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Luminogenic Materials Constructed from Tetraphenylethene Building Block: Synthesis, Aggregation-Induced Emission, Two-Photon Absorption, Light Refraction, and Explosive Detection

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**Synthesis.** Compounds 1–3 were prepared according to synthetic routes shown in Scheme 1. Detailed experimental procedures are given below.

**4-(1,2,2-Triphenylvinyl)phenylboronic acid (8).** To a stirred solution of 7 (1.00 g, 2.43 mmol) in THF (60 mL) at −78 °C under nitrogen was added n-BuLi (1.67 mL, 1.6 M in hexane, 2.67 mmol) dropwise. After stirred at −78 °C for 30 min, trimethylborate (0.76 g, 7.29 mmol) was added and the mixture was stirred for 30 min at −78 °C. The mixture was then warmed to room temperature and acidified with 50 mL of 10% aqueous hydrochloric acid solution. The organic layer was separated after stirred for 3 h and the aqueous layer was extracted with 100 mL ethyl acetate three times. The organic layers were combined and dried over Na₂SO₄. After solvent evaporation under reduced pressure, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent. White solid 8 was isolated in 54% yield. IR (KBr), ν (cm⁻¹): 3422, 3209, 3059, 3022, 1604, 1494, 1443, 1406, 1352, 1184, 1079, 1016, 755, 701. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.88 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.10 (m, 9H), 7.03 (m, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 148.26, 143.49, 143.44, 143.39, 141.75, 140.73, 134.92, 132.82, 131.30, 130.98, 130.89, 127.71, 127.65, 126.66, 126.53. HRMS (MALDI-TOF): m/z 376.1849 (M⁺, calcd 376.1635).

**1,2-Bis(4-bromophenyl)-1,2-diphenylethene (9).** Into a 250 mL two-necked round-bottom flask with a reflux condenser were placed 5.00 g (19.1 mmol) of 4-bromobenzophenone, 2.50 g (38.2 mmol) of zinc dust. The flask was evacuated under vacuum and flushed with dry nitrogen three times. 100 mL of THF was then added. The mixture was cooled to −78 °C and 3.6 g (19.1 mmol) of TiCl₄ was added dropwise by a syringe. The mixture was slowly warmed to room temperature. After stirred for 0.5 h, the mixture was refluxed for 24 h. The mixture was quenched with 10% aqueous...
K₂CO₃ solution and filtered. The filtrate was extracted with THF three times. The organic layer was washed with water and dried over Na₂SO₄. After solvent evaporation, the crude product was purified by silica gel column chromatography using petroleum ether as eluent. White solid of 9 was isolated in 75% yield. IR (KBr), \( \nu \) (cm⁻¹): 3053, 3022, 1957, 1903, 1583, 1490, 1442, 1392, 1070, 1009, 824, 754, 702, 481. \(^1\)H NMR (400 MHz, CDCl₃), \( \delta \) (TMS, ppm): 7.23 (m, 4H), 7.12 (m, 6H), 6.99 (m, 4H), 6.88 (m, 4H). \(^13\)C NMR (100 MHz, CDCl₃), \( \delta \) (ppm): 143.74, 143.61, 143.29, 143.17, 141.12, 133.62, 131.86, 131.76, 131.56, 128.72, 128.53, 128.41, 127.65, 127.53, 127.35, 121.38, 121.23. HRMS (MALDI-TOF): \( m/z \) 488.0238 (M⁺, calcd 487.9775).

