Electronic Supplementary Material (ESI) for ChemComm.

Research progress on polyoxometalate-based transition-metal–rare-earth heterometallic derived materials: synthetic strategies, structural overview and functional applications

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Supporting Information:

Table S1 The summary of major reactants, synthetic methods and product phases of reported PTRHDMs. [room temperature (RT), hour (h), day (d), week (w), month (m)]

Year	Major reactants	Phases	pH	Synthetic methods	Temp. [°C]	Time	Ref.
2004	$Na_{27}[NaAs_4W_{40}O_{140}]\cdot 60H_2O/NiCl_2\cdot 6H_2O/RE(NO_3)_3\cdot xH_2O$	$[RE(H_2O)_5\{Ni(H_2O)\}_2As_4W_{40}O_{140}]^{21-}$ (RE = Y^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III})	4.5	CASS	RT	several d	112
2004	$Na_3(CrMo_6O_{24}H_6)\cdot 8H_2O/La(NO_3)_3\cdot 7H_2O/C_5H_9NO_2$	$[La(H_2O)_7CrMo_6H_6O_{24}]^{2-}$	2.4	CASS	RT	2 w	113
2007	$K_4Na_6Mn[Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot 33H_2O/Ce(SO_4)_2\cdot 4H_2O/H_2O$	$[\{Ce(H_2O)_7\}_2Mn_4Si_2W_{18}O_{68}(H_2O)_2]^{6-}$	3.5	CASS	RT	10 d	114
2007	$Na_2WO_4\cdot 2H_2O/As_2O_3/VOSO_4\cdot 5H_2O/DyCl_3\cdot 6H_2O/KCl$	$[((VO)_2Dy(H_2O)_4K_2(H_2O)_2Na(H_2O)_2)(\alpha\text{-B-}AsW_9O_{33})_2]^{8-}$		CASS	RT	1 d	115
2007	$K_{14}[As_2W_{19}O_{67}(H_2O)]/CuCl_2\cdot 2H_2O/LaCl_3\cdot 7\ H_2O$	$\{La[As_2W_{20}CuO_{67}(H_2O)_3]\}^{3-}$		CASS	RT	1 m	116
2007	$[\{Ce_2O(H_2O)_5\}\{WO(H_2O)\}\{AsW_9O_{33}\}_2]_2^{16-}/MnCl_2\cdot 4H_2O$	$\{Mn_{0.5}[Ce_4As_4W_{41}O_{149}]\}^{23-}$	5.0	CASS	RT	1m	117
2008	$Na_2WO_4\cdot 2H_2O/Na_2HAsO_4\cdot 7H_2O/HCl/CeCl_3\cdot 7\ H_2O/HMTA/FeCl_3\cdot 6H_2O$	$[K\subset\{FeCe(AsW_{10}O_{38})(H_2O)_2\}_3]^{12-}$	4–5	CASS	RT	1 m	111
2008	$(NH_4)_6[H_2W_{12}O_{40}]\cdot 3H_2O/Ce(NO_3)_3\cdot 6H_2O/AgNO_3$	$[\{Ag_3(H_2O)_2\}\{Ce_2(H_2O)_{12}\}H_5\subset\{H_2W_{11}Ce(H_2O)_4O_{39}\}_2]\cdot 8H_2O$	3.26	CASS	RT	3 w	118
2008	$CeMn_6O_9(O_2CCH_3)_9(NO_3)\ (H_2O)_2/Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$	$[\{\alpha\text{-}P_2W^{VI}_{16}O_{57}(OH)_2\}\{Ce^{IV}Mn^{IV}_6O_9(O_2CCH_3)_8\}]^{3-}$		CASS	RT	2 d	119
2008	$Na_{12}[P_2W_{15}O_{56}]\cdot 18H_2O/[Ce^{IV}_3Mn^{IV}_2O_6(O_2CMe)_{7.5}(NO_3)_3]\cdot\ (HO_2CMe)_{0.5}(H_2O)_2$	$[\{\alpha\text{-}P_2W_{15}O_{56}\}_6\{Ce_3Mn_2(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_2\}_3(\mu_2\text{-}OH)_2(H_2O)_2(PO_4)]^{47-}$		CASS	RT	2 w	120
2008	$K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O/CuCl_2\cdot 2H_2O/Nd(NO_3)_3$	$\{Nd_2(H_2O)_{12}Cu_4(H_2O)_2(SiW_9O_{34})_2\}^{6-}$		CASS	RT	2 m	121
2008	$\alpha\text{-}K_8[GeW_{11}O_{39}]\cdot nH_2O/DyCl_3/Cu(NO_3)_2\cdot 3H_2O/$ en	$[Cu(en)_2]_2[Cu(en)_2(H_2O)]_2H_3\{[Cu(en)_2]_2[Na_2(H_2O)_{1.75}][K(H_2O)_3][Dy_2(H_2O)_2(GeW_{11}O_{39})_3]\}\cdot 6H_2O$	6.0	HT	165	144 h	122
2008	$[Cu_2(bpy)_2(\mu\text{-ox})]^{2+}/\ [Ln(PW_{11}O_{39})_2]^{11-}$	$[\{Ln(PW_{11}O_{39})_2\}\{Cu_2(bpy)_2(\mu\text{-ox})\}]^{9-}$ (Ln = La^{III}, Pr^{III}, Eu^{III}, Gd^{III}, Yb^{III})		CASS	RT	several d	123
2009	$(NH_4)_2[Ce(NO_3)_6]/Mn(OAc)_2\cdot 4H_2O/K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$	$[Ce^{IV}_3Mn^{IV}_2O_6(OAc)_6(H_2O)_9]_2[Mn^{III}_2P_2W_{16}O_{60}]_3^{20-}$	4.0	CASS	RT	1 m	124
2009	$Na_9[\alpha\text{-A-}PW_9O_{34}]\cdot 7H_2O/CuCl_2\cdot 2H_2O/Ce_2(SO_4)_3\cdot 8H_2O,\ ErCl_3\cdot 6H_2O/en$	$[\{Ce(\alpha\text{-}PW_{11}O_{39})_2\}Cu(en)_2]^{9-}$; $[Cu(en)_2\{Er(\alpha\text{-}PW_{11}O_{39})_2\}Cu(en)_2]^{7-}$		HT	120	5 d	125
