Electronic Supplementary Information

Fig. S1 (a) Monovacant $[SiW_{11}O_{39}]^{8-}$ unit obtained by removing a {WO6} 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 $[\{(H_2O)_4La(SiW_{11}O_{39})\}_2]^{10-}$ in **1** and **2**. (d) View of the two kinds of polyoxoanions $[\{(H_2O)_4Nd(SiW_{11}O_{39})\}_2]^{10-}$ and $[\{(H_2O)_3Nd(SiW_{11}O_{39})\}_2]^{10-}$ 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.**

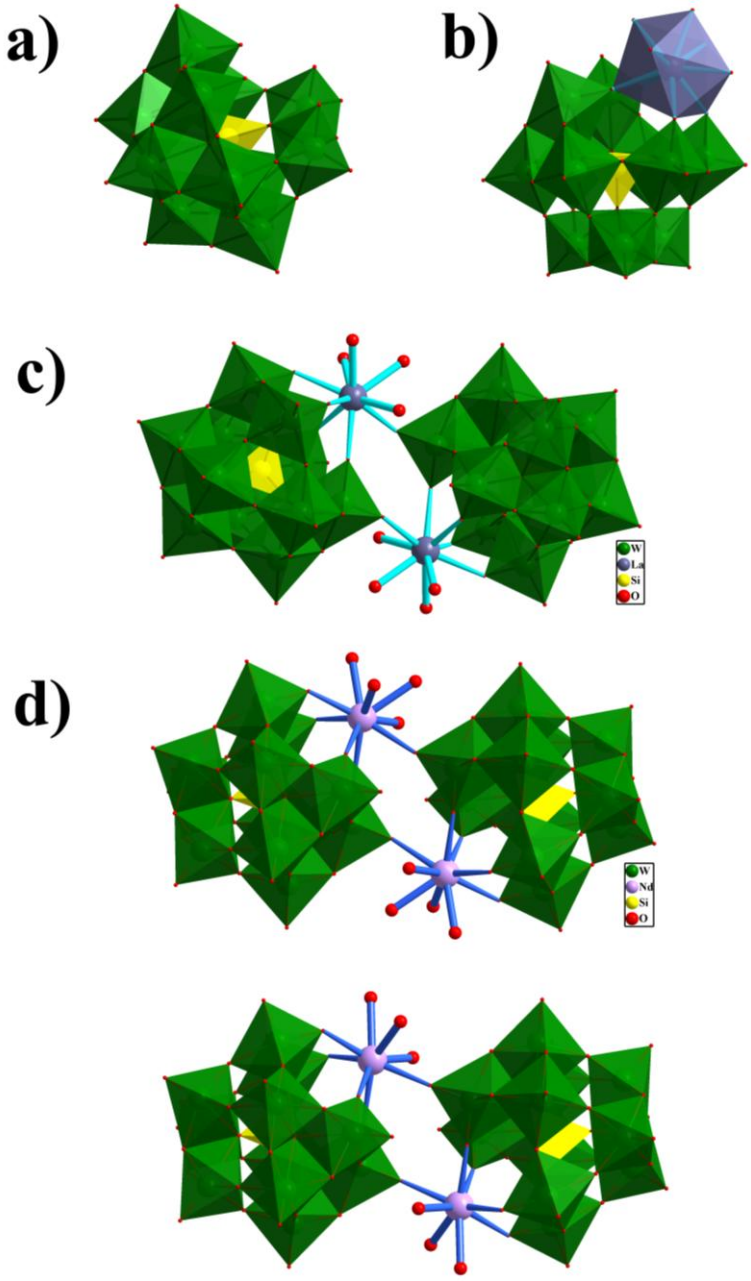
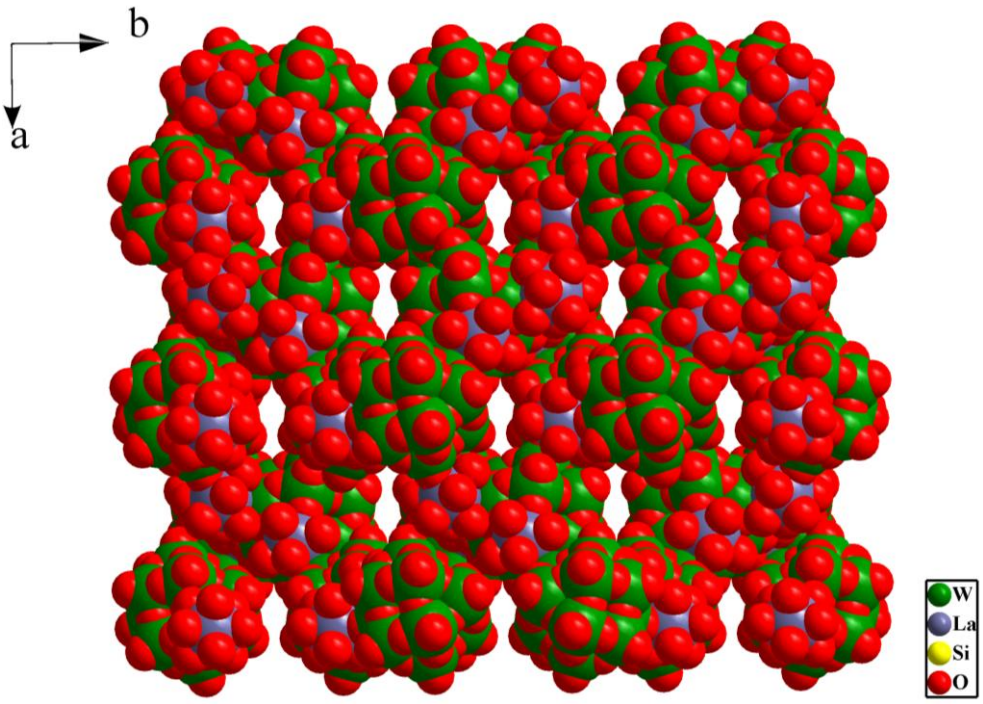


