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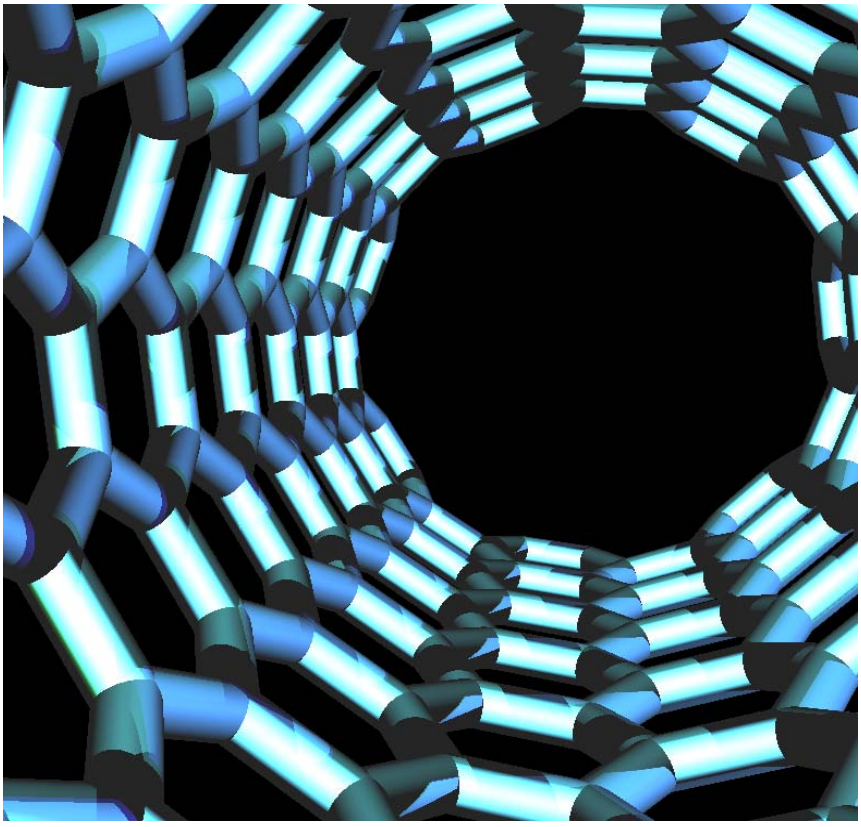
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# Direct formation of fullerene monolayers using [4 + 2] Diels–Alder cycloaddition†‡

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**The formation of covalent $C_{60}$ monolayers through [4 + 2] Diels–Alder cycloaddition between $C_{60}$ and anthracene monolayers grafted onto a silicon oxide surface was investigated by ellipsometry, fluorescence and by atomic force microscopy.**

Enhanced functionality and performance in molecule-based electronic devices will invariably require spatial control of the molecular constituents over multiple length scales, a key step in the design and construction of hierarchically organized molecular assemblies in three dimensions.[1] The controlled grafting of electro- and photoactive molecular components onto metallic and insulating substrates is thus of interest as an entryway towards building more complex architectures. In particular, monolayers of fullerene[2] or fullerene derivatives on metal surfaces[3–5] have received special attention as electronic and photonic molecular devices. However, the successful technological application of these thin films relies on novel syntheses to modify $C_{60}$ with the desired anchoring groups, as well as the ability to form highly ordered arrangements on a surface. Although monolayers of fullerene have been previously reported through covalent or non-covalent grafting, their extension towards more complex modified $C_{60}$ derivatives is synthetically challenging as it demands the preparation of multiply-substituted fulleroids. Similarly, chemisorption of modified fullerenes will be highly dependent on the physical properties of the system at hand. A more convenient approach would make use of the numerous already available fullerene derivatives, for example *via* their reaction with a suitably modified surface. With this in mind, we explored the [4 + 2] Diels–Alder reaction of fullerenes with substituted anthracenes,[6] and now report on its use to build fullerene monolayers onto silicon wafer substrates suitable for the fabrication of fullerene-based electronic devices.

