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It Takes Three to Tango: The Length of the Oligothiophene Chain Determines the Nature of the Long-Lived Excited State and the Resulting Photocytotoxicity of a Ruthenium (II) Photodrug

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TLD1433 is the first Ru(II) complex to be tested as a photodynamic therapy agent in a clinical trial. In this contribution we study TLD1433 in the context of structurally-related Ru(II)-imidazo[4,5-f][1,10]phenanthroline (ip) complexes appended with thiophene rings to decipher the unique photophysical properties which are associated with increasing oligothiophene chain length. Substitution of the ip ligand with ter- or quaterthiophene changes the nature of the long-lived triplet state from metal-to-ligand charge-transfer to $^3\pi\pi^*$ character. The addition of the third thiophene thus presents a critical juncture which not only determines the photophysics of the complex but most importantly its capacity for $^1\text{O}_2$ generation and hence the potential of the complex to be used as a photocytotoxic agent.

Recent developments highlight Ru(II) polypyridyl complexes with π -expanded ligands as a promising class of new compounds for photodynamic therapy (PDT).^[1–11] By extending the pyridyl ligands with organic chromophores, low-lying intraligand (IL) excited states become accessible, and these appear to

be crucial to the photophysical function of these systems.^[12] Our TLD1433 (**Ru-ip-3T** in this manuscript, Figure 1) is a compound of this type, having three appended thiophene rings, and has the distinction of being the first Ru(II)-based PDT agent ever to enter a human clinical trial;^[1,10,13] **Ru-ip-3T** is currently being tested in a Phase II PDT trial for non-invasive bladder cancer (ClinicalTrials.gov identifier: NCT03945162).^[10]

In vitro studies have been previously conducted on the **Ru-ip-nT** series of compounds, where *n* indicates the number of appended thiophene rings attached to an imidazo[4,5-f][1,10]phenanthroline (ip) ligand (Figure 1). Visible light illumination of SK-MEL-28 cancer cells treated with the compounds in the series led to increased photocytotoxicity with increasing *n*. The light EC_{50} values (effective concentration to reduce cell viability by 50%) were 0.72 μM , 0.26 μM , $1.9 \times 10^{-4} \mu\text{M}$ and $2.8 \times 10^{-9} \mu\text{M}$ for **Ru-ip-1T** to **Ru-ip-4T**, respectively (Figure 2d)^[11] and the corresponding PI values (ratio of dark to light EC_{50}) were 225, 434, 7.2×10^5 and 45×10^9 respectively. While these previous findings demonstrate a clear correlation between the length of the thiophene chain and the in vitro phototherapeutic effects, herein we present the key photophysical properties of the compounds in the **Ru-ip-nT** series that could be responsible for the observed photocytotoxicity.

The electronic absorption spectra of the compounds within the **Ru-ip-nT** series (Figure 2a) are characterized by IL transitions localized to the dmb and phen portion of the ip ligand below 300 nm as well as a broad metal-to-ligand charge transfer (MLCT) band in the 420–550 nm range, consistent with the spectrum of the parent $[\text{Ru}(\text{dmb})_3]^{2+}$ complex.^[14,15] An additional band centered near 370 nm is visible in **Ru-ip-2T** that shifts to longer wavelengths in **Ru-ip-3T** and **Ru-ip-4T**. This band corresponds to the $\pi\pi^*$ ^1IL transition associated with the oligothiophene.^[16] These oligothiophene-localized transitions have been computed to have substantial charge transfer character and are best described as intraligand charge transfer (ILCT) states, but are referred to herein more generally as IL.^[17,18]

The steady-state emission spectra of the complexes show a single structureless emission band centered at 625 nm (Figure 2b), suggesting a similar emissive $^3\text{MLCT}$ state for all complexes in the **Ru-ip-nT** family.^[19] The emission quantum yields (Φ_{em}) in deaerated water (five freeze pump thaw cycles under a nitrogen atmosphere) drop with increasing *n*, from 6% for **Ru-ip-1T** to below 0.1% for **Ru-ip-3T** (Table 1). Emission from **Ru-ip-4T** is barely detectable (Figure 2d). The emission

