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Intramolecular excitation energy transfer in isomeric porphyrin–anthracene dyads

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Abstract

Isomeric donor–acceptor (D–A) dyads in which an anthracene donor moiety is covalently linked, via a short ether bridge, to either *ortho*, *meta* or *para* position of one of the aryl groups of 5, 10, 15, 20-tetraphenylporphyrin have been synthesized and characterized by spectral and electrochemical methods. UV–visible and ^{1}H nuclear magnetic resonance data of these D–A systems suggest the presence of weak intramolecular π–π interaction between the porphyrin and the anthracene. Fluorescence from the anthracene subunit in each dyad is found to be quenched in comparison with the fluorescence of free anthracene. Excitation spectral data provide evidence for an intramolecular excitation energy transfer (EET) from the singlet anthracene to the porphyrin and the energy transfer efficiency is found to be dependent on the site of attachment (i.e. *ortho* > *meta* > *para*) of the donor to the acceptor. Detailed analysis of the data suggests that Förster's dipole–dipole mechanism does not adequately explain this energy transfer and that an electron-exchange-mediated mechanism can, in principle, contribute to the intramolecular EET in these short ether bridged dyads. Furthermore, arguments based on the thermodynamic considerations and also the solvent-dependent fluorescence data reveal that, while quenching of the fluorescence in the *ortho* isomer could be explained solely on the basis of EET, invoking an intramolecular electron transfer can rationalize the observed quenching in the *meta* and *para* isomers. Finally, a comparison is made of the EET reactions in these isomeric dyads with those observed for the previously reported porphyrin-based energy transfer systems which include a supramolecular, D_4–A pentad porphyrin bearing four anthracene donor subunits.

Keywords: Intramolecular excitation energy transfer; Porphyrin–anthracene dyads

1. Introduction

Studies involving the excitation energy transfer (EET) reactions of donor–acceptor (D–A) systems having short (3–6 Å) and intermediate (6–20 Å) D–A separations are of current interest [1–8]. Much of the impetus for such studies seems to have come from the importance of EET in both natural [9] and functionally active synthetic systems [10–13]. Thus, because of their relevance to many research areas including biomimetic photosynthesis and molecular electronics, EET reactions occurring in porphyrin-based systems have attracted considerable attention. Intramolecular EET has been elucidated in a great variety of bis-porphyrin and multiporphyrin arrays [9,14,15] and also in numerous porphyrin-based dyads in which a porphyrin or a metalloporphyrin is covalently linked to either an energy donor or an acceptor [14,16–21]. However, examples of porphyrin-based dyads in which detailed mechanisms of intramolecular singlet–singlet energy transfer reactions are known have been restricted to covalently linked porphyrin–cyanine dye [16], porphyrin–carotene [17–20] and porphyrin–molecular wire–anthracene [21] systems. More importantly, although studies which enquire into the influence of D–A distance and orientation on the efficiency of the intramolecular electron transfer in porphyrin-based D–A systems have been numerous [9,14], similar studies dealing with the EET in porphyrin-based energy transfer dyads are relatively unknown.

During our studies on the electron and energy transfer reactions of porphyrin-based photosynthetic model systems [22–25], it occurred to us that the synthetic manoeuvrability of porphyrins and well-defined spectral as well as photochemical properties of porphyrin and other hydrocarbon systems could provide an opportunity to build energy transfer dyads of the type "porphyrin–spacer–hydrocarbon (non-porphyrinic)" that are characterized by short or intermediate D–A separations and various mutual orientations. This has been realized in the present study which reports intramolecular EET reactions of isomeric porphyrin–anthracene dyads the molecular structures of which, as derived from the molecular mechanics (MMX) calculations, are given in Fig. 1. As seen

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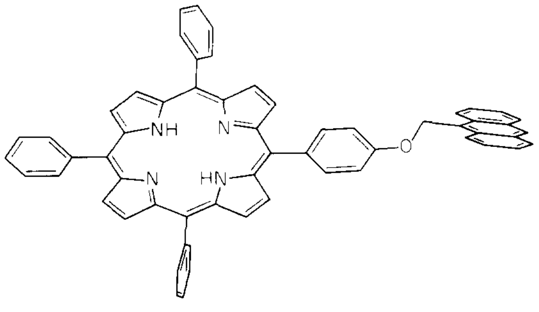
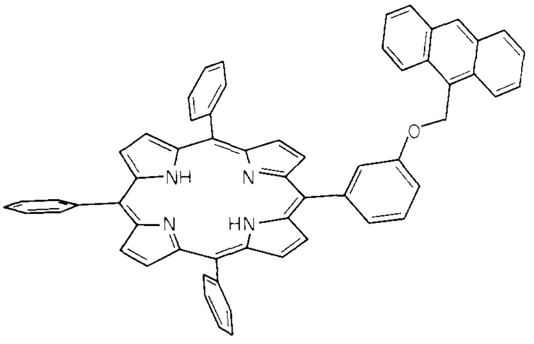


