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Research paper

Z to *E* light-activated isomerization of α -pyridyl-*N*-arylnitrone ligands sensitized by rhenium(I) polypyridyl complexes



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ARTICLE INFO	A B S T R A C T			
Keywords: Photosensitized isomerization of nitrones Rhenium(I) polypyridyl compounds Photosensors	A series of rhenium(I) polypyridyl compounds, bearing photoisomerizable nitrones as ligands, was synthesized and characterized by several techniques. The photochemical and photophysical behaviors of the compounds were investigated. Upon irradiation, acetonitrile solutions of the nitrones, or their respective complexes, exhibit changes in absorption, emission, and FTIR spectra. FTIR revealed the formation of the respective anilide as the photoproducts of irradiation of the uncoordinated nitrones, while irradiation of the complexes resulted in $Z \rightarrow E$ due to the photosensitized isomerization of the coordinated ligand, also confirmed by HPLC-MS and ¹ H NMR. The photoisomerization quantum yields are dependent on the nature of the nitrone substituent, which changes the energy of the ³ IL _{Z-NitX} excited state, which is populated by photosensitization. ³ MLCT becomes the lowest- lying excited state in the E-product and results in an increase in emission intensity. The changes in spectroscopic			

1. Introduction

The photophysical properties of rhenium polypyridyl compounds were first described in the 1970s [1]. The characteristics of these compounds have been exploited in the development of potential molecular devices, such as molecular switches [2–4], luminescent sensors [5–9], ion sensors [10], and electroluminescent layers for OLEDs [11–15]. These compounds are also valuable tools for studying push-pull systems and proton-coupled electron transfer systems [16] as well as in practical applications as triggers for the electron injection process [17,18], and non-linear optics [19].

The lowest-lying excited state of rhenium(I) polypyridyl compounds is usually the triplet metal-to-ligand charge transfer one, ³MLCT. The energy of this excited state is often sufficient to sensitize intra- or intermolecular chemical reactions, such as photocyclization [20–22] or *trans*-to-*cis* isomerization of azo or stilbene-like compounds [23–29]. Stilbene-like ligands are the most investigated group for the isomerization sensitized by rhenium(I) complexes. Modification on these ligands, such as the use of electron-withdrawing, multiple double bonds [24,30] or surfactant groups [31] was done to evaluate their effects on the photosensitized isomerization. Besides the modifications on the photoisomerizable ligands, the use of coordinated polypyridyl ligands having different substituents on the photochemical process has also been investigated [32–34], as well as binuclear compounds [35]. The dynamics of the process have also been investigated by quantum mechanics approach [36] as well as time-resolved experiments [37–39]. New compounds are sought for the development of molecular devices based on photoassisted isomerization.

properties of the Z or E coordinated nitrones can be exploited for molecular devices such as photosensors.

The photoassisted isomerization was investigated for non-polar double bonds until now. Besides the stilbene or azo groups, the use of nitrone groups can access information on the isomerization process by using a polarized, charged, and oxidized double bond of nitrones (C= N^+-O^-), since it presents structural and electronic characteristics that contribute to the comprehension of photosensitized isomerization processes. The literature reports that the direct irradiation of Z-nitrone results in its decomposition. On the other hand, by populating the ³IL state by photosensitization, the only product detected is the E-isomer. Thus these compounds are promising candidates to evaluate the photosensitization process promoted by the rhenium(I) moiety.

In this work, we report the synthesis, characterization, photochemical and photophysical properties of a new class of rhenium(I) compounds featuring nitrone-containing groups (C=N⁺-O⁻) as isomerizable ligands, Fig. 1. Photochemical and photophysical tools, associated with the rational design of nitrone-containing ligands, led to the investigation of the influence of electron-withdrawing and donating groups on the photosensitized Z- to E- isomerization process. These investigations aim to evaluate their possible use in the development of molecular devices.

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Fig. 1. Structures of the investigated Re(I) complexes (The nitrone functional group is highlighted).

