Building-up novel coordination polymer with Zn(II) porphyrin dimer: Synthesis, structures, surface morphology and effect of axial ligands

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Abstract. Highly flexible Zn(II)1,2-bis(*meso*-octaethylporphyrin)ethane (**1**) has been used as host in which two porphyrin rings are found to be face-to-face in non-coordinating solvents. Upon addition of one relatively smaller 4,4'-dipyridine (L^1) and one extended N,N'-bispyridine-4-yl-methylene ethylenediamine (L^2) guest ligands, the *syn* conformation of **1** is switched to the *anti* complexes $1 \cdot (L^1)_2$ and $1 \cdot L^2$, respectively. Single crystal X-ray structures of all the complexes are reported in which a stable one-dimensional coordination polymer is produced only in $1 \cdot L^2$ that is, to the best of our knowledge, the first structural report of 1D-coordination polymer with porphyrin dimer. Solution structures of the complexes along with binding studies in solution between **1** and L have also been investigated. The morphology of the polymeric complex $1 \cdot L^2$ on silicon wafer surface was examined by Atomic Force Microscopy (AFM) in which the crystalline islands of well defined facets of size ranging from 200–550 nm perimeter and a height of 20–40 nm have been observed.

Keywords. Zn(II)bisporphyrin; coordination polymer; binding constant; surface morphology; structure elucidation

1. Introduction

Multi-porphyrin systems have been studied extensively in recent times for their structure-induced optical and electronic properties that have application in optical switches, conductive materials and non-linear optics.^{1–10} Porphyrins and chlorophylls are often self-assembled into nanoscale superstructures to perform many essential biological functions, such as light harvesting and electron transport.¹¹ The application of these supramolecular systems would require fabrication on substrate surfaces that are smooth at the molecular level. Higher-order structures, such as wires, networks and nanodots on surfaces, are necessary for molecular electronic devices. Since porphyrins have tunable photophysical and chemical properties, the functionalities of their materials can be suitably manipulated.

While numerous multi-porphyrin systems have been reported so far, most of them rely on rigid covalent linkages to achieve the shape persistent multi-porphyrin structures.^{6,7} Although rigid connections between porphyrin pigments are useful to materialize regular arrangement of porphyrins, the synthetic procedures become inevitably complicated, tedious and also expensive. However, the preparation of supramolecular

porphyrin polymers by self-assembly is fascinating since it involves a relatively light synthetic burden and tunability for length by control of external conditions. Hence, a supramolecular self-assembly system has become an attractive and alternative strategy to build well-ordered multi-porphyrin array including models of long polymers for potential conductive wires and optical materials. Linkers that can bind two or more metalloporphyrin units into a supramolecular aggregate are particularly useful. The metal ion and spacers provide additional variants of the supramolecular structure. Recently, we have reported a large family of stable magnesium, zinc and cobalt complexes of tetranitro octaethylporphyrin¹² which bind strongly with conjugated bipyridyl axial ligands to generate different types of oligomer as well as polymeric assemblies depending on the nature of metal ions used. For example, while magnesium and cobalt mono-porphyrin form six-coordinate complexes with bipyridyl ligand in which all the porphyrin units are aligned parallel to each other to have so-called 'shish kebab' like architectures, zinc forms five-coordinate porphyrin dimer with 'wheel-and-axle' like architecture.¹² It would be interesting to investigate such studies using porphyrin dimers instead of monomeric porphyrin itself. Our design utilizes a two component system which would allow enhancing or changing the structure and property of the final polymeric system. Despite the simplicity of

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this approach, the axial ligand must meet the specific design/electronic requirements.

