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Article

Photoinduced Isomerization and Luminescence of *fac*-[Re(CO)$_3$(ph$_2$phen)(bpe)]$^+$

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O complexo *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]PF$_6$, ph$_2$phen = 4,7-difenil-1,10-fenantrolina e *trans*-bpe = *trans*-1,2-bis(4-piridil)etileno, foi sintetizado, caracterizado e seu comportamento fotoquímico e fotofísico foi investigado. Esse complexo apresenta isomerização *trans*→*cis* do ligante *trans*-bpe coordenado. Os rendimentos quânticos aparentes em CH$_3$CN, determinados através da variação espectral, são $\Phi_{313\ nm} = 0.19 \pm 0.02$, $\Phi_{365\ nm} = 0.18 \pm 0.04$ e $\Phi_{404\ nm} = 0.18 \pm 0.02$. Rendimentos quânticos maiores, denominados de reais ($\Phi_{365nm} = 0.40 \pm 0.06$), foram determinados utilizando espectroscopia de ^{1}H RMN. A coordenação do ligante *trans*-bpe ao complexo polipiridínico de rênio(I) possibilita uma isomerização fotossensibilizada sob irradiação a energias menores, onde o *trans*-bpe livre não absorve. O aumento da luminescência com a formação do fotoproduto, *fac*-[Re(CO)$_3$(ph$_2$phen)(*cis*-bpe)]$^+$, é atribuído a mudança do estado excitado de energia mais baixa de ^{3}IL para ^{3}MLCT. A emissão apresenta deslocamento hipsocrômico associado ao efeito rigidocrômico.

The *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]PF$_6$ complex, ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline and *trans*-bpe = *trans*-1,2-bis(4-pyridyl)ethylene, was synthesized, characterized and its photochemical and photophysical behavior was investigated. This complex exhibits *trans*→*cis* photoisomerization of the coordinated *trans*-bpe ligand. The apparent quantum yields in CH$_3$CN, determined by absorption changes, are $\Phi_{313\ nm} = 0.19 \pm 0.02$, $\Phi_{365\ nm} = 0.18 \pm 0.04$ and $\Phi_{404\ nm} = 0.18 \pm 0.02$. Higher true quantum yields ($\Phi_{365\ nm} = 0.40 \pm 0.06$) were determined by ^{1}H NMR spectroscopy. The coordination of the *trans*-bpe ligand to the rhenium(I) polypyridyl complex enables a photosensitized isomerization under a lower energy region irradiation, where the free ligand does not absorb. The increasing luminescence as the photoproduct, *fac*-[Re(CO)$_3$(ph$_2$phen)(*cis*-bpe)]$^+$, is formed is ascribed to the change of the lowest lying excited state from ^{3}IL to ^{3}MLCT. The emission exhibits a hypsochromic shift associated with the rigidochromic effect.

Keywords: photoisomerization, rhenium(I) carbonyl complexes, *tra*ns-bpe, luminescence, rigidochromic effect

Introduction

Rhenium(I) polypyridyl complexes are well known for their interesting photochemical and photophysical properties.[1-22] These complexes, with an adequate ^{3}MLCT excited state and fairly long lifetimes (0.1–9.0 µs), can be used as photosensitizers for a variety of reactions including photoisomerization.

A well known model of photoisomerizable molecules are the stilbene-like ligands.[2,23-27] They provide a classic example of one of the outstanding advantages of photochemistry – the possibility of selective preparation of a less stable higher energy isomer. Photoinduced isomerization of these molecules can be achieved by direct irradiation or by sensitization *via* inter- or intramolecular energy transfer processes.[2,27]

One interesting intramolecular sensitization approach is the coordination of a stilbene-like ligands to a metal center such as rhenium(I). These complexes are especially attractive over their free organic counterparts because of the additional advantage of their MLCT state tunability. This feature allows the use of visible light in the photoisomerization process, which can be conveniently exploited in the development of molecular devices, such as photoswitches.[6,7,14,18,19,28]

Moreover, the photoisomerization process of rhenium(I) polypyridyl complexes with a photoisomerizable stilbene-like ligand results in a change of the lowest excited state nature, from ^{3}IL to ^{3}MLCT, leading to the formation of emissive complexes. Their

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emission profiles can be tuned by changing the polypyridine ligand as well as by modifying the rigidity of the medium, an important feature for sensing applications.

In our previous works[10-13,16,17,21,22] the photoisomerization of *trans*-L in *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$, NN = polypyridynes and L = 1,2-bis(4-pyridyl)ethylene (bpe), or 4-styrylpyridine (stpy), and the luminescence of their photoproducts were investigated. Here, we extend our investigations by using 4,7-diphenyl-1,10-phenanthroline (ph$_2$phen) as a polypyridyl ligand in the photoisomerization of *trans*-bpe in *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ in order to observe the tunability of the photochemical and photophysical behaviors of *trans*- and *cis*-isomer complexes.

