

Light driven isomerization of coordinated ligand and modulation of *fac*-[Re(CO)₃(phen)(*trans*-bpe)]PF₆ photoluminescence in rigid media

Melina Kayoko Itokazu, André Sarto Polo, and Neyde Yukie Murakami Iha[†]

Instituto de Química, Universidade de São Paulo - Av. Lineu Prestes, 748, São Paulo, SP, 05508-900, Brazil

ABSTRACT. The excited state reactivity and photophysical properties of *fac*-[Re(CO)₃(phen)(L)]PF₆ (phen = 1,10-phenanthroline, L = *trans*- or *cis*-1,2-bis(4-pyridyl)ethylene, bpe) in PMMA (poly(methyl methacrylate)) films have been investigated and compared with those in acetonitrile solution.

313 or 365 nm irradiation of the rhenium complex in PMMA leads to UV-vis spectral changes due to the *trans* → *cis* isomerization of the coordinated bpe ligand. The *fac*-[Re(CO)₃(phen)(*cis*-bpe)]⁺ product presents a markedly enhanced luminescence due to a lower lying metal-to-ligand charge transfer (MLCT) excited state in the *cis* isomer. This emitting property can be conveniently applied as a probe or sensor.

The *cis* isomer ratio in the photostationary state (PSS) is substantially smaller in solid films than in solution. The photochemical behavior of the free *trans*-1,2-bis(4-pyridyl)ethylene in PMMA is also reported to establish comparisons with the investigation carried out in acetonitrile solution as well as with the behavior of the coordinated ligand.

1. INTRODUCTION

Applications of luminescent MLCT excited states, in especial for Re(I) polypyridyl complexes containing carbonyl ligands, have been mentioned in several areas such as solar energy conversion [1, 2], luminescence-based sensor development [3, 4] and molecular materials for non-linear optics [5, 6] or photoswitches [7, 8].

Luminescent sensors using Re(I) metal complexes are gaining much interest because of their high sensitivity and specificity. This is due to the possibility of modulating photochemical and luminescent properties of such complexes by modifying ligands and/or solvent environment which affect the excited state properties [9-12]. These characteristics are also observed and reported in polymer matrices [13, 14], for example, in the development of luminescent sensors for oxygen [15].

In previous works of our group [16-19], the red-shifted absorption of the coordinated *trans*-bpe in *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ was exploited to achieve photoassisted isomerization by irradiation in the low energy region (i.e. 365 nm), where the free ligand does not absorb. The dynamics of photoisomerization in *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ have also been investigated by transient absorption (TA) and time-resolved infrared (TRIR) spectroscopies. These measurements have provided direct evidence for a photochemical transient and detailed insight into mechanism for sensitized *trans* → *cis* isomerization of bpe in rhenium carbonyl complexes.

The present work extends our study on metal complex sensitized intraligand photochemistry by the investigation of *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺

in rigid media aiming the possible use of the photoisomerizable properties of the ligand in the design and development of photochemical molecular devices.

2. EXPERIMENTAL

2.1. Preparation. All solvents were reagent grade (Merck, Synth or Nuclear), except for those used in polymer films preparation, photophysical and photochemical measurements, in which HPLC grade solvents (Aldrich) were employed. Trifluoromethanesulfonic acid, CF₃SO₃H, ammonium hexafluorophosphate, NH₄PF₆ and poly(methyl methacrylate), PMMA (Average $M_w = 25,000$), from Aldrich, were used as received.

Purification of *trans*-1,2-bis(4-pyridyl)ethylene. The *trans*-1,2-bis(4-pyridyl)ethylene ligand, *trans*-bpe, purchased from Aldrich was recrystallized several times from a methanolic solution by addition of water. The pure *trans*-1,2-bis(4-pyridyl)ethylene was collected, washed with water and then with diethylether.

Synthesis of *fac*-[(CF₃SO₃)Re(CO)₃(phen)]. The *fac*-[(CF₃SO₃)Re(CO)₃(phen)] complex was synthesized as described in the literature [17, 20]. CF₃SO₃H (2.0 mL; 23 mmol) was added to a dichloromethane solution (35 mL) of *fac*-[ClRe(CO)₃(phen)] (1.1 g, 2.2 mmol), previously prepared [17], under inert atmosphere and stirred for 1 hour. The complex was precipitated by a slow addition of diethylether and collected by filtration. Yields 79%. *Anal. Calc.* for ReC₁₆H₈N₂O₆F₃S: C, 32.06; N, 4.67; H, 1.35%. *Found:* C, 32.28; N, 4.80; H, 1.46%.

