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Synthesis and Electrophysical Properties of the Fullerene C_{60}–1,3,5-Trimethoxybenzene Conjugate

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Abstract—A conjugate of fullerene C_{60} with methyl 3-oxo-3-(2,4,6-trimethoxyphenyl)propanoate (monoacylation product of 1,3,5-trimethoxybenzene with methyl 3-chloro-3-oxopropanoate) has been synthesized under the Bingel–Hirsch conditions. Redox properties of the conjugate have been studied by cyclic voltammetry.

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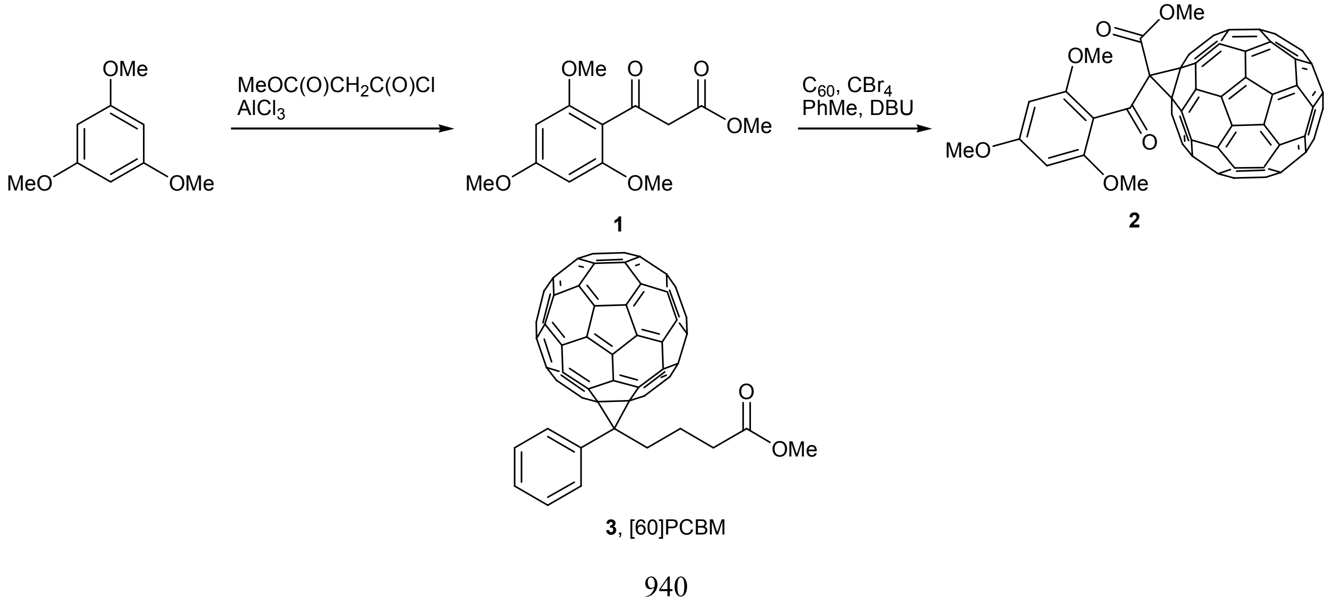
Nowadays, solar energy transduction into electrical energy is a global problem [1–3]. Bulk heterojunction solar cells utilize combinations of *p*-donor and *n*-acceptor materials [4]. Small molecules in which donor and acceptor fragments are covalently bonded to each other may be used as micro models of bulk-heterojunction photovoltaic devices [5, 6]. In this article we describe one such compound obtained from fullerene C_{60} and keto ester **1** which was prepared by Friedel–Crafts acylation of 1,3,5-trimethoxybenzene with methyl 3-chloro-3-oxopropanoate. The reaction of **1** with C_{60} under the Bingel–Hirsch conditions [7] afforded adduct **2** in more than 50% yield (Scheme 1).

Molecule **2** contains a donor trimethoxyphenyl fragment and acceptor methyl 3-oxopropanoate residue linked through C^2 to methanofullerene. Therefore, it can be regarded as a “push–pull” system where the acceptor and donor fragments are cross-conjugated, which should enable a fundamental photovoltaic process, absorption of light, generation of excitons, and charge separation within a single molecule.

The electrophysical characteristics of fullerene derivative **2** were determined by studying redox properties in *o*-dichlorobenzene by cyclic voltammetry (CV) in comparison with fullerene conjugate **3** ([60]PCBM) which is widely used in organic solar

Scheme 1.



