

A New Paradigm for Anion Trapping in High Capacity and Selectivity: Crystal-to-Crystal Transformation of Cationic Materials

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S Supporting Information

ABSTRACT: We describe a new methodology to the selective trapping of priority pollutants that occur inherently as oxo-anions (e.g., perchlorate, chromate, arsenate, pertechnetate, etc.) or organic anions (e.g., salicylate, pharmaceuticals, and their metabolites, which are often chlorinated into potentially more harmful compounds). The typical approach to trapping anions is exchange into cationic hosts such as resins or layered double hydroxides. Both capacity and selectivity are limited by the equilibrium of the process and moreover are often subject to interference, e.g. by carbonate that is always present in water from atmospheric CO₂. Our approach takes advantage of the metastability of our cationically charged materials to instead trap by recrystallization to a new structure. Exceptionally high adsorption capacities for permanganate and perrhenate—studied as models for pertechnetate—were found for a Ag(I)-based cationic extended framework. The exchange capacity reached 292 and 602 mg/g, respectively, over five times the exchange capacity compared to conventional layered double hydroxides. Our cationic material can also selectively trap these and other toxic oxo-anions when nontoxic anions (e.g., nitrate, carbonate) were present in an over 100-fold excess concentration.

Many of the metal pollutants listed as priorities by the EPA (U.S. Environmental Protection Agency) occur in water as their oxo-hydroxo anionic forms (e.g., perchlorate, chromate, selenite, etc.).¹ Radioactive technetium (Tc-99) in the form of soluble pertechnetate (TcO₄⁻) is highly problematic in low-activity waste (LAW) and separating the nuclear waste into primary solids. Its easy leakage from glass after vitrification does not meet long-term storage performance assessment requirements.² LAW also contains other nonradioactive inorganic and organic species [e.g., carbonate (CO₃²⁻), nitrate (NO₃⁻), etc.] that may interfere with immobilizing radioactive species in solid-state ion-exchange materials. Chromate is another problematic anion for vitrification because it weakens the integrity of the waste glass by forming spinels; such particles can also obstruct the glass flow within the melter during vitrification.³

Conventional ion-exchange resins with cationic groups and exchangeable counteranions are of limited thermal and chemical stability due to their organic nature, yet are still the standard ion exchanger.⁴ Layered double hydroxides (LDHs) are an isostructural set of materials consisting of cationic brucite-type layers charge

balanced by interlayer anions, with the general formula [M²⁺_{1-x}M³⁺_x(OH)₂]Aⁿ⁻_{x/n}·mH₂O. They have been extensively studied and are considered to be an ideal alternative to anion exchange resins.⁵ This group of materials, however, has limited capacity as evidenced by adsorption titration and isotherms. They also display low selectivity toward anion pollutants, especially in the presence of carbonate.⁶

Metal-organic frameworks (MOFs) are an emerging class of materials with a vast array of topologies and potential applications in gas adsorption/storage, catalysis, and drug delivery.⁷ As a subgroup of these known compounds, cationic extended frameworks have received limited investigation. Two of our previously reported cationic inorganic frameworks, [Pb₃F₅⁺][NO₃⁻] and [Pb_{4.5}F₈⁺][ClO₄⁻], exhibited anion exchange with dichromate, but with some decomposition to PbF₂ or PbCr₂O₇.^{8,9} Meanwhile, one recent development is the synthesis of cationic 3D metal borates with initial studies of TcO₄⁻ trapping. The overall adsorption capacity was not given, though the removal rate was 72% with dilute TcO₄⁻ solution, and the framework is based on slightly radioactive thorium.¹⁰ Though some exchange for anions of comparable size has been shown among other extended frameworks, the process is again guided by weak, nonspecific interaction between cationic host and anionic guest.¹¹⁻¹³ Fogg and co-workers recently reported an ytterbium oxyhydroxide 3D cationic framework with initial anion exchange but not for anionic pollutants.¹⁴

Herein, we report the unprecedented capacity and selectivity for trapping permanganate (MnO₄⁻), perrhenate (ReO₄⁻), and chromate (CrO₄²⁻) by our cationic MOF (SLUG-21, [Ag₂(4,4'-bipy)₂(O₃SCH₂CH₂SO₃)·4H₂O]).^{15,16} Unlike the strong affinity of LDHs for carbonate, SLUG-21 selectively traps these problematic oxo-anion pollutants *in record levels over all previous materials*. The mechanism of the high selectivity and adsorption capacity occurs *via* a crystal transition upon oxo-metal uptake. While crystal transformation for selective guest adsorption/desorption has been investigated for neutral materials,¹⁷⁻¹⁹ this report is the first to extend this approach to cationic materials for the trapping of anionic pollutants.