2. Experimental

2.1. General methods

FTIR spectra were obtained on a Perkin-Elmer Spectrum One spectrophotometer using an ATR accessory. ¹H NMR spectra were recorded at 300.15 K on a Bruker Avance III spectrometer operating at a frequency of 300 MHz or on a DRX-500 Bruker Avance spectrometer operating at a frequency of 500 MHz. ¹H chemical shifts are reported in parts per million (ppm), with TMS at 0 ppm as absolute standard, and residual acetonitrile as internal standard with the CH₃ peak centered at 1.96 ppm [40]. Additional ¹H and ¹³C NMR spectra were acquired in a Varian VNMRS 500 MHz spectrometer operating at a resonance frequency of 125.7 (13C) and 500 (1H) MHz, using a 5 mm liquid state 1H indirect probe. Great care was taken in shimming the magnet in order to obtain highly resolved spectra without need for spinning the samples. ¹³C chemical shifts were referenced to TMS at 0 ppm with the CN acetonitrile at 118.06 ppm as internal reference [40]. The absorption spectra were recorded using an Agilent 8453 spectrophotometer equipped with an Agilent 89090A Peltier temperature controller described elsewhere [41]. Irradiation of samples was performed using a Newport solar simulator model 96,000 with an AM1.5G filter [42,43] or a Newport system comprising a lamp house equipped with a xenon (Hg) 200 W lamp [35]. The light passes through a water filter, followed by the selection of the 405-nm wavelength by an appropriate interference filter. The light intensity was determined by the method described by Hatchard and Parker using tris-(oxalato)ferrate actinometry [44,45]. The quantum yields reported are the average of three distinct experiments. The values reported for the photostationary state, PSS, were determined by the absorbance difference of the initial and final samples, divided by the initial value. Emission and excitation spectra were recorded using a Cary Eclipse spectrofluorometer, as described elsewhere [42,43,46,47]. For all experiments, guartz cuvettes with a 1.000-cm path length and HPLC-grade solvents were employed. The HPLC-ESI-MS analyses were carried out in an Agilent Technologies 1290 Infinity equipment having a DAD (UV/Vis) detector coupled to an Agilent Technologies Electrosprav Mass Spectrometer (ESI-MS), model 6130 Quadrupole. The chromatographic profiles were collected by using an Agilent Poroshell 120 EC-C18, $2,1 \times 50$ mm, 4 μ m column at 40 °C. 10 µL of the sample was injected and it was applied a two-solvent elution gradient (A = Ultrapure Water + 0.1% TFA and B = 90%HPLC grade acetonitrile + 0.1% TFA) at a flow rate of 0.300 mL min⁻¹. The elution gradient as a function of solvent B was: 10% - 95% over 20 min; 95%-100% over 5 min; 100% for 10 min resulting in a total time of 35 min per analytical run. DAD detection was set to monitor absorption changes at 290 and 340 nm. The ESI-MS analyses were performed by using ionization in positive mode, capillary voltage 3.0 kV, capillary temperature 350 °C, ion energy 5.0 V, nitrogen gas flow 12 L min⁻¹, solvent heater 250 °C, 35 psig pressure in the nebulizer, multiplier 1.0 and cone at 35 V. The mass spectrometer was programmed for scan the mass range of 100 to 1500 Daltons. All solvents for synthesis were purchased from Synth - Brazil. All reagents for synthesis and all deuterated and HPLC solvents were purchased from Sigma-Aldrich - USA and used as received. The (Z)-3,4-dimethyl-N-(pyridin-4-ylmethylene) aniline oxide (Z-Nit-Me₂), (Z)-N-(pyridin-4-ylmethylene)aniline oxide (Z-Nit-H) and (Z)-4-chloro-N-(pyridin-4-



Scheme 1. Synthetic routes for preparation of the ligands and coordination compounds.

ylmethylene)aniline oxide (Z-Nit-Cl) were prepared and characterized as described elsewhere [48].

The compounds were prepared as depicted in Scheme 1 and described below.

2.1.1. Synthesis of fac-[Re(CO)₃(Ph₂-phen)Cl]

The *fac*-[Re(CO)₃(Ph₂-phen)Cl] complex was prepared using a slight modification of the procedure previously described for similar compounds [49–51]. To xylene (100 mL), 4,7-diphenyl-1,10-phenanthroline, Ph₂-phen, (1.08 g - 3.25 mmol) was added. The mixture was continuously stirred and heated to boiling, upon which the complete dissolution of the ligand was observed. Next, Re(CO)₅(Cl) (1.2 g - 3.25 mmol) was added, and the mixture was refluxed for 2.5 h. After the solution had reached room temperature, the formation of a solid was observed, which was filtered and dried in a desiccator, yielding 1.69 g of product, corresponding to 86% yield. The spectroscopic data for the product were coincident with those reported [52].