Experimental

All solvents were reagent grade, except those for film preparation and photochemical and photophysical measurements, when HPLC grade solvents from Aldrich were employed. [ReCl(CO)$_5$] from Strem and ph$_2$phen, trifluoromethanesulfonic acid (CF$_3$SO$_3$H), *trans*-1,2-bis(4-pyridyl)ethylene (*trans*-bpe) and poly(methyl methacrylate) (PMMA: M$_w$ = 101,000) from Aldrich were used as received. Potassium tris(oxalato)ferrate(III) was prepared and purified according to the literature procedure[29] from reagent grade potassium oxalate (Merck) and iron(III) chloride hexahydrate (Reagen).

Synthesis of fac-[ReCl(CO)$_3$(ph$_2$phen)]

The *fac*-[ReCl(CO)$_3$(ph$_2$phen)] complex was synthesized according to the procedure previously described for *fac*-[ReCl(CO)$_3$(phen)].[13,21] The [ReCl(CO)$_5$] complex (0.27 g, 0.75 mmol) and an excess of ph$_2$ phen (0.5 g, 1.5 mmol) were suspended in 30 mL of xylene (Nuclear) and heated to reflux for 6 hours. After cooling, the resulting solid was separated by filtration and washed with xylene. The crude product was recrystallized from dichloromethane (Merck) by addition of *n*-pentane (Nuclear). Yield 69%. Anal. Calc. for ReC$_{27}$H$_{16}$O$_3$N$_2$Cl: C, 50.82; H, 2.53; N, 4.39%. Found: C, 51.11; H, 2.47; N, 4.42%.^{1}H NMR for *fac*-[ReCl(CO)$_3$(ph$_2$ phen)] δ(CD$_3$CN): 9.45 (d, 2H), 8.11 (s, 2H), 7.93 (d, 2H), 7.65 (s, 10H).

Synthesis of fac-[Re(CF$_3$SO$_3$)(CO)$_3$(ph$_2$phen)]

The *fac*-[Re(CF$_3$SO$_3$)(CO)$_3$(ph$_2$phen)] complex was synthesized following the procedure previously described.[11,13,21] CF$_3$SO$_3$H (0.50 mL, 5.6 mmol) was added to a 35 mL dichloromethane suspension of *fac*-[ReCl(CO)$_3$(ph$_2$phen)] (0.30 g, 0.47 mmol) under argon. The complex was precipitated by slow addition of diethyl ether. Yield 79%. Anal. Calc. for ReC$_{28}$H$_{16}$N$_2$O$_6$F$_3$S: C, 39.11; H, 2.18; N, 3.04%. Found: C, 39.21; H, 2.45; N, 3.22%. ^{1}H NMR for *fac*-[Re(CF$_3$SO$_3$)(CO)$_3$(ph$_2$phen)] δ(CD$_3$CN): 9.46 (d, 2H), 8.16 (s, 2H), 8.01 (d, 2H), 7.68 (s, 10H).

Synthesis of fac-[Re(CO)$_3$(ph$_2$phen)(trans-bpe)]PF$_6$

The *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]PF$_6$ complex was prepared using the procedure previously described[11,13,17] with slight modifications. The *fac*-[Re(CF$_3$SO$_3$)(CO)$_3$(ph$_2$phen)] complex (0.20 g, 0.27 mmol) and *trans*-bpe (0.35 g, 1.9 mmol) were dissolved in 45 mL of methanol (Synth) and heated to reflux for 9 hours. Solid NH$_4$PF$_6$ was added to a room temperature solution to precipitate the yellow complex, which was subsequently collected by filtration and washed with water to eliminate excess of NH$_4$PF$_6$ and then with diethyl ether. Yield 50%. Anal. Calc. for ReC$_{39}$H$_{26}$N$_4$O$_3$F$_6$P: C, 50.37; H, 2.82; N, 6.03%. Found: C, 50.07; H, 2.77; N, 5.96%. ^{1}H NMR for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ δ(CD$_3$CN): 9.64 (d, 2H), 8.55 (d, 2H), 8.31 (d, 2H), 8.08 (s, 2H), 8.06 (d, 2H), 7.63 (s, 10H), 7.40 (d, 2H), 7.36 (d, 2H), 7.34 (d, 1H), 7.23 (d, 1H).

Preparation of polymer films

The PMMA-based films were prepared in the absence of humidity and light following the procedure previously described.[11,21] The *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]PF$_6$ complex was dissolved in acetonitrile, added to an acetonitrile solution of PMMA and left to dry.

Methods

Electronic absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer with quartz cuvets of 1.000 or 0.100 cm optical length.

NMR spectra were recorded on a Bruker AC-200 (200 MHz) or a DPX-300 (300 MHz) spectrometer at 300 K using CD$_3$CN as solvent. The residual CH$_3$CN signals were employed as internal standard.

