Electronic Supplementary Information

for

Enclosure of a Keggin-type heteropolyoxometalate into a tubular π-space *via* hydrogen bonds with a nonplanar Mo(V)-porphyrin complex forming a supramolecular assembly

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X-ray Crystallography. X-ray crystallography on 1. A single crystal of **1** was coated in liquid paraffin and mounted on a glass fiber with silicon grease. X-ray diffraction data were collected on a Rigaku Mercury CCD at 170 ± 2 K. All calculations for structure refinements were carried out on a personal computer using *CrystalStructure* (Rigaku Corp., Japan)[1] and SHELXL programs.[2]

Structure Refinements for 1 and 3. Refinements on F^2 were performed for all reflections. The weighted R factor (R_w) and goodness of fit (S) are based on F^2, and the conventional R factor (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. As for **3**, the restraint program "ISOR S1" was used for the refinement.

(1) *CrystalStructure 3.7.0*: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2005), The Woodlands, TX 77381, USA.

(2) *SIR 97* and *SHELX 97*: G. M. Sheldrick, *Program for Crystal Structures Refinement*, University of Göttingen, Germany, 1997.

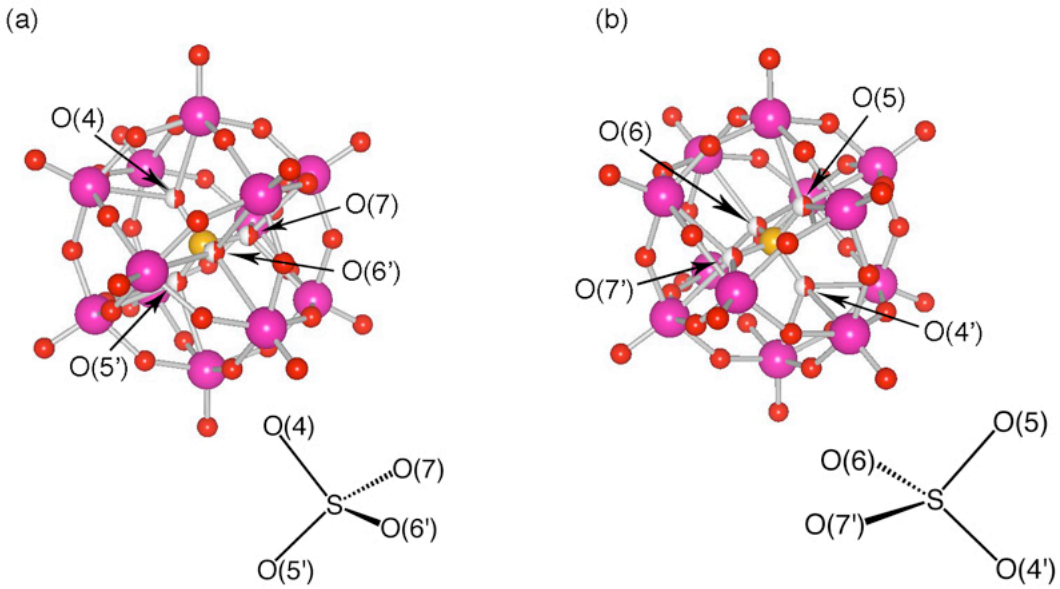

Fig. S1 Disordered two tetrahedrons around the sulfur atom in the Keggin structure. Red, oxygen; red and white, disordered oxygen; pink, tungsten; orange, sulfur.

Table S1. Selected bond distances (Å), interatomic distances (Å) and bond angles (deg) for **3.**

	3	
assignment	distance (Å)	angle (deg)
Mo(1)-O(1)	1.671(6)	–
Mo(1)-O(2)	2.371(6)	–
O(2)-O(3)	2.87(1)	–
O(2)-O(25A)	3.01(3)	–
O(25A)-O(25A')	3.22(2)	–
W(1)-O(3)	1.679(6)	–
S(1)-O(4)	1.52(1)	–
S(1)-O(5)	1.48(1)	–
S(1)-O(6)	1.46(1)	–
S(1)-O(7)	1.40(1)	–
Mo(1)-O(2)-O(3)	–	112.9(2)
O(2)-O(3)-W(1)	–	152.5(4)
O(3)-O(2)-O(25A)	–	116.2(2)
O(2)-O(25A)-O(25A')	–	105.9(7)

