Supplementary Information for:

Expansion of the Structural Diversity of f-Element Bearing Molybdate Iodates: Synthesis, Structures, and Optical Properties

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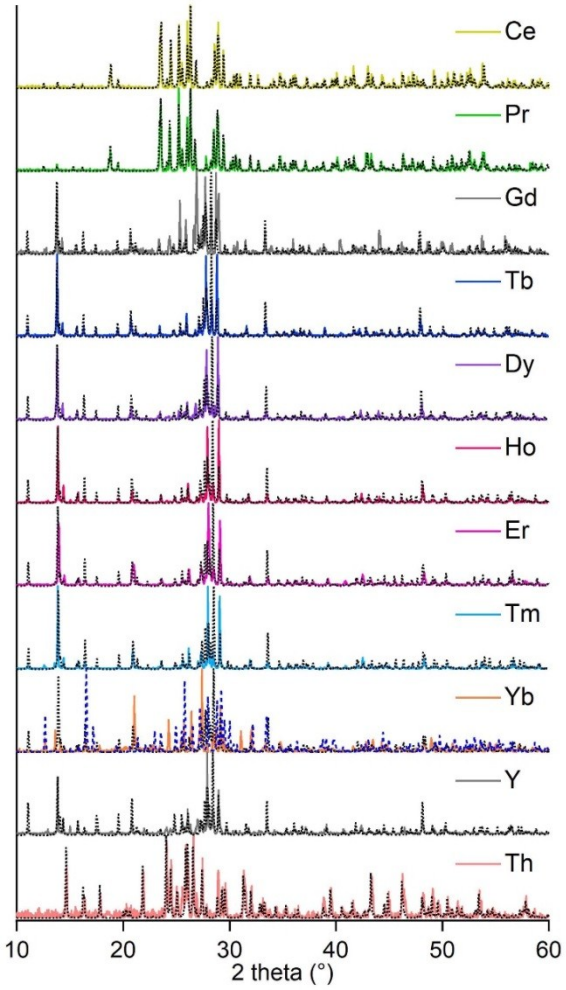

Fig. S1. Powder X-ray diffraction (PXRD) patterns showing the phase purity of for **LnMoIO-1** (Ln = Ce − Pr), **LnMoIO-2** (Ln = Gd – Yb, Y), and **ThFMoIO**. Black dashed line: simulated patterns of **LnMoIO-1**, **LnMoIO-2**, and **ThFMoIO**; blue dashed line: simulated patterns of $Yb(IO_3)_3(H_2O)_2$; solid line: experimental patterns.

