Supplementary Material (ESI) for Chemical Communications

Supplementary Information

For

A Discrete Conglomerate of a Distorted Mo(V)-Porphyrin with a Directly Coordinated Keggin-Type Polyoxometalate

Atsutoshi Yokoyama, Takahiko Kojima,* Kei Ohkubo, and

Shunichi Fukuzumi

Department of Material and Life Science, Graduate School of Engineering, Osaka University and SORST(JST), 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

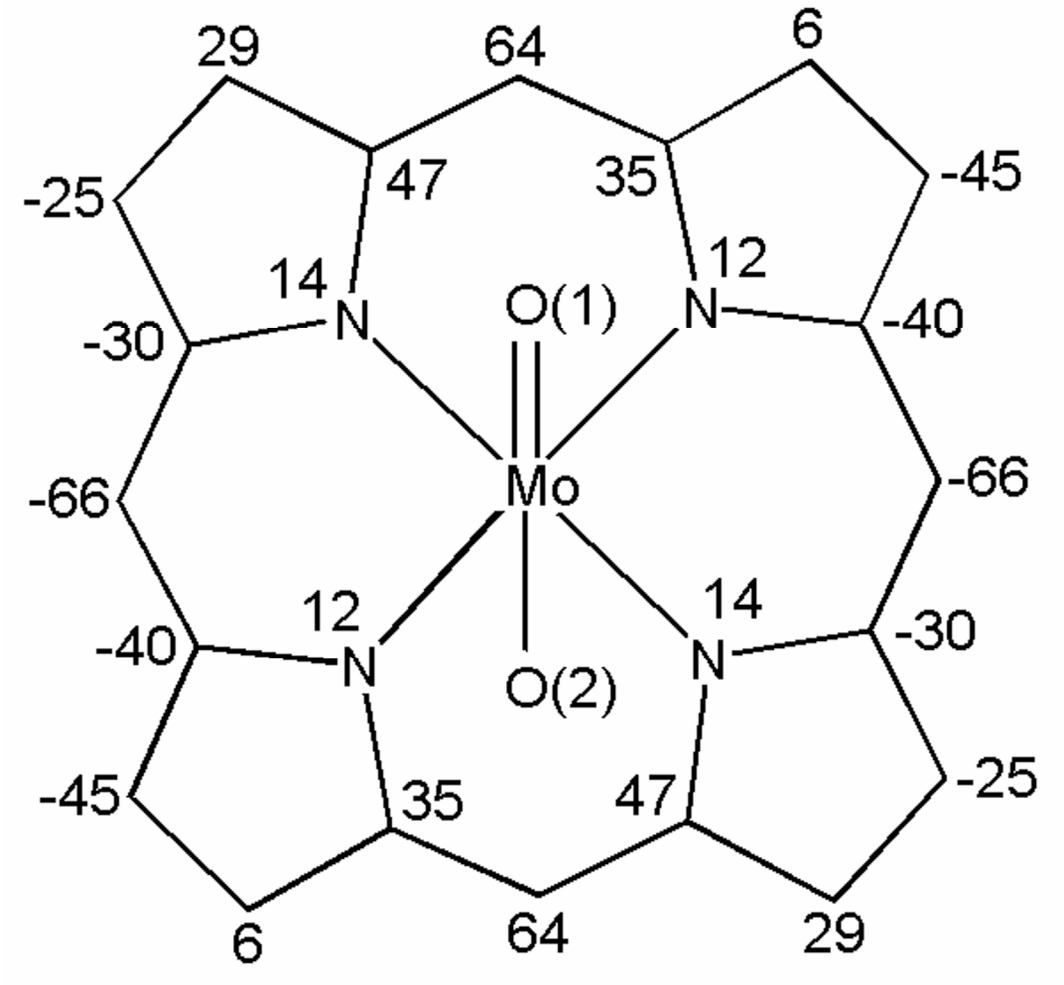


Fig. S1 The displacement of each atom from the least-squares mean plane of 24 atoms of the DPP moiety in **3** [in units of 0.01Å].

