Triplet state dynamics on isolated conjugated polymer chains

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Abstract

Triplet state behaviour has been studied with several conjugated polymers in dilute benzene solutions by flash photolysis, photoacoustic calorimetry (PAC) and pulse radiolysis/energy transfer. With polythiophenes and the ladder poly(p-phenylene) MeLPPP, singlet–triplet intersystem crossing (ISC) is relatively efficient. In contrast, it is inefficient with poly(p-phenylenevinylene)s (PPVs) and polyfluorene, while with cyano-substituted PPV, there is no evidence for any long-lived triplet state. Energy transfer from triplet biphenyl to MEH-PPV is diffusion controlled and triplet state lifetimes are typically tens or hundreds of μs. All the triplet states are quenched by molecular oxygen, leading to formation of singlet oxygen with yields which are generally close to those for triplet formation. With pulse radiolysis at high doses, it is possible to have more than one triplet state per polymer chain. This can lead to delayed fluorescence via intrachain triplet–triplet annihilation. Kinetic analysis of this shows slow movement of triplets by hopping along the chain.
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1. Introduction

Since the first reports of efficient electroluminescence from nonconjugated [1] and conjugated [2,3] organic polymers, intense activity has been devoted to the application of these systems in light emitting diodes (LEDs) [4,5], photovoltaic systems [6], polymer based lasers [7], etc. Polymer-based

LED display systems are already a reality [8], full colour RGB display systems have been presented [9] and the potential market for these materials is enormous. Our theoretical understanding of their electronic structure is also improving. Although the initial interpretation of the behaviour in these systems used a one-electron semiconductor band model where the transitions are largely delocalised [10,11], a number of experimental results are not consistent with this [12], and suggest for the description of many of the properties of excited states of conjugated polymers it is better to

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consider that excitation is localised within a relatively small conjugation length. Within this molecular exciton description, the properties of the systems are best treated within a molecular framework, corresponding to self-localisation of electron–hole pairs [13]. At this level, there is extensive electron–electron correlation, and spin is a good quantum number, such that normal concepts of spin–spin coupling, etc. are appropriate. A good discussion of the relative merits of these two descriptions is given in a series of articles in [14]. Of particular relevance to the molecular exciton model is the observation of a long-lived phosphorescence, with a lifetime close to that of typical aromatic molecules, following photoexcitation of a frozen solution of a ladder type poly(*p*-phenylene), MeLPPP [15,16]. Phosphorescence has also been observed from thin films of polyfluorene alone and blended with benzil [17,18].

The majority of conjugated polymers have nondegenerate (singlet) ground states, and within a molecular exciton description these will be associated with excited singlet and triplet state manifolds. The behaviour of the triplet states is of importance to the efficiency of devices based on these systems for a number of reasons. Firstly, electroluminescence arises from excited state formation via charge recombination between positive (P$^+$) and negative (P$^-$) charge carriers:

$$P^+ + P^- \rightarrow {}^1P^* + {}^3P^*$$

Although different estimates exist for the ratio of singlet-to-triplet excited states produced in this process [19–22], it is generally accepted that triplet state formation is one of the major causes of efficiency loss in these systems. Since electroluminescence is normally only observed from the short-lived singlet excited state, long-lived triplet states may also act as traps to reduce the concentration of these species in devices [23]. Secondly, in the presence of molecular oxygen, triplet states may sensitise the formation of singlet oxygen, which can react with polymer chains, and ultimately limit device performance and lifetime [23–27]. On the beneficial side, the electronic energy from the triplet states of these systems may, however, be captured by appropriate acceptors, and these systems show potential as electrophosphorescent devices [28–30].

Triplet state formation can occur both by charge recombination, and singlet–triplet intersystem crossing (ISC). Knowledge of the formation and decay pathways of these triplets is therefore important for a full understanding of the electroluminescence behaviour of conjugated organic polymers. We report results of polymer triplet state dynamics in dilute solution, under conditions where they can be considered to be isolated chains [31], i.e., where there are no interchain interactions, and where the time between collisions of two polymer molecules is longer than the lifetimes of the excited states being studied. Preparation of triplet states by both photoexcitation and energy transfer will be considered.

