

# Synthesis, electrochemical and spectroelectrochemical characterization of iron(III) tetraarylporphyrins containing four $\beta$ , $\beta'$ -butano and $\beta$ , $\beta'$ -benzo fused rings

Weijie Xu<sup>a</sup>, Yuanyuan Fang<sup>a</sup>, Zhongping Ou\*<sup>a,b<sup>0</sup></sup>, Mingyuan Chen<sup>a,b</sup> and Karl M. Kadish\*<sup>b<sup>0</sup></sup>

<sup>a</sup>School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, China <sup>b</sup>Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA

Received 20 March 2017 Accepted 11 April 2017

**ABSTRACT:** Six iron(III) tetraarylporphyrins containing four  $\beta$ , $\beta'$ -butano or  $\beta$ , $\beta'$ -benzo fused rings were synthesized and characterized by electrochemistry and spectroelectrochemistry in nonaqueous media. The examined compounds are represented as butano(TpYPP)FeCl and benzo(TpYPP)FeCl, where TpYPP is a dianion of the *meso*-substituted porphyrin, Y is a CH<sub>3</sub>, H or Cl substituent on the *para*-position of the four *meso*-phenyl rings and butano and benzo are the  $\beta$ , $\beta'$ -substituents on each of the four pyrrole rings of the compound. Up to three reductions are observed for each Fe(III) butano- and benzoporphyrin in CH<sub>2</sub>Cl<sub>2</sub> or pyridine containing 0.1 M TBAP, the first of which is assigned in each case to a metal-centered electron transfer. The second reduction is also metal-centered in CH<sub>2</sub>Cl<sub>2</sub> and leads to formation of an Fe(I) porphyrin, but it is porphyrin ring-centered and gives an Fe(II) porphyrin  $\pi$ -anion radical reduction product when pyridine is used as the solvent. The effects of the solvent and type of fused ring system (butano or benzo) on the UV-vis spectra and electrochemical properties of the Fe(III) porphyrins are discussed and comparisons are made to both the structurally related non- $\beta$ , $\beta'$ -substituted iron porphyrins and earlier described butano- or benzotetraarylporphyrins containing Cu(II) or Co(II) central metal ions.

**KEYWORDS:** synthesis, iron(III) tetrabutanoporphyrins, iron(III) tetrabenzoporphyrins, electrochemistry, spectroelectrochemistry, substituent effects.

# **INTRODUCTION**

Iron porphyrins are some of the most studied metalloporphyrins, in part because of their biological relevance and in part because they can be used as catalysts in a variety of reactions [1–26]. A large number of iron porphyrins with different *meso* and/or  $\beta$ -pyrrole substituents have been synthesized and electrochemically characterized over the last four decades [26–47]. However, to the best of our knowledge, only a few  $\beta$ , $\beta'$  butano or  $\beta$ , $\beta'$  benzo substituted iron tetraarylporphyrins have been reported in the literature [48, 49] and the electrochemistry

and spectroscopic properties of these compounds in their neutral, reduced or oxidized forms are virtually unknown.

We recently reported the synthesis and electrochemistry of tetraaryltetrabutano- and tetraaryltetrabenzoporphyrins containing Co(II) [50], Cu(II) [51] or Pt(II) [52] central metal ions and have now turned our attention to derivatives of Fe(III) containing these two porphyrin skeletal structures. The examined compounds are represented as butano(TpYPP)FeCl and benzo(TpYPP)FeCl, where TpYPP is a dianion of the *meso*-substituted porphyrin, Y is a CH<sub>3</sub>, H or Cl substituent on the *para*-position of the four *meso*-phenyl rings, and butano and benzo are the  $\beta$ , $\beta'$ -fused ring substituents on each of the four pyrrole groups of the compound. The structures of the newly-investigated porphyrins are shown in Chart 1 along with that of the parent iron(III)

<sup>&</sup>lt;sup>6</sup>SPP full member in good standing

<sup>\*</sup>Correspondence to: Zhongping Ou, email: zpou2003@yahoo. com or Karl M. Kadish, email: kkadish@uh.edu.



Chart 1. Structures of investigated iron(III) porphyrins

tetraarylporphyrin, represented as (TpYPP)FeCl. The effects of solvent and type of fused ring structure on the UV-vis spectra and electrochemical properties are described and comparisons made to both structurally related non- $\beta$ , $\beta'$ -substituted Fe(III) porphyrins and earlier described butano- and benzoporphyrin derivatives with Cu(II) or Co(II) central metal ions.

# **RESULTS AND DISCUSSION**

#### Synthesis

Non- $\beta$ , $\beta'$ -substituted iron(III) porphyrins, (TpYPP)FeCl **1a–1c**, were synthesized according to a procedure in the

(a) Fe(III) butanoporphyrins 2a-2c

literature [53]. The butano(TpYPP)FeCl **2a–2c** complexes were synthesized *via* a reaction between butano(TpYPP)H<sub>2</sub> [49, 54] and Fe(Cl)<sub>2</sub>·4H<sub>2</sub>Oin DMF (Scheme 1a) while the benzo(TpYPP)FeCl **3a–3c** derivatives were synthesized *via* the route shown in Scheme 1b. The free-base benzoporphyrins were obtained by demetalation of the corresponding copper benzoporphyrins [51] in acid solution and then reacted with FeCl<sub>2</sub>·4H<sub>2</sub>O in DMF to generate the desired Fe(III) benzoporphyrins **3a–3c**.

## **UV-vis spectra**

The UV-vis spectra and redox properties of each Fe(III) porphyrin in Chart 1 were measured in both the non-binding solvent  $CH_2Cl_2$  and the binding solvent pyridine. Examples of the spectra are given in Fig. 1, which compares the three types of porphyrins with *meso*-PhCH<sub>3</sub> groups (compounds **1a**, **2a** and **3a**) in the two solvents, while Fig. S1 illustrates spectra under the same two solution conditions for the three series of iron porphyrins with *meso*-Ph (**1b**, **2b** and **3b**) or *meso*-PhCl substituents (**1c**, **2c** and **3c**).

