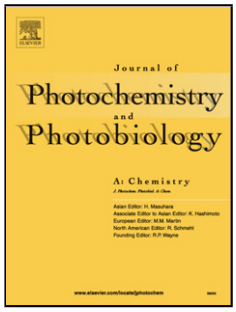

Title: Photophysical properties of [(norharmane)Re(CO)$_3$ (L)]$^+$ complexes (Lnull=nullbpy, phen or dppz). Redox behavior of the excited states and their interaction with Calf Thymus DNA.

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Photophysical properties of [(norharmane)Re(CO)$_3$(L)]$^+$ complexes (L = bpy, phen or dppz). Redox behavior of the excited states and their interaction with Calf Thymus DNA.

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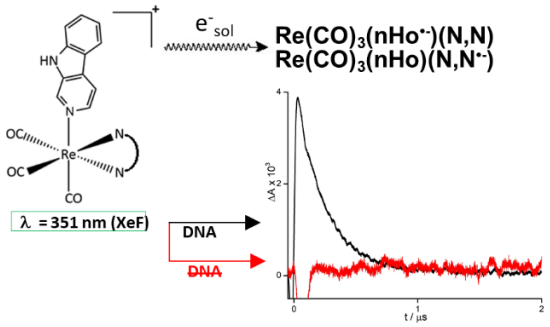
Graphical abstract



Highlights

- Photochemical and Photophysical studies of three Re^{I} tricarbonyl complexes with β-carbolines (norharmane) as ligand are detailed.
- Flash photolysis and Pulse radiolysis experiments
- Norharmane shows a dual role as electron accepting and as spectator, depending the polypyridyl (N,N') ligand.
- $[(nHo)Re(CO)_3(dppz)]^+$ complex shows an excited state accessibility to quenchers when it is intercalated in DNA.

ABSTRACT

The photochemical and photophysical properties of $[(nHo)Re(CO)_3(L)]^+$ complexes, where nHo = 9H-pyrido[3,4-b]indole and L = 2,2' bipyridine (bpy), 1,10 phenantroline (phen) or dipyridil[3,2-a:2'3'-c]phenazine (dppz) were investigated by Laser Flash Photolysis (LFF) and Pulse Radiolysis (PR) techniques. While complexes with L = bpy or phen show absorption transients compatible with $MLCT_{Re\rightarrow L}$ excited states, $[(nHo)Re(CO)_3(dppz)]^+$ showed an excited state assignable to a dppz-centered, $^3\pi\pi^*_{dppz}$. In aqueous solutions, the last complex does not generate any absorption transient. However, when Calf thymus DNA was added, the same absorption spectrum was

obtained. These results suggest that this complex can intercalate into DNA. The species generated in either reductive or oxidative conditions in LFF experiments were compared with those obtained in PR. Also, the quenching rate constants (k_q) of the excited states with MV^{2+} were calculated. The intercalation of the $[(nHo)Re(CO)_3(dppz)]^+$ into DNA, increases k_q ~100 times. This result is rationalized in terms of the conditions created by the intercalation using the biopolymer as a well-organized matrix.

1. INTRODUCTION

Rhenium (I) tricarbonyl complexes have been extensively investigated in different fields of research due to their rich photophysics and photochemistry[1-2]. These properties lead to new applications in the CO_2 photoreduction[3-6], photocatalysis [7], organic light emitting diode devices (OLEDS)[8-9], electron transfer processes [10-11], chemosensors [12] and solar energy conversion[13]. It has been established that the source of the luminescence of polypyridinic Re(I) complexes is in great part associated with metal to ligand charge transfer excited states ($MLCT_{Re\rightarrow L}$), i.e., excited states whose energy can be modulate by a judicious selection of the ligands [1, 14-19]. Insofar as these complexes exhibit good thermal and photochemical stability, they have also been used as biosensors and cellular probes.[20-21] The particular last applications are based on the formation of adducts between complexes of Re(I) and biomacromolecules such as DNA. [22-24] These are formed when the cationic transition metal complex is attracted by the phosphate groups in the periphery of the DNA.

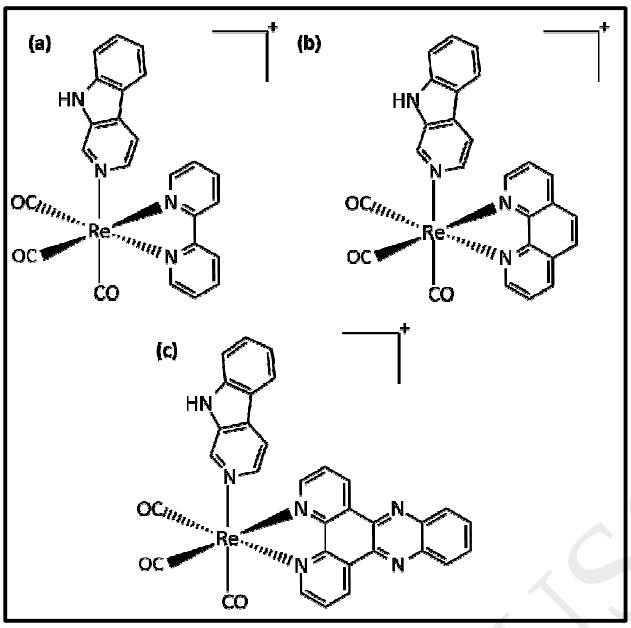
It has already been established that intercalation with DNA takes place with *fac*-Re(I) complexes containing an extended planar ligand, such as dppn (benzo[i]dipyrido[3,2-a:2′,3′-h]quinoxaline) or dppz (dipyrido[3,2-a:2′,3′-c]phenazine).[25-27] In Re(I) complexes of dppz it was

