Chapter - 5
5.1 Introduction

Aggregation induced Emission (AIE) and Aggregation Induced Emission Enhancement (AIEE) are envied as effective tools for offsetting the low quantum yields of luminogens in solid state.\textsuperscript{1} Luminogens with AIE property showed very low or no emission in solution, while emission is turned on upon aggregation.\textsuperscript{2} AIEE luminogens on the other hand showed significant emission in solution that is enhanced upon aggregation.\textsuperscript{3} A survey of recent literature on AIE/AIEE luminogens revealed that they are sensitive to micro environment.\textsuperscript{4} As a result a myriad of applications have been successfully realized from these smart materials such as; supersensitive explosive detection,\textsuperscript{5} sensors for heavy metals,\textsuperscript{6} thermo fluorochromism,\textsuperscript{7} piezochromic or mechanochromic sensors,\textsuperscript{8} and Organic Light Emitting Diodes (OLEDs).\textsuperscript{9} In the afore mentioned applications, OLED is one of the most promising aspect since AIE/AIEE luminogens can be highly emissive in thin films.

Long wavelength emitting AIE/AIEE fluorophores with color tunability are gaining importance since they can be used for undoped OLEDs and bio-imaging applications.\textsuperscript{10-14} Particularly red emitting AIE molecules have been demonstrated for sensor and OLED applications.\textsuperscript{15,16} Phenothiazine is a versatile building blocks for construction of luminogens with enhanced emission in solid state.\textsuperscript{17} It is evident from the recent literature that phenothiazine based building blocks have been utilized for red emitting AIE luminogens.\textsuperscript{18} Further, phenothiazine was also used as a structural component in molecules with AIE property along with piezochromic properties.\textsuperscript{19} The above attributes were clearly ascribed to the actuation of a transition between twisted and planar conformations of these molecules by changes in microenvironments.\textsuperscript{17-19}
The changes in the microenvironments can be brought about by external stimuli such as; change in polarity of medium and physical stress. Thus, it is possible to tune the emission properties by precise control of the microenvironment of AIE fluorophores of phenothiazine. The electron donating character in phenothiazine can be utilized to realize variety of spectral properties by versatile substitution in 3 and 7 positions.

In addition to the above advantages phenothiazine was extensively used in developing light emitting conjugated polymers and have been found to impart a reduced hole injection barrier. Thus phenothiazine based structural fragments resulted in balanced charge mobility in conjugated polymers. The balanced charge carrier mobility is due to the electron rich nature and the consequent hole transporting nature of phenothiazine unit. Copolymers of 10-alkylphenothiazine with fluorene have been explored with yellow or orange electroluminescence albeit with voltage-dependent electroluminescence owing to charge trapping. Significant attempts were made towards development of white LEDs using phenothiazine copolymers. Nevertheless, the efficiency and brightness of the devices were relatively low. In addition; these above white light emitting polymer were found to show voltage dependent electroluminescence. The inferior properties can be attributed to the charge trapping mechanism, field induced mobility and alteration of recombination zone with changing voltage.

Development of white light emitting polymers is paramount to achieving cost effective OLED technology. Single copolymers with white light emission were extensively studied by researchers using other systems. However, polyfluorenes have remained an integral part of these white emitting polymers with different covalent dopants in main chain and side chains of copolymers. Charge trapping and consequent long wavelength emission have proved to be problematic in achieving
pure white electroluminescence from conventional approach.\textsuperscript{29,30} We propose a novel polymerizable fluorophore with high quantum yield red emission and tuned white light emission from its copolymers of 9,9-dihexylfluorene with balanced charge carrier mobility and efficient white light emission.

5.2 Experimental section

Phenothiazine, phosphoryl chloride, cyanoacetic acid, piperidine, \(\text{N,N'}\)-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, 1-bromohexane, tetrabutylammonium bromide and dimethylsulfoxide were purchased from Aldrich chemical company and used as purchased without any further purification. The structural integrity of monomer and copolymers were confirmed by using \(^1\)H NMR spectroscopy, MALDI mass spectrometry and elemental analysis. Dynamic Light Scattering (DLS), Fluorescence Lifetime analysis (FLT), Atomic Force Microscopy (AFM), Grazing Incidence X-ray Diffraction (GIXRD), UV-Visible absorbance, fluorescence spectroscopy, cyclic voltammetry were performed using the same methods described in Chapter 2, Section 2.2.1. The concentration of monomer used for spectroscopic, DLS and FLT studies was \(6.91 \times 10^{-6}\) M while that of polymers was \(5 \times 10^{-3}\) g dl\(^{-1}\). Theoretical calculations were done according to procedure given in section 4.2.1 in chapter 4. The synthetic strategy for monomers and polymers are presented in Scheme 5.2.1. The detailed procedure followed for the synthesis of all intermediates, monomer and all the polymers are given in the following subsections.

Synthesis of 3,3'-(6,6'-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl))bis(oxy)bis(tetrahydro-2H-pyran) (FHTP)

About, 8.51 g (0.0339 mol, 2.2 eq.) of 3-(6-bromohexyloxy)tetrahydro-2H-pyran and 5.00 g (0.0154 mol, 1 eq.) of 2,7-dibromofluorene were dissolved in DMSO along with 2.74 g (8.5 mmol) of tetrabutylammoniumbromide. To the above
Scheme 5.2.1 Synthetic strategy of monomer FCPA and copolymers.

