Electronic Supplementary Information

Tetraphenylpyrazine-Based AIEgens: Facile Preparation and Tunable Light Emission

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Experimental Section

Materials: All commercially available chemicals were purchased from Alfa Aesar, J&K chemistry or Sinopharm Chemical Reagent Co., Ltd and used directly without further purification. Tetrahydrofuran (THF) and 1,4-dioxane were distilled from sodium benzopheone ketyl under dry nitrogen immediately before use.

Instrumentation: All $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AVANCE III 500 spectrometer using CDCl$_3$ or DMSO-$d_6$ as solvent. High resolution mass spectra (HRMS) were tested using a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV-visible absorption spectra were measured with a Varian CARY 100 Biospectrophotometer. PL spectra were recorded on a RF-5301 PC spectrofluorometer. PL quantum efficiency ($\Phi_F$) was measured with standard quinine sulfate in 0.1N H$_2$SO$_4$ ($\Phi_F = 0.54$) or anthracene in ethanol ($\Phi_F = 0.27$). The absolute $\Phi_F$ values were recorded with a Hamamatsu Quantaurus-QY C11347 spectrometer. Thermogravimetric analysis (TGA) was carried out with a PerkinElmer TGA 7 at a heating rate of 10 °C/min under dry nitrogen. Single crystal X-ray diffraction was carried out on a Gemini A Ultra diffractometer at 293K.

Synthesis of tetraphenylpyrazine (TPP): Rout A: The compound was synthesized accord to the literature with slight modification.$^1$ Into a 50 mL round bottom flask was added 2.12 g (10 mmol) of benzoin, 1.45 mL (15 mmol) of acetic anhydride, 2.32 g
(30 mmol) of ammonium acetate and 10 mL acetic acid. After refluxing for 3.5 h, the mixture was cooled down to room temperature and then filtered.

Route B:\[2\]: Into a 50 mL round bottom flask was added 212 mg (1 mmol) of 1,2-diphenylethane-1,2-diamine, 210 mg (1 mmol) of benzyl and 2 mL of acetic acid. The mixture was allowed to reflux for 4 h. Afterwards, the mixture was cooled down to room temperature and filtered. The crude products were purified with recrystallization in acetic acid three times. White crystal, yield: 33.9% (route A); 46.9% (route B). \(^1\)H NMR (500 MHz CDCl\(_3\)): \(\delta\) (TMS, ppm) 7.65 (m, 8H), 7.33 (m, 12H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm) 148.5, 138.5, 129.9, 128.7, 128.3. HRMS (MALDI-TOF): \(m/z\) 384.1664 ([M]+), calcd for C\(_{28}\)H\(_{20}\)N\(_2\) 384.1626).

**Synthesis of TPP derivative (TPP-4M):** The synthetic method was similar to that of TPP. White crystal, yield: 20%. \(^1\)H NMR (500 MHz CDCl\(_3\)): \(\delta\) (TMS, ppm) 7.61 (d, 8H), 6.86 (d, 8H), 3.82 (s, 12H). \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm) 159.9, 146.8, 131.1, 113.7, 55.3. HRMS (MALDI-TOF): \(m/z\) 504.2039 ([M]+), calcd for C\(_{32}\)H\(_{28}\)N\(_2\)O\(_4\): 504.2049).

**Synthesis of 1-(4-bromophenyl)-2-phenylethanone (8):** The product was prepared according to the literature procedure.\(^3\) Into a 250 mL round bottom flask was added 10 g (50 mmol) of 4-bromophenyl boronic acid (5), 1.32 g (2.5 mmol) of Ni(dppe)Cl\(_2\) and 5.1 g (37.5 mmol) of ZnCl\(_2\) under nitrogen. Then, 75 mL of 1,4-dioxane, 2.9 mL (25 mmol) of phenylacetonitrile (6) and 0.45 mL (25 mmol) of water was injected into the flask and the reaction was allowed to stir at 80 °C for 8 h. Afterward, the
mixture was filtered and the residue was washed with THF three times. Then the filtrate was concentrated and further dissolved in DCM, and washed with water to remove residual 1,4-dioxane. The collected organic phase was condensed and purified by a silica-gel column with ethyl acetate/hexane (1:20 by volume) as eluent. White solid 8 was obtained in 74.4% yield. 

