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Nitric oxide and singlet oxygen photo-generation by light irradiation in the phototherapeutic window of a nitrosyl ruthenium conjugated with a phthalocyanine rare earth complex

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ABSTRACT

The photochemical, photophysical and photobiological studies of a mixture containing *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] (H$_2$-dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) and Na$_4$[Tb(TsPc)(acac)] (TsPc = tetrasulfonated phthalocyanines; acac = acetylacetone), a system capable of improving photodynamic therapy (PDT), were accomplished. *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] was obtained from *cis*-[Ru(H$_2$-dcbpy)$_2$Cl$_2$]·2H$_2$O, whereas Na$_4$[Tb(TsPc)(acac)] was obtained by reacting phthalocyanine with terbium acetylacetonate. The UV–Vis spectrum of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] displays a band in the region of 305 nm (λ_{max} in 0.1 mol L^{-1} HCl)(π–π^*) and a shoulder at 323 nm (MLCT), while the UV–Vis spectrum of Na$_4$[Tb(TsPc)(acac)] presents the typical phthalocyanine bands at 342 nm (Soret λ_{max} in H$_2$O) and 642, 682 (*Q* bands). The *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] FTIR spectrum displays a band at 1932 cm^{-1} (Ru–NO$^+$). The cyclic voltammogram of the *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] complex in aqueous solution presented peaks at E = 0.10 V (NO$^{+/0}$) and E = −0.50 V (NO$^{0/-}$) versus Ag/AgCl. The NO concentration and ^{1}O$_2$ quantum yield for light irradiation in the λ > 550 nm region were measured as [NO] = 1.21 ± 0.14 μmol L^{-1} and ϕ_{OS} = 0.41, respectively. The amount of released NO seems to be dependent on oxygen concentration, once the NO concentration measured in aerated condition was 1.51 ± 0.11 μmol L^{-1} The photochemical pathway of the *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)]/Na$_4$[Tb(TsPc)(acac)] mixture could be attributed to a photoinduced electron transfer process. The cytotoxic assays of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] and of the mixture carried out with B16F10 cells show a decrease in cell viability to 80% in the dark and to 20% under light irradiation. Our results document that the simultaneous production of NO and ^{1}O$_2$ could improve PDT and be useful in cancer treatment.

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1. Introduction

The development of molecular systems that absorb light intensely in the visible region and carry out rapid and directional energy or electron transfer is an important research goal in several different areas [1,2]. Among them, phthalocyanines have proven to be an efficient dye for light absorption in the phototherapeutic window and they constitute one of the second-generation photosensitizers used in photodynamic therapy (PDT) [3]. PDT is an efficient binary treatment that combines a light source and a photosensitizing agent, resulting in the generation of singlet oxygen (^{1}O$_2$) and leading to the oxidation of many cellular constituents. This therapy is employed against various malignancies including cancer [3–5]. However, PDT has been reported to fail in hypoxic regions. Therefore, the search for other active radicals for PDT has been considered mandatory, so that this technique is improved [6]. One approach would be the use of nitrosyl metal compounds acting as nitric oxide (NO) delivery species, since NO has been described as an anti-tumor agent [7–9]. Among these compounds, nitrosyl ruthenium complexes comprise a thermodynamically stable and NO photo-labile species, especially in the ultraviolet region [7,10]. One important challenge in this field is to prepare nitrosyl ruthenium species that deliver NO in the phototherapeutic window and are also useful in PDT, which has in fact been a great deal of our research [7,10–15]. To increase the photosensitivity of such nitrosyl ruthenium complex by visible light irradiation, we have decided to utilize strongly colored dye molecules coupled to the ruthenium species [1,2]. In this work, we present a system that produces NO and ^{1}O$_2$ simultaneously. The photochemical, photophysical and photobiological studies of a mixture containing

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cis-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] (H_2-dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) and Na_4[Tb(TsPc)(acac)] (TsPc = tetrasulfonated phthalocyanines; acac = acetylacetone) are reported, and this system is suggested as an alternative for improving PDT.

