# Photosensitized Generation of Singlet Oxygen from Re(I) Complexes: A Photophysical Study Using LIOAS and Luminescence Techniques

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ABSTRACT: Quantum yields and efficiencies of $^1O_2$ ($^1\Delta_g$) production along with photophysical properties for a number of Re(I) complexes in acetonitrile solutions are reported. Two different classes of Re(I) complexes, L_S-CO_2-Re(CO)$_3$(bpy) (L_S = 2-pyrazine, 2-naphthalene, 9-anthracene, 1-pyrene, 2-anthraquinone) and XRe(CO)$_3$L (X = CF$_3$SO$_3$, py; L = bpy, phen), were probed as photosensitizers for $^1O_2$ ($^1\Delta_g$) production in air-saturated acetonitrile solutions. Depending on the nature of the Re(I) complex, the excited state responsible for the generation of $^1O_2$ ($^1\Delta_g$) is either a metal-to-ligand charge transfer (^{3}MLCT) or a ligand centered (^{3}LC) state. With L_S-CO_2-Re(CO)$_3$(bpy) complexes, $^1O_2$ ($^1\Delta_g$) is produced by oxygen quenching of ^{3}LC states of anthracene and pyrene with high quantum yields (Φ_Δ between 0.8 and 1.0), while the complexes bearing the ligands L_S = 2-anthraquinone, 2-pyrazine, and 2-naphthalene did not yield $^1O_2$. XRe(CO)$_3$L complexes generate $^1O_2$ ($^1\Delta_g$) mainly by oxygen quenching of their ^{3}MLCT luminescence with an efficiency of $^1O_2$ ($^1\Delta_g$) formation close to unity. Bimolecular rate constants for the quenching of the XRe(CO)$_3$L complexes' emission by molecular oxygen range between 1×10^9 and 2×10^9 M^{-1} s^{-1}, and they are all $\leq {}^1/_9 k_d$, in good agreement with the predominance of the singlet channel in the mechanism of $^1O_2$ ($^1\Delta_g$) generation using these Re(I) complexes as photosensitizers. All the experimental singlet oxygen efficiencies are consistent with calorimetric and luminescence data for the studied complexes. With L_S-CO_2-Re(CO)$_3$(bpy) complexes, calorimetric experiments were utilized in the calculation of the quantum yields of triplet formation; namely ϕ_T = 0.76 and 0.83 for the triplet states of anthracene and pyrene, respectively.
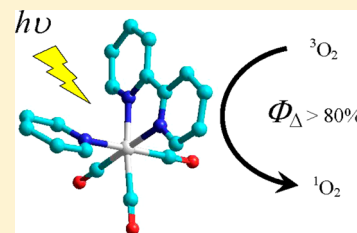
INTRODUCTION

Singlet oxygen, $^1O_2$ ($^1\Delta_g$), being a strongly oxidant reactive species, is a key intermediate in chemical processes, such as photo-oxidation reactions, as well as in biological processes, including DNA damage and photodynamic therapy of cancer.[1,2] In the latter, it is used to kill malignant tumors and to destroy other unwanted tissues. Therefore, research on sensitizers that may produce $^1O_2$ ($^1\Delta_g$) with high efficiencies is of keen interest because of its importance in both photochemistry and photobiology.[3−5] Usually, the production of $^1O_2$ ($^1\Delta_g$) involves electronic energy transfer from the triplet excited state of a sensitizer, generally an organic dye, to the triplet ground state of molecular oxygen. In addition, some transition metal complexes like those of Cr(III), Ru(II), and Os(II) have also been used as sensitizers in the generation of $^1O_2$ ($^1\Delta_g$).[6−12] In particular, those complexes of Ru(II) coordinating polypyridyl ligands have been shown to be efficient photosensitizers, with reported efficiencies >80%.[2,9] Nevertheless, little attention has been given to the use of XRe(CO)$_3$L complexes as photosensitizers in $^1O_2$ ($^1\Delta_g$) production. As far as we know, there is only one example in the literature where Re(I) complexes, one tricarbonyl (Re(phen)CN(CO)$_3$) and two tetracarbonyl (Re-(phen)(CO)$_4^+$ and Re(benzoquinoline)(CO)$_4^+$), have been used to generate $^1O_2$ ($^1\Delta_g$).[13] The scarcity of examples found in the literature of Re(I) tricarbonyl complexes functioning as $^1O_2$ ($^1\Delta_g$) sensitizers is surprising because these compounds

continue to attract the attention of researchers because of their applicability in broad research areas such as electron transfer studies,[14] solar energy conversion,[15−17] catalysis,[18] applications as luminescent sensors,[19−21] molecular materials for nonlinear optics,[22,23] and optical switching.[24] Because these complexes show exceptionally rich excited-state behavior and redox chemistry as well as thermal and photochemical stability,[25,26] they have also been used as biological labeling reagents and noncovalent probes for biomolecules and ions.[27−29] Moreover, there are potential biochemical and technical applications based on the formation of adducts between transition metal complexes of Re(I) and biological macromolecules such as DNA.[9,30] In this paper, we explore the efficiency of $^1O_2$ ($^1\Delta_g$) production using two different types of XRe(CO)$_3$L complexes: (1) nonluminescent complexes with the general formula L_S-CO_2-Re(CO)$_3$(bpy), where the spectator ligand L_s is a well-known and highly efficient $^1O_2$ ($^1\Delta_g$) sensitizer like anthracene, anthraquinone, or pyrene, and (2) luminescent XRe(CO)$_3$L complexes where photosensitized generation of $^1O_2$ ($^1\Delta_g$) occurs mainly by energy transfer from the highly emissive MLCT excited state to molecular oxygen.

Furthermore, a photoacoustic and luminescence characterization of all the Re(I) complexes used as photosensitizers is performed, using laser induced optoacoustic spectroscopy (LIOAS) and steady-state and time-resolved luminescence techniques, in order to better understand the energy factors governing singlet oxygen generation efficiency with these complexes. All the experimental singlet oxygen efficiencies are consistent with calorimetric and luminescence data for the studied complexes.

■ EXPERIMENTAL SECTION

Photophysical Measurements. UV−vis spectra were recorded on a Shimadzu UV-1800 spectrophotometer. All the photophysical experiments were performed at room temperature (295 ± 3 K). Emission spectra were obtained with a computer-interfaced Near-IR Fluorolog-3 Research Spectrofluorometer. Spectra were corrected for differences in spectral response and light scattering. Solutions were deaerated either with pure O_2 or with O_2-free nitrogen in a gastight apparatus before the spectra were recorded.

