

Supporting Information

For

White Light Emitting Single Polymer from Aggregation Enhanced Emission: A Strategy through Supra molecular Assembly

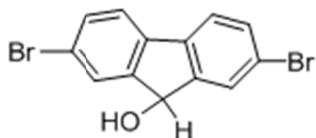
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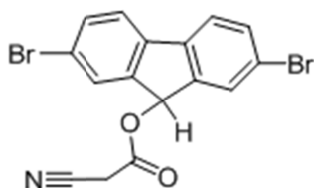
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Synthesis Procedure of Monomer and copolymers: *Synthesis of 2,7-dibromo-9H-fluoren-9-ol (FLO-OH).*



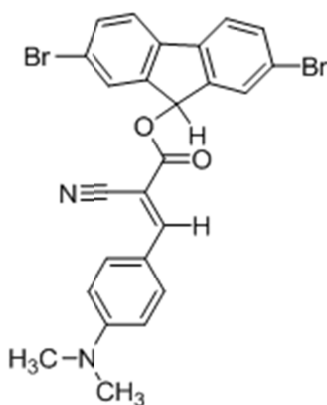
About (5g, 14.79 mmol) of 2,7-dibromo-9-fluorenone, dissolved in (75 mL) of tetrahydrofurane (THF) solvent. The reduction was carried out with (0.84 g, 22.20 mmol) of sodiumborohydride (NaBH_4). The reduction is normally carried out by rapid addition of smaller increment of the NaBH_4 to the vigorously stirring solution. The solution was stirred at room temperature for 1 hr. After the reaction time, the yellow color mixture has become colorless. The resulting organic layer was separated 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 4:1). The pure white color product was isolated 4.6 g (Yield 91.6%). ^1H NMR (400 MHz, CDCl_3 , δ): 7.14 (s, 2H, Ar H), 7.51, 7.49 (dd, $J = 1.2$ Hz, 1.6 Hz, Ar 2H), 5.47 (s, 1H, Ar H), 1.66 (s, 1H, OH); ^{13}C NMR (400 MHz, CDCl_3 , δ): 147.20, 137.93, 132.38, 128.63, 122.00, 121.42, 74.52; IR (KBr, cm^{-1}): $\nu = 3267.3$ (s), 1451.5 (s), 1414 (m), 1307.6 (s), 1265.8 (m), 1167.7 (s), 1117.6 (m), 1061.3 (s), 1030 (s); Elemental analysis calculated (%) for $\text{C}_{13}\text{H}_8\text{Br}_2\text{O}$: C, 45.9; H, 2.37; Br, 47; O, 4.71; found, C, 45.91; H, 2.36; Br, 46.93; O, 4.69.

Synthesis of 2,7 - dibromo-9H-fluoren-9yl 2-cyanoacetate (FLO-CN):



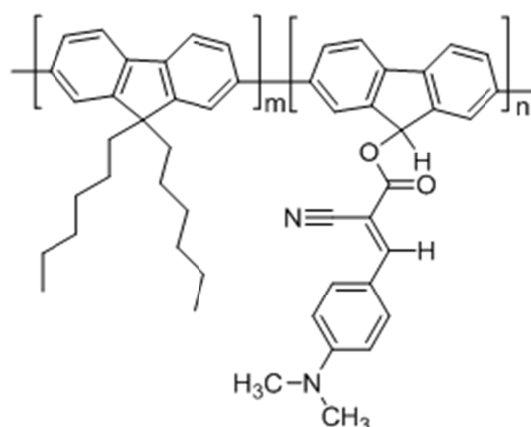
About (2.5 g, 7.38 mmol) of 2,7-dibromo-9H-fluoren-9-ol, (0.65 g, 7.38 mmol) of 2-cyanoacetic acid and (1.82 g, 9.36 mmol) of dicyclo hexyl carbodiimide are dissolved in (60 mL) of tetrahydrofuran and (0.090 g, 0.738 mmol) of dimethyl amino pyridine was finally added and stirred at room temperature for 24 hrs. The contents were filtered and the organic solution was stirred with dilute hydrochloric acid (HCL) and 2% of potassium hydroxide (KOH) solution. The resulting organic layer was separated and washed with brine solution. The organic compound was dried, washed with methanol and white solid powder was obtained 2.38 g (yield 80.79%). ¹H NMR (400 MHz, CDCl₃, δ): 7.68 (s, 2H, Ar H), 7.59, 7.57 (dd, *J* = 1.6 Hz, 2 Hz, Ar 2H), 7.50 (d, *J* = 8 Hz, Ar 2H), 6.70 (s, 1H, Ar H), 3.62 (s, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃, δ): 163.77, 142.07, 139.13, 133.42, 129.44, 122.18, 121.62, 112.42, 76.29, 24.97; IR (KBr, cm⁻¹): ν = 2986.6 (w), 2932.5 (w), 2206.5 (s) (CN), 1705.2 (s) (CO), 1613.6, (s), 1572.1 (s), 1526.3 (s), 1443.2 (s), 1382.7 (s), 1324.5 (m), 1274.5 (s), 1224.8 (s), 1166.5 (s), 1083 (m); Elemental analysis calculated (%) for C₁₆H₉Br₂NO₂: C, 47.2; H, 2.23; Br, 39.26; N, 3.44; O, 7.86; found, C, 47.27; H, 2.26; Br, 39.23; N, 3.43; O, 7.89.

Synthesis of (E)-2,7-dibromo-9H-yl 2-cyano-3(dimethylamino)phenyl)acrylate (FCP):



In to a (250 mL), two necked round bottom flask equipped with condenser were placed about (2.38 g, 5.87 mmol) of 2,7-dibromo-9H-fluorene-9-yl-2-cyanoacetate and (0.87 g, 5.87 mmol) of 4-(dimethylamino)benzaldehyde) added to the (75 mL) of ethanol. The reaction mixture was heated up to 50 °C and then did the addition of (2.5 mL, 35.22 mmol) of pyridine under vigorous stirring condition. The reaction mixture was heated at 80 °C and refluxed for 24 hours, after which the color of the reaction mixture turned wine red. After cooling, 0.5N HCL was added to the reaction mixture for removing excess of pyridine and washed with ethanol to get (E)-2,7-dibromo-9H-yl 2-cyano-3(dimethylamino)phenyl)acrylate (FCP). The product was purified on a silica gel column using petroleum ether/chloroform(v/v 1:9) as eluent. Yellow color solid was obtained (Yield 88.06). ¹H NMR (400 MHz, CDCl₃, δ): 8.14 (s, 1H, Ar H), 7.95 (d, *J* = 4 Hz, Ar 2H), 7.73 (s, 1H, Ar H), 7.52 (m, 4H, Ar H), 6.82 (s, 1H, Ar H), 6.69 (d, *J* = 8 Hz, Ar 2H), 3.12 (s, 6H, CH₃), ¹³C NMR (400 MHz, CDCl₃, δ): 154.48, 146.67, 146.07, 142.34, 138.26, 137.5, 156.53, 133.51, 131.90, 128.44, 122.96, 120.40, 118.10, 113.05, 110.64, 39.06 (C4); IR (KBr, cm⁻¹): ν = 2931 (s), 2852.5 (m), 2201 (s) (CN), 1697 (CO), (s), 1648, (s), 1611.9 (m), 1573.5 (s), 1528.9 (s), 1442.1 (m), 1375.2 (w), 1324.7 (s), 1221.3 (w), 1189 (s). Elemental analysis calculated (%) for C₂₅H₁₈Br₂N₂O₂: C, 55.79; H, 3.37; Br, 29.69; O, 5.95; found, C, 55.67; H, 3.38; Br, 29.71; O, 6.01; MALDI mass m/z: Calculated for C₂₅H₁₈Br₂N₂O₂: 537.97; found, 537.05.

Polymerization:



A series of copolymers were synthesized by Suzuki poly condensation reaction using different composition of feed ratio of the FCP monomer and comonomers (Different feed ratio in **Table S1**). The obtained conjugated copolymers with different FCP to fluorene ratios and their M_n and Poly dispersity Index (PDI) values are shown in **Table S1**. The corresponding copolymers labeled as FCP 1, FCP 2.5, FCP 5, FCP 10, FCP 25, and FCP 50 (**Scheme 1**). In a representative controlled synthetic procedure (149 mg, 0.27 mmol) of FCP along with (133 mg 0.27 mmol) of 9,9-dihexyl -2,7-dibromofluorene and (272 mg, 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester was dissolved in (65 mL) of tetrahydrofurane. To the above mixture of the reactant, (26 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 50 °C, catalytic amount of Tetrakis triphenyl phosphine palladium (0) was added to the reaction mixture under the nitrogen condition. The mixture of the content was refluxed with constant stirring for 72 hours. The resulting mixture was concentrated under vacuum and redissolved in chloroform. The chloroform solution was washed with 3N HCl solution and water. The organic layer was separated and concentrated through rotary evaporator to get crude product of copolymer **FCP 25**. The resulting crude product was purified through reprecipitation from the concentrated chloroform solution with methanol and subjected to soxhlet extraction for 6 hours to get

brown precipitate, dried and weighed. Yield 78.3%. ^1H NMR (500 MHz, CDCl_3 , δ): 8.23-7.27 (m, 44H, Ar H), 7.19-7.05 (m, 1H, Ar H), 6.73-6.57 (m, 1H, Ar H), 3.14-3.00 (m, 3H, CH_2), 2.35-1.85 (m, 22H, CH_2), 1.31-0.52 (m, 130H, CH_2).

