

Electronic Supplementary Information (ESI)

**Chiral salen-metal derivatives of polyoxometalates with asymmetric catalytic and photocatalytic activities**

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## ***Experimental Section***

**Materials and Measurements.** All starting materials and solvents were reagent grade, commercially available and used without further purification. Mn(salen)(H<sub>2</sub>O)<sub>2</sub>ClO<sub>4</sub> was synthesized according to the reported procedures.<sup>1,2</sup> The Fourier transform infrared (FT-IR) spectra were recorded in the range 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer with pressed KBr pellets (Figure S3). Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. P, Mo, and W were determined by a Leaman inductively coupled plasma (ICP) spectrometer. TG analyses were performed on a Perkin-Elmer TG-7 analyzer heated from 45 to 900 °C under a N<sub>2</sub> atmosphere at a rate of 10 °C min<sup>-1</sup> (Figure S4).

1. Shyu, H.-L.; Wei, H.-H.; Wang, Y. *Inorg. Chim. Acta.* **1999**, *290*, 8.
2. Miyasaka, H.; Clérac, R.; Ishii, T.; Chang, H.-C.; Kitagawa, S.; Yamashita, M. *J. Chem. Soc. Dalton Trans.* **2002**, 1528.

**Synthesis of 1:** H<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] (1830 mg, 1 mmol) was dissolved in 20 mL distilled water. Then, 20 mL Mn(salen)(H<sub>2</sub>O)<sub>2</sub>ClO<sub>4</sub> (1532 mg, 3 mmol) methanol solution was quickly added to above solution. The dark brown reaction mixture appeared immediately and was vigorously stirred in a rockered flask at 35°C for 2 days. After filtration, the precipitate was re-crystallized at CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH (1:1) solution. Dark-brown plate-like crystals of **1** were obtained in a week (yield: 2095 mg, 68% based on Mo). Elemental analysis (%) calcd for **1**: C 24.56, H 2.49, N 2.73, P 1.01, Mn 5.35, Mo 37.37; found: C 24.35, H 2.36, N 2.80, P 1.08, Mn 5.29, Mo 37.42.

**Synthesis of 2:** An identical procedure with **1** was followed to prepare **2** except

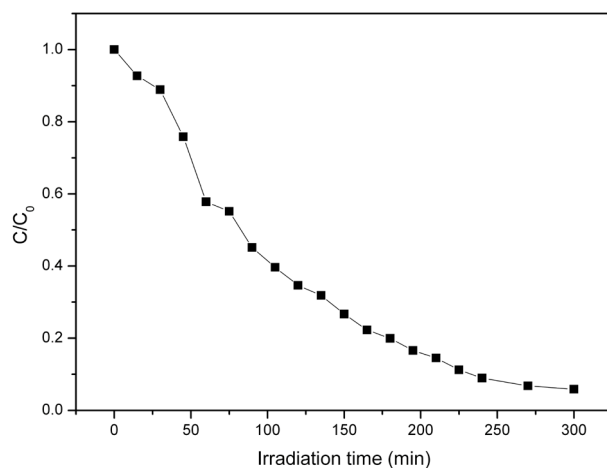
H<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] was replaced by H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (2880 mg, 1 mmol) (yield: 2895 mg, 70% based on W). Elemental analysis (%) calcd for **1**: C 18.30, H 1.85, N 2.03, P 0.75, Mn 3.99, W 53.35; found: C 18.42, H 1.76, N 2.21, P 0.79, Mn 3.85, Mo 53.41.

### ***Details for Catalytic Experiments***

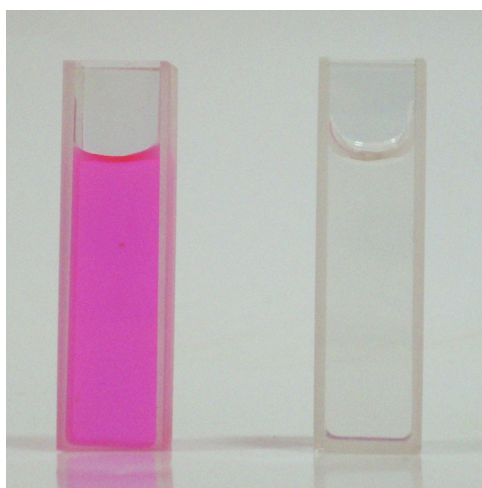
**Asymmetric epoxidation of chromene:** To a cooled solution (0 °C) of chromene (0.2 mmol), PPNO (7 mg, 0.04 mmol), and catalyst (**1** or **2**, 0.002 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), a precooled NaClO aqueous solution (0.4 mmol, 0 °C) was added portionwise. The mixture was stirred at 0 °C, and the reaction was monitored by gas chromatography. When the reaction reached a steady conversion, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The phases were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 mL × 2). The combined organic layers were washed with brine (3 mL×2) and dried over anhydrous sodium sulfate. The concentrated filtrate was purified by silica gel column chromatography to afford the corresponding epoxide.

