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In molten anthracene, solid C_{70} reacts regiospecifically in very high yield (68%) to form exclusively the 12 o'clock bis-adduct isomer, as determined by single crystal X-ray diffraction, thermal gravimetric analysis (TGA) and spectroscopy techniques.

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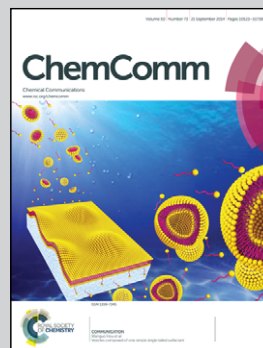
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High-yield, regiospecific bis-functionalization of C_{70} using a Diels–Alder reaction in molten anthracene†

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A regiospecific bis-adduct of C_{70} with anthracene was prepared with unusually high yield (68%) by the Diels–Alder reaction in the absence of solvent (melt). The structure of the bis-adduct was an unexpected 12 o'clock isomer, as determined by single crystal X-ray diffraction, thermal gravimetric analysis (TGA) and spectroscopy.

Regiochemical control of bis-addition reactions on fullerenes has been, and continues to be, an important synthetic challenge. Common fullerene functionalization methods such as addition-elimination of halogenated malonates and 1,3-dipolar cycloadditions of ylides lead to multiple isomeric bis- and tris-adducts which are relatively difficult to separate using conventional column chromatography.[1–3] The presence of 30 equivalent double bonds on the surface of C_{60} leads to low bis-adduct regioselectivity,[4] and in the case of C_{70} the number of possible isomers increases because there are eight different types of C–C double bonds and five different types of carbon atoms, due to the lower symmetry of this cage.[5,6] Diederich *et al.* and Hirsch *et al.* developed elegant synthetic strategies, such as the 'tether directed remote functionalization' and the 'reversible template directed activation' methods, for regioselective bis-, tris-, and tetrakis-additions to C_{60} and C_{70}.[5] In 1996, Kräutler *et al.* reported a topochemically-controlled conversion of the crystal-line C_{60}–anthracene monoadduct into the *trans*-1 bis-adduct in 96% yield.[6a] Subsequently, that group showed that heating an anthracene–C_{60} mixture at 240 °C produced the same *trans*-1 bis-adduct in 43.7% yield along with 4.5% of the monoadduct and 46.7% of unreacted C_{60} as the only products.[6b] Such anthracene adducts are useful as protecting groups in guiding multiple

additions to fullerenes.[5e] Surprisingly, similar solvent-free Diels–Alder reactions with C_{70} or other fullerenes have not been reported. Here, we report that the solvent-free addition of anthracene to C_{70} yields only one regioisomer of the bis-adduct in remarkably high yield (68%).

Diederich *et al.* introduced a simple nomenclature to describe bis-adducts of C_{70} where the addends are attached to α bonds on opposite ends of the C_{70} molecule, which is usually the observed case.[5b] These ten α double bonds radiate from the two pentagons at the poles of the molecule and are typically the most reactive. Assuming from previous observations that anthracenes will add to the more reactive [6,6] α bonds, three possible regioisomers can be formed, two of which exist as enantiomeric pairs, see Fig. 1. The three possible bis-isomers are described as 12 o'clock, 2 o'clock and 5 o'clock, depending on the relative orientation of the two adducts around the C_5 symmetry axis (see Fig. 1). The 7 o'clock and 11 o'clock bis-adducts can also form (not shown in Fig. 1), but since the adducts are identical, these correspond to enantiomers of the 5 o'clock and 2 o'clock isomers, respectively. Generally, formation of the 2 o'clock isomer is favored, as
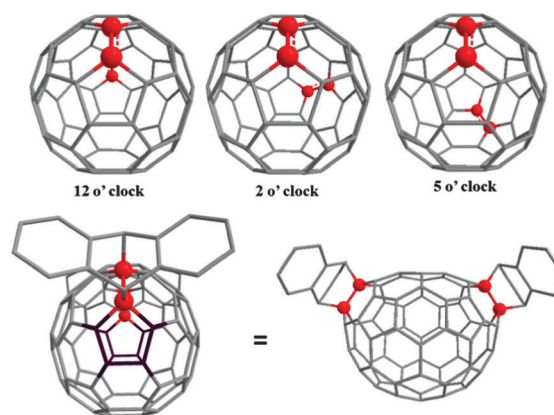
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Fig. 1 Representation of the possible bis-isomers of C_{70} (above) and the structure of the 12 o'clock regioisomer (below).

