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Energy transfer in zinc porphyrin–phthalocyanine heterotrimer and heterononamer studied by fluorescence resonance energy transfer (FRET)

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Abstract

Two or eight zinc triphenyl porphyrins were conjugated with Zn-phthalocyanine or H₂-phthalocyanine to form ZnPc–(ZnTPP)₂, ZnPc–(ZnTPP)₈, H₂Pc–(ZnTPP)₂ and H₂Pc–(ZnTPP)₈. Energy transfers from the porphyrin moiety to phthalocyanine part were quantitatively studied with the modality of fluorescence resonance energy transfer (FRET). By measuring the fluorescence increment from the phthalocyanine moiety and the decrease from porphyrin part under selective excitation at the B band of the porphyrin part in those conjugated compounds and their equimolar mixture of compositions, energy transfer efficiencies were estimated to be 90% for H₂Pc–(ZnTPP)₈ and ZnPc–(ZnTPP)₈, and 60%, 30% for ZnPc–(ZnTPP)₂ and H₂Pc–(ZnTPP)₂, respectively.

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1. Introduction

Phthalocyanines are an important class of organic compounds, which have a number of applications in different fields such as xerographic photoreceptors [1], infrared sensors [2], optical recording [3], organic photoelectronic devices [4], nonlinear optics [5] and as photosensitizers in photodynamic therapy (PDT) of cancer [6]. Phthalocyanines are stable and rigid compounds with a high quantum yield to emit red fluorescence, and can photo-induce singlet oxygen to destroy cancer cells when used in PDT. Phthalocyanines have two absorption bands, a strong O band in the red region (600-700 nm) and a mediumstrength Soret band in UV region (350 nm). Due to the attractive property of high fluorescence efficiency in red wavelength region, phthalocyanines are potentially useful as wavelength transfer devices absorbing the short wavelength and emitting longer red wavelengths. However, their poor absorption in the other visible region (except red region) limits these types of

1386-1425/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2007.07.010 applications. Furthermore, phthalocyanines such as Pc 4 have been used in clinical trials for photodynamic therapy of cancer [7], thus expanding the range of absorption (excitation) wavelengths in the visible region is of importance. With the aim of effectively capturing a wide region of visible light and efficiently emitting red light, porphyrin-phthalocyanine conjugates have been synthesized. Porphyrins have an intense B band in violet region [8], and successful energy transfer from porphyrin to phthalocyanine has been achieved [9]. To conjugate porphyrin with phthalocyanine, several links have been tested, such as ether [10], alkoxy [11], piperazinyl [12], phenylethynyl [13] and ethynyl groups [8]. However, among those linked porphyrin-phthalocyanines only a few conjugates, such as the phenylethynyl-linked dyad [13] and the meso- and β -position connected compounds [9], accomplished a remarkable energy transfer. The edge-to-edge distances for above conjugates are all similar (about a few nm). However, the results of energy transfer are different for different linkages, and no good explanation for such difference has been given. So far, no clear rule has been reported for energy transfer in linked porphyrin-phthalocyanine molecules. Thus searching a dominating rule in energy transfer would involve not only extending applications of phthalocya-

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nines but also establishing a typical photochemical model of energy transfer in chemical conjugates.

From the physics point of view, the concept of fluorescence resonance energy transfer (FRET) may help to solve the energy transfer problem in porphyrin-phthalocyanine conjugates. FRET is a photophysical process based on a non-radiative energy transfer between a fluorescent donor and a suitable energy acceptor [14]. According to the Förester theory, FRET is related to the distance separating the donor-acceptor pair, and it generally happens when such distance is approximately equal to or smaller than 5 nm [15]. Moreover, the efficiency of energy transfer depends upon the amount of overlap between the wave functions describing the donor-acceptor dipoles, e.g. the amount of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor [16]. In porphyrin-phthalocyanine compounds, porphyrin may be conjugated to phthalocyanine with a distance which can easily be controlled to be smaller than 5 nm, thus these compounds are suitable for FRET studies.

In this work, FRET was used as the modality to investigate the energy transfer from porphyrin moiety to phthalocyanine part in zinc porphyrin–phthalocyanine heterotrimer and heterononamer, synthesized in our laboratory. The efficiency of energy transfer in these compounds is evaluated in this work. Here the acceptor was either Zn-phthalocyanine (ZnPc) or H₂phthalocyanine (H₂Pc), and the donor was two or eight zinc triphenyl porphyrins that conjugated to form ZnPc–(ZnTPP)₂, Zn-(ZnTPP)₈, H₂Pc–(ZnTPP)₂ and H₂Pc–(ZnTPP)₈, respectively.

