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Photoinduced Electron Transfer in Solid C_{60} Donor/Acceptor Complexes Studied by Light-Induced Electron-Spin Resonance

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*Light-induced ESR (LESR) spectroscopy was used to study photoinduced electron transfer (PIET) in the crystals of the C_{60} donor/acceptor complexes. High-field LESR signals attributed to $C_{60}^{\bullet-}$ (g = 1.9984 − 1.9992 and $\Delta H = 3 − 6$ G at 100 K) were observed in fullerene complexes with Leuco Crystal Violet (LCV·C_{60}·C_6H_5Cl, **1**), N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPDA·C_{60}, **2**), and bianthrone ((BA)$_2C_{60}$, **3**), whereas a low-field LESR signal in **2** was attributed to TMPDA$^{\bullet+}$. Microwave power studies reveal two independent spins in **2** and show high relaxation rates for photoinduced spins on $C_{60}^{\bullet-}$. The LESR signals consist of a major long-lived "persistent" component and a minor "prompt" one, which disappears immediately after light is off. The maximal intensity of the LESR signals was observed for the excitation of **1–3** below 2 eV. This range of photon energy corresponds to direct intermolecular charge transfer from donor to C_{60} molecules. PIET is temperature activated with E_a = 23, 43 and 49 meV for **1**, **2**, and **3**, respectively. Photoinduced spin susceptibility attains the maximum at 30 K in **1** and decreases with temperature down to 4 K indicating a possible*

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*antiferromagnetic interaction of spins, while in **2** it increases with the temperature decrease down to 4 K.*

Keywords: photoinduced electron transfer; fullerene; donor-acceptor complexes

INTRODUCTION

Photoinduced electron transfer from excited semiconducting conjugated polymers to C_{60} has been intensely studied [1–4]. Excitation of polymers with photon energies higher than their π-π^{*} gap results in fast reversible charge transfer to C_{60} molecules within a picosecond time scale to form relatively long-lived charge separated states (up to milliseconds at 80 K) [1–4]. High quantum efficiency of charge transfer and metastable charge separation allow the design of heterojunction diodes and plastic solar cells based on C_{60}-conjugated polymer composites [3–6]. The LESR technique was successfully used in the studies of PIET in the composites [1,3,4,7–9]. The presence of two LESR signals attributed to positive polarons[+] on the polymer chain and to the fullerene radical anions unambiguously evidences charge transfer and charge separation [1,7–9].

Various dyads comprising fullerenes covalently attached to porphyrins [10–12], phthalocyanines [12,13], ruthenium complexes [14], and some other chromophores [15–18] also show efficient photoinduced electron transfer from an excited donor part of the dyads to fullerene to form a relatively long-lived (from 50 ps to 2.5 μs) charge separated states. Different triads were also synthesized to increase lifetime of charge separation [19,20]. The dyads and triads may be promising for the design of molecular switches.

PIET was also studied in C_{60} complexes with amines in solution [21–23]. It was shown that the C_{60} photoexcited singlet or triplet states are quenched in the presence of amines by electron transfer to form either ion radicals or ion–radical pairs (exciplexes) [21–23]. The lifetime of the ion radical pairs in chlorobenzene is 3 ns–1.18 μs [23] and is close to that for the C_{60} dyads.

Fullerene C_{60} also forms solid complexes with substituted tetrathiafulvalenes, amines, porphyrins, aromatic hydrocarbons and some other donors [24–32]. PIET is not studied well for this class of compounds. The other aspect of PIET studies in solid fullerene complexes is the design of new materials with photoinduced conductivity and/or magnetism. Most of fullerene complexes have a neutral ground state [24,26,28]. The absence of ionicity defines their insulating and diamagnetic properties [24]. At the same time C_{60} compounds in an ionic state can show metallic conductivity [33] and ferromagnetism [34].
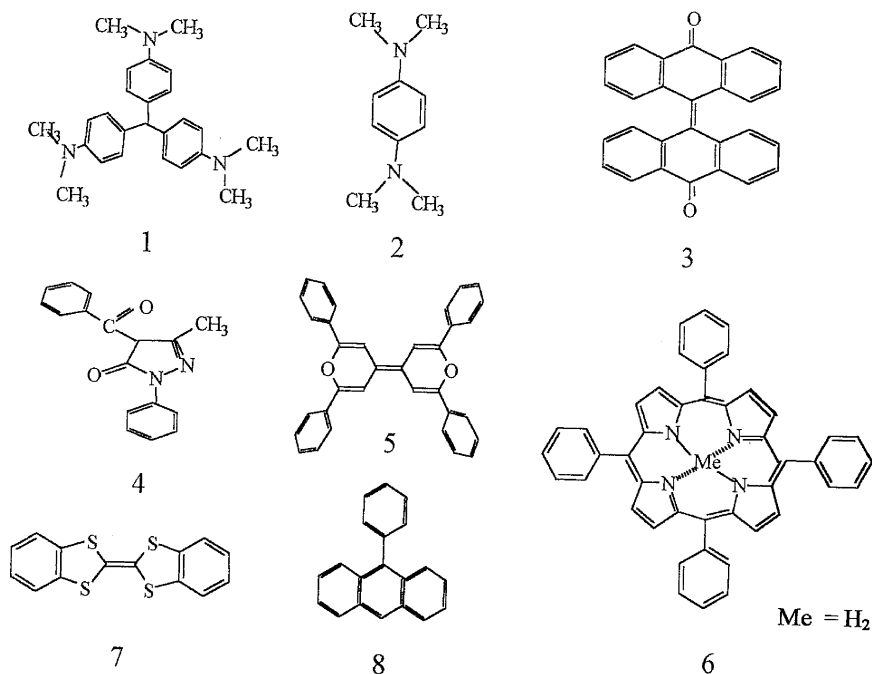
The excited state for the neutral complexes must be ionic, therefore it is possible to observe photoinduced conductivity and/or magnetism.

