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 N₂ atmosphere, was slowly added a solution of 2.5 M *n*-BuLi in *n*-hexane (180.0 mL, 0.45 mol) at -78 °C. The reaction mixture was warmed to rt and stirred for 1 h. After cooling to -78 °C, 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 °C, then slowly warmed to rt and further stirred for 2 h. The mixture was quenched with saturated NH₄Cl (500 mL), and the organic layer was separated. The aqueous layer was extracted with Et₂O (3 × 300 mL). The combined organic extracts were dried (MgSO₄), filtered, and evaporated in vacuo to afford the crude ynol (106.40 g, 96%) as an orange oil. Kugelrohr distillation (0.01 torr, 130 °C) afforded the propargyl alcohol as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 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); ¹³C NMR (100 MHz, CDCl₃): 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) (C₁₅H₁₈O₃): calcd: 246.1256; found: 246.1267; elemental analysis calcd (%) for C₁₅H₁₈O₃

(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 °C) afforded propargylic ketone as a colorless oil. ^1H 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) ($\text{C}_{15}\text{H}_{16}\text{O}_3$): calcd: 244.1099; found: 244.1092; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{16}\text{O}_3$ (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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (66.4 mL, 0.53 mol) and 1,2-ethanedithiol (37.8 mL, 0.45 mol) at -78 °C. 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, CH₂Cl₂/*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 °C; ¹H NMR (400 MHz, CDCl₃): δ = 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); ¹³C NMR (100 MHz, CDCl₃): δ = 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): ν = 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) (C₁₇H₂₀O₂S₂): calcd: 320.0905; found: 320.0910; elemental analysis calcd (%) for C₁₇H₂₀O₂S₂ (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 °C 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 °C, 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 NH₄Cl (100 mL), and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2 × 100 mL). The combined organic layer was dried (MgSO₄), filtered, and evaporated in vacuo. The resulting residue was suspended in Et₂O (6 mL) and stirred. The solid **6** was filtered, washed with a mixture of Et₂O/pentane (1:1), and collected as a fluorescent yellow powder (4.52 g, 65%). M.p. 196-197 °C; ¹H NMR (400 MHz, CDCl₃): δ = 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): $\delta = 14.0, 22.6, 25.7, 32.1, 37.5, 52.1, 111.5, 123.1, 124.0, 125.8, 128.2, 128.8, 129.2, 130.1, 134.8, 140.8, 149.3, 150.6, 166.9$; IR (KBr): $\nu = 3027, 2958, 2932, 2864, 1720, 1612, 1510, 1437, 1281, 1177, 1109, 934, 831, 772, 700, 670\text{ cm}^{-1}$; UV/Vis (CHCl_3): $\lambda_{\text{max}} (\epsilon) = 360\text{ nm}$ ($7.6 \times 10^4\text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); Emission (CHCl_3): $\lambda_{\text{em}} = 430\text{ nm}$; 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) ($\text{C}_{46}\text{H}_{46}\text{O}_6$): calcd: 694.3294; found: 694.3298; elemental analysis calcd (%) for $\text{C}_{46}\text{H}_{46}\text{O}_6$ (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 °C 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 $\times$ 200 mL), the combined filtrate was evaporated in vacuo. Water (200 mL) was added to the residue and extracted with CH_2Cl_2 (4 $\times$ 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 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.95$ (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): $\delta = 14.0, 22.6, 25.7, 32.1, 37.5, 65.2, 109.2, 123.6, 123.8, 125.5, 127.4, 128.7, 129.5, 130.3, 139.6, 140.3, 148.1, 151.4$; IR (KBr): $\nu = 3338$,