As seen in the two figures, quite different spectra are obtained for the three series of Fe(III) porphyrins with different macrocycles. The difference in UV-vis spectra



Scheme 1. Synthesis routes for preparing the Fe(III) (a) butanoporphyrins 2a-2c and (b) benzoporphyrins 3a-3c



**Fig. 1.** UV-vis spectra of  $(TpCH_3PP)$ FeCl **1a**, butano $(TpCH_3PP)$ FeCl **2a** and benzo $(TpCH_3PP)$ FeCl **3a** in (a) CH<sub>2</sub>Cl<sub>2</sub> and (b) pyridine. The spectrum of **3a** in pyridine was measured at least 5 min after dissolving the compound in solution

between CH<sub>2</sub>Cl<sub>2</sub> and pyridine can be accounted for in each case by the presence or absence of two bound pyridine molecules on the Fe(III) center of the porphyrin, giving the six-coordinate bis-pyridine adducts in pyridine, compared to the related five-coordinate chloroderivatives in CH<sub>2</sub>Cl<sub>2</sub>. This is consistent with what was previously reported for other Fe(III) porphyrins with substituted TPP or OEP skeletal structures [34, 41, 43, 45, 55]. In addition, a red shift in the Soret and Q bands is seen upon going from the parent porphyrins 1a, 1b or 1c to the corresponding butanoporphyrins 2a, 2b or 2c, and a further red shift in these bands occurs upon going from the butanoporphyrins to the benzoporphyrins 3a, 3b or 3c, the latter of which have enhanced intensity Q-band absorptions in the two solvents. The 614–618 nm Q band of the three benzoporphyrins in pyridine has a relatively high intensity compared to the single Q band of compounds in other two solvents which are weak and located at 529-539 for [(TpYPP)Fe(Py)2]+ and 561-563 nm for [butano(TpYPP)Fe(Py)<sub>2</sub>]<sup>+</sup>, respectively. This result is consistent with what was earlier reported for tetraaryltetrabenzoporphyrins containing other central metal ions under the same solution conditions [48, 50–54].

## Electrochemistry

The electrochemistry of each Fe(III) porphyrin was carried out in both  $CH_2Cl_2$  and pyridine containing 0.1 M TBAP. The reduction and oxidation potentials are given in Table 1, and the results are described below for the three porphyrins in each series, first for the tetraarylporphyrins, then for the butanoporphyrins and finally for the benzoporphyrins.

*Tetraarylporphyrins.* The electrochemistry of iron(III) porphyrins with TPP skeletal structures is well-documented in the literature [37, 45]. In general, up to three reductions are observed for these types of compounds within the solvent potential limit of  $CH_2Cl_2$  containing 0.1 M TBAP, the first of which involves, in every case, a conversion of the Fe(III) porphyrin to its Fe(II) form. In the current study this process is irreversible for the (TpYPP)Fe<sup>III</sup>Cl derivatives **1a–1c** when examined by cyclic voltammetry which showed a cathodic to anodic peak separation of about 410 mV for all three compounds at a scan rate of 0.1 V/s. The cathodic reduction peak is located at  $E_{pc} = -0.29$  to -0.38 V for a scan rate of 0.1 V/s, the exact value depending upon the

3

solvent	β,β-sub	Y		oxidatior	1	re	duction	
CH <sub>2</sub> Cl <sub>2</sub>	none	CH <sub>3</sub>		1.36 <sup>a</sup>	1.13ª	-0.38 <sup>a</sup>	-1.30 <sup>a</sup>	-1.82 <sup>a</sup>
		Н		1.42 <sup>a</sup>	1.20 <sup>a</sup>	-0.36 <sup>a</sup>	-1.20ª	-1.80 <sup>a</sup>
		Cl		1.43ª	1.28 <sup>a</sup>	-0.29 <sup>a</sup>	-1.16ª	-1.70 <sup>a</sup>
	butano	$CH_3$		1.20 <sup>a</sup>	0.62	-0.72 <sup>a</sup>	-1.28	-1.68 <sup>a</sup>
		Н		1.23 <sup>a</sup>	0.67	-0.72 <sup>a</sup>	-1.27	-1.68 <sup>a</sup>
		Cl		1.26 <sup>a</sup>	0.76	-0.68 <sup>a</sup>	-1.20	
	benzo	$CH_3$	1.13	0.94	0.67	$0.07, -0.25^{a}$	-1.72 <sup>a</sup>	
		Н		0.93	0.69	0.15, -0.19	-1.65ª	
		Cl	1.13	0.96	0.76	0.19, -0.16 <sup>a</sup>	-1.64 <sup>a</sup>	
Pyridine	none	$CH_3$				0.14	-1.62 <sup>a</sup>	-1.75
		Н				0.17	-1.57 <sup>a</sup>	-1.73
		Cl				0.23	-1.50 <sup>a</sup>	-1.68
	butano	$CH_3$			0.92 <sup>a</sup>	-0.14	-1.81 <sup>a</sup>	-1.91
		Н			0.94 <sup>a</sup>	-0.12	-1.78 <sup>a</sup>	-1.89
		Cl			0.96 <sup>a</sup>	-0.04	-1.70 <sup>a</sup>	-1.80
	benzo	$CH_3$			0.76	0.20	-1.60	
		Н			0.79	0.22	-1.59	
		Cl			0.83	0.30	-1.48 <sup>a</sup>	-1.64

**Table 1.** Half-wave potentials (V vs. SCE) of (TpYPP)FeCl, butano(TpYPP)FeCl and<br/>benzo(TpYPP)FeCl in  $CH_2Cl_2$  and pyridine containing 0.1 M TBAP

<sup>a</sup>Irreversible peak potential at a scan rate of 0.10 V/s.

specific *meso*-substituent, and this one-electron addition leads to the initial generation of  $[(TpYPP)Fe^{II}CI]^-$  which then loses the bound Cl<sup>-</sup> counterion, giving  $(TpYPP)Fe^{II}$ as a final product which is re-oxidized at  $E_{pa} = 0.12$  to 0.03 V on the return sweep of the cyclic voltammograms (see Fig. 2). The second reduction of the three parent porphyrins is also irreversible in CH<sub>2</sub>Cl<sub>2</sub>, and the cathodic peak for this process is located at  $E_{pc} = -1.30$  to -1.16 V for a scan rate of 0.10 V/s. These reductions are proposed to generate an Fe(I) porphyrin, which then reacts with the CH<sub>2</sub>Cl<sub>2</sub> solvent to give a transient  $\sigma$ -bonded complex which is described as (TpYPP)Fe(CH<sub>2</sub>Cl) [45, 56–58].

Three reductions of **1a–1c** are also observed in pyridine as shown in Fig. 3. The first one-electron addition is reversible and located at  $E_{1/2} = 0.14$  to 0.23 V. This process is assigned as a conversion of  $[(TpYPP)Fe^{II}(Py)_2]^+$  to  $(TpYPP)Fe^{II}(Py)_2$ . The second reduction has non-coupled reduction and re-oxidation peaks which are separated by 140 mV in all three compounds. Earlier mechanistic studies on related compounds showed that the two bound pyridine molecules dissociate following electron transfer, giving  $[(TpYPP)Fe^{II}]^-$  as the final reduction product in the current study, and this four-coordinate species is then re-oxidized at a more positive potential of  $E_{pa} = -1.36$  to -1.48 V on the return potential sweep.

