Supporting Information

for

Crystal Structures and Solution Properties of Discrete Complexes Composed of Saddle-Distorted Molybdenum(V)-Dodecaphenylporphyrins and Keggin-Type Heteropolyoxometalates Linked by Direct Coordination

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X-ray Crystallography. X-ray crystallography on 1 and 6: All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -170 ± 1 (**1**) and -150 ± 1 (**6**) $^{\circ}$C to a maximum 2θ value of 55.0°. A total of 1240 oscillation images were collected. A sweep of data was done using ϕ scans from -80.0 to 100.0° in 0.3° step, at $\omega = 0.0^{\circ}$ and $\chi = 0.0^{\circ}$. The exposure rate was 33.3 sec/deg. The detector swing angle was 19.80°. A second sweep was performed using ω scans from -20.0 to 28.0° in 0.3° step, at $\chi = 90.0^{\circ}$ and $\phi = 0.0^{\circ}$. The exposure rate was 33.3 sec/deg. The detector swing angle was 19.80°. The crystal-to-detector distance was 44.24 mm. Readout was performed in the 0.273 mm pixel mode. All crystallographic data are summarized in Table S1.

X-ray crystallography on 5 and 7: All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -150 ± 1°C to the maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from -70.0 to 110.0° in 0.5° step, at $\chi = 45.0^{\circ}$ and $\phi = 0.0^{\circ}$. The exposure rate was 20.0 (**5**) and 48.0 (**7**) sec/deg. The detector swing angle was 20.06°. A second sweep was performed using ω scans from -70.0 to 110.0° in 0.5° step, at $\chi = 45.0^{\circ}$ and $\phi = 90.0^{\circ}$. The exposure rate was 20.0 sec/deg. The detector swing angle was 20.06°. The crystal-to-detector distance was 44.54 mm. Readout was performed in the 0.273 mm pixel mode. All crystallographic data are summarized in Table S1.

Structure Refinements. Refinement on F^2 was performed for all reflections. The weighted R factor R_w and goodness of fit S are based on F^2, and the conventional R factors R on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ was used only for calculating R factors (gt) etc. and was not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on all data are even larger. Since the oxygen and tungsten atoms in the Keggin moieties were disordered in the crystals of **5**, **6** and **7**, each

atom was refined isotropically with occupancy of 0.5.

Table S1. Crystallographic Data for **1**, **5**, **6** and **7**.

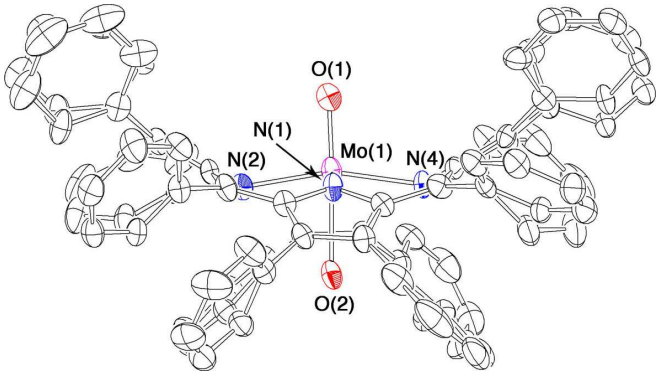
	1	**5**	**6**	**7**
Formula	$C_{92}H_{62}N_4O_6Cl$	$C_{184}H_{121}N_8O_{42}PMo_2W_{12}$	$C_{184}H_{122}N_8O_{42}SiMo_2W_{12}$	$C_{184}H_{123}N_8O_{42}BMo_2W_{12}$
F. W.	1699.67	5544.95	5543.07	5526.80
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	*P* -1	$P2_1/n$	*C*2/*m*	$P2_1/c$
T, K	103	123	123	123
a, Å	15.901(6)	17.607(15)	18.4212(11)	17.750(5)
b, Å	16.509(6)	37.654(10)	37.5328(17)	37.319(9)
c, Å	18.453(7)	18.227(5)	17.8126(11)	18.393(5)
α, deg.	104.143(3)	–	–	–
β, deg.	108.391(3)	118.664(4)	118.897(2)	118.6632(11)
γ, deg.	109.915(3)	–	–	–
V, Å^3	3972(3)	10605(5)	10782(10)	10691(5)
Z	2	2	2	2
No. of reflections	30844	75582	33298	74601
No. of observations	17703	23851	9879	23451
No. of parameters	1019	1099	560	1099
$R1$[a] ($I > 2.0\sigma(I)$)	0.123	0.135 (0.072[c])	0.077	0.158 (0.088[c])
$wR2$[b] (all data)	0.338	0.239 (0.143[c])	0.165	0.313 (0.236[c])
GOF	1.130	1.51 (1.08[c])	1.11	1.30 (1.08[c])

[a] $R1 = ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR2 = [\sum(w (F_o^2 - F_c^2)^2)/ \sum w(F_o^2)^2]^{1/2}$.

