Ethynyl-Capped Hyperbranched Conjugated Polytriazole: Click Polymerization, Clickable Modification, and Aggregation-Enhanced Emission

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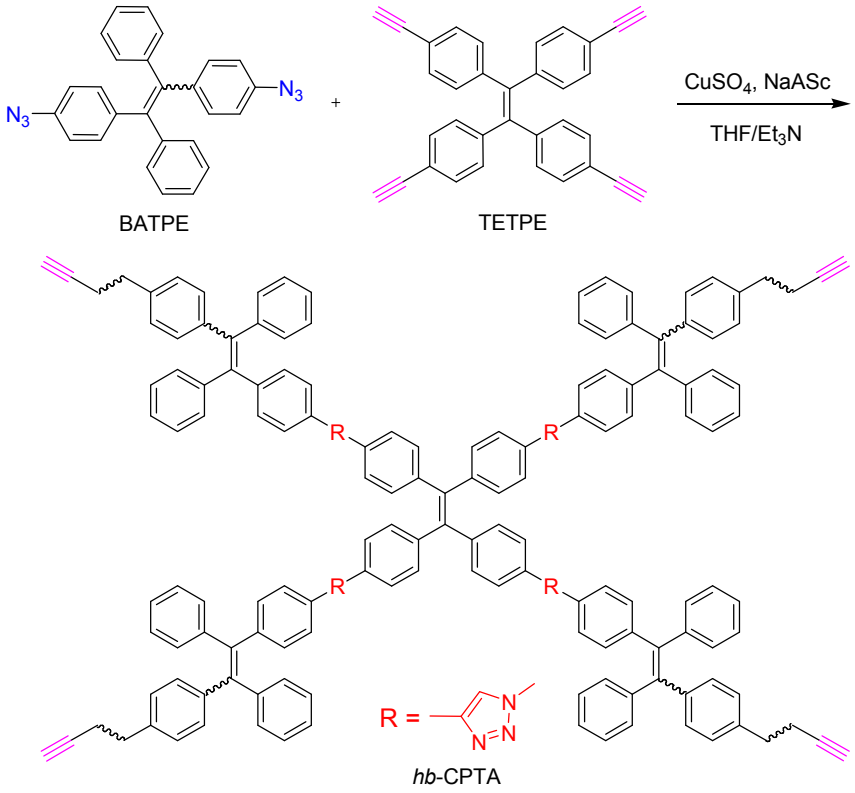
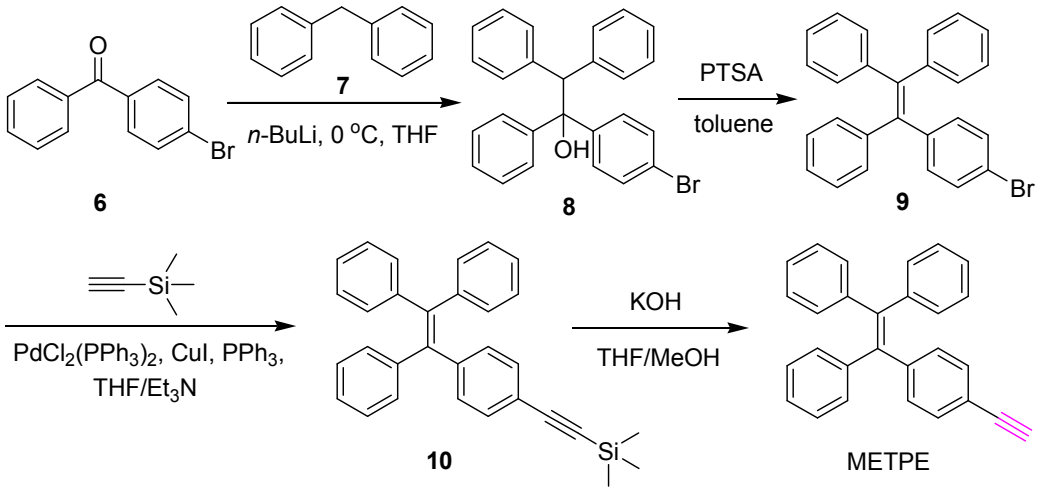
Contents

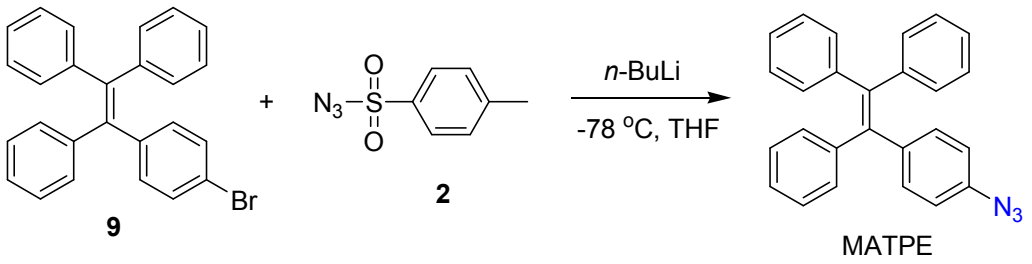
Figure S10. TEM images of (A) *hb*-CPTA, (B) *hb*-CPTA-A, and (C) *hb*-CPTA-T. Samples prepared from their chloroform solution directly, concentration: 1.0 μg/mL. (14)



