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Singlet and triplet energy transfer in a bichromophoric system with anthracene covalently linked through sulfonamide to a *meso*-tetraphenylporphyrin

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Abstract

A bichromophoric system in which anthracene has been covalently linked to *meso*-tetrakis(phenyl)porphyrin (TPP) moieties by alkylsulfonamide spacers has been synthesized and fully characterized. A spectroscopic and photophysical study of this system in dimethylformamide (DMF) has been undertaken to study electronic energy transfer between the anthracene and porphyrin units in excited singlet and triplet states. By use of steady-state and time-resolved fluorescence techniques as well as phosphorescence and laser flash phototolysis, it is shown that excitation to either the singlet or triplet states of the anthracene leads to energy transfer to the lower lying S_1 and T_1 states of TPP group. The efficiency and the rate of energy transfer have been determined. Although the estimated efficiency of the energy transfer process in the singlet manifold is high, the coexistence of fluorescence from both moieties when exciting the anthracene, together with observation of a biexponential decay of the porphyrin fluorescence when excited in the porphyrin Soret band suggest that communication exists between the two chromophores. This is discussed in terms of Förster type energy transfer and geminate radical pair mechanisms, possibly involving nonplanar (between chromophores) excited state geometry. In the flash photolysis studies, only the porphyrin triplet state was observed. The dominance of nonradiative deactivation in the overall decay of the excited singlet and triplet states is indicated.

Keywords: Porphyrins; Anthracene; Photophysics; Fluorescence; Phosphorescence; Triplet state; Singlet state

1. Introduction

The attractive electronic properties, coupled with the ease of modification by various synthetic routes, make porphyrins good candidates both for the study of energy and electron transfer reactions and as building blocks for molecular electronic and photonic devices [1–14]. Much of the research in this area has been stimulated by their relevance as model systems for photosynthesis [15]. The study of this has been particularly stimulated by the elegant structural [16] and dynamic [17,18] studies of the bacterial light harvesting systems. Many of these studies involve bichromophoric systems, frequently referred to as dyads, triads, etc., in which two isolated chromophores are present. Energy or electron transfer can occur via through-space or through-bond processes. Such bichromophoric systems provide the possibility that one of the chromophores may act as an antenna to absorb light in a spectral region where the other does not absorb, but which may then transfer this energy to the other chromophore by electronic energy transfer. Porphyrin based molecular photonic wires [5] and optoelectronic gates [7] have been reported, while the synthesis of long (ca. 106 nm), discrete coupled porphyrin arrays [12] opens up exciting possibilities in light harvesting. In addition, singlet and triplet energy transfer to porphyrins also has important applications in optimising emission yields and colour in organic [19,20] and polymer based [21,22] light emitting diodes. Porphyrins may also have an important role in the photooxidation of phenols [23] and as sensors. For example, it has been found that, with similar compounds when present in LB films, they are excellent probes for chlorine detection with detection limits of 0.2 ppm [24].

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Because of good spectral overlap, and other photophysical properties, bichromophoric molecules involving anthracene as donor and porphyrins as acceptors have been found to be particularly attractive candidates for studying energy migration, and both covalently bonded [1,25–27] and self-assembled [28] systems of these have been reported. However, whilst much valuable information has been obtained from such studies, our knowledge of processes occurring and the effect of the spacer groups are far from complete. The study of this is particularly relevant to the development of new covalently linked bichromophoric electronic and photonic devices, such as those used for tuning the colour of organic light emitting devices [29].

Chlorosulfonation has been shown to be an excellent route for functionalization of *meso*-tetrakis(phenyl)porphyrin (TPP) so that it can be covalently bonded to other molecules [30]. This involves reaction of the porphyrin with chlorosulfonic acid to produce the sulfonyl chloride. This can then be reacted with a suitable amine or hydroxy derivative to give the corresponding amide or ester. We report the preparation of the bichromophoric system involving anthracene covalently linked by an alkylsulfonamide spacer to TPP (designated Anth*as*TPP). Energy transfer has been studied in the lowest singlet and triplet states of this system, with particular emphasis on mechanistic aspects.

2. Experimental

2.1. Materials

All reagents were synthesis grade (Aldrich) and all solvents were purified by standard methods before use. Chloroform was purified by washing 2.5 dm^3 with 250 cm^3 of concentrated sulfuric acid, separating the organic layer, washing twice with distilled water ($2 \times 150\,cm^3$) followed by drying with magnesium sulfate. For pulse radiolysis studies, the $CHCl_3$ was then filtered through a pad of silica gel (bottom) and sodium carbonate (top) solid and used directly. This treatment was necessary to remove ethanol stabilizer, which interferes with formation of positive charged species in radiolysis [31].

2.1.1. Synthesis of meso-tetra-(4-(N-methyl-N-9-anthracenyl-methyl)-sulfamoylphenyl)-porphyrin (3)

Meso-tetraphenylporphyrin (**1**) was prepared by the Rothemund–Adler method [32] and purified following an established procedure [33]. *Meso*-tetra-(4-chlorosulfonyl)-phenylporphyrin (**2**) was prepared by chlorosulfonation [30] and used directly in the synthesis of porphyrin (**3**).