H_2-p-AP



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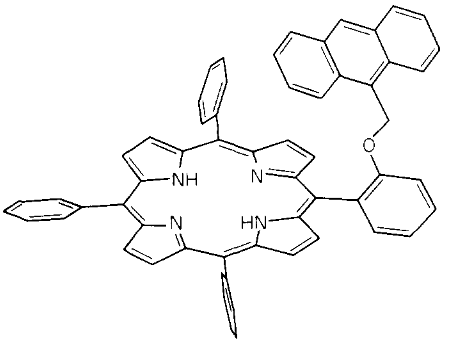

H_2-o-AP

Fig. 1. Structures of the isomeric porphyrin–anthracene dyads investigated.

by the structures given in this figure, linking an anthracene donor, via a short ether spacer moiety ($-OCH_2$), to either *ortho* (*o*), *meta* (*m*) or *para* (*p*) position of one of the phenyl groups of 5, 10, 15, 20-tetraphenylporphyrin (H_2TPP) acceptor brings about the changes in both D–A distance and mutual orientation. The centre-to-centre separation R_c and edge-to-edge R_e separations (R_c, R_e = 12.71 and 7.96 Å for H_2–*p*-AP, 10.95 and 7.20 Å for H_2–*m*-AP and 7.73 and 5.08 Å, for H_2–*o*-AP) between the porphyrin and the anthracene in these intramolecular systems can be considered to belong to intermediate or short D–A distances [1,2].

It should be noted here that the synthesis and intramolecular EET of a porphyrin bearing four anthracene donor subunits at its periphery have been reported by us recently but, owing to the structural complexity of this supramolecular species, it was not possible to elucidate the distance and orientation dependence of the EET in this D_4–A pentad [25]. On the contrary, from a structural point of view (Fig. 1), the present D–A dyads are well suited to the demonstration of distance and orientation influence on the EET. Indeed, as will be shown in this study, the efficiency of the intramolecular EET from the singlet anthracene to the porphyrin in H_2–*p*, *m*, *o*-AP is dependent on the site of attachment of the donor to the acceptor. Furthermore, on the basis of the solvent-dependent fluorescence data and thermodynamic considerations, a competing electron transfer reaction will also be shown to occur in these isomeric dyads.

2. Experimental details

2.1. Materials

The chemicals and solvents utilized in this study were purchased from either Aldrich Chemical Co. (USA) or BDH (India). The solvents utilized for spectroscopic and electrochemical experiments were further purified by the standard procedures [26].

2.1.1. Synthesis of the donor–acceptor dyads

Stirring a dimethylformamide solution containing (5-*o*,*m*,*p*-hydroxyphenyl) 10, 15, 20-(triphenyl) porphyrin [22] and excess 9-chloromethyl anthracene for 24 h at the room temperature and evaporating the solvent gave a residue which upon repeated column chromatographic separation (basic alumina, $CHCl_3$ eluent) furnished pure (as checked by thin layer chromatography, elemental analysis, UV–visible and ^1H NMR methods) samples of H_2-*o*,*m*,*p*-AP with greater than 60% yields.

2.2. Methods

The instruments and experimental conditions employed for obtaining the various spectra and electrochemical redox potentials have been described earlier [22,23,25]. The concentration of the dyads used for the absorption spectral measurements in the UV–visible region ranged from about 2×10^{-6} M (porphyrin Soret and anthracene bands) to 5×10^{-5} M (porphyrin Q bands) and that used for emission measurements was about 10^{-7} M (optical density at $\lambda_{exc} < 0.2$). The emitted quanta in the fluorescence experiments were detected at right angles to the incident beam (slit widths, 2 nm for excitation and 2 nm for emission). The fluorescence quantum yields ϕ of the dyads were estimated by integrating the areas under the fluorescence curves and by using H_2TPP ($\phi = 0.12$ in benzene [27], for excitation into the porphyrin band, 550 nm) or anthracene (A) ($\phi = 0.27$ in CH_2Cl_2 [25], for excitation into the anthracene band, 250 nm) as standards. The excitation spectra for dilute solutions of the samples were recorded and overlapped with the absorption spectra after correcting for the instrument response function and after having performed a normalization procedure as described in a previous related study [25]. Refractive index corrections have been incorporated while reporting the fluorescence spectral data in various solvents.

Care was taken to avoid the entry of direct ambient light into the samples in all the spectroscopic and electrochemical experiments. All experiments were carried out at 293 ± 3 K.