reaction mixture, 50 ml of 50% NaOH solution was added and nitrogen was purged. The reaction mixture was refluxed for 72 hours under nitrogen atmosphere with constant stirring. After the reaction time, the reaction mixture was mixed with twice the volume of water and extracted with ethyl acetate. The resulting white precipitate
was filtered off and rejected, while the pure organic medium was concentrated under vacuum to get the crude product as colorless oily liquid. The product was purified using column chromatography with hexane:ethyl acetate (v/v 9:1) as eluent. The pure product is obtained as colorless oily liquid which was triturated after 24 hours with absolute ethanol to get the product as a white powder (Yield 67%). $^1$H NMR (CDCl$_3$, 500 MHz, δ, ppm): 0.58 (m, 4 H), 1.11 (m, 8 H), 1.42 (t, 2 H), 1.52 (m, 8 H), 1.68 (m, 2 H), 1.78 (m, 2 H), 1.91 (m, 4 H), 3.27 (m, 2 H), 3.46 (m, 2 H), 3.62 (m, 2 H), 3.81 (m, 2 H), 4.51 (t, 2 H), 7.45 (m, 4 H), 7.52 (m, 2 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, δ, ppm): 19.70, 23.64, 25.49, 25.90, 29.62, 29.73, 29.74, 30.76, 40.20, 55.64, 62.32, 67.51, 98.81, 121.19, 121.52, 126.13, 130.22, 139.07 and 152.42 (Figure 5.2.1). ESI mass m/z: Calculated for C$_{35}$H$_{48}$Br$_2$O$_4$, 692.56, found: 692.27. Elemental Analysis: Calculated (%) for C$_{35}$H$_{48}$Br$_2$O$_4$: C, 60.70; H, 6.99. found: C, 60.62; H, 6.84.

**Synthesis of 6,6’-(9H-fluorene-9,9-diyl)dihexan-1-ol (FHO)**

In a representative procedure, about 2.50 g (4.7 mmol, 1 eq.) of FHTP was dissolved in 85 ml of hot ethanol and mixed with 42.5 ml of 4N hydrochloric acid. The above mixture was refluxed for about 5 hours. The reaction mixture was cooled and mixed with excess distilled water. The resulting turbid mixture was extracted with ethyl acetate and concentrated under vacuum to get crude product as colorless oily liquid. The crude product was purified by column chromatography using hexane:ethylacetate (v/v 3:2) as eluent. The pure product was obtained as colorless crystals (Yield. 93%). $^1$H NMR (CDCl$_3$, 500 MHz, δ, ppm): 0.60 (m, 4 H), 1.11 (m, 8 H), 1.36 (m, 4 H), 1.92 (m, 4 H), 3.51 (t, 4 H), 7.45 (m, 4 H), 7.51 (m, 2 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, δ, ppm): 23.61, 25.32, 29.57, 32.58, 40.07, 55.62, 62.82, 121.21, 121.52, 126.14, 130.27, 139.07 and 152.36 (Figure 5.2.1). ESI mass m/z: Calculated for
Synthesis of 6,6’-(9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl) bis(2-cyanoacetate) (FHCN)

In a representative synthesis, ca. 900.0 mg (1.7 mmoles, 1.0 eq.) of FHO and 314.7 mg (3.7 mmoles, 2.2 eq.) of Cyanoacetic acid were dissolved in 60 ml of 1:1 mixture of THF and Dichloromethane. To the above mixture 763.4 mg (3.7 mmoles, 2.2 eq.) of N,N-Dicyclohexylcorbodiimide (DCC) and 45.2 mg (0.37 mmoles, 0.22 eq.) of 4-Dimethylaminopyridine were added and the mixture was continuously stirred for 24 hours. The reaction mixture was filtered off to remove the precipitate and the organic layer was washed with dilute Hydrochloric acid. The crude product obtained by concentration of organic layer was purified using column chromatography with hexane:ethyl acetate (v/v 7:3) mixture. The pure product was obtained as viscous colorless oily liquid (Yield 84%).

\[1^H NMR (CDCl_3, 500 MHz, \delta, ppm): 0.56 (m, 4 H), 1.11 (br. s., 8 H), 1.48 (m, 4 H), 1.93 (m, 4 H), 3.42 (s, 4 H), 4.09 (t, 4 H), 7.46 (m, 4 H), 7.54 (m, 2 H), \]

\[^{13}C NMR (CDCl_3, 500 MHz, \delta, ppm): 23.44, 24.75, 25.31, 28.15, 29.28, 40.00, 55.58, 66.97, 113.06, 121.31, 121.58, 126.09, 130.37, 139.11, 152.17 and 162.93 \] (Figure 5.2.1). ESI mass m/z: Calculated for C_{31}H_{34}Br_{2}N_{2}O_{4}: 658.42, found: 658.42. Elemental Analysis: Calculated (%) for C_{31}H_{34}Br_{2}N_{2}O_{4}: C, 56.55; H, 5.20; N, 4.25. Found(%): C, 56.81; H, 5.36; N, 4.19.

Synthesis of 10-hexyl-10H-phenothiazine-3-carbaldehyde (HPTC)

5.00 g (0.0176 moles, 1.0 eq.) of N-hexylphenothiazine, prepared by literature reported method, was dissolved in 100 ml of 1,2-dichloroethane at room temperature. About 4.05 g (0.0264 moles, 1.5 eq.) of phosphoryl chloride was dissolved along with 2.03 ml (0.0264 mol, 1.5 eq.) of N,N-Dimethylformamide in 20
ml of 1,2-Dichloroethane in a dropping funnel and added drop wise through a time interval of 10 minutes. The reaction vessel was sealed and stirred for 24 hours. The crude product was isolated by washing the organic layer with excess of water for about ten times and concentrated in vacuum. The product was purified by using hexane:ethyl acetate (v/v 4:2) mixture as mobile phase in column chromatography. The pure product was dark yellow oily liquid which crystallized on standing to brown crystals (Yield 75%). $^1$H NMR (CDCl$_3$, 500 MHz, $\delta$, ppm): 0.87 (t, 3 H), 1.29 (m, 4 H), 1.43 (m, 2 H), 1.81 (quin, 2 H), 3.88 (t, 2 H), 6.88 (t, 2 H), 6.96 (t, 1 H), 7.10 (d, 1 H), 7.16 (m, 1 H), 7.58 (s, 1 H), 7.63 (d, 1 H), 9.78 (s, 1 H), $^{13}$C NMR (CDCl$_3$, 500 MHz, $\delta$, ppm): 14.00, 22.58, 26.53, 26.74, 31.40, 48.03, 114.80, 115.96, 123.58, 123.79, 125.00, 127.56, 127.57, 128.42, 130.10, 131.02, 143.45, 150.78 and 190.08 (Figure 5.2.1). ESI mass m/z: Calculated for C$_{19}$H$_{21}$NOS, 311.44, found: 311.22.