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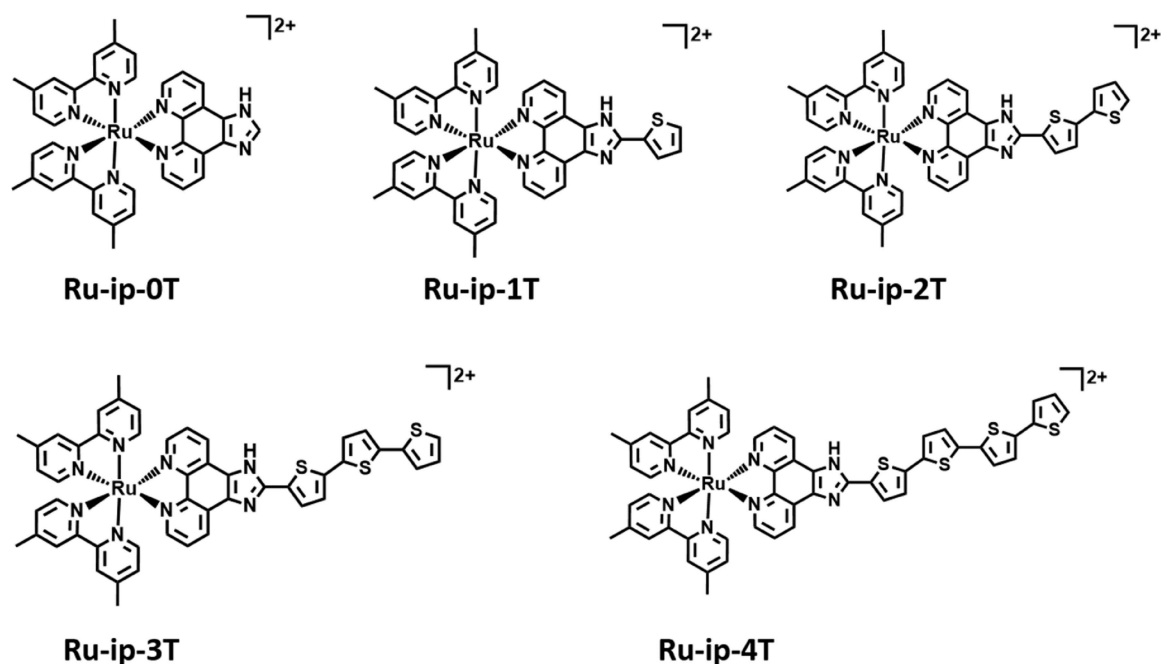
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Figure 1. Chemical structures of Ru-ip-*n*T complexes.**Table 1.** Excited state lifetimes and quantum yields for emission and singlet oxygen production for Ru-ip-*n*T under different conditions.^[a]

Complex	$\tau_{\text{em.}}^{[d]}$ Aerated/Deaerated [μs]/[μs]	$\tau_{\text{TA}}^{[d]}$ Aerated/Deaerated [μs]/[μs]	$\Phi_{\text{em.}}^{[d]}$ Aerated/Deaerated	$\Phi_{\Delta}^{[e]}$
Ru-ip-0T	0.4/0.7	0.4/0.7	0.038/0.05	0.68
Ru-ip-1T	0.4/0.8	0.4/0.7	0.044/0.06	0.61
Ru-ip-2T	0.3; 1[b]/0.6; 11[b]	1.4/14	0.006/0.04	0.71
Ru-ip-3T	0.3/0.6	1.4/48	—[c]/ 4.8×10^{-4}	0.77
Ru-ip-4T	0.3/0.6	1.4/29	—[c]/ 8.1×10^{-4}	0.81

[a] $\tau_{\text{em.}}$: emission lifetime; τ_{TA} : recovery lifetime; $\Phi_{\text{em.}}$: quantum yield of emission; Φ_{Δ} : singlet oxygen quantum yield. Singlet oxygen was determined spectroscopically by monitoring its emission centered at 1275 nm in aerated MeCN. $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ is used as the reference obtaining $\Phi_{\text{em.}}^{[27]}$ and $\Phi_{\Delta}^{[28]}$ [b] A biexponential decay of the respective signal is observed. [c] Emission is too low to obtain a reasonable estimate of the emission quantum yield. [d] Solvent used is H_2O . [e] Solvent used is MeCN.

quantum yields for Ru-ip-3T and Ru-ip-4T are extremely small and do not notably increase upon deaeration of the solvent. This suggests that collisional deactivation by $^3\text{O}_2$ is not the prime quenching process of the $^3\text{MLCT}$ state in the complexes.

