Synthesis, characterisation and magnetic behaviour of ionic metalloporphyrins: metal-tetrakis(N-octyl-4-pyridinium)-porphyrins with tetrabromoferrate(III) anions

Na Zhou^a, Zhicheng Sun^b, Qing Zhou^b, Xingmei Lu^b and Huawu Shao^a*

^aNatural Products Research Centre, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu, Sichuan 610041, P. R. China ^bBeijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China

A series of magnetic, ionic-substituted tetrapyridyl metalloporphyrins, [tetrakis(N-octyl-4-pyridinium)–metal–porphyrin][tetrabromoferrate(III)]₄ (metal=iron, cobalt, manganese, copper or zinc), have been synthesised. All compounds show weak ferromagnetic behaviour at room temperature and respond to an external neodymium magnet.

Keywords: [tetrakis(N-octyl-4-pyridinium)-metal-porphyrin][tetrabromoferrate(III)]4, magnetism, macrocycles

Metalloporphyrins, model compound of biological enzymes, have been extensively studied because of their far-ranging applications in separation, synthesis, catalysis, energy transfer, coordination chemistry and novel materials.¹⁻⁶ Being the analogues of cytochrome P450, metalloporphyrins may take a similar role in catalysing a series of oxidative reactions including epoxidation of olefins and hydroxylation of hydrocarbons under mild conditions without additional co-reductant.⁷⁻¹¹ However, the realisation of efficient catalyst separation in a reaction system is a major problem in porphyrin chemistry. Various methods, including immobilisation of homogeneous catalysts on inorganic supports, have been developed.¹²⁻¹⁶ Nevertheless, the resulting simple recovery was always at the expense of decreased reactive performance due to reduction of the active surface area of the heterogeneous catalysts.¹⁷⁻¹⁹

Recently, paramagnetic ionic liquids, composed mostly of organic ions with the special properties of showing good magnetic field response and solubility, have gained importance in ionic liquid chemistry.²⁰⁻²⁴ These paramagnetic ionic liquids have helped to provide fresh perspectives in separation and catalytic chemistry applications. With the aid of a magnetic field, they provide a completely novel tool to solve the loss of catalysts in industrial processes. In addition, magnetic properties have, to some degree, positive catalytic impacts on certain chemical reactions.

In our work, we aimed to develop a series of novel magnetic ionic metalloporphyrin catalysts by incorporating the paramagnetic anion tetrabromoferrate(III) (FeBr₄⁻) into the water soluble metalloporphyrins (Fig. 1), which can be recycled



Fig. 1 Structures of the magnetic ionic substituted tetrapyridyl metalloporphyrins:[tetrakis(N-octyl-4-pyridinium)-metal-porphyrin][tetrabromoferrate(III)]₄ [TMPyPC₈(FeBr₄)₄].

effectively by virtue of magnetic character under a magnetic field. Therefore we have prepared a series of ionic metalloporphyrins with iron, cobalt, manganese, copper or zinc as the central metal by means of the multi-steps synthetic method shown in Scheme 1 and characterised them by elemental analysis and ¹H NMR, UV-Vis, FT-IR, ES-MS and Raman spectroscopy.

We have investigated and compared the effect of the central metal ions as well as anion incorporation. Furthermore, other than the metalloporphyrin with halogenide anions, the coordination of FeBr_4^- improved water-solubility and magnetic response of the obtained products, confering weak ferromagnetic behaviour at room temperature. Interestingly, samples of the magnetic ionic metalloporphyrins showed a strong response to a neodymium magnet, making them attactive candidates as "reusable compounds" in different systems.

Results and discussion

In this paper, we use the notation 'TMPyPC₈ + (anion)₄' to represent the ionic salts which are composed of a tetrakis(N-octyl-4-pyridinium)–metal–porphyrin cation and Br⁻ or FeBr₄⁻ anions. M, (Fe, Co, Mn, Cu, or Zn), represents the central metal ion of the cation and C₈ represents the alkyl group (C_nH_{2n+1}) attached to the N-position of the pyridinium. TMPyP is used to represent the neutral metalloporphyrin of tetrakis-(4-pyridyl)–metal–porphyrin. For example, [tetrakis(N-octyl-4-pyridinium)-iron-porphyrin][tetrabromoferrate(III)]₄ is indicated as "TFePyPC₈ (FeBr₄)₄" and tetrakis-(4-pyridyl)-zinc-porphyrin as "TZnPyP".

Synthesis

The synthetic route used for the preparation of these novel water-soluble, magnetic, ionic metalloporphyrins is shown in Scheme 1. The free-base tetrakis-(4-pyridyl)-porphyrin, H₂TPyP, was synthesised, as described elsewhere,^{25–27} from the propionic acid-catalysed condensation of freshly distilled pyrrole with pyridine-4-carboxaldehyde. Then by adding excess 1-bromooctane to H₂TPyP at refluxing temperature, tetrakis(Noctyl-4-pyridinium)-porphyrin bromide, H₂TPyPC₈Br₄, was synthesised in nearly quantitative yield.^{28–29} The desired products, [tetrakis(N-octyl-4-pyridinium)-metal–porphyrin] [tetrabromo-ferrate(III)]₄, [TMPyPC₈(FeBr₄)₄], were obtained by adding a slight molar excess of FeBr₃ to TMPyPC₈Br₄, under refluxing temperature for 48 h.³⁰⁻³² A total of five water-soluble, magnetic, ionic substituted tetrapyridyl metalloporphyrins were prepared in yields above 75%.

