt;300</td>
<td>0.81</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>2-NO₂</td>
<td>&gt;300</td>
<td>0.83</td>
<td>73</td>
</tr>
<tr>
<td>14</td>
<td>3-NO₂</td>
<td>&gt;300</td>
<td>0.82</td>
<td>76</td>
</tr>
<tr>
<td>15</td>
<td>4-NO₂</td>
<td>&gt;300</td>
<td>0.84</td>
<td>72</td>
</tr>
</tbody>
</table>

In ¹H-NMR, presence of characteristic peaks in the aromatic region in the range of 8.47-6.61 ppm with distinct coupling pattern and multiplets, besides singlet obtained for four resonating protons of perylene above 8.51 ppm, marked the condensation of anilines. ¹H-NMR spectrum of compound 11 is presented in Fig. 2.33. The same case would result in ¹³C-NMR where alongside the aromatic carbons of perylene nucleus observed above 160 ppm, other aromatic carbons were also present in the range of 153.9-112.5 ppm. In case of electron-withdrawing substituted-anilines, carbon is more deshielded as compared to
electron-donating substituents. LCMS confirms the synthesis that was further proved through elemental analysis bearing closeness of found results with calculated ones.

![1H-NMR spectrum of compound 11](image)

**Figure 2.33:** $^1$H-NMR spectrum of compound 11

Following the substitution of chloro group with substituted-phenol by engaging anhydrous potassium carbonate in NMP yielded the perylene derivative in good yield (Scheme 2.18). In case of 2,5-diOMe-substituted derivative, yield was low as opposed to other derivatives probably on account of steric interactions of bulky methoxy group. The obtained perylene derivatives were soluble in common organic solvents, *i.e.*, key requirement for film formation. The much-needed solubility was achieved through attachment of bulky phenoxy substituents.

**Scheme 2.18:** Synthesis of bay-substituted PDIs
Table 2.18: Physical constants of PDIs

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R’</th>
<th>m.p. (°C)</th>
<th>R_f</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>4-CH₃</td>
<td>H</td>
<td>&gt;300</td>
<td>0.30</td>
<td>68</td>
</tr>
<tr>
<td>POM</td>
<td>4-CH₃</td>
<td>4-CH₃</td>
<td>&gt;300</td>
<td>0.28</td>
<td>67</td>
</tr>
<tr>
<td>PDM</td>
<td>2-OCH₃</td>
<td>2,5-diOMe</td>
<td>&gt;300</td>
<td>0.24</td>
<td>55</td>
</tr>
<tr>
<td>P2N</td>
<td>2-NO₂</td>
<td>4-CH₃</td>
<td>&gt;300</td>
<td>0.31</td>
<td>67</td>
</tr>
<tr>
<td>P3N</td>
<td>3-NO₂</td>
<td>4-CH₃</td>
<td>&gt;300</td>
<td>0.34</td>
<td>65</td>
</tr>
<tr>
<td>P4N</td>
<td>4-NO₂</td>
<td>4-CH₃</td>
<td>&gt;300</td>
<td>0.36</td>
<td>69</td>
</tr>
</tbody>
</table>

In FTIR, characteristic stretching vibration of C-O observed in the range of 1160-1135 cm⁻¹ demonstrated the substitution of phenol with strong stretching of aromatic C=C in the region of 1592-1586 cm⁻¹. ¹H-NMR gives additive number of peaks in the aromatic region with the protons present in the vicinity of phenolic oxygen being more shielded than other protons. Similarly, in ¹³C-NMR, the appearance of deshielded carbons in the span of 158.7-154.8 ppm was assigned to carbons close to phenolic oxygen and indicative of attachment of phenol. Results of elemental analysis were in close agreement with the calculated ones.

Figure 2.34: ¹H-NMR spectrum of POM
2.4.1 Thermal properties

As revealed by Fig 2.35, perylene derivatives bear good thermal stability with thermal decomposition temperatures around >300°C, determined by TG under nitrogen measured from 0-700°C at a heating rate of 10°C/min.

![Figure 2.35: TG curves of PDIs](image)

The results indicate that synthesized derivatives with 2-NO₂, 3-NO₂ substituted-anilines exhibit almost similar behavior, while derivatives with substitution at 4<sup>th</sup> position of aromatic ring have higher thermal stability due to symmetry, rigidity and intermolecular interactions. The first major loss occurs at around 350°C. Results of thermal studies are given in Table 2.19.

<table>
<thead>
<tr>
<th></th>
<th>PM</th>
<th>POM</th>
<th>PDM</th>
<th>P2N</th>
<th>P3N</th>
<th>P4N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T&lt;sub&gt;d&lt;/sub&gt; (°C)</strong></td>
<td>326</td>
<td>370</td>
<td>342</td>
<td>307</td>
<td>319</td>
<td>312</td>
</tr>
<tr>
<td><strong>T&lt;sub&gt;g&lt;/sub&gt; (°C)</strong></td>
<td>121</td>
<td>132</td>
<td>126</td>
<td>110</td>
<td>114</td>
<td>124</td>
</tr>
</tbody>
</table>

DSC analysis was performed to check the thermal behavior in the temperature range of 0-400°C under nitrogen. Figure 2.36 presents the DSC thermogram of dye P4N.
The $T_g$ of perylene derivatives ranged from 110-132°C. The linking of phenoxy group at bay position does not significantly influence the thermal behavior. The relatively high $T_g$ and good thermal stability provide good chances for use of these materials in organic electronic devices.

### 2.4.2 Photophysical properties

The synthesized perylene derivatives show the maximum absorption in the range of 516-578 nm with the characteristic three-band pattern associated with perylene bisimide. The clear change in absorption and emission spectra appears due to substitution on the aromatic core of perylene bisimide. The more pronounced red shift appeared in case of POM owing to the presence of electron-donating methyl substituent at bay position. Next is the PDM which gives $\lambda_{max}$ at 546 nm for the same reason. The considerable peak broadening in this case appears probably on account of loss of planarity of perylene because of steric crowding at bay area. The PDI derivatives with nitro group display $\lambda_{max}$ 520-524 nm due to $\pi-\pi^*$ transition of perylene core. The absorption and emission spectral profile of perylene dyes is presented in Fig. 2.37.
Figure 2.37: (a) Absorption spectra of PDIs in CHCl₃ 10⁻⁵ M. (b) Emission spectra of PDIs in CHCl₃ 10⁻⁵ M

In the emission spectra, all PDIs retain an almost localized single-peak pattern. The POM and PDM emit at 605 and 600 nm, respectively, in the orange region of visible spectrum corresponding to their absorption spectra. The core-substituted PDIs possess small Stoke shifts demonstrating the rigidity of molecules. Other PDIs emitted in the green region with an emission wavelength in the range of 550-553 nm. The reason for maximum emission of POM and PDM was increased conjugation length which also influenced absorption spectra in the similar fashion.

Table 2.20: Optical data of PDIs

<table>
<thead>
<tr>
<th>Entry</th>
<th>λ_max, abs (nm)</th>
<th>λ_max, em (nm)</th>
<th>Stoke shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>516, 391</td>
<td>550</td>
<td>34</td>
</tr>
<tr>
<td>POM</td>
<td>578, 545, 450</td>
<td>605</td>
<td>27</td>
</tr>
<tr>
<td>PDM</td>
<td>546, 424</td>
<td>600</td>
<td>54</td>
</tr>
<tr>
<td>P2N</td>
<td>520, 486, 425</td>
<td>550</td>
<td>30</td>
</tr>
<tr>
<td>P3N</td>
<td>524, 489, 429</td>
<td>551</td>
<td>27</td>
</tr>
<tr>
<td>P4N</td>
<td>521, 485, 424</td>
<td>553</td>
<td>32</td>
</tr>
</tbody>
</table>

2.4.3 Electrochemical properties

The electrochemical behavior of PDIs was determined by cyclic voltammetry. The cyclic voltammograms of all PDIs exhibit two reversible reduction and one irreversible oxidation waves at glassy carbon electrode in DMSO. This pattern turned up on account of easy reduction of perylene bisimide corresponding to the formation of radical dianion,
while substitution of electron donor phenoxy at bay position causes the oxidation by increasing the π-electron density on perylene bisimide core and making its oxidation easier. The values of LUMO energy levels for these π-conjugated copolymers were estimated from the values of energy band gaps which were calculated from absorption threshold of UV-Visible spectrum and the values of HOMO energy levels. The values of HOMO, LUMO and band gap are contained in Table 2.21.

**Table 2.21:** Electrochemical parameters of PDIs

<table>
<thead>
<tr>
<th>Entry</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>-5.60</td>
<td>-3.52</td>
<td>2.078</td>
</tr>
<tr>
<td>POM</td>
<td>-5.89</td>
<td>-4.09</td>
<td>1.798</td>
</tr>
<tr>
<td>PDM</td>
<td>-5.83</td>
<td>-3.91</td>
<td>1.912</td>
</tr>
<tr>
<td>P4N</td>
<td>-5.65</td>
<td>-3.60</td>
<td>2.173</td>
</tr>
<tr>
<td>P3N</td>
<td>-5.69</td>
<td>-3.60</td>
<td>2.096</td>
</tr>
<tr>
<td>P2N</td>
<td>-5.68</td>
<td>-3.47</td>
<td>2.204</td>
</tr>
</tbody>
</table>

The combined cyclic voltamogramms of perylene dyes represented in Fig. 2.38.

**Figure 2.38:** CV curves of PDIs (1mM each) recorded at glassy carbon working electrode, platinum wire (counter), sat Ag/AgCl (reference) in their DMSO solution containing 0.1M (TBAP) as a supporting electrolyte employing potential scan rate of 50 mV s⁻¹. HOMO level for PDIs ranges from 5.60-5.89 eV with the lowest value for the PDI substituted with p-methyl phenoxy at bay position and highest value for unsubstituted phenoxy at bay position. This effect may be attributed to donor-acceptor interaction of
substituent and perylene bisimide core. Almost similar trend was observed for LUMO levels with the most low-lying for POM and PDM at 4.09, 3.51 eV, respectively, besides a narrow band gap for these substances consistent with the absorption results. The result indicated that D-A-D systems had a pronounced impact on the electrochemical properties as compared to D-A systems. Nitro-substituted PDIs nearly showed the similar trend. The HOMO level of synthesized dyes was found close to the hole-transporting stuff, NPB. The low-lying LUMO levels of the synthesized PDIs augment the electron-accepting character of these materials and electron-transporting applications of these entities in OLEDs. The energy band diagram of dyes is shown in Fig. 2.39.

Figure 2.39: Energy band diagram of PDIs with respect to ITO-NPB
Chapter 3

Experimental

3.1 Chemicals and reagents
Carbazole, aluminium chloride, ammonium acetate, acetyl chloride, benzaldehyde, 3-nitro-, 3-bromo-, 3-hydroxy-benzaldehydes, N-bromosuccinimide and tetrabutyl ammonium bromide were provided commercially from Fluka. Acetonitrile, dimethyl sulfoxide, potassium carbonate and n-hexane were purchased from E. Merck. Anhydrous sodium sulfate and potassium hydroxide were products of Aldrich. n-BuLi (1.6 M in hexane) was supplied by Alfa Aesar. Tetrakis(triphenylphosphine)palladium(0), tri-isopropyl borate, anhydrous ferric chloride, bromine, 1-bromobutane, 1-bromoctane, 2,7-dibromo fluorene, 2-bromo fluorene, cuprous iodide, 18-crown6, zinc acetate and quinoline were acquired from Sigma-Aldrich. 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride was purchased from Acros. Chloroform, dichloromethane, tetrahydrofuran and methanol were supplied by Lab Scan. Acetic acid, N-methyl pyrrolidone, o-dichlorobenzene, pyridine and toluene were obtained from Riedal de Haën. Ethanol, methanol, acetone and ethyl acetate were products from commercial sources. 2-Nitroaniline, 3-nitroaniline, 4-nitroaniline and 4-methylaniline were purchased from BDH. p-Cresol, phenol, 2,5-dimethoxyphenol and 2-methoxyaniline were products of Sigma-Aldrich. The reagents were purified where necessary prior to use.

3.2 Purification of solvents
Standard methods were followed for the purification and drying of solvents. The dried solvents were stored over type 4Å molecular sieves. A brief account of the purification procedures is given below.

1) Acetone
Calcium chloride (anhydrous) was added to flask having acetone and refluxed for 3-5 hours. Pure acetone was distilled at 56°C.

2) Chloroform
Chloroform was pre-dried over anhydrous calcium chloride for 4 hours and distilled at 65-66°C.

