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Journal of Physics and Chemistry of Solids 66 (2005) 711–715
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
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Synthesis, crystal structure and photoconductivity of new molecular complex of C_{60} with tetrabenzo(1,2-bis[4H-thiopyran-4-ylidene]ethene): Bz_4BTPE C_{60}

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Received 28 June 2004; revised 10 September 2004; accepted 10 September 2004

Abstract

A new molecular complex of C_{60} with tetrabenzo(1,2-bis[4H-thiopyran-4-ylidene]ethene), Bz_4BTPE C_{60} (**1**) has been obtained. The complex has a layered structure in which closely packed hexagonal layers of C_{60} alternate with the layers composed of Bz_4BTPE molecules. The complex has a neutral ground state according to UV–vis–NIR spectrum. It has been found that single crystals of **1** show low 'dark' conductivity of $\sigma \sim 10^{-10}$ $(\Omega\,\mathrm{cm})^{-1}$. A 10^2 increase in photocurrent has been observed upon illuminating the crystal with white light. Photoconductivity of **1** is sensitive to magnetic field with $B_0 < 1$ T and increases up to 5% in magnetic field. The photoconductivity spectra of the complex indicate that free charge carriers are generated in the UV–visible range mainly by the Bz_4BTPE excitation (the peaks at 622, 562, 472 and 348 nm) with a possible contribution of charge transfer excitations between neighboring C_{60} molecules (the peak at 472 nm).

Keywords: A. Fullerenes; B. Crystal growth; D. Crystal structure; D. Optical properties

1. Introduction

Fullerenes have unique photoacceptor properties. As a result, fullerene based composites with conjugated polymers [1,2] as well as dyad and triad molecules [3,4] show effective photoinduced charge transfer (PICT) from chromophore to fullerene molecule, and relatively long-lived charge separated states form. These compounds are promising components for the development of energy transducers [5] and the modeling of artificial photosynthesis [6]. In this context electron-optical properties of pure fullerene crystals [7–9] or fullerene/conjugated polymer composites [10] are intensely studied. Charge separated states are also observed by light-induced EPR spectroscopy at photoexcitation of donor–acceptor complexes of fullerenes with amines and c halcogen-containing heterocycles [11]. Because of this, it is interesting to study electron-optical properties of such complexes. Recently a 10^3 increase in photocurrent upon illuminating by white light of the crystal of C_{60} complex with *N*,*N*,*N*′,*N*′-tetrabenzyl-*p*-phenylenediamine: $TBPDA(C_{60})_2$ has been reported [12]. The effect of magnetic field with $B_0 < 1$ T on photocurrent and the RYDMR (Reaction Yield Detected Magnetic Resonance) spectrum of $TBPDA(C_{60})_2$ were also studied [12].

This work reports on the new C_{60} complex with chromophore tetrabenzo(1,2-bis[4H-thiopyran-4-ylidene]ethene (denoted also as donor molecule in the text) (Fig. 1), Bz_4BTPE C_{60} (**1**) synthesized for the first time.

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0022-3697/$ - see front matter
doi:10.1016/j.jpcs.2004.09.005

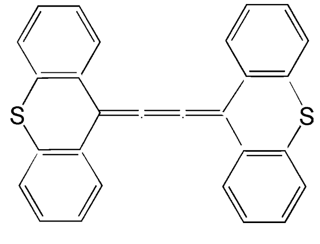

Fig. 1. The molecular structure of Bz_4BTPE.

The crystal structure, IR and UV–vis–NIR spectra of the complex are presented. Photoconductivity of the crystals was studied upon illuminating by white light and the influence of magnetic field with $B_0 < 1$ T on photoconductivity was found. The comparison of photoconductivity and absorption spectra allows possible mechanisms of photoinduced charge transfer in **1** to be elucidated.

2. Experimental details

Materials. Bz_4BTPE was synthesised previously [13]. C_{60} of 99.98% purity was used from MTR Ltd. Benzene (C_6H_6) was distilled over Na/benzophenone in the argon atmosphere.

General. FT-IR spectra were measured in KBr pellets with a Perkin–Elmer 1000 Series spectrometer (400–7800 cm^{-1}). UV–vis–NIR spectra were measured on a Shimadzu-3100 spectrometer in the 220–1600 nm range. Photoconductivity was excited using white light of a 150 W halogen tube. Photoconductivity was characterized by current, I, running through indium contacts attached to one of the faces of the samples with silver or carbon paste. To record the spectra the light beam of a xenon lamp was transmitted through a high-aperture monochromator. The contacts were under direct voltage of 10–50 V. A constant magnetic field with the induction up to 0.5 T was obtained by means of an electromagnet.

