__Supplementary information__

__For__

Offsetting the problem of charge trapping in white polymer light emitting diodes using a fluorenone based luminogen

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Materials and Methods

2,5-Dibromo-9,9-dihexylfluorene, 9,9-Dihexylfluorene-2,7-diboronic acidbis(1,3-propanediol)ester, tetrabotylammonium hexafluorophosphate and Tetrakistriphenylphosphinepalladium(0) were purchased from Sigma Aldrich chemical company and used for synthesis of polymers as obtained without further purification. The structural integrity of the FF-Br monomer and copolymers were confirmed by ^{1}H and ^{13}C NMR spectroscopic studies performed using JEOL ECA 500 MHz NMR spectrometer. $CDCl_3$ was used as solvent for NMR spectroscopic studies with Tetramethylsilane (TMS) as internal standard. MALDI mass spectra was recorded on Bruker Ultraflextreme MALDI mass spectrometerby using 4-HCCA (α-hydroxycinnamic acid) matrix. Elemental analyses were carried out using Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer. Cyclic voltammetry (CV) experiments were done using CH instruments, CHI 600D electrochemical work station with platinum disc electrode as the working electrode, Ag/AgCl electrode as reference electrode and Platinum wire electrode as counter electrode. All CV experiments were done using a degassed acetonitrile as solvent and Tetrabutylammonium hexafluorophosphate as support electrolyte.

Procedure for Synthesis of Monomer and copolymers

Synthesis of 2,7-bis(7,7'-dibromo-9H-fluoren-9-one-2-yl)-9,9-dihexyl-9H-fluorene (FF-Br$_2$)
About 1g (1.4 mmol, 1eq.) of 2,7-bis(9H-fluoren-9-one-2-yl)-9,9-dihexyl-9H-fluorene (FF) synthesized according to previously reported method [1S] was dissolved in chloroform in room temperature. To the above solution, 0.5781g (3.0 mmol, 2.1 eq.) of Bromine was added followed by catalytic amount 0.0586g (0.36 mmoles, 0.25 eq.) of $FeCl_3$ and the solution was stirred for 72 hours under dark environment. After the reaction time the mixture was treated with potassium