A solution of 1.5 g (0.007 mol) of 9-methylaminomethyl-anthracene in 25 ml in dry dichloromethane was added to a sample of 100 mg (1×10^{-4} mol) of *meso*-tetra-(4-chlorosulfonyl)-phenylporphyrin in 25 cm^3 dry dichloromethane, at room temperature. The reaction was left under moderate stirring for 4 h, and then the mixture was washed with aqueous HCl (4% solution), water and a saturated solution of sodium hydrogen carbonate. The final work-up involved chromatography on silica using dichloromethane/ethyl acetate (4/1) as eluent and crystallisation from dichloromethane/*n*-hexane, giving small red/brown crystals. Yield 70%, FAB$^+$, $[M+H]^+$ a m/z 1749. Calculated for $C_{108}H_{82}N_8O_8S_4$—C: 74.20%; H: 4.73%; N: 6.41%; O: 7.32%; S: 7.34%. Found—C: 74.63%; H: 4.98%; N: 6.29%; S: 7.34%. UV/visible spectra (DMF) (nm; ε, $cm^{-1}\,mol^{-1}$) = (350; 13,599), (368; 17,299), (387; 16,300), (419; 4.5×10^5), (513; 25,019), (548; 12,195), (588; 8471), (643; 5164). UV/visible spectra of dication ($CHCl_3$/TFA 5%) (nm; relative intensity, %) = (350; 32.2), (366; 42.9), (388; 38), (443; 100), (650; 13.6). ^1H NMR (DMF-d_7): (9.2; s; 8H; $\underline{H}_\beta$), (8.8–7.5; m; 52H; Ar$\underline{H}$), (5.6; sl; 8H; $-NC\underline{H_2}-$), (2.7; sl; 12H; $-NC\underline{H_3}$), (−2.8; s; 2H).

2.2. Methods

NMR experiments were carried out on a Bruker-AC200 instrument, and mass spectra (FAB$^+$) were measured on a Varian VG7070C spectrometer.

Absorption and luminescence spectra were recorded on Shimadzu UV-2100, Olis-Cary 14, and Horiba Jobin-Ivon SPEX Fluorog 3-22 spectrometers, respectively. For phosphorescence a 1934 D phosphorimeter accessory was used. Fluorescence and phosphorescence spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields were measured using heptathiophene in benzene as standard ($\phi_F = 0.36$) [34].

Initial laser induced transient absorption spectral measurements were made at the Free Radical Research Facility of the Paterson Institute for Cancer Research, Manchester, England using a J.K. Lasers System 2000 Nd/YAG laser for excitation and single or multiwavelength detection systems [35], and at the Instituto Superior Técnico, Lisbon using a set-up described in detail elsewhere [36]. All subsequent triplet absorption spectra and yields were obtained using an Applied Photophysics laser flash photolysis equipment pumped by a Nd:YAG laser (Spectra Physics) with excitation wavelength 355 or 266 nm [37,38]. First-order kinetics was observed for the decay of the lowest triplet state. The transient spectra (300–700 nm) were obtained by monitoring the optical density change at 5–10 nm intervals and averaging at least 10 decays at each wavelength. Pulse radiolysis experiments were carried out at the Free Radical Research Facility, Daresbury, UK using 200 ns–2 μs high-energy electron pulses from a 12 MeV linear accelerator, which were passed through solutions in a 2.5 cm optical pathlength quartz cuvette attached to a flow system. All solutions were bubbled with argon for about 30 min before experiments. The experimental set-up been described in detail elsewhere [31].

Fluorescence decays were measured using a home-built TCSPC apparatus with an N_2 filled IBH 5000 coaxial flashlamp as excitation source, Jobin-Ivon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments

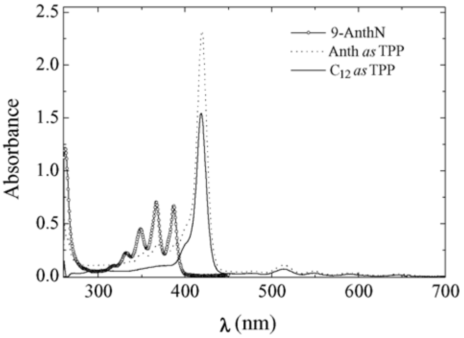


Fig. 1. Absorption spectra of Anth*as*TPP, C_{12}*as*TPP and 9-(methylaminomethyl)anthracene (9-AnthN) in DMF.

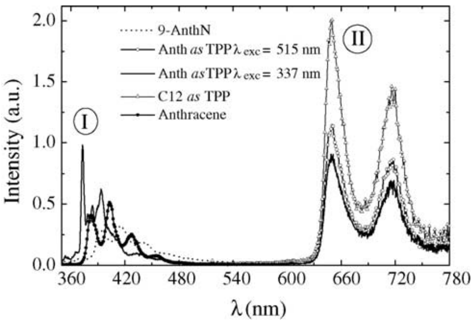


Fig. 2. Fluorescence emission spectra of Anth*as*TPP (with λ_{exc} = 337 and 515 nm), C_{12}*as*TPP, 9-AnthN and anthracene in DMF.

TAC and MCA. Alternate measurements (1000 c.p.c.) of the pulse profile at 337 nm and the sample emission were performed until 1–2 × 10^4 counts at the maximum were reached [39]. The fluorescence decays were analysed using the modulating functions method of Striker with automatic correction for the photomultiplier 'wavelength shift' [40]. Some of the decays were obtained with picosecond resolution in an apparatus described elsewhere [41].

