

Supplementary Information

Discovery of the selenotantalate building block and its lanthanide derivatives: design, synthesis, and RhB decolorization properties

Haiying Wang,^{†,‡} Junjun Sun,[†] Yachun Ma,[†] Chen Li,[†] Nan Li,[†] Pengtao Ma,[†] Dongdi Zhang,^{*,†} Guan Wang,[†] Jingping Wang,[†] and Jingyang Niu^{*,†}

[†]Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China.

[‡]Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China.

Table S1. Survey of the reported POTa clusters.

Published year	compounds
2007, 2009, 2012	$A_8[Ta_6O_{19}] \cdot nH_2O$ $A=K, Na; Rb, Cs; Na; Li; NaLi; TBA$ ^{1,2,3,4}
2001	$K_7[Re(CO)_3Ta_6O_{19}]$ $K_7[Mn(CO)_3Ta_6O_{19}]$ <i>cis</i> - $K_6[\{Mn(CO)_3\}_2Ta_6O_{19}]$ <i>trans</i> - $K_4Na_2[\{Re(CO)_3\}_2Ta_6O_{19}]$ ⁵
2011	$\{[Cu(1,3-dap)_2]_2[Cu(1,3-dap)(H_2O)]_2[Ta_6O_{19}]\} \cdot 8H_2O$ $[Cu(en)_2]_4[Ta_6O_{19}] \cdot 14H_2O$ ⁶
2012	$K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3] \cdot 17H_2O$ $K_8Na_8H_4[P_8W_{60}Ta_{12}(H_2O)_4(OH)_8O_{236}] \cdot 42H_2O$ $Cs_3K_{3.5}H_{0.5}[SiW_9(TaO_2)_3O_{37}] \cdot 9H_2O$ $Cs_{10.5}K_4H_{5.5}[Ta_4O_6(SiW_9Ta_3O_{40})_4] \cdot 30H_2O$ ⁷
2013	$TBA_6[Ta_{10}O_{28}] \cdot 6H_2O$ ⁸
2014	$Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu-O)] \cdot 39.4H_2O$ $Na_4[trans-\{(C_6H_6)Ru\}_2Ta_6O_{19}] \cdot 20H_2O$ ⁹
2014	$CsNa_2H[Cu(bpy)(H_2O)_3]_3\{[Cu(bpy)_2]_2[Cu(bpy)(H_2O)_2]_3[Ta_4O_6(SiW_9Ta_3O_{40})_4]\} \cdot 17H_2O$ $K_4Na_4H_4[Ta_4O_6(SiW_9Ta_3O_{40})_4][Cu(apy)(H_2O)_2]_4 \cdot 42H_2O$ ¹⁰
2015	$Cs_4[trans-\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$ ¹¹
2016	$Cs_{16}K_{16}Na_4[Ta_{18}P_{12}W_{90}(OH)_6(H_2O)_2O_{360}] \cdot 24H_2O$ ¹²
2016	$H_{20}[P_8W_{60}Ta_{12}(H_2O)_4(OH)_8O_{236}] \cdot 125H_2O$ ¹³
2016	$TMA_8Ti_2Ta_8O_{28} \cdot 21H_2O$ $TMA_{10}Ti_{12}Ta_6O_{44} \cdot 39H_2O$ ¹⁴
2016	$Na_4[trans-\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 24H_2O$ ⁶
2016	$Na_6[\{Cp^*Ir\}Ta_6O_{19}] \cdot 27H_2O$ $Na_4[trans-\{Cp^*Ir\}_2Ta_6O_{19}] \cdot 24H_2O$ ¹⁵
2016	$Cs_5K_2[(Si_2W_{18}Ta_6O_{78})Cr(H_2O)_4] \cdot 8H_2O$ $Cs_3K_4H_2[(Si_2W_{18}Ta_6O_{78})FeCl_2(H_2O)_2] \cdot 15H_2O$ ¹⁶
2016	$Cs_{26}K_2H_2[Yb_2Ta_{18}P_{12}W_{90}(OH)_6(H_2O)_{16}O_{360}] \cdot 52H_2O$ ¹²
2017	$Cs_5K_4\{Cr_3[Ta_3P_2W_{15}O_{62}]_2(H_2O)_{12}\} \cdot 15H_2O$ $Cs_{8.5}K_8Na_2H_{5.5}\{Cr_4[Ta_3P_2W_{15}O_{62}]_4(H_2O)_{12}\} \cdot 53H_2O$ ¹⁷
2017	$Cs_{12.5}K_{4.5}H[Ta_{12}Si_4W_{37}O_{158}] \cdot 25H_2O$ ¹⁸
2017	$Cs_3[H_9P_4Ta_6(O_2)_6O_{25}] \cdot 9H_2O$, $(CN_3H_6)_6[H_4P_4Ta_6(O_2)_6O_{24}] \cdot 4H_2O$ ¹⁹
2017	$[Ln_3(H_2O)_{22}][P_2W_{15}Ta_3O_{62}] \cdot nH_2O$ ($Ln = La; Ce; Pr; Nd$) ²⁰
2018	$Na_8K_7[(Ta_6O_{19})_4H_5Co_8O_4] \cdot 45H_2O$ ²¹
2019	$\{[CuL]_2[CuL_2]_2[Ta_6O_{19}]\} \cdot 21H_2O$ ($L = 1, 10\text{-phen}$)
2019	$Cs_3[Ln(H_2O)_6\{H_4(TaO_2)_6As_4O_{24}\}] \cdot 7H_2O$ ²³

Table S2. Bond lengths in **1–7**.

Compound 1					
Bond	Length	Bond	Length	Bond	Length
Ta(1)–O(2)	2.037(13)	Ta(2)–O(1)	1.948(16)	Ta(3)–O(5)1	2.037(14)
Ta(1)–O(7)	1.959(14)	Ta(2)–O(4)	1.976(14)	Ta(3)–O(8)	2.109(14)
Ta(1)–O(10)1	2.084(12)	Ta(2)–O(6)	1.901(3)	Ta(3)–O(13)	1.959(14)
Ta(1)–O(11)	1.979(14)	Ta(2)–O(8)	2.069(14)	Ta(3)–O(14)	1.955(14)
Ta(1)–O(12)1	2.104(13)	Ta(2)–O(9)	2.087(13)	Ta(3)–O(15)	1.919(12)
Ta(1)–O(15)	1.904(12)	Ta(2)–O(12)	2.040(13)	Ta(3)–O(16)	2.105(13)
Ta(1)–O(17)1	2.096(13)	Ta(2)–O(17)	2.078(12)	Ta(3)–O(17)	2.108(13)
Se(1)–O(9)	1.694(14)	Se(1)–O(10)	1.710(13)	Se(1)–O(16)	1.701(14)
Se(2)–O(2)	1.682(13)	Se(2)–O(3)	1.666(16)	Se(2)–O(5)	1.703(15)
Compound 2					
Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.975(9)	Ta(4)-O(10)	1.997(9)	Tb(1)-O(1)	2.382(8)
Ta(1)-O(18)	1.991(9)	Ta(4)-O(13)	2.090(8)	Tb(1)-O(4)	2.285(8)
Ta(1)-O(22)	1.892(8)	Ta(4)-O(14)	1.976(8)	Tb(1)-O(1W)	2.409(10)
Ta(1)-O(24)	2.064(8)	Ta(4)-O(15)	2.053(8)	Tb(1)-O(2W)	2.493(10)
Ta(1)-O(25)	2.054(8)	Ta(4)-O(22)	1.924(8)	Tb(1)-O(3W)	2.397(10)
Ta(1)-O(30)	2.070(8)	Ta(4)-O(29)	2.077(8)	Tb(1)-O(4W)	2.365(10)
Ta(1)-O(33)	2.061(7)	Ta(4)-O(31)	2.045(8)	Tb(1)-O(9W)	2.423(11)
Ta(2)-O(5)	1.972(8)	Ta(5)-O(2)	1.990(9)	Tb(1)-O(10W)	2.358(12)
Ta(2)-O(6)	2.000(8)	Ta(5)-O(11)	1.958(10)	Se(1)-O(20)	1.709(8)
Ta(2)-O(9)	2.049(8)	Ta(5)-O(17)	2.040(8)	Se(1)-O(25)	1.729(8)
Ta(2)-O(26)	1.843(8)	Ta(5)-O(23)	2.162(8)	Se(1)-O(27)	1.688(8)
Ta(2)-O(27)	2.145(8)	Ta(5)-O(26)	2.007(8)	Se(2)-O(13)	1.695(8)
Ta(2)-O(32)	2.088(8)	Ta(5)-O(28)	1.913(8)	Se(2)-O(21)	1.699(8)

