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Electrochemical investigation of a photochromic spiropyran containing a pyrrolidinofullerene moiety

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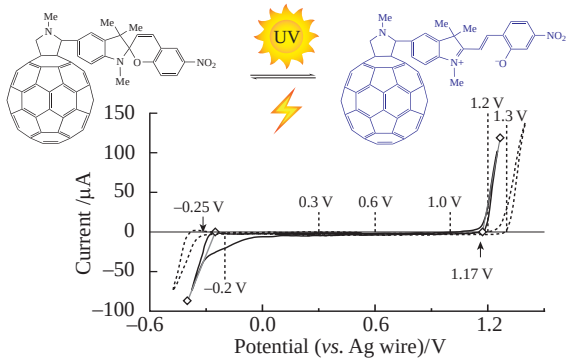
Reversible transformations of a hybrid molecule based on [60]fullerene and a spiropyran moiety under conditions of combined photo- and electrochemical exposure were found. It has been established that the electrochemical oxidation of the UV-photoinduced colored form of the hybrid spiropyran in solution significantly accelerates the discoloration process and does not affect the fullerene part of the hybrid molecule. The research results are promising for designing a photo-electrochromic device that modulates electromagnetic radiation in the visible range of the spectrum.



Keywords: [60]fullerene, pyrrolidinofullerene, spiropyrans, cyclic voltammogram, HOMO–LUMO energy gap, electrochemical study.

Photochromic transformation, which involves a reversible conversion induced by electromagnetic radiation between two forms of a molecule with different absorption spectra, is an area of growing interest for researchers around the world. To date, such spirocyclic compounds as spiropyrans and spirooxazines are among the most studied photochromic systems.[1] In compounds of this type, the spirocyclic form absorbs in the UV region of the spectrum, while the photoinduced merocyanine form absorbs in the visible region of the spectrum. Spiropyrans are unique organic compounds that exhibit not only photochromic properties as a result of structural transformations under the action of UV light, but also solvatochromism,[2] hydrochromism,[3] acidochromism,[4] thermochromism[5] and a response to the presence of metal ions.[6] The high potential of spiropyrans to respond to external influences makes them promising materials for three-dimensional optical memory elements,[7] molecular switches,[8] nanoscale optoelectronic devices,[9] nanoparticle fluorescence modulation,[10] adjustable light filters,[11] sensors[12] and photosensitive biomaterials,[13] as well as for the recognition and quantification of amino acids.[14]

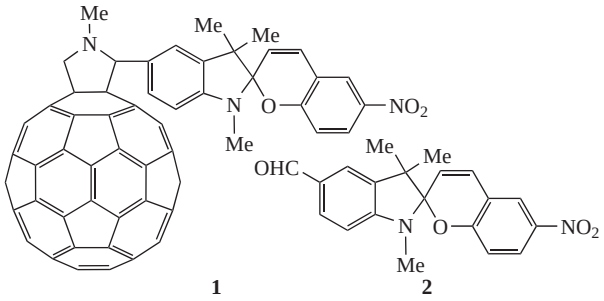
The functionality of spiropyrans can also be enhanced by electrochemical action. Indeed, the electrochemical reduction of spiropyrans leads to the opening of the spiropyran ring,[15] while under the conditions of oxidation of indole-substituted spiropyrans, their dimerization through the formation of a radical cation is observed.[16] The introduction of substituents into the indoline fragment of spiropyran blocks the dimerization of photochrome, which promotes the oxidation of spiropyran to a radical cation; in this case, the formation of merocyanine forms can be observed.[17]

To date,[18–22] we have synthesized a wide range of hybrid photochromic and acidochromic molecules based on fullerenes in combination with spiropyrans or dithienylethenes. Research has revealed the great potential of the synthesized photochromic hybrid molecules as light-regulating semiconductor layers for organic field-effect transistors.[23–25] In this case, in contrast to the initial spiropyrans, the hybrid molecules exhibited high resistance to photodegradation upon repeated switching and prolonged exposure to UV light.

