Supporting Information

Tuning fluorescence of tetraphenylethylene in dilute solution *via* modulating of multiple-hydrogen-bonding interactions between Hamilton receptor and cyanuric acid

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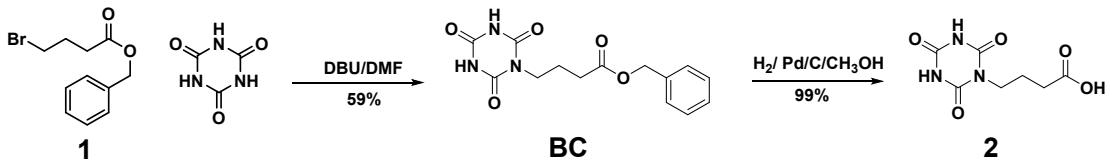
Contents

1. Material and methods

Compounds **1**[S1], **3**[S2], **4**[S3], **7**[S4] and **8**[S5] were synthesized according to published procedures. Chloroform ($CHCl_3$) was freshly distilled from P_2O_5 under normal pressure and nitrogen atmosphere to remove water and oxygen prior to use. Dimethyl sulfoxide (DMSO) with spectroscopic purity was purchased from Aladdin. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 400 MHz Digital FT-NMR spectrometer. Chloroform (δ = 7.26 ppm) was used as an internal standard for chloroform-*d*. DMSO (δ = 2.50 ppm) was used as an internal standard for DMSO-d_6. The fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrophotometer. UV-vis spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. SEM images were recorded on a Hitachi S4800 scanning electron microscope (5 kV, 10 μA).

2. Synthesis of compound **2**



Scheme S1. Synthetic route for key intermediate **2**.

2.1 Synthesis of compound **BC**

Benzyl 4-bromobutanoate **1** (1 g, 3.9 mmol) and cyanuric acid (2.52 g, 19.5 mmol) were dissolved in dry DMF (25 mL). 1, 8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.58 mL, 3.9 mmol) was added dropwise to the solution. The mixture was heated to 70 ˚C and stirred for 24 hours. The solvent was evaporated under reduced pressure. The crude mixture was triturated with methanol and the insoluble solid was filtrated off. After condensation of the filtrate, the product was purified by column chromatography (silica, dichloromethane/ethyl acetate, 6:1, *v*/*v*). The product was a white solid (0.70 g, 59%).

Mp: 155.5-156.4 ˚C.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.40 (s, 2H, N*H*), 7.37-7.34 (m, 5H, Bn-Ar*H*), 5.11 (s, 2H, Bn-CH_2), 3.92 (t, *J* = 6.6 Hz, 2H, NCH_2), 2.46 (t, *J* = 7.2 Hz, 2H, COCH_2), 2.05-1.98 (m, 2H, CH_2).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 172.8, 150.5, 149.1, 136.7, 128.9, 128.42, 128.37, 65.9, 31.2, 23.2.

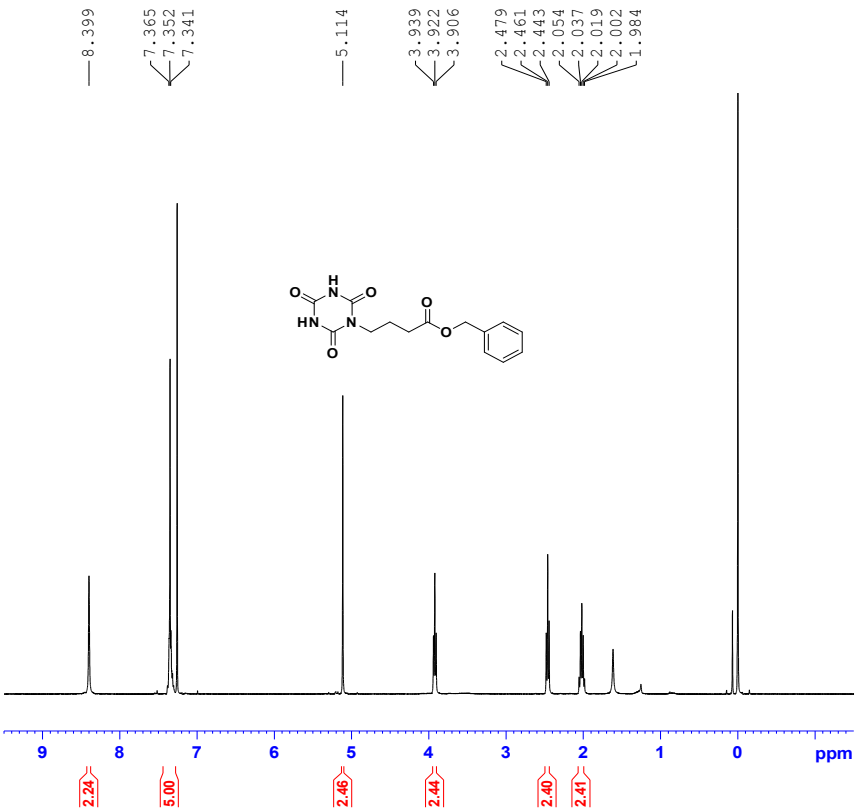


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **BC**.

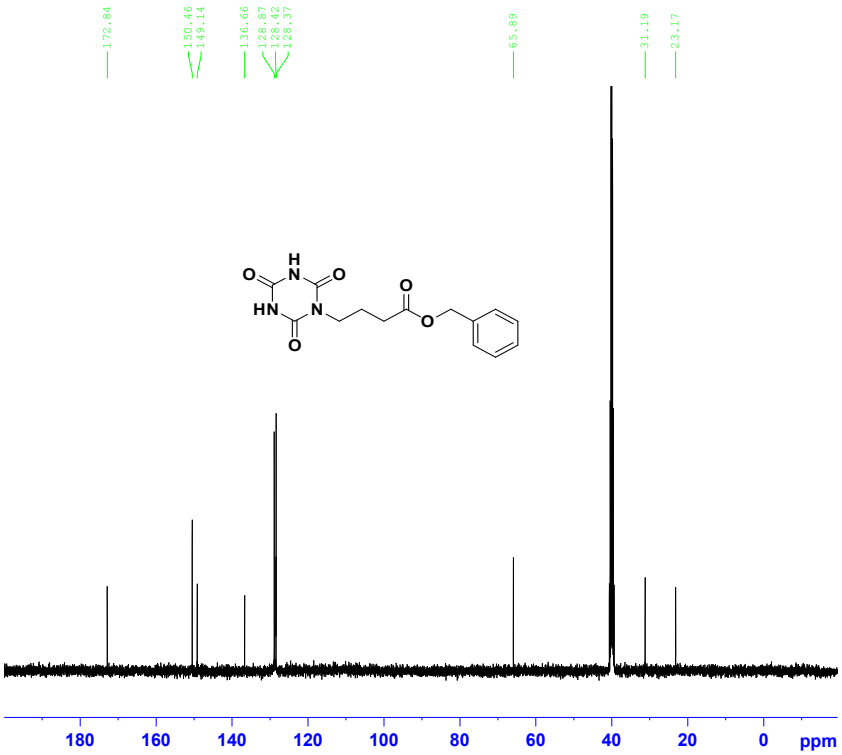


Fig. S2 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, TMS, 298 K, ppm) of compound **BC**.

