

Supporting Information

Three-dimensional assembly of pyrene dye on tetraphenylethane scaffold enhances fluorescent quantum yield

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Experimental Section

Instrumental. All the ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz JEOL LMN-EX400 instrument with tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a JASCO FT-IR 469 plus spectrometer. Melting points were obtained by a Stuart Scientific Melting Point Apparatus SMP3. MS spectra (Dart) were obtained by JEOL JMS-T100TD mass spectrometer. Elemental analyses were performed by LECO CHNS-932. High-resolution mass spectra (FAB) was obtained by JEOL JMS700 mass spectrometer. All photophysical measurements performed in solutions were carried out using dilute solutions with optical density (O.D.) around 0.1 at the maximum absorption wavelength in 1 cm path length quartz cells at room temperature (298 K). In addition, all samples solutions were deaerated by bubbling with argon gas for 15 min before the measurements. The UV-Vis spectra were recorded with a Beckman Coulter DU800 UV-Vis Spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 Spectrofluorometer. Absolute Quantum Yields were measured by a Hamamatsu Photonics Quantaurus QY. Time-resolved emission was measured on an Hamamatsu OB920. by time-correlated single-photon counting using a hydrogen flash lamp. Fluorescence lifetimes were determined by a single exponential curve fit. The MM2 calculation was performed using the Materials Studio 5.0 program (Accelrys Software Inc.).

Materials. Unless otherwise noted, all reagents and chemicals were obtained from commercially available and used without further purification. 7-*tert*-Butylpyrene-1-boronic acid pinacol ester was prepared from pyrene according to the literature [Figueira-Duarte, T. M.; Simon, S. C.; Wagner, M.; Druzhinin, S. I.; Zachariasse, K. A.; Müllen, K. *Angew. Chem. Int. Ed.*, **2008**, *47*, 10175-10178.]. Pyrene, 2-chloro-2-methylpropane, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, phenylboronic acid, 4-methylphenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, was obtained from TCI Japan (Tokyo). $\text{PdCl}_2(\text{PPh}_3)_2$ was obtained from Aldrich. AlCl_3 was obtained from Kanto Chemical Co., Inc. Cesium carbonate was obtained from Wako Pure Chem. 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane was gift from Asahi Organic Chemicals Industry Co. Ltd.

Synthesis.

1,1,2,2-Tetrakis(4-trifluoromethanesulfonylphenyl)ethane.

To a solution of 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (2.0 g, 5.0 mmol) in pyridine (24 ml) at 0 °C was slowly added trifluoromethanesulfonic anhydride. (4.2 ml, 25 mmol) the reaction mixture was stirred at 0 °C for 5 min and then allowed to warm to room temperature for 24 h. The mixture was poured into water and extracted with toluene. The toluene extract was washed sequentially with 10% aqueous hydrochloric acid, water, and saturated aqueous sodium chloride and then dried over MgSO₄ and evaporated. Recrystallization from hexane afforded 1,1,2,2-Tetrakis(4-trifluoromethanesulfonylphenyl)ethane as colorless crystals. (Yield 89%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.13 (d, *J* = 8.8 Hz, Ar-H, 8H), 7.09 (d, *J* = 8.8 Hz, Ar-H, 8H), 4.71 (s, Ar-CH-Ar, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 141.6, 130.0, 121.6 (aromatic C), 117.0 (-CF₃), 55.2 (Ar-CH-Ar) ppm. FT-IR (KBr); 3044, 3022, 1599, 1488, 1433, 1217, 1141, 1075 cm⁻¹. mp 206-208 °C.

1,1,2,2-tetrakis(7-tert-butyl(pyren-1-yl)phenyl)ethane (TPPE)

Under an argon atmosphere, 1,1,2,2-(4-trifluoromethanesulfonylphenyl)ethane (0.16 g, 0.16 mmol), 7-*tert*-butylpyrene-1-boronic acid pinacol ester (0.32 g, 0.84 mmol) and cesium carbonate (1.1 g, 3.3 mmol) were mixed together with Pd(PPh₃)₄ (40 mg, 0.032 mmol), degassed THF (15 ml). The mixture was refluxed for 18 h. After cooling to room temperature, the result mixture was extracted with chloroform. The organic extract was washed sequentially with water and brine and then dried over MgSO₄. After removal of the solvent, the residue was purified by column chromatography using chloroform/*n*-hexane (1:1, v/v) and preparative HPLC (CHCl₃). After removal of the solvent, the product was recrystallized from cyclohexane. 1,1,2,2-tetrakis(7-*tert*-butyl (pyren-1-yl)-phenyl)ethane was obtained as a pale yellow powder in 63% yield. mp 215-216 °C.; ¹H NMR (400 MHz, CDCl₃) δ 7.83-8.22 (m, Ar-H, 36H), 7.65 (d, *J* = 8.0 Hz, Ar-H, 8H), 7.59 (d, Ar-H, 8H), 5.25 (s, Ar-CH-Ar, 2H) ppm.; ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 143.1, 139.1, 137.6, 131.5, 130.5, 130.4, 129.0, 128.3, 127.6, 127.5, 127.3, 127.1, 125.0, 124.4, 123.2, 122.3, 121.9 (aromatic C), 56.5 ((Ph)₂CH-CH-(Ph)₂), 31.3 (-C(CH₃)₃), 29.8 (-C(CH₃)₃) ppm.; FT-IR (KBr); 3026, 2960, 1594, 1496, 1458,

