# PAPER

Cite this: New J. Chem., 2013, 37, 1746

Received (in Montpellier, France) 9th January 2013, Accepted 14th March 2013

DOI: 10.1039/c3nj00036b

www.rsc.org/njc

# Preparation and photophysical properties of a tetraethylene glycol-linked phthalocyanine-porphyrin dyad and triad

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Treatment of 1,4-bis(tetraethylene glycol)-substituted zinc(II) phthalocyanine with *p*-toluenesulfonyl chloride and triethylamine followed by 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin and K<sub>2</sub>CO<sub>3</sub> resulted in the formation of both a covalently linked phthalocyanine–porphyrin dyad and triad. The photophysical properties of these hetero-arrays were studied in detail using steady-state and time-resolved spectroscopic methods. Upon excitation at the porphyrin moiety, both compounds exhibited predominantly highly efficient excitation energy transfer from the excited porphyrin to the phthalocyanine core. The rate of energy transfer ( $2.4 \times 10^{10} \text{ s}^{-1}$ ) was more than 20-fold faster than the rate of electron transfer ( $1.1 \times 10^9 \text{ s}^{-1}$ ). When the phthalocyanine core of the dyad and triad was excited either directly or *via* excitation energy transfer, its singlet excited state underwent charge transfer leading to reduction in the fluorescence quantum yield and fluorescence lifetime. The rate of charge transfer for the triad ( $2.8 \times 10^8 \text{ s}^{-1}$ ) was about two-fold higher than that for the dyad ( $1.5 \times 10^8 \text{ s}^{-1}$ ) due to the presence of an additional porphyrin moiety in the triad.

# Introduction

Photoinduced energy and electron transfer are the key processes in natural photosynthesis, in which sunlight is initially absorbed by ensembles of light-harvesting chromophores and then efficiently delivered to the reaction centre where the captured energy is converted into chemical potential energy.<sup>1</sup> There has been considerable interest in the development of bioinspired molecular systems that can undergo rapid and directional energy and electron transfer processes.<sup>2,3</sup> These properties are crucial for applications in artificial photosynthesis,<sup>4</sup> photovoltaics<sup>5</sup> and molecular electronics.6 Among the various classes of chromophores being employed as the building blocks, porphyrins (Pors)<sup>2,4b,7</sup> and phthalocyanines (Pcs)<sup>4b,8</sup> are of particular interest owing to their high stability and intriguing electronic and photophysical properties. Pors are naturally occurring pigments showing a strong B band at ca. 400 nm and a number of weaker Q bands in the region of 500-600 nm, whereas Pcs are their non-natural analogues showing the B-band absorption at *ca.* 350 nm and Q-band absorption at *ca.* 670 nm. Thus a broad range of solar spectrum could be covered when these functional dyes are coupled together.<sup>9</sup> In addition, their photophysical and redox properties can also be altered readily by changing the metal centre and the peripheral substituents. These features enable the interactions between these chromophores to be systematically tuned.

A substantial number of covalent and non-covalent Por-Pc systems have been prepared and studied for their photophysical properties and intramolecular photoinduced processes.9,10 Recently, we have reported two Pc-Por triads in which two meso-tetraphenylporphyrin (MTPP;  $M = H_2$ , Zn) rings are linked to a silicon(*iv*) phthalocyanine core at the axial positions.<sup>11</sup> It has been found that the triads exhibit both photoinduced energy and electron transfer processes. The extent depends on the nature of the metal centre of the Por and the solvent. As an extension of this work, we report herein a related Pc-Por dyad and triad in which a zinc(II) phthalocyanine is covalently linked to one or two metal-free H2TPP via a tetraethylene glycol chain, including their synthesis and photophysical properties as studied by various steady-state and time-resolved spectroscopic methods. In designing artificial photosynthetic models, rigid linkers are commonly used to connect the building blocks with a view to facilitating their electronic interactions and

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having a better control of the separation and orientation of the interacting components.<sup>12</sup> However, flexible linkers also have their advantages as conformational changes of the corresponding systems can be induced readily, for example, by changing the solvents or addition of metal ions, thereby controlling the intramolecular photoinduced processes.<sup>13</sup> This kind of aliphatic linkers can also enhance the solubility of the multi-macrocyclic systems. As a result, a flexible tetraethylene glycol spacer was used in this study.