2. Experimental

2.1. Materials

4,5-Dichlorophthalonitrile [17], 5-hydroxy-10,15,20-triporphyrin [18], 4,5-di-[5-(4-phenoxy)-10,15,20phenyl triphenyl porphyrin]-1,2-dicarbonitrile [P(CNOTPP)₂] [19], 4,5-di[5-(4-phenoxy)-10,15,20-triphenyl porphyrin]-1,2dicarbonitrile zinc (II) [P(ZnCNOTPP)2] [19] were synthesized in literature. 4-Hydroxybenzaldehyde, benzaldehyde, as pyrrole, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), sodium methoxide, potassium carbonate, zinc acetate, lithium and propan-1-ol, were purchased from Sigma-Aldrich and used without further purification. Dimethylsulfoxide (DMSO) was dried over alumina before use. All other solvents were dried by standard methods prior to use. Silica gel 60 (0.04-0.063 mm) for chromatography was purchased from Merck.

2.2. Equipment

UV-vis absorption spectra were recorded on a Varian 500 UV-vis/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum 200 FTIR spectrometer. ¹H NMR spectra were recorded using a Bruker EMX 400 NMR spectrometer. Fluorescence spectra were recorded with a Varian Eclipse Spectrofluoremeter. MALDI-TOF mass spectra of the nonamer ZnPc-(ZnTPP)₈ was obtained at Tohoku University (Japan) using Perseptive Biosystem MALDI-TOF Mass Voyager DE-SI2 spectrometer with dithranol as matrix. The MALDI-TOF mass spectra of the rest of the complexes was determined using Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation and Processing Delayed Extraction Technology at the University of Cape Town in South Africa.

2.3. Synthesis

2.3.1. 2,3-Di-[5-(4-phenoxy)-10,15,20-triphenyl porphyrin zinc (II)] phthalocyanine (H₂Pc-(ZnTPP)₂) (Scheme 1) Chloro[7,12,14,19-diimino-21,5-nitrilo-5H-

tribenzo[c,h,m]-[1,16,1]triazacyclopentadecinato-(2-)- N^{22},N^{23},N^{24}] boron (SubPc) was synthesized according to literature methods [20]. SubPc (86 mg, 0.2 mmol) in DMSO (10 ml) was heated at 60 °C for 2 h with stirring under nitrogen. P(ZnCNOTPP)₂ (151 mg, 0.1 mmol) and DBU (two drops) were added to the solution. The mixture was heated to 120 °C

were added to the solution. The mixture was heated to $120 \,^{\circ}$ C for 24 h with stirring under nitrogen. After cooling to room temperature, the green reaction mixture was poured into 100 ml dichloromethane and washed three times with 100 ml water to remove DMSO. The dichloromethane layer was collected, evaporated and the solid applied to a silica gel column. A series of purple bands were eluted by dichloromethane. The desired compound (green bands) was eluted using dichloromethane containing 5% methanol. The by-product ZnPc remained on the top of column. Removal of dichloromethane and methanol by evaporation afforded 12.7 mg (6%) of a green solid. The green product H₂Pc-(ZnTPP)₂ was recrystallized from dichloromethane with methanol.

UV–vis [DMSO, λ_{max}/nm (log ε)]: 349 (4.47), 429 (5.82), 560 (4.23), 602 (4.33), 673 (5.01); ¹H NMR (400 MHz, CDCl₃), δ 9.38 (s, 2H, phthalocyanine H), δ 8.92 (m, 6H, phthalocyanine H), 8.16–8.21 (m, 16H, pyrrole H), 7.69–7.76 (m, 16H, phenyl H), 7.49–7.52 (m, 22H, phenyl H), 6.98 (s, 6H, phthalocyanine H).

