Photodriven Oxygen Removal via Chromophore-Mediated Singlet Oxygen Sensitization and Chemical Capture

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Supporting Information

ABSTRACT: We report a general, photochemical method for the rapid deoxygenation of organic solvents and aqueous solutions via visible light excitation of transition metal chromophores (TMCs) in the presence of singlet oxygen scavenging substrates. Either 2,5-dimethylfuran or an amino acid (histidine or tryptophan methyl ester) was used as the substrate in conjunction with an iridium or ruthenium TMC in toluene, acetonitrile, or water. This behavior is described for solutions with chromophore concentrations that are pertinent for both luminescence and transient absorption spectroscopies. These results consistently produce TMC lifetimes comparable to those measured using traditional inert gas sparging and freeze−pump−thaw techniques. This method has the added benefit of providing long-term stability (days to months); economical preparation due to the use of inexpensive, commercially available oxygen scrubbing substrates; and negligible size and weight footprints compared to traditional methods. Furthermore, attainment of dissolved [O2] < 50 μM makes this method relevant to any solution application requiring low dissolved oxygen concentration in solution, provided that the oxygenated substrate does not interfere with the intended chemical process.

INTRODUCTION

Widespread interest in transition metal chromophores (TMCs) continues to grow as they are applied in photocatalysis,1,2 biological sensing,3,4 dye-sensitized solar cells (DSSCs),1,5−7 photodynamic therapy (PDT),8 and nonlinear optical (NLO) applications.9,10 Their popularity arises from their synthetic and redox tunability and photophysical properties. TMCs that possess metal-to-ligand charge transfer (MLCT) excited states are of particular interest due to excited state lifetimes on the order of hundreds of nanoseconds to tens of microseconds and moderate to high photoluminescence quantum yields.11

Characterization of long-lived, luminescent chromophores is complicated by oxygen dissolved in organic solvents (1−5 mM) and water (0.3 mM) due to the efficient, collisional quenching of molecular excited states by ground state oxygen.12 In this process, ground state oxygen, which possesses a triplet spin multiplicity, 3O2, is promoted to an excited state of singlet spin multiplicity, 1O2 (1Δg), while returning the excited chromophore to its ground state, eqs 1−3.13,14 Many TMCs possess large quantum yields for 1O2 production, ΦΔ = 0.5−1.15,16. Excited state quenching decreases the observed lifetime, τobs, and the luminescence quantum yield of the chromophore; thus, care is often taken to deoxygenate samples either through inert gas sparging (N2 or Ar) or through the freeze−pump−thaw degas method.

Although this quenching process is detrimental to long lifetime and luminescence applications, the 1O2 produced can be advantageous for synthetic or photobiological applications when it reacts with substrates dissolved in solution. For instance, unity ΦΔ values are advantageous for PDT applications where directed irradiation generates 1O2, which attacks tumor cells.8,14 In terms of organic photochemistry, the Schenck ene reaction is an important pathway for the addition of oxygen atoms across carbon−carbon double bonds.17 Interestingly, this seemingly antagonistic pairing of excited state quenching and 1O2 production provides for an alternative method of oxygen removal from solution. A substrate known to react irreversibly with 1O2 is added to an aerated solution of a given chromophore. Upon irradiation, oxygen is permanently abstracted from solution as the photogenerated 1O2 reacts with the scavenging substrate. Recent literature reports demonstrated the applicability of sodium sulfite as a photochemical oxygen scavenger in aqueous solution and oleic acid, 9,10-dimethylnanthracene, and 2,5-dimethylfuran as photochemical oxygen scrubbers in liquid polyethylene glycol.18,19 Consequently, an expansion of these results to encompass a comprehensive methodology for the

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photochemical deoxygenation of polar, nonpolar, and aqueous solutions is necessary and would be valuable.

