Self-assembled construction of a sheet-type coordination polymer bearing cationic M2L4 cages: creation of channel-like space for removal of ClO4- and NO3- from aqueous solutions

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Self-assembled Construction of a Sheet-type Coordination Polymer Bearing Cationic M₂L₄ Cages: Creation of a Channel-like Space for Removal of ClO₄⁻ and NO₃⁻ from Aqueous Solutions

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Treatment of CuCl₂ with a bis-benzimidazole-type ligand, *p*-bbiteb, afforded a new 2D coordination polymer bearing cationic Cu₂L₄ cages on the sheet framework. The regular arrangement of the cages created a channel-like space for anions. The compound removed ClO₄⁻ and NO₃⁻ from aqueous solutions by exchange with Cl⁻ in the channels.

Fixation of functional discrete molecules on an infinite polymeric framework is a promising strategy for the preparation of polymer compounds that exhibit functionality due to the discrete molecular units.[1-5] For example, many types of molecular catalysts are bound to 1D organic polymers as pendant units, yielding new polymeric materials that exhibit catalytic reactivity due to the discrete units.[2] Furthermore, various heterogeneous catalysts,[3] sensors,[4] and molecular devices[5] have been prepared by attaching discrete functional molecules to the surface of 2D organic films or inorganic layer compounds.

The treatment of metal ions with organic bridging ligands, using self-assembly processes, has afforded numerous coordination polymers with well-ordered structures.[6] Although some coordination polymers incorporating polyoxometalate units in the frameworks have been synthesized,[7] the preparation of coordination polymers bearing discrete molecules as pendant units is not well developed. The one-step construction of such functional structures by the simple treatment of one type of metal source and one type of organic ligand remains a challenging topic.

Flexible bis-imidazole- and bis-benzimidazole-type ligands,[8-12] as illustrated in Scheme 1, have been used for the synthesis of coordination polymers[8] and for discrete molecules such as dinuclear[9-11] or trinuclear cage complexes.[12] In this paper, these types of bridging ligands are designated as L^B. The type of compound obtained is largely dependent on the types of metal ions, counter anions, and reaction solvents used in the synthesis.
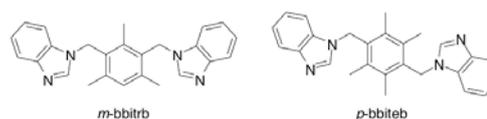
Scheme 1. Structures of *m*-bbitrb and *p*-bbiteb.

We have recently shown that $[SO_4 \subset Cu_2(m\text{-bbitrb})_4]SO_4$ (*m*-bbitrb = 1,3-bis(benzimidazol-1-yl)-2,4,6-trimethylbenzene) (Scheme 1) efficiently removes ClO₄⁻ from aqueous solutions by exchange with the counter anion SO_4^{2-} located outside the cationic cage, despite this compound being insoluble in water.[11] However, to achieve sufficient anion removal activity with $[SO_4 \subset Cu_2(m\text{-bbitrb})_4]SO_4$, it was necessary to grind the solid sample well, because the SO_4^{2-} embedded in the particle cannot be exchanged with ClO₄⁻.

Following on from this, in the present study, we found that the water-insoluble cationic $M_2L^B_4$ cages are useful units for the removal of ClO₄⁻ from aqueous solutions. We successfully synthesized and characterized a new water-insoluble coordination polymer $[Cu(p\text{-bbiteb})_2(\text{-}\mu\text{-Cl-}[Cl\cdot(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4])]Cl_4\cdot MeCN\cdot(H_2O)_8$ (**1**) (*p*-bbiteb = 1,4-bis(benzimidazol-1-yl)-2,3,5,6-tetramethylbenzene) (Scheme 1), comprising the sheet framework and the cationic Cu₂L^B₄ cages that are bound to the sheet. The regular arrangement of the cationic Cu₂L^B₄ cages creates a channel-like space surrounded by the cationic cages. This paper reports on the new self-assembly synthesis and crystal structure of compound **1**, and its NO₃⁻ and ClO₄⁻ removal functions based on the channel-like space.

Compound **1** was conveniently obtained by the treatment of CuCl₂ with *p*-bbiteb in the mixed solvent MeCN/H₂O. The compound crystallized in the tetragonal centric space groups (*P4/n*). The structure was clarified by single-crystal X-ray

