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Selective anion recognition by novel 5,10,15,20-tetrakis(*o*-ferrocenylcarbonylaminophenyl-substituted) zinc metalloporphyrin receptors

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New free-base and zinc-metallated 5,10,15,20-tetrakis(*o*-ferrocenylcarbonylaminophenyl-substituted) porphyrin atropisomers have been prepared. Proton NMR anion-binding investigations revealed the free-base porphyrins to be poor complexing agents for anions. The zinc metalloporphyrin receptors, however, strongly complex halide, nitrate and hydrogensulfate anions and stability-constant evaluations showed marked selectivity trends dependent upon the particular atropisomer. Electrochemical studies showed that these zinc metalloporphyrin receptors electrochemically sense anions *via* significant cathodic perturbations of the respective porphyrin oxidation and ferrocene redox couples.

The molecular recognition of anionic guest species of biochemical, medical and environmental importance is an area of intense current research activity and many successful examples of positively charged or neutral abiotic anion receptors are now available.[1–5] The natural extension of such work is to develop sensors for anions, molecules which will exhibit a measurable physical change on binding, but surprisingly there are very few reports in the literature.[6,7] Rare examples include redox-responsive metallocene amide[7] and optically responsive polyammonium anthracene[6] and ruthenium(II) bipyridyl amide systems.[7] Owing to its well known photo- and redox-activity the porphyrin macrocycle is an attractive building block[8] on which to append additional recognition sites for anion binding. In nature the selective binding of anions is primarily achieved by the positional alignment or direction of hydrogen-bond donor groups. For example sulfate and phosphate binding proteins selectively complex their respective anions exclusively through hydrogen bonding.[9] The attachment of ferrocenyl amide hydrogen-bonding groups to the various atropisomers of *meso*-5,10,15,20-tetrakis(*o*-phenyl-substituted) porphyrin[10] creates novel cavities that contain unique topological amide hydrogen-bonding environments. This in combination with a Lewis-acid metal, such as zinc, complexed in the porphyrin macrocyclic cavity may produce new selective redox-active sensory reagents for anions. Indeed various simple metalloporphyrins have been shown potentiometrically to sense anions with selectivity sequences solely dependent on the centrally bound metal.[11] We report here the syntheses and anion co-ordination investigations of new 5,10,15,20-tetrakis(*o*-ferrocenylcarbonylaminophenyl-substituted) zinc metalloporphyrin receptors whose anion-selective properties are dependent upon the particular metalloporphyrin atropisomer.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using the solvent deuterium signal as internal reference, fast atom bombardment (FAB) mass spectra by the EPSRC mass spectrometry service at University College, Swansea. Electrochemical measurements were carried out using an E.G. and G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

Solvent and reagent pre-treatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Dichloromethane and acetontrile were distilled from calcium hydride. (Chlorocarbonyl)ferrocene **1**[12] and the α,α,α,α-, α,α,α,β-, α,α,β,β- and α,β,α,β-atropisomers of 5,10,15,20-tetrakis(2-aminophenyl)porphyrin (**Ia**–**Id**)[10] were prepared according to literature methods.

Syntheses

α,α,α,α-5,10,15,20-Tetrakis(*o*-ferrocenylcarbonylaminophenyl)porphyrin 2. To a solution of the α,α,α,α atropisomer 5,10,15,20-tetrakis(2-aminophenyl)porphyrin **Ia** (0.27 g, 0.4 mmol) in dry dichloromethane (25 cm^3) in a round-bottom flask (50 cm^3) was added triethylamine (0.28 cm^3, 2.0 mmol). The solution was stirred under nitrogen for 10 min then (chlorocarbonyl)ferrocene (0.78 g, 2.0 mmol) was added. After 48 h of stirring the solvent was removed *in vacuo* leaving a dark brown crude product. Distilled water (25 cm^3) was added and the mixture stirred for 20 min and then filtered. The crude product was further purified by silica gel column chromatography [dichloromethane–ethyl acetate (4:1, v/v)]. The dark purple major band was collected and the pure product obtained after recrystallization from dichloromethane–hexane. Yield: 70% (0.43 g, 0.28 mmol). M.p. 290 °C (Found: C, 68.05; H, 4.4; N, 7.05. $C_{88}H_{66}Fe_4N_8O_4$ requires C, 69.4; H, 4.35; N, 7.35%). NMR: ^{1}H ($CDCl_3$) δ − 1.02 (s, 2 H, pyrrole NH), 3.21 (dd, 8 H, J = 1.9, ferrocenyl H), 3.26 (dd, 8 H, J = 1.9, ferrocenyl H), 3.35 (s, 20 H, ferrocenyl H) 7.51 (m, 4 H, J = 7.8, *o*-H of Ph), 7.9 (m, 8 H, J = 5.9, *m*,*p*-H of Ph), 8.9 (dd, 4 H, J = 8.18, *m*′-H of aryl) and 9.05 (s, 8 H, β-pyrrole); (CD_2Cl_2), δ − 1.0 (s, 2 H, pyrrole NH), 3.16 (d, d, 8 H, J = 1.8, ferrocenyl H), 3.24 (d, d, 8 H, J = 1.8 Hz, ferrocenyl H), 3.40 (s, 20 H, ferrocenyl H), 7.43 (s, br, 4 H, NHCO), 7.53 (m, 4 H, *o*-H of Ph), 7.94–7.95 (m, 8 H, *m*,*p*-H of Ph), 8.85 (d, 4 H, *m*′-H of Ph) and 9.06 (s, 8 H, β-pyrrole); ^{13}C ($CDCl_3$), δ 67.00 (ferrocenyl), 69.41 (ferrocenyl), 70.34 (ferrocenyl) 75.56 (*ipso*-C of ferrocenyl), 115.53 (*meso*-C of aryl), 120.23 (*m*′-C of Ph), 122.81 (*p*-C of Ph), 129.64 (*ipso*-C of Ph subst.), 130.39 (β-pyrrole), 132.5 (*ipso*-C of α-pyrrole), 134.89 (*o*-C of Ph), 138.75 (*ipso*-C of Ph) and 168.0 (C=O). FAB mass spectrum: m/z = 1524, [M + H^+]. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 421 (5.24), 515 (4.06), 548 (3.48), 589 (3.5) and 646 (3.07).