Thermal properties

Thermogravimetric analysis (TGA) curves for representative samples of $TMPyPC_8(FeBr_4)_4$ under a dinitrogen atmosphere

^{*} Correspondent. E-mail: shaohw@cib.ac.cn



Scheme 1 Synthesis of ionic-substituted tetrapyridylmetalloporphyrins: TMPyPC₈(FeBr₄)₄.

are shown in Fig. 2. The determined decomposition temperatures taken from the onset of weight loss are listed in Table 1. In general, the magnetic metalloporphyrin derivatives showed a progressive weight loss throughout the whole temperature scan (up to 800 $^{\circ}$ C).

More specifically, the weight losses for $TMPyPC_8(FeBr_4)_4$ were all observed above 250 °C, and the weight loss in some circumstances was followed by a second or even third decomposition during the thermal process. For example, $TMnPyPC_8(FeBr_4)_4$ decomposed first at 330 °C, showing a weight loss of 35%, then a second decomposition occurred at 580 °C. The higher temperature of the second decomposition



Fig. 2 TGA curves for $\mathsf{TMPyPC}_{\scriptscriptstyle 8}(\mathsf{FeBr}_{\scriptscriptstyle 4})_{\scriptscriptstyle 4}$ as a function of central metal ion.

 Table 1
 TGA, density and molar concentration data for the synthesised magnetic metalloporphyrin derivatives

Compounds	$T_d/^{\circ}C^{a}$	d ^b g ⁻¹ cm ⁻³	c °/mol cm ⁻³
TFePyPC ₈ (FeBr ₄) ₄	340 (580)	2.0339	7.74×10 ⁻⁴
TCoPyPC ₈ (FeBr ₄) ₄	250 (330, 590)	1.8156	6.90×10 ⁻⁴
TMnPyPC ₈ (FeBr ₄) ₄	330 (580)	1.8774	7.15×10 ⁻⁴
TCuPyPC ₈ (FeBr ₄) ₄	340 (565)	2.2134	8.40×10 ⁻⁴
TZnPyPC ₈ (FeBr ₄) ₄	250	2.1093	8.00×10 ⁻⁴
	Compounds TFePyPC ₈ (FeBr ₄) ₄ TCoPyPC ₈ (FeBr ₄) ₄ TMnPyPC ₈ (FeBr ₄) ₄ TCuPyPC ₈ (FeBr ₄) ₄ TZnPyPC ₈ (FeBr ₄) ₄	$\begin{tabular}{ c c c c } \hline C & c & c & c & c & c & c & c & c & c &$	$\begin{tabular}{ c c c c c } \hline C & C & d & b & g^{-1} & cm^{-3} \\ \hline TFePyPC_8(FeBr_4)_4 & 340 & (580) & 2.0339 \\ TCoPyPC_8(FeBr_4)_4 & 250 & (330, 590) & 1.8156 \\ TMnPyPC_8(FeBr_4)_4 & 330 & (580) & 1.8774 \\ TCuPyPC_8(FeBr_4)_4 & 340 & (565) & 2.2134 \\ TZnPyPC_8(FeBr_4)_4 & 250 & 2.1093 \\ \hline \end{tabular}$

 ${}^{a}T_{d}/TGA = decomposition temperatures, {}^{b}d = density/25 {}^{\circ}C,$ ${}^{\circ}c = molar concentration.$ can be attributed to the increased symmetry of the metalloporphyrins prepared. The above-mentioned decomposition mode suggests that the weight loss began with the paramagnetic anions FeBr₄⁻ and then turned to the metalloporphyrin cations TMPyPC₈⁺, which illustrates the ionic association in the FeBr₄⁻ salts prepared. This special phenomenon can be rationalised on the basis of the more significant nephelauxetic effect together with the lower molar concentration in the FeBr₄⁻ salts. Further experiments will be performed in our laboratories to gain more precise information about the process of decomposition.

Density

Density values of the magnetic metalloporphyrins were also obtained. Due to the greater mass of metalloporphyrin cations, the density values of the magnetic metalloporphyrin derivatives, shown in Table 1, substantially exceed that of simple FeBr_4^- salts such as [1-octyl-3-methylimidazolium][FeBr $_4^-$] (d = 1.74 g cm⁻³).²⁰⁻²³ Decreased density values were observed in the following order: TCuPyPC₈(FeBr $_4$)₄>TZnPyPC₈(FeBr $_4$)₄ > TFePyPC₈(FeBr $_4$)₄ >TMnPyPC₈(FeBr $_4$)₄ >TCoPyPC₈(FeBr $_4$)₄.

