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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

K. Barkigia (BNL) and P. Battioni, V. Riou and D. Mansuy (Univ. Paris V)

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Introduction: The roles of porphyrins in photosynthetic light harvesting and electron transfer have led to intense efforts that seek to duplicate the biological processes and more recently to fabricate synthetic arrays with a wide range of potential applications to materials chemistry as photonic devices, conductive polymers 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]. In light of some newer crystal-engineering strategies by Goldberg et al. using tetraphenylporphyrin and either amines or diamine ligands as linkers [2], we have turned to an amine-functionalized, fluorinated Zn porphyrin as a tecton for supramolecular self-assembly [3].

Methods and Materials: Single crystals of **1** were grown by diffusion of methanol vapor into a solution of **1** in methylene chloride/pentane in a closed system. Two hemispheres of data were collected at 153K by the rotation method using a MAR345 image plate detector. The data were processed and merged with Denzo/Scalepack [4] and the structure was solved and refined with the SHELXTL package [5].

Results: The molecular structure of **1** is shown in Figure 1 and its supramolecular self-assembly, mediated by the coordination of two opposite nitrogens to the Zn of an adjacent molecule, is shown in Figure 2.

Conclusions: As previously observed [6], the presence of multiple electron-withdrawing groups at the periphery of a Zn porphyrin tends to favor hexacoordination and causes a redistribution of electron density that affects the optical, redox, radical and excited state properties.

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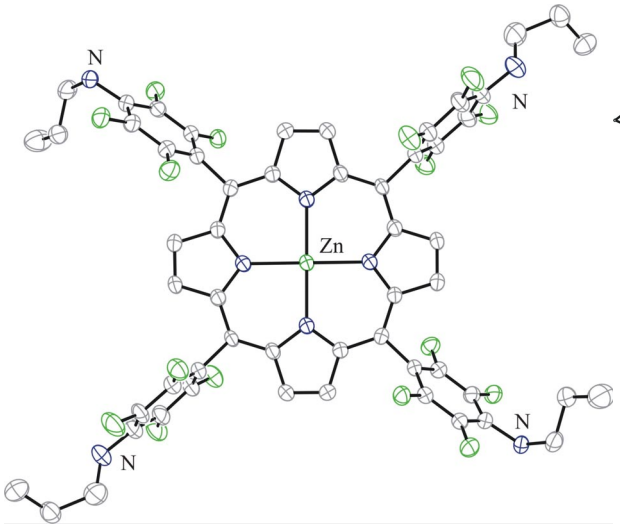

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Figure 1. Molecular structure of the basic subunit that self-assembles to form the two-dimensional array. The peripheral fluorines are shown in green.

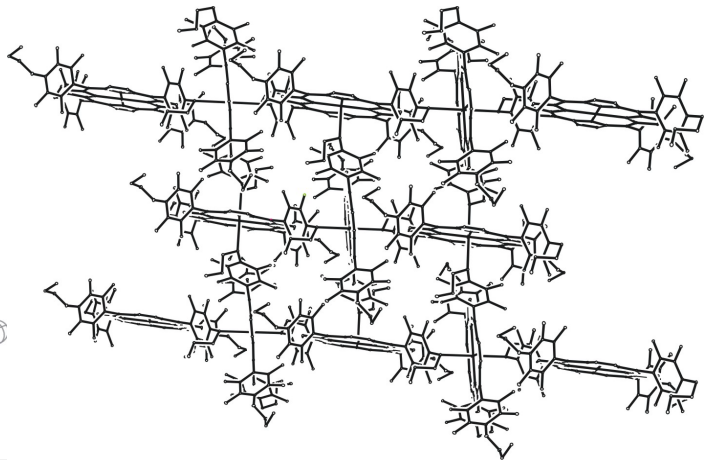

Figure 2. Illustration of the two-dimensional network formed by the self-assembly of **1**.