1,2-Bis[4'-(1,2,2-triphenylvinyl)biphenyl-4-yl]-1,2-diphenylethene (1). To a mixture of 8 (192 mg, 0.51 mmol) and 9 (100 mg, 0.20 mmol) in THF (20 mL) was added 10 mL of 2 M aqueous Na₂CO₃ solution. After degassed and purged with nitrogen, Pd(PPh₃)₄ (18 mg, 0.016 mmol) was added. The reaction mixture was refluxed for 30 h and then extracted with dichloromethane and washed with 100 mL brine solution three times. The organic layer was dried over anhydrous MgSO₄. After solvent evaporation, the crude product was purified by silica gel column chromatography using petroleum ether as eluent. Yellow solid of 1 was isolated in 62% yield. IR (KBr), \( \nu \) (cm⁻¹): 3026, 2927, 1737, 1596, 1492, 1443, 1074, 1030, 1004, 811, 764, 699. \(^1\)H NMR (400 MHz, CDCl₃), \( \delta \) (TMS, ppm): 7.31 (m, 8H), 7.09 (m, 24H), 7.04 (m, 24H). \(^13\)C NMR (100 MHz, CDCl₃), \( \delta \) (ppm): 143.76, 143.73, 142.72, 141.02, 140.60, 140.53, 138.30, 138.22, 131.74, 131.40, 131.32, 127.74, 127.64, 127.61, 126.45, 126.39, 125.99, 125.87. HRMS (MALDI-TOF): \( m/z \) 992.4176 (M⁺, calcd 992.4382).

1,2-Bis(4-methylphenyl)-1,2-diphenylethene (11). Into a 500 mL two-necked round-bottom flask with a reflux condenser were placed 4-methylbenzophenone (10) (5.00 g, 25.5 mmol) and zinc...
dust (3.33 g, 51.0 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. 150 mL of THF was then added. The mixture was cooled to −78 °C and TiCl₄ (2.80 mL, 25.5 mmol) was added dropwise by a syringe. The mixture was slowly warmed to room temperature. After stirred for 0.5 h, the mixture was refluxed for 24 h. The reaction was quenched with 10% aqueous K₂CO₃ solution and filtered. The filtrate was extracted with dichloromethane three times. The organic layer was washed with water and dried over Na₂SO₄. After solvent evaporation, the crude product was purified by silica gel column chromatography using petroleum ether as eluent to give 11 as white solid in 83% yield. IR (KBr), ν (cm⁻¹): 3049, 3021, 2919, 2950, 1895, 1809, 1596, 1510, 1489, 1442, 1183, 1112, 1073, 1028, 821, 803, 738, 700, 609, 530. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.05 (m, 10H), 6.89 (d, J = 7.1 Hz, 8H), 2.56 and 2.24 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 144.13, 140.90, 140.36, 135.88, 131.35, 131.31, 131.21, 131.16, 128.37, 128.31, 127.59, 127.53, 126.17, 21.20, 21.16. HRMS (MALDI-TOF): m/z 360.1707 (M⁺, calcd 360.1878).

1,2-Bis[4-(bromomethyl)phenyl]-1,2-diphenylethene (12). Into a 250 mL round-bottom flask with a reflux condenser were placed 11 (3.00 g, 8.3 mmol), NBS (3.11 g, 17.5 mmol), and BPO (10 mg, 0.04 mmol) followed by addition of 70 mL of CCl₄. After refluxed for 24 h, the mixture was cooled to room temperature and filtered and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether as eluent to give 12 as white solid in 48% yield. IR (KBr), ν (cm⁻¹): 3443, 3050, 3024, 2966, 2950, 1915, 1804, 1698, 1605, 1508, 1490, 1443, 1409, 1227, 1205, 1145, 1098, 1074, 1020, 977, 830, 764, 732, 700, 635, 619, 608. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.12 (m, 10H), 6.99 (m, 8H), 4.43 and 4.41 (s, 4H, CH₂Br). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 143.76, 143.16, 140.77, 135.80, 131.62,
131.37, 131.28, 128.50, 128.40, 127.81, 127.71, 126.72, 126.64, 125.98, 125.88, 33.55. HRMS (MALDI-TOF): m/z 518.0677 (M+ , calcd 518.0068).

