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Covalent binding of fullerene C_{60} to dithienylethene as a promising approach to the preparation of new photochromic compounds

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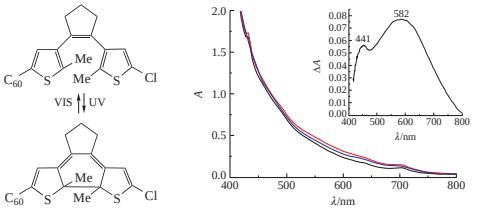
A dithienylethene-containing fullerocyclopropane was synthesized by the catalytic reaction of the carbon cluster with diazoalkane generated *in situ* by the oxidation of a corresponding photochrome hydrazone with MnO_2 in the presence of the $Pd(acac)_2$–$2PPh_3$–$4Et_3Al$ catalyst, and the photochromic properties of the synthesized methanofullerene were evaluated.



Compounds that exist as two or more thermodynamically stable isomers have found extensive use in light filters, solar protection devices, dosimeters, *etc*. Other areas of applications of photochromic compounds include molecular electronics, photonics and switchable catalytic, enzymatic and bio- and chemosensor systems.[1] 1,2-Diarylethenes – thermally irreversible photochromes with high cycling rate – are of particular interest.

A broad range of 1,2-diarylethene derivatives have been synthesized,[2] differing in ethene moiety,[3–10] the presence of electron-donating or electron-withdrawing groups in the aryl or hetaryl moiety[11–14] and the length of an alkyl chain at the α-carbon atom of the aryl group.[15,16]

Recently, extensive studies have been aimed at preparing photochromic compounds based on fullerene derivatives,[17–23] whose photochromic properties are due to electron recombination in both the fullerene cage and the attached moiety.

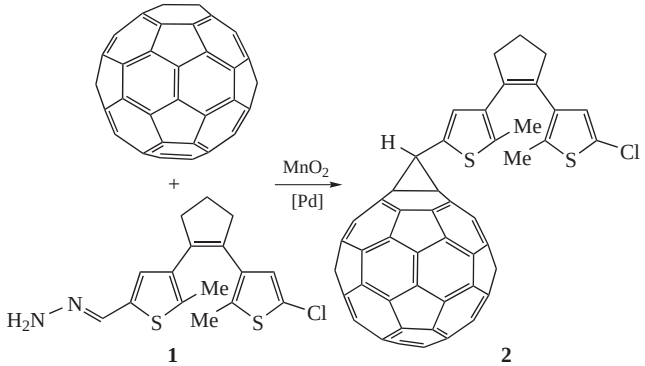
To extend the applicability of the photochromic derivatives of carbon clusters and to study a mutual influence of fullerene and diarylethene on the electronic properties and stability of a new photochromic molecule, we performed covalent binding of C_{60} to dithienylethene. The method developed was based on the catalytic cycloaddition of diazoalkanes to fullerenes under the action of a Pd catalyst, which was performed previously.[24–30]

Experiments† showed that fullerene C_{60} reacted with diazoalkane, generated *in situ* by oxidation of dithienylethene hydrazone **1** with MnO_2, in the presence of 20 mol% of a three-component $Pd(acac)_2$–PPh_3–Et_3Al catalyst (component ratio of 1:2:4) to give methanofullerene **2**‡ in ~50% yield (Scheme 1).

Methanofullerene **2** was purified by preparative HPLC. The structure of adduct **2** was established using 1D (^{1}H and ^{13}C NMR) and 2D (HHCOSY, HSQC, HMBC) NMR experiments and MALDI TOF mass spectrometry.

MALDI TOF mass spectrum of compound **2** with S_8 as a matrix showed intense peaks of the molecular ion $[M]^+$ = 1026.015 (calc. for $C_{76}H_{15}ClS_2$, 1026.030) and the fragment ion $[M-Cl]^+$ = = 991.016 (calc. for $C_{76}H_{15}S_2$, 991.061).

