Furan-Containing Oligoaryl Cyclophanene.

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Supporting Information

Experimental Section

4-(1-Hydroxy-hept-2-ynyl)-benzoic acid methyl ester. To a solution of 1-hexyne (51.6 mL, 0.45 mol) in THF (200 mL), stirred under N_2 atmosphere, was slowly added a solution of 2.5 M *n*-BuLi in *n*-hexane (180.0 mL, 0.45 mol) at -78 ºC. The reaction mixture was warmed to rt and stirred for 1 h. After cooling to -78 ºC, a solution of methyl 4-formylbenzoate (73.60 g, 0.45 mol) in THF (500 mL) was added slowly. After addition, the reaction mixture was stirred for 30 min at -78 ºC, then slowly warmed to rt and further stirred for 2 h. The mixture was quenched with saturated NH_4Cl (500 mL), and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 300 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the crude ynol (106.40 g, 96%) as an orange oil. Kugelrohr distillation (0.01 torr, 130 ºC) afforded the propargyl alcohol as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, *J* = 7.3 Hz, 3 H), 1.39 (tq, *J* = 7.1, 7.3 Hz, 2 H), 1.50 (quintet, *J* = 7.1 Hz, 2 H), 2.19-2.38 (m, 3 H, embodied a dt at δ 2.25 (*J* = 2.0, 7.1 Hz, 2 H)), 3.90 (s, 3 H), 5.47 (d, *J* = 5.6 Hz, 1 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 8.02 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 18.4, 21.9, 30.5, 52.1, 64.3, 79.4, 88.2, 126.5, 129.8, 146.1, 166.8; IR (KBr): ν = 3439, 2961, 2938, 2872, 2284, 2229, 1725, 1614, 1580, 1439, 1414, 1285, 1193, 1112, 1020, 754 cm^{-1}; MS (70 eV, EI): *m/z* (%): 246 (11) [M^+], 231 (16), 215 (34), 213 (35), 202 (41), 189 (20), 187 (100), 185 (44), 171 (20), 163 (80), 145 (36), 137 (70), 129 (54), 115 (45), 105 (68), 91 (38), 77 (65), 68 (34); HRMS (EI) ($C_{15}H_{18}O_3$): calcd: 246.1256; found: 246.1267; elemental analysis calcd (%) for $C_{15}H_{18}O_3$

(246.31): C 73.15, H 7.37; found: C 72.93, H 6.99.

4-Hept-2-ynoyl-benzoic acid methyl ester. A solution of crude 4-(1-hydroxy-hept-2-ynyl)-benzoic acid methyl ester (106.40 g, 0.43 mol) in CH_2Cl_2 (300 mL) was added slowly to a suspension of activated MnO_2 (224.30 g, 2.58 mol) in CH_2Cl_2 (400 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (5 cm) and washing with CH_2Cl_2 (5 × 300 mL), the combined filtrate was evaporated in vacuo to afford crude ynone (99.72 g, 95%) as an orange oil. Kugelrohr distillation (0.01 torr, 140 ºC) afforded propargylic ketone as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.3 Hz, 3 H), 1.49 (tq, *J* = 7.3, 7.4 Hz, 2 H), 1.65 (tt, *J* = 7.1, 7.4 Hz, 2 H), 2.50 (t, *J* = 7.1 Hz, 2 H), 3.93 (s, 3 H), 8.10 and 8.16 (AA′XX′, *J* = 8.0, 0.7, 1.7, 1.7 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 18.9, 22.1, 29.8, 52.5, 79.6, 98.1, 129.4, 129.7, 134.5, 140.0, 166.2, 177.4; IR (KBr): ν = 2962, 2940, 2875, 2239, 2204, 1730, 1652, 1439, 1410, 1282, 1267, 1195, 1120, 1106, 1019, 913, 825, 721 cm^{-1}; MS (70 eV, EI): *m/z* (%): 244 (14) [M^+], 229 (7), 215 (16), 213 (72), 202 (70), 185 (49), 171 (14), 163 (100), 157 (14), 135 (14), 115 (13), 109 (31), 103 (17), 79 (15); HRMS (EI) ($C_{15}H_{16}O_3$): calcd: 244.1099; found: 244.1092; elemental analysis calcd (%) for $C_{15}H_{16}O_3$ (244.29): C 73.75, H 6.60; found: C 73.43, H 6.86.

