Supporting Information

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(Experimental detail, Chart S1, and Figures S1 – S3)

**Reversible Sulfurization-Desulfurization of
Tungsten-Bis(dithiolene) Complexes**

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General. All reagents and solvents were used as received unless otherwise noted. MeCN and EtCN were dried over CaH_2 and then P_2O_5 , THF and ether were dried over Na in the presence of benzophenone, and these were distilled under argon prior to use. All reactions were carried out under argon in a Schlenk tube or a Miwa DB0-1KP glovebox.

Physical Measurements. FT-IR spectra were recorded with a Perkin Elmer Spectrum One. UV-vis spectra were recorded on HP-8453 spectrometer with a Unisoku thermostated cell holder. EPR and ^1H NMR spectra were measured on a JEOL-JES-FE2XG and JEOL-Lambda 300 spectrometers, respectively.

X-ray crystal structure determinations. Single crystals of $(\text{Ph}_4\text{P})_2[\text{W}^{\text{VI}}\text{O}(\text{S}_2)(\text{bdt})_2]$ (**1**) and $(\text{Et}_4\text{N})_2[\text{W}^{\text{IV}}\text{O}(\text{S}_2\text{C}_6\text{H}_8)_2]$ (**5**) were obtained by recrystallization from MeCN/ether. The crystals were mounted on a glass fiber with traces of viscous oil. The X-ray data were collected with graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71070 \text{ \AA}$) on a Rigaku/MSM Mercury CCD diffractometer at 123 K under cold nitrogen gas equipped with a Rigaku GNNP low-temperature device. All the calculations were performed using Single-Crystal Structure Analysis Software, version 3.7.0.^[1] The structures were solved by direct methods (SIR-97)^[2] and expanded using DIRDIF 99.^[3] The atoms were refined anisotropically except distorted atoms by full-matrix least squares on F^2 . The hydrogen atoms in all structures were attached at idealized positions on carbon atoms and not refined. All structures converted in the final stages of refinement showed no movement in atom positions.

References

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Chart S1. Designations of Complex Structures and Abbreviations.

Figure S1. Electronic Spectra changed upon addition of Na₂S₄ (1.0×10^{-4} M) into a solution of **3** in MeCN(2.0×10^{-4} M) at 25 °C.

Figure S2. Temperature dependence of the electronic spectrum of a MeCN-EtCN (70:30) solution containing (Et₄N)₂[WO(S₂C₆H₈)₂] (**5**: 3.3×10^{-4} M) and S₈ (0.825×10^{-4} M) recorded at 223, 233, 243, 253, 263, 273, 283, 293, and 298K.

Figure S3. Crystal structure of the anion part of $(\text{Et}_4\text{N})_2[\text{W}^{\text{IV}}\text{O}(\text{S}_2\text{C}_6\text{H}_8)_2]$ (**5**) shown with 50% ellipsoids. The hydrogen atoms were omitted for clarity.