Analogous experimental procedures were used to prepare

compounds **3**–**5** from the condensation reactions of **1** and the appropriate atropisomer **Ib**–**Id**.

α,α,α,β-5,10,15,20-Tetrakis(*o*-ferrocenylcarbonylaminophenyl)porphyrin 3. Yield 67%. M.p. 225 °C (Found: C, 66.75; H, 4.25; N, 7.15. $C_{88}H_{66}Fe_4N_8O_4{\cdot}CH_2Cl_2$ requires C, 66.5; H, 4.25; N, 6.95%). NMR ($CDCl_3$): ^{1}H, δ − 1.03 (s, br, 2 H, pyrrole NH), 2.74 [dd, 2 H, *J* = 1.8, ferrocenyl H (d)], 3.0 [s, 5 H, ferrocenyl H (d)], 3.14 [s, 5 H, ferrocenyl H (c)], 3.21 (s, 10 H, ferrocenyl H), 3.28 [dd, 2 H, *J* = 1.78, ferrocenyl H (c)], 3.3 [dd, 4 H, *J* = 1.8, ferrocenyl H], 3.52 (dd, 4 H, *J* = 1.8, ferrocenyl H), 3.64 (dd, 2 H, *J* = 1.9, ferrocenyl H), 3.91 (dd, 4 H, *J* = 1.8, ferrocenyl H), 7.23 (s, br, 4 H, NHCO), 7.45–7.55 (m, 8 H, aryl H), 7.80–8.0 (m, 4 H, aryl H), 8.94 (m, 4 H, *m′*-H of aryl) and 9.03 (t, 8 H, *J* = 4.78 Hz, β-pyrrole); ^{13}C, δ 60, 66.19, 67.10, 68.27, 69.09, 69.99, 70.29 (ferrocene), 115.67, 120.40, 122.64, 129.71, 130.35, 132.21, 135.20 (porphyrin) and 168 (C=O). FAB mass spectrum: *m/z* = 1524, $[M + H]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 421 (5.01), 515 (3.73), 547 (3.13), 590 (3.36) and 646 (2.89).

α,α,β,β-5,10,15,20-Tetrakis(*o*-ferrocenylcarbonylaminophenyl)porphyrin 4. Yield 72%. M.p. 280–285 °C (Found: C, 67.45; H, 4.6; N, 7.05. $C_{88}H_{66}Fe_4N_8O_4{\cdot}CH_2Cl_2$ requires C, 66.5; H, 4.6; N, 6.95%). NMR ($CDCl_3$): ^{1}H, δ − 1.02 (s, 2 H, pyrrole NH), 2.65 (dd, 4 H, ferrocenyl H), 3.15 (s, 20 H, ferrocenyl H), 3.38 (dd, 4 H, ferrocenyl H), 3.6 (dd, 4 H, ferrocenyl H), 3.7 (dd, 4 H, ferrocenyl H), 7.32 (s, br, 4 H, NHCO), 7.47 (t, 4 H, *o*-H of Ph), 7.88 (m, 8 H, *J* = 7.89, *m*,*p*-H of aryl), 8.9 (d, 4 H, *J* = 8.3) and 9.02 (t, 8 H, *J* = 5.39 Hz, β-pyrrole); ^{13}C, δ 67.52, (ferrocenyl), 67.82 (ferrocenyl), 68.73 (ferrocenyl), 69.02 (*ipso*-C of ferrocenyl), 115.51 (*meso*-C of aryl), 120.28 (*m′*-C of Ph), 122.51 (*p*-C of Ph), 129.46 (*ipso*-C of Ph), 130.35 (β-pyrrole), 132.10 (*ipso*-C of α-pyrrole), 134.67 (*o*-C of Ph), 138.74 (*ipso*-C of aryl) and 168.28 (C=O). FAB mass spectrum: *m/z* = 1524, $[M + H]^+$. UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 420 (5.41), 515 (4.36), 548 (3.77), 589 (3.86) and 645 (3.35).

