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Facile synthesis and supramolecular network of a Zn(II)–octaesterporphyrin

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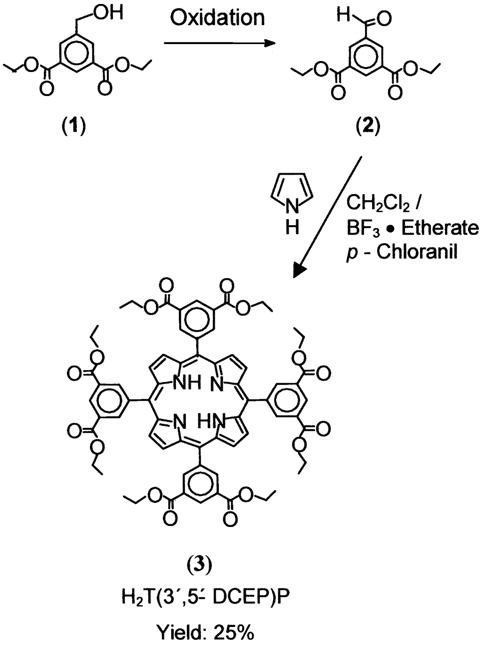
Abstract—The present work reports the synthesis of an octaester porphyrin and its Zn(II) complex which shows an unusual two-dimensional supramolecular coordination network structure. © 2002 Elsevier Science Ltd. All rights reserved.

Functionalised porphyrins are of considerable interest owing to their use as model compounds[1,2] and also for their interesting physico-chemical properties.[3] Furthermore, these multifunctionalized porphyrins are useful compounds for generation of materials with interesting properties.[4] A wide variety of *meso*-tetraphenylporphyrins with varying substituents at the *meso*-positions have been explored for the control of molecular self-assembly processes to generate functional materials with specific properties.[4] It has been shown that the effect of the carboxy group enhances the thermal stability of the resultant self-assembly in the solid state.[5] Further, the synthesis of porphyrins with appropriate functional groups at the *meta* or *ortho* positions are potentially attractive due to their three-dimensional disposition of substituents. Such molecular building blocks provide intermolecular interactions in three dimensions for the construction of robust solid networks with interesting properties. Herein, we present the facile synthesis of a multi-functionalized porphyrin 5,10,15,20 - tetrakis(3′,5′ - dicarboxyethylesterphenyl)-porphyrin, $H_2T(3',5'\text{-DCEP})P$ and examined the interesting X-ray structure of the $ZnT(3',5'\text{-DCEP})P$ complex.

The precursor 5-formylisophthalic acid diethylester[6] (**2**) was synthesized via oxidation of 5-hydroxymethyl isophthalic acid diethylester[7] (**1**) using chromium(VI) quinolinate[8] in CH_2Cl_2 or ceric(VI) ammonium nitrate in an acetic acid medium.[9] The dicarboxydiethyl ester free base porphyrin, $H_2T(3',5'\text{-DCEP})P$ (**3**) was synthesized by the condensation of pyrrole with 5-formylisophthalic acid diethylester (**2**) in dichloromethane under mild conditions (Scheme 1).[10] Its Zn(II) complex was prepared using the reported procedure.[11]

The compounds synthesized were characterized by UV–vis, ^1H NMR, mass spectroscopic and elemental analysis. $MT(3',5'\text{-DCEP})P$ complexes show a marginal red



Scheme 1.

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shift in electronic transitions relative to the corresponding MTPPs. The ^{1}H NMR spectra of the octaester porphyrin exhibited down-field *ortho*- (8.60 ppm) and *para*-phenyl (9.20 ppm) proton resonances relative to the corresponding resonances of *meso*-tetraphenylporphyrin, (H_2TPP), 8.20 and 7.60 ppm, respectively. The downfield shift of the resonances is possibly due to the electron withdrawing effect of the ester groups.

