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FULL PAPER

Synthesis, reactivity and spectroscopy of ferrocene-functionalised porphyrins, with a conjugated connection between the ferrocene and the porphyrin core

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Several new ferrocene-functionalised porphyrins and a ruthenocene-functionalised porphyrin have been synthesized and studied using electrochemistry, electronic absorbance and resonance Raman spectroelectrochemical techniques. The porphyrin and ferrocene are observed to have limited effect on each other with the properties of the porphyrin dominating the spectroscopy of these molecules.

Introduction

Compounds containing both a chromophore and a redox site incorporated into a single molecule have extensively been studied as potential chemical sensors.[1] To this end, a multitude of porphyrin systems functionalised with redox groups,[2] such as ferrocene,[3,4] have been prepared. In many cases, the utility of these compounds as chemical sensors has been limited by a lack of suitable communication between the redox group and the porphyrin core. Recently, we described the synthesis of a series of functionalised porphyrins that contain a conjugated link between the porphyrin and an aryl group.[5] These studies indicated that in some cases there is some communication between the functionality on the aryl group and the porphyrin core. Therefore, ferrocene-functionalised porphyrins connected in a similar fashion should also be able to "communicate". This work reports the synthesis and spectroscopic and electrochemical characterisation of some conjugates and their metalloporphyrin derivatives.

Results and discussion

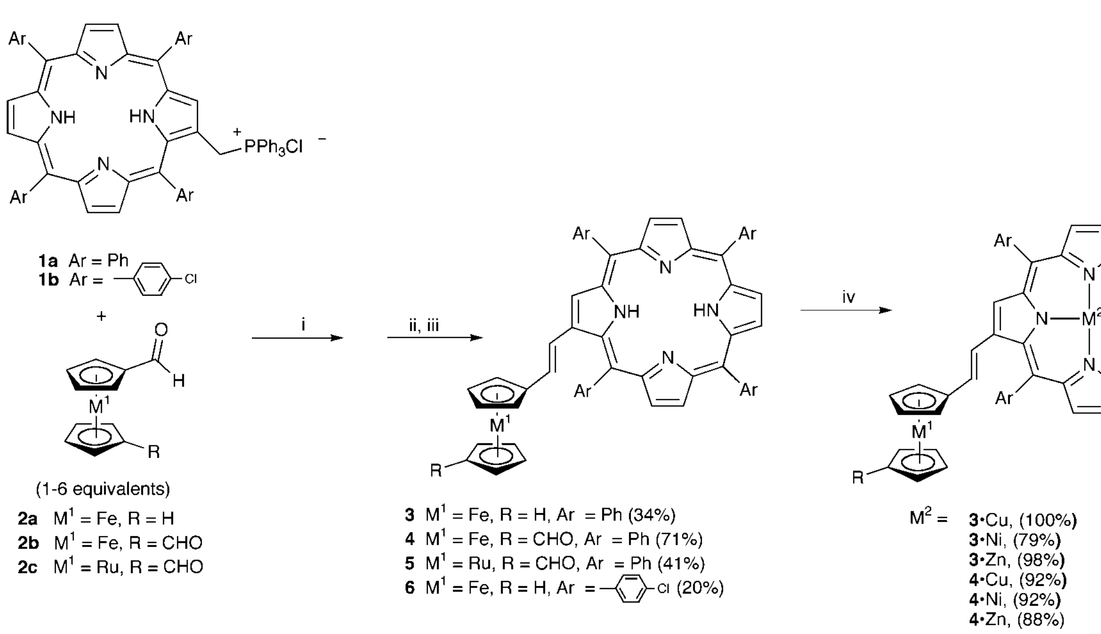
A Synthesis

The ferrocene-functionalised porphyrins **3** and **4** are prepared in good yield from the reaction of the phosphonium salt **1a**[6] with the ferrocenecarbaldehydes **2a** and **2b** respectively (Scheme 1). The initial products from these reactions are inseparable (using standard chromatography) mixtures of the *cis* and *trans* isomers of both **3** and **4**. The formation of both *cis* and *trans* isomers is apparent from an examination of the proton NMR, however treatment of the mixtures with an excess of iodine results in complete conversion into the *trans* isomer and an overall yield for the formation of **3** and **4** of 34% and 71% respectively. Thus, the ^{1}H NMR spectrum of **3** contains a pair of coupled doublets ($J = 15.9$ Hz) arising from the vinylic protons at δ 6.62 and 7.15 respectively, typical of similar porphyrin conjugates.[4,5] The ferrocene protons are also quite distinctive, giving rise to signals at δ 4.21, 4.28 and 4.32. A similar ferrocene-functionalised porphyrin has been synthesized by Morris *et al.*[7] with the same ferrocene–vinyl linkage and the ^{1}H NMR spectrum shows similarities in the ferrocene and vinylic region to that of **3**, although somewhat shifted due to the presence of the ester groups on the porphyrin. The ^{1}H NMR spectrum of **4** is similar to that of **3**, the pattern of substitution of the ferrocene changing as expected for the presence of an aldehyde on the second cyclopentadienyl (Cp) ring giving four signals of equal integrals at δ 4.35, 4.41, 4.62 and 4.81. The ferrocene proton resonances are also shifted slightly downfield relative to **3**.

