# Stereochemical Expression of Bi 6s<sup>2</sup> Lone Pairs Mediates Fluoride-ion (De)insertion in a tunnel-structured Bi<sub>2</sub>PdO<sub>4</sub> and Bi<sub>1.6</sub>Pd<sub>0.4</sub>PtO<sub>4</sub>

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#### **Experimental Section**

**Synthesis of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub>:** Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub> were synthesized via solidstate methods by adapting previously reported methods.<sup>1,2</sup> Previous work by Bettahar *et al.* has established the need for Pb-alloying to stabilize the Pt analogue.<sup>1,3</sup> Briefly, Bi<sub>2</sub>PdO<sub>4</sub>, and Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> were prepared by mixing stoichiometric amounts of Bi<sub>2</sub>O<sub>3</sub> powder (Strem chemicals, 99 % purity), PdO powder (Sigma-Aldrich, 99 % purity), PbO powder (Sigma-Aldrich, 99 % purity), and elemental platinum (Sigma-Aldrich, 99.995 % purity). The mixture was ballmilled in a Spex Certiprep ball-mill for 30 min using yttrium-stabilized zirconia balls as the milling media. The mixtures were pressed into 6 mm pellets using 1/4-inch (I.D.) dry pellet pressing die (EQ-Die-06D-B, MTI Corporation). The resulting pellets were placed in a fused silica ampoule and sealed under vacuum (0.1 MPa). The ampoules were heated to 730°C for 12 h, and then cooled to room temperature at 3 °C/h. The recovered powders of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub> appeared as well-crystallized, fine brownish powders with a uniform color and consistent texture, indicating high crystallinity and purity.

**Fluoride-ion insertion in Bi**<sub>1.6</sub>**Pb**<sub>0.4</sub>**PtO**<sub>4</sub> and Bi<sub>2</sub>**PdO**<sub>4</sub>: All fluoride-ion insertion and deinsertion reactions were performed in an argon-filled glovebox, maintained at O<sub>2</sub> and H<sub>2</sub>O levels of <0.1  $\mu$ L/L and <0.1  $\mu$ L/L, respectively. A 35 mL aliquot of dry acetonitrile (Millipore Sigma, 99.9 % purity, <50  $\mu$ L/L H<sub>2</sub>O) was added to a 100 mL round bottom flask. 0.35 g of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub> was added to the flask along with a two-fold molar excess amount of XeF<sub>2</sub> (Thermo Scientific, 99.5 % purity) at 23 °C. The mixture (placed in 3-neck round bottom flux and closed with a septum and a condenser) was refluxed in acetonitrile and stirred at 23 °C for 24 h on a Schlenk line under an argon ambient. The excess acetonitrile was decanted, and the resulting fluoridated product, black/dark brown in color was washed three times with 10 mL acetonitrile. The powder was dried and stored in a sample vial, which was then placed in a drawer at room temperature for further characterization.

**Defluoridation of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub> and Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub>**: A 0.1 g sample of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub> and Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub> was mixed with a molar excess of *n*-BuLi (Sigma-Aldrich) (in hexanes (Supelco, 95 % purity)) in a 1:5 ratio. The mixture (placed in 3-neck round bottom flux and closed with a septum and a condenser) was refluxed in hexanes and stirred at 23 °C for 24 h under a Schlenk line under an argon environment. Excess hexanes supernatant were decanted, and the obtained product was washed with hexanes and decanted thrice to remove any unreacted *n*-BuLi using a centrifuge. Each washing cycle involved stirring the powder in hexanes for 10 min. The solid product was then allowed to dry in an air ambient for 48 h at 23 °C.

