Supporting Information of

Amphiphilic Benzothiadiazole–triphenylamine-based Aggregates That Emit Red Light in Water

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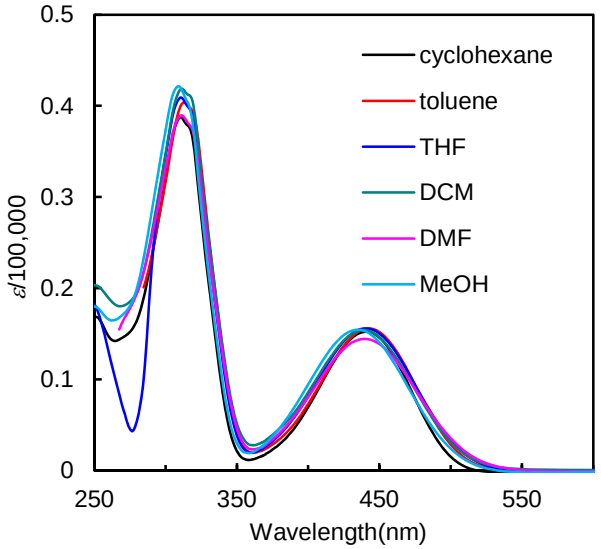


Fig. S1 UV/Vis spectra of **1** in cyclohexane, toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-5} M).

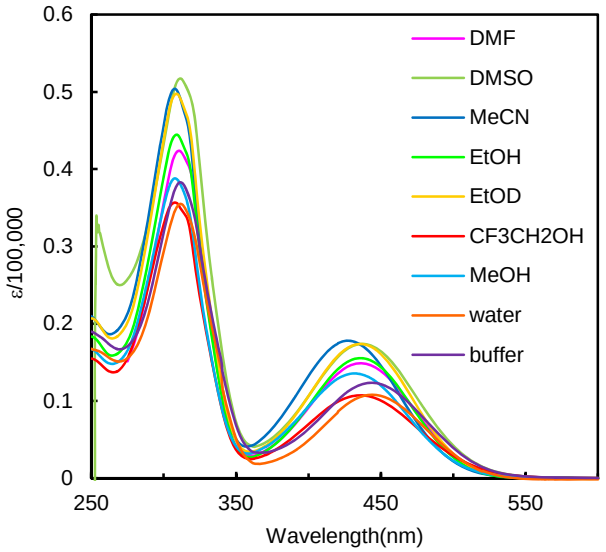


Fig. S2 UV/Vis spectra of **2** in DMF, DMSO, acetonitrile, ethanol, ethanol-d_1, 2,2,2-trifluoroethanol, methanol, water, and phosphate buffer (pH 7.4) (1.0×10^{-5} M).

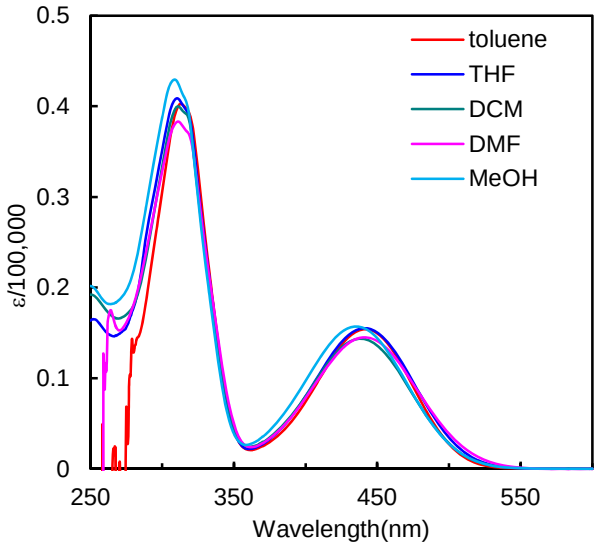


Fig. S3 UV/Vis spectra of **4** in toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-5} M).

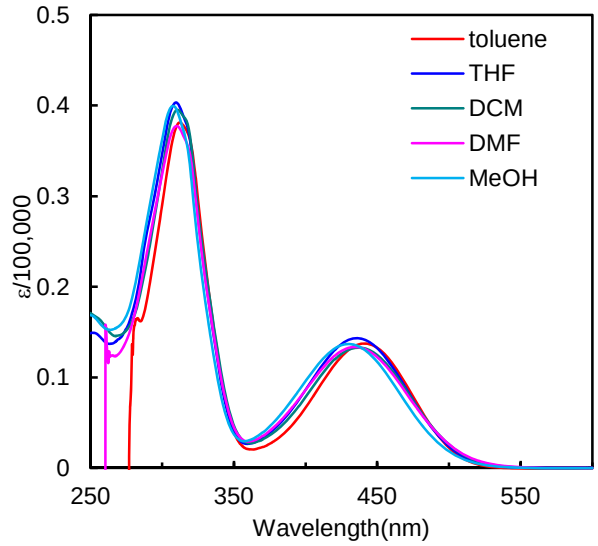


Fig. S4 UV/Vis spectra of **6** in toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-5} M).

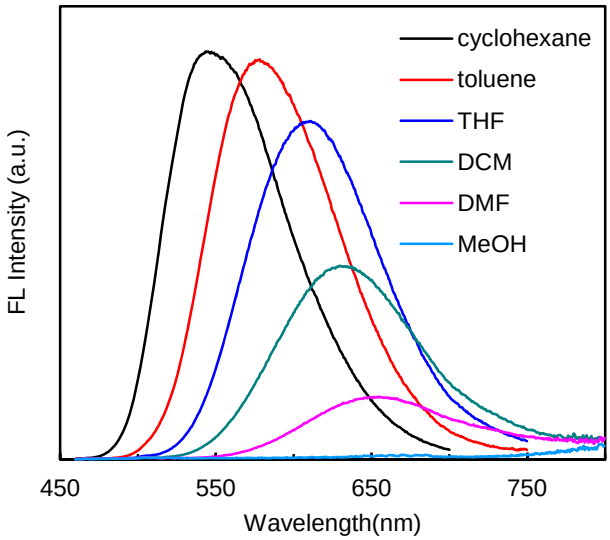


Fig. S5 Fluorescence spectra of **1** in cyclohexane, toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-6} M) excited at 440 nm.

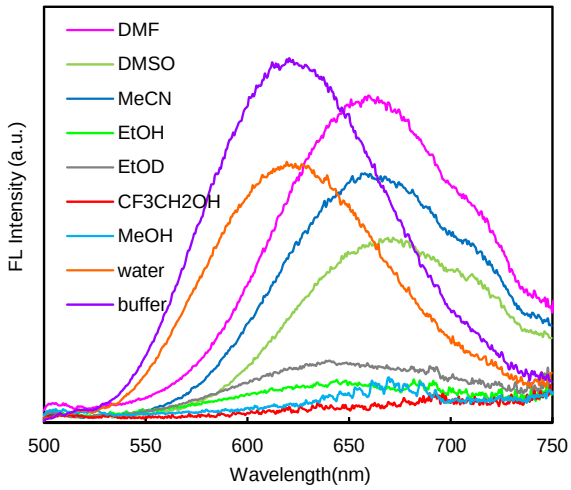


Fig. S6 Fluorescence spectra of **2** in DMF, DMSO, acetonitrile, ethanol, ethanol-d_1, 2,2,2-trifluoroethanol, methanol, water, and phosphate buffer (pH 7.4) (1.0×10^{-6} M) excited at 440 nm.

