

Photoinduced electron transfer in sexithiophene/fullerene derivative blends: evidence of long-lived spin correlated radical pairs

Luigi Pasimeni,^{*a} Anna Lisa Maniero,^a Marco Ruzzi,^a Maurizio Prato,^b Tatiana Da Ros,^b Giovanna Barbarella^c and Massimo Zambianchi^c

^a Department of Physical Chemistry, University of Padova, Via Loredan 2, I-35131 Padova, Italy

^b Department of Pharmaceutical Sciences, University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy.
E-mail: prato@univ.trieste.it

^c I.Co.CEA, Area Ricerca C.N.R., Via Gobetti 101, I-40129 Bologna, Italy

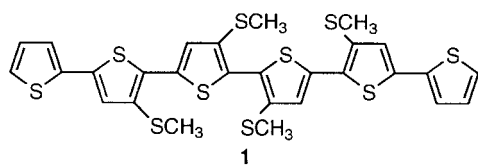
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Photoinduced electron transfer between sexithiophene and fullerene derivatives in the solid phase has been studied by transient EPR spectroscopy: spin correlated radical pairs were observed having a lifetime of 10 μ s and mean distance of 20 Å.

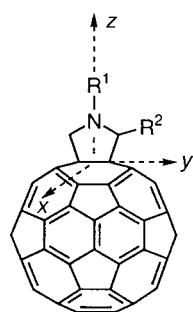
Several classes of electron donor–acceptor (D–A) systems have been investigated displaying through-bond and through-space mechanisms of photoinduced electron transfer (PET), the latter mechanism being responsible for the charge-separated state in D–A blends. Among other systems,¹ the PET process has been fully investigated in blends of thiophene polymers and oligomers and C₆₀ as building blocks.^{2,3}

The thiophene–C₆₀ combination is particularly attractive because of the tunable donor properties of the thiophenes^{4–6} (depending on their chain length and substituents) and the acceptor properties of C₆₀. PET from π -conjugated polymers and oligomers of thiophene derivatives to C₆₀ have been studied mainly by photoinduced absorption (PIA) spectroscopy and light-induced electron paramagnetic resonance (LEPR).¹ Using PIA spectroscopy, it was found that the forward electron transfer is extremely fast (ps time scale), while the rate for back electron transfer can be many orders of magnitude lower.

Compounds **1** and **2**⁸ (Scheme 1) were prepared as described previously. Mixed films of sexithiophene/fullerene composites were prepared by dissolving the donor and acceptor mixture (1 : 1 molar ratio) in toluene in quartz tubes. After evaporating the solvent at a pressure of 10^{–1} Torr, the tubes were sealed under vacuum. The EPR experiments consisted of laser excitation followed by time-resolved direction of the signal.[†]



1



2 R¹ = CH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃; R² = H

Scheme 1 Schematic view of possible structure of the 1/2 radical pair.

Field-swept spectra of 1/2 blends obtained at variable delay time from the laser pulse, are shown in Fig. 1(a) and (b). Within 0.5 μ s from the laser pulse the signal reaches its maximum, then the spectrum intensity decays to zero within several microseconds.

The spectrum at its maximum intensity, shown in Fig. 1(c), is typical of spin correlated radical pairs.^{9,10} Upon excitation and photoinduced electron transfer, the D⁺A[–] radical pair produced is characterized by two radicals having different *g* factors, *g*_D and *g*_A that interact by spin exchange and dipolar interactions, with *J* and *D* the constants that express their strength, respectively. Thorough analysis of the spectrum allows one to obtain information about the structure of the charge separated radical pair.

The basic EPR spectrum of a spin-correlated radical pair, created in a singlet or a triplet configuration, consists of four peaks arranged as two doublets with equal splittings determined by the spin–spin interaction between the radicals. Both doublets have one component emissive (e) and the other absorptive (a), reflecting the non-equilibrium populations of the four-electron