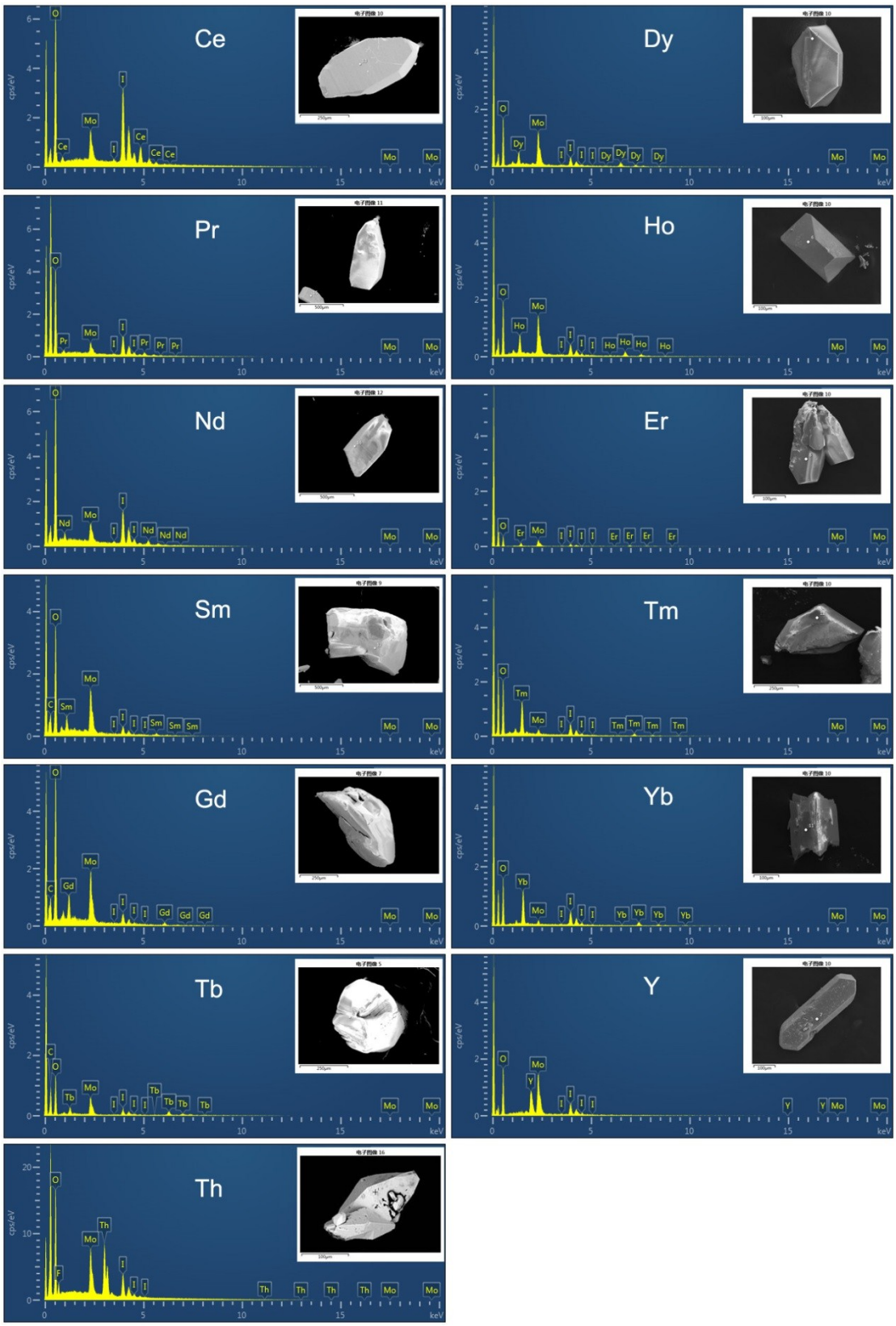

Fig. S2. SEM images and EDS spectra of **LnMoIO-1** (Ln = Ce − Sm), **LnMoIO-2** (Ln = Gd – Yb, Y), and **ThFMoIO**.

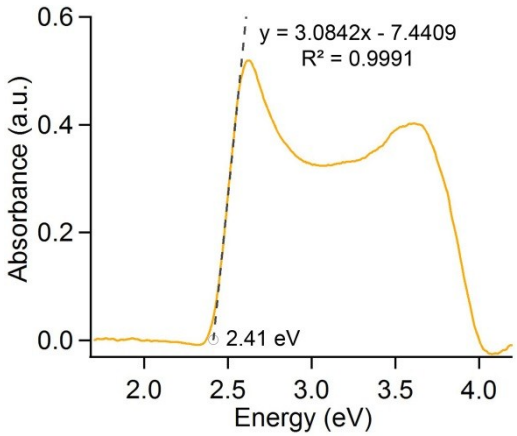

Fig. S3. Optical energy spectrum of **CeMoIO-1** used to determine the approximate band gap. The least-squares fit is shown along with the x intercept which is the calculated band gap.

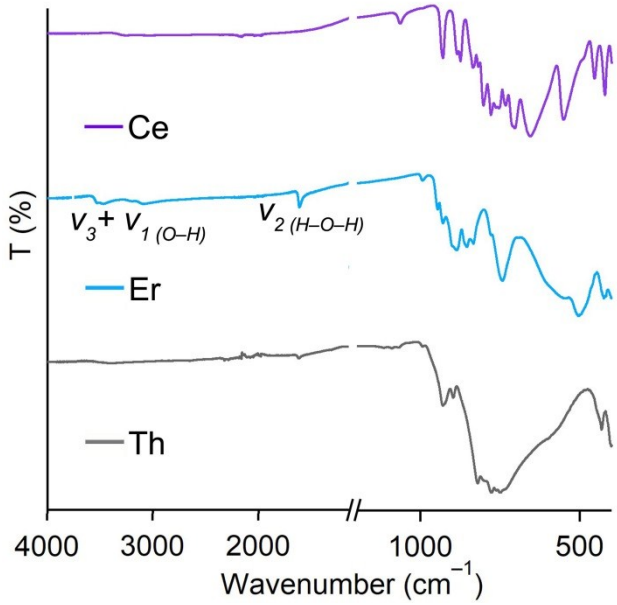

Fig. S4 IR spectra of **CeMoIO-1**, **ErMoIO-2**, and **ThFMoIO**.

