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Br_2 induced oxidative pore modification of a porous coordination network

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Iodinated pores of a Zn-based coordination network were modified by Br_2 oxidation to produce brominated pores in a polycrystalline-to-polycrystalline manner while maintaining the same network topology. Ab initio X-ray powder diffraction analysis and Raman spectroscopy revealed that the brominated pore can trap Br_2 or I_2 by strong σ/π-type interactions. A kinetic study in solution revealed that the pore modification by Br_2 oxidation is much faster than the Br_2 encapsulation process.

The interactivity of pores of coordination networks plays a key role in their fascinating properties because interactive sites can communicate with activated guest molecules and induce dynamic structural changes.[1-3] Because the pores' environment is critical in determining their role, post-modification methods have been actively investigated and developed.[4] In particular, building-block replacement methods such as methathesis,[5] ligand linker exchange,[6] and non-bridging ligand exchange[7] are promising ways to dramatically change the pore environment via simple metal/ligand exchange reactions in solution.[4e] Redox reactions are also a promising method for creating various types of pores by post-modification; many studies have emerged to show post synthetic oxidation/reduction.[4, 8] However, there is only limited types of redox induced ligand exchange; such reactions needs high reactivity toward ligand exchange as was nicely shown in Br_2[4a]

Herein, we report the post-modification of pores by Br_2 oxidation of the iodinated pores of a network which induces I/Br exchange; this process represents an unprecedented example of connector modification induced by redox reactions. The iodinated pores of the $[(ZnI_2)_3(TPT)_2]_n$ network (network **1**; Fig. S5, ESI†; TPT = 2,4,6-tris-(4-pyridyl)-1,3,5-triazine)[9,10] were modified by Br_2 oxidation, leading to the formation of a $[(ZnBr_2)_3(TPT)_2(I_2)]_n$ brominated network accompanied by I_2 generation in a polycrystalline-to-polycrystalline manner while maintaining the same network topology. Further heating of this network produced the empty brominated network $[(ZnBr_2)_3(TPT)_2]_n$, which could not be obtained by conventional synthetic methods, *e.g.*, solution- or gas-phase reactions using $ZnBr_2$ and TPT. Furthermore, we encapsulated Br_2 in these brominated pores via strong σ/π-halogen interactions. This work represents the first structural report of a Br_2-encapsulating porous coordination network, even though the literature contains several reports of post-synthetic bromination.[11] All structural transformations/guest encapsulations were investigated by ab initio X-ray powder diffraction (XRPD) and Raman spectroscopic analyses, which revealed strong halogen-halogen interactions at the interactive sites, similar to those at biological halogen-interactive sites.[12]

The post-modification of iodinated pores was accidentally discovered during attempts to encapsulate Br_2 into pores of network **1**. The Br_2 encapsulation into network **1** was performed by a solid-gas reaction under bromine vapour. Any attempts to use single crystals of network **1** failed because the single crystallinity deteriorated upon bromine exposure.[8c] Therefore, we utilized the crystalline powder of network **1** for this experiment (Fig. S6, ESI†). Network **1** and approximately 3 *eq*. of Br_2 were placed separately in the same glassware and maintained at 298 K for approximately 1 min. The colour of the powder changed from pale-yellow to reddish-brown. The XRPD patterns dramatically changed after Br_2 exposure (Fig. 1).

To determine a powder crystal structure of the resulting network, we collected high-resolution XRPD patterns in a synchrotron facility (SPring-8, BL02B2). After bromine exposure, the unit cell changed from a = 30.360 Å, b = 12.775 Å, and c = 13.5826 Å in space group *Pccn* to a = 29.997 Å, b =

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†Electronic Supplementary Information (ESI) available: ab initio XRPD analysis, Raman spectra, IR spectra, UV-Vis-NIR spectra, and TG results, adsorption kinetics and complete scheme of pore-modification, adsorption tests, TOPOS analyses, Magnified figures of Rietveld refinements and crystallographic details (CIF; also see CCDC entries 1420942 - 1420944).. See DOI: 10.1039/x0xx00000x

