Supporting information

For

A Solution ProcessableFluorene-fluorenone Oligomer with Aggregation Induced Emission Enhancement

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Experimental Details

Materials and methods

2-Bromofluorene, sodium dichromate dehydrate, 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) and Malononitrile, Tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma Aldrich and used in synthesis of oligomers as obtained. All reactions except the preparation of 2-bromofluoren-9-one were done under nitrogen atmosphere.

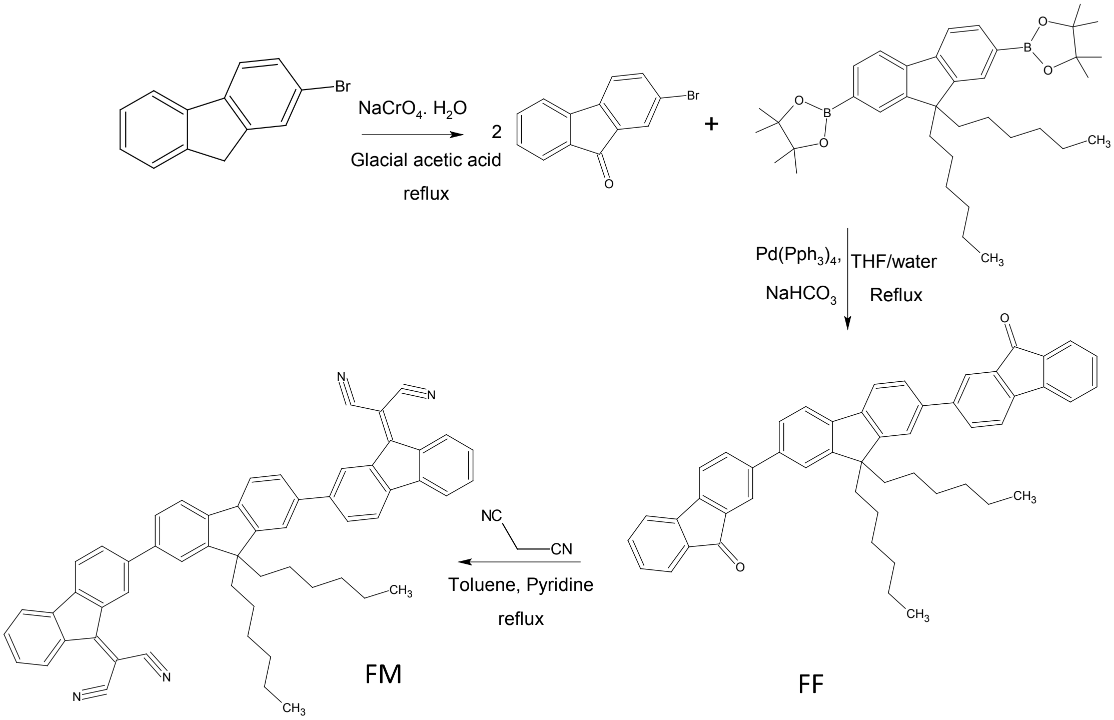
^{1}H spectra were recorded on JEOL ECA 500 MHz NMR spectrometer with tetramethylsilane as standard with respective deuterated solvents for oligomers. MALDI mass spectrometry was recorded on BrukerUltraflextreme MALDI mass spectrometerby using 4-HCCA (α-hydroxycinnamic acid) matrix. Elemental analyses of oligomers were done on Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer. UV-Visible absorption spectra were recorded on Varian Cary 50 Bio UV-Visible spectrophotometer with concentration of oligomers at 9.98x10^{-6} M. Photoluminescence (PL) spectra were measured on Varian Cary eclipse fluorescence spectrophotometer with concentration of 9.98x10-6 M. Cyclicvoltammetry were done on CH instruments, CHI600D electrochemical work station with platinum working electrode by forming a thin film of the polymers on the surface of platinum working electrode, Ag/AgCl electrode as reference and platinum wire as counter electrode. Dynamic light scattering experiments were done on dynamic light scattering instrument from Malvern instruments, UK. Fluorescence life time experiments were done on IBH Fluorescence Lifetime System (Picosecond resolution), while the exponential fitting were done using Horiba JobinYvon decay analysis software. Atomic force micrographs were obtained on Nova 1.0.26 RC1 Atomic force microscope with NT-MDT solver software for analysis, Silicon cantilever (SII) with average frequency of 260-630 kHz with force constant of 28-91 N m^{-1}were used in semi contact mode.

Light emitting diodes (LEDs) were fabricated by coating about 70-100 nm thick layer of Poly(ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) on oxygen plasma treated ITO (Thickness 110 nm and resistance 10Ω/sq) coated glass substrate and baking the coated plates at 200 °C for 1 h. FF was spin coated over PEDOT:PSS layer from chloroform solution of 2mg/ml concentration (thickness of FF film was 100 – 115 nm). Aluminum (100-140nm) was coated over FF film as cathode. I-V characterizations were done on keithley 2400 source meter. L-V characteristics were done on Type PT 168 PMT housing with drawer assembly. The Electroluminescence spectrum of LEDs were recorded on Varian Cary eclipse fluorescence spectrophotometer in chemiluminescence mode.

Absolute fluorescence quantum yield of the polymer thin films were done using FLUOROLOG3 (model FL3-II) fluorescence spectrophotometer from JOBIN YVON-SPEX instruments. S.A.Inc, USA, equipped with integrated sphere. The data treatment for absolute quantum yield measurement was carried out using HORIBA JOBIN YVON quantum yield and color calculator. The relative quantum yields of the polymer in solution state were measured by using quninesulfate standard. GIXRD measurements were done on Bruker AXS D8 Advance X-ray diffractometer by using Cu kα wavelength.

The ground and excited state geometries of the two systems were optimized by using density functional theory (DFT) based method with Becke's three-parameter functional and the Lee–Yang–Parr functional (B3LYP)[1-2] functional 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 and excited state geometries, the absorption and emission 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. All calculations were performed using Gaussian 09 program package[3]

Synthesis of Oligomers.



SCHEME S1 Synthesis of oligomers

Synthesis of 2-Bromofluoren-9-one.