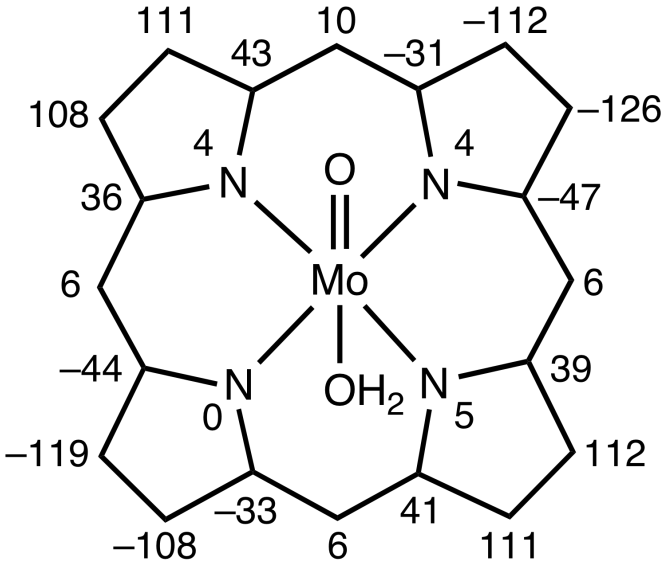

Fig. S2 The displacement of each atom from the least-squares mean plane of 24 atoms of the DPP^{2-} moiety in **3** (in unit of 0.01 Å).

