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Photoswitches and Luminescent Rigidity Sensors Based on *fac*-$[Re(CO)_3(Me_4phen)(L)]^+$

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The *fac*-$[Re(CO)_3(Me_4phen)(trans\text{-}L)]^+$ complexes, Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline and L = 4-styrylpyridine, stpy, or 1,2-bis(4-pyridyl)ethylene, bpe, were synthesized and characterized by their spectroscopic, photochemical, and photophysical properties. The complexes exhibit *trans*-to-*cis* isomerization upon 313, 334, 365, and 404 nm irradiation, and the true quantum yields can be efficiently determined by absorption changes combined with ^1H NMR data. For *fac*-$[Re(CO)_3(Me_4phen)(trans\text{-}bpe)]^+$ similar quantum yields were determined at all wavelengths investigated. However, a lower value ($\Phi_{true} = 0.35$) was determined for *fac*-$[Re(CO)_3(Me_4phen)(trans\text{-}stpy)]^+$ at 404 nm irradiation, which indicates different pathways for the photoisomerization process. The photoproducts, *fac*-$[Re(CO)_3(Me_4phen)(cis\text{-}L)]^+$, exhibit luminescence at room temperature with two maxima ascribed to the $^3IL_{Me_4phen}$ and $^3MLCT_{Re\rightarrow Me_4phen}$ excited states. The luminescence properties were investigated in different media, and the behavior in glassy EPA at 77 K showed that the contribution of each emissive state is dependent on the excitation wavelength. The photochemical and photophysical behavior of the complexes were rationalized in terms of the energy gap of excited states and can be exploited in photoswitchable luminescent rigidity sensors.

1. Introduction

In recent years, molecular devices capable of performing specific functions under the action of a defined energy input have been extensively studied.[1−3] In this context, metal complexes are very attractive compounds for photoinduced molecular machines because of their good light harvesting and redox properties.[4−6]

Rhenium(I) tricarbonyl polypyridyl complexes have been the subject of extensive investigations because of their photochemical and photophysical properties and their potential applicability in devices for solar energy conversion,[7] for luminescence sensing,[8−12] or for photosensitization of organic substrates.[13−15]

The energy states and redox properties of these complexes depend on the ligands and the media. In particular, the energy level of the metal-to-ligand charge transfer excited state, MLCT, can be tuned by changing the polypyridyl ligand,

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NN, or the medium rigidity.[16−20] The energy gap between the $MLCT_{Re\rightarrow NN}$ and the ligand-centered, IL_{NN}, excited states plays an important role in the decay pathways of these complexes.[21,22] For example, several authors have investigated the effects of aryl and methyl substitution on the polypyridyl ligand on the luminescence properties of Re(I) complexes[16,23−25] and different lifetimes, quantum yields, and temperature dependence profiles have been found. A particular case is found for Re(I) complexes having 3,4,7,8-tetramethyl-1,10-phenanthroline, Me_4phen, as the polypyridyl ligand. These complexes exhibit unusual photophysical properties, as a result of the decrease of the energy gap between the IL_{Me_4phen} and $MLCT_{Re\rightarrow Me_4phen}$ excited states[23,29] caused by the electron-donating character of methyl groups. The effects of this decrease in intramolecular energy transfer processes are not properly evaluated yet.

It has been observed that the efficiency of intramolecular charge transfer processes, such as the photoassisted isomerization of stilbene-like ligands, L, in *fac*-$[Re(CO)_3(NN)($*trans*-$L)]^+$, is dependent on polypyridyl ligands.[13,26−28] However, the influence of the isomerizable ligand on the photoreaction is not completely understood. The coordination of isomerizable ligands to a metal center is an interesting approach to sensitize the isomerization process of the organic substrate to visible light and can be applied in photoswitches or molecular memory units.[29,30]

In this work, the photochemical and photophysical behaviors of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-$L)]^+$, Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline and L = 4-styrylpyridine, stpy, or 1,2-bis(4-pyridyl)ethylene, bpe, are investigated to further understand the intramolecular energy transfer process in Re(I) complexes having Me_4phen as a polypyridyl ligand. The influence of methyl groups on the 1,10-phenanthroline ligand on the photoinduced *trans*-to-*cis* isomerization of stilbene like ligands, as well as in the luminescence of their photoproducts, are discussed in terms of the energy gaps between the excited states.