Here we present our results of the study of PIET in solid C$_{60}$ complexes with different donor molecules by LESR spectroscopy. The LESR signals were observed in the C$_{60}$ complexes with Leuco Crystal Violet, LCV·C$_{60}$·C$_6$H$_5$Cl (**1**), N,N,N′,N′-tetramethyl-*p*-phenylenediamine, TMPDA·C$_{60}$ (**2**); and bianthrone, (BA)$_2$C$_{60}$ (**3**). Preliminary data for the study of PIET in these complexes was published previously [35]. In this work we present microwave power studies for the LESR signals. The temperature dependencies of LESR signal intensity allows the activation energies of PIET in the complexes to be derived and the magnetic interaction between photoinduced spins to be studied down to 4 K. It is shown that LESR signals have "prompt" and "persistent" components and the lifetime of the "persistent" component were estimated. The dependencies of LESR signal intensity on photon energy were studied. The comparison of these dependencies with the absorption spectra of the complexes allows one to assume the mechanism for PIET in the solid fullerene complexes.

EXPERIMENTAL

The C$_{60}$ complexes with Leuco Crystal Violet, LCV·C$_{60}$·C$_6$H$_5$Cl (**1**) [27];N,N,N′,N′-tetramethyl-*p*-phenylenediamine, TMPDA·C$_{60}$ (**2**) [27]; bianthrone, (BA)$_2$C$_{60}$ (**3**) [28]; 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one, BMPP·C$_{60}$ (**4**) [29]; 2,2′,6,6′-tetraphenyldipyranylidene, TPDP(C$_{60}$)$_2$(CS$_2$)$_4$ (**5**) [28]; 5,10,15,20-tetraphenyl-21H,23H-porphyrin, H$_2$TPP(C$_{60}$)$_2$(C$_6$H$_6$)$_4$ (**6**) [30]; dibenzotetrathiafulvalene, DBTTF·C$_{60}$·C$_6$H$_6$ (**7**) [31]; and 9-phenylanthracene, PA·C$_{60}$(C$_6$H$_6$)$_{0.5}$ (**8**) [32] were obtained as crystals by evaporation of chlorobenzene (**1, 2**), benzene (**3, 4, 6, 7, 8**), and carbon disulfide (**5**) solutions containing C$_{60}$ and the corresponding donors (Fig. 1). The complexes were characterized by elemental, thermogravimetric analyses, and by IR-, UV-visible, and ESR-spectroscopy [24–22]. The crystal structures of **2** [27], **4** [29], **5** [28], **6** [30], and **7** [32] were reported.

A Bruker EMX (X-band) ESR spectrometer with an Oxford variable temperature cryostat (4-300 K operating range) was used. The g-factor was calibrated against α,α′-diphenyl-β-picrylhydrazid (DPPH). A xenon high-pressure lamp connected to a monochromator (400–900 nm range) and an optical parametric oscillator (OPO) (450–1700 nm) pumped by the third harmonic of a Nd-YAG laser were used to excite the samples through a grid on the cavity. Microwave power saturation studies and the studies of time and temperature dependencies of LESR signals intensity were carried out using a xenon lamp.

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FIGURE 1 Molecular structure of the donor molecules: (1) Leuco Crystal Violet (4,4′,4″-methylidyne tris(N,N-dimethylaniline)); (2) N,N,N′N′-tetramethyl-p-phenylenediamine; (3) bianthrone; (4) 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one; (5) 2,2′,6,6′- tetraphenyldipyranylidene; (6) 5,10, 15,20-tetraphenyl-21H,23H-porphyrin; (7) dibenzotetrathiafulvalene; and (8) 9-phenylanthracene.

The intensity of the LESR signals was estimated by a double integration of the signal. To obtain the dependence of the LESR signals intensity on photon energy we normalized the integral intensity of LESR signals on the light power and a number of photons.

The samples were put into quartz tubes. The tubes were evacuated before and during measurements to avoid the irreversible LESR signals, which appear under light excitation if some water condenses on the surface of the crystals.

The LESR experimental procedure consists of four steps. The ESR spectrum was scanned at 100 K: for a nonilluminated sample ("dark" signal) (1); under light excitation ("light on" signal) (2); when illumination is turned off ("light off" signal) (3). Switching off the excitation light does not lead to a complete disappearance of the LESR signal at

low temperatures. Therefore, the sample was heated up to room temperature, annealed for 5–10 minutes, and cooled down to 100 K ("annealed" signal) (4). To discriminate the LESR signals the "dark" signal was subtracted from the "light on" one.

RESULTS

Dark Signals

The "dark" ESR spectra of the complexes **1, 3–8** manifest weak narrow ESR signals with g = 2.0022 and $\Delta H = 1.5 - 2$ G, which cannot be attributed to $C_{60}^{\bullet-}$ (g = 1.9960 − 2.0000, the line halfwidth $\Delta H = 2 - 6$ G at 100 K [36]), indicating a neutral ground state the complexes.

