

First tether-directed regioselective bis-functionalisation of C₇₀: effects of cation complexation on the redox properties of diastereoisomeric fullerene crown ether conjugates

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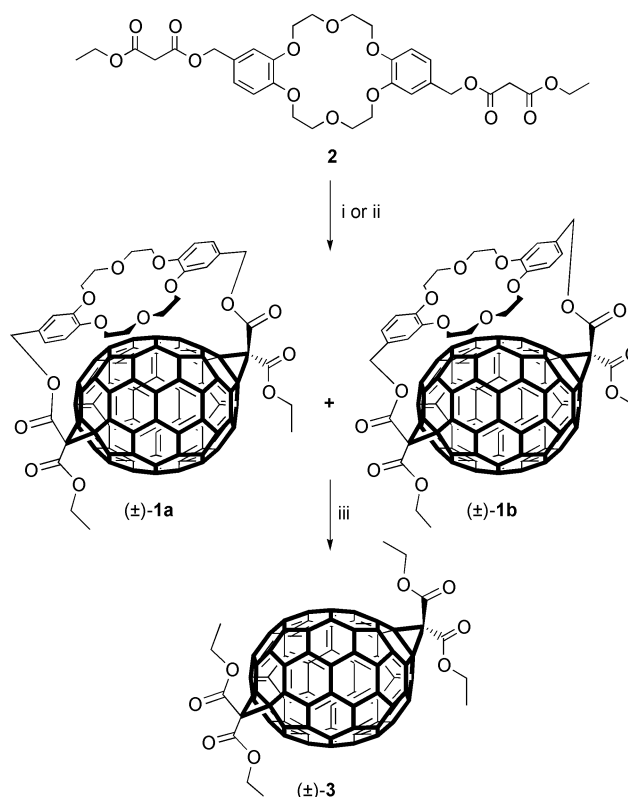
The covalently templated bis-functionalisation of C₇₀, employing a dibenzo-18-crown-6 tether, proceeds with complete regiospecificity and provides a bis-addition pattern which is disfavoured in sequential transformations.

Tether-directed remote functionalisation has proven to be a powerful tool for obtaining regiochemical control in multiple additions to buckminsterfullerene, C₆₀.^{1–4} However, up until now, this approach had not been applicable to C₇₀ or other higher fullerenes.

Double *Bingel* cyclopropanation of C₇₀⁵ occurs on opposing hemispheres at the most curved α -type⁶ 6–6 bonds (bonds at the junction between two six-membered rings) emanating from the two polar pentagons through which the C₅ symmetry axis of the higher fullerene passes. In a *Newman*-type projection looking down the C₅ axis onto the two polar pentagons, the two addends adopt a twelve, two and five o'clock geometrical relationship, respectively. Accordingly, the kinetically controlled *Bingel* bis-cyclopropanation with achiral dialkyl malonates provides three constitutional isomers, two of which (two and five o'clock) are pairs of enantiomers, in a ratio of 2.8:6.8:1.0, respectively (twelve, two and five o'clock orientation of the addends). Similar addition patterns were also obtained in other bis-functionalisation reactions, with the two o'clock geometric relationship being highly favored in each case.^{7–10} Here we report the application of the tether-directed remote functionalisation to prepare C₇₀ bis-adducts (\pm)-**1a** and (\pm)-**1b** with complete regioselectivity, featuring the kinetically disfavoured five o'clock addition pattern.

C₇₀ was reacted with dibenzo-18-crown-6- (DB18C6) linked bis-malonate **2**¹¹ under modified *Bingel*-conditions (I₂, DBU, toluene) in the presence of KPF₆ (10 eq.), which was added as a template to rigidify the tether by complexation (Scheme 1). This afforded the two products (\pm)-**1a** and (\pm)-**1b** in a 56:44 ratio with an overall yield of 41%. Both compounds were separated by column chromatography (Silica-*H*; toluene–ethyl acetate (1:1)) and fully characterised (¹H and ¹³C NMR, high-resolution MALDI-TOF-MS, IR and UV/Vis). Transesterification of the crude product mixture of (\pm)-**1a** and (\pm)-**1b** (Cs₂CO₃, THF–EtOH (1:1)) afforded only one single C₂-symmetrical bis-adduct (\pm)-**3**. The spectroscopic data (¹H and ¹³C NMR) revealed its identity with the C₇₀ bis-adduct featuring diethyl malonate addends at the two polar C(1)–C(2) and C(67)–C(68) bonds (five o'clock addition pattern), which had previously been obtained by sequential double *Bingel* addition.^{5,6b} This leads to the remarkable conclusion that reaction of C₇₀ with **2** proceeds with complete regioselectivity to give the normally kinetically least favoured regioisomer. Surprisingly, the absence of KPF₆ in the *Bingel* macrocyclisation did not affect the regioselectivity at all, although the diastereoisomeric ratio changed slightly, providing (\pm)-**1a** and (\pm)-**1b** as the only products in a ratio of 37:63 with a substantial higher yield of 68%.