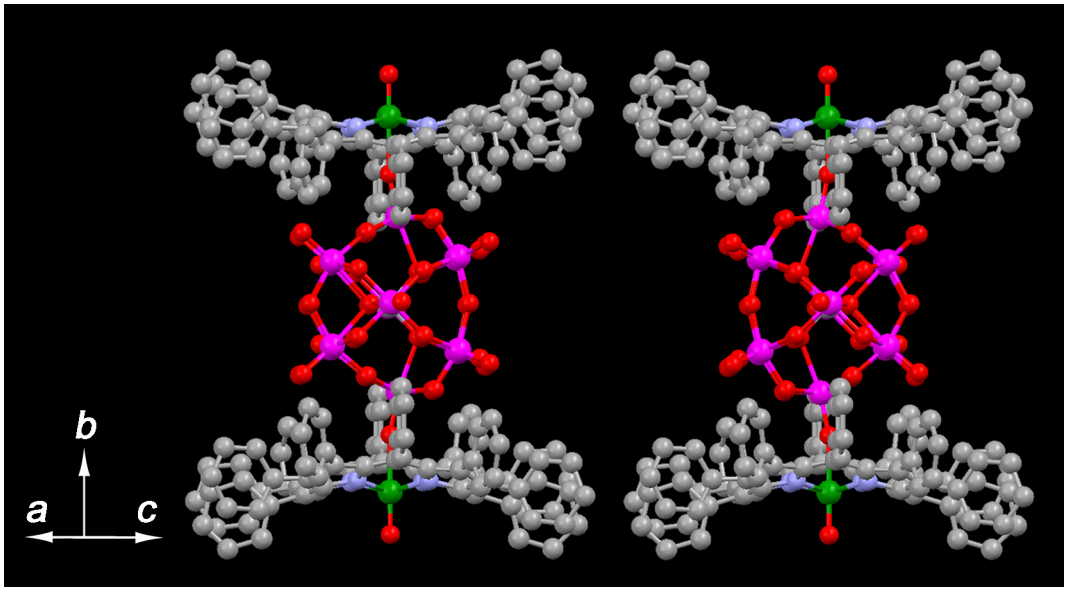


Fig. S2 Two independent isomeric structures of **3** due to the directional disorder of the Keggin moiety in the crystal.

(a)

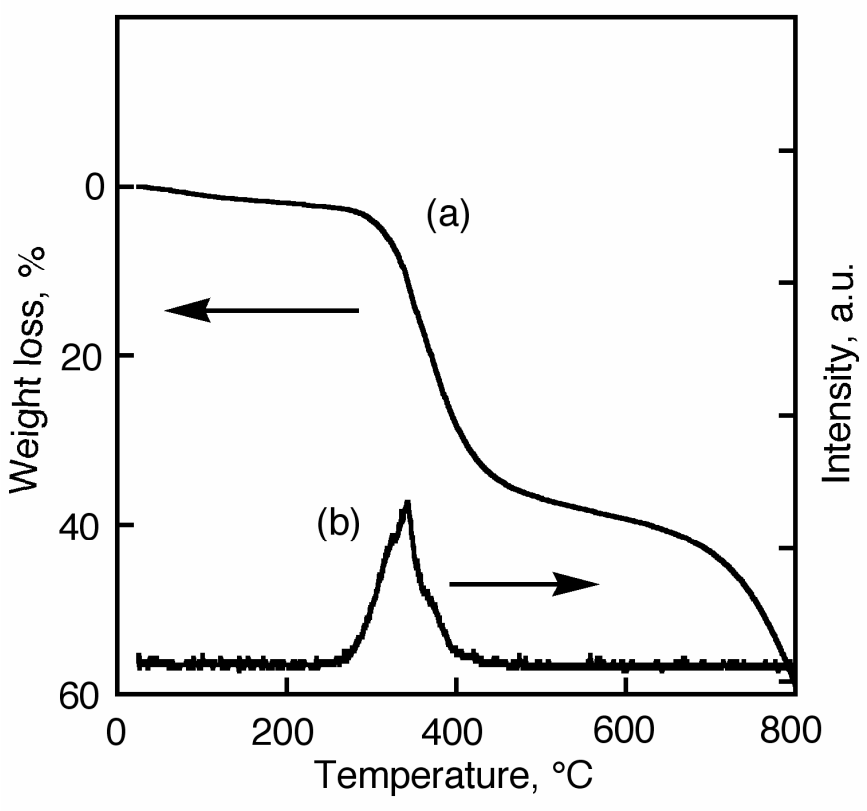


Fig. S3 TG-MS analysis of **3**: (a) TG-trace, (b) Mass spectrum of CH_3CN ($M / Z = 41$).

