DALTON
FULL PAPER

Multicomponent Zn-tetraphenylporphyrins: syntheses, characterization and their self assembly in the solid state

Atindra D. Shukla, Paresh C. Dave, Eringathodi Suresh, Amitava Das * and Parthasarathi Dastidar *

Silicates & Catalysis Division, Central Salt & Marine Chemicals Research Institute, G. B. Marg, Bhavnagar 364 002, India

Received 26th May 2000, Accepted 13th October 2000
First published as an Advance Article on the web 16th November 2000

Two multicomponent Zn-tetraphenylporphyrin (ZnTPP) based building blocks have been synthesized for designing microporous crystalline solids. Reactions of ZnTPP with 4,4′-bipyridine (4,4′-bpy) in two different molar ratios gave two coordination complexes namely $[(ZnTPP)_3\{\mu\text{-}4,4'\text{-}bpy\}_2]$ **I** and $[(ZnTPP)_2\{\mu\text{-}4,4'\text{-}bpy\}]$ **II**. Complexes **I** and **II** were characterized by spectroscopic and analytical methods. Inclusion complexes of **I** with toluene, **II** with toluene, and also with nitrobenzene have been prepared and are characterized by ^{1}H NMR and single crystal X-ray diffraction techniques. Supramolecular structural systematics of TPP-based materials are conserved in these crystals.

Introduction

In recent years, much effort has been directed towards the creation of organized self assemblies that result in microporous crystalline solids with various applications.[1] Tetraarylporphyrins (TAP) and tetraarylmetalloporphyrins (TAMP) have been recognized as potential building blocks for generating microporous crystalline solids.[2] By introducing various supramolecular synthons at strategic positions on the phenyl ring of TAP and/or TAMP, interesting supramolecular architectures have been created.[3,4] TAP and TAMP being conjugated symmetrical macrocycles possess high rigidity and high molecular symmetry that are essential for the design of good building blocks. Moreover, these molecules are thermally stable, largely unreactive, easily synthesized and chemically modified in various ways. Among the first row transition metals, ZnTPP is found to be a much better general purpose host for the design of microporous solids. Double occupation of the $d_{x^2-y^2}$ orbital of the Zn^{2+} complex tends to increase the metal–nitrogen bond distances and destabilizes the ruffled conformation of the porphyrin plane observed in TPP complexes with other first row transition metals. So, the more planar ZnTPP has higher symmetry and provides fewer orientational degrees of freedom; thereby making it a potential building block. Systematic single crystal X-ray structural studies on TPP and tetraphenylmetalloporphyrins (TPMP) revealed efficient packing of the molecules in 2-D. This induces voids in their crystal lattice, which are then occupied by guest molecules.[2] Supramolecular structural systematics of TPP-based solids are conserved in many such materials. The packing of the hosts is generally governed by intermolecular porphyrin–porphyrin interactions. Parallel chains of porphyrin units are arranged in layers and channels are located between the phenyl arms of two adjacent chains[5] [see Fig. 1(a)]. Similar supramolecular self assembly is also observed in five- and six-coordinated TPP-based materials.[5] In five coordinate species, the axial ligand and a guest molecule of the same size and shape as the axial ligand occupy alternate sites in the channels [Fig. 1(b)] whereas both axial ligands occupy the channel space in six coordinate compounds [Fig. 1(c)]. Therefore, the axial ligand plays an important role in tailoring the lattice of these microporous crystalline solids. In this context, we are interested in coupling penta- and hexa-coordinate ZnTPP in a single entity and studying the effect on the resulting self assemblies in the solid state. We have, therefore, synthesized and characterized a trimer, *i.e.* **I**, (composite of two five- and one six-coordinate species) linked through the bidentate bridging ligand, 4,4′-bipy. We have also synthesized and characterized a dimeric ZnTPP, *i.e.* **II**, (two five-coordinate species coupled together) hooked through the same bridging ligand. The plausible self assemblies of both the building blocks are depicted schematically in Fig. 1(d) and Fig. 1(e) with the hope that the gross supramolecular array of TPP-based materials [Fig. 1(a)] will also be conserved in these novel building blocks. In order to establish the molecular structures of these building blocks and characterize their supramolecular array, we have prepared the following inclusion