2.2 Synthesis of compound **2**

The benzyl derived cyanuric acid **BC** (1000 mg, 3.28 mmol) was dissolved in CH_3OH (100 mL) and 10% Pd/C (95 mg) was added. This suspension was subjected to hydrogenation until no more hydrogen was consumed. The Pd/C was filtered and CH_3OH was evaporated under reduced pressure to provide a white solid (700 mg, 99%).

Mp: 212.9-213 ˚C.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 11.37 (s, 2H, N*H*), 3.67 (t, *J* = 6.6 Hz, 2H, NCH_2), 2.24 (t, *J* = 7.2 Hz, 2H, CH_2CO), 1.77-1.72 (m, 2H, CH_2).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 174.5, 150.4, 149.2, 31.5, 23.3.

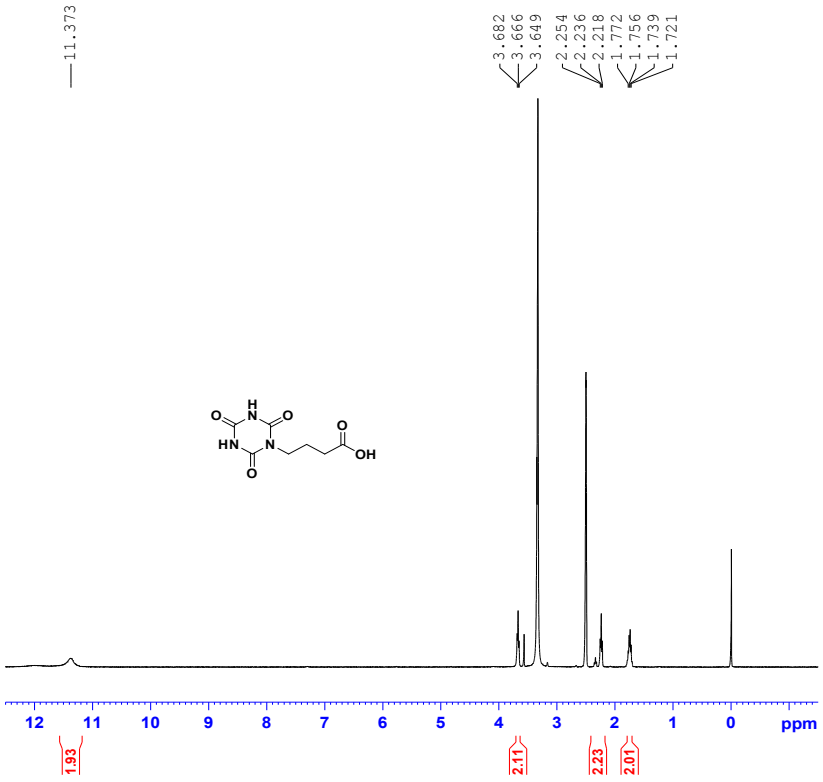


Fig. S3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, TMS, 298 K, ppm) of compound **2**.

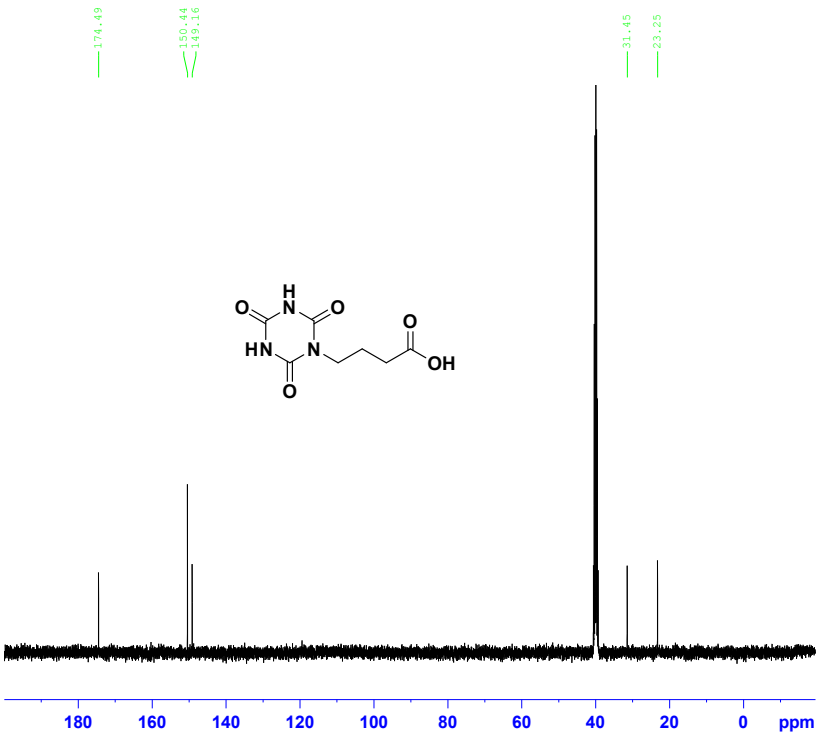
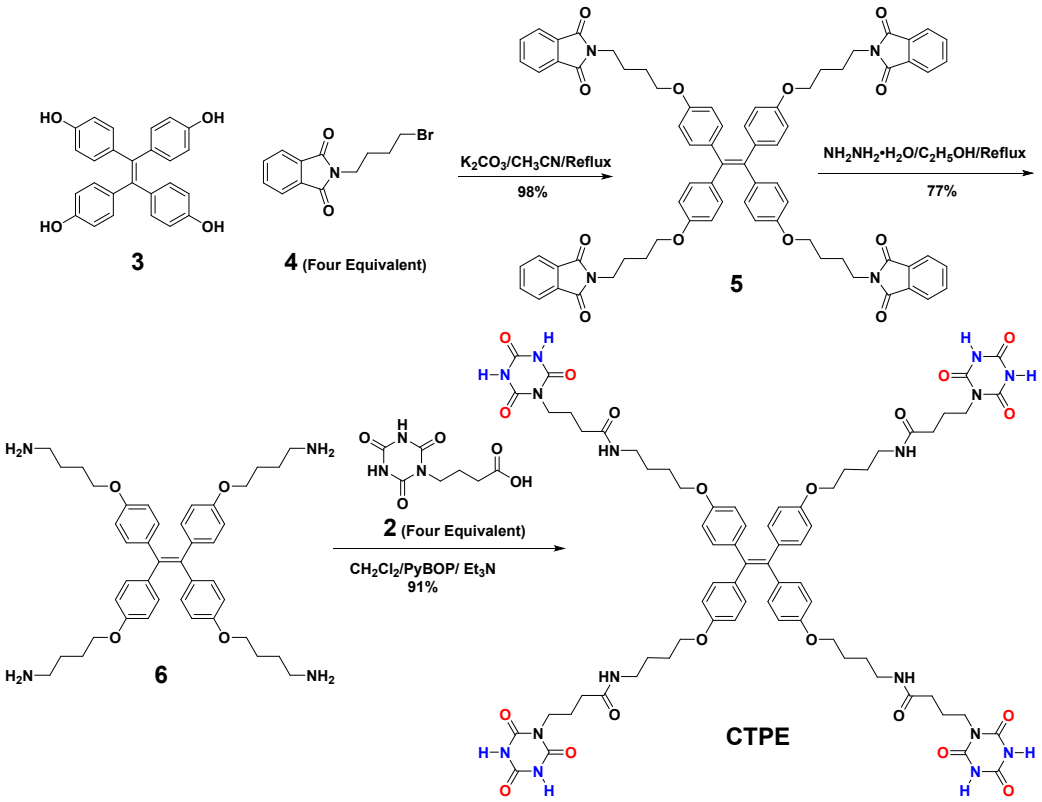


