

A Cationic Metal–Organic Framework Consisting of Nanoscale Cages: Capture, Separation, and Luminescent Probing of $\text{Cr}_2\text{O}_7^{2-}$ through a Single-Crystal to Single-Crystal Process**

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With the development of modern industry, heavy-metal contamination has become a more and more severe problem. Among common heavy-metal pollutants, hexavalent chromium [Cr^{VI}] has been a focus of concern because it causes serious damage to human health and the environment.^[1] Cr^{VI} has been widely used in the field of chromium plating, metallurgy, pigment manufacturing, leather tanning, and wood preservation.^[2] The capture and separation of Cr^{VI} from industrial waste water is extremely important. Although adsorbents,^[3] resins,^[4] and membranes^[5] have been introduced to remove Cr^{VI} and other pollutants, their inherent drawbacks, such as poor selectivity and slow process kinetics, limit their further development and application. Therefore, the exploration of new materials for the efficient capture and separation of Cr^{VI} is highly important.

As an emerging class of porous materials, metal–organic frameworks (MOFs) have recently attracted considerable attention owing to their high surface area, uniform pore size, controllable structures, and readily tailorable functions.^[6] Cationic MOFs are an appealing subclass and can be constructed by using neutral nitrogen-containing organic ligands and metal ions. The charge-balancing anions usually occupy the framework voids and are sometimes just weakly coordinated or even uncoordinated to the metal centers, potentially allowing the capture and separation of anions through anion exchange. Recently, a few cationic MOFs have been used for exchange and removal of heavy-metal pollutant anions, such as ReO_4^- , CrO_4^{2-} , and TcO_4^- ,^[7] but there has been no report of $\text{Cr}_2\text{O}_7^{2-}$ anion exchange in MOFs despite the powerful carcinogenicity and extensive application of this species. Herein, we report an unprecedented 3D cationic MOF consisting of nanoscale cages composed of $[\text{Ag}_2(\text{btr})_2] \cdot 2\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ ($\text{ABT} \cdot 2\text{ClO}_4$; ($\text{btr} = 4,4'$ -bis(1,2,4-triazole))), which shows fast exchange, high trapping capacity, and good selectivity for the capture and separation of $\text{Cr}_2\text{O}_7^{2-}$ in water. Interestingly, the exchange of $\text{Cr}_2\text{O}_7^{2-}$ in

$\text{ABT} \cdot 2\text{ClO}_4$ was performed through a single-crystal to single-crystal (SC–SC) process.

Colorless crystals of $\text{ABT} \cdot 2\text{ClO}_4$ were obtained by slow evaporation of a solution of AgClO_4 and btr in water and acetonitrile. Single-crystal X-ray diffraction analysis revealed that $\text{ABT} \cdot 2\text{ClO}_4$ crystallizes in the cubic space group $Fd\bar{3}c$. As shown in Figure 1, two independent Ag^{I} ions adopt a distorted

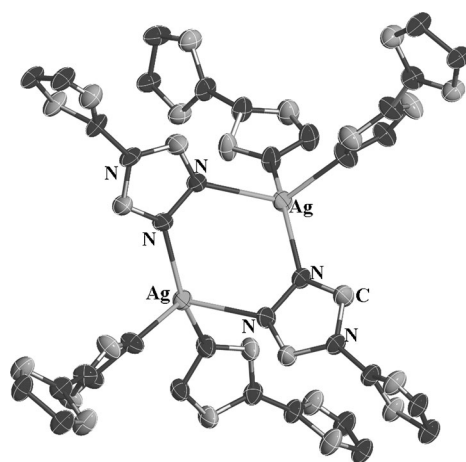


Figure 1. Crystal structure showing the coordination environments of the Ag^{I} ions in $\text{ABT} \cdot 2\text{ClO}_4$ with thermal ellipsoids set at 50% probability.