FCP 50 copolymer: (300 mg, 0.54 mmol) of FCP along with (272 mg 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 86%. ^1H NMR (500 MHz, CDCl_3 , δ): 8.23-8.13 (m, 2H, Ar H), 8.06-7.28 (m, 48H, Ar H), 7.17-6.98 (m, 2H, Ar H), 6.74-6.56 (m, 4H, Ar H), 3.16-2.89 (m, 14H, CH_2), 2.28-1.89 (m, 12H, CH_2), 1.21-0.50 (m, 73H, CH_2).

FCP 10 copolymer: (60 mg, 0.11 mmol) of FCP along with (213 mg 0.43 mmol) of 9,9-dihexyl -2,7-dibromofluorene and (272 mg, 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 78%. ^1H NMR (500 MHz, CDCl_3 , δ): 8.05-7.27 (m, 44H, Ar H), 7.19-7.05 (m, 1H, Ar H), 6.73-6.57 (m, 1H, Ar H), 3.14-3.00 (m, 3H, CH_2), 2.35-1.85 (m, 22H, CH_2), 1.31-0.52 (m, 130H, CH_2).

FCP 5 copolymer: (30 mg, 0.05 mmol) of FCP along with (240 mg 0.48 mmol) of 9,9-dihexyl -2,7-dibromofluorene and (272 mg, 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 64%. ^1H NMR (500 MHz, CDCl_3 , δ): 8.00-7.28 (m, 32H, Ar H), 3.12-3.01 (m, 1H, CH_2), 2.20-1.87 (m, 16H, CH_2), 1.27-0.53 (m, 90H, CH_2).

FCP 2.5 copolymer: (15 mg, 0.027 mmol) of FCP along with (252 mg 0.513 mmol) of 9,9-dihexyl -2,7-dibromofluorene and (272 mg, 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 83%. ^1H NMR (500 MHz, CDCl_3 , δ): 7.90-7.33 (m, 33H, Ar H), 2.23-1.92 (m, 15H, CH_2), 1.23-0.60 (m, 92H, CH_2).

FCP 1 copolymer: (6 mg, 0.01 mmol) of FCP along with (260 mg 0.53 mmol) of 9,9-dihexyl -2,7-dibromofluorene and (272 mg, 0.54 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid(1,3-propane diol)ester were used in the polymerization, yield 74.5%. ^1H NMR

(500 MHz, CDCl₃, δ): 8.00-7.31 (m, 33H, Ar H), 2.28-1.88 (m, 17H, CH₂), 1.27-0.48 (m, 102H, CH₂).

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

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

<i>Polymer</i>	<i>Feed ratio</i> ^a		^c Calculated values		<i>M_w/M_n/PDI</i> ^b
	<i>FCP</i>	<i>M</i>	<i>N</i>	<i>FCP</i>	
DHFP	0	0.50	0.50	-	24500/9673/2.4809
FCP 1	0.01	0.50	0.49	0.0092	18567/ 8652/2.1458
FCP 2.5	0.025	0.50	0.475	0.021	21001/9201/2.2823
FCP 5	0.05	0.50	0.45	0.047	16045/6856/2.3402
FCP 10	0.1	0.50	0.40	0.091	17456/7441/2.3457
FCP 25	0.25	0.50	0.25	0.22	40734/14642/2.7820
FCP 50	0.50	0.50	0	0.44	14665/7176/2.0436

^aFCP, mole fraction of FCP; 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 FCP.