Herein, we have used Zn(II)bisporphyrin as a host in which the two *meso* positions are connected through a highly flexible ethane spacer. Upon coordination of axial ligand to the zinc central ion, *syn* conformation of Zn(II)bisporphyrin is switched to either stretched *anti* conformer or 1:1 sandwich complex depending upon the type of axial ligand used for destroying the strong π - π interporphyrin interactions.¹³ The ethane spacer gives the compound enough flexibility to adjust the distance between two porphyrin units. While 1,2-diaminobenzene and 4,4'-dipyridine form 1:1-sandwich and 1:2-*anti* complex, respectively, with Zn(II)bisporphyrin the flexible and extended N,N'-bispyridine-4-yl-methylene ethylenediamine form one dimensional polymeric chain in *anti* conformation. The structure of the molecule in solution and its surface pattern on silicon has also been investigated.

2. Experimental

2.1 Materials

Zn(II)1,2-bis(*meso*-octaethylporphyrin)ethane (**1**), has been prepared by literature methods.¹³ Reagents and solvents are purchased from the commercial sources and purified by standard procedures before use. The ligand 4,4' bipyridine (L^1) has been purchased from Sigma-Aldrich while N,N'-bispyridine-4-yl-methylene ethylenediamine (L^2) has been synthesized following the reported procedure.¹⁴

2.1a Synthesis of $I \cdot (L^1)_2$: Zn(II)bisporphyrin, **1** (50 mg, 0.041 mmol) was dissolved in 5 mL distilled chloroform. 4,4' bipyridine (L^1) (20 mg, 0.13 mmol) was added to it and stirred for 5–6 min. The solution thus obtained was then filtered off to remove any solid residue, the volume reduced to nearly half and carefully layered with n-hexane in air at room temperature. On standing for 6–7 days, dark crystalline solid were precipitated out which was then isolated by filtration, washed well with hexane and dried in high vacuum for several hours. Yield: 40 mg (57 %). Anal. Calcd (found) for $C_{104}H_{114}N_{14}Zn_2$: C, 73.87 (73.72); H, 6.80 (6.92); N, 11.60 (11.78). UV-vis (chloroform) [λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)]: 427 (1.65×10^5), 438^{sh} (1.56×10^5), 561 (2.00×10^4), 601 (6.74×10^3). 1H NMR ($CDCl_3$, 295 K): δ 9.82(s, 2H, 15-*meso*-H); 9.72(s, 4H, 10,20-*meso*-H); 6.30(br, 16H, CH(L^1); 4.64(s, 4H, -CH₂(b)); 4.15–3.10 (m, 32H, -CH₂CH₃); 1.90–1.18 (m, 48H, -CH₂CH₃) ppm.

2.1b Synthesis of $I \cdot L^2$: Zn(II)bisporphyrin, **1** (50 mg, 0.041 mmol) was dissolved in 5 mL distilled chloroform. N,N'-bispyridine-4-yl-methylene ethylenediamine (L^2) (10.5 mg, 0.05 mmol) was added to it and was stirred for 5–6 min. The solution thus obtained was then filtered off to remove any solid residue, the volume reduced to nearly half and carefully layered with n-hexane in air at room temperature. On standing for 7–8 days, dark crystalline solid of the title complex were precipitated out which was then isolated by filtration, washed well with n-hexane. The solid sample was then dried in high vacuum for several hours. Yield: 40 mg (66%). Anal. Calcd (found) for $C_{88}H_{104}N_{12}Zn_2$: C, 72.36 (72.51); H, 7.17 (7.31); N, 11.50 (11.64). UV-vis(chloroform) [λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)]: 427 (1.60×10^5), 438^{sh} (1.30×10^5), 559 (2.10×10^4), 600 (9.30×10^3). 1H NMR ($CDCl_3$, 295 K): δ 9.87(s, 2H, 15-*meso*-H); 9.68 (s, 4H, 10,20-*meso*-H); 7.40 (s, 2H, CH(L^2)); 6.38(s, 4H, Py-H, L^2); 5.45 (br, 4H, Py-H, L^2); 4.71(s, 4H, -CH₂(b)); 4.07 (s, 4H, -CH₂(L^2)); 4.20–3.15 (m, 32H, -CH₂CH₃); 2.10–0.78 (m, 48H, -CH₂CH₃) ppm.