The "dark" signals are present even in starting fullerenes and may be attributed to defects due to the interaction of fullerenes with oxygen [37,38]. The intensity of these signals is 0.01–0.1% of the mass of the sample and strongly depends on methods of the fullerene preparation and storage. The position and the halfwidth of the signal are almost temperature-independent down to helium temperatures. The "dark" ESR signals remain unchanged after the light excitation and will not be considered in the further discussion.
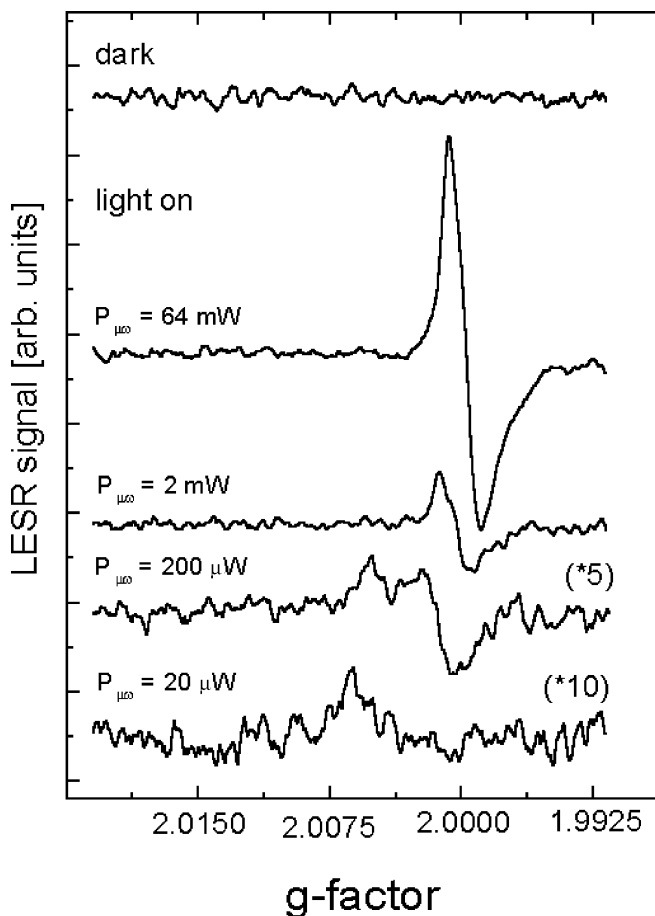
LESR Signals

We performed LESR measurements for the complexes **1-8** using white light (400–900 nm) at 100 K using the sequence described in Experimental. The LESR signals were observed only for the complexes **1–3** (Table 1). Photoexcitation of **4** yields only a weak LESR signal whose intensity is less than that of the "dark" signal.

The LESR signals with g = 1.9984 − 1.9992 and $\Delta H = 3.9 - 4.2$ G were observed at high microwave power (Figs. 2 and 3) and disappear

TABLE 1 Parameters of the LESR Signals in **1–3**

N	Complex	High-field signal		Low-field signal		E_a, meV	T_{PIET}, K
		g-factor	ΔH, G	g-factor	ΔH, G		
1	LCV · C_{60} · C_6H_5Cl	1.9992	4.2	–	–	23	170
2	TMPDA · C_{60}	1.9984	3.9	2.005	~8 G	49	120
3	$(BA)_2C_{60}$	1.9985	3.9	–	–	43	135

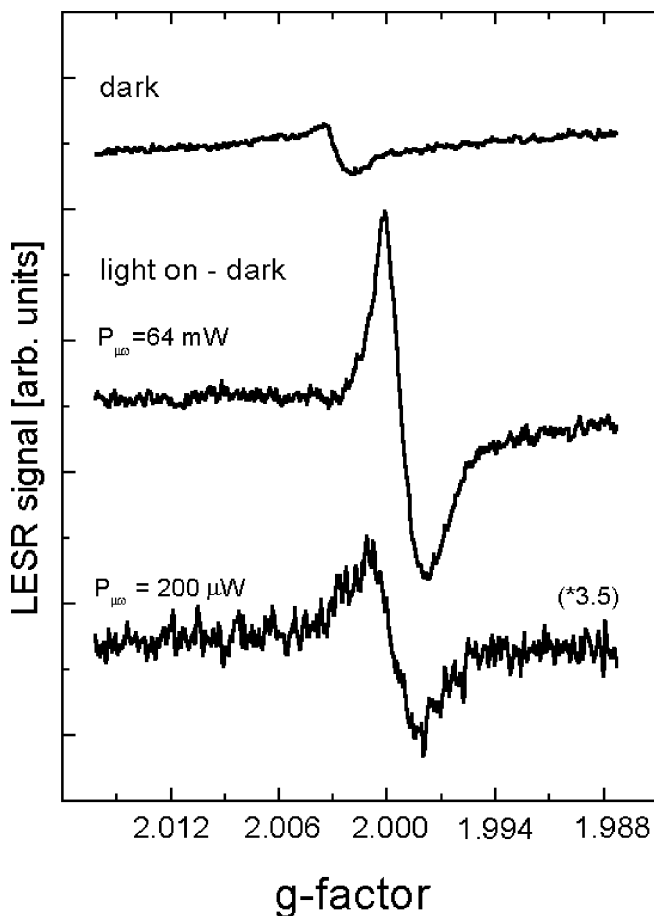T_{PIET} – the temperature of the appearance of the LESR signals.

FIGURE 2 The "dark" and "light on" ESR signals in TMPDA · C_{60} at different microwave power (57 K). Amplification of the signals is given in brackets.

below 20 μW (the high-field signals). It should be noted that all these signals are slightly asymmetrical.