The excitation spectra recorded for Ru-ip-0T, Ru-ip-1T and Ru-ip-2T using the emission signal at 640 nm resemble the respective absorption spectra (Figure 2a, b), suggesting that the emissive $^3\text{MLCT}$ state is populated regardless of whether the initially populated states are $^1\text{MLCT}$ or ^1IL (i.e., $\pi\pi^*$). The absence of excitation signals that would correspond to broad ^1IL transitions in the UV-vis spectra at 420 nm and 440 nm for Ru-ip-3T and Ru-ip-4T, respectively, indicates that excitation of the ^1IL state does not populate the emissive $^3\text{MLCT}$ state.

In addition to absorption and emission characteristics, the singlet oxygen quantum yields (Φ_{Δ}) were also measured. Values for Φ_{Δ} increase from 0.61 for Ru-ip-1T to 0.81 for Ru-ip-4T (Table 1). This trend is consistent with the trend for photocytotoxicity as reflected in the PI values that increase with *n* (see Figure 2d).^[1] This positive correlation between singlet

oxygen quantum yields and photocytotoxicity suggests that singlet oxygen is involved in their mode of action.^[20–22] Enhanced sensitivity toward oxygen is normally reflected as a drastic decrease in triplet excited state lifetime in the presence of oxygen.^[8] The relative changes of excited state lifetimes for Ru-ip-*n*T upon exposure to oxygen will be discussed in the next section.

The photophysical properties of the longer-lived excited states, from which singlet oxygen sensitization occurs, were probed by transient absorption (TA) spectroscopy yielding excited-state absorption spectra and characteristic time-constants for ground state recovery (τ_{TA}) and emission decay ($\tau_{\text{em.}}$). Table 1 summarizes these key characteristics of the long-lived excited states in aerated and deaerated water. The emission and TA lifetimes of Ru-ip-0T and Ru-ip-1T are the same, 0.4 μs , indicative of a single excited state being depopulated (Figure 3a). The fact that deaeration lengthens the lifetime by only two-fold suggests that this state is only weakly quenched by oxygen. Ru-ip-2T behaves somewhat differently than Ru-ip-0T

