

# 许慧君先生论文集

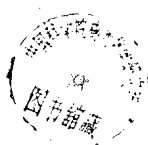
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中国科学院感光化学研究所

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2000年7月



## Singlet-singlet intramolecular energy and electron transfer in covalently-linked porphyrin-phthalocyanine heterodimers

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### Abstract

Intramolecular transfer processes in porphyrin-phthalocyanine heterodimers covalently linked by an oxygen atom (restricted conformation) and/or by a flexible chain of variable length were investigated. Fluorescence spectroscopy shows that singlet-singlet energy transfer from the porphyrin to the phthalocyanine moiety occurs. From fluorescence decay studies, it is concluded that the heterodimers exist in solution in different non-equilibrating conformations. The effects of the chain length and mutual orientation of the chromophore subunits in the heterodimers on the intramolecular energy and electron transfer efficiencies are discussed.

### 1. Introduction

The most efficient primary electron donor in bacterial photosynthesis is a bacteriochlorophyll dimer, the "special pair" [1]. Spectroscopic evidence has shown that the metalloporphyrins are held in carefully controlled orientations which optimize the efficiency of photon or electron transfer. This has prompted numerous studies on linked porphyrin compounds [2]. More recently, a mixed dimer containing a zinc porphyrin linked to a zinc phthalocyanine via an oxygen atom, with more restricted conformational changes, has been reported [3]. In this paper, we present an investigation of the intramolecular energy and electron transfer processes in porphyrin-phthalocyanine heterodimers covalently linked with a flexible chain of variable length  $\text{TTP-O-(CH}_2\text{)}_n\text{-O-Pc}$  (heterodimers II-V) (where TTP is tetraphenylporphyrin). The effects of solvent polarity, chain length and the mutual orientation of the chromophore subunits in the heterodimers on the intramolecular energy and electron transfer efficiencies are discussed in comparison with the previously synthesized  $\text{TTP-O-Pc}$  (heterodimer I) with more restricted conformation.

### 2. Experimental details

#### 2.1. Materials

The structures of the heterodimers are shown in Fig. 1. The syntheses of I and II-V have been reported previously [4, 5]. All the solvents were of analytical grade (Beijing Chemical Factory) and were used as received.

#### 2.2. Instruments and methods

The absorption spectra were measured on a Hitachi-557 spectrometer. The fluorescence spectra were recorded using a Perkin-Elmer LS-5 and/or Hitachi 850 spectrofluorometer with an excitation wavelength of 515 nm for porphyrin and 615 nm and/or 640 nm for phthalocyanine and excitation and emission slits of 5 nm. The fluorescence spectra were recorded over the 600–800 nm wavelength domain. The fluorescence quantum yields were determined by a comparative method using TTP and Pc as standards. Fluorescence lifetime measurements were determined using a Horiba NAES-1100 time-correlated single-photon counting instrument. Redox potentials were measured using a model 79-1 cyclic voltammeter (Jinan Radio No. 4 Factory) with Ag/AgCl saturated with KCl as standard electrode, Pt as counter-electrode, pyrolytic graphite as working electrode and 0.1 M LiCl in dimethylformamide (DMF) as supporting electrolyte.

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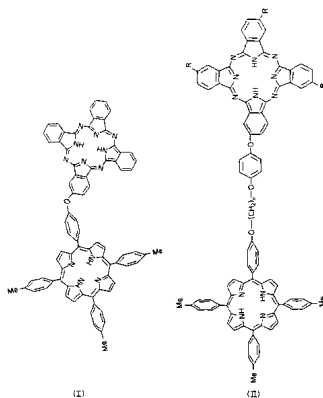


Fig. 1. Structures of the heterodimers: TTP-O-Pc (I); TTP-O-(CH<sub>2</sub>)<sub>n</sub>-O-Pc (II, *n*=2; III, *n*=3; IV, *n*=4; V, *n*=5).

### 3. Results and discussion

#### 3.1. Ground state absorption spectra

The electronic absorption spectra of the heterodimers I-V are very similar. The ground state absorption spectrum of the heterodimer TTP-O-Pc in benzene is compared with that of an equimolar mixture of TTP and Pc (tetra-isopropoxy phthalocyanine) (Fig. 2). This indicates that in dilute solution TTP-O-Pc exhibits an absorption spectrum similar to that of the TTP-Pc mixture. However, the intensity of the Soret band of the porphyrin moiety is slightly decreased and red shifted (2 nm). The heterodimer Q band can be ascribed to the sum of the monomer Q bands with a slight broadening and decrease in intensity of the porphyrin band and a blue-shifted phthalocyanine band. These absorption spectral changes can be ascribed to weak exciton coupling interaction between the two chromophores in the heterodimer in the ground state.

