Redox Characteristics of Covalent Derivatives of the Higher Fullerenes C_{70}, C_{76}, and C_{78}

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Abstract: The electrochemical properties of covalent derivatives of the higher fullerenes C_{70}, C_{76}, C_{2v}-C_{78}, and D_3-C_{78}, bearing bis(alkoxycarbonyl)methano addends, were investigated by cyclic voltammetry (CV) and/or steady-state voltammetry (SSV). Included in this study were a series of previously prepared mono- to tetrakisadducts of C_{70}, monoadducts of C_{76}, and bis- and trisadducts of C_{2v}-C_{78} and D_3-C_{78}. For all compounds, several (up to five) reduction steps and one or two oxidation steps were observed. The reduction steps usually required more energy than the corresponding processes in the parent fullerenes whereas the oxidation steps became facilitated with increasing degree of addition. A notable exception to this trend was the observation that two C_{76} monoadducts were more readily reduced than the parent fullerene and one was more difficult to oxidize. The electrochemical properties of C_{70} derivatives were found to closely resemble those of C_{60} adducts. Constitutional isomers displayed nearly identical redox characteristics. Only the first reduction process is reversible by CV or SSV in the entire series of C_{70} adducts whereas the electrochemically generated dianions of some of the derivatives underwent a rapid subsequent chemical reaction. The electrochemistry of covalent adducts of C_{76} and C_{78} differs substantially from that of the derivatives of the smaller carbon spheres C_{60} and C_{70}. Among all compounds studied, monoadducts of C_{76} are the easiest to be reduced or oxidized and their electrochemically generated multiple anions are much more stable under the conditions of the SSV and CV experiments than those of the adducts of C_{70} and the C_{78} isomers. Several of the electrochemically generated trisanions of the adducts of C_{78} isomers underwent rapid chemical reactions. Indeed, a new bisadduct of C_{2v}-C_{78}, not detected in the regular synthetic mixture, was prepared via electrolysis of a trisadduct. This C_2-symmetrical bisadduct seems to be present as an intermediate during every electrolysis of other bis- and trisadducts of C_{2v}-C_{78}.

Introduction

The discovery of a bulk preparation method for fullerenes[1] and the development of protocols for the isolation of the pure carbon spheres[2] in 1990 were rapidly followed by first reports on the investigation of the electronic properties of these molecular carbon allotropes using electroanalytical techniques such as cyclic voltammetry (CV).[3] These experimental studies demonstrated that C_{60} and the higher fullerene C_{70} displayed similar, highly solvent-dependent redox behavior, with both fullerenes undergoing up to six reversible one-electron reductions (Table 1).[4] Up to the second electron transfer, the reduction potentials of the two fullerenes are essentially the same; upon moving to higher reduction states, reduction of C_{70} becomes increasingly facilitated as compared to C_{60}.[3−5] In contrast, oxidation of the two fullerenes is much more difficult. Only one oxidation wave was observed for C_{60} whereas two one-electron oxidation waves were observed for C_{70}, with the second one occurring at the limit of the accessible potential window.[6] Thus, the electrochemical investigations confirmed theoretical predictions made soon after the mass spectrometric discovery of C_{60} in 1985.[7] Calculations in 1986 by Haddon et al. had indicated that the lowest unoccupied molecular orbital (LUMO) of C_{60} would be low-lying, triply degenerate, and,

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Table 1. Redox Parameters (CV If Not Stated Otherwise) of the Higher Fullerenes C_{70}, C_{76}, C_{2v}-C_{78}, and D_3-C_{78} in Comparison to C_{60}

fullerene	solvent^a	scan rate (V s^{-1})	$E_1^{\mathrm{Red}\ b}$	$E_2^{\mathrm{Red}\ b}$	$E_3^{\mathrm{Red}\ b}$	$E_4^{\mathrm{Red}\ b}$	$E_5^{\mathrm{Red}\ b}$	$E_6^{\mathrm{Red}\ b}$	electrode	$E_1^{\mathrm{Ox}\ b}$	$E_2^{\mathrm{Ox}\ b}$	$E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}\ c}$	ref
C_{60}	PhMe/MeCN^{d,e}	0.1	−0.98	−1.37	−1.87	−2.35	−2.85	−3.26	GCE^f	+1.26^g		2.24	4, 6
	CH_2Cl_2^{h}	0.1	−0.98 (59)^i	−1.37 (61)^i	−1.83 (60)^i				Pt				20a
C_{70}	PhMe/MeCN^{d,e}	0.1	−0.97	−1.34	−1.78	−2.21	−2.70	−3.07	GCE	+1.20^g	+1.75^g	2.17	4, 6
	CH_2Cl_2^{h}	0.1	−0.93	−1.31	−1.73	−2.09							this work
C_{76}	PhMe/MeCN (8:2)^e	2	−0.83	−1.17	−1.68	−2.10	−2.61	−3.04^j	Pt	+0.70^k		1.53	10
	$(CHCl_2)_2$^{l}		−0.83	−1.12					GCE	+0.81	+1.30^m	1.64	5h
	CH_2Cl_2^{h}		−0.83 (60)^i	−1.15 (59)^i	−1.64 (61)^i	−2.01 (68)^i			GCE	+0.84 (67)^i		1.67	this work
C_{2v}-C_{78}	PhMe/MeCN (8:2)^{e,n}	2	−0.72	−1.08	−1.79	−2.16	−2.45	−2.73^o	Pt	+0.90^p		1.62	10
	$(CHCl_2)_2$^{l}	0.1	−0.77	−1.08					GCE	+0.95	+1.43^m	1.72	5h
	CH_2Cl_2^{e}	0.1	−0.70 (62)^q	−1.04 (79)^q	−1.72(75)^q	−2.07^p (80)^q			GCE				this work
D_3-C_{78}	$(CHCl_2)_2$^{l}	0.1	−0.77	−1.08					GCE	+0.70	+1.17^m	1.47	5h
	CH_2Cl_2^{e}	0.1	−0.64 (80)^q	−0.94 (64)^q	−1.70 (82)^q	−2.05^p (94)^q			GCE	+0.74 (76)^q		1.38	this work

[a] + 0.1 M Bu_4NPF_6. [b] V vs Fc/Fc^+. [c] V, electrochemical gap. [d] At −10 °C. [e] $E = (1/2)(E_p^{\mathrm{Red}} + E_p^{\mathrm{Ox}})$. [f] GCE = glassy carbon electrode. [g] In $(CHCl_2)_2$. [h] Steady-state voltammetry (SSV, rotating disk electrode). [i] Slope $\log(I/(I_d - I)$ in mV. [j] Differential pulse voltammetry (DPV) at −15 °C, possibly irreversible. [k] In CH_2Cl_2; irreversible. [l] Osteryoung square wave voltammetry (OSWV). [m] Irreversible. [n] At −15 °C. [o] Speculated assignment. [p] Approximate potential; broad, irreversible wave. [q] ΔE_{pp} in mV.

hence, capable of accepting up to 6 electrons.[8] On the other hand, the calculated closed-shell electronic structure with an energetically low-lying, 5-fold degenerate highest occupied molecular orbital (HOMO) had suggested that the fullerene would not be readily oxidized, which is in agreement with the electroanalytical results obtained nearly five years later.