Another LESR signal together with the high-field one were resolved in the spectrum of **2** at low microwave power < 200 μW (the low-field signal) and only a weak low-field signal was manifested at 20 μW whose parameters are g ∼2.005 and $\Delta H = 8$ G (Fig. 2). The low-field signals were not observed in **1** (Fig. 3) and **3**.
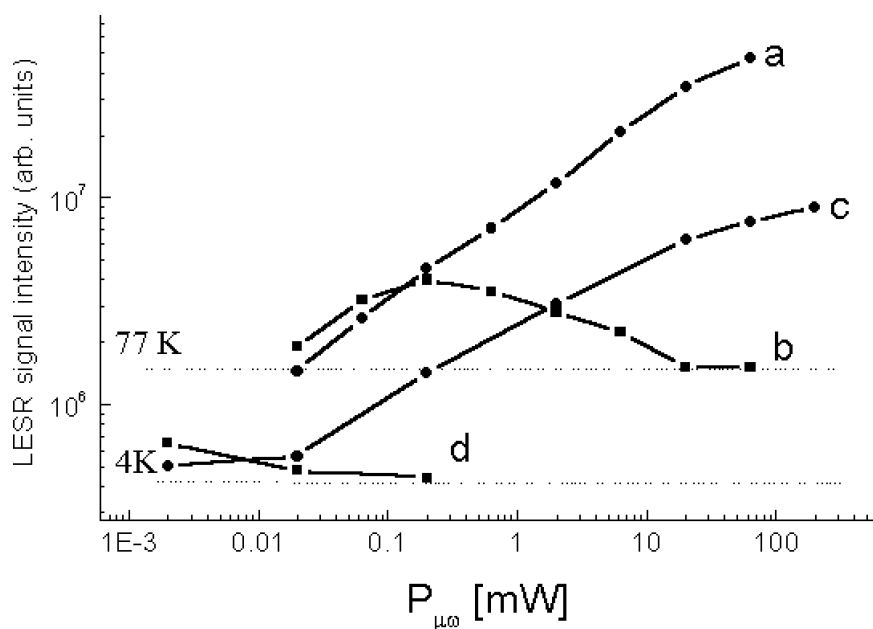
The dependencies of the intensity of the high-field LESR signals on microwave power for **1** and **2** are presented in Figures 4 and 5. These signals show nearly a square-root dependence on $P_{\mu\omega}$ and they are not

FIGURE 3 The "dark" and "light on" ESR signals in LCV·C$_{60}$·C$_6$H$_5$Cl at different microwave power (77 K). Amplification of the signals is given in brackets.

saturated up to highest available microwave power. The temperature decrease from 57–77 down to 4 K shifts the saturation maximum for signals to lower P$_{\mu\omega}$ values. However, even at 4 K, the high-field LESR signals are not saturated. We found also that the maximum of the saturation curve for high-field LESR signal in **1** is essentially shifted to higher microwave power relatively to this maximum for the "dark" signal (Fig. 5a and b).

The saturation behavior of the low- and high-field signals in **2** is also different. The maximum of the saturation curve for the low-field
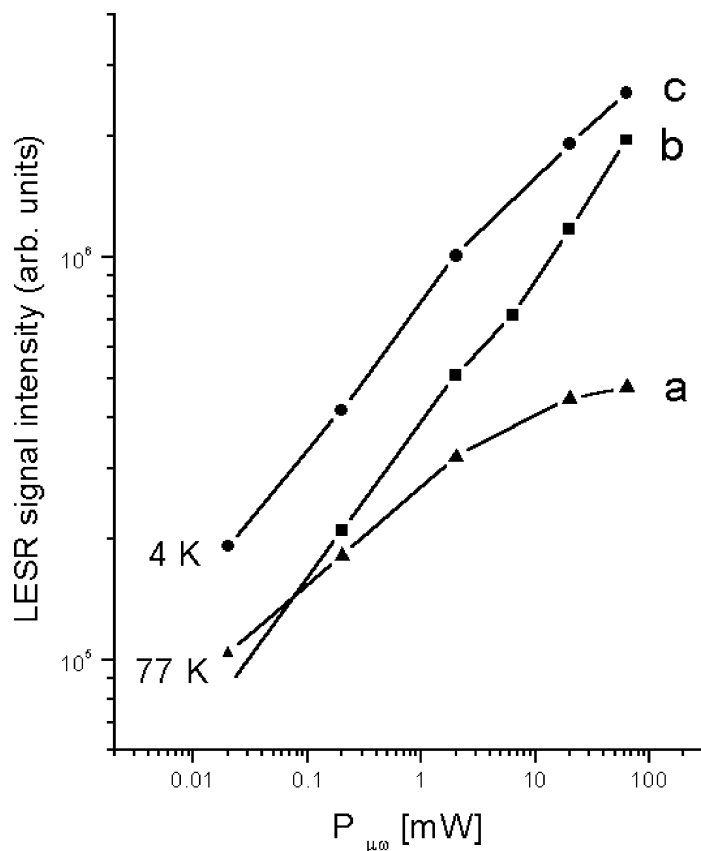
FIGURE 4 The saturation dependencies for the LESR signals in TMPDA · C_{60}: the high- (a) low-field (b) signals at 57 K; the high-(c) low-field (d) signals at 4 K.

signal is attained at 0.2 mW and at higher microwave power the signal is suppressed to zero (Fig. 4b). The temperature decrease from 57 down to 4 K shifts the saturation maximum to lower $P_{\mu\omega}$ values (Fig. 4d).

The time dependence of the high-field LESR signal intensity in **2** excited by OPO (700 nm, 30 mW, 100 K) is shown in Figure 6a. Two components of the "light on" signal can be distinguished. The first "prompt" component disappears immediately when light is off. This component has approximately 25% of the intensity of the "light on" signal. The second "persistent" component has a lifetime of several hours at 100 K (its intensity decreases by 8% for 2.25 hours).

