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Photoinduced Electron Transfer in Covalently Linked Oxomolybdenum(V) Porphyrin Systems

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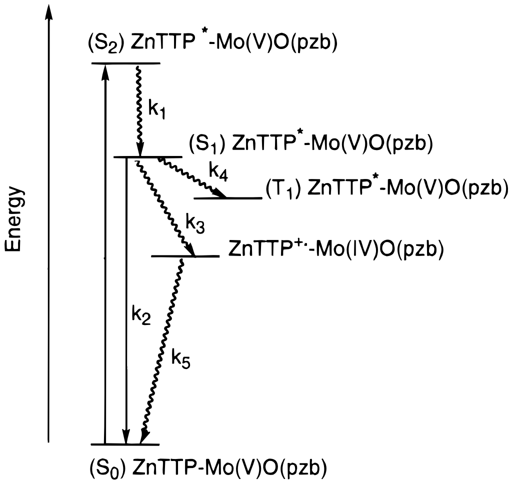
The pterin-containing molybdenum enzymes are comprised of three general classes which perform simple oxygen-atom transfer either to or from substrate (sulfite oxidase and DMSO reductase families) and the oxidative hydroxylation of various substrates (xanthine oxidase family).[1] Following oxygen-atom transfer, the resting state of the enzyme is regenerated by two sequential one-electron transfers. Therefore, it is of interest to investigate electron transfer events in oxomolybdenum systems which mimic specific structural features of the active site. Here we describe the results of our initial investigations on photoinduced electron transfer in {5,10,15-tri-*p*-tolyl-20-[2,3-[((hydrotris(3,5-dimethylpyrazolyl)borato)oxomolybdenio)dioxy]phenyl]-porphyrinato}zinc(II) (ZnTTP(2,3-Mo^VO(pzb)), **1**) and {5,10,15-tri-*p*-tolyl-20-[3,4-[((hydrotris(3,5-dimethylpyrazolyl)borato)-oxomolybdenio)dioxy]phenyl]porphyrinato}zinc(II) (ZnTTP-(3,4-Mo^VO(pzb)), **2**), where a catechol moiety is used to covalently link the donor (porphyrin) and acceptor (Mo) sites via the *meso* position of the porphyrin.[2] The incorporation of oxo−Mo(V) centers as electron acceptors make these systems effective first generation models of electron transfer processes occurring at the active site of pterin-containing oxomolybdenum enzymes.[1] The structural rigidity of the catechol linker is particularly attractive since the through-bond and through-space distances, and the relative orientation of the donor and acceptor, can be easily modified by changing the spacer group from a 2,3-catechol to a 3,4-catechol. This provides a basis for testing various theoretical aspects of electron transfer and allows for detailed spectral probing of the electronic effects of linkage isomers on electron transfer rate constants. Furthermore, peripherally metalated porphyrin systems also provide a general means of probing real-time electron transfer dynamics at redox active transition metal sites.[3] In this communication we report direct evidence for photoinduced electron transfer in covalently linked donor−acceptor molecules **1** and **2**.

Scheme 1



Since the $[Mo^VO(pzb)]^{2+}$ fragment possesses a comparatively low oscillator strength ($\epsilon < 10^3$ M^{-1} cm^{-1}), the ground-state electronic absorption spectra of **1** and **2** are dominated by the intense $\pi \rightarrow \pi^*$ transitions of the porphyrin. The room-temperature electronic absorption spectra of the nonperipherally metalated {5,10,15-tri-*p*-tolyl-20-[2,3-dimethoxyphenyl]porphyrinato}zinc(II) (ZnTTP(2,3-$(OMe)_2$), **3**) and {5,10,15-tri-*p*-tolyl-20-[3,4-dimethoxyphenyl]porphyrinato}zinc(II) (ZnTTP-(3,4-$(OMe)_2$), **4**) and the peripherally metalated derivatives **1** and **2** in DMSO are virtually identical. This indicates no significant porphyrin excited state (S_1 or S_2) electronic structural differences occur upon covalent attachment of the pendant $[Mo^VO(pzb)]^{2+}$ subunit. However, steady-state emission studies show that covalent attachment of the $[Mo^VO(pzb)]^{2+}$ pendant to the porphyrin periphery in **1** and **2** results in complete quenching of the porphyrin fluorescence as opposed to the behavior of nonperipherally metalated **3** and **4**. Since the emissive quantum yield for **1** and **2** is zero for both B (S_2) and Q (S_1) band excitation, the competing deactivation pathway originates from the lowest lying porphyrin excited state, S_1. On the basis of thermodynamic considerations, the mechanism responsible for the dramatic fluorescence quenching of **1** and **2** may be explained in terms of electron transfer from ZnTTP to $[Mo^VO(pzb)]^{2+}$ (Scheme 1).[4]