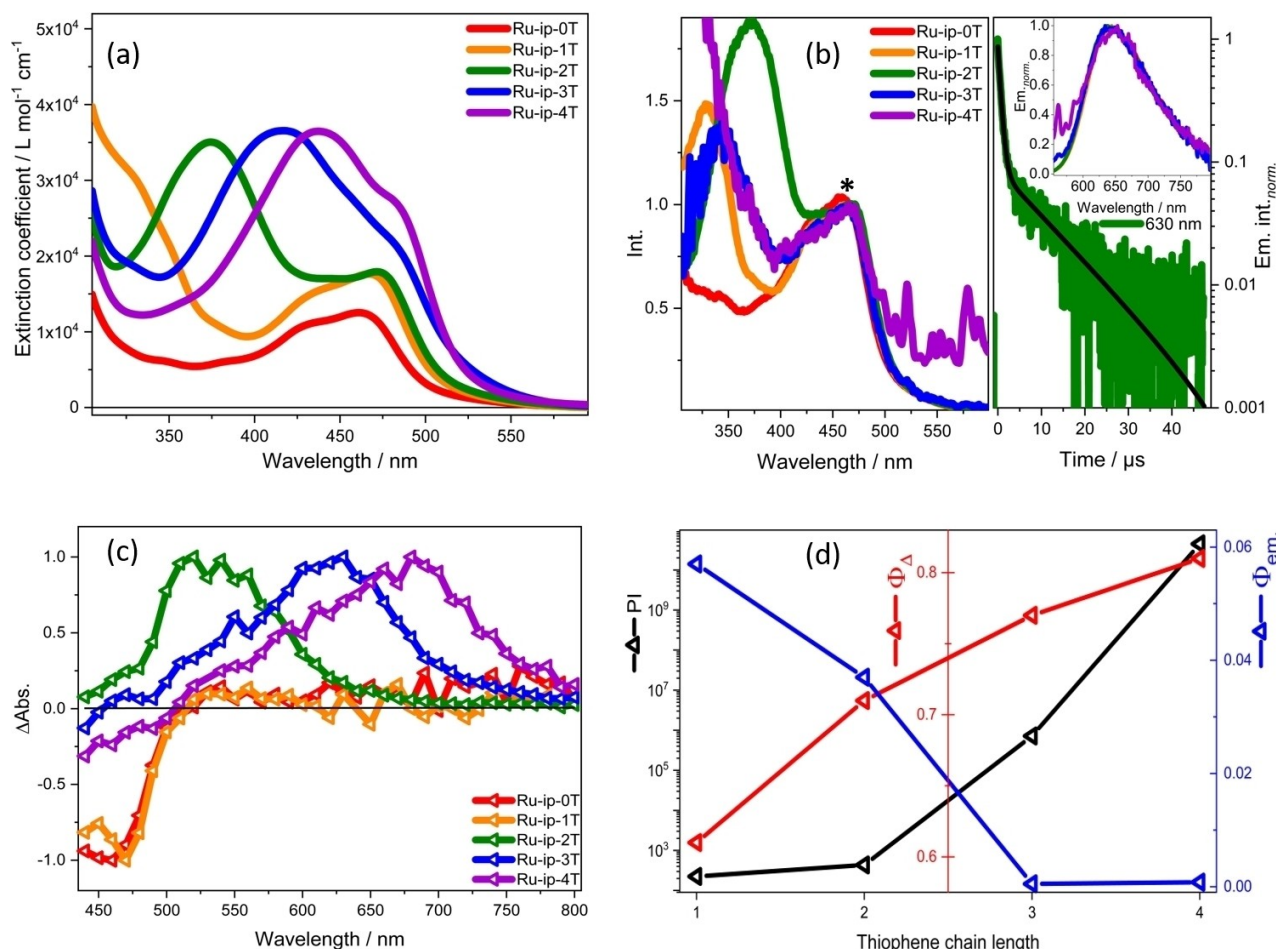


Figure 2. (a) Absorption spectra for the **Ru-ip-nT** complexes in water. (b) Excitation spectra of the **Ru-ip-nT** complexes in water at 640 nm emission normalized to the MLCT band at 480 nm (*, left); bi-exponential emission decay of **Ru-ip-2T** with lifetimes of 0.6 μs and 11 μs at 630 nm (right); Inset: Emission spectra of **Ru-ip-nT** complexes normalized to their respective maxima. (c) Nanosecond TA spectra of **Ru-ip-nT** complexes in aerated water normalized to their respective maxima at λ_{ex}: 410 nm at 300 ns. (d) Relationship between the PI values (black y-axis), singlet-oxygen quantum yield Φ_A (red y-axis) in aerated MeCN (excitation at 450 nm) and fluorescence quantum yield Φ_{em} (blue y-axis) in deaerated water (excitation at 450 nm) with increasing thiophene chain length (x-axis).^[1] The PI is defined as the ratio of EC_{50 dark} to EC_{50 visible light} values in SK-MEL-28 cells.

and **Ru-ip-1T**. In aerated aqueous solutions, τ_{em} and τ_{TA} for **Ru-ip-2T** are 1 μs and 1.4 μs, respectively. In deaerated solutions, however, the excited state(s) was much longer lived, and the emission decay was biexponential (τ_{em} = 0.6; 11 μs, τ_{TA} = 14 μs). An excited state lifetime that is ten-fold (or more) longer than the typical 1 μs lifetime of ³MLCT states in Ru(II) polypyridyl complexes and is very sensitive to O₂ is consistent with the involvement of an ³IL state.^[23,24] The second thiophene lowers the energy of this state sufficiently that the emissive ³MLCT and non-emissive ³IL states are in energetic proximity (Figure 3b). The biexponential emission decay, where the longer component matches the decay of the non-emissive state by TA, suggests that the shorter 0.6 μs component is due to prompt ³MLCT emission and the longer 11 μs lifetime corresponds to delayed emission from the ³MLCT state resulting from population of the ³MLCT from the nearly isoenergetic ³IL state (Figure 3b).^[24]

