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Stereochemical expression of Bi 6s² lone pairs mediates fluoride-ion (De)insertion in tunnel-structured Bi₂PdO₄ and Bi_{1.6}Pb_{0.4}PtO₄†

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Fluoride-ion batteries are a promising alternative to lithium-ion batteries by dint of the greater crustal abundance of fluorine and the potential to alleviate the need for metal electrodeposition. However, conventional metal fluoride cathodes typically rely on conversion-type reactions that require propagation of a reaction–diffusion front, thereby limiting cycling performance and rate capability. In contrast, the topochemical insertion of fluoride-ions in periodic solids remains a relatively unexplored approach. Here, we explore the mechanisms of fluoridation of Bi₂PdO₄ and Bi_{1.6}Pb_{0.4}PtO₄ insertion hosts that possess capacious tunnels that can accommodate fluoride-ions with a particular emphasis on elucidating the role of stereochemical expression of bismuth 6s² lone pairs in mediating anion diffusion. We reveal that the topochemical solution-phase insertion and deinsertion of fluoride-ions at room temperature is mediated by redox reactions at platinum and palladium centers but involves multi-center synergies between d- and p-block atoms across the one-dimensional (1D) tunnel structure. While Pt and Pd centers mediate redox reactions, the stereochemically active lone pair electrons of Bi³⁺ play a pivotal role in facilitating reversible fluoride-ion diffusion. Consequently, Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ can be reversibly fluoridated with full recovery of the crystal lattice and with minimal alteration of the unit cell volume. The results reveal a key principle that the stereochemical activity of p-block electron lone pairs can be harnessed to modulate anion–lattice interactions and mediate facile anion diffusion.

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Introduction

Lithium-ion batteries are the current paradigm for electrochemical energy storage across a diversity of formats; however, their widespread adoption in electromobility and grid-scale energy storage is currently stymied by materials criticality and supply chain constraints,^{1,2} which often give rise to vexatious

trade-offs between performance and cost efficiency. Recent efforts have increasingly focused on enhancing technological diversity as a means of alleviating material criticality concerns.^{3,4} Anion batteries represent an orthogonal construct to Li-ion batteries by utilizing anions, commonly fluoride- and chloride-ions, as charge carriers.⁵ Such battery concepts rival Li-ion batteries in terms of theoretical energy densities and hold promise for improved safety by entirely alleviating the need for metal electrodeposition.^{5–7} Much of the current palette of fluoride-ion anodes leverage conversion reactions to store fluoride-ions. This poses inevitable challenges of large volume changes and sluggish progression of the reaction–diffusion front, which are manifested as poor rate performance and cycle life.^{6,8–11} In contrast, the insertion chemistry of fluoride-ions in periodic solids to form mixed-anion (oxyfluorides) periodic solids remains poorly developed. As such, fully integrated fluoride-ion insertion batteries remain to be realized despite promising steps toward this goal, which is a reflection of fundamental challenges in achieving reversible topochemical fluoride-ion diffusion in redox-active insertion hosts.^{12–14}

While topochemical cation insertion is well studied as a proxy for electrochemical coupled electron–ion transport

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processes,¹⁵ anion insertion reactions in periodic inorganic crystals are much less explored.^{16,17} Beyond elucidation of fundamental mechanisms relevant to energy storage, topochemical anion insertion holds promise for accessing a rich palette of mixed-anion periodic solids,^{18,19} especially far-from-equilibrium structures with anions precisely positioned in specific interstitial or interlayer sites that can be challenging to access from direct synthesis.^{20–22} Here, we have adopted a solution-phase topochemical fluoridation approach as a proxy for electrochemical fluoridation using XeF₂ as a fluoridating agent, C₄H₉Li as a defluorinating agent and Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ hosts as model systems to understand mechanisms of charge compensation and the modulation of electronic structure changes during reversible fluoride-ion insertion.²³ We apply a broad range of X-ray scattering as well as X-ray absorption and emission spectroscopy tools to our model systems to probe the mechanistic basis of reversible fluoride-ion insertion and diffusion, as well as to unravel key design principles, an approach that would have been rather challenging to implement in fully assembled fluoride-ion batteries.

Similar to Li-ion batteries, fluoride-ion insertion requires hosts to have a high density of available interstitial sites and accessible redox centers capable of accommodating relatively large F-ions (contrast ionic radii of 1.32 Å for fluoride-ions as compared to 0.79 Å for Li-ions)²⁴ with relatively modest structural distortions. However, a crucial distinction is that fluoride-ion insertion reactions must induce oxidation rather than the reduction of the redox active sites upon ion insertion. Recent studies have indicated the synergistic role of redox reactions at d-block transition metal redox sites and electron repulsion at polarizable p-block sites in mediating reversible fluoride-ion diffusion.^{25,26} Notably, reversible fluoride-ion insertion has been achieved in schafarzikite-type FeSb₂O₄ at room temperature. Kageyama and co-workers recently demonstrated intriguing low-temperature fluoride-ion insertion in the 1D tunnels of Bi₂PdO₄.²⁷ We explore here the mechanisms underlying fluoride-ion insertion in Bi₂PdO₄ and Bi_{1.6}Pb_{0.4}PtO₄ compounds with a particular emphasis on elucidating the role of stereochemical expression of bismuth 6s² lone pairs in mediating anion diffusion.

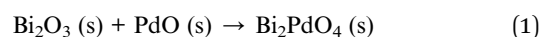
p-block cations with stereochemically active electron lone pairs manifest lattice anharmonicity and distinctive structural distortions in periodic solids because of the expression of the stereochemical activity of filled 4/5/6s² electron lone pairs.^{28–31} In both schafarzikite-type FeSb₂O₄ and Bi₂PdO₄/Bi_{1.6}Pb_{0.4}PtO₄ structures, the lone-pair repulsions of p-block cations underpin the opening of sizable one-dimensional tunnels, which can be used to accommodate fluoride-ions. As per the revised lone pair model, stereochemical expression of 4/5/6s² lone pairs is predicated on their effective hybridization with anion p states (mediated by cation 4/5/6p states), which gives rise to filled slightly anti-bonding states at the valence band maximum.²⁸ Here, we examine the electronic structure consequences of reversible room-temperature solution-phase (de)insertion of fluoride-ions in tunnel-structured insertion hosts, Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄. Using X-ray scattering and spectroscopy probes, we map structural distortions induced by anion

insertion to electronic structure modulations. Next, we use energy-variant hard X-ray photoemission spectroscopy (HAXPES) and first-principles density functional theory (DFT) calculations along with crystal orbital Hamiltonian population (COHP) analyses to examine how the stereochemical expression of Bi 6s² lone pairs and their interactions with inserted fluoride ions mediates the strength of Pd/Pt–F interactions and enables reversible fluoride-ion insertion in Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ periodic solids.

