Supporting Information

Self-assembled Construction of a Sheet-type Coordination Polymer Bearing Cationic M_2L_4 Cages: Creation of a Channel-like Space for Removal of ClO_4^- and NO_3^- from Aqueous Solutions

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1. Experimental

General information. All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. 1,4-Bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (*p*-bbiteb) was prepared according to the literature method.[1] IR spectra were recorded on Shimadzu IR Affinity-1 using KBr pellets. Solid state diffuse reflectance spectra were recorded on a Jasco V-570. Elemental analyses were measured using Euro Vector EA3000. ^{1}H (600.17 MHz) spectrum was recorded on a Jeol ECA-600 spectrometer. Chemical shifts in CD_3CN were reported in the scale relative to tetramethylsilane (0 ppm) as an internal reference, (multiplicities; s = singlet, dd = double doublet).

[1] Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Zhang, H.-X.; Kang, B.-S. *J. Chem. Soc., Dalton Trans.* **2001**, 359-361.

Synthesis of $[Cu(p\text{-bbiteb})_2(\text{-}\mu\text{-}Cl\text{-}[Cl\cdot(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4])]Cl_4\cdot(H_2O)_8\cdot MeCN$ (1). An aqueous solution (20 mL) of $CuCl_2\cdot 2H_2O$ (34 mg, 0.20 mmol) was mixed with an acetonitrile solution (20 mL) of *p*-bbiteb (158 mg, 0.40 mmol), and stood without stirring at room temperature for a few weeks, producing blue crystalline solid of **1** at 74% yield (49 mg, 0.049 mmol). Anal. Calcd. for $C_{158}H_{179}Cl_6Cu_3N_{25}O_{10}$: C, 63.43; H, 6.03; N, 11.70. Found: C, 63.31; H, 6.04; N, 11.69. IR spectrum of **1**. (KBr, cm^{-1}); 3410 (m), 3119 (w), 3059 (w), 2993 (w), 2920 (w), 1614 (m), 1591 (w), 1518 (s), 1481 (s), 1464 (s), 1395 (m), 1329 (m), 1294 (m), 1254 (m), 1233 (m), 1200 (m), 1184 (m), 1155 (w), 1126 (w), 1092 (w), 1036 (m), 1011 (m), 920 (m), 889 (w), 841 (m), 750 (s), 691 (w), 646 (w), 623 (w), 603 (w), 511 (w), 461 (m). Reflection Spectrum of **1** in the solid state. λ_{max} = 634 nm (d-d absorption).

Synthesis of $[Cu(p\text{-bbiteb})_2(\text{-}\mu\text{-}Cl\text{-}[Cl\cdot(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4])]Cl_4\cdot(H_2O)_8$ (1b). Compound **1b** was prepared by dryness of **1** under reduced pressure for 2 hours. Anal. Calcd. for $C_{156}H_{176}Cl_6Cu_3N_{24}O_{10}$: C, 63.50; H, 6.01; N, 11.39. Found: C, 63.19; H, 6.00; N, 11.31. IR spectrum of **1b**. (KBr, cm^{-1}); 3414 (m), 3011 (w), 3051 (w), 3011 (w), 2920 (w), 1612 (s), 1518 (s), 1481 (s), 1464 (s), 1398 (m), 1331 (m), 1296 (m), 1254 (m), 1233 (m), 1198 (m), 1180 (m), 1126 (w), 1096 (w), 1036 (m), 1012 (m), 920 (s), 887 (w), 843 (m), 763(s), 691 (w), 646 (w), 625 (w), 602 (w), 511 (w), 461 (m). Reflection Spectrum of **1b** in the solid state; λ_{max} = 635 nm (d-d absorption).

Anion removal experiments for ClO_4^- and NO_3^-. For the ClO_4^- removal experiment from an aqueous solution, an aqueous solution of ClO_4^- (1.0 mM) was prepared by dissolution of

$NaClO_4$ (30.6 mg, 0.25 mmol) in an ultrapure water (250 mL). The 100 mL of this solution was moved to another vessel containing 0.050 mmol of **1b** (147.5 mg). The vessel was capped with Septa Rubber, and shaken by 100 rpm in a water bath kept at 30°C. The changes of concentration of anions in the solution depending on time were monitored by ion chromatography for the solution, which was prepared by dilution of the 200 μL of the reaction solution into the 4800 μL of the ultrapure water. Concentrations of anions in the aqueous solutions were determined by Metrohm Compact IC 861 ion chromatography. Other anion removal experiments by using **1b** and anion-exchange resins were carried out by a similar procedure.