2009	$Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 19H_2O/Cu(CH_3COO)_2/Ln(NO_3)_3/en$	$\{[Cu(en)_2(H_2O)][(Cu(en)(OH))_3RE(SiW_{11}O_{39})(H_2O)]\}_2\cdot 20H_2O$ (Ln = Gd^{III}, Eu^{III}); $[Cu(en)_2][(Cu(en)(OH))_3La(SiW_{11}O_{39})]\ 20H_2O$	4.8	HT	140	40 h	126
2010	$Ce(NO_3)_3\cdot 6H_2O/GeO_2/Na_2WO_4\cdot 2H_2O/NiCl_2\cdot 6H_2O$	$[K\subset K_7Ce_{24}Ge_{12}W_{120}O_{456}(OH)_{12}(H_2O)_{64}]^{52-}$		CASS	RT	4 d	127
2010	$H_3PW_{12}O_{40}\cdot xH_2O/Ln(NO_3)_3\cdot 6H_2O/en/CuSO_4\cdot 5\ H_2O$	$[Cu(en)_2H_2O]_4[Cu(en)_2]\{[Cu(en)_2][Ln(PW_{11}O_{39})_2]\}_2^{n-}$ (Ln = Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}); $[Cu(en)_2H_2O]_4[Cu(en)_2]\{[Cu(en)_2][La(PW_{11}O_{39})_2]\}_2^{8-}$; $[Cu(en)_2]_2[Sm(PW_{11}O_{39})_2]^{7-}$		HT	150	72 h	128
2010	$K_{12}[Mn_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]/Ce(NH_4)_2(NO_3)_6$	$[\{Ce^{III}(H_2O)_2\}_2Mn^{III}_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{8-}$	1.1	CASS	RT	few w	129
2010	$Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2(Cr(OH)(H_2O))_3]_3\cdot 17H_2O/LaCl_3\cdot 7H_2O$	$[(\gamma\text{-}SiW_{10}O_{36})_2(Cr(OH)(H_2O))_3(La(H_2O)_7)_2]^{4-}$		CASS	RT	few h	130
2010	$K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O/Gd(NO_3)_3/Tart,\ (CH_3)_2NH_3\cdot HCl/\ MnCl_2,CoCl_2$	$[K_3\subset\{GdMn(H_2O)_{10}\}\{HMnGd_2(Tart)O_2(H_2O)_{15}\}\{P_6W_{42}O_{151}(H_2O)_7\}]^{11-}$; $[K_3\subset\{GdCo(H_2O)_{11}\}_2\{P_6W_{41}O_{148}(H_2O)_7\}]^{13-}$		CASS	RT	few w, 0.5 m	131
2010	$Na_{10}[\alpha\text{-}SiW_9O_{34}]/CuSO_4\cdot 5\ H_2O/en/Ln(NO_3)_3\cdot 6H_2O$	$[Cu(en)_2H_2O]_3[(\alpha\text{-}SiW_{11}O_{39})Ln(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO]\cdot nH_2O$ (Ln = Nd^{III}, n= 3.5; Ln = Sm^{III}, n = 3); $[Cu(en)_2H_2O]_8[Cu(en)_2]_3[\{(\alpha\text{-}SiW_{11}O_{39})Ce(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO\}_4]^{2-}$		HT	150, 170	72 h	132
2011	$K_{12}[Cu_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]/Ce(NH_4)_2(NO_3)_6$	$[\{Ce^{IV}(C_2H_3O_2)\}Cu^{II}_3(H_2O)(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{11-}$		CASS	RT	2 m	133
2011	$Dy_2O_3/HNO_3/CuCl_2\cdot 2H_2O/K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25\ H_2O/en$	$\{[Cu(en)_2(H_2O)][DyCu_3(en)_3(OH)_3(H_2O)_2(GeW_{11}O_{39})]\}_2\cdot 18H_2O$	5.17	HT	160	4.5 d	134
2011	$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O/CuCl_2\cdot 2H_2O/PrCl_3/H_2O/dap,$ en	$[Cu(dap)(H_2O)_2]_{0.5}[Cu(dap)_2]_4[Pr(\alpha\text{-}PW_{11}O_{39})_2]^{2-}$; $[Cu(en)_2(H_2O)]_2[Cu(en)_2]_{1.5}[Pr(\alpha\text{-}PW_{11}O_{39})_2]^{4-}$		HT	160	5 d, 6 d	135
2011	$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O/CuCl_2\cdot 2H_2O/(NH_4)_2SO_4\ Ce(SO_4)_2\cdot 2H_2O,\ DyCl_3$ /en,dap	$[Cu(en)_2]_2[Ce(\alpha\text{-}PW_{11}O_{39})_2]^{6-}$; $[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Dy(\alpha\text{-}PW_{11}O_{39})_2]\cdot 4H_2O$	4.2, 4.4	HT	160	9 d	136
2011	$Dy_2O_3,Tb_4O_7/K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ /NaCl/$FeCl_3$/en	$[Dy_6Fe_6(H_2O)_{12}(SiW_{10}O_{38})_6]^{36-}$, $[Tb_6Fe_6(H_2O)_{12}(SiW_{10}O_{38})_6]^{36-}$	5.5, 5.8	HT	160	96h	137

Table S1 Continued.

Year	Major reactants	Phases	pH	Synthetic methods	Temp. [°C]	Time	Ref.