\[ ^1H \text{NMR} (500 \text{ MHz, DMSO-}d_6): \delta (\text{TMS, ppm}) 7.99 (d, 2H), 7.76 (d, 2H), 7.26 (m, 5H), 4.39 (s, 2H). \]

\[ ^{13}C \text{NMR} (125 \text{ MHz, CDCl}_3): \delta (\text{TMS, ppm}) 196.8, 135.5, 134.4, 132.2, 130.4, 129.0, 128.6, 127.3, 45.8. \]

**Synthesis of 1-(4-bromophenyl)-2-(4-methoxyphenyl)ethanone (9):** The synthetic method was similar to that of 8. White solid, yield: 67.0 %. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3): \delta (\text{TMS, ppm}) 7.87 (d, 2H), 7.60 (d, 2H), 7.17 (d, 2H), 6.87 (d, 2H), 4.19 (s, 2H), 3.78 (s, 3H). \]

\[ ^{13}C \text{NMR} (125 \text{ MHz, CDCl}_3): \delta (\text{TMS, ppm}) 196.9, 158.6, 135.1, 131.9, 130.4, 130.2, 128.3, 126.1, 114.2, 55.3, 44.7. \]

**Synthesis of 1-(4-bromophenyl)-2-hydroxy-2-phenylethanone (10):** The product was prepared according to the literature procedure. \(^3\) Into a 250mL round bottom flask was added 6 g (22 mmol) of 9, 150 mL of dimethyl sulfoxide and 7.5 mL of water. After complete dissolution, 20.5 g (52.8mmol) of PHI(OH)OTs was added into the mixtures in two times. The reaction was kept at room temperature for 24 h. After reaction, the mixture was poured into the water and extracted with ethyl acetate. The collected organic phase was first washed with a large amount of water, and then condensed and purified by a silica-gel column with ethyl acetate/hexane (1:10 by volume) as eluent. White solid 10 was obtained in 35.4% yield. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3): \delta (\text{TMS, ppm}) 7.78 (d, 2H), 7.54 (d, 2H), 7.32 (m, 5H), 5.89 (s, 1H) 4.47 (s,
1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 198.3, 138.9, 132.3, 130.8, 129.5, 129.0, 128.0, 76.6.

**Synthesis of 1-(4-bromophenyl)-2-hydroxy-2-(4-methoxyphenyl)ethanone (11):**
The synthetic method was similar to that of 10. Yellow viscous liquid, yield: 34.4 %.
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 7.77 (d, 2H), 7.54 (d, 2H), 7.23 (d, 2H), 6.86 (d, 2H), 5.85 (s, 1H), 4.41 (s, 1H), 3.76 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 198.1, 159.9, 132.3, 132.0, 130.8, 130.6, 129.1, 114.7, 75.8, 55.3.

**Synthesis of 12:** The synthetic method was similar to that of TPP with method A. White solid, yield: 18.6 %. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$(TMS, ppm) 7.61 (m, 4H), 7.50 (m, 4H), 7.46 (m, 4H), 7.36 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 148.6, 148.4, 147.4, 147.2, 138.0, 137.2, 131.5, 131.4, 129.8, 129.0, 128.5, 123.3.

**Synthesis of 13:** The synthetic method was similar to that of TPP with method A. White solid, yield: 23.5 %. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$(TMS, ppm) 7.56 (m, 8H), 7.45 (d, 4H), 6.87 (d, 4H), 3.83 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$(TMS, ppm) 160.3, 148.0, 147.5, 146.8, 146.1, 137.6, 131.5, 131.4, 131.3, 131.2, 131.1, 130.3, 123.0, 113.9, 55.3.

**Synthesis of TPP-2P:** Into a 250 mL round bottom flask was added 120 mg (0.22 mmol) of 12, 66 mg (0.54 mmol) of benzoboric acid, 12.8 mg (0.011 mmol) of Pd(PPh$_3$)$_4$, 10 mL of THF and 1.38 g of K$_2$CO$_3$ (dissolved in 5 mL of water) under nitrogen. The mixture was allowed for stir at 80 °C for 12 h. After cooled down to room temperature, the mixture was diluted with dichloromethane and washed with...
NH₄Cl aqueous solution. The collected organic phase was condensed and purified by a silica-gel column with ethyl acetate/hexane (1:50 by volume) as eluent. White solid, yield: 58.9 %. ¹H NMR (500 MHz, CDCl₃): δ(TMS, ppm) 7.74 (m, 8H), 7.64 (d, 4H), 7.59 (d, 4H), 7.45 (t, 4H), 7.37 (m, 8H). ¹³C NMR (125 MHz, CDCl₃): δ(TMS, ppm) 148.6, 148.5, 148.2, 148.1, 141.5, 140.7, 138.7, 137.6, 130.6, 130.2, 129.1, 129.0, 128.6, 127.8, 127.3, 127.2. HRMS (MALDI-TOF): m/z 536.2248 ([M⁺], calcd for C₄₀H₂₈N₂ 536.2252 ).