Preparations of reaction products of 1b with ClO_4^- and NO_3^- in aqueous solutions. For preparation of the ClO_4^--exchanged solid sample, an aqueous solution (100 mL) of $NaClO_4$ (20.0 mM) was prepared by dissolution of $NaClO_4$ (mg, 2.0 mmol) in an ultrapure water (100 mL). This solution was moved to another vessel containing 0.050 mmol of **1b** (147.5 mg). The vessel was capped with Septa Rubber, and shaken by 100 rpm in a water bath kept at 30°C for 3 hours. The obtained solid was collected by filtration, and washed with water well. The powder was dried under air. The NO_3^--exchanged solid was obtained by similar procedure by using NO_3^- aqueous solution (100 mL) of $NaNO_3$ (20.0 mM), which was prepared by dissolution of $NaNO_3$ (mg, 2.0 mmol) in an ultrapure water (100 mL). Each powder was characterized by measurements of XRPD pattern and IR spectra.

2. Crystal structures

Single crystal of **1** was mounted on MicroMount loop (MiTeGen) with Paraton-N (Hampton Research), and was flash frozen to 173 K in a liquid nitrogen cooled stream of nitrogen. Single crystal of **2** was sealed in a glass capillary with its mother liquid. Data collections were carried out on a Rigaku VariMax Saturn (Mo $K\alpha$ radiation, 1.2-kW rotating anode). The summarized data of the X-ray measurements are given in Table S1. 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, SHELXL-97 (**1**), and refined using the SHELXL-97 tool. The disordered chloride ions were refined with occupancies as follwos; Cl(4A), 0.40; Cl(5B), 0.30; Cl(6), 0.75; Cl(7), 0.25; Cl(8); 0.25. The disordered oxygen atoms were refined with occupancies as follwos; O(1), 0.50, O(2); 0.50, O(3), 0.20; O(4), 0.35; O(5), 0.75; O(6A), 0.14; O(7B); 0.12. Although too short O—O distances are observed in the structure because of the disorders, the oxygen atoms would not exist in the short distance.

Table S1. Crystallographic Data for **1**.

formula	$C_{158}H_{179}Cl_6Cu_3N_{25}O_{10}$
fw	2991.67
lattice	tetragonal
space group	$P4/n$ (#85)
a, Å	16.3153 (19)
c, Å	30.680 (6)
V, Å^3	8167 (2)
Z	2
ρ(calcd) g cm^{-3}	1.217
μ(MoKα), mm^{-1}	0.547
radiation (λ, Å)	0.71075
temperatre (K)	173
space group	$P4/\mathrm{n}$ (#85)
reflns collected	113821
unique relfns (R$^{\mathrm{int}}$)	7948 (0.0755)
param refined,	513
R_1 [$I > 2\mathrm{s}(I)$]^a	0.0755
wR_2[all data]	0.1521
GOF on F^2	1.004

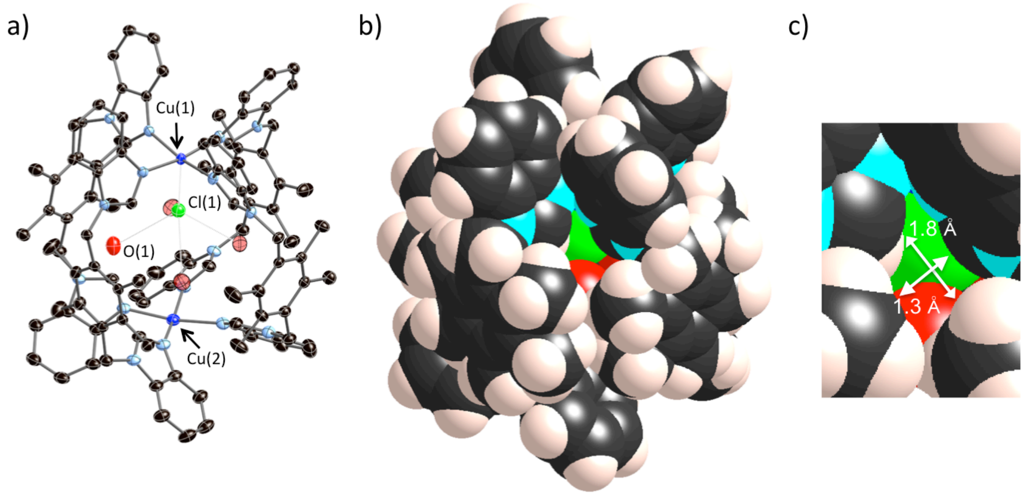

Figure S1. Structure of the cationic cage unit of **1** with a ball-and-stick model (a) and van der Waals radii model (b). The gap in the cage is shown in (c). The disordered water O(1) atoms are shown by transparent ellipsoids in (a). Color code: blue, copper; green, chlorine; red, oxygen; cyan, nitrogen; black, carbon; hydrogen, light pink. The hydrogen atoms are omitted in (a) for clarity. The structures were drawn by "Crystal Maker (version 8.76)" software.[2] The channel size (Fig. S1c) was measured by using the "Distance tool" in the software.

