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Light-induced electron paramagnetic resonance evidence of charge transfer in electrospun fibers containing conjugated polymer/fullerene and conjugated polymer/fullerene/carbon nanotube blends

Alexander I. Shames,^{1,a)} Céline Bounioux,^{2,a)} Eugene A. Katz,^{2,3,b)}
Rachel Yerushalmi-Rozen,^{3,4} and Eyal Zussman⁵

¹Department of Physics, Ben-Gurion University of the Negev, Beersheba 84105, Israel

²Department of Solar Energy and Environmental Physics, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boker Campus 84990, Israel

³Ilze Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

⁴Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

⁵Department of Mechanical Engineering, Technion, Haifa 32000, Israel

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Electrospun sub-micron fibers containing conjugated polymer (poly(3-hexylthiophene), P3HT) with a fullerene derivative, phenyl-C61-butyric acid methylester (PCBM) or a mixture of PCBM and single-walled carbon nanotubes (SWCNTs) were studied by light-induced electron paramagnetic resonance spectroscopy. The results provide experimental evidence of electron transfer between PCBM and P3HT components in both fiber systems and suggest that the presence of a dispersing block-copolymer, which acts via physical adsorption onto the PCBM and SWCNT moieties, does not prevent electron transfer at the P3HT-PCBM interface. These findings suggest a research perspective towards utilization of fibers of functional nanocomposites in fiber-based organic optoelectronic and photovoltaic devices. The latter can be developed in the textile-type large area photovoltaics or individual fiber-based solar cells that will broaden energy applications from macro-power tools to micro-nanoscale power conversion devices and smart textiles. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3693520>]

Optoelectronic devices based on conjugated polymers have been under tremendous interest due to their flexibility, lightweight, and low cost processing. Various polymer-based photodetectors,¹ phototransistors,² and organic photovoltaics (OPVs) have been demonstrated. The photo-induced charge transfer is a crucial step in the operation of all of these devices, and the morphology of the donor and acceptor components in their photoactive layer mostly controls the device efficiency.

In particular, intense research is directed towards the development of OPV with a bulk heterojunction (BHJ) between donor-type conjugated polymers and acceptor-type fullerenes, e.g., poly(3-hexylthiophene) (P3HT) and fullerene derivative, phenyl-C61-butyric acid methylester (PCBM).^{3,4} Upon illumination of these devices, light is absorbed by the conjugated polymer and fullerene moieties of the photoactive layer resulting in the formation of a neutral and stable excited state. Free carriers can be generated by exciton dissociation at a donor-acceptor interface, leaving the electron on the acceptor (fullerene in this case) and the hole on the conjugated polymer donor. In addition to such an efficient charge transfer, the donor and acceptor materials should form interpenetrating and continuous networks, "phase separated" on the scale of the exciton diffusion length ≤ 10 nm (Ref. 5) so as to enable transport of the charge carriers to the relevant electrodes.

While of great promise (efficiencies in excess of 8% have been reached in BHJ polymer-based OPV (Refs. 6 and 7)) combining high efficiency, stability and processability remains the greatest OPV challenge. For instance, morphological control of the BHJ photoactive layer is hard to achieve.

Yet, one may force the system into a desired configuration using strong external shear and electric fields such as those used in electrospinning of polymer solutions^{8,9} where a strong shear force is used to induce stretching and alignment of polymer chains. By introducing a step of fast quenching due to solvent evaporation, one is able to fabricate nanofibers of densely packed and oriented polymer chains. Fiber-based organic optoelectronic, electronic, and photovoltaic devices may attract additional interest due to their possible integration in smart textiles.¹⁰

A few recent studies reported electrospinning of conjugated polymers¹¹ and two-component system of PCBM and conjugated polymer (poly(p-phenylenevinylene) (PPV)¹² or P3HT (Ref. 13); for a review, see Ref. 14). In all these studies, a high molecular weight flexible nonconductive polymer was used to overcome the inherent low spinnability of the conjugated polymer.

Recently, we demonstrated that electrospinning may be used for the preparation of composite sub-micron thick fibers of the 2-component (P3HT/PCBM) and 3-component (P3HT/single-walled carbon nanotubes (SWCNTs)/PCBM) systems.¹⁵ It was found that the key to the formation of well shaped optically active fibers was the dispersion of both PCBM and SWCNT via a single dispersing agent, a

^{a)}Alexander I. Shames and Céline Bounioux contributed equally to this work.

^{b)}Author to whom correspondence should be addressed. Electronic mail: keugene@bgu.ac.il.