#### 3.2. Steady state fluorescence spectroscopy

On excitation of TTP-O-Pc (heterodimer I) at 515 nm, a strong decrease in the porphyrin fluorescence is observed accompanied by an increase in the phthalocyanine emission with a peak at 710

nm (Fig. 3). Similar results were obtained from heterodimers II-V but the porphyrin fluorescence is almost quenched and the increase in the intensity of the phthalocyanine fluorescence strongly depends on the length of the connecting chain. The heterodimer V with *n*=5 exhibits the strongest phthalocyanine emission indicating that energy transfer is most favourable.

Since there is considerable overlap between the fluorescence spectrum of TTP and the ground state absorption spectrum of Pc in I (Fig. 4), energy transfer should be efficient. The Forster equation can be used to determine the average donor-acceptor distance *R*<sub>0</sub> at which the rate constant for energy transfer *k*<sub>ENT</sub> equals the rate constant (τ<sub>D</sub><sup>-1</sup>) for non-radiative decay of the donor

$$R_0^6 = \frac{9(\ln 10)\kappa^2\Phi_D}{128\pi^5 N n^4} J \quad (1)$$

where Φ<sub>D</sub>=0.15 is the fluorescence quantum yield of TTP in benzene in the absence of acceptor, *n* is the refractive index of the solvent (*n*=1.424 for benzene), *N* is Avogadro's number and κ<sup>2</sup> is the orientation factor which equals  $\frac{2}{3}$  for random geometries. The numerical value of overlap *J* is

$$J = \frac{\int_0^\infty F_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)d\lambda} \approx 1.87 \times 10^{-9} \text{ mol}^{-1} \text{ cm}^6$$

for the heterodimer in benzene and *J*=1.14×10<sup>-9</sup> mol<sup>-1</sup> cm<sup>6</sup> in DMF. Both values are one order of magnitude higher than those found for ZnTTP-O-ZnPc [3].

Substituting these values into eqn. (1) results in *R*<sub>0</sub> values of 58.5 Å for the heterodimer I in benzene showing that singlet energy transfer can occur over quite large distances.

The corrected fluorescence excitation spectra of the heterodimers I and V are compared with their absorption spectra in Fig. 5. Monitoring the emission at 710 nm (Pc fluorescence) and scanning through 500-720 nm, it can be seen that, after normalizing at 668 and 702 nm, the agreement between the two spectra is good for heterodimer I in benzene indicating that energy transfer is very efficient. However, there is a discrepancy between the excitation spectrum and the ground state absorption spectrum in the 500-580 nm region where TTP absorbs for heterodimer V. It is clear that some of the photons absorbed by TTP are trans-

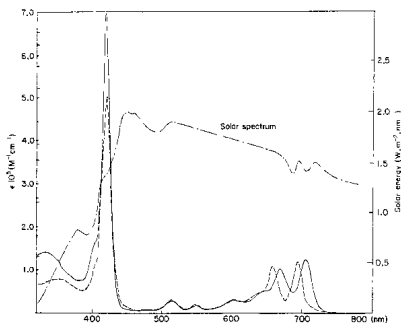


Fig. 2. Absorption spectra of TTP-Pc mixture (1:1) (—) and TTP-O-Pc (---) in benzene.

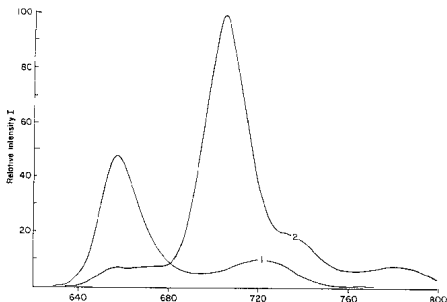


Fig. 3. Fluorescence spectra of TTP (1) and TTP-O-Pc (2) in benzene ( $\lambda_{ex}$  = 515 nm).

ferred to the Pc subunit. Similar results are obtained for heterodimers II–IV in benzene and I in DMF showing that intramolecular energy transfer is not complete, probably due to other quenching processes such as electron transfer and the formation of short-lived intermediates.

Quantitatively, the efficiency of energy transfer can be estimated from the ratio of the corrected excitation spectrum to the ground state absorption spectrum in the 500–580 nm region. The results are collected in Table 1. The energy transfer efficiency  $\Phi_{EnT}$  can be used to calculate the average

rate constant for intramolecular energy transfer  $k_{EnT}$

$$\Phi_{EnT} = k_{EnT} / (k_{EnT} + \tau_D^{-1}) \quad (2)$$

where  $\tau_D$  is the lifetime of the donor porphyrin ( $\tau_D$  = 12.3 ns in benzene). The derived values are also included in Table 1. Thus steady state fluorescence data show that intramolecular singlet-singlet energy transfer from TTP to Pc in heterodimer I occurs more efficiently in benzene than in DMF. In the heterodimers II–V, the transfer is less efficient and depends markedly on the chain

