Photo-Induced One-Electron Chloride Oxidation in Water Using a Pentacationic Ir(III) Photosensitizer

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ABSTRACT: A novel iridium(III) photosensitizer containing pyridinium-decorated terpyridines has been used for the photo-oxidation of chloride in water. Despite its abundance, the very positive one-electron reduction potential (E° $Cl^{\bullet/-}$ = 2.1-2.4 V *vs* NHE) restricted its use in energy conversion schemes and artificial photosynthesis. The kinetics of the photo-induced electron transfer process were investigated through Stern-Volmer quenching experiments and nanosecond transient absorption spectroscopy, which provided unambiguous evidence that photo-induced chloride oxidation occurred with a quenching rate constant $k_q = 5.0 \times 10^{10}$ $M^{-1}s^{-1}$. Complementary spectroelectrochemistry and photolysis experiments confirmed the formation of the reduced photosensitizer and showcased the redox and photostability of the Ir(III) photosensitizer that holds great promise for the HX splitting approach.

The production of sustainable solar fuels through the photoreduction of carbon dioxide[1] or protons[2] relies on a source of electrons that ideally would be water. However, the complex process of water oxidation, involving multiple electrons and protons,[3] has hindered the realization of solar-powered water splitting. Halides represent a realistic alternative to water and could offer a sustainable supply of electrons given their abundance on Earth.[4] Unlike water, the oxidation of halides requires only two electrons and does not involve a demand for protons, thereby circumventing the kinetic barrier associated with water oxidation. Due to favorable thermodynamic properties, HX splitting (where X = Cl^-, Br^- or I^-) has been recognized as the most desirable reaction, **Eq. 1**.[5]

$$2\ HX \rightarrow H_2 + X_2 \qquad \textbf{Eq. 1}$$

Although aqueous chloride oxidation presents greater challenges (E° $Cl^{\bullet/-}$ = 2.1-2.4 V *vs* NHE) compared to aqueous bromide or iodide oxidation (1.92 and 1.33 V *vs* NHE, respectively),[6] its abundance makes it the preferred candidate for HX splitting. Chlorine ranks as the 20th most abundant element in the Earth's crust[7] and accounts for approximately 2% of seawater's weight.[8] A major challenge for solar chloride oxidation is the need to photogenerate powerful photo-oxidants. There are only a handful of reported photosensitizers able to perform chloride oxidation. Noteworthy, these examples mostly report chloride oxidation in organic solvent[4, 9-15] or acetonitrile/water mixtures with water content up to 50%,[11] but none of these prior examples were performed in neat water. In this context, we present a unique instance of light-induced chloride oxidation in the aqueous phase mediated by a novel pentacationic iridium photosensitizer. This process has the potential to serve as the foundation for a hydrogen photoproduction system in water, eliminating the need for sacrificial electron donors.

Iridium(III)-based photosensitizers have been largely used in fields that include lighting devices[16], life sciences[17], and photoredox chemistry.[18-19] Their success can be attributed to their long-lived excited states and excellent redox and photostability.[20] There are many examples of cyclometallated tris-bidentate photosensitizers in the literature.[21] These complexes have finely tunable photo-induced properties, but sometimes suffer from a lack of water solubility. The bis-terpyridine coordinated Ir(III) photosensitizers (IrN_6) have been less extensively studied.[22-25] The reasons are that such photosensitizers require more challenging synthetic conditions and that the corresponding photosensitizers only moderately absorb visible light. However, IrN_6 complexes possess three positive charges which improves water solubility, a prerequisite for aqueous chloride oxidation. Finally, IrN_6 photosensitizers typically undergo ligand-centered reductions at potentials more positive than –1 V *vs* NHE. When combined with their relatively large $E_{0\text{-}0}$ values (up to 3 eV), these photosensitizers become potent photo-oxidants according to **Eq. 2**.[26]

$$E_{red}^{*} = E_{red} + E_{0\text{-}0} \qquad \textbf{Eq. 2}$$

To further improve water solubility and to increase the excited-state reduction potential (E_{red}*), we set our sights on the novel pentacationic $[Ir(tpy\text{-}PyMe)_2]^{5+}(PF_6^-)_5$ photosensitizer **(Figure 1)**. The synthesis proceeded in three steps with an overall yield of 13% on large scale **(SI1)**: (1) a modified Kröhnke procedure to obtain a quaterpyridine (qtpy),[27] (2) a methylation to give the ligand tpy-PyMe[28] and (3) a complexation with a suitable iridium salt to yield the desired complex.