The X-ray structure of the ZnT(3′,5′-DCEP)P[12] was examined to determine the role of the octaester groups on the self-assembly process. The crystals of ZnT(3′,5′-DCEP)P were grown by diffusing methanol into a $CHCl_3$ solution of the porphyrin. The ORTEP structure of the Zn(II) complex is shown in Fig. 1. The molecule crystallizes free of any solvent in the lattice and there are two molecules in the unit cell. Surprisingly, the Zn(II) ion is in a six coordinate geometry with the two axially ligated ester groups bonded through keto-functionalities from the two neighboring porphyrins. The ligated ester groups are from the phenyl rings positioned *trans* to one another and the bound ester groups are from opposite faces of the porphyrin. The porphyrins are arranged alternately in a slip-stack orientation to give a two-dimensional array (Fig. 2). In this orientation, the adjacent molecules show an offset orientation to induce a coordinative interaction between the Zn(II) center and the peripheral ester groups. The alternative array showed a two-dimensional coordination polymeric network with the closest inter-layer distance of 3.432 Å indicating the absence of any strong inter-layer interactions. The closest distance between the adjacent Zn(II) centers of the adjacent two-dimensional layers is 24.12 (3) Å. In this structure, the average dihedral angle formed by the phenyl groups with the porphyrin core is 75.4(2)°. The Zn(II) ion is situated almost in the plane of four nitrogen atoms with an average Zn–N distance of 2.039(3) Å. The axially ligated oxygen of the ester groups and the Zn(II) center are situated at a distance of 2.500(8) Å apart. The observed bond lengths and bond angles of the 24 atom core are not significantly different from those of the ZnTPP complex.[13]

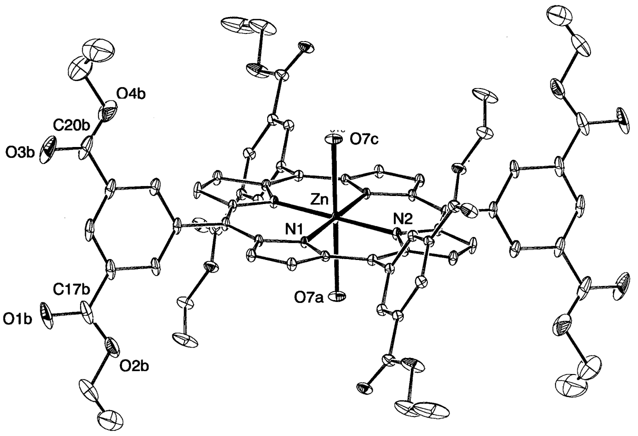

Figure 1. ORTEP structure of the complex ZnT(3′,5′-DCEP)P. Only the Zn(II), pyrrolic nitrogen and ester groups are labelled for clarity.

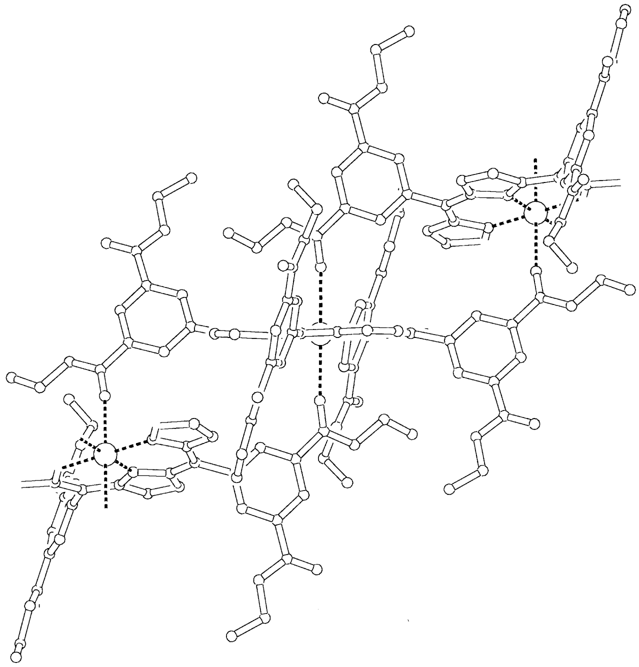

Figure 2. The coordination mode of the Zn(II) centre showing the ester groups from the neighbouring molecules. Symmetry related neighbouring molecular units are shown.

The synthesis of an octaester porphyrin has been presented. The crystal structure shows an interesting two-dimensional coordination polymeric structure in the solid state. The de-esterification of the octaester and its use in the construction of solid networks is being actively investigated. The octacarboxy porphyrin would be of interest for its strong complementary hydrogen bonding interactions and may lead to robust network solids.

Acknowledgements

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