Synthesis and photochemical characterization of a zinc phthalocyanine–zinc porphyrin heterotrimer and heterononamer

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The synthesis of two phthalocyanine–porphyrin covalently linked heteromolecules are described. Intramolecular energy transfer is investigated and quantified in terms of the quantum yield of energy transfer and found to be highly effective in both molecules. The photophysical properties of both molecules are modified greatly by the presence of the porphyrin moieties on the phthalocyanine core.

Introduction

Phthalocyanine complexes have received much attention in the literature for various photochemical applications such as infrared sensors,1 nonlinear optics,2 photodynamic therapy,3 optical recording⁴ and as xerographic photoreceptors.⁵ The phthalocyanines are generally stable, rigid compounds with varying properties dependent upon their central metals, peripheral substituents and axial substituents. Optical applications abound due to the uniquely intense red absorbing band referred to as the Q-band in these compounds. Porphyrins are naturally occurring entities and are structurally similar to phthalocyanines but are generally less rigid and less stable (chemically as well as photochemically) than phthalocyanines. Porphyrins generally have an intense B-band (~420 nm for zinc tetraphenylporphyrin) and less intense Q-band. Many porphyrins have triplet lifetimes above 1 ms and high quantum yields of triplet formation which make them interesting molecules for study in photocatalytic applications. The covalent linking of phthalocyanines to porphyrins was first achieved by Gaspard et al.⁶ A dimer of these compounds where one porphyrin unit was linked to a phthalocyanine unit were shown to exhibit interesting charge transfer properties by Tran-Thi et al.7 Metal-free8 and zinc⁸ containing covalently linked phthalocyanine-porphyrin dimers have also been reported. Ethynyl linked phthalocyanineporphyrin dimers have also been synthesised by two groups.9,10

Metal-free, zinc and magnesium containing phthalocyanine– porphyrin nonamers as a mixture of isomers due to tetrasubstitution of porphyrin dimers have also been prepared.¹¹ We have recently reported on a pentamer consisting of one phthalocyanine molecule and four porphyrin molecules containing zinc¹² or cobalt¹³ central metals. A mutual quenching of excited singlet states of both the zinc phthalocyanine (ZnPc) and zinc tetraphenylporphyrin (ZnTPP) components were observed for the zinc pentamer.¹² Intramolecular electron and energy transfer process efficiencies in covalently linked chromophores are of interest as model systems for the reaction centre of photosynthesis. In this paper we report on the synthesis and photophysical properties of a covalently linked trimer (one phthalocyanine and two porphyrins) as well as a covalently linked nonamer (one phthalocyanine and eight porphyrins).

Experimental

Materials

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4,5-Dichlorophthalonitrile¹⁴ and 5-hydroxy-10,15,20-triphenylporphyrin¹⁵ were synthesized as in the literature. 4-Hydroxybenzaldehyde, benzaldehyde, pyrrole, 1,8-diazabicyclo[5,4,0]unde-7-ene (DBU), sodium methoxide, potassium carbonate, to use. Silica gel 60 (0.04–0.063 mm) for chromatography was purchased from Merck. Equipment UV-Vis spectra were recorded on a Varian 500 UV-Vis/NIR

hydrous zinc acetate, lithium and propan-1-ol, were purchased

from Sigma-Aldrich and used without further purification.

Dimethyl sulfoxide (DMSO) was dried over alumina before

use. All other solvents were dried by standard methods prior

spectrophotometer. IR (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 excitation and emission spectra were recorded with a Varian Eclipse spectrofluorimeter. Flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (pyridine 1 dye in methanol). Single pulse energy was 2 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360). MALDI-TOF mass spectra of the nonamer ZnPc-(ZnTPP)₈ was obtained at Tohoku University using a Perseptive Biosystem MALDI-TOF Mass Voyager DE-SI2 spectrometer with dithranol as matrix. The MALDI-TOF mass spectra of the rest of the complexes were determined using Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation and Processing Delayed Extraction Technology at the University of Cape Town in South Africa.