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 ($6.3 \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); 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) ($\text{C}_{44}\text{H}_{46}\text{O}_4$): calcd: 638.3396; found: 638.3364; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{46}\text{O}_4$ (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 $^\circ\text{C}$ (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 ($5.8 \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); 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 $^+$) ($\text{C}_{44}\text{H}_{44}^{79}\text{Br}_2\text{O}_2$): calcd: 762.1707; found: 762.1687; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{44}\text{Br}_2\text{O}_2$ (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 MnO₂ (2.09 g, 24.00 mol) in CH₂Cl₂ (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 CH₂Cl₂ (5 × 120 mL), the combined filtrate was evaporated in vacuo. The resulting residue was recrystallized from Et₂O and CH₂Cl₂, to afford the dialdehyde **12** as a fluorescent yellow solid (1.21 g, 95%). M.p. 155-157 °C; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 (CHCl₃): λ_{max} (ε) = 379 nm (5.9 × 10⁴ mol⁻¹dm³cm⁻¹); Emission (CHCl₃): 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) (C₄₄H₄₂O₄): calcd: 634.3078; found: 634.3036; elemental analysis calcd (%) for C₄₄H₄₂O₄ (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), BF₃·Et₂O (0.25 mL, 2.20 mmol) and 1,2-ethanedithiol (0.20 mL, 2.00 mmol) in CH₂Cl₂ (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 CH₂Cl₂ (3 × 30 mL). The combined organic layer was washed with 10% NaOH (5 × 100 mL), then dried (MgSO₄), filtered, and evaporated in vacuo. The resulting residue was recrystallized from Et₂O and CH₂Cl₂, to afford **11** as a yellow solid (724.2 mg, 92%). M.p. 177-179 °C; ¹H NMR (400 MHz, CDCl₃): 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): $\delta = 14.0, 22.6, 25.7, 32.1, 37.5, 40.3, 56.2, 109.5, 123.6, 123.7, 125.6, 128.3, 128.7, 129.5, 130.7, 138.9, 140.4, 148.2, 151.3$; IR (KBr): $\nu = 3027, 2959, 2930, 2863, 1612, 1509, 1462, 1421, 1277, 1219, 1182, 934, 837, 758, 523\text{ cm}^{-1}$; UV/Vis (CHCl_3): $\lambda_{\text{max}} (\epsilon) = 341\text{ nm}$ ($5.6 \times 10^4\text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); Emission (CHCl_3): $\lambda_{\text{em}} = 397, 377\text{ nm}$; 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) ($\text{C}_{48}\text{H}_{50}\text{O}_2\text{S}_4$): calcd: 786.2694; found: 786.2687; elemental analysis calcd (%) for $\text{C}_{48}\text{H}_{50}\text{O}_2\text{S}_4$ (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/Et₂O (0.36 mL, 0.65 mmol) at -78 °C 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 $\times$ 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, $\text{CH}_2\text{Cl}_2/n$ -hexane 1:5) to afford cyclophane **2** (229.8 mg, 76%) as white solids. M.p. 210-211 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.00$ (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): $\delta = 14.0, 22.7, 25.6, 32.3, 38.0, 38.2, 107.9, 123.0, 123.8, 124.9, 129.1, 129.5, 129.7, 129.8, 138.9, 139.3, 148.0, 152.2$; IR (KBr): $\nu = 3026, 2957, 2931, 2862, 1615, 1509, 1463, 1446, 1216, 1186, 935, 915, 825, 758, 677, 549\text{ cm}^{-1}$; UV/Vis (CHCl_3): $\lambda_{\text{max}} (\epsilon) = 316\text{ nm}$ ($5.3 \times$