Fig. S1



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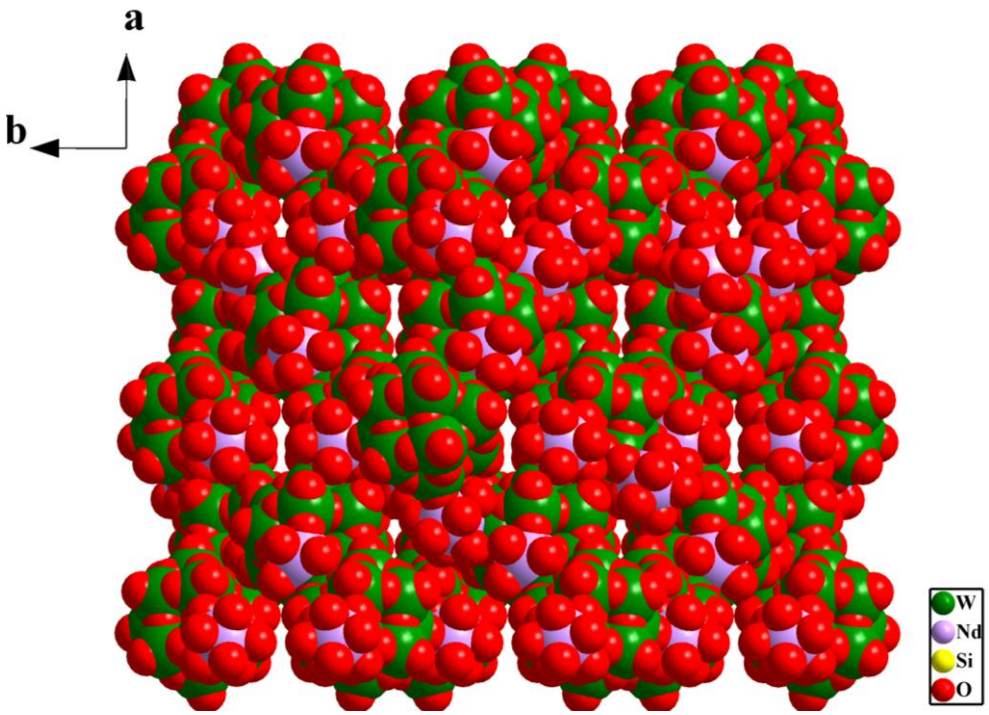

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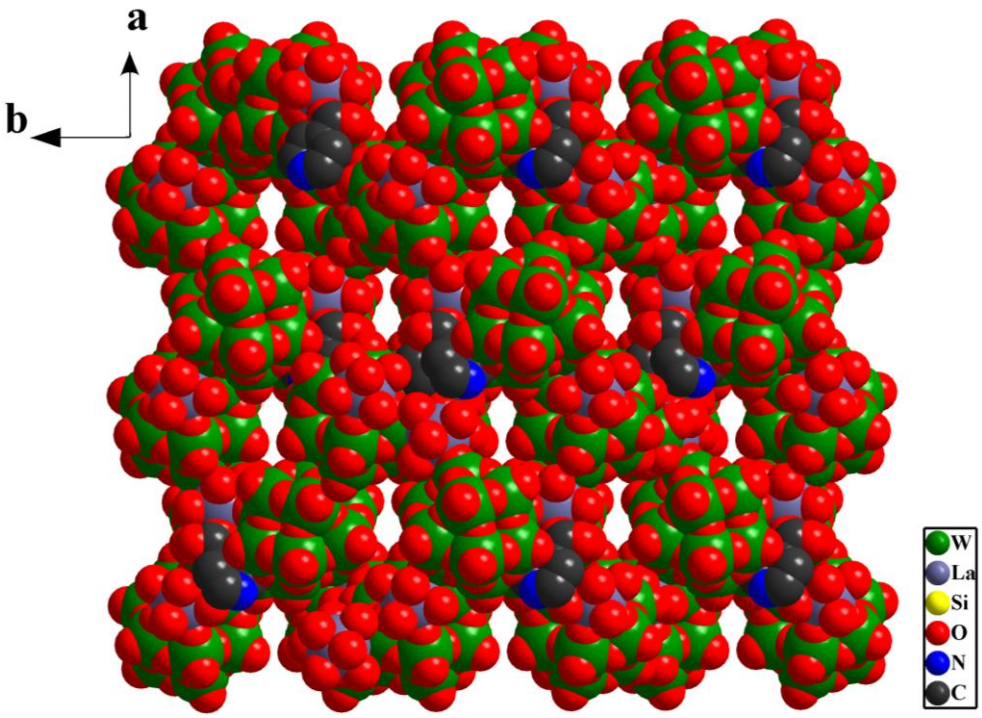

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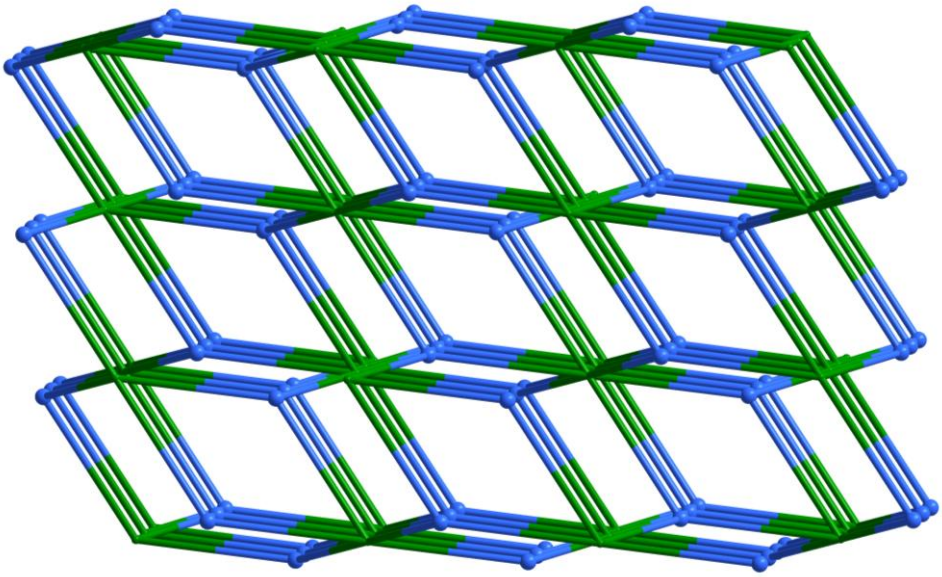