Ta(2)-O(33)	2.092(7)	Ta(5)-O(31)	2.109(8)	Se(2)-O(23)	1.706(8)
Ta(3)-O(8)	1.964(8)	Ta(6)-O(3)	1.969(9)	Se(3)-O(4)	1.638(8)
Ta(3)-O(12)	1.969(9)	Ta(6)-O(7)	1.961(9)	Se(3)-O(15)	1.714(8)
Ta(3)-O(19)	1.908(8)	Ta(6)-O(19)	1.881(8)	Se(3)-O(17)	1.722(8)
Ta(3)-O(20)	2.083(8)	Ta(6)-O(21)	2.132(8)	Se(4)-O(1)	1.665(8)
Ta(3)-O(30)	2.032(8)	Ta(6)-O(28)	1.995(8)	Se(4)-O(9)	1.722(8)
Ta(3)-O(32)	2.043(8)	Ta(6)-O(29)	2.077(8)	Se(4)-O(24)	1.722(9)
Ta(3)-O(33)	2.095(7)	Ta(6)-O(31)	2.066(8)		

Compound 3

Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.971(12)	Ta(4)-O(10)	1.983(12)	Dy(1)-O(1)	2.348(12)
Ta(1)-O(18)	1.975(12)	Ta(4)-O(13)	2.072(12)	Dy(1)-O(4)	2.260(11)
Ta(1)-O(22)	1.914(11)	Ta(4)-O(14)	1.992(12)	Dy(1)-O(1W)	2.384(14)
Ta(1)-O(24)	2.072(11)	Ta(4)-O(15)	2.064(11)	Dy(1)-O(2W)	2.465(15)
Ta(1)-O(25)	2.048(11)	Ta(4)-O(22)	1.901(11)	Dy(1)-O(3W)	2.374(15)
Ta(1)-O(30)	2.082(11)	Ta(4)-O(29)	2.077(11)	Dy(1)-O(4W)	2.341(16)
Ta(1)-O(33)	2.068(10)	Ta(4)-O(31)	2.053(10)	Dy(1)-O(9W)	2.39(2)
Ta(2)-O(5)	1.965(11)	Ta(5)-O(2)	1.963(14)	Dy(1)-O(10W)	2.337(19)
Ta(2)-O(6)	1.999(11)	Ta(5)-O(11)	1.970(16)	Se(1)-O(20)	1.715(11)
Ta(2)-O(9)	2.046(11)	Ta(5)-O(17)	2.032(11)	Se(1)-O(25)	1.715(11)
Ta(2)-O(26)	1.856(11)	Ta(5)-O(23)	2.165(12)	Se(1)-O(27)	1.680(12)
Ta(2)-O(27)	2.142(12)	Ta(5)-O(26)	1.989(11)	Se(2)-O(13)	1.690(12)
Ta(2)-O(32)	2.089(11)	Ta(5)-O(28)	1.924(11)	Se(2)-O(21)	1.706(11)
Ta(2)-O(33)	2.102(10)	Ta(5)-O(31)	2.104(10)	Se(2)-O(23)	1.710(12)
Ta(3)-O(8)	1.981(11)	Ta(6)-O(3)	1.971(12)	Se(3)-O(4)	1.646(11)
Ta(3)-O(12)	1.976(13)	Ta(6)-O(7)	1.959(12)	Se(3)-O(15)	1.686(11)
Ta(3)-O(19)	1.879(11)	Ta(6)-O(19)	1.909(11)	Se(3)-O(17)	1.718(11)

Ta(3)-O(20)	2.103(11)	Ta(6)-O(21)	2.113(11)	Se(4)-O(1)	1.674(12)
Ta(3)-O(30)	2.014(11)	Ta(6)-O(28)	1.996(12)	Se(4)-O(9)	1.708(11)
Ta(3)-O(32)	2.045(11)	Ta(6)-O(29)	2.063(11)	Se(4)-O(24)	1.720(11)
Ta(3)-O(33)	2.077(10)	Ta(6)-O(31)	2.075(10)		
Compound 4					
Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.993(11)	Ta(4)-O(10)	1.978(11)	Ho(1)-O(1)	2.366(10)
Ta(1)-O(18)	1.979(11)	Ta(4)-O(13)	2.077(11)	Ho(1)-O(4)	2.254(11)
Ta(1)-O(22)	1.906(10)	Ta(4)-O(14)	1.988(11)	Ho(1)-O(1W)	2.397(12)
Ta(1)-O(24)	2.072(11)	Ta(4)-O(15)	2.059(10)	Ho(1)-O(2W)	2.449(13)
Ta(1)-O(25)	2.061(10)	Ta(4)-O(22)	1.909(10)	Ho(1)-O(3W)	2.381(12)
Ta(1)-O(30)	2.080(10)	Ta(4)-O(29)	2.068(10)	Ho(1)-O(4W)	2.354(12)
Ta(1)-O(33)	2.058(10)	Ta(4)-O(31)	2.046(10)	Ho(1)-O(9W)	2.419(13)
Ta(2)-O(5)	1.969(11)	Ta(5)-O(2)	1.961(12)	Ho(1)-O(10W)	2.328(13)
Ta(2)-O(6)	1.991(10)	Ta(5)-O(11)	1.946(13)	Se(1)-O(20)	1.695(10)
Ta(2)-O(9)	2.056(10)	Ta(5)-O(17)	2.039(10)	Se(1)-O(25)	1.731(10)
Ta(2)-O(26)	1.835(10)	Ta(5)-O(23)	2.177(11)	Se(1)-O(27)	1.699(11)
Ta(2)-O(27)	2.160(11)	Ta(5)-O(26)	2.014(10)	Se(2)-O(13)	1.707(11)
Ta(2)-O(32)	2.087(10)	Ta(5)-O(28)	1.895(10)	Se(2)-O(21)	1.699(11)
Ta(2)-O(33)	2.088(10)	Ta(5)-O(31)	2.100(10)	Se(2)-O(23)	1.698(11)
Ta(3)-O(8)	1.976(10)	Ta(6)-O(3)	1.981(11)	Se(3)-O(4)	1.651(11)
Ta(3)-O(12)	1.966(11)	Ta(6)-O(7)	1.950(11)	Se(3)-O(15)	1.711(11)
Ta(3)-O(19)	1.890(10)	Ta(6)-O(19)	1.902(10)	Se(3)-O(17)	1.712(10)
Ta(3)-O(20)	2.100(10)	Ta(6)-O(21)	2.127(11)	Se(4)-O(1)	1.670(11)
Ta(3)-O(30)	2.027(10)	Ta(6)-O(28)	1.994(10)	Se(4)-O(9)	1.707(10)
Ta(3)-O(32)	2.048(10)	Ta(6)-O(29)	2.071(11)	Se(4)-O(24)	1.713(11)
Ta(3)-O(33)	2.107(9)	Ta(6)-O(31)	2.093(10)		

