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## **Supporting Information**

For

# Efficient white-light from single polymer system with "spring-like" selfassemblies induced emission enhancement and intramolecular charge transfer characterics

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### **Experimental:**

#### Materials:

All solvents for UV and FL analyses were used as spectroscopic grade. Column chromatography was performed on silica gel (100-200 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel F-254 plates (0.25 mm, E. Merck). Phenothiazine, 1-Bromohexane, sodium hydroxide, N-Bromosuccinimide, 4-formyl phenylboronic acid, 9,9-dihexylfluorene and tetrakis-(triphenylphosphine)palladium(0) were purchased from Sigma Aldrich and used as received for the synthesis of monomer and copolymers.

#### Instrumentation:

<sup>1H</sup> and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker spectrophotometer using CDCl<sub>3</sub> with tetramethylsilane (TMS, d = 0) as the internal standard. Mass spectra were recorded on a MALDI–TOF measurements were performed on BRUKER ULTRAFLEXTREME using 4-HCCA (a-Cyano-4-hydroxycinnamic acid) matrix. Elemental analysis was carried out using a Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer. UV-visible absorption spectra were carried out on a Varian Carey 50 Bio UV-visible spectrophotometer. Fluorescence spectra of the monomer and copolymers were recorded on a Varian Carey Eclipse fluorescence

spectrophotometer. Cyclic voltammetry measurements were done using CHI 600D electrochemical work stations using Ag/AgCl, platinum disc and platinum wire as reference, working and counter-electrodes respectively. Cyclic voltammetry was performed by coating a thin layer of BPPTA and copolymers on a platinum disc electrode and measurements were performed in acetonitrile medium with tetrabutylammonium hexafluorophosphate (0.1 M [Bu4N] PF6) as a supporting electrolyte. Dynamic light scattering (DLS) experiments were performed on a Malvern, DLS instrument. Fluorescence lifetime experiments were conducted on EDINBURGH (UK) and FLS 980 TCSPC instruments. Atomic force micrographs (AFM) were obtained on a RUSSIA model: NTEGRA PRIMA instrument under ambient conditions using NT-MDT solver software for analysis, Ireland. The high resolution scanning electron microscopy (HRSEM) analysis were performed using HITACHI S-4800. Samples for AFM and SEM were prepared by spin coating 300 microliters of the chloroform solution (2 mgml<sup>-1</sup>) and over the surface area of 1.8 cm<sup>2</sup> of an ITO coated glass substrate to simulate the end use device conditions. The absolute photoluminescence quantum yield (PLQY) was collected by measuring the total light output in all directions in an integrating sphere using EDINBURGH (UK) and FLS 980 TCSPC instruments. GIXRD studies were performed on films coated on ITO substrates using a Bruker D8 advance Xray diffractometer with a Cu Ka wavelength of 1.5406 Å. The ground and excited state geometries were determined using density functional theory (DFT) with Becke's three-parameter functional and the Lee-Yang-Parr functional (B3LYP) using the 6-31G\* basis set.

**OLEDs fabrication and measurement:** OLEDs of PNAA were fabricated using indium tin oxide (ITO) with a sheet resistance of 10  $\Omega$  square<sup>-1</sup>. The substrates were cleaned by a series of ultrasonic processing with acetone, detergent, and deionized water in an ultrasonic solvent bath. After cleaning in the solvent bath they were then baked in a heating chamber at 120 °C and treated with oxygen plasma for 25 min before use. The PEDOT-PSS (10–40 nm) solution was spin-coated on cleaned ITO substrates and baked in a heating chamber at 200 °C for one hour. After the above process 300 ml of PTNAA in CHCl3 (solution with 1 mg/ml concentration) were spin-coated at 2000 rpm for 60 seconds to get uniform film (with thickness 100–150 nm) and the aluminium was coated at 105 Torr. Current–voltage (I–V) characteristics were studied using a Keithley 2400 sourcemeter. Luminescence–voltage (L–V) characteristics of the OLEDs were performed using a NUCLEONIX type 168 PMT housing with drawer assembly. Electroluminescence spectra of the OLEDs were further measured using a Carey Eclipse fluorescence spectrophotometer. Commission Internationale de l'Eclairage (CIE) color coordinate values of the thin films of the LEDs were standardized using a Konica Minolta CS-100 Chromameter in automated mode.