Table S1. Selected bond distances and BVS for **CeMoIO-1** and **PrMoIO-1**.

CeMoIO-1		**PrMoIO-1**	
Ce(1)-O(7)#1	2.383(9)	Pr(1)-O(7)#1	2.384(6)
Ce(1)-O(9)#2	2.436(8)	Pr(1)-O(9)#2	2.427(6)
Ce(1)-O(5)	2.437(10)	Pr(1)-O(5)	2.423(6)
Ce(1)-O(2)#3	2.478(8)	Pr(1)-O(2)#3	2.481(6)
Ce(1)-O(6)#4	2.509(9)	Pr(1)-O(6)#4	2.508(6)
Ce(1)-O(15)#4	2.515(8)	Pr(1)-O(13)#5	2.511(6)
Ce(1)-O(13)#5	2.517(8)	Pr(1)-O(15)#4	2.511(6)
Ce(1)-O(14)#1	2.527(9)	Pr(1)-O(14)#1	2.525(6)
AVE	2.475	2.471	2.475
BVS of Ce	3.36	BVS of Pr	3.25
Mo(1)-O(6)	1.722(9)	Mo(1)-O(6)	1.727(6)
Mo(1)-O(4)	1.738(9)	Mo(1)-O(4)	1.732(6)
Mo(1)-O(8) (OH)	1.812(8)	Mo(1)-O(8) (OH)	1.831(6)
Mo(1)-O(1)	2.160(8)	Mo(1)-O(12)	2.177(5)
Mo(1)-O(12)	2.163(8)	Mo(1)-O(1)	2.168(6)
Mo(1)-O(10)	2.179(9)	Mo(1)-O(10)	2.171(6)
BVS of Mo	6.00	BVS of Mo	5.93
I(1)-O(14)	1.787(8)	I(1)-O(14)	1.790(6)
I(1)-O(3)	1.799(8)	I(1)-O(3)	1.799(6)
I(1)-O(11)	1.929(8)	I(1)-O(11)	1.953(6)
BVS of I	4.71	BVS of I	4.62
I(2)-O(2)	1.790(8)	I(2)-O(2)	1.809(6)
I(2)-O(15)	1.808(9)	I(2)-O(15)	1.807(6)
I(2)-O(12)	1.836(8)	I(2)-O(12)	1.836(6)
BVS of I	5.00	BVS of I	5.00
I(3)-O(5)	1.773(9)	I(3)-O(5)	1.789(6)
I(3)-O(13)	1.825(7)	I(3)-O(13)	1.829(5)
I(3)-O(10)	1.836(9)	I(3)-O(10)	1.843(6)
BVS of I	5.00	BVS of I	4.88
I(4)-O(9)	1.784(9)	I(4)-O(9)	1.796(6)
I(4)-O(7)	1.802(9)	I(4)-O(7)	1.801(6)
I(4)-O(1)	1.843(7)	I(4)-O(1)	1.848(5)
BVS of I	5.03	BVS of I	4.96

Table S2. Selected bond distances and BVS for **LnMoIO-2** (Ln = Gd – Yb, Y).

