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Photoinduced electron transfer in solid C_{60} donor/acceptor complexes.

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Abstract

Light-induced ESR spectroscopy was used to study photoinduced electron transfer (PIET) in the crystals of the C_{60} donor/acceptor complexes: TMPD·C_{60} (**1**), LCV·C_{60}·C_6H_5Cl (**2**), and $(BA)_2C_{60}$ (**3**). LESR signals from $C_{60}^{-\cdot}$ with g=1.9984-1.9992 and ΔH=3-6G (100K) for **1-3** as well as the LESR signal from $TMPD^{+\cdot}$ for **1** were observed. The LESR signals have two components: a long-lived "persistent" component and a "prompt" one, which disappears immediately after light is off. All PIET processes are temperature activated with E_a=23, 43 and 49 meV for **2**, **3**, and **1**, respectively. The temperature dependence of spin susceptibility in **1** can be described by the Bonner-Fisher model, while in **2** it corresponds to a paramagnetic behavior of isolated spins.

Keywords: Fullerene C_{60}, Donor/acceptor complexes, Photo-induced electron transfer, Light-induced ESR spectroscopy

Photoinduced electron transfer from excited semiconducting conjugated polymers to C_{60} has been studied intensely [1,2]. Excitation of polymers results in fast reversible charge transfer to C_{60} molecules to form relatively long-lived charge separated states. High quantum efficiency of charge transfer and long lived charge separation allow the design of plastic solar cells based on conjugated polymer-C_{60} composites [3]. The LESR technique was successfully used in the studies of PIET in the composites [4]. The presence of two LESR signals in the composites attributed to a polaron$^+$ on the polymer chain and to the $C_{60}^{-\cdot}$ radical anion evidencing unambiguously charge transfer and charge separation [4].

PIET was also studied for a number of charge transfer fullerene complexes with amines in solutions [5]. It is shown that C_{60} photoexcited states are quenched in the presence of amines by electron transfer to form ion radicals or exciplexes [5]. Up to now various C_{60} complexes with different organic donors have been prepared in the solid state [6]. Most of them have a neutral ground state. Since the excited state must be ionic in these complexes, it would be interesting to study PIET in these compounds.

In this work we present the results of the study of PIET in the solid C_{60} molecular complexes by light-induced ESR spectroscopy. The LESR signals were observed in TMPD·C_{60} (**1**); LCV·C_{60}·C_6H_5Cl (**2**); and $(BA)_2C_{60}$ (**3**). Microwave power and temperature dependencies of the LESR signal intensity were obtained. The temperature dependence allows the estimation of the activation energy, E_a of PIET and the study of magnetic interactions between photo-induced spins down to 4K.

The C_{60} complexes were obtained as crystals by evaporation of solutions containing C_{60} and the corresponding donors [6]. A Bruker EMX (X-band) ESR spectrometer with an Oxford variable temperature cryostat (4-300 K operating range) was used. A xenon high pressure lamp connected to a monochromator (400-900 nm) was used for excitation of the samples. The samples were put into quartz tubes which were evacuated before and during the measurements.

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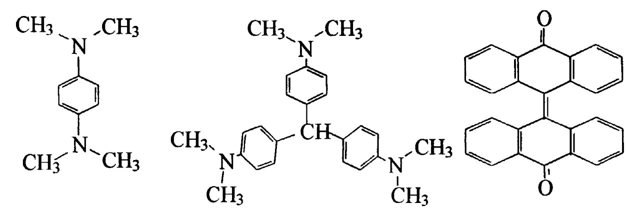

1 2 3

Fig.1. (1) N,N,N′,N′-tetramethyl-*p*-phenilenediamine; (2) Leuco Crystal Violet ; and (3) bianthrone.

Results and Discussion.

The complexes under study have a neutral ground state because the ESR signals attributed to $C_{60}^{-\cdot}$ are absent in all the samples. The dark ESR spectra of **2** and **3** manifest weak ESR signals with g= 2.0022 and ΔH=1.5-2 G which are attributed to defects due to the interaction of fullerenes with oxygen [7].

The LESR signals were observed under excitation of the complexes at 100K. The parameters of the signals are presented in Table 1. The LESR signals with g=1.9985-1.9992 and ΔH=3.9-4.2 G were observed at high microwave power (Fig. 2) and can be attributed unambiguously to the $C_{60}^{-\cdot}$ anion-radical [4,8].

A new weak LESR signal together with the high-field one are resolved in the spectrum of **1** at $P_{\mu\omega}$<200 μW (Fig. 2) and can be attributed to $TMPD^{+\cdot}$. In **2** and **3** the signals from radical

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Table 1.
The parameters of the LESR signals from C_{60} in the complexes.

