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Electron Absorption Spectroscopy Study of the Iodine Intercalated Charge Transfer Complexes of C_{60} with Organic Donors

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Electronic absorption spectroscopy was applied to study the electron processes in the iodine doped charge transfer (CT) complexes of C_{60} with two different organic donors, *i.e.*, tetramethylenedithiodimethyl-tetrathiafulvalene (TMDTDM-TTF) and 2,2′,6,6′-tetraphenyldipyranilydene (TPDP). Evolution of the electronic absorption spectra for the progressively iodine intercalated complexes has been investigated and discussed. It was shown that the iodine can intercalate the crystalline CT complexes of the fullerene under mild conditions as opposed to intercalation of the solid fullerite. The role of the charge transfer processes between the donor and C_{60}, as well as between iodine and the organic donor, is discussed. Extensive doping with iodine of a C_{60} complex leads to the increase of separation of the fullerene molecules.

Key words: fullerene, C_{60}, charge transfer, complex intercalation, electronic absorption spectroscopy

Solid C_{60} is a redox-active array of relatively weak intermolecular forces, and thus it can be a potential host for reductive intercalation chemistry [1]. Most commonly, doping of fullerene solids (or intercalation) is performed with exohedral donors. A dopant, *e.g.*, an alkali or alkaline earth metal atom, occupies interstitial positions between adjacent C_{60} molecules. Doping of fullerene with acceptors is more difficult than that with donors because of high electron affinity of C_{60} [2]. Interaction of fullerenes with halogens was extensively studied [3–9]. While bromine, which can be intercalated oxidatively into graphite, adds across the double bonds of C_{60} to form a variety of adducts with the C–Br σ bonds [9], iodine has been for a long time considered to be unable to add to the fullerene molecule, due to high ionization potential of C_{60} [10]. It has been shown, however, that special doping conditions and large excess of iodine afford a compound of the $C_{60}\,I_2$ stoichiometry [11]. Although compounds with I_2 [3,8,11], Cl_2 [12], and Br_2 [13] have been obtained, no electron transfer between C_{60} and the intercalate has been reported. An important role, played by the intercalate shape, has been found. The dumbbell-shaped I_2 molecules are accomodated in the primitive hexagonal C_{60} lattice of the $C_{60}\,I_4$ structure in full agreement with the respective van der Waals distances, and also retain many of the features of the I_2 elemental structure [3].

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We have developed a new doping strategy, and in the present article describe the possibility of acceptor intercalation of some C_{60} charge transfer complexes. Electronic spectroscopy has been chosen for investigations of the electronic states of these complexes.

Remarks on the C_{60} Complexes

The pronounced electron affinity of C_{60} [2,15] affords possibilities for its reactions with electron-rich organic molecules. Charge transfer (CT) complexes of C_{60} with some electron donors have been reported so far [14–22]. Fully ionic CT complexes of C_{60} have been prepared with very strong electron donors, such as Cr(TPP) [14] and tetrakisethylenediamine TEDA [16]. Most frequently, insulating neutral CT complexes have been synthesized [17,18,22,23]. It seems that there are two ways to increase the ionic nature of the fullerene complexes: (i) to use the strongest electron donors of formal redox potential smaller than 0 eV, or (ii) to dope the van der Waals complexes of the fullerene with strong oxidative or reductive intercalates. The latter, being strongly active agents, could modify the electronic structure of the complexes. The main problem, that can be faced on this way, is the kind of interactions between the host lattice and the dopant. Simply speaking, the question is: will C_{60} be involved in the interaction in the case of oxidative intercalation, or will the donor be involved in the case of reductive intercalation? In other words: is the complex, formed between a dopant and the molecular complex (donor-C_{60}) as a whole, or is it formed between the dopant and unbonded donor and fullerene, separately. In the CT complexes the main role is played commonly by van der Waals interactions between π-electron system of the fullerene and π-electrons of the aromatic addends or n-electrons of the donor heteroatoms. Therefore, some kind of a common electronic system arises in the complexes. Its formation is due to the overlap of the electronic clouds of both constituing parts of the complex, probably because of tight contacts formed between some atoms, belonging to both parts, that are shorter than the sum of van der Waals radii. Thus, intercalation of the complex with oxidative dopant, acting as the oxidative donor, leads to modification of the electronic structure of C_{60}. This effect is a consequence of the correlation between electronic systems of both the donor and C_{60}. In order to study this effect, some C_{60} complexes of a small charge transfer were intercalated with iodine.