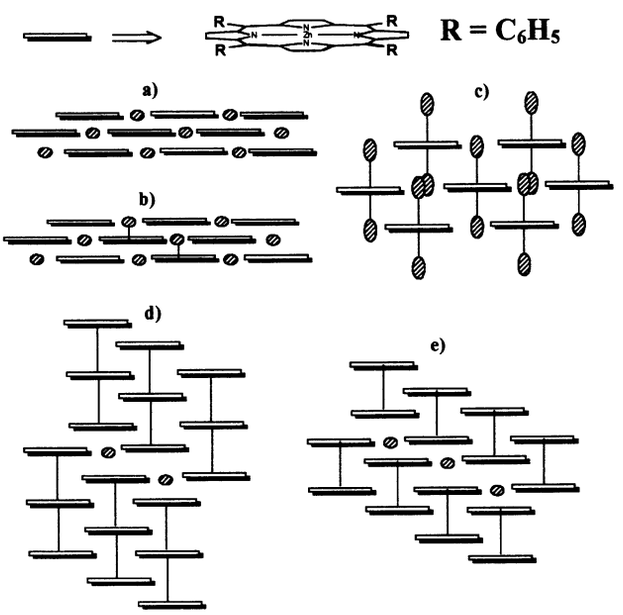

Fig. 1 Schematic representation of the packing mode observed in (a) TPP-based inclusion complexes, (b) pentacoordinate TPP-based inclusion complexes, (c) hexacoordinate TPP-based inclusion complexes; plausible packing mode of hosts (d) **I** and (e) **II**.

DOI: 10.1039/b004211k

complexes (namely **III**, **IV** and **V**) of **I** and **II** and analyzed them by ^{1}H NMR and single crystal X-ray diffraction: **III**, **I**·toluene (1 : 6); **IV**, **II**·toluene (1 : 4); **V**, **II**·nitrobenzene (1 : 4).

Experimental

Materials

All chemicals were reagent grade unless otherwise specified. Monomeric ZnTPP was synthesized according to the standard literature method.[6] Silica gel on an aluminium support (100 μm thick card, Aldrich) was used for thin layer chromatography (TLC). CH_2Cl_2, used as solvent for electrochemical studies, was dried and distilled over CaH_2 prior to use. $[Bu^t_4N]PF_6$ was used as the background electrolyte in a three electrode cell assembly with Pt as the working electrode and Ag–AgCl as the reference electrode. Yields are reported on the basis of ZnTPP used.

Physical measurements

Cyclic voltammograms were recorded on a CH660A electrochemical analyzer. Ferrocene was used as internal standard and all potentials are quoted *vs*. an Fc/Fc^+ couple. UV–Vis spectra were recorded on a Shimadzu-3101PC spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker 200 MHz spectrometer. Microanalyses were performed on a Perkin-Elmer elemental analyzer, Series II, 2400. All solution studies were performed with freshly prepared solutions.

Syntheses

[(ZnTPP)$_3${μ-4,4′-bpy}$_2$] I. ZnTPP (200 mg, 0.295 mmol) and 4,4′-bpy (190 mg, 1.2 mmol) were dissolved in 25 ml of toluene and refluxed for 1 h. The reaction mixture was then dried under vacuum and the product isolated. TLC with $CHCl_3$–n-hexane (99 : 1, v/v) as eluent showed several spots. The major spot with $R_f = 0.48$ was purified by column chromatography using SiO_2 as the stationary phase. Initially, $CHCl_3$–n-hexane (95 : 5, v/v) was used as eluent and the polarity of the eluent was gradually increased up to 100% $CHCl_3$. The major fraction was collected and dried under vacuum (yield 110 mg, 45%). Elemental analysis: $C_{152}H_{100}N_{16}Zn_3$ (found) C 77.1, H 4.2, N 9.4; (calc.) C 77.79, H 4.29, N 9.54%. UV–Vis (ε M^{-1} cm^{-1}; CH_2Cl_2): 425 (3.0×10^5), 523 (4.8×10^3), 562 (2.7×10^4) and 601 (1.37×10^3) nm. ^{1}H NMR ($CDCl_3$): δ 8.8 (24H, s, pyrrole), 8.1–8.2 (32H, m, *o*-phenyl and 4,4′-bpy), 7.5–7.7 (44H, m, *m*-, *p*-phenyl and 4,4′-bpy). $E_{\frac{1}{2}}$: 0.40(r), 0.76(r) and −1.98(r) V.