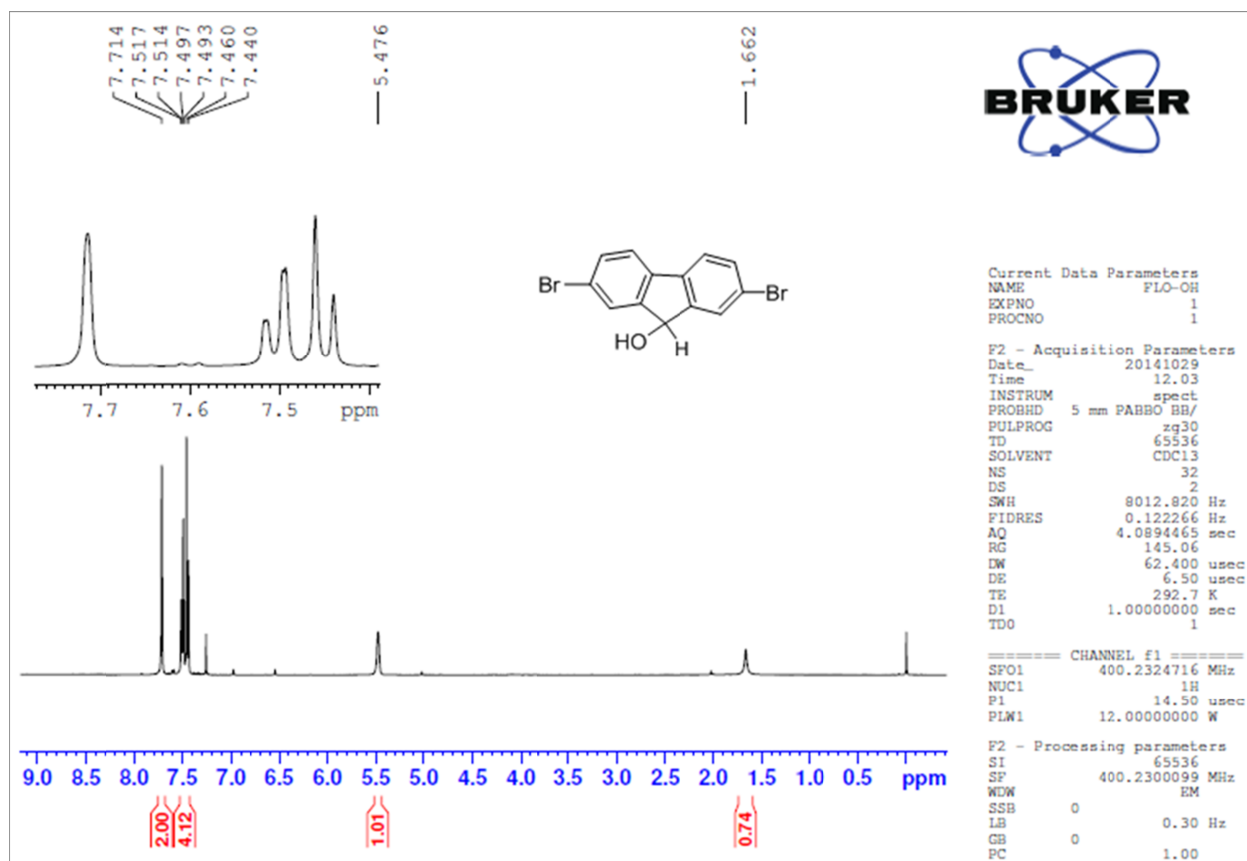


Figure S1. ^1H NMR spectrum of FLO-OH

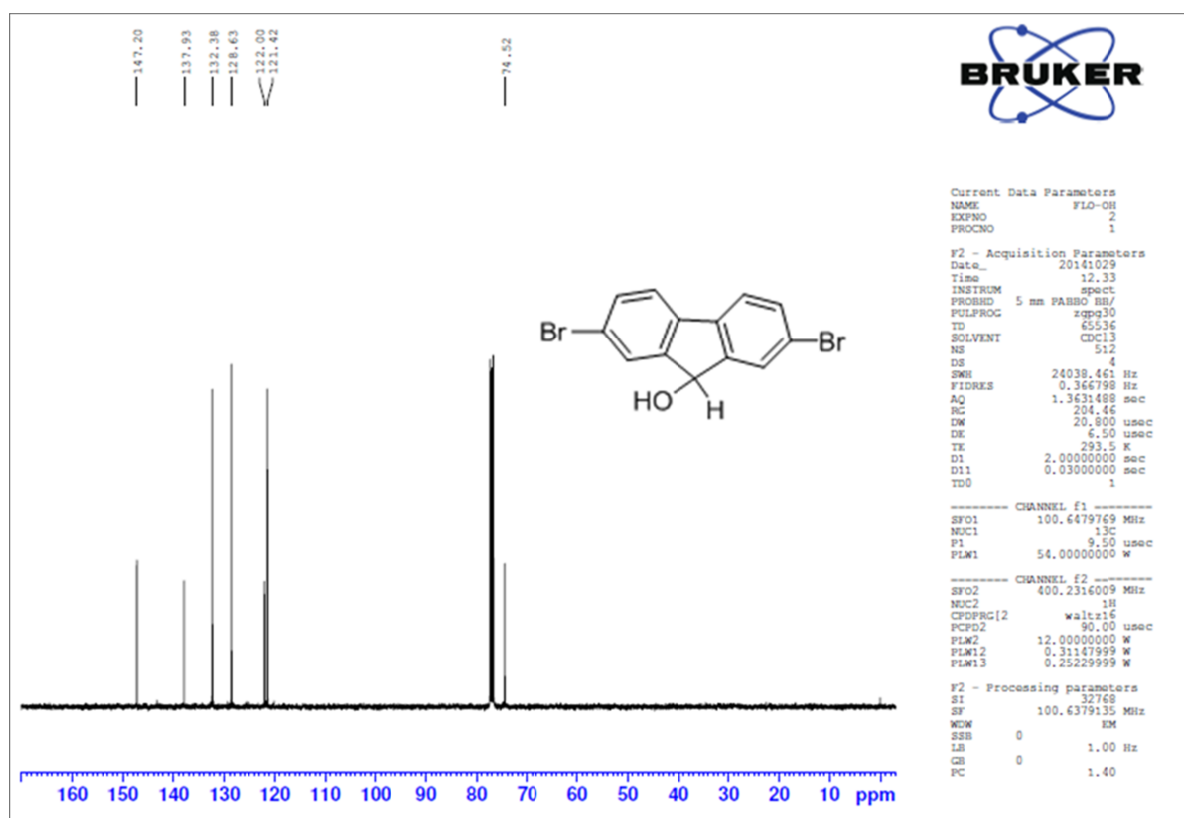


Figure S2. ^{13}C NMR spectrum of FLO-OH

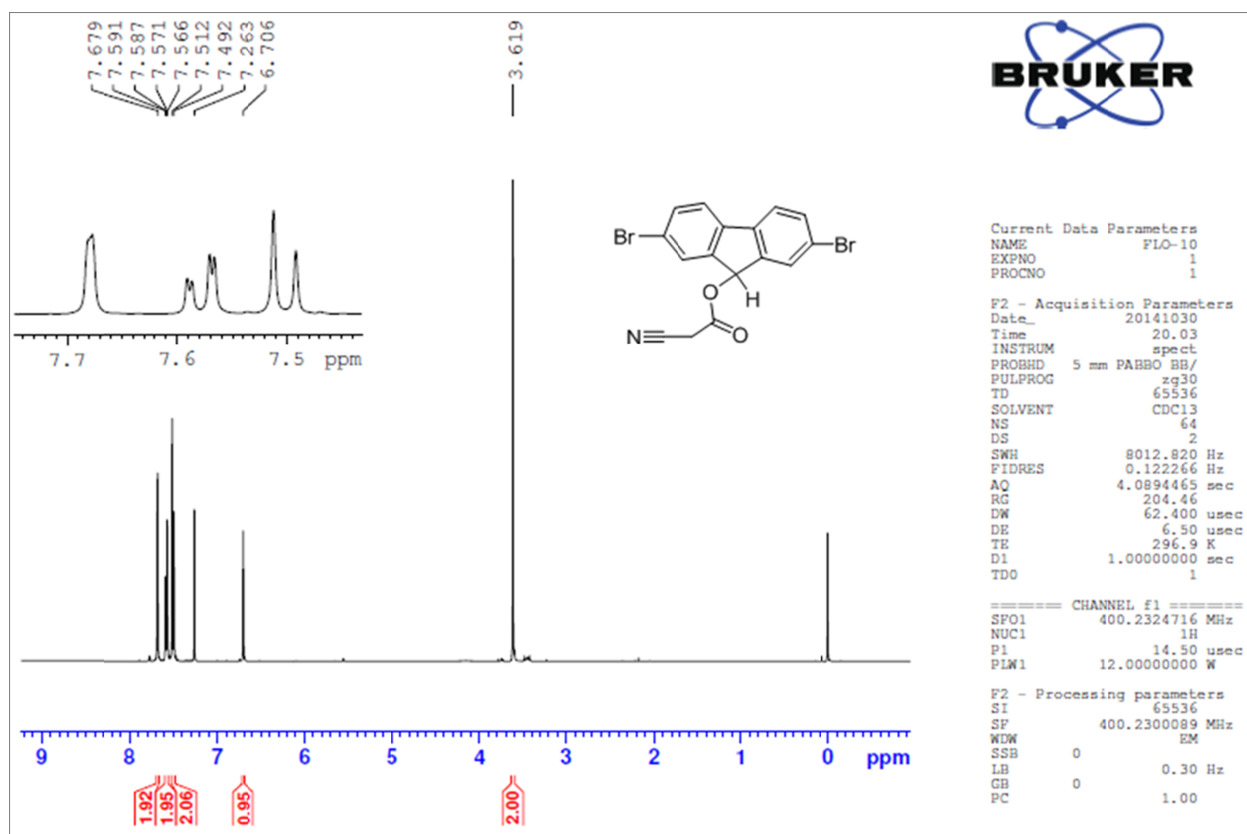


Figure S3. ^1H NMR spectrum of FLO-CN

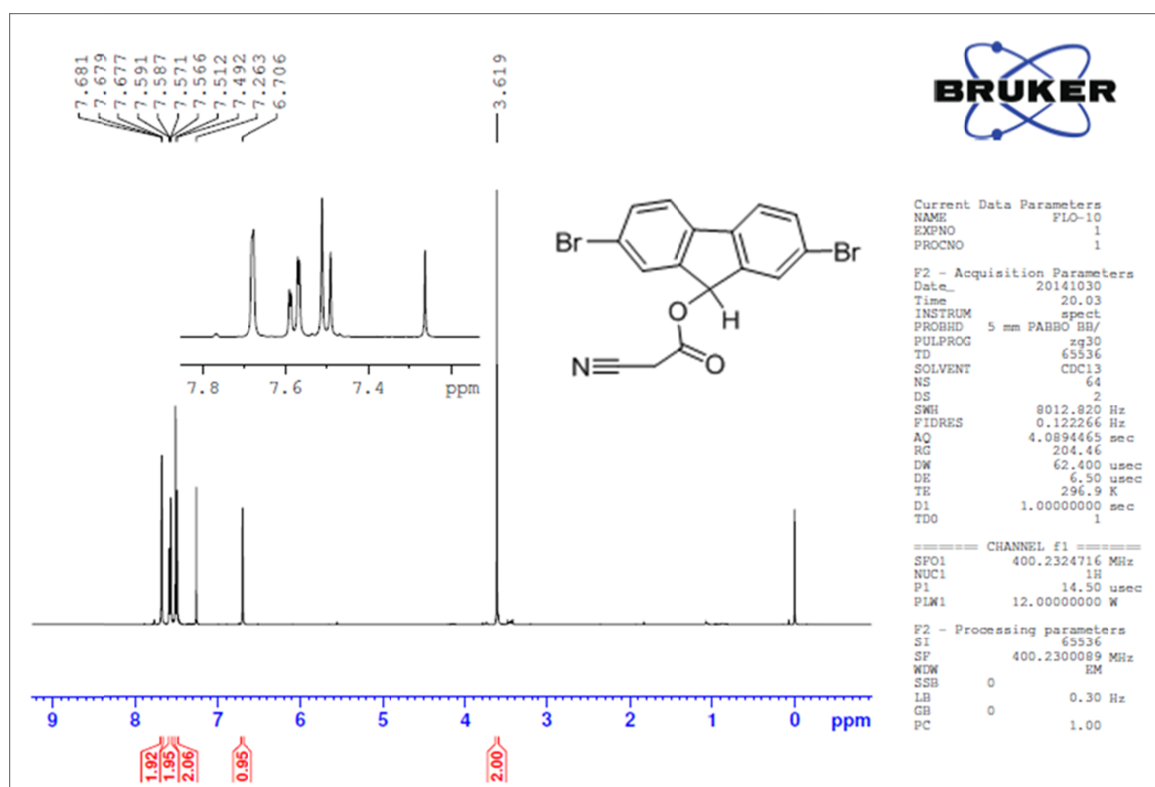