3. Results and discussion

3.1. Ground-state properties

Fig. 2 compares the ^{1}H NMR spectra ($CDCl_3$, tetramethylsilane) of the three isomeric D–A compounds. The spectra are highly characteristic for each isomer and the integrated intensity data are in conformity with the proposed structures. Salient features of the spectra that provide evidence for a proximity of the anthracene with the porphyrin in these dyads follow. Firstly, whereas the pyrrole-β protons of H_2TPP resonate at 8.83 ppm (s) [22,23], those of H_2-*p*-AP, H_2-*m*-AP and H_2-*o*-AP resonate at 8.83 (s) ppm, 8.82 (s) ppm and 8.73 (s) ppm respectively. Similarly, in comparison with the resonance due to the central imino protons of H_2TPP (−2.80 ppm, s(2H)), the corresponding resonance in the spectra of the dyads is seen to be upfield shifted by 0.01 ppm, 0.04 ppm and 0.16 ppm for *para*, *meta* and *ortho* derivatives respectively. Secondly, resonances due to protons at positions 2, 3, 6, 7 of the anthracene subunit also follow a similar trend in that the *para*, *meta* and *ortho* isomers show peaks due to these protons at 8.29 (m, 4H) ppm, 8.16 (m, 4H) ppm and 6.50 (m, 4H) ppm respectively. We analyse that this complementary shielding of the protons on the porphyrin ring and those on the anthracene ring is a consequence of the ring-current effect [28] exerted by these two aromatic moieties on each other and that the effect follows a trend that is determined by the site of attachment of the donor to the acceptor, i.e. *ortho* > *metal* > *para*. Consistent with this analysis is the trend observed for peaks due to the spacer–OCH_2 protons which occur at 6.19 (s, 2H) ppm, 6.09 (s, 2H) ppm and 5.56 (s, 2H) ppm for the *para*, *meta* and *ortho* isomers respectively (note that the corresponding peak for a model compound without porphyrin, 9-methyloxyphenyl anthracene (A–O–Ph), is located at 6.21 ppm). As the ring-current effects are known to be significant at "short" distances [28], the observed mutual shielding of protons on the constituent components of these dyads indicates the proximity of the two π systems. It should be noted here that the π system on the porphyrin might also include the meso-aryl ring on it that is linked to the anthracene moiety and that the ^{1}H NMR shifts represent an equilibrium between several D–A conformations present in solution under these experimental conditions.

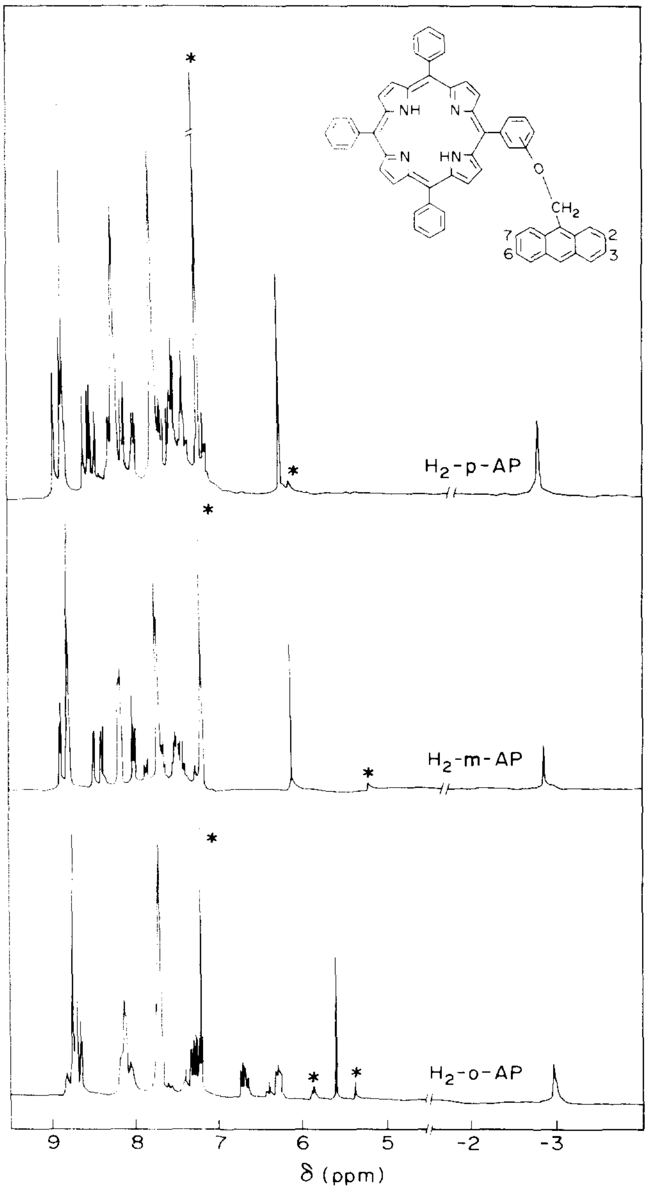

Fig. 2. ^{1}H NMR spectra ($CDCl_3$ and tetramethylsilane) of the isomeric dyads: *, peaks due to solvent impurities.