2011	$Na_9[\alpha\text{-}PW_9O_{34}]\cdot16H_2O/Na_7[\alpha\text{-}PW_{11}O_{39}]\cdot nH_2O/LnCl_3\cdot7H_2O/CuCl_2\cdot2H_2O/$ en/2,2'- bipy	$\{[Cu(en)_2]_{1.5}[Cu(en)(2,2'\text{-bipy})(H_2O)_n]Ln[(\alpha\text{-}PW_{11}O_{39})_2]\}^{6-}$ [Ln = Ce^{III}, Pr^{III}]; $\{[Cu(en)_2]_2(H_2O)[Cu(en)(2,2'\text{-bipy})]Ln[(\alpha\text{-}HPW_{11}O_{39})_2]\}^{4-}$ [Ln = Gd^{III}, Tb^{III}, Er^{III}]; $\{[Cu(en)_2]_{1.5}[Cu(en)(2,2'\text{-bipy})]Nd[(\alpha\text{-}H_5PW_{11}O_{39})_2]\}^{3-}$	4.6– 5.2	HT	170	4 d	138
2012	$K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot17H_2O/LnCl_3\cdot6H_2O/CuCl_2\cdot2H_2O/en/H_2O$	$\{[Cu(en)_2]_{1.5}Ln[(\alpha\text{-}SiW_{11}O_{39})_2]\}_2^{20-}$ [Ln = Gd^{III}, Tb^{III}, Dy^{III}, Er^{III}, Lu^{III}]; $\{[Cu(en)_2]_{1.5}Ln[(\alpha\text{-}SiW_{11}O_{39})]\}^{2-}$ [Ln = La^{III}, Ce^{III}]; $\{[Cu(en)_2(H_2O)][Cu(en)_2]_nLn[(\alpha\text{-}SiW_{11}O_{39})_2]\}^{m-}$ [(Ln, n, m) = (Pr^{III}, 2, 7), (Sm^{III}, 3, 5)]		HT	170	120 h	139
2012	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot25H_2O/CuCl_2\cdot2H_2O/LnCl_3/en$	$\{[Cu(en)_2(H_2O)][Cu_3Ln(en)_3(OH)_3(H_2O)_2](\alpha\text{-}GeW_{11}O_{39})\}_2\cdot11H_2O$ (Ln = Eu^{III}, Tb^{III}); $\{[Cu(en)_2(H_2O)][Cu_3Dy(en)_3(OH)_3(H_2O)_2](\alpha\text{-}GeW_{11}O_{39})\}_2\cdot10H_2O$; $[Cu(en)_2(H_2O)]_8\{Cu(en)_2[La(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{8-}$; $[Cu(en)_2(H_2O)_2]_5[Cu(en)_2(H_2O)]_2[Cu(en)_2]_2\{Cu(en)_2[Pr(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{6-}$; $[Cu(en)_2(H_2O)]_2[Cu(en)_2]_2\{Cu(en)_2[Er(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{6-}$		HT	160	5 d	140
2012	$K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot17H_2O/RECl_3\cdot6H_2O/CuCl_2\cdot2H_2O/H_2pzda/en/H_2O$	$[Cu(en)_2(H_2O)]_2\{[Cu(en)_2]\ [Cu(en)_2(H_2O)][(\alpha\text{-}SiW_{11}O_{39})RE(H_2O)(pzda)]\}_2^{2-}$ (RE = Y^{III}, Dy^{III}, Yb^{III}, Lu^{III}); $\{[Cu(en)_2]_2[Cu(pzda)_2][(\alpha\text{-}H_2SiW_{11}O_{39})Ce(H_2O)]_2\}^{4-}$		HT	170	117 h	141
2012	$Na_5[IMo_6O_{24}]\cdot3H_2O/[CuTb(bmaed)(H_2O)_3Cl_2]Cl$, $Na_3[AlMo_6O_{24}H_6]\cdot3H_2O/[CuTb(bmaed)(H_2O)_3Cl_2]Cl$	$[\{CuTb(bmaed)(H_2O)_3\}_2\{IMo_6O_{24}\}]Cl\cdot2MeOH\cdot8H_2O$; $[\{CuTb(bmaed)(H_2O)_2\}_2\{AlMo_6O_{18}(OH)_6\}_2]\cdot MeOH\cdot10H_2O$		CASS	RT	2 w	142
2012	Mn_{12}-acetate/$Na_9[A\text{-}\beta\text{-}SiW_9O_{34}H]\cdot23H_2O/CeMn_6O_9(O_2CCH_3)_9(NO_3)(H_2O)_2$	$[(CH_3)_2NH_2]_{20}[(A\text{-}\beta\text{-}SiW_9O_{34})_2Ce^{IV}{}_4O_2(CH_3COO)_2][(A\text{-}\beta\text{-}SiW_9O_{34})Mn^{III}{}_3Mn^{IV}O_3(CH_3COO)_3]_2^{2-}$		CASS	RT	1 w	143
2012	$FeCl_3\cdot6H_2O/LnCl_3\cdot6H_2O/K_{28}Li_5[H_7P_8W_{48}O_{184}]\cdot92H_2O$	$[Fe_{16}O_2(OH)_{23}(H_2O)_9(P_8W_{49}O_{189})Ln_4(H_2O)_{20}]^{11-}$ (Ln = Eu^{III}, Gd^{III})		CASS	RT	1 m	144
2012	$Na_8[A\text{-}\alpha\text{-}HAsW_9O_{34}]\cdot11H_2O/CuCl_2\cdot2H_2O/(NH_4)_2SO_4Ce\ (SO_4)_2\cdot2H_2O$, $LnCl_3$/en, dap	$\{Cu(en)_2[H_2Ce^{IV}(\alpha\text{-}AsW_{11}O_{39})_2]_2\}^{14-}$; $[Cu(en)_2(H_2O)][Cu(en)_2]_{1.5}[H_3Ln(\alpha\text{-}AsW_{11}O_{39})_2]^{3-}$ [Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III}]; $[Cu(dap)(H_2O)_2]_{0.5}[Cu(dap)_2(H_2O)]_2[Cu(dap)_2]_3[Ln(\alpha\text{-}AsW_{11}O_{39})_2]$ [Ln = Pr^{III}, Eu^{III}]; $[Cu(dap)_2]_{5.5}[Ln(\alpha\text{-}AsW_{11}O_{39})_2]$ [(Ln = Tb^{III}, Dy^{III}]	3.9– 5.5	HT	160	5d–6d	145
2012	$[PMo_{12}O_{36}(OH)_4\{LaH_2O)_4\}_4]^{5+}/Fe^{II}(CN)_6^{4-}$	$[\varepsilon\text{-}PMo_{12}O_{37}(OH)_3\{La(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]$		CASS	RT		146
2012	$Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot18H_2O/CuCl_2\cdot2H_2O/LnCl_3$/dap	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Ln(H_2O)_3]_2\}$ (Ln = Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Er^{III})		HT	160	6 d	147
