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Synthesis, photo and acidochromic properties of spiropyran-containing methanofullerenes†

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Spiropyran-containing methanofullerenes able to rapidly and reversibly respond to optical and chemical stimuli were synthesized for the first time by the Bingel–Hirsch reaction and catalytic cycloaddition of diazo compounds to carbon clusters. The effects of substituent structure in the new hybrid molecule and the mode of spiropyran attachment to fullerene on the spectral kinetic properties and photo- and acidochromic behavior of the synthesized fullerene derivatives was established.

Introduction

A highly important trend in modern organic chemistry is the synthesis, design and study of new photochromic molecules able to reversibly isomerize under the action of various types of stimuli. The enhanced interest in these compounds is caused by their applicability for the development of promising materials and devices with unique characteristics: memory elements,[1–3] optoelectronic and holographic devices,[4,5] and sensors.[6–11]

Spiropyrans are the best known and unique representatives of photochromic compounds, since they can be easily prepared and structurally modified and because of the possibility of targeted change of their spectral kinetic characteristics over a wide range. The isomers of spiropyrans considerably differ in their physical and optical properties, which inspired a number of studies on the use of these compounds as dynamic materials.[12] An important place is occupied by studies directed towards the development of nanomaterials with controlled properties, *e.g.*, light controlled carbon nanomolecules, fullerenes, nanotubes and graphenes.[13–15]

Recently,[16] we performed for the first time the successful chemical bonding of C$_{60}$ fullerene to spiropyrans *via* the Prato reaction and found[17] that the photochromic properties of pyrrolidinofullerenes are substantially affected by the nature of the electron-withdrawing group in the pyran ring.

In order to pursue these studies directed towards the development of efficient methods for chemical bonding of fullerenes to photochromic spiro derivatives, to obtain new dynamic materials for light-controlled field effect transistors,[18] and to

study the effects of the fullerene core and spiropyran structure in the new hybrid molecule on the response to external stimuli, we synthesized spiropyran-containing methanofullerenes and studied their photo- and acidochromic behavior.
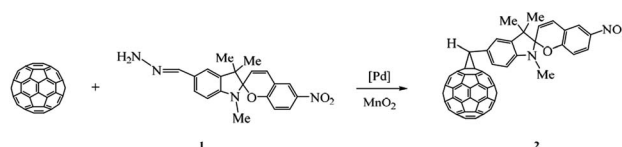
Experimental section

The target methanofullerenes were synthesized using the Bingel–Hirsch reaction and catalytic cycloaddition of diazo compounds to carbon clusters, which gave the possibility to study the effect of the mode of spiropyran attachment to fullerene on the physicochemical properties of new hybrid molecules.

The first stage of our study was concerned with chemical bonding of spiropyrans to C$_{60}$ fullerene upon catalytic cycloaddition of diazo compounds to carbon clusters.[19] The reaction of C$_{60}$ with a diazoalkane generated *in situ* by oxidation of spiropyran hydrazone **1** with MnO$_2$ in the presence of three-component Pd(acac)$_2$-2PPh$_3$-4Et$_3$Al catalyst (20 mol%) afforded methanofullerene **2** in 55% yield (Scheme 1).

The formation of 6,6-closed cycloadduct in the catalytic reaction between C$_{60}$ and diazoalkanes is in good agreement with published data[20] and is caused by the presence of a heterocyclic moiety in the molecule of the starting spiropyran hydrazone **1**.

In order to study the effect of the mode of attachment of the spiro photochrome to the carbon cluster on the
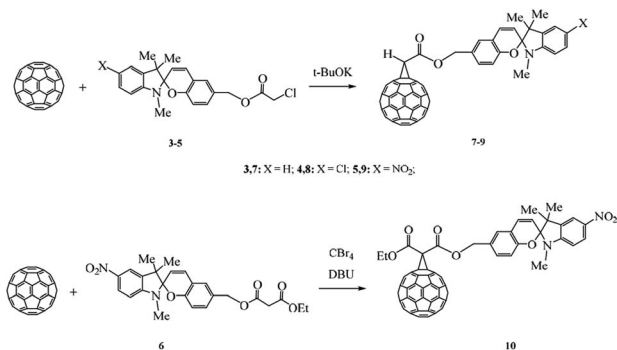
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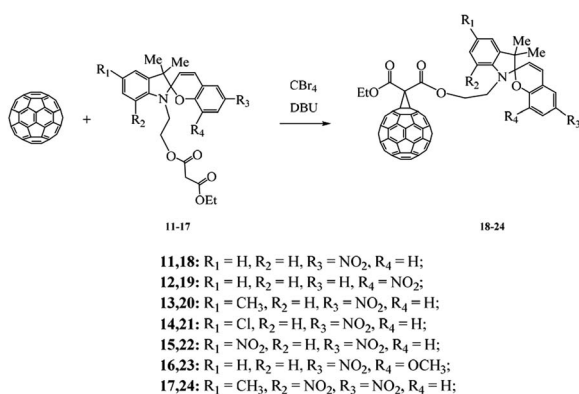
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Scheme 1 Schematic representation of the synthesis of methanofullerene **2**.

