Supplementary Information

Synthesis of Tetraphenylethylene Pillar[4]arenes and the Selective Fast Quenching of Their AIE Fluorescence by TNT

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Materials and methods: All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise specified. \(^1\)H NMR and \(^{13}\)C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in CDCl\(_3\). Infrared spectra were recorded on BRUKER EQUINAX55 spectrometer. Mass spectrum was measured on an IonSpec 4.7 Tesla FTMS instrument. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K.

Synthesis of TPE pillar[6]arenes

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\begin{align*}
&\begin{array}{c}
\text{NBS/CCl}_4 \\
\text{reflux}
\end{array} \\
&\begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}
\]

\[
\begin{align*}
&\begin{array}{c}
\text{NBS/CCl}_4 \\
\text{reflux}
\end{array} \\
&\begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}
\]

Synthesis of the key intermediate 2: It was synthesized according to the known procedure (A. Qin, L. Tang, J. W. Y. Lam, C. K. W. Jim, Y. Yu, H. Zhao, J. Sun and B. Z. Tang, Adv. Funct. Mater. 2009, 19, 1891–1900). To a flask was added 4,4’-dimethyltetraphenylethene 1 (1.08 g, 3 mmol), 1-bromosuccinimide (NBS, 1.18 g, 3.3 mmol), dibenzoyl peroxide (15 mg, 0.060 mmol) and CCl\(_4\) (20 mL). The mixture was refluxed for 12 h, and then dichloromethane (20 mL) was added. After the solution was washed with water and brine, respectively, for three times, it was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum to dryness. The residue was purified by flash chromatography (eluant, petroleum/dichloromethane 5:1 v/v) to give 2 as a slightly yellow powder (1.15 g, 74%). Mp 219.7–220.8 °C; \(^1\)H NMR(400 MHz, CDCl\(_3\)) 7.11 (m, 10 H), 7.00 (dt, \(J = 6.0, 2.3\) Hz, 4 H), 6.97 (d, \(J =\))
8.3 Hz, 4 H), 4.41 (s, 4 H); 13C NMR(100 MHz, CDCl₃) 143.7, 143.3, 142.1, 139.5, 135.9, 131.7, 131.2, 128.5, 127.8, 126.7, 33.5; IR (KBr) ν 3070, 3026, 1659, 1604, 1507, 1488, 1440, 1410, 1226, 1205, 1129, 1099, 1072, 1024, 981, 839, 760, 697, 616 cm⁻¹.

**Synthesis of TPE pillar[6]arene 3a:** To a flask was added 2 (1.20 g, 2.30 mmol), 1,4-dimethyloxylbenzene (0.38 g, 2.80 mmol), anhydrous AlCl₃ (370 mg, 2.80 mmol) and dichloromethane (210 mL). The mixture was stirred at ambient temperature for 6 h, and the resultant dark green solution was quenched with water (30 mL) and became yellow. After the yellow solution was washed with 50 mL water for three times, it was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum to dryness. The remained slurry-like solid was purified by flash chromatography (eluant, petroleum/dichloromethane 2:1 v/v). The obtained solid was recrystallized from a mixed solvent of CHCl₃ and methanol to give 3a as a white solid (230 mg, 20%). Mp >300 °C; 1H NMR (400 MHz, CDCl₃) δ 7.11 – 7.08 (m, 12 H), 7.01 – 6.99 (m, 8 H), 6.87 (q, J = 12.4, 8.6 Hz, 16 H), 6.60 (s, 4 H), 3.78 (s, 8 H), 3.66 (s, 12 H); 13C NMR (100 MHz, CDCl₃) δ 151.30, 144.29, 141.05, 140.95, 140.09, 139.37, 131.36, 131.23, 127.98, 127.79, 127.59, 126.09, 114.15, 55.15, 35.82; IR (KBr) ν 3076.93, 3048.41, 3022.06, 2989.82, 2930.59, 2902.72, 2829.42, 1601.12, 1571.49, 1505.34, 1460.78, 1437.26, 1403.28, 1334.40, 1293.88, 1250.50, 1214.75, 1179.21, 1108.72, 1073.01, 1047.17, 977.72, 952.91, 925.70, 869.49, 801.97, 760.89, 736.30, 699.32, 620.82, 594.09, 540.73, 511.38, 486.78, 461.60, 428.21 cm⁻¹; ESI+ HRMS m/z calcd for C₁₇₂H₁₆₄O₉ 988.4492 [M⁺], found 988.4496 [M⁺].

