Supporting information

Full-color tunable mechanofluorochromism and excitation-dependent emissions of single-arm extended tetraphenylethenes

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Experimental details

Materials

All raw materials (such as diphenylmethane, 4-methylbenzophenone, triethyl phosphite and various aromatic aldehydes) were purchased from commercial sources and used without further purification.

Characterization

$^1$H NMR (300 MHz) spectra were recorded on a Varian Mercury using TMS as a standard at room temperature. $^1^3$C NMR (125 MHz) spectra were recorded on a Bruker AVANCE500 using TMS as a standard at room temperature. The time of flight mass spectra was recorded using a Kratos MALDI-TOF mass system. UV-Vis absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer. The fluorescence quantum yields ($\Phi_f$) and lifetime were measured on FLS 920 lifetime and steady state spectrometer. Steady State fluorescence spectra were measured using a Shimadzu RF-5301 PC spectrophotometer. Reflection spectroscopy was performed on a Maya 2000PRO fiber optical spectrometer with Ocean DH-2000-BAL UV-Vis-NIR light source using BaSO$_4$ as background. True-color optical images were obtained by using a Canon camera. DSC experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of 10 K·min$^{-1}$. Powder XRD patterns were obtained from a PANalytical B.V. Empyrean X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å).

Synthetic scheme for monosubstituted tetraphenylethylene derivatives (group I)

Take TPE-CH$_3$ as an example, the general synthetic procedure is shown as follow: To a solution of diphenylmethane (3.8 g, 22.6 mmol, 1.0 eq) in dry THF (20 mL) was added 10 mL of n-butyllithium hexane solution (2.5 mol/L) (equivalently 25.0 mmol n-butyllithium, 1.1 eq) at 0 °C under nitrogen atmosphere. The resulting orange-red solution was stirred for one hour at that temperature. To this solution was added 4-methylbenzoate (4.0 g, 20.4 mmol, 0.9 eq) and the reaction mixture was allowed to warm to room temperature with stirring for 12 hours. Then the reaction was quenched with the addition of an aqueous solution of ammonium chloride, the organic layer was extracted with dichloromethane, and the combined organic layers were washed with a saturated brine solution and dried over anhydrous MgSO$_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in about 50 mL of toluene in a 100 mL Schlenk flask fitted with a Dean-Stark trap. A catalytic amount of p-toluenesulphonic acid (PTSA) (0.42 g, 2.4 mmol, 0.1 eq) was added, and the mixture was refluxed for 6 hours and cooled to room temperature. The toluene layer was washed with 10 % aqueous NaHCO$_3$ solution, dried over anhydrous MgSO$_4$ and evaporated to afford the crude TPE-CH$_3$. The crude product was recrystallized in alcohol to afford a white powder with the yield of 60%.
Synthetic scheme for single-arm extended tetraphenylethylene derivatives (group II)

TPE-PO(OEt)$_2$ and TPE-CHO were synthesized according to reported literatures.$^1$

The single-arm extended tetraphenylethylene derivatives were synthesized according to typical Witting-Horner reaction. Taking TPE-VB as an example, the general synthetic procedure is shown as follow: To a solution of TPE-PO(OEt)$_2$ (240 mg, 0.5 mmol, 1eq) and benzaldehyde (53 mg, 0.5 mmol, 1eq) in dry THF (10 mL) cooled to 0 °C, was stepwise added 2 mL dry THF solution of potassium tert-butoxide (70 mg, 0.6 mmol, 1.2 eq). After 10 hours, the reaction mixture was poured into a large amount of water (around 100 mL). Then the crude was filtered out and recrystallized with hot ethanol to afford white powders (yield: 77%).

TPE-VI and TPE-VBVI were synthesized as following synthetic procedure: A mixture of 1,2,3,3-tetramethyl-3H-indolium hexafluorophosphate (1 mmol) and the corresponding aldehydes (1 mmol) in ethanol (10 mL) were refluxed for 24 hours under nitrogen. When the reaction mixture was cool to room temperature, the crude was filtered out and purified with column chromatography (CH$_2$Cl$_2$/petroleum ether) to afford the target products.

Detailed characterization of tetraphenylethylene and its derivatives

$^1$H NMR (300 MHz, CDCl$_3$): δ(TMS, ppm): 7.10-7.08 (12H, m), 7.04-7.02 (8H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): δ(TMS, ppm): 143.76, 140.98, 131.38, 127.69, 126.45. MS (MALDI-TOF): m/z calcd. [M]$^+$ 332.16 found 331.95.