2.3.2. 2,3-Di-[5-(4-phenoxy)-10,15,20-triphenyl porphyrin zinc (II)] phthalocyanine zinc (II) (ZnPc-(ZnTPP)₂) (Scheme 1)

A mixture of H₂Pc-(ZnTPP)₂ (190 mg, 0.1 mmol) and anhydrous zinc acetate (92 mg, 0.5 mmol) in dimethylformamide (DMF) (30 ml) was heated at 70 °C for 1 h with stirring under nitrogen. After cooling to room temperature, the green reaction mixture was poured into 100 ml dichloromethane and washed three times with 100 ml water to remove excess zinc acetate, acetic acid and DMF. Column chromatography on silica gel with dichloromethane containing 5% methanol as eluent gave one band. Removal of dichloromethane and methanol by evaporation afforded 178 mg (91%) of a blue-green solid. The crude product was recrystallized from dichloromethane with absolute methanol. UV–vis [DMSO, $\lambda_{max}/nm (\log \varepsilon)$]: 350 (4.72), 428 (5.73), 561 (4.32), 607 (4.45), 675 (5.13); ¹H NMR (400 MHz, DMSO- d_6), δ 9.42 (s, 2H, phthalocyanine H), δ 9.05 (d, 6H, phthalocyanine H), 8.77-8.90 (m, 16H, pyrrole H), 8.07–8.25 (m, 16H, phenyl H), 7.49–7.75 (m, 22H, phenyl H), 6.74 (d, 6H, phthalocyanine H). IR(KBr) C-O-C



Scheme 1. Synthetic route for the trimers H₂Pc-(ZnTPP)₂ and ZnPc-(ZnTPP)₂.

 1202 cm^{-1} ; MALDI-TOF-MS *m*/*z*: Calcd. = 1966.98; Found = 1962.93 [*M* - 4]⁺.

2.3.3. 2,3,9,10,16,17,23,24-Octa[5-(4-phenoxy)-10,15,20triphenyl porphyrin zinc (II)] phthalocyanine (H₂Pc-(ZnTPP)₈) (Scheme 2)

A mixture of $P(ZnCNOTPP)_2$ (151 mg, 0.1 mmol) and sodium methoxide (5 mg) was added to distilled methanol

(10 ml). Anhydrous ammonia gas was bubbled through the stirred suspension for 1 h. The suspension was then refluxed for 6 h with continued addition of ammonia gas, forming the diiminoisoindole which was not isolated. The methanol was removed, then propan-1-ol (5 ml) and DBU (2 drops) were added. The mixture was refluxed for 2 h with stirring under a nitrogen atmosphere. The reaction procedure was monitored by



H₂Pc-(ZnTPP)₈

Scheme 2. Synthetic route for the nonamers H₂Pc-(ZnTPP)₈ and ZnPc-(ZnTPP)₈.

UV–vis spectroscopy. After cooling to room temperature, the purple solution was poured into 20 ml dichloromethane, washed three times with 100 ml water. The dichloromethane layer was collected, evaporated and the solid applied to a silica gel column. A series of purple bands was eluted by dichloromethane. The desired compound was eluted using dichloromethane containing 2% methanol. Removal of dichloromethane and methanol by evaporation afforded 18 mg (12%) of a dark-purple solid. The dark-purple product was recrystallized from dichloromethane with hexane. UV–vis [DMSO, $\lambda_{max}/nm (\log \varepsilon)$]: 355 (4.76), 429 (6.12), 561 (4.68), 600 (4.53), 680 (4.92); ¹H NMR (400 MHz, CDCl₃), δ 8.82 (broad s, 72H, phthalocyanine H and pyrrole H), 8.19 (broad s, 40H, phenyl H), 7.74 (broad s, 80H, phenyl H), 7.16 (broad s, 32H, phenoxy H).

2.3.4. 2,3,9,10,16,17,23,24-Octa[5-(4-phenoxy)-10,15,20triphenyl porphyrin zinc (II)] phthalocyanine zinc (II) (ZnPc-(ZnTPP)₈) (Scheme 2)

A mixture of $H_2Pc-(ZnTPP)_8$ (121 mg, 0.02 mmol) and anhydrous zinc acetate (18 mg, 0.1 mmol) in dimethylformamide (DMF) (30 ml) was heated at 70 °C for 1 h with stirring under nitrogen. After cooling to room temperature, the purple reaction mixture was poured into 100 ml dichloromethane and washed three times with 100 ml water to remove excess zinc acetate, acetic acid and DMF. Column chromatography on silica gel with dichloromethane containing 2% methanol as eluent gave one band. Removal of dichloromethane and methanol by evaporation afforded 101 mg (83%) of a purple solid. The crude product was recrystallized from dichloromethane with absolute methanol. UV–vis [DMSO, $\lambda_{max}/nm (\log \varepsilon)$]: 356 (4.97), 429 (6.31), 561 (4.91), 602 (4.69), 681 (5.09); ¹H NMR (400 MHz, CDCl₃), δ 8.87 (broad s, 72H, phthalocyanine H and pyrrole H), 8.21(broad s, 40H, phenyl H), 7.75 (broad s, 80H, phenyl H), 7.15 (broad s, 32H, phenoxy H), IR(KBr) C–O–C 1210 cm⁻¹; MALDI-TOF-MS *m*/*z*: Calcd. = 6114.79; Found = 6114.93 [*M*]⁺.