SLUG-21 crystals can be synthesized hydrothermally, under reflux or at room temperature with stirring (Supporting Information). The crystal structure of SLUG-21 (Figure 1 left) consists of a cationic layer of π-π stacked Ag-bipy chains, charge balanced by interlamellar 1,2-ethanedithiolonate (EDS) anions. Only one oxygen of each sulfonate end weakly interacts with the Ag metal center. The distance is in the range of 2.711(7) to 2.759(9) Å,

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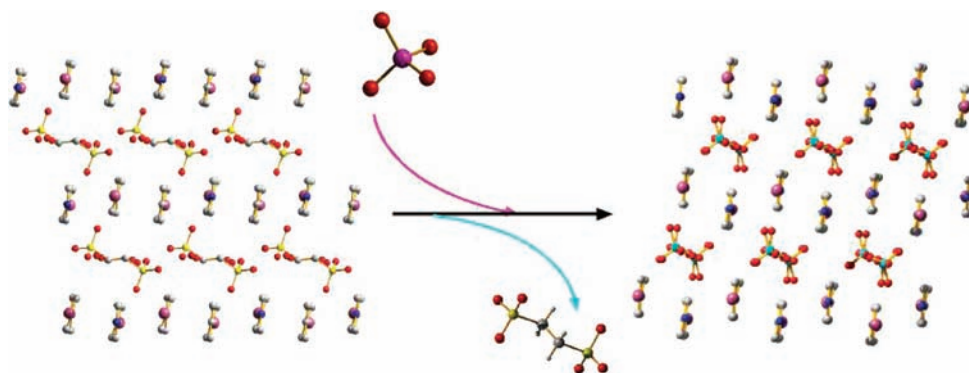


Figure 1. (Left) Crystallographic view along the $[10\bar{1}]$ direction of the SLUG-21 structure with hydrogen atoms omitted for clarity. (Right) Crystallographic view along the $[01\bar{1}]$ direction of the crystal structure after perchlorate anion exchange (hydrogen atoms omitted for clarity; Ag, purple; C, gray; S, yellow; O, red; N, blue; Cl, green). The scheme is shown for the anion exchange process of trapping oxo-anions and loss of EDS anions.

significantly longer than the accepted covalent Ag–O length (median: 2.44 Å, CSD). These distances indicate the EDS anions only electrostatically interact with the cationic layers, supporting the cationic feature and anion exchangeability of SLUG-21.

For a detailed investigation of the SLUG-21 anion uptake capacity, permanganate and perrhenate were chosen as models for pertechnetate since all are group 7 oxo-anions. As-synthesized SLUG-21 (25 mg, 3.17×10^{-5} mol) were introduced into a 50 mL solution containing KMnO_4 (10 mg, 6.33×10^{-5} mol). The molar amount of permanganate was doubled compared to the trapping material since EDS is divalent and bifunctional. The entire reaction was performed under ambient conditions with mild stirring (see Supporting Information for experimental details). As monitored by UV–vis spectroscopy, the permanganate concentration in the solution decreased by 64% and 94% with reaction intervals of 24 and 48 h, respectively, for an adsorption capacity (mol/mol) of 1.28 and 1.88 (Figure 2, Table 1). Inductively coupled plasma (ICP) gave a similar percent loss, indicating an adsorption capacity (mol/mol) of 1.30 and 1.94 (Table 1). The slight difference is likely due to experimental error and the greater uncertainty for UV–vis at low concentration. The overall adsorption capacity of permanganate trapping by SLUG-21 after 48 h is therefore 292 mg/g (by UV–vis) and 283 mg/g (by ICP, Table 1). No further decrease in anion concentration was detected after 48 h, demonstrating completion of the recrystallization process. The widely accepted adsorption capacity for oxo-anions *via* LDHs is in the range of 10–150 mg/g based on a recent review.⁶ To verify, we also carried out the anion exchange reaction with commercially available synthetic hydroxycite (magnesium aluminum hydroxycarbonate, Aldrich) in both the uncalcined and calcined form. After 48 h of exchange under the same conditions as in the case of SLUG-21, only 3% and 18% of the anions were adsorbed by LDHs, respectively. The adsorption capacity for calcined hydroxycarbonate-based LDHs is thus 36 and 42 mg/g *via* UV–vis and ICP respectively. These values are less than 14% compared to our SLUG-21 material (Table 1).

