Electronic Supplementary Material (ESI) for ChemComm.

Self-assembly and photocatalytic H_2 evolution activity of two unprecedented polytantalotungstates based on the largest $\{Ta_{18}\}$ and $\{Ta_{18}Yb_2\}$ clusters

Peng Huang,[a] Chao Qin,*[b] Yu Zhou,[a] Yu-Mei Hong,[a] Xin-Long Wang,[b] and Zhong-Min Su,*[b]

[a.] Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Department of Chemistry, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou, 221116, PR China, E-mail: huangpeng@jsnu.edu.cn

[b.] Institute of Functional Material Chemistry, National & Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China. E-mail: qinc703@nenu.edu.cn and zmsu@nenu.edu.cn

1. Materials and Methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received, except for $Cs_8K[P_2W_{15}O_{59}(TaO_2)_3]\cdot 22H_2O$, which was prepared similar to the procedure described for $K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3]\cdot 17H_2O$,[1] but by using the addition of solid CsCl to precipitate as mixed Cs/K salt (characterized by IR spectra, thermogravimetric analyses, and elemental analysis). Elemental analyses (Cs, P, K, Ta, and W) were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded on Alpha Centaurt FT/IR spectrophotometer (KBr pellets) over the region of 400–4000 cm^{-1}. PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range 3−50°. UV−vis absorption spectroscopy was obtained on a U-3010 spectrophotometer (Hitachi, Japan). Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7 analyzer heated from room temperature to 800 °C under a nitrogen gas atmosphere with a heating rate of 10 °C min^{-1}.

2. Photocatalytic Measurements.

Photocatalytic reactions were carried out in an external illumination-type reaction vessel with a magnetic stirrer and analyzed by using an automatic H_2 monitoring system at room temperature. The photoirradiation were performed using a 500 W mercury lamp for **1** and **2**. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 m) using N_2 as carrier gas.

3. Synthesis

Synthesis of 1. The mixture of $CoCl_2\cdot 6H_2O$ (10 mg), and $Cs_8K[P_2W_{15}O_{59}(TaO_2)_3]\cdot 22H_2O$ (50 mg) were put in a 4-cm high vial, which was then transferred and sealed in a Teflon-lined autoclave with 3mL HCl (aq. 1.0 M) and heated at 120 °C for 3 days followed by slow cooling to room temperature. The resulting colourless crystals were separated from the solution and washed with distilled water several times, yielding 68% based on $Cs_8K[P_2W_{15}O_{59}(TaO_2)_3]\cdot 22H_2O$. Anal. Calc: P, 1.26; Ta 11.09; W, 56.37; Cs, 7.24; K, 2.13; Na, 0.31. Found: P, 1.24; Ta 11.12; W, 56.38; Cs, 7.22; K, 2.16; Na, 0.33. IR (KBr disks): 519, 775, 910, 955, 1090 cm^{-1}.

Synthesis of 2. Compound **2** was prepared following the procedure described for **1**, except using $Yb(NO_3)_3\cdot 9H_2O$ instead of $CoCl_2\cdot 6H_2O$. The resulting products were

colorless crystals (yield: 76%). Anal. Calc: P, 1.19; Ta 10.46; W, 53.13; Yb, 1.11; Cs, 11.09; K, 0.25. Found: P, 1.47; Ta 11.88; W, 54.29; Yb, 1.02; Cs, 11.61; K, 1.05. IR (KBr disks): 525, 783, 908, 957,1090 cm^{-1}.

