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Anion Exchange of the Cationic Layered Material $[Pb_2F_2]^{2+}$

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Supporting Information

ABSTRACT: We demonstrate the complete exchange of the interlamellar anions of a 2-D cationic inorganic material. The *α,ω*-alkanedisulfonates were exchanged for *α,ω*-alkanedicarboxylates, leading to two new cationic materials with the same $[Pb_2F_2]^{2+}$ layered architecture. Both were solved by single crystal X-ray diffraction and the transformation also followed by in situ optical microscopy and ex situ powder X-ray diffraction. This report represents a rare example of metal−organic framework displaying highly efficient and complete replacement of its anionic organic linker while retaining the original extended inorganic layer. It also opens up further possibilities for introducing other anions or abatement of problematic anions such as pharmaceuticals and their metabolites.

Many pollutants listed as EPA (U.S. Environmental Protection Agency) priorities inherently occur as their anionic form, including metal oxo-anions (e.g., TcO_4^-, ClO_4^-, CrO_4^{2-}, etc.) and organic anions [e.g., salicylate (metabolite of Aspirin), carbamazepine, clofibrate, ibuprofen, etc.].[1] Recent studies have achieved successful inorganic anion pollutant trapping with high capacity and selectivity using cationic extended frameworks.[2] Custelcean and co-workers investigated the selectivity principles in anion separation with both metal−organic frameworks (MOFs) and hydrogen-bonded frameworks.[3] Solid-state anion trapping of organic pollutants, however, has been less investigated despite the growing worldwide problem of water contamination by pharmaceuticals and their metabolites, most of which are highly soluble in water and occur in anionic forms.[4] The current treatment process of chlorination often leads to even more toxic compounds such as monohalogenated and/or oxidized byproduct.[5]

Cationic inorganic layered materials are 2-D extended topologies where positively charged layers are structure-directed by charge-balancing anions.[6] Layered double hydroxides are the most widely studied example and have general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are a range of metals (e.g., Mg^{2+} and Al^{3+}) and A^{n-} are interlamellar anions (e.g., CO_3^{2-}).[7] Meanwhile, layered rare earth hydroxides are a recent series of pillared materials with eight or nine-coordinate metals as part of the positively charged architecture.[8] Both classes of materials display efficient equilibrium-driven anion exchange processes, while layered double hydroxides (LDHs) are often subject to interference by nontoxic anions that have a higher affinity for the material (e.g., carbonate and bicarbonate).[9] Furthermore, no single-crystal structure after exchange has been reported to support that the anion has exchanged and the metal hydroxide layers remain intact. Indeed, LDHs are known to partially decompose without complete heterogeneity during exchange in aqueous media.[7] Similarly, our previous lower *p*-block based cationic inorganic layered materials also displayed partial to complete decomposition of the structure upon anion exchange attempts.[10]

Anion exchange has been observed for a few cationic MOFs, although a majority were exchanged between inorganic anions of comparable size.[11] Postsynthetic modification, one of the most widely studied approaches to alter the organic linker, involves decoration of ligand functional groups and not altering the extended architecture.[12] Choe and co-workers recently reported the complete substitution of neutral N-donor organic linkers, namely, tetrakis(4-carboxyphenyl) porphyrin for 4,4′-bipyridine.[13] Very recently, Cohen and co-workers reported postsynthetic exchange of anionic organic linkers in MOFs.[14] The exchanged ligands were limited to functionalized 1,4-benzene-dicarboxylates with the same chain length, and the exchange process was ~21 to 97% over 5 d.

Herein, we report anion exchange within a cationic MOF to yield two new crystal structures where the 2-D inorganic topology is retained. This report is a rare example of the complete replacement of organic anions in a MOF and the first exchange of an *α,ω*-alkanedisulfonate for an *α,ω*-alkanedicarboxylate. The anion exchange process was monitored by both X-ray crystallography and in situ optical microscopy, which support an unconventional solvent-mediated pathway. Unlike LDHs, the heterogeneity and high crystallinity are maintained throughout the exchange process, with intact cationic inorganic layers fully characterized by X-ray crystallography. In addition, the interlayer-spacing can be tuned by carboxylate chain length.

