

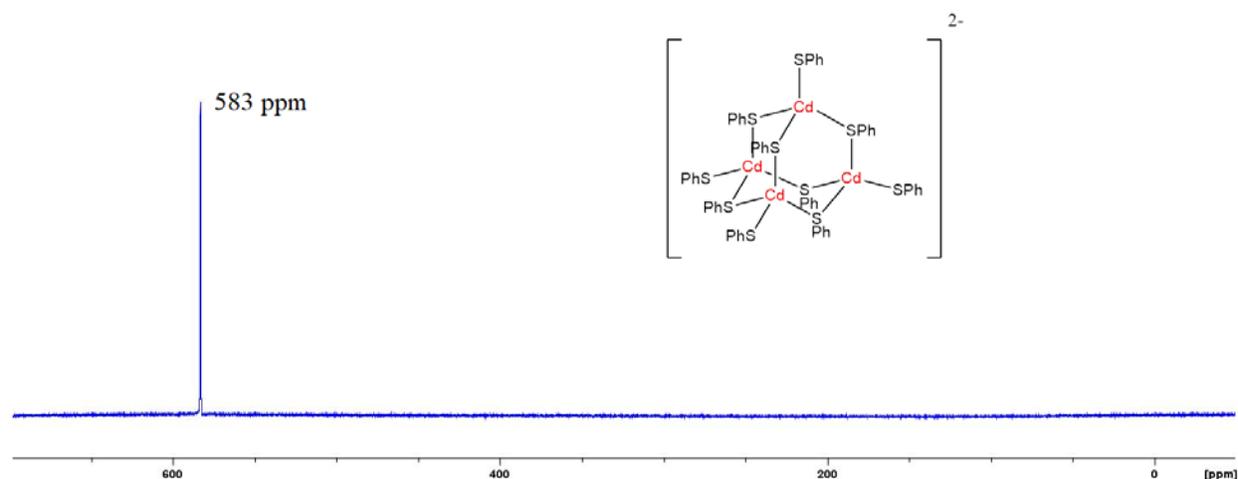
**Chemistry of Singlet Oxygen with a Cadmium-Sulfur Cluster:  
Physical Quenching vs. Photooxidation  
Supplemental Information**

David A. Cagan<sup>†</sup>, Arman C. Garcia<sup>†</sup>, Kin Li<sup>†</sup>, David Ashen-Garry<sup>†</sup>, Abigail C. Tadle<sup>†</sup>, Dong Zhang<sup>†</sup>, Katherine Nelms<sup>†</sup>, Yangyang Liu<sup>†</sup>, Jeffrey R. Shallenberger<sup>‡</sup>, Joshua J. Stapleton<sup>‡</sup>, Matthias Selke<sup>\*†</sup>

<sup>†</sup>Department of Chemistry and Biochemistry, California State University, Los Angeles

