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Photostabilization of Endogenous Porphyrins: Excited State Quenching by Fused Ring Cyanoacrylates.

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Received (in XXX, XXX) 1st January 2014, Accepted 1st XXXX 2014

⁵ First published on the web 1st XXX 2014

DOI: 10.1039/b000000x

Endogenous chromophores in human skin, when exposed to sunlight, generate harmful reactive oxygen species (ROS). Protoporphyrin IX (PpIX) is one of the common chromophores in human tissue. A series of aromatic cyanoacrylates were tested as quenchers of excited singlet and triplet states of PpIX. While the diaryl cyanoacrylate (**1**) did not quench excited singlet or triplet states of PpIX, some cyanoacrylates with fused aromatic rings showed excited singlet state quenching rate constants as high as $5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (acetonitrile solution). In addition, one of the fused ring cyanoacrylates (**5**) quenches PpIX triplet states with a rate constant of $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The observed quenching rate constants correlated well with the suppression of singlet oxygen generation from PpIX under visible light exposure in the presence of dissolved oxygen. This photostabilization of endogenous chromophores can prevent or reduce ROS generation and perhaps constitute a new approach to mitigating cutaneous oxidative stress.

Introduction

Reactive oxygen species (ROS) generated by the action of sunlight on endogenous chromophores in human skin are believed to play a significant role in skin damage and disease, including premature skin aging and cancer.¹ An important class of endogenous chromophores are porphyrins which are distributed throughout the plant and animal kingdoms where they play essential roles in biological processes including oxygen transport and storage (heme), electron transport (cytochromes), and energy conversion (chlorophylls). Protoporphyrin IX (PpIX) is the direct chemical precursor to heme, a universal component present in human tissue. For example, in human blood amounts in the order of $0.5 \mu\text{M}$ PpIX are present² and in human skin cells $5 - 27 \text{ pmol PpIX per } 10^7 \text{ cells}$ have been reported.³ Detailed photophysical studies on PpIX have been reported.⁴⁻⁶ PpIX absorbs UV and visible light below 640 nm and shows fluorescence with peaks at 630 and 698 nm with a lifetime of 19.2 ns in acetonitrile solution. PpIX singlet excited states intersystem cross into triplet states with high quantum yields ($\phi = 0.63$).⁷ These long-lived triplet states are quenched efficiently by molecular oxygen to generate singlet oxygen ($^1\text{O}_2$),^{8,9} a highly reactive form of molecular oxygen that reacts with cellular components to cause protein oxidation, lipid peroxidation, and DNA damage.^{10, 11} In addition, $^1\text{O}_2$ is the precursor of other reactive oxygen species (ROS), such as peroxide radicals, superoxide and hydroxy radicals. These energy transfer and $^1\text{O}_2$ mediated processes are termed Type II mechanisms. Electron transfer from photoexcited states can also lead to ROS (Type I mechanism).¹² Increased ROS levels generate a series of signal transduction pathways by activation of skin cell surface receptors, including receptors for

epidermal growth factor, interleukin-1, insulin, keratinocyte growth factor and tumor necrosis factor- α . Activated cell surface receptors further result in up-regulation of the expression and functional activation of the nuclear transcription factor, which results in reduced collagen gene transcription and degradation of collagenous and noncollagenous molecules in the extracellular matrix, impairing the structural integrity of the skin.¹³⁻¹⁵ Therefore, controlling the generation of ROS is an important strategy for skin anti-aging technology and prevention of skin cancer.

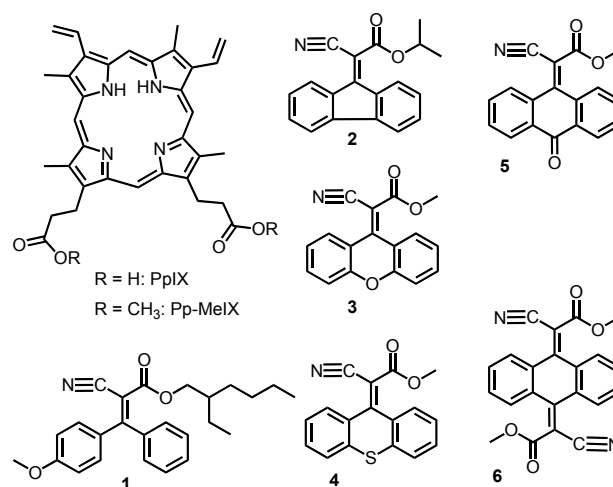


Chart 1 Structures of protoporphyrin IX (PpIX) and stabilizers 1-6.