shown that complexes such as $[(4,4´bpy)Re(CO)_3(dppz)]^+$ emitted in organic solvents but not in aqueous media. Other studies, where related Re^I-dppz complexes were used, showed that the luminescence comes from an IL($\pi\pi^*$) excited state of the dppz. This IL($\pi\pi^*$) excited state is sufficiently close in energy to the ^{3}MLCT excited state to be therefore in a quasi-equilibrium condition.[28-30] In aqueous solutions, the ^{3}MLCT excited state is strongly quenched due to the interaction of the dppz ligand with the protons of the H_2O molecule.[31] The quenching of the emission is a consequence of the rapid radiationless conversion of the ^{3}MLCT excited state to the ground state along with a consumption of the IL($\pi\pi^*$) state mediated by the pseudo equilibrium with the MLCT excited state. Different intercalation studies with similar Re^I-dppz complexes have shown that when they were stacked between DNA bases, the emission of the complexes is recovered.[25, 28, 32-33] This phenomenon where the emission can be turned on/off by intercalating this complexes into DNA strands is labeled "light switch effect". [31] It allows to use these kind of cpmplexes as luminescent DNA probes. Conversely, the intercalation modifies the photophysical properties of the Re(I) complexes, such as lifetimes and reactions of the $^3MLCT_{Re\rightarrow L}$ state, among others.[34-35] Recently, we have synthesized and full characterized three novel Re(I) complexes with norharmane (9H-Pyrido[3,4-b]indole), and a bidentate azines ligand, 2,2' bipyridine (**bpy**), 1,10 phenantroline (**phen**) and **dppz** (Scheme 1).[36, 37] Norharmane (nHo) is a naturally occurring alkaloid showing quite a broad spectrum of interesting chemical, photochemical and photophysical properties.[38-41] Moreover, nHo and other related derivatives, were shown to be active against different types of microorganisms such as parasites, fungi, etc.[42] Upon photoexcitation, nHo can act as a quite efficient photosensitizers giving rise to the photooxidation and/or damaging of molecules of biological relevance such as nucleotides and DNA.[43-44] In 2011, Tan *et.al* demonstrated that some Ru(II) complexes with nHo as ligands were successfully internalized by

HeLa cells without losing their fluorescence. Also, these complexes were cytotoxic against different cell lines.[45-46] Recently, it was demonstrated that silver(I) complexes of nHo were light stable and also cytotoxic against different cell lines[47]. Moreover, the complexes used in this work were cytotoxic against A549 cells, [37] phototoxic against *S. typhimurium* and showed photosensitizing potential against plasmid DNA[48].

Eventhough a few more metal-nHo complexes in the literature have to date been structurally characterized, [49-51] the excited states and the redox mechanisms of the photosensitizing processes where these complexes participate still need to be addressed.

In this work, we present flash photolysis observations with the three Re(I) complexes listed in Scheme 1, as well as their redox reactivity toward the sacrificial reductant TEA (triethylamine). A comparison was made between the results of these experiments and results obtained from their thermal reactions with solvated electrons using the pulse radiolysis technique. The quenching constants (k_q) of the compounds were determined by the reaction with the electron acceptor MV^{+2} (methyl-viologen). To inquire into the potential photobiological applications of these compounds, studies in presence of Calf thymus DNA (CT-DNA) were carried out. Finally, in order to study if the redox properties of these complexes can change when DNA is present, the quenching constants (k_q) were determined by the reaction of the compounds with MV^{+2} in the presence of CT-DNA.



Scheme 1: Rhenium complexes investigated in this work: **(a)** $[(nHo)Re(CO)_3(bpy)]^+$, **(b)** $[(nHo)Re(CO)_3(phen)]^+$ and **(c)** $[(nHo)Re(CO)_3(dppz]^+$.

2. MATERIAL AND METHODS

2.1 General. $[(nHo)Re(CO)_3(L)]O_3SCF_3$ complexes (where L = bpy, phen or dppz) were available from our previous works.[36-37] Methyl-Viologen was available from a previous work.[52] Calf Thymus DNA and Triethylamine (TEA) were bought from Sigma-Aldrich. HPLC grade Methanol (MeOH) was bought from Merck and used as received. KH_2PO_4 and K_2HPO_4 were purchased from J. T. Baker. Water of very low conductivity (MiliQ grade) was used.

2.2 Preparation of working solutions

2.2.1. Preparation of CT-DNA. To prepare a stock solution of CT-DNA, a few threads of CT-DNA were dissolved in a freshly prepared pH 7.4 phosphate buffer. The resulting solution of CT-

DNA was stirred for 24 hours and left in a refrigerator overnight. The concentration of CT-DNA (in molar of bases) was determined from the recorded spectrum of the solution at 260 nm ($\varepsilon = 6600$ M^{-1} cm^{-1}).[53-55] A concentration [CT-DNA] = 8×10^{-4} M was calculated for the stock solution.

2.2.2. Complex solutions with DNA. Buffered methanolic solutions (5%) of $[(nHo)Re(CO)_3(L)]O_3SCF_3$ complexes with different concentrations of DNA were prepared by adding different aliquots of CT-DNA to the complex solution, reaching a final volume of 10 ml. The concentration of the complex was kept constant in all experiments.

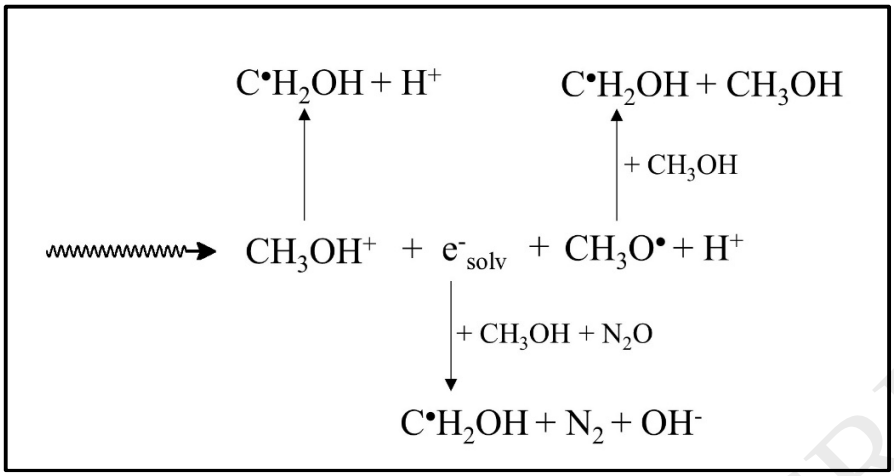
2.2.3. Solutions with Methyl-Viologen. Methanolic solutions of the rhenium complexes with different concentrations of MV^{+2} were prepared by adding different volumes of MV^{+2} to the complex solutions, reaching a final volume of 10 ml. The concentration of the complex was kept constant in all experiments.