4-(2-Hex-1-ynyl-[1,3]dithiolan-2-yl)-benzoic acid methyl ester (3). To a solution of 4-hept-2-ynoyl-benzoic acid methyl ester (107.41 g, 0.44 mol) in MeOH (700 mL) was added $BF_3 \cdot Et_2O$ (66.4 mL, 0.53 mol) and 1,2-ethanedithiol (37.8 mL, 0.45 mol) at -78 ºC. The reaction mixture was slowly warmed to rt and stirred for 12 h. After quenching with 10% NaOH (400 mL), the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layer was washed with 10% NaOH (5 × 300 mL), brine (300 mL), then dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:9) to afford **3** as a pale yellow oil. The product was dissolved in pentane and cooled in the freezer, the pure propargylic dithioacetal **3** crystallizes out as a colorless needle (87.42 g, 62%). M.p. 46-47 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.3$ Hz, 3 H), 1.43 (sextet, $J = 7.3$ Hz, 2 H), 1.56 (tt, $J = 7.1, 7.3$ Hz, 2 H), 2.35 (t, $J = 7.1$ Hz, 2 H), 3.59-3.75 (m, 4 H), 3.89 (s, 3 H), 7.98 (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.6$, 18.9, 22.0, 30.6, 41.4, 52.1, 61.7, 81.7, 88.7, 127.7, 129.4, 129.8, 145.1, 166.6; IR (KBr): $\nu = 2960$, 2934, 2870, 2226, 1726, 1610, 1437, 1408, 1280, 1193, 1111, 1021, 966, 869, 735, 496 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 320 (100) [M^+], 292 (10), 278 (14), 263 (73), 250 (89), 235 (17), 219 (22), 191 (17), 179 (14), 131 (12), 115 (12), 59 (12); HRMS (EI) ($C_{17}H_{20}O_2S_2$): calcd: 320.0905; found: 320.0910; elemental analysis calcd (%) for $C_{17}H_{20}O_2S_2$ (320.46): C 63.72, H 6.29; found: C 63.68, H 5.89.

Diester 6. Under Ar atmosphere, a solution of 2.5 M *n*-BuLi in *n*-hexane (12.0 mL, 30.0 mmol) was introduced dropwise to a solution of **3** (9.61 g, 30.0 mmol) in THF (200 mL) at -78 ºC and stirred for 50 min. To this reaction mixture was added a solution of 4,4′-diformylbibenzyl (**5**) (2.38 g, 10.0 mol) in THF (60 mL) slowly at this temperature. The reaction mixture was stirred for 1 h at -78 ºC, then gradually warmed to rt. After further stirring for 30 min at rt, TFA (4.5 mL, 60.0 mmol) was added and the mixture was stirred at rt for overnight. The reaction mixture was finally quenched with saturated NH_4Cl (100 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was suspended in Et_2O (6 mL) and stirred. The solid **6** was filtered, washed with a mixture of Et_2O/pentane (1:1), and collected as a fluorescent yellow powder (4.52 g, 65%). M.p. 196-197 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.3$ Hz, 6 H), 1.43 (sextet, $J = 7.3$ Hz, 4 H), 1.66 (tt, $J = 7.3, 7.8$ Hz, 4 H), 2.68 (t, $J = 7.8$ Hz, 4 H), 2.99 (s, 4 H), 3.91 (s, 6 H), 6.78 (s, 2 H), 7.25 (d, *J* = 8.2 Hz, 4 H), 7.61 (d, *J* = 8.2 Hz, 4 H), 7.74 and 8.03 (AA′XX′, *J* = 8.2, 0.5, 1.7, 1.7 Hz, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 32.1, 37.5, 52.1, 111.5, 123.1, 124.0, 125.8, 128.2, 128.8, 129.2, 130.1, 134.8, 140.8, 149.3, 150.6, 166.9; IR (KBr): ν = 3027, 2958, 2932, 2864, 1720, 1612, 1510, 1437, 1281, 1177, 1109, 934, 831, 772, 700, 670 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 360 nm (7.6 × 10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 430 nm; MS (70 eV, EI): *m*/*z* (%): 694 (1) [M^+], 564 (2), 534 (3), 522 (4), 492 (6), 466 (84), 435 (5), 373 (8), 347 (100), 304 (8), 288 (7), 245 (6), 217 (6), 202 (6), 163 (4), 117 (4), 91 (6); HRMS (EI) ($C_{46}H_{46}O_6$): calcd: 694.3294; found: 694.3298; elemental analysis calcd (%) for $C_{46}H_{46}O_6$ (694.87): C 79.51, H 6.67; found: C 79.53, H 6.79.