Figure S4. ^{13}C NMR spectrum of FLO-CN

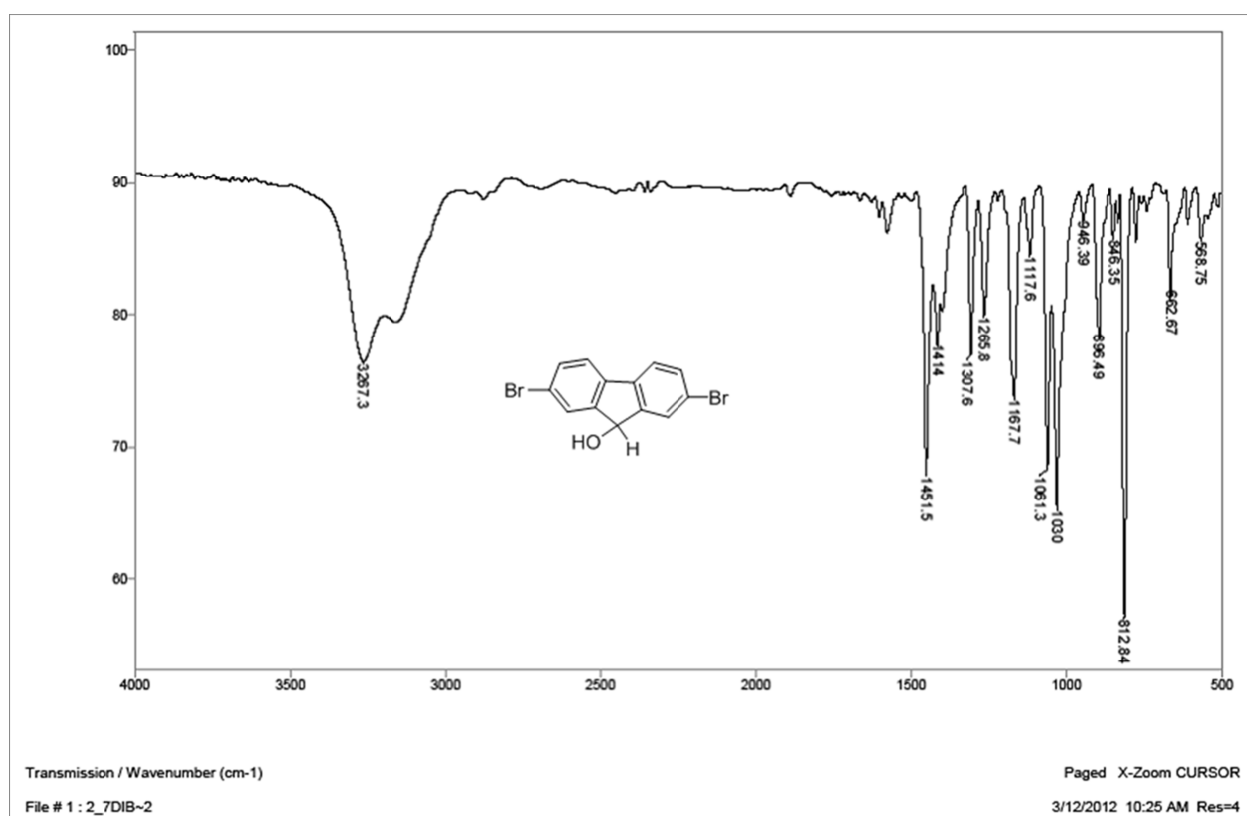


Figure S5. FT-IR spectrum of FLO-OH

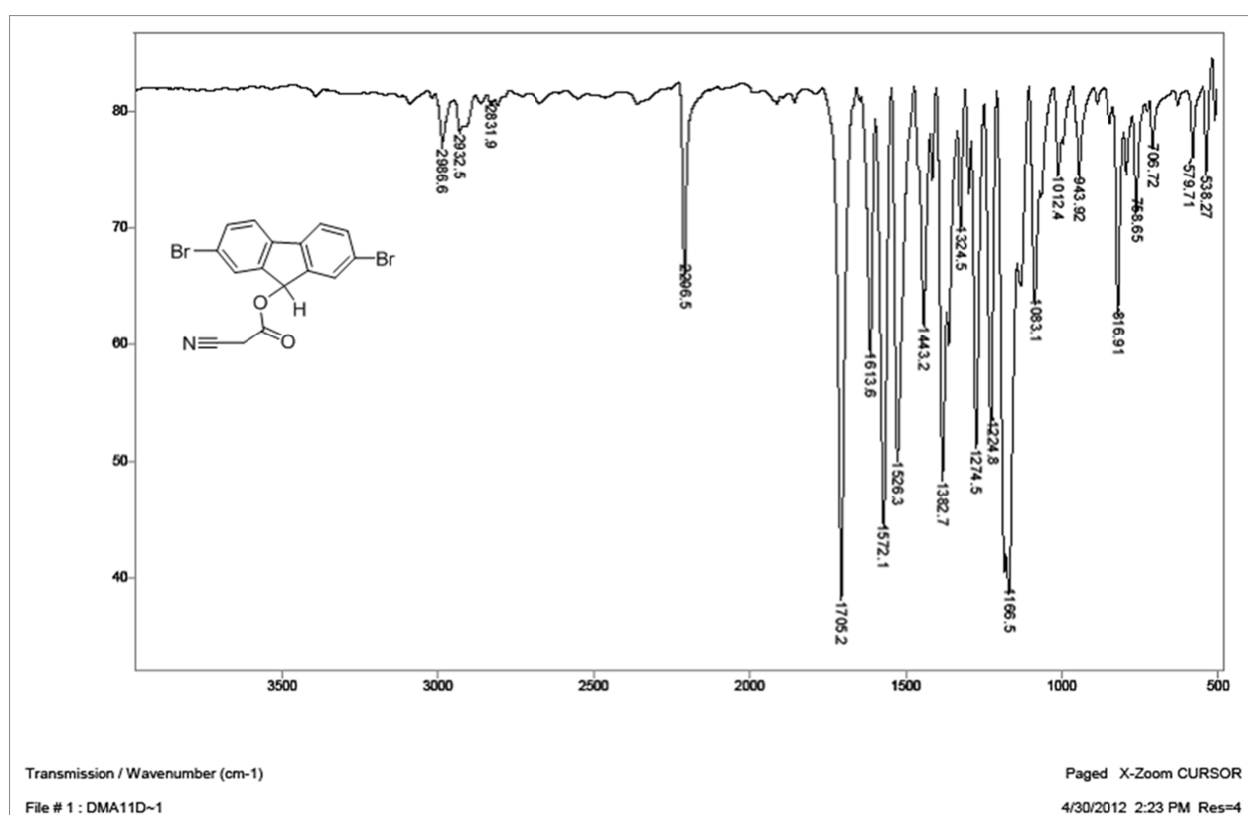


Figure S6. FT-IR spectrum of FLO-CN

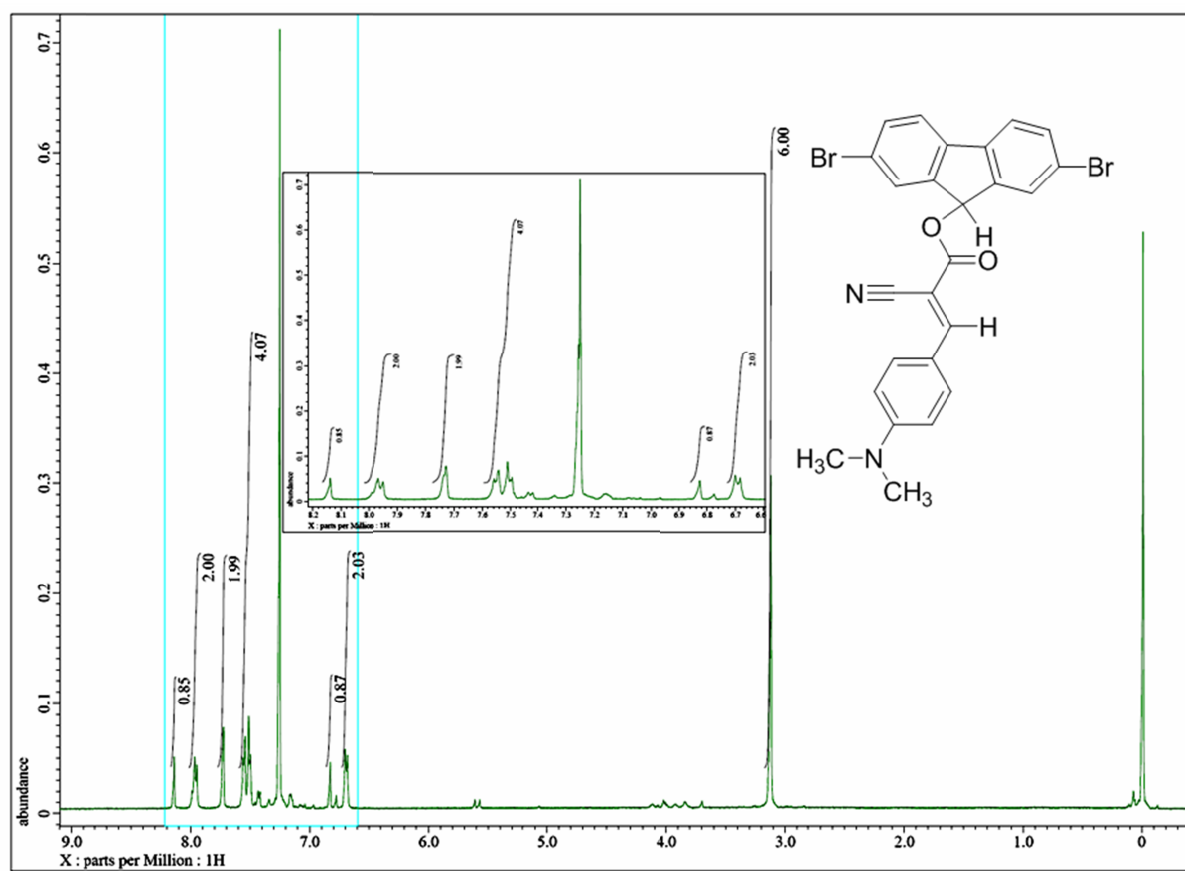


Figure S7. ^1H NMR spectra of FCP (inset, expansion of aromatic region)