The reason for the much greater uptake by our material we believe is due to crystal transformation by the host and the stability of the oxo-anion in the resultant structure, rather than undergoing a typical equilibrium-driven anion exchange. The limited adsorption capacity of LDHs also necessitates preremoval of intercalated carbonate by calcination.^{5,6} As-synthesized SLUG-21 may be used

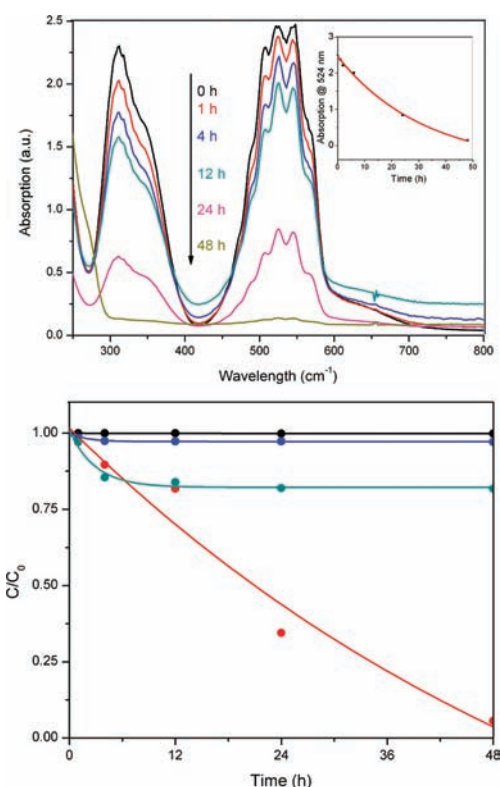


Figure 2. (Top) UV–vis absorption spectra of the permanganate solution with initial concentration of 6.33×10^{-5} mol in 50 mL solution and 3.17×10^{-5} mol SLUG-21 at various intervals. (Inset) Relative intensity of the 524 nm MnO_4^- maximum versus time. (Bottom) Concentration of permanganate (based on UV–vis) vs time for anion exchange by blank (no solid, black), uncalcined LDH (blue), calcined LDH (cyan), and SLUG-21 (red).

for the anion exchange, with a much higher adsorption capacity based on a stronger interaction toward the oxo-anion pollutant by the resultant crystal structure, which can be seen to take the place of each end of the EDS molecules (Figure 1). The incoming permanganate anion plays a crucial role in high capacity trapping by forming a thermodynamically favorable crystal structure. Indeed, the same structure forms if the nitrate- or perchlorate-containing version of SLUG-21 is used as starting material, as verified

Table 1. Adsorption Capacity of 6.33×10^{-5} mol of Permanganate or Perrhenate in 50 mL Aqueous Solution with Half Molar Ratio of SLUG-21 and Equimolar Uncalcined/Calcined LDHs during 24 or 48 h Intervals, As Monitored by ICP and UV-vis

Anion	Anion Exchanger	Time (h)	ICP			UV-vis		
			Oxoanion Removal	Ads. Cap. (mol/mol)	Ads. Cap. (mg/g)	Oxoanion Removal	Ads. Cap. (mol/mol)	Ads. Cap. (mg/g)
MnO_4^-	SLUG-21	24	65%	1.30	195.73	64%	1.28	192.72
	SLUG-21	48	97%	1.94	292.09	94%	1.88	283.06
	uncalcined LDH	48	4%	0.04	7.92	3%	0.03	5.94
	calcined LDH	48	21%	0.21	41.60	18%	0.18	35.66
ReO_4^-	SLUG-21	24	91%	1.82	576.49	N/A	N/A	N/A
	SLUG-21	48	95%	1.90	601.83	N/A	N/A	N/A
	uncalcined LDH	48	9%	0.09	37.51	N/A	N/A	N/A
	calcined LDH	48	30%	0.30	125.03	N/A	N/A	N/A

by powder X-ray diffraction (PXRD). This important distinction between SLUG-21 and LDHs is further supported by selectivity studies (*vide infra*).