About (0.0191 mol) 2-Bromofluorene was dispersed in 30ml glacial acetic acid and the temperature of was raised to 60°C to dissolve it to get a clear solution. To the above solution 9.7g (0.0325 mol)of $Na_2Cr_2O_7.2H_2O$, dissolved in 40 ml glacial acetic acid was added in one lot and the solution was refluxed for 3 hours. After refluxing the above solution for 3 hours, the solution turned dark green from orange color. The solution was cooled to room temperature and mixed with 400ml of water and the resulting precipitate was washed with plenty of distilled water, filtered and dried in vacuum to get pure 2-Bromofluorenone as bright yellow powder. Yield 93%.

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

2.16g (0.0083 mole) of 2-Bromofluoren-9-one and 2g (0.0039 mole) 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) ester were dissolved in 61ml of THF. To the above solution, 1% $NaHCO_3$in water was added and the mixture was purged with nitrogen. After raising the temperature to 75 °C, Tetrakis(triphenylphosphine)palladium(0) was added and again nitrogen was purged. The above reaction mixture was refluxed for 48 h. After 48 h the mixture was filtered after cooling to get 2,7-bis(9H-fluoren-9-one-2-yl)-9,9-dihexyl-9H-fluorene (FF) as bright yellow precipitate. The product was purified by column chromatography using hexanes/ethylacetate (2:3 – 0:1 v/v) as eluent. The oligomer FF was obtained as yellow poweder (4.6g, Yield 60%). ^1H NMR ($CDCl_3$, 500MHz, δ, ppm): 0.69 – 1.45 (m, 22H), 2.1 (m, 4H) 7.30-7.86 (m,18H) and 8.0 (m, 2H). MALDI mass m/z:Calculated for $C_{51}H_{46}O_2$,690.91; found, 691.63. Elemental analysis: Calculated (%)for $C_{51}H_{46}O_2$: C, 88.66; H, 6.71. found: C, 88.67; H, 6.75.

Synthesis of 2,7-bis((9H-fluoren-9-ylidene(malanonitrile)-2-yl)-9,9-dihexylfluorene (FM).

About 1g (1.2 mmol) of FF was dissolved in 50ml toluene along with 190 mg (2.88 mmol) of malononitrile and 569 mg (7.2 mmol) of pyridine. The above reaction mixture was refluxed for 5 h after which the color of the solution turned from yellow to wine red. After cooling, the mixture was washed with distilled water and solvent was evaporated in vacuum. The product was purified by washing with ethanol to remove excess pyridine and malononitrile to get 2,7-bis((9H-fluoren-9-ylidene(malanonitrile)-2-yl)-9,9-dihexylfluorene (FM) as brown powder (1.1g, yield 97%). ^1H NMR ($CDCl_3$, 500MHz, δ, ppm): 0.72 (t, 6H), 0.85-1.31 (m, 16H), 2.10 (m, 4H), 7.35-8.00 (m,16H), 8.37 (m, 2H) and 8.73 (m, 2H). MALDI mass m/z: Calculated for $C_{57}H_{46}N_4$, 787.00; found, 786.74. Elemental analysis: Calculated (%) for $C_{57}H_{46}N_4$: C, 86.99; H, 5.89; N, 7.12. found: C, 87.02; H, 6.79; N, 7.14.