tetrahedral coordination geometry and are coordinated by four nitrogen atoms from different btr ligands, $\text{Ag}^{\text{I}}\text{–N}$ bond lengths range from 2.237(5) Å to 2.417(6) Å. Two crystallographically independent btr molecules act as tetradentate ligands to bridge four Ag^{I} ions (Scheme S1 in the Supporting Information); the two triazolyl rings in btr are nearly perpendicular to each other, and the twisting angles between them are 85.540(3) and 74.599(3)°, respectively. A prominent structural feature of $\text{ABT} \cdot 2\text{ClO}_4$ is the presence of distorted octahedral and tetrahedral cages. The octahedral cage is made up of twelve Ag^{I} ions and twelve btr ligands (Figure 2a and S1); the overall edge length is about 2.0 nm and the inner diameter and calculated pore volume based on the van der Waals surfaces are about 4.18 Å and 305.9 Å³, respectively. Each octahedral cage has eight trigonal windows formed by three Ag^{I} ions and three btr ligands, and the aperture of these windows is about 4.0 Å. The tetrahedral cage consists of eight Ag^{I} ions and eight btr ligands and its edge length is about 1.0 nm (Figure 2b and S1). Worthy of mention is further assembly of these cages. Each octahedral cage is connected to

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[**] This work was financially supported by 973 Program (2010CB933501, 2011CBA00502), Natural Science Foundation of China (21273239) and “One Hundred Talent Project” from Chinese Academy of Sciences.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201307650>.

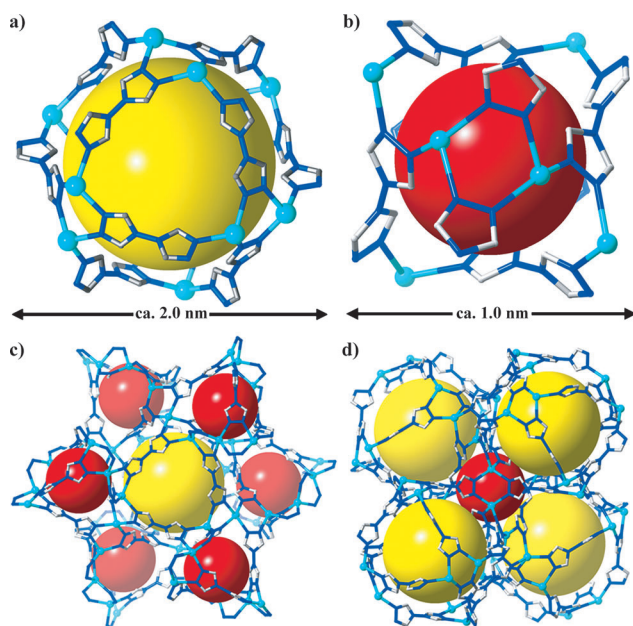


Figure 2. Ball and stick representation of the octahedral (a) tetrahedral (b) cages of ABT-2ClO₄; c) The linking mode of an octahedral cage with six tetrahedral cages; d) The linking mode of a tetrahedral cage with four octahedral cages. The large spheres indicate the sizes of the voids. N blue, C white, Ag small light-blue spheres.

six tetrahedral cages through the sharing of two Ag^I ions and two btr ligands (Figure 2c and S2), while every tetrahedral cage shares Ag^I ions and btr ligands with four octahedral cages (Figure 2d and S2). The linking of the two types of cage results in the formation of a 3D cationic framework (Figure 3 and S3). The framework possesses 1D channels with a diameter of about 7.8 Å along [1 1 1] direction, which should be accessible to anion exchange. Although a large number of cationic MOFs have been reported,^[8] cationic MOFs constructed from nanoscale coordination cages are very rare.^[9] PLATON calculation showed that the total empty volume of the cationic framework is 65 531 Å³, corresponding to 52.8 %