$10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); Emission (CHCl_3): $\lambda_{\text{em}} = 392, 372 \text{ nm}$; 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) ($\text{C}_{44}\text{H}_{44}\text{O}_2$): calcd: 604.3341; found: 604.3337; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{44}\text{O}_2$ (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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (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 ($3 \times 100 \text{ mL}$). The combined filtrate was evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 1:4) to afford thiacyclophane **9** as a white solid (388.5 mg, 61%). M.p. 190-191 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.96$ (t, $J = 7.3 \text{ Hz}$, 6 H), 1.45 (tq, $J = 7.3, 7.5 \text{ Hz}$, 4 H), 1.68 (tt, $J = 7.5, 7.8 \text{ Hz}$, 4 H), 2.71 (t, $J = 7.8 \text{ Hz}$, 4 H), 2.87 (s, 4 H), 3.74 (s, 4 H), 6.59 (s, 2 H), 6.67 (d, $J = 8.2 \text{ Hz}$, 4 H), 6.77 (d, $J = 8.3 \text{ Hz}$, 4 H), 7.40 (d, $J = 8.2 \text{ Hz}$, 4 H), 7.45 (d, $J = 8.3 \text{ Hz}$, 4 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.0, 22.7, 25.6, 32.2, 36.8, 37.9, 108.8, 123.1, 123.7, 125.1, 129.4, 129.5, 129.5, 129.6, 137.8, 139.0, 148.2, 151.6$; IR (KBr): $\nu = 3028, 2959, 2931, 2864, 1614, 1510, 1494, 1463, 1216, 934, 825, 757, 677, 519 \text{ cm}^{-1}$; UV/Vis (CHCl_3): $\lambda_{\text{max}} (\epsilon) = 322 \text{ nm}$ ($6.1 \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$); Emission (CHCl_3): $\lambda_{\text{em}} = 398, 379 \text{ nm}$; 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) ($\text{C}_{44}\text{H}_{44}\text{O}_2\text{S}$): calcd: 636.3057; found: 636.3050; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{46}\text{O}_2\text{S}$ (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 °C, and stirred for 1 h under N₂ 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 °C and stirred for 1 h. After MeI (0.25 mL, 4.0 mmol) was added at 0 °C, 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 CH₂Cl₂ (3 × 20 mL). The combined organic layer was dried (MgSO₄), filtered, and evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH₂Cl₂/*n*-hexane 1:3) to afford **10** as a white solid (1.22 g, 94%). M.p. 194-195 °C; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 (CHCl₃): λ_{max} (ε) = 318 nm (5.6 × 10⁴ mol⁻¹dm³cm⁻¹); Emission (CHCl₃): 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) (C₄₅H₄₆O₂S): calcd: 650.3213; found: 650.3202; elemental analysis calcd (%) for C₄₅H₄₆O₂S (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 CH₂Cl₂ (30 mL) under N₂ atmosphere was treated

with Me₃O·BF₄ (147.9 mg, 1.00 mmol) at 0 °C 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 NH₄Cl (50 mL), the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layer was dried (MgSO₄), filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, CH₂Cl₂/*n*-hexane 1:4) to afford **1** as a pale yellow solid (307.4 mg, 51%). M.p. 199-201 °C; ¹H NMR (400 MHz, CD₂Cl₂): 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); ¹³C NMR (100 MHz, CD₂Cl₂): 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 (CHCl₃): λ_{max} (ε) = 325 nm (5.5 × 10⁴ mol⁻¹dm³cm⁻¹); Emission (CHCl₃): 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) (C₄₄H₄₂O₂): calcd: 602.3179; found: 602.3177; elemental analysis calcd (%) for C₄₄H₄₂O₂ (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 CH₂Cl₂ (5 × 100 mL), the combined filtrate was evaporated in vacuo. The residue was purified by flash column chromatography

(silica gel, CH₂Cl₂/*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 LiAlH₄ (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 °C, 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 Et₂O (100 mL), the filtrate was dried over MgSO₄, filtered, and concentrated under vacuo. The resulting oil was purified by flash column chromatography (silica gel, CH₂Cl₂/*n*-hexane 1:3) to afford **15** (358 mg, 92%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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) (C₂₂H₂₄O): calcd: 304.1827; found: 304.1828.

Photophysical measurement. The absorption and emission spectra were measured at ambient temperature in CHCl₃. 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 ^1H NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer. The free energy barrier ($\Delta G_c^\ddagger$) was calculated by the following equation:

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

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°C , $\Delta G_c^\ddagger$ 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 $7.065 \times 10^{-2} \text{ cm}^2$ (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 ($E_{1/2} = 0.037 \text{ V}$).