reported for the addition of $Ir(CO)Cl(PPhMe_2)_2$ to C_{70} (ref. 7) and for formation of Bingel adducts of C_{70}.[5b] The synthetic procedure followed was essentially the same as that previously reported by Kräutler et al. with C_{60}.[6a] C_{70} was reacted with two equivalents of anthracene in the melted state under vacuum at 240 °C for 2 hours. Purification of the crude mixture on a silica gel column using CS_2:hexane (7:3) as eluent yielded, in order of elution, unreacted C_{70} and two compounds denoted as **1** and **2**. The major fraction of the reaction was compound **2**, which was isolated in 68% yield, followed by C_{70} and compound **1** in 22% and 10% yield, respectively. Characterization of the C_{70}–anthracene adducts was performed using field desorption mass spectrometry (FD-MS), MALDI-TOF, electrospray ionization mass spectrometry (ESI), ^1H and ^{13}C-NMR, TGA, UV/Vis, IR, cyclic voltammetry, and single crystal X-ray diffraction.

The ^1H-NMR spectrum of compound **1** showed six resonances, and was identical to the spectrum reported for an anthracene C_{70}-mono-adduct (on an α position) obtained using a flame synthesis procedure (Fig. S1, ESI†).[8] This observation conclusively showed that **1** is the mono-adduct. The ^1H-NMR spectrum of compound **2** exhibited a similar set of signals as observed for compound **1** but with significant chemical shift differences (Fig. S3, ESI†). Attempts to obtain the parent peaks in the mass spectra for compounds **1** and **2** using a variety of ionization techniques (MALDI-TOF, ESI, and FD) were unsuccessful, indicating that both compounds are very unstable after ionization in the gas phase, readily undergoing retro Diels–Alder reactions. The MALDI-TOF, ESI, and FD mass spectra of the crude mixture and of the isolated compounds exhibited only one strong peak at m/z 840 due to C_{70}.

Thermogravimetric analyses (TGA) of **1** and **2** were performed by increasing the temperature at a rate of 3 °C min⁻¹ under a flow of N_2 (Fig. 2). A 17% weight loss (calculated value for the loss of one anthracene from **1**: 17.4%) was observed for **1** (transition onset at 180 °C and midpoint at 220 °C). A 31% weight loss was observed to occur in two discrete steps for **2** (calculated value for the loss of two successive anthracene molecules for a bis-adduct is 29.7%, first transition at 160 °C and a second transition onset at 180 °C and midpoint at 220 °C). These results confirm the loss of a single anthracene
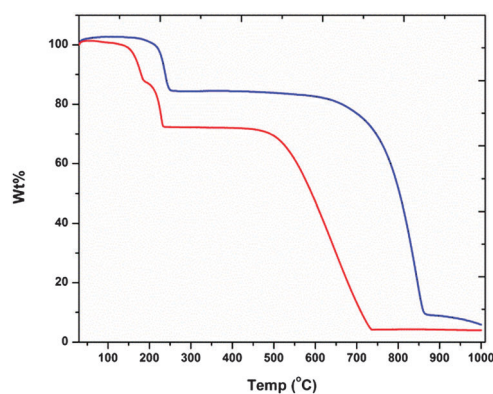
unit from **1** and of two anthracene units from **2**. C_{70} was recovered after thermal treatment of **1** and **2** at 250 °C under a N_2 atmosphere. We selectively removed only one anthracene from **2** at 190 °C, but the mass balance was not quantitative. The UV-vis spectra of compound **2** is similar to those previously reported for 12 o'clock C_{70} bis-adducts,[5e,9] exhibiting weak absorption maxima around 640 nm and a strong absorption maximum at 442 nm (Fig. S5, ESI†). The FT-IR spectra of **1**, **2** and C_{70} showed significant differences in the intensity of the bridgehead C–H stretching vibration bands (Fig. S6, ESI†).

