

## The Diversity of Zn(II) Coordination Networks Composed of Multi-Interactive Ligand TPHAP<sup>-</sup> via Weak Intermolecular Interaction

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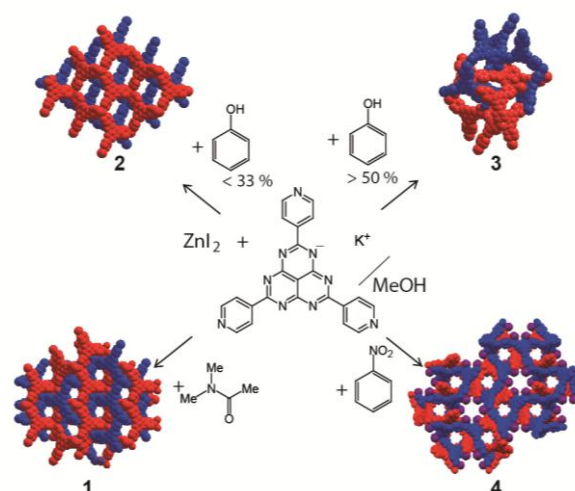
### Introduction

Coordination network is a representative subject of crystal engineering because of self-assembly of building blocks cooperated with non-covalent intermolecular interactions. Network geometry is based on the coordination geometry of metal ions and the shape of organic ligands. Furthermore, weak intermolecular interactions like hydrogen bond or  $\pi$ - $\pi$  interaction play a crucial role in networking. We focused on a hexaazaphenalenyl (HAP) skeleton to introduce weak intermolecular interactions. Recently, we succeeded in synthesizing a multi-interactive ligand, 2,5,8-tri(4'-pyridyl)-1,3,4,6,7,9-hexaazaphenalene (TPHAP<sup>-</sup>), which is responsive to weak intermolecular interaction (Scheme 1). In this study, we focused on solvent effects on networking via weak intermolecular interaction. Here, we report four kinds of coordination networks using the same starting materials of K<sup>+</sup>TPHAP<sup>-</sup> and ZnI<sub>2</sub> in various solvents (Scheme 1).

### Results and Discussion

The layering diffusion method of a methanol solution of ZnI<sub>2</sub> into a MeOH-guest solution (DMA, PhOH and PhNO<sub>2</sub>) of K<sup>+</sup>TPHAP<sup>-</sup> produced single crystals. Totally four types of different network crystals were obtained depending on the solvent systems and mixing ratio, [ZnI(TPHAP)] 3.5CH<sub>3</sub>OH (1) (from MeOH/DMA), [ZnI(TPHAP)] 3PhOH 2CH<sub>3</sub>OH (2) (from MeOH/phenol (< 33%)), [ZnI(TPHAP)] 5PhOH 2.5CH<sub>3</sub>OH (3) (from MeOH/phenol (> 50%)), and [ZnI(TPHAP)] 2PhNO<sub>2</sub> 6CH<sub>3</sub>OH (4) (from MeOH/nitrobenzene).

Although the components of 1, 2, 3 and 4 are the exactly same as [ZnI(TPHAP)], each of them has different network. Zn<sup>2+</sup> ions in each network have tetrahedral coordinate and act as a trident junction. While the zigzag sheets in 1 interpenetrate each other, that in 2 is stacked without interpenetration. In contrast, 3 forms interpenetrated 3D network composed of ZnI<sup>+</sup> and TPHAP<sup>-</sup> via  $\pi$ - $\pi$  interaction. Even though 2 and 3 were obtained from the same solvent system of PhOH/MeOH, they formed totally different networks due to the different ratio of phenol (< 33% and > 50% volumetric ratio, respectively). Because phenol has a hydrogen bond



Scheme 1 Diversity of ZnI(TPHAP) networks

donor site, it prefers hydrogen bond to  $\pi$ - $\pi$  interaction. Therefore, in > 50% volumetric ratio case, phenol formed more hydrogen bonds around TPHAP<sup>-</sup> preventing  $\pi$ - $\pi$  stacking formation, resulting in 3D interpenetrated structure 3 rather than 2. In 2 and 3, phenol works as a template, which forms triple  $\pi$ -stacking structure (TPHAP<sup>-</sup>/phenol/TPHAP<sup>-</sup>). Because of hydrogen bond donor interaction, phenols prefer hydrogen bond to  $\pi$ - $\pi$  interaction between them. On the other hand, in 4, nitrobenzene helps to form quadruple  $\pi$ -stacking structure (TPHAP<sup>-</sup>/nitrobenzene/nitrobenzene/TPHAP<sup>-</sup>), because both nitrobenzene and TPHAP<sup>-</sup> are hydrogen bond acceptor and only  $\pi$ - $\pi$  interaction works as a template effect for forming a stacking structure. Among all, thanks to nitrobenzene double layer, only 4 has a pore window large enough for guest molecules to enter.

In conclusion, we demonstrated that TPHAP<sup>-</sup> can be an excellent probe for weak intermolecular interactions and can form various networks depending on coexisting molecules. This sensitive probe can be useful for trapping kinetic state networks.

### References

[1] T. Kojima *et al.*, *CrystEngComm*. Submitted.

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