Elemental Analysis: Calculated (%) for C$_{19}$H$_{21}$NOS: C, 73.27; H, 6.80; N, 4.50; S, 10.30. Found (%): C, 73.44; H, 6.79; N, 4.61; S, 10.22.

**Synthesis of (2Z,2′Z)-6,6′-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl) bis(2-cyano-3-(10-hexyl-10H-phenothiazin-3-yl)acrylate) (FCPA)**

About 2.12 g (3.2 mmol, 1 eq.) of FHCN and 2.00 g (6.4 mmol, 2.0 eq.) of HPTC were dissolved in 150 ml of absolute ethanol at room temperature. To the above solution, 4.90 g (0.0576 moles, 18 eq.) of piperidine was added and the mixture was refluxed for 72 hours under nitrogen atmosphere. After the reaction time, the reaction mixture was concentrated, removing the solvent by refluxing in a dean-stark set up and by evaporation under vacuum to remove traces of solvent and piperidine. The resulting crude product was purified using column chromatography with hexane:ethyl acetate (v/v 9:1) mixture. The pure product FCPA was isolated as a low melting dark red colored solid (Yield 73%). $^1$H NMR (CDCl$_3$, 500 MHz, $\delta$,...
Figure 5.2.1 (a) $^1$H NMR and (b) $^{13}$C NMR of monomer and intermediates. ppm: 0.62 (m, 4 H), 0.88 (m, 6 H), 1.16 (m, 8 H), 1.31 (m, 8 H), 1.42 (m, 4 H), 1.55 (q, 4 H), 1.80 (q, 4 H), 1.95 (m, 4 H), 3.86 (t, 4 H), 4.17 (t, 4 H), 6.85 (t, 4 H), 6.95 (t, 2 H), 7.08 (dd, 2 H), 7.15 (m, 2 H), 7.48 (m, 6 H), 7.61 (d, 2 H), 7.85 (dd, 2 H), 7.99 (s, 2 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, $\delta$, ppm): 13.98, 22.57, 23.46, 25.40, 25.40, 26.50, 26.67, 28.37, 29.37, 31.36, 39.97, 48.01, 55.59, 66.36, 98.76, 114.93, 115.82, 116.23, 121.23, 121.56, 123.32, 123.68, 124.63, 125.58, 126.13, 127.55, 127.58, 130.18, 130.29, 131.26, 139.07, 143.02, 149.67, 152.25, 153.12 and 163.18 (Figure 5.2.1). MALDI mass m/z: Calculated for C$_{69}$H$_{72}$Br$_2$N$_4$O$_8$S$_2$: 1245.27, found: 1244.37
Figure 5.2.2 MALDI mass spectrum of AIEE monomer, FCPA (a) full spectrum and (b) expanded spectrum with characteristic isotopic peaks. (100.0%), 1246.37 (75%), 1245.35 (74%), 1242.36 (44%), 1247.36 (43%), 1243.35 (37%), 1248.42 (17%), 1249.35 (7.2%), 1250.37 (2%).

Elemental Analysis:
Calculated (%) for C_{69}H_{72}Br_{2}N_{4}O_{4}S_{2}: C, 66.55; H, 5.83; N, S, 5.15. Found (%): C, 66.50; H, 5.78; N, S, 5.31.

Synthesis of copolymers of (2Z,2'Z)-6,6'- (2,7-dibromo-9H-fluorene-9,9-diyl)bis(hexane-6,1-diyl)bis(2-cyano-3-(10-hexyl-10H-phenothiazin-3-yl)acrylate) (FCPA-n).

In a representative experiment, Ca. 300.0 mg (2.4x10^{-4} moles, 0.5 eq.) of FCPA and 118.6 mg (2.4x10^{-4} moles, 0.5 eq.) of 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-
propanediol) ester and 242.0 mg (4.8x10^{-4} moles, 1.0 eq.) of 2,7-Dibromo-9,9-dihexylfluorene were dissolved in 40 ml of THF at room temperature. To the above solution, 15 ml of 1% sodium bicarbonate solution was added and the temperature of the biphasic mixture was raised to 60 °C. About 54.0 mg of Tetrakistriphenylphosphinepalladium(0) was added to the above mixture under nitrogen atmosphere and the mixture was refluxed for 72 hours. After the reaction time, the mixture was evaporated under vacuum to obtain dark blue colored residue. The residue was washed with 3N hydrochloric acid and redissolved in minimum amount of chloroform. The polymer was reprecipitated from the concentrated chloroform solution in methanol and subjected to soxhlet extraction with methanol for 12 hours to get the pristine polymer (FCPA-25) as brown precipitate. Yield 89%.^1^H NMR (CDCl\textsubscript{3}, 500MHz, δ, ppm): 0.56-2.43 (m), 3.85 (m), 4.17 (m), 6.72-7.20 (m) and 7.28-8.02 (m). Elemental Analysis: Calculated (%): C, 82.95; H, 8.06; N, 2.69; S, 3.08. Found: C, 82.81; H, 8.11; N, 2.69; S, 3.08.

**FCPA-50,**^1^H NMR (CDCl\textsubscript{3}, 500MHz, δ, ppm): 0.56-2.33 (m), 3.85 (m), 4.17 (m), 6.72-7.20 (m) and 7.28-8.02 (m). Elemental Analysis: calculated (%): C, 79.51; H, 7.33; N, 3.95; S, 4.52. Found: C, 79.40; H, 7.24; N, 3.88; S, 4.44.

**FCPA-10,**^1^H NMR (CDCl\textsubscript{3}, 500MHz, δ, ppm): 0.55-2.29 (m), 3.85 (m), 4.17 (m), 6.69-7.17 (m) and 7.26-8.00 (m). Elemental analysis: Calculated (%): C, 86.52; H, 8.82; N, 1.37; S, 1.56. Found (%): C, 86.39; H, 8.71; N, 1.46; S, 1.55.

**FCPA-5,**^1^H NMR (CDCl\textsubscript{3}, 500MHz, δ, ppm): 0.57-2.31 (m), 3.86 (m), 4.19 (m), 6.76-7.19 (m) and 7.27-8.00 (m). Elemental analysis: Calculated (%): C, 88.18; H, 9.18; N, 0.75; S, 0.86. Found (%): C, 88.22; H, 9.25; N, 0.67; S, 0.81.

