Supporting Information

Hydrophobicity and CH/π-interaction-driven self-assembly of amphiphilic aromatic hydrocarbons into nanosheets

Tsuyoshi Nishikawa, Hiroki Narita, Soichiro Ogi, Yoshikatsu Sato, and Shigehiro Yamaguchi

1Department of Chemistry, Graduate School of Science, Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan.
2Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya 464-8601, Japan.

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Experimental Procedures

General
Melt points (mp) were determined with a Yanaco MP-S3 instrument (MP-S3). NMR spectra were recorded with a JEOL JNM-ECS400 (400 MHz for $^1$H, 100 MHz for $^{13}$C), or a JEOL AL-400 spectrometer (100 MHz for $^{11}$B) in CDCl$_3$. The chemical shifts in $^1$H NMR spectra are reported in $\delta$ ppm using the residual protons of the solvents as an internal standard (CDCl$_3$ $\delta$ 7.26), and those in $^{13}$C NMR spectra are reported using the solvent signals as an internal standard (CDCl$_3$ $\delta$ 77.16). The chemical shifts in $^{11}$B NMR spectra are reported using BF$_3$·OEt$_2$ as an external standard. Mass spectra were measured with a Bruker micrOTOF Focus spectrometry system with the ionization method of APCI. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thickness of silica gel 60F$_{254}$ (Merck). Column chromatography was performed using neutral silica gel PSQ100B (Fuji Silysia Chemicals). Recycling preparative gel permeation chromatography (GPC) was performed with a LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. All reactions were performed under a nitrogen atmosphere unless stated otherwise. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Anhydrous DMF and 1,4-dioxane was purchased from Wako Chemicals. Anhydrous Tetrahydrofuran (THF) and toluene was purchased from Kanto Chemicals and further purified by Glass Contour Solvent Systems. Transmission electron microscopy (TEM) was performed on a JEM-1400EM (JEOL) using an acceleration voltage of 80 kV. Atomic force microscopy (AFM) was performed on a JSPM-5200V (JEOL). Spectral imaging was performed on a confocal laser microscope (LSM780-DUO-NLO, Zeiss) equipped with a 10x objective lens (Plan-Apochromat, N.A. 0.45). The sample was excited with a 405 nm laser and acquired emission spectrum between 411-693 nm range for taking a lambda stack images. UV-vis absorption spectra were recorded using JASCO V-750 spectrometer equipped with a JASCO ETCR-762 temperature/stirring controller at 20 °C. Fluorescent spectrum was recorded using HITACHI F-2500 fluorometer. X-Ray powder diffraction analysis was carried out with a Rigaku R-AXIS IV X-ray diffractometer with monochromated CuK$\alpha$ radiation ($\lambda$ = 1.5418 Å) at RT. 9-Bromomethylanthracene, $^1$-bromo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene, $^2$ Pd$_2$(dba)$_3$·CHCl$_3$, $^3$ 4,4,5,5-tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane, $^4$ and 5-bromo-2-iodo-1,3-diisopropylbenzene $^5$ were prepared as described in the literature. Although 9-((1,1'-biphenyl)-4-yl)anthracene was prepared by the different procedure from a reported one, the structure of the product was identified based on the literature. $^6$

Synthesis of 1-(anthracen-9-yl)-2,5,8,11-tetraoxadodecane (1)

![Synthesis of 1-(anthracen-9-yl)-2,5,8,11-tetraoxadodecane (1)](image)

**Compound 1.** Triethyleneglycol monomethyl ether (0.275 g, 1.67 mmol) was added to a mixture of THF (10 mL) and NaH (55% in oil, 66.9 mg, 1.53 mmol) at 0 °C. After the stirring at RT for 10 min, 9-bromomethylanthracene (0.378 g, 1.39 mmol) dissolved in THF (10 mL) was added to the reaction solution dropwisely. After the stirring at RT for 14 h, the reaction mixture was quenched by the addition of water (30 mL). The solution was poured into a separation funnel containing AcOEt (30 mL). The organic layer was washed with water (30 mL) and brine (30 mL). The organic layer was dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The organic residue was purified by column chromatography on silica gel (CH$_2$Cl$_2$ $\rightarrow$ 80/20 CH$_2$Cl$_2$/AcOEt) to give 1 (414 mg, 1.17 mmol, 84% yield) as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.44 (s, 1H), 8.43 (d, $J$ = 8.4 Hz, 2H), 8.00 (d, $J$ = 8.4 Hz, 2H), 7.55 (d, $J$ = 7.6 Hz, 2H), 7.47 (d, $J$ = 7.4 Hz, 2H), 5.54 (s, 2H), 3.80 (t, $J$ = 4.8 Hz, 2H), 3.68 (t, $J$ = 4.8 Hz, 2H), 3.66 (t, $J$ = 4.8 Hz, 2H), 3.63 (t, $J$ = 4.8 Hz, 2H), 3.51 (t, $J$ = 5.0 Hz, 2H), 3.36 (t, $J$ = 3.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.5, 131.2, 129.1, 128.8, 128.5, 125.1, 124.6, 72.0, 71.0, 70.8, 70.7, 69.6, 65.4, 59.2, 31.1; HRMS (APCI): m/z calcd. for C$_{22}$H$_{26}$O$_4$: 354.1826 ([M$^+$]); found: 354.1827.
Synthesis of 9-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)anthracene (2)