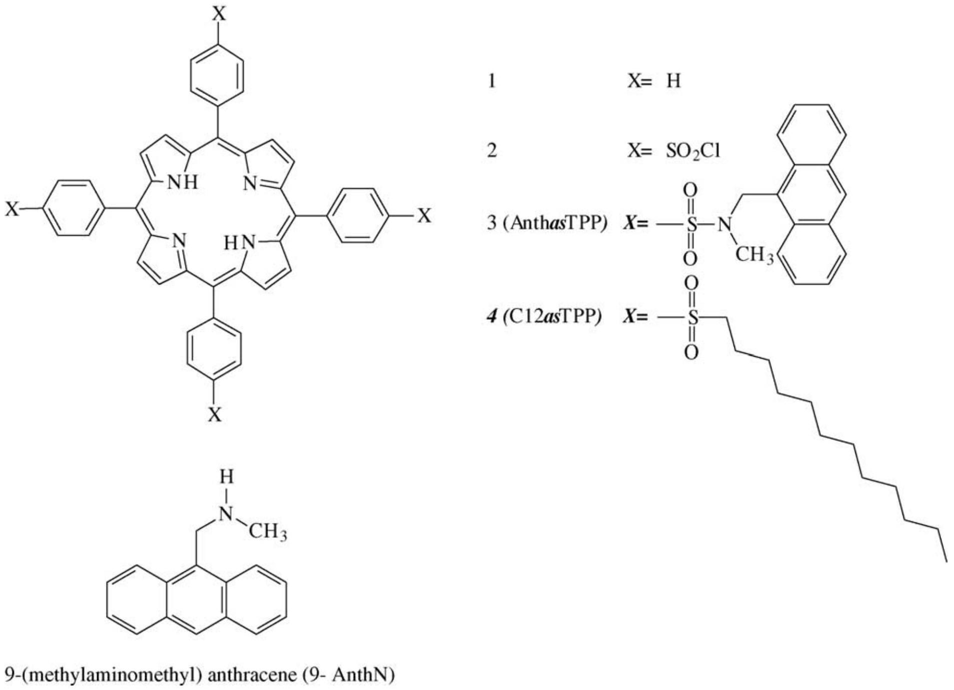
3. Results and discussion

3.1. Singlet state properties

Fig. 1 shows the absorption spectra of the system Anth*as*TPP (**3** in Scheme 1) together with the spectra of the two isolated chromophores: C_{12}*as*TPP (**4** in Scheme 1) and 9-(methylaminomethyl)anthracene, 9-AnthN in Scheme 1. Both Anth*as*TPP and C_{12}*as*TPP display characteristic free base porphyrin spectra, with a strong Soret (B) band at 420 nm and four weaker visible bands, $Q_y(1,0)$, $Q_y(0,0)$, $Q_x(1,0)$ and $Q_x(0,0)$, between 490 and 650 nm. The absorption spectrum of 9-AnthN is close to that of anthracene, revealing similar vibronic structure. The sum of the absorption spectra of the two isolated chromophores C_{12}*as*TPP and 9-AnthN can be seen to match perfectly the absorption spectrum of Anth*as*TPP, indicating that there is no significant interaction between the anthracene and porphyrin groups in the ground state.

3.1.1. Steady-state fluorescence data

Fig. 2 presents the fluorescence spectra of the three compounds studied, together with that of anthracene, all in dimethylformamide (DMF) solution. The emission spectra of



Scheme 1.

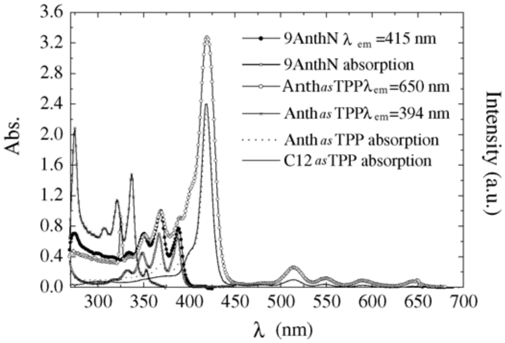


Fig. 3. Excitation and absorption spectra of Anth*as*TPP, C_{12}*as*TPP and 9-AnthN in DMF, at 293 K.

Anth*as*TPP with excitation at 515 nm consist of two bands with maxima at 650 and 718 nm, typical of free base porphyrins, and is very similar to that obtained with the same excitation wavelength for C_{12}*as*TPP, identified as II in Fig. 2. However, when excitation is made at 337 nm, in the region where the anthracene chromophore absorbs, in addition to emission at 650 and 718 nm, a new vibrationally resolved band appears with a maximum at ≅372 nm, identified with I in Fig. 2. Comparison of this new band with the emission spectra of 9-AnthN and of anthracene reveals that while the match is not perfect, the emission of Anth*as*TPP overlaps the emission of the two above, suggesting that it comes from the anthracene moiety. The blue shift of the emission band in Anth*as*TPP relative to 9-AnthN probably arises from the fact that the model compound, 9-AnthN, lacks the SO_2-Ph group, which probably induces an efficient electron withdrawing effect on the anthracene chromophore.

The appearance of bands I and II in Fig. 2 when excitation is made in the anthracene absorption region provides evidence for singlet–singlet energy transfer from anthracene to the porphyrin. Evidence against the emission arising from direct excitation of both chromophores comes from the fluorescence excitation spectrum of Anth*as*TPP with $\lambda_{em} = 650$ nm (see Fig. 3), which is identical to the absorption spectrum of Anth*as*TPP, revealing the existence of the two distinct chromophores. It is worth noting that the efficiency of energy transfer to the TPP unit is not 100% on excitation in the anthracene band. The importance of orientation of donor and acceptor groups in anthracene–porphyrin energy transfer in supramolecular systems has recently been highlighted [27], and this factor may possibly be important here.

Both intra and intermolecular energy transfer have been found to occur with Anth*as*TPP. For more concentrated solutions of Anth*as*TPP, it was found that the ratio of the fluorescence bands II/I is greater than that obtained at low concentrations. However, no dependence of the shape or emission maximum was found with different concentrations of Anth*as*TPP, showing that aggregation is not occurring.