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diffraction analysis (Fig. 1). The framework is composed of the sheet framework formulated as $[Cu(p\text{-bbiteb})_2]^{2+}$ and the cationic cages formulated as $[Cl\cdot(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4]^{3+}$. The cages are bound to each Cu^{II} site in the sheet via a μ-Cl^- bridge (*vide infra*). The structure of the cationic cage unit is shown in Fig. 1a. The two Cu^{II} centers are bridged by four *syn*-formed *p*-bbiteb. The Cu(1) and Cu(2) are essentially in the N_4 plane defined by the four nitrogen atoms in the coordination environments. The cage space is well isolated with a gap of about 1.8×1.3 Å^2 between the *p*-bbiteb in the $[Cu_2(p\text{-bbiteb})_4]^{3+}$ framework (Fig. S1 in ESI†).
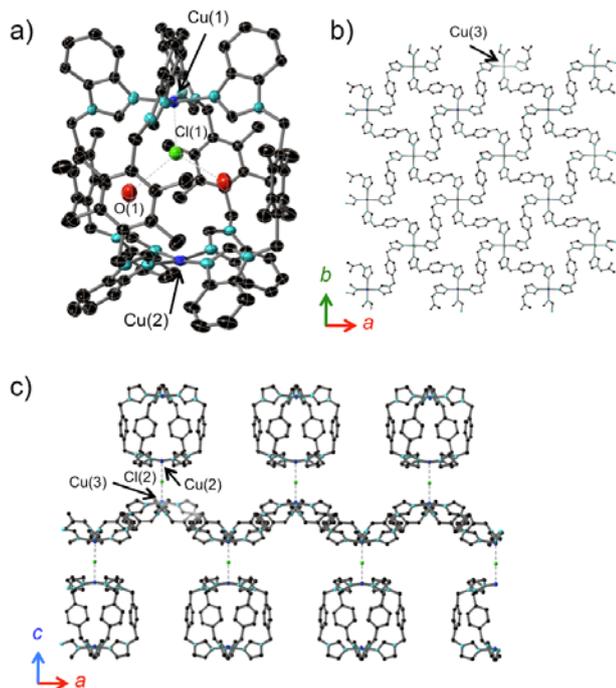

Fig. 1 Structures of the cationic cage unit (a), the sheet framework (b), and the 2D structure that bears the cationic cage units (c) of **1**. The following are omitted for clarity: hydrogen atoms and co-crystallized MeCN molecules in (a)–(c), disorders of water molecules in the cage in (a) and (c), and phenyl rings of benzimidazole and methyl groups of the *p*-bbiteb in (b) and (c). Colour code: blue, copper; green, chlorine; red, oxygen; cyan, nitrogen; black, carbon.

The cage contains a Cl^- and two water molecules. The guest anion and water molecule do not exhibit strong interaction with the cage framework. The Cl^- associates with the Cu^{II} site of the $Cu_2L^B_4$ cage (Cu(1)—Cl(1) = 2.531 (3) Å). The distance is longer than the Cu—N distances (average 2.014 Å) in the coordination environment because of the Jahn–Teller effect. The Cl^- also associates with hydrogen atoms of the imidazole ring of the *p*-bbiteb (Cl(1)---H(1) = 2.882 Å) and water molecules (Cl(1)---O(1) = 3.026 (8) Å). The water molecule is disordered at the four crystallographic equivalent positions (Fig. S1a in the ESI†). Fig. 1b shows a structure of the sheet framework of compound **1**. Each Cu^{II} ion is connected by the *anti*-formed *p*-bbiteb, providing a 2D framework in the *ab* plane. The Cu—N distances (2.015 (4) Å) are similar to those observed in the cationic cages. The sheet

waves are largely as shown in Fig. 1c. The Cu^{II} ions (Cu(3)) located at the tops of the waves are bound to the cationic $Cu_2L^B_4$ cages via the μ-Cl^- (Cl(2)) bridge on both sides of the sheet, as shown in Fig. 1c. The Cu—Cl distances are similar for Cu(3)—Cl(2) (2.504 (2) Å) and Cu(2)—Cl(2) (2.553 (2) Å). The obtained sheet bearing cationic $Cu_2L^B_4$ cages is stacked along the *c* axis (Fig. 2a). Fig. 2b shows the overall structure of the compound with van der Waals radii, exhibiting the creation of the channel-like space surrounded by the cationic cages. A channel, which has a size of about 8.3×3.4 Å^2 in the channel window, is filled with four Cl^- ions, one MeCN, and eight water molecules per three Cu^{II} ions of **1** (Fig. S3 in ESI†). Regarding the solvent molecules, MeCN was easily removed under air or reduced pressure to afford $[Cu(p\text{-bbiteb})_2(\text{-}\mu\text{-Cl-}[Cl\cdot(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4])]Cl_4(H_2O)_8$ (**1b**). Characterization by elemental analysis, powder X-ray diffraction (PXRD) measurements (Fig. S4 in the ESI†) demonstrated that **1b** retains the overall framework of **1**. Because it stores well, we used **1b** to characterize the properties of the coordination polymer bearing cationic cage units.
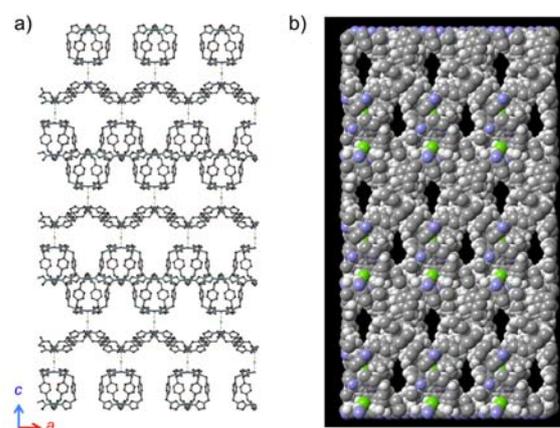

