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Photoinduced electron transfer from π -conjugated polymers onto Buckminsterfullerene, fullerooids, and methanofullerenes

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We present near-steady-state photoinduced absorption (PIA), photoluminescence, and light-induced electron spin resonance (LESR) studies on photoinduced electron transfer reactions from poly(bis-2,5-*epi*-cholestanoxo-1,4-phenylene vinylene) (BeCHA-PPV) as a donor to Buckminsterfullerene (C_{60}) and a number of functionalized fullerenes as acceptors. We show that functionalized fullerenes with a solubilizing side chain linked to C_{60} in a [5,6] (fulleroid) or [6,6] (methanofullerene) fashion, are efficient electron acceptors towards BeCHA-PPV, as evidenced from changes in the PIA, the efficient quenching of the photoluminescence, and the LESR spectra of BeCHA-PPV cation and fullerene anion radicals. The increased miscibility of the functionalized fullerenes with the conjugated polymer as compared to C_{60} , can be important for the preparation of future electrooptic devices, based on the photoinduced charge separation. © 1995 American Institute of Physics.

I. INTRODUCTION

Since the discovery that photoexcitation of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) across the π - π^* energy gap in a composite film with Buckminsterfullerene (C_{60}) results in an electron transfer reaction,^{1,2} various π -conjugated polymers and oligomers have been found to act as efficient excited state electron donors towards C_{60} .² The electron transfer to C_{60} quenches the photoluminescence of MEH-PPV by three orders of magnitude, implying that in composite films there is a process that is competing efficiently with dipole-allowed radiative emission. This provides an estimate to the electron-transfer time of less than one picosecond. Time-resolved photoinduced absorption (PIA) spectroscopy experiments, which directly measured the electron transfer rate, confirmed this estimate. By measuring the dichroic ratio an upper limit of 300 fs on the charge-transfer time has been obtained.³ Since electron transfer in polymer/ C_{60} mixtures occurs orders of magnitude faster than any competing process, the quantum efficiency for the production of charged photoexcitations is considerably enhanced. The rate for back electron transfer (i.e., recombination of electrons and holes) is many orders of magnitude lower, as evidenced from the observation of the radical ions of the conjugated polymer and C_{60} using near steady state PIA spectroscopy and light-induced electron spin resonance (LESR) spectroscopy, which detect species with lifetimes in the microsecond and millisecond domains.^{1,2(b)-2(d),4} Additional evidence for fast forward and slow back electron transfer has been obtained from the increase of both transient and steady-state photoconductivity.⁵

The enhanced efficiency for photogeneration of free charge carriers and the enhanced lifetimes for those carriers have been attributed to the excellent acceptor properties of C_{60} and the efficient stabilization of the positive charge due

to carrier delocalization and structural relaxation of the polymer chain.

The donor-acceptor couple of a semiconducting polymer and C_{60} has been incorporated in heterojunction devices such as diodes, photodiodes, and photovoltaic cells.⁶ Recently, it was demonstrated that photodiodes made from MEH-PPV, sensitized with C_{60} , show excellent sensitivity to UV-visible radiation in a three-layer device indium-tin-oxide/MEH-PPV: C_{60} /Ca. Compared to the devices made from pure MEH-PPV, the photoresponse of MEH-PPV: C_{60} devices is enhanced by more than an order of magnitude at zero bias.⁷

A problem that arises in the preparation of composite films of π -conjugated polymers with C_{60} is the intrinsic incompatibility of the two materials; at higher concentrations C_{60} usually phase segregates from the conjugated polymer matrix due to a tendency to crystallize. In order to increase the miscibility of the fullerene with conjugated polymers it seemed worthwhile to investigate the use of derivatives of C_{60} with a solubilizing side chain. Provided that the redox properties of C_{60} do not change significantly after chemical modification, it can be expected that side-chain derivatives of C_{60} form an interesting option as an acceptor in composite films with conjugated polymers.

A reliable and versatile route to fullerene functionalization has been found via the addition of diazo compounds to C_{60} .⁸ This route offers the possibility of obtaining monoaddition products across a 5,6 ring junction (fulleroid) or a 6,6 ring junction (methanofullerene). The [5,6] methanoannulene bonding preserves the 60π electrons of C_{60} , whereas the [6,6] cyclopropane bonding reduces the number of π electrons to 58.