# **Results and discussion**

The synthetic route used to prepare both the Pc–Por dyad and triad is shown in Scheme 1. The 1,4-bis(tetraethylene glycol)-substituted zinc(II) phthalocyanine 1 was prepared readily by mixed cyclisation of the corresponding phthalonitriles.<sup>14</sup> Treatment of this compound with *p*-toluenesulfonyl chloride (TsCl) in the presence of triethylamine gave the ditosylate 2 in good yield. Further treatment of compound 2 with two equiv. of hydroxyporphyrin  $3^{15}$  and K<sub>2</sub>CO<sub>3</sub> in *N*,*N*-dimethylformamide (DMF) afforded a mixture of dyad 4 (15%) and triad 5 (45%), which was separated and purified readily by column chromatography. Both compounds were soluble in a wide range of organic solvents, including CHCl<sub>3</sub>, tetrahydrofuran (THF), DMF, toluene and pyridine, and were characterised by various spectroscopic methods.

Fig. 1 shows the UV-Vis spectra of these two compounds in DMF. For comparison, the absorption spectra of the two



**Fig. 1** UV-Vis spectra of the dyad **4**, triad **5**, H<sub>2</sub>TPP and Pc **1** in DMF. The absorbance of the Q-band absorption maximum of the Pc moiety in **1**, **4** and **5**, and the absorbance of the B-band absorption maximum of H<sub>2</sub>TPP were normalised as 1.

reference compounds  $H_2$ TPP and Pc 1 are also included. The B- and Q-band absorptions of these compounds are listed in Table 1. It can be seen that the absorption positions of the dyad 4 and triad 5 are essentially the same as those of the reference compounds, showing that the Pc and Por components in these hetero-arrays exhibit negligible ground-state interactions.

The steady-state fluorescence spectra of these compounds were also recorded in DMF and the data are also summarised in Table 1. Upon excitation at 510 nm, where only the Por moiety



Scheme 1 Preparation of Pc-Por dyad 4 and triad 5.

**Table 1** Electronic absorption and fluorescence maxima, fluorescence quantum yields ( $\Phi_{fl}$ ) and fluorescence lifetimes ( $\tau_{fl}$ ) of the dyad **4**, triad **5** and the two reference compounds H<sub>2</sub>TPP and Pc **1** in DMF

				${\Phi_{\mathrm{fl}}}^b$		$\tau_{\rm fl} (\rm ns)$	
Compound	B-band (nm)	Q-band <sup>a</sup> (nm)	$\lambda_{\mathrm{fl}}$ (nm)	Por-part excitation	Pc-part excitation	Por-part excitation	Pc-part excitation
H <sub>2</sub> TPP Pc 1 Dyad 4 Triad 5	419 339 346, 419 346, 419	650 689 689 689	653, 719 697 697 697	$0.11 \ - \ < 0.01^d \ 0.20 \pm 0.02^c \ < 0.01^d$	$- \\ 0.27 \pm 0.01^{c} \\ 0.20 \pm 0.02^{c} \\ 0.16 \pm 0.02^{c}$	$\begin{array}{c} 9.72\pm 0.02 \\ \\ (31\pm 5)\times 10^{-3} \\ 1.79\pm 0.01 \\ 9.3\pm 0.1 \\ (27\pm 3)\times 10^{-3} \end{array}$	$-2.50 \pm 0.01 \\ 1.79 \pm 0.01 \\ 1.46 \pm 0.01$
				$0.15\pm0.02^c$		$\begin{array}{c} 1.46 \pm 0.01 \\ 9.7 \pm 0.1 \end{array}$	

<sup>*a*</sup> The lowest-energy band. <sup>*b*</sup> Relative to H<sub>2</sub>TPP in DMF ( $\Phi_{fl} = 0.11$ ) for Por-part emission and SiPc(OEG)<sub>2</sub> in DMF ( $\Phi_{fl} = 0.50$ ) for Pc-part emission. <sup>*c*</sup> For Pc-part emission. <sup>*d*</sup> For Por-part emission.

absorbs, both dyad 4 and triad 5 gave an emission band at 697 nm due to the Pc core (Fig. 2a). The fluorescence quantum yield of the Por part was lower than 0.01, which was much lower than that of the reference H<sub>2</sub>TPP ( $\Phi_{\rm fl} = 0.11$ ).<sup>16</sup> It clearly indicates that an efficient excitation energy transfer (EET) occurs from the excited Por unit(s) to the Pc core both in the dyad and triad.

