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Singlet–singlet Intramolecular Energy and Electron Transfer in Covalently Linked Porphyrin–fluorescein/porphyrin–eosin Heterodimers

Xiaobin Yan, Min Weng, Manhua Zhang* & Tao Shen

Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China

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ABSTRACT

Two porphyrin–xanthene (including FL–TTP and Eo–TTP) heterodimers covalently linked with a flexible polyatomic chain have been synthesized and characterized. Their Uv–vis absorption, steady-state and time-resolved fluorescence spectra were investigated. The Uv–vis absorption spectroscopy suggests that there is some weak exciton coupling between the two chromophores in these systems, whilst fluorescence spectroscopy shows that the FL or Eo unit transfer singlet-state excitation energy to the TTP. From time-resolved fluorescence studies, it is concluded that the heterodimers exist in solution in different, non-equilibrating, conformations. The effects of the solvent polarity on the intramolecular energy and electron transfer efficiencies are discussed. The results show, in apolar solvent, selective excitation of the FL/Eo chromophore, a very efficient singlet state energy transfer process from FL/Eo to TTP was observed, but in polar solvent (DMF) intramolecular electron transfer reaction also occurs in addition to the singlet state energy transfer. The difference of the intramolecular interaction in solvents of various polarity may be explained in terms of conformational change due to the nature of solvent interaction. The rate constants and efficiencies of the intramolecular energy and electron transfer reactions in different polar solvents were determined. © 1997 Elsevier Science Ltd

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*Corresponding author.

Keywords: intramolecular energy and electron transfer, porphyrin–xanthene, heterodimer.

INTRODUCTION

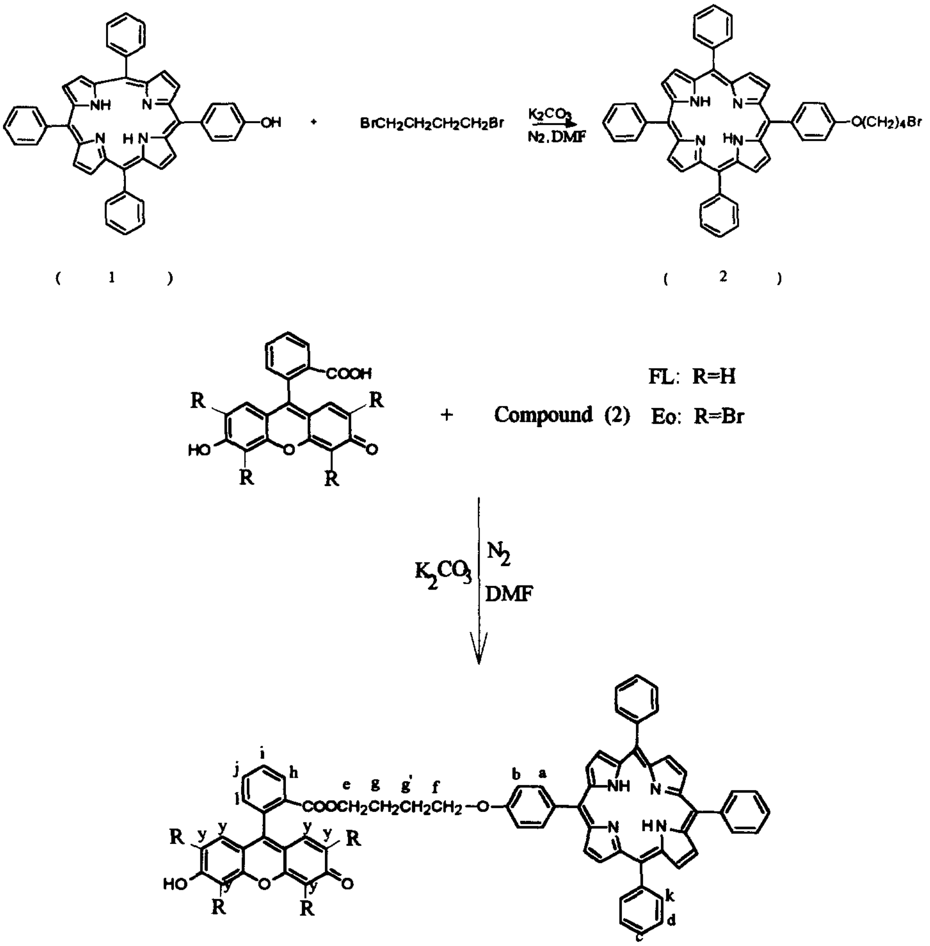
The most efficient primary electron donor in bacterial photosynthesis is a bacteriochlorophyll dimer, the "special pair" [1]. Green plant and bacterial photosynthetic organisms employ closely associated porphyrin as carriers of photons and electrons. Spectroscopic evidence has shown that the porphyrins are held in carefully controlled arrangements that optimize the efficiency of photon or electron transfers. So most of the studies devoted to this subject involve dyes [2] or porphyrin and porphyrin-like compounds linked together in a rigid manner or via flexible chains [3–9], as they can serve as model systems for the reaction center of photosynthesis. In most systems, the donor and the acceptor groups were attached, either to rigid systems such as steroids, so that their spatial relationship was known but could be varied only by using different spacers, or to a flexible chain so that their spatial relationship could not be determined. Hussoon *et al.* [10] carried out a partial intramolecular energy transfer in systems containing phenanthrene and α-diketone moieties linked in close proximity by two—$(CH_2)_2$—bridges with limited flexibility and suggested a Dexter-type exchange transfer mechanism. More recently, several mixed dimers containing zinc porphyrin linked to zinc phthalocyanine *via* an oxygen atom and/or via a flexible chain of variable length have been reported [11], and in these systems, both energy and electron transfer processes were demonstrated. More generally, the approach likely to yield such information would imply having a bichromophoric molecule consisting of a donor and an acceptor (D–A) held in proximity with specific properties: viz (i) D and A should exhibit a large difference in ground-state absorption spectrum so that each moiety could be selectively excited, (ii) D and A should be attached in such a manner that the conformation and spatial relationship could be varied and controlled.