In this paper we describe our studies using PIA, photoluminescence, and LESR on photoinduced electron transfer from poly(bis-2,5-*epi*-cholestanoxo-1,4-phenylene vinylene) (BeCHA-PPV) to C_{60} , fulleroids, and methanofullerenes shown in Fig. 1. We show that monofunctionalization in a [5,6] or [6,6] fashion, and bis-[6,6] functionalization of C_{60}

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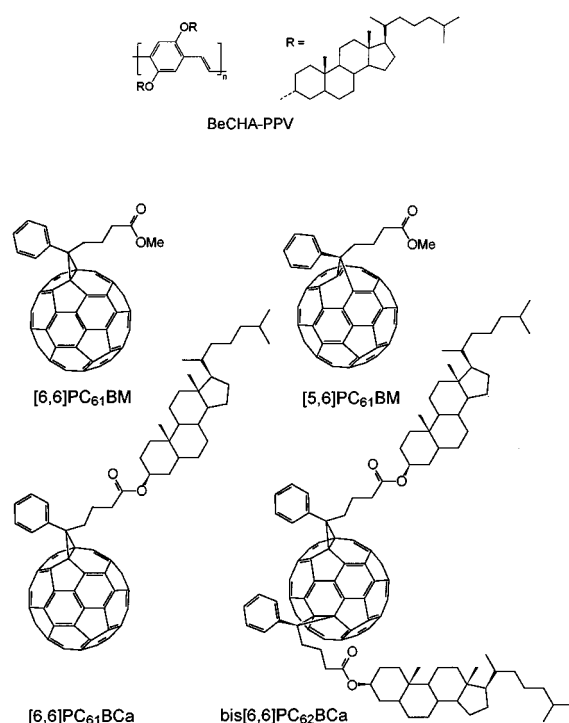


FIG. 1. Molecular structure of BeCHA-PPV, [5,6]PC₆₁BM, [6,6]PC₆₁BM, [6,6]PC₆₁BCa, and bis[6,6]PC₆₂BCa. For bis[6,6]PC₆₂BCa the relative orientations of the two substituents on the ring is not known and the actual sample probably contains various isomers.

increases the miscibility with BeCHA-PPV in composite films and affords an efficient photoinduced electron transfer reaction analogous to BeCHA-PPV:C₆₀ composites.

II. EXPERIMENT

BeCHA-PPV was prepared according to methods previously described.⁹ The synthesis and characterization of the fulleroid 1-(3-methoxycarbonyl)propyl-1-phenyl[5,6]C₆₁ ([5,6]PC₆₁BM), the methanofullerenes 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ ([6,6]PC₆₁BM), and 1-(3-cholestanoxycarbonyl)propyl-1-phenyl [6,6] C₆₁ ([6,6] PC₆₁BCa) has been described elsewhere.¹⁰ Samples for optical studies were prepared by casting from *p*-xylene solutions onto sapphire substrates and for LESR by evaporation of the solvent in a suprasil quartz tube followed by flame sealing under a vacuum of 5×10^{-6} Torr. Composite films were made by mixing solutions of BeCHA-PPV and the fullerene acceptors in *p*-xylene to obtain a 75:25 ratio by weight. Absorption spectra of the composite films are a linear superposition of the spectra of BeCHA-PPV and the fullerene; no new absorption below the π - π^* energy gap is observed.

PIA experiments used an argon ion laser as a pump beam and a tungsten-halogen white light source as a probe beam. The pump beam (488 nm, 25 mW, diameter 2 mm) was mechanically chopped (275 Hz) and the resulting modulation of the probe beam transmission (ΔT) was phase sensitively recorded using a lock in amplifier and a two-color (Si/PbS) detector. The PIA was obtained as $-\Delta T/T \approx \alpha d$ after correc-