$^1$H NMR (300 MHz, CDCl$_3$): δ(TMS, ppm): 7.23-7.19 (2H, m), 7.13-7.07 (9H, m), 7.03-6.98 (6H, m), 6.90-6.87 (2H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): δ(TMS, ppm): 143.75, 143.45, 143.36, 143.26, 142.73, 141.62, 139.68, 133.03, 131.37, 131.34, 131.29, 131.27, 130.89, 127.92, 127.82, 127.73, 127.68, 126.74, 126.69, 126.64, 126.44, 120.49. MS (MALDI-TOF): m/z calcd. [M]$^+$ 410.07 found 410.34.
\[ \text{δ(TMS, ppm): } 7.10-7.02 (15 \text{H, m), 6.90 (4H, s), 2.25 (3H, s); } \]
\[ \text{δ(TMS, ppm): } 143.98, 143.96, 140.93, 140.77, 140.48, 136.09, 131.39, 131.36, 131.26, 128.42, 127.70, 127.64, 126.37, 126.32, 21.24. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 346.17 \text{ found 346.00.} \]

\[ \text{δ(TMS, ppm): } 7.10-7.01 (15 \text{H, m), 6.93 (2H, d, J=8.9 Hz), 6.63 (2H, d, J=8.9 Hz), 3.73 (3H, s); } \]
\[ \text{δ(TMS, ppm): } 158.10, 144.07, 144.02, 144.01, 140.55, 140.11, 136.14, 132.57, 128.75, 127.82, 127.76, 127.70, 127.64, 126.39, 126.28, 113.07, 55.12. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 362.17 \text{ found 362.06.} \]

\[ \text{δ(TMS, ppm): } 7.56-7.54 (6 \text{H, m), 7.41-7.29 (5H, m), 7.14-7.02 (17 \text{H, m); } \]
\[ \text{δ(TMS, ppm): } 143.83, 143.78, 142.81, 141.17, 141.15, 140.68, 140.58, 138.90, 131.84, 131.49, 131.41, 128.75, 127.82, 127.76, 127.70, 127.21, 126.91, 126.54, 126.48, 126.26. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 408.19 \text{ found 407.93.} \]

\[ \text{δ(TMS, ppm): } 7.64-7.61 (6 \text{H, m), 7.47-7.34 (5H, m), 7.14-7.02 (17 \text{H, m); } \]
\[ \text{δ(TMS, ppm): } 143.79, 143.75, 143.74, 142.89, 141.18, 140.70, 140.53, 139.96, 139.55, 138.31, 131.86, 131.46, 131.38, 128.83, 127.80, 127.73, 127.67, 127.43, 127.34, 127.21, 127.02. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 484.22 \text{ found 484.11.} \]

\[ \text{δ(TMS, ppm): } 7.47 (2H, d, J=7.4 Hz), 7.34 (2H, t), 7.27-7.21 (4H, m), 7.13-7.00 (18H, m); \]
\[ \text{δ(TMS, ppm): } 128.55, 127.76, 127.64, 127.61, 127.54, 126.54, 126.51, 126.45, 125.84. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 434.20 \text{ found 434.58.} \]

\[ \text{δ(TMS, ppm): } 7.36 (2H, d, J=8.8 Hz), 7.20 (2H, d, J=8.4 Hz), 7.13-6.94 (18H, m), 6.81 (1H, d, J=16.2 Hz), 7.60 (2H, d, J=8.3 Hz), 2.97 (6H, s); \]
\[ \text{δ(TMS, ppm): } 143.90, 143.87, 143.81, 143.72, 140.80, 131.66, 131.46, 131.39, 131.37, 128.55, 127.76, 127.64, 127.61, 127.54, 126.44, 126.43, 126.34, 125.30, 124.14, 120.00, 112.46, 40.49. \]
\[ \text{MS (MALDI-TOF): m/z calcld. } [M]^+ 477.25 \text{ found 477.70.} \]
$^1$H NMR (300 MHz, CDCl₃): δ(TMS, ppm): 8.20 (2H, d, J=8.9 Hz), 7.58 (2H, d, J=8.9 Hz), 7.29 (1H, d, J=8.3 Hz), 7.20-7.01 (20H, m); $^{13}$C NMR (125 MHz, CDCl₃): δ(TMS, ppm): 146.68, 144.64, 143.97, 143.60, 143.53, 143.46, 141.66, 140.31, 134.16, 133.07, 131.92, 131.38, 131.35, 131.32, 127.82, 127.77, 127.68, 126.74, 126.66, 126.62, 126.40, 125.92, 124.17. MS (MALDI-TOF): m/z calcd. [M]$^+$ 479.19 found 479.66.