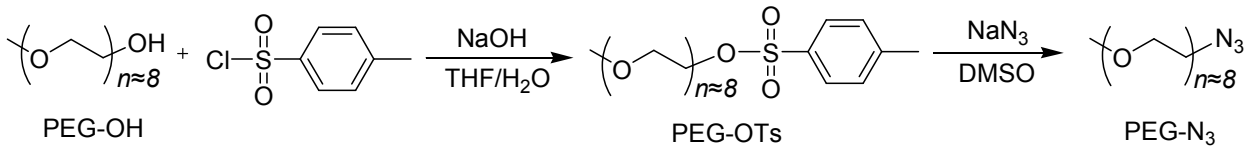
Scheme S1. Synthetic route to hyperbranched conjugated polytrizaole (*hb*-CPTA) by Cu(I)-catalyzed click polymerization of BATPE and TETPE. NaASc = sodium ascorbate.



Scheme S2. Synthtic route to monoazide METPE. PTSA = *p*-toluenesulfonic acid.



Scheme S3. Synthetic route to monoyne MATPE.



Scheme S4. Synthetic routes to monoazide-functionalized polyethylene glycol (PEG-N_3).

Preparetion of Monoazide-Functionalized Polyethylene Glycol (PEG-N_3).

The synthetic routes to the monoazide-functionalized polyethylene glycol (PEG-N_3) were shown in Scheme S2.

Into a 250 mL round-bottom flask was placed polyethylene glycol monomethylether (PEG-OH) with an average molecular weight of 350 (3.5 g, about 10 mmol) and THF (20 mL). After 3.2 g of NaOH dissolved in 10 mL water was added under stirring, the mixture was cooled to 0 ^{o}C. Then *p*-toluenesulfonyl chloride (Ts-Cl, 2.383 g, 12.5 mmol) dissolved in 30 mL THF was added into the flask dropwise in 30 min. The resultant mixture was allowed to warm to room temperature and stirred overnight. After neutralized by 6 M HCl, the mixture was extracted by DCM and the combined organic layer was washed with water and brine, and dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using ethyl acetate to acetone as eluents. Colorless liquid of PEG-OTs was obtained in 84.5% yield (4.259 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.62 (d, 2H), 7.19 (d, 2H), 3.98 (t, 2H), 3.52~3.38 (m, 28H), 3.21 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ (ppm): 144.6, 132.6, 129.6, 127.7, 71.6, 70.4, 70.3~70.2, 69.1, 68.4, 58.8, 21.4.

Into a 100 mL round-bottom flask was placed PEG-OTs (4.032 g, 8 mmol) and NaN_3 (0.65g, 10 mmol). DMSO (30 mL) was then added into the flask. After the reaction mixture was stirred at room temperature overnight, 50 mL water was added and the mixture was extracted by diethyl ether five times. The organic phases were combined and washed with brine and water, and then dried over $MgSO_4$ for an hour. The filtrate was concentrated by a rotary evaporator and the product was dried in a vacuun oven at 30 ^oC to a constant weight. Colorless liquid of PEG-N_3 was obtained in 53.7% yield (1.611 g). IR (KBr) ν (cm^{-1}): 2870, 2108 (N≡N), 1452, 1300, 1115, 943, 852. ^1H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 3.55~3.40 (m, 28H), 3.26 (d, 2H), 3.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 71.6, 70.4~70.3, 70.2, 69.7, 58.7, 50.4.

Synthesis of Starting Materials for Model Compounds.

4-Methylbenzenesulfonyl azide (2). Into a 500 mL round-bottom flask was added sodium azide (1.431 g, 22 mmol) and a mixture of ethanol/water (57 mL/3 mL). After the solid was completely dissolved, *p*-toluenesulfonyl chloride (3.813 g, 20 mmol) dissolved in 100 mL acetone was added into the flask. The mixture was stirred at room temperature overnight with a large amount of white precipitate appeared. After filtration and solvent evaporation, the organic layer was diluted with DCM, washed with water three times, and then dried over $MgSO_4$ for an hour. The filtrate was concentrated by a rotary evaporator and the product was dried in a vacuun oven at 30 ^oC to a constant weight. Colorless liquid of **2** was obtained in 92.7% yield (3.656 g). ^1H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.81 (d, 2H), 7.38 (d, 2H), 2.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.5, 135.7, 130.5, 127.7, 21.9.

1-(4-Bromophenyl)-1,2,2-triphenylethene (9). Into a 250 mL two-necked round-bottom flask was added diphenylmethane (**7**, 3.7 g, 22 mmol). After being evacuated and refilled with nitrogen three times, THF (40 mL) was injected. The mixture was cooled down to 0 ^oC, into which *n*-BuLi (13.75 mL, 22 mmol, 1.6 M in hexane) was added dropwise. The resultant red solution was stirred at 0 ^oC for 1 h, then 4-bromobenzophenone (**6**, 5.222 g, 20 mmol) dissolved

in 10 mL THF was added slowly. The reaction mixture was warmed up to room temperature and quenched by addition of a saturated NH_4Cl solution after reacting for 6 h. The crude product was extracted by DCM and the combined organic layer was washed with water and brine, and dried over $MgSO_4$. After solvent evaporation, the obtained solid was washed with hexane five times upon suction filtration to remove the residue of **7**. White solid of alcohol **8** was obtained in 78.3% yield (6.724 g), which was directly subjected to acid-catalyzed dehydration.