For **Ru-ip-3T** and **Ru-ip-4T**, the aerated and deaerated emission lifetimes were monoexponential and relatively short (τ_{em} ≈ 0.4 μs) as observed for **Ru-ip-0T** and **Ru-ip-1T**, indicating

that the emissive ³MLCT state cannot be populated from the ³IL when n = 3 or 4. **Ru-ip-3T** and **Ru-ip-4T** are barely emissive, with emission quantum yields too small to be calculated in the aerated solutions and vanishingly small in deaerated conditions. These observations point to the fact that a significant fraction of the **Ru-ip-3T** and **Ru-ip-4T** excited states must deactivate via non-emissive ³IL states. The aerated TA lifetimes for **Ru-ip-3T** and **Ru-ip-4T** were identical to that of **Ru-ip-2T**, consistent with efficient quenching of the ³IL states by O₂ and corroborated by all three being very good ¹O₂ sensitizers. The values for τ_{TA} in deaerated water were considerably longer, 48 μs and 29 μs for **Ru-ip-3T** and **Ru-ip-4T**, respectively. This is attributed to the ³IL state of both **Ru-ip-3T** and **Ru-ip-4T** being sufficiently lower in energy than the emissive ³MLCT state (Figure 3c), which remains unchanged throughout the series (evidenced by a constant emission maximum). The triplet is thereby trapped in the longer-lived ³IL state, unable to populate the ³MLCT, which is significantly uphill in energy. The ³IL relaxes much slower due to the reduced intersystem crossing rate in organic chromophores compared to transition

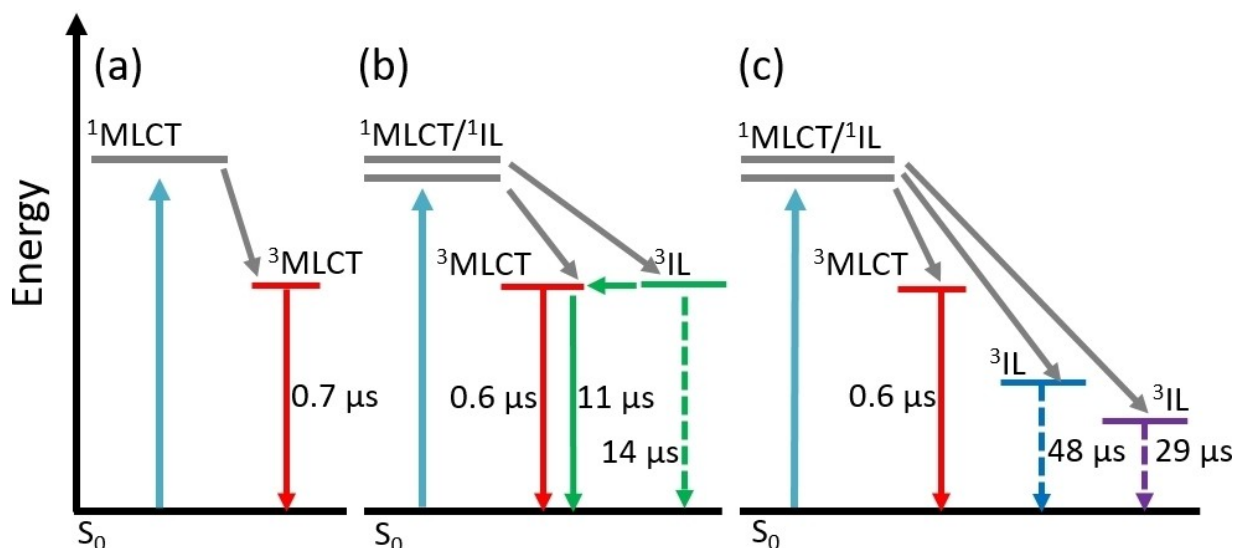


Figure 3. Jablonski diagrams depicting the photophysical models that describe the nanosecond–microsecond excited state dynamics of Ru-ip-nT complexes with 410 nm excitation in deaerated water: (a) Ru-ip-0T, Ru-ip-1T; (b) Ru-ip-2T; (c) Ru-ip-3T, Ru-ip-4T. [Note: grey arrows represent processes occurring faster than the investigated timescale.]

metal complexes, in which the heavy metal ion increases spin-orbit coupling. The lifetime of the ^3IL state for Ru-ip-4T may be shorter than the corresponding lifetime for Ru-ip-3T due to the energy gap law.^[25] However, additional relaxation pathways cannot be excluded without further investigation.