α,β,α,β-5,10,15,20-Tetrakis(*o*-ferrocenylcarbonylaminophenyl)porphyrin 5. Yield 68%. M.p. 280–285 °C (Found: C, 65.65; H, 5.1; N, 6.25. $C_{88}H_{66}Fe_4N_8O_4{\cdot}CH_2Cl_2$ requires C, 66.5; H, 4.25; N, 6.95%). NMR ($CDCl_3$): ^{1}H, δ − 1.02 (s, 2 H, pyrrole NH), 2.9 (s, 20 H, ferrocenyl H), 3.39 (dd, 8 H, *J* = 1.9, ferrocenyl H), 3.56 (dd, 8 H, *J* = 1.9 Hz, ferrocenyl H), 7.41 (t, 4 H, *o*-C of Ph), 7.89 (m, 8 H, *m*,*p*-C of Ph), 8.9 (d, 4 H, *m′*-H of aryl) and 8.99 (s, 8 H, β-pyrrole); ^{13}C, δ 67.237 (ferrocenyl), 68.747 (ferrocenyl), 70.08 (ferrocenyl), 75.64 (*ipso*-C of ferrocenyl), 115.53 (*meso*-C of aryl), 120.35 (*m′*-C of Ph), 122.6 (*p*-C of Ph), 129.73 (*ipso*-C of Ph), 130.4 (β-pyrrole), 132.10 (*ipso*-C of α-pyrrole), 134.39 (*o*-C of Ph), 138.75 (*ipso*-C of aryl) and 168.0 (C=O). FAB mass spectrum: *m/z* = 1524, $[M + H]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 421 (5.73), 516 (4.65), 547 (4.05) and 590 (4.09).

Zinc metalloporphyrin receptor 6. Compound **2** (0.025 g, 0.016 mmol) dissolved in dry dichloromethane (10 cm^3) was treated with zinc(II) acetate dihydrate (0.05 g, 0.23 mmol) in methanol (5 cm^3) and stirred at room temperature under nitrogen for 48 h. The solution was initially dark purple but a cherry red colour was observed after 5 h of stirring. The progress of the reaction was monitored by TLC analyses. After 48 h of stirring the solvent was removed *in vacuo* leaving a red residue. Distilled water (10 cm^3) was added and the mixture stirred for 30 min. It was filtered leaving a red product which was further purified by silica gel column chromatography [dichloromethane–ethyl acetate (4:1 v/v)] followed by recrystallization from dichloromethane–hexane leaving a red powder. Yield: 90% (0.023 g, 0.014 mmol) (Found: C, 64.55; H, 4.4; N, 6.65. $C_{88}H_{64}Fe_4N_8O_4Zn{\cdot}MeOH$ requires C, 65.25; H, 4.2; N, 6.9%). ^{1}H NMR ($CDCl_3$): δ 2.69 (d, d, 8 H, ferrocenyl H), 3.07 (d, d, 8 H, ferrocenyl H), 3.4 (s, 20 H, ferrocenyl H), 7.37 (s, br, 4 H, NHCO), 7.49 (t, 4 H, *o*-H of aryl H), 7.62 (t, 4 H, aryl H), 7.93 (d, 4 H, aryl H), 8.70 (d, 4 H, aryl H) and 9.03 (s, 8 H, β-pyrrole). FAB mass spectrum: *m/z* = 1587, $[M + H]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 437 (5.63), 570 (4.35) and 609 (3.93).

Analogous synthetic procedures were used to prepare zinc metalloporphyrin receptors **7**–**9**.