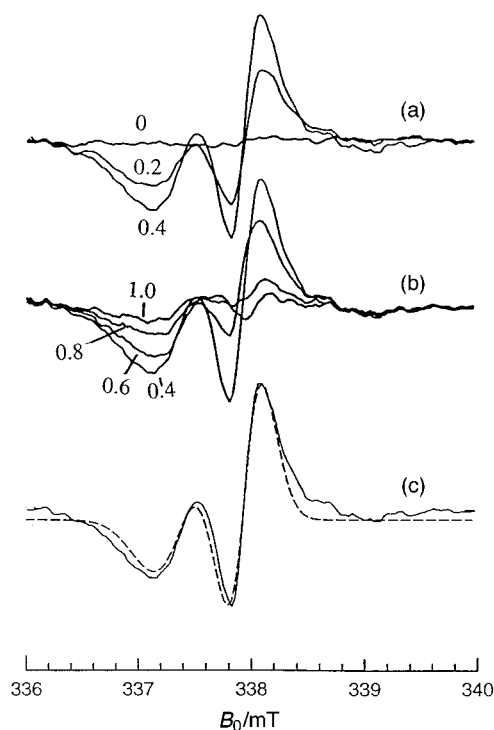
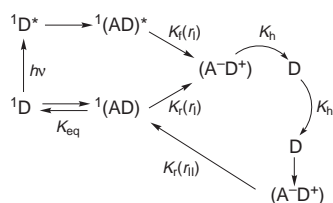


Fig. 1 Growth (a) and decay (b) of the field-swept transient EPR spectra recorded at different delay times from the laser pulse and at 120 K in 1/2 blends are shown. (c) Spectrum at the maximum intensity (delay time 0.4 μ s, solid line) and its computer simulation (dashed line). The values of *g*_D = 2.0030 and *g*_A = 1.9998 factors were used assumed as isotropic. The value of *g*_A is typical of the monoanion of a C₆₀ adduct.

spin states. In case of hyperfine interactions with magnetic nuclei of one or both radicals of the pair, each doublet may become a more complicated multiplet. For non-oriented samples, the EPR signal has to be averaged over all the orientations of the radical pair with respect to the direction of the external field.

As shown in Fig. 1(a)–(c), the characteristic e/a/e/a pattern for a singlet born radical pair was observed in the whole time range of the experiment, extending from 0.1 to 20 μ s. Simulation of the spectrum requires the knowledge of several structural parameters like the components of g_D and g_A tensors and the D and J values, although it is known that the lineshape depends most critically on the relative orientation of the principal axes of the g_D and g_A tensors and the spin–spin dipolar tensor.¹⁰ Because of the lack of structural information on the radical pair, we have calculated the spectrum lineshape for different structural arrangements and different D and J values, and the fitting reported in Fig. 1(c) gave $D = -0.15$ mT and $J = 0.01$ mT, while principal axes of g_D and g_A , and of spin–spin dipolar tensors are assumed parallel. We have found that the spectrum lineshape is rather sensitive to the relative orientation of g and dipolar tensors, but the spread of resonant fields is scarcely affected by the above assumption. An isotropic hyperfine constant of 0.06 mT due to two equivalent hydrogen nuclei on the donor was also included.¹¹ In the averaging procedure over all orientations of the radical pair the stick diagram at a fixed orientation was convoluted with an envelope function in order to mimic the line broadening due to relaxation and residual unresolved hyperfine splittings. The simulated spectrum is shown in Fig. 1(c).

In order to model the structure of the pair having the charge-separated state we calculated the electron dipolar tensor for which the spin densities on the sexithiophene and on the fullerene moieties are needed. We considered for **1** the spin distribution calculated for sexithiophene,¹¹ while that for **2** was obtained from a HF calculation on the neutral *N*-methyl analog of **2** by taking the squares of the LUMO coefficients. The dipole–dipole interaction was calculated with the point dipole approximation, justified by the large distance between the two electrons. When the sexithiophene molecule is arranged as shown in Scheme 1, coplanar with the pyrrolidine ring, and its short in-plane axis is parallel to the z axis, the experimental value of $D = -0.15$ mT is reproduced when the centers of mass of the two molecules are 20 Å apart, a distance consistent also with the $J = 0.01$ mT value. This electron–hole (e–h) separation distance seems rather large as compared to the 10.25 Å value calculated for fullerene-doped *N*-poly(vinylcarbazole).¹² This finding supports that, in our case, a secondary radical pair is formed after e–h hopping from a more tightly bound primary pair (primary pair). It is suggested that a multistep process may occur as illustrated in Scheme 2. After the absorption of light from the donor and the exciplex formation $^1(AD)^*$ the primary pair (A^-D^+) is generated by PET with the forward rate constant



Scheme 2 Schematic representation of the multistep process experienced by the electron–hole pair generated by PET. Primary pair (A^-D^+) may either recombine by rate constant $K_r(r_I)$ or may give rise by hopping of charges (K_h , hopping rate constant) to a secondary pair (A^-SD^+). The latter in turn recombines with rate constant $K_r(r_{II}) < K_r(r_I)$ or transforms into subsequent pairs until it leads to radicals trapped at impurity sites.