Molar concentration, estimated from the density and formula weight as a function of central metal ion, is presented in Fig. 3 and Table 1. Apparently, density values show similar



Fig. 3 Dependence of the molar concentration () with density () for TMPyPC_8(FeBr_4)_4.

variation trends to those of the molar concentrations. Keeping the anion constant (FeBr₄⁻), the molar concentration values of the magnetic metalloporphyrin-based cations are less than those of the salts containing smaller cations. This can be attributed to the larger van der Waals (vdW) volumes of metalloporphyrin-based cations.

Electronic absorption spectra

The UV-Vis spectra data for the prepared porphyrin derivatives are given in Table 2. The neutral porphyrin {TPyP} showed a typical electronic spectrum of a meso-substituted porphyrin in CHCl₃ with a sharp Soret band at 416 nm and four Q-bands at 512, 546, 588 and 644 nm (entry 1, Table 2). Alkylation on pyridinium of the neutral porphyrin {TPyP}, caused the Soret band of this precursor to red-shift by 10 nm (entry 1 and 2, Table 2).

Interestingly, once the central metal ions were embedded into the ionic porphyrin ligands H2TPyPC8Br4, an evident decrease of wavelength as well as intensity for the related Q bands and shift-changes of the Soret band are found, owing to the improved symmetry of the metalloporphyrin molecules. Both properties can be regarded as diagnostic for the generation of corresponding metalloporphyrins TMPyPC₈Br₄ (entries 8–12, Table 2). Specifically, for the cobalt, manganese or zinc based metalloporphyrins, the Soret bands were blue-shifted. The above mentioned shift-change on Soret bands for metalloporphyrins TMPyPC₈Br₄ can be explained by coordination chemistry theory, namely electron flow in the σ and π bonds generated by the coordination of the central metal ions with the porphyrin ring. In the σ bond, flow is from the porphyrin ring to metal ions, leading to a decreased electron density on the porphyrin ring, whereas for the π bond, electrons flow from the metal ions to porphyrin ring, which leads to an increased electron density on the porphyrin ring. Thus the decreased/ increased electron density on the porphyrin ring changes the electron energy needed to transfer to a higher/lower energy level, leading to the corresponding shift-change of the Soret band. Being more specific, when σ bonds have greater influences on the electron density on the porphyrin ring, the Soret band is blue-shifted, conversely red-shifted. This phenomenon can also be found for the neutral metalloporphyrins TMPyP (entries 3–7, Table 2). As for the final products TMPyPC₈(FeBr₄)₄, the generation of FeBr₄⁻ anions equally induces certain shift-changes of the Soret band, albeit smaller (entries 13-17, Table 2).



Fig. 4 UV-V is spectra for representative samples: $a=TPyPC_8Br_4$, $b=TCoPyPC_8Br_4$, $c=TCoPyPC_8(FeBr_4)_4$.

Figure 4 presents UV-Vis spectra for representative samples (entries 2, 9 and 14, Table 2). As shown in Fig. 4, the Soret band of TCoPyPC₈(FeBr₄)₄ is significantly broadened, and additionally its extinction coeffcients are remarkably decreased, relative to the precursor H_2 TPyPC₈Br₄ as well as TMPyPC₈Br₄. Such variations also occur for the other four compounds prepared. In summary, the typical UV-Vis spectra absorption bands illustrate, to some extent, the structural validity of the porphyrin derivatives synthesised.^{25–27}

IR spectra

Dominant IR bands for the synthesised porphyrin derivatives are listed in Table 3. It can be concluded that C–H bands for pyrrolyl and pyridyl of the synthesised porphyrin derivatives appeared mainly within the 3030–3114 cm⁻¹ range, while the frequencies of the stretching vibrations of C=C and C=N of the porphyrin are, respectively, within the 1593–1653 cm⁻¹ and 1342–1387 cm⁻¹ ranges. Peaks appearing at -793 cm⁻¹ are assigned to the 1,4-disubstituents of pyridyl on the porphyrin ring.

Raman spectroscopy

In order to study the compositions of $TMnPyPC_8(FeBr_4)_4$ in more detail, Raman spectroscopy was used to illustrate the