2.1.2. Synthesis of fac-[Re(CO)₃(Ph₂-phen)(tfms)]

The *fac*-[Re(CO)₃(Ph₂-phen)(tfms)] complex was prepared using a slight modification of the procedure described in the literature for similar compounds [49–51]. To dichloromethane (75 mL), *fac*-[Re (CO)₃(Ph₂-phen)Cl] (1.40 g – 2.2 mmol) was added, and the mixture was continuously stirred under argon for 1 h. Then, trifluoromethanesulfonic acid, Htfms, (2 mL–23 mmol) was added, followed by stirring under argon for additional 2 h. The product was obtained by adding diethyl ether until the precipitation of the complex. The solid was collected by filtration and resulted in 0.84 g of product, which corresponds to 50% yield. The spectroscopic data for the product was in agreement with those reported [52].

2.1.3. Synthesis of fac-[$Re(CO)_3(Ph_2-phen)(Z-Nit\mathbf{X})$]PF₆; $\underline{X} = Me_2$, H or Cl ($Re(Z-Nit-\mathbf{X})$)

The fac-[Re(CO)₃(Ph₂-phen)(Z-Nit-X)] ($\underline{X} = Me_2$, H or Cl) complexes were prepared using a modification of the procedure described in the literature for similar compounds using stilbene-like ligands [34,49–51]. The precursor complex, fac-[Re(CO)₃(Ph₂-phen)(tfms)], and the respective Z-nitrone ligand (3 equivalents) were added to methanol (40 mL). The mixture was heated to reflux for 5 h, followed by adding NH₄PF₆ (2 equivalents). After volume reduction, the product was collected by filtration and washed with diethylether. fac-[Re $(CO)_3(Ph_2-phen)(Z-Nit-Me_2)]PF_6$ yield 60% (Anal. calcd for C41H30F6N4O4PRe: C, 50.56; H, 3.10; N, 5.75; found: C, 50.24; H, 3.42; N, 5.60). ¹H NMR (300 MHz, CD₃CN, δ / ppm) 8.41 (dd, 2H), 8.09 (m, 2H), 8.16 (s, 1H), 7.55 (d, 1H) 2.31 (s, 6H), 7.46 (dd, 1H), 9.67 (d, 2H), 8.09 (d, 2H), 7.67 (m, 10H), 8.11 (m, 2H). fac-[Re(CO)₃(Ph₂-phen)(Z-Nit-H)]PF₆·H₂O yield 34% (Anal. calcd for C₃₉H₂₈F₆N₄O₅PRe: C, 48.60; H, 2.93; N, 5.81; found: C, 48.89; H, 2.72; N, 5.78). ¹H NMR (300 MHz, CD₃CN, δ / ppm) 8.45 (dd, 2H), 8.12 (m, 2H), 8.21 (s, 1H), 7.75 (dd, 2H), 7.55 (m, 3H), 9.68 (d, 2H), 8.09 (d, 2H), 7.68 (m, 10H), 8.12 (m, 2H). fac-[Re(CO)₃(Ph₂-phen)(Z-Nit-Cl)]PF₆·H₂O yield 51% (Anal. calcd for C₃₉H₂₇ClF₆N₄O₅PRe: C, 46.92; H, 2.73; N, 5.61; found: C, 47.09; H, 2.74; N, 5.72). ¹H NMR (300 MHz, CD₃CN, δ / ppm) 8.45 (dd, 2H), 8.10 (d, 2H), 8.19 (s, 1H), 7.75 (dd, 2H), 7.54 (dd, 2H), 9.67 (d, 2H), 8.09 (d, 2H), 7.67 (m, 10H), 8.12 (m, 2H).

3. Results and discussion

The absorption spectra of the compounds *Z*-Nit-**X**, **X** = Me₂, H or Cl, and the corresponding coordination compounds, Re(*Z*-Nit-**X**), in acetonitrile are presented in Fig. 2. The nitrone compounds exhibited absorption up to 375 nm, which can be ascribed to π - π * electronic transitions.