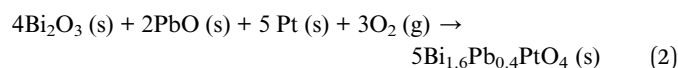
Results and discussion

Structure evolution upon topochemical fluoridation and defluoridation

Bi₂PdO₄ and Bi_{1.6}Pb_{0.4}PtO₄ have been prepared from precursor powders of stoichiometric oxides by ball milling and annealing in a fused silica ampoule as per:³²

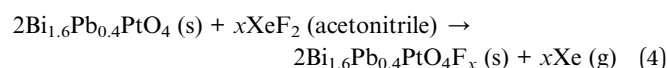
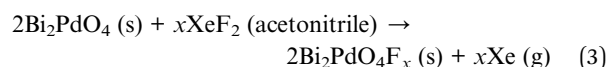


An attempt to synthesize stoichiometric Bi₂PtO₄ did not succeed; instead, partial substitution of Bi³⁺ by Pb²⁺ is needed to stabilize the Pt variant as a Bi–Pb solid-solution as per:^{32,33}

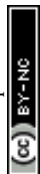


Mixed valence platinum is required to stabilize the structure, which can formally be denoted as Bi_{1.6}Pb_{0.4}Pt_{0.8}Pt_{0.2}O₄. Fig. 1 illustrates the structures of Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ as inferred from Rietveld refinements (Fig. S2C and D†) to powder X-ray diffraction (XRD) patterns shown in Fig. 2A, S2A and S2B† respectively. Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ crystallize in the tetragonal space group, *P4/ncc*; Tables S1 and S2† list the unit cell parameters and cell volume. The compounds are isostructural with Bi₂CuO₄ and comprise edge-sharing Pt/PdO₄ square-planar units bonded to corner-sharing BiO₆ octahedra that are asymmetrically distorted as a result of Bi³⁺ 6s² stereochemically active electron lone pairs. Electron lone-pair repulsions between Bi sites open sizable 1D tunnels along the [001] and [110] directions of the crystal structure (Fig. 1A). These capacious tunnels (see also structure representations in Fig. S1†) are sufficiently large to serve as diffusion channels for F-ions between interstitial sites bounded by Bi centers.^{12,25,26}

Topochemical fluoride-ion insertion has been performed by reacting the as-prepared materials with XeF₂ in acetonitrile at room temperature, as also described by Kageyama, as per:²⁷



Topochemical fluoridation serves here as a proxy for electrochemical fluoridation, which has recently been achieved for CsMnFeF₆ and ReO₃ using tetra-*n*-butylammonium fluoride (TBAF) liquid electrolyte dissolved in THF at room



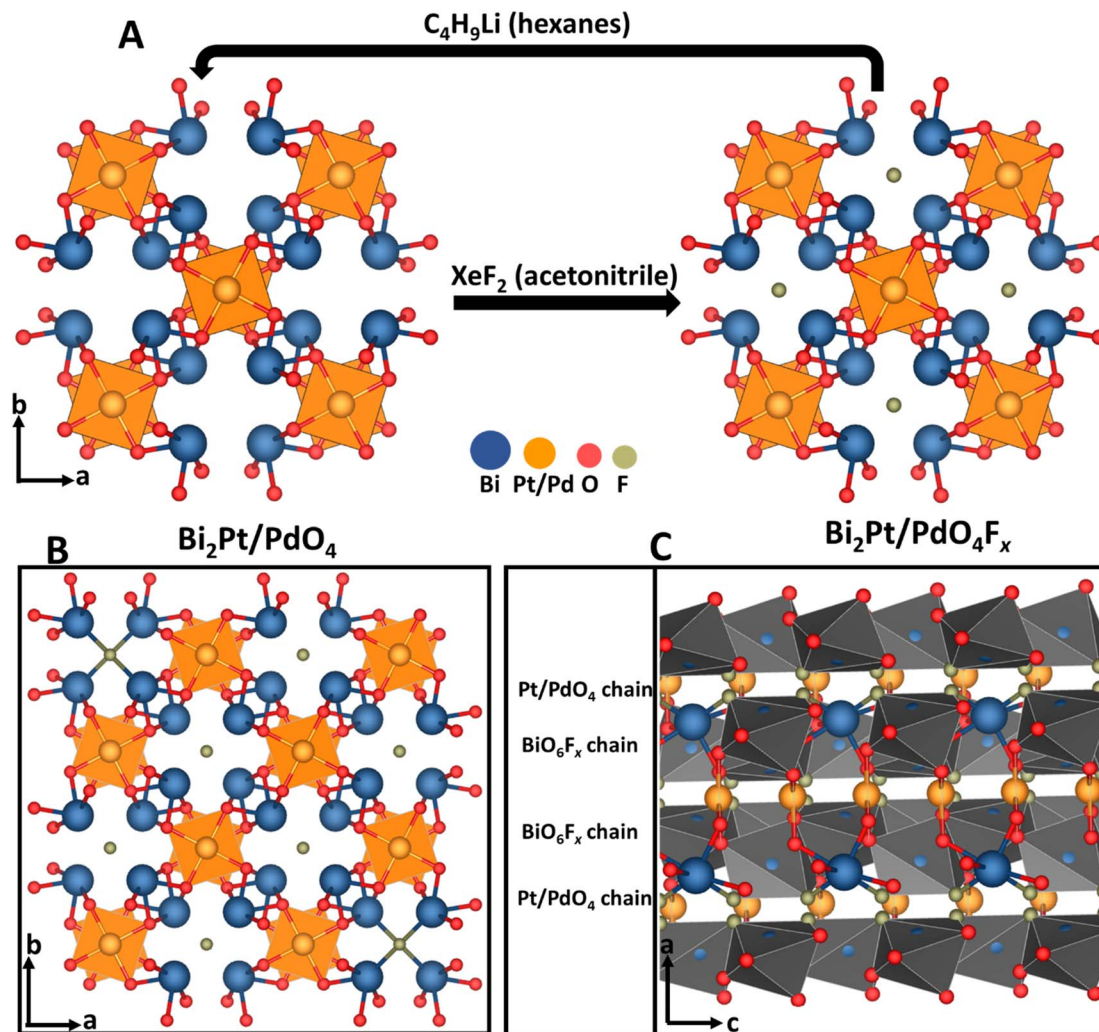
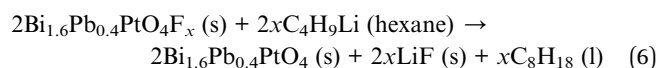
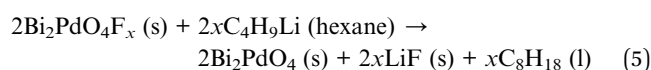