1227 cm^{-1} .; HR-MS (FAB) Calcd for $\text{C}_{106}\text{H}_{86}\text{Na}$ 1381.6627 $[\text{M}+\text{Na}]^+$, Found 1381.6534 $[\text{M}+\text{Na}]^+$.; Anal. Calcd for $\text{C}_{90}\text{H}_{54}$: C, 93.63; H, 6.37%. Found: C, 93.60; H, 6.35%.

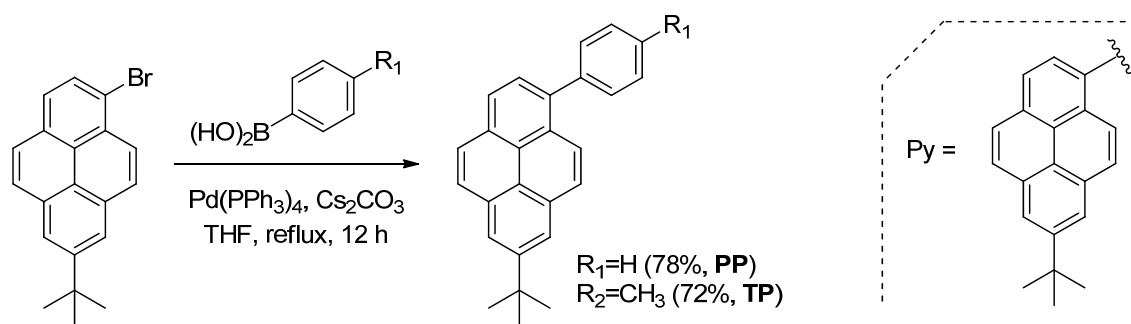
PP

Under an argon atmosphere, 2-bromo-7-*tert*-butylpyrene (0.25 g, 0.75 mmol), phenylboronic acid (0.12 g, 1.0 mmol), and cesium carbonate (0.65 g, 2.0 mmol) were mixed together with $\text{Pd}(\text{PPh}_3)_4$ (43 mg, 0.038 mmol), degassed THF (20 ml). The mixture was refluxed for 12 h. After cooling to room temperature, the result mixture was extracted with chloroform. The organic extract was washed with water and dried over MgSO_4 . After removal of the solvent, the residue was purified by column chromatography using chloroform/*n*-hexane (1:5, v/v). Subsequent recrystallization in methanol gave the objective product 7-*tert*-butyl-1-phenylpyrene as a colorless crystal in 78% yield. mp 90-92 °C.; ^1H NMR (400 MHz, CDCl_3) δ 8.22-7.65 (m, pyrene-H, 8H), 7.63-7.58 (d, $J = 7.7$ Hz, phenyl-H, 2H), 7.56-7.59 (t, $J = 7.6$ Hz, phenyl-H, 2H), 7.48-7.26 (t, $J = 7.3$ Hz, phenyl-H 1H), 1.59 (s, *tert*-butyl, 9H) ppm.; ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 141.3, 137.5, 131.3, 130.8, 130.6, 130.4, 128.33, 128.26, 127.63, 127.59, 127.24, 127.23, 125.1, 124.9, 124.4, 123.1, 122.4, 122.1 (aromatic C), 35.2 (-C(CH₃)₃), 31.9 (-C(CH₃)₃) ppm.; FT-IR (KBr) 3044, 3022, 1599, 1488, 1433, 1217, 1141, 1075 cm^{-1} .; HR-MS (EI) Calcd for $\text{C}_{26}\text{H}_{22}$ 334.1722 [M], Found 334.1719 [M].; Anal. Calcd for $\text{C}_{26}\text{H}_{22}$: C, 93.37; H, 6.63%. Found: C, 93.12; H, 6.54%.

TP (same procedure for PP)

Yield 72%; colorless crystal; mp 97-99 °C.; ^1H NMR (400MHz, CDCl_3) δ 8.21-7.91 (m, pyrene-H, 8H), 7.52-7.37 (d, $J = 7.7$ Hz, phenyl-H, 2H), 7.35-7.23 (d, $J = 7.7$ Hz, phenyl-H, 2H), 3.48 (s, tolyl-Me, 3H), 1.58 (s, *tert*-butyl, 9H) ppm.; ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 138.3, 137.5, 136.9, 131.3, 130.8, 130.4, 130.2, 129.0, 128.3, 127.51, 127.47, 127.3, 125.2, 124.9, 124.4, 123.1, 122.3, 122.0 (aromatic C), 35.2 (-C(CH₃)₃), 31.9 (-C(CH₃)₃), 21.2 (-Ph-CH₃) ppm.; FT-IR (KBr) 3023, 2959, 1592, 1497, 1457, 1378, 1361, 1227 cm^{-1} .; HR-MS (FAB) Calcd for $\text{C}_{27}\text{H}_{24}$ 348.1878 [M], Found 348.1873 [M].; Anal. Calcd for $\text{C}_{27}\text{H}_{24}$: C, 93.06; H, 6.94%. Found: C, 92.89; H, 6.94%.

