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Coordination Chemistry Reviews 250 (2006) 1669–1680

COORDINATION CHEMISTRY REVIEWS

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Review

Light driven *trans*-to-*cis* isomerization of stilbene-like ligands in *fac*-$[Re(CO)_3(NN)(trans\text{-}L)]^+$ and luminescence of their photoproducts

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Received 12 October 2005; accepted 8 December 2005

Contents

Abstract

The photochemistry and photophysics of the *fac*-$[Re(CO)_3(NN)(L)]^+$ complexes, NN = polypyridyl ligands and L = stilbene-like ligands, in acetonitrile solution and in poly(methyl methacrylate) (PMMA) polymer film have been reported. Under irradiation, the complexes exhibit *trans-to-cis* photoassisted isomerization of the coordinated stilbene-like ligand. The quantum yields are determined by absorption changes as well as by ^{1}H NMR spectra. The increasing luminescence as the photoproduct, *fac*-$[Re(CO)_3(NN)(cis\text{-}L)]^+$, is formed is assigned to the change of the lowest lying excited state from ^{3}IL to ^{3}MLCT. Changes in absorption and emission spectra are also similar for the complexes in PMMA film, a suitable medium for device application based on their properties. The emission maxima of these complexes exhibit hypsochromic shifts as the medium rigidity increases, and the result is discussed based on the luminescence rigidochromic effect.

Time-resolved infrared spectroscopy, TRIR, in combination with other techniques, characterized the excited state electronic properties of the *fac*-$[Re(CO)_3(phen)(bpe)]PF_6$ complex, where bpe is 1,2-bis(4-pyridyl)ethylene. The competitive intramolecular energy transfer is also investigated by analyzing photophysical and photochemical properties of binuclear complexes containing the $(phen)Re^I(CO)_3$ subunit bridged by *trans*-1,2-bis(4-pyridyl)ethylene.

Keywords: Photoisomerization; Rhenium carbonyl complexes; Rigidochromic effect; Luminescence; Stilbene-like ligands

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Abbreviations: EPA, ethyl ether, isopentane and ethanol (5:5:2); EtOH, ethanol; EtOH/MeOH, ethanol:methanol mixture (4:1); IL, intraligand charge transfer; *J*, coupling constant; MeOH, methanol; MLCT, metal to ligand charge transfer; NN, polypyridine ligands; NMR, nuclear magnetic resonance; t_{irr}, irradiation time; TRIR, time-resolved infrared; δ, proton chemical shift; Φ, quantum yield; ε, molar absorptivity; λ, wavelength; λ_{max}, maximum wavelength

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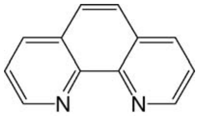
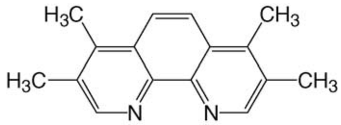
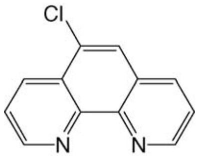
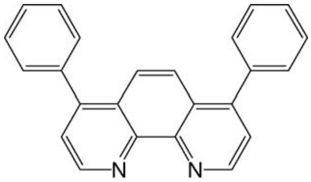
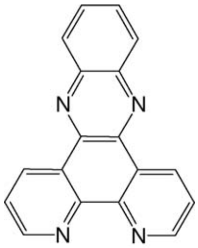
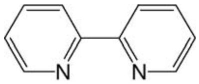
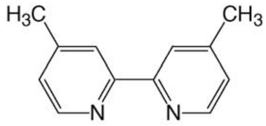
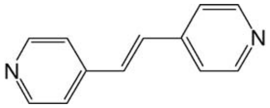
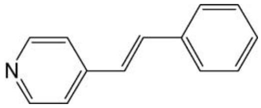
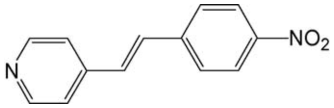
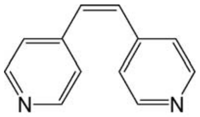
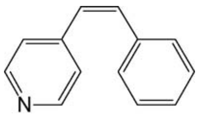
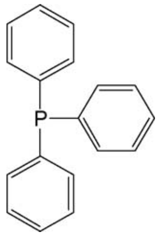
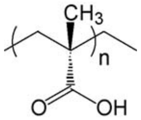
doi:10.1016/j.ccr.2005.12.015