Compound 5					
Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.975(9)	Ta(4)-O(10)	1.997(9)	Er(1)-O(1)	2.364(9)
Ta(1)-O(18)	2.000(9)	Ta(4)-O(13)	2.092(9)	Er(1)-O(4)	2.259(9)
Ta(1)-O(22)	1.899(8)	Ta(4)-O(14)	1.978(9)	Er(1)-O(1W)	2.379(10)
Ta(1)-O(24)	2.065(8)	Ta(4)-O(15)	2.055(9)	Er(1)-O(2W)	2.440(11)
Ta(1)-O(25)	2.060(8)	Ta(4)-O(22)	1.915(9)	Er(1)-O(3W)	2.357(11)
Ta(1)-O(30)	2.067(8)	Ta(4)-O(29)	2.074(8)	Er(1)-O(4W)	2.331(11)
Ta(1)-O(33)	2.062(8)	Ta(4)-O(31)	2.044(8)	Er(1)-O(9W)	2.383(12)
Ta(2)-O(5)	1.980(9)	Ta(5)-O(2)	1.984(11)	Er(1)-O(10W)	2.316(12)
Ta(2)-O(6)	1.990(9)	Ta(5)-O(11)	1.951(13)	Se(1)-O(20)	1.704(9)
Ta(2)-O(9)	2.054(9)	Ta(5)-O(17)	2.038(8)	Se(1)-O(25)	1.719(8)
Ta(2)-O(26)	1.848(9)	Ta(5)-O(23)	2.156(9)	Se(1)-O(27)	1.689(9)
Ta(2)-O(27)	2.147(9)	Ta(5)-O(26)	1.997(9)	Se(2)-O(13)	1.701(9)
Ta(2)-O(32)	2.085(8)	Ta(5)-O(28)	1.912(8)	Se(2)-O(21)	1.703(8)
Ta(2)-O(33)	2.100(8)	Ta(5)-O(31)	2.109(8)	Se(2)-O(23)	1.712(9)
Ta(3)-O(8)	1.971(9)	Ta(6)-O(3)	1.983(9)	Se(3)-O(4)	1.637(9)
Ta(3)-O(12)	1.981(9)	Ta(6)-O(7)	1.968(9)	Se(3)-O(15)	1.702(9)
Ta(3)-O(19)	1.883(8)	Ta(6)-O(19)	1.905(8)	Se(3)-O(17)	1.722(8)
Ta(3)-O(20)	2.082(9)	Ta(6)-O(21)	2.139(8)	Se(4)-O(1)	1.651(9)
Ta(3)-O(30)	2.029(9)	Ta(6)-O(28)	2.012(9)	Se(4)-O(9)	1.705(9)
Ta(3)-O(32)	2.049(9)	Ta(6)-O(29)	2.073(9)	Se(4)-O(24)	1.726(9)
Ta(3)-O(33)	2.086(8)	Ta(6)-O(31)	2.077(8)		
Compound 6					
Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.982(12)	Ta(4)-O(10)	1.978(11)	Tm(1)-O(1)	2.333(12)

Ta(1)-O(18)	1.985(12)	Ta(4)-O(13)	2.083(11)	Tm(1)-O(4)	2.217(12)
Ta(1)-O(22)	1.894(11)	Ta(4)-O(14)	1.982(12)	Tm(1)-O(1W)	2.358(14)
Ta(1)-O(24)	2.074(11)	Ta(4)-O(15)	2.047(12)	Tm(1)-O(2W)	2.434(15)
Ta(1)-O(25)	2.063(11)	Ta(4)-O(22)	1.924(11)	Tm(1)-O(3W)	2.353(13)
Ta(1)-O(30)	2.058(11)	Ta(4)-O(29)	2.055(11)	Tm(1)-O(4W)	2.316(14)
Ta(1)-O(33)	2.054(10)	Ta(4)-O(31)	2.039(11)	Tm(1)-O(9W)	2.388(16)
Ta(2)-O(5)	1.960(11)	Ta(5)-O(2)	1.972(14)	Tm(1)-O(10W)	2.316(15)
Ta(2)-O(6)	1.983(12)	Ta(5)-O(11)	1.963(14)	Se(1)-O(20)	1.711(11)
Ta(2)-O(9)	2.054(12)	Ta(5)-O(17)	2.031(11)	Se(1)-O(25)	1.718(11)
Ta(2)-O(26)	1.833(11)	Ta(5)-O(23)	2.163(11)	Se(1)-O(27)	1.693(11)
Ta(2)-O(27)	2.149(11)	Ta(5)-O(26)	2.016(11)	Se(2)-O(13)	1.687(12)
Ta(2)-O(32)	2.101(12)	Ta(5)-O(28)	1.910(12)	Se(2)-O(21)	1.687(11)
Ta(2)-O(33)	2.106(10)	Ta(5)-O(31)	2.117(11)	Se(2)-O(23)	1.713(12)
Ta(3)-O(8)	1.972(12)	Ta(6)-O(3)	1.999(13)	Se(3)-O(4)	1.672(12)
Ta(3)-O(12)	1.984(12)	Ta(6)-O(7)	1.969(12)	Se(3)-O(15)	1.712(12)
Ta(3)-O(19)	1.883(11)	Ta(6)-O(19)	1.906(11)	Se(3)-O(17)	1.723(11)
Ta(3)-O(20)	2.092(11)	Ta(6)-O(21)	2.141(11)	Se(4)-O(1)	1.666(13)
Ta(3)-O(30)	2.050(11)	Ta(6)-O(28)	2.017(12)	Se(4)-O(9)	1.728(11)
Ta(3)-O(32)	2.048(11)	Ta(6)-O(29)	2.094(11)	Se(4)-O(24)	1.717(11)
Ta(3)-O(33)	2.091(10)	Ta(6)-O(31)	2.068(11)		

Compound 7

Bond	Length	Bond	Length	Bond	Length
Ta(1)-O(16)	1.980(11)	Ta(4)-O(10)	2.009(10)	Yb(1)-O(1)	2.348(10)
Ta(1)-O(18)	1.991(10)	Ta(4)-O(13)	2.087(10)	Yb(1)-O(4)	2.225(10)
Ta(1)-O(22)	1.918(10)	Ta(4)-O(14)	2.001(10)	Yb(1)-O(1W)	2.348(11)
Ta(1)-O(24)	2.073(10)	Ta(4)-O(15)	2.056(10)	Yb(1)-O(2W)	2.426(12)
Ta(1)-O(25)	2.075(9)	Ta(4)-O(22)	1.898(10)	Yb(1)-O(3W)	2.352(12)

