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Electrochemical and electrophysical properties of aminomethano- and tetrahydropyridino-C_{60}-fullerenes

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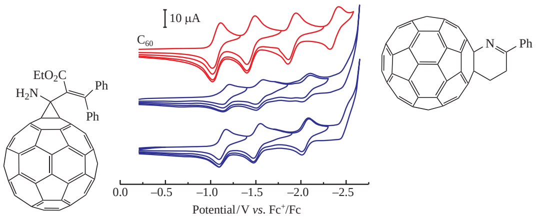
The electrochemical and electrophysical properties of fullerene C_{60} derivatives containing an amino group at the methanofullerene bridging carbon atom and a tetrahydropyridine moiety annelated to the fullerene have been determined. The electrochemical reduction of the derivatives was found to proceed less easily than that of C_{60} but more easily than that of unsubstituted methano- and pyrrolidinofullerenes.



The electrochemical and electrophysical properties of fullerenes and their derivatives are significant for the design of novel practically valuable materials[1–4] based on carbon clusters. No wonder that one of the first studies published immediately after the development of preparative methods for fullerene C_{60} synthesis was devoted to its electrochemical behavior.[5] As a result, the radical anion and dianion of fullerene C_{60} with reduction potentials of –1.01 and –1.40 V, respectively, were obtained for the first time. Subsequently, tri-,[6] tetra-,[7] penta-[8] and hexa-anions[9–11] of C_{60} were reported. It was found that difference between the reduction potentials of two successive steps is approximately the same in all cases being equal to ~0.45 V, which is in good agreement with theoretical calculations,[12] indicating that the fullerene molecule has three degenerate LUMOs.

The possibility of using fullerenes as a basis for new prospective materials for molecular wires, surface coatings and electrooptical devices stimulated research into fullerene functionalization aimed at changing the electronic properties of C_{60} carbon clusters and investigating the effect of the nature, geometry, structure and number of attached addends on the electrochemical reduction of fullerenes. Most of these studies dealing with the electrochemistry of fullerenes and their derivatives represent voltammetric measurements of their reduction because this feature dictates the scope of their practical applications. Therefore, voltammetric characteristics have been measured for almost any class of fullerene derivatives.

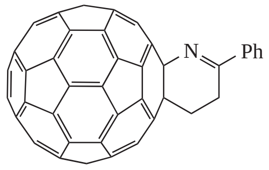
The results of electrochemical studies of fullerene and its derivatives are summarized in reviews[13–15] and monographs.[16,17] Despite the fact that the electrochemical behavior of fullerenes and their derivatives has been investigated in detail, publications appear, which report novel, previously unknown and difficult-to-prepare derivatives of carbon clusters, whose voltammetric characteristics have not been measured and studied so far.

Recently,[18,19] we reported the synthesis of previously unknown fullerotetrahydropyridine derivatives of C_{60}[18] and aminomethanofullerenes, which are otherwise difficult to prepare,[19] by the multicomponent reaction of fullerene C_{60} with nitriles and cyanoacrylates in the presence of EtMgBr and a $Ti(OPr^i)_4$ catalyst.

Here, we report the electrochemical and electrophysical properties of new classes of functionally substituted C_{60} fullerenes.

To study electrochemical reduction, we used phenyl-substituted fullerotetrahydropyridine **1** and aminomethanofullerene **2** as model compounds.

The cyclic voltammograms of C_{60} derivatives **1** and **2** were measured in dichlorobenzene with Bu_4NBF_4 as a supporting electrolyte (10^{-1} M) at room temperature (Figure 1 and Table 1).[†]



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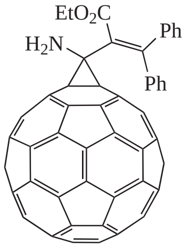

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[†] The experiments were carried out in a dry argon atmosphere. Bu_4NBF_4 from Aldrich was used without further purification. Anhydrous dichlorobenzene (Acros Organics) was distilled from phosphoric anhydride.

Cyclic voltammograms were recorded with a BASi Epsilon potentiostate (USA) at room temperature in *o*-dichlorobenzene (10^{-3} M). 0.1 M Bu_4NBF_4 was used as a supporting electrolyte, and a glassy carbon electrode was used as a working electrode. The auxiliary electrode was a platinum rod. All potentials are referred to the $Ag/AgNO_3$ redox couple and recalculated from Fc^+/Fc. The scan rate was 100 mV s^{-1}.

The resistance of films was measured with an AKIP-8602 digital resistance meter. The error of measurements was ±5%. The conductivity was determined from the resistance ($G = 1/R$). The temperature was measured to within ±1% using an APPA-107N digital multimeter.