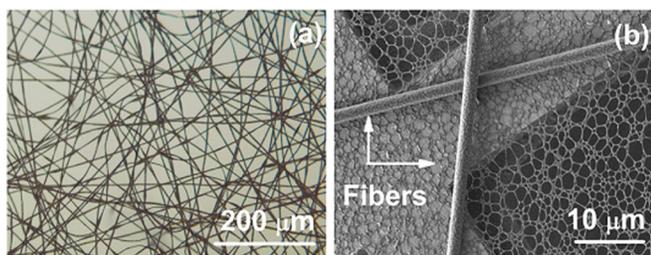


FIG. 1. (Color online) Images of electrospun P3HT fibers containing 0.1 wt. % block-copolymer, 10 wt. % PCBM, and 5 wt. % SWCNT obtained with optical microscopy (a) and SEM (b).

hexa-*p*-phenylene polyethylene oxide tri-block copolymer $(\text{PEO})_n(\text{Ph})_6(\text{PEO})_n$ (where $n = 8, 24, \text{ and } 44$). While, in previous studies,^{12,13} the insulating polymer acted as a passive component, in our study, the hexa-*p*-phenylene group of the dispersing block-copolymer was designed to physically interact with the SWCNT and PCBM moieties via π - π interactions¹⁶ (the same additive was used for the preparation of stable dispersions of individual SWCNT).

Structural characterization of these fibers indicated a high degree of ordering in the processed polymer. Furthermore, photoluminescence quenching indicated significant electronic interaction among the components. Based on these results, we speculated about the possibility of charge transfer between the donor and acceptor moieties within the fibers and suggested possible device architecture that can unify, in a single solar panel, three recently declared strategies in OPV development: BHJ solar cells based on individual fibers,¹⁷ photovoltaic textile-based solar panels,^{18,19} and OPV cells with conductive mesh grids (ITO-free devices).^{20,21}

In spite of efficient photovoltaic utilization of ternary blends with a non-conductive moiety in the standard OPV device architecture with P3HT and PCBM,²² the methods used previously in all mentioned studies of electrospun fibers^{12,13,15} do not provide univocal evidence for electron

transfer. In our fibers, as the dispersing block-copolymer acts via physical adsorption of the hexa-*p*-phenylene group onto the PCBM and SWCNT moieties,¹⁵ one may seriously suspect that the presence of the copolymer may hinder charge transfer between the P3HT and the dispersed nano-additives.

In this letter, we provide direct experimental evidence for charge transfer in P3HT/PCBM and P3HT/PCBM/SWCNT fibers using light-induced electron paramagnetic resonance (LEPR) spectroscopy.

Details of dispersions and solution preparation as well as parameters of the electrospinning process are described in Ref. 15 and supplemental material.²³ The fibers are shown in Fig. 1.

LEPR experiments at $T = 80(0.1)$ K were carried out using a Bruker EMX220 X-band ($\nu \sim 9.4$ GHz) spectrometer equipped with an Oxford Instrument ESR900 cryostat and an Agilent 53150A frequency counter. Fiber-Lite Model 3100 was used as a CW light source. Fiber samples were peeled off from the substrate with simple tape to be placed into the EPR silent 4 mm i.d. Wilmad quartz tubes sealed under 1.2 bar He pressure. Tape planes were oriented parallel to the DC magnetic field and irradiation grid directions. For the measurements described here, the spectrometer operated with 100 kHz frequency and 0.2 mT modulation amplitude, at low (200 μ W) and high (20 mW) incident microwave (MW) power levels P_{MW} . Each spectrum is a result of 25 coherent acquisitions. The g -values were calibrated against a powder sample of well purified detonation nanodiamond ($g_{\text{iso}} = 2.00282 \pm 0.00003$).²⁴ Spectra processing and parameters' calculations were done using Bruker WIN-EPR software.