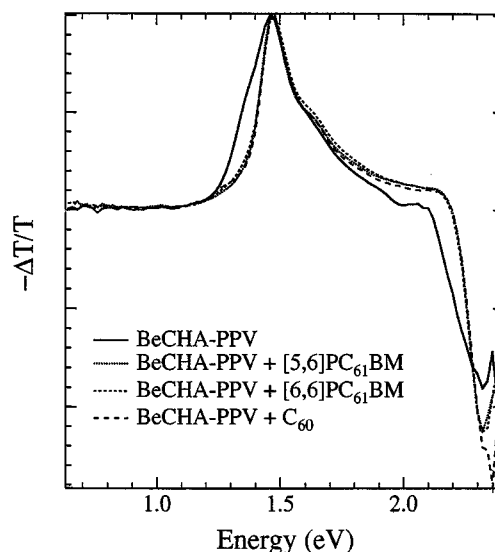


FIG. 2. PIA spectra of a pristine BeCHA-PPV film and the 75:25 wt. % composite films BeCHA-PPV:C₆₀; BeCHA-PPV:[5,6]PC₆₁BM; and BeCHA-PPV:[6,6]PC₆₁BM. Spectra were recorded at 80 K by pumping at 2.54 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to the same intensity to allow direct comparison.

tion for luminescence. Samples for PIA were mounted on a cold-finger cryostat held at 80 K under a dynamical vacuum on the order of 10^{-5} Torr.

For LESR experiments we used an argon ion laser (488 nm, 150 mW) and a Bruker ESP300 X-band spectrometer with an Oxford ITC4 variable temperature cryostat. Light was transmitted into the cavity via a 50% transmission grid. Frequencies were measured using a HP5225A frequency counter, and *g* values are calibrated against DPPH (*g* = 2.0036). LESR spectra were typically recorded at 25 K with 10 μ W microwave power, while care was taken to avoid background signals from ambient light of fluorescent lamps.

III. RESULTS AND DISCUSSION

A. Photoexcitation of pristine BeCHA-PPV

The PIA spectrum of a pristine BeCHA-PPV film recorded at 80 K (Fig. 2) exhibits a band at 1.47 eV which is attributed to the well-established triplet state photoexcitation of PPV's and dialkoxy-PPV's.¹¹ The triplet origin of the PIA band in the 1.4–1.5 eV region observed for various dialkoxy-PPV's, has been confirmed unambiguously using magneto-optical spectroscopy.¹² The triplet PIA intensity ($\Delta T/T$) increases with pump intensity (*I*) according to a $\Delta T/T \sim I^{0.65}$ power law (Fig. 3), which indicates that both monomolecular ($\Delta T/T \sim I$) and bimolecular ($\Delta T/T \sim I^{0.5}$) decay mechanisms contribute to the relaxation of the triplet state in the film. By varying the modulation frequency (ω) of the pump beam and monitoring the PIA intensity, it is possible to deduce the lifetime τ_s of this triplet BeCHA-PPV photoexcitation by fitting the $\Delta T/T$ vs ω data (Fig. 4) to the equation for bimolecular decay:¹³

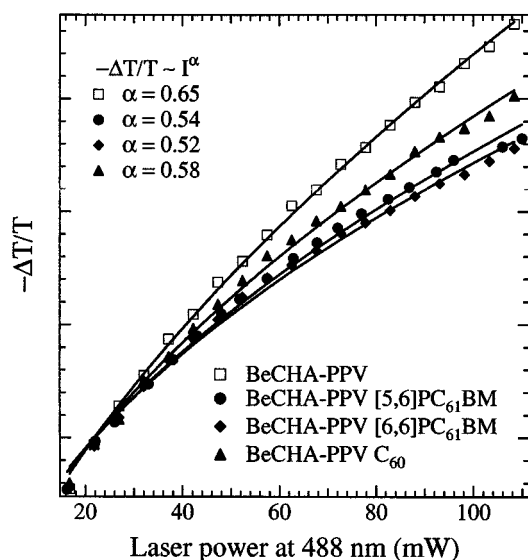


FIG. 3. Pump intensity dependence of the PIA signal at 1.47 eV for a pristine BeCHA-PPV film and the 75:25 wt. % composite films BeCHA-PPV:C₆₀; BeCHA-PPV:[5,6]PC₆₁BM; and BeCHA-PPV:[6,6]PC₆₁BM. Solid lines represent best-fit power laws, with exponents as indicated in the inset. Data were obtained at 80 K by pumping at 2.54 eV with a frequency of 275 Hz.

$$\Delta T \propto \sqrt{I/\beta} \cdot \frac{\alpha \tanh \alpha}{\alpha + \tanh \alpha}, \quad (1)$$

where $\alpha = \pi/(\omega\tau_s)$, $\tau_s = (I\beta)^{-0.5}$, and β is the bimolecular decay rate constant. This fit yields a lifetime of 2.0 ms for the triplet state of BeCHA-PPV in the film at 80 K.