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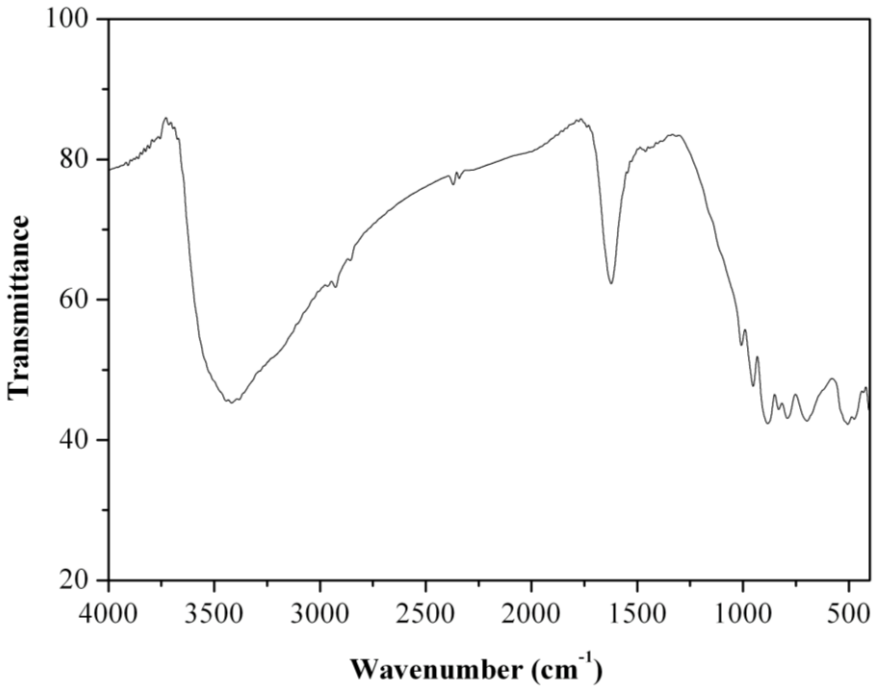


Fig. S6a

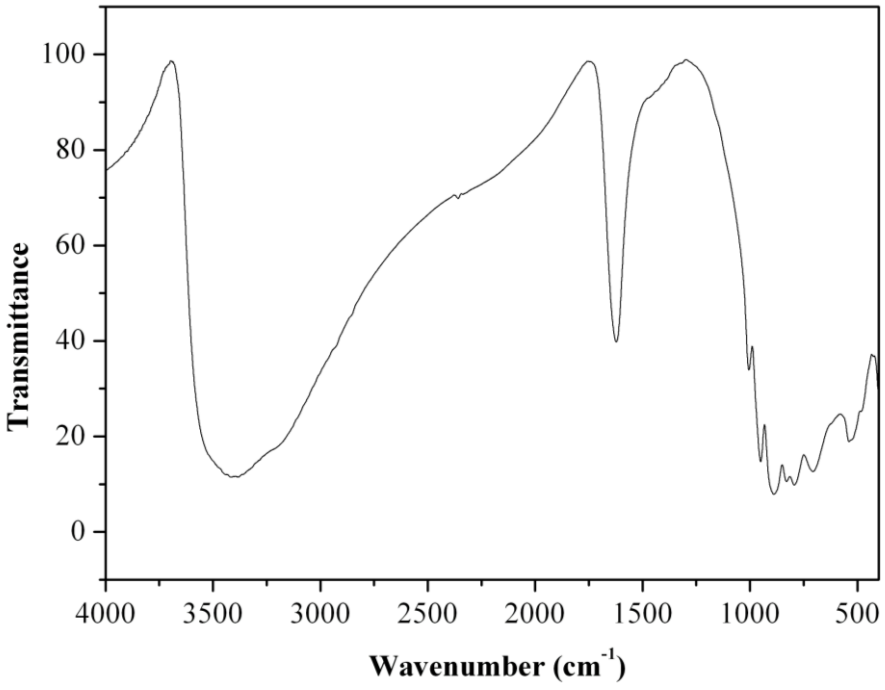


Fig. S6b

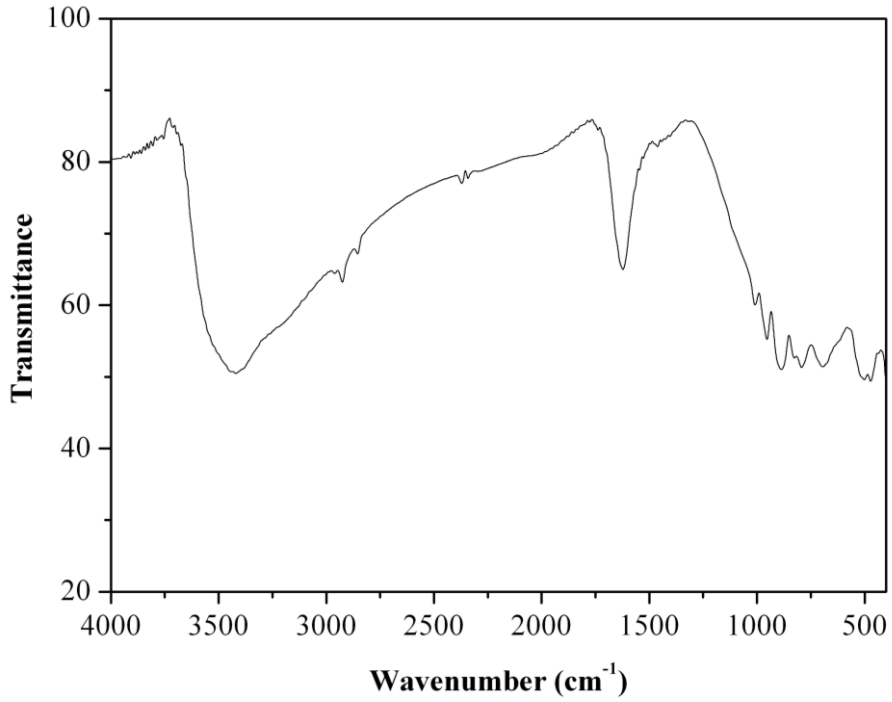
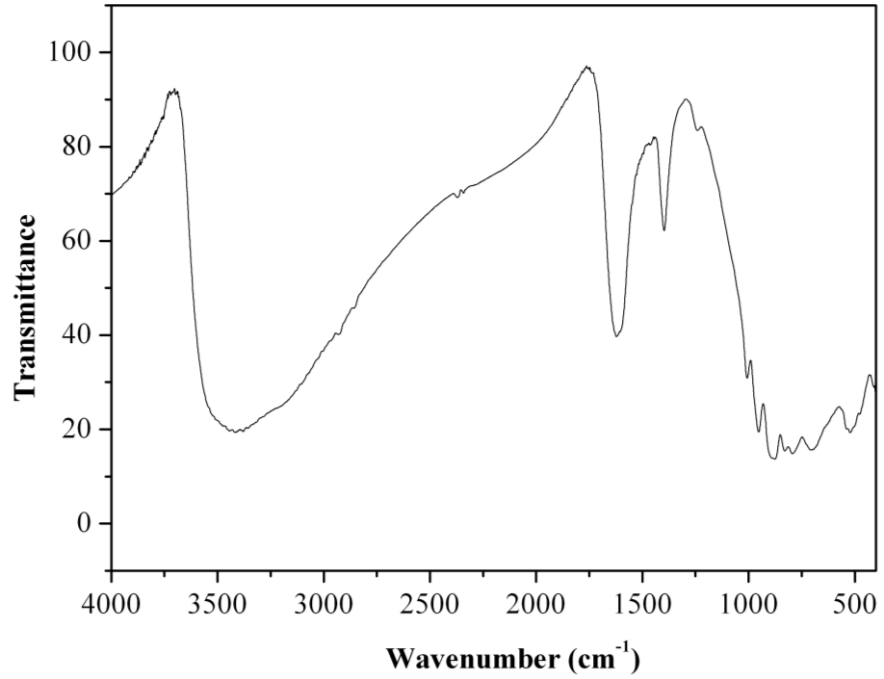