2. Experimental Section

2.1. Materials. All chemicals were reagent grade, except HPLC grade solvents used for the photochemical and photophysical measurements. 3,4,7,8-tetramethyl-1,10-phenanthroline, Me_4phen, *trans*-1,2,-bis(4-pyridyl)ethylene, *trans*-bpe, ammonium hexafluorophosphate, and trifluoromethanesulfonic acid, CF_3SO_3H, all from Aldrich and $[ClRe(CO)_5]$ from Strem were used as received. The ligand *trans*-4-styrylpyridine, *trans*-stpy, was synthesized as previously reported.[31,32] Potassium tris(oxalate)ferrate(III) employed as chemical actinometer was prepared and purified according to the literature procedure.[33]

2.2. Synthesis of *fac*-$[ClRe(CO)_3(Me_4phen)]$. The *fac*-$[ClRe(CO)_3(Me_4phen)]$ complex was prepared with slight modifications of the procedure reported for similar complexes.[34,35] An excess of Me_4phen (0.53 g, 2.2 mmol) was added with $[ClRe(CO)_5]$ (0.40 g, 1.1 mmol) in 30 mL of xylene, and the mixture was heated to reflux for 9 h. The resulting yellow solid was separated by filtration and washed with xylene. The crude product was recrystalized from CH_2Cl_2 by slow addition of *n*-hexane. Yields 66%. Anal. Calcd for $ReC_{19}H_{16}N_2O_3Cl$: C, 42.10%; N, 5.17%; H, 2.98%. Found: C, 42.13%; N, 4.99%; H, 3.34%. ^1H NMR (CD_3Cl δ/ppm): 9.11, (s, 2H); 8.14, (s, 2H); 2.78, (s, 6H); 2.61, (s, 6H).

2.3. Synthesis of *fac*-$[(CF_3SO_3)Re(CO)_3(Me_4phen)]$. The complex was synthesized following the same procedure adopted for the synthesis of *fac*-$[(CF_3SO_3)Re(CO)_3(phen)]$, phen = 1,10-phenanthroline.[35] The *fac*-$[ClRe(CO)_3(Me_4phen)]$ complex (0.25 g, 0.26 mmol), previously synthesized, was suspended in 15 mL of CH_2Cl_2, and CF_3SO_3H (0.5 mL, 5 mmol) was added under argon atmosphere. The mixture was stirred for 1 h at room temperature. The product was precipitated by slow addition of ethyl ether. Yields 68%. Anal. Calcd for $ReC_{20}H_{16}N_2O_3S$: C, 36.64%; N, 4.27%; H, 2.47%. Found: C, 36.58%; N, 4.22%; H, 2.43%. ^1H NMR (CD_3CN δ/ppm): 9.13, (s, 2H); 8.37, (s, 2H); 2.86, (s, 6H); 2.64, (s, 6H).

2.4. Synthesis of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-stpy$)]PF_6$. The synthesis of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-stpy$)]PF_6$ was based on the procedure previously described for the *fac*-$[Re(CO)_3(phen)($*trans*-stpy$)]PF_6$ complex.[31] *fac*-$[(CF_3SO_3)Re(CO)_3(Me_4phen)]$ (0.20 g, 0.31 mmol) and *trans*-stpy (0.18, 1.1 mmol) were dissolved in 90 mL of methanol and heated to reflux for 9 h. After cooling to room temperature, solid NH_4PF_6 was added to precipitate a pale yellow solid, which was further separated by filtration, washed with water and ethyl ether. Yields 53%. Anal. Calcd for $ReC_{32}H_{27}N_3O_3PF_6 \cdot 1.5H_2O$: C, 44.65%; N, 4.88%; H, 3.52%. Found: C, 44.80%; N, 4.86%; H, 3.57%. ^1H NMR (CD_3CN δ/ppm): 9.32 (s, 2H); 8.27 (s, 2H); 8.19 (dd, 2H); 7.51 (dd, 2H); 7.36 (m, 3H); 7.24 (dd, 2H); 6.97 (d, 1H); 2.67 (s, 6H); 2.27 (s, 6H).

2.5. Synthesis of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-bpe$)]PF_6$. The *fac*-$[Re(CO)_3(Me_4phen)($*trans*-bpe$)]PF_6$ complex was synthesized according to the procedure previously reported for *fac*-$[Re(CO)_3(phen)($*trans*-bpe$)]PF_6$.[35] *fac*-$[(CF_3SO_3)Re(CO)_3(Me_4phen)]$ (0.47, 0.71 mmol) and *trans*-bpe (0.37 g, 2.0 mmol) were heated to reflux in 50 mL of methanol for 6 h. After cooling, the product was precipitated by addition of solid NH_4PF_6, separated

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by filtration, washed with water and ethyl ether. Yields 59%. Anal. Calcd for $ReC_{31}H_{26}N_4O_3PF_6$: C, 44.60%; N, 6.71%; H, 3.15%. Found: C, 44.01%; N, 6.60%; H, 2.97%. ^1H NMR (CD_3CN δ/ppm): 9.34 (s, 2H); 8.60 (d, 2H); 8.57 (s, 2H); 8.32 (d, 2H); 7.46 (d, 2H); 7.35 (d, 2H); 7.29 (d, 1H); 7.22 (d, 1H); 2.82 (s, 6H); 2.68 (s, 6H).

