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Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 73–78

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photoinduced luminescence of *fac*-[Re(CO)$_3$(phen)(stpy)]$^+$ in CH$_3$CN and PMMA

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Received 31 August 2005; received in revised form 3 November 2005; accepted 8 November 2005
Available online 18 January 2006

Abstract

The photophysical and photochemical behavior of the *fac*-[Re(CO)$_3$(phen)(stpy)]$^+$ complex, where phen = 1,10-phenanthroline and stpy = 4-styrylpyridine, in acetonitrile solution and in poly(methyl methacrylate), PMMA, polymer film has been studied. Under irradiation, the complex exhibits *trans–cis* photoassisted isomerization of the coordinated ligand stpy. The apparent quantum yields determined by absorption changes in acetonitrile are $\Phi_{313} = 0.35 \pm 0.02$, $\Phi_{334} = 0.36 \pm 0.02$ and $\Phi_{365} = 0.31 \pm 0.02$. The ^{1}H NMR spectra and the increasing luminescence as the photoproduct is formed corroborate the photochemical process. The observed emission of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$, assigned to the lowest lying ^{3}MLCT state, is highly sensitive to changes in the rigidity of the medium. Similar changes in absorption and emission spectra are also observed for the complex in PMMA film, a suitable medium for developing practical molecular devices.

Keywords: Photoisomerization; Rhenium carbonyl complex; Rigid media; Luminescence; PMMA; Poly(methyl methacrylate)

1. Introduction

Photoisomerization reactions observed in some organic compounds result in photoproducts with distinct spectroscopic properties, which can be useful in development of photochemical molecular devices [1–3]. The design of such molecular devices can also be achieved by coordinating photoisomerizable ligands to metallic complexes [4,5]. The coordination of a photoisomerizable organic ligand to rhenium(I) carbonyl complexes is one of these cases. These compounds, with ^{3}MLCT excited state having adequate energy, usually allow light driven isomerization in a less energetic irradiation and/or enhance its efficiency [6–10].

Rhenium(I) polypyridyl complexes have also been the subject of a great number of studies [11–28] and many of these complexes have characteristic lowest lying ^{3}MLCT excited state. This state shows a remarkable emission [11–21] and also exists long enough to take part in electron and/or energy transfer processes [21–26]. The growing interest in employing these complexes in several applications, such as in photocatalysis [26], solar energy conversion [27] and also as molecular probes [19,23] or luminescent sensors [29,30], is associated with the tunability of this excited state.

Changes in the coordinated ligands [31] and/or the medium in which the complex is placed [11,12] can also tune the ^{3}MLCT excited state. An appropriate modification of these conditions alters the emissive state; a suitable medium can also provide additional information in processes (e.g., electron transfer [17,32]) and a rigid medium is a suitable choice for developing practical devices [33].

In this paper, we extend our previous studies on rhenium(I) polypyridyl complexes [9,13,34–37] to the investigation of the photochemical and photophysical behavior of *fac*-[Re(CO)$_3$(phen)(stpy)]$^+$ in acetonitrile solution, as well as in poly(methyl methacrylate), PMMA, aiming its possible use as a photosensor or as a molecular probe.

2. Experimental

All solvents for syntheses were reagent grade. HPLC grade solvents (Aldrich) were employed in polymer film preparation and in photophysical and photochemical measurements.

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doi:10.1016/j.jphotochem.2005.11.003

Benzaldehyde (Aldrich), 4-picoline (Aldrich), acetic anhydride (Mallinckrodt), 1,10-phenanthroline (QM), phen, ClRe $(CO)_5$ (Strem), trifluoromethanesulfonic acid (Aldrich), HTFMS, and poly(methyl methacrylate) (Aldrich, $M_w = 101{,}000$), PMMA, were used as received.

2.1. Synthesis of trans-4-styrylpyridine

Trans-4-styrylpyridine, *trans*-stpy, was prepared with slight modifications of the procedure reported in the literature [38]. Benzaldehyde (5.0 g, 0.47 mmol) and 4-picoline (5.2 ml, 0.53 mmol) were refluxed for 12 h in acetic anhydride (5.0 ml, 53 mmol). The solution was distilled under reduced pressure, and the remaining solid was extracted with diethyl ether. Yields 59%. ^{1}H NMR (CD_3CN, δ (ppm)): 8.53, d (2H); 7.62, d (2H); 7.47, d (2H); 7.41, d (1H); 7.41, t (2H); 7.34, t (1H); 7.17, d (1H).