**FCPA-1,**^1^H NMR (CDCl\textsubscript{3}, 500MHz, δ, ppm): 0.54-2.28 (m), 3.87 (m), 4.16 (m), 6.78-7.21 (m) and 7.28-7.95 (m). Elemental analysis: Calculated (%): C, 89.76; H,
Figure 5.2.3 

$^1$H NMR spectra of copolymers with the rectangular region showing characteristic methylene signals from FCPA units.

Table 5.2.1 Gel Permeation Chromatography data of polymers.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Polymer code</th>
<th>$^a M_n$</th>
<th>$^b M_w$</th>
<th>$^c PDI$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FCPA 0.5</td>
<td>9550</td>
<td>18661</td>
<td>1.95</td>
</tr>
<tr>
<td>2</td>
<td>FCPA 1.0</td>
<td>10946</td>
<td>21035</td>
<td>1.92</td>
</tr>
<tr>
<td>3</td>
<td>FCPA 5.0</td>
<td>11235</td>
<td>23571</td>
<td>2.09</td>
</tr>
<tr>
<td>4</td>
<td>FCPA 10</td>
<td>8765</td>
<td>19586</td>
<td>2.23</td>
</tr>
<tr>
<td>5</td>
<td>FCPA 25</td>
<td>7622</td>
<td>16758</td>
<td>2.19</td>
</tr>
<tr>
<td>6</td>
<td>FCPA 50</td>
<td>7232</td>
<td>14360</td>
<td>1.98</td>
</tr>
</tbody>
</table>

$^a M_n$, Number averaged molecular weight; $^b M_w$, Weight averaged molecular weight; $^c PDI$, Polydispersity index.


$^1$H NMR (CDCl$_3$, 500MHz, $\delta$, ppm): 0.56-2.30 (m), 3.85 (m), 4.14 (m), 6.79-7.20 (m) and 7.29-7.90 (m). Elemental analysis: Calculated (%): C, 89.98; H, 9.57. Found (%): C, 90.10; H, 9.62.

$^1$H and $^{13}$C NMR spectra of all precursors and monomer FCPA are presented in Figure 5.2.1. $^1$H NMR spectra of all polymers are presented in Figure 5.2.3. MALDI MASS spectrometry data of monomer FCPA are presented in Figure 5.2.2.
along with isotopic peaks. Gel Permeation Chromatography (GPC) data of all polymers are presented in Table 5.2.1.

5.3 Results and discussion

5.3.1 Spectral properties of FCPA

Recently a series of phenothiazine based chromophore was reported by Yang et al with a dye coded as Pt-C6 among others with enhanced absorbance. The structure of FCPA can be viewed as two (Pt-C6) units dangled to the termini of hexyl groups in 9,9-Dihexylfluorene through ester linkage. The solubility of polymerizable AIEE luminogen FCPA in solvent with wide polarity range was helpful in complete characterization of the spectral and electronic properties. The absorption spectra of FCPA were recorded in different solvents as presented in Figure 5.3.1. The lowest energy absorption of FCPA shifted between 400 nm in cyclo hexane to 453 nm in chloroform indirectly revealed that the peak at 440-452 nm is due to intramolecular charge transfer (CT). The CT band exhibited initial bathochromic shift followed by hypsochomatic shift, characteristic of inverted solvatochromic character due to solvent-induced change of electronic structure in ground state. The emission spectra of FCPA recorded in solvents with different polarity elicited a red shift from 568 nm to 658 nm with increase in polarity as observed for donor-acceptor systems. The red shift in emission of FCPA in polar solvents (Figure 5.3.1) is due to the emission from solvent relaxed state. In addition to the above observation, Lippert-Mataga plot presented in Figure 5.3.1 showed a high slope implicit of a charge transfer transition in FCPA. The photoluminescence quantum yield of FCPA showed a steady decrease with increase in solvent polarity. The reduced quantum yield is implicit of relaxation of excited state through torsional coordinates thus leading to twisted intramolecular charge transfer state (TICT) as observed for AIE luminogens.
The thin films of FCPA elicited an intense red emission as shown in the photograph in Figure 5.3.2. Emission spectrum of FCPA in thin film elicited emission maximum at 636 nm ($\varphi_{TF} = 37.5\%$, Table 5.3.1) which is very close to the solution emission in dichloromethane. When the emission wavelength in thin film of FCPA and is compared with the solution emission of FCPA, it is evident that local polarity in thin film state of FCPA is close to that of dichloromethane.\(^{36}\)

5.3.2 Spectral properties of copolymers

FCPA was copolymerized by Suzuki polycondensation with 9,9-Dihexylfluorene as depicted in Scheme 5.2.1. The absorption and emission spectra of all copolymers in chloroform solution are presented in Figure 5.3.2. The absorption spectra of copolymers showed more characteristic absorption of poly 9,9-Dihexylfluorene.\(^{37}\) The CT absorption of FCPA units are observed only in case of FCPA-50 polymer while it was not observable for other polymers owing to lower content of FCPA units and relatively weak absorption coefficient of CT band (Table 5.3.1).

