Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Synthesis and Properties of Open-Cage Fullerene C_{60} Derivatives: Impact of the Extended π-Conjugation

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1. General

Melting points were determined on a Yanaco MP-500D apparatus. The ^{1}H and ^{13}C NMR measurements were carried out at room temperature with Varian MERCURY 300 and JEOL JNM ECA500 instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.00 ppm in ^{13}C NMR), CD_2Cl_2 (δ 5.32 ppm in ^{1}H NMR), and C_6D_6 (δ 7.15 ppm in ^{1}H NMR, δ 128.00 ppm in ^{13}C NMR). APCI mass spectra were measured on JEOL MStation JMS-700 and Bruker micrOTOF-Q II. UV-vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Cyclic voltammetry was conducted on a BAS Electrochemical Analyzer ALS620C using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out under N_2 atmosphere using benzonitrile solutions of 1.0 mM samples and 0.10 M tetrabutylammonium tetrafluoroborate (*n*-$Bu_4N{\cdot}BF_4$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene used as an internal standard which was added after each measurement. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (two directly connected columns; 250 mm in length, 20 mm in inner diameter) for preparative purpose. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B or PSQ 100B (Fuji Silysia).

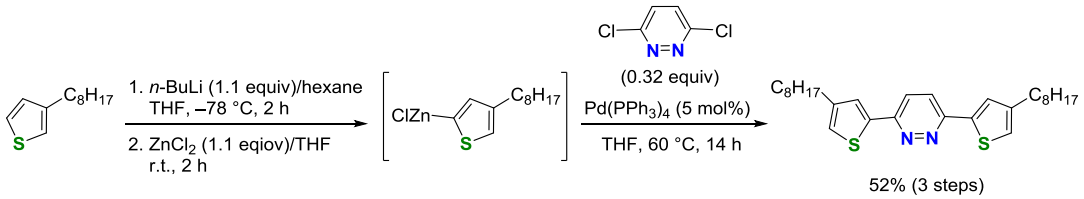
All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification.

2. Computational Methods

All calculations were conducted using the Gaussian 09 program. For calculations of HOMO-LUMO energy levels, the structures were optimized at the B3LYP/6-31G(d) level of theory without any symmetry assumptions. Using these optimized geometries, TD DFT calculations were carried out at the CAM-B3LYP/6-31G(d) level of theory. NICS(0) values were calculated at the HF/6-311G(d,p) level of theory. All structures at the stationary and transition states were confirmed by the frequency analyses at the same level of theory.

3. Synthesis of Pyridazine Derivatives

3.1. Synthesis of 3,6-Bis(4'-*n*-octylthiophen-2'-yl)pyridazine



To the solution of 3-octylthiophene (5.00 g, 25.0 mmol) in THF (25 mL), *n*-butyllithium (16.7 mL of a 1.6 M solution in hexane, 26.7 mmol, 1.1 equiv) was slowly added at −78 °C. The solution was stirred at −78 °C for 2 h. Then, $ZnCl_2$ (3.75 g, 28.0 mmol, 1.1 equiv) in THF (15 mL) was slowly added into the flask at −78 °C. After stirred at −78 °C for 10 min, the reaction mixture was allowed to warm up to room temperature for 2 h. To the resulting mixture, 3,6-dichloropyridazine (1.19 g, 7.99 mmol, 0.32 equiv vs. 3-octylthiophene) and $Pd(PPh_3)_4$ (462 mg, 400 μmol, 5 mol% vs. 3,6-dichloropyridazine) were added at room temperature. After stirred at 60 °C for 14 h, the reaction mixture was quenched with distilled water and extracted with $CHCl_3$. The organic layer was collected and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography ($CHCl_3$/hexane (7:1)) afforded 3,6-bis(4'-*n*-octylthiophen-2'-yl)pyridazine as yellow powder (3.03 g, 6.46 mmol, 52% based on 3-octylthiophene).

3,6-bis(4'-*n*-octylthiophen-2'-yl)pyridazine: mp. 110.3−111.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 2H, vinyl), 7.51 (d, J = 1.2 Hz, 2H, thienyl), 7.08 (s, 2H, thienyl), 2.64 (t, J = 7.7 Hz, 4H, CH_2), 1.71−1.63 (m, 4H, CH_2), 1.38−1.31 (m, 20H, CH_2), 0.88 (t, J = 6.5 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.47, 144.62, 140.45, 127.42, 124.20, 122.48, 32.09, 30.72, 30.67, 29.64, 29.50, 29.47, 22.88, 14.32; HRMS (EI, positive ion mode) calcd for $C_{28}H_{40}N_2S_2$ ($M^{\bullet+}$) 468.2633, found 468.2633.

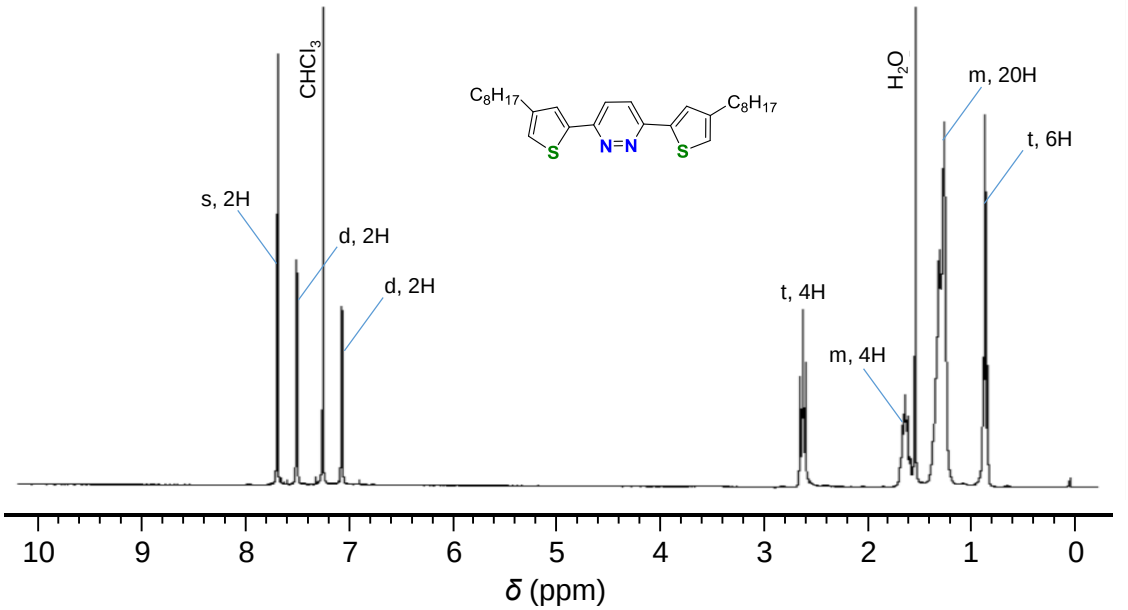


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3,6-bis(4'-*n*-octylthiophen-2'-yl)pyridazine.

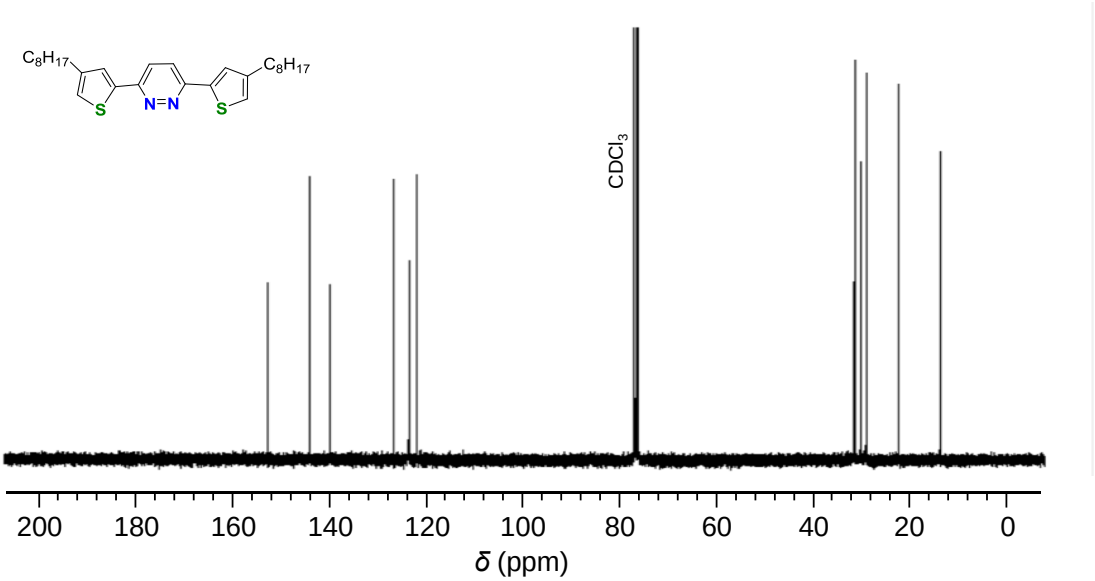
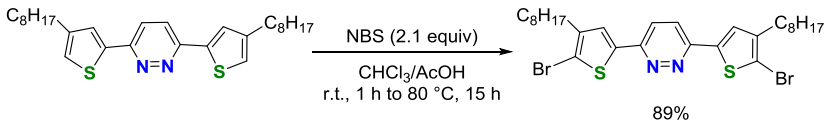


Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 3,6-bis(4'-*n*-octylthiophen-2'-yl)pyridazine.

3.2. Synthesis of 3,6-Bis(5’-bromo-4’-*n*-octylthiophen-2’-yl)pyridazine



To the solution of 3,6-bis(4’-*n*-octylthiophen-2’-yl)pyridazine (1.52 g, 3.20 mmol) in $CHCl_3$ (50 mL) and acetic acid (50 mL), *N*-bromosuccinimide (1.16 g, 6.56 mmol, 2.1 equiv) was added at room temperature. The solution was stirred at room temperature under dark for 1 h and then heated at 80 °C for 15 h. After reaction, the resulting mixture was poured into the distilled water and extracted with $CHCl_3$. The organic layer was washed with sat. $NaHCO_3$ aq. and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography ($CHCl_3$/hexane (3:2)) gave 3,6-bis(5’-bromo-4’-*n*-octylthiophen-2’-yl)pyridazine as white powder (1.79 g, 2.86 mmol, 89%).

3,6-bis(5’-bromo-4’-*n*-octylthiophen-2’-yl)pyridazine: mp. 80.8−81.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H, phenyl), 7.33 (s, 2H, thienyl), 2.59 (t, J = 7.4 Hz, 4H,CH_2), 1.65−1.57 (m, 4H, CH_2), 1.33−1.28 (m, 20H, CH_2), 0.88 (t, J = 6.5 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.90, 143.55, 139.94, 126.84, 121.96, 114.30, 32.08, 29.87, 29.59, 29.45, 22.88, 14.35; HRMS (APCI, negative ion mode) calcd for $C_{28}H_{38}N_2S_2Br_2$ ($M^{\bullet-}$) 624.0849 found 624.0825.

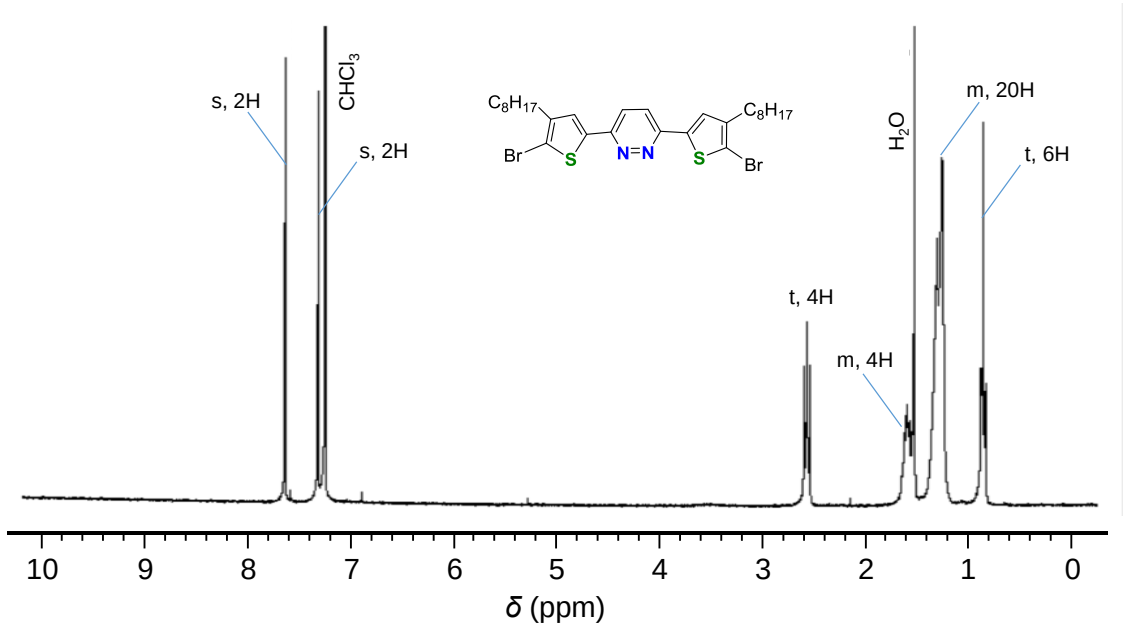


Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3,6-bis(5'-bromo-4'-*n*-octylthiophen-2'-yl)pyridazine.

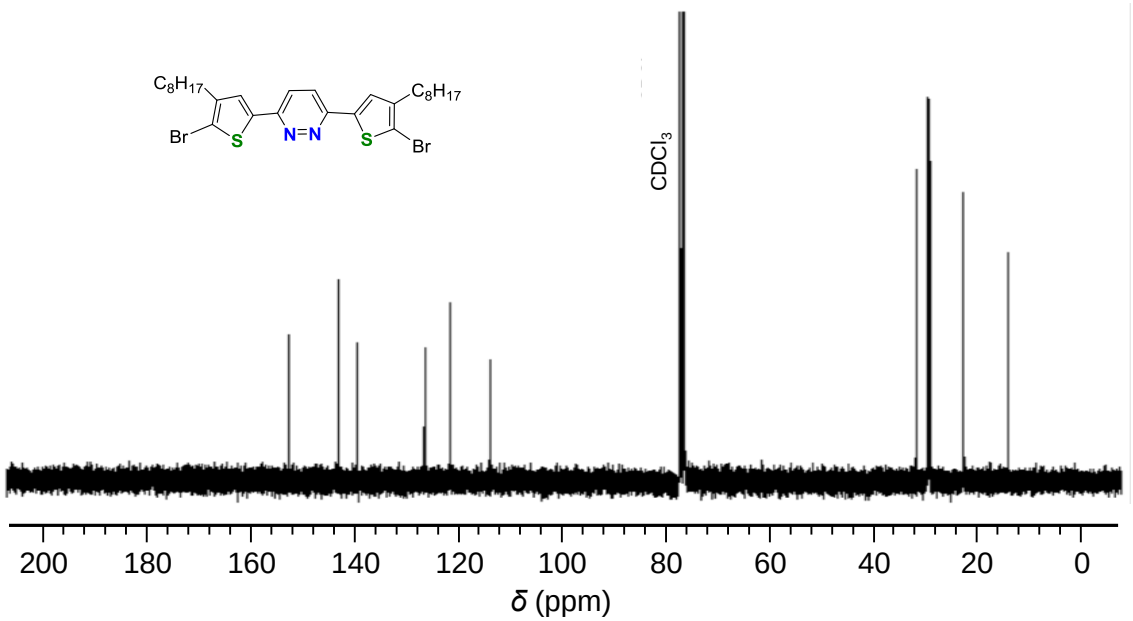
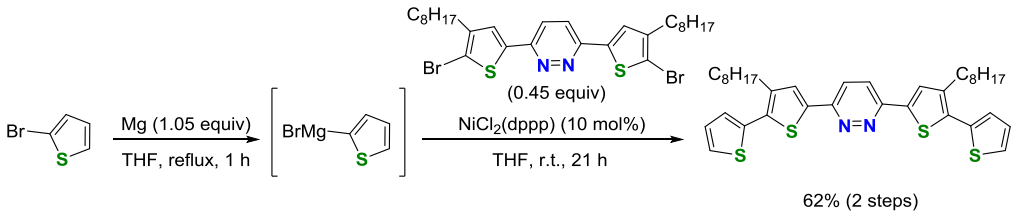


Figure S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 3,6-bis(5'-bromo-4'-*n*-octylthiophen-2'-yl)pyridazine.