Until recently, relatively little effort has been devoted to studies of mixed dimers containing porphyrin and xanthene. In that regard, our present interest is focused on a system consisting of a porphyrin linked together with fluorescein and/or eosin via a flexible polyatomic chain (FL—O—$(CH_2)_4$—O-TTP,Eo—O—$(CH_2)_4$—O—TTP). Moreover, the porphyrin–xanthene heterodimers present the peculiarity of having a ground-state absorption spectrum that covers the entire visible part of the solar energy spectrum, while allowing selective excitation of each individual chromophore. In the present paper, a study of the intramolecular energy and electron transfer processes in heterodimers is reported.

EXPERIMENTAL DETAILS

Materials

The structures of the heterodimers are shown in Scheme 1. FL, Eo were purchased from Beijing chemical plant, China. All the solvents used were of analytical grade and were used as received. Any required high-purity solvents were prepared by further purification of the commercial products, and no impurities were detected by absorption and/or fluorescence spectroscopies.



Compound (3):R=H,FL-C_4-TTP(heterodimer I)
Compound (4):R=Br,Eo-C_4-TTP(heterodimer II)

Scheme 1.

Synthesis

1. The model compounds, viz ethyl ester of FL(FLEt) and ethyl ester of Eo(EoEt)

   With reference to Acree and Slagle [12], they were synthesized from the disodium salts of FL and Eo. For FLEt, UV–vis (MeOH): $\lambda_{max} = 500\,nm$. IR(KBr): $\nu_{max}(C{=}O) = 1710\,cm^{-1}$. ^1H NMR($CDCl_3$): 0.9(t,3H,CH_3); 4.1(q,2H,CH_2); and 6.5–8.3 ppm (m, 10H). For EoEt, Uv–vis (MeOH): $\lambda_{max} = 530\,nm$. IR (KBr): $\nu_{max}(C{=}O) = 1720\,cm^{-1}$. ^1H NMR ($CDCl_3$): 1.0 (t,3H,CH_3); 4.2(q,2H,CH_2) and 6.9–8.5 ppm (m,6H).
2. Compound 2 (Br—$(CH_2)_4$–O–TTP)