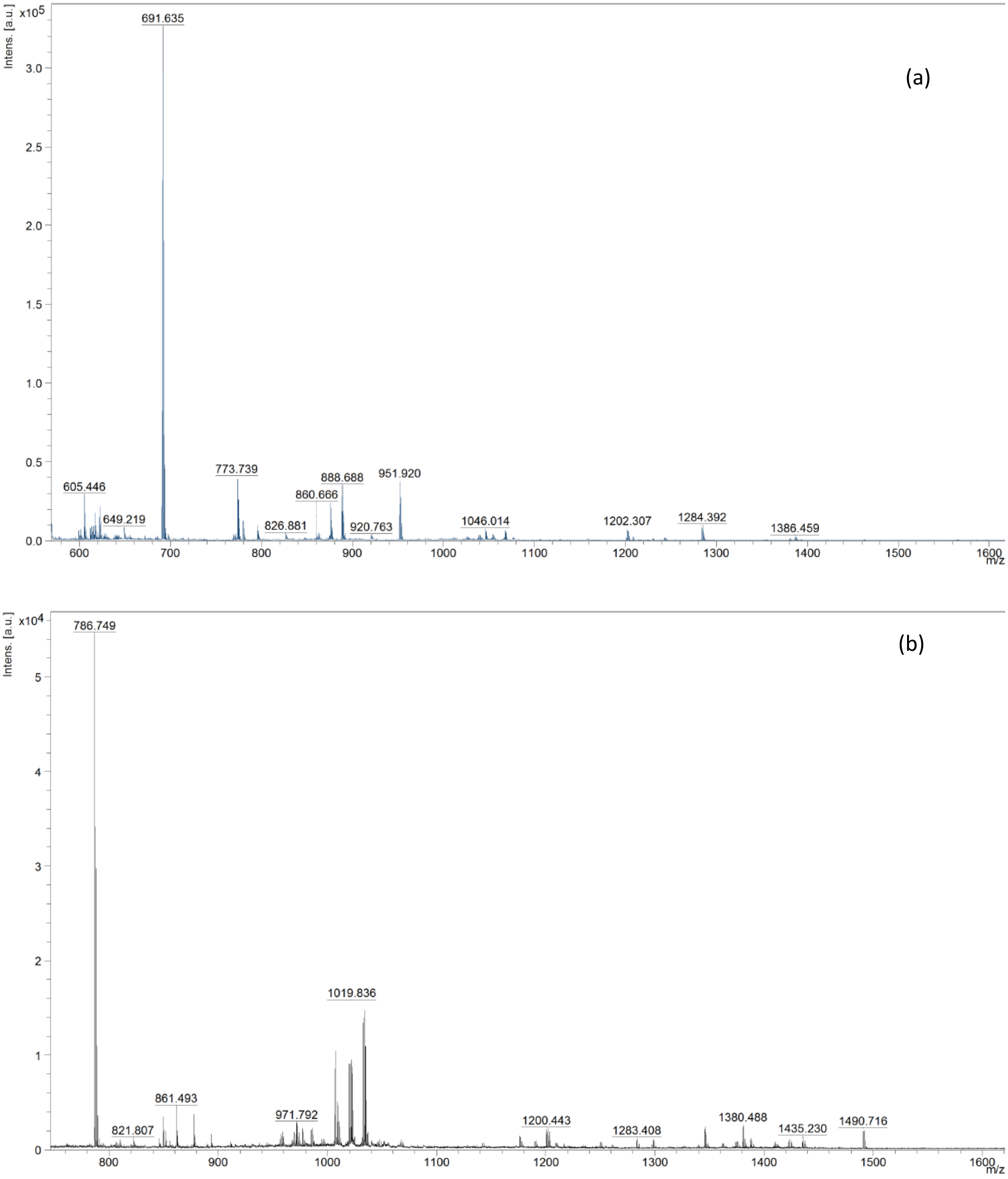


Figure 1S. MALDI mass spectrometry of (a) FF and (b) FM

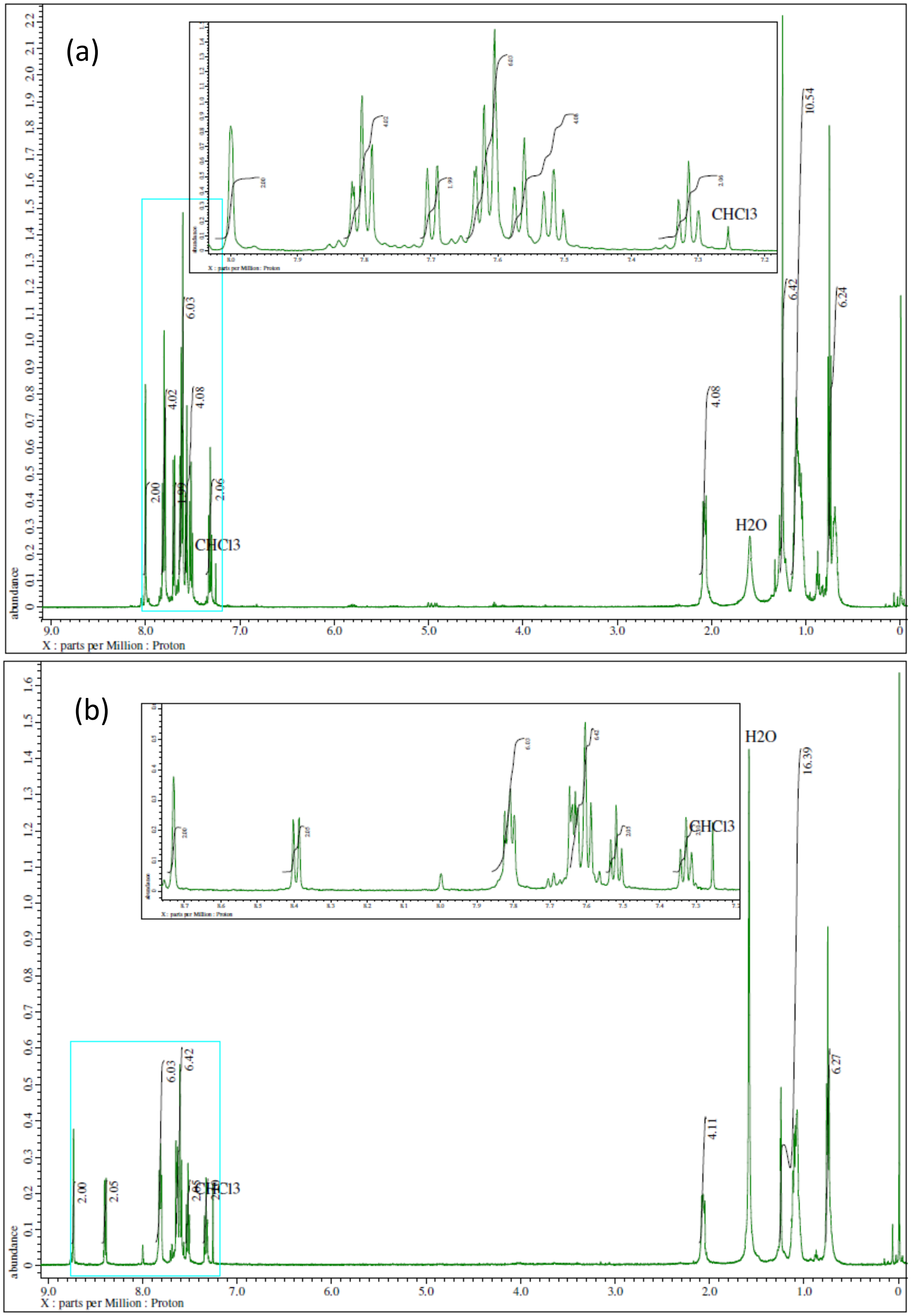


Figure 2S. ^{1}H NMR spectra of (a) FF and (b) FM (inset, expansion of aromatic region)

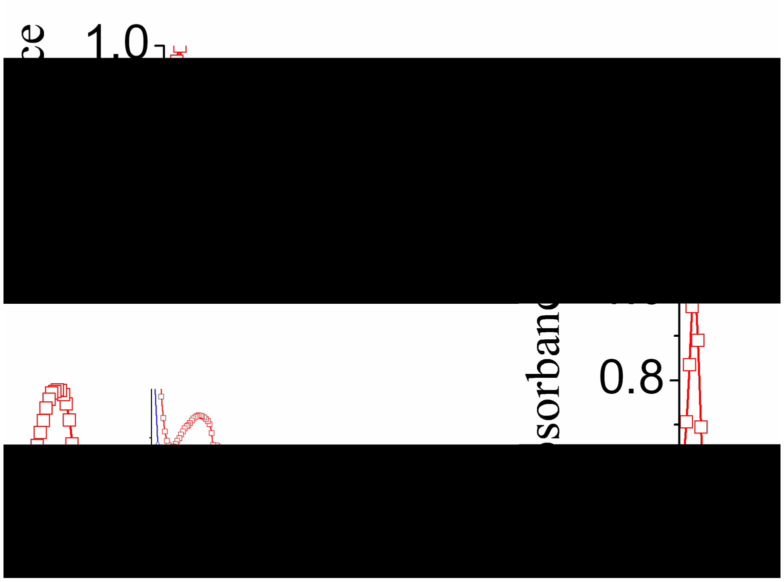


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Figure 3S. Absorbance spectrum of FF (red, squares) and FM (blue, triangle) in chloroform, Inset showing zoomed CT band of FF and FM