UV–visible spectral data of the covalently linked dyads and that of their constituent individual components (i.e. H_2TPP and A or A–O–Ph) are summarized in Table 1 and the spectra of H_2-*p*-AP and H_2TPP are given in Fig. 3(a). From a comparison of the spectra given in this figure, it is clear that the anthracene part of the dyad strongly absorbs between 200 and 300 nm, a region in which H_2TPP shows minimum absorption. Further, the data given in Table 1 reveal that neither A nor A–O–Ph absorbs beyond about 400 nm and that both H_2TPP and porphyrin part of each dyad show their B and Q bands between 400 and 700 nm. Taken together, these observations suggest that opportunity exists for excitation into either an exclusive anthracene absorption band (about 250 nm) or an exclusive porphyrin absorption band (about 550 nm) in these dyads. Data given in Table 1 also suggest that, while the λ_{max} values of these dyads are within the same range as those of their constituent individual components, their log ϵ (ϵ is the molar extinction coefficient) values are altered in comparison with those of A (or A–O–Ph) or H_2TPP. Furthermore, the log ϵ values, in general seem to follow the order *ortho* < *meta* < *para*. These observations are similar to those reported by us earlier for a series of

Table 1
UV–visible absorption spectral data in CH_2Cl_2

Compound	λ (nm) (log ε) for the following porphyrin transitions					λ (nm) (log ε) for the following anthracene transitions		
	Q_1	Q_2	Q_3	Q_4	B	I	II	III
A						378(3.84)	359(3.88)	255(5.19)
A–O–Ph						387(4.07)	367(4.09)	257(5.29)
H_2TPP	645(3.67)	590(3.68)	549(3.84)	514(4.22)	417(5.56)			
H_2–*p*-AP	648(3.66)	592(3.67)	552(3.83)	517(4.21)	419(5.67)	373(4.72)	355(4.61)	259(5.38)
H_2–*m*-AP	648(3.53)	591(3.53)	551(3.73)	516(4.03)	419(5.55)	368(4.57)	355(4.34)	257(5.25)
H_2–*o*-AP	645(3.51)	591(3.72)	551(3.82)	516(4.24)	418(5.41)	368(4.31)	355(4.06)	258(4.95)

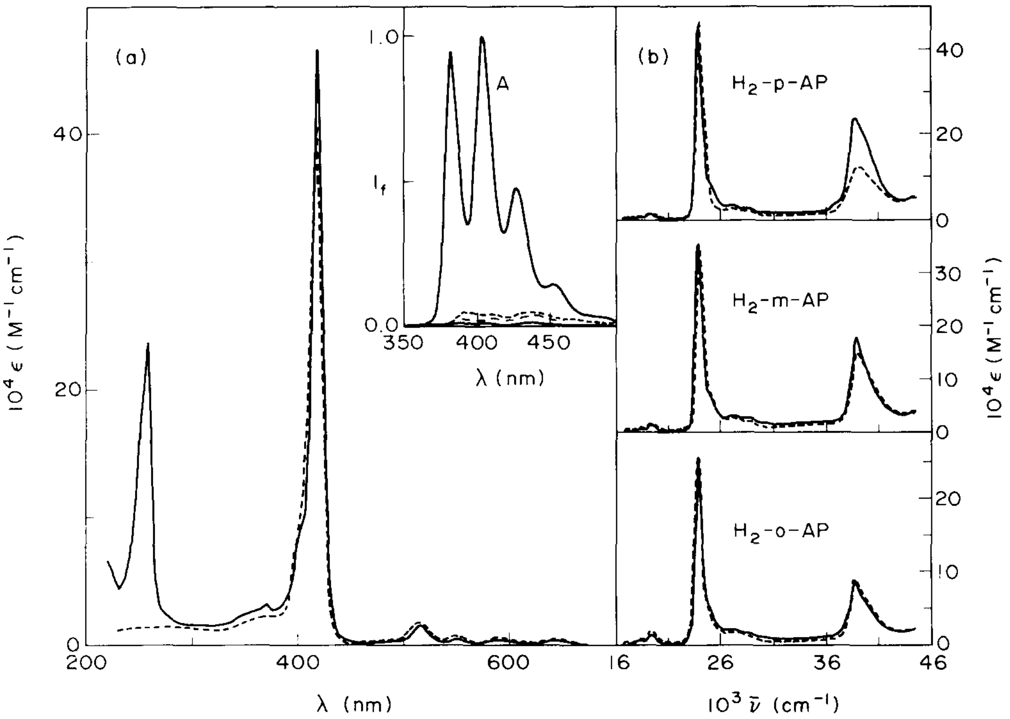

Fig. 3. (a) UV–visible spectra of H_2TPP (– – –) and H_2–*p*-AP (——). The inset shows the fluorescence spectra (λ_{ex} = 250 nm) of anthracene (——) and of H_2–*p*-AP (– – –), H_2–*m*-AP (– – –) and H_2–*o*-AP (——). (b) Overlap of the absorption (——) and excitation (– – –) (λ_{em} = 650 nm) spectra of the dyads. CH_2Cl_2 was used as the solvent for taking all the spectra in this figure.

isomeric porphyrin–nitroarene electron transfer dyads [22,24] and are consistent with the presence of weak π–π interaction between the two π-systems in the present series of dyads.