[(ZnTPP)$_2${μ-4,4′-bpy}] II. ZnTPP (200 mg, 0.295 mmol) and 4,4′-bpy (70 mg, 0.45 mmol) were used for the reaction. Isolation and purification of the product was similar to that adopted for **I** ($R_f = 0.6$; yield 156 mg, 65%). Elemental analysis: $C_{98}H_{64}N_{10}Zn_2$ (found) C 77.2, H 4.1, N 8.9; (calc.) C 77.82, H 4.26, N 9.26%. UV–Vis (ε M^{-1} cm^{-1}; CH_2Cl_2): 422 (3.1×10^5), 5.13 (7.0×10^3), 549 (3.0×10^4), 598 (8.3×10^3) nm. ^{1}H NMR ($CDCl_3$): δ 8.95 (16H, s, pyrrole), 8.2–8.25 (20H, m, *o*-phenyl and 4,4′-bpy), 7.71–7.77 (28H, m, *m*-, *p*-phenyl and 4,4′-bpy). $E_{\frac{1}{2}}$: 0.39(r), 0.73(r) and −2.18(r) V.

^{1}H NMR spectra of III, IV and V

Freshly grown crystals were used to record ^{1}H NMR spectra in $CDCl_3$ in order to assess the stoichiometry of the inclusion complexes.

III [3($C_{44}H_{28}N_4Zn$)·2($C_{10}H_8N_2$)·6(C_7H_8)]. δ 8.85 (24H, s, pyrrole), 8.19–8.15 (32H, m, *o*-phenyl, 4,4′-bpy), 7.72–7.69 (44H, m, *m*-, *p*-phenyl, 4,4′-bpy), 7.25–7.15 (30H, m, toluene), 2.35 (18H, s, Me of toluene).

IV [2($C_{44}H_{28}N_4Zn$)·($C_{10}H_8N_2$)·4(C_7H_8)]. δ 8.76 (16H, s, pyrrole), 8.08–8.04 (20H, m, *o*-phenyl, 4,4′-bpy), 7.69–7.58 (28H, m, *m*-, *p*-phenyl, 4,4′-bpy), 7.27–7.13 (20H, m, toluene), 2.34 (12H, s, Me of toluene).

V [2($C_{44}H_{28}N_4Zn$)·($C_{10}H_8N_2$)·4($C_6H_5NO_2$)]. δ 8.83 (16H, s, pyrrole), 8.24 (8H, d, *J* 8.2 Hz, *o*-nitrobenzene), 8.15–8.10 (20H, m, *o*-phenyl, 4,4′-bpy), 7.73–7.70 (32H, m, *m*-, *p*-phenyl, *p*-nitrobenzene), 7.59–7.55 (8H, t, *m*-nitrobenzene).

Crystallography

Single crystals of inclusion complexes of **III**, **IV** and **V** were obtained by slow evaporation from respective guests as solvents. Data collection, (CAD4 diffractometer, Mo-Kα, $\lambda = 0.7107$ Å, crystals sealed in a glass capillary), data reduction, structure solution and refinement were carried out using the programs CAD-4 PC,[7] NRCVAX program,[8] SHELX97[9] and PLATON[10] respectively.