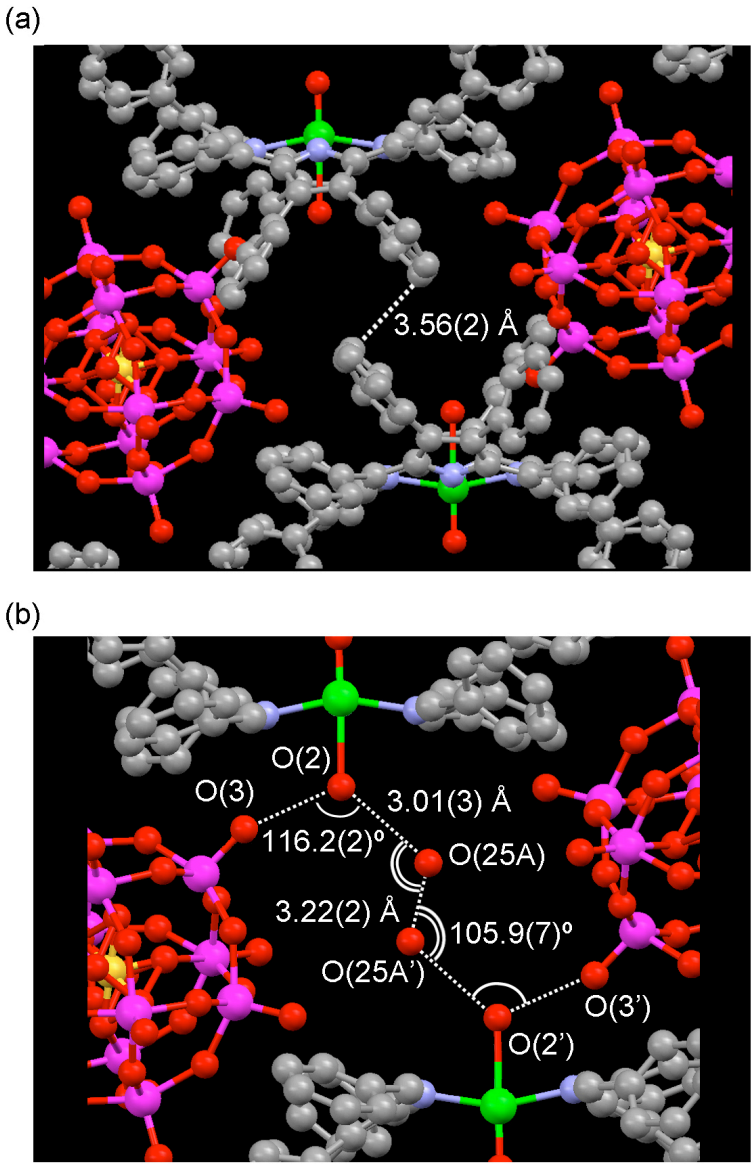

Fig. S3 (a) Intermolecular π-π interaction between peripheral phenyl groups of two Mo(V)-porphyrin units. (b) A hydrogen bonding network involving water molecules of crystallization (O(25)). Gray, carbon; blue, nitrogen; red, oxygen; green, molybdenum; pink, tungsten; orange, sulfur.

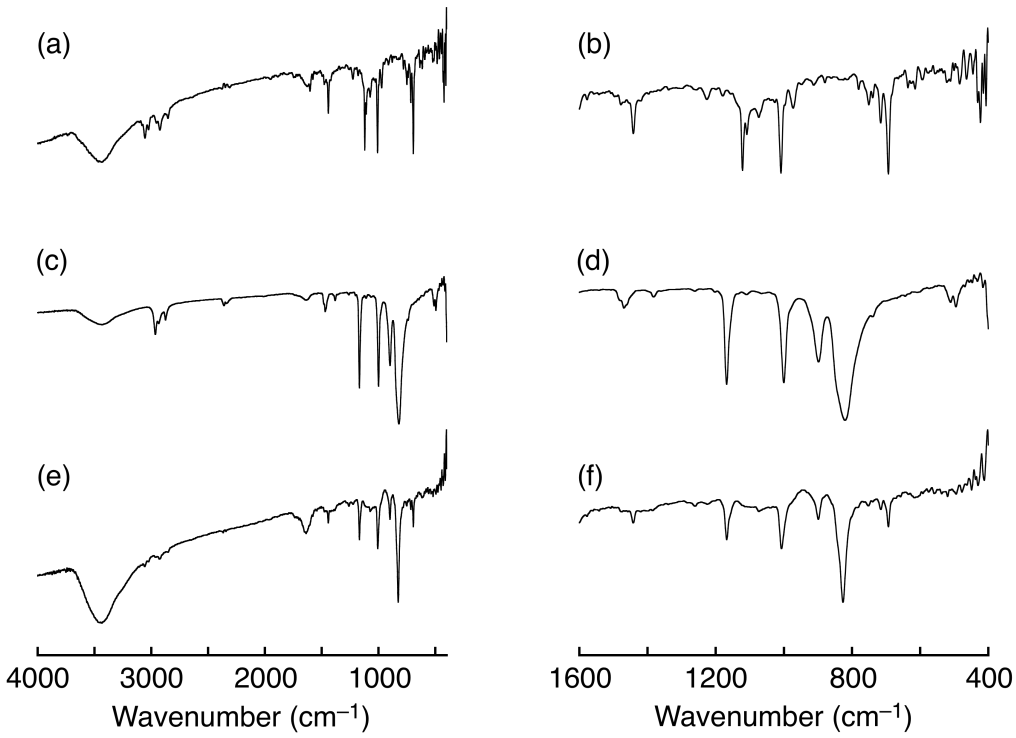

Fig. S4 IR spectra (KBr) of **1** ((a), (b)), **2** ((c), (d)) and **3** ((e), (f)).