2.6. Methods. Electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. ^1H NMR spectra were recorded on a DRX-500 (500 MHz) Bruker Avance spectrometer using CD_3CN as solvent. Residual CH_3CN signals were used as an internal standard.

The photolyses at 313, 334, 365, and 404 nm were carried out as previously reported,[26,35,36] using an Oriel 200 W Hg(Xe) system by selecting the wavelength using appropriate interference filters. Solutions of *trans*-complexes were adjusted to absorb more than 99.99% of the incident light and were kept under stirring while irradiated. Absorption changes during the photolysis (less than 10% of conversion) of each complex investigated were monitored at three different wavelengths selected where the absorption of the *cis*-isomer was minimal. Apparent quantum yields (average of at least three independent experiments) were determined based on the absorbance decay of the *trans*-isomer at each probe wavelength, and the procedure has been described in detail elsewhere.[26,35,36] Samples were irradiated in a 1.000 cm quartz cuvette connected to a second quartz cuvette (0.1000 cm) for absorption measurements. Light intensities were determined by tris(oxalate)ferrate(III) actinometry before and after each photolysis.

Emission experiments were performed, as previously reported,[31] by using an ISS-PC1 photon counting spectrofluorometer. Degassed fluid solutions in a 1.000 quartz cuvette were employed for room temperature measurements, whereas low temperature spectra were obtained in glassy EPA (ethyl ether-isopentane-ethanol, 5:5:2) at 77 K, using a tube placed in a quartz Dewar flask filled with liquid nitrogen.

3. Results and Discussion

Electronic Absorption Spectra. The electronic spectra of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-L$)]^+$, L = stpy, bpe are shown in Figure 1 and their spectral data, as well as those for the free and protonated ligands, are listed in Table 1.

Intense bands in the highest energy region (200−300 nm) are ascribed to ligand centered transitions of Me_4phen, IL_{Me_4phen}. These bands are red-shifted in comparison to the non-substituted phen ligand.[13,31,35] The lowest energy bands (300−400 nm) are ascribed to the metal to ligand charge transfer transition, $MLCT_{Re\rightarrow Me_4phen}$. However, the molar absorptivities determined for *fac*-$[Re(CO)_3(Me_4phen)$-($\textit{trans}$-L$)]^+$ in this region are much higher than those commonly reported for MLCT transitions in other rhenium(I) polypyridyl complexes.[11,12,37] This fact suggests a contribution from intraligand transition, $IL_{\pi\rightarrow\pi^*}$, of photoisomerizable ligands, *trans*-L, which are red-shifted after coordination, similarly to shifts observed after their protonation.[13,26,36] As it can be seen in Figure 1, protonated *trans*-stpy absorbs at lower energy than protonated *trans*-bpe, thus the overlap between the $IL_{trans\text{-stpy}}$ and the MLCT bands in *fac*-$[Re(CO)_3(Me_4phen)($*trans*-stpy$)]^+$ is extended up to 380 nm, in contrast to what is observed in *fac*-$[Re(CO)_3(Me_4phen)($*trans*-bpe$)]^+$ with an overlap of $MLCT_{Re\rightarrow Me_4phen}$ and IL_{bpe} up to 350 nm.

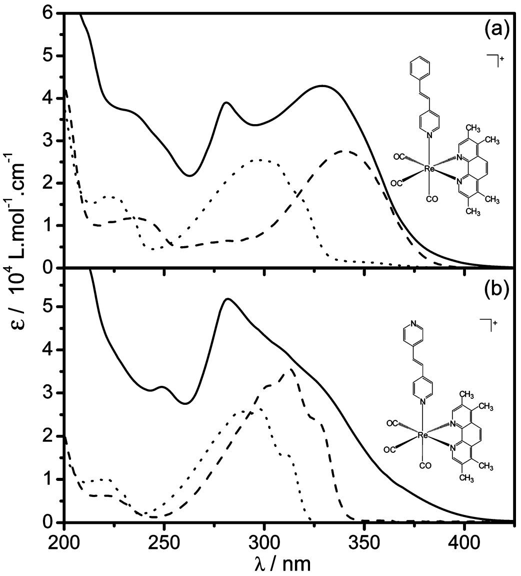
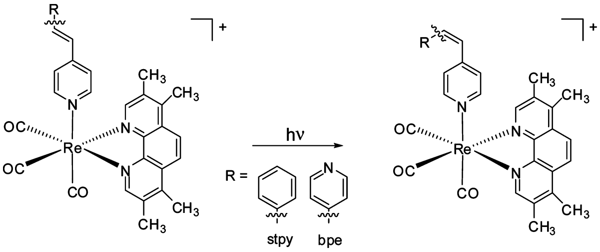


Figure 1. Electronic spectra of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-L$)]^+$ (solid line), and free (dotted line) and protonated (dashed line) *trans*-L in acetonitrile. (a) L = stpy; (b) L = bpe.

