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Optical spectroscopy of C_{60} complexes.

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Abstract

Complexes of fullerene C_{60} with different organic donors have been studied by optical absorption spectroscopy in solutions and in solid state. Charge transfer bands were found for C_{60} complexes with tetrathiafulvalenes, pyranylidene and xantenyl in the 600-1300 nm range. It is shown that the energies corresponding to the maxima of charge transfer bands ($h\nu_{CT}$) for C_{60} complexes in solution are almost independent of solvent polarity. The $h\nu_{CT}$ values for the complexes in solid state are ~0.15-0.20 eV less than in solution. The dependence of the $h\nu_{CT}$ values on donor ionization potentials (I_P) for C_{60} complexes with tetrathiafulvalenes in solid state was found to be $h\nu_{CT} = 0.82\ I_P - 3.93$ eV. The lowering of the intensity was observed for the C_{60} transitions at 420-540 nm in absorptoin spectra of single crystals of some C_{60} complexes obviously due to isolation of C_{60} molecules.

Keywords: single crystal growth, UV-VIS-NIR spectroscopy, fullerenes, charge transfer complexes.

Introduction.

Fullerenes as acceptors [1] form various donor-acceptor complexes some of which exhibit ferromagnetic and superconducting properties [2,3]. By now a great number of complexes with fullerenes has been prepared [4-10]. Complex formation of fullerenes with various donors in solution is also intensively studied [11,12]. Due to weak acceptor properties of fullerenes most compounds of this type have only weak charge transfer. But their optical absorption spectra show the presense of charge transfer bands, therefore they may be considered as charge transfer complexes (CTC).

The dependence of $h\nu_{CT}$ energies on IP of donors is usually close to a linear one for π-complexes formed by the same acceptor with a series of donors. Such dependences are known for many organic planar π-acceptors [13]. For C_{60} complexes such investigations are carried out for substituted anilines [11] and substituted naphthalenes [12] in toluene. According to these data [11,12] an almost linear dependence of $h\nu_{CT}$ on donor I_Ps is observed in 7.2-8.2 eV IP range.

For some C_{60} complexes in solid state the $h\nu_{CT}$ energies are determined by optical spectroscopy [4-9] and the dependence of $h\nu_{CT}$ values on redox potentials of donors is considered [5].

Now the processes of charge transfer in C_{60}-polymer composites [14] and fullerene complexes with organic donors [5, 15, 16] are intensely studied, therefore the derivation of general dependencies of the changes of the $h\nu_{CT}$ energy in fullerene complexes is very important.

This paper reports the studies of C_{60} complexes with a wide range of donors in solution and in solid state by optical spectroscopy. The changes in intensity of the absorption in 420-540 nm range associated with forbidden transitions of C_{60} in the complexes are discussed. The $h\nu_{CT}$ values for C_{60} complexes in solution and in solid state are obtained. The dependencies of $h\nu_{CT}$ on I_P of donors are derived. The influence of solvent polarity and the transition from solution to solid state upon the $h\nu_{CT}$ values is studied for C_{60} complexes.

Experimental

Complexes of C_{60} were obtained by evaporation of fullerenes and donors solutions in carbon disulfide, benzene or pyridine (Py) under argon. The composition of the complexes was determined by elemental, thermogravimetric and X-ray analyses [6-10]. The complexes under study are presented in Table 1.

The analysis of IR- [15] and ESR spectra of the compounds under discussion shows that all of them to be a neutral complexes.

Absorption spectra were registered with "Perkin Elmer Lambda 19 UV-VIS-NIR" spectrophotometer in 220-2000 nm range.

The samples in solid state were prepared in KBr pellets at the 1:2000 ratio. To determine more precisely the maxima of the bands we discriminated charge transfer bands (CTBs) by a subtraction of a normalized spectrum of the individual fullerene from that of the complex

The solutions of C_{60} with 0.5 mg/mL concentration were put in a 0.5 cm thick hermetic quatrz cell. CTBs were discriminated by a subtraction of the spectra of the starting fullerene solution from that of the same solution containing the donor with ~6-8 mg/mL concentration.

It should be noted that the absorption bands of fullerene and the donors are absent in 680-1300 nm range.

The reflection spectra of C_{60} complexes single crystals were measured by a two-beam spectroreflectometer in 250-1100 nm range. Absorption spectra were obtained by the Kramers-Kronig transformation of the reflection spectra.