We previously reported the hydrothermal synthesis of $[Pb_2F_2][O_3SCH_2CH_2SO_3]$ (SLUG-6).[15] This material can be synthesized with high yield and purity and is chemically stable in pH 4−10 aqueous solution. The crystal structure consists of cationic single $[Pb_2F_2]^{2+}$ layers pillared by 1,2-ethanedisulfonate (EDS) anions (Figure 1, center). The organic EDS linker is aligned perpendicular to adjacent layers with two oxygens of each sulfonate end covalently bonded to two Pb metal centers. This orientation gives rise to a large *d*-spacing between the cationic layers, while the weakly bonding nature known for organosulfonates gives rise to possible anion exchangeability and intercalation chemistry.[16]

Succinate $[^-O_2C(CH_2)_2CO_2^-]$ and glutarate $[^-O_2C(CH_2)_3CO_2^-]$ were chosen as initial examples of *α,ω*-

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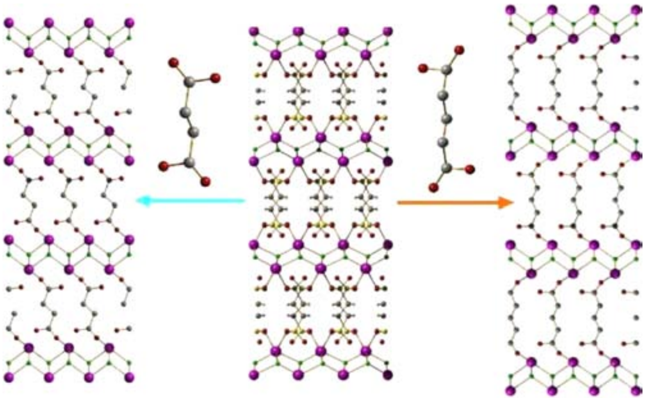

Figure 1. Scheme of the anion exchange process of the cationic lead fluoride structure. (Left) Crystallographic view of SLUG-32 along the *a*-axis. (Center) Crystallographic view of the original SLUG-6 along the *c*-axis. (Right) Crystallographic view of SLUG-33 along the *a*-axis (Pb purple, F green, S yellow, O red, C gray, H white).

alkanedicarboxylate carbon chain length. Immersion of as-synthesized SLUG-6 crystals in an aqueous solution of 2-fold molar excess disodium succinate under static ambient conditions afforded the highly crystalline phase $[Pb_2F_2][O_2C(CH_2)_2CO_2]$ (which we denote as SLUG-32 for University of California, Santa Cruz, Structure No.32; see Supporting Information for experimental details). In situ optical microscopy was employed to monitor the transformation between the two crystalline phases (Figure 2). The formation of SLUG-32 was observed on the surface of the SLUG-6 crystals after 30 min in the dicarboxylate solution (Figure 2b). The competitive crystallization allows SLUG-32 to gradually grow in expense of the original SLUG-6 crystal to form an entirely new phase and crystal morphology after 4 h. No further change in crystal morphology occurs after 4 h (Figure 2f), supporting the completion of the anion exchange process. Unlike the solid-state equilibrium-driven anion exchange process for LDHs, the in situ optical microscopy indicates our material undergoes a solvent-mediated anion exchange with a possible exfoliation and recrystallization pathway. Figure 3 shows the ex situ powder X-ray diffraction (PXRD) versus time for the solid from a 20 mL aqueous solution of 1.0×10^{-4} mol SLUG-6 and 0.01 M sodium glutarate. After 1 h, the new SLUG-33 phase $[Pb_2F_2][O_2C(CH_2)_3CO_2]$ is clearly present [e.g., (001) peak at 7.4° (2θ), Figure 3b]. On the basis of the peak area of the majority peak, the glutarate exchange was over 90% complete after 2 h and phase-pure SLUG-33 after 24 h, with no peaks of the original SLUG-6 remaining (Figure 3c,d). The anion exchange process is also supported by FTIR (Figure S3) and elemental analysis (Table S3).