7: Yield 97% (Found: C, 64.8; H, 4.3; N, 6.6. $C_{88}H_{64}Fe_4N_8O_4Zn{\cdot}MeOH$ requires C, 65.25; H, 4.2; N, 6.7%). ^{1}H NMR ($CDCl_3$): δ 2.45 (dd, 2 H, ferrocenyl H), 2.85 (dd, 2 ferrocenyl H), 2.97 (dd, 4 H, ferrocenyl H), 3.15 (s, 5 H, ferrocenyl H), 3.16 (s, 5 H, ferrocenyl H), 3.26 (s, 10 H, ferrocenyl H), 3.35 (dd, 4 H, ferrocenyl H), 3.53 (dd, 2 H, ferrocenyl H), 3.65 (dd, 2 H, ferrocenyl H), 7.2 (s, br, 4 H, NHCO), 7.32–7.47 (m, 8 H, aryl H), 7.7–7.98 (m, 4 H, *o*-H of Ph), 8.63–8.72 (m, 4 H, aryl H) and 9.0–9.85 (m, 8 H, β-pyrrole). FAB mass spectrum: *m/z* = 1587, $[M + H]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 437 (5.68), 570 (4.57) and 609 (3.33).

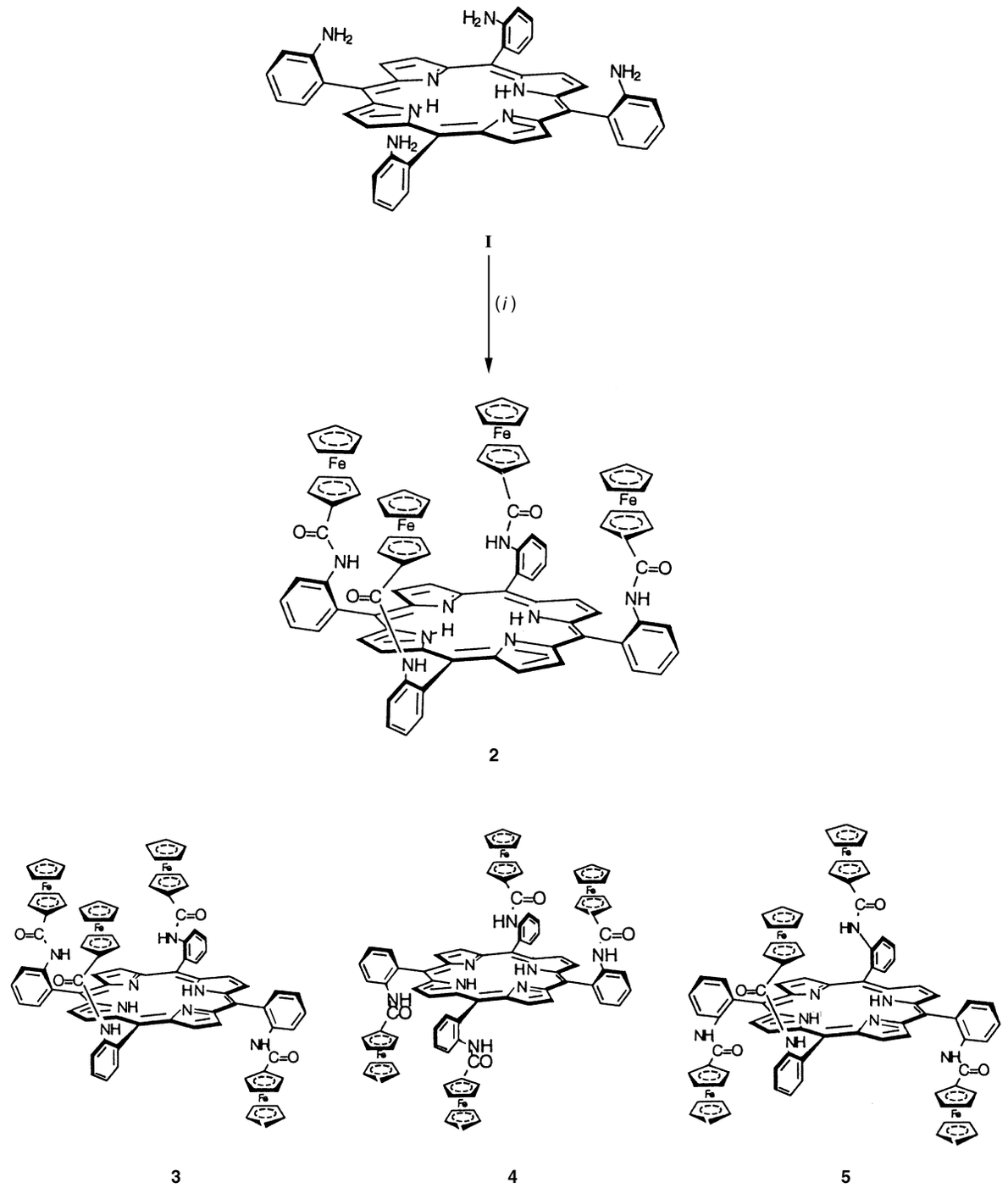
8: Yield 97% (Found: C, 65.3; H, 4.25; N, 6.85. $C_{88}H_{64}Fe_4N_8O_4Zn{\cdot}MeOH$ requires C, 65.25; H, 4.2; N, 6.9%). ^{1}H NMR ($CDCl_3$): δ 2.8 (t, 4 H, ferrocenyl H), 3.27 (s, 20 H, ferrocenyl H), 3,34 (t, 4 H, ferrocenyl H), 3.49 (t, 4 H, ferrocenyl H), 3.57 (t, 4 H, ferrocenyl H), 7.37 (s, br, 4 H, NHCO), 7.45 (t, 4 H, *o*-H of aryl), 7.90 (q, 8 H, *J* = 7.8, *m*,*p*-H of aryl), 8.89 (dd, 4 H, *J* = 8.34, *m′*-H of Ph) and 9.14 (dd, *J* = 8.34 Hz, 8 H, β-pyrrole). FAB mass spectrum: *m/z* = 1586, M^+; 1587, $[M + H]^+$; 1609, $[M + Na]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 437 (5.64), 5.71 (4.59) and 609 (3.41).

