

Photostable Polynuclear Ruthenium(II) Photosensitizers Competent for Dehalogenation Photoredox Catalysis at 590 nm

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ABSTRACT: Higher nuclearity photosensitizers produced dehalogenation yields greater than 90% in the reported $[\text{Ru}(\text{bpy})_3]^{2+}$ -mediated dehalogenation of 4-bromobenzyl-2-chloro-2-phenylacetate to 4-bromobenzyl-2-phenylacetate with orange light in 7 hours, whereas after 72 hours yields of 49% were obtained with $[\text{Ru}(\text{bpy})_3]^{2+}$. Dinuclear (**D1**), trinuclear (**T1**) and quadrinuclear (**Q1**) ruthenium 2,2'-bipyridine based photosensitizers were synthesized, characterized and investigated for their photoreactivity. Three main factors were shown to lead to increased yields: i) the red-shifted absorbance of polynuclear photosensitizers, ii) the more favorable driving force for electron transfer, characterized by more positive $E_{1/2}(\text{Ru}^{2+*/+})$ and iii) the smaller population of the ^3MC state ($< 0.5\%$ for **D1**, **T1** and **Q1** vs. 48% for $[\text{Ru}(\text{bpy})_3]^{2+}$ at room temperature). Collectively, these results highlight the potential advantages of using polynuclear photosensitizers in phototriggered redox catalysis reactions.

The increased reactivity of sensitizers upon light excitation has contributed to the drastic development of the field of photoredox catalysis, where they have been harnessed to perform challenging organic transformations, difficult to achieve without the use of photoactive catalysts.¹⁻⁷ While some organic sensitizers have been reported, most are based on mononuclear transition metal complexes, including iridium, copper and ruthenium. Iridium(III) complexes are usually highly photostable and can be tuned to achieve a wide range of catalytic reactions.^{5, 8-9} However, their low molar absorption coefficients in the visible region has limited their widespread application. Copper(I) bipyridine complexes exhibit long-lived Metal-to-Ligand Charge Transfer (MLCT) excited states compatible with photoredox catalysis.¹⁰⁻¹³ Nonetheless, copper complexes are often associated with low molar absorption coefficients (ϵ) in the visible region and Jahn-Teller distortions accompanying changes in the oxidation states, which often leads to ligand-loss or scrambling, particularly problematic for heteroleptic complexes.¹⁴⁻¹⁶ In contrast, ruthenium(II) polypyridyl sensitizers absorb visible light typically with ϵ greater than $10000 \text{ M}^{-1}\text{cm}^{-1}$ and exhibit relatively long-lived excited states.¹⁷⁻²⁰ Larger ϵ are obtained with polynuclear photosensitizers (PS), which have been known to undergo excited-state electron transfer with catalysts in the presence of sacrificial electron donors or acceptors.^{17, 21-32} Ruthenium complexes exhibit greater stability than Cu complexes, but are typically more prone to ligand-loss than iridium complexes. This is often attributed to population of a metal-centered (^3MC) state.³³⁻³⁶ Hence, i) better control of the deactivation pathways, ii) the development of photosensitizers that absorb more visible light, allowing to decrease to amount of photosensitizer, iii) the use of low energy visible light and iv)

the development of stable photosensitizers represent challenges upon which photoredox catalysis could be further improved.

Here, a series of polynuclear photosensitizers was investigated for the reported visible light-induced dehalogenation of 4-bromobenzyl-2-chloro-2-phenylacetate (**1**) in the presence of a sacrificial electron donor and compared to the performance of the parent compound, $[\text{Ru}(\text{bpy})_3]^{2+}$.³⁷ These dehalogenation reactions are of synthetic and environmental importance.^{3, 11, 38-40} Fundamental understanding was garnered through Stern-Volmer analysis and variable temperature time-resolved photoluminescence spectroscopies. In comparison to $[\text{Ru}(\text{bpy})_3]^{2+}$, polynuclear complexes were stronger photo-oxidants, produced larger yields with low energy visible light and smaller catalyst loadings. In addition, they exhibited less ligand-loss photochemistry, making them a real alternative to common photoredox catalysts.