In continuation of our research on the development of approaches to the synthesis and study of the properties of new hybrid molecules based on fullerenes and spiropyrans,[18–20] as well as taking into account the prospects of photochromic compounds and fullerenes for various areas of science and technology, we for the first time conducted electrochemical studies of pyrrolidinofullerene containing a spiropyran fragment. Preliminary experiments have shown that by using electrochemical influence, the discoloration time of the photogenerated colored form of the hybrid spiropyran can be significantly reduced compared with the spontaneous discoloration time. The electrochemical studies are aimed at optimizing this process and choosing the appropriate voltages for electrochemical action.

Photochromic pyrrolidino[60]fullerene **1** and its precursor, spiropyran **2**, were chosen as the objects of study. The synthesis, structure and photochromic properties of compounds **1** and **2** were described in detail earlier.[18]

The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)



1 **2**

were measured by cyclic voltammetry (CV), the corresponding energy gaps, E_g (EC), were calculated and compared with those, E_g (opt), determined from the absorption spectra (for details, see Online Supplementary Materials).

Compound **1** was initially studied by CV as a film on a platinum electrode in a non-aqueous acetonitrile (AN) electrolyte.† In Figure 1(*a*), a pair of redox peaks corresponding to LUMO is observed in the cathode region. In this pair, the intersection of the tangents gives the LUMO level value of −4.15 eV. An unstable voltammogram in the region of 0.8–1.6 V, observed upon transition to the anode region [Figure 1(*b*)], is associated with the decomposition of one of the fragments of the compound **1** molecule. Further advance into the anode region leads to stabilization of the CV curve at a HOMO value of −6.69 eV. The obtained LUMO and HOMO values for the film of compound **1**, as well as the shapes of the CV curves, are in good agreement with the fullerene derivatives.[26–28] According to CV experiments, the energy gap between the LUMO and HOMO is estimated as E_g (EC) = 2.54 eV.

To elucidate the nature of the instability of the CV curves in the anode region of 0.8–1.6 V [see Figure 1(*b*)], CV of compounds **1** and **2** was carried out in solution.‡ CV study of compound **1** in solution revealed irreversible electrochemical processes in the cathode and anode regions [Figure S1(*a*), see Online Supplementary Materials]. However, the CV curve is quite reproducible, since the content of the substance in the solution significantly exceeds the content in the film, and the concentration near the electrode is maintained due to the diffusion of molecules from the bulk. Importantly, the tangents to the fronts of the cathodic currents in Figures 1(*a*) and S1(*a*) intersect with the potential axis at the same point −0.86 V. Therefore, it is reasonable to assume that these sections of the CV curves reflect the same electrochemical process.

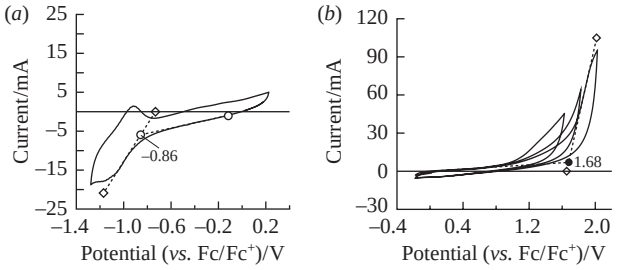


Figure 1 CV curves of compound **1** as a film on a Pt electrode in the (*a*) cathode and (*b*) anode regions in the presence of a supporting electrolyte (0.2 M NBu_4BF_4 in AN).

† To obtain a film, the electrode was sequentially poured with a solution of compound **1** in *o*-dichlorobenzene, dried in air and then in a fore vacuum for 15 min to remove residual solvent.

‡ Since compound **2** is soluble in AN, CV was performed at a concentration of 0.005 M in the same electrolyte solution as for the film of compound **1**. To carry out CV study of compound **1**, which is insoluble in AN or 1 : 1 AN/dichloromethane (DCM), we used its 5×10^{-4} M solution in a DCM-based electrolyte containing 0.2 M NBu_4BF_4.