Metalloporphyrin derivatives of **3** and **4** were also prepared from metal acetate salts.[8] Derivatives **3**·Cu, **3**·Ni, **3**·Zn, **4**·Cu, **4**·Ni and **4**·Zn are obtained in essentially quantitative yield. The ^{1}H NMR spectra of the metalloporphyrin derivatives are similar to those of **3** and **4**, with the absence of the NH pyrrole resonances being the most obvious difference. The presence of Zn causes slight downfield shifts in the β-pyrrolic proton resonances while Ni has a slight shielding effect on the vinyl and porphyrin protons, with these resonances moving upfield by 0.1–0.2 ppm.

A related compound **6** was synthesized from the phosphonium salt of 5,10,15,20-tetra(4-chlorophenyl)porphyrin (**1b**) and ferrocenemonocarbaldehyde (**2a**). The ^{1}H NMR spectrum of **6** is similar to that of **3** with the largest changes being the expected absence of the *para* proton resonances and the upfield shift of the *ortho* proton resonances from the phenyl ring. This demonstrated ability to attach different porphyrins to the ferrocene *via* the vinyl link should facilitate tuning of this molecular system's photo- and redox-active properties.

Ferrocene is not the only metallocenecarbaldehyde that can be treated with phosphonium salt **1a**. This synthetic strategy also works well with 1,1′-diformylruthenocene **2c**.[9] The Wittig reaction and isomerisation was carried out in the same manner as described for **3** and **4** to produce *trans*-porphyrinylruthenocenemonocarbaldehyde **5**. Stabilities and solubilities of this compound paralleled those of *trans*-porphyrinylferrocene **4**. The two highly shielded nitrogen protons in the centre of the aromatic porphyrin ring occur as a broad singlet (δ −2.62). The signals for the non-equivalent protons of the Cp rings are split into four equivalent resonances (δ 4.71, 4.76, 4.89, 5.12). The resonances of the substituted Cp rings are apparent triplets due to splitting from non-equivalent magnetic pathways, typical of an AA′BB′ splitting pattern. The signal from the vinylic protons H_a (δ 6.53) and H_b (δ 6.88) can be seen as an AB quartet (15.7 Hz). The assignment of H_a as the upfield proton has been made on the basis of a small coupling ($^4J = 0.6$ Hz) to the β-pyrrolic H^3 proton in the nickel and zinc metal-



Scheme 1 *Reagents*: (i) DBU; (ii) I_2; (iii) $Na_2S_2O_3$ (aq); (iv) $M(OAc)_2{\cdot}xH_2O$.

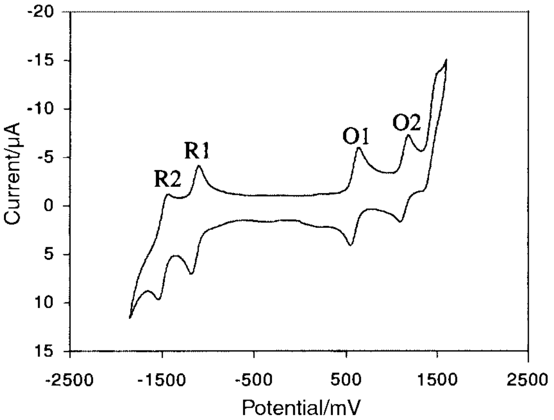


Fig. 1 Cyclic voltammogram of adduct **3**·Cu in CH_2Cl_2; O denotes an oxidation and R a reduction.

loporphyrin derivatives of **3**. The porphyrin and aldehyde resonances are found to be similar in position to those of the ferrocene analogue, **4**.

B Physical measurements

The electrochemistry of strongly coupled units shows large shifts in the $E^{\circ\prime}$ values of the coupled species from those of the parent monomer species.[10] Electrochemical studies performed on **3**, **3**·Cu, **3**·Ni and **3**·Zn showed these compounds to undergo little redox centre communication (Table 1, Fig. 1). All oxidations and reductions observed are reversible one electron processes. The first oxidation, centred on ferrocene, is observed to remain at a very similar value of $E^{\circ\prime}$ to that of unsubstituted ferrocene for all four compounds. This suggests that the porphyrin moiety has very little influence on the ferrocene. The remaining two oxidations and two reductions are those of the porphyrin moiety and are largely unchanged from free TPP.[11]

The UV-visible spectra of compounds **3**, **4**, **5**, **6** and the metalloporphyrin derivatives of **3** and **4** are consistent with the assigned structure but are otherwise unremarkable (Table 2). The ferrocene moiety is seen to have little effect on the absorption spectra of the porphyrin, with the porphyrin bands completely dominating. The free-base compounds show four Q bands and the metallated compounds only two in accordance with the D_{2h} and D_{4h} symmetry of the porphyrin core.[12] The Soret bands of these compounds have a reduced absorption coefficient in comparison to that of TPP but are broadened

Table 1 Electrochemical data for compounds (1×10^{-3} M) in dichloromethane

	$E^{\circ\prime\,a}$/V				
Compound	Oxidation			Reduction	
3	0.48	1.07	1.18	−1.20	−1.49
3·Cu	0.48	1.03	1.31	−1.32	−1.70
3·Ni	0.48	1.10	1.23	−1.27	−1.65
3·Zn	0.48	0.98	1.20	−1.34	−1.72

[a] *vs.* SCE; supporting electrolyte 0.1 mol L^{-1} NBu_4BF_4; scan rate 200 mV s^{-1}.

