

Facile synthesis, spectroscopic and electrochemical properties, and theoretical calculations of porphyrin dimers with a bridging amide-bonded xanthene moiety

Xu Liang^{a,b}, Li Xu^a, Minzhi Li^a, John Mack^{*c0}, Justin Stone^c, Tebello Nyokong^{c0}, Yu Jiang^a, Nagao Kobayashi^{*b0} and Weihua Zhu^{*a0}

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China ^b Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan ^c Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

Received 22 December 2014 Accepted 13 February 2015

ABSTRACT: A free base porphyrin dimer bridged by a flexible amide-bonded xanthene moiety and its binuclear zinc(II) complex zinc(II) complex were synthesized and characterized. Structural characterization by MS and ¹H NMR spectroscopy confirmed the bridged porphyrin dimer structure. The properties of the dimers were characterized by IR, UV-visible absorption, fluorescence and magnetic circular dichroism (MCD) spectroscopy, and electrochemistry studies. Theoretical calculations were carried out to analyze the electronic structures of porphyrin dimers with a bridging amide-bonded xanthene moiety.

KEYWORDS: xanthene, porphyrin dimers, spectroscopy, TD-DFT calculations, electrochemistry.

INTRODUCTION

Porphyrin oligomers with macrocyclic rings that are covalently linked in a cofacial configuration have received considerable attention in recent years due to their unique electronic structures and novel optical properties [1]. Several types of conjugated porphyrin oligomers have been reported such as, doubly- or triply-fused co-planar porphyrins [2], alkyne-bridged porphyrin strands [3], and π -phenylene-bridged twisted/planar porphyrin dimers [4]. Interest of porphyrin dimers with linking moieties, especially those that adopt a face-to-face manner has been increasing in recent years. Porphyrin dimers with face-toface conformations exhibit an increased ability to bind two metals ions in a suitable geometry, opening up the possibility of mimicking the activity of heme and nonheme iron and copper-binding bioproteins such as oxidase, oxygenase, and oxygen transport proteins, which have binuclear active sites [5]. Xanthenes, have found widespread use as synthetic dyes in a wide range of applications, and their spectroscopic properties have been extensively studied [6]. Xanthene moieties have usually been introduced to porphyrin arrays through direct C-C bonds at the mesopositions and the electronic structures, and optical and magnetic properties of these compounds have been studied in depth [7]. In contrast, porphyrin xanthenes with flexible bridges such as alkyl chains and amines have received considerably less attention [8], and their spectroscopic properties and electrochemical properties have not been reported. Given the progress that has been made in xanthene-bridged cofacial porphyrin dimers, the goal of this study was to synthesize new compounds with flexible amide bridging units and to investigate their spectroscopic and electrochemical properties to develop an in-depth understanding of their electronic structures.

EXPERIMENTAL

Chemicals

Spectral grade *o*-dichlorobenzene for electrochemical measurements was purchased from the

^oSPP full member in good standing

^{*}Correspondence to: Weihua Zhu, email: sayman@ujs.edu. cn, tel/fax: +86 511-8879-1928; John Mack, email: j.mack@ ru.ac.za, fax: +27 46-622-5109; Nagao Kobayashi, email: nagaok@m.tohoku.ac.jp, fax: +81 22-795-7719.

Aladdin Reagent Company of Shanghai. Other chemicals and solvents were of analytical pure grade and were obtained from the Shanghai Guoyao Co. All solvents were dried and distilled prior to use, and 5,10,-15,20-tetraphenylporphyrin was synthesized according to standard literature procedures [9].

Synthesis

5-*p*-Nitrophenyl-10,15,20-triphenylporphyrin (2)[10]. Nitrosonitric acid (3.2 mL) was slowly added to a solution of 300 mL CH₂Cl₂ and 5,10,15,20tetrahenylporphyrin (3.00 g, 4.88 mmol) and the mixture was stirred at 0~5 °C in an ice-bath for 4 h. The reaction mixture was neutralized with ammonia solution to ca. pH = 7.0, and the organic layer was washed with brine and dried with anhydrous MgSO₄. After removal of the solvent, the residue was recrystallized from CH₂Cl₂ and MeOH and finally purified by Al₂O₃ gel chromatography (eluent: CH_2Cl_2 /hexane = 2:1) to give 5-*p*-nitrophenyl-10,15,20-triphenylporphyrin as a purple solid. Yield 2.0 g (62.6%). ¹H NMR (CDCl₃, 298 K): $\delta_{\rm H}$, ppm 8.89 (2H, d, J = 4.0 Hz), 8.86 (4H, s), 8.73 (2H, d, J = 4.0 Hz), 8.62 (2H, d, J = 8.0 Hz), 8.38 (2H, d, J = 8.0 Hz), 8.21 (6H, d, J = 8.0 Hz, 7.83–7.77 (9H, m), -2.74 (2H, s).