2. Experimental

The structures and abbreviations of the polymers used in this study are shown in Fig. 1. In addition to the MEH-PPV shown, two other poly(*p*-phenylenevinylene)s (PPVs), poly(2,5-hexyloxyphenylenevinylene) (DHO-PPV) and poly(2,5-octyloxyphenylenevinylene) (DOO-PPV), were also studied. These differ from MEH-PPV in the alkoxyl substituents on the phenyl rings. These compounds were generous gifts from Covion (MEH-PPV), Professor M. de Long (DHO- and DOO-PPV), Professor M. Anderson (polythiophenes), Professor U. Scherf (PFO and MeLPPP), and Professor A.B. Holmes (CN-MEHPPV). Other reagents were of the purest grade available, and were generally used without further treatment. All photophysical measurements were made on benzene solutions. Except where stated, these were degassed by bubbling with argon or nitrogen.

Absorption and luminescence spectra, used for optical matching, and obtaining singlet energies and fluorescence data were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3-22 spectrometers, respectively [23]. Flash photolysis experiments were performed with an Applied Photophysics LKS.60 Laser Flash Photolysis Spectrometer attached to a Hewlett–Packard Infinum oscilloscope, using the third harmonic (355 nm) of the pulse from a Spectra-Physics Quanta Ray GCR-130 Nd/YAG laser for
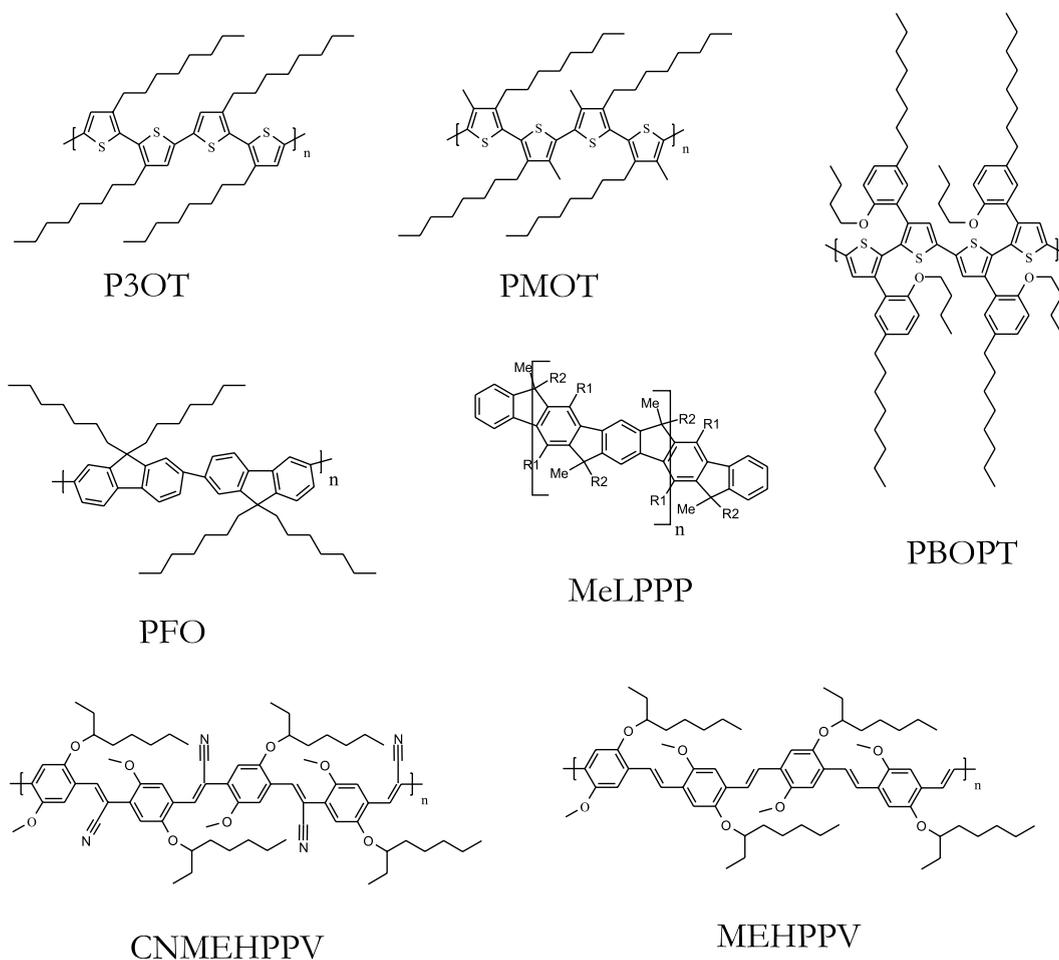
Fig. 1. Schematic structures of polymers used with their corresponding acronyms. For MeLPPP, $R_1 = n\text{-}C_6H_{13}, R_2 = 1,$ $4\text{-}(C_6H_4)\text{-}n\text{-}C_{10}H_{21}$.