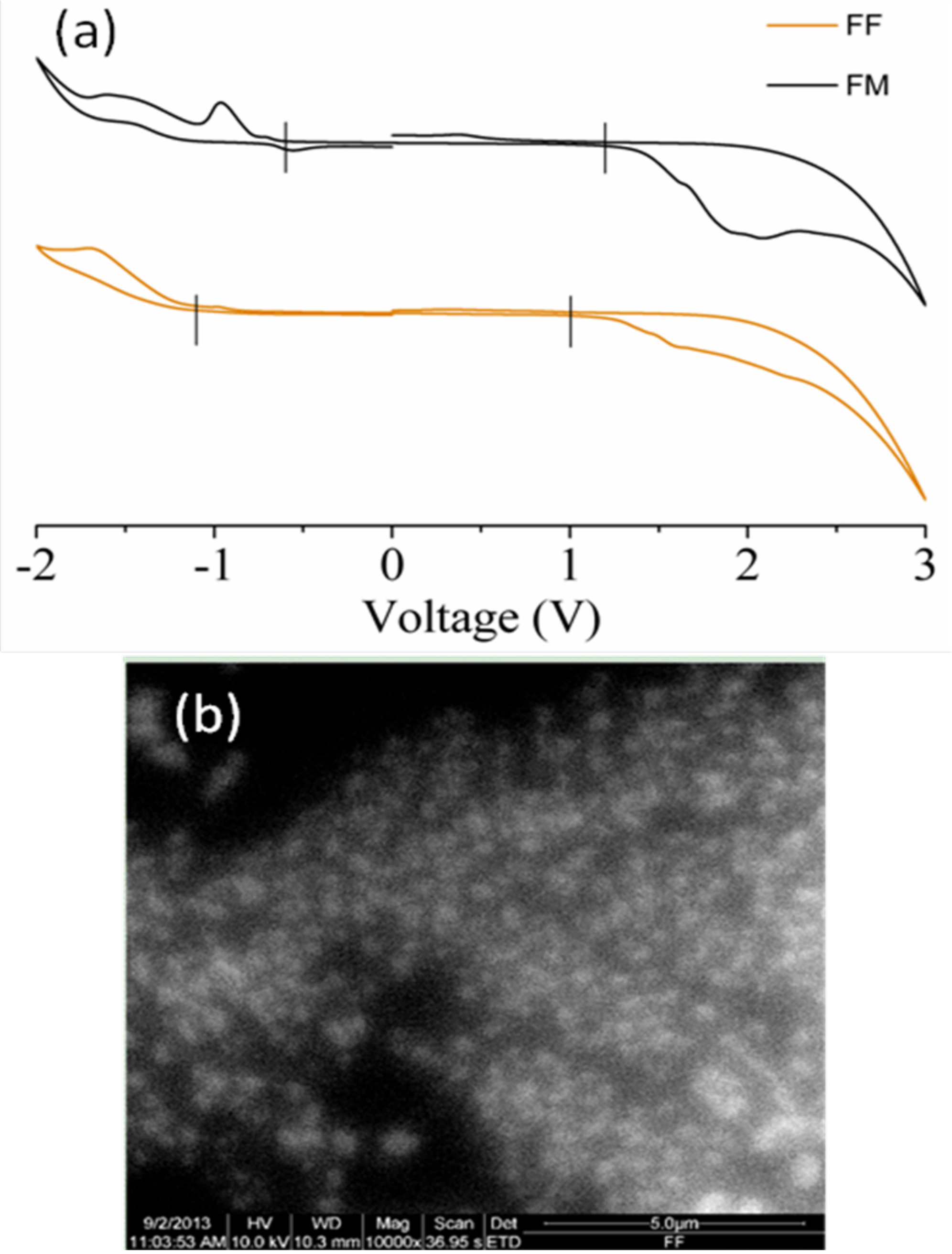

Figure 4S. (a) Cyclic voltammetry traces of FF and FM; (b) SEM micrograph (10000X) of FF aggregates from pure THF solution showing aggregates of size (300-400nm).

Table 1S.Experimental and calculated spectral and electronic properties of FF and FM.

compound	$^{a}\lambda_{abs}{}^{TF}/\lambda_{abs}{}^{sol}/\varepsilon$	$^{b}\lambda_{abs}{}^{calc}/f_{obs}$	$^{c}\lambda_{emi}{}^{TF}/\lambda_{emi}{}^{sol}$ $\lambda_{emi}{}^{calc}(f^{emi})$	^{d} $\Phi_{PL}{}^{TF}$	^{e} $\Phi_{PL}{}^{Sol}$	$^{f}E^{HOMO}{}_{exp}/E^{HOMO}{}_{calc}$	^{g} $E^{LUMO}{}_{exp}/E^{LUMO}{}_{calc}$	$^{h}E_g{}^{ele}/E_g{}^{op}/E_g{}^{calc}$
FF	448/419/2.5x10^4 375/349/2.9x10^5 317/305/2.2x10^5 260/-/-	375/1.41 264/0.027 301/0.024	555/530/ 598(0.180)	79.6%	0.32	-5.71 /-5.44	-3.60 /-3.04	2.11/2.12/2.40
FM	575/517/2.1x10^3 352/339/1.1x10^5 264/-/-	353/1.38 265/0.43	-/421,529/ 852(0.054)	1.3%	0.02	-5.90 /-5.59	-4.116 /-3.20	1.79/1.80/2.38

$^{a}\lambda_{abs}{}^{TF}/\lambda_{abs}{}^{exp}$, observed absorption maxima in thin film/THF solution nm;ε, molar extinction coefficient l mol^{-1}cm^{-1} in solution. $^{b}\lambda_{abs}{}^{calc}$, Calculated absorption maxima nm; f ^{obs}, Oscillator strength for calculated absorption. $^{c}\lambda_{emi}{}^{TF}/\lambda_{emi}{}^{sol}$, Observed emission maxima in thin film/THF solution nm; $\lambda_{emi}{}^{calc}$, Calculated emission maxima, nm; f ^{emi}, Oscillater strength of calculated emission. $^{d}\Phi_{PL}{}^{TF}$, Absolute quantum yield of spun thin film. $^{e}\Phi_{PL}{}^{Sol}$, Relative quantum yield with respect to qunine sulfate in 0.5N H_2SO_4. $^{f}E^{HOMO}{}_{exp}$, Energy of highest occupied molecular orbital from cyclic voltammetry eV; $E^{HOMO}{}_{calc}$, Calculated energy of highest occupied molecular orbital eV. $^{g}E^{LUMO}{}_{exp}$, Energy of lowest unoccupied molecular orbital from cyclic voltammetry eV; $E^{LUMO}{}_{calc}$, Calculated energy of lowest unoccupied molecular orbital eV. $^{h}E_g{}^{ele}$, Electrochemical band gap eV; $E_g{}^{op}$, Optical band gap; $E_g{}^{calc}$, Calculated band gap.