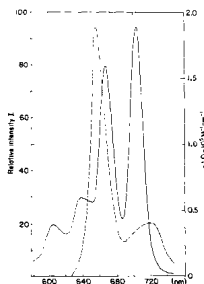


Fig. 4. Absorption spectrum of Pc (—) and fluorescence spectrum (---) of TTP in benzene ( $\lambda_{ex}$  = 515 nm).

length. The difference in behaviour on going from benzene to DMF for heterodimer **I** may be explained in terms of conformational changes due to solvent interactions. It is suggested that heterodimer **I** may vary from an extended conformation with the two chromophores well separated in benzene to a somewhat folded conformation in DMF which allows partial overlap of the orbitals of each chromophore favouring intramolecular electron transfer. In the heterodimers **II-V**, the flexible nature of the connecting chain allows a

whole family of conformations to be adopted, ranging from fully extended to a closed form with the two chromophores held in close proximity. Thus electron transfer occurs in competition with energy transfer processes.

Finally, the solvent dependence of the intramolecular fluorescence quenching in heterodimer **V** was investigated. The results (Fig. 6) show that the porphyrin fluorescence is quenched almost completely and the intensity of the phthalocyanine fluorescence decreases with increasing polarity of the solvent, indicating that the interactions responsible for intensity quenching are related to electron transfer.

### 3.3. Fluorescence quenching and intramolecular electron transfer

As mentioned above, the porphyrin fluorescence is quenched by phthalocyanine through intramolecular energy and electron transfer, whereas the phthalocyanine fluorescence is quenched by porphyrin via electron transfer. The free enthalpy change on one-electron transfer from a singlet excited donor molecule  $D^*$  to an electron acceptor molecule  $A$  can be calculated from the equation

$$\Delta G_{D^*A} = E(D/D^+) - E(A^-/A) - E_s - C \quad (3)$$

where  $E_s$  indicates the excitation energy (1.90 V for TTP and 1.77 V for Pc) and  $C$  denotes the small additional coulombic stabilization of the  $D^+A^-$  pair (0.06 eV in DMF). The one-electron oxidation potential  $E(D/D^+)$  is 1.05 V for TTP

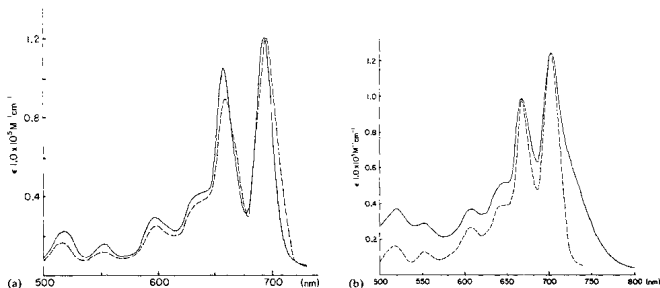


Fig. 5. Comparison of the excitation ( $\lambda_{em}$  = 710 nm) (---) and absorption (—) spectra recorded in dilute benzene solution: (a) TTP-O-Pc; (b) TTP-O-(CH<sub>2</sub>)<sub>5</sub>-O-Pc. The spectra were normalized at 702 nm.

TABLE 1. Parameters derived from steady state fluorescence spectra in benzene

Compound	$\Phi_{\text{ET}} (\%)$	$k_{\text{ET}} (\text{s}^{-1})$
I	73.3	$2.2 \times 10^8$
I (in DMF)	37.8	$5.0 \times 10^7$
II	29.8	$3.5 \times 10^7$
III	30.0	$3.5 \times 10^7$
IV	26.3	$2.9 \times 10^7$
V	37.9	$5.0 \times 10^7$

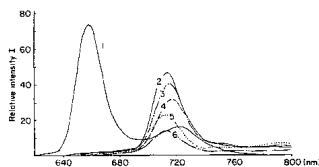
Fig. 6. Fluorescence spectra of TTP-O-(CH<sub>2</sub>)<sub>4</sub>-O-Pc in solvents of different polarity: 1, TTP in benzene; 2, benzene; 3, CHCl<sub>3</sub>; 4, pyridine; 5, CH<sub>2</sub>Cl<sub>2</sub>; 6, DMF.