9: Yield 90% (Found: C, 64.35; H, 4.15; N, 6.75. $C_{88}H_{64}Fe_4N_8O_4Zn{\cdot}MeOH$ requires C, 65.25; H, 4.2; N, 6.9%). ^{1}H NMR ($CDCl_3$): δ 3.12 (s, 20 H, ferrocenyl H), 3.26 (dd, 8 H, *J* = 1.9, ferrocenyl H), 3.5 (dd, 8 H, *J* = 1.9, ferrocenyl H), 7.44 (t, 4 H, *J* = 7.96, *o*-H of aryl), 7.64 (t, 4 H, *J* = 8.36, *m*,*p*-H of aryl), 8.77 (d, 4 H, *J* = 8.15 Hz, *m′*-H of aryl) and 9.07 (s, 8 H, β-pyrrole). FAB mass spectrum: *m/z* = 1587, $[M + H]^+$. UV/VIS (CH_2Cl_2): λ_{max}/nm (log ε) 437 (5.69), 571 (4.58) and 609 (3.52).

Table 1 Crystal data and structure refinement for compound **6**·$CHCl_3$·2MeOH

Empirical formula	$C_{91}H_{73}Cl_3Fe_4N_8O_6Zn$
M	1768.30
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.924(11)
b/Å	21.177(13)
c/Å	29.193(22)
β/°	94.48(1)
U/Å^3	7965.5
Z	4
D_c/Mg m^{-3}	1.510
μ/mm^{-1}	1.173
F(000)	3740
Crystal size/mm	0.3 × 0.2 × 0.2
θ range/° for data collection	3.18–25.13
hkl Ranges	0–15, −25 to 25, −34 to 34
Reflections collected	23305
Independent reflections	13323 (R_{int} = 0.080) 7868 reflections had $I > 2\sigma$
Refinement method	Full-matrix least squares on F^2
Weighting scheme parameters *a*,*b**	0.152, 15.546
Data, parameters	13323, 1047
Goodness of fit on F^2	1.135
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0786, 0.2129
(all data)	0.1258, 0.2604
Largest difference peak and hole/e Å^{-3}	0.895, −0.573

Weighting scheme parameter $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 1 (*i*) 4 equivalents (chlorocarbonyl)ferrocene, CH_2Cl_2, NEt_3, room temperature

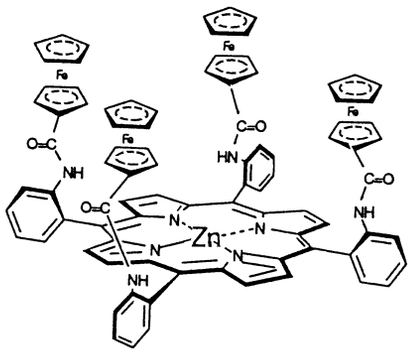
Crystallography

Crystal data for compound **6** are given in Table 1, together with refinement details. Data were collected with Mo-Kα radiation (λ 0.71070 Å) using the MARresearch image-plate system. The crystal was positioned 75 mm from the plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[13] The structure was solved using direct methods with the SHELXS 86 program.[14] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions. The structure was then refined using SHELXL.[15] Some of the carbon atoms, particularly in the cyclopentadiene groups, had high thermal motion but no suitable disordered model could be found. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/347.