Herein we report our surprising finding that several fused ring cyanoacrylate derivatives **2-6** (Chart 1) have the ability

to quench the excited states (singlet and triplet) of the endogenous chromophore PpIX and by doing so significantly reduce its photo-generation of singlet oxygen. Under the same condition, the non-fused ring derivative **1**, Chart 1, did not quench excited states of PpIX. Several cyanoacrylates are widely used as additives in skin care products. For example octocrylene, which has a similar structure to **1**, but lacks the methoxy substituent, is used in sunscreens. **1** is used as stabilizer for retinol, an active ingredient in anti-aging creams.

Results and Discussion

Singlet-excited state quenching of PpIX by cyanoacrylates **1-6** was studied by time-resolved fluorescence quenching. PpIX fluorescence decay traces were recorded at 690 nm after pulsed excitation at 496 nm in the absence and presence of various concentrations of **1-6**. The fluorescence lifetimes of PpIX were determined at each quencher concentration. The bimolecular quenching rate constants k_q^S were determined from the slope of the plots of the inverse fluorescence lifetimes vs. the quencher concentrations (Fig. 1). High quenching rate constants of $\sim 4\text{-}5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ were found for **2, 3, 5**, and **6**. The sulfur bridged cyanoacrylate **4** showed a one order of magnitude lower quenching rate constant. The non-bridged cyanoacrylate **1** did not show any observable PpIX singlet excited state quenching.

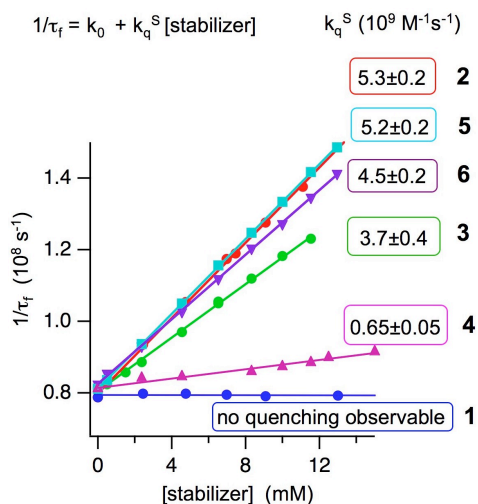


Fig. 1 Determination of the bimolecular quenching rate constants k_q^S of quenching of PpIX fluorescence in acetonitrile by cyanoacrylates **1-6** from the slope of the plot of the inverse fluorescence lifetime vs. the quencher concentration. $\lambda_{\text{ex}} = 496 \text{ nm}$, $[\text{PpIX}] = 8 \mu\text{M}$.

Because of the longer lifetime of PpIX triplet states compared to singlet excited states, reactions and phototoxicity are more likely to occur from triplet states. The kinetics of PpIX triplet state reactivity can be followed by laser flash photolysis. Fig. 2 shows the transient absorption spectrum of PpIX in acetonitrile solutions after pulsed laser excitation. At 400 nm the ground state

bleaching of PpIX is observable. The absorbance at 440 nm was assigned to the triplet state.¹⁶ In deoxygenated acetonitrile solutions, the triplet decayed with a lifetime of 52 μs with simultaneous recovery of the ground state absorption (Fig. 2, right).

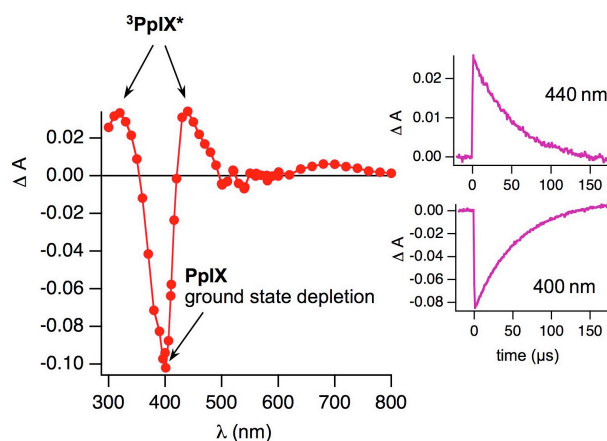


Fig. 2 Transient absorption spectrum of an argon saturated acetonitrile solution of PpIX ($8 \mu\text{M}$) recorded 0.1 to 1.5 μs after pulsed laser excitation (532 nm, 7 ns pulse width). Kinetic traces monitored at 400 and 440 nm are shown on the right.