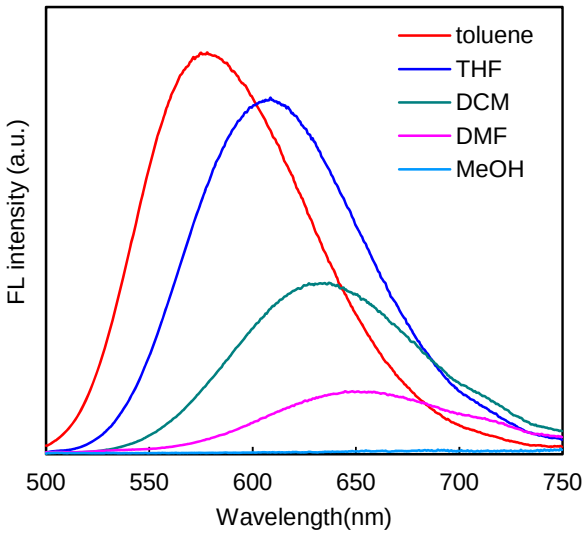


Fig. S7 Fluorescence spectra of **4** in toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-6} M) excited at 440 nm.

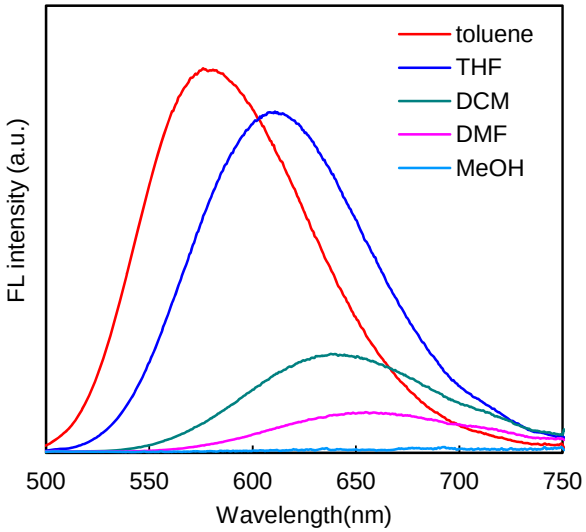


Fig. S8 Fluorescence spectra of **6** in toluene, THF, dichloromethane, DMF, and methanol (1.0×10^{-6} M) excited at 440 nm.

Fig. S9 Fluorescence images of **1** in cyclohexane, toluene, THF, dichloromethane, DMF, and methanol (from left to right) at 1.0×10^{-5} M under UV light irradiation.

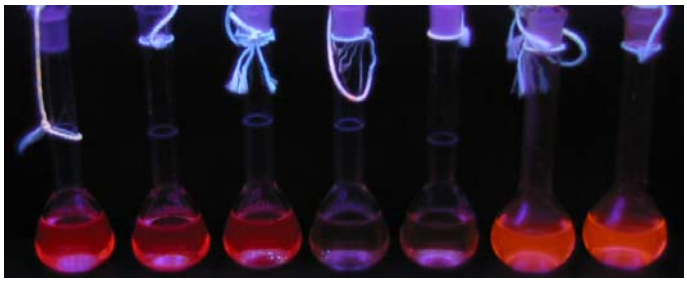


Fig. S10 Fluorescence images of **2** in polar solvents (DMF, DMSO, acetonitrile, ethanol, ethanol-d_1, water, and phosphate buffer (pH 7.4), from left to right) at 1.0×10^{-5} M under UV light irradiation.

Fig. S11. Fluorescence images of **4** in toluene, THF, dichloromethane, DMF, and methanol (from left to right) at 1.0×10^{-5} M under UV light irradiation.

Fig. S12 Fluorescence images of **6** in toluene, THF, dichloromethane, DMF, and methanol (from left to right) at 1.0×10^{-5} M under UV light irradiation.

Fig. S13. Fluorescence images of **1**, **2**, **4**, and **6** (from left to right) in the bulk state under the UV light irradiation.

Table S1. Spectral data of **1**, **2**, **4**, and **6**.

Comp.	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	$\Delta\lambda$
1	cyclohexane	442	547	0.75	105
	toluene	443	578	0.73	135
	THF	441	611	0.65	170
	dichloromethane	439	637	0.50	198
	DMF	440	655	0.23	215
	methanol	434	640	0.005	206
	bulk	-	610	0.69	
2	cyclohexane	437	544	0.85	107
	toluene	439	575	0.88	136
	THF	436	615	0.77	179
	dichloromethane	437	635	0.53	198
	DMF	435	661	0.19	226
	DMSO	437	669	0.14	232
	acetonitrile	427	660	0.15	233
	ethanol	436	642	0.014	206
	ethanol-d_1	436	642	0.025	206
	methanol	433	647	0.005	214
	2,2,2-trifluroroethanol	437	648	0.002	221
	water	444	622	0.20	178
	phosphate buffer (pH 7.4)	444	621	0.21	177
	bulk	-	628	0.67	
4	toluene	443	578	0.94	135
	THF	442	608	0.54	166
	dichloromethane	439	637	0.40	198
	DMF	442	648	0.22	206
	methanol	436	642	0.003	206
	bulk	-	628	0.56	-
6	toluene	441	577	0.81	136
	THF	436	612	0.66	176
	dichloromethane	438	640	0.23	202
	DMF	435	655	0.12	220
	MeOH	431	645	0.003	214
	bulk	-	589	0.10	-

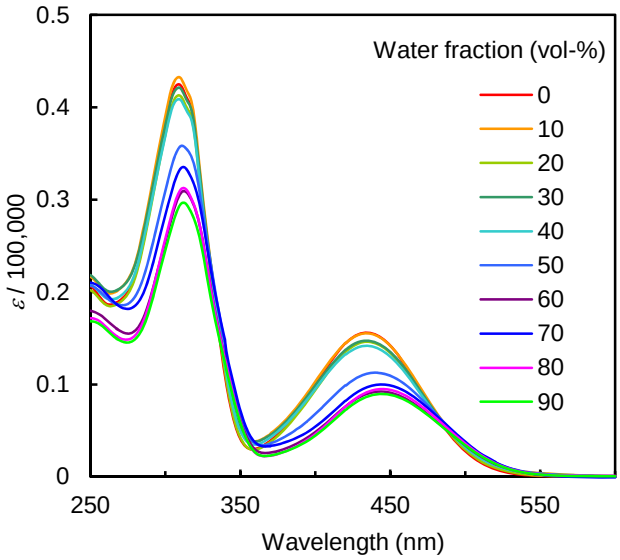


Fig. S14 UV/Vis spectra of **1** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M.

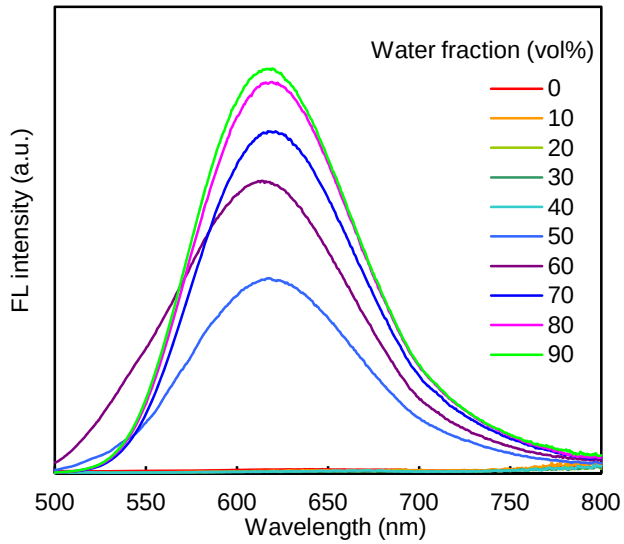


Fig. S15 Fluorescence spectra of **1** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M exited at 440 nm.