List of compounds

Compound	Abbreviation	Structure
1,10-Phenanthroline	phen	
3,4,7,8-Tetramethyl-1,10-phenanthroline	Me_4phen	
5-Chloro-1,10-phenanthroline	Cl-phen	
4,7-Diphenyl-1,10-phenanthroline	ph_2phen	
Dipyrido[3,2-a:2′,3′-c]phenazine	dppz	
2,2′-Bipyridine	bpy	
4,4′-Dimethyl-2,2′-bipyridine	Me_2bpy	
trans-1,2-Bis(4-pyridyl)ethylene	*trans*-bpe	
trans-4-Styrylpyridine	*trans*-stpy	
trans-4-(4-Nitrostyryl)pyridine	NO_2-stpy	
cis-1,2-Bis(4-pyridyl)ethylene	*cis*-bpe	
cis-4-Styrylpyridine	*cis*-stpy	

Compound	Abbreviation	Structure
Triphenylphosphine	PPh_3	
Poly(methyl methacrylate)	PMMA	

1. Introduction

Rhenium(I) tricarbonyl polypyridyl complexes, *fac*-$[Re(CO)_3(NN)(L)]^+$, NN = polypyridyl ligands and L = ancillary ligand, have been extensively studied due to their stability, redox properties, luminescence, and excited state reactivities, which can determine their applicability towards devices based on solar energy conversion and luminescence sensing. These rhenium complexes have been useful for studies of intramolecular energy and electron transfer in chromophore-quencher complexes as well as for rigid medium effects [1–19].

The emitting state energies and excited state redox properties of these complexes can be very sensitive to the coordinating ligands and solvent properties. One of the attractive features of rhenium tricarbonyl polypyridyl complexes is the possibility to vary one or more of these factors in order to tune their photophysical and photochemical properties. The strong MLCT absorption in the UV to visible regions is easily tunable by substitution at the polypyridyl (NN) or ancillary (L) ligands by a well established synthetic methodology using concepts of molecular engineering. The sensitivity of their photophysical properties to the environment has made rhenium complexes promising sensors for microscopic environmental conditions, such as polarity and rigidity. Furthermore, the large Stokes shift between excitation and emission wavelengths allows for easier detection of luminescence changes in sensing applications.

Rhenium(I) tricarbonyl polypyridyl complexes with a photoisomerizable organic ancillary ligand L have potential applications in light activated molecular switching devices. Photoinduced reactions of coordinated ligands have also been the subject of extensive investigation [4,20–32], and is an interesting approach to photosensitization of organic substrates. Thus, the properties of these complexes are suited for performing light-driven functions and hold promise for application in signal processing and information storage.

In this work, an outline of investigations carried out on photophysical and photochemical properties of rhenium(I) tricarbonyl polypyridyl complexes containing polypyridyl ligands in the Laboratory of Inorganic Photochemistry and Energy Conversion at the Chemistry Institute of the University of São Paulo will be reviewed. In particular, the luminescence properties of *fac*-$[Re(CO)_3(NN)(cis\text{-}L)]^+$, L = 1,2-bis(4-pyridyl)ethylene, bpe, or 4-styrylpyridine, stpy, obtained upon the irradiation of the coordinated *trans*-L, will be discussed and exploited to design photoresponsive species capable of performing light induced functions. This feature is useful in the development of photochemical molecular devices, such as photoluminescence sensors and molecular machines.