4. Single-Crystal Studies

Intensity data of **1** and **2** were collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Absorption corrections were applied using multiscan techniques. Their structures were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[2] Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception of some oxygen atoms. Hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules were estimated by thermogravimetry, and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. **1**: $H_{58}Cs_{16}K_{16}Na_4P_{12}Ta_{18}W_{90}O_{392}$, *M*r = 29348.6, triclinic, *P-1*, a = 22.058(5) Å, b = 24.286(5) Å, c = 26.664(5) Å, α = 66.926(5)°, β = 83.401(5)°, γ = 72.665(5)°, V = 12544(5) $Å^3$, Z = 1, ρ_{calcd} = 3.877 g cm^{-3}, final R_1 = 0.0701 and wR_2 = 0.2024(R_{int} = 0.0652) for 30509 independent reflections ($I > 2\sigma(I)$). **2**: $H_{144}Cs_{26}K_2Yb_2P_{12}Ta_{18}W_{90}O_{434}$, *M*r = 31143, Monoclinic, *c2/m*, a = 44.234(5) Å, b = 26.671(5) Å, c = 22.026(5) Å, α = 90.000(5)°, β = 115.231(5)°, γ = 90.000(5)°, V = 23506(7) $Å^3$, Z = 2, ρ_{calcd} = 4.380 g cm^{-3}, final R_1 = 0.0684 and wR_2 = 0.1829 (R_{int} = 0.1492) for 17261 independent reflections ($I > 2\sigma(I)$). CCDC 1002180 (**1**) and 1058414 (**2**), contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif for **1** and **2**.

Table 1. Polyoxometalates photocatalysts for photocatalytic H_2 evolution activity.

Catalysts	Cocatalyst	Light source	Reaction solution	Reaction time (h)	H_2 evolution rates (μmol h^{-1} g^{-1})	Ref.
1	None	500 W Hg	H_2O + CH_3OH	18	8301.3	
2	None	500 W Hg	H_2O + CH_3OH	18	6494.4	
$\{P_2W_{18}O_{62}\}$	None	500 W Hg	H_2O + CH_3OH	4	552.7	3
$\{P_2W_{15}O_{59}(TaO_2)_3\}$	None	500 W Hg	H_2O + CH_3OH	10	1088.6	
$\{Ta_6O_{19}\}$	None	500 W Hg	H_2O + CH_3OH	10	233.4	

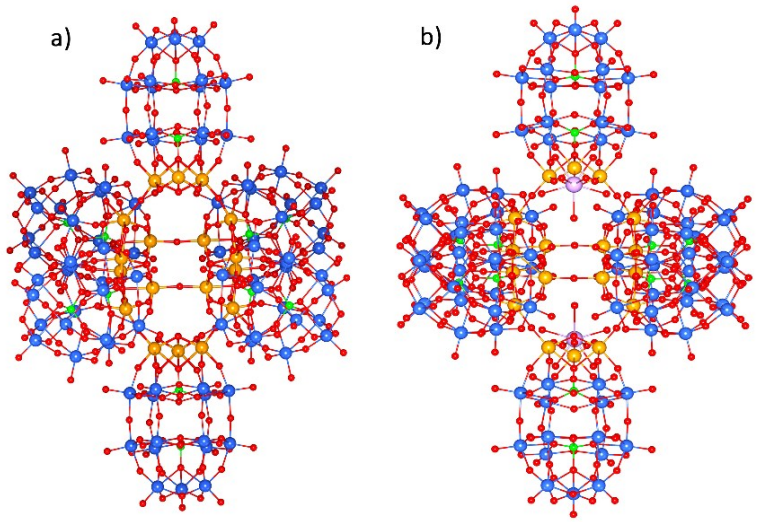

Fig. S1 Ball-and-stick presentations of **1** and **2,** respectively.

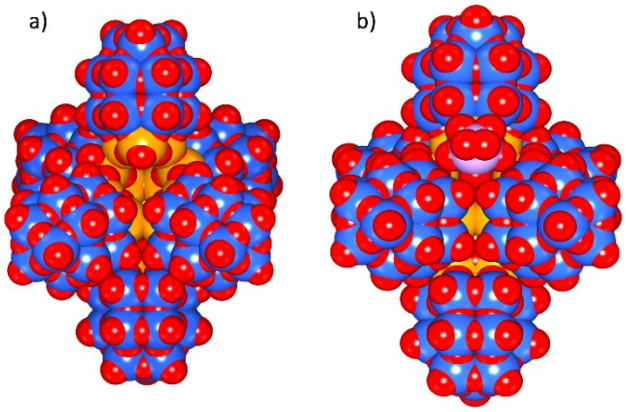

Fig. S2 Ball-and-stick presentations of **1** and **2,** respectively.