Proton NMR titrations

A solution of the receptor (volume 500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in CD_2Cl_2. The initial ^1H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mole equivalent was added in 20 μl. After each addition and mixing the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of displacement in



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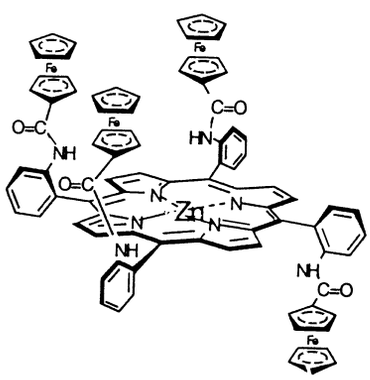

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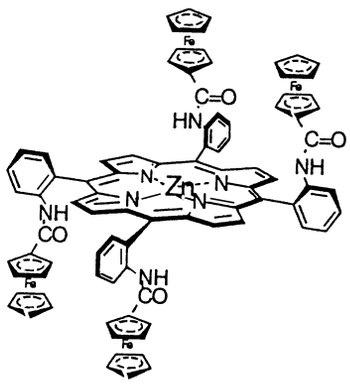

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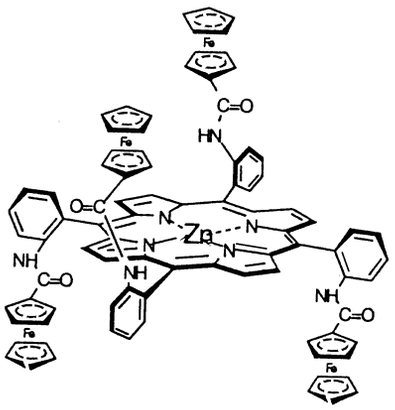

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chemical shift as a function of the amount of added anion, which was subjected to analysis by curve fitting since the shape of the titration curve is indicative of the stability constant for the complex. The computer program EQNMR[16] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point.

Results and Discussion

Syntheses

The condensation of an excess amount of (chlorocarbonyl)-ferrocene **1**[12] and the appropriate atropisomer 5,10,15,20-tetrakis(2-aminophenyl)porphyrin **Ia**–**Id**[10] in dry dichloromethane in the presence of triethylamine gave crude products which were purified *via* column chromatography (silica) using dichloromethane–ethyl acetate (4:1, v/v) eluent to give **2**–**5** as purple microcrystalline solids in good yields ranging from 67 to 72% (Scheme 1). The zinc metalloporphyrin receptors **6**–**9** were prepared in near-quantitative yields by stirring the free-base porphyrins with zinc acetate in dichloromethane–methanol (2:1, v/v). All of the receptors were characterised by ^{1}H NMR, fast atom bombardment mass spectrometry and elemental analyses (see Experimental section).

X-Ray structural investigation of compound 6

Crystals of compound **6** suitable for X-ray structural investigation were grown from dilute dichloromethane–methanol solutions of the receptor. The molecule is shown in Fig. 1(*a*) and 1(*b*) which are respectively projections through the porphyrin plane and perpendicular to it. The zinc atom is bonded to the four nitrogen atoms of the porphyrin at distances of 2.041(7), 2.044(6), 2.048(7) and 2.091(8) Å and to a methanol molecule at 2.091(8) Å. The metal atom is 0.27 Å above the plane of the four nitrogen atoms towards the methanol oxygen atom. The four phenyl rings intersect this plane of four nitrogen atoms at angles of 71.9, 68.7, 83.5 and 74.9° respectively. There is a significant difference between the positions of one of the carbonyl oxygen atoms and the other three, thus O(39) is directed into the cavity and the other three O(59), O(79) and O(99) are directed outwards.

There are three intramolecular hydrogen bonds in the structure, all involving the solvent methanol molecules. Thus the co-ordinated methanol oxygen O(5) forms a hydrogen bond to an oxygen atom of the solvent methanol O(5)···O(200) 2.60 Å and two carbonyl oxygen atoms also bond to oxygen atoms of the solvent methanols, (O79)···O(200) $(\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$ 2.66 and O(99)···O(301) $(x + 1, y, z)$ 2.72 Å.

Anion co-ordination studies: stability constant determinations from ^{1}H NMR titrations

The addition of tetrabutylammonium salts $Bu_4N^+X^-$ (X^- = Cl^-, Br^-, NO_3^- or HSO_4^-) to CD_2Cl_2 ^{1}H NMR solutions of compounds **6**–**9** resulted in significant shifts of the respective amide, ferrocene, aromatic and porphyrin protons of all four receptors. Substantial downfield shifts of the amide protons are noteworthy. For example, amide-proton perturbations of $\Delta\delta = 0.40$ and 0.64 ppm were observed for **6** and **9** after the addition of 1 equivalent of nitrate and bromide anions respectively. Analogous anion ^{1}H NMR titration investigations with **2**–**5** and zinc tetraphenylporphyrin **10** in CD_2Cl_2 revealed only negligible perturbations ($\Delta\delta \leqslant 0.05$ ppm) of these compounds protons suggesting the combination of both amide hydrogen-bonding groups and the Lewis-acid zinc metal centre is essential for successful anion binding in these neutral receptor systems.