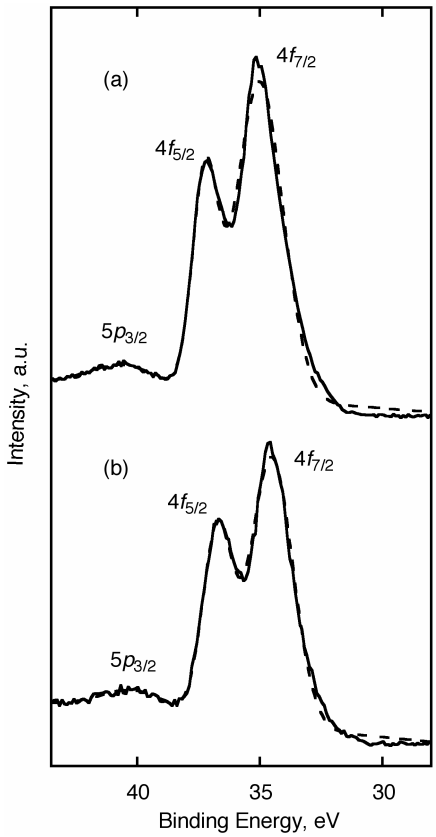


Fig. S4 XPS spectra of **2** (a) and **3** (b) in boron nitride pellets. Dotted lines represent computer simulations.

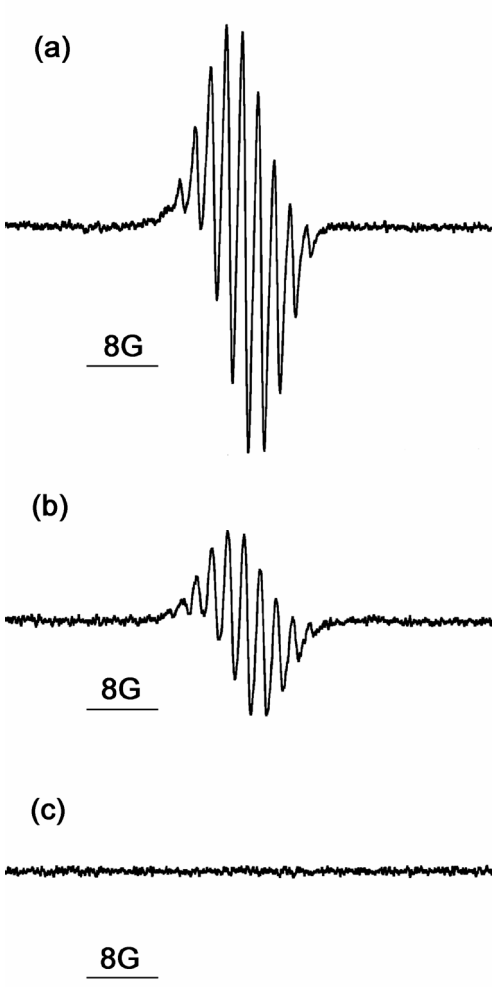
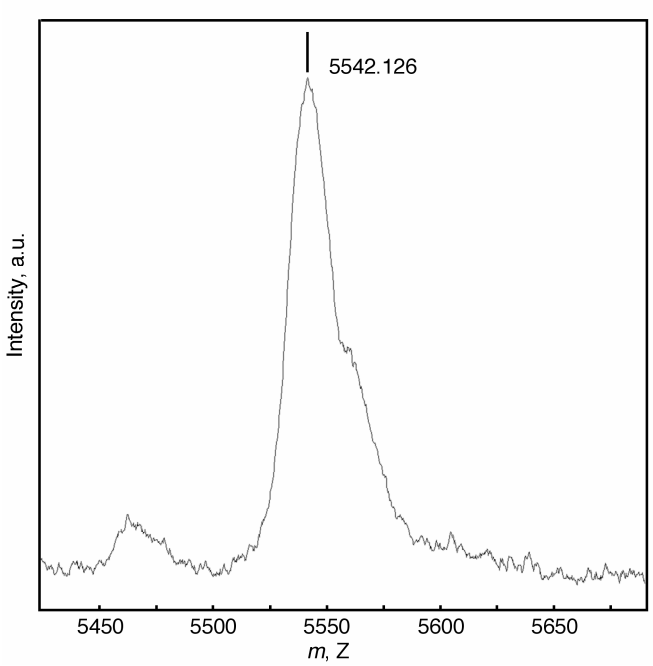