The redox properties of **1**, **2** and C_{70} were determined using cyclic voltammetry (CV) at a scan rate of 100 mV s⁻¹ and by square wave voltammetry (SWV) in o-dichlorobenzene solutions using 0.05 M of n-Bu_4NPF_6 as supporting electrolyte, see Fig. 3. The CV results are summarized in Table 1. The electrochemical behavior of **1** showed three reversible reduction waves, which are cathodically shifted compared to those of C_{70} under the same experimental conditions. Compound **2** also showed three reversible reduction waves, which were further cathodically shifted compared to those of compound **1**. These results agree with previous reports of successive cathodic shifts upon double bond saturation by chemical functionalization.[10] Compounds **1** and **2** showed one reversible oxidation wave.

The regiochemistry of bis-adduct **2** was unambiguously established using X-ray crystallography.‡ Black crystals grew as thin rectangular plates from a diffusion of hexane into a carbon disulfide solution of **2**. Crystallographic data were collected at the Advanced Light Source, Lawrence Berkeley Laboratory. The structure was solved in the tetragonal crystal system, space group $P4_2/ncm$ (no. 138) and revealed one-quarter of the molecule of **2** in the asymmetric unit. The crystallographic site symmetry of 2mm confirmed that the molecule is the unexpected 12 o'clock bis-isomer with C_{2v} point symmetry, as shown in Fig. 4(a). The 2-fold axis is vertical. The two perpendicular mirror planes pass through this axis. The structure contains a disordered interstitial hexane molecule with the same site symmetry. The utility SQUEEZE[11] was applied to
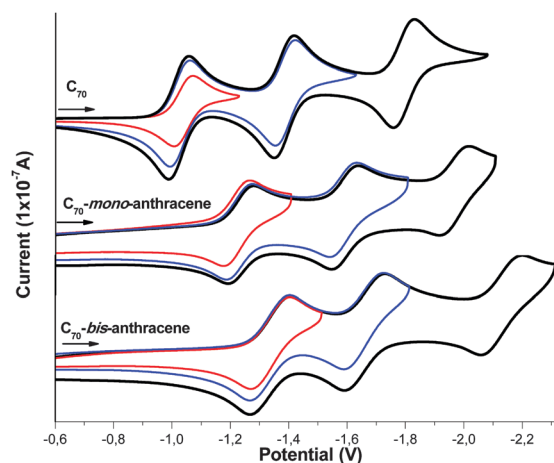

Fig. 2 TGA of **1** (blue) and **2** (red) obtained up to 1000 °C using a linear 3 °C min⁻¹ ramp method.

Fig. 3 Cyclic voltammetry of 0.05 mM of C_{70}, C_{70}-mono-anthracene (**1**) and C_{70}-bis-anthracene (**2**) (o-DCB containing 0.05 M n-Bu_4NPF_6 at 100 mV s⁻¹; using the redox couple Fc/Fc⁺ as internal reference).