3. Results and discussion

The synthetic route to the compounds is presented in Schemes 1 and 2. The compounds are abbreviated as indicated in the experimental section. The synthesis of the porphyrin-phthalocyanine trimer H₂Pc-(ZnTPP)₂ was done from the reaction of P(ZnCNOTPP)₂ with unsubstituted subphthalocyanine (SubPc) to give the desired product in low yield (6%). The low yield is partly due to the extensive purification procedure required. The ¹H NMR spectrum of $H_2Pc-(ZnTPP)_2$ compound showed the resonances belonging the phthalocyanine ring protons at 9.38 ppm as singlet, 8.92 ppm as multiplets and 6.98 ppm as broad peak, integrating for 2, 6 and 6, respectively, giving a total of 14 protons as expected for H₂Pc-(ZnTPP)₂. The resonance belonging the pyrrole protons were observed between 8.16 and 8.21 ppm as multiplets, integrating 16 protons as expected and the phenyl protons were observed between 7.69–7.76 and 7.49–7.52 ppm as multiplets, integrating for 16 and 22, respectively and totalling 38 protons as expected for H₂Pc-(ZnTPP)₂. The synthesis of ZnPc-(ZnTPP)₂ using a general phthalocyanine metallation reaction with anhydrous zinc acetate in DMF gave a satisfactory yield (91%). The ¹H NMR spectrum of this compound showed the resonances due to the phthalocyanine ring protons at 9.42 ppm as singlet, 9.05 ppm as a doublet and 6.74 ppm as a doublet, integrating for 2, 6 and 6, respectively, giving a total of 14 protons as expected for $ZnPc-(ZnTPP)_2$. The resonances belonging the pyrrole protons were observed between 8.77 and 8.90 ppm as multiplets, integrating for 16 protons as expected and the phenyl protons were observed between 8.07-8.25 and 7.49-7.75 ppm as multiplets, integrating for 16 and 22, respectively and totalling 38 protons as expected for ZnPc-(ZnTPP)₂. Mass spectroscopy revealed a molecular ion peak at 1962.93 $m/z [M-4]^+$ which is 4 less than the calculated molar mass of 1966.98 g/mol. The synthesis of the porphyrin-phthalocyanine nonamer H₂Pc-(ZnTPP)₈ was done from P(ZnCNOTPP)₂ which was firstly converted into the diiminoisoindoline precursor by bubbling the phthalonitrile with ammonia gas and after chromatography gave a 12% yield of the target phthalocyanine product. The resonances belonging the phthalocyanine ring and pyrrole protons of H₂Pc-(ZnTPP)₈ complex were observed at 8.82 ppm as a broad peak, integrating for a total of 72 protons as expected for $H_2Pc-(ZnTPP)_8$. The resonance belonging the phenyl protons were observed 8.19 and 7.74 ppm as a broad peak, integrating for 40 and 80 protons, respectively, giving a total of 120 protons as expected and the phenoxy protons were observed at 7.16 ppm as a broad peak, integrating for 32 protons as expected for H₂Pc-(ZnTPP)₈. The synthesis of ZnPc-(ZnTPP)₈ using a general phthalocyanine metallation reaction with anhydrous



Fig. 1. The spectra of $H_2Pc-(ZnTPP)_2$ and an equimolar mixture of its components in DMSO. (a) UV–vis absorption spectra; (b) fluorescence spectra by selective excitation of the porphyrin part at 429 nm. The dotted line is for an equimolar H_2Pc .

zinc acetate in DMF gave a good yield (83%). The ¹H NMR spectrum of this compound showed the resonances belonging the phthalocyanine ring and pyrrole protons at 8.87 ppm as a broad peak, integrating for a total of 72 protons as expected for (ZnPc–(ZnTPP)₈). The resonances belonging to the phenyl protons were observed at 8.21 and 7.75 ppm as broad peaks, integrating for 40 and 80 protons respectively giving a total of 120 protons as expected and the phenoxy protons were observed at 7.15 ppm as a broad peak, integrating for 32 protons as expected for (ZnPc–(ZnTPP)₈). The mass spectrum of this compound displayed a molecular ion peak at 6114.93 *m*/*z*, which was in agreement with the calculated value of 6114.93 g/mol.