A number of structurally related *meso-* and/or  $\beta$ -pyrrole substituted iron(III) tetraarylporphyrins have



**Fig. 2.** Cyclic voltammograms showing the reduction of (a) (TpCH<sub>3</sub>PP)FeCl **1a**, (b) (TPP)FeCl **1b** and (c) (TpClPP)FeCl **1c** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at a scan rate of 0.10 V/s



**Fig. 3.** Cyclic voltammograms showing the reduction of (a) (TpCH<sub>3</sub>PP)FeCl **1a**, (b) (TPP)FeCl **1b** and (c) (TpClPP)FeCl **1c** in pyridine 0.1 M TBAP at a scan rate of 0.10 V/s

also been examined as to their spectroscopic properties after electroreduction in nonaqueous media [32, 35, 46, 55, 59–61]. As mentioned above, the first one-electron reduction is invariably metal-centered to give an Fe(II) porphyrin. The addition of a second electron may also involve a metal-centered reaction to give an Fe(I) porphyrin with an unreduced macrocycle, but this is not always the case and an Fe(II) porphyrin  $\pi$ -anion radical may also be formed, depending upon the type and number of *meso* and/or  $\beta$ -pyrrole substituents, the type and number of axial ligands and the specific electrochemical solvent utilized [37, 45]. 5

Figure 4 shows the spectroelectrochemical data for the first two reductions of  $(TpCH_3PP)Fe^{III}Cl$  **1a** in  $CH_2Cl_2$  and pyridine containing 0.1 M TBAP. In both solvents, the spectral changes during the first reduction are similar to what has been reported for other structurally related Fe(III) tetraarylporphyrins and are consistent with the generation of a four-coordinate Fe(II) porphyrin in  $CH_2Cl_2$  and a six-coordinate bis-pyridine derivative in



**Fig. 4.** Cyclic voltammograms and UV-vis spectral changes of (TpCH<sub>3</sub>PP)FeCl **1a** obtained during the first two controlled potential reductions in (a)  $CH_2Cl_2$  and (b) pyridine containing 0.1 M TBAP



Fig. 5. Cyclic voltammograms of (a) butano(TpCH<sub>3</sub>PP)FeCl 2a, (b) butano(TPP)FeCl 2b and (c) butano(TpClPP)FeCl 2c in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

pyridine [45, 46]. The final spectra, after completion of the second reduction, are also consistent with what has been reported for structurally related porphyrins giving an unstable [Fe<sup>III</sup>(CH<sub>2</sub>Cl)]  $\sigma$ -bonded porphyrin product in CH<sub>2</sub>Cl<sub>2</sub> and an Fe(II) porphyrin  $\pi$ -anion radical in pyridine. Compared to (TpCH<sub>3</sub>PP)Fe<sup>III</sup>Cl **1a**, similar spectral changes are observed for (TPP)Fe<sup>III</sup>Cl **1b** and (TpCIPP)Fe<sup>III</sup>Cl **1c** during the first two controlled potential reductions in CH<sub>2</sub>Cl<sub>2</sub> (Fig. S2), indicating that the same reduction mechanism can be proposed for compounds **1a–1c** under the given solution conditions.

The large separation in cathodic and anodic peaks for the second reduction of **1a** in pyridine are similar to what was previously reported upon reduction of ( $F_{20}$ DPP)FeCl ( $F_{20}$ DPP = the dianion of 2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetra(pentafluorophenyl)porphyrin) in PhCN or pyridine [55]. In both of these solvents, the first reduction was assigned as metal-centered to give an Fe(II) porphyrin, while the second reduction was assigned as a ring-centered process to give an Fe(II) porphyrin  $\pi$ -anion radical as the main product. Little to no difference is seen in the UV-vis spectral changes obtained during reduction of compounds **1b** or **1c** in pyridine (Fig. S3), and the assignments of electron transfer sites should be the same as all three porphyrins in the (TpYPP)FeCl series.

Butanoporphyrins. The three butano(TpYPP)FeCl complexes 2a-2c exhibit mainly ill-defined reductions in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 5). The first reduction peak is located at  $E_{\rm pc} = -0.72$  V for **2a**, -0.74 V for **2b** and -0.68 V for **2c** at a scan rate of 0.10 V/s and a re-oxidation peak is then observed at  $E_{pa}$  values between 0.06 and 0.18 V when the potential scan direction is reversed. The separation between  $E_{pc}$  and  $E_{pa}$  ranges from 780 to 860 mV compared to the (TpYPP)FeCl complexes, where  $\Delta E_{\rm p}$ is equal to 410 mV as mentioned earlier and shown in Fig. 2. The strong binding of Cl<sup>-</sup> to the Fe(III) form of the butanoporphyrins leads to a larger negative shift in the cathodic peak potential for the first reduction compared to the three TPP derivatives, but far smaller shifts are seen in the re-oxidation peaks, where the difference in  $E_{\rm pa}$  values between the two series of compounds amounts to only 30-70 mV.

The second reduction of the butanoporphyrins is quasi-reversible and located at  $E_{1/2}$  values of -1.28 V (2a) to -1.20 V (2c) in CH<sub>2</sub>Cl<sub>2</sub>. The cathodic peak potentials for these reductions are quite similar to the cathodic peak potentials for the irreversible reduction of the corresponding derivatives **1a–1c**, thus indicating only a small effect of the butano groups on this redox reaction involving the four-coordinate Fe(II) porphyrins.



**Fig. 6.** Cyclic voltammogram and UV-vis spectral changes of butano(TpClPP)FeCl **2c** during the reductions at -0.8 and -1.5 V, and the oxidations at 0.9 and 1.4 V in  $CH_2Cl_2$  containing 0.1 M TBAP

Two oxidations are observed for three butanoporphyrins, the first of which is reversible and located at  $E_{1/2} = 0.62$  V for **2a**, 0.67 V for **2b** and 0.76 V for **2c**, respectively (Fig. 5). The cyclic voltammetric data indicates the lack of a chemical reaction coupled to the first electron abstraction in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP, but this is not the case for the second oxidation where an irreversible process is observed as indicated by the lack of a re-reduction peak after generation of the Fe(III) porphyrin dication.