2.2 Instrumentation

UV-vis spectra were recorded on a PerkinElmer UV/vis spectrometer. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400II elemental analyzer. 1H NMR spectra were recorded on a JEOL 500 MHz instrument. The residual 1H resonances of the solvents were used as a secondary reference. PXRD data were collected on an XPERT-PRO diffractometer using CuK α radiation (λ 413 = 1.540598 Å) at 295 K.

2.3 Atomic force microscopy

The samples were imaged using Agilent Technologies Atomic Force Microscopy (AFM) operating under the Acoustic AC mode (AAC) and the sample was mounted on the XY stage of the AFM and the integral video camera (NAVITAR, Model N9451A-USO6310233) with the Fiber-lite source. MI-150 high intensity illuminator from Dolan-Jenner Industries was used to isolate the marked regions imbedded with the microscope. Micro fabricated silicon nitride cantilevers (PPP-NCL-20) and scanner model N9524A-USO7480132. x m l/N9520A-USO7480152.xml were used for imaging. The images were taken at room temperature in air with a scan speed of 2.0 lines/sec. Repeated scanning of the sample confirmed that no physical damage occurred during scanning. Data acquisition and analysis was carried out using Pico View 1.8.2. The Images were processed by using Pico Image basic software.

2.4 X-ray structure solution and refinement

Single crystal of the complexes were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of Bruker SMART APEX CCD diffractometer equipped with CRYO industries low-temperature apparatus. Intensity data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) while SAINT software¹⁵ was used for data integration and reduction. An absorption correction was applied.¹⁶ The structures were solved by the direct method using SHELXS-97 and were refined on F² by full-matrix least-squares technique using the SHELXL-97 program package.¹⁷ Non-hydrogen atoms were refined anisotropically. In the refinement, the hydrogen atoms were included in geometrically calculated positions and were refined according to the 'riding model.' Crystal data and data collection parameters are given in table 1. The structures of **1**·(L¹)₂, and **1**·L² contain several severely disordered solvent molecules which could not be modelled properly due to weakly diffracting nature of the crystals and thus, the SQUEEZE¹⁸ routine of PLATON was used to remove such unbound and

highly disordered solvent molecules (three CHCl₃ and one H₂O molecules per unit cell in **1**·(L¹)₂ while three CHCl₃ and two H₂O molecules per unit cell in **1**·L²) but the reported formula includes the solvents.

3. Results and Discussion

Zn(II)1,2-bis(*meso*-octaethylporphyrinyl)ethane **1** was prepared using the procedure reported previously.¹³ Two porphyrin rings in **1** are found to be in face-to-face in non-coordinating solvent. This spatial arrangement is extremely stable with no observable changes in conformation even upon heating up to 110°C. Strong π - π interaction between two planar chromophoric moieties generates this high stability.¹³ The UV-vis spectrum of **1** show Soret and Q-bands at 400 and 551 nm, respectively. Additions of excess 4,4' bipyridine (L¹) to the chloroform solution of **1** results large spectral change which includes the red shift and splitting of the Soret band into two well-resolved^{13c,19} B_I and B_{II} transitions at 427 and 438 nm as the host: guest ratio changes from 1:0.1 to 1:3760 due to the formation of **1**·(L¹)₂ which has been isolated as solid. Figure 1

Table 1. Crystal data and data collection parameters of **1**·(L¹)₂ and **1**·L².