Synthesis of *fac*-[Re(CO)₃(phen)(*trans*-bpe)]PF₆·H₂O. The *fac*-[Re(CO)₃(phen)(*trans*-bpe)]PF₆ complex was synthesized following an improved modifica-

[†] E-mail: neydeiha@iq.usp.br

tion of the procedure previously described [17]. In 60 mL of methanol, 0.30 g (0.50 mmol) of *fac*-[(CF₃SO₃)Re(CO)₃(phen)] and 0.64 g (3.5 mmol) of *trans*-1,2-bis(4-pyridyl)ethylene were dissolved and heated to reflux for 4 hours. Saturated aqueous solution of NH₄PF₆ was added to a room temperature solution to precipitate yellow solid. The solid complex was stirred in water for 15 minutes to eliminate the excess of NH₄PF₆, separated by filtration, washed first with water and then with diethylether. Yields 60%. *Anal. Calc.* for ReC₂₇H₂₀O₄N₄F₆P: C, 40.72; N, 7.04; H, 2.51%. *Found:* C, 40.61; N, 6.99; H, 2.39%. ¹H NMR for *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺, (CD₃CN, δ (ppm)): 9.62, dd (2H); 8.84, dd (2H); 8.54, dd (2H); 8.17, s (2H); 8.12, q (2H); 8.22, dd (2H); 7.39, dd (2H); 7.30, dd (2H); 7.30, d (1H); 7.18 d (1 H).

PMMA based films. 4.2 mg of the complex *fac*-[Re(CO)₃(phen)(*trans*-bpe)]PF₆·H₂O was dissolved in acetonitrile (2–3 mL), added to an acetonitrile solution of PMMA and left to dry. Usually, films prepared using this procedure have 30–40 μm of thickness [21].

Preparation of PMMA films with the complex should be carried out in absence of humidity to obtain a clean, homogeneous and transparent film. Also, the light exposure should be avoided during the preparation and the samples kept in dark to prevent the formation of the *cis*-bpe complex.

2.2. Methods. Emission experiments were performed by using an ISS Model PC1 photon-counting spectrofluorometer, with a photomultiplier-based photon counting detector. The emission spectra of polymer films were obtained by using a front face arrangement for solid samples with the light focused at the same region where the photolyses had been carried out. Low-temperature emission experiments were made in EPA (diethyl ether-isopentane-ethanol, 5:5:2) solutions in a quartz tube at 77 K.

The electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer.

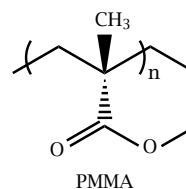
The photolyses were carried out with an Oriel 200 W Hg(Xe) arc lamp Oriel. Irradiation at 313 or 365 nm was obtained by using an appropriate interference filter. The photochemical system and photolysis procedures for solution were described in detail elsewhere [22].

Photochemical experiments in polymer films were performed in parallel to those in acetonitrile solution. The photoreaction was followed for both having the same absorbance at the irradiation wavelength ($A_{\text{film}} = A_{10\text{mm optical path solution}}$).

3. RESULTS AND DISCUSSION

The electronic spectrum of the complex *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ in PMMA film (Figure 1(a)) exhibits intense absorption bands in the

250–300 nm region assigned to intraligand transitions (IL) $\pi \rightarrow \pi^*$. The 300–350 nm absorption bands correspond to intraligand (IL) $\pi \rightarrow \pi^*_{\text{trans-bpe}}$ and metal-to-ligand charge transfer (MLCT) $d\pi_{\text{Re}} \rightarrow \pi^*_{\text{trans-bpe}}$ and $d\pi_{\text{Re}} \rightarrow \pi^*_{\text{phen}}$ transitions, similarly to those previously assigned in solution [17].



The irradiation of *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ in poly(methyl methacrylate), PMMA, at 313 or 365 nm results in UV-vis spectral changes with isosbestic points at 267 and 389 nm (Figure 1(b)). These spectral changes are associated to the *trans* → *cis* isomerization of the coordinated bpe ligand, equation (1), as reported in methanolic solution [17, 19].

