Supporting information

Construction of Aromatic-Ring-Layered Structures
Using the Terphenylene-layered Polymer as the Scaffold

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Contents

Synthesis of 1, M1, M2d, and D2d ............................................. S–1

1H and 13C NMR spectra of S1–S3, 1, M1, D1, P1, D2d, and P2a–e (Figures S1–S26) ............................................. S–6

FT-IR spectra of P1 and P2a–e (Figure S27) ................................... S–19

MALDI-TOF-Mass spectra of P1 and P2d (Figures S28 and S29) ............................................. S–19

UV-vis absorption and fluorescence spectra of M1, D1 and P1 (Figure S30) ............................................. S–20

X-ray diffraction analysis (XRD) patterns of D1, P1, D2d and P2d (Figure S31 and Table S1) ............................................. S–21

Fluorescence emission spectra of D2d and P2d in different concentrations (Figure S32) ............................................. S–22

Fluorescence decay analysis of M2d, D2d, and P2d (Figures S33–S35 and Table S2) ............................................. S–23

Fluorescence emission spectra of P2d in 2-methyltetrahydrofuran (Figures S36 and S37) ............................................. S–25
Synthesis of monomer 1

1,4-Dibromo-2,3,5,6-tetramethoxybenzene (S1).
1,4-Dihydroxy-p-benzoquinone (7.79 g, 55.6 mmol) was suspended in EtOH (200 mL), and Br₂ (5.66 mL, 111.2 mmol) was added dropwise to the suspension. The mixture was stirred at room temperature overnight. Red precipitation was formed, which was collected by filtration. The crude product was washed with CHCl₃, and then, it was dried in vacuo. The product was dissolved in EtOAc (400 mL). Aqueous Na₂S₂O₄ (1 M, 200 mL) was added dropwise to the solution, and the mixture was stirred at room temperature overnight. The organic layer was extracted with EtOAc (100 mL × 2), and the combined organic layer was dried over Na₂SO₄. After Na₂SO₄ was removed, the solution was concentrated in vacuo. The crude product was dissolved in acetone (50 mL). (MeO)₂SO₂ (21 mL, 222.4 mmol) and K₂CO₃ (30.7 g, 222.4 mmol) were added to the solution, and the mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into H₂O (200 mL) to precipitate the product. The precipitation was collected by filtration, and it was dried in vacuo. The crude product was purified by recrystallization from CHCl₃/MeOH to afford S1 as a white crystal (15.51 g, 43.6 mmol, 78% for 3 steps). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.88 (s, 12 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 148.0, 112.9, 61.0.

1,4-Bis(4'-trimethylphenyl)-2,3,5,6-tetramethoxybenzene (S2).
A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)trimethylsilylbenzene (6.63 g, 24.0 mmol), S1 (3.56 g, 10.0 mmol), Pd₂(dba)₃ (230 mg, 0.25 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-phos) (410 mg, 1.0 mmol), and K₂CO₃ (4.15 g, 30.0 mmol) was dissolved in toluene (50 mL), EtOH (20 mL), and H₂O (30 mL). The solution was refluxed for 24 h. H₂O (50
(30 mL × 3). The combined organic layer was dried over MgSO₄. After removal of MgSO₄, the solution was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/CHCl₃ = 1:1, Rf = 0.2) and by recrystallization from CHCl₃/MeOH to afford 1,4-bis(4'-trimethylphenyl)-2,3,5,6-tetramethoxybenzene (S2) as a white crystal (3.61 g, 7.29 mmol, 73%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.59 (d, J = 8.0 Hz, 4 H), 7.39 (d, J = 8.0 Hz, 4 H), 3.62 (s, 12 H), 0.31 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.0, 139.0, 134.3, 132.9, 130.2, 129.3, 60.9, –1.0. MS (APCI) m/z: 495.2378 (calcd for C₂₈H₃₈O₄Si₂, [M + H]⁺ 495.2381). Anal. calcd. for C₂₈H₃₈O₄Si₂: C 67.97, H 7.74; found: C 67.71, H 7.81.

1,4-Bis(4'-iodophenyl)-2,3,5,6-tetramethoxybenzene (1).