Scheme S1



Scheme S1. Synthesis of PP and TP.

Figures

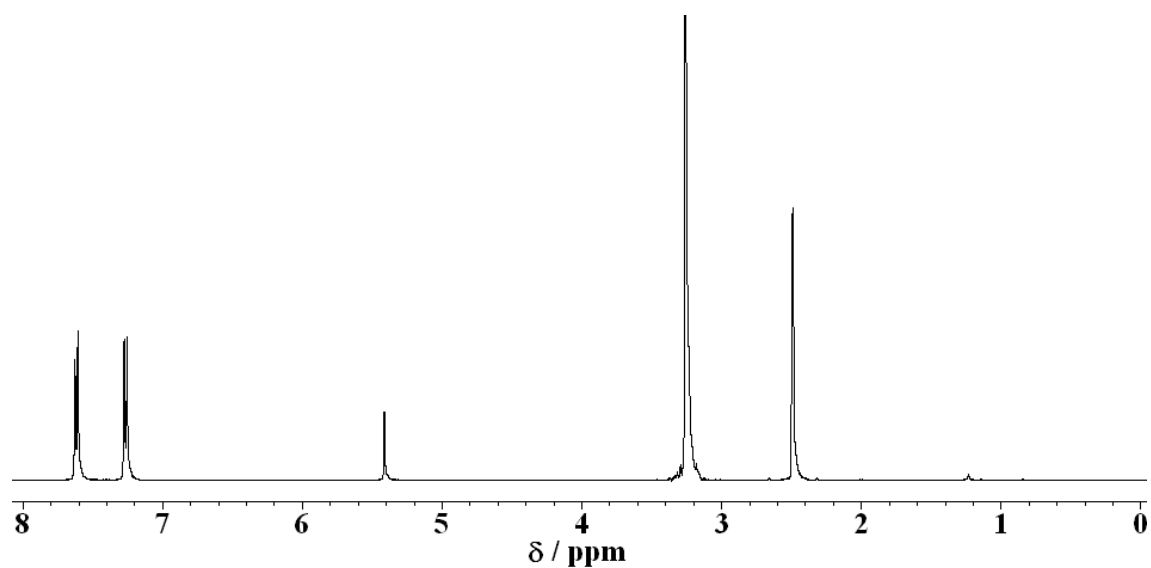


Figure S1. ¹H NMR spectrum of
1,1,2,2-Tetrakis(4-trifluoromethanesulfonylphenyl)ethane.
(400 MHz, DMSO-*d*₆)

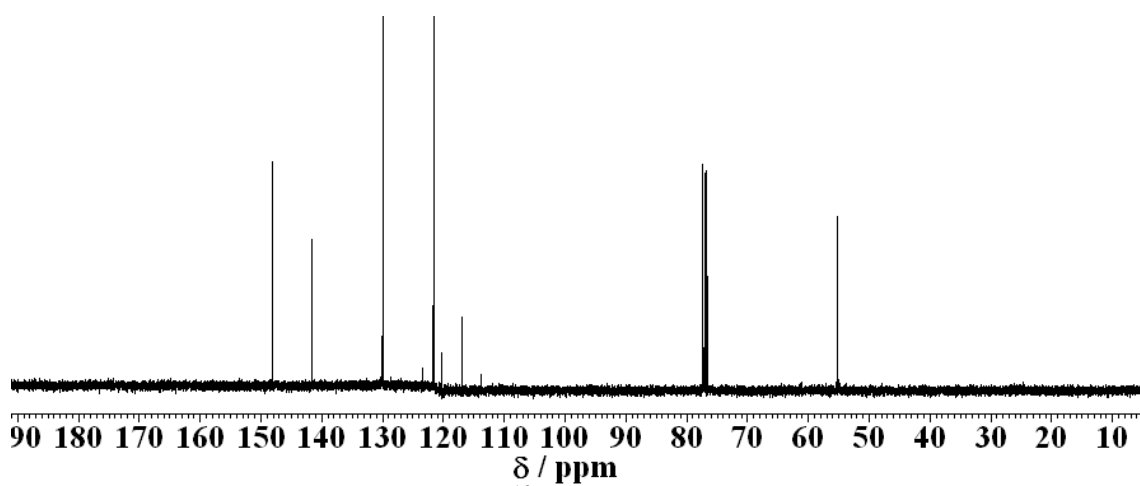


Figure S2. ¹³C NMR spectrum of
1,1,2,2-Tetrakis(4-trifluoromethanesulfonylphenyl)ethane.
(100 MHz, CDCl₃)