Our general, photochemical approach focused on the deoxygenation of tolune, acetonitrile, and water solutions containing TMCs and either 2,5-dimethylfuran (organic solvents) or an amino acid (aqueous solutions of tryptophan and histidine). The oxygen removal substrates are inexpensive and available on the kilogram scale from major chemical suppliers (2,5-dimethylfuran ~ $1.00 per gram; histidine ~ $0.60 per gram; and l-tryptophan methyl ester ~ $5.00 per gram; see Supporting Information). The convenience and economical nature of this procedure make it applicable as an alternative deoxygenation method for photochemical systems when Ar or N2 is not available or samples are required to remain deoxygenated for long time periods (e.g., days to months). Moreover, unlike large inert gas tanks and cumbersome vacuum pumps, there are no space requirements or maintenance costs associated with this method. This method could serve as a solution deoxygenation technique for any application requiring low dissolved oxygen concentrations as long as the oxygenated substrate does not interfere with the intended chemical process.

$$\text{TMC} \xrightarrow{hv} \text{TMC}^*$$  \hspace{1cm} (1)

$$\text{TMC}^* \xrightarrow{k_2} \text{scavenger}$$  \hspace{1cm} (2)

$$\text{TMC}^* + \text{O}_2 (\Delta g) \xrightarrow{3} \text{scavenger} \cdot \text{O}_2 \cdot \text{complex}$$  \hspace{1cm} (4)

### EXPERIMENTAL SECTION

**General.** Tris(2,2′-bipyridine)ruthenium(II) dichloride and all other reagents and solvents were purchased from Sigma-Aldrich and used as received. Tris(2,2′-bipyridine)ruthenium(II) dihexafluorophosphate was prepared from the anion metathesis reaction of tris(2,2′-bipyridine)ruthenium(II) dichloride with potassium hexafluorophosphate. 1H NMR spectra were measured on a Bruker 600 MHz Avance NMR spectrometer, referenced to the internal residual solvent peak, and processed using TopSpin 3.5 software. Argon gas (Airgas, 99.999%) was used to sparge spectroscopic samples.

**Synthesis of [Ir(III)(pbt)2(dpm)]0**. The compound was synthesized using previously reported procedures.20,21 The free ligand 2,2′,6,6′-tetrakis(3,5-heptanedione, dpm, (0.80 mL, 3.8 mmol) was added to a suspension of [Ir(pbt)2Cl]2 dimer (0.2501 g, 0.19 mmol) in tetramethyl-3,5-heptanedione, dpm, (0.80 mL, 3.8 mmol) was added to the mixture which was subsequently refluxed for 1 h to yield an orange microcrystalline powder. The precipitate was induced precipitation. The suspension was cooled in a refrigerator (3 °C) for 9.0 mmol) was added to the mixture which was subsequently refluxed for 16 h under nitrogen. After being cooled to room temperature, the crude reaction mixture was filtered through a silica plug using dichloromethane as the eluent. The solution volume was decreased by filtration on a Buchner funnel, washed with cold ethanol, diethyl ether, and hexanes, and dried in a vacuum oven (55 °C) to recover 0.2394 g of orange powder (3.0 mmol, 78% yield). 1H NMR ((CD3)2CO, 600 MHz): 8.16 (dd, 2H, J = 7.8, 0.6 Hz), 8.02 (d, 2H, J = 7.8 Hz), 7.75 (dd, 2H, J = 7.2, 0.6 Hz), 7.52 (td, 2H, J = 7.8, 1.2 Hz), 7.45 (td, 2H, J = 7.8, 1.2 Hz), 6.86 (td, 2H, J = 7.2, 1.2 Hz), 6.62 (td, 2H, J = 7.2, 1.8 Hz), 6.50 (d, 2H, J = 7.8 Hz), 5.49 (s, 1H), 0.82 (s, 18H).

**RESULTS AND DISCUSSION**

Experiments to establish the viability of this photochemical deoxygenation methodology were performed in iterative fashion. Initial studies were carried out in 2 mm cuvettes and characterized using a nanosecond transient absorption (TA) geometry in which the pump and probe beams are separated by a small angle. This work was then expanded to include a thorough characterization of the chemical deoxygenation process in 1 cm cuvettes with TMC concentrations pertinent to both luminescence and TA spectroscopies.