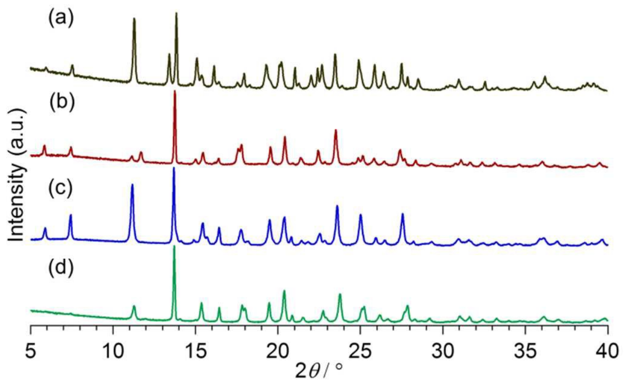

Fig. 1. XRPD patterns of (a) network **1**, (b) I_2@network **2**, (c) network **2**, (d) Br_2@network **2** (λ = 1.54056 Å, Cu $K_{\alpha1}$)

12.8596 Å, and *c* = 12.8188 Å in space group *Pccn* (as determined using the program DICVOL[13]). We solved the initial structure using a model of the original network **1** and Br_2 via a simulated annealing method (using the program DASH[14]); however, I^- was exchanged with Br^-, forming an I_2-encapsulating ZnBr-network, $[(ZnBr_2)_3(TPT)_2(I_2)]_n$ (I_2@network **2**; network **2**, $[(ZnBr_2)_3(TPT)_2]_n$). The I_2@network **2** model provided better refinement results and agreed with other experimental results (*vide infra*). Therefore, after obtaining the I_2-encapsulating ZnBr-network model, we refined the structure by the Rietveld method[15] using soft restraints for geometrical parameters (using the program RIETAN-FP[16] and VESTA[17]; see ESI[†] for more details). The correctness of this model was further confirmed by vibrational spectroscopy, elemental analysis, and Thermogravimetry (TG) (*vide infra*). The good agreement between the experimental and calculated diffraction patterns indicates the correctness of the structure (Fig. 2; Fig. S2, ESI[†]).

This structural analysis unveiled the post-modification of the pores: iodinated pores were modified to brominated pores in a polycrystalline-to-polycrystalline manner while maintaining the same network topology. Thus, the following I/Br exchange reaction occurred:

$$[(ZnI_2)_3(TPT)_2] + 3Br_2 \longrightarrow [(ZnBr_2)_3(TPT)_2(I_2)] + 2I_2$$

We confirmed the presence of I_2 in network **2** by Raman spectroscopy;[3a, 18] the spectrum showed sharp peaks at 174 cm^{-1} and 194 cm^{-1}, corresponding to I_2 in a pore and I_2 attached to the surfaces of crystals, respectively (Fig. S10(d), ESI[†]). The surface I_2 cannot be avoided because the reaction produces 2 *eq*. of free I_2. The elemental analysis results indicate that the chemical formula of the network product is $[(ZnBr_2)_3(TPT)_2(I_2)](I_{2\text{-surface}})_{0.67}$. We also confirmed the amount of I_2 by TG analyses (Fig. S7, ESI[†]) of the network, which showed weight decreases in two steps; the first step corresponds to I_2 desorption from the surface, whereas the second one corresponds to the loss of I_2 from the pores. The overall weight decrease until 575 K was approximately 25.3%, which agrees with the overall I_2 amount (24.6%) calculated on the basis of the formula $[(ZnBr_2)_3(TPT)_2(I_2)](I_{2\text{-surface}})_{0.67}$. The I_2 in a pore interacts with the Br^- sites of the network. The I···Br distance is 3.61 Å, which is shorter than the sum of the van der Waals radii of I and Br (3.75 Å),[19] and the I-I-Br angle is 153°(non-linear), which indicates a π-type interaction with some contributions of a σ-type interaction. The I_2 absorption band at 280 nm indicates strong charge transfer interaction between Br^- and I_2, which was not clearly observed in I_2@network **1**, indicating only σ-type interaction between I^- sites of the network and I_2 (Fig. S8, ESI[†]).[9b] The brominated network **2** shows significantly stronger affinity for I_2 because of this σ/π- interactions compared with the iodinated pore in network **1** which encapsulates I_2 only via σ-interaction.