The time dependence of the LESR signal intensity in **1** excited by white light is presented in Figure 6b. The contribution of the "prompt" component is only about 4%. Thus, white light of relatively low intensity produces mainly the "persistent" component whose lifetime is also more than 2 hours at 100 K. However, this persistent LESR signal intensity decreases faster in **1** than in **2** (by 50% for 2 hours). The two components of the "light on" signal were observed in **3** as well. The parameters (g-factors and ΔH) and the saturation behavior of
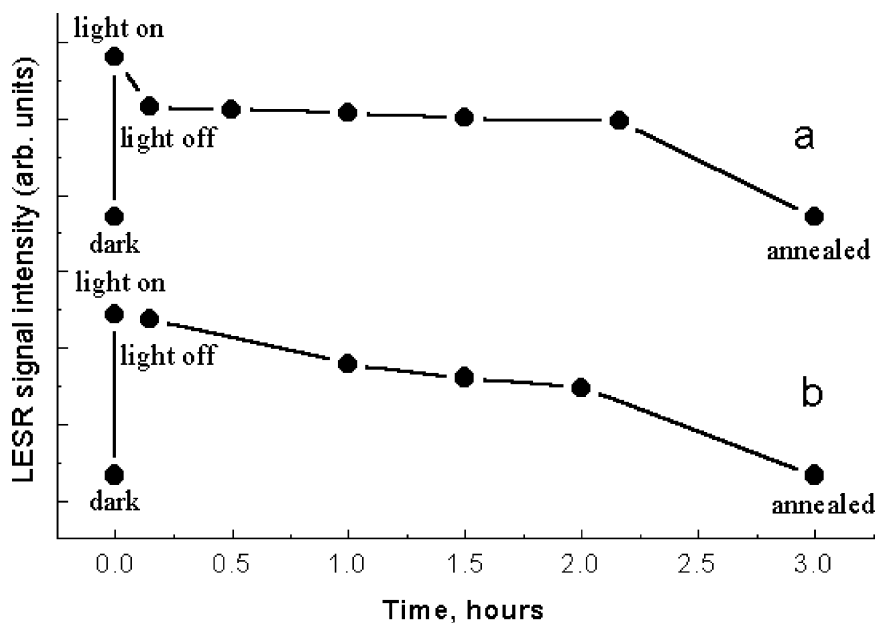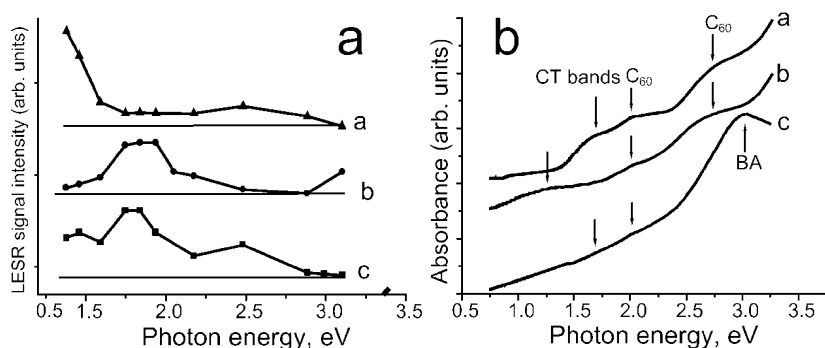
FIGURE 5 The saturation dependencies for the "dark" and LESR signals in LCV·C$_{60}$·C$_6$H$_5$Cl: (*a*) the "dark" ESR signal at 77 K; the high-field LESR signal at 77 (*b*) and 4 K (*c*).

the "persistent" components are similar to those of the "light on" signal. In all cases the lifetime of the "persistent" component becomes shorter with the temperature increase and disappears completely on annealing the sample for ten minutes at room temperature.

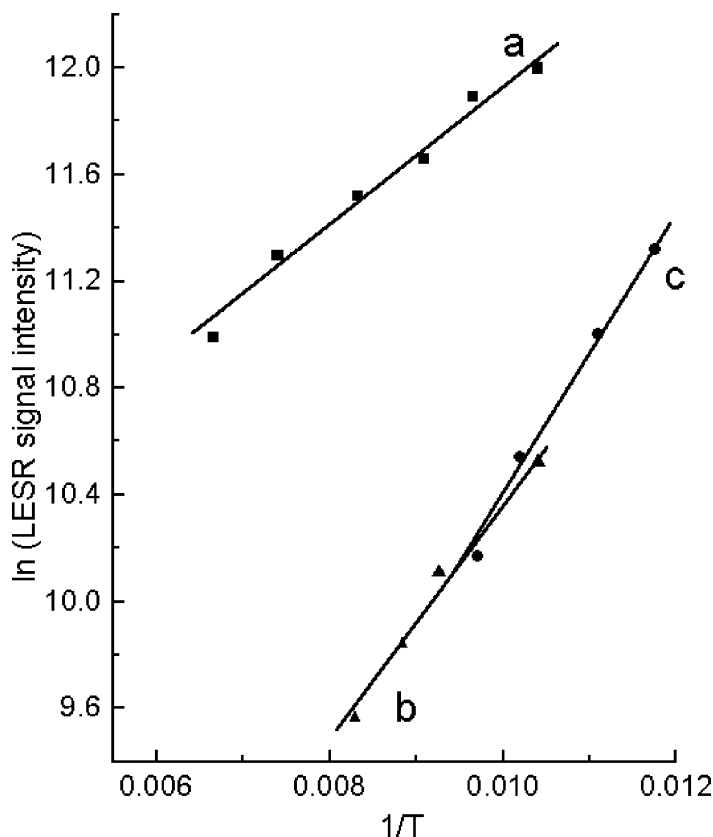The dependencies of the LESR signal intensity on photon energy are presented in Figure 7a. It is seen that all maxima lie at energies lower than 2.00 eV, though the positions of the maxima are different. The maxima for **2** and **3** are located in the 2.00–1.65 eV range, whereas the maximum for **1** lies at photon energy smaller than 1.46 eV. Figure 7b show the absorption spectra of the complexes **1–3** for comparison.