$^1$H NMR (300 MHz, CDCl₃): δ(TMS, ppm): 8.23 (2H, d, J=8.9 Hz), 7.63 (2H, d, J=8.9 Hz), 7.53 (2H, d, J=8.7 Hz), 7.49 (2H, d, J=8.8 Hz), 7.29-7.24 (3H, m), 7.17-7.01 (20H, m); $^{13}$C NMR (125 MHz, CDCl₃): δ(TMS, ppm): 146.70, 143.91, 143.74, 143.70, 143.63, 143.59, 141.27, 140.53, 138.07, 135.35, 135.09, 132.90, 131.82, 131.44, 131.39, 131.38, 129.18, 127.81, 127.74, 127.63, 127.44, 126.93, 126.84, 126.58, 126.56, 126.51, 125.99, 125.96, 124.21. MS (MALDI-TOF): m/z calcd. [M]$^+$ 581.24 found 581.03.

$^1$H NMR (300 MHz, CDCl₃): δ(TMS, ppm): 8.01 (1H, d, J=16.3 Hz), 7.61-7.53 (6H, m), 7.33 (1H, d, J=15.7 Hz), 7.20-7.11 (11H, m), 7.17-7.00 (6H, m), 4.11 (3H, s), 1.76 (6H, s); $^{13}$C NMR (125 MHz, CDCl₃): δ(TMS, ppm): 182.14, 152.78, 149.05, 144.08, 143.31, 143.19, 142.96, 142.93, 142.28, 140.22, 133.13, 132.04, 131.24, 131.23, 131.10, 130.43, 129.89, 129.44, 128.53, 128.52, 128.37, 127.60, 127.43, 127.42, 123.33, 115.66, 113.40, 52.60, 34.88, 25.70. HRMS (ESI, positive): m/z calcd. [M-PF$_6^-$]$^+$ 516.2686 found 516.2685.

$^1$H NMR (300 MHz, CDCl₃): δ(TMS, ppm): 8.41 (1H, d, J=16.3 Hz), 8.22 (2H, d, J=8.3 Hz), 7.91-7.86 (2H, m), 7.78 (2H, d, J=8.2 Hz), 7.72-7.62 (3H, m), 7.48-7.42 (3H, m), 7.30 (1H, d, J=16.6 Hz), 7.18-7.13 (9H, m), 7.03-6.93 (8H, m), 4.16 (3H, s), 1.80 (6H, s); $^{13}$C NMR (125 MHz, CDCl₃): δ(TMS, ppm): 182.05, 152.88, 144.06, 143.89, 143.66, 143.58, 143.46, 142.65, 142.33, 141.48, 140.67, 135.30, 134.11, 131.91, 131.68, 131.53, 131.22, 131.17, 131.13, 129.82, 129.45, 128.40, 128.37, 128.29, 127.96, 127.61, 127.19, 127.15, 127.09, 126.92, 123.32, 115.60, 112.99, 52.59, 34.88, 25.82. HRMS (ESI, positive): m/z calcd. [M-PF$_6^-$]$^+$ 618.3155 found 618.3154.
Figure S1. (a) Optimized structures of TPE and its group I derivatives using B3LYP/6-31G (d,p) by Gaussian 09. (b) Long-to-short axis ratio (LSAR) of TPE and its group I derivatives.

Long-to-short axis ratio (LSAR) is obtained through molecular long axis divided by molecular short axis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>TPE</th>
<th>TPE-Br</th>
<th>TPE-CH₃</th>
<th>TPE-OCH₃</th>
<th>TPE-Phen</th>
<th>TPE-Diphen</th>
</tr>
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<tbody>
<tr>
<td>Long-to-short axis ratio</td>
<td>1.00</td>
<td>1.07</td>
<td>1.07</td>
<td>1.17</td>
<td>1.37</td>
<td>1.75</td>
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</tbody>
</table>
Figure S2. (a) Optimized structures of single-arm extended TPE derivatives (group II) using B3LYP/6-31G (d,p) by Gaussian 09\textsuperscript{2}. (b) Long-to-short axis ratio (LSAR) and dipole moments of these six single-arm extended TPE derivatives (group II).