[c] Structure refinements using the "Squeeze" method.

(a)



(b)

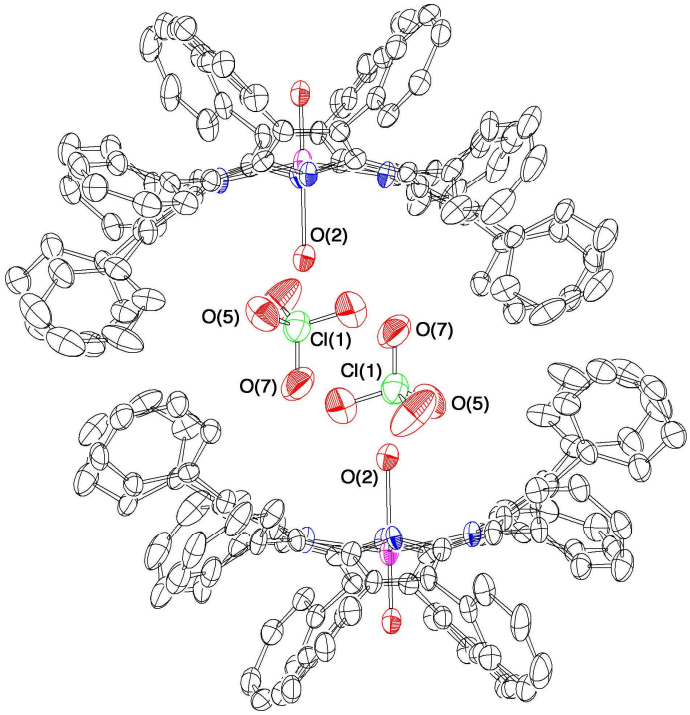


Figure S1. Crystal Structures of [Mo(DPP)(O)(H_2O)]ClO_4 (**1**) with 50% probability thermal ellipsoids.

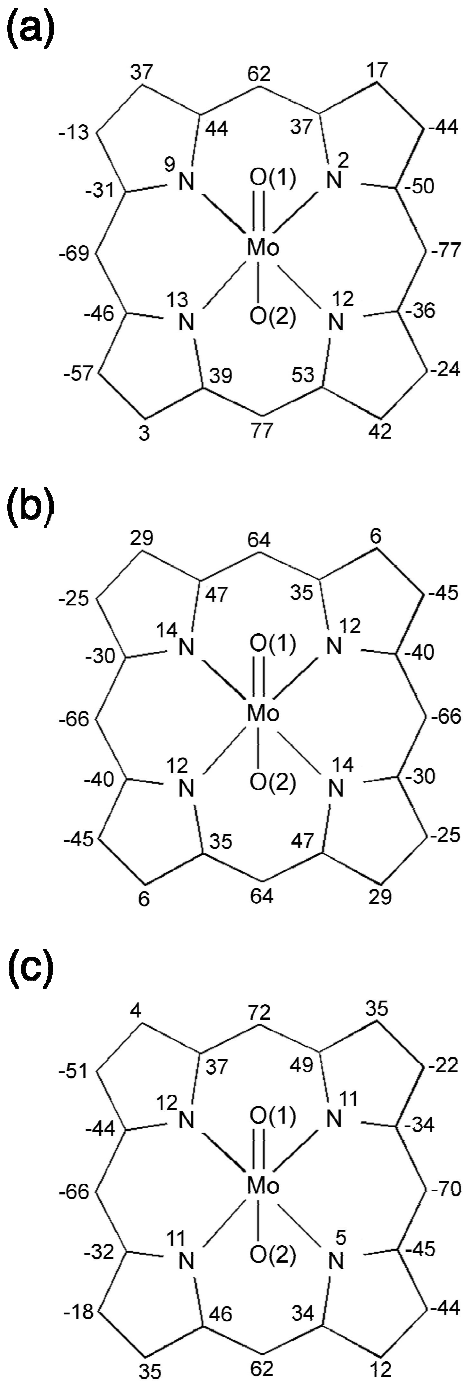


Figure S2. The displacement of each atom from the least-squares mean plane of 24 atoms of the DPP moiety in **5**(a), **6**(b) and **7**(c) (in units of 0.01Å).