Into a 100 mL round-bottom flask was placed the obtained alcohol **8** and a catalytic amount of *p*-toluenesulfonic acid. Toluene (20 mL) was added to the flask and the mixture was refluxed overnight. After cooled to room temperature, the toluene was evaporated and the crude product was purified by a silica gel column using petroleum ether as eluent. White powder of **9** was obtained in total 67.9% yield (5.585 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.22 (d, 2H), 7.10 (m, 9H), 7.01 (m, 6H), 6.90 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 143.6, 143.5, 143.4, 142.9, 141.8, 139.9, 133.2, 131.5~131.4, 131.1, 128.1, 128.0, 127.9, 126.9~126.8, 120.6.

1-[4-(2-Trimethylsilylethynyl)phenyl]-1,2,2-triphenylethene (10). Into a 250 mL round-bottom flask was added $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol), CuI (38.1 mg, 0.2 mmol), PPh_3 (78.7 mg, 0.3 mmol), **9** (2.057 g, 5 mmol), and a mixture of THF/TEA/piperidine (5:4:1 v/v/v) (100 mL) under nitrogen. After the catalysts were completely dissolved, trimethylsiylacetylene (0.85 mL, 6 mmol) was injected into the flask. After stirred at 50 ^{o}C for 24 h, the formed solid was removed by filtration and washed with diethyl ether. The filtrate was concentrated by a rotary evaporator and the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of **10** was obtained in 94.7% yield (2.03 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.21 (d, 2H), 7.10 (m, 9H), 7.01 (m, 6H), 6.96 (d, 2H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.5, 143.7, 143.6, 143.5, 141.9, 140.5, 131.6, 131.5, 131.45, 128.0, 127.94, 127.9, 126.9~126.8, 121.1, 105.5, 94.5, 0.2.

1-(4-Ethynylphenyl)-1,2,2-triphenylethene (METPE). Into a 250 mL round-bottom flask was placed **10** (1.715 g, 4 mmol) and THF (50 mL). Then KOH (0.898 g, 16 mmol) dissolved in methanol (25 mL) was added. The mixture was stirred at room temperature overnight. After most

of the solvent was evaporated, 1M HCl solution (20 mL) was added, then extracted by DCM three times. The organic layer was combined and washed with water and brine, and then dried over $MgSO_4$ for an hour. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of METPE was obtained in 91.7% yield (1.307 g). IR (KBr) ν (cm^{-1}): 3287 (≡C-H stretching), 3024, 2106 (C≡C stretching), 1594, 1493, 1380, 1074, 765, 699, 624. ^{1}H NMR (500 MHz, $CDCl_3$) δ (TMS, ppm): 7.24 (d, 2H), 7.11 (m, 9H), 7.02 (m, 8H), 3.05 (s, 1H, HC≡). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 144.6, 143.6, 143.5, 143.4, 141.9, 140.2, 131.6~131.4, 128.0, 127.9, 127.8, 126.8~126.7, 120.0, 83.9 (≡C-Ar), 77.4 (≡C-H).

1-(4-Azidophenyl)-1,2,2-triphenylethene (MATPE). Into a 250 mL round-bottom flask was placed **9** (1.028 g, 2.5 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After THF (20 mL) was added, the solution was cooled down to -78 ^{o}C, into which *n*-BuLi (1.72 mL, 2.75 mmol, 1.6 M in hexane) was added dropwise. The mixture was kept at -78 ^{o}C for 1 h, then 0.543 g (2.75 mmol) of 4-methylbenzenesulfonyl azide (**5**) dissolved in 5 mL THF was added into the flask dropwise. After reacting at -78 ^{o}C for 1 h, the mixture was warmed slowly to room temperature and stirred overnight. Afterward, saturated NH_4Cl solution (50 mL) was added to stop the reaction. After THF was evaporated, DCM was added to extract the product for three times. The organic layer was combined and washed with water and brine, and then dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of MATPE was obtained in 89.0% yield (0.831 g). IR (KBr) ν (cm^{-1}): 3054, 2120 (azide stretching), 1597, 1499, 1291, 1181, 1115, 824, 754, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ (TMS, ppm): 7.08 (m, 9H), 6.99 (m, 8H), 6.75 (d, 2H, Ar-H proton adjecent to the azide group). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 143.8, 143.6~143.5, 141.3, 140.7, 139.9, 138.0, 132.8, 131.4, 131.3, 127.9, 127.8, 127.7, 126.7, 126.6, 126.5, 118.4.

Table S1. Crystal data and structure refinement for TETPE.