Fig. S6c



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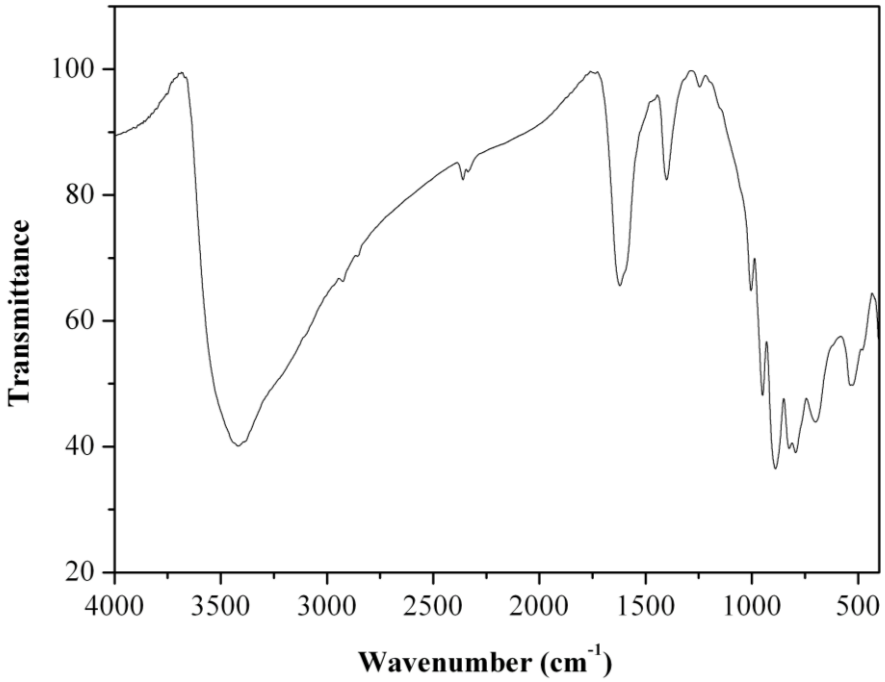

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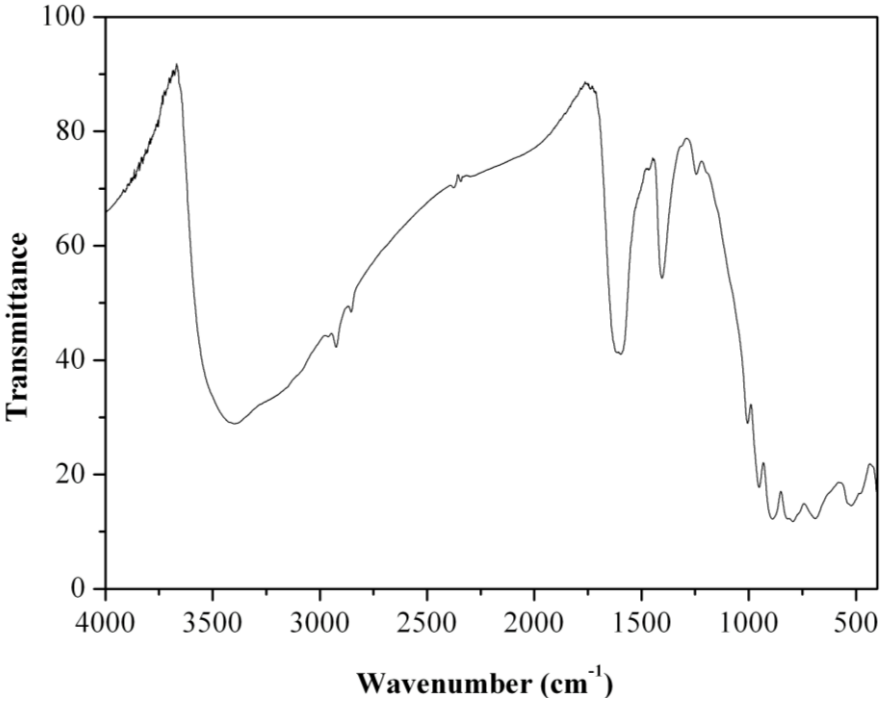


