

## Supporting Information

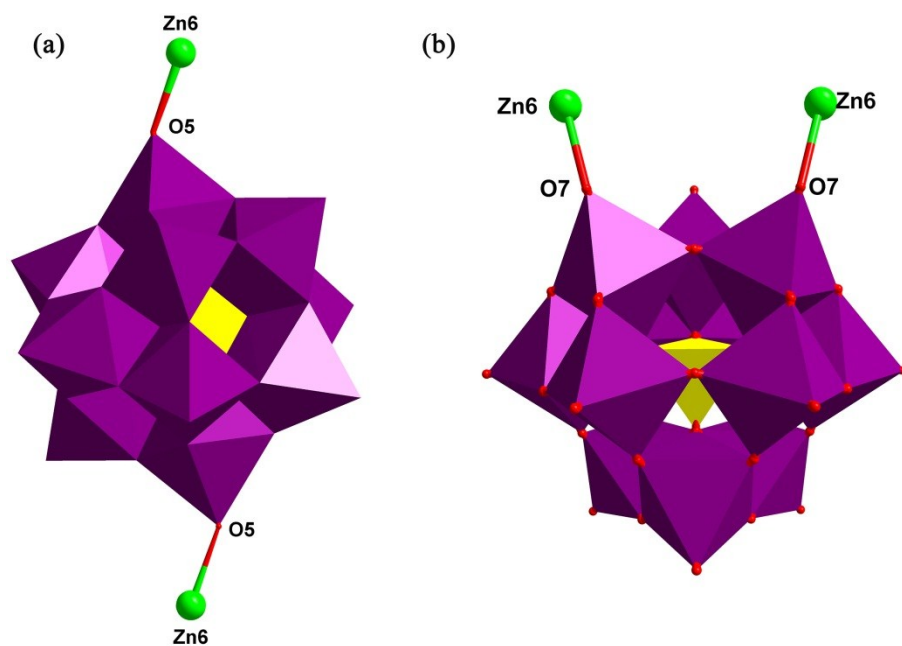
### **Assembly of two novel 3D organic–inorganic hybrids based on Keggin-type polyoxometalates: syntheses, crystal structures and properties**

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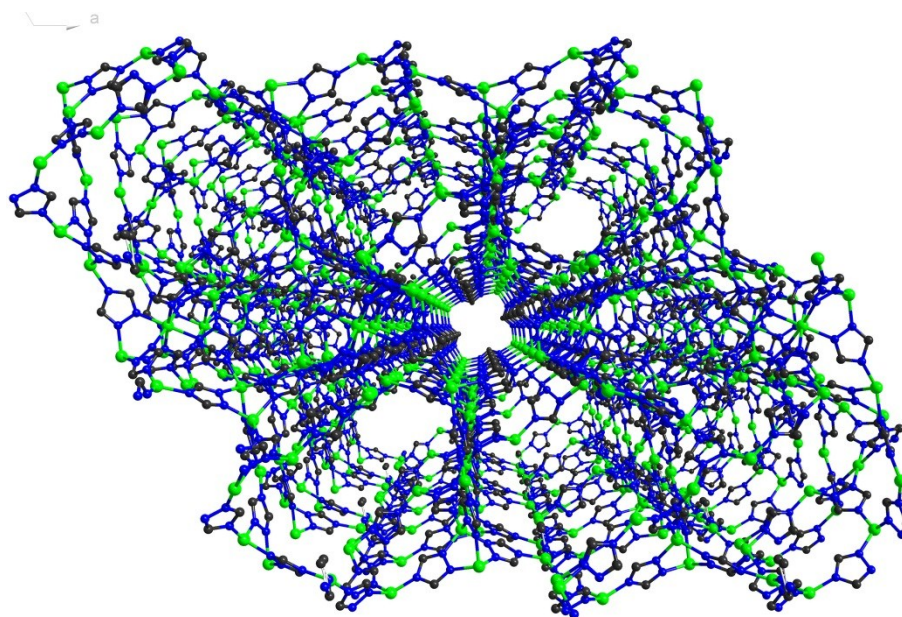
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**Fig. S1** The coordination mode of POM in compound **1**: (a) the linear coordination mode; (b) the swing coordination mode.



**Fig. S2** The 3D structure of compound **1** without POM along b axis.

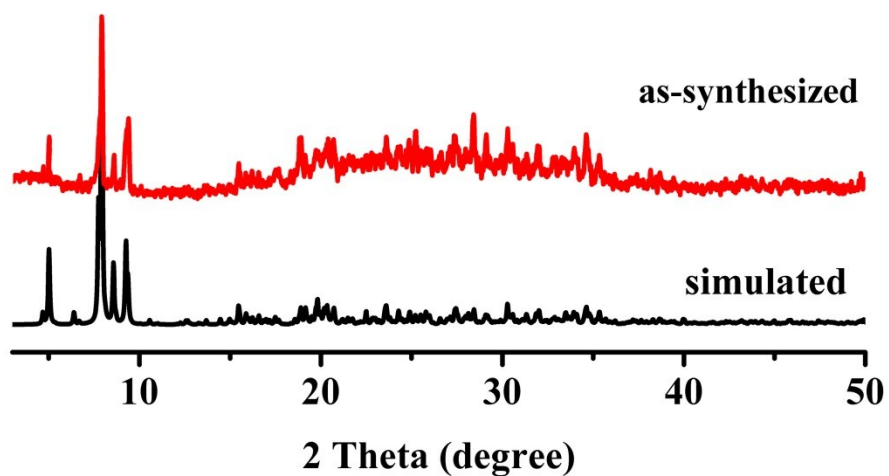


Fig. S3 PXRd patterns of compound 1.

