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Synthesis, characterisation and X-ray structure of a novel porphyrin array employing Zn–O and O–H...O bonding motifs

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Abstract

The preparation and characterisation of the free-base and zinc metallated derivatives of 5,10,15,20-tetrakis(4-(2-(2-hydroxyethoxy)phenyl)porphyrin **1** is described. The X-ray crystal structure of the Zn(II) adduct **2** dimerises in the solid state *via* an intermolecular polyether oxygen–Zn(II) interaction (O. . .Zn = 2.124(4) Å). The porphyrin dimers form discrete layers defined by a distance of 5.10 Å between the porphyrin planes in adjacent layers. A bilayer sheeting arrangement of the porphyrin macrocyclic units is achieved through cooperative hydrogen bonding of the ethoxyethanol arms to form 11-membered macrocycles containing four hydrogen bonds. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Metalloporphyrins; Zn(II) complex; Hydrogen bonding; Coordination network; X-ray structure

1. Introduction

Controlling the arrangement of porphyrin macrocycles into well-defined solid-state arrays through the processes of self-assembly and self-organisation is necessary to advance the development of surface bound porphyrin devices with applications in surface sensing, size exclusion, light harvesting and heterogeneous porphyrin catalysis [1-6]. Desired control may be executed by utilising "intelligent" porphyrins in which non-covalent interactions are pre-programmed into the porphyrin structure to aid molecular alignment in either a pseudo 1-D or 2-D and 3-D arrays [7–10]. In particular, new porphyrin systems capable of forming either hydrogen bonded or coordinative 2D sheet networks from a single molecular entity are desirable. In this paper we report on preliminary studies using ethoxyethanol side chains for this goal (Fig. 1). Such functionality could potentially self-assemble at the porphyrin periphery in a non-covalent way cooperatively, forming two distinct intermolecular hydrogen bonds per ethoxyethanol set leading to discrete assemblies or 2-D supramolecular arrays.

2. Results and discussion

5,10,15,20-Tetrakis(4-(2-(2-hydroxyethoxy)ethoxy)phenyl)porphyrin (1, H₂TEEP) was prepared in 83% yield by the alkylation of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin with 2-(2-chloroethoxy)ethanol [11]. Compound 1 is surprisingly insoluble in the usual aprotic solvents used for dissolving porphyrins (CHCl₃, CH₂Cl₂, toluene, etc). This insolubility can be attributed to extensive intermolecular hydrogen bonding interactions, which are desirable but uncontrolled to this point. The problem is alleviated by the addition of a small amount of a solvent capable of interfering with hydrogen bonding (e.g., methanol or pyridine)¹. Zinc metallation of 1 was achieved using the acetate method [12] producing 5,10,15,20-tetrakis(4-(2-(2-hydroxyethoxy)ethoxy)phenyl)porphinato zinc(II) (2, ZnTEEP) in 89% yield as a light purple solid. Solubility of the porphy-

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¹ Despite this fix, crystals of **1** suitable for X-ray crystallography have not been forthcoming.



Fig. 1. Utilising the potential of ethoxyethanol groups on the porphyrin periphery could lead to a range of supramolecular constructs through concentration and surface dependency.





Fig. 2. ORTEP diagram of the molecule displaying the atom labelling scheme used with in paper. Ellipsoids are drawn at 50% probability level. Coordinating alcohol removed for clarity.

Table 1 Selected bond lengths (Å) and bond angles (°) for ${\bf 2}$

	•	0 ()	
Bond distances			
M-N(1)	2.056(4)	M-N(4)	2.071(4)
M-N(2)	2.059(4)	M-O(6)	2.124(4)
M-N(3)	2.050(4)		
Bond angles			
N1–Zn1–N2	88.76(14)	N3–Zn1–O6	99.34(14)
N1–Zn1–N3	163.25(15)	N1–Zn1–O6	97.41(14)
N1–Zn1–N4	88.86(14)	N2–Zn1–O6	97.84(14)
N2–Zn1–N3	89.23(14)	N4–Zn1–O6	98.35(14)
N2–Zn1–N4	163.80(15)		
N3–Zn1–N4	88.45(14)		

rin 2 was also only possible in a mixed solvent system in which a solvent capable of competing with ethoxyethanol hydrogen bonding was employed. Using this technique, crystals suitable for X-ray crystallography were grown by the slow diffusion of diethyl ether into dichloromethane/ methanol (see Scheme 1).