5-p-Aminophenyl-10,15,20-triphenylporphyrin (3) [11]. $SnCl_2 \cdot 2H_2O$ (2.0 g, 1.62 mmol) was added to a 100 mL solution concentrated HCl and 5-p-nitrophenyl-10,15,20-triphenylporphyrin (916 mg, 0.400 mmol). The mixture was vigorously stirred in a preheated oil bath 70°C for 2 h, and then neutralized with ammonia solution to ca. pH = 8.0. The reaction mixture was quenched by 50 mL ice-water and the water phase was extracted with ethylacetate $(3 \times 100 \text{ mL})$. The combined organic layers were dried with anhydrous MgSO₄. After removal of the organic solvent, the residue was purified through recrystallization by adding MeOH to the CH₂Cl₂ solution to afford pure 5-p-aminophenyl-10,15,20triphenylporphyrin 3 as a purple solid. Yield 767 mg (87.3%). ¹H NMR (CDCl₃, 298 K): $\delta_{\rm H}$, ppm 8.93 (2H, d, *J* = 4.0 Hz), 8.84 (6H, s), 8.20 (2H, d, *J* = 8.0 Hz), 7.98 $(2H, d, J = 8.0 \text{ Hz}), 7.74 \sim 7.80 (9H, m), 7.06 (2H, d, J =$ 8.0 Hz), 4.02 (2H, s), -2.76 (2H, s).

2,7-Di-*tert*-butyl-9,9-dimethyl-4-[10,15,20-triphenylporphyrin-10-(*N*-4-phenylamido-acyl)]-5xanthenecarboxylic acid amide (4). A mixture of 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-xanthene-dicarboxylic acid (41 mg, 0.10 mmol) and SOCl₂ (5 mL) was refluxed for 2 h. After excess SOCl₂ was removed, the xanthene acyl chloride was dried and dry CH_2Cl_2 (5 mL) was added. The mixture was stirred at room temperature and a mixture of 5-*p*-aminophenyl-10,15,20-triphenylporphyrin (3) (57 mg, 0.10 mmol) in CH_2Cl_2 (15 mL) and 2 drops of Et_3N was then added dropwise to the resulting light yellow solution and a white vapor was observed to form in the reaction flask. The mixture was stirred for 2 h at 0°C. The crude product was purified directly by silica gel column chromatography (eluent: CH₂Cl₂/hexane = 2:1) to give the free base porphyrin dimer **4** as a dark-red solid. Yield 65 mg (68%). IR (KBr): v, cm⁻¹ 3405 (s, br), 3300 (s), 3043 (m), 2960 (s), 2350 (s), 1798 (w), 1666 (s), 1590 (s), 1506 (vs), 1471 (vs), 1437 (vs), 1395 (m), 1346 (s), 1221 (s), 1166 (m), 1110 (w), 1055 (w), 964 (vs), 783 (vs), 735 (vs), 700 (vs), 651 (w), 512 (w), 415 (w). ¹H NMR (CDCl₃, 298 K): $\delta_{\rm H}$, ppm 9.27 (2H, s), 8.74 (4H, d, *J* = 6.0 Hz), 8.70 (4H, d, *J* = 6.0 Hz), 8.36 (4H, s), 8.25 (8H, dd, *J*₁ = 8 Hz, *J*₂ = 12 Hz), 8.17 (4H, d, *J* = 8.0 Hz), 8.14 (2H, d, *J* = 4.0 Hz), 7.88 (4H, d, *J* = 4.0 Hz), 7.77~7.73 (10H, m), 7.02 (10H, d, *J* = 15 Hz), 6.67 (8H, t, *J*₁ = 8 Hz, *J*₂ = 16 Hz), 1.86 (6H, s), 1.49 (18H, s), -3.01 (4H, s). MS (MALDI-TOF): *m/z* 1635.64 (calcd. [M + H]⁺ 1635.00).