The use of anthracene as a fullerene-selective functional tether presents several advantages: (1) the reaction is reversible at room temperature, allowing self-assembly of the fullerene monolayer to achieve close packing; (2) anthracene is generally unreactive towards common dienophiles and other functional groups; (3) anthracene monolayers are easily lithographed through photoinduced oxidation[7] or photodimerization reactions.[8] The latter point is particularly interesting in view of obtaining spatially-resolved fullerene layer-by-layer assemblies. Monolayer formation and modification was monitored using fluorescence, ellipsometry, and AFM. We initially focused on 9-alkoxy substituted anthracene derivatives, which are readily available through O-alkylation of anthrone. However, the resulting monolayers did not bind $C_{60}$ reproducibly, presumably due to the sensitivity of the cycloaddition reaction to anthracene substitution. The fullerene is likely to be non-covalently bound to the surface, as it is easily removed by washing the substrate. We therefore turned to 1-substituted anthracenes, as shown in Scheme 1. Grafting of the anthracene layer was achieved through reaction of the corresponding acyl chloride with an amino-terminated alkylsilane monolayer, prepared using 3-aminopropyltriethoxysilane (APTES).[9]

The synthesis of **7** was achieved by alkylation of 1-hydroxyanthracene. Once obtained, **4** is immediately treated with ethyl 4-bromobutanoate to obtain **5**. Saponification of **5** in ethanol followed by purification by column chromatography (hexane/ethyl acetate 80 : 20) gives **6** in 78% isolated yield. Conversion to the acyl chloride **7** was followed by grafting onto the amino-terminated alkylsilane monolayer (see ESI‡). For characterization purposes, the 1 : 1 adduct between $C_{60}$ and **6** was independently synthesized in 43% yield by the reaction of **6** with $C_{60}$ in toluene (see ESI‡).

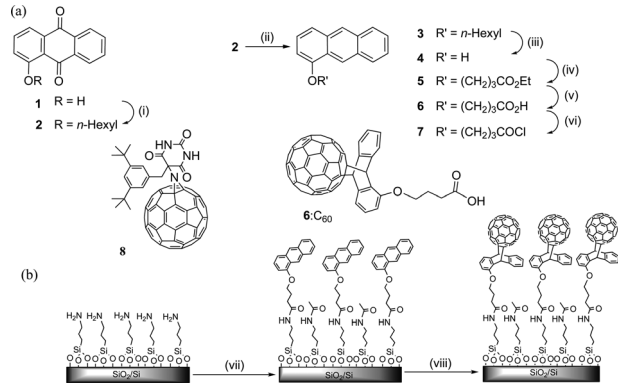
It was anticipated that a close-packed anthracene layer would not be able to accommodate the more bulky fullerene adducts and would favour the formation of multiple fullerene adducts. Therefore, the anthracene-functionalized acyl chloride tethers were mixed with varying proportions of acetyl chloride (10–50% mol/mol **7**:AcCl) during grafting onto the silicon wafers. Typical anthracene fluorescence emission was detected from the anthracene-modified monolayers (Fig. S13, ESI‡). Compared to the emission of **6** in solution, the emission from

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‡ Electronic supplementary information (ESI) available: Synthetic details. Characterization of monolayer by ellipsometry and AFM. UV-vis spectra and cyclic voltametric data for **6**:$C_{60}$ adduct in solution. See DOI: 10.1039/c0cc04899b

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**Scheme 1** (a) Synthesis of **7** and (b) $C_{60}$ addition to **7** on surface. Conditions: (i) *n*-$C_6H_{13}Br$, $K_2CO_3$, DMF, 100 °C, 24 h, 91%; (ii) Zn, AcOH, 115 °C, 12 h, 60%; (iii) $BBr_3$, $CH_2Cl_2$, −70 °C, 2 h, 100%; (iv) $Br(CH_2)_3CO_2Et$, NaH, DMF, 70 °C, 24 h, 77%; (v) NaOH, EtOH, 60 °C, 12 h, HCl, 78%; (vi) $(COCl)_2$, DMF (cat.), 12 h, RT, 100%; (vii) **7**, AcCl, MeCN, 24 h, rt, Ar; (viii) $C_{60}$, toluene, 48 h, RT, Ar.

the anthracene monolayers undergoes a slight loss of vibrational features and, in the case of the more concentrated anthracene monolayers, exhibits a small shoulder at 470 nm assigned to emission from anthracene excimers.[8] Excimer emission is not observed in the more diluted anthracene monolayers (20%), indicating that the anthracene-terminated tethers are evenly dispersed on the surface and not aggregated into islands.

