Electronic Supplementary Information

Characterization of charge transfer luminescence for $[WO_6]^{6-}$ octahedron in Ca_3WO_6 and $[WO_5]^{4-}$ square pyramid in $Ca_3WO_5Cl_2$

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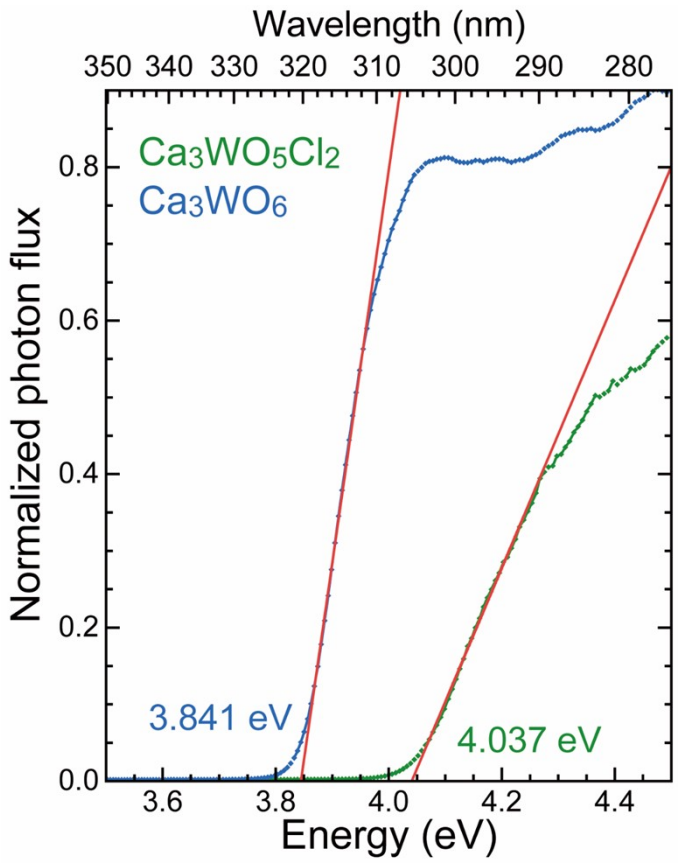

Fig. S1 Linear fitting for the absorption edge of the PLE spectra at 4 K.

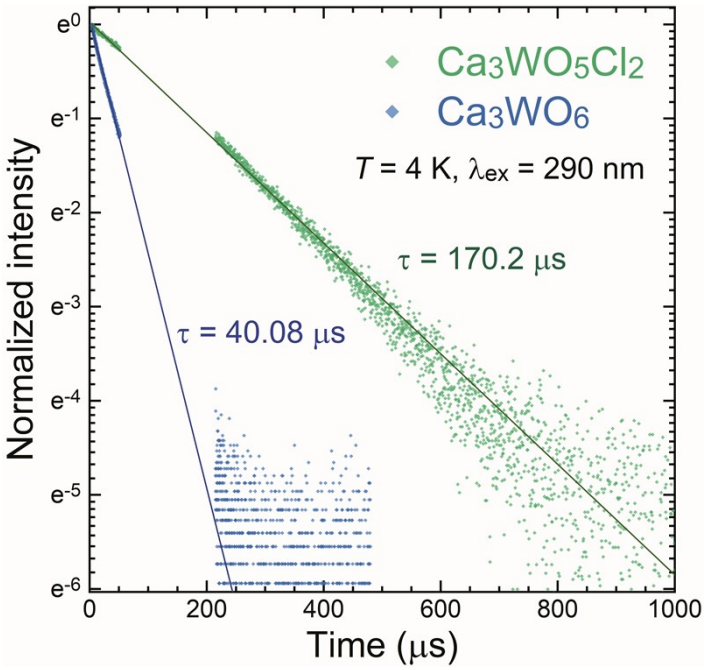

Fig. S2 Luminescence decay curves of the single-crystal samples, measured at 4 K. Data in the range of 50–200 ns is missing due to a problem with the measurement setup.

