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Dynamic Behaviour of a Tetrapyrindine-Based Crystalline Supramolecular Organic Framework

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In recent years, supramolecular organic frameworks (SOFs) have emerged as an important class of functional porous materials, alongside metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) [1,2]. Herein we report a dynamic responsive SOF obtained through the self-assembly of rigid aromatic tetrahedral molecules (tetra-4-(4-pyridyl)phenylmethane, **TPPM**) *via* van der Waals interaction and non-conventional hydrogen bonds. In its crystalline form it presents a responsive behaviour based on the reversible switch from an empty to a filled phase (and *vice-versa*), when exposed to specific organic solvent vapours and heat, respectively.

The phase transition between the filled and the empty phase occurs through a single-crystal to single-crystal transformation. However, the crystals of the empty phase were too small and defective to be characterized by standard X-ray diffraction experiments. They were therefore analysed through 3D electron diffraction (3D ED) [3,4] working in low dose mode with a parallel nanobeam of 150 nm in size, which matches perfectly with the grain size of the compound. The structural model obtained *ab-initio* by 3D ED was also refined taking into account dynamical scattering to a final R-value of 13%, with thermal parameters that mimic the rotational flexibility of the biaryl wings.

[1] Atwood, J. L.; Barbour, L. J.; Jerga, A. A New Type of Material for the Recovery of Hydrogen from Gas Mixtures. *Angew. Chem. Int. Ed.* 2004, 43, 2948–2950.

[2] Yang, W.; Greenaway, A.; Lin, X.; Matsuda, R.; Blake, A. J.; Wilson, C.; Lewis, W.; Hubberstey, P.; Kitagawa, S.; Champness, N. R.; Schröder, M. Exceptional Thermal Stability in a Supramolecular Organic Framework: Porosity and Gas Storage. *J. Am. Chem. Soc.* 2010, 132, 14457–14469.

[3] Gruene, T.; Wennmacher, J. T. C.; Zaubitzer, C.; Holstein, J. J.; Heidler, J.; Fecteau-Lefebvre, A.; De Carlo, S.; Müller, E.; Goldie, K. N.; Regeni, I.; Li, T.; Santiso-Quinones, G.; Steinfeld, G.; Handschin, S.; van Genderen, E.; van Bokhoven, J. A.; Clever, G. H.; Pantelic, R. Rapid Structure Determination of Microcrystalline Molecular Compounds Using Electron Diffraction. *Angew. Chem. Int. Ed.*, 2018, 57, 16313-16317.

[4] Gemmi, M.; Mugnaioli, E.; Gorelik, T. E.; Kolb, U.; Palatinus, L.; Boullay, P.; Hovmoller, S.; Abrahams, J. P. 3D Electron Diffraction: The Nanocrystallography Revolution. *ACS Cent. Sci.*, 2019, 5, 1315-1329.

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