Fluorescence quantum yields were obtained for dilute solutions (optical density at the excitation wavelength less than 0.1) of Anth*as*TPP and the model compound C_{12}*as*TPP. In both cases excitation was at 465 nm, region where the anthracene does not absorb. The values obtained were 0.047 and 0.051 for Anth*as*TPP and C_{12}*as*TPP, respectively. These are essentially identical within the experimental error for this type of measurement (typically 5%). Moreover, the low absorbance values used for the emission studies make it very unlikely that there is any contribution from intermolecular energy transfer, such that only intramolecular processes are being followed.

3.1.2. Time-resolved fluorescence data

The fluorescence lifetimes of the two isolated chromophores, the porphyrin (C_{12}*as*TPP) and the anthracene [9-(methylaminomethyl)anthracene] moieties, were obtained in DMF. In both cases, good monoexponential decays were observed, giving the values of 2.2 and 9.8 ns, respectively, see Table 1.

Upon excitation of Anth*as*TPP with $\lambda_{exc} = 417$ nm, i.e. at longer wavelength than the absorption of the anthracene chromophore, and observation of emission from the TPP unit at 650 nm, the fluorescence decay was double exponential, with lifetimes of 2.2 ns (≅20% of the decay) and 12.4 ns (≅80% of the overall fluorescence decay). These two decay times can be attributed to the two lifetimes of the individual chromophores. However, in the steady-state emission spectral studies, excitation at this wavelength, corresponding to the absorption region of the porphyrin moiety, only generates the characteristic fluorescence of TPP with maxima at 650 and 715 nm. Upon excitation of Anth*as*TPP at 337 nm and observation of emission at 430 nm (where the anthracene chromophore should emit) a double exponential decay was observed, with lifetimes of 2.7 ns (≅20% of the decay) and 10.2 ns (≅80% of the decay). These results are summarised in Table 1. However, it seems likely that direct excitation of the anthracene moiety in Anth*as*TPP can be excluded. From Fig. 1 it can be observed that the anthracene-like absorption of Anth*as*TPP is slightly red-shifted relative to anthracene itself. However, the shift in the maxima of the two is ca. 2 nm and the on-

Table 1
Fluorescence decay times and normalized pre-exponential factors obtained for the compounds studied in DMF, at $T = 293$ K, also presented are the χ^2 values

Compound	λ_{exc} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2
Anth*as*TPP	337	430	2.69	10.17	0.485	0.514	1.25
	417	650	2.20	12.41	0.60	0.40	1.00
C_{12}*as*TPP	417	650	2.21	–	1.00	–	1.15
9-AnthN	337	430	–	9.83	–	1.00	1.08

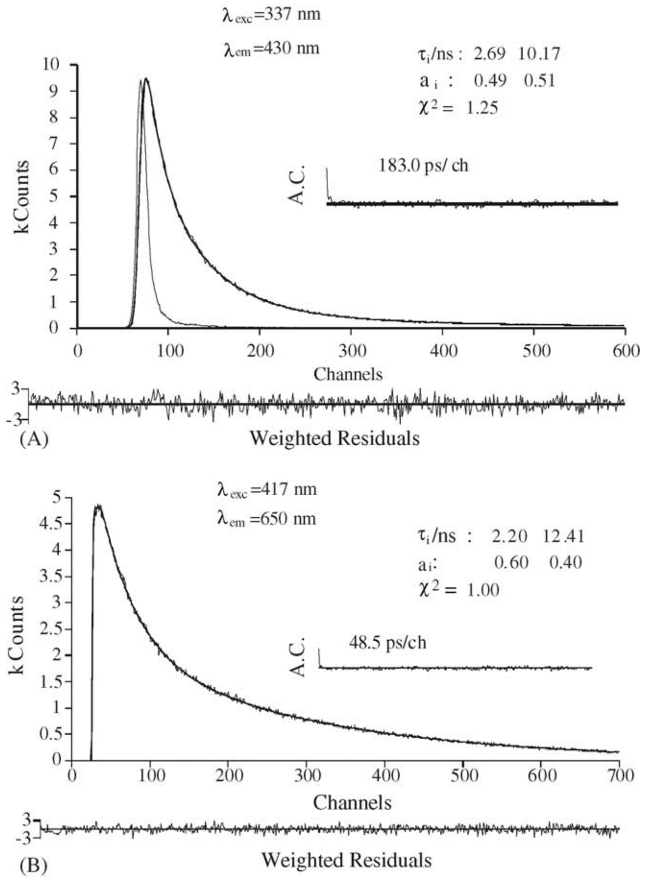


Fig. 4. Fluorescence decays of (A) Anth*as*TPP with $\lambda_{\text{exc}} = 337$ nm and emission at 430 nm and (B) with $\lambda_{\text{exc}} = 417$ and emission at 650 nm. Shown as inserts are the auto-correlation functions (A.C.). Below each decay, the weighted residuals are also presented.

set of the anthracene absorption is found at ≈406 nm; from this, it is likely that the on-set for absorption with anthracene in Anth*as*TPP will be in the 408–410 nm region, which is a markedly shorter wavelength than the 417 nm used to excite the emission in Fig. 4B. At the low photon fluxes used in these experiments, it is unlikely that processes such as triplet–triplet annihilation are involved. In addition, there is no evidence for this in the steady-state fluorescence measurements. Various other possibilities can then be considered to explain the observed biexponential decays. First, we will consider the possibility that it involves an excited state equilibrium between two possible conformations of Anth*as*TPP. In this case, with $\lambda_{\text{exc}} = 337$ nm we excite the anthracene chromophore, which would than decay normally with its inherent lifetime ($\tau_{\text{9-AnthN}}$ ca. 10 ns), in addition to energy (or electron) transfer to the porphyrin chromophore, that would than decay with a decay time which is the sum of the rate constant for the energy (or electron) transfer and the lifetime of the porphyrin ($1/\tau_{\text{Porph}}$). Due to the back reaction, although we observe emission at 430 nm, where only the anthracene emits, it may also be possible to follow the decay time of the porphyrin moiety. However, this model fails to explain the decay observed upon excitation at 417 nm.