Figure 6 illustrates the UV-vis spectral changes obtained during the first two controlled potential reductions and oxidations of butano(TpClPP)FeCl 2c in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. During the first controlled potential reduction at -0.8 V, the 394 nm Soret band of the neutral porphyrin decreases in intensity as a new Soret band associated with the Fe(II) porphyrin grows in at

429 nm. This Fe(II) porphyrin Soret band then decreases in intensity during the second reduction at -1.5 V and a split band for the doubly reduced porphyrin appears at 436 and 463 nm. The result is consistent with a metal-centered reaction to give the Fe(I) porphyrin, as was reported for other structurally related iron porphyrins under similar solution conditions [46, 62].

The spectral changes during controlled potential oxidation of compound 2c in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP are also shown in Fig. 6 and are consistent with two stepwise porphyrin ring-centered electron abstractions giving an Fe(III) porphyrin  $\pi$ -cation radical and dication, respectively, in this solvent.

Similar to (TpYPP)FeCl **1a–1c** and ( $F_{20}$ DPP)FeCl [55], the butano(TpYPP)FeCl derivatives **2a–2c** also undergo three reductions in pyridine containing 0.1 M TBAP, with the first and third being reversible as shown

7



**Fig. 7.** Cyclic voltammograms of (a) butano(TpCH<sub>3</sub>PP)FeCl **2a**, (b) butano(TPP)FeCl **2b** and (c) butano(TpClPP)FeCl **2c** in pyridine containing 0.1 M TBAP at a scan rate of 0.10 V/s

by the cyclic voltammograms of these compounds in Fig. 7. The peak potentials for the second irreversible reduction are located at  $E_{\rm pc} = -1.81$  V (**2a**), -1.79 V (**2b**) and -1.70 V (**2c**) at a scan rate of 0.10 V/s, and in each case these processes are coupled with re-oxidation peaks at  $E_{\rm pa} = -1.40$  V (**2a**), -1.38 V for (**2b**) or -1.30 V (**2c**). The hardest reduction (most negative potential) is seen for **2a** which contains an electron-donating CH<sub>3</sub> group on each *meso*-phenyl ring of the compound, while the easiest reduction (most positive  $E_{1/2}$ ) is seen for **2c** which contains an electron-withdrawing Cl group on the four *meso*-phenyl rings of the porphyrin macrocycle.

The first reduction of butano(TpClPP)Fe<sup>III</sup>Cl 2c in pyridine is assigned as generating an Fe(II) porphyrin on the basis of the spectral changes shown in Fig. 8, where the initial Soret band at 429 nm is red shifted to 439 nm and slightly increased in intensity. This contrasts with the second controlled potential reduction where the 439 nm Soret band of the Fe(II) porphyrin is significantly decreased in intensity upon electroreduction. There is also a new weak band for the doubly reduced porphyrin at 374 nm as shown in the figure. The final spectrum obtained after the second reduction suggests that an Fe(II) porphyrin  $\pi$ -anion radical is the main reduction product in the second electron addition, as was previously reported for (CN)<sub>4</sub>(TPP)FeCl [35] and F<sub>x</sub>DPPFeCl [55], where DPP = the dianion of dodecaphenylporphyrin and x is the number of fluorine groups on the four *meso*-phenyl rings of the macrocycle.

Similar UV-vis spectral changes as described above were obtained during controlled potential reduction of the Fe(III) butanoporphyrins **2a** and **2b** in the two solvents.



**Fig. 8.** Cyclic voltammogram and UV-vis spectral changes of butano(TpCIPP)FeCl **2c** obtained during the first two controlled potential reductions in pyridine containing 0.1 M TBAP

These data are shown in Figs S4 ( $CH_2Cl_2$ ) and S5 (pyridine). The electrochemical and spectroelectrochemical data are thus self-consistent in the two solvents. The proposed reduction mechanisms in  $CH_2Cl_2$  and pyridine are illustrated in Scheme 2.

In summary, the first one-electron reduction of each butano(TpYPP)Fe<sup>III</sup>Cl complex is metal-centered to initially give the [butano(TpYPP)Fe<sup>II</sup>Cl]<sup>-</sup> form of the porphyrin in CH<sub>2</sub>Cl<sub>2</sub>. This electron transfer is then followed by chloride dissociation to generate butano(TpYPP)Fe<sup>II</sup>, which can then be further reduced to an Fe(I) porphyrin anion at more negative potentials or re-oxidized to give the original Fe(III) porphyrin at more positive potentials, as shown in Scheme 2a.

The reduction mechanism in pyridine (Scheme 2b) differs from that in  $CH_2Cl_2$  for the same compound. The initial form of the butanoporphyrin is given as [butano-(TpYPP)Fe<sup>III</sup>(Py)<sub>2</sub>]<sup>+</sup> which undergoes two stepwise oneelectron reductions, leading to butano(TpYPP)Fe<sup>II</sup>(Py)<sub>2</sub> and [butano(TpYPP)Fe<sup>II</sup>(Py)<sub>2</sub>]<sup>-</sup>, respectively. The two pyridine axial ligands dissociate after generation of doubly reduced [butano(TpYPP)Fe<sup>II</sup>(Py)<sub>2</sub>]<sup>-</sup> to give [butano(TpYPP)Fe<sup>II</sup>]<sup>-</sup>, which can be reversibly reduced at more negative potentials



(b) in pyridine

$$[PorFe^{II}(Py)_{2}]^{+} \xrightarrow{+e} PorFe^{II}(Py)_{2} \xrightarrow{+e} [PorFe^{II}(Py)_{2}]^{-}$$

$$-0.04 V \qquad \uparrow -1.70 V \qquad \downarrow -2Py \qquad \downarrow -2$$

Scheme 2. Proposed reduction mechanism of butano(TpYPP)FeCl in (a)  $CH_2Cl_2$  and (b) pyridine containing 0.1 M TBAP. The listed potentials are for compound 2c



**Fig. 9.** Cyclic voltammograms of benzo(TpCH<sub>3</sub>PP)FeCl **3a** and benzo(TpClPP)FeCl **3c** in (a)  $CH_2Cl_2$  and (b) pyridine containing 0.1 M TBAP at a scan rate of 0.10 V/s

leading to [butano(TpYPP)Fe<sup>I</sup>]<sup>2-</sup> or re-oxidized to give back butano(TpYPP)Fe<sup>II</sup>, prior to re-association of the two pyridine molecules.