Ta(1)-O(30)	2.074(10)	Ta(4)-O(29)	2.086(10)	Yb(1)-O(4W)	2.315(12)
Ta(1)-O(33)	2.061(9)	Ta(4)-O(31)	2.062(9)	Yb(1)-O(9W)	2.389(13)
Ta(2)-O(5)	1.962(10)	Ta(5)-O(2)	1.988(12)	Yb(1)-O(10W)	2.294(13)
Ta(2)-O(6)	1.999(10)	Ta(5)-O(11)	1.958(12)	Se(1)-O(20)	1.697(9)
Ta(2)-O(9)	2.061(10)	Ta(5)-O(17)	2.043(9)	Se(1)-O(25)	1.705(9)
Ta(2)-O(26)	1.848(10)	Ta(5)-O(23)	2.166(10)	Se(1)-O(27)	1.703(10)
Ta(2)-O(27)	2.148(10)	Ta(5)-O(26)	2.000(10)	Se(2)-O(13)	1.692(10)
Ta(2)-O(32)	2.091(10)	Ta(5)-O(28)	1.898(10)	Se(2)-O(21)	1.694(10)
Ta(2)-O(33)	2.094(9)	Ta(5)-O(31)	2.093(9)	Se(2)-O(23)	1.709(10)
Ta(3)-O(8)	1.967(10)	Ta(6)-O(3)	1.983(11)	Se(3)-O(4)	1.652(10)
Ta(3)-O(12)	1.979(11)	Ta(6)-O(7)	1.963(10)	Se(3)-O(15)	1.712(10)
Ta(3)-O(19)	1.897(9)	Ta(6)-O(19)	1.891(9)	Se(3)-O(17)	1.718(9)
Ta(3)-O(20)	2.090(9)	Ta(6)-O(21)	2.150(9)	Se(4)-O(1)	1.658(10)
Ta(3)-O(30)	2.034(9)	Ta(6)-O(28)	2.022(10)	Se(4)-O(9)	1.727(10)
Ta(3)-O(32)	2.047(10)	Ta(6)-O(29)	2.076(10)	Se(4)-O(24)	1.718(10)
Ta(3)-O(33)	2.100(9)	Ta(6)-O(31)	2.064(9)		

Table S3. The selected Ta-O-Ta bond angle in **1–7**.

	1		2	3	4	5	6	7
Ta2—O6—Ta2 ⁱ	164.1(11)	Ta6—O19—Ta3	162.8(5)	163.3(7)	162.8(6)	163.5(5)	163.3(7)	163.2(6)
Ta2—O8—Ta3	107.0(6)	Ta1—O22—Ta4	163.1(5)	164.4(7)	163.6(6)	164.0(5)	163.2(6)	163.2(6)
Ta2—O12—Ta1 ⁱ	107.7(6)	Ta2—O26—Ta5	167.5(5)	168.4(6)	169.3(6)	168.1(5)	167.8(7)	167.8(6)
Ta1—O15—Ta3	159.7(8)	Ta5—O28—Ta6	109.7(4)	109.9(5)	110.5(5)	109.7(4)	109.3(5)	109.3(5)
Ta1 ⁱ —O17—Ta3	142.3(6)	Ta6—O29—Ta4	106.8(4)	107.5(5)	107.4(5)	107.0(4)	107.1(5)	106.4(4)
Ta2—O17—Ta1 ⁱ	106.5(5)	Ta3—O30—Ta1	108.2(4)	108.3(5)	108.3(5)	108.7(4)	108.2(5)	108.1(4)
Ta2—O17—Ta3	106.7(5)	Ta4—O31—Ta5	146.2(4)	145.9(5)	147.4(5)	146.5(4)	146.3(6)	146.2(5)
		Ta4—O31—Ta6	108.4(3)	107.9(5)	107.4(4)	108.0(3)	108.7(5)	107.8(4)
		Ta6—O31—Ta5	99.9(3)	100.4(4)	99.3(4)	100.1(3)	99.9(5)	100.6(4)
		Ta3—O32—Ta2	108.2(4)	108.1(5)	108.1(4)	108.1(4)	107.7(5)	107.9(4)
		Ta1—O33—Ta2	143.9(4)	143.3(5)	144.8(5)	143.3(4)	143.7(5)	143.9(5)
		Ta1—O33—Ta3	106.2(3)	106.5(5)	106.1(4)	106.7(4)	106.7(5)	106.1(4)
		Ta2—O33—Ta3	106.1(3)	106.4(4)	105.9(4)	106.2(3)	105.9(4)	105.9(4)

The Ta-O-Ta bond angle of the monoprotonated O atoms are highlighted in red. The Ta-O-Ta bond angle of the unprotonated O atoms with the same coordination environment are highlighted in green.

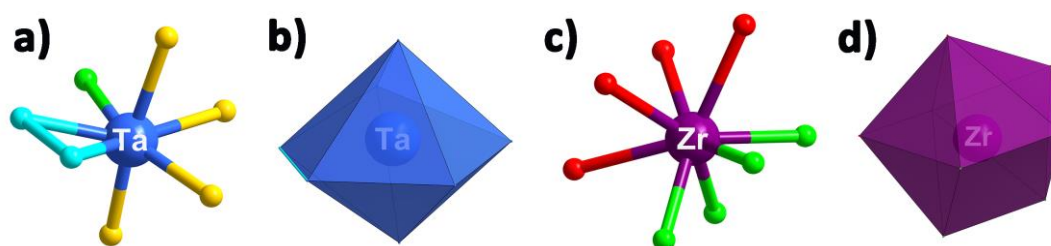


Figure S1. Coordination mode of **Ta** and **Zr**. Color code: peroxide, turquoise; hydroxide, green; oxo, gold; aqua, red; Ta, blue; Zr, violet.

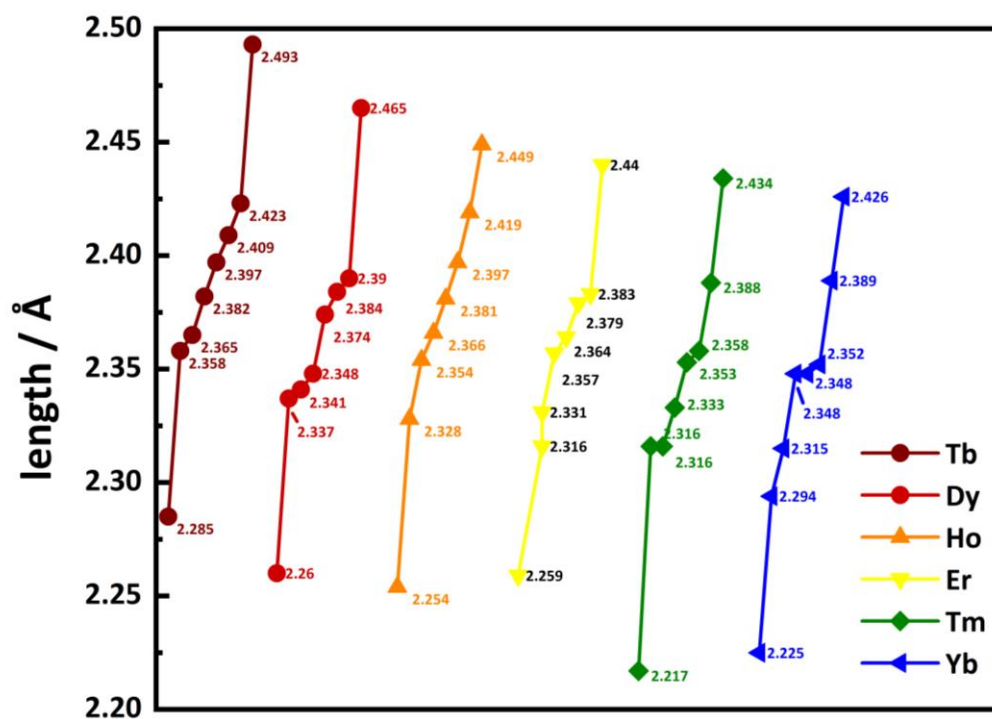


Figure S2. Ln-O bond lengths in 2-7.