2. Experimental

2.1. Apparatus

The ultraviolet–visible (UV–Vis) spectra were recorded on a Hitachi U-3501. Infrared spectra were registered on a Protegé 460 series FTIR spectrometer, using solid samples pressed in KBr pellets. Cyclic voltammetry was performed with an AUTOLAB® Model PGSTAT 30 potentiostat/galvanostat, by employing a conventional three-electrode cell arrangement with a glassy carbon disk working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. The pH measurements were accomplished by means of a DM-20 pH meter from Digimed. The photochemical experiments were carried out using an Osram 150 W/l system equipped with a Xenon Lamp, in an 8500 model with selective filter λ_{max}/550 nm (transmit > 90% above 550 nm). Luminescent measurements were performed using a FLUOROLOG 3 ISA/Jobin-Yvon spectrofluorimeter equipped with an R928P Hamamatsu photomultiplier and Xenon Lamp 450 W/ozone free. A Corning filter (transmit > 90% in the 250–400 nm range; with no transmission in the visible range) was used in the light beam entrance. Excitation and emission slits were 8 and 4 nm, respectively. The singlet oxygen yield values were determined in an apparatus consisting of a Nd-YAG laser (Continuum, Santa Clara, CA) with excitation (8 nm half life) provided by the third harmonic at 355 nm. The luminescent decay kinetics was detected by employing a germanium detector operating at liquid nitrogen temperature. A silicon filter was used to avoid any fluorescent signal interfering with the singlet oxygen measurements. Pheophorbide-a in deuterated ethanol was used as reference [16]. NO release was measured with an ISO–NOP NO meter from Word Precision Instruments.

2.2. cis-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] synthesis

The *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] complex was prepared using *cis*-[Ru(dcbpyH$_2$)$_2$Cl$_2$]·2H$_2$O as the starting reagent. *cis*-[Ru(H_2-dcbpy)$_2$Cl$_2$]·2H$_2$O was obtained according to the procedure previously employed to synthesize *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O [17]. *cis*-[Ru(H_2-dcbpy)$_2$Cl$_2$]·2H$_2$O (0.100 g, 0.14 mmol) was dissolved in distilled H_2O, and this solution was degassed for 30 min for oxygen removal. Gaseous NO was then generated by reaction between nitric acid solution (50%V/V) and metallic copper. The produced gaseous mixture was passed through a concentrated NaOH solution, to eliminate NO_2^- traces. The nitric oxide was then bubbled through the *cis*-[Ru(H_2-dcbpy)$_2$Cl$_2$]·2H$_2$O complex solution for 40 min, and the reaction mixture was stirred for another 6 h. This operation was repeated for three times, and a precipitate was formed during this procedure. The resulting brown precipitate was collected by filtration, washed with diethyl ether, and stored under vacuum in the dark. A typical yield for *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] (53.6%) was obtained. (*Anal.* Calc. for $C_{24}H_{16}N_5O_9ClRu$: C, 43.96; H, 2.14; N, 10.68. Found: C, 42.77; H, 2.26; N, 10.32%).

2.3. Na$_4$[Tb(TsPc)(acac)] synthesis

The Na_4[Tb(TsPc)(acac)] complex was synthesized using terbium acetylacetonate, Tb(acac)$_3$, as the starting reactant. The latter complex was prepared as described in the literature [18]. Then, the sodium salt of phthalocyanine-tetrasulfonate (0.100 g, 0.10 mmol), Na_4(TsPc), was dissolved in dimethylsulfoxide (DMSO, 0.5 mL), under stirring. The reaction was carried out under argon flux for 4 h, by refluxing stoichiometric amounts of (TsPc)$^{4-}$ and Tb(acac)$_3$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 30 μL). It seems that the role of DBU in this reaction is the formation of the phthalocyanine dianion (TsPc)$^{6-}$, which reacts with terbium acetylacetonate. Propanone (80.0 mL) was added after the reflux, and the mixture was frozen overnight. The obtained green precipitate was filtered and washed with propanone and diethyl ether, and dried under vacuum. Na_4[Tb(TsPc)(acac)] (47%). *m/z* 358.9602 (Tb^{3+} fragment).

2.4. Cell culture and MTT assay

The B16F10 murine melanoma was purchased from the ATCC (Rockville, MD) and grown in RPMI-1640 medium supplemented with 10% fetal bovine serum. To determine cell growth *in vitro*, B16F10 cells were plated at an amount of 10 000 cells/well on a 96-well plate. Cells were grown in MEM + 10% FBS + nonessential amino acids. Cell numbers were determined at 24 h intervals, by replacing the culture medium with 0.1 mL of an MTT solution in serum-free DMEM without phenol red [0.5 mg of MTT (Sigma, St. Louis, MO) per mL]. Cells were incubated at 37 °C for 2 h, and then 200 μL of solubilizing solution (80% isopropanol, 20% DMSO, and 4% Tween 20) were added to each well. After mixing, absorbance was determined at 562 nm with a plate reader.

