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Synthesis and photochromic properties of fullerene C_{60} adducts with dithienylethenes

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ABSTRACT

A number of adducts of C_{60} with dithienylethenes were synthesized for the first time using the Prato reaction and their photochromic properties studied. It was found that the positions of the absorption bands for the ring-closed forms of diarylethenes incorporated fullerene adducts and the efficiency of their photochromic transformations were dependent on the nature of the substituents on the second thiophene ring.

The swift development of the chemistry of photochromic diheteroarylethenes in recent years has been due to the prospects of using these compounds as light-sensitive and light-controlled materials for various purposes.[1]

Currently, a broad range of 1,2-diarylethene derivatives have been synthesized,[2,3] differing in the nature of the ethene moiety,[4–10] the presence of electron-donating or electron-withdrawing groups on either the aryl or heteroaryl moiety,[11–14] and the length of the alkyl chain at the active carbon atom of the aryl substituent.[15,16] This has made it possible to determine the effect of both the nature and structure of the diarylethene substituents on the spectral and luminescence properties of the two isomers which undergo reversible photoinduced interconversion and also the thermal stability of the isomers, quantum yields of reversible photoisomerization, cyclability, and photodegradation efficiency.

The extension of scope for the applicability of photochromic diarylethenes of the design of photo switches for various purposes based on photochromic nanoparticles,[17] still requires further research. Therefore, the synthesis of new, promising photochromic diheteroarylethenes, especially those based on carbon clusters, is an important task.

Therefore, a novel method for the preparation of new and effective photochromic molecules may be desired from fullerene chemistry.[18–20] The photochromic properties of the resulting carbon cluster adducts can be caused by electron recombinations both in the fullerene cage[21] and in the attached moiety, in particular, the heteroarylethene ring.[22–24]

In order to extend the scope of applicability of photochromic derivatives based on carbon clusters and to study the mutual influence of fullerene and diarylethene motifs on the electronic properties and stability of the new photochromic molecule, we have synthesized a number of fulleropyrrolidine-containing dithienylethenes using the Prato reaction.[25]

1,3-Dipolar cycloaddition of dithienylethene **1** or **2**[14] to fullerene C_{60} in the presence of sarcosine afforded fulleropyrrolidines **3** and **4** in 60% and 55% yield, respectively, (see Scheme 1).

Compounds **3** and **4** could be isolated from the reaction mixture by column chromatography (SiO_2). Using toluene as the eluent, unreacted C_{60} was isolated and elution of the column with pyridine gave the target adducts **3** and **4** in 100% purity. Structures of fulleropyrrolidines **3** and **4** were determined by 1D (^1H and ^{13}C) and 2D (H-HCOSY, HSQC, HMBC) NMR spectroscopy as well as MALDI TOF/TOF mass spectrometry.

Thus, the pyrrolidine ring was assigned signals at δ_C of 69.93 (C5), 79.48 (C2), and 40.13 (N-CH_3) which correlated in the HSQC experiment with the proton signals at δ_H 4.22 (H_A-C5), 4.96