The fluorescence quantum yields of the Pc-part emission were found to be 0.20 and 0.15 for the dvad 4 and triad 5 respectively, with respect to bis(oligoethylene glycol)-substituted silicon(w) phthalocyanine [SiPc(OEG)<sub>2</sub>] (the average molecular weight of OEG = *ca.* 750) ( $\Phi_{\rm fl} = 0.50$ )<sup>11*a*</sup> when the Por-part was excited. Similar values were obtained when the Pc-part was directly excited (see Fig. 2b and Table 1). These values are lower compared with that of the reference Pc 1 ( $\Phi_{\rm fl}$  = 0.27). Based on these results, two conclusions can be drawn: (i) the probability of EET from the initially photoexcited Por unit to the Pc core in its ground state is close to unity for both dyad 4 and triad 5; (ii) for both of these hetero-arrays, there is an additional quenching process for the first excited singlet state of the Pc moiety, resulting in reduction of its fluorescence quantum yield compared with that of Pc 1. Moreover, the probability of this quenching process is higher for the triad than for the dyad. Since the energy transfer for  ${}^{1}Pc^{*} \rightarrow Por$  is energetically unfavourable (the energy of  $S_{0,0} \rightarrow S_{1,0}$  transition is 1.79 eV

for Pc 1 and 1.92 eV for  $H_2$ TPP according to their absorption and fluorescence emission positions), the quenching should be mainly due to a charge transfer (CT) process.

The photoinduced intramolecular processes of these compounds were also investigated by time-resolved fluorescence spectroscopy. The fluorescence decays of the reference compounds Pc 1 and H<sub>2</sub>TPP were found to be mono-exponential with decay times of 2.50 ns and 9.72 ns respectively (see Table 1). Upon excitation at the Por-part ( $\lambda_{ex}$  = 532 nm), both dyad 4 and triad 5 gave three resolved decay-associated fluorescence (DAF) spectra (see Fig. 3a and c). The one with the shortest lifetime (31 ps for 4 and 27 ps for 5) has a positive amplitude in the Por-part emission, but became negative at longer wavelengths where the Pc fluorescence is dominant. The negative amplitude indicated an increase in fluorescence intensity. Hence, this decay time could be attributed to the EET process from the excited Por to Pc in its ground state. The longest-life decay spectrum (9.3 ns for 4 and 9.7 ns for 5) with very low amplitude has a lifetime similar to that of H2TPP and could be assigned to the Por-part fluorescence decay. The remaining one showed the maximum at 697 nm which could be attributed to the decay of the first excited singlet state of the Pc moiety. It is worth noting that this decay follows the order: Pc 1 (2.50 ns) > dyad 4 (1.79 ns) > triad 5 (1.46 ns). Moreover, upon direct excitation of the Pc moiety at 620 nm, only one DAF spectrum was detected



Fig. 2 Steady-state fluorescence spectra of the dyad 4, triad 5 and H<sub>2</sub>TPP (or Pc 1) in DMF upon excitation at (a) the Por-part and (b) the Pc-part.

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for the dyad 4 and triad 5 with decay times of 1.79 and 1.46 ns respectively (see Fig. 3b and d and Table 1). The shortening of the Pc-part fluorescence lifetime is in good agreement with the reduction of the Pc-part fluorescence quantum yield observed in steady-state measurements.

As mentioned above, the observed results could be explained by two photoinduced processes, namely EET and CT. The Dexter exchange EET mechanism was excluded on the basis of the long separation between the Por and Pc moieties, which prevents the two  $\pi$ -electron clouds from overlapping. Thus, the Förster mechanism was assumed to be responsible for the EET from the initially photoexcited Por unit to the Pc core in its ground state. By using a well-established procedure,<sup>9c</sup> the Förster radius,  $R_0$ , for Por  $\rightarrow$  Pc fluorescence resonance energy transfer (FRET) was calculated to be 5.3 nm. The FRET rate,  $k_{\text{FRET}}$ , was estimated using the following equation:

$$k_{\text{FRET}} = \frac{1}{\tau_0} k^2 \left(\frac{R_0}{R}\right)^6,\tag{1}$$

where *R* is the centre-to-centre distance between the energy donor and acceptor,  $\tau_0$  is the donor fluorescence lifetime in the absence of acceptor and  $k^2$  is the orientation factor, which depends on the relative orientation of the dipole moments of the interacting molecules. According to molecular dynamic simulations using the HyperChem 5.0 programme package, the centre-to-centre distance between the donor and acceptor chromophores was estimated to be ca. 2 nm. Due to the high flexibility of the tetraethylene glycol chain between the Por and Pc chromophores in the dyad and triad, the value of the orientation factor was taken to be 2/3 as first approximation. This average value of the orientation factor is commonly used for solutions with uniform distribution of the transition dipole moments of the interacting chromophores. As a result, the rate of FRET was estimated to be  $2.4 \times 10^{10}$  s<sup>-1</sup>. It is worth noting that this value is very close to the Por first excited singlet state depopulation rate  $(3.2 \times 10^{10} \text{ s}^{-1})$  determined by taking the reciprocal value of the fluorescence lifetime of the Por moiety measured by time-resolved fluorescence spectroscopy (ca. 30 ps). FRET is therefore a dominant pathway of the Por-part fluorescence quenching.

