

## Supplementary Information

(Experimental details, Tables S1-S2 and Figs. S1-S8)

### **Oxo-carboxylato-molybdenum(VI) complexes possessing dithiolene ligand related to the active site of type II class of DMSOR family of molybdoenzymes**

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## Experimental Section

**General.** All reagents and solvents were used as received unless otherwise noted. All reactions were carried out under argon in a Miwa DB0-1KP glovebox except for preparation of  $[\text{Mo}^{\text{VI}}\text{O}(\text{S}_2\text{C}_6\text{H}_8)_2]$  ( $\text{Mo}^{\text{VI}}\text{OL}_2$ ),  $[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_6\text{H}_8)_2]$  ( $\text{Mo}^{\text{IV}}\text{OL}_2$ ) and  $\text{Et}_4\text{N}(p\text{-H-OBz})$  were prepared according to the literature.<sup>1,2</sup>

**Synthesis of tetraethylammonium *para*-chloro-benzoate ( $\text{Et}_4\text{N}(p\text{-Cl-OBz})$ ).** 4.4 ml of 25%  $\text{Et}_4\text{NOH}$ -methanol solution was added to a methanol solution containing *para*-chlorobenzoic acid (1.01 g, 6.48 mmol). The obtained solution was evaporated to dryness. The white residue was dissolved in minimum volume of acetonitrile and any unsolved powder was removed by filtration. Diffusion of dithylether into the filtrate gave white crystals. Yield; 0.88 g (48 %).  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.87 ppm (d,  $J$  = 8.4 Hz, 2H), 7.22 (d, 8.8, 2H), 3.14 (q, 7.2, 8H), 1.17 (t, 7.4, 12H). The solid was highly hygroscopic.

**Synthesis of tetraethylammonium *para*-methoxy-benzoate ( $\text{Et}_4\text{N}(p\text{-OMe-OBz})$ ).** This compound was prepared according to the method for the chloro derivative but *para*-methoxybenzoic acid (1.00 g, 6.60 mmol) was used instead of *para*-chlorobenzoic acid. Yield; 0.55 g (30 %).  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.83 ppm (d,  $J$  = 9.2 Hz, 2H), 6.75 (d, 8.8, 2H), 3.74 (s, 3H), 3.13 (q, 7.2, 8H), 1.17 (t, 7.4, 12H). The solid was highly hygroscopic.

**Synthesis of  $\text{Mo}^{\text{IV}}(\text{OBz})\text{L}_2$ :** The complex was synthesised by the reaction of  $\text{Mo}(\text{CO})_2(\text{S}_2\text{C}_2\text{C}_4\text{H}_8)_2$ <sup>1</sup> with  $\text{Et}_4\text{N}(p\text{-H-OBz})$ , referring the procedure for the bis( $\text{S}_2\text{C}_2\text{Me}_2$ )benzoatomolybdenum(IV) complex.<sup>2</sup> Anal. Calcd for  $\text{C}_{27}\text{H}_{41}\text{NO}_2\text{S}_4\text{Mo}$  (mol wt. 635.84): C, 51.00; H, 6.50; N, 2.20. Found: C, 50.92; H, 6.76; N, 2.16.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  1.17 ppm (t,  $J$  = 7.1 Hz, 12H), 2.5 ~ 3.1 (br, 16 H), 3.11 (q, 7.3, 8H), 7.44 (t,  $J$  = 7.8 Hz, 2H), 7.55 (t, 7.4 Hz, 1H), 8.00 (d, 7.2 Hz, 2H). UV-vis spectrum ( $\text{CH}_3\text{CN}$ , 30°C):  $\lambda_{\text{max}}$  = 328 nm ( $\epsilon$  = 3900  $\text{M}^{-1} \text{cm}^{-1}$ ), 373 (3700), 422 (4300), 499 (3400), 770 (400).