#### Synthesis of intermediates, monomers and polymers

A multi-step synthetic rout was followed to achieve the synthesis of all key intermediates, monomers and all polymers. The structural integrity of intermediates, monomers and polymers were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, elemental analysis and Maldi-mass analysis. All reactions were carried out under nitrogen atmosphere unless entirely stated. A detailed synthetic strategy (Scheme 1) for all Intermediates, monomers and polymers are we used specific procedures followed for each steps are given in the following subsections.



**Scheme 1** Synthetic route to AIE monomer of BPPTA and copolymers (i) NaOH/DMSO in THF, RT for 48 hrs; (ii) NBS, Acetic acid/Toluene, RT stirred for 6 hrs; (iii) Pd(pph<sub>3</sub>)<sub>4</sub>–K<sub>2</sub>CO<sub>3</sub> reflux for 48 hrs; (iv) Ni(COD)<sub>2</sub>/DMF 52° for 12 hrs (v) NaOH/THF 50° C, for 24 hrs; (vi) Pd(pph<sub>3</sub>)<sub>4</sub>–NaHCO<sub>3</sub> reflux for 72 h.



Phenothiazine (10 g, 0.0501 mol), 1-Bromohexane (9.92 g, 0.0601 mol), sodium hydroxide (13.0 g, 0.3256 mol), and DMSO (100 mL) were placed in a 250-mL, two-necked round-bottom flask and the reaction mixture was stirred for 48 hrs at room temperature. The mixture was extracted with ethylacetate/brine and then dried with anhydrous MgSO<sub>4</sub>. The resulting liquid was purified by column chromatography, as a light yellow solid of PT-Al (10.92 g, 0.038 mol, yield = 77%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.11 (t, *J* = 6.9 Hz, 4H), 6.91 – 6.80 (m, 4H), 3.80 (t, *J* = 7.0 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.45 – 1.35 (m, 2H), 1.33 – 1.22 (m, 4H), 0.85 (t, *J* = 5.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.38, 127.47, 127.23, 124.95, 122.37, 115.45, 47.49, 31.55, 26.96, 26.74, 22.68, 14.09. Elemental analysis: Calculated (%) for C<sub>18</sub>H<sub>21</sub>NS: C, 76.28%; H, 7.47%; N, 4.94%; S, 11.31%. Found: C, 76.04%; H, 7.65%; N, 4.62%; S, 10.11%.



Figure S1. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 10-hexyl-10H-phenothiazine (PT-Al)

#### 3,7-dibromo-10H-phenothiazine (PT-Br<sub>2</sub>)



In to a (100 mL), two necked round bottom flask were placed NBS (7.83 g, 0.044 mol) was added to a solution of 10-hexyl-10H-phenothiazine (5 g, 0.0176 mol) in toluene (20 mL) and acetic acid (30 mL). The reaction mixture was then stirred for 6 hrs at room temperature. The resulting mixture was extracted with ethyl acetate/ brine and then dried with anhydrous MgSO4. After filtration, the solvent was concentrated in a rotary evaporator to obtain the crude product as yellow amorphous solid and residue was purified by column chromatography using silica gel and *n*-hexane/ethylacetate (19/1; v/v) as the eluent to give PT-Br<sub>2</sub> as a little yellow viscous liquid after 2 days it was concentrated and converted as a solid crystal form (6.91 g, 0.1411 mol, yield = 89.5%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.16 (m, 4H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.72 (t, *J* = 7.0 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.35 (dd, *J* = 29.3, 22.5 Hz, 6H), 0.86 (t, *J* = 6.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.15, 130.12, 129.71, 126.47, 116.66, 114.76, 47.65, 31.39, 26.66, 26.52, 22.58, 13.99. Elemental analysis calcd for C<sub>18</sub>H<sub>19</sub>Br<sub>2</sub>NS: C, 49.00%; H, 4.34%; N, 3.17%; S, 7.27%. Found: C, 50.09%; H, 4.45%; N, 3.29%; S, 6.82%.



Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 3,7-dibromo-10H-phenothiazine (PT-Br)

#### 4-(7-bromo-10hexyl-10h-phenothiazine-3-yl) benzaldehyde PTP-CHO



In to a (250 mL), two necked round bottom flask equipped with condenser were placed *PT-Br*<sub>2</sub> (5 g, 0.0114 mol) was added to a solution of (3.17 g, 0.0136 mole) 4-formyl phenylboronic acid (3.17g 0.0137 mole) in THF. 2 M K<sub>2</sub>CO3 in water was added to the reaction mixture and degassed by nitrogen. After raising the temperature to 70 °C, a catalytic amount of (2.6 g, 0.0023 mole) Pd(PPh<sub>3</sub>)<sub>4</sub> was added and again nitrogen was purged. The resulting reaction mixture was refluxed for 48 hours. After 48 hours the reaction mixtures was allowed to cool room temperature and filtered the crude product, then evaporate the solvent through rotary evaporator. The crude product was poured into a separating funnel and then 100 ml of CH<sub>2</sub>Cl<sub>2</sub> was added followed by washing with water (3 x 100 ml). The resulting organic layer was separate and concentrated in a rotary evaporator to obtain the crude product of organic phase and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Further, the solvent was removed and the residue was purified by column chromatography eluting with hexane/ethylacetate (9:1, v/v). The pure product **PTP-CHO** was isolated (4.95 g, 0.0107 mol, yield = 93.4%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.95 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.19 – 7.15 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.66 – 6.61 (m, 1H), 3.79 – 3.72 (m, 2H), 1.78 – 1.67 (m, 2H), 1.35 (dd, *J* = 14.8, 7.1 Hz, 2H), 1.28 – 1.19 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.74, 144.71, 144.26, 142.89, 133.94, 132.96, 129.33, 129.04, 128.69, 125.81, 125.45, 125.01, 123.83, 115.60, 114.70, 113.76, 76.32, 76.00, 75.68, 46.67, 30.39, 25.69, 25.53, 21.55, 12.95.

Elemental analysis: Calculated (%)for C<sub>25</sub>H<sub>24</sub>BrNOS, C, 64.38; H, 5.19; Br, 17.13; N, 3.00; O, 3.43; S, 6.87. Found: C, 62.46; H, 4.98; N, 2.74.00; S, 6.44.



**Figure S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 4-(7-bromo-10hexyl-10h-phenothiazine-3-yl) benzaldehyde (PTP-CHO)

#### 2,2'-([1,1'biphenyl]4,4'-diyl)acetonitrile (BP-ACN)



In to a (50 mL), single necked round bottom flask were placed about 1 g (0.0051 mol) of and 2.17 g (0.0076 mole) of Ni(COD)<sub>2</sub> are added to the 30 ml of anhydrous dimethylformamide (DMF), then the mixture was stirred for 12 hrs. The crude product was poured into a separating funnel and then 50 ml of CHCl<sub>3</sub> was added followed by washing with water (3 x 100 ml). Then the reaction mixture was washed with water and brine solution. resulting organic layer was concentrated in a rotary evaporator to obtain the crude product. The crude product was purified by column chromatography using petroleum ether/ethylacetate (v/v 9:1). The pure white color solid was isolated (4.9 g, 0.0211 mol, yield = 87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.57 (m, 4H), 7.41 (d, J = 8.5 Hz, 4H), 3.80 (s, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.09, 129.26, 128.46, 127.74, 117.70, 23.11.

Elemental analysis: Calculated (%) for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>: C, 82.73; H, 5.21; N<sub>1</sub>12.06; Found: C, 82.06; H, 5.12; N<sub>1</sub>11.87.