ZnTEEP (2) crystallises in the triclinic space group $P\overline{1}$. The molecular structure of 2 is shown in Fig. 2 and selected bond distances and angles for 2 are listed in Table 1. The square pyramidal Zn(II) centre is somewhat distorted with the four inner peripheral nitrogens of the porphyrin defining the pyramid base and the apical position occupied by a coordinated (intermolecularly) alcohol side chain (see Fig. 3). The metal to nitrogen bond distances vary from 2.050(4) to 2.071(4) Å (average value 2.059 Å), with the axially coordinated Zn-O bond displaying a longer distance of 2.124(4) Å. These values fall into the ranges observed in other Zn(II) porphyrin systems [13]. The Zn(II) metal ion resides 0.29 Å above the porphyrin least squares plane and toward the coordinating alcohol. The large dihedral angles observed between the meso phenyl rings and the mean porphyrin plane (69.9-88.3°) are also typical, the difference from orthogonal attributed to crystal packing forces [14]. Despite their inherent flexibility, the ethoxyethanol chains are extended and relatively well ordered. Each



Fig. 3. Representation of the dimer formed in the crystal structure of 2 (H-atoms and CH₂Cl₂ solvent molecule have been omitted for clarity).



Fig. 4. Bilayer sheeting arrangement observed in the crystal structure of 2. The shaded area highlights the organisation and intra-layer thickness (3.45 Å), with inter-layer separation of 5.10 Å (H-atoms have been omitted for clarity).



Fig. 5. Representation of the hydrogen bonding motif observed above the zinc coordination site (hydrogen atoms have been omitted for clarity).

Table 2 Hydrogen bonding parameters of **2**

O–H	0	O–H $(Å)^a$	$H{\cdots}O\;(\mathring{A})$	O···O (Å)	O−H···O (°)
O-H(3)	O5	0.84	2.16	2.791(6)	132.2
O-H(6)	O9	0.84	1.92	2.626(6)	159.8
O-H(9)	O12	0.84	1.89	2.677(6)	155.9
O-H(12)	O3	0.84	1.82	2.686(6)	150.2

^a All non-hydrogen atoms were refined anisotropic, while all hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they are attached.

OCH₂CH₂OH group forms a staggered *gauche* arrangement while the internal OCH₂CH₂O groups are not as well defined, forming both *extended* and *gauche* arrangements.

Interestingly, ZnTEEP forms a C_2 symmetric dimer in which the OH group from the ethoxyethanol side chain of one porphyrin coordinates to the Zn(II) centre of an adjacent porphyrin molecule [15]. A representation of this dimer is shown in Fig. 3. The observed Zn...Zn separation between the two porphyrins within the dimer is 13.39 Å, with the mean plane of the porphyrins aligned parallel to one another at a distance of 3.45 Å (Fig. 3). The two *meso* phenyl groups used to form the 28-membered macrocycle are parallel to each other but do not provide further Van der Waals stabilisation through π - π interactions.

The dimeric arrays occur within a plane represented by the grey regions in Fig. 4 and alternate in an up-and-down fashion. Each bilayer is separated by an intervening space of thickness 5.10 Å (porphyrin plane to porphyrin plane). The dimers within one layer are interconnected through a hydrogen bonding motif involving the ethoxyethanol chains not involved in dimerisation. A representation of this motif and the extended layer is shown in Fig. 5. Selected hydrogen bonding data are listed in Table 2.

The bilayer sheeting arrangement of the porphyrin macrocyclic units is achieved through cooperative hydrogen bonding of the ethoxyethanol arms to form 11-membered macrocycles containing four hydrogen bonds. Hence, all ethoxyethanol groups are employed in the formation of the overall structure. The longest of the hydrogen bonds O3–H...O5 differs from the others (Table 2) in that it is an ether oxygen rather than hydroxy oxygen atom that partakes in the noncovalent bonding.

3. Concluding remarks

A novel supramolecular structure utilising hydrogen bonding and Zn(II)–N and Zn(II)–O coordination was determined. Despite the use of hydrogen bonding (available through the ethoxyethanol side chains) to form a layered structure, this present result was more complex than anticipated by design. We are continuing our quest to form hydrogen bonded arrays based on the ethoxyethanol motif for surface adhesion, but recognise that the use of free-base or metalloporphyrins in which axial coordination is not possible (i.e. using four coordinate metal ions or strong donor ligands) may be necessary to achieve this goal. These experiments are underway.

4. Experimental

4.1. General

Synthesis reagents including solvents were used as purchased. Melting points (m.p.) were measured on a Stuart Scientific SMP 3 melting point apparatus. UV–Vis spectra were recorded on a Varian model Cary 100 Bio UV–Visible Spectrophotometer, with the solvent systems used stated in the synthesis description. ¹H and ¹³C nuclear magnetic resonance (n.m.r.) spectra were recorded using a Bruker DPX 300 MHz spectrometer (300 MHz ¹H, 75 MHz ¹³C) or a Bruker DRX 400 MHz spectrometer (400 MHz ¹H, 100 MHz ¹³C), as solutions in the deuterated solvents specified. Deuterated chloroform (CDCl₃) was base washed with anhydrous Na₂CO₃ prior to use. High-resolution electrospray mass spectra (HRMS) were recorded on a Bruker BioApex 47e Fourier transform mass spectrometer.