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FIGURE 6 Intensity of the "light on", and "light off" signals and the time dependence for the LESR signal after light is turned off: (a) TMPDA$\cdot$C$_{60}$; (b) LCV$\cdot$C$_{60}\cdot$C$_6$H$_5$Cl.

FIGURE 7 (a) The dependence of the LESR signal intensity on the photon energy: (a) LCV$\cdot$C$_{60}\cdot$C$_6$H$_5$Cl; (b) TMPDA$\cdot$C$_{60}$; (c) (BA)$_2$C$_{60}$. (b) Absorption spectra of (a) LCV$\cdot$C$_{60}\cdot$C$_6$H$_5$Cl; (b) TMPDA$\cdot$C$_{60}$; (c) (BA)$_2$C$_{60}$ in the 0.75–3.25 eV range. The arrows show the position of charge transfer (CT), BA (c) and C$_{60}$ bands.

FIGURE 8 The dependence of the hyperbolic logarithm (ln) of the intensity of the LESR signals vs. the inverted temperature (1/T): (a) LCV · C$_{60}$ · C$_6$H$_5$Cl; (b) (BA)$_2$C$_{60}$; (c) TMPDA · C$_{60}$.

The intensity of the LESR signal is temperature-dependent. The LESR signals can be observed only below 170 K for **1** and below 135 and 120 K for **3** and **2**, respectively. The temperature dependencies reflect the Arrhenius behavior (Fig. 8). The estimation of the PIET activation energies in the complexes (Table 1) yields the E$_a$ value for **1–3** equal to 23, 49, and 43 meV, respectively. Below 50 K the temperature dependencies of LESR signals intensity deviate from the Arrhenius behavior (Fig. 9). The intensity of the high-field LESR signal in **2** attains maximum at 30 K and then decreases with temperature down to 4 K, whereas the ΔH of the signal changes from 3.9 G at 100 K to 3.4 G at 4 K. The LESR signal intensity increases in **1** with

FIGURE 9 The temperature dependence of doubly integrated LESR signal from $C_{60}^{\bullet-}$ in TMPDA $\cdot$ C_{60} at $P_{\mu\omega} = 20\,\mathrm{mW}$ in the 100–4 K range.

the temperature decrease down to 4 K, whereas ΔH of the signal decreases from 7 G at 150 K down to 3.5 G at 4 K.

DISCUSSION

It is known [36] that the ESR signal from $C_{60}^{\bullet-}$ has a g-value between 1.996 and 2.000 and ΔH between 20 and 50 G at room temperature and it is narrowed to 4–10 G with the temperature decrease down to 77 K. The high-field LESR signals with g = 1.9984 − 1.9992 and $\Delta H = 3.9 − 4.2\,\mathrm{G}$ (77 K) observed in the complexes can unambiguously be attributed to $C_{60}^{\bullet-}$. Anisotropy of these signals is probably associated with polycrystallinity of the samples. Similar anisotropy was also observed for the LESR signals from the $C_{60}^{\bullet-}$ in C_{60}-conjugated polymer composites [7]. A weak low-field LESR signal in **2** with g = 2.005 can be attributed to TMPDA$^{\bullet+}$. Thus, two signals from $C_{60}^{\bullet-}$ and TMPDA$^{\bullet+}$ with different g-factors and ΔH are distinguished in **2**, whereas only one LESR signal from $C_{60}^{\bullet-}$ is detected in **1** and **3**. A different saturation behavior of LESR signals from $C_{60}^{\bullet-}$ and TMPDA$^{\bullet+}$ in **2**, and the "dark" ESR and the LESR signals from $C_{60}^{\bullet-}$ in **1** and **3** allows them to be attributed to independent spins.
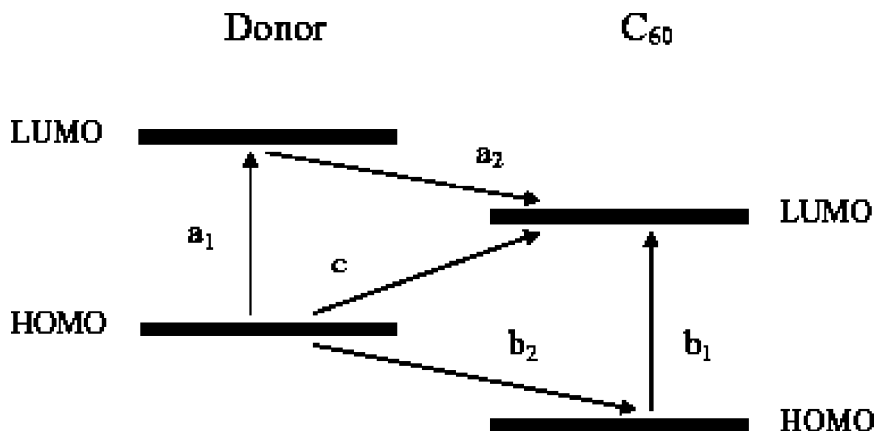
All LESR signals attributed to $C_{60}^{\bullet-}$ are characterized by short relaxation times (τ_1) because the saturation maxima for these signals lie at

microwave power higher than 200 mW. This value is at least 100 times higher than the saturation maximum for the LESR signal from TMPDA$^{\bullet+}$ (0.2 mW). Thus, τ_1 for C$_{60}^{\bullet-}$ is more than 10 times shorter than that for TMPDA$^{\bullet+}$. Such short relaxation times were reported earlier for C$_{60}^{\bullet-}$ in solution [39], in solid state [40] and for the LESR signals in C$_{60}$-conjugated polymer composites [7]. The unsaturation of C$_{60}^{\bullet-}$ LESR signal can be explained by the Jahn-Teller distortion of C$_{60}^{\bullet-}$, which splits the C$_{60}$ T$_{1u}$ level into two closely spaced energy levels. Thermal averaging over these states would provide a dominant relaxation channel for the spins on C$_{60}^{\bullet-}$.