Figure S4. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 2,2'-([1,1'biphenyl]diacetonitrile (BPDAC)

Synthesis of (2Z,2'Z)-2,2'-([1,1'-biphenyl]-4,4'-diyl)bis(3-(4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)phenyl)acrylonitrile) (BPPTA)



In a 50 mL Schlenk flask, 4-(7-bromo-10hexyl-10h-phenothiazine-3-yl) benzaldehyde (0.12 mmol, 39 mg) and 2,2'-([1,1'biphenyl]4,4'-diyl)acetonitrile (0.18 mmol, 42 mg) were dissolved in THF (24 mL). To this solution, NaOH (0.12 mmol, 5.0 mg) was added. After heating at 50°C, the reaction mixtures stirred for 24 hours, the resulting precipitates were retrieved by centrifugation, washed with water and stirred with methanol 15 mins, filter the precipitate and dried under vacuum.

<sup>1</sup>H NMR (500 MHz, )  $\delta$  7.96 – 7.73 (m, 4H), 7.72 – 7.39 (m, 14H), 7.38 – 7.22 (m, 5H), 7.20 – 7.02 (m, 4H), 6.86 – 6.74 (m, 2H), 6.58 (d, J = 8.8 Hz, 1H), 3.89 – 3.53 (m, 4H), 1.69 (s, 4H), 1.24 (t, J = 41.1 Hz, 12H), 0.80 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.84, 143.34, 141.57, 140.94, 139.92, 133.86, 132.61, 129.90, 129.50, 128.98, 128.55, 128.06, 127.74, 127.64, 127.57, 127.11, 126.50, 118.06, 117.68, 116.57, 115.74, 110.75, 48.05, 31.44, 29.70, 23.37, 22.69, 14.12. MALDI-Tof mass m/z: Calculated for C<sub>66</sub>H56Br<sub>2</sub>N<sub>4</sub>S<sub>2</sub>; 1128.23; found, 1128.10. Elemental analysis: Calculated (%) for C<sub>66</sub>H56Br<sub>2</sub>N<sub>4</sub>S<sub>2</sub>: C, 70.21; H, 5.00, Br, 14.15, N, 4.96; S, 5.68: Found: C, 69.48; H, 5.07; N, 4.87; S, 5.59.

![](_page_12_Figure_0.jpeg)

**Figure S5.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of (2Z,2'Z)-2,2'-([1,1'-biphenyl]-4,4'-diyl)bis(3-(4-(7-bromo-10-hexyl-10H-phenothiazin-3-yl)phenyl)acrylonitrile) (BPPTA).

![](_page_13_Figure_0.jpeg)

Figure S6. Maldi – Tof mass spectrum of BPPTA.

#### **Polymerization:**

![](_page_14_Figure_1.jpeg)

A series of copolymers were synthesized by Suzuki polymerization reaction using different composition of feed ratios of the BPPTA monomer and 9'9-dihexyl fluorene. The obtained conjugated copolymers with different BPPTA and fluorene ratios show M<sub>n</sub> and Poly dispersity Index (PDI) values are shown in Table S1. The corresponding copolymers are labeled as BPPTA 0.1, BPPTA 0.25, BPPTA 0.5, BPPTA 5, BPPTA 25, BPPTA 50, (Scheme 1). In a representative controlled synthetic procedure of BPPTA combined copolymers are, about 250 mg (0.00022 mole) of BPPTA along with 110 mg (0.00022 mole) 9,9-dihexylfluorene-2,7-diboronic acid (1,3-propane diol) ester was dissolved in (50 mL) of of tetrahydrofurane. To the above mixture of the reactant, (20 mL) 1% saturated sodium bicarbonate solution was added; the resulting biphasic mixture was degassed with nitrogen. On heating when the reaction mixture temperature reached to 60 °C, catalytic amount of Tetrakis triphenyl phosphine palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub> was added to the reaction mixture under the nitrogen condition. The reaction mixture was refluxed with constant stirring for 72 hrs. After ending the reaction allowed to cool at room temperature. Then concentrated under vaccum and redissolved in chloroform. The chloroform solution was washed with 3 N HCl solution and water. The organic layer was separated and concentrated through rotary evaporator to get crude product of copolymer BPPTA 50. The resulting crude product was purified through reprecipitation from the concentrated chloroform solution with methanol and subjected to soxhlet extraction for 6 hrs to get red precipitate, dried and weighed. Yield 85 %.