3) Dichloromethane
It was dried by same procedure used for chloroform and distilled at 39-40°C.
4) **Ethyl Acetate**  
It was dried by stirring with anhydrous calcium hydride and distilling at 77°C.

5) **Ethanol**  
Ethanol was refluxed over activated calcium oxide for 4-6 hours followed by distillation at 77-78°C.

6) **Methanol**  
Calcium oxide was introduced into a round bottom flask containing methanol. It was refluxed for 4 hours and distilled at 64°C.

7) **Tetrahydrofuran and Diethyl ether**  
Both solvents were dried upon reflux on sodium wire using benzophenone as an indicator, followed by distillation at 66°C and 34-36°C respectively, when color changes to violet blue. THF was freshly distilled each time before use.

8) **Acetonitrile**  
The solvent was dried upon molecular sieves (4Å) by standing overnight and fractionally-distilling at 80-81°C.

3.3 **Instruments used**  
Melting points were determined using digital Gallenkamp (Sanyo) model MPD BM 3.5 with digital thermometer and are uncorrected. Infrared spectra were recorded employing a Shimadzu IR 460 as KBr pellets and FTX 3000 MX spectrophotometer applying ATR method. \(^1\)H-NMR and \(^1^3\)C-NMR spectra were obtained utilizing a Bruker AM (300 MHz, 75 MHz) and (400 MHz, 100 MHz) spectrophotometers, in CDCl\(_3\), DMSO-d\(_6\), CD\(_3\)OD-d\(_4\) solution. Chemical shifts are given in δ-scale (ppm). Abbreviations s, d, dd, t, at and m stand for singlet, doublet, double doublet, triplet, apparent triplet and multiplet, respectively. Mass spectra were recorded on GC-MS 6890N instrument of Agilent technologies (EI, 70eV), APCI-MS on Agilent 6210 TOF while MALDI-MS on AB Sciex TOF/TOF 5800, mixing sample solution with dithranol.  
Molecular weights of the polymers were determined by laser light-scattering (LLS) technique using a commercial light-scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-τ digital time correlator) with a solid-state laser (ADLAS DPY 425II, output power ≈ 400 mW at \(λ = 532\) nm) as light source. Thermogravimetry (TG) was performed employing a PerkinElmer Thermal Analysis System 409. Differential
Scanning Calorimetry (DSC) was accomplished through Bruker Reflex II thermosystem. The TG and DSC measurements were made in a nitrogen atmosphere at a heating rate of 10°C/min.

Elemental analyses were conducted on CHNS 932 LECO instrument. UV-VIS spectra were taken by CECIL-7400 UV/Visible spectrophotometer and fluorescence spectra were recorded utilizing the Hitachi FL solutions 7000 fluorescence spectrophotometer. Cyclic voltammetry was performed on CH-800 C potentiostat employing 0.1M TBAP as internal reference in DMSO and DCM (purged with argon for 10 minutes) on glassy carbon, platinum (0.2 mm diameter) as working electrode versus Ag/AgCl reference electrode and platinum wire as counter electrode at room temperature.

3.4 CHROMATOGRAPHIC TECHNIQUES

3.4.1 Thin Layer Chromatography (TLC)
The progress of reactions was monitored through thin layer chromatography by using precoated silica gel aluminium sheets 2.0 x 5.0 cm (layer thickness 0.2 mm, HF254, Reidal-de-Haen from Merck). Chromatograms were sensed by ultraviolet light (254-360 nm). For development of chromatograms, different solvent systems were employed:

- n-Hexane:Ethyl acetate (4:1)
- n-Hexane:DCM (6:1)
- n-Hexane:Ethyl acetate (9:1)
- DCM:Methanol (10:1)

3.4.2 Column Chromatography
Column was packed with silica gel (0.063-0.200 mm from Merck). Slurry was prepared in hexane, covered with sand, hexane was eluted after which sample solution was loaded over sand and eluted by utilizing different mobile phases. Fractions were collected, evaporated and dried under vacuum.

3.5 Experimental Procedures

**General procedure for synthesis of N-alkylcarbazoles**
To an equimolar mixture of carbazole and corresponding bromoalkane (10 mmol), were added TBAB (0.1g), 50% KOH solution (20 mL) and 10 mL of benzene. It was stirred for 3 hours at 80 °C. The reaction mixture was cooled to room temperature. The benzene layer was separated, diluted with 20 mL of ethyl acetate, washed three times with 50 mL
portions of water and dried over anhydrous MgSO₄. Solvents were removed in vacuo to afford the product which was purified by recrystallization from ethanol.

### 3.5.1 N-Butylcarbazole (1a)

![N-Butylcarbazole](image)

White crystals; Yield: 90%; Rf: 0.91; m.p.: 49°C; IR (KBr, ν/cm⁻¹): 3071 (sp² C-H stretching), 2972, 2862 (sp³ C-H stretching), 1584 (Ar C=C), 1326 (C-N); ¹H-NMR (CDCl₃, 300MHz): δ 8.16 (d, J = 7.81 Hz, 2H, Ar-H), 7.51-7.49 (m, 4H, Ar-H), 7.28 (d, J = 7.68 Hz, Ar-H), 4.35 (t, J = 7.21 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 140.7, 125.5, 122.8, 120.3, 118.7, 108.6, 42, 31.1, 20.6, 13.9.

### 3.5.2 N-Octylcarbazole (2a)

![N-Octylcarbazole](image)

Light yellow oil; Yield: 87%; IR (NaCl cell, ν/cm⁻¹): 3065 (sp² C-H stretching), 2965, 2905 (sp³ C-H stretching), 1601 (Ar C=C), 1320 (C-N); ¹H-NMR (CDCl₃, 300 MHz): δ 8.35 (d, J = 7.81 Hz, 2H, Ar-H), 7.69-7.64 (m, 4H), 7.59 (d, J = 8.1 Hz, 2H, Ar-H), 4.41 (t, J = 7.20 Hz, 2H, N-CH₂), 2.03-1.91 (m, 2H, N-CH₂-CH₂), 1.51-1.30 (m, 10H), 1.14 (t, J = 7.24 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75 MHz): δ 140.5, 125.8, 123.0, 120.5, 118.9, 108.9, 49.1, 32.1, 30.6, 29.4, 29.2, 27.5, 22.9, 14.4.

### 3.6 General procedure for the synthesis of 3,6-diacetyl-N-alkylcarbazole

Aluminum chloride, 4.0 g (3.0 mmol) and acetyl chloride, 2.35 g (3.0 mmol) were added successively to 10 mL of dry chloroform. The mixture was stirred for 10 minutes at 0°C to get a clear solution. A solution of suitable N-alkylcarbazole (2 mmol) in 10 mL of dry chloroform was added drop-wise to the above solution at 0°C during 15 minutes. The reaction mixture was stirred at room temperature for three hours. After the completion of the reaction (TLC control), the reaction mixture was poured into a stirred-solution of 10% HCl (50 mL). The organic layer was separated, washed with 80 mL portions of distilled water three times and treated with anhydrous Na₂SO₄. The solvent was removed in vacuo to leave a solid which was recrystallized from ethanol.

### 3.6.1 3,6-Diacetyl-N-butylcarbazole (1b)

![3,6-Diacetyl-N-butylcarbazole](image)

Dull green solid; Yield: 85%; m.p.: 145°C; Rf: 0.28; IR (KBr, ν/cm⁻¹): 3074 (sp² C-H stretching), 2945, 2852 (sp³ C-H
stretching), 1718 (C=O), 1328 (C-N); $^1$H-NMR (CDCl$_3$, 300 MHz): δ 8.79 (s, 2H, Ar-H), 8.18 (dd, $J$ = 8.42, 1.89 Hz, 2H, Ar-H), 7.45 (d, $J$ = 8.42 Hz, 2H, Ar-H), 4.35 (t, $J$ = 7.22 Hz, 2H, N-CH$_2$), 2.75 (s, 6H, COCH$_3$), 1.87-1.79 (m, 2H), 1.42-1.32 (m, 2H), 0.97 (t, $J$ = 7.22 Hz, 3H, CH$_3$); $^{13}$C-NMR (CDCl$_3$, 75 MHz): δ 197.4, 143.9, 129.6, 127.0, 122.8, 122.0, 108.9, 43.3, 31.0, 26.6, 20.4, 13.8; GC-MS (m/z): 307 (M$^+$), 264 (100%), 221, 178, 43, 29.

3.6.2 3,6-Diacetyl-N-octylcarbazole (2b)

White solid; Yield: 88%; Rf: 0.25; m.p.: 139°C; IR (KBr, υ/cm$^{-1}$): 3064 (sp$^2$ C-H stretching), 2939, 2861 (sp$^3$ C-H stretching), 1715 (C=O), 1329 (C-N); $^1$H-NMR (CDCl$_3$, 300 MHz): δ 8.75 (s, 2H, Ar-H), 8.18 (dd, $J$ = 8.40 Hz, 2H, Ar-H), 7.45 (d, $J$ = 8.40 Hz, 2H, Ar-H), 4.34 (t, $J$ = 7.2 Hz, 2H, N-CH$_2$), 2.75 (s, 6H, COCH$_3$), 1.86-1.81 (m, 2H, N-CH$_2$-CH$_2$), 1.44-1.30 (m, 10H), 0.86 (t, $J$ = 6.94 Hz, 3H, CH$_3$); $^{13}$C-NMR (CDCl$_3$, 75 MHz): δ 198.1, 142.4, 128.9, 127.0, 121.8, 120.3, 109.9, 43.1, 31.0, 29.3, 28.9, 27.2, 22.4, 13.8; GC-MS (m/z): 363 (M$^+$), 264 (100%), 348, 221, 178, 43, 29.

3.7 General procedure for polymer synthesis

Ammonium acetate (10 mmol) was added portion-wise to a stirred-equimolar mixture of 3,6-diacetyl-N-alkylcarbazole and benzaldehyde in acetic acid (10 mL). The reaction mixture was refluxed for 18 hours. Upon completion of reaction (TLC control), the reaction mixture was cooled to room temperature, poured into distilled water (20 mL) and stirred efficiently for five minutes. The precipitated solid was filtered and washed well with a plenty of distilled water to remove acetic acid and salt completely. The resulting solid was dissolved in THF and precipitated by adding methanol to remove the oligomers. The precipitation process was repeated three times and the obtained polymers were dried in a vacuum oven at 70°C overnight.

3.7.1 Poly[3,6-N-butylcarbazole-4-phenylpyridine-2,5-diyl] (P1a)

Yellow solid; Yield: 44%; m.p.: 138-140°C; Rf: 0.35; IR (KBr, υ/cm$^{-1}$): 3055 (sp$^2$ C-H stretching), 2930, 2860 (sp$^3$ C-H stretching), 1641 (C=N), 1584 (Ar C=C), 1326 (C-N); $^1$H-NMR (CDCl$_3$, 300 MHz): δ 8.94 (s, Ar-H), 8.55 (dd, $J$ = 8.43, 1.92 Hz, Ar-H), 8.0-7.5 (br m, Ar-H), 8.28 (d, $J$ = 8.43 Hz, Ar-H), 8.0-7.5 (br m, Ar-H), 4.4 (t, $J$
$J = 6.91 \text{ Hz, 2H, N-CH}_2$, 1.79-1.41 (m, 4H), 1.02 (t, $J = 6.96 \text{ Hz, 3H, CH}_3$); $^{13}\text{C-NMR (CDCl}_3$, 75MHz): $\delta$ 148.6, 146.2, 144.1, 142.3, 139.8, 137.2, 129.0, 128.7, 127.5, 120.5, 119.1, 116.7, 109.5, 146.2, 144.1, 142.3, 139.8, 137.2, 129.0, 128.7, 127.5, 120.5, 119.1, 116.7, 109.5, 33.2, 29.9, 29.2, 28.7, 27.2, 21.9, 14.8; Anal. Calcd (%) C = 86.6, H = 5.8, N = 7.4, Found C = 84.3, H = 5.9, N = 7.1; $M_w (10^5)$: 0.57; UV/VIS (CHCl$_3$) $\lambda_{abs}$, max (nm): 301; PL (CHCl$_3$) $\lambda_{em}$, max (nm): 417.

