

Supporting Information

Efficient Removal of Perchlorate Ion from Water by Water-insoluble M₂L₄ Type Compound

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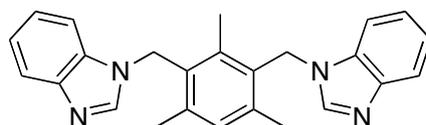
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1. General Information

All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. The water was used ion-exchanged water. ^1H (600.17 MHz), ^{13}C NMR (150.92 MHz) spectra were recorded on a Jeol ECA-600 spectrometer. Chemical shifts in CDCl_3 were reported in the scale relative to tetramethylsilane (0 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to CDCl_3 (77.0 ppm) as an internal reference, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, br = broadened). IR spectra were recorded on Shimadzu IRAffinity-1 using KBr pellets. UV/Vis absorption spectra were recorded on a Jasco V-570. Elemental analyses were measured using Euro Vector EA3000. ICP-MS was recorded on Varian VISTA – MPX. Optical Microscope Images were recorded on NIKON Eclipse E800. Concentrations of anions in the aqueous solutions were determined by Metrohm Compact IC 861 ion chromatography. Crystallographic data were collected by Rigaku CCD mercury system using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

2. Experimental

1,3-Bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (*m*-bbitrb) was prepared according to literature (See the reference 2c).

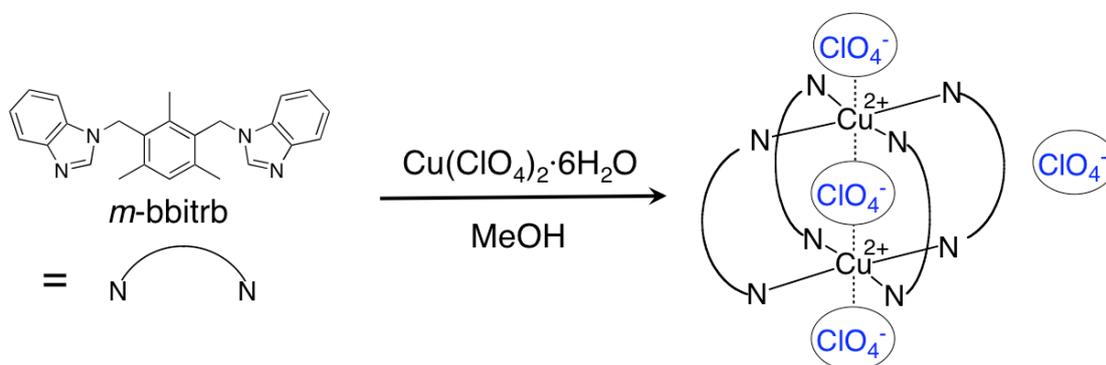


m-bbitrb

Scheme S1.

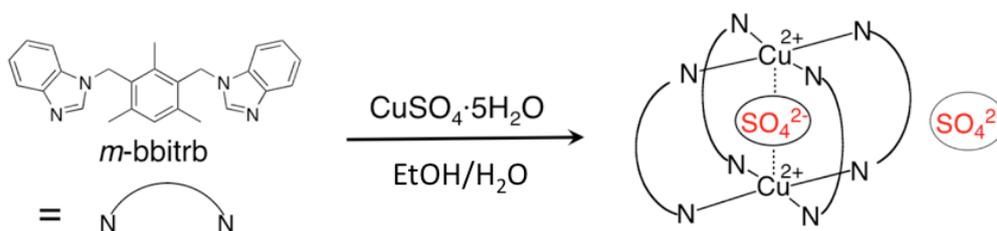
Synthesis of $[\text{ClO}_4 \subset \text{Cu}_2(\textit{m}\text{-bbitrb})_4(\text{ClO}_4)_2](\text{ClO}_4)$ (**2**).

$[\text{ClO}_4 \subset \text{Cu}_2(\textit{m}\text{-bbitrb})_4(\text{ClO}_4)_3]$ (**2**) was prepared according to literature (See the reference 1).



Scheme S2.