Two complexes of C_{60} with 2,2′,6,6′-tetraphenyldipyranilydene (TPDT) and tetramethylenedithiodimethyl-tetrathiafulvalene (TMDTDM-TTF) have been chosen for investigations. Their synthesis and structural details were described elsewhere [20,21,24]. Both donors can form cation-radicals with suitable acceptor molecules. In view of the pronounced fullerene electron affinity [2,5], the charge transfer is very likely in these complexes. In fact, a weak but very broad band at about 810 nm has been observed for $TPDP\cdot(C_{60})_2\cdot 4CS_2$ and at about 900 nm for $(TMDTDM\text{-}TTF)_2\cdot C_{60}\cdot 3CS_2$.

In both solid C_{60} complexes, the solvent, CS_2, used for preparation of the complexes, is built in their crystal structure, being coordinated to C_{60} molecules. Besides, formal redox potentials of both chosen donors are relatively low and can be oxidized by iodine, thus yielding cation radicals [25]. The above mentioned features of the complexes of C_{60} with TPDP or TMDTDM-TTF resolved on the choice of the compounds for iodine intercalation. Iodine was chosen not only because of its chemical properties but also because of the dumbbell or linear shape of its ions. Moreover, close values of the van der Waals radii of iodine (1.98 Å) and component atoms of CS_2 (C, 1.70 Å; S, 1.80 Å) are also very important. Geometrical similarity between I_2 or I_3 and CS_2 could promote replacement of the occluded solvent molecules by iodine. The ability of iodine to oxidize the donor can result in the expected replacements. Also, the iodine is suitable for the complex intercalation because of its low ability to form covalent bonds with C_{60} [3,10 and 11].

Iodine intercalation of the chosen C_{60} complexes has been studied by electronic absorption spectroscopy. Recently, iodine doping of the $TPDP{\cdot}(C_{60})_2{\cdot}4CS_2$ complex was investigated by photoelectron spectroscopy [9]. It has been shown that the doping leads to significant changes of the electronic structure of the complex. The electronic absorption spectroscopy is a very adequate technique for the study of electron distribution, because electronic excitation bands of the C_{60} molecule are typical and well resolved in the spectra of the C_{60} complexes. Besides, the absorption bands of the donors are not observed in the spectral range of 240 to 400 nm. Thus, electronic absorption spectra can be useful for investigation of the electron states of the fullerene and their changes during intercalation of the C_{60} complexes. Also, it is possible to find whether the C_{60} molecules interact with iodine during the doping or not. We would like to emphasize that iodine interacts very weakly with C_{60}; very small charge transfer has been found in the compound of $C_{60}\,I_x$ stoichiometry, where $0.2 < x < 1.5$ [1]. Weak interaction between the C_{60} and iodine molecules corroborate with the analysis of the temperature of the iodine release from the complex, which is close to the temperature of the iodine sublimation.

EXPERIMENTAL

Doping of the complexes has been performed at room temperature, under normal pressure, in the iodine vapour for 3, 6, 9 or 12 days. The data of elemental analysis are following: $TPDP{\cdot}(C_{60})_2{\cdot}4CS_2$ complex after 6-day doping has a composition: $TPDP{\cdot}(C_{60})_2{\cdot}\ 2CS_2{\cdot}I_5$ (% I = 33.0) and 12-day doping – $TPDP{\cdot}(C_{60})_2CS_2{\cdot}I_{10}$ (% I = 39.9; % S = trace). *Atomic ratio* $[C/I]^{XP}$ calculated from *integral intensities* of C1s and $I3d_{5/2}$ correlate with the elemental analysis data. The number of iodine atoms on one molecule of the complex is: 6-day doped: 5.0; 12-day doped: 10.5. Elemental analysis of $(TMDTDM\text{-}TTF)_2C_{60}{\cdot}3CS_2$ complex after 3-day doping shows its composition: $(TMDTDM\text{-}TTF)_2\,C_{60}{\cdot}7.5I$ (% I = 39.1). The absence of CS_2 solvent was confirmed by IR spectroscopy.