Fig. S4 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, TMS, 298 K, ppm) of compound **2**.

3. Synthesis of compound **CTPE**



Scheme S2. Synthetic route for **CTPE**.

3.1 Synthesis of compound **5**

A suspension of tetrakis(4-hydroxyphenyl)ethylene **3** (800 mg, 2 mmol), potassium carbonate (3.31 g, 24 mmol) and N-(4-bromobutyl)phthalimide **4** (2.25 g, 8 mmol) in 50 mL acetonitrile was heated to reflux under nitrogen atmosphere for 24 hours. The solid was filtrated off and washed thoroughly with CH_2Cl_2. After evaporation of the organic solvent the residue was recrystallized from methanol to give the product as a light yellow solid (1.74 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 7.84 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 8H, Ar*H*), 7.71 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 8H, Ar*H*), 6.87 (d, *J* = 8.8 Hz, 8H, Ar*H*), 6.59 (d, *J* = 8.4 Hz, 8H, Ar*H*), 3.90 (t, *J* = 5.6 Hz, 8H, OCH_2), 3.75 (t, *J* = 6.8 Hz, 8H, NCH_2), 1.87-1.79 (m, 16H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 168.4, 157.0, 138.2, 136.8, 133.9, 132.5, 132.0, 123.2, 113.5, 66.9, 37.7, 26.6, 25.4.

HRMS (ESI$^+$)calcd. for $[C_{74}H_{64}N_4O_{12}+Na]^+$1223.4418, found: 1223.4428.

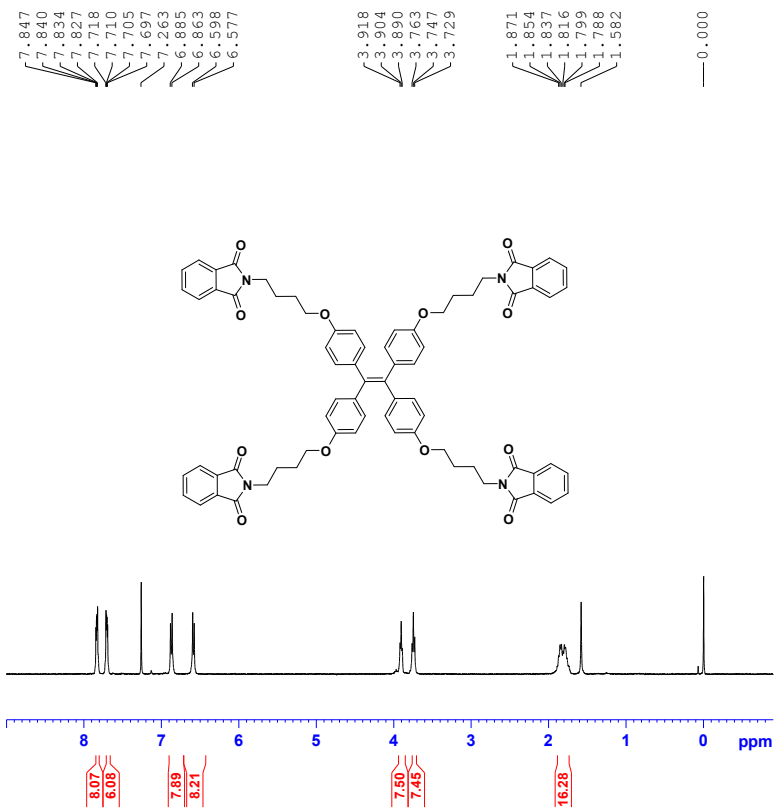


Fig. S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **5**.

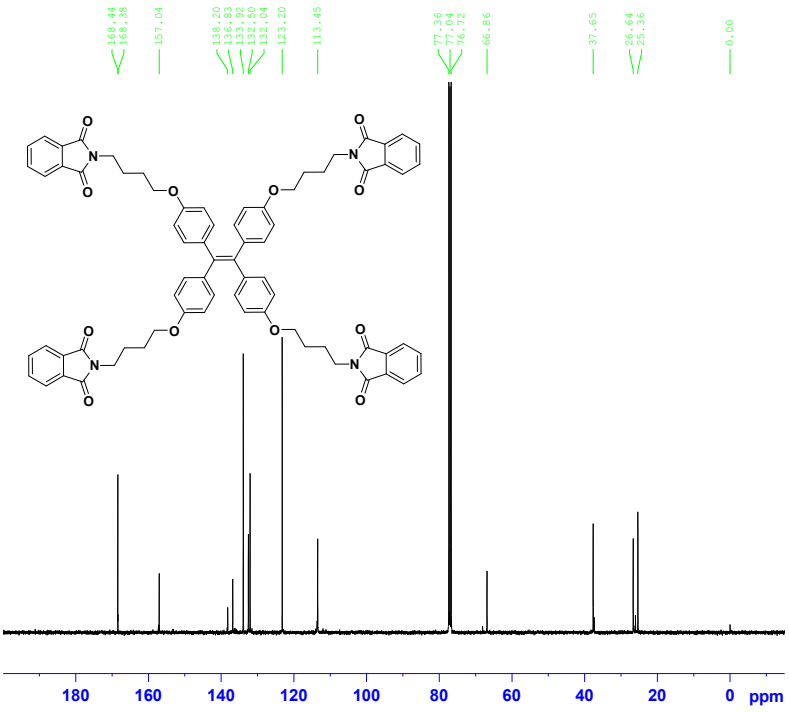


Fig. S6 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **5**.