   A mixture of compound 1 (0.291 g/0.46 mmol),1.4-dibromobutane (5.45 ml/50.8 mmol), anhydrous potassium carbonate (0.5 g) and DMF (20 ml) was stirred at 80°C for 24 h under a nitrogen atmosphere and the reaction mixture was then poured into water (170 ml) leaving a residue which was chromatographed on a 254 silica gel column using chloroform as eluant to give two bands. The first band was collected and stripped on a rotary evaporator to give compound 2 (0.185 g), yield 53%. ^1H NMR ($CDCl_3$): 8.8–8.9(m,8H, β-H); 8.2–8.4 (m, 6H, d); 8.0–8.3 (d, 2H, b); 7.2–7.8 (m, 11H, a, c, k); 3.95 (t,2H,—CH_2—O); 3.25(t,2H,—CH_2—Br); -2.89(m,2H, —HN—), and 1.6–1.8 ppm (m,4H,—CH_2—).
3. Heterodimer I (FL—TTP)

   A mixture of compound 2 (0.098 g/0.125 mmol), fluorescein (0.4 g/ 1.25 mmol), DMF (25 ml), anhydrous potassium carbonate (0.5 g) and potassium iodide (0.1 g) was refluxed for 48 h under a nitrogen atmosphere. The reaction mixture was poured into water(150 ml), filtered, and the residue, washed with water and was then chromatographed on a 254 silica gel column using chloroform as eluant to give three bands. The second band was collected, stripped on a rotary evaporator and was then rechromatographed on a 254 silica gel column; on elution with benzene, the first band was collected and stripped on a rotary evaporator (0.02 g), yield 15.6%. Uv–vis (CH_3Cl): λ_{max}(nm) = 420,460,515,592,646; IR(cm^{-1})(KBr): 3417,2918,1716 and 1501; ^1H NMR($CDCl_3$):8.8(m,8H, β—H), 8.0–8.2(d,7H,d,1), 7.8–8.0(d,2H,b), 7.6(m,11–H,a,c,k), 7.2–7.5(m,2H,i,j), 7.0(d,1H,h), 6.5–6.8 (m, 6H, y), 3.9(t, 2H, e), 3.7–3.8 (t, 2H, f), 1.4(t, 2H, g) and 0.8 ppm (t, 2H, g′); MS(FD): 1019 (M-1).
4. Heterodimer II (Eo–TTP)

   The heterodimer II (Eo–TTP) was prepared by a procedure analogous to that given for the preparation of (FL–TTP) except that ethyl acetate was used as eluant. Uv–vis (CH_3Cl): λ_{max}(nm) = 419,512,544,592,646; IR(cm^{-1})(KBr):3420,1724 and 1594;^1H NMR($CDCl_3$):8.8–8.9(m,8H, β—H),8.3(m,7H,d,1), 8.1(d,2H,b),7.8(m, 11H, a, c, k), 7.5(m, 2H, i, j), 7.2(d,1H,h),6.8(s,2H,y),3.9(t,2H,e),3.7–3.8(t, 2H,f), 2.2(t,2H,g) and 0.8 ppm (t,2H,g′);MS(FD): 1335(M-1).

Instruments and methods

The absorption spectra were measured on a Hitachi-557 spectrometer. IR spectra were performed with a Perkin Elmer 557 grating spectrophotometer. ^{1}H NMR spectra were run on a Varian XL-400 spectrometer and unless otherwise specified, the solvent was deuteriochloroform with TMS as an internal standard. The chemical shifts, δ, are given in ppm. Mass spectra were performed on a Hitachi 80(FD). Fluorescence spectra were recorded using a Perkin-Elmer LS-5 and/or Hitachi 850 spectrofluorometer with excitation and emission slits of 5 nm. The fluorescence quantum yields were determined by a comparative method using TTP as standard. Fluorescence lifetime measurements were determined using a Horiba NAES-1100 time-correlated single-photon counting instrument.