#### **Structure Elucidation**

Powder X-ray diffraction (XRD) data were collected using a using a Bruker D8-Focus diffractometer (Cu K $\alpha$ :  $\lambda$  = 1.5418 Å; 40 kV voltage; 25 mA current). Data were collected over the angle range 10° ≤ 2 $\vartheta$  ≤90° with a step width of 0.008° and step rate of 0.0557°/s at room temperature. Rietveld refinements were performed using FULLPROF software.<sup>4</sup> Atomic positions, profile terms, lattice parameters, and inserted metal occupancies were refined from laboratory XRD data using isotropic thermal parameters. All crystal structure renditions were prepared using the Vesta III software suite (JP-Minerals).<sup>5</sup>

#### **Electron Microscopy**

Scanning electron microscopy (SEM) images of  $Bi_{1.6}Pb_{0.4}PtO_4F_x$  and  $Bi_2PdO_4F_x$  were obtained using a JEOL JSM-7500F FE-SEM equipped with an Oxford energy-dispersive X-ray spectrometer (EDS). SEM images were collected at an accelerating voltage of 5 kV; EDS spectra were collected at an accelerating voltage of 20 kV. Low-magnification transmission electron microscopy (TEM) images were collected using a JEOL JEM-2010 electron microscope at an operating voltage of 200 kV. Prior to imaging, powder materials were affixed to conductive carbon tape (SEM) or dispersed in 2-propanol and drop-cast onto a copper grid (TEM).

#### **HAXPES Measurements**

HAXPES measurements were performed at the National Institute of Standards and Technology (NIST) beamline SST-2 of the National Synchrotron Light Source II of Brookhaven National Laboratory. Measurements were performed at approximately 2 keV photon energy with a pass energy of 200 eV and a step size of 0.85 eV with the analyzer axis oriented parallel with the photoelectron polarization vector. HAXPES data at 5 keV was collected with a 500 eV energy filter. The higher excitation energy of HAXPES circumvents deleterious charging issues that are ubiquitous in ultraviolet and soft X-ray photoelectron spectroscopy.<sup>6</sup> Photon energy selection was accomplished using a double Si (111) crystal monochromator. No evidence of charging was observed during our measurements. The beam energy was aligned to the Fermi level of a silver foil before measurements.

#### **Magnetic Measurements**

Magnetic measurements of  $Bi_{1.6}Pb_{0.4}PtO_4$  and  $Bi_2PdO_4$  powders and their fluoridated variants were carried out on a Quantum Design Magnetic Property Measurement System using the Quantum Design superconducting quantum interference device (SQUID) magnetometer option. Both zero-field cooled (ZFC) and field-cooled (FC) measurements were performed in the temperature range of 2 K and 400 K with an applied field up to 0.1 T. Field-dependent magnetization measurements were performed at 2K and above room temperature under an applied magnetic field ranging from -7 T to +7 T.

#### **Computational Methods**

Electronic structure calculations were performed using density functional theory as implemented in the Vienna ab initio simulation package (VASP).<sup>7–9</sup> Initial atomic positions for  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ ,  $Bi_2PdO_4F_x$ ,  $Bi_{1.6}Pb_{0.4}PtO_4$ , and  $Bi_2PdO_4$  were obtained from structure solutions derived from highresolution powder XRD. The projected augmented wave (PAW) formalism was used to model electron-ion interactions.<sup>10</sup> A kinetic energy cutoff of 520 eV was used for plane-wave basis restriction. Electronic exchange and correlation effects were included using the generalized gradient approximation based on the Perdew–Burke–Ernzerhof functional (GGA-PBE).<sup>11</sup> A Hubbard correction of U = 6.0 eV was used to account for strong electron correlation in the Pt 5*d* and Pd 4*d* electrons as benchmarked in a previous study.<sup>12</sup> A Monkhorst–Pack reciprocal grid of 3×3×4 points was used for the relaxation of 1×1×2 supercell structures. The structures were relaxed when each Cartesian force component was less the 0.01 eV/Å unless otherwise noted. Electron localization function plots were produced by the VASP output in Vesta.<sup>13</sup> COHP analyses were performed using the software package Local Orbital Suite Toward Electronic-Structure Reconstruction (LOBSTER).<sup>14–16</sup> LOBSTER-recommended basis functions were used for the projection calculations accounting for 2*s* and 2*p* orbitals of oxygen and fluorine; 4*d* and 5*s* orbitals of palladium; 5*d* and 6*s* orbitals of platinum; and 5*d*, 6*s*, and 6*p* orbitals of Bi. The absolute charge spilling is <1.96 % in all cases.