3.3. Synthesis of 3,6-Bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine



2-Bromothiophene (5.18 g, 31.7 mmol) was added to magnesium turnings (810 mg, 33.3 mmol, 1.05 equiv) in THF (30 mL). The reaction mixture was heated at reflux temperature for 1 h. The thus obtained Grignard reagent was added dropwisely into another flask containing 3,6-bis(5'-bromo-4'-*n*-octylthiophen-2'-yl)pyridazine (9.04 g, 14.4 mmol, 0.45 equiv vs. 2-bromothiophene) and diphenylphosphinopropane nickel (II) chloride (781 mg, 144 μmol, 10 mol% vs. 3,6-bis(5'-bromo-4'-*n*-octylthiophen-2'-yl)pyridazine) in THF (100 mL). The reaction mixture was stirred at room temperature for 21 h. After reaction, the resulting mixture was poured into distilled water and extracted with $CHCl_3$. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography ($CHCl_3$/hexane (3:2)) gave 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine as yellow powder (6.22 g, 9.83 mmol, 62% based on 2-bromothiophene).

3,6-bis(3'-n-octyl-[2',2''-bithiophen]-5'-yl)pyridazine: mp. 96.0−96.8 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.75 (s, 2H, phenyl), 7.52 (s, 2H, thienyl), 7.40 (d, J = 5.1 Hz, 2H, thienyl), 7.27 (d, J = 3.5 Hz, 2H, thienyl), 7.12 (dd, J = 3.6 Hz, 4H,CH_2), 2.81 (t, J = 7.5 Hz, 4H,CH_2), 1.73−1.65 (m, 4H, CH_2), 1.41−1.29 (m, 20H, CH_2), 0.88 (t, J = 6.7 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.00, 140.58, 137.92, 136.04, 134.79, 128.93, 127.76, 126.55, 126.07, 122.11, 32.08, 30.73, 29.77, 29.62, 29.47, 22.88, 14.35; HRMS (APCI, negative ion mode) calcd for $C_{36}H_{44}N_2S_4$ ($M^{\bullet-}$) 632.2393, found 632.2392.

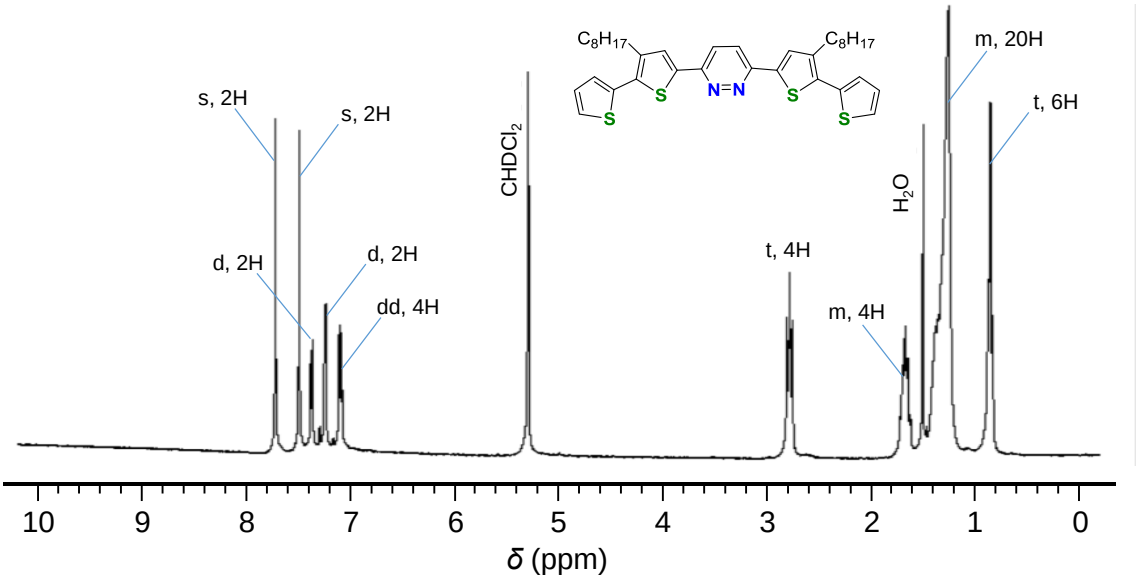


Figure S5. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine.

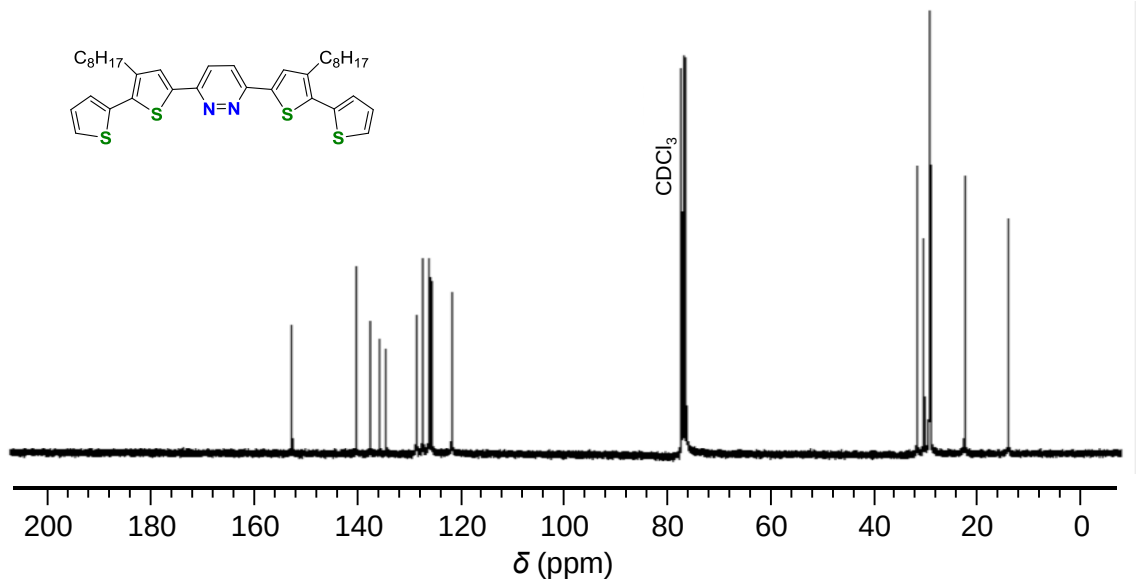
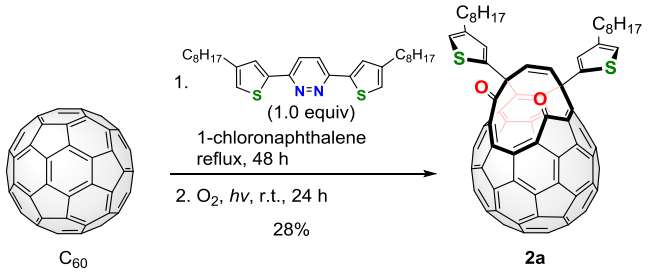


Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine.

4. Synthesis of Open-Cage C_{60} Derivatives

4.1. Synthesis of Asymmetric Diketo Derivative 2a



The solution of C_{60} (541 mg, 0.751 mmol) and 3,6-bis(4'-*n*-octylthiophen-2'-yl)pyridazine (355 mg, 0.757 mmol, 1.0 equiv) in 1-chloronaphthalene (25 mL) was refluxed at 255 °C for 48 h. After the resulting solution was diluted with CS_2 (50 mL) and bubbled with O_2 for 15 min, the reaction mixture was irradiated by a xenon-lamp (500 W) from a distance of 30 cm for 24 h. The chromatographic purification using silica gel column chromatography (toluene/hexane (1:1)) gave **2a** as dark brown solids (241 mg, 0.208 mmol, 28%).

2a: mp. 120.7−127.5 °C; IR (KBr) ν = 1690, 1746 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1H, thienyl), 7.00 (d, J = 9.9 Hz, 1H, vinyl), 6.97 (s, 1H, thienyl), 6.91 (d, J = 9.9 Hz, 1H, vinyl), 6.90 (s, 2H, thienyl), 2.59−2.53 (m, 4H, CH_2), 1.60−1.51 (m, 4H, CH_2), 1.28−1.26 (m, 20H, CH_3), 0.89−0.84 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.20, 191.56, 153.40, 153.32, 150.26, 148.98, 148.46, 148.13, 148.03, 147.61, 147.16, 146.61, 146.43, 146.28, 146.15, 146.05, 145.97, 145.85, 145.58, 145.31, 145.08, 145.04, 144.87, 144.62, 144.30, 144.12, 143.65, 143.22, 142.88, 142.81, 142.56, 142.31, 142.25, 141.84, 141.32, 140.97, 140.59, 140.14, 139.92, 139.71, 139.11, 138.68, 137.77, 137.51, 136.56, 136.35, 135.71, 134.44, 133.58, 132.59, 132.18, 131.97, 131.50, 130.92, 130.70, 129.46, 127.22, 120.94, 120.39, 55.78, 49.41, 32.08, 30.86, 30.72, 30.40, 29.63, 29.55, 29.49, 22.90, 14.36; HRMS (FAB, positive ion mode) calcd for $C_{88}H_{40}O_2S_2$ ($M+H^+$) 1193.2550, found 1193.2546.

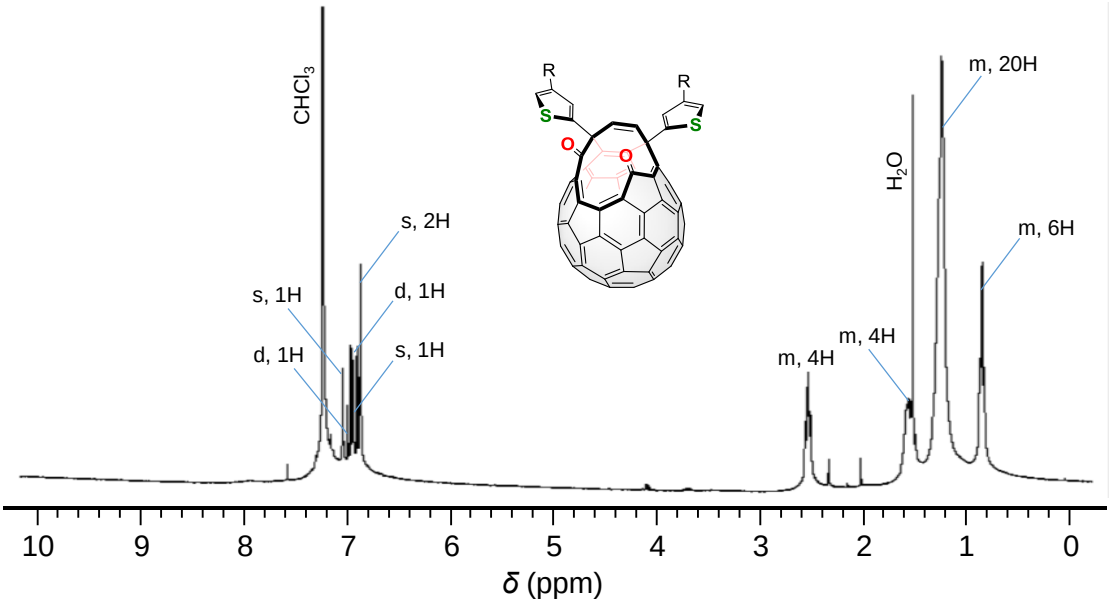


Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2a**.

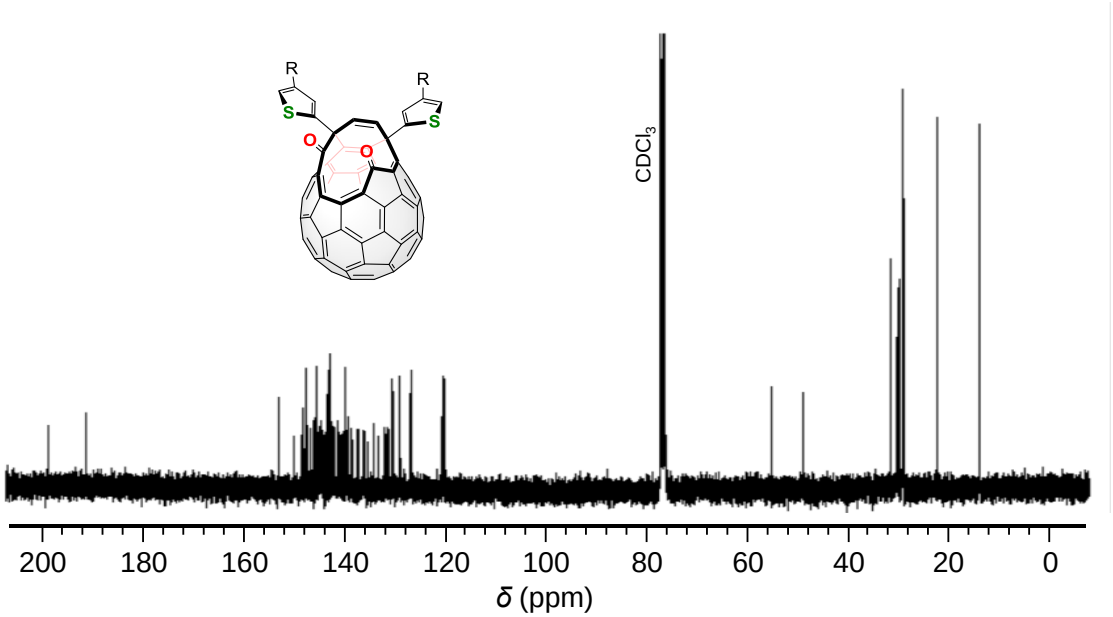


Figure S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2a**.

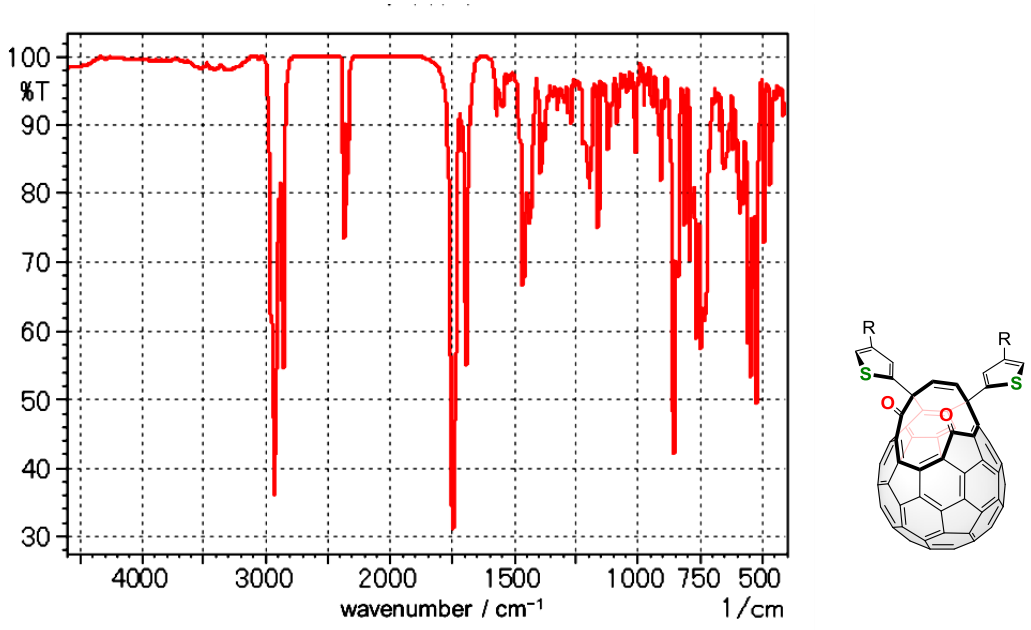
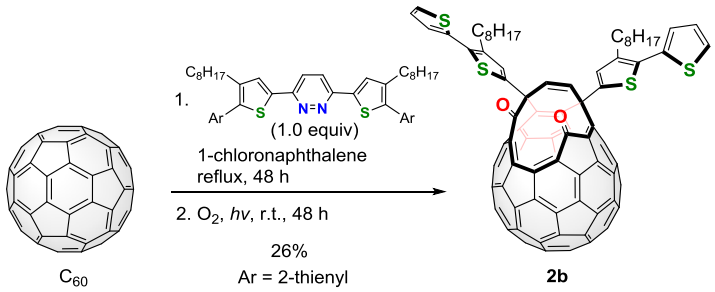


Figure S9. IR spectrum (KBr) of **2a**.

4.2. Synthesis of Asymmetric Diketo Derivative 2b



The solution of C_{60} (2.00 g, 2.78 mmol) and 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine (1.76 g, 2.78 mmol, 1.0 equiv) in 1-chloronaphthalene (100 mL) was refluxed at 255 °C for 48 h. After the resulting solution was diluted with toluene (200 mL) and bubbled with O_2 for 15 min, the reaction mixture was irradiated by a LED lamp from a distance of 10 cm for 48 h. The chromatographic purification using silica gel column chromatography (toluene/hexane (1:1)) gave **2b** as dark brown solids (948 mg, 0.715 mmol, 26%).

