Synthesis and Complexation Study of New ExTTF-Based Hosts for Fullerenes

Supporting Information

Hassan Iden, Jean-François Morin* and Frédéric-Georges Fontaine*

jean-francois.morin@chm.ulaval.ca, frederic.fontaine@chm.ulaval.ca

a) Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada, G1V 0A6

b) Centre de Recherche sur les Matériaux Avancés (CERMA), Université Laval

c) Centre de Catalyse et Chimie Verte (C3V), Université Laval
General

All solvents (ACS grade) were distilled and put through a Vacum Atmosphere Company (CA, USA) solvent purification system. All the reagents were purchased from Sigma Aldrich Co., TCI America or Oakwood Products and used as received. All reactions were carried out under an atmosphere of argon with freshly distilled solvents, unless otherwise noted. Microwave heating was performed in the single-mode microwave cavity of a Monowave 300 (Anton Paar Co.), and all microwave-irradiated reactions were conducted in a heavy-walled glass vials sealed with Teflon septa. Silica gel (SiliaFlash ® P-60) was used for column chromatography. NMR spectra were recorded at 25 °C on Brucker 400 and 500 MHz instruments and calibrated with tetramethylsilane (TMS) as an internal reference. Mass spectra were performed by the Mass Spectrometry Facilities at Laval University.

Synthesis and characterization of organic compounds

![Bis((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methyl) isophthalate](image)

Compounds 1 was prepared according to previously reported synthetic procedures in 84% yield. 1H NMR (400 MHz, CDCl3) δ ppm 8.86 (m, 1H), 7.79 (m, 2H), 7.68 (s, 1H), 7.68-7.63 (m, 5H), 7.52 (t, J = 7.8 Hz, 1H), 7.31 (m, 2H), 7.27-7.24 (m, 6H), 5.41 (d, J = 3.8 Hz, 4H), 6.24 (s, 4H), 6.16 (d, J = 6.8 Hz, 4H). 13C NMR: 165.5, 135.6, 135.1, 135.0, 135.0, 134.2, 133.8, 132.7, 131.1, 130.6, 128.7, 126.3, 125.9, 125.8, 125.72, 125.60, 125.2, 123.21, 123.1, 120.9, 66.7. m/z [M+H]+ calcd for C50H31O4S8 950.9983 found 950.9981. (Fernández, G.; Pérez, E. M.; Sánchez, L.; Martín, N. Angew. Chem. Int. Ed. 2008, 47, 1094.).
Benzo[d][1,3]dithiole-2-thione 7

1,2 Benzenedithiol (3.7 g, 26 mmol) was suspended in dry pyridine (100 mL) and carbon disulfide (20 mL) was added over a period of 5 minutes and stirred for 4 hours at room temperature. Solvent was removed under reduced pressure and the crude material purified by precipitation in hexanes, dried under high vacuum to yield the desired product 1 as a yellow solid (3.7g, 77%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.41-7.37 (m, 2H), 7.48 (m, 2H). $^{13}$C NMR: 212.2, 141.3, 127.6, 122.0. (Richter, A. M.; Beye, N.; and Fanghänel, E., Synthesis 1990, 1990, 1149-1151).

((9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)methoxy)(tert-butyl)dimethylsilane 10

To a solution of dimethyl 1,3-dithiol-2-yl-phosphonate (4.4 mmol) in dry THF (30 ml) at -78 °C and under argon atmosphere, n-BuLi (1.6 M, 12.6 mmol) was added. After 0.5 h, 2-(tert-butyldimethylsilyloxy)methyl)-anthraquinone (3.00 g, 11.4 mmol) suspended in dry THF (15 ml) was added with a syringe into the solution of the phosphonate carbanion. The mixture was stirred for 1 h at -78 °C then allowed to warm to room temperature before it was left to stand overnight. The THF was evaporated under reduced pressure, water (75 ml) was added and the residue extracted with CH$_2$Cl$_2$ (3 X 50 ml). The combined organic layers were dried (MgSO$_4$),
filtered and the solvent removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel with 10% EtOAc/hexanes to yield the desired product 10 as a yellow solid (75%, 2.1 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 7.78-7.72 (m, 3H), 7.70 (d, J = 7.9 Hz, 1H), 7.39-7.34 (m, 2H), 7.32-7.28 (m, 1H), 7.19 (m, 4H), 7.09-7.03 (m, 4H), 4.92-4.78 (m, 2H), 1.03-0.99 (s, 9H), 0.21-0.15 (s, 6H). <sup>13</sup>C NMR: 140.0, 135.5, 135.5, 135.4, 134.2, 132.3, 131.7, 126.5, 125.9, 125.9, 125.7, 124.0, 123.5, 121.2, 121.1, 65.1, 26.3, 18.7. m/z [M+H]<sup>+</sup> calcd for C<sub>35</sub>H<sub>33</sub>OS<sub>4</sub>Si 625.1178 found 625.1154.