iodide solution and washed with 5% sodium thiosulphate solution to remove excess bromine. The resulting organic layer was separated and concentrated in a rotary evaporator to obtain the crude product as yellow amorphous solid (Scheme S1). The crude product was purified by column chromatography using hexane/ethyl acetate (v/v 1:1). The pure product was isolated as bright yellow powder and typically with slight difference in fluorescence color due to bromination (Yield 82.5%). ^{1}H NMR (CDCl$_3$, 500 MHz, δ, ppm): 0.86 (m, 6H), 1.13 (m, 4H), 1.92 (m, 12H), 2.05 (m, 4H), 7.34 (m, 2H), 7.64 (m, 12H), 7.84 (m, 2H) and 8.22 (d, 2H). ^{13}C NMR (CDCl$_3$, 500 MHz, δ, ppm): 14.01, 22.50, 22.71, 29.74, 31.05, 40.55, 55.59, 120.30, 120.78, 121.12, 123.04, 124.67, 125.71, 129.08, 133.25, 134.48, 134.87, 138.86, 140.51, 142.67, 143.06, 144.36, 151.98 and 193.89 ESI mass m/z: Calculated for C$_{51}$H$_{44}$Br$_2$O$_2$, 848.70, found, 848.98. Elemental analysis, calculated (%) for C$_{51}$H$_{44}$Br$_2$O$_2$: C, 72.17; H, 5.23. Found (%): C, 72.19; H, 5.28. The ^{1}H NMR spectrum of FF-Br$_2$ is presented in Figure S1. MALDI mass spectrum of FF-Br$_2$ is presented in Figure S2.
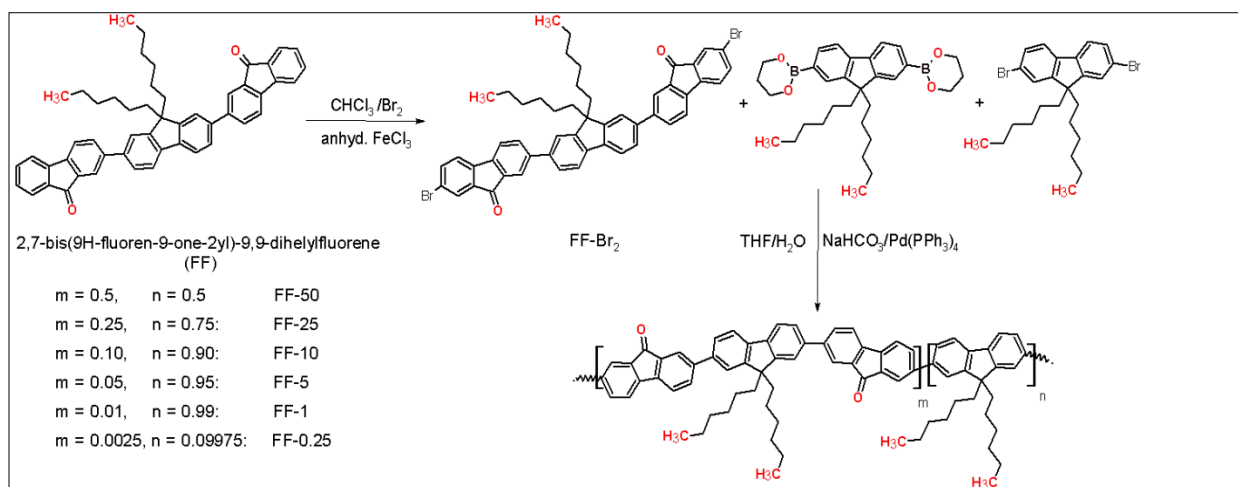
Scheme S1. Synthetic strategy for monomer and copolymers of FF with name designations for copolymers.
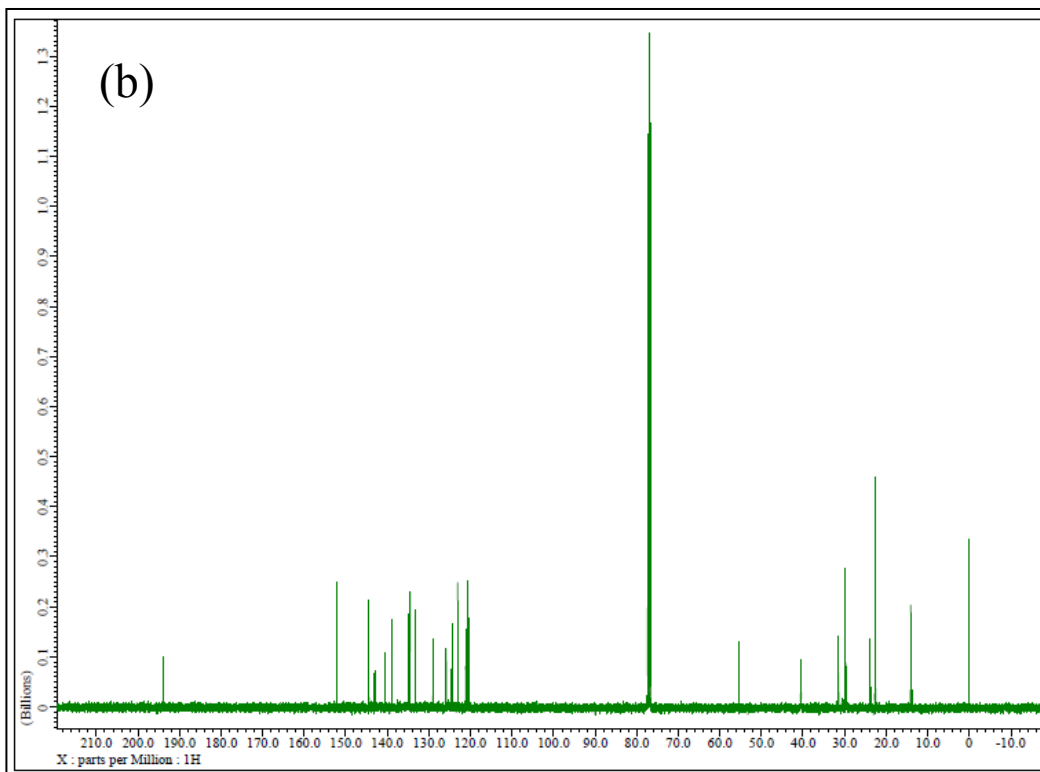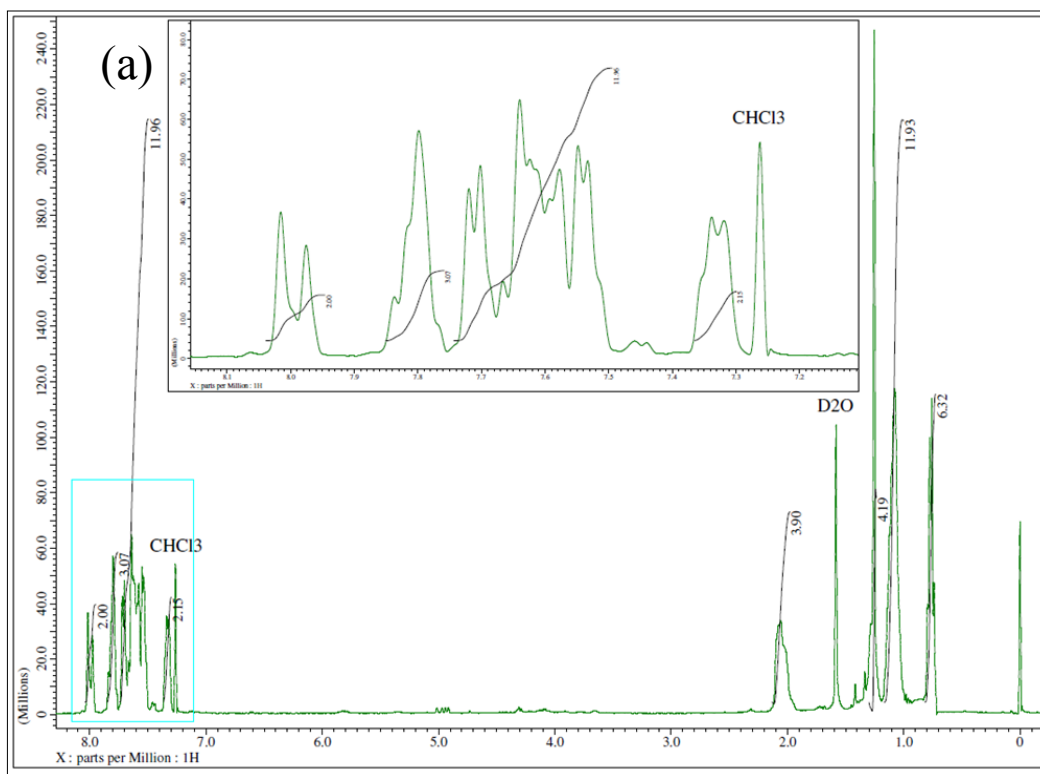
Figure S1 (a) ^{1}H and (b) ^{13}C NMR spectrum of FF-Br$_2$, inset showing the expanded region marked in blue rectangular region.
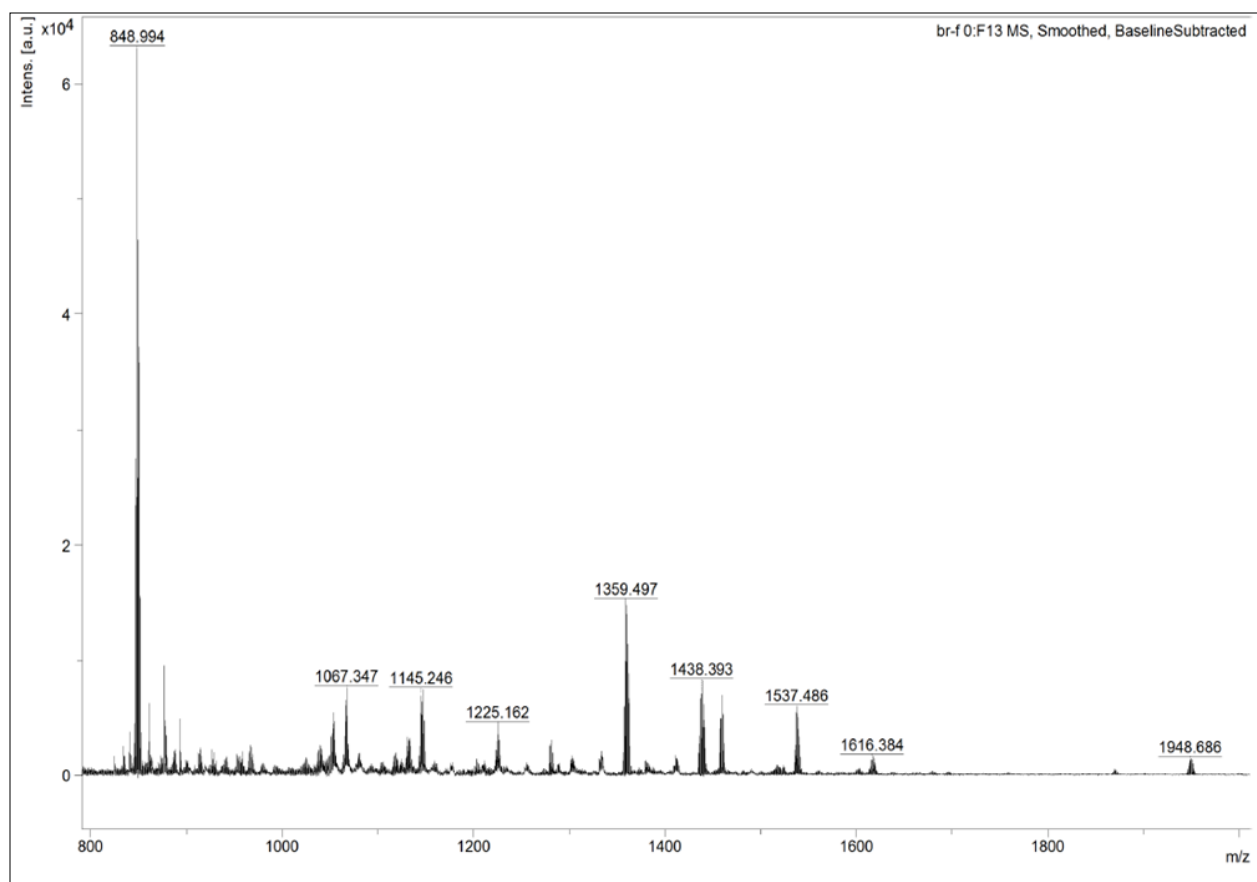
Figure S2. MALDI mass spectrum of FF-Br$_2$

