

# Near IR photoluminescence in mixed films of conjugated polymers and fullerenes

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The photoinduced electron transfer between conjugated polymers and a series of functionalized fullerenes was studied. A new photoluminescence signal was observed in the near IR ( $\sim 1.4$  eV). This weak IR photoluminescence does not result from direct excitation of the fullerene, but from radiative electron-hole recombination between the fullerene excited state and the polymer ground state. The intensity of this recombination luminescence depends on the electrochemical nature of the functional group; it is observed only for fullerenes with first reduction potential higher than that of  $C_{60}$ . © 1997 American Institute of Physics. [S0021-9606(97)51331-6]

## I. INTRODUCTION

Photoinduced electron transfer between semiconducting  $\pi$ -conjugated polymers and fullerenes was shown to be an efficient process, with a quantum yield for charge separation close to unity.<sup>1-4</sup> Electron transfer has been demonstrated to occur in blends of  $C_{60}$  with semiconducting polymers from the polythiophene and poly(*p*-phenylene-vinylene) families<sup>5</sup> as well as with various oligomers.<sup>6</sup> The charge separated state is metastable; although the forward charge transfer occurs on the sub-picosecond time scale, the back charge transfer rate is many orders of magnitude slower.

The development of fullerene chemistry has led the way to the synthesis of various fullerenes, methanofullerenes,<sup>7,8</sup> and heterofullerenes (where a carbon atom in the  $C_{60}$  cage was replaced with a nitrogen).<sup>9</sup> As described elsewhere,<sup>10</sup> the functional group bonding can be realized either by breaking a carbon-carbon bond between two six membered rings (a methanofullerene with 58  $\pi$  electrons) or by breaking the bond between a six membered ring and a five membered ring (a fulleroid with 60  $\pi$  electrons). The heterofullerenes form a different class of molecules and have 60  $\pi$  electrons.

With the availability of a number of functionalized fullerenes (Fig. 1), it becomes possible to investigate more deeply the photophysics of conjugated polymer/fullerene mixtures. The acceptors shown in Fig. 1 vary in the nature of the side groups added to them, thereby leading to somewhat different electronic and optical properties. We report here on the observation of near-IR (NIR) photoluminescence (PL) from blends of the fullerenes and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV). In all of the samples studied, the intense PL of MEH-PPV in the blend was quenched by  $\sim 3$  orders of magnitude, compared to the neat polymer. This quenching effect results from nonradiative decay of the excitation energy on the polymer

as a result of efficient electron transfer to the fullerene.<sup>1</sup> Thus, in all samples studied, efficient electron transfer takes place upon excitation. In a previous report, electron transfer between a conjugated polymer and fullerenes **7** and **12** (synthesized for improved miscibility in polymer/fullerene blends) was described.<sup>11</sup> The main conclusion was that the near steady-state photoinduced absorption (PIA) spectra of the electron transfer products were not significantly changed by using a functionalized fullerene. This was interpreted in terms of the small perturbation by the side group on the  $C_{60}$  electronic structure. For example, the relatively high electron affinity of  $C_{60}$  is maintained in the functionalized fullerenes regardless of the addition of side groups. Although the degeneracy is lifted, the actual splitting between formerly degenerate energy levels is small.

In the polymer/fullerene mixtures studied here, NIR PL was not detected for all blends under identical conditions. This indicates that although the electronic perturbation is small, the nature of the fullerene modification plays a role in the photophysics of the system. Despite the small intensity of the NIR PL (of the order of magnitude of the quenched polymer PL signal), it may serve as a probe into the electronic processes which occur in the excited state and thus help in understanding the photophysics of polymer/fullerene blends.