Fig. S6f

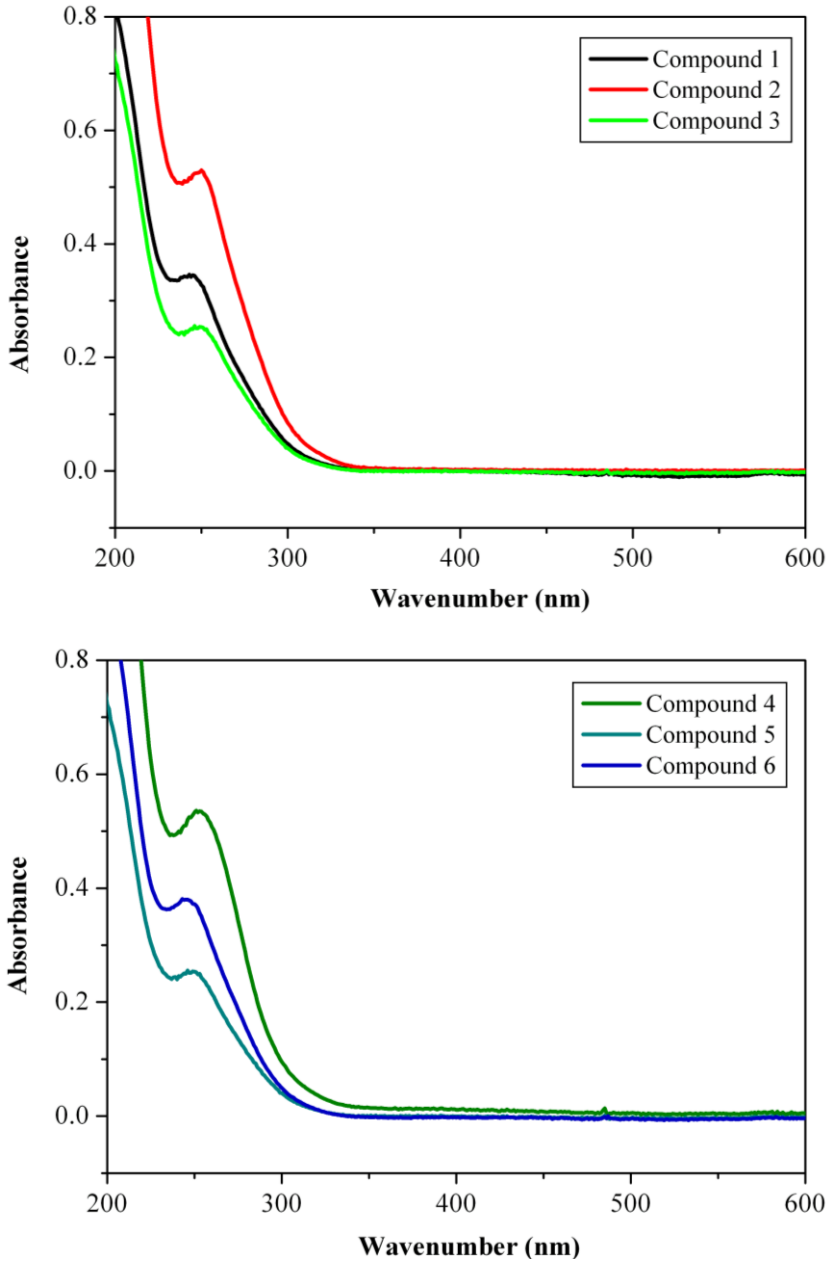


Fig. S7

UV-vis spectra

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.[16,22] 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 $p_{\pi}(Ob,c) \rightarrow d_{\pi^*}(W)$ charge transfer transition.