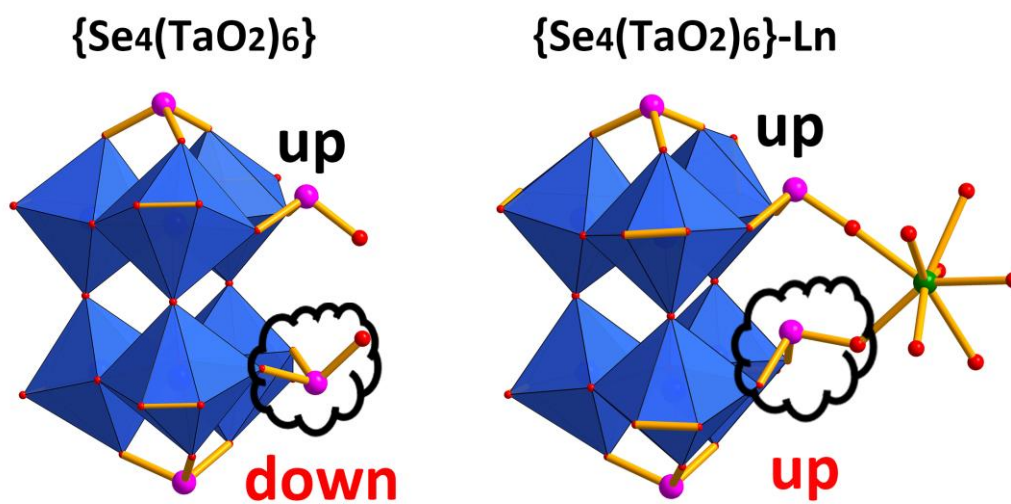


Figure S3. The position of the Se atoms.

Table S4. BVS calculation results for **1**.

Atom	Bond Valence Sum	Atom	Bond Valence Sum	Atom	Bond Valence Sum
Ta1	5.46	O4	0.89	O12	1.33
Ta2	5.58	O5	2.07	O13	0.93
Ta3	5.41	O6	2.105	O14	0.94
Se1	4.03	O7	0.93	O15	2.05
Se2	4.24	O8	1.27	O16	1.95
O1	0.96	O9	2.01	O17	1.88
O2	2.15	O10	1.96		
O3	1.55	O11	0.880		

The Op atoms are highlighted in red, and the monoprotonated O atoms in green.

Table S5. BVS calculation results for **2–7**.

Atom	2	3	4	5	6	7
Ta1	5.49	5.44	5.39	5.44	5.48	5.34
Ta2	5.42	5.39	5.45	5.38	5.46	5.40
Ta3	5.52	5.57	5.50	5.56	5.48	5.49
Ta4	5.36	5.41	5.44	5.38	5.45	5.30
Ta5	5.38	5.45	5.51	5.45	5.41	5.45
Ta6	5.60	5.55	5.51	5.42	5.34	5.45
Ln	3.23	3.34	3.18	3.19	3.24	3.13
Se1	3.96	4.02	3.96	4.01	3.97	4.03
Se2	4.05	4.03	4.03	4.00	4.11	4.07
Se3	4.17	4.25	4.16	4.21	4.03	4.13
Se4	4.02	4.05	4.10	4.13	4.02	4.05
O1	1.89	1.88	1.86	1.93	1.89	1.89
O2	1.86	1.99	2.00	1.91	1.89	1.90
O3	1.85	1.87	1.78	1.77	1.73	1.81
O4	2.13	2.11	2.08	2.11	2.01	2.06

O5	1.87	1.88	1.87	1.85	1.93	1.91
O6	1.81	1.80	1.82	1.83	1.88	1.83
O7	1.87	1.90	1.85	1.80	1.80	1.86
O8	1.83	1.79	1.79	1.74	1.82	1.85
O9	1.98	2.03	2.02	2.03	1.94	1.94
O10	1.86	1.82	1.88	1.83	1.85	1.80
O11	1.94	1.98	2.04	1.99	1.92	1.97
O12	1.82	1.80	1.82	1.72	1.79	1.82
O13	2.00	2.05	1.98	1.98	2.04	2.02
O14	1.90	1.81	1.85	1.88	1.84	1.82
O15	2.00	2.08	2.00	2.04	2.02	2.00
O16	1.85	1.94	1.77	1.83	1.77	1.82
O17	1.99	2.02	2.03	2.00	2.01	2.00
O18	1.81	1.93	1.80	1.78	1.77	1.79
O19	2.14	2.15	2.13	2.15	2.14	2.14
O20	1.96	1.91	1.98	1.98	1.94	1.99
O21	1.92	1.92	1.93	1.89	1.95	1.91
O22	2.07	2.07	2.07	2.07	2.06	2.07
O23	1.85	1.83	1.86	1.84	1.82	1.84
O24	1.95	1.94	1.97	1.93	1.95	1.94
O25	1.94	2.01	1.93	1.97	1.97	1.99
O26	2.02	2.02	2.03	2.02	2.04	2.02
O27	1.94	1.97	1.87	1.93	1.91	1.88
O28	1.84	1.80	1.89	1.80	1.80	1.82
O29	1.31	1.33	1.34	1.32	1.32	1.29
O30	1.40	1.42	1.40	1.42	1.39	1.39
O31	1.99	1.96	1.95	1.97	1.98	1.99
O32	1.35	1.35	1.34	1.35	1.32	1.34
O33	1.94	1.94	1.93	1.93	1.93	1.92
O1W	0.38	0.39	0.36	0.37	0.38	0.37

O2W	0.30	0.31	0.32	0.31	0.31	0.30
O3W	0.39	0.40	0.38	0.39	0.38	0.37
O4W	0.42	0.44	0.41	0.42	0.42	0.41
O9W	0.36	0.38	0.34	0.36	0.35	0.34
O10W	0.43	0.44	0.44	0.44	0.43	0.43

The monoprotonated O atoms are highlighted in green.

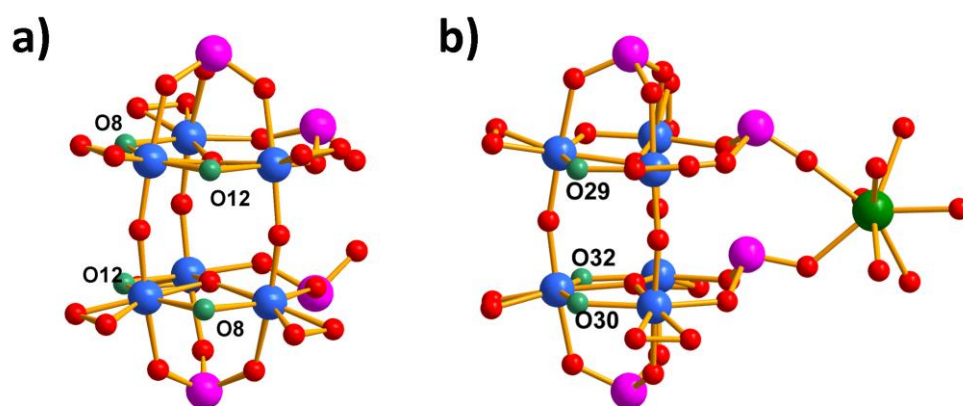


Figure S4. The monoprotonated O atoms in **1** (a) and **2-7** (b).