Zn(II)-2,7-di-tert-butyl-9,9-dimethyl-4-[10,15,20triphenylporphyrin-10-(N-4-phenylamido-acyl)]-5xanthenecarboxylic acid amide (5). 10 mL of a MeOH solution of zinc acetate (44 mg, 0.2 mmol, 10 eq.) was slowly added to a 50 mL CHCl₃ solution of the xanthene-bridged free base porphyrin dimer 4 (32.6 mg, 0.02 mmol), and the reaction mixture was stirred and refluxed at 60 °C for 1 h. After the removal of the organic solvent, the residue was purified by silica gel column chromatography with CH₂Cl₂ as the eluent to provide the Zn(II)-porphyrin dimer 5 as a green-purple solid. Yield 35.2 mg (92.9%). IR (KBr): v, cm⁻¹ 3372 (s), 30052 (m), 2955 (s), 2356 (s), 1807 (w), 1675 (s), 1585 (s), 1508 (vs), 1476 (vs), 1435 (vs), 1393 (m), 1327 (s), 1230 (s), 1112 (w), 1070 (m), 1070 (m), 1000 (vs), 798 (s), 743 (s), 701 (s), 656 (w), 529 (w), 438 (w). ¹H NMR (CDCl₃, 298 K): $\delta_{\rm H}$, ppm 9.25 (2H, s), 8.90 (4H, d, J = 6.0 Hz), 8.80 (4H, d, J = 6.0 Hz), 8.53 (4H, d, J = 6.0 Hz), 8.25 (8H, dd, $J_1 =$ 8 Hz, $J_2 = 12$ Hz), 8.17 (4H, d, J = 8.0 Hz), 8.13 (2H, d, *J* = 4.0 Hz), 8.02 (4H, d, *J* = 4.0 Hz), 7.77~7.69 (8H, m), 7.28 (8H, d, J = 12 Hz), 6.93 (4H, d, J = 15 Hz), 6.80 (8H, d, J = 12 Hz), 6.80 (8H, d, J = 12t, $J_1 = 8$ Hz, $J_2 = 16$ Hz), 1.88 (6H, s), 1.47 (18H, s). MS (MALDI-TOF): *m/z* 1761.53 (calcd. [M + H]⁺ 1761.70).

Materials and equipment

Cyclic voltammetry was performed in a three-electrode cell using a BiStat or Chi-730C electrochemistry station. A glassy carbon disk electrode was utilized as the working electrode while a platinum wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. An "H" type cell with a fritted glass layer to separate the cathodic and anodic sections of the cell was used during bulk electrolysis. The working and counter electrodes were made from platinum mesh and the reference electrode was an SCE. The working and reference electrodes were placed in one compartment while the counter electrode was placed in the other. UV-visible absorption spectra were recorded with a HP 8453A diode array spectrophotometer. All of the electrochemical measurements were carried out under a nitrogen atmosphere. Magnetic circular dichroism (MCD) spectra were measured with a JASCO J-820 equipped with a 1.6 T (tesla) permanent magnet by using both the parallel and anti-parallel fields. The conventions of Piepho and Schatz are used to describe MCD intensity and the Faraday terms [12, 13]. MALDI-TOF mass spectra (MS) were collected using Bruker Daltonics autoflexII MALDI-TOF MS spectrometer. Fourier transform infrared (FT-IR) spectra were recorded using Bruker Vector 22 FT-IR spectrometer (using KBr pellets) in the 400–4000 cm⁻¹ region. ¹H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (operating at 400.13 MHz) using the residual solvent as an internal reference for ¹H (δ = 7.26 ppm for CDCl₃).

Theoretical calculations

The density functional theory (DFT) method was used to carry out geometry optimizations for free base 5,10,15,20-tetraphenylporphyrin (**H**₂**TPP**) and its Zn(II) complex (**ZnTPP**), and for **4** and **5** with the B3LYP functional of the Gaussian09 program package [14] and 6-31G(d) basis sets. To simplify the calculations the *t*-butyl groups on the xanthene bridging moieties were replaced with methyls, since replacing one alkyl group with another is unlikely to make a significant difference in this context, since there is no scope for steric interactions. The CAM-B3LYP functional was used to calculate the electronic absorption properties based on the time-dependent (TD-DFT) method, since it includes a long-range correction of the exchange potential, which incorporates an increasing fraction of Hartree–Fock (HF) exchange as the interelectronic separation increases. This makes it more suitable for studying compounds where there is significant charge transfer in the electronic excited states. 3