ICl in CH₂Cl₂ solution (1 M, 4 mL) was added dropwise to the solution of S2 (825 mg, 1.67 mmol) in CH₂Cl₂ (20 mL) at room temperature. The mixture was stirred at room temperature overnight to form precipitation. The precipitation was collected by filtration, and it was washed with hexane. The crude product was purified by recrystallization from CHCl₃/MeOH to afford 1 as a white crystal (781 mg, 1.30 mmol, 78%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.77 (d, J = 8.3 Hz, 4 H), 7.18 (d, J = 8.3 Hz, 4 H), 3.57 (s, 12 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 147.2, 137.3, 133.4, 132.5, 129.5, 93.5, 61.2. MS (APCI) m/z: 602.9519 (calcd for C₂₂H₂₀O₄I₂, [M + H]⁺ 602.9524). Anal. calcd. for C₂₂H₂₀O₄I₂: C 43.88, H 3.35, O 10.63, I 42.15; found: C 43.79, H 3.37, O 10.79, I 41.58.
Synthesis of compound M1

2-Hexyloxybenzeneboronic acid (S3).

$n$-BuLi (24 mL, 1.6 M hexane solution) was added dropwise to a solution of 2-hexyloxybromobenzene (6.2 g, 24 mmol) in Et$_2$O (70 mL) at −78 °C. After stirring for 2 h, B(OiPr)$_3$ (9.2 mL, 40 mmol) was added dropwise to the solution at −78 °C, and it was stirred at room temperature overnight. 1 N HCl was added to the solution to quench the reaction, and then, the organic layer was extracted with Et$_2$O three times. The organic layer was dried over MgSO$_4$. After removal of MgSO$_4$, the solution was dried in vacuo. The crude product was purified by recrystallization from CHCl$_3$/hexane to afford 2-hexyloxybenzeneboronic acid (S3) as a white crystal (1.96 g, 8.8 mmol, 37%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.66 (s, 2 H), 7.57 (d, $J = 7.0$ Hz, 1 H), 7.34 (t, $J = 7.6$ Hz, 1 H), 6.96 (d, $J = 8.5$ Hz, 1 H), 6.91 (t, $J = 7.2$ Hz, 1 H), 4.01 (t, $J = 6.4$ Hz, 2 H), 1.73 (m, 2 H), 1.40 (m, 2 H), 1.30 (m, 4 H), 0.86 (t, $J = 6.4$ Hz, 3 H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) 162.9, 135.4, 131.6, 120.3, 111.2, 67.7, 34.8, 30.9, 28.6, 25.2, 22.0, 13.9.

1,4-Bis(2'-hexyloxy-1,1'-biphenyl-4-yl)-2,3,5,6-tetramethoxybenzene (M1).

A mixture of 1 (150 mg, 0.25 mmol), S3 (222 mg, 1.0 mmol), Pd$_2$(dba)$_3$ (10 mg, 0.012 mmol), S-Phos (21 mg, 0.05 mmol ), and K$_2$CO$_3$ (138 mg, 1.0 mmol) was dissolved in toluene (5 mL), EtOH (2 mL), and H$_2$O (3 mL). The solution was refluxed overnight. H$_2$O (20 mL) was added to the solution, and the product was extracted with CHCl$_3$ (20 mL × 3). The organic layer was dried over
MgSO₄. After removal of MgSO₄, the solution was concentrated in vacuo. The residue was plugged through short silica gel column (CHCl₃, Rf = 0.5), and the product was purified by recrystallization from CHCl₃/MeOH to give M1 (73%, 129 mg, 0.18 mmol) as a white crystal. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.66 (d, J = 8.2 Hz, 4 H), 7.48 (d, J = 8.2 Hz, 4 H), 7.44 (d, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.8 Hz, 2 H), 7.00 (m, 4 H), 3.99 (t, J = 6.4 Hz, 4 H), 3.64 (s, 12 H), 1.75 (m, 4 H), 1.43 (m, 4 H), 1.30 (m, 8 H), 0.88 (t, J = 6.6 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.1, 147.1, 137.3, 132.1, 130.8, 129.9, 129.6, 129.0, 128.4, 120.7, 112.6, 68.4, 60.9, 31.5, 29.3, 25.8, 22.6, 14.1. MS (APCI) m/z: 703.3973 (calcd for C₄₆H₅₄O₆, [M + H]⁺ 703.3993). Anal. calcd. for C 78.60, H 7.74, O 13.66; found: C 78.65, H 7.81, O 13.89.