3. Results and discussion

The nitrosyl ruthenium complex was ascribed as *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] mainly on the basis of elemental analysis with one deprotonated bipyridine type ligand. Addition of 0.1 M aqueous HCl or HPF_6 resulted in precipitation, which we tentatively ascribed as *cis*-[Ru(H-dcbpy)$_2$(Cl)(NO)]Cl$_2$ or *cis*-[Ru(H-dcbpy)$_2$-(Cl)(NO)](PF$_6$)$_2$. The electronic absorption data (Fig. 1) of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] displays a band at 305 nm (λ_{max}0.1 mol L^{-1} HCl; log ε 4.13) and a shoulder at 323 nm (log ε 3.97). The highest energy band is attributed to intraligand transitions involving NO and the H_2-dcbpy ligands, while the shoulder at 323 nm is due to the metal ligand charge transfer band (MLCT) with contributions from the $d\pi(Ru^{II}) \rightarrow \pi^*(NO)$ and $d\pi(Ru^{II}) \rightarrow \pi^*$(H-dcbpy$^-$) transitions [10]. In pH ⩾ 9.0 the UV–Vis spectrum of an aqueous solution containing *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] shows band in the 450 nm region (NaOH), which is characteristic of bonded nitrite obtained by electrophilic attack of the hydroxide ion [7,10,12–13]. The

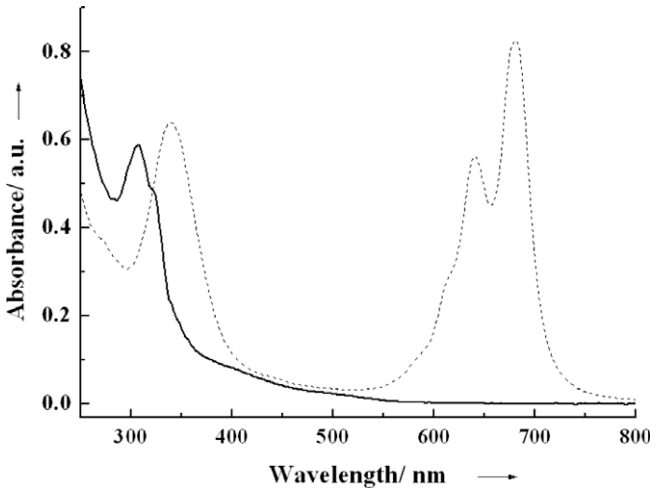


Fig. 1. Absorption spectrum in the UV–vis region: (—) *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)], 5.2×10^{-5} mol L^{-1}, in HCl 0.1 mol L^{-1}; (- - - -) Na_4[Tb(TsPc)(acac)], 1.2×10^{-5} mol L^{-1}, in aqueous solution.

nitrosyl ruthenium complex was also characterized by FTIR. The spectrum displays the typical NO frequency stretching at 1932 cm^{-1} (Ru–NO^+), as previously described for similar systems [10,12]. The cyclic voltammogram of the *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] complex was performed in aqueous solution using KCl (0.1 mol L^{-1}) as the supporting electrolyte (Supplementary data: Fig. 1). A reversible cathodic wave can be seen at 0.10 V (versus Ag/AgCl), attributed to the redox process of the nitrosyl group ($NO^{+/0}$), and there is an irreversible wave at −0.50 V (versus Ag/AgCl), due to the $NO^{0/-}$ redox process. The electronic spectrum of Na_4[Tb(TsPc)(acac)] (Fig. 1) in aqueous solution displays absorption bands at 342 nm (λ_{max} in H_2O; log ε 4.54), 642 (log ε 4.49) and 682 (log ε 4.64), typical of phthalocyanine. These bands are designated as *B* band or Soret in the case of $\lambda_{max}(H_2O)$/nm 342, and *Q* bands for $\lambda_{max}(H_2O)$/nm 642 and 682 [19,20].