	1 ·(L ¹) ₂	1 ·L ²
T, K	100(2)	100(2)
Formula	C ₁₁₇ H ₁₂₇ Cl ₉ N ₁₆ O Zn ₂	C ₉₁ H ₁₁₁ Cl ₉ N ₁₂ O ₂ Zn ₂
Crystal size (mm ³)	0.22 x 0.16 x 0.10	0.20 x 0.15 x 0.12
Formula weight	2223.14	1854.71
Crystal system	Triclinic	Triclinic
Colour	Dark Red	Dark red
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	13.914(4)	12.547(5)
<i>b</i> , Å	16.036(5)	14.520(5)
<i>c</i> , Å	16.284(5)	14.749(5)
α , deg	108.348(6)	78.036(5)
β , deg	110.071(6)	85.912(5)
γ , deg	105.289(6)	66.718(5)
<i>V</i> , Å ³	2944.2(16)	2414.4(15)
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)
<i>Z</i>	1	1
<i>d</i> _{calcd} , g·cm ⁻³	1.254	1.276
μ , mm ⁻¹	0.665	0.797
<i>F</i> (000)	1162	970
No. of unique data	10137	8184
No. of parameters Refined	617	479
GOF on <i>F</i> ²	1.003	0.934
<i>R</i> 1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0760	0.0708
<i>R</i> 1 ^a (all data)	0.0998	0.1017
<i>wR</i> 2 ^b (all data)	0.2100	0.1957
Largest diff. peak and hole	1.450 and -0.787 e.Å ⁻³	0.897 and -0.993 e.Å ⁻³

^a $R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}$; ^b $wR2 = \sqrt{\frac{\sum [w(Fo^2 - Fc^2)^2]}{\sum [w(Fo^2)^2]}}$

Figure 1. UV-visible spectral changes of **1** in chloroform upon addition of 4,4'-bipyridine (L^1) as the host-guest ratio changes from 1:0.1 to 1:3760 at 295 K.

demonstrates such spectral change with clear isosbestic points at 414, 472 and 580 nm. Such splitting in the Soret band region, as observed here, are also in good agreement with Kasha's exciton coupling theory²⁰ and associated with the *anti* form of the complex in solution which has been isolated as solid and structurally characterized (*vide infra*). The splitting of the Soret band was often observed for various porphyrin dimers and trimers in linear spatial orientations.

However, addition of excess L^2 to chloroform solution of **1** also produces similar red shifts of the Soret and Q-bands to 427, 559 nm, respectively, although the band at 438 nm has been converted to a weak shoulder. The spectral change is due to the formation of polymeric complex $1 \cdot L^2$ which has been isolated as solid and structurally characterized. Figure 2 displays the spectral change of **1** in chloroform upon addition of L^2 as the host: guest ratio changes from 1:0.1 to 1:1068 in which isosbestic points at 415 and 589 nm are clearly visible. Figure 3, however, compared the

Figure 2. UV-visible spectral changes of **1** in chloroform upon addition of L^2 as the host-guest ratio changes from 1:0.1 to 1:1068 at 295 K.

Figure 3. UV-visible spectral changes of $1 \cdot (L^1)_2$ (red), $1 \cdot L^2$ (blue) in chloroform at 295 K.

Scheme 1. Synthetic outline of the complexes.

Scheme 2. List of guest ligand used.

UV-visible spectra as appeared for $1 \cdot (L^1)_2$ and $1 \cdot L^2$. Addition of 1,2-diaminobenzene (ODAB) to the chloroform solution of **1** produces 1:1-sandwich complex **1**·ODAB which has been reported earlier by us.¹⁹ Scheme 1 shows the synthetic outline of the complexes reported here along with their abbreviations while scheme 2 lists the axial ligand used in the present investigation and their abbreviations. However, detailed synthetic procedures along with the spectroscopic characterizations for all the complexes reported here are given in the Experimental Section.

