# *Supporting Information*

## Dual halogen layers diversify band engineering in Sillén oxyhalide photocatalysts: electronic structure control of $SrBi_3O_4X_3$ (X = Cl, Br, I) *via* halogen substitution

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### Experimental section

#### Materials

$SrCO_3$ (99.99%), BiOCl (95.0%), NaBr (99.5%), NaI (97%), $Bi_2O_3$ (99.9%), $CH_3COONa$ (99.0%), $CH_3COOH$ (99.7%), and $Na_2SO_4$ (99.0%) were purchased from FUJIFILM Wako Pure Chemical. $Bi(NO_3)_3 \cdot 5H_2O$ (99.5 %) was purchased from Kanto Chemical. $SrI_2$ (99.99 %) was purchased from Sigma Aldrich.

#### Sample synthesis

$SrBi_3O_4X_3$ (X = Cl, Br, and I) was prepared *via* solid-state reactions based on previously reported methods.[1,2] $SrBi_3O_4Cl_3$ was synthesized from a stoichiometric mixture of $SrCO_3$ and BiOCl. The mixture was then loaded into an alumina crucible and calcined at 973 K for 12 h in air. $SrBi_3O_4Br_3$ was prepared by heating a pellet of a stoichiometric mixture of $SrCO_3$ and BiOBr in an evacuated silica tube at 1073 K for 12 h. $SrBi_3O_4I_3$ was synthesized by calcining a mixture of $SrI_2$, $Bi_2O_3$, and BiOI in a molar ratio of 1.1:1:1 in an evacuated silica tube at 1073 K for 12 h. We used the as-purchased BiOCl and prepared BiOX (X = Br, I), which was synthesized by following a previously reported soft liquid deposition method.[3]

#### Characterization

Powder X-ray diffraction (MiniFlex II, Rigaku, CuK$\alpha$ X-ray source), UV–visible diffuse reflectance spectrometry (V–650, JASCO), and scanning electron microscopy (SEM; NVision 40, Carl Zeiss-SIINT) were used to characterize the samples. The scanning electron microscope was equipped with an energy-dispersive X-ray spectrometer. VESTA software was used to construct crystal structures.[4]

#### Electrochemical measurements

Mott−Schottky plots were measured using a three-electrode cell equipped with a Pt wire counter-electrode and Ag/AgCl reference electrode in a $Na_2SO_4$ solution (0.1 M, pH = 2.0, adjusted with 0.1 M $H_2SO_4$ aq.) using an electrochemical analyzer (VersaSTAT 4, Princeton Applied Research) with an amplitude of 10 mV and frequency of 500 and 1000 Hz. Electrodes were prepared using the squeegee method. A particulate sample containing a small amount of water was coated onto a fluorine-doped tin oxide conductive substrate and dried overnight at room temperature.

#### DFT calculations

The electronic structures of $SrBi_3O_4X_3$ (X = Cl, Br, I) were calculated using the Cambridge Serial Total Energy Package (CASTEP).[5] The calculated models of $SrBi_3O_4X_3$ assumed that $Bi^{3+}$ and $Sr^{2+}$ are ordered at the Bi2/Sr2 site in a $\sqrt{2}\times\sqrt{2}\times1$ supercell (Fig. S5). The Perdew–Burke–Ernzerhof functional (PBE)

generalized gradient approximation (GGA) was used as the exchange-correlation functional,[6] and the electronic states were expanded using a plane-wave basis set with a cutoff of 630 eV. The k-point meshes were set as 3 × 3 × 1. Before the partial density of states (PDOS) calculation, geometry optimization was performed using the Broyden–Fletcher–Goldfarb–Shannon (BFGS) algorithm. The crystal orbital Hamilton population (COHP) was calculated using the Quantum Espresso package[7] and Local-Orbital Basis Suite Toward Electronic-Structure Reconstruction (LOBSTER) package.[8] The PBE functional for solids (PBEsol) GGA was used as the exchange-correlation functional.[9] A cutoff energy of 100 Ry (~1361 eV) and 6 × 6 × 2 k points were used. We confirmed that the calculated PDOS was similar to that calculated using CASTEP, as described above.