 Table 2
 UV-Vis absorption data for for the synthesised porphyrin derivatives

Entry 1	Compound	Solvents CHCl ₃	λ _{max} , nm (ε×10 ⁻³ , M ⁻¹ cm ⁻¹)					
			Soret band		Q bands			
			416	512	546	588	644	
2	TPyPC ₈ Br₄	CH ₃ CŇ	424	517	551	590	645	
3	TFePyP	CHCl ₃ /CH ₃ COOH	413	505	640			
4	TCoPyP	CHCl ₃ /CH ₃ COOH	434	548	653			
5	TMnPyP	CHCl ₃ /CH ₃ COOH	476	578	610			
6	TCuPyP	CHCl ₃ /CH ₃ COOH	414	538	656			
7	TZnPyP	CHCl ₃ /CH ₃ COOH	422	558	602			
8	TFePyPC ₈ Br₄	ČH ₃ ČN	414	569				
9	TCoPyPC ₈ Br ₄	CH ₃ CN	456	578	625	680		
10	TMnPyPC ₈ Br ₄	CH ₃ CN	475	581				
11	TCuPyPC ₈ Br ₄	CH ₃ CN	417	542	575			
12	TZnPyPC ₈ Br ₄	CH ₃ CN	440	564	607	658		
13	TFePyPC ₈ (FeBr ₄) ₄	CH ₃ CN	422	571				
14	TCoPyPC ₈ (FeBr ₄) ₄	CH ₃ CN	445	558	693			
15	TMnPyPC ₈ (FeBr ₄) ₄	CH ₃ CN	480	581	679			
16	TCuPyPC ₈ (FeBr ₄) ₄	CH ₃ CN	419	542				
17	TZnPyPC ₈ (FeBr ₄) ₄	CH₃CN	429	563				

 Table 3
 Dominant infrared bands for the synthesised porphyrin derivatives

Entry	Compounds	vN−Hª	vC=C-H ^b	$vC_n-H_{2n+1}^c$	$vC=C^d$	$vC=N^d$	vN−H/M ^e	<i>v</i> P–Py ^f
1	TPvP	3325 (m)	3091 (w)		1593 (s)	1351 (s)	971 (s)	
2	TPyPC ₈ Br₄	3330 (m)	3030 (w)	2924, 2854 (m)	1636 (s)	1352 (s)	970 (s)	799(s)
3	TFePyP	_	3114 (w)	_	1652 (s)	1351 (s)	993 (s)	_
4	TCoPyP	_	3114 (w)	_	1653 (s)	1351 (s)	997 (s)	_
5	TMnPyP	_	3114 (w)	_	1647 (s)	1343 (s)	1006 (s)	_
6	TCuPyP	_	3114 (w)	_	1630 (s)	1348 (s)	1001 (s)	_
7	TZnPyP	_	3114 (w)	_	1608 (s)	1342 (s)	996 (s)	_
8	TFePyPC ₈ Br₄	_	3054 (w)	2924, 2853 (m)	1634 (s)	1358 (s)	1000 (s)	799 (s)
9	TCoPyPC ₈ Br ₄	_	3110 (w)	2926, 2854 (m)	1653 (s)	1382 (s)	1001 (s)	798 (s)
10	TMnPyPC ₈ Br ₄	_	3109 (w)	2924, 2853 (m)	1636 (s)	1387 (s)	1011 (s)	802 (s)
11	TCuPyPC ₈ Br ₄	_	3035 (w)	2923, 2852 (m)	1610 (s)	1347 (s)	1000 (s)	800 (s)
12	TZnPyPC ₈ Br ₄	_	3082 (w)	2926, 2855 (m)	1611 (s)	1342 (s)	995 (s)	793 (s)
13	TFePyPC ₈ (FeBr ₄) ₄	_	3078 (w)	2925, 2854 (m)	1632 (s)	1360 (s)	1001 (s)	797 (s)
14	TCoPyPC ₈ (FeBr ₄) ₄	_	3113 (w)	2926, 2854 (m)	1652 (s)	1360 (s)	1006 (s)	796 (s)
15	TMnPyPC ₈ (FeBr ₄) ₄	_	3114 (w)	2925, 2854 (m)	1635 (s)	1374 (s)	1012 (s)	797 (s)
16	TCuPyPC ₈ (FeBr ₄) ₄	_	3059 (w)	2924, 2854 (m)	1631 (s)	1359 (s)	1000 (s)	794 (s)
17	TZnPyPC ₈ (FeBr ₄) ₄	_	3110 (w)	2925, 2853 (m)	1630 (s)	1367 (s)	996 (s)	793 (s)

^aN–H stretching vibration of pyrrolyl. ^bC–H stretching vibration of pyrrolyl and pyridyl. ^cC–H stretching vibration of alkyl chain. ^dC=C and C=N stretching vibration of porphyrin. ^eStretching vibration of central metal ions with N on pyrrolyl. ^fC–H stretching vibration of 1,4-disubstituted pyridyl derivatives.



Fig. 5 Raman spectra for representative samples: a = $TFePyPC_8Br_4$, b = $TFePyPC_8(FeBr_4)_4$, c = $TCoPyPC_8(FeBr_4)_4$, d = $TMnPyPC_8(FeBr_4)_4$, e = $TCuPyPC_8(FeBr_4)_4$, f = $TZnPyPC_8(FeBr_4)_4$.

formation of the paramagnetic FeBr₄⁻ anions. Raman spectra of TMnPyPC₈(FeBr₄)₄ (M=Fe, Co, Mn, Cu and Zn), shown in Fig. 5, all exhibit an intense band at -203 cm^{-1} , corresponding well with literature values for the anion FeBr₄⁻ as a solid or in solution.³³ Moreover, weak broad bands at 306 cm⁻¹, the feature of symmetry vibrations of Fe₂Br₇⁻, were not observed, reinforcing the specifity of FeBr₄⁻. Additionally, the observed Raman spectra of TMPyPC₈(FeBr₄)₄ have a similar pattern to those of TFePyPC₈Br₄.