Photochemical Behavior. Irradiation of *fac*-$[Re(CO)_3(Me_4phen)($*trans*-L$)]^+$, L = stpy or bpe, upon 313, 334, 365, or 404 nm results in spectral changes with clear and well-defined isosbestic points, Figure 2, ascribed to the *trans*-to-*cis* isomerization of the stilbene-like ligands, eq 1.



(1)

The efficient sensitization of the stilbene-like ligands by the rhenium polypyridyl complex via intramolecular energy transfer is ascertained by the photoisomerization achieved under 404 nm irradiation, where the free ligands do not absorb. Additionally, the use of visible light to promote the photoreaction is an interesting approach for application in light-induced molecular devices such as sensitization of organic substrates, photoswitches, and photosensors.

The photoisomerization quantum yields determined by absorption changes are apparent since the photoproducts, *fac*-$[Re(CO)_3(Me_4phen)($*cis*-L$)]^+$, absorb in the same region of the *trans*-complexes although with a lower molar absorptivity. The true quantum yields can be efficiently determined by ^1H NMR technique, since the chemical shifts of the *trans* and *cis* complexes are reasonably different, as can be seen in the ^1H NMR spectra of *fac*-$[Re(CO)_3(Me_4phen)(stpy)]^+$, Figure 3. Spectral data in CD_3CN for all the ligands and for all the complexes are available in the Supporting Information.

To reduce the number of experiments with ^1H NMR measurements to determine true quantum yields at each

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Table 1. Spectral Data of the Re(I) Complexes and of the Free Ligands in Acetonitrile

compound	λ_{max}/nm (ε/10^4 L mol^{-1} cm^{-1})
trans-stpy	224(1.7), 227(1.6)^a, 300(2.5), 318(1.6)^a
protonated *trans*-stpy	236(1.2), 274(0.6), 341(2.7)
trans-bpe	220(1.4), 290(3.0), 310(1.7)^a
protonated *trans*-bpe	224(0.6), 302(3.2)^a, 313(3.6), 326(2.4)^a
Me_4phen	205(2.9), 242(4.2), 269(3.8), 283(1.6)^a, 303(0.6)
protonated Me_4phen	216(4.3) 230(2.8), 283(4.2), 313(1.0)
fac-[ClRe(CO)$_3$(Me$_4$phen)]	211(5.1), 263(2.8)^a, 279(3.6), 299(1.5)^a, 355(0.6)
fac-[Re(CO)$_3$(Me$_4$phen)(*trans*-stpy)]$^+$	201(7.0), 234(3.6), 281(3.8), **330(4.2)**^{b}
fac-[Re(CO)$_3$(Me$_4$phen)(*trans*-bpe)]$^+$	199(7.3), 249(3.1), 282(5.2), **320(3.1)**^{a,b}

^{a} Shoulder. ^{b} Contributions of MLCT and IL transitions.

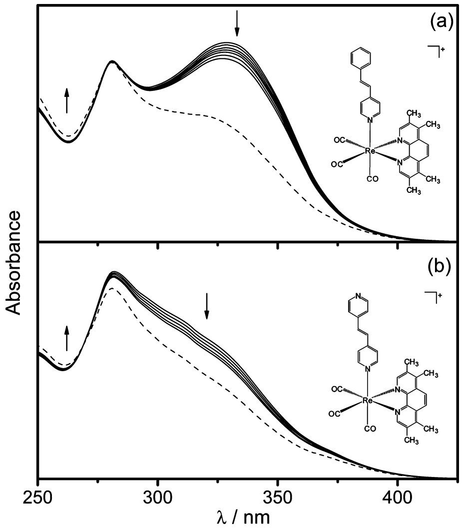

Figure 2. Spectral changes of *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-L)]$^+$ in acetonitrile upon irradiation at 365 nm (solid line), (a) L= stpy (1.5×10^{-4} mol L^{-1}; $\Delta t = 4$ s), (b) L = bpe (1.9×10^{-4} mol L^{-1}; $\Delta t = 8$ s) and after 300 s of photolysis (dashed line). $I_0 = 6.2 \times 10^{15}$ quanta s^{-1}.