To reveal whether the decrease in fluorescence quantum yield and fluorescence lifetime for the Pc unit in the dyad 4 and triad 5 is due to a photoinduced CT process, the free energy change of charge separation was calculated by using the Rehm-Weller equation:17

$$\Delta G_0^{D/A} = e \left( E_{1/2}^{\text{oxd}}(D/D^{\bullet+}) - E_{1/2}^{\text{red}}(A/A^{\bullet-}) \right) - E_{0,0}^{D/A} - \frac{e^2}{4\pi\epsilon_0\epsilon_s R} - \frac{e^2}{8\pi\epsilon_0} \left[ \frac{1}{r_{D^{\bullet+}}} + \frac{1}{r_{A^{\bullet-}}} \right] \left[ \frac{1}{\epsilon_{\text{ref}}} - \frac{1}{\epsilon_s} \right],$$
(2)

where  $\Delta G_0^{D/A}$  is the change in free energy of charge separation with selective excitation of the electron donor D (i.e. Pc) or the

 $\label{eq:table 2} \mbox{ Table 2} \mbox{ Electrochemical data of the dyad 4, triad 5, Pc 1 and H_2 TPP^a$ 

Compound	$E_{1/2}$ (oxd. 2)	$E_{1/2}$ (oxd. 1)	$E_{1/2}$ (red. 1)	$E_{1/2}$ (red. 2)
H <sub>2</sub> TPP Pc 1 Dyad 4 Triad 5	$1.10^b$ $1.05^b$ $1.04^b$	$1.05^b$ 0.56 0.57^b 0.57 <sup>b</sup>	$-0.95^b$ -1.10 -1.06 -1.05 <sup>b</sup>	-1.62 -1.77 <sup>b</sup>

<sup>*a*</sup> Recorded with [Bu<sub>4</sub>N][PF<sub>6</sub>] as an electrolyte in DMF (0.1 M) at ambient temperature. Potentials were obtained by cyclic voltammetry with a scan rate of 100 mV s<sup>-1</sup>, and are expressed as half-wave potentials ( $E_{1/2}$ ) in volts relative to the saturated calomel electrode (SCE) unless otherwise stated. <sup>*b*</sup> By differential pulse voltammetry.

electron acceptor A (*i.e.* Por),  $E_{1/2}$  is the half-wave reduction potential of the donor  $(D/D^{\bullet^+})$  or acceptor  $(A/A^{\bullet^-})$  couple in volts,  $E_{0,0}^{D/A}$  is the energy of  $S_{0,0} \rightarrow S_{1,0}$  transition of the donor or acceptor, *R* is the separation between the donor and acceptor moieties,  $\varepsilon_s$  and  $\varepsilon_{ref}$  are the dielectric constants of the solvents in which the spectroscopic and electrochemical measurements were performed, respectively,  $r_{D^{\bullet+}}$  and  $r_{A^{\bullet-}}$  are the effective radii of the radical cation and anion, respectively,  $\varepsilon_0$  is the vacuum permittivity and *e* is the charge of the transferred electron. Since the spectroscopic and electrochemical studies were performed in the same solvent (*i.e.* DMF), the last term in eqn (2) vanishes. Moreover, the contribution of  $\frac{e^2}{4\pi\varepsilon_0\varepsilon_8R}$  term is negligibly small due to the high polarity of the solvent used as well as the long separation between the donor and acceptor moieties (20, Å as estimated by using the HumerChem 5.0

well as the long separation between the donor and acceptor moieties (20 Å as estimated by using the HyperChem 5.0 programme package). The electrochemical potentials of the dyad **4** and triad **5**,

as well as the reference compounds Pc 1 and H<sub>2</sub>TPP, were studied by cyclic voltammetry and differential pulse voltammetry. The data are compiled in Table 2. According to these data,  $E_{1/2}^{\text{oxd}}(\text{D/D}^{\bullet+}) = 0.57 \text{ V}$  and  $E_{1/2}^{\text{red}}(\text{A/A}^{\bullet-}) = -1.06 \text{ V}$  for the dyad 4. By substituting the energies of  $S_{0,0} \rightarrow S_{1,0}$  transition  $E_{0,0}^{\text{D}}$  (1.79 eV) and  $E_{0,0}^{\text{A}}$  (for Por-part excitation) were determined to be -0.16and -0.29 eV respectively. The values for the triad 5 were virtually the same. Thus photoinduced CT is thermodynamically favourable both upon Pc- and Por-part excitation for both the hetero-arrays.