Table 1 Redox potentials (V)[a] of **1**, **2** and C_{70}

Compound	C_{70}	1	2
$E^{0/+1}$	—	0.97	0.91
$E^{0/-1}$	−1.05	−1.18	−1.21
$E^{-1/-2}$	−1.41	−1.54	−1.53
$E^{-2/-3}$	−1.83	−1.92	−1.99

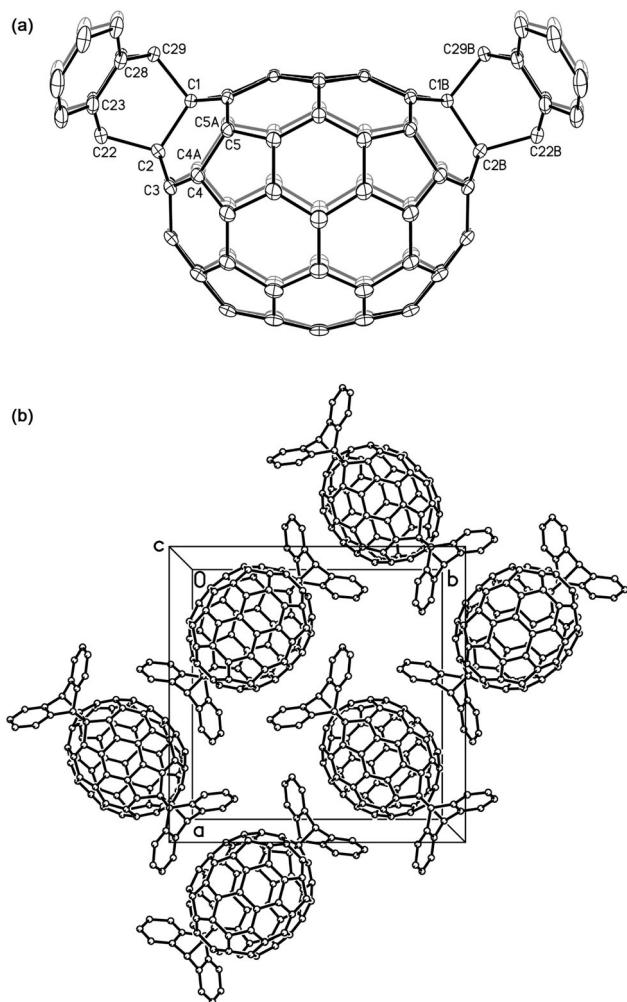[a] Values obtained by SWV in V vs. Fc/Fc$^+$.

Fig. 4 (a) The molecular structure of the C_{70} bis-anthracene adduct, **2**. Hydrogen atoms are not shown for clarity. Thermal parameters are shown at the 30% probability level. (b) A layer perpendicular to the c axis showing intermolecular interactions between anthracene and C_{70}.

remove its contribution from the structure. The fullerene [6:6] bond (C1–C2) at the site of the cycloaddition is elongated to 1.601(3) Å. The bonds C1–C29 and C2–C22 are also stretched, at 1.590(3) and 1.586(3) Å, respectively. As shown in Fig. 4(b), viewed down the c axis, adjacent molecules efficiently pack in a wavy manner with the concave surface of anthracene well matched to the flattened convex part of C_{70}. This interaction can be viewed in the ESI† as a movie in mpg format. These remarkable shape-complementary interactions are less perfect in the reported bis- and tris-adducts of C_{60} and anthracene.[12]

The intermolecular distances are typical for π···π stacking with values in the range 3.18–3.45 Å. The layers above and below this layer follow the crystallographic 4_2 operation and yield the shortest fullerene···fullerene contact of 3.118(3) Å. It is important to note that bis-Diels–Alder additions to C_{60} and C_{70} always result in multiple regioisomers (5 or 6 for C_{60}, see ref. 6b, c and 8 in the case of C_{70}, see ref. 9b), thus it is remarkable that only one bis-adduct isomer is observed in the present case.

A remarkably high yield of only one regioisomeric bis-adduct of C_{70} with anthracene was isolated for the first time from a reaction in the melt. The two anthracene molecules added to [6,6] double bonds in a 12 o'clock arrangement. Further synthetic evolution of this compound is under investigation in our laboratories, in efforts to prepare tris and higher adducts regioselectively.

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