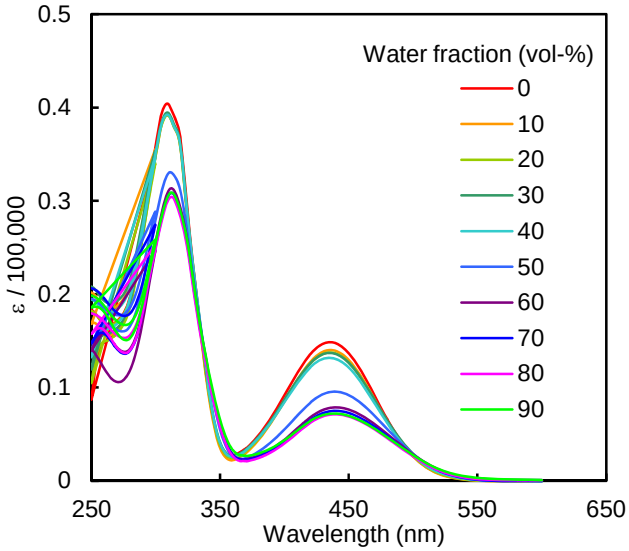


Fig. S16 UV/Vis spectra of **4** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M.

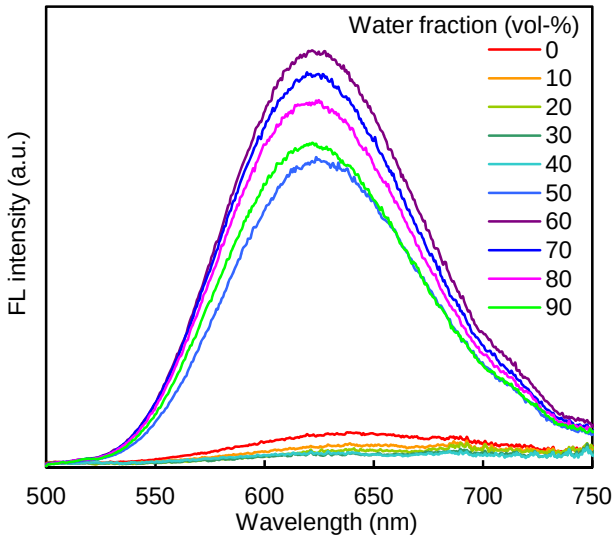


Fig. S17 Fluorescence spectra of **4** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M exited at 440 nm.

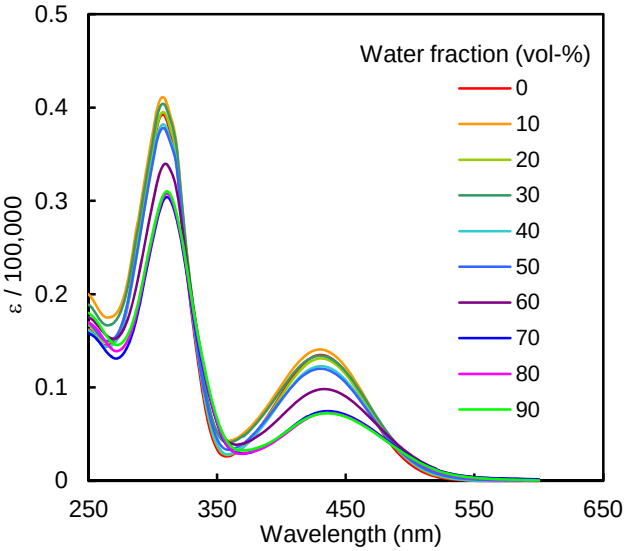


Fig. S18 UV/Vis spectra of **6** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M.

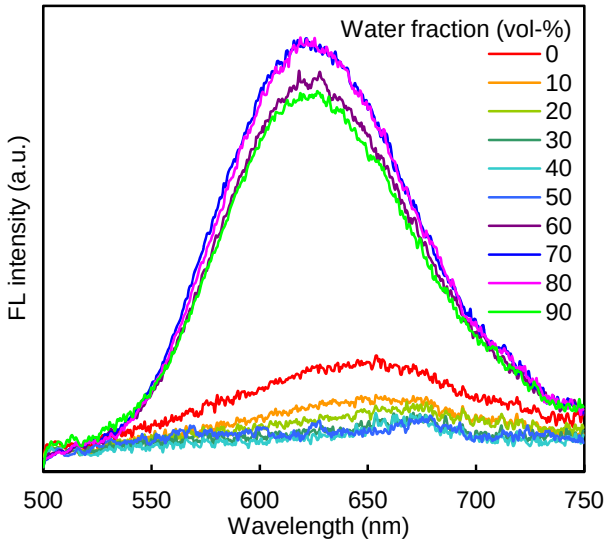


Fig. S19 Fluorescence spectra of **6** in methanol/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9, (v/v)) at 1.0×10^{-5} M exited at 440 nm.

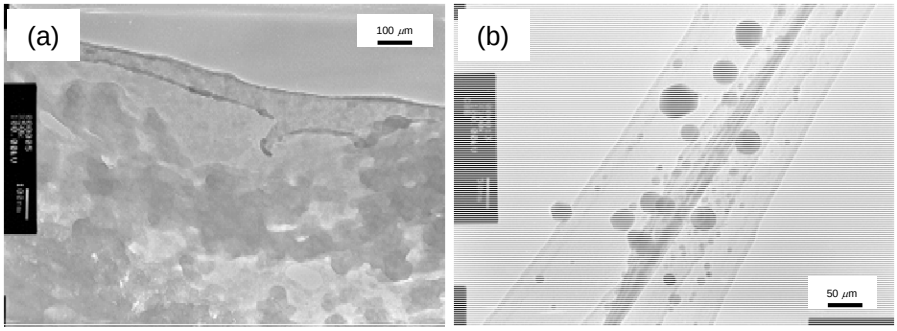


Fig. S20 TEM images of (a) **4** and (b) **6**. The samples were obtained by drop-casting from 1.0×10^{-4} M methanol/water (1:9 (v/v)) solution on carbon-coated copper grid. In **6**, the spherical aggregate with size of 30−50 nm was observed. In **4**, the structural-less aggregate was observed. Probably, the spherical aggregate was re-aggregated and re-formed during the sample preparation process.

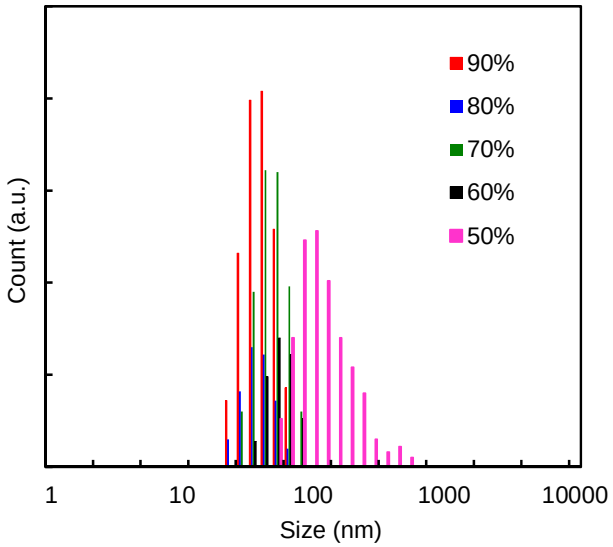


Fig. S21 DLS charts of **1** in methanol/water (50, 60, 70, 80, and 90% water fraction) at 1.0×10^{-5} M. The detected particle sizes are 130 nm (50%), 60 nm (60%), 50 nm (70%), 40 nm (80%), and 40 nm (90%).

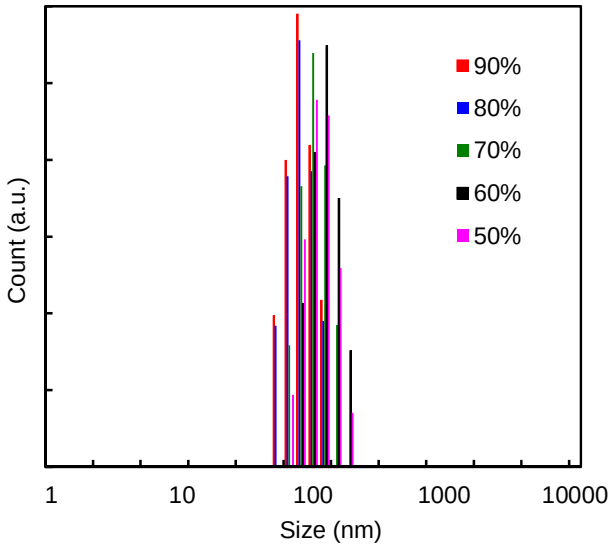


Fig. S22 DLS charts of **4** in methanol/water (50, 60, 70, 80, and 90% water fraction) at 1.0×10^{-5} M. The detected particle sizes are 110 nm (50%), 120 nm (60%), 100 nm (70%), 80 nm (80%), and 80 nm (90%).