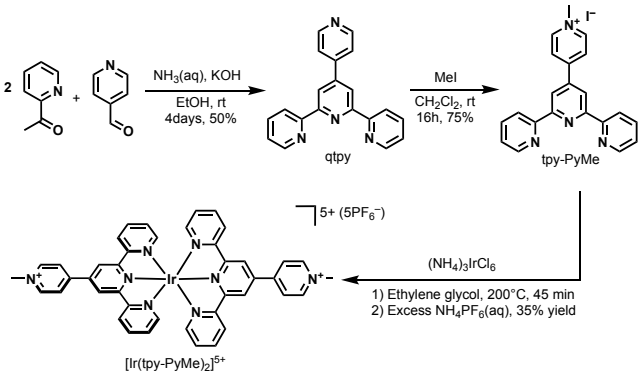

Figure 1. Synthetic route to obtain the pentacationic $[Ir(tpy\text{-}PyMe)_2]^{5+}$ $(PF_6^-)_5$.

Figure 2 depicts the UV-vis absorption and emission spectra of the photosensitizer in water. Before describing these properties, it is first necessary to comment on the solubility of $[Ir(tpy\text{-}PyMe)_2]^{5+}(PF_6^-)_5$. For the specific investigations into photo-oxidation, it was imperative to employ non-oxidizable anions, such as hexafluorophosphates. However, to conduct the experiments in an aqueous medium, this complex is first dissolved in the minimum amount of CH_3CN and then diluted with MilliQ water to obtain a final concentration of 0.5 %vol CH_3CN. The photophysics of this complex exhibit similarities to previously reported compounds.[23] The absorption spectrum displays distinct, high-energy absorption bands with significant molar absorption coefficients at wavelengths below 360 nm. Beyond this wavelength, there is a lower-energy absorption band with a shoulder. Based on the spectral characteristics, molar extinction coefficients, and relevant literature,[25] we attribute the high-energy absorption bands primarily to ligand-centered (LC) transitions, while the lower-energy band is attributed to dominant charge-transfer (CT) transitions. By introducing a methylated pyridine on the 4' position of the terpyridine ligand, we have, by a factor of ten, enhanced the molar absorption coefficient of the lowest-energy transition, compared to the reference $[Ir(tpy)_2]^{3+}$, where tpy is 2,2':6',2"-terpyridine.[22]

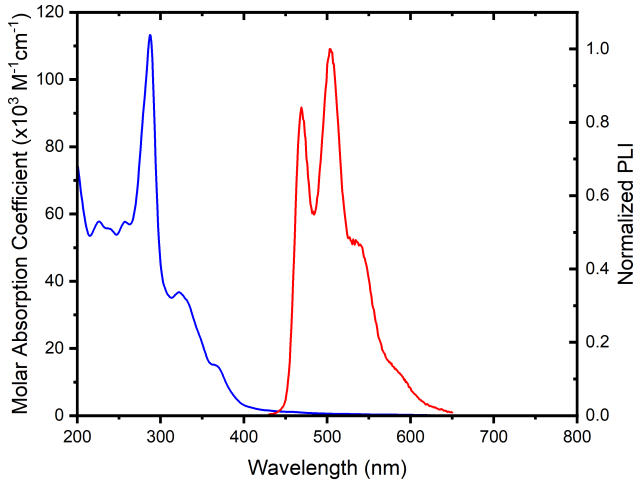

Figure 2. UV-Visible absorption (blue) and emission (red) (excitation at 365 nm) spectra of $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (7 µM) recorded at 293 K in MilliQ water with 0.5 %vol of CH_3CN used to pre-dissolve the photosensitizer.

The emission spectrum of the photosensitizer exhibits a well-resolved high-energy vibronic structure. This observation is attributed to a predominant ^{3}LC excited-state.[22-23] Moreover, this new compound exhibits an excited-state lifetime of 1.2 µs in water under air, competent for photo-induced electron transfer. An $E_{0\text{-}0}$ value of 2.63 eV was determined **(SI2)** which, using the experimentally determined ground-state reduction potential **(SI1)** and using **Eq. 2**, led to the corresponding E_{red}^* = 2.40 V *vs* NHE. This value is large and supports the photo-oxidation of chlorides in aqueous conditions. In comparison to $[Ir(tpy)_2]^{3+}$, which exhibits an E_{red}^* value of 2.1 V, $[Ir(tpy\text{-}PyMe)_2]^{5+}$demonstrates a substantial enhancement in photo-oxidizing ability while also improving its absorption properties.