Identification code	TETPE	
Empirical formula	$C_{34}H_{20}$	
Formula weight	428.50	
Temperature	173.00(14) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	I2	
Unit cell dimensions	a = 11.0905(9) Å	α= 90°.
	b = 8.7191(3) Å	β= 93.429(13)°.
	c = 12.8638(16) Å	γ = 90°.
Volume	1241.69(19) $Å^3$	
Z	2	
Density (calculated)	1.146 mg/m^3	
Absorption coefficient	0.494 mm^{-1}	
F(000)	448	
Crystal size	0.4 x 0.32 x 0.28 mm^3	
Theta range for data collection	9.65 to 66.47°.	
Index ranges	-11<= *h* <=13, -10<= *k* <=10, -15<= *l* <=13	
Reflections collected	4296	
Independent reflections	1148 [R(int) = 0.0265]	
Completeness to theta = 66.47°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81145	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1148/1/154	
Goodness-of-fit on F^2	1.003	
Final R indices [$I > 2\text{sigma}(I)$]	R1 = 0.0261, wR2 = 0.0801	
R indices (all data)	R1 = 0.0262, wR2 = 0.0804	
Largest diff. peak and hole	0.107 and -0.098 e.$Å^{-3}$	

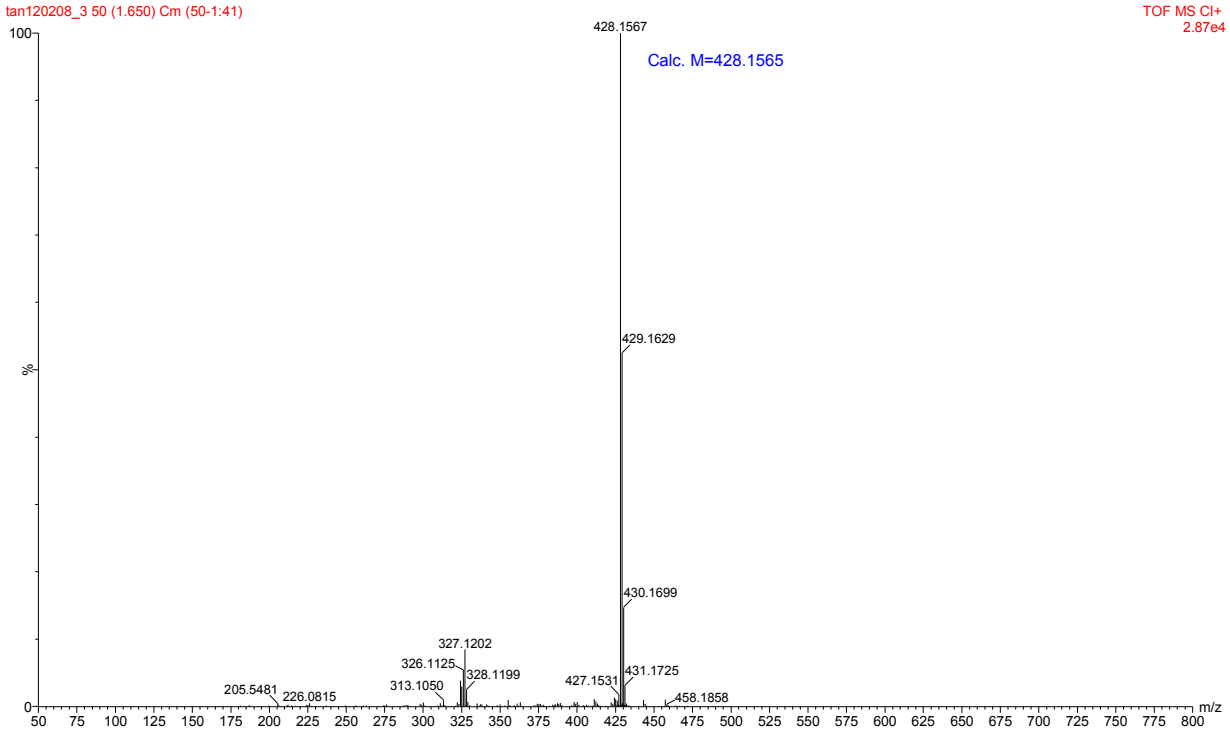


Figure S1. High resolution mass spectrum of TETPE.