The syntheses of the polynuclear photosensitizers (**Figure 1a**) were achieved through coordination of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ to the desired bridging ligand, itself synthesized via transition-metal catalyzed coupling between 4-bromo-2,2'-bipyridine and 4,4'-dibromo-2,2'-bipyridine derivatives (**SI**). The photosensitizers exhibited ground-state absorption spectra (**Figure 1b**) and steady-state photoluminescence (**Figure 1c-d**) typical for ruthenium(II) polypyridyl complexes. The molar absorption coefficients of the MLCT transition gradually increased from $11,900 \text{ M}^{-1}\text{cm}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ to $54,900 \text{ M}^{-1}\text{cm}^{-1}$ for **Q1**, concomitant with increased absorption at longer wavelengths (**Table 1** and **Figure S32**). The excited-state lifetime (**Table 1**) was longest for **D1** (1920 ns) and decreased according to **T1** > **Q1** > $[\text{Ru}(\text{bpy})_3]^{2+}$.

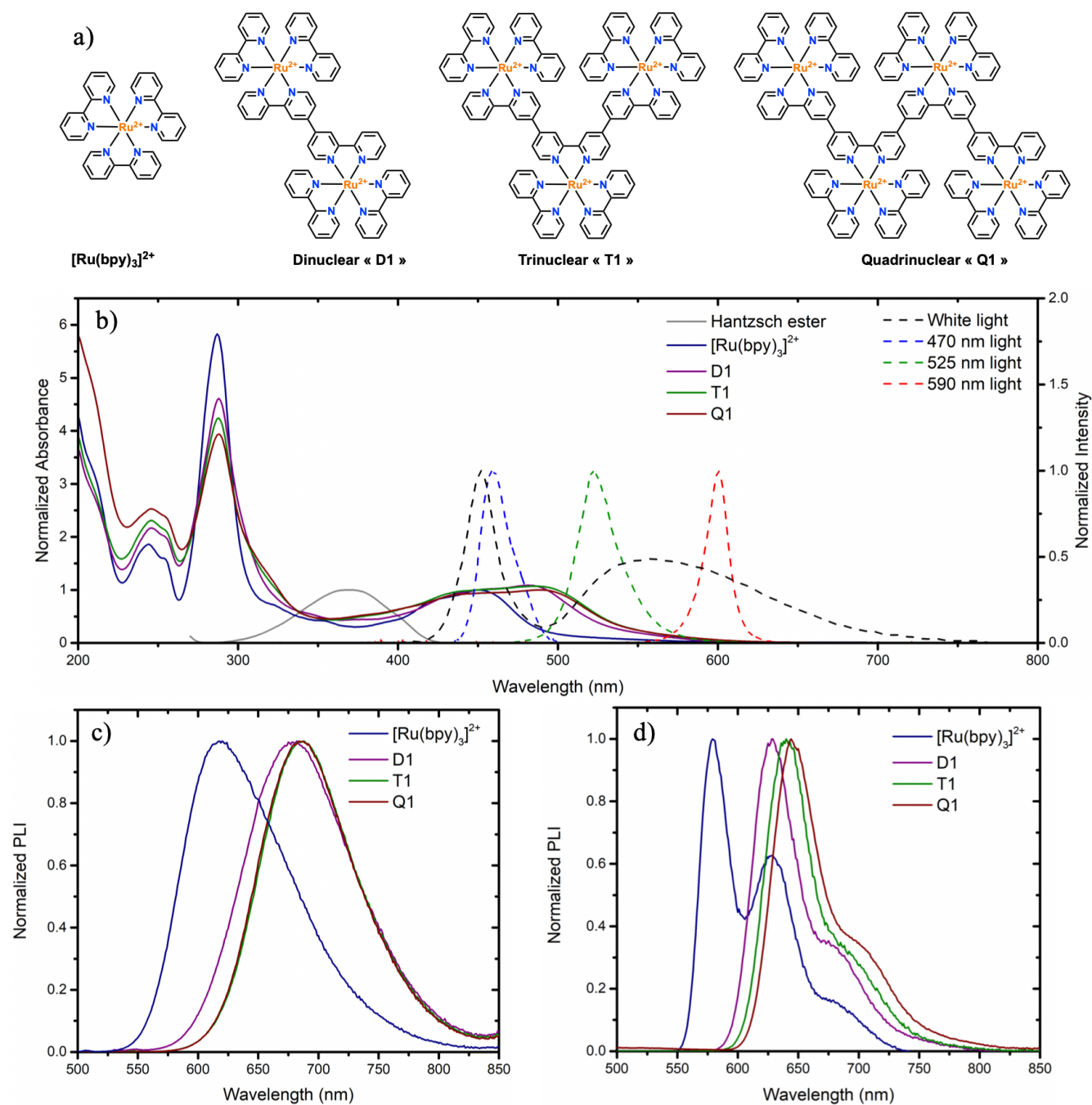


Figure 1. a) Structures of photosensitizers [Ru(bpy)₃]²⁺, D1, T1 and Q1. b) UV-Vis absorption spectra (solid lines) of the photosensitizers recorded in acetonitrile at room temperature and emission profiles (dashed lines) of the different light sources.⁴¹ Steady-state photoluminescence of the indicated photosensitizers in acetonitrile at room temperature under argon (c) and in butyronitrile at 77K (d).

