Supporting Information

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

Dong-Hui Wang, Deng-Jie Zhu, Wen Ding, Min Xue and Yong Yang

a School of Science, Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China.
b School of Science, Department of Physics, Zhejiang Sci-Tech University, Hangzhou 310018, China.

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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$_2$O$_5$ under normal pressure and nitrogen atmosphere to remove water and oxygen prior to use. Dimethyl sulfoxide (DMSO) with spectroscopic purity was purchased from Aladdin. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 400 MHz Digital FT-NMR spectrometer. Chloroform ($\delta = 7.26$ ppm) was used as an internal standard for chloroform-$d_6$. DMSO ($\delta = 2.50$ 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 $\mu$A).
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): $\delta$ 8.40 (s, 2H, NH), 7.37-7.34 (m, 5H, Bn-ArH), 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): $\delta$ 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$_3$OH (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$_3$OH was evaporated under reduced pressure to provide a white solid (700 mg, 99%).

M.p: 212.9-213 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$, TMS, 298 K, ppm): $\delta$ 11.37 (s, 2H, NH), 3.67 (t, $J = 6.6$ Hz, 2H, NCH$_2$), 2.24 (t, $J = 7.2$ Hz, 2H, CH$_2$CO), 1.77-1.72 (m, 2H, CH$_2$).

$^{13}$C NMR (100 MHz, DMSO-$d_6$, TMS, 298 K, ppm): $\delta$ 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.](image-url)
**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 CH₂Cl₂. 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%).

¹H NMR (400 MHz, CDCl₃, TMS, 298 K, ppm): δ 7.84 (dd, J = 5.2 Hz, J = 2.8 Hz, 8H, ArH), 7.71 (dd, J = 5.2 Hz, J = 3.2 Hz, 8H, ArH), 6.87 (d, J = 8.8 Hz, 8H, ArH), 6.59 (d, J = 8.4 Hz, 8H, ArH), 3.90 (t, J = 5.6 Hz, 8H, OCH₂), 3.75 (t, J = 6.8 Hz, 8H, NCH₂), 1.87-1.79 (m, 16H, CH₂).

¹³C NMR (100 MHz, CDCl₃, 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 [C₇₄H₆₄N₄O₁₂⁺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$_2$Cl$_2$ 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): $\delta$ 6.93 (d, $J$ = 8.5 Hz, 8H, ArH), 6.64 (d, $J$ = 8.6 Hz, 8H, ArH), 3.92 (t, $J$ = 6.3 Hz, 8H, OCH$_2$), 2.77 (t, $J$ = 7.0 Hz, 8H, NH$_2$CH$_2$), 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): $\delta$ 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$_4$O$_4$+H]$^+$ 681.4380, found: 681.4379.

Fig. S7 $^1$H NMR spectrum (400 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$_3$N (300 mg, 3 mmol) in 30 mL CH$_2$Cl$_2$ 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%).


$^1$H NMR (400 MHz, DMSO-$d_6$, TMS, 298 K, ppm): δ 11.55-11.00 (br, 8H, NH), 7.81 (t, $J = 5.6$ Hz, 4H, CONH), 6.82 (d, $J = 8.4$ Hz, 8H, ArH), 6.66 (d, $J = 8.8$ Hz, 8H, ArH), 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, CH₂Cl₂/CH₃OH = 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 °C.

¹H NMR (400 MHz, CDCl₃, TMS, 298 K, ppm): δ 8.46 (s, 8H, NH), 8.30 (s, 8H, NH), 8.03 (d, J = 8.0 Hz, 8H, Py-H), 7.96 (d, J = 8.0 Hz, 8H, Py-H), 7.91 (s, 4H, ArH), 7.68 (t, J = 8.0 Hz, 8H, ArH), 7.61 (s, 8H, ArH), 6.93 (d, J = 8.4 Hz, 8H, ArH), 6.64 (d, J = 8.4 Hz, 8H, ArH), 3.96 (d, J = 20 Hz, 16H, ArOCH₂), 2.25 (s, 8H, CH), 1.86 (s, 16H, OCH₂CH₂), 1.75-1.70 (m, 16H, CHCH₂), 1.60-1.54 (m, 16H, CHCH₂), 1.31-1.26 (m, 32H, CH₂CH₂), 0.96 (t, J = 7.4 Hz, 24H, CH₃), 0.86 (s, 24H, CH₃).

¹³C NMR (100 MHz, CDCl₃, TMS, 298 K, ppm): δ 175.5, 164.5, 159.7, 157.1, 150.0, 149.1,
Fig. S12 $^1$H NMR spectrum (400 MHz, CDCl$_3$, TMS, 298 K, ppm) of compound HTPE.

Fig. S11 $^1$H NMR spectrum (400 MHz, CDCl$_3$, TMS, 298 K, ppm) of compound HTPE.

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$, TMS, 298 K, ppm) of compound HTPE.

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

![Fluorescence spectra](image)

**Fig. S15** Fluorescence spectra for HTPE: CTPE = 1:1 (each $5 \times 10^{-7}$ M) in 4‰ DMSO/CHCl$_3$ with addition of methanol, from 0 to 12% methanol, $\lambda_{ex} = 335$ nm.

![Fluorescence spectra](image)

**Fig. S16** Fluorescence spectra of HTPE: CTPE = 1:1 (each $5 \times 10^{-7}$ M) in 4‰ DMSO/CHCl$_3$ with addition of 20 equivalents of different metal ions, $\lambda_{ex} = 335$ nm.
**Fig. S17** Quenching of Stern–Volmer curve of Cu$^{2+}$ to the fluorescence of HTPE: CTPE = 1:1 (each $5 \times 10^{-7}$ M in 4‰ DMSO/CHCl$_3$), $\lambda_{ex} = 335$ nm.
Fig. S18 Time-dependent fluorescence spectra of (a) HTPE: CTPE = 1:1 (each $5 \times 10^{-7}$ 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$_3$OH to the above equilibrated system, $\lambda_{ex} = 335$ nm.
7. References