In the presence of the quenchers **2-6** the triplet lifetime decreased and the ground state absorption, monitored at 400 nm, was recovered. From the plot of the inverse triplet lifetimes vs. the quencher concentration the bimolecular triplet quenching rate constants k_q^T were determined (Fig. 3).

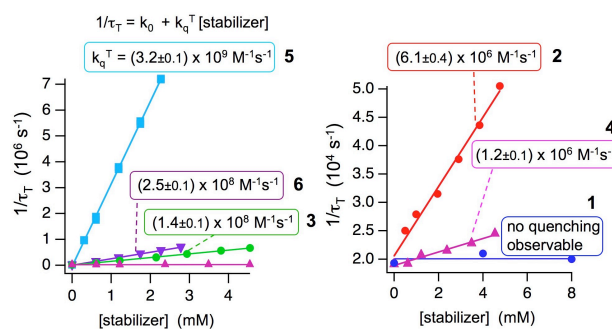


Fig. 3 Determination of the bimolecular quenching rate constants k_q^T of quenching of PpIX triplet states in acetonitrile by **1-6** from the slope of the plot of the inverse triplet lifetime (monitored at 440 nm) vs. the quencher concentration. $[\text{PpIX}] = 8 \mu\text{M}$.

Table 1 summarizes the measured quenching rate constants. Although for PpIX singlet excited state quenching, the rate constants for quenchers **2, 3, 5** and **6** are similar ($k_q^S \sim 4\text{-}5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), the rate constants for triplet state quenching cover a range over several orders of magnitude. The highest rate constant was observed for **5** ($k_q^T = 3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) whereas **2** shows a rate constant of only $6.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. Consistent with the singlet excited state quenching, the sulfur bridged cyanoacrylate **4** shows an even lower triplet quenching rate constant ($k_q^T = 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) and the non-bridged cyanoacrylate **1** did not quench PpIX triplet states.

Table 1 Rate constants of quenching of singlet and triplet excited states of PpIX (k_q^S and k_q^T , respectively) by stabilizers **1-6**. Stern-Volmer constant (K_{ST}) of suppression of 1O_2 phosphorescence by stabilizers **1-6**.

stabilizers	k_q^S (10^9 $M^{-1}s^{-1}$)	k_q^T (10^9 $M^{-1}s^{-1}$)	K_{ST} (M^{-1})
1	- ^a	- ^a	0.2
2	5.3	0.0061	30
3	3.7	0.14	27
4	0.65	0.0012	1.2
5	5.2	3.2	240
6	4.5	0.25	31

^a no quenching observable.

Possible mechanisms of quenching of PpIX excited states involve energy or electron transfer. Because of the low singlet and triplet energies of PpIX ($E_S = 191$ kJ/mol, $E_T = 150$ kJ/mol),⁵ which are expected to be well below the singlet and triplet energies of cyanoacrylates, energy transfer mechanisms are unlikely. Therefore, the probable quenching mechanism involves electron transfer. Because in laser flash photolysis experiments simultaneous recovery of the ground state absorption of PpIX was observed in the PpIX triplet quenching by **2-6**, and no major photodecomposition was observed in the presence of cyanoacrylates, the electron transfer is probably followed by fast back-electron transfer re-generating PpIX in the ground state. The differences in the quenching rate constants of PpIX singlet and triplet excited states should be reflected in the redox potentials of the cyanoacrylates, which we were not able to determine reliably at the current stage.

Singlet oxygen phosphorescence measurements were performed to investigate if the large differences in triplet quenching rate constants have an impact on the observed singlet oxygen yields generated from PpIX photoexcited states. Singlet oxygen, the first excited state of molecular oxygen, shows a characteristic phosphorescence at 1270 nm.¹⁷ The dimethyl ester derivative of PpIX (Pp-MeIX, Chart 1) was selected as sensitizer, because of better solubility in a solvent with long singlet oxygen lifetime ($CDCl_3$). Singlet oxygen lifetimes up to 8.9 ms have been reported in $CDCl_3$.¹⁸ The excited state properties of protoporphyrin IX are not affected significantly by the methyl ester functionality. Air saturated $CDCl_3$ solutions of Pp-MeIX were irradiated with a pulsed Nd-YAG laser with visible light at 532 nm, a wavelength where the stabilizers are transparent. Fig. 4 shows the generated kinetic traces of singlet oxygen phosphorescence in the absence and presence of stabilizers.