2. Spectral characteristics of *fac*-$[Re(CO)_3(NN)(trans\text{-}L)]^+$

2.1. Electronic absorption spectra

The spectral parameters of rhenium(I) tricarbonyl polypyridyl complexes, *fac*-$[Re(CO)_3(NN)(trans\text{-}L)]^+$ and ligands in acetonitrile solution are listed in Table 1. Higher energy bands of the *fac*-$[ClRe(CO)_3(NN)]$ complexes, NN = phen, ph_2phen, Cl-phen or dppz, are assigned to α-diimine (NN) intraligand transitions, IL ($\pi \rightarrow \pi^*$), of polypyridyls. The lower energy absorption bands are ascribed to a metal to ligand charge transfer transition, MLCT ($d\pi_{Re} \rightarrow \pi_{NN}^*$). These spectral characteristics of the complexes are typical of *fac*-rhenium tricarbonyl polypyridyl compounds [26,27,33–37].

Further analysis of absorption bands and molar absorptivities of *fac*-$[Re(CO)_3(NN)(trans\text{-}L)]^+$ complexes, L = bpe, stpy, reveals an additional transition in the 300–400 nm region with molar absorptivities about 10 times higher than the $10^3\ L\ mol^{-1}\ cm^{-1}$ commonly observed for rhenium to polypyridine MLCT transitions. In fact, the free ligands, *trans*-bpe and *trans*-stpy, already exhibit a strong absorption around 300 nm assigned to IL transitions, which are red-shifted upon protonation. A similar shift is observed upon coordination of either *trans*-bpe or *trans*-stpy to rhenium tricarbonyl polypyridyl complexes. These facts indicate a contribution of the red-shifted transition of the coordinated *trans*-bpe or *trans*-stpy ($\pi_L \rightarrow \pi_L^*$) in the 300–400 nm region. Therefore, the lowest energy absorption bands in *fac*-$[Re(CO)_3(NN)(trans\text{-}L)]^+$ complexes have the contribution of the intraligand $IL_{(L)}$ and MLCT transitions as previously reported [16,25–28,31,32,37,38]. This contribution is easily observed in the absorption spectrum

Table 1
Spectral parameters of *fac*-$[Re(CO)_3(NN)(L)]^+$ and ligands in acetonitrile solution

Compound	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]
trans-stpy	224(1.7)[a], 227(1.6)[a], 300(2.5), 318(1.6)[a]
protonated *trans*-stpy	200(4.3), 236(1.2), 274(0.6), 341(2.7)
phen	197(1.9), 225(4.2)[a], 250(4.9), 263(2.9), 275(1.6)[a]
ph_2phen	219(4.8), 272(4.8), 300(1.6)[a]
Cl-phen	198(1.8)[a], 231(4.6), 265(3.4), 300(6.0)[a]
dppz	240(2.4), 270(3.9), 293(1.5), 359(0.9), 367(0.8), 379(1.0)
fac-$[ClRe(CO)_3(phen)]$	200(4.5), 216(4.1), 265(2.4), 290(1.1)[a], 365(0.34)
fac-$[ClRe(CO)_3(ph_2phen)]$	220(4.8)[a], 280(3.3), 350(0.63)[a]
fac-$[ClRe(CO)_3$(Cl-phen)]	200(4.3), 218(4.1) 272(2.7), 375(0.41)
fac-$[ClRe(CO)_3(dppz)]$	280(6.7), 322(1.5), 360(1.3)
fac-$[Re(CO)_3$(phen)(*trans*-bpe)]$^+$	224(3.9)[a], 255(2.3)[a], 277(3.8), 301(3.4)[a], **330(2.7)**[a,b]
fac-$[Re(CO)_3$(phen)(*trans*-stpy)]$^+$	200(7.8), 225(4.1), 275(2.9), **332(3.9)**[b]
fac-$[Re(CO)_3(ph_2phen)$(*trans*-bpe)]$^+$	220(5.5)[a], 295(6.8), **330(3.6)**[a,b]
fac-$[Re(CO)_3(ph_2phen)$(*trans*-stpy)]$^+$	220(5.0)[a], 294(5.2), **332(4.8)**[b]
fac-$[Re(CO)_3$(Cl-phen)(*trans*-bpe)]$^+$	200(7.8), 234(3.7)[a] 280(4.5) **325(3.0)**[a,b]
fac-$[Re(CO)_3$(dppz)(*trans*-bpe)]$^+$	280(7.6), 322(3.9)[a], **380(1.4)**[b]