The redox properties of the less abundant higher fullerenes C_{76}, C_{78}, and C_{84} were investigated as soon as pure samples became available, and again, these were found to be highly dependent on the nature of the solvent. Four reversible reduction waves were observed by CV for C_{76} in THF, PhCN, or CH_2Cl_2,[9] whereas up to six reduction waves were found in PhMe/MeCN (8:2) at high scan rates (Table 1).[10] Two oxidation waves, with only the first one being reversible, were observed by Osteryoung square wave voltammetry (OSWV) in 1,1,2,2-tetrachloroethane,[5h] whereas only one oxidation step was observed by CV in the same solvent.[11] CV studies on the most abundant constitutional isomer of C_{78}, C_{2v}-C_{78}, in PhMe/MeCN (8:2) at −15 °C revealed six reversible one-electron reductions and one irreversible oxidation step.[10] A mixture of the two most abundant constitutional isomers of C_{78}, C_{2v}-C_{78} and D_3-C_{78}, was also investigated by OSWV (Table 1).[5h] The reduction waves of both isomers overlapped, and the minor isomer, D_3-C_{78}, was found easier to oxidize than the major C_{2v}-symmetrical isomer, in agreement with calculated HOMO−LUMO energies.[12] Measurements by differential pulse voltammetry (DPV) on mixtures of the two major isomers of C_{84}, a D_2- and a D_{2d}-symmetrical one, afforded up to 10 reduction steps in pyridine.[5h,10,11,13] The two pure constitutional isomers have only become available very recently.[14] In general, both reduction and oxidation become increasingly facilitated upon moving from C_{60} to the larger fullerenes. The electrochemical gap, i.e., the experimentally determined difference between the first oxidation and reduction potential ($E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}$) generally becomes smaller as the fullerene size increases,[5h] and correlates well with the calculated HOMO−LUMO gap which also decreases with increasing fullerene size.[12,15,16] Thus, the value of $E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}$ decreases from about 2.2−2.3 eV in C_{60} to 1.7−1.9 eV in C_{76}[5h] whereas the HOMO−LUMO gap, obtained from theoretical and experimental studies, decreases by about 20% in the same direction.

With the explosive development of the covalent chemistry of buckminsterfullerene,[17] the redox properties of numerous monoadducts and multiple adducts of C_{60} have been determined

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by CV and steady-state voltammetry (SSV).[18−21] As major trends in these various studies, it was found that with increasing degree of functionalization of the fullerene, reduction becomes increasingly more difficult and the number of reversible one-electron reduction steps decreases. Thus, the first reduction of monoadducts of C_{60} is 0.1−0.2 V cathodically shifted relative to the first electron transfer to C_{60}. Hexakisadducts of the fullerene with a pseudooctahedral array of the adducts no longer undergo a reversible reduction on the CV time scale, and irreversible electron transfer occurs at ca. 0.9 V more negative potential compared to C_{60}.[20a,b] In contrast, reversible oxidation becomes somewhat facilitated upon increasing the number of addends on the fullerene surface. The electroanalytical properties of covalent C_{60} derivatives are affected not only by the degree of addition but also by the pattern of the addends on the surface and by the nature of the addends.[20b] In general, the first reduction potential correlates with the calculated LUMO energy which increases upon enhancing the degree of functionalization.[20b]

In contrast, only a few papers on the electrochemical properties of functionalized higher fullerenes[22] have appeared. Besides the mixture $C_{70}F_x$ [$x = 52$, 54 (major component), 56, and 58],[23] only monoadducts of C_{70} have been investigated, and they all exhibited electrochemical characteristics quite close to those of unfunctionalized C_{70}. Thus, the first reversible one-electron reduction of two dihydrofullerenes $C_{70}H_2$,[24] three isomeric isoxazoline-fused C_{70} derivatives,[25] and two methano[70]fullerenes[26] occurred at ca. 0.1 V more negative potential than the reduction of the parent fullerene. Here, we report the first comprehensive electrochemical study by CV and/or SSV of the redox properties of covalent adducts of C_{70} (**1** to (±)-**7**), C_{76} (**8** to **12**), and the C_{2v}- and D_3-isomers of C_{78} ((±)-**13** to (±)-**19**) as a function of the degree and pattern of addition. Whereas the redox properties of covalent C_{60} and C_{70} adducts display many similarities, those of derivatives of the higher fullerenes C_{76} and C_{78} are found to differ substantially from those of the functionalized smaller carbon spheres.

Experimental Section

Synthesis. Compounds **1** to (±)-**7** were prepared according to ref 27, compounds **8** to **12** according to ref 28, and compounds (±)-**13** to (±)-**18** according to ref 29. No structures are shown for (±)-**13** and (±)-**18** because they remain unassigned. The parent higher fullerenes C_{70} and C_{76} were obtained as previously described.[27,28] The C_2-symmetry of (S,S,^{f}A)-**8** and (S,S,^{f}C)-**8** was further confirmed by their ^{13}C NMR spectra (see the Supporting Information).

Electrosynthesis. The C_{2v}-isomer of C_{78} was prepared by the recently discovered retro-Bingel reaction, the electrochemical removal of bis(alkoxycarbonyl)methano addends from fullerene derivatives.[30] Thus, trisadduct (±)-**15** (13 mg, 0.010 mmol) and supporting electrolyte Bu_4NPF_6 (0.8 g) were added into a home-built electrochemical cell, and the cell was degassed and pumped to 10^{-6} mmHg before the solvent CH_2Cl_2 (17 mL), which had also been degassed and pumped to the same pressure, was vapor-transferred into the cell, directly from CaH_2. Controlled potential electrolysis (CPE) at 293 K on a Pt mesh (100 mesh, 6.5 cm^2) working electrode at −1.8 V vs a Ag wire pseudo reference electrode, separated from the solution using a Vycor tip, was performed for 30 min, after which the solution was reoxidized at 0 V vs Ag for the same length of time. Removal of the electrolyte by passing the mixture through a short column (SiO_2, toluene), followed by HPLC (Buckyclutcher I Trident-Tri-DNP (10 μm), 500 × 21.1 mm i.d.; *n*-hexane/toluene 1:1), provided C_{2v}-C_{78} (3 mg, 31%), identical to material previously obtained by HPL chromatographic separation of soot enriched with higher fullerenes.[29] The isomeric D_3-C_{78} was obtained by HPLC of a mixture of C_{2v}- and D_3-C_{78} as previously described.[29,31a]

For the identification of (±)-**13** as a bisadduct of C_{2v}-C_{78}, the compound was subjected to the retro-Bingel reaction as described above at −1.7 V (vs Ag) for 30 min to yield the parent fullerene which was subsequently identified by its HPLC retention time. Similarly, retro-Bingel adduct removal from (±)-**18** at −1.7 V (vs Ag) for 30 min established this trisadduct to be a derivative of D_3-C_{78} (HPLC retention time).