2b: mp. 148.1−155.8 °C (decomp.); IR (KBr) ν = 1692, 1746 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.27 (m, 2H, thienyl), 7.10−7.09 (m, 3H, thienyl), 7.06 (d, J = 9.9 Hz, 1H, vinyl), 7.04−7.01 (m, 2H, thienyl), 6.97 (d, J = 9.8 Hz, 1H, vinyl), 6.97 (s, 1H, thienyl), 2.75−2.67 (m, 4H, CH_2), 1.62−1.55 (m, 4H, CH_2), 1.25−1.22 (m, 20H, CH_3), 0.90−0.83 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.87, 191.55, 152.96, 151.48, 150.24, 148.96, 148.12, 148.00, 147.85, 147.59, 147.13, 146.61, 146.48, 146.36, 146.28, 146.11, 146.03, 145.99, 145.93, 145.85, 145.57, 145.32, 145.03, 144.87, 144.62, 144.26, 144.11, 143.19, 142.86, 142.82, 142.57, 142.34, 142.28, 141.84, 141.36, 140.92, 140.56, 140.31, 140.20, 140.16, 139.88, 139.83, 139.75, 139.35, 139.25, 138.73, 137.68, 137.50, 136.59, 136.29, 135.77, 135.72, 134.16, 133.58, 132.47, 132.04, 131.89, 131.81, 131.46, 130.95, 130.83, 128.69, 127.60, 126.55, 126.40, 125.90, 125.78, 55.66, 49.35, 32.09, 32.06, 30.78, 30.71, 29.80, 29.70, 29.62, 29.52, 29.50, 22.9, 14.38; HRMS (APCI, negative ion mode) calcd for $C_{96}H_{44}O_2S_4$ ($M^{\bullet-}$) 1356.2230, found 1356.2210.

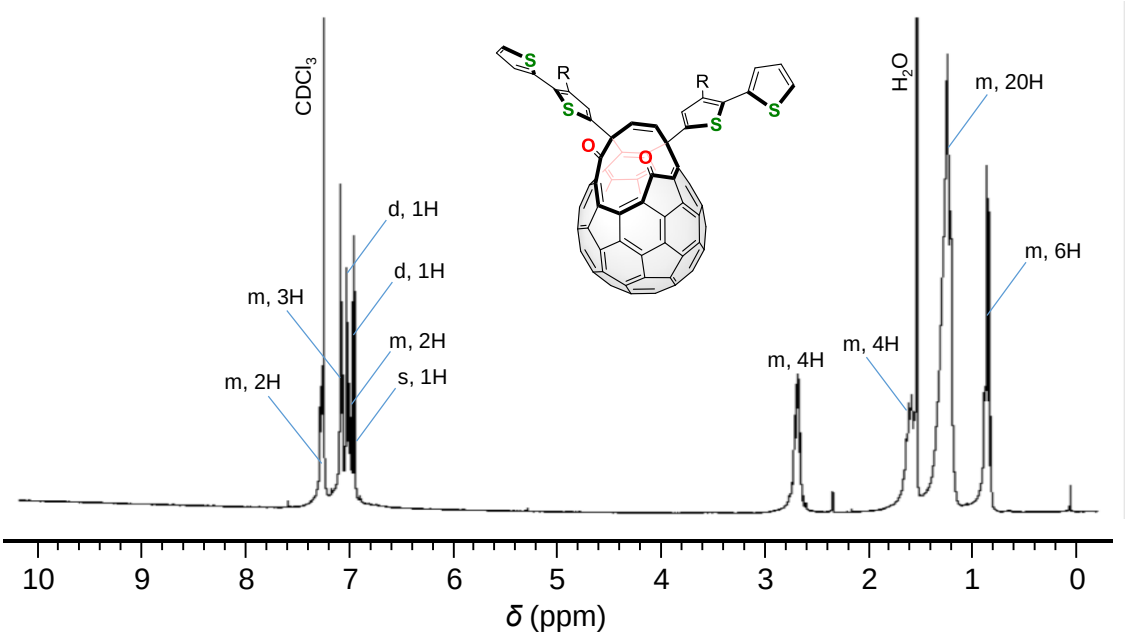


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2b**.

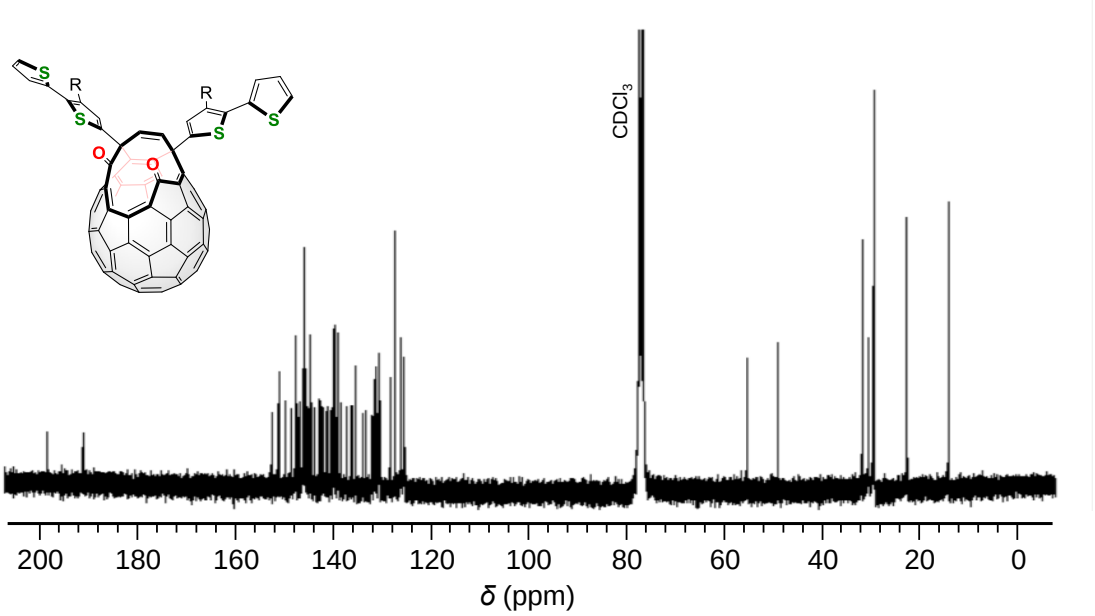


Figure S11. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2b**.

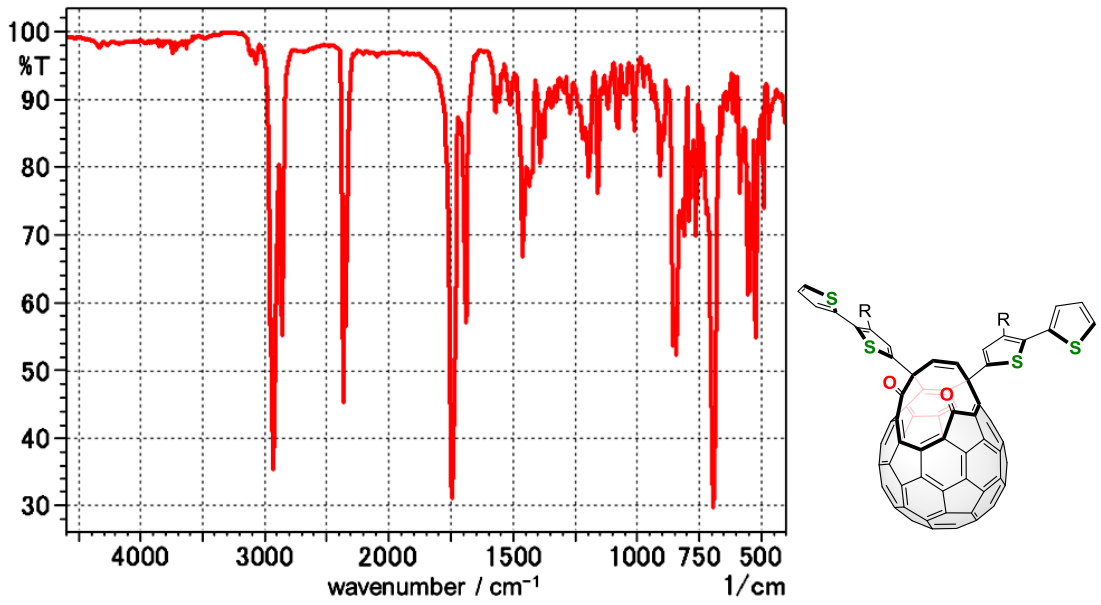
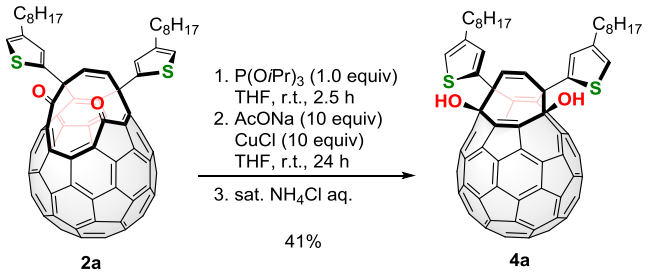


Figure S12. IR spectrum (KBr) of **2b**.

4.3. Synthesis of Diol Derivative 4a



To the solution of **2a** (200 mg, 0.172 mmol) in THF (16 mL), triisopropyl phosphite (41.3 μL, 0.179 mmol, 1.0 equiv) was added and the resulting solution was stirred at room temperature for 2.5 h. The reaction progress was monitored by HPLC equipped with the Buckyprep column using toluene as eluent at 30 °C and epoxy intermediate **3a** was eluted at 3.68 min while **2a** was detected at 4.71 min. To this reaction mixture, the solution of copper chloride (168 mg, 1.70 mmol, 9.9 equiv) and sodium acetate (138 mg, 0.168 mmol, 9.8 equiv) in THF (80 mL) was slowly added at room temperature over 1 h. The reaction mixture was further stirred at room temperature for 24 h. After reaction, the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with toluene. The organic layer was collected and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography (toluene) gave **4a** as dark brown solids (83.0 mg, 0.0713 mmol, 41%).

4a: mp. 121.5−128.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 1.2 Hz, 2H, thienyl), 6.95 (s, 4H, vinyl, thienyl), 4.53 (s, 2H, alcohol), 2.58 (t, J = 7.8 Hz, 4H, CH_2), 1.58 (m, 4H, CH_2), 1.27−1.24 (m, 20H, CH_3), 0.86 (t, J = 6.6 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.54, 148.40, 147.73, 147.12, 146.83, 146.13, 145.65, 145.33, 145.26, 145.23, 144.93, 144.74, 144.61, 144.36, 144.16, 143.77, 143.39, 143.33, 143.10, 142.89, 142.16, 141.82, 140.97, 140.65, 139.38, 139.05, 138.94, 138.76, 138.25, 136.78, 135.06, 132.78, 131.64, 130.56, 121.03, 88.73, 49.72, 32.10, 30.77, 30.47, 29.66, 29.61, 29.53, 22.90, 14.36; HRMS (FAB, positive ion mode) calcd for $C_{88}H_{42}O_2S_2$ ($M+H^+$) 1195.2706, found 1195.2709.

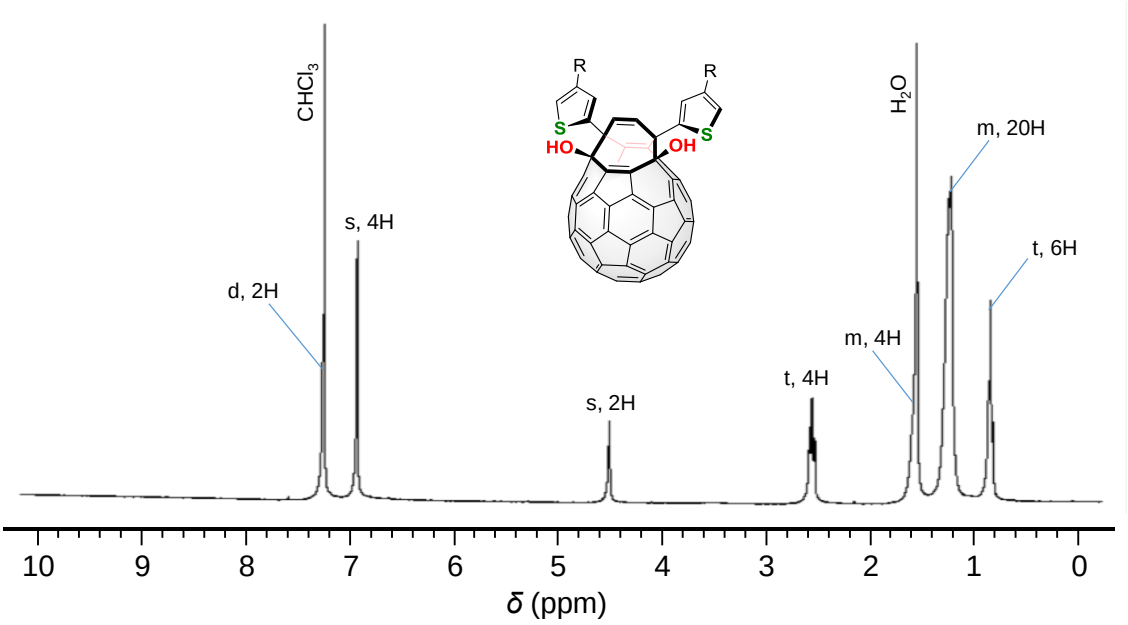


Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4a**.

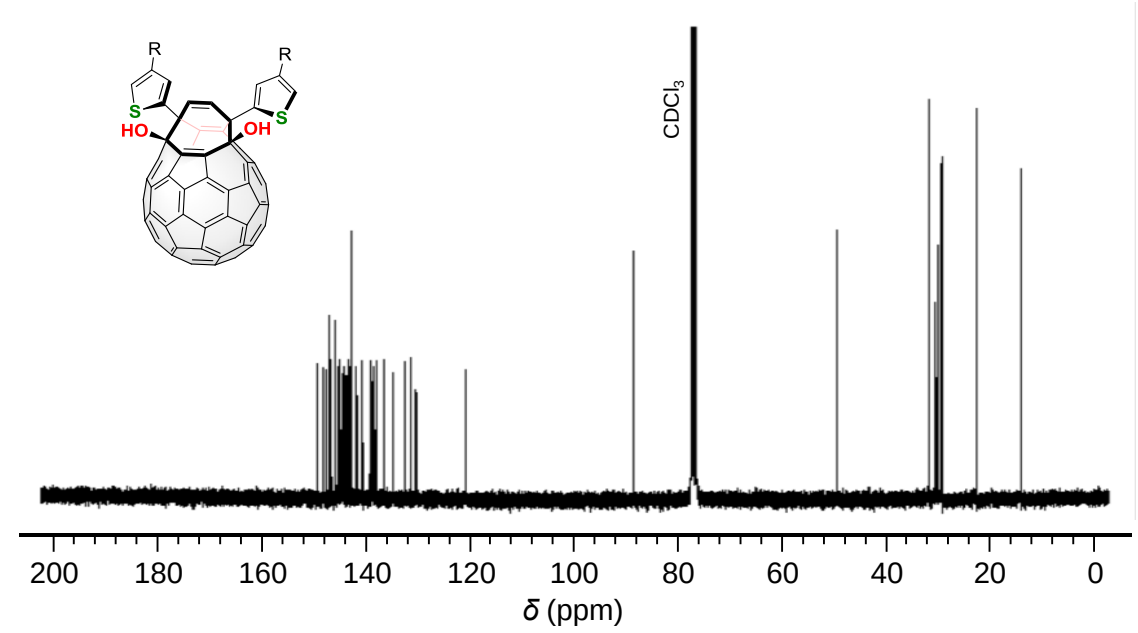
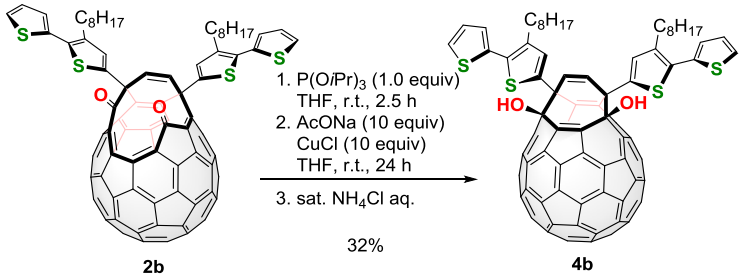


Figure S14. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4a**.

