Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

For

Self-assembly of White-light Emitting Polymer with Aggregation Induced Emission Using Simplified Derivatives of Tetraphenylethylene

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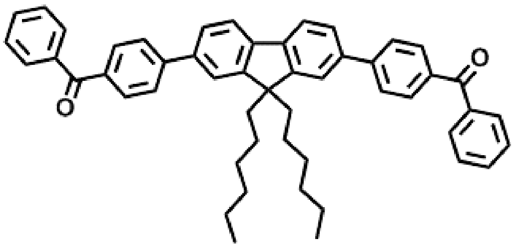
Synthesis Procedure of Monomer and copolymers:

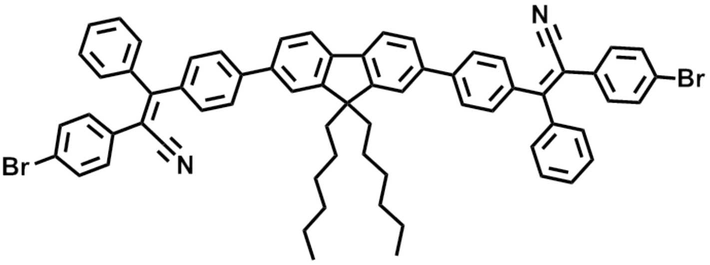
Synthesis of ((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(3,1- phenylene)) bis(phenylmethanone)) (FBPM)



5 g (0.0099 mole) of 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol)ester and 6.5 g (0.025 mole) of 4-Bromo benzophenone were dissolved in 70 ml of Toluene. To the above solution, 2 M K_2CO_3 in water was added and the mixture was degased by nitrogen. After raising the temperature to 70 °C, 2.2 g (0.002 mole) $Pd(PPh_3)_4$ was added and again nitrogen was purged. The resulting reaction mixture was refluxed for 48 hrs. After 48 hrs the reaction mixture 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 150 ml of CH_2Cl_2 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 unhydrous sodium sulphate. Solvent was then removed and the residue was purified by column chromatography eluting with hexane/ethylacetate (19:1, v/v). The pure product ((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(3,1-phenylene) bis(phenylmethanone)) was isolated as a bright white solid (Yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.94 (d, J = 8.0 Hz, 4H), 7.89 – 7.76 (m, 10H), 7.69 – 7.57 (m, 6H), 7.51 (t, J = 7.5 Hz, 4H), 2.14 – 2.03 (m, 4H), 1.11 (dd, J = 16.3, 9.5 Hz, 12H), 0.75 (t, J = 6.6 Hz, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 196.31, 152.02, 145.64, 140.77, 139.10, 137.86, 136.13, 132.40, 130.83, 130.04, 128.34, 127.01, 126.45, 121.69, 120.45, 55.49, 40.42, 31.47, 29.69, 23.86, 22.58, 14.01. IR (KBr, cm^{-1}): ν = 2926, 2853, 2210, 1660, 1603, 1487, 1466, 1402, 1248, 1183, 1079, 1010, 816, 764, 703, 481. MALDI mass m/z: Calculated for $C_{51}H_{46}O_2$,694.38; found,

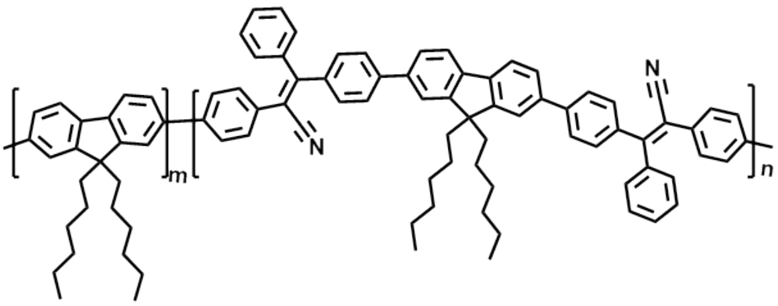
695.29. Elemental analysis: Calculated (%)for $C_{51}H_{50}O_2$, 88.14; H, 7.25, O; 4.60. Found: C, 88.37; H, 7.17; O, 4.65.

Synthesis of (2Z,2'Z)-3,3'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(3,1-phenylene))bis(2-(4-bromophenyl)-3-phenylacrylonitrile). **(FBPAN)**



In to a (250 mL), two necked round bottom flask equipped with condenser were placed about 3 g (0.0043 mole) of ((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(3,1-phenylene))bis(phenylmethanone)) and 1 g (60%, 0.0258 mole) of NaH are added to the 30 ml of benzene, then the mixture was refluxed for 10 minutes under the nitrogen. Then 2 g (0.0108 mole) of 4- Bromophenyl acetonitrile in benzene (60 ml) was added dropwise over 1hr under reflux. Evolved H_2 was observed at the oil bubler and the reaction was lasted for another 2 hrs. Upon cooling to room temperature 100 ml of water was added to the mixture. The resulting organic layer was filtered and 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 yellow color powder was isolated (Yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 – 7.69 (m, 5H), 7.65 – 7.45 (m, 12H), 7.45 – 7.29 (m, 5H), 7.28 – 7.21 (m, 5H), 7.19 – 7.12 (m, 2H), 7.12 – 7.05 (m, 3H), 2.04 (d, J = 16.7, 8.2 Hz, 4H), 1.16 – 0.97 (m, 12H), 0.79 – 0.61 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.09, 156.79, 147.07, 146.06, 145.24, 143.51, 142.35, 139.12, 137.01, 136.87, 136.74, 136.26, 135.51, 134.81, 133.74, 131.97, 127.20, 124.73, 114.92, 84.44, 60.32, 36.02, 35.89, 34.09, 28.61, 27.12, 18.95. IR (KBr, cm^{-1}): ν = 2926, 2853, 1656, 1599, 1466, 1445, 1401, 1314, 1175, 1150, 921, 857, 820, 790, 748, 697, 635. MALDI mass m/z: Calculated for $C_{67}H_{58}Br_2N_2$; 1050.29; found, 1050.87. Elemental analysis: Calculated (%)for $C_{67}H_{58}Br_2N_2$: C, 76.57; H, 5.56, Br_2, 15.21, N, 2.67; Found: C, 77.13; H, 5.46; Br_2, 15.33, N, 2.37.

***<u>Polymerization</u>*:**



A series of copolymers were synthesized by Suzuki polymerization reaction using different composition of feed ratio of the FBPAN monomer and comonomers (Different feed ratio in **Table S1**). The obtained conjugated copolymers with different FBPAN to fluorene ratios and their M_n and Poly dispersity Index (PDI) values are shown in **Table S1**. The corresponding copolymers labeled as FBPAN 0.5, FBPAN 1, FBPAN 5, FBPAN 10, FBPAN 25, FBPAN 50, (**Scheme 1).** In a representative controlled synthetic procedure of FBPAN copolymers are, about 250 mg (0.00024 mole) of FBPAN along with 120 mg (0.00024 mole) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester was dissolved in (50 mL) 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) 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 **FBPAN 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 yellow precipitate, dried and weighed. Yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96 – 7.27 (m, 38H, ArH), 7.23 – 7.01 (m, 4H, ArH), 2.03 (m, 8H, ArH), 1.05 (m, 24H, CH_2), 0.80 – 0.58 (m, 20H, CH_2).

FBPAN 25 copolymer: (126 mg, 0.00012 mol) of FBPAN along with (59 mg, 0.00012 mol) of 9,9-dihexyl -2,7-dibromofluorene and (120 mg, 0.00024 mol) of of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.28 (m, 23H, Ar H), 7.14 (m, 1H, ArH), 2.05 (m, 8H, CH_2), 1.11 (m, 24H, CH_2), 0.80 (m, 20H, CH_2).

FBPAN 10 copolymer: (50 mg, 0.000048 mol) of FBPAN along with (95 mg 0.000192 mol) of 9,9-dihexyl -2,7-dibromofluorene and (120 mg, 0.00024 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 78%. ^{1}H NMR (400 MHz, CDCl3, δ) 7.90 – 7.33 (m, 20H, Ar H), 7.18 (m, 1H Ar H), 2.15 – 1.91 (m, 8H, CH_2), 1.11 (m, 24H, CH_2), 0.89 – 0.60 (m, 20H, CH_2).

FBPAN 5 copolymer: (25 mg, 0.000024 mol) of FBPAN along with (106 mg 0.000216 mol) of 9,9-dihexyl -2,7-dibromofluorene and (120 mg, 0.00024 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 (m, 19H, Ar H), 2.04 (m, 8H, CH_2), 0.88 (m, 44H, CH_2).

FBPAN 1 copolymer: (2 mg, 0.00000192 mol) of FBPAN along with (471 mg 0.000958 mol) of 9,9-dihexyl -2,7-dibromofluorene and (480 mg, 0.00096 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.88 – 7.34 (m, 17H, ArH), 2.08 (m, 8H, CH_2), 0.95 (m, 44H, CH_2).

FBPAN 0.5 copolymer: (10 mg, 0.0000096 mol) of FBPAN along with (468 mg 0.0009504 mol) of 9,9-dihexyl -2,7-dibromofluorene and (480 mg, 0.000960 mol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 83%. 1H NMR

(400 MHz, $CDCl_3$, δ): 7.89 – 7.27 (m, 17H, ArH), 2.05 (m, J = 23.3, 8H, CH_2), 1.23 – 0.52 (m, 44H, CH_2).