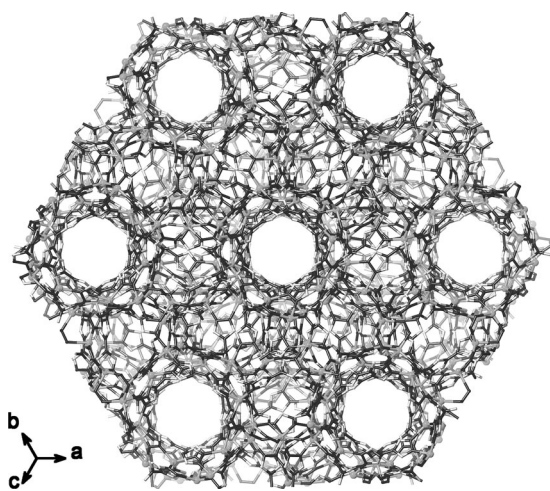


Figure 3. 3D cationic framework with 1D channels along [1 1 1] direction in ABT-2ClO₄.

of the total crystal volume (124 045 Å³). The cavities and channels were filled with highly disordered ClO₄[−] anions and lattice water molecules that cannot be completely mapped by single-crystal X-ray diffraction, which is often observed in high-symmetry structures.^[10]

Crystalline ABT-2ClO₄ is stable in water and common organic solvents. The good agreement between the experimental pattern and the simulated pattern for the powder X-ray diffraction (PXRD) indicates phase purity of ABT-2ClO₄ (Figure 4). PXRD also indicated that ABT-2ClO₄ can keep its

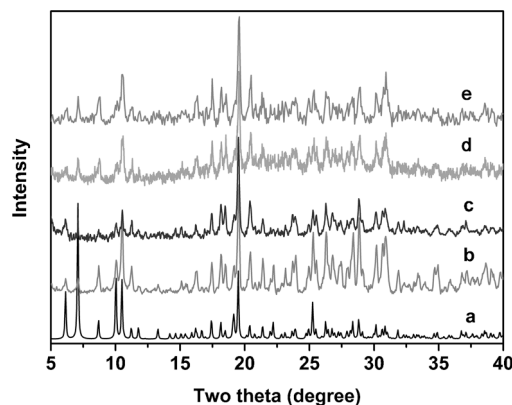


Figure 4. PXRD patterns for: a) simulated ABT-2ClO₄; b) as-synthesized ABT-2ClO₄; c) ABT-2ClO₄ immersed in equimolar aqueous K₂Cr₂O₇ solution for 48 h; d) ABT-2ClO₄ immersed in aqueous solution of excess K₂Cr₂O₇; e) ABT-2ClO₄ immersed in aqueous solution of equimolar K₂Cr₂O₇, with double the molar amount of BF₄[−], CF₃SO₃[−], and NO₃[−] ions.

crystallinity after immersion in aqueous solutions of HClO₄ and NaOH with pH values ranging from zero to ten for 24 h (Figure S4). Thermogravimetric analysis (TGA; Figure S5) of ABT-2ClO₄ showed a weight loss of 7.10 % over the temperature range 30–220 °C, corresponding to the removal of lattice water molecules (calcd 7.29 %). Above 220 °C, framework collapse was observed, which is further supported by variable-temperature PXRD (Figure S6). In the IR spectrum of ABT-2ClO₄ (Figure S7), characteristic vibration bands arising from charge-balancing ClO₄[−] were located at 1050–1150 cm^{−1},^[11] which is consistent with the single-crystal structural analysis.