The resulting anion titration curves with compounds **6**–**9** all suggested a receptor–anion stoichiometry of 1:1. The computer program EQNMR[16] was used to estimate the stability constants from the ^{1}H NMR titration data and the results are summarised in Table 2. Clearly the unique topological

Table 2 Stability constant data for compounds **6**–**9** and anions in CD_2Cl_2

Receptor	Anion	K*/dm^3 mol^{-1}
6	Br^-	6200
	NO_3^-	2300
	HSO_4^-	2100
7	Cl^-	3200
	NO_3^-	5000
	HSO_4^-	2000
8	Cl^-	5600
	Br^-	1600
	NO_3^-	900
	HSO_4^-	1000
9	Br^-	5800
	NO_3^-	1300
	HSO_4^-	600

* Errors ≤ 10%.

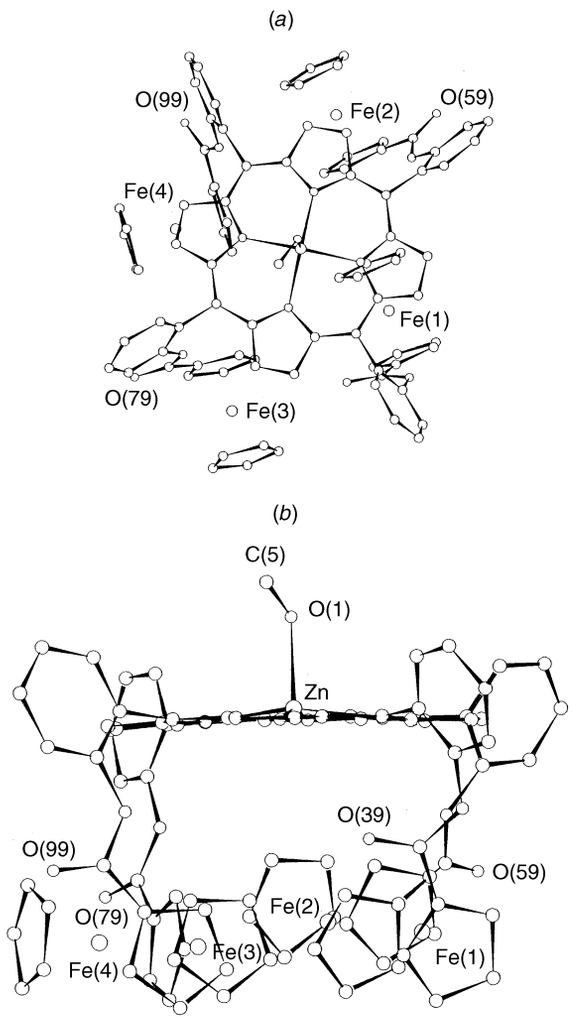

Fig. 1 Structure of compound **6**: projections (*a*) through and (*b*) perpendicular to the porphyrin plane

arrangement of the ferrocene amide hydrogen-bonding moieties of each metalloporphyrin atropisomer play a crucial role in determining the anion-selectivity trend the particular receptor displays. It is noteworthy that the α,α,α,β isomer **7** exhibits the rare selectivity preference for nitrate over chloride and hydrogensulfate anions indicating that a complementary trigonal host cavity exists for nitrate with this receptor. In contrast the other atropisomeric receptors selectively bind spherical halide anions with the tetrahedrally shaped HSO_4^- guest generally forming the weakest complexes.

Table 3 Electrochemical data[a] for compounds **2**–**9**

	E/V		
Compound	Porphyrin oxidation[b]	Ferrocene oxidation	Porphyrin reduction
2	0.78	0.53[c]	−1.26, −1.68
3	0.93	0.50[d], 0.45	−1.08, −1.49
4	0.84	0.43[c]	−1.21, −1.67
5	0.90	0.44[c]	−1.22, −1.58
6	0.71	0.43[c]	−1.26, −1.68
7	0.69	0.48,[d] 0.43	−1.08, −1.49
8	0.67	0.43[c]	−1.37, −1.78
9	0.71	0.44[c]	−1.18, −1.79

[a] Obtained in dichloromethane–acetontrile solution (3:2, v/v) containing 0.2 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. Solutions were *ca.* 5×10^{-4} mol dm^{-3} in compound and potentials were determined with reference to a Ag–Ag$^+$ electrode. [b] Two-electron process. [c] Four-electron process. [d] Three-electron process.