### ***Details for Photocatalytic Experiments***

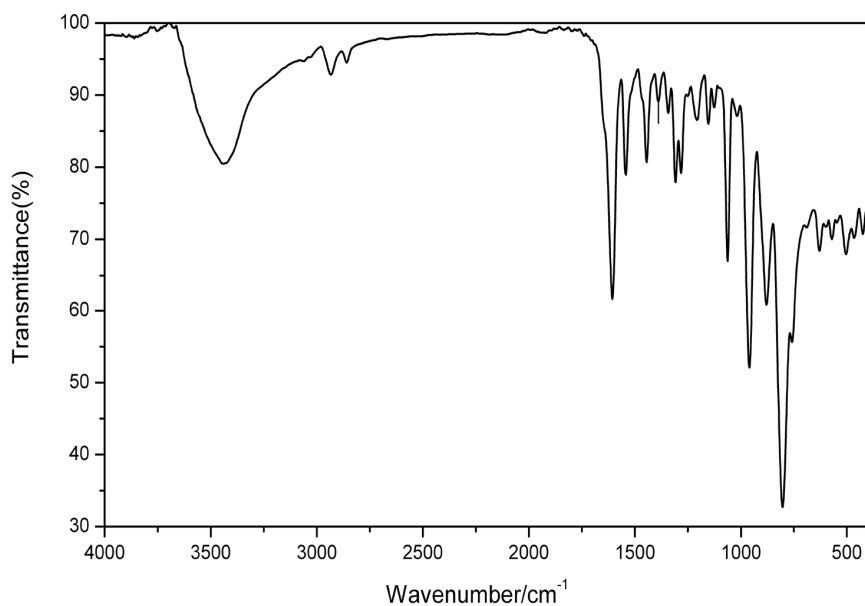
Compound **1** ( $1 \times 10^{-5}$  mol) was dispersed in the solutions ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) at pH 3.5 including RhB which was adjusted with dilute aqueous solutions of either NaOH or HClO<sub>4</sub>, then magnetically stirred in the dark for about 10 min. the solution was then exposed to UV irradiation from a 125 W Hg lamp at a distance of 4–5 cm between the liquid surface and the lamp. The solution was kept stirring during irradiation. Every 15min, 3.0 ml of samples were taken out of the beaker for analysis.



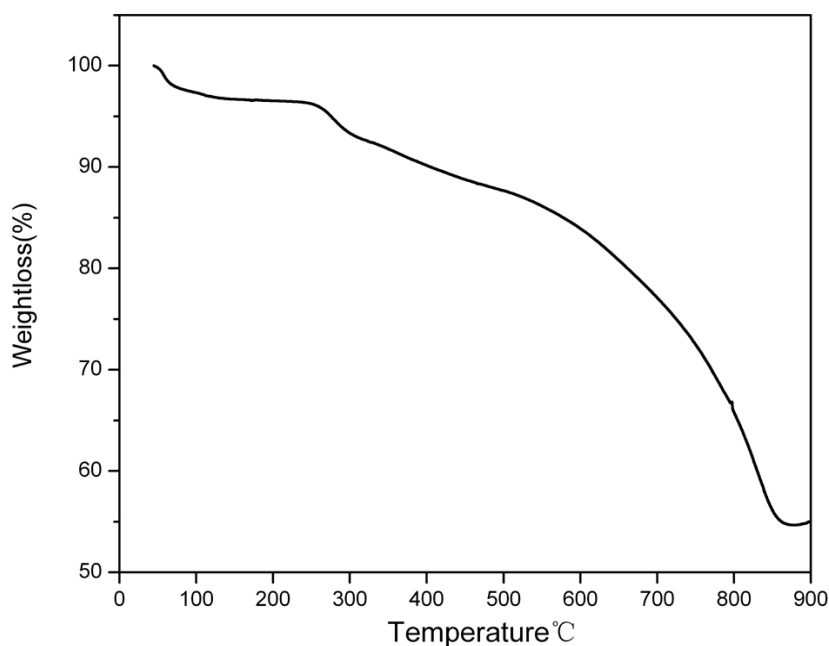
**Fig. S1** Changes in  $C/C_0$  plot of 100 ml RhB solution ( $2.0 \times 10^{-5}$  M at a pH of 3.5) versus reaction time in the presence of  $1 \times 10^{-5}$  mol **1**. The conversions of RhB(K) can be expressed as  $K = (C_0 - C_t)/C_0$ , where  $C_0$  represents the UV-vis intensity of RhB at the original reaction time ( $t = 0$ ), while  $C_t$  is the UV-vis absorption intensity at a certain irradiation time  $t$ .



