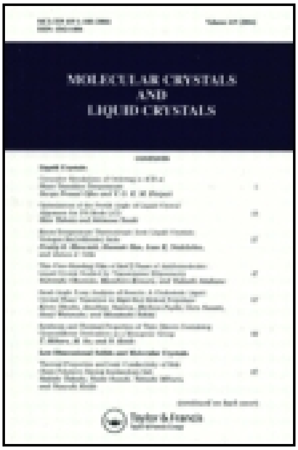

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New Photovoltaic Composite Materials Containing Fullerene Derivatives

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*A series of new nitrogen-containing fullerene derivatives: 2-azahomo[60]fullereno-(**1**) nitropyrimidine, (**2**)-phosphate, (**3**)-isocyanurate derivatives and five poly (amino)[60]fullerenes has been synthesized. Composite materials based on blends of conjugated polymer poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene (MEH-PPV) and new fullerene derivatives have been studied. We have found that the photoluminescence of MEH-PPV is quenched by a small admixture of the fullerene derivative which assumes a high efficiency of charge separation in the composite material. Photovoltaic (PV) devices based on MEH-PPV/(**1**) blends have been studied.*

Keywords: conjugated polymers; fullerenes; photovoltaics; solar cells

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INTRODUCTION

The synthesis of new materials for photovoltaic (PV) devices based on composites of conjugated polymers and fullerene derivatives is intensively investigated nowadays [1–4]. In materials of this type, the effective interaction between a conjugated polymer acting as a donor and [60]fullerene or its derivative acting as an electron acceptor takes place in the entire volume of a heterojunction. Since the semiconducting polymers are mainly processed from solutions, the search for new fullerene derivatives has to be concentrated on its solubility and the electron acceptor behavior. For this reason, we synthesized new soluble nitrogen-containing fullerene adducts by the reaction of organic azides and amines with the [60]fullerene:

(**1**) 2-azahomofullereno-5-nitropyrimidine – $C_{60}N{-}(C_4N_2H_2){-}NO_2$; AFNP

(**2**) 2-azahomofullereno-O,O-dibutylphosphate – $C_{60}N{-}PO(C_4H_9O)_2$; AFDBP

(**3**) 2-azahomofullereno-dipropyl isocyanurate pentyl – $C_{60}N{-}C_5H_{10}{-}(C_3N_3O_3(C_3H_5)_2)$; AFDPIP

(**4**) tetrakis(benzilamine)octahydro[60]fullerene – $C_{60}H_4[NH(CH_2{-}C_6H_5)]_4$; $C_{60}(ba)_4$

(**5**) tris(cycloheptylamine)hexahydro-[C_{60}]fullerene – $C_{60}H_3[NH(C_7H_{13})]_3$; $C_{60}(cha)_3$

(**6**) tetrakis(heptylamine)octahydro-[C_{60}]fullerene – $C_{60}H_4[NH(C_7H_{15})]_4$; $C_{60}(ha)_4$;

(**7**) tetrakis(dibenzylamine)octahydro[C_{60}]fullerene – $C_{60}H_4[N(CH_2{-}C_6H_5)_2]_4$; $C_{60}(dba)_4$;

(**8**) tris(cyclopentylamine)hexahydro-[C_{60}]fullerene – $C_{60}H_3[NH(C_5H_9)]_3$; $C_{60}(cpa)_3$;

The synthesized fullerene derivatives **1–8** are better electron acceptors than C_{60} and PCBM (where PCBM – 1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]C_{61} – the methanofullerene derivative which is widely used in PV devices [1–4]). In photoluminescence experiments, the current-voltage measurements were performed on the prototypes of PV cells based on MEH-PPV and blends MEH-PPV/fullerene derivative to investigate the charge transfer process.

EXPERIMENTAL

MEH-PPV was synthesized by the method of Ref. [5]. The synthesis of azahomofullerenes and poly(amino)fullerenes is described elswere [6–8]. The cyclic voltammograms (CV) of fullerene derivatives were measured in the mixture of o-dichlorobenzene/MeCN with glassy carbon electrode and 0.1 M Bu_4NBF_4 supporting electrolyte vs

0.01 M Ag/AgNO$_3$ reference electrode as described elsewhere [7]. Composite films of MEH-PPV/fullerene derivative were prepared from toluene or chlorobenzene solutions containing MEH-PPV and fullerene in a proper proportion by the spin cast method. Photoluminescence (PL) measurements were performed with a high-power 450-nm light-emitting diode as a light source and a PC1000 plug-in spectrometer (Ocean Optics). For the current-voltage measurements, thin films (100–150 nm) were spin-casted on ITO coated glass substrates, vacuum-dried at $t = 100^\circ$C, and an aluminum electrode was evaporated on top. The technique of photocurrent measurements is described in Ref. [9]. The photocurrent measurements were performed at a pressure of about 10^{-5} Torr at room temperature. The light source consisted of a high-pressure xenon lamp and a set of filters that transmitted the 400–650-nm light with a power of 20 mW/cm^2 [9].