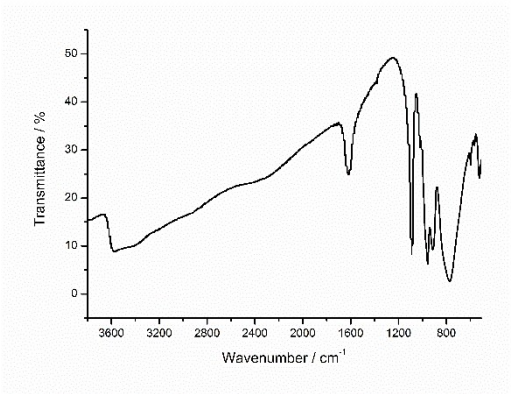

Fig. S3 IR spectra of **1**.

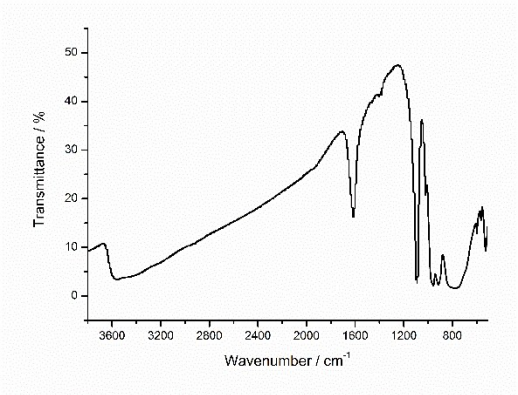

Fig. S4 IR spectra of **2**.

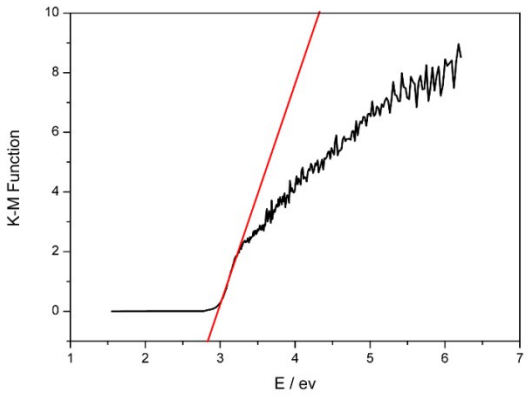

Fig. S5 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **1**.

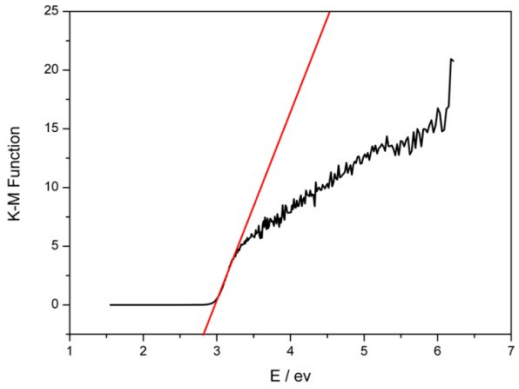

Fig. S6 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compound **2**.

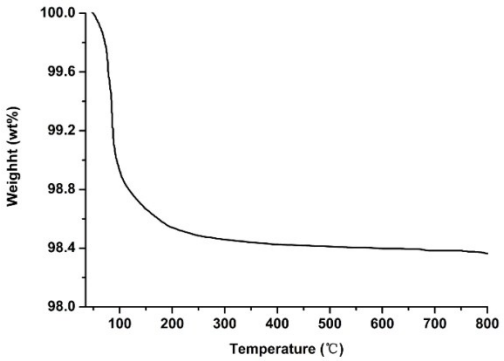

Fig. S7 TGA curve of **1**.