RESULTS AND DISCUSSION

Ground state absorption spectra

The electronic absorption spectra of the TTP(418,515,551,592,646 nm), eosin (504,544 nm) and fluorescein (456,482 nm) overlap significantly throughout the visible region. The ground state absorption spectra of the heterodimers (FL—O—$(CH_2)_4$—O— TTP,Eo—O—$(CH_2)_4$—O—TTP) in dilute benzene solution are compared with those of an equimolar mixture of TTP and model compound FLEt or EoEt (Figs 1 and 2.). These indicate that in dilute solution, the heterodimers FL–TTP and Eo–TTP exhibit absorption spectra similar to those of the 1:1 molar mixture of FLEt and TTP or EoEt and TTP, respectively. However, close examination of the spectra shows that the molar extinction coefficients of the porphyrin in the dimers are only *ca* 75–80% of the corresponding bands in the mixture of monomers, and the B-bands of the dimers have a slight bathochromic shift (2 nm) in dilute benzene solution; in addition, the molar extinction coefficient of the Eo moiety in Eo-TTP is obviously increased. Thus absorption spectroscopy provides evidence for electronic interaction between the two chromophores in the heterodimers in the ground state. There are many similar examples in the literature, Little [13], found that for the $n=3$ porphyrin dimer the B-band intensity is only *ca* 70% of the expected value, and for a ZnTTP attached to four H_2P units, Milgrom [14] found a 25% reduction in the intensity of the

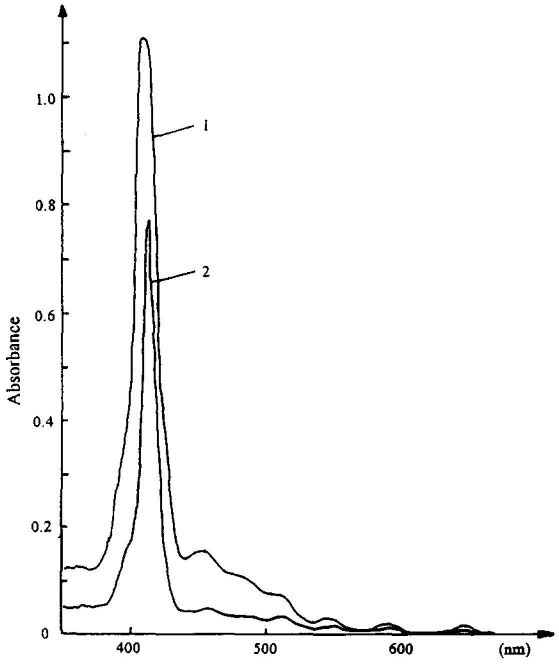


Fig. 1. Absorption spectra of FL–TTP mixture (1:1) (1) and FL—C_4—TTP, (2) in benzene.

B-band with respect to a mixture of monomers. So in our system, these absorption spectral changes can be ascribed to weak exciton coupling interaction between the porphyrin ring and the xanthene ring in the heterodimers.

Steady state fluorescence spectroscopy

On excitation of FL—C_4—TTP (heterodimer I) at 460 nm, a strong decrease in the FL fluorescence is observed accompanied by an increase in the TTP emission with a peak at 656.5 nm (Fig. 3). A similar result is obtained on excitation of Eo—C_4—TTP (heterodimer II) at 528 nm (Fig. 4). Since there is considerable overlap between the fluorescence of FLEt or EoEt and the ground-state absorption spectra of TTP (Fig. 5), singlet-singlet excitation energy transfer from FL or Eo to TTP should be extremely efficient:

$$FL^*(Eo^*) + TTP \xrightarrow{k_{ENT}} FL(Eo) + TTP^*$$

From room temperature spectra and assuming a random orientation of reactants in dilute benzene solution, the *Förster* equation can be used to determine the average donor–acceptor distance R_0 at which the rate constant

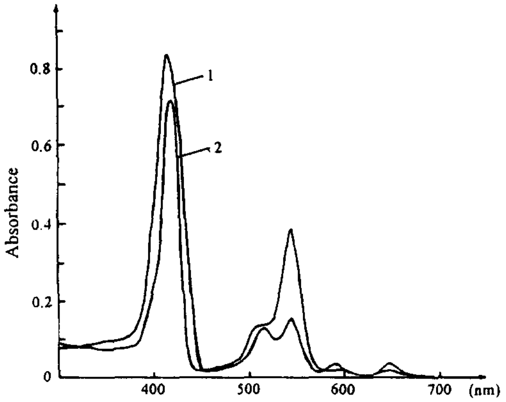


Fig. 2. Absorption spectra of Eo–TTP mixture (1:1) (1) and Eo—C_4—TTP, (2) in benzene.