Diol 7. To a solution of diester **6** (5.16 g, 7.42 mmol) in THF (200 mL) stirred under Ar atmosphere was added slowly a solution of 1.0 M diisobutylaluminum hydride in *n*-hexane (45.0 mL, 45.0 mmol) at 0 ºC and stirred for 3 h. The reaction was quenched by pouring it into a saturated NH_4Cl solution (200 mL), and stirred for 30 min. After passing through a silica gel bed (1 cm) and washing with CH_2Cl_2 (5 × 200 mL), the combined filtrate was evaporated in vacuo. Water (200 mL) was added to the residue and extracted with CH_2Cl_2 (4 × 200 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting material was recrystallized from Et_2O and CH_2Cl_2, affording diol **7** as a fluorescent yellow solid (4.46 g, 94%). M.p. 120-122 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 6 H), 1.43 (tq, *J* = 7.3, 7.4 Hz, 4 H), 1.60-1.71 (m, 6 H), 2.68 (t, *J* = 7.8 Hz, 4 H), 2.98 (s, 4 H), 4.69 (s, 4 H), 6.64 (s, 2 H), 7.23 (d, *J* = 8.2 Hz, 4 H), 7.36 (d, *J* = 8.2 Hz, 4 H), 7.60 (d, *J* = 8.2 Hz, 4 H), 7.69 (d, *J* = 8.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 32.1, 37.5, 65.2, 109.2, 123.6, 123.8, 125.5, 127.4, 128.7, 129.5, 130.3, 139.6, 140.3, 148.1, 151.4; IR (KBr): ν = 3338, 3030, 2959, 2932, 2867, 1617, 1511, 1461, 1377, 1213, 1183, 1046, 1011, 832, 807, 758, 678 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 335 nm (6.3×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 388, 370 nm; MS (70 eV, EI): *m*/*z* (%): 638 (16) [M^+], 620 (10), 606 (10), 492 (4), 422 (6), 408 (6), 319 (78), 303 (100), 231 (10), 213 (12), 202 (10), 185 (14), 171 (10), 157 (10), 135 (20), 129 (20); HRMS (EI) ($C_{44}H_{46}O_4$): calcd: 638.3396; found: 638.3364; elemental analysis calcd (%) for $C_{44}H_{46}O_4$ (638.85): C 82.72, H 7.26; found: C 82.38, H 7.38.