2.2. Synthesis of fac-[ClRe(CO)$_3$(phen)]

The complex was synthesized as previously reported [34] by refluxing $ClRe(CO)_5$ and 1,10-phenanthroline, in xylene for 6 h. The yellow solid was recrystallized from dichloromethane by slow addition of *n*-pentane. Yields 77%. Anal. Calc. for $C_{15}H_8N_2O_3ClRe$: C, 37.08; N, 5.77; H, 1.66%. Found: C, 37.12; N, 5.70; H, 1.77%. ^{1}H NMR (CD_3CN, δ (ppm)): 9.39, dd (2H); 8.76, dd (2H); 8.17, s (2H); 7.97, dd (2H).

2.3. Synthesis of fac-[(TFMS)Re(CO)$_3$(phen)]

The complex was prepared as previously reported [34] by suspending *fac*-[ClRe(CO)$_3$(phen)] in dichloromethane and adding trifluoromethanesulfonic acid, in 10-fold excess. The solution was stirred for an hour, and the product was obtained by slow addition of diethyl ether. Yields 79%. Anal. Calc. for $C_{16}N_2H_8SO_6F_3Re$: C, 32.06; N, 4.67; H, 1.34%. Found: C, 32.28; N, 4.80; H, 1.46%.

2.4. Synthesis of fac-[Re(CO)$_3$(phen)(trans-stpy)]PF$_6$

The complex was synthesized following the procedure reported [37] for *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$, replacing *trans*-bpe with *trans*-stpy. The *fac*-[(TFMS)Re(CO)$_3$(phen)] complex (0.20 g, 0.33 mmol) and *trans*-stpy, (0.42 g, 2.3 mmol) were mixed in methanol (90 ml) and heated to reflux for 5 h. After cooling to room temperature, a saturated aqueous solution of NH_4PF_6 was added to precipitate the complex as a yellow solid, which was filtered. The excess of NH_4PF_6 was removed by stirring the solid in water for 15 min. The yellow complex was collected by filtration and washed with water and then with diethyl ether. Yields 70%. Anal. Calc. for $ReC_{27}H_{20}O_4N_3F_6P$: C, 43.28; N, 5.41; H, 2.46%. Found: C, 43.55; N, 5.41; H, 2.77%. ^{1}H NMR (CD_3CN, δ (ppm)): 9.62, dd (2H); 8.84, dd (2H); 8.17, dd (2H); 8.16, d (2H); 8.12, s (2H); 7.52, d (2H); 7.37, d (1H); 7.35, m (2H); 7.35, m (1H); 7.26, d (2H); 6.97, d (1H).

2.5. Preparation of polymer films

The compounds were dissolved in acetonitrile (e.g. 4.5 mg of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]PF$_6$ in 2 ml of acetonitrile), added to an acetonitrile solution of PMMA (250 mg:5 ml), and then left to dry. Preparation of PMMA based films were carried out in the absence of humidity in order to obtain clear and transparent film. Exposure to light was avoided in order to prevent photoisomerization of the complex in the polymer matrix [34,37].

2.6. Methods

Absorption spectra were recorded using a Hewlett-Packard 8453 diode array spectrophotometer with quartz cuvets of 1.000 or 0.100 cm optical length. Absorption spectra of films were performed by exposing them directly to the light beam.

NMR spectra were recorded at 300 K in a DRX-500 (500 MHz) Bruker Avance spectrometer using CD_3CN as deuterated solvent. Tetramethylsilane or the residual CH_3CN signals were employed as internal standards.

Emission experiments were performed by using an ISS model PC1 photon-counting spectrofluorometer with a photomultiplier based, photon-counting detector. Quartz cuvets of 1.000 cm path length were used for solutions, while the spectra of polymer films were directly obtained by using a front face arrangement for solid samples, in which the excitation light was always focused at the same region where the photolyses were carried out. Low-temperature emission experiments were performed in glassy EPA (diethyl ether–isopentane–ethanol, 5:5:2) at 77 K, with the sample in a quartz tube placed in a Dewar flask filled with liquid nitrogen.