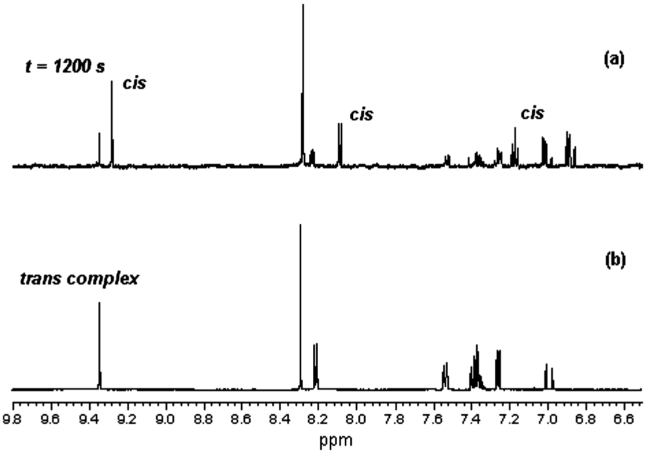

Figure 3. ^{1}H NMR spectra of *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-stpy)]$^+$ in CD$_3$CN before (a) and after (b) irradiation at 365 nm. (T = 298 K, 500 MHz).

irradiation wavelength, the molar absorptivities of *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-L)]$^+$, $\varepsilon_{cis}(\lambda)$, were determined based on the concentration of the *trans* and *cis* isomers determined by ^{1}H NMR data, eq 2, where A is the absorbance of the irradiated solution, $\varepsilon_{trans}(\lambda)$ is the molar absorptivities of trans-isomer, b is the optical length, and C_{trans} and C_{cis} are the molar concentrations of *trans* and *cis* isomers in the solution. Thus, the contribution of *cis* isomers in the absorption spectra during photolysis can be determined, and the true quantum yields, Φ_{true}, for both complexes investigated were obtained and compared to the apparent ones, $\Phi_{apparent}$, Table 2.

Table 2. *trans*-to-*cis* Photoisomerization Quantum Yields of *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-L)]$^+$

trans-L	λ_{irr}/nm	Φ_{true}	$\Phi_{apparent}$
bpe	313	0.32 ± 0.05	0.16 ± 0.02
	334	0.29 ± 0.04	0.17 ± 0.01
	365	0.33 ± 0.04	0.17 ± 0.02
	404	0.29 ± 0.03	0.17 ± 0.01
stpy	313	0.52 ± 0.06	0.25 ± 0.03
	334	0.57 ± 0.05	0.28 ± 0.02
	365	0.57 ± 0.06	0.27 ± 0.03
	404	0.35 ± 0.02	0.19 ± 0.01

$$\varepsilon_{cis}(\lambda) = \frac{A - \varepsilon_{trans}(\lambda) \cdot b \cdot C_{trans}}{C_{cis} \cdot b} \qquad (2)$$

For both complexes, the true quantum yields are about twice the apparent ones. Moreover, one can observe that quantum yields determined for *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-bpe)]$^+$ are constant at all irradiation wavelengths. On the other hand, the *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-stpy)]$^+$ complex exhibits a lower quantum yield at 404 nm, which is similar to the value determined for *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-bpe)]$^+$. This indicates that different pathways for the photoisomerization process are occurring in *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-stpy)]$^+$.

The occurrence of both singlet and triplet mechanisms for the isomerization of stilbene-like compounds has been reported.[32,38,39] However, in Re(I) complexes, the triplet pathway becomes more competitive because of the heavy atom effect. In these systems, the typical triplet mechanism involves the energy transfer from the ^{3}MLCT$_{Re\rightarrow NN}$ to the ^{3}IL$_{trans\text{-}L}$ excited state, which is responsible for isomerization.[14,40] Thus, the energy gap between these states, as well as the presence of other excited states close to them, influence directly the population of the lowest lying excited state, ^{3}IL$_{trans\text{-}L}$, and, consequently, the efficiency of photoisomerization.

The isomerization quantum yields determined for the *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-L)]$^+$ complexes are lower than

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Table 3. Apparent *trans*-to-*cis* Isomerization Quantum Yields Determined for *fac*-$[Re(CO)_3(NN)(\textit{trans}\text{-L})]^+$

NN	*trans*-L	$\Phi_{313\ nm}$	$\Phi_{334\ nm}$	$\Phi_{365\ nm}$	$\Phi_{404\ nm}$
phen	bpe	0.41[a]		0.39[a]	0.38
Me_4phen		0.16	0.17	0.17	0.17
phen	stpy	0.35[a]	0.36[a]	0.31[a]	0.29[b]
Me_4phen		0.25	0.28	0.27	0.19

[a] ref 13. [b] ref 41.

those for *fac*-$[Re(CO)_3(phen)(\textit{trans}\text{-L})]^+$ [13,41], as can be seen in the Table 3.

The less efficient process observed for the Me_4phen complexes arises from the electron-donating character of the methyl groups, which increases the energy of the MLCT excited state and stabilizes the $\pi\pi^*$ ligand centered transition. Thus, the IL_{Me_4phen} and $MLCT_{Re\rightarrow Me_4phen}$ excited states become closer in energy in *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-L})]^+$. This proximity increases the competitive relaxation to ground state, affecting the population of the lowest lying excited state, $^3IL_{\textit{trans}\text{-L}}$, and decreasing the isomerization quantum yield.