### Hard X-ray XANES and EXAFS Spectroscopy

Pd K-edge and Pt L<sub>III</sub>-edge X-ray absorption spectroscopy scans were acquired on beamline 7-BM of the National Synchrotron Light Source II of Brookhaven National Laboratory. Samples were prepared for analyses by uniformly spreading powders onto a piece of polyimide tape. The tape was then loaded onto a metal bar sample holder, and 20 scans were performed at 30 s per scan and subsequently averaged to improve the signal-to-noise ratio. Before sample acquisition, the beamline was calibrated by placing vanadium, copper and lead foils and measuring the edge position. Both fluorescence yield and transmittance data were collected for each sample. The Athena suite from the IFEFFIT package was used for data sanitization. Data in the k-range of 2.5 Å<sup>-1</sup> to 11.0 Å<sup>-1</sup> were Fourier transformed to obtain R-space data. The R-space data were used to perform shell fitting. Fittings were performed for Pt—O, Pt—Pt shells in the R-space range from 1.1 Å to 4.0 Å. Multishell least-squares fitting of Pd K- and Pt L<sub>III</sub>-edge EXAFS data were performed using the ARTEMIS module of the IFEFFIT software package.<sup>17</sup> The photoelectron mean free path, scattering amplitude, and phase functions were calculated using the FEFF6 program. Atomic coordinates and lattice parameters obtained from crystallography data were used to build initial models for EXAFS fitting.

#### Soft X-ray XANES Spectroscopy

Fluorine and oxygen K-edge XANES spectroscopy measurements were carried out at the National Synchrotron Light Source II of Brookhaven National Laboratory beamline SST-1 operated by the National Institute of Standards and Technology with a spot size of 25  $\mu$ m and a detector grid bias of -300 V. An electron flood gun was used to prevent sample charging. Measurements were performed in partial electron yield (PEY) mode with a nominal resolution of 0.1 eV. The PEY signal was normalized to the incident beam intensity of a clean gold grid to eliminate the effects of any incident beam fluctuations and optics absorption features.



Figure S1. Crystal structure representations of  $Bi_2PdO_4$  and  $Bi_{1.6}Pb_{0.4}PtO_4$  illustrating the coordination environment of bismuth centers. (A, B) Bi adopts a capped trigonal prismatic geometry characterized by 6 Bi—O bonds and one electron lone pair. The two long Bi–O (2.803 Å) interactions omitted from Figure 1 are included here to show the full Bi connectivity. (C) Expanded view of the framework. (D) Views down the crystallographic b axis which shows chains of edgesharing square planar MO<sub>4</sub> joined by corner-sharing BiO<sub>6</sub> octahedra.



**Figure S2.** Structure elucidation of  $Bi_2PdO_4$  and  $Bi_{1.6}Pb_{0.4}PtO_4$ . Powder XRD patterns collected for (A)  $Bi_{1.6}Pb_{0.4}PtO_4$  and (B)  $Bi_2PdO_4$ . Rietveld refinement of powder XRD data collected for (C)  $Bi_{1.6}Pb_{0.4}PtO_4$  and (D)  $Bi_2PdO_4$ . Refinement statistics, lattice parameters, and atom positions for the refinements of (C)  $Bi_{1.6}Pb_{0.4}PtO_4$  and (D)  $Bi_2PdO_4$  and (D)  $Bi_2PdO_4$  are provided in Tables (S1, S6, S8) and (S2, S7, S9), respectively.