Dibromide 8. A solution of diol **7** (4.34 g, 6.79 mmol) in benzene (170 mL) stirred under N_2 atmosphere was treated with PBr_3 (0.65 mL, 5.43 mmol) at rt and stirred for 6 h. After quenching with water (200 mL), the reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was recrystallized from Et_2O and CH_2Cl_2, to afford the dibromide **8** as a yellow solid (4.97 g, 97%). M.p. 144-146 ºC (dec.); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 6 H), 1.43 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.66 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.68 (t, *J* = 7.8 Hz, 4 H), 2.98 (s, 4 H), 4.51 (s, 4 H), 6.66 (s, 2 H), 7.24 and 7.39 (AA′XX′, *J* = 8.0, 0.4, 1.8, 1.8 Hz, 8 H), 7.60 and 7.66 (AA′XX′, *J* = 8.0, 0.4, 1.9, 1.9 Hz, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 32.1, 33.7, 37.5, 109.9, 123.7, 123.9, 125.6, 128.7, 129.5, 131.0, 136.3, 140.5, 148.4, 151.1; IR (KBr): ν = 3031, 2960, 2933, 2866, 1616, 1511, 1493, 1462, 1227, 1203, 1184, 1098, 935, 835, 758, 678, 601, 501 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 346 nm (5.8×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 470 nm; MS (FAB^+): *m*/*z* (%): 764 (5) [M^+], 685 (5) [M^+-Br], 683 (4), 307 (35), 289 (17), 154 (100), 136 (62), 107 (18); HRMS (FAB^+) ($C_{44}H_{44}{}^{79}Br_2O_2$): calcd: 762.1707; found: 762.1687; elemental analysis calcd (%) for $C_{44}H_{44}Br_2O_2$ (764.64): C 69.12, H 5.80; found: C 69.01, H 5.55.

Dialdehyde 12. A solution of diol **7** (1.28 g, 2.00 mmol) in CH_2Cl_2 (20 mL) was added slowly to a suspension of activated MnO_2 (2.09 g, 24.00 mol) in CH_2Cl_2 (30 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (2 cm) and washing with CH_2Cl_2 (5 × 120 mL), the combined filtrate was evaporated in vacuo. The resulting residue was recrystallized from Et_2O and CH_2Cl_2, to afford the dialdehyde **12** as a fluorescent yellow solid (1.21 g, 95%). M.p. 155-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 6 H), 1.44 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.67 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.69 (t, *J* = 7.8 Hz, 4 H), 3.00 (s, 4 H), 6.83 (s, 2 H), 7.26 (d, *J* = 8.3 Hz, 4 H), 7.62 (d, *J* = 8.3 Hz, 4 H), 7.82 and 7.87 (AB_q, *J* = 8.4 Hz, 8 H), 9.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.6, 25.7, 32.1, 37.5, 112.4, 123.6, 124.2, 125.8, 128.8, 129.1, 130.3, 134.6, 136.1, 140.9, 149.8, 150.2, 191.4; IR (KBr): ν = 3028, 2960, 2933, 2867, 2833, 2739, 1699, 1607, 1575, 1510, 1391, 1216, 1167, 932, 833, 757 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 379 nm (5.9×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 467 nm; MS (EI): *m*/*z* (%): 634 (1) [M^+], 602 (2), 520 (10), 436 (5), 415 (3), 368 (7), 353 (2), 317 (19), 313 (22), 285 (4), 236 (4), 192 (59), 177 (100), 150 (25), 145 (42), 120 (32), 107 (18), 69 (21); HRMS (EI) ($C_{44}H_{42}O_4$): calcd: 634.3078; found: 634.3036; elemental analysis calcd (%) for $C_{44}H_{42}O_4$ (634.81): C 83.25, H 6.67; found: C 83.02, H 6.68.