[2] https://www.hulinks.co.jp/software/c-maker/

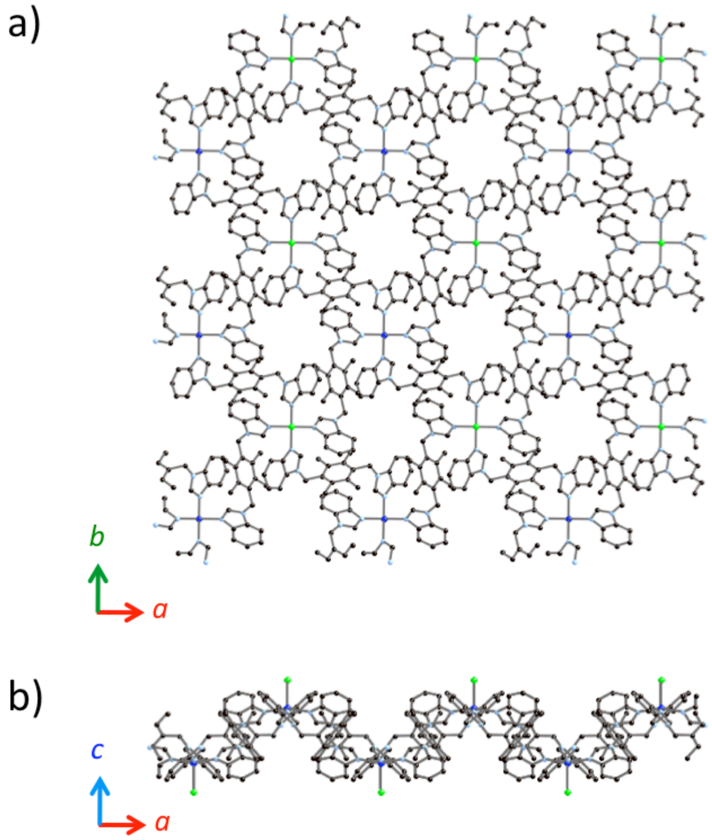

Figure S2. Structure of the sheet framework of **1** along the *c* axis (a) and *b* axis (b).

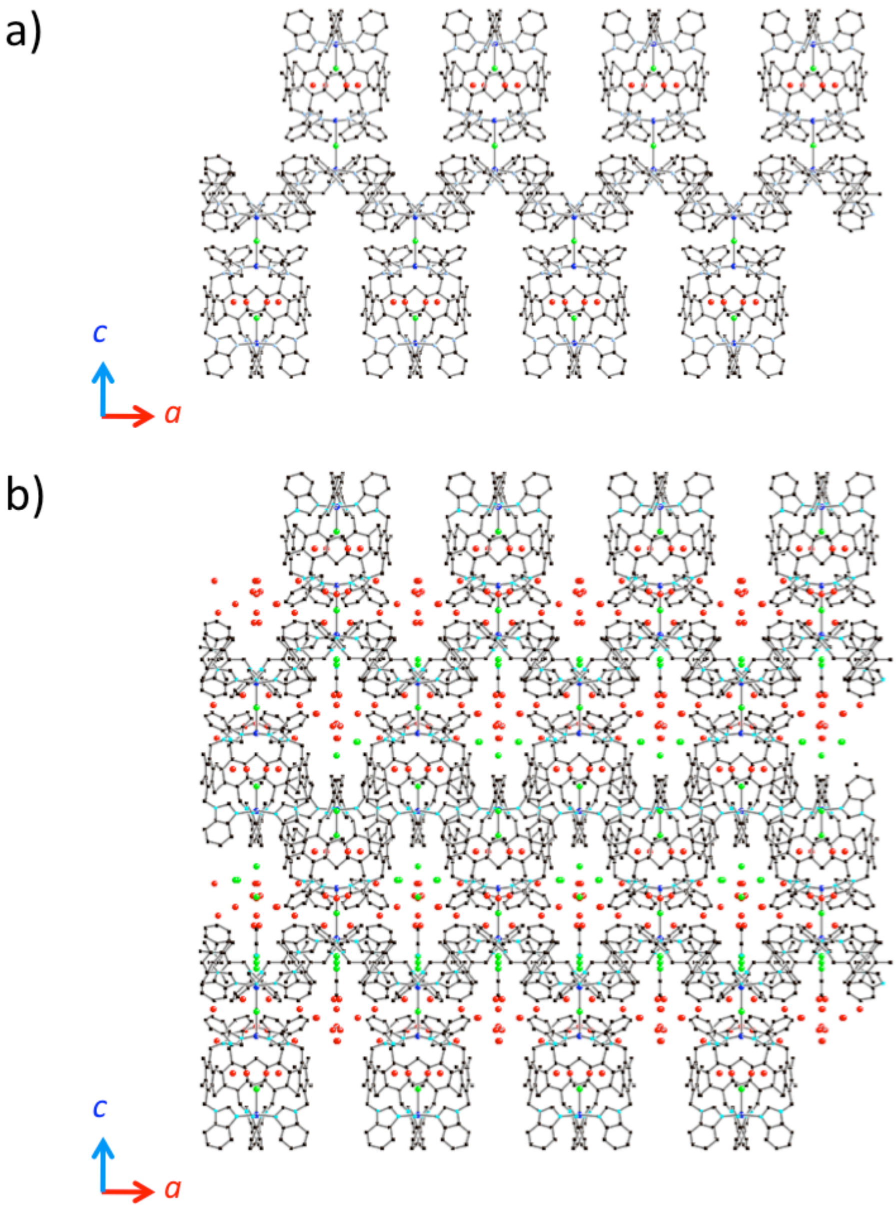

Figure S3. 2D structure that bears cationic cage unit of **1** (a) and the structure of the channel filled with guest counter anions Cl⁻, water molecules, and MeCN molecules (b).