The change in the nature of the long-lived photobiologically active excited states is also supported by the spectral shape of the ns TA spectra within the Ru-ip-nT series. The TA spectra of Ru-ip-0T and Ru-ip-1T show a ground-state bleach below 510 nm plus a very weak, unstructured excited-state absorption extending from 510 to 800 nm (Figure 2c). This signature is typical for the $^3\text{MLCT}$ states of Ru(II) polypyridyl complexes that lack π -extended ligands and thus low-lying ^3IL states.^[26] The TA spectra change substantially for Ru-ip-2T through Ru-ip-4T, which have very strong and much more structured excited state absorptions with maxima at 550, 630, and 680 nm, respectively. This systematic red-shift of the excited state absorption with increasing n , by over 100 nm, is characteristic of oligothiophene-based ^3IL states.^[5,17] Thus, the ns TA spectra indicate that the character of the long-lived state changes from $^3\text{MLCT}$ for Ru-ip-0T and Ru-ip-1T to predominantly ^3IL with additional thiophene rings.

This study highlights the photophysical properties of the lowest lying excited states in a series of Ru(II) complexes, which underlie their previously reported photocytotoxicity. The results show that the spectroscopic signatures of the long-lived excited states and the biological activity in this series of complexes are determined by the energy of the non-emissive ^3IL state relative to the energy of the emissive $^3\text{MLCT}$ state. This energy depends on the length of the oligothiophene chain and determines the TA absorption and emission lifetimes, emission quantum yields and light EC_{50} values. In Ru-ip-0T and Ru-ip-1T the energy of the ^3IL is too high and the state does not contribute to the ns-/μs-photophysics and photobiology of the

complexes. Ru-ip-2T represents the situation where the $^3\text{MLCT}$ and ^3IL states are close in energy. In this case, the ^3IL state serves as an excited state reservoir for populating the $^3\text{MLCT}$ state and results in delayed $^3\text{MLCT}$ emission. In Ru-ip-3T and Ru-ip-4T the ^3IL state is the lowest-lying triplet and plays a predominant role in the excited state relaxation. The oxygen-sensitive ^3IL state appears to be responsible for the increased photocytotoxicity of these complexes. This is manifested in a sharp increase in the photocytotoxicity and efficiency of singlet oxygen sensitization upon increasing the length of the oligothiophene chain.

Experimental Section

All samples were dissolved in the respective solvent and measured in a 1 cm quartz cell. All solvents were deaerated by freeze pump thaw cycles for five times using nitrogen as inert gas. For measuring Φ_{em} and Φ_{A} samples with an OD of about 0.05 were used. Quantum yields were calculated according to the equation $\Phi_{\text{s}} = \Phi_{\text{r}} \cdot \frac{I_{\text{s}}}{I_{\text{r}}} \cdot \frac{\text{OD}_{\text{r}}}{\text{OD}_{\text{s}}} \cdot \frac{\eta_{\text{s}}^2}{\eta_{\text{r}}^2}$ where Φ_{s} and Φ_{r} are the quantum yields of the sample and a reference, respectively. I_{s} and I_{r} are the integrated emission intensity of the sample and the references, while OD, and OD_{s} are the optical densities of the sample and the reference at the excitation wavelength. η_{r} and η_{s} refer to the refractive indices of the media in the sample and the reference. Since the same medium is used for measuring the sample and the reference $\frac{\eta_{\text{s}}^2}{\eta_{\text{r}}^2}$ equals 1.

UV-vis absorption measurements utilized a Jasco V-670 spectrophotometer and emission measurements were carried out on a FLS980 spectrophotometer (Edinburgh Instruments). $^1\text{O}_2$ emission was detected using a FLS980 spectrophotometer equipped with a NIR detector with parameters upon excitation at 450 nm.

Nanosecond transient absorption measurements used a 10 Hz Nd:YAG laser (Surelite) combined with an OPO for excitation. The Transient data was recorded by a commercial detection system

(Pascher Instruments AB) with a time resolution of 10 ns. The OD of the samples at the excitation wavelength was ~ 0.25 in a 1-cm cuvette. The integrity of the samples after nanosecond measurements were checked by measuring absorption spectra before and after the measurement. No degradation was observed. Time resolved emission measurements utilized time correlation single photon counting (TCSPC, Becker & Hickl GmbH) upon excitation at 390 nm.

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Conflict of Interest

S. A. M. has a potential research conflict of interest due to a financial interest with Theralase Technologies, Inc. and Photo-Dynamic, Inc. A management plan has been created to preserve objectivity in research in accordance with UTA policy.

Keywords: excited states • photodynamic therapy • ruthenium • singlet oxygen • TLD1433 • triplet states

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