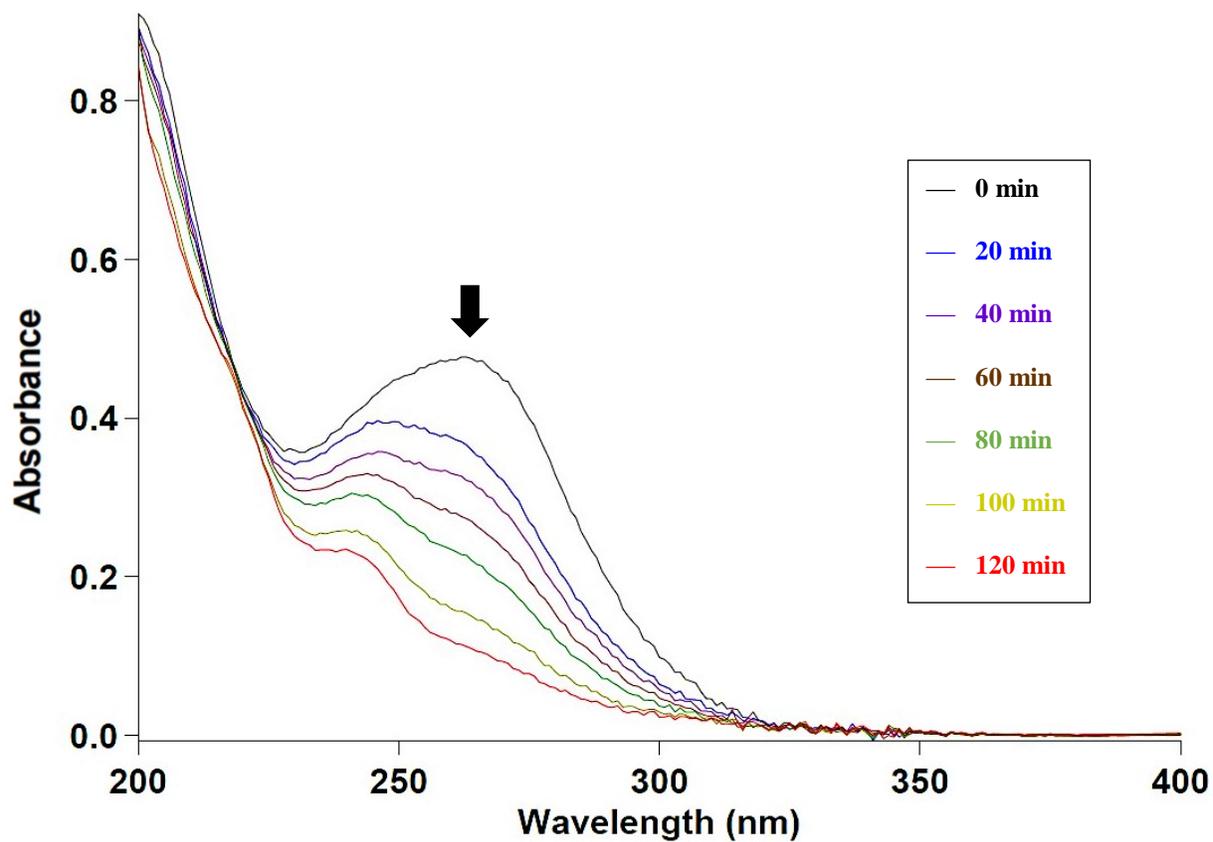
<sup>‡</sup> Materials Characterization Laboratory, The Pennsylvania State University, University Park PA

**Part 1: Characterization of (Me<sub>4</sub>N)<sub>2</sub>[Cd<sub>4</sub>(SPh)<sub>10</sub>] (1) and its Photooxidation Product**



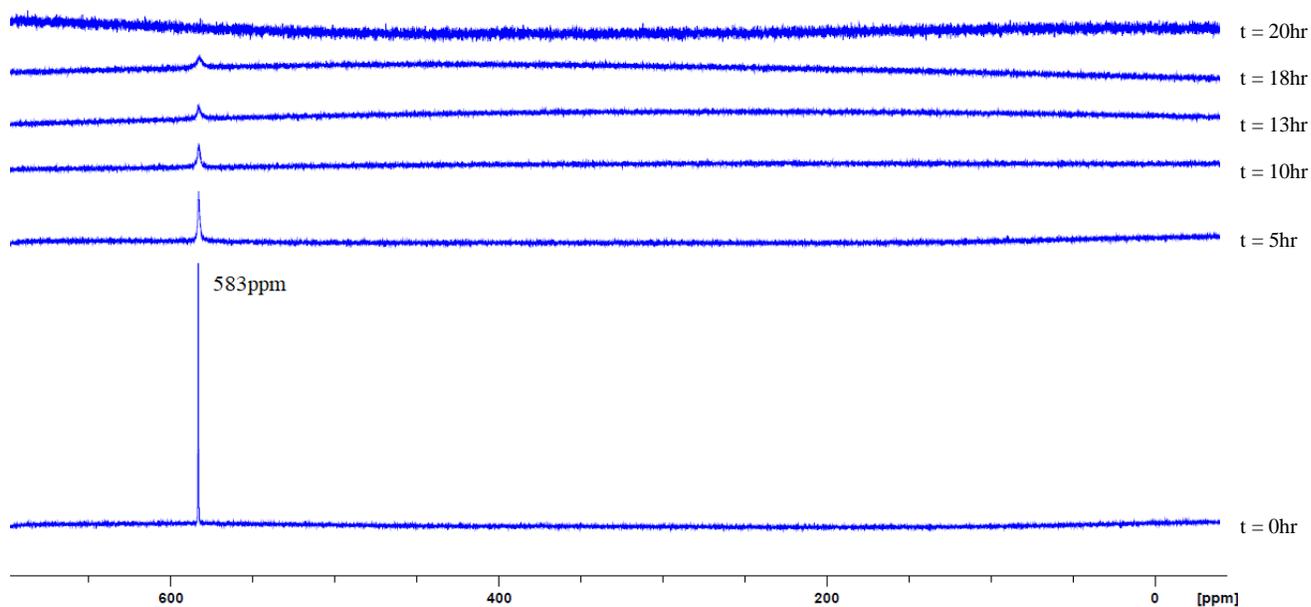
**Figure S1:** <sup>113</sup>Cadmium NMR of Cluster **1** in acetonitrile at room temperature. Since all Cadmium atoms are equivalent, only one peak is observed.

