

## Supplemental Material

### Experimental Details

**1. Photooxidation of Complexes 1 and 2.** Complex 1 and 2 were photooxidized using methylene blue or rose bengal as sensitizer, an Oriel Tungsten-Halogen 300 W lamp, cut-off filter at 492 nm as an irradiation source. The reaction can be carried out in test tubes or directly in NMR tubes. Generally, a steady stream of oxygen is bubbled through the reaction mixture. The temperature is controlled by using a Dewar flask with a quartz window.

**2. Time-resolved measurements of  $k_t$ .** Singlet oxygen quenching rates were measured using a Nd:YAG laser at an excitation wavelength of 532 nm (New Wave Research Mini-Laser II) with pulse energies of 2-4 mJ/pulse. Singlet oxygen luminescence decay signals were recorded at right angle using a liquid nitrogen cooled Ge photodiode detector (Applied Detector Corp. Model 403S). Signals were digitized by a LeCroy 9350CM oscilloscope. All experiments were run in deuterated solvents in the presence of methylene blue or rose bengal as photosensitizers. Substrate concentrations generally ranged from 0.005 mM to 0.1 mM for complexes **1** and **2**, and up to 1 mM for complex **5**. Typically, we used 2 ml solution of the complex and sensitizer in a 4 ml quartz cell.

**3. Competition experiments.** The starting Co complexes **1** and **2** were irradiated in the presence of singlet oxygen acceptors with a known reaction rate constant with  $^1\text{O}_2$ . 9, 10-dimethylanthracene (DMA) and the disodium salt of 3-(10-(2-carboxy-ethyl)-

anthracen-9-yl)-propionic acid (DMA-p) were used as competitors. These compounds remove singlet oxygen by chemical reaction only so that  $k_t = k_r$ . We remeasured the  $k_t$  value of these reference compounds in the various solvents by singlet oxygen luminescence quenching. For DMA, the  $k_r$  values thus obtained were  $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{CD}_3\text{OD}$ , and  $2.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  in  $\text{DMF-d}_7$ . For the disodium salt of 3-(10-(2-carboxyethyl)-anthracen-9-yl)-propionic acid (DMA-p), a  $k_r$  value of  $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  was obtained in  $\text{D}_2\text{O}$ . Experiments with DMA in  $\text{CD}_3\text{OD}$  and  $\text{DMF-d}_7$  were monitored by a combination of  $^1\text{H}$  NMR and UV/vis spectroscopy while those between DMA-p and the Co complexes in water were monitored spectrophotometrically. Conversion of each compound was generally kept between 20 – 80%. Irradiation conditions were as described above (part 1). The rate equations for the reactions of DMA and the Co-thiolato complexes with singlet oxygen are given by equations (1) and (2):

$$-\frac{d[\text{DMA}]}{dt} = k_r(\text{DMA}) [\text{DMA}] [^1\text{O}_2] \quad (1)$$

$$-\frac{d[[\text{Co}(\text{en})_2(\text{S-R})]^{2+}]}{dt} = k_r(\text{Co}(\text{en})_2(\text{S-R})^{2+}) [[\text{Co}(\text{en})_2(\text{S-R})]^{2+}] [^1\text{O}_2] \quad (2)$$

Where  $k_r(\text{DMA})$  is the rate constant for the reaction of DMA with singlet oxygen, and  $k_r(\text{Co}(\text{en})_2(\text{S-R})^{2+})$  is the rate constant for the reaction of the Co-thiolato complex with singlet oxygen. Under conditions of continuous irradiation under an oxygen atmosphere, the equations can simply be rearranged, integrated from initial to final irradiation time and thence solved for  $[^1\text{O}_2]$ . Taking the rate ratios then leads to the Higgins equation (3):

$$\frac{\log\{[\text{Co(en)}_2(\text{S-R})]^{2+}_f/[\text{Co(en)}_2(\text{S-R})]^{2+}_0\}}{\log\{[\text{DMA}]^f/[\text{DMA}]^0\}} = \frac{k_r(\text{Co(en)}_2(\text{S-R})^{2+})}{k_r(\text{DMA})} \quad (3)$$

Starting and final concentrations of the both competitors and Co complexes were substituted into the Higgins equation, and measured rate constants for the DMA reference were then used to calculate the rate constants for the Co complexes.