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Cationic M₂L₄ Cages for Perchlorate Removal from Aqueous Solutions and Preferential Perchlorate Incorporation in Hydrophilic Solutions

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†Electronic supplementary information (ESI) available: Figure S1-S2 show the crystal structures of **1a**, **1b**, **2a**, and **2b**; Figure S3 shows anion removal chart by **1b**. CCDC 1451229 (**1a**), 1451228 (**1b**), 1451231 (**2a**), and 1451230 (**2b**). Crystallographic data in CIF or other electronic format see DOI:

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Abstract

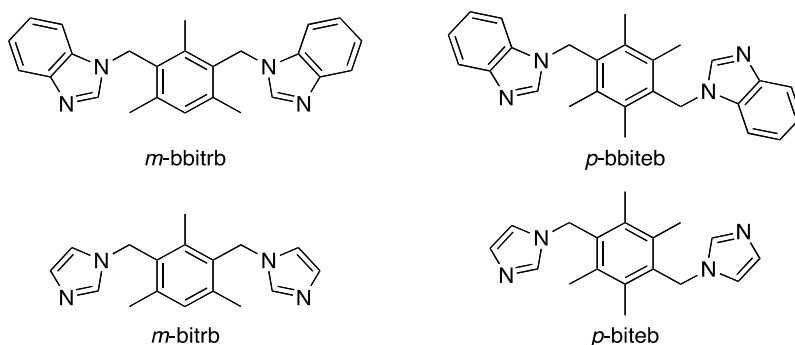
Four new cage-type compounds, [A ⊂ Cu₂(*m*-bbitrb)₄]A₃ (A = Cl[−] (**1a**), Br[−] (**1b**), *m*-bbitrb = 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene), and [SO₄ ⊂ Cu₂(*m*-bbitrb)₄]A₂ (A = Cl[−] (**2a**), Br[−] (**2b**)), were synthesized and characterized. These compounds have a M₂L₄-type cationic cage, incorporating an anion in the cage. Although the four compounds are insoluble in water, they exhibit ClO₄[−] removal activity from aqueous solutions by exchange with anions located outside the cage. The [Cl ⊂ Cu₂(*m*-bbitrb)₄]³⁺ cage removes ClO₄[−] from aqueous solutions preferentially. To study the selective removal process by the cationic cage, the affinity of the [Cu₂(*m*-bbitrb)₄]⁴⁺ cage for ClO₄[−] was studied by measuring solid-state reflectance spectra, absorption spectra, and ESI-TOF mass spectra in solutions of MeCN and MeCN/H₂O for [SO₄ ⊂ Cu₂(*m*-bbitrb)₄](ClO₄)₂ (**2d**). Results indicated that the SO₄^{2−} in [SO₄ ⊂ Cu₂(*m*-bbitrb)₄]²⁺ was retained in MeCN solution, whereas in MeCN/H₂O solution the SO₄^{2−} was exchanged with the ClO₄[−] located outside the cage. This is because an increase in the hydrophilicity of the solution promotes the incorporation of hydrophobic ClO₄[−] into the

hydrophobic cage, meaning that the preferential removal of ClO_4^- from aqueous solutions is due to the higher affinity of the hydrophobic space created outside the $\text{M}_2\text{L}^{\text{B}}_4$ cages in the solid state.

Introduction

Many cage-type coordination compounds have attracted great attention as molecular capsules to recognize and separate target molecules or ions.¹⁻¹⁶ Many metal complexes provide various cage frameworks. Coordination bonds between metal ions and organic bridging ligands generally construct these frameworks. When the cages are constructed by metal ions and neutral organic bridging ligands, the obtained coordination cages have positive charges, which are useful for the trapping of anions.¹⁷

Flexible bis-imidazole- and bis-benzimidazole-type neutral ligands, designated as L^{B} , have yielded many cage-type coordination compounds such as $\text{M}_2\text{L}^{\text{B}}_4$,^{5, 18-23} $\text{M}_2\text{L}^{\text{B}}_3$,⁵ $\text{M}_3\text{L}^{\text{B}}_4$,^{24, 25} and $\text{M}_4(\mu\text{-OR})_4\text{L}^{\text{B}}_4$ frameworks.²⁶ Among them, the $\text{M}_2\text{L}^{\text{B}}_4$ cages have generally been isolated with an anion trapped in the cationic cages. The following bridging ligands have often been used for the synthesis of $\text{M}^{\text{II}}_2\text{L}^{\text{B}}_4$ cage-type compounds: 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (*m*-bbitrb), 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (*p*-bbiteb), 1,3-bis(imidazol-1-ylmethyl)-2,4,6-tetramethylbenzene (*m*-bitrb), and 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (*p*-biteb) (Scheme 1).



Scheme 1. Ligand structures.

The perchlorate ion (ClO_4^-) is highly toxic, particularly in infants and children, because ingestion of this anion disturbs the uptake of iodine by the thyroid gland, inhibiting the formation of growth hormone.²⁷⁻²⁹ Nevertheless, this anion has often been detected, worldwide, in environmental water, agricultural products, and tap water used for drinking.²⁹⁻³³ Therefore,

the development of methods for ClO_4^- removal from aqueous solutions constitutes an important subject in the field of host–guest chemistry as well as in environmental science.³⁴

The host materials that capture the target anions selectively are known as anion hosts. Their host frameworks usually recognize the target anions by forming hydrogen bonds and/or coordination bonds with the target anions.¹⁷ However, recognition of ClO_4^- by anion hosts is quite difficult because of the remarkably low ability of this anion to form chemical bonds.³⁵

Previously, we investigated ClO_4^- removal methods by using cationic $\text{Cu}^{\text{II}}_2\text{L}^{\text{B}}_4$ cages.^{21–23, 36} We have shown, for example, that ClO_4^- is removed from aqueous solutions preferentially by formation of the water-insoluble cage-type compound $[\text{ClO}_4 \subset \text{Cu}_2(p\text{-biteb})_4(\text{ClO}_4)_2]\text{ClO}_4$.²¹ We also found that the water-insoluble $\text{M}_2\text{L}^{\text{B}}_4$ -type compound $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{SO}_4$ (**2c**) removes ClO_4^- from aqueous solutions by anion-exchange reactions. In this treatment, the SO_4^{2-} in the cage remains after the reactions.²³ **More recently, we have shown that 2D coordination polymers bearing cationic $\text{Cu}^{\text{II}}_2\text{L}^{\text{B}}_4$ cages on the 2D framework remove ClO_4^- preferentially by anion-exchange reactions.**³⁶ These previous studies have shown that the water-insoluble cationic $\text{M}_2\text{L}^{\text{B}}_4$ cages are useful cationic units for the removal of ClO_4^- .