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Table 1. Ionization potentials (I_P) of the donors, I_P estimated in this work ($I_{P(est.)}$), the maxima of CTBs (λ_{CT}, nm) and $h\nu_{CT}$ energies of C_{60} complexes in solid state.

Donor	I_P eV	$I_{P(est..)}$ eV	Complex	N	λ_{CT}, nm	$h\nu_{CT}$, eV	References
TPDP	-	-	$D(C_{60})_2(CS_2)_4$	1	1240	0.98	8,15,16
OMTTF	6.3[17]		$D{\cdot}C_{60}{\cdot}C_6H_6$	2	1040	1.20	5
			$D{\cdot}C_{60}{\cdot}Py$	3	980	1.26	-
TMTTF	6.38[18]		-	-		-	-
DMDPh-TTF	-	6.4	$(D)_2{\cdot}C_{60}{\cdot}C_6H_6$	4	940	1.32	15
EDY-BEDT-DT	-	6.4	$D{\cdot}C_{60}{\cdot}C_6H_6$	5	935	1.32	15, 16
EDT-TTF	-	6.5	$(D)_2C_{60}{\cdot}CS_2$	6	900	1.35	7,15
			$D{\cdot}C_{60}{\cdot}C_6H_6$	7	920	1.38	7,15
BEDO-TTF	6.46[19]		$D{\cdot}C_{60}{\cdot}C_6H_6$	8	900	1.38	5
DPhTTF	-	6.5	$D{\cdot}C_{60}{\cdot}C_6H_6$	9	895	1.38	15
TMDTDM-TTF	-	6.5	$(D)_2C_{60}(CS_2)_3$	10	900	1.39	7, 15, 16
BEDT-TTF	6.70[19]		$(D)_2C_{60}(Py)_2$	11	820	1.51	-
DBTTF	6.81[20]		$D{\cdot}C_{60}{\cdot}C_6H_6$	12	735	1.69	6, 15
			$D{\cdot}C_{60}{\cdot}Py$	13	750	1.64	6
BTX	-	-	$D{\cdot}C_{60}{\cdot}CS_2$	-	625	1.98	10, 16
TPC	-	-	$D{\cdot}C_{60}$	-	-	-	-

Abbreviations for the donors: TPDP-3,3′,5,5′-tetraphenyldipyranylidene; OMTTF-octamethylenetetrathiafulva-lene (TTF); TMTTF- tetramethyl-TTF; DMDPh-TTF-trans-4,4′-dimethyl-5,5′-diphenyl-TTF; EDY-BEDT-DT- 2,2′-ethanediilidene -bis(4,5-ethylene-1,3-dithiol); EDT-TTF - ethylenedithio-TTF; BEDO-TTF - bis(ethylenedioxo)-TTF; DPhTTF - trans-4,4′-diphenyl -TTF; TMDTDM-TTF - tetramethylenedithio-4,5-dimethyl-TTF; BEDT-TTF - bis(ethylenedithio)-TTF; DBTTF - dibenzo-TTF; BTX - 9,9′-trans-bis(telluraxantenyl); TPC - triptycene.

Results and Discussion.

The absorption spectra of C_{60} complexes with DBTTF, TPC and BTX were studied for single crystals.

As these complexes are typical molecular crystals, their absorption spectra show a good correlation with the spectra of pure C_{60} and the donors. The absorption spectra presented in Figs.1 and 2 exhibit two strong bands at 267 nm and 345 nm which can be attributed to dipole-allowed transitions of C_{60} and are not influenced by the interaction in the complexes.

The main changes relatively to the spectrum of C_{60} are observed in the spectra of the complexes in 420-540 nm range. The donors have no noticeable absorption in this range. CTBs are also absent for this polarization for $DBTTF{\cdot}C_{60}{\cdot}C_6H_6$ (Fig.1, curve 2) and $BTX{\cdot}C_{60}{\cdot}CS_2$ (Fig.2. curve R_1). We can see that in C_{60} complexes with TPC, DBTTF (Fig.1) and BTX (Fig.2, R_1) the absorption in 420-540 nm range is considerably less intensive than in the spectrum of pure C_{60} single crystals.

The origin of the absorption in C_{60} spectrum at 420-540 nm is still under discussion. This absorption can be attributed to the h_u—t_{1g} dipole-allowed transitions [21] as well as to the h_u—t_{1u} forbidden transitions [22].