The second possibility is that excitation transfer from anthracene to porphyrin involves more than one process. Energy transfer (ET) is commonly treated in terms of either dipole–dipole (Förster) [42] or electron exchange (Dexter) [43] mechanisms. In the case of the ET occurring through the Förster mechanism, the rate constant for energy transfer (k_{ET}) in solution is given by:

$$k_{\text{ET}} = \frac{9000 \ln 10}{128\pi^5 N} \frac{k^2\phi_{\text{D}}}{n^4\tau_{\text{D}} R^6} \underbrace{\int_0^\infty F_{\text{D}}(\bar{\nu})\varepsilon_{\text{A}}(\bar{\nu})\frac{\text{d}(\bar{\nu})}{\bar{\nu}^4}}_{J(\bar{\nu})} \tag{1}$$

where N is the Avogadro's number, ϕ_{D} and τ_{D} are the fluorescence efficiency and radiative lifetime of the donor (D), k an orientation factor relating the geometry of the D–A dipoles, n the refractive index of the media, and in the above integral, [$J(\bar{\nu})$ the overlap integral], $F_{\text{D}}(\bar{\nu})$ the spectral distribution of donor emission and $\varepsilon_{\text{A}}(\bar{\nu})$ the molar extinction of the acceptor. For random geometry, as obtained in solutions and/or gaseous systems, $k^2 = 2/3$ [44].

The rate constant for energy transfer can also be related with the critical transfer distance parameter, R_0 (which is characteristic of a given D–A acceptor pair) through Eq. (2):

$$k_{\text{ET}} = \frac{1}{\tau_{\text{D}}}\left(\frac{R_0}{R}\right)^6 \tag{2}$$

Simple manipulation of Eqs. (1) and (2) leads to:

$$R_0\,(\text{Å}) = 0.211[k^2 n^{-4}\phi_{\text{D}} J(\lambda)]^{1/6} \tag{3}$$

From this equation it can be seen that R_0 only depends on the experimental observables $J(\bar{\nu})$, overlap integral and ϕ_{D}, the fluorescence quantum yield of the donor.

The Förster critical distance, R_0, was calculated according to Eq. (3) with an overlap integral $J(\lambda) = 3.022 \times 10^{15}$ M^{-1} cm^{-1} nm^4, $n(\text{DMF}) = 1.43047$ and $\phi_{\text{D}} \equiv \phi_{\text{9-AnthN}} = 0.11$, leading to a value for the critical distance for energy transfer of 38 Å. Using Eq. (4), the lower limit for energy transfer efficiency, corresponding to the maximum interchromophoric distance of $R = 18.7$ Å (obtained from molecular modelling with Hyperchem6 from Hypercube software) is $\eta = 0.986$

$$\eta = \frac{R_0^6}{R_0^6 + R^6} \tag{4}$$

The ET efficiency can also be obtained from the ratio of the fluorescence quantum yields of the compound Anth*as*TPP and of its parent 9-AnthN, according to Eq. (4)

$$1 - \frac{\phi_{\text{Anth}as\text{TPP}}}{\phi_{\text{9-AnthN}}} = \eta_{\text{E}} \tag{5}$$

The use of the fluorescence quantum yields of the parent compound $\phi_{\text{9-AnthN}} = 0.01$ (in DMF) and of compound Anth*as*TPP, $\phi_{\text{Anth}as\text{TPP}} = 0.047$, leads to an impossible value for η_{E} from Eq. (5). However, other workers [45] have found a pronounced dependence of 9-AnthN ϕ_{F} values upon the polarity (and hydrogen ion concentration) of the media. It appears, therefore, that in DMF 9-AnthN does not act as a good parent compound since its ϕ_F value is less than that of Anth*as*TPP. If instead we use $\phi_F = 0.11$ [45] for 9-AnthN in methylcyclohexane a value of $\eta_E = 0.57$ is obtained. The issue of the correct parent compound for this type of system has been discussed elsewhere [46].

According to Eq. (6), the two η_E values can now be used to calculate the k_{ET} value.

$$\eta_{ET} = \frac{k_{ET}}{k_{ET} + k_F + \sum k_i} \tag{6}$$

When this is done, considering that the fluorescence lifetime of the donor in the absence of the acceptor is that obtained for the parent 9-AnthN (9.8 ns), the values obtained are:

$$k_{ET} = 1.35 \times 10^8\,\mathrm{s}^{-1} \quad \text{for} \quad \eta = 0.57$$

and

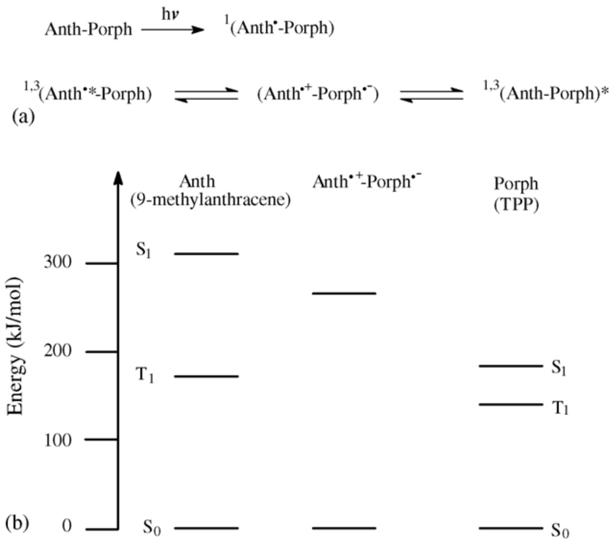
$$k_{ET} = 7.16 \times 10^9\,\mathrm{s}^{-1} \quad \text{for} \quad \eta = 0.986$$