1H NMR (400 MHz, CDCl3) δ 8.23 – 6.61 (m, 44H, ArH), 3.78 (m, 3H, CH<sub>2</sub>), 1.95 (m, 1H, CH<sub>2</sub>), 1.34 – 0.89 (m, 35H), 0.88 – 0.41 (m, 25H, CH<sub>2</sub>).

**BPPTA 25 copolymer:** (124 mg, 0.00011 mol) of BPPTA along with (54 mg, 0.00011 mol) of 9,9dihexyl -2,7-dibromofluorene and (110 mg, 0.00022 mol) of of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 75 %.

1H NMR (400 MHz, CDCl3) δ 8.13 – 6.69 (m, 31H, ArH), 4.09 – 3.62 (m, 2H, CH<sub>2</sub>), 2.18 – 0.90 (m, 56H, CH<sub>2</sub>), 0.82 – 0.30 (m, 25H, CH<sub>2</sub>).

**BPPTA 5 copolymer:** (25 mg, 0.000022 mol) of BPPTA along with (97 mg 0.000198 mol) of 9,9-dihexyl -2,7-dibromofluorene and (110 mg, 0.00022 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 74%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.24 (m, 20H, ArH), 2.00 (m, 10H, CH<sub>2</sub>), 1.15 – 0.85 (m, 29H, CH<sub>2</sub>), 0.82 – 0.44 (m, 24H, CH<sub>2</sub>).

**BPPTA 0.5 copolymer:** (2.5 mg, 0.0000022 mol) of FBPAN along with (107 mg 0.000218 mol) of 9,9dihexyl -2,7-dibromofluorene and (110 mg, 0.00022 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3propane diol)ester were used in the polymerization, yield 87%.

1H NMR (400 MHz, CDCl3) δ 7.98 – 7.23 (m, 20H, ArH), 2.30 – 1.78 (m, 11H), 1.15 – 0.86 (m, 29H, CH<sub>2</sub>), 0.83 – 0.43 (m, 24H, CH<sub>2</sub>).

**BPPTA 0.25 copolymer:** (5.6 mg, 0.0000049 mol) of BPPTA along with (486 mg 0.000985 mol) of 9,9dihexyl -2,7-dibromofluorene and (500 mg, 0.00099 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 85%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ) 7.89 – 7.32 (m, 20H, ArH), 2.08-1.67 (m, 10H, CH<sub>2</sub>), 1.30-0.41 (m, 30H, CH<sub>2</sub>), 0.78 – 0.41 (m, 24H, CH<sub>2</sub>).

**BPPTA 0.1 copolymer:** (2.23 mg, 0.00000198 mol) of BPPTA along with (486 mg 0.000988 mol) of 9,9-dihexyl -2,7-dibromofluorene and (500 mg, 0.00099 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 89%.

1H NMR (400 MHz, CDCl3) δ 7.96 – 7.22 (m, 20H, ArH), 2.26 – 1.79 (m, 11H, CH<sub>2</sub>), 1.30 – 0.87 (m, 30H, CH<sub>2</sub>), 0.82 – 0.32 (m, 24H, CH<sub>2</sub>).

Gel Permission Chromatography data and feed ratio of the copolymers are presented in Table S1.

![](_page_16_Figure_2.jpeg)

Figure S7 <sup>1</sup>H NMR spectrum of BPPTA in various copmposition of copolymers with 9'9dihexylfluorene

	Feed ra	ntio <sup>a</sup>		<sup>c</sup> Calculated values	$M_w/M_n/PDI^{b}$
Polymer	RDDTA	М	N	R P P T A	
BPPTA 0.1	0.001	0.50	0.499	0.00076	25980/ 14456/1.79
BPPTA 0.25	0.0025	0.50	0.4975	0.0018	18530/12686/1.46
BPPTA 0.5	0.005	0.50	0.495	0.0043	9310/8824/1.05
BPPTA 5	0.050	0.50	0.450	0.0417	11156/9900/1.13
BPPTA 25	0.250	0.50	0.250	0.1975	17598/13004/1.35
BPPTA 50	0.500	0.50	0.000	0.413	16868/12700/1.43