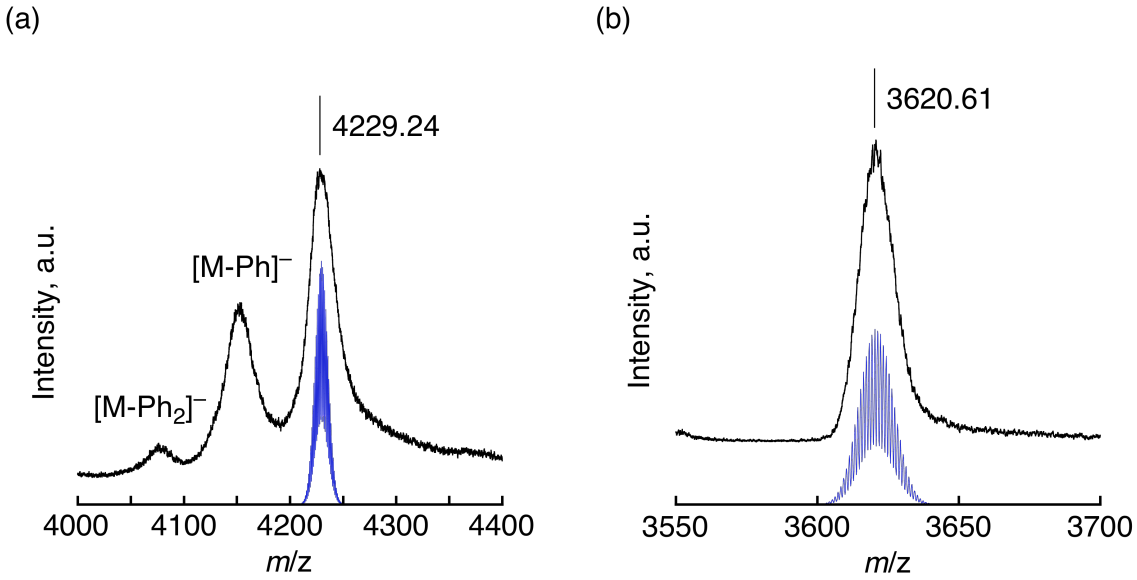

Fig. S5 (a) MALDI-TOF-MS spectrum of **4** (m/z = 4229.24) and computer simulation ([{Mo(DPP)(O)(H_2O)($SW_{12}O_{40}$)}$^-$, 4229.59 m/z] in CH_2Cl_2. (b) MALDI-TOF-MS spectrum of **6** (m/z = 3620.61) and computer simulation ([{Mo(TPP)(O)(H_2O)($SW_{12}O_{40}$)}$^-$, 3620.81 m/z] in CH_2Cl_2. (linear negative mode, matrix; α-cyano-4-hydroxycinnamic acid (CHCA)).