RESULTS AND DISCUSSION

We have synthesized a series of azahomofullerenes and poly(amino)-fullerenes **1–8**. The structures of the adducts were characterized by ^{13}C NMR, ^{1}H NMR, UV- and IR spectroscopies, and cyclic voltammetry. Peak potentials of the first waves in CV of **1–8** are by 10–120 mV less negative than that of parent C$_{60}$. (Peak potential of C$_{60}$ measured under the same conditions is −0.83 V.) This means that the synthesized fullerene derivatives are better electron acceptors than C$_{60}$ itself and of PCBM (the potential of PCBM is by 0.09 V more negative than that of C$_{60}$).

The UV-VIS and IR spectra of MEH-PPV/fullerene derivatives composite films are simple superpositions of those of the components. As an example, the UV-VIS spectra of MEH-PPV and MEH-PPV/**1** spectra are shown in Figure 1. This means that there is no ground-state interaction between the components. It is known that the MEH-PPV/C$_{60}$ system is characterized by a strong interaction between the excited state of MEH-PPV and C$_{60}$, which leads to the photoinduced electron transfer from the excited state of MEH-PPV onto C$_{60}$ [1–4]. One of the consequences of this interaction is the strong quenching of the originally effective photoluminescence (PL) of MEH-PPV [4]. We have studied the PL of our MEH-PPV/fullerene composite films.

Figure 2 shows the dependences of the intensities of the MEH-PPV PL band at 585 nm in MEH-PPV/fullerene films on the contents of the fullerene derivatives. In all the cases, the PL band intensity decreases with increase in fullerene contents. The most strong quenching is observed in the composites with **1** and **2** (PL of MEH-PPV is almost completely quenched by less than 7% admixture of the fullerene

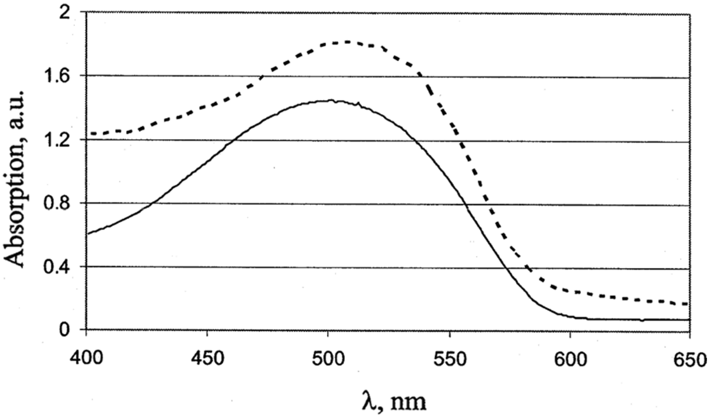

FIGURE 1 UV-VIS absorption spectra of the films of MEH-PPV (solid line) and of the blend containing MEH-PPV and 50 wt.% of **1** (dashed line).

derivative), which implies the most strong photoinduced electron transfer from MEH-PPV to these fullerene derivatives [6].

Solid lines in Figure 2 represent a fit of the Stern-Volmer type $I/I_0 = 1/(1+kC)$ where C is the fullerene concentration in weight % and k is constant for the given fullerene. Parameters k for the fullerene derivatives studied are listed in Table 1. This parameter can be a measure of acceptor properties of fullerene derivatives. For comparison, an analogous fit gives $k = 3.21$ for C_{60} and $k = 2.56$ for PCBM [10]. Thus, compound **1** is a stronger acceptor than C_{60} and PCBM, and compounds **2**, **6**, and **7** have acceptor properties comparable to those of PCBM.