The absorption spectra of the complexes included intense absorption bands in the higher-energy region (200–300 nm) due to the presence of intraligand π - π * transitions of the Ph₂-phen ligand [52]. The



Fig. 2. Absorption spectra of Re(Z-Nit-X) (solid lines) and Z-Nit-X (dashed lines), $X = Me_2$, H, or Cl in acetonitrile.

absorption in the lower-energy region (ca. 300–450 nm) exhibited molar absorptivities higher than those typically observed for rheniumpolypyridyl compounds [1,53]. The high molar absorptivities can be ascribed to a red-shift of nitrone absorption after coordination to the rhenium(I) center, resulting in a mixture of IL (π - π *_{Nit}) and MLCT ($d\pi$ _{Re}- π *_{Ph2-phen}) transitions in this region. This behavior was previously observed for similar compounds with stilbene-like ligands [30,54].

The presence of electron-withdrawing or electron-donating substituents on the nitrones had little influence on their absorption maxima. However, small changes were observed for the complexes, which featured maxima in the lower-energy region of 345, 341, and 340 nm for ReNit-X, $X = Me_2$, H, or Cl, respectively.

Irradiation of deaerated acetonitrile solutions of Z-Nit-**X** or Re(*Z*-Nit-**X**) by AM1.5G simulated sunlight initially verified the behavior of the prepared compounds. The absorption spectral changes in *Z*-Nit-**X** upon irradiation are exemplified by *Z*-Nit-**Me**₂, Fig. 3a, while those observed for the complexes are exemplified by the changes in Re(*Z*-Nit-**Me**₂), Fig. 3b.

Absorption changes for the pyridyl-nitrone solution resulted in isosbestic points at 232, 239, and 265 nm (Fig. 3a). The FTIR spectra of the compounds revealed the difference in the products obtained through direct irradiation of the pyridyl-nitrone or by irradiation of the coordination compound, Fig. 4. The pyridyl-nitrone solution exhibited a peak at 1555 cm^{-1} characteristic of the nitrone and, after irradiation, a new intense peak at 1666 cm^{-1} typical of an amide carbonyl group, Fig. 4a. The photochemistry of nitrones depends on the reaction conditions and can result in its geometric isomerization or its interconversion. This last reaction can lead the nitrone into oxazirane or the respective anilide [55]. Direct irradiation of the nitrone results in the identification of the anilide species, by its intense characteristic peak at 1300 cm^{-1} region [56] for the respective oxazirane is not observed in the spectra, indicating a major presence of the anilide species.

Irradiation of the Re(*Z*-Nit-**X**) solution also leads to absorption changes as a function of time. The FTIR of the photochemical products exhibits the characteristic nitrone peak at 1555 cm⁻¹, while it is not observed the benzanilide IR peak, at 1666 cm⁻¹, Fig. 4b.

The *E* isomer is the exclusive product when intermolecular tripletsensitized isomerization occurs [56]. This pathway avoids the formation of other products, such as the anilide observed after direct irradiation of the pyridyl-nitrone by FTIR (Fig. 4). The absence of different isomers than the geometric ones, as it is registered by FTIR, is an indication of the nitrone functional group stability under the



Fig. 3. Absorption changes upon irradiation of Z-Nit-**Me**₂ (a) (conc. = 5.8×10^{-5} mol L⁻¹) or Re(Z-Nit-**Me**₂) (b) (conc. = 3.2×10^{-5} mol L⁻¹) in acetonitrile. (P_{irr} = 100 mW cm⁻²; room temp; Δt = 15 s; red line t = 300 s). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. FTIR of *Z*-Nit-**Me**₂ (a) or Re(Z-Nit-**Me**₂) (b) (black lines) and after 10-min irradiation (red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photosensitization promoted by the rhenium(I) polypyridyl moiety.

Photochemical experiments using 405 nm irradiation, where the light is only absorbed by rhenium(I) moiety, were also conducted. Changes in absorption spectra confirm the occurrence of the photosensitized process (supporting information). Besides these changes, HPLC-MS experiments were conducted aiming to identify and quantify the products formed, Fig. 5.