A C_2-symmetrical (^1H and ^{13}C NMR) bisadduct of C_{2v}-C_{78}, (±)-**19** (structure not shown), was also prepared via an electrochemical retro-Bingel removal of one of the addends from (±)-**15** (3 mg, 0.002 mmol). The CPE at −1.3 V for 30 min yielded (±)-**19** (1.46 mg, 55%). Figure 1 shows the electrochemical transformation of (±)-**15** into (±)-**19**, as evidenced by a pronounced change of the CV. For the trisadduct, only the first reduction is reversible, while three reversible couples are observed for the product bisadduct, Figure 1. It should be noted that the first reduction of (±)-**19** is approximately 500 mV anodically shifted (easier to reduce) compared to the corresponding process for (±)-**15**. During the electrolysis of (±)-**13** (see above) to yield the retro-Bingel

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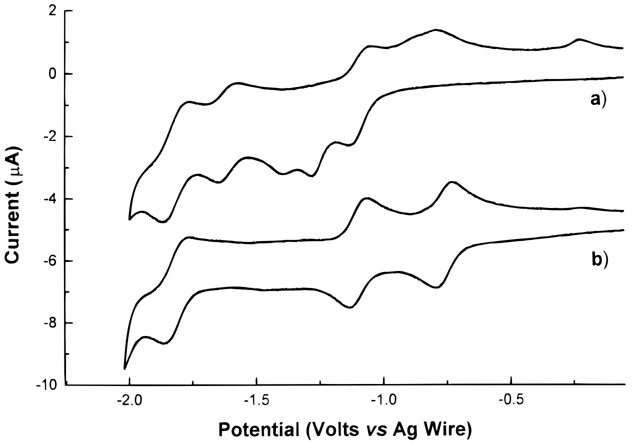

Figure 1. Cyclic voltammograms in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6) under vacuum, scan rate 0.1 V s^{-1}, referenced to a Ag wire pseudo reference electrode for (a) trisadduct (±)-**15** and (b) the retro-Bingel product (±)-**19**.

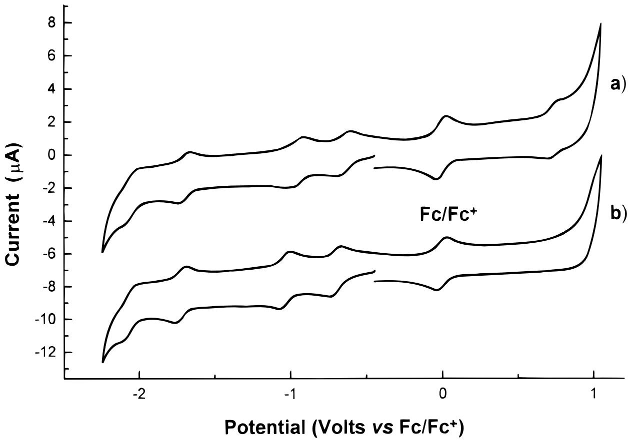

Figure 2. Cyclic voltammograms in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6), scan rate 0.1 V s^{-1}: (a) D_3-C_{78}, (b) C_{2v}-C_{78}.

product, C_{2v}-C_{78}, voltammograms such as that of (±)-**19** shown in Figure 1b were recorded, suggesting that this bisadduct is also an intermediate in this reaction. Furthermore, electrolysis of (±)-**18** to give D_3-C_{78} seems also to proceed via a bisadduct with electrochemical properties very similar to those measured for (±)-**19**. This matter is under further investigation. ^{13}C NMR ($CDCl_3$, 125.8 MHz, $Cr(acac)_3$ added): δ 162.78, 162.22, 150.62, 149.71, 149.52, 148.65, 147.15, 146.73, 146.58, 146.52, 146.35, 145.72, 145.54, 145.39, 145.36, 144.51, 144.48, 144.3, 143.16, 142.79, 141.37, 140.93, 140.31, 139.87, 139.22, 139.19, 138.59, 138.38, 137.63, 137.3, 136.68, 136.62, 136.06, 134.36, 133.53, 133.35, 133.21, 131.59, 131.51, 130.16, 74.97, 63.25, 63.11, 53.41, 48.52, 14.02, 13.88. ^1H NMR ($CDCl_3$, 500 MHz): δ 4.54−4.51 (m, 4 H, CH_2), 4.37−4.33 (m, 4 H, CH_2), 1.45 (t, J = 7.1 Hz, 6 H, CH_3), 1.35 (t, J = 7.1 Hz, 6 H, CH_3). UV−vis λ_{max} (ϵ) [CH_2Cl_2, nm (M^{-1} cm^{-1})]: 634 (960), 521 (3860), 420 (5310), 396 (5820), 332 (9210). FAB MS: calculated for $C_{92}H_{20}O_8$ 1253.18 [M^+], found 1253.1.

Electroanalytical Investigations. The electrochemical experiments were carried out at room temperature in a classical three-electrode cell in CH_2Cl_2 containing 0.1 M Bu_4NPF_6. The working electrode was a glassy carbon disk electrode (∅ 2 mm, EDI-type, SOLEA-Tacussel, Villeurbanne, France, or 3 mm from BAS) used either motionless (for CV from 0.01 to 10 V s^{-1}) or as a rotating disk electrode (RDE). The auxiliary electrode was a Pt wire, and an aqueous Ag/AgCl electrode was used as the reference electrode. The electrochemical cell was connected to a computerized multipurpose electrochemical device DACFAMOV (Microtec-CNRS, Toulouse, France) interfaced with an Apple II microcomputer or to a PAR Model 263A potentiostat/galvanostat interfaced with a PC computer. The accessible range of potentials was +1.2 to −2.2 V vs the ferrocene/ferricinium couple (Fc/Fc^+) in CH_2Cl_2. All the potentials given are referenced to the Fc/Fc^+ couple used as the internal standard.

Results and Discussion

The redox properties of all compounds considered in this investigation were determined by CV and/or by steady-state voltammetry (SSV) on a glassy carbon electrode in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6). The data determined by both methods were uniformly found to be in very good agreement.

A. Redox Characteristics of the Parent Higher Fullerenes. We first determined the redox properties of the parent higher fullerenes to calibrate our data with respect to published ones and to obtain redox potentials in the same solvent (CH_2Cl_2 + 0.1 M Bu_4NPF_6) used for the subsequent analysis of the redox properties of covalent derivatives. Table 1 depicts the redox potentials measured for C_{70}, C_{76}, C_{2v}-C_{78}, and D_3-C_{78} by various methods and in various solvents in comparison to the data reported for C_{60}. The redox properties of pure D_3-C_{78} were determined for the first time as part of this study. Generally, the redox characteristics of fullerenes measured in CH_2Cl_2 are in good agreement with those published for other solvents.

Figure 2 shows the CVs of C_{2v}-C_{78} and D_3-C_{78}. While the cathodic electrochemistry of these two isomers is reasonably similar, especially the third and fourth reductions, the first two reductions are easier for the D_3-C_{78} isomer, by 60 and 100 mV, respectively. The most striking difference is observed in the anodic scan, where the D_3-isomer exhibits a reversible one-electron oxidation at +0.74 V, while the C_{2v}-isomer does not have any observable oxidation within the potential window accessible.