excitation. Further details have been reported previously [32,33]. Time-resolved photoacoustic calorimetry (PAC) measurements were performed in a home built apparatus following the front-face irradiation design described by Arnaut et al. [34]. Both the experimental method and details of data analysis are described in detail elsewhere [23,33,35–37]. MEH-PPV was excited at 500 nm, while for all the other polymer solutions, excitation was at 337 nm. Pulse radiolysis experiments were carried out at the Free Radical Research Facility of the Paterson Institute for Cancer Research (Manchester, UK) using, typically, 50 ns, ca. 7.5 Gy pulses from a 10 MeV electron linear accelerator. Transient absorption difference spectra were observed using a xenon source and gated diode array or photomultiplier for detection. General details of the set-up are given in [26,38]. Singlet oxygen ($^1\Delta_g$) yields and lifetimes were obtained by direct measurement of the phosphorescence at 1270 nm following irradiation of an aerated solution of the polymers in benzene with a frequency tripled pulse (355 nm) from a Nd:YAG laser, as described in detail elsewhere [23,39]. The quantum yield of singlet oxygen formation was determined by comparison of the initial emission intensity for optically matched solutions at the excitation wavelength ($A_{355} = 0.5$)

with 1*H*-phenalen-1-one taken as standard, using $\Phi_\Delta = 0.93$ in benzene solution [40].

3. Results and discussion

3.1. Laser flash photolysis studies

Following photoexcitation of the polythiophenes PBOPT and P3OT in benzene solution with the third harmonic of a Nd/YAG laser (355 nm), reasonably intense transient absorptions were observed in the visible and near infrared, with spectra identical to those observed for the same compounds by pulse radiolysis/energy transfer in benzene solution with biphenyl as sensitiser [41]. These are assigned to their triplet states, suggesting relatively high $S_1 \rightsquigarrow T_1$ ISC quantum yields. The spectrum for PBOPT is shown in Fig. 2. This was fully formed within the rise-time of our system (≈ 10 ns), and under the conditions of the flash photolysis experiment decayed exponentially with a lifetime ≈ 14 μs. Efficient ISC has previously been reported for a regiorandom poly(3-octylthiophene) and a regioregular poly(3-hexylthiophene in xylene solution [42].

In contrast, although photoexcitation of MEH-PPV solutions produced a transient absorption, with lifetime $370 \leqslant \tau \leqslant 530$ μs, in the region where the triplet spectrum is expected from pulse radiolysis studies [26], the absorption was very weak, indicating that ISC is inefficient with this polymer.
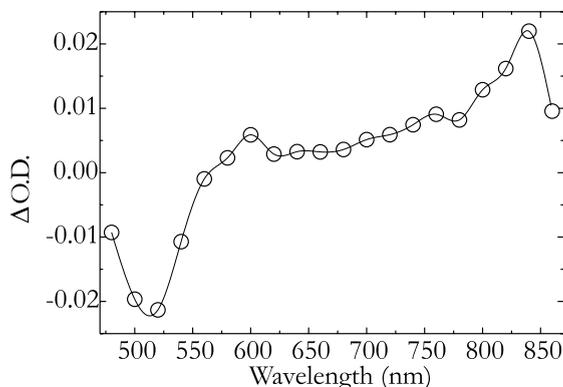
Fig. 2. Transient absorption spectrum observed following flash photolysis ($\lambda_{\text{excitation}} = 355$ nm) of a solution of PBOPT in benzene.

3.2. Time-resolved photoacoustic calorimetry

PAC has proved to be an excellent technique for studying $S_1 \rightsquigarrow T_1$ ISC in conjugated polymers [23] and oligomers [36,37]. This measures the heat evolved following excitation. From this, together with fluorescence quantum yields, singlet (E_S) and triplet (E_T) energies, it is possible to determine $S_1 \rightsquigarrow T_1$ ISC quantum yields (Φ_T). Values of Φ_T determined by this method, together with the singlet (S_1) and triplet (T_1) energies (from [41]) of a number of conjugated polymers in benzene solution are given in Table 1.