Bisdithioacetal 11. A mixture of dialdehyde **12** (636.8 mg, 1.00 mmol), $BF_3 \cdot Et_2O$ (0.25 mL, 2.20 mmol) and 1,2-ethanedithiol (0.20 mL, 2.00 mmol) in CH_2Cl_2 (50 mL) was stirred at rt for 12 h. After quenching with 10% NaOH (50 mL), the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with 10% NaOH (5 × 100 mL), then dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was recrystallized from Et_2O and CH_2Cl_2, to afford **11** as a yellow solid (724.2 mg, 92%). M.p. 177-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 6 H), 1.43 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.66 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.67 (t, *J* = 7.8 Hz, 4 H), 2.97 (s, 4 H), 3.28-3.56 (m, 8 H), 5.65 (s, 2 H), 6.63 (s, 2 H), 7.24 (d, *J* = 8.1 Hz, 4 H), 7.63 and 7.52 (AB_q, *J* = 8.3 Hz, 8 H), 7.59 (d, *J* = 8.1 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 32.1, 37.5, 40.3, 56.2, 109.5, 123.6, 123.7, 125.6, 128.3, 128.7, 129.5, 130.7, 138.9, 140.4, 148.2, 151.3; IR (KBr): ν = 3027, 2959, 2930, 2863, 1612, 1509, 1462, 1421, 1277, 1219, 1182, 934, 837, 758, 523 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 341 nm (5.6×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 397, 377 nm; MS (EI): *m*/*z* (%): 786 (< 1) [M^+], 699 (2), 634 (1), 602 (20), 551 (8), 523 (9), 495 (4), 442 (10), 410 (61), 368 (43), 335 (18), 313 (24), 289 (21), 236 (24), 193 (38), 177 (60), 168 (62), 135 (47), 129 (33), 97 (55), 83 (64), 69 (75), 57 (90), 55 (100); HRMS (EI) ($C_{48}H_{50}O_2S_4$): calcd: 786.2694; found: 786.2687; elemental analysis calcd (%) for $C_{48}H_{50}O_2S_4$ (787.17): C 73.24, H 6.40; found: C 72.89, H 6.62.

Teraryl [2.2]cyclophane 2. To a solution of dibromide **8** (382.3 mg, 0.50 mmol) in THF (500 mL), stirred under Ar atmosphere, was added dropwise a solution of 1.8 M PhLi in cyclohexane/Et_2O (0.36 mL, 0.65 mmol) at -78 ºC and stirred for 2 h at this temperature. After quenching with water (10 mL), the solvent was evaporated. Water (30 mL) was added, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo. This crude product was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:5) to afford cyclophane **2** (229.8 mg, 76%) as white solids. M.p. 210-211 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.3 Hz, 6 H), 1.49 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.72 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.75 (t, *J* = 7.8 Hz, 4 H), 2.83 (s, 4 H), 2.89 (s, 4 H), 6.55 (d, *J* = 7.9 Hz, 4 H), 6.58 (s, 2 H), 6.68 (d, *J* = 8.0 Hz, 4 H), 7.39 (d, *J* = 7.9 Hz, 4 H), 7.42 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.7, 25.6, 32.3, 38.0, 38.2, 107.9, 123.0, 123.8, 124.9, 129.1, 129.5, 129.7, 129.8, 138.9, 139.3, 148.0, 152.2; IR (KBr): ν = 3026, 2957, 2931, 2862, 1615, 1509, 1463, 1446, 1216, 1186, 935, 915, 825, 758, 677, 549 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 316 nm (5.3 ×

10^4 mol^{-1}dm^{3}cm^{-1}); Emission ($CHCl_3$): λ_{em} = 392, 372 nm; MS (70 eV, EI): *m*/*z* (%): 604 (100) [M^+], 562 (4), 368 (2), 315 (5), 302 (34), 259 (8), 245 (6), 215 (10), 185 (5), 129 (12), 115 (14), 91 (18), 83 (19), 69 (26), 55 (32); HRMS (EI) ($C_{44}H_{44}O_2$): calcd: 604.3341; found: 604.3337; elemental analysis calcd (%) for $C_{44}H_{44}O_2$ (604.83): C 87.38, H 7.33; found: C 87.15, H 7.48.