Fig. 1 Reversible topochemical fluoridation of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 . (A) Reaction scheme for topochemical fluoride-ion insertion in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 . (B) Expanded view of fluoridated $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 along the c -axis indicating F-ion positions along the 1D tunnel defined by Bi lone-pair repulsions; and (C) a view down the crystallographic axis, showing chains of edge-sharing square planar $\text{PtO}_4/\text{PdO}_4$ units sharing two oxygens with BiO_6 octahedra that are asymmetrically distorted owing to the stereochemically expressed Bi^{3+} $6s^2$ electrons. The $\text{PtO}_4/\text{PdO}_4$ and BiO_6 structural motifs separate the redox site from the F-ion binding site. Bi adopts a capped trigonal prismatic electron geometry with one vertex occupied by an electron lone pair (see Fig. S1†). Two long Bi–O (2.803 Å) bonds are weakly coordinated, and as such, have been removed to highlight the 1D tunnels with interstitial sites that accommodate F-ions.

temperature.^{11,35} In this study, by examining the mechanisms of reversible topochemical insertion of F-ions into the quasi-1D tunnels of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 , we have attempted to identify the interplay between atomistic and electronic structure required to mediate fluoride-ion insertion with a view towards designing generalizable design principles. Solution-phase topochemical fluoridation provides a means to explore the mechanistic basis for F-ion insertion and diffusion within periodic inorganic solids without having to identify a suitable electrolyte compatible with the positive and negative electrodes or assembling a complete electrochemical cell. Defluorination has been performed by reaction with n -butyllithium as per^{25,26} and the nominally defluorinated products are denoted with the modifier ($\text{Bi}_2\text{PdO}_{4-n}\text{-BuLi}$ and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_{4-n}\text{-BuLi}$):



Rietveld refinement of powder XRD data shown in Fig. 2A and S3A† for fluoridated samples infers a nominal stoichiometry (x) of 0.5 ± 0.02 in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4\text{F}_x$, with notable disorder observed in F-ion sites arrayed along the 1D tunnel (Tables S3 and S4†). The tetragonal ($P4/ncc$) structure is preserved, albeit with some modification. The (211), (220), (411), and (420) reflections of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ are shifted to lower 2θ values upon F-ion insertion (Fig. 2B and S3BD† shows comparable data for Bi_2PdO_4 before and after fluoridation), indicating an anisotropic expansion of the 1D tunnel. This



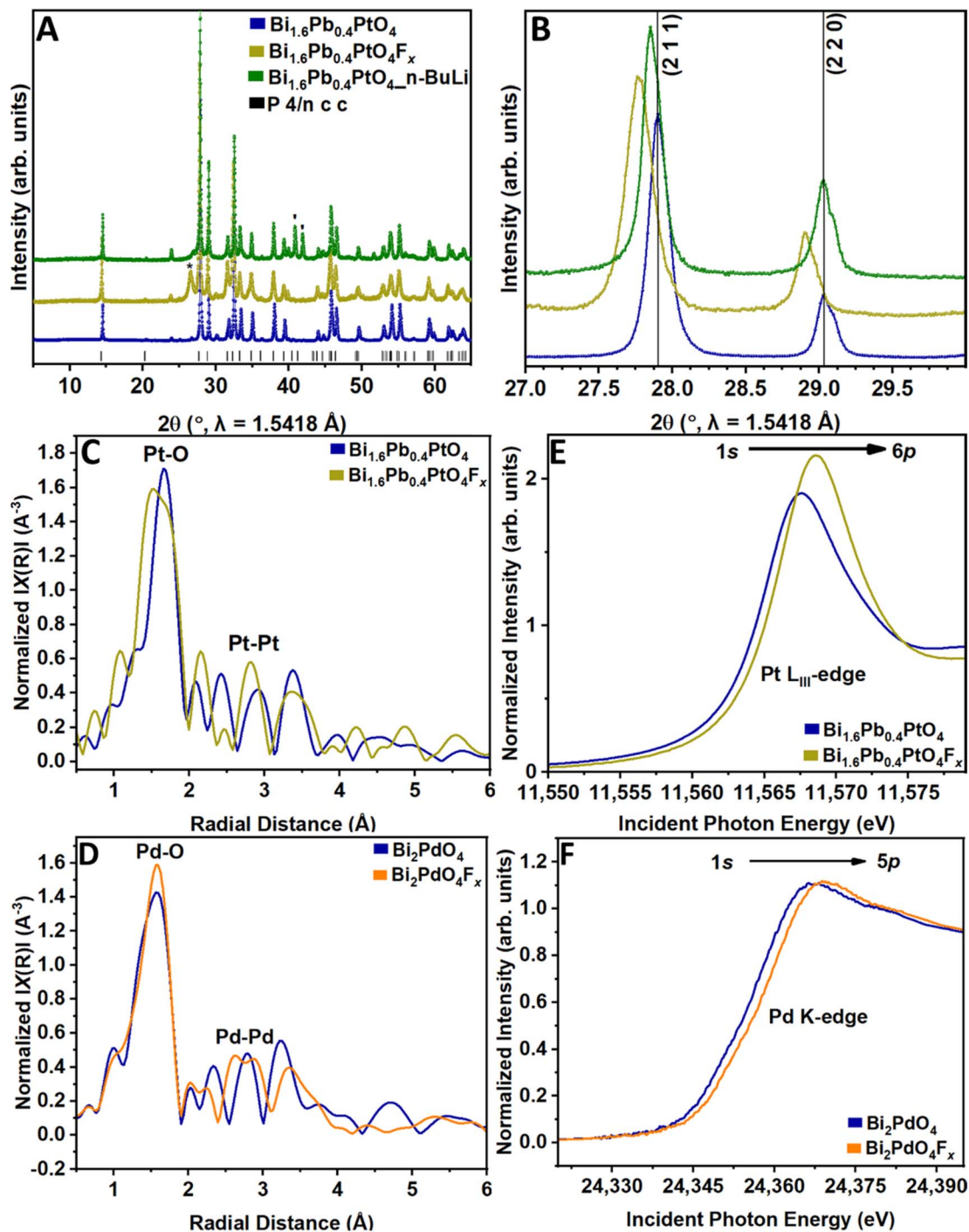


Fig. 2 Structure evolution of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 upon topochemical fluoride-ion insertion. (A) Comparison of powder XRD patterns collected for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$, $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ obtained by treatment with XeF_2 in acetonitrile, and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ recovered after treatment with *n*-butyllithium. The reflections observed around $2\theta = 26^\circ$ (denoted with *) for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ were similar to that observed by Kageyama *et al.* and can be ascribed to interphasic products (e.g. PtF_2 , PtF_4 , BiF_3 , BiOF).^{14,27} The reflection at $2\theta = 43^\circ$ (denoted with ′) for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_{4-n}\text{BuLi}$ is further likely an interphasic lithiated species.^{26,34} (B) Expanded view showing evolution of the (211) and (220) reflections across the F-ion insertion and deinsertion reactions. Normalized k^3 -weighted Fourier-transformed *R*-space data extracted from (C) Pt L_{III}-edge EXAFS spectra for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$; and (D) Pd K-edge EXAFS spectra for Bi_2PdO_4 , and $\text{Bi}_2\text{PdO}_4\text{F}_x$. Comparison of normalized (E) Pt L_{III}-edge XANES spectra for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$; and (F) Pd K-edge XANES spectra for Bi_2PdO_4 and $\text{Bi}_2\text{PdO}_4\text{F}_x$.