Given that a great deal of ClO₄[−] is located in the voids of the framework of ABT-2ClO₄ and that enough large channels are available for anion access, anion exchange experiments were performed using Cr₂O₇^{2−} as a model. The exchange process was monitored by UV/Vis spectroscopy at intervals based on the intensity variation of the maximum adsorption peak of Cr₂O₇^{2−} in solution (257 nm).^[12] As shown in Figure 5, when crystals of ABT-2ClO₄ (0.05 mmol) were immersed in a 20 mL aqueous solution of equimolar K₂Cr₂O₇, the Cr₂O₇^{2−} concentration in solution decreased by 37 % and 60 % after 1 h and 3 h, respectively, results corresponding to capture capacities of 0.37 and 0.60 mol mol^{−1}, respectively. Subsequently, a slow decrease in Cr₂O₇^{2−} concentration was observed, and there were no obvious changes in anion concentration and solution color between 24 h and 48 h

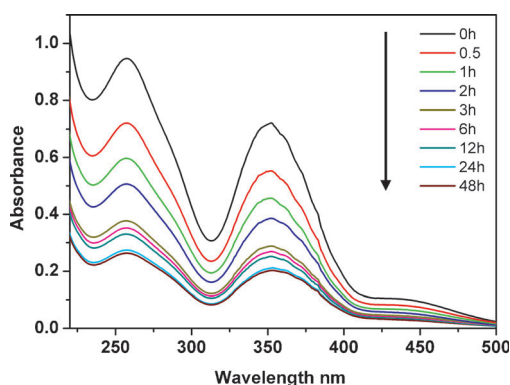


Figure 5. UV/Vis spectra of aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ solution during exchange with equimolar $\text{ABT} \cdot 2\text{ClO}_4$.

(Figure 5 and S8). The overall capacity of $\text{ABT} \cdot 2\text{ClO}_4$ to capture $\text{Cr}_2\text{O}_7^{2-}$ is $0.73 \text{ mol mol}^{-1}$ after 48 h, which is consistent with inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis ($0.71 \text{ mol mol}^{-1}$). To date, anion exchange of $\text{Cr}_2\text{O}_7^{2-}$ by cationic crystalline materials has rarely been reported. The only example is a layered inorganic lead fluoride material,^[12] which exhibited only a $0.52 \text{ mol mol}^{-1}$ exchange capacity for $\text{Cr}_2\text{O}_7^{2-}$ in a 50% excess concentration of aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ solution after 7 days; moreover, some concomitant decomposition to PbF_2 or PbCr_2O_7 was found. By comparison, $\text{ABT} \cdot 2\text{ClO}_4$ has a superior performance for $\text{Cr}_2\text{O}_7^{2-}$ capture with fast exchange and high capacity.

When using double the molar amount of $\text{ABT} \cdot 2\text{ClO}_4$ with respect to $\text{Cr}_2\text{O}_7^{2-}$ under the same conditions, 66% and 90% of $\text{Cr}_2\text{O}_7^{2-}$ were exchanged after 0.5 h and 6 h, respectively (Figure S9). The UV/Vis adsorption intensity of $\text{Cr}_2\text{O}_7^{2-}$ remained almost constant after 6 h, thus indicating completion of the exchange process. During exchange, the solution changed from yellow to colorless (Figure S10). The total adsorption capacity after 48 h as defined by UV/Vis spectroscopy and ICP–AES analysis are 0.93 and $0.92 \text{ mol mol}^{-1}$, respectively.

The $\text{Cr}_2\text{O}_7^{2-}$ capture ability was further investigated in more dilute aqueous solutions. As shown in Figure S11, when excess $\text{ABT} \cdot 2\text{ClO}_4$ was placed in a 14.7 ppm aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$, the crystals changed from colorless to yellow after 48 h. UV/Vis spectroscopy showed that the characteristic adsorption peak of $\text{Cr}_2\text{O}_7^{2-}$ in solution vanished completely (Figure S12), and ICP–AES analysis showed that the concentration of remnant $\text{Cr}_2\text{O}_7^{2-}$ was 0.09 ppm, thus suggesting almost complete capture of $\text{Cr}_2\text{O}_7^{2-}$ (99.4%) by $\text{ABT} \cdot 2\text{ClO}_4$. These results imply that $\text{ABT} \cdot 2\text{ClO}_4$ is a promising material for the removal of low-concentration $\text{Cr}_2\text{O}_7^{2-}$ from waste water.