Synthesis of $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4]\text{SO}_4 \cdot 8\text{H}_2\text{O}$ (1-SO₄**).**

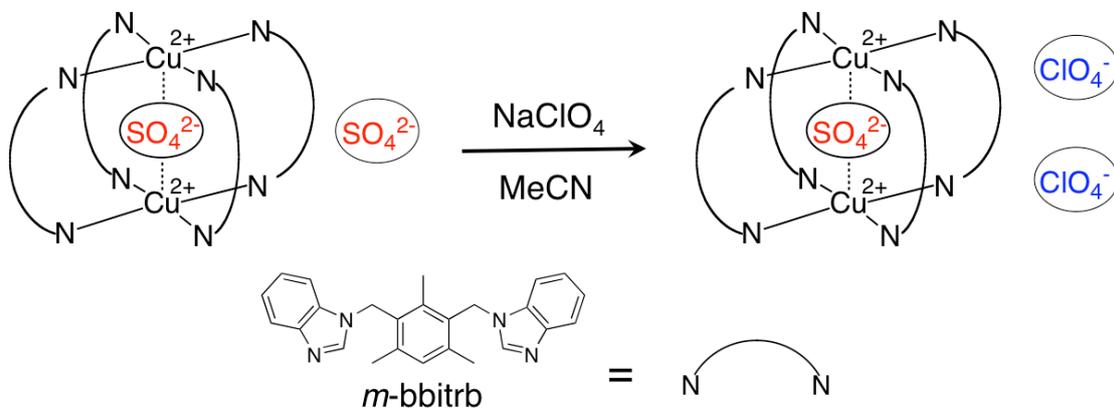


Scheme S3.

A ethanol (20.0 mL) solution of *m*-bbitrb (114 mg, 0.300 mmol) was added to a water (20.0 mL) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (37.5 mg, 0.150 mmol). The reaction mixture was left standing at room temperature for several days to give the blue block crystals (103 mg, 69.0 %). IR (KBr, cm^{-1}) 3628, 3387, 3066, 2974, 2918, 1647, 1616, 1517, 1481, 1465, 1402, 1328, 1315, 1298, 1238, 1215, 1182, 1105, 1083, 1055, 1012, 968, 921, 885, 848, 763, 746, 661, 611, 597, 574, 565, 530, 480, 460, 428; Anal. Calcd for $\text{C}_{100}\text{H}_{112}\text{Cu}_2\text{N}_{16}\text{O}_{16}\text{S}_2$ (1985.29): C, 60.50; H, 5.69; N, 11.29. Found: C, 60.87; H, 5.26; N, 11.37.

Microcrystal of **1-SO₄** was prepared by slow evaporation of an EtOH solution of **1-SO₄**. The identification was carried out by measurements of Elemental analysis and XRPD, IR, UV/Vis spectra.

Synthesis of $[\text{SO}_4 \subset \text{Cu}_2(m\text{-bbitrb})_4](\text{ClO}_4)_2 \cdot 4\text{MeCN}$ (1- ClO_4).



Scheme S4.

A water (100 mL) of NaClO₄ (730 mg, 5.96 mmol) was added **1-SO₄** (550 mg, 0.277 mmol). The reaction mixture was stirred at room temperature for 1 day. The reaction mixture was filtrated and washed water (3 × 30 mL). The blue crystals were obtained by recrystallization of blue powder from acetonitrile (340 mg, 58.2%). IR (KBr, cm⁻¹) 3385, 3064, 2972, 1614, 1517, 1481, 1465, 1402, 1298, 1238, 1105, 1085, 1049, 921, 879, 746, 621, 480, 399; Anal. Calcd for C₁₀₈H₁₀₈Cl₂Cu₂N₂₀O₁₂S (2108.20): C, 61.53; H, 5.16; N, 13.29. Found: C, 61.51; H, 4.69; N, 13.05.

3. Crystal Structures.

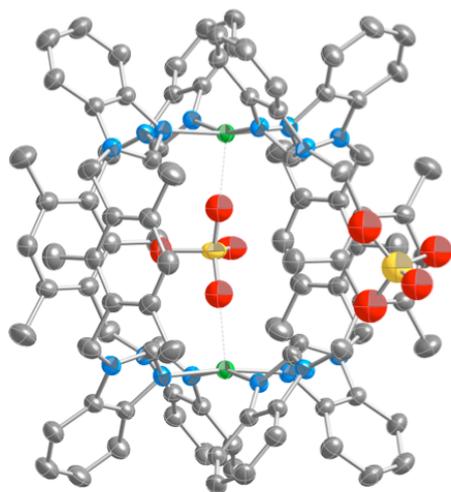
X-ray Diffraction Studies.

Single crystal of **1-SO₄** was sealed in a glass capillary with its mother liquid for X-ray diffraction analysis at room temperature, while single crystal of **1-CIO₄** was mounted on loop for X-ray diffraction analysis at 173 K. Data collections were carried out on a Rigaku CCD mercury system fitted with a monochromatic Mo *K* α radiation source ($\lambda = 0.71069$ Å). The summarized data of the X-ray measurements are given 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 (Rigaku), and the empirical absorption correction was applied for the data. The structures were solved by direct methods, SIR-92 program and refined using the SHELXL-97 tool.