**Synthesis of TPE pillar[6]arene 3b:** To a flask was added 2 (1.20 g, 2.30 mmol), 1,4-di(n-pentanoxy)benzene (0.70 g, 2.80 mmol), anhydrous AlCl₃ (370 mg, 2.80 mmol) and dichloromethane (210 mL). The mixture was stirred at ambient temperature for 12 h, and the resultant dark brown solution was quenched with 30 mL water and it became yellow. After the yellow solution was washed with water (50 mL) for three times, it was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 7:1 v/v). The obtained solid was
recrystallized from CHCl$_3$ and methanol to give 3b as a white solid (220 mg, 16%). Mp 270.8 – 271.4 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 (m, 12 H), 7.01 – 6.99 (m, 8 H), 6.85 (q, $J$ = 13.2, 8.5 Hz, 16 H), 5.57 (s, 4 H), 3.77 (s, 8 H), 3.75 (t, $J$ = 6.7 Hz, 8 H), 1.63 (m, 8 H), 1.33 – 1.29 (m, 16 H), 0.88 (t, $J$ = 5.9 Hz, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.6, 144.4, 141.2, 140.9, 139.9, 139.5, 131.4, 131.2, 128.0, 127.9, 127.6, 126.1, 114.9, 86.7, 36.1, 29.2, 28.2, 22.4, 14.0; IR (KBr) ν 3048.74, 3021.73, 2928.62, 1599.68, 1504.15, 1468.10, 1433.76, 1405.91, 1326.01, 1251.15, 1213.06, 1110.38, 1072.17, 1024.84, 929.95, 870.24, 800.84, 761.40, 699.97, 627.74 cm$^{-1}$; ESI$^+$ HRMS m/z calcd for C$_{88}$H$_{93}$O$_4$ 1213.7074 [M+H]$^+$, found 1213.7022 [M+H]$^+$.

Synthesis of TPE pillar[6]arene 3c: To a flask was added 2 (1.79 g, 3.46 mmol), 1,2,4,5-tetramethoxybenzene (0.82 g, 4.15 mmol), anhydrous AlCl$_3$ (0.55 mg, 4.15 mmol) and dichloromethane (320 mL). The mixture was stirred at reflux for 3 days, and the resultant dark brown solution was quenched with 50 mL water and became yellow. After the yellow solution was washed with water (70 mL) for three times, it was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 1:3 v/v). Then the solid was recrystallized from CHCl$_3$ and methanol to give 3c as a white solid (60 mg, 3.2%). Mp > 300 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 (m, 12 H), 6.99 – 6.97 (m, 16 H), 6.87 (d, $J$ = 8.0 Hz, 8 H), 3.80 (s, 8 H), 3.59 (s, 24 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.4, 144.5, 141.0, 140.9, 140.5, 139.6, 131.4, 131.2, 128.3, 128.2, 127.6, 127.2, 126.1, 60.2, 30.0; IR (KBr) ν 3075, 3052, 3022, 2991, 2968, 2934, 2828, 1600, 1507, 1460, 1407, 1327, 1299, 1253, 1184, 1110, 1064, 1018, 978, 959, 920, 860, 836, 811, 790, 758, 734, 698, 660, 638, 618, 577, 514, 480, 461 cm$^{-1}$; ESI$^+$ HRMS m/z calcd for C$_{76}$H$_{68}$KO$_8$ 1147.4551 [M+K]$^+$, found 1147.4528 [M+K]$^+$.