Similar quantum yields determined for *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-bpe})]^+$ at all irradiation wavelengths investigated, Table 2, indicate that the population of $^3IL_{\textit{trans}\text{-bpe}}$ by internal conversion from $^3MLCT_{Re\rightarrow Me_4phen}$ is the only pathway for the photoreaction. On the other hand, the quantum yields determined for *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-stpy})]^+$ depend on the irradiation wavelength. In the region where the isomerizable ligand does not absorb (404 nm), the population of $^3IL_{\textit{trans}\text{-stpy}}$ occurs exclusively by internal conversion from $^3MLCT_{Re\rightarrow Me_4phen}$. In others, there is a contribution of the *trans*-stpy intraligand transitions, and the isomerization quantum yields are higher.

This behavior suggests that the photoisomerization process in the region where the *trans*-stpy ligand absorbs can also be achieved by different pathways. One possibility is the enhancement of the population of $^3IL_{\textit{trans}\text{-L}}$ by the intersystem crossing from $^1IL_{\textit{trans}\text{-stpy}}$ due to the coordination. However a direct singlet reaction taking place upon excitation in the region of stpy absorption should also be considered. The photochemical behavior of *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-L})]^+$ can be summarized in the simplified energy diagram, Figure 4.

It was also observed that the back *cis*-to-*trans* isomerization in both complexes occurs for *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-L})]^+$ upon 254 nm excitation of photostationary state solutions. The quantum yield estimated by ^1H NMR for this reaction is about 0.15, in accordance with values reported by Wenger et al.[29] The ease of observation of the *cis*-to-*trans* isomerization process from the $^3IL_{\textit{cis}\text{-L}}$ excited state for *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-L})]^+$ is because of the proximity of this state with the $^3MLCT_{Re\rightarrow Me_4phen}$ one, which is the lowest lying excited state after *trans*-to-*cis* isomerization.[13]

Photophysical Behavior. The *trans*-to-*cis* photoisomerization process in *fac*-$[Re(CO)_3(Me_4phen)(\textit{trans}\text{-L})]^+$ can be also followed by the luminescence spectra, Figure 5, since the *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-L})]^+$ complexes exhibit emission in degassed acetonitrile at room temperature, while the *trans* isomers are nonemissive. The molecular motion of stilbene-like ligands coordinated to metal center can act as a luminescence on−off switch. As mentioned before, this process is reversible, which makes possible its use in photoinduced molecular devices.

Both complexes exhibit two emission maxima, in contrast to the broad and non-structured ^3MLCT emission typically observed for other rhenium(I) polypyridyl complexes.[12,13,24,35,42]

To evaluate the nature of emissive states in *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-L})]^+$, the emission spectra of the complexes and the free ligand, Me_4phen, were obtained in acetonitrile at 298 K and in glassy EPA at 77K. The emission spectra of *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-stpy})]^+$ in both media are shown in Figure 6a, and a similar behavior is observed for the *cis*-bpe complex.[43]

The emission maximum at 525 nm of the *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-stpy})]^+$ spectrum at 298 K, Figure 6a, is similar to that observed for *fac*-$[Re(CO)_3(Me_4phen)(py)]^+$, py = pyridine,[24] and is ascribed mainly to the ^3MLCT lowest lying excited state. In glassy EPA at 77 K, the emission spectrum of *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-stpy})]^+$ resembles the phosphorescence of the free Me_4phen ligand, Figure 6b, which does not exhibit emission in this region at room temperature. On the basis of the profile observed for all spectra, the maximum at 498 nm for *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-L})]^+$ at 298 K can be assigned to the contribution of the $^3IL_{Me_4phen}$ excited state.

The changes observed in the emission spectrum of *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-stpy})]^+$ in rigid medium have been described previously for some other rhenium complexes[13,18,12] and are known as the rigidochromic effect which is related to changes in dipolar interactions between the complex and the medium. In the long-lived ^3MLCT excited state, the dipole moment is reversed in comparison to the ground state. Consequently, the solvent molecules reorient themselves around the complex to best accommodate the new dipole formed. For a fluid medium, the orientational motions occur promptly, but they are restrained in a rigid medium; consequently, the energy of the ^3MLCT excited state is increased,[31] while the $^3IL_{NN}$ state is less affected by the medium's rigidity because of its centro-symmetric character.[21]

Another interesting aspect observed in the emission spectrum of *fac*-$[Re(CO)_3(Me_4phen)(\textit{cis}\text{-L})]^+$ in glassy EPA at 77 K is the dependence on excitation wavelengths, Figure 7, different to that observed at room temperature.

Excitation at lower wavelengths leads to emission spectra that resemble the phosphorescence of the Me_4phen ligand itself. As the excitation wavelength is increased, the luminescence band becomes structureless, and the relative intensity of emission in the lower energy region (around 520 nm) increases.