This observation is in excellent agreement with the previously published anodic electrochemistry of a mixture of these C_{78} isomers, which reported the first oxidation of the D_3-isomer at 0.70 V (in 1,1,2,2-tetrachloroethane) while the corresponding process for the C_{2v}-isomer occurred 250 mV more positive, at 0.95 V.[5h]

B. Changes in the Redox Properties of C_{70} Monoadducts and Multiple Adducts as a Function of the Degree of Addition and the Nature of the Addition Pattern. The C_s-symmetrical monoadduct **1**, the three bisadducts (±)-**2** (C_2-symmetry) (±)-**3** (C_2-symmetry), and **4** (C_{2v}-symmetry), the C_s-symmetrical trisadduct **5**, the achiral tetrakisadduct **6** (C_{2v}-symmetry), and the chiral constitutional isomer (±)-**7** (C_2-symmetry) had been earlier prepared and isolated in pure form as part of an investigation of the regioselectivity of multiple cyclopropanations of C_{70} and the chiroptical properties of optically active fullerene derivatives with a chiral addition pattern.[27] In monoadduct **1**, the fullerene is cyclopropanated at one of its most curved 6−6 bonds (bond at the intersection between two six-membered rings) close to the pole; we have previously defined these most reactive bonds as α-type bonds.[32] A second nucleophilic Bingel cyclopropanation[33] of C_{70} preferentially occurs at one of the five α-type bonds at the opposite pole and leads to the constitutionally isomeric bisadduct (±)-**2**, (±)-**3**, and **4**. Successive nucleophilic additions to functionalized poles of C_{70} occur regioselectively at the less curved, less reactive β-type 6−6 bonds and generate the tris- and tetrakisadducts **5**, **6**, and (±)-**7**, respectively. The different environment of α- and β-type bonds in fullerenes is illustrated in Figure 3: fusion of four pentagons to the naphthalene substructure

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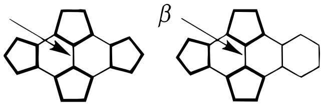
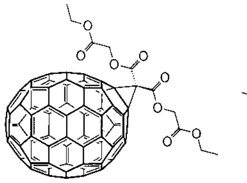


Figure 3. Illustration of the different environments of α- and β-type 6−6 bonds near the polar regions of higher fullerenes. In C_{60}, all bonds are of the α-type. With increasing fusion of pentagons to naphthalene-type fragments, the central 6−6 bond becomes more curved and more reactive against nucleophilic attack.[32]

generates a more curved, more reactive α-type 6−6 bond at its center, whereas fusion of only three pentagons leads to a less curved, less reactive β-type 6−6 bond.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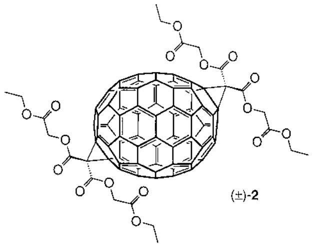
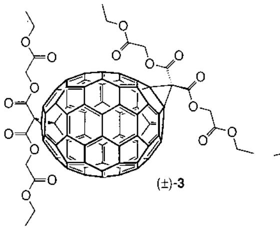
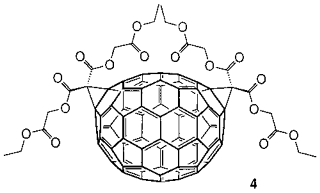

(±)-**2**


(±)-**3**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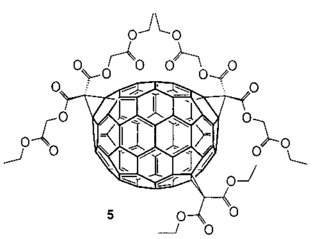
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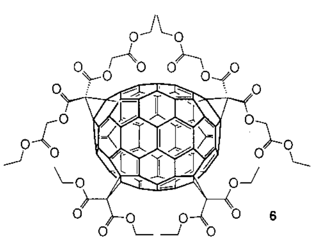
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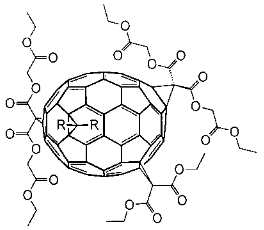


(±)-**7** R = COOEt

The redox properties of **1** to (±)-**7**, determined by SSV, are summarized in Table 2. A characteristic cyclic voltammogram of monoadduct **1** is depicted in Figure 4. As a general trend, the first reduction becomes more difficult with increasing number of addends, whereas the first oxidation becomes facilitated. Upon moving from C_{70} (Table 1) to tetrakisaddduct (±)-**7**, the first reduction step shifts by 300 mV to more negative potential whereas the first oxidation potential is lowered by ca. 270 mV (Table 2). There exist no significant differences between the redox properties of the constitutionally isomeric bisadducts (±)-**2**, (±)-**3**, and **4**, or between those of the constitutionally isomeric tetrakisadducts **6** and (±)-**7**, respectively. The electrochemical gap ($E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}$) is remarkably invariant over the entire series of C_{70} derivatives and adopts values of 2.13 ± 0.04 V.

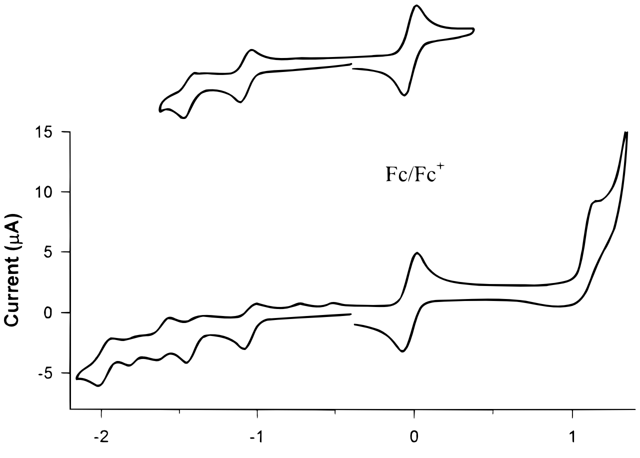
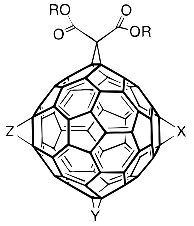


Figure 4. Cyclic voltammogram of C_{70} monoadduct **1** in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6), scan rate 0.1 V s^{-1}, for different potential windows: (top) +0.4 to −1.6 V, (bottom) +1.4 to −2.2 V.