<table>
<thead>
<tr>
<th>Compound</th>
<th>TPE-VB</th>
<th>TPE-VBA</th>
<th>TPE-VBN</th>
<th>TPE-VI</th>
<th>TPE-VBVBN</th>
<th>TPE-VBVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-to-short axis ratio</td>
<td>1.57</td>
<td>1.76</td>
<td>1.65</td>
<td>1.71</td>
<td>2.22</td>
<td>2.28</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
<td>0.13</td>
<td>3.83</td>
<td>7.11</td>
<td>12.73</td>
<td>7.71</td>
<td>24.02</td>
</tr>
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</table>
Figure S3. Molecular orbital amplitude plots of HOMO and LUMO energy levels of the six single-arm extended tetraphenylethylene derivatives (group II) calculated using B3LYP/6-31G(d,p) by Gaussian 09\textsuperscript{2}.
**Table S1.** Summary of crystal data and intensity collection parameters for TPE-VBN and TPE-VBVBN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>TPE-VBN</th>
<th>TPE-VBVBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₃₄H₂₅NO₂</td>
<td>C₄₂H₃₁NO₂</td>
</tr>
<tr>
<td>Formula mass</td>
<td>479.55</td>
<td>581.68</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁</td>
<td>P -1</td>
</tr>
<tr>
<td>a/ Å</td>
<td>10.202(5)</td>
<td>9.396(5)</td>
</tr>
<tr>
<td>b/ Å</td>
<td>18.970(7)</td>
<td>17.959(6)</td>
</tr>
<tr>
<td>c/ Å</td>
<td>13.263(5)</td>
<td>18.690(7)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>98.310(15)</td>
</tr>
<tr>
<td>β/°</td>
<td>98.310(15)</td>
<td>83.610(15)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>86.117(15)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2539.9(18)</td>
<td>3082(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ/g.cm⁻³</td>
<td>1.254</td>
<td>1.254</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>1008</td>
<td>1224</td>
</tr>
<tr>
<td>Temp, (K)</td>
<td>153(2)</td>
<td>153(2)</td>
</tr>
<tr>
<td>Absorption coefficient, μ/mm⁻¹</td>
<td>0.077</td>
<td>0.076</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>23987</td>
<td>23103</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>9887</td>
<td>10341</td>
</tr>
<tr>
<td>Rint</td>
<td>0.0554</td>
<td>0.0575</td>
</tr>
<tr>
<td>Final R₁ values (I &gt; 2σ(I))</td>
<td>0.0539</td>
<td>0.0674</td>
</tr>
<tr>
<td>Final wR(F²) values (I &gt; 2σ(I))</td>
<td>0.1241</td>
<td>0.1864</td>
</tr>
<tr>
<td>Final R(I) values (all data)</td>
<td>0.0840</td>
<td>0.1355</td>
</tr>
<tr>
<td>Final wR(F²) values (all data)</td>
<td>0.1391</td>
<td>0.2445</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.018</td>
<td>0.987</td>
</tr>
<tr>
<td>CCDC numbers</td>
<td>1053198</td>
<td>1053197</td>
</tr>
</tbody>
</table>