Complex	g-factor	ΔH	E_a, meV	T, K
1	1.9984	3.9	49	120
2	1.9992	4.2	23	170
3	1.9985	3.9	43	135

T - the temperature of the appearance of the LESR signals.

cations are absent even at low microwave power ($P_{\mu\omega}$<200 μW) probably due to its weak intensity at these $P_{\mu\omega}$ values.

The LESR signals at 57-77 K from $C_{60}^{\cdot-}$ are not saturated up to highest microwave power (64-200 mW) and are characterized by short relaxation times. The maximum of the saturation curve for LESR signal from $TMPD^{+\cdot}$ in **1** is attained at 200 μW and the signal is suppressed to zero at higher $P_{\mu\omega}$. The temperature decrease down to 4 K shifts the maximum of the saturation curves for $C_{60}^{\cdot-}$ and $TMPD^{+\cdot}$ LESR signals to lower $P_{\mu\omega}$ values. However, even near 4K, the signals from $C_{60}^{\cdot-}$ are not saturated.

When the excitation light is switched off, the intensity of the LESR signals decreases, but does not vanish completely. Hence we distinguish two components of the "light on" signal. One component disappears immediately when light is off. This "prompt" component has approximately 5-25% of the intensity of the "light on" signal. The second "persistent" component gives the main contribution to the "light on" signal and lives very long at 100K (its intensity decreases only by 10-50 % for 2 hours). Probably the "persistent" component can be attributed to trapped photo-induced spins [4]. The parameters (g-factors and ΔH) and the saturation behaviour of 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. The signal disappears completely on annealing the sample for several minutes at room temperature.

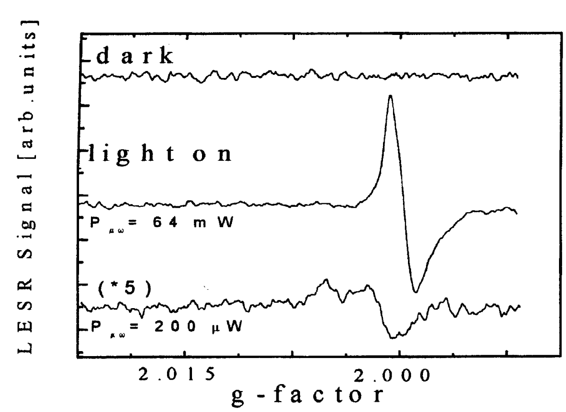

Fig. 2. The dark and "light on" LESR signals in **1** at different values of microwave power (57 K).

The intensity of the LESR signal strongly depends on temperature. The LESR signals can be observed only below 170K for **2** and below 135 and 120 K for **3** and **1**, respectively. At T>60 K the dependencies show the Arrhenius behaviour and can be presented in ln(integral intensity of the LESR signal) - 1/T coordinates. The slope of the linear dependencies allows the estimation of E_a of PIET in the complexes (Table 1). The smallest E_a value in **2** is equal to 23 meV and E_a= 43 - 49 meV for two other complexes. Thus, the E_a values in the complexes are larger than that in the composites (E_a=15 meV for C_{60}-MEH-PPV (poly(methoxy-5-(2'-ethylhexoxy)-p-phenylene)-vinylene) [9]).

Photoinduced paramagnetic susceptibility of the sample is proportional to the doubly integrated LESR signal. It increases with the temperature decrease and attains the maximum at about 30 K. With the further temperature decrease, spin susceptibility decreases. This temperature dependence can be described by the Bonner-Fisher model for antiferromagnetic interactions of spins [10].

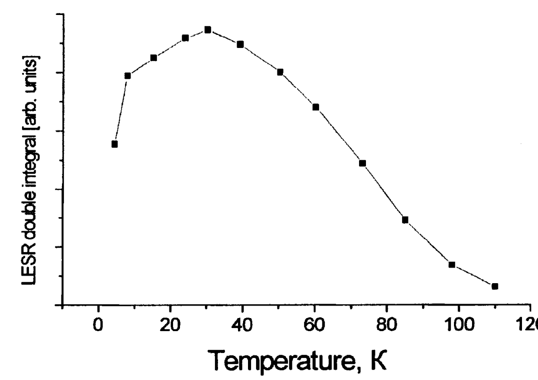

Fig. 3. The temperature dependence of doubly integrated LESR signals of $C_{60}^{\cdot-}$ in **1** at $P_{\mu\omega}$= 20 mW.

The behavior of spin susceptibility of photoinduced spins in **2** differs from that in **1**. One observes the increase of the value of spin susceptibility with the temperature decrease in **2** in the whole temperature range (170 – 4K). Such a dependence indicates a paramagnetic behavior of isolated spins [10].

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