Synthesis of copolymers of 2,7-bis(7,7'-dibromo-9H-fluoren-9-one-2-yl)-9,9-dihexyl-9H-fluorene (FF-n).

The polymers were synthesized by Suzuki polycondensation reaction by varying the feed ratio of the monomer and comonomers as shown in **Table S1**. In a representative synthetic procedure, 300.0 mg (0.353 mmol, 0.5 eq.) of FF-Br$_2$ was dissolved in 70 ml of THF along with 394.0 mg (0.706 mmoles, 1.0 eq) of 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 173. 7 mg (0.353 mmol, 0.5 eq.) of 9,9-Dihexyl-2,7- dibromofluorene. To the above solution of reactants, 28ml of 1% sodium bicarbonate solution was added and the resulting biphasic mixture was degassed to remove air from the reaction setup. The temperature of the above mixture was raised to 50 ˚C under nitrogen atmosphere and Tetrakistriphenylphosphinepalladium(0) was added in catalytic amount. The above mixture was refluxed under nitrogen atmosphere with constant stirring for 72 hours. After the reaction time the reaction mixture was evaporated under vacuum and redissolved in dichloromethane. The solution of dichloromethane was washed with 3N HCl solution and the organic layer was concentrated under vacuum to get crude polymer (FF-25). The crude polymer was purified by soxhlet extraction acetone/methanol (v/v 1:3) for 5 hours. The resulting pristine polymer (FF-25) was dried under vacuum and weighed. (Yield 86.4%). ^{1}H NMR (CDCl$_3$, 500MHz, δ, ppm): 8.22-6.95 (m, 9H), 2.24-1.90 (m, 4H) and 0.66-1.37 (m, 9H). Elemental analysis, calculated (%): C, 89.78; H, 8.31.Found (%):C, 88.92; H, 8.46. **FF-10**: ^{1}H NMR (CDCl$_3$, 500MHz, δ, ppm): 8.09-7.10 (m, 18H), 2.20-1.61 (m, 10H) and 1.37-0.27 (m, 55H). Elemental analysis, calculated (%): C, 90.09; H, 9.03.Found (%): C, 91.66; H, 8.59.

FF-5: ^{1}H NMR (CDCl$_3$, 500MHz, δ, ppm): 8.16-7.20 (m, 33H), 2.18-1.78 (m, 20H) and 1.31-0.29 (m, 110H). Elemental analysis, calculated (%): C, 90.22; H, 9.31.Found (%): C, 90.77; H, 9.98.

Table S1. Feed ratio, composition and GPC data of copolymers

Polymer	Feed ratio [a]			M_w/M_n/PDI [b]
	FF	A	M	
FF-0.25	0.0025	0.50	0.4975	8401/16910
FF-1	0.01	0.50	0.49	9238/27876
FF-5	0.05	0.50	0.45	10783/22240
FF-10	0.1	0.50	0.40	7973/16192
FF-25	0.25	0.50	0.25	8563/14371
FF-50	0.50	0.50	0	7232/14360

[a]*FF,* mole fraction of FF; *A,* mole fraction of 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) ester; *M,* 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.

FF-1: ^{1}H NMR (CDCl$_3$, 500MHz, δ, ppm): 8.23-7.27 (m, 3H), 2.49-1.77 (m, 2H) and 1.40-0.27 (m, 11H). Elemental analysis, calculated (%): C, 90.33; H, 9.57.Found (%): C, 91.51; H, 10.11.