All the structures were solved by direct methods. Guest molecules were found to be severely disordered in all cases. The asymmetric unit of **III** contains half of the trimer molecule (space group $P\bar{1}$). The central Zn atom occupies the special position, namely the centre of symmetry. Disordered toluene molecules could be located approximately in the difference Fourier map. The Me group of one of the toluene molecules could not be located. Crystals **IV** and **V** are isostructural. All non-hydrogen atoms of the host moieties could be located on a difference Fourier map only in space group *C*2. Two half-dimer moieties in the asymmetric unit are found to be related by a non-crystallographic center of symmetry approximately at 0.249, 0.632, 0.252 which suggests that a centrosymmetric space group *C*2/*c* could be possible. The coordinates of *C*2 were then transformed into *C*2/*c* and refined.

Isotropic refinements of **III** and **IV** were converged at $R1 = 0.185$ and 0.125 respectively. Considerably large asymmetric units in **III** and **IV**, limited resolution of the diffraction and severe disorder of the solvent molecules did not allow an anisotropic refinement of the full structures. Constraints applied on the phenyl rings of the ZnTPP moiety did not improve the refinement. As we are mainly interested in studying supramolecular self assemblies of the host components, we decided to carry out further refinement calculations on the host moieties using a "bypass" technique in which the overall contribution of all the guest molecules to the diffraction pattern is subtracted from the observed data.[11] With these resulting "noisefree" data and less refinable parameters, it was then possible to carry out anisotropic refinement on most of the non-hydrogen atoms of the host molecules. The resulting refinement on the host moieties converged at considerably low *R*1 values (Table 1) without significantly affecting the porphyrin structures. It may be pointed out here that in recent years, the "bypass" technique has been successfully used to refine several disordered structures of TAP-based supramolecular materials.[12] Anisotropic refinement of **V**† was carried out in a routine manner and converged to a reasonably low *R* factor (see Table 1).

CCDC reference number 186/2234.

See http://www.rsc.org/suppdata/dt/b0/b004211k/ for crystallographic files in .cif format.

Results and discussion

Syntheses and characterization of I and II

Coordination of pyridine and substituted pyridine to Zn in ZnTPP is a well known phenomenon in solution[13] and few

† After we submitted this paper for publication, it was brought to our notice that R. Krishna Kumar, Y. Diskin-Posner and I. Goldberg (*J. Incl. Phenom.*, 2000, **37**, 219) have reported the structure of **V** recently.

Table 1 Crystallographic data and refinement parameters for crystals **III**, **IV** and **V**

	III	**IV**	**V**
Formula	$(C_{44}H_{28}N_4Zn)\cdot(C_{10}H_8N_2)(C_{22}H_{14}N_2Zn_{0.5})\cdot 3(C_7H_8)$	$(C_{44}H_{28}N_4Zn)\cdot(C_5H_4N)\cdot 2(C_7H_8)$	$(C_{44}H_{28}N_4Zn)\cdot(C_5H_4N)\cdot 2(C_6H_5NO_2)$
Formula weight	1449.70	940.43	1002.39
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
Z	2	8	8
a/Å	11.065(9)	18.458(8)	18.523(28)
b/Å	13.425(5)	13.614(4)	13.473(11)
c/Å	28.068(11)	40.599(10)	40.290(11)
α/°	96.60(3)	—	—
β/°	92.23(5)	98.98(3)	99.75(06)
γ/°	102.99(5)	—	—
V/Å^3	4027(4)	10077(6)	9910(17)
D_c/g cm^{-3}	1.196	1.261	1.344
T/K	293	293	293
Total reflections, R_{int}	10245, 0.00	6443, 0.00	6454, 0.00
Final $R1$, observed data [$I \geqslant 2\sigma(I)$]	0.105, 5085 [a]	0.066, 3248 [a]	0.084, 4425
Final $wR2$ on all data	0.316	0.167	0.239

[a] Using a "bypass" technique. $R1 = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$; $wR2 = [\Sigma(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

single crystal X-ray structures are available for penta- and hexa-coordinated ZnTPP(py) (py is pyridine or substituted pyridine) complexes.[14a] To date no examples have been reported for isolated trinuclear ZnTPP complexes using 4,4′-bpy or its derivatives as a bridging ligand. In the presence of a large excess of 4,4′-bpy, the presumably hexacoordinated species, ZnTPP(4,4′-bipy)$_2$, is initially formed which then reacts with free ZnTPP to yield the trinuclear coordination complex **I**.