The introductory set of 2 mm cuvette samples were prepared by dissolving the TMC of interest in the appropriate solvent in cuvettes equipped with stir bars. Care was taken to minimize the headspace in the cuvettes, and PTFE stops were used to seal the cells. We estimate that the oxygen content of a 5 μL air bubble present in the headspace of a cuvette would be less than 5% of the total amount of oxygen initially dissolved in solution (see Supporting Information for detailed analysis). Samples containing oxygen scavenging substrates were stirred and irradiated with a 450 nm CW laser in order to deoxygenate the
solution via eqs 1–4. Samples were irradiated until the maximum TMC lifetime was achieved.

Initial experiments were carried out in the nonpolar solvent toluene using the TMC [IrIII(pbt)2(dpm)]0, where pbt is 2-phenylbenzothiazole and dpm is dipivaloylmethanato, with 2,5-dimethylfuran as the oxygen scavenging substrate. 2,5-Dimethylfuran was chosen because of its high solubility in common organic solvents and prior research that demonstrated rapid chemical reactivity with 1O2 which results in the formation of a stable diketone product and hydrogen peroxide.

Experimental UV–vis absorption spectra of [IrIII(pbt)2(dpm)]0 in aerated toluene solutions with and without 250 mM 2,5-dimethylfuran are shown in Figure 1A. The dominant absorption bands between 400–575 nm were assigned to MLCT electronic transitions of mixed singlet and triplet character based on relatively weak extinction coefficients, ε ≈ 5000 M<sup>−1</sup> cm<sup>−1</sup> (see Figure S1), and analogy to the related [IrIII(pbt)2(acac)]<sup>0</sup> compound. Normalized TA spectra obtained 5 ns after pulsed 400 nm excitation of the [IrIII(pbt)2(dpm)]<sup>0</sup> samples at room temperature are presented in Figure 1B. Excited state absorption (ESA) features were observed from 400–900 nm regardless of the presence of 2,5-dimethylfuran, and the TA spectra were superimposable for all time delays. Single wavelength kinetics were monitored at the 525 nm ESA maximum (Figure 1C) and exhibited single exponential decay behavior. The excited state lifetime of the TMC-only in toluene was 90 ns in the presence of dissolved oxygen. In contrast, [IrIII(pbt)2(dpm)]<sup>0</sup> in 250 mM 2,5-dimethylfuran toluene solution exhibited a lifetime of τ = 1.29 μs following 450 nm irradiation for 30 min.

The superimposable nature of the transient spectra and single exponential decay kinetics indicates relaxation of a single excited state back to the ground state. Additionally, a lack of chemical interaction between 2,5-dimethylfuran and [IrIII(pbt)2(dpm)]<sup>0</sup>, in either the ground or excited state, is inferred from the spectrally indistinguishable UV–vis-absorption and TA spectra when comparing the TMC-only and 250 mM 2,5-dimethylfuran toluene solutions (shown in Figure S2).

The stability and longevity of the photochemically deoxygenated samples were investigated by intermittently measuring τ<sub>obs</sub> over a period of several days to weeks after initial preparation. Samples were stored in the dark between measurements. Individual data points are presented with 10% error bars in Figure 1D along with the average τ<sub>obs</sub> and associated 10% error (dashed line and gray shaded region, respectively). The TMC-only lifetime in toluene is represented by the dotted line for reference. Excellent long-term stability was demonstrated for the 250 mM 2,5-dimethylfuran toluene solution sample with τ<sub>obs</sub> averaging 1.21 μs over measurements spanning 21 days and τ<sub>obs</sub> = 1.10 μs after 60 days. In order to validate the method in polar solvents, the quintessential d⁶ TMC [Ru(bpy)₃]²⁺, where bpy is 2,2’-bipyridine, was chosen for use in either acetonitrile as the
hexafluorophosphate (PF$_6$) salt with 2,5-dimethylfuran or aqueous solutions as the chloride salt with an amino acid due to extensive photophysical characterization of both the TMC and oxygen scavenging substrates available in the literature.$^{22,25,26}$