Table 1. Photophysical and Electrochemical Characterization of the Photosensitizers (PS).

PS	ϵ (M ⁻¹ cm ⁻¹) ^a	τ ^b	Φ ^c	$E_{1/2}(L^{0/-})$ ^d	$E_{1/2}(Ru^{III/II})$ ^d	E_{00} ^e	$E_{1/2}(Ru^{2+*/+})$ ^d
[Ru(bpy) ₃] ²⁺	11900 (450)	1020	0.094	- 1.31	1.30	579	0.83
D1	21800 (480)	1920	0.077	- 0.99	1.33	629	0.98
T1	40100 (485)	1580	0.121	- 0.93	1.38	640	1.01
Q1	54900 (490)	1470	0.098	- 0.83	1.37	644	1.10

^a values in parenthesis indicate the corresponding wavelength in nm. ^b in ns in argon purged DMF. ^c measured in CH₃CN under argon by comparative actinometry using [Ru(bpy)₃]²⁺.2PF₆⁻ (Φ = 0.018) in CH₃CN under air as a standard.⁴² ^d V vs Ag/AgCl. ^e nm

Table 2. Photocatalysis Results with White, Blue, Green and Orange LEDs

	[PS] (mol%)	Eq. Ru center (mol%)	White light (6500K) ^a	Blue (470 nm) ^a	Green (525 nm) ^a	Orange (590 nm) ^a
[Ru(bpy) ₃] ²⁺	2.50	2.5	77 %	80 % (5h)	78 % (7h)	31 % ^b
D1	1.25	2.5	92 %	91 % (2h)	91 % (2.5h)	91 % (6.5h)
T1	0.83	2.5	91 %	93 % (2h)	93 % (2.5 h)	94 % (7h)
Q1	0.63	2.5	93 %	95% (2h)	96% (2.5h)	95 % (7h)
No PS	0	0	1% ^c	---	---	---

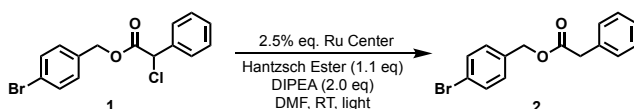
^aIsolated yields of (**2**) after column chromatography (time required for full conversion (determined by ¹H NMR)). ^b after 7 hours, 58% of starting material recovered. The yield reached 49% after 72h of irradiation, with 33% of starting material recovered. ^c 96% of starting material recovered.

