

Electronic Supplementary Information of
The photoluminescence of isolated and paired Bi³⁺ ion in layered
LnOCl crystals: A first-principles study

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TABLE S1. Calculated (calc.) and reported experimental (expt.) lattice parameters of LnOCl (Ln = Y, Gd, La) and BiOCl crystals

System	Space group	Method	a (\AA)	c (\AA)	α, β, γ (deg)	volume (\AA^3)
YOCl	P4/nmm	calc.	3.86	6.56	90, 90,90	98.01
		expt. [1]	3.90	6.60	90, 90,90	100.4
GdOCl	P4/nmm	calc.	3.89	6.50	90, 90,90	100.08
		expt. [2]	3.95	6.67	90, 90,90	104.05
LaOCl	P4/nmm	calc.	4.07	6.84	90, 90,90	113.42
		expt. [3]	4.12	6.87	90, 90,90	116.48
BiOCl	P4/nmm	calc.	3.88	7.35	90, 90,90	110.46
		expt. [4]	3.89	7.35	90, 90,90	110.95

TABLE S2. The optimized Bi pair distances in LnOCl crystals (in units of \AA)

	YOCl	GdOCl	LaOCl
Pair-1	3.58	3.59	3.62
Pair-2	3.85	3.88	4.08

TABLE S3. Formation energies of isolated and paired Bi and binding energies of Bi pairs (in units of eV)

	Formation energy			Binding energy	
	single	pair-1	pair-2	pair-1	pair-2
YOC1	-0.39	-0.75	-0.79	-0.035	0.004
GdOC1	-0.23	-0.44	-0.46	-0.027	-0.007
LaOC1	0.24	0.46	0.56	0.030	-0.007

TABLE S4. The experimental and calculated excitation (Exc.), emission (Emi.), and the Stokes shift (ΔS) of Bi pair-2 in LnOC1 hosts (in units of eV)

Host	Method	Exc.	Emi.	ΔS
YOC1	GGA	4.05	3.19	0.86
	Expt.	4.87	3.00	1.87
GdOC1	GGA	4.01	3.21	0.80
	Expt.	4.82	2.79	2.03
LaOC1	GGA	3.76	2.70	1.06
	Expt.	4.48	2.65	1.83

TABLE S5. The average Bi–O bond lengths of $[\text{BiO}_4]$ in the geometric structure of excitonic state of BiOC1 crystal (in units of Å)

Layers	Average Bi–O bond lengths							
Layer-1	2.310	2.310	2.310	2.310	2.310	2.310	2.311	2.309
Layer-2	2.270	2.284	2.274	2.277	2.305	2.305	2.307	2.307
Layer-3	2.300	2.300	2.300	2.300	2.299	2.300	2.299	2.300
Layer-4	2.299	2.302	2.301	2.301	2.301	2.301	2.301	2.301

* The partial charge density of KS orbitals show that the hole is distributed on the layer-2 and the electron is extended over layer-1 and layer-2 in the main text.