To further explore whether the ClO_4^- in the framework of $\text{ABT} \cdot 2\text{ClO}_4$ can be completely exchanged, as-synthesized crystals were immersed in an aqueous solution containing excess $\text{K}_2\text{Cr}_2\text{O}_7$. After anion exchange, the resultant orange-yellow crystals (denoted as $\text{ABT} \cdot \text{Cr}_2\text{O}_7$) were collected by filtration, rinsed with deionized water, and dried in air. Interestingly, the apparent morphology of the crystals showed

no obvious change (Figure S13). ICP–AES analysis of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ revealed that the molar ratio of Ag to Cr is 1:1, suggesting that ClO_4^- was fully exchanged by $\text{Cr}_2\text{O}_7^{2-}$. The PXRD pattern of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ was identical with that of $\text{ABT} \cdot 2\text{ClO}_4$ (Figure 4). In the IR spectrum of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ (Figure S7), the emergence of the characteristic adsorption band arising from $\text{Cr}_2\text{O}_7^{2-}$ at about 771 cm^{-1} ^[13] and the concomitant disappearance of the broad band arising from ClO_4^- at 1090 cm^{-1} were observed, thus indicating that $\text{Cr}_2\text{O}_7^{2-}$ from the solution entered the framework of $\text{ABT} \cdot 2\text{ClO}_4$ by complete exchange with ClO_4^- . TGA analysis showed that $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ was stable up to 210°C , a slightly lower temperature than that measured for $\text{ABT} \cdot 2\text{ClO}_4$ (Figure S5). In contrast to $\text{ABT} \cdot 2\text{ClO}_4$, a sharp drop was observed in the TGA curve of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ after 210°C , which was attributed to the drastic decomposition of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$. To further confirm the framework stability and the anion exchange process, a crystal of $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ was subject to single-crystal X-ray diffraction. As shown in Figures S14 and S15, the whole cationic framework is still intact after anion exchange; $\text{Cr}_2\text{O}_7^{2-}$ fills the voids in the framework to balance the charge. These observations indicate that anion exchange took place through a SC–SC process. To our knowledge, SC–SC transformation of heavy metal pollutant anions has not been explored, although a few examples of solid–solid exchange have been reported.^[7] Moreover, $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ is the first reported example of a 3D MOF able to take up $\text{Cr}_2\text{O}_7^{2-}$ counter anions.

In comparison with anion exchange, anion selectivity may be more important and challenging. Selective exchange experiments were examined for mixtures of anions. When the crystals of 0.05 mmol $\text{ABT} \cdot 2\text{ClO}_4$ were immersed in a 20 mL aqueous solution containing 0.1 mmol BF_4^- , 0.1 mmol CF_3SO_3^- , 0.1 mmol NO_3^- and 0.05 mmol $\text{Cr}_2\text{O}_7^{2-}$ for 24 h, the crystals gradually turned yellow. In the IR spectrum of the resultant crystals (Figure S16), only the characteristic band arising from $\text{Cr}_2\text{O}_7^{2-}$ was found; no characteristic adsorption bands arising from NO_3^- (1385 cm^{-1}), CF_3SO_3^- (1265 cm^{-1}), or BF_4^- (1080 – 1030 cm^{-1}) were observed,^[11,14] thus suggesting good selectivity for $\text{Cr}_2\text{O}_7^{2-}$ over NO_3^- , CF_3SO_3^- , and BF_4^- ions. The selectivity of $\text{ABT} \cdot 2\text{ClO}_4$ may be attributed to a stronger interaction of $\text{Cr}_2\text{O}_7^{2-}$ with the cationic framework than NO_3^- , CF_3SO_3^- , and BF_4^- ions.^[18c]