**Benzoporphyrins.** Cyclic voltammograms of the Fe(III) benzoporphyrins in CH<sub>2</sub>Cl<sub>2</sub> and pyridine containing 0.1 M TBAP are shown in Fig. 9 and Figs. S6–S7. Two reductions are observed for each porphyrin between +0.20 and -0.25 V in CH<sub>2</sub>Cl<sub>2</sub>. The first is located at  $E_{1/2} = 0.07$  V for **3a** and 0.19 V for **3c** as seen in Fig. 9a and is assigned as a one-electron addition to the benzoporphyrin with a dissociated Cl<sup>-</sup> axial ligand, *i.e.* [benzo(TpYPP) Fe<sup>III</sup>]<sup>+</sup>. The second reduction is also assigned as Fe(III)/Fe(II) process, in this case involving the conversion of benzo(TpYPP))<sub>4</sub>Fe<sup>III</sup>Cl to [benzo(TpYPP)Fe<sup>II</sup>Cl]<sup>-</sup> which then rapidly losses the axial Cl<sup>-</sup> ligand. The

four-coordinate Fe(II) product, benzo(TpYPP)Fe<sup>II</sup>, is then re-oxidized at  $E_{pa} = 0.10$  V for **3a** and 0.22 V for **3c** upon reversing the potential scan, as shown in Fig. 9. The Fe(II) porphyrin can also be further reduced at more negative potentials, but this process is ill-defined as shown in Figs S6 and S7.

The three benzoporphyrins all exhibit reversible Fe(III)/ Fe(II) processes when pyridine is used as the solvent. As seen in Fig. 9b, the first one-electron oxidation of **3a** and **3c** is also reversible. The one-electron addition to the benzoporphyrin gives  $benzo(TpYPP)Fe^{II}(Py)_2$  and the one-electron abstraction gives  $[benzo(TpYPP)Fe^{III}(Py)_2]^{2+}$ .

It is well-known that *meso*-phenyl substituents can significantly shift the redox potentials of iron porphyrins [45], and this also the case for the currently examined

9



**Fig. 10.** Thin-layer UV-vis spectral changes of benzo(TpYPP)FeCl **3a–3c** obtained during the first controlled potential reduction in (a) CH<sub>2</sub>Cl<sub>2</sub> and (b) pyridine containing 0.1 M TBAP

benzoporphyrins. As seen in Fig. 9a, the first oxidation and first reduction of compound **3c**, which has four electron-withdrawing Cl substituents on the four *meso*phenyl rings, are shifted positively by 90 mV in CH<sub>2</sub>Cl<sub>2</sub> as compared to potentials for the same redox reaction of compound **3a**, which has four electron-donating CH<sub>3</sub> substituents on the macrocycle. A 70–100 mV difference in  $E_{1/2}$  values is also seen for the first oxidation and first reduction of the same two porphyrins in pyridine (Fig. 9b).

The first reduction of the three benzoporphyrins 3a-3c was examined by thin-layer spectroelectrochemistry in CH<sub>2</sub>Cl<sub>2</sub> and pyridine containing 0.1 M TBAP, and the spectral changes obtained during the controlled potential reduction are shown in Fig. 10. As seen in Fig. 10a, the Soret and Q bands of the Fe(III) porphyrins which are

located at 434–438 and 565–607 nm in  $CH_2Cl_2$  decrease in intensity, while two new bands of the Fe(II) porphyrin grow in at 470–478 and 650–657 nm upon the first reduction.

Figure 10b shows the spectral changes of **3a–3c** during the first controlled potential reduction in pyridine, 0.1 M TBAP. The split Soret band at 399–402 and 461–463 nm, as well as the major Q band at 614–618 nm of the initial six-coordinate compounds, benzo(TpYPP)  $Fe(Py)_2]^+$  all decrease in intensity, while two new absorption bands grow in at 439–441 and 649–655 nm. The original spectrum of the Fe(III) benzoporphyrin could be recovered when the controlled potential was set back to 0.0 V, and this behavior is consistent with the reversible reductions observed by cyclic voltammetry of the compounds in the same solvent (see Fig. 9b).



**Fig. 11.** Cyclic voltammograms of (a) (TpCIPP)FeCl **1c**, (b) butano(TpCIPP) FeCl **2c** and (c) benzo(TpCIPP)FeCl **3c** in pyridine containing 0.1 M TBAP



**Fig. 12.** Cyclic voltammograms showing the first reduction and first oxidation of (a) (TpCH<sub>3</sub>PP)FeCl **1a**, (b) butano(TpCH<sub>3</sub>PP)FeCl **2a** and (c) benzo(TpCH<sub>3</sub>PP)FeCl **3a** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

## Effect of the butano- and benzo-substituents

It was earlier demonstrated that adding fused  $\beta$ , $\beta'$ butano or  $\beta$ , $\beta'$ -benzo groups on a porphyrin macrocycle has a significant effect on the individual reduction and oxidation potentials of cobalt [50] and copper [51] tetraarylporphyrins, and this is also the case for the currently investigated Fe(III) butanoporphyrins and benzoporphyrins. This is shown by the cyclic voltammograms of (TpClPP)FeCl **1c**, butano(TpClPP)FeCl **2c** and benzo(TpClPP)FeCl **3c** in Fig. 11 where the measurements were carried out in pyridine containing 0.1 M TBAP.

All three reductions of butano(TpClPP)FeCl **2c** are negatively shifted by 120–270 mV compared to potentials for the same redox reactions of (TpClPP)FeCl **1c** in pyridine (Fig. 11). This is consistent with the fact that  $\beta$ , $\beta'$ -butano is an electron-donating substituent, which leads to harder reductions compared to the corresponding porphyrins without butano substituents. A 220–260 mV positive shift is seen for the first two reductions of the benzo(TpClPP)FeCl **3c** compared to the same electron transfer process of butano(TpClPP)FeCl **2c** in pyridine (Fig. 11). This positive shift results from the extended  $\pi$ -system of the benzoporphyrins and distortion of the macrocycle [63, 64].

A comparison between potentials for the first reduction and first oxidation of  $(TpCH_3PP)FeCl$ **1a**, butano $(TpCH_3PP)FeCl$  **2a** and benzo- $(TpCH_3PP)FeCl$  **3a** in pyridine is shown in Fig.12. The first reduction of butano $(TpCH_3PP)FeCl$ **2a** is negatively shifted by 340 mV compared to the same electrode reactions of **1a**, while the first oxidation is negatively shifted by 510 mV. The first reduction and first oxidation of **3a** are also positively shifted compared to the related redox reactions of **2a**, with the magnitude of the shift being 50 mV for oxidation and 470 mV for reduction.