In this work, we have synthesized four new $\text{M}_2\text{L}^{\text{B}}_4$ cage-type compounds $[\text{A} \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{A}_3$ ($\text{A} = \text{Cl}$ (**1a**), Br (**1b**)) and $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{A}_2$ ($\text{A} = \text{Cl}$ (**2a**), Br (**2b**)), and characterized the removal of ClO_4^- from aqueous solutions. The effect of solvent on the affinity of the cationic cage $[\text{Cu}_2(m\text{-bbitrb})_4]^{4+}$ for ClO_4^- was also investigated during the study of the ClO_4^- removal process by the $\text{M}_2\text{L}^{\text{B}}_4$ -type cage. This paper describes the syntheses, structures, and the anion-inclusion properties of the $[\text{Cu}^{\text{II}}_2(m\text{-bbitrb})_4]^{4+}$ cages.

Experimental

General. All chemicals and organic solvents were purchased from commercial sources and used without further purification. The ligand *m*-bbitrb was prepared according to a literature method. Compounds $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2](\text{ClO}_4)$,⁵ **2c**,²³ and **2d**²³ were prepared according to previously reported methods. IR spectra were recorded on a Shimadzu IR Affinity-1 FT-IR spectrophotometer, using KBr pellets. Solid-state reflectance spectra and absorption spectra were recorded on a Jasco V-570 spectrophotometer. Elemental analyses were measured using a Euro Vector EA3000 elemental analyzer. The electrospray ionization time-of-flight (ESI-TOF) mass spectra were recorded on a Jeol JMS-T100LP mass spectrometer, using a positive-mode ESI-TOF method. Samples were eluted with a mobile phase comprising MeCN or MeCN/ H_2O mixed solvent (MeCN/ H_2O).

Caution: Although we experienced no difficulties while working with the perchlorate salts, they should be regarded as potentially explosive and handled with care.

Synthesis of $[\text{Cl} \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{H}_2\text{O})_2]\text{Cl}_3$ (1a). An aqueous solution (10 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (25.6 mg, 0.15 mmol) was mixed with an EtOH solution (10 mL) of *m*-bbitrb (114.1 mg, 0.30 mmol). The solution was left to stand without stirring for two weeks. This yielded blue crystals. One of the crystals was used for the X-ray crystal structure determination study; the residual crystals were used for other measurements. Yield: 103 mg (75.3%). Anal. Calcd for $\text{C}_{100}\text{H}_{100}\text{Cl}_4\text{Cu}_2\text{N}_{16}\text{O}_2$: C, 65.74; H, 5.52; N, 12.27. Found: C, 65.72; H, 5.30; N, 12.16. IR (KBr, cm^{-1}): 3410 (m), 3119 (w), 3059 (w), 3017 (w), 2993 (w), 2920 (w), 1614 (s), 1591 (w), (s), 1481 (s), 1464 (s), 1394 (m), 1329 (m), 1294 (m), 1254 (m), 1233 (s), 1200 (w), 1184 (w), 1126 (w), 1092 (w), 1036 (m), 1011 (m), 920 (m), 889 (w), 841 (m), 750 (s), 691 (w), 646 (w), 623 (m), 604 (m), 511 (m), 461 (m).

Synthesis of $[\text{Br} \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{H}_2\text{O})_2]\text{Br}_3$ (1b). An EtOH solution (30 mL) of *m*-bbitrb (110 mg, 0.30 mmol) was slowly added to an aqueous solution (30 mL) of CuBr_2 (33 mg, 0.15 mmol) and left to stand for a few weeks. This yielded blue-plate crystals. One of the crystals was used for the X-ray crystal structure determination study; the residual crystals were used for other measurements. Yield: 116 mg (78.8%). Anal. Calcd for $\text{C}_{100}\text{H}_{96}\text{Br}_4\text{Cu}_2\text{N}_{16}$: C, 61.01; H, 4.92; N, 11.38. Found: C, 61.02; H, 4.60; N, 11.40. IR (KBr, cm^{-1}): 3356 (w), 2970 (w), 2908 (w), 1612 (m), 1517 (s), 1479 (s), 1462 (s), 1398 (m), 1327 (w), 1292 (m), 1232 (s), 1195 (m), 1182 (m), 1012 (w), 921 (w), 576 (w), 480 (w), 428 (w).

Synthesis of $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (2a). An EtOH solution (20 mL) of *m*-bbitrb (110 mg, 0.30 mmol) was mixed with an aqueous solution (30 mL) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (37.5 mg, 0.15 mmol) and an EtOH/ H_2O (1/1; v/v) solution (30 mL) of NaCl (8.0 mg, 0.15 mmol). The solution was left to stand without stirring for two weeks. This yielded blue-block crystals. Yield: 91.2 mg (68.1%). Anal. Calcd for $\text{C}_{100}\text{H}_{98}\text{Cl}_2\text{Cu}_2\text{N}_{16}\text{O}_5\text{S}$: C, 65.49; H, 5.39; N, 12.22. Found: C, 65.56; H, 5.19; N, 12.34. IR (KBr, cm^{-1}): 3342 (w), 3064 (w), 2972 (w), 1612 (w), 1516 (w), 1463 (s), 1402 (m), 1388 (w), 1296 (m), 1236 (w), 1203 (m), 1138 (m), 1107 (m), 1083 (m), 1043 (m), 1010 (w), 920 (w), 744 (s), 611 (w), 480 (w), 418 (m).