The photosensitizers were electrochemically characterized in 0.1 M TBAPF₆/DMF electrolytes. The first ligand-centered reductions occurred at -0.99, -0.93 and -0.83 V vs Ag/AgCl for **D1**, **T1** and **Q1** respectively, *i.e.* >300 mV more positive than [Ru(bpy)₃]²⁺. The metal centered oxidation events were less influenced by the increased nuclearity, *i.e.* $E_{1/2}(\text{Ru}^{\text{III/II}}) = 1.33$, 1.38 and 1.37 V vs Ag/AgCl for **D1**, **T1** and **Q1** respectively. The excited-state reduction potentials were estimated using **equation 1**, with E_{00} , the energy stored in the excited-state, determined through Franck-Condon lineshape analysis of the photoluminescence spectra. These potentials are gathered in **Table 1** and highlight that the polynuclear photosensitizers were more potent photo-oxidants than [Ru(bpy)₃]²⁺.⁴³

$$E_{1/2}(\text{Ru}^{n+/n-1}) = E_{1/2}(\text{Ru}^{n/n-1}) + E_{00} \quad (\text{Eq. 1})$$

The photosensitizers were evaluated as photoredox catalysts in the dehalogenation reaction reported by C. Stephenson *et al.* (**Scheme 1**).^{37, 44} This reaction was proposed to occur by photo-induced electron transfer from diisopropylethylamine (DIPEA) to [Ru(bpy)₃]²⁺, followed by dehalogenation of 4-bromobenzyl-2-chloro-2-phenylacetate to 4-bromobenzyl-2-phenylacetate. Yields around 75% were obtained with [Ru(bpy)₃]²⁺ as photosensitizer. In this model reaction, the effects of the i) driving force for photoinduced electron transfer ii) impact of multiple ruthenium centers, iii) irradiation wavelength and iv) population of the ³MC state on the overall yield and efficiency were studied.

Scheme 1. Dehalogenation Reaction as Reported by C. Stephenson *et al.*³⁷



First, the photosensitizers were evaluated in conditions similar to those reported. The overall concentration of each polynuclear photosensitizer was adjusted to 2.5 mol% of ruthenium center. Therefore, the number of absorbed photons was similar in all cases. White light illumination during 24h of a DMF solution containing **1** in the presence of 2 equiv. DIPEA, 1.1 equiv. of Hantzsch ester (HE) and 2.5 mol% of [Ru(bpy)₃]²⁺ led to the formation of **2** in 77% yield, matching the reported yield.³⁷ Excitingly, with the polynuclear photosensitizers the isolated yields increased to >90% (**Table 2**). As expected, in the absence of any photosensitizer, 96% of starting material was recovered.

The effect of blue, green and orange LED illumination (**Figure 1**) on the dehalogenation reaction was then investigated. Blue light irradiation yielded similar results as white light illumination, which was not surprising considering the spectral overlap between the LED emission profile and the MLCT absorption band of the photosensitizers. Noteworthy, the use of both green, and especially orange LEDs resulted in efficient dehalogenation, with yields >90% with **D1**, **T1** and **Q1**. Albeit, with orange illumination, 7 hours were required compared to the 2-3 hours required with blue or green LEDs. This was in stark contrast to [Ru(bpy)₃]²⁺, that only reached 31% yield of **2** after 7 hours orange illumination (**Table 2**).

Given the promising results obtained with the polynuclear complexes, the photosensitizer loading was lowered to 0.1 mol% equivalent of ruthenium center (**Table 3**). This resulted in a decreased yield and incomplete conversion⁴⁵ with [Ru(bpy)₃]²⁺ after 24 hours, while excellent yields of around 90% were still obtained with **D1**, **T1** and **Q1**.

Table 3. Photocatalysis Results at Lower PS Concentration

PS	[PS] (mol %)	Eq. Ru center (mol %)	White light (6500K) ^a
[Ru(bpy) ₃] ²⁺	0.1	0.1	66 % ^b
D1	0.05	0.1	90 %
T1	0.03	0.1	87 %
Q1	0.023	0.1	91%

^a Isolated yields of (**2**) after 24h of reaction. ^b Incomplete conversion, 10% starting material recovered.