Details concerning X-ray photoelectron spectroscopy measurements have been given elsewhere [9,26]. Results of the photoelectron spectroscopy of iodine doping of the $TPDP(C_{60})_2{\cdot}4CS_2$ complex have been presented by Konarev *et al.* [9]. On the contrary $(TMDTDM\text{-}TTF)_2{\cdot}C_{60}{\cdot}3CS_2$ complex was not investigated by this method so far.

Electronic absorption spectra of the fullerene, C_{60}, its complexes with two different donors, and the iodine doped complexes have been recorded with the Lambda 19 Perkin Elmer UV VIS NIS spectrometer. All the spectra have been recorded on KBr pellets containing dispersed samples of typical complex concentration of 1:2000, at room temperature, in the spectral range of 240 nm to 1200 nm.

RESULTS

Figure 1 presents electronic absorption spectra of the (TMDTDM-TTF)$_2$·C$_{60}$·3CS$_2$ complex and the pristine fullerene, C$_{60}$. Electronic spectrum of C$_{60}$ consists of strong absorption bands at 262 and 343 nm, corresponding to electric dipole-allowed transitions between occupied (bonding) and unoccupied (antybonding) molecular orbitals (either the $h_u \rightarrow t_{1g}$ transition or the $h_g \rightarrow t_{1u}$ transition) [25]. Also, a weak absorption band is seen in the 400 to 630 nm region. It is identified with the forbidden electronic transition between h_u HOMO level of the H_u symmetry and the one-electron t_{1u} LUMO level of the T_{1u} symmetry [25]. In the spectrum of the complex, the main absorption bands at 262 and 343 nm are broaden, but their maximum wavelengths are nearly the same as these for C$_{60}$. The broadening of the electronic bands in the spectra of complexes is donor dependent. In general, it depends on the donor-acceptor interaction. In the spectrum of the complex, the large band between 400 and 630 nm is screened by strong electronic absorption above 300 nm. A weak, but very broad band at about 900 nm has been observed in the spectrum of the complex of C$_{60}$ with TMDTDM-TTF. The appearance of this band is most clearly seen at the second derivative of the absorption (not shown). This band can be attributed to a charge transfer. According to Saito *et al.* [27], the CT band appears between 800 and 1000 nm in the spectra of the complexes of C$_{60}$ with various electron donors. Location of this band depends on the redox potential of the donor. A weak band at about 621 nm, typical for the pristine C$_{60}$, is shifted down to 613 nm and strongly masked in the spectrum of the complex.

Figure 2 affords opportunity of comparison of the electronic spectra of the native (TMDTDM-TTF)$_2$·C$_{60}$·3CS$_2$ complex and the same complex after 3-days of doping by the iodine vapour. Both strong electronic absorption bands are shifted to longer

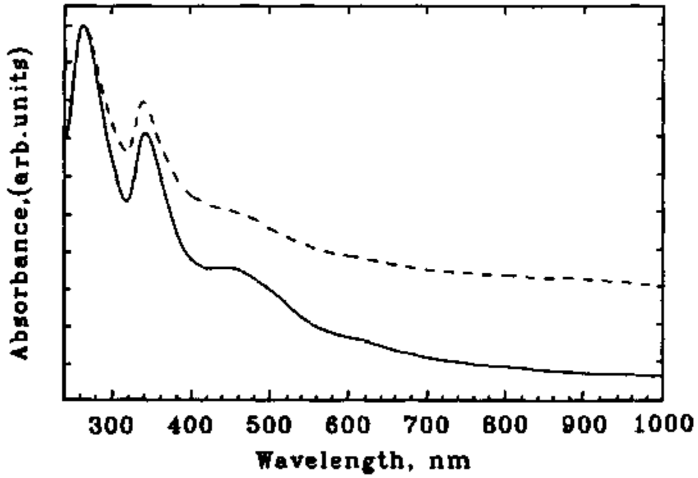

Figure 1. Electronic absorption spectra of C$_{60}$ (—) and (TMDTDM-TTF)$_2$·C$_{60}$·3CS$_2$ (- - -) for KBr pellets.