Figures 2(a) and 2(b) show typical EPR spectra recorded at $P_{\text{MW}} = 200 \mu$ W for electrospun fiber samples containing, respectively, P3HT only and P3HT-PCBM. In the dark (under ambient light conditions), the P3HT sample reveals very weak EPR signal with $g_{\text{iso}} = 2.0024(2)$ (trace 1 in Fig. 2(a)). The signal saturates at $P_{\text{MW}} = 20$ mW (Fig. 3(a)). The EPR signal in the P3HT fiber demonstrates poor sensitivity to CW photoexcitation and fast decay of the LEPR signal

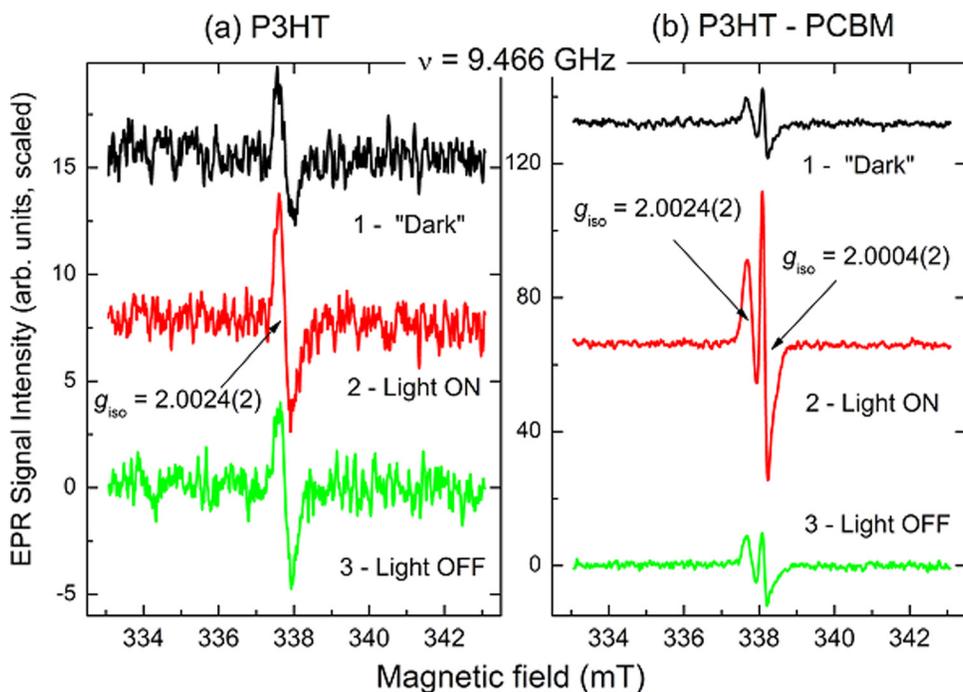


FIG. 2. (Color online) EPR and LEPR spectra of two fiber samples containing P3HT only (a) and P3HT-5% PCBM composition (b) recorded at $P_{\text{MW}} = 200 \mu$ W and $T = 80$ K. Black traces 1—spectra recorded in “dark” conditions, red traces 2—spectra recorded under CW photoexcitation (light source ON), and green traces 3—spectra recorded after the light source had been switched OFF.

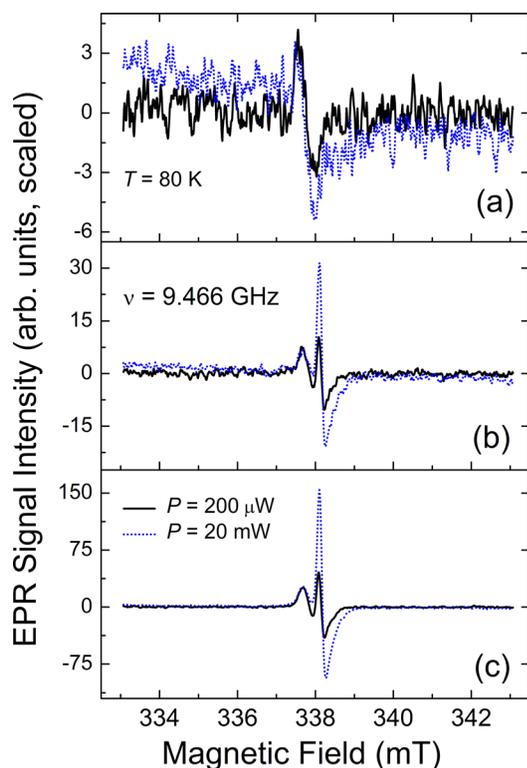


FIG. 3. (Color online) EPR and LEPR spectra recorded at $T=80$ K, $P_{MW}=200$ μ W (solid trace), and $P_{MW}=20$ mW (dotted trace): (a) fiber sample containing P3HT only, dark signal; (b) fiber sample containing P3HT-5% PCBM composition, dark signal; and (c) fiber sample containing P3HT-5% PCBM composition, light source ON.