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

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

Polymer	***Feed ratio*** [a]			**[c]Calculated values**	$M_w/M_n/PDI$ [b]
	FBPAN	***M***	***N***	***FBPAN***	
FBPAN 0.5	0.005	0.50	0.495	0.0041	14734/ 9039/1.63
FBPAN 1	0.010	0.50	0.490	0.0095	12466/7164/1.74
FBPAN 5	0.050	0.50	0.450	0.0463	19346/10688/1.81
FBPAN 10	0.100	0.50	0.400	0.0935	13344/7790/1.67
FBPAN 25	0.250	0.50	0.250	0.2270	18496/9202/2.01
FBPAN 50	0.500	0.50	0.000	0.4751	24324/12603/1.93

[a] FBPAN, mole fraction of FBPAN; M, mole fraction of 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) ester; *N,* mole fraction of 9,9-Dihexyl-2,7-dibromofluorene. [b] M_w, Weight averaged molecular weight; M_n, number averaged molecular weight; *PDI,* Polydispersity index. [c] Calculated mole fraction of FBPAN using proton NMR spectrum.

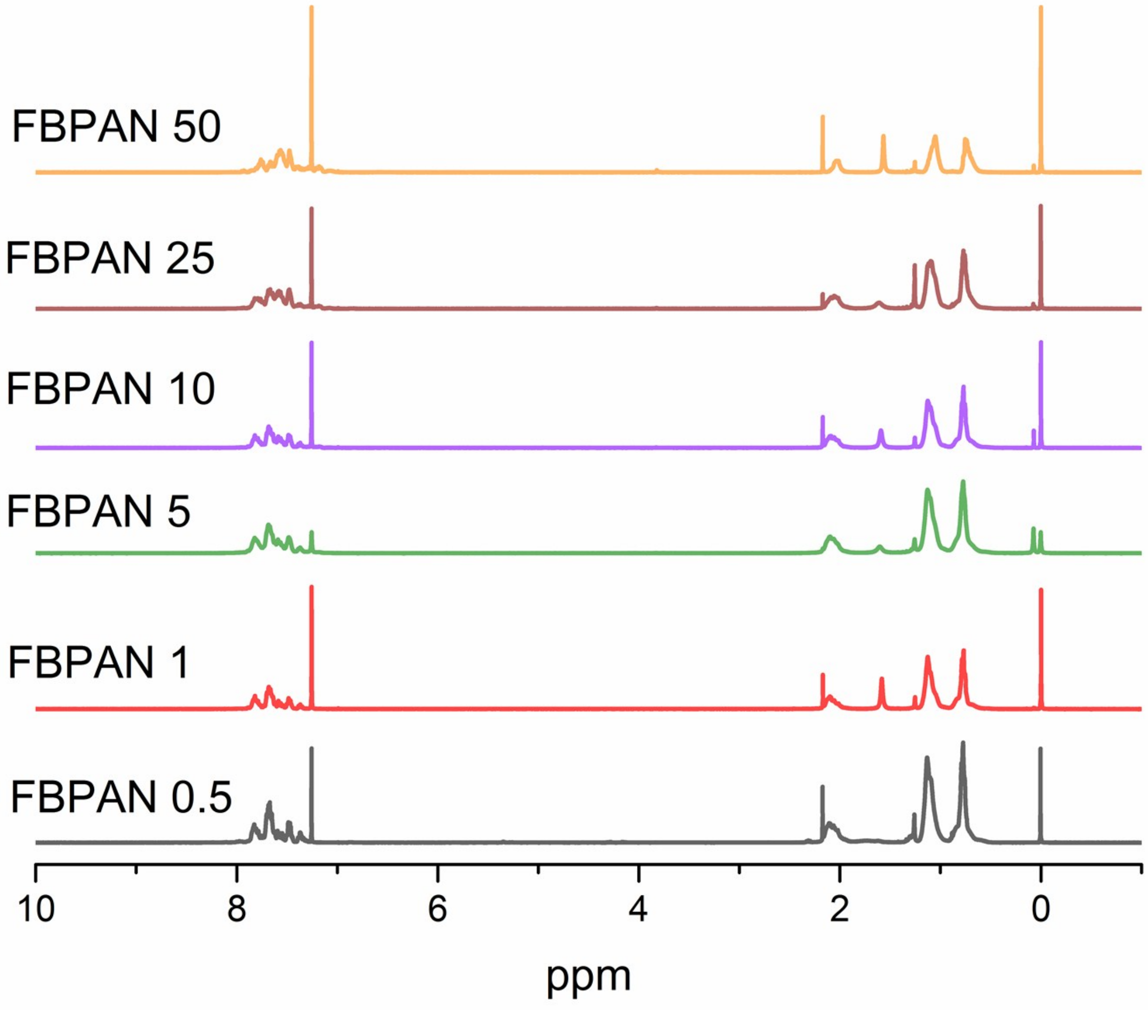


Figure S1. ^{1}H NMR spectrum of copolymers.

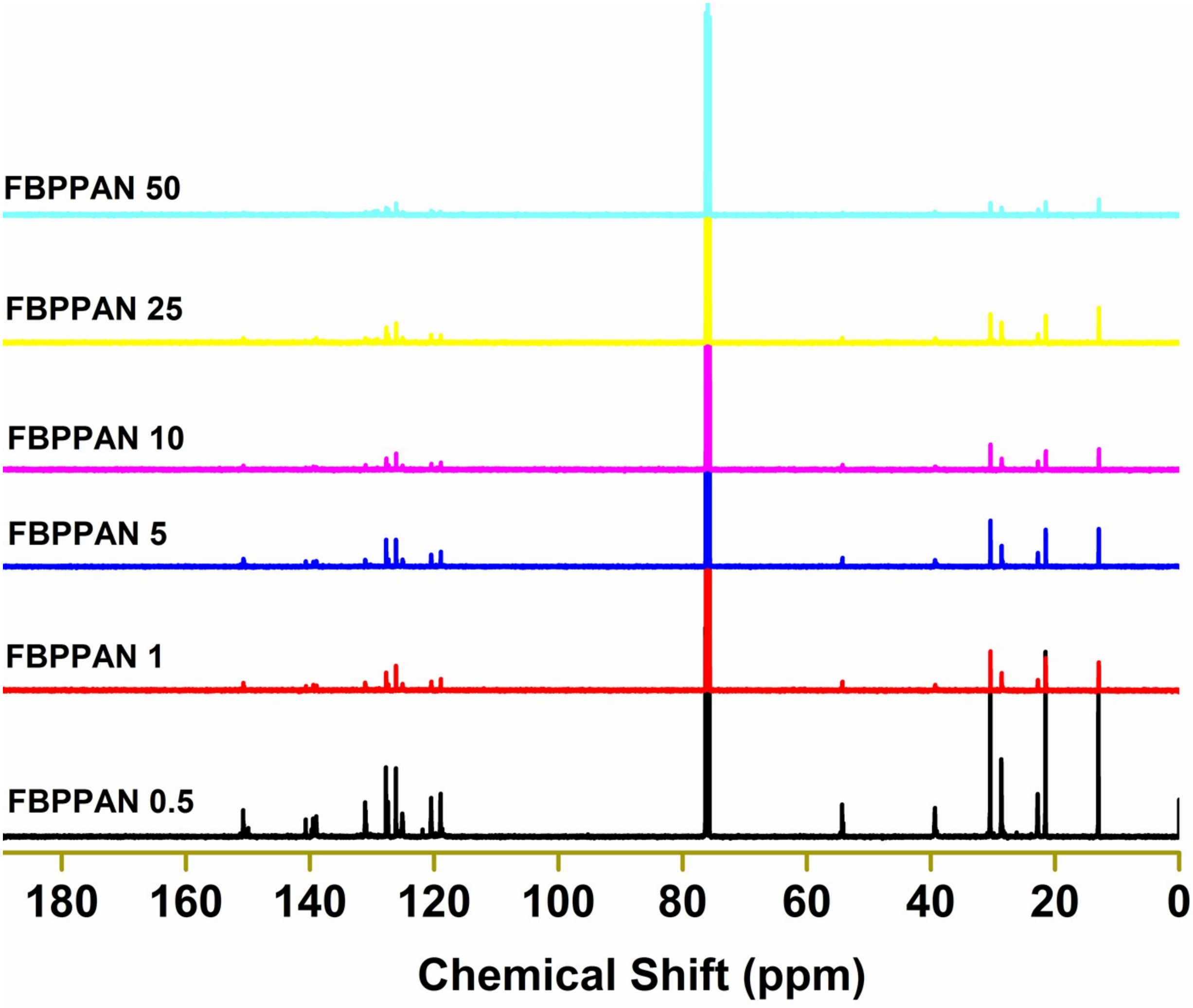


Figure S2. ^{13}C NMR spectrum of copolymers.