Table S1. Atom positions, fractional occupancies, and thermal parameters obtained from Rietveld refinement of the pristine Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>. Refinement statistics and lattice parameters are included in the table header.

α = b = 8.7617(4) Å, c = 5.6644(2) Å, α = β = γ = 90°; Volume = 435.01(3) Å <sup>3</sup> ; χ2 = 3.076; R <sub>wp</sub> = 8.70 %; R <sub>w</sub> = 6.25 %								
Atom Label	AtomSiteLabelMultiplicityxYzUiso*100							
Bi	8 -0.0862(12) 0.0863(13) 0.2500 1.13(11)							
Pb	Pb 8 -0.0862(12) 0.0863(13) 0.2500 1.25(10)							
Pt	Pt 4 0.2500 0.2500 0.0871(5) 1.30(14)							
0	16	0.4726(19)	0.1369(18)	0.1131(3)	2.41(13)			

Table S2. Atom positions, fractional occupancies, and thermal parameters obtained from Rietveld refinement of the pristine Bi<sub>2</sub>PdO<sub>4</sub>. Refinement statistics and lattice parameters are included in the table header.

a = b = 8.6220(4) Å, $c = 5.9070(3)$ Å, $α = β = γ = 90^{\circ}$ ; Volume = 439.12(2) Å <sup>3</sup> ; $\chi 2 = 3.110$ ; $R_{wp} = 8.01$ %; $R_w = 6.21$ %								
Atom Label	AtomSiteLabelMultiplicityxYzUiso*100							
Bi	Bi 8 -0.0794(8) 0.0794(8) 0.2500 1.16(1)							
Pd	Pd 4 0.2500 0.2500 0.0819(5) 1.16(3)							
0	O 16 0.4580(2) 0.1400(2) 0.0890(2) 2.17(7)							



Figure S3. Structure evolution of  $Bi_2PdO_4$  and  $Bi_{1.6}Pb_{0.4}PtO_4$  upon fluoride-ion insertion and deinsertion. (A) Comparison of powder XRD patterns collected for  $Bi_2PdO_4$ ,  $Bi_2PdO_4F_x$ , and  $Bi_2PdO_4$ recovered after treatment with n-butyllithium. Expanded views showing evolution of (B) the (411) and (420) reflections of  $Bi_{1.6}Pb_{0.4}PtO_4$ ; (C) the (110) and (200) reflections; and (D) the (220) and (002) reflections of  $Bi_2PdO_4$  upon F-ion insertion and deinsertion, respectively.



**Figure S4. Structure elucidation of fluoridated,**  $Bi_2PdO_4F_x$  and  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ . Rietveld refinement of powder X-ray diffraction data collected for (A)  $Bi_{1.6}Pb_{0.4}PtO_4F_x$  and (B)  $Bi_2PdO_4F_x$ . For fluoridated  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ , a broad reflection marked with an asterisk appears (\*) at  $2\vartheta = 27^\circ$  attributed by Kageyama et al to an interphasic product.<sup>18,19</sup> Refinement statistics, lattice parameters, and atom positions for the refinements of  $Bi_{1.6}Pb_{0.4}PtO_4F_x$  and  $Bi_2PdO_4F_x$  are shown in Tables (S3, S6, S8) and (S4, S7, S9) respectively.

Table S3. Atom positions, fractional occupancies, and thermal parameters obtained from Rietveld refinement of the  $Bi_{1.6}Pb_{0.4}PtO_4F_x$  structure. Refinement statistics and lattice parameters are included in the table header.

