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Supramolecular self-assembly of a fluorinated Zn porphyrin. Molecular structure of a two-dimensional network of amine-functionalized, hexacoordinated Zn porphyrins

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[5,10,15,20-Tetrakis(4-*n*-propylamino-2,3,5,6-tetrafluorophenyl)porphyrinato]zinc(II) self-assembles into a two-dimensional supramolecular array in which each porphyrin is linked to four orthogonally-oriented chromophores.

The crucial roles of porphyrins in photosynthetic light harvesting and electron transfer, as carriers of small diatomic molecules (O_2, CO, NO), and as catalysts in a wide variety of enzymatic reactions have naturally led to intense efforts that seek to duplicate the biological processes, and more recently, to fabricate synthetic arrays with an equally wide range of potential applications to materials chemistry as photonic devices, conductive polymers, chemical sensors, and molecular wires. Ideally, such arrays would self-assemble and their targeted properties achieved by synthetically modifying the porphyrins and/or changing the metal in metalloporphyrins.[1] The vast literature that now exists for such multiporphyrin assemblies has recently been extensively reviewed.[2] Goldberg and coworkers have described crystal-engineering strategies for the rational design of self-assembled metalloporphyrin materials and have made judicious use of 5,10,15,20-tetraphenylporphyrins (TPPs) and related chromophores to construct rigid supramolecular networks.[3] More recently, Goldberg and coworkers reported the various porphyrin architectures that can be achieved by axially linking TPPs to each other *via* amine or diamine ligands.[4] They also noted that it has been more difficult to construct extended coordination arrays with ZnTPP building blocks because of the low affinity of the Zn ion for hexacoordination.

We have thus turned to an amine-functionalized, fluorinated Zn porphyrin, [5, 10,15,20-tetrakis(4-*n*-propylamino-2,3,5,6-tetrafluorophenyl)porphyrinato]zinc(II) **1**, as a 'tecton'[3] for supramolecular assembly for the following reasons: (a) [5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]zinc(II) (ZnTPPF20) is readily synthesized (H_2TPPF20 is available commercially). Battioni *et al.*[5] have reported that ZnTPPF20 reacts with *n*-propylamine in one step and in high yield to form **1**; (b) Zn porphyrins bearing multiple electron-withdrawing groups tend to form hexacoordinated complexes,[6] unlike the general preference for pentacoordination found in less electron-deficient porphyrins;[4] (c) fluorinated porphyrins exhibit both ground and excited state properties that differ from those typically observed in TPPs and which arise from the fact that the peripheral fluorines change the highest occupied molecular orbital of the chromophores from a_{2u}, normally found in TPPs,[7] to a_{1u} with a concomitant redistribution of electron density that affects optical, redox, radical and excited state properties.[8,9] We report here crystallographic results which demonstrate that **1** self-assembles to form a supramolecular, two-dimensional array in which the Zn ion is indeed hexacoordinated by the amine nitrogens of its two nearest neighbors, and in which each porphyrin is linked to four orthogonally aligned nearest neighbors.

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The molecular structure[10] and labelling of the independent atoms of **1** which form the basic, repeating subunit of the array are shown in Fig. 1. The Zn ion lies strictly in the porphyrin plane with Zn–N1 and Zn–N2 distances of 2.062(4) and 2.058(4) Å, respectively. The molecule is planar with maximum

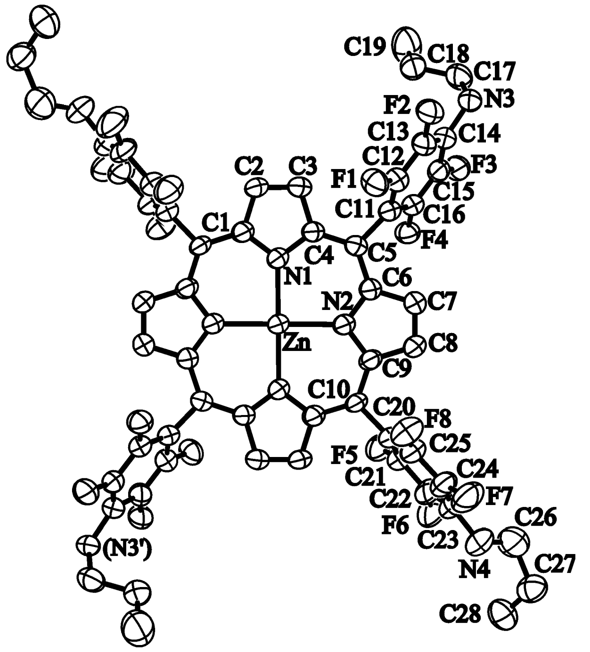

Fig. 1 Molecular structure and labelling of the unique atoms of the building blocks of **1**. Thermal ellipsoids enclose 50% probabilities, and hydrogens are omitted for clarity.