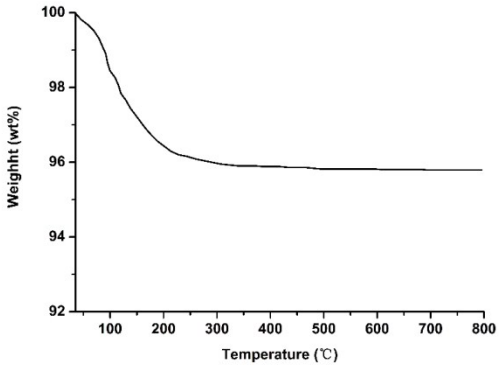

Fig. S8 TGA curve of **2**.

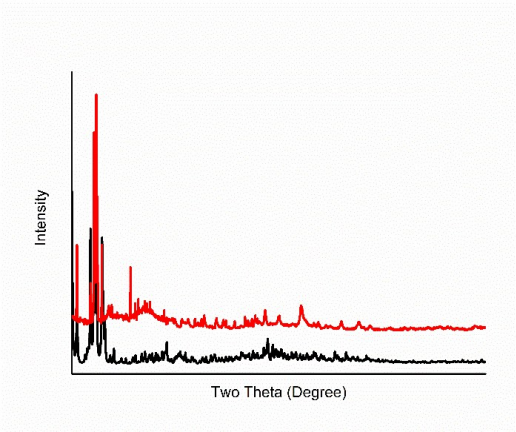

Fig. S9 The XRPD patterns for as-synthesized (top) and simulated (bottom) **1**.

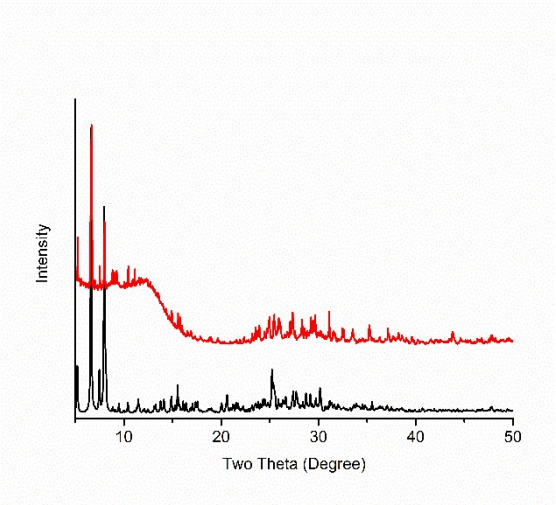

Fig. S10 The XRPD patterns for as-synthesized (top) and simulated (bottom) **2**.

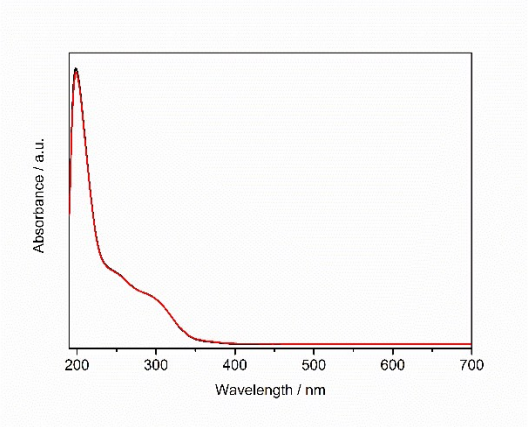

Fig. S11 UV-Vis spectra of compound **1** before (black) and after (red) three runs of the photocatalytic reactions.

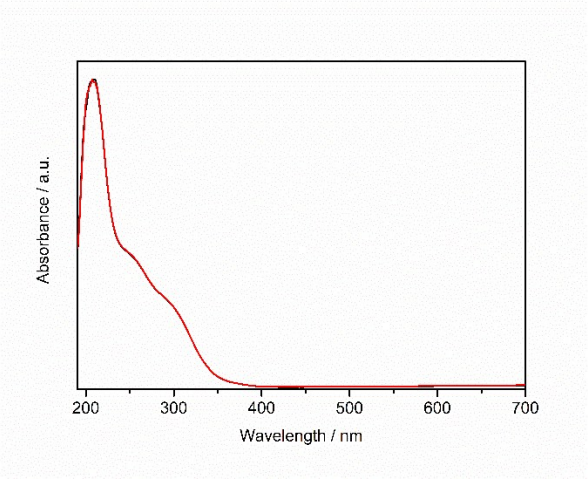

Fig. S12 UV-Vis spectra of compound **2** before (black) and after (red) three runs of the photocatalytic reactions.