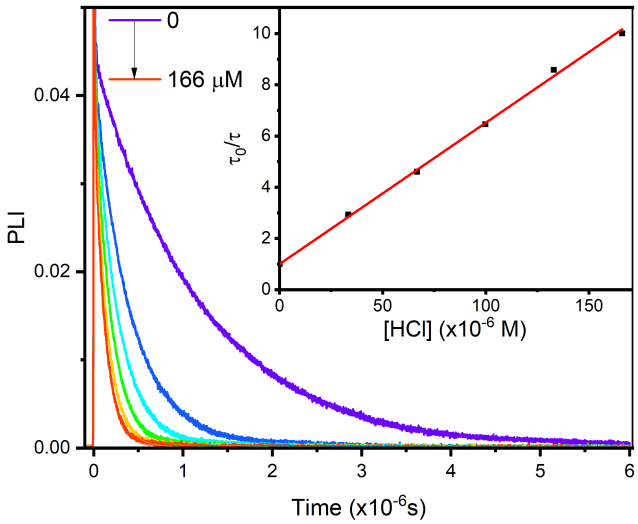

Figure 3. Time-resolved photoluminescence quenching monitored at 505 nm for $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (7 µM) in the presence of increasing amounts of hydrochloric acid (excitation at 355 nm). The inset shows the corresponding Stern-Volmer plot from which $k_q = 4.7 \times 10^{10}$ $M^{-1}s^{-1}$ was determined. Experiments were carried out in MilliQ water with 0.5 %vol CH_3CN.

Excited-state quenching experiments were carried out in water using HCl as quencher **(Figure 3)**. The excited-state quenching was monitored by time-resolved photoluminescence which showed a drastic decrease of the excited-state lifetime upon the addition of acid. Stern-Volmer analysis **(Eq. 3)** yielded a linear relationship from which a quenching rate constant (k_q) of 4.7 ±0.5x10^{10} $M^{-1}s^{-1}$ was determined.

$$\frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] \qquad \textbf{Eq. 3}$$

Since the initial amplitude of the photoluminescence intensity (PLI) remained unchanged, the observed linear relationship between the excited-state lifetime and the concentration of the quencher indicated that the quenching process was solely governed by dynamic quenching. Similar experiments were performed using KI, KBr and KCl **(SI3)** which provided quenching rate constants of 6.2 ±0.2 x10^{10} $M^{-1}s^{-1}$, 5.7 ±0.4 x10^{10} $M^{-1}s^{-1}$ and 5.0 ±0.5 x10^{10} $M^{-1}s^{-1}$, respectively. The large k_q were in line with the favorable driving force for halide oxidation, estimated between 1.17 and 0.3-0 eV for iodide and chloride oxidation, respectively.

As Stern-Volmer quenching experiments do not inform on the nature of the quenching process, we turned to nanosecond transient absorption spectroscopy. The excited-state absorption spectrum was first recorded in argon-purged water **(Figure 4A)** and displayed intense positive features across the entire visible spectrum.[29-31] Similar experiments were then carried out in the presence of HCl. This revealed the appearance of a novel

species, assigned to the mono-reduced complex (*vide infra*), which underwent second-order recombination in 137 µs in these conditions **(Figure 4B)**. Recombination occurred in 100 µs, 158 µs and 159 µs when iodide, bromide and chloride were used, respectively. Note that these are observed rates at one concentration and not actual rate constants. To further support our assignment, the measurements were repeated using ascorbic acid, a well-known reducing agent. The obtained difference spectrum exhibited identical features, thereby corroborating our initial assignment of reductive electron transfer. Similar spectra were also obtained with iodide, bromide and chloride, confirming the excited-state electron transfer process. The formation of mono-reduced complex was also confirmed by spectroelectrochemistry, where the appearance of an absorption band with a maximum centered at 400 nm was observed as the potential was gradually shifted negatively **(Figure 4C)**.