The rate of CT upon initial excitation of the Pc moiety of the dyad 4,  $(k_{\text{CT}}^{\text{Pc}})_{\text{dyad}}$ , was calculated by using the results of the DAF measurements as  $(k_{\text{CT}}^{\text{Pc}})_{\text{dyad}} = \frac{1}{\tau_{\text{Pc}}^{\text{dyad}}} - \frac{1}{\tau_{\text{ZnPc}}^{0}} = 1.5 \times 10^8 \text{ s}^{-1}$ ,

where  $\tau_{Pc}^{dyad}$  and  $\tau_{ZnPc}^{0}$  are the fluorescence lifetimes of the Pc-part fluorescence of the dyad (1.79 ns) and of the reference Pc **1** (2.5 ns) respectively. The corresponding value for the triad **5**,  $(k_{CT}^{Pc})_{triad}$ , was found to be  $2.8 \times 10^8 \text{ s}^{-1}$ . Since there is one additional Por unit in the triad **5**, it is expected that  $(k_{CT}^{Pc})_{triad}$  should be approximately two-fold faster than  $(k_{CT}^{Pc})_{dyad}$ . Hence the values obtained are in good agreement.

Estimation of the electron transfer (ET) rate upon excitation of the Por moiety,  $k_{\text{ET}}^{\text{Por}}$ , is more complicated because this process competes with the FRET. Nevertheless, the following indirect approach was used and the ratio between  $k_{\rm ET}^{\rm Por}$  and  $k_{\rm CT}^{\rm Pc}$  could be calculated as follows:<sup>11a</sup>

$$\frac{k_{\rm ET}^{\rm Por}}{k_{\rm CT}^{\rm Pc}} = \exp\left[\frac{\left(\Delta G_0^{\rm D} - \Delta G_0^{\rm A}\right)\left(\Delta G_0^{\rm D} + \Delta G_0^{\rm A} + 2\lambda\right)}{4k_{\rm B}T\lambda}\right],\tag{3}$$

where  $\lambda = \lambda_{I} + \lambda_{S}$  is the total nuclear reorganisation energy which can formally be divided into an intramolecular part,  $\lambda_{I}$ , and a contribution from inertial solvent reorganisation,  $\lambda_{S}$ , which is given by eqn (4) according to the classical treatment of Marcus:<sup>18</sup>

$$\lambda_{\rm S} = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{n^2} - \frac{1}{\epsilon_{\rm s}} \right) \left( \frac{1}{2r_{\rm A^{\bullet^-}}} + \frac{1}{2r_{\rm D^{\bullet^+}}} - \frac{1}{R} \right) \tag{4}$$

where *n* is the refractive index of the solvent used. By using the following parameters:  $r_{A^{\bullet-}} = 4.3$  Å,  $r_{D^{\bullet+}} = 4.6$  Å, R = 20 Å,  $\varepsilon_s = 37$ , n = 1.43 and  $\lambda_I = 0.3$  eV,<sup>19</sup> the ratio  $\frac{k_{ET}^{Por}}{k_{CT}^{Pc}}$  was calculated to be 8.9, resulting in  $k_{ET}^{Por} = 1.1 \times 10^9 \text{ s}^{-1}$ . This value is significantly lower compared to the above estimated rate of FRET ( $2.4 \times 10^{10} \text{ s}^{-1}$ ). This further supports that FRET is a dominant process in depopulation of the first excited singlet state of the Por moiety for both dyad 4 and triad 5.

### Conclusion

In summary, we have prepared a novel Pc–Por dyad and triad and studied in detail their photophysical properties. Upon Por-part excitation, both compounds exhibit competitive photoinduced excitation energy and electron transfer processes. The probability of FRET was found to be more than one order of magnitude higher than that of electron transfer. When the first excited singlet state of the Pc-part is populated either directly or *via* FRET, it undergoes transition to the charge-separated state resulting in reduction of the fluorescence quantum yield as well as shortening of the fluorescence lifetime of the Pc moiety for both the hetero-arrays.

#### Experimental

#### General procedure

All the reactions were performed under an atmosphere of nitrogen. Toluene and THF were distilled from sodium and sodium benzophenone ketyl respectively. The electrolyte  $[Bu_4N][PF_6]$  was recrystallised from THF three times prior to use. Electronic absorption and fluorescence spectroscopic spectra were measured in DMF (Sigma-Aldrich, spectroscopic grade). All other solvents and reagents were used as received. Compounds  $1^{14}$  and  $3^{15}$  were prepared as described. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz). Deuterated solvents were used as the lock and residual non-deuterated solvents as the internal references. Mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer.