3. Powder X-ray Diffraction (PXRD) patterns

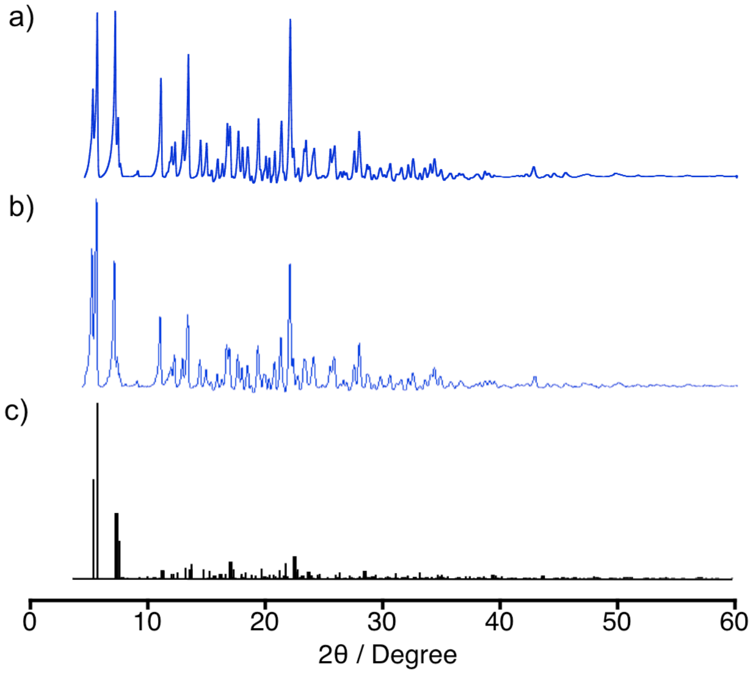

Figure S4. PXRD pattern of **1** (a), **1b** (b), and the simulated pattern based on the crystal structure of **1** (c).

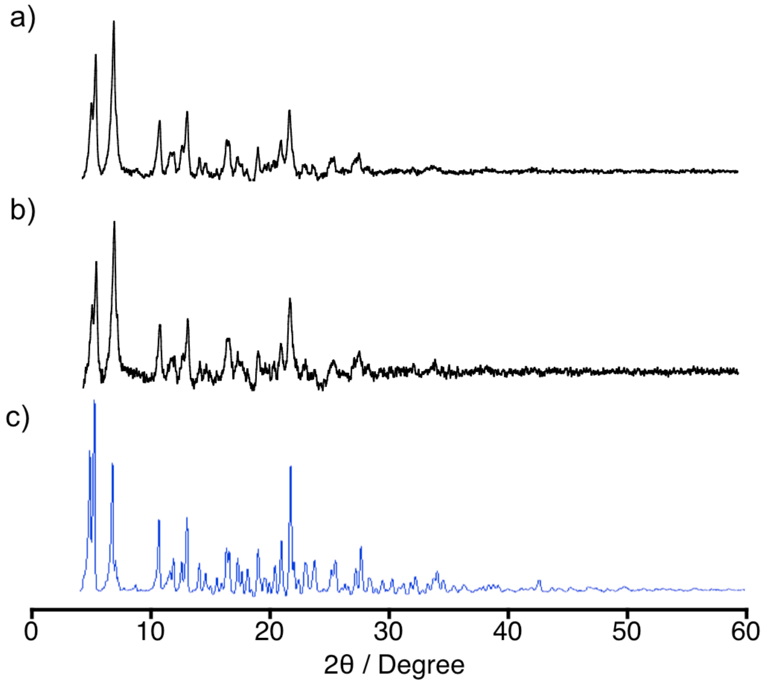

Figure S5. PXRD patterns of powder sample obtained by treatment of **1b** with 10 equiv. of $NaClO_4$ (a) or $NaNO_3$ (b) in an aqueous solution, and **1b** (c).