**Compound 2.** Pd$_2$(dba)$_3$:CHCl$_3$ (3.00 mg/mL in THF, 679 μL, 1.97 μmol) was added to a mixture of 1-bromo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (31.4 mg, 98.4 μmol), XPhos (3.00 mg/mL in THF, 1.25 mL, 7.87 μmol), K$_3$PO$_4$ (23.0 mg, 108 μmol), and (anthracen-9-yl)boronic acid (53.9 mg, 118 μmol) in THF (3.9 mL) and water (2.0 mL). The reaction mixture was stirred at 80 ºC for 18 h. The reaction mixture was poured into a separation funnel containing AcOEt (30 mL) and water (30 mL). The aqueous phase was extracted with AcOEt (3 × 50 mL). The combined organic layer was washed with brine (30 mL). The organic layer was dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (CH$_2$Cl$_2$ → 90/10 CH$_2$Cl$_2$/AcOEt) to give 2 (40.7 mg, 98.3 μmol, 99% yield) as pale yellow solid. Mp: 79.5–80.4 ºC; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.48 (s, 1H), 8.04 (d, $J$ = 8.4 Hz, 2H), 7.70 (d, $J$ = 8.8 Hz, 2H), 7.45 (t, $J$ = 7.4 Hz, 2H), 7.34 (t, $J$ = 8.4 Hz, 2H), 7.13 (d, $J$ = 8.4 Hz, 2H), 4.28 (t, $J$ = 4.8 Hz, 2H), 3.96 (t, $J$ = 4.8 Hz, 2H), 3.82 (dd, $J$ = 6.0, 3.6 Hz, 2H), 3.75 (dd, $J$ = 6.0, 3.6 Hz, 2H), 3.71 (dd, $J$ = 5.8, 3.8 Hz, 2H), 3.59 (dd, $J$ = 5.6, 4.0 Hz, 2H), 158.3, 136.9, 132.4, 131.5, 131.1, 130.6, 128.4, 127.0, 126.5, 125.3, 125.2, 114.6, 72.1, 71.0, 70.9, 70.8, 67.6, 59.3; HRMS (APCI): m/z calcd. for C$_{27}$H$_{28}$O$_4$: 416.1982 ([M]+); found: 416.1990.

Synthesis of 9-(4'-(2-(2-(2-methoxyethoxy)ethoxy)-[1,1'-biphenyl]-4-yl)anthracene (3)

**Compound S1.** A mixture of 4'-bromo-[1,1'-biphenyl]-4-ol (700 mg, 2.81 mmol), TsO-R (1.16 g, 3.65 mmol) and K$_2$CO$_3$ (777 mg, 5.62 mmol) was dissolved in DMF (7.5 mL). The reaction mixture was stirred at 80 ºC for 12 h. The reaction mixture was poured into a separation funnel containing AcOEt (50 mL) and water (50 mL). The aqueous phase was extracted with AcOEt (50 mL). The combined organic layer was washed with brine (50 mL). The organic layer was dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (CH$_2$Cl$_2$ → 85/15 CH$_2$Cl$_2$/AcOEt) to give S1 (1.08 g, 2.72 mmol, 97% yield) as white solid. Mp: 79.5–80.4 ºC; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.53 (d, $J$ = 8.8 Hz, 2H), 7.47 (d, $J$ = 8.8 Hz, 2H), 7.41 (d, $J$ = 8.8 Hz, 2H), 6.98 (d, $J$ = 9.2 Hz, 2H), 4.17 (t, $J$ = 4.8 Hz, 2H), 3.88 (t, $J$ = 5.0 Hz, 2H), 3.76 (dd, $J$ = 5.6, 3.6 Hz, 2H), 3.70 (dd, $J$ = 5.8, 3.4 Hz, 2H), 3.66 (dd, $J$ = 5.6, 3.6 Hz, 2H), 3.56 (dd, $J$ = 5.6, 3.6 Hz, 2H), 3.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.7, 139.7, 132.6, 131.9, 128.4, 127.0, 126.5, 125.3, 125.2, 114.6, 72.1, 71.0, 70.9, 70.8, 70.0, 67.6, 59.3; HRMS (APCI): m/z calcd. for C$_{19}$H$_{23}$BrO$_4$: 394.0774 ([M]+); found: 394.0766.

