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The Diversity of Network Topology Composed of Zn(II) and Multi-Interactive Ligand TPHAP$^-$ via Weak Intermolecular Interaction

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1 Introduction

In coordination polymers, not only the coordination geometry of metal ions and the shape of organic ligands but also weak intermolecular interactions like hydrogen bond and π-π interactions play a crucial role for making various network topology. Even same components of metal ions and organic ligands can produce several kinds of networks depending on an energy landscape directed by experimental conditions, e.g. solvent, guest molecule, temperature, reaction speed, and so on. In this study, we investigated solvent effects on network topology by using our multi-interactive ligand, 2,5,8-tri(4-pyridyl)-1,3,4,6,7,9-hexaazaphenalene which can induce weak intermolecular interactions during self-assembly.

2 Experiment

The layering diffusion method of a methanol solution of ZnI_2 into a MeOH–guest solution of K^+TPHAP^- produced single crystals. Totally seven types of different network crystals were obtained depending on solvent and the mixing ratio (MeOH/additive solvent): [ZnI(TPHAP)] $3.5CH_3OH$ (**1**) (from MeOH/DMA), $[ZnCl_{0.5}I_{0.5}(TPHAP)H_2O]$ $7H_2O$ (**2**) (from MeOH/DMA+water), [ZnI(TPHAP)] 3PhOH $2CH_3OH$ (**3**) (from MeOH/phenol (< 33%)), [ZnI(TPHAP)] 5PhOH $2.5CH_3OH$ (**4**) (from MeOH/phenol (> 50%)), [ZnI(TPHAP)] $2PhNO_2$ $6CH_3OH$ (from MeOH/nitrobenzene) (**5**), [ZnI(TPHAP)CH_3OH] $3PhNH_2$ (**6**) (from MeOH/aniline), and $[(ZnI)_2(TPHAP)(HCON(CH_3)_2)_3(CH_3OH)_2]^+[(ZnI_2)_2(TPHAP)(HCON(CH_3)_2)]^-$ $(HCON(CH_3)_2)$ $4CH_3OH$ (**7**) (from MeOH/ DMF).

3 Results and Discussion

We obtained four kinds of topology (interpenetrating 6^3-**hcb**, non-interpenetrating 6^3-**hcb**, interpenetrating 10^3-**srs**, and interpenetrating 8^3-**etf**) except for **7**. All networks are composed of the same component, ZnI(TPHAP), in which both ZnI^+ and $TPHAP^-$ act as 3-connected nodes. Topological mechanism was explained on the basis of symmetry of node and the weak intermolecular interactions between $TPHAP^-$ and guest molecules. Because **1** was obtained from the non-aromatic solvent system (methanol/DMA), π-π interaction may dominate intermolecular interactions within only $TPHAP^-$ molecules, followed by interpenetrating network formation. On the other hand, because **3** and **6** were obtained from aromatic solvent (methanol/phenol and methanol/aniline, respectively), the solvent molecules were encapsulated in a void via π-π interaction with $TPHAP^-$, leading to non-interpenetrating network.

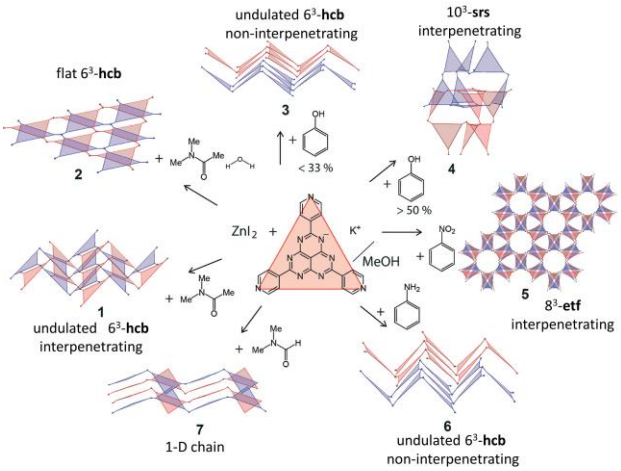

Figure 1. Diversity of ZnI(TPHAP) networks

The 10^3-**srs** network **4**, which is strong isotropic symmetry, obtained from phenol-rich solution (> 50% volumetric ratio) has a large void occupied by solvent through hydrogen bond and π-π interaction, in which phenol prefers hydrogen bond to π-π interaction, probably preventing TPHAP dimer formation. Especially, although **3** and **4** were obtained from the same solvent system (PhOH/MeOH), different networks were formed due to the different solvent ratio. This fact indicates that a slight difference in experimental conditions makes a big difference in networking thanks to multi-interactivity of $TPHAP^-$ to weak intermolecular interactions.

5 forms 3-periodic 2-fold interpenetrating 8^3-**etf** network which is the first example in the database of TOPOS& RCSR. Among all, thanks to nitrobenzene double layer, only **5** has a pore window large enough for guest molecules to enter.

In conclusion, we demonstrated that $TPHAP^-$ can be an excellent probe for weak intermolecular interactions and can form various networks depending on coexisting molecules.

References

[1] T. Kojima *et al*., *CrystEngComm.* **16**, 6335 (2013).

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