Magnetic susceptibility

Magnetic properties of TMPyPC₈(FeBr₄)₄ were examined using the SQUID method. Small samples, (typically 10–30 mg), were placed in gelatine capsules and the magnetic moments were determined in a magnetic field range between -50,000and 50,000 Oe. Figure 6 shows the obtained results of compounds synthesised including TMPyPC₈(FeBr₄)₄ (Fig. 6a) and TMPyPC₈Br₄ (Fig. 6b) at 300 K.

It can be observed that $TMPyPC_8(FeBr_4)_4$ show non-linear responses to magnetic field, which is typical for ferromagnetic materials (Fig. 6a). An increased magnetic response was



Fig. 6 SQUID magnetisation of representative samples: TMPyPC₈ (FeBr₄)₄ (a) and TMPyPC₈Br₄ (b). Inset shows an expansion at temperature of 300 K in the range of –3000 to 3000 Oe.

shown in the order: TCuPyPC₈(FeBr₄)₄ \leq TZnPyPC₈(FeBr₄)₄<TMnPyPC₈(FeBr₄)₄<TCoPyPC₈(FeBr₄)₄<TFePyPC₈(FeBr₄)₄, as a function of the various central metal ions. The corresponding bromides, TMPyPC₈Br₄, are in most cases paramagnetic materials, showing linear responses to magnetic field (Fig. 6b).

Special attention should be given to TFePyPC₈Br₄ and TCuPyPC₈Br₄, which present performance of ferromagnetism and diamagnetism respectively. Magnetic susceptibility, an indicator of paramagnetic strength for magnetic materials calculated from gradients of magnetic field dependence, is used to explain their magnetic performance, giving magnetic susceptibility values TMnPyPC₈Br₄, 32.3×10⁶ emu g⁻¹; TCoPyPC₈Br₄, 12.8×10⁶ emu g⁻¹; TCuPyPC₈Br₄, 2.3×10⁶ emu g⁻¹; 7TOPyPC₈Br₄, -0.8×10⁶ emu g⁻¹. The above greater magnetism diversity between TMPyPC₈(FeBr₄)₄ and TMPyPC₈Br₄, from ferromagnetism to paramagnetism, suggests the obvious influence of the paramagnetic anions FeBr₄⁻⁻ on the magnetic performance.

Figure 7 show the strong magnetic response of compounds $TMPyPC_8(FeBr_4)_4$ to a neodymium magnet $[TFePyPC_8(FeBr_4)_4$ is an example]. According to this special magnetism feature, we may forecast that $TMPyPC_8(FeBr_4)_4$ are potentially interesting candidates for reusable catalysts or material precursors in separation chemistry with the aid of an outside magnetic field.

Experimental

Measurement and analysis

The elemental analyses were performed using a Vario EL cube microanalyser. Electron spray mass spectrometry was recorded on a Bruker 300 spectrophotometer in acetonitrile/water mixture (1:1 by volume). ¹H NMR (600.17 MHz) spectra were recorded on a JEOL ECA-600 spectrometer and chemical shift values were referenced to SiMe₄. UV-Vis spectroscopy was recorded on a Shimadzu UV-2550 spectrophotometer. FT-IR spectra were recorded as KBr pellets on a Nicolet FTIR-380 spectrophotometer. Raman measurements were carried out on a Horiba Jobin Yvon inVia Raman spectrometer at a wavelength of 514 nm. Thermogravimetric analyses (TGA) were performed on 5-10 mg samples in platinum pans, using a TGA Q5000 thermogravimetric analyser under a dinitrogen atmosphere at 10 °C min-1 heating rate. Density values were determined using an AccuPyc 1340 densimeter. Magnetic measurements were conducted on a SQUID Quantum Design PPMS-9 magnetometer at 300 K and samples were loaded into a gelatine capsule (Quantum Design). Organic solvents were purchased as reagent grade and used as received.

Synthesis of [tetrakis(N-octyl-4-pyridinium)-metal-porphyrin] [tetrabromoferrate(III)]₄ [TMPyPC₈(FeBr₄)₄]

Tetrakis-(4-pyridyl)-porphyrin] (H₂TPyP) (1): In an N₂ atmosphere, propionic acid (120 mL) was added into a 250 mL three-neck roundbottom flask equipped with stirrer, reflux exchanger and dropping funnel. The solvent was stirred at refluxing temperature (150 °C) for 30 min. Subsequently, pyridine-4-carboxaldehyde (6.43 g, 60 mmol) and freshly distilled pyrrole (4.07 g, 60 mmol), dissolved in 10 mL propionic acid, were simultaneously added into the flask dropwise over 15 min. After refluxing for another 1 h, the reaction mixture was cooled to room temperature and then the propionic acid in the reaction mixture was evaporated absolutely. The resultant black crude products were poured into DMF (30 mL) and allowed to stand overnight. The resultant purple precipitates were separated by centrifugation and washed with DMF. The terminal product tetrakis-(4-pyridyl)-porphyrin [H₂TPyP], 1, was purified by Al₂O₃ column chromatography (CHCl₃ and CH₃OH as the eluents) and dried under vacuum (70 °C, 12 h) with a yield of 21%. ¹H NMR (CDCl₃): δ 9.1 (d, 8H, pyridyl, CHNCH), 8.9 (s, 8H, pyrrolyl, β-H), 8.2 (d, 8H, pyridyl, CHCCH), -2.9 (s, 2H, 2NH) ppm. Anal. Calcd for C40H26N8: C, 77.67; H, 4.21; N, 18.12. Found: C, 76.90; H, 4.29; N, 1 8.85%.