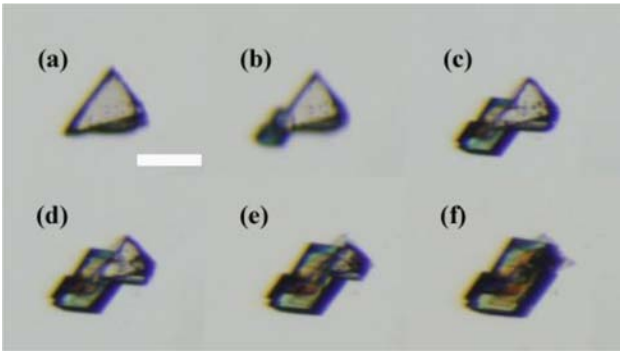

Figure 2. In situ optical micrographs of a single crystal of SLUG-6 in sodium succinate solution for 10 (a), 30 (b), 60 (c), 90 (d), 120 (e), and 240 min (f). Scale bar is 20 μm.

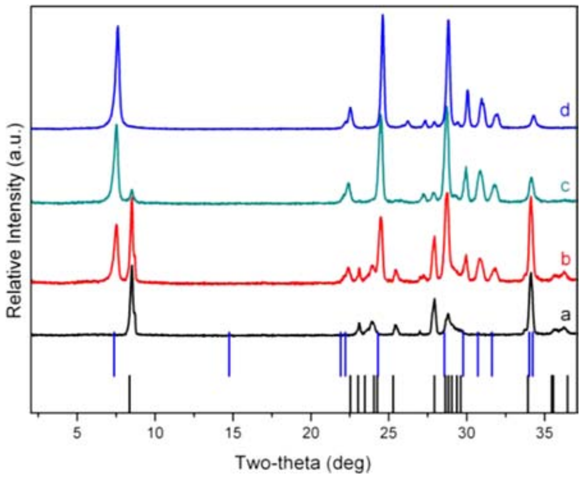

Figure 3. Ex situ PXRD measurement of SLUG-6 anion exchange products from sodium glutarate solution after 0 (a, black), 1 (b, red), 2 (c, cyan), and 24 h (d, blue). Theoretical patterns of SLUG-6 (black) and SLUG-33 (blue) are shown at the bottom as bars.

The crystals after anion exchange were manually separated and structurally characterized by single-crystal X-ray crystallography. SLUG-32 crystallizes in the high-symmetry tetragonal crystal system with $I4/m$ space group. The $[Pb_2F_2]^{2+}$ layer remains intact, with the same formula as the cationic layers in SLUG-6. The SLUG-32 cationic layer possesses slightly more condensed intralayer Pb−F connectivity in the *ab* plane (Figure 4) with decreasing *a* and *b* dimensions [a = 4.6185(2) Å and b = 4.4226(2) Å for SLUG-6; $a = b$ = 4.1371(7) Å for SLUG-32]. SLUG-32 is slightly more elongated along the *c*-axis (Figure 1 left vs center) since only one oxygen of each carboxylate group bonds to the layers [Pb−O bond length ranges between 2.620(20) and 2.635(19) Å] compared to two oxygens for SLUG-6. The distance between lead and the nonbonded oxygens on the carboxylates ranges from 2.814(23) to 2.826(23) Å, exceeding the accepted Pb−O covalent range provided by the Cambridge Structural Database [CSD, 2.60(19) Å]. This singly bonded feature for SLUG-32 is likely due to the known stronger coordination of carboxylates versus sulfonates, with one covalent metal−oxygen bond sufficient to