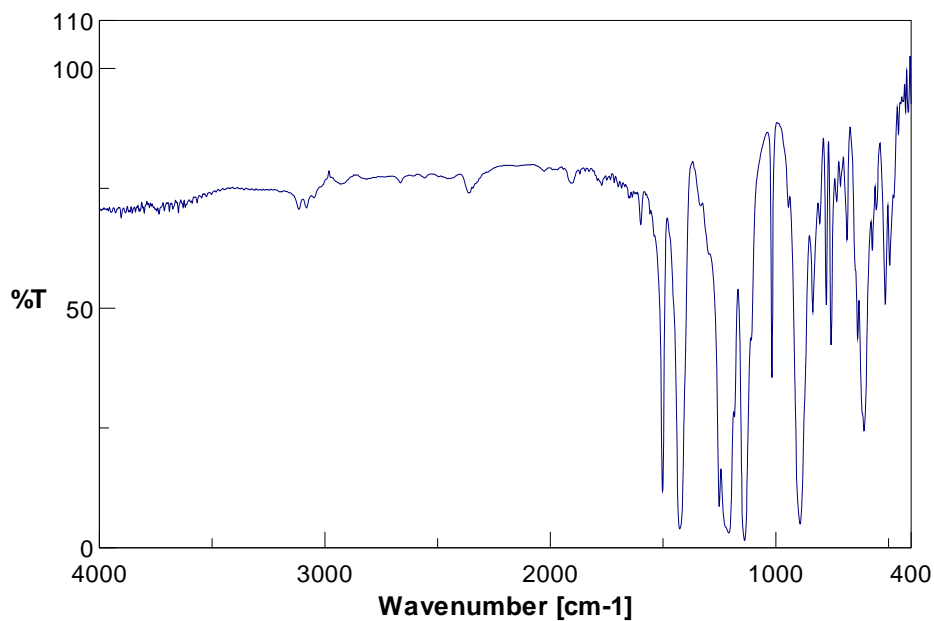


Figure S3. FT-IR spectrum of 1,1,2,2-tetrakis(4-trifluoromethanesulfonylphenyl)ethane (KBr).

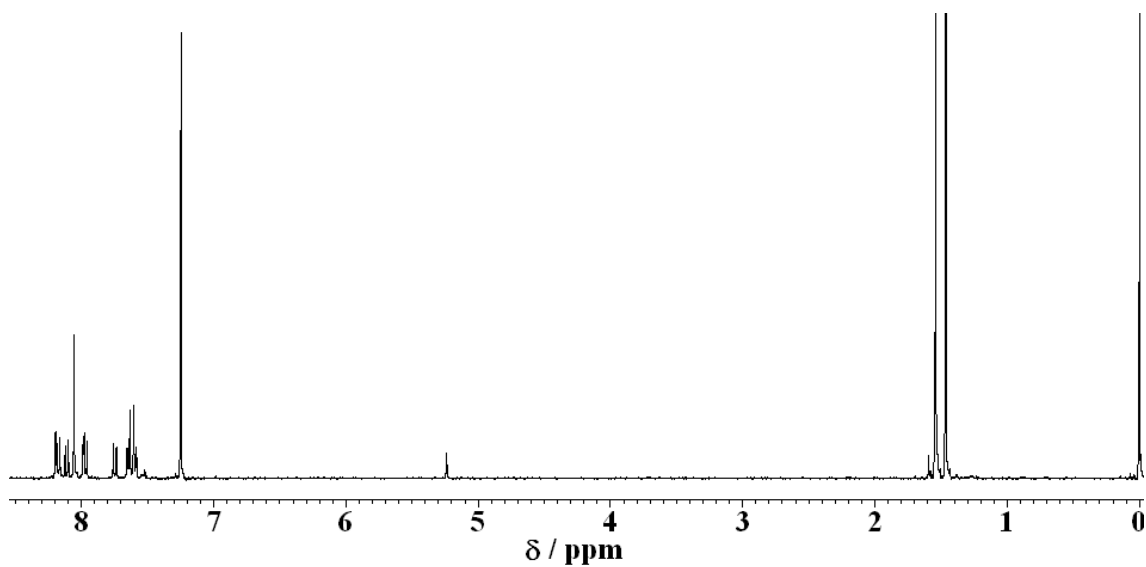


Figure S4. ^1H NMR spectrum of 1,1,2,2-tetrakis(7-*tert*-butyl(pyren-1-yl)phenyl)ethane. (TPPE, 400 MHz, CDCl_3)