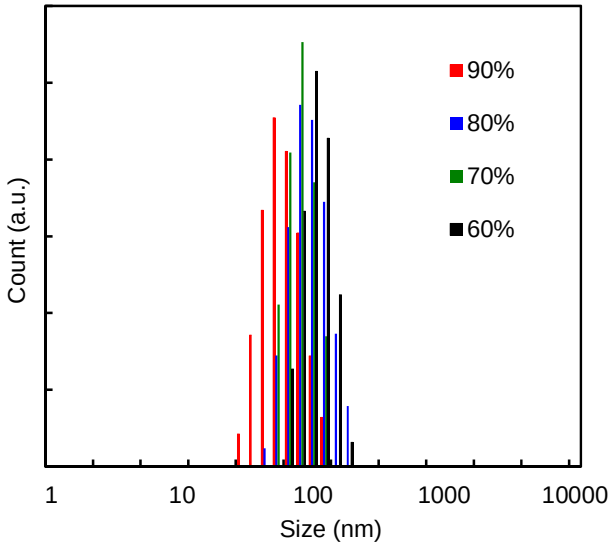


Fig. S23 DLS charts of **6** in methanol/water (60, 70, 80, and 90% water fraction) at 1.0×10^{-5} M. The detected particle sizes are 110 nm (60%), 80 nm (70%), 100 nm (80%), and 60 nm (90%).

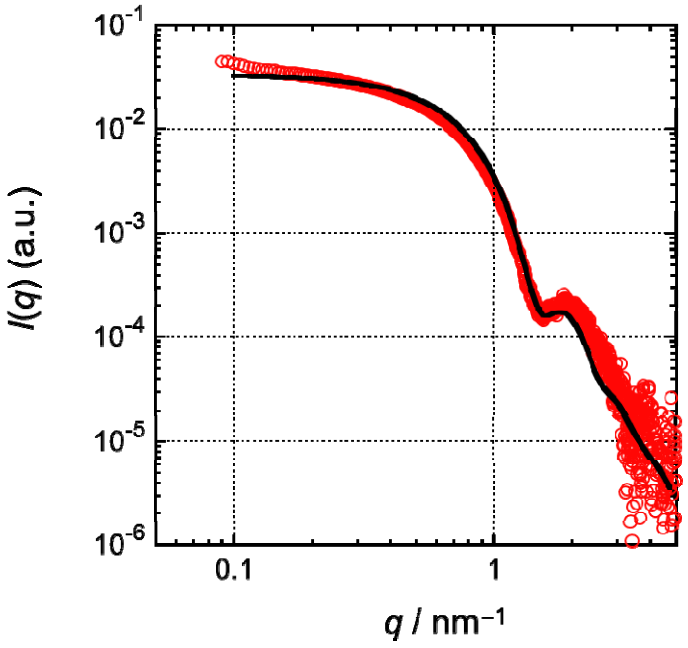


Fig. S24 Small-angle X-ray scattering profile of **2** in water at 1.0×10^{-5} M.

The analysis of the profile revealed a formation of micellar-type aggregate with a diameter of ca. 5.7 nm (shown with a solid line). The size of the micellar-type aggregate coincides with a model predicted from the molecular size (extended molecular size of ca. 4 nm and aromatic core size of ca. 1.7 nm).

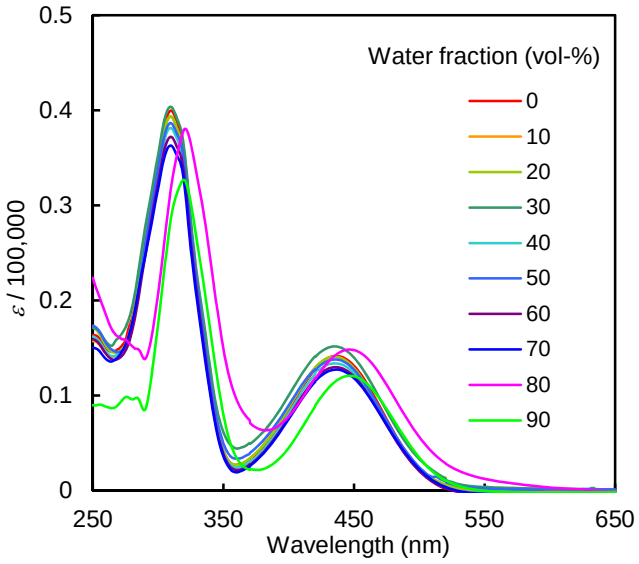


Fig. S25 UV/Vis spectra of **6** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 (v/v)) at 1.0×10^{-5} M.

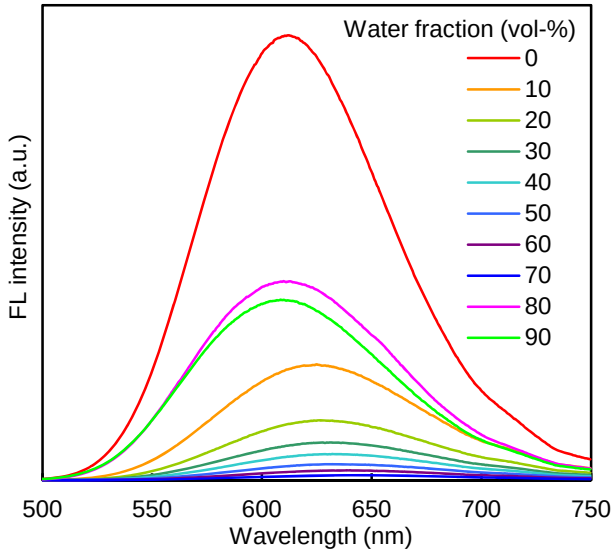


Fig. S26 Fluorescence spectra of **6** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 (v/v)) at 1.0×10^{-5} M exited at 440 nm.