### 3.7.2 Poly[3,6-N-butylcarbazole-4-(3-nitrophenylpyridine)]-2,5-diyl (P1b)

Yellow powder; Yield: 49%; m.p.: 158-160°C; R$_f$: 0.45; IR (KBR, $\nu$/cm$^{-1}$): 3035 (sp$^2$ C-H stretching), 2930, 2890 (sp$^3$ C-H stretching), 1631 (C=N), 1585 (Ar C=C), 1523, 1345 (unsymmetric and unsymmetric NO$_2$); $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.96 (s, Ar-H), 8.58 (s, Ar-H), 8.27 (m, Ar-H), 8.00 (d, $J = 7.81 \text{ Hz, Ar-H}$), 7.92 (s, Ar-H), 7.66 (d, $J = 7.81 \text{ Hz, Ar-H}$), 7.54 (m, Ar-H), 4.4 (t, $J = 7.14 \text{ Hz, 2H, N-CH}_2$, 1.91-1.84 (m, 2H), 1.46-1.31 (m, 2H), 1.01 (t, $J = 7.22 \text{ Hz, 3H, CH}_3$); $^{13}$C-NMR (CDCl$_3$, 75MHz): $\delta$ 148.9, 144.5, 142.0, 137.1, 134.3, 130.5, 130.0, 127.8, 124.9, 124.5, 123.3, 122.1, 108.7, 33.5, 29.3, 27.6, 22.6, 14.8; Anal. Calcd (%) C = 77.3, H = 5.0, N = 10.0, Found C = 76.9, H = 4.7, N = 9.8; $M_w (10^5)$: 0.56; UV/VIS (CHCl$_3$) $\lambda_{abs}$, max (nm): 282; PL (CHCl$_3$) $\lambda_{em}$, max (nm): 424.

### 3.7.3 Poly[3,6-N-butylcarbazole-4-(3-hydroxyphenylpyridine)]-2,5-diyl (P1c)

Dark brown powder; Yield: 40%; m.p.: 151-153°C; R$_f$: 0.27; IR (KBR, $\nu$/cm$^{-1}$): 3415 (O-H), 3082 (sp$^2$ C-H stretching), 2955, 2860 (sp$^3$ C-H stretching), 1633 (C=N), 1584 (Ar C=C), 1146 (C-O); $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.79 (s, Ar-H), 8.21 (dd, $J = 9.05, 1.90 \text{ Hz, Ar-H}$), 7.47-7.41 (m, Ar-H), 7.31-7.18 (m, Ar-H), 7.02-6.99 (m, Ar-H), 5.10 (s, OH), 4.34 (t, $J = 8.04 \text{ Hz, 2H, N-CH}_2$, 1.93-1.79 (m, 2H), 1.44-1.35 (m, 2H), 0.97 (t, $J = 9.02 \text{ Hz, 3H, CH}_3$); $^{13}$C-NMR (CDCl$_3$, 75MHz): $\delta$ 150.1, 147.1, 144.3, 141.6, 139.7, 137.8, 134.4, 131.1, 129.3, 126.2, 125.4, 122.9, 120.4, 117.1, 109.3, 36.2, 29.3, 28.5, 28.1, 25.5, 22.2, 14.6; Anal. Calcd (%) C = 83.0, H = 5.6, N = 7.1, Found C = 82.6, H = 5.3, N = 6.8; $M_w (10^5)$: 0.75; UV/VIS (CHCl$_3$) $\lambda_{abs}$, max (nm): 285; PL (CHCl$_3$) $\lambda_{em}$, max (nm): 397 (491).
3.7.4 Poly[3,6-N-butylcarbazole-4-(3-bromophenylpyridine)]-2,5-diyi] (P1d)

Yellow precipitates; Yield: 66%; m.p.: 99-102°C; Rf: 0.45; IR (KBr, ν/cm⁻¹): 3065 (sp² C-H stretching), 2960, 2890 (sp³ C-H stretching), 1632 (C=N), 1596 (Ar C=C), 664 (C-Br); ¹H-NMR (CDCl₃, 300 MHz): δ 8.91 (s, Ar-H), 8.28 (dd, J = 8.71 Hz, Ar-H), 7.78 (d, J = 4.2 Hz, Ar-H), 7.55-7.41 (m, Ar-H), 7.33 (at, Ar-H), 4.38 (t, J = 7.2 Hz, 2H, N-CH₂), 1.91-1.87 (m, 2H), 1.42-1.34 (m, 2H), 0.98 (t, J = 7.24 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 145.6, 143.2, 136.5, 134.1, 133.7, 131.4, 130.5, 130.3, 127.5, 126.2, 123.2, 123.0, 122.6, 109.1, 32.7, 29.1, 27.3, 22.4, 14.8; Anal. Calcd (%) C = 71.5, H = 4.6, N = 6.1, Found C = 69.3, H = 4.3, N = 6.0; Mᵣ (10⁵): 0.12; UV/VIS (CHCl₃) λₑₑₑ, max (nm): 300; PL (CHCl₃) λₑₑₑ, max (nm): 421.

3.7.5 Poly[3,6-N-octylcarbazole-4-phenylpyridine-2,5-diyi] (P2a)

Yellow powder; Yield: 39%; m.p.: 104°C (dec); Rf: 0.55; IR (KBR, ν/cm⁻¹): 3060 (sp² C-H stretching), 2950, 2862 (sp³ C-H stretching), 1639 (C=N), 1590 (Ar C=C), 1326 (C-N); ¹H-NMR (CDCl₃, 300 MHz): δ 8.94 (s, Ar-H), 8.54-7.47 (m, Ar-H), 4.38 (t, J = 7.32 Hz, 2H, N-CH₂), 1.93-1.84 (m, 2H, N-CH₂-CH₂), 1.39-1.27 (m, 10H), 0.88 (t, J = 7.12 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 150.6, 148.3, 147.1, 144.4, 139.8, 136.5, 129.0, 127.3, 126.2, 120.7, 118.1, 116.1, 110.5, 35.2, 30.1, 29.2, 28.7, 27.2, 21.9, 14.8; Anal. Calcd (%) C = 86.5, H = 6.9, N = 6.5, Found C = 83.3, H = 6.7, N = 6.1; Mᵣ (10⁵): 1.28; UV/VIS (CHCl₃) λₑₑₑ, max (nm): 291; PL (CHCl₃) λₑₑₑ, max (nm): 426.

3.7.6 Poly[3,6-N-octylcarbazole-4-(3-nitrophenylpyridine)]-2,5-diyi] (P2b)

Yellow powder; Yield: 46%; m.p.: 107-109°C; Rf: 0.25; IR (KBR, ν/cm⁻¹): 3070 (sp² C-H stretching), 2950, 2840 (sp³ C-H stretching), 1631 (C=N), 1586 (Ar C=C), 1535, 1338 (unsymmetric and symmetric NO₂); ¹H-NMR (CDCl₃, 300 MHz): δ 8.96 (s, Ar-H), 8.58 (s, Ar-H), 8.33-8.22 (m, Ar-H), 8.00 (d, J = 7.87 Hz, Ar-H), 7.92 (s, Ar-H), 7.66 (at, Ar-H), 7.52 (d, J = 8.74 Hz, Ar-H), 4.4 (t, J = 6.96 Hz, 2H, N-CH₂), 1.93-1.81 (m, 12H), 0.86 (t, J = 6.96 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 148.7, 144.1, 141.0, 136.9, 134.3, 130.1, 130.0, 127.6, 124.6, 124.5, 123.1, 122.4, 109.5, 31.7, 29.3, 29.1, 28.4, 27.2, 22.6, 14.0; Anal. Calcd (%) C = 78.3, H
= 6.1, N = 8.8, Found C = 77.1, H = 5.9, N = 8.2; Mw (10^5): 2.43; UV/VIS (CHCl₃) λabs, max (nm): 284; PL (CHCl₃) λem, max (nm): 435.

### 3.7.7 Poly[3,6-N-octylcarbazole-4-(3-hydroxyphenylpyridine)]-2,5-diyl (P2c)

Brownish-black solid; Yield: 42%; m.p.: 131-134°C; Rf: 0.15; IR (KBR, μ/cm⁻¹): 3345 (O-H), 3085 (sp² C-H stretching), 2925, 2840 (sp³ C-H stretching), 1631 (C=N), 1589 (Ar C=C), 1152 (C-O); ¹H-NMR (CDCl₃, 300 MHz): δ 8.94 (s, Ar-H), 8.89 (m, Ar-H), 8.84-8.81 (m, Ar-H), 8.22-8.17 (m, Ar-H), 7.49-7.46 (m, Ar-H), 5.31 (s, OH), 4.36 (t, J = 7.14 Hz, 2H, N-CH₂), 2.20-1.91 (m, 2H), 1.45-1.34 (m, 10H), 0.87 (t, J = 7.27 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 153.1, 145.2, 144.3, 141.1, 139.0, 137.2, 134.4, 132.1, 129.3, 127.2, 125.3, 122.6, 120.2, 117.3, 108.2, 39.2, 29.4, 28.6, 28.2, 26.3, 22.5, 15.1; Anal. Calcd (%) C = 83.4, H = 6.7, N = 6.2, Found C = 82.1, H = 6.4, N = 6.0; Mw (10^5): 1.73; UV/VIS (CHCl₃) λabs, max (nm): 291; PL (CHCl₃) λem, max (nm): 400 (524).

### 3.7.8 Poly[3,6-N-octylcarbazole-4-(3-bromophenylpyridine)]-2,5-diyl (P2d)

Dark Yellow precipitates; Yield: 40%; m.p.: 118°C (dec); Rf: 0.47; IR (KBR, μ/cm⁻¹): 3051 (sp² C-H stretching), 2960, 2855 (sp³ C-H stretching), 1629 (C=N), 1587 (Ar C=C), 668 (C-Br); ¹H-NMR (CDCl₃, 300 MHz): δ 8.92 (s, Ar-H), 8.28 (d, J = 7.55 Hz, Ar-H), 7.92-7.88 (m, Ar-H), 7.63-7.49 (m, Ar-H), 7.33 (at, Ar-H), 4.37 (t, J = 6.69 Hz, 2H, N-CH₂), 1.92-1.87 (m, 2H, N-CH₂-CH₂), 1.36-1.26 (m, 10 H), 0.87 (t, J = 6.97 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 144.0, 142.2, 137.2, 133.1, 130.8, 130.4, 130.3, 127.5, 127.3, 123.2, 123.1, 123.0, 122.2, 109.3, 31.7, 29.3, 29.1, 28.9, 27.3, 22.6, 14.1; Anal. Calcd (%) C = 73.0, H = 5.6, N = 5.5, Found C = 70.0, H = 5.4, N = 5.2; Mw (10^5): 1.29; UV/VIS (CHCl₃) λabs, max (nm): 289; PL (CHCl₃) λem, max (nm): 431.

### 3.8 3,3’-Bi(9-octylcarbazole) (3a)

Under nitrogen atmosphere, a solution of N-octylcarbazole (6g, 22 mmol) in chloroform was added slowly to a solution of anhydrous ferric chloride (18g, 111 mmol) in 40 mL of chloroform. This mixture was stirred for 25 hours at room temperature, filtered,
washed with chloroform, stirred in water:ammonia mixture (60 mL:30 mL) for half-anhour and then extracted with dichloromethane. The extract was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated in vacuo to get off white precipitates which were recrystallized in hexane to afford pure white crystals Yield: 72 %; m.p.: 75°C; R$: 0.38;

$^1$H-NMR (CDCl$_3$, 300MHz): $\delta$ 8.43 (d, $J = 7.43$ Hz, 2H, Ar-H), 8.22 (d, $J = 7.87$ Hz, 2H, Ar-H), 7.91-7.76 (m, 2H, Ar-H), 7.54-7.44 (m, 6H, Ar-H), 7.37-7.21 (m, 2H, Ar-H), 4.36 (t, $J = 7.24$ Hz, 4H, N-CH$_2$), 1.92-1.81 (m, 4H), 1.36-1.21 (m, 20H), 0.89 (t, $J = 7.03$ Hz, 6H, CH$_3$); $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 140.8, 139.5, 133.3, 125.5, 123.3, 123.0, 120.4, 118.9, 118.7, 108.7, 43.2, 31.8, 29.4, 29.2, 29.0, 27.4, 22.6, 14.1; Anal. Calcd (%) C = 86.28, H = 8.69, N = 5.03, Found C = 86.19, H = 8.51, N = 5.02.

3.9  6,6'-Diacetyl-N-octyl-3,3'-biscarbazole (3b)

The monomer was prepared by same procedure as described earlier.