## II. EXPERIMENT

MEH-PPV (Uniax Corporation) and polystyrene (Aldrich) were used as received. The syntheses of **1**,<sup>12(a)</sup> **2-5**,<sup>12(b)</sup> **6**, **7**, **12**,<sup>12(c)</sup> **9**,<sup>12(d)</sup> **10**,<sup>12(e)</sup> **11**,<sup>12(f)</sup> and **8**, **13-16**<sup>12(g)</sup> are described elsewhere. Films of the fullerene/polymer blend (5 wt % of fullerene) were prepared by spin-casting from *o*-dichlorobenzene (ODCB) solutions onto sapphire substrates. Films of the fullerenes in polystyrene (1 wt %) were prepared by drop casting from an ODCB solution. The

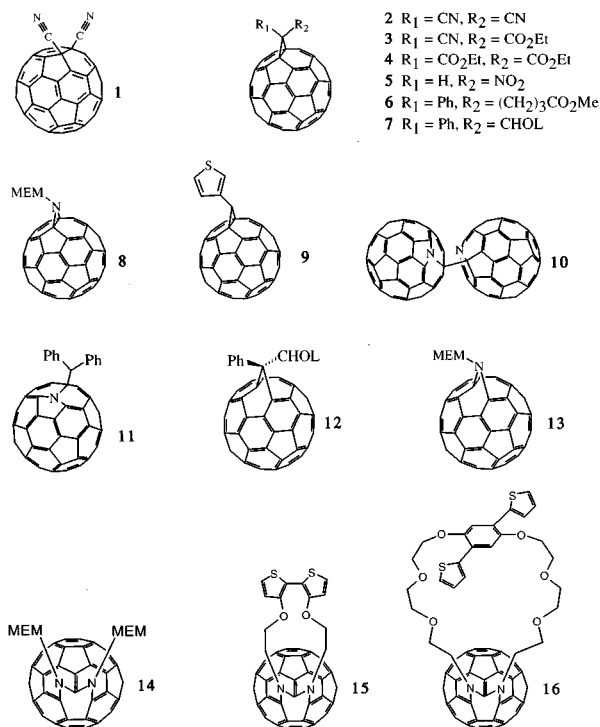


FIG. 1. Structures of the fullerene acceptors used in this study.

samples were mounted on a cryostat held at 80 K in high vacuum ( $\sim 10^{-5}$  Torr). Photoluminescence measurements were performed by exciting the films with an Argon-ion laser (488 nm, 50 mW) and dispersing the emission with a grating monochromator. The beam was mechanically chopped (15–4000 Hz) and the modulated signal was phase sensitively recorded using a lockin amplifier and a two-color (Si/PbS) detector.

### III. RESULTS AND DISCUSSION

Photoexcitation of MEH-PPV in a polymer/ $\text{C}_{60}$  mixture leads to formation of the  $\text{C}_{60}$  radical anion,  $\text{C}_{60}^-$ , and a radical cation on the polymer. The PL spectrum which is observed from such mixtures is predominantly that of the highly luminescent polymer, i.e., from pair excitations which did not transfer an electron. The MEH-PPV emission spectrum is characterized by a 0–0 transition at 2.05 eV and two other vibronic transitions with a separation of  $\sim 0.18$  eV (Fig. 2).

The lowest electronic transitions in  $\text{C}_{60}$  are dipole forbidden because both the electronic ground state and the first excited state have the same parity ( $A_g$  and  $T_{1g}$ , respectively). The weak PL observed in  $\text{C}_{60}$  was explained in terms of a Herzberg–Teller coupling where the first excited state acquires *ungerade* character via adiabatic vibronic coupling with higher states, making the transition partially dipole allowed.<sup>13</sup> Emission from  $\text{C}_{60}$  films peaks at 1.69 eV with a shallow tail extending to the NIR spectral range.<sup>14</sup> Therefore, one expects the emission from the photoexcited polymer and from  $\text{C}_{60}$  to overlap. NIR PL from the  $\text{C}_{60}$  radical anion was reported for electrochemically reduced fullerenes in solution.<sup>15</sup> It was assumed that the odd electron is located in