wavelengths. That is, the band at 262 nm is shifted largely, *i.e.*, by 9 nm and the band at 343 nm shows a smaller shift of about 2 nm. Both bands are significantly broadened. These spectral changes suggest substantial reorganization of the electronic structure of the fullerene as a result of doping. Additionally, strong absorption band appears at 435 nm. A similar, but weaker band is observed at about 455 nm in the spectrum of pristine C_{60}. Thus, intercalation of the complex by iodine causes not only a significant increase of the intermolecular interactions in the complex, manifested by broadening of the absorption bands, but also leads to the changes of the electronic structure of the C_{60} molecule, manifested by the bands shifts. The significant shift of the forbidden electron transition at 455 nm, for pristine C_{60} accompanied by a distinct increase of the intensity of appropriate band suggests activation of the $h_u \rightarrow t_{1u}$ transition, previously forbidden. It follows from the latter that the symmetry of the C_{60} molecule is reduced.

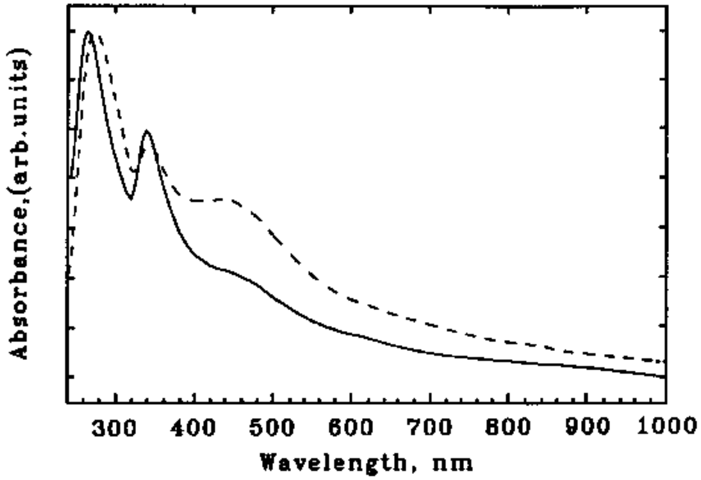

Figure 2. Electronic absorption spectrum of $(TMDTDM\text{-}TTF)_2{\cdot}C_{60}{\cdot}3CS_2$ after 3-day intercalation in the iodine vapour (- - -); for comparison the spectrum of native complex is shown (—). All spectra are recorded at room temperature, for KBr pellets.

Evolution of the C_{60} electronic absorption spectrum after formation of the complex with TPDP donor and during doping the complex with iodine is shown in Figure 3. The intercalation is shown for longer doping periods *i.e.*, up to 12 days. In general, the spectrum of $TPDP{\cdot}(C_{60})_2{\cdot}4CS_2$ is similar to that discussed above. Noticeably, some broadening appears of the allowed C_{60} bands, in particular the band at 343 nm. A pronounced band at 452 nm results from superposition of the C_{60} band at about 455 nm and the donor band centered at 453 nm. The band at 620 nm is slightly down shifted. At about 810 nm, a CT band is observed. During the intercalation of the complex with iodine the absorption band of the donor is vanishing as a result of its oxidation. Simultaneously, a new band, centered at 735 nm, appears. This feature can be attributed to a charge transfer between the TPDP donor and the iodine acceptor.

The main bands of the fullerene are virtually insensitive to doping. This suggests that the fullerene coordination is not changed during doping. In the spectrum of the 9-day doped sample, some narrowing of the electronic bands of the C_{60} is observed, mainly of the 262 nm band. It corroborates the conclusion presented above and indicates that the distance between the C_{60} molecules is increased when large amount of iodine is inserted into the complex.