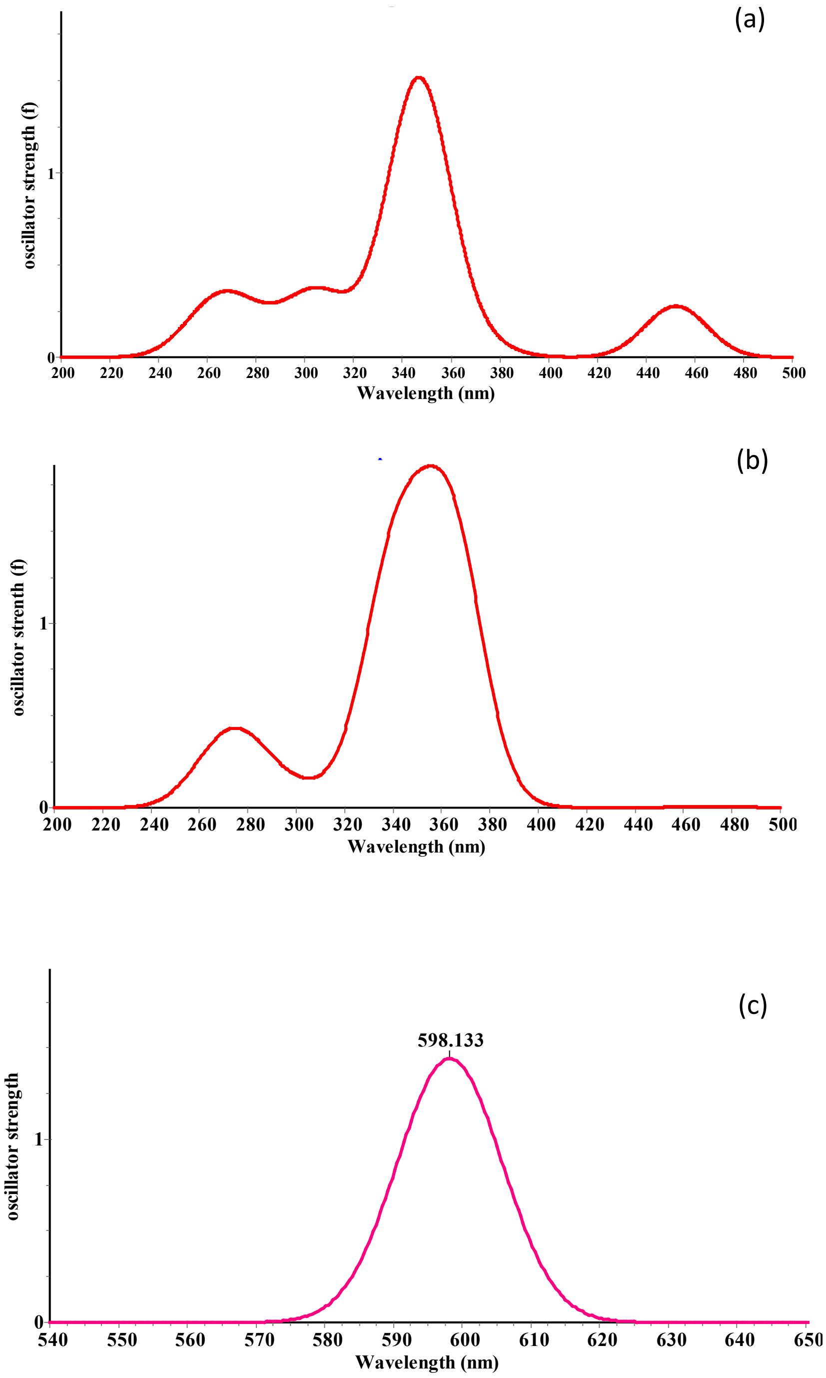

Figure 5S. Theoretically calculated (a) Absorption spectra of FF , (b) FM (c) Emission spectrum of FF

Peak assignments for computational data and experimental overlap.

Both molecules show absorption maxima with different oscillator strength (f) close to experimental values. For FF, all the experimental peaks are reproduced theoretically (Table 1 and Figure 5S, support information). The maximum absorption peak at 349 nm (f =1.50) arise from HOMO to LUMO+2 transition and intramolecular charge transfer peak at 452 nm (f =0.27) arises from the HOMO to LUMO transition. In FM, the maximum absorption peak is observed at 355 nm and it originated from the combination of 364 nm (f =1.26) and 340nm (f =1.05) peaks. These bands are due to the transition of electron from HOMO-4 to LUMO and HOMO to LUMO+2. In addition, a CT band at 265 nm for FM can also be noted (HOMO-1 to LUMO+5). Emission spectra of the two compounds were calculated from the optimized excited state geometries. For FF, LUMO toHOMO transition mainly contributes to emission at 598 nm (f=0.18) which is close to the experimental value of 572 nm. However, for FM, a significant deviation (220 nm) in calculated value (852 nm (f=0.05)) with respect to experimental peak (571 nm) is observed as reported previously for tetracyano systems.[4] we calculated HOMO and LUMO energy values and band gap (Eg) of FF and FM (Table. 1).The HOMO and LUMO values are underestimated and Eg values are overestimated with reference to the experimental values. However, the trends with calculated findings are in accordance with experimental values.The ground and excited state dipole moments of FF were calculated to be 1.15 D and 1.17 D respectively while, for FM it was 2.45 D and 2.98 D.

Fluorescence Life time and DLS Data

Fluorescence life time data was done on $9.98x10^{-6}$ M concentration of FF in varying proportion of THF-water mixture. The same concentration was used for both UV-visible absorption and Fluorescence. DLS was also done at the same solution used for fluorescence life time experiment.