We have utilized single-pulse pump−probe picosecond transient resonance Raman[5] and nanosecond transient absorption spectroscopies to assess the nature of the competing pathways leading to enhanced S_1 state relaxation and complete fluorescence quenching. The transient absorption spectrum[6] of **3** (Figure 1) is typical of nonperipherally metalated porphyrins. The spectrum displays a clear bleach of the ground state S_2 (B band) absorption with a concomitant increase in absorption to lower energy, indicating the formation of the porphyrin triplet state (T_1).[7] In marked contrast to **3**, the transient absorption

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(4) This observation is consistent with the calculated thermodynamic driving force ($\Delta G°$) for photoinduced electron transfer,

$$\Delta G° = E_{1/2}(\mathrm{ZnTTP}^{0/+}) - E_{h\nu} - E_{1/2}(\mathrm{Mo}^{\mathrm{V/IV}})$$

where $E_{1/2}(\mathrm{ZnTTP}^{0/+})$ is the oxidation potential for **3** and **4** (850 and 800 mV, respectively, vs SCE), $E_{h\nu}$ is the first excited singlet state energy of **3** and **4** (determined to be 2.0 eV above the ground state by emission spectroscopy), and $E_{1/2}(\mathrm{Mo}^{\mathrm{V/IV}})$ is the reduction potential for the Mo redox couple (determined to be −698 and −736 mV vs SCE, respectively, for compounds **1** and **2**. These values yield very favorable $\Delta G°$'s of −452 and −464 mV for compounds **1** and **2**.

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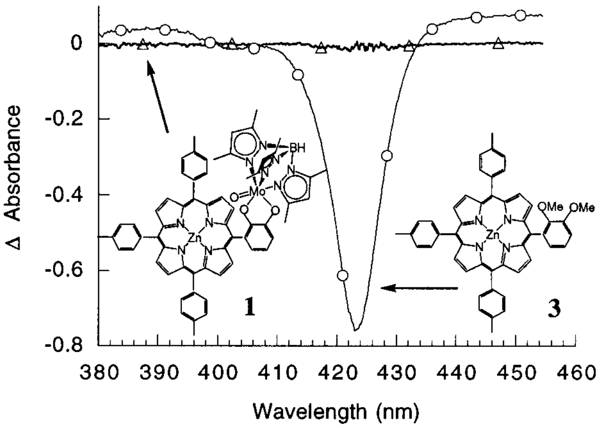

Figure 1. Transient absorption spectra (416 nm excitation) of **1** and **3** in DMSO showing the absence of triplet (T_1) state formation for **1**. The detector response time was 50 ns.

spectrum of **1** (Figure 1) is completely flat and displays no evidence for the formation of a triplet state *via* intersystem crossing.[8] Therefore, both the emissive (k_2) and intersystem crossing (k_4) relaxation pathways of Scheme 1 are being completely superseded by an additional deactivation pathway. Transient resonance Raman spectroscopy is a very powerful probe of the electronic structure of excited state intermediates and can be viewed as complementary to transient absorption spectroscopy. Specifically, the resonance selectivity of the Raman experiment will result in the enhancement of vibrational modes associated with excited states possessing appreciable absorption at the probe wavelength.[9] The 30 ps transient resonance Raman spectra of **1** are presented in Figure 2.[10] Low laser fluence excitation at 416 nm yields spectra dominated by in-plane totally symmetric macrocycle modes of the porphyrin core.[11] Upon increase of the photon fluence, spectral changes become readily evident which are attributable to the formation of a transient excited state. The difference spectrum displays appreciable shifts (5−10 cm^{-1}) to lower energy for the in-plane macrocycle modes. These are consistent with the formation of a porphyrin π-cation radical[12] and corroborate the existence of electron transfer (k_3) from the S_1 state of ZnTTP to [Mo^{V}O(pzb)]$^{2+}$.