4.4. Synthesis of Diol Derivative 4b



To the solution of **2b** (38.8 mg, 0.0286 mmol) in THF (10 mL), triisopropyl phosphite (7.2 μL, 0.029 mmol, 1.0 equiv) was added and the resulting solution was stirred at room temperature for 2.5 h. To this reaction mixture, the solution of copper chloride (28.7 mg, 0.290 mmol, 10 equiv) and sodium acetate (23.8 mg, 0.290 mmol, 10 equiv) in THF (16 mL) was slowly added at room temperature over 1 h. The reaction mixture was further stirred at room temperature for 24 h. After reaction, the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with toluene. The organic layer was collected and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography (toluene) gave **4b** as dark brown solids (12.5 mg, 0.00921 mmol, 32%).

4b: mp. 150.7−159.1 °C; ^{1}H NMR (300 MHz, CS_2/C_6D_6 (1:1)) δ 7.28 (d, J = 2.1 Hz, 2H, thienyl), 6.99 (d, J = 1.5 Hz, 2H, thienyl), 6.94 (d, J = 5.4 Hz, 2H, thienyl), 6.78 (dd, J = 2.1, 5.4 Hz, 2H, thienyl) 6.68 (s, 2H, vinyl) 3.90 (s, 2H, alcohol) 2.64 (t, J = 7.4 Hz, 4H, CH_2), 1.54−1.49 (m, 4H, CH_2), 1.19 (m, 20H, CH_2), 0.87−0.83 (t, J = 6.5 Hz, 6H, CH_3); ^{13}C NMR (150 MHz, CS_2/C_6D_6 (1:1)) δ 149.90, 148.76, 148.09, 147.21, 146.54, 146.36, 146.20, 146.02, 145.75, 145.68, 145.63, 145.26, 145.10, 145.03, 144.79, 144.59, 144.23, 143.79, 143.47 142.65, 142.21, 141.37, 141.12, 139.93, 139.52, 139.37, 139.24, 138.66, 137.33, 136.52, 135.38, 133.54, 133.25, 132.67,130.70, 126.66, 126.11, 88.90, 50.27, 32.85, 31.63, 30.56, 30.43, 30.36, 30.16, 23.77, 15.06; HRMS (FAB, positive ion mode) calcd for $C_{96}H_{46}O_2S_4$ ($M^{\bullet+}$) 1358.2381, found 1358.2340.

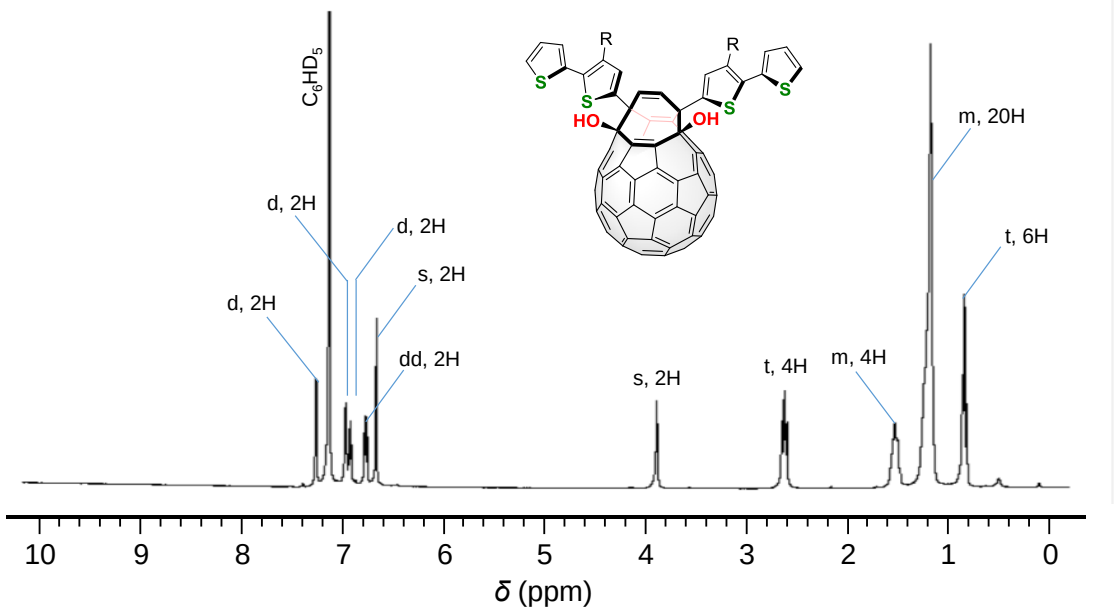


Figure S15. ^{1}H NMR spectrum (300 MHz, CS_2/C_6D_6 (1:1)) of **4b**.

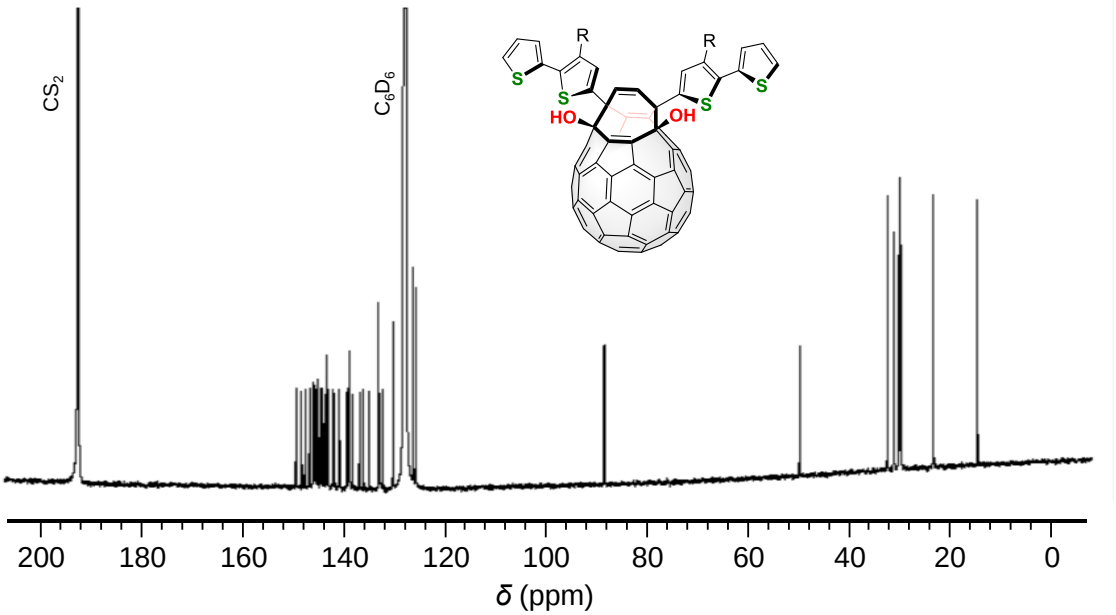
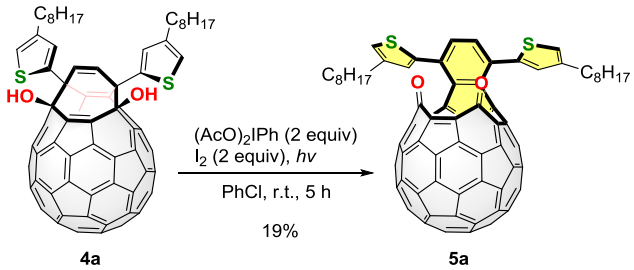


Figure S16. ^{13}C NMR spectrum (75 MHz, CS_2/C_6D_6 (1:1)) of **4b**.

4.5. Synthesis of Symmetric Diketo Derivative 5a



To the solution of **4a** (34.6 mg, 0.0289 mmol) in chlorobenzene (15 mL), (diacetoxyiodo)benzene (18.7 mg, 0.0581 mmol, 2.0 equiv) and iodine (22.1 mg, 0.0871 mmol, 3.0 equiv) were added. The resulting solution was stirred at room temperature for 5 h under irradiation by a halogen lamp. The reaction mixture was quenched with 3% $NaHSO_3$ aq. and extracted with toluene. The organic layer was collected and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography (toluene/hexane (1:1)) gave **5a** as dark brown solids (6.6 mg, 0.0055 mmol, 19%).

5a: mp. 120.5−128.0 °C; IR (KBr) ν = 1703 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 2H, phenyl), 7.22 (s, 2H, thienyl), 6.89 (s, 2H, thienyl), 2.53 (t, J = 7.4 Hz, 4H, CH_2), 1.50−1.49 (m, 4H, CH_2), 1.25−1.19 (m, 20H, CH_2), 0.84 (t, J = 6.5 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.83, 149.42, 149.19, 148.61, 148.49, 147.55, 146.46, 145.53, 145.30, 145.09, 145.02, 144.72, 144.38, 144.35, 144.09, 143.65, 143.53, 143.11, 142.90, 141.51, 140.56, 140.42, 139.78, 139.46, 138.41, 137.41, 136.25, 135.90, 135.84, 134.95, 131.96, 130.62, 129.62, 121.16, 32.13, 30.68, 30.51, 29.69, 29.52, 29.36, 22.92, 14.39; HRMS (FAB, positive ion mode) calcd for $C_{88}H_{40}O_2S_2$ ($M+H^+$) 1193.2550, found 1193.2533.

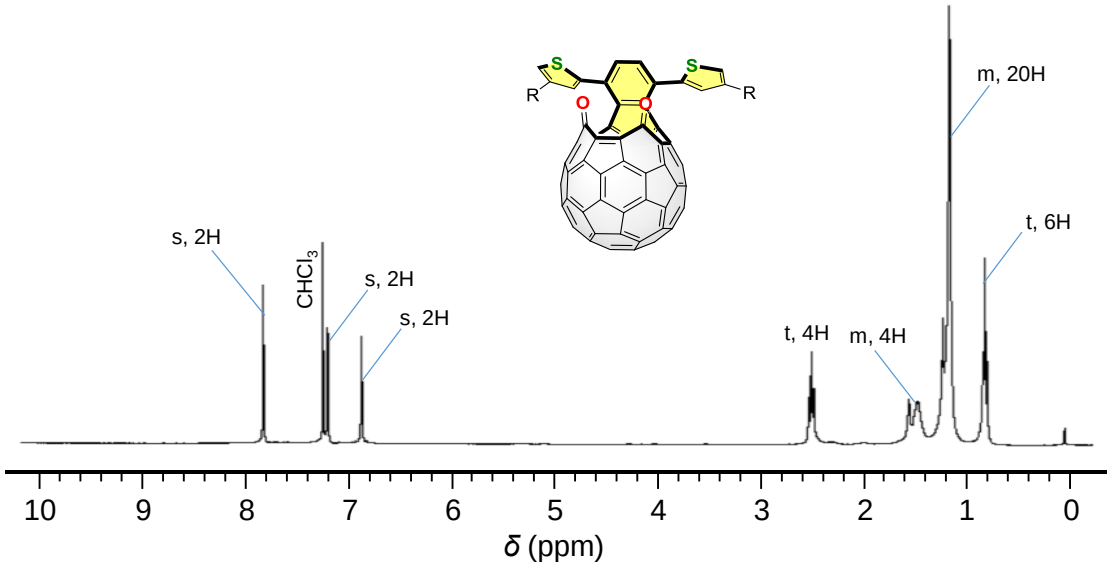


Figure S17. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5a**.

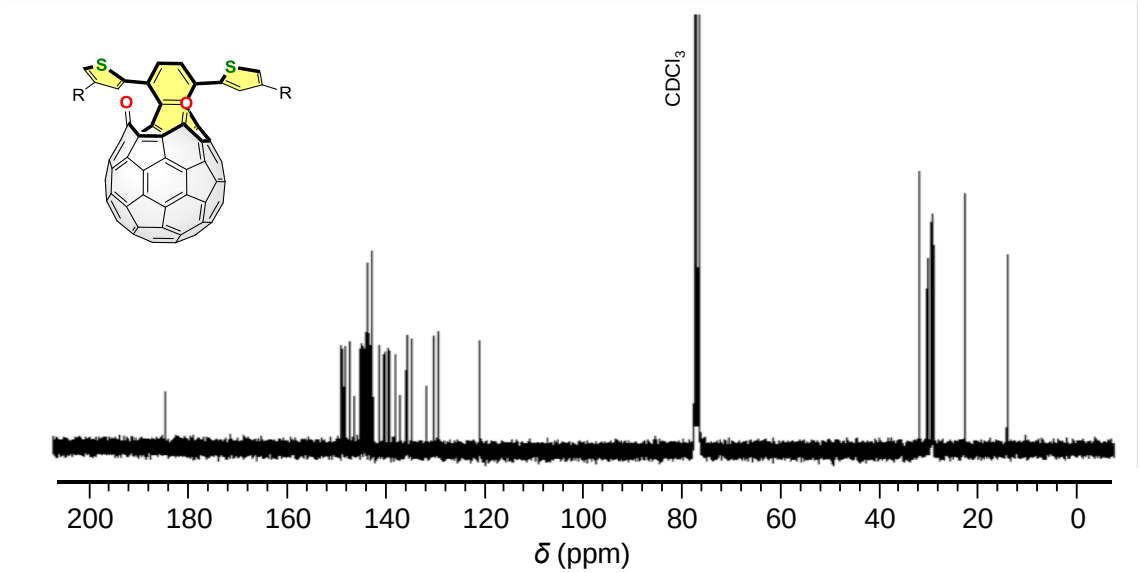


Figure S18. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5a**.

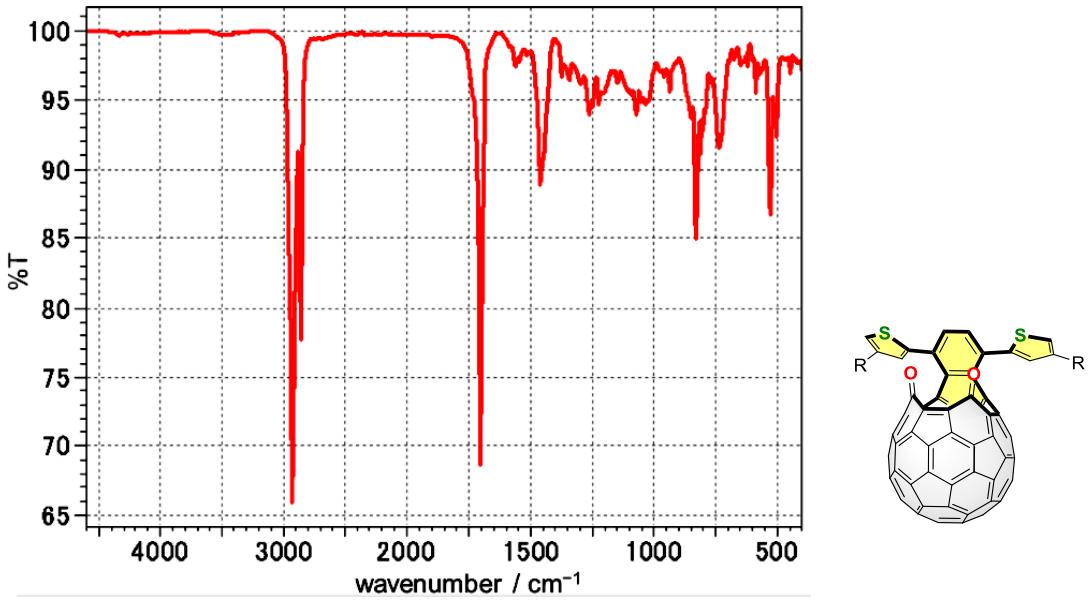
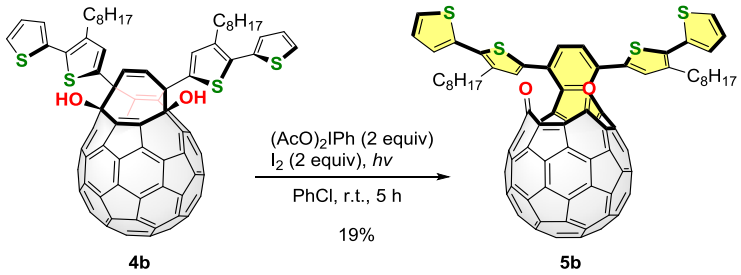


Figure S19. IR spectrum (KBr) of **5a**.

4.6. Synthesis of Symmetric Diketo Derivative 5b



4b **5b**

To the solution of **4b** (9.5 mg, 0.070 mmol) in chlorobenzene (2 mL), (diacetoxyiodo)benzene (4.5 mg, 0.014 mmol, 2.0 equiv) and iodine (3.6 mg, 0.014 mmol, 2.0 equiv) were added. The resulting solution was stirred at room temperature for 5 h under irradiation by a halogen lamp. The reaction mixture was quenched with 3% $NaHSO_3$ aq. and extracted with toluene. The organic layer was collected and dried over anhydrous Na_2SO_4. The chromatographic purification using silica gel column chromatography (toluene/hexane (1:1)) and then HPLC equipped with the Buckyprep column (toluene) gave **5b** as dark brown solids (1.8 mg, 0.0013 mmol, 19%).