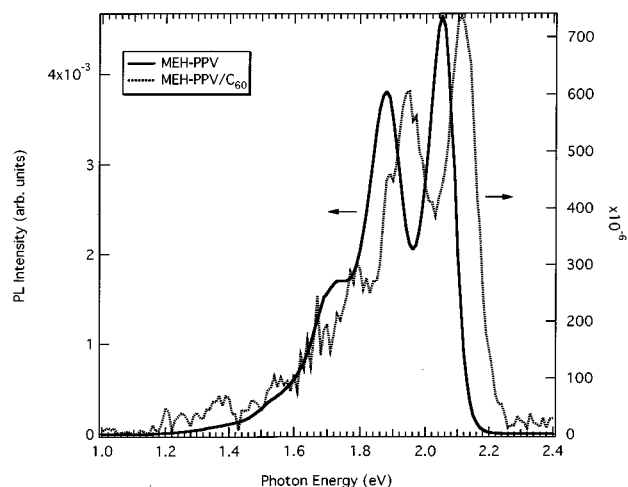


FIG. 2. Photoluminescence spectra of MEH-PPV film (left-hand axis) and MEH-PPV/ $\text{C}_{60}$  mixture (right-hand axis). Excitation at 80 K from the 488 nm line of an  $\text{Ar}^+$  ion laser at  $50 \text{ mW/cm}^2$ , chopped at 273 Hz.

all three  $t_{1u}$  LUMO states and in the  $t_{1g}$  LUMO+1 states, and that the observed transition is:  ${}^2T_{1g} \rightarrow {}^2T_{1u}$ . We find, however, that the PL spectrum of the blend is composed entirely of emission from the highly luminescent polymer, with no apparent contribution from  $\text{C}_{60}^-$  (Fig. 2).<sup>1</sup> Nonradiative decay of the unpaired electron on  $\text{C}_{60}^-$  occurs via a reverse electron transfer that returns the neutral species to the ground state within a few milliseconds.

Inspection of the mixture and neat polymer PL traces shows that they are identical, except for a blue shift of the blend PL with respect to the neat polymer PL. This shift is a typical feature found in the emission spectrum of MEH-PPV/ $\text{C}_{60}$  or in those of MEH-PPV and acceptors 1–16, and varies between 10 and 70 meV. The source for this shift is inferred from quantum chemical calculation of the changes in geometry of the polymer when  $\text{C}_{60}$  is introduced into the matrix.<sup>16</sup> These calculations show that intermolecular interactions cause the polymer to modify its equilibrium geometry in order to accommodate the  $\text{C}_{60}$  within its vicinity. The smaller Stokes shift implies that the lattice relaxation is reduced giving rise to the blue shifted emission.

The PL spectra of MEH-PPV mixtures with acceptors 9 and 16 are shown in Fig. 3(a), along with that of neat MEH-PPV. It is quite clear that in these blends, there is an additional broad NIR PL signal between 1.1 and 1.6 eV, with a peak at  $\sim 1.4$  eV. Similar spectra were detected for many of the other acceptors; the results are summarized in Table I. In polymer mixtures with a number of methanofullerenes, fulleroids and both heterofullerenes [see Fig. 3(b)], the emission spectrum was identical to that of MEH-PPV/ $\text{C}_{60}$  and no NIR PL was detected concurrently with that of the polymer (see also Table I). The occurrence of the NIR PL does not result from transitions within the fullerenes (i.e., from direct photoexcitation of the molecules). We have measured the emission spectra from several different fullerenes (2, 4, 5, and 6 of Fig. 1) dispersed in polystyrene; i.e., without conjugated polymer. In each case, the emission peaks at

