# **Electronic Supplementary Information**

## Direct formation of fullerene monolayers using [4+2] Diels-Alder cycloaddition

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#### Experimental

General: Solvents and reagents were obtained from commercial suppliers and used without further purification. Fullerene (99.5%) was obtained from MTR Ltd. And used without further purification. Spectroscopic grade solvents were used for the spectrophotometric measurements. Anhydrous solvents were dried by the usual procedures and used directly. Preparation of all compounds was carried out under an atmosphere of dry nitrogen (except for carboxylic acid derivatives) and in the dark to minimize anthracene photooxidation. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker DPX 300, DPX 400 MHz spectrometer and are referenced in ppm with respect to TMS using the residual solvent signal as internal reference. Steady state fluorescence measurements were recorded on a FL3-22 SPEX spectrofluorometer. Mass spectral analyses were carried out on a VG Autospec Q mass spectrometer. Ellipsometry measurements of the layers were made on silicon wafers and performed on a Nanofilm ellipsometer ( $\lambda = 360 - 900$  nm) assuming a refractive index of 1.5 for the monolayer over the silicon oxide layer. Raster scans were taken over 10 points per silicon wafer and their values averaged. The atomic force microscopy was performed using an Autoprobe CP Research (ThermoMicroscope) instrument equipped with a PPP-NCL tip (Nanosensors) operating in taping mode. Kelvin force probe microscopy and heights profile measurements was performed on an Agilent 5500 instrument equipped with a conducting Cr/Pt tip (Budget Sensor Multi 75E-G, 75 kHz, 3 N/m). Cyclic voltammetry of 6:C60 adduct were performed on a 1mM solution of the adduct in ACN/toluene (50/50, v/v with 0.1M NBu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte) on a 1 mm diameter gold electrode with a scan rate of 0.2 V/s. Contact angles (3 µL water drops) were obtained on a Krüss goniometer (drop shape analysis system DSA 10 Mk2) at 20 °C in static mode. The results correspond to the average of three measurements. The energies of the HOMO and LUMO of 6:C<sub>60</sub> were calculated from the measured reduction potential and the onset of the fluorescence emission in solution.<sup>3</sup> **Substrate Preparation** 

Silicon wafers were washed and successively sonicated in acetone and 2-propanol (twice in each solvent). Substrates were then dried under Ar stream and transferred to a Jelight Company Inc. UVO Cleaner 42 - 220 for surface cleaning for 25 min. Subsequently substrates were immersed into the 3-aminopropyltriethoxysilane (APTES) solution for the formation of amine terminated self assembled monolayer under Ar.

## Silanization

Amine terminated monolayer was prepared following the literature method.<sup>1</sup> NH<sub>2</sub>-monolayer were prepared by immersing clean, dry silicon substrates under Ar into a toluene solution of freshly prepared surfactant APTES (10 mM in dry toluene) in clean 2 mL vials. The vials were capped, placed under vacuum for 45 min at RT. All reactions were carried out under an atmosphere of Ar or vacuum. After the substrates were taken from the solution, it was sonicated with toluene to remove excess silane and avoid polymerization. The substrates were also sonicated with ethanol and dichloromethane to remove physisorbed material. The above cleaning protocol was repeated twice. The NH<sub>2</sub>-monolayers were then dried under Ar stream and kept under an Ar atmosphere.

#### Post modification of the NH<sub>2</sub>-monolayer

The functionalization of amino-terminated monolayers with 1-substituted anthracene was achieved by immersing the NH<sub>2</sub>-monolayer in a 25 mM acetonitrile solution of carbonyl chloride functionalized anthracene derivative, 7 and acetyl chloride in a fixed composition for 48 h at RT. For each solution, 0.1 mL of triethylamine was added to the reaction mixture. All reactions were carried out under an atmosphere of Ar. After the substrates were taken out from the solution they were rinsed and sonicated with CH<sub>3</sub>CN, EtOH, and CH<sub>2</sub>Cl<sub>2</sub> to remove physisorbed material. The anthracene-terminated monolayers were then dried under an Ar stream and kept in dark to avoid photooxidation.

#### 1-Hexyloxyanthraquinone (2)

A solution of 3 g (13.3 mmol) of 1-hydroxyanthraquinone (1), 6 ml of bromohexane (40 mmol) and 3 g (20.7 mmol) of K<sub>2</sub>CO<sub>3</sub> in 50 ml dimethylformamide (freshly distilled over CaH<sub>2</sub>) was heated at 100 °C for overnight under a nitrogen atmosphere. The solution was poured into 300 ml of aqueous solution of NaOH (pH 11). The precipitated was filtered and washed with water. Crystallization of the crude product in CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether gave pure 1-hexyloxyanthraquinone **2** (4.7 g, 91 %). M.p. 100 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.90 (t, 3H, *J* = 5.6 Hz), 1.34-1.39 (m, 4H), 1.53-1.60 (m, 2H), 1.91-1.96 (m, 2H), 4.14 (t, 2H, *J* = 6.7 Hz), 7.30 (d, 1H, *J* = 7.6 Hz), 7.63-7.92 (m, 3H), 8.19 (d, 1H, *J* = 7.5 Hz), 8.24 (dd, 2H, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 7.7 Hz); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  14.0, 22.5, 25.6, 29.1, 31.5, 69.7, 119.1, 119.5, 121.6, 126.5, 127.2, 132.5, 133.0, 134.1, 134.8, 135.1, 135.7, 160, 182.2, 183.6; Elemental analysis calc (%) for C<sub>20</sub>H<sub>20</sub>O<sub>3</sub> C, 77.9; H, 6.5, Found 77.8; 6.1.