FF-0.25[1]H NMR (CDCl$_3$, 500MHz, δ, ppm): 8.24-7.27 (m, 60H), 2.36-1.84 (m, 40H) and 1.37-0.29 (m, 250H). Elemental analysis, calculated (%): C, 90.35; H, 9.62.Found (%):C, 89.69; H, 10.35.

GPC data and feed ratios of the copolymers are presented in **Table S1.**

Table S2. Spectral Properties of copolymers.

Polymer	$\lambda_{abs}{}^{sol}(\varepsilon)$ [a]	[b]$\lambda_{emi}{}^{sol}$ (nm)	[c]$\lambda_{abs}{}^{TF}$ (nm)	[d]$\lambda_{emi}{}^{TF}$ (nm)	[e]$\Phi_{PL}{}^{Sol}$	[f]$\Phi_{PL}{}^{TF}$
FF- 0.25	$377(7.30\times10^6)$	416,440,465	384,216	440, 550	39.5	64.0
FF-1	$381(1.02\times10^7)$	418,437,468	390, 219	436, 545	43.5	72.8
FF-5	$468(1.86\times10^5),374(6.95\times10^6)$	417,434,468	458,382,314,216	555	32.3	74.7
FF-10	$450(2.17\times10^5),368(2.76\times10^6)$	416,435,466	458,380,217	555	33.6	75.8
FF-25	$441(4.17\times10^5),350(4.84\times10^6),$ $309(4.28\times10^6)$	410,432,465,588	451,358,314,220	556	20.2	62.6
FF- 50	$350(7.53\times10^6),308(7.60\times10^6),$ $438(1.25\times10^6)$	427,570	458,355,309,257,228	555	20.1	76.2
PFH	$370(1.72\times10^6)$	469, 438, 415	384, 215	442	60.5	35.4

[a]$\lambda_{abs}{}^{sol}$, Absorption maxima in THF solution in nm; ε, extinction coefficient in dL g^{-1} cm^{-1}. [b]$\lambda_{emi}{}^{sol}$, Emission maxima inTHF solution in nm. [c]$\lambda_{abs}{}^{TF}$, Absorption maxima in spun thin film. [d]$\lambda_{emi}{}^{TF}$, Emission maxima in spun thin film. [e]$\Phi_{PL}{}^{Sol}$, Quantum yield in THF solution relative to qunine sulfate in %. [f]$\Phi_{PL}{}^{TF}$, Absolute quantum yield in spun thin film in %.

Table S3. Device characteristics of Copolymers and FF.

Polymer	HOMO (eV) [a]	LUMO (eV) [b]	E^{ele} (eV) [c]	E^{opt} (eV)[d]	μ [e] (cm^2 V^{-1} s^{-1})	[f]$\eta_c{}^{max}$ (cd/m^2)	[g]$\eta_p{}^{max}$ (Lm/W)	[h]L^{max} (cd/m^2)	[i]CIE^{EL}	[j]CIE^{PL}	[k] V_{on}/V_{max} /V_{obs}	[l] EQE (%)
FF	-5.72	-3.60	2.12	2.24	1.28×10^{-6}	12.31	7.82	26551	0.46,0.52	0.46,0.51	3.5/14.0 /12	6.25
FF-0.25	-6.1653	-4.1671	1.9982	2.1364	1.26×10^{-6}	5.17	4.12	9106	0.30, 0.31	0.35, 0.29	4.1/10.5 /8.0	3.10
FF-1	-6.0800	-4.1490	1.9310	2.0981	1.59×10^{-6}	6.24	5.44	9570	0.31, 0.36	0.34, 0.46	4.1/11.0 /18.0	3.61
FF-5	-6.1000	-4.1890	1.9110	1.9771	1.43×10^{-6}	4.38	3.97	10219	0.33, 0.38	0.33, 0.48	4.0/10.0 /8.0	3.58
FF-10	-6.0582	-4.1786	1.8796	1.9562	1.44×10^{-6}	5.17	4.72	11618	0.30, 0.36	0.30, 0.36	4.0/11.3/ 8.0	3.55
FF-25	-5.8037	-4.1198	1.6839	1.7124	1.76×10^{-6}	4.61	4.16	11843	0.38, 0.44	0.38, 0.43	4.0/11.4 /8.0	3.41
FF-50	-5.7947	-4.1288	1.6659	1.6983	1.97×10^{-6}	6.31	5.77	10976	0.38, 0.45	0.38, 0.45	4.1/12.0 /8.0	4.21
PFH-FF	-	-	-	-	8.9×10^{-6}	4.12	3.01	9002	0.30, 0.34	0.38, 0.42	4.0/11.4 /8.0	2.14
PFH	-5.5036	-2.3741	3.1295	3.1316	6.2×10^{-7}	1.24	3.10	1604	0.23, 0.19	0.22, 0.17	4.3/11.3 /8.0	1.24