Fig. S5 ESR spectral changes of **3** (a) for the Mo^{V} ($I = 0$) signal upon addition of 1 eq (b) and 2 eq (c) of $Me_4SQ^{-\bullet}$ (tetramethylsemiquinone) as a reducing agent at room temperature, respectively: Frequency, 9.112 GHz; Power, 0.998 mW; Modulation, 100.00 kHz, 0.016 mT.

(a)



(b)

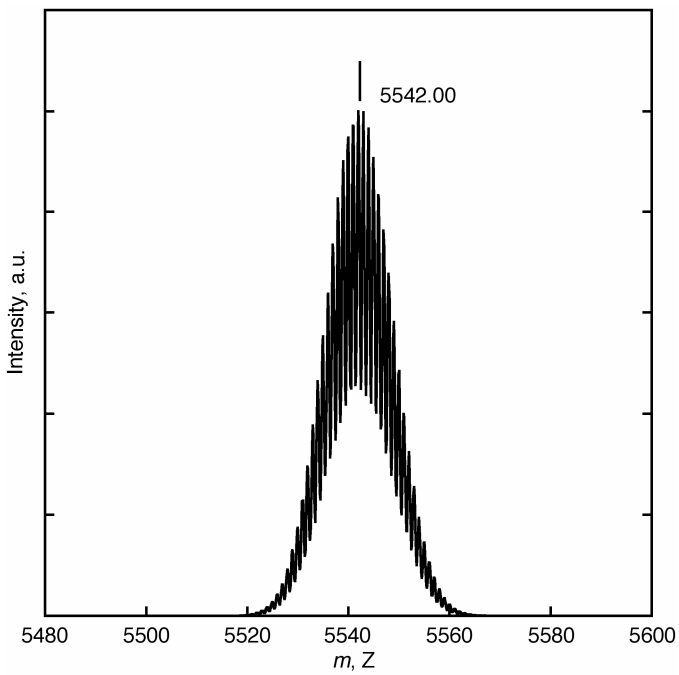


Fig. S6 MALDI-TOF-MS spectrum of **3** in CH_2Cl_2 (matrix; α-cyano-4-hydroxycinnamic acid (CHCA)): (a) observed spectrum; (b) Computer simulation.