Table 2 Electronic spectral data for porphyrins and their oxidised and reduced products in dichloromethane at room temperature

Compound	λ/nm ($\varepsilon \times 10^{-3}$/$M^{-1}$ cm^{-1})				
3	423 (263)	521 (19)	572 (11)	604 (12)	655 (3.4)
$\mathbf{3}^{+}$	423 (230)	521 (19)	572 (11)	604 (12)	655 (3.4)
$\mathbf{3}^{2+}$	444 (157)				666 (24)
3·Cu	420 (275)		550 (21)	591 (15)	
3·Cu^{+}	420 (246)		550 (21)	591 (15)	
3·Cu^{2+}	417 (80)				
3·Ni	423 (209)		540 (18)	584 (14)	
3·Zn	425 (282)		560 (20)	598 (12)	
4	424 (263)	524 (24)	568 (15)	601 (12)	655 (3)
4·Cu	421 (234)		549 (21)	587 (15)	
4·Ni	424 (178)		540 (17)	580 (12)	
4·Zn	425 (148)		557 (11)	595 (6)	
6	425 (250)	521 (20)	570 (11)	604 (13)	654 (5)
5	422 (240)	525 (22)	564 (13)	599 (8.3)	655 (2.1)

giving similar integrated absorbances. This is typical of β-vinyl substituted porphyrins.[5,13]

UV-Visible spectroelectrochemistry was performed on compounds **3** and **3**·Cu (Table 2). Importantly the oxidation of the ferrocene moiety had very little effect on the electronic absorption spectra, providing further evidence for the lack of communication between the moieties. The second oxidation probed the first oxidation of the porphyrin moiety. For **3** this resulted in a red shift of the Soret band to 444 nm and the growth of a band at 666 nm. These features are characteristic of the formation of a dication species.[5,13,14] For **3**·Cu the Soret band was observed to decrease in intensity with a small blue shift. These features are typical of the formation of porphyrin π cation radicals.[13,15,16] Reduction of **3** and **3**·Cu showed no observable

Table 3 Frequencies (cm^{-1}) for Raman bands of porphyrins in dichloromethane

TPP[a]	7[b]	3	3^+	3^{2+}	3·Cu	3·Cu^+	3·Cu^{2+}	Assignment[c]	Label[a]
	1624s	1621s	1614s	1627s	1616w			Vinyl[d]	
1597	1598w	1601w		1599w	1598s	1599s	1595s	Phenyl	φ_4
					1580w	1579w	1579w		
1550	1551s	1553s	1553s	1545s	1561s	1560s	1559s	$\nu(C_\beta C_\beta)$	ν_2
1499	1505w	1506w	1507w	1506w				$\nu(C_\beta C_\beta)$	ν_{12}
1438	1449w	1446w	1450w	1448w	1463w	1460w	1461w	$\nu_{asym}(C_\alpha C_m)$	ν_{11}
1357	1380w	1380s	1381s	1383s	1370s	1370s	1365s	$\nu_{sym}(C_\alpha N)$	ν_4
	1330w	1332w	1332w		1343w	1343w	1346w		
1292	1306w	1308w	1312w	1312w	1303w	1304w	1304w	$\nu(C_\alpha C_\beta)$	ν_3
1234	1236s	1237s	1239s	1238s	1240s	1239s	1237s	$\nu(C_\alpha Ph)$	φ_3
1076		1078w	1082w	1078w	1077w	1078w	1080w	$\delta_{sym}(C_\beta H)$	ν_5

s, strong; w, weak. [a] Taken from ref. 17. [b] Taken from ref. 5. [c] Assignments taken from refs. 17, 5 and 13. [d] Assigned as a styryl band for compound **7**.

