Supporting Information

Hydrated Zirconium Coordination Enhanced the Photoluminescence Performance in 0D Cadmium Manganese Based Perovskites

Panheng Wang,[a] Xiaoming Zhang,[a] Qinglin Meng,[a] Mosheng Cai,[a] Ziqiao Wu,[b] Chengjing Huang,[a] Jiandong Fan,[a,b,c,*] Wenzhe Li [a,b,c,*]

[a] Institute of New Energy Technology, Jinan University, Guangzhou 510632, China

[b] Institute of New Energy Technology, College of Physics & Optoelectronic Engineering, Jinan University, Guangzhou, 510632, China.

[c] Guangdong Provincial Key Laboratory of Nanophotonic Manipulation, Jinan University, Guangzhou 511443, China.

E-mail: (Jiandong Fan) jdfan@jnu.edu.cn; (Wenzhe Li) li_wz16@jnu.edu.cn.

Table S1. Crystallographic data and structure refinement details for $[ZrO(H_2O)_2]Cl_2 \cdot xH_2O$ (Zr), $[ZrO(H_2O)_8]_2CdCl_6$ (Cd), $[ZrO(H_2O)_8]_2MnCl_6$ (Mn), and $[ZrO(H_2O)_8]_2Cd_{0.7}Mn_{0.3}Cl_6$ (CdMn).

Crystal	Zr	Cd	Mn	CdMn
CCDC No.	2553895	2526960	2526961	2526962
Measurement temperature (K)	293(2)			
Crystal system	tetragonal	triclinic		
Space group name	P-4 21c	P-1		
Lattice parameters	a = 17.0492(4) Å	a = 7.8062(2) Å	a = 7.7794(2) Å	a = 7.7950(2) Å
	b = 17.0492(16) Å	b = 8.83610(16) Å	b = 8.7334(2) Å	b = 8.8048(2) Å
	c = 7.6920(3) Å	c = 10.5429(3) Å	c = 10.5215(2) Å	c = 10.5327(3) Å
	α = 90°	α = 75.6310(19)°	α = 75.951(2)°	α = 75.711(2)°
	β = 90°	β = 73.694(3)°	β = 74.131(2)°	β = 73.841(2)°
	γ = 90°	γ = 85.147(2)°	γ = 85.376(2)°	γ = 85.243(2)°
Unit-cell volume	2235.87 $Å^3$	676.04(3) $Å^3$	666.95(3) $Å^3$	672.78(3) $Å^3$
Z	2	1	1	1
Final R indexes	R1= 0.0537	R1= 0.0288	R1= 0.0333	R1= 0.0352
[All data]	wR^2 = 0.1470	wR^2 = 0.0651	wR^2 = 0.0763	wR^2 = 0.0844
Goodness-of-fit On F^2	1.062	1.065	1.049	1.046

Table S2. Zr-O bond lengths in $[ZrO(H_2O)_8]_2CdCl_6$.

O atom	Zr1-O (Å)	Zr2-O (Å)
O1 (μ_2-O)	2.10072	2.16405
O2 (μ_2-O)	2.16405	2.10072
O3	2.25353	
O4		2.25353
O5	2.23640	
O6		2.23640
O7	2.24542	
O8		2.24542
O9	2.19146	
O10		2.19146
O11	2.16314	
O12		2.16314
O13	2.17340	
O14		2.17340

Table S3. Elemental concentrations and calculated Cd/Mn molar composition of CdMn ($[ZrO(H_2O)_8]_2Cd_xMn_{1-x}Cl_6$) crystals.

Sample	Cd (ppm)	Mn (ppm)	Calculated Cd:Mn molar ratio	Normalized composition
$[ZrO(H_2O)_8]_2Cd_xMn_{1-x}Cl_6$	9.562	1.983	0.702:0.298	$Cd_{0.7}Mn_{0.3}$

Table S4. Selected bond lengths (Å) and bond angles (°) for the $[BCl_6]^{4-}$ (B = Cd/Mn) octahedra in $[ZrO(H_2O)_8]_2CdCl_6$ (Cd), $[ZrO(H_2O)_8]_2MnCl_6$ (Mn), and $[ZrO(H_2O)_8]_2Cd_{0.7}Mn_{0.3}Cl_6$ (CdMn). Symmetry codes are given where applicable.