**Synthesis of TPP-2PM**: The synthetic method was similar to that of TPP-2P. White solid, yield: 68.2 %. ¹H NMR (500 MHz, CDCl₃): δ(TMS, ppm) 7.72 (m, 8H), 7.57 (d, 4H), 7.52 (d, 4H), 7.35 (m, 6H), 6.97 (d, 4H), 3.85 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ(TMS, ppm) 159.6, 148.5, 148.4, 148.2, 148.0, 141.2, 138.8, 137.0, 133.2, 130.5, 130.1, 128.9, 128.6, 128.3, 126.7, 114.5, 55.6. HRMS (MALDI-TOF): m/z 596.2462 ([M⁺], calcd for C₄₂H₃₂N₂O₂ 596.2464 ).

**Synthesis of TPP-2MP**: The synthetic method was similar to that of TPP-2P. White solid, yield: 79.3 %. ¹H NMR (500 MHz, CDCl₃): δ(TMS, ppm) 7.77 (d, 4H), 7.66 (m, 8H), 7.60 (d, 4H), 7.45 (t, 4H), 7.36 (t, 2H), 6.89 (d, 4H), 3.83 (6H). ¹³C NMR (125 MHz, CDCl₃): δ(TMS, ppm) 160.1, 147.7, 147.4, 147.2, 146.9, 141.1, 140.6, 137.9, 131.3, 130.9, 130.2, 128.8, 127.5, 127.1, 127.0, 113.8, 55.3. HRMS (MALDI-TOF): m/z 596.2457 ([M⁺], calcd for C₄₂H₃₂N₂O₂ 596.2464 ).

**Synthesis of TPP-2MPM**: The synthetic method was similar to that of TPP-2P. White solid, yield: 62.9 %. ¹H NMR (500 MHz, CDCl₃): δ(TMS, ppm) 7.74 (d, 4H), 7.65 (d, 4H), 7.58 (d, 4H), 7.53 (d, 4H), 6.99 (d, 4H), 6.88 (d, 4H), 3.86 (s, 6H), 3.83
(s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 160.1, 159.4, 147.5, 147.3, 147.2, 146.9, 140.6, 137.2, 133.0, 131.3, 131.0, 130.2, 128.1, 126.4, 114.3, 113.7, 55.4, 55.3. HRMS (MALDI-TOF): $m/z$ 656.2658 ([M]$^+$, calcd for C$_{44}$H$_{36}$N$_2$O$_4$ 656.2675).

Synthesis of TPP-2PCN: Into a 100 mL round bottom flask was added 60 mg (0.11 mmol) of 12, 48 mg (0.33 mmol) of 15 and 12.8 mg (0.011 mmol) of Pd(PPh$_3$)$_4$, 10 mL of toluene, 5 mL of EtOH and 1.38 g K$_2$CO$_3$ (dissolved in 5 mL of water) under nitrogen. The mixture was reacted at 110 °C for 6 h. Afterwards, solvent was removed by reduced pressure distillation and the residue was washed with dichloromethane and water. The collected organic phases were concentrated and the product was purified by a silica-gel column with dichloromethane/hexane (4:5 by volume) as eluent. White solid TPP-2PCN was obtained in 80% yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (TMS, ppm) 7.72 (m, 16H), 7.59 (m, 4H), 7.39 (m, 6H).
**Figure S1.** $^1$H NMR spectrum of TPP in CDCl$_3$. The solvent peak is marked with asterisk.

**Figure S2.** $^{13}$C NMR spectrum of TPP in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of TPP-4M in CDCl$_3$. The solvent peak is marked with asterisk.

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Figure S16. $^{13}$C NMR spectrum of 13 in CDCl$_3$. The solvent peak is marked with an asterisk.
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Figure S18. $^{13}$C NMR spectrum of TPP-2P in CDCl$_3$. 
**Figure S19.** $^1$H NMR spectrum of TPP-2PM in CDCl$_3$. The solvent peak is marked with asterisk.