We have studied the photovoltaic properties of the composite films of MEH-PPV containing azahomofullerene **1**. Films MEH-PPV/C_{60} prepared under the same conditions were also studied for comparison. Figure 3 show the dependences of the photocurrent on the electric field strength for the MEH-PPV/**1** and MEH-PPV/C_{60} based PV devices with different fullerene contents. The data were obtained with the illumination in the spectral region of 400–650 nm which is the region of the absorption of polymer/fullerene composite films (Fig. 1). The photocurrent increases strongly when fullerene is added to pure MEH-PPV. For the mixture with 75% of **1**, the short-circuit current is by more than two orders of magnitude higher than that of a pure MEH-PPV device (Fig. 3a).

For the composite film containing C_{60}, we see that the photocurrent increases with the fullerene content up to 50% and decreases at a

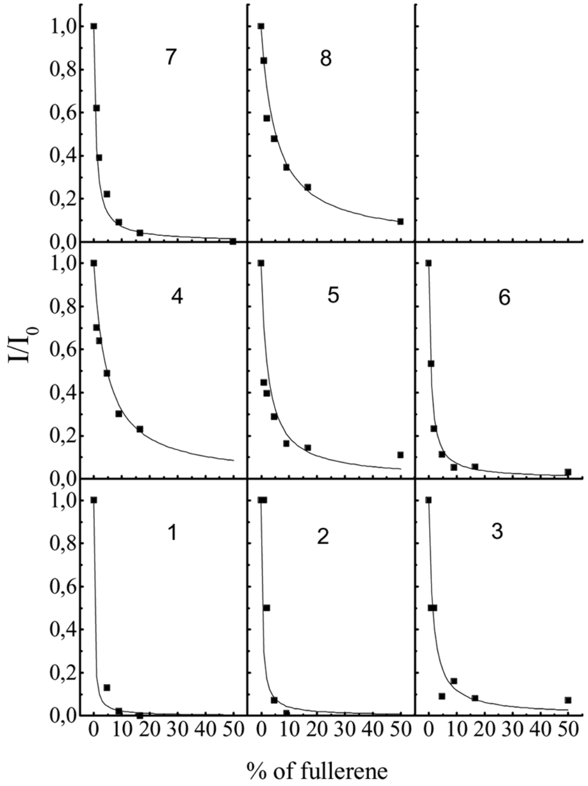

FIGURE 2 Dependences of relative intensities of the MEH-PPV PL band in MEH-PPV/fullerene films on the contents of fullerene. 1 – AFNP; 2 – AFDBP; 3 – AFDPIP; 4 – $C_{60}(ba)_4$; 5 – $C_{60}(cha)_3$; 6 – $C_{60}(ha)_4$; 7 – $C_{60}(dba)_4$; 8 – $C_{60}(cpa)_3$. Solid curves represent Stern-Volmer fits.

higher C_{60} content (75%) (Fig. 3b). On the contrary, for the MEH-PPV/**1** composite, the photocurrent at the 75% fullerene content is much higher than that for the 50% content (Fig. 3a). Such a discrepancy between the properties of C_{60} and **1** containing composites may

TABLE 1 The Parameters of Stern-Volmer Fits

Fullerene	k	Fullerene	k
(**1**) AFNP	4.53	(**5**) $C_{60}(cha)_3$	0.20
(**2**) AFDBP	2.74	(**6**) $C_{60}(ha)_4$	1.31
(**3**) AFDPIP	0.33	(**7**) $C_{60}(dba)_4$	1.32
(**4**) $C_{60}(ba)_4$	0.22	(**8**) $C_{60}(cpa)_3$	0.19