Synthesis of $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{Br}_2 \cdot \text{H}_2\text{O}$ (2b). An EtOH solution (20 mL) of *m*-bbitrb (114 mg, 0.30 mmol) was added to an aqueous solution (20 mL) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (37.5 mg, 0.15 mmol) and an EtOH/ H_2O solution of NaBr (15.4 mg, 0.15 mmol). The resulting mixture was left to stand at room temperature for several days. This yielded blue-block crystals (100 mg, 69.5%). Anal. Calcd for $\text{C}_{100}\text{H}_{98}\text{Cu}_2\text{Br}_2\text{N}_{16}\text{O}_5\text{S}$: C, 62.46; H, 5.14; N, 11.65. Found: C, 62.44; H, 5.13; N, 11.17. IR (KBr, cm^{-1}): 3375 (w), 3053 (m), 3018 (m), 2968 (w), 2954 (w), 1614 (w), 1514 (s), 1465 (s), 1402 (m), 1330 (w), 1298 (m), 1236 (m), 1215 (m), 1186 (w), 1143 (m), 1105 (m), 1083 (w), 1053 (s), 1012 (w), 920 (m), 763 (m), 742 (s), 615 (w), 476 (w), 428 (w). This compound was also obtained by treatment of **2c** with excess NaBr. An EtOH solution (20 mL) of **2c** (199 mg, 0.10 mmol) and an aqueous solution (20 mL) of NaBr (206 mg,

2.00 mmol) were mixed. The solution was exposed to the air to allow slow evaporation. Within a week, blue-plate crystals were obtained (133 mg, 69.4%). Identification of this compound was carried out by determination of the cell parameters: tetragonal, $a = b = 16.920$ (5) Å, $c = 32.49$ (1) Å, $V = 9301.9$ (4) Å³.

Crystal structure determination. A single crystal of each compound was sealed in a glass capillary with its mother liquid. Data collection was carried out on a Rigaku CCD Mercury system fitted with a monochromatic MoK α radiation source ($\lambda = 0.71069$ Å). Data from the X-ray measurements are summarized in Table 1. Eighteen preliminary data frames were measured at 0.5° increments of ω to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω . The intensity images were integrated using the CrystalClear program package, and the empirical absorption correction was applied for the data. The structures were solved by direct methods, SHELX-97, and refined using the SHELXL-97 (**1a**, **1b**, and **2b**) or SHELXL2013 (**2a**) programs. The crystallographic parameters are summarized in Table 1.

Anion removal experiments. For the ClO₄[−] removal from an aqueous solution experiment, an aqueous solution of ClO₄[−] (1.0 mM) was prepared by dissolving NaClO₄ (30.6 mg, 0.25 mmol) in ultrapure water (250 mL). A 100 mL volume of this solution was transferred to another vessel containing 0.1 mmol of the cage-type compound. The vessel was capped with a rubber septum and then shaken (100 rpm) in a water bath at 30 °C. Changes in the concentrations of the anions in the solution over time were monitored by ion chromatography analysis of the solution. Samples for analysis were prepared by dilution of 200 μL aliquots of the reaction solution into 4800 μL of the ultrapure water. Concentrations of the anions in the aqueous solutions were determined using a Metrohm Compact IC 861 ion chromatography instrument. Other anion removal experiments were carried out using a similar procedure.

Table 1. Crystallographic data for **1a**, **1b**, **2a**, and **2b**

complexes	1a	1b	2a	2b
formula	C ₁₀₀ H ₁₀₀ Cl ₄ Cu ₂ N ₁₆ O ₂	C ₁₀₀ H ₁₀₀ Br ₄ Cu ₂ N ₁₆ O ₂	C ₁₀₀ H ₉₈ Cl ₂ Cu ₂ N ₁₆ O ₅ S	C ₁₀₀ H ₉₈ Br ₂ Cu ₂ N ₁₆ O ₅ S
fw	1826.90	2004.70	1834.04	1922.94
lattice	tetragonal	tetragonal	tetragonal	tetragonal
space group	<i>I4/m</i> (No. 87)	<i>I4/m</i> (No. 87)	<i>P4/ncc</i> (No. 130)	<i>P4/ncc</i> (No. 130)
<i>a</i> , Å	15.2312(8)	15.3248(10)	16.689(4)	16.918(2)
<i>c</i> , Å	23.338(2)	23.354(3)	32.737(8)	32.534(5)
<i>V</i> , Å ³	5414.2(7)	5484.6(8)	9118(4)	9312(2)
<i>Z</i>	2	2	4	4
ρ (calcd) g cm ⁻³	1.121	1.214	1.336	1.372
μ (MoK α), mm ⁻¹	0.542	1.899	1.836	1.402
radiation (λ , Å)	0.71069	0.71069	0.71069	0.71069
temp, °C	25	25	25	25
reflns collected	20493	16804	57180	66405
unique reflns	2556	2398	4361	5355
<i>R</i> _{int}	0.0701	0.0805	0.1974	0.1271
param refined	175	172	295	304
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0783	0.0933	0.1463	0.0974
w <i>R</i> ₂ [all data]	0.0829	0.1855	0.3398	0.1442
GOF on <i>F</i> ²	1.051	1.180	1.387	1.018

Results and discussion

Syntheses and structures of 1a and 1b. Compounds **1a** and **1b** were conveniently prepared by the reaction of CuCl₂·2H₂O or CuBr₂ with *m*-bbitr_b. Figure 1 shows the molecular structure of **1a**. The crystallographic C₄ axis runs through the two Cu^{II} centers in the cage framework, and the crystallographic mirror exists in the equatorial plane of the cage. Two Cu^{II} ions are connected by four *m*-bbitr_b to yield the cationic Cu^{II}₂L^B₄ cage, which is similar to the cages of the M₂L^B₄-type compounds previously reported. Compound **1a** incorporates a Cl⁻ inside the cage and has three Cl⁻ outside the cage. The Cl⁻ in the cage is disordered at the six positions, namely, the four crystallographically equivalent positions for Cl(1A) and the two crystallographically equivalent positions for Cl(1B). The occupancies of the Cl(1A) and Cl(1B) were refined as 0.2 and 0.1, respectively. The Cl(1A) associates with the imidazole hydrogen atom (Cl(1A)⋯H(1) = ca. 2.77 Å) as illustrated in Figure 1b. Although Cl(1B) is located at the axial site of the Cu(1) environment (Figure 1a and 1b), the interaction with Cu(1) is weak

(Cu(1)---Cl(1B) = 2.97 (3) Å).