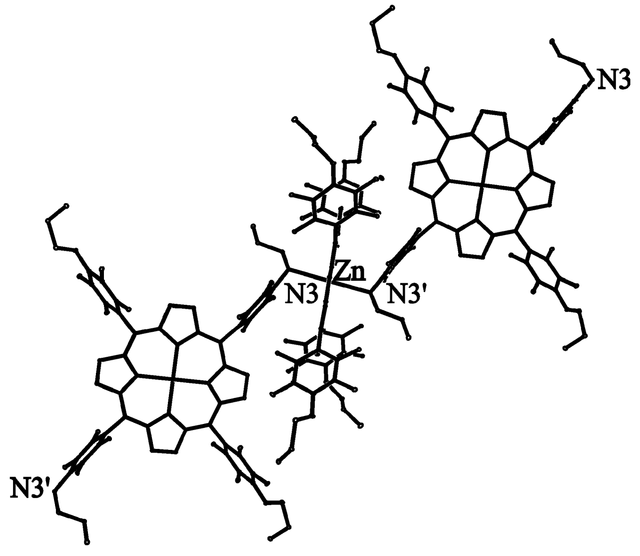

Fig. 2 Illustration of the aggregation mode and hexacoordination of each Zn ion *via* the amine nitrogens (N3 and N3') and of the orthogonal orientations of the nearest-neighbor porphyrins.

deviations of 0.05 Å at any one macrocycle carbon, and average dihedral angles of 70.3° between the phenyl rings and the porphyrin plane. For comparison, in ZnTPPF20,[11] Zn–N = 2.036 Å and the phenyl dihedral angles average 72.6°.

The aggregation mode is illustrated in Fig. 2. The Zn ion of each porphyrin is ligated by the amine nitrogens N3 and N3' of two nearest chromophores such that the Zn is hexacoordinated, with Zn–N axial distances of 2.473(5) Å, and the two ligating porphyrins are oriented perpendicular to the plane of the ligated molecule. In addition, both amines of the antipodal phenyl rings of each ligated porphyrin bind to the Zn of their nearest neighbors to yield an architecture which propagates in both the horizontal and vertical planes and results in alternating parallel and perpendicular alignments of the molecules in any one row and direction, with each porphyrin surrounded by four orthogonally aligned neghboring porphyrins[12] with Zn$\cdots$Zn distances of 10.6 Å, Fig. 3. (Note that only two of the four amines of **1** participate in the self-assembly.) The optical spectrum of the array shifts from 421 and 546 nm for the monomer in solution[5] to 439 and 594 nm in the (ground-up) crystals.

Battioni *et al.*[5] reported that ZnTPPF20 also reacts readily with alkoxide and thiol nucleophiles to yield the equivalents of **1** with OR and SR functions at the *para* phenyl positions. Further, the same regioselectivity is observed[5] in the reaction of the nonplanar[13] β-octabromo-TPPF20 with *n*-propylamine. Nonplanar porphyrins exhibit significantly altered (photo)-physical and chemical properties,[14] and brominated nonplanar Zn porphyrins are being actively studied as optical limiters.[15] The nonplanar, and oxygen or sulfur functionalized porphyrins may thus provide facile entry into new supramolecular arrays whose properties are further modulated by the nonplanarity of the chromophores or by the oxygen and sulfur ligation.

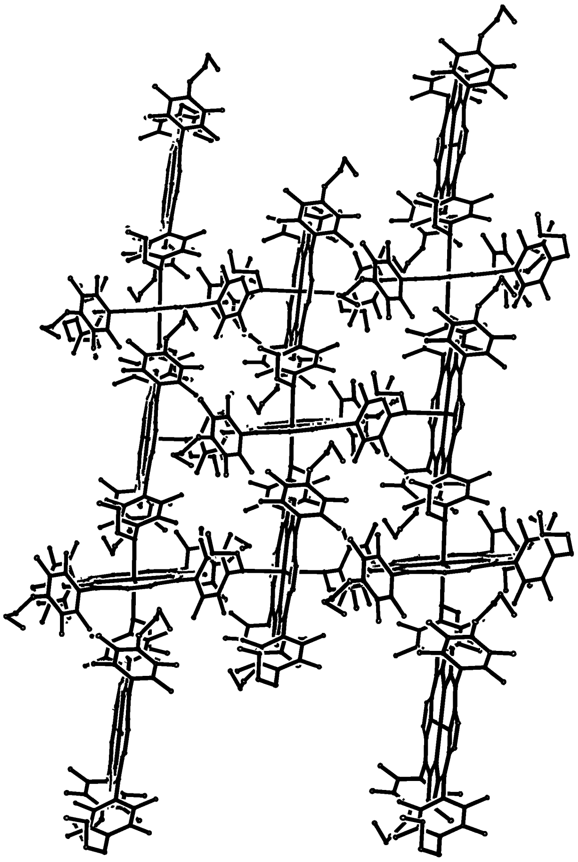

Fig. 3 Illustration of the two-dimensional network formed by the self-assembly of **1**.

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10 *Crystallographic details*: crystals of **1** were obtained by diffusion of methanol vapor into a solution of **1** in CH_2Cl_2/pentane in a closed system. *Crystal data* for **1** ($ZnC_{56}N_8F_{16}H_{40}$, M = 1194.33) were collected at beamline X7B at the National Synchrotron Light Source at 153 K using $\lambda = 0.9273$ Å. **1** crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 12.038(1), b = 13.284(2), c = 16.600(2) Å, β = 111.08(1)°, V = 2476.9(5) Å^3, Z = 2. A total of 36418 reflections ($\pm h, \pm k, \pm l$) were measured on a MAR345 image plate detector in the range $2.64 \leqslant \theta \leqslant 31.37°$ and processed and merged with Denzo Scalepack to give 3306 unique and 3080 with $I > 2(\sigma(I)$. The structure was solved and refined with the SHELXTL Version 5 programs. Hydrogen atoms were refined with riding models. Final R factors were $R1$ = 0.073 (observed data) and $wR2$ = 0.214 (all data). CCDC reference number 181654. See http://www.rsc.org/suppdata/cc/b2/b202513m/ for crystallographic data in CIF or other electronic format.

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