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic pathway used to prepare porphyrin dimers with a bridging amide-bonded xanthene moiety is shown in Scheme 1. A nitro group is added at the para-positions of one of the phenyl substituents of tetraphenylporphyrin to form 1, which is then reduced to form the amino group of 2. Reaction with xanthene acyl chloride results in the formation of an amide-bonded xanthene-bridged porphyrin dimer. The MALDI-TOFmass spectra reveals a strong parent peak at m/z = 1635.64(calcd. $[M + H]^+ = 1635.00$) for the xanthene-bridged free base porphyrin 4, providing direct evidence that the target molecule was obtained. The parent peak of the Zn(II) porphyrin dimer 5 at m/z = 1761.53 (calcd. [M + H^{+} = 1761.70) was also observed. The ¹H NMR spectrum of 4 contains several peaks in the aromatic region from both the porphyrins and xanthene moieties (Fig. 1). The assignment of the proton signal at -3.50 ppm to the inner N-H protons of the porphyrin rings was further confirmed by D₂O exchanged ¹H NMR measurements. The proton signals at $\delta = 1.50$, 1.85 were assigned to the -*t*Bu and -CH₃ substituents on the xanthene bridging moiety,



Scheme 1. Synthesis of the amide-bonded xanthene-bridged porphyrin dimers 4 and 5. Synthetic procedure: (i) nitrosonitric acid, CH₂Cl₂, 0~5 °C, 4 h; (ii) SnCl₂·2H₂O, HCl, 70 °C, 2 h; (iii) SOCl₂, reflux, 2 h; CH₂Cl₂, Et₃N, 0 °C, 2 h; (iv) Zn(OAc)₂·2H₂O, CHCl₃/ MeOH, reflux, 1 h



Fig. 1. ¹H NMR spectra of 4 (top) and 5 (bottom) in CDCl₃ (left) and for the D₂O exchange experiment for 4 (right)



Fig. 2. Infrared spectra of **4** (bottom, red) and **5** (top, black). Boxes are used to highlight peaks at *ca.* 3300 and 1000 cm⁻¹ confirm the presence of the inner N–H protons of **4** and the coordination of Zn(II) ions in the context of **5**

respectively. Similar proton peaks were observed in the spectrum of the Zn(II) porphyrin complex **5**. Solid-state infrared spectra (IR) (Fig. 2) were measured to obtain further information about the coordination environment of these two compounds. The peak at 3300 cm⁻¹ confirms the presence of an amide moiety. The 3320 cm⁻¹ band of **4**, which is not observed in the IR spectrum of **5**, can be assigned to the inner N–H bonds of the macrocyclic ring and is often used as a diagnostic peak for free base porphyrins. The shift of the peaks at around 1000 cm⁻¹ also confirms the coordination interaction between the Zn(II) ion and porphyrin rings.

Optical spectroscopy and TD-DFT calculations

UV-visible absorption spectra were recorded in CH₂Cl₂ at room temperature (Fig. 3). UV-visible absorption spectroscopy is one of the most useful methods for characterizing porphyrins and their analogues, due to the presence of the forbidden and allowed Q and B-bands of Gouterman's 4-orbital model [15] in the 500-600 and 400–450 nm regions, respectively. A D_{16h} symmetry $C_{16}H_{16}^{2}$ -species can be regarded as the parent hydrocarbon perimeter for describing and rationalizing the optical properties of tetrapyrrolic porphyrinoids. The π -system contains a series of MOs arranged with $M_L = 0, \pm 1, \pm 2$, $\pm 3, \pm 4, \pm 5, \pm 6, \pm 7$ and 8 nodal properties in ascending energy terms based on the magnetic quantum number for the cyclic perimeter, M_L . The frontier π -MOs have M_L = ± 4 and ± 5 nodal properties, respectively. The four spinallowed $M_L = \pm 4 \rightarrow \pm 5$ excitations result in two orbitally degenerate ${}^{1}E_{u}$ excited states, due to the $\Delta M_{L} = \pm 9$, and $\Delta M_{L} = \pm 1$ transitions. This results in the forbidden and allowed Q and B-bands of Gouterman's 4-orbital model for porphyrins [15], since an incident photon can provide only one quantum of orbital angular momentum. MCD spectroscopy can be used to identify the main electronic Q(0,0) and B(0,0) bands, due to the presence of intense derivative-shaped Faraday \mathcal{A}_{1} terms or, in the context of lower symmetry compounds, coupled pairs of Gaussianshaped Faraday \mathcal{B}_0 terms [13]. The MCD spectra of 4 and 5 are very similar to those of H_2TPP and ZnTPP [14a] (Fig. 3), since the relative energies of the frontier π -MOs of the free base and Zn(II) complexes are very similar. Derivative-shaped positive pseudo- \mathcal{A}_1 terms are observed in the MCD spectrum of 5 for the Q(0,0), Q(0,1)and B(0,0) bands at 597, 556 and 420 nm. It is noteworthy, however, that the signal is significantly less symmetrical than in the B-band region than is typically observed