5b: mp. 148.0−155.5 °C; IR (KBr) ν = 1703 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.84 (s, 2H, phenyl), 7.31 (d, J = 5.0 Hz, 2H, thienyl), 7.20 (s, 2H, thienyl), 7.14 (d, J = 3.0 Hz, 2H, thienyl), 7.06 (dd, J = 3.0, 5.0 Hz, 4H, thienyl), 2.75−2.65 (m, 4H, CH_2), 1.50 (m, 4H, CH_2), 1.20 (m, 20H, CH_2), 0.84 (t, J = 6.4 Hz, 6H, CH_3); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 184.62, 149.24, 149.02, 148.43, 148.30, 147.36, 146.47, 145.36, 145.10, 144.92, 144.85, 144.55, 144.20, 143.92, 143.50, 143.37, 142.71, 141.91, 141.35, 140.39, 140.28, 139.68, 139.30, 139.13, 138.27, 137.33, 136.12, 136.04, 135.53, 135.33, 134.86, 131.67, 131.57, 130.99, 130.25, 127.33, 125.81, 125.20, 77.23, 77.02, 76.81, 31.94, 30.41, 29.51, 29.34, 29.29, 29.23, 22.72, 14.19; HRMS (APCI, negative ion mode) calcd for $C_{96}H_{44}O_2S_4$ ($M^{\bullet-}$) 1356.2230, found 1356.2180.

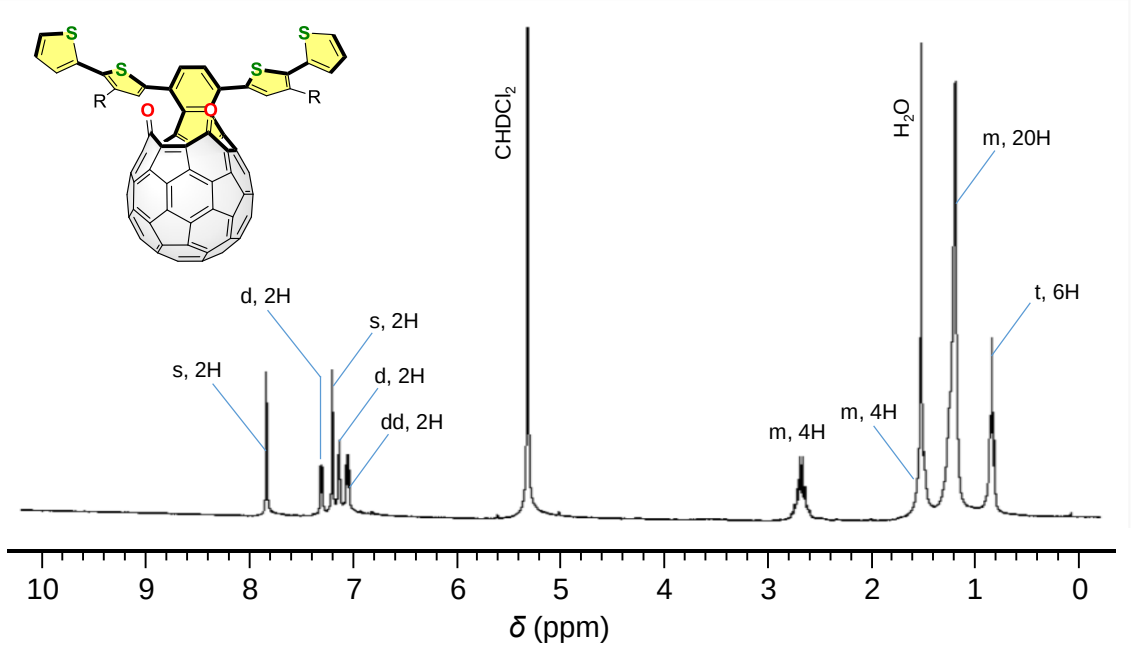


Figure S20. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **5b**.

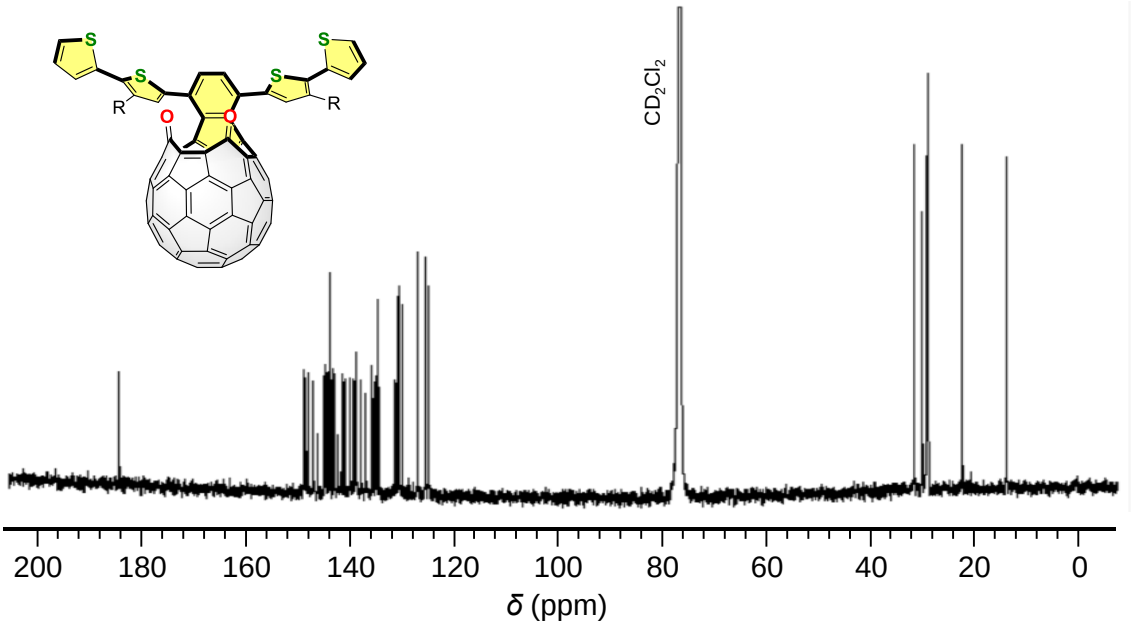


Figure S21. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of **5b**.

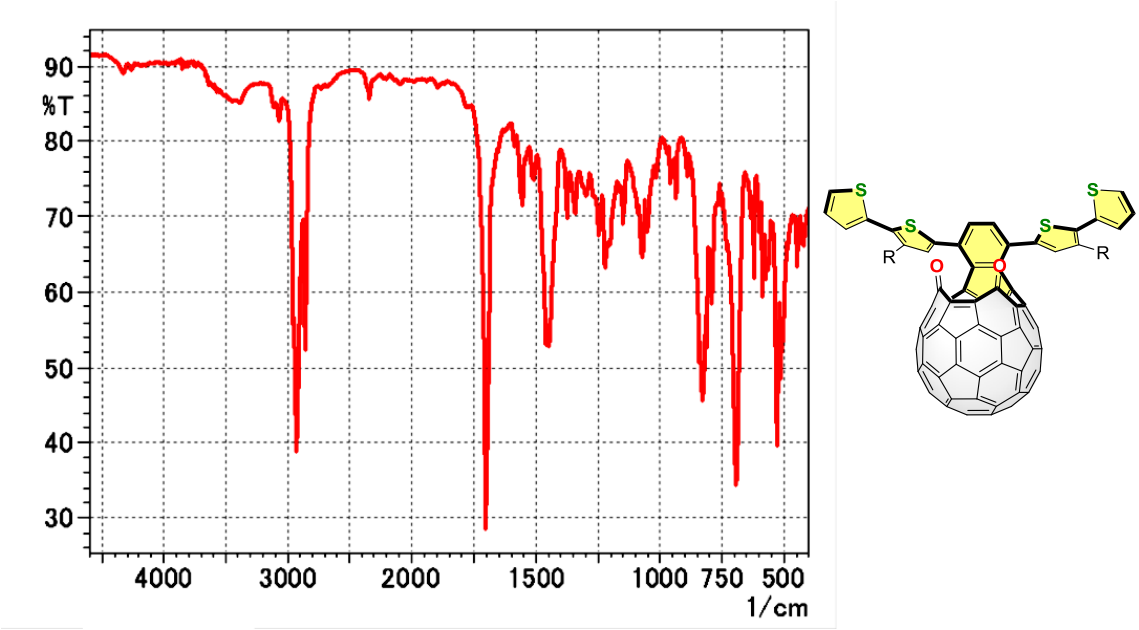


Figure S22. IR spectrum (KBr) of **5b**.

5. Cyclic Voltammetry

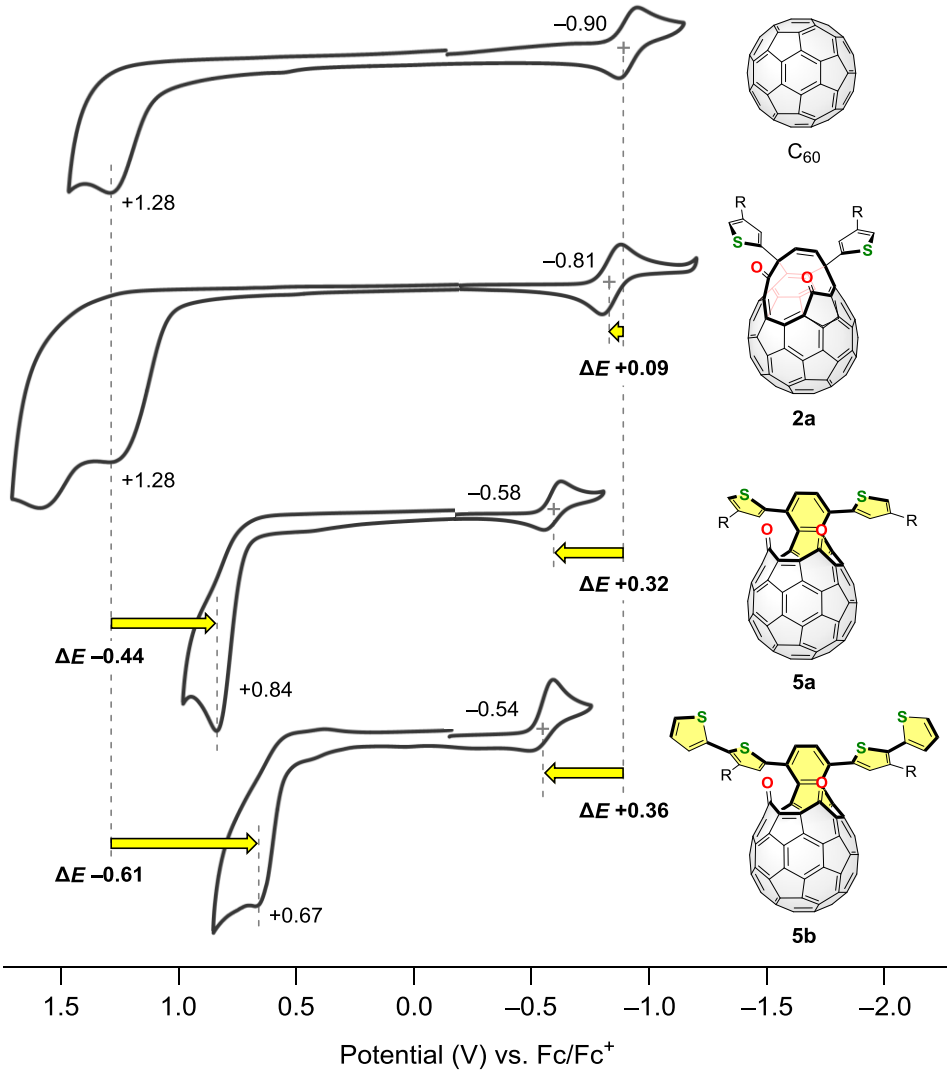


Figure S23. Cyclic voltammograms of C_{60}, **2a**, **5a** and **5b** using 1.0 mM samples with 0.10 M *n*-$Bu_4N{\cdot}BF_4$ in benzonitrile at a scan rate of 20 mV s^{-1}.

6. UV-Vis Absorption

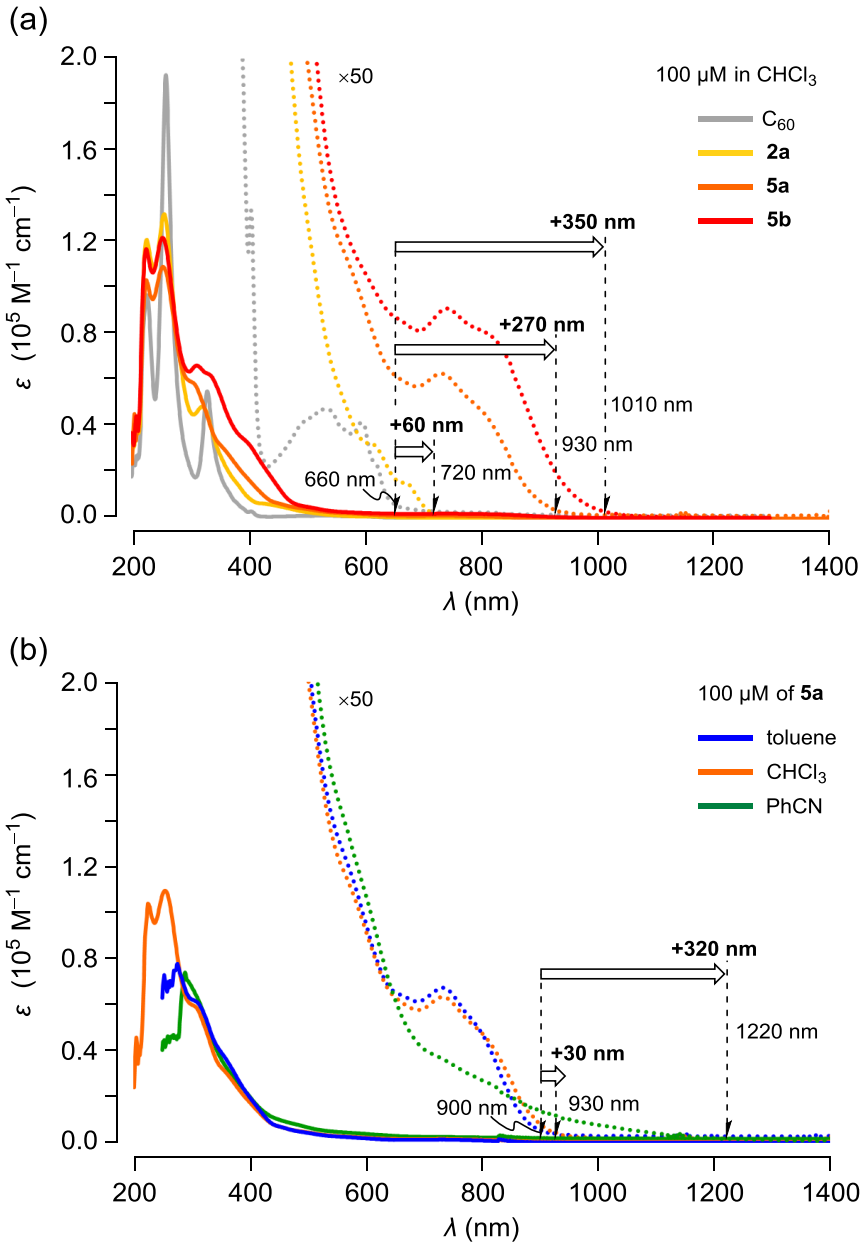


Figure S24. UV-vis absorption spectra for 100 μM solutions of (a) C_{60}, **2a**, **5a** and **5b** in chloroform and (b) **5a** in toluene, chloroform and benzonitrile.

7. X-Ray Structural Analysis

Single crystals of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine were obtained from an acetone solution by slow evaporation. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 8919 reflections were measured at the maximum 2θ angle of 50.1°, of which 6371 were independent reflections (R_{int} = 0.0222). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). The one of two *n*-octyl groups was partially disordered, which was solved using appropriate models. Thus, two sets of ethylene moieties, i.e., (C12–C13) and (C15–C16), were placed and their occupancies were refined to be 0.77 and 0.23, respectively. The two terminal thiophene rings are also disordered, i.e., [(S6-C3-C4-C5-C1) and (S3-C1-C2-C3-C4-S3)] and [(S4-C7-C8-C9-C10) and (S5-C7-C6-C10-C9)], in which the occupancies were refined to be 0.88 and 0.12 for the former and 0.62 and 0.38 for the latter, respectively. All non-hydrogen atoms except for the minor components of two terminal thiophene rings were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{39}H_{50}N_2OS_4$; FW = 691.05, crystal size 0.82 × 0.28 × 0.17 mm^3, triclinic, *P*-1, a = 7.622(3) Å, b = 14.074(5) Å, c = 18.644(7) Å, α = 108.820(4)°, β = 99.259(5)°, γ = 95.596(3)°, V = 1844.4(12) Å^3, Z = 2, D_c = 1.244 g cm^{-3}. The refinement converged to R_1 = 0.0411, wR_2 = 0.0926 ($I > 2\sigma(I)$), GOF = 1.099.