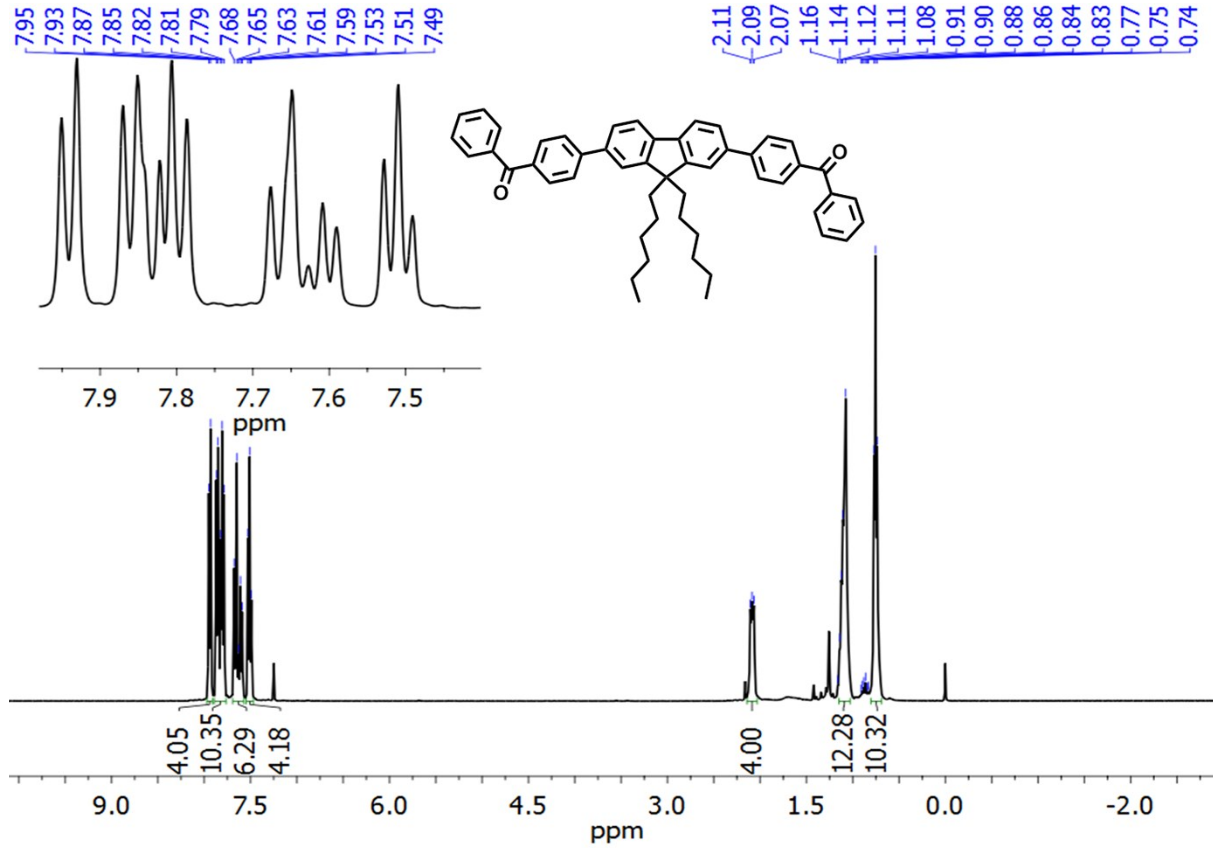


Figure S3. ^{1}H NMR spectrum of FBPM.

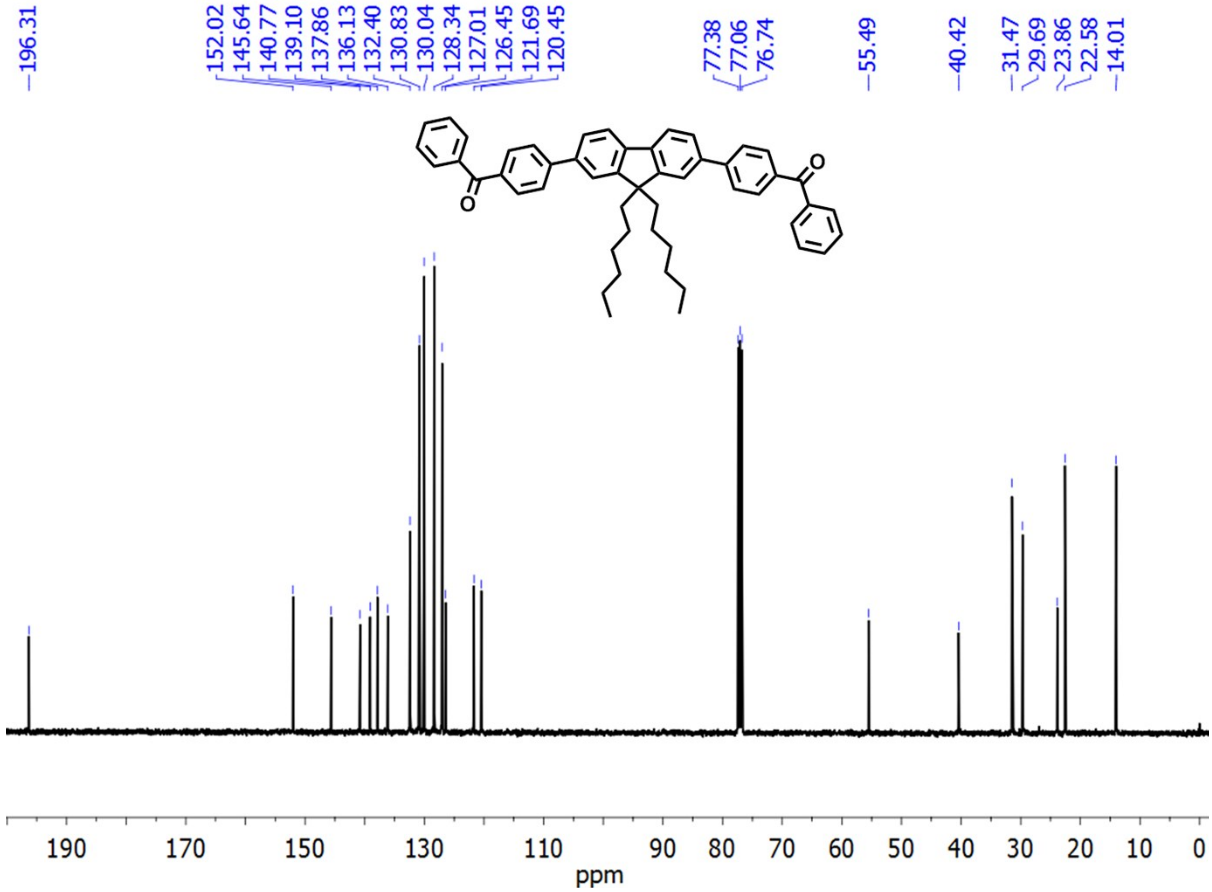


Figure S4. ^{13}C NMR spectrum of FBPM.

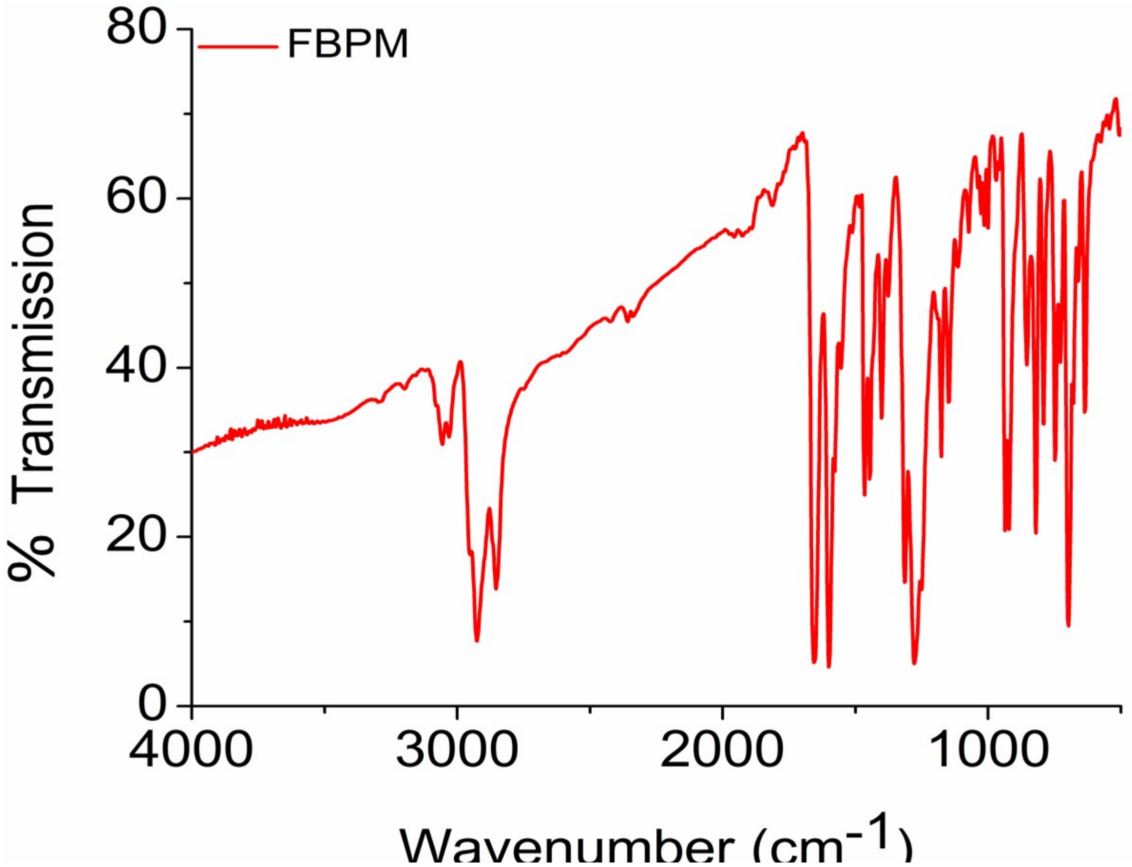


Figure S5. FT-IR spectrum of FBPM.