Synthesis. Bz_4BTPE C_{60} (**1**) was obtained by a slow evaporation of benzene solution (30 mL) containing C_{60} (0.035 mmole, 25 mg) and an equimolar amount of Bz_4BTPE (0.035 mmole, 14.5 mg). The solvent was decanted after 1 week and the crystals were washed with hexane yielding large hexagonal plates (up to $0.1\times0.5\times1$ mm^3 size) with characteristic copper luster (yield 70%). Elemental analysis: found; %: $S=5.85$, calc.; %: $S=5.63$. The composition of the complex was justified by X-ray diffraction on a single crystal.

X-ray crystallography. The intensity data for the structural analysis were collected on a MAC Science DIP-2020K oscillator type X-ray imaging plate diffractometer with graphite monochromated Mo K_α radiation at room temperature (293 (2) K). Raw data reduction to F^2 was carried out using the DENZO program [14]. The structures were solved by a direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97 [15].

3. Results and discussion

The crystals of **1** were obtained by a slow evaporation of benzene solution containing C_{60} and an equimolar amount of Bz_4BTPE. The crystals appeared as large hexagonal plates with characteristic copper luster. The 1:1 (Bz_4 BTPE:C_{60}) composition of the complex was determined from elemental analysis and was justified by X-ray diffraction on a single crystal.

The complex has a monoclinic lattice [16]. The Bz_4-BTPE molecule is ordered whereas C_{60} one is statistically disordered and was refined as a superposition of two orientations with 65/35% occupancy. However, the complicated disorder pattern could not be resolved completely as a superposition of two orientations (probably the third C_{60} orientation with a small occupancy factor is also presented). This results in a relatively high value of R-factor for this crystal structure ($R_1=0.1167$).

The complex **1** has a layered structure. Closely packed hexagonal layers of C_{60} alternate with the layers composed of Bz_4BTPE (Fig. 2). Each C_{60} has six neighbors in the layer with the center-to-center distances of 9.93 (two neighbors) and 10.06 Å (four neighbors) and the shortened van der Waals C···C contacts in the 3.22–3.36 Å range. These distances are close to those in pure C_{60} crystal at 153 K (the center-to-center distance is 9.94 Å) [17].

The projection of the Bz_4BTPE layer on the bc-plane is shown in Fig. 3. Bulky Bz_4BTPE molecules slightly overlap in the layers by the edges of C_9SH_4 fragments (Fig. 3), which are nearly parallel to each other (the corresponding dihedral angle is 171°) and form shortened van der Waals C···C contacts in the 3.41–3.60 Å range. So one-dimensional chains of the Bz_4BTPE molecules passing along the b-direction within the layer are clearly pronounced. The Bz_4BTPE molecule has nearly planar conformation with slight 'batterfly' deviations of the $C_{13}SH_8$ fragment

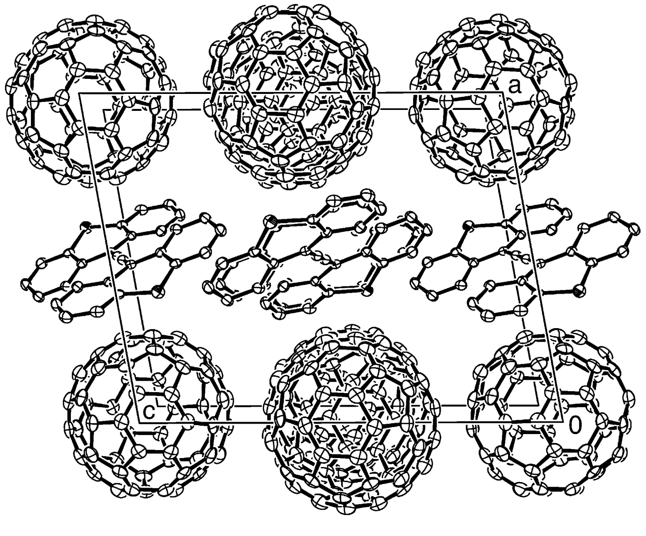

Fig. 2. The projection of the crystal structure of **1** along the b-axis. Only major orientation of C_{60} molecules is shown.