Methods

Fluorescence quantum yields were determined in DMSO by the comparative method^{16,17} using either zinc phthalocyanine (ZnPc, $\Phi_{\rm F} = 0.23^7$) or zinc tetraphenylporphyrin (ZnTPP, $\Phi_{\rm F} =$ 0.039⁷) as references. Fluorescence lifetimes were determined from the absorbance and emission spectra using the Strickler– Berg equation as described previously.¹⁸ Triplet lifetimes ($\tau_{\rm T}$) were determined by exponential fitting of the laser flash photolysis experimental data using OriginPro 7.5 software. Triplet quantum yields ($\Phi_{\rm T}$) were determined by a comparative method^{19,20} (singlet depletion) using zinc phthalocyanine (0.65⁷) as standard with a laser flash photolysis setup described above. Deaerated solutions were introduced into a 10 mm × 10 mm spectrophotometric cell and irradiated at the relevant Q-band maxima. The relevant equations will be given at the sections where they are required.

Synthesis

Preparation of 4,5-bis[5-(4-phenoxy)-10,15,20-triphenyl porphyrin]-1,2-dicarbonitrile ligand P(CNOTPP)₂. A mixture of 5-hydroxy-10,15,20-triphenylporphyrin (P-OH)PP, 126.2 mg, 0.2 mmol), 4,5-dichlorophthalonitrile (13.2 mg, 0.066 mmol) and K₂CO₃ (138 mg, 1 mmol) in dry DMSO (20 ml) was heated at 90 °C for 6 h with stirring under a nitrogen atmosphere. The reaction progress was monitored by thin layer chromatography (TLC). After cooling to room temperature, the purple reaction mixture was poured into 100 ml dichloromethane and washed three times with 100 ml water. The dichloromethane was removed by evaporation. Column chromatography on silica gel with dichloromethane as eluent gave two bands; the first band was found to be the product. The second band was the starting material. Evaporation of the dichloromethane afforded 83.4 mg (91%) of purple solid. The purple crude product was recrystallized from dichloromethane with absolute methanol. UV-Vis [CHCl₃, λ_{max}/nm (log ε)]: 420 (5.72), 515 (4.45), 551 (4.14), 591 (3.99), 646 (3.91); ¹H NMR (400 MHz, CDCl₃), δ 8.84–8.89 (m, 16H, pyrrole H), 8.15–8.39 (m, 16H, phenyl H), 7.84 (s, 2H, phthalonitrile H), 7.59-7.80 (m, 22H, phenyl H), -2.73 (s, 4H, N-H). IR(KBr) CN 2230, COC 1210 cm⁻¹; MALDI-TOF-MS m/z: Calc. = 1385.61; Found = 1387.61 $[M + 2]^+$.

Preparation of 4,5-bis[5-(4-phenoxy)-10,15,20-triphenyl porphyrin]-1,2-dicarbonitrile zinc(II) P(ZnCNOTPP)₂. A mixture of P(CNOTPP)₂ (138.6 mg, 0.1 mmol) and hydrous zinc acetate (108 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 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 as eluent gave one band. Removal of dichloromethane by evaporation afforded 144.5 mg (97%) of a vivid red solid. The crude product was recrystallized from dichloromethane with absolute methanol. UV-Vis [CHCl₃, λ_{max}/nm (log ε)]: 428 (5.97), 522 (3.81), 561 (4.62), 600 (4.30); ¹H NMR (400 MHz, CDCl₃), δ 8.94–9.00 (m, 16H, pyrrole H), 8.16–8.40 (m, 16H, phenyl H), 7.84 (s, 2H, phthalonitrile H), 7.59-7.81 (m, 22H, phenyl H); IR(KBr) CN 2232, COC 1206 cm⁻¹; MALDI-TOF-MS m/z: Calc. = 1513.18; Found = 1512.17 [M]⁺.