White solid; Yield:71%; m.p.:196°C; R$: 0.16; IR (KBR, cm$^{-1}$): 3081 (sp$^2$ C-H stretching), 2971, 2847 (sp$^3$ C-H stretching), 1705 (C=O), 1586 (Ar C=C); $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta$ 8.57-8.45 (m, 4H, Ar-H), 8.15-8.01 (m, 2H, Ar-H), 7.44-7.33 (m, 4H, Ar-H), 7.28 (d, $J = 7.21$ Hz, 2H, Ar-H), 4.12 (t, $J = 6.96$ Hz, 4H, N-CH$_2$), 2.71 (s, 6H, COCH$_3$), 1.83 (m, 4H, N-CH$_2$-CH$_2$), 1.27 (m, 20H), 0.85 (t, $J = 6.92$ Hz, 6H, CH$_3$); $^{13}$C-NMR (CDCl$_3$, 75 MHz): $\delta$ 197.6, 147.1, 143.2, 140.1, 134.5, 128.0, 127.5, 126.7, 125.1, 122.1, 110.7, 108.6, 106.3, 43.2, 31.7, 29.3, 27.3, 26.6, 22.6, 14.0; Anal. Calcd (%) C = 82.50, H = 8.12, N = 4.37, Found C = 82.49, H = 8.09, N = 4.38.

3.10 General procedure for the synthesis of polymers

Polymers were synthesized by above described method upon 30 hours reflux and precipitates were filtered through a short plug of basic alumina to remove traces of iron chloride and dried in vacuum oven overnight.

3.10.1 Poly[6,6'-{3,3'-N-octylbiscarbazole-4-phenylpyridine}-2,5-diyl] (P3a)

Light brown solid; Yield: 68%; m.p.: 160-162°C; R$: 0.27; IR (KBR, cm$^{-1}$): 3060 (sp$^2$ C-H stretching), 2950, 2862 (sp$^3$ C-H stretching), 1628 (C=N), 1590 (Ar C=C), 1326 (C-N); $^1$H-NMR (CDCl$_3$, 300MHz): $\delta$ 8.70 (s, Ar-
H), 8.30-7.31 (m, Ar-H), 4.25 (t, J = 7.54 Hz, 4H, N-CH₂), 2.74-1.34 (m, 24H), 0.87 (t, J = 7.04 Hz, 6H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 144.4, 142.3, 140.1, 139.3, 134.2, 133.5, 130.2, 129.3, 127.0, 126.7, 125.5, 123.8, 123.2, 121.1, 119.6, 118.2, 116.4, 113.3, 111.5, 108.4, 106.3, 44.2, 31.9, 30.4, 29.3, 27.2, 22.3, 14.1; Anal. Calcd (%) C = 65.56, H = 7.49, N = 5.94 Found C = 85.99, H = 7.33, N = 5.96; Mₜ (10⁵): 3.36; UV/VIS (CHCl₃) ʎᵣₐₛₜₜ, max (nm): 326, (389); PL (CHCl₃) ʎₑₘₜₜ, max (nm): 402.

3.10.2 Poly[6,6’-{3,3’-N-octylbiscarbazole-4(3-bromophenylpyridine)}-2,5-diyl] (P3b)

Reddish brown solid; Yield: 60%; m.p.: 233°C (dec); Rᵢ: 0.25; IR (KBR, cm⁻¹): 3020 (sp² C-H stretching), 2960, 2855 (sp³ C-H stretching), 1631 (C=N), 1587 (Ar C=C), 668 (C-Br); ¹H-NMR (CDCl₃, 300MHz): δ 8.55 (s, Ar-H), 8.41-7.37 (m, Ar-H), 4.2 (t, J = 7.53 Hz, 4H, N-CH₂), 2.72-1.39 (m, 24H), 1.24 (t, J = 7.27 Hz, 6H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 144.2, 140.5 139.8, 134.4, 133.2, 131.2, 130.5, 129.3, 127.4, 126.7, 126.0, 125.2, 123.1, 121.4, 119.1, 118.0, 116.1, 113.4, 111.3, 108.2, 106.1, 43.1, 31.8, 30.2, 29.4, 27.1, 22.7, 14.3; Anal. Calcd (%) C = 78.86, H = 6.61, N = 5.34, Found C = 77.24, H = 6.59, N = 5.37; Mₜ (10⁵): 1.38; UV/VIS (CHCl₃) ʎᵣₐₛₜₜ, max (nm): 323, (400); PL (CHCl₃) ʎₑₘₜₜ, max (nm): 406.

3.10.3 Poly[6,6’-{3,3’-N-octylbiscarbazole-4(3-nitrophosphorpyridine)}-2,5-diyl] (P3c)

Yellowish brown solid; Yield: 51%; m.p.: 151°C (dec); Rᵢ: 0.13; IR (KBR, cm⁻¹): 3070 (sp² C-H stretching), 2950, 2840 (sp³ C-H stretching), 1624 (C=N), 1586 (Ar C=C), 1536, 1341 (unsymmetric and symmetric NO₂); ¹H-NMR (CDCl₃, 300MHz) δ (ppm): 8.68 (s, Ar-H), 8.30 (d, J = 8.00 Hz, Ar-H), 8.18-8.07 (m, Ar-H), 7.38-7.34 (m, Ar-H), 4.24 (t, J = 8.02 Hz, 4H, N-CH₂), 2.73-1.35 (m, 24H), 1.02 (t, J = 7.12 Hz, 6H, CH₃); ¹³C-NMR (CDCl₃, 75MHz) δ (ppm): 144.8, 140.2, 140.0, 139.6, 134.9, 133.5, 130.2, 129.4, 127.2, 126.8, 125.8, 123.7, 123.2, 122.6, 122.0, 118.4, 116.4, 113.0, 111.2, 108.6, 106.2, 44.0, 31.9, 30.4, 29.3, 27.4, 22.8, 14.2; Anal. Calcd (%) C = 81.38, H = 6.91, N = 7.44, Found C = 81.19, H = 6.79, N = 7.47; Mₜ (10⁵): 1.61; UV/VIS (CHCl₃) ʎᵣₐₛₜₜ, max (nm): 343, (411); PL (CHCl₃) ʎₑₘₜₜ, max (nm): 442.
3.10.4 Poly[6,6’-{3,3’-N-octylbiscarbazole-4(3-hydroxyphenylpyridine)}-2,5-diyl] (P3d)

Light brown solid; Yield: 56%; m.p.: 191-193°C; Rf: 0.12;
IR (KBR, cm⁻¹): 3345(O-H), 3085 (sp² C-H stretching),
2925, 2840 (sp³ C-H stretching), 1621 (C=N), 1589 (Ar
C=C). ¹H-NMR (CDCl₃, 300MHz): δ 8.42 (s, Ar-H), 8.21 (d,
J = 7.84 Hz, Ar-H), 7.86 (dd, J= 8.73, 1.80Hz, Ar-H), 7.53-
7.43 (m, Ar-H), 7.27 (dd, J = 3, 14 Hz Ar-H), 5.31 (br s,
OH), 4.36 (t, J = 6.91 Hz, 6H, N-CH₂), 2.2-1.80 (m, 4H, N-CH₂-CH₂), 1.6-1.2 (m, 20H),
0.89 (t, J = 6.91 Hz, 6H, CH₃); ¹³C-NMR (CDCl₃, 75MHz): δ 144.4, 140.8, 140.4, 139.5,
134.7, 133.3, 129.2, 126.9, 125.6, 123.3, 123.0, 122.6, 122.2, 118.9, 111.0, 108.8, 106.4,
43.2, 31.8, 29.4, 27.3, 26.6, 22.6, 14.1; Anal. Calcd (%) C = 84.64, H = 7.33, N = 5.80,
Found C = 84.25, H = 7.30, N = 5.86; M_w (10⁵): 1.59; UV/VIS (CHCl₃) λₘₐₓ (nm): 342, (409); PL (CHCl₃) λₑₘ, max (nm): 435.

3.11 3,6-Dibromo-N-octylcarbazole (1)

To a mixture of N-octylcarbazole (5g, 18mmol) and acetic acid (15
mL) was added bromine (1.9 mL, 36.7 mmol) dropwise (15
minutes). The mixture was stirred at room temperature for 3 hours.
The precipitates formed were filtered and recrystallized from
ethanol affording white crystals (6.7g, 85%).
Yield: 85%; m.p.: 78-79°C; IR (w/cm⁻¹, ATR): 3064 (sp² C-H stretching), 2965, 2835
(sp³ C-H stretching), 1583 (Ar C=C), 1464 (CH₂ bend), 1376 (CH₃ bending), 1316 (C-
N); ¹H- NMR (CDCl₃, 400 MHz): δ 8.15 (d, J = 1.96 Hz, 2H, Ar-H), 7.56 (dd, J = 8.72,
1.96 Hz, 2H, Ar-H), 7.29 (d, J = 8.72 Hz, 2H, Ar-H), 4.24 (t, J = 7.20 Hz, 2H, N-CH₂),
1.85-1.81 (m, 2H, N-CH₂-CH₂), 1.32-1.24 (m, 10H), 0.87 (t, J = 6.76 Hz, 3H, CH₃); ¹³C-
NMR (CDCl₃, 100 MHz): δ 139.2, 129.7, 123.3, 122.8, 118.2, 111.7, 55.4, 32.7, 30.5,
29.2, 28.8, 26.7, 22.6, 14.1; GC-MS (70eV): 437(439, 435 isotopic pattern) (M⁺, 100%).

3.12 3-Bromo-9-octylcarbazole (3)

A solution of N-octylcarbazole (1g, 3.6 mmol) in dry chloroform
(15 mL) was stirred under nitrogen in a covered flask at 0°C. To
this flask, solution of NBS (0.64g, 3.6 mmol) in dry CHCl₃ (25 mL)
was added in two portions at 0°C. After complete addition, flask
was warmed to room temperature and stirred for 6 hrs under inert atmosphere. On the completion of reaction the mixture was poured into water and extracted, concentrated in vacuo to give brown oil that was purified by column chromatography on silica gel by eluting with hexane to afford a colourless oil (1.15g, 90%).

Yield: 90%; IR (υ/cm⁻¹, ATR): 3081 (sp² C-H stretching), 2961, 2815 (sp³ C-H stretching), 1584 (Ar C=C), 1466 (CH₂ bending), 1375 (CH₃ bending), 1319 (C-N), 690 (C-Br); ¹H-NMR (CDCl₃, 400 MHz): δ 8.21 (d, J = 1.4 Hz, 1H, Ar-H), 8.00 (d, J = 7.71 Hz, 1H, Ar-H), 7.55-7.41 (m, 2H, Ar-H), 7.36-7.27 (m, 3H, Ar-H), 4.36 (t, J = 7.31 Hz, 2H, N-CH₂), 1.92-1.87 (m, 2H, N-CH₂-CH₂), 1.41-1.25 (m, 10H), 0.89 (t, J = 6.91 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 100 MHz): δ 140.3, 139.2, 128.6, 126.3, 124.8, 123.3, 121.7, 120.6, 119.8, 115.4, 110.2, 109.5, 51.3, 31.8, 29.6, 29.0, 28.2, 27.4, 22.6, 14.3.

3.13 2,7-Dibromo-9,9'-dioctyl-9H-fluorene (5)

2,7-Dibromofluorene (3g, 9.2 mmol) was dissolved in DMSO (15 mL). To this 1-bromoctane (3.7g, 19.1 mmol) and KI (0.17g, 1.0 mmol) were added, mixture was degaseed and filled with nitrogen thrice. Then powdered KOH (2.3g, 41 mmol) was added at once, degassing and refilling with nitrogen were carried out again. The mixture was stirred under inert atmosphere for 6 hours, poured into water, precipitates were collected by filtration and recrystallized from ethanol to give pale yellow needle-like crystals (4.1g, 81%).

Yield: 81%; Rₓ: 0.81; m.p.: 51-51.5°C; ¹H-NMR (CDCl₃, 400 MHz): δ 7.53 (d, J = 7.76, 1.1 Hz, 2H, Ar-H), 7.47 (d, J = 1.8 Hz, 2H, Ar-H), 7.44 (d, J = 1.1 Hz, 2H, Ar-H), 1.94-1.89 (m, 4H, C-CH₂), 1.25-1.05 (m, 20H), 0.81 (t, J = 7.24 Hz, 6H, CH₃), 0.56 (quint, 4H). ¹³C-NMR (CDCl₃, 100 MHz): δ 153.2, 139.8, 131.2, 126.2, 122.3, 121.1, 46.4, 41.8, 31.7, 29.6, 29.0, 23.9, 22.8, 14.1; Anal for CₙHₙBr₂: Calcd (%) C = 63.51, H = 7.35, Found C = 63.41, H = 7.33.