[a] Highest Occupied Molecular Orbital. [b] Lowest Unoccupied Molecular Orbital. [c] E^{ele}, Electrochemical band gap. [d] E^{opt}, Optical band gap. [e] μ, Charge carrier mobility determined by Space Charge Limited Current (SCLC) method. [f] $\eta_c{}^{max}$, Luminous efficiency. [g] $\eta_p{}^{max}$, Power efficiency. [h] L^{max}, Maximum brightness. [i] *Commission internationale de l'Eclairage* coordinates for EL. [j] *Commission internationale de l'Eclairage* coordinates for PL. [k] V_{on}, Turn on voltage, V_{max},Voltage at maximum brightness and V_{obs}, Voltage at which $\eta_c{}^{max}$, $\eta_p{}^{ma}$, [h] L^{max} and [i]CIE^{EL} were measured. [l] EQE, External Quantum efficiency observed at brightness of 1000 cd m^{-1}.

Table S4. Quantum yield of copolymers in various THF-water mixtures.[a]

Polymer	FF-50	FF-25	FF-10	FF-5	FF-1	FF-0.25	PFH
Pure THF	20.1	20.2	33.6	32.3	43.5	39.5	60.5
10% H_2O in THF	9.6	1.5	27.5	32.1	43.8	44.1	40.3
20% H_2O in THF	1.2	1.4	45.3	30.9	25.7	36.4	30.1
30% H_2O in THF	1.1	1.4	54.7	21.5	20.1	28.8	29.7
40% H_2O in THF	1.0	1.3	48.6	15.3	12.3	15.1	20.8
50% H_2O in THF	0.9	2.2	15.4	6.9	7.4	6.4	12.3
60% H_2O in THF	12.3	30.6	6.1	3.3	50.3	5.7	9.0
70% H_2O in THF	48.6	54.1	5.8	29.6	41.2	6.0	3.6
80% H_2O in THF	33.8	5.2	20.2	6.21	28.6	29.1	1.5
90% H_2O in THF	2.7	4.7	8.1	5.1	13.6	9.3	0.5

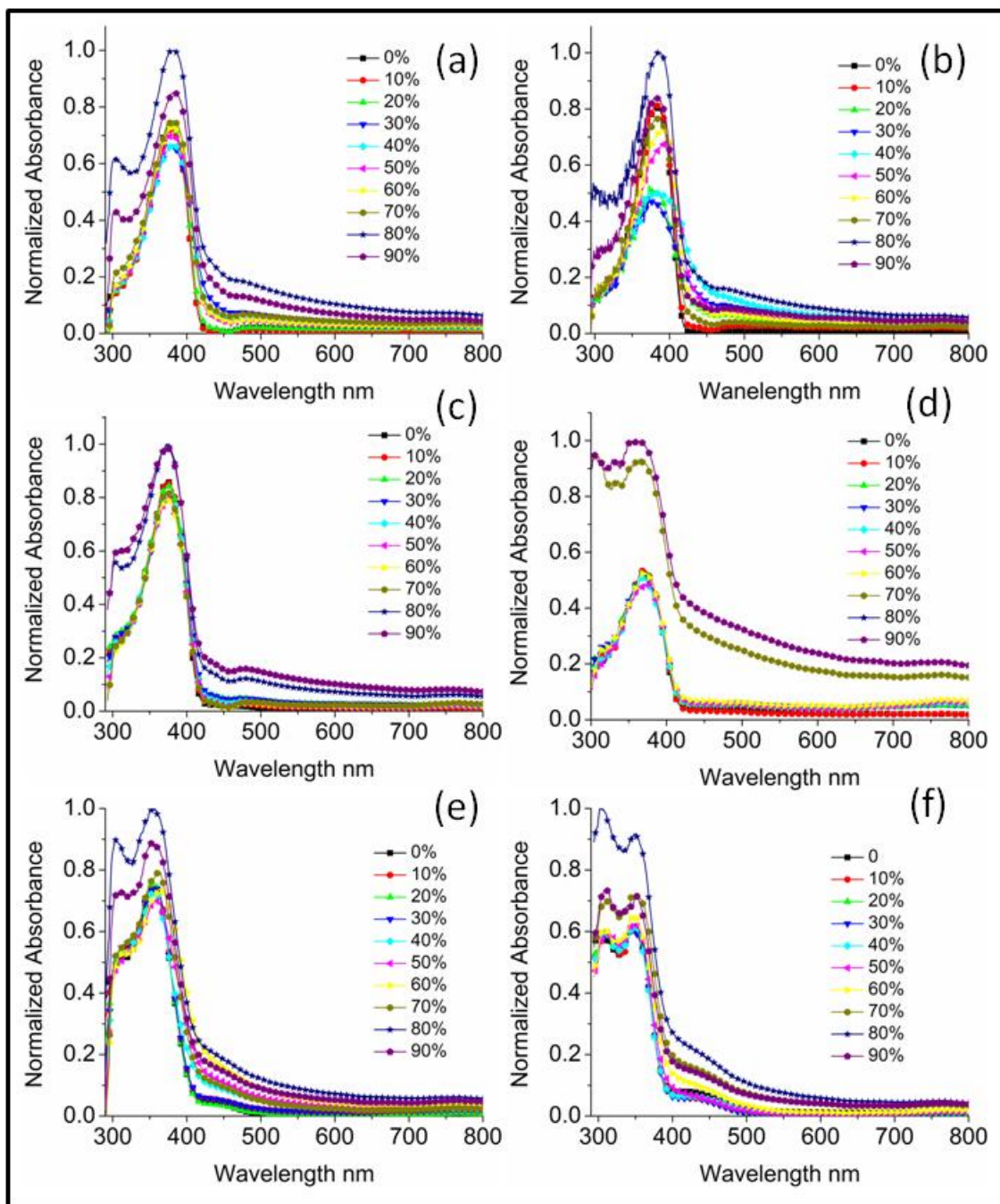[a] Relative quantum yield with respect to qunine sulfate.