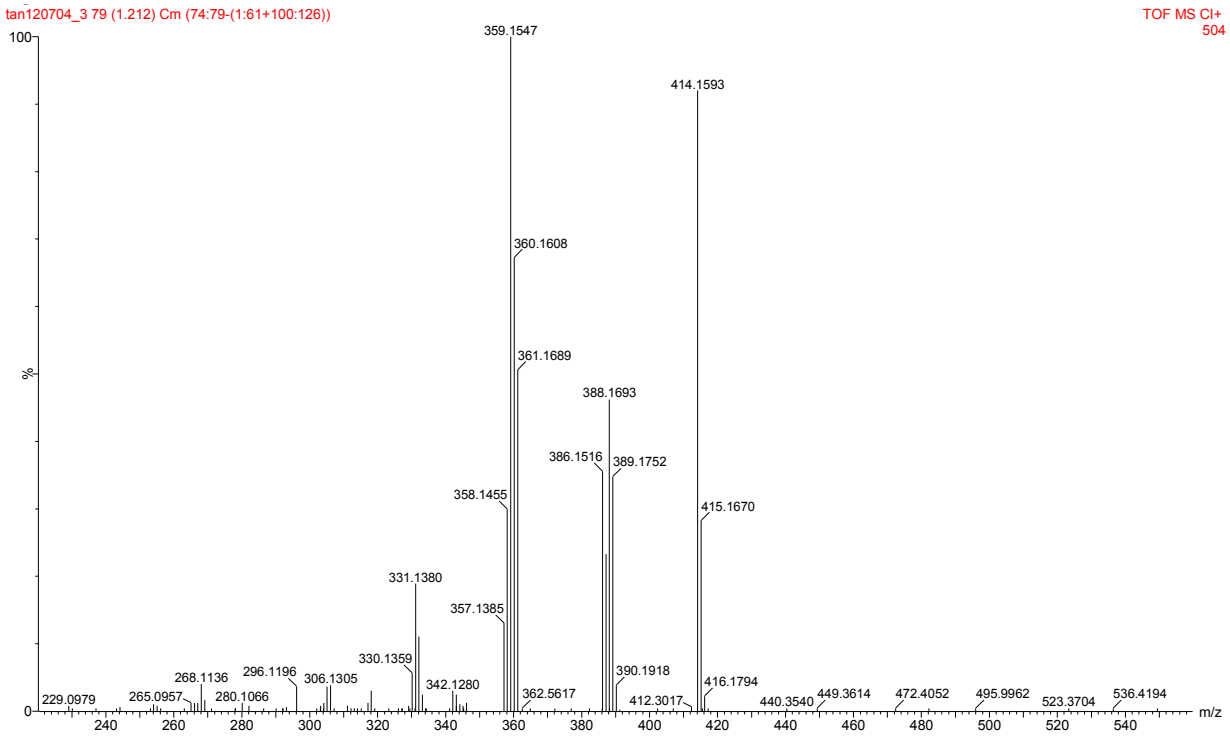


Figure S2. High resolution mass spectrum of BATPE.

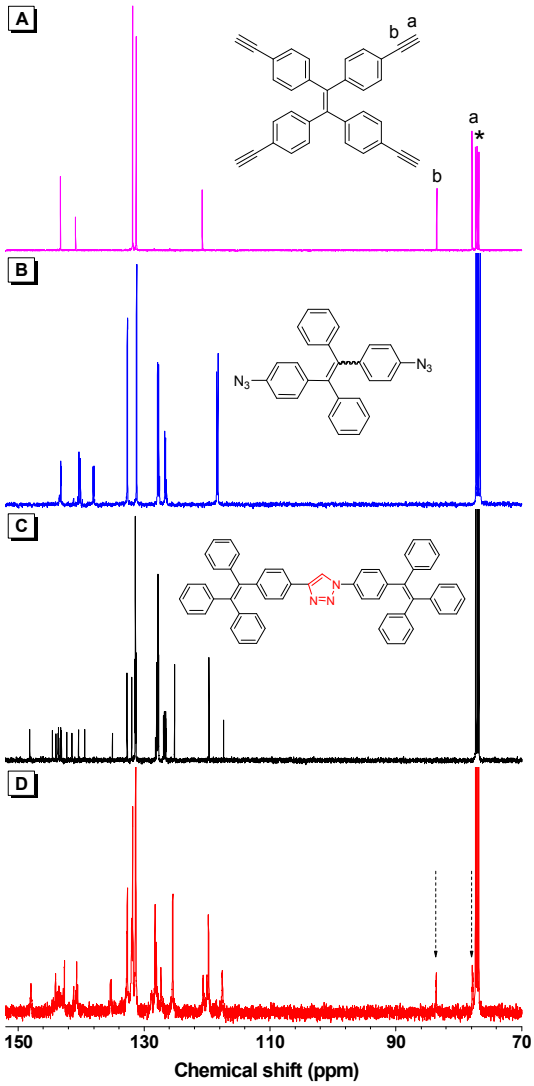


Figure S3. ^{13}C NMR spectra of (A) TETPE, (B) BATPE, (C) M1, and (D) *hb*-CPTA in $CDCl_3$. The solvent peaks are marked with asterisks.

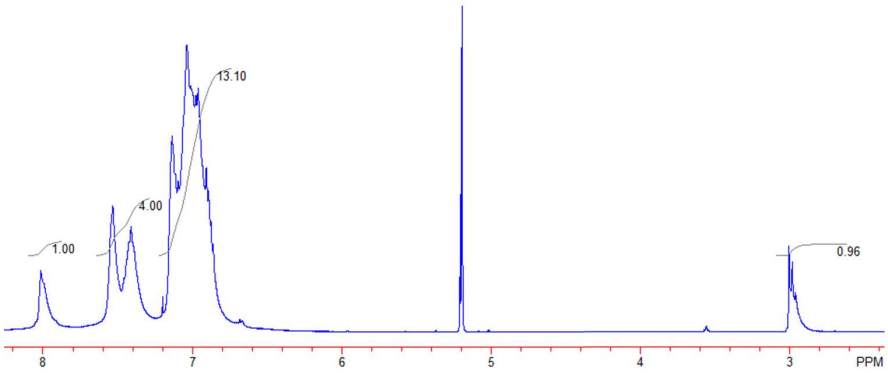


Figure S4. ^{1}H NMR spectra of *hb*-CPTA in DCM-d_2.

