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Received 26 August 2006, revised 1 November 2006, accepted 1 November 2006 Published online 7 November 2006

PACS 72.20.Jv, 72.40.+w, 72.80.Rj

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### phys. stat. sol. (RRL) 1, No. 2, R56-R58 (2007) / DOI 10.1002/pssr.200600015





## On the photoconductivity of layered molecular complex of fullerene $C_{60}$ with saturated amine TMPDA



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**1 Introduction** The formation of long-lived metastable charge separated states, arising from an efficient photoinduced electron transfer from chromophores to the fullerene molecules, makes donor–acceptor complexes of  $C_{60}$  attractive materials for the applications in molecular electronics [1, 2].

The visible-near infrared (Vis-NIR) range photoexcitation of these complexes gives rise to the excitons. The excitons may dissociate into free charge carriers, or recombine to fluoresce, or relax by some non-radiative channel. It is known that the multiplicity of these intermediate states essentially affects fast processes when the time scale is shorter than the spin-lattice relaxation time [3]. Therefore, the modification of electron-hole pairs' spin state by an external applied magnetic field (MF) can result in changes in photoconductivity magnitude and fluorescence intensity. Thus, a high-speed, contactless, and selective controlling of the optoelectronic properties of fullerene-based materials can be manifested.

The work reports on the intermediate magnetosensitive stage of free charge carriers photogeneration in layered molecular complex of fullerene  $C_{60}$  with saturated amine TMPDA (N,N,N',N'-tetramethyl-*p*-phenylenediamine): TMPDA  $\cdot C_{60}$  (1).

**2 Experimental** The measuring cell containing a single crystal of complex 1 in a quartz ampoule was placed into the cavity of a RadioPan SE/X 2547 ESR spectrometer. 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 and followed Ohm's law. The photoconductivity spectrum was recorded using the illumination of a high pressure short-arc xenon lamp transmitted through the monochromator and normalized on the light intensity. The light intensity was  $10^{12}-10^{14}$  photons cm<sup>-2</sup> s<sup>-1</sup>. Photoconductivity remaind unchanged for a long period of time. This fact proves the absence of any nonequilibrium processes connected with chemical or structural transformations in the sample. All the measurements were carried out at room temperature.

**3 Results** The photoconductivity spectrum of **1**, containing an intensive band near 419 nm (2.96 eV), is shown in Fig. 1. The photoconductivity of **1** excited by white light was sensitive to an external MF with induction B < 1 T. The relative change of photocurrent  $\Delta I$  was characterized by sign inversion at  $B \approx 0.13$  T and saturation was reached near  $B \sim 0.5$  T as shown in Fig. 2. The magnitude and other features of the magnetic field effect (MFE) did not





**Figure 1** Photoconductivity spectrum of TMPDA  $\cdot$  C<sub>60</sub>. The insert shows the absorption spectrum of this molecular complex [4].

depend on the bias and the mutual orientation of electric and magnetic fields.

**4 Discussion** In molecular crystals direct interband absorption resulting in the occurrence of free electrons and holes does not really take place in contrast to the direct band photoconductors. Therefore, the photoconductivity of **1** is caused by the exciton dissociation process. There are several possible mechanisms for the generation of these intermediate states being precursors of free charge carriers:

(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, TMPDA has no absorption in the 260–850 nm range.

(ii) Direct photoinduced intermolecular charge transfer from the HOMO level of the donor molecule to the LUMO level of the acceptor one is due to the overlapping of  $\pi$ -orbitals of TMPDA and C<sub>60</sub>. It leads to the appearance of light-induced ESR signals attributed to C<sup>-</sup><sub>60</sub> and TMPDA<sup>+</sup> [4]. The charge transfer band with the maximum at 1.27 eV (976 nm) occurs in the absorption spectrum of **1** (Fig. 1, insert). Thus, we can conclude that the lowmagnitude photocurrent at the wavelength of the exciting light higher than 600 nm is caused by dissociation of charge transfer excitons (CT-excitons) characterized by the localization of an electron and a hole on the acceptor and the donor molecules correspondingly.

All the aforesaid indicates that the photoconductivity spectrum of **1** most probably originates due to intermolecular electronic processes in the fullerene layers. Indeed, the band near 419 nm (2.96 eV) does not correspond to intramolecular transitions in  $C_{60}$  [5]. It disappears in the absorption spectrum of  $C_{60}$  in solution [6] and in the spectra of solid  $C_{60}$  complexes with isolated packing of the fullerene molecules [7], but manifests itself in the absorption spectrum of **1** (Fig. 1, insert). Thus, it can be ascribed



**Figure 2** Magnetic field effect on the photoconductivity of TMPDA  $\cdot$  C<sub>60</sub> excited by white light.

to CT-excitons caused by photoinduced intermolecular electron transfer between HOMO and LUMO levels of  $C_{60}$  molecules.