Synthesis of compound M2d

BBr₃ in CH₂Cl₂ solution (1 M, 0.25 mL) was added dropwise to the solution of M1 (28 mg, 0.04 mmol) in CH₂Cl₂, and the mixture was stirred at room temperature for 2 h. 1-Pyreneboronic acid (3d) (0.5 mmol) in CH₂Cl₂/MeOH (v/v = 1:1) was added to the solution and stirred overnight. Excess MeOH was added to the mixture to precipitate the product. The precipitation was collected by filtration, and it was washed with MeOH and hexane. The product was dried in vacuo to obtain M2d as a white powder (39 mg, 0.036 mmol, 91%). MS (APCI) m/z: 1089.4452 (calcd for C₇₄H₆₀B₂O₆, [M + Na]⁺ 1089.4468).
Synthesis of compound D2d

BBr₃ in CH₂Cl₂ solution (1 M, 0.25 mL) was added dropwise to the solution of D1 (10 mg, 5.7 mmol) in CH₂Cl₂, and the mixture was stirred at room temperature for 2 h. Compound 3d (1.0 mmol) in CH₂Cl₂/MeOH (v/v = 1:1) was added to the solution and stirred overnight. Excess MeOH was added to the mixture to precipitate the polymer, which was collected by centrifugation. After filtration, the product was washed with MeOH and hexane. It was purified by silica gel column chromatography (hexane/CHCl₃ = 1:1, Rf = 0.5) to afford D2d as a yellow powder (13 mg, 5.2 mmol, 91%).

1H NMR (400 MHz, CDCl₃): δ (ppm) 8.56 (d, J = 9.0 Hz, 4 H), 8.22 (d, J = 8.0 Hz, 8 H), 7.98 (d, J = 7.6 Hz, 4 H), 7.80 (d, J = 7.3 Hz, 4 H), 7.70 (d, J = 9.0 Hz, 4 H), 7.65 (d, J = 8.0 Hz, 8 H), 7.59 (t, J = 7.5 Hz, 4 H), 7.52 (d, J = 7.6 Hz, 4 H), 7.47 (d, J = 7.6 Hz, 4 H), 7.37 (d, J = 7.0 Hz, 4 H), 7.21 (t, J = 8.4 Hz, 8 H), 7.00 (d, J = 8.8 Hz, 4 H), 2.19 (m, 8 H), 1.36 (m, 80 H), 0.88 (t, J = 6.7 Hz, 12 H). 13C NMR (100 MHz, CDCl₃): δ (ppm) 149.1, 141.1, 137.6, 135.5, 133.2, 130.4, 130.2, 130.0, 129.6, 129.2, 127.8, 126.5, 126.0, 125.0, 124.8, 123.5, 123.2, 122.9, 111.2, 44.9, 43.0, 32.0, 31.6, 30.3, 29.9, 29.8, 29.5, 25.0, 22.7, 14.2. MS (APCI) m/z: 2480.2561 (calcd for C₁₇₄H₁₆₄B₄O₁₀,[M + Na]⁺ 2480.2594).
Figure S1. $^1$H NMR spectrum of S1, 400 MHz, CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum of S1, 100 MHz, CDCl$_3$. 
**Figure S3.** $^1$H NMR spectrum of S2, 400 MHz, CDCl$_3$.

**Figure S4.** $^{13}$C NMR spectrum of S2, 100 MHz, CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 1, 400 MHz, CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum of 1, 100 MHz, CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of S3, 400 MHz, DMSO-$d_6$.

Figure S8. $^{13}$C NMR spectrum of S3, 100 MHz, DMSO-$d_6$. 
Figure S9. $^1$H NMR spectrum of M1, 400 MHz, CDCl$_3$.

Figure S10. $^{13}$C NMR spectrum of M1, 100 MHz, CDCl$_3$. 

S-10
Figure S11. $^1$H NMR spectrum of D1, 400 MHz, CDCl₃.

Figure S12. $^{13}$C NMR spectrum of D1, 100 MHz, CDCl₃.
Figure S13. $^1$H NMR spectrum of P1, 400 MHz, CDCl$_3$.

Figure S14. $^{13}$C NMR spectrum of P1, 100 MHz, CDCl$_3$. 
Figure S15. $^1$H NMR spectrum of D2d, 400 MHz, CDCl$_3$.

Figure S16. $^{13}$C NMR spectrum of D2d, 100 MHz, CDCl$_3$. 
**Figure S17.** $^1$H NMR spectrum of P2a, 400 MHz, CDCl$_3$.

**Figure S18.** $^{13}$C NMR spectrum of P2a, 100 MHz, CDCl$_3$. 
Figure S19. $^1$H NMR spectrum of P2b, 400 MHz, CDCl$_3$.

Figure S20. $^{13}$C NMR spectrum of P2b, 100 MHz, CDCl$_3$. 

S-15
**Figure S21.** $^1$H NMR spectrum of P2c, 400 MHz, CDCl$_3$.

**Figure S22.** $^{13}$C NMR spectrum of P2c, 100 MHz, CDCl$_3$. 
Figure S23. $^1$H NMR spectrum of P2d, 400 MHz, CDCl$_3$.