1,2-Bis{4-[(bromotriphenylphosphoranylmethyl)phenyl]-1,2-diphenylethene (13). Into a 250 mL round-bottom flask with a reflux condenser were placed 12 (1.00 g, 1.93 mmol) and PPh3 (2.02 g, 7.72 mmol). 50 mL of DMF was then added. After heated to 100 °C for 24 h, the mixture was cooled to room temperature and poured into toluene. The precipitates were filtered and washed with toluene to give 13 as white solid in 83% yield. Compound 13 was used for the next reaction without further purification. IR (KBr), ν (cm⁻¹): 3402, 3052, 3019, 2860, 2770, 1618, 1484, 1437, 1113, 847, 752, 717, 690, 567. 13C NMR (100 MHz, CDCl3), δ (ppm): 135.25, 135.05, 134.35, 134.31, 134.26, 134.21, 131.06, 130.91, 130.31, 130.18, 130.05, 127.72, 126.82, 118.02, 117.17, 34.69. HRMS (MALDI-TOF): m/z 961.2246 [(M-Br)+], calcd 961.1911.

4-(1,2,2-Triphenylvinyl)benzaldehyde (14). To a stirred solution of 7 (1.50 g, 3.64 mmol) in 50 mL anhydrous THF was added n-BuLi (2.7 mL, 1.6 M in hexane, 4.36 mmol) at −78 °C under nitrogen. The mixture was first stirred for 2 h at this temperature and then warmed to room temperature. After stirred for 1 h, the flask was cooled again to −78 °C and N-formylpiperidine (0.62 g, 5.46 mmol) was injected in one portion. The solution was stirred overnight and warmed to room temperature gradually. The reaction was quenched by adding 100 mL of 2 M aqueous hydrochloric acid solution. The organic layer was separated and the aqueous layer was extracted with 100 mL ethyl ether three times. The organic layers were combined and dried over Na2SO4. After solvent evaporation, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give the desired product as a yellow solid in 80% yield. IR (KBr), ν (cm⁻¹): 3054, 3021, 2833, 2728, 1698, 1599, 1489, 1439, 1306, 1215, 1166, 1069, 826, 746,
696, 630. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 9.90 (s, 1H, CHO), 7.61 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.11 (m, 9 H), 7.02 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$(ppm): 191.91, 150.54, 143.02, 142.96, 142.86, 139.72, 134.24, 131.92, 131.27, 129.14, 127.90, 127.72, 127.02, 126.87, 126.84. HRMS (MALDI-TOF): m/z 361.1588 [(M+1)$^+$, calcd 360.1514].

1,2-Bis[4-(1,2,2-triphenylvinyl)styryl]phenyl-1,2-diphenylethene (2). To a three-necked, round-bottom flask was added 13 (193 mg, 0.18 mmol) in 5 mL of dry DMF under nitrogen in an ice-water bath. Potassium tert-butoxide (80 mg, 0.72 mmol) was then added under stirring. The intense orange solution was stirred at room temperature for 30 min, after which a solution of 14 (200 mg, 0.55 mmol) in 5 mL of dry DMF was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into ice water and the yellow precipitates were collected. The crude product was washed by cold ethanol. The residue was purified by silica gel column using petroleum ether as eluent to give 2 as a yellow solid in 91% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3021, 1948, 1678, 1597, 1491, 1443, 1075, 748, 698, 629. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 7.20 (m, 4H), 7.10 (m, 46H), 6.93 (m, 4H), 6.87 (m, 4H), 6.43 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$(ppm): 143.71, 143.61, 143.10, 142.56, 141.08, 140.86, 140.72, 140.59, 135.38, 131.66, 131.39, 131.29, 131.08, 129.87, 128.29, 128.13, 127.72, 127.66, 127.61, 126.45, 126.40, 125.71. HRMS (MALDI-TOF): m/z 1044.6278 (M$^+$, calcd 1044.4695).