For the coordination circumstance around the Cu^{II} center, a H₂O molecule outside the cage associates with the metal center (Cu(1)---O(1) = 2.637 (5) Å) (Figure S1a). This distance is significantly shorter than the Cu(1)---Cl(1B) distance, but longer than the Cu—N bond distances (Cu(1)—N(1) = 2.002 (4) Å), giving the distorted square pyramidal or elongated octahedral geometry around the Cu^{II} center. One of the counter anions (Cl(2)) located outside the cage is disordered at the four positions by the crystallographic C₄ axis. This anion, whose occupancy was refined as 0.25, bonds with a H₂O molecule (O(1)) by hydrogen bonding (Cl(2)···O(1) = 3.113 (12) Å). The other counter anions are located between the cationic cages and have no significant interactions with the cage.

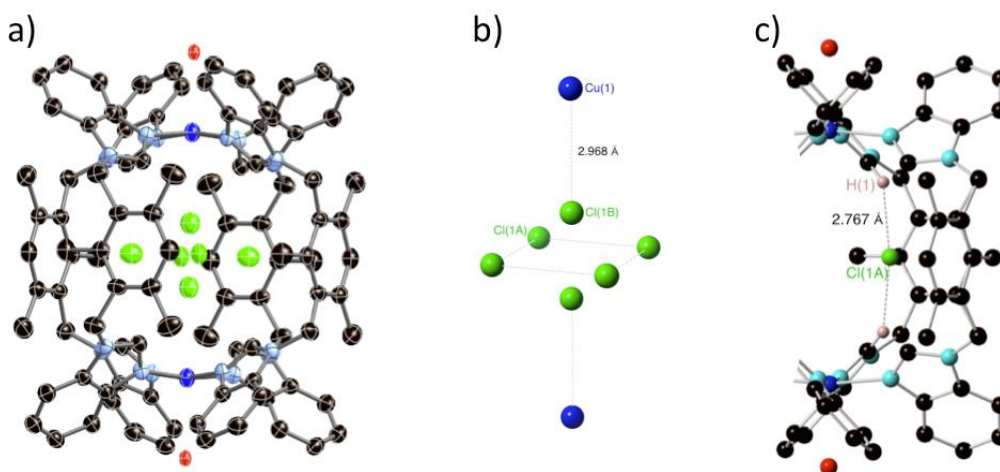


Figure 1. Thermal ellipsoids of the molecular structure of the cationic part of **1a** at 30% probabilities (a), view of the arrangement of the disordered Cl[−] in the cage (b), and Cl[−]···H–C interactions for Cl(1A) with an imidazole hydrogen atom (c). Hydrogen atoms, except for H(1) in (c), are omitted for clarity. Color code: blue, copper; red, oxygen; green, chlorine; cyan, nitrogen; black, carbon.

Compound **1b** crystallized with similar cell parameters and the same tetragonal space group (*I4/m*, # 87) as **1a**. Although **1b** has a similar structure to that of **1a**, the anion disorder inside the cage is significantly different. Figure 2 shows the molecular structure of **1b**. This compound also has the crystallographic C₄ axis that runs through the Cu(1) and Cu(2) atoms in the cage framework, and the crystallographic mirror in the equatorial plane of the cage. The cationic cage of **1b** contains a Br[−], which is disordered at the eight positions (four crystallographically equivalent positions for Br(1A) and four crystallographically equivalent positions for Br(1B)). The occupancies of the Br(1A) and Br(1B) were refined as 0.14 and 0.11,

respectively. The Br[−] in the eight disordered positions in the cage interacted with an imidazole hydrogen atom (Br(1A)⋯H(1) = ca. 2.80 Å, Br(1B)⋯H(1) = ca. 3.06 Å). In contrast to in **1a**, Br[−] was not observed in the axial position in the coordination environment of the Cu^{II} center in **1b**.

As observed in **1a**, a water molecule (O(1)) outside the cage associates weakly with the Cu^{II} center. The Cu⋯O bond distance (2.658 (10) Å) is close to that of **1a**, and significantly longer than that of Cu—N bonds (Cu(1)—N(1) = 1.992 (4) Å) in the coordination environment. The Cu^{II} center is based on the square pyramidal geometry due to the coordinations of four imidazole nitrogen atoms at the basal positions and a water molecule in the apical position. Similar to in **1a**, a Br[−] located outside the cage interacted with the water (Br(2A)⋯O(1) = 3.143 (9) Å) (Figure S1b). The Br(2A) is disordered at the four positions by the crystallographic C₄ axis, and was refined as 0.25. The other Br[−] was located between the Cu^{II}₂L^B₄ cages without significant interactions with the cationic cage.