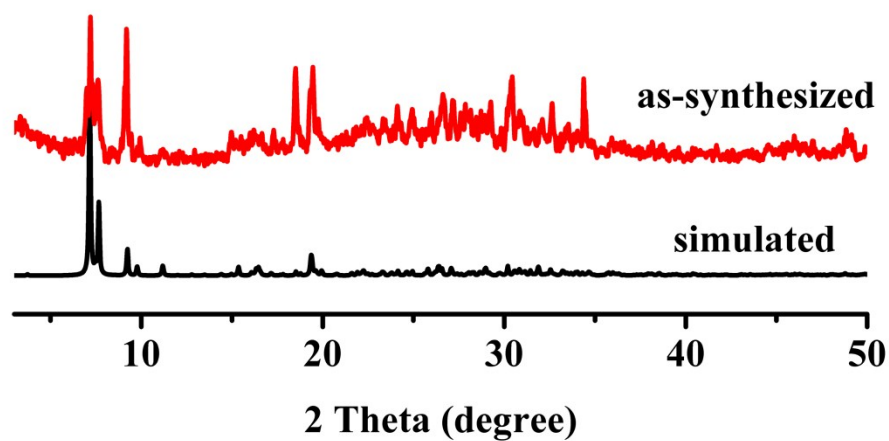


Fig. S4 PXRd patterns of compound 2.

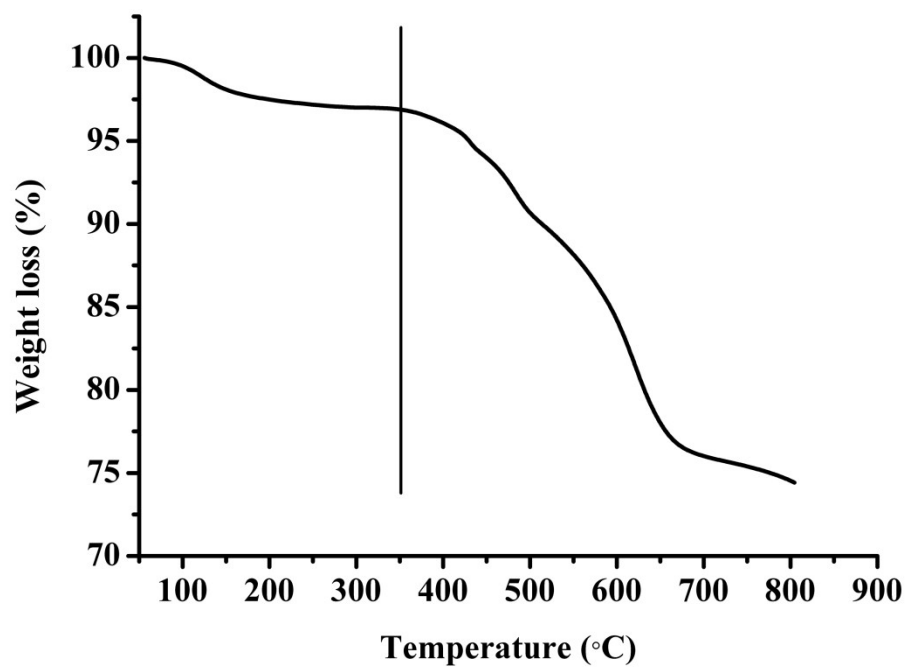


Fig. S5 TG curves of compound 1.