UV−vis absorption spectra of the [Ru(bpy)$_3$](PF$_6$)$_2$ acetonitrile system are shown in Figure 2A. The dominant absorption bands between 400−575 nm are attributed to MLCT electronic transitions, [Ru$^{II}$(bpy)$_3$]$^{2+}$ →[Ru$^{III}$(bpy$^-$)(bpy)$_2$]$^{2+}$. Normalized TA spectra obtained 5 ns after pulsed 400 nm excitation of the [Ru(bpy)$_3$](PF$_6$)$_2$ samples at room temperature are presented in Figure 2B. The observed transient bleach of the MLCT band and long-wavelength ESA features were superimposable for all time delays monitored and consistent with previous results.$^{25}$ Excited state relaxation kinetics were monitored at the 450 nm bleach and well described by single exponential decay behavior with $\tau = 160$ ns for the TMC-only solution (Figure 2C). The 2,5-dimethylfuran-containing acetonitrile sample exhibited a 5-fold enhancement of the excited state lifetime with $\tau = 840$ ns. The photophysical characteristics of aqueous [Ru(bpy)$_3$]Cl$_2$ solutions containing 260 mM L-tryptophan methyl ester were identical to the [Ru(bpy)$_3$](PF$_6$)$_2$ acetonitrile solutions (Figure S3). However, the excited state lifetimes differed for the aqueous samples with $\tau = 370$ ns for the TMC-only sample which increased to 630 ns for the 260 mM L-tryptophan methyl ester sample after irradiation. Analogous to the iridium system, no spectroscopic evidence of chemical interaction between [Ru(bpy)$_3$]$^{2+}$ and the oxygen scavenging substrates was observed, and the samples were stable over periods of days to weeks following the initial sample irradiation.

It is worthwhile to note that the excited-state lifetimes of argon sparged samples, which were sealed with rubber septa as opposed to PTFE stoppers, decreased to the aerated, TMC-only value after a single day of storage.

While the above measurements were performed in 2.0 mm cuvettes using a TA geometry in which the pump and probe beams were separated by a small angle, the versatility of this method was confirmed and expanded using standard 1.0 cm cuvettes in a T-shaped photoluminescence setup. This instrumental arrangement allowed for variation of the irradiation source between a 450 W Xe arc lamp and a Q-switched Nd:YAG laser equipped with an OPO tuned to 450 nm (6.6−8.8 mJ/cm$^2$ per pulse) while permitting the convenient collection of lifetime data. Furthermore, the method was verified to work for samples with ground state absorption values pertinent for both luminescence ($A_{450\text{nm}} = 0.2$) and pulsed laser ($A_{450\text{nm}} = 0.6$) measurements.

For the 1.0 cm cuvette measurements, the TMC samples were prepared as before with small magnetic stir bars, minimized headspace, and PTFE screw caps to seal the cells. The stirred sample solutions were irradiated for a period of time (30−60s of 10 Hz laser pulses or CW arc lamp photolysis, depending on the sample) followed by measurement of the luminescence lifetime. This process was continued until a constant $\tau_{\text{obs}}$ was reached. These experiments were conducted at high and low TMC

Figure 2. Photophysical data for [Ru$^{II}$(bpy)$_3$](PF$_6$)$_2$ in 250 mM 2,5-dimethylfuran acetonitrile solution following irradiation at 450 nm compared to TMC-only in acetonitrile: (A) normalized UV−vis absorbance spectra; (B) normalized transient absorbance (TA) spectra; (C) normalized TA kinetics monitored at 450 nm; (D) excited-state lifetimes monitored after sample preparation. See text for additional detail.
concentrations using both the arc lamp and laser irradiation sources for \([\text{Ir}^{III}(\text{pbt})_2(\text{dpm})]_0\) in 250 mM 2,5-dimethylfuran toluene solution; \([\text{Ru}^{III}(\text{bpy})_3](\text{PF}_6)_2\) in 250 mM 2,5-dimethylfuran acetonitrile solution; and \([\text{Ru}^{III}(\text{bpy})_3]\text{Cl}_2\) in 250 mM aqueous L-histidine. Kinetic data plots shown in terms of both luminescence lifetime or dissolved oxygen concentration as a function of irradiation time are presented for all of the combinations studied in Figure 3.