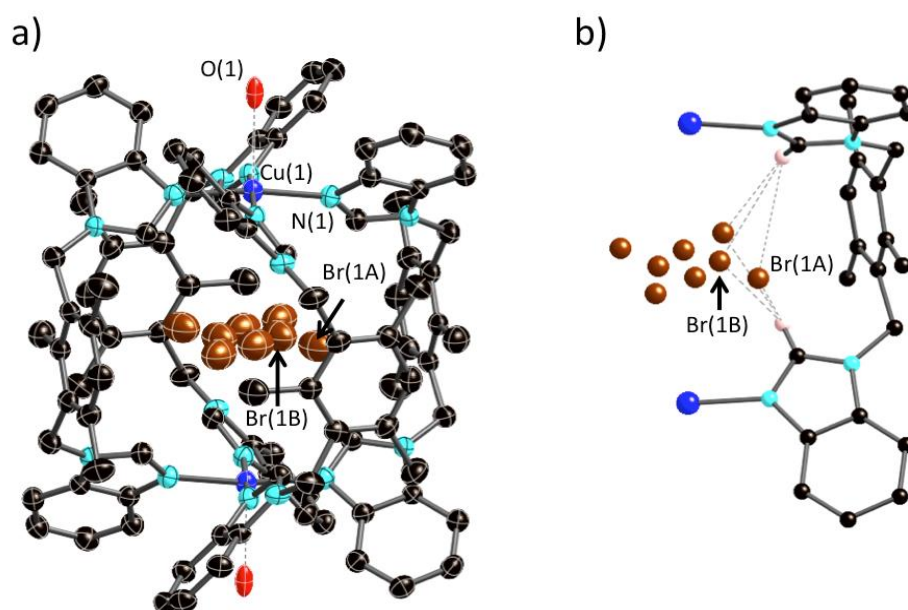


Figure 2. Thermal ellipsoids of the molecular structure of the cationic part of **1b** at 30% probabilities (a). View of the arrangement of disordered Br[−] in the cage, and Br[−]⋯H—C interactions for Br(1A) and Br(1B) (b). Hydrogen atoms, except for H(1) in (b), are omitted for clarity. Color code: blue, copper; red, oxygen; brown, bromine; cyan, nitrogen; black, carbon.

Syntheses and structures of 2a and 2b. Compounds **2a** and **2b** were obtained by the treatment of CuSO₄·5H₂O with *m*-bbitr_b and NaCl (**2a**) or NaBr (**2b**). Single-crystal X-ray diffraction studies and elemental analyses demonstrated that these two compounds are

constructed by the cationic part $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]^{2+}$ and the counter anions Cl^- or Br^- . These two compounds were isolated from an EtOH/H₂O (1/1; v/v) solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $m\text{-bbitrb}$, and the inorganic salt NaCl or NaBr. Results indicated that the space outside the cationic cage $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]^{2+}$ has higher affinity for Cl^- and Br^- than for SO_4^{2-} . Compounds **2a** and **2b** are crystallographically isostructural. As resolution of the structure of **2b** was of higher quality, we will use the structure of this compound for our description of the structure.

Figure 3 shows the molecular structure of **2b**, which crystallized in the tetragonal space group ($P4/ncc$, # 130). The crystallographic C₄ axis runs through the two Cu^{II} atoms in the cage framework and the two Cu^{II} ions are connected by four $m\text{-bbitrb}$. The obtained cationic cage incorporates a SO_4^{2-} , which is disordered by the imposed C₄ axis. The structure of this cationic part is essentially the same as in **2c** and **2d**.²³ The SO_4^{2-} in the cage is coordinated to the two Cu^{II} ions (Cu(1)—O(1) = 2.173(5), Cu(2)—O(2) = 2.164(5) Å). The two counter anions per one cationic cage (Br(1) and Br(2)) are included among the cationic cages. This compound also includes a water molecule, which is disordered at the two positions, among the cages. The water molecule was refined as 0.25 and 0.125 for O(5A) and O(5B). For the two Br⁻, Br(2) forms hydrogen bonds with the water molecule as shown in 3 (Br(2)⋯O(5A) = 3.43(4) Å and Br(2)⋯O(5B) = 3.17(4) Å).

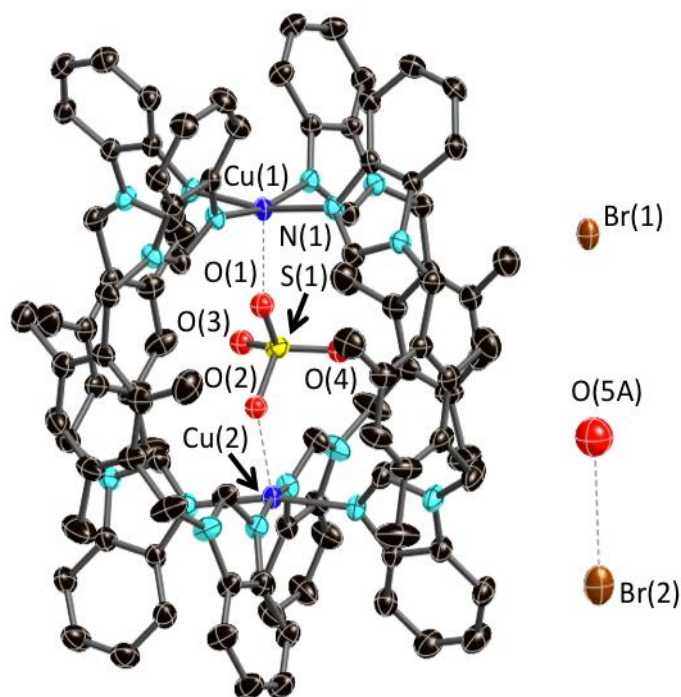


Figure 3. Thermal ellipsoids of the molecular structure of **2b** at 30% probabilities. Disorders of

SO_4^{2-} , disordered water molecules, and hydrogen atoms are omitted for clarity. Color code: blue, copper; yellow, sulfur; red, oxygen; cyan, nitrogen; black, carbon.

Perchlorate removal by 1a, 1b, 2a, and 2b. The four compounds prepared in this work (**1a**, **1b**, **2a**, and **2b**) are insoluble in water. Perchlorate removal from aqueous solutions by the four compounds was studied. Figure 4 shows the change in concentration of ClO_4^- (1.0 mM) in aqueous solutions (100 mL) of NaClO_4 (0.10 mmol) after the addition of well-ground powder samples of each of the compounds (0.10 mmol). The change in the concentration of the anions in each of the solutions was determined by ion chromatography. The figure clearly shows that all the compounds reduced the concentration of ClO_4^- in aqueous solution significantly and that the compounds had comparable activities. For all treatments, the release of Cl^- (**1a**, **2a**) or Br^- (**1b**, **2b**) was observed in response to the removal of ClO_4^- (Figure 4). In the experiments, the concentrations of ClO_4^- at 180 min were 0.30 mM, 0.32 mM, and 0.38 mM for **1b**, **2a**, and **2b**, respectively. Although their activity would be affected by the particle size, compound **1a** had the highest activity for ClO_4^- removal among the four compounds investigated. In the experiment, the concentration of Cl^- (Cl^- was not included in the initial solution) was observed at 10 min (0.37 mM), and then increased to 0.83 mM at 180 min. For example, in the case of **1a**, 1.0 mM of ClO_4^- was reduced to 0.44 mM at 30 min and then to 0.27 mM at 180 min. These results indicated that the obtained cage compounds removed ClO_4^- by anion-exchange reactions.