3.1 Crystallographic characterization of $1 \cdot (L^1)_2$

Dark brown crystals of the complex are obtained *via* slow diffusion of n-hexane into the chloroform solution of the molecule in air and one such crystal was chosen to mount on the Goniometer head for X-ray structure determination. The molecule crystallizes in the triclinic crystal system with *P*-1 space group. A perspective view of the molecule is shown in figure 4. The complex has a five coordinate square-pyramidal geometry in which the Zn-atom is displaced by 0.38 Å from the least-squares plane of the C₂₀N₄ porphyrinato core. The average Zn-N_p and Zn-N_{ax} distances are found to be 2.069(3) and 2.154(3) Å, respectively. The non-bonding distances between two Zn atoms are found to be 9.89 Å. Figure 5 represents the packing diagram of $1 \cdot (L^1)_2$ which also shows the unbound 4,4'-bipyridine (*L*¹) that is present in the crystal lattice.

Figure 4. A perspective view of $1 \cdot (L^1)_2$ showing 50% thermal contours for all non-hydrogen atoms at 100 K. H-atoms have been omitted for clarity. The molecule also contains unbound *L*¹ in the crystal lattice which is not shown.

Figure 5. Molecular packing of $1 \cdot (L^1)_2$ in the unit cell which also includes the unbound *L*¹. H-atoms have been omitted for clarity.

3.2 Crystallographic characterization of $1 \cdot L^2$

Dark brown crystals of the molecule are obtained *via* slow diffusion of n-hexane into the chloroform solution of the complex in air at room temperature and one such crystal was mounted on the Goniometer head for X-ray structure determination. The molecule crystallizes in the triclinic crystal system with *P*-1 space group. The complex has a five coordinate square-pyramidal geometry in which the Zn-atom is displaced by 0.31 Å from the least-squares plane of the C₂₀N₄ porphyrinato core. The average Zn-N_p and Zn-N_{ax} distance are found to be 2.069(4) and 2.179(4) Å, respectively, which are similar to other five-coordinate Zn(II) porphyrin reported here. The non-bonding distance between two Zn atoms is found to be 10.03 Å. Figure 6 illustrates the molecular packing which shows the formation of one-dimensional (1D) chain. To the best of our knowledge, this is the first structural report of such 1D-coordination polymer with porphyrin dimers. Crystal data and data collection parameters for all the complexes reported here are listed in table 1 while the selected bond distances and angles are given in table 2.

The salient structural features of the complexes reported here along with Zn(II)bisporphyrin **1** reported earlier^{13d} are compared in table 3. Zn is present on the mean porphyrin plane in **1** but the metal is significantly displaced in five-coordinate complexes; the metal displacement in $1 \cdot (L^1)_2$ is more compared to the polymeric species $1 \cdot L^2$. As can be seen, Zn···Zn non-bonding distance increases from 9.89 Å in $1 \cdot (L^1)_2$ to 10.03 Å in $1 \cdot L^2$. The average Zn-N(L) distance also increases from 2.154(3) Å to 2.179(4) Å in the same order. Moreover, the porphyrin rings are distorted more in five-coordinate species. X-ray structure

Figure 6. Molecular packing of $1 \cdot L^2$. H-atoms have been omitted for clarity.

of 1:1 sandwich complexes $1 \cdot \text{DACH}$ ^{13e} and $1 \cdot \text{ODAB}$ ^{19a} have been reported earlier which, however, enable us to compare with the structural parameters of the complexes reported here. As can be seen from table 3, Zn–N (por) and metal displacements from the mean porphyrin plane (Δ_{24}^{Zn}) are more or less similar in the five-coordinate complexes. However, Zn···Zn separation is found to be 5.55 Å in $1 \cdot \text{ODAB}$ while the values are 9.89 and 10.03 Å for $1 \cdot (L^1)_2$ and $1 \cdot L^2$, respectively, which shows the unusual ability of the Zn(bisporphyrin) platform to ‘open’ and ‘close’ its binding pockets, leading to facile *syn-anti* conformational switching with very high vertical flexibility.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $1 \cdot (L^1)_2$ and $1 \cdot L^2$.