Table S1. Crystallographic data for **1-SO₄** and **1-CIO₄**

compound	1-SO₄	1-CIO₄
formula	C ₁₀₀ H ₁₁₂ Cu ₂ N ₁₆ O ₁₆ S ₂	C ₁₀₈ H ₁₀₈ Cl ₂ Cu ₂ N ₂₀ O ₁₂ S
fw	1985.29	2108.23
lattice	monoclinic	triclinic
<i>a</i> , Å	19.508(15)	13.3355(11)
<i>b</i> , Å	22.484(19)	14.6602(11)
<i>c</i> , Å	13.377(12)	15.0833(10)
α , °		67.191(5)
β , °	126.072(7)	75.636(6)
γ , °		89.943(7)
<i>V</i> , Å ³	5164(8)	2618.2(4)
space group	<i>C</i> 2/ <i>m</i> (No. 12)	<i>P</i> -1 (No. 2)
<i>Z</i>	2	1
ρ (calcd), g cm ⁻³	1.277	1.337
μ (MoK α), mm ⁻¹	0.522	0.548
radiation (λ , Å)	0.7107	0.7107
temp, K	293	173
reflns collected	18816	22727
unique reflns	5880	9049
param refined	323	766
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0831	0.0871
<i>wR</i> ₂ [all data]	0.1826	0.1943
GOF	1.051	1.013

(side view)



(Top view)

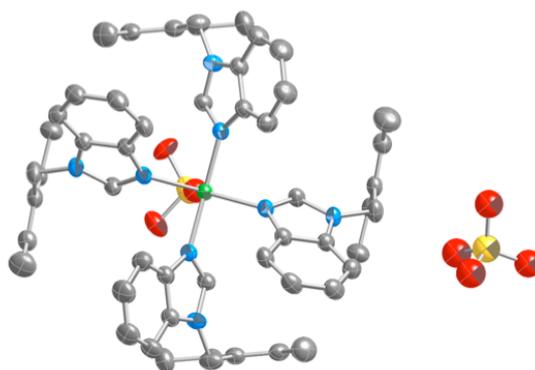


Figure S1. X-ray structure of **1-SO₄** represented by thermal ellipsoids of 30% probability. Hydrogen atoms, and solvents are omitted for clarity. Color code: green, copper; red, oxygen; yellow, sulfur; blue, nitrogen; gray, carbon. Although SO₄²⁻ in and outside the capsule are disordered, they are not shown for clarity.