In order to further demonstrate the potential application of SLUG-21 toward pertechnetate abatement, perrhenate was also investigated. The resultant exchange solution was monitored only by ICP due to the overlap between EDS and perrhenate in the UV region. ReO_4^- trapping by SLUG-21 is even more rapid than MnO_4^- , reaching over 90% removal from solution in only 24 h, saturating in 48 h with 95% removal. Although the crystals were not suitable for single crystal analysis, the overall adsorption capacity of 1.90 (mol/mol) is comparable with the previous permanganate study, as expected. The adsorption capacity based on weight, however, reaches an exceptionally high 602 mg/g based on the molecular weight of ReO_4^- as compared to that of MnO_4^- . Meanwhile, the adsorption capacity of the uncalcined and calcined LDHs is only 37 and 125 mg/g, respectively, a mere 6% and 20% with respect to SLUG-21.

Chromate exchange and adsorption capacity were also studied for SLUG-21. UV-vis shows that 25%, 33%, and 41% of the chromate were exchanged after 8, 24, and 48 h, respectively (Figure S4). The adsorption capacity for chromate was thus 0.41 mol/mol and 60 mg/g, while the capacity for uncalcined LDHs and calcined LDHs was 6 mg/g and 17 mg/g. Fourier transform infrared spectroscopy (FTIR) of the solid products after exchange support that chromate exchanged into the structure, with a prominent Cr-O stretch band and concomitant reduced intensity of the sulfonate absorption band (Figure S3). The broad absorption located at $\sim 1200 \text{ cm}^{-1}$ and singlet at $\sim 1050 \text{ cm}^{-1}$ before anion exchange is characteristic of the sulfonate (RSO_3^{2-}) groups in the original SLUG-21. The disappearance of these two bands after anion exchange, along with survival of the 4,4'-bipyridine stretches (1605s, 1535s, 1490s, 1418s, aromatic C=C and C=N), further support the anion exchange process. No nitrate or carbonate absorption bands (~ 1300 or $\sim 1420 \text{ cm}^{-1}$) are observed in the solid after anion exchange. PXRD demonstrates the structure after exchange retained its layered feature with prominent (010) and (020) peaks and no structural decomposition to Ag_2CrO_4 (Figure S3, top).

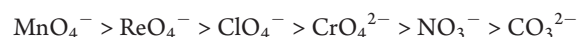
Equally important to capacity is anion selectivity for controlling the anion that is captured. Selectivity has been a long-term problem for LDHs, mainly owing to the high affinity of the cationic layers to carbonate as well as a variety of other anions

that may be present in solution. The affinity obeys the following order:²⁰



Calcination is usually necessary to partially remove the carbonate anions in LDHs before anion exchange. It is therefore never possible to remove all anions and/or introduce complete selectivity. Meanwhile, the selectivity of anion trapping in SLUG-21 was studied with multiple competing anions of varying excess concentration in the presence of a low concentration of the target anion pollutant. A selective reaction with 78.8 mg (0.1 mmol) of SLUG-21 was introduced into a 50 mL aqueous solution consisting of 47.4 mg (0.3 mmol) of KMnO_4 and 2.55 g (30 mmol) of NaNO_3 . FTIR and PXRD measurements of crystals after anion exchange indicate only MnO_4^- entered the cationic material to replace the EDS anions. No NO_3^- is present inside the solid (Figure 3c, top). Indeed, the PXRD pattern is identical to the material after exchange in a permanganate-only solution (Figure 3, bottom). Furthermore, the theoretical PXRD pattern of AgMnO_4 (shown as bars at the bottom of Figure 3) indicates no structural decomposition occurred during the anion exchange. Similarly, carbonate in a 100-fold excess did not interfere with permanganate, which was again selectively trapped by SLUG-21 (Figure 3d). This high selectivity is based on its unconventional recrystallization upon anion trapping, unlike the host-guest equilibrium driven process of LDHs and resins. PXRD indicates a crystal transition from SLUG-21 to the postanion exchange products with a specific new pattern. Selectivity toward perrhenate was also carried out with both of the competing nitrate and carbonate anions, with the same trapping behavior as permanganate (Figure S1, Supporting Information).