Bond	Angle (°)		
	Cd	Mn	CdMn
Cl(1)-B-Cl(2)	87.79(3)	88.17(3)	92.10(4)
Cl(1)-B-Cl(2)#1	87.69(4)	88.26(4)	92.14(4)
Cl(1)-B-Cl(2)#2	92.31(4)	91.74(4)	87.86(4)
Cl(1)-B-Cl(2)#3	92.21(3)	91.83(3)	87.90(4)
Cl(2)-B-Cl(2)#1	91.36(4)	90.95(4)	88.76(4)
Cl(2)#1-B-Cl(2)#2	88.64(4)	89.05(4)	91.24(4)
Cl(2)#2-B-Cl(2)#3	91.36(4)	90.95(4)	88.76(4)
Cl(2)#3-B-Cl(2)	88.64(4)	89.05(4)	91.24(4)
Cl(1)#1-B-Cl(2)	87.79(3)	88.17(3)	92.10(4)
Cl(1)#1-B-Cl(2)#1	87.69(4)	88.26(4)	92.14(4)
Cl(1)#1-B-Cl(2)#2	92.21(3)	91.83(3)	87.90(4)
Cl(1)#1-B-Cl(2)#3	92.31(4)	91.74(4)	87.86(4)
Bond	Lengths (Å)		
	Cd	Mn	CdMn
Cl(1)-B	2.5796(9)	2.5955(9)	2.5578(10)
Cl(1)#1-B	2.5796(9)	2.5955(9)	2.5578(10)
Cl(2)-B	2.6715(9)	2.5504(11)	2.6489(11)
Cl(2)#3-B	2.6715(9)	2.5504(11)	2.6489(11)
Cl(2)#1-B	2.6289(11)	2.5027(9)	2.6037(13)
Cl(2)#2-B	2.6289(11)	2.5027(9)	2.6037(13)

Table S5. ICP analysis of Cd crystals

Sample	Product	
	Cd (ppm)	Mn (ppm)
$[ZrO(H_2O)_8]_2CdCl_6$	5.364	0.024

Table S6. Bi-exponential fitting parameters and derived lifetimes from TRPL.

Model: $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + y_0$.

Average lifetime: $\langle \tau \rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$.

TRPL monitored at **620** nm (units: ms)

Crystal	A_1	τ_1 (ms)	A_2	τ_2 (ms)	τ (ms)
Cd	0.58928 ± 0.04200	0.24161 ± 0.03500	0.33091 ± 0.02200	3.89317 ± 0.33300	1.55 ± 0.15
Mn	0.20866 ± 0.00519	0.60055 ± 0.02427	0.78740 ± 0.00526	3.26153 ± 0.01750	2.70 ± 0.02
CdMn	0.10236 ± 0.00409	0.58453 ± 0.04156	0.88338 ± 0.00395	3.64370 ± 0.01434	3.33 ± 0.02

Table S7. Bi-exponential fitting parameters and derived lifetimes from TRPL.

Model: $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + y_0$.

Average lifetime: $\langle \tau \rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$.

