

Photogeneration of free charge carriers in the donor–acceptor complex TBPDA·(C₆₀)₂

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The effect of a weak magnetic field with $B_0 < 10000$ G on the photoconductivity of the layered donor–acceptor complex TBPDA·(C₆₀)₂ has been studied. The Reaction Yield Detected Magnetic Resonance (RYDMR) spectrum provides evidence of a spin nature of the mechanism of free charge carrier generation in magnetic fields. A model of triplet–triplet annihilation of charge transfer excitons has been suggested. The model interprets the effect of a weak magnetic field on photoconductivity in TBPDA·(C₆₀)₂. The photoconductivity spectrum of the complex shows two peaks at 470 and 700 nm. The comparison of this spectrum with the optical absorption one indicates that both intermolecular charge transfer between neighboring C₆₀ molecules and direct charge transfer from the TBPDA to the C₆₀ molecules contribute to free charge carrier generation in TBPDA·(C₆₀)₂.

Introduction

Fullerene C₆₀ is a π -acceptor, which essentially differs from other planar π -acceptor molecules by its large size, spherical shape, high symmetry and polarizability.¹ These features certainly affect the donor–acceptor interactions of C₆₀ providing the design of materials possessing unusual magnetic and conductive properties.^{2–4} Fullerenes also have unique photoacceptor properties. Different fullerene based composites with conjugated polymers, dyad and triad molecules with covalently and noncovalently attached porphyrins, phthalocyanines and other molecules show efficient electron transfer from chromophores to fullerenes and the formation of long-lived charge separated states (up to tens of ms).^{5–7} This makes fullerene based compounds promising materials for use in modeling artificial photosynthesis⁸ and in photovoltaic devices.⁹ In this context it seems important to study the electro-optical properties of fullerene compounds. While the electro-optical properties of pure fullerene crystals^{10–12} and conjugated polymer/fullerene composites¹³ have been studied, information on electro-optical properties of donor–acceptor complexes of fullerenes is absent. We chose the C₆₀ charge transfer complex with *N,N,N',N'*-tetrabenzyl-*p*-phenylenediamine, TBPDA·(C₆₀)₂¹⁴ for photoconductivity measurements since in C₆₀ complexes with amines under photoexcitation by white light the excited ionic state can be detected by light-induced EPR spectroscopy.^{14,15} The goal of this work was to study the effect of weak static and microwave magnetic fields on the photoconductivity of the complex and to elucidate the mechanisms of free charge carrier generation.

Results and discussion

TBPDA·(C₆₀)₂ has a layered structure.¹⁴ Fullerenes form deformed puckered layers arranged along a diagonal to the *ac* plane (Fig. 1). Each C₆₀ molecule has 5 neighboring C₆₀ ones in the layer with center-to-center distances of 9.77–10.67 Å, several of them being shorter than the van der Waals diameter of the C₆₀ molecule (10.18 Å). Due to the strong puckering of the C₆₀ layers, each C₆₀ molecule also has two neighboring C₆₀ ones from the adjacent layer with a center-to-center distance of 10.25 Å. TBPDA molecules occupy cavities between the C₆₀ layers (Fig. 1) and form van der Waals contacts with C₆₀ molecules by phenyl (molecule I) and central phenylene groups (molecule II).

The UV-vis-NIR spectrum of TBPDA·(C₆₀)₂ is a superposition of the spectra of parent TBPDA and C₆₀ (Fig. 2). The bands with the maxima at 260, 346, 470 and 610 nm are ascribed to the C₆₀ chromophore and can be observed in the spectrum of the C₆₀ single crystal as well.¹⁶ Whereas the bands

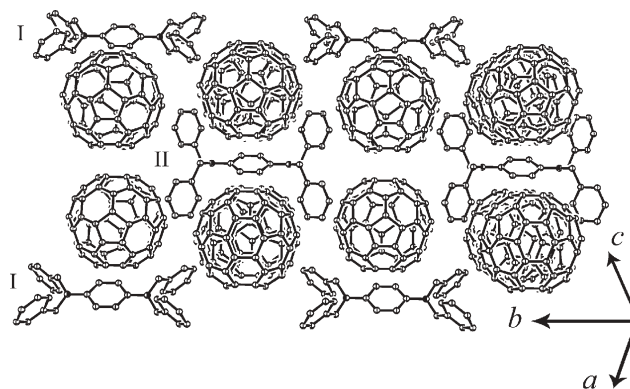


Fig. 1 The projection of the crystal structure of TBPDA·(C₆₀)₂ along a diagonal to the *ac* plane.¹⁴