Perchlorate is another problematic anion that diffuses rapidly and widely, emitted from rocket fuel waste along with other sources including pyrotechnics.^{21,22} A mixed anion solution indicates perchlorate is preferred over nitrate by SLUG-21 (Figure S2, Supporting Information). The anion affinity for SLUG-21 thus displays the following order, with the problematic metalate pollutants topping the list:



In addition to the exceptionally high adsorption capacity and selectivity toward problematic anions, there are two other properties that make SLUG-21 advantageous over LDHs: (i) SLUG-21 remains heterogeneous throughout the anion exchange at the

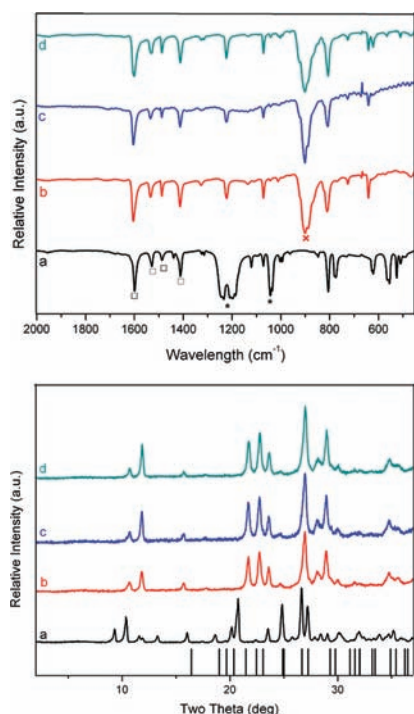


Figure 3. FTIR (top) and PXRD (bottom) of (a) as-synthesized SLUG-21; (b) SLUG-21 after exchange with permanganate; (c) SLUG-21 after exchange with permanganate and 100-fold molar excess of nitrate; (d) SLUG-21 after exchange with permanganate and 100-fold molar excess of carbonate. Theoretical pattern of AgMnO_4^- is shown as bars. (□) The aromatic C=C and C=N stretches of 4,4'-bipyridine; (×) the Mn–O stretch; (*) sulfonate stretches.

bottom of the aqueous solution and can be recovered without centrifuging. LDHs often form a paste, and *ca.* 30 min of centrifuging are required for total separation from the solution. (ii) As-synthesized SLUG-21 can be directly employed in anion exchange without pretreatment. LDHs require calcination up to 450 °C to partially remove the carbonate and render the layers more basic in order to facilitate the anion exchange. Moreover, this state is metastable: calcined LDH retains its optimized adsorption capacity only within 24 h after calcination due to the memory effect, where the layers rehydrate and reintercalate anions into the interlayer.⁶

In conclusion, our cationic material shows superior performance over the extensively studied LDHs and anion exchange resins. SLUG-21 has the potential to selectively trap pertechnetate in high capacity for the treatment of radioactive waste (*cf.* 292 and 602 mg/g for permanganate and perrhenate, respectively). With the formation of a new crystal structure driving the reaction, the anions would be permanently trapped. Reuse of the material would in fact be undesirable for a highly problematic radionuclide. Under the same experimental conditions, the calcined form of hydrotalcites only reaches 42 mg/g for permanganate and 125 mg/g for perrhenate. Our cationic material therefore overcomes both the low capacity and retention problems of hydrotalcites. It also displays high selectivity toward group 7 oxo-anions over other nonradioactive and nontoxic anions such as nitrate and carbonate, even in a 100-fold excess. Other advantageous properties include complete heterogeneity and no need for pretreatment. Further investigation of this and related cationic extended frameworks is underway to evaluate and exploit their anion trapping properties.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, additional FTIR and PXRD for solids before and after anion exchange, UV–vis absorption spectra monitored for chromate exchange, and ICP detail intensity data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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