Irradiation at 313, 334 or 365 nm was performed using an Oriel 200 W Hg(Xe) arc lamp and the wavelength selection was obtained by means of appropriate interference filters. The light intensity was determined by chemical actinometry with tris(oxalate)ferrate(III). The photochemical system and photolysis procedures have been described in detail elsewhere [34,37]. Photochemical experiments in polymer films were always performed in parallel with those in acetonitrile solution under a similar condition of irradiation ($A_{\text{film}} = A_{\text{sol}}$).

3. Results and discussion

The absorption spectra of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$, *trans*-stpy, and protonated *trans*-stpy, in acetonitrile solution, are shown in Fig. 1a. The spectrum of *trans*-stpy exhibits the characteristic intraligand transitions, IL, in the near UV region ($\lambda_{\max} = 300$ nm). The protonation of pyridinic nitrogen stabilizes the excited state and shifts these transitions to a lower energy region ($\lambda_{\max} = 340$ nm).

Molar absorptivity of $10^4\ \text{l mol}^{-1}\ \text{cm}^{-1}$ of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$, from 330 to 375 nm, is much higher than usually observed for rhenium carbonyl complexes with α-diimine ligands. Such complexes are characterized by an intense metal-to-ligand charge transfer transition, MLCT, in the UV–vis region ($\varepsilon \approx 10^3\ \text{l mol}^{-1}\ \text{cm}^{-1}$) and its energy depends on the

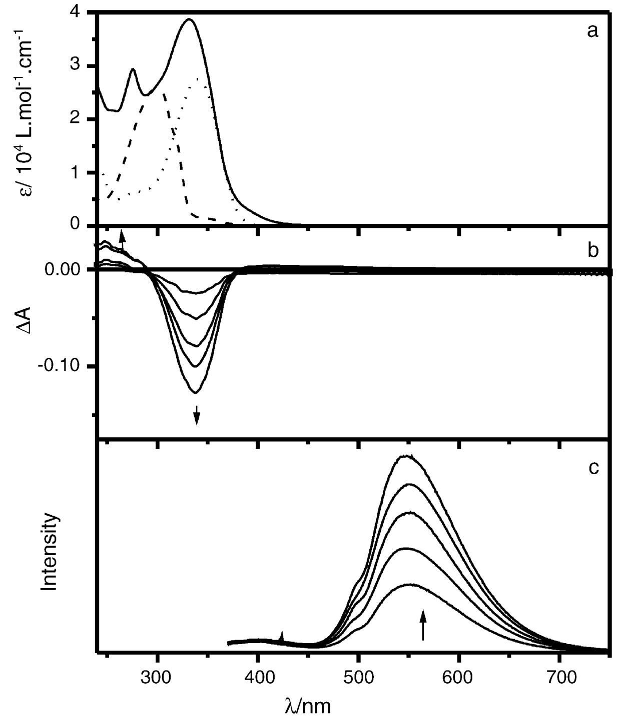


Fig. 1. (a) Absorption spectra of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ (—), *trans*-stpy (- - -) and protonated *trans*-stpy (· · ·), (b) difference absorption spectra of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ ($\Delta t_{irr} = 2$ s at 365 nm) and (c) changes in emission spectra ($\lambda_{ex} = 365$ nm) of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ ($\Delta t_{irr} = 2$ min at 365 nm), as a function of photolysis time, in CH$_3$CN solution.