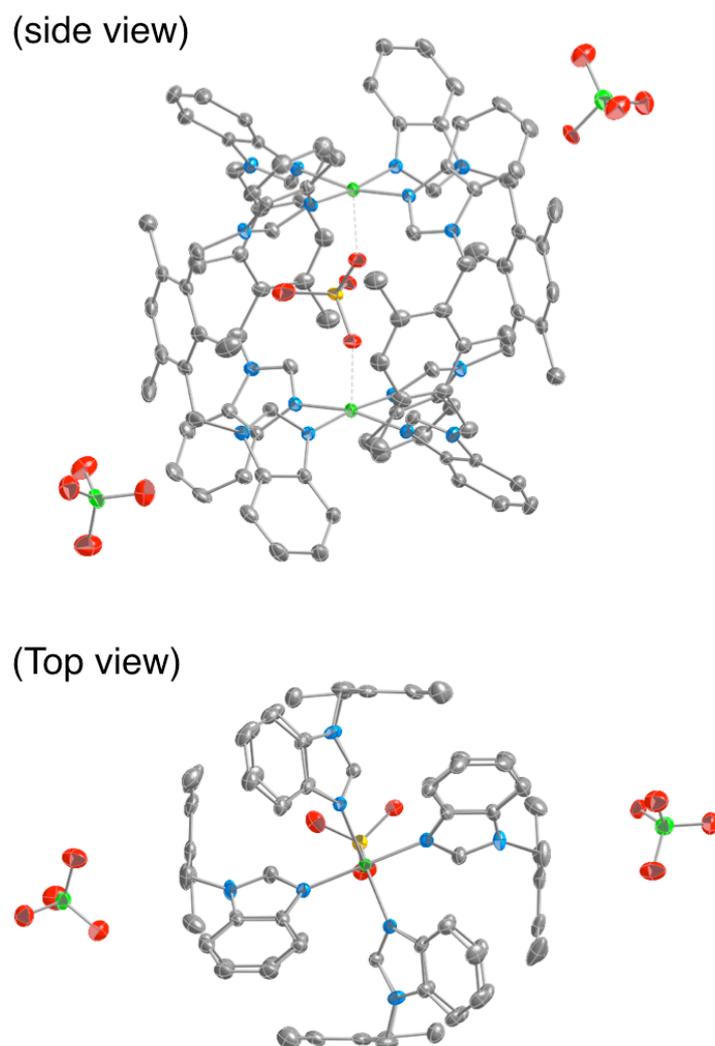


Figure S2. X-ray structure of **1-ClO₄** represented by thermal ellipsoids of 30% probability. Hydrogen atoms, and solvents are omitted for clarity. Although SO_4^{2-} in the capsule and ClO_4^- outside the capsule are disordered, they are not shown for clarity. Color code: green, copper; yellow green, chlorine; red, oxygen; yellow, sulfur; blue, nitrogen; gray, carbon.

4. X-ray Diffraction Powder Patterns of 1-SO₄.

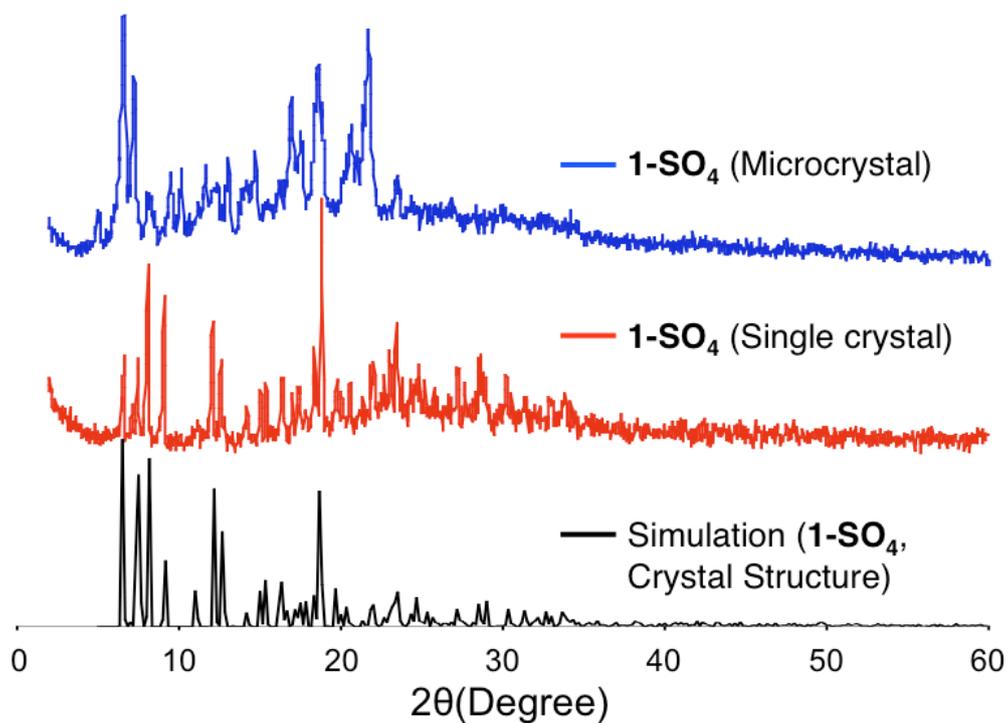


Figure S3. XRPD patterns of microcrystal: 1-SO₄ (blue), single crystal: 1-SO₄ (red), and simulation (black) based on the crystal structure.