expansion brings about an outwards flexion of PtO_4 and PdO_4 units concomitantly with the inward buckling of BiO_6 octahedra, as depicted in Fig. 1. Rietveld refinements to powder

XRD data for fluoridated samples are shown in Fig. S4; Tables S3 and S4† show that the *a* and *b* lattice parameters are increased upon fluoridation, whereas the *c* parameter is



decreased. Beyond the reflections corresponding to topochemical fluoridation, some additional reflections are also observed corresponding to interphasic products. Analogous to topochemical cation reactions, the formation of corrosion products competes with insertion reactions at high local chemical potentials.^{14,36}

The unit cell volume of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$, decreases from $435.01(3) \text{ \AA}^3$ to $434.84(5) \text{ \AA}^3$, a change of 0.17 \AA^3 (0.04%), whereas in Bi_2PdO_4 , the volume decreases from $439.12(2) \text{ \AA}^3$ to $439.082(19) \text{ \AA}^3$, a change of 0.038 \AA^3 (0.009%). Overall, fluoride-ion insertion induces a modest (<1%) lattice contraction, which is characteristic of oxidative insertion.^{25,26} These minimal volume changes upon fluoride-ion insertion reflect the structural resilience afforded by the stereochemical expression and polarizability of $6s^2$ lone pairs on Bi and Pb centers,³⁷ which introduce localized lattice distortions that accommodate fluoride ions ameliorating the need for large structural distortions or phase transformations. In this regard, while Bi and Pb both express stereochemical activity proportionate to the strength of $6s$ – $2p$ hybridization with O $2p$ states,³⁸ as quantified by ΔE_{s-p} .²⁸ Since Pb $6s$ atomic states (-11.9 eV) closer to O $2p$ states as compared to Bi $6s$ (-14.4 eV), the introduction of Pb induces a greater lone pair distortion.³⁹ An empirical estimate of the extent of lone pair distortion can also be derived from the fractional contribution of O $2p$ to lowest metal ns valence band states (*vide infra*).³⁹ As such, Pb–F interactions are stronger than Bi–F interactions. The stronger Pb–F hybridization induces relatively greater lattice distortions and contributes to the larger volume contraction observed in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ as compared to Bi_2PdO_4 .

Corroboration of F-ion reactivity with $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 is derived from energy dispersive spectroscopy (EDS) mapping (Fig. S5 and S6[†]), which shows a homogeneous spatial distribution of F-atoms co-localized with Bi and Pt/Pd in the fluoridated materials. Upon reaction with *n*-butyllithium as per eqn (5) and (6), Fig. 2A, B and S3A–D[†] illustrate restoration of the starting crystal structure of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 , respectively (see also Tables S6 and S7[†]). These results demonstrate the facile reversibility of the solution-phase F-ion insertion reaction.

Extended X-ray absorption fine structure (EXAFS) spectroscopy data collected at Pt L_{3-} and Pd K-edges for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 , respectively, have further been used to obtain a local structure perspective of structural modifications induced by fluoridation. The EXAFS data has been fitted starting from initial structural models derived from Rietveld refinements of the powder XRD patterns. Fourier-transformed R-space EXAFS data for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 with and without fluoridation are presented in Fig. 2C and D, respectively. Two prominent features at Pt L_{3-} and Pd K-edges are assigned to Pt–O/Pd–O (*ca.* 2.0 \AA) and Pt–Pt/Pd–Pd (*ca.* 3.0 \AA) scattering paths. The fitting results in Fig. S7[†] indicate that upon fluoridation, the Pt–O bond correlations are reduced from 2.000 \AA to 1.986 \AA ; Pd–O bond distances are similarly decreased from 2.010 \AA to 1.991 \AA . The reduced bond lengths are consistent with oxidation of the platinum and palladium centers. Models of PtO_4 and PdO_4 square-planar coordination environments shown in Fig. S7E

and F[†] have been constructed based on the Pt–O and Pd–O distances derived from EXAFS fits in Fig. S7 and Table S5.[†] Further evidence for topochemical insertion of F-ions derives from F K-edge XANES spectra of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4\text{F}_x$ shown in Fig. S8A and B,[†] respectively, which are overlapped with Bi N_{III} -edge (Bi $4d_{3/2} \rightarrow \text{Bi } 6p$) resonances. The local structure results thus show that fluoride-ion insertion in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 causes reversible, anisotropic structural changes, expanding the 1D tunnels and contracting the *a* and *b* lattices as a result of shortened Pt–O and Pd–O bonds. Topochemical anion insertion oxidizes Pt and Pd centers whilst maintaining tetragonal symmetry, which is fully reversible upon defluoridation.

Electronic structure implications of topochemical fluoridation and defluoridation

X-ray absorption and emission spectroscopies have been employed to investigate the electronic structure changes in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 upon F-ion insertion. Pt L_3 (Pt $1s \rightarrow \text{Pt } 6p$) and Pd K-edge (Pd $1s \rightarrow \text{Pd } 5p$) XANES spectra in Fig. 2E and F, respectively, reveal a shift in the primary white-line absorption features to higher energies by *ca.* 2 eV upon fluoride-ion insertion, which is indicative of the oxidation of nominally divalent Pt and Pd centers.⁴⁰ This observation further squares with the observed shrinkage of Pd–O and Pt–O bonds in the EXAFS measurements. Soft X-ray Pt N_{III} -edge (Pt $4d_{3/2} \rightarrow \text{Pt } 6p$), Pd M_{III} -edge ($3d_{3/2} \rightarrow \text{Pd } 5p$), and O K-edge ($1s \rightarrow 2p$) XANES spectra for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4/\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4/\text{Bi}_2\text{PdO}_4\text{F}_x$ are shown in Fig. S8C and D.^{†41–43} Consistent with the redox activity of the transition-metal centers, Pt and Pd N_{III}/M_{III} -edge features are shifted to higher energy upon topochemical F-ion insertion.