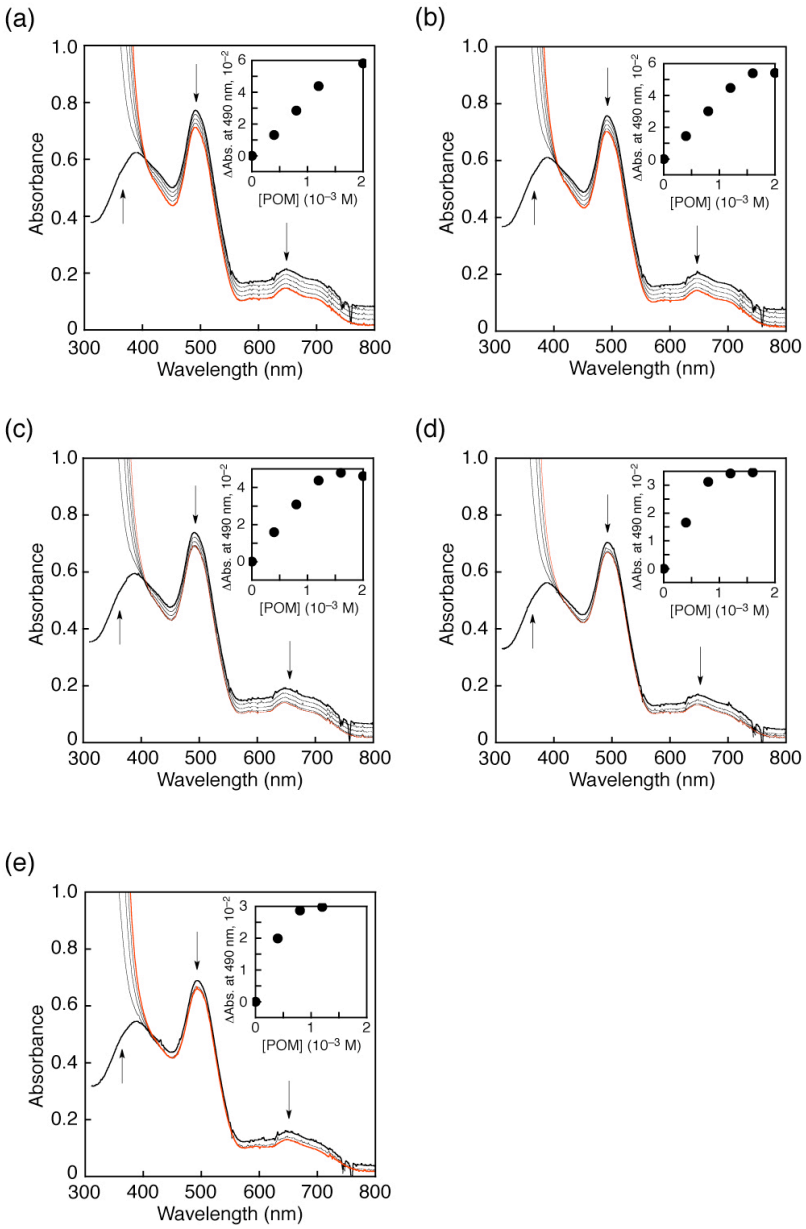

Fig. S6 UV-vis spectral titration of **1** (1.0×10^{-5} M) upon addition of **2** in PhCN at 265 K (a), 273 K (b), 283 K (c), 303 K (d) and 313 K (e). Each ΔAbs ($A - A_0$) at 490 nm was plotted as insets.

