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Iodine doping of C_{60} charge transfer complexes

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Abstract.

Iodine doping of C_{60} complexes with organic donors were carried out. The solvent was gradually substituted by the iodine with the formation of $TPDP(C_{60})_2I_{10}$, $(TMDTDM\text{-}TTF)_2C_{60}I_{7.5}$, and $DBTTFC_{60}I_9$ compounds. The doping results in strong changes in the donor electron state but only indirectly affects the C_{60} electron system.

Keywords: Fullerene, Doping, Charge transfer complexes, Iodine.

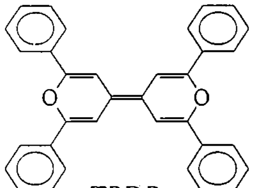
1. Introduction

Geometric sizes together with steric properties of organic donors enable the design of compounds with various C_{60} packing in a crystal [1-4]. However most organic donors form with C_{60} weak charge transfer complexes (CTC) since fullerene is a weak acceptor [5]. C_{60} molecule may be reduced with the formation of a radical anion only by donors with the potential E_{ox1} more than -0.45 eV[5].The electron state of weak CTC may be changed by doping them by strong reductants analogously to the doping of a neat C_{60}. The doping of $OMTTFC_{60}C_6H_6$ complex by alkali metals leads to a superconductivity in this compound [6].

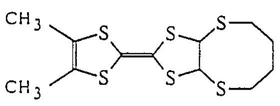
This paper reports the doping of next complexes: $TPDP(C_{60})_2(CS)_4$ (1), TPDP - tetraphenyldipyranylidene [2], $(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ (2), TMDTDM-TTF - tetramethylenedithiodimethyltetrathiafulvalene [3], and $DBTTFC_{60}C_6H_6$ (3), DBTTF - dibenzotetrathiafulvalene [4] by iodine and the study of the electron state of these CTC after doping.

2. Experimental

The presence of solvent molecules in the complex composition is the important condition for doping. The thermogravimetric analysis showed that the heating of 1-3 results in the removal of a solvent. The compound (1) completely losses CS_2 at 125-200°C [1], (2) within 80-200°C [3] and (3) losses benzene in 160-200°C [4] temperature range.



TPDP



TMDTDM-TTF

$(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ has a layered structure [3], C_{60} layers alternating with the layers of the TMDTDM-TTF donor molecules packed head-to-tail in dimers. Two CS_2 molecules are located in the donor and one in the fullerene layer.The crystal structures of 1 and 3 are now under study.

We used solvent containing samples for its gradual substitution in the doping. The samples 1-3 were exposed in a saturated iodine vapour under the ambient pressure at room temperature. The compounds obtained are listed in Table 1.

3. Results and discussion

It is seen that the 6 days long doping results in the inclusion of five iodine atoms but the solvent is yet present (1a). After 12 days iodine completely substitutes the solvent (1b). The further doping for a month does not result in the increase of iodine content (1c). The preliminary evacuation 1 in heating (80-120°C, 1-2 Torr for 1) enables the total removal of the solvent. In this case the rate of doping increases and after 5 days the sample contains the maximal quantity of iodine (1T).

The process of doping is accompanied by a solid-phase oxidation of the donor component of the complex with the formation of radical cations and in some cases dications of the donor.

$$TPDP(C_{60})_2(CS_2)_4 + I_2 \Rightarrow TPDP^{+}(C_{60})_2(CS_2)_x(I_n^{-}) + I_2 \Rightarrow TPDP^{2+}(C_{60})_2(I_n^{-})_2$$

The changes in the donor component and the formation of a radical cation and dication states are well pronounced in IR and ESR spectra.

Both the location and the ratio of the intensities of the absorption bands attributed to C_{60} vibration modes (526, 576, 1182, and 1428 cm^{-1}) in doping samples remain practically unchanged as compared with the same absorption bands in the starting complex. The absorption bands of the solvent (1508 cm^{-1} for CS_2, 668 and 1480 cm^{-1} for C_6H_6) vanish at the maximal degree of doping (Table). The greatest changes in IR spectra of doping samples are observed for the absorption bands of the characteristic vibrations of the central ν(C=C) bond of the donors (Table 1). The shift of these bands is attributed to the formation of a radical cation or probably dication of the donor, for example for TPDP[7].