Fig. 3. UV-visible absorption (bottom, solid line), fluorescence spectra (bottom, dashed gray line), and MCD (top) spectra of H_2TPP and **ZnTPP** in CHCl₃, and of **4** and **5** in CH₂Cl₂. TD-DFT spectra for the B3LYP optimized geometries were calculated by using the CAM-B3LYP functional with 6–31G(d) basis sets (Table 1) and are plotted against a secondary axis. The Q and B-bands of Gouterman's 4-orbital model [13] are highlighted with dark gray diamonds, while bands associated with transitions between the two porphyrin ring moieties are highlighted with light gray diamonds



Fig. 4. Energies of the frontier π -MOs for the B3LYP geometries of **H**₂**TPP**, **ZnTPP**, **4** and **5** calculated with the CAM-B3LYP functional and 6–31G(d) basis sets. In each case, the HOMO–LUMO gap is plotted against a secondary axis with a large gray diamond. In the context of **4** and **5**, MOs associated with the two porphyrin ring moieties are offset to the left and right, while those that are localized on the xanthene bridging moiety are not. Small black diamonds are used to highlight occupied MOs

for **ZnTPP** and radially symmetric analogues of Zn(II) tetraphenylporphyrins [16]. When molecular modeling calculations (Figs 4 and 5 and Table 1) were carried out it soon became obvious that the flexible amide bonds enable access to conformations in which the two porphyrin rings lie orthogonal to one another, so that there is considerably less scope for the strong exciton interactions that are observed for cofacial porphyrin dimers [17]. In TD-DFT calculations this results in two sets of Q- and B-bands, which are very similar in energy to those predicted for the parent tetraphenylporphyrin monomers (Figs 3-5 and Table 1). Michl's a, s, -a and -s nomenclature (Fig. 5) for the four frontier π -MOs of porphyrinoids with differing symmetries [18] facilitate the comparison with the spectra of H_2TPP and ZnTPP (Fig. 3 and Table 1). No bands associated with transitions involving MOs localized on the xanthene bridging moiety are predicted to have significant intensity in the visible region (Fig. 3 and Table 1). The xanthene-bridged free base porphyrin dimer 4 has fluorescence emission bands at 656 and 717 nm, while the corresponding Zn(II)porphyrin complex has bands at 607 and 649 nm (Fig. 3).



Fig. 5. Nodal patterns and energies of the frontier π -MOs of **4** and **5**. H and L denote the HOMO and LUMO (bottom), respectively. A and B superscripts are used to denote MOs localized on the two porphyrin moieties. Nodal patterns of the four frontier π -MOs of zinc tetraazaporphyrin at an isosurface value of 0.04 a.u (top). Michl [19] introduced **a**, **s**, **-a** and **-s** nomenclature to describe the four frontier π -MOs with $M_L = \pm 4$ and ± 5 nodal patterns based on whether there is a nodal plane (**a** and **-a**) or an antinode (**s** and **-s**) on the *y*-axis. This makes it easier to compare MOs of porphyrin complexes with differing symmetries (Table 1)

If the relative intensities of the two major bands are ignored in each case, the fluorescence spectra of **4** and **5** can be viewed as near mirror images of the emission bands of the related porphyrin monomers, and there are relatively small Stokes shifts of 9 and 11 nm, respectively, as is normally the case with monomeric porphyrins [15], which suggests that the S_1 state is localized on a single porphyrin ring moiety in each case.