Figure S3. Absorption spectrum of (a) FF-0.25, (b) FF-1, (c) FF-5, (d) FF-10, (e) FF-25 and (f) FF-50 in different compositions of water-THF mixtures.
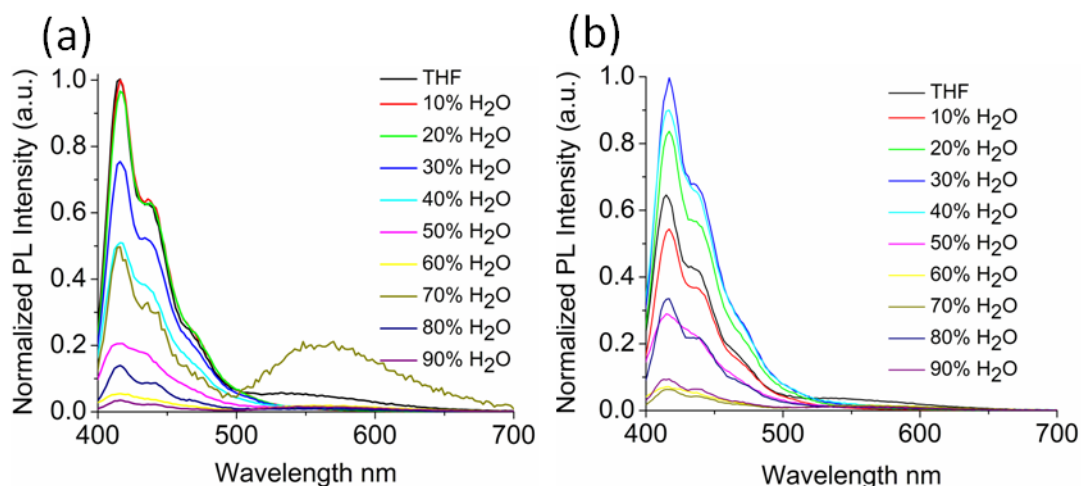
Figure S4 Photoluminescence spectra of (a) FF-5 and (b) FF-10 in different THF-water mixtures
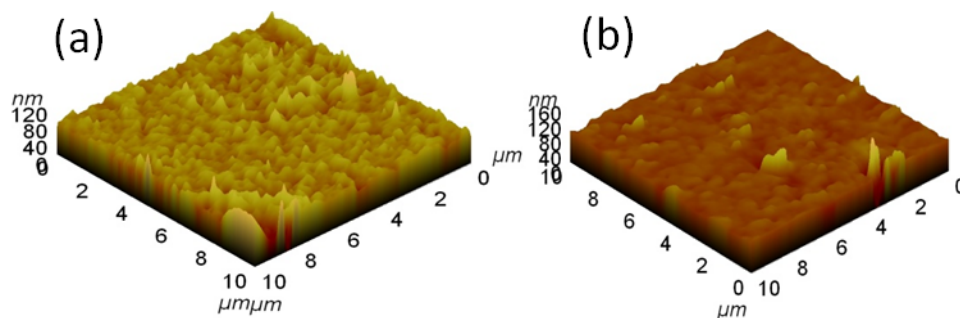