**Synthesis of  $(\text{Et}_4\text{N})[\text{Mo}^{\text{V}}\text{O}(\text{S}_2\text{C}_6\text{H}_8)_2]$ :**  $\text{FcPF}_6$  (33.4 mg, 0.101 mmol) was added to a  $\text{CH}_3\text{CN}$  solution (8 mL) of  $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{C}_2\text{C}_4\text{H}_8)_2]$  (66.9 mg, 0.101 mmol) and the solution was stirred for 20 minutes. The grey solution obtained was concentrated to approximately 1.5 mL. After removal of any undissolved solid by filtration, diffusion of diethylether into the filtrate gave grey microcrystals, which were collected by filtration and dried in vacuo. Yield; 40.4 mg (75%). Anal. Calcd for  $\text{C}_{20}\text{H}_{36}\text{NOS}_4\text{Mo}$  (mol wt. 530.73): C, 45.26; H, 6.84; N, 2.64. Found: C, 45.06; H, 6.72; N, 2.71.

**Synthesis of  $\text{Mo}^{\text{VI}}\text{OL}_2$ :**  $\text{FcPF}_6$  (16.6 mg, 0.050 mmol) was added to a THF solution (10 mL) of  $(\text{Et}_4\text{N})[\text{Mo}^{\text{V}}\text{O}(\text{S}_2\text{C}_2\text{C}_4\text{H}_8)_2]$  (26.7 mg, 0.050 mmol) at  $-40\text{ }^\circ\text{C}$  under an Ar atmosphere. The yellow solution was concentrated to approximately 2.0 mL. Diffusion of hexane into the concentrated solution gave white-grey powders, which were collected by filtration and dried in vacuo. The isolated pale grey powder was very hygroscopic in air and decomposed at room temperature. The cyclic voltammogram was identical to that of  $\text{Mo}^{\text{IV}}\text{OL}_2$  except that the isolated complex possessed a rest potential in the region of the molybdenum(VI) ion. This confirms that the molybdenum(VI) centre has a square-pyramidal structure as found in  $\text{Mo}^{\text{IV}}\text{OL}_2$ .

**Electronic structure calculations.** Gas-phase geometry optimizations and electronic structure calculations for  $\text{Mo}^{\text{VI}}\text{O}(p\text{-X-OBz})\text{L}_2$  ( $\text{X} = \text{OMe}, \text{H}, \text{Cl}$ ) and Intermediate A were performed at the density functional level of theory (DFT) using the Gaussian 09 revision C.01 software package.<sup>3</sup> The calculations utilized the PBE<sup>4-5</sup> exchange-correlation functional with the def2-tzvp basis set<sup>6</sup> for all atoms and an effective core potential on Mo.<sup>7</sup> The def2-tzvp basis set was obtained from the EMSL basis set exchange website.<sup>8-9</sup> Orbital compositions were obtained using the Mulliken population analysis method as implemented in Gaussian 09.<sup>10</sup> Orbital compositions were determined by subtracting the electron density of the ground state from the one electron reduced state without allowing for any electronic relaxation. The experimental electronic absorption spectra were analyzed using time dependent DFT (TD-DFT) methods as implemented in Gaussian 09.<sup>11-17</sup>

