Electronic Supplementary Information

Fig. S1 (a) Monovacant [SiW$_{11}$O$_{39}$]$^{8-}$ unit obtained by removing a {WO$_6$} octahedron in the cap site of the parent Keggin structure. (b) Polyhedral view of mono-Ln-substituted Keggin anions. (c) Polyhedral and ball-stick representation of the lanthanide-substituted double-Keggin-type polyoxoanion $\left\{ (H_2O)_4La(SiW_{11}O_{39}) \right\}_{2}^{10-}$ in 1 and 2. (d) View of the two kinds of polyoxoanions $\left\{ (H_2O)_4Nd(SiW_{11}O_{39}) \right\}_{2}^{10-}$ and $\left\{ (H_2O)_3Nd(SiW_{11}O_{39}) \right\}_{2}^{10-}$ in 3 (color code: Si, yellow; W, green; La, blue gray; Nd, pink; O, red).

Fig. S2 A space-filling diagram of the 3D channel framework of 1, (color code: Si, yellow; W, green; La, blue gray; O, red). Other atoms have been omitted for clarity.

Fig. S3 A space-filling diagram of the 3D channel framework of 3, (color code: Si, yellow; W, green; Nd, pink; O, red). Other atoms have been omitted for clarity.

Fig. S4 A space-filling diagram of the 3D channel framework of 4 (color code: Si, yellow; W, green; La, blue gray; O, red; N, oxford blue; C, dark gray). Other atoms have been omitted for clarity.

Fig. S5 Schematic representation of the rutile topology of compound 4.

Fig. S6 (a) IR spectrum for compound 1. (b) IR spectrum for compound 2. (c) IR spectrum for compound 3. (d) IR spectrum for compound 4. (e) IR spectrum for compound 5. (f) IR spectrum for compound 6.

Fig. S7 UV-vis spectra and analysis for compounds 1-6.

Fig. S8 (a) TG curve for compound 1. (b) TG curve for compound 2. (c) TG curve for
compound 3. (d) TG curve for compound 4. (e) TG curve for compound 5. (f) TG curve for compound 6.

**Fig. S9** (a) The calculated and experimental PXRD patterns for compound 1. (b) The calculated and experimental PXRD patterns for compound 2. (c) The calculated and experimental PXRD patterns for compound 3. (d) The calculated and experimental PXRD patterns for compound 4. (e) The calculated and experimental PXRD patterns for compound 5. (f) The calculated and experimental PXRD patterns for compound 6.
Fig. S1
Fig. S2
Fig. S3
Fig. S4
Fig. S5
Fig. S6a

Fig. S6b
Fig. S6c

Fig. S6d
Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2012

Fig. S6e

Fig. S6f
The UV-vis spectra of compounds 1-6 are shown in Fig. S7, ranging from 190 to 600 nm. The plots display an intense absorption band for O→W charge transfer, which is characteristic of Keggin-type polyoxoanion. The bands at 245 nm for 1, 250 nm for 2, 249 nm for 3, 251 nm for 4, 249 nm for 5, and 246 nm for 6 are assigned to the $p_d(\text{Ob,c}) \rightarrow d_{e^*}(W)$ charge transfer transition.
Fig. S8a

Fig. S8b
Fig. S8c

Fig. S8d
Fig. S8e

Fig. S8f
Fig. S9a

Compound 1

Calculated pattern

Experimental pattern

2 Theta/degree

Fig. S9b

Compound 2

Calculated pattern

Experimental pattern

2 Theta/degree
**Fig. S9c**

**Compound 3**

Calculated pattern

Experimental pattern

2 Theta/degree

**Fig. S9d**

**Compound 4**

Calculated pattern

Experimental pattern

2 Theta/degree
Fig. S9e

Compound 5

Calculated pattern

Experimental pattern

2 Theta/degree

Fig. S9f

Compound 6

Calculated pattern

Experimental pattern

2 Theta/degree