

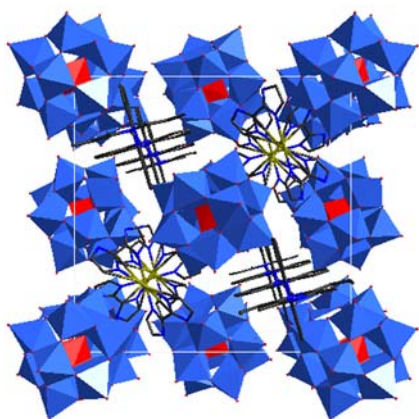
Supplemental Material for:

## Assembly of Multinuclear Ag complexes and Keggin Polyoxometalates Adjusted by Organic Ligands: Syntheses, Structures and Luminescence

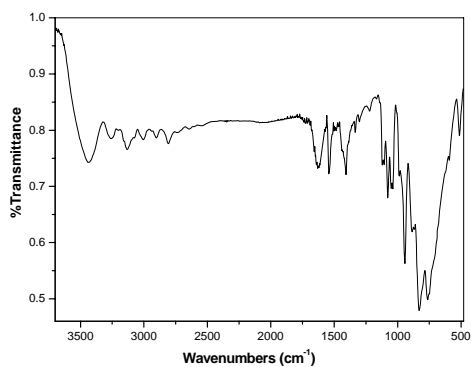
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**The bond valence sum calculations for W atoms in compounds 1 and 2:** For **1**, bond valence sum calculations for W1, W2, W3, W4, W5, W6, W7, W8, W9, W10 and W11, are 5.83, 6.03, 5.78, 6.32, 6.40, 6.10, 5.85, 6.28, 5.81, 6.03 and 6.16, respectively. For **2**, W1, W2, W3, W4, W5, W6, are 6.41, 6.52, 6.42, 6.35, 6.41, 6.46, respectively.

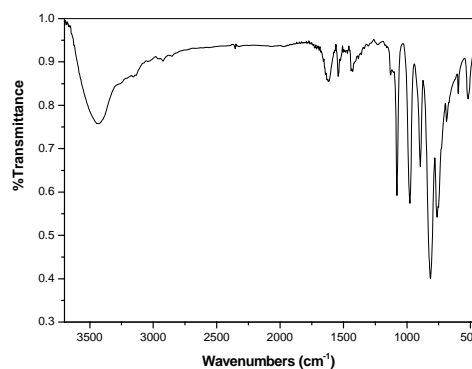
**Fig. S1** View of 3D supramolecular structure of compound **2**.