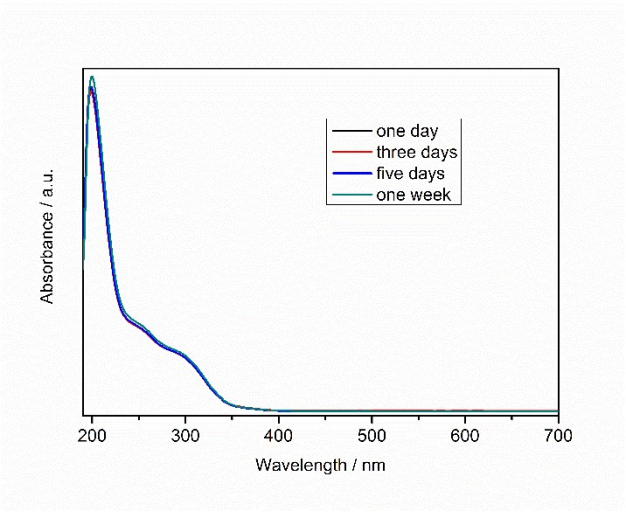

Fig. S13 UV-Vis spectra of compound **1** kept at room temperature.

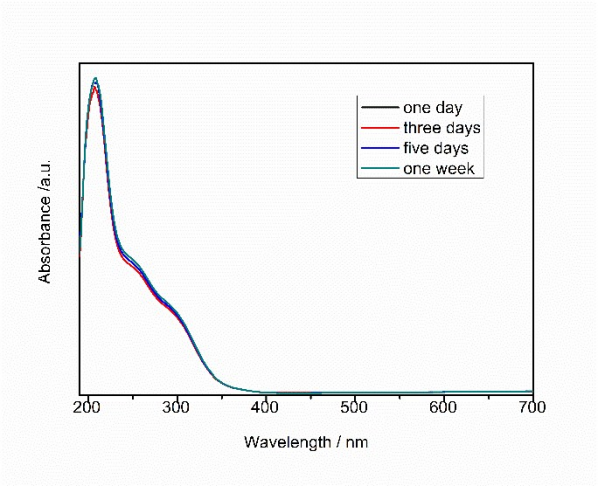

Fig. S14 UV-Vis spectra of compound **2** kept at room temperature.

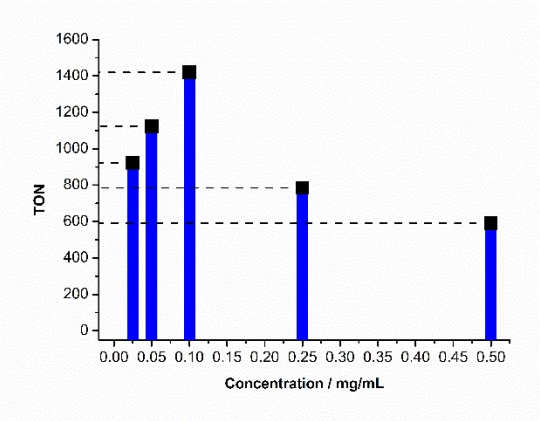

Fig. S15 Turnover number (TON) over different concentrations of **1**. **1** (5.75, 11.5, 23, 57.5, 115 mg) dissolved in 230 mL of 20% methanol solution under ultraviolet irradiation using a 500 W Hg lamp.