$K_r(r_I)$, where r_I is the distance of closest approach between donor and acceptor molecules. Then, the primary (e–h) state evolves in time either by recombining to the neutral $^1(AD)$ state with backward rate constant $K_r(r_I)$ or it transforms into a secondary (A^-SD^+) pair where the active role of spacer neutral molecules (S) is to increase the e–h distance. In our case the primary pair eludes observation, since its lifetime must be < 100 ns, as shown by the signal growth in Fig. 1. In the secondary pair the dipolar and exchange interactions as well as the recombination rate constant $K_r(r_{II})$ are reduced and its lifetime falls into the ms domain. Further hopping of charges within the material eventually leads to radicals trapped at impurity sites, providing probably the light-induced EPR signals observed under continuous illumination.¹³

The phenomenon described in this work seems to be peculiar to the specific sexithiophene **1**. In fact, attempts to reproduce the same results with other methylsulfanyl-sexithiophenes¹⁴ were unsuccessful.

In conclusion, we have shown that in blends of sexithiophene **1** with fullerene derivatives **2**, radical pairs are generated by PET that evolve in the ms domain as detected by transient EPR spectra. The resulting charge separated states are much longer than for covalently linked dyads¹⁴ and this suggests that, analogously to other systems,¹ the blends presented here might be well suited for use in photovoltaic and optoelectronic systems.

Notes and references

† The sample was irradiated by a Lambda Physik LPX 100 XeCl excimer laser ($\lambda = 308$ nm, ≈ 10 mJ pulse⁻¹) which fed a Coumarin 47 dye laser with emitting light at 450 nm (pulse duration ≈ 20 ns). A modified Bruker ER 200D X-band (9.5 GHz) EPR spectrometer was used equipped with a fast microwave preamplifier and a broad band (10 kHz–6.5 MHz) video amplifier, whose upper frequency value limits the time resolution of the experimental to ca. 150 ns. The time-dependent EPR signal was digitized in a transient recorder (LeCroy 9450 digital oscilloscope) at a maximum acquisition rate of 400 megasamples s⁻¹. Typical two-dimensional (2D) EPR spectra have been recorded by collecting the time profile of the signal at different settings of the resonant magnetic field through the spectrum.

- N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.
- K. Yoshino, X. Hong Yin, S. Morita and A. A. Zakhidov, *Jpn. J. Appl. Phys.*, 1993, **32**, L140.
- R. A. J. Janssen, M. P. T. Christiaans, K. Pakbaz, D. Moses, J. C. Hummelen and N. S. Sariciftci, *J. Chem. Phys.*, 1995, **102**, 2628 and references therein.
- G. Horowitz, F. Garnier, A. Yassar and R. Hajlaoui, *Adv. Mater.*, 1996, **52**, 52.
- D. Fichou, J.-M. Nunzi, F. Charra and N. Pfeffer, *Adv. Mater.*, 1994, **6**, 64.
- S. C. Veenstra, G. G. Malliaras, H. J. Brouwer, F. J. Esselink, V. V. Krasnikov, P. F. van Hutten, J. Wildeman, H. T. Jonkman, G. A. Sawatzky and G. Hadziioannou, *Synth. Met.*, 1997, **84**, 971.
- G. Barbarella, M. Zambianchi, R. Di Toro, M. Colonna, L. Antolini and A. Bongini, *Adv. Mater.*, 1996, **8**, 325.
- P. Wang, B. Chen, R. M. Metzger, T. Da Ros and M. Prato, *J. Mater. Chem.*, 1997, **7**, 2397.
- J. R. Norris, A. L. Morris, M. C. Thurnauer and J. Tang, *J. Chem. Phys.*, 1990, **92**, 4239.
- G. Kothe, S. Weber, E. Ohmes, M. C. Thurnauer and J. R. Norris, *J. Am. Chem. Soc.*, 1994, **116**, 7729.
- M. Bennati, K. Nemeth, P. R. Surjan and M. Mehring, *J. Chem. Phys.*, 1996, **105**, 4441.
- Y. Wang and A. Suna, *J. Phys. Chem. B*, 1997, **101**, 5627.
- A. L. Maniero, L. Pasimeni, G. Barbarella, M. Zambianchi and M. Prato, in *Fullerenes and Photonics IV*, ed. Z. H. Kafafi, SPIE Proceedings, San Diego, 1997, vol. 3142, p. 112.
- H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537.

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