The proportions of DIPEA and HE were then modified with [Ru(bpy)₃]²⁺ as photosensitizer in order to investigate factors influencing the conversion and the achievable yields (**Table S1-S2**). Surprisingly, in the absence of DIPEA, but with increasing amounts of HE (**Table S1**, entries 5-7), the reaction reached quantitative conversion and isolated yields around 80% after column chromatography. Similar results were obtained with polynuclear complexes but with yields greater than 90% (**Table S2**). Moreover, without HE, but in the presence of DIPEA, a conversion of 81% was observed, corresponding only to a 33% isolated yield, which showed that the catalytic cycle proceeded partially under these conditions, however with predominant side reactions (**Table S1**, Entry 9).

Table 4. Photophysical Characterization and Excited-State Quenching Rate Constants for the PS

PS	k_q^a ($M^{-1}s^{-1}$)	k_q^b ($M^{-1}s^{-1}$)	ΔG_{et}^a (eV)	ΔG_{et}^b (eV)	% 3MC (298 K)
[Ru(bpy) ₃] ²⁺	2.5×10^6	1.3×10^6	− 0.07	+ 0.09	48 %
D1	3.3×10^7	8.1×10^6	− 0.22	− 0.06	< 0.5 %
T1	2.6×10^7	4.6×10^7	− 0.24	− 0.09	< 0.5 %
Q1	1.3×10^7	2.6×10^8	− 0.33	− 0.18	< 0.5 %

^a with DIPEA ($E_{1/2} = 0.765$ V vs Ag/AgCl)¹¹, ^b with Hantzsch ester ($E_{1/2} = 0.92$ V vs Ag/AgCl in 0.1M TBAPF₆ DMF electrolyte)