Time course of reaction of singlet oxygen with  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  followed by UV/vis spectroscopy.



**Figure S2.** Time course of photooxidation of  $(\text{NH}_4)_2[\text{Cd}_4(\text{SPh})_{10}]$  in  $\text{CH}_3\text{CN}$  (sensitizer = Rose Bengal, cutoff filter at 496 nm).

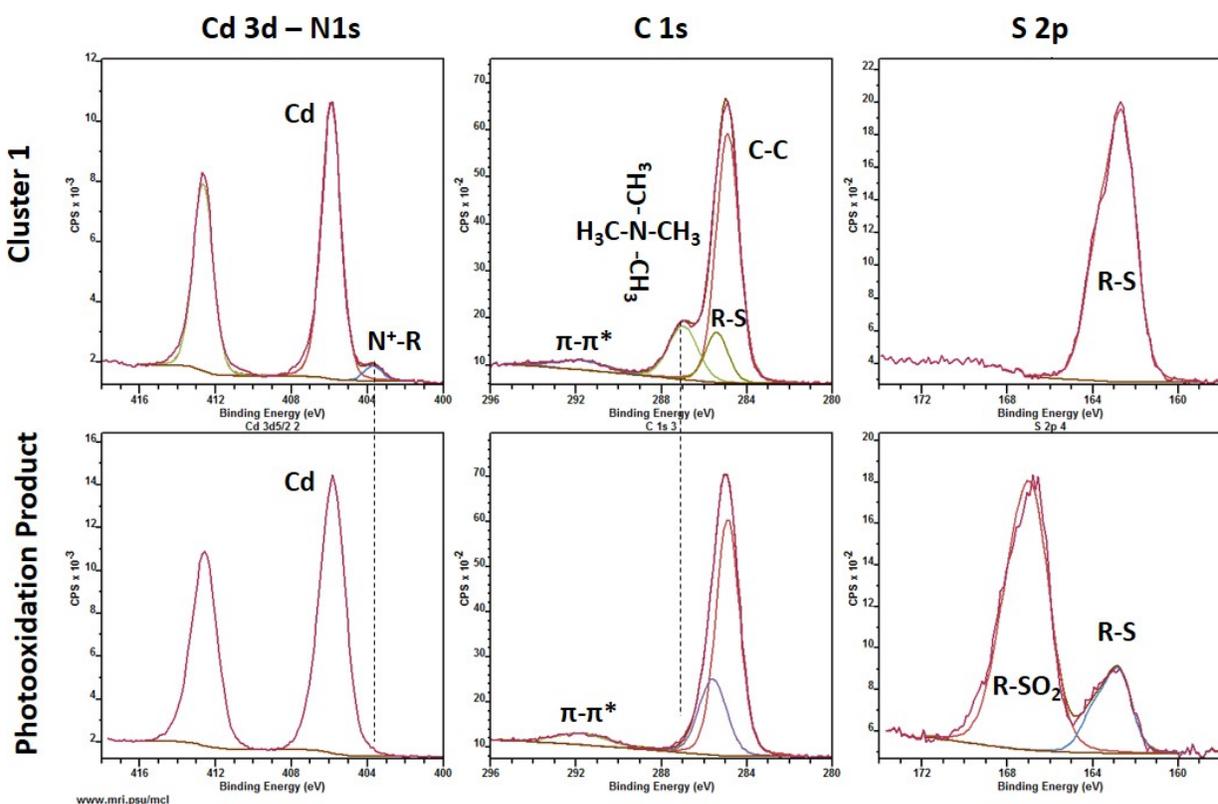
Time course of reaction of singlet oxygen with  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  followed by  $^{113}\text{Cd}$  NMR.