Fig. 2 Overall structure of **1** viewed along the *b* axis, illustrated with a ball-and-stick model (a) and van der Waals radii model (b). The following are omitted for clarity in (a): hydrogen atoms, phenyl rings of the benzimidazole, methyl groups of the *p*-bbiteb, and Cl^- and water molecules in the cage. The following are omitted for clarity in (a) and (b): Cl^-, water, and MeCN molecules in the channels.

The inorganic anions ClO_4^- and NO_3^- are toxic to humans, and are particularly harmful to infants and children.[13,14] The former anion disturbs the uptake of iodide in the thyroid gland, inhibiting the formation of growth hormone,[13] while the latter anion disturbs the transport of oxygen by hemoglobin.[14] Recent reports also suggest that NO_3^- causes various cancers.[15] These anions have been detected in the environment and in drinking water, therefore the development of new materials that can be used to remove these anions is very important. However, these anions are difficult to remove from aqueous solutions because of their high solubility.

As mentioned, we have previously shown that water-insoluble cationic $Cu_2L^B_4$ complexes are useful for ClO_4^- removal from aqueous solutions by anion-exchange reactions.[11] To determine whether **1** exhibits useful properties based on the cationic cages arranged on the 2D sheet, we

studied the ClO_4^- and NO_3^- anion removal properties of **1b**. Fig. 3a and 3b show changes in the concentration of ClO_4^- and NO_3^- (1.0 mM) in an aqueous solution (100 mL) as a function of time after the addition of **1b** (147.5 mg, 0.05 mmol) with different particle sizes. When a powdered sample of **1b** (147.5 mg, 0.05 mmol) was added to an aqueous solution of $NaClO_4$ (0.1 mmol in 100 mL), the concentration of ClO_4^- was reduced from 1.0 mM to 0.43 mM after 10 min, and then to 0.26 mM after 180 min (Fig. 3a). Similarly, the concentration of NO_3^- was reduced from 1.0 mM to 0.58 mM after 10 min, and then to 0.28 mM after 180 min. The anion removal activity was significantly increased when the microcrystalline form of **1b** was used. The powdered sample of **1b** became aggregated during the treatment, but the microcrystalline sample did not, leading to the better activity of the latter. In contrast to the case of $[SO_4 \subset Cu_2(m\text{-bbitrb})_4]SO_4$, **1b** showed less dependency of the particle size on the anion removal activity. This is ascribed to the effects of the channel frameworks, as generally observed in porous materials with channel frameworks, such as zeolites, graphite, and metal–organic frameworks.[6, 16]
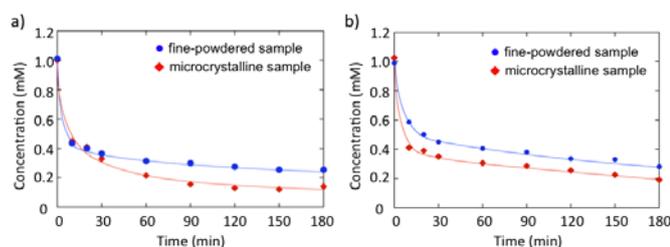

Fig. 3 Changes in concentrations of ClO_4^- (1.0 mM) (a) and NO_3^- (1.0 mM) (b) in an aqueous solutions (100 mL) as a function of time after the addition of a fine-powdered (blue) and microcrystalline sample (red) of **1b** (147.5 mg, 0.05 mmol).
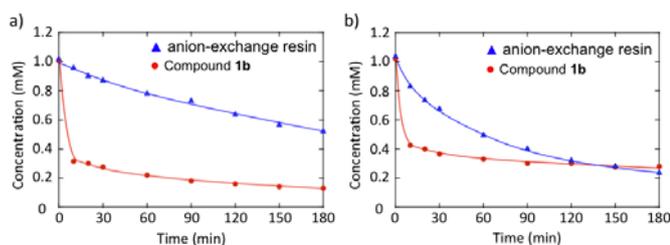

Fig. 4 Changes in concentrations of ClO_4^- (1.0 mM) (a) and NO_3^- (1.0 mM) (b) in aqueous solutions (100 mL) that mimic groundwater as a function of time after the addition of **1b** (299 mg) (red) or anion-exchange resins (blue): Purolite A530E (299 mg) (a) and Purolite A520E (299 mg) (b).