# Electronic absorption and steady-state fluorescence spectroscopy

The ground-state absorption spectra were recorded using a commercial spectrophotometer Shimadzu UV-2501PC. Steadystate fluorescence spectra were measured in quartz cells (1 cm thickness) using a combination of a cw-Xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as the detector system (Lot-Oriel, Instaspec IV).<sup>20</sup> For determination of the fluorescence quantum yields, solutions of H<sub>2</sub>TPP<sup>16</sup> and SiPc(OEG)<sub>2</sub><sup>11a</sup> in DMF were used as the references ( $\Phi_{\rm fl} = 0.11$  and 0.50 respectively).

#### Time-resolved fluorescence spectroscopy

Excited-state lifetimes and DAF spectra were measured using a time-correlated single photon counting (TCSPC) technique in combination with scanning of the detection wavelength as described previously.<sup>11b</sup> The light of a Nd:VO<sub>4</sub> laser (Cougar, Time Bandwidth Products) operating at 60 MHz at a wavelength of 532 nm and producing pulses with a duration of 12 ps was used directly for excitation of the Por-part of the samples or to synchronously pump a dye laser (Model 599, Coherent) tuned to 620 nm for the Pc-part excitation. Fluorescence was detected at the magic polarisation angle (54.7°) relative to excitation with a thermo-electrically cooled micro-channel plate (R3809-01, Hamamatsu). Detection wavelength was chosen using a computercontrolled monochromator (77200, Lot-Oriel). Electrical signals were processed by a PCI TCSPC controller card (SPC630, Becker & Hickl). The instrument response function was 42 ps as measured at an excitation wavelength using Ludox. The data were analysed by a home-made programme described previously.<sup>11b</sup> Decay times and time shifts were linked through all measurements of one scan sampled every 3 nm.

#### **Electrochemical measurements**

These were carried out using a BAS CV-50W voltammetric analyser. The cell comprised inlets for a platinum-sphere working electrode, a platinum-plate counter electrode and a silverwire pseudo-reference electrode. Typically, a 0.1 M solution of  $[Bu_4N][PF_6]$  in DMF containing the sample was purged with nitrogen for 15 min, then the voltammograms were recorded at ambient temperature with a scan rate of 100 mV s<sup>-1</sup>. Potentials were referenced to SCE using ferrocene as an internal standard  $(E_{1/2} = +0.38 V \nu s. SCE).^{21}$ 

**Pc 2.** A mixture of **1** (0.50 g, 0.52 mmol), TsCl (1.0 g, 5.2 mmol) and triethylamine (10 mL) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was stirred at room temperature overnight. The volatiles were removed under reduced pressure, and then the residue was chromatographed on a silica gel column using CHCl<sub>3</sub>–CH<sub>3</sub>OH (15:1, v/v) as the eluent to give the product as a green solid (0.56 g, 85%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  9.25–9.38 (m, 4H, Pc-H<sub>α</sub>), 9.22 (d, *J* = 7.2 Hz, 2H, Pc-H<sub>α</sub>), 8.15–8.25 (m, 6H, Pc-H<sub>β</sub>), 7.69 (d, *J* = 7.5 Hz, 4H, ArH), 7.58 (s, 2H, Pc-H<sub>β</sub>), 7.36 (d, *J* = 7.5 Hz, 4H, ArH), 4.83 (t, *J* = 4.5 Hz, 4H, OCH<sub>2</sub>), 4.35 (t, *J* = 4.5 Hz, 4H, OCH<sub>2</sub>), 3.85–4.05 (m, 8H, OCH<sub>2</sub>), 3.60–3.75 (m, 8H, OCH<sub>2</sub>),

3.40–3.55 (m, 8H, OCH<sub>2</sub>), 2.50 (s, 6H, CH<sub>3</sub>).  ${}^{13}C^{1}$ {H} NMR:  $\delta$  153.3, 153.1, 153.0, 152.6, 150.5, 145.9, 139.1, 138.8, 138.7 133.4, 131.1, 130.7, 129.9, 128.6, 126.9, 126.6, 126.0, 123.3, 123.0, 116.0, 71.4, 71.1 71.0, 70.8, 70.7, 69.8, 69.3, 68.9, 64.2. HRMS (FAB) calcd for C<sub>62</sub>H<sub>61</sub>N<sub>8</sub>O<sub>14</sub>S<sub>2</sub>Zn (MH<sup>+</sup>): 1269.3035; found: 1269.3026.