TABLE 2. Parameters derived from fluorescence decay measurements

Compound	Solvent	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{f}}$ (nm)	$\tau_1$ (ns)	$k_{\text{ET}} (\text{s}^{-1})$	$\Phi_{\text{ET}} (\%)$
Pc	Benzene	640	710	7.5	—	—
	DMF	640	710	6.8	—	—
I	Benzene	515	650	5.1	—	—
			710	7.2	—	—
	DMF	640	710	7.5	—	—
		640	710	3.2(7.3)	$1.7 \times 10^8$	53.1
II	Benzene	515	710	6.5	—	—
		640	710	6.2	$2.8 \times 10^7$	17.3
III	Benzene	515	710	5.8	—	—
		640	710	5.8	$3.9 \times 10^7$	22.6
IV	Benzene	515	710	5.8	—	—
		640	710	5.8	$3.9 \times 10^7$	22.6
V	Benzene	515	710	6.1	—	—
		640	710	6.0	$3.4 \times 10^7$	20.4

and 1.13 V for Pc and the one-electron reduction potential  $E(\text{A}^-/\text{A})$  is  $-1.17$  V for TTP and  $-0.61$  V for Pc relative to the saturated calomel electrode. From the  $\Delta G$  values, we can see that on excitation of either TTP or Pc, electron transfer from TTP to Pc is possible, whereas electron transfer from Pc to TTP is thermodynamically unfavourable. Table 2 shows that, on selective excitation of either TTP at 515 nm or Pc at 640 nm of heterodimer

I in benzene, the lifetime of the porphyrin is shortened but the lifetime of the phthalocyanine subunit remains unchanged, demonstrating that only energy transfer occurs in benzene. However, in DMF, the fluorescence decay measurements exhibit two components, one short-lived (3.2 ns) and one long-lived (7.3 ns). The short lifetime results from intramolecular electron transfer reactions. Transient absorption studies on the picosecond time scale in DMF confirm the formation of the porphyrin radical cation in the 590–630 nm region [6]. The electron transfer efficiency can be calculated from the equation

$$k_{\text{ET}} = 1/\tau_1 - 1/\tau_0^{\text{f}} \quad (4)$$

where  $\tau_0^{\text{f}}$  and  $\tau_1$  denote the fluorescence lifetimes of the Pc monomer and Pc in the heterodimer respectively. However, the lifetime of the Pc moiety in the heterodimers II–V is shortened even in benzene in contrast with heterodimer I in which the lifetime of the Pc subunit remains unchanged. The difference in behaviour of the two kinds of heterodimer may result from the existence of different conformers. When a porphyrin is linked to a phthalocyanine subunit via an oxygen atom, the conformational changes are more restricted as in heterodimer I. The heterodimers II–V undergo conformation changes more freely on excitation due to the flexibility of the methylene chain. The distance between the two chromophores and their mutual orientation during the lifetime of the excited states determine the electron transfer efficiency. In heterodimer IV with  $n=4$ , the two chromophores are held in a closely packed conformation on excitation which accounts for the efficient intramolecular electron transfer reaction. In contrast, heterodimer V with  $n=5$  probably exists in a partially folded form. The fully extended form of heterodimer II with  $n=2$  shows very little electron transfer because of the unfavourable orientation factor.

#### Acknowledgments

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SYNTHESES AND SPECTROSCOPIC PROPERTIES OF  
PORPHYRIN-PHTHALOCYANINE WITH FLEXIBLE POLYATOMIC CHAINS

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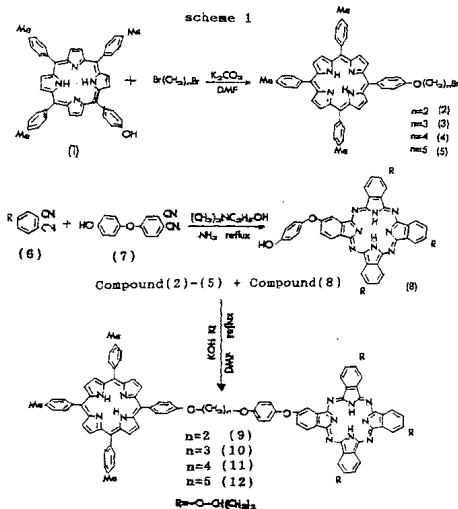
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ABSTRACT: The syntheses of porphyrin-phthalocyanine heterodimers with flexible polyatomic chains especially designed for the studies of intramolecular photoinduced processes are presented along with the effect of mutual orientation of the chromophore subunits on intramolecular energy transfer efficiency.

The most efficient primary electron donor in bacterial photosynthesis is a bacteriochlorophyll dimer, the "special pair"<sup>1</sup>. This has prompted numerous studies on cofacial<sup>2</sup>, hinged<sup>3</sup> or singly linked and folded dimer porphyrins<sup>4,5</sup> or dimer phthalocyanines<sup>6-8</sup>. More recently, a mixed dimer consisting of a porphyrin linked with a phthalocyanine via an oxygen atom with more restricted conformational change has been reported<sup>9,10</sup>. As part of our continuing interest in the studies of photoinduced electron transfer processes sensitized by phthalocyanines<sup>11,12</sup>, we report here the syntheses of four porphyrin-phthalocyanine heterodimers covalently linked with flexible polyatomic chains and the effect of mutual orientation of the chromophore subunits in the heterodimer influencing the intramolecular energy transfer efficiency is discussed.