The thickness of the mixed monolayers was analyzed by spectroscopic ellipsometry (360–900 nm) and the data are summarized in Table 1. The initial thickness measurements of the $-NH_2$ terminated layers (0.4–0.5 nm) are consistent with the formation of an ω-aminopropylsilane monolayer on the native oxide surface of the silicon wafer.[9] Subsequent modification of the amine layer with **7** and acetyl chloride resulted in an increment of the average thickness of the monolayer when analysed by ellipsometry. The observed increment in thickness was found to be proportional to the concentration of **7** in the solution, consistent with the formation of monolayers in which both components are in competition for surface functionalization.

The straightforward grafting of fullerenes onto modified surfaces was a central goal of this work. We therefore placed the various anthracene-grafted substrates in saturated toluene solutions of $C_{60}$ at rt for 48 h (Scheme 1b). After thorough cleaning, the increment in height was measured by spectroscopic ellipsometry (Table 1). The observed increment in height (0.7–1.1 nm) is in agreement with the deposition of a single layer of fullerene, whose molecular diameter is 1 nm. The lower value (0.7 nm) obtained for S1 is consistent with only partial coverage of the surface, due to the lower surface concentration of anthracene sites. Control experiments in which anthracene-terminated substrates are incubated in a solvent devoid of fullerene showed no detectable increase in layer thickness. The stability of the fullerene monolayer to washing contrasts that observed for the 9-alkoxyanthracene monolayers initially investigated, and strongly supports covalent grafting of the fullerene in this case. The overall thickness of the monolayers was also independently measured using AFM by mechanically dislocating the monolayer, giving values of 2.9 nm and 4.0 nm for S3 and S3 + $C_{60}$, respectively (Fig. S15 and S16, ESI‡). These values are in excellent agreement with those obtained by ellipsometry considering the thickness of the APTES layer.

**Table 1** Increment in layer thickness upon surface modification of aminosilane substrates[a]

| Substrate | Composition[b] 7:AcCl | Thickness increment/nm Alone[c] | +$C_{60}$[d] | +**8**[d] |
|---|---|---|---|---|
| S1 | 10% | 1.3 ± 0.1 | 0.7 ± 0.1 | |
| S2 | 20% | 1.9 ± 0.1 | 0.9 ± 0.1 | |
| S3 | 50% | 2.5 ± 0.1 | 1.1 ± 0.1 | |
| S4 | 50% | 2.4 ± 0.1 | | 0.9 ± 0.1 |

[a] As determined by spectroscopic ellipsometry (see ESI‡). [b] Composition (mol/mol) of **7**:AcCl in solution. [c] Average thickness of the anthracene/AcO layer. [d] Average thickness increase of the anthracene layer upon incubation with $C_{60}$ or **8** (48 h).

The kinetics of surface binding of $C_{60}$ was investigated by monitoring the change in average thickness of the layer as a function of time. The results for a single substrate S3 incubated in a toluene solution of fullerene in the dark are presented in Fig. 1, and show a steady increase in surface thickness over a period of *ca.* 30 h, which then levels off to a maximum value of 1.1 nm. This behaviour confirms that the binding of $C_{60}$ to the surface of the anthracene-modified substrates leads to the deposition of a single layer of fullerene molecules, in agreement with the proposed covalent attachment of $C_{60}$ *via* a thermal [4+2] cycloaddition. The reaction proceeds according to pseudo-first order kinetics, with a time constant of $1.7 \times 10^{-5}$ $s^{-1}$. The latter is comparable to that determined using absorption spectroscopy by Sarova and Berberan-Santos for the cycloaddition of anthracene to $C_{60}$ in toluene solution at 49 °C ($2.3 \times 10^{-5}$ $s^{-1}$), but faster than that observed at rt ($1.8 \times 10^{-6}$ $s^{-1}$).[10] Clearly, the substitution pattern of the acene and the molecular environment of the reaction affect the rate constant for the cycloaddition.