Atom Label	AtomSitexyZUiso*100OccupancyLabelMultiplicityxyZUiso*100Occupancy								
Bi	Bi 8 -0.0870(19) 0.0870(19) 0.2500 1.48(16) 0.80								
Pb	Pb 8 -0.0870(19) 0.0870(19) 0.2500 1.48(16) 0.20								
Pt	Pt 4 0.2500 0.2500 0.0869(6) 5.40(20) 1.00								
0	16	0.6380(2)	0.5290(2)	0.1491(5)	3.30(10)	1.00			
F	4	0.2500	0.7500	0.00000	1.26(11)	0.51(5)			

Table S4. Atom positions, fractional occupancies, and thermal parameters obtained from Rietveld refinement of the  $Bi_2PdO_4F_x$  structure. Refinement statistics and lattice parameters are included in the table header.

a = b = 8.7392(2) Å, $c = 5.7492(16)$ Å, $α = β = γ = 90^{\circ}$ ; Volume = 439.082(19) Å <sup>3</sup> ; $\chi 2 = 3.012$ ; $R_{wp} = 7.05$ %; $R_w = 5.44$ %									
Atom Label	AtomSiteLabelMultiplicityxyZUiso*100Occupancy								
Bi	Bi 8 0.91750 0.0829 0.2500 2.10(6) 1.00								
Pd	Pd 4 0.2500 0.2500 0.0873 2.00(12) 1.00								
0	16	0.4552	0.1436	0.0787	2.50(6)	1.00			
F	4	0.2500	0.7500	0.0000	4.40(19)	0.50(8)			



**Figure S5. Energy dispersive X-ray spectroscopy mapping analysis of Bi**<sub>1.6</sub>**Pb**<sub>0.4</sub>**PtO**<sub>4</sub>**F**<sub>x</sub>. Energy dispersive X-ray spectrum acquired for Bi<sub>1.6</sub>**Pb**<sub>0.4</sub>**PtO**<sub>4</sub>**F**<sub>x</sub> (top left). Elemental mapping showing (top right and bottom panels) superimposed maps and spatial distribution of Pt, O, F, Pb, and Bi.



**Figure S6. Energy dispersive X-ray spectroscopy mapping analysis of Bi\_2PdO\_4F\_x.** Energy dispersive X-ray spectrum acquired for  $Bi_2PdO_4F_x$  (top left). Homogenous spatial distribution of inserted fluoride-ions in the synthesized material (top right). Elemental mapping showing (bottom panels) superimposed maps and spatial distribution of Pd, F, and Bi.

Lattice Parameter	Bi <sub>1.6</sub> Pb <sub>0.4</sub> PtO <sub>4</sub>	Bi <sub>1.6</sub> Pb <sub>0.4</sub> PtO <sub>4</sub> F <sub>x</sub>	Bi <sub>1.6</sub> Pb <sub>0.4</sub> PtO <sub>4</sub> _n-BuLi
a = b (Å)	8.7617(4)	8.8121(9)	8.7598(3)
<i>c</i> (Å)	5.6644(2)	5.4243(5)	5.6526(1)
V (ų)	435.01(3)	434.84(5)	435.52(2)

Table S6. Lattice constants obtained from fitting lattice parameters of the powder X-ray diffraction patterns for Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>, Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub>, and Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> recovered.

Table S7. Lattice constants obtained from fitting lattice parameters of the powder X-ray diffraction for  $Bi_2PdO_4$ ,  $Bi_2PdO_4F_x$ , and  $Bi_2PdO_4$  recovered.

Lattice Parameter	Bi <sub>2</sub> PdO <sub>4</sub>	Bi <sub>2</sub> PdO <sub>4</sub> F <sub>x</sub>	Bi <sub>2</sub> PdO <sub>4</sub> _n-BuLi
a = b (Å)	8.6220(4)	8.7392(2)	8.6192(6)
<i>c</i> (Å)	5.9070(3)	5.7492(16)	5.8923(10)
V (ų)	439.12(2)	439.082(19)	439.15(7)