The differences between the experimental (Eq. (5)) and theoretical (Eq. (4)) values are clearly significant. This could be due to the fact that with Eq. (4), the calculated value, corresponding to the maximum interchromophoric distance, could be even higher leading to a lower η value. Another explanation can lie in the fact that we are assuming a value of $k^2 = 2/3$. However, as discussed elsewhere [27], this is not necessarily the case with these supramolecular systems, and two limiting conditions may be considered: (1) D and A moieties have orthogonal transition moments, i.e., $k^2 = 0$ and the D is unable to transfer energy to the A moiety; (2) D and A moieties have parallel transition moments, $k^2 = 4$ and consequently the efficiency of the process will be high. In fact, if this was so, the determined R_0 value (from Eq. (3)) will be equal to 55 Å, and $\eta_E = 0.999$. Since the transition moments of both molecules in solution should be in between the two situations, it is predicted that the actual value for η_E will lie between the above-mentioned values.

In both cases, the process of energy transfer from the peripheral anthracenes to the porphyrin should be efficient, and probably close to 100% in efficiency, as has been found with similar anthracene–porphyrin supramolecular systems [27]. However, the steady-state fluorescence results show this is not the case. This suggests that energy transfer does not simply involve the Förster dipole–dipole mechanism.

It is, however, also possible to treat the mechanism in terms of an actual electron transfer to form a geminate radical pair, which then undergoes back electron transfer to produce the appropriate excited states [47]. This situation would correspond to a series of three steps:

1. The porphyrin moiety is excited.
2. The anthracene group can transfer an electron to the porphyrin moiety.
3. The anthracene-porphyrin radical pair is now in equilibrium with the porphyrin as in the previous situation in Scheme 2.



Scheme 2.

Electron transfer has previously been suggested with anthracene–porphyrin dyads, is feasible on energetic grounds, [25,26] and is also likely to be favoured by the anthracene and porphyrin rings not being coplanar. Photoinduced charge separation has also been proposed for other bichromophoric anthracene containing systems [48]. Using electrochemical redox potentials for related systems measured in dichloromethane [26], and literature data for singlet and triplet energies of TPP and 9-methylanthracene [49], the approximate energy diagram shown in Scheme 2b can be obtained. It should be noted in this that energy for the radical pair has been calculated ignoring any solvent effect or electrostatic interactions, since these are very dependent on the relative orientations of anthryl and porphyrin groups in Anth*as*TPP, and difficult to estimate for highly polar media such as DMF. These effects will probably go in different directions, but imply a considerable uncertainty in the energy of this state. Nevertheless, while the back electron transfer to produce singlet state excitation on anthracene is energetically unfavourable, communication still exists through the charge separated state between singlet excited anthracene and singlet excited TPP. This is illustrated in Scheme 2a. Because of this, a channel is opened when during observation of the decay of the porphyrin moiety, the decay time of the anthracene segment is involved. This requires rapid back electron transfer between the charge separated state and anthracene. However, it is worth noting that rapid endothermic energy transfer processes have been observed in other systems [50,51].

An important consequence of involvement of the charge separated radical pair as an intermediate is that if the electron spins are no longer correlated, it can decay to form either the singlet or the triplet state. If this is purely governed by spin statistics, as in simple organic systems, this will be in the ratio 1:3 [52]. However, it has been suggested, based on theoretical data in polymeric systems, that higher singlet:triplet ratios may be observed on charge recombination, and that these depend on structural and energetic parameters [53–57]. A more detailed understanding of the spin dependence of charge recombination is of great theoretical and practical importance in relation to its application in organic and polymeric light emitting devices.

3.2. *Triplet state properties*

3.2.1. *Phosphorescence*

Phosphorescence spectra of 9-AnthN and Anth*as*TPP in toluene are presented in Fig. 5. It can be observed that no phosphorescence of Anth*as*TPP can be observed when $\lambda_{exc} \geq 400$ nm. This means that the porphyrin moiety does not phosphoresce or, if it does, it has a phosphorescence quantum yield lower than the sensitivity of our system ($\leq 10^{-4}$). In general, free base porphyrins do not show significant phosphorescence. Although there have been reports of the observation of TPP phosphorescence with a maximum at ≅860–865 nm, the ϕ_{Ph} values are very low (4×10^{-5}) [58,59].

Attempts were made to look for phosphorescence from the anthracene part. From the triplet energy of 9-methylanthracene (1.79 eV [49,60,61]), this would be expected to be observed around 700 nm. No emission was observed at this wavelength. Instead, upon excitation at 370 nm, a structured emission was observed in the region 400–600 nm. Similar emission was observed with 9-AnthN. These are shown in Fig. 5. The measured luminescence lifetimes for 9-AnthN and Anth*as*TPP were 4.13 and 4.3 ms, respectively. Within the experimental error these two values can be considered to be identical. Although both 9-AnthN and Anth*as*TPP showed good analytical data suggesting reasonable purity, it is not possible to rule out the emission in both cases coming from some impurity. However, it is known with 9-methyl anthracene P-type delayed fluorescence is efficient [62], and if the triplet state is formed this may be the preferred decay route. As this was not the primary objective of our study, this was not pursued further.