Previously it was found that the photoconductivity of the molecular complex of fullerene  $C_{60}$  with another saturated amine LCV (Leuco Crystal Violet) is also magnetosensitive [8]. However, the different features of MFEs indicate various mechanisms of the effect of MF on the photoconductivity of LCV  $\cdot C_{60} \cdot C_6H_5Cl$  and TMPDA  $\cdot C_{60}$ .

The influence of MF on the photogeneration of free charge carriers in 1 can be described in the following way. Light absorption induces mainly singlet (S) CT-excitons, characterized by the separation of an electron and a hole at the distance R satisfying the condition  $r \leq R < R^*$ , where r = 10.02 Å and  $R^* \sim 100$  Å are the distance between neighbouring  $C_{60}$  molecules and the Onzager radius for 1 correspondingly. A part of the singlet excitons transfers to the triplet state (T) due to the interaction with the lattice and the lattice defects. In the thermodynamic equilibrium the populations of S and T states of CT-excitons are defined by their statistical weights and lifetimes. Dense packing of the C<sub>60</sub> molecules in the fullerene layers of 1 allows one to propose the interaction between triplet excitons that leads to the formation of singlet ones. The kinetic model of the triplet-triplet annihilation process is described by the following reaction [9]:

$$T + T \xrightarrow[k_{-1}]{k_1} 1,3,5 (T \dots T) \xrightarrow{k} S + S_0$$

where  $k_1$ ,  $k_{-1}$ , k are the rate constants of the collision, back scattering and the formation of singlet products; S<sub>0</sub> is the ground-state of the C<sub>60</sub> molecule.

The excitons are not assumed to interact unless the intermediate complex  $(T \dots T)$  is produced. The lifetime of this pair is taken to be noticeably shorter than the spin– lattice relaxation time. Hence the reaction rate depends strongly on the multiplicity of the pair. A contact complex consisting of two triplets has nine spin states forming a



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singlet, a triplet and a quintuplet. The process of scattering is independent of the spin. In contrast, the spin conservation principle is essential to the annihilation process. The total rate constant of the T-T annihilation is defined as

$$\gamma = \frac{k_1}{9} \sum_{i=1}^{9} \frac{k|S_i|^2}{k_{-1} + k|S_i|^2}$$

where  $S_i$  is the amplitude of a singlet component in *i*-th spin state.

At B = 0 only three spin states contain a singlet component. An external MF with B < H (H is dipole zero-field tensor) distributes the singlet component over a greater number of states that results in the increase of  $\gamma$ . Over the range of a strong field (B > H) the Zeeman splitting greatly exceeds that in a zero field, so that the latter can be taken as a perturbation. Under these conditions spin states are quantized along an external field and only two states exhibit singlet character (i.e., less than in a zero field) that leads to the decrease of  $\gamma$  in strong fields. All the stated above reveals a nonmonotonic behavior of the  $\gamma(B)$  function and allows one to conclude that magnetosensitivity of the photoconductivity of 1 is mainly due to the effect of MF on the total rate constant  $\gamma$  of the triplet CT-excitons annihilation process. Besides, the field dependence of the photocurrent indicates the dominating role of singlet CTexcitons in the photogeneration of free charge carriers in 1. Indeed, the concentration of singlet CT-excitons grows in weak fields due to the increase of  $\gamma$ . In strong fields  $\gamma$  decreases and it reduces the concentration of such states.

**5** Conclusion Intermolecular electronic processes in the fullerene layers were found to cause the photoconductivity of **1** mainly. Similar bands near 419 nm (2.96 eV) were observed in the photoconductivity spectrum of another layered molecular complex, too: TBPDA  $\cdot$  (C<sub>60</sub>)<sub>2</sub> (TBPDA: N,N,N',N'-tetrabenzyl-*p*-phenylenediamine) [10] single-crystal sample (**2**). However, the response associated with direct photoinduced intermolecular charge transfer from the donor molecule to the fullerene sphere detected in the photoconductivity spectrum of **2** is absent in the spectrum of **1** in spite of that both complexes have relatively intense charge transfer bands in the Vis– NIR range. Thus, we can suppose that the replacement of benzyl substituents by alkyl ones in the donor molecules affects the mechanisms of free charge carriers photogeneration in the complexes. This fact indicates the creation possibility of novel  $C_{60}$ -based materials with required optoelectronic properties.

The MFE on the photoconductivity of **1** reveals an intermediate magneto-sensitive stage in the photogeneration of free charge carriers due to the effect of MF on the triplet CT-exciton annihilation process and indicates that dissociation of singlet CT-excitons leads to the appearance of free charge carriers.

In summary, it should be noted that fullerene  $C_{60}$ -based materials possessing the sign inversion MFEs on the photoconductivity could be used for the fabrication of field-dependent photoconductive optical switches.

**Acknowledgement** The work was supported by Rosnauka (State contract No. 02.442.11.7470).

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