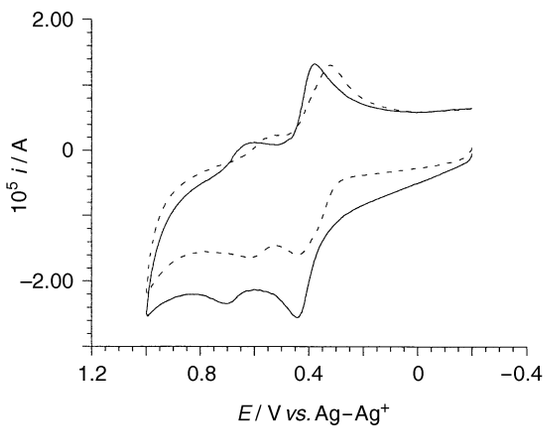

Fig. 2 Cyclic voltammograms in dichloromethane–acetonitrile (3:2, v/v) of compound **8** in the absence (——) and presence (– – –) of 1 equivalent of hydrogensulfate anion

Electrochemical anion-recognition studies

The electrochemical properties of the free base porphyrin derivatives **2**–**5** and metalloporphyrin receptors **6**–**9** were investigated by cyclic and square-wave voltammetries (Table 3). All the compounds exhibited typical 'picket fence' porphyrin redox chemistry;[17] a single two-electron porphyrin oxidation wave in the range 0.67–0.93 V and two one-electron reduction waves in the range −1.08 to −1.79 V respectively. The respective four ferrocene moieties of **2**, **4**–**6**, **8** and **9** exhibit a single four-electron oxidation wave which suggests the metallocene redox centres are electronically equivalent and undergo independent reversible one-electron transfers at the same potential. Among the various ferrocene-appended porphyrin systems reported,[18] a related *meso*-tetrakis(4-ferrocenylphenyl)porphyrin also exhibits a single four-electron oxidation wave for the four ferrocene redox centres.[19] With **3** and **7** two oxidation waves for the ferrocene moieties were observed with peak-current ratios of 1:3 indicating the least anodic redox couple corresponds to the β-ferrocene amide group and the other three metallocenes oxidize simultaneously at a more positive potential.

Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions of compounds **6**–**9** and the results are summarized in Table 4. Significant one-wave cathodic shifts of the respective porphyrin oxidation waves and the poly(ferrocene) redox couples of all four metalloporphyrin receptors are observed with all anionic guest species (Fig. 2); the complexed anion effectively stabilizes the respective oxidized redox

Table 4 Cathodic shifts of porphyrin oxidation and ferrocene redox couples on addition of anions[a]

		ΔE/mV			
Receptor	Oxidation	Cl^-	Br^-	NO_3^-	HSO_4^-
6	Porphyrin	115	85	110	100
	Ferrocene	30	20	25	60
7	Porphyrin	90	75	100	125
	Ferrocene[b]	25	20	20	50
8	Porphyrin	95	80	75	175
	Ferrocene	25	25	20	110
9	Porphyrin	70	65	60	150
	Ferrocene	20	20	15	105

[a] Cathodic shift in redox wave produced by the presence of anions (up to 5 equivalents) added as their tetrabutylammonium salts. [b] Average shift of both ferrocene waves.

components of **6**–**9**. In all cases the anion-induced magnitude of cathodic perturbations of the porphyrin oxidation wave are much larger than those of the ferrocene redox couple. The polarising power, *i.e.* charge to radius ratio of the anionic guest species, dictates the cathodic shift values observed. For example the general ΔE trend of decreasing shift magnitude for the porphyrin oxidation wave is $HSO_4^- > Cl^- > Br^- > NO_3^-$ with each receptor. Interestingly, the respective porphyrin reduction waves are not significantly perturbed ($\Delta E \leqslant 5$ mV) with any anionic guest. Although the addition of anions to electrochemical solutions of **2**–**5** did not perturb the respective oxidation peak potentials (E_{Pa}) of the porphyrin or ferrocene redox couples relatively small cathodic perturbations (ΔE 5–20 mV) of the corresponding reduction peak potentials were observed. These results indicate that a degree of anion binding takes place in the compounds oxidized states and not in their neutral states which is consistent with the ^{1}H NMR investigations described earlier.

Conclusion

New free-base and zinc-metallated 5,10,15,20-tetrakis(*o*-ferrocenylcarbonylaminophenyl-substituted)porphyrin atropisomers have been prepared. Proton NMR anion-binding studies revealed the free base compounds to be poor complexing agents for anions. In contrast the zinc metalloporphyrin receptors strongly complex anionic guests and stability constant evaluations in dichloromethane display selectivity trends that are dependent upon the topological arrangement of the ferrocene amide groups of a particular atropisomer. For example the α,α,α,β isomer **7** exhibits the selectivity sequence $NO_3^- > Cl^- > HSO_4^-$ whereas the α,α,α,α isomer **6** is bromide selective. Electrochemical investigations show that compounds **6**–**9** can electrochemically recognize anions *via* significant cathodic perturbations of the respective porphyrin oxidation and ferrocene redox couples.

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