The changes in the emission profile observed at different excitation wavelengths indicate that the two emitting states,

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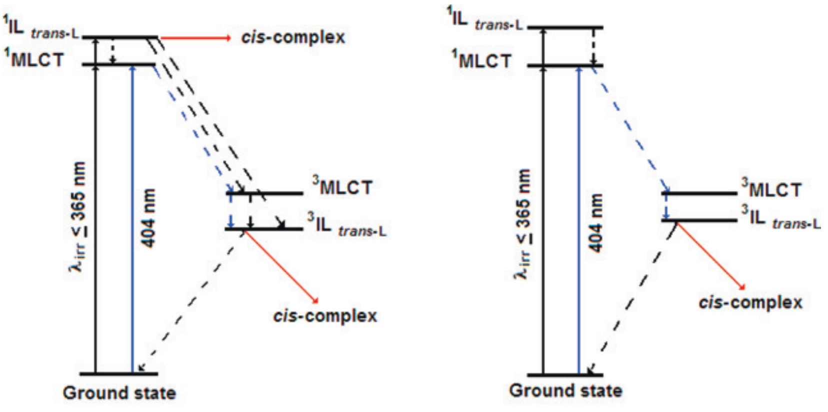

fac-[Re(CO)$_3$(Me$_4$phen)(trans-stpy)]$^+$ fac-[Re(CO)$_3$(Me$_4$phen)(trans-bpe)]$^+$

Figure 4. Simplified energy diagram for the photochemical behavior of *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-stpy)]$^+$ and *fac*-[Re(CO)$_3$(Me$_4$phen)(*trans*-bpe)]$^+$.

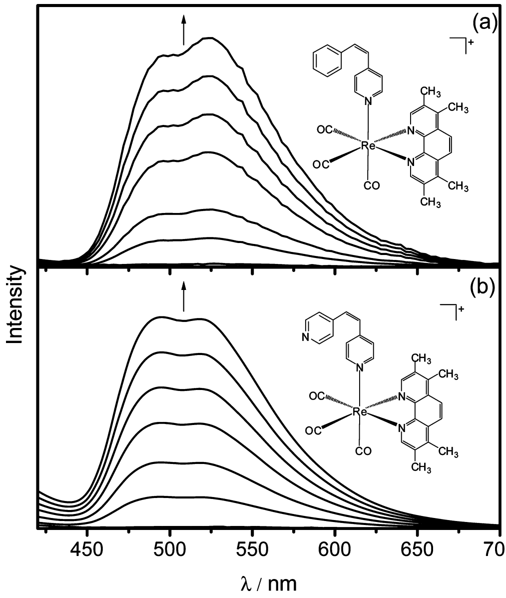

Figure 5. Changes in emission spectra of *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-L)]$^+$ in acetonitrile as a function of photolysis time upon 365 nm irradiation. (a) L = stpy; (b) L = bpe. (λ_{exc} = 300 nm, Δt = 5 s).

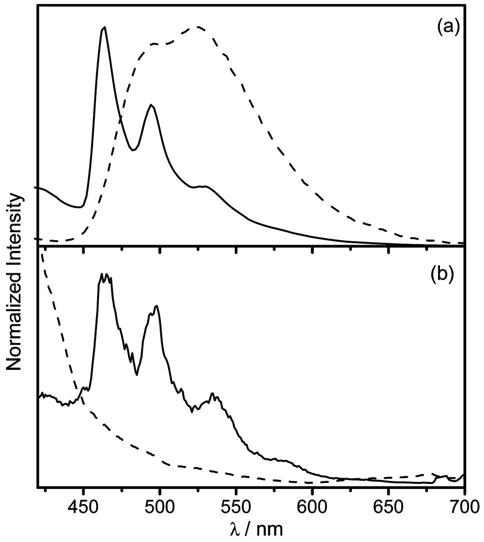

Figure 6. Emission spectra in glassy EPA at 77 K (solid line) or in acetonitrile at 298 K (dashed line) of (a) *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-stpy)]$^+$ (λ_{exc} = 300 nm) and (b) Me$_4$phen (λ_{exc} = 285 nm).

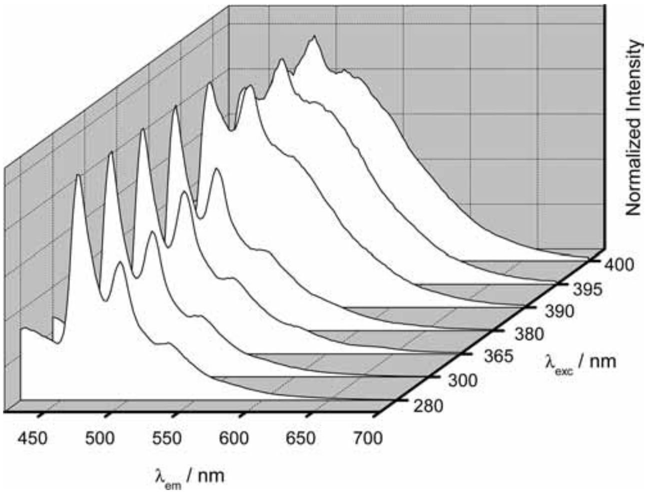

Figure 7. Emission spectra of *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-stpy)]$^+$ in EPA at 77 K at different excitation wavelengths.