Band ^a	# ^b		Calcd. ^c		Ex	p ^d	Wave function ^e =
H ₂ TPP							
_	1		_		_	_	Ground state
Q_x	2	16.8	596	(0.01)	15.6	641	59% s \rightarrow -a; 40% a \rightarrow -s;
Q_y	3	18.5	540	(0.03)	18.4	544	$58\% \text{ s} \rightarrow -\text{s}; 41\% \text{ a} \rightarrow -\text{a}; \dots$
В	4	27.1	369	(1.26)	24.0	416	56% a \rightarrow -s; 35% s \rightarrow -a;
	5	27.9	359	(1.66)	24.0	410	59% a \rightarrow -a; 43% s \rightarrow -s; 9% H–3 \rightarrow -a;
	7	32.8	305	(0.62)		—	$80\% \text{ H}-3 \rightarrow -a; 8\% \text{ s} \rightarrow -a; \dots$
ZnTPP							
	1		_		_	_	Ground state
Q	2	18.5	542	(0.01)	16.0	502	53% s \rightarrow -a/-s; 47% a \rightarrow -a/-s;
	3	18.5	542	(0.01)	10.9	392	53% a \rightarrow -a/-s; 47% s \rightarrow -a/-s;
В	4	27.8	360	(1.50)	23.8	421	53% a \rightarrow -a/-s; 46% s \rightarrow -a/-s;
	5	27.8	360	(1.50)	23.0	721	53% s \rightarrow -a/-s; 46% a \rightarrow -a/-s;
4							
_	1		—		_	_	Ground state
$Q_x^{\ A}$	2	16.7	599	(0.02)	15.4	648	$ \begin{array}{l} 51\% \ s^{A} \rightarrow -s^{A}; \ 34\% \ a^{A} \rightarrow -a^{A}; \\ 9\% \ s^{A} \rightarrow -a^{A}; \ 6\% \ a^{A} \rightarrow -s^{A}; \ \ldots \end{array} $
$Q_x^{\ B}$	3	16.7	597	(0.01)			$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Q_y^A	4	18.4	543	(0.04)	18.1	551	$\begin{array}{l} 50\% \ s^{A} \rightarrow -a^{A}; \ 34\% \ a^{A} \rightarrow -s^{A}; \\ 9\% \ s^{A} \rightarrow -s^{A}; \ 6\% \ a^{A} \rightarrow -a^{A}; \ \dots \end{array}$
$Q_y^{\ B}$	5	18.5	542	(0.04)			$ \begin{array}{c} 51\% \ s^B \rightarrow -a^B; \ 35\% \ a^B \rightarrow -s^B; \\ 8\% \ s^B \rightarrow -s^B; \ 5\% \ a^B \rightarrow -a^B; \ \ldots \end{array} $
$\mathbf{B}_{x}^{\mathbf{A}}$	6	26.8	373	(1.67)			$\begin{array}{c} 26\% \ a^{A} \rightarrow -a^{A}; \ 19\% \ a^{B} \rightarrow -a^{B}; \ 15\% \ s^{A} \rightarrow -s^{A}; \\ 12\% \ s^{B} \rightarrow -s^{B}; \ 12\% \ a^{A} \rightarrow -s^{A}; \ 7\% \ s^{A} \rightarrow -a^{A}; \ \dots \end{array}$
$\mathbf{B}_{x}^{\mathbf{B}}$	7	27.0	370	(1.87)	24.0	417	$\begin{array}{l} 35\% \ a^B \rightarrow -a^B; \ 21\% \ s^B \rightarrow -s^B; \ 15\% \ a^B \rightarrow -a^B; \\ 9\% \ s^A \rightarrow -s^A; \ 6\% \ a^B \rightarrow -s^B; \ \ldots \end{array}$
$\mathbf{B}_{y}^{\mathbf{A}}$	8	27.6	363	(1.57)			$\begin{array}{c} 25\% \ a^{A} \rightarrow -s^{A}; \ 18\% \ a^{B} \rightarrow -s^{B}; \ 18\% \ s^{A} \rightarrow -a^{A}; \\ 16\% \ a^{A} \rightarrow -a^{A}; \ 13\% \ s^{B} \rightarrow -a^{B}; \ 11\% \ s^{A} \rightarrow -s^{A}; \ \ldots \end{array}$
$\mathbf{B}_{y}^{\mathbf{B}}$	9	16.7	599	(1.33)			$34\%~a^B \rightarrow \text{-}s^B; 24\%~s^B \rightarrow \text{-}a^B; 21\%~a^A \rightarrow \text{-}s^A; 15\%~s^A \rightarrow \text{-}a^A; \ldots$
_	16	32.2	311	(0.24)	_	_	$44\% \text{ H}4^{Xan} \rightarrow \text{-}s^{B}; 29\% \text{ H}7^{B} \rightarrow \text{-}s^{B}; \ldots$
_	17	32.6	307	(0.61)	—	—	$62\% \text{ H-}11^{\text{A}} \rightarrow \text{-s}^{\text{A}}; 11\% \text{ H-}11^{\text{A}} \rightarrow \text{-a}^{\text{A}}; 6\% \text{ s}^{\text{A}} \rightarrow \text{-a}^{\text{A}}; \dots$
—	20	33.2	302	(0.28)	—	—	$\begin{array}{c} 32\% \ H{-}7^B \rightarrow {-}s^B; \ 29\% \ H{-}4^{Xan} \rightarrow {-}a^B; \\ 16\% \ H{-}4^{Xan} \rightarrow {-}s^B; \ 9\% \ H{-}7^B \rightarrow {-}a^B; \ \ldots \end{array}$
5							
	1					_	Ground state
Q_x^A	2	18.3	545	(0.01)			55% s ^A \rightarrow -a/-s ^A ; 45% a ^A \rightarrow -a/-s ^A ;
Q_x^A	3	18.4	544	(0.01)	16.8	597	53% s ^A \rightarrow -a/-s ^A ; 46% a ^A \rightarrow -a/-s ^A ;
Q_y^{B}	4	18.5	542	(0.01)			$52\% \text{ s}^{\text{B}} \rightarrow \text{-a/-s}^{\text{B}}; 46\% \text{ a}^{\text{B}} \rightarrow \text{-a/-s}^{\text{B}}; \ldots$
$Q_y^{\ B}$	5	18.5	541	(0.01)			$53\% \text{ s}^{\text{B}} \rightarrow \text{-a/-s}^{\text{B}}; 47\% \text{ a}^{\text{B}} \rightarrow \text{-a/-s}^{\text{B}}; \ldots$