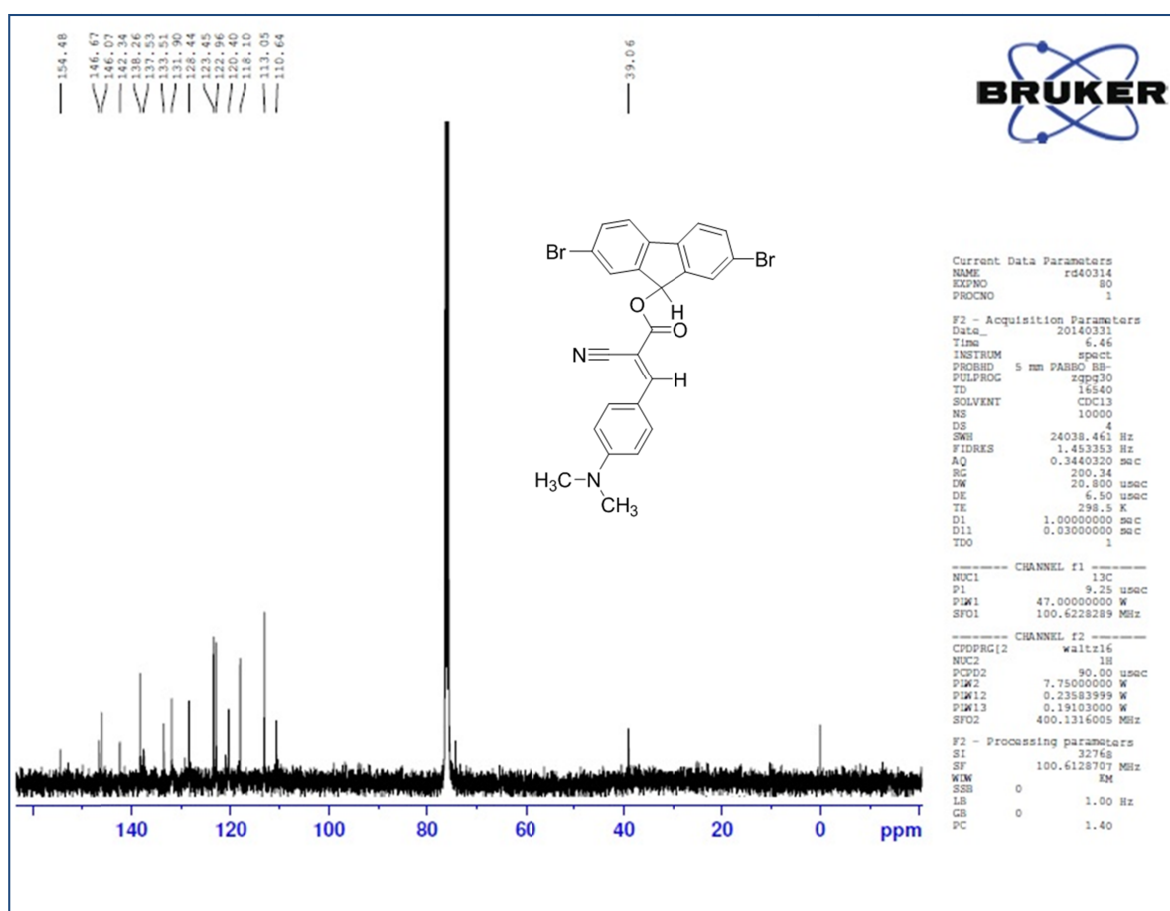


Figure S8. ¹³C NMR spectra of FCP

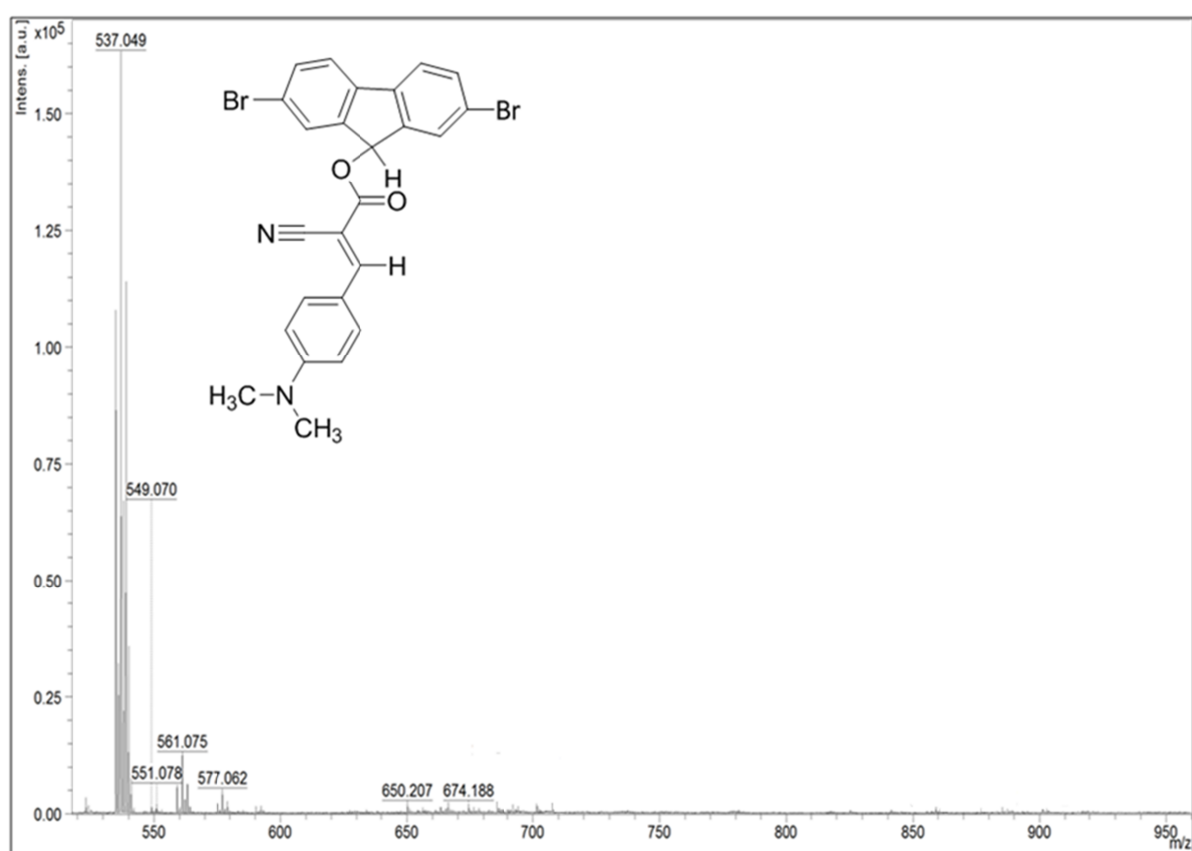


Figure S9. MALDI mass spectrometry of FCP.