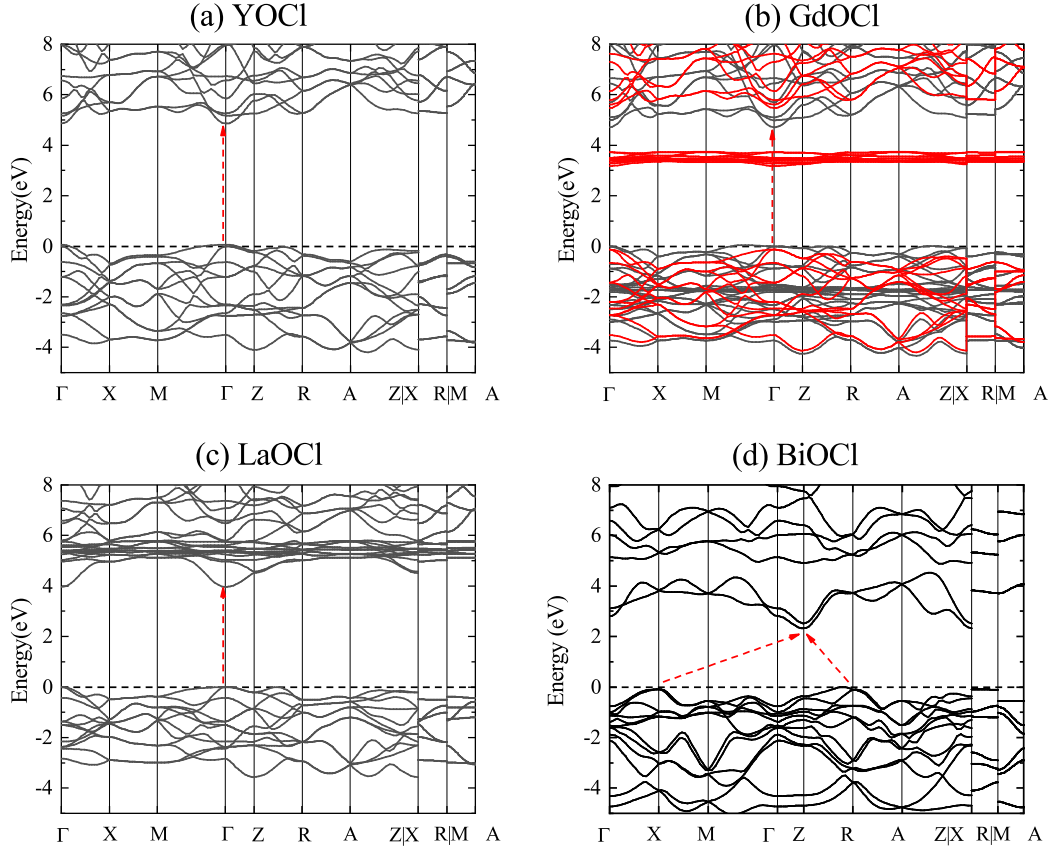


FIG. S1. Electronic band structures of YOCl (a), GdOCl (b), LaOCl (c) and BiOCl (d) obtained by GGA-PBEsol method.

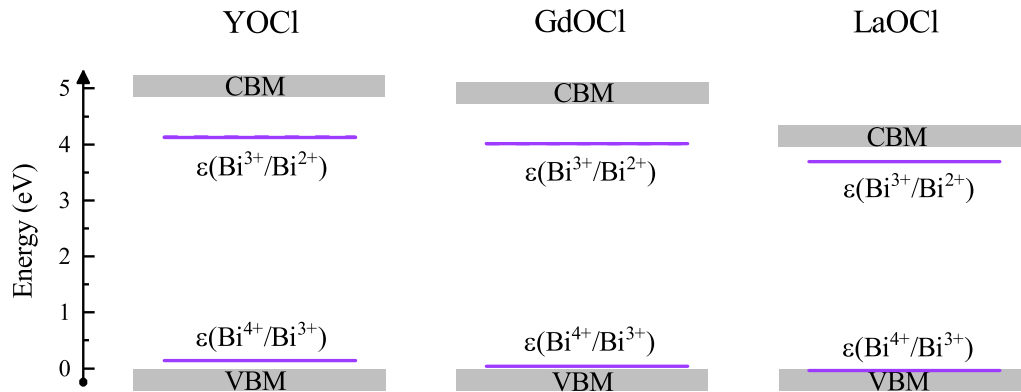


FIG. S2. Thermodynamic charge-state transition levels of single Bi dopant in LnOCl (Ln = Y, Gd, La) crystals calculated by GGA-PBEsol method.

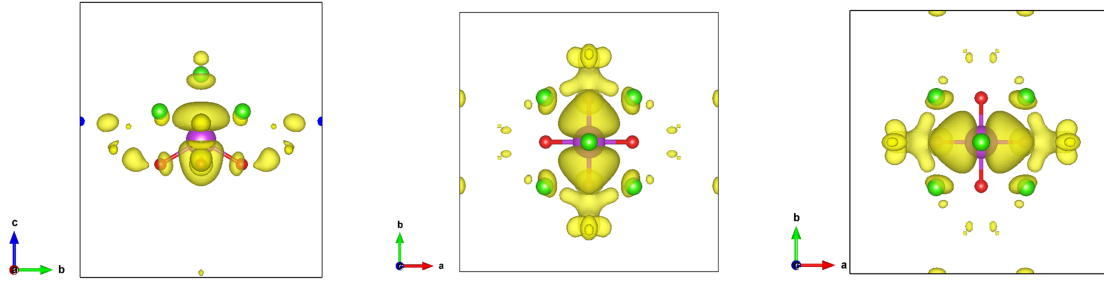


FIG. S3. The partial charge density distributions of Bi-6*p* orbitals of A_1 (left) and E (right two) levels without SOC.

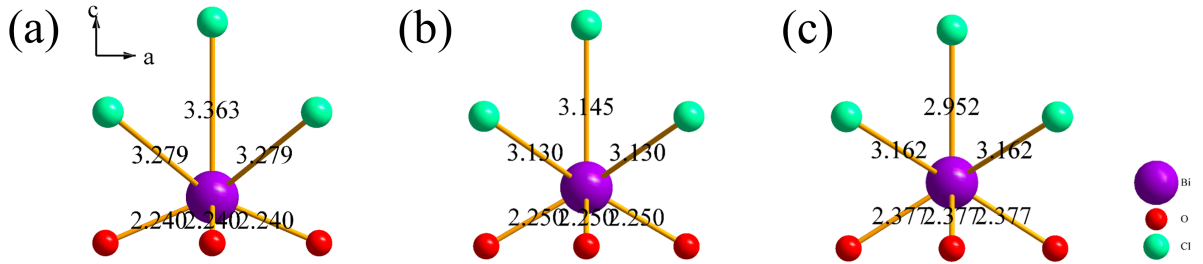


FIG. S4. The equilibrium geometric configurations of excited state without SOC (a), ground state with SOC (b) and excited state with SOC (c).