On the contrary, differential pulse voltammetry experiments revealed that the electrochemical redox potentials of these systems are insensitive to their molecular structures. While the porphyrin part of each compound could be oxidized and reduced at 1.02 ± 0.03 V and −1.24 ± 0.03 V respectively, the anthracene part could be oxidized at 1.41 ± 0.03 V and the reduction of it was not observed within the solvent limit (about −1.8 V) under the experimental conditions employed in this study (CH_2Cl_2; 0.1 M tetrabutylammonium chloride; saturated calomel electrode). Nonetheless, from the consistency observed in the UV–visible and ^1H NMR data described above, it can be suggested that there exists a weak π–π interaction between the donor and the acceptor in these systems and that the extent of this interaction is sensitive to a change in the D–A distance and the orientation (i.e. *ortho* > *meta* > *para*).

3.2. Singlet-state properties

The existence of weak π–π interaction can, in principle, manifest itself in the formation of an exciplex but no evidence for the separate emission from an exciplex was noticed for these weakly fluorescent (vide infra) dyads. However, full widths at half-maxima and wavelengths of maximum fluorescence observed in the anthracene emission region (280–450 nm; λ_{exc} = 250 nm) of the three dyads, with the spectra being measured in hexane, CH_2Cl_2 and CH_3CN, were found to be altered (broadened or shifted by about 3–5 nm) in comparison with the corresponding spectral parameters observed for A. On the contrary, E_{0-0} (0–0 spectroscopic transition energy) values for the porphyrin (2.01 ± 0.05 eV) and the anthracene (3.20 ± 0.05 eV) parts of these dyads, as estimated from an overlap of their absorption and emission spectra, were found to be in the same range as the E_{0-0} values for H_2TPP and A respectively [25].

A major difference between the fluorescence data of the dyads and those of H_2TPP and A lies in the magnitude of ϕ values. Whereas ϕ for an excitation into the porphyrin moiety ($\phi = 0.12 \pm 0.1$) was similar to that of H_2TPP [27], fluorescence from the anthracene part of each dyad was found to be strongly quenched (up to 99%) in comparison with the fluorescence of A [25] in all the three solvents investigated. Representative spectra showing this latter observation are given in the inset of Fig. 3(a) and the evaluated quenching efficiency Q

$$Q = \frac{\phi(\mathrm{A}) - \phi(\mathrm{H_2}\text{–}o,m,p\text{-AP})}{\phi(\mathrm{A})} \tag{1}$$

and k_{obs} values

$$k_{\mathrm{obs}} = \frac{Q/(1-Q)}{\tau(\mathrm{A})} \tag{2}$$

are given in Table 2. ϕ(A) and $\phi(\mathrm{H_2}$–o,m,p-AP) refer to the fluorescence quantum yields for A and the three isomeric dyads ($\lambda_{\mathrm{exc}} = 250$ nm) respectively and τ(A) is the singlet-state lifetime of A (equal to 4.9 ns, 5.2 ns and 5.3 ns in hexane, CH_2Cl_2 and CH_3CN respectively [25]).

There exists a strong overlap between the emission of anthracene and the absorption of porphyrin in these dyads and this suggests that quenching of the fluorescence of the anthracenes in them can be due to an intramolecular EET from the singlet anthracene to the porphyrin. Indeed, excitation of approximately 10^{-7} M solution of each dyad at 250 nm resulted in the appearance of well-defined porphyrin emission bands in all the three solvents. On the contrary, only weak fluorescence could be seen when a solution of H_2TPP having the same concentration was excited at the same wavelength. Furthermore, when the fluorescence was monitored at the porphyrin emission maximum ($\lambda_{\mathrm{em}} = 650$ nm), the excitation spectrum taken for these dyads showed bands characteristic of anthracene absorption. Collectively, these observations provide evidence for intramolecular EET in these bichromophoric compounds. It should be noted that a solution containing 1:1 (mole/mole) intermolecular mixture of H_2TPP and A did not show quenching of the fluorescence due to A ($\lambda_{\mathrm{exc}} = 250$ nm) nor did it suggest energy transfer in the excitation spectrum. Clearly, EET is more efficient here in an intramolecular than in an intermolecular situation.