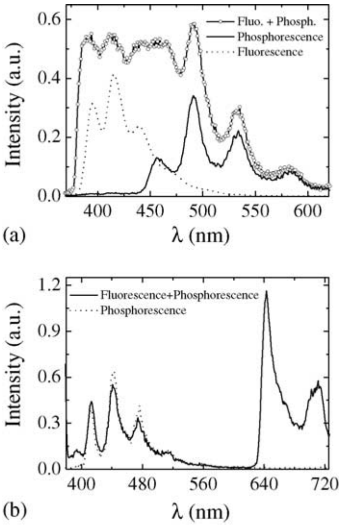


Fig. 5. Fluorescence plus phosphorescence and phosphorescence spectra of (a) 9-anthN in an ethanol:methanol 1:1 mixture and of (b) Anth*as*TPP in toluene with excitation at 370 nm.

3.2.2. *Triplet state absorption*

Argon saturated solutions of Anth*as*TPP (10^{-6} M) in DMF were excited with 15 ns pulses of a frequency tripled Nd:YAG laser ($\lambda_{exc} = 355$ nm). With this excitation wavelength, it is expected that predominantly the anthracene moiety will absorb light. Loss of the ground state Soret band at 430 nm and formation of a new band at 470 nm was observed (Fig. 6a). The new band was assigned by comparison with literature data for related compounds [63,64] to the lowest triplet state of the porphyrin group. The absorption maximum of the triplet state of the anthracene moiety (420–430 nm) may be obscured by the intense Soret band of the porphyrin. Attempts were made to observe depletion of the anthracene absorption resulting from triplet state formation at 365 nm, where the porphyrin does not absorb excessively (Fig. 6). However, these were inconclusive due to light scattering from the laser. The transient absorption at 450 nm was fully formed within the detection time of the system (ca. 30 ns). If any anthracene triplet state is formed, it must have decayed within this time. Decay of the porphyrin absorptions at 450 nm and the weaker band at 700 nm matched recovery of the ground state absorption at 420 nm (Fig. 6a). The decay/recovery followed good first-order kinetics, with $\tau_T = 64$ μs.

If all the excited Anth*as*TPP that has not decayed by fluorescence is producing the porphyrin triplet state, an estimation of the differential extinction coefficient of this at 450 nm can be made from the depletion of the ground-state Soret absorption at 420 nm, and the experimental extinction coefficient of $\varepsilon = 4.6 \times 10^5$ M^{-1} cm^{-1} for the Soret band. A value of $\Delta\varepsilon = 55{,}000$ M^{-1} cm^{-1} was obtained. The estimated error is fairly large (±50%). However, the value is close to that observed for other porphyrins [65]. An estimate of the

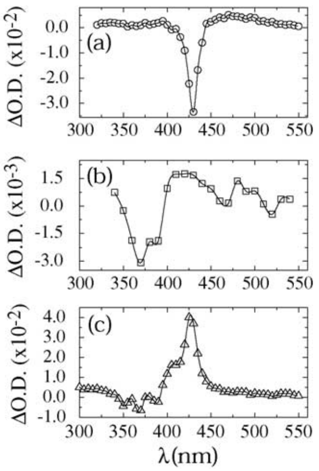


Fig. 6. Triplet–triplet spectra of (a) Anth*as*TPP, (b) C_{12}*as*TPP and (c) 9-AnthN in *N*,*N*-dimethylformamide 2 μs after the flash.

yield of Anth*as*TPP triplet state in DMF was made from the study of the initial absorption of its transient at 450 nm compared with the absorbance of triplet state of anthracene at 422 nm following photolysis of optically matched argon saturated solutions in cyclohexane, using the method described by Amand and Bensasson [66], and values for anthracene of $\Delta\varepsilon_{422} = 64{,}700\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ [67] and $\phi_\mathrm{T} = 0.71$ [65]. A value for Anth*as*TPP of $\phi_\mathrm{T} = 0.25$ was obtained. Although there is considerable experimental uncertainty in this value, comparison with the quantum yield for fluorescence (0.047) strongly suggests that excitation energy is being transferred from anthracene to the porphyrin unit.

Support for the absence of significant anthracene triplet production in Anth*as*TPP comes from comparison with laser flash photolysis data from the model compounds in which the anthracene and TPP chromophores are studied separately (Fig. 6b and c). In both cases the transients were assigned as triplets since they decay with first order kinetics and were quenched by oxygen with $k_\mathrm{ox} = (0.5\text{–}2) \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, typical for this process [68]. It can be seen that the isolated porphyrin (C_{12}*as*TPP) has a different singlet–triplet difference spectrum from Anth*as*TPP. Also the triplet–triplet absorption spectrum of 9-AnthN with maxima at 430 nm (Fig. 6c) cannot be seen in the spectrum of Anth*as*TPP. In particular, it can be noted that the depletion of the Soret band is observed in the case where the anthracene chromophore is present; indicating that the energy transfer process from the anthracene to the porphyrin moiety must be efficient.