Photolyses at 313, 365 or 404 nm were carried out with an Oriel 200 W Hg(Xe) arc lamp powered by an Oriel universal power supply model 68700 by selecting the wavelength using appropriate interference filters. Light intensities were determined by tris(oxalato)ferrato(III) actinometry before and after each photolysis experiment. The photochemical system and photolysis procedure have been described in detail elsewhere.[13,17] The irradiations were performed in a 1.000 cm optical length quartz cuvet connected to another 0.100 cm optical length quartz cuvet for measurements of the absorption spectra.

Emission experiments were performed by using an ISS photon counting spectrofluorometer, model PC1, with a photomultiplier-based photon counting detector. The photophysical system and procedures have been described in detail elsewhere.[11,21] The emission spectra were obtained using a 1.000 cm path length quartz cuvet and a front face arrangement for polymer films.

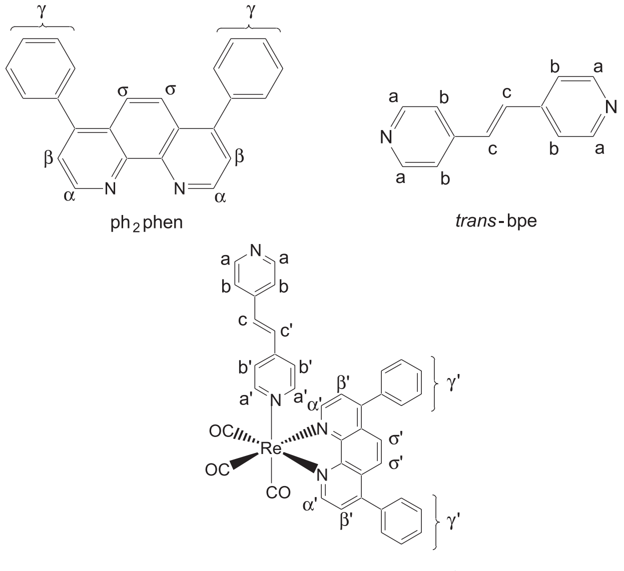
Results and Discussion

^{1}H NMR spectra

The ^{1}H NMR spectral data in CD$_3$CN for the ligands and complexes, represented as follow, are listed in Table 1.

The signals of aromatic protons for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ were assigned by comparison of ^{1}H NMR spectra of the free ligands and *fac*-[ReCl(CO)$_3$(ph$_2$phen)]. The H-H COSY spectrum of *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ (see Figure 1) corroborated the assignments.

The α-diimine proton signals in *fac*-[ReCl(CO)$_3$(ph$_2$phen)] are shifted to high frequency in comparison to the corresponding proton of the free ph$_2$phen. The same behavior has been reported for *fac*-[ReCl(CO)$_3$(phen)][11,13] and other complexes.[30,31] After the coordination of *trans*-bpe to the metal center, the proton signals of the bound pyridyl ring are shifted to low frequency in comparison



Scheme 1.

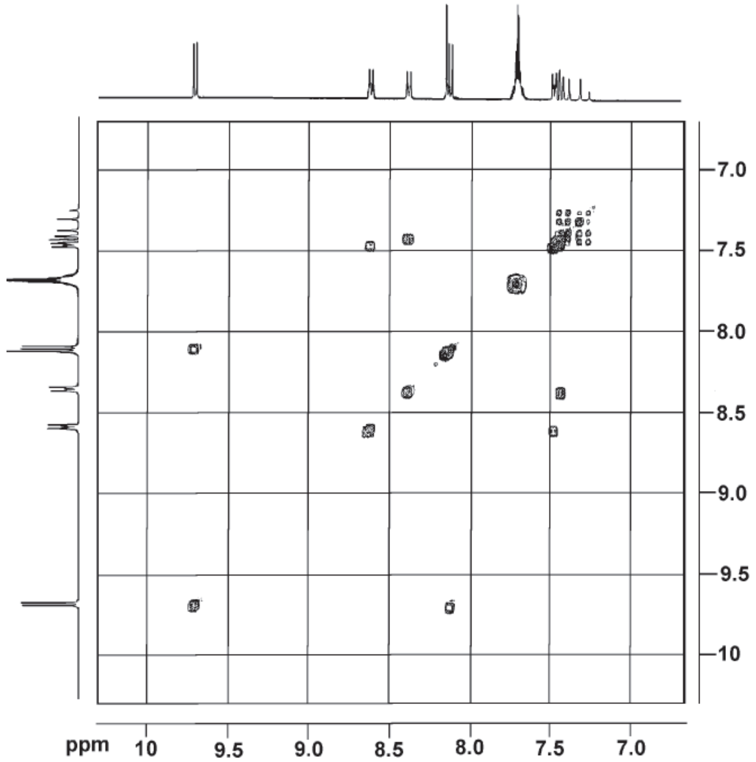


Figure 1. COSY NMR spectrum (300 MHz) of *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ in CD$_3$CN.

to its unbound pyridyl ring, leading to a higher electronic perturbation in Ha', Hb' and Hc' signals due to the anisotropic effect of the α-diimine ligand.[13,17,32]

Electronic absorption spectra

The spectral data of the rhenium(I) polypyridyl complexes and of the free ligands in acetonitrile solution are summarized in Table 2. The absorption spectra in acetonitrile are shown in Figure 2.