Table S1. Feed ratios, calculated mole fractions and GPC datas of BPPTA copolymers:

<sup>*a*</sup> BPPTA, mole fraction of BPPTA; M, mole fraction of 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) ester; N, mole fraction of 9,9-Dihexyl-2,7-dibromofluorene. <sup>*b*</sup> $M_w$ , Weight averaged molecular weight;  $M_n$ , number averaged molecular weight; *PDI*, Polydispersity index. <sup>*c*</sup> Calculated mole fraction of BPPTA

#### Lippert- mataga study:

Solvatochromism is a characteristic behavior of dipolar molecules. In general, different polarity of solvent provides a usefull frame work for study of solvent dependent spectral shift. Using Lippertmataga study the influence of different polarity of solvents environment on photophysical property of organic luminogen can be understood.<sup>1</sup> Lippert- mataga study reveals that the interactions between the solvent and dipolmoment of solute and the equation can be given as follows.

$$hc(v_{a} - v_{f}) = hc(v_{a}^{0} - v_{f}^{0}) - \frac{2(\mu_{e} - \mu_{g})}{a^{3}} \left[ \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^{2} - 1}{2n^{2} + 1} \right]$$
$$a = (3M/4N\pi d)^{1/3}; \left[ \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^{2} - 1}{2n^{2} + 1} \right] = f(\varepsilon, n)$$
$$\mu_{g} = (m_{2} - m_{1}/2) [hca^{3}/2m_{1})^{1/2}$$
$$\mu_{e} = (m_{1} + m_{2}/2) [hca^{3}/2m_{1})^{1/2}$$

Where *h* is the Planck's constant (6.625x10<sup>-7</sup> ergs), *c* is the velocity of light (2.997x10<sup>10</sup> cm/s), "a' is the Radius of the cavity in which the fluorophore resides, derived from the Avogadro number (N), molecular weight(M), and density (d=1.0 g/cm<sup>3</sup>);  $v_a$  and  $v_f$  is wavenumber (cm<sup>-1</sup>) of the absorption and emission respectively;  $v_a^0$  and  $v_f^0$  are corresponds to the stokes shift when *f* is Zero;  $\mu_e$  is the excited state dipole moment,  $\mu_g$  is the ground state dipole moment; *f* is the orientation polarizability of the solvent;  $\varepsilon$  and n are the solvent dielectric and the solvent refractive intex, respectively. The detailed data are listed in Table S2.

						BPPTA
Solvents	3	n	<i>f</i> (ε,n)			Stroke shift
				$\lambda_a(nm)$	$\lambda_f(nm)$	$(\lambda_a - \lambda_f) (\mathrm{cm}^{-1})$
Cyclohexane	1.9	1.375	-0.0014	436	555	4917
Toluene	2.38	1.49	0.014	438	562	5033
Diethyl ether	4.34	1.35	0.167	435	568	5383
Tetrahydrofurane	7.58	1.40	0.210	439	576	5418
Dichloromethane	8.93	1.42	0.217	442	580	5501
N'N-Dimethyl formamide	37	1.427	0.276	445	585	5477
Acetone	20.7	1.35	0.284	438	582	5649
Acetonitrile	37.5	1.34	0.305	436	587	5900
Methanol	33	1.33	0.308	438	595	5972

Table S2. Detailed study of absorption and emission peak position of BPPTA in different polar solvents.

Where,  $\varepsilon$  and n are the solvent dielectric constant and the corresponding solvent refractive index, respectively; *f* is the orientational polarizability of the solvent;  $\lambda_a$  and  $\lambda_f$  absorption and emission maximum respectively.