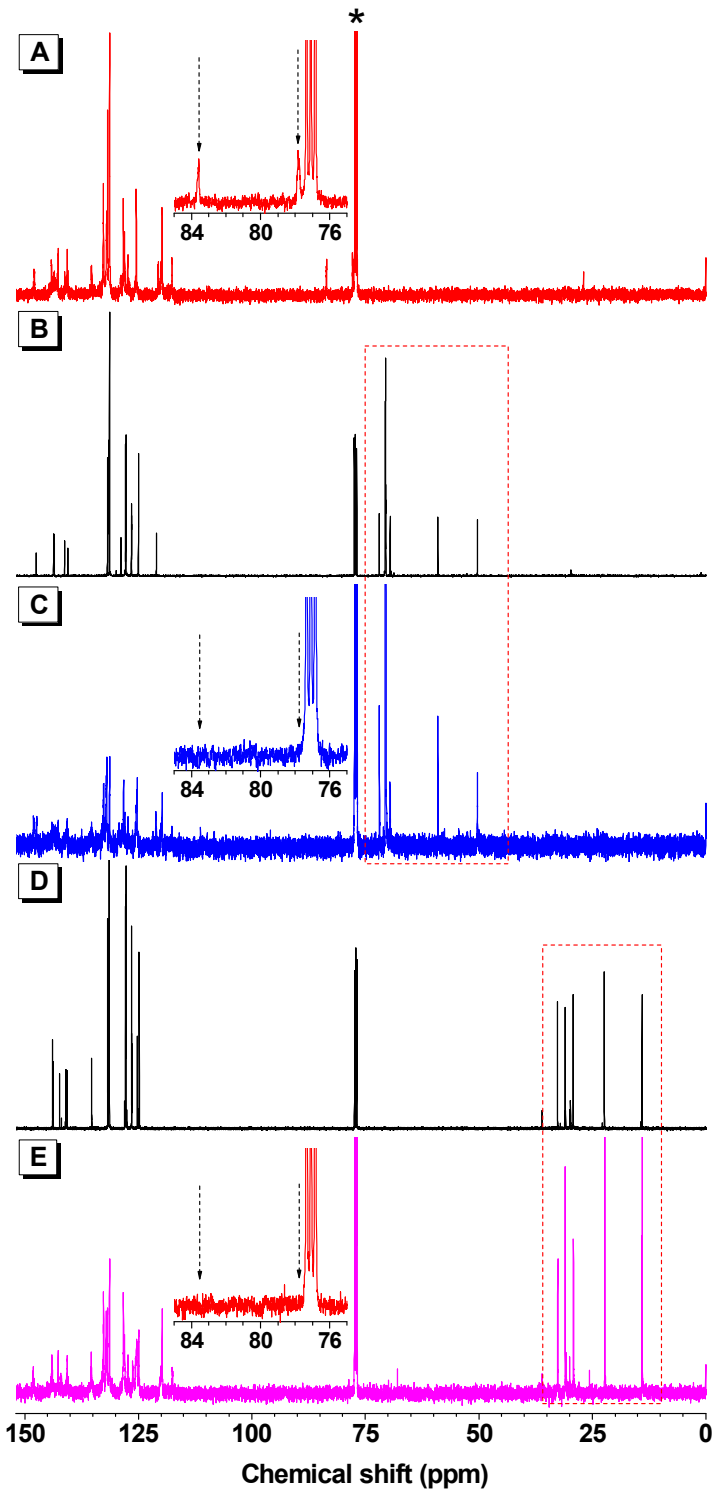


Figure S5. ^{13}C NMR spectra of (A) *hb*-CPTA, (B) M2, (C) *hb*-CPTA-A, (D) M3, and (E) *hb*-CPTA-T in $CDCl_3$. The solvent peaks are marked with asterisks.

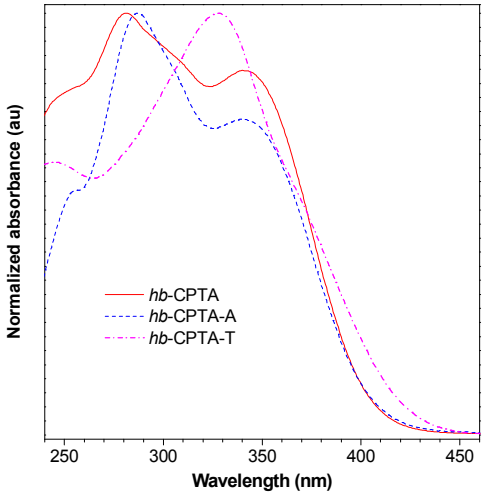


Figure S6. Normalized absorption spectra of *hb*-CPTA, *hb*-CPTA-A, and *hb*-CPTA-T in THF solution. Concentration: 10 μg/mL.