The higher energy bands of *fac*-[ReCl(CO)$_3$(ph$_2$phen)] can be associated with electronic transitions localized mainly in the ligand and assigned to ph$_2$phen intraligand transitions (IL, $\pi \rightarrow \pi^*$). The lower energy absorption bands (300-450 nm) are ascribed to a metal to ligand charge transfer transition (MLCT, $d\pi_{Re} \rightarrow \pi^*_{ph2phen}$). Such spectral characteristics are typical of *fac*-tricarbonyl diimine compounds and the assignments were made in comparison to the literature.[1,3,11,13,17,21,22,33,34]

The absorption spectrum of *trans*-bpe (λ_{max} = 290 nm) shows a characteristic intraligand transition (IL) band which is red shifted (λ_{max} = 312 nm) upon protonation. A similar shift is observed upon coordination of *trans*-bpe to the rhenium tricarbonyl polypyridyl complexes. Molar absorptivity of 10^4 L mol^{-1} cm^{-1} in the 300-365 nm region for the *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ complex is much higher than the 10^3 L mol^{-1} cm^{-1} commonly observed for rhenium diimine MLCT transitions.[34,35] The higher molar absorptivity for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ and the presence of a similar low energy absorption band in protonated free *trans*-bpe indicate a contribution of the intraligand transition of the coordinated *trans*-bpe. Therefore, the absorption bands in the 300-365 nm region for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ have the contributions of the intraligand (IL$_{bpe}$) $\pi \rightarrow \pi^*_{bpe}$ and MLCT transitions, Figure 2.[6,7,11-14,17,18,20] The tail extending to *ca.* 425 nm for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ is ascribed to a metal to ligand charge transfer transition (MLCT, $d\pi_{Re} \rightarrow \pi^*_{ph2phen}$) based on comparison with the spectra of *fac*-[ReCl(CO)$_3$(ph$_2$phen)].

Table 1. ^{1}H NMR spectral data for the free ligands and the rhenium(I) complexes in CD$_3$CN

Compounds	Proton	δ / (ppm)	*J* / (Hz)
ph$_2$phen	Hα (d, 2H)	9.17	4.5
	Hβ (d, 2H)	7.65	4.5
	Hγ (s, 10H)	7.56	
	Hσ (s, 2H)	7.86	
trans-bpe	Ha (d, 4H)	8.58	4.5
	Hb (d, 4H)	7.50	4.5
	Hc (s, 2H)	7.39	
fac-[ReCl(CO)$_3$(ph$_2$phen)]	Hα' (d, 2H)	9.45	5.4
	Hβ' (d, 2H)	7.93	5.4
	Hγ' (s, 10H)	7.65	
	Hσ' (s, 2H)	8.11	
fac-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$	Ha (d, 2H)	8.55	6.3
	Hb (d, 2H)	7.40	6.3
	Hc (d, 1H)	7.34	16.2
	Ha' (d, 2H)	8.31	6.7
	Hb' (d, 2H)	7.36	6.7
	Hc' (d, 1H)	7.23	16.2
	Hα' (d, 2H)	9.64	5.4
	Hβ' (d, 2H)	8.06	5.4
	Hγ' (s, 10H)	7.63	
	Hσ' (s, 2H)	8.08	

Table 2. Spectral data for the rhenium(I) complexes and the free ligands in CH$_3$CN

Compounds	λ_{max} / nm (ε / (10^4 L mol^{-1} cm^{-1}))
trans-bpe	220(1.4)^a, 290(3.0), 310(1.7)^a
protonated *trans*-bpe	220(0.6)^a, 301(3.2)^a, 312(3.6), 327(2.4)^a
ph$_2$phen	219(4.8), 272(4.8), 300(1.6)^a
fac-[ReCl(CO)$_3$(ph$_2$phen)]	220(4.8)^a, 280(3.3), 350(0.63)^a
fac-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$	220(5.5)^a, 295(6.8), 330(3.6)^{a,b}

^{a} shoulder; ^{b} contributions of MLCT and IL transitions.

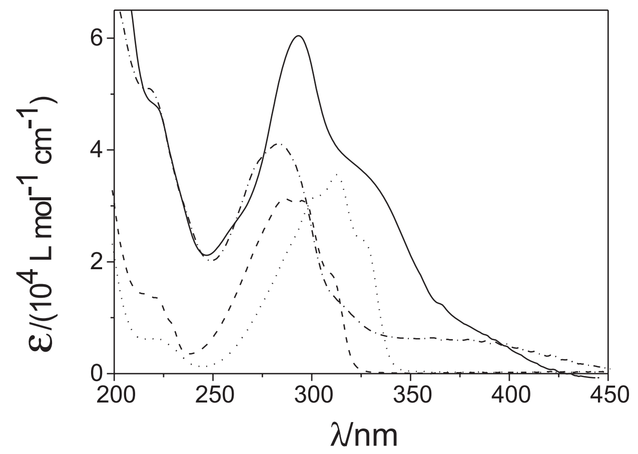


Figure 2. Absorption spectra of *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$(—), *trans*-bpe (---), protonated *trans*-bpe (···) and *fac*-$[ClRe(CO)_3(ph_2phen)]$ (- · -) in acetonitrile solution.