3.2 Synthesis of compound **6**

A suspension of hydrazine monohydrate (1 mL) and tetrakis(phthamide)TPE **5** (1.66 g, 1.38 mmol) in 40 mL ethanol was heated to reflux overnight. The organic solvent was evaporated under reduced pressure. The residue was triturated with CH_2Cl_2 and the solid was filtrated off. The organic phase was washed with aqueous sodium hydroxide solution. After dried over anhydrous sodium sulfate and evaporation of the organic solvent, the product was obtained by trituration with petroleum ether as a yellow solid (0.72 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 6.93 (d, *J* = 8.5 Hz, 8H, Ar*H*), 6.64 (d, *J* = 8.6 Hz, 8H, Ar*H*), 3.92 (t, *J* = 6.3 Hz, 8H, OCH_2), 2.77 (t, *J* = 7.0 Hz, 8H, NH_2CH_2), 1.86-1.76 (m, 8H, CH_2), 1.66-1.57 (m, 8H, CH_2), 1.50-1.30 (br, 8H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 157.2, 138.3, 136.9, 132.6, 113.5, 67.5, 42.0, 30.4, 26.7.

HRMS (ESI$^+$) calcd. for $[C_{42}H_{56}N_4O_4+H]^+$681.4380, found: 681.4379.

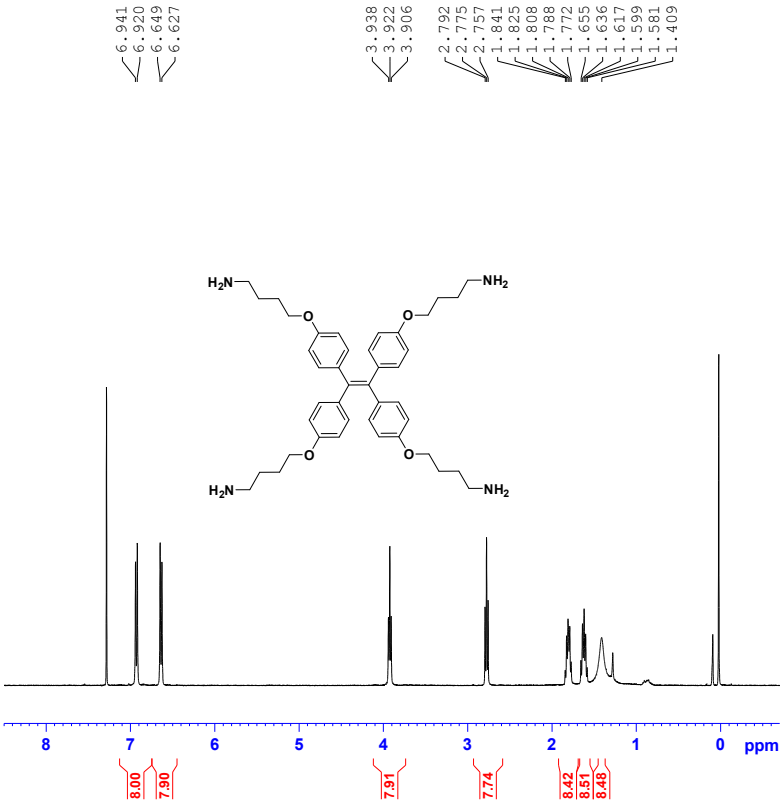


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **6**.

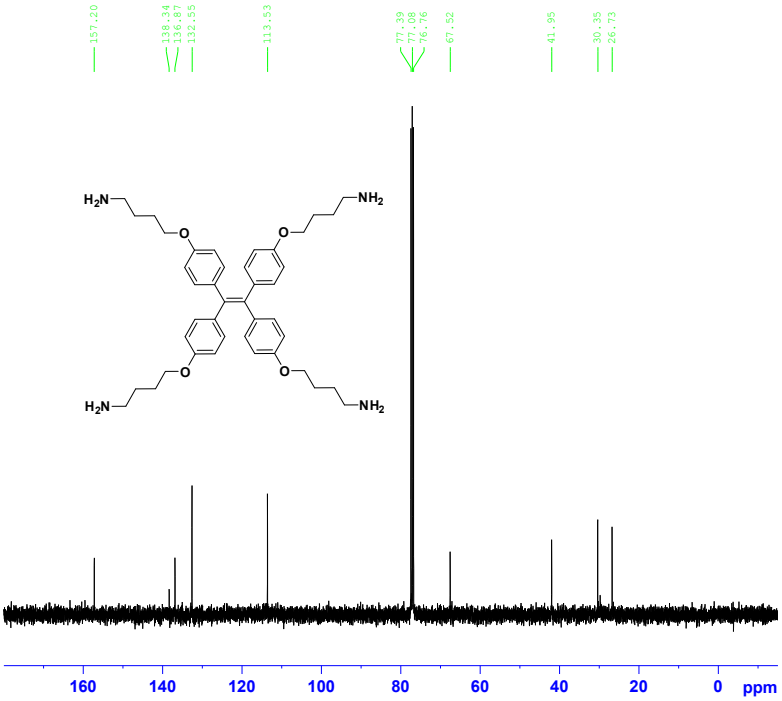


Fig. S8 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **6**.

3.3 Synthesis of compound **CTPE**

A suspension of tetraaminoTPE **6** (204 mg, 0.3 mmol), butyric acid derived cyanuric acid **2** (258 mg, 1.2 mmol, 4 eq), PyBOP (780 mg, 1.5 mmol), Et_3N (300 mg, 3 mmol) in 30 mL CH_2Cl_2 was stirred at room temperature. The suspension became clear in about 2 hours. A solid precipitated and adhered on the flask. The mixture was then heated to reflux overnight. After evaporation of the solvent, the residue was triturated with hot acetonitrile and methanol successively to give the product as a light yellow solid (400 mg, 91%).

M.p: > 237 ºC, decomposition.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 11.55-11.00 (br, 8H, N*H*), 7.81 (t, *J* = 5.6 Hz, 4H, CON*H*), 6.82 (d, *J* = 8.4 Hz, 8H, Ar*H*), 6.66 (d, *J* = 8.8 Hz, 8H, Ar*H*), 3.86 (t, *J* = 5.8 Hz, 8H, OCH_2), 3.63 (t, *J* = 7.0 Hz, 8H, NCH_2), 3.07-3.02 (m, 8H, NHCH_2), 2.06 (t, *J* = 7.6 Hz, 8H, COCH_2), 1.76-1.69 (m, 8H, CH_2), 1.68-1.61 (m, 8H, OCH$_2$CH_2), 1.53-1.45 (m, 8H, CH_2).

^{13}C NMR (100 MHz, DMSO-d_6, TMS, 298 K, ppm): δ 171.3, 156.8, 150.2, 149.2, 137.9, 136.2, 132.0, 113.6, 66.9, 38.1, 32.8, 26.2, 25.8, 23.7.