The crystallographic data of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine co-crystalized with an acetone molecule has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1577019. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

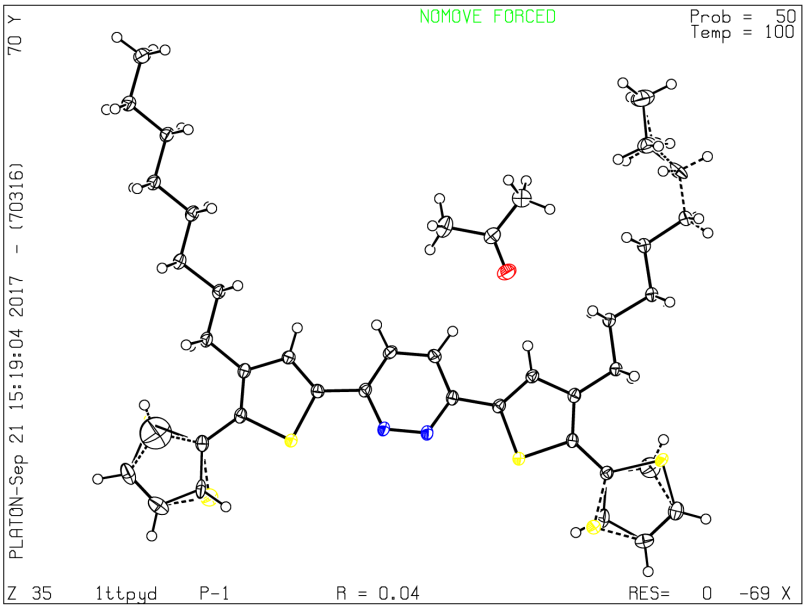


Figure S25. ORTEP drawing of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine with 50% probability of thermal ellipsoids.

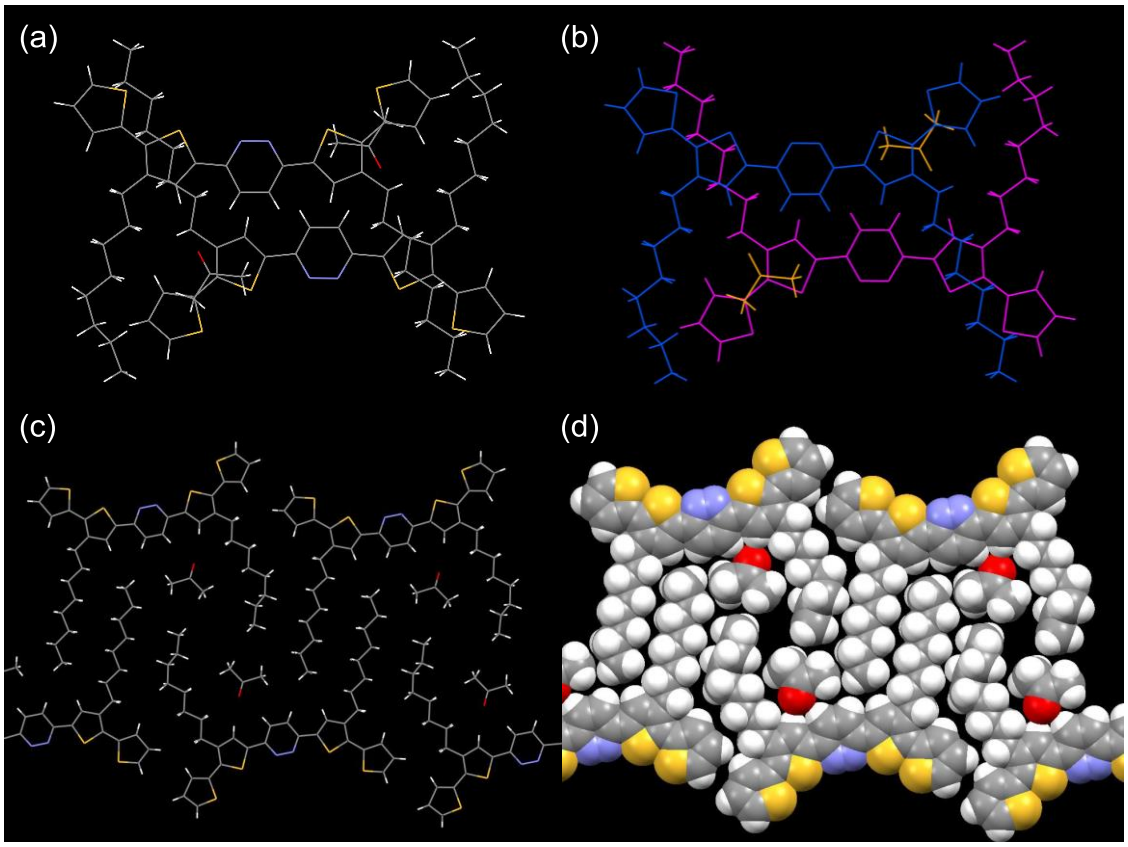


Figure S26. (a–c) Packing structures of 3,6-bis(3'-*n*-octyl-[2',2''-bithiophen]-5'-yl)pyridazine and (d) the van der Waals model.

8. DFT Calculations

8.1. HOMO-LUMO

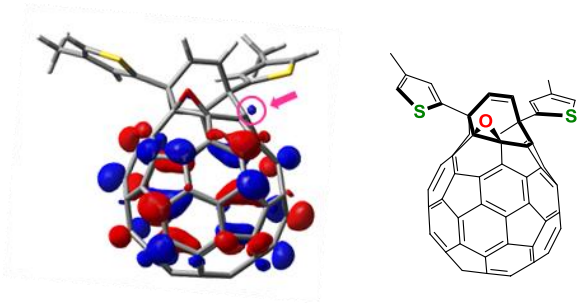


Figure S27. LUMO of **3a'** calculated at the B3LYP/6-31G(d) level of theory. The *n*-octyl groups in **3a** were replaced with methyl groups for calculations.

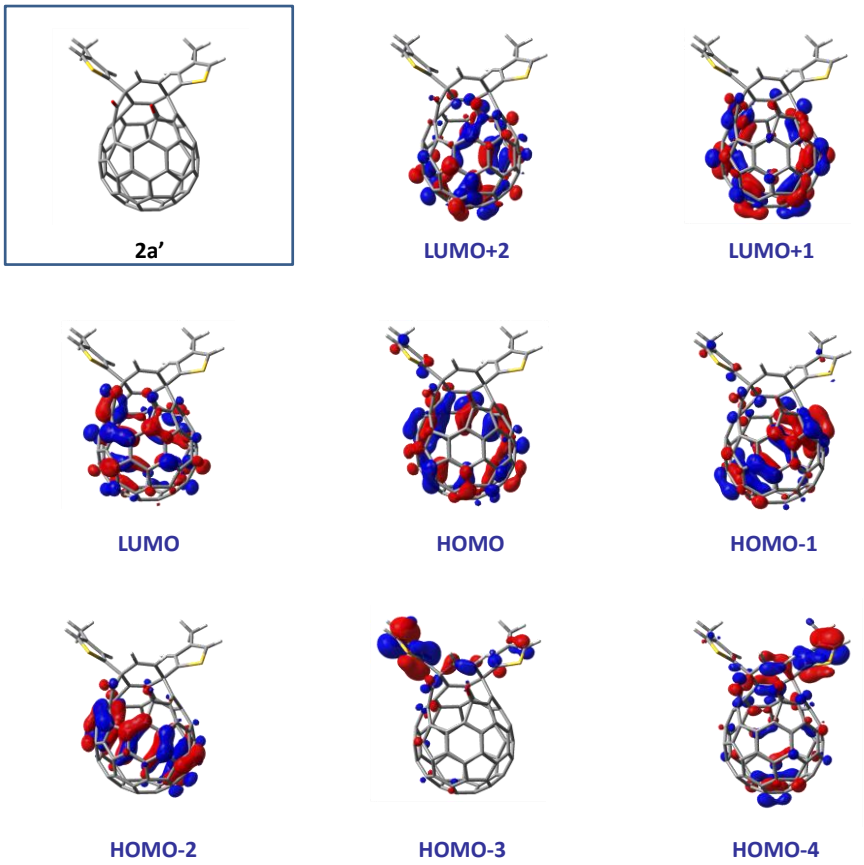


Figure S28. HOMOs and LUMOs of **2a'** calculated at the B3LYP/6-31G(d) level of theory.

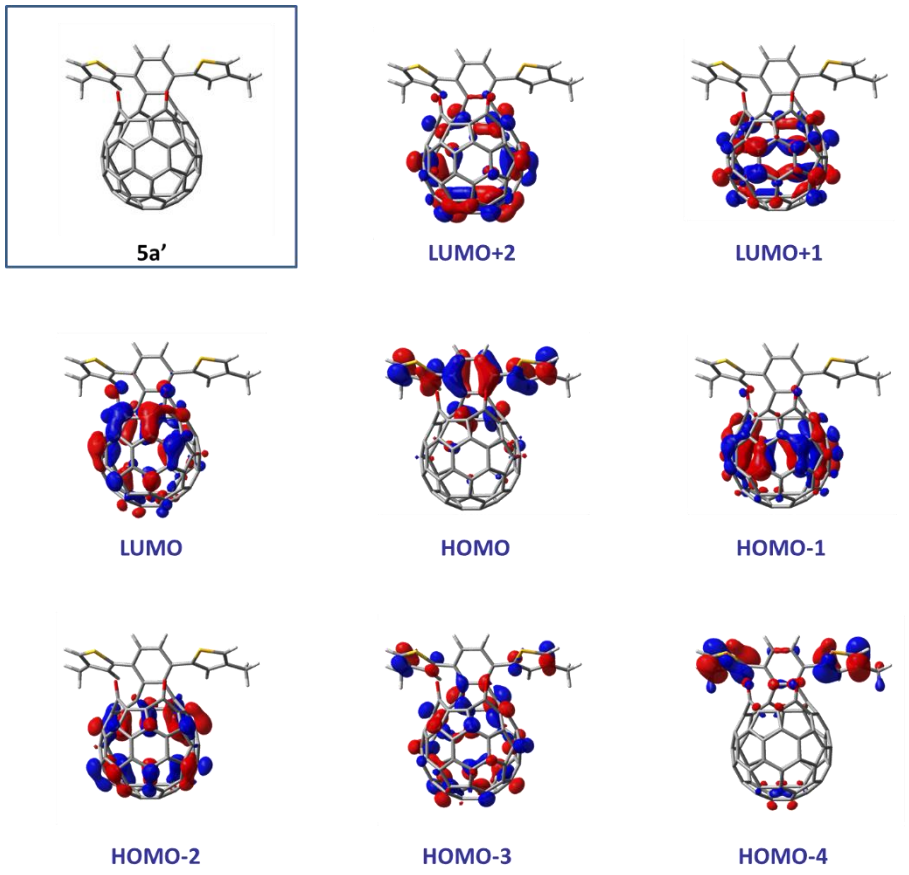


Figure S29. HOMOs and LUMOs of **5a'** calculated at the B3LYP/6-31G(d) level of theory.

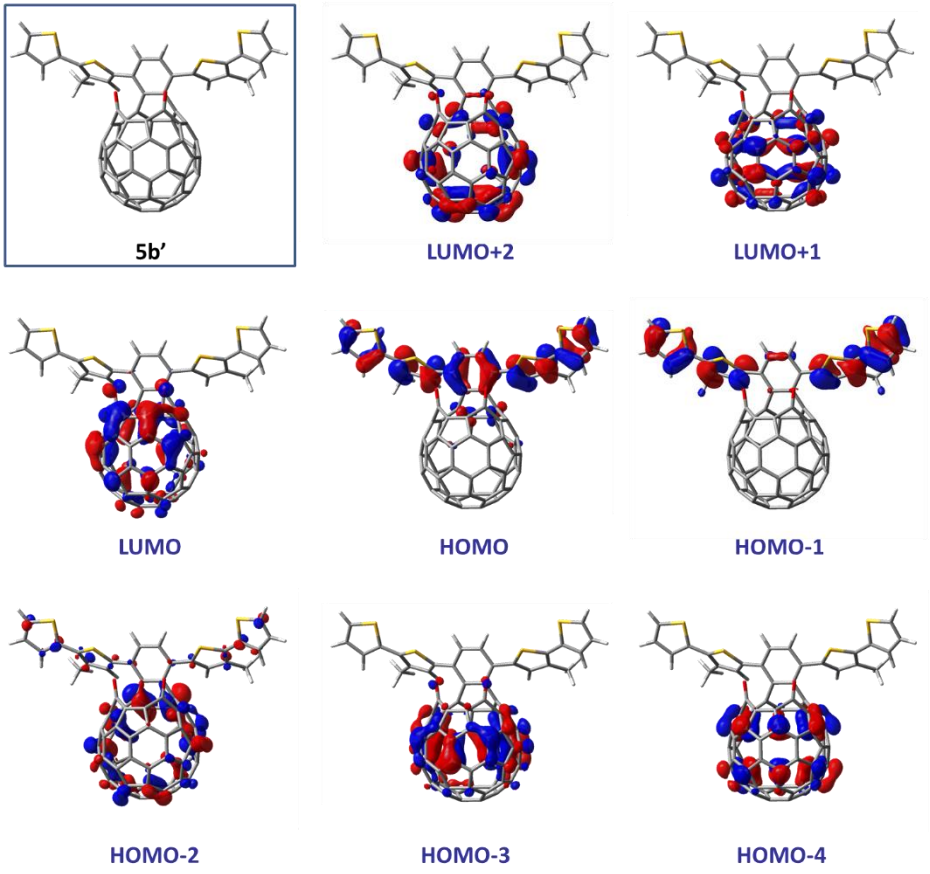


Figure S30. HOMOs and LUMOs of **5b'** calculated at the B3LYP/6-31G(d) level of theory.

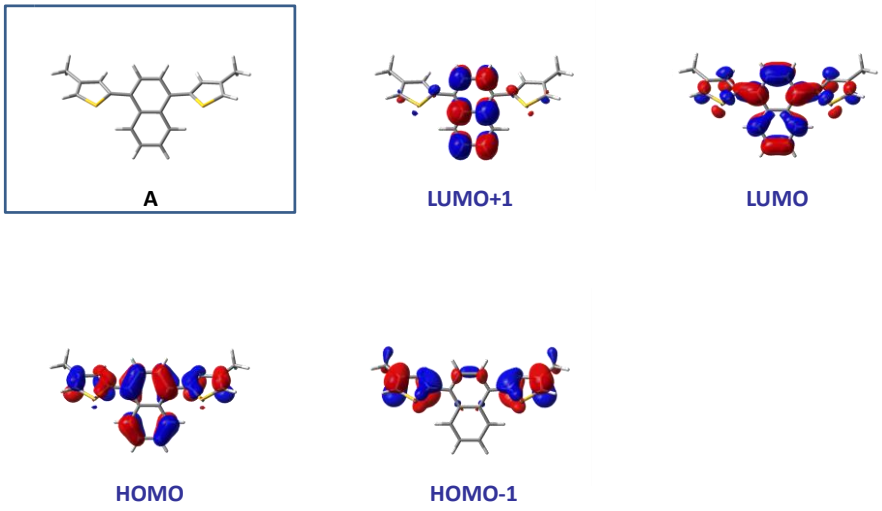


Figure S31. HOMOs and LUMOs of 1,4-bis(4'-methylthiophen-2'-yl)naphthalene) (**A**) calculated at the B3LYP/6-31G(d) level of theory.