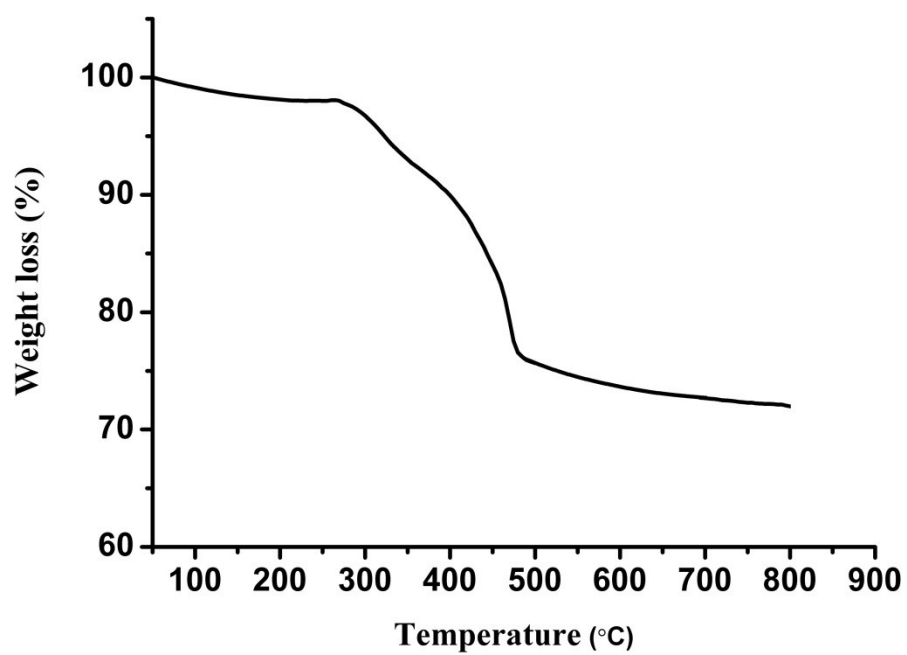
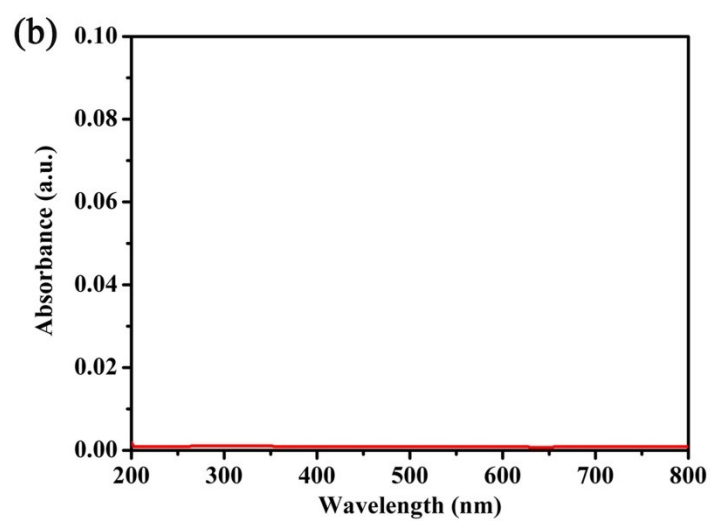
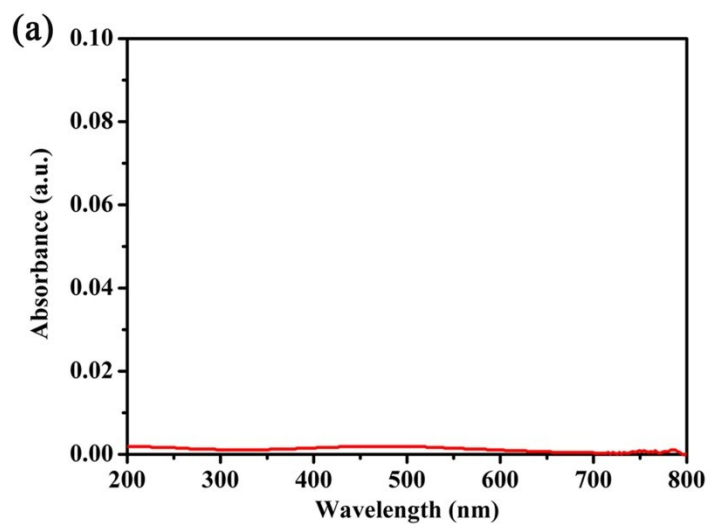
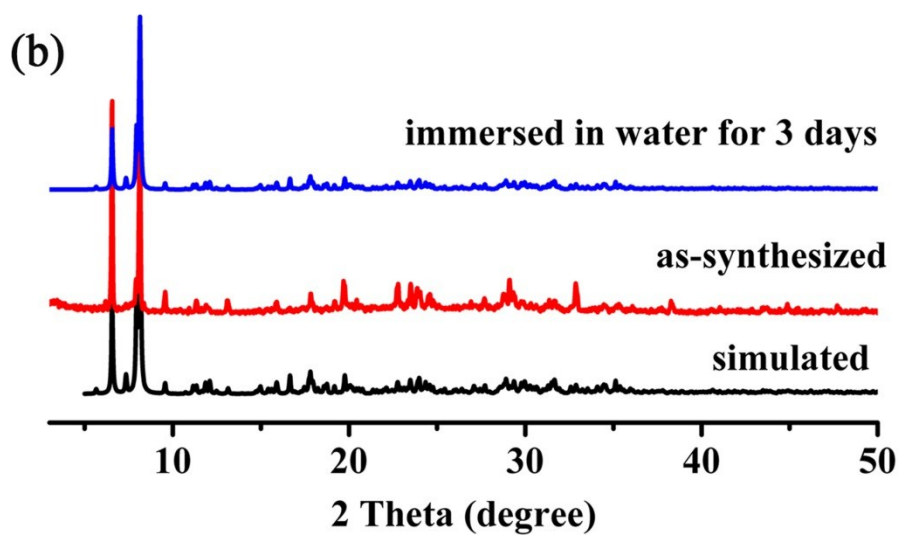
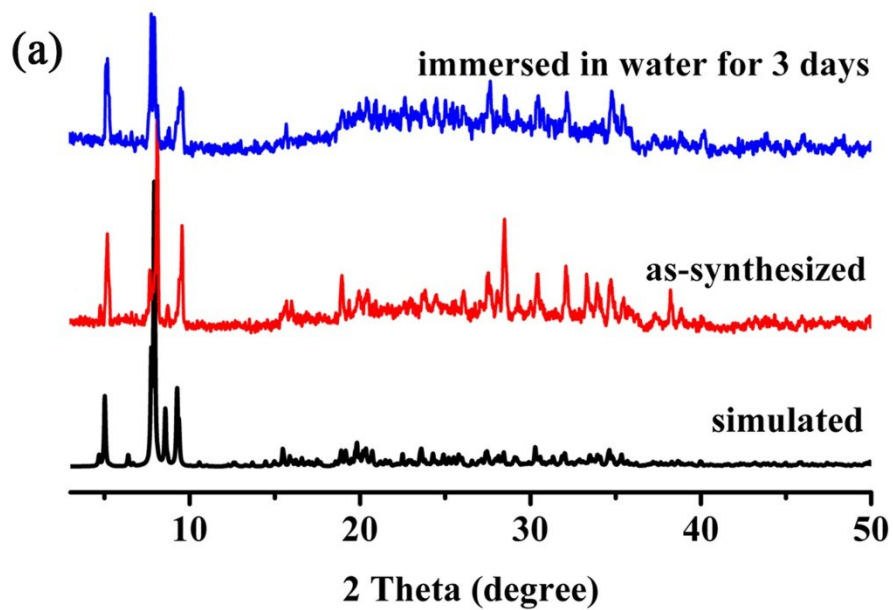