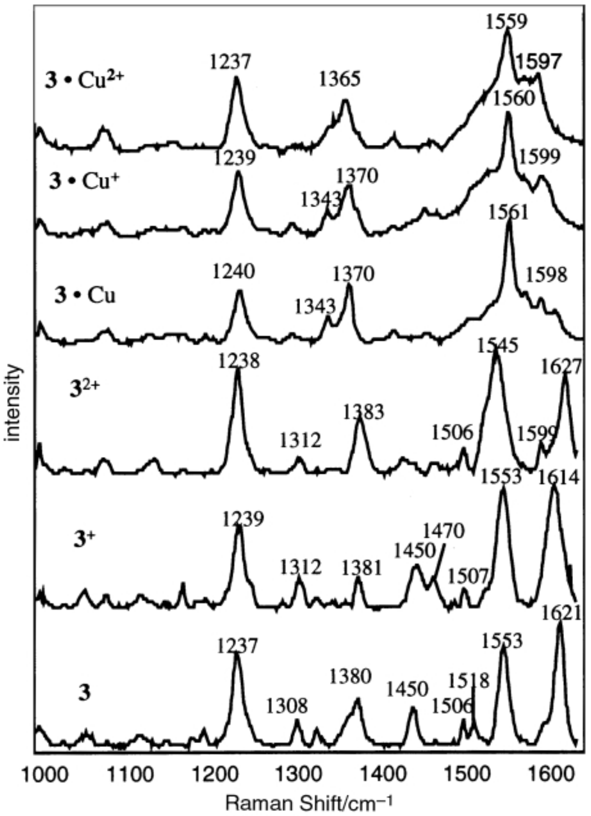
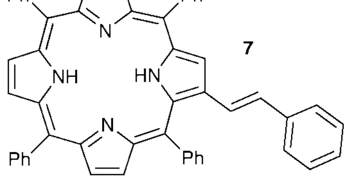


Fig. 2 Resonance Raman spectra of compounds **3**, $\mathbf{3}^+$, $\mathbf{3}^{2+}$, **3**·Cu, **3**·Cu^+ and **3**·Cu^{2+} in dichloromethane (1 mM). Excitation wavelength 457.9 nm (20 mW).

changes in the spectrum although a current was observed indicating that some form of redox process was occurring.

Resonance Raman spectra were recorded of compounds **3** and **3**·Cu (Table 3, Fig. 2). The figure shows all bands to be intense with the solvent peaks obscured by the porphyrin features in the spectra. The band positions of **7** are included in the table for comparison purposes. Both spectra have intense bands at approximately 1553, 1380 and 1237 cm^{-1} while **3** has an additional strong band at 1621 cm^{-1}. The common features of these spectra may be assigned by comparison with the previously assigned spectra of H_2TPP[17] and a series of styryl-substituted TPP porphyrins.[5] These ferrocene porphyrins contain only the vinyl part of the styryl linkage in comparison to the porphyrins studied by Bonfantini *et al.*[5] as illustrated by **7** (Table 3). However, **3** still has the strong 1621 cm^{-1} feature assigned by Bonfantini *et al.*[5] as resulting from the styryl linkage. The fact that the band appears in these ferrocene porphyrins suggests that it is actually associated with the vinylic part of the linkage. The strong features at 1553 cm^{-1} for **3** and 1561 cm^{-1} for **3**·Cu are assigned to be the C_β–C_β stretch (labelled ν_2)[17a] of the porphyrin ring system. Bands at 1446 cm^{-1} for **3** and 1463 cm^{-1} for **3**·Cu are ascribed to the porphyrin ring C_α–C_m stretch (ν_{11} for H_2TPP).[17a] The 1506 cm^{-1} band of **3** is assigned to be the $\nu(C_\beta–C_\beta)$ stretch (ν_{12}) while the band at approximately 1300 cm^{-1} for both is the $\nu_{sym}(C_\alpha–C_\beta)$ stretch (ν_3).[17a] The weak band at 1601 cm^{-1} for **3** and strong 1598 cm^{-1} band for **3**·Cu are the φ_4 phenyl vibration. The strong bands at 1380 (**3**) and 1370 cm^{-1} (**3**·Cu) are ν_4, the symmetric C_α–N stretch.[17a] It can been seen that there are very few differences between the spectra of **3** and **7**, with the most significant being the enhancement of the 1380 cm^{-1} band of **3**. No bands that could be attributed to ferrocene are evident. This is further evidence for the lack of communication between the porphyrin and ferrocene moieties. Some shifts are seen in the positions of the ν_2, ν_{11} and ν_4 bands on substitution of copper into the porphyrin ring.



7

Resonance Raman spectra were also recorded of the electrochemically reduced and oxidised species of **3** and **3**·Cu (Table 3, Fig. 2). The first oxidation of both species results in very few changes. This is to be expected as it is localised on the ferrocene moiety. The second oxidation of **3**, of the porphyrin moiety, results in formation of the porphyrin dication with strong bands at 1545 and 1383 cm^{-1} as previously observed for other porphyrins.[5] Oxidation of the porphyrin moiety of **3**·Cu shows several small changes from the neutral species spectrum, with the biggest shift being in ν_4 from 1370 to 1365 cm^{-1}. This down shift in wavenumber for ν_4 has been observed previously,[18] and for TPP derivatives results in the loss of an electron from an a_{2u} orbital. Reduction of **3** and **3**·Cu has also been carried out but results again in negligible changes.

Conclusion

The synthesis of several new ferrocenyl and ruthenocenyl derivatised porphyrins has been described. Spectroscopic and electrochemical studies have shown there to be no evidence of strong communication between the moieties.