Comparing the positions of the fronts of the anodic currents on the potential axis in Figure S1(*a*),(*b*), we should mention that the anodic process in a solution of compound **1** proceeds at a higher potential (0.81 V) than for compound **2** (0.56 V). Considering that fullerene is an acceptor, such a shift seems to be quite expected. Therefore, the CV curve instability region near 0.8–1.6 V in the case of the film [see Figure 1(*b*)] can be associated with the oxidation process in the spiropyran fragment of compound **1**. The irreversible process of spiropyran oxidation, which causes a gradual decrease in the oxidation current, was also observed for nitro-substituted spiropyran and was explained by the degradation of the formed radical cation.[29,30] Upon the complete decomposition of the spiropyran fragment of compound **1** in the film, the fullerene oxidation current front on the CV curve of compound **1** was recorded near 1.68 V [see Figure 1(*b*)]. The presence of the spiropyran fragment in hybrid compound **1** does not affect the cathodic process involving the fullerene fragment, since the cathodic process in spiropyran **2** occurs at more negative potentials of about −1.48 V [Figure S1(*b*)]. Due to the narrower range of electrochemical stability of DCM compared to AN, CV of compound **1** in DCM solution did not register the processes of cathodic reduction of the spiropyran fragment and anodic oxidation of the fullerene fragment.

Based on the results of CV experiments with a solution of compound **2**, it is possible to calculate the energy parameters characterizing the HOMO level of −5.57 eV, the LUMO level of −3.52 eV and E_g (EC) = 2.04 eV. These values and the shape of the CV curve are quite typical for spiropyrans.[29] Thus, the presence of the spiropyran fragment in the hybrid fullerene compound **1** creates an additional energy level of −5.74 eV in the energy structure, which is within the energy gap of the fullerene fragment. The obtained energy characteristics for compounds **1** and **2** are summarized in Table 1.

The energies of the frontier orbitals of compounds **1** and **2** were additionally calculated using the PBEPBE/6-311G(d,p) quantum chemical method implemented in the GAUSSIAN 09 (Revision D.01) program and proposed earlier.[31–33] As can be seen from Table 1, the theoretical values of the energies of the boundary orbitals for both compounds, calculated both in the gas phase and taking into account the influence of the solvent, are in good agreement with the experimental data (the difference is from 0.22 to 0.34 eV). A slightly overestimated difference between the theoretical and experimental HOMO energies (1.51 eV) is characteristic of compound **1**. This is due, in our opinion, to the fact that the experimental values of the HOMO for this compound were determined in the film, and in quantum chemical calculations of the energies of the frontier orbitals, it is impossible to take into account the influence of various kinds of intermolecular interactions occurring in a given state of aggregation. Thus, the experimental

Table 1 Energy characteristics of pyrrolidinofullerene **1** and its precursor **2**.

Compound	Conditions	LUMO energy/eV	HOMO energy/eV	E_g (EC)/eV	E_g (opt)/eV
1	Film/AN	–4.13	–6.67	2.54	
1	DCM solution	–4.07	–5.74	1.67	3.96 3.08 1.97
2	AN solution	–3.52	–5.57	2.04	–
1	Computed	–4.05[a]	–5.15[a]		
2	Computed	–3.18[a] –3.30[b]	–5.46[a] –5.32[b]		

[a] Theoretical value in the gas phase, calculated by the PBEPBE/6-311G(d,p) method. [b] Theoretical value calculated by the same method, but taking into account the influence of the solvent (acetonitrile) within the framework of the polarization continuum model.

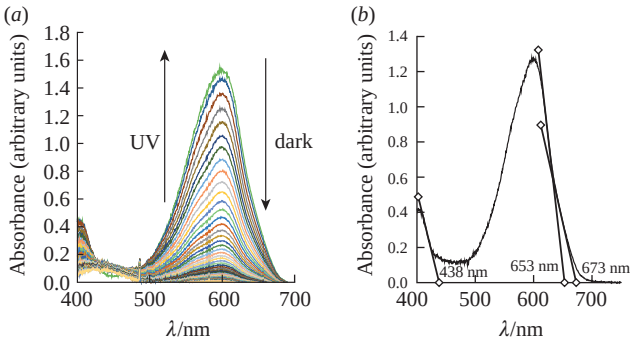


Figure 2 (*a*) UV photoinduced and spontaneous (in the dark) transformations of compound **1** (1×10^{-3} M) in *o*-dichlorobenzene containing 0.1 M NBu_4BF_4 and (*b*) analysis of bathochromic slopes in the absorption spectrum of the colored form of compound **1**.