Examples of the hexacoordinated ZnTPP complex with pyridine-based ligands are scarce[14b] and the relatively rare occurrence of the hexacoordinated ZnTPP complex is due to the higher lability of the N-donor heterocycle in the sixth coordination position. The high lability of the second 4,4′-bpy ligand also restricts the formation of a linear coordination polymer and provides the synthetic edge in designing tri- and bi-nuclear complexes such as **I** and **II**. Interestingly, **I** is also the first example of an isolated ZnTPP complex with both penta- and hexa-coordinated ZnTPP moieties. It should be noted that all attempts to synthesize the desired binuclear complex **II** using the exact stoichiometry of reactants required were unsuccessful. In the presence of a slight excess of 4,4′-bipy, ZnTPP exists as pentacoordinated species [ZnTPP(4,4′-bipy)] which reacts with one equivalent of ZnTPP to form binuclear complex **II**. Formation of the pentacoordinated binuclear species in relatively high yield perhaps signifies the relatively high thermodynamic stability of the binuclear complex.[15]

The proposed formulation for complexes **I** and **II** is well supported by elemental analyses and ^{1}H NMR data (see Experimental). The ^{1}H NMR signal for the 2,2′,6,6′ protons of free 4,4′-bpy appears at $\delta \approx 8.73$ whereas the 3,3′,5,5′ protons resonate at $\delta \approx 7.53$. However, the 2,2′,6,6′ protons of 4,4′-bpy in **I** and **II** are found to be resonating at $\delta \approx 8.17$ and ≈ 8.22 respectively whereas signals for 3,3′,5,5′ protons remained unchanged at around $\delta \approx 7.53$. The significant difference in chemical shift of the 2,2′,6,6′ protons of 4,4′-bpy in complexes **I** and **II** indicates that they are shielded. The distances of these protons, as calculated from single crystal X-ray studies, from the centroid of the porphyrin core (namely the Zn metal ion) are in the range of 3.099–3.329 Å and 3.158–3.258 Å in **I** and **II** respectively. These data clearly suggest that due to the coordination of the ring nitrogens of the 4,4′-bpy ligand bridging to the Zn metal ion of the porphyrin core, the 2,2′,6,6′ protons fall within the shielding zone of the porphyrin ring and, therefore, are significantly shielded.

Cyclic voltammograms for complexes **I** and **II** do not show any significant change in redox potential or any additional feature when compared with that of ZnTPP.[16] This clearly shows that there is no significant electronic interaction between two individual ZnTPP units across the 4,4′-bpy spacer. It was also not possible to separate any redox process for individual ZnTPP units by using differential pulse voltammetry experiments for complexes **I** and **II**. Further, if one considers the weak hexa-coordination of 4,4′-bpy to ZnTPP [Zn–N in Zn(4,4′-bpy)$_2$ is 2.42 Å whereas the corresponding distance in the pentacoordinated porphyrin moiety is 2.16 Å], then no significant interaction either between the two terminal ZnTPP units or between the terminal and central ZnTPP units is expected in complex **I**.

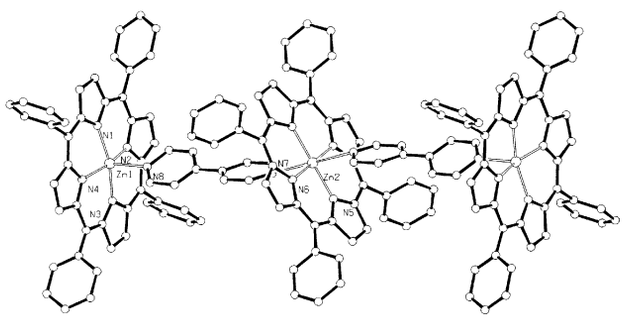

Fig. 2 Perspective view of the host **I** in crystal **III**. Only heteroatoms are numbered. Hydrogen atoms are not shown.