The emission spectra of polymers in solution also indicate a predominant blue emission at ~ 416 nm alongside low energy shoulders at ~ 435 and 466 nm from 9,9-dihexylfluorene moiety.\(^{37}\) The observed predominant blue emission can be attributed to high quantum yield of 9,9-dihexylfluorene moiety and low quantum yield of FCPA in chloroform solution (Table 5.3.1). In thin film state the copolymers showed slight
Table 5.3.1 Spectral properties of FCPA and its copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{abs}^{sol}$ (ε) $^a$</th>
<th>$\lambda_{abs}^{sol}$ (nm)</th>
<th>$\epsilon_{\lambda_{abs}}^{sol}$</th>
<th>$\lambda_{emi}^{sol}$ (nm)</th>
<th>$\epsilon_{\lambda_{emi}}^{sol}$</th>
<th>$\Phi_{PL}^{Sol}$</th>
<th>$\phi_{PL}^{TF}$</th>
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</thead>
<tbody>
<tr>
<td>FCPA</td>
<td>454(1.41x10$^6$), 315(2.92x10$^6$)</td>
<td>627</td>
<td>468,318,287</td>
<td>636</td>
<td>0.096</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>FCPA-0.5</td>
<td>373(7.85x10$^6$)</td>
<td>467,434,416</td>
<td>382,218</td>
<td>569,436</td>
<td>0.590</td>
<td>59.4</td>
<td></td>
</tr>
<tr>
<td>FCPA-1</td>
<td>378(8.04x10$^6$)</td>
<td>466,435,416</td>
<td>386,222</td>
<td>573,436</td>
<td>0.368</td>
<td>52.8</td>
<td></td>
</tr>
<tr>
<td>FCPA-5</td>
<td>381(9.36x10$^6$)</td>
<td>465,438,416</td>
<td>393,219</td>
<td>578,443</td>
<td>0.472</td>
<td>51.9</td>
<td></td>
</tr>
<tr>
<td>FCPA-10</td>
<td>378(6.47x10$^6$)</td>
<td>468,438,416</td>
<td>383,217</td>
<td>581,436</td>
<td>0.423</td>
<td>49.4</td>
<td></td>
</tr>
<tr>
<td>FCPA-25</td>
<td>464(4.37x10$^4$), 375(5.86x10$^5$)</td>
<td>468,439,417</td>
<td>384,214</td>
<td>580</td>
<td>0.281</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>FCPA-50</td>
<td>458(4.45x10$^5$), 378(6.73x10$^5$)</td>
<td>630,470,438,417</td>
<td>465,390,232</td>
<td>611</td>
<td>0.133</td>
<td>45.1</td>
<td></td>
</tr>
</tbody>
</table>

$^a\lambda_{abs}^{sol}$. Absorption maxima in THF solution in nm; ε. extinction coefficient in dL g$^{-1}$ cm$^{-1}$.

Emission maxima in CHCl$_3$ solution in nm. $\lambda_{emi}^{sol}$. Absorption maxima in thin film. $\lambda_{emi}^{TF}$. Emission maxima in thin film. $\epsilon_{\lambda_{emi}}^{sol}$. Quantum yield in CHCl$_3$ solution relative to quinine sulfate in.

$\phi_{PL}^{TF}$. Absolute quantum yield in spun thin film in %.

red shifted absorption at 380-390 nm and the CT band observed in FCPA-50 copolymers merged with the high energy absorption due to broadening.

The emission spectra of the copolymers in thin film were completely different from that in solution state. FCPA-50 copolymers exhibited a predominant emission at 611 nm which can be attributed to increase in quantum yield of FCPA in thin film state. Similarly, emission maxima of copolymers FCPA-25, FCPA10 and FCPA-5 were observed at ~580nm that is very close to emission of FCPA in cyclohexane and heptane, implicit of reduced local polarity due to alkyl groups present in 9,9-dihexylfluorene units of copolymers. Thus it can be concluded that the decreased local polarity in copolymers, FCPA25, FCPA-10 and FCPA-5 resulted in enhanced emission from FCPA units with consequent predominant emission at ~580nm. In case of copolymers with very low compositions of FCPA units like FCPA-1 and FCPA-0.5, emissions were observed at ~570 nm and ~436 nm resulting in white emission with Commission internationale de l’Eclairage (CIE) coordinates of (0.31, 0.32) and (0.30, 0.33) respectively as shown in photograph presented in Figure 5.3.2.
5.3.3 Aggregation Induced Enhanced Emission (AIEE) Property of FCPA

It is clear from the above observations that the fluorescence and absorption studies of that FCPA showed high quantum yield in thin film state than in solution state. The FCPA monomer was studied for AIEE property by measuring the emission properties of FCPA in THF-water mixtures of varying compositions. Dynamic light scattering and Fluorescence Lifetime were also recorded simultaneously to understand the dynamics of emission process and monitor the extent of precipitation in the THF-water mixtures (Figure 5.3.3). Emission of FCPA was initially observed at 624 nm in pure THF solution. As composition of water was increased to 10%, a bathochromic shift was observed and the emission maximum was observed at 634 nm. The bathochromic shift was observed to increase with the water content till the content of water reached 40% with emission maximum at 647 nm. The corresponding Dynamic Light Scattering (DLS) traces elicited a change from polydisperse distribution in pure THF solution to unimodal distribution of hydrodynamic radii ($R_h$) in 40% water in THF. The corresponding Fluorescence spectra of mixtures showed a steady decrease
in the intensity. The emission intensity decreased and reached a minimum intensity at 50% water-THF mixture with emission maximum observed at 642 nm and the DLS showed narrower size distribution. The quenching in emission of FCPA in THF-water mixtures till 50% was accompanied by appearance of ultrafast decay channel in Fluorescence Lifetime signifying non-radiative decay (Figure 5.3.3 and Table 5.3.2). Emission intensity of FCPA increased with further increase in water content to 60% and a hypsochromic shift of emission maximum to 634 nm was observed. The hypsochromic shift progressively increased with further increase of water content in mixtures. Maximum intensity of emission and a maximum blue shift to 622 nm was observed for 90% water in THF. The DLS traces of mixtures with 60 to 90% water content showed a remarkable narrow distribution of size indicating formation of uniform sized particles. Fluorescence Lifetime of same mixtures with high water contents showed a disappearance of ultrafast decay component indicating an increased
Table 5.3.2 Fluorescence Lifetime data of FCPA in various proportions of THF-water mixture.