3.14 2-Bromo-9,9'-dioctyl-9H-fluorene (7)

It was synthesized according to above-reported method stirring 2-bromofluorene (1.0g, 4.07 mmol), DMSO (10 mL), 1-bromoctane (1.8g, 9.3 mmol), KI (0.07g, 0.4 mmol), KOH (1.2g, 20 mmol) overnight at room temperature. Reaction mixture was
diluted with ethyl acetate and organic layer was washed with water, separated and concentrated in vacuo. Crude product was purified by column chromatography using hexane as eluent to afford the light yellow oil.

Yield: 88%; \(^1\)H-NMR (CDCl\(_3, 400\) MHz): \(\delta\) 7.69-7.68 (m, 1H, Ar-H), 7.57 (dd, \(J = 7.88, 1.4\) Hz, 1H, Ar-H), 7.49-7.46 (m, 2H, Ar-H), 7.35-7.33 (m, 3H, Ar-H), 1.98-1.91 (m, 4H, C-CH\(_2\)), 1.27-1.10 (m, 20H), 0.91 (t, \(J = 7.34\) Hz, 6H, CH\(_3\)), 0.79 (quint, 4H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.5, 148.2, 141.6, 140.3, 135.5, 131.7, 130.2, 128.7, 127.9, 126.4, 122.1, 44.1, 43.3, 31.8, 30, 6, 29.9, 29.2, 24.2, 22.6, 14.2; Anal for C\(_{29}\)H\(_{41}\)Br: Calcd (%) C = 74.18, H = 8.80, Found C = 74.27, H = 8.79.

3.15 General procedure for synthesis of boronic acid

The synthesized brominated compounds were dissolved in dry THF (30 mL) in an oven dried 100 mL flask and cooled to -78°C. To this, n-BuLi was added dropwise (15 minutes) and stirred for 1 hour. Afterward tri-isopropyl borate was added and reaction mixture was stirred overnight at room temperature, quenched with 2 M HCl (20 mL), stirred further for one hour and extracted with diethyl ether. Organic layers were separated, dried over anhydrous MgSO\(_4\), concentrated and vacuum-dried for one hour in oven at room temperature and used without further purification. For each Suzuki-coupling the corresponding boronic acid was synthesized separately.

3.15.1 9-Octyl-9H-carbazol-3,6-di-yl-boronic acid (2)

Compound was synthesized by same method employing 3,6-dibromo-N-octylcarbazole (0.5g, 1.14 mmol), n-BuLi (1.6 M in hexane, 1.71 mL, 2.73 mmol, 2.4 eq), THF (20 mL), B(OCH\(_3\))\(_3\) (0.96g, 5.10 mmol, 4.5 eq) with the exception that after concentrating the solvent, there appeared an oil that afforded product as white solid by dropwise addition of hexane by drop wise addition to afford white solid (0.25g, yield 63%) and used further as such.

3.15.2 9-Octylcarbazole-3-boronic acid (4)

The compound was prepared, by same procedure utilizing 3-bromo-9-octylcarbazole (2g, 5.6 mmol), n-BuLi (1.6 M in hexane, 4.2 mL, 6.72 mmol, 1.2 eq), THF (20 mL), tri-isopropyl borate (2.4g 12.8 mmol, 2.3 eq) as white solid (1.1g, 61%) and used as obtained.
3.15.3 9,9-Dioctyl-9H-fluoren-2,7-diylboronic acid (6)

The compound was prepared, by general method using 2,7-dibromo-9,9-dioctyl-9H-fluorene (0.3g, 0.54 mmol), n-BuLi (1.6 M in hexane, 0.81 mL, 1.29 mmol), THF (20 mL), tri-isopropyl borate (0.46g, 2.44 mmol) (reaction required vigorous stirring in contrast to above procedures), as white solid (0.16g, 61%) having m.p. > 350°C and used without further purification.

3.15.4 9,9-Dioctyl-9H-fluoren-2-ylboronic acid (8)

It was synthesized, by same method using n-BuLi (1.6 M in hexane, 0.8 mL, 1.27 mmol), 2-bromo-9,9-dioctyl-9H-fluorene (0.5g, 1.06 mmol), THF (15 mL), tri-isopropyl borate (0.46g, 2.44 mmol) upon vigorous stirring. Product was collected after sonication for one hour at 1200/rpm as white fine powder (0.25g, 54%) having m.p.: 69-71°C and used immediately obviating purification.

3.16 9-(7-Bromo-9,9-dioctylfluoren-2-yl)-9H-carbazole (10)

A mixture of 2,7-dibromo-9,9-dioctylfluorene (10g, 18.2 mmol), carbazole (2.6g, 15.5 mmol), cuprous iodide (0.3g, 1.57 mmol), 18-crown-6 (0.14g, 0.53 mmol), K2CO3 (4.3g, 31 mmol) was suspended in o-dichloro benzene (10 mL) and heated at 180°C for four days under nitrogen atmosphere. Upon completion of reaction, the reaction mixture was cooled, diluted with dichloromethane, filtered through a short silica plug to remove CuI and concentrated in vacuo to give orange brown oil. The o-dichloro benzene was removed upon vacuum distillation and the resulting brown mixture was purified by column chromatography (Hexane/DCM 6:1) to afford a colorless oil (5.6g, 57%).

Yield: 57%; Rf: 0.46; 1H-NMR (CDCl3, 400 MHz): δ 8.18 (2H, dt, J = 1.9 Hz, 7.7 Hz), 7.88 (dd, J = 0.44 Hz, 7.96 Hz, 1H, Ar-H), 7.64 (d, J = 8.5 Hz, 1H, Ar-H), 7.56-7.52 (m, 4H, Ar-H), 7.44-7.42 (m, 4 H), 7.33–7.30 (m, 2H), 2.00-1.96 (m, 4H), 1.21–1.11 (m, 20H), 0.83 (t, J = 7.10 Hz, 6H, CH3), 0.75-0.73 (m, 4H); 13C-NMR (CDCl3, 100 MHz): δ 153.2, 152.5, 141.0, 139.3, 139.0, 130.3, 129.7, 126.4, 126.1, 125.9, 123.4, 121.8,
129.2, 120.9, 120.3, 119.9, 109.7, 55.6, 40.2, 31.8, 29.9, 29.2, 23.9, 22.6, 14.1; MS (m/z, APCI): 634.3 (M⁺), 636.3 (M²).

3.17 9-(6-Bromo-9-octyl-9H-carbazol-3-yl)-9H-carbazole (9)

It was prepared according to above-reported method using N-octyl-3,6-dibromocarbazole (7.55g 17.2 mmol), carbazole (2.2g, 13.2 mmol), cuprous iodide (0.27g, 1.42 mmol), 18-crown-6 (0.13g, 0.49 mmol), K₂CO₃ (3.4g, 24.6 mmol), o-dichloro benzene (10 mL).

Crude product was purified by column chromatography (Hexane/DCM 7:1) to obtain compound as white solid (4.9g, 71%).

Yield: 71%; m.p.:141-143°C; Rf: 0.39; ¹H-NMR (CDCl₃, 400 MHz): δ 8.30 (d, J = 1.8 Hz, 1 H, Ar-H), 8.21 (d, J = 2.0 Hz, 1 H, Ar-H), 8.12 (d, J = 7.8 Hz, 2H, Ar-H), 7.84 (d, J = 8.1 Hz, 1H, Ar-H), 7.72–7.62 (m, 3 H, Ar-H), 7.44–7.36 (m, 4 H, Ar-H), 7.29 (dt, J₁ =1.4 Hz, J₂ =7.9 Hz, 2H, Ar-H), 4.25 (t, J = 7.2 Hz, 2H, N-CH₂), 1.85–1.80 (m, 2 H), 1.71–1.24 (m, 10 H), 0.87 (t, J = 7.1 Hz, 3H, CH₃); ¹³C-NMR (CDCl₃, 100 MHz): δ 141.9, 139.7, 133.1, 129.3, 125.9, 123.4, 122.6, 121.7, 120.2, 119.6, 117.4, 112.0, 111.9, 110.5, 110.0, 109.7, 43.7, 31.8, 30.7, 29.3, 27.4, 22.6, 14.1; MS (m/z, APCI): 523.2 (M⁺), 525.1 (M²).

3.18 General procedure for Pd-catalyzed Suzuki coupling

Boronic acid (1.0 eq) and bromo derivative (2.26 eq) were dissolved in toluene (15 mL). To this, were added 2 M K₂CO₃ (20 mL). The mixture was evacuated and filled with nitrogen thrice to remove air. Then Pd(PPh₃)₄ (0.05g, 0.04 mmol, 5 mol%) was added in three portions and after each addition, successive degassings were carried out. The mixture was refluxed for 72 hrs under nitrogen and filtered through a short silica plug to remove the catalyst. The filtered-mixture was extracted with dichloromethane. Organic phase was separated, dried over MgSO₄, evaporated on rotary evaporator and crude product was purified by column chromatography on silica gel engageing different mobile phases and vacuum-dried.
3.18.1 9-(7-(6-(7-(9H-Carbazol-9-yl)-9,9'-dioctyl-9H-fluoren-2-yl)-9-octyl-9H-carbazol-3-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9H-carbazole (CFT)

The compound was synthesized by same procedure using corresponding boronic acid 2 (0.2g, 0.54 mmol), 9-(2-bromo-9,9-dioctylfluoren-7-yl)-9H-carbazole 10 (0.78g, 1.23 mmol), toluene (15 mL), 2 M K$_2$CO$_3$ (20 mL), Pd(PPh$_3$)$_4$ (0.05g, 0.04 mmol, 5 mol%). Crude product was purified by column chromatography on silica gel (Hexane:DCM =7:1) to obtained as off-white solid (0.45g, 67%).

Yield: 67%; m.p.: 88°C; Rf: 0.27; IR (υ/cm$^{-1}$, ATR): 3074 (sp$^2$ C-H stretching), 2991, 2865 (sp$^3$ C-H stretching), 1600 (Ar C=C), 1464 (CH$_2$ bending), 1376 (CH$_3$ bending), 1311 (C-N); $^1$H-NMR (CDCl$_3$, 400 MHz): δ 8.52 (2H, d, $J = 7.56$ Hz), 8.20-8.18 (m, 4H, Ar-H), 7.96 (d, $J =8.64$Hz, 2H, Ar-H), 7.90-7.79 (m, 6H, Ar-H), 7.76-7.75 (m, 2H, Ar-H), 7.58-7.51 (m, 6H, Ar-H), 7.48-7.42 (m, 8H, Ar-H), 7.34-7.31 (m, 4H, Ar-H); 4.42 (t, $J = 7.23$ Hz, 2H, N-CH$_2$), 2.24-2.07 (m, 10H), 1.21-1.19 (m, 10H), 1.14-1.05 (m, 40H), 0.91 (quint, 8H), 0.88 (t, $J = 7.11$ Hz, 15H, CH$_3$); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 152.6, 150.2, 141.3, 140.9, 140.2, 138.5, 136.0, 132.3, 131.5, 129.9, 128.7, 126.0, 125.4, 123.9, 121.8, 121.0, 120.6, 118.8, 116.6, 109.7, 108.9, 55.7, 45.4, 41.2, 31.9, 29.6, 28.2, 27.3, 22.1, 14.1; MS (m/z, APCI): calcd 1385.9 (M$^+$), found 1387.9 (M+2); Anal for C$_{102}$H$_{119}$N$_3$ (%): Calcd C = 88.32, H = 8.65, N = 3.03, Found C = 88.30, H = 8.62, N = 8.64; UV/VIS (CHCl$_3$) $\lambda_{abs}$ max (nm): 352, (292); PL (CHCl$_3$) $\lambda_{em}$, max (nm): 400.

3.18.2 9-(6-(6-(6-(9H-Carbazol-9-yl)-9-octyl-9H-carbazol-3-yl)-9-octyl-9H-carbazol-3-yl)-9-octyl-9H-carbazol-3-yl)-9H-carbazole (CCP)

It was synthesized by method reported above employing corresponding boronic acid 2 (0.2g, 0.54 mmol), 9-(6-bromo-9-octyl-9H-carbazol-3-yl)-9H-carbazole 9 (0.65g, 1.24 mmol), Pd(PPh$_3$)$_4$ (0.05g, 0.04 mmol, 5 mol%), toluene (15 mL), 2M K$_2$CO$_3$ (20 mL) and purifying by column chromatography on silica gel (Hexane:DCM= 5:1) to afford very light yellow solid (0.37g, 59%).