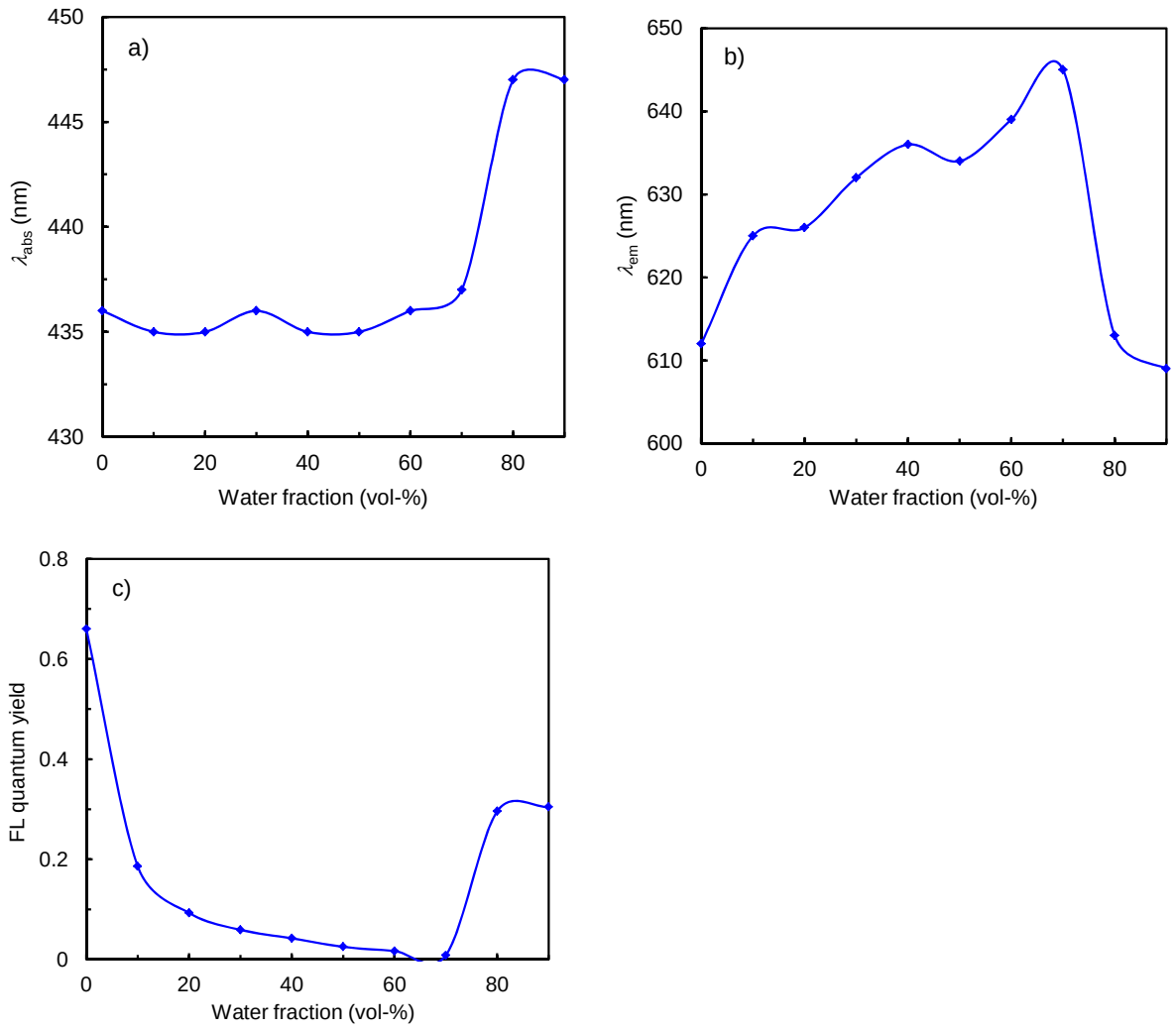


Fig. S27 Plots of (a) the absorption band, (b) the fluorescence band, and (c) the fluorescence quantum yield versus the water fraction of **6** in THF/water at 1.0×10^{-5} M.

Fig. S28 Fluorescence images of **6** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 (v/v), from left to right) at 1.0×10^{-5} M under UV light irradiation.

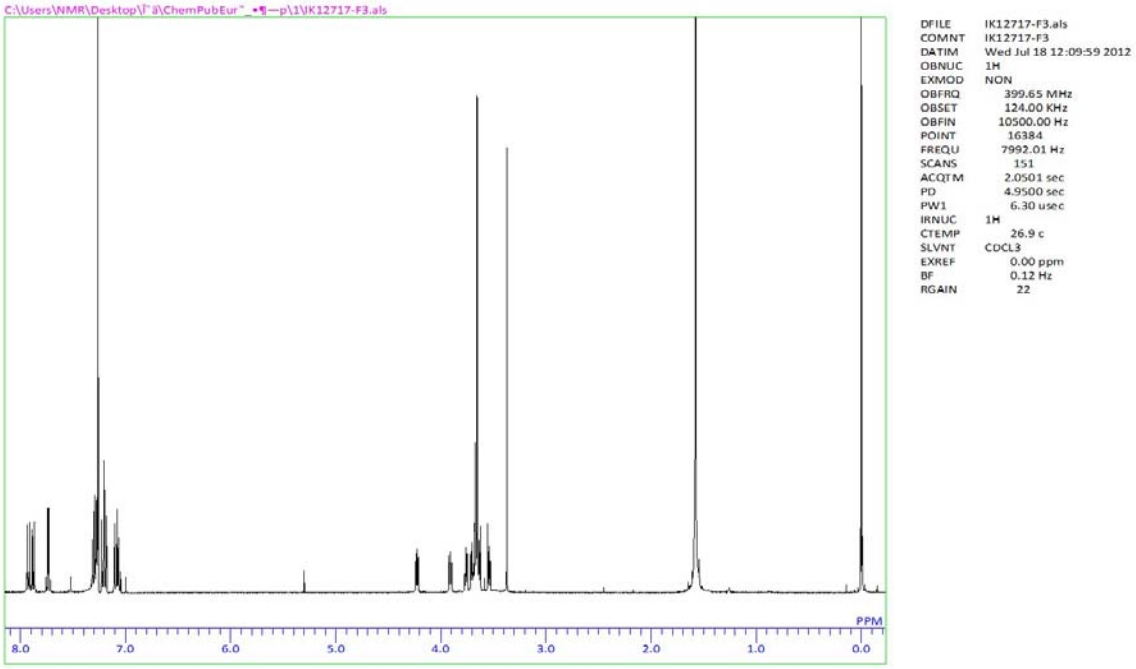
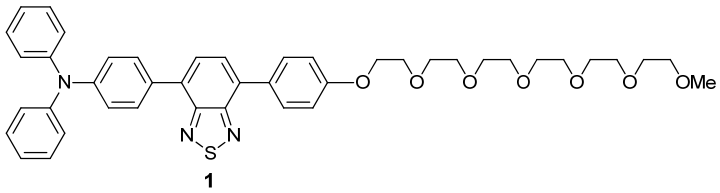


Fig. S29 ^{1}H NMR spectrum of **1** in $CDCl_3$.



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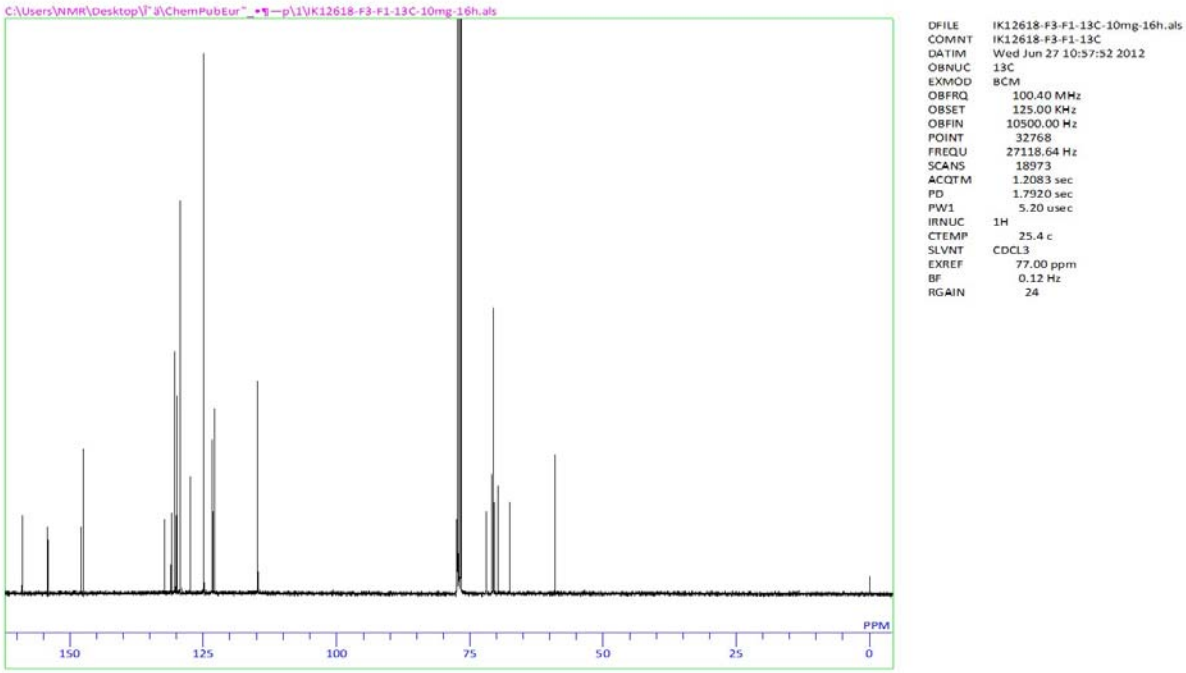


Fig. S30 ^{13}C NMR spectrum of **1** in $CDCl_3$.

