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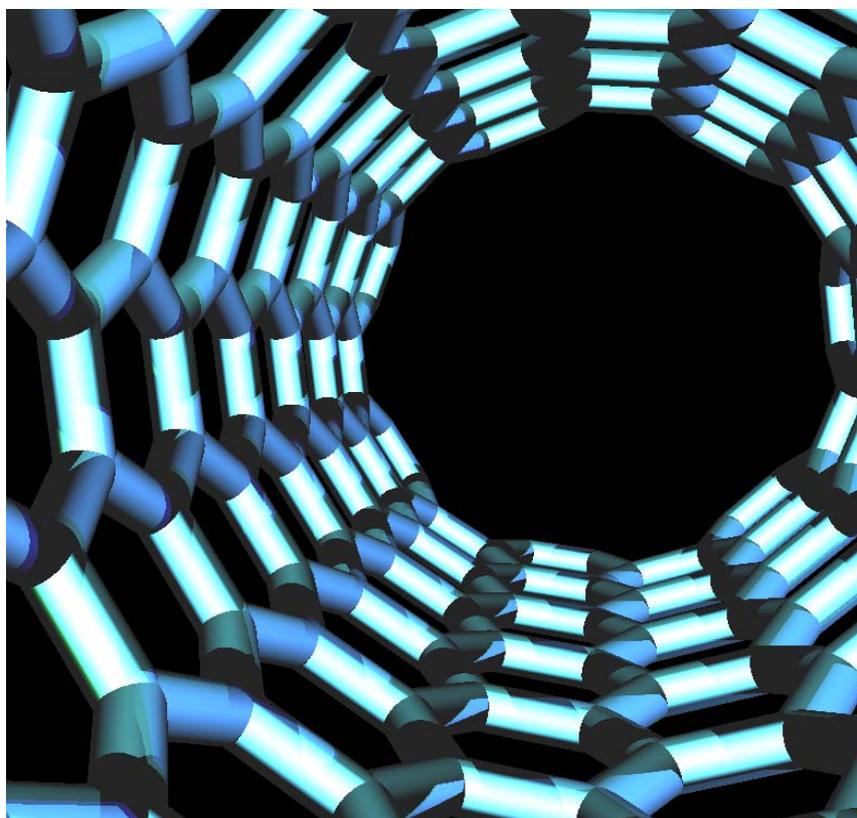
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Direct formation of fullerene monolayers using [4 + 2] Diels–Alder cycloaddition†‡

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The formation of covalent C₆₀ monolayers through [4 + 2] Diels–Alder cycloaddition between C₆₀ 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 fullerene² 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 C₆₀ 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 C₆₀ derivatives is synthetically challenging as it demands the preparation of multiply-substituted fullerenoids. 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 oxidation⁷ 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 C₆₀ 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 C₆₀ and **6** was independently synthesized in 43% yield by the reaction of **6** with C₆₀ 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**:C₆₀ adduct in solution. See DOI: 10.1039/c0cc04899b

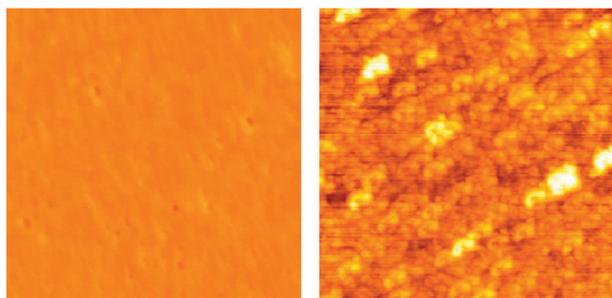


Fig. 2 AFM images ($0.5 \times 0.5 \mu\text{m}$, tapping mode) of substrate S3 before (left) and after (right) grafting of the fullerene monolayer.

microroughness ($0.5 \pm 0.1 \text{ nm}$) 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 + C₆₀ (Fig. S17 and S18, ESI†) shows that the surface potential is homogeneous throughout the sample.

The spectroscopic and redox properties of the 6:C₆₀ adduct were investigated in solution. In a toluene : acetonitrile (1 : 1) solution, the adduct exhibits a first reversible oxidation wave at $-1.062 \text{ V vs. Fc/Fc}^+$, 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:C₆₀ 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 C₆₀ and anthracene.¹⁰ Fluorescence emission from substrate S3 + C₆₀ is very similar to that of 6:C₆₀ 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 C₆₀ 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 + C₆₀, 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 C₆₀-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:C₆₀ are calculated to be -3.56 and -5.44 eV , respectively.

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