The collisional, energy transfer quenching of molecular excited states is governed by the Stern–Volmer relationship (eq 5).^{26–28}

\[
\frac{I}{I_0} = \frac{\tau_0}{\tau} = 1 + k_q [Q] = 1 + K_{SV} [Q]
\]

The fraction of excited states quenched is related to the lifetime of the chromophore in the absence of quencher \((\tau_0)\), the quencher concentration in solution \(([Q])\), and the bimolecular quenching rate constant \((k_q)\). The Stern–Volmer constant, \(K_{SV}\),

Figure 3. Excited state lifetime (left column) or dissolved oxygen concentration (right column) measured as a function of irradiation time for the TMC/scavenger/solvent combinations studied. The irradiation source used was either a 450 W Xe arc lamp (colored symbols) or pulsed 532 nm laser light (dark gray symbols). The sample absorbance at 450 nm was either 0.2 (open symbols) or 0.6 (filled symbols) in 1 cm path length cuvettes.
is the product of $k_0$ and $\tau_0$. The lifetime of the TMC and the bimolecular quenching constant of a TMC by ground state oxygen can be independently measured. Therefore, the solution oxygen concentration, i.e. [Q], can be determined after any duration of photolysis using eq 5.

The rate of oxygen removal from the system is dependent on the quantum yield of $^{1}$O$_2$ production (eq 3) for a particular chromophore/solvent combination and the bimolecular reaction of $^{1}$O$_2$ with the scavenger molecule in solution (eq 4). The secondary, bimolecular reaction occurs under pseudo-first-order conditions ([scavenger] $\gg$ [O$_2$]) and will be constant throughout the photolysis. The quantum yield of $^{1}$O$_2$ production will vary depending on the concentration and lifetime of the chromophore excited-state and the $^{3}$O$_2$ concentration in solution. Explicit quantum yield values for oxygen removal were not determined for any of the chromophore solvent combinations tested because this value would change as the oxygen concentration in solution changes and detailed actinometry experiments were not performed. It is clear from the data that quantum yield values for oxygen removal vary across the chromophore/solvent systems. [Ir$^{III}$(pbt)$_2$(dpm)]$^0$ has the longest lifetime and was tested in toluene (2.1 mM $[^3$O$_2$]), resulting in the fastest rate of oxygen removal. An increase in the number of photons absorbed by or delivered to the system will result in an increase in the TMC excited-state concentration and the resulting oxygen capture rate. Empirically, the 450 W Xe arc lamp provides a greater photon flux than the pulsed Nd:YAG/OPO source, although detailed actinometry experiments were not conducted on either irradiation source. Additionally, the rate of oxygen removal necessarily decreases as the dissolved oxygen concentration in solution diminishes. For all data sets, an initial, rapid decrease in the ground state oxygen concentration in solution is observed (see Figure 3). The rate of the chemical capture process starts to diminish appreciably when the Stern–Volmer quenching ratio ($\tau_o/\tau$) approaches 1.10 which is the point when only 10% of excited states are quenched and when the intrinsic lifetime of the chromophore becomes the dominant relaxation pathway of the excited state. Further photolysis results in continued oxygen consumption until a plateau is reached when the Stern–Volmer quenching ratio reaches: 1.01–1.03 (1–3% excited states quenched) for [Ir$^{III}$(pbt)$_2$(dpm)]$^0$ and 250 mM 2,5-dimethylfuran in toluene; 1.05–1.10 (5–10% excited states quenched) for [Ru(bpy)$_3$](PF$_6$)$_2$ and 250 mM 2,5-dimethylfuran in acetonitrile; or 1.01–1.05 (1–5% excited states quenched) for [Ru(bpy)$_3$]Cl$_2$ and 250 mM L-histidine in water. In the scope of this work, we chose the irradiation time required to reach the maximum lifetime value as a simple, semiquantitative metric for sample deoxygenation. These irradiation times are provided in Table 1 for the different TMC/scavenger/solvent systems along with lifetime values obtained for aerated and freeze–pump–thaw degassed solutions for comparison.