The energy transfer efficiencies T_{obs} for these dyads that are obtained by comparing an overlap of the excitation and absorption spectra in each investigated solvent are collected in Table 2 and representative spectra showing this overlap in CH_2Cl_2 are given in Fig. 3(b). Table 2 also contains data on k_{EN}(obs) values where

$$k_{\mathrm{EN}}(\mathrm{obs}) = \frac{T_{\mathrm{obs}}/(1-T_{\mathrm{obs}})}{\tau(\mathrm{A})} \tag{3}$$

An inspection of Fig. 3(b) and also Table 2 suggests that k_{EN}(obs) (and T_{obs}) values follow the order *ortho* > *meta* > *para* and that, in the case of *meta* and *para* isomers, they are less than the k_{obs} (or Q) values. In what follows now we shall try to arrive at a mechanistic interpretation of the EET occurring in these isomeric dyads by employing the obtained data.

EET reactions in bichromophoric D–A systems can proceed mainly through two types of mechanism: (i) over large D–A separations and in the absence of any interchromophore interactions, they may occur via a coulombic interaction

Table 2
Energy transfer data [a]

Compound	%Q	%T_{obs}	k_{obs} ($\times 10^9$ s^{-1})	$k_{\mathrm{EN}}^{\mathrm{obs}}$ ($\times 10^9$ s^{-1})	$k_{\mathrm{F\ddot{o}rster}}$ [c] ($\times 10^9$ s^{-1})		
					K^2(I)	K^2(II)	K^2(III)
	Hexane ($n = 1.375$; $\epsilon = 1.88$) [b]						
H_2–p-AP	97	60	6.60	0.31	1.30	2.61	0.69
H_2–m-AP	98	84	10.00	1.07	4.75	3.15	1.69
H_2–o-AP [d]	99	100	20.20	20.20	20.11	13.13	13.68
	CH_2Cl_2 ($n = 1.425$; $\epsilon = 8.930$) [b]						
H_2–p-AP	91	52	1.94	0.21	0.77	1.55	0.41
H_2–m-AP	93	82	2.60	0.86	2.82	1.87	1.00
H_2–o-AP [d]	99	100	19.04	19.04	11.95	7.80	8.13
	CH_3CN ($n = 1.344$; $\epsilon = 37.50$) [b]						
H_2–p-AP	97	42	6.10	0.14	1.40	2.80	0.74
H_2–m-AP	98	85	9.20	1.07	5.10	3.38	1.82
H_2–o-AP [d]	99	100	18.70	18.70	21.60	14.10	14.67

[a] Error limits: %Q, k_{obs}, ±5%; %T_{obs}, $k_{\mathrm{EN}}^{\mathrm{obs}}$, ±10%; $k_{\mathrm{F\ddot{o}rster}}$, ±7%.

[b] n and ϵ refer to refractive index and dielectric constant respectively of the solvents.

[c] K^2(I) and K^2(II) values are 1.25, 1.82, 0.28 and 2.59, 1.20, 0.64 respectively for H_2–p-AP, H_2–m-AP and H_2–o-AP. K^2(III) = 2/3 in all the cases.

[d] Considering that %Q is 99 and that %$T_{\mathrm{obs}} = 100$ for this isomer, k_{obs} is taken as $k_{\mathrm{EN}}^{\mathrm{obs}}$ in these cases.

between the transition dipoles of excited donor and ground-state acceptor (Förster [29] mechanism) and (ii) in situations where there is some degree of interchromophore orbital overlap they can also be mediated by overlap dependent electronic coupling, one of which is the quantum mechanical exchange interaction (Dexter [30] mechanism). Both the Förster and the Dexter mechanisms require, among other things, that the rate of energy transfer be proportional to a spectral overlap J of the donor emission and the acceptor absorption [29,30]. Overlap integrals $J_{\text{Förster}}$ given by

$$J_{\text{Förster}}=\frac{\int F(\nu)\epsilon(\nu)\epsilon^{-4}\,\mathrm{d}\nu}{\int F(\nu)\,\mathrm{d}\upsilon} \tag{4}$$

and J_{Dexter} given by

$$J_{\text{Dexter}}=\frac{\int F(\nu)\epsilon(\nu)\,\mathrm{d}\nu}{\int F(\nu)\,\mathrm{d}\nu\ \epsilon(\nu)\,\mathrm{d}\nu} \tag{5}$$

($F(\nu)$ is the fluorescence intensity of the energy donor at wavenumber ν (cm^{-1}), and ϵ (mmol^{-1} cm^{-1}) is the molar extinction coefficient of the energy acceptor) for the present D–A pair in the three solvents investigated have been estimated to be $(2.64\pm0.12)\times10^{-16}$ cm^6 mmol^{-1} [25] and $(1.40\pm0.08)\times10^{-4}$ cm respectively and, in both cases, no direct correlation of these integrals could be made with the k_{EN}(obs) (or T_{obs}) values.