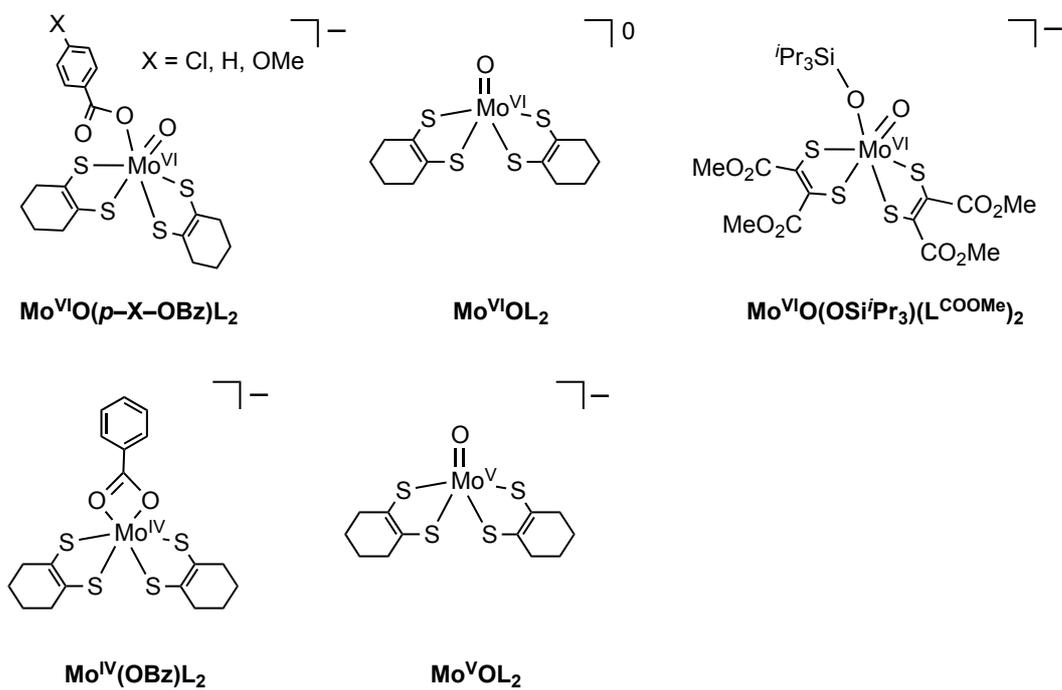
**Physical measurements.** UV-vis spectra were recorded on a Hewlett Packard 8453 photo diode array spectrophotometer equipped with a UNISOK thermo-Stated cell holder. CSI-MS (coldelectrospray ionization mass spectra) measurements were performed on a BRUKER cryospray micrOTOFII.  $^1\text{H}$  NMR spectra were recorded on a JEOL ECP400 or a JEOL ECS400.

**CSI-mass measurement of  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$ .**  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$  was generated *in-situ* in  $\text{C}_2\text{H}_5\text{CN}$  at  $-60\text{ }^\circ\text{C}$  by the reaction of  $\text{Mo}^{\text{VI}}\text{OL}_2$  and  $\text{Et}_4\text{N}(p\text{-OMe-OBz})$  in a Schlenk tube under a dry dinitrogen atmosphere. The temperature of the solution was kept constant using a dry ice-acetone bath. One end of a capillary was connected to the CSI-mass detector and another end was dipped into the complex solution at  $-80\text{ }^\circ\text{C}$  through a septum cap. The  $\text{C}_2\text{H}_5\text{CN}$  solution was sprayed into the detector using a syringe.