3.2.3. Triplet–triplet energy transfer and radical cation formation

Triplet states can be selectively produced [69] by energy transfer following pulse radiolysis of benzene (Bz) solutions of Anth*as*TPP in the presence of appropriate sensitisers (biphenyl, Bp, for example)

$$\mathrm{Bz} + \mathrm{e}^* \sim> {}^1\mathrm{Bz}^* + {}^3\mathrm{Bz}^* + \mathrm{e}^*$$

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

$${}^1\mathrm{Bz}^* + \mathrm{Bp} \rightarrow \mathrm{Bz} + {}^1\mathrm{Bp}^*$$

$${}^3\mathrm{Bz}^* + \mathrm{Bp} \rightarrow \mathrm{Bz} + {}^3\mathrm{Bp}^*$$

$${}^1\mathrm{Bp}^* \rightarrow {}^3\mathrm{Bp}^*$$

$${}^3\mathrm{Bp}^* + \mathrm{Anth}\mathit{as}\mathrm{TPP} \rightarrow \mathrm{Bp} + {}^3\mathrm{Anth}\mathit{as}\mathrm{TPP}^*$$

This is subject to the kinetically demanded concentration ratio [Bz] ≫ [Bp] ≫ [Anth*as*TPP] [70].

An argon-saturated solution of Anth*as*TPP was studied by pulse radiolysis in benzene solution in the presence of biphenyl (0.01 M). Following pulse radiolysis, an initial absorption at 360 nm due to biphenyl triplet was replaced by new absorptions in the 440–560 nm region due to the triplet of Anth*as*TPP (see Fig. 7), accompanied by bleaching of the Soret band of this compound at 420 nm. This new absorption is very similar to that seen in flash photolysis, and is assigned to a triplet state predominantly localised on the porphyrins. It was not possible to see the main anthracene triplet state maximum at 430 nm [49] due to intense ground state absorption by the strong Soret band of the porphyrin moiety. The absorption band at 390 nm may be due in part to the anthracene triplet, but this decayed at almost the same rate as the biphenyl triplet [$k\,(360\ \mathrm{nm}) = 3.27 \times 10^4\ \mathrm{s}^{-1}$, $k(390\ \mathrm{nm}) = 3.08 \times 10^4\ \mathrm{s}^{-1}$]. From the above data we can conclude that if there is any anthracene triplet formed, it decays at a rate close to that of the sensitiser, biphenyl, triplet state.

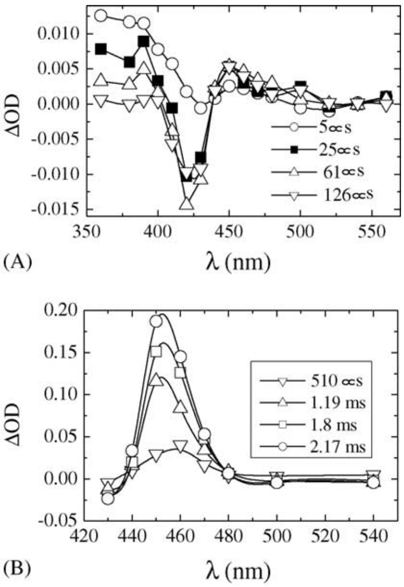


Fig. 7. Pulse radiolysis spectra obtained for different delays after flash of Anth*as*TPP in (A) in biphenyl (0.01 M) benzene solution and (B) chloroform solution.

However, on pulse radiolysis of chloroform solutions of Anth*as*TPP an absorption at ≈450 nm is observed (Fig. 7B). This is assigned to the anthracene radical cation from the known radiation chemistry of chloroform [71], where radiolysis leads to solute radical cation formation through the reaction sequence

$$\mathrm{CHCl_3} + \mathrm{e}^* \sim> \mathrm{CHCl_3}^{\bullet+} + {}^\bullet\mathrm{CCl_3} + \mathrm{Cl}^-$$

$$\mathrm{CHCl_3}^{\bullet+} + \mathrm{Anth}\mathit{as}\mathrm{TPP} \rightarrow \mathrm{CHCl_3} + \mathrm{Anth}\mathit{as}\mathrm{TPP}^{\bullet+}$$

This is in good agreement with one of the main bands reported in the literature for the radical cation [72]. We were unable to observe the long wavelength band of anthracene radical cation around 700 nm because of the response of the detector used in pulse radiolysis measurements. The ready formation of this species gives additional credibility to the mechanism proposed in Scheme 2b.

Table 2
Photophysical data for Anth*as*TPP in DMF

ϕ_F	0.047
τ_F (ns)	2.20
ϕ_T	0.25
τ_T (μs)	64
k_F (ns^{-1})	0.021
k_{IC} (ns^{-1})	0.32
k_{ISC} (ns^{-1})	0.114

3.3. Rate constants for the deactivation processes in AnthasTPP

With the above photophysical data it is possible to obtain all the rate constants for the deactivation processes occurring with Anth*as*TPP. Table 2 summarizes the data. It can clearly be seen that the rate constants for the radiationless processes are dominating the photophysics of Anth*as*TPP.

4. Conclusions

The photophysical behaviour of a new porphyrin–anthracene derivative in which, the chromophores are linked by a sulfonamide group has been undertaken. It has been shown that efficient energy and/or electron transfer processes occurs between the anthracene and the porphyrin moieties in both excited singlet and triplet states. These processes are discussed in terms of possible mechanisms. Although a Förster mechanism is possible for the singlet–singlet energy transfer, the observed data are not consistent with this being the only mechanism. Instead, it is suggested that a model involving the formation of a radical pair is compatible with the biexponential decay law found for fluorescence when Anth*as*TPP is excited in either the anthracene or porphyrin moieties. A complete set of deactivation rate constants has been determined for Anth*as*TPP and shows that the major contribution to excited state decay comes from the radiationless processes (k_{IC} and k_{ISC}).

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