Table 1. TD-DFT spectra of the B3LYP optimized geometries for H_2 TPP, ZnTPP, 4 and 5 calculated with the CAM-B3LYP functional and 6-31G(d) basis sets

(Continued)

Table 1. (Continued)							
Band ^a	# ^b	Calcd. ^c			$\mathrm{Exp}^{\mathrm{d}}$		Wave function ^e =
$\mathbf{B}_{x}^{\mathbf{A}}$	6	27.3	367	(2.41)			$\begin{array}{c} 35\% \ a^{\rm A} \to -a/{\rm -s}^{\rm A}; \ 28\% \ s^{\rm A} \to -a/{\rm -s}^{\rm A}; \\ 17\% \ a^{\rm B} \to -a/{\rm -s}^{\rm B}; \ 16\% \ s^{\rm B} \to -a/{\rm -s}^{\rm B}; \ \dots \end{array}$
$\mathbf{B}_{y}^{\mathbf{A}}$	7	27.6	363	(1.50)	23.8	420	$\begin{array}{l} 47\% \ a^{A} \rightarrow -a/\text{-}s^{A}; \\ 4\% \ a^{B} \rightarrow -a/\text{-}s^{B}; \\ 4\% \ s^{B} \rightarrow -a/\text{-}s^{B}; \\ \ldots \end{array}$
$\mathbf{B}_{x}^{\mathbf{B}}$	8	27.8	360	(2.24)			$\begin{array}{c} 41\% \ a^{B} \rightarrow -a/\text{-}s^{B}; \ 36\% \ s^{B} \rightarrow -a/\text{-}s^{B}; \\ 12\% \ a^{A} \rightarrow -a/\text{-}s^{A}; \ 9\% \ s^{A} \rightarrow -a/\text{-}s^{A}; \ \dots \end{array}$
$\mathbf{B}_{y}^{\mathbf{B}}$	9	27.9	358	(0.40)			$\begin{array}{c} 43\% \ a^{B} \rightarrow -a/\text{-}s^{B}; \ 37\% \ s^{B} \rightarrow -a/\text{-}s^{B}; \\ 8\% \ a^{A} \rightarrow -a/\text{-}s^{A}; \ 7\% \ s^{A} \rightarrow -a/\text{-}s^{A}; \ \dots \end{array}$
_	15	31.0	322	(0.10)	_		$93\% \text{ H}-12^{Xan} \rightarrow -a/-s^A; \dots$
	16	31.2	321	(0.09)	—		$93\% \text{ H-}12^{Xan} \rightarrow -a/\text{-s}^{A}; \dots$

^aBand assignment described in the text. ^bThe number of the state assigned in terms of ascending energy within the TD-DFT calculation. ^cCalculated band energies (10^3 .cm⁻¹), wavelengths (nm) and oscillator strengths in parentheses (f). ^dObserved energies (10^3 .cm⁻¹) and wavelengths (nm) in Figs 3 and 4. ^cThe wave functions based on the eigenvectors predicted by TD-DFT. One-electron transitions associated with the four frontier π -MOs of Gouterman's 4-orbital model [13] are highlighted in bold. H and L refer to the HOMO and LUMO, respectively. A and B superscripts are used to denote the two porphyrin rings, while a Xan superscript is used to denote MOs that are localized primarily on the xanthene bridging moiety. Michl's **a**, **s**, **-a** and **-s** nomenclature for the four frontier π -MOs [18] is used to facilitate comparison of the transition of porphyrinoids with differing symmetries.