We assume that this absorption in the C_{60} spectrum of single crystals can be basically attributed to forbidden transition. Their intensity is quite high due to breaking of fullerene symmetry because of interaction between neighboring C_{60} molecules. Since in the crystals of the complexes C_{60} molecules are separated by donor ones the distances between C_{60} molecules are greater. Thus the interaction of C_{60} molecules with neighboring C_{60} molecules is considerably weaker in these complexes than in pure C_{60} crystals.

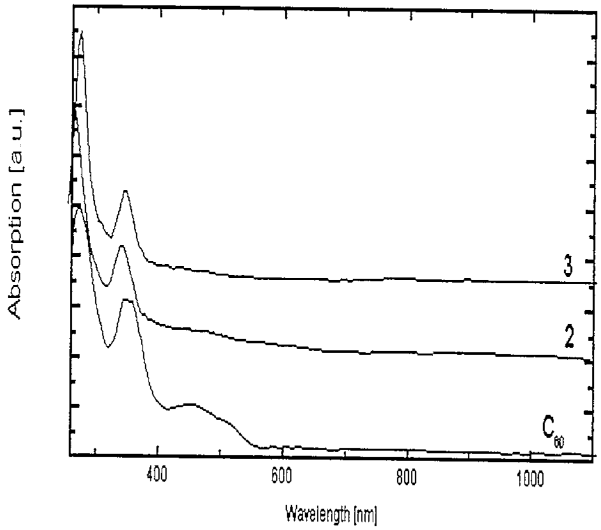

Fig.1. Absorption spectra of C_{60}, $DBTTF{\cdot}C_{60}{\cdot}C_6H_6$ (2) and $TPC{\cdot}C_{60}$ (3) single crystals.

The complexes under study actually have the isolated packing of C_{60} molecules with the shortest distances between them close to or greater than C_{60} Van der Waals radius (10.18Å): 10.17Å for $TPC{\cdot}C_{60}$ [24], 10.40 Å for $DBTTF{\cdot}C_{60}C_6H_6$ [6] and 10.31Å $BTX{\cdot}C_{60}{\cdot}CS_2$ [23].

To find the CT band the spectra for three polarizations of well-shaped $BTX{\cdot}C_{60}{\cdot}CS_2$ single crystals were studied. Absorption spectra polarized along the crystal R_2 (*E//a*), R_1 (*E//b*) and R_3 (*E//c*) axes are shown in Fig.2.

The weak bands of BTX at 290 nm were observed for R_2 and R_3 polarizations together with high-intensity fullerene bands. A new band at 625 nm (1.98 eV) appears in the absorption spectrum with R_3 (*E//c*) polarization.

Since neither C_{60} bands nor BTX ones are observed in this range and due to high anisotropy of this band, it is suggested that it is to be attributed to band of charge transfer from BTX to fullerene. The fact that the maximum of intensity appears in polarization parallel to the c-axis of the crystal is in agreement with the structural data which indicate that the shortened C_{60} - donor contacts are arranged in the direction of *c*-axis of the crystal [23].

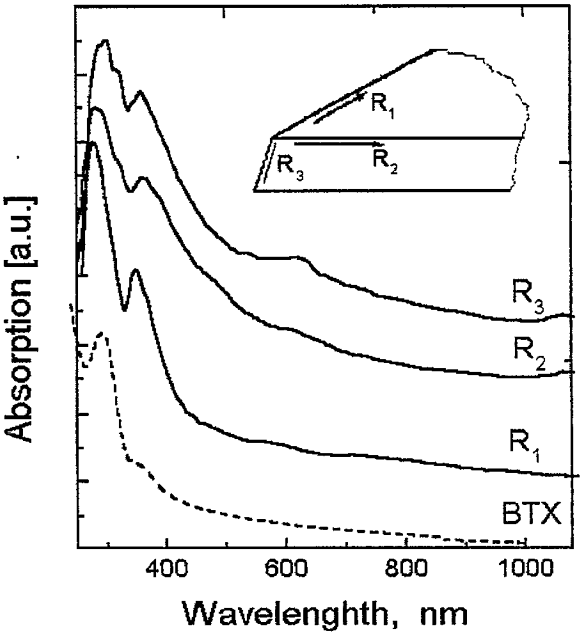

Fig.2. Polarized absorption spectra of BTX·C_{60}·CS_2 single crystals measured along the crystal R_2 (*E//a)*, R_1 (*E//b*) and R_3 *(E//c)* axes.

