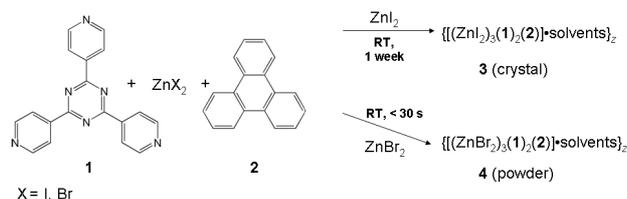


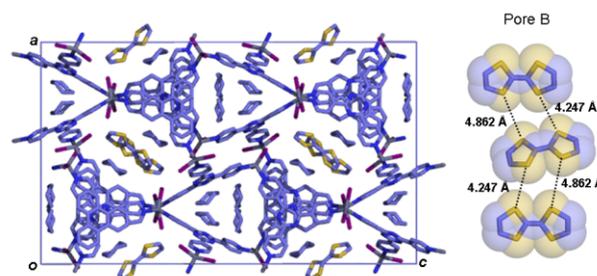
## Structure analysis of biporous network encapsulating TTF molecules in a pore

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Tetrathifulvalene (TTF) molecules can form dimmers, highly-ordered stacks, or two-dimensional sheets, which are stabilized by intermolecular  $\pi$ - $\pi$  interactions and non-bonded S...S interactions. Intensive studies have focused on TTF for the preparation of new materials in bulk and thin film states. One important aspect to achieve unique physical properties like conductivity is how to control the arrangement of molecules to bring them in proper orientations. Despite the wide variety of applications found in porous coordination network controlling the stacking of molecules upon confinement has not been reported so far. Here we report an arrangement of TTF using the confined space in porous coordination network  $[(ZnI_2)_3(1)_2(2)]_n$  (**3**) which was characterized by single crystal X-ray diffraction at AR NW2A. Its isostructural ZnBr<sub>2</sub> network (**4**) prepared by instant synthesis also successfully encapsulated TTFs as guest (Scheme 1) [1].

**Results**

When a single crystal of (**1**) was immersed in a cyclohexane/TTF solution (20 mL; 12.26 mg, 0.06 mmol) for 12 hours at 300 K, the light green crystal turned dark green overnight. Although the single crystal cracked into several parts, a piece with good crystallinity was isolated from the solution suitable for X-ray analysis. Synchrotron X-ray crystallography revealed the coordination network  $[(ZnI_2)_3(1)_2(2)]_n \cdot (TTF)_3 \cdot (C_6H_{12})$  (**3•TTF**). The solvent nitrobenzene molecules were unambiguously replaced by TTF and cyclohexane. Interestingly, TTFs are selectively included in the larger pore A, whereas cyclohexane molecules are located in both pores A and B (Figure 1). The TTF molecules within the pore are aligned parallel to each other forming one-dimensional columns along the *b*-axis. The S...S distances between stacked TTF molecules are 4.247 Å and 4.862 Å. But such distances are too large to expect conductivity along the one-dimensional array of TTF molecules and in fact the conductivity measurements in single crystals of (**3•TTF**) did not show electron transport.



**Figure 1.** Synchrotron X-ray structure of **3•TTF**. The inclusion of TTF molecules is only in one pore. The TTF are stacked along the *b*-axis with a shortest S...S contact of 4.247 Å.

On the other hand, as like in (**3**) when yellow microcrystalline powder of network (**4**) was immersed in a cyclohexane/TTF solution (20 mL; 12.26 mg, 0.06 mmol) for 12 hours at 300 K, compound (**4**) also turned dark-green overnight whilst maintaining good crystallinity. Elemental analyses suggested the inclusion of two TTFs and one cyclohexane molecules. We fully determined the crystal structure by *ab initio* structure determination using the simulated annealing (SA) method, followed by Rietveld refinement. The powder crystal structure  $[(ZnBr_2)_3(1)_2(2)]_n \cdot (TTF)_2 \cdot (C_6H_{12})$ , (**4•TTF**) has the same topology of that of (**3•TTF**). In pore A the TTF molecules stack nearly orthogonal to each other and the S...S distances between TTF molecules are 3.744 Å and 4.727 Å. In pore B, the TTF molecules stack on top of each other forming one-dimensional arrays along the *c*-axis. The S...S distances between stacked TTFs are 3.370 Å and 4.431 Å.

Our strategy allows the formation of short S...S contacts among TTF guest molecules within the well-defined porous space. Thus, we have demonstrated that how to control the packing of TTF molecules using biporous coordination networks which may be applied to many other guests molecules.

**References**

[1] J. Martí-Rujas et al., *Angew. Chem. Int. Ed.* In press.

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