The chromatographic profile of the non-irradiated sample exhibits a major peak at the retention time of 1 min, Fig. 5A. The mass spectrum of this sample reveals two peaks, the first one at m/z = 710 and a second one at m/z = 829, Fig. 5C. The first peak (m/z = 710) is ascribed to a fragment of the Re(Z-Nit-Me₂), as depicted in the inset of Fig. 5C, probably due to the ionization process of ESI-MS, and the second one is ascribed to the molecular ion of the compound Re(Z-Nit-Me₂). Both peaks exhibit the characteristic isotopic pattern of the rhenium metallic center, indicating the presence of the metal center in both fragments detected [57]. After irradiation of the sample at 405 nm, Fig. 5B, it is observed a new peak on the chromatographic profile. Still, the mass spectra for both peaks exhibited in the chromatogram are similar and coincident to the ones of the non-irradiated sample (Fig. 5A and C). Unfortunately, the low affinity of Re(Z-Nit-Me₂) to the stationary phase did not allow the separation and quantification of the Z and E isomers after irradiation.

On the other hand, this technique reinforces the absence of other photoproducts. Possible different products should have a distinct interaction with the stationary phase, resulting in the observation of other peaks; Fig. 5b exhibits only two peaks having very close retention time. Due to these reasons, the chromatograms emphasize the absence of by-photoproducts.

The photoisomerization of the Re(*Z*-Nit-**Cl**) was also verified by ¹H NMR, Fig. 6. The assignment of the resonance peaks, indicated in the inset, was derived from the ¹H–¹H COSY experiments and comparative analysis with the ¹H spectrum of the ligand (Figs. S3–S5). In this experiment, the sample was irradiated for 80 min at 405 nm and achieved 15% of isomerization, determined by absorption changes, Fig. S9 The ¹H NMR of the irradiated sample exhibits new peaks at 9.96, 8.65, and 7.62 ppm, in comparison to the spectrum of Re(*Z*-Nit-**Cl**) and are ascribed to the signal of Ha', Hc' and Hd' of the Re(*E*-Nit-**Cl**) isomer formed. No further signals are observed in the spectrum of the irradiated sample, confirming the absence of by-products, as was indicated by HPLC-MS. Using the integral of Ha and Ha' the conversion of Z to E isomer achieved around 35%. This difference in the photolysis percentage is due to the absorption of both isomers in the same absorption region, whilst they are well separated in the ¹H NMR spectrum.

The photosensitized isomerization quantum yields of the complexes determined by the absorption changes at 370 nm were $\Phi_{\text{Re}(Z-\text{Nit-Me2})} = (12.7 \pm 0.2) \times 10^{-3}$, $\Phi_{\text{Re}(Z-\text{Nit-H})} = (8.8 \pm 0.7) \times 10^{-3}$, and $\Phi_{\text{Re}(Z-\text{Nit-Cl})} = (7.5 \pm 0.2) \times 10^{-3}$. Irradiation to their respective photostationary state, PSS, in which there is not observed any further absorption changes, resulted in photolysis percentage for Re(Z-Nit-Me2) = 55%; Re(Z-Nit-H) = 53% and Re(Z-Nit-Cl) = 48%. Correspondence between Φ and PSS values was observed. After reaching their PSS, the absorption spectra of the samples were monitored for one hour at 25, 35, 40, 45, 50, and 60 °C. No significant changes were observed, discarding the thermal reversibility.

Changes in photophysical properties are also observed after the $Z \rightarrow E$ photoisomerization of the coordinated pyridyl-nitrones. Initially, Re (*Z*-Nit-**X**) exhibits low-intensity luminescence in acetonitrile solution (Fig. 7). As the sensitized isomerization of the coordinated ligand proceeds, there is an increase in the emission intensity of the samples due to the presence of *E*-isomer in higher concentrations. It is observed similar behavior to rhenium(I) compounds using stilbene or azo ligands [24,32].

All three complexes have the same broad and non-structured emission profile and maxima after photoisomerization, indicating that a common lowest-lying excited state is achieved for all *E*- isomers. The



Fig. 5. Chromatograms of Re(Z-Nit-Me₂) before (A) and after (B) irradiation at 405 nm (λ = 340 nm) and the mass spectra of the samples before (C) and after (D) irradiation at 405 nm. Fig. 5C inset: expansion of the mass spectrum peaks and the respective fragment proposed.