[2.3]Thiacyclophane 9. To a dilute suspension of dibromide **8** (764.6 mg, 1.00 mmol) in absolute EtOH (1.5 L) was added $Na_2S{\cdot}9H_2O$ (288.2 mg, 1.20 mmol) and the reaction mixture was stirred at reflux temperature for overnight. After removal of the solvent, the residue was treated with CH_2Cl_2 (50 mL) and $MgSO_4$. The suspension was passed through a silica gel bed (1 cm), and the silica gel bed was washed with CH_2Cl_2 (3 × 100 mL). The combined filtrate was evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:4) to afford thiacyclophane **9** as a white solid (388.5 mg, 61%). M.p. 190-191 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.3 Hz, 6 H), 1.45 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.68 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.71 (t, *J* = 7.8 Hz, 4 H), 2.87 (s, 4 H), 3.74 (s, 4 H), 6.59 (s, 2 H), 6.67 (d, *J* = 8.2 Hz, 4 H), 6.77 (d, *J* = 8.3 Hz, 4 H), 7.40 (d, *J* = 8.2 Hz, 4 H), 7.45 (d, *J* = 8.3 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.7, 25.6, 32.2, 36.8, 37.9, 108.8, 123.1, 123.7, 125.1, 129.4, 129.5, 129.5, 129.6, 137.8, 139.0, 148.2, 151.6; IR (KBr): ν = 3028, 2959, 2931, 2864, 1614, 1510, 1494, 1463, 1216, 934, 825, 757, 677, 519 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 322 nm (6.1×10^4 mol^{-1}dm^{3}cm^{-1}); Emission ($CHCl_3$): λ_{em} = 398, 379 nm; MS (70 eV, EI): *m*/*z* (%): 636 (100) [M^+], 333 (4), 318 (12), 303 (30), 285 (4), 241 (6), 197 (3), 146 (3); HRMS (EI) ($C_{44}H_{44}O_2S$): calcd: 636.3057; found: 636.3050; elemental analysis calcd (%) for $C_{44}H_{46}O_2S$ (636.89): C 82.98, H 6.96; found: C 82.58, H 6.87.

Thiomethoxy-substituted [2.2]cyclophane 10. A solution of LDA in THF was first prepared by slowly adding a 2.5 M solution of *n*-BuLi in *n*-hexane (1.20 mL, 2.8

mmol) to a solution of di-*i*-propylamine (0.40 mL, 2.8 mmol) in THF (15 mL) at 0 ºC, and stirred for 1 h under N_2 atmosphere. This freshly prepared LDA solution was slowly introduced into a solution of **9** (1.27 g, 2.0 mmol) in THF (10 mL) at 0 ºC and stirred for 1 h. After MeI (0.25 mL, 4.0 mmol) was added at 0 ºC, the reaction mixture was slowly warmed to rt and stirred for a further 1 h. Finally, water (10 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:3) to afford **10** as a white solid (1.22 g, 94%). M.p. 194-195 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.3 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.40-1.53 (m, 4 H), 1.61-1.77 (m, 4 H), 2.04 (s, 3 H), 2.61-2.70 (m, 7 H, embodied two triplets centered at δ 2.71 (t, J = 7.8 Hz, 2 H) and 2.74 (t, J = 7.8 Hz, 2 H)), 3.07 (d, J = 8.7 Hz, 2 H), 3.24 (dd, J = 4.1, 12.4 Hz, 1 H), 3.80 (dd, J = 4.1, 10.7 Hz, 1 H), 6.50 (d, J = 8.1 Hz, 2 H), 6.55 (s, 1 H), 6.58 (s, 1 H), 6.65 (d, J = 8.1 Hz, 2 H), 6.66 (d, J = 8.1 Hz, 2 H), 6.70-7.00 (br, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.40 (d, J = 8.1 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.0, 15.1, 22.6, 22.7, 25.6, 25.7, 32.2, 32.3, 37.9, 38.0, 44.2, 54.6, 108.2, 108.5, 123.0, 123.1, 123.7, 124.2, 124.9, 125.0, 128.8 (br), 129.4, 129.5, 129.6, 129.9, 130.6, 137.1, 138.9, 139.0, 148.2, 148.4, 152.0, 152.1; IR (KBr): ν = 3028, 2959, 2930, 2863, 1613, 1508, 1463, 1445, 1216, 1185, 1103, 934, 825, 758, 555 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 318 nm (5.6×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 393, 375 nm; MS (70 eV, EI): *m*/*z* (%): 650 (100) [M^+], 603 (66), 333 (12), 325 (21), 303 (18), 241 (4), 85 (4); HRMS (EI) ($C_{45}H_{46}O_2S$): calcd: 650.3213; found: 650.3202; elemental analysis calcd (%) for $C_{45}H_{46}O_2S$ (650.92): C 83.04, H 7.12; found: C 83.06, H 7.13.