Electrochemical properties of methanofullerenes **2** and **3**[a]

Compound no.	E^{1}_{red}, V	E^{2}_{red}, V	E^{3}_{red}, V	E^{4}_{red}, V	$E^{\mathrm{on}}_{\mathrm{red}}$,[b] V	E_{LUMO}, eV (DFT)[c]	E_{HOMO}, eV (DFT)[d]	E_{g}, eV (DFT)
2	–0.86	–1.28	–1.77	–2.07	–0.75	–4.05 (–3.75)	–5.70 (–5.52)	1.65 (1.77)
3	–0.88	–1.35	–1.94	–	–0.78	–4.02 (–3.68)	–5.61 (–5.48)	1.59 (1.80)

[a] The reduction potentials E_{red} were determined against Fc/Fc^{+} redox couple (internal standard) using Ag/Ag^{+} electrode.

[b] $E^{\mathrm{on}}_{\mathrm{red}}$ is the reduction wave onset potential relative to Fc/Fc^{+} according to the CV data.

[c] $E_{\mathrm{LUMO}} = -(E^{\mathrm{on}}_{\mathrm{red}} + 4.8)$ (eV) [9].

[d] $E_{\mathrm{HOMO}} = -(E^{\mathrm{on}}_{\mathrm{ox}} + 4.8)$ (eV).

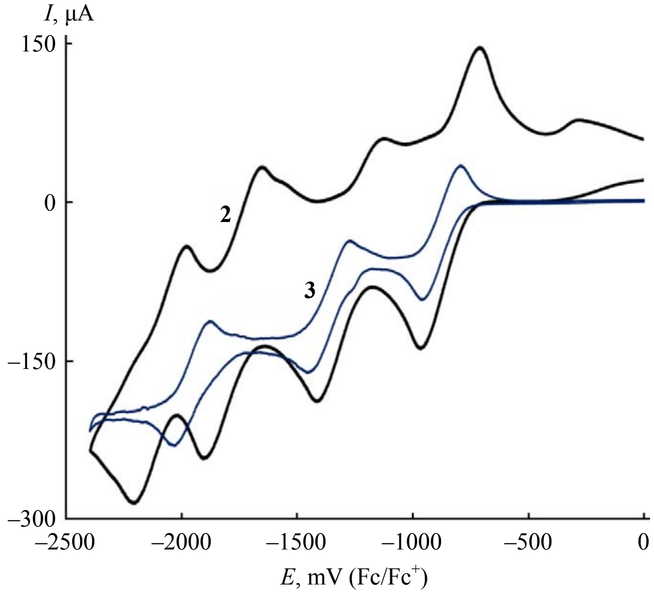
cells [7, 8]. On the basis of the data of cyclic voltammetry we determined the electron affinities of **2** and **3** (first reduction potential, E^{1}_{red}) which is related to the energy of the lowest unoccupied molecular orbital (LUMO) and its ionization potential (first oxidation potential) which is related to the energy of the highest occupied molecular orbital. The difference in the LUMO and HOMO energies is the width of the forbidden band gap of the acceptor (E_{g}) (see table).

The first reduction potentials of compounds **2** and **3** are close to each other. This means that fullerene derivatives are characterized by similar LUMO levels. The LUMO and HOMO energies of **2** and **3** determined by cyclic voltammetry are consistent with those calculated for the isolated molecules in terms of the density functional theory (see table). The LUMO energy of **2** is lower by 0.03 eV than that of **3**. Presumably, the powerful donor effect of the trimethoxyphenyl fragment is compensated to a somewhat greater extent by the electron-withdrawing effect of the carbonyl group, which is responsible for the close LUMO energies of compounds **2** and **3**.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer from samples prepared as thin films. The UV spectra were measured on a Shimadzu UV-1800 UV-Vis spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker AM-300 spectrometer at 300.13 MHz from solutions in $CDCl_3$ using tetramethylsilane as internal reference. The ^{13}C NMR spectra were taken on a Bruker Avance-500 spectrometer at 125.77 MHz. The MALDI mass spectra were obtained on a Voyager-D STR TOF instrument. The progress of reactions was monitored by TLC on Sorbfil plates (Russia); spots were detected by calcination or treatment with an alkaline solution of potassium permanganate. The products were isolated by column chromatography on silica gel using 30–60 g of the sorbent per gram of substrate; freshly distilled solvents were used as eluents. Cyclic voltammograms were recorded for 10^{-3} M solutions of **2** and **3** in *o*-dichlorobenzene in an inert atmosphere at room temperature on a P-30JM Elins potentiostat–galvanostat equipped with a three-electrode cell (working vitreous glass electrode, $d = 5$ mm^{2}, opposite platinum electrode, and reference Ag/Ag^{+} electrode, 0.01 mol/L in MeCN; scan rate 50 mV/s; supporting electrolyte 0.1 M Bu_4NPF_6 in acetonitrile); ferrocene (Fc) was used as internal standard. The electronic structures of **2** and **3** were calculated at the DFT B3LYP/6-31G(*d*) level of theory using Gaussian 09 software package.