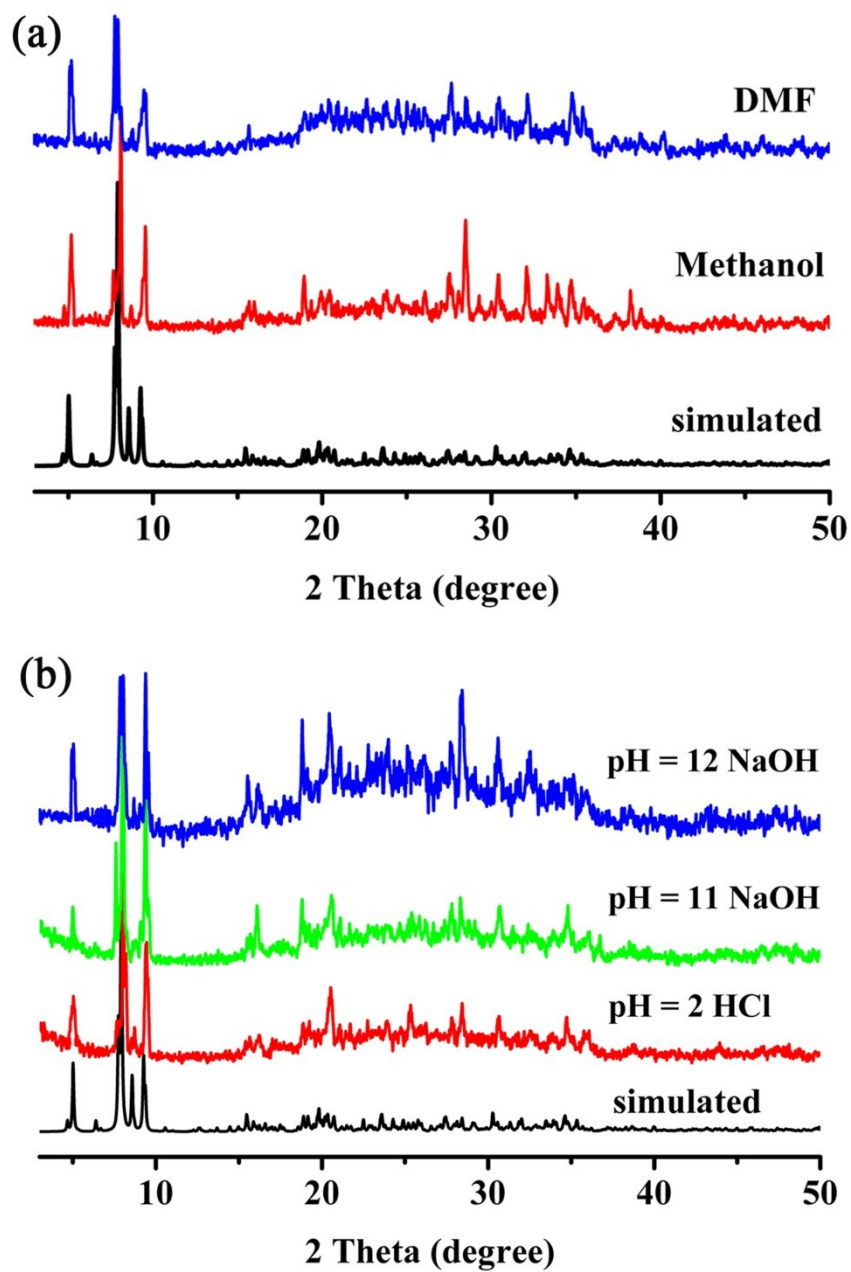
Fig. S6 TG curves of compound 2.