Experimental

Physical measurements

The instrumentation used in the measurement of UV-visible, electrochemical and resonance Raman properties and the protocols have been described elsewhere.[13,19] The electronic absorption spectra of oxidised and reduced species were measured using an optically transparent thin layer electrode (OTTLE) cell with a platinum grid as the working electrode.[20] In these experiments the potential applied was stepped through the redox processes collecting a spectrum at each step. For Raman spectra of oxidised and reduced species a similar cell was employed. In these experiments the potential applied was sufficient to ensure complete reduction of the sample in the irradiated volume.

The ^{1}H nuclear magnetic resonance spectra were obtained at 270 MHz using a JEOL GX270 FT-NMR spectrometer with Tecmag Libra upgrade. Data are expressed in parts per million downfield shift from tetramethylsilane as an internal reference and are reported as position (δ_H), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, and m = multiplet), relative integral, coupling constant (J/Hz) and assignment. All spectra were recorded in deuteriated chloroform. Mass spectra were recorded using a Varian VG70-250S double focusing magnetic sector mass spectrometer with an ionisation potential of 70 eV. Major fragmentations are given as percentages relative to the base peak intensity. Flash chromatography employed Merck Kieselgel 60 (230–400 mesh) with the indicated solvents. Thin-layer chromatography was performed using precoated silica gel plates (Merck Kieselgel $60F_{254}$). The synthesis of compounds **1a**,[6] **7**,[5] **2b**[21] and **2c**[9] has been reported previously. Ferrocenemonocarbaldehyde **2a** was obtained from Strem Chemicals.

Preparations

***trans*-2-Ferrocenylvinyl-5,10,15,20-tetraphenylporphyrin 3.** A solution of phosphonium salt **1a** (500 mg, 0.54 mmol) and ferrocene carbaldehyde **2a** (460 mg, 2.2 mmol) in CCl_4 (60 mL) was heated to reflux under nitrogen when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.32 mL) was added and reflux continued for 10 min. The solution was cooled and solvent removed under reduced pressure. The residue was chromatographed (3 : 1 CH_2Cl_2–hexane) and the product precipitated and dried under high vacuum to yield a *cis*/*trans* mixture (0.5 : 9.5 ratio) of a purple powder. This mixture (240 mg, 0.29 mmol) was dissolved in $CHCl_3$ (30 mL), I_2 (120 mg, 0.47 mmol) added and stirred for 3 h at room temperature. A saturated solution of $Na_2S_2O_3$ (30 mL) was added and stirred vigorously for 20 min. The organic layer was separated and dried (K_2CO_3), and solvent removed under reduced pressure. The residue was chromatographed (2 : 3 CH_2Cl_2–hexane), the product precipitated and dried under vacuum to yield *trans*-product **3** as a purple powder (181 mg, 34%). ^{1}H NMR (270 MHz): δ −2.54 (br s, 2 H, NH), 4.21 (s, 5 H, Cp H), 4.28 (app t, 2 H, J = 1.9, Cp H), 4.32 (app t, 2 H, J = 1.9, Cp H), 6.62 (d, 1 H, ^3J = 15.9, $H_{\textit{trans}\text{-ethenyl}}$), 7.15 (d, 1 H, ^3J = 15.9, $H_{\textit{trans}\text{-ethenyl}}$), 7.71–8.00 (m, 12 H, $H_{m,p\text{Ph}}$), 8.18–8.84 (m, 8 H, $H_{o\text{Ph}}$), 8.69 and 8.77 (ABq, 2 H, ^3J = 4.9, $H^{7,8}$ or $H^{18,17}$), 8.77 and 8.81 (ABq, 2 H, ^3J = 4.9, $H^{7,8}$ or $H^{18,17}$), 8.86 (app t, 2 H, ^3J = 5.2 Hz, $H^{12,13}$) and 8.98 (s, 1 H, H^3). FAB HRMS: m/z = 825.2678 (MH^+, 100%). Calculated for $C_{56}H_{41}FeN_4$, MH^+: m/z = 825.2681.