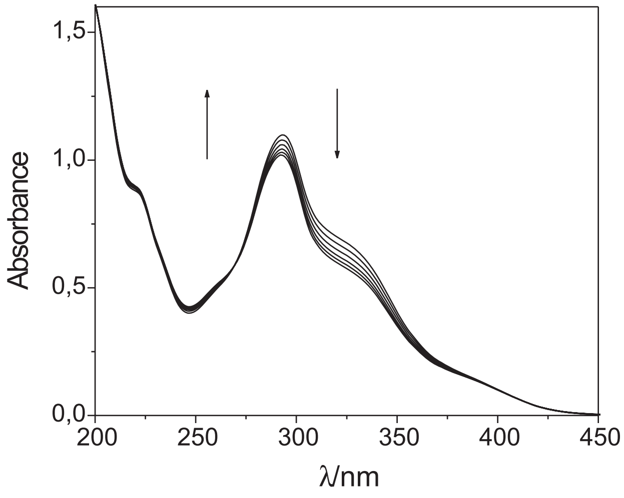


Figure 3. Spectral changes of *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$ in acetonitrile upon irradiation at 365 nm (Δt = 4 s).

Photoinduced isomerization

Irradiation of *trans*-bpe at 313 nm can be followed by changes in absorption spectra, which show clear and well-defined isosbestic points and are in accordance with those reported in the literature.[13,23-25,27]

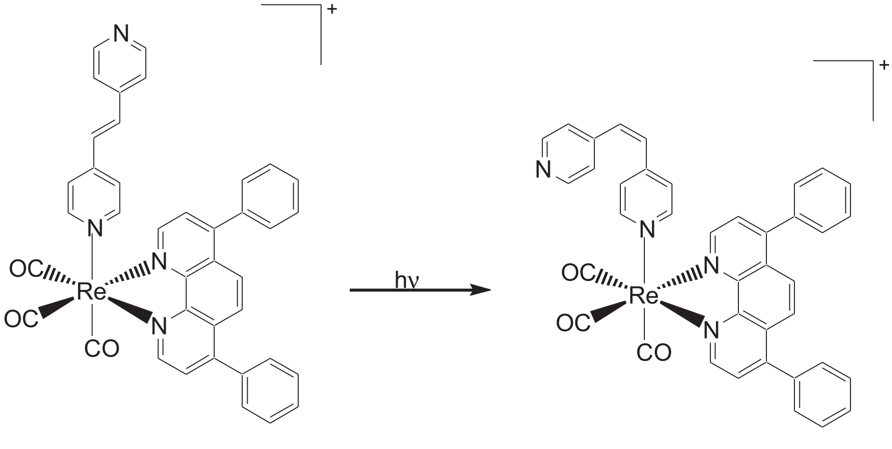
The *trans→cis* isomerization of the coordinated *trans*-bpe ligand can be followed by absorption changes observed for *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$, Figure 3, upon 313, 365 or 404 nm irradiation.

The quantum yields, determined by absorption spectral changes, are 0.19 ± 0.02, 0.18 ± 0.04 or 0.18 ± 0.02, respectively for 313, 365 or 404 nm irradiation and constant within experimental error.

This photochemical behavior is consistent with the IL lowest lying excited state. Time-resolved infrared (TRIR) measurements performed with *fac*-$[Re(CO)_3(phen)(trans\text{-}bpe)]^+$ corroborate the nature of the lowest lying excited state being bpe localized ($^3IL_{trans\text{-}bpe}$), which is responsible for the *trans→cis* isomerization process.[16]

Quantum yields based on absorption spectral changes for *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$ are apparent, Φ_{app}, since the reactant and the photoproduct absorb in the same region. In this case, the photoisomerization process can be better followed by ^1H NMR spectroscopy. For both isomers, chemical shifts and coupling constants of the protons, specially for the olefinic ones, are fairly different. Upon irradiation of *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$, the *trans*-isomer signals at 7.50 - 7.20 ppm decrease, while the *cis*-isomer signals at 7.00 - 6.50 ppm gradually build up in intensity, as can be observed in Figure 4. The quantum yields are determined using the integral of the olefinic proton signals of the *cis*-isomer. In this way, much higher quantum yields, the true ones, are determined by ^1H NMR experiments with $\Phi_{365nm} = 0.40 \pm 0.06$.[22,36]

Trans-cis photoisomerization of *fac*-$[Re(CO)_3(ph_2phen)(trans\text{-}bpe)]^+$ can be achieved even under 404 nm irradiation due to the efficient sensitization of the stilbene-like ligand *via* intramolecular energy transfer from the MLCT to the IL_{bpe} excited state.