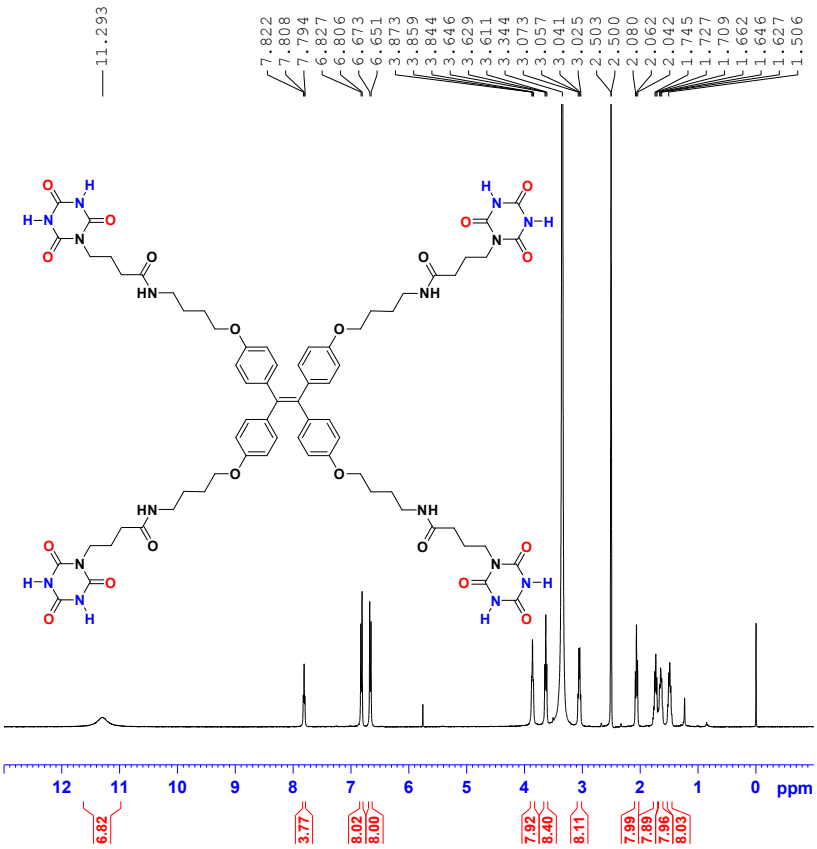


Fig. S9 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, TMS, 298 K, ppm) of compound **CTPE**.

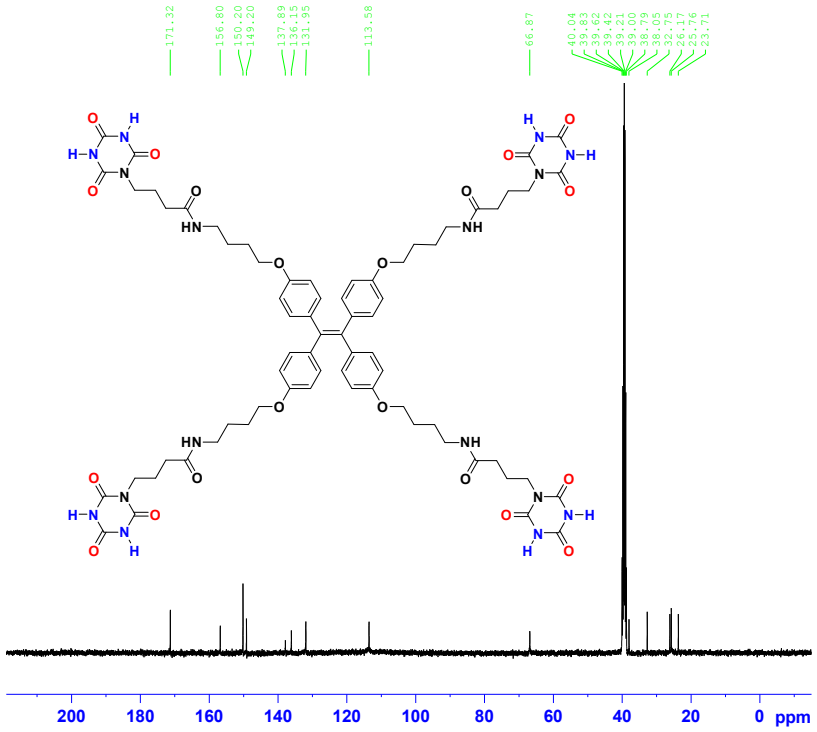
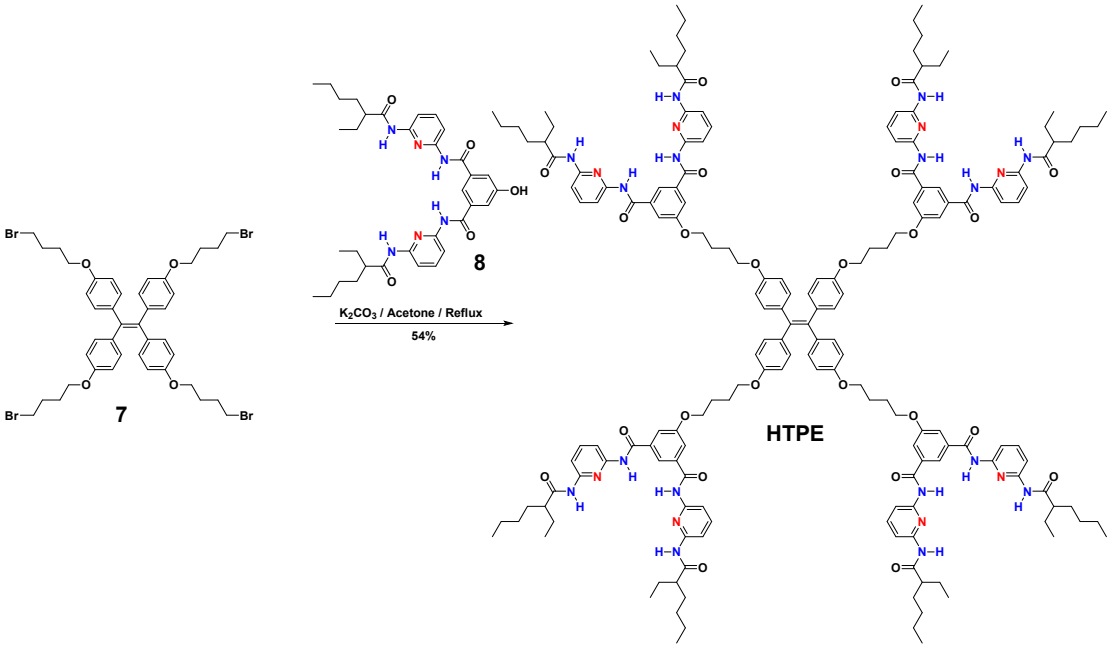


Fig. S10 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, TMS, 298 K, ppm) of compound **CTPE**.