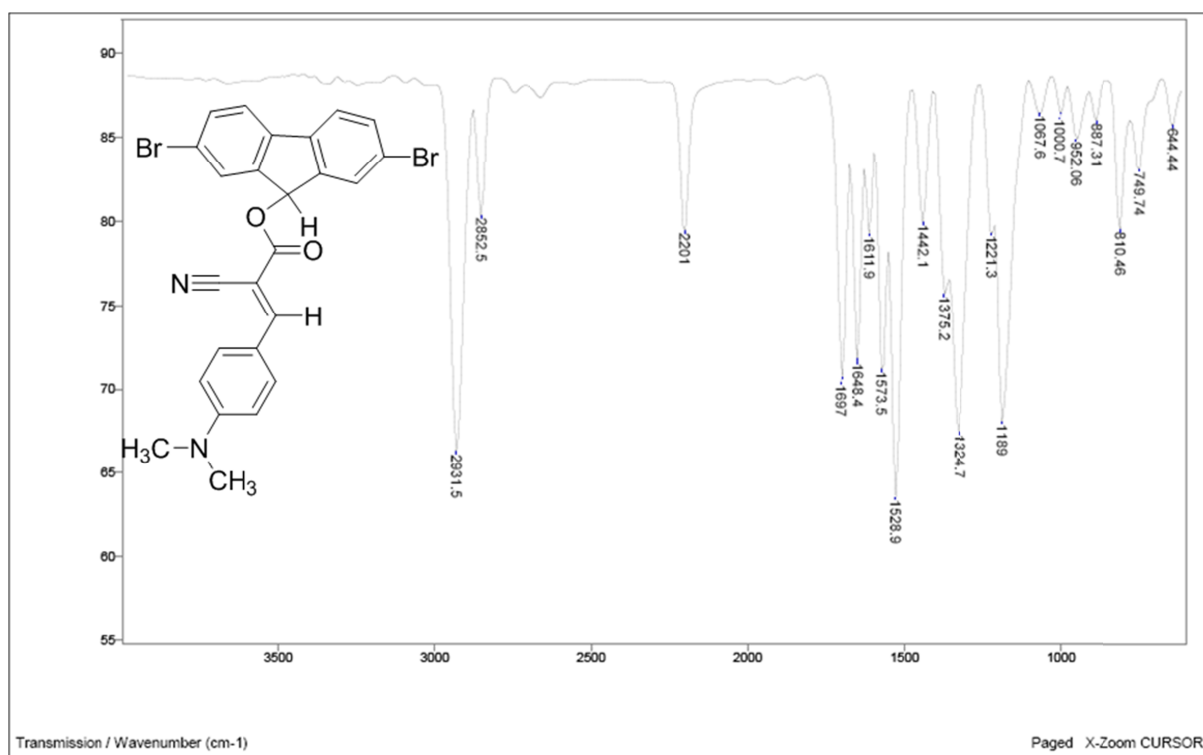


Figure S10. FT-IR spectrum of FCP

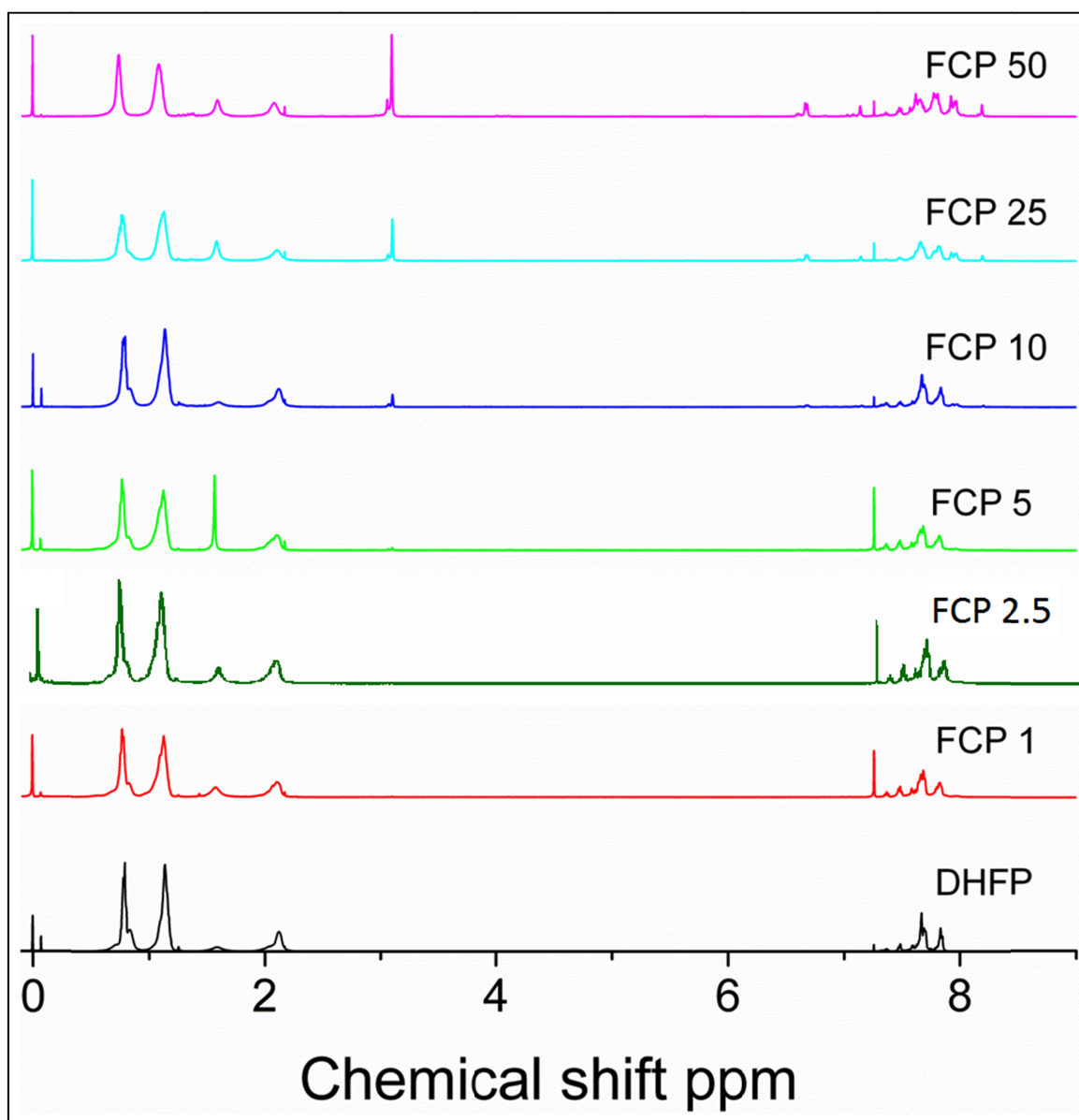


Figure S11. ^1H NMR spectrum of DHFP and copolymers

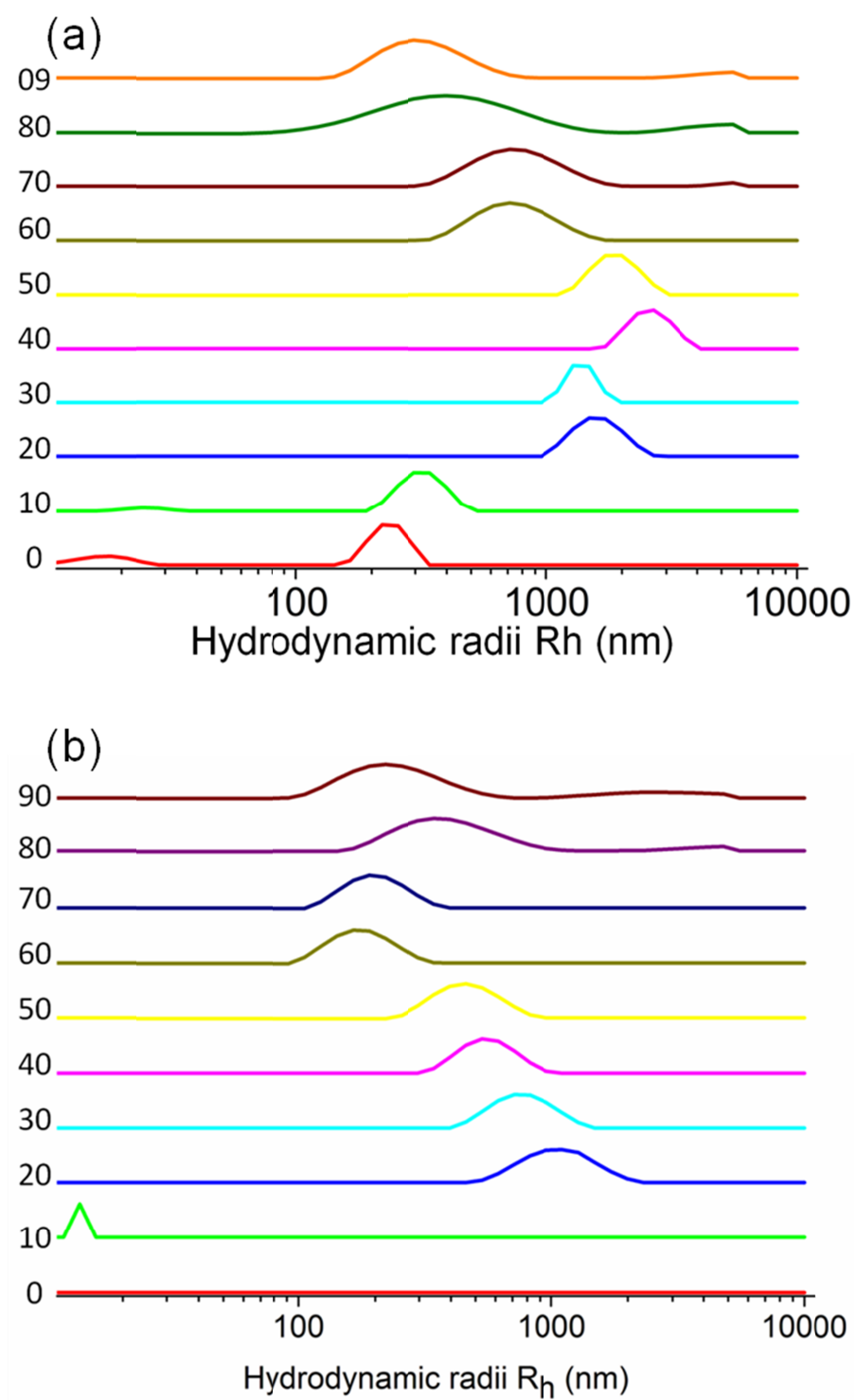


Figure S12. (a) and (b) DLS traces of copolymers FCP 50 and FCP 25

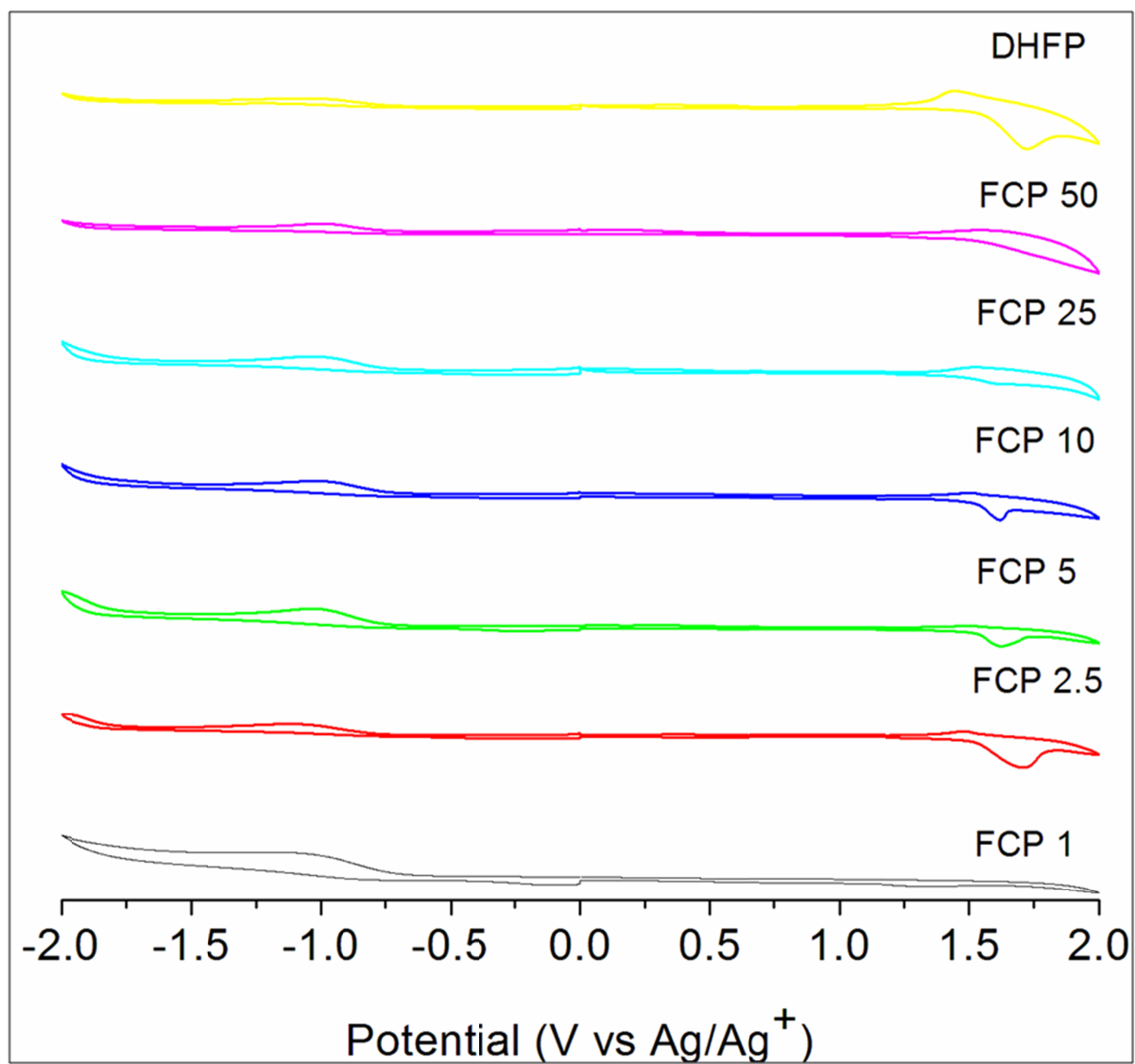


Figure S13. Cyclic voltammetry spectrum of DHFP and copolymers