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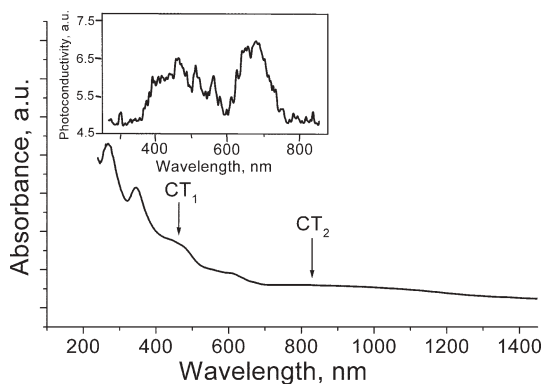


Fig. 2 Optical absorption spectrum of TBPDA·(C₆₀)₂ in the 240–1450 nm range in KBr pellets. The insert shows the photoconductivity spectrum of TBPDA·(C₆₀)₂ in the 280–850 nm range.

at 260, 346 and 610 nm are attributed to intramolecular transitions in the C₆₀ molecule,^{1,17} the band at 470 nm can be ascribed to intermolecular charge transfer between neighboring C₆₀ molecules (CT₁ in Fig. 2).^{17,18} Indeed, this band disappears in the solution spectrum of C₆₀¹⁷ and the spectra of solid C₆₀ complexes with isolated packing of C₆₀ molecules.^{16,19} A broad and weak band in the 700–1300 nm range can be attributed to direct intermolecular charge transfer from TBPDA to C₆₀ upon the absorption of light quantum (CT₂ in Fig. 2). However, the IR and EPR spectra of TBPDA·(C₆₀)₂ indicate the absence of any charge transfer from TBPDA to C₆₀ in the ground state.¹⁴ Thus, TBPDA·(C₆₀)₂ is a neutral CT complex.

In compliance with a neutral ground state it was found that the TBPDA·(C₆₀)₂ single crystals show low “dark” conductivity, $\sigma \sim 10^{-12} (\Omega \text{ cm})^{-1}$. Upon illuminating the sample with white light one observed a 10^3 increase of the photocurrent, which remained unchanged for 10^4 s. The photoconductivity of TBPDA·(C₆₀)₂ was found to be sensitive to the magnetic field (MF) with $B_0 < 10^4$ G. The dependence of photocurrent on B_0 is characterized by the sign inversion at 3000 G (Fig. 3) and conceivably attains saturation at 10^4 G. The sign inversion field dependence is characteristic of processes associated with the effect of the MF on the concentration of triplet charge transfer excitons in molecular crystals.²⁰

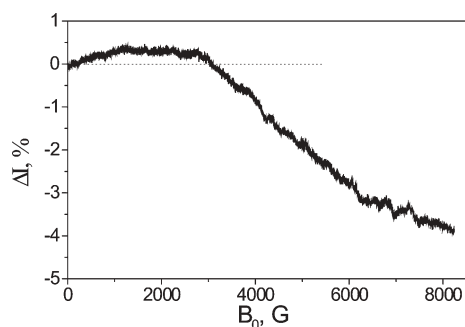


Fig. 3 The dependence of the relative change of the photocurrent ΔI in TBPDA·(C₆₀)₂ on the magnetic field with induction B_0 .

The CT-exciton is formed upon photoexcitation of the complex. Depending on the mutual orientations of spins of the components (electrons and holes), the CT-exciton can be either a singlet or a triplet one. Free charge carriers are formed in molecular crystals mainly due to thermal or impurity dissociation of triplet CT-excitons.²¹

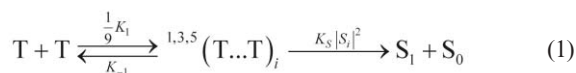
The spin nature of the effect of MF on photogeneration of free charge carriers was verified under experimental conditions of the registration of a EPR spectrum detected by photoconductivity measurements (Reaction Yield Detected Magnetic Resonance (RYDMR) spectrum) of TBPDA·(C₆₀)₂. The spectrum (Fig. 4) contains two resonance peaks of negative polarity at 1890 and 3120 G, the peak halfwidth is 90 G. The second peak has a fine structure.