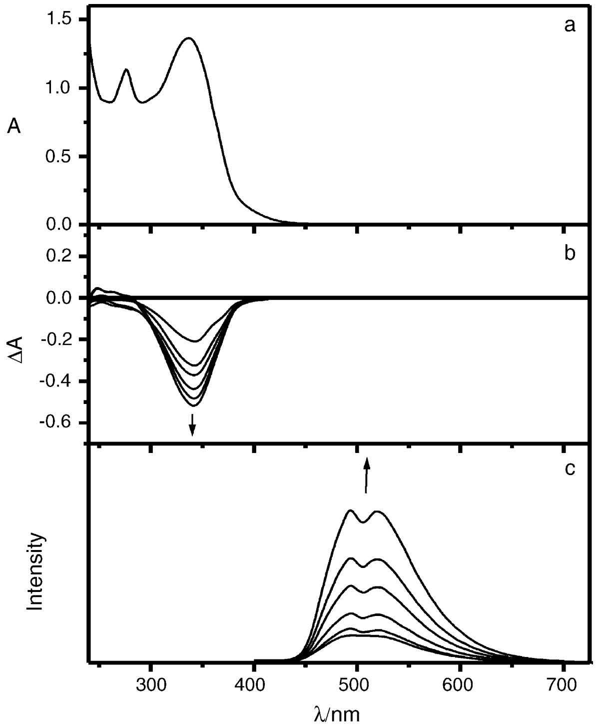
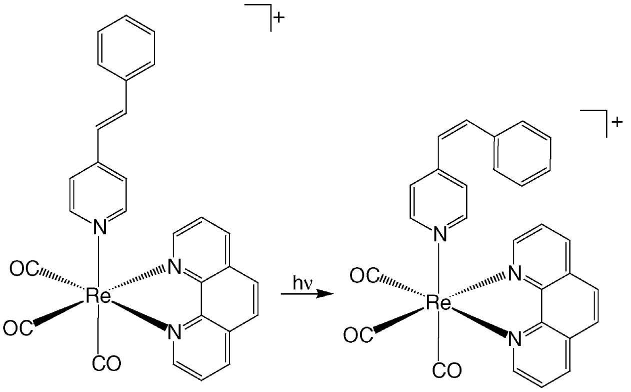


Fig. 2. (a) Absorption spectrum of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$, (b) difference absorption spectra of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ and (c) changes in emission spectra of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ ($\lambda_{ex} = 365$ nm), as a function of photolysis time, in PMMA films. ($t_{irr} = 2$, 6, 60, 360, 660, 1260 s at 365 nm).

ligands and the polarity of the solvent employed [31]. The coordination of *trans*-stpy to the metal center shifts the absorption to a lower energy region, similar to those observed after protonation of the ligand itself. Thus, the absorption from 330 to 375 nm has contributions from the IL and the MLCT charge transfers. This has also been reported for similar complexes with other photoisomerizable ligands [9,10,37,39,40].

The electronic absorption spectrum of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ in PMMA matrix is shown in Fig. 2a. The spectrum is slightly shifted to lower energy ($\lambda_{max} = 335$ nm) but its profile is very similar to the one in acetonitrile solution and leads to the same assignments. The polarities of the PMMA matrix and the acetonitrile solution are different, resulting in small shifts of the absorption maxima due to changes in the energy of MLCT. This excited state can be stabilized in a polar environment due to a better interaction between the media dipoles and those formed upon excitation of the complex [11,12,31].

The photoisomerizaton process of the *trans*-stpy ligand was followed by changes in electronic spectra, with clear and well-defined isosbestic points, upon irradiation at 313 nm (Fig. 3). This behavior is in accord with those reported in the literature [41] and similar to the photochemical behavior of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ under excitation at either 313, 334 or 365 nm. The absorption changes observed for irradiation at 365 nm in acetonitrile or in PMMA (Figs. 1b and 2b), respectively, are consistent with *trans*-to-*cis* isomerization of the coordinated *trans*-stpy ligand, represented by Eq. (1).



(1)

The quantum yields for the photoisomerization, $\Phi_{trans\text{–}cis}$, of *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ in acetonitrile are similar at all excitation wavelengths investigated, as can be seen in Table 1. The apparent $\Phi_{trans\text{–}cis}$, determined by spectral variation, are

Table 1
Quantum yields for the photoisomerization of free and coordinated *trans*-stpy in acetonitrile solution

Compound	$\Phi_{313\,nm}$	$\Phi_{334\,nm}$	$\Phi_{365\,nm}$
trans-stpy	0.34 ± 0.04 0.37–0.39[b]	[a]	[a]
fac-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$	0.35 ± 0.02	0.36 ± 0.02	0.31 ± 0.02

[a] *Trans*-stpy does not absorb in this wavelength.
[b] CH$_2$Cl$_2$ solution [6].

