Keywords: asymmetric synthesis · cyclizations · domino reactions · Lewis acids · radicals

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Regioselective Synthesis of *trans*-1 Fullerene Bis-Adducts Directed by a Crown Ether Tether: Alkali Metal Cation Modulated Redox Properties of Fullerene–Crown Ether Conjugates[**]

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Monia Fibbioli, Ernö Pretsch,[*] and
François Diederich[*]

Since the introduction of the tether-directed remote functionalization of fullerenes,[1–3] a variety of bis(cyclopropanated) [60]fullerene derivatives have been synthesized both regio- and stereoselectively[2] by macrocyclization of the carbon sphere by a double Bingel addition.[4] This reaction has provided ready access to bis(methano)fullerenes with *cis*-2, *cis*-3, *e*, *trans*-4, and *trans*-3 addition patterns (Figure 1).[5]

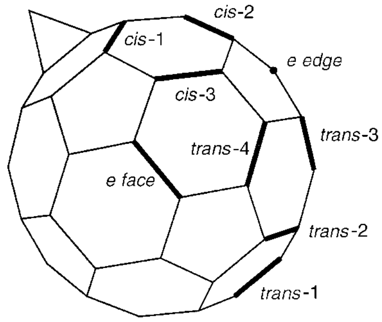

Figure 1. Position notation for bis-adducts of C$_{60}$.

However, it has proven quite challenging to develop extended tethers with a suitable degree of conformational homogeneity that would span the carbon sphere and direct the second addend into the *trans*-2 and, in particular, the *trans*-1 positions on the opposite pole.[6] Among the up to eight regioisomeric C$_{60}$ bis-adducts isolated from various sequential (nontethered) double additions,[7, 8] the *trans*-1 derivative is almost always the least abundant for both kinetic and statistical reasons. Thus, the stepwise Bingel reaction with diethyl 2-bromomalonate, reported by Hirsch and co-workers,[5, 7] gave the *trans*-1 bis-adduct in only 0.8–2% yield after tedious regioisomer separation. Regioselective access to a *trans*-1 bis-adduct was achieved by Kräutler et al. in a most elegant topochemical reaction in which anthracenes are added by cycloaddition to the two poles of the fullerene.[9]

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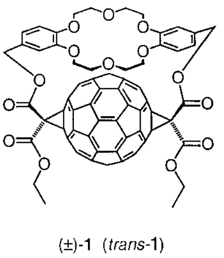
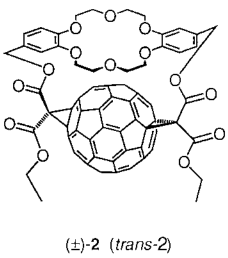
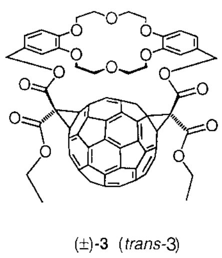
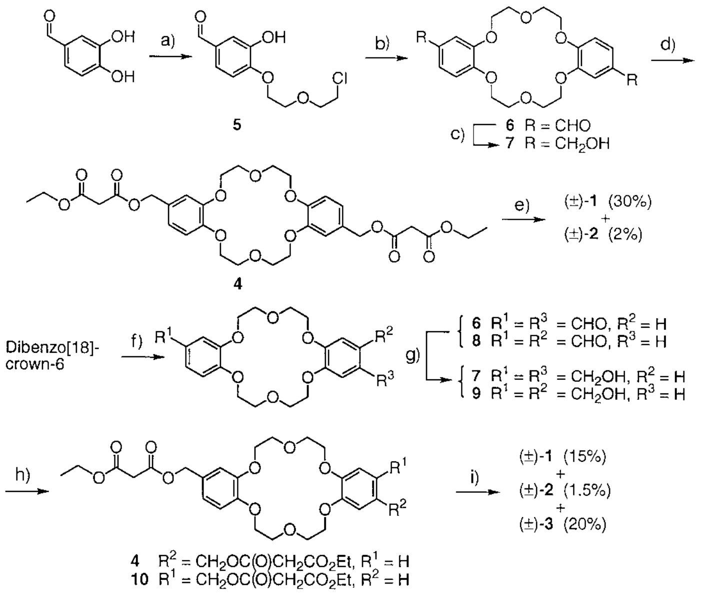