4-(2-Trimethylsilytlethynyl)benzophenone (15). Into a 100 mL two-necked round-bottom flask were added 70.1 mg (0.1 mmol) of Pd(PPh$_3$)$_2$Cl$_2$, 19 mg (0.1 mmol) of CuI, 13 mg (0.05 mmol) of PPh$_3$, 1.3 g of 5 (5 mmol), and 55 mL of THF/Et$_3$N (1:10 v/v) in an atmosphere of nitrogen. After the catalysts were completely dissolved, 0.9 mL (6.5 mmol) of (trimethylsilyl)acetylene was injected into the flask and the mixture was stirred at 70 °C for 24 h. The formed solid was removed by
filtration and washed with diethyl ether. After solvent evaporation, the crude product was purified by silica gel column chromatography using hexane as eluent. A pale brown solid was obtained in 86% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3061, 2958, 2900, 2156 (C≡C), 1650 (C=O), 1599, 1446, 1403, 1307, 1279, 1251, 1221, 1176, 1145, 939, 923, 851, 789, 761, 742, 697, 649, 532. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 7.77 (d, $J = 7.2$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.57 (m, 3H), 7.48 (m, 2H), 0.27 [s, 9H, Si(CH$_3$)$_3$]. $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 195.96 (C=O), 137.34, 136.93, 132.55, 131.76, 129.94, 129.89, 128.34, 127.31, 104.04 (≡C–Ar), 97.82 (≡C–Si), −0.18 [Si(CH$_3$)$_3$]. HRMS (MALDI-TOF): $m/z$ 278.0110 (M$^+$, calcd 278.1127).

1,2-Bis[4-(2-(trimethylsilyl)ethynyl]phenyl]-1,2-diphenylethene (16). Into a 250 mL two-necked round-bottom flask with a reflux condenser were placed 12.1 g (18 mmol) of zinc dust and 4.18 g (15 mmol) of 15. The flask was evacuated under vacuum and flushed with dry nitrogen three times. 100 mL of THF was then added. The mixture was cooled to $-78$ °C and 1 mL (9 mmol) of TiCl$_4$ was slowly added. The mixture was slowly warmed to room temperature, stirred for 0.5 h, and then refluxed overnight. The reaction was quenched with 10% aqueous K$_2$CO$_3$ solution and large amount of water was added until the solid turned to grey or white. The mixture was extracted with DCM for three times. The organic layers were combined and washed with brine twice. After solvent evaporation, the crude product was purified on a silica gel column using hexane as eluent. A yellow solid was obtained in 90% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3076, 3059, 3031, 2958, 2898, 2156 (C≡C stretching), 1599, 1499, 1443, 1404, 1249, 1224, 1178, 1108, 1073, 871, 863, 843, 761, 699, 645, 629, 570. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 7.21 (m, 4H), 7.10 (m, 6H), 6.96 (m, 8H), 0.22 and 0.24 [18H, Si(CH$_3$)$_3$]. $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 143.94, 143.82, 143.00, 142.95, 140.88, 131.44, 131.34, 131.30, 131.19, 127.88, 127.73, 126.83, 126.74, 121.14, 120.97, 120.97.
105.16 and 105.11 (≡C–Ar), 94.55 and 94.42 (≡C–Si), –0.06 [Si(CH₃)₃]. HRMS (MALDI-TOF): \textit{m/z} 524.2887 (M⁺, calcd 524.2356).