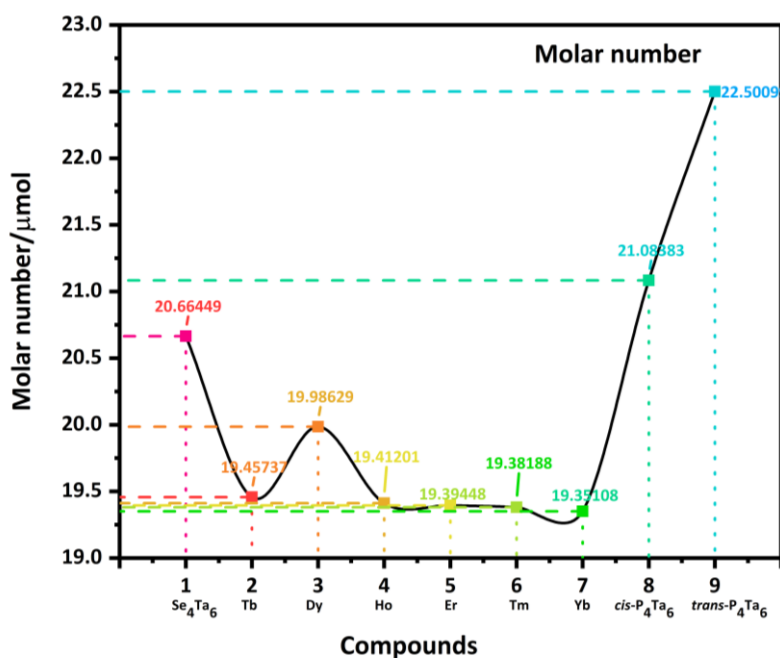


Figure S5. The comparison of molar quantities with 50 mg catalyst for compounds **1-7**, $\text{cis-P}_4\text{Ta}_6$ and $\text{trans-P}_4\text{Ta}_6$.

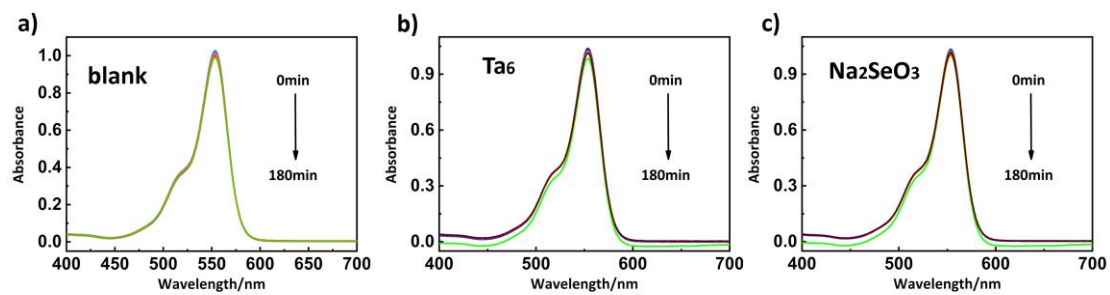


Figure S6. The comparison of photocatalytic degradation of RhB by blank, 50 mg Ta₆ and Na₂SeO₃.

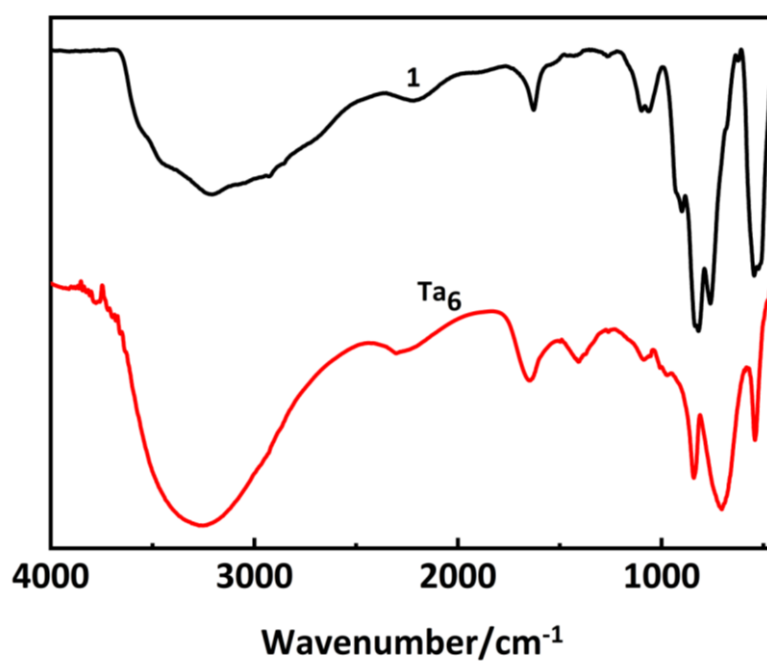


Figure S7. IR spectra of compound **1**, Ta₆ in the region between 4000 to 450 cm⁻¹.

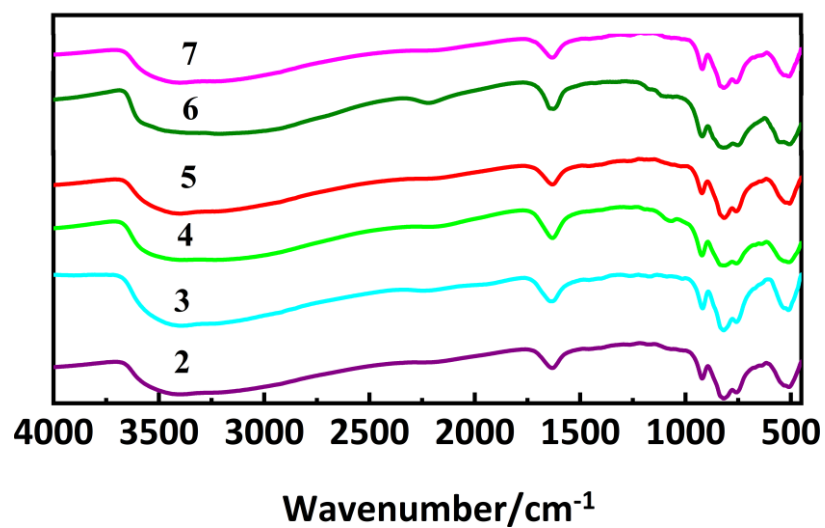


Figure S8. IR spectra of compounds 2-7 in the region between 4000 to 450 cm^{-1} .

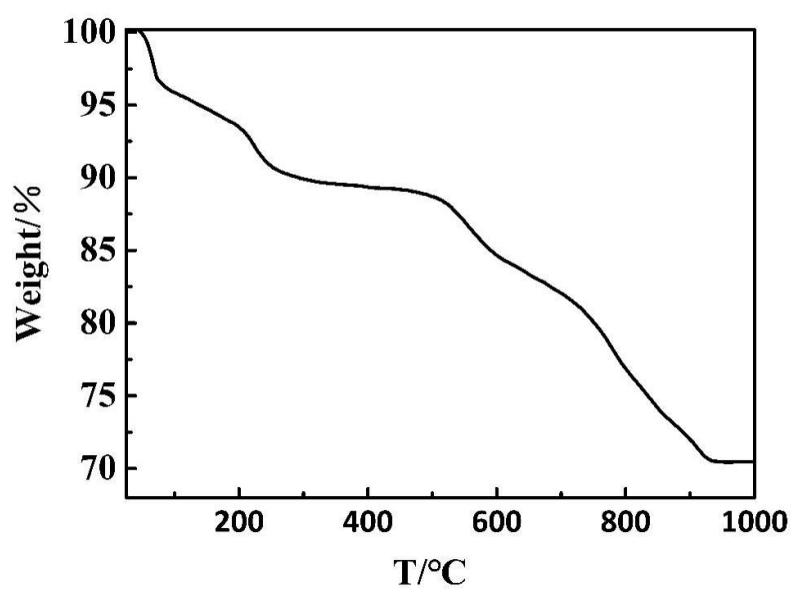


Figure S9. The TG curve of 1.