At the beginning of the irradiation (~ 1–6 seconds), the isomerization reaction in PMMA films presents a higher photolysis percentage than that in fluid solution. After that, the *cis*-complex isomer was found to form in smaller quantities in PMMA than in acetonitrile solution.

According to the literature, this behavior is typical

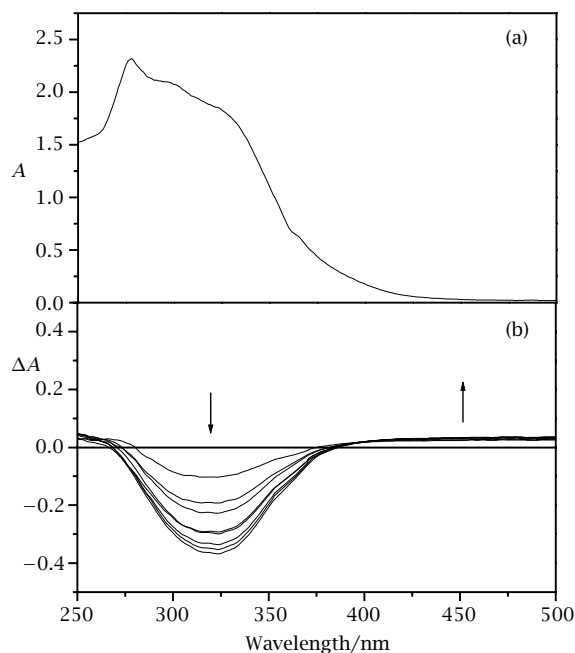
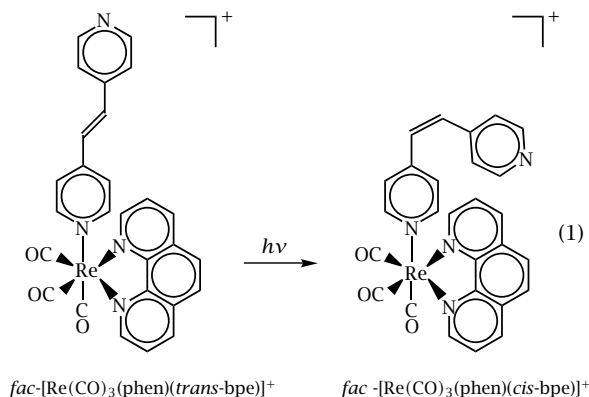


Figure 1. (a) Absorption spectrum of the complex *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ in PMMA. (b) UV-visible difference absorption spectra ($\Delta A = A_t - A_0$, where $t = \text{irradiation time}$) of *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ in PMMA as a function of photolysis time ($\lambda_{\text{irr}} = 365 \text{ nm}$).



of the photoisomerization inhibition due to a relatively small free volume in a solid matrix compared with that in a fluid solution. Imai *et al.* reported smaller *cis* isomer ratios in the photochemical stationary state for azobenzene isomerization in organic-inorganic polymer hybrids [23]. In our case, this effect is also observed, but the apparent small conversion rate is also related to the effect of a decreasing local concentration of the $fac-[Re(CO)_3(phen)(trans-bpe)]^+$ species as the photolysis time increase.

One can see, in Figure 2, that photolyses of $fac-[Re(CO)_3(phen)(trans-bpe)]^+$ in PMMA polymer films result in a markedly enhanced luminescence as the *cis* isomer is formed. The spectrum displays a broad emission profile characteristic of a MLCT excited state [24-26].

The distinct emissive characteristic in both bpe isomer species is due to the different lowest lying excited states in these complexes. For $fac-[Re(CO)_3(phen)(cis-bpe)]^+$, the ordering of lowest lying states is reversed and ${}^3MLCT < {}^3\pi\pi_{cis}^*$ (${}^3\pi\pi_{cis}^*$

is the $\pi\pi^*$ state localized on the *cis*-bpe ligand), which results in the growth of the emission.

Photolyses of the free *trans*-bpe were performed at 313 nm in order to further analyze the process. Irradiation of the *trans*-bpe ligand in PMMA also leads to the *trans* \rightarrow *cis* isomerization, Figure 3, with similar spectral changes to those described in fluid solutions for those described in fluid solutions for absorption and emission [17, 19, 27-29]. Although the emission intensity is greatly enhanced as a function of photolysis time, Figure 3(b), its feature is distinct of the MLCT emission previously described for the *cis*-bpe complex.