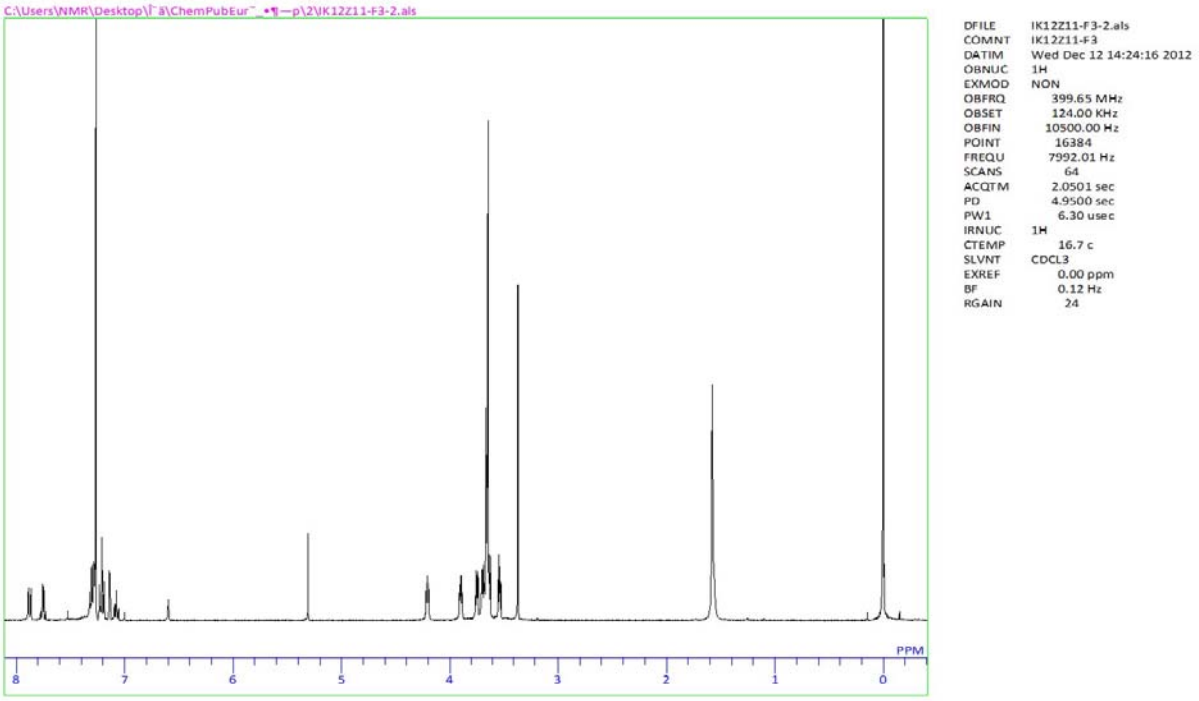
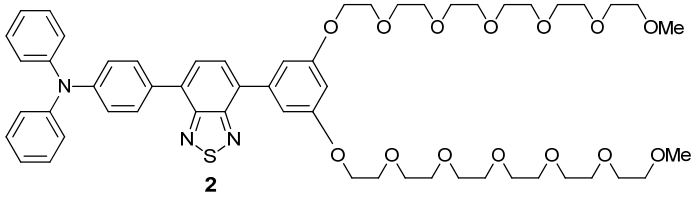


Fig. S31 ^{1}H NMR spectrum of **2** in $CDCl_3$.



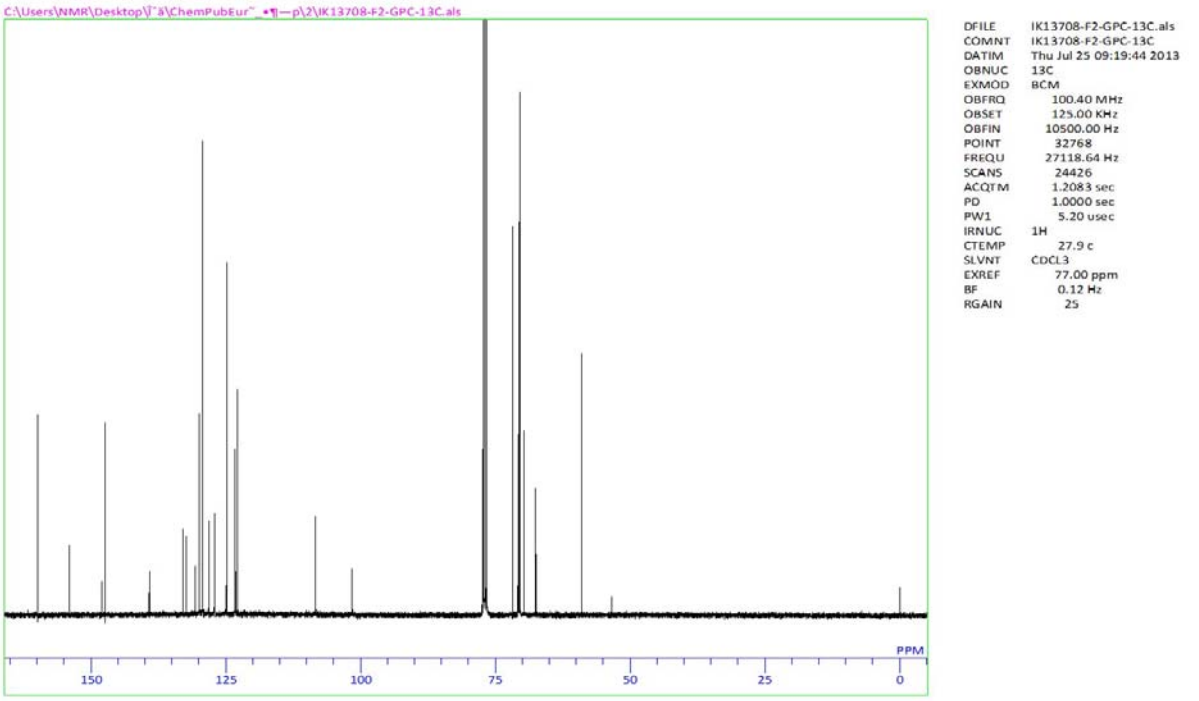


Fig. S32 ^{13}C NMR spectrum of **2** in $CDCl_3$.

