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Intramolecular Rotation in a Porphyrin Dimer Controls Singlet Oxygen Production

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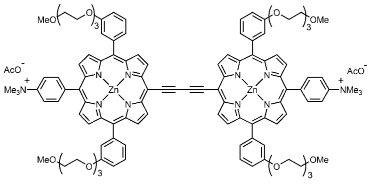
Singlet oxygen, $O_2(a^1\Delta_g)$, the lowest excited state of molecular oxygen,[1,2] reacts with a wide range of organic molecules, including biomolecules.[1] These reactions can have many consequences, including irreversible cellular damage and cell death.[3]

We recently reported that conjugated porphyrin dimers, such as **1**, can efficiently produce $O_2(a^1\Delta_g)$ by photosensitization.[4,5] In this process, either one- or two-photon activation of the porphyrin dimer is followed by intersystem crossing to produce a triplet state which, in turn, transfers its energy to ground state oxygen, $O_2(X^3\Sigma_g^-)$. Here, we demonstrate that the wavelength of light used to excite **1** is reflected in the quantum yield of $O_2(a^1\Delta_g)$ production. To our knowledge, such a wavelength-dependent effect is unprecedented and offers an additional degree of control in the photosensitized production of $O_2(a^1\Delta_g)$.



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The absorption, emission and excitation spectra of **1** in two solvents of different viscosity, methanol ($\eta = 0.6$ cP) and 1:4 methanol/glycerol (v/v, $\eta = 250$ cP), are shown in Figure 1. The most striking feature of these data is the two emission maxima at 640 and 700 nm, observed for **1** in a viscous glycerol solution, Figure 1d. The excitation spectra obtained for these emission peaks are likewise strikingly different, Figure 1b.

Based on previous reports for similar dimers,[6,7] we assign the two emission peaks to two excited-state conformations of **1**, defined by the torsional angle about the central butadiyne bridge (i.e., a twisted and a planar form). Although there is a continuous distribution of conformations, the behavior can be understood by considering just these two extremes. The emission maxima of the twisted and planar conformations are at 640 and 700 nm, respectively. The lower-energy planar conformer can be selectively excited at the red edge of the Soret and Q bands; see Figure 1b. At these excitation energies, the higher energy twisted form cannot be accessed. Conversely, 450 nm excitation predominantly produces the twisted excited state.

Emission from the planar conformer is strongly preferred in nonviscous media. Therefore, even selective excitation of the twisted state at 450 nm in methanol results in predominant emission from the planar form, Figure 1c. The excitation spectra recorded for the planar conformer emission in methanol, Figure 1b, closely match the absorption spectra, illustrating a near quantitative conversion of the twisted state to the lower-energy planar form in the excited state.

However, such conversion does not occur in viscous glycerol solution, where the characteristic 640 nm emission of the twisted state is observed along with 700 nm emission, Figure 1d. The excitation spectra (750 nm detection) obtained in viscous solution no longer match the absorption spectra and lack the 450 nm peak assigned to the twisted state (i.e., the selectively excited twisted state cannot convert to the lower-energy planar form due to a viscosity-dependent inhibition of torsional rotation about the butadiyne bridge). These data demonstrate that, in viscous media, each conformer of **1** can be excited selectively.

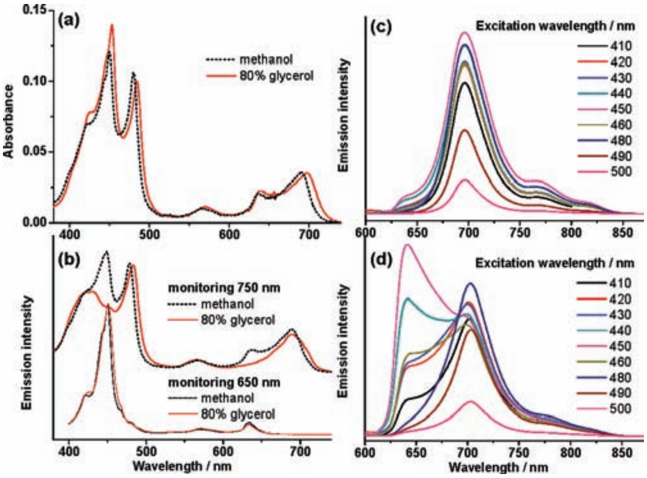

Figure 1. Absorption (a) and excitation (b) spectra of **1** in methanol (--) and 1:4 methanol/glycerol (v/v) (red —). Emission spectra of **1** in methanol (c) and 1:4 methanol/glycerol (d) following excitation at wavelengths over the range 410−500 nm.

Note that the spectra of the twisted conformation resemble those of a porphyrin monomer.[8] This is consistent with limited communication between the two perpendicular porphyrin units.

To enable efficient production of $O_2(a^1\Delta_g)$, the sensitizer must readily produce a long-lived triplet state following light absorption. It is known that, in a given molecule, particularly those containing flexible molecular bridges, conformational dynamics can influence a variety of photophysical processes, including those that influence triplet state yields.[8,9] Therefore it is possible that the rotational dynamics in **1** can alter the efficiency of photosensitized $O_2(a^1\Delta_g)$ production. Indeed, in a series of porphyrin oligomers we have demonstrated that the oligomer triplet quantum yield and, in turn,

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the $O_2(a^1\Delta_g)$ yield decrease from 1.0 to 0.3 with increasing number of linked porphyrin units (*N* between 1 and 8), suggesting complex conformational dynamics in longer arrays.[8]