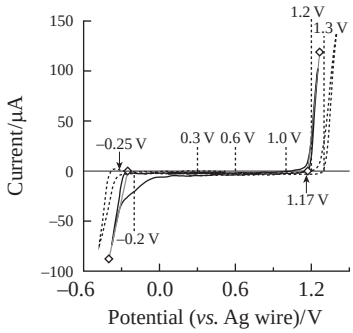


Figure 3 Cyclic voltammograms of compound **1** (1×10^{-3} M) in *o*-dichlorobenzene containing 0.1 M NBu_4BF_4, measured in a three-electrode photoelectrochromic cell before UV irradiation (dashed curve) and under constant UV irradiation (solid curve). The potential sweep rate was 50 mV s^{-1}.

approach used in this work to determine the energies of boundary orbitals is reliable.

Conceivably, the value of the energy gap between the LUMO and HOMO, determined from electrochemical measurements, E_g (EC), should coincide with the same value determined by the position of the optical absorption edge, E_g (opt).

In the absorption spectrum of a solution of compound **1** in DCM (Figure S2), three segments of the absorption decay slopes are clearly distinguished: the first (sharp) in the region of 250–320 nm, the second (shoulder) in the region of 350–450 nm and the third (moderate) in the region of 450–650 nm. The tangents to the absorption decay slopes in these three ranges give three values of the optical energy gaps presented in Table 1. The second value E_g (opt) = 3.08 eV is slightly larger than E_g (EC) = 2.54 eV for compound **1** in the film, and the third value (1.97 eV) is slightly larger than E_g (EC) = 1.67 eV for compound **1** in solution. Underestimation of the energy gap in electrochemical measurements is common for organic compounds in solution or films,[34] since the energy levels in solution have a Gaussian dispersion and, accordingly, the current through the electrode begins to flow before reaching the maximum on the Gaussian distribution curve. Meanwhile, the state of the substance in solution may differ from its state in the film, which means that the absorption spectrum may also be somewhat different.

Since the determination of the position of the third (moderate) slope of the absorption band is associated with a large error, we can assume that the values of E_g (opt) = 1.97 eV and E_g (EC) = 1.67 eV, given the underestimation of the values of E_g (EC) mentioned above, characterize the same electronic transition, namely, the excitation of an electron from the LUMO level of the fullerene fragment (4.07 eV) to the HOMO level of the spiropyran fragment (5.57 eV). An alternative explanation may be the existence of intramolecular charge-transfer complexes, but this fact requires additional evidence.

Under the action of UV radiation, hybrid compound **1** in solution undergoes photochromic transformations [Figure 2(*a*)] due to reversible photoinduced dissociation of the C–O bond in the pyran fragment and subsequent *cis–trans* isomerization with the formation of a colored merocyanine form (Figure S3). The solution spontaneously returns to its original state upon turning off the light and heating [see Figure 2(*a*)]. Analyzing the shape of the absorption band of the colored form of compound **1** [Figure 2(*b*)], one can see that the bathochromic slope has a complex shape with possible two tangents in the range of 650–675 nm. This indicates the existence of two close energy levels, the nature of which cannot be established at present.