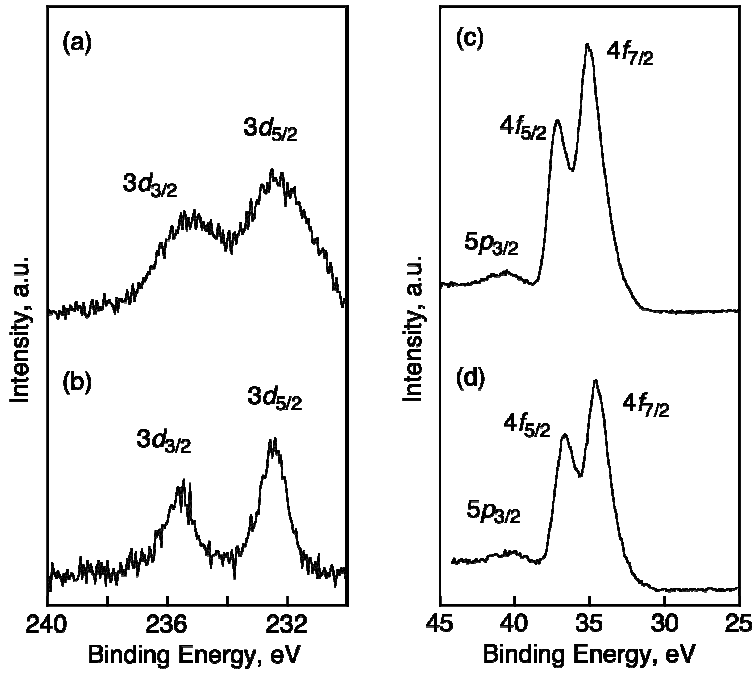


Figure S3. XPS spectra of **1**(a), **3**(c) and **6**(b),(d) in boron nitride pellets. Spectra of (a) and (b) are assigned to Molybdenum atom ($3d_{3/2}$, $3d_{5/2}$). (c) and (d) are assigned to tungsten atom ($5p_{3/2}$, $4f_{5/2}$, $4f_{7/2}$).