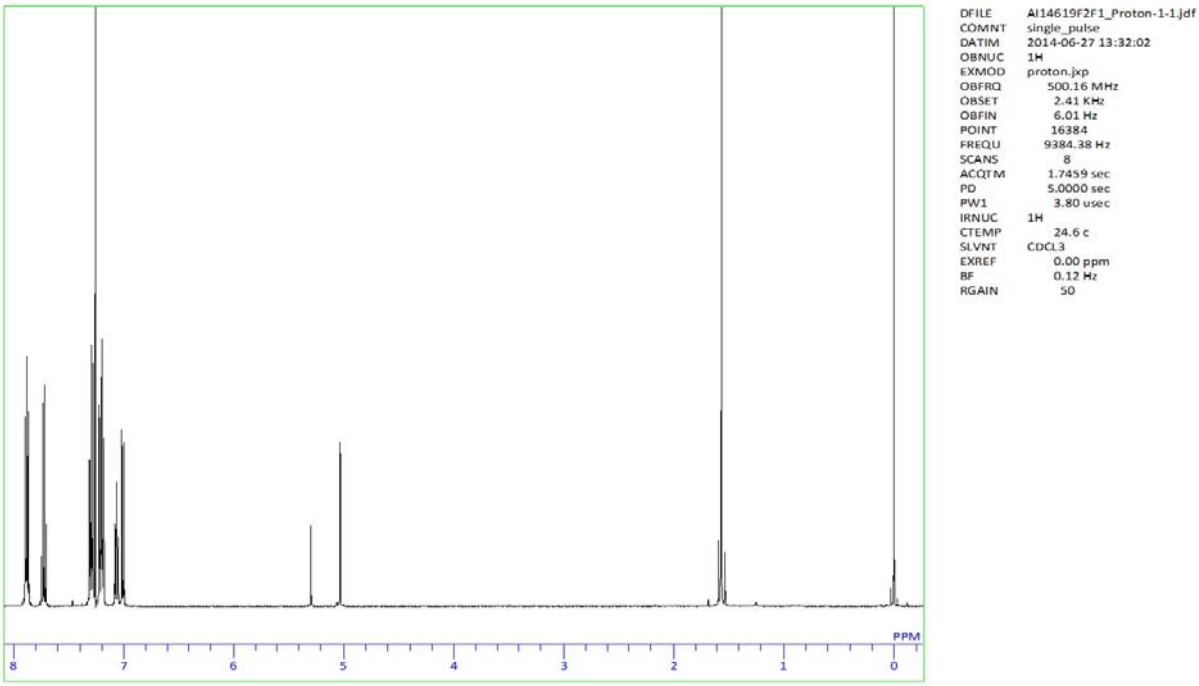
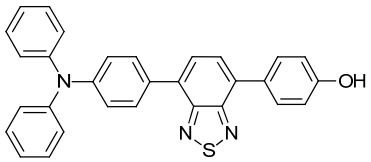


Fig. S33 ^{1}H NMR spectrum of **4** in $CDCl_3$.



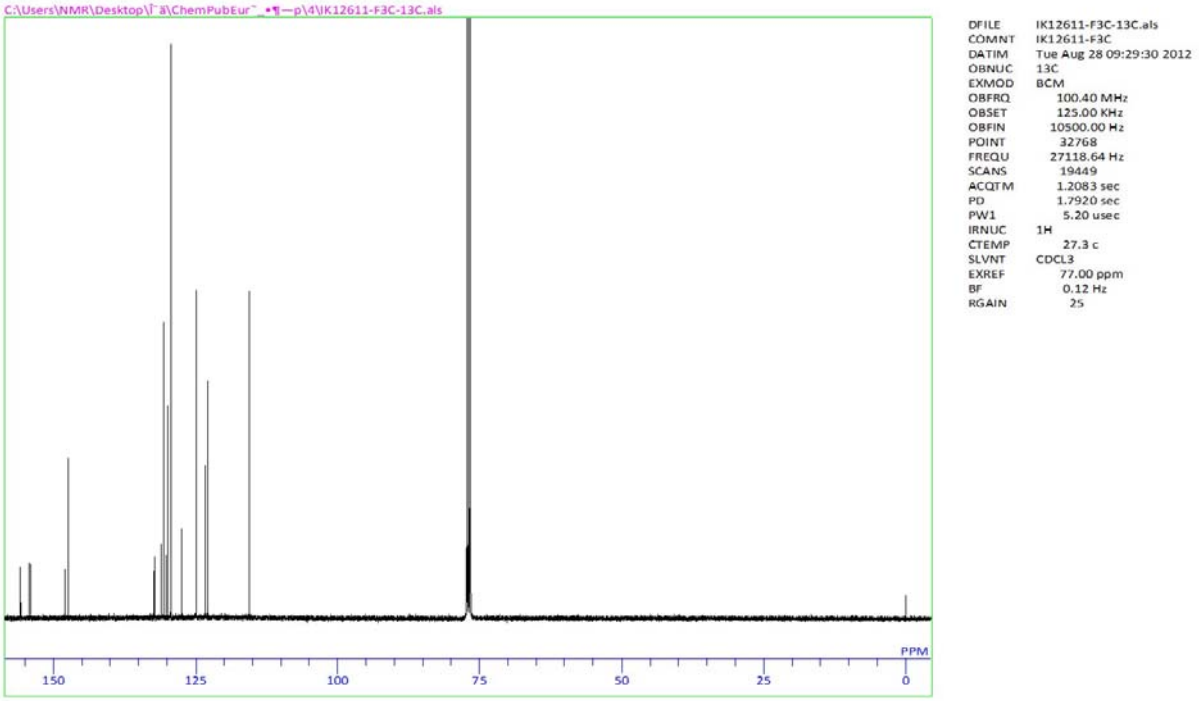


Fig. S34 ^{13}C NMR spectrum of **4** in $CDCl_3$.

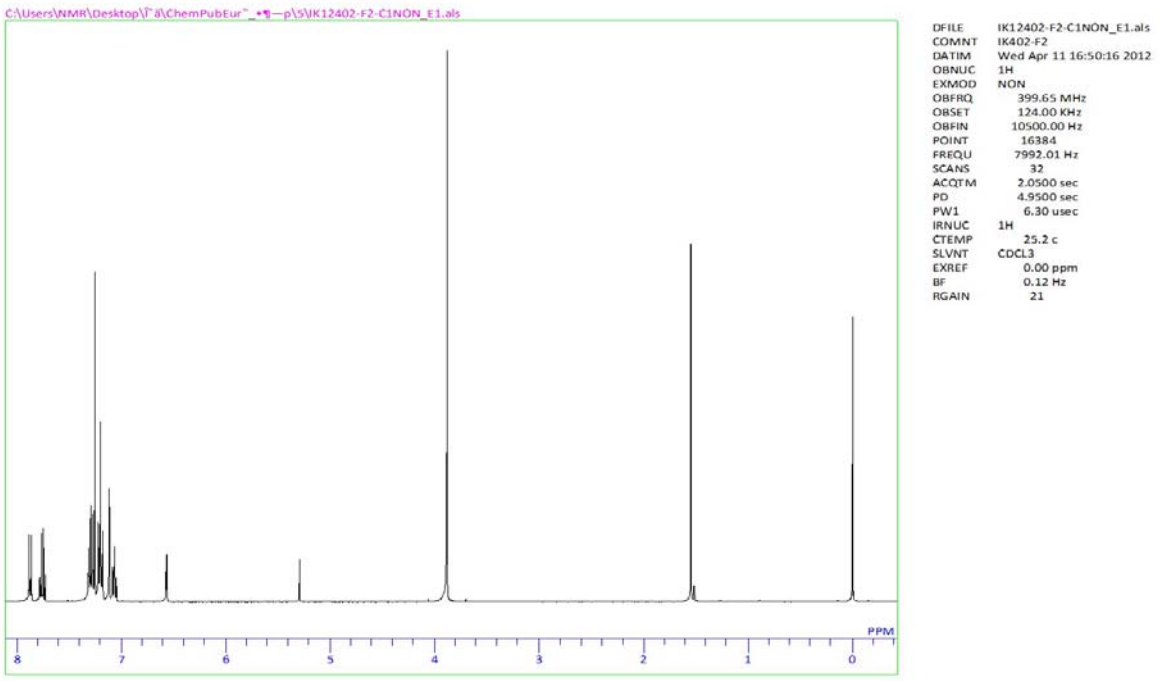
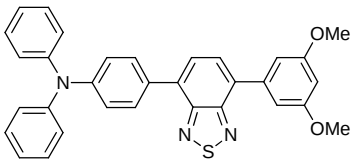


Fig. S35 ^{1}H NMR spectrum of **5** in $CDCl_3$.