The effect of anion exchange on luminescence was also explored. As shown in Figure 6, $\text{ABT} \cdot 2\text{ClO}_4$ emitted a bluish-violet light under UV irradiation, whereas the $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ emission is almost invisible to naked eye. The solid-state emission spectrum of $\text{ABT} \cdot 2\text{ClO}_4$ at room temperature displays a broad emission band centered at 450 nm upon excitation at 345 nm, a value in agreement with the emission observed under UV irradiation. The emission may be attributed to ligand-to-metal charge transfer (LMCT) transition.^[15] However, the luminescent emission was largely suppressed after the exchange of ClO_4^- by $\text{Cr}_2\text{O}_7^{2-}$. The disappearance of the luminescent emission in $\text{ABT} \cdot \text{Cr}_2\text{O}_7$ is probably because the electron-transfer transitions of $\text{Cr}_2\text{O}_7^{2-}$ decrease the energy transfer from the btr ligand to Ag^+ .^[7b] $\text{ABT} \cdot 2\text{ClO}_4$ may thus be considered a luminescent probe for

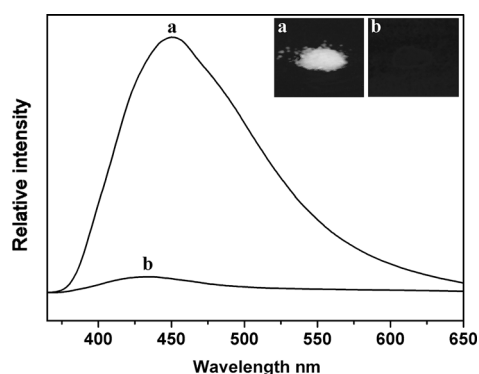


Figure 6. Room-temperature solid-state emission spectra upon excitation at 345 nm for a) ABT-2ClO₄ and b) ABT-Cr₂O₇. Insert: fluorescent images under UV irradiation for a) ABT-2ClO₄ and b) ABT-Cr₂O₇.

Cr₂O₇²⁻, an application that has not hitherto been reported for MOFs.

In conclusion, an unprecedented 3D cationic MOF consisting of distorted octahedral and tetrahedral cages has been successfully prepared. Anion exchange studies showed that the complex sets a record for fast capture and removal of Cr₂O₇²⁻, moreover, Cr₂O₇²⁻ exchange took place through SC-SC transformation. The use of MOFs that are able to take up pollutant anions could thus prove an effective strategy for dealing with pollutants of this type that are difficult to remove through established methods. ABT-2ClO₄ exhibits a bluish violet luminescence that is distinctly quenched upon Cr₂O₇²⁻ exchange; ABT-2ClO₄ may thus be used as a luminescent probe for Cr₂O₇²⁻. This work not only enriches the structural diversity of MOFs, but also widens the application of MOFs to the capture, enrichment, and luminescence-based detection of Cr₂O₇²⁻.

Experimental Section

Crystal data for ABT-2ClO₄: C₈H₁₄N₁₂O₁₁Cl₂Ag₂, Cubic, *Fd*3̄c, *a* = 49.8724(6) Å, *V* = 124045(3) Å³, *Z* = 192, *ρ* = 1.904 g cm⁻³, *F*(000) = 69504, GOF = 1.039, *R*₁ = 0.0618, *wR*₂ = 0.1752. Crystal data for ABT-Cr₂O₇: C₈H₁₀N₁₂O₈Cr₂Ag₂, Cubic, *Fd*3̄c, *a* = 49.869(2) Å, *V* = 124022(9) Å³, *Z* = 192, *ρ* = 1.856 g cm⁻³, *F*(000) = 66816, GOF = 1.237, *R*₁ = 0.0604, *wR*₂ = 0.1517. Full experimental details are given in the Supporting Information. CCDC 927379 and 939626 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: August 30, 2013

Published online: October 31, 2013

Keywords: anion exchange · dichromate · luminescence · metal-organic frameworks · single-crystal to single-crystal transformation

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