Figure S24. $^{13}$C NMR spectrum of P2d, 100 MHz, CDCl$_3$. 
Figure S25. $^1$H NMR spectrum of P2e, 400 MHz, CDCl₃.

Figure S26. $^{13}$C NMR spectrum of P2e, 100 MHz, CDCl₃.
Figure S27. FT-IR spectra of polymers P1 and P2a-e (film on KBr).

Figure S28. MALDI-TOF-Mass spectrum of P1 using DCTB as a matrix.

Figure S29. MALDI-TOF-Mass spectrum of P2d using DCTB as a matrix.
Figure S30. (A) UV-vis absorption spectra of M1, D1, and P1 in CHCl₃ (1.0 × 10⁻⁵ M). (B) Fluorescence emission spectra of M1, D1, and P1 in CHCl₃ (1.0 × 10⁻⁵ M), excited at each absorption maximum.
Figure S31. X-ray powder diffraction patterns of (A) D1, (B) P1, (C) D2d, and (D) P2d.

Table S1. Powder X-ray Diffraction results

<table>
<thead>
<tr>
<th>Compounds</th>
<th>observed peaks / Å</th>
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<tr>
<td>D1</td>
<td>26.67</td>
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<tr>
<td></td>
<td>9.64, 8.43, 7.34</td>
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<td></td>
<td>6.72, 6.22, 4.84, 4.66, 4.54</td>
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<tr>
<td>P1</td>
<td>27.08</td>
</tr>
<tr>
<td></td>
<td>8.09, 7.03</td>
</tr>
<tr>
<td></td>
<td>6.05, 4.88, 4.43</td>
</tr>
<tr>
<td>D2d</td>
<td>22.02, 17.45, 10.79</td>
</tr>
<tr>
<td></td>
<td>6.15, 3.65, 3.42</td>
</tr>
<tr>
<td>P2d</td>
<td>25.59, 20.82, 16.79</td>
</tr>
<tr>
<td></td>
<td>8.47</td>
</tr>
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<td></td>
<td>3.49</td>
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**Figure S32.** Normalized fluorescence emission spectra of (A) \( \text{P2d} \) and (B) \( \text{D2d} \) in CHCl\(_3\) (1.0 \times 10^{-3}, 1.0 \times 10^{-4}, 1.0 \times 10^{-5}, 1.0 \times 10^{-6}, \) and 1.0 \times 10^{-7} M), excited at each absorption maximum.
Figure S33. Time-resolved emission spectra of M2d in CHCl₃ (1.0 × 10⁻⁵ M).

(A)  

(B)  

Figure S34. Time-resolved emission spectra of D2d (A) in CHCl₃ (1.0 × 10⁻⁵ M) and (B) the film.

(A)  

(B)  

Figure S35. Time-resolved emission spectra of P2d (A) in CHCl₃ (1.0 × 10⁻⁵ M) and (B) the film.
Table S2. Results of fluorescence decay analysis

<table>
<thead>
<tr>
<th>Compound (observed λ&lt;sub&gt;em&lt;/sub&gt;)</th>
<th>τ / ns</th>
<th>χ²</th>
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<tbody>
<tr>
<td>M2d (410 nm)</td>
<td>2.4</td>
<td>1.24</td>
</tr>
<tr>
<td>D2d (415 nm)</td>
<td>τ₁ = 1.9 (28.3%)</td>
<td>1.02</td>
</tr>
<tr>
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<td>τ₂ = 7.8 (71.7%)</td>
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<tr>
<td>D2d (520 nm)</td>
<td>τ₁ = 6.9 (8.0%)</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>τ₂ = 34.5 (92.0%)</td>
<td></td>
</tr>
<tr>
<td>P2d (420 nm)</td>
<td>τ₁ = 1.5 (25.5%)</td>
<td>1.28</td>
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<tr>
<td></td>
<td>τ₂ = 8.7 (74.5%)</td>
<td></td>
</tr>
<tr>
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<td>τ₁ = 8.1 (7.7%)</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>τ₂ = 34.9 (92.3%)</td>
<td></td>
</tr>
<tr>
<td>P2d film (520 nm)</td>
<td>τ₁ = 2.4 (21.0%)</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>τ₂ = 12.2 (78.9%)</td>
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</table>
**Figure S36.** Fluorescence emission spectra of P2d in 2-methyltetrahydrofuran (1.0 × 10^{-5} M) at 303 K and 77 K.

**Figure S37.** Normalized fluorescence emission spectra of P2d in 2-methyltetrahydrofuran (1.0 × 10^{-3}, 1.0 × 10^{-4}, 1.0 × 10^{-5}, and 1.0 × 10^{-6} M), excited at each absorption maximum.