**Figure S3.** Time course of photooxidation of cluster **1** by  $^{113}\text{Cd}$  NMR spectra of **1** in acetonitrile over a period of 20 hours. The  $^{113}\text{Cd}$  NMR measurements were performed using a Bruker Advance 400 MHz NMR Spectrometer using cadmium nitrate as an external reference and  $d_3$ -acetonitrile as solvent.

While no new peaks were observed in the  $^{113}\text{Cd}$  NMR, formation of a precipitate was observed. This product formed as a solid at the bottom of the vessel, and it was insoluble in the following solvents: acetone, acetonitrile, chloroform, dichloromethane, dimethylformamide, dimethyl sulfoxide, methanol, toluene, and water. The product was dried and analyzed by X-ray photoelectron spectroscopy (XPS) and FT-IR at the Materials Characterization Laboratory at Penn State University.

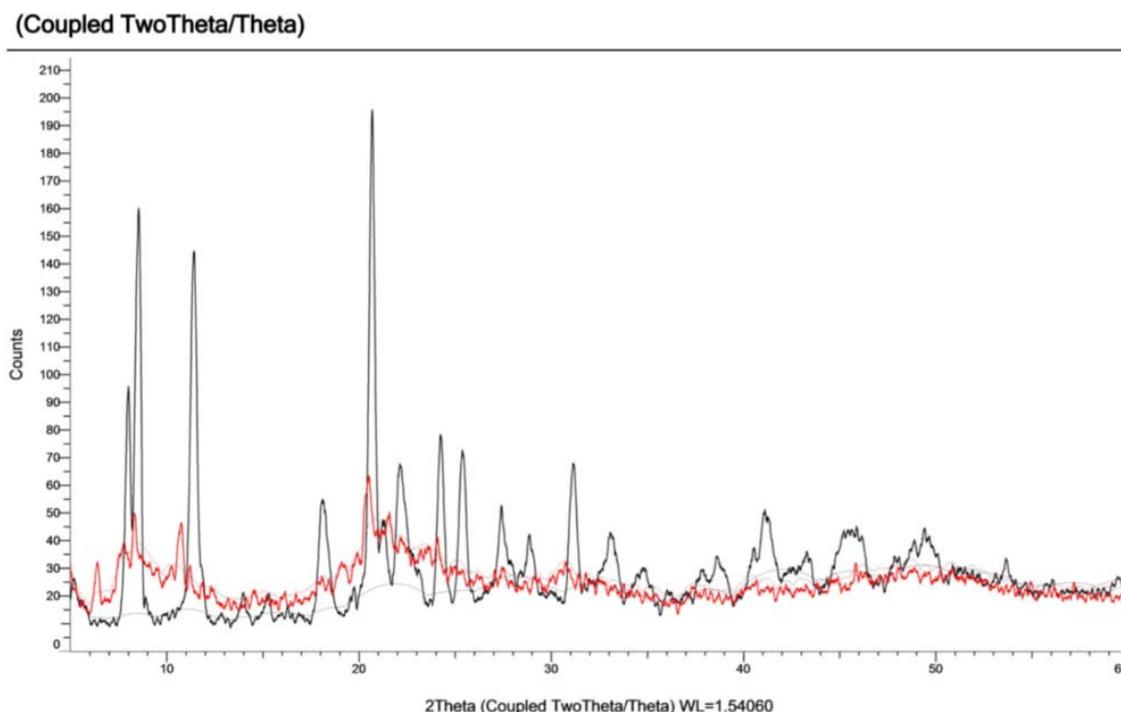
XPS analyses of precipitate formed upon reaction of singlet oxygen with  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$ .



**Figure S4:** High resolution photoemission spectra from Cluster 1 (top row) and photooxidation product (bottom row). Photooxidation product shows lack of signal from  $\text{Me}_4\text{N}$  groups in both the N 1s (original peak at 403.7 eV is not present in photooxidation product) and C 1s spectra (C-N band at 286.9 eV is missing) as well as presence of  $\text{SO}_2$  groups.

XPS experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al  $\text{K}\alpha$  x-ray source ( $h\nu = 1,486.7$  eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu  $2p_{3/2} = 932.7$  eV, Cu  $2p_{3/2} = 75.1$  eV). Peaks were charge-referenced to the  $\text{CH}_x$  band in the carbon 1s spectra at 284.8 eV. Measurements were made at a takeoff angle of  $45^\circ$  with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons.