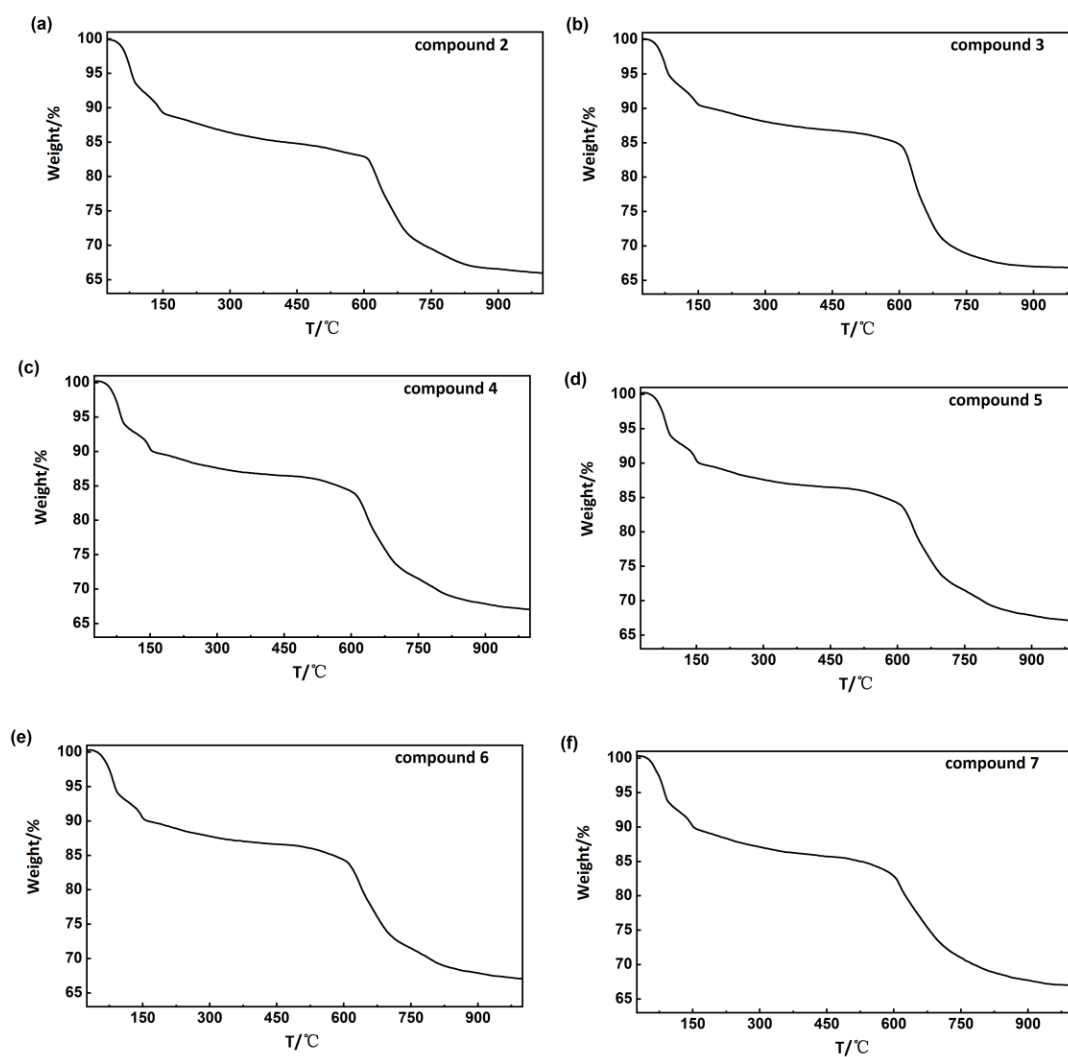


Figure S10. The TG curves of **2-7**.

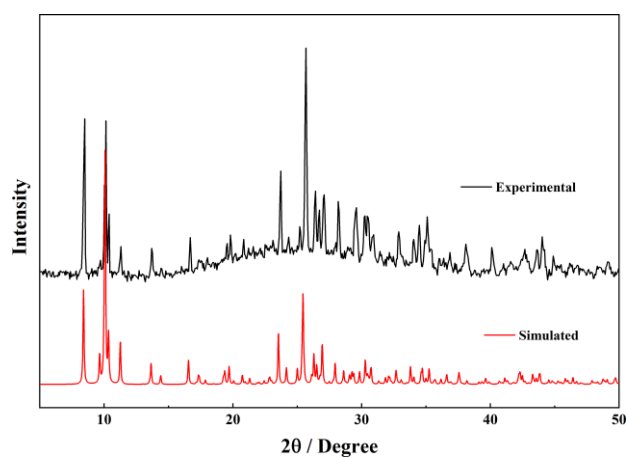


Figure S11. Comparison of experimental (black) and simulated (red) PXRD of compound **1**.

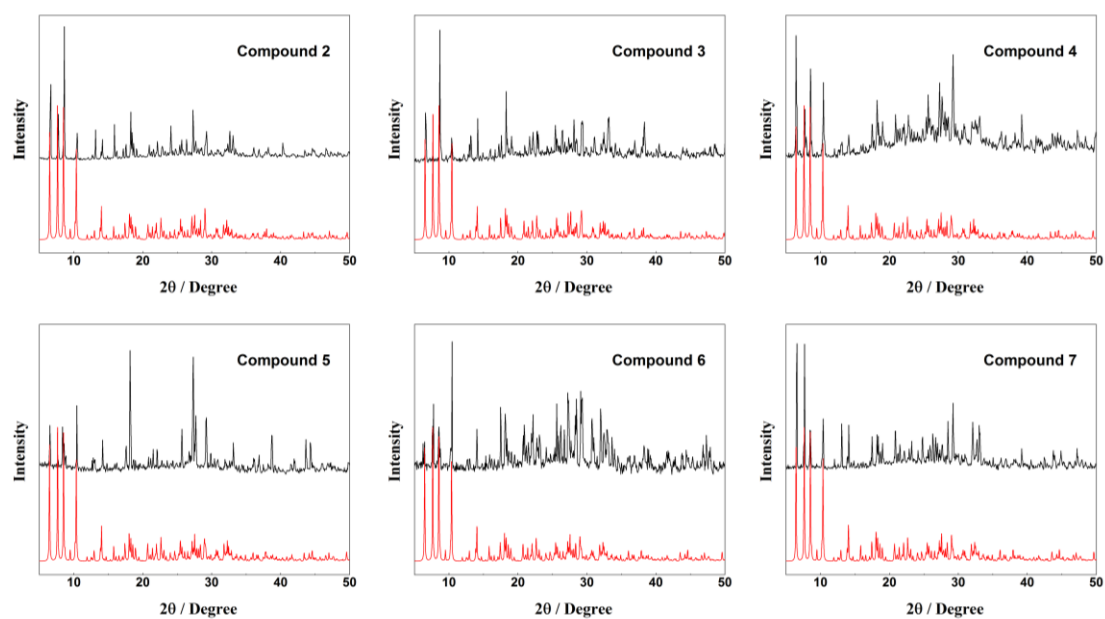


Figure S12. Comparison of experimental (black) and simulated (red) PXRDs of compounds 2-7.