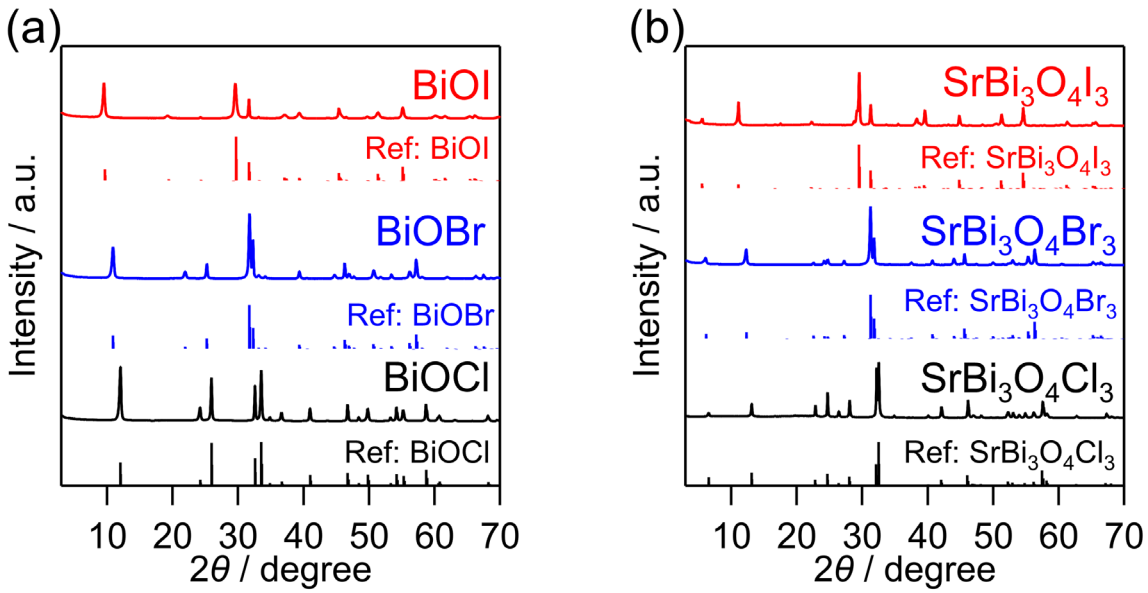


**Fig. S1** XRD patterns of (a) BiOX (X = Cl, Br, I) and (b) $SrBi_3O_4X_3$, along with reference patterns of BiOCl (COD #4509949), BiOBr (COD #1010421), BiOI (COD #4341500), $SrBi_3O_4Cl_3$ (previous report[10] ), $SrBi_3O_4Br_3$ (COD #1539104), and $SrBi_3O_4I_3$ (ICSD #76963).

**Table S1** Average Sr/Bi and X/Bi atomic ratios in $SrBi_3O_4X_3$ (X = Cl, Br, I), determined from energy-dispersive X-ray spectroscopy mapping at three locations for each sample.

| $SrBi_3O_4X_3$ | Sr/Bi | X/Bi |
|---|---|---|
| X = Cl | 0.30 | 0.82 |
| X = Br | 0.30 | 0.96 |
| X = I | 0.31 | 1.01 |