2.3 Photochemical Measurements

Absorbance changes, ΔA, occurring in a time scale longer than 10 ns were investigated with a flash photolysis apparatus described elsewhere[56-57]. In these experiments, 10 ns flashes of 351 nm light were generated with a Lambda Physik SLL -200 excimer laser. The energy of the laser flash was attenuated to values equal to or less than 20 mJ/pulse by absorbing some of the laser light in a filter solution of $Ni(ClO_4)_2$ having the desired optical transmittance, $T = I_t / I_0$ where I_0 and I_t are respectively the intensities of the light arriving to and transmitted from the filter solution. Th×e transmittance, $T = 10^{-A}$, was routinely calculated by using the spectrophotometrically measured absorbance, *A*, of the filter solution. A right-angle configuration was used for the pump and the probe beams. Concentrations of the photolytes were adjusted to provide homogeneous concentrations of photogenerated intermediates over the optical path, l = 1 cm, of the probe beam.

To satisfy this optical condition, solutions were made with an absorbance equal to or less than 0.8 over the 0.2 cm optical path of the pump. The dimensionless parameter ξ (see the pulse radiolysis procedure) was used in the treatment of the reaction kinetics.

2.4 Pulse radiolysis. Pulse radiolysis experiments were carried out with a model TB-8/16-1S electron linear accelerator, LINAC. The instrument and computerized data collection for time-resolved UV-Vis spectroscopy and reaction kinetics have been described elsewhere in the literature. [58-59] Thiocyanate dosimetry was carried out at the beginning of each experimental session. The details of the dosimetry have been reported elsewhere. [58, 60] The procedure is based on the concentration of $(SCN)_2^{\bullet-}$ radicals generated by the electron pulse in a N_2O saturated 10^{-2} M SCN^- solution. In the procedure, the calculations were made with G = 6.13 and an extinction coefficient, $\varepsilon = 7.58 \times 10^3\ M^{-1}\ cm^{-1}$ at 472 nm, for the $(SCN)_2^{\bullet-}$ radicals.[58, 60] In general, the experiments were carried out with doses that in N_2 saturated aqueous solutions resulted in $(2.0 \pm 0.1) \times 10^{-6}$ M to $(6.0 \pm 0.3) \times 10^{-6}$ M concentrations of e^-_{sol}. In all the experiments with the Re complexes, solutions in methanol were deaerated under vacuum in a gas tight cell. In methanolic and methanolic/aqueous solution the radiolysis with ionizing radiation has been reported elsewhere in the literature. [61-62] In this experimental condition the radiolytic pulse yield e^-_{solv} and $C^{\bullet}H_2OH$ radicals according to the following reactions scheme:



Thereby, in pulse radiolysis of methanolic solutions under a N_2 atmosphere, the main reducing species formed are e^-_{solv} and $C^{\bullet}H_2OH$. As these species have large reduction potentials (-0.92 V for $C^{\bullet}H_2OH$ and -2.8 V for e^-_{solv}, both against NHE) they have been used for the study of both electron transfer and reduction reactions of different species like coordination complexes of different transition metals. The G-value of e^-_{solv} in MeOH ($G \approx 1.2$) is approximately one third part of the yield in the radiolysis of H_2O ($G \approx 2.8$) [62]. When the e^-_{solv} is scavenged with N_2O, the $C^{\bullet}H_2OH$ radical is the predominant product (yield >90%) of the reaction between $O^{\bullet-}$ and CH_3OH. [61] The reaction kinetics were investigated by following the absorbance change at given wavelengths of the spectrum and incorporating those changes in the dimensionless parameter, $\xi = (\Delta A_{inf} - \Delta A_t)/(\Delta A_{inf} - \Delta A_0)$. In ξ, ΔA_0 is the absorbance change at the beginning of the reaction, ΔA_t is determined at an instant t of the reaction and ΔA_{inf} is determined at the end of the reaction.

3. RESULTS AND DISCUSSION

3.1 Flash irradiation of the $[(nHo)Re(CO)_3(L)]^+$ complexes. Flash irradiation of the **$[(nHo)Re(CO)_3(dppz)]O_3SCF_3$** complex in deaerated 5% MeOH/H_2O, produce no optical transients in a time scale t > 10 ns. However, a transient spectrum attributed to an excited state of the complex is

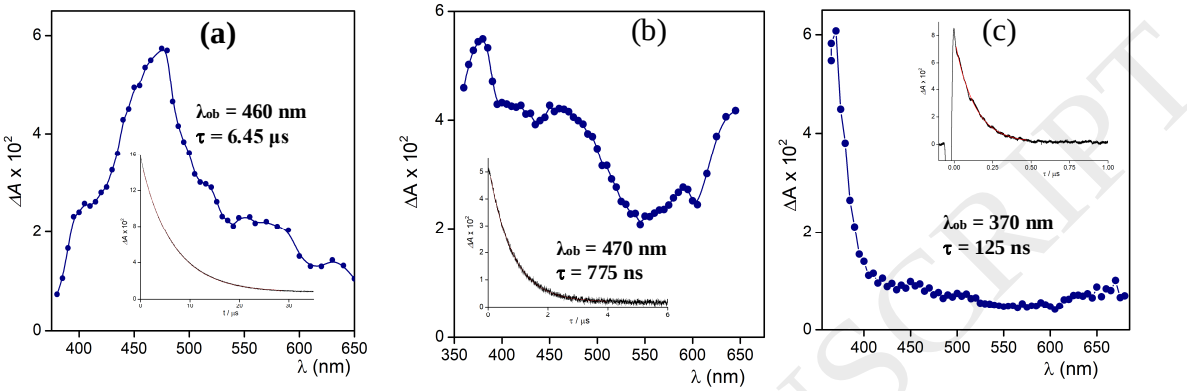


Figure 1. Transient spectra recorded after flash irradiation (λ_{ex} = 351 nm) of deaerated neat MeOH solution of: **(a)** $[(nHo)Re(CO)_3(dppz)]^+$ (2×10^{-5} M), **(b)** $[(nHo)Re(CO)_3(phen)]^+$ (3×10^{-5} M), and **(c)** $[(nHo)Re(CO)_3(bpy)]^+$ (4×10^{-5} M). *Insets*: representative examples of oscillographic traces showing the decay of the excited-state absorbance (*ΔA*).generated in deaerated neat MeOH, Figure 1a. The decay of the spectrum was followed at different