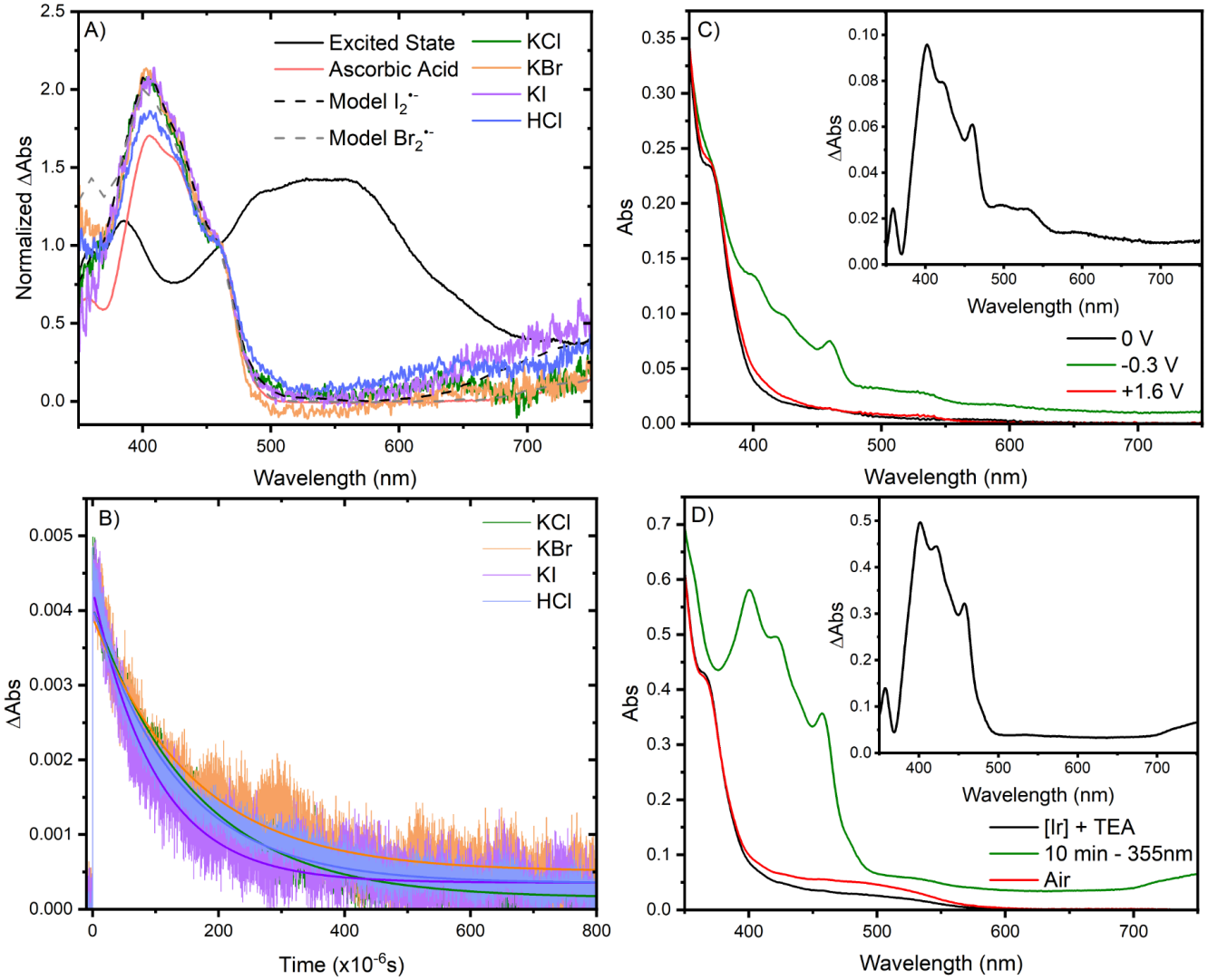

Figure 4. A) Nanosecond transient absorption spectra, normalized at 460 nm, recorded after 50 ns in water following pulsed 355 nm (20 mJ/pulse) light excitation of $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (black) (35 µM) and in the presence of 450 mM of ascorbic acid (red), iodide (purple), bromide (orange), chloride (green) and hydrochloric acid (blue). The spectra were modeled using a 1:1 ratio (0.23 µM of each) of Ir(II) to $Br_2^{\bullet-}$ (dashed grey) or to $I_2^{\bullet-}$ (dashed black). **B)** Corresponding single wavelength absorption changes recorded at 410 nm. Experiments were carried out in MilliQ water with 0.5 %vol of CH_3CN used to pre-dissolve the photosensitizer. **C)** Spectroelectrochemistry of $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (800 µM) recorded in 0.3 M $TBAPF_6$ CH_3CN electrolyte. Color code: $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (black), $[Ir(tpy\text{-}PyMe)_2]^{5+}$ reduced at a potential of –0.3 V *vs* Ag pseudo-reference (green) and after applying a potential of +1.6 V *vs* Ag pseudo-reference (red). The difference spectrum between the reduced state and the ground-state is shown in the inset. **D)** UV-Visible absorption spectra of $[Ir(tpy\text{-}PyMe)_2]^{5+}$ (30 µM) before (black) and after (green) irradiation at 355 nm in the presence of TEA (300 µM) in argon-purged MilliQ water. The red spectrum shows recovery of the initial product following exposure to air. The inset represents the difference spectrum (between green and black lines) leading to the spectrum of the singly reduced Ir photosensitizer.