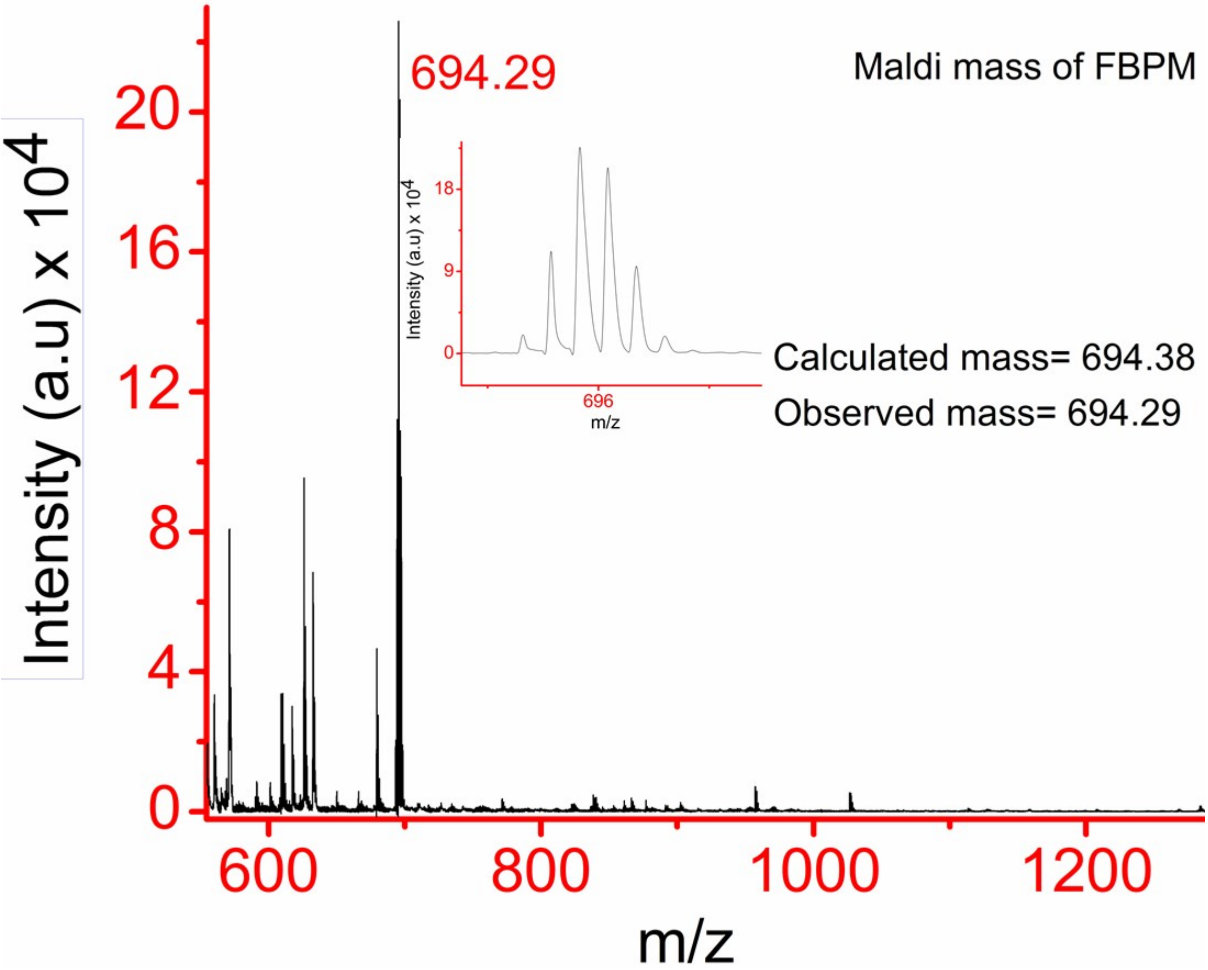


Figure S6. Maldi mass spectrometry of FBPM.

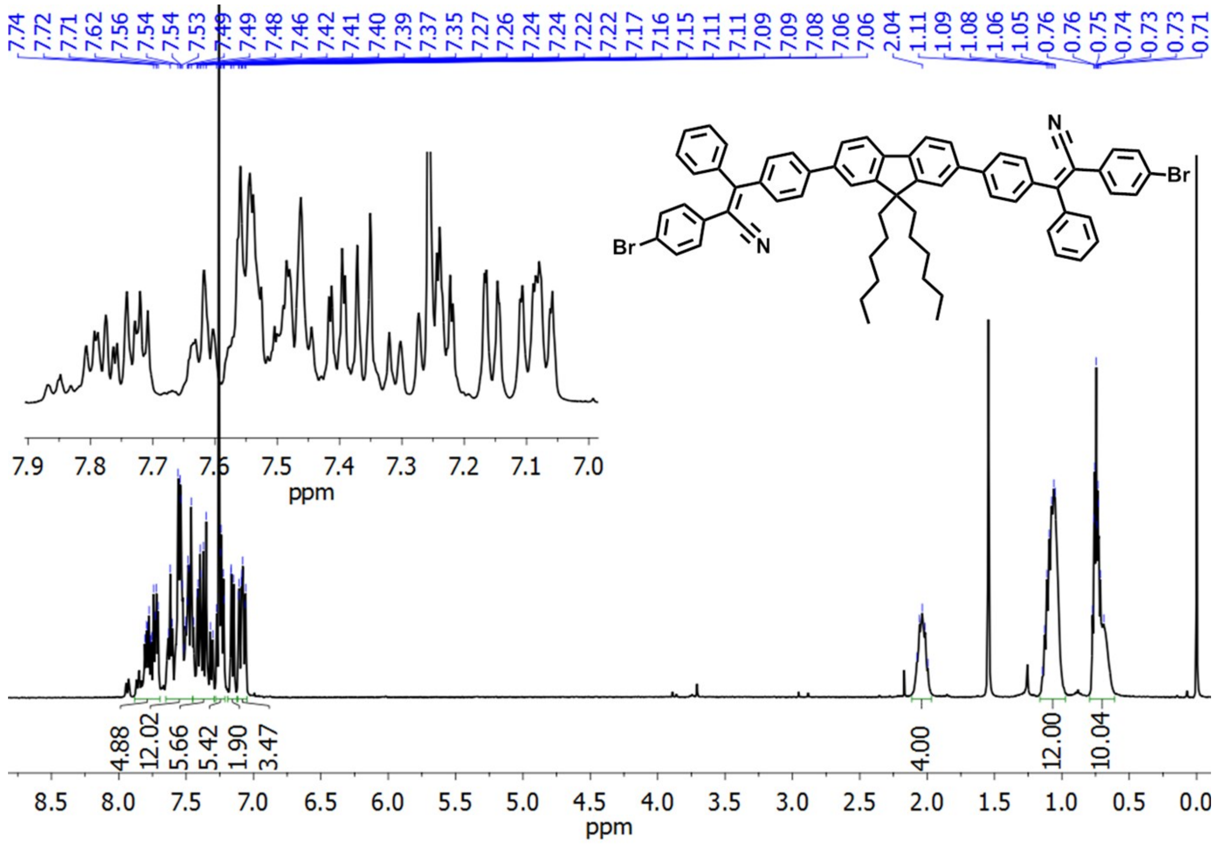


Figure S7. ^{1}H NMR spectrum of FBPAN.

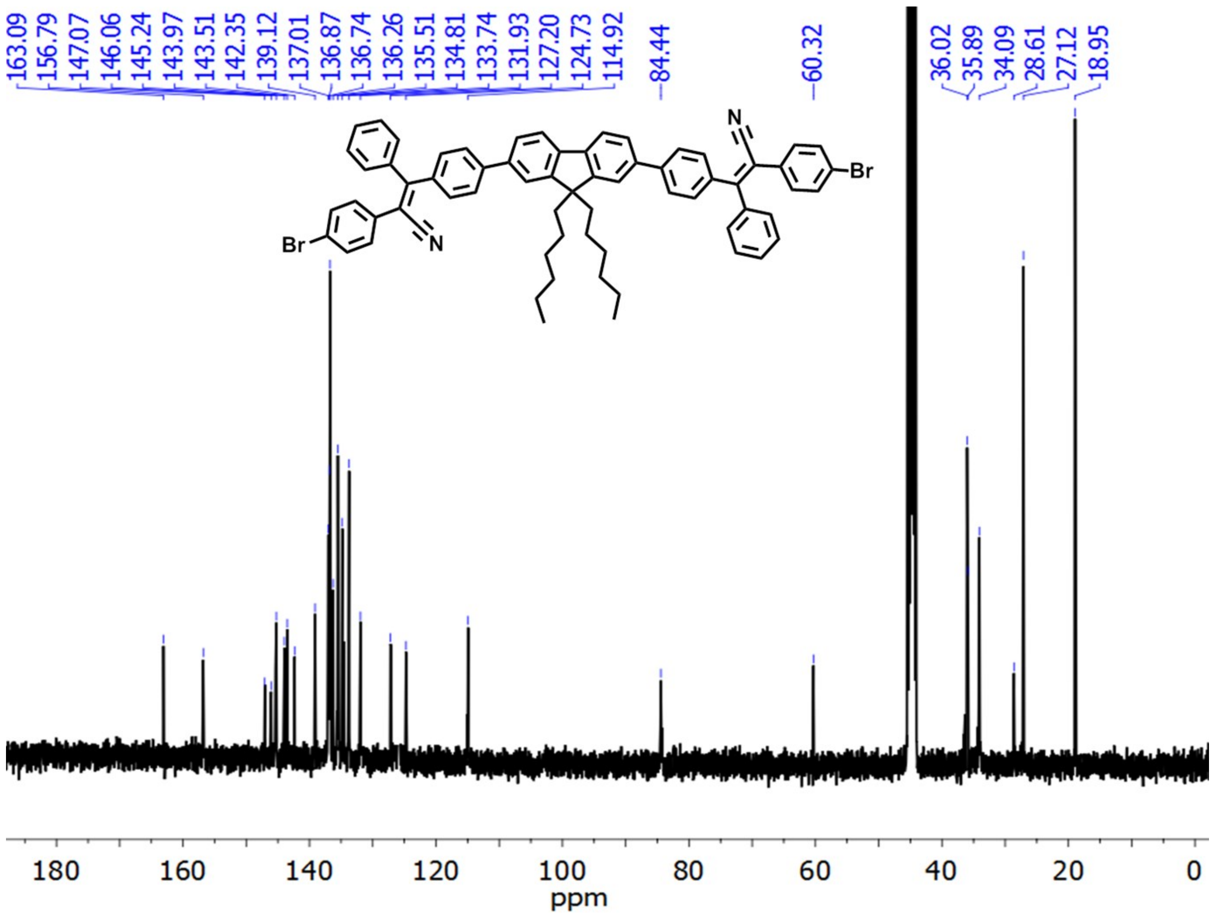


Figure S8. ^{13}C spectrum of FBPAN.