1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (17). Into a 100 mL round bottom flask was placed 40 mL of THF solution of 16 (1.57 g, 3 mmol), followed by addition of 12 mL of 1 M THF solution of TBAF. After stirring for 3 h, 40 mL of water was added and the mixture was extracted with 200 mL of DCM three times. The DCM solution was washed with brine twice. The mixture was dried over 5 g of anhydrous sodium sulfate for 2 h. After solvent evaporation, the crude product was purified on a silica gel column using hexane as eluent. A light yellow solid of 17 was obtained in 92% yield. IR (KBr), \( \nu \text{(cm}^{-1}) \): 3339 (≡C–H stretching), 3027, 3025, 2928, 2109 (C≡C stretching), 1601, 1497, 1444, 1404, 1247, 1107, 1072, 1019, 862, 818, 698, 627, 601. \(^1\)H NMR (400 MHz, CD₂Cl₂), \( \delta \text{(TMS, ppm)} \): 7.23 (m, 4H), 7.12 (m, 6H), 6.98 (m, 8H), 3.05 and 3.04 (2H, HC≡). \(^13\)C NMR (100 MHz, CD₂Cl₂), \( \delta \text{(TMS, ppm)} \): 144.91, 143.76, 141.73, 132.28, 132.14, 131.97, 131.94, 128.66, 128.51, 127.65, 127.52, 120.94, 84.17 (Ar–C ≡ ), 78.13 ( ≡C–H). HRMS (MALDI-TOF): \textit{m/z} 380.1525 (M⁺, calcd 380.1565).

1,2-Bis(4-[2-[4-(1,2,2-triphenylvinyl)phenyl]ethynyl]phenyl)-1,2-diphenylethene (3). Into a two-necked flask were added 7 (1.30 g, 3.15 mmol), 16 (0.40 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (59 mg, 0.07 mmol), PPh₃ (27 mg, 0.11 mmol), and CuI (12 mg, 0.06 mmol). After degassed and purged with nitrogen, a mixture of 30 mL of THF and 15 mL of Et₃N was added by a syringe. The mixture was stirred under reflux for 24 h under nitrogen. The reaction was cooled to room temperature and washed with saturated aqueous NH₄Cl solution. The mixture was extracted with DCM and washed with brine. The organic layers were combined and dried over anhydrous MgSO₄. After solvent...
evaporation under reduced pressure, the residue was purified by silica gel column chromatography using petroleum ether as eluent. Yellow solid of 3 was isolated in 95% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3074, 3019, 1945, 1893, 1490, 1443, 1393, 1261, 1072, 1013, 814, 751, 696, 478. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 7.23 (d, $J$ = 6.8 Hz, 8H), 7.11 (m, 24 H), 7.02 (m, 24 H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$(ppm): 143.88, 143.50, 143.42, 143.33, 143.11, 141.63, 140.95, 140.28, 131.33, 131.30, 131.00, 130.90, 127.80, 127.72, 127.64, 126.74, 126.65, 126.57, 121.41, 121.06. HRMS (MALDI-TOF): $m/z$ 1040.4373 (M$^+$, calcd 1040.4382).

**Polymerization.** Scheme 2 shows the synthetic routes for the preparation of P1–P3. Detailed synthetic procedures are shown below.

**4,4'-(1,2-Diphenyl-1,2-ethylenediphenylboronic acid (18).** To a stirred solution of 9 (2.00 g, 4.08 mmol) in THF (100 mL) at $-78$ °C under nitrogen was added n-BuLi (2.8 mL, 1.6 M in hexane, 4.49 mmol) dropwise. After stirred at $-78$ °C for 30 min, trimethylborate (1.27 g, 12.24 mmol) was added and the mixture was stirred for 30 min at $-78$ °C. The mixture was warmed to room temperature and acidified with 50 mL of 10% aqueous hydrochloric acid solution. After stirred for 3 h, the organic layer was separated and the aqueous layer was extracted with 100 mL ethyl acetate three times. The organic layers were combined and dried over Na$_2$SO$_4$. After solvent evaporation under reduced pressure, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give 8 as a white solid in 74% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3391 (OH), 3053, 3022, 1703, 1605, 1548, 1509, 1491, 1402, 1344, 1182, 1108, 1074, 1017, 838, 817, 751, 698, 652, 478. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 8.04 (d, $J$ =
7.2 Hz, 4H), 7.44 (m, 4H), 7.10 (m, 6H), 7.02 (m, 4H). HRMS (MALDI-TOF): m/z 420.1884 (M⁺, calcd 420.1704).