The crystal data for TPE-VBN and TPE-VBVBN were deposited into Cambridge Crystallographic Data Centre with CCDC numbers of 1053198 and 1053197, respectively.
Figure S4. Single-crystal X-ray structure of TPE-VBN and TPE-VBVBN (50% probability ellipsoids).
Figure S5. (a) Absorption spectra and (b) fluorescent spectra of TPE-VB (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of TPE-VB with different water fractions). (c) Absorption spectra and (d) fluorescent spectra of TPE-VBA (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of TPE-VBA with different water fractions).
Figure S6. (a) Absorption spectra and (b) fluorescent spectra of TPE-VI (1\times10^{-5} \text{ M}) in THF and hexane mixtures with different hexane fractions (inset: real fluorescent images of TPE-VI with different hexane fractions). (c) Absorption spectra and (d) fluorescent spectra of TPE-VBVI (1\times10^{-5} \text{ M}) in THF and hexane mixtures with different hexane fractions (inset: real fluorescent images of TPE-VBVI with different hexane fractions).
Figure S7. (a) Absorption spectra and (b) fluorescent spectra of TPE-VBN (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of TPE-VBN with different water fractions). (c) Absorption spectra and (d) fluorescent spectra of TPE-VBVBN (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of TPE-VBVBN with different water fractions).
Figure S8. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra ($\lambda_{\text{Ex}}=365$ nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of TPE-VBA in different states.
Figure S9. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra ($\lambda_{\text{Ex}}=365$ nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of TPE-VBN in different states.
Figure S10. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra ($\lambda_{\text{ex}}=365$ nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of TPE-VBVBN in different states.
Figure S11. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra ($\lambda_{\text{Ex}}=500$ nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of TPE-VI in different states.
Figure S12. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra ($\lambda_{\text{Ex}}=500$ nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of TPE-VBVI in different states.
Figure S13. (a) Emission spectra of unground TPE with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S14. (a) Emission spectra of unground TPE-Br with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-Br with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-Br with different excitation lights (inset: the corresponding excitation spectrum). (d) Emission spectra of fumed TPE-Br with different excitation lights (inset: the corresponding excitation spectrum).
Figure S15. (a) Emission spectra of unground TPE-CH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground TPE-CH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-CH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-CH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S16. (a) Emission spectra of unground TPE-OCH$_3$ with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-OCH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-OCH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-OCH$_3$ with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S17. (a) Emission spectra of unground TPE-Phen with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-Phen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-Phen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-Phen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S18. (a) Emission spectra of unground TPE-Diphen with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-Diphen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-Diphen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-Diphen with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S19. (a) Emission spectra of unground TPE-VB with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-VB with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VB with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VB with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S20. (a) Emission spectra of unground TPE-VBA with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-VBA with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VBA with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VBA with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S21. (a) Emission spectra of unground TPE-VBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground TPE-VBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S22. (a) Emission spectra of unground TPE-VBVBN with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-VBVBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VBVBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VBVBN with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S23. (a) Emission spectra of unground TPE-VI with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground TPE-VI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
Figure S24. (a) Emission spectra of unground TPE-VBVI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground TPE-VBVI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed TPE-VBVI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed TPE-VBVI with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).
**Figure S25.** (a) Normalized emission spectra of TPE-VB in THF solution \((1 \times 10^{-5} \text{ M})\) with different excitation lights. (b) Normalized excitation spectrum of TPE-VB in THF solution \((1 \times 10^{-5} \text{ M})\).

**Figure S26.** (a) Normalized emission spectra of TPE-VBA in THF solution \((1 \times 10^{-5} \text{ M})\) with different excitation lights. (b) Normalized excitation spectrum of TPE-VBA in THF solution \((1 \times 10^{-5} \text{ M})\).
Figure S27. (a) Normalized emission spectra of TPE-VBN in THF solution ($1 \times 10^{-5}$ M) with different excitation lights. (b) Normalized excitation spectrum of TPE-VBN in THF solution ($1 \times 10^{-5}$ M).

Figure S28. (a) Normalized emission spectra of TPE-VBVBN in THF solution ($1 \times 10^{-5}$ M) with different excitation lights. (b) Normalized excitation spectrum of TPE-VBVBN in THF solution ($1 \times 10^{-5}$ M).
Figure S29. (a) Normalized emission spectra of TPE-VI in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of TPE-VI in THF solution (1×10^{-5} M).

Figure S30. (a) Normalized emission spectra of TPE-VBVI in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of TPE-VBVI in THF solution (1×10^{-5} M).
Figure S31. (a) Normalized emission spectra of Rhodamine 6G in THF solution \((1 \times 10^{-5} \text{ M})\) with different excitation lights. (b) Normalized excitation spectrum of Rhodamine 6G in THF solution \((1 \times 10^{-5} \text{ M})\).

Figure S32. (a) Normalized emission spectra of Anthracene in THF solution \((1 \times 10^{-5} \text{ M})\) with different excitation lights. (b) Normalized excitation spectra of Anthracene in THF solution \((1 \times 10^{-5} \text{ M})\) with different emission wavelengths.
Figure S33. (a) Normalized emission spectra of **Rhodamine 6G** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **Rhodamine 6G** in PMMA film (ω%=1%) with different emission wavelengths.

Figure S34. (a) Normalized emission spectra of **Anthracene** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **Anthracene** in PMMA film (ω%=1%) with different emission wavelengths.
Figure S35. (a) Normalized emission spectra of TPE in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE in PMMA film (ω%=1%) with different emission wavelengths.

Figure S36. (a) Normalized emission spectra of TPE-Br in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-Br in PMMA film (ω%=1%) with different emission wavelengths.
Figure S37. (a) Normalized emission spectra of TPE-CH$_3$ in PMMA film ($\omega\%$=1\%) with different excitation lights. (b) Normalized excitation spectra of TPE-CH$_3$ in PMMA film ($\omega\%$=1\%) with different emission wavelengths.