5. IR Spectra.

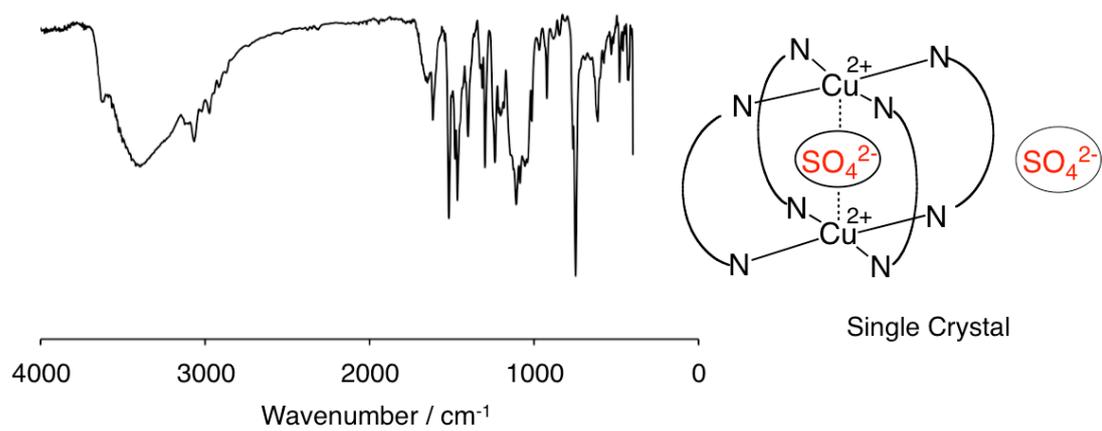


Figure S4. IR spectrum of 1-SO₄ (single crystal).

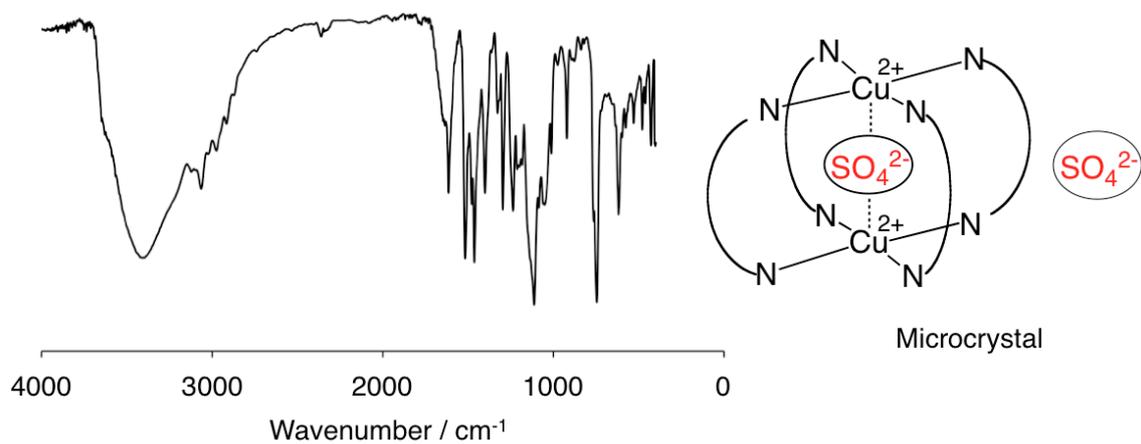


Figure S5. IR spectrum of 1-SO₄ (microcrystal).

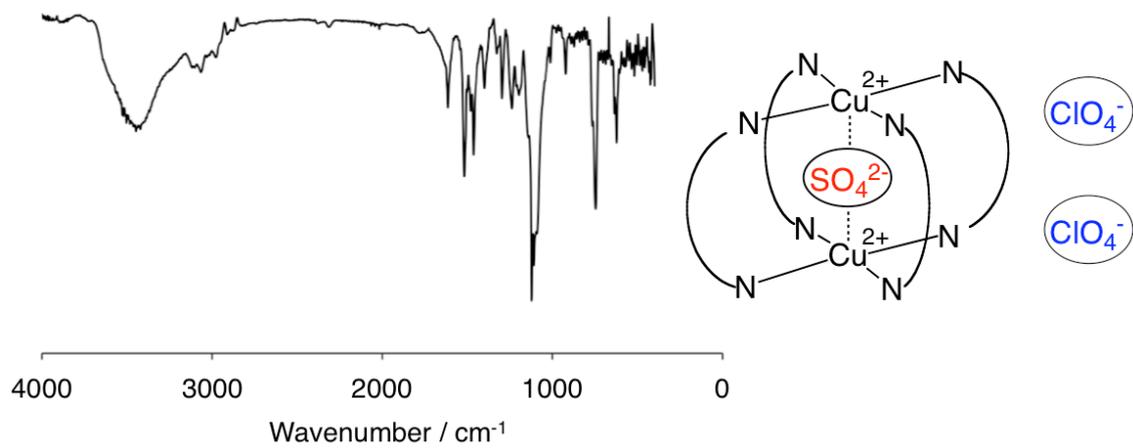


Figure S6. IR spectrum of **1-CuO₄**.

6. Anion Removal Experiments.

Removal by using 1-SO₄.