Of particular relevance is the high efficiency of triplet state formation observed with polythiophenes. This is probably due to efficient spin–orbit coupling induced by the sulphur heteroatom [43]. In agreement with the flash photolysis experiments, the yield of ISC with MEH-PPV was very small, while with DHO-PPV and DOO-PPV, although it was not possible to extract reliable Φ_T data from the PAC measurements, data from singlet oxygen measurements suggests this process is also inefficient. With CN-MEHPPV, there was no evidence for any long-lived triplet state formation either from either PAC or singlet oxygen studies. In contrast, with the ladder polymer MeLPPP, a reasonable triplet quantum yield was observed, consistent with the observation of phosphorescence on photoexcitation of this polymer in low temperature glasses [15,16] or films [44]. Although other factors may be involved, we wish to suggest that, as with typical aromatic systems [45–47], the decrease in the S_1–T_1 energy separation on going from MEH-PPV, through PFO to MeLPPP increases the rate of ISC. Recently, a similar energy gap dependence has been reported for nonradiative decay from the triplet state of Pt-containing conjugated polymers and monomers [48].

3.3. Pulse radiolysis/energy transfer

Triplet states can be selectively produced [49,50] by energy transfer following pulse radiolysis of benzene solutions of polymers (S) in the presence of appropriate sensitisers (A)

$$\text{Bz} + \text{e}^* \rightsquigarrow {}^1\text{Bz}^* + {}^3\text{Bz}^* + \text{e}^*$$

Table 1
Triplet state formation and decay of conjugated polymers in benzene solution

Compound	E_S[a] (eV)	E_T[b] (eV)	$\Delta E(S_1–T_1)$ (eV)	Φ_T	T–T absorption[c] (eV)	τ[c] (µs)
PBOPT	2.52	1.60	0.92	0.47	1.38	57
PMOT	3.77	2.20	1.57	0.66	1.85	62
P3OT	2.83	1.65	1.03	0.77	1.50	21
MEH-PPV	2.48	1.27	1.21	0.0125	1.50	92
DHO-PPV	2.58	1.50	1.08	[d]	1.62	176
DOO-PPV	2.59	1.50	1.09	[d]	1.55	134
PFO	3.22	2.30	0.92	0.031	1.65	108
MeLPPP	2.70	2.05	0.65	0.37	1.34	170
CN-MEHPPV	2.72	1.45[e]	1.27	0	[f]	

[a] From maximum of absorption band.
[b] From energy transfer.
[c] From pulse radiolysis.
[d] See text.
[e] Estimated from singlet energy and correlation in Ref. [41].
[f] Not observed.

$$^1Bz^* \rightarrow {}^3Bz^*$$

$$^1Bz^* + A \rightarrow Bz + {}^1A^*$$

$$^3Bz^* + A \rightarrow Bz + {}^3A^*$$

$$^1A^* \rightarrow {}^3A^*$$

$$^3A^* + S \rightarrow A + {}^3S^*$$
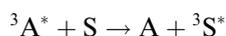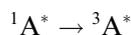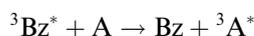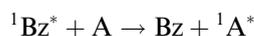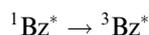
This is subject to the kinetically demanded concentration ratio $[Bz] \gg [A] \gg [S]$. We have previously reported spectra and energies of the triplet states of these polymers generated in this way [26,27,31,41]. The technique has also been used to study some *p*-phenylenevinylene oligomers [51] and broken conjugation polymers [52]. Absorption maxima and lifetimes for the polymers in the present study are given in Table 1.

3.4. Some kinetic considerations on triplet energy transfer to conjugated polymers

Under the experimental conditions used for the pulse radiolysis/energy transfer experiments, the concentration of excited triplet sensitiser ($[^3A^*] \approx 7 \times 10^{-8}–6 \times 10^{-6}$ M) is greater than that of the conjugated polymer ($1–3 \times 10^{-8}$ M). The rate of formation of MEH-PPV triplet state by energy transfer from biphenyl as a function of radiation dose is given in Table 2, and is typically $\approx 10^{11}$

Table 2
Kinetics of formation and decay of MEH-PPV triplet states by energy transfer from biphenyl as a function of radiation dose

Dose (Gy)	Formation	Decay[a]	
	k_2 (10^{11} M^{-1} s^{-1})	k_T (10^4 s^{-1})	$2\gamma/\varepsilon l$ (10^4 s^{-1})
1.73	1.97	0.97	–
3.28	1.32	1.03	–
7.76	0.91	1.12	–
16.04	0.83	1.20	0.76
33.75	0.67	1.34	1.16

[a] The decay has been analysed as competing first- and second-order kinetics assuming the decay of triplets follows the rate law $dn_T/dT = -k_T n_T - \gamma n_T^2$. From the data analysis both components have the units (time)$^{-1}$. For simplicity, the relationship between the measured value for the second component and the rate constant for triplet–triplet annihilation in three dimensions is given. As discussed in the text, the actual process may have rather lower dimensionality.