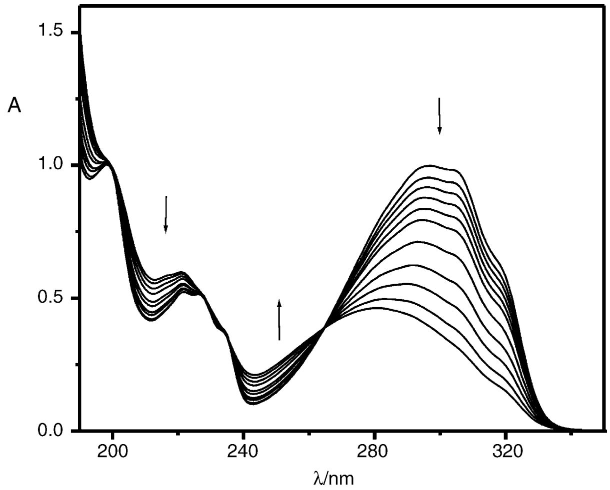


Fig. 3. Spectral changes of *trans*-stpy as a function of photolysis time in CH_3CN solution (Δt_{irr} = 6 s at 313 nm).

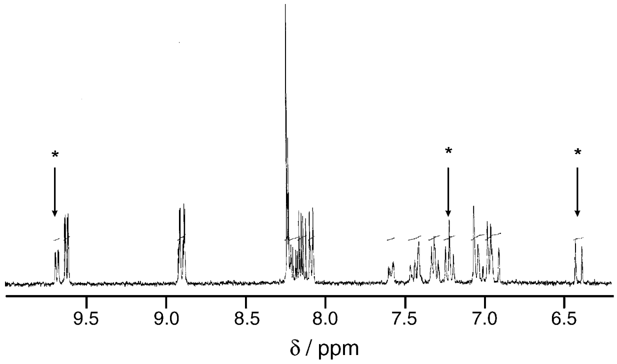


Fig. 4. ^{1}H NMR spectrum of the *fac*-$[Re(CO)_3(phen)(stpy)]^+$ complex in CD_3CN after 10 min of irradiation at 365 nm (T = 298 K, 300 MHz) (* peaks assigned to the *cis*-complex).

similar to those determined for the free ligand. However, the actual value, so called true quantum yield, for the complex is higher than those determined by changes in electronic spectra, since the *cis* isomer absorbs also at the same wavelengths employed in determination of $\Phi_{trans–cis}$ and will be further discussed with ^{1}H NMR results. The observed isomerization at 334 or 365 nm irradiation indicates that the coordination sensitizes *trans*-stpy to the excited state responsible for the process, allowing the photoassisted isomerization. The photosensitized isomerization of *trans*-styrylpyridine has also been reported for other complexes, such as *fac*-$[ClRe(CO)_3($*trans*-stpy$)_2]$ [6] and *cis*-$[W(CO)_4($*trans*-stpy$)_2]$ [42].

It has been reported that both singlet and triplet pathways are present in the photoisomerization of stilbene-like compounds; although, when a functional group increases the coupling between singlet and triplet manifolds, the triplet pathway becomes more competitive [43]. The metal center acts as a substituent, besides the heavy atom effect which enhances the triplet mechanism, and acts as a sensitizer, transferring energy to the ^{3}IL state responsible for isomerization. The adequate energy levels of the complex lead to sensitization of the ^{3}p* state, as has already been reported for the similar *fac*-$[Re(CO)_3(phen)($*trans*-bpe$)]^+$ complex [36]. The photoassisted isomerization has been reported to occur, even with excitation at lower energies, exclusively by the triplet mechanism [39] for *fac*-$[Re(CO)_3(bpy)($*trans*-stpy$)]^+$ and for *fac*-$[ClRe(CO)_3($*trans*-stpy$)_2]$.

Exhaustive irradiation, conducted in either acetonitrile or PMMA showed that the photostationary state, PSS, is substantially smaller in solid films (25%) than in solution (55%). This behavior has also been reported for azo dyes in rigid matrices, and the inhibition of the photoisomerization has been ascribed to a relatively small free volume in solid medium in comparison to a fluid solution [44–46].

The photoisomerization process for the coordinated stpy ligand was also monitored by ^{1}H NMR spectroscopy following chemical shifts and coupling constants of the protons. This technique is particularly adequate as the olefinic proton signals of the *cis* and *trans* configurations are fairly different. The ^{1}H NMR spectrum of *fac*-$[Re(CO)_3(phen)($*trans*-stpy$)]^+$ showed a clear electronic communication of a metal center across the ring of coordinated *trans*-stpy, whereas the spectrum revealed the characteristic ^{1}H NMR signals shifted upfield for the *cis*-isomer.