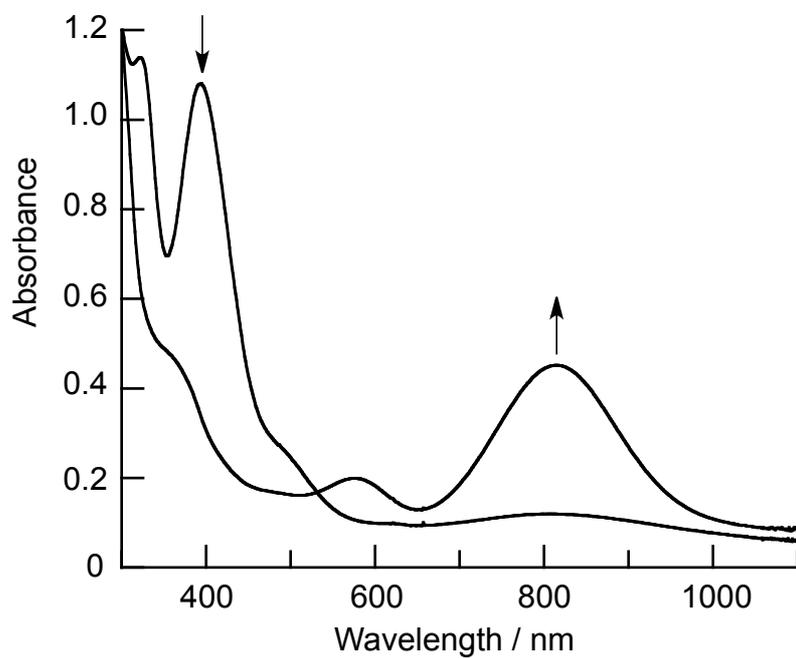
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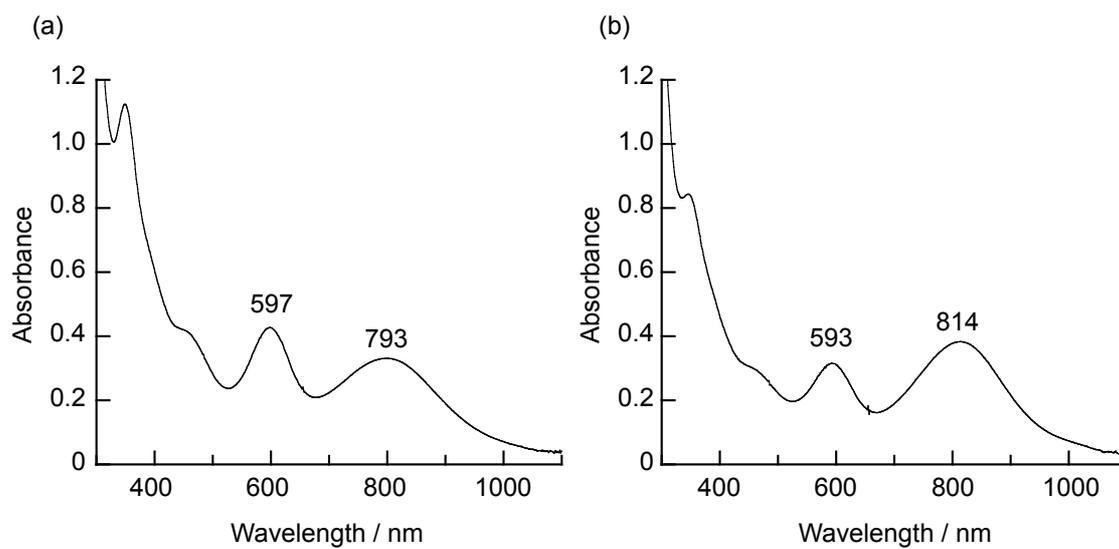
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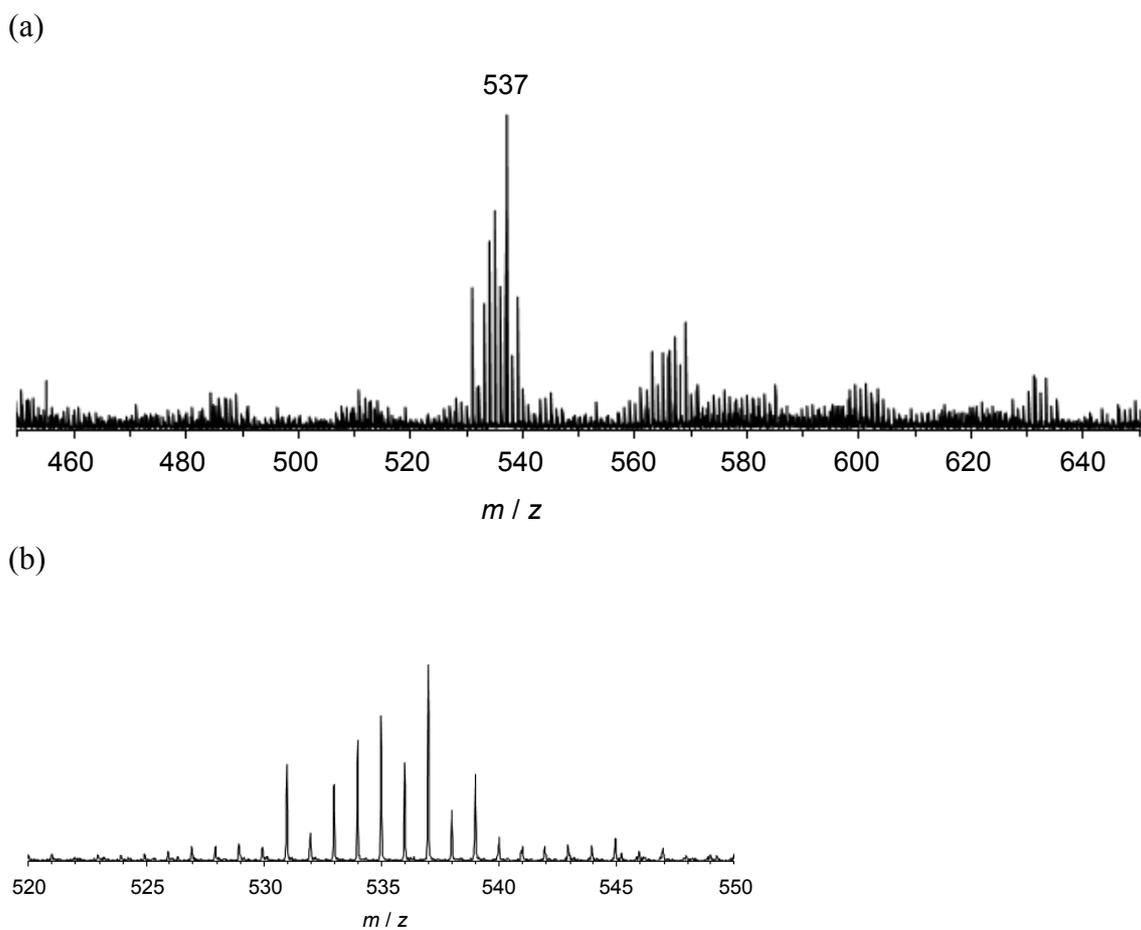
**Chart S1** ChemDraw structures of the molybdenum complexes.