Further corroboration of transition-metal redox accompanying topochemical fluoride-ion insertion in these systems is derived from core-level hard X-ray photoemission spectroscopy (HAXPES) measurements (Fig. 3 and S9[†]). The high incident photon energy of HAXPES (as compared to surface-sensitive laboratory X-ray photoemission spectroscopy) enhances the kinetic energy of the emitted electron, and consequently, its inelastic mean free path,⁴⁴ enabling interrogation of bulk (and not just surface) electronic structure.^{44,45} Fig. 3A and B plot high-resolution core-level Pt $4f$ and Pd $3d$ spectra, respectively. Both features are shifted to higher binding energy upon fluoride-ion insertion but restored upon removal of fluoride-ions by treatment with *n*-BuLi. These results attest to the oxidation of the transition metal centers upon fluoridation and reduction upon fluoride-ion de-insertion. In contrast, high-resolution Bi $4d_{5/2}$ core-level HAXPES spectra in Fig. 3C and D show features centered at *ca.* 440.2 eV corresponding to trivalent Bi centers in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 , which remain essentially unmodified by fluoride-ion insertion and de-insertion. Fig. S9A and B[†] show core-level F $1s$ HAXPES spectra obtained for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4\text{F}_x$, further corroborating bulk fluoridation, with the fluorine position for both compounds at 685 eV . This binding energy is typical of ionic fluoride species in metal oxide matrices.⁴⁶ These results attest to the transition metal centers,



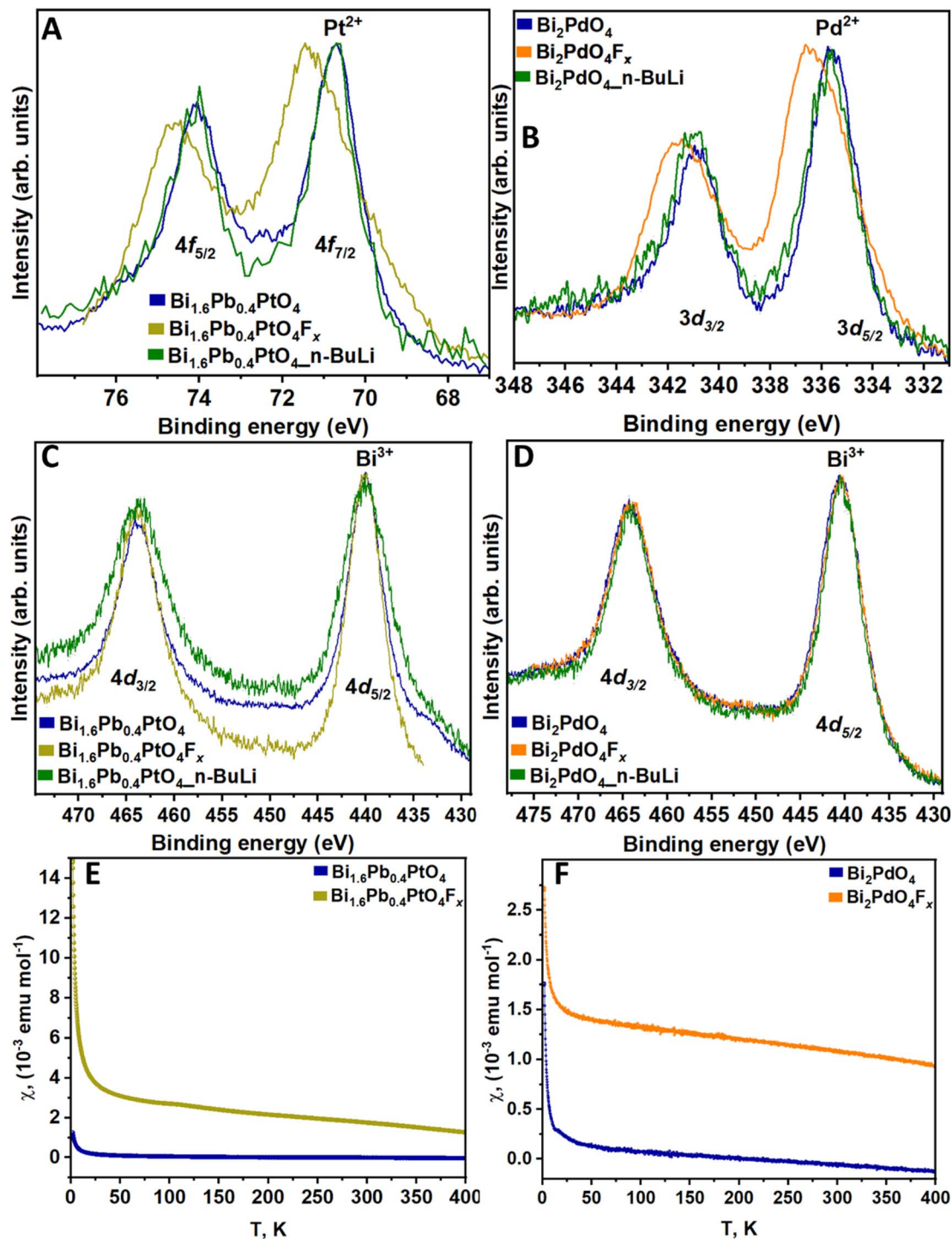


Fig. 3 HAXPES and magnetic measurements to probe evolution of electronic structure upon topochemical fluoridation. High-resolution core-level HAXPES plots at 2 keV incident energy for (A) Pt 4f, (B) Pd 3d, and Bi 4d core excitations collected for (C) Bi_{1.6}Pb_{0.4}PtO₄, Bi_{1.6}Pb_{0.4}PtO₄F_x, and Bi_{1.6}Pb_{0.4}PtO₄ recovered after treatment with *n*-butyllithium and (D) Bi₂PdO₄, Bi₂PdO₄F_x, and Bi₂PdO₄ recovered after treatment with *n*-butyllithium. FC magnetic susceptibility as a function of temperature for (E) Bi_{1.6}Pb_{0.4}PtO₄/Bi_{1.6}Pb_{0.4}PtO₄F_x and (F) Bi₂PdO₄/Bi₂PdO₄F_x under an applied field of 0.1T.

Pt and Pd, mediating redox reactivity upon fluoride-ion insertion, whereas the p-block cation, Bi, remains nominally redox innocent.