Preparation of 2,3-bis[5-(4-phenoxy)-10,15,20-triphenyl porphyrin zinc(II)] phthalocyanine zinc(II) (ZnPc-(ZnTPP)₂). Chloro[7,12,14,19-diimino-21,5-nitrilo-5H-tribenzo[c,h,m]-[1,16,1]triazacycloopentadecinato- $(2-)-N_{22},N^{23},N^{24}]$ boron (SubPc) was synthesized according to literature methods.²¹ SubPc (86.4 mg, 0.2 mmol) in DMSO (10 ml) was heated at 60 °C for 2 h with stirring under nitrogen. P(ZnCNOTPP)₂ (151.6 mg, 0.1 mmol), DBU (2 drops) and hydrous zinc acetate (43.2 mg, 0.2 mmol) were added to the solution. The mixture was heated to 120 °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 excess zinc acetate, acetic acid and DMF. 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 (blue bands) was eluted using dichloromethane with 5% methanol. The biproduct ZnPc remained on the top of column. Removal of dichloromethane and methanol by evaporation afforded 12.7 mg (6%) of a blue solid. The blue product $ZnPc-(ZnTPP)_2$ was recrystallized from dichloromethane with methanol. UV-Vis [DMSO, λ_{max}/nm (log ε)]: 350 (4.72), 428 (5.73), 561 (4.32), 607 (4.45), 675 (5.13); ¹H NMR (400 MHz, DMSO-d₆), δ 9.42 (s, 2H, phthalocyanine H), 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) COC 1202 cm⁻¹; MALDI-TOF-MS m/z: Calc. = 1966.98; Found = 1962.93 [M - 4]⁺.

Preparation of 2,3,9,10,16,17,23,24-octakis[5-(4-phenoxy)-10, 15,20-triphenylporphyrin zinc(II)] phthalocyanine zinc(II) (ZnPc-(ZnTPP)₈). A mixture of P(ZnCNOTPP)₂ (151.6 mg, 0.1 mmol) and sodium methoxide (5 mg) was added to distilled methanol (10 ml). Anhydrous ammonia gas was bubbled through the strirred suspension for 1 hour. 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 hydrous zinc acetate (43.2 mg, 0.2 mmol), DBU (2 drops) and propan-1-ol (10 ml) were added. The mixture was heated at 95 °C for 2 h with stirring under a nitrogen atmosphere. The reaction procedure was monitored by UV-Vis spectroscopy. After cooling to room temperature, the purple solution was poured into 20 ml dichloromethane, and 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 with 2% methanol. Removal of dichloromethane and methanol by evaporation afforded 21.7 mg (14%) of a dark-purple solid. The dark-purple product was recrystallized from dichloromethane with hexane. UV-Vis [DMSO, λ_{max} /nm (log ε)]: 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) COC 1210 cm⁻¹; MALDI-TOF-MS m/z: Calc. = 6114.79; Found = 6114.93 [M]⁺.

Results and discussion

Synthesis

The synthetic route to the compounds presented is shown in Schemes 1 and 2. The compounds are abbreviated as indicated in the Experimental section. The synthesis of $P(CNOTPP)_2$ using a standard chloride group displacement reaction was completed sooner than expected with very high yield (91%). Most of the porphyrin reagent was converted to product, the lost yield is attributed to the purification procedure. The high yield may be due to the increased nucleophilic nature of the attacking oxygen on the porphyrin species. This compound was characterised by IR (CN stretch at 2230 cm⁻¹ and aromatic ether at 1210 cm⁻¹), UV-Vis spectroscopy (porphyrin B-band at 420 nm, and a split Q-band at 591 nm and 646 nm) as well as ¹H NMR. The synthesis of P(ZnCNOTPP)₂ using a general porphyrin metallation reaction with hydrous zinc acetate in DMF gave a satisfactory yield (96%). This compound was characterized by IR (CN stretch at 2232 cm⁻¹ and aromatic ether at 1206 cm⁻¹), UV-Vis spectroscopy (porphyrin B-band at 428 nm, and a split Q-band at 561 nm and 600 nm) as well as ¹H NMR sectroscopy. The mass spectrum revealed a molecular ion peak $[M]^+$ at 1512.18 m/z which is in good agreement with the calculated molecular weight of 1513.18 g mol⁻¹. An attempt was made to synthesise the cobalt product P(CoCNOTPP)₂ using the P(CNOTPP)₂ ligand and hydrous cobalt acetate in DMF. This compound was found to be unstable upon purification as it slowly decomposed to the starting materials. This is probably due to the cobalt porphyrin being acid-sensitive as well as oxygen sensitive. The synthesis of the porphyrin-phthalocyanine trimer ZnPc-(ZnTPP)₂ was done from $P(ZnCNOTPP)_2$ 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. An attempt was also made to synthesise the trimer ZnPc-(ZnTPP)₂ using the statistical condensation method with P(ZnCNOTPP)₂ and phthalonitrile, but the yield was found to be far lower than with the SubPc method. The ¹H NMR



