Supporting Information

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

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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 PXRD patterns of compound 1 immersed in different organic solvents and aqueous solution of different pH.
Fig. S10 (a) Cyclic voltammograms of the I-CPE in 1 M H$_2$SO$_4$ 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$^{-1}$, respectively). (b) The dependence of anodic peak (II) and cathodic peak (II$'$) currents of I-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) Comparision 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.