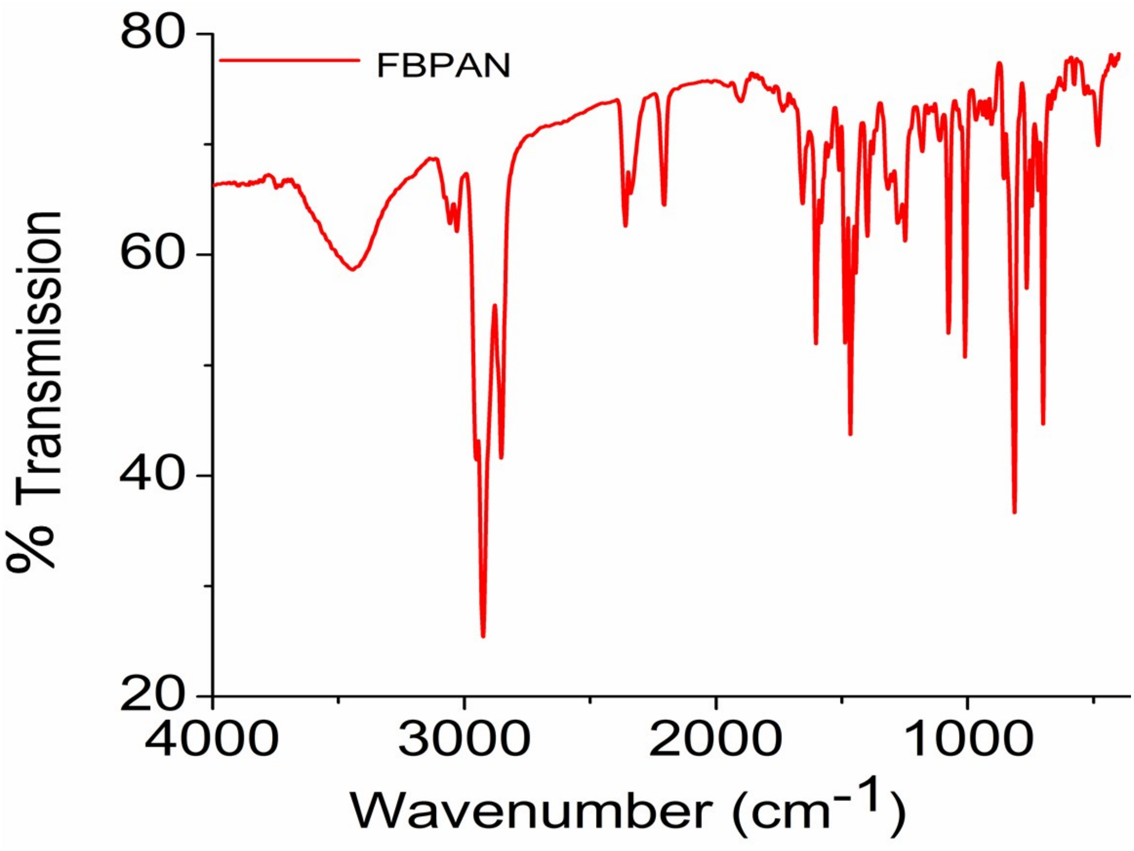


Figure S9. FT-IR spectrum of FBPAN.

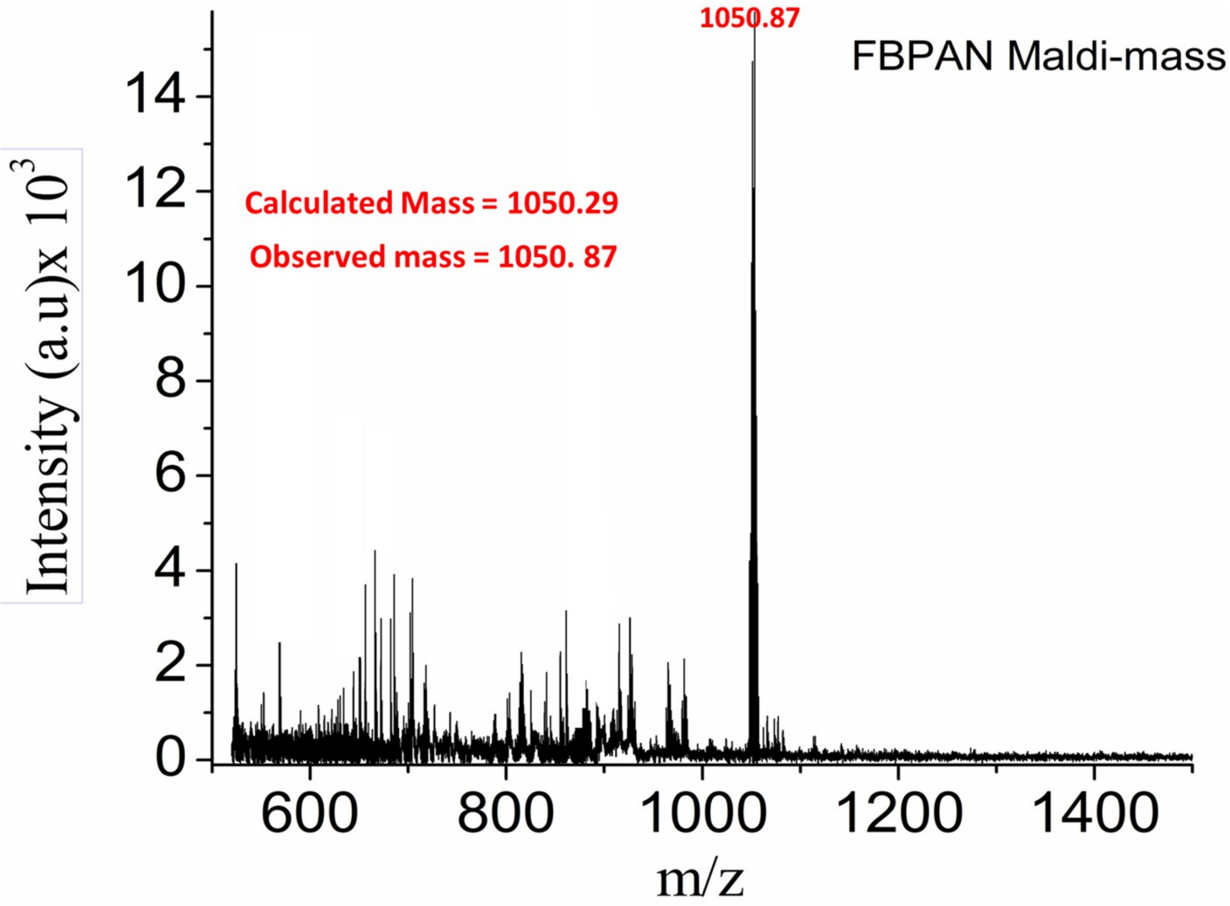


Figure S10. Maldi mass spectrometry of FBPN.

Solvatochromic effect (Lippert–Mataga study):

Solvatochromism is a typical behaviour of dipolar molecules. In general, the different polarities of solvents offer a worthwhile framework for studying solvent reliant spectral shifts to some organic luminogens. Using the Lippert–Mataga study, the effect of different polarities of solvent environments on the photo physical properties of organic luminogens can be implied.[S1] The lowest energy absorption of FBPAN was observed at 359 nm in hexane (lowest polarity of the solvent) and at 368 nm in N'N-Dimethyl formamide (highest polarity of the solvent). The observed result clearly reveals that the presence of twisted intramolecular charge transfer (TICT)[S2] due to solvent-induced change of electronic structure in ground state **(Figure S11 (a)** supporting information).[S3] In addition to that the emission spectra of FBPAN recorded in solvents with different polarity triggered a obvious solvatochromic effect with a uniform pathochromic shift of 44 nm (408-452 nm) while increase in polarity as observed for donor-acceptor systems.[S4] These red shift in emission spectra of FBPAN in polar solvents **Figure S11 (b)** is attributed to the emission from solvent relaxed state. Notably, based on the above observation, Lippert-Mataga plot presented in **Figure S11 (c)** in supporting information, shows a linear relationship as the solvent polarity increases. A plot of orientational polarizability (f) versus Stoke's shift (υ_a - $\upsilon_{f)}$ exhibited a positive slope and linear correlation coefficient was observed (R=0.9197). The above observation indicates that the resulting transitions involve significant charge transfer (CT) characteristic and with a high transition dipole moment.