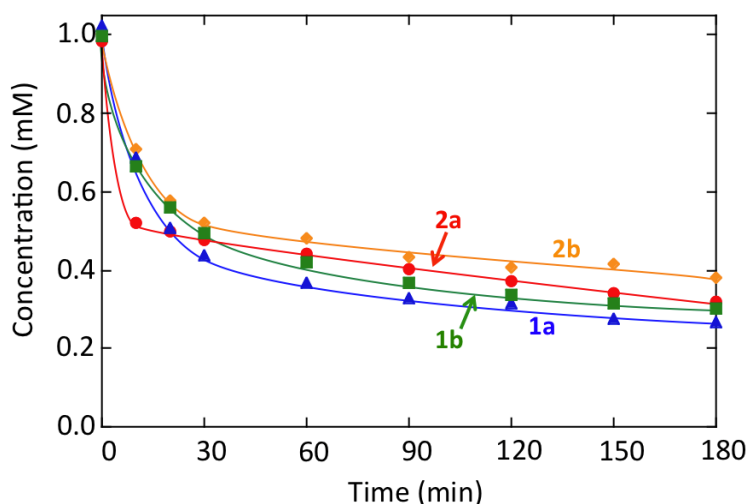


Figure 4. Change in concentrations of ClO_4^- over time in aqueous solutions (100 mL) after addition of each of the cage compounds (0.1 mmol). Color code: **1a** (blue), **1b** (green), **2a** (red), and **2b** (orange).

We also studied the anion removal selectivity of **1a** in aqueous solutions. Figure 5

shows changes in the concentrations of anions depending on the time after addition of **1a** (0.10 mmol) in aqueous solutions (100 mL) containing NaF, NaCl, NaBr, NaNO₃, NaClO₄, and Na₂SO₄ (all 1.0 mM). The ClO₄⁻ was removed preferentially; it was reduced from 1.0 mM to 0.63 mM at 30 min and then to 0.41 mM at 180 min. The other anions, NO₃⁻, NO₂⁻, and Br⁻, were also significantly reduced, from 1.00 mM to 0.79 mM, 0.88 mM, and 0.93 mM, respectively, at 180 min. Concentrations of F⁻ and SO₄²⁻ were essentially not reduced. The concentration of Cl⁻ increased from 1.00 mM to 2.10 mM at 180 min due to the release from **1a** by exchange with the anions removed. The total amount of anions reduced from the aqueous solutions was about 0.10 mmol. This value is close to the amount of Cl⁻ released (0.11 mmol). **Compound 1b** showed similar anion removal selectivity to that of **1a** (Figure S3 in ESI). The removal selectivity of **1a** and **1b** is similar to that of **2c**: ClO₄⁻ > NO₃⁻ > Br⁻ > F⁻.

Although **2a**, **2b**, and **2c** have the same cationic part [SO₄ ⊂ Cu₂(*m*-bbitr_b)₄]²⁺, their ClO₄⁻ removal activity differs. Compound **2c** showed remarkably high activity. This result indicated that the ClO₄⁻ removal activity is affected by the types of counter anions that are exchanged with ClO₄⁻. As the anion removal reaction proceeds under heterogeneous conditions, the SO₄²⁻, being larger in size than Cl⁻ or Br⁻, would provide more space for the incorporation of ClO₄⁻.

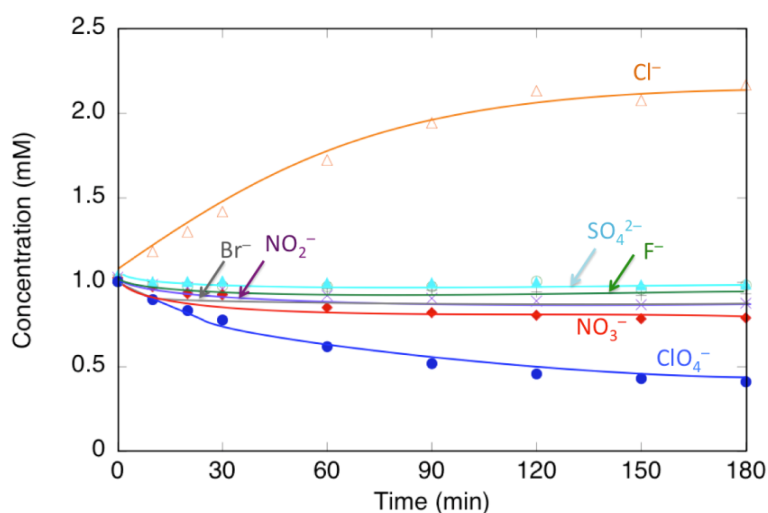


Figure 5. Change in concentrations of anions over time in aqueous solutions (100 mL) containing NaF, NaCl, NaBr, NaNO₃, NaClO₄, and Na₂SO₄ (all 0.1 mmol) after the addition of **1a** (0.1 mmol). Color code: orange, Cl⁻; cyan, SO₄²⁻; green, F⁻; purple, NO₂⁻; gray, Br⁻; red, NO₃⁻; blue, ClO₄⁻.

Exchange of anions inside and outside the cage. Our previous works and this work show that cationic M₂L^B₄ cage-type compounds remove ClO₄⁻ preferentially from aqueous

solutions by incorporating the anion inside the cage, or including anion among the cationic cages. To study the affinity of the space created by the cationic cage $[\text{Cu}_2(m\text{-bbitrb})_4]^{4+}$ toward anions, we studied the exchange of SO_4^{2-} inside the cage, with ClO_4^- located outside the cage, using **2d**. Figure 6 shows the following for **2d** and $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2]\text{ClO}_4$: (a) solid-state reflectance spectra, and (b and c) absorption spectra in MeCN and MeCN/H₂O.