2012	$K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot14H_2O/Cu(NO_3)_2/Dy_2O_3$,$Ho_2O_3$/en	$[Cu(en)_2]_9\{K_4Na_2[Dy(SiW_{11}O_{39})_2]_2\}^{2-}$; $[Cu(en)_2]_9\{K_4Na_2[Ho(SiW_{11}O_{39})_2]\ _2\}^{2-}$		HT	160	96 h	148
2013	$K_{12}[\gamma\text{-}SiW_{10}O_{38}]\cdot12H_2O/\ MnCl_2/Dy_2O_3$	$[\{Dy^{III}Mn^{III}{}_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)(CO_3)\}(\beta\text{-}SiW_8O_{31})_2]^{13-}$	9.51	CASS	RT	3 d	149
2013	$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot7H_2O/Tb(OAc)_3\cdot6H_2O/K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot24H_2O/$ ox/$CuCl_2\cdot2H_2O$/en	$[Cu(en)_2(H_2O)][Cu(en)_2][Tb(\alpha\text{-}PW_{11}O_{39})(H_2O)_2(ox)Cu(en)]\cdot6H_2O$		HT	80	6 d	150
2013	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot25H_2O/CuCl_2\cdot2H_2O/GdCl_3$,$YCl_3$/en	$[Cu(en)_2]_5[Cu(en)_2(H_2O)]_2[RE_4Ge_4W_{46}O_{164}(H_2O)_3]^{10-}$ (RE = Gd^{III}, Y^{III})		HT	160	6d,9d	151
2013	$Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot19H_2O/Tb(OAc)_3\cdot6H_2O/H_2C_2O_4/CuCl_2\cdot2H_2O$ /en; $K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot25H_2O/Cu(OAc)_2\cdot H_2O/C_4H_6O_4/Eu(OAc)_3\cdot6H_2O$/en; $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot7H_2O/CuSO_4\cdot5H_2O/Sm(OAc)_3\cdot6H_2O/H_2C_2O_4$/en; $K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot25H_2O/Tb(OAc)_3\cdot6H_2O/C_4H_6O_4$/en	$[Cu(en)_2(H_2O)]_2[Tb(\alpha\text{-}HSiW_{11}O_{39})\ (H_2O)_3]\cdot12H_2O$; $[Cu(en)_2(H_2O)]_2[Eu(\alpha\text{-}HGeW_{11}O_{39})(H_2O)_3]\cdot12H_2O$; $Na_2[Cu(en)_2(H_2O)]_4[Sm(\alpha\text{-}PW_{11}O_{39})(CH_3COO)(H_2O)]_2\cdot10H_2O$; $[Cu(en)_2(H_2O)]_5[Cu(en)_2][Tb(\alpha\text{-}GeW_{11}O_{39})(CH_3COO)(H_2O)]_2\cdot14H_2O$	6.1; 5.9; 4.8; 5.3	HT	80; 80; 100; 100	4 d; 5 d; 7 d; 5 d	152
2013	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot25H_2O/Mn(NO_3)_2/Ce(NH_4)_2(NO_3)_6/C_2H_2O_4$	$[Ce_2(ox)_3(H_2O)_2]_2\{[Mn(H_2O)_3]_2[Mn_4(GeW_9O_{34})_2(H_2O)_2]^{8-}$	6.1	HT	120	3 d	153

Table S1 Continued.

Year	Major reactants	Phases	pH	Synthetic methods	Temp. [°C]	Time	Ref.
2013	$Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$/ dpdo/$Ce(NO_3)_3\cdot 6H_2O$	$[Ce_4(H_2O)_{22}(dpdo)_5](Mn_2HP_2W_{15}O_{56})_2^{2-}$	4.0	HT	160	4 d	154
2013	$K_{12.5}Na_{1.5}[Na(H_2O)P_5W_{30}O_{110}]\cdot 15H_2O$/ $Sm(NO_3)_3\cdot 6H_2O$/$Mn(ClO_4)_2\cdot 6H_2O$/ $C_2H_4O_3$; $K_{12.5}Na_{1.5}[Na(H_2O)P_5W_{30}O_{110}]\cdot 15H_2O$/$Sm(NO_3)_3\cdot 6H_2O$/$CuCl_2\cdot 5H_2O$/ $C_4H_7NO_4$	$[\{Sm_6Mn(\mu\text{-}H_2O)_2(OCH_2COO)_7(H_2O)_{18}\}\{Na(H_2O)P_5W_{30}O_{110}\}]^{8-}$; $\{[\{Sm_4Cu_2(gly)_2(ox)(H_2O)_{24}\}\{NaP_5W_{30}O_{110}\}]Cl_2\}^{4-}$	5.5; 3.6	HT	120	5 d	155
2013	$Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$/ $CuCl_2\cdot 2H_2O$/YCl_3/dap	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Y(H_2O)_2]_2\}\cdot 10H_2O$		HT	160	5 d	156
2013	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25H_2O$/ $CuCl_2\cdot 2H_2O$/$EuCl_3$,$LaCl_3$/en	$[Cu(en)_2(H_2O)]_2[Cu(en)_2]_2\{Cu(en)_2[Eu(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{16-}$; $[Cu(en)_2(H_2O)]_2[Cu(en)_2]_6[Cu(en)_2]\{Cu(en)_2[La(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{8-}$		HT	160	5 d	157
2013	$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$/$CuCl_2\cdot 2H_2O$/ $SmCl_3$,$ErCl_3$/dap	$[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Sm(\alpha\text{-}PW_{11}O_{39})_2]\cdot 5\ H_2O$; $[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Er(\alpha\text{-}PW_{11}O_{39})_2]\cdot 4H_2O$		HT	160	5 d	158