Differences in the electrochemical behavior of spiropyran in the initial colorless form and the UV-induced colored form were studied by the CV method. Figure 3 shows CV curves for a solution of compound **1** in *o*-dichlorobenzene (1×10^{-3} M) without and under constant UV irradiation. The CV curves obtained without irradiation show the current fronts of the anodic process near 1.28 V (oxidizing, corresponding to the HOMO level) and the cathodic process near –0.35 V (reducing, corresponding to the LUMO level), which gives $E_g = e[1.28 - (-0.35)] = 1.69$ eV. This value is in good agreement with the value obtained in the DCM solution (1.67 eV, see Table 1). We purposely did not expand the scan limits of the cathodic and anodic potentials, since the solution turns yellow when scanning in the range of potentials that are significantly higher than the potentials for the onset of redox processes. CV for the colored form of compound **1** gives the value $E_g = e[1.17 - (-0.25)] = 1.42$ eV. The corresponding value, determined from the optical spectrum in Figure 2(*b*), is 1.84 eV. The potential values corresponding to the HOMO and LUMO levels measured for the colored and uncolored forms of compound **1** in a photoelectrochromic sandwich cell differ significantly from those measured in an electrochemical cell, which is quite appropriate given the differences in the electrode material (SnO_2), counter electrode (bare Ag wire) and the solvent used, as well as the proximity of the electrodes and the limited volume of the cell. Despite these facts, the obtained values of E_g differ little from the values obtained from the absorption spectra of the colored and uncolored forms of compound **1** and seem to be quite reasonable, indicating the appearance of new electronic levels in the system upon irradiation, which is accompanied by the convergence of the HOMO and LUMO levels.

On the CV curve obtained under UV irradiation, it is possible to identify safe potential regions (see Figure 3, vertical dashed lines), in which electrochemical action can lead to discoloration of the colored product without irreversible degradation of compound **1**. These potentials were applied to decolorize the photoinduced form of spiropyran.

Analysis of the absorbance transients of the electrochemical discoloration of compound **1** [Figure 4(*a*)] reveals that 90% of the discoloration range is reached in 150 s at a voltage of +1.3 V, which is 25% faster than in the case of spontaneous discoloration. Linearization of the dependences of absorbance on the square root of time makes it possible to identify time intervals when discoloration processes are predominantly controlled by diffusion. From Figure 4(*b*), it is easy to see that in the case of electrochemical discoloration (curve *6*), the diffusion of the colored form to the electrode plays a significant role.

Thus, for the first time we have carried out electrochemical studies of a photochromic hybrid molecule based on [60]fullerene and spiropyran. We determined the energy characteristics of the hybrid molecule in the cyclic form and compared them with those of the parent spiropyran. The theoretical values of the energies of the frontier orbitals of the compounds under study, obtained using quantum chemical calculations are in good agreement

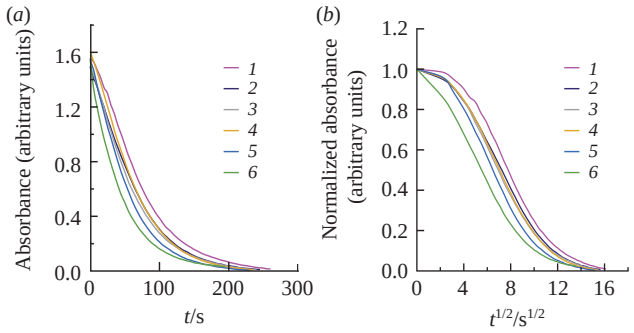


Figure 4 Dependences of absorbance on (*a*) time and (*b*) square root of time for (*1*) spontaneous and (*2*)–(*6*) electrochemical discoloration of the photoinduced colored form (λ_{max} = 600 nm) of compound **1** (1×10^{-3} M) in *o*-dichlorobenzene containing 0.1 M NBu_4BF_4, at a voltage of (*2*) 0.3, (*3*) 0.6, (*4*) 1.0, (*5*) 1.2 and (*6*) 1.3 V.

with the experimental data. The results of an electrochemical study of a solution of the hybrid molecule prove the possibility of electrically controlling the rate of discoloration of the photoinduced form. Further intensification of electrochemical discoloration can be achieved by modifying the structure of the hybrid spiropyran to suppress electrochemical degradation at higher anodic potentials and by introducing substituents that improve solubility in more polar solvents (*e.g.*, acetonitrile).

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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.2023.06.021.

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