In a 50 ml round bottom flask, 5% HCl (1 mL) was added to a solution of 10 (1.25 g, 2.00 mmol) in THF (8 mL)/MeOH (1 mL) and stirred at room temperature for 3 hours. After reaction completion as monitored by TLC, the crude mixture was poured onto 250 ml of methanol and the precipitate was filtered, washed with methanol and dried under high vacuum to provide the desired product 11 (1.00 g, 98%) as a bright yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm 7.79-7.71 (m, 4H), 7.37 (m, 3H), 7.23-7.16 (m, 4H), 7.09-7.05 (m, 4H), 4.81 (d, J = 5.7 Hz, 2H), 1.85 (br t, 1H). <sup>13</sup>C NMR: 139.1, 135.6, 135.2, 135.1, 135.1, 135.0, 134.7, 132.3, 132.0, 126.3, 125.9, 125.7, 125.6, 124.8, 124.2, 123.51, 123.49, 120.9, 65.3. m/z [M+H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>19</sub>OS<sub>4</sub> 511.0313 found 511.0319.
bis((9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methyl) isophthalate 2

N-(3-Dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC) (0.053 g, 0.275 mmol) was added portionwise to a previously cooled solution (0 °C) of (9,10-di(benzo[d][1,3]dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methanol (0.127 g, 0.25 mmol), isophthalic acid (0.021 g, 0.125 mmol) and 4-dimethylaminopyridine (DMAP) (0.034 g, 0.275 mmol) in dry dichloromethane (5 mL) under argon atmosphere. The mixture was allowed to warm up to room temperature and stirred overnight. After evaporation of the solvent under reduced pressure the residue was purified by column chromatography (CHCl₃/hexanes, 8/2) affording 2 as a yellow solid (0.1 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ ppm 8.93 (m, 1H), 8.36 (dd, J = 7.8, 1.7 Hz, 2H), 7.83 (m, 2H), 7.75-7.67 (m, 6H), 7.58 (t, J = 7.8 Hz, 1H), 7.45-7.39 (m, 2H), 7.38-7.31 (m, 4H), 7.20-7.13 (m, 6H), 7.11-7.08 (m, 2H), 7.07-6.99 (m, 8H), 5.52-5.42 (m, 4H). ¹³C NMR: 165.5, 135.6, 135.2, 135.2, 135.1, 135.0, 134.7, 134.2, 133.8, 132.7, 130.6, 128.7, 126.3, 125.8, 125.7, 125.6, 125.2, 123.2, 123.1, 120.9, 66.7. m/z [M+H]⁺ calcd for C₆₆H₃₉O₄S₈ 1151.0609 found 1151.0591.

2-azidoanthracene-9,10-dione 14

To a mixture of 2-aminoanthracene-9,10-dione (2.23 g, 10.0 mmol) in AcOH (9.2 mL) and concentrated H₂SO₄ (4.3 mL) was added sodium nitrite (0.70 g, 10 mmol) in water (5 mL)
dropwise under vigorous stirring at 0-5 °C. After 10 min, aqueous urea was added to the reaction mixture to remove excess sodium nitrite. Then sodium azide (7.70 g, 118 mmol) in water (50 mL) was added to the reaction mixture at 0-5 °C for 3 h. The reaction mixture was poured into ice water and the resulting mixture was basified with sodium hydroxide and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated to give the corresponding crude azide 14, which was purified by column chromatography (DCM/hexanes, 6/4) to yield pure azide (36%, 0.90 g) as a off-white solid. \(^1^H\) NMR (400 MHz, \(CDCl_3\)) \(\delta\) ppm 7.36-7.33 (m, 1H), 8.29 (m, 3H), 7.90-7.88 (m, 1H), 7.82-7.78 (m, 2H). \(^1^3^C\) NMR: 182.7, 182.0, 146.7, 135.3, 134.6, 134.3, 133.7 133.5, 130.3, 129.8, 127.5, 127.51, 124.6, 117.0.