UV-vis spectra of H₂Pc-(ZnTPP)₂ and an equimolar mixture of the monomers of H₂Pc and ZnTPP are shown in Fig. 1a, while their corresponding fluorescence spectra are depicted in Fig. 1b. The conjugation did not affect the B band absorption of the ZnTPP moiety in H₂Pc-(ZnTPP)₂, but altered the Q band of the H₂Pc moiety by combining the separated two peaks into one peak (Fig. 1a) which is shifted to the blue compared to the mixture, reflecting that the electronic interaction between the different ring systems occurred in this complex. The effect of the electronic interaction was also exhibited by fluorescence spectra, in that the second emission peak at 657 nm of the ZnTPP moiety disappeared and a 15 nm blue-shift in emission peak of the H₂Pc moiety occurred on conjugation. The energy transfer from (ZnTPP)₂ moiety to H₂Pc occurred in $H_2Pc-(ZnTPP)_2$ (Fig. 1b), as evidenced by the remarkable enhancement of fluorescence intensity from the H₂Pc moiety compared to the un-conjugated equimolar mixture, at the excitation wavelength of 429 nm which is the B band peak absorption

of the ZnTPP moiety. The energy transfer efficiency can be estimated by the two factors, the donor factor and the acceptor factor. Comparing the emission spectrum of H₂Pc-(ZnTPP)₂ with that of the un-conjugated equimolar mixture of its compositions, the decreased value (ΔI_1) of integrated fluorescence intensities from corrected fluorescence spectra (whole emission bands at 605 and 657 nm) form the ZnTPP moiety (donor) was obtained, and the percentage of transferred energy from the donor is $P_d = \Delta I_1 / I_1$, where the I_1 is integrated fluorescence intensities of un-conjugated ZnTPP. For the acceptor, the percentage of accepted energy is $P_a = \Delta I_2 / \Delta I_1 \Phi_F$, where ΔI_2 is the increased value of integrated fluorescence intensities (the emission band of 680 nm) form H₂Pc part in H₂Pc-(ZnTPP)₂ compared with un-conjugated H₂Pc and Φ_F is the fluorescence quantum yield of the acceptor. Combining these two factors, the efficiency (E) of energy transfer from the donor to the acceptor can be given by Eq. (1):

$$E = P_{\rm d} P_{\rm a} = \frac{\Delta I_2}{I_1 \Phi_{\rm F}} \tag{1}$$

The $\Phi_{\rm F}$ of H₂Pc is 0.77, as reported [21]. Thus, the efficiency of energy transfer in H₂Pc–(ZnTPP)₂ was calculated to be about 30% from the data in Fig. 1b and using Eq. (1).

When H₂Pc was conjugated to eight ZnTPPs in H₂Pc–(ZnTPP)₈, the molecule is more symmetrical than H₂Pc–(ZnTPP)₂, this may result in balance the electronic interaction between the H₂Pc and ZnTPP, resulting in a decreased wavelength shift of both the absorption and emission bands (Fig. 2). As seen in Fig. 2b, the energy transfer was more pronounced in H₂Pc–(ZnTPP)₈, and the efficiency (*E*) of energy transfer can reach 90%.

Fig. 3 shows the absorption and fluorescence spectra of $ZnPc-(ZnTPP)_2$ and the equimolar mixture of the ZnPc and ZnTPP. Here the effect of the conjugation of ZnPc and $(ZnTPP)_2$ on spectra was much weaker as compared with that of H₂Pc-(ZnTPP)₂ (Fig. 1). Only a slight broadening of Q absorption band of ZnPc moiety in ZnPc-(ZnTPP)2 was found, and three emission bands of ZnPc-(ZnTPP)2 all appeared in fluorescence spectra (Fig. 3b) in which the first two bands (607 and 657 nm) are attributed to the ZnTPP moiety and the other (682 nm) is typical ZnPc emission, with no obvious wavelength shift compared with that of the equimolar mixture of the ZnPc and ZnTPP. The energy transfer efficiency in ZnPc-(ZnTPP)₂ was calculated to be about 60% by using the data in Fig. 3b and the $\Phi_{\rm F}$ of 0.3 for ZnPc [22]. When eight ZnTPPs are conjugated to ZnPc (ZnPc-(ZnTPP)₈,), the energy transfer efficiency also increased to 90% (Fig. 4b). However the aggregation occurred in ZnPc-(ZnTPP)₈, as shown in Fig. 4a, with a typical Pc aggregation peak of 640 nm. The aggregation peak was evident even when the ZnPc-(ZnTPP)₈, sample was diluted to a very low concentration (OD = 0.01 at 680 nm), demonstrating that the presence of a large number of ZnTPPs conjugated to ZnPc made the ZnPc-(ZnTPP)8, to become very aggregative. Considering the aggregation effect, the ZnPc-(ZnTPP)₈, is not a good compound for the model of energy transfer.

