

## Single-crystal growth of coordination networks via the gas phase

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## 1 Introduction

To achieve high performance of various applications in porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), not only functionality but also thermal stability of networks is important. To create thermally stable networks, it is essential to develop networking methods. Most of the MOFs have been prepared from solution phase reaction such as solvothermal synthesis because solvent readily assists in forming a coordination bond and making a large pore. However, sometimes the network containing a number of solvents in a large pore is so fragile that it cannot retain a framework. Therefore, we paid attention to the networking via gas phase reaction as a solvent-free method. Herein we report the single crystal growth of thermally stable coordination network via gas phase.<sup>1</sup>

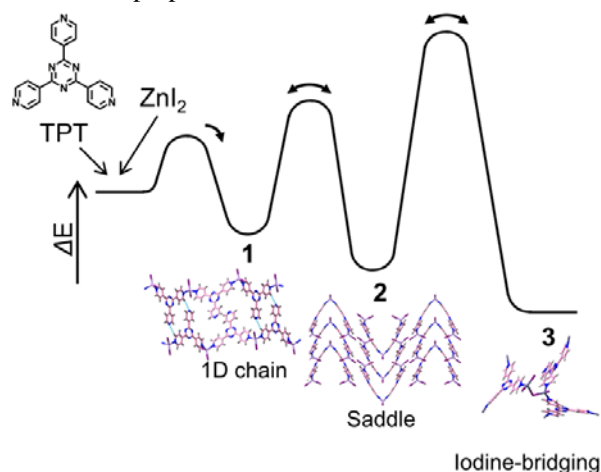
## 2 Experiment

We observed rapid vaporization of starting materials and deposition of white crystalline powder on the inside surface of the glass ampule within 10 seconds on rapidly heating of ZnI<sub>2</sub> and TPT (TPT = 2,4,6-tris(4-pyridyl)triazine) together (at the mole ratio of 2:1) at 850 K under reduced pressure (~0.1 Torr) in a glass ampule. Afterward, the white crystalline powder turned stepwise light yellow to dense yellow for 2 min. Three kinds of crystalline phases were found by powder X-ray diffraction. By optimizing experimental conditions of temperature, reaction time, and mole ratio of ZnI<sub>2</sub> and TPT, we successfully isolated each single crystal, [(ZnI<sub>2</sub>)(TPT)]<sub>n</sub> (**1**), [(ZnI<sub>2</sub>)<sub>3</sub>(TPT)<sub>2</sub>]<sub>n</sub> (**2**), and [(ZnI<sub>2</sub>)(μ-I)(ZnI)(TPT)]<sub>n</sub> (**3**) in Table 1.

The single crystal X-ray structure analysis revealed each structural detail. **1** has a stacking structure of 1D undulated chains composed of ZnI<sub>2</sub> and TPT, [(ZnI<sub>2</sub>)(TPT)]<sub>n</sub>. **2** has a stacking structure of 1D saddle-type unit. Two TPTs connected by ZnI<sub>2</sub> form a saddle-type unit and each saddle-type unit forms a 1D chain through ZnI<sub>2</sub> connectors, [(ZnI<sub>2</sub>)<sub>3</sub>(TPT)<sub>2</sub>]<sub>n</sub>. Thanks to the saddle-type unit, 1D channels form in the structure with pore volume of 293.4 Å<sup>3</sup> per unit cell. To the best of our knowledge, this is the first example of single crystal growth of porous coordination network via gas phase. The single crystal X-ray structure analysis of **3** revealed a new type of iodide single-bridging coordination mode, (ZnI<sub>2</sub>)(μ-I)(ZnI).

Crystal structure analysis provides an insight of relative thermal stability of each network regarding bond dissociation energy. TG curves support each thermal stability by the decomposition temperatures, **1** < **2** < **3**.

This result indicates that, to control each phase, reaction temperature and mole ratio of ZnI<sub>2</sub> and TPT are crucial in selectivity of single crystal growth as shown in Table 1. Therefore, the energy diagram for three-step reactions in scheme 1 was proposed.



Scheme 1. Proposed energy diagram via gas phase.

Table 1. Dependence of selectivity of single crystal growth on reaction temperature and mole ratio<sup>a</sup>

Mole ratio of ZnI <sub>2</sub> :TPT	Reaction temperature / K					
	673	708	723	743	788	843
1:1	<b>1</b>	<b>1</b>	<b>1, 2</b>	<b>2</b>	× <sup>c</sup>	× <sup>c</sup>
3:2	× <sup>b</sup>	<b>1, 2</b>	<b>1, 2</b>	<b>2</b>	× <sup>c</sup>	× <sup>c</sup>
2:1	× <sup>b</sup>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2, 3<sup>d</sup></b>	<b>3<sup>d</sup></b>

[a] All reaction times (except 2:1, 788K and 843K) are 2 hours leading to thermal equilibrium state. [b] No reaction. [c] Decomposition. [d] 5 min

In summary, we have successfully prepared three kinds of single crystals via gas phase. Especially, **2** is the first example of single crystal growth of a porous coordination network via gas phase, which can trap small molecules in a pore. Furthermore, the equilibrium among three networks can be controlled by temperature and stoichiometry. This synthetic method via gas phase can be applied to the materials which cannot be available in solution phase, for example, because of low solubility.

## References

[1] T. Kojima *et al.*, *Chem. Commun.*, 2014, **50**, 13793-13796.

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