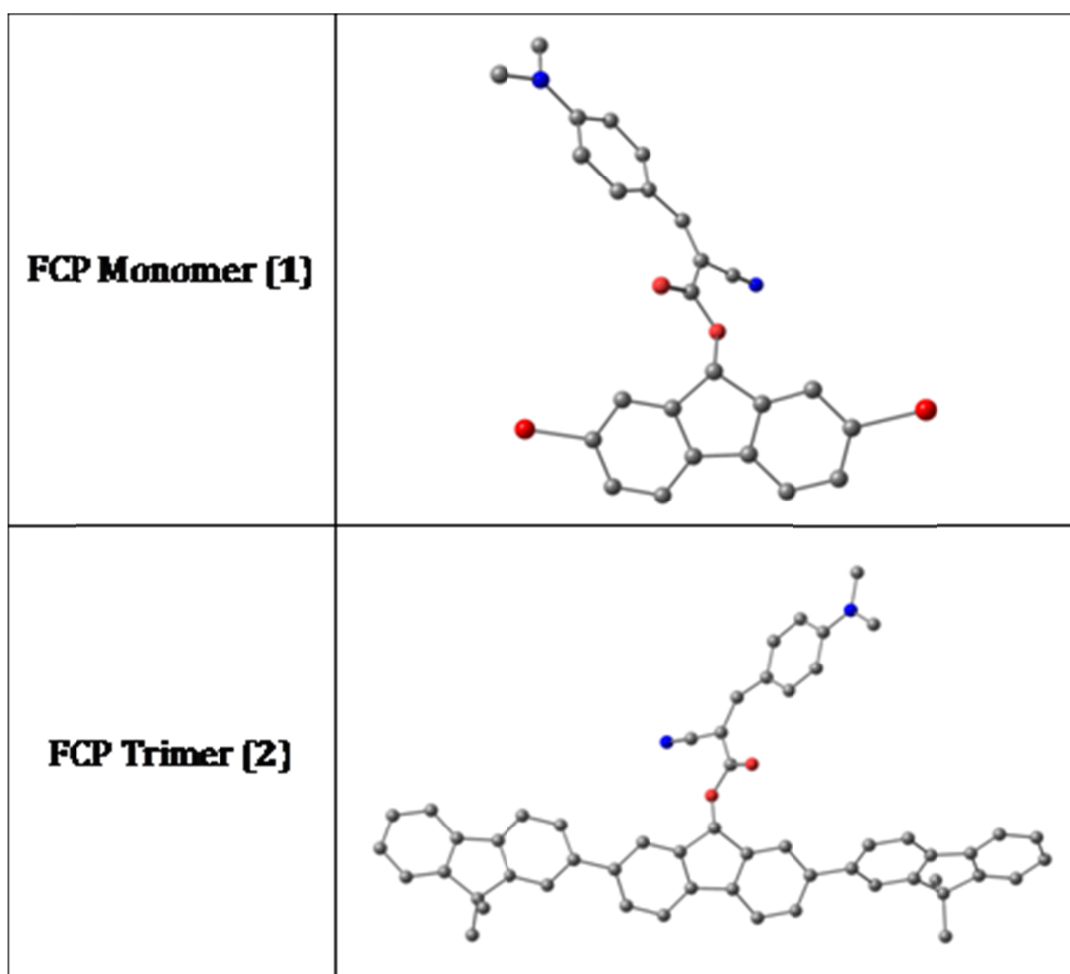


Figure S14. Optimized geometry of the FCP monomer (1) and FCP trimer (2) at the B3LYP/6-31G* level. The hydrogen atoms are omitted here for clarity.

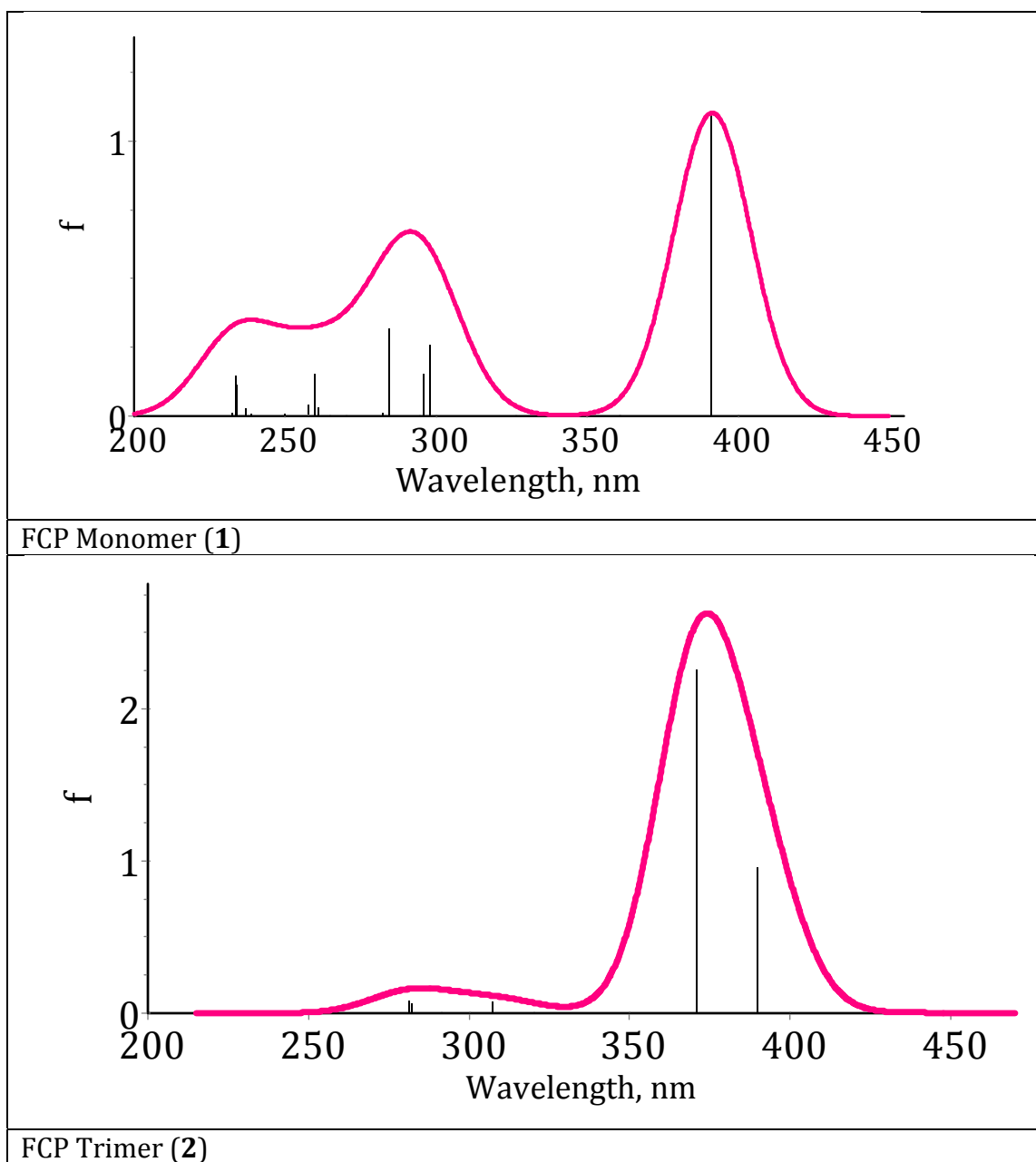


Figure S15. Theoretically calculated absorption spectra of FCP Monomer (1) and FCP trimer (2) at B3LYP/6-31G* level.