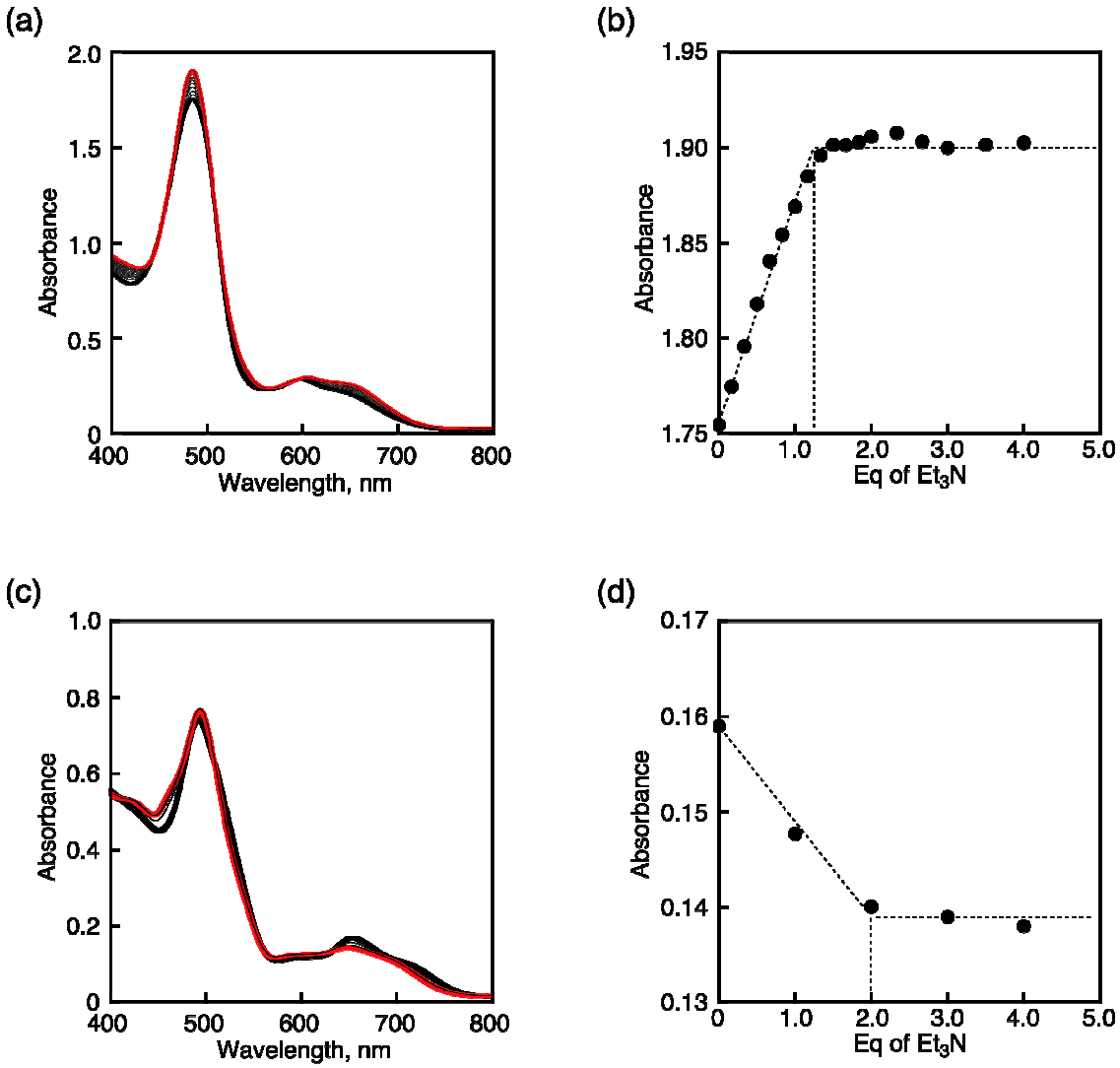


Figure S4. UV-vis spectral changes of (a) **5** (1.0×10^{-5} M) and (c) **6** (1.0×10^{-5} M) upon addition of triethylamine (1 mM). Changes of absorbance at 484.5 nm for **5** (b) and 653 nm for **6** (d) are depicted.

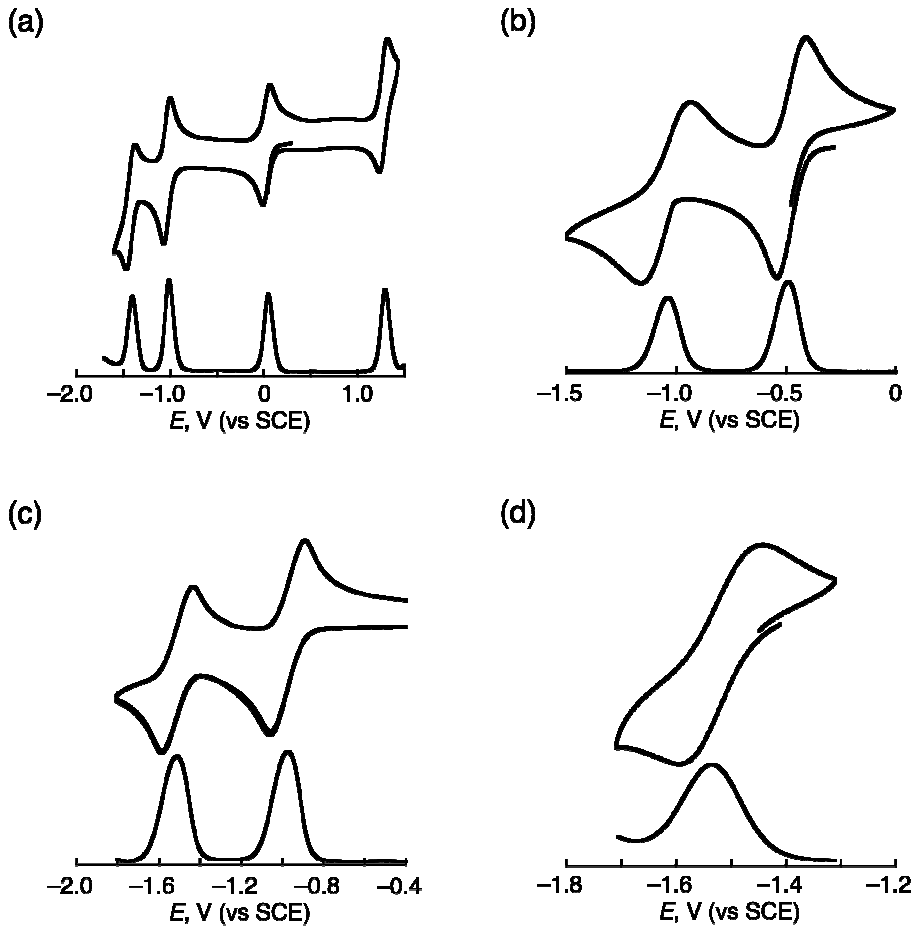


Figure S5. Cyclic voltammograms and differential plus voltammograms for **1**(a), **2**(b), **3**(c), and **4**(d) in PhCN at room temperature under Ar in the presence of 0.1 M $TBAPF_6$ as an electrolyte.