The EPR data for the complexes and corresponding donors doped by iodine are listed in Table. The differences of parameters (g-factor and the line width ΔH) in EPR spectra of donors and complexes were observed during doping process. It would be associated with different types of packing and the donor molecule location in the crystal of individual donor and in the complexes. The donor molecules are distorted in the complexes by the coordination with C_{60}. This may cause a break in a conjugation

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	Composition of the samples	doping time, days	% of iodine	IR - spectra absorbtion bands		EPR spectra			
				solvent	donor	complex		individual donor	
				cm^{-1}	cm^{-1}	g-factor	ΔH, G	g-factor	ΔH, G
1	TPDP$(C_{60})_2(CS_2)_4$	0	0	1508	1662	2.0033*	3.0	2.0033*	1.6
-	-	2	-	-	-	2.0032 2.0095	4.0 15.2	2.0036	4.5
1a	TPDP$(C_{60})_2(CS_2)_xI_5$	6	33.0	1508	1621	2.0032 2.0088	4.0 10.7	2.0039	4.0
1b	TPDP$(C_{60})_2I_{10}$	12	39.9	trace	1600	2.0039	4.0	2.0039	3.4
1c	TPDP$(C_{60})_2I_{10}$	30	39.8	-	1595	2.0039	4.0	2.0039	3.0
1T	TPDP$(C_{60})_2I_{10}$	5	40.6	-	1595	-	-	not measured	
2	(TMDTDMTTF)$_2C_{60}(CS_2)_3$	0	0	1508	1429	-	-	-	-
2a	(TMDTDMTTF)$_2C_{60}I_{7.5}$	3	39.1	-	1339	2.0067	20.5	2.0067	25.5
3	DBTTF·C_{60}·C_6H_6	0	0	668, 1480	1440	-	-	-	-
3a	DBTTF·C_{60}·$(C_6H_6)_xI_{3.5}$	10	30.67	668, 1480	1440, 1322	2.0069	19.5	2.0030	26.5
3b	DBTTF·C_{60}·I_9	20	44.2	-	1320	2.0071	18.5	2.0030	26.5

* *impurity of donor TPDP*

and the differences in electron delocalization in the doping. The g-value shift to the larger quantities in 1 and 3 would be the result of increase overlaping of iodine and donor electron orbitals in complexes. This leads to a stronger spin-orbital interaction in the complexes doped. The EPR signals corresponding to $C_{60}^{+\cdot}$ and $C_{60}^{-\cdot}$ were absent.

The loss spectra in the range of the excitation of plasma oscillations of all valence electrons exhibits the decrease of the energy of the basic plasmon with the increase of iodine content in the sample under doping. This may be associated with the decrease of the valence electrons density in the range of plasma oscillations. The positions of $I3d_{5/2}$ peak in X-ray photoelectron spectra of 1a - 1T correspond to the same in I_5^- salts [8].

The iodine was removed from TPDP$(C_{60})I_{10}$ in two temperature ranges: 200-260°C (17.4% w/w) and 325-450°C (24% w/w). It depends probably on the strength of iodine binding in the complexes. It was shown earlier that iodine is removed from the iodine doped C_{60} under severe conditions at 200-260°C [9].

The resistances of 1 and 3 single crystals decrease in doping by 10-25 times (by a standard two-probe technique).

The doping results in strong changes in the donor electron state but some changes in the electron structure of fullerene are observed in electron spectra also. An essential broadening of absorption bands at 262 and 343 nm is observed with the preservation of their location with the increase of the absorption in the whole wave-length range for the fully doped TPDP$(C_{60})I_{10}$ (1b). The intensity of the fundamental electron band of TPDP (460 nm) decreases and a new absorption band (730 nm) attributed to radical cation TPDP$^+$ appears [7]. The shift to lower energies is observed in addition to a quite noticeable broadening of the fundamental bands of C_{60} in (TMDTDM-TTF)$_2C_{60}I_{7.5}$,: 9 nm for 262 nm and 2 nm for 343 nm, respectively. The spectrum exhibits the increase of the absorption at 450 nm [10]. The measurements of the reflection spectra of DBTTF$C_{60}C_6H_6$ single crystals before and after doping [4] showed the similar changes in the absorption bands attributed to C_{60}. The broadening of fundamental electron bands of C_{60} together with the increase of the intensity of forbidden in symmetry bands at 450 nm take place that may be associated with a significant decrease of the fullerene molecule symmetry. The spectra of (TMDTDM-TTF)$_2C_{60}I_{7.5}$, and DBTTF$C_{60}I_9$ exhibit the shift of the fundamental electron bands of C_{60} by 0.05-0.20 eV to lower energies.

All these effects can be associated with the oxidation of the donor molecule by iodine and with the formation of a positive charge at it. TMDMDT-TTF is coordinated with C_{60} by S atoms by a sandwich type in 2a and has shortened contacts with C_{60} The fullerene molecules are involved in a strong positive field generated by two TMDMDT-TTF radical cations. This results in the decrease of the energy of C_{60} electron levels and the distortion of its symmetry. TPDP is probably coordinated with C_{60} by phenyl substituents which come out of the plane of dipyranylidene skeleton. The positive charge seems to be far away from C_{60} and cannot cause the changes in the energy of electron levels.

These changes are not associated with the charge transfer and C_{60}^{-} or C_{60}^{+} formation is not observed in doping. Therefore one could assume that the process of doping by iodine only indirectly affects the C_{60} electron system.

Acknowledgments

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