(±)-1 (*trans*-1)


(±)-2 (*trans*-2)


(±)-3 (*trans*-3)

Here we report the regioselective Bingel macrocyclization of C_{60} with a bis-malonate containing a novel dibenzo[18]-crown-6 tether, which yields up to 30% of the planar-chiral *trans*-1 bis-adduct (±)-**1**. Electrochemical investigations of the series of isomeric *trans*-1, *trans*-2, and *trans*-3 bis-adducts (±)-**1**, (±)-**2**, and (±)-**3** revealed, for the first time, substantial effects of cation complexation on the redox properties of the carbon sphere in a fullerene–crown ether conjugate.[2c, 10] This is a result of the close proximity of the fullerene to the ion bound to the crown ether. Dibenzo[18]-crown-6 was chosen as tether since computer modeling indicated that its dimensions and shape would be appropriate to direct the second Bingel addition of bis-malonate **4** into the *trans*-1 position.[11] In the *trans*-1 product (±)-**1**, the crown macrocycle essentially adopts a tangential orientation relative to the fullerene sphere.

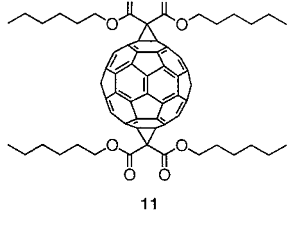
In the synthesis of (±)-**1**, 3,4-dihydroxybenzaldehyde was regioselectively alkylated[12] to give **5** (Scheme 1). Macrocyclization of **5**, templated by K^+ ions,[13] yielded dialdehyde **6**, which was reduced to diol **7** and subsequently transformed into bis-malonate **4**.[14] A modified Bingel reaction[2a, b] of **4** with C_{60} yielded *trans*-1 bis-adduct (±)-**1** (30%) and a minor amount of the *trans*-2 derivative (±)-**2** (2%). Preliminary observations suggest that the regioselectivity in the addition of **4** to C_{60} is further increased by addition of KPF_6, but the yield of the overall reaction decreases. This template effect of the metal ion is under further investigation. When dibenzo[18]crown-6 was diformylated by the Smith modification[15] of the Duff reaction,[16] a 1:1 mixture of *anti* and *syn* isomers **6** and **8** was obtained.[17] Their reduction to **7** and **9**, conversion into the bis-malonates **4** and **10**, and treatment of the mixture under modified Bingel reaction conditions afforded the *trans*-1 ((±)-**1**, 15%), *trans*-2 ((±)-**2**, 1.5%), and *trans*-3 ((±)-**3**, 20%) isomers, which were separated by column chromatography (SiO_2 (5–40 μm), AcOEt/PhMe 1/1). Thus, conversion of the *syn* isomer **10**, with the smaller extension of its tether, provided the *trans*-3 derivative (±)-**3** regioselectively.



Scheme 1. Synthesis of the fullerene–crown ether conjugates (±)-**1**–(±)-**3**. a) $Cl(CH_2)_2O(CH_2)_2Cl$, K_2CO_3, DMF, 80 °C, 36 h, 20%; b) K_2CO_3, DMF, KPF_6, 80 °C, 36 h, 45%; c) $NaBH_4$, MeOH, 20 °C, 1 h, 70%; d) $ClCOCH_2CO_2Et$, pyridine, CH_2Cl_2, 20 °C, 1 h, 70%; e) C_{60}, I_2, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 20 °C, 1 h; f) hexamethylenetetramine $[(CH_2)_6N_4]$, CF_3COOH, 80 °C, 24 h, 20%; g) $NaBH_4$, $CHCl_3$, 20 °C, 36 h, 55%; h) $ClCOCH_2CO_2Et$, NEt_3, DMF, 20 °C, 1 h, 75%; *i*) C_{60}, I_2, DBU, PhMe, 20 °C, 12 h.