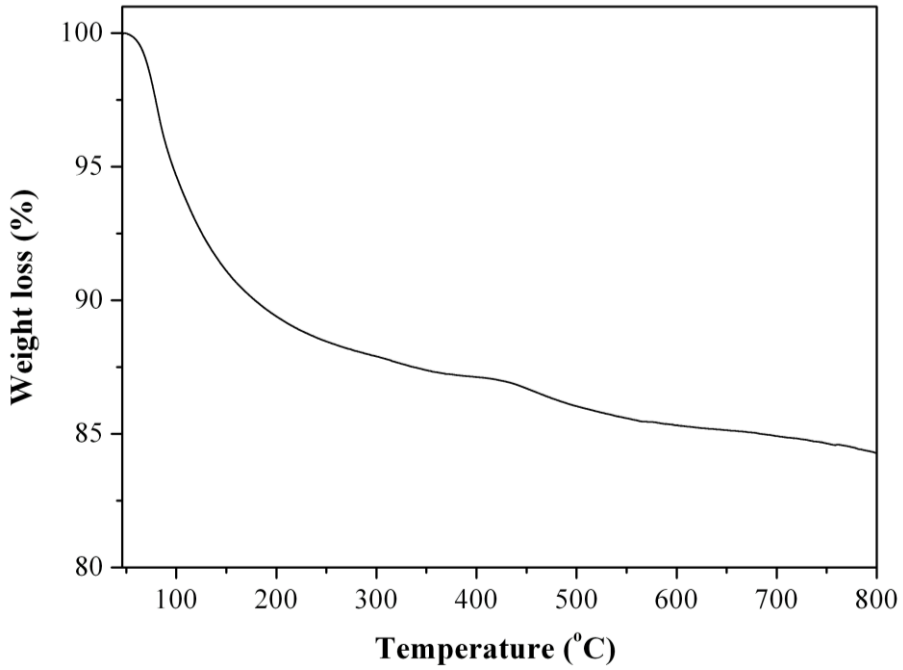


Fig. S8a

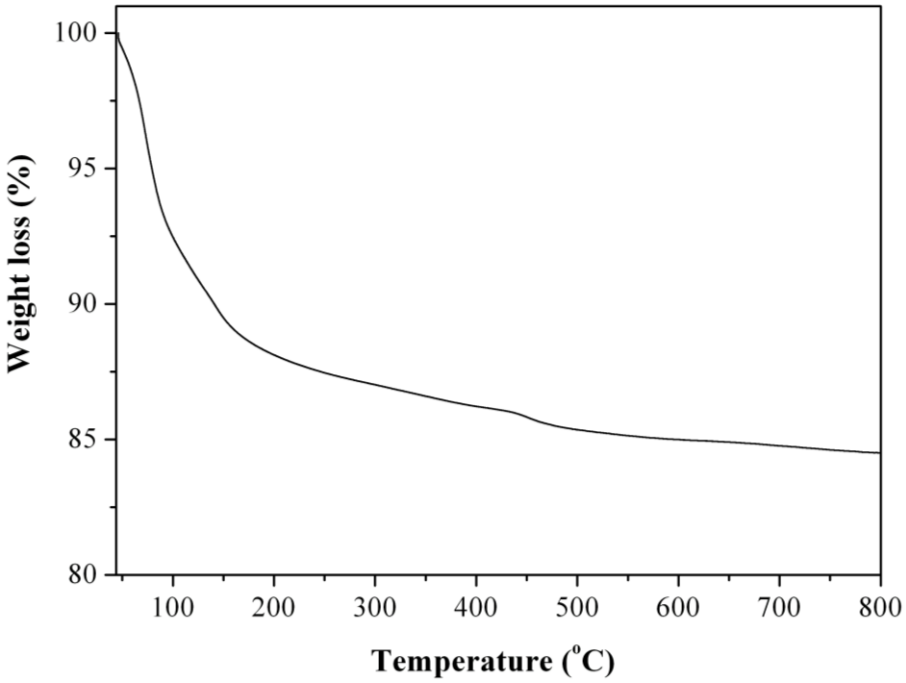


Fig. S8b

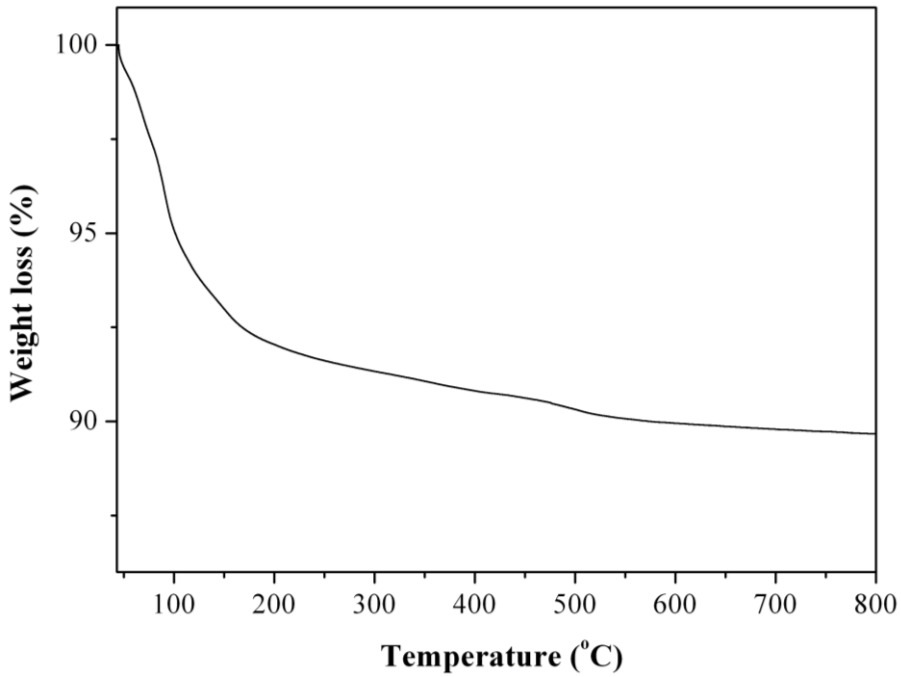


Fig. S8c

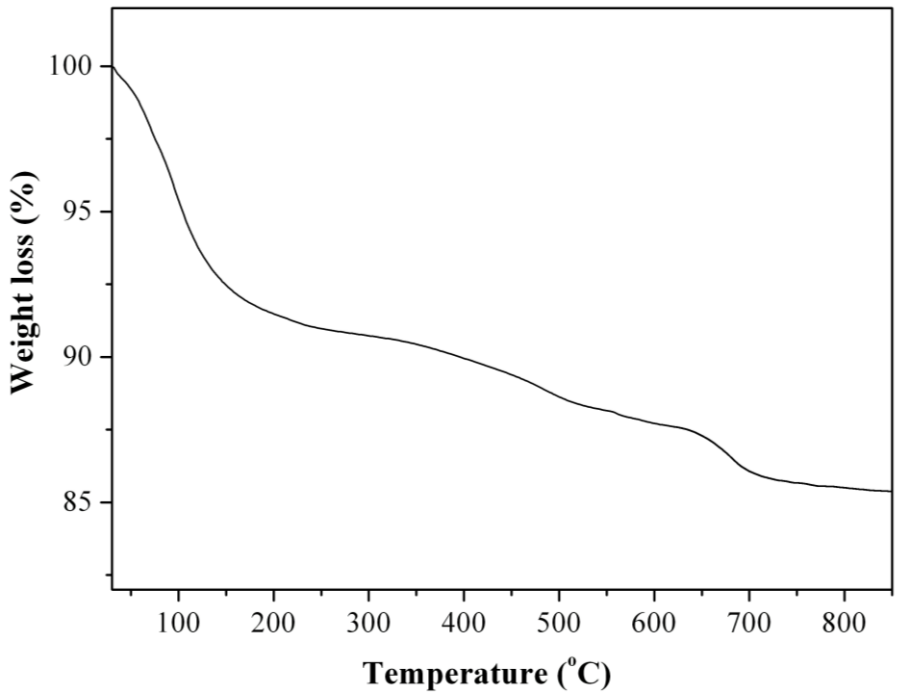
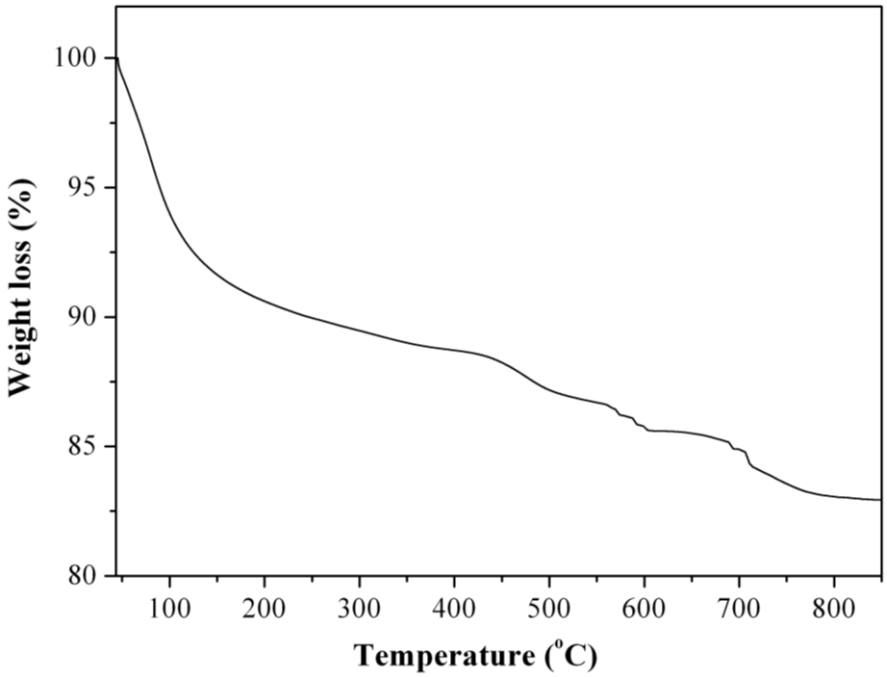