In the ClO_4^- removal experiment in Fig. 3, Cl^- appeared, and increased, in response to the removal of ClO_4^- (Fig. S6 in the ESI†) (and hence a reduction in its concentration). This indicated that the anions are removed in anion-exchange reactions. To study the ClO_4^- and NO_3^- removal process by **1b**, we characterized the reaction products obtained by the treatment of **1b** with 10 equiv ClO_4^- or NO_3^- in aqueous solution. The PXRD measurements showed intense peaks, and the patterns of the reaction products were practically identical to those of **1** and **1b** (Fig. S5 in the ESI†). This indicated that

the framework of **1** is retained after the anion-exchange reactions. The inclusion of ClO_4^- and NO_3^- in the products was conveniently confirmed by IR spectroscopy; the IR spectra showed new intense peaks, ascribed to ClO_4^- and NO_3^-, at around 1100 cm^{-1} and 1400 cm^{-1} (Fig. S7 in the ESI†).

Because of the increased d_{x2-y2} orbital level caused by the weak crystal field of the ClO_4^-, the d–d absorption of the Cu^{II} ions of the $Cu_2L^B_4$ cage, which include ClO_4^-, is observed at the higher-energy region compared with $Cu_2L^B_4$ cages that include SO_4^{2-} or Cl^-. The d–d absorptions characterized by reflectance spectra of the reaction products were similar for **1** and **1b** (Fig. S8 in the ESI†), indicating that Cl^- in the cationic $Cu_2(p\text{-bbiteb})_4$ cage was not exchanged with ClO_4^- or NO_3^- during the anion removal experiments. Only Cl^- in the channel-like space is exchanged with ClO_4^- and NO_3^- by the anion-exchange reactions. We then investigated whether **1b** could remove ClO_4^- and NO_3^- from an aqueous solution that mimicked groundwater. We used a solution containing $NaHCO_3$ (3.0 mM), $CaCl_2$ (1.0 mM), $MgCl_2$ (0.5 mM), Na_2SO_4 (0.5 mM), and KNO_3 (0.5 mM). For the removal experiments, $NaClO_4$ or $NaNO_3$ (0.10 mmol) was dissolved in 100 mL of this solution. Fig. 4a and Fig. 4b show the changes in concentrations of ClO_4^- and NO_3^- as a function of time after the addition of **1b** (299 mg, 0.10 mmol). The concentration of ClO_4^- was reduced from 1.0 mM to 0.32 mM after 10 min and then to 0.13 mM after 180 min (Fig. 4a), while the concentration of NO_3^- was reduced from 1.0 mM to 0.42 mM after 10 min and then to 0.28 mM after 180 min (Fig. 4b). The higher ClO_4^- removal activity by **1b** is due to the higher affinity of the anion to the hydrophobic space surrounded by the cationic cages. Although many coordination polymers showed anion exchange property,[17] the selective removals for ClO_4^- and NO_3^- from aqueous solutions were unprecedented.

We studied the recovery process of **1b** from the anion-exchanged products by the simple reverse anion-exchange reactions or the chemical degradation process. The yields of **1b** recovered from the ClO_4^-- and NO_3^--absorbed products by treatments with excess NaCl in aqueous solutions were estimated to be 12% and 40% from ion chromatograph measurements (Fig. S11 in the ESI†). Lower yield for ClO_4^--included product is the result of high affinity of ClO_4^- in the channel space. As shown in the ESI†, it was also shown that analytically pure p-bbiteb was recovered by a general chemical degradation procedure from the anion-exchanged product in 47% (Fig. S12). The ligand could be used for re-preparation of **1b**.

For comparison, we carried out the ClO_4^- and NO_3^- removal experiments with the mimicked solutions using the anion-exchange resins Purolite A530E (299 mg) and A520E (299 mg). These resins are widely used for the removal of ClO_4^- and NO_3^- from aqueous solutions. The results are shown in Fig. 4a and 4b. The removal of ClO_4^- and NO_3^- is remarkably faster in the case of **1b** compared with the resins. This result means that **1b** is superior in terms of ClO_4^- and NO_3^- removal; removal with **1b** takes place within a shorter period than with the anion-exchange resins.

In conclusion, we have shown, for the first time, a one-step self-assembled construction of a 2D coordination polymer **1** which bears the regular arrangement of cationic $Cu_2L^B_4$ cages on the sheet framework, creating a channel-like space for anions among the cationic cages. We have shown that the channels have high anion removal activity for the removal of ClO_4^- and NO_3^- from aqueous solutions via anion-exchange reactions. Furthermore, and significantly, the removal takes place within a shorter period than with anion-exchange resins.

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