**Compound 3.** Pd$_2$(dba)$_3$:CHCl$_3$ (48.0 mg, 46.4 μmol) was added to a mixture of S1 (917 mg, 2.32 mmol), XPhos (88.4 mg, 186 μmol), K$_3$PO$_4$ (541 mg, 2.55 mmol), and (anthracen-9-yl)boronic acid (618 mg, 2.78 mmol) in THF (93 mL) and water (46 mL), followed by stirring at 80 ºC for 18 h. The resulting mixture was poured into a separation funnel containing AcOEt (50 mL) and water (50 mL). The organic layer was washed with water (50 mL) and brine (50 mL). The organic layer was dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The mixture was purified by column chromatography on silica gel (CH$_2$Cl$_2$ → 85/15 CH$_2$Cl$_2$/AcOEt), followed by preparative GPC to give 3 (724 mg, 1.47 mmol, 63% yield) as pale yellow solid. Mp:
108.8–109.6 °C; 1H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.76 (dd, J = 7.6, 6.0 Hz, 4H), 7.69 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.8, Hz, 2H), 4.23 (t, J = 4.8 Hz, 2H), 3.92 (t, J = 5.2 Hz, 2H), 3.80–3.77 (m, 2H), 3.74–3.68 (m, 4H), 3.58 (dd, J = 5.6, 3.6 Hz, 2H), 4.30 (s, 3 H); 13C NMR (100 MHz, CDCl₃): δ 158.6, 139.9, 137.2, 136.9, 133.6, 131.8, 131.5, 130.4, 128.5, 128.2, 127.0, 125.5, 125.2, 115.1, 72.1, 71.0, 70.8, 70.7, 69.9, 67.6, 59.2, one signal was not observed due to the overlap with the other signal; HRMS (APCI): m/z calcd. for C₃₃H₃₂O₄: 492.2295 ([M]+); found: 492.2308.

Synthesis of 9-([1,1'-biphenyl]-4-yl)anthracene

9-([1,1'-biphenyl]-4-yl)anthracene. Pd₂(dba)₃·CHCl₃ (13.3 mg, 12.9 μmol) was added to a mixture of 4-bromo-1,1'-biphenyl (150.0 mg, 644 μmol), XPhos (24.5 mg, 51.5 μmol), K₃PO₄ (150.2 mg, 707.8 μmol), and (anthracen-9-yl)boronic acid (171.4 mg, 772 μmol) in THF (26 mL) and water (13 mL). The reaction mixture was stirred at 80 °C for 6 h. The mixture was poured into a separation funnel containing Et₂O (50 mL) and water (2 × 50 mL) and brine (50 mL). The organic layer was dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (n-hexane) to give 6 (206.7 mg, 625.6 μmol, 97% yield) as white solid. 1H NMR (400 MHz, CDCl₃): δ 8.42 (s, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.74–7.66 (m, 6H), 7.45–7.26 (m, 9H). These chemical shifts were identical with those reported in the literature.

Synthesis of 9-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10-phenylanthracene (4)