Dyad 4 and triad 5. A mixture of 2 (0.20 g, 0.16 mmol), 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (3) (0.20 g, 0.32 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.5 g, 3.62 mmol) in DMF (5 mL) was stirred at 80 °C overnight. The volatiles were removed under reduced pressure, and then the residue was chromatographed on a silica gel column using CHCl<sub>3</sub>-CH<sub>3</sub>OH (10:1, v/v) as the eluent to give 4 as a blue-green solid (38 mg, 15%) and 5 as a blue solid (157 mg, 45%). Dyad 4: <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  $9.62-9.71 (m, 6H, Pc-H_{\alpha}), 9.01 (s, 8H, Por-H_{\beta}), 8.38-8.54 (m, 6H,$ Ph), 8.05–8.28 (m, 8H, Pc-H<sub>β</sub> and p-C<sub>6</sub>H<sub>4</sub>), 7.70–7.86 (m, 9H, Ph), 7.64 (s, 2H, Pc-H<sub> $\beta$ </sub>), 7.35 (d, *J* = 8.4 Hz, 2H, *p*-C<sub>6</sub>H<sub>4</sub>), 5.08 (br. s, 2H, OCH<sub>2</sub>), 4.62 (br. s, 2H, OCH<sub>2</sub>), 4.47 (br. s, 2H, OCH<sub>2</sub>), 4.22-4.34 (m, 4H, OCH<sub>2</sub>), 4.11 (br. s, 2H, OCH<sub>2</sub>), 3.68-4.02 (m, 20H, OCH<sub>2</sub>), -2.53 (s, 2H, NH). HRMS (FAB) calcd for C<sub>92</sub>H<sub>77</sub>N<sub>12</sub>O<sub>10</sub>Zn (MH<sup>+</sup>): 1573.5172; found: 1573.5181. UV-Vis (DMF)  $[\lambda_{max} nm (log \epsilon)]$ : 346 (4.98), 419 (5.69), 515 (4.00), 689 (5.28). Triad 5: <sup>1</sup>H NMR (pyridine- $d_5$ ):  $\delta$  9.80 (d, J = 7.5 Hz, 2H,  $Pc-H_{\alpha}$ , 9.64 (d, J = 7.5 Hz, 2H,  $Pc-H_{\alpha}$ ), 9.52–9.55 (m, 2H,  $Pc-H_{\alpha}$ ), 9.06 (s, 16H, Por-H<sub>B</sub>), 8.36-8.41 (m, 12H, Ph), 8.11-8.26 (m, 8H, Pc-H<sub>B</sub> and p-C<sub>6</sub>H<sub>4</sub>), 7.96–7.99 (m, 2H, Pc-H<sub>B</sub>), 7.72–7.80 (m, 18H, Ph), 7.50 (s, 2H, Pc-H<sub> $\beta$ </sub>), 7.28 (d, J = 8.4 Hz, 4 H, p-C<sub>6</sub>H<sub>4</sub>), 4.93  $(t, J = 4.5 \text{ Hz}, 4H, \text{ OCH}_2), 4.50 (t, J = 4.5 \text{ Hz}, 4H, \text{ OCH}_2),$ 4.16-4.22 (m, 8H, OCH<sub>2</sub>), 3.82-3.96 (m, 8H, OCH<sub>2</sub>), 3.70-3.78 (m, 8H, OCH<sub>2</sub>), -2.52 (s, 4H, NH). HRMS (FAB) calcd for  $C_{136}H_{105}N_{16}O_{10}Zn$  (MH<sup>+</sup>): 2186.7519; found: 2186.7501. UV-Vis (DMF)  $[\lambda_{\text{max}} \text{ nm } (\log \epsilon)]$ : 346 (5.13), 419 (6.01), 515 (4.49), 689 (5.27).

# Acknowledgements

We thank The Chinese University of Hong Kong for a Research Fellowship to X. Leng and the DFG for financial support (grant no. ER 588/1-1).

## References

- 1 V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, 1, 26.
- 2 (a) M. R. Wasielewski, Acc. Chem. Res., 2009, 42, 1910;
  (b) N. Aratani, D. Kim and A. Osuka, Acc. Chem. Res., 2009, 42, 1922;
  (c) S. Fukuzumi and K. Ohkubo, J. Mater. Chem., 2012, 22, 4575;
  (d) J. Yang, M.-C. Yoon, H. Yoo, P. Kim and D. Kim, Chem. Soc. Rev., 2012, 41, 4808.
- 3 R. Ziessel and A. Harriman, Chem. Commun., 2011, 47, 611.
- 4 (a) D. G. Nocera, *Acc. Chem. Res.*, 2012, 45, 767; (b) G. Bottari,
  O. Trukhina, M. Ince and T. Torres, *Coord. Chem. Rev.*, 2012, 256, 2453.
- 5 (a) Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, 41, 4245;
  (b) A. Mishra and P. Bauerle, *Angew. Chem., Int. Ed.*, 2012, 51, 2020.