2013	$\alpha\text{-}K_8SiW_{11}O_{39}\cdot 13H_2O$/$AgNO_3$/ $Ce(NO_3)_3\cdot 6H_2O$,$Pr(NO_3)_3\cdot 6H_2O$	$\{[Ag\{Ag_2(H_2O)_4\}\{Ln(H_2O)_6\}_2H\subset\{SiW_{11}Ln(H_2O)_4O_{39}\}_2]\cdot nH_2O$(Ln = Ce^{III}, n= 7;, Ln = Pr^{III}, n = 3)	3.26	CASS	60	3 w; 2 w	159
2014	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25H_2O$/ $FeSO_4\cdot 7H_2O$/$Sm(NO_3)_3\cdot 6H_2O$/en	$[Fe_6Sm_6(H_2O)_{12}(\alpha\text{-}GeW_{10}O_{38})_6]^{36-}$	5.0	HT	160	5 d	160
2014	$K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot 24H_2O$/ $Cu(Ac)_2\cdot H_2O$/$H_2C_2O_4$/$Tb(Ac)_3\cdot 6H_2O$, $Eu(Ac)_3\cdot 6H_2O$, $Sm(Ac)_3\cdot 6H_2O$, $(NH_4)_2SO_4\cdot Ce(SO_4)_2\cdot 4H_2O$/en	$[Cu(en)_2][Ln(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{15-}$ (Ln = Tb^{III}, Eu^{III}, Sm^{III}, Ce^{III})	4.9– 5.3	HT	80	5 d	161
2014	$Na_9[B\text{-}\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$/ $FeCl_3\cdot 6H_2O$/$LnCl_3$/L-thr	$[Ln(H_2O)_8]_2[Fe_4(H_2O)_8(thr)_2][B\text{-}\beta\text{-}SbW_9O_{33}]_2\cdot 22H_2O$ (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III}, Lu^{III}, thr = threonine)	1.09– 1.17	CASS	80	Several d	162
2014	$K_7[MnV_{13}O_{38}]\cdot 18H_2O$/$LaCl_3$, $Ce(NO_3)_3\cdot 6H_2O$,$Nd(NO_3)_3$, $PrCl_3$	$[\{La_2(DMF)_5(H_2O)_4\}\{MnV_{13}O_{38}\}]^-$; $[\{Ce_2(DMF)_2(H_2O)_7\}\{MnV_{13}O_{38}\}]^-$; $\{Nd(DMF)(H_2O)_3\}\{MnV_{13}O_{38}\}]^{4-}$; $[\{Ln_2(C_6H_5NO_2)_3(H_2O)_6\}[MnV_{13}O_{38}]^-$ (Ln = La^{III}, Ce^{III}); $[\{Pr(C_6H_5NO_2)(H_2O)_{3.5}\}\{Pr_{0.5}(H_2O)_2\}\{MnV_{13}O_{38}\}]^{2.5-}$		CASS	40	2 w	163
2014	$(NH_4)_6[Co_2Mo_{10}H_4O_{38}]\cdot 7H_2O$/$GdCl_3$,$TbCl_3$	$[Ln(H_2O)_7][Ln(H_2O)_5][Co_2Mo_{10}H_4O_{38}]\cdot 5H_2O$ (Ln = Gd^{III}, Tb^{III}); $(NH_4)_3[Ln(H_2O)_6][Co_2Mo_{10}H_4O_{38}]\cdot 6H_2O$ (Ln = Gd^{III}, Tb^{III})	3.10; 3.05	CASS	85	Several d	164
2014	$K_8Na_2[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 25H_2O$/ $CuCl_2\cdot 2H_2O$/$LnCl_3$/dap	$[Cu(dap)_2]_{0.5}[Cu(dap)_2(H_2O)][Ln(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]^{2-}$ (Ln = La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III}, Er^{III})		HT	160	5 d	165
2014	$K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$/ $MnCl_2\cdot 4H_2O$/Ln_2O_3,$Ce(OH)_4$	$[\{LnMn^{III}_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)(CO_3)\}(\beta\text{-}SiW_8O_{31})_2]^{13-}$ (Ln = Ho^{III}, Tm^{III}, Yb^{III}); $[\{LnMn^{III}_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)(CO_3)\}(\beta\text{-}SiW_8O_{31})_2]^{13-}$ (Ln = Sm^{III}, Gd^{III}, Er^{III}); $[\{Ce^{IV}Mn^{III}_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)(CO_3)\}(\beta\text{-}SiW_8O_{31})_2]^{12-}$	9.40– 9.47	CASS	75	96– 100 h	166
2014	$(NH_4)_6[H_2W_{12}O_{40}]\cdot 3H_2O$/$AgNO_3$/$La(NO_3)_3\cdot 6H_2O$	$(H_3O)[Ag_6La(H_2O)_6L_4(H_2W_{12}O_{40})]$ (L = 2-pyrazinecarboxylic acid)		HT	120	4 d	167
2015	$K_{14}[As_2W_{19}O_{67}(H_2O)]$/$FeCl_3\cdot 6H_2O$/ $LnCl_3$/L-leucine/L-alanine/NaCl	$[Ln(H_2O)_7][Fe_4(H_2O)_{10}(B\text{-}\beta\text{-}AsW_9O_{33})_2]^{3-}$ (Ln = La^{III}, Pr^{III}, Nd^{III}, Sm^{III}); $[Ln(H_2O)_8]_2[Fe_4(H_2O)_8(L\text{-}thr)_2(B\text{-}\beta\text{-}AsW_9O_{33})_2]\cdot 20H_2O$ (Ln = La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Er^{III})		HT	100	5 d	168
2015	$Na_9[B\text{-}\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$/ $FeCl_3\cdot 6H_2O$/$LnCl_3$/HCl	$[Pr(H_2O)_8][Pr(H_2O)_6][Fe_4(H_2O)_{10}(B\text{-}\beta\text{-}SbW_9O_{33})_2]\cdot 16H_2O$; $[RE(H_2O)_7]_2[Fe_4(H_2O)_{10}(B\text{-}\beta\text{-}SbW_9O_{33})_2]\cdot 22H_2O$ [RE = Tb^{III}, Dy^{III}, Lu^{III}, Y^{III}]		CASS	80	Several d	169

Table S2 The summary of magnetic information of some PTRHDMs.