(Figs. 2(a) and 4, trace 1). “Dark” EPR signal in the P3HT-PCBM sample is of the same order of magnitude as the corresponding P3HT signal (trace 1 in Fig. 2(b)). However, this signal consists of two components: a fast saturating component with $g_{iso}=2.0024(2)$ and another component with $g_{iso}=2.0004(2)$ that shows only slight saturation at high $P_{MW}=20$ mW (trace 1 in Fig. 3(b)). The most important result is that, in contrast with the P3HT fiber sample, the LEPR signal in P3HT-PCBM fiber is 3 times stronger (by doubly integrated intensity) than the corresponding “dark” EPR signal (trace 2 in Fig. 2(b)). Rise and decay times of both components of this LEPR signal on switching the light source ON and OFF are also very fast (traces 2–4 in Fig. 4). No signs of the persistent LEPR signals were found. The latter points out to the efficient photoinduced charge separation and absence of deeply trapped charges.²⁵

Both EPR and LEPR signals found in the fiber samples under study belong to well known types of signals observed in conjugated polymer-fullerene composites.^{26–30} Thus, the fast saturating signal with $g_{iso}=2.0024(2)$ originates from the positively charged polaron with spin $S=1/2$ formed on the polymer backbone and the slightly saturating one with $g_{iso}=2.0004(2)$ originates from the negatively charged methanofullerene (also with $S=1/2$).

Observation of “dark” EPR signals in both fiber samples indicates the presence of some impurities and chain defects or trapped positive polarons³¹ appeared due to sample preparation techniques and/or aging. Appearance of a weak LEPR signal in the P3HT sample may also originate from the inter-chain charge transfer.²⁶

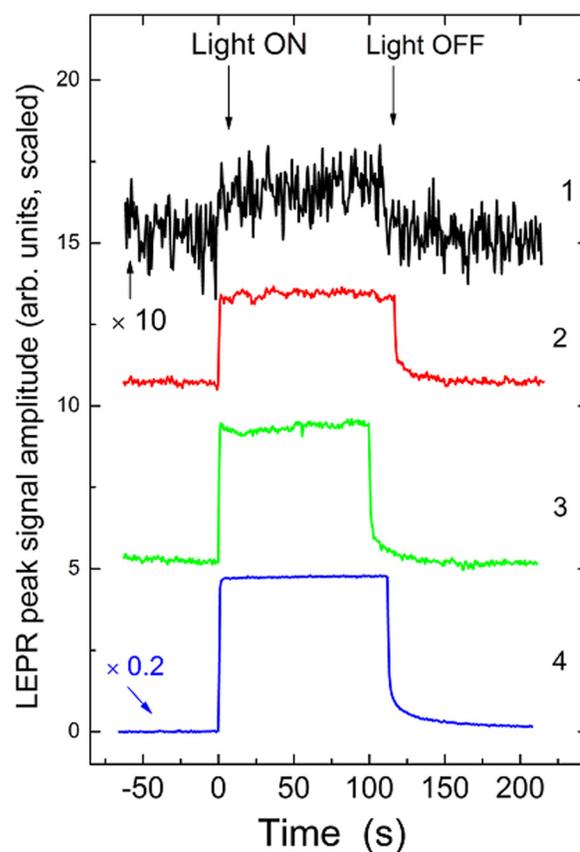


FIG. 4. (Color online) Rise and decay of the peak intensity of LEPR signals recorded at $T=80$ K: Black trace 1—fiber sample containing P3HT only, $P_{MW}=200$ μ W; red trace 2—fiber sample containing P3HT-PCBM composition, $g=2.0004$ component, $P_{MW}=200$ μ W; green trace 3—fiber sample containing P3HT-PCBM composition, $g=2.0024$ component, $P_{MW}=200$ μ W; blue trace 4—fiber sample containing P3HT-PCBM composition, $g=2.0004$ component, $P_{MW}=20$ mW.

Adding of 0.1% SWCNT to the PCBM-P3HT fiber material described above did not affect its LESR spectra that was found to be similar to those shown in Fig. 2(b).

In conclusion, the LEPR results together with the PL quenching observed previously¹⁵ provide experimental evidence of electron transfer between PCBM and P3HT components in two-component (P3HT/PCBM) and three-component (P3HT/PCBM/SWCNT) fibers and suggest that the presence of the dispersing block-copolymer does not prevent the efficiency of the electron transfer at the P3HT-PCBM interface in PCBM-P3HT and SWCNT-PCBM-P3HT fibers. Further studies of electronic transport in the fibers and, especially, the effect of the SWCNT content to electronic properties are required.

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