<table>
<thead>
<tr>
<th>% water in THF</th>
<th>$^{a}\tau_1/\tau_2$</th>
<th>$^{b}a_1/a_2$</th>
<th>$^{c}\Phi_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.13/2.25</td>
<td>2.85/97.15</td>
<td>0.08663</td>
</tr>
<tr>
<td>10</td>
<td>5.22/0.92</td>
<td>4.30/95.70</td>
<td>0.06335</td>
</tr>
<tr>
<td>20</td>
<td>5.63/0.72</td>
<td>4.93/95.07</td>
<td>0.04688</td>
</tr>
<tr>
<td>30</td>
<td>4.99/6.42</td>
<td>7.61/92.39</td>
<td>0.03974</td>
</tr>
<tr>
<td>40</td>
<td>4.64/0.61</td>
<td>9.48/90.52</td>
<td>0.03234</td>
</tr>
<tr>
<td>50</td>
<td>3.73/0.53</td>
<td>14.53/85.47</td>
<td>0.02987</td>
</tr>
<tr>
<td>60</td>
<td>4.25/0.89</td>
<td>6.04/93.96</td>
<td>0.03732</td>
</tr>
<tr>
<td>70</td>
<td>4.55/1.01</td>
<td>3.53/96.47</td>
<td>0.05962</td>
</tr>
<tr>
<td>80</td>
<td>6.94/1.27</td>
<td>1.60/98.40</td>
<td>0.07847</td>
</tr>
<tr>
<td>90</td>
<td>3.48/1.62</td>
<td>10.43/89.57</td>
<td>0.11884</td>
</tr>
</tbody>
</table>

$^{a}\tau_1/\tau_2$, Lifetime of decay channels 1 and 2 $\times 10^{-9}$ sec. $^{b}a_1/a_2$, contribution of decay channels in %. $^{c}\Phi_f$, quantum yield relative to quinine sulfate.

The increased quantum yield observed in 90% water-THF mixture confirmed the presence of AIEE property in FCPA. The initial quenching of emission of FCPA in mixtures with lower content of water in THF is attributed to initial increase in polarity and also supported by red shift of emission. Increased emission in higher composition can be attributed to formation of aggregates with hydrophobic alkyl chains forming the core with low polarity. Herein we propose that the low local polarity in aggregates due to aliphatic chains actuated the enhanced emission in mixtures with high water content. The reduced local polarity in mixtures with 60-90% water content is supported by a hypsochromic shift of emission of FCPA similar to that observed in low polarity solvents.

5.3.4 AIEE property in copolymers

Owing to the AIEE property of FCPA, the polymers were also studied for the same attribute. The enhanced emission was observed in the case of FCPA-50 copolymer.
with maximum intensity of emission was observed at 70% water in THF. However the emission wavelength was completely shifted from 416 nm to 616 nm signifying the Dual Channel Fluorescence Response (DCFR) property of FCPA-50. \textsuperscript{45} Other copolymers with lower composition of FCPA moieties did not exhibit any DCFR phenomenon. However it is interesting to note that the FCPA-25 copolymer elicited a maximum emission intensity of emission at 30% water in THF and steadily showed a decrease until it slightly enhanced at 70% water content. The above observation can be attributed to the formation of random amorphous aggregates that lead to precipitation of polymer.\textsuperscript{46} Other polymers did not show enhancement of emission upon aggregation owing to low composition of FCPA.\textsuperscript{45} Further, the emission property of the polymers with 25-0.5% content of FCPA showed emission spectra in aggregates identical to that in solution state. This can be attributed to strong solvent-solute interactions. Nevertheless it is interesting to note that, the
Table 5.3.3 Fluorescence Lifetime data of copolymers in solution and thin film.

<table>
<thead>
<tr>
<th>Monomer/polymer</th>
<th>$\frac{\tau_1}{\tau_2}$</th>
<th>$\frac{T_1/T_2/T_3}{A_1/A_2/A_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCPA</td>
<td>8.13/2.25 (2.85/97.15)</td>
<td>3.34/1.75 (2.61/65.39)</td>
</tr>
<tr>
<td>FCPA-0.5</td>
<td>3.77/0.56 (1.99/98.01)</td>
<td>7.27/0.19 (1.39/98.61)</td>
</tr>
<tr>
<td>FCPA-1</td>
<td>3.94/5.48 (1.94/98.06)</td>
<td>5.35/0.19 (3.03/96.97)</td>
</tr>
<tr>
<td>FCPA-5</td>
<td>3.20/0.55 (2.78/97.22)</td>
<td>5.08/1.76 (41.15/89.89)</td>
</tr>
<tr>
<td>FCPA-10</td>
<td>4.02/0.57 (2.11/97.89)</td>
<td>4.6/1.46 (40.51/59.49)</td>
</tr>
<tr>
<td>FCPA-25</td>
<td>2.98/0.59 (1.98/98.02)</td>
<td>4.10/1.80 (2.05/97.95)</td>
</tr>
<tr>
<td>FCPA-50</td>
<td>4.91/2.23 (6.16/93.84)</td>
<td>2.61/1.02 (59.51/40.49)</td>
</tr>
</tbody>
</table>

$\frac{\tau_1}{\tau_2}$, Lifetime of decay channels 1 and 2 X10$^{-9}$ sec and $\frac{a_1/a_2}{a_1/a_2}$, contribution of decay channels in % for solution state. $\frac{T_1/T_2/T_3}{A_1/A_2/A_3}$, Lifetime of decay channels 1, 2, 3 and $\frac{A_1/A_2/A_3}{A_1/A_2/A_3}$, contribution of different decay channels in % for thin films.

Emission spectra of copolymers in thin film are completely different from the aggregates. The thin films spin coated on quartz substrates exhibited higher quantum yield than in solution state. Fluorescence Lifetime data presented in Table 5.3.3 from solution and thin film indicate a longer average lifetime for thin films implicit of dominant radiative decay process. Thus, the presence of FCPA in smaller proportions resulted in decreased $\pi-\pi$ interaction and higher emission quantum yield.

FCPA with AIEE property was thus used for white emission with high quantum yield in FCPA-1 and FCPA-0.5. White emission using AIE luminogen as comonomer is highly desirable but is seldom reported. Here the local polarity induced hypsochromic shift of FCPA emission towards orange color and consequent enhancement of quantum yield was used to generate white light emission.

5.3.5 Morphology and intermolecular interaction

The monomer FCPA and the copolymers were studied using X-ray diffraction analysis (XRD) and Atomic force microscopy (AFM). The above studies were used to
understand the intermolecular interactions and correlate the observation with the spectral and electronic properties. A comparison of copolymers by their morphology and X-ray diffraction patterns revealed that the change in composition of FCPA units had a strong effect on the intermolecular interactions. FCPA did not show any peaks in XRD suggesting that FCPA is completely amorphous (Figure 5.3.5). In fact the DSC of FCPA revealed that the melting point of FCPA was 48.7 °C and absence of crystallization peak on cooling cycle indicate that the compound is highly amorphous. This observation is in contrast to the previous AIE molecules reported with phenothiazine and bulky aromatic groups. The absence of significant morphological features in AFM micrograph of FCPA also indicate the amorphous nature of FCPA in thin film state.