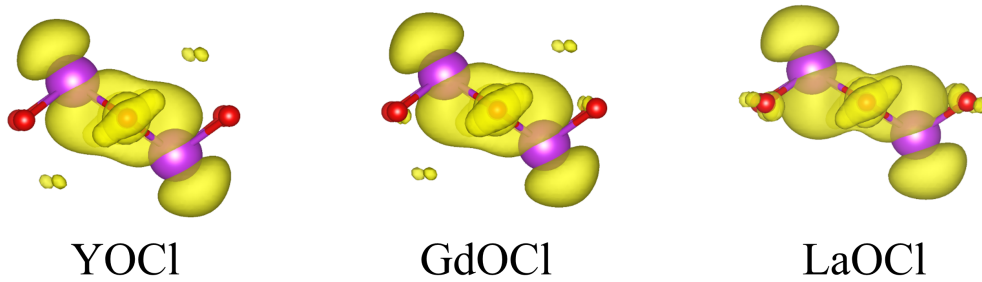


FIG. S5. The partial charge density distributions of occupied *p* orbitals of Bi pair-1 without SOC in YOCl, GdOCl and LaOCl hosts, which show the orbital hybridization between Bi pair and are remarkably different from the partial charge density distribution of Bi pair with SOC, as discussed in Fig. 3(b) of main text.

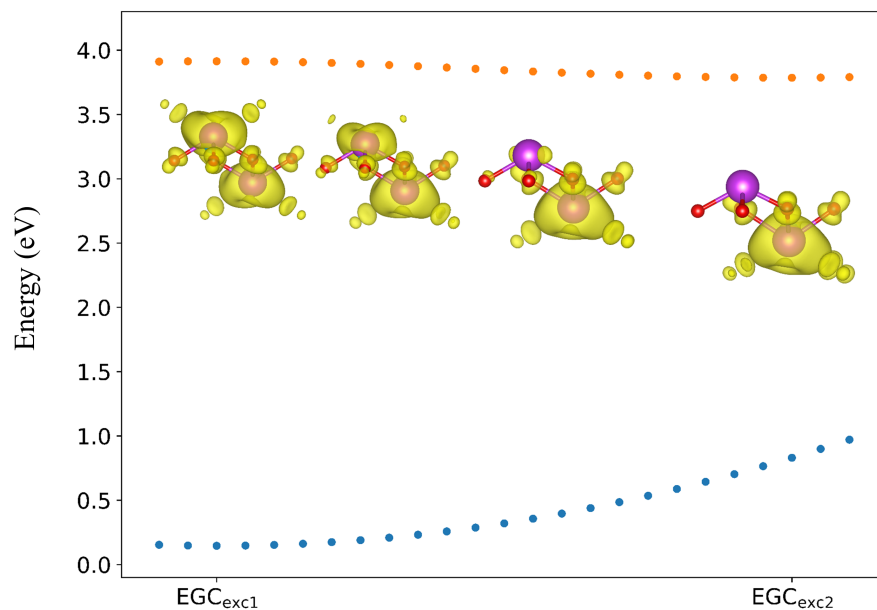


FIG. S6. Configuration coordination diagram along the geometric configuration path of ‘exc1’ and ‘exc2’ excited states and the insets are the $6p$ partial charge density distributions.

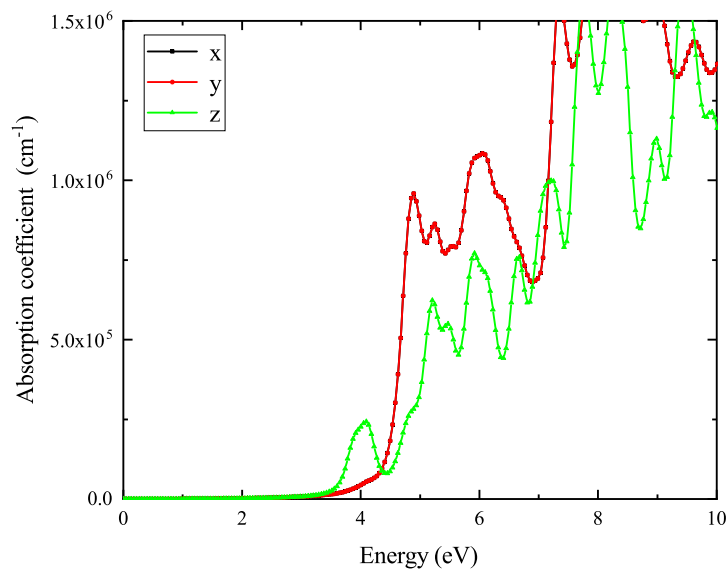


FIG. S7. The absorption coefficients of BiOCl by HSE06 calculations. The x and y polarizations are the same due to axial symmetry.

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