The LESR signals consist of the "prompt" and "persistent" components. The "persistent" component can be attributed to photoinduced spins localized on the defects. Two types of defect states can contribute to the "persistent" component: (defect$^{\bullet+}$)·(C$_{60}^{\bullet-}$) or (Donor$^{\bullet+}$)·(defect$^{\bullet-}$) pairs. The defect states in the complexes can be assigned to the (defect$^{\bullet+}$)·(C$_{60}^{\bullet-}$) pairs since the "persistent" component consists of LESR signals from C$_{60}^{\bullet-}$. This may be also a reason for the absence the LESR signals from radical cations of donors in **1** and **3** due to possible trapping of photoinduced holes on the defect states. The reversible "prompt" component can be attributed to the LESR signal from the (Donor$^{\bullet+}$)·(C$_{60}^{\bullet-}$) pairs. At a low power of exciting light the saturation of the defect states occurs mainly and the "persistent" component makes the main contribution to the "light on" signal. The "prompt" component of the LESR signal is evidently generated after the saturation of the defect states.

Different mechanisms for the generation of the LESR signals under light excitation are possible in fullerene donor/acceptor complexes (Fig. 10):

1). Photoexcitation of the donor component with photon energy higher than the HOMO-LUMO gap (Fig. 10a$_1$) results in electron transfer from an excited donor molecule to C$_{60}$ (Fig. 10a$_2$). The formation of charge separated states in C$_{60}$-conjugated polymer composites is observed in the whole range of photon energies higher than the HOMO-LUMO gap of polymers (>2 eV) [3–4].
2). Photoexcitation of C$_{60}$ (Fig. 10b$_1$) can also result in electron transfer from the HOMO level of the donor molecule to the HOMO level of excited C$_{60}$ (Fig. 10b$_2$) due to that C$_{60}$ is a stronger acceptor in the excited state than in the ground state [41]. Photoexcitation of C$_{60}$ is possible at energies higher than its HOMO-LUMO gap. Direct HOMO-LUMO transitions (the band around 2 eV in the absorption spectra, Fig. 7b, curves *a* and *b*) are symmetry forbidden and have very low intensity [42]. The photoexcitation of C$_{60}$ is

FIGURE 10 The diagram of possible mechanisms of PIET in the C_{60} donor/acceptor complexes: (a) excitation of the donor component; (b) excitation of C_{60} followed by electron transfer from the donor to the excited C_{60} molecule; (c) direct intermolecular charge transfer from the donor to the C_{60} molecule.

mainly realized at energies higher than 2 eV (the bands attributed to the symmetry-allowed transitions in the absorption spectrum of C_{60} are at 3.60 and 4.68 eV [42]).

3). The third possibility is direct intermolecular charge transfer from the HOMO level of the donor to the LUMO level of C_{60} (Fig. 10c). Wide and relatively weak charge transfer bands (CTB) are observed in the spectra of fullerene complexes in visible and near-IR ranges below 2 eV [43] (Fig. 7b).

LCV and TMPDA are transparent and have no absorption in the 400–900 nm range, while BA manifests intense absorption at 2.98 eV (Fig. 7b, curve *c*). To determine precisely the position of CTB we discriminated them by a subtraction of a normalized C_{60} spectrum from those of **1** and **2** or normalized C_{60} and BA spectra from that of **3**. The determined CTB maxima are located at 1.26 eV for **2** and 1.7 eV for **1** and **3**. The main difference of the absorption spectra of **4–9** which do not show LESR signals under light excitation is the absence of CTBs (**4, 6, 7**) or their low intensity (**5, 8**) [28]. Intense absorption associated with donors is observed in the visible range at 2.68 eV for **5**, and at 2.86 eV for **6**.

The LESR signals were observed under photoexcitation of the complexes with photon energy lower than 2.75 eV with the maxima below 2 eV (Fig. 7a). Photoexcitation of the donor molecules (LCV, TMPDA

and BA) as well as C$_{60}$ is possible only at higher energy (>2.7 eV). Therefore, the PIET mechanism can be attributed mainly to direct intermolecular charge transfer from the donor to the C$_{60}$ molecule. This is an unexpected result, particularly, for the C$_{60}$ complexes with BA, TPDP, and H$_2$TPP due to that absorption associated with donor in the visible range is an order of magnitude more intense than that associated with intermolecular charge transfer.

The activation energies of PIET are different in the complexes. The E$_a$ value for **1** is two times smaller than those for **2** and **3**. This difference can be associated with different intensity of CTBs. For example, CTB in the absorption spectrum of **1** has the highest intensity among **1–9** if we compare the normalized spectra.

