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Evidence of high charge mobility in photoirradiated polythiophene–fullerene composites

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Interpenetrating networks of polythiophenes and fullerene derivatives give rise to charge transfer after irradiation with visible light. The resulting radical ion pairs have been studied by time-resolved EPR spectroscopy. At low temperatures (20 K), the radical pairs are spin correlated and locked at a distance of 27.1 Å, whereas an increase of temperature causes the electron and the hole to move further away from each other.

The photoirradiation of conjugated polymer films generates intra-chain singlet excitations that evolve either into triplet intra-chain excitations, or transfer an electron to the neighbouring chain giving rise to inter-chain ion pairs.[1] In polythiophenes, electron or hole transfer can occur with rate constants as fast as 10^{12}–10^{13} s^{-1}.[2] Photoinduced electron transfer (PET), which is markedly enhanced between conjugated polymers and fullerenes, has attracted considerable attention, mainly in connection with manufacturing plastic solar cells.[3] In polymer–fullerene blends, fast electron transfer occurs from the donor polymer to the acceptor fullerene upon light excitation. The back electron transfer is considerably slower, allowing collection of charges at the electrode.[3] Two factors are responsible for this behaviour: (i) the low reorganization energy of fullerenes in electron transfer reactions accelerates forward and decelerates back electron transfer, compared to planar electron acceptors[4] and (ii) well-structured polymers facilitate charge delocalization within their structures.[5]

The charge transport in these systems is a crucial prerequisite for efficient photovoltaic behaviour. The role of the morphology is especially significant, since the composite is made of two active components.[3] We have recently shown that amorphous thioalkyl-functionalised oligothiophene donors interact much more efficiently with modified, soluble fullerene derivatives than crystalline oligothiophenes, by preventing phase segregation.[6]

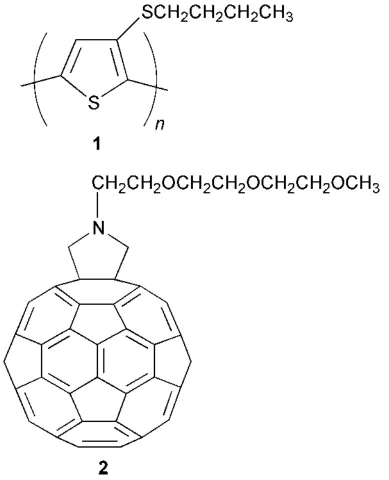
Here we report clear evidence that charges indeed move fast in alkylsulfanyl-functionalised polythiophene–fullerene blends at room temperature, using time-resolved EPR spectroscopy.

Head-to-tail poly[3-(*n*-butylsulfanyl)thiophene] **1** and the *N*-(methoxyethoxyethoxyethyl)fullerenopyrrole derivative **2** (Scheme 1) were prepared according to previous reports.[7,8] Both compounds were chosen for their structural characteristics, mainly to improve their relative miscibility.[6] The active films were prepared by mixing toluene solutions containing 1 : 1 ratios of **1** and **2** in weight, followed by evaporation of the solvent. This mixture corresponds to a molar ratio of about 19% fullerene per monomer unit.

The films were first studied by transient absorption spectrophotometry on a nanosecond time-scale at room temperature, following a short 532 nm pulse. A transient is formed, which shows a strong absorption centered at 900 nm. This can be attributed to the polymer radical cation, based on a complementary set of pulse radiolytic oxidation experiments.†The radical anion of the fullerene derivative, usually observed at around 1000 nm,[4] was overshadowed by the strong polymer radical cation absorption. In deaerated conditions, a lifetime of 4.6 μs was measured for the charge-separated state.

In EPR experiments, excitation at 581 nm (Rhodamine 6G dye) resulted in the formation of radical species. A typical EPR transient spectrum, taken at 20 K, is shown in Fig. 1, together with its computer simulation. The small width of the spectrum, which is limited to 4 mT, rules out the possible formation of a triplet excited state of the polythiophene or the fullerene component, characterized by spectrum widths of 112 mT[9] and 19 mT,[10] respectively.