wavelengths between 375 and 650 nm. Traces were fitted to a single exponential, *i.e.*, $\xi = \exp(-t/\tau)$ with a lifetime τ = 6.45 µs, at any of the probing wavelengths. Differences were observed between the UV-Vis spectrum in Figure 1a and the published excited-state spectrum of $[(4,4'\text{-bpy})Re(CO)_3(dppz)]^+$ complex[30]. In the photolysis of $[(4,4'\text{-bpy})Re(CO)_3(dppz)]^+$, the observed transient spectrum has been described as a convolution of the $MLCT_{Re\rightarrow L}$, L = dppz and 4,4'-bpy, charge transfer spectra. In contrast with [(4,4'-lowest lying dppz-centered excited state, $^3\pi\pi^*_{dppz}$, spectrum with either or both the $bpy)Re(CO)_3(dppz)]^+$, the features of the spectrum depicted in Figure 1a and the observed lifetime are in better agreement with those of a dppz-centered, $^3\pi\pi^*_{dppz}$, of $[(nHo)Re(CO)_3(dppz)]^+$ [63]. The $MLCT_{Re\rightarrow L}$, L = dppz, and nHo, excited states of $[(nHo)Re(CO)_3(dppz)]^+$ may not be observed either because they decay in a time scale shorter than

10 ns or for being in equilibrium with the slower decaying dppz-centered, $^3\pi\pi^*_{dppz}$, excited state. Therefore, different contributions to the transient spectrum from the spectator ligands, *i.e.* nHo and 4,4'-bpy in $[(nHo)Re(CO)_3(dppz)]^+$ and $[(4,4'\text{-bpy})Re(CO)_3(dppz)]^+$, respectively, are **(a)** most likely responsible for the observed differences.

In deaerated neat MeOH, the 351 nm flash irradiations of **$[(nHo)Re(CO)_3(phen)]^+$** and **$[(nHo)Re(CO)_3(bpy)]^+$**, induces the formation of transients with lifetimes τ = 775 ns and 125 ns, respectively. For **$[(nHo)Re(CO)_3(phen)]^+$**, Figure 1b, the bands observed in $\lambda \approx 370$ nm and $\lambda \approx$ 460 nm are in agreement with the previously attributed $^3MLCT_{Re\rightarrow phen}$ excited state for the related complex $[(L)Re(CO)_3(phen)]^+$.[17,64] Therefore, is possible to assign the photogenerated transient in our complex to the $^3MLCT_{Re\rightarrow phen}$ state. The spectra of **$[(nHo)Re(CO)_3(bpy)]^+$** , Figure 1c, shows one intense band in $\lambda \approx 385$ nm, previously attributed to the $^3MLCT_{Re\rightarrow bpy}$ excited state in the $[(py)Re(CO)_3(bpy)]^+$ complex.[65] Based on these spectroscopic similarities, it is possible to assign the photogenerated transient to the $^3MLCT_{Re\rightarrow bpy}$ excited state in **$[(nHo)Re(CO)_3(bpy)]^+$.**

3.2. Excited states of Re^I-nHo complexes in the presence of CT-DNA.

The excited-state spectrum of $[(nHo)Re(CO)_3(dppz)]^+$ was only observed when the MeOH/H_2O solution had concentrations of MeOH equal to or larger than 75% (v/v). The excited-state spectrum of $[(nHo)Re(CO)_3(dppz)]^+$ was also recorded in a 25% MeOH/H_2O solution flash irradiated in the

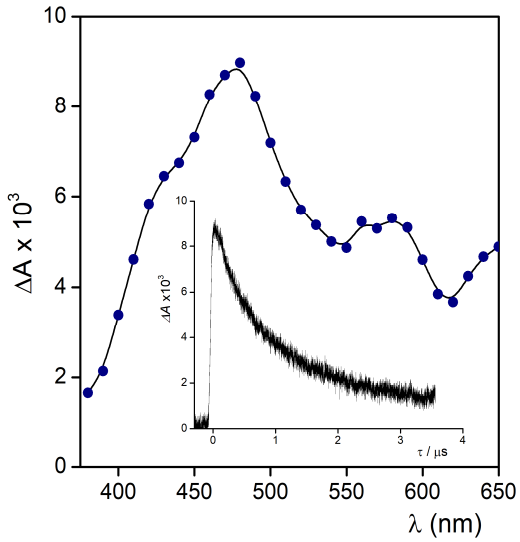


Figure 2. Transient spectrum of a 2×10^{-4} M of $[(nHo)Re(CO)_3(dppz)]^+$ 25% MeOH/H_2O solution with 3×10^{-4} M of CT-DNA upon irradiation (λ_{ex} = 351 nm) *Inset*: oscillographic trace recorded at λ_{ob} = 460 nm showing the decay of the excited-state absorbance (ΔA), with a lifetime τ = 0.89 μs.

presence of 3×10^{-4} M CT-DNA (Figure 2). The spectra recorded in presence of CT-DNA and in neat MeOH (Figure 1a) were indistinguishable. Thus, the transient spectra observed in the presence of CT-DNA was assigned to the excited states of $[(nHo)Re(CO)_3(dppz)]^+$ described above. However, the observed lifetimes in both conditions were not the same. While in neat MeOH the lifetime of the decay is τ = 6.54 μs, in the aqueous solution with CT-DNA the lifetime decay was τ = 0.88 μs. This lifetime disparity can be attributed to differences in the environments of the excited state which increase the rate of radiationless relaxation in the latter experimental

conditions. By comparing the photophysical behaviors of $[(nHo)Re(CO)_3(dppz)]^+$ observed in the absence and presence of DNA, we can conclude that the complex is interacting with the CT-DNA, presumably by intercalation. This is consistent with a previous study where the intercalation of $[(4,4'\text{-bpy})Re(CO)_3(dppz)]^+$ in DNA was demonstrated.[32] The association of $[(nHo)Re(CO)_3(dppz)]^+$ with CT-DNA must be assisted by an electrostatic interaction between a negatively charged CT-DNA backbone and the cationic complex. Moreover, this kind of interaction must provide some sort of hydrophobic environment which protects the complex from solvent molecules an allows the observation of the excited states of $[(nHo)Re(CO)_3(dppz)]^+$.