Further corroboration of redox insertion is derived from magnetic susceptibility measurements. Fig. 3E and F show the

temperature-dependent magnetic susceptibilities of Bi_{1.6}Pb_{0.4}PtO₄/Bi_{1.6}Pb_{0.4}PtO₄F_x and Bi₂PdO₄/Bi₂PdO₄F_x, during field cooling (FC), and reveal that F-ion insertion and subsequent Pt²⁺ and Pd²⁺ oxidation bring about a noteworthy alteration in magnetic behavior. Both Bi_{1.6}Pb_{0.4}PtO₄ and Bi₂PdO₄ exhibit



diamagnetic behavior, which is in stark contrast to the paramagnetic behavior of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4\text{F}_x$. This pronounced alteration of magnetic structure upon F-ion insertion is consistent with the change from d^8 (M^{2+}) to nominally d^7 (M^{3+}) electronic structure. The extracted effective magnetic moment on the basis of the CW fit in the temperature range between 100 K and 350 K is increased from $\mu_{\text{eff}} = 0$ of ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4) to $1.30 \mu_{\text{B}}$ ($\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$) and $1.25 \mu_{\text{B}}$ ($\text{Bi}_2\text{PdO}_4\text{F}_x$), which is consistent with a change in magnetic spins from $S = 0$ to almost $S = \frac{1}{2}$ upon F-ion insertion.

Stereochemical expression of Bi $6s^2$ lone pairs

Energy-variant valence band (VB) HAXPES measurements have been performed on $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 before and after reaction with XeF_2 to examine the role of electronic structure modulations in mediating fluoride-ion insertion and to elucidate fundamental design principles associated with specific anion-cation interactions. Photoionization cross-sections in photoemission spectroscopy are generally suppressed as a function of incident photon energy; however, the steepness of the decrease is greater for subshells with higher orbital angular momentum. As such, HAXPES spectra obtained at higher incident photon energies more prominently manifest orbital contributions from subshells with lower angular momentum values (e.g., s and p orbitals). In the context of periodic solids, energy-variant HAXPES serves as an excellent probe to selectively spotlight filled $4f/5f/6s^2$ -derived states of p-block cations at the valence band edge.^{28,38,44,47}

Fig. 4 and S10[†] display VB HAXPES spectra for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 acquired at two distinct incident photon energies, 2.0 keV and 5.0 keV, before and after F-ion insertion. HAXPES features have been assigned based on COHP calculations shown in Fig. 4E, F, S10C and D[†] and DFT-calculated atom-projected density of states plotted in Fig. S11.[†] The VB of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 comprises O 2p states hybridized with Pt 5d, Pd 4d, and Bi 6s; additional contributions from F 2p states appear after F-ion insertion. Notably, the relative intensity of the features at ca. 14 eV for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and ca. 12 eV for Bi_2PdO_4 increases with higher incident photon energy (Fig. 4A and B), suggesting pronounced $6s^2$ contributions derived from bonding and anti-bonding Bi-O interactions.^{25,28,38} As per the revised lone pair model,²⁸ Bi 6s-O 2p bonding states occur deep in the valence band (at ca. 14 eV and ca. 12 eV as shown in Fig. 4F and S10D[†]), whereas Bi 6s, 6p-O 2p antibonding states are positioned at the top of the VB (at ca. 4.0 eV and 3.9 eV), just below Pt 5d-O 2p and Pd 4d-O 2p AB states, respectively. The latter anti-bonding states manifest the stereochemical expression of Bi $6s^2$ lone pairs.^{28,38}

Fig. S10A and B[†] contrast analogous spectra acquired at 2 and 5 keV for Bi_2PdO_4 and $\text{Bi}_2\text{PdO}_4\text{F}_x$. At an incident photon energy of 2 keV, where considerable spectral weight derives from transition metal d-states, VB HAXPES spectra show a notable decrease in the intensity of the states at the VB maximum upon fluoride-ion insertion. The loss of intensity at the valence band maximum corresponds to emptying of filled Pd/Pt 4d/5d states at the valence band edge upon oxidative F-ion

insertion. Bonding Pt 5d-O 2p and Pd 4d-O 2p are concomitantly shifted to higher binding energies, which further corroborates oxidation of Pt and Pd centers, respectively. COHP analyses of Pt-O and Pd-O interactions in Fig. 4E and S10C[†] illustrate that fluoride-ion insertion significantly reduces Pt 5d-O 2p and Pd 4d-O 2p anti-bonding interactions at the valence band maximum, while introducing new anti-bonding interactions at the bottom of the conduction band in the case of Pt 5d-O 2p.

Conversely, VB HAXPES spectra acquired at an incident photon energy of 5 keV, which feature enhanced contributions from Bi $6s^2$ states show the opposite trend upon fluoride-ion insertion.^{28,47,48} The occupied electronic states at the valence band edge are higher for the F-ion-inserted compounds as compared to the pristine $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 insertion hosts (Fig. 4F and S10D[†]). With the loss of anti-bonding Pt/Pd-O 2p states, the lone-pair-derived anti-bonding states constitute the valence band edge. Furthermore, new Bi-F-derived bonding and anti-bonding interactions appear with the latter contributing considerable spectral weight at the valence band maximum. Fig. S12[†] shows that Bi-F anti-bonding interactions emerge at higher binding energies as compared to Bi-O interactions.

In contrast to La-ions in LaSrMnO_4 and La_2CoO_4 , which primarily play a structural role, stereochemically active Bi^{3+} centers play an important role in facilitating F-ion (de)insertion. Energy-variant HAXPES spectra in Fig. 4 provide insights into the modification of hybrid Bi 6s, Bi 6p-O 2p states upon fluoride-ion insertion. Upon fluoride-ion insertion, the Bi $6s^2$ lone pairs are further hybridized with F 2p states near the VBM in the mixed anion compound as evident in Fig. 4D and S10B[†] (which have been assigned with the help of COHP analyses in Fig. S12A and S12B[†]). F 2p states are nominally lower in energy as compared to O 2p states because of the higher electronegativity of fluorine as compared to oxygen. As such, given the lower ΔE_{s-p} values, these states are well positioned to hybridize with filled Bi $6s^2$ states through dative covalent interactions.⁴⁹ The electron lone pairs on fluoride-ions back-donate electron density to the Bi centers.⁵⁰ COHP analysis of Bi-O interactions in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ (Fig. 4F and S12A[†]) and $\text{Bi}_2\text{PdO}_4\text{F}_x$ (Fig. S10D and S12B[†]), reveals these newly occupied Bi 6s, 6p-O 2p lone pair states at the VBM, alongside the Bi 6s, 6p-F 2p lone pair states. Considering that Bi 6s, 6p-O 2p lone pair states have a strong antibonding character at the VBM, addition of electron density upon fluoride-ion insertion results in the decrease of the Bi-O bond order, which is evident in the elongation of Bi-O bonds (Tables S8 and S9[†]). Notably, the Pb $6s^2$ lone pairs exhibit stronger lone pair distortions as compared to Bi $6s^2$ for both oxide and fluoride ion interactions, as can be quantified by the fractional contribution of O 2p states to the lowest valence band metal ns state.^{28,38,39} Comparing PbO and Bi_2O_3 , Walsh and co-workers have determined values of ca. 0.4 and 0.2, respectively, attesting to the much stronger anion hybridization of Pb $6s^2$ states. This differential contributes to the larger lattice contraction observed for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ as compared to $\text{Bi}_2\text{PdO}_4\text{F}_x$.





