

Photoconductivity of crystalline molecular complex of fullerene C_{60} with amine LCV

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A molecular complex of fullerene C_{60} with amine LCV: $LCV \cdot C_{60} \cdot C_6H_5Cl$ was studied. A comparative analysis of the photoconductivity spectrum allowed to reveal possible mechanisms of generating free charge carriers in $LCV \cdot C_{60} \cdot C_6H_5Cl$.

The influence of a weak magnetic field on the photoconductivity of the compound was observed and a model taking into account the spin nature of this effect was proposed.

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1 Introduction The great attention to fullerene-based compounds is attracted due to not only the unusual conductivity and magnetic properties of the C_{60} salts, but also possible application of neutral composites comprising fullerenes in low-cost photovoltaic devices and photodetectors [1]. Thus, it seems interesting to study the electron-optical properties of photoactive fullerene C_{60} -based molecular complexes characterized by a high quantum efficiency of charge transfer and long-lived charge separation. The present work reports on the mechanism of photoconductivity of fullerene C_{60} compound with organic donor LCV (Leuco Crystal Violet or 4, 4', 4''-methylidynetris (N,N-dimethylaniline)).

2 Experimental The measuring cell containing a single crystal sample in a quartz ampoule was placed into the cavity of a standard ESR spectrometer RadioPan SE/X 2547. Silver contacts, attached to one of the surfaces of the sample, were under a direct voltage of 10–50 V. Current was measured with an electrometric amplifier. The photoconductivity spectrum was recorded by using the illumination of a xenon lamp transmitted through the monochromator and normalized on the light intensity. The light intensity was 10^{12} – 10^{14} photons/cm²s. All the measurements were carried out at room temperature.

3 Results The photoconductivity spectrum of $LCV \cdot C_{60} \cdot C_6H_5Cl$ (1), containing one intensive peak near 830 nm, is shown in Fig. 1. It was found that the photoconductivity excited by monochromatic light with the wavelength of 830 nm was sensitive to a weak magnetic field (MF) with induction $B < 1$ T. The relative increase of photocurrent ΔI saturated at $B > 0.1$ T with the maximum magnitude of the effect 2% (Fig. 2).

4 Discussion Photoinduced electron transfer (PIET) in the molecular complex of C_{60} with photoactive donor LCV was studied by light-induced ESR spectroscopy in [2]. It was found that the LESR signal can be attributed to the C_{60}^- radical anion and the dependence of its intensity on photon energy had a maximum at the wavelength of the excitation light higher than 620 nm. Various mechanisms for the generation of the LESR spectrum are possible in the fullerene donor/acceptor complex (1):

(i) Photoexcitation of the donor component with the photon energy higher than the HOMO–LUMO gap results in electron transfer from the excited donor molecule to C_{60} . However, LCV is transparent and has no absorption in the 400–900 nm range.

(ii) Photoexcitation of C_{60} can also result in the electron transfer from the HOMO level of the donor mole-

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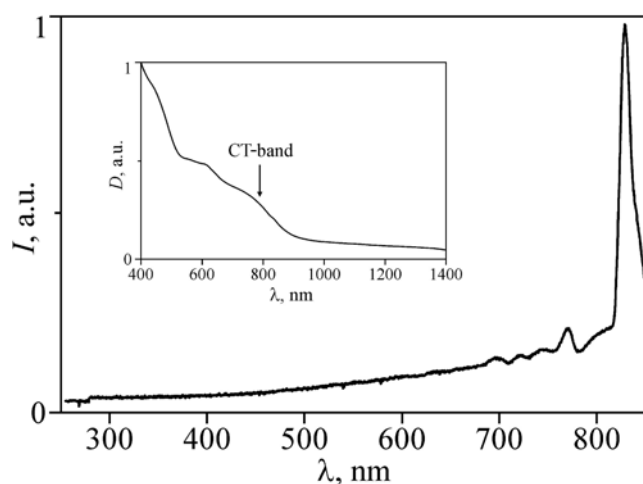


Figure 1 Photoconductivity spectrum of LCV · C₆₀ · C₆H₅Cl. The insert shows the absorption spectrum of this molecular complex [2].

cule to the HOMO level of the excited C₆₀ since fullerene is a stronger acceptor in the excited state than in the ground one, but photoexcitation of C₆₀ mainly occurs at wavelengths of the exciting light below 620 nm (the bands attributed to the symmetry-allowed intramolecular transitions in the absorption spectrum of C₆₀ are at 260 nm and 346 nm) [3].