Summarizing the discussion above on the four porphyrin-phthalocyanine conjugates, FRET seems a good way



Fig. 2. The spectra of $H_2Pc-(ZnTPP)_8$ and an equimolar mixture of its components in DMSO. (a) UV–vis absorption spectra; (b) fluorescence spectra by selective excitation of the porphyrin part at 429 nm. The dotted line is for an equimolar H_2Pc .



Fig. 3. The spectra of $ZnPc-(ZnTPP)_2$ and an equimolar mixture of its components in DMSO. (a) UV–vis absorption spectra; (b) fluorescence spectra by selective excitation of the porphyrin part at 429 nm. The dotted line is for an equimolar ZnPc.



Fig. 4. The spectra of $ZnPc-(ZnTPP)_8$ and an equimolar mixture of its components in DMSO. (a) UV–vis absorption spectra; (b) fluorescence spectra by selective excitation of the porphyrin part at 429 nm. The dotted line (in b) is for an equimolar ZnPc and the curve is enlarged in inset.

to study the energy transfer from porphyrin to phthalocyanine and evaluating the energy transfer efficiency quantitatively. The energy transfer efficiency is certainly correlated with the physical properties of the donor and the acceptor. The degree of overlap of energy levels of the donor and acceptor plays an important role on energy transfer. Fig. 5 shows the emission spectrum of ZnTPP (donor) and the absorption spectra of H_2Pc or ZnPc (acceptors). The Q band absorption of H_2Pc overlaps well with the second emission band of ZnTPP, which can



Fig. 5. Spectral overlapping of the donor and acceptors. The emission spectrum of ZnTPP (donor, solid line) excited at 429 nm; the absorption spectra of two acceptors of ZnPc (broken line) and H_2Pc (dotted line).

explain the good energy transfer efficiency in H₂Pc–(ZnTPP)₂ and H₂Pc–(ZnTPP)₈. While in the case of ZnPc–(ZnTPP)₂, in addition to a good overlap of the main absorption (the Q band) with the second emission band, the absorption peak at 607 nm of ZnPc also overlaps with the first emission band of ZnTPP, providing the reason of higher efficiency *E* (60%) in ZnPc–(ZnTPP)₂ as compared with that (30%) in H₂Pc–(ZnTPP)₂.

Another effect involved in the energy transfer, which we term, the conjugating effect, could be found from above results. When energy levels of both the donor and the acceptor are not disturbed by the conjugation (e.g. the absorption bands do not shift after the conjugation), as is the case in $ZnPc-(ZnTPP)_2$ and H₂Pc-(ZnTPP)₈, efficient energy transfer would be fulfilled. In contrast in the case of $H_2Pc-(ZnTPP)_2$, the absorption spectrum was seriously changed by the conjugation (Fig. 1a), resulting in a low efficiency of energy transfer. This conjugating effect is consistent with previous literature data [8,23,24]. The energy transfer occurred in the porphyrin-phthalocyanine conjugate linked with phenyle-thynyl, where the absorption spectrum of the conjugate was just the sum of two components [23,24]. While for the ethynyl-linked heterodyad of porphyrin-phthalocyanine conjugate, its absorption spectrum differed considerably from the sum of two components and no energy transfer was found [8]. So, to obtain the efficient energy transfer the conjugating effect should be properly satisfied, e.g. the absorption spectrum is not considerably altered by the conjugation.

4. Conclusions

We found that H₂Pc–ZnTPP and ZnPc–ZnTPP are suitable photochemical models to demonstrate the energy transfer according to the FRET principles. The conjugating effect, measured by the absorption spectrum comparison between the conjugate and its components, also plays an important role in energy transfer. In addition, the ZnPc–(ZnTPP)₂ and H₂Pc–(ZnTPP)₈ were found to be excellent compounds to efficiently carry out the energy transfer from porphyrin moiety to phthalocyanine part, which expands the absorption region to obtain the fluorescence emission from phthalocyanine moiety and could broaden the applications of phthalocyanines in several different fields such as for light harvesting materials and photodynamic therapy.

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