Scheme 2 Schematic representation of the synthesis of methanofullerenes **7–10**.

Scheme 3 Schematic representation of the synthesis of methanofullerenes **18–24**.

physicochemical properties of a new synthesized hybrid molecule, in the next stage of our study, we performed chemical bonding of C_{60} fullerene to spiropyran *via* the chromene moiety.

This aim was pursued using the nucleophilic addition of α-halo carbanions to C_{60} (Bingel–Hirsch reaction). The anions were generated *in situ* by the reaction of spiropyran chloroacetic **3–5** and malonic **6** acid esters with bases to give the corresponding methanofullerenes **7–10** in 60–70% yields (Scheme 2).

A similar approach was used to prepare hybrid molecules **18–24** in which fullerene was linked to the photochrome through the indole nitrogen atom of the starting spiropyran (Scheme 3). This approach to the preparation of C_{60} fullerene–spiropyran hybrid molecules gave hope, according to published data,[21,22] that the prepared methanofullerenes **18–24** would possess negative photochromism (Scheme 3).

All of the C_{60}- and spiropyran-based hybrid molecules **2, 7–10, 18–24** were isolated from the reaction mixture by column chromatography or preparative HPLC with ∼100% purity.

The structures of hybrid compounds **2, 7–10, 18–24** were reliably established by 1D (^{1}H and ^{13}C) and 2D (H-HCOSY, HSQC, HMBC) NMR spectroscopy and MALDI TOF/TOF mass spectrometry (see ESI†).

Results and discussion

In view of high sensitivity of initial spiropyrans to a broad range of external stimuli[10,23–30] and to pursue our research aimed at the development of efficient synthetic routes to new molecular switches based on fullerenes and photochromic compounds,[14–16,31–33] we investigated photochromic and acidochromic behaviors of methanofullerenes **2, 7–10, 18–24**.

The results of studying photochromic properties of the obtained compounds are presented in Table 1 (the Table 1 gives

Table 1 Characteristics of the UV/Vis absorption of methanofullerenes that exhibit photochromic properties

Compound	$\lambda_A^{max\,a}$ (nm)	ε^b ($M^{-1}\,cm^{-1}$)	$\lambda_B^{max\,a}$ (nm)	$\Delta D_B^{max\,c}/D_A^{max\,c}$	$\tau_{1/2}^{phdgr\,d}$, s
2	330	50 000	615	0.4	185
	431				
18	328	45 500	608	0.30	260
	428				
	608				
19	328	33 000	605	0.15	135
	428				
	472				
20	330	40 500	610	0.30	205
	428				
21	330	42 850	615	0.31	170
	428				
	465				
22	330	48 000	615	0.005	200
	428				
	482				
23	330	36 450	605	0.34	235
	428				
	462				