20 R = *t*-Bu; X = Y = Z = –
21 R = Et; X = C(COOEt)$_2$; Y = Z = –
22 R = Et; X = Z = C(COOEt)$_2$; Y = –
23 R = Et; X = Y = Z = C(COOEt)$_2$

The redox characteristics of the C_{70} adducts (Table 2) closely resemble those of C_{60} derivatives, such as **20**−**23**, in which one to four methano bridges were sequentially added to 6−6 bonds along the equator.[20b] In the C_{60} series **20**−**23**, oxidation also becomes slightly facilitated with increasing degree of functionalization, with the potential shifting from +1.23 V in monoadduct **20** to +0.98 V in tetrakisadduct **23**.[20b] Upon changing from pure C_{60} to tetrakisadduct **23**, the first reduction potential becomes more negative by 210 mV. In another series of derivatives, with one to four methano adducts placed in a different array of equatorial positions, a shift of 270 mV was observed.[20c] The redox characteristics of constitutionally isomeric C_{60} bismethano adducts were also found to be nearly identical.[20b,c] The electrochemical gap in the series of C_{60} adducts is slightly larger and varies to a somewhat greater extent with the degree of addition; thus, $E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}$ determined by SSV changes from 2.31 V in **20** to 2.17 V in **23**.[20b] Although different C_{60} and C_{70} addition patterns[20a−c] as well as different addends[20b] are expected to generate different redox characteristics, we conclude with confidence from this comparison that, in general, the redox characteristics of the C_{60} and C_{70} adducts show many similarities. This was, in some way, expected given the similar redox properties of the parent fullerenes (Table 1).

At scan rates higher than 1 V s^{-1}, the steady-state voltammograms of all C_{70} adducts exhibited two well-defined, reversible reduction steps. These reduction steps are separated by 0.36 ± 0.03 V for all adducts except tetrakis-functionalized (±)-**7**. For this compound, the reduction waves are ill-resolved and the half-wave potentials corresponding to the two first reductions are only separated by 0.2 V. Note that the separation of the two first reduction steps in C_{60} mono- to trisadducts also amounts to 0.38 ± 0.03 V.[20]

Although the three first reduction steps are well defined in SSV, only the first reduction in cyclic voltammetry is a reversible one-electron transfer in the entire series of C_{70} adducts. The second reduction step was reversible in adducts **4** to (±)-**7** (see Figures 1 and 2 in the Supporting Information) whereas in adducts **1** to (±)-**3**, the second electron transfer was

Table 2. Redox Characteristics of Covalent Adducts of C_{70} Obtained by Steady-State Voltammetry (SSV) on a Glassy Carbon Working Electrode in CH_2Cl_2 + 0.1 M Bu_4NPF_6[a]

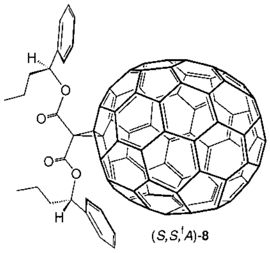
compound	E_1^{Red}	E_2^{Red}	E_3^{Red}	E_4^{Red}	E_5^{Red}	E_1^{Ox}	$E_1^{Ox} - E_1^{Red}$ [b]
1	−1.05 (62) $n = 1$	−1.44 (67) $n = 1$	−1.84 (59) $n = 1$	−2.02 (59) $n = 0.5$	−2.26 (78) $n = 0.5$	+1.12 (72) $n = 1$	2.17
(±)-**2**	−1.11 (66) $n = 1$	−1.47 (64) $n = 1$	−1.88 (54) $n = 1$	−2.06 (70) $n = 1$		+0.98 (63)	2.09
(±)-**3**	−1.12 (64) $n = 1$	−1.45 (63) $n = 1$	−1.90 (59) $n = 1$	−2.04 (50)		+1.00 (64)	2.12
4	−1.08 (65) $n = 1$	−1.45 (65) $n = 1$	−1.85 (61) $n = 1$			+1.02 (68)	2.10
5	−1.13 (77) $n = 1$	−1.52 (82) $n = 1$	−2.15 (135)			+0.97 (95)	2.10
6	−1.19 (80) $n = 1$	−1.61 (121) $n = 1$	−2.1			+0.92 (74)	2.11
(±)-**7**	−1.23 (71) $n = 1$	−1.45 (95) $n = 1$	−1.65 (95)			+0.93 (89)	2.16

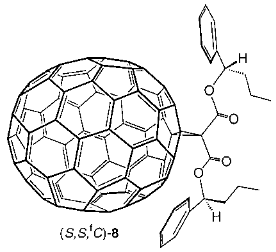
[a] V vs Fc/Fc^+; slope $\log(I/(I_d - I))$ in mV in parentheses; n = number of electrons transferred. [b] Electrochemical gap (V).

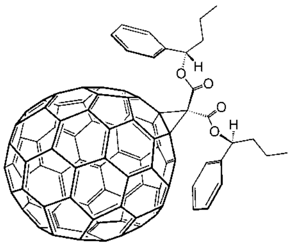
irreversible (Figure 4). For the latter adducts, the potential difference between the reduction and the corresponding reoxidation peaks increased with the potential scan rate, and also, the current of the reoxidation peak was always less than that of the reduction peak. Careful analysis of these parameters leads to the conclusion that the second reduction of **1** to (±)-**3** occurs through an EC mechanism, i.e., the sequence of an electrochemical (E) electron-transfer step followed by a subsequent chemical (C) reaction. This chemical step consumes the dianion resulting from the second electron transfer. Species generated by this chemical reaction are reduced at more negative potentials (peak around −1.6 V; see Figure 4). However, these species are not stable, as documented by the observation that their electrochemical reduction could only be detected on the short-time CV time scale at scan rates from 10 mV s^{-1} to 0.5 V s^{-1}, whereas no reduction signal was detected on the longer time scale of SSV.

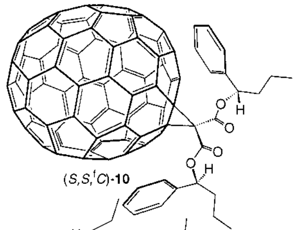
We had previously observed that the dianions of bis(methano)[60]fullerenes with cis-addition patterns, which were generated under CV conditions, were also unstable,[20b,c] and this observation recently led to the discovery of the retro-Bingel reaction, a general preparative electrochemical method for the removal of bis(alkoxycarbonyl)methano bridges from methanofullerenes.[30] Thus, monoadduct **1** was converted by electrolysis at the potential of the second, irreversible reduction step (−1.3 V vs Ag in CH_2Cl_2) in 70% yield into C_{70}. We propose that losses of one or more bis(alkoxycarbonyl)methano bridges are also among the chemical steps leading to the decomposition of the electrochemically generated dianions of (±)-**2** and (±)-**3** and of more highly reduced species of **4** to (±)-**7**.