The efficiency of the effect of magnetic field on spin-dependent reactions in solids is based on the performance of the following condition:²² the time τ_{pair} particles stay in a pair state must be longer than the time needed to mix spin states τ_{ev} , but shorter than the relaxation time τ_{rel} with the value typical for molecular crystals, which is equal to 10^{-6} – 10^{-8} s:

$$\tau_{\text{ev}} < \tau_{\text{pair}} < \tau_{\text{rel}}$$

The time τ_{ev} depends on the mechanism of spin evolution. For the dipole–dipole mechanism $\tau_{\text{ev}} = \hbar/g\mu D$, where D is the dipole–dipole energy of interaction and μ is the Bohr magneton. For TBPDA·(C₆₀)₂ the following values were calculated: $\tau_{\text{ev}} = 2.7 \times 10^{-11}$ s and $\tau_{\text{pair}} = 3.1 \times 10^{-9}$ s.

The RYDMR spectrum of the TBPDA·(C₆₀)₂ crystals is interpreted by a model, which considers external-field modulation of a triplet–triplet exciton annihilation rate constant.²¹ The kinetic model of triplet–triplet exciton annihilation can be presented as follows:



where $(T \dots T)_i$ is the intermediate pair state formed in one of nine possible, i th, spin state; K_1 and K_{-1} are the rate constants of collision and back scattering; $K_S |S_i|^2$ is the rate constant of annihilation for the i th spin state; and S_i is the amplitude of singlet components in this state.

In magnetic fields with $B_0 > 10^3$ G only two mixed singlet and quintuplet levels, SQ₁ and SQ₂, generally contain a singlet component S, which defines the transition of a pair to a final

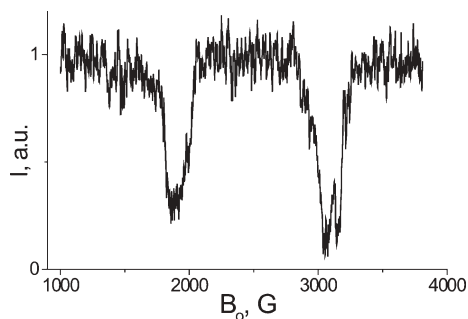


Fig. 4 The RYDMR spectrum for TBPDA·(C₆₀)₂. Microwave magnetic field frequency $\nu = 8.96$ GHz.

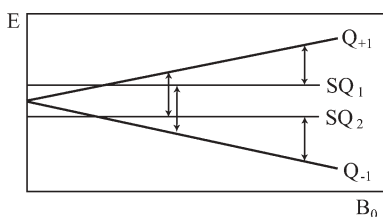


Fig. 5 The scheme of resonance transitions in the (T...T) complex.

singlet state. These transitions cause partial emptying of the SQ_1 and SQ_2 levels. Microwave magnetic field stimulates mainly transitions from the quintuplet levels Q_{+1} and Q_{-1} to the SQ_1 and SQ_2 ones (Fig. 5), whose occupancy increases. Since the total rate constant (1) defined as

$$\gamma = \frac{1}{9} K_1 \sum_i \frac{K_S |S_i|^2}{K_{-1} + K_S |S_i|^2}$$

is a function of stationary occupancies of the levels of the (T...T) complex, the above mentioned resonance transitions result in the increase of γ .

The increased yield of the reaction products of (1) results in a lower concentration of triplet excitons and, consequently, a lower number of free charge carriers formed in molecular crystals that is justified by two resonance peaks of negative polarity in the RYDMR spectrum of TBPDA·(C₆₀)₂.

Free charge carriers are generated in the complex at the dissociation of CT-excitons. Two ways for the formation of CT-excitons are possible upon photoexcitation of TBPDA·(C₆₀)₂ by white light: intermolecular photoinduced charge transfer between neighboring C₆₀ molecules and from TBPDA to C₆₀ molecules. The first way is realized in pure C₆₀ crystals²³ and it is also possible in TBPDA·(C₆₀)₂ because of the close packing of the C₆₀ molecules in the layer. The second way can be realized by three schemes depending on the photon energy of excited light (Fig. 6):

1. The photoexcitation of the donor component (Fig. 6a₁) results in electron transfer from the excited donor to the C₆₀ molecule (Fig. 6a₂) (TBPDA absorbs only in the UV range > 310 nm).
2. The photoexcitation of C₆₀ (Fig. 6b₁) can also result in electron transfer from the donor to the excited C₆₀ molecule (Fig. 6b₂) since the C₆₀ molecule is a stronger acceptor in the excited state rather than in the ground state.²⁴ Direct HOMO–LUMO transitions in C₆₀ are symmetry forbidden and photoexcitation of C₆₀ is possible mainly at energies