![Chemical Structure](image)

**2-(2-azido-10-(1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidene)-1,3-dithiole 16**

Method A: Compound 16 was prepared according to the reported synthetic procedures described for compound 10 in 13% yield. Method B: To a solution of triazene 18 (0.48 g, 1.0 mmol) and KHSO\(_4\) (1.36 g, 10.0 mmol) in CH\(_2\)Cl\(_2\)/H\(_2\)O (16/8 mL) was added NaN\(_3\) (0.33 g, 5.0 mmol) at room temperature. The reaction mixture was stirred vigorously 3 days at room temperature. The biphasic mixture was poured onto 100 ml of methanol and the precipitate was filtered, washed with methanol and dried under high vacuum to give the pure product 16 (0.30 g, 71%) as a brown-yellow solid. \(^1^H\) NMR (500 MHz, \(CDCl_3\)) \(\delta\) ppm 7.72-7.68 (m, 3H), 7.37 (d, \(J = 2.3\) Hz, 1H), 7.31-7.29 (m, 2H), 6.95 (dd, \(J = 8.3, 2.3\) Hz, 1H), 6.32 (s, 2H), 6.31 (s, 2H). \(^1^3^C\) NMR: 137.4, 137.1, 135.5, 135.3, 135.0, 132.5, 126.4, 126.1, 124.9, 121.4, 121.2, 117.3, 117.3, 117.1, 116.2, 115.6 \(m/z\) [M+H]\(^+\) calcd for C\(_{20}\)H\(_{11}\)N\(_3\)S\(_4\) 420.983 found 420.9805.
2-(2-(pyrrolidin-1-yl)diazenyl)anthracene-9,10-dione 17

A solution of 2-aminoanthraquinone (1.11g, 5.0 mmol) in 2 mL of conc. HCl was cooled in an ice bath while a solution of NaNO₂ (0.35 mg, 5.25 mmol) in cold water (20 mL) was added dropwise. The resulting solution of the diazonium salt was stirred at 0 °C for 30 min and then added at once to a solution of pyrrolidine (710 mg g, 10 mmol) and K₂CO₃ (3.45 g, 25 mmol) in 1:2 acetonitrile/water (25 mL). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The organic layer was washed twice with brine, dried over MgSO₄, filtered, and concentrated by evaporation. The crude product was purified by flash chromatography over silica gel using EtOAc/hexanes (2/8) giving the pure product as a brown-yellow solid in 60% yield. ¹H NMR (500 MHz, CDCl₃) δ ppm 8.31-8.26 (m, 2H), 8.25 (m, 2H), 7.78-7.72 (m, 3H), 4.00 (t, J = 6.1 Hz, 2H), 3.72 (t, J = 6.2 Hz, 2H), 2.07 (m, 4H). ¹³C NMR: 183.4, 182.473, 156.1, 134.5, 133.8, 133.7, 133.5, 129.7, 128.7, 127.0, 125.6, 51.6, 46.8, 23.8, 23.5. m/z [M+H]+ calcd for C₁₈H₁₆N₅O₂ 307.1268 found 307.1286. (See Liu, C.-Y.; Knochel, P. Org. Lett. 2005, 7, 2543.)

(5E)-1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-3-yl)-2-(pyrrolidin-1-yl)diazene 18

Compound 18 was prepared according to the reported synthetic procedures described for compound 10 in 70% yield. ¹H NMR (500 MHz, DMSOd₆) δ ppm 7.66-7.60 (m, 3H), 7.58 (d, J = 8.3 Hz, 1H), 7.37-7.31 (m, 2H), 7.27 (m, 1H), 6.74-6.69 (m, 4H), 3.98-3.77 (m, 2H), 3.56 (br d, 2H), 1.97 (br s, 4H). ¹³C NMR: 149.6, 137.0, 136.1, 135.8, 135.4, 135.3, 132.0, 126.8, 126.8,
125.4, 121.5, 121.4, 118.8, 118.7, 116.5, 79.8, 23.8. \( m/z \) [M+H]\(^+\) calcd for \( C_{24}H_{20}N_3S_4 \) 479.0562 found 479.0554.