Fig. 4 Evolution of the electronic structure of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 upon F-ion insertion, examined using valence-band HAXPES and COHP analysis. Overlay of valence-band HAXPES spectra collected at incident photon energies of 2.0 keV and 5.0 keV for (A) $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ (Pb $6s^2$ states also contribute to bonding (B) and anti-bonding (AB) interactions) and (B) Bi_2PdO_4 . Differentials in spectral weight as a function of incident photon energy are shaded in light blue. High-resolution HAXPES data collected for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ at incident photon energy of (C) 2 keV and (D) 5 keV. All valence-band HAXPES spectra have been normalized to internal core level $\text{Bi } 5d_{5/2}$ peak at a binding energy of 24 eV near the valence band. COHP analysis of (E) Pt–O and (F) Bi–O interactions.

To further examine the changes in electronic and atomistic structure resulting from F-ion insertion, we have calculated charge density differences (CDD) and electron localization

function (ELF) plots for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 before and after fluoride-ion insertion. Fig. 5A, B, S13A and B† illustrate the ELFs for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 with and without inserted



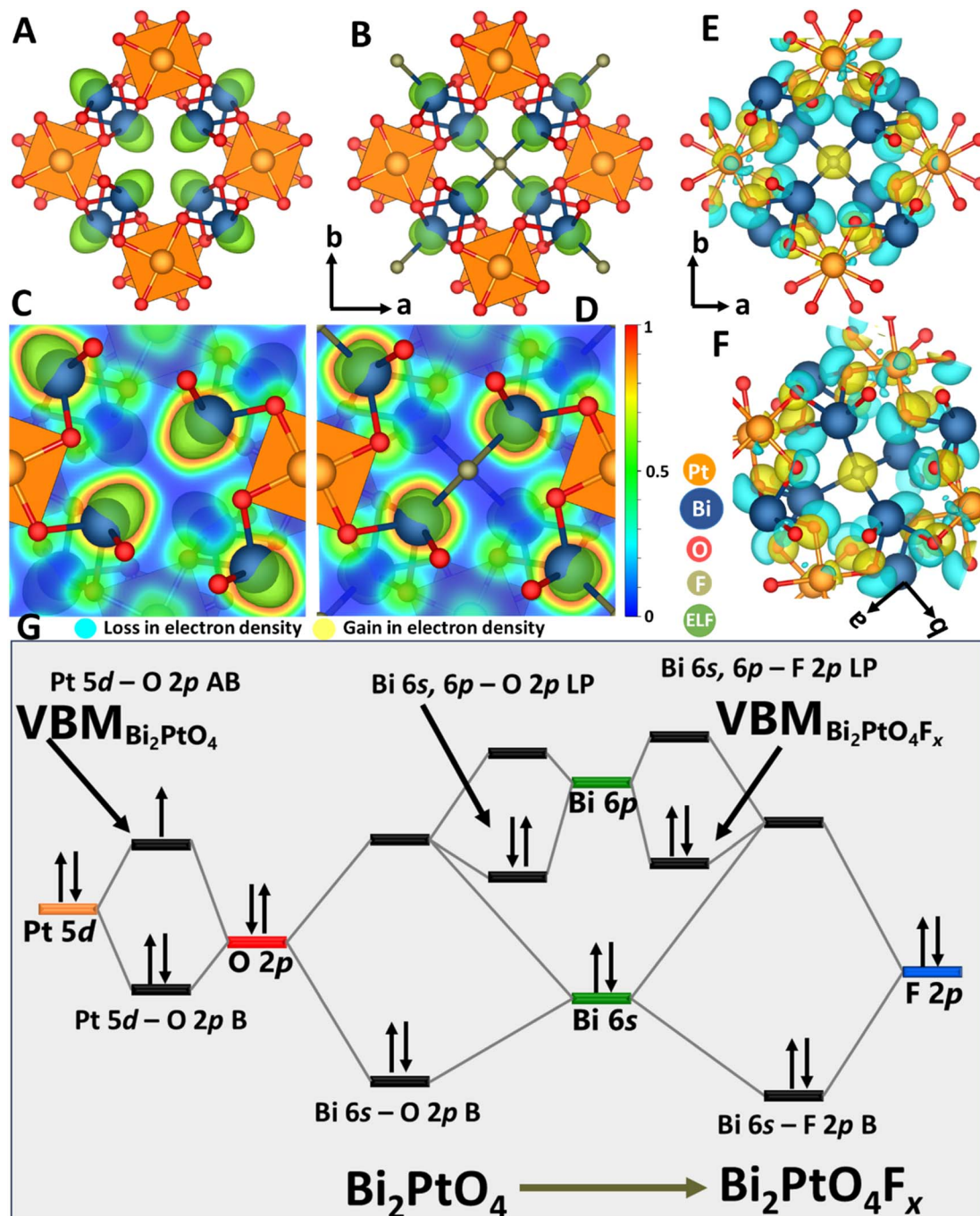


Fig. 5 Charge distribution and molecular orbital perspective of topochemical fluoride-ion insertion. Electron localization function (ELF) map of (A) $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$, and (B) $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$. A 2-D cross-section of the 3-D ELF map shown in (C) A and (D) B. (E) Charge density difference (CDD) of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ with a fluoride ion inserted. (F) Charge redistribution around the oxidized Pt atoms. (G) Molecular orbital sketch showing the relative position of Bi 6s, 6p–O 2p, and Bi 6s, 6p–F 2p lone pair states relative to the Pt 5d–O 2p AB states.

fluoride-ions. The stereochemical expression of Bi $6s^2$ lone pairs in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PtO_4 define the 1D open tunnels (Fig. 5A and S13A[†]). After insertion of a fluoride-ion, repulsions between Bi–O and Bi–F bonding pairs induce significant polarization of Bi $6s^2$ electron density in the vicinity of the fluoride-ion (Fig. 5B and S13B[†]). Additionally, Fig. 5C, D, S13C and D[†] present a 2D cross-section of the 3D ELF map shown in

Fig. 5A, B, S13A and B[†] highlighting the local changes in Bi $6s^2$ electron density upon fluoride-ion bonding.