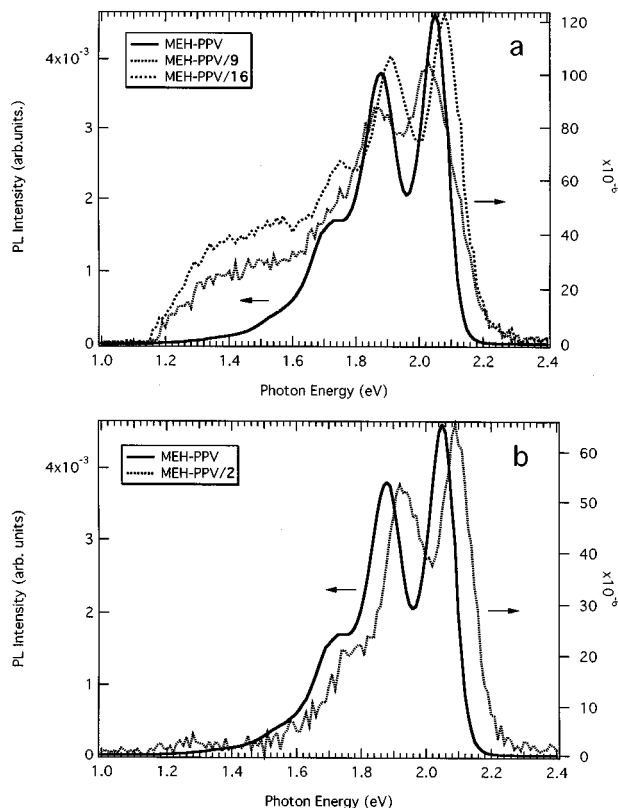


FIG. 3. (a) Photoluminescence spectra of MEH-PPV/fullerenes **9** and **16**; (b) PL spectra of MEH-PPV/2. Experimental conditions as in Fig. 2.

$\sim 1.7$  eV, as with  $C_{60}$ ,<sup>14</sup> consistent with the assumption that the functionalization of fullerenes does not lead to a large perturbation in the electronic structure of  $C_{60}$ . As an additional check, we measured the PL spectra from a series of MEH-PPV/**12** samples, where the fullerene weight fraction was varied between 5% and 50% [Fig. 4(a)]. As the fullerene concentration is increased, the polymer PL is quenched until it is almost unobservable in the 50% blend, indicating that electron transfer is competing efficiently with radiative recombination within the polymer. The NIR PL at 1.38 eV is detectable at all concentrations. In Fig. 4(b), we compare the

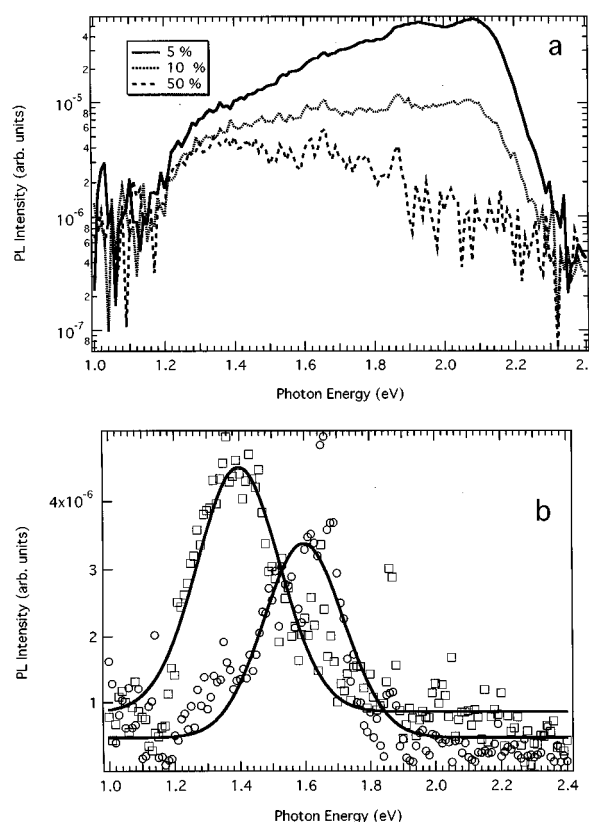


FIG. 4. (a) Photoluminescence of MEH-PPV/**12** at 5, 10, and 50 wt % of the fullerene; (b) circles: PL from a drop cast film of **12**, squares: PL from the MEH-PPV/**12** (50%) blend. The superimposed lines are the result of a fit to a Gaussian and serve to guide the eye. Experimental conditions as in Fig. 2.