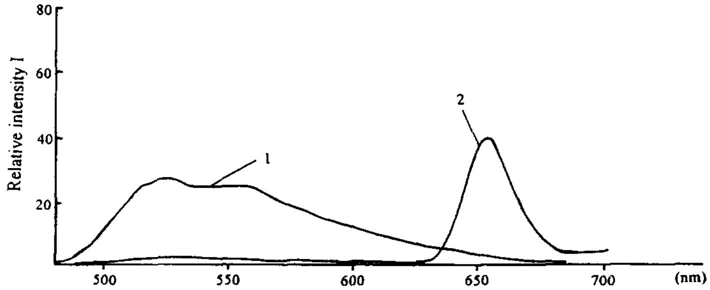


Fig. 3. Fluorescence spectra of FLEt (1) and FL—C_4—TTP, (2) in benzene (λ ex = 460 nm).

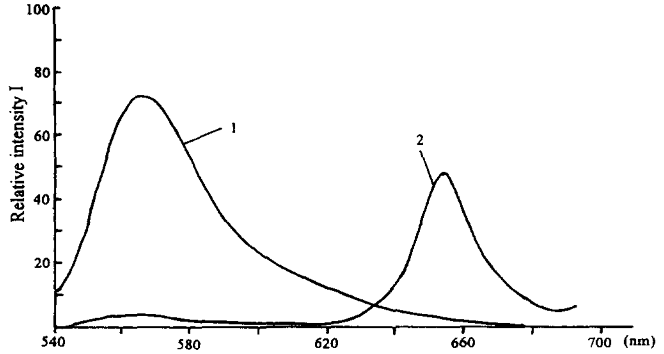


Fig. 4. Fluorescence spectra of EoEt (1) and Eo—C_4—TTP, (2) in benzene (λ ex = 528 nm).

for energy transfer (k_{ENT}) equals the rate constant for non-radiative decay of the donor.

$$R_o^6 = \frac{9\ln 10K^2\phi_D}{128\pi^5 Nn^4} J \qquad (1)$$

TABLE 1
Parameters Derived from Steady Fluorescence Spectra

Compound	*Solvent*	ϕ_{ENT} (%)	k_{ENT} (s^{-1})	ϕ_q (%)	k_q (s^{-1})	J $(mol^{-1}cm^6)$	R_0 (Å)	R (Å)
FLTTP	C_6H_6	98.4	1.25×10^{10}	97.8	1.21×10^{10}	1.26×10^{-9}	66.8	34.9
FLTTP	C_6H_6/CH_3CN_3(1/1)	98.2	1.23×10^{10}	97.6	1.19×10^{10}	1.23×10^{-9}	65.2	33.2
FLTTP	CH_3CN	98.2	1.23×10^{10}	97.4	1.17×10^{10}	1.23×10^{-9}	65.2	33.2
EoTTP	C_6H_6	94.1	5.3×10^{9}	94.2	5.4×10^{9}	0.91×10^{-9}	55.4	34.8
EoTTP	C_6H_6/DMF(1/1)	85.2	1.9×10^{9}	93.8	5.2×10^{9}	0.7×10^{-9}	42.6	31.8
EoTTP	DMF	70.3	7.9×10^{8}	94.1	5.3×10^{9}	0.53×10^{-9}	32.3	27.8

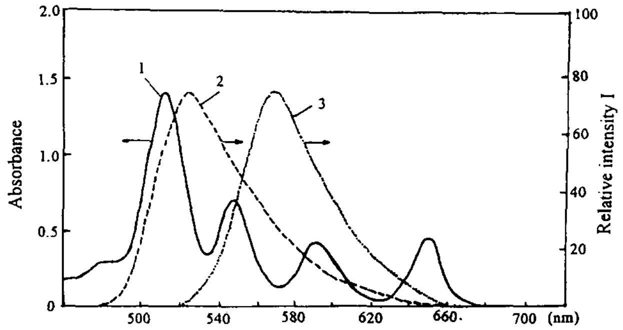


Fig. 5. Absorption spectra of TTP (1), fluorescence spectra of FLEt, (2) (λ ex = 460 nm) and EoEt (3) (λ ex = 528 nm) in benzene.

where ϕ_D are the fluorescence quantum yield of FLEt and EoEt in benzene in the absence of acceptor, respectively, n is the refractive index of the solvent ($n = 1.424$ for benzene), N is Avogadro's constant and K^2 is the orientation factor that equals 2/3 for random geometries. The numerical value of overlap J may be calculated from following equation:

$$J = \frac{\int_0^\infty F_D(\lambda)\,\varepsilon_A(\lambda)\,\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)\,d\lambda} \qquad (2)$$

Substituting the value of J into eqn (1) results in an R_o value of 66.8Å for FL–TTP and 55.4Å for Eo–TTP in benzene, showing that singlet energy transfer can occur over quite large distances. The values of R_o and J for FL–TTP/Eo–TTP in different solvents are listed in Table 1.