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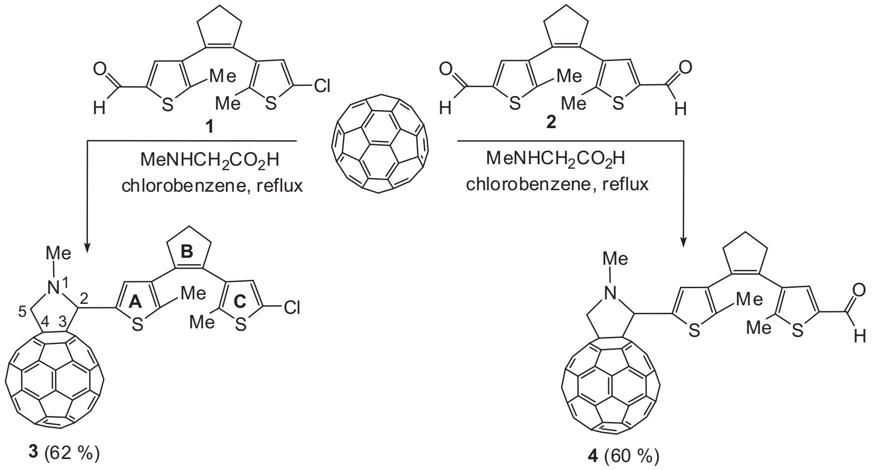
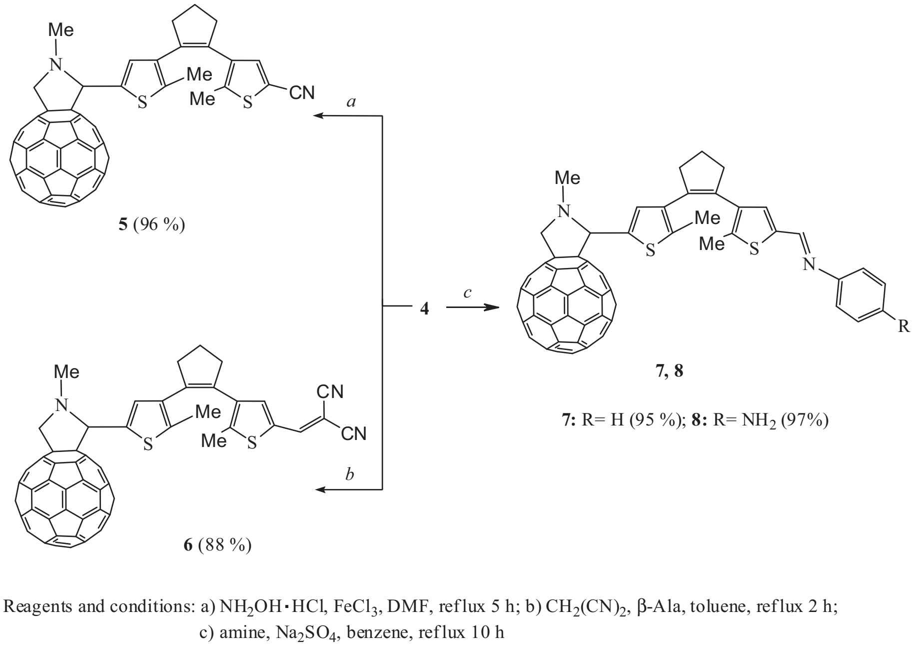


Scheme 1. Prato reaction of photochromic aldehydes **1** and **2** with C_{60}.



Reagents and conditions: a) $NH_2OH{\cdot}HCl$, $FeCl_3$, DMF, reflux 5 h; b) $CH_2(CN)_2$, β-Ala, toluene, reflux 2 h; c) amine, Na_2SO_4, benzene, reflux 10 h

Scheme 2. Synthesis of the heteroarylfulleropyrrolidines **5**–**8**, containing electron-donating and electron-withdrawing groups on the second thienyl moiety.

(H_B-C5), 5.11 (H-C2), and 2.88 (N-CH_3) ppm, respectively. The thiophene rings **A** and **C** of the attached moiety accounted for ten low-field signals at 135–153 ppm, which overlapped with 48 signals of the fullerene cage. Additionally there were three signals for the sp^3-hybridized atoms of cyclopentene ring **B**. Cross-peaks between the geminal proton signals (δ_H 4.22 and 4.96 ppm) and the carbon signals of the fullerene cage (δ_C 153.92 and 155.91 ppm) in the HMBC experiment as well as a cross-peak between the H-C2 signal (δ_H 5.11 ppm) and one of the low-field signals of the sp^2-hybridized C_{60} carbons (δ_C 153.20 ppm) confirmed the annulation of the pyrrolidine moiety with the fullerene cage in molecule **3**.

The structure of fulleropyrrolidine **3** was also reliably established by MALDI TOF/TOF mass spectrometry which showed an intense fragment ion peak [M–H] at $m/z = 1068.061$.

The free aldehyde group present in compound **4** was utilized to synthesize various heteroarylfulleropyrrolidines **5**–**8** containing electron-donating and electron-withdrawing groups in order to elucidate the effect that the nature of the substituent on the second thienyl moiety had on the photochromic properties of the new hybrid molecules (Scheme 2).

The structures of the fulleropyrrolidines **5**–**8** were reliably established by classical physicochemical methods (IR, UV, and NMR spectroscopy and MALDI TOF/TOF mass spectrometry).

The photochromic properties of dithienylethene pyrrolidinofullerenes **3**–**8** were studied at room temperature in toluene solutions ($c = 4{\cdot}10^{-4}$ M) and for homogenization, the mixtures were ultrasonicated for 2 min. Photochemical experiments with all photochromic compounds were carried out under identical conditions of photoactivation. The results were compared with the data reference compound, dithienylethene **2**.

Results of the spectral kinetic study are presented in Figures 1–4 and in Table 1. Figure 1 shows the photoinduced variations of the absorption spectra of the starting diarylethene **2** used to prepare hybrid compound **4**.

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