A similar PIA band can be observed at ambient temperature in solutions of BeCHA-PPV in various organic solvents, e.g., in *p*-xylene (0.5 mg/ml), where the PIA band is centered at 1.50 eV, slightly blue-shifted as compared to the film at 80 K. In contrast to the solid film, the PIA intensity of

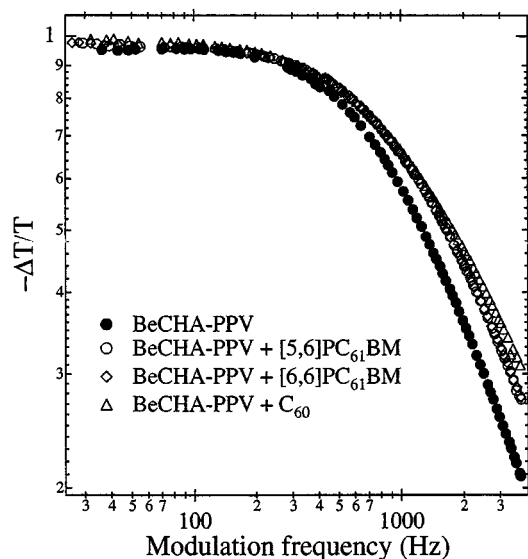


FIG. 4. Normalized intensity dependence of the PIA signals shown in Fig. 2 as a function of the modulation frequency. Data were obtained at 80 K by pumping at 2.54 eV with a 25 mW excitation beam.

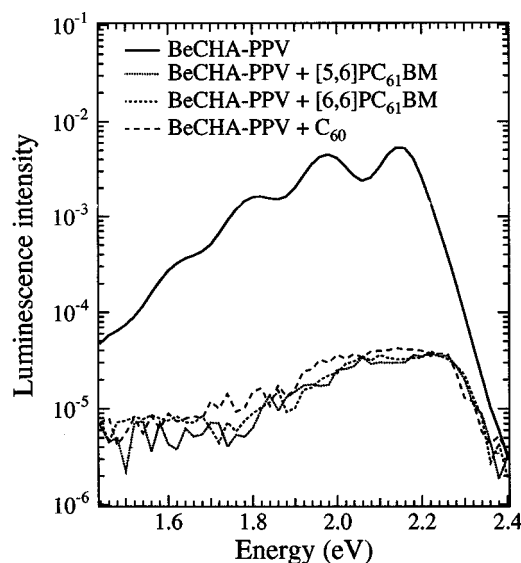


FIG. 5. Luminescence intensity of a pristine BeCHA-PPV film and the 75:25 wt. % composite films BeCHA-PPV:C₆₀; BeCHA-PPV:[5,6]PC₆₁BM; and BeCHA-PPV:[6,6]PC₆₁BM. Spectra were recorded at 80 K by excitation with a 25 mW beam at 2.54 eV.

BeCHA-PPV in *p*-xylene depends linearly on the pump intensity ($\Delta T/T \sim I^{0.92}$) and, hence, relaxation is predominantly monomolecular. The lifetime, τ , in solution as deduced from the modulation frequency dependence of ΔT assuming monomolecular decay:^{11(a)}

$$\Delta T \propto \frac{I\tau}{(1 + \omega^2\tau^2)^{1/2}} \quad (2)$$

is 1.0 ms. This PIA band is completely quenched when the solution is exposed to air, due to a triplet energy transfer reaction with molecular oxygen. The observed quenching gives further evidence to the assignment that the PIA band is due to a $T \rightarrow T^*$ absorption of a triplet state photoexcitation.

The partly bimolecular decay ($\Delta T/T \sim I^{0.65}$) of the triplet state photoexcitation in the film as compared to the monomolecular decay ($\Delta T/T \sim I^{0.92}$) in solution is an indication for an increased triplet-triplet annihilation in the solid state, likely to be caused by the mobility of photoexcitations.