Molecular structures of I and II, and their self assemblies in the solid state

In order to establish the proposed formulation of **I** and **II** and study their self assembly modes in the solid state, inclusion crystals **III**, **IV** and **V** have been prepared and their crystal structures were determined by single crystal X-ray diffraction. Host **I** can be best described as a ZnTPP trimer in which ZnTPP units are hooked together by two bidentate ligands, namely 4,4′-bpy (Fig. 2). The Zn(2) atom of the central Zn–porphyrin moiety (hereafter, CPM) occupies a special position (crystallographic center of symmetry at 0,1/2,1/2). The terminal ZnTPP moiety (hereafter, TMP) is a pentacoordinated species whereas the CPM is a hexacoordinated one. The Zn(2) atom is located exactly at the center of the porphyrin core as it is occupying the crystallographic center of symmetry. It is interesting to note that the CPM is not parallel with the TPM; the angle between the mean planes of these two porphyrin moieties is 25.6°. A tilt angle of 25.6° of the CPM and TPM could be because of the packing requirement. Tilt angles have also been observed

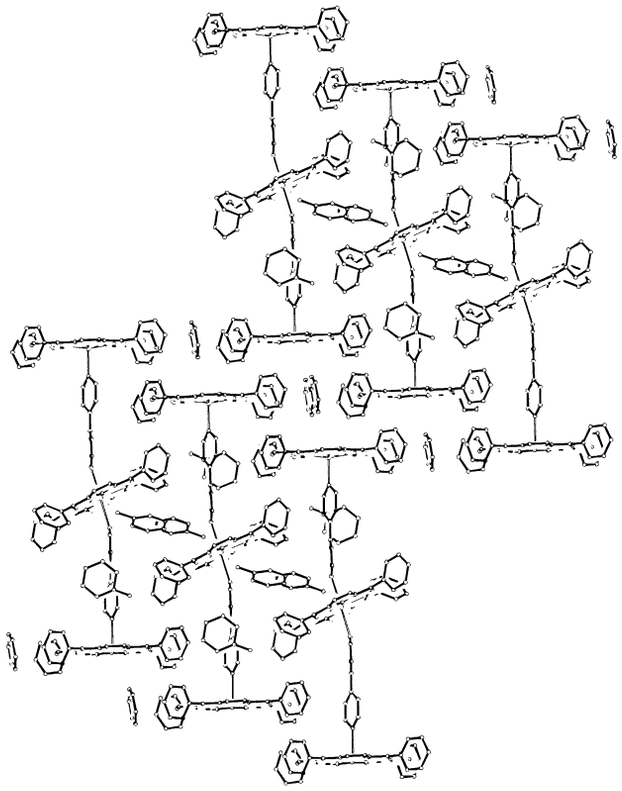

Fig. 3 Supramolecular array of **I** in crystal **III** viewed down the *b*-axis. Approximate positions of the disordered toluenes are shown. Hydrogen atoms are not shown.

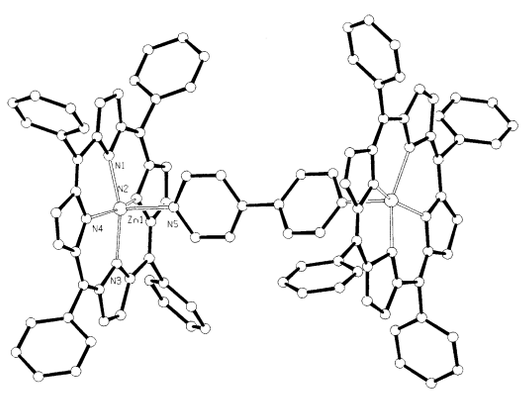

Fig. 4 Perspective view of the host **II** in crystals **IV** and **V**. Crystal **V** is isostructural with **IV** and not shown separately. Numbering for heteroatoms is given. Hydrogen atoms are not shown.

earlier in Zn–py porphyrin structures.[17] A close inspection of the packing diagram of **III** (Fig. 3) reveals that the whole trimer molecule is approximately oriented along the longest *c*-axis of the unit cell. The molecules are, therefore, packed along the *c*-axis leading to the formation of an end-to-end "staircase"-like chain. Open channels are created as a result of such arrangements within the peripheral phenyl arms of the TPM. When these chains are closely packed in the crystal, another open channel surrounded by the CPM of adjacent chains appears to form.