The ^{1}H and ^{13}C NMR spectra of individual cycloadduct **2** exhibit signals characteristic of the fullerene cage (130–150 ppm) and dithienylethene linked to the C_{60} molecule *via* the bridging carbon atom of the cyclopropane moiety (δ_C 38.04 ppm). Simul-



Scheme 1

† *Catalytic cycloaddition of diazo dithienylethene to [60]fullerene*. Solutions of $Pd(acac)_2$ (0.00278 mmol) in chlorobenzene (0.4 ml) and PPh_3 (0.00556 mmol) in chlorobenzene (0.4 ml) were mixed in a glass flask, and a solution of Et_3Al (0.01112 mmol) in toluene (0.1 ml) was added dropwise with stirring to the mixture under a stream of nitrogen at –5 °C. The color of the solution changed from pale yellow to light brown. A solution of [60]fullerene (0.0139 mmol) in chlorobenzene (2 ml) was added to the resultant catalyst at room temperature, and the color of the solution turned dark green. A solution of hydrazone **1** (0.0695 mmol) and MnO_2 (1 mmol) was added. The reaction mixture was stirred for 30 min at ambient temperature; then, it was treated with aqueous HCl and extracted with toluene (7 ml). The organic layer was passed through a short silica gel column.

‡ *Methanofullerene* **2**: brown powder. ^{1}H NMR [500 MHz, $CDCl_3$–CS_2 (1:5)] δ: 1.97 (s, 3H), 2.11–2.15 (m, 2H), 2.17 (s, 3H), 2.81 (t, 2H, *J* 5 Hz), 2.92 (t, 2H, *J* 5 Hz), 5.30 (s, 1H), 6.63 (s, 1H), 7.20 (s, 1H). ^{13}C NMR [125 MHz, $CDCl_3$–CS_2 (1:5)] δ: 14.64, 14.68, 23.40, 38.04, 38.77, 38.82, 75.34, 125.80, 126.78, 131.05, 131.65, 133.37, 134.41, 134.87, 134.94, 135.15, 136.56, 138.98, 141.01, 141.20, 142.17, 142.23, 142.39, 142.71, 143.08, 143.19, 143.87, 144.50, 144.56, 144.60, 144.79, 145.22, 145.28, 145.31, 145.45, 145.74, 147.31, 149.29.

taneously, the ^{13}C NMR signals of the sp^3-hybridized carbons of the fullerene cage (δ_C 75.34 ppm) and the ^1H NMR signals for the methine proton (δ_H 5.30 ppm) correlated in the HMBC experiment with the *trans*-arranged carbons of C_{60} (δ_C 149.29 ppm) unambiguously attest to the formation of the cyclopropane moiety of methanofullerene **2**, which is consistent with published data[30] for the cycloaddition of heterocyclic diazoalkanes to carbon clusters catalyzed by Pd complexes. The dithienylethene fragment of methanofullerene **2** in the ^1H NMR spectrum was characterized by two singlets (δ_H 1.97 and 2.17 ppm), which belong to the hydrogen atoms of two methyl groups. Three proton signals [δ_H 2.11–2.15 (m), 2.81 (t) and 2.92 (t)] of the methylene groups of a cyclopentene fragment and two singlets at δ_H 6.63 and 7.20 ppm, corresponding to the resonances of the hydrogen atoms of the thiophene ring, fully confirm the proposed structure of **2**.

To obtain tentative data on the photochromic properties of methanofullerene **2** and in view of the fact that the possibility of ring closure in the initial diarylethene molecule depends on the mutual positions of thiophene rings and a distance between the carbon atoms involved in the ring closure,[31] we performed DFT calculations of the geometric parameters and molecular orbitals of fullerene derivative **2** by the RBLYP method with the 3-21G basis set using the Gaussian software.[32]

The distance between the thiophene carbon atoms involved in ring closure in **2o** (Figure 1) to give closed form **2c** is 3.534(1) Å. The dihedral angle between the thiophene rings is 52.12(3)°, and the angles between the cyclopentene and thiophene moieties are 49.21(0)° and 44.66(2)°. The presented geometric parameters of open methanofullerene **2o**, according to published data,[33] indicate that compound **2** should exhibit photochromic properties.