#### Effect of central metal ions

Table 2 lists potentials for the first oxidation and first reduction of (TPP)M, butano(TPP)M and benzo(TPP)M (M = Fe<sup>III</sup>Cl, Co<sup>II</sup> or Cu<sup>II</sup>) in CH<sub>2</sub>Cl<sub>2</sub>. The site of electron transfer is given in parenthesis as M or R to indicate a metal or ring-centered electron transfer. The values of  $\Delta E_{ox1}$  and  $\Delta E_{red1}$  shown in the table are the potential differences between the first oxidations and first reductions of butano(TPP)M or benzo(TPP)M and (TPP)M. As seen from the table, all the  $\Delta E_{ox1}$  values are negative for the butano(TPP)M and benzo(TPP)M derivatives, indicating that the butano and benzo groups both lead to an easier oxidation of the porphyrins compared to (TPP)M. The  $\Delta E_{red1}$  values are also negative for butano(TPP)M and consistent with harder

**Table 2.** Comparisons of potentials (V *vs.* SCE) for the first oxidation and reduction between the (TPP)M, butano(TPP)M and benzo(TPP)M ( $M = Fe^{III}Cl, Co^{II} \text{ or } Cu^{II}$ ) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

М	β–β′-sub	1st ox <sup>a</sup>	$\Delta E_{\rm ox1}  ({\rm V})^{\rm b}$	1st red <sup>a</sup>	$\Delta E_{\rm red1} ({\rm V})^{\rm l}$
Fe(III)	none	1.20 (R)		-0.36 (M)	
	butano	0.67 (R)	-0.53	-0.72 (M)	-0.36
	benzo	0.69 (R)	-0.51	-0.19 (M)	+0.17
Co(II) <sup>c</sup>	none	0.70 (M)		-0.88 (M)	
	butano	0.39 (R)	-0.31	-1.02 (M)	-0.14
	benzo	0.44 (M)	-0.26	-0.61 (M)	+0.27
Cu(II) <sup>d</sup>	none	1.04 (R)		-1.28 (R)	
	butano	0.49 (R)	-0.55	-1.55 (R)	-0.27
	benzo	0.55 (R)	-0.49	-1.22 (R)	+0.06

<sup>a</sup>M and R represent a metal-centered and porphyrin ring-centered electron transfer process, respectively.

 $^{\rm b}$  Potential shifts from corresponding reactions of the non- $\beta-\beta'$ -substituted compound.

<sup>c</sup>Data taken from Ref. 50.

<sup>d</sup>Data taken from Ref. 51.

reductions occurring for the Fe(III), Co(II) and Cu(II) butanoporphyrins. However, positive  $\Delta E_{red1}$  values are seen for all the benzo(TPP)M derivatives, indicating that these compounds are easier to reduce in CH<sub>2</sub>Cl<sub>2</sub> than the non- $\beta$ , $\beta'$ -substituted porphyrins (TPP)M under the same solution conditions.

The results discussed above indicate that the effect of butano and benzo groups on the first oxidation and first reduction follow the same trend as all the Fe(III), Co(II) and Cu(II) porphyrins. However, the magnitude of the effect varies with the central metal ions. For example, Cu(II) porphyrins have almost the same  $\Delta E_{ox1}$  values (-0.55 V for butano(TPP)Cu and -0.49 V for benzo(TPP)Cu) as that of Fe(III) derivatives ( $\Delta E_{ox1} = -0.53$  for butano(TPP)FeCl and -0.51 V for benzo(TPP)FeCl). This is probably because the site of electron transfer for the first oxidation is the same on the porphyrin macrocycle for all the Fe(III) and Cu(II) porphyrins. In the case of Co(II) porphyrins, the  $\Delta E_{ox1}$  values are smaller (-0.31 for the butano(TPP)Co and -0.26 V for benzo(TPP)Co) than that of Fe(III) and Cu(II) porphyrins, which may be due to the fact that the oxidation sites of the cobalt(II) derivatives differ from the Fe(III) and Cu(II) porphyrins.

## EXPERIMENTAL

#### Chemicals

Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>,  $\geq$ 99.8%), pyridine (Py,  $\geq$ 99.9%) and tetra-*n*-butylammonium perchlorate (TBAP,  $\geq$ 99.0%) were purchased from Sigma-Aldrich and used as received. The investigated Fe(III) porphyrins were prepared according to procedures in the literature [49–51] and are described below. MS spectra of the porphyrins are shown in Supporting information (see Figs S8–S10).

## Synthesis of (TpYPP)FeCl 1a-1c [53]

(TpYPP)H<sub>2</sub>(0.075 mmol) and excess FeCl<sub>2</sub>·4H<sub>2</sub>O (0.75 mmol) were refluxed in *N*,*N*-dimethylformamide under nitrogen as the progress of the reaction was monitored by UV-vis spectroscopy. After 1h, the resulting solution was washed with HCl (4.7 wt%, 200 mL) and H<sub>2</sub>O (200 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The raw product was chromatographed with a silica gel column using a mixture of ethyl acetate/dichloromethane as eluent (v/v = 1/2). The brown fraction was collected and roto-evaporated to dryness.

 $(TpCH_3PP)FeCl$  1a. Yield, 47.2 mg, 83%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 381$ , 418, 511 nm; MS (MALDI-TOF), *m/z* calcd for [M - Cl]<sup>+</sup> 724.23; found 724.43.

(*TPP*)*FeCl* 1b. Yield, 46.0 mg, 87%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 378$ , 417, 508 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 668.17; found 668.29.

(TpClPP)FeCl 1c. Yield, 54.0 mg, 86%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 380$ , 415, 510 nm; MS (MALDI-TOF), *m/z* calcd for [M - Cl]<sup>+</sup> 804.01; found 806.22.

#### Synthesis of butano(TpYPP)FeCl 2a–2c [49, 54]

Excess FeCl<sub>2</sub>·4H<sub>2</sub>O (0.3 mmol) was added into a N,N-dimethylformamide solution which contained butano(TpYPP)H<sub>2</sub> (0.03 mmol). The reaction solution was refluxed under nitrogen for 2 h and then washed with HCl (4.7 wt%, 200 mL) and H<sub>2</sub>O (200 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated under vacuum, the raw product was purified on a neutral alumina column using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The brown fraction was collected and evaporated under vacuum to dryness.

*Butano*(*TpCH*<sub>3</sub>*PP*)*FeCl* 2*a*. Yield, 16.7 mg, 57%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 399$ , 431 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 941.06; found 941.13.

*Butano*(*TPP*)*FeCl* 2b. Yield, 10.2 mg, 37%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 396$ , 429 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 884.95; found 885.05.

*Butano*(*TpClPP*)*FeCl* 2*c*. Yield, 7.9 mg, 25%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 394$ , 430 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 1022.72; found 1022.92.