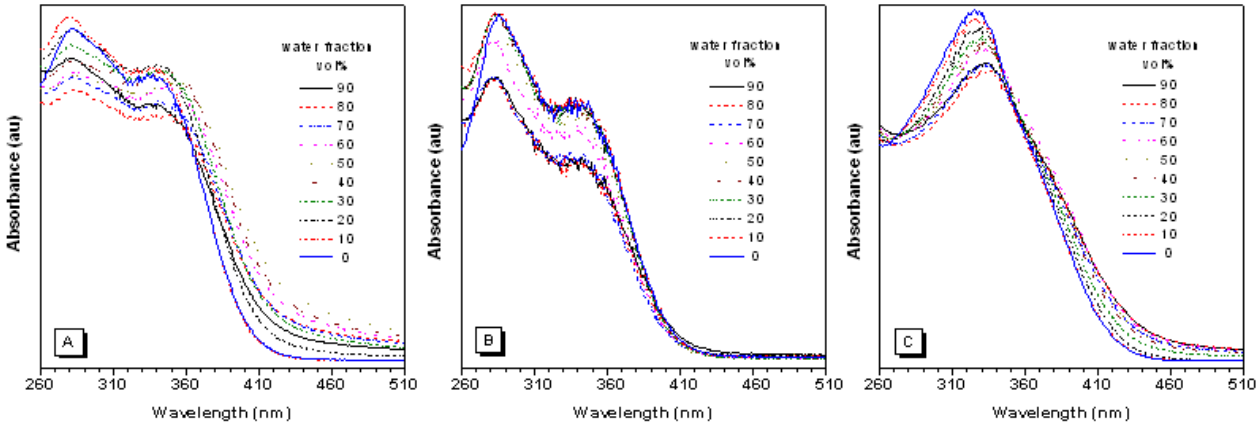


Figure S7. Absorption spectra of (A) *hb*-CPTA, (B) *hb*-CPTA-A, and (C) *hb*-CPTA-T in the THF/water mixtures with different fractions of water. Concentration: 10 μg/mL.

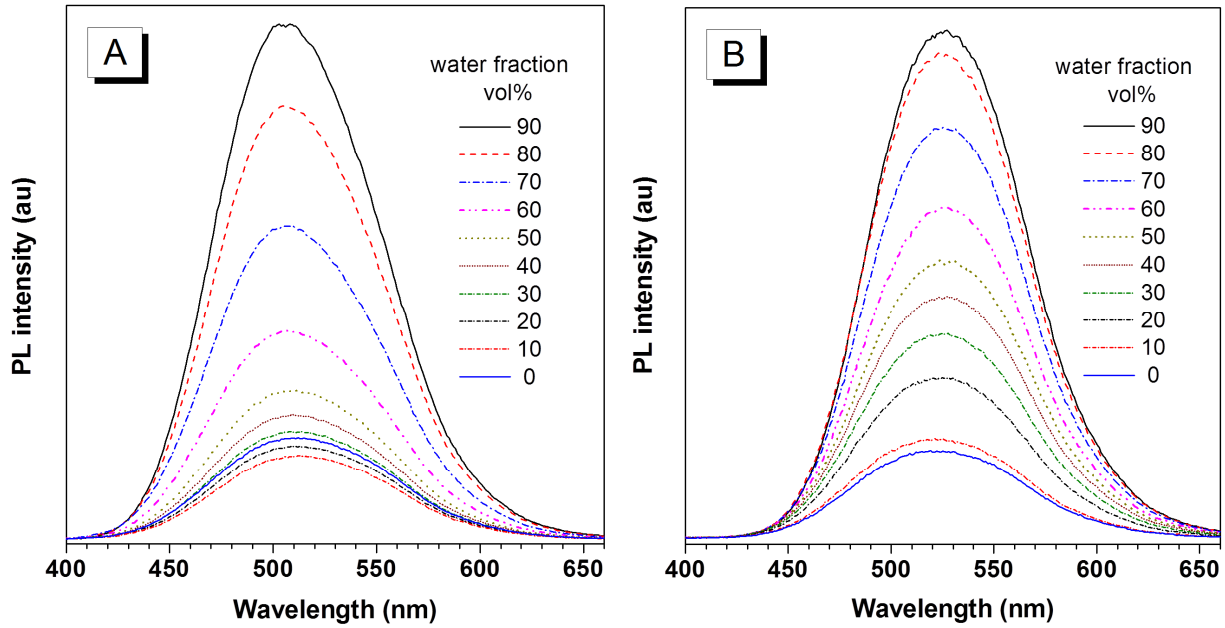


Figure S8. PL spectra of (A) *hb*-CPTA-A and (B) *hb*-CPTA-T in the THF/water mixtures with different fractions of water (f_w). Concentration: 10 μg/mL; excitation wavelength: 340 nm.