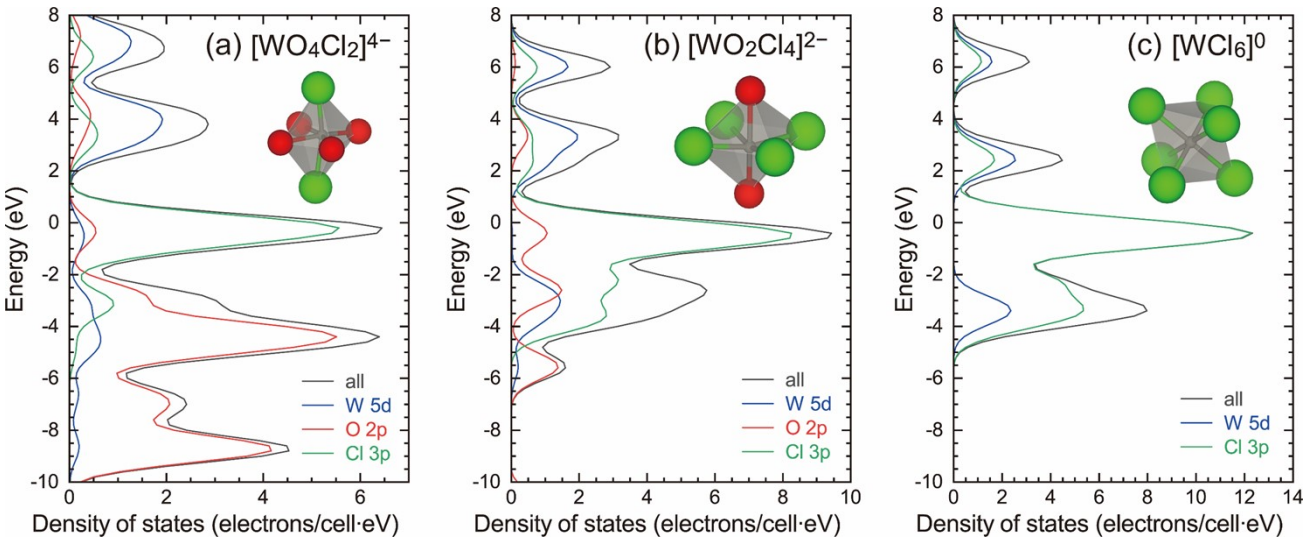

Fig. S3 Total and partial density of electronic states for (a) a $[WO_4Cl_2]^{4-}$ cluster in WO_2Cl_2 (ICSD 28510), (b) a $[WO_2Cl_4]^{2-}$ cluster in $WOCl_4$ (ICSD 25519), and (c) a $[WCl_6]$ cluster in WCl_6 (ICSD 425147), which were calculated by the relativistic DV-Xα method. The HOMO mainly composed of Cl 3p orbitals is set at 0 eV.

Table S1 Lattice constants and interatomic distances between W^{6+} and ligands before and after DFT geometry optimization

		$Ca_3WO_5Cl_2$ (*Pbnm*)		Ca_3WO_6 ($P2_1/n$)	
		CIF	Optimized	CIF	Optimized
lattice constants		*a* = 11.820(2) Å *b* = 11.132(1) Å *c* = 5.587(1) Å	*a* = 11.8007 Å *b* = 11.0789 Å *c* = 5.5574 Å	*a* = 5.5518(3) Å *b* = 5.8100(3) Å *c* = 8.0066(4) Å *β* = 89.808(1)°	*a* = 5.5065 Å *b* = 5.7905 Å *c* = 7.9640 Å *β* = 90.1846°
bonding[a]	W^{6+}-O^{2-}_{I}	1.724(15) Å	1.73113 Å	1.9273(7) Å	1.93016 Å
	W^{6+}-O^{2-}_{II}	1.887(11) Å	1.88707 Å	1.9134(6) Å	1.90982 Å
	W^{6+}-O^{2-}_{III}	1.911(11) Å	1.90258 Å	1.9358(8) Å	1.92416 Å
	W^{6+}-Cl^{-}	3.404(8) Å	3.26617 Å	—	—

[a]The different O^{2-} ions are labeled with Roman numerals, I–III, shown in Fig. 1.

Table S2 Results of compositional analysis of MO levels calculated by the relativistic DV-Xα calculation (unit: %)[a]

	top1[b]	top2[b]	top4[b]	$5d_1$	$5d_2$	$5d_3$	$5d_4$	$5d_5$
W 5d	0.04	0.03	0.01	80.00	68.67	71.08	49.95	70.68
O 2p	11.14	17.59	14.10	19.88	29.07	26.63	23.53	25.95
Cl 3p	88.57	82.21	85.19	0.00	0.04	0.02	1.22	0.00

[a]Note that the total percentages are less than 100% because of small contributions of other orbitals, such as O 2s, W 6s, and W 6p orbitals.

[b]The first, second, and fourth levels of the HOMO level are labeled top1, top2, and top4, respectively, in order of decreasing energy, mainly composed of the Cl $3p_x$, $3p_y$, and $3p_z$ orbitals.

Confirmation of k-points convergence

In order to confirm the validity of these k-points grids, the DFT single-point SCF calculations with the double k-points grids (2×2×4 for $Ca_3WO_5Cl_2$ and 6×6×4 for Ca_3WO_6) were performed with the CASTEP module. The results are summarized in Table S3. Because the total energies are well converged even with smaller k-points mesh, the smaller k-points grids (1×1×3 for $Ca_3WO_5Cl_2$ and 3×3×2 for Ca_3WO_6) are enough for the property calculations.

Table S3. Comparison of the SCF converged energy with different sizes of k-point grids

	$Ca_3WO_5Cl_2$		Ca_3WO_6	
	1×1×3	2×2×6	3×3×2	6×6×4
SCF converged energy (eV)	−33652.0430	−33652.0192	−15917.9952	−15917.9203