#### Synthesis of benzo(TpYPP)FeCl 3a–3c [49, 54]

Excess  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.3 mmol) was added into a solution of benzo(TpYPP)H<sub>2</sub> (0.03 mmol) in *N*,*N*dimethylformamide. The mixture was refluxed under nitrogen for 2 h and then cooled to room temperature. The reaction solution was diluted with  $CHCl_3$  and washed with HCl (4.7 wt%, 200 mL) and H<sub>2</sub>O (200 mL). After drying with  $Na_2SO_4$ , the solution was evaporated with vacuum to remove the solvent. The raw product was purified on a neutral alumina column using  $CHCl_3$  as eluent. The green fraction was collected and roto-evaporated to dryness.

**Benzo**(**TpCH**<sub>3</sub>**PP**)**FeCl 3a.** Yield, 4.0 mg, 14%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 436$ , 606 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 924.93; found 924.88.

**Benzo(TPP)FeCl 3b.** Yield, 16.3 mg, 60%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 430$ , 606 nm; MS (MALDI-TOF): *m/z* calcd for [M – Cl]<sup>+</sup> 868.23; found 868.68.

**Benzo**(**TpClPP**)**FeCl 3c.** Yield, 16.2 mg, 52%; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max} = 434$ , 607 nm; MS (MALDI-TOF), *m/z* calcd for [M – Cl]<sup>+</sup> 1006.59; found 1006.65.

#### Instrumentation

Cyclic voltammetry was carried out at 298 K using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture.

Thin-layer UV-vis spectroelectrochemical experiments were performed using a home-built thin-layer cell, which had a transparent platinum net working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. High purity  $N_2$  from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

# CONCLUSION

 $\beta$ , $\beta'$ -butano and  $\beta$ , $\beta'$ -benzo substituted Fe(III) tetraarylporphyrins were synthesized and the electrochemical and spectroelectrochemical properties of the porphyrin characterized in CH<sub>2</sub>Cl<sub>2</sub> and pyridine containing 0.1 M TBAP. The Fe(III) porphyrins can be singly, doubly or triply reduced to generate Fe(II), Fe(II) porphyrin  $\pi$ -anion radicals or Fe(I) anions and dianions with the exact form of the generated reduction product depending upon the solvent utilized and the potential applied during electroreduction. The  $\beta$ , $\beta'$ -butano and  $\beta$ , $\beta'$ -benzo substituents of Fe(III) porphyrins have a significant effect on the UV-vis spectra and the reduction/oxidation potentials.

#### Acknowledgments

We gratefully acknowledge support from the National Natural Science Foundation of China (Grants 21501070 and 21071067), the Jiangsu University Foundation (Grants 15JDG131 and 05JDG051), the China Postdoctoral Science Foundation (Grant 2017M611707) and the Robert A. Welch Foundation (K.M.K., Grant E-680).

#### Supporting information

Figures S1–S10 are given as supplementary material. This material is available free of charge *via* the internet at http://www.worldscinet.com/jpp/jpp.shtml.

# REFERENCES

- Rao H, Schmidt LC, Bonin J and Robert M. *Nature* 2017; **548**: 74–77.
- Zhang W, Lai W and Cao R. *Chem. Rev.* 2017; 117: 3717–3797.
- Chatterjee S, Sengupta K, Mondal B, Dey S and Dey A. Acc. Chem. Res. 2017; 50: 1744–1753.
- Ascenzi P and Brunori M. J. Porphyrins Phthalocyanines 2016; 20: 134–149.
- Costentin C, Robert M and Saveant JM. Acc. Chem. Res. 2015; 48: 2996–3006.
- Samanta S, Das PK, Chatterjee S and Dey A. J. Porphyrins Phthalocyanines 2015; 19: 92–108.
- 7. Manbeck GF and Fujita E. J. Porphyrins Phthalocyanines 2015; **19**: 45–64.
- Oszajca M, Franke A, Brindell M, Stochel G and Eldik R. *Coord. Chem. Rev.* 2016; **306** (Part 2): 483–509.
- 9. Boehm P and Groeger H. *ChemCatChem* 2015; 7: 22–28.
- Oohora K and Hayashi T. *Curr. Opin. Chem. Biol.* 2014; **19**: 154–161.
- Zhu WH, Ni C, Liang LL, Li JW, Li MZ, Ou ZP and Kadish KM. J. Porphyrins Phthalocyanines 2014; 18: 519–527.
- Zhang Y, Shen W, Ou ZP, Zhu WH, Fang YY and Kadish KM. *Electroanalysis* 2013; 25: 1513–1518.
- 13. Azcarate I, Costentin C, Robert M and Saveant JM. *J. Am. Chem. Soc.* 2016; **138**: 16639–16644.
- 14. Sengupta K, Chatterjee S and Dey A. *ACS Catalysis* 2016; **6**: 6838–6852.
- Choi J, Benedetti TM, Jalili R, Walker A, Wallace GG and Officer DL. *Chem. —Eur. J.* 2016; 22: 14158–14161.
- Römelt C, Song J, Tarrago M, Rees JA, Gastel M, Weyhermüller T, DeBeer S, Bill E, Neese F and Ye S. *Inorg. Chem.* 2017; 56: 4745–4750.
- Mihara N, Yamada Y, Takaya H, Kitagawa Y, Aoyama S, Igawa K, Tomooka K and Tanaka K. *Chem. —Eur. J.* 2017; 23: 7508–7514.
- Rana A, Mondal B, Sen P, Dey S and Dey A. *Inorg. Chem.* 2017; 56: 1783–1793.
- Ambre RB, Daniel Q, Fan T, Chen H, Zhang B, Wang L, Ahlquist MSG, Duan L and Sun L. *Chem. Commun.* 2016; **52**: 14478–14481.