**Figure S7.** Local structure of Bi<sub>2</sub>PdO<sub>4</sub>/Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub> and Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>/Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub> as derived from **EXAFS Spectroscopy:** R-space data with their respective fitting profiles for (A) Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>, (B) Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub>, (C) Bi<sub>2</sub>PdO<sub>4</sub>, and (D) Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub>. EXAFS fitting was performed with four equal fitting parameters for both the pristine and fluoridated compounds. The fitting window was kept constant in all four systems. The fitting results related to the primary scattering paths are provided in Table S5. (E) Structural models of the Pt local coordination environment generated from fitted EXAFS data for Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>2</sub>PtO<sub>4</sub>F<sub>x</sub>. (F) Structural models of the Pd coordination environment generated from fitted EXAFS data for Bi<sub>2</sub>PdO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub>.

Table S5. Tabulated Pt L<sub>3</sub>-edge and Pd K-edge EXAFS fitting parameters of Bi<sub>2</sub>PdO<sub>4</sub>/Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub> and Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>/Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub>. Atom positions obtained from Rietveld refinement of high-resolution powder X-ray diffraction patterns (Tables S1—S4) were used as initial structural models to fit the EXAFS data.

Sample	Path	N	R(Å)	σ²	<b>S</b> <sub>0</sub> <sup>2</sup>	E <sub>0</sub> (eV)	R-factor (%)
				(Å) <sup>2</sup>			
Bi <sub>2</sub> PtO <sub>4</sub>	Pt—O	4	2.000	0.001	0.9	8.24 ± 3.50	0.50
	Pt—Pt	4	2.821	0.001			
Bi <sub>2</sub> PtO <sub>4</sub> F <sub>x</sub>	Pt—O	4	1.986	0.003	0.9	3.21 ± 1.57	0.55
	Pt—Pt	4	2.774	0.003			
Bi <sub>2</sub> PdO <sub>4</sub>	Pd—O	4	2.010	0.002	0.9	7.71 ± 1.45	0.65
	Pd—Pd	4	2.987	0.002			
Bi <sub>2</sub> PdO <sub>4</sub> F <sub>x</sub>	Pd—O	4	1.991	0.010	0.9	8.02 ± 1.99	0.75
	Pd—Pd	4	2.869	0.010			



Figure S8. Soft X-ray spectroscopy characterization of topochemical fluoridation of  $Bi_2PdO_4/Bi_2PdO_4F_x$ and  $Bi_{1.6}Pb_{0.4}pto_4/Bi_{1.6}Pb_{0.4}Pto_4f_x$ . XANES spectra spanning the F K-edge and Bi  $N_{III}$ -edge for (A)  $Bi_{1.6}Pb_{0.4}PtO_4F_x$  and (B)  $Bi_2PdO_4F_x$ . (C) XANES spectra spanning the Pt  $N_{III}$ -edge and O K-edge for  $Bi_{1.6}Pb_{0.4}PtO_4$ , and  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ . (D) XANES spectra spanning the Pd  $M_{III}$ -edge and O K-edge for  $Bi_2PdO_4$ , and  $Bi_2PdO_4F_x$ .



Figure S9. Mapping bulk fluoridation in  $Bi_2PdO_4$  and  $Bi_{1.6}Pb_{0.4}PtO_4$ , upon fluoride-ion insertion using HAXPES. High-resolution core-level F 1s HAXPES spectra acquired for (A)  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ , and (B)  $Bi_2PdO_4F_x$  at incident photon energies of 2.0 keV.



**Figure S10. Evolution of the electronic structure of Bi\_2PdO\_4 upon F-ion insertion**. High-resolution HAXPES spectra collected for  $Bi_2PdO_4$ , and  $Bi_2PdO_4F_x$  at an incident photon energy of **(A)** 2 keV, and **(B)** 5 keV. COHP analyses of **(C)** Pt-O, **(D)** Bi-O interactions in  $Bi_2PdO_4$ , and  $Bi_2PdO_4F_x$ . Interactions are plotted such that B interactions between two species are negative along the y-axis, whereas AB interactions are positive along the y-axis.