Similar to PPV and other dialkoxy-PPV's, BeCHA-PPV is an excellent photoluminescent material.⁹ The radiative emission of BeCHA-PPV occurs from the excited $\pi-\pi^*$ singlet state (fluorescence). Despite the formation of triplet state photoexcitations, as evidenced from PIA, phosphorescence has not been reported for PPV's. Figure 5 shows the luminescence spectrum of a BeCHA-PPV film at 80 K, which is characterized by a 0-0 transition at 2.15 eV and (at least) three other vibronic transitions at lower energies separated by 0.17 eV.

B. Photoexcitation of composite films

Composite films of BeCHA-PPV with [5,6]PC₆₁BM or [6,6]PC₆₁BM are appreciably less phase-segregated than a composite film of BeCHA-PPV with C₆₀ as evidenced from the reduced scattering observed in the linear absorption spectrum above 700 nm.

The composite BeCHA-PPV:C₆₀; BeCHA-PPV:[5,6]PC₆₁BM; and BeCHA-PPV:[6,6]PC₆₁BM films (75:25 wt. %) exhibit an efficient quenching of the photoluminescence (Fig. 5); the intensity drops by two orders of magnitude.

In Fig. 2, we plot the normalized PIA spectra of the composite films for a direct comparison with the spectrum of the pristine material. This reveals that despite the dramatic change in the photoluminescence efficiency, the changes in PIA seem small, but it is important to note that the absolute PIA intensity of the 1.47 eV band in the composite films is consistently larger by a factor of 2–4 than in the pristine film. The PIA spectra obtained for each of the three composite films are fully superimposable, irrespective of the nature of the fullerene derivative. Hence, we are prompted to conclude that [5,6]PC₆₁BM and [6,6]PC₆₁BM bring about the same changes in the photophysics of BeCHA-PPV as those caused by C₆₀.

Although the PIA spectra in the millisecond to microsecond domain as probed by our modulation technique show only minor differences for pristine and composite films, time-resolved PIA spectroscopy on BeCHA-PPV:C₆₀ has clearly indicated a different origin.^{3(c)} Femtosecond time-resolved PIA spectroscopy has shown that in BeCHA-PPV:C₆₀ a well-defined absorption band peaking at 1.45 eV is formed with a rise time that is resolution limited (less than 1 ps), while the early time PIA in the pristine BeCHA-PPV film, on the other hand, is red-shifted and shows no peak at 1.45 eV.^{3(c)} Hence, the dramatic changes in the photophysics of the composite films as compared to the pristine film that appear from the efficient quenching of the photoluminescence, is supported by time-resolved PIA spectroscopy and consistent with an ultrafast photoinduced electron transfer reaction.

In principle, energy transfer from the photoexcited polymer to the three fullerene derivatives can occur. In fact, triplet energy transfer has recently been observed for poly(3-alkylthiophene) and C₆₀ in solution.^{2(f)} Triplet energy transfer from BeCHA-PPV in the composite films, however, is unlikely to occur in the present case, because this would require an unexpectedly fast intersystem crossing rate to explain the quenching of photoluminescence and the subpicosecond rise of the band at 1.47 eV in time-resolved PIA. Singlet energy transfer to low lying states of C₆₀ and the fullerene derivatives can occur, but their high rate for intersystem crossing would produce the metastable fullerene triplet states that have been observed previously using PIA and direct excitation of these acceptors.¹⁴ The absence of the triplet PIA bands at 1.65 eV for BeCHA-PPV:C₆₀ and at 1.73 eV for BeCHA-PPV:[5,6]PC₆₁BM or BeCHA-PPV:[6,6]PC₆₁BM, however, is at variance with both singlet and triplet energy transfer.