#### 1-hexyloxy anthracene (3)

To a suspension of **2** (1.0 mmol) in glacial AcOH (30 mL) was added zinc dust (26 mmol) in one portion. The reaction mixture was refluxed for 12 h. After the reaction was complete (monitored by TLC), the mixture was poured into ice water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was washed with H<sub>2</sub>O and sat. aq solution of NaHCO<sub>3</sub> respectively and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent in vacuum, the residue was purified by column chromatography over silica gel to afford the corresponding 1-hexyloxyanthracene, **3** as a pale green solid. M.p. 65 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.94 (t, 3H, *J* = 7.08 Hz, -CH<sub>3</sub>), 1.39-1.51 (m, 4H), 1.59-1.64 (m, 2H), 1.97-2.02 (m, 2H), 4.19 (t, 2H, *J*= 6.42 Hz), 6.70 (d, 1H, *J* = 7.17 Hz), 7.33 (dd, 1H, *J* = 8.49 Hz), 7.42-7.46 (m, 2H), 7.55 (d, 1H, *J* = 8.49 Hz), 7.97 (d, 1H, *J* = 9.24 Hz), 8.04 (d, 1H, *J* = 9.63 Hz), 8.34 (s, 1H), 8.84 (s, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  14.85, 23.42, 26.79, 30.04, 32.44, 68.99, 103.04, 109.47, 120.92, 121.87, 125.77, 126.16, 126.32, 126.34, 128.65, 129.57, 131.93, 132.69, 133.44, 155.69; Elemental analysis calc (%) for C<sub>20</sub>H<sub>22</sub>O C, 86.3; H, 7.9; Found C, 86.4, H, 7.8.

#### 1-hydroxy anthracene (4)

To a stirred and degassed solution of 1-hexyloxyanthracene, **3** (2.3 g, 8.26 mmol) in  $CH_2Cl_2$  at -70 °C was slowly added BBr<sub>3</sub> (10 mL of 1M solution in  $CH_2Cl_2$ ). The resulting mixture was then stirred at room temperature for 2 h. The mixture was poured into 100 ml of water

and extracted with methylene chloride (100 mL  $\times$  3). After removal of the solvent under reduced pressure the unstable crude 1-hydroxyanthracene, 4 (greenish yellow solid, 100 % yield), was rapidly used without further purification.

## 4-(1-anthryloxy)-butanoic acid (6)

At room temperature 0.31 g (12.5 mmol) of NaH and 1.8 mL (12.7 mmol) of ethyl 4bromobutanoate were consecutively added to a stirred solution of compound 5 (1.65 g, 8.5 mmol) in 20 mL of dry DMF. After addition the mixture was then stirred for 24 h at 70 °C. After the usual workup the residue was purified by flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>). The resultant product (5a) was dissolved in 20 mL of ethanol and 2M NaOH solution of water was added to it. The mixture was stirred at 60 °C for overnight. Ethanol was evaporated by reduced pressure and water was added to the mixture. The solution was neutralized with 2M HCl and extracted with  $CH_2Cl_2$  (3  $\times$  50 mL). The organic phase was dried with anhydrous MgSO<sub>4</sub> and evaporated to dryness. The crude product (1.5 g) was crystallized from ethyl acetate and hexane which affords a pale green solid, 6 (1.3 g, 78 %). M.p. 95 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.17-2.22 (m, 2H), 2.61 (t, 2H, J = 7.24 Hz), 4.14 (t, 2H, J = 6.01 Hz), 6.61 (d, 1H, J = 7.71 Hz), 7.24 (dd, 1H,  $J_1 = 8.49$  Hz,  $J_2 = 8.67$  Hz), 7.34  $(dd, 2H, J_1 = 6.42 Hz, J_2 = 6.6 Hz), 7.47 (d, 1H, J = 8.1 Hz), 7.88 (d, 1H, J = 9.78 Hz), 7.95$ (d, 1H, J = 9.15 H z), 8.26 (s, 1H), 8.71 (s, 1H), 11.31 (s, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ 24.44, 30.92, 66.98, 102.42, 120.37, 120.84, 125.01, 125.17, 125.38, 125.58, 125.68, 127.81, 128.68, 131.17, 131.92, 154.48, 179.17; Elemental analysis calc (%) for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub> C, 77.2; H, 5.7% and Found C, 76.4; H, 5.9%, FAB-MS: m/z calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub> + Na 303.1, Found 303.0998 (M+Na).