Compound 4. Pd₂(dba)₃·CHCl₃ (3.00 mg/mL in THF, 800 μL, 2.32 μmol) was added to a mixture of 1-bromo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (37.0 mg, 116 μmol), XPhos (3.00 mg/mL in THF, 1.47 mL, 9.27 μmol), K₃PO₄ (27.1 mg, 128 μmol), and 4,4,5,5-tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane (52.9 mg, 139 μmol) in THF (4.6 mL) and water (2.3 mL). The reaction mixture was stirred at 80 °C for 14 h. The reaction mixture was poured into a separation funnel containing AcOEt (30 mL) and water (30 mL). The aqueous phase was extracted with AcOEt (2 × 30 mL). The combined organic layer was washed with brine (30 mL) and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (CH₂Cl₂) to give 4 (49.7 mg, 101 μmol, 87% yield) as pale yellow solid. Mp: 126.6–127.4 °C; 1H NMR (400 MHz, CDCl₃): δ 7.75–7.72 (m, 2H), 7.70–7.67 (m, 2H), 7.62–7.52 (m, 3H), 7.49–7.47 (m, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.34–7.32 (m, 4H), 7.15 (d, J = 8.8 Hz, 1H), 4.30 (t, J = 4.8 Hz, 2H), 3.97 (t, J = 4.8 Hz, 2H), 3.83 (dd, J = 6.0, 3.2 Hz, 2H), 3.75 (dd, J = 6.4, 4.0 Hz, 2H), 3.71 (dd, J = 5.4, 3.8 Hz, 2H), 3.59 (dd, J = 5.8, 3.8 Hz, 2H), 3.41 (s, 3 H); 13C NMR (100 MHz, CDCl₃): δ 158.3, 139.2, 137.02, 137.00, 130.4, 128.5, 128.2, 127.0, 125.5, 125.2, 115.1, 72.1, 71.0, 70.8, 70.7, 69.9, 67.6, 59.2, one signal was not observed due to the overlap with the other signal; HRMS (APCI): m/z calcd. for C₃₃H₃₂O₄: 492.2295 ([M]+); found: 492.2308.
132.4, 131.4, 131.3, 130.0, 128.5, 127.5, 127.1, 127.0, 125.1, 125.0, 114.6, 72.1, 71.0, 70.8, 70.7, 69.9, 67.6, 59.2; HRMS (APCI): \( m/z \) calcd. for \( \text{C}_{33}\text{H}_{32}\text{O}_{4} \): 492.2295 ([M]+); found: 492.2302.

Synthesis of 9-(3,5-diisopropyl-4’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) -[1,1’-biphenyl]-4-yl)-anthracene (5)

Compound S2. A hexane solution of n-BuLi (1.6 mol/L, 3.49 mL, 5.59 mmol) was added dropwisely to a solution of 5-bromo-2-iodo-1,3-diisopropylbenzene (2.05 g, 5.59 mmol) in toluene (28 mL) at 0 °C. The mixture was stirred at RT for 2 h. A toluene (28 mL) solution of anthrone (1.10 g, 5.59 mmol) was added to the reaction mixture dropwisely. The mixture was stirred at reflux (125 °C) for 36 h. After addition of saturated \( \text{NH}_{4}\text{Cl} \) aq (100 mL), the mixture was poured into a separation funnel containing \( \text{CHCl}_{3} \) (150 mL). The organic layer was washed with water (2 × 100 mL) and brine (100 mL). The resulting mixture was purified by column chromatography on silica gel (\( \text{n-hexane} \)) to give S3 (1.00 g, 2.41 mmol, 43% yield) as white solid. Mp: 268.7–269.5 °C; \( \text{H} NMR (400 \text{ MHz, CDCl}_{3}) \): \( \delta \) 8.50 (s, 1H), 8.06 (d, \( J = 8.8 \text{ Hz, 2H} \)), 7.49 (s, 2H), 7.48–7.45 (m, 4H), 7.33 (dd, \( J = 8.0, 6.0 \text{ Hz, 2H} \)), 2.04 (sep, \( J = 6.8 \text{ Hz, 2H} \)), 0.86 (d, \( J = 6.8 \text{ Hz, 2H} \)), 1H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 151.0, 134.0, 131.5, 130.7, 128.7, 126.8, 126.7, 125.6, 125.5, 123.1, 31.0, 24.3, one signal was not observed due to the overlap with the other signal; HRMS (APCI): \( m/z \) calcd. for \( \text{C}_{26}\text{H}_{25}\text{Br} \): 416.1134 ([M]+); found: 416.1147.