Table 1 Electrochemical characteristics of the reduction of compounds **1**, **2** and C_{60}.[a]

Compound	Peak no.	Cyclic voltammetry						Differential pulse voltammetry				
		Reduction					Oxidation	Reduction	Oxidation	E_{LUMO}/eV	E_{HOMO}/eV	ΔE/eV
		E_{pc}/V	E_{pa}/V	i_{pa}/i_{pc}	ΔE/V	$E_{1/2}$/V	E_{pa}/V	E_{red}/V	E_{ox}/V			
1	1	–1.21	–1.13	0.51	0.08	–1.17	1.21	–1.10	1.10	–3.70	–5.90	2.20
	2	–1.58	–1.50	0.86	0.08	–1.54	–	–1.47	–	–	–	–
	3	–2.11	–2.01	0.72	0.10	–2.06	–	–1.99	–	–	–	–
	4	–2.52	n/a	n/a	n/a	n/a	–	–2.40	–	–	–	–
2	1	–1.17	–1.09	0.95	0.08	–1.13	1.06	–1.06	0.98	–3.74	–5.78	2.11
	2	–1.55	–1.47	1.00	0.08	–1.51	–	–1.44	–	–	–	–
	3	–2.09	–2.01	0.95	0.08	–2.05	–	–1.99	–	–	–	–
	4	–2.53	n/a	n/a	n/a	n/a	–	–2.43	–	–	–	–
C_{60}	1	–1.11	–1.02	0.95	0.09	–1.07	1.25	–0.99	1.08	–3.81	–5.88	2.14
	2	–1.49	–1.40	1.00	0.09	–1.45	–	–1.37	–	–	–	–
	3	–1.95	–1.86	1.00	0.09	–1.91	–	–1.84	–	–	–	–
	4	–2.42	–2.32	0.76	0.10	–1.37	–	–2.31	–	–	–	–

[a] The data for C_{60} are close to reported values[16] obtained under similar conditions. Due to proximity of the fourth peak to the solvent (*o*-dichlorobenzene) discharge line, the calculation of i_{pa}/i_{pc} is in some cases not appropriate (designated as n/a). The HOMO/LUMO energy (in eV) was calculated as $E = -(E_{\text{DPV } vs.\ \text{Fc}^+/\text{Fc}} + 4.8)$.[17]

Cycloadducts **1** and **2** can reversibly add four electrons in four steps (Figure 1) to give stable multianions.

$$\mathrm{A} + e \xrightleftharpoons{E_1} \mathrm{A}^{\cdot-} + e \xrightleftharpoons{E_2} \mathrm{A}^{2-} + e \xrightleftharpoons{E_3} \mathrm{A}^{3-} + e \xrightleftharpoons{E_4} \mathrm{A}^{4-}$$

The first reduction potentials of fullerenes **1** and **2** are somewhat more negative than that of fullerene C_{60} due to the effect of substituents (Table 1). The fourth reduction peak is easily discernible for compound **2**, while it is nearly merged with the background for cycloadduct **1**. The stability of the electrochemically reduced fullerene species (a radical anion formed in the first step and polyanions formed in the subsequent steps) can be evaluated from the ratio of anodic and cathodic currents in the i_{pa}/i_{pc} peak. The reduced form of **1** is less stable than that of **2**.

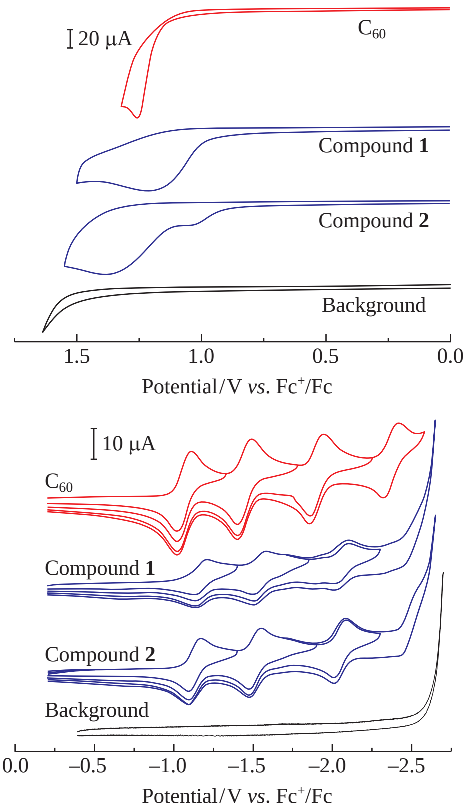

Figure 1 Cyclic voltammograms of C_{60} and its derivatives **1** and **2** (10^{-3} M in 1,2-dichlorobenzene, Bu_4NBF_4).