***trans*-2-(1′-Formylferrocenylvinyl)-5,10,15,20-tetraphenylporphyrin 4.** A solution of phosphonium salt **1a** (1.0 g, 1.1 mmol) and 1,1′-ferrocenedicarbaldehyde **2b** (810 mg, 3.4 mmol) in 1,2-dichloroethane (90 mL) was heated to reflux. The compound DBU (0.68 mL) was added, and reflux continued for 10 min. The solution was cooled and solvent removed under reduced pressure. The residue was chromatographed (2 : 1 CH_2Cl_2–hexane). Solvent was removed under reduced pressure to yield a *cis*/*trans* mixture of a purple solid (^{1}H NMR, 0.5 : 9.5). The mixture (810 mg, 0.95 mmol) was dissolved in CH_2Cl_2 (50 mL), I_2 (500 mg, 2.0 mmol) added and stirred for 3 h at room temperature. A saturated solution of $Na_2S_2O_3$ (30 mL) was added and stirred vigorously for 30 min. The organic layer was separated and washed (water, 2 × 50 mL), then dried (K_2CO_3) and solvent removed under reduced pressure. The product was precipitated from a solution of $CHCl_3$ with MeOH and dried under high vacuum to yield *trans*-product **4** as a purple powder (680 mg, 71%). ^{1}H NMR (270 MHz): δ −2.58 (br s, 2 H, NH), 4.35 (app t, 2 H, J = 1.7, Cp H), 4.41 (app t, 2 H, J = 1.7, Cp H), 4.62 (app t, 2 H, J = 1.8, Cp $H_{\text{Cp-CHO}}$), 4.81 (app t, 2 H, J = 1.8, Cp $H_{\text{Cp-CHO}}$), 6.64 (d, 1 H, ^3J = 15.9, $H_{\textit{trans}\text{-ethenyl}}$), 7.01 (d, 1 H, ^3J = 15.9 Hz, $H_{\textit{trans}\text{-ethenyl}}$), 7.72–7.98 (m, 12 H, $H_{m,p\text{Ph}}$), 8.14–8.30 (m, 8 H, $H_{o\text{Ph}}$), 8.69–8.83 (m, 4 H, $H^{7,8,17,18}$), 8.85 (s, 2 H, $H^{12,13}$), 8.98 (s, 1 H, H^3) and 9.97 (s, 2 H, H_{CHO}). FAB HRMS: m/z = 853.2670 (MH^+, 100%). Calculated for $C_{57}H_{41}FeN_4O$, MH^+: m/z = 853.2630.

(*trans*-2-Ferrocenylvinyl-5,10,15,20-tetraphenylporphyrinato)copper(II) 3·Cu. To a solution of porphyrinylferrocene **3** (12 mg, 0.02 mmol) in $CHCl_3$ (20 mL) was added a solution of $Cu(OAc)_2 \cdot H_2O$ (4 mg) in MeOH (3 mL) and the mixture heated to reflux under nitrogen and then cooled. The organic layer was washed with water–MeOH (1 : 1, 50 mL × 2), separated and dried (K_2CO_3), filtered and solvent removed to yield product **3**·Cu as a purple solid (13 mg, 100%). FAB HRMS: m/z = 885.1730 (M^+, 100%). Calculated for $C_{56}H_{38}CuFeN_4$, M^+: m/z 885.1742.

[*trans*-2-(1′-Formylferrocenylvinyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) 4·Cu. Porphyrinylferrocene **4** (22 mg, 0.03 mmol) was dissolved in $CHCl_3$ (8 mL) and a solution of $Cu(OAc)_2 \cdot H_2O$ (11 mg) in MeOH (1 mL) added. The mixture was heated to reflux temperature and after 10 min the red solution was cooled and solvent removed under reduced pressure. The residue was chromatographed (CH_2Cl_2) and the solvent removed under reduced pressure, then dried under high vacuum to yield product **4**·Cu as a purple solid (21 mg, 92%). FAB HRMS: m/z = 913.1922 (M^+, 64%). Calculated for $C_{57}H_{38}CuFeN_4O$, M^+: m/z 913.1691.

(*trans*-2-Ferrocenylvinyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) 3·Ni. Porphyrinylferrocene **3** (60 mg, 0.073 mmol) was dissolved in $CHCl_3$ (10 mL) and a solution of $Ni(OAc)_2 \cdot 4H_2O$ (170 mg) in MeOH (1 mL) added, followed by DBU (0.10 mL). The mixture was heated to reflux under nitrogen. After 16 h reaction was judged complete and the resulting deep red solution allowed to cool. Solvent was reduced and the residue adsorbed onto silica and chromatographed (2 : 3 CH_2Cl_2–hexane). The first band was collected, the solvent removed under reduced pressure, and the product precipitated from a CH_2Cl_2–MeOH solution. This was then filtered off and dried under high vacuum to yield product **3**·Ni as a purple powder (51 mg, 79%). ^{1}H NMR (270 MHz): δ 4.16 (s, 5 H, Cp H), 4.20 (t, 2 H, J = 1.8, Cp H), 4.27 (t, 2 H, J = 1.8, Cp H), 6.45 (dd, 1 H, ^3J = 15.9, ^4J = 0.8, $H_{\textit{trans}\text{-ethenyl}}$), 6.95 (d, 1 H, ^3J = 15.9, $H_{\textit{trans}\text{-ethenyl}}$), 7.63–7.91 (m, 12 H, $H_{m,p\text{Ph}}$), 7.96–8.08 (m, 8 H, $H_{o\text{Ph}}$), 8.66–8.74 (m, 6 H, $H^{7,8,12,13,17,18}$) and 8.83 (d, 1 H, ^4J = 0.8 Hz, H^3). FAB HRMS: m/z = 880.1770 (M^+, 100%). Calculated for $C_{56}H_{38}FeN_4Ni$, M^+: m/z = 880.1799.