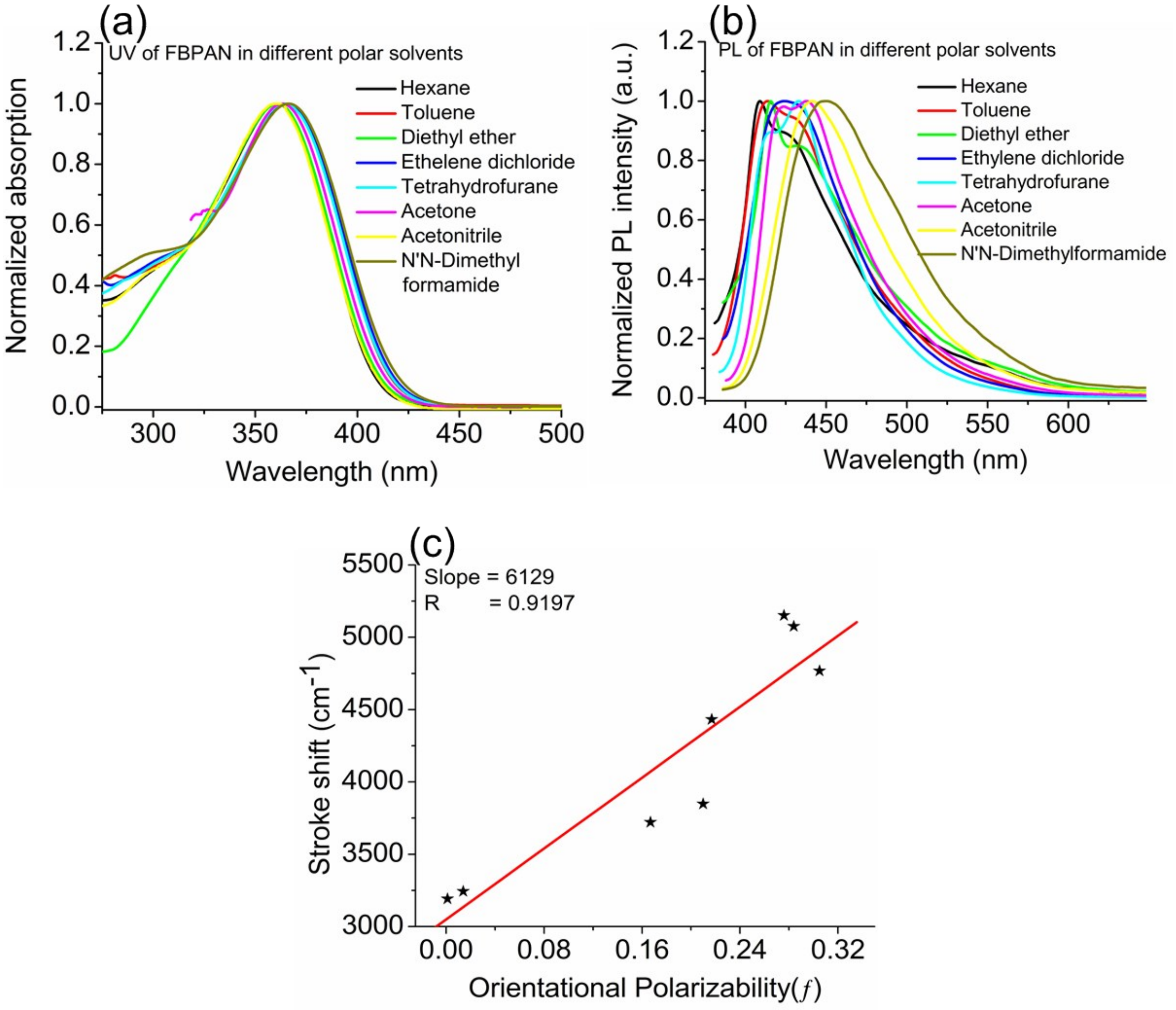


Figure S11 (a) and (b), UV and PL spectra of FBPAN monomer, measured in different solvents with increasing polarity (the orientational polarizability of solvent, *f*, is presented in **Table 2** supporting information); (c) linear correlation of the orientational polarizability (*f*) of different solvents media with the Stokes shift (υ_a - υ_f) for FBPAN.

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

Solvents	ε	n	$f(\varepsilon,n)$	FBPAN		
				λ_a (nm)	λ_f(nm)	Stroke shift (λ_a - λ_f) (cm^{-1})
Hexane	1.9	1.375	0.0012	361	408	3191
Toluene	2.38	1.49	0.014	365	414	3243
Diethyl ether	4.34	1.35	0.167	361	417	3720
Methylene chloride	8.93	1.42	0.217	366	426	3848
Tetrahydrofurane	7.58	1.40	0.210	364	434	4431
Acetone	20.7	1.35	0.284	363	439	4767
Acetonitrile	37.5	1.34	0.305	361	442	5076
N'N-Dimethyl formamide	37	1.427	0.276	368	452	5150

Where, ε and n are the solvent dielectric and the solvent refractive index, respectively; f is the orientational polarizability of the solvent; λ_a and λ_f absorption maximum and emission maximum respectively.

Thermal properties:

Thermal properties of these copolymers were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen flow at a heating rate of 10 ˚C min^{-1}. The TGA curves of the copolymers are presented in **Fig. S12 (a)**. All the copolymers exhibited a very good thermal stability with onset decomposition temperature (Td, corresponding to 5% weight loss) of 304-390 ˚C. This high thermal stability is essential for their application in OLEDs fabrication and DSC analysis demonstrating the high morphological stability of their amorphous phase in a spun thin film presented in **Fig. S12 (b)** .

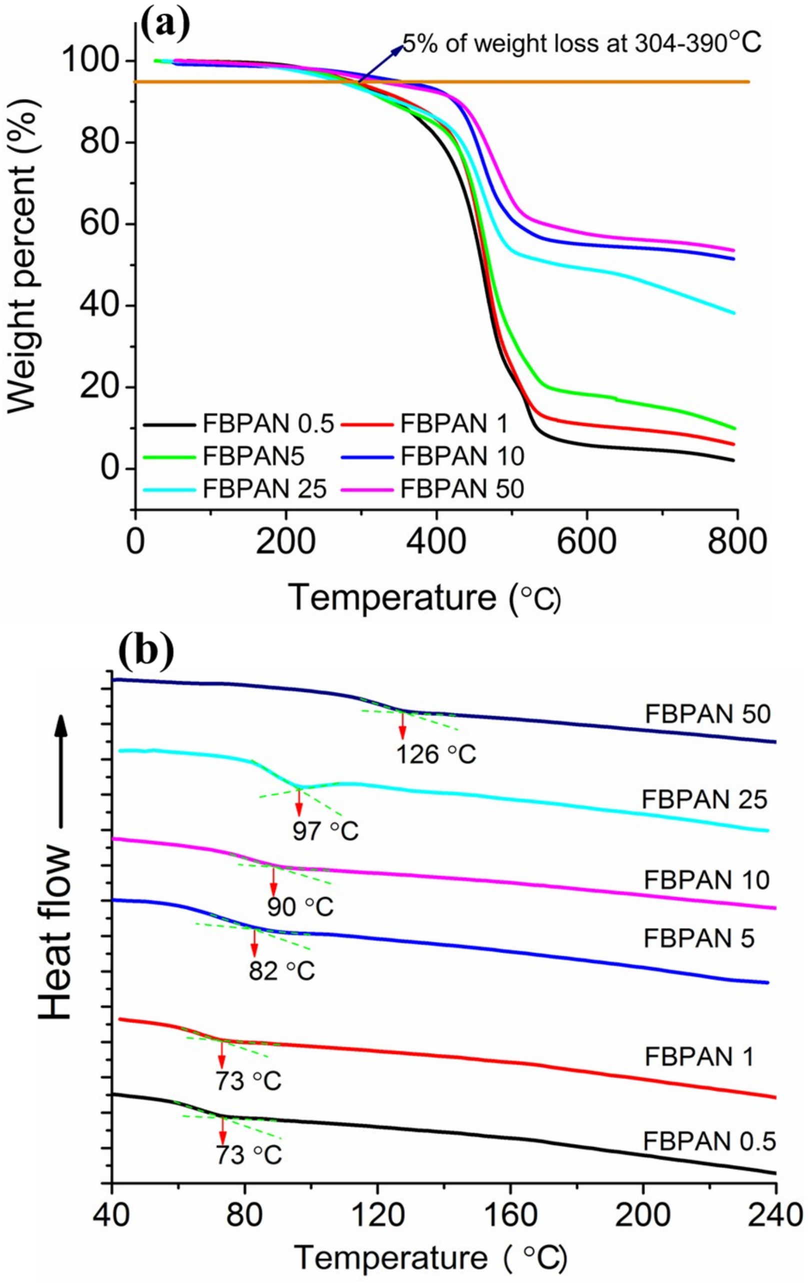


Figure S12 (a) TGA curves of copolymers; (b) DSC spectra of copolymers

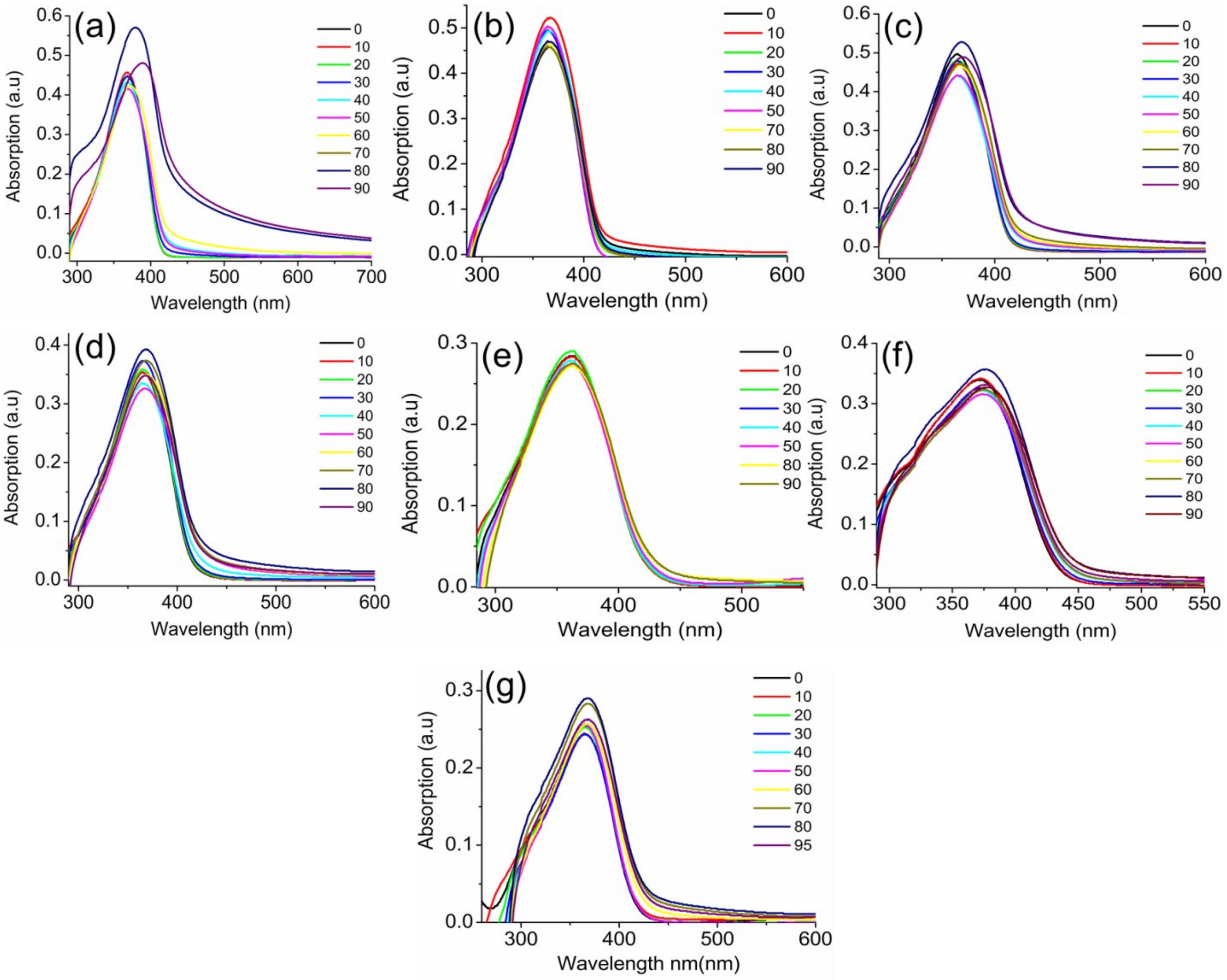


Figure S13 Absorption spectrum of (a) FBPAN 0.5, (b) FBPAN 1, (c) FBPAN 5, (d) FBPAN 10, (e) FBPAN 25 and (f) FBPAN 50, (g) FBPAN in different composition of water-THF mixtures.