	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
Ln(1)-O(2)	2.341(6)	2.324(6)	2.307(3)	2.299(4)	2.285(3)	2.276(2)	2.282(5)	2.293(3)
Ln(1)-O(3)#1	2.341(5)	2.330(6)	2.314(3)	2.307(4)	2.297(3)	2.289(2)	2.272(6)	2.308(3)
Ln(1)-OW1	2.343(7)	2.320(7)	2.324(4)	2.301(4)	2.293(3)	2.279(3)	2.276(6)	2.298(3)
Ln(1)-O(6)#2	2.363(6)	2.347(6)	2.338(4)	2.322(4)	2.315(3)	2.306(3)	2.299(6)	2.330(3)
Ln(1)-O(10)	2.377(6)	2.366(7)	2.355(4)	2.340(4)	2.333(3)	2.328(3)	2.315(6)	2.344(3)
Ln(1)-O(5)#3	2.395(6)	2.380(6)	2.370(3)	2.357(4)	2.349(3)	2.335(3)	2.326(6)	2.361(3)
Ln(1)-O(1)#4	2.453(6)	2.434(7)	2.415(3)	2.399(5)	2.391(3)	2.377(3)	2.378(6)	2.403(3)
Ln(1)-O(4)#3	2.521(6)	2.525(6)	2.508(4)	2.512(4)	2.498(3)	2.488(3)	2.495(6)	2.505(3)
AVE	2.392	2.378	2.366	2.355	2.345	2.335	2.330	2.355
BVS of Ln	3.35	3.33	3.31	3.31	3.28	3.28	3.20	3.23
Mo(1)-O(8)	1.700(7)	1.699(8)	1.697(4)	1.697(5)	1.697(3)	1.698(3)	1.718(7)	1.698(3)
Mo(1)-O(4)	1.744(6)	1.746(6)	1.742(4)	1.745(4)	1.746(3)	1.749(3)	1.750(6)	1.747(3)
Mo(1)-O(2)	1.860(6)	1.871(6)	1.867(3)	1.866(4)	1.870(3)	1.870(2)	1.864(5)	1.871(3)
Mo(1)-O(1)	1.933(5)	1.937(6)	1.937(3)	1.936(4)	1.937(3)	1.936(2)	1.937(5)	1.936(3)
Mo(1)-O(3)#4	2.164(6)	2.166(6)	2.168(3)	2.163(4)	2.165(3)	2.159(3)	2.165(6)	2.162(3)
BVS of Mo	5.87	5.82	5.86	5.86	5.83	5.83	5.74	5.83
Mo(2)-O(9)	1.704(6)	1.710(7)	1.709(4)	1.708(5)	1.706(3)	1.710(3)	1.715(6)	1.712(3)
Mo(2)-O(5)	1.740(6)	1.746(6)	1.735(3)	1.744(4)	1.736(3)	1.741(3)	1.746(6)	1.736(3)
Mo(2)-O(3)	1.874(5)	1.879(6)	1.879(3)	1.877(4)	1.880(3)	1.883(2)	1.895(6)	1.876(3)
Mo(2)-O(1)	1.975(5)	1.981(6)	1.980(3)	1.980(4)	1.978(3)	1.980(2)	1.977(5)	1.977(3)
Mo(2)-O(2)#5	2.173(5)	2.169(6)	2.177(3)	2.171(4)	2.174(3)	2.172(3)	2.167(6)	2.172(3)
Mo(2)-OW2	2.376(7)	2.359(7)	2.387(4)	2.372(5)	2.371(3)	2.360(3)	2.365(7)	2.365(3)
BVS of Mo	6.00	5.93	5.95	5.95	5.98	5.94	5.87	5.98
I(1)-O10	1.799(6)	1.801(7)	1.791(4)	1.794(4)	1.794(3)	1.794(3)	1.803(6)	1.791(3)
I(1)-O(6)	1.811(6)	1.824(6)	1.815(4)	1.813(4)	1.816(3)	1.813(3)	1.819(6)	1.808(3)
I(1)-O(7)	1.824(6)	1.830(6)	1.823(4)	1.816(4)	1.819(3)	1.821(3)	1.825(6)	1.817(3)
BVS of I	5.00	4.90	5.02	5.05	5.02	5.02	4.94	5.08

Table S3. Selected bond distances and BVS for **ThFMoIO**.

	Bond distance
Th(1)-F(1)	2.321(6)
Th(1)-F(1)#1	2.342(6)
Th(1)-O(7)	2.367(8)
Th(1)-O(3)#2	2.430(8)
Th(1)-O(4)#3	2.451(7)
Th(1)-O(6)	2.463(8)
Th(1)-O(8)#4	2.491(8)
Th(1)-O(5)#1	2.515(8)
Th(1)-O(2)#5	2.516(8)
BVS of Th	4.17
Mo(1)-O(8)	1.734(8)
Mo(1)-O(7)	1.749(8)
Mo(1)-O(4)	1.768(7)
Mo(1)-O(3)	1.792(8)
BVS of Mo	5.95
I(1)-O(6)	1.790(9)
I(1)-O(5)	1.796(9)
I(1)-O(2)	1.809(8)
BVS of I	5.18

Table S4. Crystallographic data for **LnMoIO-1** (Ln = Ce − Pr), **LnMoIO-2** (Ln = Gd – Yb, Y), and **ThFMoIO**.