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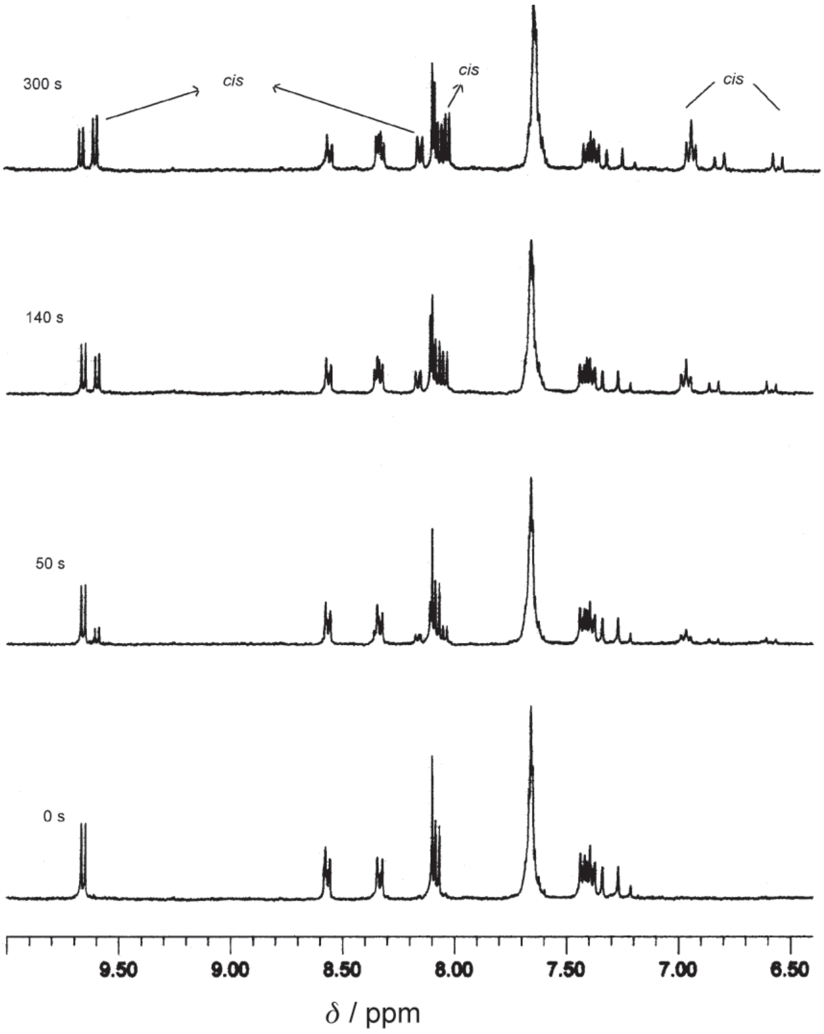

Figure 4. ^{1}H NMR spectra (300 MHz) of *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ in CD$_3$CN upon photolyses at 365 nm.

It has been reported[37] that the singlet and triplet mechanisms are always present in the photoisomerization process of stilbene-like compounds. However, a functional group increases the coupling between the singlet and triplet manifolds, and the triplet mechanism becomes more competitive. For the rhenium(I) complexes, the metal centers enhance the intersystem crossing, either through the heavy atom effect or as a functional group, favoring the triplet mechanism by transferring the energy from the ^{3}MLCT to the ^{3}IL excited state, which is responsible for the isomerization.[2,16,21]

The lower quantum yields for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ in comparison to *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ [21] are a result of a less efficient sensitization of the ^{3}IL$_{bpe}$ excited state due to the lower energy of the ^{3}MLCT which is stabilized by the two phenyl groups. Thus, the ^{3}MLCT$_{Re\rightarrow ph2phen}$ decay manifold can compete with the ^{3}IL$_{bpe}$ lowest lying excited state in deactivation processes.

The photoisomerization process can also be followed by the increasing luminescence as the photoproduct, *fac*-[Re(CO)$_3$(ph$_2$phen)(*cis*-bpe)]$^+$, is formed upon irradiation of the *trans*-complex, Figure 5. The broad and structureless band in acetonitrile solution at room temperature is typically a ^{3}MLCT emission of rhenium(I) compounds.[1,3,5,8,11,13,17,21,33,34,38,39]

In order to understand the nature of the emissive state, the investigation was also carried out in different media, e.g., PMMA at 298 K and EPA (diethyl ether-isopentane-ethanol, 5:5:2) at 77 K, Figure 6.