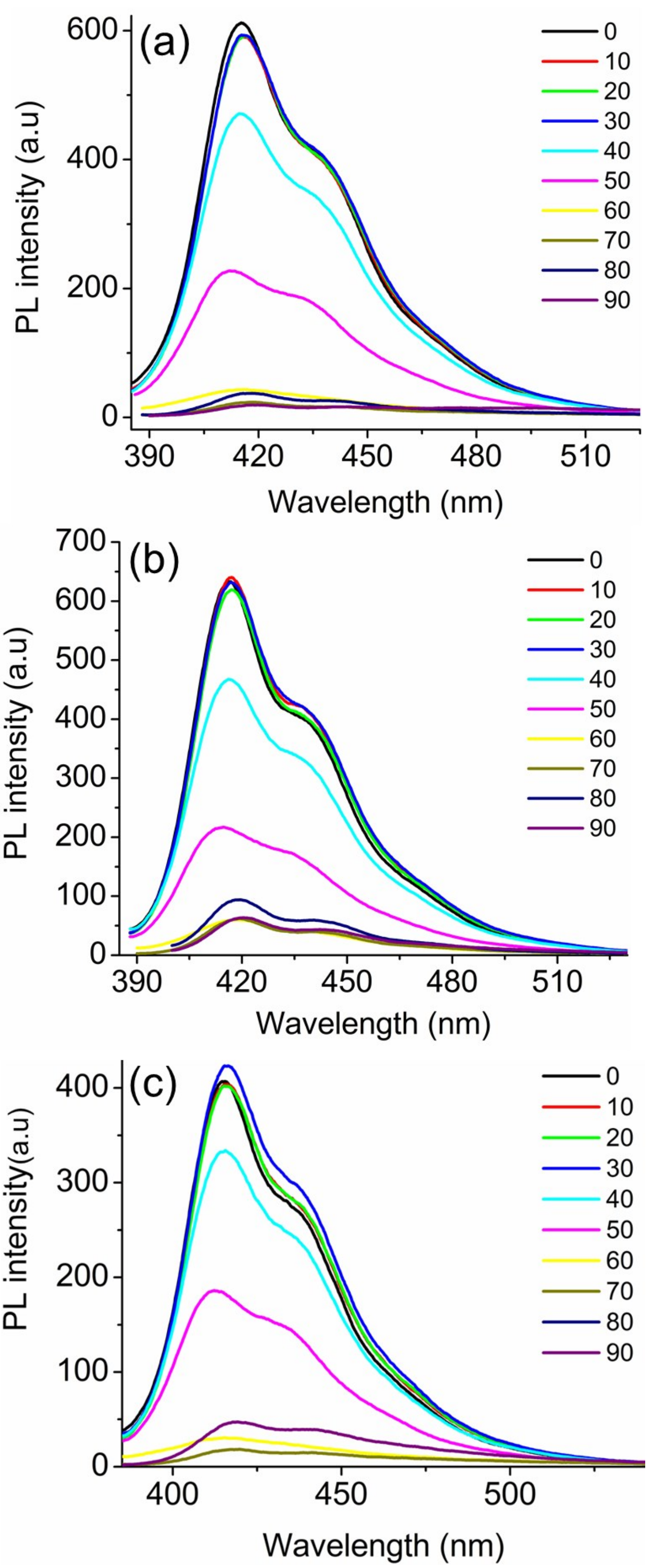


Figure S14 (a), (b), (c) PL spectra of FBPAN 1, FBPAN 5, FBPAN 10 in THF and water mixtures with different water fractions (f_w).

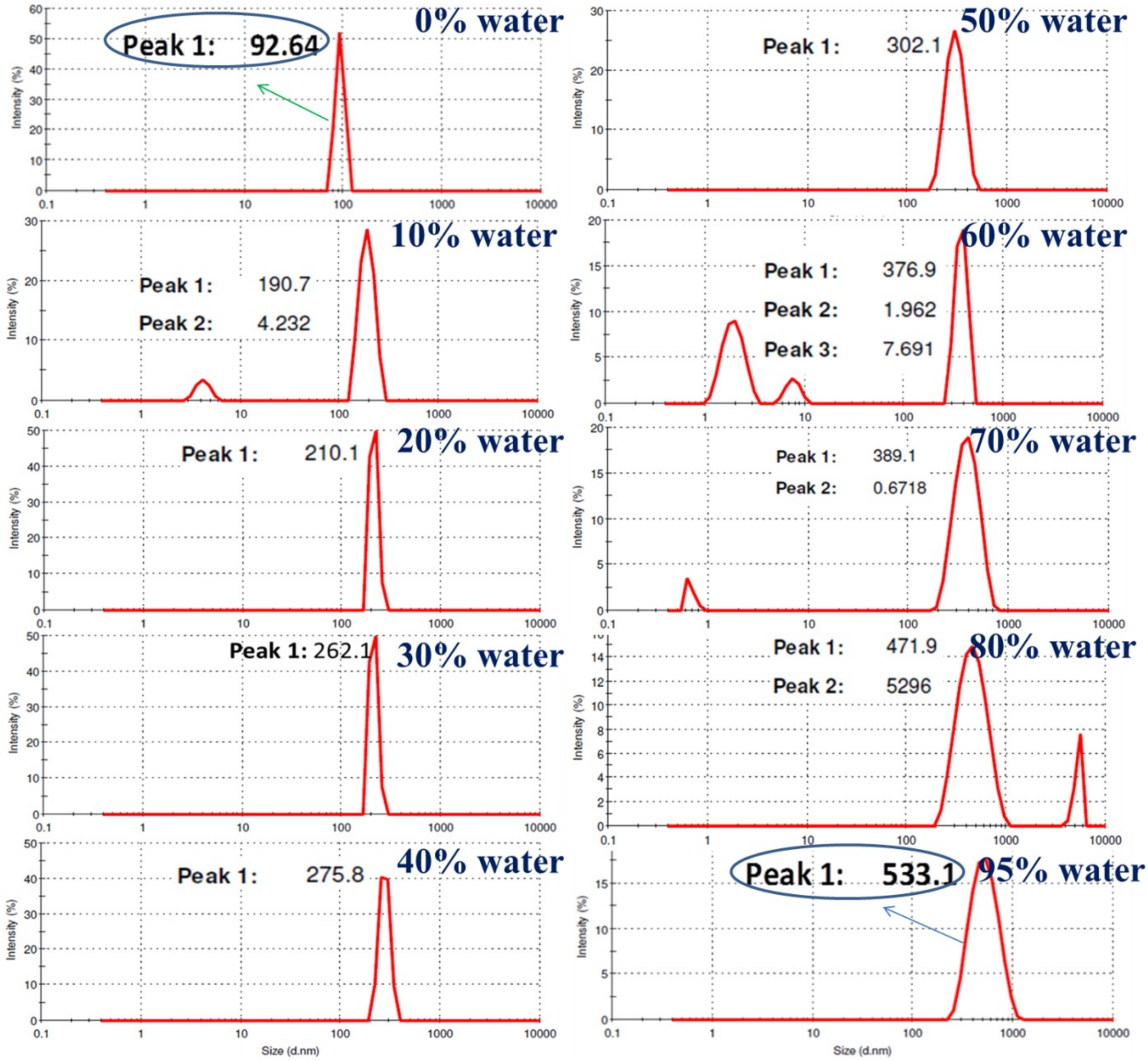


Figure S15 DLS traces of monomer FBPAN in different THF-water mixtures with different water fraction.