^{3}MLCT and ^{3}IL$_{Me_4phen}$, are not equilibrated.[44] The internal conversion between ^{3}IL$_{NN}$ and ^{3}MLCT has been reported to be controlled by the degree of electronic and vibronic coupling between the states,[21] and it is slower when the states are close in energy. In *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-L)]$^+$, the methyl groups of Me$_4$phen decrease the energy gap between the ^{3}MLCT and ^{3}IL$_{Me_4phen}$ excited states, and the internal conversion from ^{3}IL$_{Me_4phen}$ to ^{3}MLCT should be slower. Consequently, radiative decays from both states can be observed. From the changes observed in the emission profile as a function of excitation wavelenght in EPA at 77 K, Figure 7, it can be inferred that the contribution of the ^{3}MLCT luminescence increases at lower excitation wavelengths when the ^{1}MLCT excited state is directly populated and followed by a preferential intersystem crossing to ^{3}MLCT.

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[44] The multiple non-equilibrated emissions can be also confirmed by application of excitation spectra method described by Sackesteder et al (*Inorg. Chem.* **1990**, *29*, 4335−4340; *Inorg. Chem.* **1989**, *28*, 1787−1792). Plots of R(λ) for *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-stpy)]$^+$ in EPA at 77 K and in acetonitrile at 298 K support that two emitting states are no equilibrated in rigid medium (Supporting Information, Figure B).

At room temperature, the energy of ^{3}MLCT is lowered, and the internal conversion from $^3IL_{Me_4phen}$ is enhanced. Thus, the luminescence is dominated by the lowest lying ^{3}MLCT excited state and is independent of the excitation wavelength. The two emission maxima can also be explained by the presence of $^3IL_{Me_4phen}$ and the proximity of $^3IL_{cis\text{-}L}$, responsible for the *cis*-to-*trans* isomerization, which competes with radiative decay from $^3MLCT_{Re\rightarrow Me_4phen}$. Consequently, the contribution from the $^3IL_{Me_4phen}$ excited state becomes more evident for *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-L)]$^+$.

4. Conclusions

The photochemical and photophysical behaviors of *fac*-[Re(CO)$_3$(Me$_4$phen)(L)]$^+$, L = bpe or stpy, depend on the energy gap among three triplet excited states: $^3MLCT_{Re\rightarrow Me_4phen}$, ^3IL_L, and $^3IL_{Me_4phen}$. For the *trans* isomers the lowest lying excited state is $^3IL_{trans\text{-}L}$; thus, upon 313, 334, or 365 nm irradiation, *trans*-to-*cis* isomerization of the stilbene like ligand is observed. This process is observed even at 404 nm irradiation, where the ligand itself does not absorb, and the role of the metal complex to the sensitization of ^{3}IL of isomerizable ligand becomes clear. After photoisomerization, ^3IL_L is destabilized and $^3MLCT_{Re\rightarrow Me_4phen}$ becomes the lowest lying excited state. Excitation of *cis* isomer complexes leads to a broad emission band with two maxima ascribed to $^3MLCT_{Re\rightarrow Me_4phen}$ and to a contribution of the $^3IL_{Me_4phen}$. These states are close in energy and exhibit slow internal conversion rates. Furthermore, the *cis*-to-*trans* isomerization observed upon irradiation at 254 nm confirms that the decay from $^3IL_{cis\text{-}L}$ state competes with luminescence from $^3MLCT_{Re\rightarrow Me_4phen}$.

In rigid media, the energy of $^3MLCT_{Re\rightarrow Me_4phen}$ is raised, and the electronic and vibrational coupling between this state and $^3IL_{Me_4phen}$ decreases. As a consequence, the emissive states are not equilibrated, and the emission profile is dependent on the excitation wavelength with a preferential emission from ^{3}MLCT being observed at higher excitation wavelengths.

The reversible *trans*-to-*cis* isomerization of coordinated ligands acts as on−off switch of the luminescence of complexes, which can be exploited for the application in photoinduced molecular machines.

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Supporting Information Available: ^{1}H NMR spectral data in CD$_3$CN for ligands and complexes, emission spectra of *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-bpe)]$^+$ in EPA at 77 K and in acetonitrile at 298 K, and plot of $R(\lambda)$ as a function of excitation wavelength for *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-stpy)]$^+$ in EPA at 77 K and in acetonitrile at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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