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**Figure S21.** $^1$H NMR spectrum of TPP-2MP in CDCl$_3$. The solvent peak is marked with asterisk.

**Figure S22.** $^{13}$C NMR spectrum of TPP-2MP in CDCl$_3$. The solvent peak is marked with asterisk.
Figure S23. $^1$H NMR spectrum of TPP-2MPM in CDCl$_3$. The solvent peak is marked with asterisk.

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Figure S26. HRMS spectra of TPP-4M.
Figure S27. HRMS spectra of TPP-2P.

Figure S28. HRMS spectra of TPP-2PM.
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Figure S33. PL spectra of pristine and treated TPP in THF/water mixtures with ~90% water fractions. Concentration: $10^{-5}$ M. $\lambda_{ex}$: 338 nm. The acid and base are 0.1 mL HCl or NaOH aqueous solution (1M), respectively.

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**Figure S37.** PL spectra of TPP-2PM in THF/water mixtures with different water fraction. Concentration: $10^{-5}$ M, $\lambda_{ex} = 352$ nm.

**Figure S38.** PL spectra of TPP-2MPM in THF/water mixtures with different water fraction. Concentration: $10^{-5}$ M, $\lambda_{ex} = 362$ nm.
**Figure S39.** PL spectra of TPP-2MP in THF/water mixtures with different water fraction. Concentration: $10^{-5}$ M, $\lambda_{ex} = 359$ nm.

**Figure S40.** PL spectra of TPP-4M in THF/water mixtures with different water fraction. $10^{-5}$ M, $\lambda_{ex} = 360$ nm.
**Figure S41.** Molecular structures and torsion angles of TPP.

**Figure S42.** Molecular structures and torsion angles of TPP-4M.
**Figure S43.** Molecular structures and torsion angles of TPP-2P.

θ₁ = 50.81°  
θ₂ = 38.46°  
θ₃ = 38.23°  
θ₄ = 47.01°  
θ₅ = 39.59°  
θ₆ = 29.71°

**Figure S44.** Molecular structures and torsion angles of TPP-2PM.

θ₁ = 51.57°  
θ₂ = 45.65°  
θ₃ = 33.81°  
θ₄ = 55.21°  
θ₅ = 31.04°  
θ₆ = 40.93°
**Figure S45.** Normalized PL spectra of TPP derivatives in THF. Concentration: 10 μM.

**Scheme S1.** Synthetic route to TPP-2PCN.
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Figure S47. PL spectra of TPP-2PCN in THF/water mixtures with different water fraction. Concentration: $10^{-5}$ M, $\lambda_{ex} = 347$ nm.

Table S1. Optical and thermal properties of TPP and its derivatives.
\[ \lambda_{ab}/\text{nm} \quad \lambda_{em,s}/\text{nm} \quad \lambda_{em,f}/\text{nm} \quad \Phi_{F,\text{sol}}/\% \quad \Phi_{F,\text{agg}}/\% \quad \Phi_F/\% \quad T_d/^\circ \text{C} \]

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<th>( \lambda_{em,f}/\text{nm} )</th>
<th>( \Phi_{F,\text{sol}}/% )</th>
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\(^a\) Measured using anthracene in ethanol as standard (\( \Phi_F = 0.27 \)). \(^b\) Measured using quinine sulfate in 0.1N \( \text{H}_2\text{SO}_4 \) as standard (\( \Phi_F = 0.54 \)). \(^c\) Aggregates formed in THF/water mixtures with \( f_w \) of 90%. \(^d\) Aggregates formed in THF/water mixtures with \( f_w \) of 80%. \(^e\) Measured using Hamamatsu Quantaurus-QY C11347 spectrometer.

### Table S2. Particle sizes of TPP-based AIEgens in THF/water mixtures.\(^a\)

<table>
<thead>
<tr>
<th>( f_w (%) )^b</th>
<th>TPP</th>
<th>TPP-2P</th>
<th>TPP-2PM</th>
<th>TPP-2MPM</th>
<th>TPP-2MP</th>
<th>TPP-4M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>140</td>
<td>72</td>
<td>64</td>
<td>84</td>
<td>207</td>
<td>287</td>
</tr>
<tr>
<td>90</td>
<td>220</td>
<td>32</td>
<td>31</td>
<td>40</td>
<td>37</td>
<td>139</td>
</tr>
</tbody>
</table>

\(^a\) Measured by DLS, the unit for the particle size is nm. \(^b\) \( f_w \) = water fraction.

### References