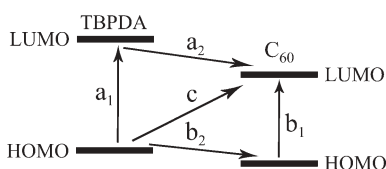


Fig. 6 A diagram of the possible mechanisms of photoinduced charge transfer in the C₆₀ complex with TBPDA: (a) excitation of the TBPDA component; (b) excitation of C₆₀ followed by electron transfer from TBPDA to the excited C₆₀ molecule; (c) direct charge transfer from TBPDA to the C₆₀ molecule.

higher than 410 nm (the bands in the absorption spectrum at 260 and 346 nm (Fig. 2)).

3. Direct intermolecular charge transfer from the TBPDA to the C₆₀ molecule is also possible (Fig. 6c). As it was mentioned above, the charge transfer band in the spectrum of TBPDA·(C₆₀)₂ was observed in the 700–1300 nm range.

The photoconductivity spectrum of the complex is shown in Fig. 2, insert. There are two separate high- and low-energy peaks of photoconductivity with maxima around 470 and 700 nm, respectively. The position of the high-energy peak is close to that in the photoconductivity spectrum of pure C₆₀ crystals²³ and coincides with the band ascribed to intermolecular charge transfer between neighboring C₆₀ molecules in the absorption spectrum of TBPDA·(C₆₀)₂ (maximum at 470 nm). The low-energy peak is not observed in the photoconductivity spectrum of pure C₆₀ crystals²³ and can be associated with photoinduced charge transfer from TBPDA to the C₆₀ molecule. The position of this peak is close to that of the charge transfer band (700–1300 nm) and intramolecular HOMO–LUMO transitions in the C₆₀ molecule (maximum at 610 nm) in the absorption spectrum of TBPDA·(C₆₀)₂. However, at wavelengths higher than 380 nm, where the photoexcitation of C₆₀ is also possible, photocurrent is not observed. This allows one to conclude that the second peak of photoconductivity is most probably due to direct charge transfer from TBPDA to the C₆₀ molecule. Previously it was also shown that the excited ionic state observed by light-induced EPR spectroscopy upon photoexcitation of C₆₀ complexes by white light is realized mainly by direct charge transfer from the donor to the C₆₀ molecule.¹⁴

Conclusion

The effect of a weak magnetic field with $B_0 < 10^4$ G on the photoconductivity of the donor–acceptor layered complex TBPDA·(C₆₀)₂ has been studied. The RYDMR spectrum provides evidence of a spin nature of the mechanism of free charge carrier generation in magnetic fields. The information on structure, energy and time performances of short-lived intermediate charge transfer states can be received from the analysis of the RYDMR spectrum. A model of triplet–triplet annihilation of charge transfer excitons has been suggested. The model interprets the effect of a weak magnetic field on the photoconductivity in TBPDA·(C₆₀)₂. The photoconductivity spectrum of the complex shows two high- and low-energy peaks around 470 and 700 nm. The first peak is also observed in pure C₆₀ crystals and can be attributed to intermolecular charge transfer between neighboring C₆₀ molecules, whereas the second peak is most probably associated with direct intermolecular charge transfer from TBPDA to the C₆₀ molecule.

Experimental

Synthesis of single crystals of TBPDA·(C₆₀)₂ was described previously.¹⁴ The UV-vis-NIR spectrum was measured on a Shimadzu-3100 spectrometer in the 220–1600 nm range. Photoconductivity of the complex was studied by excitation using white light from a 150 W halogen tube. The flux of light through the monochromator was 10^{12} – 10^{14} photons cm⁻² s⁻¹.

Photoconductivity was characterized by the current I running through indium contacts attached to one of the facets of a single crystal of TBPDA·(C₆₀)₂ with silver paste. The contacts were under a direct voltage of 10–50 V. The RYDMR spectrum of TBPDA·(C₆₀)₂ was measured in a cell with the crystal inserted into a resonator of a standard Radiopan SE/X 2547 spectrometer. The photoconductivity spectrum was recorded by using the light beam of a xenon lamp transmitted through a high-aperture monochromator.

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