The instrumentation for time-resolved luminescence has been described elsewhere.[31] Lifetime measurements were made using the third harmonic (355 nm) of a pulsed Nd:YAG laser (Litron Optical Nano S 130-10) and monitoring the signal at different wavelengths between 500 and 600 nm. A modified 1P28 photomultiplier tube circuit with ca. 1 ns response time was used as the detector for the green emission dispersed through a monochromator. The signal was directly measured on a fast digitizing oscilloscope (Rigol model DS1 102E), and the overall time resolution was ca. 20 ns.

Photoacoustic measurements were performed using a setup already described.[32,33] A Q-switched Nd:YAG laser (7 ns fwhm) operating at 355 nm was used as the excitation source (1 mm diameter in the cell). A homemade ceramic PZT-based piezoelectric transducer (4 × 4 mm) with an appropriate amplifier was used to detect the acoustic signals. The resolution time of the experiments, determined by our experimental setup, was $\tau_R = 1\ \mu$s. Measurements were performed averaging the acoustic signals generated by 64 laser shots for a better signal-to-noise ratio. The UV−vis spectrum of the solutions was checked before and after each set of laser shots. 2-Hydroxybenzophenone was used as a calorimetric reference.[34] For the experiments, sample and reference solutions were matched within 2% to absorbance values between 0.1 and 0.2 at the laser wavelength. Experiments were performed under a controlled atmosphere, bubbling N_2 or O_2 in the solution, for 15 min. In principle, all the excited species with lifetimes $\tau \leq \frac{1}{5}\tau_R$ release their heat content as prompt heat, whereas excited species that live longer than $5\tau_R$, that is with a lifetime of $\tau \geq 5\tau_R$, function as heat storage within the time resolution of the LIOAS experiment.

For the handling of the LIOAS signals, we used eq 1, which relates the peak-to-peak amplitude of the first optoacoustic signal (H) with the fraction of the excitation laser fluence (F) absorbed by the sample[35]

$$H = K\alpha F(1 - 10^{-A}) \tag{1}$$

In this equation, the experimental constant K contains the thermo-elastic parameters of the solution as well as instrumental factors, A is the absorbance of the sample at the excitation wavelength, and α is the fraction of the energy released to the medium as prompt heat within the time

resolution of the experiment (1 μs). In LIOAS experiments, linear relationships were obtained between H and F for samples and references at various A values in a fluence range between 1 and 30 J/m². The slopes of these lines gave the energy-normalized optoacoustic signal, H/F, which was plotted against $1 - 10^{-A}$, yielding straight lines. The ratio between the slopes of these lines for sample and reference yielded the values of α for the samples. This procedure was carried out under oxygen (O_2) or nitrogen (N_2) atmosphere.

The efficiency of the Re(I) complexes toward singlet oxygen sensitization was assessed by the direct measurement of the $^1O_2$ ($^1\Delta_g$) near-IR luminescence. After the irradiation of aerated solutions of complexes, the generation of $^1O_2$ ($^1\Delta_g$) was evidenced by the appearance of the characteristic $^1O_2$ ($^1\Delta_g$) → $^3O_2$ phosphorescence at 1270 nm. Time-resolved phosphorescence detection was used for singlet oxygen detection. The near-IR luminescence of $^1O_2$ ($^1\Delta_g$) was observed at 90° geometry through a 5 mm thick antireflective coated silicon metal filter with a wavelength pass >1.1 μm and an interference filter at 1.27 μm by means of a preamplified (low impedance) Ge-photodiode (Applied Detector Corporation, time resolution 1 μs). Simple exponential analysis of the emission decay was performed with the exclusion of the initial part of the signal. The quantum yield of $^1O_2$ ($^1\Delta_g$) formation, Φ_Δ, was determined by measuring its phosphorescence intensity using an optically matched solution of phenalenone ($\Phi_\Delta = 0.98$[36]) as a reference sensitizer.

Materials. Spectrograde and HPLC grade acetonitrile was purchased from J. T. Baker and was used without further purification. 2-Hydroxybenzophenone, 9-anthracene-COOH, 1-pyrene-COOH, and 2-anthraquinone-COOH were purchased from Aldrich at the highest purity available and were used as received. The complexes fac-L_S-CO_2-Re(CO)$_3$(bpy) (with L_S = 2-pyrazine, 2-naphthalene, 9-anthracene, 1-pyrene, 2-anthraquinone), CF$_3$SO$_3$Re(CO)$_3$(bpy), CF$_3$SO$_3$Re-(CO)$_3$(phen), and [pyRe(CO)$_3$(bpy)]CF$_3$SO$_3$ (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, py = pyridine) were available from previous works.[37−40] Hereafter, for the sake of simplicity, the complexes and organic compounds will be denoted by the acronyms shown in bold: 2-hydroxybenzophenone (**2-HBP**), 9-anthracene-COOH (**9-an**), 1-pyrene-COOH (**1-pyr**), 2-anthraquinone-COOH (**2-aq**), 2-pyrazine-CO_2-Re-(CO)$_3$(bpy) (**Re-pz**), 2-naphthalene-CO_2-Re(CO)$_3$(bpy) (**Re-na**), 9- anthracene-CO_2-Re(CO)$_3$(bpy) (**Re-an**), 1-pyrene-CO_2-Re(CO)$_3$(bpy) (**Re-pyr**), 2-anthraquinone-CO_2-Re-(CO)$_3$(bpy) (**Re-aq**), CF$_3$SO$_3$Re(CO)$_3$(bpy) (**Re-1**), CF$_3$SO$_3$Re(CO)$_3$(phen) (**Re-2**), and [pyRe(CO)$_3$(bpy)]-CF$_3$SO$_3$ (**Re-3**) (Scheme 1).
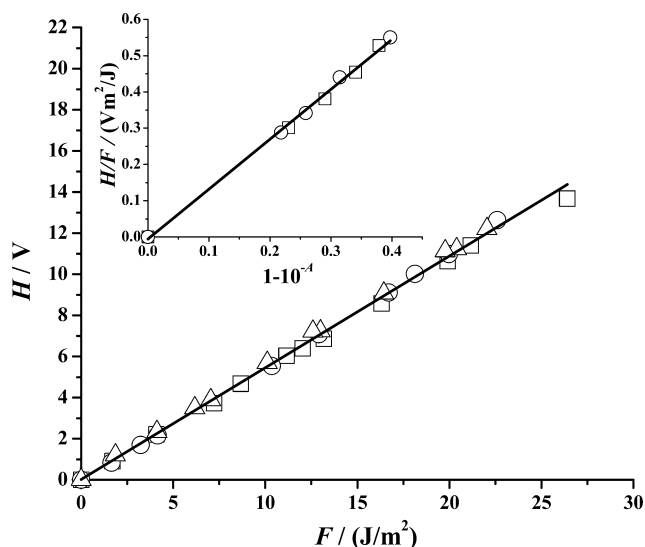
■ RESULTS AND DISCUSSION