The reaction of 5-(4-hydroxyphenyl)-10,15,20-tritolyl-porphyrin(1)<sup>13</sup> with  $\text{Br}(\text{CH}_2)_n\text{Br}$  where  $n=2-5$  gave compound (2)  $n=2$ , (3)  $n=3$ , (4)  $n=4$ , (5)  $n=5$  (Scheme 1). Compound (2)-(5) were identified by field desorption (FD) mass spectra. Their molecular ions were observed at  $m/z$  781 (calcd. 779 for  $n=2$ ),  $m/z$  794 (calcd. 793 for  $n=3$ ),  $m/z$  809 (calcd. 807 for  $n=4$ ) and  $m/z$  821 (calcd. 821 for  $n=5$ ). Compound (8) was prepared by refluxing 4-isopropoxy-phthalonitrile (6)<sup>7</sup> with 4-(4'-hydroxyphenoxy)-phthalonitrile(7)<sup>14</sup> in  $N,N$ -dimethylaminoethanol for 24 hrs. during which a steady stream of ammonia gas was passed into the solution, the reaction mixture was poured into water and filtered. The crude product containing compound (8) and a large amount of tetra-isopropoxyphthalocyanine was washed with water, dried, then dissolved in chloroform and chromatographed on a silica gel column. Elution with chloroform gave two bands. The more polar compound was assigned as compound (8) FD-MS  $m/z$  797 (calcd. 796).

Coupling of (2)-(5) with (8) was carried out by refluxing in dried DMF in the presence of potassium hydroxide and a small amount of potassium iodide under nitrogen atmosphere for 48 hrs.



The reaction mixture was poured into water, filtered and the residue washed with water, dried and chromatographed on silica gel column. Elution with acetone to remove the unreacted porphyrin (pink band), then with chloroform gave the heterodimer contaminated with small amount of impurities. The solvent was evaporated and the crude product was taken with benzene and chromatographed on silica gel column. Upon elution with benzene the first green band was assigned as the heterodimer (monitored by UV-visible spectroscopy Fig.1). The crude product was dissolved in chloroform and purified by chromatography on Sephadex LH-20 and eluted with chloroform. The first band was the heterodimer (9)-(12). All the heterodimers exhibited parent ions in their mass spectra using FD mode. The molecular ions were observed at  $m/z$  1494 (calcd. 1494  $n=2$ ),  $m/z$  1507 (calcd. 1508  $n=3$ ),  $m/z$  1521 (calcd. 1522  $n=4$ ),  $m/z$  1535 (calcd. 1536  $n=5$ ) respectively for compounds (9)-(12).

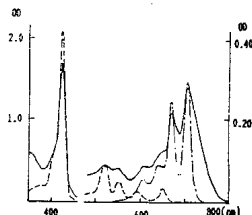


Fig.1. UV-visible spectra of compound (12) —, TTP --- and  $H_2PC$  ..... in benzene ( $3.2 \times 10^{-6}$  mol/L)

The electronic absorption spectra of compound (9)-(12) in benzene are very similar. Fig.1 gives the uv-visible spectra of equimolar mixture of free base of tetratolylporphyrin(TTP) and tetraisopropoxy-phthalocyanine( $H_2PC$ ) as well as compound (12) in benzene. It is indicated that the intensity of the Soret or B band of porphyrin moiety is significantly decreased. Whereas the heterodimer Q bands can be ascribed as the sum of the monomers Q bands with a little broadening and slight intensity decrease of both porphyrin and phthalocyanine Q bands. These absorption spectral changes can be ascribed to weak exciton coupling interaction between the two chromophores in the heterodimer.

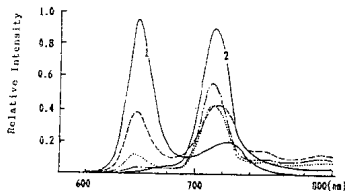


Fig.2. Fluorescence spectra of compounds (9)-(12) and TTP in benzene ( $\lambda_{exc}=512nm$ ) (9)--- (10)..... (11) - - - (12) — 2 TTP — 1