Upon irradiation, the proton signals CH=CH for the *trans* isomer at 6.97 and 7.37 ppm were found to decrease gradually. At the same time, the signal ascribed to the *cis* isomer at 6.41 and 7.22 ppm built up (Fig. 4). The characteristic ^{1}H NMR coupling constants for the *cis* isomer (12 Hz) were observed, besides those for the existent *trans* isomer (16 Hz).

Irradiation at 365 nm achieved 50% of *trans–cis* conversion after 10 min, calculated by ^{1}H NMR data. The true quantum yields determined by ^{1}H NMR are at least twice as high as than those determined by absorption changes [47]. The higher quantum yields for the coordinated stpy in comparison to the free ligand indicate the role of metal complex in the photosensitized isomerization.

Intense emission was observed upon irradiation due to the formation of the *cis*-isomer. The changes in the emission spectra of *fac*-$[Re(CO)_3(phen)($*trans*-stpy$)]^+$ both in acetonitrile and in PMMA are shown in Figs. 1c and 2c, respectively. The distinct emissive characteristic of the *cis*-complex can be ascribed to the change of the lowest lying excited state. The ^{3}MLCT state is assigned as the lowest lying one for *fac*-$[Re(CO)_3(phen)($*cis*-stpy$)]^+$ due to the typical broad and non-structured emission at 298 K [36,37].

For *fac*-$[Re(CO)_3(phen)($*trans*-stpy$)]^+$, the ^{3}MLCT energy level is higher than the $^3IL_{trans\text{-}stpy}$ state; therefore, the deactivation pathway leads to the lowest lying ^{3}IL excited state, responsible for the *trans–cis* isomerization [36]. A dihedral angle between the pyridyl and benzyl rings in *trans*-stpy allows the π clouds to interact, while for the *cis* photoproduct this angle is changed, dramatically reducing such interaction. As a consequence, the energy of the $^3IL_{cis\text{-}stpy}$ state is raised in comparison to the $^3IL_{trans\text{-}stpy}$ state. The destabilization of ^{3}IL leads ^{3}MLCT as the lowest lying excited state, which is responsible for the emission observed in solution at 298 K.

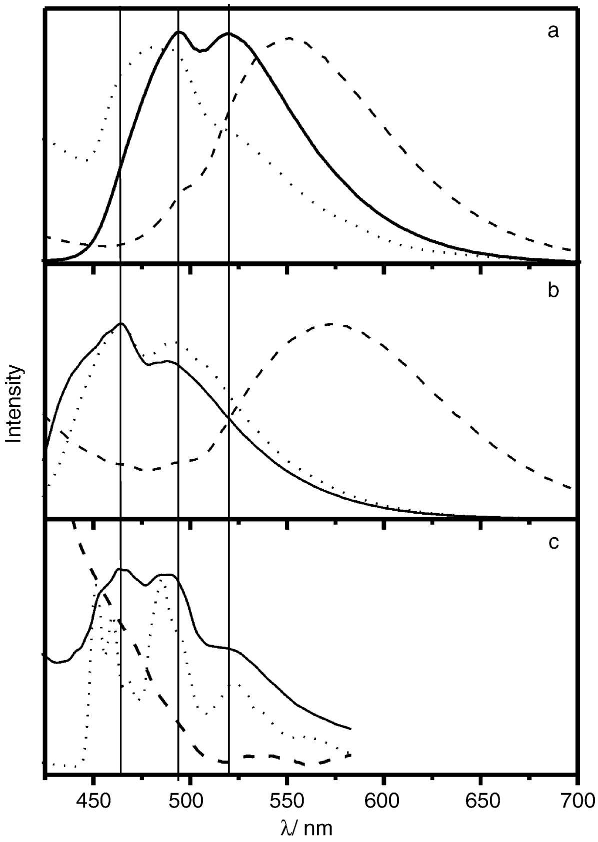


Fig. 5. Emission spectra in PMMA film (—) or fluid solution (- - -) at 298 K, and in EPA at 77 K (· · ·) of (a) *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ (λ_{ex} = 365 nm), (b) *fac*-[(TFMS)Re(CO)$_3$(phen)] (λ_{ex} = 300 nm), and (c) 1,10-phenanthroline (λ_{ex} = 285 nm).