An aqueous solution which contained various anions (1.0 mM) was prepared by dissolution of NaClO₄ (61.2 mg, 0.500 mmol), NaBr (51.5 mg, 0.500 mmol), NaNO₃ (42.5 mg, 0.500 mmol), Na₂SO₄ (71.0 mg, 0.500 mmol) in an ultrapure water (500 mL). The 100 mL of the solution was moved to another vessel containing micro crystal of **1-SO₄** (199 mg, 0.100 mmol). The vessel was capped by using Septa Rubber, and set in water bath to keep the solution at 30°C. The vessel was shaken by 100 rpm. The changes of concentrations of anions in the solution depending on time were monitored by ion chromatography. The chart which shows the change of the concentration of anions is shown in manuscript (Figure 2a).

Removal by using Anion-Exchange Resin.

Anion removal experiment by anion-exchange resin (Purolite A530E, 199 mg) was carried out by similar procedure using **1-SO₄** mentioned above. The resin was used for the experiment by grinding and without grinding. The chart which shows the change of the concentration of anions is shown in manuscript (Figure 2b).

Removal by using Syringe Filter.

The micro crystal of **1-SO₄** (0.20 g, 0.10 mmol) was suspended in water (40 mL). The solution was moved to syringe, and then filtered by the commercially available syringe filter (ϕ 40 mm, 2 μ m pore size). The filter was dried under reduced pressure at room temperature for 24 hours. The photograph was shown in Figure S15. An aqueous solution (6 mL) of NaClO₄ (0.010 mM, ca. 1,000 ppb for ClO₄⁻) was passed through the filter by hand-pressure. The change of the concentration of ClO₄⁻ in the filtrate was determined by ion chromatography.



Figure S7. Photograph of prepared filter fixed with the micro crystal **1-SO₄** (left), and the syringe (right) attached with the filter.

Ion Chromatography Charts

Anion Removal by **1-SO₄** and Ground Anion-Exchange Resin

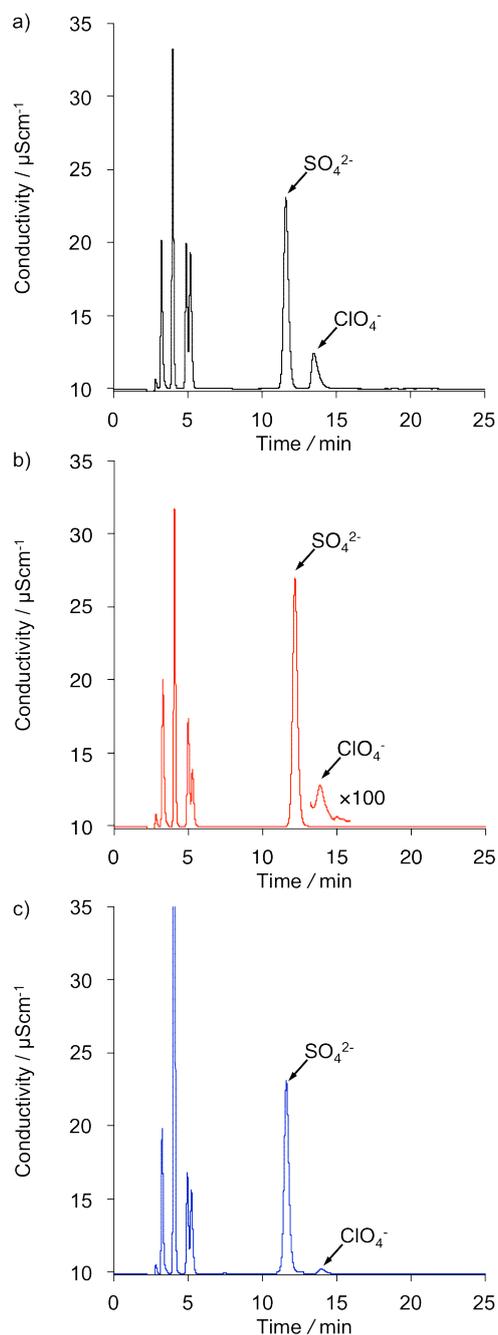


Figure S8. Ion chromatograph chart a) of an aqueous solution containing various salts in all 1 mM. Ion chromatograph chart when the solution was treated by the microcrystal of **1-SO₄** (199 mg, 0.100 mmol) b) for 180 min, and well-ground anion-exchange resin (199 mg) c) for 180 min.