4. Changes of anion in an aqueous solution

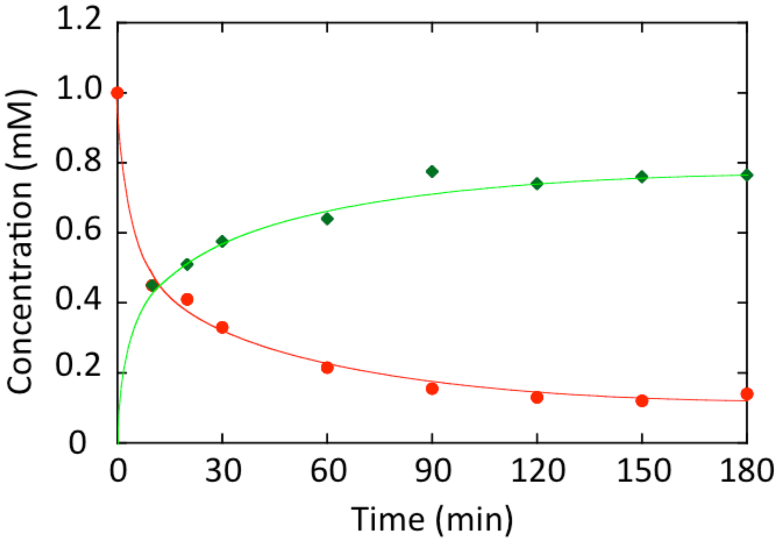

Figure S6. Changes in concentrations of Cl^- (green) and ClO_4^- (red) when **1b** (147.5 mg, 0.05 mmol, microcrystalline sample) was added in an aqueous solution of ClO_4^- (1.0 mM, 100 mL).

5. IR spectra

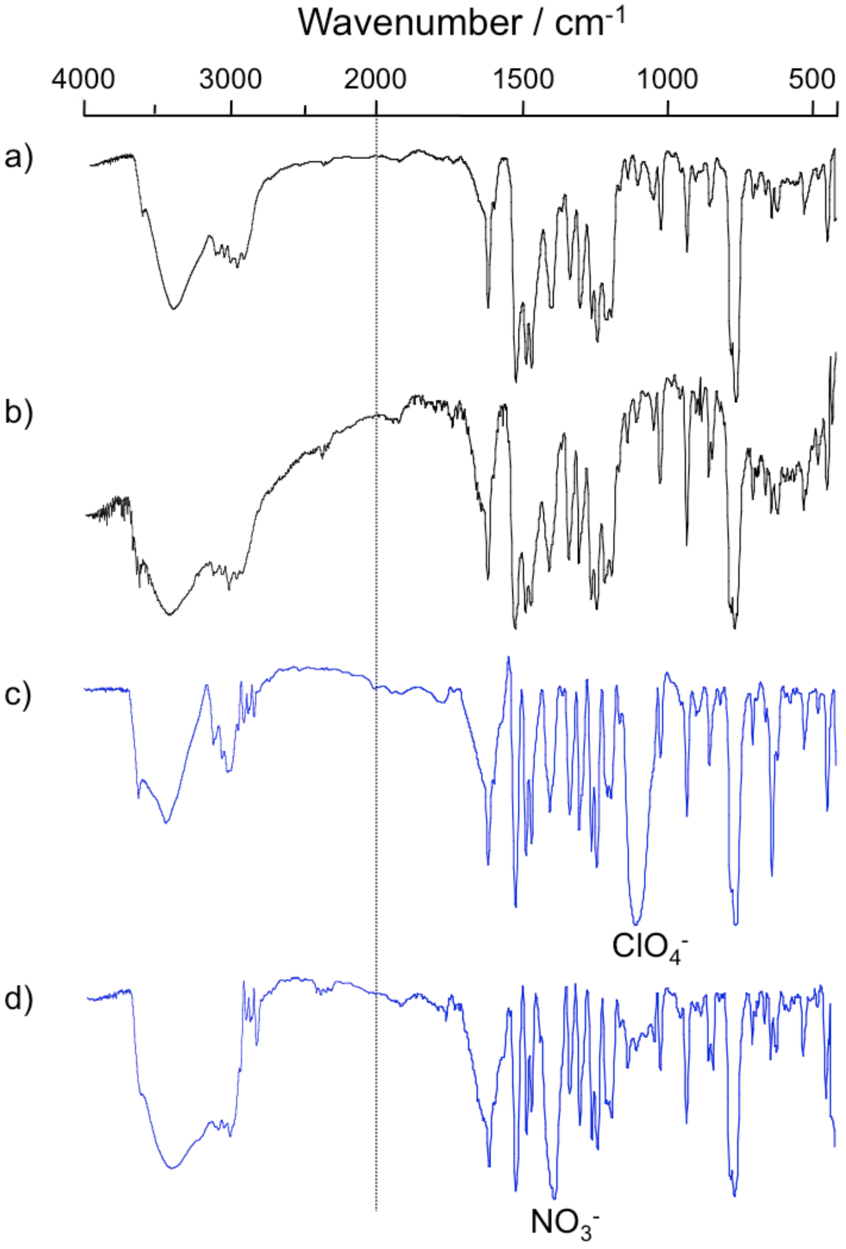

Figure S7. IR spectra of **1** (a), **1b** (b), solid samples obtained by treatments with excess $NaClO_4$ (c) and $NaNO_3$ (d) in aqueous solutions.