On the contrary, the Förster mechanism predicts the rate constant $k_{\text{Förster}}$ for the EET to follow

$$k_{\text{Förster}}=\frac{8.8\times10^{-25}K^2\phi_{\text{D}}J_{\text{Förster}}}{n^4\tau R^6} \tag{6}$$

Here, n is the solvent refractive index, ϕ_{D} and τ (s) are the fluorescence quantum yield and the fluorescence lifetime of the isolated donor, K^2 is an orientation factor and R (cm) is the distance. The possibility that the Förster mechanism is operative in the EET of these dyads can be tested by comparing the experimental rates k_{EN}(obs) of energy transfer with the rates $k_{\text{Förster}}$ calculated by the application of Eq. (6). While doing so, we have assumed that $R=R_{\text{c}}$ and that the orientation factor K^2 given by

$$K^2=(\cos\gamma-3\cos\alpha\cos\beta)^2 \tag{7}$$

(where α and β are the angles made by the transition dipoles of anthracene and porphyrin in these dyads with the line joining the centres of the transitions, and γ is the angle between the two transition dipoles), cannot be uniquely defined for the present intramolecular systems. It was found necessary to employ three different K^2 values while applying Eq. (6) for these bichromophoric molecules and the rationale behind this is briefly discussed below.

While the transition dipole of the ^{1}S state of anthracene lies on the molecule's short axis [2], that of the porphyrin is known to lie along a line joining two opposing pyrrole nitrogens [31]. Thus for a given anthracene conformation in these dyads there are two possibilities (essentially equally populated) depending upon which nitrogen atoms are protonated [18]. Assuming that the orientation between donor and acceptor π planes is the same as that shown in Fig. 1, two K^2 (K^2(I) and K^2(II)) values can be calculated for each dyad. On the contrary, it can be argued that the anthracene moiety assumes an average orientation in its excited state with respect to the porphyrin plane and in such a case, K^2(III) will be 2/3 [29]. Thus, substitution of these K^2 values into Eq. (6) gave three different $k_{\text{Förster}}$ values for each dyad in each solvent investigated (Table 2). A comparison of the $k_{\text{Förster}}$ with the k_{EN}(obs) values in Table 2 reveals that no correlation between the theory and experiment can be made for these dyads under any given set of parameters (i.e. isomer, K^2 and solvent). Similarly, k_{EN}(obs) values did not show a good correlation with the $k_{\text{Förster}}$ values calculated for EET from the ^{2}S state of anthracene (evaluation of J and K^2 values pertaining to the long-axis polarized transition [2]). In addition, the data given in Table 2 also suggest that k_{EN}(obs) values do not bear an inverse relationship with the refractive index n of the solvents as dictated by Eq. (6). Collectively, all these observations clearly suggest that the rates of EET in these systems are inadequately explained by Förster mechanism.

On the contrary, arguments based on the redox potential data of these dyads reveal that the porphyrin highest occupied molecular orbital (HOMO) (1.02 ± 0.03 eV) and lowest unoccupied molecular orbital (LUMO) (-1.24 ± 0.03 eV) are sandwiched between the HOMO (1.41 ± 0.03 eV) and the LUMO (less than -1.8 eV) of anthracene. If it can be argued that electron exchange reactions between the donor and the acceptor in a D–A compound involve radical intermediates (of the type D^+A^- and D^-A^+) and that neither electron transfer step can occur to an orbital at a higher energy level, the observed orbital energy level scheme for the porphyrin–anthracene dyads suggests the possibility that an electron exchange mechanism is operative in these cases [16,25]. Furthermore, it can be expected that the weak intramolecular π–π interaction observed for these dyads (vide supra) is likely to contribute to the electron exchange mechanism. Despite these, we note that it is not generally correct to consider exclusively a Förster or a Dexter mechanism for a singlet–singlet interchromophore EET and that this is especially so for systems having intermediate D–A separations such as those investigated in this study. Thus, on the basis of the analysis of the EET data presented here, it is reasonable to expect that contribution from the exchange-mediated mechanism increases as one moves from *para* to *meta* to *ortho* isomer in these D–A systems with the *ortho* isomer showing the highest contribution. Finally, it is possible that intramolecular EET can also proceed via a ''through-bond'' mechanism, but currently there exists no experimental evidence to suggest the participation of this mechanism in these systems