Table 2. Redox potentials *vs.* SCE (in V) for **4** and **5**. The $E_{\frac{1}{2}}$ values are taken from DPV measurements

	$E^{Ox}_{^{1\!\!/_2}}{}^{2}$	$E^{Ox}_{{}^{l\!\!/_2}}{}^{1}$	$E^{Red}_{l\!\!/_2}{}^1$	$E^{Red}_{1\!\!/_2}\!$
4	+1.53	+1.10	-1.11	-1.46
5	+1.22	+0.89	-1.26	-1.60

Cyclic voltammetry measurements

Electrochemical measurements were carried out in o-dichlorobenzene containing 0.1 M TBAP to gain further insight into the electronic properties. Table 2 provides the redox potentials $E_{\frac{1}{2}}$ values derived cyclic and differential pulse voltammetry (CV and DPV) measurements. The voltammograms for xanthenebridged free base porphyrin dimer 4 (Fig. 6) contain two reversible one-electron reduction steps at -1.11 V for $[H_2Por]/[H_2Por]^-$ and at -1.46 V for $[H_2Por]^-/$ $[H_2Por]^{2-}$, respectively, under these experimental conditions. Two reversible one-electron oxidation curves are also observed at +1.10 and +1.53 V for the 1st and 2nd oxidation steps. In the voltammograms of the xanthenebridged Zn(II) porphyrin dimer 5 (Fig. 6) two reversible one-electron reduction processes were observed at -1.26 and -1.60 V for the [Zn(II)Por]/[Zn(II)Por]⁻ and [Zn(II) Por]⁻/[Zn(II)Por]²⁻ steps, respectively. Two oxidation processes are also observed at +0.89 and +1.22 V which are similar to those observed for monomeric Zn(II) 5,10,15,20-tetraphenylporphyrins [19]. The i_n^{Red} and i_p^{Ox} values, determined from CV measurements for 4 and 5 made at various scan-rates from 20–500 mV



Fig. 6. CV (bottom) and DPV (top) measurements of 4 (left) and 5 (right) in *o*-dichlorobenzene



Fig. 7. Cyclic voltammetry measurements for **4** and **5** in *o*-dichlorobenzene at different scan rates

(Fig. 7), provide an insight into the reversibility of the system on an experimental time-scale. The good linear correlations observed for plots of peak current *vs.* $v^{\frac{1}{2}}$ for **4** and **5** (Fig. 8) confirm that all of the oxidation and reduction processes are diffusion controlled.

CONCLUSION

A free base porphyrin dimer with a bridging amidebonded xanthene moiety and its binuclear Zn(II) complex have been synthesized through a facile reaction of 5-p-aminophenyl-10,15,20-triphenylporphyrin and xanthene chloride. A detailed characterization by IR, UV-visible absorption, MCD, and fluorescence spectroscopy was carried out and further insights into the electronic structures were obtained from theoretical calculations and various electrochemistry measurements. The optical spectroscopy of 4 and 5 is very similar to that of regular meso-tetraphenylporphyrin monomers, since the flexible amide-bonded xanthene bridging moiety enables access to energetically stable conformations in which the porphyrin rings lie in an orthogonal arrangement with respect to each other. Since porphyrin dimers with functional bridging units have potential applications in the field of energy conversion and catalytic chemistry, the detailed analysis of their spectroscopic and redox



Fig. 8. The dependence of square root of the scan-rate (v^{i_2}) on the peak current (i_p) for the 1st and 2nd reduction and 1st and 2nd oxidation steps during cyclic voltammetry measurements of 4 and 5

properties should assist the design and investigation of other bridged porphyrin dimers. Further research is currently being pursued in this regard.

Acknowledgements

Financial support was provided by the National Scientific Foundation of China (No. 21171076). The authors thank Prof. Zhen Shen of Nanjing University for the MCD spectral measurement. The theoretical calculations were carried out at the Centre for High Performance Computing in Cape Town, South Africa.

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