LIOAS Experiments. The photoacoustic signal of all the samples studied showed the same behavior: no time shift or changes of shape with respect to the calorimetric reference signal (Figure 1). For the cases of **Re-pz**, **Re-na**, and **Re-aq**, the behavior of H versus F, measured at the same absorbance (A) under O_2 or N_2 atmospheres, showed a linear dependence with the same slope. When compared with the calorimetric reference, **2-HBP**, at the same A, the same slope was obtained, as shown in Figure 2 for **Re-aq**. Good reproducibility of these measurements was observed for different A and $F \leq 30$ J/m². For the complexes **Re-an**, **Re-pyr**, **Re-1**, **Re-2**, and **Re-3**, slopes depended on the specific atmosphere (O_2 or N_2) and/or were different from the calorimetric reference (Figure 3). From these

**Scheme 1. Structural Formulas and Abbreviations Used for the Re(I) Complexes**

Re-pz   Re-na   Re-an

Re-pyr   Re-aq

Re-1   Re-2   Re-3
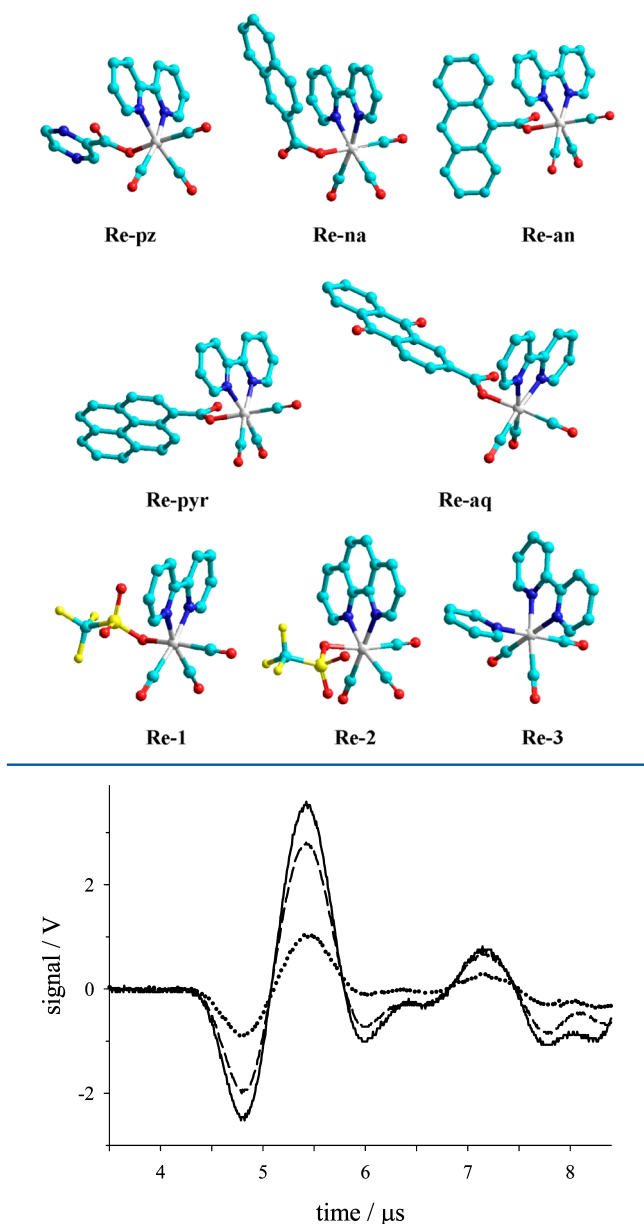
Figure 1. Photoacoustic signals of **2-HBP** (solid line) and **Re-2** (N$_2$, dotted line; O$_2$, dashed line).

Figure 2. Amplitude of the photoacoustic signals as a function of laser fluence for acetonitrile solutions of **Re-aq** (N$_2$, $\bigcirc$; O$_2$, $\triangle$) and **2-HBP** (air, $\square$). The solutions of **Re-aq** and **2-HBP** were matched within 2% to absorbance at 355 nm. Inset: amplitude of the fluence-normalized photoacoustic signals as a fraction of the absorbed energy for acetonitrile solutions of **Re-aq** (N$_2$, $\bigcirc$) and **2-HBP** (air, $\square$). See text for details.
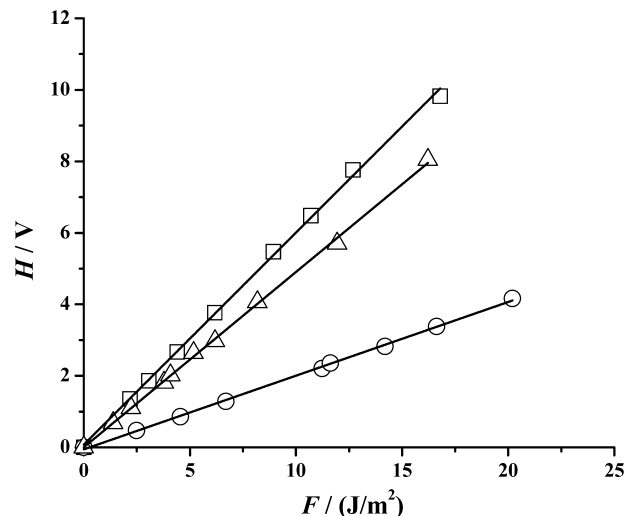
Figure 3. Amplitude of the photoacoustic signals as a function of laser fluence for acetonitrile solutions of **Re-2** (N$_2$, $\bigcirc$; O$_2$, $\triangle$) and **2-HBP** (air, $\square$). The solutions of **Re-2** and **2-HBP** were matched within 2% to absorbance at 355 nm. See text for details.

plots, considering that the fraction of the energy released to the medium as prompt heat (α) is $\alpha_R = 1$ for **2-HBP**, the ratio of H/F values obtained for sample and reference gave the α values listed in Tables 1 and 2. Therefore, α values equal to 1.00 ± 0.05 (in either O$_2$ or N$_2$) were obtained for **Re-pz**, **Re-na**, and **Re-aq**. Consequently, these complexes released to the medium all the absorbed energy as prompt heat (integrated by the transducer) in processes faster than $\tau_R/5$. For **Re-pyr** values of $\alpha(O_2) = 0.72 \pm 0.05$ and $\alpha(N_2) = 0.50 \pm 0.05$ were obtained, while for **Re-an** the corresponding values were $\alpha(O_2) = 0.78 \pm 0.05$ and $\alpha(N_2) = 0.60 \pm 0.05$. On the other hand, for **Re-1**, **Re-2**, and **Re-3** complexes, the obtained values for the fraction of energy dissipated are $\alpha(O_2) = 0.81 \pm 0.05$, $\alpha(N_2) = 0.60 \pm 0.05$; $\alpha(O_2) = 0.80 \pm 0.05$, $\alpha(N_2) = 0.33 \pm 0.05$; and $\alpha(O_2) = 0.81 \pm 0.05$, $\alpha(N_2) = 0.83 \pm 0.05$, respectively. These values