In Figure 6a, **2d** and $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2]\text{ClO}_4$ exhibit d–d absorptions in the solid state at $\lambda_{\text{max}} = 628$ and 568 nm, respectively. The Cu^{II} center of $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2]\text{ClO}_4$ is based on the elongated octahedral geometry with four imidazole nitrogen atoms at the equatorial positions and two oxygen atoms of ClO_4^- at the axial positions. The higher d–d absorption energy of this compound is the result of the increased $d_{x^2-y^2}$ orbital due to the weak crystal field of ClO_4^- .

The λ_{max} of $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2]\text{ClO}_4$ was observed at 573 nm in MeCN and MeCN/H₂O (Figure 6b and 6c). Here, the d–d absorption shifted 5 nm to a longer wavelength compared with that in the solid-state spectrum (568 nm), and the λ_{max} is quite different to that of **2d**, which exhibited a $\lambda_{\text{max}} = 629$ nm. This indicates that ClO_4^- is retained in the $[\text{Cu}^{\text{II}}_2(m\text{-bbitrb})_4]^{4+}$ cage in MeCN and in MeCN/H₂O.

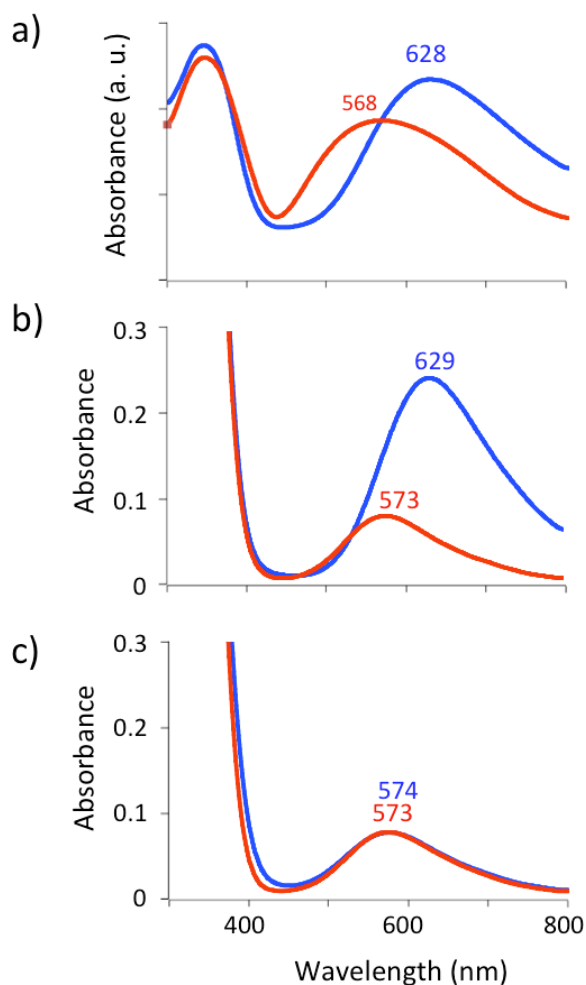
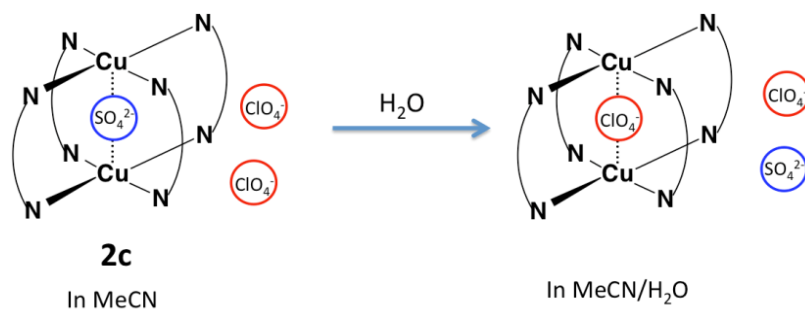


Figure 6. Solid-state reflectance spectra (a) and absorption spectra in MeCN (1.0 mM) (b) and MeCN/H₂O (v/v; 1/1) (1.0 mM) (c) for **2d** (blue) and [ClO₄ ⊂ Cu₂(*m*-bbitrb)₄(ClO₄)₂]ClO₄ (red).

For **2d**, the λ_{max} of the spectrum in MeCN solution (629 nm, Figure 6b) is similar to that of the solid-state reflectance spectrum; yet, when measured in MeCN/H₂O, the λ_{max} is remarkably shifted to a shorter wavelength (574 nm, Figure 6c). Figure 6c shows that the spectrum of **2d** in MeCN/H₂O is quite similar to that of [ClO₄ ⊂ Cu₂(*m*-bbitrb)₄(ClO₄)₂]ClO₄. This result indicated that SO₄²⁻ in the [Cu₂(*m*-bbitrb)₄]⁴⁺ cage is not exchanged with ClO₄⁻ in MeCN, but is exchanged with the anion in MeCN/H₂O. This reaction is illustrated schematically in Scheme 2.



Scheme 2. Schematic illustration of the exchange of SO_4^{2-} inside the cage with ClO_4^- outside the cage in response to an increase in the hydrophilicity of the solution.

To confirm this anion-exchange reaction, we measured the ESI-TOF mass spectrum of **2d** in MeCN and MeCN/H₂O (Figure 7). In MeCN solution, **2d** showed two intense peaks, assigned to $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]^{2+}$ and $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_3]^{2+}$ at m/z 872.3 (Calcd 872.3) and m/z 682.2 (Calcd 682.2). In MeCN/H₂O, these two intense peaks were not observed; there were intense peaks at m/z 923.2 and m/z 582.5, assigned to $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)]^{2+}$ (Calcd 923.3) and $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]^{3+}$ (Calcd 582.5). These results are consistent with the anion-exchange reaction illustrated in Scheme 2, and proposed based on the results of the absorption spectra change mentioned above.