Photoinduced paramagnetic susceptibility of the complexes is proportional to the doubly integrated LESR signal. The C$_{60}^{\bullet-}$ LESR signal has a nearly square-root dependence of intensity on P$_{\mu\omega}$ up to 64 mW in the 80–4 K range (Figs. 4 and 5). Therefore, we studied the temperature dependencies of LESR signal intensity down to 4 K at 20 mW. The behavior of spin susceptibility of photoinduced spins in **2** (Fig. 9) indicates an antiferromagnetic interaction of photoinduced spins. The behavior of spin susceptibility of photoinduced spins in **1** may correspond to a paramagnetic behavior of non-interacting spins. The study of PIET by the LESR technique in solid fullerene complexes shows some similarity with PIET in C$_{60}$-conjugated polymer composites [7]. Two independent photoinduced spins with different spin-relaxation times corresponding to the high- and low-field LESR signals were observed in **2** and in the composites, though we observed only one high-field LESR signal in two other complexes. The unsaturated high-field LESR signals are attributed to C$_{60}^{\bullet-}$. At low microwave power <200 μW the LESR signals attributed to the donor$^{\bullet+}$ or polaron$^{\bullet+}$ are resolved. The LESR signal from C$_{60}^{\bullet-}$ has close g-factor values (g = 1.9995 in the composites [6] and 1.9984–1.9992 in the complexes) and high relaxation rates, which are attributed to the Jahn-Teller distortion of the fullerene molecule. The LESR signals of the donor$^{+\cdot}$ and the positive polaron$^{+\cdot}$ in the conjugated polymer backbone [7] have spin relaxation time (τ_1) more than 10 times longer than those of C$_{60}^{\bullet-}$.

In both cases the "prompt" and "persistent" components are found in the "light on" signal. The "persistent" component is attributed to photoinduced spins localized on defect states. It is independent of light intensity, has a long lifetime (several hours) at T <200 K and depends probably on the amount of the defect states in the sample [7].

The mechanisms of PIET are different in the composites and complexes. The main contribution to PIET in the composites is made by

excitation of conjugated polymers. However, PIET by photoexcitation of donor is less realized even for C_{60} complexes with chromophore BA, TPDP, and H_2TPP. The generation of the LESR signals in the complexes **1–3** is mainly realized by direct intermolecular charge transfer from donor to C_{60} molecules. From this point of view the C_{60} complexes with intense CTBs in visible or near IR range are the most promising compounds for which PIET can be observed under light excitation. The difference in the PIET mechanisms results in higher activation energies of PIET in the complexes ($E_a = 23 - 49$ meV) than in the composites ($E_a = 15$ meV for MEH-PPV $- C_{60}$, where MEH-PPV is poly(methoxy-5-(2′-ethylhexoxy)-p-phenylene)-vinylene) [3]), since absorption associated with HOMO-LUMO transitions in the conjugated polymers is orders of magnitude more intense than that associated with intermolecular charge transfer transitions in the complexes.

The magnetic interaction between photoinduced $C_{60}^{\bullet-}$ spins is insignificant for composites with relatively low C_{60} content and large distances between the C_{60} molecules [7]. In contrast to the composites, **2** has a layered structure with close packing of the C_{60} molecules in the layer [27]. This is proposed to give an antiferromagnetic behavior of photoinduced spins. Previously, the antiferromagnetic interaction of spins was observed in the C_{60} complexes with ionic ground state: antiferromagnetic modification of TDAE·C_{60} salt (TDAE: tetrakis(dimethylamino)ethylene) with one-dimensional packing of $C_{60}^{\bullet-}$ [44], C_{60} salt with 2,2′-bi(1,3-dimethylhexahydropyrimidine-2-yl) [45] and a multi-component ionic complex of tetrabenzyl-p-phenylenediamine with TDAE·C_{60}: (TBPDA)$_2$· TDAE·C_{60} [46].

CONCLUSION

Light-induced ESR spectroscopy was used to study PIET in the solid C_{60} donor/acceptor complexes. The LESR signals were observed for LCV·C_{60}·C_5H_5Cl, TMPDA·C_{60}, and (BA)$_2$$C_{60}$. Microwave power studies allow one to distinguish two independent photoinduced spins in TMPDA·C_{60} and only one such spin in LCV·C_{60}·C_5H_5Cl and (BA)$_2$$C_{60}$. The LESR signals in the complexes with g = 1.9984 − 1.9992 and $\Delta H = 3 - 6$ G (100 K) are attributed to $C_{60}^{\bullet-}$ and that with g $\sim$ 2.005 and $\Delta H = 8$ G in TMPDA·C_{60} to TMPDA$^{\bullet+}$. Photoinduced spins localized on $C_{60}^{\bullet-}$ show high relaxation rates, which are explained by the Jahn-Teller distortion of $C_{60}^{\bullet-}$.

It was shown that the "light on" LESR signals consist of two components. The "persistent" component with a long lifetime (>2 hours at 100 K) and the "prompt" one, which disappears immediately after light

is off. The "persistent" component is mainly attributed to the $(defect^{\bullet+})C_{60}^{\bullet-})$ pairs. The dependencies of the LESR signals intensity on photon energy have the maxima below 2.00 eV. According to the absorption spectra of the complexes intermolecular charge transfer from the donor to the C_{60} molecule can be realized in this energy range. Other C_{60} complexes **4–8**, for which PIET is not observed at 100 K, do not have CTBs in the absorption spectra or they have low intensity. All PIET processes are temperature activated with $E_a = 23$, 49, and 43 meV for $LCV \cdot C_{60} \cdot C_5H_5Cl$, $TMPDA \cdot C_{60}$, and $(BA)_2C_{60}$, respectively. PIET in the complexes shows some similarities with PIET studied earlier for the C_{60}-conjugated polymer composites [7]. However, the mechanism of PIET in the complexes is realized via intermolecular charge transfer between donor and C_{60} molecules, whereas in the composites that is mainly the photoexcitation of the conjugated polymer donors. The E_a values are also higher for the complexes than for the composites.

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