Compound S3. A mixture of S2 (200 mg, 479 \( \mu \)mol), \( \text{PdCl}_{2}(\text{PPPh}_{3}) \) (16.8 mg, 24.0 \( \mu \)mol), AcOK (141 mg, 1.44 mmol) and \( \text{B}_{2}\text{pin}_{2} \) (183 mg, 719 mmol) was dissolved in 1,4-dioxane (3.4 mL). The reaction mixture was stirred at 80 °C for 15 h. The mixture was poured into a separation funnel containing \( \text{Et}_{2}\text{O} \) (30 mL) and water (30 mL). The organic layer was washed with water (2 × 30 mL) and brine (50 mL) and dried over \( \text{Na}_{2}\text{SO}_{4} \). After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (\( \text{n-hexane} \rightarrow 70/30 \text{n-hexane/CHCl}_{3} \)) to give S3 (176 mg, 378 \( \mu \)mol, 79% yield) as white solid. Mp: 226.2–227.0 °C; \( \text{H} NMR (400 \text{ MHz, CDCl}_{3}) \): \( \delta \) 8.50 (s, 1H), 8.06 (d, \( J = 8.8 \text{ Hz, 2H} \)), 7.49 (s, 2H), 7.48–7.45 (m, 4H), 7.33 (dd, \( J = 8.0, 6.0 \text{ Hz, 2H} \)), 2.04 (sep, \( J = 6.8 \text{ Hz, 2H} \)), 0.86 (d, \( J = 6.8 \text{ Hz, 12H} \)), 13C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 151.0, 134.0, 131.5, 130.7, 128.7, 126.8, 126.7, 125.6, 125.5, 123.1, 31.0, 24.3, one signal was not observed due to the overlap with the other signal; HRMS (APCI): \( m/z \) calcd. for \( \text{C}_{32}\text{H}_{37}\text{BO}_{2} \): 464.2881 ([M]+); found: 464.2869.
**Compound 5.** Pd$_2$(dba)$_3$·CHCl$_3$ (3.00 mg/mL in THF, 800 μL, 2.32 μmol) was added to a mixture of S3 (52.9 mg, 139 μmol), 1-bromo-4-(2-[(2-methoxyethoxy)ethoxy]ethoxy)benzene (37.0 mg, 116 μmol), XPhos (3.00 mg/mL in THF, 1.47 mL, 9.27 μmol), and K$_2$PO$_4$ (27.1 mg, 128 μmol) in THF (4.6 mL) and water (2.3 mL). After the reaction mixture was stirred at 80 °C for 14 h, the mixture was poured into a separation funnel containing AcOEt (30 mL) and water (30 mL). The aqueous phase was extracted with AcOEt (2 × 30 mL). The combined organic layer was washed with brine (30 mL), and dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (CH$_2$Cl$_2$) to give 5 (49.7 mg, 101 μmol, 87% yield) as pale yellow solid. Mp: 126.6–127.4 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.50 (s, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.56 (s, 2H), 7.46 (t, J = 7.0 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 4.24 (t, J = 4.8 Hz, 2H), 3.94 (t, J = 4.8 Hz, 2H), 3.82–3.79 (m, 2H), 3.70–3.73 (m, 2H), 3.70 (dd, J = 5.8, 4.0 Hz, 2H), 3.59 (dd, J = 5.6, 4.0 Hz, 2H), 3.41 (s, 3H), 2.13 (sept, J = 6.8 Hz, 2H), 0.93 (d, J = 6.8 Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.4, 148.9, 140.7, 135.4, 134.7, 133.6, 131.9, 130.9, 128.5, 128.3, 127.0, 126.2, 125.4, 125.2, 121.8, 115.0, 72.1, 71.0, 70.8, 70.7, 69.9, 67.6, 59.2, 31.1, 24.6; HRMS (APCI): m/z calcd. for C$_{39}$H$_{44}$O$_4$: 576.3234 ([M]+); found: 576.3251.

**Synthesis of 9-(4'(2-(2-hydroxyethoxy)ethoxy)ethoxy)-[1,1'-biphenyl]-4-yl)anthracene (6)**

![Reaction scheme for the synthesis of 6](https://via.placeholder.com/100)

**Compound S4.** 4-Bromo-4'-hydroxy-1,1'-biphenyl (0.996 g, 4.00 mmol), 2-(2-(2-hydroxyethoxy)ethoxy)ethyl p-toluenesulfonate (1.01 g, 3.33 mmol), and K$_2$CO$_3$ (1.66 g, 12.0 mmol) were dissolved in acetone (33 mL), and the mixture was stirred at 70 °C for 31 h. The resulting mixture was extracted with CH$_2$Cl$_2$ (3 × 20 mL), and the combined organic layer was washed with brine, and dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The mixture was purified by column chromatography on silica gel (80/20 CH$_2$Cl$_2$·EtOAc) to give S1 (1.01 g, 2.64 mmol, 79% yield) as a white solid. Mp: 98.5–99.3 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.51 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 4.17 (t, J = 4.6 Hz, 2H), 3.88 (t, J = 4.8 Hz, 2H), 3.70–3.75 (m, 6H), 3.62 (t, J = 4.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.7, 139.8, 132.9, 131.9, 128.4, 128.1, 121.0, 115.2, 72.6, 71.0, 70.5, 69.9, 67.6, 61.9; HRMS (APCI): m/z calcd. for C$_{18}$H$_{20}$BrO$_4$: 380.0618 ([M]+); found: 380.0601.