**Figure S11. Electronic structure modulation of**  $Bi_2PdO_4$  **and**  $Bi_{1.6}Pb_{0.4}PtO_4$  **upon F-ion insertion**. Total and atom-projected density of states calculated using density functional theory for **(A)**  $Bi_{1.6}Pb_{0.4}PtO_4$ , **(B)**  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ , **(C)**  $Bi_2PdO_4$ , and **(D)**  $Bi_2PdO_4F_x$ . The total density of states is plotted in green. Atom projected density of states for Pt, Pd, Bi, and O are plotted in gold, orange, black, and blue, respectively. The atom-projected density of states plots indicates that Pt–O and Pd–O hybrid states lie at the top of the valence band, higher in energy than the Bi–O states, and are thus preferentially oxidized upon F-ion insertion. Upon oxidation, Pt 5d – O 2p and Pd 4d – O 2p hybrid states appear at the bottom of the conduction band.



Figure S12. Evolution of the electronic structure of  $Bi_{1.6}Pb_{0.4}PtO_4$  and  $Bi_2PdO_4$  upon F-ion insertion. Comparison of Bi-F and Bi-O interactions in (A)  $Bi_{1.6}Pb_{0.4}PtO_4F_x$ , and (B)  $Bi_2PdO_4F_x$ .

Table S8. Bond lengths obtained from Rietveld refinement of Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub> and Bi<sub>1.6</sub>Pb<sub>0.4</sub>PtO<sub>4</sub>F<sub>x</sub>.

Polyhedron	Bond Vector	Bi <sub>1.6</sub> Pb <sub>0.4</sub> PtO <sub>4</sub> (Å)	Bi <sub>1.6</sub> Pb <sub>0.4</sub> PtO <sub>4</sub> F <sub>x</sub> (Å)
	Pt—O(1)	2.194(17)	2.024(19)
PtO <sub>4</sub>	Pt—O(1)	2.194(17)	2.0234(19)
square planar	Pt—O(1)	2.194(17)	2.0234(19)
	Pt—O(1)	2.194(17)	2.0234(19)
	Bi—O(1)	2.326(17)	2.520(3)
BiO <sub>6</sub>	Bi—O(1)	2.164(17)	2.115(19)
octahedra	Bi—O(1)	2.164(17)	2.115(19)
	Bi—O(1)	2.326(17)	2.520(3)

Table S9. Bond lengths obtained from Rietveld refinement of Bi<sub>2</sub>PdO<sub>4</sub> and Bi<sub>2</sub>PdO<sub>4</sub>F<sub>x</sub>.

Polyhedron	Bond Vector	Bi₂PdO₄ (Å)	Bi₂PdO₄F <sub>x</sub> (Å)
	Pt—O(1)	2.029(18)	2.0206(5)
PtO <sub>4</sub>	Pt—O(1)	2.029(18)	2.0206(5)
square planar	Pt—O(1)	2.029(18)	2.0206(5)
	Pt—O(1)	2.029(18)	2.0206(5)
	Bi—O(1)	2.319(14)	2.2587(5)
BiO <sub>6</sub>	Bi—O(1)	2.141(17)	2.2327(5)
octahedra	Bi-O(1)	2.141(17)	2.2353(5)
	Bi—O(1)	2.319(14)	2.2562(5)



**Figure S13. Mapping charge distribution upon fluoride-ion insertion of Bi<sub>2</sub>PdO<sub>4</sub>. (A)** Electron localization function (ELF) map of (A)  $Bi_2PdO_4$ , and (B)  $Bi_2PdO_4F_x$ . 2-D cross-section of 3-D ELF map shown in (C) A and (D) B. (E) Charge density difference (CDD) of  $Bi_2PdO_4$  with a fluoride ion inserted. (F) Charge redistribution around the oxidized Pd atoms.

## Disclaimer

Commercial names mentioned in this paper are for the purpose of illustration and not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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