**1,3-bis(prop-2-ynyloxy)benzene 19**

A mixture of resorcinol (3.0 mmole, 0.33g), propargyl bromide (9.0 mmole, 1.070g) and anhydrous potassium carbonate (4.14g, 30 mmole) in dry acetone (40 ml) was refluxed for 12 h. The reaction mixture was cooled and diluted with 500 ml of water and extracted thoroughly with DCM (3x15 mL). The organic layer was washed with 10% sodium hydroxide, water and dried over \( \text{MgSO}_4 \), filtered, and concentrated by evaporation. The residue was purified by silica gel column chromatography to yield the desired product 7 as a clear oil (0.35 g, 56%). \(^1\)H NMR (500 MHz, \( \text{CDCl}_3 \)) \( \delta \) ppm 7.25-7.20 (m, 1H), 6.66-6.62 (m, 3H), 4.69 (s, 2H), 4.67(s, 2H), 2.56-2.52 (m, 2H). \(^{13}\)C NMR: 158.7, 129.9, 107.9, 102.4, 78.4, 75.6, 55.8. API \( m/z \) [M+H]\(^+\) calcd for \( C_{7}H_{4}S_{3} \) 187.0754 found 187.0745.

**1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)-4-((3-((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-7-yl)-1H-1,2,3-triazol-4-yl)methoxy)phenoxy)methyl)-1H-1,2,3-triazole 3**

To a 5 mL flask charged with \( \text{Et}_3\text{N} \) (5.5 \( \mu \)L, 0.04 mmol), azide 16 (92 mg, 0.22 mmol), DMSO (1.5 mL) and CuI (2 mg, 0.01 mmol) were added into the mixture under \( \text{N}_2 \) atmosphere. The
flask was charged with acetylene (0.1 mmol, 19 mg) and then the mixture was stirred under a pressure of nitrogen at room temperature. After 2 days, the mixture was diluted with 25 mL of EtOAc and washed with 20 mL of H2O four times then with brine. The organic phase dried over anhydrous Na2SO4. After removal of the solvent under reduced pressure, the residue was purified on SiO2 with DCM-hexanes (6:4) to yield the desired product as an orange-yellow solid in 41% yield. 1H NMR (500 MHz, CDCl3) δ ppm 8.07 (s, 2H), 7.98 (br s, 2H), 7.75-7.70 (m, 2H), 7.69-7.65 (m, 4H), 7.56 (m, 2H), 7.31-7.26 (m, 5H), 6.80-6.76 (m, 1H), 6.69 (dd, J = 8.2, 2.3 Hz, 2H), 6.30-6.23 (m, 8H), 5.31 (s, 4H). 13C NMR: 159.4, 144.7, 138.1, 137.5, 136.9, 135.8, 135.0, 134.8, 134.1, 130.2, 126.2, 125.0, 124.9, 121.0, 120.8, 120.6, 117.6, 117.5, 117.3, 117.2, 117.1, 116.8, 107.9, 102.2, 62.0. m/z [M+H]+ calcd for C52H33N6O2S8 1029.0425 found 1029.0389.

1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-4-((3,5-bis((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-1H-1,2,3-triazol-4-yl)methoxy)phenoxy)methyl)-1H-1,2,3-triazole 5

1,3,5-tris(prop-2-ynyloxy)benzene (19 mg, 1 equiv), compound 16 (134 mg, 4.0 equiv), CuI (4 mg, 0.33 equiv), and N-ethylidioiso- propylamine (0.068 mL, 6 equiv) were dissolved in 3 mL of DMF in an 10 mL glass vial equipped with magnetic stirring bar. The mixture was then irradiated for 1 h at 80 °C using microwave irradiation. After cooling, the mixture was dissolved in CH2Cl2, washed with water and brine. The organic extract was dried (MgSO4), concentrated, and then purified by column chromatography (SiO2, MeOH/CH2Cl2, 5/95 ) to yield a yellow solid (60% yield). 1H NMR (400 MHz, DMSOδ6) δ ppm 8.98 (s, 3H), 8.18 (s, 3H), 7.86-7.78 (m, 6H), 7.71-7.63 (m, 6H), 7.39-7.33 (m, 6H), 6.76 (m, 12H), 6.48 (s, 3H), 5.25 (s, 6H). 13C NMR: 159.9, 143.9, 138.7, 138.1, 136.1, 134.8, 134.5, 133.9, 126.5, 126.1, 124.8, 122.9, 119.6, 118.4, 117.7, 116.2, 109.4, 79.2. m/z [M+H]+ calcd for C75H46N9O3S12 1504.0367 found 1504.0386.
1,3,5-tribromo-2,4,6-tris(prop-2-ynyloxy)methyl)benzene 21