Figure 5.3.5 AFM micrographs, (a) X-Ray Diffraction (XRD) traces and (b) Differential Scanning Caloriemetry (DSC) traces of copolymers.
The copolymers on the other hand showed XRD patterns that are very similar to that of dialkylfluorene that changed progressively with the increase in composition of FCPA. For example, the copolymer, FCPA-0.5 showed a reflection at 6.77° 2θ corresponding to the β-phase of dialkylfluorene; however, the peak was not clearly observed in the case of FCPA-25 and FCPA-50 copolymers. The reflection corresponding to the β-phase formation in the copolymers correspond to the distance of 13.04 Å which is very close to that observed for poly(9,9-dihexylfluorene) systems. In addition to the reflection, a broad rise in the base line with onset at around 16.79° 2θ corresponds to the amorphous halo that is characteristic of the presence of amorphous phase in dialkylfluorene polymers. The XRD patterns of FCPA-25 and FCPA-50 showed very weak reflections that are not clearly observable signifying a similarity to pure FCPA film in the property due to its higher content in backbone.

AFM micrograph of the copolymers showed a progressive change from FCPA-0.5 with more lamellae like structures to terraced morphology in FCPA-10. As the composition of FCPA units further increased in FCPA-25 and FCPA-50, the AFM morphology change to fibrillar lamellae structure and amorphous pattern respectively (Figure 5.3.5).

### 5.3.6 Theoretical study on FCPA

To gain more insight on the nature of transitions, the frontier molecular orbitals (FMO) distributions of FCPA was studied using Density Functional Theory (DFT) at B3LYP/6-31G* level. Figure 5.3.6, presents the optimized geometry of FCPA in hexane and acetonitrile with the FMO distributions indicating a ‘bow and arrow’ geometry of FCPA. The optimized ground state geometries did not show much variation as the solvent polarity was changed. The HOMO of FCPA is localized on
Figure 5.3.6 Frontier Molecular Orbital distribution of FCPA in different solvents. phenothiazine unit, while the LUMO is localized on cyanoacetate moiety indicating a intramolecular charge transfer between donor (phenothiazine) to acceptor (cyanoacetate moiety). TD-DFT calculations were also performed to find out the orbitals involved in the dominant electronic transitions and their corresponding energies with oscillator strength; the calculated results are presented in Table 5.3.4. It is clear from Table 5.3.4 that, the low energy band constitutes transitions from HOMO→LUMO+1 (50%) and HOMO-1→LUMO (47%). The corresponding FMO distribution showed that HOMO-1 and HOMO were localized on phenothiazine moiety while, LUMO and LUMO+1 were localized on cyanoacetate moiety. It is also to be noted that the charge transfer is observed only within the same red emitting unit. All absorption bands calculated using TD-DFT calculations closely matched with that of the experimental values. Thus, the linear dependence of the stoke’s shift in Lippert-Mataga plot and charge transfer nature of low energy transition confirm that the enhanced emission of FCPA in solid film is induced by reduced local polarity.
Table 5.3.4 Results from TD-DFT calculations with experimental values.

<table>
<thead>
<tr>
<th>solvent</th>
<th>States</th>
<th>${{\lambda}_{abs}}^{calc}$</th>
<th>E$^{calc}$</th>
<th>f</th>
<th>(%) contribution</th>
<th>${{\lambda}_{abs}}^{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>S$_1$</td>
<td>474.9</td>
<td>2.61</td>
<td>0.6058</td>
<td>H$\rightarrow$L+1 (50%), H-1$\rightarrow$L (47%)</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>S$_2$</td>
<td>474.4</td>
<td>2.61</td>
<td>0.1673</td>
<td>H-1$\rightarrow$L (50%), H$\rightarrow$L+1 (47%)</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>S$_{15}$</td>
<td>299.1</td>
<td>4.15</td>
<td>0.7004</td>
<td>H-5$\rightarrow$L (47%), H-6$\rightarrow$L+1 (46%)</td>
<td>440</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>S$_1$</td>
<td>467.5</td>
<td>2.65</td>
<td>0.5559</td>
<td>H$\rightarrow$L+1 (50%), H-1$\rightarrow$L (47%)</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>S$_2$</td>
<td>467.1</td>
<td>2.65</td>
<td>0.1429</td>
<td>H-1$\rightarrow$L+0 (50%), H$\rightarrow$L+1 (47%)</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>S$_{17}$</td>
<td>292.4</td>
<td>4.24</td>
<td>0.7219</td>
<td>H-2$\rightarrow$L+2 (95%)</td>
<td>313</td>
</tr>
</tbody>
</table>

$\lambda_{abs}^{calc}$, Calculated absorption using TD-DFT calculations. E$^{calc}$, Calculated transition energy. f, Oscillator strength. H denotes HOMO and L denotes LUMO. $\lambda_{abs}^{exp}$, Experimental absorption of FCPA.

5.3.7 OLED device characteristics of monomer and copolymers

The monomer, FCPA and the copolymers were used to fabricate OLEDs with device configuration of ITO/PEDOT:PSS/polymer/Al by solution processing. OLEDs of polymers elicited a broad electroluminescence spectrum that had same spectral width as the corresponding PL spectra. The EL spectrum of FCPA was observed to be wider than the PL spectrum which can be attributed to the formation of exciplex. Further the energy level diagram presented in Figure 5.3.7 show that the electron injection barrier for FCPA is 0.63 eV and hole injection barrier was found to be 0.46 eV. Hence, FCPA would constitute holes as majority charge carriers leading to imbalance in charge injection. However, the 9,9-dihexylfluorene backbone has a LUMO and HOMO energies of -2.4 eV and -5.5 eV hence FCPA can be expected to act as trap for electrons. The copolymers with low composition of FCPA units namely: FCPA-0.5 and FCPA-1 showed a hybrid character of energy levels that is intermediate between 9,9-dihexylfluorene and FCPA monomer. Thus FCPA-0.5 and FCPA-1 elicited LUMO levels closer to that of FCPA monomer.