As shown in Figs 3 and 4, with selective excitation at 460 nm of the FL–TTP(λex = 528 nm in Eo–TTP), a drastic decrease of the FL fluorescence at 526.5 nm (Eo fluorescence is at 566 nm) is observed concomitant with an obvious increase of the TTP fluorescence (at about 656.5 nm), indicating that a very efficient intramolecular singlet–singlet energy trasfer process from FL* or Eo* to TTP occurs. At the same time, due to some overlap of the absorption spectra of TTP and FL/Eo at 426 and 528 nm, the controlled experiments were carried out as follows:- on excitation of TTP solution at 460 and 528 nm, respectively, the very weak intensities of fluorescence at 656.5 nm were recorded and submitted to correct the data obtained from heterodimers. Comparison of the fluorescence from the monomers with fluorescence spectra recorded for the FL–TTP or Eo–TTP dimers in dilute benzene solution (Figs 3 and 4) shows that, in all cases, the dimers show a drastic decrease in fluorescence associated with the FLEt(λ em = 526.5 nm) or EoEt(λ em = 566 nm), and a corresponding increase in fluorescence associated with the TTP(λ em = 656.5 nm). This observation is consistent with singlet energy transfer from the FL or Eo to the covalently linked TTP. ϕ_{ENT} can be determined by the following equation derived from the kinetic scheme of Figs 3 and 4.

$$\phi_{\mathrm{ENT}} = \frac{F_A \mid \phi_A}{F_A \mid \phi_A + F_D \mid \phi_D} \tag{3}$$

where F_D and F_A are the fluorescence intensity of FL/Eo and TTP in the dimer on excitation of FL or Eo, respectively, ϕ_{D} and ϕ_{A} are the fluorescence quantum yield of FLEt/EoEt and TTP in monomers respectively; these are measured from the normalized and corrected fluorescence spectra by using the known value ($\phi_f = 0.92$) of the standard compound (FL in benzene). The energy transfer efficiency ϕ_{ENT} can be used to calculate the average rate constant for intramolecular energy transfer k_{ENT}

$$\phi_{\mathrm{ENT}} = \frac{k_{\mathrm{ENT}}}{k_{\mathrm{ENT}} + \tau^{-1}_D} \tag{4}$$

where τ_D is the fluorescence lifetime of FLEt or EoEt monomer. At the same time, k_q and ϕ_q can be determined by the following equations

$$k_q = \tau^{-1}_D \left(\frac{\phi_D}{\gamma_{DA}} - 1\right) \qquad \phi_q = \frac{k_1}{k_q + \tau^{-1}_D} \tag{5}$$

where τ_D is the fluorescence lifetime of FLEt or EoEt monomer, ϕ_D and ϕ_{DA} are the fluorescence quantum yield of FL or Eo chromophore in the monomer and heterodimer respectively, k_q and ϕ_q are the quenching rate constant and quenching efficiency by which FL/Eo fluorescence is quenched by TTP in heterodimers, respectively.

The results are listed in Table 1. The steady state fluorescence data show that intramolecular singlet-singlet energy transfer from FL/Eo to TTP occurs in a weakly polar solvent more efficiently than in a polar solvent. In the heterodimer I (FL–TTP), the value of ϕ_{ENT} is nearly equal to the value of ϕ_q indicating the singlet–singlet energy transfer process is only one pathway of FL fluorescence quenching. However in the Eo–TTP heterodimer, the value of ϕ_{ENT} is smaller than the value of ϕ_q in dilute DMF solution, which is probably due to other quenching processes such as electron transfer and the formation of short-lived intermediates.