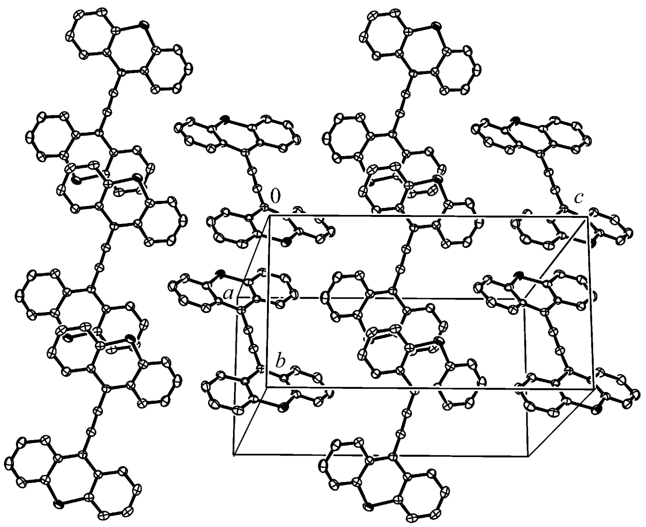

Fig. 3. The projection of the donor layer on the *bc*-plane.

(the dihedral angle between the planes of two phenylene (C_6H_4) groups in this fragment is 160°).

The effective packing of the Bz_4BTPE molecules with the spherical C_{60} ones is attained by the occupation of the voids formed in closely packed hexagonal layers of C_{60} by outer phenylene groups of Bz_4BTPE. Previously the formation of similar layered structures was observed for the C_{60} complex with 9,9′-diphenylanthracene [18] and the multi-component C_{60} complex with planar bis(ethylenedithio)tetrathiafulvalene cation and I_3^- [19]. Two C_9SH_4 fragments of Bz_4BTPE form shortened van der Waals contacts with hexagons of two C_{60} molecules belonging to adjacent layers (Fig. 4, the C⋯C contacts are in the 3.40–3.53 Å range and the shortest S⋯C(C_{60}) contact is 3.57 Å).

The IR spectrum of **1** is a superposition of the spectra of starting Bz_4BTPE and C_{60}. The bands at 452, 474, 612, 625, 723, 762, 774, 850, 938, 1036, 1075, 1125, 1156, 1264, 1293, 1428 (coincides with the C_{60} band), 1456, and 1574 cm^{-1} are attributed to Bz_4BTPE. Parent Bz_4BTPE has the bands in the IR spectrum at 452, 473, 611, 625, 713, 753, 776, 852, 933, 1040, 1078, 1127, 1158, 1262, 1297, 1430, 1459, and 1580 cm^{-1}. The shift of up to 10 cm^{-1} of some Bz_4BTPE bands relative to the starting donor indicates noticeable changes in its initial geometry in the complex with C_{60}. The bands at 526, 576, 1181, and 1428 cm^{-1} are attributed to C_{60}.

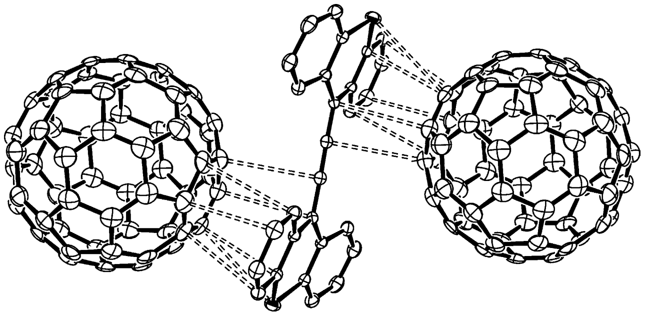

Fig. 4. Van der Waals contacts (<3.6 Å) between Bz_4BTPE and C_{60} molecules (dashed lines). Only major orientation of C_{60} molecules is shown.

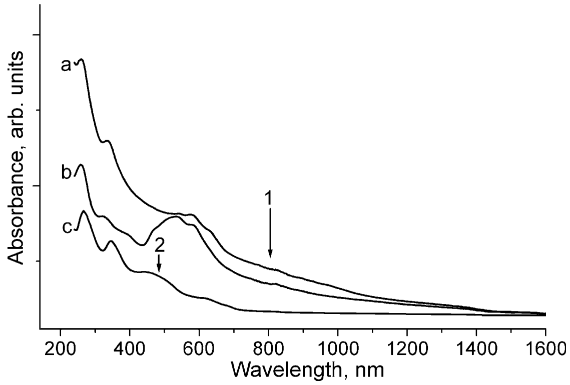

Fig. 5. UV–vis–NIR spectra of the complex **1** (a), starting Bz_4BTPE (b) and pure C_{60}(c) in KBr pellets in the 240–1600 nm range. The arrows 1 and 2 show the position of charge transfer (CT) band attributed to transitions between Bz_4BTPE and C_{60} in **1** and intermolecular CT transitions in pure C_{60}, respectively.