1,3,5-tribromo-2,4,6 tris (hydroxymethyl)benzene (200 mg, 0.5 mmol) was added in portions to a suspension of NaH (70 mg, 1.75 mmol, 60% in mineral oil) in DMF (3 mL) at 0°C. After 30 minutes, propargyl bromide (297 mg, 2.5 mmol) was added and the resulting mixture was stirred at room temperature overnight. The mixture was poured onto ice and then diluted by DCM (30 mL) and washed by HCl 1N (30 mL) and dried on MgSO₄. The reaction mixture was then concentrated to obtain the desired compound (160 mg, 56%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.30 (s, 3H), 4.61 (s, 6H), 4.19 (t, J = 2.4 Hz, 6H), 2.50-2.41 (m, 3H). ¹³C NMR: 137.9, 127.1, 79.5, 74.8, 71.2, 57.3. API m/z M⁺ calcd for C₁₈H₁₈O₃ 282.125 found 282.1242.

1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-4-((3,5-bis(((1-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)-1H-1,2,3-triazol-4-yl) methoxy) methyl) benzyloxy)methyl)-1H-1,2,3-triazole 6

The product was prepared according to the procedure described for compound 5 with the following exception, 1,3,5-tris(prop-2-ynyloxy)benzene was replaced for 1,3,5-tris((prop-2-
ynyloxy)methyl)benzene. Product was purified by column chromatography (39% yield). 

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ ppm 8.03 (s, 3H), 7.92 (s, 3H), 7.72-7.57 (m, 9H), 7.57-7.50 (m, 3H), 7.40 (s, 3H), 7.26-7.20 (m, 6H), 6.29-6.16 (m, 12H), 4.78 (s, 6H), 4.69 (s, 6H). 

$^{13}$C NMR: 145.7, 138.4, 137.4, 136.7, 135.6, 134.9, 134.1, 126.9, 126.2, 124.9, 124.8, 120.8, 120.5, 117.5, 117.3, 117.2, 116.6, 72.3, 63.6. 

$m/z$ [M+H]$^+\text{calcd for C}_{78}H_{51}N_{9}O_{3}S_{12}$ 1546.0786 found 1546.0898.

---

2-(2-((3-bromophenoxy)methyl)-10-(1,3-dithiol-2-ylidene)anthracen-9(10H)-ylidene)-1,3-dithiole 23

A 50 mL round-bottomed flask was charged with triphenylphosphine (PPh$_3$) (1.57 g, 6.0 mmol), and THF (12 mL). The flask is immersed in an ice bath and diethyl azodicarboxylate (1.04 g, 6 mmol) was added dropwise. Upon completion of the addition, the solution was allowed to stir at 0 °C for 15 min. Alcohol 22 (1.64 g, 4.0 mmol) and 3-bromophenol (0.69 g, 4.0 mmol) were then added and the mixture was allowed to stir for further 18 hours at room temperature. Excess solvent was removed under reduced pressure. The resulting solid was suspended in 100 mL of isopropanol, the resulting yellow solid was filtered under vacuum and the filter cake was washed with isopropanol. The solid was purified by flash chromatography and eluted with 40% DCM-hexanes to yield 1.0 g (44%) of pure ether 23 as a yellow solid. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ ppm 7.74 (br d, 1H), 7.73-7.68 (m, 3H), 7.33-7.29 (m, 3H), 7.21-7.19 (m, 1H), 7.17-7.13 (m, 1H), 7.12-7.09 (m, 1H), 6.93 (m, 1H), 6.29 (d, $J = 2.0$ Hz, 2H), 6.29 (s, 2H), 6.28 (br m, 2H), 5.11 (s, 2H). $^{13}$C NMR: 159.4, 135.9, 135.7, 135.2, 135.1, 134.0, 130.6, 126.0, 125.2, 124.9, 124.88, 124.8, 124.0, 123.9, 122.8, 121.8, 121.7, 118.3, 117.2, 117.1, 113.9, 70.0. $m/z$ [M+H]$^+\text{calcd for C}_{27}H_{18}BrOS_4$ 564.9418 found 564.9414.
2-(3-((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 24