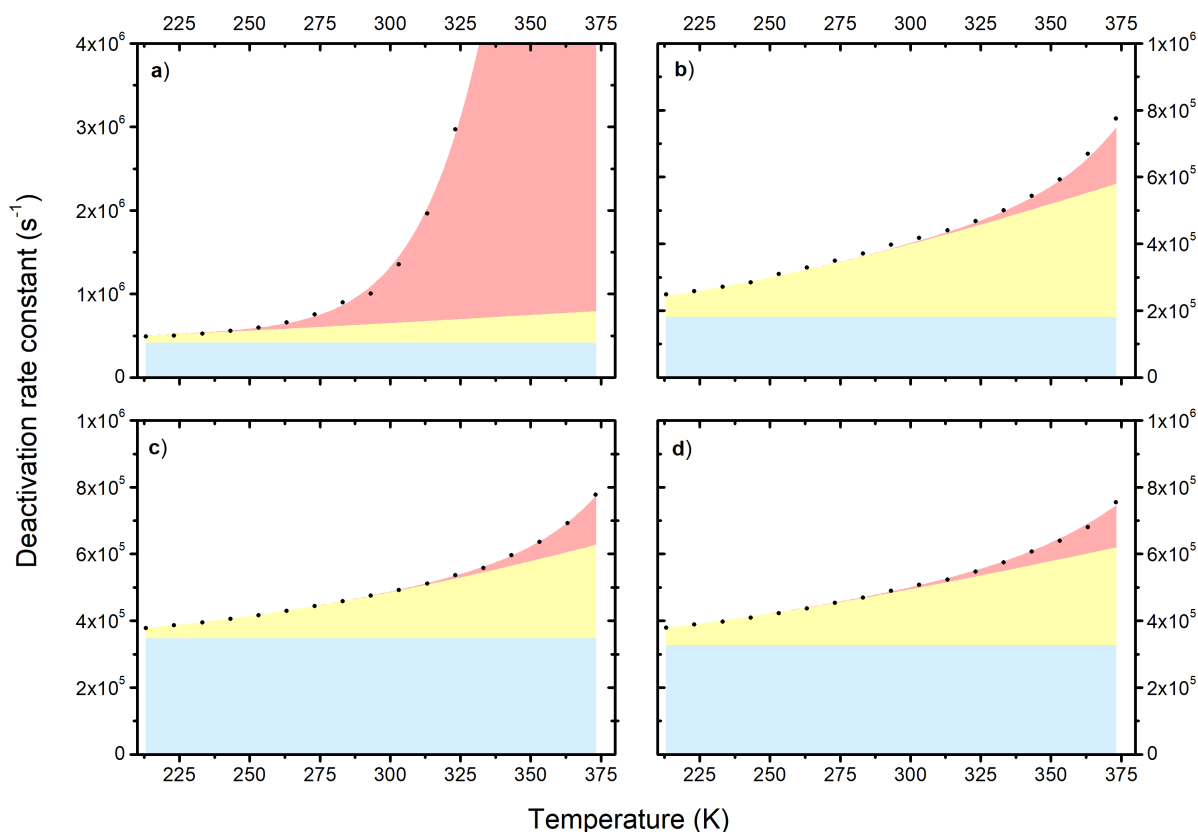


Figure 2. Excited-state deactivation rate constant for [Ru(bpy)₃]²⁺ (a), D1 (b), T1 (c), Q1 (d); (blue) direct radiative and nonradiative rate constants ($k_{dr} + k_{dnr}$), (yellow) thermally activated deactivation via the upper lying 3MLCT , (red) thermally activated deactivation via the 3MC and (dot) experimental data. Variable temperature measurements were performed in argon purged butyronitrile.

The larger yields obtained with the polynuclear photosensitizers, together with the good yield observed in the absence of DIPEA, prompted excited-state quenching experiments (Figures S33-S34).⁴⁶⁻⁴⁷ Quenching rate constants (k_q) of 2.53×10^6 $M^{-1}s^{-1}$ and 1.32×10^6 $M^{-1}s^{-1}$ were determined with [Ru(bpy)₃]²⁺ and DIPEA or HE respectively (Table 4). These quenching rate constants were one order of magnitude larger for **D1**, **T1** and **Q1** than for [Ru(bpy)₃]²⁺. Hence, as absorptivity was similar for the four photosensitizers, the larger yields could originate from these larger quenching rate constants. Note that Stern-Volmer experiments do not provide information about the quenching mechanism, *i.e.* electron transfer or energy transfer for example. Nonetheless, the driving force for electron transfer was estimated using equation 2,⁴⁸⁻⁴⁹ where $E_{1/2}(D^{+/0})$ is the one-electron

redox potential of the electron donor, and F is Faraday's constant. Table 4 highlights that the photoinduced electron transfers to the excited-state polynuclear photosensitizers from HE or DIPEA¹¹ were consistently more favorable than to [Ru(bpy)₃]²⁺.

$$\Delta G_{ET} = [E_{1/2}(D^{+/0}) - E_{1/2}(Ru^{n*/n-1})]F \quad (\text{Eq. 2})$$

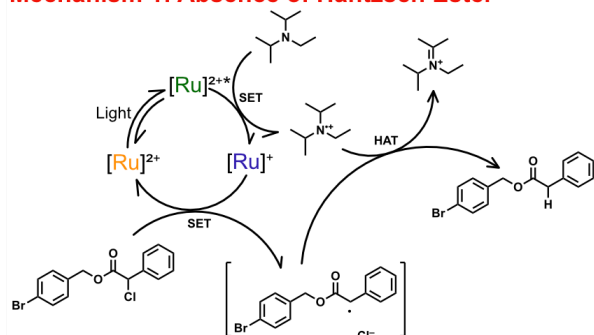
Additionally, ligand-loss photochemistry was observed for [Ru(bpy)₃]²⁺ during prolonged white light illumination reactions (Figure S35). This observation was rationalized through population of the dissociative triplet metal-centered (3MC) state from the 3MLCT excited state.³³⁻³⁶ [Ru(bpy)₂Cl₂] and [Ru(bpy)₂(DMF)₂]²⁺ were unable to perform significant catalysis (Table S1, Entries 3-4). Variable temperature time-resolved photoluminescence measurements (Figures S39-S50) were

performed to estimate the activation energy required to cross from the $^3\text{MLCT}$ to the ^3MC , as well as the percentage ^3MC population at room temperature, **Figure 2** (see SI for additional explanation).⁵⁰⁻⁵¹ Polynuclear complexes exhibited $< 0.5\%$ of ^3MC state population at room temperature, whereas population reached 48% in $[\text{Ru}(\text{bpy})_3]^{2+}$.