[a] λ_A^{max}, λ_B^{max} – are absorption maxima of the initial and photoinduced forms, respectively. [b] ε – molar extinction coefficient. [c] D_A^{max}, ΔD_B^{max} are, respectively, the optical density at the absorption maximum of the initial form and change of the optical density after UV irradiation. [d] $\tau_{1/2}^{phdgr}$ – the time during which the optical density of the photo-induced form is reduced by half under the influence of unfiltered radiation.
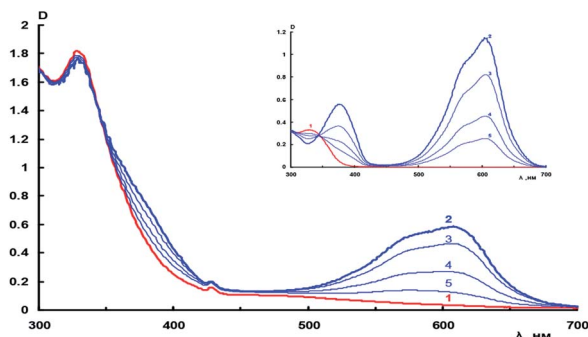
Fig. 1 Absorption spectra of methanofullerene **18** in toluene before (1) and during irradiation through a UFS-1 light filter (2) and after the subsequent bleaching in the dark (3–5). The inset shows the absorption spectra of the initial spiropyran **11** before and after irradiation.
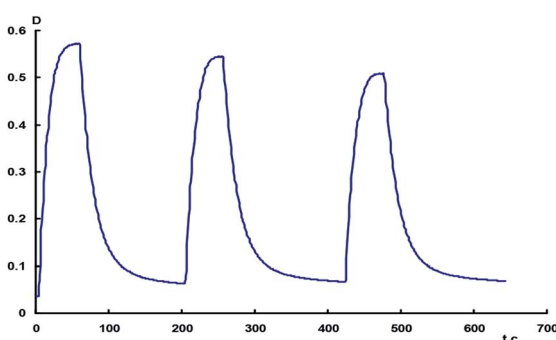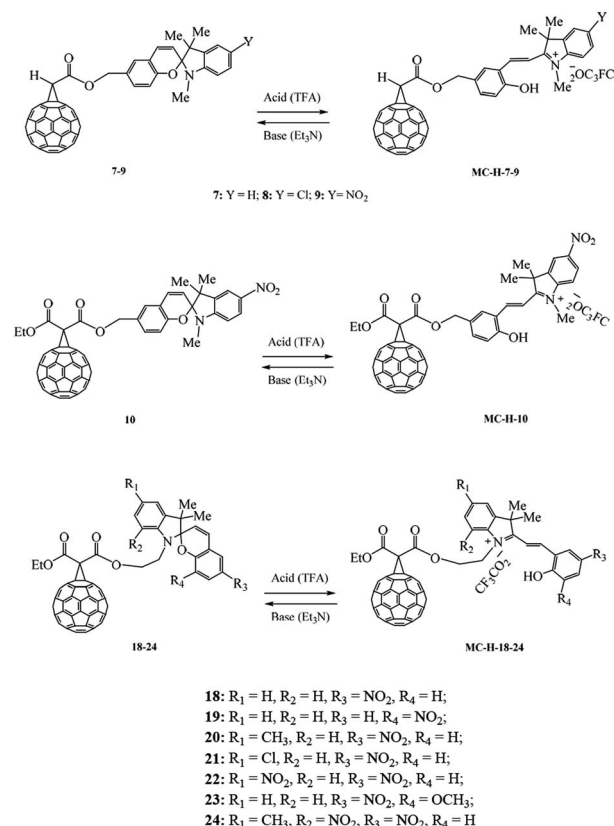

Fig. 2 Kinetics of the alternating photocoloration of methanofullerene **18** in toluene measured at 608 nm under irradiation through a UFS-1 light filter and during bleaching in the dark.

only characteristics of compounds that exhibit photochromic properties, namely, **2**, **18–23**).

Fig. 1 (inset) depicts the photoinduced spectral changes of the starting spiropyran **11** in toluene; it can be seen that the absorption spectrum of the photoinduced merocyanine form shows an absorption maximum in the visible region at 605 nm. During dark relaxation, the intensity of photoinduced absorption bands gradually decreases. Photoinduced spectral changes of this type are also manifested for hybrid compound **18** in toluene. In this case, the long-wavelength absorption maximum occurs at 608 nm.

The decrease in the amplitude of intensity changes of the absorption bands of the photoinduced merocyanine form of spiropyran in methanofullerene **18** indicates that the latter undergoes photochromic transformations with gradual photodecomposition (Fig. 2).

A comparison of the curves presented in Fig. 1 demonstrates the absence of significant spectral differences between nitro-substituted spiropyran **11** and spiropyran–fullerene hybrid compound **18**, which is apparently indicative of weak interaction between the spiropyran and fullerene moieties. A difference is observed for light sensitivity defined by the $\Delta D_B^{phot}/D_A^{max}$ ratio (Table 1). This ratio reflects the photoinduced change in the absorbance at the absorption maximum of the

Scheme 4 Schematic representation of the acid–base switching of synthesized methanofullerenes.

merocyanine form normalized to the maximum absorption intensity of the starting spiro form, which absorbs the activating radiation. It follows from Table 1 that light sensitivity of hybrid compounds **2**, **18–23** is lower than that of their precursors. This difference is quite significant for methanofullerene **22** and precursor **15**. It is characterized by photoinduced spectral changes for spiropyran **15** and minor changes in the absorption spectra of hybrid **22** in the long-wavelength spectral region.

A considerable difference was found for the photodegradation of photochromic methanofullerenes and the starting spiro photochromes. Hybrid compounds are more stable against irreversible phototransformations than the starting spiropyrans (see ESI†).