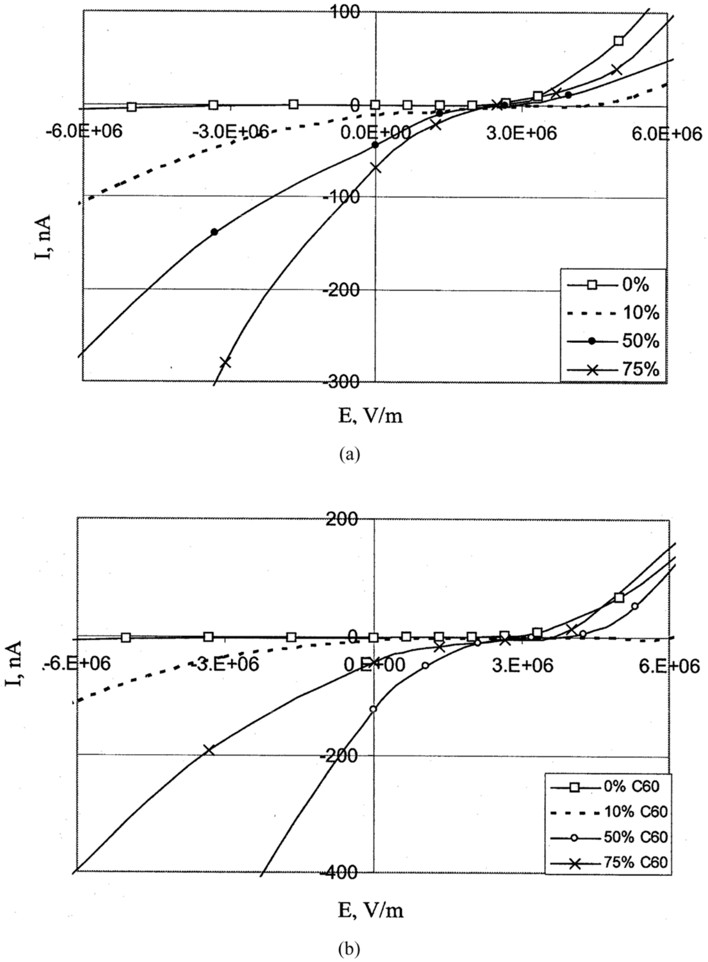

FIGURE 3 Dependences of the photocurrent on the electric field strength for PV devices: (a) MEH-PPV/**1** based devices with fullerene contents of 0, 10, 50, and 75 wt.%. (b) MEH-PPV/C_{60} based PV devices with fullerene contents 0, 10, 50, and 75 wt.%.

be due to differences in the morphology of the fullerene species in the polymer matrix.

Figure 4 shows the transmission electron micrographs (TEM) of the composite films comprising the **1** additive. It is seen that the aggregation of the **1** molecules at low concentrations (up to 10 w/w%) results in the appearance of large rod-like formations, whose characteristic thickness is approximately 100 nm and the length is of several

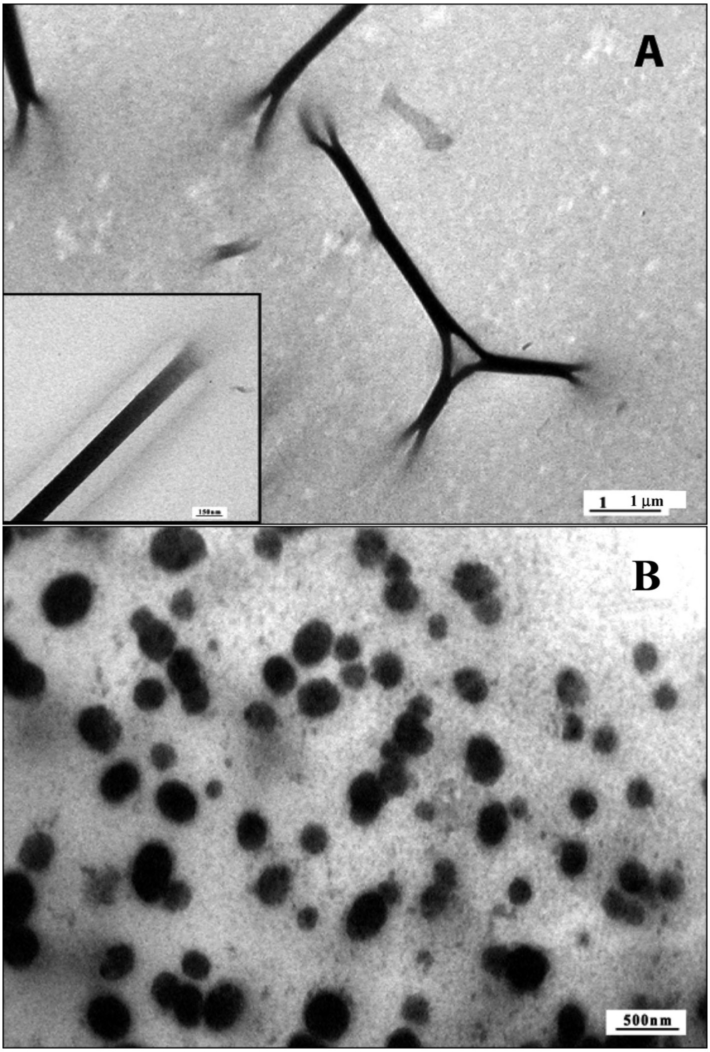

FIGURE 4 TEM image of MEH-PPV/**1** composite films with the contents of the fullerene derivative: 10 w/w% (A) and 50 w/w% (B).