Fig. 6. ¹H NMR spectra of Re(Z-Nit-Cl) at t = 0 min and after 80 min of irradiation at 405 nm. (initial conc. = 6.62×10^{-4} mol L⁻¹).

excited state responsible for the observed luminescence was confirmed by the emission spectrum of *fac*-[Re(CO)₃(Ph₂-phen)(py)]⁺, py = pyridine, recorded under the same conditions. The normalized spectra were superimposed, Fig. 8, confirming the nature of the lowest-lying excited state as the ³MLCT_{Re-Ph2-phen} one, as reported for *fac*-[Re (CO)₃(Ph₂-phen)(py)]⁺ [58].

Considering the photosensitized isomerization process, the distinct photophysical properties of the rhenium(I) compounds having the *Z*- or *E*-pyridyl-nitrone isomer and emission characteristics of the E-isomer, a qualitative energy diagram can be proposed, Fig. 9. In this diagram, for the *Z*-isomer, ³MLCT_{Re-Ph2-phen} is more energetic than ³IL_{*Z*-Nit-X}, the excited state responsible for the isomerization process. Thus, the energy harvested by the metal complex can be transferred to ³IL_{*Z*-Nit-X},



Fig. 7. Emission spectral changes as a function of irradiation time of *Z*-Nit-Me₂ (\longrightarrow) and Re(*Z*-Nit-Me₂) (\blacksquare) acetonitrile solutions. ($\lambda_{exc.} = 350$ nm; v = 600 nm min⁻¹; $\Delta t_{irr} = 15$ s).

sensitizing this excited state responsible for the photoisomerization process. However, due to the proximity of these states, a low-intensity emission is observed from ${}^{3}MLCT_{Re-Ph2-phen}$, even for the Z-isomers. It deactivates this excited state, resulting in photochemical low quantum yield values. After the isomerization, the new ${}^{3}IL_{E-Nit-x}$ is more energetic than ${}^{3}MLCT_{Re-Ph2-phen}$. Thus, the excitation of the *E*-isomer results in the observed emission spectrum instead of the isomerization process. The photochemical and photophysical data are summarized in Table 1.

The results of Φ and PSS suggest a dependence of the photochemical behavior on the substituent on the pyridyl-nitrone. Lower Φ and PSS values are observed for Re(*Z*-Nit-**Cl**), whereas a higher Φ and PSS are observed for Re(*Z*-Nit-**Me**₂). These results are in agreement with the absorption spectra of the complexes; the lowest energy maximum was observed for Re(*Z*-Nit-**Me**₂) (345 nm), and Re(*Z*-Nit-**H**) and Re(*Z*-Nit-**Cl**) had approximately the same energy (341 and 340 nm, respectively), resulting in similar isomerization quantum yields. The absorption



Fig. 8. Emission spectra of Re(*Z*-Nit-**X**); **X** = **Me**₂, **H**, or **Cl** after irradiation and *fac*-[Re(CO)₃(Ph₂-phen)(py)]⁺ (dashed line) in acetonitrile. ($\lambda_{exc.}$ = 350 nm; v = 600 nm min⁻¹).

spectra of these compounds have contributions from both $IL_{Z\text{-Nit-X}}$ and $MLCT_{Re^-Ph2-phen}$ electronic transitions in this region. Thus, the different maxima observed for this series of compounds are due to changes in $IL_{Z\text{-Nit-X}}$ energy, and such effects can be extended to ${}^{3}IL_{Z\text{-Nit-X}}$, the excited-state responsible for the isomerization process.

Changes in the energy of ${}^{3}IL_{Z-Nit-X}$ will alter the ${}^{3}MLCT_{Re-Ph2-phen}$ deactivation pathways. After reaching the ${}^{3}MLCT_{Re-Ph2-phen}$ excited-state, it can be deactivated by two pathways. The first one is through phosphorescence, resulting in the low emission observed for the complex having the Z-nitrone ligand. The second deactivation pathway is by transferring energy to ${}^{3}IL_{Z-Nit-X}$ responsible for the isomerization process. The energy-gap between the ${}^{3}IL_{Z-Nit-X}$ and ${}^{3}MLCT_{Re-Ph2-phen}$ has a close relationship to these pathways. If the energy-gap is small, phosphorescence and photosensitization become more competitive, activating both pathways. On thv other hand, as the ${}^{3}IL_{Z-Nit-X}$ state became more stabilized, the energy-gap increases, favoring the photosensitization process. As previously discussed, Re(Z-Nit-Me_2) has the more stabilized ${}^{3}IL_{Z-Nit-X}$ excited-state among the compounds investigated. Consequently, the energy transfer pathway to ${}^{3}IL_{Z-Nit-Me2}$ is favored, and its Φ and PSS are the highest values in the series. For Re(Z-Nit-H)

Table 1

Photochemical and photophysical data determined for the complexes investigated.