Tetrakis-(*N*-octyl-4-pyridinium)-iron-(porphyrin) bromide [*TFePy* PC_8Br_4] (**3**): In an N₂ atmosphere, a mixture of **2** (0.26 g, 0.19 mmol) and FeCl₂4H₂O (0.38 g, 1.9 mmol) in DMF (25 mL) was heated at 100 °C for 8 h. After removal of the solvent *in vacuo*, the residues were recrystallised with methanol/diethyl ether and dark-yellow solid TFePyPC_8Br_4, **3** was obtained, yield 92%. Due to the influence of the Fe quadrupolar nucleus and the paramagnetism of **3**, the signals in the ¹H NMR of **3** were broadened to flatness. ESI C₇₂H₉₂N₈FeBr₄ (*m*/z^{+/-}): Cation 1125.28.

Tetrakis-(*N*-octyl-4-pyridinium)-cobalt-(porphyrin) bromide TCoPy PC_8Br_4 (4): TCoPyPC_8Br_4 was synthesised according to the above procedure from **2** and CoCl₂6H₂O (0.45 g, 1.9 mmol) as a dark-green solid in 88% yield. Due to the influence of the Co quadrupolar nucleus and the paramagnetism of **4**, the signals in its ¹H NMR were broadened to flatness. ESI $C_{72}H_{92}N_8COBr_4$ ($m/z^{+/-}$): Cation 1127.00.

Tetrakis-(*N*-octyl-4-pyridinium)-manganese-(porphyrin) bromide $[TMnPyPC_8Br_4]$ (**5**): TMnPyPC_8Br₄ was synthesised according to the above procedure from **2** and MnCl₂ (0.24 g, 1.9 mmol) as a dark-green in 87% yield. Due to the influence of the Mn quadrupolar nucleus and the paramagnetism of **5**, its signals in the ¹H NMR were broadened to flatness. ESI C₇₂H₉₂N₈MnBr₄ (*m*/*z*^{+/-}): Cation 1123.00.

Tetrakis-(N-octyl-4-pyridinium)-copper-(porphyrin) bromide [TCuPy PC_8Br_4] (6): {TCuPyPC_8Br_4} was synthesised according to the above procedure from **2** and Cu(CH₃COO)₂.H₂O (0.38 g, 1.9 mmol) as a dark-red solid in 92% yield. The signals in the ¹H NMR of **6** were broadened to flatness. ESI $C_{72}H_{92}N_8CuBr_4$ ($m/z^{+/-}$): Cation 1133.00.

Tetrakis-(N-octyl-4-pyridinium)-zinc-(porphyrin) bromide [*TZn* $PyPC_8Br_4$] (7): TZnPyPC_8Br₄ was synthesised according to the above procedure from **2** and Zn(CH₃COO)₂.2H₂O (0.42 g, 1.9 mmol) as a dark-brown solid in 90% yield. The signals in the ¹H NMR of **7** were broadened to flatness. ESI $C_{72}H_{92}N_8ZnBr_4$ ($m/z^{+/-}$): Cation 1133.00.

Tetrakis-(N-octyl-4-pyridinium)-iron-(porphyrin) tetrabromoferrate(III) [TFePyPC₈(FeBr)₄] (8): In an N₂ atmosphere, a mixture of **3** (0.10 g, 0.07 mmol) and FeBr₃ (0.09 g, 0.315 mmol) in acetonitrile (20 mL) was heated at 85 °C for 48 h. After removal of the solvent *in vacuo*, the residues were recrystallised with diethyl ether several times until the solvent was colourless. Dark-brown, solid **8** was obtained in 80% yield. ESI C₇₂H₉₂N₈Fe₅Br₁₆ ($m/z^{+/-}$): Cation 1125.28, Anion 375.61.

Tetrakis-(*N*-octyl-4-pyridinium)-cobalt-(porphyrin) tetrabromoferrate(*III*) [*TCoPyPC*₈(*FeBr*₄)₄] (**9**): TCoPyPC₈(FeBr₄)₄ was synthesised according to the above procedure from **4** (0.10 g, 0.07 mmol) and FeBr₃ (0.09 g, 0.315 mmol). The dark-brown solid **9** was obtained in 80% yield. ESI C₇₂H₉₂N₈CoFe₄Br₁₆ ($m/z^{+/-}$): Cation 1127.00, Anion 375.61.

