



## Supporting Information

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## Ordered Self-Assembly and Electronic Behavior of

### **C<sub>60</sub>-Anthrylphenylacetylene Hybrid<sup>\*\*</sup>**

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Buckminsterfullerene (C<sub>60</sub>) was purchased from Bucky USA and used as received. All other reagents purchased from Aldrich were used without further purification unless otherwise indicated. <sup>1</sup>H NMR spectra were recorded on a AF 300 (300 MHz) or a DMS 750 (750 MHz) spectrometer with the solvent proton signal as standard. <sup>13</sup>C NMR spectra were recorded at 188 MHz on the same instrument using the solvent carbon signal as a reference. Mass spectra were recorded on a JEOL HX-110 mass spectrometer.

Synthesis of 10-bromoanthracene-9-ester (**6**). To a solution of *t*-butyl alcohol (20 mmol) and pyridine (30 mmol) in dry CHCl<sub>3</sub> was slowly added 10-bromo-9-anthracene carbonyl chloride (**5**)<sup>[1]</sup> (15 mmol) at room temperature. After the reaction for 2 days at room temperature, the solvent was removed and the residue was extracted with ethyl ether, washed with brine and water. Etheral layer was dried over MgSO<sub>4</sub>, and then was removed to give a crude product. Purification was carried out by silica gel column chromatography eluting with hexane/ethyl acetate = 10/1. Yield 72%. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 8.62 (d, 2H), 7.98 (d, 2H), 7.42-7.73 (m, 4H), 1.91 (s, 9H).

Synthesis of 10-trimethylsilylacetyleneanthracene-9-ester (**7**). In a three-neck flask were charged compound **6** (5 mmol), diisopropylethylamine (5 mL), CuI (3 mol%), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mol%), trimethylsilylacetylene (1 mL) and dry THF (1 mL). This reaction mixture was kept for stirring at room temperature for 4 days. After removing the solvent, ether was added to the residue. The resulting suspension was filtered, and the filtrate was washed with water, brine and then dried over MgSO<sub>4</sub>, and concentrated to give target compound. This crude product can be either further purified by recrystallization from hexane or used without purification. Yield 42%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.64 (d, 2H), 8.06 (d, 2H), 7.42-7.63 (m, 4H), 1.91 (s, 9H), 0.24 (s, 9H).

Synthesis of 10-acetyleneanthracene-9-ester (**8**) For the desilylation, the compound **7** was dissolved in dry  $\text{CH}_2\text{Cl}_2$  and cooled to  $0\text{ }^\circ\text{C}$ . Tetrabutylammonium fluoride (1.5 equiv, 1.0 M in THF) was added, and the reaction mixture was stirred for 3 hours. The reaction mixture was then subjected to an aqueous workup and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . After drying the combined organic layers over  $\text{MgSO}_4$ , the solvent was removed. The crude product was then purified by silica gel column chromatography eluting with hexane/ethyl acetate = 9/1. Yield 95%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (d, 2H), 8.01 (d, 2H), 7.44-7.73 (m, 4H), 3.43 (s, 1H), 1.91 (s, 9H).

Synthesis of 9-(4-thioesterphenyl)acetyleneanthracene-10-ester (**1**). The mixture of compound **8** (2.0 mmol), 4-iodophenylthioester<sup>[2]</sup> (2.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol%), and diisopropylethylamine (20 mL) was heated at reflux overnight under nitrogen. After removing the solvent,  $\text{CH}_2\text{Cl}_2$  was added to the residue. The resulting suspension was filtered, and the filtrate was washed with water, brine and then dried over  $\text{MgSO}_4$ , and concentrated. This crude was further purified by silica gel column chromatography eluting with hexane/ $\text{CH}_2\text{Cl}_2$  = 9/1. Yield 38%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (d, 2H), 8.01 (d, 2H), 7.44-7.73 (m, 4H), 7.32 (d, 2H), 7.08 (d, 2H) 2.43 (s, 3H), 1.91 (s, 9H).