Simultaneously, it was found that unlike the starting spiropyrans, methanofullerenes **7–10**, **24** do not possess photochromism. This may be due not only to the nature of the substituent and its position in the aromatic ring, but also to the effect of the fullerene core, which destabilizes the merocyanine form and, as a consequence, leads to high thermal relaxation rate and formation of spirocyclic forms.

The results provide the conclusion that the light sensitivity, the rate constant of dark relaxation of the photoinduced merocyanine form, and stability to photodegradation of hybrid molecules are affected by both the nature of substituents in the indoline and chromene moieties and the proper fullerene core.

Recently, it was shown[34] that spiropyran-containing pyrrolidinofullerenes undergo reversible isomerization not only on
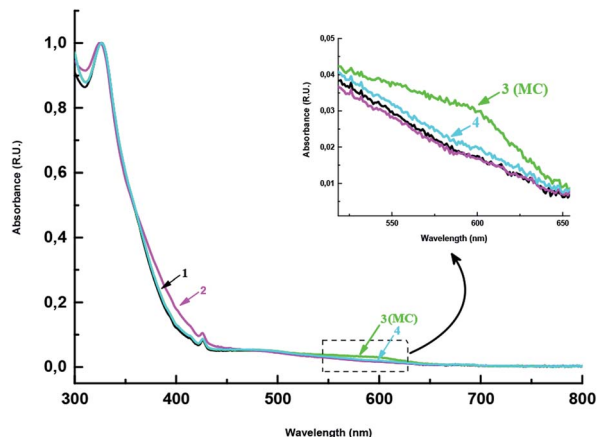
Fig. 3 Absorption spectra of methanofullerene **18** in chloroform before (1) and after addition of TFA (2) and after the subsequent neutralization with triethylamine (3 and 4).

exposure to UV light, but also upon the acid–base switching. Therefore, we studied the acidochromic behavior of methanofullerenes **2**, **7–10**, **18–24** (Scheme 4).

The experiments showed that on treatment with equimolar amounts of trifluoroacetic acid (TFA), cycloadducts **2**, **7–10**, **18–24** are converted to protonated merocyanines MC-H-**2**, **7–10**, **18–24** (Fig. 3 and ESI†), which are characterized by hyperchromic effect in the 365–445 nm range of absorption spectra. Treatment of these compounds in solutions with a base (Et$_3$N) restores the initial hybrids **2**, **7–10**, **18–24** as a result of TFA neutralization. According to published data,[35] the conversion of protonated merocyanine to spiropyran involves the formation of neutral merocyanine *via* deprotonation of phenolic hydroxyl. The intermediate formation of merocyanine upon amine treatment of protonated open form of spiropyran MC-H-**18** is indicated, for example, by the absorption maximum at 603 nm in the absorption spectrum of this compound (Fig. 3, inset, curve 3).

The acid-induced opening of spiropyran addends in the synthesized hybrid molecules **2**, **7–10**, **18–24** was demonstrated not only by UV spectroscopy, but also using NMR spectroscopy. TFA-induced spiropyran ring opening in **18** was indicated by disappearance of both the singlets at 1.31 and 1.19 ppm (see ESI†), corresponding to two methyl protons of the indole moiety, and the multiplets for the two spacer methylene groups at 3.69, 4.51, 4.59 and 4.73 ppm from the ^{1}H NMR spectra of the hybrid molecules. After TFA neutralization with an equimolar amount of Et$_3$N, the initial form of the ^{1}H NMR spectrum is restored (see ESI†). Similar results were obtained in our previous study for photochromic pyrrolidinofullerenes.[34]

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hybrid molecules. After TFA neutralization with an equimolar amount of Et$_3$N, the initial form of the ^{1}H NMR spectrum is restored (see ESI†). Similar results were obtained in our previous study for photochromic pyrrolidinofullerenes.[34]

Quite unexpected results were obtained for spiropyrans and their fullerene hybrids containing two NO$_2$ groups. Indeed, the starting spiropyrans **15** and **17** and methanofullerenes **22** and **24** do not undergo acid-induced isomerization to the corresponding protonated merocyanines even in the presence of a large excess of the acid (see ESI†). Apparently, the presence of two electron-withdrawing groups in the spiropyran molecule makes oxygen at the spiro atom electron-deficient and thus not susceptible to protonation.[34,35]

Conclusions

Thus, we synthesized for the first time cyclopropane derivatives of C$_{60}$ fullerene containing spiropyran addends and studied them for photo- and acidochromic behaviours. The effect of structural factors on the spectral and kinetic characteristics of the photochromic transformations of the synthesized fullerene hybrids was established. It was found that the photochromic and acidochromic behaviors of the resulting hybrid molecules are affected by the substituent nature and position in the chromene or indole aromatic rings and by the fullerene to spiropyran binding mode.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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