M^{-1} s^{-1}. This is close to the value 1.2×10^{11} M^{-1} s^{-1} calculated from the Debye–Smoluchowski equation [53,54] for a diffusion controlled process between biphenyl triplet state and the polymer in benzene

$$k_{diff} = (2RT/3000\eta)(2 + r_a/r_b + r_b/r_a),$$

where η is the solvent viscosity and r_a and r_b are the solute radii (taken as 0.5 nm for biphenyl and 21.5 nm for MEH-PPV). This behaviour is typical for triplet energy transfer occurring by the Dexter

electron exchange mechanism [55] when the triplet energy levels of the donor and acceptor are separated by more than 12 kJ mol^{-1} (125 meV) [56,57]. Note that the rate of energy transfer decreases with increasing dose. This will be discussed later.

3.5. Oxygen quenching and singlet oxygen formation

On bubbling solutions, with 0.4% O$_2$, the transient absorptions attributed to triplet states decayed more rapidly. The second-order decay rate constants for quenching of triplet states by oxygen (k_q) are presented in Table 3. Quenching of excited triplet states by molecular oxygen can either occur via electron transfer (Type I reaction) or energy transfer (Type II reaction) [58]. Evidence that the Type II process

$$^3S^* + O_2(^3\Sigma_g^-) \rightarrow S + O_2^*(^1\Delta_g)$$
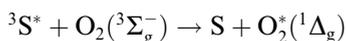
is involved with these systems comes from the direct observation of the phosphorescence of singlet oxygen at 1 eV (1270 nm) following excitation of aerated solutions of conjugated polymers with pulses from a frequency doubled or tripled Nd:YAG laser. From the study of the singlet oxygen luminescence intensity as a function of laser intensity [39], and comparison with 1H-phenalen-1-one as standard [40], it has been possible to estimate quantum yields for its formation (Φ_Δ).

These are given in Table 3, and vary from about 2.5% with MEH-PPV to nearly 70% with the polythiophene PMOT. In general, these are close to the yields of triplet state formation determined by PAC, as expected if quenching of singlet states by oxygen is quantitative. The main exception is MeLPPP, where the value of Φ_Δ is significantly smaller than the ISC yield determined by PAC. As we have discussed elsewhere [23,27], plots of singlet oxygen luminescence against excitation were nonlinear for P3OT, PFO and MeLPPP. This may have been due to some complexing of the polymers with molecular oxygen, as has been reported for poly(3-alkylthiophenes) [59].

The rate constants for quenching the triplet states of the polymers by oxygen are close to those observed with oxygen quenching of the triplet states of many small organic molecules [60], and are in the range 0.5–2.5×10^9 M^{-1} s^{-1}, approximately 1/9th the diffusion controlled limit in benzene solution (10^{10} M^{-1} s^{-1} [61]). This factor of 1/9th arises from spin multiplicity considerations when a ground state molecule and singlet oxygen are formed from two triplet states [60,62,63], and results from the fact that while interaction of the triplet state of the substrate and oxygen ($^3\Sigma_g^-$) will produce complexes with quintet, triplet and singlet multiplicity, these are formed reversibly and only the singlet complex leads to quenching (i.e., 1 in every 9 collisions is effective).

3.6. Triplet–triplet annihilation and delayed fluorescence

With the data in Table 2, the decrease in energy transfer rate with increasing dose can be explained in terms of more than one triplet excitation being transferred per chain. As discussed elsewhere [64], we estimate for MEH-PPV there can be a maximum of about 30 triplets per isolated polymer chain. When this happens, it is possible to have intrachain triplet–triplet annihilation. With the decay of the MEH-PPV triplet–triplet absorption at high radiation doses (Table 2) it is no longer possible to fit the decay of triplet absorption to a single exponential, but the data can be fitted to two competing processes. The second process is suggested to be bimolecular. If this is due to

Table 3
Rates for quenching of triplet states of conjugated polymers by oxygen and quantum yields for singlet oxygen formation in benzene solution

Compound	k_q[a] (10^9 M^{-1} s^{-1})	Φ_Δ[b]
PBOPT	1.2	0.535
PMOT	1.1	0.69
P3OT	1.4	0.41
MEH-PPV	2.5	0.025
DHO-PPV	1.7	0.024
DOO-PPV	2.2	0.041
PFO	0.5	0.031
MeLPPP	0.7	0.085
CN-MEHPPV	[c]	0

[a] From decay of triplet state in presence and absence of oxygen.
[b] From singlet oxygen luminescence.
[c] Not observed.