Synthesis of MPAA- $\text{CO}_2\text{H}$  (**2**). A suspension of **1** (174 mg, 0.38 mmol) in trifluoroacetic acid (1.5 mL), water (0.4 mL), and acetonitrile (3.8 mL) was stirred vigorously at room temperature overnight under a nitrogen atmosphere. The reaction mixture was diluted with water. The mixture was filtered, and washed with water and hexane to afford an orange solid. Yield: 138 mg (91%).  $^1\text{H}$  NMR (750 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.69 (d, 2H), 8.10 (d, 2H), 7.97 (d, 2H), 7.79 (m, 4H), 7.59 (d, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (188 MHz,  $\text{DMSO}-d_6$ ): 193.88, 170.72, 170.53, 135.49, 133.71, 133.58, 133.22, 132.86, 132.21, 129.88, 128.57,

127.79, 127.19, 127.07, 126.63, 124.08, 118.20, 101.88, 87.81, 31.18. MS (FAB)  $m/z = 396.1$  ( $M^+$ ).

Synthesis of  $C_{60}$ -OH (**3**). A solution of  $C_{60}$  (0.500 g, 0.69 mmol), paraformaldehyde (0.104 g, 3.45 mmol), and *N*-(4-hydroxyphenyl)glycine (0.231 g, 1.39 mmol) in toluene (300 mL) was stirred at reflux temperature for 2 h, then the solvent was removed in vacuo. The crude product was purified by flash chromatography eluting with 4:1 toluene/ethyl acetate. Yield: 0.189 g (32%).  $^1H$  NMR (750 MHz,  $CDCl_3$ - $CS_2$  1:1):  $\delta$  7.22 (m, 2H), 7.12 (d, 1H), 6.93 (d, 1H), 5.05 (s, 4H).  $^{13}C$  NMR (188 MHz,  $CDCl_3$ - $CS_2$  1:1): 154.84, 150.63, 147.83, 146.79, 146.59, 146.13, 146.07, 146.07, 145.80, 145.07, 143.63, 143.18, 142.72, 142.60, 142.43, 142.38, 140.79, 137.96, 136.77, 129.53, 128.79, 125.90, 118.82, 116.91, 70.46, 64.76. MS (FAB)  $m/z = 855.4$  ( $M - H^+$ ).

Synthesis of  $C_{60}$ -MPAA (**4**). To a solution of **3** (14.0 mg, 16.4  $\mu$ mol) in benzene (25 mL) was added trifluoroacetic anhydride (0.01 mL, 65.4  $\mu$ mol), and stirred at 40 °C under nitrogen. **2** (6.5 mg, 16.4  $\mu$ mol) was added and the mixture was stirred for 24 h. The reaction mixture was cooled and evaporated. The crude product was purified by flash chromatography eluting with 1:3 hexane/ $CH_2CH_2$ . Yield: 7.1 mg (35%).  $^1H$  NMR (750 MHz,  $CDCl_3$ - $CS_2$  1:1):  $\delta$  8.71 (m, 2H), 8.26 (m, 2H), 7.80 (d, 2H), 7.68 (m, 4H), 7.56 (m, 4H), 7.51 (d, 2H), 5.22 (s, 4H), 2.47 (s, 3H).  $^{13}C$  NMR (188 MHz,  $CDCl_3$ - $CS_2$  1:1): 193.72, 170.48, 153.25, 148.52, 146.51, 146.03, 145.25, 144.93, 144.77, 144.47, 143.71, 142.30, 141.84, 141.36, 141.25, 141.10, 139.47, 135.37, 133.45, 132.33, 131.46, 131.14, 130.86, 128.36, 127.53, 127.22, 124.74, 101.11, 90.13, 68.91, 29.80. MS (FAB)  $m/z = 1234.6$  ( $M + H^+$ ).

The solutions of **4** (50  $\mu$ M) or a mixture of **4** and **MPAA-Ac** (1:9, 50  $\mu$ M) in THF/ethanol (1:10) were prepared, bubbled with nitrogen and ammonium hydroxide (1.0  $\mu$ L

(28.0-30.0% NH<sub>3</sub>) per mL of solution) was added. Then gold substrates were immediately immersed into the solution for 24 h, followed by rinsing with ethanol and drying with a nitrogen stream. Electrochemical experiments were carried out in a single-compartment, three-electrode glass cell. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements were performed on a Nanosurf EasyScan system operated in air at room temperature. Freshly cut Pt-Ir tips (0.2 mm) were used. STM images and STS curves were obtained with typical tip-sample bias voltages of 200 mV and tunneling currents of 100 pA. Average scan rate is 20 Hz and resolution is 512x512. Imaging the relevant surface area before and after the STS measurements is an essential point for measuring reliable STS data in order to exclude tip or sample alterations. The images of the same area reveal no changes before and after STS in our experiments except a small lateral drift of the sample between two scans.

## References

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