PL trace of the 50 wt % blend with that of pure fullerene **12**. In the blend, the NIR PL signal is red shifted by about 0.2 eV with respect to the neat film. We conclude, therefore, that the NIR PL found in these mixtures results from the photoinduced electron transfer and not from a transition induced by direct excitation of the fullerene. Therefore, two questions arise. What is the mechanism leading to the NIR emission? Why is the NIR emission detected from blends with specific

TABLE I. Photoluminescence properties of MEH-PPV fullerene blends.

Fullerene	$\Delta E_1^a$	PL <sup>b</sup>	$\pi$ electrons	Fullerene	$\Delta E_1^a$	PL <sup>b</sup>	$\pi$ electrons
$C_{60}$	0	–	60	<b>9</b>	(–)	+	58
<b>1</b>	+121	–	58	<b>10</b>	+131	–	60
<b>2</b>	+156	–	58	<b>11</b>	+41	–	60
<b>3</b>	–10	+	58	<b>12</b>	(–)	+	60
<b>4</b>	–41	+	58	<b>13</b>	(–)	+	60
<b>5</b>	–40	+	58	<b>14</b>	–40	+	60
<b>6</b>	–110	+	58	<b>15</b>	–57	+	60
<b>7</b>	(–)	+	58	<b>16</b>	–53	+	60
<b>8</b>	(–)	+	58				

<sup>a</sup> $\Delta E_1 = E_1(x) - E_1(C_{60})$  in meV ( $x = \mathbf{1-16}$ ),  $E_1$  is the first reduction potential of the functionalized fullerene. Signs in parentheses are used where a complete CV has not been measured. From the similarity of some functional groups, a reasonable estimate of the sign of  $\Delta E$  can be made.

<sup>b</sup>PL in the NIR, a “+” sign indicates that NIR PL was detected, a “–” sign means that the only PL measured was that of MEH-PPV.

derivatives of  $C_{60}$  but not from blends with other functionalized fullerenes?

### A. Nature of the NIR PL signal

The current picture of electron transfer in polymer/fullerene blends is one where a charge separated state is formed within few hundreds fs. This state is metastable and relaxes by a reverse electron transfer from the fullerene LUMO to the polymer HOMO (relaxation to the fullerene HOMO cannot take place as that level is filled). Within this framework, there are two possible mechanisms for the observed emission:

- (i) Radiative transition from an excited state of the fullerene anion; and
- (ii) radiative transition between the fullerene LUMO and the polymer HOMO.

In the first case, a radiative transition of the unpaired electron between two of the energy levels of the fullerene anion would precede a nonradiative recombination of the electron-hole pair (the reverse electron transfer). Since this transition cannot be a LUMO→HOMO recombination, it would necessarily be between the fullerene excited states. The transition energy between the first two excited states of  $C_{60}(t_{1g} \rightarrow t_{1u})$  was found to be 1.1 eV.<sup>17</sup> Upon modification of the molecule, the symmetry is lowered, and these levels are expected to split. A recent calculation of the heterofullerene  $C_{59}N$  has shown that lowering of the symmetry splits the triply degenerate  $t_{1u}$  state into one singlet and a twofold degenerate level.<sup>18</sup> A similar splitting scheme can be assumed for the higher energy levels. Since the perturbation to the electronic structure of  $C_{60}$  was found to be small, we can rule out a transition within the states derived from either  $t_{1u}$  or  $t_{1g}$  (between the singlet and twofold degenerate states), as that would lead to a PL signal at about 0.5 eV. We can assume that the observed NIR PL is occurring between new levels which originate from  $t_{1g}$  to new levels which originate from  $t_{1u}$  in  $C_{60}$ . Such a scheme could explain the ~1.4 eV energy difference inferred from the PL.