Scheme 1 Synthesis of the trimer $ZnPc-(ZnTPP)_2$.

spectrum of this compound displayed two sets of signals of the non-peripheral protons on the phthalocyanine at 9.42 ppm (2H as a singlet) and 9.05 ppm (6H as a doublet). This is typical of a disubstituted phthalocyanine as the two protons at 9.42 ppm are present on the ring that contains the two porphyrin moeities and the other 6H are present on the unsubstituted benzene rings where they have one neighbouring proton that splits them into a doublet. 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⁻¹. The synthesis of the porphyrin-phthalocyanine nonamer ZnPc-(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 14% yield of the target phthalocyanine product. The ¹H NMR spectrum of this compound (Fig. 1) displayed four broad peaks due to the extensive overlapping of the numerous protons in this molecule. The integration of these peaks, however, revealed that all protons could be accounted for. The broad peak at 8.87 ppm integrated for 72 protons and this was due to the 64 pyrrole protons on the porphyrin ring as well as the 8 non-peripheral phthalocyanine protons. The broad peaks at 8.21 ppm and 7.75 ppm were due to the phenyl protons on the porphyrin rings and integrated for 120 protons. Finally, the broad peak at 7.15 ppm integrated for 32 protons and this was due to the phenyl protons on the phenoxy groups that connect the porphyrin moeities to the phthalocyanine core. The mass spectrum of this compound displayed a molecular ion peak at 6114.93 m/z, Fig. 2. which was in agreement with the calculated value of 6114.93 g mol⁻¹. It has been shown by Marcuccio²² *et al.* that large phthalocyanine type structures do not always give satisfactory elemental analysis.

Absorption properties

The UV-Vis spectrum confirms the formation of a phthalocyanine ring by the appearance of a phthalocyanine Q-band. Fig. 3 shows the electronic absorption spectra of $ZnPc-(ZnTPP)_2$, $ZnPc-(ZnTPP)_8$, ZnTPP and ZnPc in DMSO. The UV-Vis spectrum of a metallophthalocyanine-metalloporphyrin conjugate should represent the spectrum of each of the components ZnPc and ZnTPP. The UV-Vis spectrum of $ZnPc-(ZnTPP)_2$ and $ZnPc-(ZnTPP)_8$ (Fig. 3) does indeed show a combination of the respective spectra of ZnTPP and ZnPc with a slight bathochromic (red) shift for the Q-bands of the ZnPc moieties (from 670 nm to 675 nm for ZnPc in $ZnPc-(ZnTPP)_2$ and 670 nm to 681 nm for ZnPc in $ZnPc-(ZnTPP)_8$). The shifting



Scheme 2 Synthesis of the nonamer ZnPc-(ZnTPP)₈.