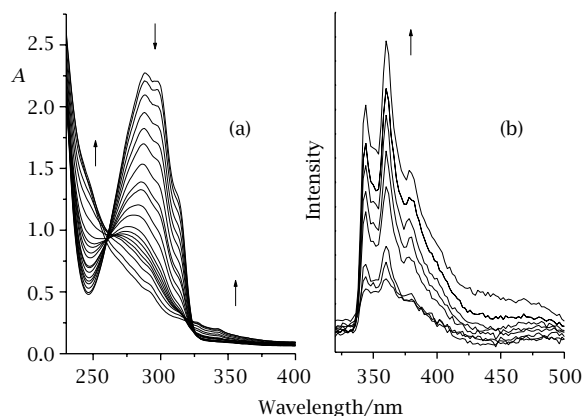


Figure 3. (a) UV-vis spectral changes and (b) emission spectral changes of bpe in PMMA as a function of photolysis time ($\lambda_{irr} = 313$ nm).

The emission properties for the complex $fac-[Re(CO)_3(phen)(cis-bpe)]^+$ in PMMA, in acetonitrile solution at room temperature, and in EPA at 77 K [18, 30] are summarized in Figure 4. In the PMMA

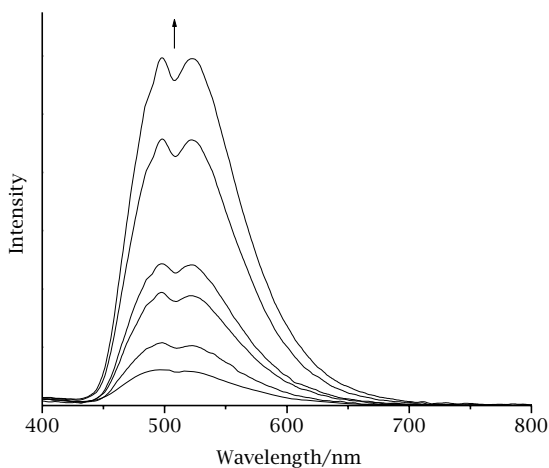


Figure 2. Growth of emission spectra of the photoproduct $fac-[Re(CO)_3(phen)(cis-bpe)]^+$ in PMMA as a function of photolysis time ($\lambda_{irr} = 365$ nm).

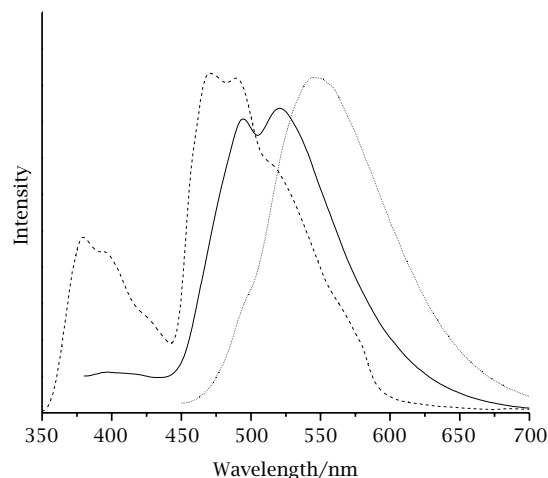


Figure 4. Emission spectra of $fac-[Re(CO)_3(phen)(cis-bpe)]^+$ in PMMA (—), in acetonitrile solution at room temperature (---) and in EPA at 77 K (.....).

film, the emission maximum is ~ 42 nm shifted toward higher energy region in comparison to that in acetonitrile solution. A similar shift, although more pronounced (70 nm), is also observed for the emission spectrum of the complex in EPA at 77 K. The observed shifts to higher energy are a consequence of changes in the rigidity of the polymer matrix/solvent medium, so called luminescence rigidochromism. This effect, observed by Wrighton and Morse in several Re(I) complexes at 77 K, has been assigned to a difference in solvent dipole orientations between glass and fluid solution [31].

This study showed that the photoisomerization of the *fac*-[Re(CO)₃(phen)(*trans*-bpe)]⁺ complex can be promoted even in rigid media. The enhanced luminescence of the *cis* photoproduct and the strong environmental sensitivity of this Re(I) complex are characteristics that can be conveniently exploited in luminescence-based sensors or photoswitches.