A flask charged with palladium acetate (7 mg, 0.03 mmol), X-phos (29 mg, 0.06 mmol), KOAc (550 mg, 5.6 mmol), and bis-pinacolatodiboron (400 mg, 1.575 mmol) was flushed with nitrogen. Dioxane (5 mL) and compound 23 (0.85 g, 1.5 mmol) were then added. After being stirred at 80 °C for 12 h, the product was extracted with DCM, washed with water, and dried over anhydrous magnesium sulfate. Purification on silica gel (DCM/hexanes, 4/6) yields the desired product (0.35 g, 38% yield) as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.78 (br d, , 1H), 7.73-7.67 (m, 3H), 7.50-7.42 (m, 2H), 7.36 (m 1H), 7.32 (m, 1H), 7.30 (m, 2H), 7.14-7.08 (m, 1H), 6.31- (s, 2H), 6.26 (m, 2H) 5.18-5.14 (s, 2H), 1.37 (s, 12H). $^{13}$C NMR: 158.2, 136.0, 135.6, 135.3, 134.9, 134.8, 129.0, 127.4, 125.9, 125.9, 125.1, 124.9, 124.9, 123.9, 121.9, 121.9, 119.9, 118.6, 117.2, 117.1, 117.1, 117.0, 83.8, 69.7, 24.9. m/z [M+H]$^+$ calcd for C$_{33}$H$_{30}$BO$_3$S$_4$ 613.1171 found 613.1188.
3,3′-Di[(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methoxy]biphenyl 4

Product 4 was isolated as side product of Suzuki-cross coupling reaction in 26% yield, purified on silica gel (DCM/hexanes, 4/6). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.77-7.72 (m, 2H), 7.67 (m, 6H), 7.33 (s, 2H), 7.31 (s, 2H), 7.29-7.24 (m, 4H), 7.24-7.15 (m, 4H), 6.98 (br d, 2H), 6.22 (d, $J = 4.2$ Hz, 4H), 6.15 (m 4H), 5.18-5.12 (br s, 4H). $^{13}$C NMR: 159.0, 136.3, 135.7, 135.2, 134.9, 134.6, 129.7, 125.9, 125.2, 124.9, 123.9, 121.7, 119.9, 117.2, 117.1, 114.3, 113.9, 69.8. 

$m/z$ [M+H]$^+$ calcd for C$_{54}$H$_{34}$O$_2$S$_8$ 971.0319 found 971.0398.
Figure S1: Complexation of C\textsubscript{60} by receptor 1 [22 µM] in chlorobenzene

Figure S2: Job’s plot of 1 with C\textsubscript{60} in chlorobenzene at a fixed [1]+[C\textsubscript{60}]=1.1x10\textsuperscript{-5} M
**Figure S3:** Complexation of $C_{60}$ by receptor 1 [12 µM] in toluene

![Graph showing the complexation of $C_{60}$ by receptor 1 in toluene. The graph includes a Job's plot with a Ka value of 667 M$^{-1}$ and a R$^2$ of 0.997.]

**Figure S4:** Job’s plot of 1 with $C_{60}$ in toluene at a fixed [1]+[C$_{60}$]=1.1x10$^{-5}$ M

![Graph showing the Job’s plot for the complexation of 1 with $C_{60}$ in toluene. The plot includes a linear fit with the Ka and R$^2$ values as indicated.]
**Figure S5:** Complexation of C\textsubscript{60} by receptor 1 [11 µM] in DCM/toluene 1:2

![Complexation of C\textsubscript{60} by receptor 1](image)

**Figure S6:** Job’s plot of 1 with C\textsubscript{60} in DCM/toluene 1:2 at a fixed [1]+[C\textsubscript{60}]=1.1x10\textsuperscript{-5} M

![Job’s plot of 1 with C\textsubscript{60}](image)
**Figure S7:** Complexation of C$_{60}$ by receptor 1 [11 µM] in CS$_2$

**Figure S8:** Job’s plot of 1 with C$_{60}$ in CS$_2$ at a fixed [1]+[C$_{60}$]=1.1x10$^{-5}$ M
**Figure S9:** Complexation of C$_{70}$ by receptor 1 [11 µM] in chlorobenzene

![Graph showing absorbance vs. wavelength for different concentrations of C$_{70}$]