Anion Removal by Anion-Exchange Resin without Grinding

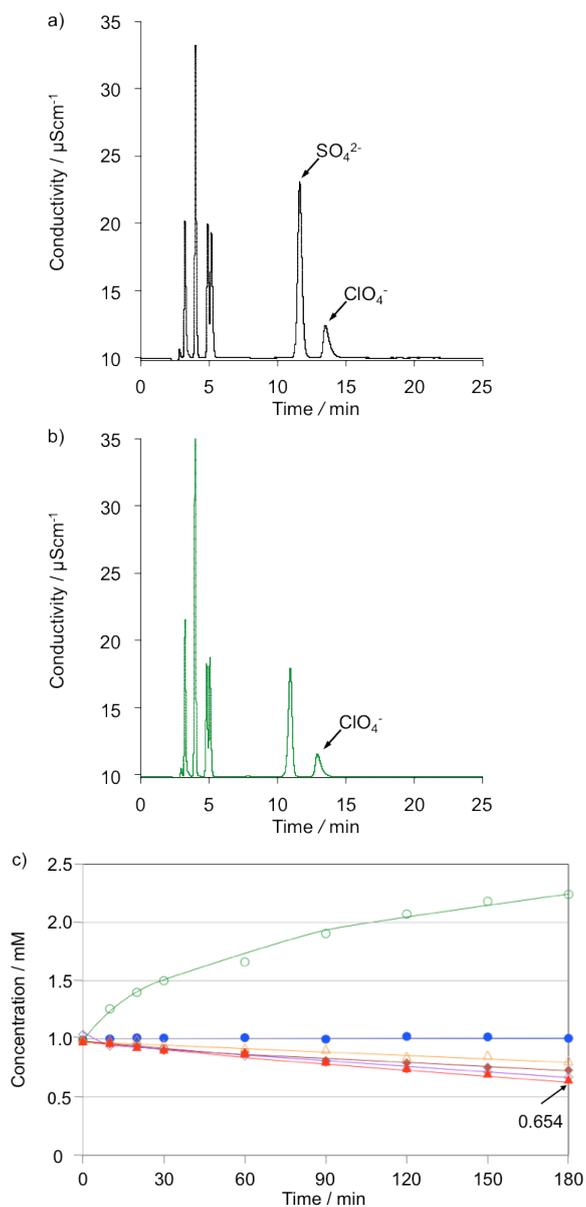


Figure S9. Ion chromatograph charts of an aqueous solution containing various salts before a) and after b) treatments by anion-exchange resin without grinding for 180 min. Plots of change of concentrations of anions in an aqueous solution containing F^- (blue), Cl^- (green), Br^- (brown), NO_3^- (purple), SO_4^{2-} (orange), ClO_4^- (red), after addition of anion-exchange resin without grinding c).