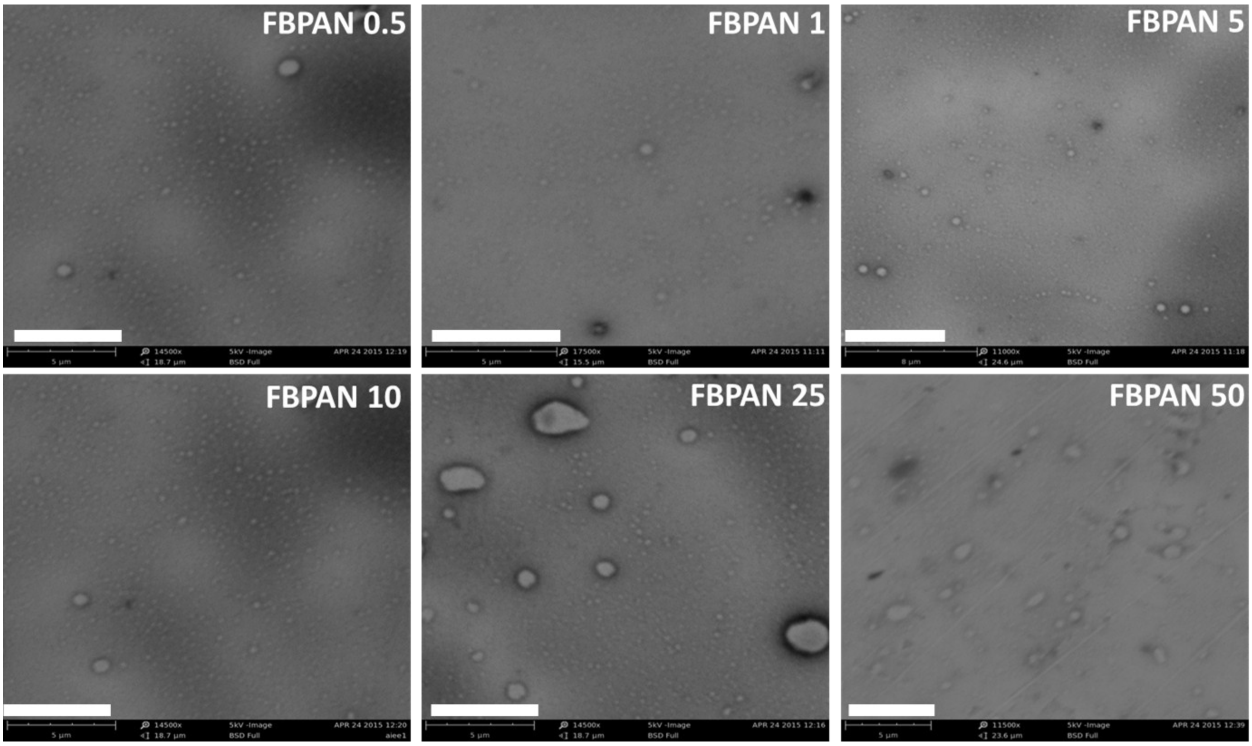


Figure S16 Scaning electron micrograph (SEM) image of FBPAN copolymers with 5μm scale bars.

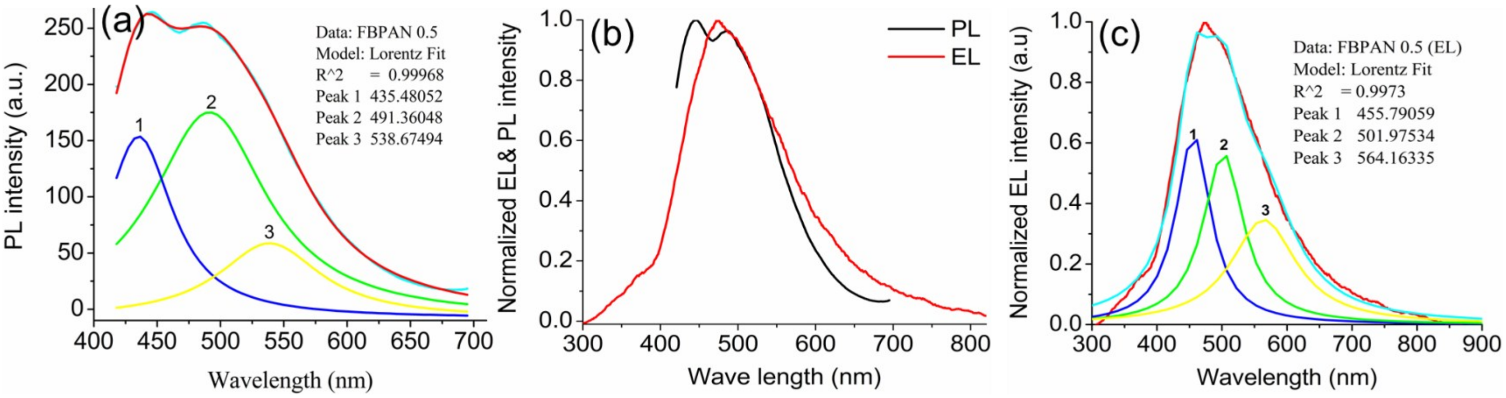


Figure S 17 (a) PL Deconvolution spectra of white liht emitting copolymer FBPAN 0.5; (b) (a) PL and EL spectra of FBPAN 0.5; (c) EL Deconvolution spectra of white liht emitting copolymer FBPAN 0.5

Table S3. Device characteristics of FBPAN monomer and copolymers.

Polymer	*HOMO [a] (eV)*	*LUMO [b] (eV)*	*E^{ele}/E^{opt} [c] (eV)*	*[d] η_c^{max} (cd/A)*	*[e] η_p^{max} (Lm/W)*	*[f]L^{max} (cd/m^2)*	*Turn-on Voltage (V)*	*[g]CIE^{EL}*	*[h] CIE^{PL}*
FBPAN 0.5	-5.99	-3.42	2.57/2.79	7.8	5.9	13455	1.4	0.32, 0.31	0.30, 0.31
FBPAN 1	-5.93	-3.39.	2.54/2.77	6.01	5.03	6324	1.4	0.34, 0.37	0.23, 0.27
FBPAN 5	-5.91	-3.48	2.43/2.45	8.17	6.79	8574	2.9	0.33, 0.39	031, 0.36
FBPAN 10	-5.86	-3.49	2.37/2.38	5.58	4.97	7865	1.5	0.35, 0.38	0.35, 0.36
FBPAN 25	-5.87	-3.50.	2.37/2.35	6.88	5.33	10432	1.6	0.37, 0.41	0.39, 0.38
FBPAN 50	-5.77	-3.45	2.32/2.34	9.12	8.33	17342	1.7	0.43, 0.45	0.39, 0.41
FBPAN	-5.81	-3.42	2.39/2.31	12.43	7.99	16673	1.4	0.37, 0.39	0.37, 0.40

[a]Highest Occupied Molecular Orbital.[b]Lowest Unoccupied Molecular Orbital. [c]E^{ele}/E^{opt}, Electrochemical band gap/Optical band gap. [d]η_c^{max}, Luminous efficiency. [e]η_p^{max}, Power efficiency. [f]L^{max}, Maximum luminance. [g]CIE coordinates for EL. [h]CIE coordinates for PL.

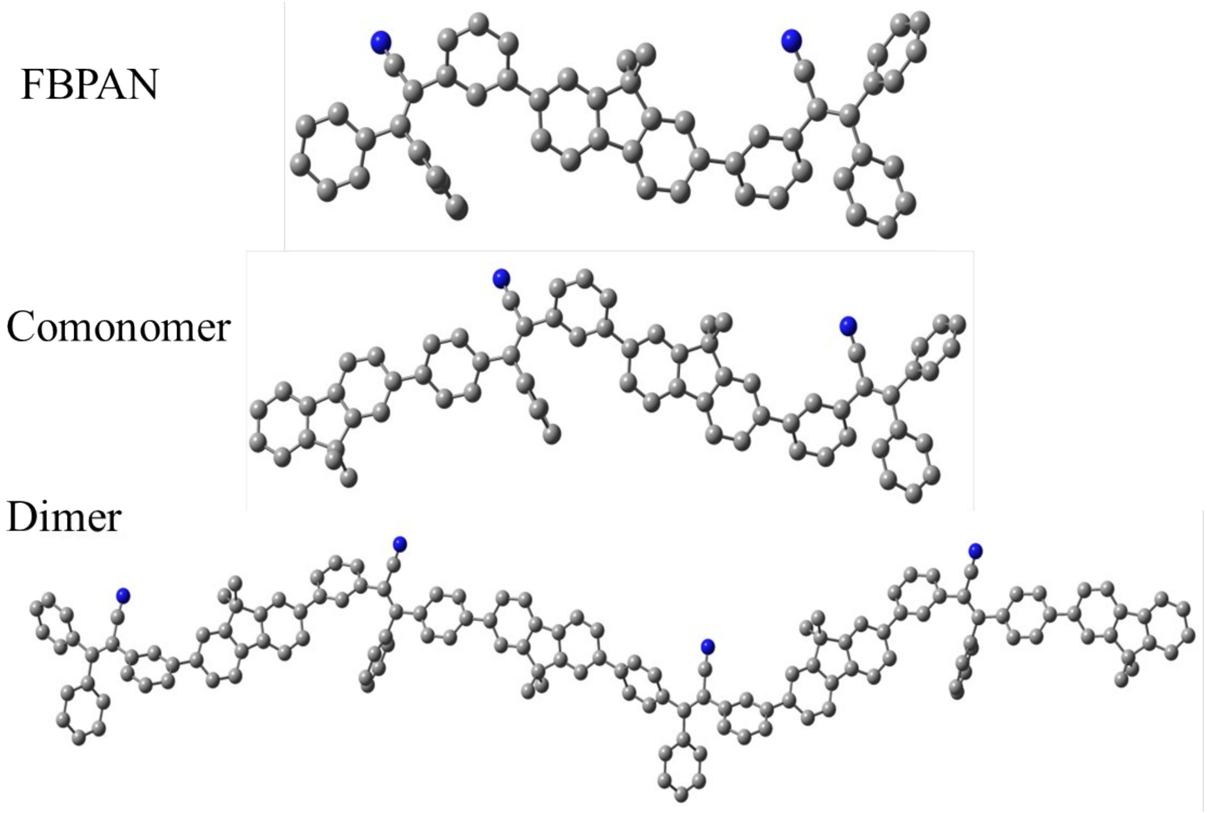


Figure 18 Optimized geometry of the model system at B3LYP/6-31G* level of theory.

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.[S5-S7] 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 modeled as methyl group due to computation limitation. On basis of gas phase optimized ground geometry, the absorption spectra in tetra hydro furan (THF) were calculated by time dependant density functional theory (TD-DFT) method with Polarizable Continuum Model (PCM) at B3LYP 6-31G* level. The SWizard program has been employed to evaluate the contribution of singly excited state configurations to each electronic transition.[S8] The reorganization energies for electrons (λ_e) and holes (λ_h) of model oligomer were computed using Gaussian 09 program along with B3LYP/6-31G* levels of theory.

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