Polymers -	$a\lambda_{max}$ (Ab	$^{a}\lambda_{max}$ (Abs) (nm)		<sup>c</sup> λ <sub>max</sub> (Emi) (nm)		nce life time		
	Solution ${}^{b}(\varepsilon)$	Thin film	Solution(Exc)	Thin film (Exc)	Solution $(\tau_1/\tau_2)$	Thin film $(T_1/T_2)$	${}^{e}\Phi_{PL}{}^{SOL}$	${}^{\mathrm{f}}\Phi_{PL}{}^{\mathrm{TF}}$
BPPTA 0.1	365	375	416 (366)	424, 519 (375)	1.63	0.25/7.58	49.3	79.5
BPPTA 0.25	370	374	414 (370)	422, 530 (374)	1.77	0.22/5.89	51.2	59.9
BPPTA 0.5	370, 417	378, 442	416 (370)	423, 539 (378)	1.68	0.26/14.93	33.4	63.5
BPPTA 5	355, 419	360, 443	413, 573 (419)	420, 546 (443)	1.57	3.46	29.7	71.4
BPPTA 25	363, 427	347, 444	410, 577 (427)	422, 565 (444)	3.4/6.8	4.08	37.1	59.3
ВРРТА 50	355, 429	369, 450	413, 590 (429)	576 (450)	2.9/7.3	4.30	32.3	64.8
ВРРТА	320, 432	306, 386	462, 570 (432)	601 (386)	3.8/12.1	4.77	19.2	69.1

**Table S3.** Device characteristics of BPPTA monomer and copolymers.

 ${}^{a}\lambda_{max}$  (Abs), absorption maxima for solutions and thin films in nm;  ${}^{b}(\varepsilon)$ , extinction coefficient in dL g<sup>-1</sup> cm<sup>-1</sup>.  ${}^{c}\lambda_{max}$  (Emi), emission maxima for solutions and thin films in nm.  ${}^{d}\tau_{1}/\tau_{2}$  and  $T_{1}/T_{2}$ , lifetime of different decay channels from fluorescence lifetime experiment in ns for solutions and thin films;  ${}^{e}$  and  ${}^{f}\Phi_{PL}^{SOL}$  and  $\Phi_{PL}^{TF}$ , The solution and thin film absolute PL quantum yields were measured using an integrating sphere.

![](_page_20_Figure_3.jpeg)

Absorption spectra

of BPPTA in different composition of water in THF mixtures.

Figure S8

![](_page_21_Figure_0.jpeg)

**Figure S9** (a) AFM micrograph of spun thin films from chloroform solution of BPPTA; (b) HRSEM micrograph ((scale bar for image is 2 μm); (c) GIXRD traces of BPPTA in thin film.

![](_page_21_Figure_2.jpeg)

Figure S10 DSC traces of various composition of BPPTA in copolymers

**Computational Details** 

The ground state geometries were optimized by density functional theory (DFT) at the B3LYP/6-31G\* level of theory as implemented in the Gaussian 09 package.<sup>S5-S7</sup> All the optimized structures were characterized by a frequency analysis and were shown to be all positive frequencies. The solubilizing hexyl groups from fluorene were represented as methyl group due to computation limitation. On basis of gas phase optimized ground geometry, the absorption spectra were calculated by a time-dependent density functional theory (TD-DFT) program with at B3LYP 6-31G\* level.

![](_page_22_Figure_1.jpeg)

**Figure S11** (a) and (b) Optimized geometry of the BPPTA and copolymer model systems at B3LYP/6-31G\* level of theory.

![](_page_23_Figure_0.jpeg)

Figure S12 Theoretically calculated absorption spectra of BPPTA Monomer (a) and BPPTA copolymer model system (b) at B3LYP/6-31G\* level.

**Table 4** Summary of the excited state electronic transitions obtained from the TD-DFT calculations at the B3LYP/6-31G\* level

Model systems	States	Absorption (nm)	Energy (eV)	Oscillator strength (F)	Dominant contribution <sup>a</sup> (%)	Exp. (nm)
BPPTA	$\mathbf{S}_1$	366	3.3832	3.8088	H-2→LUMO (27%),	320, 432
	S <sub>20</sub>	240	5.1734	0.3841	HOMO→LUMO (39%), H-5→L+1 (9%)	
BPPTA copolymer	$\mathbf{S}_1$	372	3.3317	4.0658	H-2→LUMO (29%), H- 1→L+1 (13%), HOMO→LUMO (29%); H-1→L+2 (10%), H-1→L+6 (12%).	
	$S_8$	280	4.4178	0.8530		370

<sup>a</sup>H denotes HOMO and L denotes LUMO.

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