4. Synthesis of compound **HTPE**



Scheme S3. Synthetic route for **HTPE**.

A suspension of 1, 1, 2, 2-tetrakis(4-(4-bromobutoxy)phenyl)ethylene **7** (300 mg, 0.322 mmol), OH-derived Hamilton receptor **8** (793.8 mg, 1.288 mmol) and potassium carbonate (712 mg, 5.152 mmol) in 50 mL acetone was heated to reflux under nitrogen atmosphere for 30 hours. After filtration of the solid and evaporation of the solvent, the crude product was purified by column chromatography (silica, CH_2Cl_2/CH_3OH = 80:1, *v*/*v*). The product as a light yellow solid (500 mg, 51%) was further purified via trituration with acetonitrile.

M.p: 147.3-148.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.46 (s, 8H, N*H*), 8.30 (s, 8H, N*H*), 8.03 (d, *J* = 8.0 Hz, 8H, Py-*H*), 7.96 (d, *J* = 8.0 Hz, 8H, Py-*H*), 7.91 (s, 4H, Ar*H*), 7.68 (t, *J* = 8.0 Hz, 8H, Py-*H*), 7.61 (s, 8H, Ar*H*), 6.93 (d, *J* = 8.4 Hz, 8H, Ar*H*), 6.64 (d, *J* = 8.4 Hz, 8H, Ar*H*), 3.96 (d, *J* = 20 Hz, 16H, ArOCH_2), 2.25 (s, 8H, C*H*), 1.86 (s, 16H, OCH_2CH_2), 1.75-1.70 (m, 16H, $CHCH_2$), 1.60-1.54 (m, 16H, $CHCH_2$), 1.31-1.26 (m, 32H, CH_2CH_2), 0.96 (t, *J* = 7.4 Hz, 24H, CH_3), 0.86 (s, 24H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 175.5, 164.5, 159.7, 157.1, 150.0, 149.1,

140.7, 138.5, 136.9, 135.7, 132.6, 117.6, 117.1, 113.7, 110.5, 109.6, 68.2, 67.0, 50.3, 32.4, 29.8, 26.1, 25.7, 22.8, 14.0, 12.1.

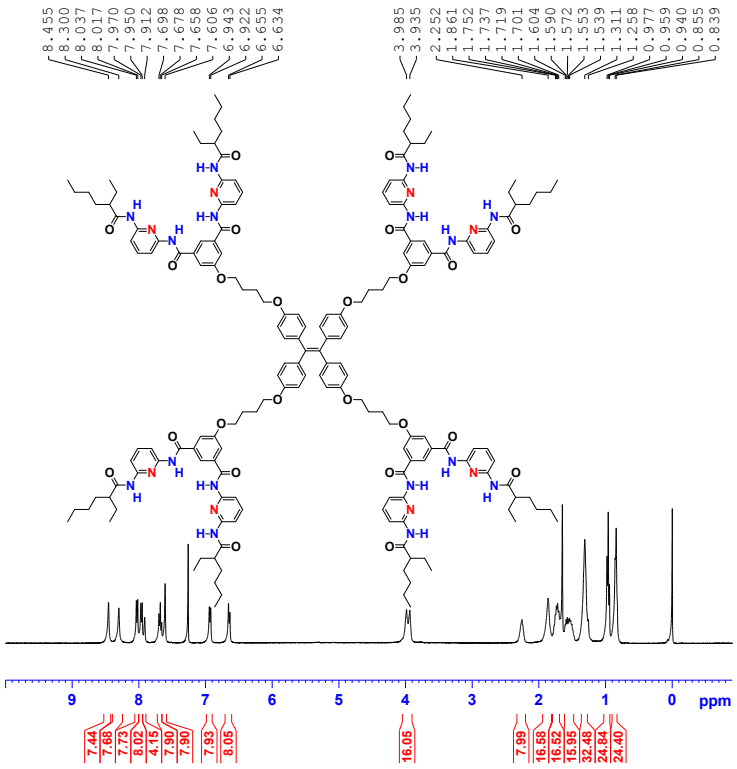


Fig. S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **HTPE**.

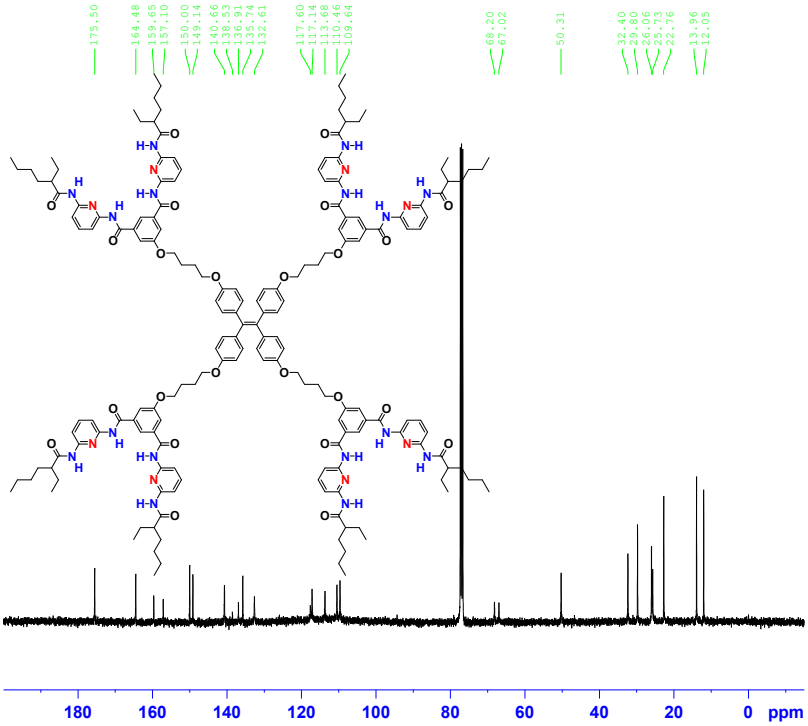


Fig. S12 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS, 298 K, ppm) of compound **HTPE**.