Table 1. Calorimetric and Singlet Oxygen Data of L$_S$-CO$_2$-Re(CO)$_3$(bpy) Complexes and Related Ligands in Acetonitrile (λ_{exc} = 355 nm)

compound	$\alpha(N_2)$ (± 0.05)	$\alpha(O_2)$ (± 0.05)	Φ_Δ (air) (± 0.05)
Re-pz	1.00	1.00	<0.05
Re-na	1.00	0.95	<0.05
Re-an	0.60	0.78	0.78
Re-pyr	0.50	0.72	0.95
Re-aq	0.99	0.99	<0.05
9-an	–	–	0.25
1-pyr	–	–	0.27
2-aq	–	–	0.49

Table 2. Calorimetric and Singlet Oxygen Data of XRe(CO)$_3$L Complexes in Acetonitrile (λ_{exc} = 355 nm)

compound	$\alpha(N_2)$ (±0.05)	$\alpha(O_2)$ (±0.05)	Φ_Δ (air) (±0.05)	$P^T_{O_2} = 1 - \tau/\tau_0$	$P^T_{O_2} = 1 - I/I_0$	$P^T_{O_2}$	$f^T_{O_2}$
Re-1	0.60	0.81	0.63	0.68	0.63	0.66	0.95
Re-2	0.33	0.80	0.89	0.84	0.84	0.84	1.02
Re-3	0.83	0.81	0.51	0.49	0.50	0.50	1.02

Table 3. Emission Wavelengths (λ_{em}), Emission Lifetimes (τ_{em}),[a] Bimolecular Rate Constants (k_q),[b] Overall Rate Constants (k_D),[b] Calculated Rate Constants ($k^{nCT}_{\Delta E}$), and Relative Weights of Charge Transfer Deactivation (p_{CT}) of Singlet Oxygen Sensitization by Re-1, Re-2, and Re-3 Complexes in Acetonitrile

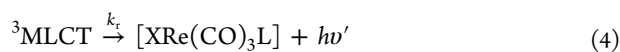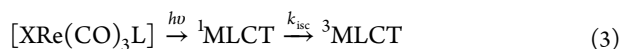| compound	λ_{em} (nm)	τ_{em}, N$_2$ (ns)	τ_{em}, air (ns)	τ_{em}, O$_2$ (ns)	k_q (10^9 M^{-1} s^{-1})	k_D (10^9 s^{-1})	$k^{nCT}_{\Delta E}$ (10^9 s^{-1})	p_{CT}
Re-1	538	519	167	45	2.0	2.1	1.9	0.10
Re-2	539	1690	263	73	1.3	1.4	1.9	0.00
Re-3	557	245	126	44	1.9	2.0	2.1	0.00

[a]Standard deviation: $\pm2\%$. [b]Standard deviation: $\pm10\%$.

combined with fluorescence data and singlet oxygen quantum yield production (see below) fit the energy balance of eq 2:
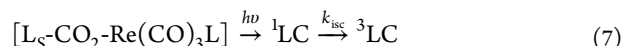
$$E_a = \Phi_f E_f + \alpha E_a + \Phi_{st} E_{st} \tag{2}$$

where Φ_f is the fluorescence quantum yield, E_f is the 0-0 luminescence energy, E_a is the molar energy of the laser pulse (hc/λ_{exc}), and E_{st} is the molar energy content of the species formed with a quantum yield Φ_{st} which stores energy for a time longer than the heat integration time and decays with a lifetime τ. For the case of a triplet state, Φ_{st} equals the quantum yield of triplet formation (Φ_T), E_{st} is the triplet content energy (E_T), and τ is the triplet lifetime (τ_T). When singlet oxygen acts as the storing species, the corresponding values for this species are $\Phi_f = 0$, $\Phi_{st} = \Phi_\Delta$, and $\tau = \tau_\Delta$. Because in acetonitrile $\tau_\Delta \sim 40$ μs,[41] $^1O_2$ ($^1\Delta_g$) acts as an energy store within the time resolution of the LIOAS experiment.

Singlet Oxygen Generation. In order to find an expression for the quantum yield of $^1O_2$ ($^1\Delta_g$) production as a function of the excited-state parameters of the sensitizer, the various photophysical and photochemical pathways involved have to be considered. After optical excitation of XRe(CO)$_3$L complexes with photonic energies ≤340 kJ/mol (i.e., in an energy region where LC states are usually not populated), the first excited singlet state, ^{1}MLCT, yields the ^{3}MLCT by intersystem crossing (ISC) in a few hundred femtoseconds,[25] leaving the ^{3}MLCT exited state to decay by monomolecular radiative and nonradiative processes (eqs 3−5)

$$[XRe(CO)_3L] \xrightarrow{h\nu} {}^1MLCT \xrightarrow{k_{isc}} {}^3MLCT \tag{3}$$

$$^3MLCT \xrightarrow{k_r} [XRe(CO)_3L] + h\nu' \tag{4}$$

$$^3MLCT \xrightarrow{k_{nr}} [XRe(CO)_3L] \tag{5}$$

Equations 3−5 reflect the photophysical behavior of XRe-(CO)$_3$L complexes (i.e., Re-1, Re-2, and Re-3) with L = bpy or phen and X = CF$_3$SO$_3$ and/or py, because bpy, phen, py, and CF$_3$SO$_3$ do not have significant LC states at energies ≤340 kJ/ mol ($\lambda_{exc} \geq 350$ nm). However, this is not always the case within the family of complexes with the general formula fac-L$_S$-CO$_2$-Re(CO)$_3$L, because Re-an, Re-pyr, and Re-aq still have significant LC absorptions[37,40] at energies ≤340 kJ/mol; therefore after photonic excitation, both MLCT and LC excited states are produced (eqs 6 and 7)

$$[L_S-CO_2-Re(CO)_3L] \xrightarrow{h\nu} {}^1MLCT \xrightarrow{k_{isc}} {}^3MLCT \tag{6}$$

$$[L_S-CO_2-Re(CO)_3L] \xrightarrow{h\nu} {}^1LC \xrightarrow{k_{isc}} {}^3LC \tag{7}$$