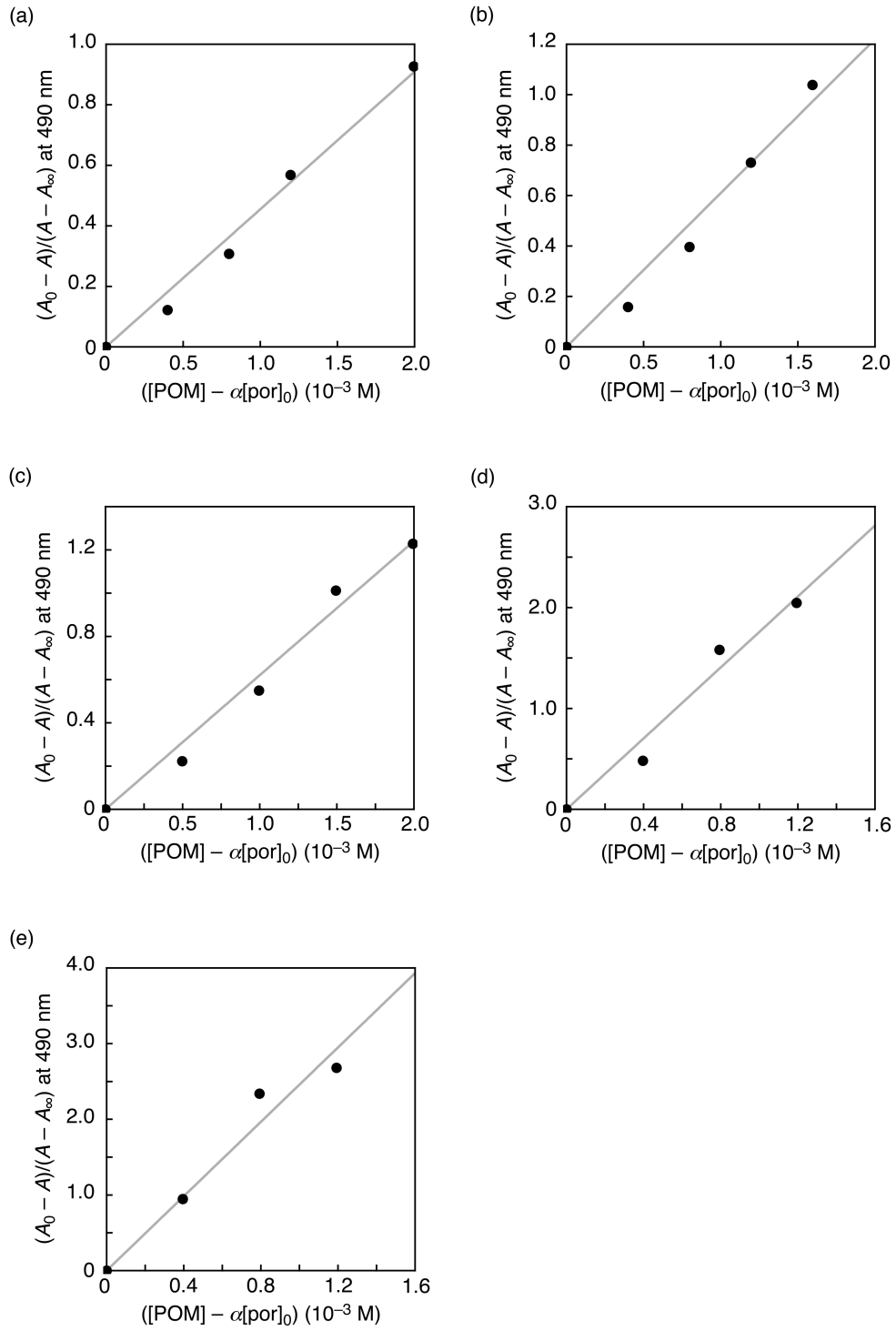

Fig. S7 Plots of $(A - A_0)/(A_\infty - A)$ *versus* ([POM] – α[por]$_0$) for the spectroscopic titration of **1** upon addition of **2** in PhCN using absorbance at 490 nm; (a) 265 K, (b) 273 K, (c) 283 K, (d) 303 K and (e) 313 K.