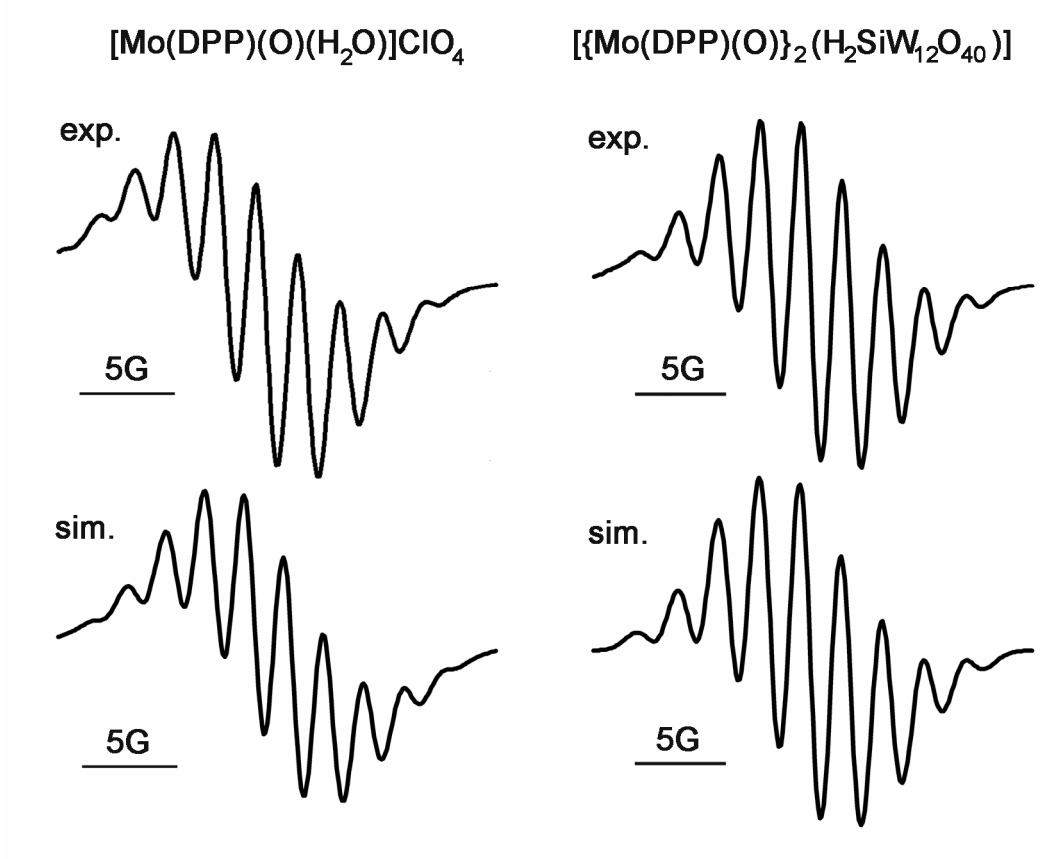
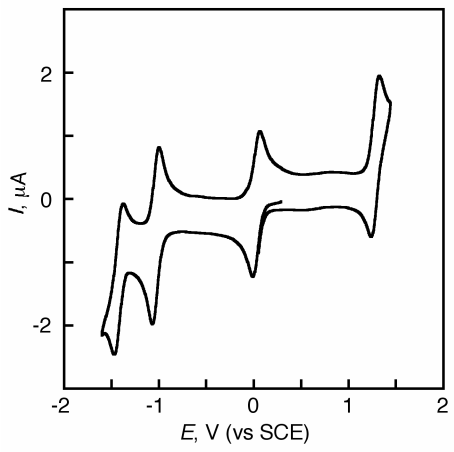


Fig. S7 ESR spectra of $[Mo(DPP)(O)(H_2O)]ClO_4$ (left) and $[\{Mo(DPP)(O)\}_2(H_2SiW_{12}O_{40})]$ (right) in CH_2Cl_2 at room temperature: Frequency, 9.454 GHz; Power, 1.026 mW; Modulation; 100.00 kHz, 0.1 mT.

(a)



(b)

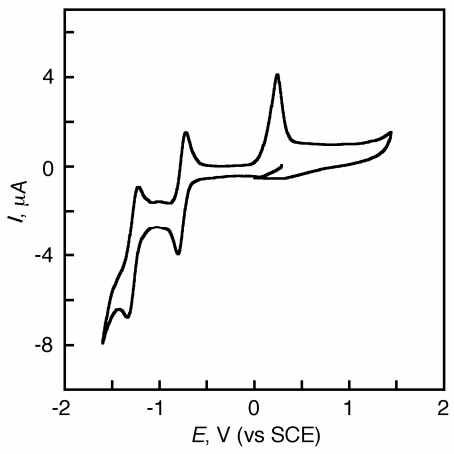


Fig. S8 CV traces for **1** (a) and **2** (b) in PhCN and CH_3CN, respectively, at room temperature under Ar in the presence of 0.1 M $TBAPF_6$.