That efficient singlet energy transfer does occur in these systems is confirmed by the corrected excitation spectra. The corrected fluorescence excitation spectra of the heterodimer I or II was compared with their absorption spectra. Monitoring the emission at 656.5 nm (TTP fluorescence) and scanning through 440–660 nm, it can be seen that, after normalizing at 456 nm (FL–TTP) or 544 nm (Eo–TTP), the agreement between the two spectra is good for heterodimers in benzene indicating that energy transfer is very efficient. For FL–TTP the spectra almost coincide, showing that energy transfer fron FL to TTP is nearly quantitative, but for the Eo–TTP, energy transfer from Eo to TTP is slightly less efficient than FL–TTP. These excitation spectra give good support to the values of ϕ_{ENT} collected in Table 1. The efficiency of the intramolecular singlet–singlet energy transfer in heterodimers in DMF is less efficient than in benzene, probably due to other quenching process such as an electron transfer process in polar solvents. The difference in behaviour on going from benzene to DMF for Eo–TTP may be explained in terms of conformational changes due to solvent interactions. It is suggested that heterodimers may vary from an extended conformation with the two chromophores well separated in benzene, to a somewhat folded conformation in DMF. The values obtained from steady-state fluorescence spectroscopy can be used to estimate the average separation distance(R) between TTP and FL/Eo units.

$$k_{\mathrm{ENT}=\tau_D^{-1}(R_0/R)^6} \tag{6}$$

The steady-state fluorescence data given in Table 1 show that excitation energy transfer from FL/Eo to a covalently-linked TTP can occur with high efficiency. The actual efficiency (ϕ_{ENT}) depends upon the orientation and separation distance between the two rings; our derived R values suggest that the two chromophores reside between 2.7–3.4 nm apart. For the heterodimer, spacing-filling molecular models show that the extended separation

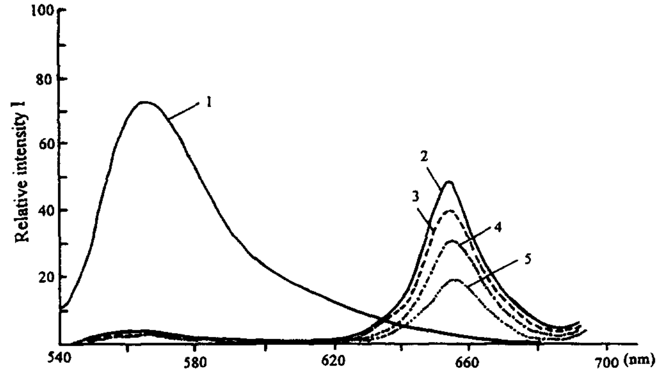


Fig. 6. Fluorescence spectra of Eo—C_4—TTP in solvents of different polarity: (1) EoEt in benzene, (2) benzene, (3) $CHCl_3$, (4) CH_3OH, (5) DMF.

distance is 3.6 nm [15]. The value of *R* in FL–TTP is 3.4 nm which is nearly equal to the calculated value; however the values of *R* in Eo–TTP derived from steady state fluorescence measurement are 3.2 nm (in C_6H_6/DMF = 1/1) and 2.8 nm (in DMF), respectively. They are smaller than those calculated from space-filling models for fully extended conformations and this may imply that the conformation of Eo–TTP is somewhat folded in DMF, which allows partial overlap of the orbitals of each chromophore, thus favouring intramolecular electron transfer. The flexible nature of the linkages used to bind together the two chromophores permit a whole family of conformations to be adopted, ranging from the fully extended form to a closed form with the two chromophores held in close proximity; thus electron transfer occurs in competition with an energy transfer process in DMF for the Eo–TTP dimer. Finally, the solvent dependence of the intramolecular fluorescence quenching in Eo–TTP was investigated. The results (Fig. 6) show that the Eo fluorescence is quenched almost completely, and that the intensity of the porphyrin fluorescence decreases with increasing polarity of the solvent, indicating that the interactions responsible for intensity quenching are related to electron transfer.