Formula	TM	RE	measured $\chi_M T$ ($cm^3 \cdot K \cdot mol^{-1}$)	theory $\chi_M T$ ($cm^3 \cdot K \cdot mol^{-1}$)	g_{TM} g_{RE}	magnetic behavior	Ref
$[K\subset\{FeCe(AsW_{10}O_{38})(H_2O)_2\}_3]^{14-}$	$3Fe^{III}$	$3Ce^{III}$	14.01	14.25	2.00, 6/7	AFM	111
$[((VO)_2Dy(H_2O)_4K_2(H_2O)_2Na\ (H_2O)_2)(\alpha\text{-}B\text{-}AW_9O_{33})_2]^{8-}$	$2V^{IV}$	Dy^{III}	15.36	14.88	1.95 1.33	AFM	115
$[\{\alpha\text{-}P_2W^{VI}{}_{16}O_{57}(OH)_2\}\{Ce^{IV}Mn^{IV}{}_6O_9(O_2CCH_3)_8\}]^{8-}$	$6Mn^{IV}$	Ce^{IV}	not given	not given	2.06, 0	AFM	119
$[\{\alpha\text{-}P_2W_{15}O_{56}\}_6\{Ce_3Mn_2(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_2\}_3(\mu_2\text{-}OH)_2(H_2O)_2(PO_4)]^{47-}$	$2Mn^{IV}$	$3Ce^{IV}$	not given	not given	1.98, 0	AFM	120
$\{[Cu(en)_2(H_2O)][(Cu(en)(OH))_3Gd(SiW_{11}O_{39})(H_2O)]\}_2\cdot 20H_2O$	$4Cu^{II}$	Gd^{III}	9.25	9.375	2.00, 2.00	The coexistence of AFM and FM	126
$[Cu(en)_2][(Cu(en)(OH))_3La(SiW_{11}O_{39})]$	$4Cu^{II}$	La^{III}	1.31	1.5	2.00 0	AFM	126
$[Ni(H_2O)_6]_3[K\subset K_7Ce_{24}Ge_{12}W_{120}O_{456}(OH)_{12}(H_2O)_{64}]^{46-}$	$3Ni^{II}$	$24Ce^{III}$	20.4	21	not given, not given	AFM	127
$[Cu(en)_2H_2O]_4[Cu(en)_2]\{[Cu(en)_2][La(PW_{11}O_{39})_2]\}_2^{8-}$	$6Cu^{II}$	La^{III}	3.03	2.62	2.00 0	AFM	128
$[Cu(en)_2H_2O]_4[Cu(en)_2]\{[Cu(en)_2][Ce(PW_{11}O_{39})_2]\}_2^{8-}$	$6Cu^{II}$	Ce^{III}	4.69	4.23	2.00, 6/7	AFM	128
$[Cu(en)_2H_2O]_4[Cu(en)_2]\{[Cu(en)_2][Nd(PW_{11}O_{39})_2]\}_2^{8-}$	$6Cu^{II}$	Nd^{III}	5.85	5.89	2.00, 8/11	AFM	128
$[\{Ce(H_2O)_2\}_2Mn_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{8-}$	$2Mn^{III}$	$2Ce^{III}$	8.2	7.6	2.00 6/7	The coexistence of AFM and FM	129
$[K_3\subset\{GdMn(H_2O)_{10}\}\{HMnGd_2(Tart)O_2(H_2O)_{15}\}\{P_6W_{42}O_{151}(H_2O)_7\}]^{11-}$	$2Mn^{II}$	$3Gd^{III}$	36.6	not given	not given, not given	AFM	131
$[K_3\subset\{GdCo(H_2O)_{11}\}_2\{P_6W_{41}O_{148}(H_2O)_7\}]^{13-}$	$2Co^{II}$	$2Gd^{III}$	30.73	not given	not given, not given	AFM	131
$[Cu(en)_2H_2O]_3[(\alpha\text{-}SiW_{11}O_{39})Nd(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO]\cdot 3.5H2O$	$3Cu^{II}$	$2Nd^{III}$	3.23	4.39	2.00, 8/11	AFM	132
$[Cu(en)_2H_2O]_8[Cu(en)_2]_3[\{(\alpha\text{-}SiW_{11}O_{39})Ce(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO\}_4]^{2-}$	$7Cu^{II}$	$2Ce^{III}$	6.48	7.35	2.00, 6/7	AFM	132
$[\{Ce^{IV}(OAc)\}Cu^{II}{}_3(H_2O)(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{11-}$	$3Cu^{II}$	Ce^{IV}	1.66	0.99	2.22 0	AFM	133
$[Dy_6Fe_6(H_2O)_{12}(SiW_{10}O_{38})_6]^{36-}$	$6Fe^{III}$	$6Dy^{III}$	107.4	111.27	2.00 4/3	AFM	137
$[Tb_6Fe_6(H_2O)_{12}(SiW_{10}O_{38})_6]^{36-}$	$6Fe^{III}$	$6Tb^{III}$	94	97.11	2.00 3/2	AFM	137
$[\{CuTb(bmaed)(H_2O)_3\}_2\{IMo_6O_{24}\}]Cl\cdot 2MeOH\cdot 8\ H_2O/[\{CuTb(bmaed)(H_2O)_2\}_2\{AlMo_6O_{18}(OH)_6\}_2]\cdot MeOH\cdot 10H_2O$	$2Cu^{II}$	$2Tb^{III}$	22.2	24.375	2.00 3/2	SMM	142
$[(A\text{-}\beta\text{-}SiW_9O_{34})_2Ce^{IV}{}_4O_2(CH_3COO)_2][(A\text{-}\beta\text{-}SiW_9O_{34})Mn^{III}{}_3Mn^{IV}O_3(CH_3COO)_3]_2^{22-}$	$2Mn^{IV}$+ $6Mn^{III}$	$4Ce^{IV}$	17.55	24.75	2.00, 0	SMM	143
$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Pr(H_2O)_3]_2\}\cdot 10H_2O$	$3Cu^{II}$	$2Pr^{III}$	4.20	4.33	2.00, 4/5	The depopulation of the higher Stark levels	147
$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Nd(H_2O)_3]_2\}\cdot 10H_2O$	$3Cu^{II}$	$2Nd^{III}$	4.42	4.41	2.00, 8/11	The depopulation of the higher energy state	147
$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Gd(H_2O)_3]_2\}\cdot 9H_2O$	$3Cu^{II}$	$2Gd^{III}$	16.88	16.87	2.00, 2.00	The coexistence of AFM and FM	147
$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Gd(H_2O)_3]_2\}\cdot 8H_2O$	$3Cu^{II}$	$2Dy^{III}$	29.93	29.47	2.00, 4/3	The coexistence of AFM and FM	147
$[Cu(en)_2]_9\{K_4Na_2[Dy(SiW_{11}O_{39})_2]_2\}^{2-}$	$9Cu^{II}$	Dy^{III}	16.7	17.5	2.00 4/3	Spin-orbit coupling of lanthanide ion	148
$[Cu(en)_2]_9\{K_4Na_2[Ho\ (SiW_{11}O_{39})_2]_2\}^{2-}$	$9Cu^{II}$	Ho^{III}	17.6	17.43	2.00 5/4	The spin-orbit coupling of Ho^{III} ion.	148
$[\{Dy^{III}Mn^{III}{}_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2\ (H_2O)(CO_3)\}(\beta\text{-}SiW_8O_{31})_2]^{13-}$	$4Mn^{III}$	Dy^{III}	26.44	26.17	2.00 4/3	AFM (SMM)	149

Table S2 Continued.