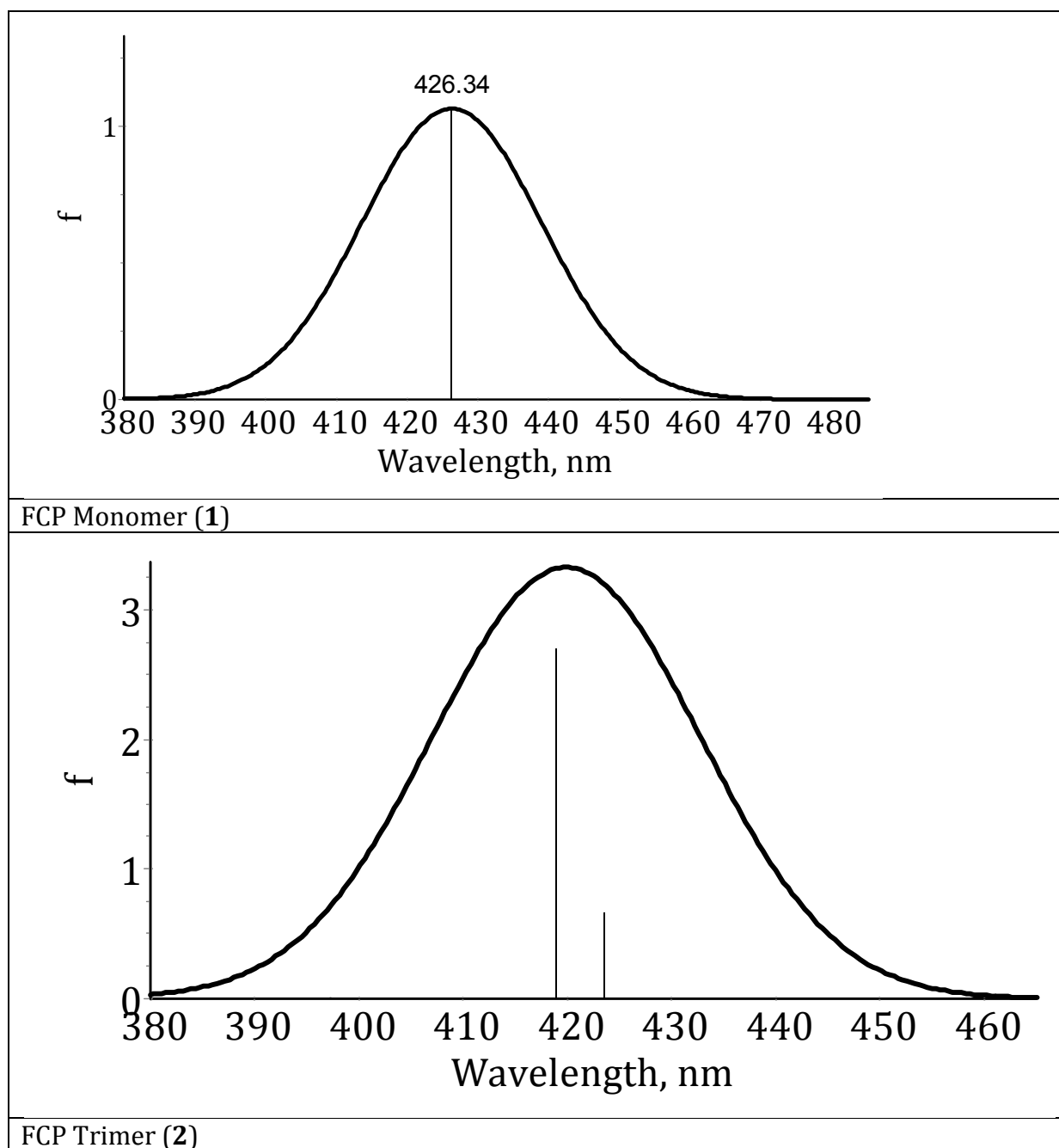


Figure S16. Theoretically calculated emission spectrum of FCP Monomer (1) and FCP trimer (2) at B3LYP/6-31G* level.

Table S2. Detailed study of absorption and emission peak position of FCP in different polar solvents and Lippert-mataga study.

Solvents	ϵ	n	$f(\epsilon, n)$	FCP		
				λ_a (nm)	λ_f (nm)	Stroke shift ($\lambda_a - \lambda_f$) (cm^{-1})
Toluene	2.38	1.49	0.01	427	465	1914
Diethyl ether	4.34	1.35	0.16	420	465	2304
Ethyl acetate	6.02	1.37	0.20	424	478	2665
Tetrahydrofurane	7.58	1.40	0.21	427	477	2455
Methylene chloride	8.93	1.42	0.21	433	480	2261
Acetone	20.7	1.35	0.28	430	487	2723
Acetonitrile	37.5	1.34	0.30	431	489	2751

Table S3. Device characteristics of monomer (FCP) and copolymers.

<i>Polymer</i>	<i>HOMO</i> (eV) ^a	<i>LUMO</i> (eV) ^b	<i>E^{ele}/E^{opt}</i> (eV) ^c	μ^d ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	<i>e</i> η_c^{max} (cd/m^2)	<i>f</i> η_p^{max} (Lm/W)	<i>g</i> L^{max} (cd/m^2)	<i>Turn-on</i> <i>Voltage</i> (V)	<i>^hCIE^{EL}</i>	<i>ⁱCIE^{PL}</i>
FCP 1	-5.82	-3.18	2.59/2.54	6.89×10^{-6}	5.13	4.45	8956	3.6	0.30, 0.31	0.25, 0.27
FCP 2.5	-5.81	-3.17	2.56/2.64	1.02×10^{-6}	6.34	4.83	9332	3.9	0.33, 0.34	0.31, 0.32
FCP 5	-5.86	-3.37	2.52/2.49	1.02×10^{-6}	3.12	5.93	8567	4.3	0.30, 0.38	0.32, 0.37
FCP 10	-5.80	-3.27	2.49/2.53	0.53×10^{-6}	4.38	3.98	10456	4.1	0.43, 0.42	0.41, 0.38
FCP 25	-5.85	-3.38	2.47/2.47	1.77×10^{-6}	4.79	4.67	11234	3.7	0.36, 0.41	0.37, 0.43
FCP 50	-5.83	-3.32	2.44/2.51	2.21×10^{-6}	6.12	4.83	12456	3.9	0.38, 0.44	0.37, 0.44
FCP	-5.91	-3.53	2.37/2.48	2.11×10^{-6}	11.91	5.77	18746	4.3	0.44, 0.49	0.45, 0.51

^aHighest Occupied Molecular Orbital. ^bLowest Unoccupied Molecular Orbital. ^c E^{ele}/E^{opt} , Electrochemical band gap/Optical band gap. ^d μ , Charge carrier mobility determined by Space Charge Limited Current (SCLC) method. ^f η_c^{max} , Luminous efficiency. ^f η_p^{max} , Power efficiency. ^g L^{max} , Maximum brightness. ^hCIE coordinates for EL. ⁱCIE coordinates for PL.

Table S4. Quantum yield of FCP monomer and copolymers in various THF/water mixtures.^a

<i>Monomer and polymer</i>	<i>FCP</i>	<i>FCP 50</i>	<i>FCP 25</i>	<i>FCP 10</i>	<i>FCP 5</i>	<i>FP 2.5</i>	<i>FCP 1</i>	<i>DHFP</i>
Pure THF(0% of water)	0.01	0.55	0.55	20.9	50.4	65.7	69.8	71.7
30%+70% H ₂ O	39.1	18.3	21.1	9.3	8.3	8.9	6.0	7.1
20%+80% H ₂ O	51.7	27.1	16.2	23.1	12.7	11.2	7.8	1.6
10%+90% H ₂ O	42.3	29.4	31.2	14.2	15.4	13.5	9.3	0.9

^a Relative quantum yield with respect to quinine sulfate.

Computational details

Density functional theory (DFT) has been noteworthy successful at providing a means for computing a range of ground-state properties with an accuracy which rivals that of the post Hartree-Fock methods. Calculated structures and properties of organic electronic materials in the ground and excited states with Lee–Yang–Parr functional (B3LYP)^{S1, S2} functional often provide good agreement with experiment compared to other functional. Hence, the ground and excited state geometries of the two systems were optimized by DFT based method with B3LYP 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. The SWizard program has been employed to evaluate the contribution of singly excited state configurations to each electronic transition.^{S3} All calculations were performed using Gaussian 09 program package.^{S4}

References

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