[*trans*-2-(1′-Formylferrocenylvinyl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) 4·Ni. Porphyrinylferrocene **4** (330 mg, 0.39 mmol) was dissolved in $CHCl_3$ (50 mL) and a solution of $Ni(OAc)_2 \cdot 4H_2O$ (1.4 g) in MeOH (5 mL) added. The mixture was heated to reflux under nitrogen and after 9.5 h reaction was judged complete and the resulting deep red solution allowed to cool overnight. The reaction mixture was washed with water–MeOH (9 : 1, 50 mL × 2) then water (50 mL). The organic layer was separated and dried (K_2CO_3), filtered and solvent removed under reduced pressure. The product was purified by precipitation from a solution of CH_2Cl_2 with MeOH, filtered and dried under high vacuum to yield product **4**·Ni as a purple powder (322 mg, 91.5%). ^{1}H NMR (270 MHz): δ 4.29 (app t, 2 H,

$J = 1.7$, Cp H), 4.37 (app t, 2 H, $J = 1.7$, Cp H), 4.58 (app t, 2 H, $J = 1.9$, Cp $H_{Cp\text{-}CHO}$), 4.78 (app t, 2 H, $J = 1.9$, Cp $H_{Cp\text{-}CHO}$), 6.51 (dd, 1 H, $^3J = 15.9$, $^4J = 0.6$, $H_{trans\text{-ethenyl}}$), 6.85 (d, 1 H, $^3J = 15.9$, $H_{trans\text{-ethenyl}}$), 7.68–7.83 (m, 12 H, $H_{m,pPh}$), 7.99–8.08 (m, 8 H, H_{oPh}), 8.69–8.74 (m, 6 H, $H^{7,8,12,13,17,18}$), 8.88 (d, 1 H, $^4J = 0.6$ Hz, H^3) and 9.94 (s, 1 H, H_{CHO}). FAB HRMS: $m/z = 908.1763$ (M^+, 100%). Calculated for $C_{57}H_{38}FeNiO$, M^+: $m/z = 908.1748$.

(*trans*-2-Ferrocenylvinyl-5,10,15,20-tetraphenylporphyrinato)zinc(II) 3·Zn. Porphyrinylferrocene **3** (100 mg, 0.12 mmol) was dissolved in $CHCl_3$ (15 mL) and a solution of $Zn(OAc)_2{\cdot}2H_2O$ (260 mg) in MeOH (1 mL) added. After 2 min stirring at room temperature reaction was complete and the resulting red solution filtered through a plug of silica gel and solvent diminished under reduced pressure. The product was precipitated from a solution of CH_2Cl_2 with MeOH, filtered and dried under high vacuum to yield product **3**·Zn as a purple powder (110 mg, 98%). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 4.19 (s, 5 H, Cp H), 4.27 (app t, 2 H, $J = 1.5$, Cp H), 4.29 (app t, 2 H, $J = 1.5$, Cp H), 6.45 (dd, 1 H, $^3J = 15.8$, $^4J = 0.6$, $H_{trans\text{-ethenyl}}$), 7.09 (d, 1 H, $^3J = 15.8$, $H_{trans\text{-ethenyl}}$), 7.71–7.99 (m, 12 H, $H_{m,pPh}$), 8.18–8.30 (m, 8 H, H_{oPh}), 8.78 and 8.89 (ABq, 2 H, $^3J = 4.6$, $H^{7,8}$ or $H^{18,17}$), 8.89 and 8.94 (ABq, 2 H, $^3J = 4.6$, $H^{7,8}$ or $H^{18,17}$), 8.91 (s, 2 H, $H^{12,13}$) and 9.05 (d, 1 H, $^4J = 0.6$ Hz, H_3). FAB HRMS: $m/z = 886.1722$ (M^+, 100%). Calculated for $C_{56}H_{38}FeN_4Ni$, M^+: $m/z = 886.1737$.

[*trans*-2-(1′-Formylferrocenylvinyl)-5,10,15,20-tetraphenylporphyrinato]zinc(II) 4·Zn. Porphyrinylferrocene **4** (35 mg, 0.038 mmol) was dissolved in $CHCl_3$ (10 mL). While stirring, a solution of $Zn(OAc)_2{\cdot}2H_2O$ (10 mg) in MeOH (1 mL) was added. After 20 min stirring at room temperature solvent was removed under reduced pressure. The residue was chromatographed (CH_2Cl_2) and the product precipitated from CH_2Cl_2 with MeOH, filtered and dried under high vacuum to yield product **4**·Zn as a purple powder (33 mg, 88%). ^{1}H NMR (270 MHz): δ 4.34 (app t, 2 H, $J = 1.8$, Cp H), 4.38 (app t, 2 H, $J = 1.8$, Cp H), 4.61 (app t, 2 H, $J = 1.8$, Cp $H_{Cp\text{-}CHO}$), 4.78 (app t, 2 H, $J = 1.8$, Cp $H_{Cp\text{-}CHO}$), 6.66 (dd, 1 H, $^3J = 15.8$, $^4J = 0.6$, $H_{trans\text{-ethenyl}}$), 6.96 (d, 1 H, $^3J = 15.8$, $H_{trans\text{-ethenyl}}$), 7.75–7.93 (m, 12 H, $H_{m,pPh}$), 8.19–8.29 (m, 8 H, H_{oPh}), 8.78–8.96 (m, 6 H, $H^{7,8,12,13,17,18}$), 9.06 (d, 1 H, $^4J = 0.6$ Hz, H^3) and 9.87 (s, 1 H, H_{CHO}). FAB HRMS: $m/z = 914.1661$ (M^+, 100%). Calculated for $C_{57}H_{38}FeN_4OZn$, M^+: $m/z = 914.1686$.