As a semi-quantitative study to ascertain if the $[(nHo)Re(CO)_3(dppz)]^+$ complex is able to intercalate into the CT-DNA double helix, a displacing experiment of a known fluorescent intercalator, Ethidium Bromide (EB), was carried out. When EB is intercalated into a CT-DNA, the fluorescence of the formed adduct increases around 25 times. [66] In the presence of a DNA intercalating compound, which can compete with EB for the DNA intercalating sites, the fluorescence of EB-DNA adduct may be quenched as the new compound is displacing the EB from the DNA. As seen in Figure S1, increasing concentrations of $[(nHo)Re(CO)_3(dppz)]^+$ to a solution of EB and CT-DNA decreases the fluorescence intensity of the adduct, showing that the mode of interaction between this complex and CT-DNA is the same as EB, typically by intercalation (full details of this experiment can be found in the supplementary material).

The excited-state transient spectra of $[(nHo)Re(CO)_3(bpy)]^+$ or $[(nHo)Re(CO)_3(phen)]^+$ showed no changes when the complexes were flash irradiated in a 25% MeOH/H_2O solutions containing 3×10^{-4} M CT-DNA (Figure S2a and S2b). When comparing the lifetime of the excited-states of these two complexes observed in 25% MeOH/H_2O solutions (τ = 28.8 ns and τ = 179.0 ns for $[(nHo)Re(CO)_3(bpy)]^+$ and $[(nHo)Re(CO)_3(phen)]^+$, respectively) with that observed in neat MeOH (τ = 125 ns and τ = 775 ns for $[(nHo)Re(CO)_3(bpy)]^+$ and $[(nHo)Re(CO)_3(phen)]^+$, respectively) a clear decrease was observed. Conversely, lifetimes were the same whether the complex was irradiated in the presence or absence of CT-DNA.

This experimental observation suggests the association between $[(nHo)Re(CO)_3(bpy)]^+$ and $[(nHo)Re(CO)_3(phen)]^+$ with CT-DNA is null or weak, and also suggests that the decrease of lifetimes is due to the solvent, *e.g.* due to the polarity and/or the formation of strong H-bonds. In addition, data indicates that the ligand dppz would be playing a key role in the intercalation of the complex into DNA with no major contribution of the spectator nHo ligand.

3.3. Redox behavior of the excited states

The ability of the $^3MLCT_{Re\rightarrow L}$ excited states to participate in redox reactions has been abundantly documented in the literature.[7,10,60,67] To ascertain if $^3MLCT_{Re\rightarrow dppz}$ excited states of $[(nHo)Re(CO)_3(dppz)]^+$ in the presence of CT-DNA were able to participate in similar chemical reactions, their electron transfer reactions with the electron donor TEA and with the electron acceptor MV^{2+} were investigated. Also, photoinduced reactions of $[(nHo)Re(CO)_3(L)]^+$, L = bpy, phen, were studied in order to establish the role of nHo ligand in the excited state redox reactions.

3.3.1. Reductive quenching of $[(nHo)Re(CO)_3(L)]^+$ excited states.

$[(nHo)Re(CO)_3(phen)]^+$ complex was flash irradiated in a neat MeOH solution containing 0.1 M TEA. The generated transient spectrum (Figure 3a) was longer lived than the excited states (τ > 10 μs) and the characteristic absorptions band of the $phen^{\bullet-}$ chromophore described for other related complexes (*e.g.*, $[pyRe(CO)_3(phen^{\bullet-})]$) is clearly missing. [17, 64] Therefore, the spectrum