The fluorescence measurements in aqueous solution indicate that the emission of the nitrosyl ruthenium complex is silent when it is excited at 376 nm, although [Tb(TsPc)(acac)]$^{4-}$ presents an emission band at 691 nm (λ_{em} in H_2O; Fig. 2). The fluorescence intensity of the phthalocyanine chromophore is lower than that of the rare earth phthalocyanine compound, and the emission of the Tb^{3+} ion is observed only when the excitation is performed at 356 nm (λ_{ex} in H_2O), using a filter which transmits above λ_{max} = 550 nm (Supplementary data: Fig. 2) [21].

The photolysis of an aqueous solution containing equimolar amounts of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] and Na_4[Tb(TsPc)(acac)] in phosphate buffer solution (pH 5.0) is fascinating. NO release, accounted for by NO-sensor measurement, is observed during light irradiation at $\lambda_{max} \geqslant 550$ nm (Fig. 3). A similar experiment was performed with *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] (Fig. 3) in the presence of an equimolar amount of Na_4(TsPc), but no signal was detected using NO-sensor.

NO release from *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] in the presence of [Tb(TsPc)(acac)]$^{4-}$ during photolysis at $\lambda_{max} \geqslant 550$ nm was quantitatively analyzed under argon atmosphere. The experiment was conducted until a maximum of 30 min, to avoid chemical filter interference. The measured NO concentration using NO-sensor after 30 min was 1.21 ± 0.14 μmol L^{-1}, which corresponds to 4% of the starting *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] concentration. The amount of NO release seems to be dependent on oxygen concentration, once the NO concentration measured in aerated condition was 1.51 ± 0.11 μmol L^{-1}, which suggests an effect of oxygen on the photochemical pathway of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] when it is photolysed in the presence of [Tb(TsPc)(acac)]$^{4-}$. The most probable photochemical pathway for NO release from the aerated

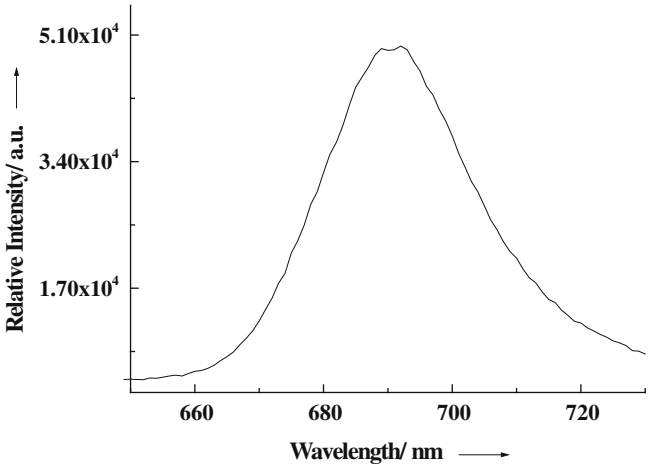


Fig. 2. Na_4[Tb(TsPc)(acac)] emission spectrum (λ_{ex}= 376 nm in H_2O) in aqueous solution. [complex] = 2.4 × 10^{-5} mol L^{-1}.

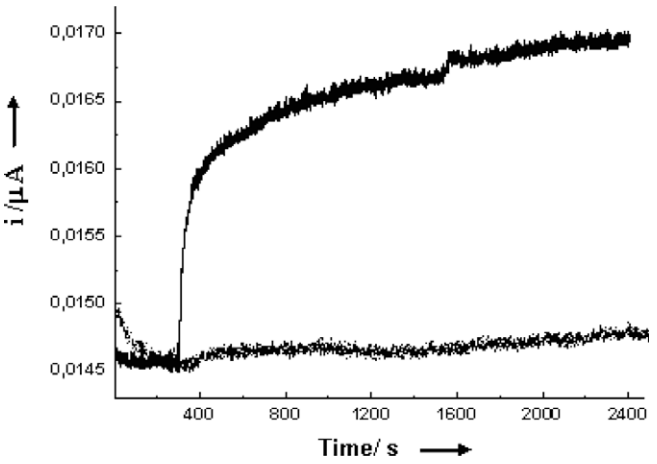
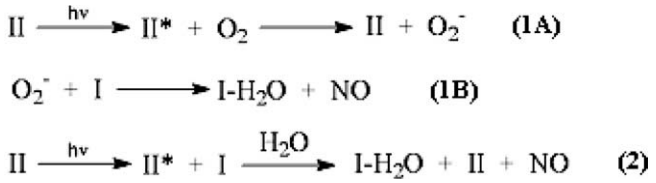