**Fig. S2** IR spectra of compounds **1** and **2**.

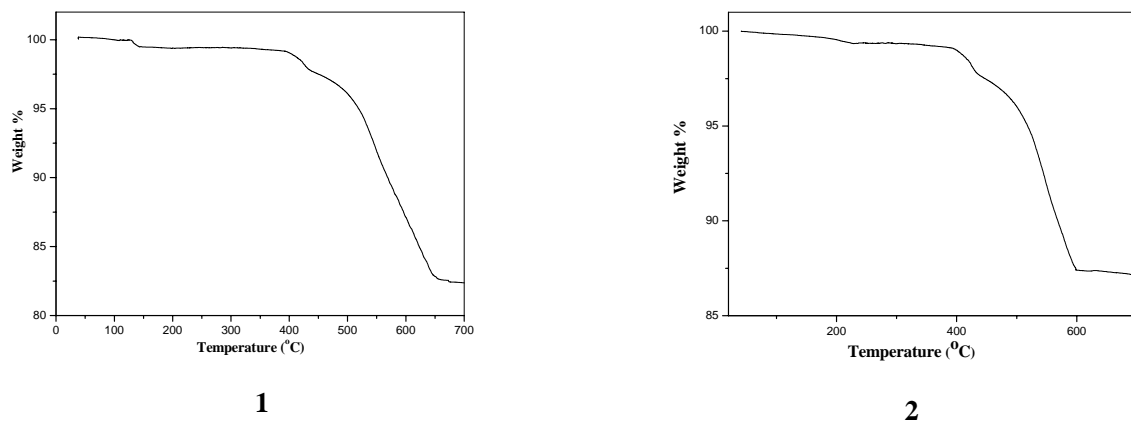


**1**

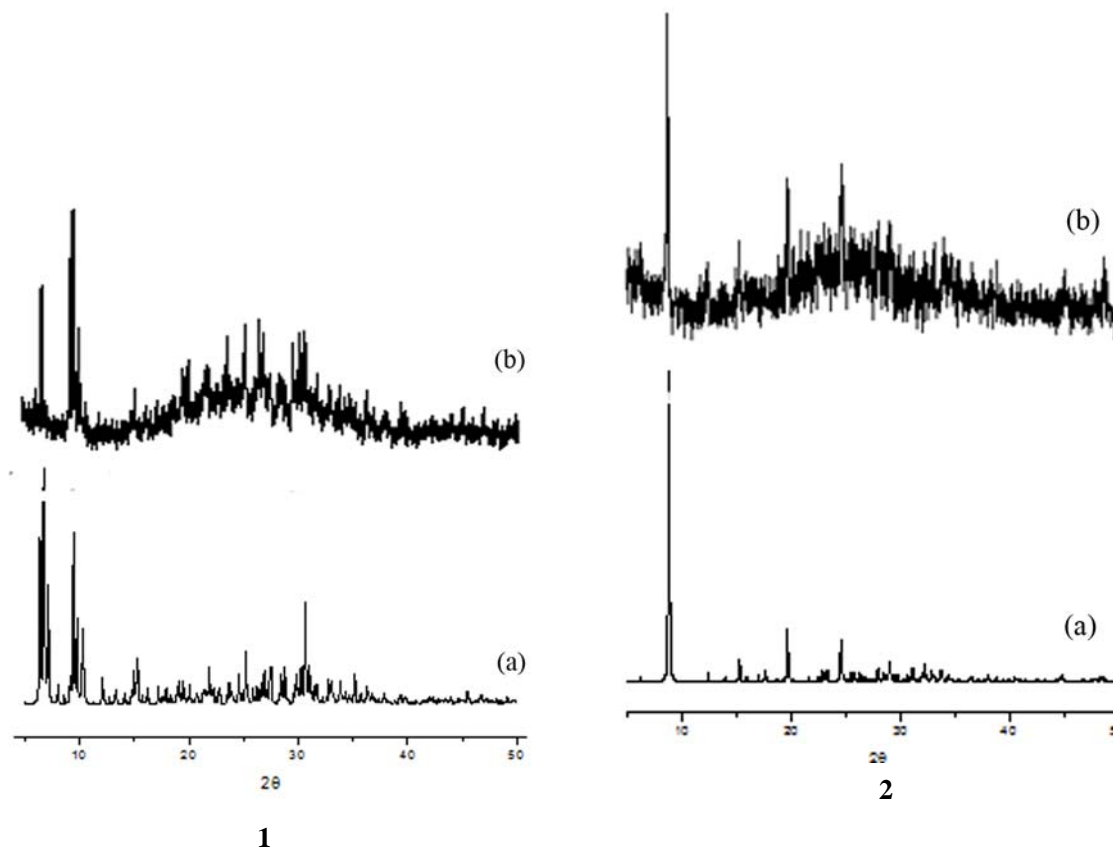


**2**

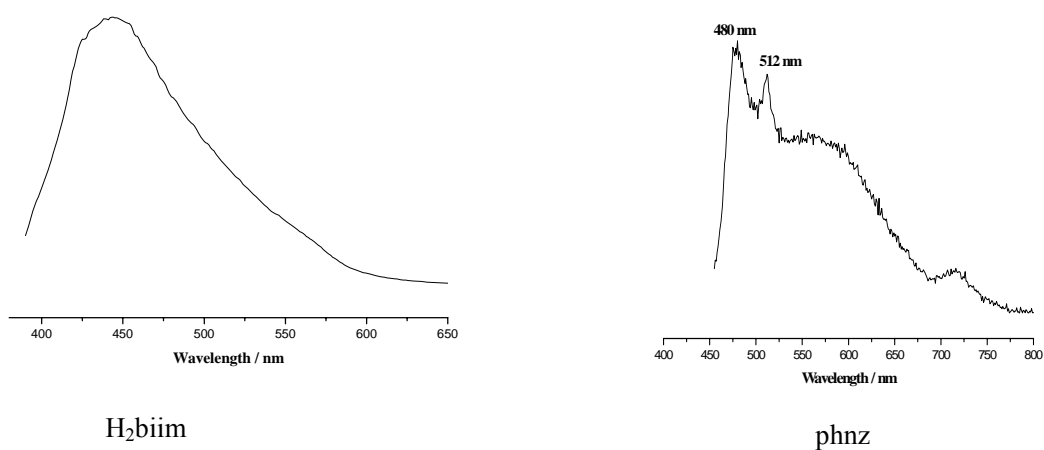
**Fig. S3** TG curves of compounds **1** and **2**.



**Fig. S4** PXRD patterns of compounds **1** and **2** under different states: a) simulated from single-crystal data, b) as-synthesized sample.



**Fig. S5** The fluorescence emission spectra of ligands H<sub>2</sub>biim ( $\lambda_{\text{ex}} = 370$  nm) and phnz ( $\lambda_{\text{ex}} = 445$  nm) in the solid state at room temperature.



**Fig. S6** The fluorescence emission spectra of compounds **1** ( $\lambda_{\text{ex}} = 336$  nm) and **2** ( $\lambda_{\text{ex}} = 370$  nm) in the solid state at room temperature.