6. Solid state reflectance spectra

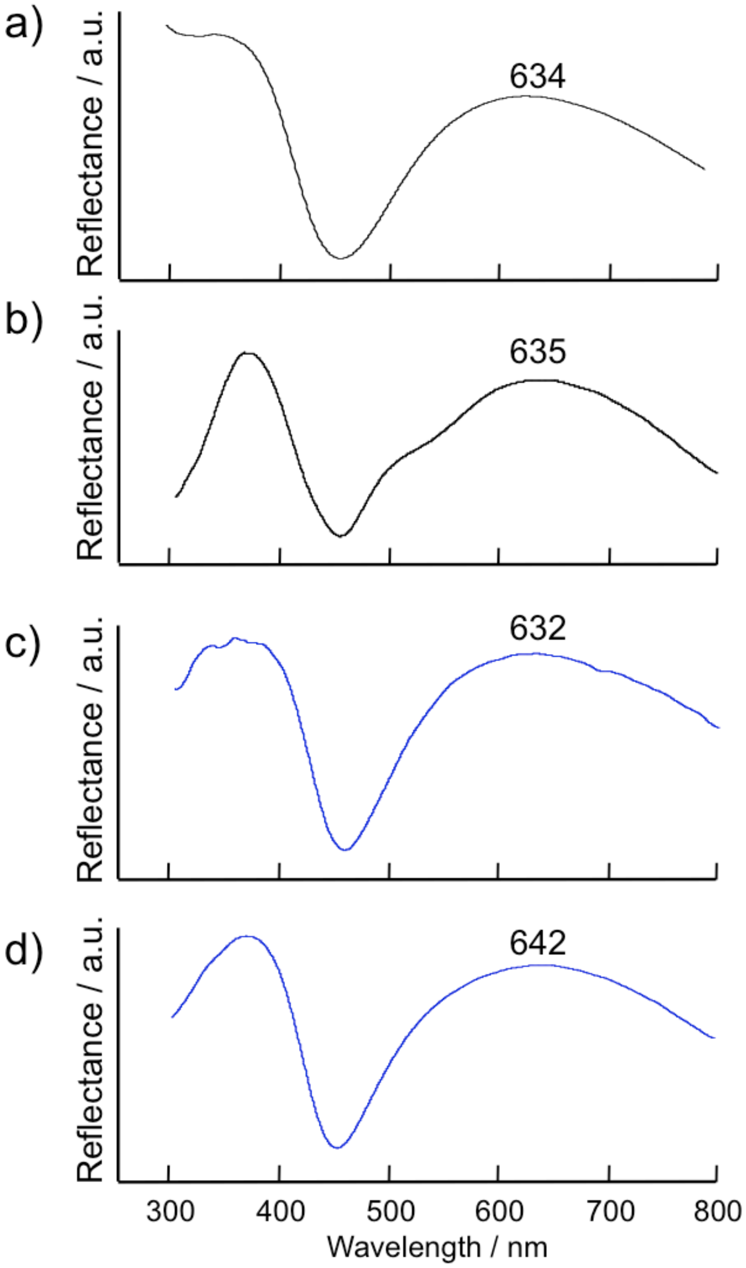

Figure S8. Solid state reflectance spectra of **1** (a), **1b** (b), solid samples obtained by treatments with excess $NaClO_4$ (c) and $NaNO_3$ (d) in aqueous solutions.

7. TG charts

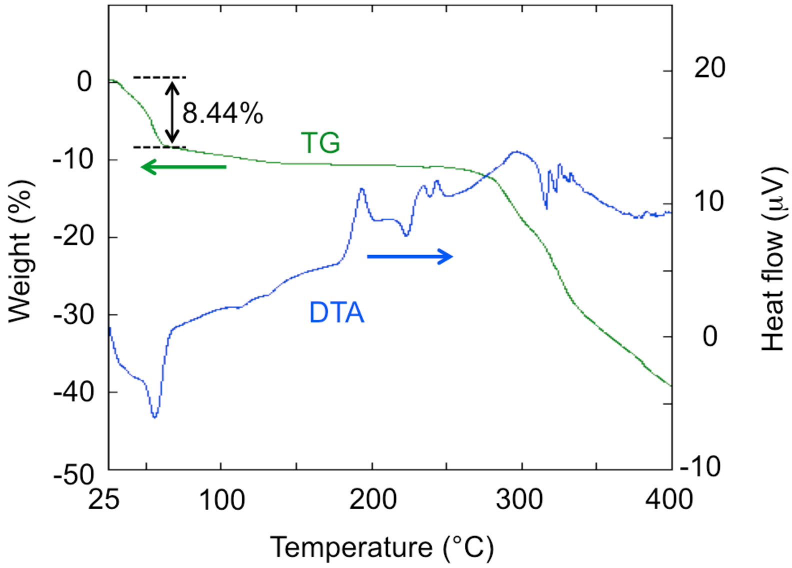

Figure S9. TGA data of crystalline sample of **1**. Decrease of 8.44% up to 80°C would be due to the releases of guest molecules acetonitrile and water molecules. The observed percentage (8.4%) was larger than the estimated value based on single crystal X-ray analysis and elemental analysis (6.8%) because of the hygroscopic property of the sample.