(iii) Intermolecular optical transition between HOMO and LUMO levels of neighboring molecules of fullerene can lead to the appearance of C₆₀[−] too, however, this process takes place at the photon energy corresponding to 470 nm [3].

(iv) The fourth possibility is direct intermolecular charge transfer from the HOMO level of the donor to the LUMO level of the acceptor due to overlapping of π -orbitals of amine LCV and fullerene C₆₀. A wide charge transfer (CT) band occurs in the absorption spectrum of (1) around 800 nm (Fig. 1, insert).

The LESR signal was observed under photoexcitation of (1) by light with the wavelength higher than 620 nm, therefore, the PIET mechanism can be attributed mainly to direct intermolecular charge transfer from the donor molecule to the fullerene sphere.

The position of the intensive peak in the photoconductivity spectrum of (1) coincides with the CT-band in the absorption spectrum of a given molecular complex. It allows concluding that free charge carriers in (1) are generated due to impurity or thermal dissociation of dipole charge transfer excitons (CT-excitons) characterized by localization of an electron and a hole on the acceptor and the donor molecules, correspondingly. Some details of the involved mechanisms of generating new states in the LCV–C₆₀ system related to the permanent photoinduced hydride transfer are proposed in [4].

CT-excitons can be a singlet or a triplet depending on the mutual spin orientation of their components. It is known, that multiplicity of these intermediate states has an

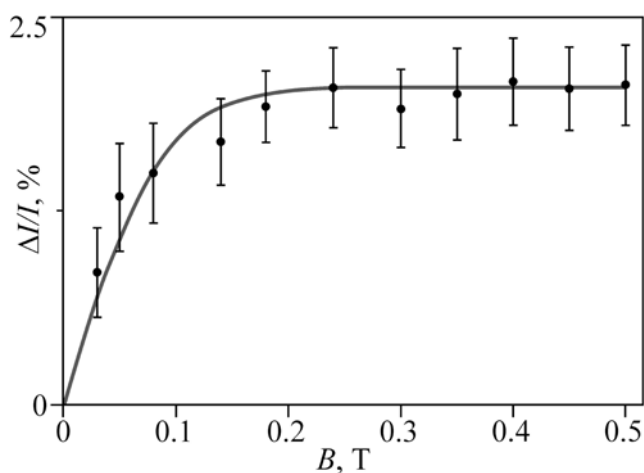


Figure 2 Magnetic field effect on the photoconductivity of LCV · C₆₀ · C₆H₅Cl excited by 830 nm light.

essential influence on the fast processes when the time scale is shorter than the spin-lattice relaxation time [5].

It was previously revealed that the effect of MF on the photoconductivity of layered molecular complex of fullerene C₆₀ with another saturated amine TBPDA (N,N,N',N'-tetrabenzyl-p-phenylenediamine) is spin related [6]. The observed magnetic field effect (MFE) on the photoconductivity of (1) indicates that the photogeneration of free charge carriers in this material is a spin-sensitive process, too.

The influence of a weak MF on the photoconductivity of (1) can be described in the following scheme. According to the principle of spin conservation, light absorption induces intermolecular charge transfer from LCV to C₆₀ forming singlet (S) dipole CT-excitons. Some part of the singlet dipoles transfers to the triplet state (T) because of interaction with the lattice and the lattice defects. As a rule, in molecular crystals the recombination from the S state occurs more effectively than from the T state. The role of MF is in increase of the concentration of triplet CT-excitons due to S–T intercombination transitions caused by the difference of g-factors of ionic states forming CT-excitons. It results in an increase of the probability of dissociation of intermediate pairs of paramagnetic particles into free charge carriers and in an enhancement of photoconductivity as a consequence.

5 Conclusion Thus, an analysis of the photoconductivity, LESR and the optical absorption spectra of the molecular complex of fullerene C₆₀ with the photoactive donor LCV allowed to reveal a possible mechanism of the formation of the intermediate excitonic states. Their dissociation leads to the appearance of free charge carriers in (1), and the positive MFE on the photoconductivity indicates the dependence of this process on the multiplicity of dipole CT-excitons.

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