CDD induced as a result of F-ion insertion have been plotted in Fig. 5E and F, S13E and F[†] as per

$$\Delta\rho(r) = \rho_{\text{Bi}_2\text{MO}_4\text{F}_{0.25}}(r) - \rho_{\text{Bi}_2\text{MO}_4}(r) - \rho_{\text{F}}(r) \quad (7)$$



where $\rho_{\text{Bi}_2\text{MO}_4\text{F}_{0.25}}(r)$ represents the charge density for a $1 \times 1 \times 2$ Bi_2MO_4 superlattice inserted with one fluoride-ion; and $\rho_{\text{Bi}_2\text{MO}_4}(r)$ is the charge density acquired for a Bi_2MO_4 unit cell without F-ion insertion. Fig. 5E and S13E† depict a fluoride-ion in a tetrahedral interstitial site bonded to four pendant Bi atoms. A modest charge redistribution is observed at each of the Bi centers, which reflects distortion of the Bi $6s^2$ lone pair upon fluoride-ion insertion. More significant redistribution of electron density is observed around the Pt and Pd centers. Fig. 5E, F, S13E and F† demonstrate changes in electron density on the Pt and Pd atoms, indicating a gain of electron density along Pt–O and Pd–O bonds, consistent with the strengthening of bond lengths seen in EXAFS measurements, and transition metal oxidation observed in core-level HAXPES and Pt L_{III} -edge and Pd K-edge XANES measurements.

Fig. 5G sketches a simplified molecular orbital diagram to summarize the electronic structure modulation of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 upon fluoride-ion insertion based on electronic structure calculations in conjunction with HAXPES, XANES, and COHP analysis. Anti-bonding Pt $5d\text{--}O$ $2p$ and Pd $4d\text{--}O$ $2p$ states are the highest occupied states in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 respectively, as also observed in the DOS plots in Fig. S11A and S11C.† These states are positioned in close proximity of but higher in energy as compared to Bi $6s^2$ -derived lone-pair states. Fluoride-ion insertion results in oxidation of Pt and Pd, which brings about loss of electron density from the Pt $5d\text{--}O$ $2p$ and Pd $4d\text{--}O$ $2p$ AB states at the valence band edge. Oxidation of the transition metal centers is observed as contraction of Pt–O and Pd–O bonds in powder XRD and EXAFS measurements. Filled Bi–F AB states emerge at the VBM as F-ions form dative covalent bonds with Bi atoms lining the edges of the 1D tunnel. The BiO_6LP polyhedra is transformed to a distorted BiO_6FLP polyhedra, with considerable polarization of the Bi $6s^2$ lone pair density.^{23,51} In essence, the polarization of Bi lone pairs stabilizes the inserted F-ions within the 1D tunnel of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 and mediates the redox reaction at the Pt and Pd centers (Fig. 4, S10 and S12†). The repulsions between Bi $6s^2$ and F $2p$ lone pairs yield a relatively weak Bi–F bond that can be formed and broken at room temperature. As such, the stereochemical expression of the Bi $6s^2$ lone pair is pivotal to enabling bulk diffusion and homogenous F-ion insertion as observed in the EDS data.

Conclusions

In summary, we evidence reversible room-temperature topochemical insertion and bulk diffusion of fluoride-ions in tetragonal $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4$ and Bi_2PdO_4 . Solution-phase fluoridation using XeF_2 yields a nominal fluoride-ion stoichiometry of $x \approx 0.5$ in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{PtO}_4\text{F}_x$ and $\text{Bi}_2\text{PdO}_4\text{F}_x$; fluoride-ions can be extracted by reaction with *n*-butyllithium at room-temperature. Powder XRD measurements reveal that the inserted F-ions reside in interstitial sites within one-dimensional tunnels defined by electrostatic repulsions between stereochemically active $6s^2$ electron lone pairs of four bismuth centers. Fluoride-ion insertion is mediated by oxidation of Pt and Pd centers and brings about a modest contraction of the

unit cell volume (<1% change), a significant improvement over conventional conversion electrodes, suggesting potential viability as an insertion electrode for fluoride-ion batteries.

Based on X-ray scattering and spectroscopy characterization of modulations of local atomistic and electronic structure upon fluoride-ion insertion, several fundamental design principles can be delineated. While Pt and Pd centers mediate redox reactions, the stereochemically active lone pair electrons of Bi^{3+} play a critical role in facilitating reversible fluoride-ion diffusion. Although Bi centers are not formally oxidized, Bi $6s^2$ (and Pb $6s^2$) electron lone pairs interact with F $2p$ states, resulting in the emergence of new states in the valence band. The inserted fluoride-ions polarize the Bi $6s^2$ lone pairs and donate electron density through covalent dative interactions, thereby weakening Bi–O bonds. The repulsions between Bi $6s^2$ and F $2p$ lone pairs in BiO_6FLP polyhedra gives rise to a relatively weak Bi–F bond, which can be formed and broken at room temperature resulting in facile F-ion diffusion along 1D tunnels. Decoupling the transition metal (Pt, Pd) redox-active center from the fluoride-ion coordination site (Bi) enables the uniform distribution of the structural distortions between the Pt/PdO₄ and BiO_4 structural units within the lattice, which is critical to the small volume change and topochemical nature of anion insertion. As such, insertion hosts combining transition metal redox centers with p-block cations expressing stereochemical activity represent a promising design motif for fluoride-ion insertion batteries. Future work will explore electrochemical fluoridation in full cell configurations and implement *operando* cells for X-ray spectroscopy and scattering investigations under electrochemical fluoridation from solid or liquid electrolytes.

Data availability

All experimental procedures, computational sections, and associated data are included in the article and ESI.†

Author contributions

S. B. directed the research. G. A. and S. B. conceptualized and designed the experiments. G. A. conducted and analyzed the data from powder X-ray diffraction. G. A. performed Rietveld analysis of the powder X-ray diffraction data. A. P., W. Z., and S. P. performed and analyzed the DFT calculations. G. A., S. H., A. G., and J. D. P. conducted and analyzed the data from HAXPES, EXAFS, and XANES. C. W., C. J., and D. A. F. helped with setting up HAXPES and XANES experiments and data collection. S. G. A. conducted the magnetic measurements and analyzed the data. J. R. A. conducted and analyzed the data from EDS. G. A. and S. B. contributed to writing the paper. H. S. B., M. A., G. A., and S. B. revised the paper. All authors discussed the results and contributed to the manuscript preparation.

Conflicts of interest

There are no conflicts to declare.



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