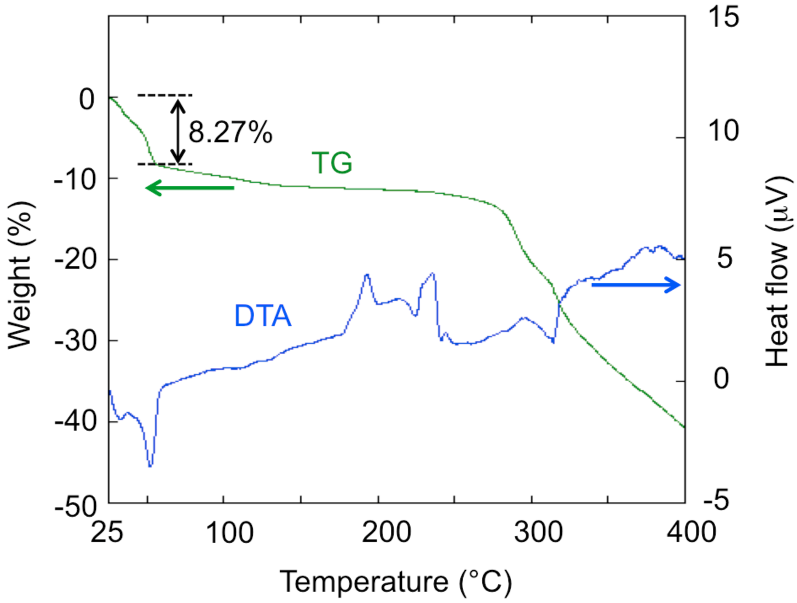

Figure S10. TGA data of crystalline sample of **1b**. Decrease of 8.3% up to 80°C would be due to the releases of guest molecules acetonitrile and water molecules. The observed percentage (8.3%) was larger than the estimated value based on single crystal X-ray analysis and elemental analysis (5.5%) because of the hygroscopic property of the sample.

8. Treatments of the anion removal reaction products with NaCl.

Anion-exchanged product of **1b** was prepared by reaction method mentioned in the manuscript with using excess $NaClO_4$ or $NaNO_3$. Compound **1b** (100 mg, 0.034 mmol) was treated with 10 equiv. of $NaClO_4$ (41 mg, 0.33 mmol) or $NaNO_3$ (29 mg, 0.34 mmol) in aqueous solution (100 mL). Their reaction products were collected by filtration and dried under reduced pressure. The ClO_4^- exchanged product (40 mg, about 0.01 mmol) was immersed in an aqueous solution (100 mL) of NaCl (7.3 mg, 0.1 mmol). The solution was stirred for 3 hours. The released ClO_4- was monitored by ion chromatograph (Figure S11a), indicating the release of about 0.005 mmol of ClO_4^- from the anion-exchanged products. This result indicated that about 12% of ClO_4^- was estimated to be replaced with Cl^- in the reaction to recover **1b**.

Similar treatment was carried out for NO_3^- exchanged **1b**. When the NO_3^- exchanged **1b** (38 mg, about 0.01 mmol) was treated with 10 equiv. of NaCl (7.3 mg, 0.1 mmol) in an aqueous solution (100 mL), release of about 0.016 mmol NO_3^- was observed (Figure S11b). This result indicates that about 40% of NO_3^- was estimated to be replaced with Cl^- in the reaction to recover **1b**.