Fluorescence quenching and intramolecular electron transfer

As noted above, the FL or Eo fluorescence is quenched by porphyrin through intramolecular energy and electron transfer processes, whereas, on selective excitation of heterodimers or of a 1:1 M mixture of FL/Eo and TTP at 592 nm, only the porphyrin chromophore was excited in dimers or monomer. Comparison of the fluorescence spectra from the 1:1 M mixture with those recorded for the FL–TTP or Eo–TTP dimers in dilute DMF solution

TABLE 2
Photophysical and Electrochemical Data of TTP, FL and Eo

Compound	*Es(ev)*	$E(D/D^+)(v)$	$E(A/A^-)(v)$	$\Delta G_{ET}(ev)$
FL	2.42	1.11	—	−0.04 (TTP*)
Eo	2.31	1.00	—	−0.15 (TTP*)
TTP	1.90	—	−0.81	—

shows that the fluorescence intensity of TTP at 656.5 nm in the dimers was lower than in the monomers. Electronic energy transfer, exciplex formation and electron transfer processes can be perceived as possible pathways of the TTP fluorescence quenching in these systems. As the singlet-state energy level of porphyrin lies below the FL or Eo's level, there is no spectral overlap between the emission of the porphyrin and the absorption of the FL or Eo. Hence, the intramolecular singlet–singlet energy transfer from TTP to FL/Eo could not occur and the fluorescence spectra show no evidence for the formation of exciplex, and it is therefore suggested that the porphyrin fluorescence is quenched by FL/Eo via intramolecular electron transfer. The standard free energy change (ΔG_{ET}) value on one electron transfer from a singlet excited donor molecule D^* to an electron acceptor molecule A can be calculated from the Weller's equation. Photophysical and electrochemical datas of the FL, Eo, and TTP are listed in Table 2.

$$\Delta G_{\mathrm{ET}} = E(D/D^+) - E(A^-/A) - E_s - C$$

where E_s indicates the excitation energy and C denotes the small additional coulombic stabilization of the D^+A^- pair (0.06 ev in DMF).

From the ΔG values, it is apparent that on excitation of TTP, electron transfer from FL/Eo to TTP is possible in a polar solvent, whereas electron transfer from TTP to FL/Eo is thermodynamically unfavourable. Table 3 shows that on selective excitation of TTP at 592 nm of the heterodimer I (FL–TTP) in benzene, the fluorescence lifetime of the porphyrin remains unchanged, demonstrating that electron transfer could not occur in benzene, but for the heterodimer II (Eo–TTP), the fluorescence lifetime of the porphyrin was shortened. In dilute DMF solution, the fluorescence decay measurements exhibit two components, one short-lived component (4.50 ns) and one long-lived component (11.7 ns) in Eo–TTP; the same result was obtained for FL–TTP dimer (one is 9.20 ns, the other is 11.6 ns). The electron transfer rate constant can be calculated from the equation

$$k_{\mathrm{ET}} = 1/\tau_f - 1/\tau_f^0 \tag{7}$$

TABLE 3
Parameters Derived from Fluorescence Decay Measurements

Compound	*Solvent*	$\lambda ex(nm)$	$\lambda em(nm)$	$\tau_f(ns)$	$k_{ET}(s^{-1})$	$\phi_{Et}(\%)$
TTP	C_6H_6	592	658	11.8	—	—
TTP	CH_3CN	592	658	11.5	—	—
FLTTP	C_6H_6	592	658	11.8	—	—
FLTTP	CH_3CN	592	658	9.2(11.6)	2.21×10^7	20.4
EoTTP	C_6H_6	592	658	8.3(11.7)	3.51×10^7	29.3
EoTTP	DMF	592	658	4.5(11.7)	1.36×10^8	61.5

where τ_f^0 and τ_f denote the fluorescence lifetimes of the TTP monomer and TTP in the heterodimer respectively, and the results are listed in Table 3.

From Table 3, it can be seen that the fluorescence lifetime of the porphyrin moiety in the heterodimers is shortened in a polar solvent. This behaviour may result from the existence of different conformations. The intramolecular D–A compounds studied in this work are linked by flexible chain and this gives rise to a flexibility of the distance and orientation of the FL/Eo with respect to the porphyrin plane, and permits the possibility of several conformations. The distance between the two chromophores and their mutual orientation during the lifetime of the excited states determine the electron transfer efficiency. In a polar solvent such as DMF, the two chromophores of dimers are held in a closely packed conformation on excitation, which accounts the efficient intramolecular electron transfer reaction. But in an apolar solvent such as benzene, the extended conformation of the heterodimers shows very little electron transfer efficiency because of the unfavourable orientation factor. It is of interest to note that the life time of all the long-lived components in heterodimers are about 11.7 ns, coincident with the lifetime of the TTP monomer, which may arise from unfavourable conformation to electron transfer of the two moieties adopted in heterodimers.

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