The pump intensity dependence (Fig. 3) of the 1.47 eV PIA band observed in the composite films follows approximately a square-root behavior, indicating predominant bimolecular decay. Such bimolecular decay is as expected for a full charge separation, since decay of photoexcitations involves non-geminate recombination of electrons and holes. Likewise, we observe a change in the modulation frequency

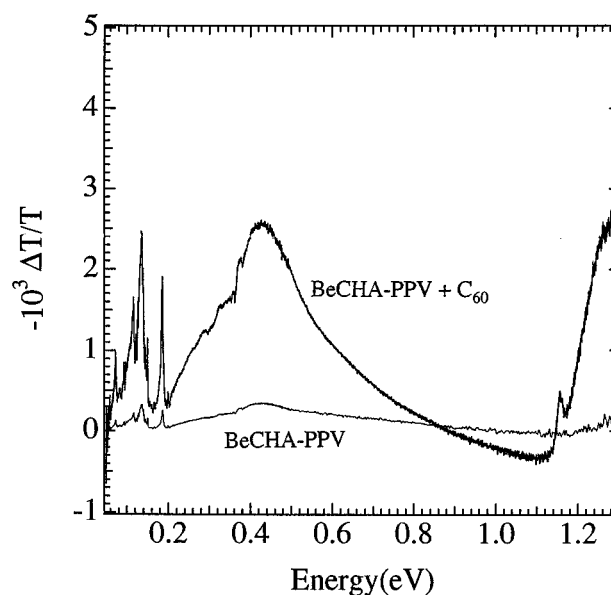


FIG. 6. Photoinduced IR absorption spectra of BeCHA-PPV and BeCHA-PPV:C₆₀ obtained by pumping at 80 K with an argon ion laser at 2.41 eV with 50 mW/cm².

dependence of the 1.47 eV band in the composite films (Fig. 4); the lifetime is reduced from 2.0 to 1.4–1.5 ms for the composite films of BeCHA-PPV with the three fullerene derivatives.

Similar changes in the PIA spectra have also been observed in a previous study on MEH-PPV. Absorption detected magnetic resonance (ADMIR) experiments on MEH-PPV and MEH-PPV/C₆₀ have shown unambiguously that despite the almost invariant position, the nature of the 1.40 eV PIA band changes completely in the presence of C₆₀: from being associated with a $S=1$ (triplet) photoexcitation in the pristine film to a $S=\frac{1}{2}$ (doublet) photoexcitation in the composite film.¹⁵ This is the expected behavior for charge separation upon photoexcitation.

Photoinduced absorption measurements using Fourier transform infrared (FTIR) spectroscopy on BeCHA-PPV:C₆₀ composite films at 80 K reveal a subgap electronic absorption at 0.43 eV and an enhancement (by nearly an order of magnitude) of the infrared active vibrational modes (Fig. 6). The IRAV modes result from the self-localization of polaronic and bipolaronic states. When such excitations are created, their associated structural distortions cause the symmetrical (Raman active) modes to become infrared active vibrational modes.⁴ The strong enhancement in IRAV mode intensity is consistent with the long-living charge separation. In addition, a small signal at 1.16 eV reveals the presence of C₆₀⁻. The combined PIA spectra indicate that two polaronic/bipolaronic absorptions are present in BeCHA-PPV:C₆₀ at 0.43 and 1.47 eV, respectively.

LESR experiments were performed as an independent spectroscopic technique to establish whether whole electron transfer occurs from the photoexcited BeCHA-PPV on to the acceptors. LESR spectra were recorded at 25 K, while irradiating continuously at 488 nm. In this experiment we probe the steady state concentration of (long-lived) radicals corre-

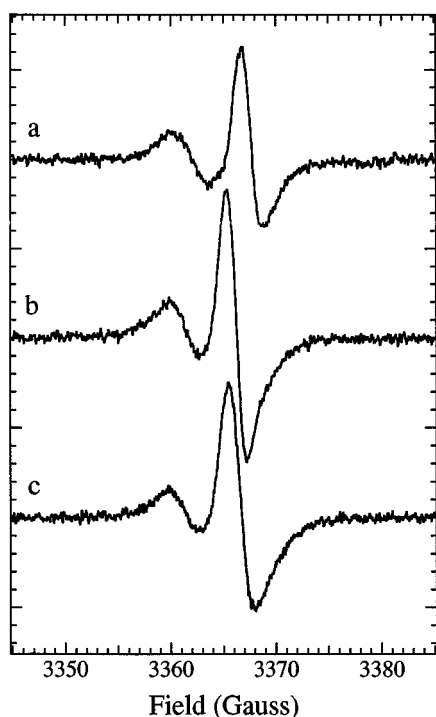


FIG. 7. ESR spectra of 75:25 wt. % composite films (a) BeCHA-PPV:C₆₀; (b) BeCHA-PPV:[6,6]PC₆₁BM; and (c) BeCHA-PPV:[5,6]PC₆₁BM. Spectra (25 cumulative scans) were recorded at 25 K while continuously irradiating the sample at 488 nm with 150 mW through a 50% transmission grid and are corrected for dark signal. Microwave power was 10 μ W.