**Figure S10:** Job’s plot of 1 with C$_{70}$ in chlorobenzene at a fixed [1]+[C$_{70}$]=1.75x10$^{-5}$ M

![Graph showing absorbance difference vs. [Host]/[Host]+[C$_{70}$]]
**Figure S11:** Job’s plot of 3 with C$_{60}$ in chlorobenzene at a fixed [3]+[C$_{60}$]=1.1x$10^{-5}$ M

![Job's plot](image)

**Figure S12:** Complexation of C$_{60}$ by receptor 3 [22 µM] in chlorobenzene (305.5 K)

![Complexation plot](image)

$K_a = 343$ M$^{-1}$

$R^2 = 0.999$
**Figure S13:** Complexation of C$_{60}$ by receptor 3 [22 µM] in chlorobenzene (315.5 K)

![Graph showing complexation of C$_{60}$ by receptor 3](image)

$K_a = 285 \text{ M}^{-1}$  
$R^2 = 0.999$

0 eq. C$_{60}$  
115 eq. C$_{60}$

**Figure S14:** Complexation of C$_{60}$ by receptor 3 [22 µM] in chlorobenzene (325.5 K)

![Graph showing complexation of C$_{60}$ by receptor 3](image)

$K_a = 254 \text{ M}^{-1}$  
$R^2 = 0.999$

0 eq. C$_{60}$  
115 eq. C$_{60}$
Thermodynamic parameters

![Graph showing Van’t Hoff plots of the Host 3-C\textsubscript{60} complexes in chlorobenzene](image)

**Figure S15**: Van’t Hoff plots of the Host 3-C\textsubscript{60} complexes in chlorobenzene

**Table S1**: Thermodynamic parameters of the Host 3-C\textsubscript{60} complexes in chlorobenzene

<table>
<thead>
<tr>
<th>Complexes</th>
<th>( \Delta H ) (Kcal/mol)</th>
<th>( \Delta S ) (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host 3-C\textsubscript{60}</td>
<td>-2.95</td>
<td>1.89</td>
</tr>
</tbody>
</table>
**Figure S16:** Complexation of C$_{60}$ by receptor 3 [22 µM] in toluene

**Figure S17:** Job’s plot of 3 with C$_{60}$ in toluene at a fixed [3]+[C$_{60}$]=1.1x10$^{-5}$ M
Figure S18: Complexation of C$_{60}$ by receptor 3 [22 µM] in DCM/toluene 1:2

Figure S19: Job’s plot of 3 with C$_{60}$ in DCM/toluene 1:2 at a fixed [3]+[C$_{60}$]=1.1x10$^{-5}$ M
Figure S20: Complexation of C$_{60}$ by receptor 3 [11 µM] in CS$_2$

![Figure S20: Complexation of C$_{60}$ by receptor 3 [11 µM] in CS$_2$]

Figure S21: Job’s plot of 3 with C$_{60}$ in CS$_2$ at a fixed [3]+[C$_{60}$]=1.1x10$^{-5}$ M

![Figure S21: Job’s plot of 3 with C$_{60}$ in CS$_2$ at a fixed [3]+[C$_{60}$]=1.1x10$^{-5}$ M]
Figure S22: Job’s plot of 3 with C70 in chlorobenzene at a fixed [3]+[C70]=1.75x10^{-5} M

Figure S23: Complexation of C60 by receptor 4 [16 µM] in chlorobenzene
**Figure S24:** Job’s plot of 4 with C\textsubscript{60} in chlorobenzene at a fixed [4]+[C\textsubscript{60}]=1.75x10\textsuperscript{-5} M

![Job's plot](image)

**Figure S25:** Complexation of C\textsubscript{60} by receptor 4 [16 µM] in toluene/DCM 2/1

![Complexation plot](image)
Figure S26: Job’s plot of 4 with C₆₀ in toluene/DCM 2/1 at a fixed [4]+[C₆₀]=1.75x10⁻⁵ M

![Graph showing the Job's plot](image)

Figure S27: Complexation of C₆₀ by receptor 4 [16 µM] in CS₂

![Graph showing complexation](image)
**Figure S28:** Job’s plot of 4 with C$_{60}$ in CS$_2$ at a fixed [4]+[C$_{60}$]=1.75x10$^{-5}$ M

![Figure S28: Job’s plot of 4 with C$_{60}$ in CS$_2$ at a fixed [4]+[C$_{60}$]=1.75x10$^{-5}$ M](image1)