Preliminary studies by fluorescence spectroscopy showed obvious decrease of the intensity of porphyrin emission at 660 nm and increase of the intensity of phthalocyanine emission at 710 nm upon excitation of the porphyrin moiety at 512 nm as shown in Fig.2. This behavior was different from the fluorescence of equimolar mixture of porphyrin and phthalocyanine where no notable increase of emission at 710 nm was detected. The results show very efficient intramolecular energy transfer from the porphyrin to the phthalocyanine chromophore in compound (9)-(12). It is also indicated

in Fig. 2 that the amount of increase of fluorescence from the phthalocyanine moiety depends upon the length of the connecting chain. It appears that the flexible nature of the linkage ensures that compound (9)-(12) undergo conformational changes upon excitation and the distance between the two chromophores and their mutual orientation to be reached during the life-time of the excited states determine the energy transfer efficiency. It is suggested that compound (10) with  $n=3$  and (12) with  $n=5$  can attend closed conformations, whereas the two chromophores in (12) are held in very close proximity that accounts for the most efficient intramolecular energy transfer efficiency. Compound (9) with  $n=2$  and (11) with  $n=4$  probably exist in "Z-shape" conformation with the two chromophores held some distance apart, so that energy transfer is less efficient. The results reported here also demonstrate that the length of the linkage between the two chromophores is not a sufficient condition for intramolecular energy transfer. There is also a strong geometrical requirement.

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PHOTOINDUCED ELECTRON TRANSFER AND ENERGY  
TRANSFER IN SUPRAMOLECULAR SYSTEM CONSIST-  
ING OF PORPHYRIN AND PHTHALOCYANINE

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ABSTRACT

In the first part, intramolecular energy and electron transfer processes in porphyrin-phthalocyanine heterodimers covalently linked by an oxygen atom with more restricted conformation and/or by a flexible chain of variable length are investigated. Fluorescence spectroscopy shows that singlet-singlet energy transfer from the porphyrin to the phthalocyanine moiety occurs. From fluorescence decay studies, it is concluded that the heterodimers exist in solution in different non-equilibrating conformations. The effect of solvent polarity, chain length and mutual orientation of the chromophore subunits in the heterodimers influencing the intramolecular transfer efficiencies are discussed.

In the second part, novel Langmuir-Blodgett films consisting of amphiphilic zinc phthalocyanine and hydrophobic porphyrin have been successfully fabricated. Surface pressure-area isotherms and uv-vis absorption spectra measurements show that the porphyrin molecules are arranged voluntarily into the cavity between the long alkyl chains of the AmZnPc in one layer of the LB film. Polarized uv-vis and FT-IR spectroscopic studies indicate that the AmZnPc macroring plane lies nearly parallel to the substrate surface, while the long alkyl chains of AmZnPc are orientated nearly perpendicular to the substrate surface. Multilayer of the mixed LB film are built onto SnO<sub>2</sub> electrode. The photoelectric effects obtained is more than two times larger than that of the individual AmZnPc LB films.

INTRODUCTION

Porphyrin and phthalocyanine have unique properties for their redox behaviors. It seems that they can provide fascinating properties when their functionalities are combined. Moreover, the absorption spectra of porphyrin and phthalocyanine cover the entire visible region of the solar spectrum so that it can harvest a large fraction of the energy available in the solar spectrum. We report here: In the first part, intramolecular energy and electron transfer in porphyrin-phthalocyanine heterodimers. In the second part, formation, characterization of a novel mixed LB film consisting of an amphiphilic zinc phthalocyanine and a hydrophobic porphyrin and its photoelectric behaviors.

EXPERIMENTAL

Materials: The heterodimer I and II-V as well as the amphiphilic zinc phthalocyanine (AmZnPc) ( Fig.1 ) were synthesized in our laboratory and details syntheses will have been

described elsewhere<sup>11a</sup>. All the solvents were of analytical grade purchased from Beijing Chemical Factory and were used as received.