A second possible mechanism involves direct recombination of the transferred electron on the fullerene with the hole in polymer ground state. Since the NIR PL signal is very weak, we assume that this radiative recombination takes place concurrently and in competition with reverse nonradiative electron transfer; the latter being the main decay route. In this case, all transitions within the fullerene excited states are nonradiative and an electronic matrix element exists which couples the wave functions of the hole and the electron in their respective states. Such a transition is possible only if there is overlap between the polymer and fullerene wave functions such that a dipole transition is allowed.

In order to differentiate between the two mechanisms, we have repeated the NIR photoluminescence experiments using blends of the fullerenes and a different conjugated polymer, poly(2-butyl,5-(2'-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV). The advantage of using BuEH-PPV is that its emission spectrum is blue shifted with respect to that

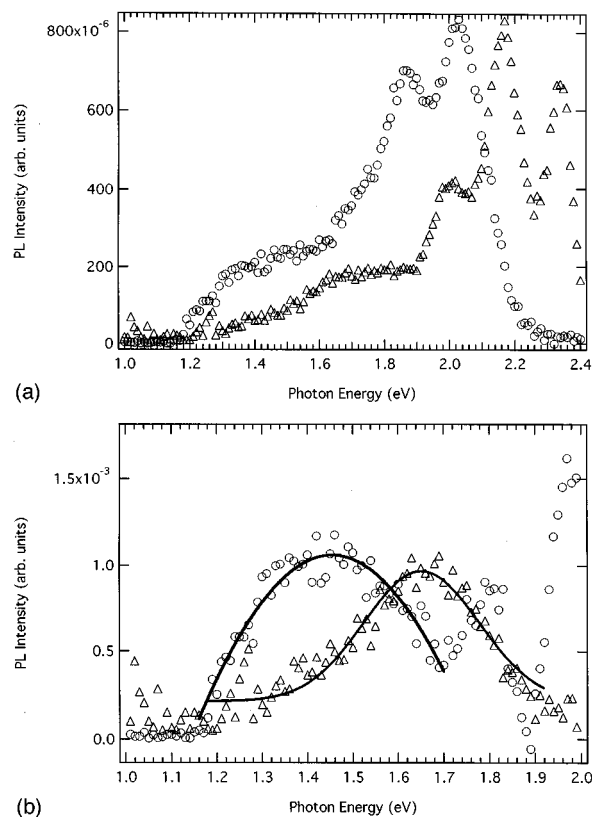


FIG. 5. (a) Photoluminescence of BuEH/9 (circles) and MEH-PPV/9 (triangles); (b) same as in a but with the neat polymer PL subtracted from the blend PL. Experimental conditions as in Fig. 2.

of MEH-PPV. The PL spectrum of the BuEH/9 mixture is shown in Fig. 5(a) and compared with that of MEH-PPV/9. It is clear that the peak of the NIR PL has shifted from ~1.4 eV in MEH-PPV blends to ~1.65 eV in BuEH blends. The blue shift of the NIR PL is more clearly seen in Fig. 5(b) where the PL spectrum of the neat polymer was subtracted from that of the blend for both polymers. The PL peak is blue shifted by 0.2 eV in BuEH/9. If this transition were between fullerene energy levels, changing the polymer should not have had any effect on the NIR spectrum. Apparently, all transitions between the fullerene excited-state levels (described above) are nonradiative. Thus, we attribute the origin of the NIR PL to electron-hole recombination between the polymer and fullerene.