It is well known that the effect of substituents in a C_{60} molecule on the reduction potentials is composed of two effects, namely, a change in the electronic properties of the proper fullerene sphere as a result of disruption of the common π-system of conjugation and the electron-donating or -withdrawing properties of the substituents. For example, the substituents at the *exo*-carbon atom of C_{60} in methanofullerene **2** are not involved in the common fullerene π-system, which can be regarded as a reaction center for the electron transfer because of two σ-bonds; therefore, they affect only slightly the reduction potentials of the C_{60} derivatives. The potential shift reported for this class of carbon clusters is in the limits of up to 200 mV.[21] Meanwhile, strong electron-withdrawing substituents in methano-[22] or azahomofullerenes[23] can overcompensate for the loss of electron affinity as a result of conjugation π-system disruption. The introduction of a cyclopropane group into the C_{60} molecule makes electron transfer to the fullerene sphere more difficult by 120 mV.[24] Thus, the three-membered ring of the methanofullerene molecule is not involved in the delocalization of an excess negative charge, only the fullerene cage π-system being involved in this process. The cyclopentane and cyclohexane derivatives of C_{60} are 100 and 80 mV more difficult to reduce than parent C_{60},[25] while the presence of a nitrogen atom in fulleropyrrolidines has a slight influence on the potentials of the first two reduction steps compared with cyclopentane derivatives.[26,27]

The electrochemical reduction of C_{60} derivatives **1** and **2** occurred at more negative potentials than that of the parent C_{60} (the difference is 60–90 mV). This distinguishes compounds **1** and **2** from unsubstituted methano- and pyrrolidinofullerene. These results indicate that the introduction of an amino group or an acrylate substituent into the three-membered ring of **2** compensates, to a certain extent although not completely, for the loss of the electron affinity caused by the disruption of the conjugation π-system.

The oxidation waves of fullerene C_{60} and compounds **1** and **2** are multielectron and irreversible; this may be caused by sample polymerization under conditions of electrochemical measurements and is typical[17] of fullerene and its derivatives in *o*-dichlorobenzene. The potentials are close to the literature data.[17,28,29]

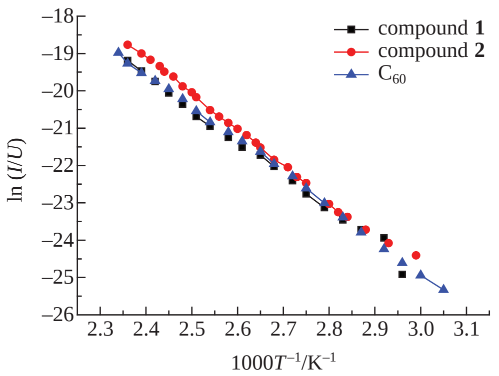

Figure 2 Temperature dependence of the conductivity of films of compounds **1** and **2**.

The E_{HOMO}, E_{LUMO} and the energy gap between the frontier orbitals ΔE were calculated based on differential pulse voltammetry experiments. The energy gap found for the test compounds was 2.1–1.2 eV. For fullerene C_{60}, ΔE = 2.14 eV is larger than that determined from the temperature dependent microwave conductivity, 1.86 eV,[30] probably, due to the solvent effect.

The band gap width can be determined by electrophysical methods, in particular, from the temperature dependence of the film conductivity G in a range of 300–450 K: $G = G_0\exp(-\Delta E/2kT)$. From the slope of the linear segments, it was possible to calculate ΔE for each sample; the result was about 1.70 eV, which is consistent with published data for pyrrolidine and aminomethanofullerenes. Meanwhile, the value of ΔE can be interpreted as E_g (the gap between the LUMO and the HOMO).

Furthermore, Table 2 indicates that the conductivities of samples differ little from one another and change by approximately two or three orders of magnitude (from 1.4×10^{-11} to 2.5×10^{-11} S) on heating from 60 to 150 °C.

Table 2 Conductivity of compounds **1**, **2** and C_{60} at 60 °C.

Compound	G/Ω^{-1} (at 60 °C)	ΔE/eV
1	1.5×10^{-11}	1.67
2	2.5×10^{-11}	1.70
C_{60}	1.4×10^{-11}	1.63

Thus, we studied in detail the electrochemical and electrophysical properties of carbon cluster derivatives, tetrahydropyridino- and aminomethanofullerenes. The electrochemical reduction of these C_{60} derivatives occurs less easily than that of C_{60} but more easily than that of unsubstituted methano- and pyrrolidinofullerenes, which may imply that the introduction of new substituents into the three-membered ring of methanofullerene or the addition of a tetrahydropyridine addend to C_{60} compensates somewhat for the loss of electron affinity of the fullerene cage. Relying on the obtained results, one can predict and control the electrochemical and electrophysical properties of new C_{60} derivatives.

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