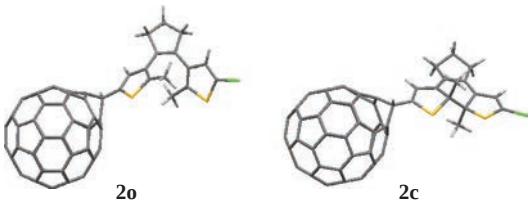


Figure 1 Open **2o** and closed **2c** forms of methanofullerene **2** in the antiparallel conformation state.

Simultaneously, the molecular orbital calculation for open form **2o** demonstrated that electron transition from the lowest unoccupied molecular orbital (LUMO) located on the electron-withdrawing fullerene cage to the highest occupied molecular orbital (HOMO), which is mainly located on the hetarylethene moiety, is 2.46 eV (Figure 2). In anti-conformation isomer **2c**, the HOMO to LUMO transition energy is 1.68 eV, which also favors the fluorescent-resonance energy transition, *i.e.*, this attests to the possibility of photoswitching. The more so that in the synthesis of the potential photochrome based on fullerene C_{60}, we utilized an approach promoting an increase in the quantum yield of the closed form, namely, the introduction of crowded (bulky) substituents into heterocyclic moieties.[2]

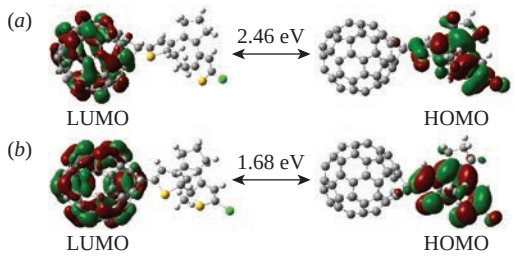


Figure 2 LUMO and HOMO of (*a*) open **2o** and (*b*) closed **2c** forms of methanofullerene **2**.

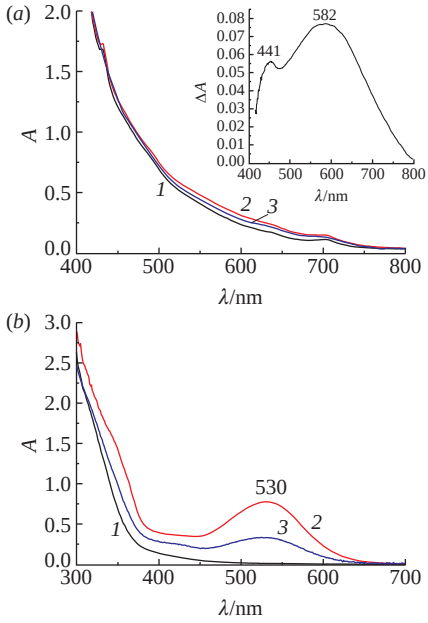


Figure 3 Absorption spectra of (*a*) compound **2** and (*b*) compound **1** in toluene ($C = 4\times10^{-4}$ M) measured in a 10-mm cell (*1*) before and (*2*) after UV irradiation through a UFS-1 filter and (*3*) after subsequent visible light irradiation through a ZhS-16 filter. The inset presents the difference absorption spectrum between curves *2* and *1* for compound **2**.

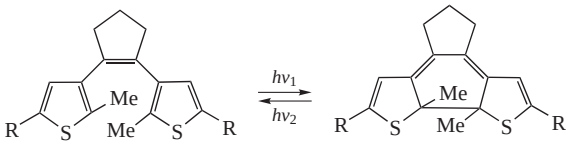
Table 1 Spectral characteristics of the test solutions.[a]

Compound	λ_A^{max}/nm	λ_B^{max}/nm	ΔD_B^{phot}
1	327 (sh.)	350	0.74
		530	0.76
2	330 (sh.)[b]	441[c]	0.02
		582[c]	0.08

[a] λ_A^{max}, λ_B^{max} are the absorption maxima wavelengths of the initial and photo-induced forms of the compound, respectively; ΔD_B^{phot} is the change in the absorbance during UV irradiation measured at the absorption maximum of the closed isomer. [b] For dilute solution. [c] Determined from the difference spectrum for concentrated solution ($C = 4\times10^{-4}$ M).