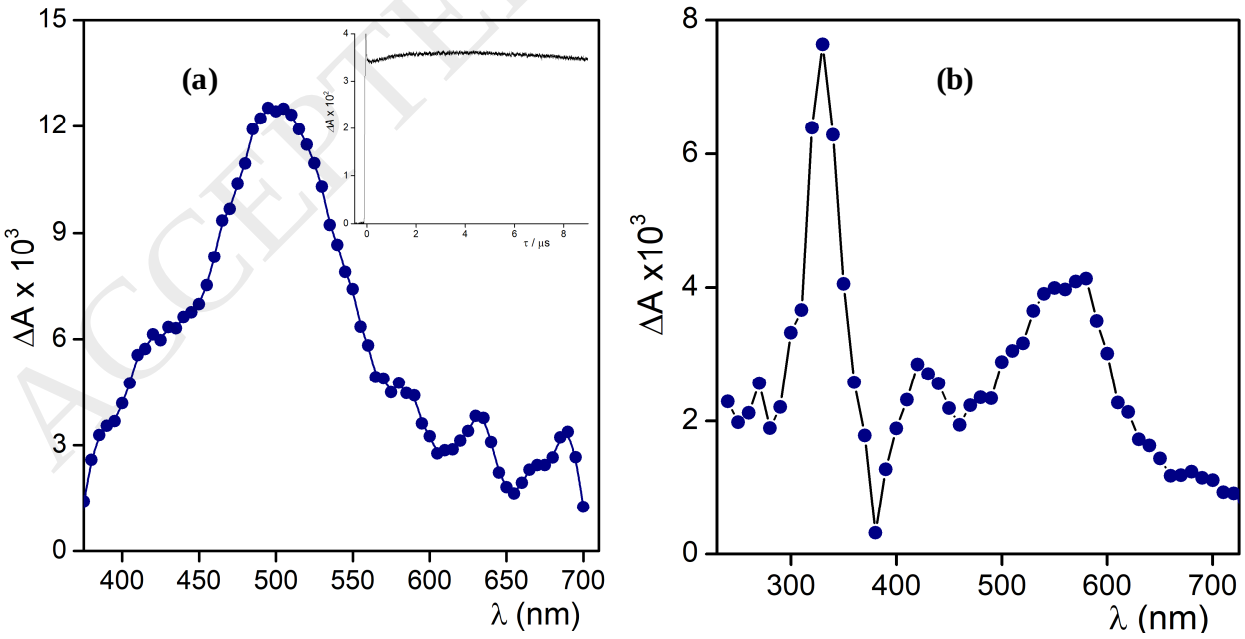


Figure 3. (a) Transient spectrum of [(nHo$^{\bullet-}$)Re(CO)$_3$(phen)] recorded upon flash irradiation (λ_{ex} = 351 nm) of 2 × 10^{-4} M [(nHo)Re(CO)$_3$(phen)]$^+$ in MeOH containing 0.1 M TEA. *Inset:* oscillographic trace recorded at λ_{ob} = 500 nm showing the slow decay of [(nHo$^{\bullet-}$)Re(CO)$_3$(phen)]. **(b)** Transient spectrum recorded 35 μs after the e^-_{sol} reacts with [(nHo)Re(CO)$_3$(phen)]$^+$.

in Figure 3a cannot be ascribed to the radical [(nHo)Re(CO)$_3$(phen$^{\bullet-}$)]. A comparison of the spectra generated when nHo is both flash photolyzed and pulse radiolyzed is made Figure S3. It shows that the latter techniques produce different species. These species can be products of the e^-_{sol} reaction, i.e., nHo$^{\bullet-}$, in pulse radiolysis and of the H-atom abstraction, i.e, nHoH$^{\bullet}$, in the flash photochemical experiment. This experimental observation strongly suggests that the spectrum in Fig. 3a is a convolution of the spectra of the complexes corresponding to the products of nHo, i.e., one [(nHo$^{\bullet-}$)Re^{I}(CO)$_3$(phen)] and the other, [(nHoH$^{\bullet}$)Re^{I}(CO)$_3$(phen)]$^+$. In the convoluted spectrum of Figure 3a, it appears that [(nHo$^{\bullet-}$)Re^{I}(CO)$_3$(phen)] makes a smaller contribution than [(nHo$^{\bullet-}$)Re^{I}(CO)$_3$(phen)].

The pulse radiolysis technique was also used to generate the spectrum of the species produced by the reaction of [(nHo)Re(CO)$_3$(phen)]$^+$ with e^-_{solv}. Solutions ~ 7 × 10^{-5} M of [(nHo)Re(CO)$_3$(phen)]$^+$ in neat MeOH were used in the radiolysis experiments after the deaeration with streams of N_2 (Figure 3b). The absence of the phen$^{\bullet-}$ features in the product of the reductive quenching of [(nHo)Re(CO)$_3$(phen)]$^+$ and the improbableness of generating a Re(0) intermediate suggests that the spectrum in the Figure 3b corresponds to an adduct of the •CH_2OH radical to [(nHo)Re(CO)$_3$(phen)]$^+$.

In contrast to [(nHo)Re(CO)$_3$(phen)]$^+$, the electron accepting role of nHo appears diminished in the reductive quenching of the respective excited states of [(nHo)Re(CO)$_3$(L)]$^+$, L = bpy, dppz. The reaction products of the quenching reactions of the excited states of these compounds were investigated combining experimental information obtained from flash photolysis and pulse radiolysis experiments, done under similar medium conditions. The typical excited-state spectrum of [(nHo)Re(CO)$_3$(bpy)]$^+$ was observed in a time scale $\tau \leq 70$ ns when the complex

was flash photolyzed in a solution containing 0.1 M TEA in MeOH (Figure 4a). [68] The transient spectrum evolves in time passing through an intermediate step and the final transient spectrum is observed in a time scale, $\tau \geq 570$ ns.

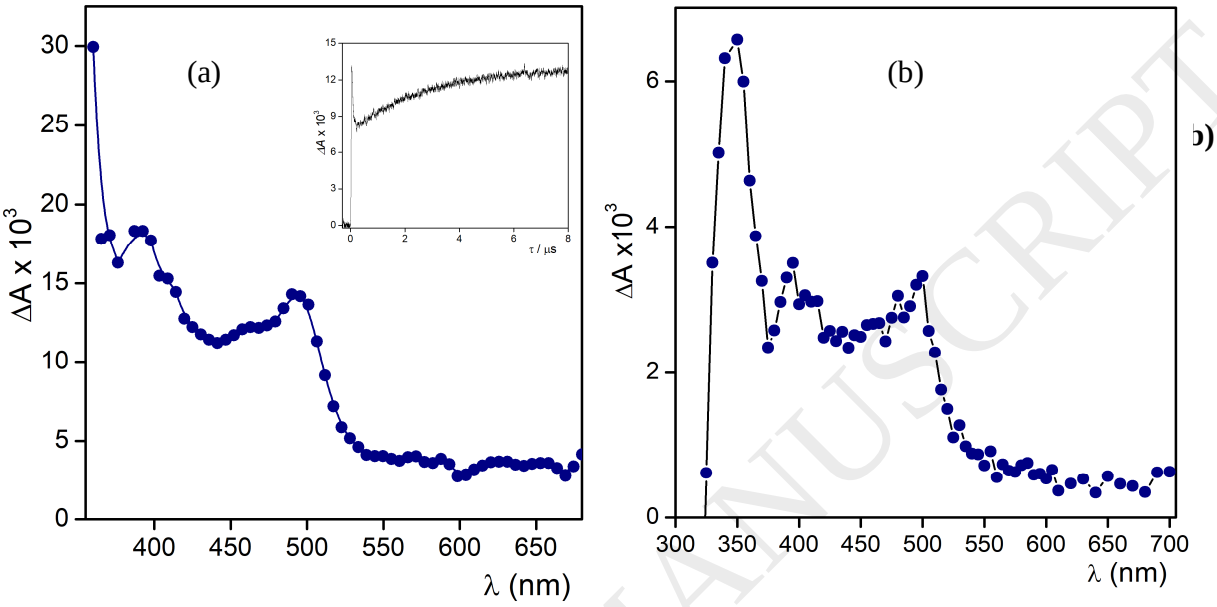


Figure 4. (a) Transient spectrum of [(nHo)Re(CO)$_3$(bpy$^{\bullet-}$)] recorded 8 μs after flash irradiation (λ_{ex} = 351 nm) of 2 × 10^{-4} M of [(nHo)Re(CO)$_3$(bpy)]$^+$ in MeOH containing 0.1 M TEA *Inset*: oscillographic trace recorded at λ_{ob} = 450 nm showing the formation of [(nHo)Re(CO)$_3$(bpy$^{\bullet-}$)] radical. **(b)** Transient spectra recorded 5 μs after a radiolytic pulse of [(nHo)Re(CO)$_3$(bpy)]$^+$ in MeOH.