Fig. 1 1 H NMR (aromatic region on top and complete spectrum below) of ZnPc-(ZnTPP) $_{8}$.

of the ZnPc Q-bands in ZnPc– $(ZnTPP)_2$ and ZnPc– $(ZnTPP)_8$ to longer wavelengths compared to ZnPc alone suggests that ZnTPP peripheral substituents exert electron-donating effects on the ZnPc, since electron-donating peripheral substituents on the MPc complexes gives rise to red shifts in the Q absorption wavelengths.²³ The intensity of the B-band relative to the Qband is lower for ZnTPP compared to the trimer and nonamer (Fig. 3). The position of the porphyrin B-bands in terms of wavelength did not shift at all. The fact that the B-band of the ZnTPP components did not shift excludes the possibility of a charge transfer interaction in the ground states of these two molecules. A decrease in the B-band intensity is due to conformational changes of the porphyrin moeity upon bonding to the phthalocyanine,⁷ hence the observation of an intense Bband relative to Q-band for the porphyrin is an indication that



Fig. 2 Mass spectrum of ZnPc–(ZnTPP)₈.

there are no conformation changes. The molecules synthesised obey Beers law up to 1×10^{-5} M for ZnPc–(ZnTPP)₂ and 2×10^{-5} M for ZnPc–(ZnTPP)₈ in DMSO. The deviation from linearity was observed at the phthalocyanine Q-band, at high concentrations, thus indicating that aggregation occurs through the phthalocyanine moeities.

Fluorescence properties

The fluorescence spectra of both the ZnPc–(ZnTPP)₂ (Fig. 4) and ZnPc–(ZnTPP)₈ (Fig. 5) showed extensive energy transfer between the porphyrin and phthalocyanine moeities. For both these compounds, irradiation of the porphyrin B-band vibration at 403 nm led to emission at the porphyrin B- and Q-bands as well as the Q-band of the phthalocyanine (678 nm) (Fig. 4). This excitation leads to the formation of a π – π * singlet state of the porphyrin which results in the fluorescence from the porphyrin molecule. From the fact that emission is observed



Fig. 3 The UV-Vis spectrum of ZnTPP $(2.7 \times 10^{-6} \text{ M})$, ZnPc $(4.9 \times 10^{-6} \text{ M})$, ZnPc–ZnTPP₂ $(3.9 \times 10^{-6} \text{ M})$ and ZnPc–ZnTPP₈ $(1.7 \times 10^{-6} \text{ M})$ in DMSO. Insert: expansion of the Q-band region of the ZnTPP.



Fig. 4 Normalized (Q-band) electronic absorption, excitation and fluorescence spectra of 1.8×10^{-6} M ZnPc–(ZnTPP)₂ in DMSO. Insert: expansion of the Q-band region.

also from the phthalocyanine molecule suggests that the excited porphyrin molecule transfers energy to the phthalocyanine molecule. These two processes are in competition with the internal conversion processes. In both cases the porphyrin Bband had a far lower fluorescence intensity than expected, due to charge transfer to the Pc molecule. This effect was amplified in $ZnPc-(ZnTPP)_{8}$ (3× more than in $ZnPc-(ZnTPP)_{2}$) as seen in Fig. 4 and 5 for the former compound, thus indicating a more efficient intramolecular energy transfer process taking place in this molecule. The excitation spectra (emission monitored at 720 nm) (Fig. 4 and 5) for both complexes displayed two interesting features. The first was the relatively low ratio of the intensity of the porphyrin B-band to the phthalocyanine Q-band in the excitation spectra of both complexes. This phenomenon is indicative of the extensive energy transfer taking place. Secondly, the excitation spectra was slightly different from the absorption spectra in terms of Q-band absorbtion wavelength for both compounds, suggesting that changes in the nature of the



Fig. 5 Normalized (Q-band) electronic absorption, excitation and fluorescence spectra of 2.0×10^{-6} M ZnPc–(ZnTPP)₈ in DMSO. Insert: expansion of the Q-band region.

molecules follow upon excitation. Fluorescence quantum yields were determined using the following eqn (1):

$$\boldsymbol{\Phi}_{\mathrm{F}}^{x} = \boldsymbol{\Phi}_{\mathrm{F}}^{\mathrm{std}} \frac{F_{x} \cdot A_{\mathrm{std}} \cdot \eta^{2}(x)}{F_{\mathrm{std}} \cdot A_{x} \cdot \eta^{2}(\mathrm{std})}$$
(1)