micrometers. Thus, it is seen that fullerene derivatives **1** (AFNP) can form linear extended structures. Considering the great interest in extended nanosize structures (for example, carbon nanotubes and quantum wires), one could expect that this compound would widely be used in modern science and technology. It is also seen from the micrograph that there are no smaller **1** aggregates between rod-like ones that allows us to conclude that all or almost all acceptor molecules introduced were involved in the formation of aggregates. The further increase in the concentration of **1** resulted in essential changes in the composite system morphology. For example, the film containing 50 w/w% of an acceptor is observed to comprise ball-shaped aggregates with 100÷400-nm characteristic sizes. Seemingly, the increase in the amount of the acceptor in the film changed the character of the intermolecular interaction of azahomofullerene, which resulted in changes in the film morphology. On the whole, though the aggregates are distributed uniformly enough in the bulk, some adjacent aggregates are observed to agglomerate.

The study of the morphology of composite films comprising C_{60} as an acceptor showed the latter one to exhibit an essentially lower tendency to the aggregation in contrast to **1**. Figure 5 shows the TEM electron micrographs of a MEH-PPV/C_{60} film with the 50% concentration of C_{60}. It is seen from Figure 5 that fullerene is arranged uniformly enough in the film. Light spots seem to be holes, which appeared as a result of the film separation from a quartz support during the preparation of samples to be studied in a transmission electron microscope. The insert shows a portion of the film on the 25-nm scale. One

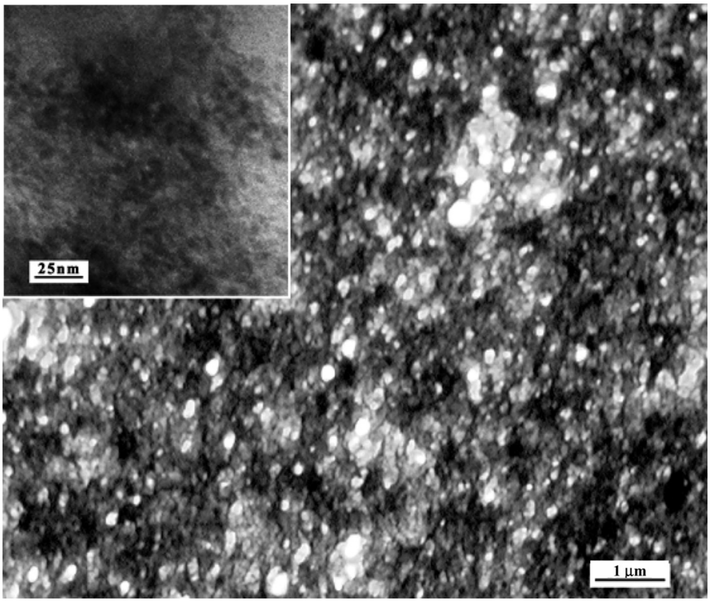

FIGURE 5 TEM image of a MEH-PPV/C_{60} composite film with a fullerene content of 50 w/w%.

can conclude that fullerene is insignificantly aggregated in the film. This is in concordance with the data of Ref. [11], where TEM investigations of MEH-PPV/C_{60} composite films revealed nanoparticles of C_{60} with dimensions around 10 nm and showed that the finest phase separation takes place at compositions of near 1:1 by weight.

CONCLUSION

We have synthesized 8 new azahomofullerenes and poly(amino)fullerens and investigated their charge transfer and photovoltaic properties in composite films MEH-PPV/fullerene. The variation of the polymer PL intensity by changing the volume percent of fullerene offers a useful tool to study the acceptor properties of fullerene derivatives. According to this test, compounds **1** and **2** showed a stronger acceptor strength comparing to those of C_{60} and PCBM. Compound **1** showed the results comparable with those for C_{60} in the photovoltaic cells based on MEH-PPV/fullerene composite fims. The morphologies of **1** and C_{60} species in the MEH-PPV matrix are sufficiently different. It is of interest to study the charge transfer and photovoltaic properties of the new fullerene derivatives in composites with other conjugated polymers.

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