where ^{3}LC represents the triplet excited states of anthracene, pyrene, and anthraquinone in L$_S$-CO$_2$-Re(CO)$_3$L complexes. Because naphthalene has no significant absorptions at $\lambda_{exc} \geq$ 350 nm, only ^{1}MLCT is populated after photonic excitation of Re-na with energies ≤340 kJ/mol.[37] In fact, the photophysical properties of L$_S$-CO$_2$-Re(CO)$_3$(bpy) are quite different from those of Re-1, Re-2, and Re3: whereas L$_S$-CO$_2$-Re(CO)$_3$(bpy) are nearly nonluminescent ($\Phi_{lum} \leq 5 \times 10^{-3}$),[37,40] Re-1, Re-2, and Re-3 are quite good luminophores, with reported Φ_{lum} values ranging between 0.3 and 0.5 in a N$_2$ atmosphere for Re-1 and Re-3 in aprotic solvents like dichloromethane and acetonitrile.[42−44] Under an O$_2$ atmosphere, however, their luminescence is strongly quenched (Table 3). On the other hand, after photonic excitation, the generated excited states in Re-an and Re-pyr complexes are mainly of LC character corresponding to the triplets of the free L$_s$ ligands (9-an and 1-pyr) with reported triplet lifetimes of τ_T = 6.9 and 7.4 μs for Re-an and Re-pyr, respectively.[40] With the complex Re-aq, however, LC absorptions are displaced to shorter wavelengths (relative to MLCT absorptions), and after photonic excitation, the MLCT excited state is mainly populated, with only minor (<10%) contributions from LC absorptions of the ligand 2-aq.[37] The triplet-state lifetime of the anthraquinone ligand in the Re-aq complex is τ_T = 4.9 μs.[37] In the presence of oxygen, XRe(CO)$_3$L complexes may be used as sensitizers, and $^1O_2$ ($^1\Delta_g$) may be produced by energy transfer from the ^{3}MLCT (or ^{3}LC) to molecular oxygen (eq 8)

$$^3S + O_2(^3\Sigma^-_g) \xrightarrow{k_\Delta} {}^1S + {}^1O_2(^1\Delta_g) \tag{8}$$
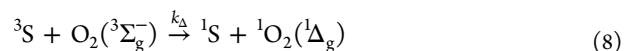
where k_Δ stands for the rate constant of the energy transfer process from ^{3}S (^{3}MLCT or ^{3}LC in XRe(CO)$_3$L or L$_S$-CO$_2$-Re(CO)$_3$(bpy) complexes, respectively) to yield $^1O_2$ ($^1\Delta_g$). The mechanism of quenching by oxygen of the excited triplet state of a sensitizer S is given in eqs 9−11.
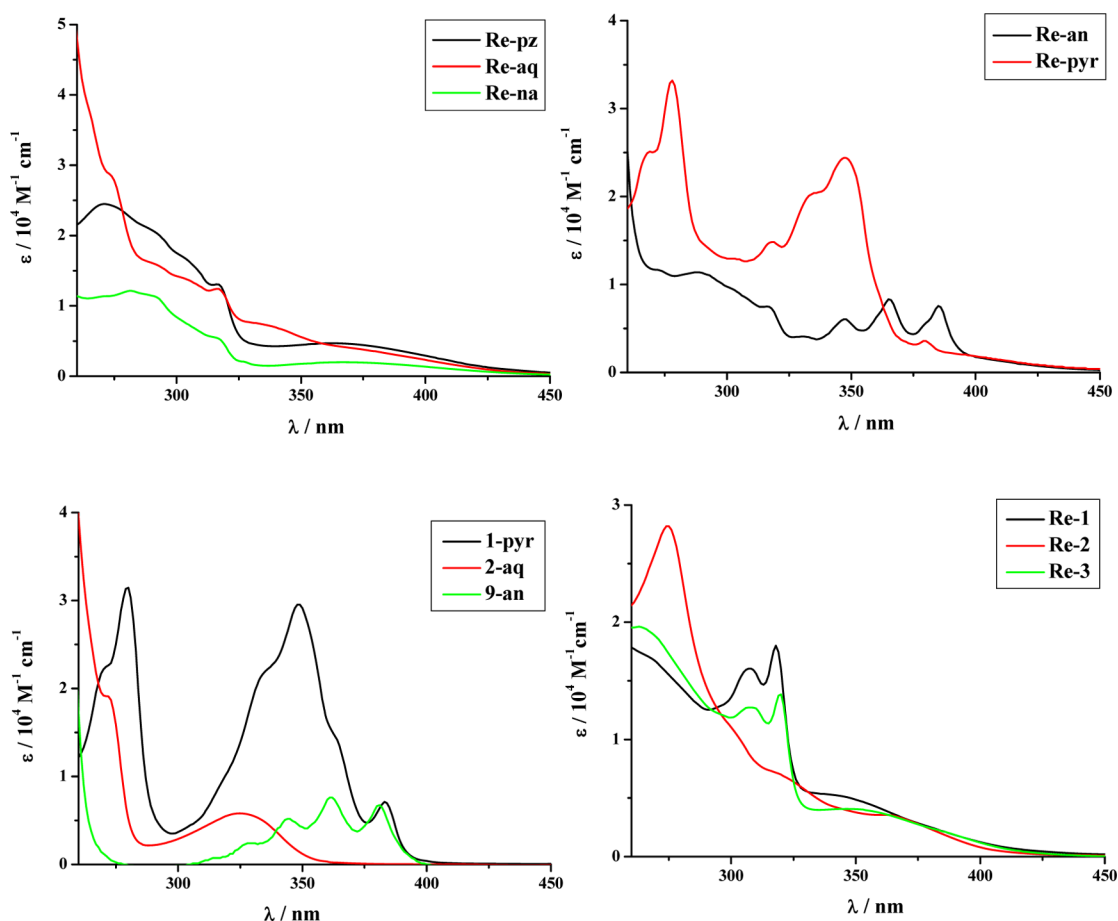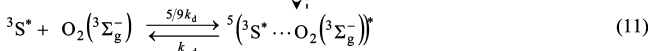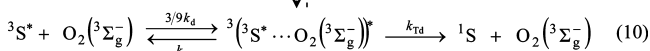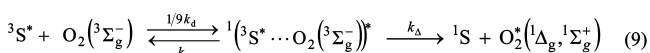
Figure 4. Absorption spectra of Re(I) complexes and related ligands in acetonitrile.