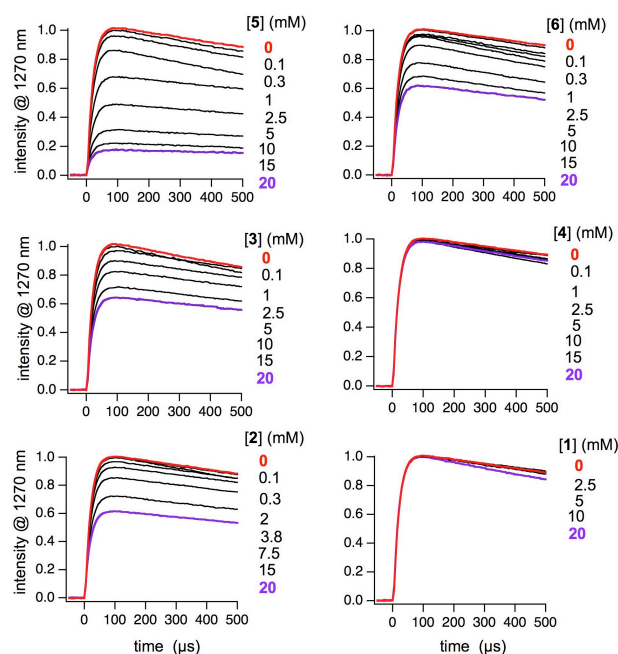


Fig. 4 Singlet oxygen phosphorescence traces monitored at 1270 nm generated by pulsed laser excitation at 532 nm of Pp-MeIX (17 μM) in air saturated $CDCl_3$ solutions in the absence (red) and presence of variable amounts of stabilizers **1-6**.

Comparison of these kinetic traces shows major differences in signal intensity for the different stabilizers. The non-bridged stabilizer **1** did not suppress singlet oxygen generation. The lack of singlet oxygen suppression is consistent with the lack of observable quenching of singlet or triplet excited states of PpIX by **1** (Table 1). The bridged stabilizers suppressed singlet oxygen generation to different degrees with **5** showing the largest suppression.

Stern-Volmer analysis of the data shown in Fig. 4 was performed to quantify the suppression of singlet oxygen generation by the stabilizers. The singlet oxygen phosphorescence intensity in the absence of stabilizer (I_0) divided by the singlet oxygen phosphorescence intensity in the presence of stabilizer (I) was plotted against the stabilizer concentration (Fig. 5). From the slope of these plots the Stern-Volmer constants were extracted and listed in Table 1. The Stern-Volmer constants are a direct measure of the singlet oxygen suppression efficiency of the stabilizers. The values of the Stern-Volmer constants can be grouped into three different ranges. For **1** and **4** only negligible singlet oxygen suppression and low Stern-Volmer constants were observed, which is probably caused by the low PpIX singlet and triplet quenching rate constants of these stabilizers. For **2**, **3**, and **6** Stern-Volmer constants of ~ 30 M^{-1} were observed. For these three stabilizers high PpIX singlet quenching rate constants ($k_q^S \sim 5 \times 10^9$ $M^{-1}s^{-1}$) but low triplet quenching rate constants ($k_q^T < 10^9$ $M^{-1}s^{-1}$) were observed. For **2**, **3**, and **6**, the singlet oxygen suppression is probably dominated by Pp-MeIX singlet excited state quenching by these stabilizers. The highest Stern-Volmer constant was observed for **5** (240 M^{-1}). Because of the very high PpIX triplet quenching rate constant ($k_q^T = 3.2 \times 10^9$ $M^{-1}s^{-1}$), the high singlet oxygen

suppression efficiency of **5** is probably dominated by triplet quenching.