The emission spectra of *fac*-[Re(CO)$_3$(ph$_2$phen)(*cis*-bpe)]$^+$ exhibit hypsochromic shift as the medium rigidity increases due to the ^{3}MLCT destabilization. This behavior has already been reported for other rhenium polypyridyl complexes[1,5,8,11,17,21,22,39] and is known as the rigidochromic effect. This effect arises from variations in the dipolar interactions between the excited molecule

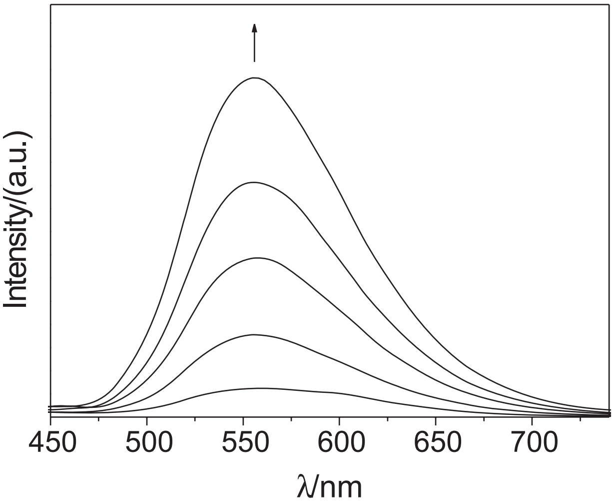

Figure 5. Changes in emission spectra of *fac*-$[Re(CO)_3(ph_2phen)(cis\text{-}bpe)]^+$ in acetonitrile as a function of photolysis time (λ_{exc} = 365 nm, Δt = 5 min).

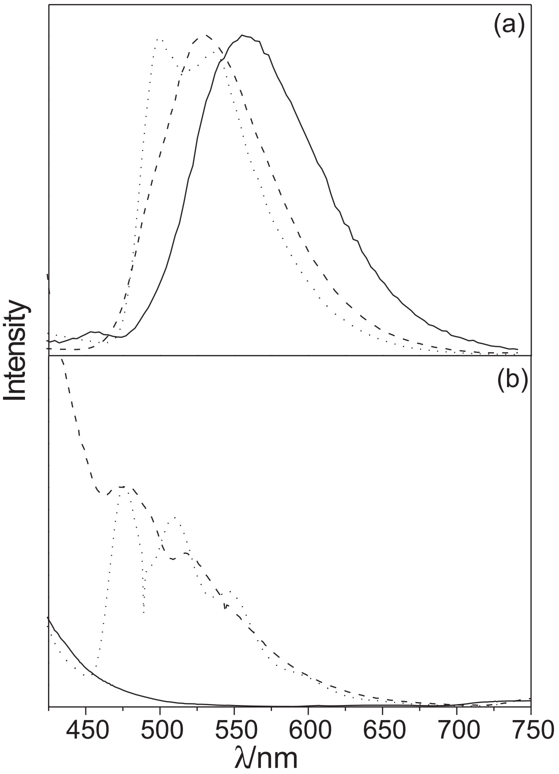

Figure 6. Emission spectra of *fac*-$[Re(CO)_3(ph_2phen)(cis\text{-}bpe)]^+$ (a) and ph_2phen (b) in acetonitrile (–) or in PMMA (--) at 298 K and in EPA (···) at 77 K.

and the solvent dipoles of the surrounding medium. While the ^3MLCT excited state is strongly dependent on solvent organization due to its polar nature, the energy of the ^3IL state is insensitive due to its centro symmetric character.[17,21,39] Thus, the observed shifts are due to the destabilization of the $^3MLCT_{Re\rightarrow ph2phen}$ excited state as the rigidity of the medium increases, as can be observed in the spectrum of *fac*-$[Re(CO)_3(ph_2phen)(cis\text{-}bpe)]^+$ in acetonitrile and in PMMA, Figure 6a. The emission spectrum of *fac*-$[Re(CO)_3(ph_2phen)(cis\text{-}bpe)]^+$ in EPA at 77 K resembles that of the free ph_2phen ligand, Figure 6b, due to the contribution of the $^3IL_{ph2phen}$ excited state to the ^3MLCT emission.

Conclusion

The coordination of the *trans*-bpe unit to the rhenium(I) tricarbonyl polypyridyl complex is an interesting approach to photosensitize an isomerization to visible light, *e.g.* at 404 nm, where the free ligand does not absorb. This feature can be exploited in designing photoresponsive species capable of performing light induced functions, which are useful in the development of photochemical molecular devices.

The photoisomerization of coordinated bpe leads to a change of the lowest excited state nature, from $^3IL_{bpe}$ to ^3MLCT, resulting in an emissive *cis*-complex. Moreover, this luminescence is highly sensitive to changes in medium rigidity, by destabilizing the ^3MLCT excited state with the increase in rigidity. Such behavior can be conveniently exploited in the development of luminescent sensors.