**Compound 6.** A mixture of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (764 mg, 2.51 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (470 mg, 2.21 mmol) and K$_2$PO$_4$ (380 mg, 3.00 mmol), XPhos (76.6 mg, 161 μmol), and K$_3$PO$_4$ (470 mg, 2.21 mmol) was dissolved in THF (80 mL) and water (40 mL), and stirred at 80 °C for 19 h. The mixture was extracted with CH$_2$Cl$_2$ (3 × 30 mL), and the combined organic layer was washed with brine, and dried over Na$_2$SO$_4$. After filtration, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (50/50 CH$_2$Cl$_2$·EtOAc), followed by preparative GPC (CHCl$_3$) to give 1 (694 mg, 1.45 mmol, 73% yield) as a white solid. Mp: 135.3–136.0 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.51 (s, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.74–7.78 (m, 4H), 7.69 (dd, J = 6.6, 2.1 Hz, 2H), 7.45–7.49 (m, 4H), 7.35–7.39 (m, 2H), 7.07 (dd, J = 6.9, 2.3 Hz, 2H), 4.24 (t, J = 4.8 Hz, 2H), 3.93 (t, J = 4.8 Hz, 2H), 3.73–3.80 (m, 6H), 3.66 (dd, J = 5.5, 3.7 Hz, 2H), 2.34 (t, J = 6.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.5, 139.9, 137.2, 136.9, 133.7, 131.8, 131.5, 130.4, 128.5, 128.3, 127.0, 125.3, 125.5, 121.8, 72.6, 71.0, 70.8, 70.6, 69.9, 67.8, 62.3; one signal was not observed due to the overlap with the other signal; HRMS (APCI): m/z calcd. for C$_{39}$H$_{38}$O$_4$: 478.2139 ([M]+); found: 478.2152.
Preparation of TEM samples

A TEM substrate (Elastic carbon ELS-C10) was fixed on a glass dish by a double-sided tape. A droplet of a sample solution was put on the TEM substrate. After 5 min, the droplet was removed by tilting the substrate on a filter paper (without heating). It was dried under vacuum for 30 min before taking TEM images.

![Figure S1. A schematic procedure for preparation of a TEM sample.](image)

Self-Assembly of 1 in 10/90 (v/v) 1-PrOH/H₂O

A 5.0 mM solution of 1 in 1-PrOH was diluted with distilled water to give a solution of 1 in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of 5 × 10⁻⁴ M. After the brief shaking, self-assembling behavior was monitored by UV-vis absorption spectroscopy at 20 °C for 12 h. The morphology of the aggregates was observed by TEM.

![Figure S2. (a) Time-dependent UV-vis absorption spectra of 1 in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of 5 × 10⁻⁴ M at 20 °C; (b) time-dependent absorbance change of 1 at 385.5 nm.](image)
Figure S3. A TEM image of the aggregates of 1 prepared in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-4}$ M.

Time-Dependent Transition of the Morphology of the Aggregates of 3

A solution of 3 in 1-PrOH was diluted with distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-5}$ M. After the brief shaking, the sample was allowed to stand at RT for 10 min. A small amount of the solution was used for preparation of a TEM sample.

Figure S4. A TEM image of the aggregates of 3 at 10 min later after mixing of the 1-PrOH solution of 3 with water.
Time-Dependent UV-Vis Absorption Spectroscopy During the Aggregation of 3

A $5 \times 10^{-5}$ M solution of 3 in 1-propanol (1-PrOH) was diluted with distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-6}$ M. After the brief shaking, self-assembling behavior was monitored by UV-vis absorption spectroscopy at 20 °C for 12 h.

![Figure S5. (a) Time-dependent UV-vis absorption spectra of 3 in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-6}$ M at 20 °C; (b) time-dependent absorbance change of 3 at 395.0 nm.](image)

Preparation of an AFM Sample

A solution of 3 in 1-PrOH was diluted with distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-6}$ M. After the brief shaking, the solution was allowed to stand at RT for 18 h. A droplet of the sample solution was put on a silicon wafer. After keeping it for 5 min, the droplet was removed by tilting the substrate on a filter paper. After repeating this operation 5 times, the sample was dried under vacuum for 30 min prior to taking AFM images.

Preparation of a Sample for Spectral Imaging by a Confocal Laser Microscope

A solution of 3 in 1-PrOH was diluted with the distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H$_2$O with a total concentration of $5 \times 10^{-6}$ M. After the brief shaking, the solution was allowed to stand at RT for 15 h. A droplet of the solution was put on a cover glass. After keeping it for 5 min, the droplet was removed by tilting the substrate on a filter paper (without heating), followed by drying under vacuum for 30 min prior to taking spectral images.
A Fluorescence Spectrum of a Solution of Sheet-like Aggregates of 3

A solution of 3 in 1-PrOH was diluted with distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of 5 × 10⁻⁶ M. After the brief shaking, the solution was allowed to stand at RT for 15 h prior to the measurement of a fluorescence spectrum.