## 4-(1-anthryloxy)-butanoyl chloride (7)

To a stirred solution of 4-(1-anthryloxy)-butanoic acid, **6** (70 mg, 0.25 mmol) and dry DMF (cat.) in dry dichloromethane (5 mL) at room temperature was slowly added oxalyl chloride (0.04 mL, 0.5 mmol). The resulting mixture mixture was stirred at room temperature for 6h. Excess solvent was removed under Ar pressure and dried under vacuum. The compound is used as soon as possible without any further characterization.

#### 6:C<sub>60</sub> adduct

The 1:1 adduct of  $C_{60}$  and **6** was prepared by mixing these molecules in toluene under Ar. Thirty milligrams (0.04 mmol) of  $C_{60}$  and 40 mg (0.4 mmol) of **6** were mixed in 30 mL of toluene and stirred at 40 °C for 1 week. After 1 week, the solvent was removed under reduced pressure, and the resulting brown powder was purified by silica-gel column chromatography using toluene/ethyl acetate (9:1) as eluent. After the solvent was removed under nitrogen gas flow, a dark brown powder was obtained (0.018 g, 43.2%).

The anthracene proton signals [ $\delta$  6.61 (d, 1H), 7.24 (dd, 1H), 7.34 (dd, 2H), 7.47 (d, 1H), 7.88 (d, 1H), 7.95 (d, 1H), 8.26 (s, 1H), 8.71 (s, 1H)] of 7 in C<sub>6</sub>D<sub>6</sub> disappeared and new singlet peaks of methine protons appeared at 5.6 and 6.5 ppm respectively and aromatic protons [ $\delta$  6.61 (d, 2H *J* = 7.74 Hz), 7.23 (d, 2H, *J* = 6.4 Hz), 7.35-7.42 (m, 1H), 7.5 (1H, *J* = 8.85 Hz), 7.61 (d, 1H, *J* = 8.67 Hz)] were observed.







**Fig. S4.** <sup>13</sup>C-NMR spectrum of compound **3**.



**Fig. S6.** <sup>13</sup>C-NMR spectrum of compound 6.



Fig. S7. TOF-MS spectrum of compound 6.



**Fig. S8** Cyclic voltammetry of a 1mM solution of **6**:C<sub>60</sub> in ACN/toluene (50/50, v/v) using a 1mm diameter gold electrode. Scan rate 0.2 V/s. Supporting Electrolyte 0.1M NBu<sub>4</sub>PF<sub>6</sub>. (---) background current. Potentials are versus the ferrocene/ferrocenium couple.



Fig. S9 UV-vis spectrum of adduct  $6:C_{60}$  (1.2 × 10<sup>-5</sup> M) in toluene.



Fig. S10. Variation of ellipsometric parameters  $\Delta$  (top) and  $\Psi$ (bottom) with wavelength ( $\lambda$ ). In above figure top, middle and bottom line represents the bank sample (SiO<sub>2</sub>/Si), anthracenemonolayer as well as C<sub>60</sub>-monolayer, respectively.



Fig. S11. Atomic force microscopy image of an anthracene-terminated monolayer (substrate S3) and corresponding height profile at line 1. Image is  $0.5 \times 0.5 \mu m$ .



Fig. S12. Atomic force microscopy image of a fullerene-terminated monolayer (substrate  $S3+C_{60}$ ) and corresponding height profile at line 1. Image is  $0.5\times0.5\mu$ m.



**Fig. S13** Normalized fluorescence emission ( $\lambda_{ex} = 350$  nm) from anthracene-modified substrate S3 (—) and of 6 (- - ) in dichloromethane.



**Fig. S14.** Normalized fluorescence emission ( $\lambda_{ex}$ = 310 nm) of 6:C<sub>60</sub> adduct (red line) in toluene and from a C<sub>60</sub>-SAM (substrate S3+C<sub>60</sub>, black line).



Fig. S15. AFM image (left,  $5 \times 5 \mu m$ ) and height profile (right) of substrate S3 where the organic layer was mechanically removed.



**Fig. S16.** AFM image (left,  $5 \times 5 \mu m$ ) and height profile (right) of substrate S3+C<sub>60</sub> where the organic layer was mechanically removed.



**Fig. S17.** Top: KFPM image (left,  $20 \times 20 \ \mu$ m) and corresponding topography (right) of an area of substrate S3 (the organic layer was mechanically removed in the center area to allow comparison with the surface potential of the bare substrate). Bottom: Profile of the surface potential.



**Fig. S18.** Top: KFPM image (left,  $30 \times 30 \ \mu$ m) and corresponding topography (right) of an area of substrate S3+C<sub>60</sub> (the organic layer was mechanically removed on the right to allow comparison with the surface potential of the bare substrate). Bottom: Profile of the surface potential.

#### References

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