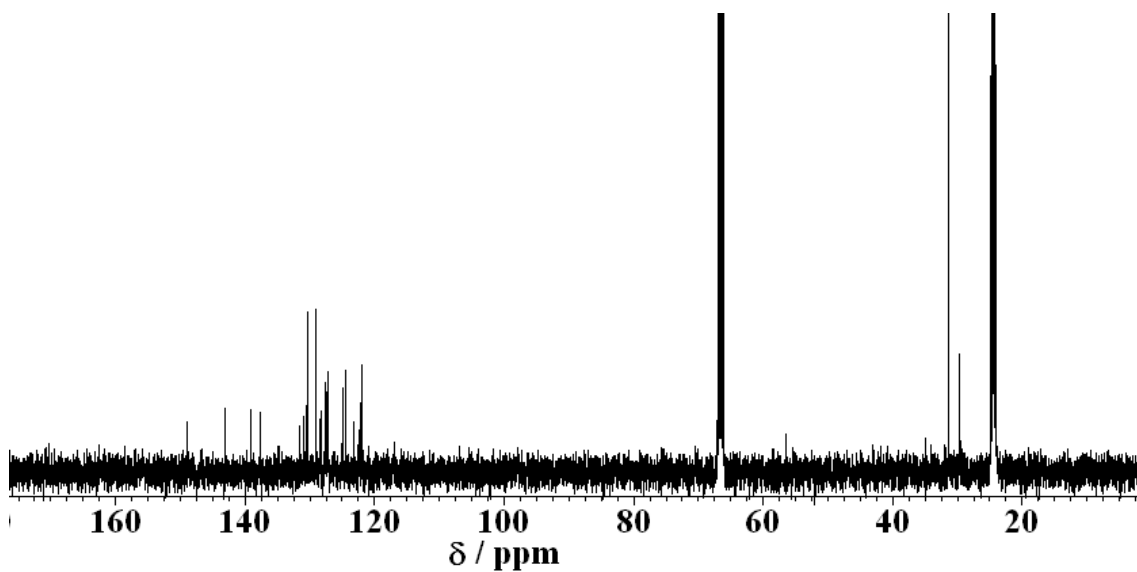


Figure S5. ^{13}C NMR spectrum of
1,1,2,2-tetrakis(7-*tert*-butyl(pyren-1-yl)phenyl)ethane.
(**TPPE**, 100 MHz, $\text{THF-}d_8$)

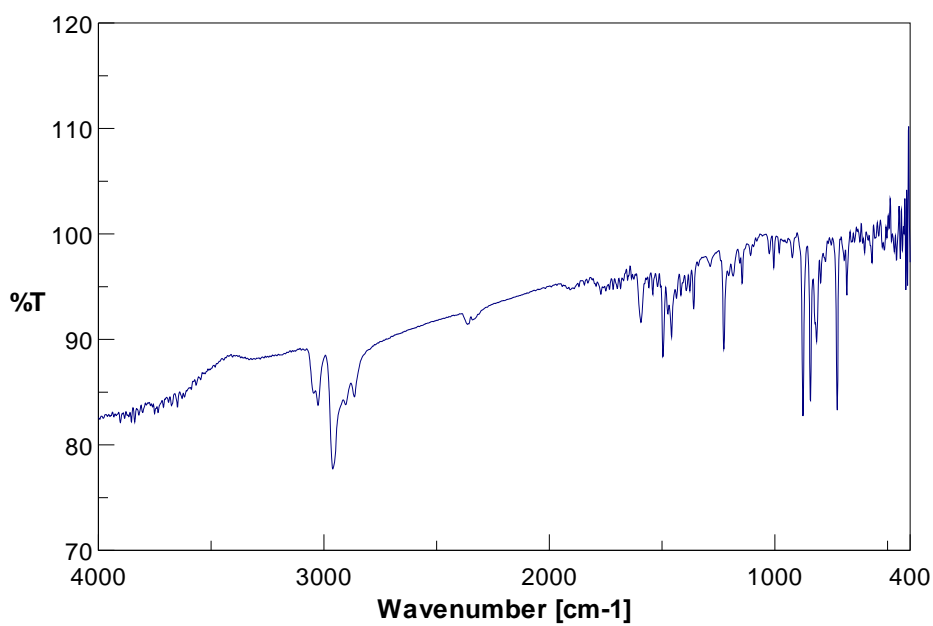


Figure S6. FT-IR spectrum of 1,1,2,2-tetrakis(7-*tert*-butyl(pyren-1-yl)phenyl)ethane
(**TPPE**, KBr).