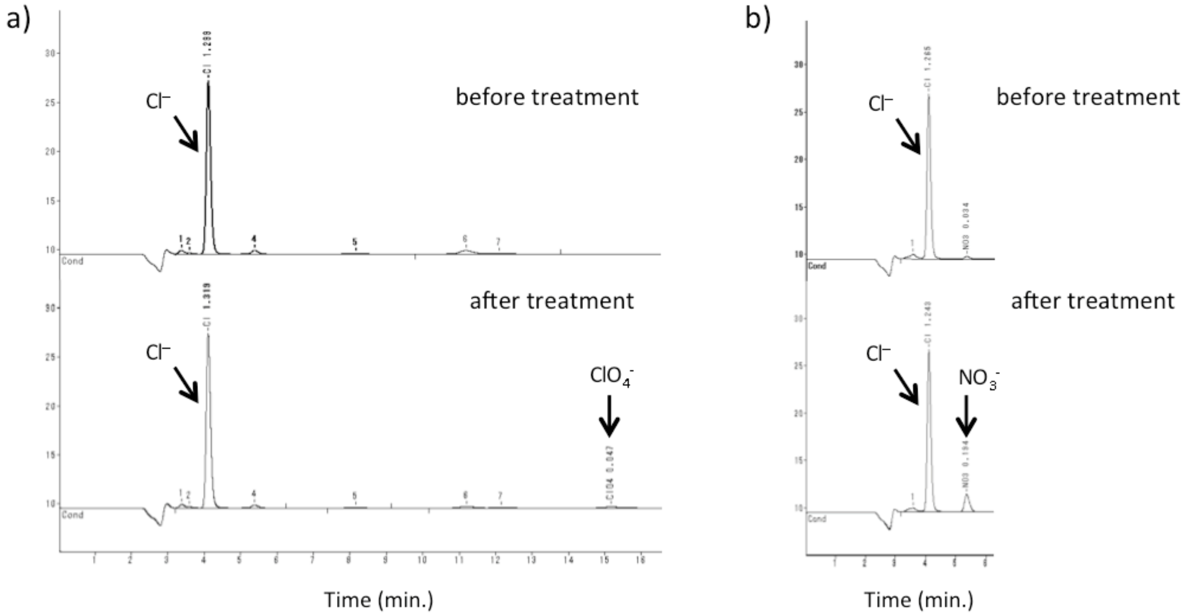

Figure S11. Ion chromatograph charts of the supernatant of the aqueous solution before and after treatments (180 min.) of an aqueous solution (100 mL) containing NaCl (0.1 mmol) with ClO_4- exchanged **1b** (about 0.01 mmol) (a) and NO_3^- exchanged **1b** (about 0.01 mmol) (b).

9. Isolation of *p*-bbiteb from the anion-exchanged product by chemical degradation process. The ClO_4^- - included product (400 mg, about 0.1 mmol) obtained by treatment of **1b** with excess $NaClO_4$ (mentioned in p. S12) was added in 100 mL of acetonitrile. An aqueous solution (4 mL) of NaOH (400 mg, 10 mmol) was added in the solution. The solution was heated for 30 min. at 70°C, and then evaporated. The crude product was dissolved in 100 mL of acetonitrile, and then filtered. The filtrate was evaporated carefully, giving white crystals of *p*-bbiteb (110 mg, 0.28 mmol) (47% yield). The identification was carried out by measurement of ^{1}H-NMR spectrum in CD_3CN (Figure S11). ^{1}H NMR (CD_3CN) δ 7.682 (d, 2 H) , 7.57 (dd, 2 H) , 7.51 (s, 2 H) , 7.329 (dd, 2 H) , 7.270 (dd, 2 H) , 5.456 (s, 4 H) , 2.24 (s, 12 H) .

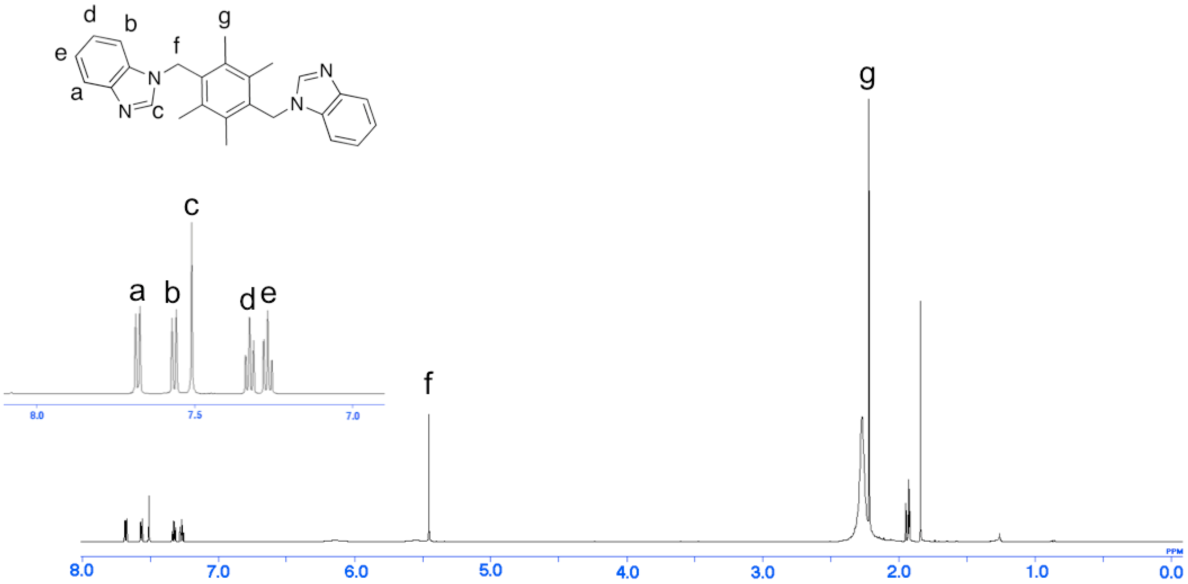

Figure S12. ^{1}H-NMR spectrum of white crystals obtained by chemical degradation of the ClO_4^--exchanged product of **1b**. The compound was identified to be *p*-bbiteb by this measurement.