Compound	**Ce**	**Pr**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Y**	**Th**
Formula Mass	$CeI_4M_oO_{15}$ 983.66	$PrI_4M_oO_{15}$ 984.45	$GdIMo_2O_{12}$ 668.03	$TbIMo_2O_{12}$ 669.70	$DyIMo_2O_{12}$ 673.28	$HoIMo_2O_{12}$ 675.71	$ErIMo_2O_{12}$ 678.04	$TmIMo_2O_1{}_2$ 679.71	$YbIMo_2O_1{}_2$ 683.82	$YIMo_2O_{12}$ 599.69	$ThIMoFO_7$ 585.88
Color	Purple	Green	Colorless	Colorless	Colorless	Pink	Purple	Colorless	Colorless	Colorless	Colorless
Habit	Tablet	Tablet	Tablet	Tablet	Tablet	Tablet	Tablet	Tablet	Tablet	Tablet	Octahedral
Space Group	$P2_1$	$P2_1$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	$P2_1/_n$	*Pbca*
a (Å)	6.9831(10)	6.9871(12)	7.6068(10)	7.5995(12)	7.5804(4)	7.5555(4)	7.5508(4)	7.5360(6)	7.5242(16)	7.5639(6)	7.261(3)
b (Å)	14.1056(19)	14.114(2)	11.3865(15)	11.3847(18)	11.3583(6)	11.3438(6)	11.3352(6)	11.3220(9)	11.321(2)	11.3372(9)	8.769(4)
c (Å)	7.0752(9)	7.0873(12)	11.3561(15)	11.3300(19)	11.2975(6)	11.2690(6)	11.2366(6)	11.1946(9)	11.203(2)	11.2573(10)	21.820(8)
α (deg)	90	90	90	90	90	90	90	90	90	90	90
β (deg)	115.325(4)	115.065(4)	92.129(3)	92.142(4)	92.2852(17)	92.2717(15)	92.3336(16)	92.284(2)	92.308(7)	92.219(2)	90
γ (deg)	90	90	90	90	90	90	90	90	90	90	90
V (Å^3)	629.94(15)	633.11(19)	982.9(2)	979.6(3)	971.95(9)	965.09(9)	960.94(9)	954.39(13)	953.5(3)	964.63(14)	1389.3(9)
Z	2	2	4	4	4	4	4	4	4	4	8
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Max. 2θ (°)	27.580	27.537	27.559	27.535	27.569	27.649	27.575	27.565	27.550	27.597	27.527

ρ_{calcd} (g cm^{-3})	5.186	5.164	4.514	4.541	4.601	4.651	4.687	4.730	4.764	4.129	5.602
μ (Mo Kα) (mm^{-1})	14.448	14.629	12.379	12.871	13.383	13.935	14.494	15.096	15.614	11.785	27.645
Flack factor	0.120(16)	0.041(10)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
GoF on F^2	1.113	1.103	1.452	1.216	1.129	1.060	1.165	1.156	1.118	1.137	1.200
R_{int}	0.0518	0.0499	0.0588	0.0642	0.0426	0.0404	0.0376	0.0383	0.0745	0.0572	0.0431
R_1,[a] wR_2 [I >	0.0254,	0.0175,	0.0387,	0.0319,	0.0219,	0.0150,	0.0165,	0.0161,	0.0329,	0.0201,	0.0343,
2σ(I)][b]	0.0617	0.0412	0.1136	0.1110	0.0474	0.0324	0.0373	0.0387	0.0959	0.0464	0.0902
R_1,[a] wR_2 (all data)[b]	0.0256,	0.0178,	0.0431,	0.0333,	0.0284,	0.0168,	0.0184,	0.0171,	0.0436,	0.0213,	0.0417,
	0.0618	0.0413	0.1290	0.1143	0.0489	0.0328	0.0378	0.0390	0.1056	0.0467	0.0928
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e	1.462,	1.240,	5.136,	2.170,	1.139,	1.022,	0.939,	1.103,	2.539 ,	0.884,	1.627,
Å^{-3}	-1.486	-0.911	-5.649	-3.021	-1.161	-0.589	-0.872	-1.162	-3.532	-0.708	-3.106