Fig. S8d



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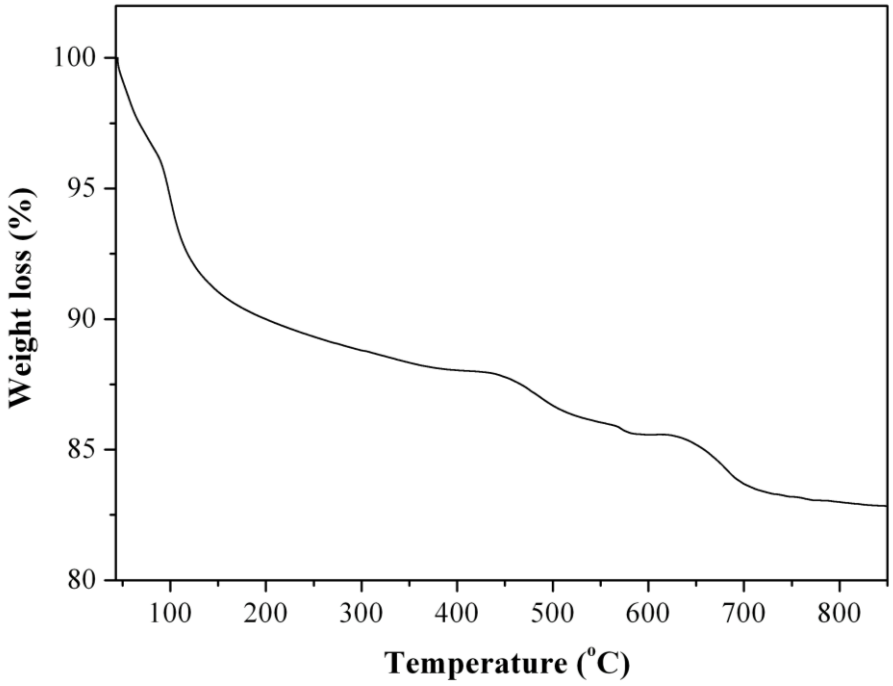


Fig. S8f

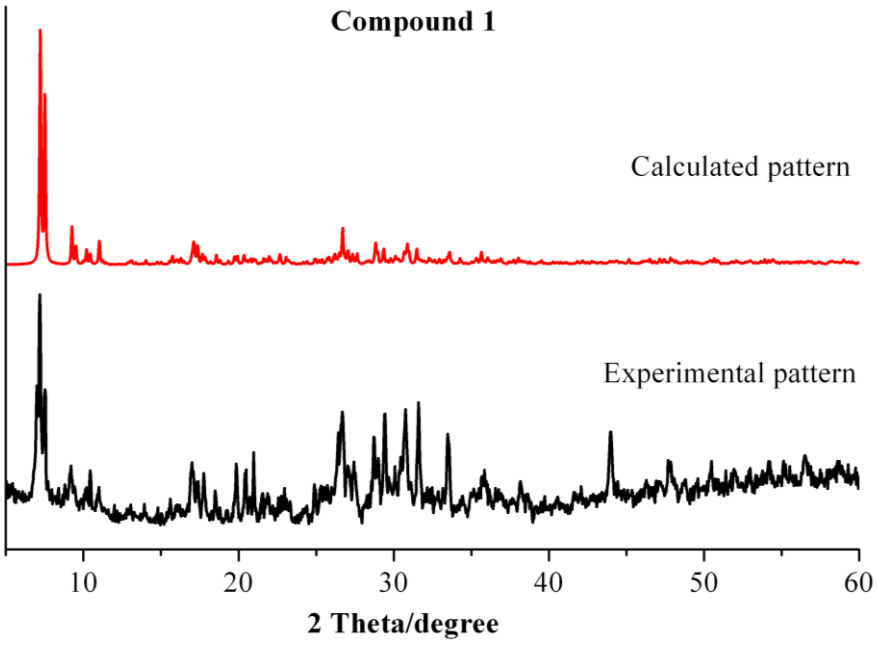


Fig. S9a

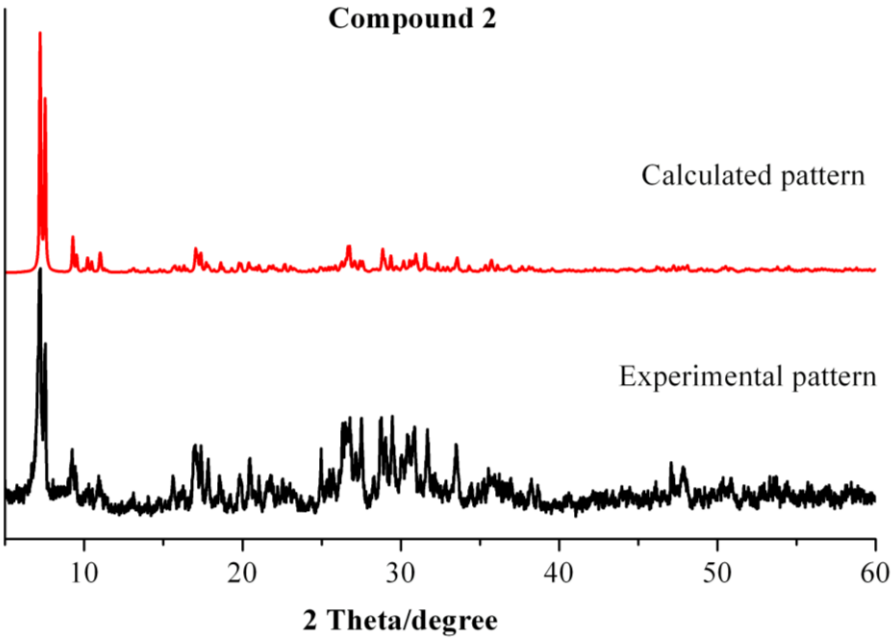
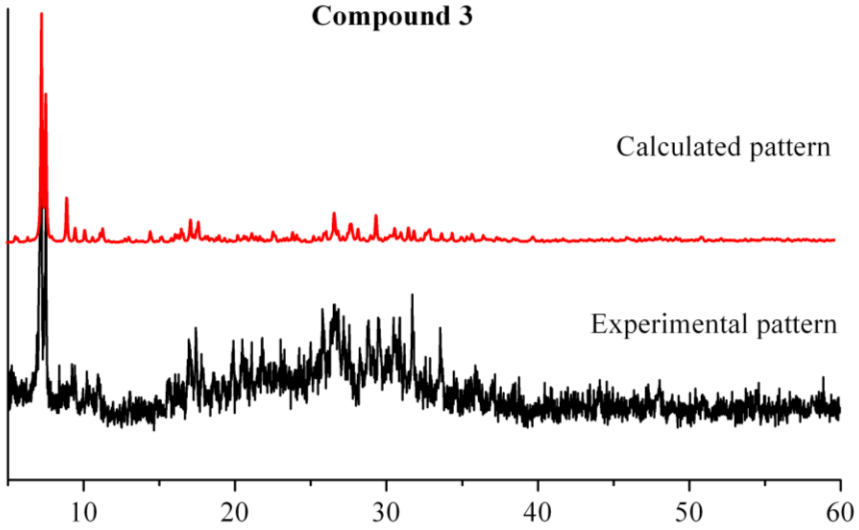