Measurements of the NIR PL intensity dependence on the pump chopping frequency show no frequency dependence up to  $10^4 \text{ s}^{-1}$ , implying that the radiative emission occurs within a time period less than about 100  $\mu\text{s}$  after the initial charge transfer. The longer lived charge transferred species [observed, for example, in photoinduced absorption and in photoinduced ESR (electron spin resonance) experiments] decay nonradiatively. One possibility is that the NIR emission takes place immediately after charge transfer, before the self trapping (polaron effects) which subsequently inhibit the reverse electron transfer.

## B. Dependence of the NIR PL on the fullerene addend group

A model which explains the difference between NIR emitting and nonemitting fullerenes on the basis of differences in the electronic structure can be eliminated. These molecules can be grouped into two categories, the first being fullerenes with 60  $\pi$  electrons, and the second those with 58  $\pi$  electrons (Table I). The occurrence of NIR PL in both molecules **8** and **13**, for example, which are the azamethanofullerene and azafulleroid versions of a methoxyethoxymethyl (MEM) substituted fullerene, respectively, clearly demonstrates that the number of  $\pi$  electrons is not important, nor is the nature of the side-group bonding to the  $C_{60}$  (bonding by cleavage of a C–C bond between two six member rings vs bonding by cleavage the bond between a six member ring and a five member ring).

A similar argument demonstrates that the NIR PL is not related to the difference in solubilities of the different acceptors (which could enhance optical features through film quality). A very soluble fullerene such as **12** gave practically the same NIR PL as a weakly soluble fullerene such as **13**. Moreover, in all cases (including the ones where no NIR PL is found), the PL of the polymer is quenched by  $\sim 3$  orders of magnitude, indicating that good mixing was achieved such that the polymer and fullerene electronic wave functions overlap and efficient electron transfer occurs.

Depending on the nature of the side group, the redox properties of fullerenes **1–16** vary; some are easier to reduce than  $C_{60}$  while others are more difficult to reduce. From Table I, a clear correlation is seen between the first reduction potential ( $E_1$ ) of each fullerene and its NIR emission spectrum: All fullerenes whose first reduction potential is higher than that of  $C_{60}$  give rise to the NIR PL, while  $C_{60}$  itself and the more electronegative fullerenes do not. The effect of the side group on the fullerene redox properties results from the existence of a balance between the side-group electrochemical properties (i.e., electron withdrawing or donating) and the negative shift of the  $C_{60}$  reduction potential following saturation of a double bond.<sup>12(b)</sup> Recent theoretical studies on the influence of donor–acceptor substitution in phenylene vinylene oligomers have shown that the frontier levels are shifted from their nonsubstituted positions.<sup>19</sup> Similar arguments can be applied here. Substitution with an electron withdrawing group stabilizes the HOMO and LUMO while substitution with an electron donating group destabilizes them. In both cases a red shift occurs in the absorption. Although this shift of the energy levels may give rise to the NIR PL, we can rule it out since that would imply that PL from photoexcited fullerene films will occur also in the NIR. As described above, this is not the case (the PL in the neat fullerene films results from electron-hole recombination within the fullerene HOMO and LUMO). In the case of fullerenes **1–16**, the energy shifts and the degree of their asymmetry are directly linked to the electrochemical nature of the side group. In the case of fullerenes with an electron donating side group, the destabilization of the frontier energy levels apparently leads to the required coupling between the

fullerene LUMO and the polymer HOMO such that the radiative recombination can take place. The opposite is true for fullerenes with an electron withdrawing side group where the stabilization of the frontier levels (e.g., lowering of the gap energy) inhibits the radiative recombination.

## IV. SUMMARY AND CONCLUSION

We have described the detection of PL in the NIR region in mixtures of conducting polymers and substituted fullerenes. Although the exact mechanism leading to this PL is not clear, the available evidence implies that it arises from direct electron-hole recombination between the fullerene and polymer. This radiative recombination occurs prior to, or concurrently with the dominant nonradiative electron transfer. The dependence of the PL signal on the nature of the substituent group results from the stabilization–destabilization effect that an electron donating or withdrawing group has on the fullerene electronic structure.

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