The emission spectra of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ in acetonitrile solution and PMMA matrix, both at 298 K, and in glassy EPA, at 77 K, are shown in Fig. 5a. In order to investigate the changes in different media and to better understand the nature of the emissive state, the spectra of *fac*-[(TFMS)Re(CO)$_3$(phen)] and of 1,10-phenanthroline, are presented in Fig. 5b and c, respectively, under the same conditions. The emission of the free *cis*-stpy, either protonated or not, is observed only in 330–440 nm region.

For both complexes, the broad and structureless emission has to originate from ^{3}MLCT$_{\text{Re-phen}}$ as this is the only possibility for *fac*-[(TFMS)Re(CO)$_3$(phen)]. The spectra of both complexes (Fig. 5a and b), exhibit hypsochromic shifts as the medium rigidity increases due to ^{3}MLCT being very sensitive to the rigidity of the medium. This effect has already been described for other rhenium(I) complexes and is known as the "rigidochromic" effect [6,29,48].

This rigidochromic effect is associated with the changes in the dipolar interactions between the complex and the medium [19,34,49]. The energy shifts depend on the variations in dipole moment between the initial and final states. In a liquid medium, the solvent molecules can easily be reoriented around the new dipole formed in the long-lived ^{3}MLCT state. In a rigid medium, orientational motions are frozen, and the charge transfer occurs with solvent dipoles oriented for the initial state, increasing the energy of the ^{3}MLCT state. For ^{3}IL excited states, the shifts are typically small due to their centro-symmetric character, and difference in the emission maxima of PMMA and EPA is negligible, as can be seen in Fig. 5c [17,32].

The energy of the lowest lying ^{3}MLCT excited state raises due to the solvent reorganizational energy added to the free energy [17]. This destabilization of ^{3}MLCT can be observed by comparing the spectra of the complexes in PMMA and in acetonitrile. In both cases the increase in the rigidity of the medium results in a more structured spectra, with two maxima, and shifts toward higher energy region. A defined structure can be associated with the spectrum of 1,10-phenanthroline in PMMA, where the contribution of the ligand phosphorescence in the same region is observed. In a more rigid medium, e.g. EPA at 77 K, the emission spectra for both complexes are shifted even more to higher energy. Particularly, the emission spectrum of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ at 77 K is structured and resembles the ligand one in a rigid medium. The less structured spectrum of *fac*-[(TFMS)Re(CO)$_3$(phen)] in EPA at 77 K can be explained by lower energy of its ^{3}MLCT excited state in comparison to that of the *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$.

The increasing in the energy of the ^{3}MLCT state of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ through augmentation of medium rigidity leads to an approximation of this energy level to ^{3}IL$_{\text{phen}}$, or even a complete inversion of the lowest lying excited state. Such effect has already been observed for other rhenium carbonyl complexes. Sacksteder et al. [29] investigated the emission properties of a series of *fac*-[XRe(CO)$_3$(L)], X = Cl$^-$, Br$^-$, or I$^-$ and L = α-diimines, at room temperature and in glassy EPA at 77 K. The compounds in a room temperature solution exhibit broad and non-structured emission spectra, typical of ^{3}MLCT, while in glassy EPA presented a highly structured spectrum, ascribed to the phosphorescence of ^{3}IL$_{\alpha\text{-diimine}}$ showing a complete inversion of the lowest lying excited state.

4. Conclusion

The photoassisted isomerization of *trans*-stpy can be achieved by the coordination of the ligand to *fac*-[Re(CO)$_3$(phen)]$^+$. The quantum yields higher than those determined for the free ligand are evidence of the sensitization promoted by the metal complex. Photoisomerization was also achieved in a rigid medium with a lower ratio in the photostationary state.

The isomerization leads the ^{3}MLCT$_{\text{Re-phen}}$ to become the lowest lying excited state in the *cis* complex and is responsible for the luminescence observed as the photoprocess proceeds. The energy of ^{3}MLCT excited state increases as medium rigidity increases. The emission spectrum of *fac*-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$ in EPA at 77 K exhibits a wide contribution of ^{3}IL$_{\text{phen}}$, suggesting that the energy of this state and ^{3}MLCT$_{\text{Re-phen}}$ are closer or that the ^{3}IL$_{\text{phen}}$ became the lower state. Such behavior can be exploited in the development of photochemical molecular devices aiming for possible use in practical applications, such as a molecular probe to monitor polymerization processes [19] by following the emission maxima.

Acknowledgements

The authors are grateful to the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, and Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, for financial support.

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