The photoinduced spectral changes for a solution of hybrid compound **2** are presented in Figure 3(*a*).§ The initial absorption spectrum shows several weakly pronounced absorption maxima (curve *1*, Table 1).

The successive exposure to filtered UV light and visible light induces reversible changes in the absorption spectra (curves *2* and *3*). The difference photoinduced absorption spectrum [inset in Figure 3(*a*)] shows two absorption bands at 441 and 582 nm. The latter resembles the photoinduced absorption band of diarylethene **1** in toluene arising on exposure to UV light [Figure 3(*b*), curve *2*] and known[2] to belong to the ring-closed isomer formed upon photochromic transformations.



In the case of compound **2**, the photoinduced absorption maximum of the closed isomer is shifted hypsochromically by

§ The photochemical properties of compound **2** and its precursors (fullerene and photochromic diarylethene **1**) were studied in toluene (Scharlau, analytical grade, ACS) at room temperature. The solutions were homogenized by ultrasonication for 10 min. The solutions were transparent with no precipitate or suspension. For more details, see Online Supplementary Materials.

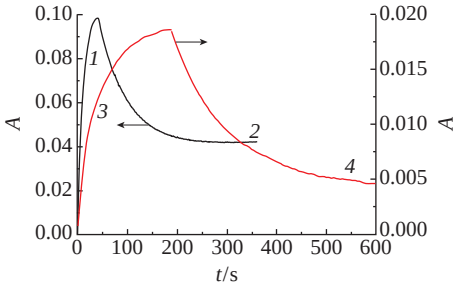


Figure 4 Kinetic curves for (*1*, *3*) photocoloring and (*2*, *4*) photobleaching in the solutions of diarylethene **1** and hybrid compound **2** in toluene (C = = 2×10^{-4} M) measured at the absorption maximum wavelengths of the photoinduced closed form.

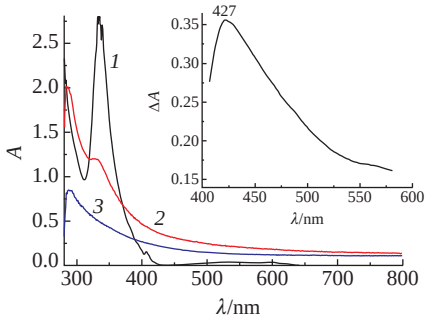


Figure 5 Absorption spectra of fullerene C_{60} in toluene (C = 2×10^{-4} M) measured in a 2 mm-thick cell (*1*) before and (*2*, *3*) after irradiation with unfiltered light with longer exposure. The inset presents the difference absorption spectrum between curves *2* and *1*.

52 nm with respect to the maximum of the corresponding absorption band of photochromic precursor **1**.

Figure 4 shows the kinetic curves for UV-induced photocoloring and the subsequent photobleaching induced by visible light in both compounds. Like the photoinduced spectral changes, the curves attest to the reversibility of phototransformations.

The short-wavelength absorption band is attributable to the photoinduced irreversible photochemical transformations of fullerene giving rise to intermediate photoproducts. Figure 5 shows that, during the irradiation of a fullerene solution in toluene with unfiltered light, the absorption band intensity at 333 nm (curve *1*) gradually decreases (curve *2*) until disappearance (curve *3*). This gives rise to an absorption band at 427 nm (inset in Figure 5), which disappears on further irradiation (*cf*. curves *2* and *3*).

The results of a comparative spectral kinetic study of diarylethene **1**, fullerene and hybrid compound **2** indicate that the hybrid compound undergoes photochromic transformations similar to those of the photochromic precursor. However, the efficiency of photochromic transformations is low, which may be due to a short distance between the fullerene and diarylethene moieties. Attention is drawn to the photochemical instability of fullerene, which is manifested as a photoinduced change in the absorption spectra during photochromic transformations of hybrid compound **2**.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.021.

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