Synthesis of acyclic analogue 4: To a flask was added 2 (1.20 g, 2.30 mmol), 1,4-dimethoxybenzene (1.92 g, 13.9 mmol), anhydrous AlCl$_3$ (370 mg, 2.80 mmol) and dichloromethane (70 mL). The mixture was stirred at ambient temperature for 2 h, and the resultant dark brown solution was quenched with water (30 mL) and became yellow. After the yellow solution was washed with water (70 mL) for three times, it
was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 1:2 v/v). Then the solid was recrystallized from CHCl$_3$ and methanol to give 4 as a white solid (710 mg, 48%). Mp 67.1 – 68.3 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (m, 6 H), 7.02 – 7.00 (m, 4 H), 6.91 (s, 8 H), 6.76 (d, $J = 8.8$ Hz, 2 H), 6.69 (dt, $J = 8.8$, 2.8 Hz, 2 H), 6.54 (d, $J = 2.8$ Hz, 2H), 3.83 (s, 4 H), 3.71 (s, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.5, 151.7, 144.0, 141.3, 140.9, 140.2, 138.7, 131.3, 131.2, 128.3, 127.5, 126.1, 116.6, 111.5, 111.2, 56.1, 55.6, 35.6; IR (KBr) $\nu$ 3021, 2993, 2953, 2830, 1598, 1498, 1464, 1436, 1412, 1314, 1297, 1275, 1219, 1178, 1155, 1108, 1076, 1046, 1025, 978, 949, 914, 852, 801, 756, 730, 700, 673, 636, 592, 578, 546, 486, 451 cm$^{-1}$; ESI$^+$ HRMS m/z calcd for C$_{44}$H$_{40}$KO$_4$ 671.2564 [M+K]$^+$, found 671.2550 [M+K]$^+$. 

Fig. S1. $^1$H NMR spectrum of 3a in CDCl$_3$. 

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Fig. S2. $^{13}$C NMR spectrum of 3a in CDCl$_3$.

Fig. S3. IR spectrum of 3a.
**Fig. S4.** ESI$^+$-HRMS spectrum of 3a.

**Fig. S5.** $^1$H NMR spectrum of 3b in CDCl$_3$. 
Fig. S6. $^{13}$C NMR spectrum of 3b in CDCl$_3$.

Fig. S7. IR spectrum of 3b.
Fig. S8. ESI$^+$-HRMS spectrum of 3b.

Fig. S9. $^1$H NMR spectrum of 3c in CDCl$_3$. 
Fig. S10. $^{13}$C NMR spectrum of 3c in CDCl$_3$.

Fig. S11. IR spectrum of 3c.
Fig. S12. ESI+−HRMS spectrum of 3c.

Fig. S13. 1H NMR spectrum of 4 in CDCl3.
Fig. S15. $^{13}$C NMR spectrum of 4 in CDCl$_3$.

Fig. S15. IR spectrum of 4.
Fig. S16. ESI+HRMS spectrum of 4.

Fig. S17. Change of the fluorescence spectrum of 3a (1.0 × 10⁻⁵ M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 472 nm vs. the water fraction in THF. \( \lambda_{ex} = 342 \) nm, ex/em slid widths = 3/3 nm.
Fig. S18. Change of the fluorescence spectrum of 3b (1.0 × 10⁻⁵ M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 472 nm vs. the water fraction in THF. λ<sub>ex</sub> = 339 nm, ex/em slid widths = 3/3 nm.

Fig. S19. Change of the fluorescence spectrum of 3c (1.0 × 10⁻⁵ M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 464 nm vs. the water fraction in THF. λ<sub>ex</sub> = 343 nm, ex/em slid widths = 3/3 nm.
**Fig. S20.** Change of the fluorescence spectrum of 4 (1.0 × 10⁻⁵ M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 467 nm vs. the water fraction in THF. \( \lambda_{ex} = 339 \text{ nm} \), ex/em slid widths = 3/3 nm.

**Fig. S21.** Partial short contacts between molecules of 4.