$$^{3}S^{*} + O_{2}(^{3}\Sigma_{g}^{-}) \underset{k_{-d}}{\overset{1/9k_{d}}{\rightleftharpoons}} {}^{1}\left(^{3}S^{*}\cdots O_{2}(^{3}\Sigma_{g}^{-})\right)^{*} \xrightarrow{k_{\Delta}} {}^{1}S + O_{2}^{*}(^{1}\Delta_{g}, {}^{1}\Sigma_{g}^{+}) \quad (9)$$

$$^{3}S^{*} + O_{2}(^{3}\Sigma_{g}^{-}) \underset{k_{-d}}{\overset{3/9k_{d}}{\rightleftharpoons}} {}^{3}\left(^{3}S^{*}\cdots O_{2}(^{3}\Sigma_{g}^{-})\right)^{*} \xrightarrow{k_{Td}} {}^{1}S + O_{2}(^{3}\Sigma_{g}^{-}) \quad (10)$$

$$^{3}S^{*} + O_{2}(^{3}\Sigma_{g}^{-}) \underset{k_{-d}}{\overset{5/9k_{d}}{\rightleftharpoons}} {}^{5}\left(^{3}S^{*}\cdots O_{2}(^{3}\Sigma_{g}^{-})\right)^{*} \quad (11)$$

In this mechanism, $^{3}S^{*}$ represents the excited triplet state of the sensitizer, k_{d} and k_{-d} represent the diffusion-controlled rate constants for encounter and separation, respectively, of the complexes $^{1,3,5}(^{3}S^{*}\cdots{}^{3}O_{2})$, and k_{Td} represents the catalyzed triplet decay by molecular oxygen. The superscripts give the multiplicity values of the individual molecules and the bimolecular collision complexes. The encounter complexes $^{1,3}(^{3}S^{*}\cdots{}^{3}O_{2})$ may eventually evolve toward charge transfer complexes, that is, $^{1,3}(^{2}S^{\delta+}\cdots{}^{2}O_{2}^{\delta-})$, which are not represented in the scheme of eqs 9−11, as it was previously described by Gijzman et al.[45] and Wilkinson el al.[46] by a model that assumes the competition between a noncharge transfer (nCT) and a CT deactivation channel. The fractions $^{1}/_{9}$, $^{3}/_{9}$, and $^{5}/_{9}$ are the spin statistical factors, which reflect the statistical probability of formation of a spin state (singlet, triplet, or quintet) when an encounter complex is formed by collision of two molecules in triplet states.[45] Equation 9 includes direct production of $^{1}O_{2}$ ($^{1}\Delta_{g}$) from oxygen quenching as well as $^{1}O_{2}$ ($^{1}\Delta_{g}$) formed from any $^{1}O_{2}$ ($^{1}\Sigma_{g}^{+}$) resulting initially. The dotted arrows represent

induced ISC, possibly enhanced by the heavy atom effect exerted by Re(I) ion among the singlet, triplet, and quintet channels.

The quantum yield of singlet oxygen production (Φ_{Δ}) from the quenching of the triplet state by oxygen is given by eqs 12−17:

$$\Phi_{\Delta} = \Phi_{T} P_{O_{2}}^{T} f_{O_{2}}^{T} \quad (12)$$

$$P_{O_{2}}^{T} = \frac{k_{q}[O_{2}]}{k_{r} + k_{nr} + k_{q}[O_{2}]} = \tau k_{q}[O_{2}] = 1 - \frac{\tau}{\tau_{0}} = 1 - \frac{I}{I_{0}} \quad (13)$$

$$k_{D} = k_{\Delta} + k_{Td} \quad (14)$$

$$f_{O_{2}}^{T} = \frac{k_{\Delta}}{k_{D}} \quad (15)$$

$$\tau = \frac{1}{k_{r} + k_{nr} + k_{q}[O_{2}]} \quad (16)$$

$$\tau_{0} = \frac{1}{k_{r} + k_{nr}} \quad (17)$$

where Φ_{T} is the quantum yield of triplet formation; k_{q} is the total quenching rate constant of triplet state by oxygen; $P_{O_{2}}^{T}$ is the proportion of triplet states quenched by O_{2}; $f_{O_{2}}^{T}$ is the fraction of triplet states quenched by O_{2} which yield $^{1}O_{2}$ ($^{1}\Delta_{g}$) ($f_{O_{2}}^{T}$ is also named as the efficiency of singlet oxygen

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formation); and τ_0, τ, I_0, and I are the triplet lifetimes and luminescence intensities in the absence and presence of oxygen, respectively. The mechanism shown in eqs 9−11 was originally derived for singlet oxygen generation from the triplet states of organic sensitizers; therefore, ISC among the complexes $^{1,3,5}(^3S^*...^3O_2)$ of different spin multiplicity was not taken into account.[45] Considering that mechanism, $f^T_{O_2}$ from the excited triplet state should be 1 and $k_q \leq {}^1/_9 k_d$ if only the singlet channel were involved, whereas $f^T_{O_2} = 0.25$ and $k_q \leq {}^4/_9 k_d$ if both singlet and triplet channels were equally involved.

The quantum yields of singlet oxygen production for the complexes **Re-pz**, **Re-na**, **Re-an**, **Re-pyr**, **Re-aq**, **Re-1**, **Re-2**, and **Re-3** and for the ligands **9-an**, **1-pyr**, and **2-aq** are reported in Tables 1 and 2. **Re-pz** and **Re-na** were unable to generate $^1O_2$ ($^1\Delta_g$), in accordance with the lack of LC states available for population at $\lambda_{exc} = 355$ nm and the low luminescence quantum yields from their MLCT states. On the other hand, **Re-pyr** generated $^1O_2$ ($^1\Delta_g$) with a Φ_Δ close to unity while **Re-an** showed $\Phi_\Delta = 0.78$. Because neither **Re-pyr** nor **Re-an** has significant luminescence that may be quenched by oxygen, that is, $\Phi_{lum} \sim 4 \times 10^{-3}$, the production of $^1O_2$ ($^1\Delta_g$) in those complexes can come only from energy transfer of their ^{3}LC states, which as stated before, are mainly populated at $\lambda_{exc} = 355$ nm after ISC from ^{1}LC. The values of Φ_Δ for the free ligands **9-an** and **1-pyr**, which are both around 0.25, reflect the fact that both singlet (eq 9) and triplet channels (eq 10) are equally involved in $^1O_2$ ($^1\Delta_g$) production. The much higher Φ_Δ values observed for **Re-an** and **Re-pyr** compared to those for the corresponding free ligands are indicative of the induced ISC exerted by Re(I) ion among the singlet, triplet, and quintet channels in the kinetic scheme of eqs 9−11.