Crystals **IV** and **V** are isostructural (see Table 1). The host **II** in these crystals is a dimeric ZnTPP linked through 4,4′-bpy (Fig. 4). The Zn atom is a pentacoordinated species in this dimer and the equatorial Zn–N distances in the coordination sphere are in the normal range. The packing diagram (Fig. 5) of the crystal **IV** (**V**, being isostructural with **IV**, displays identical packing) reveals that the dimers are arranged approximately along the longest, *c*, -axis of the unit cell. Intermolecular aggregation of dimeric building blocks in the crystal lattice is such that an open channel is formed running down the *b*-axis.

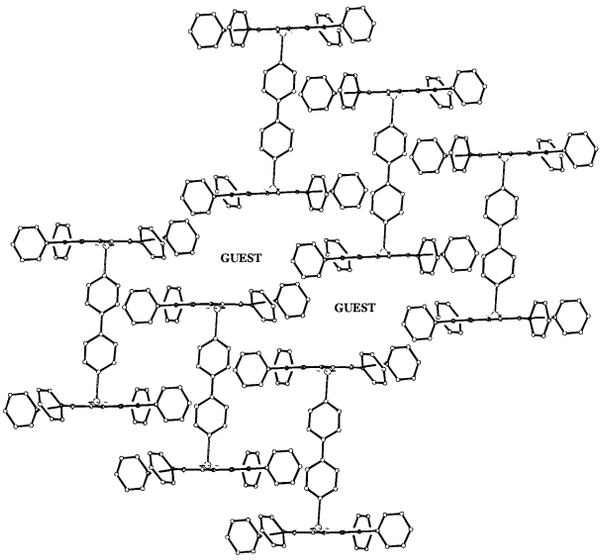

Fig. 5 Supramolecular array of host **II** in crystal **IV** viewed down the *b*-axis. Disordered guest molecules and hydrogen atoms are not shown. Packing of host **II** in **V** is identical as **IV** and **V** are isostructural.

Supramolecular self assemblies of both the hosts **I** and **II** in their crystals (Figs. 3 and 5) show remarkable similarities with the gross packing arrangement of TPP-based materials [Fig. 1(a)]. In these cases, the TPP units are self assembled in layers creating channels between the phenyl arms of two adjacent chains. Interestingly, an extra channel is also formed in the crystal **III** around CPM because of the tilt of this unit (discussed above). In **IV** and **V**, guest molecules and the axial ligand 4,4′-bpy occupy alternate channel position as found in five coordinated TPP-based materials [Fig. 1(b)]. A similar observation is noted in **III** around the TPM layer.

Conclusion

Synthetic protocols have been successfully adopted for generating multicomponent ZnTPP-based building blocks using bidentate bridging ligand 4,4′-bpy by exploiting the novel coordination properties of Zn^{2+}. ^1H NMR and crystallographic data are consistent with the proposed formulation of these two novel building blocks. Supramolecular structural systematics found in many TPP-based solids are conserved in the present multicomponent porphyrin host systems. However, in the trimer, *i.e.* in crystal **III**, an extra channel is also formed around the central porphyrin moiety due to its unprecedented tilt with respect to the terminal porphyrin unit.

Acknowledgements

We thank all the referees for their suggestions and comments. A. D. S. and P. C. D. thank CSIR for a research fellowship, A. D. thanks the Department of Science and Technology (DST), Government of India for financial support. Our sincere thanks go to Dr P. K. Ghosh and Dr R. V. Jasra for their keen interest and encouragement in this work.