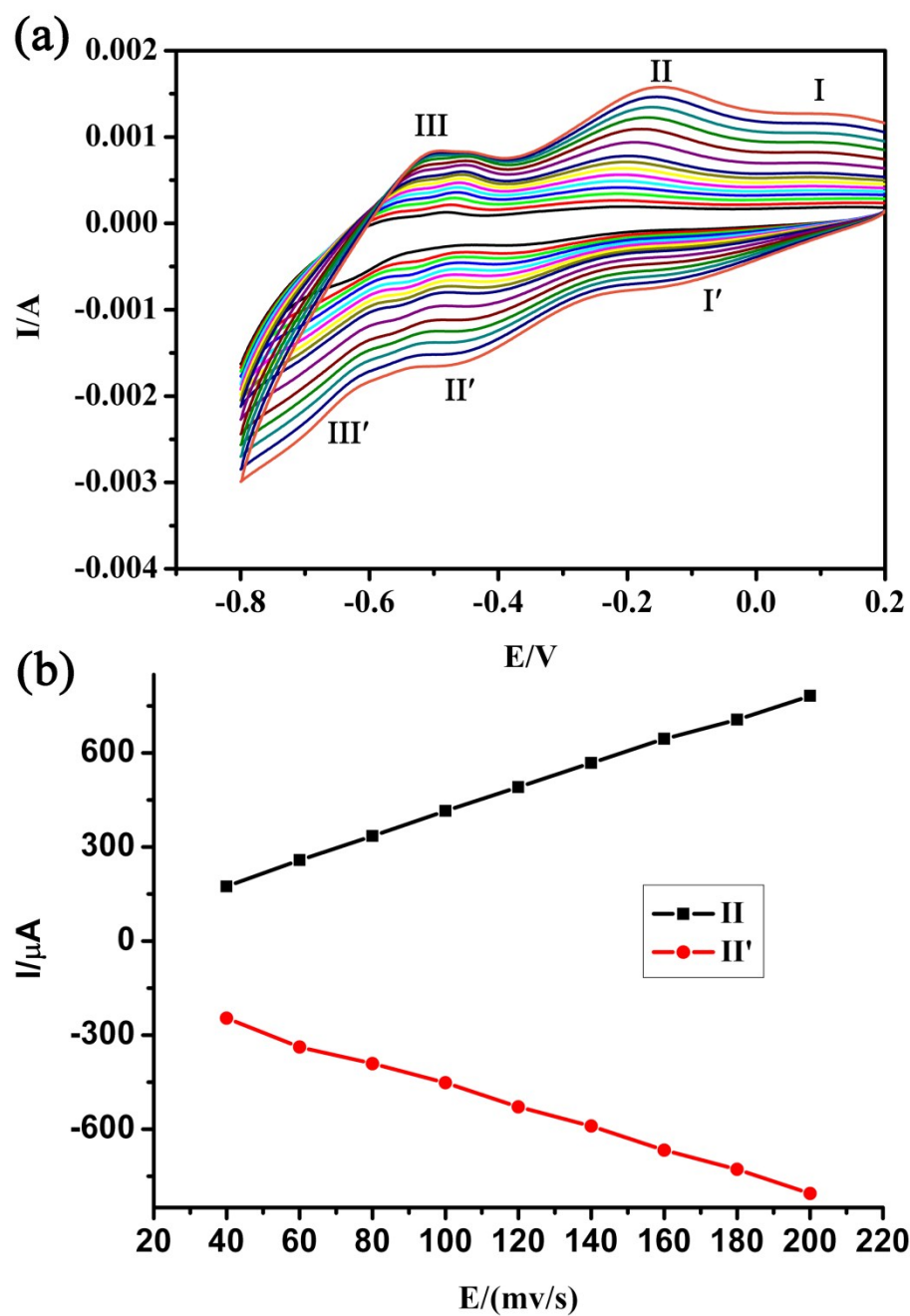
**Fig. S7** UV-vis absorbance of compound **1** (a), **2** (b) after immersed in deionized water for three days.