With calorimetric data (α values in N_2) and the energy balance of eq 2, values for the quantum yield of triplet formation, $\Phi_T = 0.76$ and 0.83, can be calculated for **Re-an** and **Re-pyr**, respectively. A value of $\Phi_T = 0.76$ for **Re-an** is in good agreement with, though a bit greater than, the literature value for anthracene, which is between 0.66 and 0.72.[47] A value of $\Phi_T = 0.83$ for **Re-pyr** is more than 2 times greater than Φ_T for pyrene,[48] indicating an enhancement of ISC due to the heavy metal effect in **Re-pyr**. The heavy metal effect on Φ_T is much more pronounced in **Re-pyr** than in **Re-an**. This is probably due to the extinction coefficient of pyrene being higher than that of anthracene[40] (Figure 4) at the laser excitation wavelength (355 nm) used in LIOAS experiments. Because of this fact, the fraction of the laser fluence absorbed by the ^{1}LC states (relative to the laser fluence absorbed by the ^{1}MLCT states) is higher in **Re-pyr** than in **Re-an**. Therefore, the fraction of the energy released to the medium as prompt heat from direct population of ^{1}MLCT states is lower in **Re-pyr** than in **Re-an**, and the enhancement of ISC due to the heavy metal effect is more pronounced in **Re-pyr** than in **Re-an**. On the other hand, with α values in O_2, again using the energy balance of eq 2, values for the quantum yield of singlet oxygen production, $\Phi_T = 0.79$ and 1.00, can be calculated for **Re-an** and **Re-pyr**, respectively. Those calculated values of Φ_T from calorimetric data are in very good agreement with the experimental ones (Table 1). **Re-aq** did not yield $^1O_2$ ($^1\Delta_g$) while $\Phi_\Delta = 0.49$ for the corresponding free ligand **2-aq**. This apparent discrepancy can be rationalized in terms of the UV−vis absorption spectrum of **Re-aq** because at $\lambda_{exc} = 355$ nm the main absorption comes from the MLCT (which, in addition, is a very weak luminophore, $\Phi_{lum} \sim 2 \times 10^{-4}$) with a small
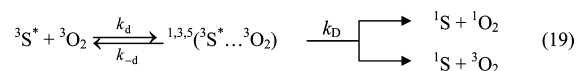
contribution from the LC states[6] (Figure 4). Complexes **Re-1**, **Re-2**, and **Re-3** have Φ_Δ values ranging between 0.5 and 0.9, which compare well with Φ_Δ values reported for similar Re(I) complexes: $Re(phen)CN(CO)_3$ ($\Phi_\Delta = 0.56$), $Re(phen)(CO)_4^+$ ($\Phi_\Delta = 0.69$), and $Re(benzoquinoline)(CO)_4^+$ ($\Phi_\Delta = 0.51$).[13] **Re-1**, **Re-2**, and **Re-3** complexes reflect the opposite photophysical behavior of **Re-pyr** and **Re-an** because they generate $^1O_2$ ($^1\Delta_g$) exclusively from the oxygen quenching of their luminescent MLCT states. Because it has been reported that Φ_T is unity because of the high degree of spin−orbit coupling in such heavy metal systems,[13] it follows that eq 12 reduces to eq 18:

$$\Phi_\Delta = P^T_{O_2} f^T_{O_2} \tag{18}$$

The values of $P^T_{O_2}$ were calculated for **Re-1**, **Re-2**, and **Re-3** using eq 13 and either the luminescence lifetimes or the luminescence intensities in N_2 and in air (Tables 2 and 3). The corresponding (mean) values are 0.66, 0.84, and 0.50 for **Re-1**, **Re-2**, and **Re-3**, respectively. When compared to Φ_Δ, these $P^T_{O_2}$ values reflect essentially the fact that $f^T_{O_2}$ is unity for **Re-2** and **Re-3** and is 0.95 for **Re-1** (Table 2).

The bimolecular rate constants for the quenching of the **Re-1**, **Re-2**, and **Re-3** emission by oxygen (k_q, Table 3) have been determined from the slopes of the linear Stern−Volmer plots ($\tau_0/\tau = 1 + k_q \tau_0 [O_2]$) calculated with the values of the emission lifetimes in the absence and presence of oxygen (τ_0 in N_2 and τ in air and in O_2, respectively). There are three different literature values, 8.1, 12.1, and 9.6 mM,[49a] for the saturated oxygen solubility at 1.013 bar in acetonitrile. We decided to use the mean value, 10 ± 2 mM, in the calculation of k_q. The oxygen solubility at 1.013 bar of air was calculated according to $[O_2] = 0.21(P_A - P_v)[O_2]_{P=1}$,[49b] where P_A and P_v are the atmospheric pressure and the vapor pressure of the solvent, respectively, and $[O_2]_{P=1}$ is the oxygen concentration of the solvent at 1.013 bar of O_2 partial pressure. The values of k_q obtained for **Re-1**, **Re-2**, and **Re-3**, which range between 1×10^9 and 2×10^9 M^{-1} s^{-1}, are in good agreement with k_q values reported for similar Re(I) complexes with $f^T_{O_2}$ close to unity.[13] Because k_d in acetonitrile is around 3×10^{10} M^{-1} s^{-1},[13,50] the values of k_q obtained for **Re-1**, **Re-2**, and **Re-3** are found to be $\leq {}^1/_9 k_d$. They are in good agreement with the unity values obtained for $f^T_{O_2}$ and with a predominance of the singlet channel, eq 9, in the mechanism of singlet oxygen generation using these Re(I) complexes as photosensitizers.

The total quenching rate constant of the triplet state by oxygen k_q, which is a second order rate constant, should not be confused with $k_D = k_\Delta + k_{Td}$ which is a first order rate constant. In order to obtain an expression for k_D from the experimental k_q values, a simplification of the mechanism of eqs 9−11, eq 19, can be considered:

$$^3S^* + {}^3O_2 \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^{1,3,5}(^3S^*...^3O_2) \xrightarrow{k_D} \begin{array}{l} ^1S + {}^1O_2 \\ ^1S + {}^3O_2 \end{array} \tag{19}$$

In the first step of the quenching, the excited sensitizer $^3S^*$ and $^3O_2$ ($^3\Sigma_g^-$) diffuse together to form the excited encounter complexes $^{1,3,5}(^3S^*...^3O_2)$ with spin multiplicity $m = 1, 3$, and 5 with a diffusion-controlled rate constant k_d (note that $k_d = \sum k_{d,i}$ of eqs 9−11). These complexes dissociate with rate constant k_{-d} or react in a forward direction: (1) $^1(^3S^*...^3O_2)$ toward singlet ground-state sensitizer ^1S and $^1O_2$ ($^1\Sigma_g^+$) or $^1O_2$ ($^1\Delta_g$) or (2) $^3(^3S^*...^3O_2)$ to ^1S and $^3O_2$ ($^3\Sigma_g^-$). The quintet complex,