Figure S38. (a) Normalized emission spectra of TPE-OCH$_3$ in PMMA film ($\omega\%$=1\%) with different excitation lights. (b) Normalized excitation spectra of TPE-OCH$_3$ in PMMA film ($\omega\%$=1\%) with different emission wavelengths.
Figure S39. (a) Normalized emission spectra of **TPE-Phen** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-Phen** in PMMA film (ω%=1%) with different emission wavelengths.

![Normalized emission spectra of **TPE-Phen** in PMMA film (ω%=1%)](image1)

![Normalized excitation spectra of **TPE-Phen** in PMMA film (ω%=1%)](image2)

Figure S40. (a) Normalized emission spectra of **TPE-Diphen** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-Diphen** in PMMA film (ω%=1%) with different emission wavelengths.

![Normalized emission spectra of **TPE-Diphen** in PMMA film (ω%=1%)](image3)

![Normalized excitation spectra of **TPE-Diphen** in PMMA film (ω%=1%)](image4)
Figure S41. (a) Normalized emission spectra of TPE-VB in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VB in PMMA film (ω%=1%) with different emission wavelengths.

Figure S42. (a) Normalized emission spectra of TPE-VBA in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VBA in PMMA film (ω%=1%) with different emission wavelengths.
Figure S43. (a) Normalized emission spectra of TPE-VBN in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VBN in PMMA film (ω%=1%) with different emission wavelengths.

Figure S44. (a) Normalized emission spectra of TPE-VBVBN in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VBVBN in PMMA film (ω%=1%) with different emission wavelengths.
Figure S45. (a) Normalized emission spectra of TPE-VI in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VI in PMMA film (ω%=1%) with different emission wavelengths.

Figure S46. (a) Normalized emission spectra of TPE-VBVI in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of TPE-VBVI in PMMA film (ω%=1%) with different emission wavelengths.
Figure S47. Summary on the maximum emission wavelengths of the studied fluorescent compounds in different states.

For TPE-VI and TPE-VBVI, their as-prepared (unground) samples exhibit relatively large maximum wavelength differences, which might be ascribed to the diversified molecular configurations in the non-ignorable surfaces, interfaces and defects of poorly-crystallized powders (broad and weak X-ray diffraction peaks in Figure S11c and S12c).

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ungrounded</th>
<th>Grounded</th>
<th>Annealed</th>
<th>Formed</th>
<th>1% PMMA Film</th>
<th>THF solution</th>
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<tbody>
<tr>
<td>TPE</td>
<td>446 nm</td>
<td>447-457 nm</td>
<td>446-466 nm</td>
<td>447-468 nm</td>
<td>439-465 nm</td>
<td>10 nm</td>
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<td>TPE-Br</td>
<td>457 nm</td>
<td>457-471 nm</td>
<td>457-461 nm</td>
<td>452-458 nm</td>
<td>455-481 nm</td>
<td>21 nm</td>
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<tr>
<td>TPE-CH₃</td>
<td>455 nm</td>
<td>457-478 nm</td>
<td>453-469 nm</td>
<td>454-489 nm</td>
<td>453-484 nm</td>
<td>9 nm</td>
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<tr>
<td>TPE-OCH₃</td>
<td>459 nm</td>
<td>458-486 nm</td>
<td>458-468 nm</td>
<td>453-485 nm</td>
<td>453-476 nm</td>
<td>10 nm</td>
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<tr>
<td>TPE-Phen</td>
<td>481 nm</td>
<td>487-493 nm</td>
<td>466-484 nm</td>
<td>460-470 nm</td>
<td>453-471 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>TPE-Diphen</td>
<td>456 nm</td>
<td>462-496 nm</td>
<td>452-479 nm</td>
<td>453-476 nm</td>
<td>452-470 nm</td>
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<td>464-508 nm</td>
<td>457-507 nm</td>
<td>453-492 nm</td>
<td>453-480 nm</td>
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<td>506-519 nm</td>
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<td>539-550 nm</td>
<td>555 nm</td>
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<tr>
<td>Rhodamine 6G</td>
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<td>309 nm, 491 nm, 420 nm, 430 nm</td>
</tr>
</tbody>
</table>
$^1$H NMR, $^{13}$C NMR and mass spectra of TPE and its derivatives
Reference