Teraryl [2.2]cyclophanene 1. Method A. A well-stirred suspension solution of **10** (650.9 mg, 1.00 mmol) in CH_2Cl_2 (30 mL) under N_2 atmosphere was treated with $Me_3O{\cdot}BF_4$ (147.9 mg, 1.00 mmol) at 0 ºC and stirred for 2 h. The reaction mixture was gradually warmed to rt and stirred for 12 h. To this clear solution was added *t*-BuOK (224.5 mg, 2.00 mmol) at rt and stirred for 30 min, followed by the addition of THF (10 mL). Stirring was allowed to continue at rt for a further 12 h. After quenching with saturated NH_4Cl (50 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:4) to afford **1** as a pale yellow solid (307.4 mg, 51%). M.p. 199-201 ºC; ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.98 (t, *J* = 7.3 Hz, 6 H), 1.47 (tq, *J* = 7.3, 7.5 Hz, 4 H), 1.70 (tt, *J* = 7.5, 7.8 Hz, 4 H), 2.74 (t, *J* = 7.8 Hz, 4 H), 2.86 (s, 4 H), 6.63 (s, 2 H), 6.69 (AA′XX′, *J* = 8.0, 0.4, 1.8, 1.8 Hz, 4 H), 6.78 (s, 2 H), 6.94 (AA′XX′, *J* = 8.0, 0.4, 1.8, 1.8 Hz, 4 H), 7.42 (d, *J* = 8.4 Hz, 8 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 14.3, 23.2, 26.1, 32.9, 38.5, 109.2, 124.0, 124.5, 125.6, 130.2, 130.3, 130.3, 130.7, 131.6, 136.8, 139.7, 149.1, 152.5; IR (KBr): ν = 3081, 3016, 2959, 2932, 2863, 1667, 1607, 1508, 1497, 1463, 1219, 1183, 1105, 1052, 934, 884, 824, 757, 678 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 325 nm (5.5×10^4 $mol^{-1}dm^3cm^{-1}$); Emission ($CHCl_3$): λ_{em} = 501 nm; MS (70 eV, EI): *m*/*z* (%): 602 (100) [M^+], 560 (5), 523 (5), 509 (3), 368 (41), 353 (9), 313 (7), 301 (32), 279 (9), 264 (19), 236 (26), 213 (12), 185 (13), 152 (14), 129 (25), 111 (35), 97 (59), 83 (71), 69 (79), 57 (94), 55 (98); HRMS (EI) ($C_{44}H_{42}O_2$): calcd: 602.3179; found: 602.3177; elemental analysis calcd (%) for $C_{44}H_{42}O_2$ (602.81): C 87.67, H 7.02; found: C 87.59, H 6.75.

