# Crystal engineering of molecular networks. Hydrogen bonding driven two-dimensional assemblies of tetrapyridylporphyrin with benzene tri- and tetra-carboxylic acids

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# SUPPLEMENTARY MATERIAL

## Synthetic and crystallization procedures.

All reagents and solvents were purchased from commercial sources and used without further purification. Crystals of compounds 1-3 were prepared using the layering technique at room temperature. The FT-IR spectra were recorded in the range of 400-4000 cm<sup>-1</sup> from KBr pellets (Aldrich 99%+, FT-IR grade), using a BRUKER PS15 spectrophotometer.

Compound 1: This compound was obtained by layering a dilute DMF solution of 1,2,4,5benzenetetracarboxylic acid, B4CA,  $(7.87 \times 10^{-3} \text{ M}, 4 \text{ ml})$  over a dilute solution of free-base tetra(4-pyridyl)porphyrin, H<sub>2</sub>TPyP, in a 3:1 solubilizing mixture of 1,2-dichlorobenzene and methanol. This reaction mixture was left at room temperature for several days. The formation of deep-red crystals of **1** on the walls and on the bottom of the reaction vessel was noted. The crystals were recovered by filtration, washed with the dichlorobenzene/methanol mixture, and dried in air. IR (KBr/cm<sup>-1</sup>): 1714m (v<sub>COOH</sub>); 1596s, 1423m, 1143w, 1095m, 969m, 800s.

Compound **2**: First, 10 mL of a  $1.47 \times 10^{-3}$  M solution of zinc tetra(4-pyridyl)porphyrin, ZnTPyP, in a mixture of tetrachloroethane and ethanol was placed at the bottom of a glass tube. Next, 2 ml of pure ethanol was carefully layered on top of it. Finally a 4 ml layer of a  $7.87 \times 10^{-3}$  M ethanol solution of B4CA was layered on top. The solutions were left to diffuse into one another through the buffering ethanol zone at room temperature. Deep red crystals appeared after a few days, were collected by filtration, washed with tetrachloroethane and dried in air. IR (KBr/cm<sup>-1</sup>): 1700w, 1717m (split band) (v<sub>COOH</sub>); 1649s, 1596m, 1522m, 1482m, 1201m, 1170m, 1002s, 992s, 752s, 718m.

Compound **3**: A methanol solution (3 ml) of 1,3,5-benzenetricarboxylic acid, B3CA, (0.014 g, 0.06 mmol) was carefully layered over a solution (5 ml) of H<sub>2</sub>TPyP (0.01 g, 0.016 mmol) dissolved in a 1:1 mixture of tetrachloroethane and methanol. After slow evaporation in room temperature deep red crystal were obtained. IR (KBr/cm<sup>-1</sup>): 1701w, 1723m (split band) ( $v_{COOH}$ ); 1650s, 1591s, 1537s, 1467m, 1070w, 971m, 883m, 802s, 724m, 653m.

The FT-IR spectra of 1-3 reveal the presence of carboxylic acid groups and confirm, through the typical stretching modes as well as several other modes attributed to the carboxylic moiety, that in the B4CA and B3CA components these groups are not deprotonated (lack of intensity bands in the 1420-1300 cm<sup>-1</sup> region). In addition to the band data listed above, the spectra exhibit a medium intensity broad band ranging from 2200 to 2800 cm<sup>-1</sup>, which is due to the O-H stretching of strongly hydrogen bonded carboxylic acid entity.

## **Crystal Structure Determinations**

The X-ray measurements (Nonius KappaCCD diffractometer, MoK $\alpha$  radiation) were carried out at 110 K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder and related thermal motion effects, and to optimize the precision of the structural results. These structures were solved by direct methods (SIR-97) and refined by full-matrix least-squares (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were located in idealized/calculated positions and were refined using a riding model, with U<sub>iso</sub> = 1.2 U<sub>eq</sub> of the parent atom. Those attached to O-atoms were either found in difference-Fourier maps or positioned to optimize the hydrogen bonding. The O-H distances were restrained to common values.



**Figure 4S.** Projection of the crystal structure of **1** down the **a**-**c** axis of the crystal, showing edge-on the stacked hydrogen bonded molecular layers. Note the offset shift between adjacent layers, so that the TPyP and B4CA moieties alternate along  $\mathbf{a}+\mathbf{c}$ . The DCB solvent is omitted.



**Figure 5S.** Crystal structure **1** viewed down the a-axis, showing the solvent channels that propagate through the stacked molecular layers.

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### Figure 6S.

Compound 2. View of the penetration of the axial ligand of the lower layer into the interporphyrin void of the upper (inversion-related) layer, next to the dichlorobenzene solvent.





#### Figure 7S.

The (bi)layered arrangement of the molecular networks in 2 viewed edgeon. The layers are aligned parallel to the (bc) plane of the crystal. Molecules of the dichlorobenzene are omitted.

#### Figure 8S.

Crystal structure of 2 viewed down the a+c axis, showing aggregation of the dichlorobenzene species in channels propagating parallel to this axis through the molecular layers.





**Figure 9S**. View of crystal structure **3**, showing edge-on the supramolecular layers aligned in the horizontal direction. The TCE and MeOH solvent species are omitted. Note that every porphyrin unit is sandwiched between two parallel molecules of B3CA.



Figure 10S. Crystal structure 3 viewed down the c-axis, showing the solvent channels.