sponding to a different time regime as modulated PIA studies, which detect species with lifetimes in the microsecond and millisecond domain. The results for the BeCHA-PPV:C₆₀, BeCHA-PPV:[5,6]PC₆₁BM, and BeCHA-PPV:[6,6]PC₆₁BM composite films are shown in Fig. 7. Each of the spectra reveals two transitions. The low-field signal is observed at $g=2.0026(2)$ for BeCHA-PPV:C₆₀ and at $g=2.0029(2)$ for BeCHA-PPV:[5,6]PC₆₁BM and BeCHA-PPV:[6,6]PC₆₁BM. These g values are close to that of the free electron and are readily attributed to the BeCHA-PPV polaron (radical cation). Consistent with this assignment, the g value of the low-field signal is almost invariant to the nature of the acceptor in the composite film. The signal at high field corresponds to the acceptor anion radical. The g value of C₆₀⁻ ($g=1.9992(2)$) [Fig. 7(a)] is in agreement with the value known from literature.¹⁶ For [6,6]PC₆₁BM⁻ and [5,6]PC₆₁BM⁻ g values are 2.0000(2) and 1.9995(2), respectively [Fig. 7(b) and 7(c)].

ESR spectra of the composite films were readily detected in the temperature range from 4.2–100 K. Pristine BeCHA-PPV shows no ESR signals under similar conditions. [6,6]PC₆₁BM and PC₆₁BM, on the other hand, reveal ESR spectra similar to those shown in Figs. 7(b) and 7(c) but their intensity is significantly lower. The formation of charged states as detected using ESR, is significantly enhanced in films containing both a good electron donor (BeCHA-PPV) and a good electron acceptor (fullerene/fulleroid/methanofullerene). The ESR results are consistent with our conclusion that photoinduced electron transfer oc-

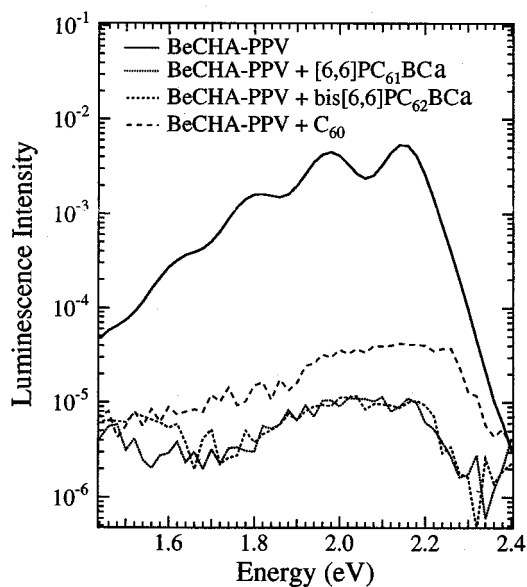


FIG. 8. Luminescence intensity of a pristine BeCHA-PPV film and the 75:25 wt. % composite films BeCHA-PPV:C₆₀; BeCHA-PPV:[6,6]PC₆₁BCa; and BeCHA-PPV:bis[6,6]-PC₆₂BCa. Spectra were recorded at 80 K by excitation with a 25 mW beam at 2.54 eV.

cur readily to the all fullerene acceptors. The fact that pristine [6,6]PC₆₁BM and [5,6]PC₆₁BM also give rise to two ESR transitions near $g=2.002$ – 2.003 and $g=1.999$ – 2.000 can possibly be explained by an intramolecular charge transfer reaction from the 1-(3-methoxycarbonyl)propyl-1-phenyl substituent to the excited C₆₁ moiety.