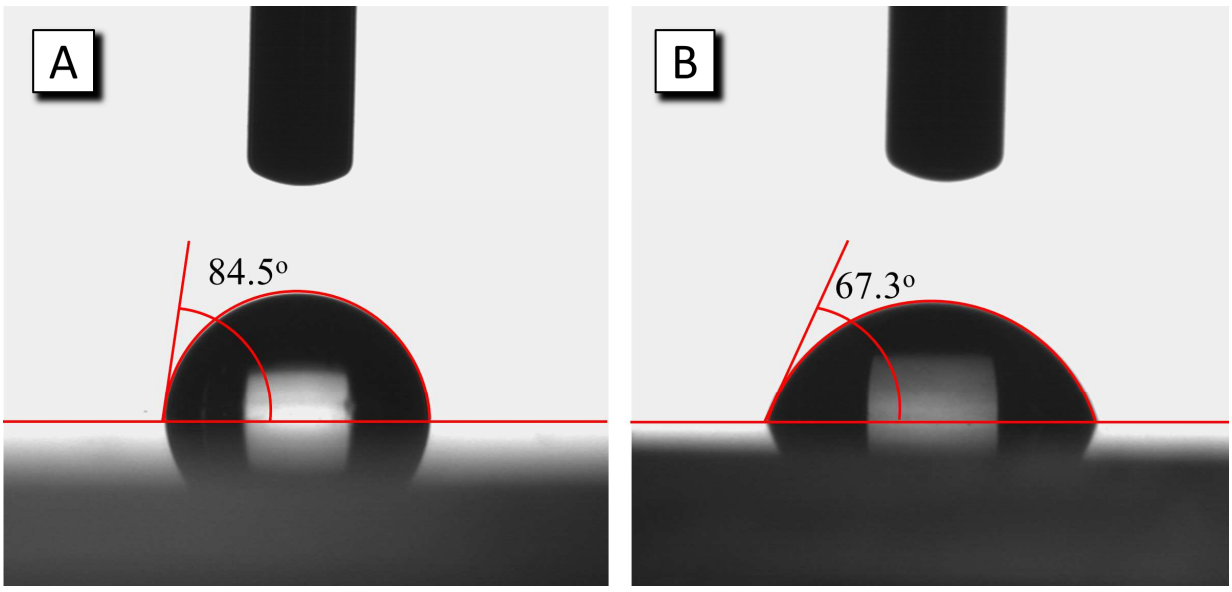


Figure S9. The contact angle images of the films of (A) *hb*-CPTA and (B) *hb*-CPTA-A.

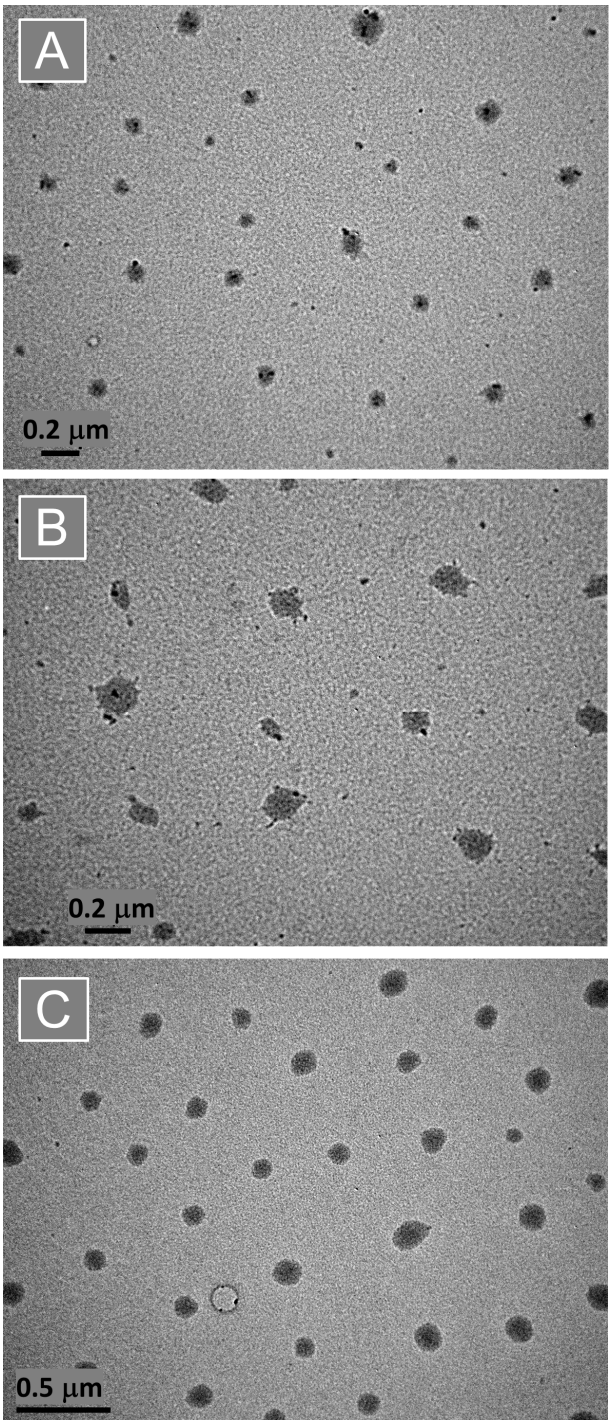


Figure S10. TEM images of (A) *hb*-CPTA, (B) *hb*-CPTA-A, and (C) *hb*-CPTA-T. Samples prepared from their chloroform solution directly, concentration: 1.0 μg/mL.