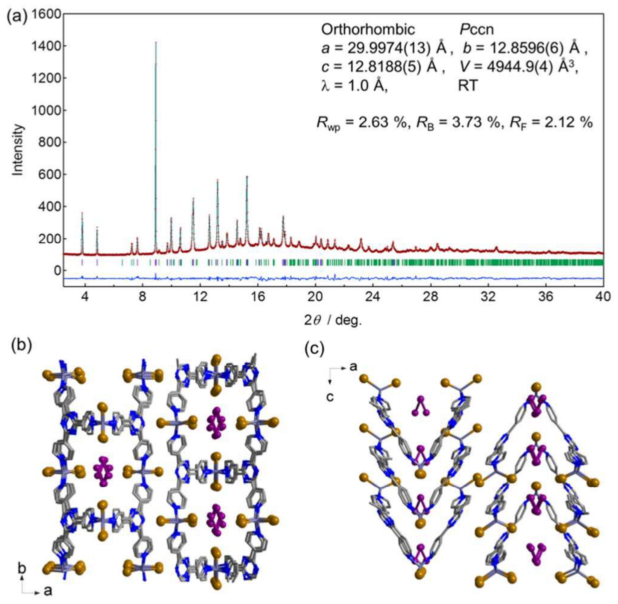

Fig. 2. Experimental (red), calculated (black), and difference (blue) XRPD profiles from the final Rietveld refinement of the I_2@network **2**. Crystal structure: (b) view along the *c*-axis. I_2 (occupancy 0.5) occupies two symmetrically related positions. (c) View along the *b*-axis. Color codes: C, grey; N, blue; Zn, pale-blue; I, purple; and Br, brown.

This post-modification of a pore arises from the oxidation ability of bromine; Br_2 has an oxidation potential of *E* = +1.087 V (vs. SHE), which is higher than that of I_2 (+0.54 V vs. SHE). Therefore, it can oxidize I^- to I_2.[20] This post-modification is the first example of redox induced ligand exchange for building block replacement. This unique pore modification enables the drastic change of the species in the interactive pores from I^- to Br^-.

A kinetic study indicated that this post-modification process was quite fast in solution. Approximately 3 *eq*. of powdered network **1** was immersed in a Br_2/cyclohexane solution (0.48 mM), and the change in the UV-Vis spectrum was monitored (Fig. S1, ESI[†]). The Br_2 absorption band at 418 nm decreased in intensity, and new bands corresponding to I_2 appeared at 310 nm and 496 nm. Therefore, the post-modification of a pore occurred in solution as well. We propose the following reaction scheme: (a) 1 *eq*. of Br_2 diffuses into a pore because the pore window is too small for cyclohexane, and the pore accommodates one Br_2; (b) Br_2 oxidizes I^- to generate I_2, with only one of the three ZnI_2 species being modified; and (c) I_2 escapes from the pore. Through this process from (a) to (c), one ZnI_2 species is modified to $ZnBr_2$:

$$[(ZnI_2)_3(TPT)_2] + 3Br_2 \longrightarrow [(ZnI_2)_3(TPT)_2(Br_2)] + 2Br_2 \ (1)$$

$$\longrightarrow [(ZnI_2)_2(ZnBr_2)(TPT)_2(I_2)] + 2Br_2 \ (2)$$

$$\longrightarrow [(ZnI_2)(ZnBr_2)_2(TPT)_2] + Br_2 + 2I_2 \ (3)$$

$$\longrightarrow [(ZnBr_2)_3(TPT)_2] + 3I_2 \ (4)$$

These reactions continue until all of the Br_2 are consumed (ESI†). This process comprises three steps because one unit of the network consists of three ZnI_2 units.