intrachain triplet–triplet annihilation (TTA), it would be expected to lead to delayed fluorescence (DF). Confirmation of this is given in Fig. 3, where the time-dependent DF signal monitored at 2.23 eV is shown following pulse radiolysis of solutions of MEH-PPV in benzene in the presence of biphenyl [64]. There is an initial very fast emission, which arises from Čerenkov radiation, probably together with some prompt fluorescence from MEH-PPV. At the same wavelength, a new emission grows-in over a few μs, and then decays in tens of μs. This is due to DF from the polymer arising from intrachain triplet–triplet annihilation [64], and is ompletely quenched by molecular oxygen. In agreement with the interpretation that DF arises from TTA, its intensity increases, while its lifetime decreases on increasing radiation dose. This is a result of the increase in the triplet state concentration on each isolated chain. We have observed delayed fluorescence arising from intrachain TTA from other polymers, including MeLPPP and PFO [27,64]. In studies using a series of broken conjugation MEH-PPV derivatives Candeias et al. [52] have shown that there is no evidence for any triplet

energy transfer between different isolated conjugation segments on a microsecond timescale. In our intrachain TTA results, triplet energy must then migrate by hopping. Complications arise in analysis of data due to problems of dimensionality, and further work is in progress. However, for the rigid rod polymer MeLPPP, from the observed DF traces we have estimated a triplet hopping rate of 10^5–10^6 nm s^{-1} [27].

4. Conclusions

Triplet states have been produced on isolated chains of conjugated polymers in benzene solution by optical excitation and by energy transfer from appropriate donors. The triplet lifetimes vary from ca. 20 to 200 μs, with shorter lifetimes commonly being observed with the polythiophene derivatives. The triplet states are quenched by molecular oxygen with formation of singlet molecular oxygen. The efficiency of $S_1 \rightarrow T_1$ ISC in the polymers has been studied by PAC and by measuring singlet oxygen yields. The highest yields are observed with the polythiophenes, and it is probable that both the high triplet yields and short lifetimes of these compounds is due to efficient spin–orbit coupling of the sulphur atom affecting the spin-forbidden radiationless processes. Comparison between the yields of triplet formation with *p*-phenylenevinylene polymers, polyfluorene and MeLPPP suggests that, where no heteroatom is present, ISC may depend on the singlet–triplet energy gap. All these results suggest that the photophysics of conjugated polymers is closer to that of typical small organic molecules than to semiconductors.

However, very distinct behaviour is observed when a number of triplet excitations is introduced onto each chain by energy transfer. The polymers can accept several triplet excitations before they eventually become saturated. Each triplet can then move rather slowly along the chain by hopping until it eventually encounters another triplet, resulting in triplet–triplet annihilation and delayed fluorescence. This has no analogy in small molecules, but has many similarities with what is observed in organic crystals [65].
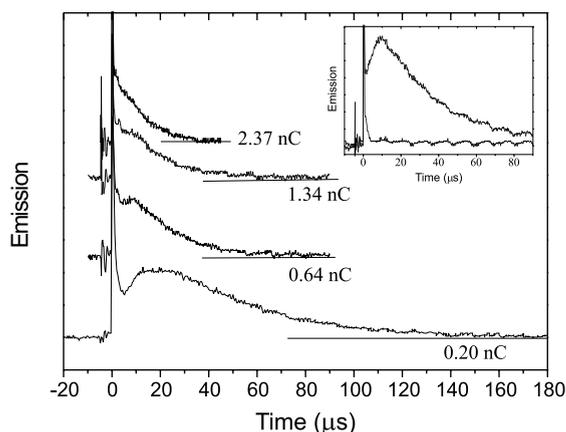
Fig. 3. Time-dependent DF of MEH-PPV observed at 555 nm at various radiation doses following pulse radiolysis of argon-saturated benzene solutions in the presence of biphenyl (10 mM). Intensities are not normalised, however the peak signal at 1.34 nC was ca. six times that at 0.2 nC. The inset shows the effect of bubbling with oxygen: top trace, Ar saturated; bottom trace, oxygen bubbled. Reprinted from A.P. Monkman, H.D. Burrows, I. Hamblett, S. Navaratnam, Chem. Phys. Lett. 340 (2001) 467, Copyright (2001) with permission from Elsevier Science.

Acknowledgements

References

[1] R.H. Partridge, UK Pat. 74/44704; Chem. Abs. 86 (1974) 11261.

[2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539.

[3] D. Braun, A.J. Heeger, Appl. Phys. Lett. 58 (1991) 1982.