Acknowledgments

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References

1. Wrighton, M.; Morse, D. L.; *J. Am. Chem. Soc.* **1974**, *96*, 998.
2. Wrighton, M. S.; Morse, D. L.; Pdungsap, L.; *J. Am. Chem. Soc.* **1975**, *97*, 2073.
3. Giordano, P. J.; Wrighton, M. S.; *J. Am. Chem. Soc.* **1979**, *101*, 2888.
4. Lees, A. J.; *Chem. Rev.* **1987**, *87*, 711.
5. Stufkens, D. J.; *Comments Inorg. Chem.* **1992**, *13*, 359.
6. Yam, V. W. W. ; Lau, V. C. Y.; Cheung, K. K.; *J. Chem. Soc., Chem. Commun.* **1995**, 259.
7. Yam, V. W. W.; Lau, V. C. Y.; Wu, L. X.; *J. Chem. Soc., Dalton Trans.* **1998**, 1461.
8. Lees, A. J.; *Coord. Chem. Rev.* **1998**,*177*, 3.
9. Stufkens, D. J.; Vlček Jr., A.; *Coord. Chem. Rev.* **1998**, *177*, 127.
10. Garcia, C. G.; Lima, J. F.; Murakami Iha, N. Y.; *Coord. Chem. Rev.* **2000**, *196*, 219.
11. Itokazu, M. K.; Polo, A. S.; Murakami Iha, N. Y.; *Int. J. Photoenergy* **2001**, *3*, 143.

12. Argazzi, R. A.; Bertolasi, E.; Chiorboli, C.; Bignozzi, C. A.; Itokazu, M. K.; Murakami Iha, N. Y.; *Inorg. Chem.* **2001**, *40*, 6885.
13. Itokazu, M. K.; Polo, A. S.; Araújo de Faria, D. L.; Bignozzi, C. A.; Murakami Iha, N. Y.; *Inorg. Chim. Acta* **2001**, *313*, 6885.
14. Yam, V. W. W.; Lau, V. C. Y.; Zhang, J.; Chu, B. W. K.; Zhu, N.; *Organometallics* **2001**, *20*, 4911.
15. Sun, S. S.; Lees, A. J.; *Coord. Chem. Rev.* **2002**, *230*, 171.
16. Dattelbaum, D. M.; Itokazu, M. K.; Murakami Iha, N. Y.; Meyer, T.J.; *J. Phys. Chem. A.* **2003**, *107*, 4092.
17. Itokazu, M. K.; Polo, A. S.; Murakami Iha, N. Y.; *J. Photochem. Photobiol. A.* **2003**, *160*, 27.
18. Wenger, O. S.; Henling, L. M.; Day, M. W.; Winkler, J. R.; Gray, H. B.; *Inorg. Chem.* **2004**, *43*, 2043.
19. Wenger, O. S.; Henling, L. M.; Day, M. W.; Winkler, J. R.; Gray, H. B.; *Polyhedron* **2004**, *23*, 2955.
20. Busby, M.; Matousek, P.; Towrie, M.; Vlček Jr., A.; *J. Phys. Chem. A.* **2005**, *109*, 3000.
21. Polo, A. S.; Itokazu, M. K.; Murakami Iha, N. Y.; *J. Photochem. Photobiol. A.* **2006**, *181*, 73.
22. Polo, A. S.; Itokazu, M. K.; Frin, K. M.; de Patrocínio, A. O. T.; Murakami Iha, N. Y.; *Coord. Chem. Rev.* **2006**, *250*, 1669.
23. Whitten, D. G.; McCall, M. T.; *J. Am. Chem. Soc.* **1969**, *91*, 5097.
24. Whitten, D. G.; Lee, Y. J.; *J. Am. Chem. Soc.* **1970**, *92*, 415.
25. Lee, Y. J.; Whitten, D. G.; Pedersen, L.; *J. Am. Chem. Soc.* **1971**, *93*, 6330.
26. Bartocci, G.; Bortolus, P.; Mazzucato, U.; *J. Phys. Chem.* **1973**, *77*, 605.
27. Görner, H.; Kuhn, H. J.; *Advances in Photochemistry*, John Wiley & Sons: New York,1995, vol.19.
28. Sans, M. Q.; Belser, P.; *Coord. Chem. Rev.* **2002**, *229*, 59.
29. Hatchard, C. G.; Parker, C. A.; *Proc. R. Soc. Lond. A* **1958**, *235*, 518.
30. Sarneski, J. E.; Rickson, L. E.; Reilley, C. N.; *Inorg. Chem.* **1981**, *20*, 2137.
31. Kamath, S. S.; Uma, V.; Srivastava, S.; *Inorg. Chim. Acta* **1989**, *161*, 49.
32. Orrell, K. G.; Osborne, A. G.; Silva, M. W. ; Hursthouse, M. B.; Coles, S. J.; *Polyhedron* **1997**, *16*, 3003.
33. Fredericks, S. M.; Luong, J. C.; Wrighton, M. S.; *J. Am. Chem. Soc.* **1979**, *101*, 7415.
34. Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A.; *Inorg. Chem.* **1990**, *29*, 4335.
35. Shaw, J. R.; Schmehl, R. H.; *J. Am. Chem. Soc.* **1991**, *113*, 389.
36. Frin, K. M.; Itokazu, M. K.; Murakami Iha, N. Y.; unpublished results.
37. Waldeck, D. H.; *Chem. Rev.* **1991**, *91*, 415.
38. Leasure, R. M.; Sacksteder, L.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B.A.; *Inorg. Chem.* **1991**, *30*, 3722.
39. Chen, P.; Meyer, T. J.; *Chem. Rev.* **1998**, *98*, 1439.

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