Fig. S9b



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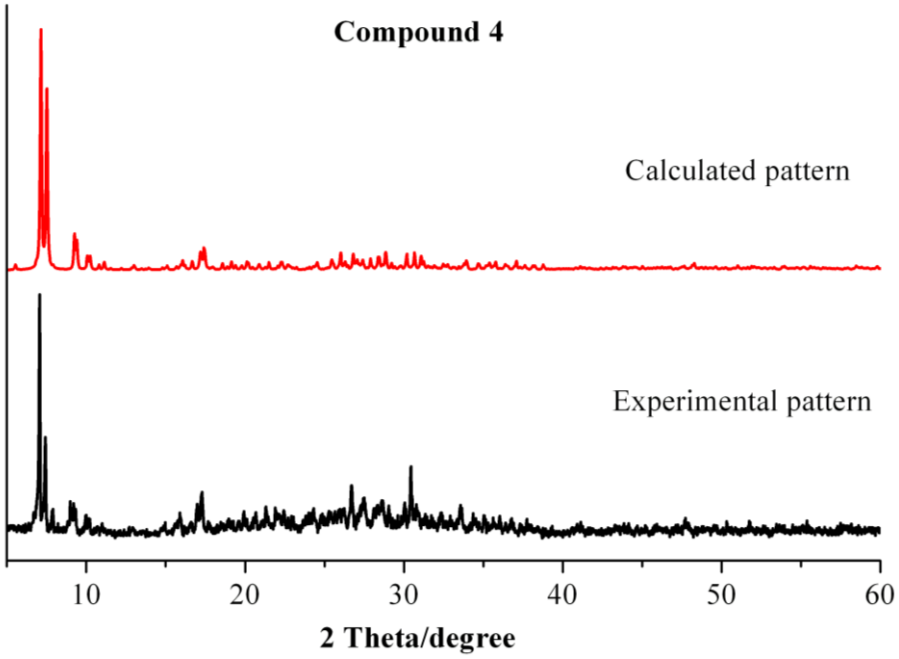

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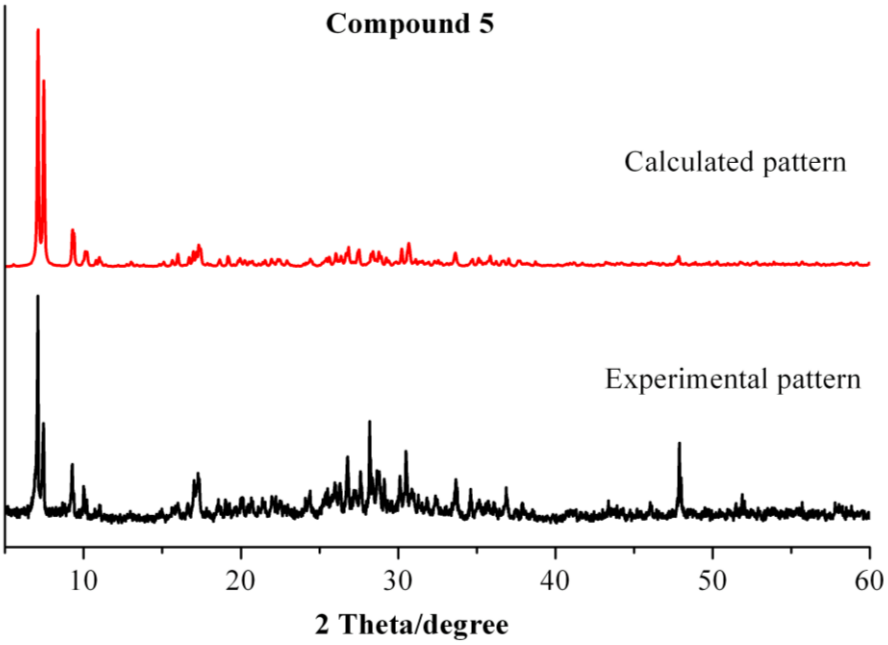

Fig. S9e

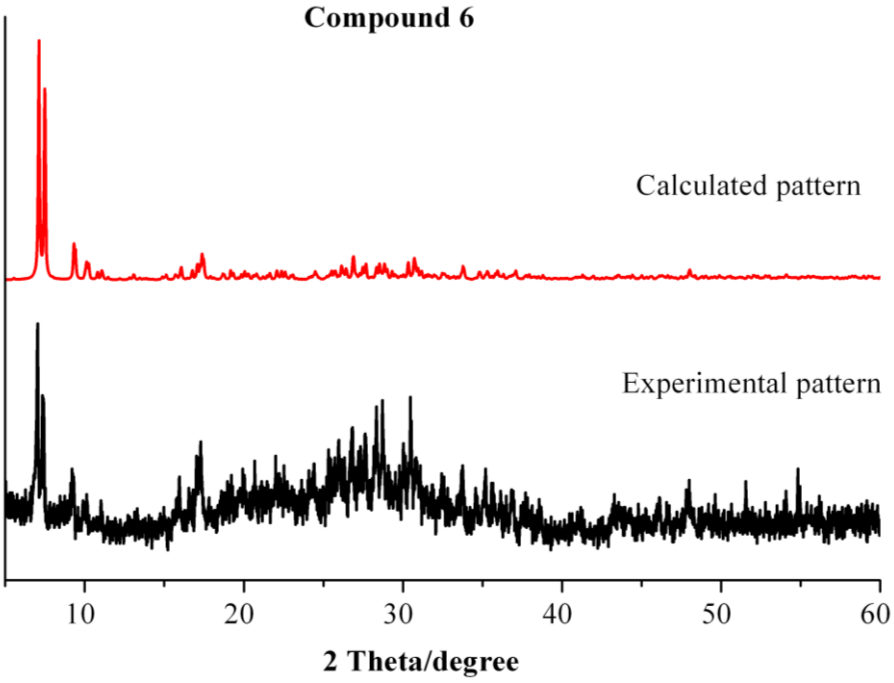

Fig. S9f