Fig. 3. Chronoamperograms of NO release by photolysis ($\lambda_{max} \geqslant 550$ nm): (**A**) *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] complex and (**B**) the mixture of nitrosyl ruthenium and the terbium phthalocyanine complexes. [nitrosyl complex] = [terbium phthalocyanine complex] = 3.0 × 10^{-5} mol L^{-1}, in phosphate buffer solution (pH 5.0).

aqueous solution mixture containing *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] and [Tb(TsPc)(acac)]$^{4-}$ involves a photoinduced electron transfer that is most likely a chemical reduction of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] (Scheme 1) by former superoxide. The assumption for superoxide formation (Scheme 1- Eq. 1A and 1B) is based on the qualitative assay using ferrocytochrome-C, a well-known superoxide scavenger [22]. Knowing that the superoxide reduction potential is −0.31 V versus Ag/AgCl, we can suppose that there is a favorable driving force for the reduction of *cis*-[Ru(H-dcbpy$^-$)$_2$- (Cl)(NO)] [23]. The second possible explanation for the photoinduced NO release comes from intermolecular photoinduced electron transfer (Scheme 1 Eq (2)), an assumption that is based mainly on the results from luminescence spectroscopy.

Changes in the fluorescence spectrum of [Tb(TsPc)(acac)]$^{4-}$ in phosphate buffer solution pH 5.0 (λ_{exc} = 376 nm) upon addition of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] can be observed. Differences in the shape and position of the fluorescence bands when only free [Tb(TsPc)(acac)]$^{4-}$ is present in the medium and when it is in the presence of the nitrosyl ruthenium complex are small, but the fluorescence intensity is diminished by 20% for an equimolar amount of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)]. This quenching efficiency might be caused by hydrogen bonding interaction. From the Stern–Volmer analysis of I_0/I versus [*Q*] plots, it can be seen that the interaction [Tb(TsPc)(acac)]$^{4-}$–*cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] obeys a Stern–Volmer type analysis, forming a 1:1 stoichiometric association in aqueous solution. Fig. 4 depicts the Stern–Volmer plots based on the relation $I_0/I = 1 + K_D[Q]$, where $K_D = 9.0 \times 10^3$ is the interaction constant for a 1:1 stoichiometry [24], which we have tentatively ascribed to hydrogen bonding interaction taking place as represented in Fig. 5.

Phthalocyanines are known to generate singlet oxygen ($^1O_2$) upon photoirradiation, which was also observed for the terbium phthalocyanine tetrasulfonate compound when it was irradiated at λ_{max} = 691 nm [3]. The measured singlet oxygen quantum yield



Scheme 1. Photochemistry intermolecular electron transfer mechanism; **I** is *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] and **II**, the sensitizer Na_4[Tb(TsPc)(acac)] complex.

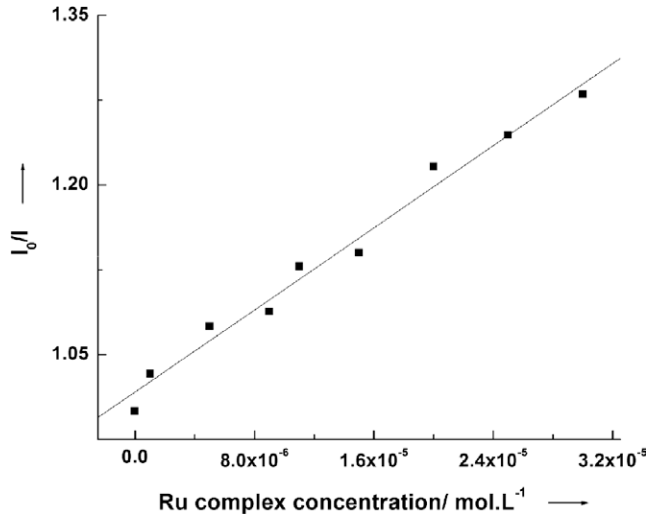


Fig. 4. Stern–Volmer plot for quenching of the fluorescence of ([Tb(TsPc)(acac)]$^{4-}$ (1.4×10^{-6} mol L^{-1}) in the presence of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)], monitored at λ_{em} = 691 nm (λ_{ex} = 376 nm).