**Fig. S8** PXRd patterns of compound 1 (a) and 2 (b) after immersed in deionized water for three days.

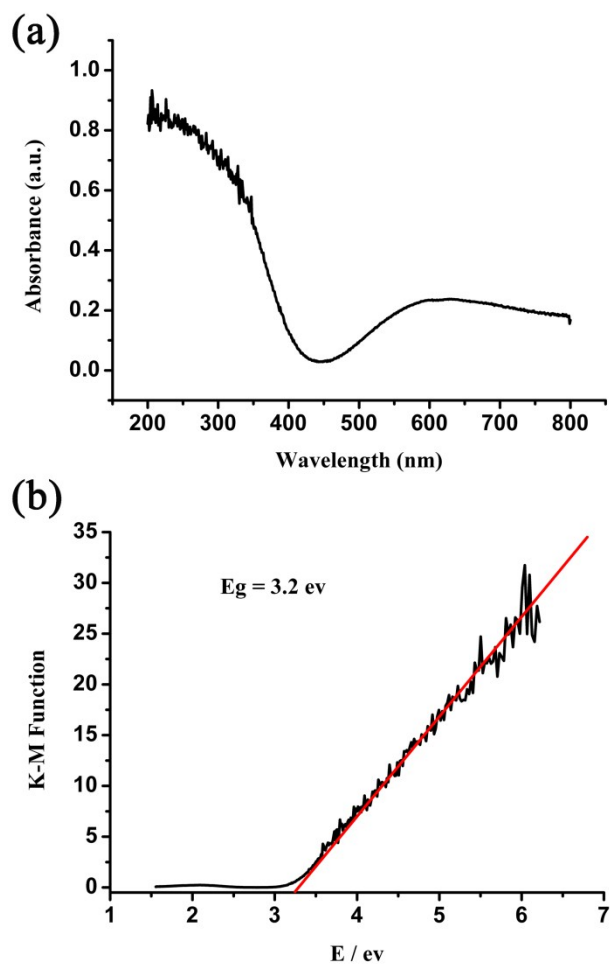


**Fig. S9** PXR D patterns of compound 1 immersed in different organic solvents and aqueous solution of different pH.

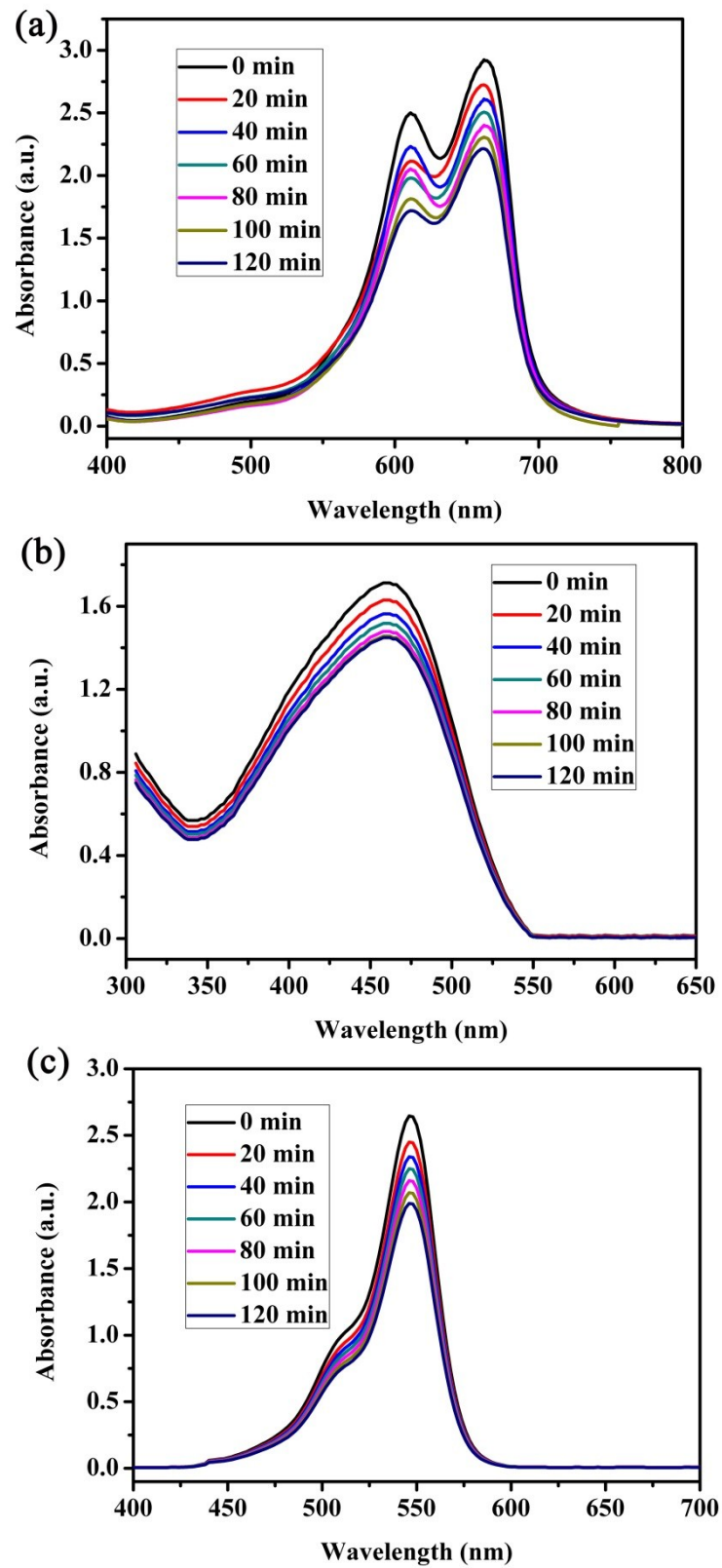


**Fig. S10** (a) Cyclic voltammograms of the 1-CPE in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450 and 500 mV·s<sup>-1</sup>, respectively). (b) The dependence of anodic peak (II) and cathodic peak (II') currents of 1-CPE on the scan rate.