5. ^{1}H NMR analysis of interaction between **BH** and **CTPE**, **HTPE** and **CTPE**

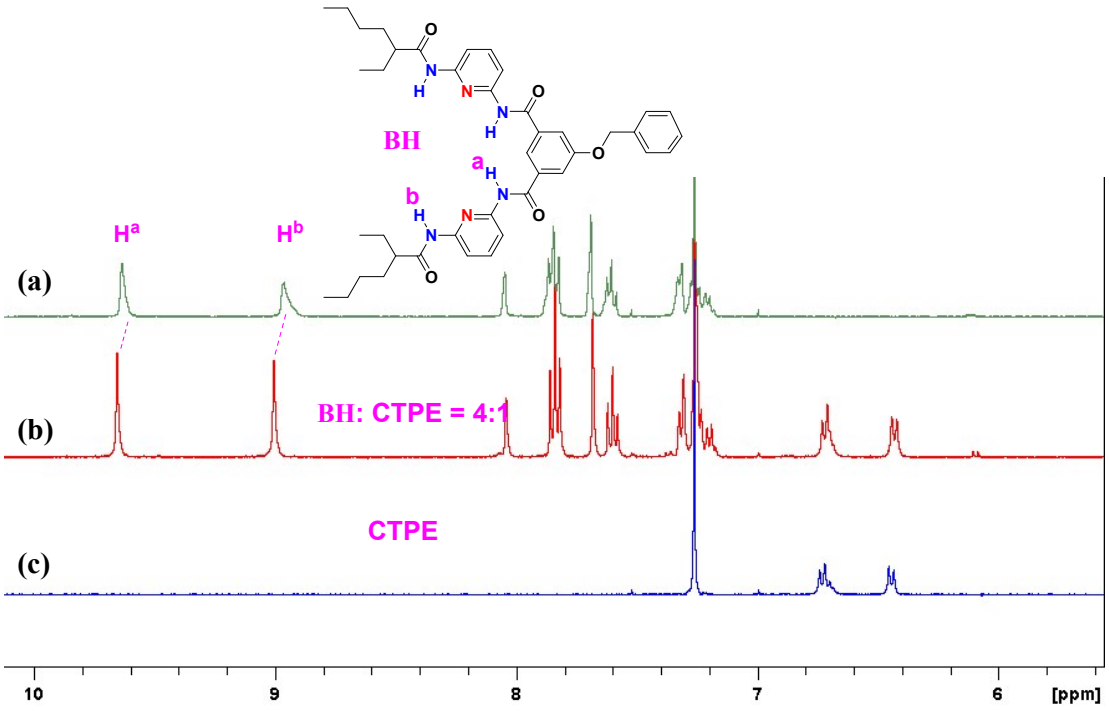


Fig. S13 ^{1}H NMR spectra (10% DMSO-d_6/$CDCl_3$, *v*/*v*, 298 K, 400 MHz) of (a) **BH** (4 mM); (b) **CTPE** (1 mM) and **BH** (4 mM); (c) **CTPE** (1 mM).

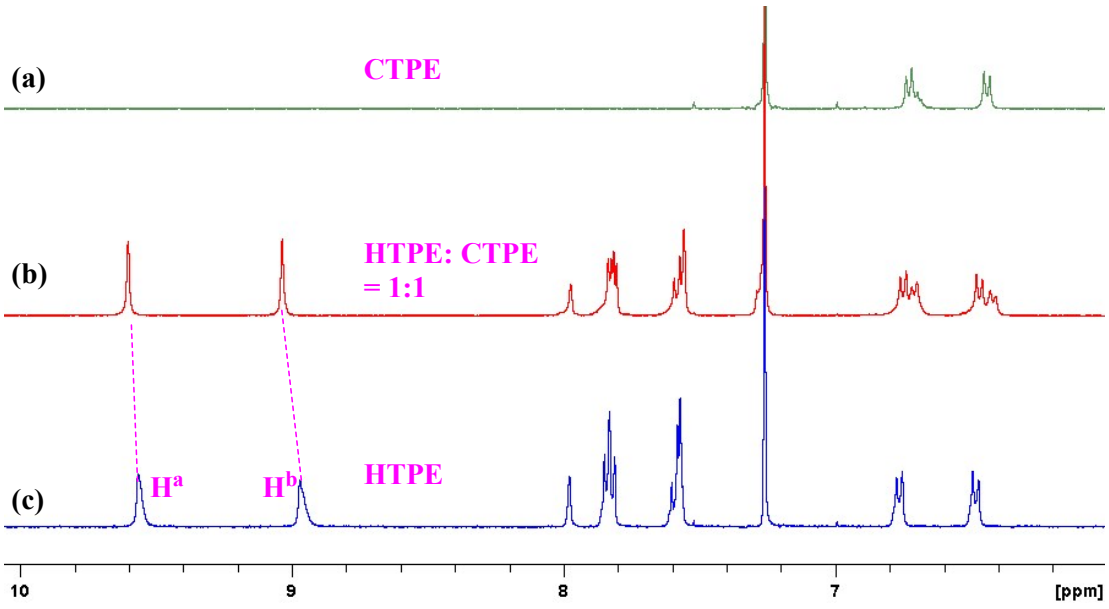


Fig. S14 ^{1}H NMR spectra (10% DMSO-d_6/$CDCl_3$, *v*/*v*, 298 K, 400 MHz) of (a) **CTPE** (1 mM); (b) **CTPE** (1 mM) and **HTPE** (1 mM); (c) **HTPE** (1 mM).

6. Fluorescence spectra of **HTPE/CTPE** on the different conditions

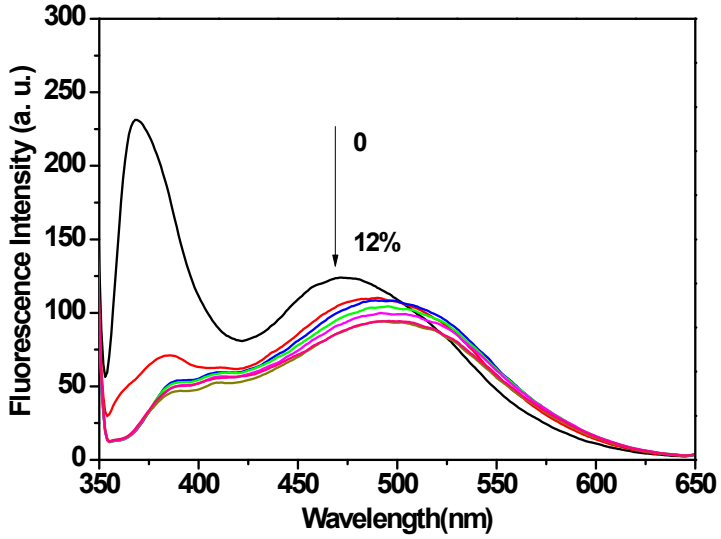


Fig. S15 Fluorescence spectra for **HTPE**: **CTPE** = 1:1 (each 5 × 10^{-7} M) in 4‰ DMSO/$CHCl_3$ with addition of methanol, from 0 to 12% methanol, λ_{ex} = 335 nm.