	$1 \cdot (L^1)_2$	$1 \cdot L^2$
Zn(1)–N(1)	2.069(3)	2.078(4)
Zn(1)–N(2)	2.071(3)	2.078(4)
Zn(1)–N(3)	2.069(3)	2.064(4)
Zn(1)–N(4)	2.065(3)	2.058(4)
Zn(1)–N(5)	2.154(3)	2.179(4)
N(1)–Zn(1)–N(2)	89.77(13)	90.32(15)
N(1)–Zn(1)–N(3)	161.37(13)	164.13(13)
N(1)–Zn(1)–N(4)	86.93(13)	87.01(15)
N(2)–Zn(1)–N(3)	87.19(13)	87.96(15)
N(2)–Zn(1)–N(4)	162.65(12)	163.49(14)
N(3)–Zn(1)–N(4)	90.51(13)	90.17(15)
N(1)–Zn(1)–N(5)	95.88(13)	97.73(14)
N(2)–Zn(1)–N(5)	99.36(12)	96.43(14)
N(3)–Zn(1)–N(5)	102.75(13)	98.14(14)
N(4)–Zn(1)–N(5)	97.92(12)	100.07(14)

It would be interesting to discuss now the various molecular structures that can be generated designing suitable bidentate ligand L with the Zn-1,2-bis(*meso*-octaethylporphyrinyl)ethane (**1**). Upon coordination of 1,2-diaminocyclohexane (DACH) and 1,2-diaminobenzene (ODAB), 1:1 sandwich complexes are formed where Zn···Zn separation are found to be 5.60 and 5.55 Å, respectively.^{13e,19a} Here two coordinating nitrogens are perfectly suitable to form a stable chelate with **1**. In contrast, 4,4′ bipyridine (L^1) whose internitrogen distance between two binding sites is 7.10 Å can only form the *anti*-complex $1 \cdot (L^1)_2$ (figures 4 and 5). Similarly, coordination of N,N′-bispyridine-4-yl-methylene ethylenediamine (L^2) whose internitrogen distance between two binding sites is 13.44 Å also produces the *anti*-complex at first which eventually self-assembled to form 1D coordination polymer $1 \cdot L^2$ (figure 6). Formation of such polymer with L^1 is not possible since it would invite severe steric interaction between two porphyrin rings due to smaller size of the ligand.

Figure 7 compare the powder X-ray diffraction (PXRD) pattern of the bulk sample of $1 \cdot L^2$ with the simulated pattern obtained from the single crystal X-ray structure. As can be seen, the bulk powder sample of the complex also has the same polymeric structures obtained from the single crystal X-ray diffraction study.

3.3 ^1H NMR

^1H NMR titration experiments were carried out at 295K in CDCl_3 to investigate the structure of complex in solution as shown in figure 8. Trace A shows the well

Table 3. Selected structural parameters.

Complex		Zn-N _p ^a	Zn-N _{ax} ^a	Δ_{24}^{Znb}	Δ_{24}^{c}	Zn...Zn ^d	Ref.
1	core-I	2.037(3)		0.03	0.06	5.91	13d
	core-II	2.038(3)		0.04	0.09		
1 ·DACH ^e	core-I	2.079	2.170	0.47	0.11	5.60	13e
	core-II	2.073	2.186	0.40	0.10		
1 ·ODAB ^f	core-I	2.062(5)	2.256(5)	0.30	0.09	5.55	19a
	core-II	2.056(5)	2.258(5)	0.26	0.08		
1 ·(L ¹) ₂		2.069(3)	2.154(3)	0.38	0.12	9.89	Tw
1 ·L ²		2.069(4)	2.179(4)	0.31	0.12	10.03	Tw