4.1.1. 5,10,15,20-Tetrakis(4-(2-(2-hydroxyethoxy)) ethoxy)phenyl)porphyrin (1)

To a stirred DMF solution (50 mL) of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (100 mg, 0.15 mmol), anhydrous K₂CO₃ (410 mg, 2.96 mmol) and 2-(2-chloroethoxy)ethanol (0.2 mL, 1.89 mmol) were added and the resulting solution was heated to 80 °C and left to stir for 4 days. After cooling, the porphyrin was precipitated by the addition of water (50 mL), filtered and washed with water $(3 \times 5 \text{ mL})$. Further purification by column chromatography (SiO₂, CHCl₃/MeOH, 9:1 ratio) eluted 1 as a purple solid (128.5 mg, 83%). m.p. 261-262 °C, UV-Vis (CHCl₃/MeOH, 9:1) λ_{max} (log ε): 403 sh (4.79); 422 (560); 520 (4.16); 556 (4.09); 594 (3.88); 649 nm (3.90). ¹H n.m.r (400 MHz, CDCl₃/MeOH, 4:1): δ 3.66 (m, 8H, OCH₂); 3.72 (m, 8H, OCH₂); 3.19 (t, J 4.6 Hz, 8H, OCH₂); 4.29 (t, J 4.5 Hz, 8H, OCH2); 7.17 (ABq, J 8.2 Hz, 8H, ArH); 7.98 (ABq, J 8.2 Hz, 8H, ArH); 8.69 (s, 8H, β-pyrrolic-H); inner NH not observed. HR-MS (ESI, +ve, DCM/ MeOH): calculated m/z 1053.4262; observed m/z1053.4230 [M+Na]⁺.

4.1.2. [5,10,15,20-Tetrakis(4-(2-(2-hydroxyethoxy)) ethoxy)phenyl)porphinato]zinc(II) (2)

To a solution of 1 (15 mg, 0.015 mmol) in $CHCl_3/MeOH$ (3 mL, 4:1 ratio) was added a saturated $Zn(OAc)_2$ in MeOH (5 mL) and stirred at reflux for 3 h in darkness. Upon completion, the solvent system was removed by

rotary evaporation. Water and THF were added and the THF was removed by rotary evaporation to precipitate the porphyrin. The purple suspension was filtered and washed with water $(3 \times 5 \text{ mL})$. The sample was dried under high vacuum pump to remove the residual solvent giving 2 as a purple solid (14.2 mg, 89%). X-ray quality crystals were grown by the slow diffusion of diethyl ether into a CH₂Cl₂/MeOH solvent system (4:1), resulting in elongated hexagonal red plates. m.p. 223–225 °C. UV–Vis (THF) λ_{max} (log ε): 406 sh (4.63); 426 (6.07); 558 (4.94); 599 nm (4.60). ¹H n.m.r (400 MHz, CDCl₃/MeOD 9:1): δ 3.53 (m, 16H, OCH₂); 3.76 (m, 8H, OCH₂); 4.14 (m, 8H, OCH₂); 7.00 (ABq, J 8.6 Hz, 8H, ArH); 7.83 (ABq, J 8.6 Hz, 8H, ArH); 8.56 (s, 8H, β-pyrrolic-H). ¹³C n.m.r (75 MHz, CDCl₃/MeOD 9:1): δ 61.5, 67.8, 69.9, 73.0, 112.6, 120.1, 131.5, 135.6, 136.4, 150.3, 158.2. HR-MS (ESI, +ve, DCM/MeOH): calculated m/z 1115.3397; observed m/z 1115.3414 [M+Na]⁺.

4.1.3. X-ray structure determination

4.1.3.1. Data collection and processing. X-ray measurements were made using a Bruker X8 Apex II CCD diffractometer using monochromated Mo K α radiation (0.71073 Å). The collection temperature was maintained at 123 K using an Oxford Cryostream open-flow N₂ cryostat. Solution was obtained by direct methods (SHELXS 97)[15] followed by successive Fourier-difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97) [16]. Hydrogen atom thermal parameters were tied to those of the atom to which they are attached.

Crystal data for **2**: $C_{61}H_{62}Cl_2N_4O_{12}Zn$, M = 1179.42, red plate, $0.20 \times 0.20 \times 0.02$ mm, triclinic, space group $P\bar{1}$, a = 11.6110(5), b = 13.3604(5), c = 17.6703(8) Å, $\alpha =$ 87.943(2), $\beta = 86.938(2)$, $\gamma = 88.317(2)^\circ$, V = 2734.4(2) Å³, Z = 2, $D_c = 1.432$ g/cm³, $F_{000} = 1232$, T = 123(2) K, $2\theta_{max} = 55.1^\circ$, 60320 reflections collected, 12539 unique ($R_{int} = 0.0751$). Final Goodness-of-fit = 1.117, $R_1 =$ 0.0891, $wR_2 = 0.1995$, R indices based on 9409 reflections with $I > 2\sigma(I)$ (refinement on F^2), 721 parameters. Lp and absorption corrections applied, $\mu = 0.616$ mm⁻¹.

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Appendix A. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC (awaiting No.) for structures of **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). The ¹H n.m.r. spectrum of **2** is also presented. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.06.002.

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