The UV–vis–NIR absorption spectra of **1**, starting Bz_4BTPE and C_{60} are shown in Fig. 5. Complex **1** reveals the bands at 258, 334, 541, 574, 632 and 800 nm (Table 1, Fig. 5a). The bands at 541, 574 and 632 nm can be ascribed to Bz_4BTPE since the starting donor also absorbs in visible range with the maxima at 474, 534 and 578 nm (Table 1, Fig. 5b). It is seen that Bz_4BTPE bands are noticeably red-shifted in the complex (by 67–40 nm or 0.16–0.35 eV) to lower energies. These shifts can be associated with a noticeable interaction of π-systems of Bz_4BTPE and C_{60}. The bands in the spectrum of **1** in the UV-range at 258 and 334 nm can be attributed mainly to C_{60} (stating C_{60} shows

Table 1
The positions of the absorption bands in the spectra of C_{60}, Bz_4BTPE, and **1**, and the peaks in the photoconductivity spectrum of **1** and their assignment

	Position (nm)						
Absorption spectra							
1	258	334	–[a]	541	574	632	800w (CT band)
Bz_4 BTPE	256	318	–	474	534	578	–
C_{60}	265	345	470 (CT band)	–	–	620w	–
Photoconductivity spectrum							
1	–	348	472	562	622		
Assignment		Bz_4 BTPE excitation	Bz_4BTPE excitation with possible contribution of C_{60} CT excitation	Bz_4 BTPE excitation			

w, Weak absorption band.

[a] The broad band of C_{60} at 470 nm is probably hidden by the Bz_4BTPE absorption at 541 nm.

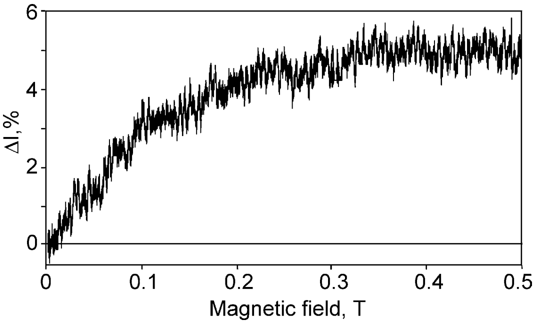

Fig. 6. Dependence of photocurrent increment ΔI caused by the static magnetic field vs. the induction of magnetic field (B).

the bands at 265 and 345 nm, Table 1). Broad and weak absorption near 800 nm (Fig. 5a, arrow 1) can be attributed to charge transfer from Bz_4BTPE to C_{60} at the absorption of light quantum. However, this absorption is relatively weak as compared to that observed in the spectra of C_{60} complexes with amines [20]. Characteristic bands of the C_{60} radical anion are not observed at 930 and 1070 nm in the spectrum of the complex (Fig. 5a). Thus, **1** has a neutral ground state.

The single crystals of **1** show low 'dark' conductivity $\sigma \sim 10^{-10}$ $(\Omega\,\text{cm})^{-1}$. Upon illuminating the sample with white light one observes a 10^2 increase of photocurrent, which remains unchanged for 10^3 s. It was found that photoconductivity of **1** is sensitive to magnetic field (MF) with $B < 1$ T. The increase in photoconductivity up to 5% was observed in MF. The main peculiarity of the ΔI (B) dependence is ΔI saturation attained at $B_0 > 0.2$ T (Fig. 6). The 'dark' current was not sensitive to MF. The effect of MF on the charge carrier generation in **1** can be represented by the following scheme. Light absorption leads to the formation of excitons. Excitons can dissociate on the surface, lattice oscillations, defects and impurities producing free charge carriers. Light generates mainly singlet excitons. However, MF can change a spin state of an electron and a hole in the exciton and produce triplet excitons from singlet ones. As a rule, dissociation of excitons from triplet state occurs more effectively than that from singlet one. Because of this the population of a triplet state results in the increase of probability of electron–hole pair dissociation into free charge carriers and, as a consequence, an enhancement of photoconductivity in MF. Spin nature of the effect of MF on photogeneration of free charge carries demands further experimental confirmation. Thus, MF is able to govern electronic processes of charge carriers photogeneration in the single crystals of **1**.