- 20. Azcarate I, Costentin C, Robert M and Saveant JM. *J. Phys. Chem. C* 2016; **120**: 28951–28960.
- 21. Kim S and Kim H. *Catalysis Today* 2017; **295**: 119–124.
- 22. Elhamifar D, Badin P and Karimipoor G. J. Colloid Interface Sci. 2017; **499**: 120–127.
- 23. Zhao R, Wang J, Zhang D, Sun Y, Han B, Tang N, Wang N and Li K. *Appl. Cat.*, A2017; **532**: 26–31.
- 24. Deng X, Fang Y, Lin S, Cheng Q, Liu Q and Zhang X. ACS Appl. Mater Interfaces 2017; 9: 3514–3523.
- 25. Zanatta LD, Barbosa IA, Zanardi FB, de Sousa Filho PC, Bolzon LB, Ramos AP, Serra OA and Iamamoto Y. *RSC Adv.* 2016; **6**: 104886–104896.
- Rebelo SLH, Silva AMN, Medforth CJ and Freire C. *Molecules* 2016; 21: 481/1–481/12.
- Nakamura M, Ohgo Y and Ikezaki A. In *Handbook* of *Porphyrin Science*, Vol. 7, Kadish KM, Smith KM and Guilard R. (Eds.), World Scientific: New Jersey, 2010, pp. 1–146.
- Mittra K, Singha A and Dey A. Dalton Transactions 2016; 45: 18796–18802.
- Weiss R, Gold A, Trautwein AX and Terner J. In *The Porphyrin Handbook*, Vol. 4. Kadish KM, Smith KM and Guilard R. (Eds.), Academic Press: San Diego, 2000; pp. 65–96.
- Fukuzumi S, Nakanishi I, Tanaka K, Suenobu T, Tabard A, Guilard R, Van Caemelbecke E and Kadish KM. J. Am. Chem. Soc. 1999; 121: 785–790.
- 31. Kadish KM, Autret M, Ou ZP, Tagliatesta P, Boschi T and Fares V. *Inorg. Chem.* 1997; **36**: 204–207.
- Kadish KM, Van Caemelbecke E, D'Souza F, Medforth CJ, Smith KM, Tabard A and Guilard R. *Inorg. Chem.* 1995; 34: 2984–2989.
- Kadish KM, D'Souza F, Van Caemelbecke E, Villard A, Lee JD, Tabard A and Guilard R. *Inorg. Chem.* 1993; 32: 4179–4185.
- Kadish KM, Tabard A, Lee W, Liu YH, Ratti C and Guilard, R. *Inorg. Chem.* 1991; **30**: 1542–1549.
- Kadish KM, Boisselier-Cocolios B, Simonet B, Chang D, Ledon H and Cocolios P. *Inorg. Chem.* 1985; 24: 2148–2156.
- Bottomley LA, Olson L and Kadish KM. Adv. Chem. Ser. 1982; 201: 279–311.
- Kadish KM. In *Iron Porphyrins*, Part 2. Lever ABP and Gray HB (Eds.) Addison-Wesley Publishing Co: London, 1983; pp. 161–249.
- Bottomley LA and Kadish KM. *Inorg. Chem.* 1981;
   20: 1348–1357.
- Kadish KM and Bottomley LA. *Inorg. Chem.* 1980; 19: 832–836.
- Kadish KM and Larson G. *Bioinorg. Chem.* 1977; 7: 95–105.
- Kadish KM and Bottomley LA. J. Am. Chem. Soc. 1977; 99: 2380–2382.
- Kadish KM, Morrison MM, Constant LA, Dickens L and Davis DG. J. Am. Chem. Soc. 1976; 98: 8387–8390.

- 43. Kadish KM, Bottomley LA and Beroiz D. *Inorg. Chem.* 1978; **17**: 1124–1129.
- Kadish KM, D'Souza F, Villard A, Van Caemelbecke E, Bianco P, Antonini A and Tagliatesta P. *Inorg. Chem.* 1994; 33: 5169–5170.
- 45. Kadish KM, Van Caemelbecke E and Royal G. In *The Porphyrin Handbook*, Vol. 8, Kadish KM, Smith KM and Guilard R (Eds.) Academic Press: San Diego, 2000; pp. 1–144.
- Yang SB, Sun B, Ou ZP, Meng DY, Lu GF, Fang YY and Kadish KM. J. Porphyrins Phthalocyanines 2013; 17: 857–869.
- Rahman MH and Ryan MD. *Inorg. Chem.* 2017; 56: 3302–3309.
- 48. Carvalho CMB, Brocksom TJ and de Oliveira KT. *Chem. Soc. Rev.* 2013; **42**: 3302–3317.
- Ikeue T, Handa M, Chamberlin A, Ghosh A, Ongayi O, Vicente MGH, Ikezaki A and Nakamura M. *Inorg. Chem.* 2011; **50**: 3567–3581.
- Ye L, Ou Z, Fang Y, Xue S and Kadish KM. *Inorg. Chem.* 2017; **57**: 13613–13626.
- 51. Ye L, Ou Z, Fang Y, Xue S, Song Y, Wang L, Wang M and Kadish KM. *RSC Adv.* 2015; **5**: 77088–77096.
- Chen P, Finikova OS, Ou Z, Vinogradov SA and Kadish KM. *Inorg. Chem.* 2012; **52**: 6200–6210.
- Lindsey JS. In *The Porphyrin Handbook*, Vol. 1, Kadish KM, Smith KM and Guilard R. (Eds.), Academic Press: San Diego, 2000; pp. 62–65.
- 54. Finikova OS, Cheprakov AV, Beletskaya IP, Carroll PJ and Vinogradov SA. *J. Org. Chem.* 2004; **69**: 522–535.
- Kadish KM, Van Caemelbecke E, D'Souza F, Lin M, Nurco DJ, Medforth CJ, Forsyth TP, Krattinger B, Smith KM, Fukuzumi S, Nakanishi I and Shelnutt JA. *Inorg. Chem.* 1999; 38: 2188–2198.
- 56. Lexa D, Mispelter J and Saveant J-M. J. Am. Chem. Soc. 1981; **103**: 6806–6812.
- 57. Gueutin C, Lexa D, Momenteau M and Saveant J-M. J. Am. Chem. Soc. 1990; **112**: 1874–1880.
- Zhang Y, Shen W, Ou Z, Zhu W, Fang Y and Kadish KM. *Electroanalysis* 2013; 25: 1513–1518.
- Tagliatesta P, Li J, Autret M, Van Caemelbecke E, Villard A, D'Souza F and Kadish KM. *Inorg. Chem.* 1996; **35**: 5570–5576.
- Pellegrino J, Hübner R, Doctorovich F and Kaim W. *Chem. —Eur. J.* 2011; **17**: 7868–7874.
- Kadish KM, Shao J, Ou Z, Zhan R, Burdet F, Barbe JM, Gros CP and Guilard R. *Inorg. Chem.* 2005; 44: 9023–9038.
- 62. Kadish KM, Larson G, Lexa D and Momenteau M. *J. Am. Chem. Soc.* 1975; **97**: 282–288.
- 63. Finikova OS, Cheprakov AV, Carroll PJ, Dalosto S and Vinogradov SA. *Inorg. Chem.* 2002; **41**: 6944–6946.
- 64. Cheng RJ, Chen YR, Wang SL and Cheng C. Y. *Polyhedron* 1993; **12**: 1353–1360.