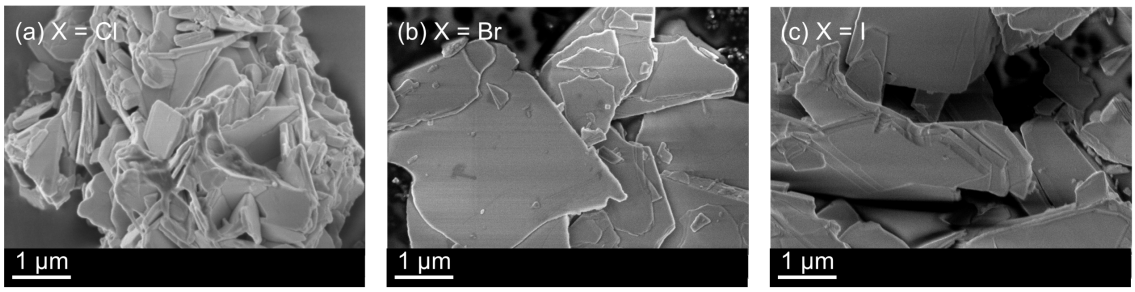


**Fig. S2** SEM images of $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I).

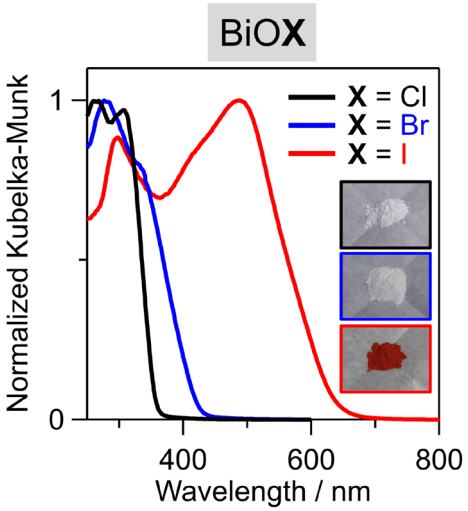


**Fig. S3** UV-vis diffuse reflectance spectra of BiOX (X = Cl, Br, I).

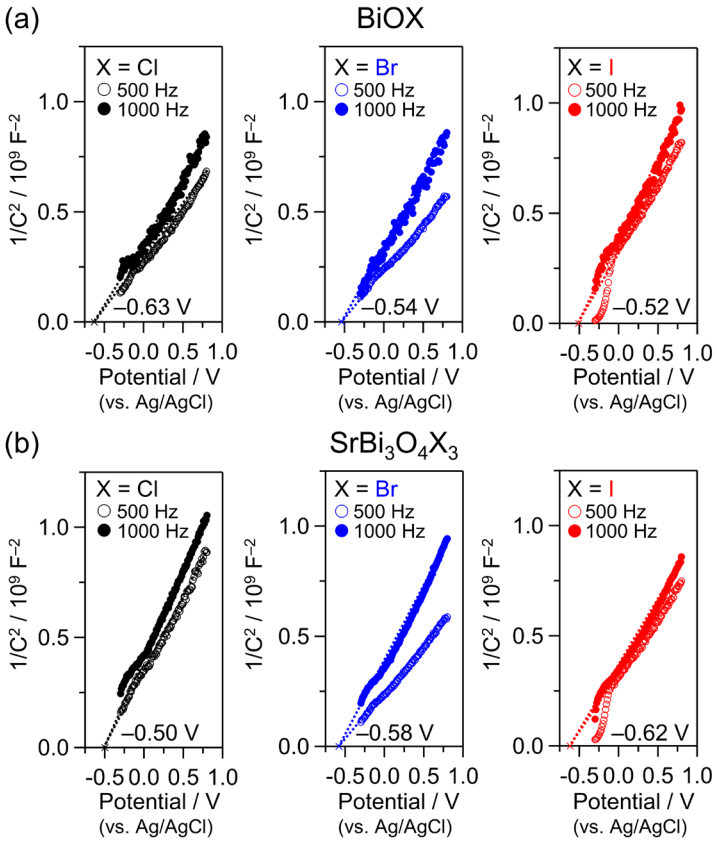


**Fig. S4** Mott–Schottky plots for (a) BiOX (X = Cl, Br, I) and (b) $SrBi_3O_4X_3$.

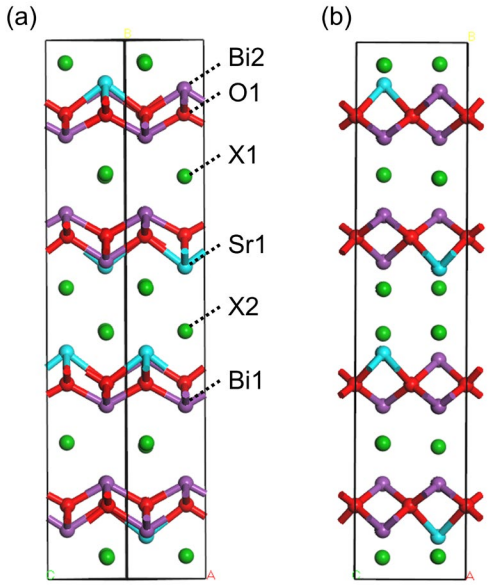


**Fig. S5** Structural models of $SrBi_3O_4X_3$ (X = Cl, Br, I) used for the DFT calculations, viewed from two different directions corresponding to the [100] and [110] directions of the original structures.