Absorption spectra of C_{60} complexes with DBTTF, BEDT-TTF, TMTTF, and OMTTF with known IPs were studied in toluene and benzonitrile. Low solubility of BEDT-TTF in toluene and benzonitrile did not allow us to determine the position of CTBs in the BEDT-TTF complexes with C_{60}. New bands are observed after adding donors to fullerene solutions. These bands are absent in the spectra of the donors and the starting C_{60} solution. Since the positions of the maxima of new absorption bands depend on IPs of donors and their intensity proportionally depends on donor concentration, the appearance of new bands seems to be associated with the formation of CTCs.

Table 2. $h\nu_{CT}$ energies in solutions of C_{60} complexes.

Donor	I_P, eV	$h\nu_{CT}$, eV	
		Toluene	Benzonitrile
OMTTF	6.3	1.44	1.43
TMTTF	6.38	1.48	1.47
DBTTF	6.81	1.85	1.85

The energies of charge transfer corresponding to the maximum CTB ($h\nu_{CT}$) in C_{60} complexes in toluene and benzonitrile solutions are presented in Table 2. Figure 3 (14-15) shows the dependence of $h\nu_{CT}$ on I_P of the donors in C_{60} complexes in toluene. A good correlation between I_P of the donors and the $h\nu_{CT}$ energies in solutions can be seen.

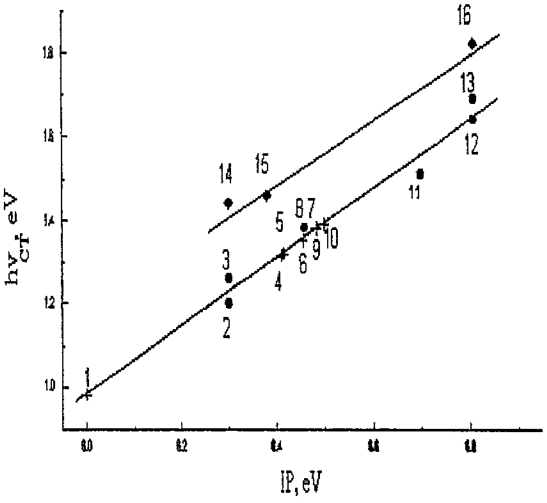

Fig. 3. The dependence of the $h\nu_{CT}$ energies on vertical IP of the donors in the C_{60} complexes .
Points are numbered according to Table 1.
(•) - C_{60} complexes of donors with known IPs in solid state.
(+) - C_{60} complexes of donors with estimated IPs in solid state. Points are put in the obtained line in accordance with the $h\nu_{CT}$ values.
(♦) C_{60} complexes of OMTTF (14), TMTTF (15), DBTTF (16) in toluene.

The dependence of $h\nu_{CT}$ on I_P for C_{60} complexes with tetrathiafulvalenes is close to those obtained earlier for C_{60} complexes with substituted anilines and naphthalenes [11, 12]. Using these data one can derive the general dependence of $h\nu_{CT}$ on I_P of donors within the 6.3-8.2 eV range. This dependence is linear and is well described by the expression: $h\nu_{CT} = 0.90\ I_P - 4.28$ eV.

It was shown [13] that a polar solvent can stabilize the excited ionic state of π-complexes that results in the decrease of $h\nu_{CT}$ at transition from nonpolar solvent to a polar one. To estimate the influence of solvent polarity on the $h\nu_{CT}$ energy we measured similar absorption spectra for C_{60} complexes in more polar benzonitrile. The $h\nu_{CT}$ values are presented in Table 2. It is seen that the $h\nu_{CT}$ energy remains unchanged at transition from toluene to benzonitrile. Thus the $h\nu_{CT}$ energy is almost independent of solvent polarity in fullerene complexes in contrast to other π-acceptors.

Absorption spectra of C_{60} complexes in solid state were studied. The CTBs discriminated from the spectra of a number of C_{60} complexes are shown in Fig.4. It is seen that these bands are wide, asymmetric, they are absent in the spectra of starting donors and fullerenes and therefore can be attributed to CTBs.