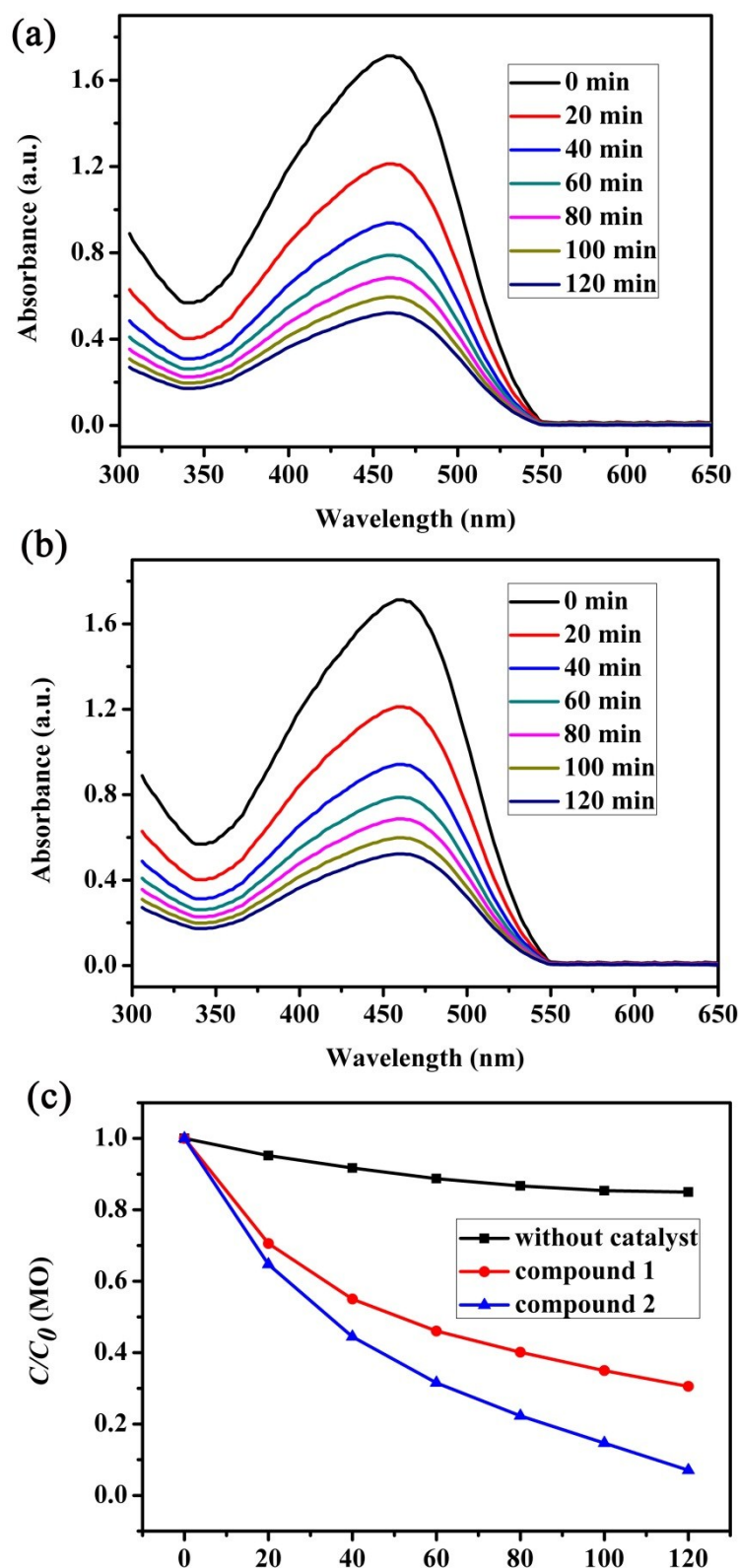




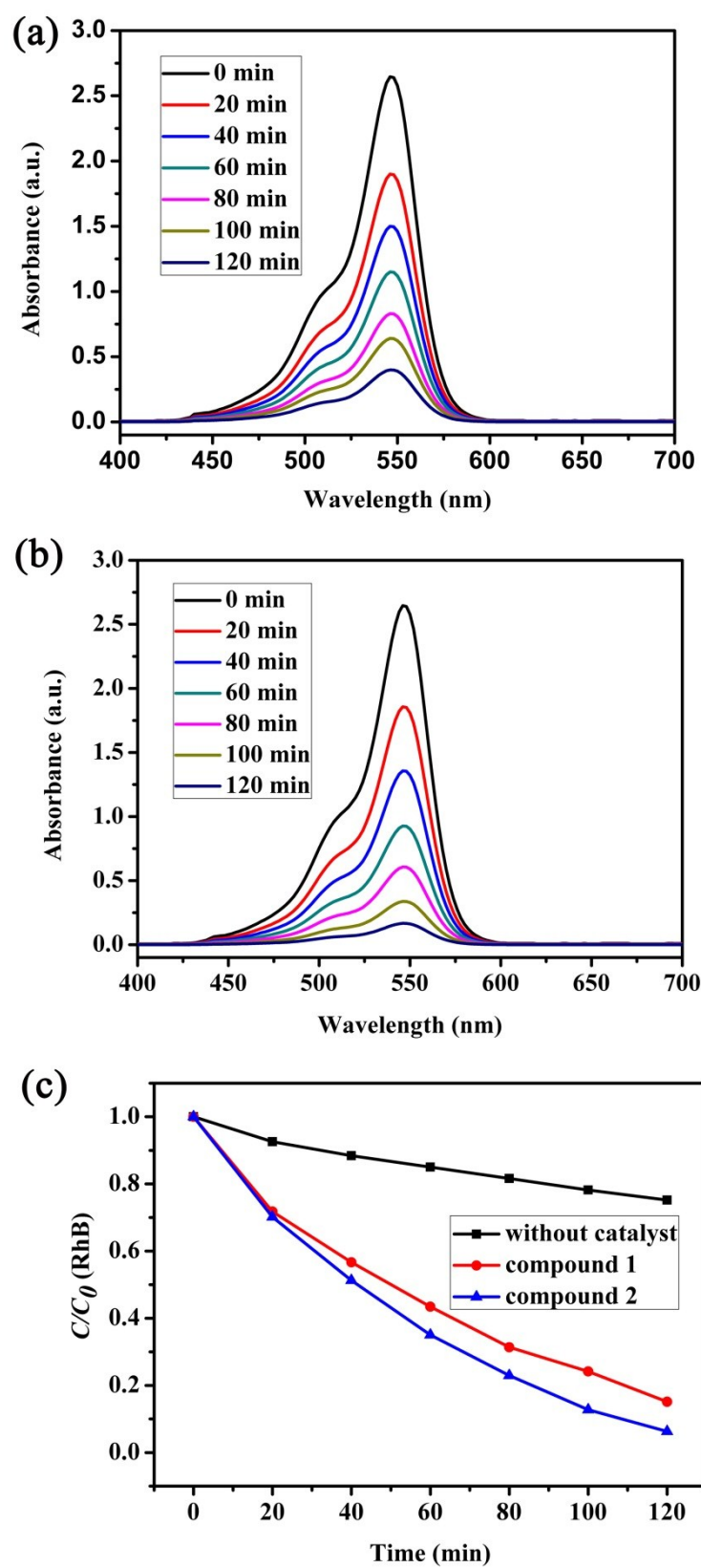
**Fig. S11** (a) The diffuse reflectance UV-Vis absorption spectrum of compound **2**. (b) The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **2**.