Where $\Phi_{\rm E}^{\chi}$ and $\Phi_{\rm E}^{\rm std}$ are the fluorescence quantum yields of the sample and standard respectively; F_x and F_{std} the areas under the emission curves of the sample and standard respectively; A_x and A_{std} , the absorbances of the sample and standard at the excitation wavelength respectively (absorbance ranged between 0.04 and 0.05) and $\eta^2(x)$ and $\eta^2(\text{std})$ are the refractive indices of the solvents used for the sample and standard respectively. Both the sample and the standard were excited at the same relevant wavelength. The $\Phi_{\rm F}$ values obtained were the average of three independent experiments in DMSO. The fluorescence quantum yields (using the phthalocyanine emission for calculations) upon excitation at 603 nm (porphyrin Q-band) (Table 1) were found to decrease in the following order: single molecule ZnTPP $(0.039)^7$ > trimer ZnPc-(ZnTPP)₂ (0.009 ± 0.001) > nonamer $ZnPc-(ZnTPP)_8$ (0.005 ± 0.001). This decrease was expected as the steady-state emission spectra clearly showed energy transfer taking place from the porphyrin units to the phthalocyanine moeity. The fluorescence quantum yield ($\Phi_{\rm F}$) calculated for the zinc phthalocyanine moeity (excitation at 640 nm) in the heteromers had lower values compared to the ZnPc single molecule (0.14 for ZnPc-(ZnTPP)₂ and 0.06 for ZnPc-(ZnTPP)₈). This may result from fluorescence quenching due to the porphyrin rings on the periphery of the phthalocyanine by charge transfer.⁷ Fluorescence lifetimes were determined using the Strickler-Berg equation utilising the absorbance and fluorescence spectra of dilute solutions of ZnPc-(ZnTPP)2 and ZnPc-(ZnTPP)8. The Strickler-Berg equation has been shown to be accurate for nonaggregated phthalocyanines.14 The same trend observed for the fluorescence quantum yields was obtained for the fluorescence lifetimes as follows: single molecule $(2.7 \pm 0.3 \text{ ns}) > \text{ZnPc}$ - $(ZnTPP)_2$ (1.6 ± 0.3 ns) > ZnPc-(ZnTPP)₈ (1.2 ± 0.2 ns). To quantify the energy transfer process one may determine the energy transfer constant $(k_{\rm Et})$ and concurrently the energy transfer quantum yield ($\Phi_{\rm Et}$) from the fluorescence quantum

 Table 1
 Photophysical data of the single molecules and heteromers used in this study. Solvent = DMSO

Molecule	$\Phi_{\rm F}$ (Exciting $\lambda_{\rm max}$)	$\tau_{\rm F}/{ m ns}$	$arPsi_{ ext{T}}$	$\tau_{\rm T}/\mu s$	$k_{\rm Et}/(imes 10^9~{ m s}^{-1})$	$oldsymbol{\Phi}_{ ext{Et}}$
ZnPc	0.23 (640)	4.75ª	0.65	330	_	_
ZnTPP	0.039 (603)	2.7	0.83	1400		
$ZnPc-(ZnTPP)_2$	0.009 ± 0.001 (603)	1.6 ± 0.3	0.10 ± 0.02	260 ± 30	1.2 ± 0.1	0.77 ± 0.08
$ZnPc-(ZnTPP)_2$	0.14 ± 0.05 (640)		_			
$ZnPc-(ZnTPP)_{8}$	0.005 ± 0.001 (603)	1.2 ± 0.2	0.04 ± 0.01	170 ± 30	2.5 ± 0.2	0.95 ± 0.1
ZnPc-(ZnTPP)	0.06 ± 0.02 (640)					

" From ref. 20.

yields of the respective single molecules and heteromers as well as the fluorescence lifetime of the single molecule $(2.7 \text{ ns})^{24}$ from eqn (2) and (3), which have been derived before:⁷