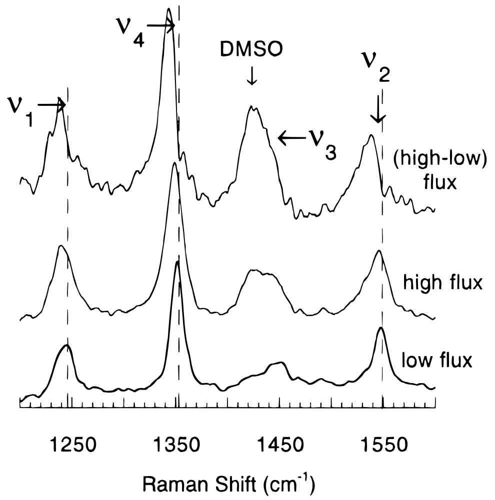

Figure 2. Laser fluence dependent picosecond transient Raman spectra of **1** in DMSO using 416 nm laser excitation. The difference spectrum displays frequency shifts, $\Delta\nu_1 = -5$ cm^{-1}, $\Delta\nu_2 = -11$ cm^{-1}, and $\Delta\nu_4 = -8$ cm^{-1}, consistent with the formation of a porphyrin π-cation radical.[12]

In summary, the photoinduced electron transfer observed for **1** and **2** is consistent with Scheme 1. Compounds **1** and **2** possess biologically relevent oxo−Mo(V) acceptors and represent first generation models for investigating real-time electron transfer dynamics in pterin-containing molybdenum enzymes. Furthermore, the judicious substitution of other biomimetic transition metal complexes coupled with appropriate modifications to the porphyrin−metal linkage results in a general approach to probing electron transfer dynamics relevant to the redox behavior of a variety of metalloenzyme active sites. The results presented here clearly demonstrate that transition metal acceptors can be photoactivated in porphyrin-based supramolecular systems *via* an antenna-mediated electron transfer process. Finally, extension of this methodology allows for the potential photochemical and photophysical exploitation of the unique reactivity and catalytic activity of transition metal systems in general.

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(6) Transient absorption was performed in DMSO using a Spex Model 1877 triple spectrograph with a PAR Model 1420 OMA gated detector and PAR Model 1463 controller. The samples were made anaerobic via three freeze/pump/thaw cycles. Excitation at 416 nm was provided by Raman shifting the output of a tripled Nd−YAG laser Model DCR-2 in a high pressure hydrogen gas cell. The probe light source was a PTI Model 220 75 W xenon arc lamp.

(7) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500−6506.

(8) Intersystem crossing between the S_1 and T_1 states could potentially be enhanced by increased spin−orbit coupling mediated by the pendant [Mo^{V}O(pzb)]$^{2+}$ group.

(9) (a) The S_1 and T_1 states of (5,10,15,20-tetraphenylporphinato)zinc(II) (ZnTPP) possess absorption maxima at 450 and 460 nm, respectively, well to the red of the 416 nm probe employed in the transient resonance Raman experiment (for example, see ref 12). As a result, resonance enhancement of the S_1 and T_1 states for **1** and **2** is not anticipated. Furthermore, there is no evidence for a long-lived T_1 excited state in the transient absorption spectra of **1** and **2**. ZnTPP$^{\bullet+}$ has been shown to absorb maximally at 410 nm (Buranda, T.; Soice, N.; Lin, S.; Larson, R.; Ondrias, M. *J. Phys. Chem.* **1996**, *100*, 18868−18874). Therefore, an appreciable resonance enhancement for the porphyrin π-cation radical of **1** and **2** may be expected with a 416 nm probe.

(10) Raman shifts for the excited state transient of **2** are virtually identical to **1**.

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(12) The resonance Raman frequency shifts between the ground and excited state of **1** and **2** are $\Delta\nu_1 = -5$ cm^{-1}, $\Delta\nu_2 = -11$ cm^{-1}, and $\Delta\nu_4 = -8$ cm^{-1}. These values compare very favorably with those for electrochemically generated ZnTPP$^{\bullet+}$, $\Delta\nu_1 = 0$ cm^{-1}, $\Delta\nu_2 = -7$ cm^{-1}, and $\Delta\nu_4 = -12$ cm^{-1} (Yamaguchi, H.; Nakano, M.; Itoh, K. *Chem Lett.* **1982**, 1397−1400), and are not similar to the frequency shifts observed for the T_1 state of ZnTPP, $\Delta\nu_1 = 0$ cm^{-1}, $\Delta\nu_2 = -34$ cm^{-1}, and $\Delta\nu_4 = +32$ cm^{-1} (de Paula, J. C.; Walters, V. A.; Nutaitis, C.; Lind, J.; Hall, K. *J. Phys. Chem.* **1992**, *96*, 10591−10594). The S_1 state frequency shifts are anticipated to be very similar to those of the T_1 state due to the similar orbital nature of the S_1 and T_1 wave functions (Kreszowski, D. H.; Deinum, G.; Babcock, G. T. *J. Am. Chem. Soc.* **1994**, *116*, 7463−7464).