**Figure S29:** Complexation of C$_{70}$ by receptor 4 [16 µM] in chlorobenzene

![Figure S29: Complexation of C$_{70}$ by receptor 4 [16 µM] in chlorobenzene](image2)
Figure S30: Job’s plot of 4 with C$_{70}$ in chlorobenzene at a fixed [4]+[C$_{70}$]=1.75x10$^{-5}$ M
**Figure S31:** $^1$H NMR spectrum of compound 1 (400 MHz, $CDCl_3$)

**Figure S32:** $^{13}$C{$^1$H} NMR spectrum of compound 1 (400 MHz, $CDCl_3$)
Figure S33: $^1$H NMR spectrum of compound 2 (400 MHz, CDCl$_3$)

Figure S34: $^{13}$C{$^1$H} NMR spectrum of compound 2 (400 MHz, CDCl$_3$)
Figure S35: $^1$H NMR spectrum of compound 3 (500 MHz, CDCl$_3$)

Figure S36: $^{13}$C{$^1$H} NMR spectrum of compound 3 (500 MHz, CDCl$_3$)
Figure S37: $^1$H NMR spectrum of compound 4 (500 MHz, CDCl$_3$)

Figure S38: $^{13}$C\{$^1$H\} NMR spectrum of compound 4 (500 MHz, CDCl$_3$)
Figure S39: $^1$H NMR spectrum of compound 5 (400 MHz, DMSOd$_6$)

Figure S40: $^{13}$C$^1$H NMR spectrum of compound 5 (500 MHz, DMSOd$_6$)
Figure S41: $^1$H NMR spectrum of compound 6 (400 MHz, CDCl$_3$)

Figure S42: $^{13}$C{$^1$H} NMR spectrum of compound 6 (400 MHz, CDCl$_3$)
Figure S43: $^1$H NMR spectrum of compound 7 (400 MHz, CDCl$_3$)

Figure S44: $^{13}$C{$^1$H} NMR spectrum of compound 7 (400 MHz, CDCl$_3$)
Figure S45: $^1$H NMR spectrum of compound 10 (400 MHz, CDCl$_3$)

Figure S46: $^{13}$C{$^1$H} NMR spectrum of compound 10 (400 MHz, CDCl$_3$)
Figure S47: $^1$H NMR spectrum of compound 11 (500 MHz, $CDCl_3$)

Figure S48: $^{13}$C{$^1$H} NMR spectrum of compound 11 (500 MHz, $CDCl_3$)
Figure S49: $^1$H NMR spectrum of compound 14 (400 MHz, CDCl$_3$)

Figure S50: $^{13}$C{$^1$H} NMR spectrum of compound 14 (400 MHz, CDCl$_3$)
Figure S51: $^1$H NMR spectrum of compound 16 (500 MHz, $CDCl_3$)

Figure S52: $^{13}$C{$^1$H} NMR spectrum of compound 16 (500 MHz, $CDCl_3$)
Figure S53: $^1$H NMR spectrum of compound 17 (500 MHz, CDCl$_3$)

Figure S54: $^{13}$C{$^1$H} NMR spectrum of compound 17 (500 MHz, CDCl$_3$)
Figure S55: $^1$H NMR spectrum of compound 18 (500 MHz, DMSO$_d_6$)

Figure S56: $^{13}$C{$^1$H} NMR spectrum of compound 18 (500 MHz, DMSO$_d_6$)
Figure S57: $^1$H NMR spectrum of compound 19 (500 MHz, $CDCl_3$)

Figure S58: $^{13}$C{$^1$H} NMR spectrum of compound 19 (500 MHz, $CDCl_3$)
Figure S59: $^1$H NMR spectrum of compound 21 (400 MHz, CDCl$_3$)

Figure S60: $^{13}$C{$^1$H} NMR spectrum of compound 21 (400 MHz, CDCl$_3$)
Figure S61: $^1$H NMR spectrum of compound 23 (500 MHz, CDCl$_3$)

Figure S62: $^{13}$C($^1$H) NMR spectrum of compound 23 (500 MHz, CDCl$_3$)
Figure S63: $^1$H NMR spectrum of compound 24 (500 MHz, CDCl$_3$)

Figure S64: $^{13}$C{$^1$H} NMR spectrum of compound 24 (500 MHz, CDCl$_3$)