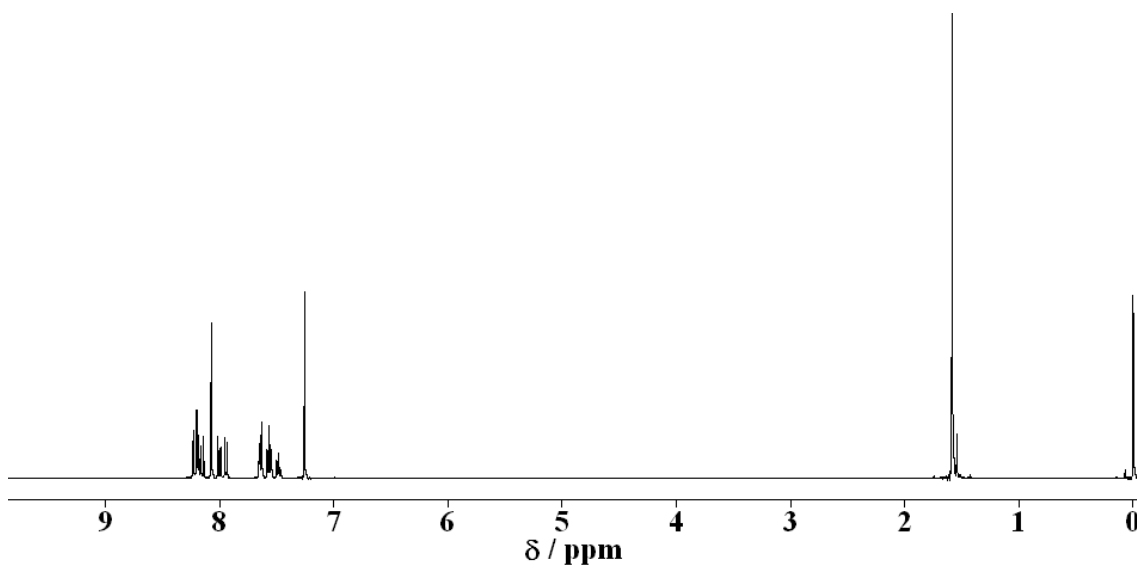


Figure S7. ¹H NMR spectrum of 7-*tert*-butyl-1-phenylpyrene (**PP**, 400 MHz, CDCl₃).

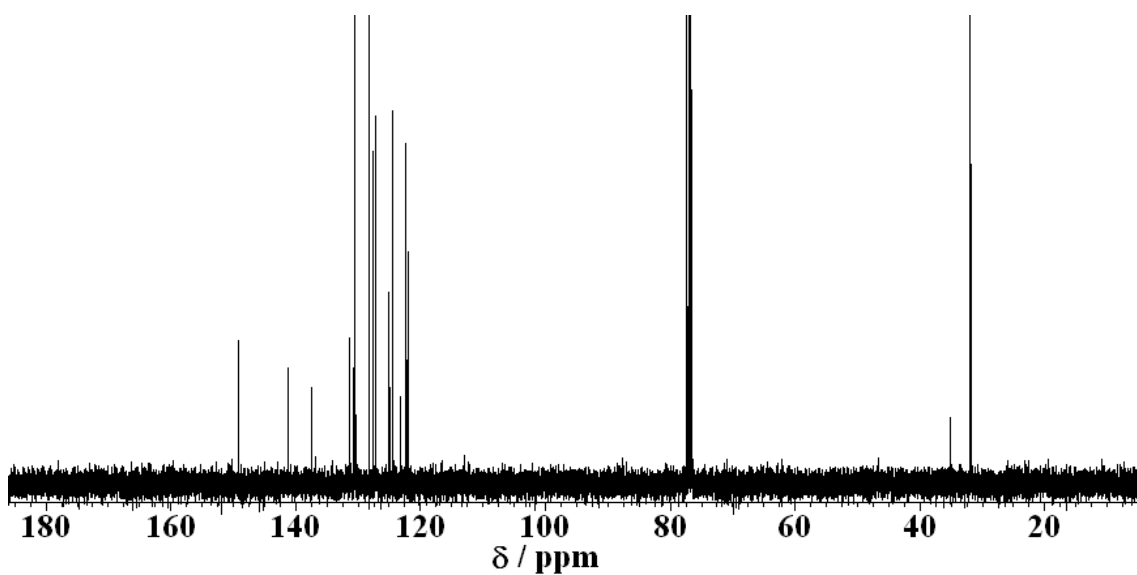


Figure S8. ¹³C NMR spectrum of 7-*tert*-butyl-1-phenylpyrene (**PP**, 100 MHz, CDCl₃).

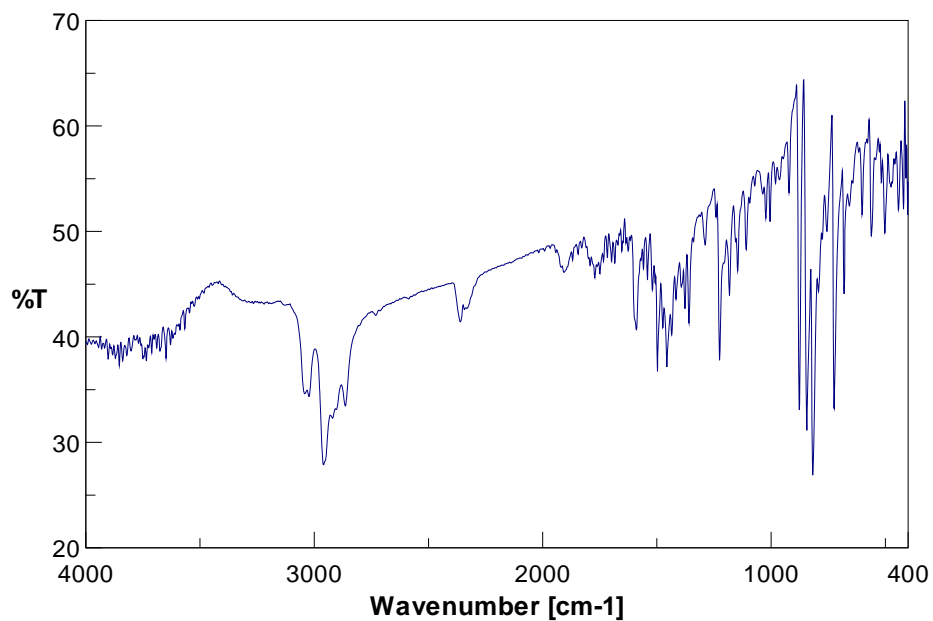


Figure S9. FT-IR spectrum of 7-*tert*-butyl-1-phenylpyrene (**PP**, KBr).