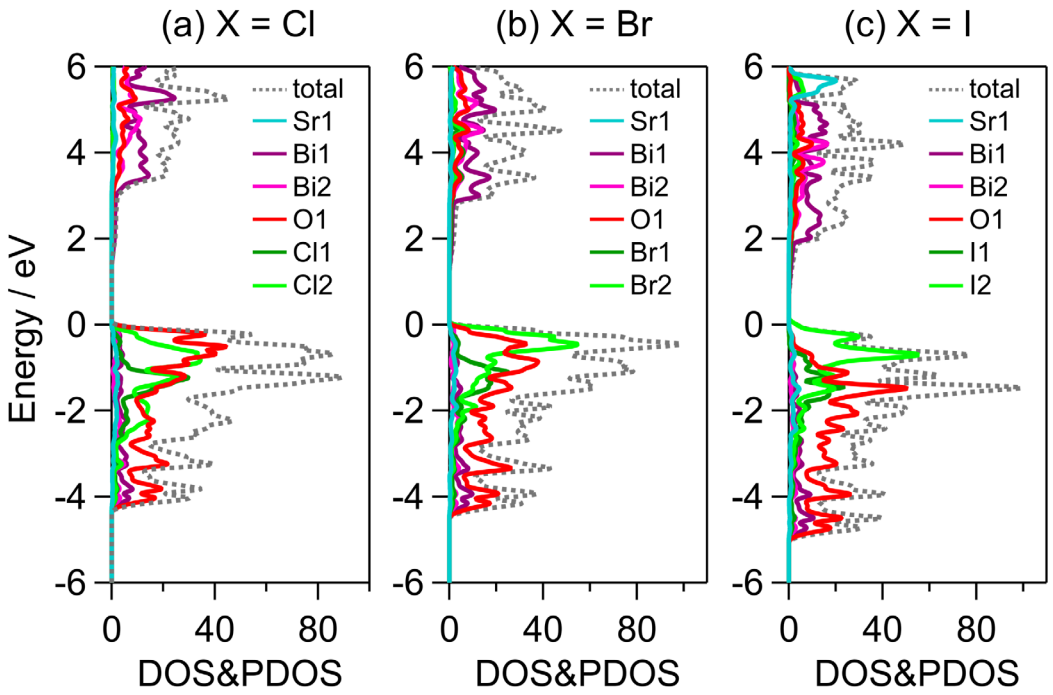


**Fig. S6** DOS and PDOS near the VBM and CBM of $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I), calculated using the structural models shown in Fig. S5.