The relative position of the two cyclopropane rings on the C_{60} surface in the three fullerene–crown ether conjugates was established by ^1H NMR, ^{13}C NMR, and UV/Vis spectroscopy. In particular, the crown ether tethers do not perturb the UV/Vis absorptions of the carbon spheres above 300 nm, and the spectra of the three isomers correspond to those previously reported for *trans*-1, *trans*-2, and *trans*-3 bis(diethyl malonate) adducts.[2a, b, 7, 8] The ^1H and ^{13}C NMR spectra support the C_2 symmetry of (±)-**1** and (±)-**2** and the C_1 symmetry of (±)-**3**. These symmetry assignments clearly establish that (±)-**1** and (±)-**2** are *out-out* isomers with respect to the orientation of the two ethoxycarbonyl residues at the methano bridge carbon atoms.[2a, b] Although experimental proof was not obtained, molecular modeling also strongly supports the *out-out* structure for (±)-**3**. The formation of (±)-**2** occurred with high diastereoselectivity, since only one of two possible diastereoisomers, which differ by the orientation of the dibenzo[18]crown-6 tether, could be isolated.

The *trans*-1 derivative (±)-**1** was transesterified with Cs_2CO_3 in anhydrous 1-hexanol/THF (1/1; 20 °C, 3.5 h) to yield the D_{2h}-symmetrical bis-adduct **11** (34%). Its ^{13}C NMR spectrum displayed only nine resonances for the fullerene C atoms and the expected peaks for four equivalent hexyl residues. Of all possible regioisomeric bis-adducts of C_{60}, only the *trans*-1 compound displays this high symmetry.[5] The facile conversion of (±)-**1** into **11** by transesterification of the *trans*-1 bis-adduct of C_{60} demonstrates that the crown ether tether route provides a versatile entry into diverse molecular scaffolding.


11

The ionophoric properties of (±)-**1** were investigated with an ion-selective electrode, the membrane of which was composed of the fullerene–crown ether conjugate, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), bis(2-ethylhexyl) sebacate (DOS), and poly(vinyl chloride) (PVC) of high molecular weight.[18] This electrode is selective for K^+, with close to Nernstian response to all monovalent ions investigated. The potentiometric selectivity coefficients, $\log K^{pot}_{K,J}$, were determined by the separate solution method[19] with J = Rb^+: -0.7 ± 0.2, NH_4^+: -0.9 ± 0.2, Na^+: -1.7 ± 0.2, Cs^+: -2.3 ± 0.4, H^+: -2.4 ± 0.3, Li^+: -2.7 ± 0.3, Mg^{2+}: < -3.5, Ca^{2+}: < -4.0, Sr^{2+}: < -4.3. The selectivity sequence observed clearly deviates from that of a membrane based on an ion exchanger (Hofmeister series) [18a] and clearly demonstrates that (±)-**1** acts as an ionophore. Effective complex formation constants, K^{eff}_{IL} (I: alkali metal ion, L: ligand), in the same solvent polymeric phase were obtained by comparing the responses of two membranes, one with the H^+-selective ionophore ETH 2439 (see Experimental Section) and NaTFPB, and the other with these components and (±)-**1**.[18b] If a 1:1 stoichiometry is assumed, the $\log K^{eff}_{IL}$ values for the following alkali metal ions I were found to be: K^+: 5.4 ± 0.2, Na^+: 4.0 ± 0.2, Cs^+: 3.3 ± 0.5, Li^+: 2.9 ± 0.3. The values for K^+, Na^+, and Li^+ are lower by 3.9, 2.7, and 3.8 orders of magnitude, respectively, than for valinomycin as ligand in the same membrane matrix.[18b, c]