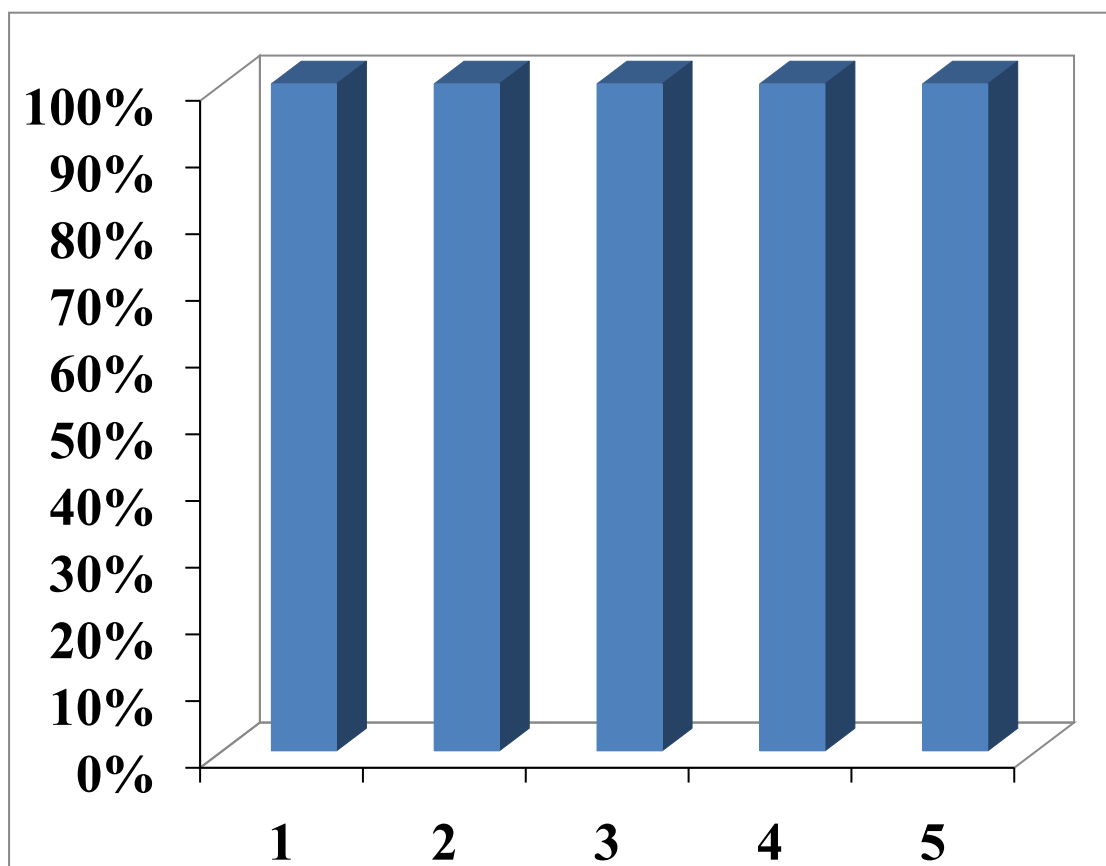
**Fig. S12** UV-Vis absorption spectra of the MB (a), MO (b), and RhB (c) solutions degraded without photocatalysts under UV irradiation (254 nm) at different time intervals.



**Fig. S13** (a) Curves of absorbance of the MO solution decomposed by **1** under UV irradiation. (b) Curves of absorbance of the MO solution decomposed by **2** under UV irradiation. (c) Comparison of decomposition rate of the MO solution with and without catalyst.



**Fig. S14** Curves of absorbance of the RhB solution decomposed by **1** under UV irradiation. (b) Curves of absorbance of the RhB solution decomposed by **2** under UV irradiation. (c) Comparison of decomposition rate of the RhB solution with and without catalyst.



**Fig. S15** The reproducible ability of compound **1** for photodegradation of MB for 5 cycles.