Photoconductivity spectra of the single crystal of **1** both in and out of MF are shown in Fig. 7. The decomposition of the spectra into Lorentz components allows us to select four optical transitions at 622, 562, 472 and 348 nm (Table 1). The comparison of the photoconductivity and the UV–vis–NIR spectra of **1** indicates that the most intense photoconductivity peaks at 622 and 562 nm and the absorption bands in the spectrum of **1** at 632 and 574 nm ascribable to Bz_4BTPE have close positions. C_{60} has no intense absorption in this range. Thus, these peaks of photoconductivity can be associated with the photoexcitation of Bz_4BTPE. A similar mechanism of the generation of free charge carriers is observed in fullerene/conjugated polymer composites, where the primary step of PICT is mainly the excitation of conjugated polymers [2].

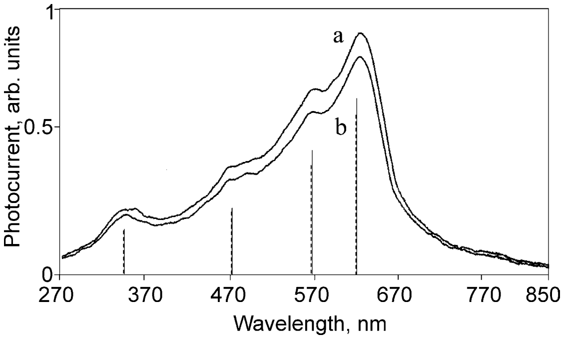

Fig. 7. Photoconductivity spectra of **1** in the absence (b) and in the presence (a) of the magnetic field with $B_0 = 0.5$ T. Continuous and dotted vertical lines show positions of optical transitions in the magnetic field and its absence, respectively.

C_{60} has four bands in the UV–visible range at 265, 345, 470 nm and a weak band near 620 nm (Fig. 5c, Table 1). Among these bands the band at 470 nm (Fig. 5c, arrow 2) is attributed to intermolecular CT excitations [21] and the position of this band coincides with the maximum of photoconductivity in pure C_{60} crystals [22]. The C_{60} molecules are also closely arranged in **1** and this mechanism of free charge carrier generation can contribute to photoconductivity (the peak at 472 nm) together with photoexcitation of Bz_4BTPE. A weak peak of photoconductivity at 348 nm can be assigned mainly to photoexcitation of Bz_4BTPE because C_{60} can be excited in the UV-range at 265 and 345 nm. However, weak photocurrent is observed only at 348 nm and is absent at 270 nm.

It should be noted that photoconductivity is nearly absent at wavelengths of excited light larger than 670 nm. Because of the charge transfer band observed in this range (the maximum at around 800 nm), we can conclude that direct charge transfer from Bz_4BTPE to C_{60} does not contribute to the generation of free charge carries in **1**.

4. Conclusions

Thus, the new complex of C_{60} with chromophore Bz_4BTPE has been synthesized for the first time. According to the UV–vis–NIR spectrum **1** has a neutral ground state. X-ray diffraction on a single crystal affords a layered structure, where closely packed hexagonal layers of C_{60} alternate with the layers of Bz_4BTPE. The Bz_4BTPE molecules form infinite one-dimensional chains within the layers with weak overlapping between the molecules.

Photoexcitation of **1** by white light results in a 10^2 increase of photocurrent. It was found that weak magnetic field ($B_0 < 1$ T) enhances photoconductivity in **1** (up to 5%). Dissociation of excitons from a triplet state occurs more effectively, than that from a singlet one. MF can populate a triplet state by changing spin state of an electron and a hole in the exciton thus increasing the probability of electron–hole pair dissociation into free charge carriers. The primary step of PICT was deduced to be photoexcitation of Bz_4BTPE with a possible contribution of intermolecular CT excitation between the C_{60} molecules. It is interesting to note that in previously studied C_{60} complexes with amines the probable mechanism of PICT at the excitation by white light (400–900 nm) was direct electron transfer from amine to C_{60}. Amines have no absorption in the visible range and only charge transfer bands are observed in the range of energies, where light-induced EPR signals are generated [20]. An important factor for the realization of photoconductivity in the resulting complex is a closely packed layered structure. The electron has the possibility to move through the C_{60} layers, whereas the holes can move through the Bz_4BTPE chains. Previously studied $TBPDA(C_{60})_2$ complex showing a 10^3 increase of photocurrent under illumination by white light also has a closely packed layered structure [12].

Acknowledgements

The work was partly supported by a Grant-in-Aid Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (152005019, 21st Century COE, and Elements Science 12CE2005) and the RFBR grants N 03-03-32699a, and 02-02-17571).

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