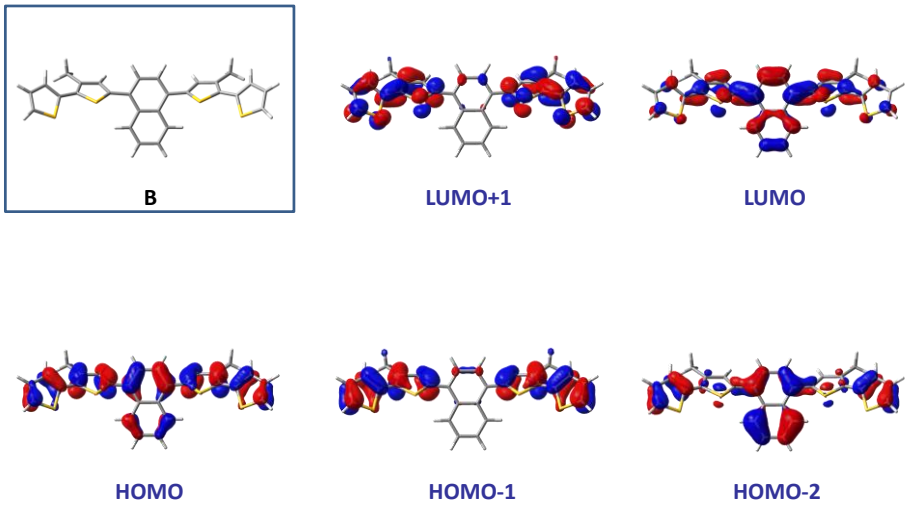


Figure S32. HOMOs and LUMOs of 1,4-bis(4'-methyl-5'-thienylthiophen-2'-yl)naphthalene (**B**) calculated at the B3LYP/6-31G(d) level of theory.

8.2. TD DFT Calculations

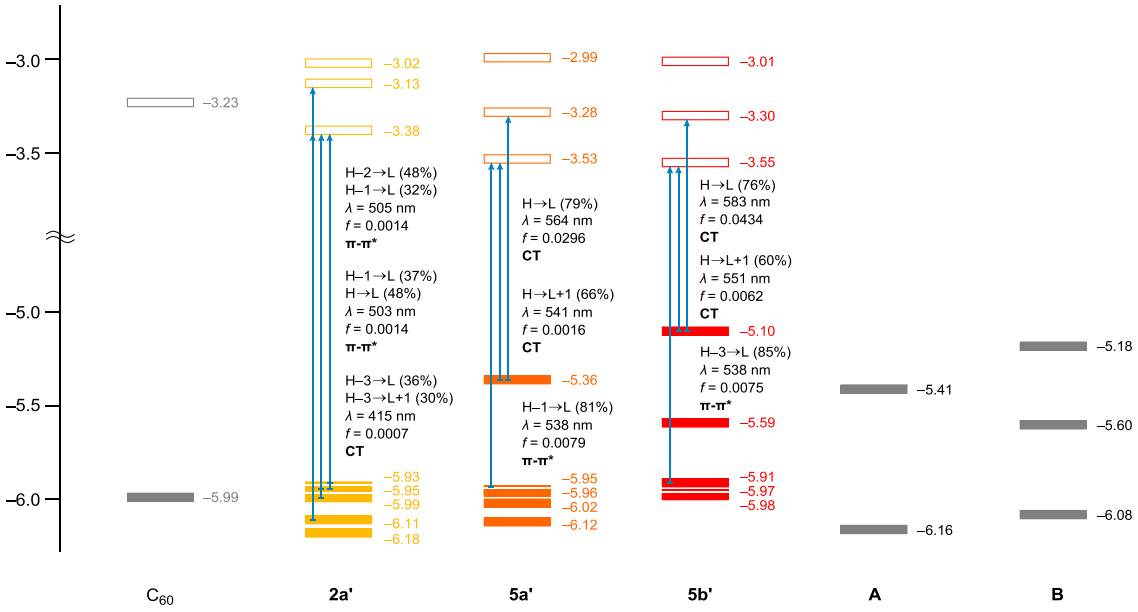


Figure S33. A plot of Kohn-Sham HOMO and LUMO levels (B3LYP/6-31G(d)) and optical transitions with oscillator strengths (TD CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d)) of C_{60}, **2a'**, **5a'**, **5b'**, **A** (1,4-bis(4'-methylthiophen-2'-yl)naphthalene), and **B** (1,4-bis(4'-methyl-5'-thienylthiophen-2'-yl)naphthalene). The transition energies were calibrated by using a factor of 0.75. The *n*-octyl groups in **2a**, **5a** and **5b** were replaced with the methyl groups in **2a'**, **5a'** and **5b'**.

8.3. NICS(0) Calculations

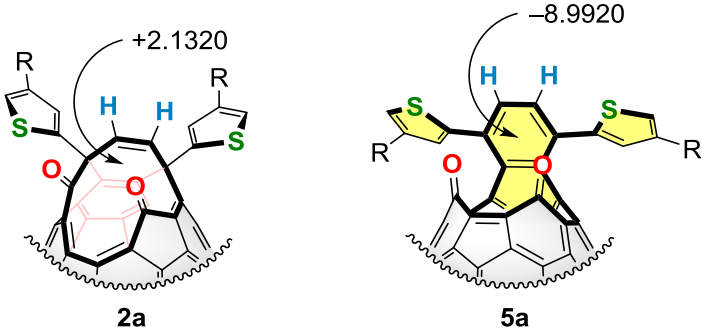
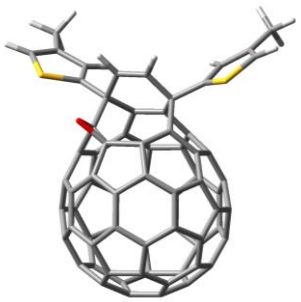


Figure S34. NICS(0) calculations of **2a** and **5a**, calculated at the HF/6-311G(d,p)// B3LYP/6-31G(d) level of theory.

Table S1. Optimized structure of **3a'** (B3LYP/6-31G(d))

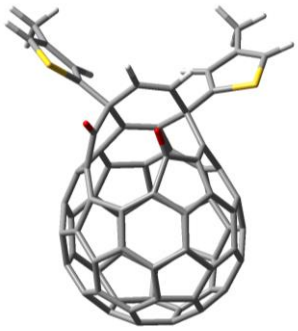


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.061382	-1.229524	3.093534
2	6	0	-2.384372	-0.033587	3.567631
3	6	0	-0.993794	0.003185	3.600261
4	6	0	-0.225213	-1.141828	3.154686
5	6	0	-0.862922	-2.272723	2.669420
6	6	0	-2.313865	-2.329190	2.659322
7	6	0	-3.121750	1.124251	3.092711
8	6	0	-0.282908	1.186530	3.156243
9	6	0	0.961842	-0.669862	2.489129
10	6	0	-0.359754	-2.925739	1.469948
11	6	0	-2.714639	-3.057250	1.473476
12	6	0	-4.231950	-0.810491	2.344364
13	6	0	0.786659	-2.456891	0.786992
14	6	0	1.526523	-1.342785	1.400637
15	6	0	0.828614	-2.575953	-0.673123
16	6	0	2.459092	-0.596474	0.599155
17	6	0	-2.431590	2.260394	2.657586
18	6	0	0.927204	0.778227	2.492443
19	6	0	1.807574	-1.693535	-1.403640
20	6	0	1.455962	1.482791	1.404746
21	6	0	-0.980663	2.283016	2.669082
22	6	0	-1.506576	-3.435544	0.758744
23	6	0	-3.851514	-2.666936	0.764182
24	6	0	-2.874986	2.968374	1.473012
25	6	0	-4.621324	-1.518290	1.205120
26	6	0	-4.270529	0.644636	2.344313
27	6	0	-3.835841	-2.664185	-0.690223
28	6	0	-5.077675	-0.802054	0.023762
29	6	0	-4.700328	1.331320	1.207674
30	6	0	2.415771	0.782850	0.590762
31	6	0	-1.495187	-3.442973	-0.631211
32	6	0	-0.509016	2.965497	1.472007
33	6	0	-4.598803	-1.513377	-1.146611
34	6	0	-5.118733	0.594590	0.026075
35	6	0	-3.994269	2.522279	0.766375
36	6	0	-3.986630	2.525958	-0.686566
37	6	0	-1.692569	3.412590	0.758180
38	6	0	0.662538	2.560659	0.799600
39	6	0	0.670246	2.614776	-0.678448
40	6	0	-4.684120	1.335666	-1.144337
41	6	0	-4.227596	0.652111	-2.274119
42	6	0	-3.059091	1.133498	-2.987208
43	6	0	-4.182988	-0.803343	-2.275120
44	6	0	-0.325108	-2.988222	-1.334499
45	6	0	-0.505764	2.997052	-1.331371
46	6	0	-2.682326	-3.049404	-1.371364
47	6	0	-2.247137	-2.318996	-2.544946
48	6	0	-1.691260	3.421379	-0.627801
49	6	0	1.598992	1.713203	-1.360974
50	6	0	1.098752	0.842146	-2.338144
51	6	0	-2.856271	2.976197	-1.370297
52	6	0	-2.380360	2.267752	-2.542199
53	6	0	-2.988696	-1.216521	-2.989134
54	6	0	-2.300005	-0.023954	-3.420469
55	6	0	-0.924929	2.293974	-2.514766
56	6	0	-0.800083	-2.277517	-2.532670
57	6	0	1.181692	-0.724988	-2.424911
58	6	0	-0.189525	1.178932	-2.911712
59	6	0	-0.161856	-1.122288	-2.935499
60	6	0	-0.906363	0.009472	-3.357853
61	6	0	2.935918	1.553490	-0.620130
62	6	0	3.066903	-1.354368	-0.562170
63	6	0	3.558156	2.889680	-0.230863
64	6	0	3.777141	-2.629632	-0.118631
65	16	0	3.615615	4.230882	-1.353685
66	6	0	4.268013	3.183007	0.900959
67	6	0	4.861268	4.490024	0.901853
68	6	0	4.591499	5.161886	-0.258894
69	6	0	3.958352	0.789423	-1.423506
70	6	0	4.030900	-0.532788	-1.384906
71	6	0	5.671828	5.041357	2.044249
72	8	0	2.130917	-1.755616	-2.795692
73	1	0	4.370435	2.484445	1.725427
74	1	0	4.892662	6.165655	-0.529589
75	1	0	4.634495	1.375857	-2.037753
76	1	0	4.761823	-1.077211	-1.971985
77	1	0	6.030482	6.051763	1.825850
78	1	0	6.547092	4.413314	2.252506
79	1	0	5.080933	5.087814	2.967536
80	6	0	4.376301	-2.885061	1.084745
81	6	0	5.055264	-4.147531	1.149472
82	6	0	4.958825	-4.826916	-0.033991
83	6	0	5.774233	-4.650241	2.372692
84	1	0	4.334996	-2.192284	1.919017
85	1	0	5.360609	-5.803260	-0.272714
86	1	0	6.224571	-5.631293	2.193713
87	1	0	5.091735	-4.745948	3.226442
88	1	0	6.575442	-3.964499	2.675518
89	16	0	4.054670	-3.953801	-1.231653

The total electronic energy was calculated to be –3698.4051993 Hartree.

Table S2. Optimized structure of **2a'** (B3LYP/6-31G(d))

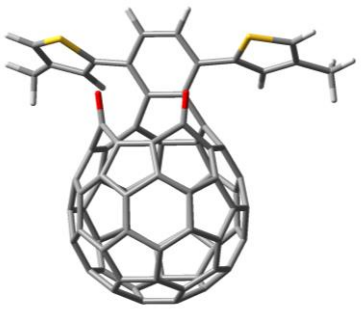


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.546471	1.634440	3.066585
2	6	0	-1.101658	1.740027	2.989727
3	6	0	-0.316885	0.630483	3.262878
4	6	0	-0.932634	-0.644098	3.579580
5	6	0	-2.320306	-0.762801	3.607573
6	6	0	-3.146267	0.404813	3.354729
7	6	0	-0.750860	2.616708	1.885072
8	6	0	0.860251	0.392145	2.469369
9	6	0	-0.123989	-1.669246	2.953540
10	6	0	-2.958123	-1.911624	2.983039
11	6	0	-4.308392	-0.023479	2.595451
12	6	0	-3.105262	2.494799	2.043227
13	6	0	-2.174437	-2.884504	2.354462
14	6	0	-0.729548	-2.758469	2.342993
15	6	0	-2.577648	-3.415420	1.065154
16	6	0	-0.239271	-3.194010	1.050078
17	6	0	0.371641	2.366688	1.065966
18	6	0	1.003509	-1.040754	2.306836
19	6	0	-1.377303	-3.575315	0.263050
20	6	0	1.579102	-1.541741	1.140609
21	6	0	1.242033	1.244404	1.425921
22	6	0	-4.184122	-1.452649	2.356646
23	6	0	-4.848610	0.807234	1.611853
24	6	0	0.284647	2.700623	-0.366815
25	6	0	-4.247466	2.101315	1.340367
26	6	0	-1.999346	3.117684	1.341839
27	6	0	-5.292218	0.247219	0.345501
28	6	0	-4.343127	2.351519	-0.086613
29	6	0	-2.099215	3.374401	-0.016131
30	6	0	0.877209	-2.614728	0.430138
31	6	0	-4.586988	-1.988148	1.129317
32	6	0	2.175406	0.717013	0.454220
33	6	0	-4.987607	1.202840	-0.704097
34	6	0	-3.298754	2.998864	-0.747553
35	6	0	-0.949335	3.161613	-0.859621
36	6	0	-1.442068	2.704428	-2.138096
37	6	0	1.209807	2.029526	-1.284431
38	6	0	2.391263	-0.641372	0.356592
39	6	0	2.252749	-2.181755	-1.607238
40	6	0	-2.882511	2.558085	-2.061173
41	6	0	-3.496871	1.453248	-2.653397
42	6	0	-2.679432	0.455683	-3.321506
43	6	0	-4.558948	0.754680	-1.957924
44	6	0	-3.759893	-2.978847	0.469990
45	6	0	0.989846	0.207557	-3.229090
46	6	0	-5.154068	-1.122612	0.105919
47	6	0	-4.682229	-1.584245	-1.185202
48	6	0	0.683840	1.504181	-2.458304
49	6	0	0.927971	-2.535068	-1.025577
50	6	0	-0.265562	-2.650997	-1.754585
51	6	0	-0.676479	1.779416	-2.823336
52	6	0	-1.303679	0.604949	-3.402389
53	6	0	-4.386597	-0.671800	-2.196217
54	6	0	-3.197152	-0.847645	-3.011410
55	6	0	-0.375883	-0.494114	-3.272326
56	6	0	-3.797594	-2.711079	-0.958503
57	6	0	-1.396789	-3.251213	-1.094970
58	6	0	-0.841544	-1.730693	-2.826293
59	6	0	-2.630241	-2.829789	-1.709424
60	6	0	-2.297143	-1.887656	-2.746771
61	6	0	2.585654	1.670418	-0.666403
62	6	0	3.215036	-1.291646	-0.734453
63	6	0	3.859393	-0.270013	-1.643358
64	6	0	3.552406	1.023379	-1.633781
65	6	0	4.293973	-2.189538	-0.121889
66	6	0	3.273748	2.918900	-0.112391
67	8	0	2.618920	-2.635021	-2.673128
68	8	0	1.975681	-0.133589	-3.829704
69	6	0	4.050481	3.024062	1.009136
70	6	0	4.664113	4.309481	1.181743
71	6	0	4.339725	5.159736	0.159978
72	16	0	3.289341	4.421804	-1.009557
73	16	0	5.079772	-3.454237	-1.047531
74	6	0	6.138460	-3.818151	0.277240
75	6	0	5.912620	-3.026721	1.370390
76	6	0	4.853882	-2.091900	1.125153
77	6	0	5.547061	4.666510	2.347569
78	6	0	6.667575	-3.117179	2.669588
79	1	0	4.557105	-0.662572	-2.375003
80	1	0	4.017881	1.693366	-2.350708
81	1	0	4.190248	2.202357	1.704194
82	1	0	4.643959	6.190703	0.033236
83	1	0	6.865636	-4.613973	0.176637
84	1	0	4.525151	-1.366997	1.862426
85	1	0	5.910521	5.695624	2.270114
86	1	0	5.009571	4.571854	3.299439
87	1	0	6.421422	4.006086	2.403498
88	1	0	5.997722	-3.351072	3.506639
89	1	0	7.434914	-3.896189	2.628802
90	1	0	7.165959	-2.169673	2.910263

The total electronic energy was calculated to be –3773.65965998 Hartree.