In order to achieve the freeze–pump–thaw lifetime for any of the TMC/scavenger/solvent combinations tested, the dissolved oxygen concentration would have to decrease below 1 $\mu$M in solution. Although this method was unable to reach the 1 $\mu$M threshold, dissolved [O$_2$] < 50 $\mu$M was consistently realized, which yielded TMC lifetimes within 10% of the freeze–pump–thaw values. The results for [Ir$^{III}$(pbt)$_2$(dpm)]$^0$ with 2,5-dimethylfuran in toluene and [Ru(bpy)$_3$]Cl$_2$ with L-histidine in water are particularly remarkable, as the lifetime values following

<p>| Table 1. Summary of Photochemical Deoxygenation Parameters for TMC/O$_2$ Scavenger Systems |</p>
<table>
<thead>
<tr>
<th>sample</th>
<th>solvent</th>
<th>absorption (450 nm)</th>
<th>irradiation source</th>
<th>maximum lifetime (ns)</th>
<th>time to max lifetime (min)</th>
<th>[O$_2$] at max lifetime ($\mu$M)</th>
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<td><a href="PF$_6$">Ru(bpy)$_3$</a>$_2$ + 2,5-dimethylfuran</td>
<td>water</td>
<td>0.2</td>
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<td>29</td>
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<td></td>
<td>acetonitrile</td>
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<td>lamp</td>
<td>590</td>
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<td>10</td>
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<tr>
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<td>lamp</td>
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<td>29 $^b$</td>
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<td></td>
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<td></td>
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<td>Aerated Lifetime</td>
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<td>1</td>
<td>2000$^b$</td>
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<td></td>
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<td>Freeze–Pump–Thaw Lifetime</td>
<td>910</td>
<td>0.5$^b$</td>
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<tr>
<td>[Ir(pbt)$_2$(dpm)] + 2,5-dimethylfuran</td>
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<td>0.1$^b$</td>
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</table>

$^a$Lifetimes given with $\pm$10% error. $^b$Determined using $K_{SV}$ and lifetime data and in agreement with literature values in Handbook of Photochemistry, 3rd ed., 2006. $^c$Estimated using a value of $K_{SV}$ and lifetime data and in agreement with literature values in Handbook of Photochemistry, 3rd ed., 2006.

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irradiation are all within 5% of the freeze–pump–thaw lifetime. Not only does this chemical capture method achieve low concentrations of dissolved oxygen, it does so in rapid fashion. Suitable oxygen removal using traditional methods require 10–15 min of inert gas sparging or 30–60 min of freeze–pump–thaw degas cycles. This chemical capture method achieves acceptable levels of oxygen removal within this time frame, and, in some instances, achieves the requisite oxygen concentration levels of less than 50 μM in under 10 min. Along with clear applicability as a photochemical deoxygenation method for spectroscopy, this method could also prove useful for any application requiring low dissolved oxygen concentration in solution such as synthetic organic chemistry.

**CONCLUSION**

In summary, a method for the rapid, in situ deoxygenation of aqueous and organic solutions was demonstrated using visible light irradiation of TMCs in the presence of oxygen scavenging substrates, namely, 2,5-dimethylfuran, L-tryptophan methyl ester, and L-histidine. Enhanced excited state lifetimes in comparison with those obtained via inert gas sparging and freeze–pump–thaw techniques, were observed for sealed samples over the duration of several days to months. This method should be compatible with other known oxygen scavengers such as butylated hydroxytoluene (BHT) in organic solvents or the amino acid methionine in water. Furthermore, a plethora of TMCs and organic chromophores capable of sensitizing \( \text{O}_2 \) should behave similarly to the exemplars described herein. By employing inexpensive substrates and low-power laser light, this method provides a portable, cost-effective alternative to traditional inert gas sparging and freeze–pump–thaw degassing techniques for solution deoxygenation.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01226.

Bulk prices of additives; \( ^1 \text{H} \) NMR spectrum of \([\text{Ir}^{III}(\text{pbt})_2(\text{dpm})]^{3+}\); analysis of \( \text{O}_2 \) headspace content; molar absorption spectrum of \([\text{Ir}^{III}(\text{pbt})_2(\text{dpm})]^{3+}\); UV–visible absorption spectra for samples before and after laser irradiation; photophysical data for \([\text{Ru}(\text{bpy})_3]^{2+}\) in 260 mM L-tryptophan methyl ester aqueous solution (PDF)

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**ABBREVIATIONS**

ESA, excited state absorption; CW, continuous wave; MLCT, metal-to-ligand charge transfer; TA, transient absorption; TMC, transition metal chromophore

**REFERENCES**