To analyze the effect of cation complexation on the redox properties of the fullerene–crown ether conjugates (±)-**1**–(±)-**3**, cyclic voltammetric (CV) studies were performed in CH_3CN/CH_2Cl_2 (1/1).[20] The CV of (±)-**1** is shown in Figure 2, both in the presence of one equivalent of [2.2.2]cryptand and in the presence of ten equivalents of KPF_6. The cryptand was added to try to ensure that the species observed initially was uncomplexed, since peaks corresponding to the Na^+ and K^+ complexes were observed in the FAB mass spectrum of free (±)-**1**. The first fullerene-based reduction process of uncomplexed (±)-**1** is quasireversible ($\Delta E_{pp} = 70$ mV) and occurs at $E_{1/2} = -1.04$ V versus ferrocene/ferricinium (Fc/Fc^+; Table 1). The second fullerene-based reduction process is somewhat more complicated, and exhibits what appear to be two closely spaced waves. Because of these observations, we did not attempt to quantify $E_{1/2}$ for this process.

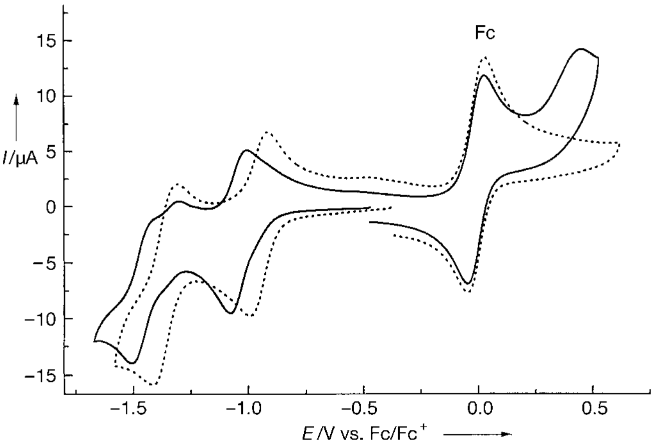


Figure 2. Cyclic voltammograms for (±)-**1** recorded at $100\,mV\,s^{-1}$ on a glassy carbon working mini-electrode; solid line: solution of free (±)-**1** with one equivalent of [2.2.2]cryptand present; dotted line: solution of (±)-**1** with ten equivalents of KPF_6.

Table 1. Redox potentials [V vs Fc/Fc+] for (±)-**1**–(±)-**3** and **11**.[a]

	+ [2.2.2]cryptand[b]		+ KPF_6[c]	
	$E^1_{1/2}$	$E^2_{1/2}$	$E^1_{1/2}$	$E^2_{1/2}$
(±)-**1**	– 1.04 (70)	– 1.51[d]	– 0.95 (79)	– 1.36 (104)
(±)-**2**	– 1.02 (79)	– 1.48[d]	– 0.97 (75)	– 1.43[d]
(±)-**3**	– 1.05 (83)	– 1.47[d]	– 1.01 (77)	– 1.46[d]
11	– 0.94 (77)	– 1.36 (80)	– 0.95 (85)	– 1.36 (93)

[a] In CH_3CN/CH_2Cl_2 (1/1) in the presence of 0.1 M Bu_4NPF_6. Fc/Fc^+ was used as the internal reference, and measurements were made with a glassy carbon working mini-electrode. Values for ΔE_{pp} [mV] are given in parenthesis. [b] One equivalent of [2.2.2]cryptand. [c] Ten equivalents of KPF_6. [d] Only the cathodic potential is given.

A closer examination of this voltammogram suggests that the first wave exhibits a shoulder at more positive potentials, although it is not as clearly resolved as in the second reduction. The chemically irreversible oxidation at about +0.4 V corresponds to the added cryptand. Addition of KPF_6 results in a large anodic shift of the reduction processes, with the first one shifting to –0.95 V versus Fc/Fc^+; this is a shift in potential of 90 mV relative to that of the uncomplexed compound and is attributed to the electrostatic effect of K^+ bound in close proximity to the carbon sphere. The shifted couples due to complexation of K^+ correspond well with the small shoulders previously mentioned. The second redox process has $\Delta E_{pp} = 100$ mV and $E_{1/2} = -1.36$ V versus Fc/Fc^+. Addition of ten equivalents of [2.2.2]cryptand reversed the voltammetric response to the original voltammogram, observed in the absence of KPF_6, which indicates that the K^+ binding process with (±)-**1** is reversible.