Table S3. Optimized structure of **5a'** (B3LYP/6-31G(d))

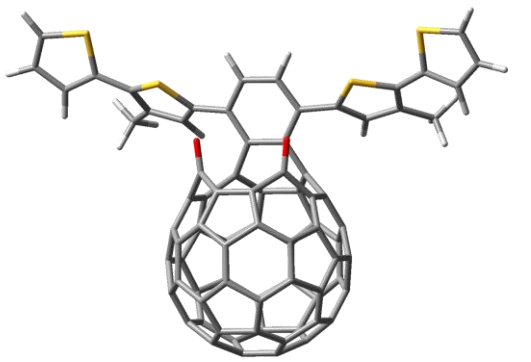


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.076740	2.290443	-2.698436
2	6	0	0.640467	2.266443	-2.497091
3	6	0	-0.082212	1.156513	-2.902725
4	6	0	0.590957	-0.000016	-3.452055
5	6	0	1.969094	-0.000029	-3.618785
6	6	0	2.732611	1.179751	-3.244429
7	6	0	0.321350	2.870059	-1.217821
8	6	0	-1.207185	0.736677	-2.129601
9	6	0	-0.082231	-1.156533	-2.902725
10	6	0	2.732592	-1.179819	-3.244423
11	6	0	3.984491	0.727336	-2.669731
12	6	0	2.657939	2.990805	-1.574029
13	6	0	2.076702	-2.290497	-2.698425
14	6	0	0.640429	-2.266474	-2.497086
15	6	0	2.657887	-2.990862	-1.574010
16	6	0	0.321301	-2.870082	-1.217816
17	6	0	-0.743965	2.393721	-0.387712
18	6	0	-1.207200	-0.736675	-2.129607
19	6	0	1.569038	-3.354684	-0.683632
20	6	0	-1.655611	-1.402107	-0.988649
21	6	0	-1.655584	1.402114	-0.988637
22	6	0	3.984478	-0.727422	-2.669726
23	6	0	4.558497	1.423618	-1.599912
24	6	0	-0.509498	2.440425	1.059722
25	6	0	3.884990	2.584480	-1.047876
26	6	0	1.569098	3.354654	-0.683652
27	6	0	5.174737	0.698365	-0.503848
28	6	0	4.096432	2.582349	0.390614
29	6	0	1.775105	3.351766	0.687439
30	6	0	-0.744010	-2.393720	-0.387720
31	6	0	4.558470	-1.423706	-1.599900
32	6	0	-2.825582	0.717253	-0.393805
33	6	0	4.904303	1.422176	0.728539
34	6	0	3.067767	2.979205	1.241062
35	6	0	0.731521	2.873258	1.542647
36	6	0	1.399910	2.240345	2.705020
37	6	0	-1.328982	1.659191	2.091117
38	6	0	-2.825584	-0.717241	-0.393791
39	6	0	-1.329028	-1.659074	2.091081
40	6	0	2.830005	2.277153	2.483452
41	6	0	3.626790	1.173710	2.824279
42	6	0	3.008207	-0.000004	3.405298
43	6	0	4.668762	0.729061	1.915671
44	6	0	3.884941	-2.584551	-1.047856
45	6	0	-0.488150	-0.689947	2.872107
46	6	0	5.174722	-0.698455	-0.503842
47	6	0	4.904271	-1.422250	0.728551
48	6	0	-0.488126	0.690052	2.872136
49	6	0	-0.509552	-2.440372	1.059708
50	6	0	0.731451	-2.873228	1.542655
51	6	0	0.828484	1.145548	3.316618
52	6	0	1.635989	0.000012	3.649036
53	6	0	4.668745	-0.729121	1.915676
54	6	0	3.626760	-1.173737	2.824285
55	6	0	0.828443	-1.145498	3.316608
56	6	0	4.096376	-2.582409	0.390636
57	6	0	1.775032	-3.351775	0.687461
58	6	0	1.399848	-2.240311	2.705021
59	6	0	3.067698	-2.979231	1.241084
60	6	0	2.829945	-2.277160	2.483464
61	6	0	-3.977681	1.427684	0.029882
62	6	0	-3.977682	-1.427659	0.029927
63	6	0	-5.058623	-0.694027	0.533889
64	6	0	-5.058625	0.694071	0.533864
65	6	0	-4.106378	-2.885810	-0.134805
66	6	0	-4.106344	2.885836	-0.134857
67	8	0	-2.517683	-1.803822	2.289945
68	8	0	-2.517638	1.803953	2.289979
69	16	0	-4.839070	3.879948	1.108198
70	6	0	-4.722547	5.295012	0.115027
71	6	0	-3.904001	-6.069382	-2.171375
72	6	0	-4.144215	5.038661	-1.100582
73	6	0	-3.799162	3.656227	-1.232322
74	6	0	-3.799179	-3.656216	-1.232256
75	6	0	-4.144249	-5.038645	-1.100511
76	6	0	-4.722620	-5.294977	0.115084
77	16	0	-4.839183	-3.879897	1.108225
78	6	0	-3.903925	6.069395	-2.171439
79	1	0	-5.947383	-1.224866	0.860548
80	1	0	-5.947383	1.224922	0.860507
81	1	0	-5.071127	6.248169	0.491812
82	1	0	-4.415854	-5.803644	-3.104834
83	1	0	-2.835904	-6.162867	-2.404769
84	1	0	-4.265344	-7.054945	-1.862178
85	1	0	-3.364134	3.240627	-2.135089
86	1	0	-3.364106	-3.240635	-2.135010
87	1	0	-5.071210	-6.248128	0.491873
88	1	0	-4.415044	5.803219	-3.105172
89	1	0	-4.266041	7.054787	-1.862599
90	1	0	-2.835739	6.163492	-2.404191

The total electronic energy was calculated to be –3773.66566033 Hartree.

Table S4. Optimized structure of **5b'** (B3LYP/6-31G(d))

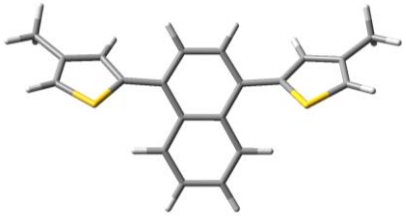


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.368469	-3.112475	-2.597031
2	6	0	2.305045	-1.665526	-2.520081
3	6	0	1.175757	-1.011803	-2.984553
4	6	0	0.037950	-1.761397	-3.470499
5	6	0	0.075941	-3.148135	-3.517649
6	6	0	1.276330	-3.843480	-3.081301
7	6	0	2.900117	-1.220197	-1.274913
8	6	0	0.724485	0.163264	-2.310143
9	6	0	-1.136883	-1.075212	-2.978726
10	6	0	-1.082198	-3.908303	-3.075333
11	6	0	0.858982	-5.052835	-2.399231
12	6	0	3.084989	-3.574589	-1.428455
13	6	0	-2.210417	-3.238478	-2.585208
14	6	0	-2.225834	-1.790331	-2.508317
15	6	0	-2.894386	-3.739373	-1.412951
16	6	0	-2.837686	-1.378121	-1.260045
17	6	0	2.394430	-0.100622	-0.538781
18	6	0	-0.747909	0.123100	-2.306590
19	6	0	-3.288115	-2.587958	-0.619057
20	6	0	-1.425140	0.651303	-1.207326
21	6	0	1.377171	0.727553	-1.214277
22	6	0	-0.595167	-5.092880	-2.395656
23	6	0	1.571289	-5.512428	-1.285537
24	6	0	2.448574	-0.208101	0.923242
25	6	0	2.713635	-4.762269	-0.797039
26	6	0	3.419221	-2.403429	-0.636400
27	6	0	0.863452	-6.051086	-0.138573
28	6	0	2.717841	-4.849066	0.654498
29	6	0	3.422764	-2.490426	0.747461
30	6	0	-2.391492	-0.231830	-0.526435
31	6	0	-1.275127	-5.591044	-1.278424
32	6	0	0.661181	1.925549	-0.721438
33	6	0	1.579928	-5.655890	1.063843
34	6	0	3.086007	-3.739943	1.411900
35	6	0	2.916101	-1.390134	1.510366
36	6	0	2.301472	-1.972317	2.727702
37	6	0	1.645906	0.675856	1.882066
38	6	0	-0.772506	1.886804	-0.718537
39	6	0	-1.674255	0.584623	1.891010
40	6	0	2.377226	-3.414663	2.630354
41	6	0	1.296222	-4.208868	3.041423
42	6	0	0.106227	-3.574670	3.569756
43	6	0	0.880601	-5.338127	2.228099
44	6	0	-2.454250	-4.904512	-0.783731
45	6	0	-0.680558	-0.158303	2.737201
46	6	0	-0.532970	-6.089750	-0.135023
47	6	0	-1.263940	-5.734084	1.071083
48	6	0	0.698995	-0.120291	2.733560
49	6	0	-2.432134	-0.342133	0.935954
50	6	0	-2.830123	-1.548253	1.525180
51	6	0	1.191116	-1.380084	3.289703
52	6	0	0.068311	-2.186955	3.693864
53	6	0	-0.577040	-5.378339	2.231814
54	6	0	-1.049777	-4.273497	3.047305
55	6	0	-1.099253	-1.443336	3.295563
56	6	0	-2.446239	-4.990895	0.667754
57	6	0	-3.279419	-2.674801	0.764737
58	6	0	-2.178239	-2.095671	2.739157
59	6	0	-2.871108	-3.903867	1.427259
60	6	0	-2.174972	-3.539945	2.642107
61	6	0	1.340362	3.128846	-0.398698
62	6	0	-1.513364	3.052658	-0.394124
63	6	0	-0.808869	4.190525	0.021180
64	6	0	0.577874	4.227582	0.019145
65	6	0	-2.970669	3.131514	-0.574656
66	6	0	2.791244	3.283073	-0.581599
67	8	0	-1.849857	1.782239	1.982747
68	8	0	1.758788	1.880865	1.975243
69	16	0	3.761805	4.171771	0.568156
70	6	0	5.200063	4.019295	-0.424889
71	6	0	-6.091262	2.675163	-2.653459
72	6	0	4.934707	3.292189	-1.574479
73	6	0	3.571378	2.885310	-1.643901
74	6	0	-3.730275	2.692806	-1.635572
75	6	0	-5.111767	3.033259	-1.567431
76	6	0	-5.412352	3.750670	-0.420374
77	16	0	-3.983731	3.973135	0.573791
78	6	0	6.457894	4.600640	0.012551
79	6	0	-6.696441	4.273464	0.014122
80	6	0	7.737790	4.108118	-0.136566
81	6	0	5.929961	2.986708	-2.662362
82	6	0	8.743180	4.954674	0.412105
83	6	0	8.231984	6.087341	0.984032
84	16	0	6.505333	6.149416	0.846045
85	6	0	-7.952898	3.725773	-0.141171
86	6	0	-8.996574	4.526083	0.405548
87	6	0	-8.537883	5.678849	0.981789
88	16	0	-6.815166	5.817387	0.850327
89	1	0	-1.362953	5.088994	0.274197
90	1	0	1.084196	5.154249	0.270619
91	1	0	-6.568465	1.702821	-2.469673
92	1	0	-6.889019	3.419823	-2.734515
93	1	0	-5.585167	2.606476	-3.622459

94	1	0	3.168171	2.348984	-2.496052	101	1	0	8.764289	6.888328	1.479282
95	1	0	-3.301278	2.174236	-2.486080	102	1	0	-8.116550	2.758027	-0.600450
96	1	0	7.945504	3.147903	-0.593853	103	1	0	-10.044376	4.246430	0.380891
97	1	0	6.711553	3.750550	-2.716681	104	1	0	-9.106943	6.454424	1.476627
98	1	0	6.426515	2.020092	-2.501579						
99	1	0	5.432785	2.934127	-3.637088	The total electronic energy was calculated to be –4877.29067834 Hartree.					
100	1	0	9.802329	4.721133	0.392414						

Table S5. Optimized structure of 1,4-bis(4’-methylthiophen-2’-yl)naphthalene) (B3LYP/6-31G(d))

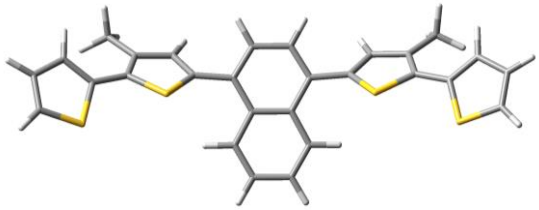


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.703298	-1.461714	0.250528
2	6	0	0.703345	-1.461695	0.250517
3	6	0	1.430495	-0.303674	0.029426
4	6	0	0.719836	0.913284	-0.257943
5	6	0	-0.719852	0.913266	-0.257921
6	6	0	-1.430475	-0.303708	0.029456
7	6	0	-2.903588	-0.392607	0.085359
8	6	0	2.903608	-0.392557	0.085312
9	6	0	1.395789	2.118220	-0.593964
10	6	0	0.705443	3.269892	-0.898033
11	6	0	-0.705554	3.269875	-0.897998
12	6	0	-1.395855	2.118184	-0.593903
13	6	0	3.700420	-1.294607	-0.575571
14	6	0	5.092165	-1.218123	-0.243557
15	6	0	5.330144	-0.246363	0.691028
16	16	0	3.883166	0.581094	1.173198
17	6	0	-3.700430	-1.294498	-0.575697
18	6	0	-5.092173	-1.218037	-0.243655
19	6	0	-5.330115	-0.246457	0.691123
20	16	0	-3.883105	0.580862	1.173452
21	6	0	6.151024	-2.095162	-0.856967
22	6	0	-6.151052	-2.094970	-0.857183
23	1	0	-1.233420	-2.381802	0.477118
24	1	0	1.233491	-2.381769	0.477114
25	1	0	2.478780	2.118573	-0.628808
26	1	0	1.249043	4.174825	-1.155771
27	1	0	-1.249189	4.174797	-1.155706
28	1	0	-2.478849	2.118502	-0.628689
29	1	0	3.298781	-1.993129	-1.303423
30	1	0	6.281754	0.038267	1.121614
31	1	0	-3.298820	-1.992879	-1.303700
32	1	0	-6.281713	0.038115	1.121774
33	1	0	6.190583	-1.971817	-1.946542
34	1	0	7.142497	-1.859910	-0.458098
35	1	0	5.954675	-3.156636	-0.660031
36	1	0	-5.955046	-3.156442	-0.659885
37	1	0	-6.190207	-1.971917	-1.946804
38	1	0	-7.142599	-1.859355	-0.458712

The total electronic energy was calculated to be –1568.1464395 Hartree.

Table S6. Optimized structure of 1,4-bis(4’-methyl-5’-thienylthiophen-2’-yl)naphthalene (B3LYP/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.702765	1.774151	-0.127672
2	6	0	-0.702735	1.774161	-0.127682
3	6	0	-1.431094	0.705853	0.371895
4	6	0	-0.719982	-0.401916	0.953482
5	6	0	0.719965	-0.401933	0.953475
6	6	0	1.431098	0.705827	0.371905
7	6	0	2.901458	0.781233	0.288860
8	6	0	-2.901446	0.781279	0.288821
9	6	0	-1.395215	-1.484075	1.581235
10	6	0	-0.705280	-2.523942	2.162861
11	6	0	0.705227	-2.523968	2.162838
12	6	0	1.395179	-1.484120	1.581200
13	6	0	-3.691350	1.844734	0.654853
14	6	0	-5.082330	1.691726	0.376797
15	6	0	-5.357717	0.481744	-0.236580
16	16	0	-3.889501	-0.454091	-0.467258
17	6	0	3.691367	1.844630	0.655045
18	6	0	5.082352	1.691636	0.376996
19	6	0	5.357732	0.481731	-0.236533
20	16	0	3.889497	-0.454051	-0.467358
21	6	0	-6.106393	2.727427	0.758223
22	6	0	6.106424	2.727268	0.758585
23	6	0	-6.639767	-0.049894	-0.670154
24	6	0	6.639777	-0.049878	-0.670155
25	6	0	-7.708002	0.618984	-1.229740
26	6	0	-8.817480	-0.223825	-1.527316
27	6	0	-8.593810	-1.533400	-1.202386
28	16	0	-7.022400	-1.759301	-0.505989
29	16	0	7.022370	-1.759314	-0.506195
30	6	0	8.593794	-1.533361	-1.202543
31	6	0	8.817498	-0.223751	-1.527308
32	6	0	7.708034	0.619045	-1.229645
33	1	0	1.231995	2.607980	-0.578699
34	1	0	-1.231944	2.607991	-0.578730
35	1	0	-2.477900	-1.476022	1.618432
36	1	0	-1.249492	-3.335066	2.638855
37	1	0	1.249424	-3.335119	2.638802
38	1	0	2.477866	-1.476104	1.618361
39	1	0	-3.284766	2.719578	1.153091
40	1	0	3.284784	2.719420	1.153379
41	1	0	-5.804334	3.251015	1.671834
42	1	0	-6.227785	3.488734	-0.024356
43	1	0	-7.088020	2.275761	0.929879
44	1	0	5.804374	3.250707	1.672284
45	1	0	7.088049	2.275568	0.930161
46	1	0	6.227815	3.488703	-0.023869
47	1	0	-7.682005	1.678926	-1.454053
48	1	0	-9.738202	0.131107	-1.977873
49	1	0	-9.255014	-2.379759	-1.331476
50	1	0	9.254981	-2.379719	-1.331731
51	1	0	9.738236	0.131217	-1.977806
52	1	0	7.682065	1.679016	-1.453830

The total electronic energy was calculated to be –2671.7709505 Hartree.

9. References

(1) Sheldrick, G. M. *SHELX-97*; University of Gӧttingen: Gӧttingen, Germany, 1997.