- 6 V. Balzani, A. Credi and M. Venturi, *Chem.-Eur. J.*, 2008, **14**, 26.
- 7 (a) J.-Y. Liu, M. E. El-Khouly, S. Fukuzumi and D. K. P. Ng, *Chem.-Eur. J.*, 2011, 17, 1605; (b) M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, 256, 2601; (c) R. Jono and K. Yamashita, *J. Phys. Chem. C*, 2012, 116, 1445.
- 8 (a) J.-Y. Liu, E. A. Ermilov, B. Röder and D. K. P. Ng, *Chem. Commun.*, 2009, 1517; (b) E. A. Ermilov, J.-Y. Liu, D. K. P. Ng and B. Röder, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6430; (c) G. Bottari, G. de la Torre, D. M. Guldi and T. Torres, *Chem. Rev.*, 2010, **110**, 6768.
- 9 (a) P.-C. Lo, X. Leng and D. K. P. Ng, Coord. Chem. Rev., 2007, 251, 2334; (b) J.-Y. Liu, P.-C. Lo and D. K. P. Ng, Struct. Bond., 2010, 135, 169; (c) E. A. Ermilov, R. Menting, J. T. F. Lau, X. Leng, B. Röder and D. K. P. Ng, Phys. Chem. Chem. Phys., 2011, 13, 17633; (d) R. Menting, J. T. F. Lau, H. Xu, D. K. P. Ng, B. Röder and E. A. Ermilov, Chem. Commun., 2012, 48, 4597; (e) R. Menting, D. K. P. Ng, B. Röder and E. A. Ermilov, Phys., 2012, 14, 14573.
- 10 (a) P. D. Harvey, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2003, vol. 18, pp. 63–250; (b) S. Fukuzumi, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, 2010, vol. 10, pp. 183–243; (c) P. D. Harvey, C. Stern and R. Guilard, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, 2011, vol. 11, pp. 1–179.
- 11 (a) E. A. Ermilov, S. Tannert, T. Werncke, M. T. M. Choi,
   D. K. P. Ng and B. Röder, *Chem.Phys.*, 2006, 328, 428;

(b) S. Tannert, E. A. Ermilov, J. O. Vogel, M. T. M. Choi, D. K. P. Ng and B. Röder, *J. Phys. Chem. B*, 2007, **111**, 8053.

- 12 (a) D. Holten, D. F. Bocian and J. S. Lindsey, Acc. Chem. Res., 2002, 35, 57; (b) A. Satake and Y. Kobuke, Org. Biomol. Chem., 2007, 5, 1679.
- 13 (a) D. I. Schuster, S. MacMahon, D. M. Guldi, L. Echegoyen and S. E. Braslavsky, *Tetrahedron*, 2006, 62, 1928; (b) L. Flamigni, A. M. Talarico, B. Ventura, C. Sooambar and N. Solladié, *Eur. J. Inorg. Chem.*, 2006, 2155; (c) M. E. El-Khouly, J. Hasegawa, A. Momotake, M. Sasaki, Y. Araki, O. Ito and T. Arai, *J. Porphyrins Phthalocyanines*, 2006, 10, 1380; (d) T. D. M. Bell, K. P. Ghiggino, A. Haynes, S. J. Langford and C. P. Woodward, *J. Porphyrins Phthalocyanines*, 2007, 11, 455; (e) A. Takai, M. Chkounda, A. Eggenspiller, C. P. Gros, M. Lachkar, J.-M. Barbe and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, 132, 4477.
- 14 J.-Y. Liu, X.-J. Jiang, W.-P. Fong and D. K. P. Ng, *Org. Biomol. Chem.*, 2008, **6**, 4560.
- 15 P. Osswald, C.-C. You, V. Stepanenko and F. Würthner, *Chem.-Eur. J.*, 2010, **16**, 2386.
- 16 P. G. Seybold and M. Gouterman, J. Mol. Spectrosc., 1969, 31, 1.
- 17 D. Rehm and A. Weller, Isr. J. Chem., 1970, 8, 259.
- 18 R. A. Marcus, J. Chem. Phys., 1956, 24, 966.
- 19 (a) I. R. Gould, D. Ege, J. E. Moser and S. Farid, *J. Am. Chem. Soc.*, 1990, 112, 4290; (b) I. R. Gould, R. H. Young, R. E. Moody and S. Farid, *J. Phys. Chem.*, 1991, 95, 2068.
- 20 O. Korth, T. Hanke, I. Rückmann and B. Röder, *Exp. Tech. Phys.*, 1995, **41**, 25.
- 21 R. T. Boeré, K. H. Moock and M. Parvez, Z. Anorg. Allg. Chem., 1994, 620, 1589.