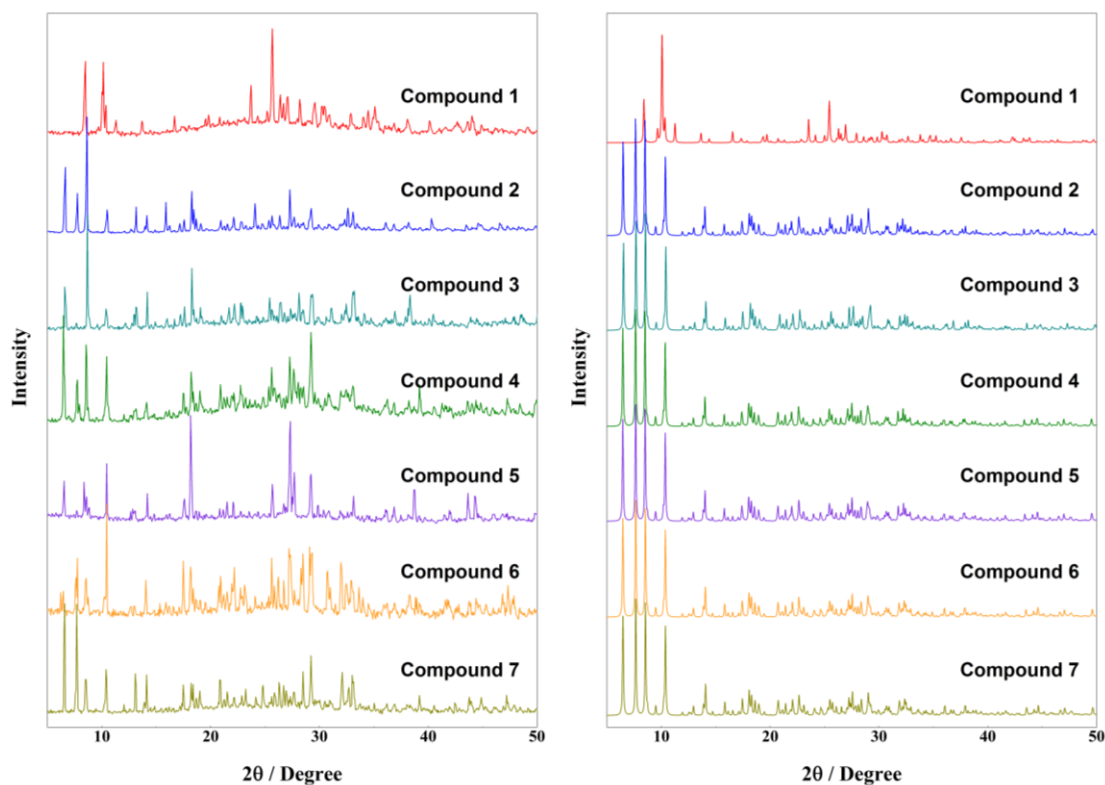


Figure S13. Comparison of experimental (left) and simulated (right) PXRDs of compounds 1-7, highlighting the difference between compound 1 and compounds 2-7.

The simulated pattern of compound 1 is obviously different from those of compounds

2-7, shown in the Figure S13 (right column), as well as the experimental results (left column in Figure S13). This difference is mainly attributed to the introduction of Lanthanide ions in compounds **2-7** ($\{\text{LnSe}_4(\text{TaO}_2)_6\}$, Figure S3), resulting in the different structures from compound **1** ($\{\text{Se}_4(\text{TaO}_2)_6\}$, Figure S3).

The simulated patterns of compounds **2-7** are almost same to each other because they are isostructural, whereas the experimental patterns of them have a little difference among them. However, the experimental and simulated PXRDs match well with each other.

Reference

- 1 T. M. Anderson, M. A. Rodriguez, F. Bonhomme, J. N. Bixler, T. M. Alam and M. Nyman, *Dalton Trans.*, 2007, 4517–4522.
- 2 M. Nyman, T. M. Anderson and P. P. Provencio, *Cryst. Growth Des.*, 2009, **9**, 1036–1040.
- 3 L. Shen, Y.-Q. Xu, Y.-Z. Gao, F.-Y. Cui and C.-W. Hu, *J. Mol. Struct.*, 2009, **934**, 37–43.
- 4 M. Matsumoto, Y. Ozawa and A. Yagasaki, *Inorg. Chem.*, 2012, **51**, 5991–5993.
- 5 A. V. Besserguenev, M. H. Dickman and M. T. Pope, *Inorg. Chem.*, 2001, **40**, 2582–2586.
- 6 G.-L. Guo, Y.-Q. Xu, B.-K. Chen, Z.-G. Lin and C.-W. Hu, *Inorg. Chem. Commun.*, 2011, **14**, 1448–1451.
- 7 S. Li, S. Liu, S. Liu, Y. Liu, Q. Tang, Z. Shi, S. Ouyang and J. Ye, *J. Am. Chem. Soc.*, 2012, **134**, 19716–19721.
- 8 M. Matsumoto, Y. Ozawa, A. Yagasaki and Y. Zhe, *Inorg. Chem.*, 2013, **52**, 7825–7827.
- 9 P. A. Abramov, M. N. Sokolov, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, E. V. Peresypkina, A. V. Virovets, C. Vicent, N. B. Kompankov, A. A. Zhdanov, O. V. Shuvaeva and V. P. Fedin, *Inorg. Chem.*, 2014, **53**, 12791–12798.
- 10 T.-Z. Zhang, S. Yao, Z.-M. Zhang, Y. Lu, Y.-G. Li and E.-B. Wang, *ChemPlusChem*, 2014, **79**, 1153–1158.
- 11 P. A. Abramov, M. N. Sokolov, A. V. Virovets, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, C. Vicent and V. P. Fedin, *Dalton Trans.*, 2015, **44**, 2234–2239.
- 12 P. Huang, C. Qin, Y. Zhou, Y.-M. Hong, X.-L. Wang and Z.-M. Su, *Chem. Commun.*, 2016, **52**, 13787–13790.
- 13 S. Li, Q. Peng, X. Chen, R. Wang, J. Zhai, W. Hu, F. Ma, J. Zhang and S. Liu, *J. Solid State Chem.*, 2016, **243**, 1–7.
- 14 J.-H. Son and W. H. Casey, *Chem. - Eur. J.*, 2016, **22**, 14155–14157.
- 15 P. A. Abramov, C. Vicent, N. B. Kompankov, A. L. Gushchin and M. N. Sokolov, *Eur. J. Inorg. Chem.*, 2016, **2016**, 154–160.
- 16 P. Huang, X.-G. Han, X.-L. Li, C. Qin, X.-L. Wang and Z.-M. Su, *CrystEngComm*, 2016, **18**, 8722–8725.
- 17 P. Huang, X.-J. Wang, J.-J. Qi, X.-L. Wang, M. Huang, H.-Y. Wu, C. Qin and Z.-M. Su, *J. Mater. Chem. A*, 2017, **5**, 22970–22974.

- 18 P. Huang, H.-Y. Wu, M. Huang, M. Du, C. Qin, X.-L. Wang and Z.-M. Su, *Dalton Trans.*, 2017, **46**, 10177–10180.
- 19 D. Zhang, Z. Liang, S. Liu, L. Li, P. Ma, S. Zhao, H. Wang, J. Wang and J. Niu, *Inorg. Chem.*, 2017, **56**, 5537–5543.
- 20 Q. Peng, S. Li, R. Wang, S. Liu, L. Xie, J. Zhai, J. Zhang, Q. Zhao and X. Chen, *Dalton Trans.*, 2017, **46**, 4157–4160.
- 21 Z. Liang, S. Zhao, P. Ma, C. Zhang, J. Sun, T. Song, J. Niu and J. Wang, *Inorg. Chem.*, 2018, **57**, 12471–12474.
- 22 Y. Ma, J. Sun, C. Li, N. Li, P. Ma, D. Zhang, G. Wang and J. Niu, *Inorg. Chem. Commun.*, 2019, **101**, 6–10.
- 23 Z. Liang, H. Wu, V. Singh, Y. Qiao, M. Li, P. Ma, J. Niu and J. Wang, *Inorg. Chem.*, 2019, **58**, 13030–13036.