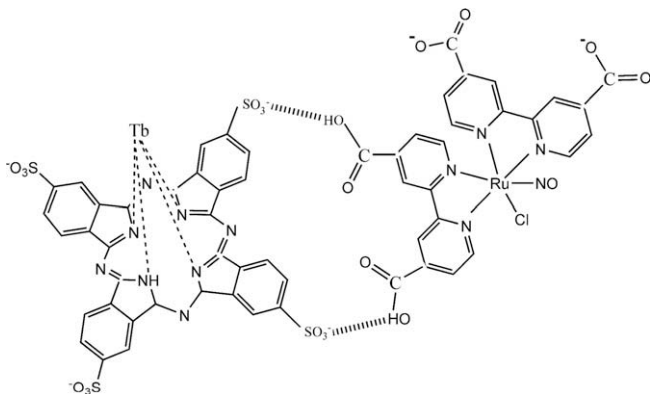


Fig. 5. Schematic diagram assumed for the self-assembled structure.

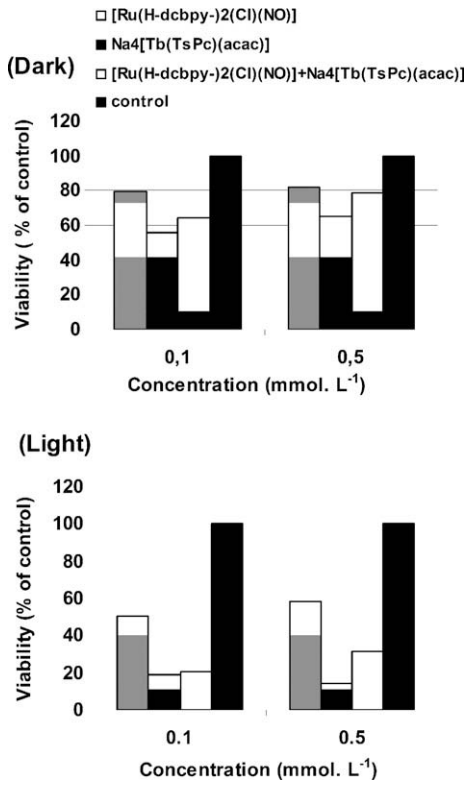


Fig. 6. Cell viability of the B16F10 cell line after treatment with *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] and [Tb(TsPc)(acac)]$^{4-}$, as measured via the MTT assay. Results are represented as a percentage of the relative absorbance with respect to the control cells (100%, in black).

was 0.41, a value that can be taken as promising for a photosensitizer to be applied in the photodynamic therapy (PDT) of cancer [3–5]. To investigate whether [Tb(TsPc)(acac)]$^{4-}$–*cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)], a NO release and $^1O_2$ producing agent, inhibits its cell viability, we have performed experiments using B16F10 cells. Fig. 6 depicts the cell viability experiment showing the cytotoxic effects of *cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] in the presence of an equal amount of [Tb(TsPc)(acac)]$^{4-}$ under visible light irradiation in B16F10 cells, which was performed using 100–500 μmol L^{-1} of each complex. The solution containing [Tb(TsPc)(acac)]$^{4-}$–*cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] strongly inhibits the cell viability in a light irradiation-dependent manner. The best result was achieved when the concentration of 100 μmol L^{-1} was used, which reduced cell viability to 20% of the control. The hypothesis for the cancer cell activity (não seria melhor mudar esta palavra pois o cancer é destruído) obtained by using [Tb(TsPc)(acac)]$^{4-}$–*cis*-[Ru(H-dcbpy$^-$)$_2$(Cl)(NO)] mainly involves $^1O_2$ formation, a well-known anticancer agent. The concomitant production of NO in this system could also improve its anticancer capacity due to the corroborative effect of NO, once it can induce apoptosis in a variety of cell types [7–10]. Apparently, as the concentration of *cis*-[Ru(H-dcbpy$^-$)$_2$- (Cl)(NO)] increases in the solution containing [Tb(TsPc)(acac)]$^{4-}$, cell activity decreases. Maybe NO is consumed by $^1O_2$ in a typical oxidation process, which could explain the cell viability decrease when a mixture of rare earth and nitrosyl ruthenium complexes was used as sensitizer [25]. On the other hand, the NO release agent itself decreases cell viability, which could be an indication that at low oxygen concentration the system could improve anticancer activity.

4. Conclusion

Our results document the effect of the concomitant formation of NO and $^1O_2$ on a cancer cell line. The amount of species employed in the cell viability experiments is around 1% of IC_{50}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.051.

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