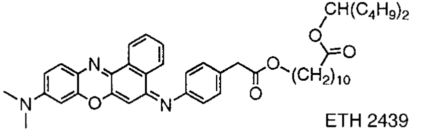
Very similar results were obtained from the CV studies of (±)-**2** and (±)-**3**, but the observed anodic shifts for the first redox couple upon complexation with K^+ were smaller (50 mV for (±)-**2** and 40 mV for (±)-**3**, Table 1). The reduction of the anodic shift from 90 mV (in (±)-**1**) to 40 mV (in (±)-**3** can be readily explained with an increasing averaged distance, evidenced by molecular modeling,[11] between the cation bound to the crown ether and the fullerene sphere as the addition pattern changes from *trans*-1, to *trans*-2, and to *trans*-3.

This investigation demonstrates that a significant perturbation of the electronic structure of the fullerene occurs only when the bound cation is positioned closely and tightly on the fullerene surface as seen in (±)-**1** and, to a lesser extent, in (±)-**2** and (±)-**3**. In previous fullerene–crown ether conjugates, the ionophore moiety was positioned at a much greater distance from the fullerene surface and, correspondingly, significant cation-mediated electrochemical effects were not detected. The Bingel macrocyclization reaction should also provide a highly effective method for positioning other organic chromophores[2c] such as porphyrins in sufficiently close proximity to the fullerene sphere to induce profound changes in the photophysical and redox properties of the carbon allotrope.

Experimental Section

Membrane preparation and EMF (electromotive force) measurements: Ion-selective electrode (ISE) membranes were prepared by dissolving the carrier(s) and NaTFPB, together with DOS and PVC (2/1 w/w), in THF (1.5 mL), pouring this solution into a glass ring (∅ = 26 mm) on a glass plate, and allowing the solvent to evaporate overnight. The three membrane compositions were (concentrations [mmol kg^{-1}] in parentheses,): (±)-**1** (6.3), ETH 2439 (6.6), and NaTFPB (3.1); (±)-**1** (7.4) and NaTFPB (3.7); ETH 2439 (6.6) and NaTFPB (3.3). Three 6-mm discs were punched from each membrane and mounted in Philips electrode bodies (IS-561, Glasbläserei Möller, Zürich). The internal filling solution was 0.01 M KCl for the ISE membrane based on (±)-**1** as only carrier, and 0.1 M KCl buffered to pH 3.9 with 5×10^{-3} M AcOH/AcOK for the other two. Before measurements, the ISEs were equilibrated with the respective internal filling solution overnight. The pH values were determined with Metrohm glass and reference electrodes. All EMF measurements were performed at room temperature (21.5 ± 0.5 °C) in stirred solutions.

ETH 2439:



Selectivity coefficients, $K^{\text{pot}}_{\text{H,J}}$, were obtained on 0.1 M chloride solutions with the separate solution method.[19] Effective complex formation constants, $K^{\text{eff}}_{\text{IL}}$ were calculated by Equation (1) from the $K^{\text{pot}}_{\text{H,J}}$ values of two ISEs based on ETH 2439 (measured at pH 11.0), one with and the other without ligand (±)-**1** (L).[18b] A 1:1 stoichiometry of the complex IL was assumed, and L_T

$$K^{\text{eff}}_{\text{IL}} = \frac{1}{L_T - R^-_T} \frac{K^{\text{pot}}_{\text{H,J}}(\text{with L})}{K^{\text{pot}}_{\text{H,J}}(\text{without L})} \tag{1}$$

and R^-_T are the total concentrations of (±)-**1** and NaTFPB, respectively. The standard deviations given were calculated from the results obtained with three ISEs from the same membrane. A measuring station of our own design, with an adapted LabView program, was used for EMF measurements.

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