102
Yield: 59%; m.p.: 91°C; Rf: 0.21; IR (υ/cm\(^{-1}\), ATR): 3077 (sp\(^2\) C-H stretching), 2972, 2849 (sp\(^3\) C-H stretching), 1598 (Ar C=C), 1465 (CH\(_2\) bending), 1375 (CH\(_3\) bending), 1312 (C-N); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): 8.26-8.25 (m, 2H, Ar-H), 8.19 (ddd, \(J = 6.4, 4.1, 1.4\) Hz, 6H, Ar-H), 7.61-7.59 (m, 6H, Ar-H), 7.55-7.49 (m, 6H, Ar-H), 7.42-7.39 (m, 8H, Ar-H), 7.33-7.29 (ddd, \(J = 6.4, 4.1, 1.4\) Hz, 6H, Ar-H), 4.41 (t, \(J = 7.30\) Hz, 6H, N-CH\(_2\)), 2.09-1.92 (m, 6H, N-CH\(_2\)- CH\(_2\)), 1.41-1.24 (m, 30H), 0.91 (t, \(J = 7.13\) Hz, 9H, CH\(_3\)); \(^1^3\)C- NMR (100 MHz, CDCl\(_3\)): \(\delta 145.9, 141.0, 138.4, 133.5, 131.2, 129.9, 125.7, 124.9, 122.1, 120.6, 119.8, 119.1, 117.2, 114.4, 112.5, 111.3, 109.8, 109.0, 61.1, 38.4, 31.8, 29.4, 27.3, 22.6, 14.0; MS (m/z, APCI): calcd 1163.7 (M\(^+\)), found 1164.8 [M+H]\(^+\);

Analytical data for C\(_{88}H_{85}N_5\) (%): Calcd C = 86.63, H = 7.36, N = 6.01, Found C = 86.65, H = 7.35, N = 6.02; UV/VIS (CHCl\(_3\)) \(\lambda_{abs}\), max (nm): 343, (297); PL (CHCl\(_3\)) \(\lambda_{em}\), max (nm): 400.

3.18.3 9-(9-Octyl-6-(9-octyl-9H-carbazol-3-y1)-9H-carbazol-3-y1)-9H-carbazole (CCT)

The compound was synthesized by the same method employing boronic acid 4 (1.0g, 3.1 mmol), 9-(6-bromo-9-octyl-9H-carbazol-3-y1)-9H-carbazole 9 (1.8g, 3.4 mmol), 2M K\(_2\)CO\(_3\) (30 mL), toluene (20 mL), Pd(PPh\(_3\))\(_4\) (0.05g, 0.04 mmol, 5 mol%) except the reaction time was 48 hours and purified by column chromatography (Hexane:DCM 6:1) as white semi-solid (1.34g).

Yield: 61%; m.p.: 79°C; Rf: 0.39; IR (υ/cm\(^{-1}\), ATR): 3082 (sp\(^2\) C-H stretching), 2971, 2859 (sp\(^3\) C-H stretching), 1595 (Ar C=C), 1466 (CH\(_2\) bending), 1375 (CH\(_3\) bending), 1317 (C-N); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta 8.26\) (d, \(J = 7.34\) Hz, 2H, Ar-H), 8.19-8.02 (m, 2H, Ar-H), 7.87-7.76 (m, 4H, Ar-H), 7.67 (d, \(J = 8.23\) Hz, 2H, Ar-H), 7.58-7.49 (m, 2H, Ar-H), 7.44-7.40 (m, 5H, Ar-H), 7.31 (ddd, \(J = 6.3, 4.1, 1.5\) Hz, 4H, Ar-H), 4.41 (t, \(J = 7.3\) Hz, 4H, N-CH\(_2\)), 2.04-1.91 (m, 4H, N-CH\(_2\)-CH\(_2\)), 1.51-1.25 (m, 20H), 0.91 (t, \(J = 6.9\) Hz, 6H, CH\(_3\)); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta 148.2, 143.4, 139.6, 136.5, 133.1, 129.2, 127.3, 125.6, 124.3, 123.6, 122.4, 120.8, 118.2, 116.9, 115.7, 115.1, 114.3, 59.4, 35.6, 32.1, 29.9, 28.1, 23.3, 14.2; MS (m/z, APCI): calcd 721.4 (M\(^+\)), found 722.4 [M+H]\(^+\); Analytical data for C\(_{52}H_{55}N_3\) (%): Calcd C = 86.50, H = 7.68, N = 5.82, Found C = 86.47, H = 7.66, N = 5.83; UV/VIS (CHCl\(_3\)) \(\lambda_{abs}\), max (nm): 337, (290); PL (CHCl\(_3\)) \(\lambda_{em}\), max (nm): 450, (508).
3.18.4 9-(9,9'-Dioctyl-7-(9-octyl-9H-carbazol-3-yl)-9H-fluoren-2-yl)-9H-carbazole (CCF)

The compound was obtained by above-reported method utilizing boronic acid 4 (1.0g, 3.1 mmol), 9-(7-bromo-9,9-dioctyfluoren-2-yl)-9H-carbazole 10 (2.16g, 3.4 mmol) under Suzuki coupling conditions as white solid (1.60g, 62%) after column chromatography (Hexane:DCM 6:1).

Yield: 62%; m.p.: 72°C; Rf: 0.43; IR (υ/cm⁻¹, ATR): 3087 (sp² C-H stretching), 2971, 2852 (sp³ C-H stretching), 1596 (Ar C=C), 1465 (CH₂ bending), 1375 (CH₃ bending), 1318 (C-N); ¹H-NMR (CDCl₃, 400 MHz): δ 8.21-8.18 (m, 4H, Ar-H), 7.97 (dd, J = 8.01, 3.72 Hz, 2H, Ar-H), 7.73-7.59 (m, 4H, Ar-H), 7.36-7.29 (m, 3H, Ar-H), 7.19-7.07 (m, 8H, Ar-H), 4.37 (t, J = 7.11 Hz, 2H, N-CH₂), 2.09-2.01 (m, 4H, C-CH₂), 1.94-1.82 (m, 2H, N-CH₂-CH₂), 1.41-1.22 (m, 30H), 0.97 (t, J = 7.89 Hz, 9H, CH₃), 0.81 (quint, 4H); ¹³C-NMR (100 MHz, CDCl₃): δ 151.2, 149.4, 144.1, 141.9, 140.3, 139.9, 138.9, 138.8, 136.0, 132.5, 130.5, 128.7, 126.2, 125.8, 123.3, 122.9, 121.7, 120.6, 120.1, 119.8, 118.9, 109.7, 108.8, 55.5, 43.5, 40.1, 31.7, 30.4, 29.9, 29.2, 22.5, 14.1; MS (m/z, APCI): calcld 832.5 (M⁺), found 833.5 [M+H]⁺; Anal for C₆₁H₇₂N₂ (%): Calcld C = 87.93, H = 8.71, N = 3.36, Found C = 87.91, H = 8.70, N = 3.38; UV/VIS (CHCl₃) λₑₚ, max (nm): 334, (293); PL (CHCl₃) λₑₚ, max (nm): 452, (506).

3.18.5 9-(7-(7-(9H-Carbazol-9-yl)-9,9'-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-9H-carbazole (CFD)

The compound was prepared by same method using corresponding boronic acid 6 (0.17g, 0.35 mmol), 9-(7-bromo-9,9-dioctyfluoren-2-yl)-9H-carbazole 10 (0.51g, 0.80 mmol), 2M K₂CO₃ (20 mL), toluene (15 mL), Pd(PPh₃)₄ (0.05g, 0.043 mmol) and purified by column chromatography over silica gel using (Hexanes:DCM 6:1) as light yellow solid (0.35g, 66%) yield.

Yield: 66%; m.p.: 77°C; Rf: 0.29; IR (υ/cm⁻¹, ATR): 3077 (sp² C-H stretching), 2982, 2861 (sp³ C-H stretching), 1599 (Ar C=C), 1465 (CH₂ bending), 1376 (CH₃ bending), 1314 (C-N); ¹H-NMR (CDCl₃, 400 MHz): δ 8.21-8.17 (m, 4H, Ar-H), 8.01-7.92 (m, 2H,
Ar-H), 7.89-7.75 (m, 2H, Ar-H), 7.70-7.68 (m, 4H, Ar-H), 7.64 (m, 4H, Ar-H), 7.59-7.52 (m, 6H, Ar-H), 7.47-7.41 (m, 8H, Ar-H), 7.35-7.30 (m, 4H, Ar-H), 2.14-2.03 (m, 12H), 1.22-1.15 (m, 60H), 0.82-0.73 (m, 30H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.3, 148.8, 141.6, 140.2, 139.7, 138.4, 136.2, 132.8, 130.9, 129.5, 126.7, 125.2, 123.9, 122.7, 121.8, 120.6, 119.7, 116.4, 114.2, 112.8, 45.7, 42.4, 33.5, 31.2, 30.4, 29.7, 23.8, 14.3; MS (m/z, MALDI): calcd 1496.1 (M\(^+\)), found 1498 [M\(^+\)+2]; Anal for C\(_{111}\)H\(_{156}\)N\(_2\) (%): Calcd C = 88.98, H = 9.15, N = 1.87, Found, C = 88.99, H = 9.06, N = 1.84; UV/VIS (CHCl\(_3\)) \(\lambda\)\(_{\text{abs, max}}\) (nm): 350, (292); PL (CHCl\(_3\)) \(\lambda\)\(_{\text{em, max}}\) (nm): 400.

3.1.6.9-\((9,9'^{\prime}\)-Dioctyl-7-\((9,9'^{\prime}\)-dioctyl-9H-fluorene-2-yl)-9H-fluorene-2-yl)-9H-carbazole (CFM)

The compound was synthesized by same procedure employing corresponding boronic acid 8 (0.18g, 0.41 mmol), 2MK\(_2\)CO\(_3\) (15 mL), 9-\((7\)-bromo-9,9'-dioctylfluoren-2-yl)-9H-carbazole 10 (0.29g, 0.45 mmol), toluene (20 mL), Pd(PPh\(_3\))\(_4\) (0.05g, 0.04 mmol, 5 mol\%) for reaction time of 48 hours, purified by column chromatography upon silica gel (Hexane:DCM 5:1) as white solid (0.25g, 64%).

Yield: 64%; m.p.: 69°C; Rf: 0.48 ; IR (\(\nu/cm^{-1}\), ATR): 3071 (sp\(^2\) C-H stretching), 2984, 2873 (sp\(^3\) C-H stretching), 1594 (Ar C=C), 1465 (CH\(_2\) bending), 1375 (CH\(_3\) bending), 1314 (C-N); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.20 (d, \(J = 7.76\) Hz, 2H, Ar-H), 7.97 (d, \(J = 8.36\) Hz, 2H, Ar-H), 7.90-7.87 (m, 2H, Ar-H), 7.76-7.70 (m, 4H, Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.51-7.43 (m, 5H, Ar-H), 7.34 (ddd, \(J = 8.04, 7.52, 1.4\) Hz, 4H, Ar-H), 2.16-2.07 (m, 8H, C-CH\(_2\)), 1.14-1.07 (m, 40H), 0.93 (t, \(J = 7.1\) Hz, 12H, CH\(_3\)), 0.86 (quint, 8H, CH\(_2\)-CH\(_3\)); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.5, 148.2, 147.6, 143.4, 141.6, 140.8, 138.8, 136.9, 132.4, 131.3, 130.1, 129.6, 128.7, 126.5, 125.8, 123.6, 122.5, 121.7, 120.7, 119.8, 117.2, 114.4, 48.2, 42.7, 34.1, 31.3, 29.7, 26.4, 23.5, 14.3; MS (m/z, APCI): calcd 943.7 (M\(^+\)), found 944.7 [M+H\(^+\)]\(^+\); Anal for C\(_{70}\)H\(_{85}\)N\(_2\) (%): Calcd C = 89.02, H = 9.50, N = 1.48, Found C = 88.98, H = 9.54, N = 1.47; UV/VIS (CHCl\(_3\)) \(\lambda\)\(_{\text{abs, max}}\) (nm): 340, (291); PL (CHCl\(_3\)) \(\lambda\)\(_{\text{em, max}}\) (nm): 402, (507).
3.18.7 2,7-(6-(9-Octyl-9H-carbazolyl)3-yl)9,9'-dioctyl-9H-fluorene (CFC)

The compound was synthesized by same method utilizing boronic acid 6 (0.2g, 0.41 mmol), 9-(6-bromo-9-octyl-9H-carbazol-3-yl)-9H-carbazole 9 (0.5g, 0.95 mmol), 2M K$_2$CO$_3$ (20 mL), toluene (15 mL), Pd(PPh$_3$)$_4$ (0.05g, 0.04 mmol, 5 mol%), purifying by column chromatography (Hexane:Ethyl acetate 9:1) and obtaining light yellow solid (0.36g, 68%).