**Fig. S2** Colour changes of RhB solution before and after photocatalysis.

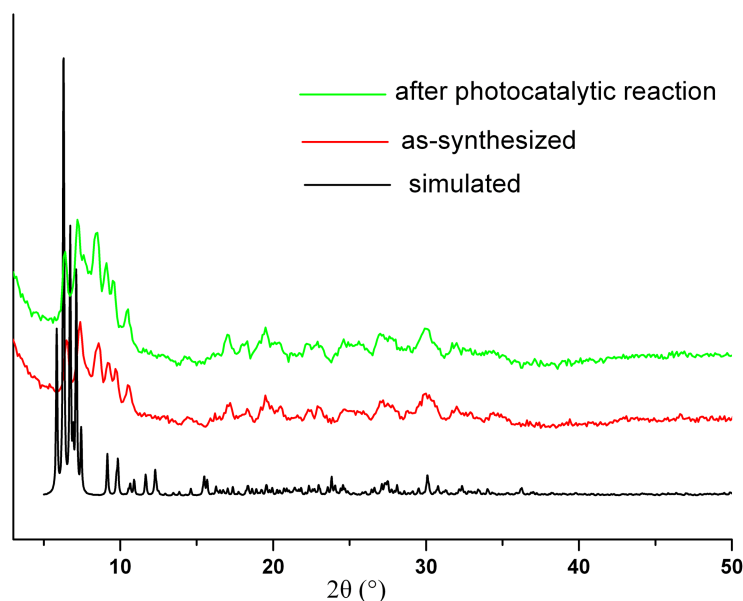


**Fig. S3** IR spectrum of compound **1**



**Fig. S4** TG curve of **1**

The TG curve of complex **1** shows two weight loss steps. The first weight loss in the temperature range of 45–250 °C might be attributed to the loss of coordinated methanol molecule and water molecule. The complete decomposition is finished up to 870 °C with unidentified decomposition products.



**Fig. S5** PXRD patterns of compound **1**

Crystal data for **1**:  $C_{63}H_{76}N_6O_{51}PMo_{12}Mn_3$ ,  $M_r = 3080.37$ , monoclinic, space group  $C2$ ,  $a = 28.281(8) \text{ \AA}$ ,  $b = 17.947(6) \text{ \AA}$ ,  $c = 23.917(10) \text{ \AA}$ ,  $\beta = 96.866(6)^\circ$ ,  $V = 12052(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.693 \text{ g cm}^{-3}$ , final  $R_1 = 0.0804$  and  $wR_2 = 0.2490$  ( $R_{\text{int}} = 0.0728$ ) for 20588 independent reflections [ $I > 2\sigma(I)$ ]. **2**:  $C_{63}H_{76}N_6O_{51}PW_{12}Mn_3$ ,  $M_r = 4135.29$ , monoclinic, space group  $C2$ ,  $a = 27.671(5) \text{ \AA}$ ,  $b = 17.834(5) \text{ \AA}$ ,  $c = 23.899(5) \text{ \AA}$ ,  $\beta = 95.821(5)^\circ$ ,  $V = 11733(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.341 \text{ g cm}^{-3}$ , final  $R_1 = 0.0742$  and  $wR_2 = 0.2276$  ( $R_{\text{int}} = 0.0673$ ) for 19162 independent reflections [ $I > 2\sigma(I)$ ]. The Flack parameters of 0.00(5) and 0.02(2) for **1** and **2** indicate that the absolute configurations are correct. CCDC 798437 for **1** and CCDC 798438 for **2**.

Data were collected on a Bruker Apex CCD diffractometer at 298(2) K for **1** and **2**, with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and refined by full-matrix least-squares methods with SHELXL.<sup>3</sup> Some H atoms of the ligand could not be introduced in the refinement but

were included in the structure factor calculation. The solvent molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the \*.hkp files produced using the SQUEEZE routine.

3 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.