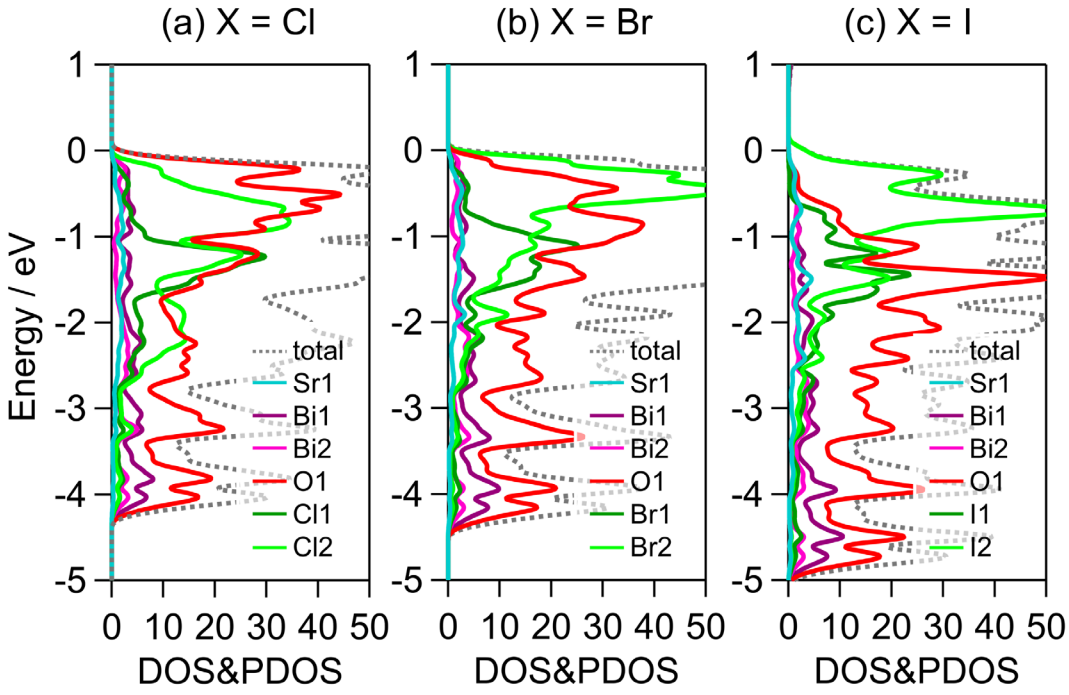


**Fig. S7** Enlarged DOS and PDOS near the VBM of $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I), based on the structural models shown in Fig. S5.

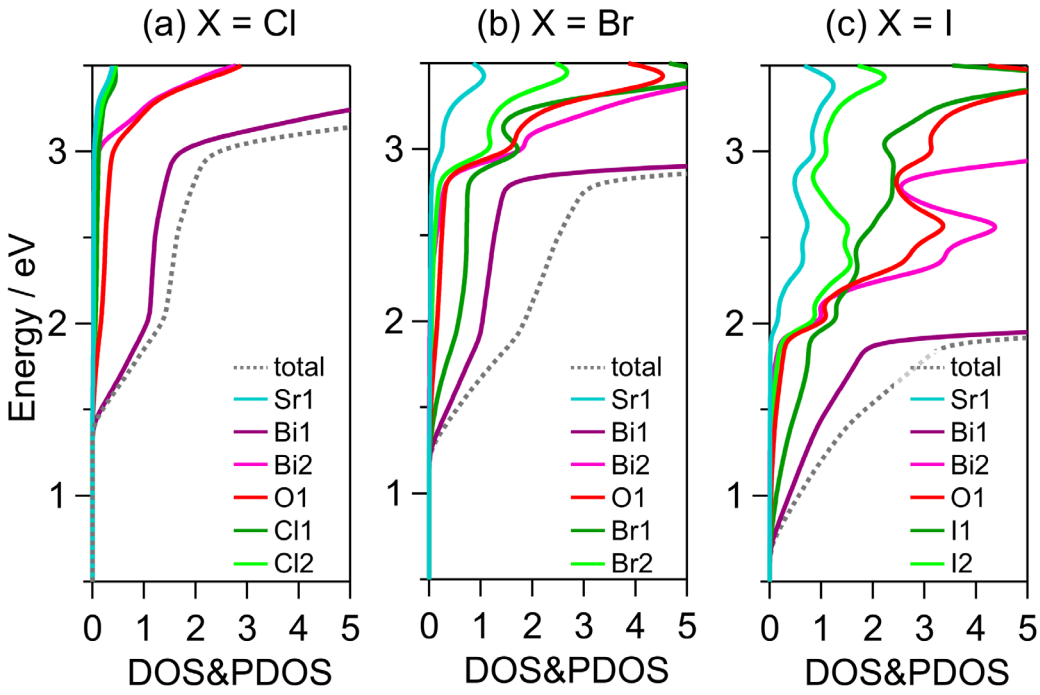


**Fig. S8** Enlarged DOS and PDOS near the CBM of $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I), based on the structural models shown in Fig. S5.