TRPL monitored at **445 nm** (units: ns)

Crystal	A_1	τ_1(ns)	A_2	τ_2(ns)	τ(ns)
Cd	0.93924 ± 0.00900	0.78791 ± 0.01280	0.13740 ± 0.00900	4.53447 ± 0.25890	1.27 ± 0.04
Mn	0.91538 ± 0.00920	0.76369 ± 0.01490	0.17122 ± 0.00790	5.85345 ± 0.29730	1.57 ± 0.06
CdMn	0.84045 ± 0.00810	0.74702 ± 0.01320	0.21813 ± 0.00770	4.86846 ± 0.16380	1.60 ± 0.04

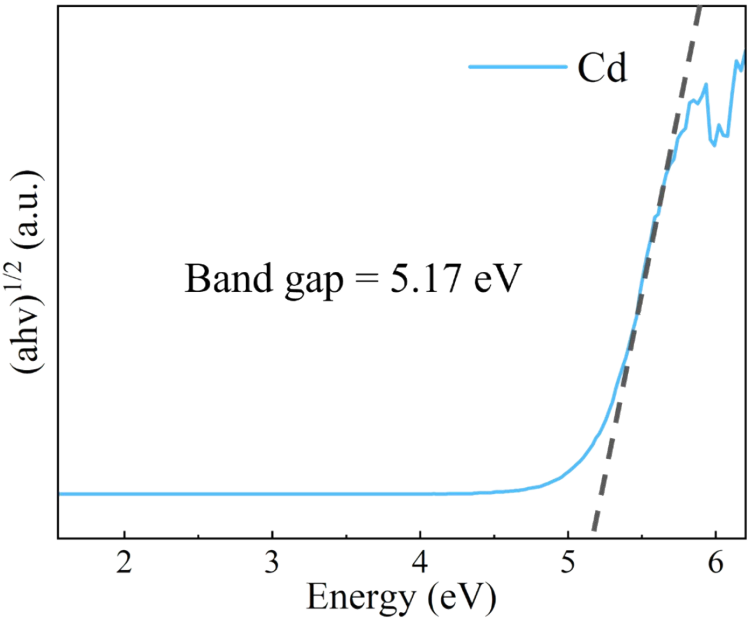

Fig. S1. Corresponding Tauc plot of Cd.

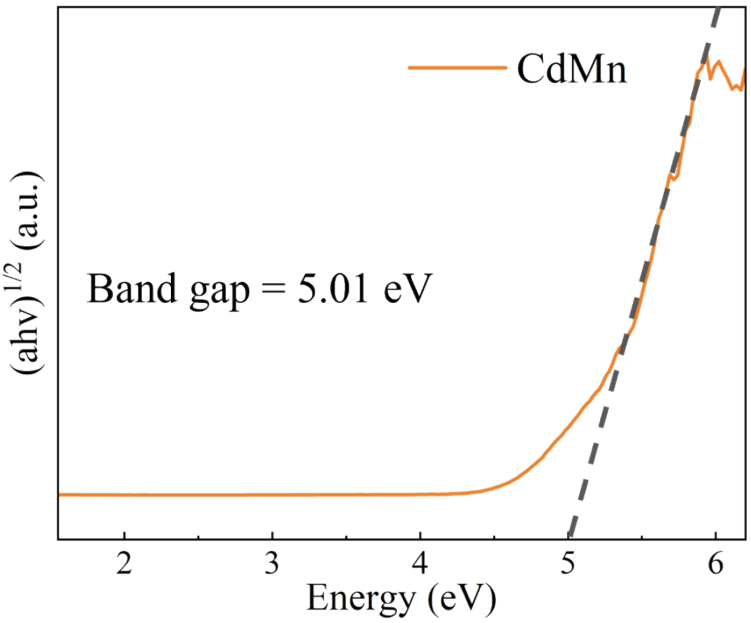

Fig. S2. Corresponding Tauc plot of CdMn.