Table S2. Fluorescence life time data of FF in THF-water mixture and quantum yield

%water (v/v)	τ_1/τ_2 [a]	A_1/A_2 [b]	[c] χ^2	Quantum yield
100% THF	4.53x10-9/1.81x10-8	21.4/78.6	1.02	0.323
10%	$3.93x10^{-10}$/-	100/-	0.95	0.0013
20%	$6.56x10^{-10}$/-	100/-	0.97	0.001
30%	$5.48x10^{-10}$	100/-	0.97	$7.1x10^{-4}$
40%	$2.89x10^{-10}/1.15x10^{-9}$	70.63/29.37	0.95	$6.7\ x10^{-4}$
50%	$6.81x10^{-10}/2.72x10^{-9}$	94.52/5.48	0.91	$4.9\ x10^{-4}$
60%	$5.9x10^{-9}$	100/-	1.09	0.130
70%	$5.39x10^{-9}$	100/-	1.12	0.512
80%	$5.02x10^{-9}$	100/-	1.16	0.117
90%	$4.81x10^{-9}$	100/-	1.13	0.141
Thin film	$4.42x10^{-9}$	100/-	0.98	78%

[a] τ_1/τ_2, life time of different decay channels. [b] A_1/A_2, %composition of different decay channels [c] χ^2,Correlation of exponential fit.

Table S3. Photophysical properties in different solvents and Lippert-Mataga study

Solvent	λ_{max}[a] nm		λ_{emi}[b] nm		Stoke shift cm^{-1}		Quantum yield	
	FF	FM	FF	FM	FF	FM	FF	FM
Diethyl ether	351	337	521	519	9296	10405	0.69	0.011
Ethyl acetate	353	333	531	529	9496	11126	0.36	0.007
THF	349	339	530	528	9785	10559	0.32	0.028
DCM	352	338	521	545	9215	11237	0.0985	0.009
DMF	353	346	556	557	10343	11044	0.19344	0.005
Acetone	352	341	552	546	10293	11010	0.27143	0.004
aceonitrile	353	337	563	572	10566	12191	0.26674	0.005

[a] λ_{max}, Absorption maxima . [b] λ_{emi}, %composition of different decay channels

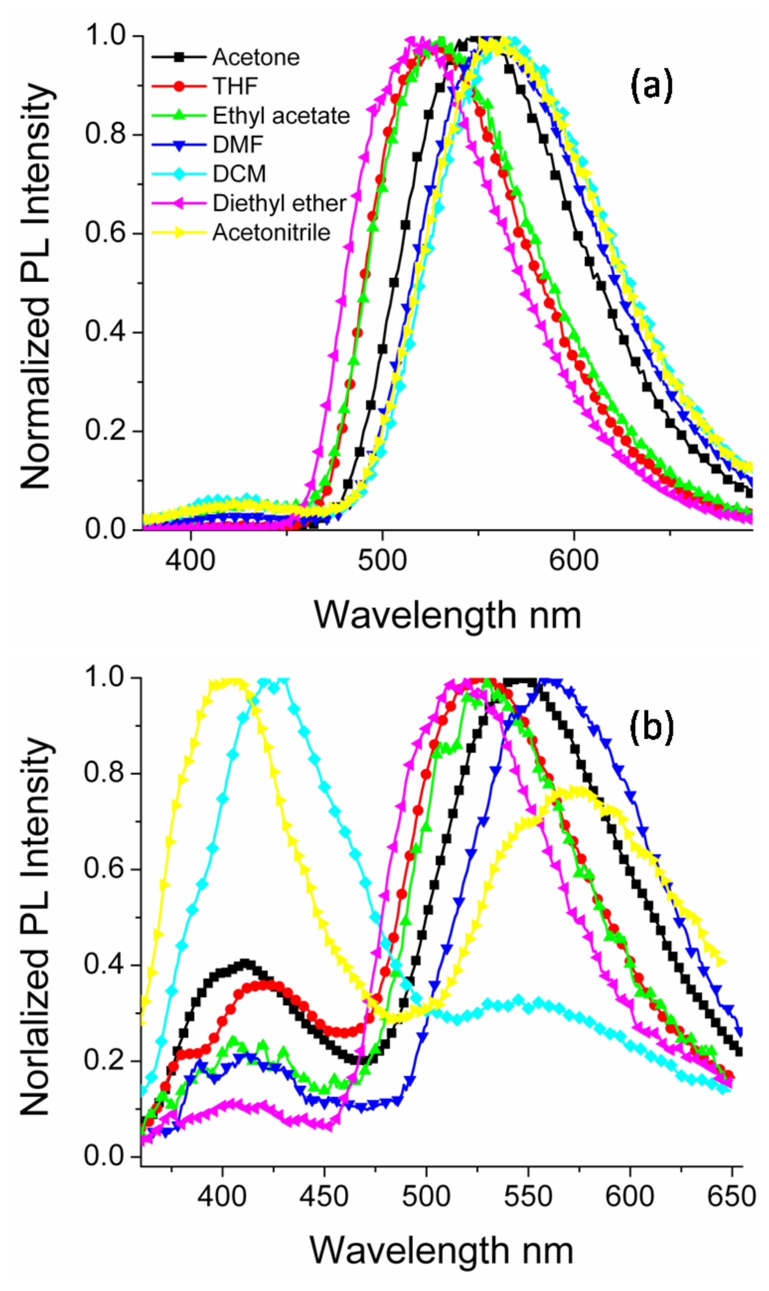

Figure 6S. Emission spectra of (a) FF at6.71x10^{-6} M concentration and (b) FM at 6.36x10^{-6} M concentration in different solvents.(FM showed dual emission behavior in all solvents and a blue shifted emission in acetonitrile, due to specific solvent interactions, concentration is fixed for all solvents)