Formula	TM	RE	measured $\chi_M T$ ($cm^3 \cdot K \cdot mol^{-1}$)	theory $\chi_M T$ ($cm^3 \cdot K \cdot mol^{-1}$)	g_{TM} g_{RE}	magnetic behavior	Ref
$[Cu(en)_2(H_2O)][Cu(en)_2][Tb(\alpha\text{-}PW_{11}O_{39})(H_2O)_2(ox)Cu(en)]\cdot 6H_2O$	$3Cu^{II}$	Tb^{III}	13.04	12.94	2.00, 3/2	AFM	150
$[Cu(en)_2(H_2O)]_2[Tb(\alpha\text{-}HSiW_{11}O_{39})(H_2O)_3]\cdot 12H_2O$	$2Cu^{II}$	Tb^{III}	12.88	12.94	2.00, 3/2	FM	152
$[Cu(en)_2(H_2O)]_4[Sm(\alpha\text{-}PW_{11}O_{39})(CH_3COO)(H_2O)]_2^{2-}$	$4Cu^{II}$	$2Sm^{III}$	2.64	not given	not given, not given	AFM	152
$[Ce_4(H_2O)_{22}(dpdo)_5](Mn_2HP_2W_{15}O_{56})_2^{2-}$	$4Mn^{II}$	$4Ce^{III}$	24.22	20.71	2.00, 6/7	AFM	154
$[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Sm(\alpha\text{-}PW_{11}O_{39})_2]\cdot 5H_2O$	$5.5Cu^{II}$	Sm^{III}	3.29	2.15	2.00, 2/7	The depopulation of the higher Stark levels of the Sm^{III} cation	158
$[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Er(\alpha\text{-}PW_{11}O_{39})_2]\cdot 4H_2O$	$5Cu^{II}$	Er^{III}	14.77	14.21	2.00, 6/5	The thermal depopulation of the Er^{III} excited states	158
$\{[Ag\{Ag_2(H_2O)_4\}\{Ce(H_2O)_6\}_2H\subset\{SiW_{11}Ce(H_2O)_4O_{39}\}_2]\cdot 7H_2O$	$3Ag^{I}$	$4Ce^{III}$	3.3	3.2	0, 6/7	The spin–orbit coupling of the Ce^{III} ions and crystal field effects	159
$\{[Ag\{Ag_2(H_2O)_4\}\{Pr(H_2O)_6\}_2H\subset\{SiW_{11}Pr(H_2O)_4O_{39}\}_2]\cdot 3H_2O$	$3Ag^{I}$	$4Pr^{III}$	6.6	6.4	0, 4/5	The spin–orbit coupling of the Pr^{III} ions and crystal field effects	159
$[Fe_6Sm_6(H_2O)_{12}(\alpha\text{-}GeW_{10}O_{38})_6]^{36-}$	$6Fe^{III}$	$6Sm^{III}$	28.3	26.78	2.00, 2/7	AFM	160
$[Cu(en)_2][Tb^{III}(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{15-}$	Cu^{II}	Tb^{III}	16.17	12.20	2.00, 3/2	The coexistence of the $S_{Tb} = 3$ local spins align along the same direction and the thermal depopulation of the Stark sublevels of the Tb^{III} cation	161
$[Sm(H_2O)_8]_2[Fe_4(H_2O)_8(thr)_2][B\text{-}\beta\text{-}SbW_9O_{33}]_2\cdot 22H_2O$	$4Fe^{III}$	$2Sm^{III}$	20.16	17.68	2.00 0.29	The depopulation of the Kramers doublets of the Sm^{III} ions	162
$[Dy(H_2O)_8]_2[Fe_4(H_2O)(thr)_2][B\text{-}\beta\text{-}SbW_9O_{33}]_2\cdot 22H_2O$	$4Fe^{III}$	$2Dy^{III}$	48.16	45.84	2.00 1.33	The coexistence of the $S_{Fe} = 5/2$ or $S_{Dy} = 9/2$ local spins align along the same direction and the intermolecular AFM interactions	162
$[\{Ce_2(DMF)_2(H_2O)_7\}\{MnV_{13}O_{38}\}]^-$	Mn^{IV}	$2Ce^{III}$	3.472	3.481	2.00 6/7	AFM	163
$[Gd(H_2O)_7][Gd(H_2O)_5][Co_2Mo_{10}H_4O_{38}]$	$2Co^{III}$	$2Gd^{III}$	16.08	15.75	0, 2.00	AFM	164
$[Tb(H_2O)_7][Tb(H_2O)_5][Co_2Mo_{10}H_4O_{38}]$	$2Co^{III}$	$2Tb^{III}$	23.08	23.64	0, 3/2	The gradual depopulation of the highest level of Tb^{III} ion	164
$[Gd(H_2O)_6][Co_2Mo_{10}H_4O_{38}]^{3-}$	$2Co^{III}$	Gd^{III}	8.40	7.875	0, 2.00	AFM	164
$[Tb(H_2O)_6][Co_2Mo_{10}H_4O_{38}]^{3-}$	$2Co^{III}$	Tb^{III}	11.87	11.82	0, 3/2	The depopulation of the highest level of Tb^{III} ion	164
$[Cu(dap)_2]_{0.5}[Cu(dap)_2(H_2O)][Pr(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]^{2-}$	$1.5Cu^{II}$	Pr^{III}	2.29	2.16	2.00 4/5	The depopulation of the Stark levels of Pr^{III} ions	165
$[Cu(dap)_2]_{0.5}[Cu(dap)_2(H_2O)][Sm(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]^{2-}$	$1.5Cu^{II}$	Sm^{III}	0.81	0.65	2.00 2/7	The depopulation of the Kramers doublets of the Sm^{III} ions	165
$[Cu(dap)_2]_{0.5}[Cu(dap)_2(H_2O)][Er(H_2O)_3(\alpha\text{-}GeW_{11}O_{39})]^{2-}$	$1.5Cu^{II}$	Er^{III}	12.33	12.04	2.00 6/5	The $S_{Er} = 11/2$ local spins align along the same direction.	165

Table S3 The photoluminescence data of fractional PTHRDMs.