The surface morphology of the anthracene monolayer and the $C_{60}$-grafted monolayer was investigated using atomic force microscopy (Fig. 2). In the case of the anthracene monolayer S3, the substrate is uniformly smooth with an rms roughness of 0.14 ± 0.1 nm, corresponding to a molecularly flat surface. The $C_{60}$-terminated monolayer differs dramatically from the anthracene monolayer, confirming the surface modification induced by the cycloaddition reaction. The increased

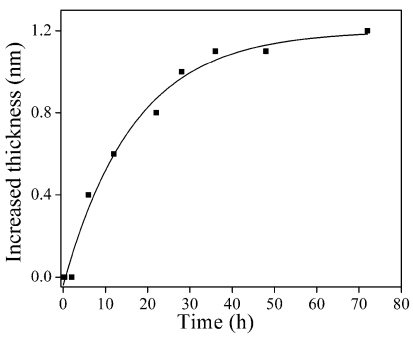



**Fig. 1** Thickness increment upon incubation of an anthracene-modified substrate (S3) with a saturated toluene solution of $C_{60}$ in the dark as a function of time. The solid line represents the best fit to a pseudo first-order reaction with a time constant of $1.7 \times 10^{-5}$ $s^{-1}$ ($r$ = 0.989).

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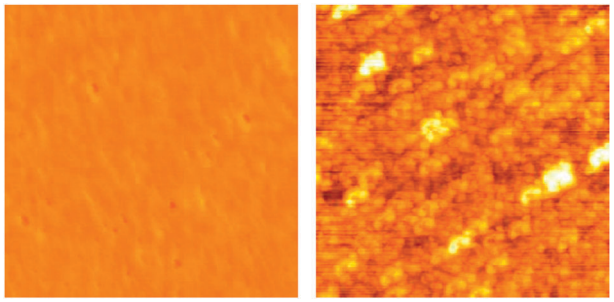


**Fig. 2** AFM images (0.5 × 0.5 μm, tapping mode) of substrate S3 before (left) and after (right) grafting of the fullerene monolayer.

microroughness (0.5 ± 0.1 nm) is the same as that observed by Tsukruk *et al.* for tightly packed covalently-bound fullerene monolayers.[11] Kelvin force probe microscopy of S3 and S3 + $C_{60}$ (Fig. S17 and S18, ESI‡) shows that the surface potential is homogeneous throughout the sample.

The spectroscopic and redox properties of the **6**:$C_{60}$ adduct were investigated in solution. In a toluene : acetonitrile (1 : 1) solution, the adduct exhibits a first reversible oxidation wave at –1.062 V *vs.* $Fc/Fc^+$, followed by a series of reversible and irreversible waves (Fig. S8, ESI‡). This behaviour is comparable to that observed by Ilhan and Rotello for the reduction of the anthracene:$C_{60}$ adduct-containing polymers.[12] The UV-vis spectrum of the adduct in toluene shows absorption bands at 433 and 704 nm (Fig. S9, ESI‡) and emission at 740 nm, which are characteristic of the mono-adduct of $C_{60}$ and anthracene.[10]§ Fluorescence emission from substrate S3 + $C_{60}$ is very similar to that of **6**:$C_{60}$ in solution, confirming the formation of a covalent adduct, and does not exhibit noticeable broadening that could be indicative of a high proportion of multiple fullerene adducts being formed (Fig. S14, ESI‡).

To probe whether cycloaddition of $C_{60}$ to surface-bound anthracene is also applicable to substituted fullerenes, we employed a fullerene–barbituric acid adduct of interest for the construction of hierarchical supramolecular assemblies.[13] Anthracene-terminated monolayers incubated in the presence of **8** show an increase in surface thickness characteristic of the attachment of the fullerene derivative to the surface (entry S4, Table 1). Water contact angles for S3, S3 + $C_{60}$, and S4 (88.0°, 90.9°, and 87.5°, respectively), indicate that the presence of **8** decreases the hydrophobicity of the surface and that therefore the barbiturate is at least partially exposed to the surface.

In summary, we have demonstrated that fullerene SAMs can be easily obtained through $C_{60}$–anthracene cycloaddition. Anthracene-terminated monolayers are inert towards most functional groups and can be readily patterned prior to the formation of the fullerene monolayer, which may be of interest for the construction of OFET devices and sensors.

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## Notes and references

§ Based on the reduction potential and onset of the fluorescence emission, the energies of the HOMO and LUMO of **6**:$C_{60}$ are calculated to be −3.56 and −5.44 eV, respectively.


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