In $\tau \sim 8$ μs, the transient spectrum in the Figure 4a is similar to the one obtained in the pulse radiolysis experiment, Figure 4b, comparing well with the literature spectrum of [BrRe(CO)$_3$(bpy$^{\bullet-}$)], a related complex.[68] The comparison shows that the respectively generated species via pulse radiolysis (eq. 1) and flash photolysis (eqs. 2-4) have the same bpy$^{\bullet-}$ chromophore. In the photolysis experiment, the multistep trace shown as inset in Figure 4a is in agreement with the set of reactions described in eqs. 2-4.

$$[(nHo)Re(CO)_3(bpy)]^+ \xrightarrow{e^-_{sol}} [(nHo)Re(CO)_3(bpy^{\bullet-})] \qquad \textit{eq. (1)}$$

$[(nHo)Re(CO)_3(bpy)]^+ \xrightarrow{h\nu} [(nHo)Re(CO)_3(bpy)]^{+}*$ ***eq. (2)***

$[(nHo)Re(CO)_3(bpy)]^{+}* \xrightarrow{-h\nu,\ -\Delta} [(nHo)Re(CO)_3(bpy)]^+$ ***eq. (3)***

$[(nHo)Re(CO)_3(bpy)]^{+}* \xrightarrow[-\ TEA^{\bullet+}]{+\ TEA} [(nHo)Re(CO)_3(bpy^{\bullet-})]$ ***eq. (4)***

The photoreduction spectra of $[(nHo)Re(CO)_3(dppz)]^+$ with TEA in MeOH (Figure 5) produces a spectrum that can be compared with that previously obtained for the $dppz^{\bullet-}$ radical [69]. Therefore, the spectra recorded in the reductive quenching of the excited state by TEA is assigned to the $[(nHo)Re(CO)_3(dppz^{\bullet-})]$ radical.

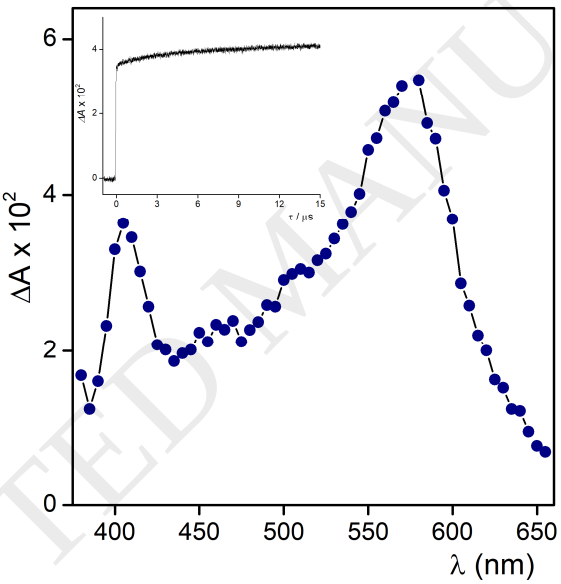


Figure 5. Transient spectrum of $[(nHo)Re(CO)_3(dppz^{\bullet-})]$ radical recorded upon flash irradiation (λ_{ex} = 351 nm) of 2 × 10^{-4} M of $[(nHo)Re(CO)_3(dppz)]^+$ in MeOH, containing 0.1 M TEA. *Inset*: oscillographic trace recorded at λ_{ob} = 540 nm showing the formation of $[(nHo)Re(CO)_3(dppz^{\bullet-})]$ radical.

3.3.2. Oxidative quenching of the complexes.

Excited states of $[(nHo)Re(CO)_3(L)]^+$ complexes were generated in the presence of MV^{2+}. The formation of the $MV^{\bullet+}$ radical was evident from the absorptions at ˜600 nm. As a representative

example, the spectra of $[(nHo)Re(CO)_3(phen)]^+$ with MV^{+2} is shown in the Figure 6. The mechanism of formation is descripted in equations 5 and 6.

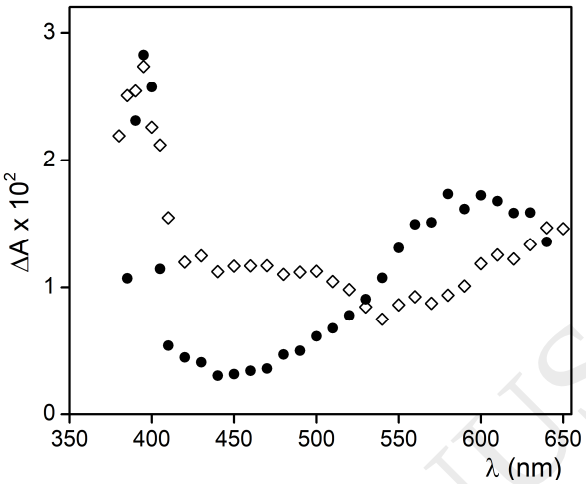


Figure 6. Transient spectra of $[(nHo)Re(CO)_3(phen)]^+$ (5×10^{-5} M) at 0.75 μs (white diamonds) and 20 μs (black circles) upon irradiation (λ_{ex} = 351 nm) with an excess of MV^{+2} (3.5×10^{-4} M). The formation of the $MV^{\bullet+}$ radical is seen at 600 nm.