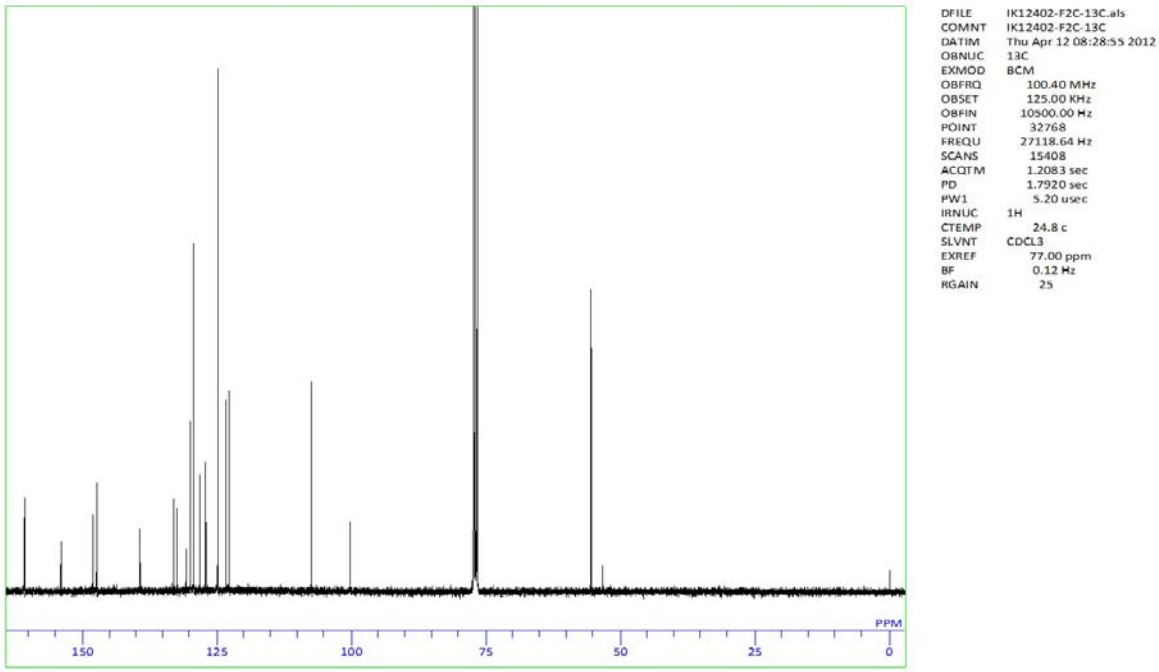


Fig. S36 ^{13}C NMR spectrum of **5** in $CDCl_3$.

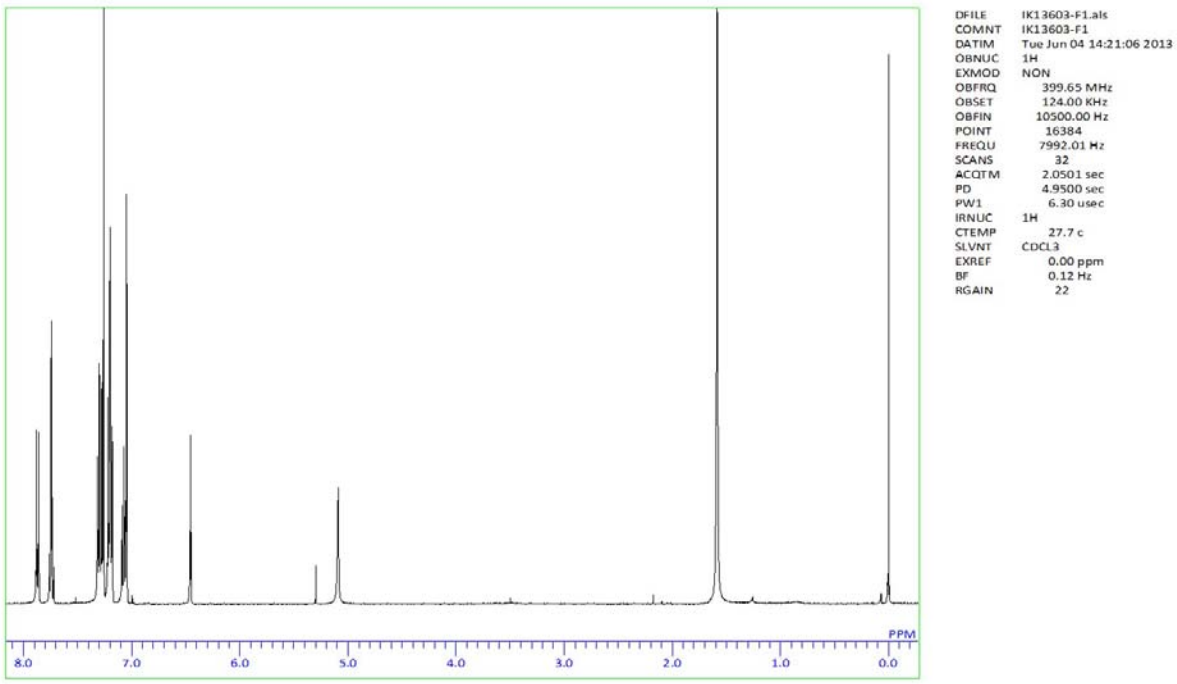
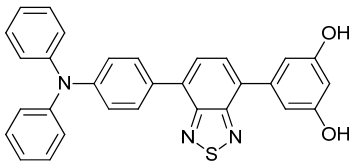


Fig. S37 ^{1}H NMR spectrum of **6** in $CDCl_3$.



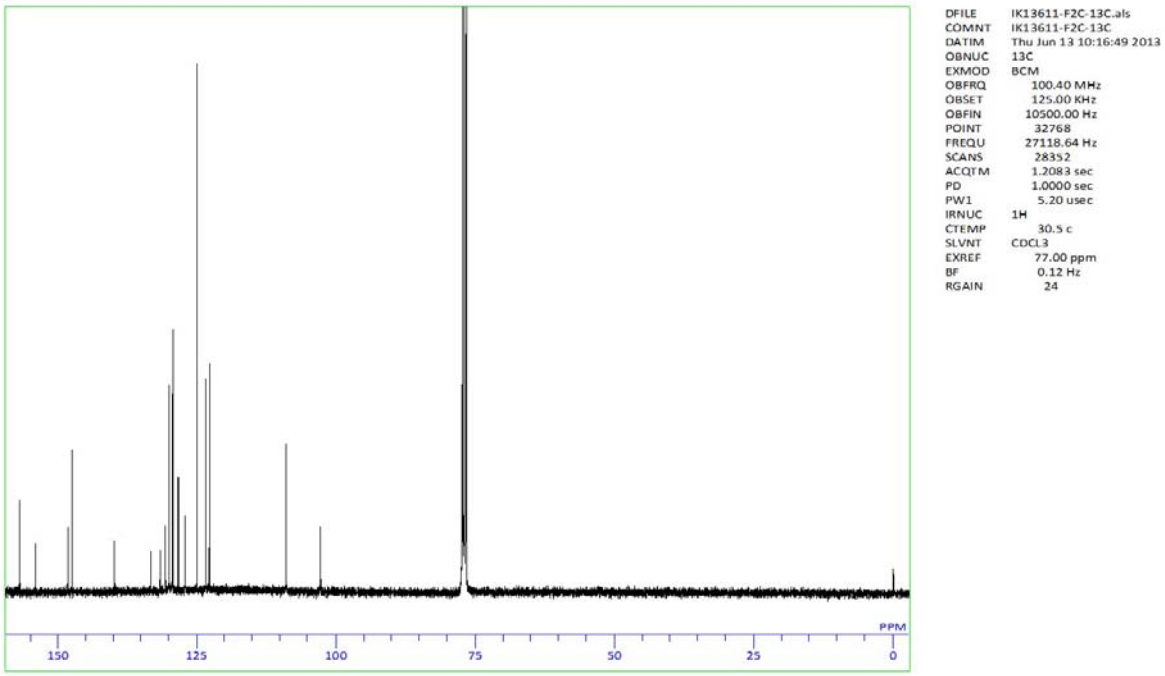


Fig. S38 ^{13}C NMR spectrum of **6** in $CDCl_3$.