Anion Removal by Single Crystals of 1-SO_4

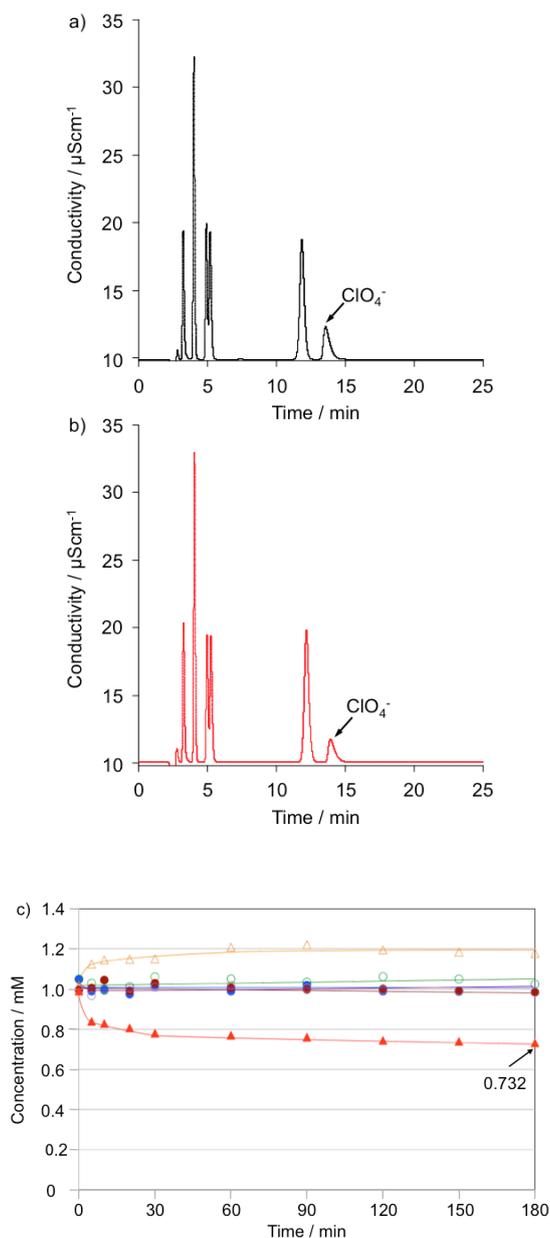


Figure S10. Ion chromatograph charts of an aqueous solution containing various salts before a) and after b) treatments by single crystals of 1-SO_4 for 180 min. Plots of change of concentrations of anions in an aqueous solution containing F^- (blue), Cl^- (green), Br^- (brown), NO_3^- (purple), SO_4^{2-} (orange), ClO_4^- (red), after addition of single crystalline sample of 1-SO_4 (c).

7. Optical Microscope Images of 1-SO₄.

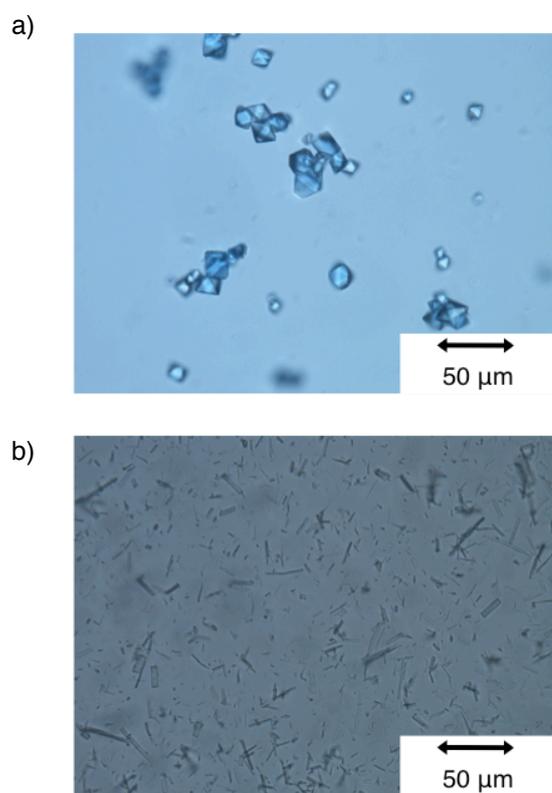
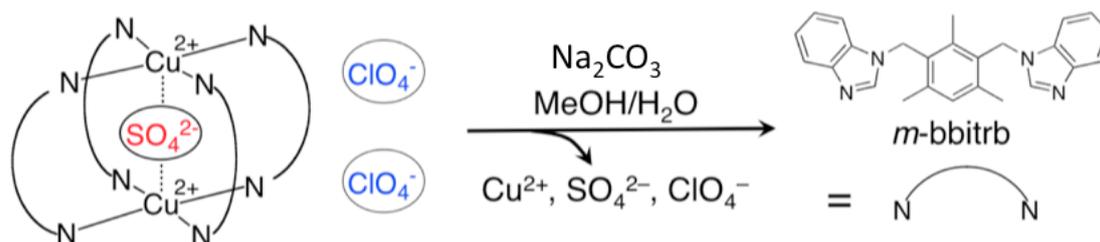


Figure S11. Optical Microscope Images of 1-SO₄: single crystals a) and microcrystal b).

8. Recovery of *m*-bbitrb after Anion Removal Experiment of 1-SO₄.



Scheme S5.

The powder obtained after anion removal experiment mentioned above was collected by filtration. The crude product was dissolved in MeOH (200 mL) and added water (10 mL) of Na₂CO₃ (8.23 g, 77.6 mmol). The reaction mixture was filtered and evaporated. The residual product was extracted with CH₂Cl₂ (200 mL). The white crystals were obtained by recrystallization from acetone/H₂O (80.5 mg, 52.9 %). ¹H NMR (600 MHz, CDCl₃) δ 7.82 (dd, 2H), 7.44 (m, 4H), 7.35-7.31 (m, 4H), 5.34 (s, 4H), 2.36 (s, 6H), 2.14 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) d 144.0, 141.5, 135.1, 134.0, 131.2, 123.0, 122.4, 120.4, 44.2, 16.5; Anal. Calcd for C₂₅H₂₄N₄ (380.48): C, 78.92; H, 6.36; N, 14.73 Found: C, 78.90; H, 6.43; N, 14.64.