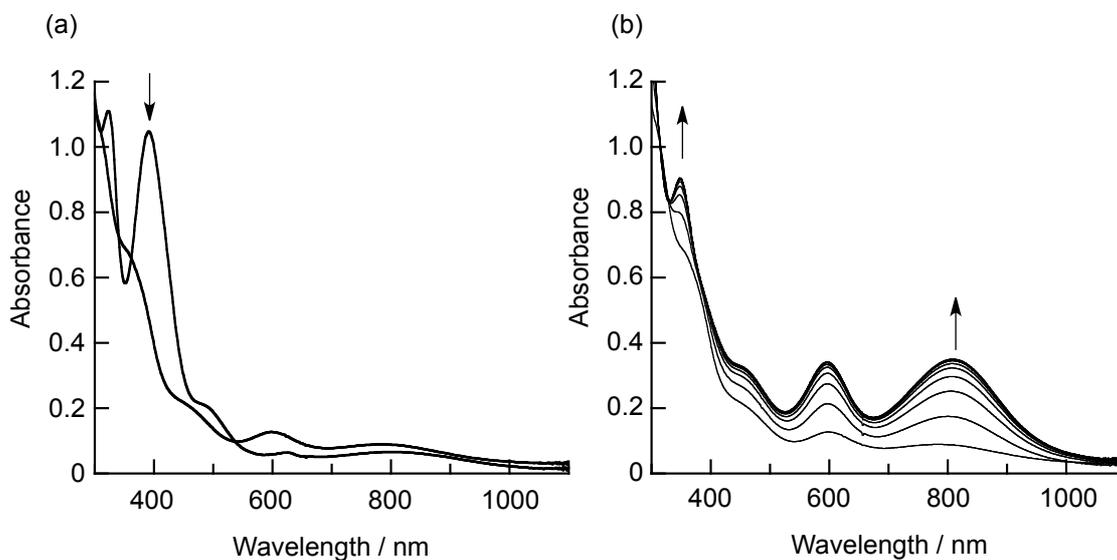
**Fig. S1** Formation of the oxomolybdenum(V) complex,  $\text{Mo}^{\text{V}}\text{OL}_2$ , by the treatment of  $\text{Mo}^{\text{VI}}\text{OL}_2$  (0.2 mM) with 1 equiv. of  $\text{Et}_4\text{N}(p\text{-H-OBz})$  in  $\text{C}_2\text{H}_5\text{CN}$  at room temperature.