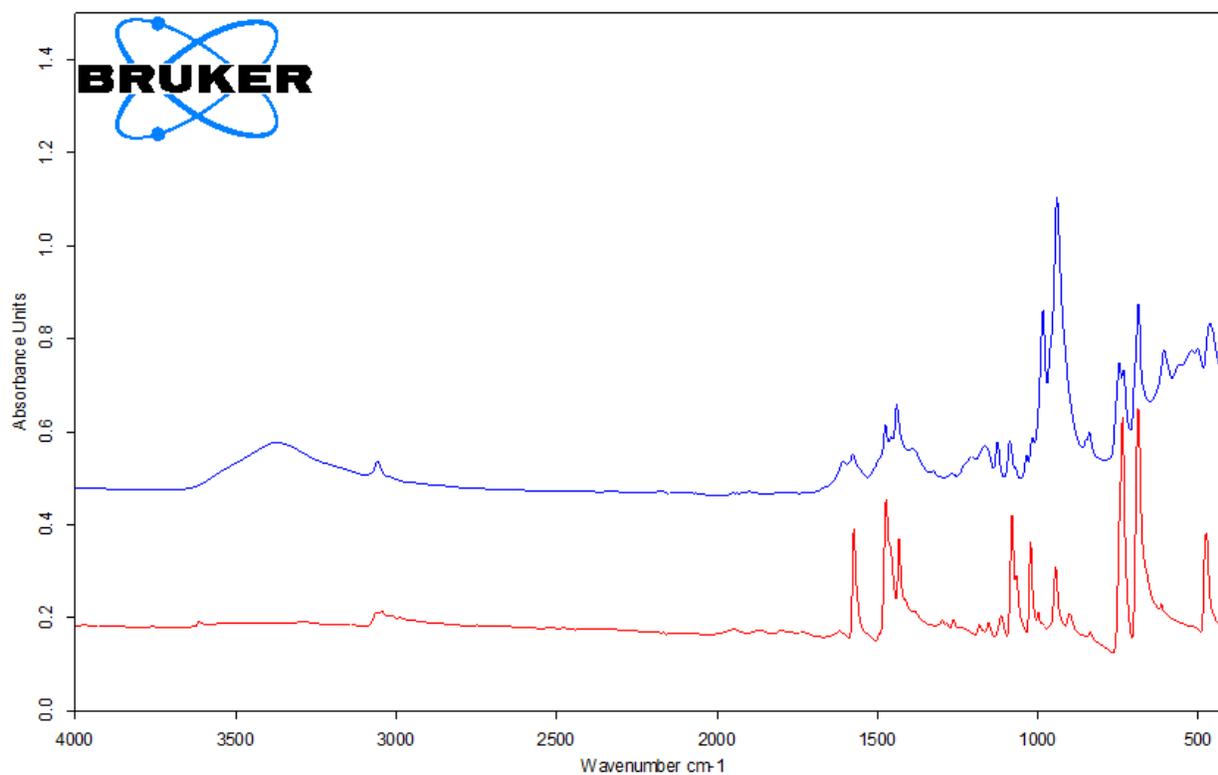
PXRD analyses of precipitate formed upon reaction of singlet oxygen with  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$



**Figure S5.** The Powder X-ray Diffraction patterns for  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  (in black) and the oxidation product (in red).

Powder X-ray Diffractions were measured for  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  (**1**) and the photooxidation product on a Bruker D2 Phaser. The PXRD of  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  (**1**) matches the simulated patterns.<sup>S1</sup> The PXRD of the precipitate formed after photooxidation product shows significant decrease in the peak intensity, which indicates loss of crystallinity. The appearance of bumps in the PXRD baseline means that the product is a mixture of crystalline and amorphous material. Comparison between the PXRD of the oxidation product and that of  $\text{CdSO}_4$  confirmed that there is no  $\text{CdSO}_4$  in the product.<sup>S2</sup> Additionally, the diffraction peak around  $2\theta = 6.5^\circ$  of the product indicates a larger unit cell is present in the crystalline part of the oxidation product. As the oxidation product is not soluble in any solvent or water, we believe that an inorganic polymer containing both Cd-S and Cd-O bonds was formed.