Because the reactions are consecutive, analysis of the kinetics is difficult. However, when we plotted time vs. $\ln(A_t - A_\infty)$ by monitoring the absorbance of Br_2 at 418 nm, the plot was linear; the overall Br_2 decrease was therefore assumed to be a pseudo-first-order reaction with a rate constant of 1.0×10^{-3} min^{-1}. According to adsorption kinetics, this reaction corresponds to the physisorption of Br_2.[21] This observation of a first-order reaction suggests that the physisorption of Br_2 is the rate-limiting step. These results suggest that immediately after Br_2 reaches the inside a pore, the oxidation reaction occurs rapidly. Because of this fast oxidation reaction, we could not obtain intermediate states of the reaction, such as a Br_2-encapsulating ZnI-network **1**.

When I_2@network **2** was heated at 573 K, the powder turned white and the encapsulated I_2 was removed. The ab initio XRPD structural analysis of the white powder revealed network **2**, $[(ZnBr_2)_3(TPT)_2]_n$, to be isostructural with network **1** (Fig. 3(a),(b); Fig. S3, ESI†). The pore window of network **2** is 2.6 × 4.6 Å^2, which is larger than that of network **1** because the ionic radius of Br^- is smaller than that of I^-. We modified iodinated pores to brominated pores while retaining the topology. Network **2** exhibits a saddle-type structure with $4^2{\cdot}6$ point-symbol topology (as calculated using TOPOS;[22] ESI†). However, we could not obtain this network starting from $ZnBr_2$ and TPT by solution-phase synthesis or by crystallization via vapour; in such cases, we always obtained an interpenetrating network.[9,23] Therefore, we could prepare network **2** only via I_2@network **2** obtained by Br_2 oxidation of network **1**. Network **2** was stable to 673 K under N_2, which was confirmed by TG measurements (Fig. S7, ESI†). We further confirmed the structural similarity between networks **1** and **2** using IR and Raman spectroscopy (Figs. S9 and S10, ESI†).

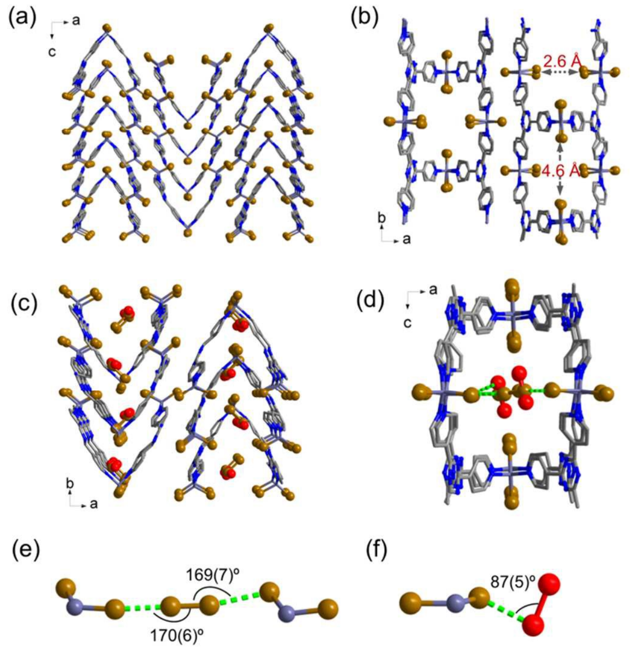

Fig. 3. Crystal Structure of network **2**: (a) view along the *c*-axis. (b) View along the *b*-axis. Crystal Structure of Br_2@network **2**: (b) view along the *b*-axis. Green dotted lines show interactions. (c) Linear interactions between Br_2 and Br^- ions. (d) Perpendicular interactions between Br_2 and Br^- ions. Colour codes: C, grey; N, blue; Zn, pale-blue; and Br, brown and red to distinguish disordered molecules.

