

# Isolation and Evolution of Labile Sulfur Allotropes via Kinetic Encapsulation in Interactive Porous Networks

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## 1 Introduction

Cryogenic trapping methods have been widely used to investigate transient chemical species. These methods, however, do not always allow the observation of very labile reactive intermediates. To go around this problem, we propose encapsulation of transient species in an interactive porous network under non-equilibrium conditions. Our approach involves the stabilization of transient species via the active sites located in the channels of porous coordination networks. Here we report the first direct X-ray observation of extremely reactive  $S_2$  species and their conversion towards bent- $S_3$  via  $cyclo-S_3^{2+}$  on an interactive site in a channel of a porous coordination network. We utilized a kinetically assembled porous coordination network  $[(CuI)_2(TPPM)]_n$  (**1**, TPPM = tetra-4-(4-pyridyl)phenylmethane) and thermally more stable isomer  $[(Cu_2I_2)(TPPM)]_n$  (**2**)<sup>1,2</sup> for kinetic trapping of sulfur species.

## 2 Experiment

Sulfur-gas was encapsulated in the porous coordination networks **1** and **2** under kinetic conditions; an excess amount of elemental sulfur and desolvated network **1** or **2** were placed at different sites of a glass tube. The glass tube was then sealed with vacuum and heated by flame at the site containing the sulfur. Shortly after heating the sulfur powder, the yellow crystals of network **1** turned dark yellow, whereas the crystals of network **2** did not display a color change. Within five minutes from the color change, X-ray diffraction of these crystals were measured. In the case of network **1**, The structure was solved in the tetragonal  $P-4$  space group. To investigate the transient nature of sulfur species in the channels of network **1**, we collected two additional sets at 300 K and 350 K using a heating rate of 10 K/min between measurements. Diffraction data at 300 K showed a space group change from  $P-4$  to  $I-4$ , a sharpening of diffraction spots and the almost entire disappearance of diffuse scattering which indicates that successive reaction of sulfur species had taken place on heating.

## 3 Results and Discussion

The crystal structure analysis at 250 K clearly unveiled the existence of physisorbed  $S_2$  and bent- $S_3$  species onto the iodide sites of the framework channels (Fig. 1). The geometry of  $S_3$  was found to be in good agreement with that previously reported. Furthermore, analysis of the 300 K structure revealed formation of  $cyclo-S_3^{2+}$  chemisorbed

on bridging iodide sites and the presence of physisorbed bent- $S_3$  and physisorbed  $cyclo-S_3$  in the network **1** channels (Fig. 1). The  $cyclo-S_3$  allotrope has been predicted to be less stable than the bent- $S_3$  structure, yet energetically accessible, by theoretical calculations but it had never been observed before. A structure redetermination of the single crystal at even higher temperature, 350 K, revealed only bent- $S_3$  species in network **1**, suggesting a complete transformation of chemisorbed  $cyclo-S_3^{2+}$  to bent- $S_3$  species.

Kinetic trapping of gas-sulfur in network **2** resulted in physisorbed  $S_2$  species only, with no evidence of  $S_3$ . X-ray analysis at 30 K revealed that  $S_2$  physisorbed on two different sites of network **2**: i) aligned in the 1D-channel of the structure presenting severe disorder and ii) within small cavities adjacent to the  $Cu_2I_2$  units. Only physisorption of  $S_2$  was observed on iodide sites in this network because of the steric hindrance around iodide sites.

The method reported here provides a new means for future investigations of other labile reaction intermediates. Indeed, this method enables to find out new reactions of sulfur allotropes.<sup>1</sup>

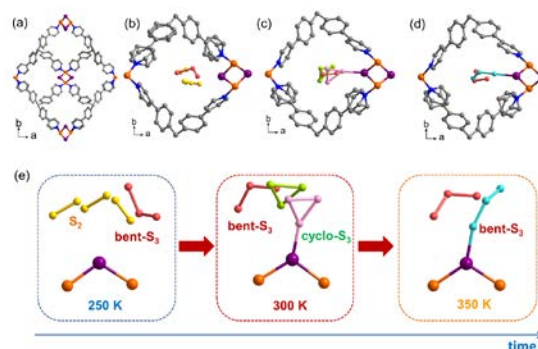


Fig. 1: Pore description in crystal structure of (a) network **1**, (b) network **1** after sulfur encapsulation at 250K, (c) 300K and (d) 350 K. (e) The crystal structure of Sulphur-encapsulating network **1** showing parts of  $\{CuI\}$  unit and sulfur species.

## 4 References

- [1] H. Kitagawa, H. Ohtsu, A. J. Cruz-Cabeza, M. Kawano, *IUCrJ*, **3**, 232 (2016).
- [2] H. Kitagawa, H. Ohtsu, M. Kawano, *Angew. Chem. Int. Ed.* **52**, 12395 (2013).

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