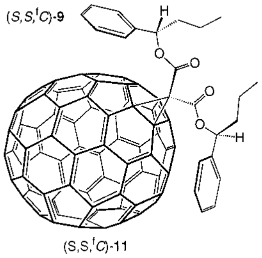
C. Redox Characteristics of C_{76} Monoadducts. Fullerene C_{76} is the smallest, intrinsically chiral carbon sphere.[34−36] As part of our program exploring the various origins of fullerene chirality and the chiroptical properties of optically active fullerene derivatives,[37] we prepared three constitutionally isomeric pairs of diastereoisomeric monoadducts together with one other constitutional isomer by nucleophilic Bingel cyclopropanation[33] with an optically active 2-bromomalonate.[28] Of these seven optically active products, only the structures for the pair of C_2-symmetrical diastereoisomers (*S*,*S*,^{f}*A*)-**8** and (*S*,*S*,^{f}*C*)-**8** (for the configurational specification, see ref 37b) could be assigned with confidence as the products arising from addition to the polar α-type bond lying on one of the three C_2 axes of the D_2-symmetrical fullerene. The other two pairs of C_1-symmetrical diastereoisomers could not be unambiguously assigned. It can be assumed that one corresponds to the products (*S*,*S*,^{f}*C*)-**9** and (*S*,*S*, ^{f}*A*)-**9**, arising from addition to the second α-type 6−6 bond near the pole, whereas the other pair results from attack at *β*-type bonds, which can theoretically produce the three pairs of diastereoisomers (*S*,*S*,^{f}*C*)-**10** and (*S*,*S*, ^{f}*A*)-**10**, (*S*,*S*,^{f}*C*)-**11** and (*S*,*S*, ^{f}*A*)-**11**, and (*S*,*S*,^{f}*C*)-**12** and (*S*,*S*,^{f}*A*)-**12**.

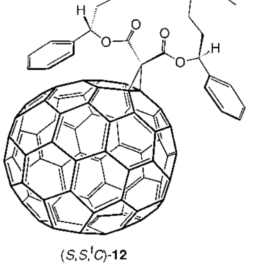

(*S*,*S*,^{f}*A*)-**8**


(*S*,*S*,^{f}*C*)-**8**


(*S*,*S*,^{f}*C*)-**9**


(*S*,*S*,^{f}*C*)-**10**


(*S*,*S*,^{f}*C*)-**11**


(*S*,*S*,^{f}*C*)-**12**

For the first ever electrochemical investigations of C_{76} derivatives, we considered one of the C_2-symmetrical diastereoisomers (*S*,*S*,^{f}*A*)-**8** and (*S*,*S*,^{f}*C*)-**8**, and one component (diastereoisomer) of each of the two most abundant pairs of C_1-symmetrical diastereoisomers which we specify as **A** (**9**−**12**) and **B** (**9**−**12**) to make it clear that the constitutionally different compounds **A** and **B** could be components of any one of the four C_1-symmetrical pairs of diastereoisomers **9**−**12**. No

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Table 3. Redox Characteristics of Covalent Monoadducts of C_{76} Obtained by Steady-State Voltammetry (SSV) on a Glassy Carbon Working Electrode in CH_2Cl_2 + 0.1 M Bu_4NPF_6[a]

compound	E_1^{Red}	E_2^{Red}	E_3^{Red}	E_4^{Red}	E_1^{Ox}	E_2^{Ox}	$E_1^{Ox} - E_1^{Red}$ [b]
8[c]	−0.79 (58) $n = 1$	−1.10 (59) $n = 1$	−1.65 (57) $n = 1$	−2.02 (58) $n = 1$	+0.84 (63) $n = 1$	+1.2 (87) $n > 1$	1.63
A (9−12)[d]	−0.79 (58) $n = 1$	−1.10 (58) $n = 1$	−1.66 (61) $n = 1$	−2.06 (62) $n = 1$	+0.78 (58) $n = 1$	+1.18 (100)	1.57
B (9−12)[d]	−0.87 (58) $n = 1$	−1.23 (60) $n = 1$	−1.69 (65) $n = 1$	−1.99 (61) $n = 1$	+0.87 (59) $n = 1$	+1.12 $n > 1$	1.74

[a] V vs Fc/Fc$^+$; slope $\log(I/(I_d - I))$ in mV in parentheses; n = number of electrons transferred. [b] V, electrochemical gap. [c] (*S*,*S*,^{f}*A*)-**8** or (*S*,*S*,^{f}*C*)-**8**. [d] Optically pure diastereoisomer which can be **9**, **10**, **11**, or **12**; an unambiguous structural assignment was not yet possible.[28]

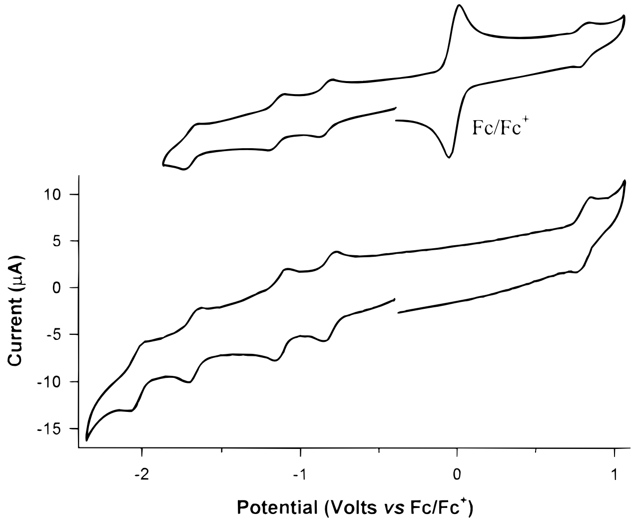


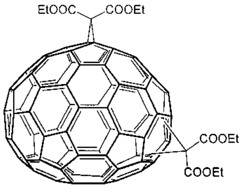
Figure 5. Cyclic voltammogram of C_{76} monoadduct (*S*,*S*,^{f}*A*)-**8** in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6), scan rate 0.1 V s^{-1}, for different potential windows: (top) +1.1 to −1.9 V, (bottom) +1.1 to −2.4 V.

differences in the electrochemistry are expected for the two components of one pair of diastereoisomers, since the electroactive fullerene cores in each pair are enantiomeric. Table 3 shows electrochemical results, and Figure 5 depicts the CV of monoadduct (*S*,*S*,^{f}*A*)-**8**.

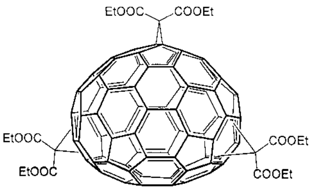
At first view, one notices that the four reductions measured in CH_2Cl_2 for the parent fullerene (Table 1) and the three C_{76} monoadducts (Table 3) occur at comparable potentials. Remarkably, monoadducts **8** and **A** (**9−12**) are slightly more readily reduced than the parent fullerene (Table 1), which is in sharp contrast to the results obtained for methano-bridged derivatives of all other fullerenes studied thus far. The four reduction steps correspond to reversible electron transfers only in the cases of **8** and **A** (**9−12**) whereas the third reduction of **B** (**9−12**) is only reversible at high potential scan rates (≥0.5 V s^{-1}). At variance with similar C_{60} and C_{70} derivatives, discussed above, the generated dianions and trianions of the C_{76} monoadducts are much more chemically stable. This is evidenced by the observation that the third reduction step of the monoadduct of C_{70} with the same addition pattern as in **1** but with the optically active malonate addend used in the C_{76} derivatives exhibits reversibility in CV only at scan rates beyond 1 V s^{-1}, while the third reduction of the studied C_{76} derivatives behaves reversibly at all scan rates. In agreement with a significantly higher stability, we also observed that the retro-Bingel reaction, i.e., the electrolytic removal of the bis(alkoxycarbonyl)methano bridges in **8**, **A** (**9−12**), and **B** (**9−12**), occurs sluggishly and only in low yield.[30]

All three C_{76} monoadducts undergo a first reversible and a second irreversible oxidation step, in analogy to the reported behavior for the parent fullerene.[5h] The first oxidation potentials of the parent fullerene and its monoadducts are also rather close, with the oxidation of **A (9−12)** occurring somewhat easier. Since reduction of **A (9−12)** is also slightly more facile, the electrochemical gap becomes considerably smaller than that of the parent fullerene or the other two monoadducts. At variance with all other covalent fullerene derivatives studied, monoadduct **B (9−12)** is more difficult to oxidize than the parent fullerene. In sharp contrast to the isomeric C_{70} monoadducts (Table 2), the electrochemical gaps of the C_{76} monoadducts differ significantly from one another. They could, therefore, become useful diagnostic tools in the quite challenging structural assignment of covalent derivatives of functionalized derivatives of C_{76}.