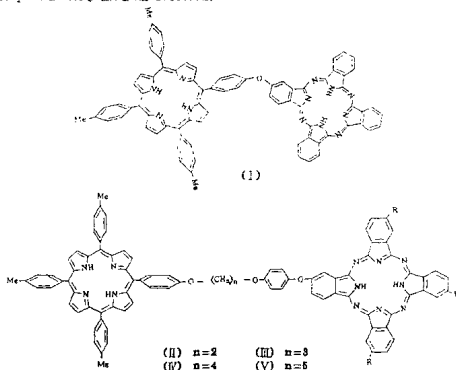


Fig.1 The structures of the heterodimers

**Instruments and methods:** The absorption spectra were measured on a Hitachi-657 Spectrophotometer. Fluorescence spectra were recorded using Perkin-Elmer LS-8 and Hitachi-850 spectrofluorometers. Fluorescence life-time measurements were determined using a Horiba NAES-1100 time-correlated single-photon counting instrument. Redox potentials were measured using a Model 79-1 cyclic voltammeter (Jinan Radio No.4 Factory) with Ag/AgCl saturated with KCl, as reference electrode, Pt as counterelectrode, pyrolytic graphite as working electrode and 0.1 M LiCl in DMF as supporting electrolyte. Monolayer of AmZnPc was spread on pure water subphase (pH ca. 5.6-5.8) from a solution of equimolar of AmZnPc and TTP in  $\text{CHCl}_3$  ( $1 \times 10^{-4}$  M). Surface-pressure isotherm were measured in a Joyle-Loebel Langmuir-Trough 4 at 25°C, compressed at a speed of  $2(\text{mN m}^{-1}) \text{ min}^{-1}$ . Multilayers were prepared on  $\text{CaF}_2$  slides with dipping speed of  $5 \text{ mm min}^{-1}$ , resulted in a fairly good deposition of a typical Y-type film with a transfer ratio of 0.95. Polarized absorbance were recorded on a Hitachi-657 Spectrophotometer with a polarizer. The orientation of the LB film with respect to the substrate was determined by the dichroic ratio of the absorbance of the film for polarized light with electric vectors parallel and perpendicular to the dipping direction using Yoneyama's expression<sup>9</sup>. Infrared measurements were performed on a Nicolet 208X FT-IR spectrophotometer equipped with a TGS detector with a resolution of  $4 \text{ cm}^{-1}$ . A ZnSe wire grid polarizer (Spectra Tech. 60.) was used. For the IR-transmission measurements, the number of interferogram accumulation was 400 at the angle of incidence at 0° and 45° respectively. According to Vandevyver's procedures<sup>8</sup>, the orientation of the LB film with an angle with respect to the substrate can be calculated.

## RESULTS AND DISCUSSIONS

### 1. Energy and electron transfer in porphyrin-phthalocyanine heterodimers.

#### 1.1 Electronic absorption spectra

The electronic absorption spectra of heterodimers I-V are very similar.

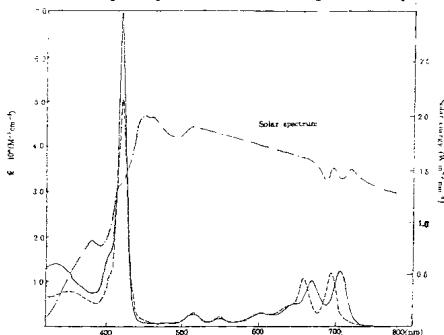


Fig.2 Absorption spectra of 1:1 molar mixture of TTP+Pc(—) and TTP-Q-Pc(---) in benzene

The ground-state absorption spectrum of the heterodimer I in benzene compared with equimolar mixture of TTP and Pc (Fig.2) indicates that in dilute solution, I exhibits the absorption spectrum that is similar to that of the mixture of TTP and Pc. However, the Soret band of the porphyrin moiety is slightly decreased and red-shifted. While the heterodimer Q band can be ascribed as the sum of the monomers Q bands with a little broadening and intensity decreased of the porphyrin and blue-shifted of phthalocyanine Q band. The results can be ascribed to weak exciton coupling interactions between the two chromophores in the heterodimer in ground state.

#### 1.2 Steady-State Fluorescence Spectroscopy

Excitation of heterodimer I at 615nm, a drastic decrease of the porphyrin fluorescence is observed accompanied with the increase of phthalocyanine emission with a peak at 710 nm (Fig. 3). Similar results were obtained from heterodimers I-V, but the porphyrin fluorescence is almost quenched and the increase of the intensity of the phthalocyanine fluorescence depends markedly upon the length of the connecting chain. The heterodimer V exhibits the strongest phthalocyanine emission indicating that energy transfer is most favorable. The corrected excitation spectrum of the heterodimer I and V is compared with its absorption spectrum respectively (Fig.4). Monitoring the emission at 710 nm (phthalocyanine fluorescence) and scanning through 500-740 nm region of the excitation spectrum shows that after normalizing at 702 nm, the agreement between the two spectra is seen to be good for the heterodimer I in benzene indicating that energy transfer is very efficient. However, there is a discrepancy between the excitation spectrum and the ground-state absorption spectrum in the 500-580 nm region where the TTP absorbs for the heterodimer V.

It is clear that some of the photons absorbed by TTP are transferred to the Pc substrate. Similar results are obtained for the heterodimer **I**–**V** in benzene and **I** in DMF showing

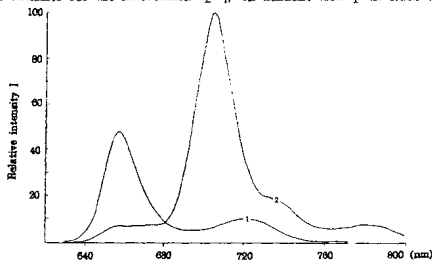


Fig.3 Fluorescence spectra of TTP (1) and TTP-O-Pc (2) in benzene ( $\lambda_{exc} = 612$  nm).