Yield: 68%; m.p.: 66°C; R$_f$: 0.24; IR (υ/cm$^{-1}$, ATR): 3069 (sp$^2$ C-H stretching), 2982, 2857 (sp$^3$ C-H stretching), 1598 (Ar C=C), 1463 (CH$_2$ bending), 1375 (CH$_3$ bending), 1314 (C-N); $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.32 (m, 2H, Ar-H), 8.15-8.07 (m, 4H, Ar-H), 7.94 (d, $J = 7.76$ Hz, 2H, Ar-H), 7.78 (d, $J = 7.76$ Hz, 2H, Ar-H), 7.66-7.58 (m, 2H, Ar-H), 7.51-7.49 (m, 4H, Ar-H), 7.40-7.34 (m, 6H, Ar-H), 7.31-7.29 (m, 2H, Ar-H), 7.19-7.17 (m, 2H, Ar-H), 7.12-7.07 (m, 8H, Ar-H); 4.10 (t, $J = 7.7$ Hz, 4H, N-CH$_2$), 2.15.2.12 (m, 4H, N-CH$_2$-CH$_2$), 2.02-1.99 (m, 4H), 1.41-1.33 (m, 20H), 1.18-1.09 (m, 20H), 0.98 (t, $J = 7.81$ Hz, 12H, CH$_3$), 0.79 (quint, 4H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 151.2, 142.1, 140.6, 139.5, 138.3, 135.4, 133.8, 130.9, 129.8, 128.8, 126.1, 125.6, 124.7, 123.1, 121.5, 120.3, 119.8, 119.3, 118.7, 114.6, 109.9, 108.6, 55.3, 43.7, 40.5, 31.9, 30.1, 29.4, 27.2, 23.9, 22.6, 14.1; MS (m/z, APCI): calcd 1274.8 (M$^+$), found 1275.8 [M+H]$^+$; Anal for C$_{93}$H$_{102}$N$_4$ (%): Calcd C = 87.55, H = 8.06, N =4.39, Found C = 87.52, H = 8.08, N = 4.36; UV/VIS (CHCl$_3$) $\lambda_{abs}$, max (nm): 346, (295); PL (CHCl$_3$) $\lambda_{em}$, max (nm): 400.

3.19 General procedure for synthesis of N,N-disubstituted-aryl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide

1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (1.0 eq), suitably-substituted anilines (4.2 eq) and zinc acetate (as catalyst) were dissolved in quinoline (15 mL). The solution was heated with stirring under inert atmosphere at 160°C for 24 hours. After cooling to room temperature, the solid reaction mixture was filtered and precipitates were washed successively with water, ethanol and vacuum-dried at 100°C overnight.
3.19.1 N,N-Di-p-tolyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (11)

The compound was synthesized by above method using 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (1.0g, 1.89 mmol), p-toluidine (0.85g, 7.94 mmol), zinc acetate (0.35g, 1.91 mmol), quinoline (15 mL) and getting product as dark brown powder (1.1g, 83%).

Yield: 83%; m.p.: >300°C; R_f: 0.78; IR (v/cm⁻¹, ATR): 2914, 2856 (sp³ C-H unsymmetric and symmetric), 1704 (C=O), 1587 (Ar-C=C), 1375 (CH₃ bending), 1312 (C-N); ¹H-NMR (300 MHz,CDCl₃): δ 8.73 (s, 4H, Ar-H), 6.96 (d, J = 8.19 Hz, 4H, Ar-H), 6.61 (d, J = 8.19 Hz, 4H, Ar-H), 2.23 (s, 6H, CH₃); ¹³C-NMR (75 MHz, CDCl₃): δ 162.5, 137.2, 135.4, 134.2, 131.3, 129.9, 128.1, 126.5, 125.2, 124.3, 122.4, 27.4; LCMS (m/z): [M⁺] calcd 706.1, found 706.9 (positive mode); Anal for C₃₈H₁₈Cl₄N₂O₄ (%): Calcd C = 64.43, H = 2.56, N = 3.95, Found C = 64.38, H = 2.51, N = 4.02.

3.19.2 N,N-Di-2-methoxyphenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (12)

Compound was prepared by general procedure utilizing 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (1.0g, 1.89 mmol), 2-methoxyaniline (0.95g, 7.72 mmol), zinc acetate (0.35g, 1.91 mmol), quinoline (15 mL) to produce reddish brown powder (0.97g, 70%).

Yield: 70%; m.p.: >300°C; R_f: 0.81; IR (v/cm⁻¹, ATR): 2970, 2833 (sp³ C-H unsymmetric and symmetric), 1710 (C=O), 1586 (Ar-C=C), 1376(CH₃ bending), 1311 (C-N); ¹H-NMR (300 MHz,CDCl₃): δ 8.74 (s, 4H, Ar-H), 7.84-7.81 (m, 2H, Ar-H), 7.51-7.34 (m, 6H, Ar-H), 3.81 (s, 6H, OCH₃); ¹³C-NMR (75 MHz, CDCl₃): δ 162.2, 153.9, 136.1, 135.4, 131.7, 129.7, 128.8, 127.2, 126.6, 125.0, 123.8, 121.1, 112.5, 55.8; LCMS (m/z): [M⁺] calcd 738.4, found 739.2 (positive mode); Anal for C₃₈H₁₈Cl₄N₂O₆ (%): Calcd C = 61.65, H = 2.45, N = 3.78, Found C = 61.62, H = 2.40, N = 4.01.
3.19.3 N,N-Di-2-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (13)

The compound was synthesized according to general method engaging 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (1.0 g, 1.89 mmol), 2-nitroaniline (1.1 g, 7.97 mmol), quinoline (15 mL), zinc acetate (0.35 g, 1.91 mmol) to attain yellow powder (1.06 g, 73%).

Yield: 73%; m.p.: >300°C; R$_f$: 0.83; IR (υ/cm$^{-1}$, ATR): 1708 (C=O), 1587 (Ar-C=C), 1315 (C-N), 1527, 1340 (unsymmetric and symmetric NO$_2$); $^1$H-NMR (300 MHz, DMSO-d$_6$): δ 8.60 (s, 4H, Ar-H), 8.33-8.30 (m, 2H, Ar-H), 8.02-7.95 (m, 2H, Ar-H), 7.74-7.65 (m, 2H, Ar-H), 7.54-7.39 (m, 2H, Ar-H); $^{13}$C-NMR (75 MHz, DMSO-d$_6$): δ 163.4, 150.3, 139.6, 138.1, 135.9, 134.0, 132.6, 131.3, 130.8, 128.7, 127.1, 124.4, 122.1; LCMS (m/z): [M$^+$] calcd 767.9, found 768.8 (positive mode); Anal for C$_{36}$H$_{12}$Cl$_4$N$_4$O$_8$ (%): Calcd C = 56.13, H = 1.57, N = 7.27, Found C = 56.02, H = 1.51, N = 7.33.

3.19.4 N,N-Di-3-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (14)

The compound was prepared by the same procedure employing 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (1.0 g, 1.89 mmol), 3-nitroaniline (1.1 g, 7.97 mmol), quinoline (15 mL), zinc acetate (0.35 g, 1.91 mmol) to gain dark yellow powder (1.1 g, 76%).

Yield: 76%; m.p.: >300°C; R$_f$: 0.82; IR (υ/cm$^{-1}$, ATR): 1707 (C=O), 1589 (Ar-C=C), 1316 (C-N), 1536, 1343 (unsymmetric and symmetric NO$_2$); $^1$H-NMR (300 MHz, DMSO-d$_6$): δ 8.59 (s, 4H, Ar-H), 8.47-8.41 (m, 2H, Ar-H), 8.04-7.97 (m, 2H, Ar-H), 7.80-7.53 (m, 4H, Ar-H); $^{13}$C-NMR (75 MHz, DMSO-d$_6$): δ 163.1, 150.2, 141.0, 136.1, 135.5, 133.6, 131.8, 130.7, 129.9, 128.6, 126.7, 123.6, 122.8; LCMS (m/z): [M$^+$] calcd 767.9, found 768.6 (positive mode); Anal for C$_{36}$H$_{12}$Cl$_4$N$_4$O$_8$ (%): Calcd C = 56.13, H = 1.57, N = 7.27, Found C = 56.09, H = 1.55, N = 7.31.

3.19.5 N,N-Di-4-nitrophenyl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (15)

The compound was prepared by the same procedure utilizing 1,6,7,12-tetrachloroperylene-
3,4,9,10-tetracarboxylic acid dianhydride (1.0g, 1.89 mmol), 4-nitroaniline (1.1g, 7.97 mmol), quinoline (15 mL), zinc acetate (0.35g, 1.91 mmol) to get dark yellow powder (1.05g, 72%).

Yield: 72%; Rf: 0.84; m.p.: >300°C; IR (ν/cm⁻¹, ATR): 1711 (C=O), 1588 (Ar-C=C), 1309 (C-N), 1529, 1343 (unsymmetric and symmetric NO₂); ¹H-NMR (300 MHz, DMSO-d₆): δ 8.61 (s, 4H, Ar-H), 8.19 (d, J = 8.15 Hz, 4H, Ar-H), 7.95 (d, J = 8.15 Hz, 4H, Ar-H); ¹³C-NMR (75 MHz, DMSO-d₆): δ 163.5, 151.1, 145.3, 137.5, 135.8, 129.4, 127.4, 126.7, 125.9, 123.6, 121.5; LCMS (m/z): [M⁺] calcd 767.9, found 768.9 (positive mode); Anal for C₃₆H₁₂Cl₄N₄O₈ (%): Calcd C = 56.13, H = 1.57, N = 7.27, Found C = 56.04, H = 1.56, N = 7.29.

3.20 General procedure for synthesis of N,N-disubstitutes-aryl-1,6,7,12-tetra(substituted phenoxy)-3,4,9,10-perylenedicarboximide
To a suspension of N,N-disubstituted-aryl-1,6,7,12-tetrachloro-3,4,9,10-perylenedicarboximide (1.0 eq) in NMP (10 mL), were added K₂CO₃ (in excess with respect to phenol) and phenol (10.5 eq). The mixture was stirred at 90°C for 24 hours under inert atmosphere. After cooling to room temperature precipitates were filtered, stirred in 150 mL of water and vacuum-dried overnight at 100°C.

3.20.1 N,N-Di-p-tolyl-1,6,7,12-tetraphenoxy-3,4,9,10-perylenedicarboximide (PM)
The compound was prepared according to general method using corresponding perylenediimide 11 (1g, 1.41 mmol), phenol (1.4g, 14.8 mmol), K₂CO₃ (2.4g, 17.39 mmol), NMP (10 mL), obtaining brown powder (0.9g, 68%).

Yield: 68%; m.p.: >300°C; Rf: 0.30; IR (ν/cm⁻¹, ATR): 2931, 2877 (sp³ C-H unsymmetric and symmetric), 1700 (C=O), 1588 (Ar-C=C), 1376 (CH₃ bending), 1326 (C-N), 1137 (C-O); ¹H-NMR (300 MHz, CDCl₃): δ 8.37 (s, 4H, Ar-H), 7.58 (d, J = 8.0 Hz, 4H, Ar-H), 7.21-7.12 (m, 8H, Ar-H), 6.98 (d, J = 8.0 Hz, 4H, Ar-H), 6.82-6.74 (m, 12H, Ar-H), 2.29 (s, 6H, CH₃); ¹³C-NMR (75 MHz, CDCl₃): δ 162.3, 158.2, 152.4, 136.3, 134.6, 133.9, 130.8, 129.9, 128.7, 125.4, 124.6, 122.4, 121.7, 119.3, 26.2; LCMS (m/z): [M⁺] calcd 938.3, found 939.4 (positive mode);
Anal for C_{62}H_{38}N_{2}O_{8} (%): Calcd C = 79.31, H = 4.08, N = 2.98, Found C = 79.23, H = 4.01, N = 2.94; UV/VIS (CHCl_{3}) \( \lambda_{\text{abs}} \), max (nm): 516, (391); PL (CHCl_{3}) \( \lambda_{\text{em}} \), max (nm): 550.

3.20.2 N,N-Di-p-tolyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximide (POM)

The compound was prepared by same procedure employing corresponding perylenediimide 11 (0.5g, 0.70 mmol), \( p \)-cresol (0.8g, 7.4 mmol), K_{2}CO_{3} (1.2g, 8.69 mmol), NMP (10 mL), attaining dark blue powder (0.47g, 67%).