It is interesting to note that the g value of the methanofullerene radical anion with $(58+1)\pi$ electrons deviates more from the g value of C₆₀⁻ than the g value of the corresponding fulleroid radical anion which possesses $(60+1)\pi$ electrons. The importance of electron count on electronic properties of methanofullerenes and fulleroids is also reflected in the linear absorption. The electronic spectrum in the visible region of fulleroids (60π) is almost identical to that of C₆₀, whereas the absorption spectrum of methanofullerenes (58π) exhibits a clear hypsochromic shift.

In order to further enhance the miscibility and compatibility of BeCHA-PPV with functionalized C₆₀ derivatives, fullerenes with cholestanoxo side chains ([6,6]PC₆₁BCa and bis[6,6]PC₆₂BCa, Fig. 1) were prepared and mixed with the polymer. The luminescence spectra of the composite BeCHA-PPV:[6,6]PC₆₁BCa and BeCHA-PPV:bis[6,6]PC₆₂BCa films (75:25 wt. %) shown in Fig. 8 reveal a very efficient quenching of the photoluminescence superior to the quenching observed for the C₆₀, [5,6]PC₆₁BM, or [6,6]PC₆₁BM acceptors. The PIA spectra (Fig. 9) are fully analogous to those obtained for [5,6]PC₆₁BM and [6,6]PC₆₁BM. The PIA band is centered at 1.47 eV and exhibits an increased intensity by a factor of about 3–4 as compared to the band observed for pristine BeCHA-PPV with a square root pump intensity dependence. The lifetimes for bimolecular decay of the 1.47 eV PIA bands are 1.46 and 1.61 ms for the [6,6]PC₆₁BCa and bis[6,6]PC₆₂BCa composites, respectively. We conclude that photoinduced electron

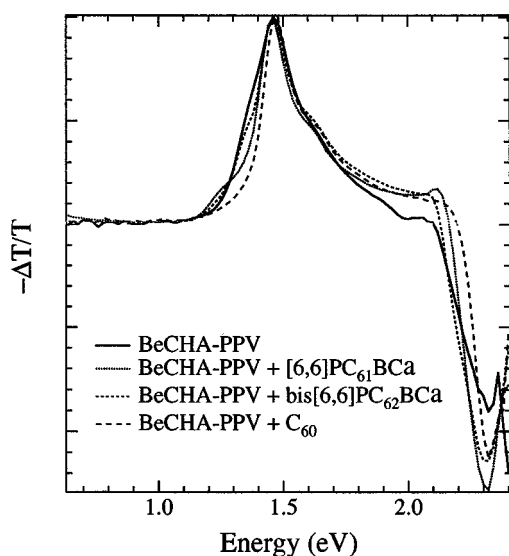


FIG. 9. PIA spectra of a pristine BeCHA-PPV film and the 75:25 wt. % composite films BeCHA-PPV:C₆₀; BeCHA-PPV:[6,6]PC₆₁BCa; and BeCHA-PPV:bis[6,6]PC₆₂BCa. Spectra were recorded at 80 K by pumping at 2.54 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are normalized to the same intensity to allow direct comparison.

transfer from BeCHA-PPV also occurs to these mono- and bischolestanoxo functionalized C₆₀ derivatives.

IV. CONCLUSIONS

We have shown that functionalized fullerenes with a solubilizing side chain which increases the miscibility of the fullerene with the π -conjugated polymer matrix, act as efficient electron acceptors in photoinduced electron transfer processes in composite films with BeCHA-PPV. The PIA spectrum of the composite films is more intense by a factor of 2–4 than the PIA spectrum of the pristine BeCHA-PPV film, and the nature of the 1.47 eV band has changed from a neutral triplet photoexcited state to a charged polaronic/bipolaronic state. Quenching of the photoluminescence is observed for all acceptors and is more efficient for the cholestanoxo substituted fullerenes. In addition, LESR spectra give evidence for the formation of BeCHA-PPV polarons and C₆₀⁻ radical anions. The *g* values of the functionalized fullerene anions are found to depend on the number of π electrons and type of bonding. The fact that the BeCHA-PPV photoluminescence is quenched by at least 2 orders of magnitude is consistent with a fast forward photoinduced electron transfer process. This is supported by the results from time-resolved PIA studies.³ The increased miscibility of the functionalized fullerenes with π -conjugated polymers offers the possibility to study the dependence of the photoinduced electron transfer on the concentration of the acceptors in more detail and can be advantageous in the preparation of electrooptic devices.

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