References

1 D. M. I. Goodgame, D. A. Grachvogel and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 153; D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1999, 1; J. A. Swift, A. M. Piovovar, A. M. Reynolds and M. D. Ward, *J. Am. Chem. Soc.*, 1998, **120**, 5887; S. G. Bodige, R. D. Rogers and S. C. Blackstock, *Chem. Commun.*, 1997, 1669; P. Brunet, M. Simard and J. D. Wuest, *J. Am.*

Chem. Soc., 1997, **119**, 2737; K. Eudo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda and Y. Aoyama, *J. Am. Chem. Soc.*, 1997, **119**, 4117; D. Venkataraman, S. Lee, J. Zhang and J. S. Moore, *Nature*, 1994, **371**, 591; R. K. Kumar, S. Balasubramanian and I. Goldberg, *Chem. Commun.*, 1998, 1435.
2 M. P. Byrn, C. J. Curtis, Y. Hsiou, S. I. Khan, P. A. Sawin, A. Terzis and C. E. Strouse, in *Comprehensive Supramolecular Chemistry*, vol. 6, ed. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, p. 715.
3 P. Dastidar, H. Krupitsky, Z. Stein and I. Goldberg, *J. Incl. Phenom.*, 1996, **24**, 241.
4 P. Dastidar, Z. Stein, I. Goldberg and C. E. Strouse, *Supramol. Chem.*, 1996, **7**, 257; P. Dastidar and I. Goldberg, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 1976; H. Krupitsky, Z. Stein and I. Goldberg, *J. Incl. Phenom.*, 1995, **20**, 211; P. Bhyrappa, S. R. Wilson and K. S. Suslick, *J. Am. Chem. Soc.*, 1997, **119**, 8492; C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger and R. D. Rogers, *J. Am. Chem. Soc.*, 1999, **121**, 1137; B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727.
5 M. P. Byrn, C. J. Curtis, S. I. Khan, P. A. Sawin, R. Tsurumi and C. E. Strouse, *J. Am. Chem. Soc.*, 1990, **112**, 1865.
6 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
7 CAD-4 Software, version 5, Enraf-Nonius, Delft, 1989.
8 E. I. Gabe, Y. Le Page, I. P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
9 G. M. Sheldrick, SHELX97, Program for Crystal Structure Solution and Refinement, University of Göttingen, 1997.
10 PLATON-97, A. L. Spek, University of Utrecht, The Netherlands, 1997.
11 P. Van der Sluis and A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 194.
12 R. Krishna Kumar and I. Goldberg, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 3027; Y. Diskin-Posner and I. Goldberg, *Chem. Commun.*, 1999, 1961; Y. Diskin-Posner, S. Dahal and I. Goldberg, *Chem. Commun.*, 2000, 585; Y. Diskin-Posner, S. Dahal and I. Goldberg, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 1288.
13 K. M. Kadish, L. R. Shine, R. K. Rhodes and L. A. Bottomley, *Inorg. Chem.*, 1981, **20**, 1247; K. M. Kadish and R. K. Rhodes, *Inorg. Chem.*, 1981, **20**, 2961; *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 5.
14 (*a*) S. Adserson, H. L. Anderson, A. Bashall, M. McPartlin and J. K. M. Sanders, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1096; W. R. Scheidt, M. E. Castner and K. Hatano, *Inorg. Chem.*, 1978, **17**, 706; *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2; (*b*) W. R. Scheidt, C. W. Eigenbrot, M. Ogiso and K. Katano, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3529; M. P. Byrn, C. J. Curtis, Yu. Hsiou, S. I. Khan, P. A. Sawin, S. K. Tendick, A. Terzis and C. E. Strouse, *J. Am. Chem. Soc.*, 1993, **115**, 9480; P. N. Taylor, A. P. Wylie, J. Huuskonen and H. L. Anderson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 986; M. O. Senge and K. M. Smith, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1108; H. Krupitsky, Z. Stein, I. Goldberg and C. E. Strouse, *J. Incl. Phenom.*, 1994, **18**, 177.
15 A. Das, J. P. Maher, J. A. McCleverty, J. A. N. Badiola and M. D. Ward, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 681.
16 M. Ravikant and T. K. Chandrashekar, *J. Photochem. Photobiol.*, 1993, **74**, 181.
17 E. B. Fleischer and M. Shachter, *Inorg. Chem.*, 1991, **30**, 3763.