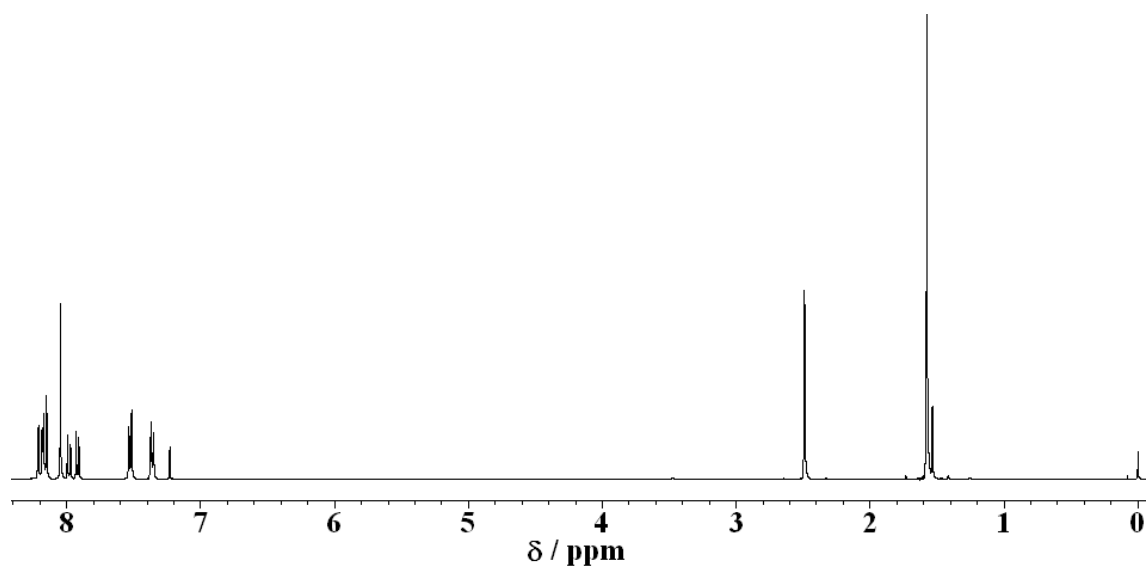


Figure S10. ¹H NMR spectrum of 7-*tert*-butyl-1-tolylpyrene (**TP**, 400 MHz, CDCl₃).

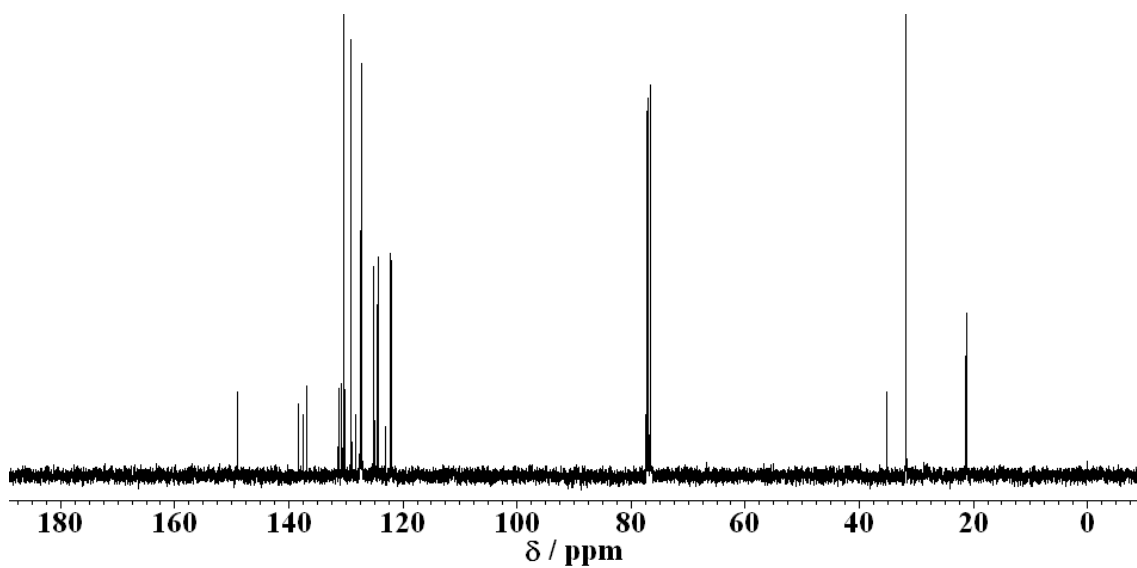


Figure S11. ^{13}C NMR spectrum of 7-*tert*-butyl-1-tolylpyrene (TP, 100 MHz, CDCl_3).