The $h\nu_{CT}$ energies for C_{60} complexes are presented in Table 1. The dependence of $h\nu_{CT}$ on I_P of donor (Fig.3, (•)) was built for C_{60} complexes with OMTTF, BEDT-TTF, BEDO-TTF and DBTTF (with known I_P values). This dependence can be described by the equation $h\nu_{CT} = 0.82\ I_P - 3.93$ eV.

A linear behaviour of the dependence enables the estimation of I_Ps of other tetrathiafulvalenes by using the values of the energy of charge transfer in C_{60} complexes. The C_{60} complexes with donors whose I_Ps are unknown are arranged in the dependence in accordance with the values of the energy of charge transfer (Fig.3 (×)). Vertical I_{PS} of these donors estimated from this dependence are given in Table 1 but the accuracy of this method is rather low.

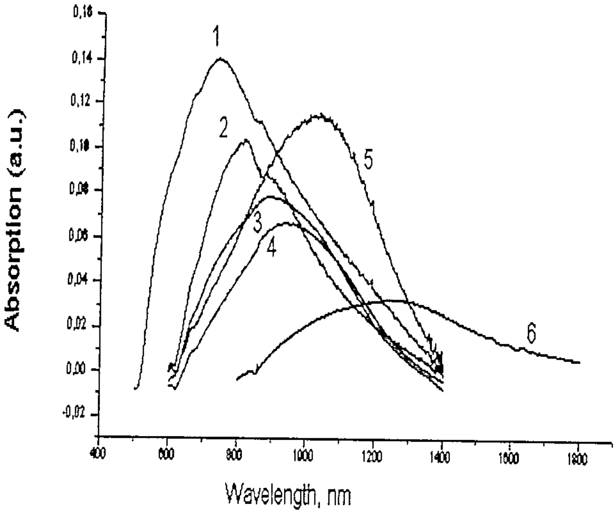

Fig.4. CTBs discriminated in absorption spectra of C_{60} complexes in solid state in the 400-1600 nm range:

1- DBTTF·C_{60}·C_6H_6
2- (BEDT-TTF)$_2$ C_{60}(Py)$_2$
3- EDY-BEDT-DT·C_{60}·C_6H_6
4- EDT-TTF·C_{60}·C_6H_6
5- OMTTF·C_{60}·C_6H_6
6- TPDP (C_{60})$_2$(CS$_2$)$_4$

The decrease of $h\nu_{CT}$ energies by ~0.15-0.20 eV was observed for C_{60} complexes with tetrathiafulvalenes at transition from a solution to solid state. The similar decrease of the $h\nu_{CT}$ energies (~0.2 eV) was observed earlier for TCNE complexes [25]. The decrease of the $h\nu_{CT}$ energy is suggested to result in the increase of ionicity of fullerene complexes at transition from a solution to solid state.

Conclusion

The complexes of fullerene C_{60} with different organic donors whose ionization potentials vary in 6.3-6.8 eV range were studied in solutions and in solid state by optical absorption spectroscopy. The lowering of absorption intensity at 420-540 nm range was observed in some molecular complexes obviously due to low intensity of forbidden transition of fullerene. We suggest that the interaction of C_{60} with its surroundings is considerably weaker in these complexes than in pure C_{60} crystal because fullerene molecules are isolated from the neighbouring C_{60} by donor molecules. Charge transfer bands are discriminated in the spectra of C_{60} complexes in the 680-1300 nm range. It is shown that the dependence of the $h\nu_{CT}$ energy on IPs of donors in C_{60} complexes with tetrathiafulvalenes is close to the similar dependence in C_{60} complexes with substituted anilines and naphthalenes. These dependencies are well approximated by the expression: $h\nu_{CT} = 0.90\ I_P - 4.28$ eV. The $h\nu_{CT}$ energies in C_{60} complexes are almost independent of solvent polarity. It is shown that for C_{60} complexes in solid state $h\nu_{CT}$ is ~0.15-0.20 eV lower than $h\nu_{CT}$ values in solution.

The dependence of the $h\nu_{CT}$ energy on I_P of tetrathiafulvalenes is derived to be $h\nu_{CT} = 0.82\ I_P - 3.93$ eV for C_{60} complexes in solid state. A linear behaviour of this dependence allows the estimation of I_P of other tetrathiafulvalenes.

Acknowledgements

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