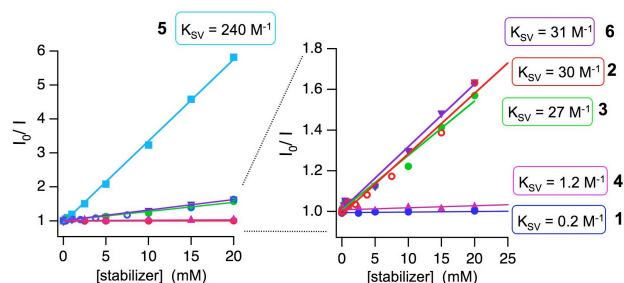


Fig. 5 Stern-Volmer plots of singlet oxygen phosphorescence data from Fig. 4.

The bimolecular quenching rate constants for singlet and triplet PpIX state quenching by molecular oxygen (O_2) were determined to be able to model the entire competitive kinetics of PpIX quenching and singlet oxygen suppression by the stabilizers. Both, singlet excited and triplet states of PpIX are quenched by molecular oxygen. The quenching rate constants of singlet excited state quenching of PpIX by molecular oxygen were determined by time correlated single photon counting using fluorescence decay traces of PpIX after pulsed excitation (496 nm). Variation of the oxygen concentration in the solvent was achieved by bubbling the sample solution with different O_2/N_2 gas mixtures. The bimolecular quenching rate constants were extracted from the plots of the inverse singlet lifetimes vs. the oxygen concentrations (Fig. S1, ESI†). The rate constants of PpIX triplet state quenching were determined by laser flash photolysis using triplet absorption decay traces of PpIX at different O_2 concentration (Fig. S2, ESI†). As consistent with the literature for other chromophores, the rate constant of PpIX singlet excited state quenching by O_2 are slightly higher than for quenching of PpIX triplet states. However, because singlet excited states of PpIX have a significantly shorter lifetime ($\tau_s = 19$ ns) compared to triplet states ($\tau_T = 52$ μ s), singlet state quenching is only effective at higher oxygen concentrations. Table 2 summarizes the singlet and triplet lifetimes in the absence of O_2 and air saturated conditions to illustrate this effect.

Table 2 Rate constants of quenching of singlet and triplet excited states of PpIX and Pp-MeIX ($k_{O_2^S}$ and $k_{O_2^T}$, respectively) by molecular oxygen. Singlet and triplet lifetimes (τ_s and τ_T , respectively) of PpIX and Pp-MeIX in the absence and presence of oxygen.

solvent	acetonitrile	$CHCl_3$
sensitizer	PpIX	Pp-MeIX
$k_{O_2^S}$ (10^9 $M^{-1}s^{-1}$)	17	9.1
$k_{O_2^T}$ (10^9 $M^{-1}s^{-1}$)	2.1	1.2
τ_s (deoxygenated)	19.2 ns	12.5 ns
$\tau_s^{O_2}$ (air saturated)	11.7 ns ^a	9.8 ns ^b
τ_T (deoxygenated)	52 μ s	37 μ s
$\tau_T^{O_2}$ (air saturated)	0.21 μ s ^a	0.33 μ s ^b

^a $[O_2] = 1.9$ mM^{19} ; ^b $[O_2] = 2.4$ mM^{19}

With the knowledge of all rate constants involved in the PpIX excited state quenching by molecular oxygen and stabilizers **1-6** the kinetics can now be modeled. The pseudo-first order decay rate constant of PpIX singlet excited states (k_s^{obs}) is given by eq 1 and is determined from the fluorescence lifetime in the absence of oxygen and quencher (τ_s^0), the quenching rate constants ($k_{O_2^S}$ and k_q^S) and the concentrations of oxygen and stabilizer.

$$k_s^{obs} = 1/\tau_s^0 + k_{O_2^S} [O_2] + k_q^S [\text{stabilizer}] \quad (1)$$

$$k_T^{obs} = 1/\tau_T^0 + k_{O_2^T} [O_2] + k_q^T [\text{stabilizer}] \quad (2)$$