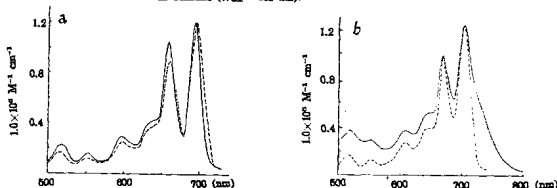


Fig.4 Comparison of excitation ( $\lambda_{exc} = 710$  nm) (---) and absorption (—) spectra recorded in dilute benzene solution: (a) TTP-O-Pc, (b) TTP-O-(CH<sub>2</sub>)<sub>4</sub>-O-Pc. The spectra have been normalized at 702 nm.

that intramolecular energy transfer is not complete probably due to other quenching processes such as electron transfer and the formation of short-lived intermediates. Quantitatively, the efficiency of energy transfer can be estimated from the ratio of the corrected excitation spectrum to the ground-state absorption spectrum in the 500–680 nm region. The results are collected in Table I. The energy transfer efficiency  $\phi_{EET}$  can be used to calculate the average rate constant for intramolecular energy transfer  $k_{EET}$ :

$$\phi_{EET} = k_{EET} / (k_{EET} + \tau_D^{-1})$$

Where  $\tau_D$  is the life-time of the donor-porphyrin ( $\tau_D = 12.3$  ns in benzene). The derived values are also included in the Table I. Thus, Steady-state fluorescence data show that intramolecular singlet-singlet energy transfer from TTP to Pc in the heterodimer **I** occurs more efficiently in benzene than in DMF. While in the heterodimers **I**–**V**, the transfer is less efficient and depends markedly upon the chain length. The difference in behaviors when going from benzene to DMF for the heterodimer **I** could be explained in terms of conformational changes due to solvent interactions. It is suggested that the heterodimer **I** may vary from an extended conformation with the two chromophores well separated in benzene to a somewhat folded conformation in DMF which allows partially overlapping of the



orbitals of end chromophores that favors intramolecular electron transfer processes. In the heterodimers I-V, the flexible nature of the connecting chain allows a whole family of conformation to be adopted ranging from fully extended to a closed form with the two chromophores held in a closed proximity. Thus, electron transfer occurs in competition with energy transfer processes.

Table 1 Parameter derived from steady-state fluorescence spectra in benzene

Compound	$\Phi_{\text{ISC}}(\%)$	$k_{\text{ISC}}(\text{s}^{-1})$
I	73.3	$2.2 \times 10^8$
I in DMF	37.8	$5.0 \times 10^7$
II	30.0	$3.5 \times 10^7$
III	30.0	$3.5 \times 10^7$
IV	26.3	$2.9 \times 10^7$
V	37.9	$5.0 \times 10^7$

### 1.3 Fluorescence decay studies

As mentioned above, the porphyrin fluorescence has been observed to be quenched by phthalocyanine through intramolecular energy and electron transfer, while the fluorescence of phthalocyanine is quenched by porphyrin via electron transfer. The free enthalpy change upon one-electron transfer from a singlet excited donor molecule  $D^*$  to an acceptor molecule A can be calculated from the equation:

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

Here,  $E_s$  indicates the excitation energy which amounts to 1.90V for TTP and 1.77V for Pc, while C denotes the small additional coulombic stabilization of the  $D^+A^-$  pair which amounts to 0.06 eV in DMF. The one-electron oxidation potential  $E(D/D^+)$  equals to 1.05 V for TTP and 1.13 V for Pc and one-electron reduction potential  $E(A^+/A)$  equals to -1.17 V for TTP and -0.61V for Pc relative to the saturated calomel electrode. From the  $\Delta G$  Values, we can see that excitation of either TTP or Pc, electron transfer from TTP to Pc is possible, while electron transfer from Pc to TTP is thermodynamically unfavorable. Table 2 shows that

Table 2 Parameters derived from fluorescence decay measurements

Compound	solvent	$\lambda_{\text{exc}}$ nm	$\lambda_{\text{f}}$ nm	$\tau_{\text{f}}$ ns	$k_{\text{ET}}$ $\text{s}^{-1}$	$\Phi_{\text{ET}}$ %
Pc	benzene	640	710	7.5	-	-
	DMF	640	710	6.8	-	-
I	benzene	515	650	5.1	-	-
			710	7.2	-	-
		640	710	7.5	-	-
II	DMF	640	710	3.2(7.3)	$1.7 \times 10^8$	53.1
	benzene	515	710	6.5	-	-
		640	710	6.2	$2.8 \times 10^7$	17.3
III	benzene	515	710	5.8	-	-
		640	710	5.8	$3.9 \times 10^7$	22.6
IV	benzene	515	710	5.8	-	-
		640	710	5.8	$3.9 \times 10^7$	22.6
V	benzene	515	710	6.1	-	-
		640	710	6.0	$3.4 \times 10^7$	20.4