Figure 4A unambiguously confirms the occurrence of excited-state electron transfer between the halides and the excited photosensitizer. The halogen atom, $X^{\bullet}$ cannot be observed within the investigated spectral window, but $X_2^{\bullet-}$ usually exhibits appreciable absorption features in the visible.[4] The transient absorption spectra recorded with KI and KBr were modelled using authentic spectra of the monoreduced Ir photosensitizer and $I_2^{\bullet-}$ or $Br_2^{\bullet-}$, respectively (**Figure 4A** and Figure **S6-S7**). This highlighted that both species were formed in a 1:1 ratio, with a respective concentration of 0.23 µM. Similar modelling could not be performed on the transient absorption data recorded in the presence of chloride as we do not have access to

authentic spectra of $Cl_2^{\bullet-}$. Nevertheless, we hypothesize that the reduced Ir photosensitizer is formed in similar concentrations. The cage-escape yields were quantified by transient absorption spectroscopy[32-37] **(SI0)** using the knowledge of the respective contribution of the reduced Ir photosensitizer and $X_2^{\bullet-}$ at the investigated wavelength. Cage-escape yields of 0.04 for each halide was determined. These yields are low compared to values recorded in acetonitrile or other organic solvents for photosensitizers where $X_2^{\bullet-}$ was clearly observed, where values range 0.25-0.96.[11, 38-39] The yields are however in line with the low cage-escape yields recently obtained with Ir(III) binuclear complexes for halide oxidation in acetonitrile/water mixtures.[11] Note that low cage-escape yields around 0.04 with observation of $I_2^{\bullet-}$ in acetonitrile have been reported using Ru(II) and Fe(III) photosensitizers.[40-41]

Finally, the stability of the mono-reduced photosensitizer was investigated. We were unable to photo-accumulate reduced photosensitizers with halides as electron donors. This probably stems from the non-sacrificial nature of halides upon one-electron oxidation, or from the formation of the corresponding X_2 that should be capable of oxidizing the reduced photosensitizer. Hence, we decided to study the stability of the mono-reduced photosensitizer in the presence of triethylamine as sacrificial reagent (**Figure 4D**) The solution was subjected to 5 or 10 minutes of irradiation at 355 nm under argon. Upon irradiation for either 5 or 10 minutes, the obtained spectra remained identical, indicating that the reaction has reached completion, and the resulting spectrum corresponds to the mono-reduced photosensitizer. Notably, the process exhibits reversibility upon exposure to air, highlighting the excellent photostability of the complex in storing electrons and hence their promise as efficient photosensitizers for applications in reductive catalysis and solar fuel production.

In conclusion, a novel photosensitizer, $[Ir(tpy\text{-}PyMe)_2]^{5+}$, displayed significantly enhanced absorption compared to its non-substituted counterpart, resulting in high-energy emission and the formation of a highly photo-oxidizing species. The quenching of the photosensitizer's excited-state by hydrochloric acid and halides was investigated through time-resolved spectroscopic techniques. The quenching rate constant agreed with a diffusion limited process, *i.e.,* $k_q = 4.7 \times 10^{10}\ M^{-1}s^{-1}$. Spectroelectrochemistry coupled to nanosecond transient absorption spectroscopy experiments in the presence of hydrochloric acid, chloride, bromide, iodide, or ascorbic acid confirmed the occurrence of a photo-induced electron transfer. The cage-escape yields were low (0.04) but the photo-oxidation of chloride and bromide in water represents an exciting novelty in the field of energy conversion for solar fuel formation. Steady-state photolysis experiments demonstrated that the new iridium complex exhibited great photostability, which is crucial for catalysis, particularly to produce solar fuels.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. ^{1}H NMR of novel compounds, materials and methods, additional excited-state quenching experiments and modelling of transient absorption spectra.

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