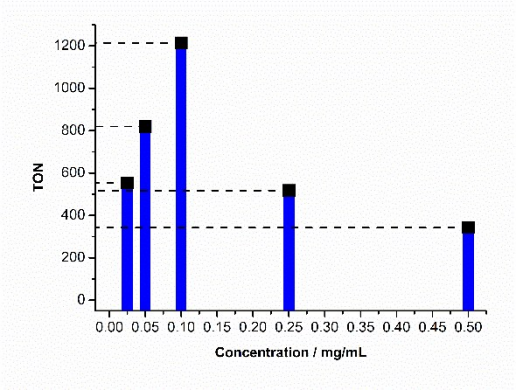

Fig. S16 Turnover number (TON) over different concentrations of **2**. **2** (5.75, 11.5, 23, 57.5, 115 mg) dissolved in 230 mL of 20% methanol solution under ultraviolet irradiation using a 500 W Hg lamp.

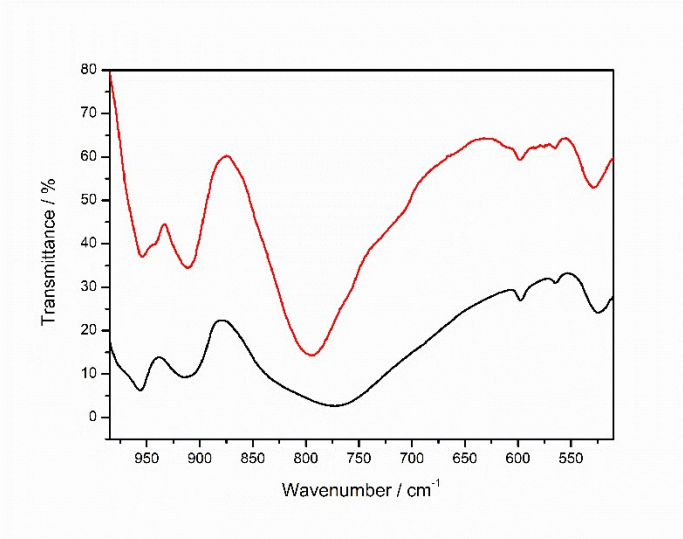

Fig. S17 IR spectra of **1** (black) and the samples recycled form photocatalytic reactions (red).

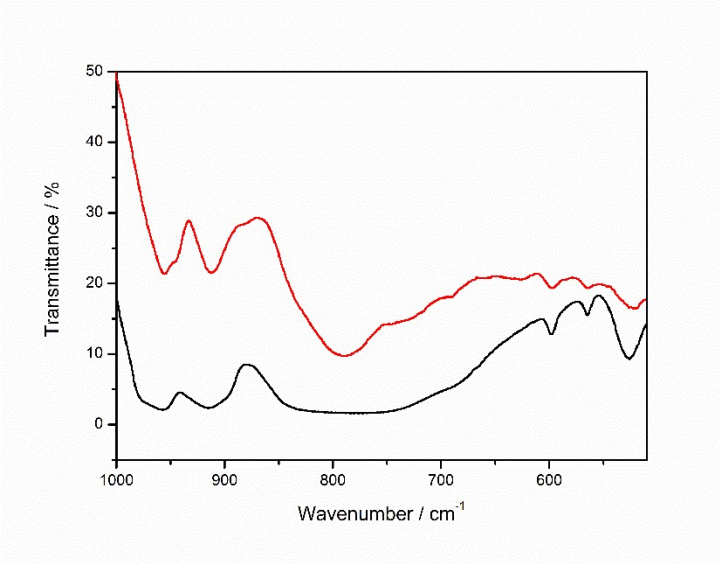

Fig. S18 IR spectra of **2** (black) and the samples recycled form photocatalytic reactions (red).

References

1. S. J. Li, S. M. Liu, S. X.Liu, Y. W. Liu, Q. Tang, Z. Shi, S. X. Ouyang, and J. H. Ye, *J. Am. Chem. Soc.,* 2012, **134**, 19716.

2. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure;* University of Göttingen, Göttingen, Germany, 1997.

3. Y. Q. Jiao, C. Qin, X. L. Wang, F. H. Liu, P. Huang, C. G. Wang, K. Z. Shao, and Z. M. Su, *Chem. Comm.* 2014, **50**, 5961.