Because network **2** contains Br^- ions as interactive pore sites, we attempted to trap Br_2 in the pores. For these experiments, we also used Br_2 vapour diffusion, which is the same method used for the exposure of network **1** to Br_2. After the exposure of network **2** to Br_2, the powder turned from white to yellow and the XRPD pattern clearly changed (Fig. 1). The ab initio XRPD structural analysis of the yellow powder revealed the structures of the Br_2@network **2** (Fig. 3(c)-(f); Fig. S4, ESI†), the ZnBr-network and the disordered guest Br_2. The Br_2 was physically adsorbed into a pore and strongly interacted with Br^- in the pore, with $Br\cdots Br$ distances of 3.44 Å, 3.55 Å, and 3.22 Å; these distances are shorter than the sum of the van der Waals radii of Br (3.70 Å).[19] One of the disordered Br_2 molecules exhibits an almost linear geometry (Fig. 3(e)), which is a typical σ-type halogen-halogen interaction;[24] in contrast, the other disordered Br_2 exhibits an almost perpendicular geometry (Fig. 3(f)), which indicates a π-type interaction with an elongated Br_2 bond (2.38(14) Å). Therefore, Br_2 can interact with Br^- not only through a σ-hole but also through π-orbitals. These results indicate the diversity of halogen bonding with interactive pore sites, similar to that demonstrated in the case of Br_2@CB[6].[25] This strong interaction was also observed by Raman spectroscopy. A Br_2 symmetric band was observed at 236 cm^{-1} (Fig. S10(e), ESI†), which is a significantly lower wavenumber than that of the band for free Br_2 (319 cm^{-1}).[26] This result is consistent with the elongation of the Br_2 bond. This strong interaction was confirmed by an affinity test; network **2** adsorbs Br_2 faster than I_2 in cyclohexane (Fig. S7, ESI†).‡ This strong affinity for Br_2 indicates a new means by which Br^--interactive sites contain reactive species. We compared the affinity of I_2 and Br_2 against network **2** by Raman spectra. The energy shift from free-state is 18 % for I_2 and 26 % for Br_2. The larger energy shift for Br_2 indicates stronger interaction for Br_2 than for I_2.

In this work, we demonstrated that iodinated pores of a Zn-based coordination network were modified by Br_2 oxidation to produce brominated pores in a polycrystalline-to-polycrystalline manner while maintaining the same network topology. This work represents the first example of redox induced ligand exchange for building block replacement. The brominated pores are thermally stable up to 673 K and the pore size is larger than the original iodinated pores because of the smaller van der Waals radius of Br^- ions than that of I^- ions. The brominated pore can trap Br_2 or I_2 by strong σ/π-type interactions. A kinetic study in solution revealed that the oxidative pore modification by Br_2 is much faster than the Br_2

encapsulation process. This post-modification method opens new pathways to create interactive porous networks. This study also demonstrates that various polycrystalline materials can be investigated using ab initio XRPD analysis.

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‡Because cyclohexane adsorption was competitive, we could not determine the kinetics of this adsorption process.

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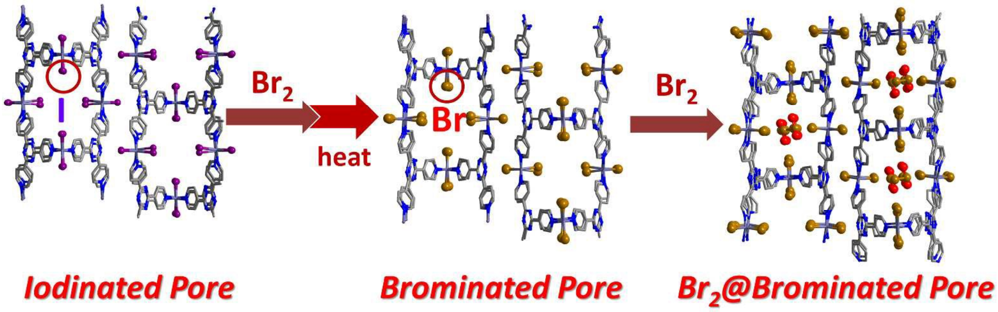

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