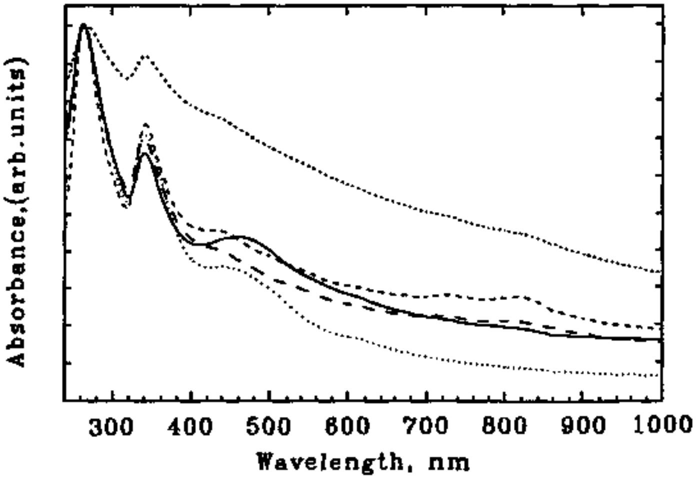

Figure 3. Electronic absorption spectra of native (—) and iodine intercalated $TPDP{\cdot}(C_{60})_2{\cdot}4CS_2$ after 6-day (---), 9-day (– – –), and 12-day (----) doping; for comparison the spectrum of pristine C_{60} is shown (.....). All spectra are recorded at room temperature, for KBr pellets.

Subsequent iodine intercalation of the complex of C_{60} with TPDP leads to the increase of the electronic absorption in the whole investigated spectral range and the bands discussed above are masked. In accord with both the photoelectron spectroscopy and elemental analysis, strong intercalation of the complex of C_{60} with TPDP leads to formation of the compound $TPDP{\cdot}(C_{60})_2{\cdot}I_{10}$, where iodine is present as I_5^-.

CONCLUSIONS

Best to our knowledge, electronic absorption spectroscopy has been used for the first time in the present paper for investigation of the doping process of the complexes of C_{60} with organic donors. Two complexes, *i.e.*, $(TMDTDM\text{-}TTF)_2{\cdot}C_{60}{\cdot}3CS_2$ and $TPDP{\cdot}(C_{60})_2{\cdot}4CS_2$, have been selected. On one hand both TMDTDM-TTF and TPDP donors form CT complexes with fullerene [21,22] and on the other, they can be easily oxidized by iodine. Note, we investigated the intercalation in the samples where some charge transfer occurs. We have shown, that doping of the C_{60} complexes leads not only to the subsequent oxidation of the donors but also to the pronounced changes of the electronic structure of the C_{60} molecule itself. Distinct shifts of the electric dipole-allowed bands at 262 and 343 nm accompanying intercalation have been observed. These large shifts, observed mainly for the complex of C_{60} with TMDTDM-TTF, are caused by modification of the C_{60} electron levels in the electric field produced by the TMDTDM-TTF cation-radical, formed as a result of the doping. Such large shifts are commonly observed in electronic absorption spectra of ionic crystals. The broadening of these electronic bands of the fullerene in CT complexes is governed mainly by the intermolecular interactions of the donor-acceptor type. Some role of the structural disorder also plays a role. Two configurations of the fullerene molecules are possible, *i.e.*, 6–5 and 6–6. However, energies of these configurations are nearly the same. Thus, the disorder mentioned above could smear the electronic energy levels, and cause broadening of the absorption bands. The extensive doping leads to replacement of the solvent molecules in the crystal lattice by the iodine ions and to appreciable oxidation of the donor. As a result, strong CT interaction occurs between the organic donor and the intercalating agent; the fullerene molecules seem to be more isolated and ordered. The increase of ordering and isolation of the C_{60} is manifested by narrowing of electronic absorption bands.

Thus, we have shown that the electronic absorption spectroscopy provides new information about intercalation with iodine of the complexes of C_{60} with organic donors. This method appeared to be particularly suitable for study of the electronic structure evolution which accompany the CT complex formation. Nevertheless, some issues remain still not clear, for instance: why intensity of the CT band in the structure of the C_{60} complexes is so weak or what is the origin of the strong, continuous absorption observed up to 1000 nm.

In conclusion, the problem of the acceptor intercalation of the C_{60} derivatives is very interesting and promising. It seems that the acceptor intercalation of the CT complexes of the fullerene is as interesting as the donor intercalation of the fullerite. The acceptor intercalation of the C_{60} and its derivatives shows basic as well as applicational aspects. On the one hand it should give information on main intermolecular interactions, structural disorder and changes in the electron-molecular vibration couplings in the iodine intercalated CT complexes of C_{60}, on the other hand it is a method of iodine intercalation of the fullerene derivatives as opposed to intercalation of the solid fullerite.

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