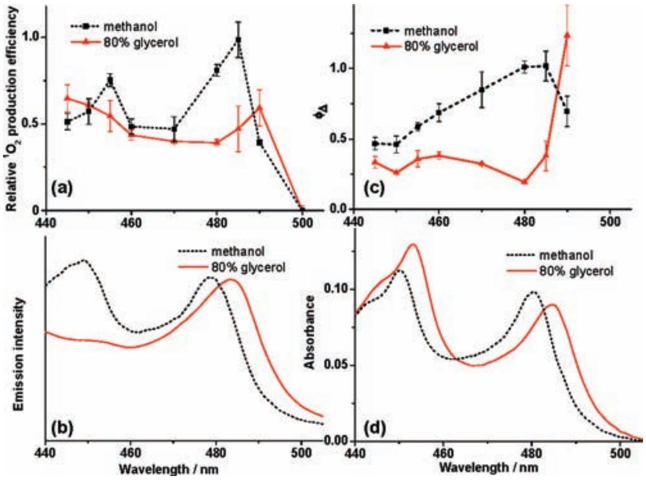

Figure 2. (a) $O_2(a^1\Delta_g)$ excitation spectra and (b) 750 nm fluorescence excitation spectra; (c) wavelength-dependent $O_2(a^1\Delta_g)$ quantum yields and (d) absorption spectra of **1** in methanol (--) and 1:4 methanol/glycerol (red —).

Using the time-resolved 1270 nm phosphorescence of $O_2(a^1\Delta_g)$ as a probe, we quantified the $O_2(a^1\Delta_g)$ production efficiencies photosensitized by **1** upon irradiation over the 445−500 nm spectral range in both nonviscous and viscous solutions. Figure 2 compares absorption spectra recorded in this region with fluorescence and $O_2(a^1\Delta_g)$ excitation spectra. It is clear that the $O_2(a^1\Delta_g)$ excitation spectrum in methanol differs from that in glycerol, and neither spectrum exactly matches the absorption spectra of **1**. A key point is that, in the $O_2(a^1\Delta_g)$ excitation spectra (Figure 2a), the 450 nm band assigned to excitation of the twisted state is much less intense than that seen in the absorption spectra. Moreover, the $O_2(a^1\Delta_g)$ excitation spectra obtained in both methanol and glycerol solutions (Figure 2a) match well the respective excitation spectra obtained using the fluorescence of the planar conformer of **1**, Figure 2b. This is further substantiated by the wavelength-dependent $O_2(a^1\Delta_g)$ quantum yields, Figure 2c. These data directly demonstrate that only the planar conformer of **1** produces significant amounts of $O_2(a^1\Delta_g)$.

The singlet state lifetimes of both conformations of the dimer (τ < 2 ns) are too short to be quenched by $O_2(X^3\Sigma_g^-)$ under our conditions. Thus, a key to understanding the behavior of **1** with respect to $O_2(a^1\Delta_g)$ production lies in the process of $S_1 \rightarrow T_1$ intersystem crossing. Low temperature EPR measurements on dimers similar to **1** suggest that the triplet state excitation is localized predominantly on a single porphyrin unit,[10] which is opposite to that for the singlet state where the excited state is highly delocalized.[11] Indeed, transient absorption measurements have shown a compound-independent T−T absorption maximum for related porphyrin monomers,[10] dimers,[8,10] and longer oligomers[8] at *ca.* 420 nm. This is in stark contrast to the ground-state absorption spectrum where the observed band maximum shifts to longer wavelengths with an increased degree of conjugation.[8]

We performed triplet state absorption measurements on **1** both in a viscous solution of 1:4 methanol/glycerol and in pure methanol. At probe wavelengths over the range 400−700 nm, we detected only monoexponential signal decays, independently of whether (i) the twisted or planar singlet excited state conformer was populated and (ii) the solutions were air- or nitrogen-saturated. Moreover, the triplet state absorption kinetics were always mirrored by the kinetics of ground state recovery; see Supporting Information. Based on these results, we conclude that only one triplet state species is present in both viscous and nonviscous solutions.

Given that a common triplet state is populated following excitation of both planar and twisted conformers of **1**, the wavelength-dependent $O_2(a^1\Delta_g)$ quantum yield must reflect an $S_1 \rightarrow T_1$ intersystem crossing efficiency that is much lower for the twisted singlet state than for the planar state. We measured the relative concentrations of the triplet state following 450 and 480 nm irradiation of **1** ($[T]^{450}$ and $[T]^{480}$) in pure methanol and 1:4 methanol/glycerol. In both solvents, $[T]^{450} \approx 1/2[T]^{480}$, and $[T]^{\mathrm{glycerol}} < [T]^{\mathrm{methanol}}$. These data are consistent with the $O_2(a^1\Delta_g)$ excitation spectra and with our hypothesis that the singlet state twisted conformer does not efficiently lead to triplet state production.

In summary, we have demonstrated that the quantum yield with which **1** sensitizes $O_2(a^1\Delta_g)$ production depends on the irradiation wavelength. The differences in the $O_2(a^1\Delta_g)$ quantum yield are particularly striking in viscous media, where the conformational dynamics of **1** plays a larger role in its photophysics. Such a viscosity- and wavelength-dependent $O_2(a^1\Delta_g)$ production efficiency could play a crucial role in many applications, including photoinduced cell death. We have recently shown that the viscosity of intracellular domains can be as high as 300 cP.[7,12] Thus, it is certainly reasonable to expect the wavelength-dependent behavior of **1** in a cell. The unique wavelength dependent properties of **1** may also be beneficial for applications requiring the controlled release of oxidizing/oxygenating species in viscous polymeric systems.

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Supporting Information Available: Experimental details, additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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