RE	complex	Assignment / nm						Ref.
		λ_{ex}	λ_{em}					
Sm^{III}			$^4G_{5/2}\rightarrow{}^6H_{5/2}$	$^4G_{5/2}\rightarrow{}^6H_{7/2}$	$^4G_{5/2}\rightarrow{}^6H_{9/2}$			
	$\{[Cu(en)_2(H_2O)][Cu(en)_2]_3Sm\ [(\alpha\text{-}SiW_{11}O_{39})_2]\}^{5-}$	377	567	597	643			139
	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Sm(H_2O)_3]_2\}$	302	570	603	635			147
	$[\{Sm_6Mn(\mu\text{-}H_2O)_2(OCH_2COO)_7(H_2O)_{18}\}\{Na(H_2O)P_5W_{30}O_{110}\}]^{8-}$	410	561	595	641			155
	$[\{Sm_4Cu_2(gly)_2(ox)(H_2O)_{24}\}\{NaP_5W_{30}O_{110}\}]^{2-}$	400		597				155
Eu^{III}			$^5D_0\rightarrow{}^7F_0$	$^5D_0\rightarrow{}^7F_1$	$^5D_0\rightarrow{}^7F_2$	$^5D_0\rightarrow{}^7F_3$	$^5D_0\rightarrow{}^7F_4$	
	$[Cu(en)_2(H_2O)][Cu(en)_2]_{1.5}[H_3Eu(\alpha\text{-}AsW_{11}O_{39})_2]^{3-}$	315		586	627	660	688	145
	$[Cu(dap)(H_2O)_2]_{0.5}[Cu(dap)_2(H_2O)]_2[Cu(dap)_2]_3[Eu(\alpha\text{-}AsW_{11}O_{39})_2]$	315		590	626	663	695	145
	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Eu(H_2O)_3]_2\}$	310	575	589	623	653	688	147
	$[Cu(en)_2(H_2O)]_2[Cu(en)_2]_2\{Cu(en)_2[Eu(\alpha\text{-}GeW_{11}O_{39})_2]_2\}^{16-}$	392	573	593	612	645	706	157
	$[Eu(H_2O)_8]_2[Fe_4(H_2O)_8(thr)_2][B\text{-}\beta\text{-}SbW_9O_{33}]_2$	310	564	594	618	648	700	162
	$[Eu(H_2O)_8]_2[Fe_4(H_2O)_8(L\text{-}thr)_2(B\text{-}\beta\text{-}AsW_9O_{33})_2]\cdot 20H_2O$	394	558	585	617	651	697	168
Tb^{III}			$^5D_4\rightarrow{}^7F_6$	$^5D_4\rightarrow{}^7F_5$	$^5D_4\rightarrow{}^7F_4$	$^5D_4\rightarrow{}^7F_3$		
	$\{[Cu(en)_2]_2(H_2O)[Cu(en)(2,2'\text{-bipy})]Tb[(\alpha\text{-}HPW_{11}O_{39})_2]\}^{4-}$	366	487	550	567	611		138
	$\{[Cu(en)_2]_{1.5}Tb[(\alpha\text{-}SiW_{11}O_{39})_2]\}_2^{20-}$	298	492	547	594	622		139
	$[Cu(en)_2(H_2O)][Cu(en)_2]_{1.5}[H_3Tb(\alpha\text{-}AsW_{11}O_{39})_2]^{3-}$	285	501	568	596	616		145
	$[Cu(dap)_2]_{5.5}[Tb(\alpha\text{-}AsW_{11}O_{39})_2]$	285	494	567	597	622		145
	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2[\alpha\text{-}H_2SiW_{11}O_{39}Tb(H_2O)_3]_2\}$	320	484	550	582	630		147
	$[Tb(H_2O)_8]_2[Fe_4(H_2O)_8(L\text{-}thr)_2(B\text{-}\beta\text{-}AsW_9O_{33})_2]\cdot 20H_2O$	379		549	590	625		168
Dy^{III}			$^4F_{9/2}\rightarrow{}^6H_{15/2}$	$^4F_{9/2}\rightarrow{}^6H_{13/2}$	$^4F_{9/2}\rightarrow{}^6H_{11/2}$			
	$[Cu(dap)_2(H_2O)][Cu(dap)_2]_{4.5}[Dy(\alpha\text{-}PW_{11}O_{39})_2]$	370	482	572				136
	$\{[Cu(en)_2]_{1.5}Dy[(\alpha\text{-}SiW_{11}O_{39})_2]\}_2^{20-}$	356	481	577	632			139
	$\{[Cu(en)_2][Cu(en)_2(H_2O)][(\alpha\text{-}SiW_{11}O_{39})Dy(H_2O)(pzda)]\}_2^{6-}$	356	485	578				141
	$[Cu(dap)_2(H_2O)]_2\{Cu(dap)_2\ [\alpha\text{-}H_2SiW_{11}O_{39}Dy(H_2O)_3]_2\}$	310	488	585				147