**P1.** To a mixture of **9** (117 mg, 0.24 mmol) and **18** (100 mg, 0.24 mmol) in THF (8 mL) was added 8 mL of 2 M aqueous solution of Na₂CO₃. After degassed and purged with nitrogen, Pd(PPh₃)₄ (22 mg, 0.019 mmol) was added. The mixture was refluxed for 30 h and then extracted with DCM and washed with 100 mL brine three times. The organic layers were combined and dried with anhydrous MgSO₄. After solvent evaporation, the residue was dissolved in THF and added into 200 mL of methanol to obtain P1 as a yellow solid in 79% yield. Mᵣ 6100; Mᵣ/Mₘ 1.73. IR (KBr), $\nu$ (cm⁻¹): 3023, 1597, 1493, 1442, 1394, 1113, 1073, 1004, 808, 766, 699. $^1$H NMR (400 MHz, CDCl₃), $\delta$ (ppm): 7.30 (m, 4H), 7.09 (m, 14H). $^{13}$C NMR (100 MHz, CDCl₃), $\delta$(ppm): 143.74, 142.77, 141.03, 140.61, 138.29, 138.21, 132.03, 131.76, 131.41, 131.32, 128.66, 128.47, 128.35, 127.96, 127.77, 127.64, 126.84, 126.52, 126.45, 126.17, 126.00, 125.87.

**4,4’-(1,2-Diphenyl-1,2-ethylenedibenzaldehyde (19).** To a stirred solution of **9** (2.00 g, 4.08 mmol) in 50 mL anhydrous THF was added n-BuLi (6.4 ml, 1.6 M in hexane, 10.2 mmol) at ~78 °C under nitrogen. The mixture was first stirred for 2 h at this temperature and then warmed to room temperature. After stirred for 1 h, the mixture was cooled again to ~78 °C and N-formylpiperidine (1.39 g, 12.24 mmol) was added in one portion. The solution was stirred overnight and allowed to warm to room temperature gradually. 100 mL of 2 M aqueous hydrochloric acid solution was added to quench the reaction. After stirred for 2 h, the organic layer was separated and the aqueous layer was extracted with 100 mL ethyl ether three times. The organic layer was dried over Na₂SO₄. After solvent evaporation under reduced pressure, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give the desired product as
a yellow solid in 66% yield. IR (KBr), $\nu$ (cm$^{-1}$): 3063, 3023, 2816, 2727, 1693, 1599, 1306, 1210, 1163, 829, 763, 699. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 9.92 (s, 2H, CHO), 7.63 (d, J = 8.2 Hz, 4H), 7.19 (d, J = 8.2 Hz, 4H), 7.14 (m, 6H), 7.01 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$(ppm): 191.69 (CHO), 149.62, 142.23, 141.68, 134.73, 131.91, 131.86, 131.15, 129.31, 128.02, 127.31. HRMS (MALDI-TOF): m/z 389.1531 [(M+1)$^+$], calcd 388.1463.

**P2.** To a three-necked, round-bottom flask was added 13 (139 mg, 0.13 mmol) in 3 mL of dry DMF under nitrogen in an ice-water bath. Potassium tert-butoxide (45 mg, 0.40 mmol) was then added under stirring. The intense orange solution was stirred at room temperature for 30 min, after which a solution of 19 (52 mg, 0.13 mmol) in 2 mL of dry DMF was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into ice water and the yellow precipitates were collected. The crude product was washed with cold ethanol. The residue was dissolved in THF and added into 200 mL of petroleum ether. Yellow solid of P2 was obtained in 85% yield. $M_w$ 11800; $M_w/M_n$ 2.56. IR (KBr), $\nu$ (cm$^{-1}$): 3021, 1597, 1509, 1491, 1442, 1384, 961, 827, 761, 699, 607. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$(TMS, ppm): 7.18 (m, 2H), 7.00 (m, 15H), 6.85 (m, 2H), 6.41 (m, 1H).