The spectrum consists of four lines, partly in emission (E) and partly in absorption (A), with a characteristic antiphase pattern E/A/E/A. The spectrum was assigned to a charge-separated state and the origin of the antiphase character is understood on the basis of the spin-correlated radical pair theory,[11] comprising two unpaired electrons that interact by



Scheme 1

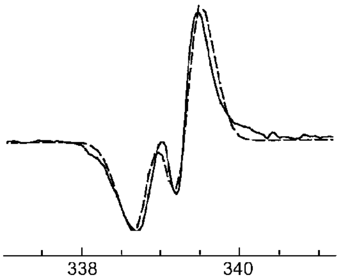


Fig. 1 Experimental EPR spectrum (solid line) of **1**–**2** film detected at 20 K 0.5 μs after the laser pulse and its simulation (dotted line). The latter was obtained as a sum of spectra calculated at a given orientation of the dipolar axis of the pair with respect to the common frame for *g*-tensors of single radicals. For each calculated spectrum the following values $D/g\beta = -0.139$ mT and $J/g\beta = 3.2$ μT for dipolar and spin exchange coupling constants were used, corresponding to a distance of 27.1 Å between radicals in a pair.

spin exchange and dipolar interactions with coupling constants J and D, respectively. Fitting to the spectrum was achieved using the values $D = -0.139$ mT and $J = 3.2$ μT. This corresponds to a mean distance of 27.1 Å between the centres of the opposite charges.[12]

The spectrum changes with increasing temperature above 150 K, losing the antiphase spin polarisation and consisting of two lines with opposite E/A spin polarisation (Fig. 2).

At 250 K such a spectrum is typical of a radical pair in which the two unpaired electrons have ceased to interact and each radical carries spin polarization supplied by the CIDEP effect.[11c] The spectral features are compatible with the picture that the original geminate pair, in which PET took place and where polarization was acquired, dissociates into free carriers inheriting the non-equilibrium populations from the precursor pair. It was ascertained that the difference in the resonant fields between the two lines was that expected for the isotropic *g*-factor values of the cation and anion without any additional contribution from dipolar and spin exchange coupling constants. Lineshape analysis indicates that the positive charge signal maintains a Gaussian profile as in the low temperature spectrum while the line for the negative carrier changes from Gaussian to Lorentzian. Within a random walk model of charge diffusion,[13] this result supports the picture that positive charges can move preferentially along a polymer chain, whereas motion of the negative charges can be described as hopping within C_{60} molecules and polymer chains. The linewidth for the fullerene anion line narrows to 0.20 mT at 250 K from the value of 0.38 mT at 20 K, yielding an estimated value of about 10^{-8} s for the correlation time of the random walk motion.

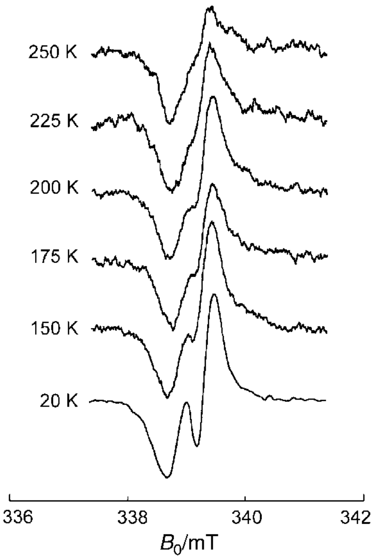


Fig. 2 Temperature dependence of EPR spectra due to radical pairs generated by photoinduced electron transfer in **1**–**2** composite deposited as a film. As the temperature was raised, the inner spectrum lines disappeared and at about 250 K the typical antiphase structure was completely lost. Microwave field, $B_1 = 50$ μT; microwave frequency $\omega/2\pi = 9.5081$ GHz.

In conclusion, since the photogenerated charges inside a polythiophene–fullerene blend survive from recombination in the microsecond range, they can be suitably studied by time-resolved EPR spectroscopy. We have shown that, at low temperatures, ion pairs are trapped at well-defined inter-radical distances. However, at room temperature, electrons and holes move sufficiently fast, thus corroborating the argument in favour of using these components for photovoltaic applications.[14]

Acknowledgements

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Notes and references

†Pulse radiolysis was used to investigate the selective one-electron transfer, for example, to $[CH_2Cl_2]^{\cdot +}$ and $\cdot OOCH_2Cl/\cdot OOCHCl_2$ peroxyl radicals in oxygenated dichloromethane solutions. The initial product of solvent ionization (*i.e.*, $[CH_2Cl_2]^{\cdot +}$) and the resulting radicals (*i.e.*, $\cdot OOCHCl_2$ and $\cdot OOCH_2Cl$) provide the means for the rapid oxidation of poly[3-(*n*-butylsulfanyl)thiophene]. This procedure leads to suitable spectral references.

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