Compound	$\lambda_{max,abs} (nm) / \epsilon (10^4 L mol^{-1} cm^{-1})^a$	Φ_{Z-E}	PSS (%)	$\lambda_{max,em}^{\qquad b}$
Re(Z-Nit- Me ₂)	345 / 3.5	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	55	560
Re(Z-Nit- H)	341 / 4.3		53	560
Re(Z-Nit- Cl)	340 / 3.1		48	560

a. Absorption of the band having MLCT + IL mixture;

b. Emission of the E-isomer after irradiation of the respective Z-isomer.

and Re(*Z*-Nit-**Cl**), ³IL_{*Z*-Nit-**X**} is destabilized in comparison to ³IL_{*Z*-Nit-**Me2**}, making the ³IL_{*Z*-Nit-**X**} and ³MLCT_{Re-Ph2-phen} excited-states closer. In this case, the competition between phosphorescence and photoisomerization decreases the Φ and PSS values. Importantly, the energy of ³MLCT_{Re-Ph2-phen}, which is responsible for sensitizing $Z \rightarrow E$ isomerization, is identical for all compounds. Thus, the difference in Φ can be due to the substituents on the nitrone ligands.

The photoassisted isomerization quantum yields determined for Re (*Z*-Nit-**X**) are lower than those reported for stilbene-like ligands in similar compounds using the same equatorial ligand, Ph₂-phen [32,34,52]. The lower quantum yield values are probably due to the presence of the phosphorescence deactivation pathway, which is not observed for compounds having stilbene-like ligands.

4. Conclusions

A series of rhenium(I) polypyridyl compounds with photoisomerizable pyridyl-aryl-nitrone ligands were synthesized and characterized. The lower-energy region of the absorption spectrum of the complexes exhibited a mixture of $IL_{Z-Nit-X}$ and $MLCT_{Re-Ph2phen}$ transitions. Due to the $IL_{Z-Nit-X}$ contribution to this absorption band, the use of different substituents on the nitrones resulted in changes in the absorption maxima, which were ascribed to the nature of the substituent on the nitrone. Irradiation of the complexes led to the $Z \rightarrow E$ nitrone isomerization pathway, avoiding other products, as confirmed by HPLC-MS and ¹H NMR. This pathway is due to photosensitization promoted by the Re(Ph₂-phen) moiety. The isomerization quantum yields are also dependent on the substituent on the nitrone. Thus, the quantum yield can be modulated by changing the substituent on the nitrone. The *E* isomer exhibits a more intense emission in comparison to the *Z* isomer. Thus, the emission intensity increases as a function of



Fig. 9. Qualitative energy diagrams for the photoassisted isomerization of Re(Z-Nit-X) compounds and the emission of their products.

photolysis time because of the concentration of the E isomer increases. Since nitrones are efficient, OH^{•-} scavengers, the different emission properties of the isomers and the possibility of promoting $Z \rightarrow E$ isomerization in situ make these compounds promising candidates for molecular devices to detect this radical. Further investigation of the chemistry and photochemistry of these compounds in the presence of $OH^{\bullet-}$ and the isomerization quantum yields of new compounds with similar ligands will be carried out to explore the potential of these compounds as photosensors.

CRediT authorship contribution statement

Julia F. Mamud: Data curation. Investigation. Methodology. Writing - original draft. Giovanna Biazolla: Data curation, Investigation, Methodology, Writing - original draft. Caroline S. Marques: Data curation, Methodology, Writing - original draft. Giselle Cerchiaro: Investigation, Methodology, Funding acquisition, Writing review & editing. Thiago B. Queiroz: Investigation, Methodology, Funding acquisition, Writing - review & editing. Artur F. Keppler: Conceptualization, Data curation, Funding acquisition, Investigation, Writing - original draft, Writing - review & editing. André S. Polo: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.ica.2020.120009.

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