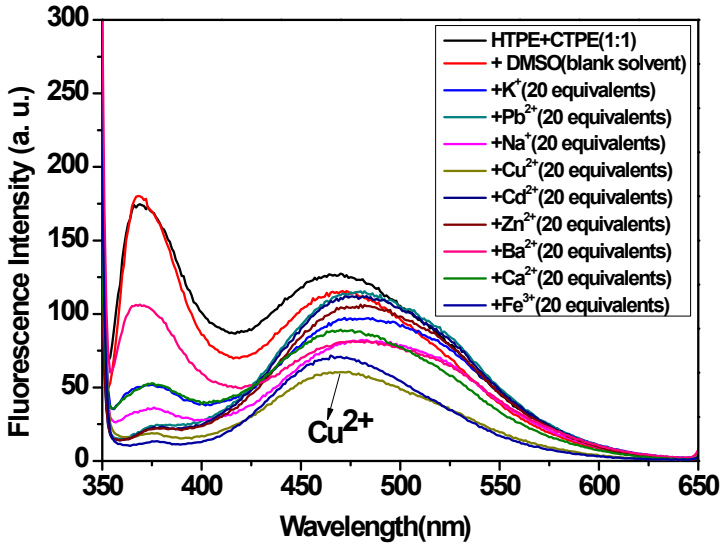


Fig. S16 Fluorescence spectra of **HTPE**: **CTPE** = 1:1 (each 5 × 10^{-7} M) in 4‰ DMSO/$CHCl_3$ with addition of 20 equivalents of different metal ions, λ_{ex} = 335 nm.

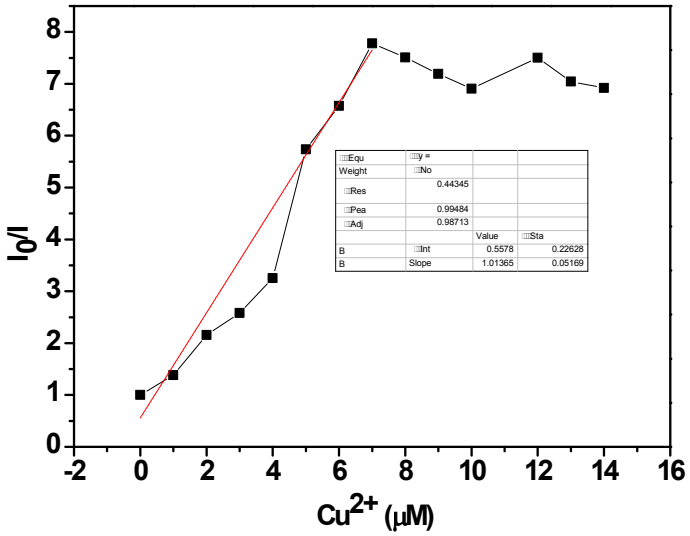


Fig. S17 Quenching of Stern–Volmer curve of Cu^{2+} to the fluorescence of **HTPE**: **CTPE** = 1:1 (each 5×10^{-7} M in 4‰ DMSO/$CHCl_3$), λ_{ex} = 335 nm.

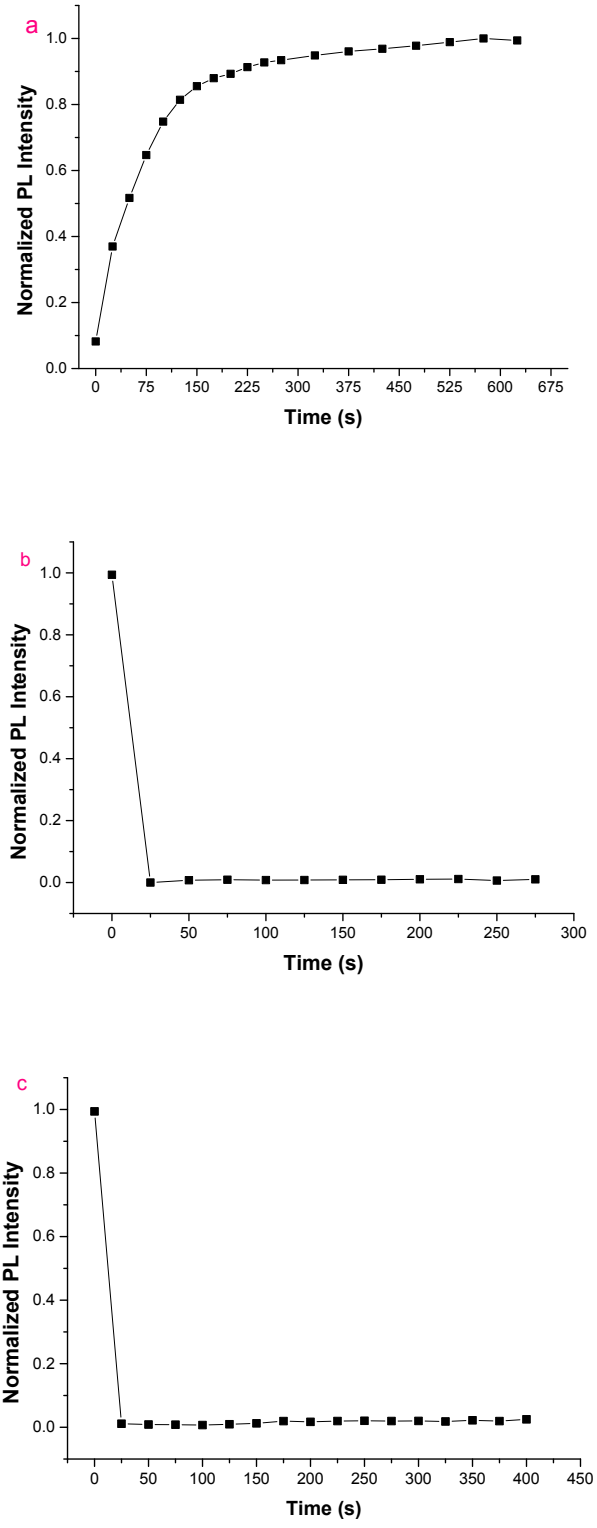


Fig. S18 Time-dependent fluorescence spectra of (a) **HTPE**: **CTPE** = 1:1 (each 5×10^{-7} M in 4‰ DMSO/$CHCl_3$); (b) With addition of 20 equivalents of Cu^{2+} to the above equilibrated system; (c) With addition of 2% CH_3OH to the above equilibrated system, $\lambda_{ex} = 335$ nm.

7. References

S1. M. Albrecht, M. Baumert, H. Winkler and C. Schalley, *Synthesis*, 2010, **2010**, 953-958.

S2. T. Noguchi, T. Shiraki, A. Dawn, Y. Tsuchiya, L. T. Ngoc Lien, T. Yamamoto and S. Shinkai, *Chem. Commun*., 2012, **48**, 8090-8092.

S3. D.-R. Hou, H.-Y. Cheng and E.-C. Wang, *J. Org. Chem*., 2004, **69**, 6094-6099.

S4. Y.-C. Liu, Y.-Y. Wang, H.-W. Tian, Y. Liu and D.-S. Guo, *Org. Chem. Front*., 2016, **3**, 53-61.

S5. C. Dethlefs, J. Eckelmann, H. Kobarg, T. Weyrich, S. Brammer, C. Näther and U. Lüning, *Eur. J. Org. Chem*., 2011, **2011**, 2066-2074.