The energy level diagram presented in Figure 5.3.7 show the LUMO energy level of FCPA-0.5 and FCPA-1 to be -3.68 and -3.69 eV respectively. The HOMO levels of FCPA-0.5 and FCPA-1 were found to be -5.74 and 5.76 eV respectively.
Electron and hole injection barrier values from Figure 5.3.7 was found to be 0.52 eV and 0.54 eV respectively for FCPA-0.5 while FCPA-1 also showed almost same values. The above injection barrier values for hole and electrons in case of FCPA-0.5 and FCPA-1 are almost equal. The above observation clearly points to a balanced charge carrier injection and recombination which is also supported by nearly same wavelength of PL and EL for these polymers. The absence of surplus long wavelength emission in Electroluminescence as observed previously for some white light emitting single polymers can be attributed to ambipolar charge injection. The maximum brightness of the white OLEDs fabricated from FCPA-0.5 and FCPA-1 were found to be 5862 and 6184 cd/m² respectively. CIE coordinates of the above two copolymers in EL was found to be 0.30, 0.33 and 0.31, 0.32 respectively that closely correspond to the pure white light emission. The luminous efficacy of the OLEDs with FCPA-0.5 and FCPA-1 were found to be 4.6 and 4.5 cd/m² (Table 5.3.5). Thus the copolymers constitute a unique class of single white light emitting polymers with covalently linked AIEE luminogen. The copolymers with higher compositions of FCPA in the back bone also exhibited near white light with FCPA-5 showing a CIE coordinate of 0.34,0.45 and FCPA-10 with 0.38,0.40. The CIE coordinates of EL from FCPA-10 and FCPA-5 were found to be close to that of white light emission from single polymers reported previously. FCPA, FCPA25 and FCPA-50 were found to show a red, yellow and orange electroluminescence however the performance of the LEDs was lower than that of FCPA-0.5 and FCPA-1 copolymers due to imbalance in charge injection (Table 5.3.5). All the copolymers and monomer showed a turn on voltage of 5 V (Figure 5.3.7) and charge carrier mobilities measured by Space Charge Limited Current was also found to be higher for FCPA-0.5 ad FCPA-1 compared to other polymers (Table 5.3.5).
Figure 5.3.7 (a) Electroluminescence (EL), (b) energy level diagram, (c) current-voltage characteristics and (e) luminescence-voltage characteristics of copolymers and FCPA.

Table 5.3.5 Device characteristics of OLEDs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E^\text{ele}$ (eV)</th>
<th>$E^\text{opt}$ (eV)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\eta_c^{\text{max}}$ (cd/m$^2$)</th>
<th>$\eta_p^{\text{max}}$ (Lm/W)</th>
<th>$L^{\text{max}}$ (cd/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCPA-0.5</td>
<td>-5.53</td>
<td>-3.85</td>
<td>1.68</td>
<td>1.70</td>
<td>5.5540X10$^{-6}$</td>
<td>4.6</td>
<td>4.3</td>
<td>5862</td>
</tr>
<tr>
<td>FCPA-1</td>
<td>-5.53</td>
<td>-3.85</td>
<td>1.68</td>
<td>1.71</td>
<td>6.0826X10$^{-6}$</td>
<td>4.5</td>
<td>4.1</td>
<td>6184</td>
</tr>
<tr>
<td>FCPA-5</td>
<td>-5.53</td>
<td>-4.17</td>
<td>1.36</td>
<td>1.39</td>
<td>8.4954X10$^{-7}$</td>
<td>3.2</td>
<td>2.6</td>
<td>4217</td>
</tr>
<tr>
<td>FCPA-10</td>
<td>-5.52</td>
<td>-4.14</td>
<td>1.38</td>
<td>1.40</td>
<td>6.9828X10$^{-7}$</td>
<td>3.1</td>
<td>2.6</td>
<td>3109</td>
</tr>
<tr>
<td>FCPA-25</td>
<td>-5.52</td>
<td>-4.18</td>
<td>1.34</td>
<td>1.38</td>
<td>1.9757X10$^{-6}$</td>
<td>2.7</td>
<td>2.1</td>
<td>3010</td>
</tr>
<tr>
<td>FCPA-50</td>
<td>-5.50</td>
<td>-4.15</td>
<td>1.35</td>
<td>1.37</td>
<td>1.0982X10$^{-6}$</td>
<td>2.9</td>
<td>2.2</td>
<td>2846</td>
</tr>
<tr>
<td>FCPA</td>
<td>-5.49</td>
<td>-4.18</td>
<td>1.31</td>
<td>1.33</td>
<td>8.4820X10$^{-7}$</td>
<td>1.8</td>
<td>0.8</td>
<td>1398</td>
</tr>
</tbody>
</table>

$^a$Highest Occupied Molecular Orbital. $^b$Lowest Unoccupied Molecular Orbital. $^c$Electrochemical band gap. $^d$Optical band gap. $^e$Charge carrier mobility determined by Space Charge Limited Current (SCLC) method. $^f$Luminous efficiency. $^g$Power efficiency. $^h$Maximum brightness.

5.4 Conclusions

A polymerizable red emitting monomer with phenothiazine based donor-acceptor system was designed with AIEE property. The AIEE monomer is unique since its
AIEE property is attributed to the local polarity of donor-acceptor system in condensed state. Reports with AIEE property actuated exclusively by local polarity alone are relatively very rare.\textsuperscript{43} Most of the systems with AIEE property relied on restricted intermolecular rotation as a principle way to trigger the property. The actuation of AIEE by low polarity is evident from the hypsochromic shift of FCPA, PL emission maxima relative to that in polar solvents. Copolymers of FCPA copolymer with different content of FCPA units were demonstrated to tune the quality of white light in OLEDs. Further, the copolymers FCPA-0.5 and FCPA-10 elicited a minimized charge carrier trapping resulting in stable electroluminescence. Till date the polymers systems with even best efficiency in OLEDs were found to suffer from charge trapping and consequent surplus long wavelength emission.\textsuperscript{55} However, such surplus long wavelength emission is not observed in the present system. Thus balanced charge injection was used successfully to offset the excess long wavelength emission in single polymer white LEDs.
References