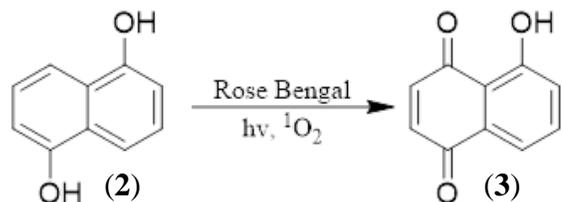
FTIR analyses of precipitate formed upon reaction of singlet oxygen with  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$



**Figure S6.** FT-IR measurement of **1** (red) and its photooxidation product (blue). Note the formation of two new peaks in the product at  $984\text{ cm}^{-1}$  and  $942\text{ cm}^{-1}$ . These are assigned to be O,O-bound  $\text{SO}_2$  peaks based on comparison with literature sulfenato and sulfinato complexes, as referenced in the main text.<sup>S3-S6</sup>

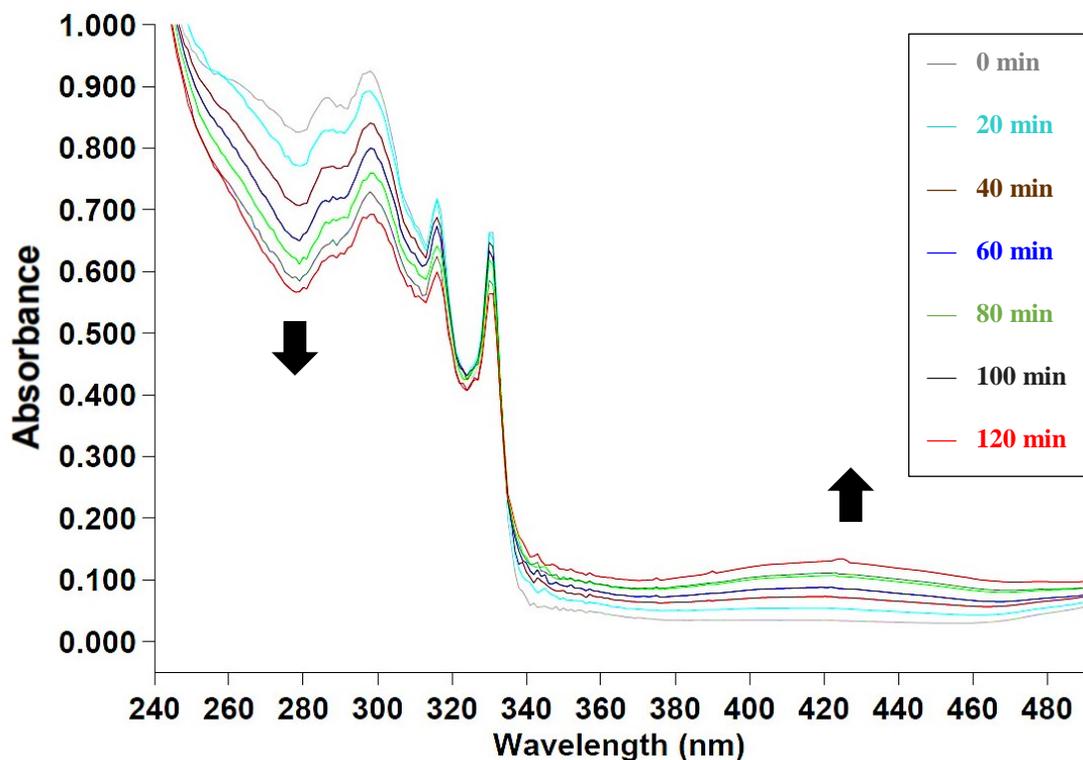
## Part II. Competition Kinetics Experimental Section

1,5-dihydroxynaphthalene (DHN, **2**) was used as a singlet oxygen co-acceptor, as previously described in the literature.<sup>S7</sup> This compound reacts with singlet oxygen forming quinone **3** as shown below, with a chemical reaction rate constant of  $1.5 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$ .