^aAverage value in Å. ^bDisplacement (in Å) of Zn from the least-square plane of the C₂₀N₄ porphyrinato core. ^cAverage displacement (in Å) of atoms from the least-square plane of the C₂₀N₄ porphyrinato core. ^dNon-bonding distance in Å. ^eDACH, 1,2-diaminocyclohexane. ^fODAB, 1,2-diaminobenzene

resolved spectra of **1** in CDCl₃ alone. Trace B shows the ¹H NMR spectra of polycrystalline sample of **1**·(L¹)₂. Trace C corresponds to the ¹H NMR spectra of free L¹. CH protons of L¹ primarily resonate at 8.73 and 7.52 ppm which upon complexation shifted upfield^{21,22} to 6.30 ppm with a broad signal. The 10,20-*meso* protons of the porphyrin macrocycle show a downfield shift of 1.55 ppm as the identical 10 and 20-*meso* protons are strongly shielded by the ring current effect of the two face-to-face porphyrin subunits in **1**. In the *anti*-complex, however, the 15-*meso* proton is out of such shielding effect and thus remains mostly unaffected. There is also an upfield shift of 0.56 ppm for the

bridging -CH₂ proton signals. Similar trends in ¹H NMR shifts of the porphyrin subunits are also reported for the *anti*-**1**·(CNPY)₂ in CDCl₃.^{19a}

Figure 9 shows the ¹H NMR spectra coming from the reaction between **1** with L². Trace A shows the ¹H NMR signal of **1**. Trace B shows the ¹H NMR spectra of

Figure 7. PXRD profiles of **1**·L²: (a) simulated pattern obtained from X-ray structure at 100 K and (b) bulk powder sample of the complex at 295 K.

Figure 8. ¹H NMR spectra (in CDCl₃ at 295 K) of (a) **1**, (b) polycrystalline sample of **1**·(L¹)₂ and (c) free L¹. Porphyrin numbering scheme is shown in scheme 1.

Figure 9. ^1H NMR spectra (in CDCl_3 at 295 K) of (a) **1**, (b) polycrystalline sample of **1**·**L**² and (c) **L**². Porphyrin numbering scheme is shown in scheme 1.

polycrystalline sample of **1**·**L**² in CDCl_3 while trace C represents the ^1H NMR of free ligand **L**². The py-*H* of **L**² is noticeably upfield shifted by $\Delta\delta$ 3.20 and 1.16 ppm. C-*H* proton of **L**² is also upfield shifted by 0.84 ppm while CH_2 proton does not show any noticeable change. The 10,20-*meso* protons of the porphyrin macrocycle show a downfield shift of 1.51 ppm as the identical 10 and 20-*meso* protons are strongly shielded by the ring current effect of the two face to face porphyrin subunits in **1**. However, the 15-*meso* protons are out of such shielding effect and are thus nearly identical. There is also an upfield shift of 0.48 ppm for the bridging- CH_2 proton signals.

3.4 Binding constant determination

Binding constant between **1** and **L** was also determined by the UV–visible spectroscopic titration method. The addition of **L**¹ (10^{-6} to 10^{-2} M) to the chloroform solution of **1** (5×10^{-6} M) at 295 K results in the red shift of Soret (400 to 427 nm) and Q bands (551 to 561 nm), due to the formation of 1:2 *anti* complex. Binding

constant was calculated using the HypSpec computer program (Protonic Software, U.K.)²³ and species distribution plots of the complex were calculated using the program HySS2009 (Protonic Software, U.K.).²³ Two sets of UV–visible titration data were analyzed, considering a binding model with two coloured stoichiometric states of Zn(II)-bisorphyrin (**1**) and **1**·(**L**¹)₂ complex as shown in Scheme 1. Binding constant *K* is found to be $(1.4 \pm 0.1) \times 10^2 \text{ M}^{-2}$ (figure 10).

Similarly the addition of **L**² (10^{-7} to 10^{-3} M) to the chloroform solution of **1** (5×10^{-6} M) at 295 K results in the red shift of Soret (400 to 427 nm) and Q bands (551 to 559 nm), due to the formation of 1D coordination polymer (1:1 binding ratio).²² *K* is found to be (7.6

Figure 10. (a) Calculated UV–visible spectra of **1** (black-line), **1**·(**L**¹)₂ (red-line). Green dotted line represents the observed UV-visible spectra of **1**. (b) Fits of the absorbance data at selected wavelengths of 400 and 427 nm. (c) Species distribution plots of **1** and **1**·(**L**¹)₂.