The space in the cationic cage is hydrophobic because it is surrounded by the hydrophobic ligands *m*-bbitrb. While ClO_4^- has a highly hydrophobic surface, SO_4^{2-} is a typical hydrophilic anion.²⁹ Despite the hydrophilicity of SO_4^{2-} , this anion is incorporated into the hydrophobic cage by forming coordination bonds to the two Cu^{II} centers. Although the solid-state structure of **2d** is retained in MeCN, an increase in hydrophilicity of the solution upon the addition of H₂O causes the exchange of ClO_4^- outside the cage, with the hydrophilic SO_4^{2-} inside the cage. This is because the hydrophobic ClO_4^- has a higher affinity in the hydrophobic space inside the cage than the hydrophilic space created by addition of H₂O outside the cage. In the solid state, or in MeCN solution, the spaces created inside and outside the $[\text{Cu}^{\text{II}}_2(m\text{-bbitrb})_4]^{4+}$ cage are both hydrophobic. Therefore, when the water-insoluble **2c** comes into contact with ClO_4^- in aqueous solution, ClO_4^- is incorporated into the hydrophobic space created among the cages, and then the hydrophilic SO_4^{2-} is released to the aqueous solution.

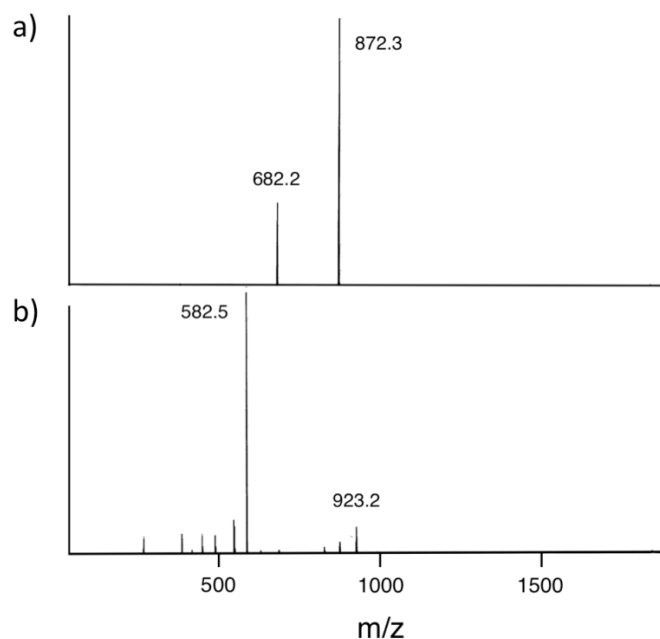


Figure 7. ESI-TOF mass spectra of **2d** measured in MeCN (a) and MeCN/H₂O (1:1, v/v) (b)).

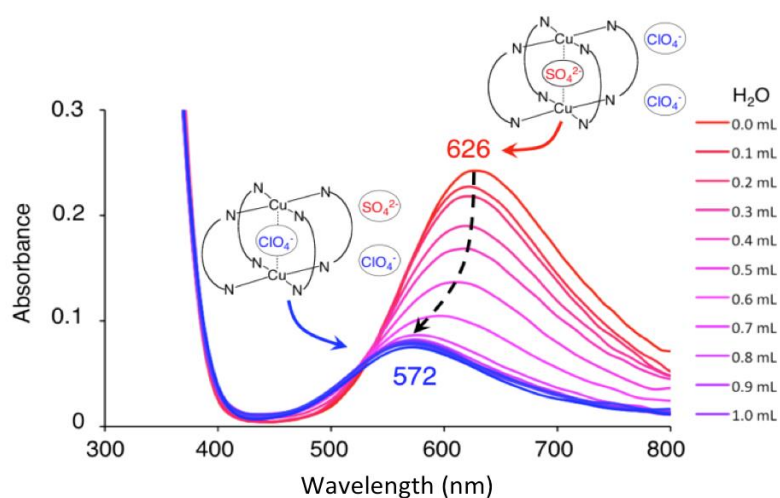


Figure 8. Absorption titration spectra of **2d** in MeCN (2.0 mL) upon sequential addition of 0.1 mL aliquots of water.

We also monitored changes in the absorption spectrum of a MeCN solution of **2d** after the sequential addition of aliquots (0.1 mL) of H₂O (see Figure 8). The intensity of absorption at $\lambda_{\text{max}} = 629 \text{ nm}$ was reduced; it gradually shifted to the higher energy region upon the addition of H₂O. Change in the absorption spectrum essentially ceased when 0.8 mL H₂O was added to 2.0 mL MeCN solution. The absorption spectrum finally obtained was consistent with that of $[\text{ClO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4(\text{ClO}_4)_2](\text{ClO}_4)$, indicating that the anions are exchanged fully when about 30%

H₂O was present in the MeCN solution.

Conclusions

In summary, we have synthesized and characterized four new Cu^{II}₂L^B₄-type compounds. Compounds **1a** and **1b** incorporate Cl[−] or Br[−] in the cationic cages, while **2a** and **2b** incorporate SO₄^{2−} in the cages. These four compounds contain Cl[−] or Br[−] as the counter anions outside the cage; they also exhibited ClO₄[−] removal activity from aqueous solutions by anion-exchange reactions. Compounds **1a** and **1b** exhibited preferential removal of ClO₄[−] from aqueous solutions. The effect of hydrophilicity of the solvent on the affinity of the [Cu^{II}₂(*m*-bbtrb)₄]⁴⁺ cage for the anions located inside and outside the cage was studied using **2d**. Results of absorption studies and ESI-TOF mass spectra for **2d** indicated that SO₄^{2−} inside the cage and ClO₄[−] outside the cage of **2d** were retained in MeCN, but exchanged in MeCN/H₂O. This is because an increase in the hydrophilicity of the solution promotes the incorporation of hydrophobic ClO₄[−] into the hydrophobic cage. Preferential removal of ClO₄[−] would be the result of the preferential inclusion of ClO₄[−] into the hydrophobic space created among the cages in the solid state.

Acknowledgements

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