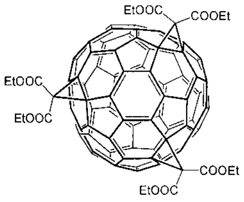
D. Redox Characteristics of Covalent Derivatives of the Isomeric Fullerenes *C*$_{2v}$-C_{78} and *D*$_3$-C_{78}. C_{78} is the smallest fullerene for which several isomers have been isolated that satisfy the isolated pentagon rule.[31] Multiple cyclopropanation of an isomeric mixture of C_{2v}- and D_3-C_{78} (ca. 3:1) with diethyl 2-bromomalonate (2 equiv) evidenced a high reactivity of the two isomeric fullerenes toward nucleophilic attack and yielded two C_1-symmetrical bisadducts together with at least eight isomeric trisadducts.[29] The most abundantly formed products were chosen for this electrochemical study, namely, two C_1-symmetrical bisadducts of C_{2v}-C_{78}, (±)-**13**, of unknown structure (thus not drawn), and (±)-**14**, C_{2v}-C_{78} trisadduct (±)-**15** with C_2-symmetry, a C_3-symmetrical tris-adduct of D_3-C_{78} of either structure (±)-**16** or structure (±)-**17**, a C_1-symmetrical trisadduct of D_3-C_{78}, (±)-**18**, of unknown structure (thus not drawn), and the C_2-symmetrical bisadduct (±)-**19** (exact structure also unknown), prepared via electrolytic retro-Bingel of trisadduct (±)-**15**. As indicated in the compound drawings, three structures are possible for (±)-**14** and (±)-**15**, respectively, one of which is preferred on the basis of π-bond order considerations.[29,38] Such considerations also suggest that structure (±)-**17** is preferred for the C_3-symmetrical trisadduct of D_3-C_{78}. The electrochemical data for these compounds are summarized in



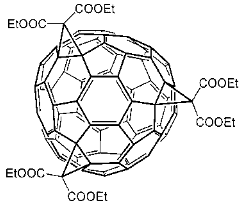
(±)-**14**



(±)-**15**



(±)-**16**



(±)-**17**

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Table 4. Redox Characteristics of Covalent Adducts of C_{2v}-C_{78} and D_3-C_{78} Obtained by Steady-State Voltammetry (SSV) or Cyclic Voltammetry (CV) on a Glassy Carbon Working Electrode in CH_2Cl_2 + 0.1 M Bu_4NPF_6[a]

compound	E_1^{Red}	E_2^{Red}	E_3^{Red}	E_4^{Red}	E_5^{Red}	E_1^{Ox}	$E_1^{Ox} - E_1^{Red}$ [b]
(±)-**13**	−0.92 (68) $n = 1$	−1.29 (80) $n = 1$	−1.86 (75) $n = 1$	−2.08 (88) $n = 1$		+0.86 (80) $n = 1$	1.78
(±)-**14**	−1.07 (59) $n = 1$	−1.30 (62) $n = 1$	−1.78 (70) $n = 1$	−1.89 (60) $n = 1$	−2.06 (62) $n = 1$	+0.85 (68) $n = 1$	1.92
(±)-**15**	−1.14 (67) $n = 1$	−1.34 (58) $n = 1$	−1.76 (110) $n > 1$	−1.90 (52) $n = 1$	−2.11 (66) $n = 1$	+0.77 (60) $n = 1$	1.91
(±)-**16** or (±)-**17**	−1.09 (70) $n = 1$	−1.40 (70) $n = 1$	−1.64 (70) $n = 1$	−1.91 (90) $n = 1$		+0.81 (62) $n = 1$	1.90
(±)-**18**	−1.07 (69)	−1.39 (67)	−1.98 (83)[c]	−2.27 (104)[c]		+0.78 (71)	1.85
(±)-**19**	−0.81 (73)	−1.14 (80)	−1.86 (96)[c]	−2.06 (104)[c]		+0.81 (80)	1.62

[a] V vs Fc/Fc$^+$; slope $\log(I/(I_d - I))$ in mV in parentheses; n = number of electrons transferred. [b] V, electrochemical gap. [c] Badly resolved.

Table 4. The CV of (±)-**15** along with that of its retro-Bingel bisadduct product (±)-**19** is presented in Figure 1.

All six C_{78} adducts studied here exhibited four one-electron reduction steps and one oxidation step, while bisadduct (±)-**14** and trisadduct (±)-**15** displayed an additional fifth reduction step (Table 4). The oxidation step is a reversible, or close to reversible, one-electron process, similar to the one observed for the free C_{78} isomers in 1,1,2,2-tetrachloroethane and for the D_3-isomer in this study.[5h] Oxidation of trisadduct (±)-**15** is clearly facilitated as compared to that of the bisadducts (±)-**13** and (±)-**14**.

Among the reduction steps, the first two and the last one are all one-electron transfers. The first is either reversible or quasi-reversible, and this holds also for the second reduction step in bisadducts (±)-**13** and (±)-**19** and in trisadduct (±)-**18**. The third reduction is a one-electron step, close to reversibility in bisadducts (±)-**13** and (±)-**19** and trisadducts (±)-**16**/(±)-**17** and (±)-**18**, whereas stationary voltammetry revealed an additional one-electron step in bisadduct (±)-**14**, the two half-wave reduction potentials being separated by 110 mV only. Similarly, in stationary voltammetry, the third reduction wave of (±)-**15** had the amplitude of a two-electron process, whereas an additional one-electron reduction step was observable close to the third one ($\Delta E_{1/2}$ = 140 mV). These additional reduction signals were not detected on the shorter CV time scale. Thus, it is reasonable to ascribe them to species resulting from chemical reactions of the electrochemically generated dianions of (±)-**14** and (±)-**15**. Again, this analytical observation correlates well with the ready formation of C_{2v}-C_{78} by retro-Bingel reaction of (±)-**15** under controlled potential electrolysis, which was used to generate the pure fullerene for this study.