Friedel–Crafts acylation of 1,3,5-trimethoxybenzene with methyl 3-chloro-3-oxopropanoate. Methyl 3-chloro-3-oxopropanoate, 0.19 mL (1.78 mmol), was added in one portion under stirring to a suspension of 0.23 g (1.78 mmol) of anhydrous aluminum chloride in 20 mL of anhydrous dichloroethane, cooled to 0°C, and a solution of 0.3 g (1.78 mmol) of 1,3,5-tri-



Cyclic voltammograms of methanofullerenes **2** and **3**.

methoxybenzene in 5 mL of dichloroethane was then added dropwise. When the reaction was complete (TLC), the mixture was treated with 20 mL of cold water and stirred for 10 min, and 2 mL of concentrated aqueous HCl was added. The organic phase was separated, and the aqueous phase was extracted with several portions of dichloroethane. The extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to silica gel column chromatography (petroleum ether–ethyl acetate, 2:1) to isolate 0.39 g (82%) of methyl 3-oxo-3-(2,4,6-trimethoxyphenyl)propanoate (**1**) as pale rose crystals with mp 85.0°C. IR spectrum, ν, cm^{-1}: 3004, 2954, 2845, 1735, 1581, 1123, 1029, 814. ^1H NMR spectrum, δ, ppm: 3.85 s (3H, OMe), 3.95 (3H, OMe), 4.00 (6H, OMe), 6.15 (2H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 52.89 (CH_2), 55.36 (OMe), 55.89 (OMe), 56.18 (2C, OMe), 90.69 (C^i), 91.05 (C^m), 162.29 (C^o), 162.92 (C^p), 167.06 (C=O).

Bingel–Hirsch reaction of compound 1 with fullerene C_{60}. Fullerene C_{60}, 0.1 g (0.138 mmol), was dissolved in 30 mL of toluene, 0.037 mL (0.138 mmol) of compound **1**, 0.045 g (0.138 mmol) of carbon tetrabromide, and 0.021 mL (0.138 mmol) of diazabicyclo[4.2.0]undec-7-ene (DBU) were added, and the mixture was stirred for 2 h at room temperature. The mixture was filtered, the filtrate was washed with 5% aqueous HCl, and the organic phase was separated, dried over $MgSO_4$, and evaporated. The residue was subjected to silica gel column chromatography using toluene as eluent to isolate 0.07 g (51%) of compound **2** as a dark brown powder and 0.03 g of unreacted fullerene C_{60}.

Methyl 3′-(2,4,6-trimethoxybenzoyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene-3′-carboxylate (2). UV spectrum ($CHCl_3$), λ_{max}, nm (logε): 327.5 (4.53), 429.5 (3.37), 490.0 (3.17). IR spectrum, ν, cm^{-1}: 1750, 1670, 1600, 1233, 1131, 731, 520. ^1H NMR spectrum, δ, ppm: 3.84 s (3H, OMe) 3.96 s (3H, OMe), 4.00 s (6H, OMe), 6.20 s (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.42 (OMe), 55.57 (OMe), 56.45 (2C, OMe), 60.94 ($C^{3'}$), 73.97 (C^1, C^9), 90.86 (C^m), 109.87 (C^i); 137.60, 140.15, 140.72, 140.84, 141.65, 141.88, 142.11 (2C), 142.86 (4C), 143.79 (2C), 144, 31 (2C), 145.54 (2C), 144.65 (2C), 145.00 (4C), 145.46, 145.58, 147.08 (C_{60}); 162.18 (C^o), 165.19 (C^p), 165.30 (CO_2), 185.45 (C=O). Mass spectrum: *m*/*z* 986.010 $[M]^+$. $C_{73}H_{14}O_6$. Calculated: *M* 986.079.

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