Yield: 67%; m.p.: >300°C; R_{f}: 0.28; IR (\nu/cm\(^{-1}\), ATR): 2990, 2884 (sp\(^{3}\)C-H unsymmetric and symmetric), 1702 (C=O), 1586 (Ar-C=C), 1374 (CH\(_{3}\) bending), 1319 (C-N), 1142 (C-O); \(^{1}\)H-NMR (300 MHz,CDCl\(_{3}\)): \( \delta \) 8.34 (s, 4H, Ar-H), 7.34 (d, \( J =8.5\)Hz, 4H, Ar-H), 7.09-7.03 (m, 12H, Ar-H), 6.83 (d, \( J =8.37\)Hz, 8H, Ar-H), 2.31 (s, 18H, CH\(_{3}\)); \(^{13}\)C-NMR (75 MHz, CDCl\(_{3}\)): \( \delta \) 162.5, 157.4, 151.6, 135.9, 133.7, 132.5, 129.9, 128.7, 127.9, 124.3, 122.7, 121.2, 120.4, 119.1, 25.4; LCMS (m/z): [M\(^{+}\)] calcd 994.4, found 995.1 (positive mode); Anal for C\(_{66}\)H\(_{46}\)N\(_{2}\)O\(_{8}\) (%): Calcd C = 79.66, H = 4.66, N = 2.82, Found C = 78.98, H = 4.61, N = 2.79; UV/VIS (CHCl\(_{3}\)) \( \lambda_{\text{abs}} \), max (nm): 578, 545, 450; PL (CHCl\(_{3}\)) \( \lambda_{\text{em}} \), max (nm): 605.

3.20.3 N,N-Di-2-methoxyphenyl-1,6,7,12-tetra(2,5-dimethoxyphenoxy)-3,4,9,10-perylene dicarboximide (PDM)

The compound was prepared according to above reported procedure engaing corresponding perylenediimide 12 (0.5g, 0.67 mmol), 2,5-dimethoxy phenol (1.1g, 7.1 mol), K_{2}CO_{3} (1.1g, 7.8 mmol), NMP (10 mL), producing red powder (0.45g, 55%).

Yield: 55%; m.p.: >300°C; R_{f}: 0.24; IR (\nu/cm\(^{-1}\), ATR): 2982, 2856 (sp\(^{3}\)C-H unsymmetric and symmetric), 1707 (C=O), 1586 (Ar-C=C), 1375 (CH\(_{3}\) bending), 1316 (C-N), 1155 (C-O); \(^{1}\)H-NMR (300 MHz,CDCl\(_{3}\)): \( \delta \) 8.31 (s, 4H, Ar-H), 7.74-7.69 (m, 2H, Ar-H), 7.43-7.31 (m, 2H, Ar-H),
6.94-6.86 (m, 8H, Ar-H), 6.58 (d, J = 8.3Hz, 8H, Ar-H), 3.78 (s, 30H, OCH_3); ^13^C-NMR (75 MHz, CDCl_3): δ 162.3, 154.8, 153.0, 151.8, 135.3, 134.7, 133.2, 128.4, 126.5, 124.3, 123.6, 122.1, 121.3, 120.4, 118.6, 116.2, 113.4, 56.1; LCMS (m/z): [M^+] calcd 1210.4, found 1211.2 (positive mode); Anal for C_{70}H_{54}N_2O_{18} (%): Calcd C = 69.42, H = 4.49, N = 2.31, Found C = 69.40, H = 4.42, N = 2.28; UV/VIS (CHCl_3) δ_{abs}, max (nm): 546, (424); PL (CHCl_3) δ_{em}, max (nm): 600.

3.20.4 N,N-Di-2-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarb-oximide (P2N)

The compound was prepared by same method utilizing corresponding perylenediimide 13 (0.5g, 0.65 mmol), p-cresol (0.74g, 6.85 mmol), K_2CO_3 (2.0g, 14.49 mmol), NMP (10 mL), producing dark orange powder (0.46g, 67%).

Yield: 67%; m.p.: >300°C; R_f: 0.31; IR (υ/cm\(^{-1}\), ATR): 2987, 2862(\(sp^3\) C-H unsymmetric and symmetric), 1705 (C=O), 1592 (Ar-C=C), 1375 (CH_3 bending), 1312 (C-N), 1530, 1348 (unsymmetric and symmetric NO_2), 1160 (C-O); ^1^H-NMR (300 MHz, DMSO-d_6): δ 8.35 (s, 4H, Ar-H), 8.24-8.19 (m, 2H, Ar-H), 7.97-7.89 (m, 2H, Ar-H), 7.76-7.64 (m, 2H, Ar-H), 7.38-7.27 (m, 2H, Ar-H), 7.11 (d, J = 8.31 Hz, 8H, Ar-H), 6.97 (d, J = 8.31 Hz, 8H, Ar-H), 2.34 (s, 12H, CH_3); ^13^C-NMR (75 MHz, DMSO-d_6): δ 163.1, 155.9, 152.8, 147.2, 138.4, 136.5, 134.7, 133.4, 132.6, 130.4, 127.6, 126.2, 125.3, 123.7, 122.9, 120.1, 118.4, 25.2; LCMS (m/z): [M^+] calcd 1056.4, found 1057.3 (positive mode); Anal for C_{69}H_{40}N_2O_{12} (%): Calcd C = 72.72, H = 3.81, N = 5.30, Found C = 72.70, H = 3.76, N = 5.25; UV/VIS (CHCl_3) δ_{abs}, max (nm): 520, (486, 425); PL (CHCl_3) δ_{em}, max (nm): 550.

3.20.5 N,N-Di-3-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarb-oximide (P3N)

The title compound was prepared by above quoted procedure as orange powder (0.44g, 65%).

Yield: 65%; m.p.: >300°C; R_f: 0.34; IR (υ/cm\(^{-1}\), ATR): 2976, 2869 (\(sp^3\) C-H unsymmetric and symmetric), 1706 (C=O), 1588 (Ar-C=C), 1374 (CH_3 bending),
1319 (C-N), 1534, 1335 (unsymmetric and symmetric NO₂), 1135 (C-O); ¹H-NMR (300 MHz, DMSO-d₆): δ 8.59-8.54 (m, 2H, Ar-H), 8.34 (s, 4H, Ar-H), 8.08-7.97 (m, 2H, Ar-H), 7.82-7.56 (m, 4H, Ar-H), 7.06 (d, J = 8.8 Hz, 8H, Ar-H), 6.94 (d, J = 8.8Hz, 8H, Ar-H), 2.37 (s, 12H, CH₃); ¹³C-NMR (75 MHz, DMSO-d₆): δ 162.4, 156.3, 152.2, 150.1, 143.2, 135.4, 134.6, 133.2, 131.8, 130.6, 128.8, 125.4, 123.9, 122.1, 120.2, 119.4, 117.8, 25.4; LCMS (m/z): [M⁺] calcd 1056.4, found 1057.4 (positive mode); Anal for C₆₄H₄₀N₂O₁₂ (%): Calcd C = 72.72, H = 3.81, N = 5.30, Found C = 72.71, H = 3.78, N = 5.26; UV/VIS (CHCl₃) λₓ, max (nm): 524, (489, 429); PL (CHCl₃) λₓ, max (nm): 551.

3.20.6 N,N-Di-4-nitrophenyl-1,6,7,12-tetra(4-methylphenoxy)-3,4,9,10-perylenedicarboximid (P4N)

The compound was prepared by above procedure as dark orange powder (0.47g, 69%).

Yield: 69%; m.p.: >300°C; Rₛ: 0.36; IR (υ/cm⁻¹, ATR): 2981, 2876 (sp³ C-H unsymmetric and symmetric), 1708 (C=O), 1591 (Ar-C=C), 1372 (CH₃ bending), 1314 (C-N), 1528, 1341 (unsymmetric and symmetric NO₂), 1128 (C-O); ¹H-NMR (300 MHz, DMSO-d₆): δ 8.38 (s, 4H, Ar-H), 8.28 (d, J = 8.42 Hz, 4H, Ar-H), 7.93 (d, J = 8.42 Hz, 4H, Ar-H), 7.16 (d, J = 8.18 Hz, 8H, Ar-H), 6.98 (d, J = 8.18Hz, 8H, Ar-H), 2.37 (s, 12H, CH₃); ¹³C-NMR (75 MHz, DMSO-d₆): δ 163.1, 157.2, 154.1, 150.3, 146.3, 136.7, 135.9, 134.6, 128.9, 125.6, 124.8, 123.2, 121.4, 119.8, 118.6, 25.2; LCMS (m/z): [M⁺] calcd 1056.4, found 1057.2 (positive mode); Anal for C₆₄H₄₀N₄O₁₂ (%): calcd C = 72.72, H = 3.81, N = 5.30, Found C = 72.71, H = 3.78, N = 5.26; UV/VIS (CHCl₃) λₓ, max (nm): 521, (485, 424); PL (CHCl₃) λₓ, max (nm): 553.
Conclusions

Two new series of a new class of carbazole-pyridine copolymers were successfully synthesized by an efficient and cost-effective method devoid of any metal catalyst. The copolymers were characterized by FTIR, NMR, SLLS and elemental analysis. Their photophysical, thermal and electrochemical properties have been investigated. Their chain length had a pronounced effect on thermal behavior while optical properties were influenced by the electron-donating/withdrawing nature of the substituent on aromatic backbone of copolymers. The newly-synthesized copolymers are thermally stable, glass forming amorphous materials necessary for the film formation which, in turn, enhances the life time of devices, if fabricated utilizing them. The copolymers exhibit blue emissive properties and good charge-transporting properties according to their HOMO and LUMO level, due to presence of carbazole and pyridine scaffolds. The copolymers possess enhanced thermal stability and better emissive properties due to presence of various substituents in comparison to copolymers based only on carbazole-pyridine contents by oxidative coupling reaction. The P3 series of copolymers exhibits still higher thermal stability and glass transition temperature owing to presence of bicarbazolyl unit and HOMO levels are more close to that of ITO, i.e., anodic material. The new classes of polymers have the potential as multifunctional stuff like charge transporting/ blue luminescent material for organic light-emitting diodes. Moreover, the good solubility of polymers renders them solution processable.

Small molecular materials were synthesized by Suzuki-coupling methodology. The effect of changing the carbazole/fluorene cores on their properties was studied. Furthermore, monosubstituted and disubstituted analogs were synthesized and their properties compared. The synthesized dyes are thermally stable and possess good solubility behavior with blue emission. The disubstituted analogs show pure blue emission with increased thermal and electrochemical stability while monosubstituted derivatives have broad emission peaks and less stability. The derivatives containing carbazole/fluorene hybrids demonstrate much better properties than carbazole-only molecular species on account of combination of fluorene and carbazole units. Also, the hybrids are electrochemically and thermally more stable than the existing carbazole/fluorene-based compounds. Moreover, the carbazole-only materials have improved optical and thermal
properties in contrast to carbazolic pentamers or trimers probably due to attachment of terminal carbazole at nitrogen rather than aromatic core. Therefore, these blue light-emitting fluorescent materials are expected to show good device performance in OLEDs as emissive layer.

Perylene-based small molecular materials were also synthesized utilizing imide and bay positions with different substituted anilines and phenols and their effect on properties was probed. All substances are thermally stable and amorphous in nature. The solubility behavior was suppressed when imidization with electron-withdrawing substituent was carried out. On the contrary, the electron donor groups improved the solubility. The optical properties were improved by the electron donor groups and the emission ranged from yellow to orange. Variation of substituent from donor to acceptor, their different attachment positions and substitution of aromatic nuclei at imide position instead of aliphatic ones revealed better optical properties than the reported ones and a comparison of solubility behavior was also affected since it was important for processing. The low LUMO levels estimated from UV and cyclic voltammetry account for their possible use as electron transport and emissive material for OLEDs.
References


20. Harrop, P.; Das, R. Organic electronics forecasts, players & opportunities, IDTechEx, **2006**.


75. Kim, J. Y.; Yasuda, T.; Yang, Y. S.; Adachi, C. Bifunctional star-burst amorphous molecular materials for OLEDs: Achieving highly efficient solid-state


118. Brunner, K.; Van Dijken, A.; Borner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: Tuning the HOMO level without


177. (a) Schmidt, R.; Ling, M. M.; Oh, J. H.; Winkler, M.; Kçnemann, M.; Bao, Z.; Würthner, F. Core-fluorinated perylene bisimide dyes: Air stable n-channel


List of Publications