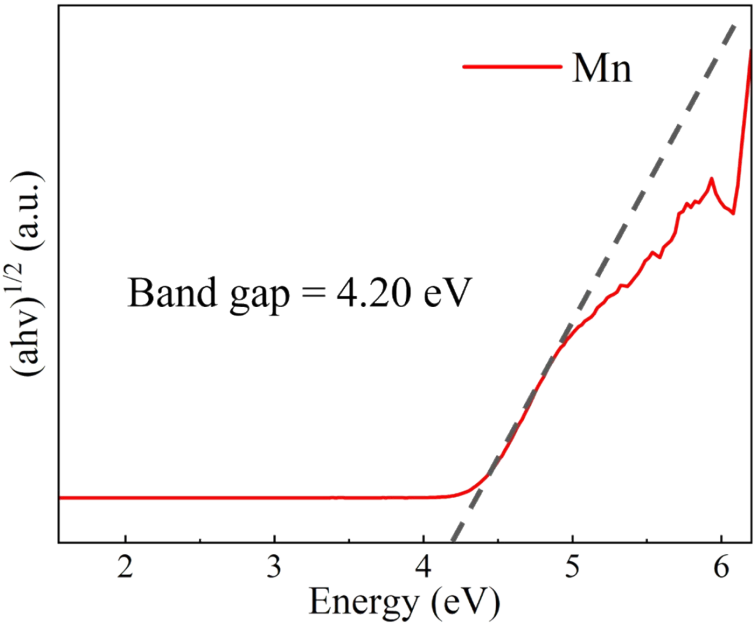

Fig. S3. Corresponding Tauc plot of Mn.

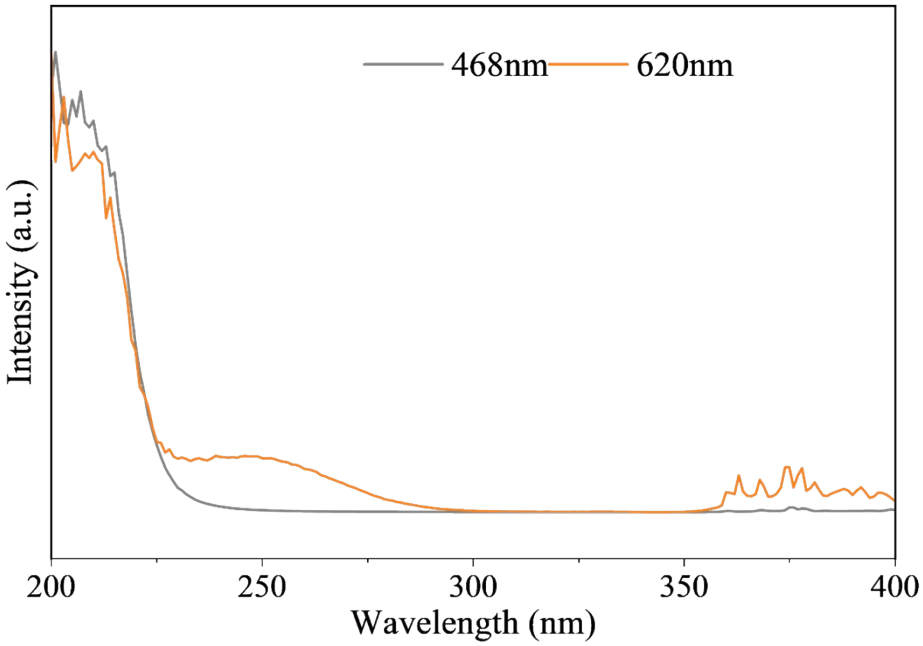

Fig. S4. PLE spectra of CdMn monitored at 468 and 620 nm (200-400 nm).