The presence of the inherently chiral five o'clock addition pattern and the *out-out* orientation of the EtOOC groups in



Scheme 1 Reagents and conditions: i, C₇₀, I₂, DBU, KPF₆ (10 equiv.), toluene, rt, 23% (\pm)-**1a**, 18% (\pm)-**1b**; ii, C₇₀, I₂, DBU, toluene, rt, 25% (\pm)-**1a**, 43% (\pm)-**1b**; iii, Cs₂CO₃, THF–MeOH (1:1), rt, 2 h.

(\pm)-**1a** was unequivocally established by X-ray crystallography (Fig. 1).[†] The fullerene core in this first crystal structure of a cyclopropanated C₇₀ derivative has a spheroidal shape with a distance of 8.03 Å along the principal axis. As a consequence of cyclopropanation, the carbon atoms C(1), C(2), C(67) and C(68) are pulled out of the C₇₀-surface leading to a slightly longer distance along the main axis than observed for the complex (η^2 -C₇₀)Ir(CO)Cl(PPh₃)₂ (7.90 Å).¹⁴ Distances from the carbon atoms at the equator to the center of the sphere range from 3.52–3.56 Å with a mean value of 3.54 Å. The bond lengths between the bridgehead atoms C(1)–C(2) and C(67)–C(68) of 1.605(9) and 1.596(10) Å, respectively, are strongly elongated compared to the analogous bonds reported for several η^2 -transition metal C₇₀-complexes (1.512–1.523 Å).⁸ However, they are similar to the lengths of the corresponding bonds reported for a *trans*-1 bis-cyclopropanated C₆₀ crown ether conjugate (1.606–1.610 Å),^{11b} and a Diels–Alder mono-adduct of C₇₀ (1.603 Å).¹⁵ Most geometrical features of **1a** are comparable to those of the latter Diels–Alder adduct.

The crown ether moiety exists in a conformation different from the four conformations reported so far in the literature for

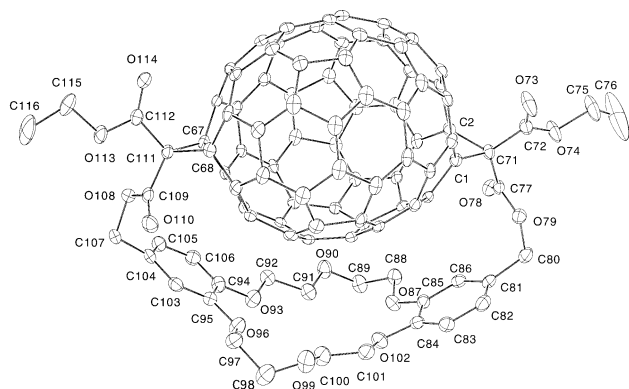


Fig. 1 Molecular structure of (±)-**1a** in the crystal. Atomic displacement parameters obtained at 233 K are drawn at the 30% probability level.

uncomplexed DB18C6.¹⁶ In order to bridge the fullerene poles, it adopts an ‘umbrella shaped’ geometry with a distorted C_2 -symmetry. The approximate dihedral angle between the two aromatic planes is about 124° . This is comparable to the value reported for DB18C6 complexes (128 – 102°),^{11b,16b,c} but considerably larger than for uncomplexed C_{2v} -symmetrical DB18C6 (98.8°).^{16c} Several close contacts between the DB18C6 tether and the fullerene surface are observed.

