Electric Supplemental Information for:

## Monolacunary Keggin Polyoxometalates Connected to Ten 4d or

## 4f Metal Atoms

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**Fig. S1.** Coordination modes of  $Ce^{3+}$  and  $Ag^+$  cations in **1**.



**Fig. S2.** The detailed coordination environments of  $Ag1^+$  and  $Ag2^+$  cations.



Fig. S3. Combined polyhedral/ball/stick and space-filling diagrams of 1 showing the 2D channels along [100] (left) and [010] (right) directions.

Compound 1	atom	$R_0$	BVS	Compound 2	atom	$R_0$	BVS
(Ag-Ce-SiW <sub>11</sub> )	Ag1	1.805	1.06	(Ag-Pr-SiW <sub>11</sub> )	Ag1	1.805	1.28
	Ag2	1.805	0.95		Ag2	1.805	0.98
	Ce1	2.094	2.67		Pr1	2.138	3.26
	Ce2	2.094	2.75		Pr2	2.138	3.32
	W1	1.921	6.38		W1	1.921	6.15
	W2	1.921	6.26		W2	1.921	5.88
	W3	1.921	6.25		W3	1.921	6.11
	W4	1.921	6.07		W4	1.921	5.90
	W5	1.921	6.02		W5	1.921	6.19
	W6	1.921	6.20		W6	1.921	6.39
	W7	1.921	5.93		W7	1.921	6.36
	W8	1.921	6.24		W8	1.921	6.26
	W9	1.921	6.22		W9	1.921	6.30
	W10	1.921	6.09		W10	1.921	6.42
	W11	1.921	6.45		W11	1.921	6.38

Table S1. Summary of calculated values from BVS for the metal centers in 1 and 2



Fig. S4. The UV spectra of 1, with control experiments of  $K_8SiW_{11}O_{39}$ ·13H<sub>2</sub>O,

AgNO<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> aqueous solutions.



Fig. S6. The simulated (red) and experimental (black) XRPD patterns of 1 and 2.