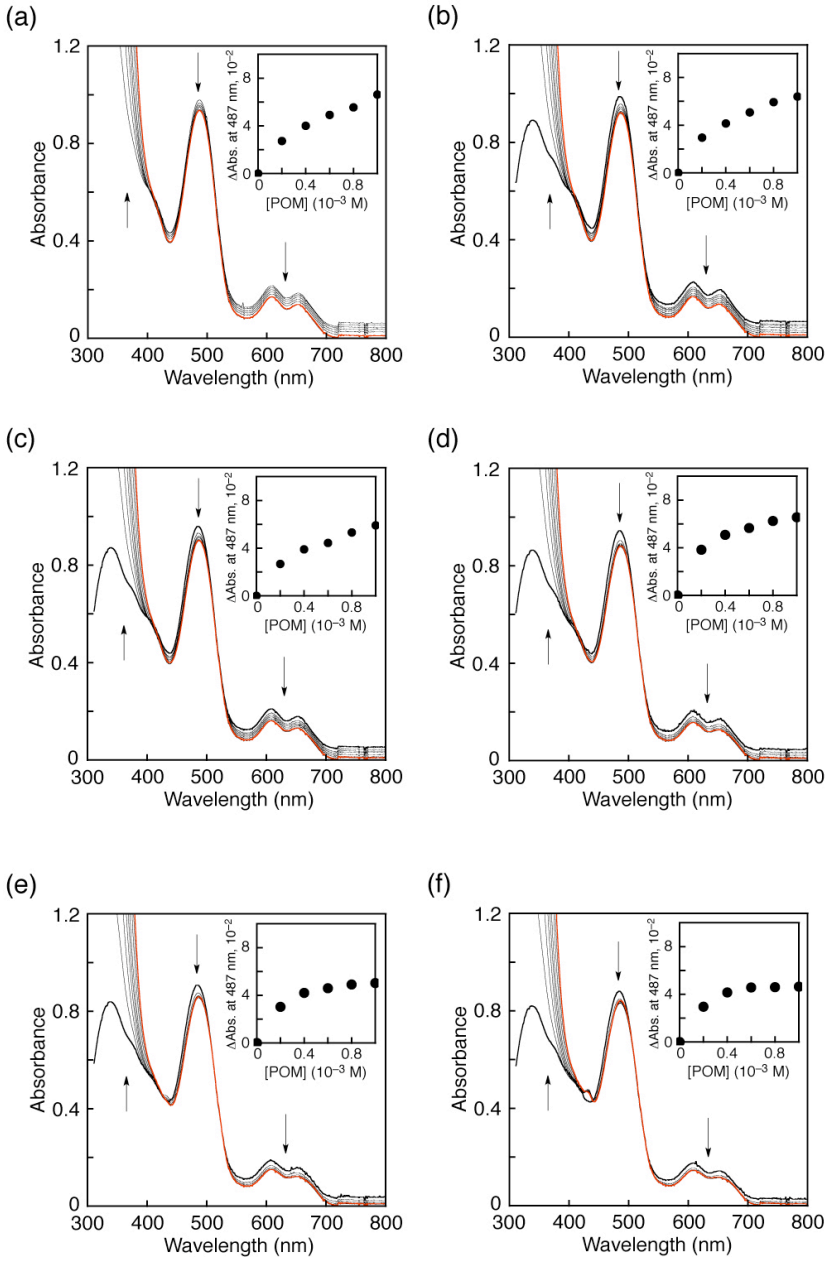

Fig. S8 UV-vis spectral titration of **4** (2.0×10^{-5} M) upon addition of **2** in PhCN at 265 K (a), 273 K (b), 283 K (c), 293 K (d), 303 K (e) and 313 K (f). Each ΔAbs ($A - A_0$) at 487 nm was plotted as insets.