[4] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed. 37 (1998) 402.

[5] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Löglund, W.R. Salaneck, Nature 397 (1999) 121.

[6] G. Yu, Y. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.

[7] F. Hide, M.A. Díaz-Garciá, B.J. Schwartz, A.J. Heeger, Acc. Chem. Res. 30 (1997) 430.

[8] R.J. Visser, Philips J. Res. 51 (1998) 467.

[9] H. Kobayashi, S. Kanbe, S. Seki, H. Kigchi, M. Kimura, I. Yudasaka, S. Miyashita, T. Shimoda, C.R. Towns, J.H. Burroughes, R.H. Friend, Synth. Met. 111/112 (2000) 125.

[10] W.-P. Su, J.R. Schreiffer, A.J. Heeger, Phys. Rev. Lett. 42 (1979) 1698.

[11] K. Fesser, D.R. Bishop, D.K. Campbell, Phys. Rev. B 27 (1983) 4804.

[12] U. Rauscher, H. Bässler, D.D.C. Bradley, M. Hennecke, Phys. Rev. B 42 (1990) 9830.

[13] B. Schweitzer, H. Bässler, Synth. Met. 109 (2000) 1.

[14] N. Sariciftci (Ed.), Primary Photoexcitations in Conjugated Polymers: Molecular Exciton Versus Semiconductor Band Model, World Scientific, Singapore, 1997.

[15] Yu.V. Romanovskii, H. Bässler, Chem. Phys. Lett. 326 (2000) 51.

[16] D. Hertel, S. Setayesh, H.-G. Nothofer, U. Scherf, K. Mullen, H. Bässler, Adv. Mater. 13 (2001) 65.

[17] C. Rothe, A.P. Monkman, Phys. Rev. B 65 (2002) 073201.

[18] C. Rothe, R. Guentner, U. Scherf, A.P. Monkman, J. Chem. Phys. 115 (2001) 9557.

[19] M.A. Baldo, D.F. O'Brien, M.E. Thompson, S.R. Forrest, Phys. Rev. B 60 (1999) 14422.

[20] Y. Cao, I.D. Parker, C. Yu, C. Zhang, A.J. Heeger, Nature 397 (1999) 414.

[21] Z. Shuai, D. Beljonne, R.J. Silbey, J.L. Brédas, Phys. Rev. Lett. 84 (2000) 131.

[22] M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha, Z.V. Vardeny, Nature 409 (2001) 494; Nature 411 (2001) 617.

[23] H.D. Burrows, J. Seixas de Melo, C. Serpa, L.G. Arnaut, A.P. Monkman, I. Hamblett, S. Navaratnam, J. Chem. Phys. 115 (2001) 9601.

[24] R.D. Scurlock, B. Wang, P.R. Ogilby, J.R. Sheats, R.L. Clough, J. Am. Chem. Soc. 117 (1995) 10194.

[25] N. Dam, R.D. Scurlock, B. Wang, L. Ma, M. Sundahl, P.R. Ogilby, Chem. Mater. 11 (1999) 1302.

[26] A.P. Monkman, H.D. Burrows, M.G. Miguel, I. Hamblett, S. Navaratnam, Chem. Phys. Lett. 307 (1999) 303.

[27] A.P. Monkman, H.D. Burrows, I. Hamblett, S. Navaratnam, U. Scherf, C. Schmitt, Chem. Phys. Lett. 327 (2000) 111.

[28] V. Cleave, G. Yahioglu, P. LeBarny, R.H. Friend, N. Tessler, Adv. Mater. 11 (1999) 285.

[29] D.F. O'Brien, C. Giebeler, R.B. Fletcher, A.J. Cadby, L.C. Palilis, D.G. Lidzey, P.A. Lane, D.D.C. Bradley, W. Blau, Synth. Met. 116 (2001) 379.

[30] I.H. Campbell, D.L. Smith, S. Tretiak, R.L. Martin, C.J. Neef, J.P. Ferraris, Phys. Rev. B 65 (2002) 085210.

[31] H.D. Burrows, M. da G. Miguel, A.P. Monkman, I. Hamblett, S. Navaratnam, J. Mol. Struct. 563–564 (2001) 41.

[32] D. Murtinho, M. Pineiro, M.M. Pereira, A.M.d'A. Rocha Gonsalves, L.G. Arnaut, M. da G. Miguel, H.D. Burrows, J. Chem. Soc., Perkin Trans. 2 (2000) 2441.

[33] C. Serpa, L.G. Arnaut, J. Phys. Chem. A 104 (2000) 11075.