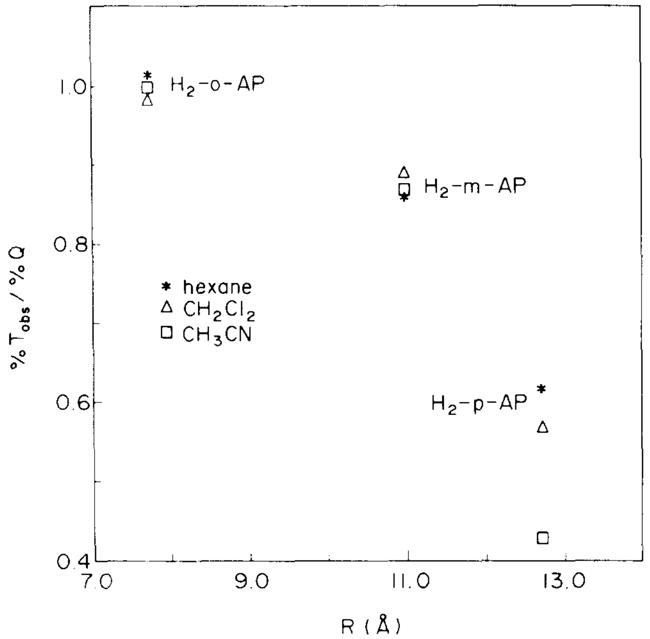

Fig. 4. Illustration of the D–A structure as well as solvent dependence of the intramolecular energy and electron transfer reactions in the investigated isomeric dyads (see text for details).

wherein the donor and acceptor are linked by "flexible" bonds.

Another interesting aspect of the singlet-state activity of our dyads is concerned with the following two observations which can be made from the data given in Table 2: (i) k_{EN}(obs) (or T_{obs}) is less than k_{obs} (or Q) for the *meta* and more so for the *para* isomer in each solvent investigated and (ii) the ratio $\%T_{obs}/\%Q$ seems to depend on the D–A distance and orientation as well as on the solvent polarity. The latter observation is illustrated in Fig. 4, an analysis of which clearly suggests that, while the observed quenching of the anthracene fluorescence in H_2-*o*-AP can be explained almost entirely on the basis of an EET ($\%T_{obs}/\%Q = 1$), the $\%T_{obs}/\%Q$ (< 1) values of the *meta* and *para* isomers imply a parallel quenching mechanism to be operative in these isomers. In addition, the figure also suggests a solvent polarity dependence of $\%T_{obs}/\%Q$; the more polar the solvent, the lower is the ratio. The free energy change ΔG for an electron transfer from the singlet anthracene to the porphyrin in these systems as calculated by employing their redox potential and E_{0-0} data is found to be exoergic (-0.54 ± 0.05 eV in CH_2Cl_2). This suggests that a photoinduced electron transfer can compete with the EET in these porphyrin–anthracene dyads. In principle, involving this competing electron transfer mechanism can explain the excess quenching observed for the *meta* and *para* isomers that cannot be reconciled solely on the basis of an energy transfer quenching. In this case, the observed trend for the $\%T_{obs}/\%Q$ (i.e. *ortho* > *meta* > *para*) implies that, while the energy transfer is the dominant quenching mechanism at shorter distances, it is the electron transfer that takes over at larger distances. Interestingly, the co-occurrence of energy and electron transfer observed for these porphyrin–anthracene dyads and also for the previously reported tetranthracenyl pentad system [25] is reminiscent of what has been noticed earlier for natural chlorophyll–carotene [32,33] and synthetic porphyrin–carotene [17–19] systems.

Comparison between the EET reactions of the present series of dyads and those of the previously reported analogous porphyrin-based energy transfer systems [16–21,25] is interesting. While the dipole–dipole-induced "through-space" mechanism was found to explain the EET in porphyrin–ether–carotene [19] systems adequately, it was essential to invoke a "through-bond" mechanism in the case of the porphyrin–molecular wire–anthracene [21] dyad. On the contrary, an electron-exchange-mediated mechanism, with a distance- and orientation-dependent fall-off in its contribution, seems to be involved in the EET of the present set of short-ether-linked isomeric porphyrin–anthracene dyads. Finally, in the previously reported [25] supramolecular D_4–A pentad porphyrin, anthracene subunits have been connected at the *meta* positions of all the four phenyl rings of a tetraphenyl porphyrin and the fluorescence properties of this compound can be compared with those of H_2-*m*-AP. Such a comparison suggests that, as was the case with the supramolecular porphyrin, invoking both energy and electron transfer processes is essential to explain the fluorescence quenching of the anthracene chromophores in H_2-*m*-AP. However, EET efficiency $\%T_{obs}$ for the pentad porphyrin is lower (hexane, 76%; CH_2Cl_2, 64%; CH_3CN, 36%) than that for H_2-*m*-AP which shows about 82–85% efficiency in the solvents investigated. It is possible that the D–A orientation is conducive for an EET in the dyad whereas, as suggested earlier [25], the presence of several D–A orientations that are a consequence of linking four anthracene subunits might promote excited-state processes other than the EET in the supramolecular porphyrin.

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