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$$k_{\rm Et} = \frac{1}{\tau_{\rm S}} \left(\frac{\Phi_{\rm F}(\rm monomer)}{\Phi_{\rm F}(\rm heteromer)} - 1 \right)$$
(2)

$$\Phi_{\rm Et} = \frac{k_{\rm Et}}{k_{\rm Et} + \frac{1}{r_{\rm S}}} \tag{3}$$

Where $\Phi_{\rm F}$ (single molecule) is the fluorescence quantum yield of the single molecule (ZnPc of ZnTPP), $\tau_{\rm S}$ is the lifetime of the excited singlet state. Using the fluorescence data above, efficiency of the energy transfer process was calculated using eqn (2) and (3) and $k_{\rm Et}$ of 1.2 (± 0.1) × 10⁹ s⁻¹ for ZnPc–(ZnTPP)₂ was observed. This value increases for ZnPc–(ZnTPP)₈ to 2.5 (± 0.2) × 10⁹ s⁻¹ indicating an increase by a factor of two, on going from the trimer to the nonamer. These values were then used to calculate the quantum yield of energy transfer ($\Phi_{\rm Et}$) using eqn (3) and found to be 0.77 (± 0.08) for ZnPc–(ZnTPP)₂ and near unity (0.95 ± 0.1) for ZnPc–(ZnTPP)₈, showing that the nonamer experiences more quenching than the trimer.

Triplet properties

The influence of the porphyrin rings upon the triplet properties of the zinc phthalocyanine moeity was studied by laser flash photolysis. Excitation for these studies was performed at 640 nm (the Pc absorption) only due to intrumental limitations. Unsubstituted zinc phthalocyanine has a triplet quantum yield of 0.657 in DMSO and a triplet lifetime of 330 µs7 in DMSO. The triplet lifetime of the studied compounds was determined by laser flash photolysis and the analysis of the decays was done by fitting a single exponential function to the decays. It was found that for both studied compounds the triplet lifetime decreased somewhat, compared to the respective single molecules, and this decrease was dependant on the number of porphyrin rings present on the molecules. The ZnPc-(ZnTPP)2 had a triplet lifetime of 260 (\pm 30) µs and ZnPc–(ZnTPP)₈ 170 (\pm 30) µs. Triplet quantum yields for the zinc phthalocyanine moieties were determined by the following eqn (4):

$$\Phi_{\rm T}^{\rm sample} = \Phi_{\rm T}^{\rm std} \frac{\Delta A_{\rm S}^{\rm sample} \varepsilon_{\rm S}^{\rm std}}{\Delta A_{\rm S}^{\rm std} \varepsilon_{\rm S}^{\rm sample}}$$
(4)

Where $\Delta A_{\rm s}^{\rm sample}$ and $\Delta A_{\rm s}^{\rm sid}$ are the changes in the singlet state absorbance of the sample and ZnPc, respectively. $\varepsilon_{\rm s}^{\rm sample}$ and $\varepsilon_{\rm s}^{\rm sid}$ are the singlet state extinction coefficients for the sample and ZnPc, respectively; $\Phi_{\rm T}^{\rm sid}$ is the triplet quantum yield for ZnPc.

As with the lifetimes, the triplet quantum yields (due to the ZnPc component) decreased with an increase in porphyrin rings attached peripherally to the zinc phthalocyanine unit. These were found to be 0.10 (\pm 0.02) for ZnPc–(ZnTPP)₂ and 0.04 (\pm 0.01) for the ZnPc–(ZnTPP)₈. All these data confirm that effective energy transfer takes place and that the porphyrin units in turn act as quenchers of the photophysical processes taking place in these molecules.

Conclusion

Phthalocyanine–porphyrin conjugates that are linked through covalent linkers are effective light harvesters. The porphyrins are especially efficient at transferring energy to phthalocyanines upon excitation at their B- or Q-bands. The zinc phthalocyanine used in this study was also a good acceptor of this energy and its photophysical properties were modified greatly by the presence of the porphyrins on its periphery. The nonameric molecule, $ZnPc-(ZnTPP)_8$, which had eight porphyrins linked to the phthalocyanine had an energy transfer quantum yield of unity which is quite remarkable.

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