The structure of the other isomer ((±)-**1b**) was deduced from MM2-calculations,¹⁷ which indicated that the *in-out* and *in-in* isomers are not feasible because of their much higher steric energy. Thus, (±)-**1a**, and (±)-**1b** are diastereoisomeric pairs of enantiomers, differing only in the orientation of the DB18C6 tether as a result of planar chirality.

To determine the effects of cation complexation on the redox properties of (±)-**1a** and (±)-**1b**, cyclic voltammetric (CV) studies were performed in toluene–MeCN (4:1) in the absence and presence of KPF_6 and $NaBF_4$ (Table 1). Based on the ΔE_{pp} values and the cathodic:anodic current ratio, the first reduction waves of (±)-**1a** and (±)-**1b** are electrochemically and chemically reversible. However, the second reduction is chemically irreversible as judged by an additional oxidation wave observed on the reverse scan. Consequently, ion binding effects were monitored only for the first reduction. Similar to the behavior of the previously reported C_{60} –DB18C6 conjugate,^{11b} addition of sub-stoichiometric amounts of Na^+ ions to the solution of (±)-**1a** causes the appearance of a new poorly resolved, yet clearly discernible redox wave which is anodically shifted by 70 mV relative to that for the free compound.¹¹ This new redox couple, assigned to the cation complex, grows at the expense of the one for the uncomplexed species as the concentration of Na^+ ions increases. This was firmly established by the observation of isotopotential points on both the forward and reverse scans. Addition of one eq. of Na^+ ions causes the redox wave of the free compound to disappear completely, and further addition

Table 1 Redox potentials (vs. ferrocene–ferricinium couple) of (±)-**1a** and (±)-**1b** in absence and presence of alkali metal cations^a

	E_1/V	E_2/V	+ KPF_6^b E_1/V	+ $NaBF_4^c$ E_1/V
(±)- 1a	−1.13 (67)	−1.57 ^d	−1.05 (65)	−1.06 (68)
(±)- 1b	−1.14 (68)	−1.58 ^d	−1.07 (68)	−1.06 (67)

^a Measurements were performed under Ar in toluene–MeCN (4:2) containing 0.1 M Bu_4NPF_6 as the supporting electrolyte, using a concentration of 0.3 mM for (±)-**1a** and 0.2 mM for (±)-**1b**. Glassy carbon working electrode. Non-aqueous Ag/Ag^+ reference electrode Pt wire counter electrode. The scan rate was 100 mV s^{-1} . Values in parentheses are the ΔE_{pp} in mV. ^b 1.0 eq. of KPF_6 . ^c 1.0 eq. of $NaBF_4$. ^d Cathodic peak potential.

causes no further observable changes in the voltammetry. This behavior implies strong complexation between the crown ether conjugate and one Na^+ ion.¹⁸ The anodic shift must be attributed to the electrostatic effect of the Na^+ ion which is bound to the DB18C6 inophore in close proximity to the fullerene surface. The behavior with K^+ ions was very similar (Table 1), and the same was observed for (±)-**1b** with either cation.

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Notes and references

† *Crystal data*: **1a**: $C_{102}H_{36}O_{14} \cdot 6CHCl_3$, $M_r = 2201.52$, monoclinic space group $P2_1/n$ (no. 14), $Z = 4$, $a = 14.395(4)$, $b = 33.405(9)$, $c = 19.277(6)$ Å, $\beta = 108.67(2)^\circ$, $V = 8782(4)$ Å³, $T = 233$ K. A semi-empirical absorption correction, based on psi-scans was applied to the data ($T(\max) = 0.99$, $T(\min) = 0.78$). The structure was solved by direct methods (SIR92)¹² and refined by full-matrix least-squares analysis (SHELXL-97),¹³ using an isotropic extinction correction, and $w = 1/[\sigma^2(F_o^2) + (0.115P)^2 + 43.34P]$, where $P = (F_o^2 + 2F_c^2)/3$. It consists of one ordered molecule of (±)-**1a** and six slightly disordered $CHCl_3$ molecules. All heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.077$, $wR(F^2) = 0.205$ for 1262 parameters, and 7220 reflections with $I > 2\sigma(I)$ and $2.6 < \theta < 53.0^\circ$ (corresponding R -values based on all 9732 reflections are 0.105 and 0.234, respectively). CCDC 182/1756. See <http://www.rsc.org/suppdata/cc/b0/b006066f/> for the crystallographic file in .cif format.

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