In air saturated acetonitrile solutions the first order decay rate constant of PpIX singlet excited states ($1/\tau_s^0 + k_{O_2^S} [O_2]$) has a value of 8.5×10^7 s^{-1} . If 20 mM of **4** is added, a decay rate constant of 9.8×10^7 s^{-1} is calculated from eq 1, which is similar to the rate constant in the absence of **4**. This demonstrates that 20 mM of **4** is not sufficient to quench PpIX singlet excited states which subsequently intersystem cross into triplet states followed by oxygen quenching to generate singlet oxygen. The poor singlet excited state quenching by **4** is consistent with the low Stern-Volmer constant for singlet oxygen suppression (Table 1). If stabilizer **2** is present at a concentration of 20 mM a rate constant of $k_s^{obs} = 1.9 \times 10^8$ s^{-1} is calculated from eq 1, which is approximately twice as fast as in the absence of **2**. Therefore, the PpIX triplet formation and singlet oxygen generation is reduced to about half. This is consistent with the observed singlet oxygen reduction in Fig. 4 and modest Stern-Volmer constant of singlet oxygen suppression of 30 M^{-1} . However, the first order rate constant for PpIX triplet decay (k_T^{obs}), calculated from eq 2, is similar in presence (4.9×10^6 s^{-1}) and absence (4.8×10^6 s^{-1}) of **2**. This indicates that 20 mM of **2** do not quench PpIX triplet states. Cyanoacrylate **5** shows the highest quenching rate constant of PpIX triplet states. The first order triplet decay rate constant (k_T^{obs}), calculated from eq 2, is one order of magnitude larger in the presence of 20 mM of **5** (6.9×10^7 s^{-1}). Therefore, PpIX triplet states are efficiently quenched, which subsequently prevents the formation of singlet oxygen (Fig. 4). Consistently, a high Stern-Volmer constant for singlet oxygen suppression was observed (240 M^{-1}).

Finally, the question remains if stabilizers **1-6** can directly quench 1O_2 . For two representative cyanoacrylates, **1** (non-bridged) and **2** (bridged) the 1O_2 quenching rate constants were determined by time-resolved 1O_2 phosphorescence measurements. 1O_2 was generated by sensitization with tetraphenylporphyrin. CCl_4 was selected as solvent, because of its long 1O_2 lifetime which enables the measurements of very low quenching rate constants. The observed low 1O_2 quenching rate constants of 6×10^3 $M^{-1}s^{-1}$ and 5×10^3 $M^{-1}s^{-1}$ by **1** and **2**, respectively, are too low to contribute to the overall quenching kinetics (Fig. S3, ESI†).

In conclusion, the cyanoacrylates with fused aromatic rings **2**, **3**, **5**, and **6** are effective quenchers of PpIX's singlet

excited state. PpIX singlet excited state quenching prevents the formation of PpIX triplet states which subsequently can generate toxic singlet oxygen. In addition, **5** is also an effective quencher of PpIX triplet states. With the help of these cyanoacrylates, the formation of toxic singlet oxygen can be significantly suppressed, indicating that photostabilizing endogenous porphyrins is a potentially effective strategy for reducing cutaneous oxidative stress in human skin.

Experimental

Spectroscopy and measurements: Steady-state luminescence spectra were recorded on a Fluorolog-3 fluorometer (HORIBA Jobin Yvon). Fluorescence lifetimes were measured by time correlated single photon counting on an OB920 spectrometer (Edinburgh Analytical Instruments) in conjunction with a pulsed LED (PicoQuant) as excitation light source (496 nm). Singlet oxygen phosphorescence measurements were performed on a modified Fluorolog-3 spectrometer (HORIBA Jobin Yvon) in conjunction with a liquid nitrogen cooled Ge-diode detector (Model 403S, Applied Detector Corp.). A Spectra Physics GCR-150-30 Nd:YAG laser (532 nm, ca 5 mJ/pulse, 7 ns) was used for pulsed excitation to collect $^1\text{O}_2$ phosphorescence decay traces at 1270 nm which were stored on a digital oscilloscope (TDS 360 from Tektronics). Laser flash photolysis experiments employed the pulses from a Nd:YAG laser (532 nm, 7 ns pulse width) and a computer-controlled system, as described previously.²⁰

Materials: Stabilizers **1-6** were obtained from HallStar Company. All other materials were purchased from commercial sources and used as received.

Acknowledgments

S.J. thanks the National Science Foundation for financial support through grant CHE 1111392.

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†Electronic supplementary information (ESI) available: Determination of the quenching rate constants of PpIX singlet and triplet excited states by molecular oxygen; determination of $^1\text{O}_2$ quenching rate constants by **1** and **2**.

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Graphical Contents Entry:

TOC: Tricyclic cyanoacrylates quench singlet and triplet excited states of the endogenous chromophore protoporphyrin IX to prevent harmful singlet oxygen generation.