Figure S6. A fluorescence spectrum of the whole solution of the aggregate of 3 (excitation wavelength: 374.0 nm, excitation slit: 2.5 nm, fluorescence slit: 2.5 nm)

Preparation of the Sample for X-ray Powder Diffraction

A solution of 3 in 1-PrOH was diluted with distilled water to give a solution of 3 in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of 5 × 10⁻⁵ M. After the brief shaking, the solution was allowed to stand at RT for 19 h. The formation of sheet-type aggregates in this condition was confirmed by TEM and AFM measurements (Figure S7 and S8). Then, the solvent was removed by freeze dry. The remained white powder was used for the measurement of X-ray powder diffraction.

Figure S7. A TEM image of the aggregates of 3 prepared in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of 5 × 10⁻⁵ M.
Figure S8. (a) An AFM image of the aggregates of 3 prepared in 10/90 (v/v) 1-PrOH/H2O with a total concentration of 5 × 10⁻⁵ M; (b) the height profile of the red line in the AFM image.

X-ray Crystallographic Analyses

X-ray Crystallographic Analysis of 3. Plate-shaped colourless single crystals were grown from a homogenous hot solution of 3 in 1-PrOH in the process of gradual cooling to RT. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoKα radiation (λ = 0.71075 Å). A total of 30182 reflections were measured with the maximum 2θ angle of 55.0°, of which 12004 were independent reflections (Rint = 0.0181). The structures were solved by a direct method (SHELXT)⁷ and refined by a full-matrix least-square method on F² for all reflections (SHELXL-2017/1).⁸ Only the part of hydrogen atoms in the ethylene oxide chain were placed using AFIX instructions, while all other atoms (containing the hydrogen atoms in the aromatic hydrocarbon moiety) were refined anisotropically. Although the CIF check reports contained alert A originating the disorder of the part of the ethylene oxide chain, it does not affect to the discussion in the main text about the molecular packing of the aromatic hydrocarbon moieties. Therefore, we did not carry out further refinement. The crystal data are as follows: C₃₃H₃₂O₄, FW = 492.58, crystal size = 0.5 × 0.07 × 0.04 mm³, triclinic, P¹ (#2), a = 9.6509(10) Å, b = 16.0605(17) Å, c = 18.319(2) Å, α = 85.627(4)°, β = 76.636(3)°, γ = 75.927 (4)°, V = 2679.1(5) Å³, Z = 4, Dc = 1.221 g cm⁻³, μ = 0.079 mm⁻¹, R¹ = 0.0440 (I > 2σ(I)), wR² = 0.1457 (all data), GOF = 1.081. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 1824326. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S9. Two types of intermolecular CH/π interactions between the anthracene and biphenyl units of 3.
X-ray Crystallographic Analysis of 9-((1,1'-biphenyl)-4-yl)anthracene. Colorless block single crystals were grown from the homogenous hot solution of 9-((1,1'-biphenyl)-4-yl)anthracene in 1-PrOH in the process of gradual cooling to RT. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoKα radiation (λ = 0.71073 Å). A total of 17262 reflections were measured with the maximum 2θ angle of 55.0°, of which 4010 were independent reflections (Rint = 0.0284). The structures were solved by a direct method (SHELXT) and refined by a full-matrix least-square method on $F^2$ for all reflections (SHELXL-2017/1). The crystal data are as follows: C_{26}H_{18}, FW = 330.40, crystal size = 0.2 × 0.1 × 0.05 mm$^3$, monoclinic, $P2_1/n$ (#14), $a = 10.4610(4)$ Å, $b = 7.4395(2)$ Å, $c = 22.5216(7)$ Å, $β = 94.046(3)^°$, $V = 1748.37(10)$ Å$^3$, $Z = 4$, $D_c = 1.255$ g cm$^{-3}$, $µ = 0.071$ mm$^{-1}$, $R_1 = 0.0390$ ($I > 2σ(I)$), $wR_2 = 0.0988$ (all data), GOF = 1.032. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 1953600. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S10. X-ray crystal structure of 9-((1,1'-biphenyl)-4-yl)anthracene.