The electrochemical behavior of (±)-**19** deserves special attention and is presented in Figure 6 along with the CV of the parent C_{2v}-C_{78}. The four reduction steps as well as the one-electron oxidation are reversible or quasi-reversible. In many ways, including the actual potential values, this bisadduct is similar to the parent compound. The two adducts result only in a cathodic shift of ~100 mV, and the spacing between the first three reductions is very similar in (±)-**19** to the corresponding values for C_{2v}-C_{78}. Coulometric experiments show that the dianion of (±)-**19** is stable but the trianion (beyond −1.9 V) decomposes and eventually leads to the formation of C_{2v}-C_{78} if exhaustively electrolyzed. Interestingly, during CPE of bisadduct (±)-**13**, an intermediate voltammogram very similar to that of (±)-**19** (Figure 6a) was also observed. This could mean that this particular bisadduct isomer is energetically favored and accessible electrochemically, by removal of an addend from a trisadduct derivative, or perhaps by isomerization of the malonates after electron transfer. Evidence of such electrochemically induced "shuffling" of malonate adducts on the surface of C_{60} has recently been obtained and is being reported separately. We believe that a similar mechanism is operative when any bismalonate adduct of C_{78} is coulometrically reduced with two electrons per molecule. Preliminary measurements indicate that the retro-Bingel reaction of trisadduct (±)-**18** to give D_3-C_{78} also proceeds via a bisadduct displaying a similar voltammogram to that obtained for (±)-**19**. This matter is under further investigation.

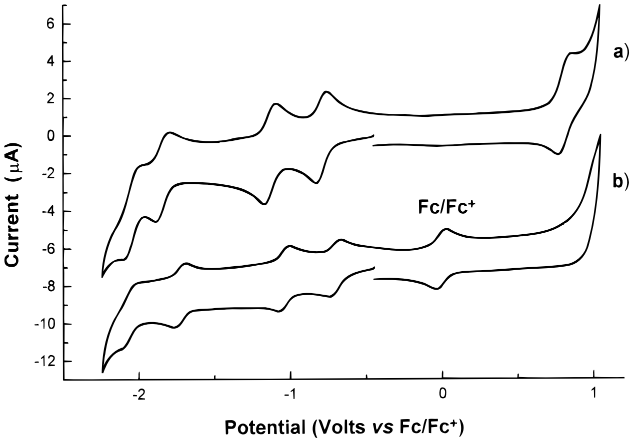

Figure 6. Cyclic voltammograms in CH_2Cl_2 (+ 0.1 M Bu_4NPF_6), scan rate 0.1 V s^{-1}, of (a) bisadduct (±)-**19** and (b) C_{2v}-C_{78}.

In general, reduction of functionalized C_{78} requires more energy than that of the parent fullerene, whereas the oxidation is facilitated. This is in agreement with the findings for C_{60} and C_{70} but contrasts with some of the remarkable observations made for C_{76} monoadducts which, depending on the addition pattern, are more readily reduced or more difficult to oxidize than the parent fullerene.

Interesting differences in the relative energies of the two first unoccupied orbitals in the various adducts become apparent from the measured data. Whereas the separation between the first and second reduction steps in bisadduct (±)-**13** and trisadducts (±)-**16**/(±)-**17** and (±)-**18** amounts from 0.31 to 0.37 V, this difference is only 0.23 V in bisadducts (±)-**14** and 0.20 V in trisadduct (±)-**15**. In analogy to the findings for the other higher fullerene derivatives (Tables 2 and 3) the second and third reductions are separated by a wider gap than the first and second ones. The electrochemical gap ($E_1^{Ox} - E_1^{Red}$), which correlates well with the HOMO−LUMO energy separation in fullerenes,[5h] increases by 0.1−0.5 V upon changing from the pure C_{78} isomers to the covalent derivatives.

It is worth noticing that the redox pattern of some of the C_{78} bis- and trisadducts is diagnostic and should be of use in their unambiguous identification. Thus, bisadducts (±)-**13** and (±)-**14** are specifically recognized by the large difference in their first reduction potential, which is 150 mV less negative for the former than for the latter. Similarly, among the trisadducts, (±)-**15** is much more difficult to reduce than the other two derivatives (Table 4).

Conclusions

This first comprehensive investigation of the redox properties of covalent adducts of the higher fullerenes bearing similar bis(alkoxycarbonyl)methano addends has revealed a series of interesting trends. A number of features are common to lower adducts (mono- to tetrakisadducts) of all the fullerenes studied, including C_{60}. All derivatives undergo several electrochemical reduction and one or two oxidation steps. For a given fullerene, the first one-electron reduction usually becomes more difficult with increasing degree of addition whereas oxidation becomes facilitated. A notable exception to this general trend was observed in the series of isomeric monoadducts of C_{76}, where the two derivatives **8** and **A** (**9**−**12**) were reduced more readily than the parent fullerene and the derivative **B (9**−**12)** was more difficult to oxidize. Both the first reduction and oxidation steps are the most facilitated in C_{76} derivatives, followed presumably (as extrapolated from the data measured for bis- and trisadducts) by derivatives of the C_{78} isomers, C_{70}, and finally C_{60}. Similarly, the electrochemical gap ($E_1^{\mathrm{Ox}} - E_1^{\mathrm{Red}}$) for comparable covalent adducts seems to diminish in the sequence $C_{60} > C_{70} > C_{2v}$- and D_3-$C_{78} > C_{76}$. These trends resemble those observed experimentally (Table 1) and predicted by theory[15,39] for the pure carbon spheres.

A large number of similarities were encountered in the redox characteristics of derivatives of C_{60} and C_{70}, at variance with the adducts of the larger carbon spheres C_{76} and C_{78}. Thus, the redox characteristics (first reduction and oxidation potential, electrochemical gap) of constitutionally isomeric adducts are nearly identical. In contrast, the potentials for electron transfer to and from constitutionally isomeric adducts of C_{76} and C_{78} differ significantly and thus bear diagnostic value.

During this study, a notable instability of electrochemically generated dianions and higher anions of the bis(alkoxycarbonyl)methano adducts was observed, and this instability was found to correlate nicely with the propensity of these compounds to undergo loss of the methano bridges in the recently discovered retro-Bingel reaction,[30] a preparatively useful electrosynthetic process. This new electrosynthetic method allowed us to obtain a new C_{2v}-C_{78} bisadduct that was not present in the regular Bingel reaction. Furthermore, this bisadduct seems to correspond to an intermediate that is formed during retro-Bingel reactions of other tris- and bisadducts of C_{2v}-C_{78}, as a result of either removal of a bismalonate moiety or shuffling of the latter moieties around the C_{78} sphere.

For C_{60} multiple adducts, useful correlations between the electrochemical characteristics, the computed LUMO energy and electron affinity, and the reactivity of fullerenes toward nucleophiles and carbenes and as dienophiles in cycloaddition reactions have been established.[20b] Similarly, this electrochemical study makes a substantial contribution to the understanding of electronic and reactivity properties of the covalent derivatives of higher fullerenes. We are now extending these investigations to derivatives of fullerene C_{84} as well as to derivatives of higher fullerenes with a very high degree of addition.

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Supporting Information Available: ^{13}C NMR spectra of (S,S,^{f}A)-**8** and (S,S,^{f}C)-**8** and cyclic voltammograms of C_{70} bisadduct **4** and C_{70} tetrakisadduct **6** (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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