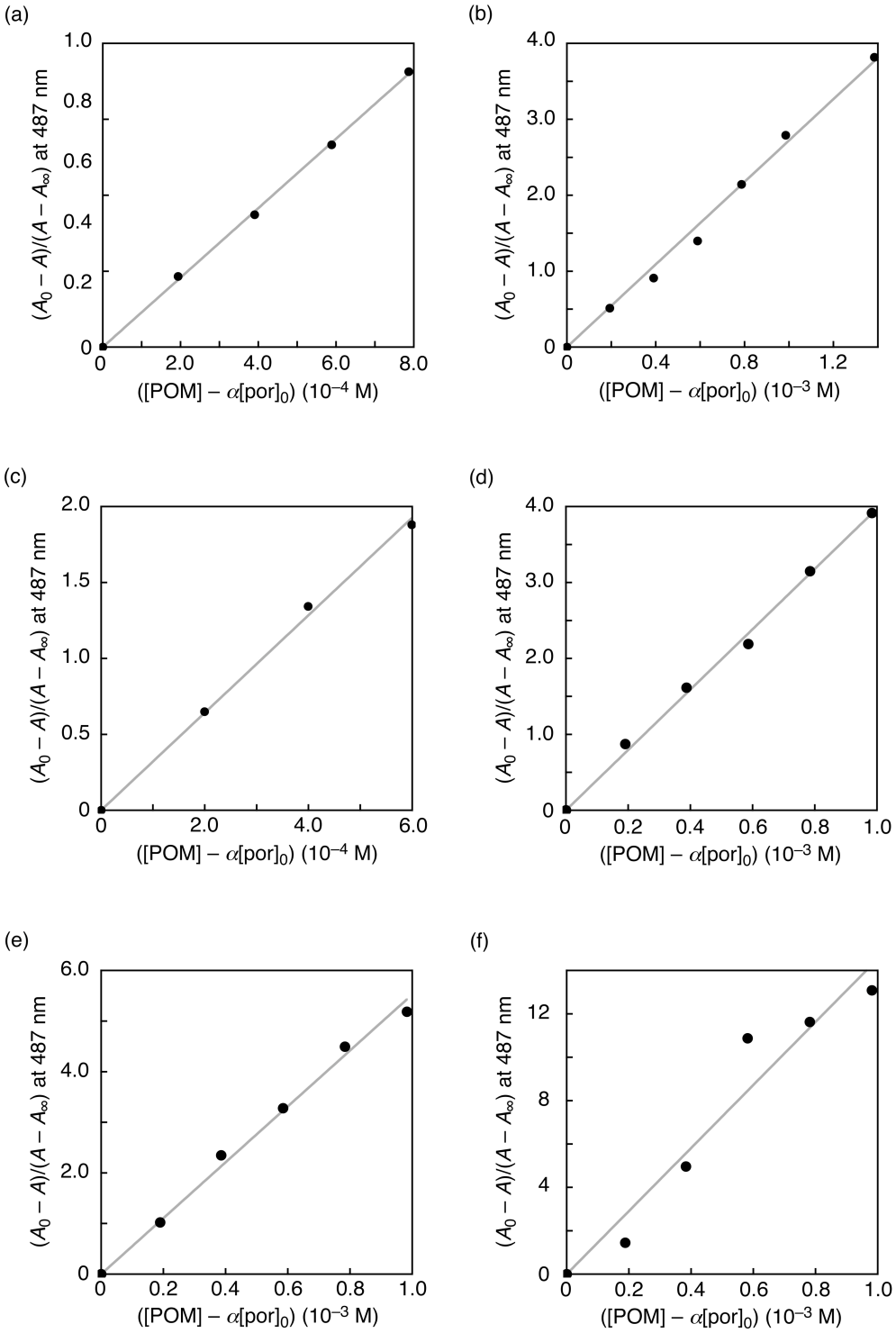

Fig. S9 Plots of $(A - A_0)/(A_\infty - A)$ *versus* ([POM] – α[por]$_0$) for the spectroscopic titration of **4** upon addition of **2** in PhCN using absorbance at 487 nm; (a) 265 K, (b) 273 K, (c) 283 K, (d) 298 K, (e) 303 K and (f) 313 K.

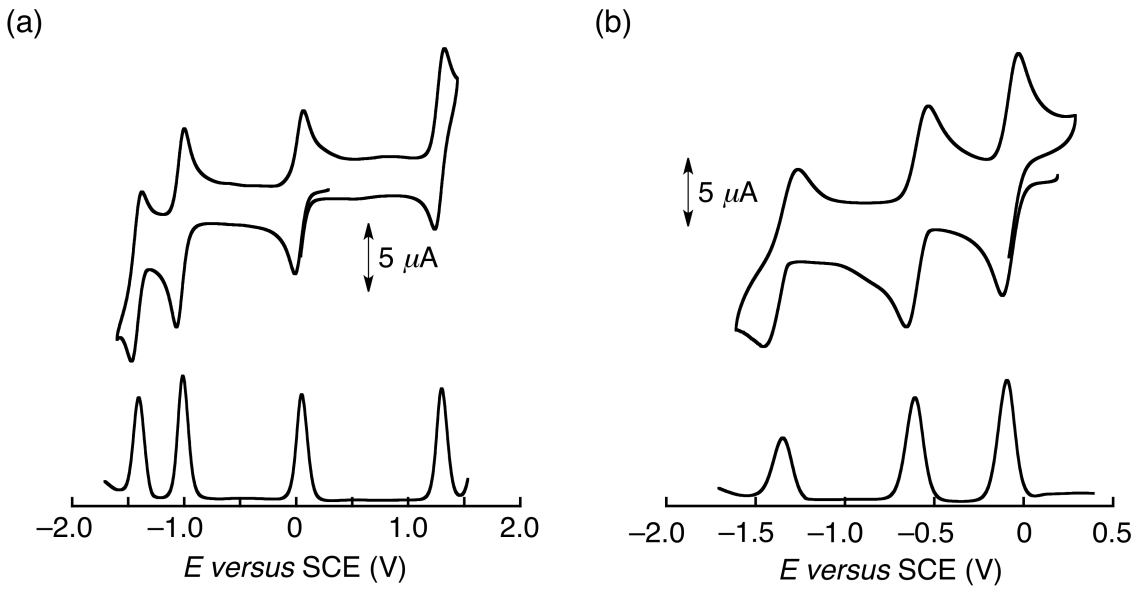

Fig. S10 Cyclic voltammograms (upper) and differential pulse voltammograms (bottom) for (a) **1** (1.0 mM) and (b) **2** (1.0 mM) under Ar in the presence of 0.1 M $TBAPF_6$ in PhCN at room temperature.