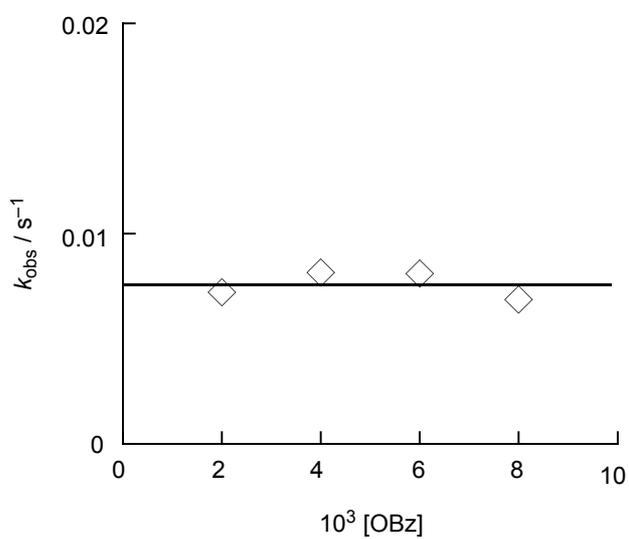
**Fig. S2** Absorption spectra of  $\text{Mo}^{\text{VI}}\text{O}(p\text{-Cl-OBz})\text{L}_2$  (a) and  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$  (0.2 mM) in  $\text{C}_2\text{H}_5\text{CN}$  at  $-60\text{ }^\circ\text{C}$ .



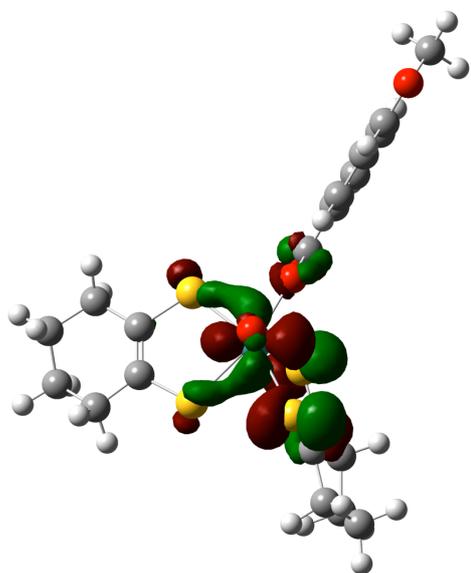
**Fig. S3** Cold-mass spectra of  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$  (0.2 mM) in  $\text{C}_2\text{H}_5\text{CN}$  at  $-60\text{ }^\circ\text{C}$ :  
(a) 450 to 650  $m/z$  range and (b) 520 to 550  $m/z$  range.



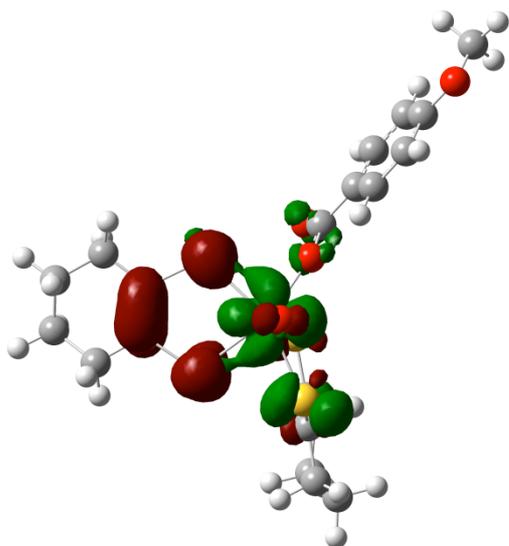
**Fig. S4** a) Absorption spectral changes (a) for the first step (0 s → 20 sec) and (b) for the second step (20 s → 800 sec) in the formation of  $\text{Mo}^{\text{VI}}\text{O}(p\text{-H-OBz})\text{L}_2$  by the reaction of  $\text{Mo}^{\text{VI}}\text{OL}_2$  (0.2 mM) with  $\text{Et}_4\text{N}(p\text{-H-OBz})$  (2.0 mM) at  $-60\text{ }^\circ\text{C}$ .