Method B. A mixture of **11** (393.6 mg, 0.50 mmol) and $W(CO)_6$ (791.8 mg, 2.25 mmol) in PhCl (100 mL) was stirred at reflux for 48 h. After passing through a silica gel bed (1 cm) and washing with CH_2Cl_2 (5 × 100 mL), the combined filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:4) to afford **1** (75.4 mg, 25%) as a pale yellow solid.

3-butyl-2,5-bis(4-tolyl)furan 15. To a suspension of $LiAlH_4$ (97 mg, 2.56 mmol) in THF (10 mL) was added slowly a THF solution (10 mL) of 2,5-bis-(4-bromomethylphenyl)-3-butylfuran (591 mg, 1.28 mmol) under Ar atmosphere at 0 ºC, then stirred at rt for 2 h. The reaction was quenched by adding water (0.2 mL), 10% NaOH (0.2 mL), and water (0.2 mL) to obtain a white suspension solution. After passing through a silica gel bed (0.5 cm) and washing with Et_2O (100 mL), the filtrate was dried over $MgSO_4$, filtered, and concentrated under vacuo. The resulting oil was purified by flash column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:3) to afford **15** (358 mg, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H), 1.43 (sextet, *J* = 7.3 Hz, 2 H), 1.65 (tt, *J* = 7.3, 7.7 Hz, 2 H), 2.35 (s, 3 H), 2.37 (s, 3 H), 2.67 (t, *J* = 7.7 Hz, 3 H), 6.57 (s, 1 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.57 (d, *J* = 8.2 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.3, 22.7, 25.8, 25.9, 32.3, 108.5, 123.4, 123.7, 125.6, 128.4, 129.3, 129.4, 129.5, 136.6, 137.0, 147.9, 160.0; MS (FAB): *m*/*z* (%): 304 (100) [M^+], 290 (5), 261 (12), 218 (5); HR-MS (EI) ($C_{22}H_{24}O$): calcd: 304.1827; found: 304.1828.

Photophysical measurement. The absorption and emission spectra were measured at ambient temperature in $CHCl_3$. The fluorescence quantum yields were obtained by comparing the integrated intensity of the unknown sample to that of a reference Coumarin 1 fluorescent standard (Φ_f = 0.99 in EtOAc). The quantum yield of the unknown sample was calculated by the following equation:

$$\Phi_s = \Phi_{ref} \times (I_s / I_{ref}) \times (A_{ref} / A_s) \times (n_s / n_{ref})^2$$

Where Φ is the quantum yield, *I* is the integrated intensity, A is the absorbance at the excitation wavelength, and *n* is the refractive index. The subscript *s* refers to the unknown sample, and *ref* refers to the reference fluorophore of known quantum yield.

Variable temperature NMR spectra. Dynamic ^{1}H NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer. The free energy barrier ($\Delta G_c^{\neq}$) was calculated by the following equation:

$$\Delta G_c^{\neq} = 4.58 \times T_c \times \left(10.32 + \log \frac{T_c}{k_c}\right), \text{ Where } \; k_c = \frac{\pi \cdot \Delta \nu}{\sqrt{2}} = 2.22 \times \Delta \nu$$

Where, T_c is the coalescence temperature in K, k_c is the rate constant of coalescence, and $\Delta\nu$ is the frequency difference of two exchange signals. Since the exact $\Delta\nu$ can not be determined up to -95 ^{o}C, $\Delta G_c^{\neq}$ can only be estimated in this study.

Electrochemical measurements. An EG&G (PAR 273A) potentiostat/galvanostat was used to control the potential applied to the working electrode. A conventional three-electrode configuration was used for cyclic voltammetry experiments. A glassy carbon electrode with an area of 7.065×10^{-2} cm^2 (1.5 mm diameter), a Pt wire, and a Ag/Ag$^+$ (0.1 M $AgNO_3$) electrode were used as the working, counter, and reference electrode, respectively. The potentials reported were corrected with the reference to ferrocene ($E_{1/2}$ = 0.037 V).