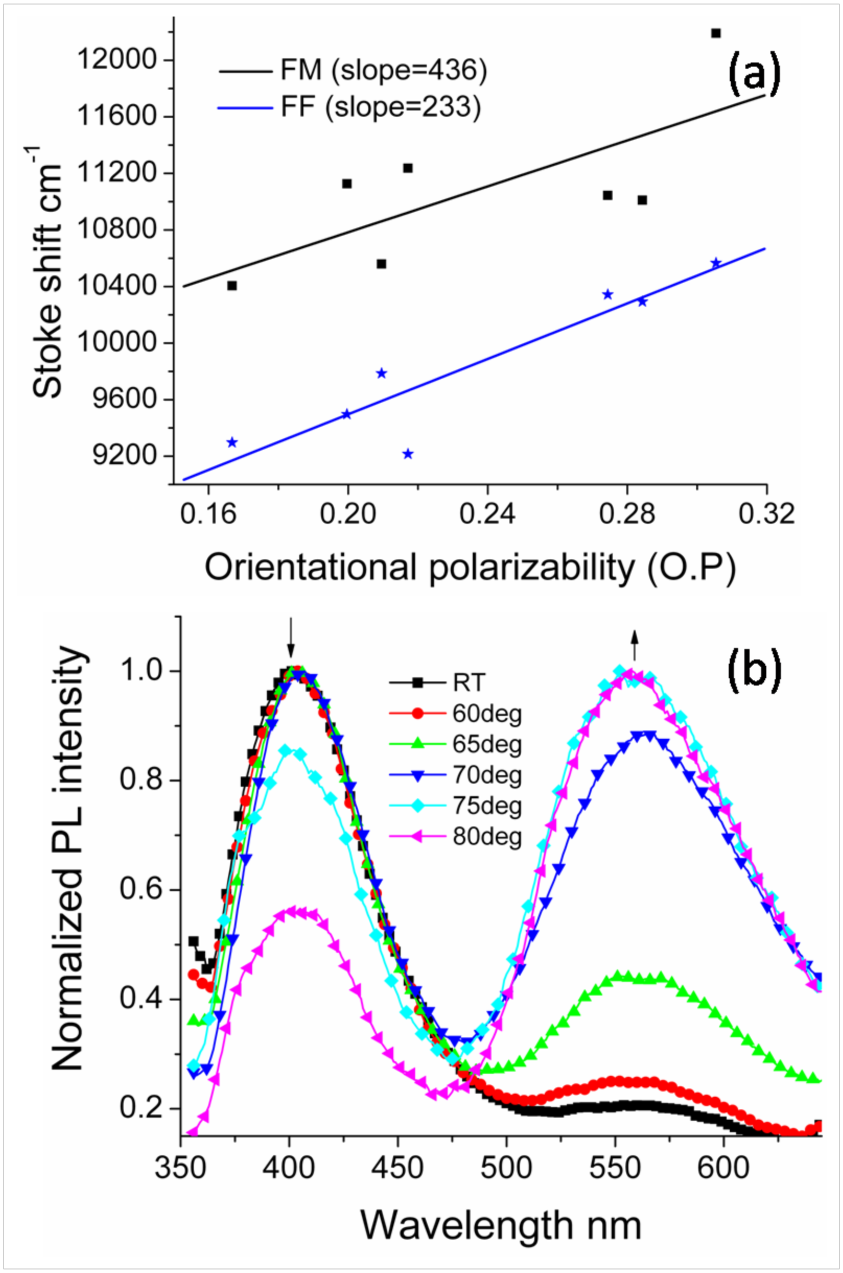

Figure7S (a) Lippert-Mataga plot and (b) Emission spectra of FM in acetonitrile at different temperatures. (The long wavelength emission increases with increasing temperature at same concentration used forLippert-Mataga study)

Discussions on Lippert-Mataga study (Figure 7S)

Particularly in acetonitrile, a high intensity of emission at 402nm and low emission at ~560nm were observed for FM. The intensity of emission at 560nm increased with increasing temperature accompanied by decrease in intensity at 420nm (Figure 7S) due to reduced dielectric friction and local viscosity with resultant solvent relaxation at higher temperatures.[5, 6]The presence of one isobestic point in variable temperature fluorescence of FM in acetonitrile showed that, there are only two emitting species (Local excited state and solvent relaxed state).

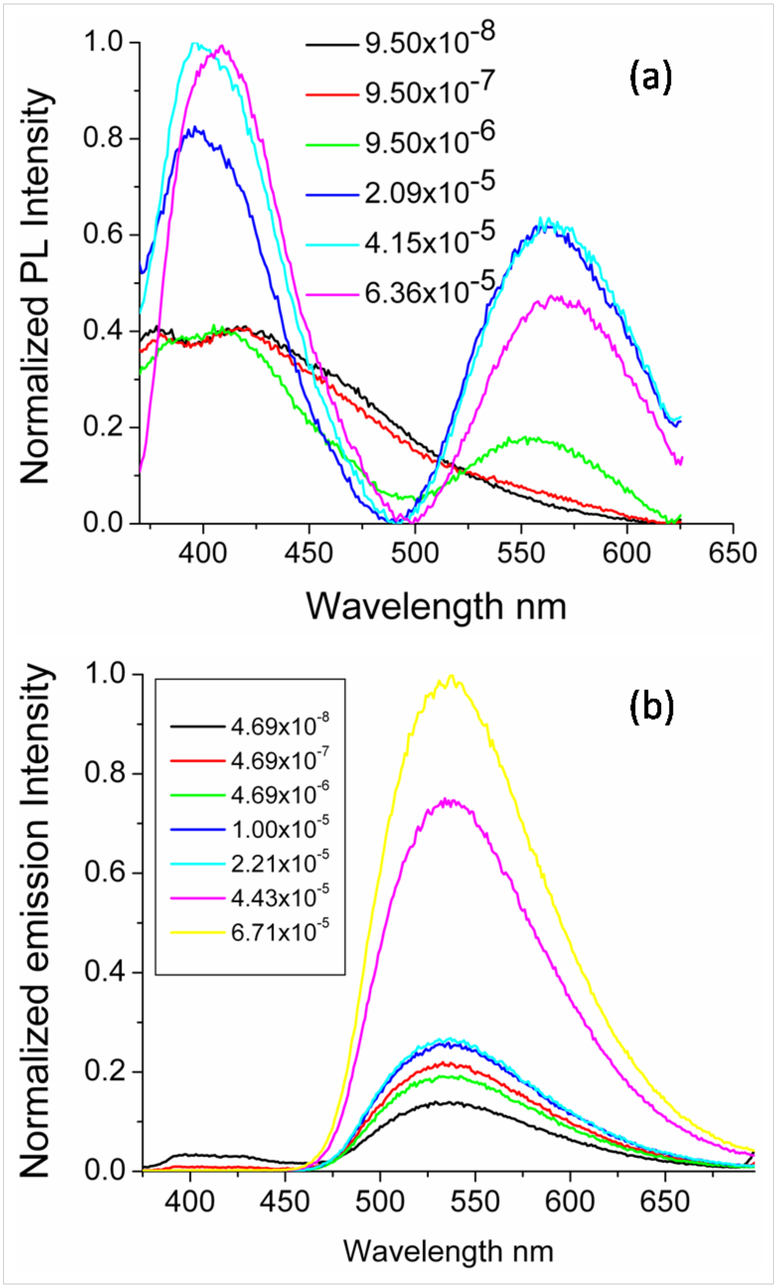

Figure 8S. Effect of concentration on emission spectra of (a) FM and (b) FF. (FM showed shift in emission to blue at sub micromolar concentrations due to high dielectric friction and local viscosity at low concentrations)