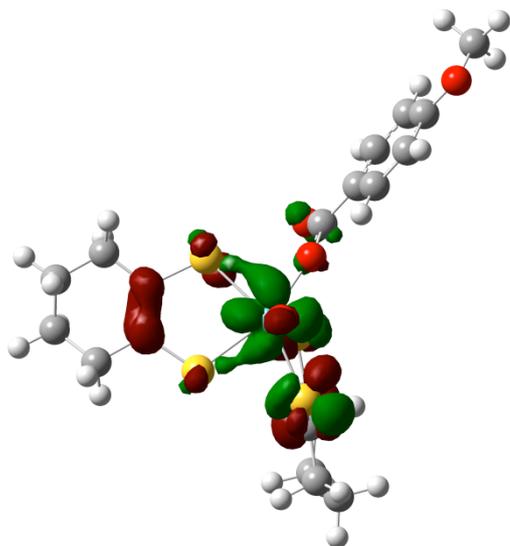
**Fig. S5** Zeroth-order dependence of the observed rate constants,  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ), versus the concentration of  $\text{Et}_4\text{N}(\text{p-}H\text{-OBz})$ .



**Fig. S6** Lowest unoccupied molecular orbital wavefunction for  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$  plotted at a 0.04 isovalue.



**Fig. 7** Electron density difference map (EDDM) for the transition that is responsible for band 1 in  $\text{Mo}^{\text{VI}}\text{O}(\text{p}\text{-OMe-OBz})\text{L}_2$ . The density value of the plot is 0.002. The oscillator strength for this transition is calculated to be  $f = 0.0134$ . Red indicates a loss of electron density in the transition, and green indicates a gain in electron density for the transition.



**Fig. S8** Electron density difference map (EDDM) for the transition that is responsible for band 2 in  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$ . The density value of the plot is 0.002. The oscillator strength for this transition is calculated to be  $f = 0.0391$ . Red indicates a loss of electron density in the transition, and green indicates a gain in electron density for the transition.

**Table S1.** Molecular orbital compositions for  $\text{Mo}^{\text{VI}}\text{O}(p\text{-Cl-OBz})\text{L}_2$ .

Molecular orbital	Fragment Character (%)				
	Mo	Oxo	OBz	S <sub>2</sub> C <sub>4</sub> H <sub>8</sub> A <sup>a</sup>	S <sub>2</sub> C <sub>4</sub> H <sub>8</sub> B <sup>a</sup>
LUMO+2	6	0	91	1 (1)	1 (1)
LUMO+1	59	22	5	8 (4)	6 (5)
LUMO	40	1	11	9 (8)	37 (29)
HOMO	5	5	1	63 (37)	26 (17)
HOMO-1	18	4	4	24 (11)	50 (26)

<sup>a</sup> Values in parentheses are the S contribution from the dithiolene.

**Table S2.** Molecular orbital compositions for  $\text{Mo}^{\text{VI}}\text{O}(p\text{-OMe-OBz})\text{L}_2$

Molecular orbital	Fragment Character (%)				
	Mo	Oxo	OBz	S <sub>2</sub> C <sub>4</sub> H <sub>8</sub> A <sup>a</sup>	S <sub>2</sub> C <sub>4</sub> H <sub>8</sub> B <sup>a</sup>
LUMO+2	7	0	88	2 (2)	1 (1)
LUMO+1	59	22	5	8 (4)	6 (5)
LUMO	42	1	10	10 (9)	38 (29)
HOMO	5	5	1	63 (37)	27 (18)
HOMO-1	18	4	4	24 (12)	49 (26)

<sup>a</sup> Values in parentheses are the S contribution from the dithiolene.