ACKNOWLEDGMENTS

The authors would like to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for support of this research.

References

- [1] Energy Resources Through Photochemistry and Catalysis, M. Grätzel (ed.), Academic Press, New York, 1983.
- [2] K. Kalyanasundaram, *Coord. Chem. Rev.* **46** (1982), 159.
- [3] Y. B. Shen and B. P. Sullivan, *J. Chem. Educ.* **74** (1997), 685.
- [4] M. H. Keefe, K. D. Benkstein, and J. T. Hupp, *Coord. Chem. Rev.* **205** (2000), 201.
- [5] T. T. Ehler, N. Malmberg, K. Carron, B. P. Sullivan, and L. J. Noe, *J. Phys. Chem.* **101** (1997), 3174.
- [6] J. C. Calabrese and W. Tam, *Chem. Phys. Lett.* **133** (1987), 244.
- [7] V. W. W. Yam, V. C. Y. Lau, and K. K. Cheung, *J. Chem. Soc., Chem. Commun.* (1995), 259.
- [8] V. Goulle, A. Harriman, and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* (1993), 1034.
- [9] S. M. Fredericks, J. C. Luong, and M. S. Wrighton, *J. Am. Chem. Soc.* **101** (1979), 7415.
- [10] L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas, and B. A. DeGraff, *Inorg. Chem.* **29** (1990), 4335.
- [11] L. A. Sacksteder, M. Lee, J. N. Demas, and B. A. DeGraff, *J. Am. Chem. Soc.* **115** (1993), 8230.
- [12] D. J. Stufkens and A. Vlček Jr, *Coord. Chem. Rev.* **177** (1998), 127.
- [13] S. Draxler, M. E. Lippitsch, I. Klimant, H. Kraus, and O. S. Wolfbeis, *J. Phys. Chem.* **99** (1995), 3162.
- [14] W. Paw, W. B. Connick, and R. Eisenberg, *Inorg. Chem.* **37** (1998), 3919.
- [15] T. G. Kotch, A. J. Lees, S. J. Fuerniss, K. I. Papathomas, and R. W. Snyder, *Inorg. Chem.* **32** (1993), 2570.
- [16] C. G. Garcia, J. F. Lima, and N. Y. Murakami Iha, *Coord. Chem. Rev.* **196** (2000), 219.
- [17] M. K. Itokazu, A. S. Polo, D. L. Araújo de Faria, C. A. Bignozzi, and N. Y. Murakami Iha, *Inorg. Chim. Acta* **313** (2001), 149.
- [18] D. M. Dattelbaum, M. K. Itokazu, N. Y. Murakami Iha, and T. J. Meyer, *J. Phys. Chem.* in press.
- [19] R. Argazzi, C. Chiorboli, C. A. Bignozzi, M. K. Itokazu, and N. Y. Murakami Iha, submitted.
- [20] B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.* (1984), 1244.
- [21] S. Masuda, N. Sertova, and I. Petkov, *J. Polym. Sci. Pol. Chem.* **35** (1997), 3683.
- [22] N. Y. Murakami Iha and J. F. Lima, *Inorg. Chem.* **30** (1991), 4576.
- [23] Y. Imai, K. Naka, and Y. Chujo, *Macromolecules* **32** (1999), 1013.
- [24] L. A. Worl, R. Duesing, P. Y. Chen, L. D. Ciana, and T. J. Meyer, *J. Chem. Soc., Dalton Trans.* (1991), 849.
- [25] G. Tapolsky, R. Duesing, and T. J. Meyer, *Inorg. Chem.* **29** (1990), 2285.
- [26] P. J. Giordano and M. S. Wrighton, *J. Am. Chem. Soc.* **101** (1979), 2888.
- [27] D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.* **91** (1969), 5097.
- [28] D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.* **92** (1970), 415.
- [29] Y. J. Lee, D. G. Whitten, and L. Pedersen, *J. Am. Chem. Soc.* **93** (1971), 6330.
- [30] D. M. Dattelbaum, M. K. Itokazu, N. Y. Murakami Iha, and T. J. Meyer, in preparation.
- [31] M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.* **96** (1974), 998.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