There is an isosbestic point at 277 nm during the photooxidation of compound **2** to **3**. Since the Cadmium cluster  $(\text{NH}_4)_2 [\text{Cd}_4(\text{SPh})_{10}]$  (**1**) absorbs strongly at that wavelength ( $\epsilon_{277} = 5.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$  in methanol), we used that wavelength to monitor the disappearance of the Cd cluster **1** during the competition experiment. Formation of the quinone adduct **3** was monitored at 427 nm ( $\epsilon_{427} = 3810 \text{ M}^{-1} \text{ cm}^{-1}$ ), where the Cadmium cluster **1** does not absorb. The competition experiments were carried out under ambient conditions with Rose Bengal as singlet oxygen sensitizer and a cutoff filter at 496 nm such that neither the Cadmium cluster **1** nor the 1,5-dihydroxynaphthalene **2** nor its photooxidation product **3** were excited.

During the competition experiments, methanol solutions (2 ml in UV/vis cuvettes) with initial concentrations of DHN (**2**) and cluster **1** were  $8.5 \times 10^{-5} \text{ M}$  and  $5.7 \times 10^{-6} \text{ M}$  were irradiated with a 12-A xenon lamp for up to 120 minutes. Every 20 minutes, UV-Vis scans of the reaction cells were taken using a Varian Cary 300 Bio Spectrophotometer (Figure S8). The cell volume was maintained at 2.00 mL by addition of solvent via micro syringe.



**Figure S7.** Sample an electronic spectrum of the competition kinetics experiments. Scans were taken every 20 minutes up to 120 minutes. Initial concentrations used were as follows:  $[\text{Cd}_4(\text{SPh})_{10}]^2 = 5.7 \times 10^{-6} \text{M}$ ,  $[\text{DHN}]^0 = 8.5 \times 10^{-5}$ .

Final concentration of DHN (**2**) was determined by subtracting the final concentration of product **3** from the initial concentration of **2**. The initial and final concentrations of cluster **1** and DHN were then substituted into the Higgins equation S-E1 below. Once the ratio of rate constants was determined, we were able to solve for the chemical quenching rate constant of the cadmium cluster,  $k_{r,cluster}$ , using the known value for DHN ( $k_{r,DHN} = 1.5 \times 10^6 \text{M}^{-1} \text{s}^{-1}$ ) which had been determined by direct measurement of its disappearance in the presence of singlet oxygen and absolute actinometry.

$$\frac{k_{r,cluster}}{k_{r,DHN}} = \frac{\log\left(\frac{[\text{cluster}]_t}{[\text{cluster}]_0}\right)}{\log\left(\frac{[\text{DHN}]_t}{[\text{DHN}]_0}\right)} \quad (\text{S-E1})$$

## References

- S1) Vittal, J.J.; Dean, P.A.W.; Payne, N.C. Metal selenolate chemistry: Stereochemistry of adamantane-type clusters of formula  $[(\mu\text{-SePh})_6(\text{MeSePh})_4]^{2-}$  *Can. J. Chem.* **1992**, *70*, 792-801.
- S2) Theppitak, C.; Chainok, K. Crystal structure of  $\text{CdSO}_4(\text{H}_2\text{O})$ : a redetermination *Acta Cryst.E* **2015**, *71*, i8-i9.
- S3) Carey, N. A. D.; Clark, H. C. Reaction of sulfur dioxide with dimethylzinc and dimethylmercury *Can. J. Chem.* **1968**, *46*, 649-651.
- S4) Vitzthum, G.; Lindner, E. Sulfinato complexes *Angew. Chem. Int. Edit.* **1971**, *10*, 315-326.
- S5) Conversely, S-bound sulfinato complexes show two peaks in the range of 1,000 -1,150  $\text{cm}^{-1}$ . Farmer, P.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D.H. Reibenspies, J.H.; Darensbourg, M.Y. Isotopic labeling investigation of the oxygenation of nickel-bound thiolates by molecular oxygen *J. Am. Chem. Soc.* **1992**, *114*, 4601-4605.
- S6) Tamura, M.; Tsuge, K.; Igashira-Kamiyama, A.; Konno, T. Bis(bipyridine)-ruthenium(II) Complexes with an aliphatic sulfinato donor: Synthesis, characterization, and properties *Inorg. Chem.* **2011**, *50*, 4764-4771.
- S7) Croux, S.; Maurette, M.-T. Kinetic Parameters of the Reactivity of Dihydroxy Naphthalenes with Singlet Oxygen *New J. Chem.* **1990**, *14*, 161-167.