X-ray Crystallographic Analysis of 6. Colorless block single crystals were grown by slow diffusion of hexane into a solution of 6 in CH$_2$Cl$_2$. Intensity data were collected at 90 K on synchrotron radiation (λ = 0.8104 Å) at the BL40XU beam line in Spring-8 (JASRI, projects 2018B1084, 2018B1275). A total of 52946 reflections were measured with the maximum 2θ angle of 58.0°, of which 4531 were independent reflections (Rint = 0.0814). The structure was solved by direct methods (SHELXT-2018/2) and refined by the full-matrix least-squares on $F^2$ (SHELXL-2018/3). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions excluding H0. The crystal data are as follows: C$_{32}$H$_{30}$O$_4$, FW = 478.56, crystal size = 0.01 × 0.01 × 0.01 mm$^3$, tetragonal, $P4_2/n$ (#86), $a = 23.03320(10)$ Å, $b = 23.03320(10)$ Å, $c = 9.5130(10)$ Å, $V = 5048.14(7)$ Å$^3$, $Z = 8$, $D_c = 1.259$ g cm$^{-3}$, $µ = 0.108$ mm$^{-1}$, $R_1 = 0.0543$ ($I > 2σ(I)$), $wR_2 = 0.1506$ (all data), GOF = 1.033. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 1953601. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Out-of-plane XRD analysis

A solution of 3 in 1-PrOH was diluted with distilled water to give a solution in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of $5 \times 10^{-5}$ M. After the brief shaking, the solution was allowed to stand at RT for 19 h. A droplet of the solution was put on the silicon wafer (1 × 1 cm). After keeping it for 1 h with a cover (The solvent was evaporated partially.), the droplet was removed by tilting the substrate on a filter paper. After repeating this operation 6 times, the sample was dried under vacuum for 1 h prior to the measurement of X-ray diffraction.

![Graph](image)

**Figure S11.** An out-of-plane XRD pattern of 3 in the aggregated state.

The Morphology of the Aggregates of Reference Compounds

A solution of each reference compound (4, 5, and 6) in 1-PrOH was diluted with the distilled water to give a 5.0 μM solution in 10/90 (v/v) 1-PrOH/H₂O. After the brief shaking, the solution was allowed to stand at RT for 12 h and then the morphology of the aggregates were observed by TEM and AFM.

![Images](image)

**Figure S12.** TEM images of the aggregates of (a) 4 and (b) 5 in 10/90 (v/v) 1-PrOH/H₂O with a total concentration of $5 \times 10^{-6}$ M.
Figure S13. TEM images of aggregates prepared from the solution of 6 in 1-PrOH/H₂O (1:9, v/v) at concentration of 5 µM after being aged at 20 °C for (a) 5 min, (b) 12 h, and (c) 24 h.

Figure S14. (a) An AFM height image of aggregated 6; (b) a cross-section analysis along the white arrow; (c) a cross-section analysis along the black arrow.

Figure S15. Measured and simulated XRD patterns of 6 in the aggregate state (red line) and in the single crystal (blue line).
Figure S16. X-ray crystal structure of 6: (a) top view and (b) side view (thermally ellipsoids at 50% probability).

References

1H, 13C, and 11B NMR Spectra

Figure S17. 1H NMR spectrum of 1 (400 MHz, CDCl3).

Figure S18. 13C NMR spectrum of 1 (100 MHz, CDCl3).
Figure S19. $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$).

Figure S20. $^{13}$C NMR spectrum of 2 (100 MHz, CDCl$_3$).
Figure S21. $^1$H NMR spectrum of S1 (400 MHz, CDCl$_3$).

Figure S22. $^{13}$C NMR spectrum of S1 (100 MHz, CDCl$_3$).
Figure S23. $^1$H NMR spectrum of 3 (400 MHz, CDCl$_3$).

Figure S24. $^{13}$C NMR spectrum of 3 (100 MHz, CDCl$_3$).
Figure S25. $^1$H NMR spectrum of 4 (400 MHz, CDCl$_3$).

Figure S26. $^{13}$C NMR spectrum of 4 (100 MHz, CDCl$_3$).
Figure S27. $^1$H NMR spectrum of S2 (400 MHz, CDCl$_3$).

Figure S28. $^{13}$C NMR spectrum of S2 (100 MHz, CDCl$_3$).
Figure S29. $^1$H NMR spectrum of S3 (400 MHz, CDCl$_3$).

Figure S30. $^{13}$C NMR spectrum of S3 (100 MHz, CDCl$_3$).
**Figure S31.** $^{11}$B NMR spectrum of S3 (100 MHz, CDCl$_3$).

**Figure S32.** $^1$H NMR spectrum of 5 (400 MHz, CDCl$_3$).
Figure S33. $^{13}$C NMR spectrum of S (100 MHz, CDCl$_3$).

Figure S34. $^1$H NMR spectrum of S (400 MHz, CDCl$_3$).
Figure S35. $^{13}$C NMR spectrum of S4 (100 MHz, CDCl$_3$).

Figure S36. $^1$H NMR spectrum of 6 (400 MHz, CDCl$_3$).
Figure S37. $^{13}$C NMR spectrum of 6 (100 MHz, CDCl$_3$).