[*trans*-5,10,15,20-Tetra(4-chlorophenyl)-2-ferrocenylvinyl]porphyrin 6. The compound DBU (0.014 mL) was added over 30 min to a solution of phosphonium salt[22] **1b** (17 mg, 0.016 mmol) and ferrocenemonocarbaldehyde **2a** (21 mg, 0.098 mmol) in $CHCl_3$ (3 mL) while stirring at room temperature. Iodine (24 mg, 0.095 mmol) was then added and the reaction mixture stirred for 3 h at room temperature. A saturated solution of $Na_2S_2O_3$ (3 mL) was added and the mixture stirred vigorously for 20 min. The organic layer was separated and dried (K_2CO_3), filtered and the solvent removed under reduced pressure. The residue was chromatographed (1 : 2 CH_2Cl_2–hexane), the product collected in the second band and then precipitated from a solution of CH_2Cl_2 with MeOH, filtered and dried under high vacuum to yield a *trans*-product **6** as a purple powder (3 mg, 20%). ^{1}H NMR (270 MHz): δ −2.66 (br s, 2 H, NH), 4.25 (s, 5 H, Cp H), 4.32 (app t, 2 H, $J = 1.7$, Cp H), 4.39 (app t, 2 H, $J = 1.7$, Cp H), 6.53 (d, 1 H, $^3J = 15.9$, $H_{trans\text{-ethenyl}}$), 7.19 (d, 1 H, $^3J = 15.9$, $H_{trans\text{-ethenyl}}$), 7.72–7.88 (m, 8 H, H_{mPh}), 8.10–8.20 (m, 8 H, H_{oPh}), 8.70 and 8.75 (ABq, 2 H, $^3J = 4.9$, $H^{7,8}$ or $H^{17,18}$), 8.75 and 8.79 (ABq, 2 H, $^3J = 4.9$ Hz, $H^{7,8}$ or $H^{17,18}$), 8.84 (s, 2 H, $H^{12,13}$) and 8.90 (s, 1 H, H^3). FAB HRMS: $m/z = 962.1051$ (M^+, 100%). Calculated for $C_{56}H_{36}Cl_4FeN_4$, M^+: $m/z = 962.1013$.

***trans*-(1′-Formylruthenocenylvinyl)-5,10,15,20-tetraphenylporphyrin 5.** The compound DBU (0.25 mL) was added to a solution of phosphonium salt **1a** (260 mg, 0.28 mmol) and ruthenocene-1,1′-dicarbaldehyde **2c** (80 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) at room temperature under nitrogen. After 15 min the reaction was complete and solvent removed under reduced pressure. The residue was chromatographed ($CHCl_3$) and solvent removed under reduced pressure and high vacuum to yield a *cis*/*trans* mixture of a purple solid (^{1}H NMR, 2.5 : 7.5). The mixture (115 mg, 0.13 mmol) was dissolved in $CHCl_3$ (30 mL), I_2 (65 mg, 0.26 mmol) added, and stirred for 3 h at room temperature. A saturated solution of $Na_2S_2O_3$ (10 mL) was added and stirred vigorously overnight. The organic layer was separated and washed (water, 2 × 30 mL), separated and dried (K_2CO_3), filtered and solvent removed under reduced pressure. The product was precipitated from CH_2Cl_2 with MeOH, and dried under high vacuum to yield *trans*-product **5** as a purple powder (93 mg, 41%). ^{1}H NMR (270 MHz): δ −2.616 (br s, 2 H, NH), 4.71 (app t, 2 H, $J = 1.5$, Cp H), 4.76 (app t, 2 H, $J = 1.7$, Cp H), 4.89 (app t, 2 H, $J = 1.7$, Cp $H_{Cp\text{-}CHO}$), 5.12 (app t, 2 H, $J = 1.8$, Cp $H_{Cp\text{-}CHO}$), 6.53 (dd, 1 H, $^3J = 15.7$, $^4J = 0.6$, $H_{trans\text{-ethenyl}}$), 6.88 (d, 1 H, $^3J = 15.7$ Hz, $H_{trans\text{-ethenyl}}$), 7.72–7.92 (m, 12 H, $H_{m,pPh}$), 8.15–8.27 (m, 8 H, H_{oPh}), 8.68–8.90 (m, 7 H, $H^{3,7,8,12,13,17,18}$) and 9.71 (s, 1 H, H_{CHO}). FAB HRMS: $m/z = 898.2367$ (MH^+, 100%). Calculated for $C_{57}H_{41}N_4ORu$, MH^+: $m/z = 898.2336$.

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