$^5(^3S^*...^3O_2)$, has no direct product channel.[49] The overall rate constant $(k_D = k_\Delta + k_{Td})$ is calculated by eq 20:

$$k_D = \frac{k_{-d}k_q}{k_d - k_q} \tag{20}$$

The dissociative rate constant, k_{-d}, is calculated according to $k_{-d}/k_d = 1$ M, where M is the unit mole per liter, as was previously done by Schmidt, Gijzeman et al., and Wilkinson et al.,[49] with the value of $k_d = 3.1 \times 10^{10}$ M^{-1} s^{-1} for the diffusion-controlled rate constant for bimolecular processes of O$_2$ in acetonitrile.[13] The calculated values of k_D from the values of k_q for **Re-1**, **Re-2**, and **Re-3** are listed in Table 3. The multiplicity-normalized rate constants, $k_{\Delta E}^{nCT}/m$ (i.e., $k_{\Delta E}^{^1\Sigma}/1$, $k_{\Delta E}^{^1\Delta}/1$, and $k_{\Delta E}^{^3\Sigma}/3$), depend for $^3S^*$ sensitizers with high oxidation potentials and minimum CT interactions between $^3S^*$ and O$_2$ on the excess energy (ΔE) for formation of $^1O_2$ $(^1\Sigma_g^+)$, $^1O_2$ $(^1\Delta_g)$, and $^3O_2$ $(^3\Sigma_g^-)$ in a common way.[49] With the known values of the triplet sensitizers' energies, the absolute contribution from the non-charge transfer path (nCT) to deactivation, eq 21, can be calculated with the aid of the polynomial expression of eq 22 via the corresponding excess energies ΔE (in kJ/mol):[49]

$$k_{\Delta E}^{nCT} = k_{\Delta E}^{^1\Sigma} + k_{\Delta E}^{^1\Delta} + k_{\Delta E}^{^3\Sigma} \tag{21}$$

$$\begin{aligned}\log(k_{\Delta E}^{nCT}/m)(s^{-1}) &= 9.05 + 9 \times 10^{-3}\Delta E \\ &- 1.15 \times 10^{-4}\Delta E^2 + 1.15 \times 10^{-7}\Delta E^3 \\ &+ 9.1 \times 10^{-11}\Delta E^4\end{aligned} \tag{22}$$

where the excess energies are $\Delta E = E_T - 157$, $\Delta E = E_T - 94$, and $\Delta E = E_T$ for $\log(k_{\Delta E}^{^1\Sigma})$, $\log(k_{\Delta E}^{^1\Delta})$, and $\log(k_{\Delta E}^{^3\Sigma})$, respectively, because the excited state energies of $^1O_2$ $(^1\Sigma_g^+)$ and $^1O_2$ $(^1\Delta_g)$ are 157 and 94 kJ/mol above the ground state of molecular oxygen, O$_2$ $(^3\Sigma_g^-)$, respectively (Scheme 2). The relative

Scheme 2. Relative Energies of $^1O_2$ $(^1\Sigma_g^+)$, $^1O_2$ $(^1\Delta_g)$, and $^{1,3}(^3S^*...^3O_2)$
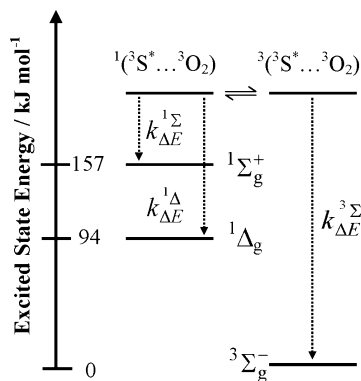
importance of charge transfer (CT) and non-charge transfer (nCT) deactivation mechanisms can be assessed by the quantity p_{CT}, which is defined by eq 23 as the relative weight of charge transfer deactivation referred to the overall deactivation of the excited state by O$_2$:

$$p_{CT} = \frac{k_D - k_{\Delta E}^{nCT}}{k_D} \tag{23}$$

The calculated values of $k_{\Delta E}^{nCT}$ for **Re-1**, **Re-2**, and **Re-3** are 1.9 $\times 10^9$, 1.9 $\times 10^9$, and 2.1 $\times 10^9$ s^{-1} (Table 3), respectively.

Thus, the calculated values of $k_{\Delta E}^{nCT}$ are very close to the experimental k_D values, with $p_{CT} \sim 0.10$, 0.00, and 0.00 for **Re-1**, **Re-2**, and **Re-3**, respectively, implying a dominance of the nCT mechanism in the overall deactivation of the excited state by O$_2$.

■ CONCLUDING REMARKS

Besides showing exceptionally rich excited-state behavior and photochemical stability, tricarbonyl Re(I) complexes coordinating polypyridyl ligands are excellent photosensitizers for the generation of singlet oxygen, and their use in photodynamic therapy can be envisaged in the near future. In this regard, the synthesis of a series of bioconjugated *fac* tricarbonyl rhenium bis-imine complexes with amino acid ester derivatives and their application in fluorescent microscopy cell imaging have recently been reported.[51]

We have examined the photophysical properties of a number of Re(I) complexes in dilute acetonitrile solutions along with the efficiencies of singlet oxygen production. In the singlet oxygen photosensitization using Re(I) complexes, $^1O_2$ $(^1\Delta_g)$ can be efficiently produced either from the nonemissive **Re-pyr** and **Re-an** or from the highly emissive **Re-1**, **Re-2**, and **Re-3** complexes. Depending on the nature of the Re(I) complex, the excited state responsible for the generation of singlet oxygen, via energy transfer to molecular oxygen, is either ^{3}MLCT (in **Re-1**, **Re-2**, and **Re-3** complexes) or a ^{3}LC state (in **Re-pyr** and **Re-an** complexes). The much higher Φ_Δ values observed for **Re-an** and **Re-pyr** compared to those for the corresponding free ligands are indicative of the induced intersystem crossing exerted by Re(I) ion among the singlet, triplet, and quintet channels in the kinetic scheme of singlet oxygen production. Calorimetric data were used to calculate the quantum yields of triplet formation, $\Phi_T = 0.76$ and 0.83 for **Re-an** and **Re-pyr**, respectively. Values of Φ_Δ calculated from calorimetric experiments were in very good agreement with the experimental ones. With the highly emissive complexes, **Re-1**, **Re-2**, and **Re-3**, unity values for efficiency of singlet oxygen formation were obtained. The bimolecular rate constants for the quenching of the **Re-1**, **Re-2**, and **Re-3** emission by oxygen range between 1×10^9 and 2×10^9 M^{-1} s^{-1}. The fact that $k_q < {}^1/_9 k_d$ is in good agreement with the nearly unity values obtained for $f_{O_2}^T$ and with a predominance of the singlet channel in the mechanism of singlet oxygen generation using these Re(I) complexes as photosensitizers. The calculated values of $k_{\Delta E}^{nCT}$ are very close to the experimental k_D values, with a minimal contribution of the charge transfer mechanism in the overall deactivation of the excited state by O$_2$.

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F.R. and H.H.M.S. contributed equally to the experimental part of this work.

Notes

The authors declare no competing financial interest.

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