*Tetrakis-(N-octyl-4-pyridinium)-manganese-(porphyrin) tetrabromoferrate(III) [TMnPyPC*₈(*FeBr*₄)₄] (**10**): TMnPyPC₈(FeBr₄)₄ was synthesised according to the above procedure from, **5** (0.10 g, 0.07 mmol) and FeBr₃ (0.09 g, 0.315 mmol). Dark-brown solid **10** was obtained in 80% yield. ESI $C_{72}H_{92}N_8MnFe_4Br_{16}$ (*m/z^{+/-}*): Cation 1123.00, Anion 375.61.



Fig. 7 Response of a block of FeTPyPC₈(FeBr₄)₄ to a neodymium magnet.

450 JOURNAL OF CHEMICAL RESEARCH 2013

Tetrakis-(N-octyl-4-pyridinium)-copper-(porphyrin) tetrabromoferrate(III) [*TCuPyPC*₈(*FeBr*₄)₄] (**11**): TCuPyPC₈(FeBr₄)₄ was synthesised according to the above procedure from **6** (0.10 g, 0.07 mmol) and FeBr₃ (0.09 g, 0.315 mmol). Dark-purple solid **11** was obtained in 80%yield. ESI C₇₂H₉₂N₈CuFe₄Br₁₆ (*m/z*^{+/-}): Cation 1133.00, Anion 375.61.

Tetrakis-(N-octyl-4-pyridinium)-zinc-(porphyrin) tetrabromoferrate(*III)* [*TZnPyPC*₈(*FeBr*₄)₄] (**12**). TZnPyPC₈(FeBr₄)₄ was synthesised according to the above procedure from **7** (0.10 g, 0.07 mmol) and FeBr₃ (0.09 g, 0.315 mmol). Dark-purple, solid **12**, yield 75%. ESI $C_{72}H_{92}N_8ZnFe_4Br_{16}$ (*m*/z^{+/-}): Cation 1133.00, Anion 375.61.

Synthesis of tetrakis-(4-pyridyl)-metal-(porphyrin) (TMPyP)

Tetrakis-(4-pyridyl)-iron-(porphyrin) (TFePyP) (13): In an N₂ atmosphere, a solution of 1 (0.5 g, 0.8 mmol) in DMF (80 mL) was added to FeCl₂·4H₂O (1.59 g, 8 mmol). After refluxing 6 h, the resultant crude products were poured into H₂O (200 mL) and allowed to stand overnight. The purple precipitates were obtained by centrifugation and washed with deionized water. The dark-brown solid 13 was dried under vacuum (70 °C, 12 h), yield 92%.

Tetrakis-(4-pyridyl)-cobali-(porphyrin) (TCoPyP) (14): TCoPyP was synthesised according to the above procedure from 1 and $CoCl_26H_2O$ (1.90 g, 8 mmol). The dark-green solid 14 was obtained in yield of 88%.

Tetrakis-(4-pyridyl)-manganese-(porphyrin) (TMnPyP) (**15**): TMnPyP was synthesised according to the above procedure from **1** and $MnCl_2$ (1.00 g, 8 mmol). Dark-green, solid **15** was obtained in yield of 88%.

Tetrakis-(4-pyridyl)-copper-(porphyrin) (TCuPyP) (16): TCuPyP was synthesised according to the above procedure from 1 and $Cu(CH_3COO)_2H_2O$ (1.60 g, 8 mmol). Dark-purple solid 16 was obtained in yield 90%.

Tetrakis-(4-pyridyl)-zinc-(porphyrin) (*TZnPyP*) (**17**): TZnPyP was synthesised according to the above procedure from **1** and $Zn(CH_3COO)_22H_2O$ (1.76 g, 8 mmol). Dark-purple solid **17** was obtained in yield 85%.

Conclusions

A series of novel magnetic, ionic metalloporphyrins, [TMPyPC₈(FeBr₄)₄], (M = iron, cobalt, manganese, copper or zinc), have been synthesised. UV-Vis studies revealed the generation of metalloporphyrins cations, while Raman spectroscopy was used as a characterisation method for the paramagnetic anions FeBr₄⁻. The FeBr₄⁻ paramagnetic anions improved water-solubility and magnetic response of the determined products, particularly making them show weak ferromagnetic behaviour at room temperature. An increased magnetic performance was observed in the order TCuPyPC₈(FeBr₄)₄ \leq TZnPyPC₈(FeBr₄)₄<TMnPyPC₈(FeBr₄)₄<TCoPyPC₈(FeBr₄)₄<TFePyPC₈(FeBr₄)₄<TCoPyPC₈(reBr₄)₄<TFePyPC₈(FeBr₄)₄<Timples of the prepared magnetic ionic metalloporphyrins showed a strong response to a neodymium magnet, making them attactive candidates as "reusable compounds" in different systems.

The work was supported by the National Natural Science Foundation of China (grant No. 21206171 and 21276006), the Special Funds of the National Natural Science Foundation of China (grant No. 21127011) and the Petrochmical Joint Funds of NSFCACNPC (grant No. U1162106).