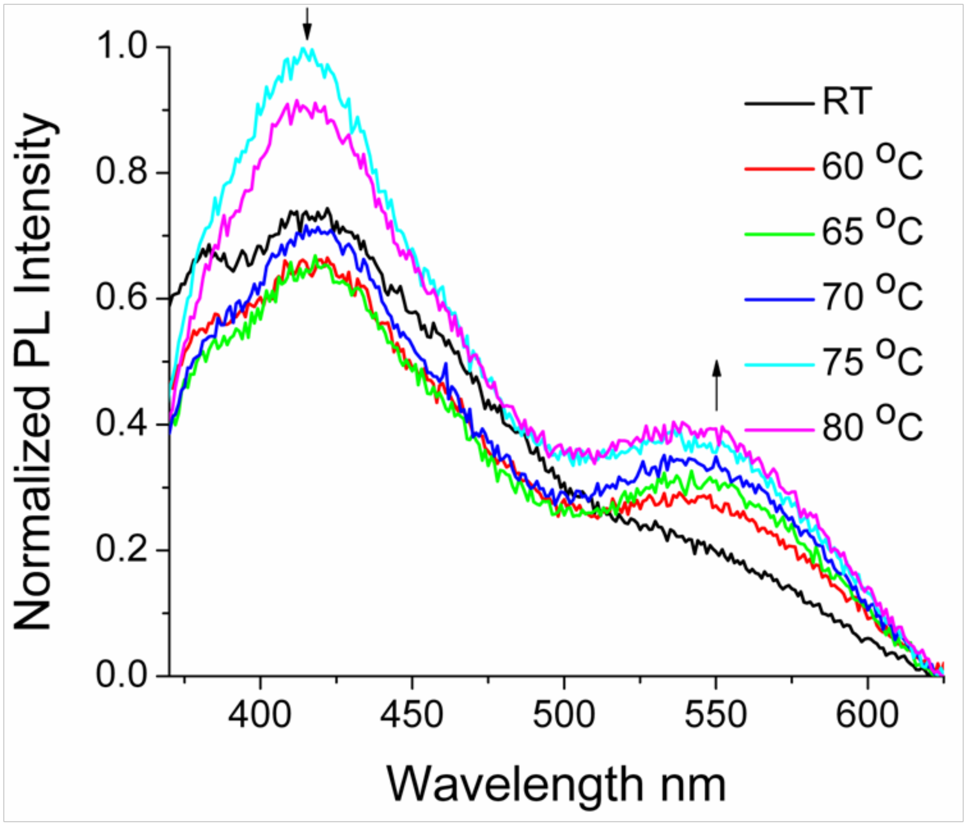

Figure 9S. Emission spectra of 9.5×10^{-8} M solution of FM at different temperature (long wavelength emission increases with temperature signifying high local viscosity)

Discussions on variable temperature fluorescence study at 9.5×10^{-8}M.

Blue shift in dilute solutions of FM below 10^{-6}M concentration and increased vibronic features raised doubt that long wavelength emission arise from eximer (Figure 6S). However, at higher temperatures the same solutions started to show increased long wavelength emission due lowering of local viscosity with increasing temperature (Figure 8S, 9S).

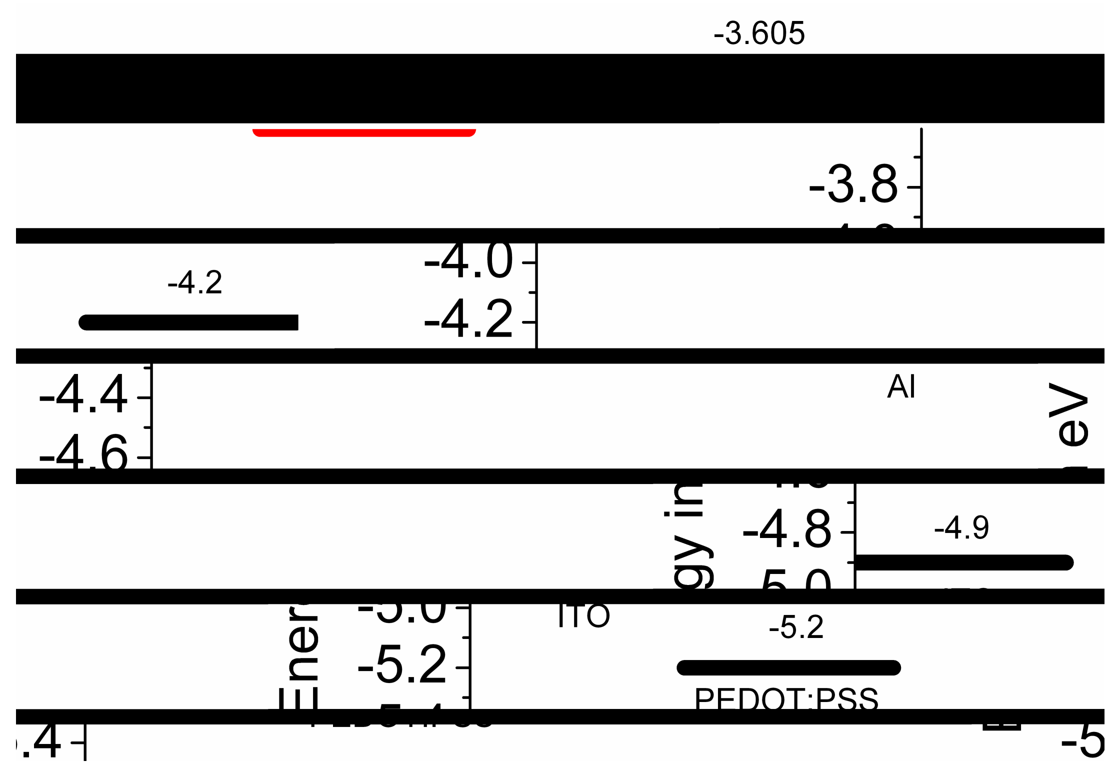

Figure 10S. Energy level diagram of LED fabricated with FF as emissive layer

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