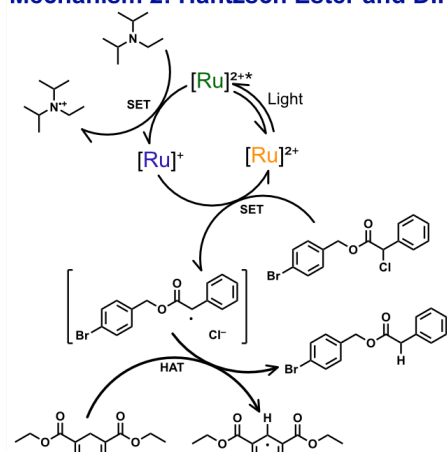
The results obtained herein were rationalized according to three proposed mechanisms (**Scheme 2**). In all cases, the photo-reduced ruthenium complexes performed dehalogenation of **1** leading to the corresponding radical. In the absence of HE (**Mechanism 1**), this radical performed hydrogen atom transfer (HAT) from oxidized DIPEA. In the absence of DIPEA (**Mechanism 3**), HE served both as excited-state reductant and as HAT reagent.⁵² The intermediate **mechanism 2** is similar to the one reported,⁵³ where DIPEA is a reducing agent prone to photooxidation in the presence of excited photosensitizers, whereas HE acts as a HAT reagent.³⁷

Scheme 2. Proposed Reaction Mechanisms.

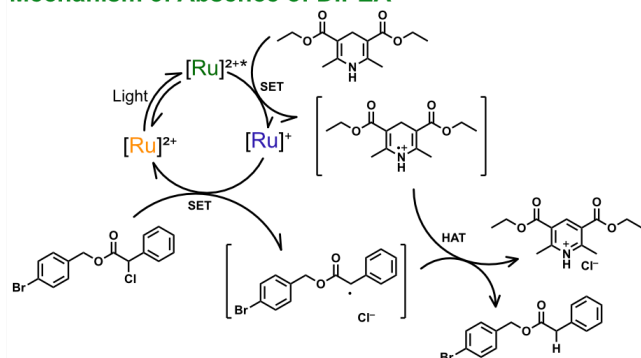
Mechanism 1: Absence of Hantzsch Ester



Mechanism 2: Hantzsch Ester and DIPEA Present



Mechanism 3: Absence of DIPEA



In conclusion, dinuclear, trinuclear and quadrinuclear ruthenium(II) photosensitizers were synthesized and investigated for a reported light-induced dehalogenation reaction. Altogether, the increased photostability, larger quenching rate constants, shorter reaction time and more favorable driving force for electron transfer contributed to the increased isolated yields for the light-induced dehalogenation reaction of **1** into **2**. Importantly, catalyst loadings were decreased down to 0.02 mol% while still achieving dehalogenation yields greater than 90%. Variable temperature measurements showed that $< 0.5\%$ of the polynuclear excited-states reached the ^3MC , which correlated with increased photostability observed under steady-state illumination. In addition, this reaction proceeded with similar yields when orange illumination was used, whereas $[\text{Ru}(\text{bpy})_3]^{2+}$ only partially converted **1** into **2** in 72 hours.

ASSOCIATED CONTENT

Supporting Information

Experimental section, Electrochemistry, Variable temperature time-resolved photoluminescence measurements, Stern-Volmer plots and additional references (PDF).^{50-51, 54-66} The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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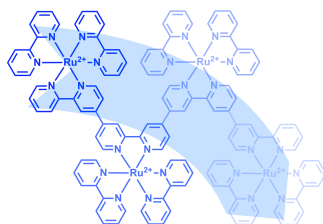
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- ✔ Mononuclear to tetranuclear Ru complexes
- ✔ Catalysts loading of 0.02 mol%
- ✔ Dehalogenation yields > 90% with 590 nm light excitation
- ✖ $[\text{Ru}(\text{bpy})_3]^{2+}$: 48% population ^3MC at 298 K
- ✔ Polynuclear: < 0.5 % population ^3MC at 298 K