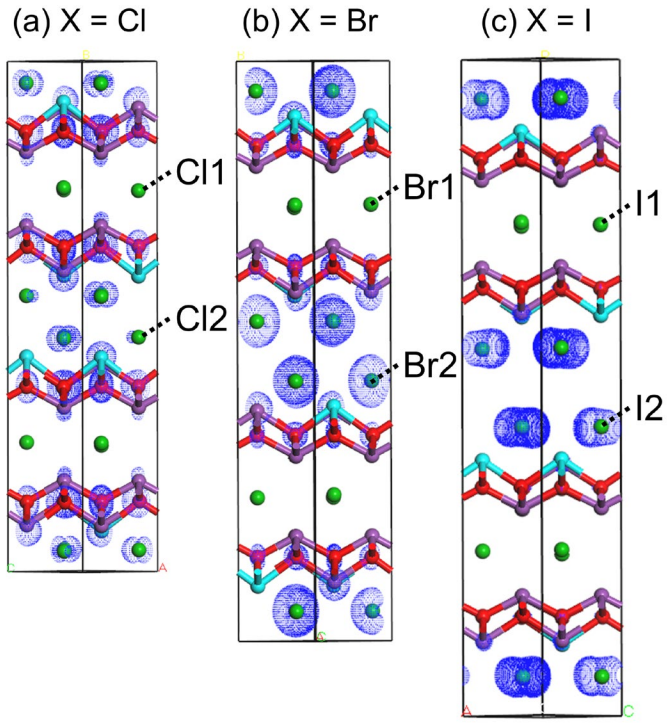


**Fig. S9** Orbital distributions of the VBM (blue dots) estimated by DFT calculations for $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I) (isosurface values: 0.0075 e/Å$^3$).

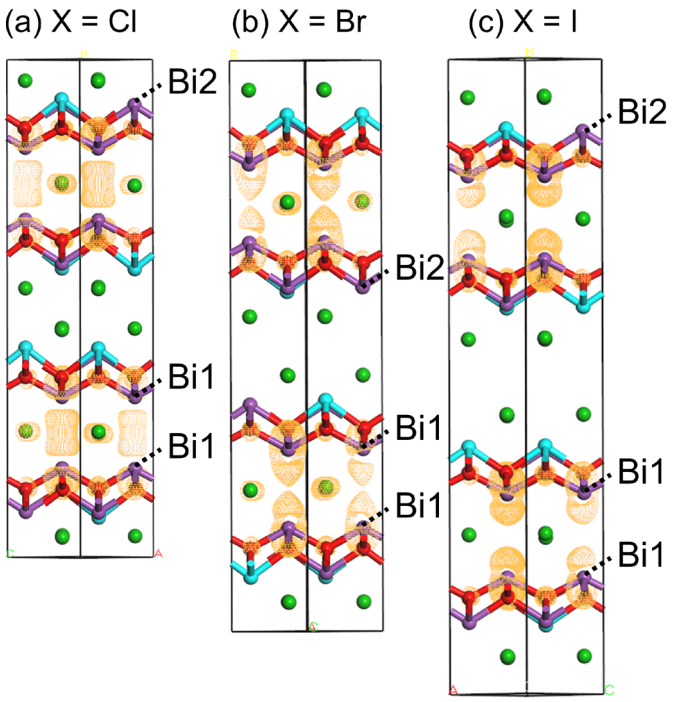


**Fig. S10** Orbital distributions of the CBM (orange dots) estimated by DFT calculations for $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I) (isosurface values: 0.0075 e/Å$^3$).

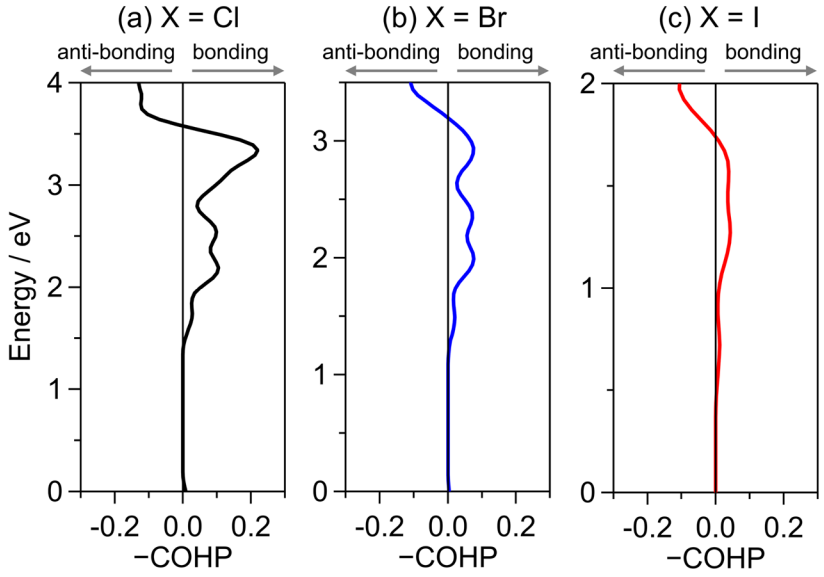


**Fig. S11** COHPs for interlayer Bi1($6p_z$)–Bi1($6p_z$) interaction in $SrBi_3O_4X_3$ (X = (a) Cl, (b) Br, (c) I).

**References**

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