Figure S5 Atomic Force micrograph of (a) FF-50 and (b) FF-25

AIEE Property of copolymers

It is clear from the PL spectra of FF-5 and FF-10 in different THF-water mixtures that the maximum intensity of emission is observed at lower composition of water (Figure S5). The above observation can be attributed to the increased hydrophobic nature of the copolymers due to higher content of 9,9-dihexylfluorene groups. Thus low composition of water in THF lead to quick precipitation of polymers from their solutions.

Computational Details

The ground (S_0) and excited singlet state(S_1) geometries of the polymers were optimized by using density functional theory (DFT) based method with Becke's three-parameter functional and the Lee-Yang-Parr functional (B3LYP)[S1-S2] with 6-31G* basis set. Frequency calculations were also executed at the same level of theory. The optimizations and the vibrational data confirmed that the structures were true minima on the potential energy surface because there were no imaginary frequencies. The solubilizing hexyl groups from fluorene were modeled as methyl group due to computation limitation. On basis of gas phase optimized ground state geometry, the absorption spectral properties 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 progam was used to evaluate the singly excited

state configurations to each electronic transition.[S3] All the calculations were carried out using Gaussian 09 program package.[S4]

DFT-TD-DFT calculations

TD-DFT calculations were also performed to ascertain the orbitals involved in the dominant excited state electronic transitions and their corresponding energies and oscillator strength. The calculated results are presented in Table S5. From the Table S5, have been summarized in Table xxx. From the Table xxx, we can see that, for all the polymers the low energy band constitutes the transition from HOMO→LUMO.

Table S5 Summary of the excited state electronic transitions obtained from the TD-DFT calculations.

Compounds	States	^{a} λ_{abs}^{calc}	^{b} E_g^{calc}	^{c} f	^{d} (%) contribution	^{e} λ_{abs}^{exp}
	S_1	506.21	2.45	0.7487	H→L (68%), H-1→L+1(16%)	
	S_4	445.51	2.78	0.0094	H-1→L+1(64%), H2→L+0(28%)	441
CpFF-7	S_8	390.87	3.17	0.6132	H-3→L+1(59%), H-1→L+3(40%),	
	S_{12}	368.8	3.36	0.1671	H-0-→L+3(45%), H-1→L+2(44%)	350
	S_{15}	349.29	3.55	0.4617	H-1-→L+3(40%), H-2→L+2(30%)	309
	S_1	509.05	2.43	0.4285	H→L (77%), H-2→L (18%)	
	S_5	390.86	3.17	4.9455	H→L+1(73%)	455
FLO-7	S_7	377.3	3.29	0.1908	H-1-→L+1(49%), H-0-→L+2(43%)	
	S_9	353.33	3.51	0.6104	H-1→L+2(50%), H→L+3(23%)	370
	S_{12}	337.8	3.67	0.1540	H-2→L+1(57%)	

^{a} λ_{abs}^{calc} , Calculated absorption using TD-DFT calculations. ^{b} E_g^{calc}, Calculated Band gap, ^{c} f, Oscillator strength. ^{d} H denotes HOMO and L denotes LUMO, ^{e} λ_{abs}^{exp}, Experimental absorption of FF-25 copolymer since it corresponded to the nearest composition, for FLO-7 the values of absorption correspond to that reported for fluorenone cointaining pentamer reported in reference S5.
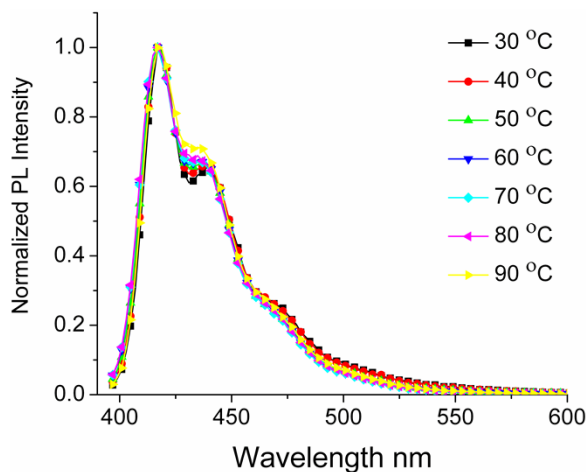

Figure S6 Fluorescence spectra of FF-0.25 in THF at different temperature under ambient conditions

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