Received 21 March 2013; accepted 25 May 2013 Paper 1301852 doi: 10.3184/174751913X13727033282329 Published online: 9 August 2013

References

- 1 H.J. Lu and X.P. Zhang, Chem. Soc. Rev., 2011, 40, 1899–1909.
- 2 P. Kumari, N. Sinha, P. Chauhan and S.M.S. Chauhan, *Current organic synthesis*, 2011, 8, 393.
- 3 J.S. Lindsey, In: *The porphyrin handbook*, eds. K.M. Kadish, K.M. Smith and R. Guilard. Academic Press, San Diego, 2000, Vol. 1, pp. 45–118.
- 4 S. Mandal, S. Bhattacharyya, V. Borovkov and A. Patra, J. Phys. Chem. C, 2012, 116, 11401.
- 5 D.S. Bohle, E.L. Dodd, T.B.J. Pinter and M.J. Stillman, *Inorg. Chem.*, 2012, **51**, 10747.
- 6 L. Chen, Y. Yang, Z.Q. Guo and D.L. Jiang, *Adv. Mater.*, 2011, 23, 3149.
 7 D. Meyer, T. Leifels, L. Sbaragli and W.D. Woggon, *Biochem. Biophys.*
- *Res. Commun.*, 2005, **338**, 372.
- 8 C.M. Che, V. K-Y. Lo, C.Y. Zhou and J.S. Huang, *Chem. Soc. Rev.*, 2011, 40, 1950.
- 9 Y. Li, J.S. Huang, Z.Y. Zhou, C.M. Che and X.Z. You, J. Am. Chem. Soc., 2002, 124, 13185.
- 10 G.S. Nunes, I. Mayer, H.E. Toma and K. Araki, *Journal of Catalysis*, 2005, 236, 55.
- 11 S. Nimri and E. Keinan, J. Am. Chem. Soc., 1999, 121, 8978.
- 12 E.Y. Jeong and S.E. Park, Res Chem Intermed, 2012, 38, 1237.
- 13 M.H. Alkordi, Y.L. Liu, R.W. Larsen, J.F. Eubank and M. Eddaoudi, J. Am. Chem. Soc., 2008, 130, 12639.
- 14 L. Chen, Y. Yang and D.L. Jiang, J. Am. Chem. Soc., 2010, 132, 9138.
- 15 L. Chen, Y. Yang, Z.Q. Guo and D.L. Jiang, Adv. Mater., 2011, 23, 3149.
- 16 Z.C. Sun, Y.B. She, Y. Zhou, X.F. Song and K. Li, *Molecules*, 2011, 16, 2960.
- 17 J. Bernadou and B. Meunier, Chem. Commun., 1998, 2167.
- 18 H. Imai, H. Munakata, Y. Uemori and N. Sakura, *Inorg. Chem.*, 2004, 43, 1211.
- 19 R.J. Balahura, A. Sorokin, J. Bernadou and B. Meunier, *Inorg. Chem.*, 1997, 36, 3488.
- 20 Y. Yoshida and G. Saito, J. Mater. Chem., 2006, 16, 1254.
- 21 R.E. Del Sesto, T.M. McCleskey, A.K. Burrell et al. Chem. Commun., 2008, 447.
- 22 T. Peppel, M. Köckerling, M. Geppert-Rybczyńska, R.V. Ralys, J.K. Lehmann, S.P. Verevkin and A. Heintz, *Angew. Chem. Int. Ed.*, 2010, 49, 7116.
- 23 Y. Funasako, T. Mochida, T. Inagaki et al., Chem. Commun., 2011, 47, 4475.
- 24 S. Hayashi and H. Hamaguchi, Chem. Lett., 2004, 33, 1590.
- 25 Y. Ito, K. Kunimoto, S. Miyachi and T. Kako, *Tetrahedron Lett.*, 1991, 32, 4007.
- 26 I.C.M.S. Santos, S.L.H. Rebelo, M.S.S. Balula et al. J. Molec. Catal. A, 2005, 231, 35.
- 27 N.M. Berezina, M.I. Bazanov, A.S. Semeikin, and M.B. Berezin, *Russ. J. of Phys. Chem.*, A, 2009, 83, 785.
- 28 Y. Liu, H.J. Zhang, Y. Lu, Y.Q. Cai and X.L. Liu, Green Chem., 2007, 9, 1114.
- 29 H.J. Zhang, Y. Liu, Y. Lu, X.S. He, X. Wang and X. Ding, J. Molec. Catal. A, 2008, 287, 80.
- 30 T. Kominami, T. Matsumoto, K. Ueda et al. J. Mater. Chem., 2001, 11, 2089.
- 31 Y. Yoshida and G. Saito, J. Mater. Chem., 2006, 16, 1254.
- 32 Z.C. Sun, Y.B. She and R.G. Zhong, Front. Chem. Eng. China, 2009, 3, 457.
- 33 M. Döbbelin, V. Jovanovski, I. Llarena et al. Polym. Chem., 2011, 2, 1275.

Copyright of Journal of Chemical Research is the property of Science Reviews 2000 Ltd. and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.