[34] L.G. Arnaut, R.A. Caldwell, J.E. Elbert, L.A. Melton, Rev. Sci. Instrum. 63 (1992) 5381.

[35] M. Pineiro, A.L. Carvalho, M.M. Pereira, A.M.d'A. Rocha Gonsalves, L.G. Arnaut, S.J. Formosinho, Chem. Eur. J. 4 (1998) 2299.

[36] J. Seixas de Melo, L.M. Silva, L.G. Arnaut, R.S. Becker, J. Chem. Phys. 111 (1999) 5427.

[37] J. Seixas de Melo, F. Elisei, C. Gartner, G.G. Aloisi, R.S. Becker, J. Phys. Chem. A 104 (2000) 6907.

[38] J. Butler, B.W. Hodgson, B.M. Hoey, E.J. Land, J.S. Lea, E.J. Lindley, F.A.P. Rushton, A.J. Swallow, Radiat. Phys. Chem. 34 (1989) 633.

[39] J.P. Keene, D. Kessel, E.J. Land, R.W. Redmond, T.G. Truscott, Photochem. Photobiol. 43 (1986) 117.

[40] E. Oliveros, P. Suardi-Murasecco, T. Aminian-Saghafi, A.M. Braun, H.-J. Hansen, Helv. Chim. Acta 74 (1991) 79.

[41] A..P. Monkman, H.D. Burrows, L.J. Hartwell, L.E. Horsburgh, I. Hamblett, S. Navaratnam, Phys. Rev. Lett. 86 (2001) 1358.

[42] B. Kraabel, D. Moses, A.J. Heeger, J. Chem. Phys. 103 (1995) 5102.

[43] D. Beljonne, Z. Shuai, G. Pourtois, J.L. Bredas, J. Phys. Chem. A 105 (2001) 3899.

[44] Yu.V. Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R.I. Personov, H. Bässler, Phys. Rev. Lett. 84 (2000) 1027.

[45] G.W. Robinson, R.P. Frosch, J. Chem. Phys. 38 (1963) 1187.

[46] W. Siebrand, J. Chem. Phys. 47 (1967) 2411.

[47] R. Englman, J. Jortner, Mol. Phys. 18 (1970) 145.

[48] J.S. Wilson, N. Chawdhury, M.R.A. Al-Mandhary, M. Younus, M.S. Khan, P.R. Raithby, A. Köhler, R.H. Friend, J. Am. Chem. Soc. 123 (2001) 9412.

[49] E.J. Land, Proc. R. Soc. A 305 (1968) 457.

[50] R. Bensasson, E.J. Land, Trans. Faraday Soc. 67 (1971) 1904.

[51] L.P. Candeias, J. Wildeman, G. Hadziioannou, J.M. Warman, J. Phys. Chem. B 104 (2000) 8366.

[52] L.P. Candeias, G. Padmanaban, S. Ramakrishnan, Chem. Phys. Lett. 349 (2001) 394.

[53] M. Smoluchowski, Z. Phys. Chem. 92 (1917) 129.

[54] P. Debye, Trans. Electrochem. Soc. 82 (1942) 265.

[55] D.L. Dexter, J. Chem. Phys. 21 (1953) 836.

[56] H.L.J. Bäckstrom, K. Sandross, Acta Chem. Scand. 12 (1958) 823.

[57] R.V. Bensasson, E.J. Land, T.G. Truscott, in: Excited States and Free Radicals in Biology and Medicine, Oxford University Press, Oxford, 1993, p. 42.

[58] Ref. [57], p. 255.

[59] M.S.A. Abdou, F.P. Orfno, Y. Son, S. Holdcroft, J. Am. Chem. Soc. 119 (1997) 4518.

[60] O.L.J. Gijzeman, F. Kaufman, G. Porter, J. Chem. Soc., Faraday Trans. 269 (1973) 708.

[61] S.L. Murov, I. Carmichael, G.L. Hug, in: Handbook of Photochemisry, second ed., Marcel Dekker, New York, 1993, p. 208.

[62] S.J. Formosinho, Mol. Photochem. 7 (1976) 13.

[63] F. Wilkinson, Pure Appl. Chem. 69 (1997) 851.

[64] A.P. Monkman, H.D. Burrows, I. Hamblett, S. Navaratnam, Chem. Phys. Lett. 340 (2001) 467.

[65] M. Pope, C.E. Swenberg, in: Electronic Processes in Organic Crystals and Polymers, second ed., Oxford University Press, New York, 1999, p. 64.