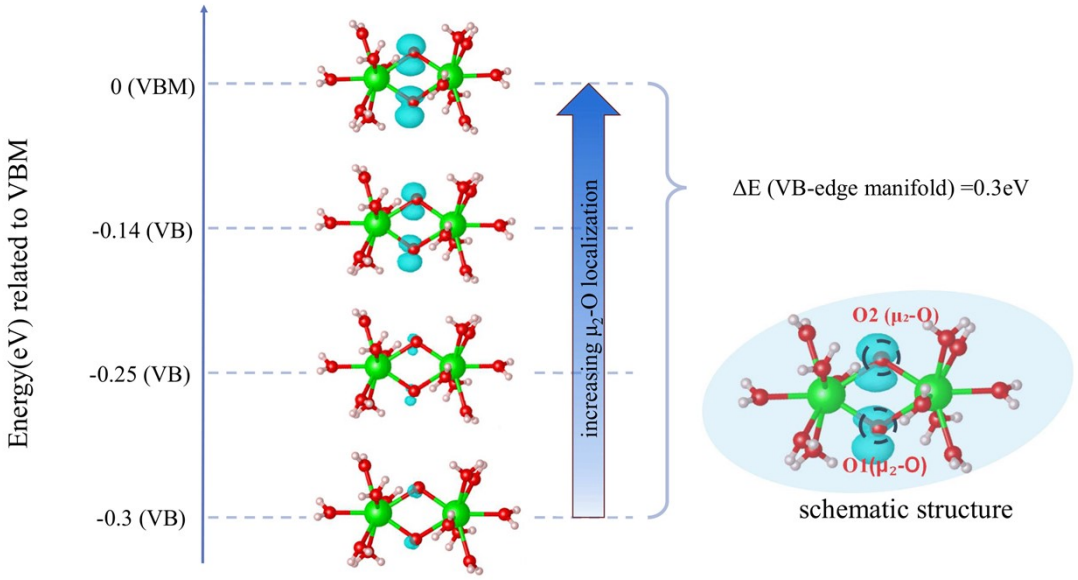

Fig. S5. Band-decomposed hole-density isosurfaces for VBM and VB (energies relative to VBM), plotted at the same isovalue ($\rho = 6\times10^{-7}$; units as in the charge-density file).

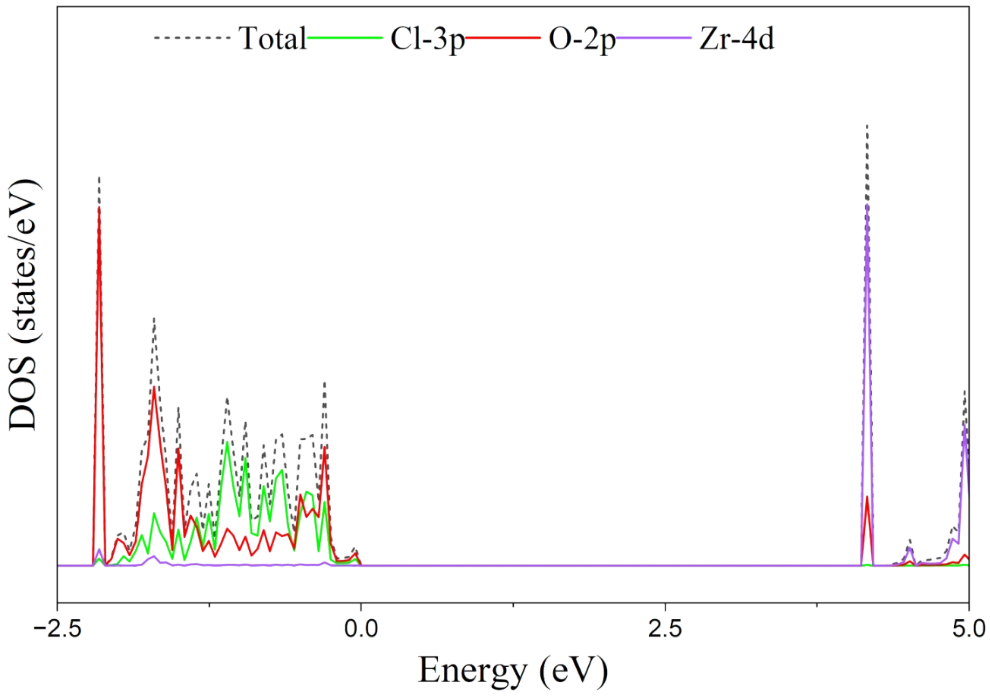

Fig. S6. Corresponding total and projected density of states (DOS) for $[ZrO(H_2O)_2]Cl_2\cdot xH_2O$.