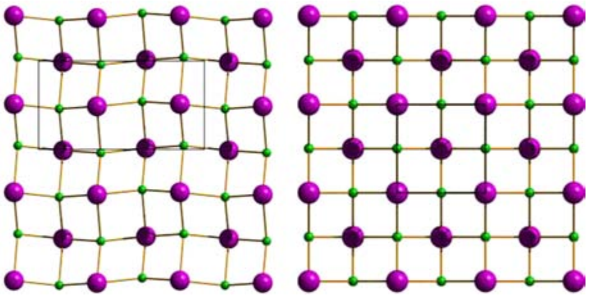

Figure 4. (Left) Crystallographic view of one $[Pb_2F_2]^{2+}$ layer of SLUG-6 along the crystallographic *a*-axis. (Right) View of one $[Pb_2F_2]^{2+}$ layer of SLUG-32 along the crystallographic *c*-axis (Pb purple, F green).

hold the interlamellar anionic linkers in place. This interaction is also evidenced by the elongation of the $[Pb_2F_2]^{2+}$ layers along *c* axis due a stronger carboxylate-lead interaction

In addition to anion exchange, SLUG-32 can be synthesized by a conventional hydrothermal reaction and corresponding molar ratio (see Supporting Information), yielding a similar tetragonal crystal morphology. PXRD confirms that both synthesis methods give the identical high purity SLUG-32 phase, with experimental PXRD matching the powder pattern simulated from the crystallographic data (Figure S2a,b). Interestingly, perchlorate is necessary in the hydrothermal method to obtain the same phase as post-anion exchange, likely acting as a stabilizer.[10b] Reaction without perchlorate produced α-PbF_2 (ICDD PDF# 41-1086).

To investigate the generality of this crystal-to-crystal anion intercalation chemistry, we employed glutarate as a longer dicarboxylate chain to intercalate between adjacent $[Pb_2F_2]^{2+}$ layers. X-ray crystallography of crystals after anion exchange confirms the formation of SLUG-33 with the same layer topology as SLUG-32 (Figure 1). Both SLUG-32 and SLUG-33 share the *I*4/*m* space group and the unit cell dimensions in the *ab* plane differ by only 0.51% [SLUG-32, $a = b = 4.1371(7)$ Å; SLUG-33, $a = b = 4.116(3)$ Å]. Moreover, they afford the same feature of singly bonded carboxylates. This feature implies that further possible anion exchangeability with other dicarboxylates and anions is possible. The cell dimension along the *c*-axis increased from 21.477(4) Å for SLUG-32 to 24.003(15) Å for SLUG-33. This 11.8% increase agrees well with the carboxylate chain length difference of 13.9%. Again, SLUG-33 can be synthesized hydrothermally and both methods give a high purity product as evidenced by PXRD (Figure S2c,d). Anion exchange with even longer α,ω-alkanedicarboxylates such as sebacate, $[^{-}O_2C(CH_2)_8CO_2^{-}]$, was also followed by PXRD and FTIR (Figure S4). Although structure solution from single crystal data was not possible, the (00*l*) peaks indicate that the material is also layered and *d*-spacing increasing to ~15.9 Å.

In conclusion, we have introduced the first cationic lead fluoride layered compound exhibiting high capacity anion exchange. The postexchange products were solved crystallographically and the solvent-mediated process was monitored by in situ optical microscopy. The new materials represent rare examples of MOFs that completely and efficiently replace its anionic organic linker while retaining the cationic inorganic layered structure. The post-anion exchange products were solved crystallographically and prove the survival of the cationic layers. The ability to exchange for varying length carboxylate chain indicates that rich intercalation chemistry is possible including the trapping of more complex species such as pharmaceutical or photoluminescent anions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, tables containing crystal data and refinement details, ORTEP diagrams, additional characterization data and crystallographic information file (CIF, containing refinement parameters, fractional atomic coordinates and bond lengths and angles for both structures). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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