Figure 11. (a) Calculated UVvisible spectra of **1** (black-line), $1 \cdot L^2$ (red-line). Green dotted line represents the observed UVvisible spectra of **1**. (b) Fits of the absorbance data at selected wavelengths of 400 and 427 nm. (c) Species distribution plots of **1** and $1 \cdot L^2$.

$\pm 0.2) \times 10^2 \text{ M}^{-1}$ (figure 11). Larger binding constant was obtained in $1 \cdot L^2$ compared to that of *anti* complex $1 \cdot (L^1)_2$ which suggest cooperativity of binding of L^2 to form 1D-polymeric chain in the former.

3.5 AFM images

The morphology of the polymeric complex $1 \cdot L^2$ on silicon wafer surface was examined by Atomic Force Microscopy (AFM). Silicon (100) surface was cleaned by soap water, distilled water and acetone. The complex were dissolved in distilled chloroform (10^{-5} M) which was then applied on the silicon surface by drop casting method and consequently dried under ambient conditions. After evaporation of solvent, the surface was examined by AFM. Figure 12 shows typical topograph, (a) amplitude (b) and phase-shift (c) images of polymeric complex deposited on surface.

Typical AFM topographs show islands of size ranging from 200–550 nm perimeter and a height of ≈ 20 –40 nm. Majority of the islands show well-defined facets along few lateral growth directions. This indicates a crystalline²⁴ behaviour for the small islands. However, aggregation of islands seems to occur and limit us from determining the exact facets along all directions. The general overview suggests a possible quasi-hexagonal packing in the islands.

4. Conclusions

We have used Zn-1,2-bis(*meso*-octaethylporphyrin)ethane (**1**) as a host complex in a which the two porphyrin rings are in a face-to-face arrangement due to strong π - π interporphyrin interactions and thus stabilized in *syn* conformation. Upon addition of one relatively smaller 4,4'-dipyridine (L^1) and one extended N,N'-bispyridine-4-yl-methylene ethylenediamine ligand (L^2), the *syn* conformation of Zn-1,2-bis(*meso*-octaethylporphyrin)ethane (**1**) is switched to the *anti*

Figure 12. AFM images (a) topograph, (b) amplitude and (c) phase-shift of $1 \cdot L^2$ (drop casted) polymeric complex onto silicon (100) wafer surface from 10^{-5} M solution in chloroform. A non-contact mode was used for obtaining the images.

complexes $1 \cdot (L^1)_2$ and $1 \cdot L^2$, respectively, with the respective binding constants of $(1.4 \pm 0.1) \times 10^2 \text{ M}^{-2}$ and $(7.6 \pm 0.2) \times 10^2 \text{ M}^{-1}$. However, with the extended L^2 ligand, the *anti*-form of the complex self-assembled further to generate stable 1D coordination polymer $1 \cdot L^2$. Single crystal X-ray structures of $1 \cdot (L^1)_2$ and $1 \cdot L^2$ are reported here along with their solution structures using ^1H NMR spectroscopy. To the best of our knowledge, $1 \cdot L^2$ is the first structural report of such 1D-coordination polymer with porphyrin dimers. The morphology of the polymeric complex $1 \cdot L^2$ on silicon wafer surface was examined by Atomic Force Microscopy (AFM) in which islands of well-defined facets of size ranging from 200–550 nm perimeter and a height of ≈ 20 –40 nm have been obtained. However, aggregation of islands seem to occur and limit us from determining the exact facets along all directions. The general overview suggests a possible quasi-hexagonal packing in the islands.

Supplementary Information

CCDC-999047 and 999048 contain the X-ray crystallographic details in CIF format for compound $1 \cdot (L^1)_2$ and $1 \cdot L^2$, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

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