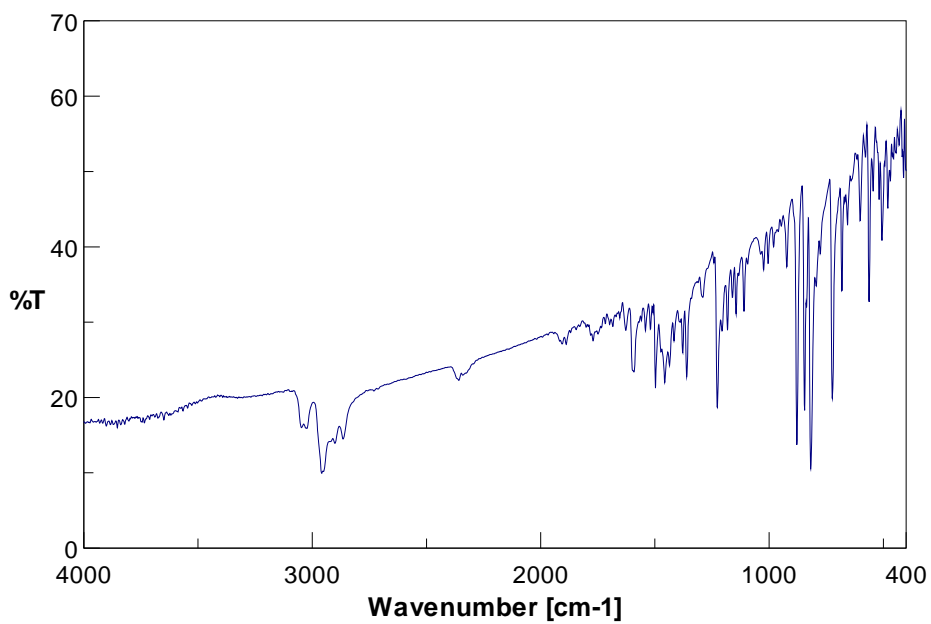


Figure S12. FT-IR spectrum of 7-*tert*-butyl-1-tolylpyrene (TP, KBr).

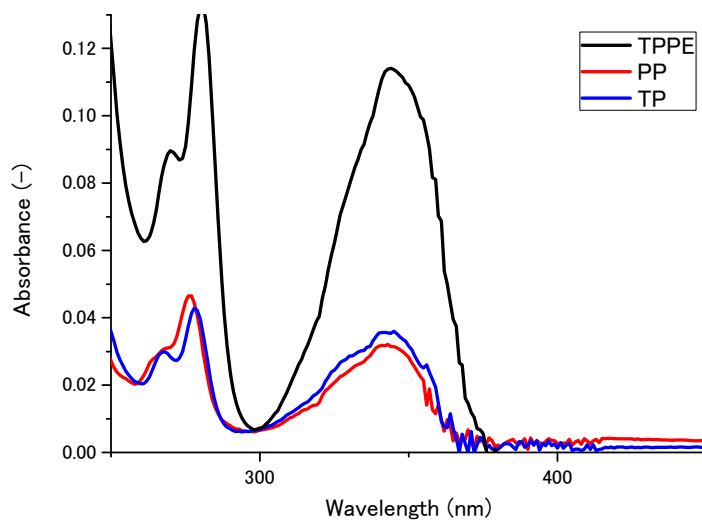


Figure S13. UV-vis spectra of **TPPE**, **PP**, and **TP** (THF; $c = 1.0 \times 10^{-6}$ M).

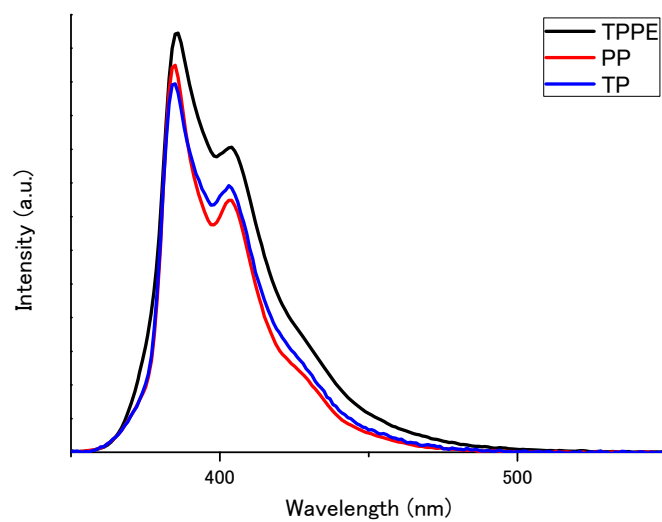


Figure S14. Fluorescence spectra of **TPPE**, **PP**, and **TP**.
(CH₂Cl₂; Abs = 0.1; $\lambda_{\text{ex}} = \lambda_{\text{max}}$)