**P3.** Into a two-necked flask were added 9 (77 mg, 0.16 mmol), 17 (60 mg, 0.16 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (9 mg, 0.012 mmol), PPh$_3$ (4 mg, 0.016 mmol), and CuI (2 mg, 0.010 mmol). After degassed and purged with nitrogen, a solution of Et$_3$N (2 mL) in 4 mL of THF was added by a syringe. The reaction was refluxed for 24 h and then washed with 20 mL of saturated NH$_4$Cl solution. The mixture was extracted with 50 mL of DCM and washed with 50 mL brine three times. The organic layers were combined and dried over anhydrous MgSO$_4$. After solvent evaporation
under reduced pressure, the residue was dissolved in THF and added into 200 mL of methanol to give P3 as a yellow solid in 76% yield. $M_n$ 7500; $M_w/M_n$ 1.69. IR (KBr), $\nu$ (cm$^{-1}$): 3055, 3026, 1948, 1909, 1596, 1511, 1491, 1443, 1073, 1011, 840, 811, 762, 698, 628, 573. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 7.16 (m, 4H), 7.05 (m, 6H), 6.93 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 143.04, 142.42, 142.31, 140.39, 139.78, 132.27, 131.10, 130.59, 130.53, 130.29, 130.13, 129.29, 127.88, 127.24, 127.09, 126.19, 126.07, 120.70, 89.02 (Ar−C≡).

Fig. S1 HRMS spectrum of 1.
Fig. S2 HRMS spectrum of 2.

Fig. S3 HRMS spectrum of 3.
Fig. S4  (A) Photographs of 2 in THF/water mixtures with different fractions of water ($f_w$) taken under UV illumination. (B) Emission spectra of 2 in THF/water mixtures. (C) Plot of ($I/I_o$) values versus the compositions of the aqueous mixtures. $I_o$ = emission intensity in pure THF solution. Solution concentration: 10 µM; excitation wavelength: 360 nm.
Fig. S5 (A) Photographs of 3 in THF/water mixtures with different fractions of water ($f_w$) taken under UV illumination. (B) Emission spectra of 3 in THF/water mixtures. (C) Plot of ($I/I_o$) values versus the compositions of the aqueous mixtures. $I_o = $ emission intensity in pure THF solution. Solution concentration: 10 M; excitation wavelength: 352 nm.
Fig. S6 (A) Photographs of P2 in THF/water mixtures with different fractions of water ($f_w$) taken under UV illumination. (B) Emission spectra of P2 in THF/water mixtures. (C) Plot of ($I/I_o$) values versus the compositions of the aqueous mixtures. $I_o$ = emission intensity in pure THF solution. Solution concentration: 10 µM; excitation wavelength: 382 nm.
**Fig. S7** (A) Photographs of P3 in THF/water mixtures with different fractions of water ($f_w$) taken under UV illumination. (B) Emission spectra of P3 in THF/water mixtures. (C) Plot of ($I/I_o$) values versus the compositions of the aqueous mixtures. $I_o$ = emission intensity in pure THF solution.

Solution concentration: 10 µM; excitation wavelength: 360 nm.
**Table S1.** Theoretical Calculations of Energy Levels of 1–3

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<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
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Abbreviation: HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital, and $E_g$ = energy band gap = LUMO–HOMO.

Fig. S8 Molecular orbital amplitude plots of HOMO and LUMO energy levels of *cis* 1–3 calculated using B3LYP/6-31G(d) basis set.
Fig. S9 (A) Emission spectra of P1 in THF/water mixtures (1/1 v/v) and (B) THF solution containing different amounts of picric acid (PA). Concentration: 10 µM; excitation wavelength: 356 nm.