$$[(nHo)Re^{I}(CO)_3(phen)]^+ + h\nu \longrightarrow [(nHo)Re(CO)_3(phen)]^{+}* \qquad \textit{eq. (5)}$$

$$[(nHo)Re(CO)_3(phen)]^{+}* + MV^{+2} \rightarrow [(nHo)Re^{II}(CO)_3(phen)]^{+2} + MV^{\bullet+} \qquad \textit{eq. (6)}$$

Solutions of the complexes with MV^{+2} were flash irradiated at 351 nm. The rate constants of the quenching reactions were determined by varying the concentration of MV^{+2} while keeping the complex concentration constant. The kinetics of the reactions were investigated under a pseudo-first order regime in MV^{+2} concentration. For all complexes, single exponential decays, $\Delta A_{(t)} = \Delta A_{(0)} e^{-kd.t}$ of the excited state with a rate constant k_d corresponding to a pseudo first order dependence on MV^{+2} concentration were obtained. The quenching rate constants (k_q) were calculated from the slope of the plot k_d vs MV^{+2} concentration for each case. As an example, the

plot of $[(nHo)Re(CO)_3(bpy)]^+$ is shown in Figure S4. The quenching experiments yield the quenching rate constants $k_q = 2.1 \times 10^9\ M^{-1}\ s^{-1}$, $k_q = 1.3 \times 10^9\ M^{-1}\ s^{-1}$ and $k_q = 1.4 \times 10^8\ M^{-1}s^{-1}$ for the excited states of $[(nHo)Re(CO)_3(bpy)]^+$, $[(nHo)Re(CO)_3(phen)]^+$ and $[(nHo)(Re(CO)_3(dppz)]^+$, respectively. These values are in agreement with the k_q obtained for structurally related $Re(CO)_3(L)$ complexes. [70-71]

3.4. Interaction between $[(nHo)Re(CO)_3(L)]^+$ complexes with CT-DNA and MV^{+2}.

Besides the formation of stable radicals, MV^{+2} can also intercalate into DNA. [72] In order to find out if the presence of methyl-viologen could lead to different processes or change the phochemical behavior of the complexes, 20% MeOH (v/v) aqueous solutions of $[(nHo)Re(CO)_3(dppz)]^+$ (7×10^{-5} M), containing also 3×10^{-4} M of CT-DNA and different MV^{+2} concentrations, were flash irradiated at 351 nm. In each solution, a fast-single exponential decay of the λ_{ob} = 460 nm absorbance was observed together with the appearance of the characteristic NIR spectrum of the $MV^{\bullet+}$ radical (Figure 5). The rate constants were calculated as before. The quenching rate constant, $k_q = 1.42 \times 10^{10}\ M^{-1}\ s^{-1}$, was also calculated from the slope of the plot k_d vs MV^{2+} concentration (Figure 7). This ~100 × fold increment of the k_q in the presence of MV^{+2} shows that both molecules (Re-dppz complex and MV^{+2}) are immersed in an environment where they interaction is favored. This can be possible due to the interaction of both species with the DNA, using the biopolymer as a well-organized matrix. Similar flash photolytic experiments were carried out with $[(nHo)Re(CO)_3(bpy)]^+$ and $[(nHo)Re(CO)_3(phen)]^+$. Analyses of the traces collected when the complexes were in the presence and absence of CT-DNA and MV^{+2} showed no differences between the quenching rate constants k_q. These results indicate that the presence of intercalated

MV^{+2} has no effect on the interaction between these complexes and the genetic material. This is probably the consequence of different types of interaction and/or the lack of intercalation.

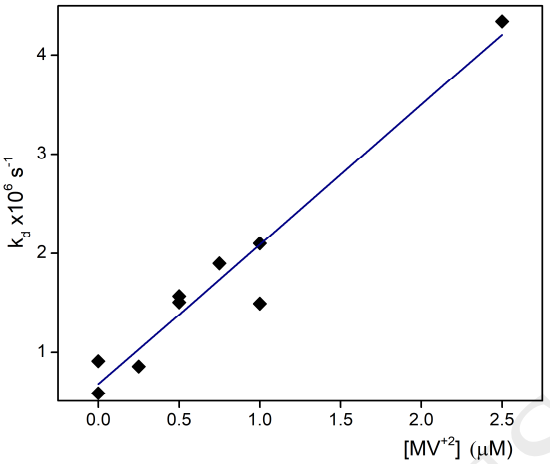


Figure 7. Dependence of the $[(nHo)Re(CO)_3(dppz)]^+$ decay rate constant k_d on the MV^{+2} concentration. The excited state was flash generated in an $[(nHo)Re(CO)_3(dppz)]^+$ 20% $MeOH/H_2O$ solution (1×10^{-4} M) of the complex containing 3×10^{-4} M of CT-DNA.

CONCLUSIONS

Two main conclusions can be derived from the previous section. One is the dual role of the spectator ligand nHo and the other is the $[(nHo)Re(CO)_3(dppz)]^+$ excited state accessibility to quenchers when it is intercalated in a biopolymer, *e.g.*, DNA. With regard to the photoinduced transfer of charge, nHo relinquish its role of spectator and acts as an electron acceptor when it competes against phen ligand. However, nHo proves to be a poorer electron acceptor when competes with dppz and bpy ligands. Since the dual behavior appears in the ground and excited state, it cannot be only attributed to the position of the MLCT excited sates. Energy considerations, *e.g.* based on the redox potentials of the ligands, as well as different symmetry restrictions must be considered. Several matters should be taken into account with regard to the excited state

accessibility. The intercalation of the $[(nHo)Re(CO)_3(dppz)]^+$ complex (the guest) in DNA (the host) shows that conditions created by the intercalation modify the photophysical and photochemical properties of the guest. In addition to the host DNA used here, it is possible that other polymers that are also able to form adducts with photoactive complexes will alter the properties of the guest complex. A necessary condition in all these cases is that in an environment provided by the host the photochemical or thermal reactivity of the guest complex differs from the one exhibited in aqueous or organic media. It is possible to imagine that this manner of altering the chemical properties of the guest may find many biotechnological applications, such as cell probes or photodynamic therapy, among other biological purposes. Also, these chemical modifications can lead to applications in areas of CO_2 reduction, drug design and delivery as well in catalysis.

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