[a] Shoulder.

[b] Contributions of MLCT and IL transitions.

of *fac*-$[Re(CO)_3$(phen)(*trans*-bpe)]$^+$ along with the spectra of *trans*-bpe, protonated *trans*-bpe, and *fac*-$[ClRe(CO)_3(phen)]$ in acetonitrile solutions, Fig. 1. The absorption spectra of *fac*-$[Re(CO)_3$(phen)(*trans*-L)], L = bpe or stpy, in poly(methyl methacrylate), PMMA, resemble those measured in fluid solution, leading to the same assignments.

The electronic spectrum of the binuclear complex, $[(CO)_3$(phen)Re(*trans*-bpe)Re(phen)$(CO)_3]^{2+}$ [37], is similar to the mononuclear one, although with higher molar absorptivities [25,39,40].

2.2. ^{1}H NMR spectra

The ^{1}H NMR spectral data for *fac*-$[Re(CO)_3$(phen)(*trans*-L)]$^+$, L = bpe or stpy, [27,29,32,37] and for *fac*-$[Re(CO)_3(ph_2phen)$(*trans*-L)]$^+$ complexes, L = bpe or stpy [41–43], as well as *trans*-L ligands, are summarized in Table 2 .

The proton signals in spectra of *fac*-$[Re(CO)_3$(NN)(*trans*-L)]$^+$, NN = phen or ph_2phen and L = bpe or stpy, were assigned by analysis and comparison with the ^{1}H NMR spectra of *fac*-$[ClRe(CO)_3(NN)]$ and of the free ligands NN and L. The assignments for *fac*-$[Re(CO)_3$(phen)(*trans*-L)]$^+$ complexes are corroborated also by the H–H COSY method. The spectrum for the *fac*-$[Re(CO)_3$(phen)(*trans*-bpe)]$^+$ complex is shown in Fig. 2.

The 1,10-phenanthroline proton signals in *fac*-$[ClRe(CO)_3(phen)]$ are downfield shifted in comparison to the corresponding protons of the free ligand, and are in accordance with the

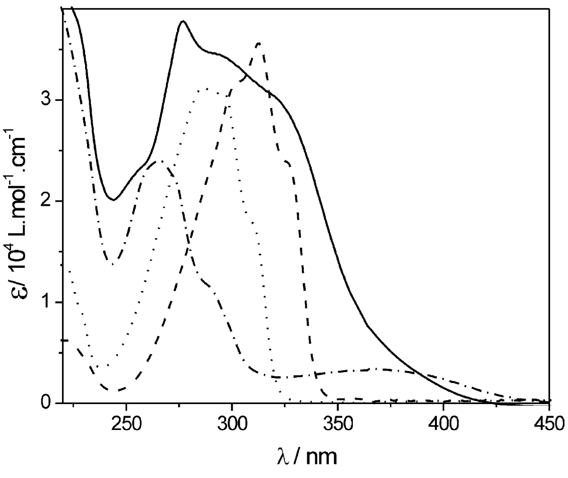


Fig. 1. Electronic spectra of *fac*-$[Re(CO)_3$(phen)(*trans*-bpe)]$^+$ (—), protonated *trans*-bpe (- - -), *trans*-bpe (· · ·) and *fac*-$[ClRe(CO)_3(phen)]$ (-·-·-·) in acetonitrile solution.

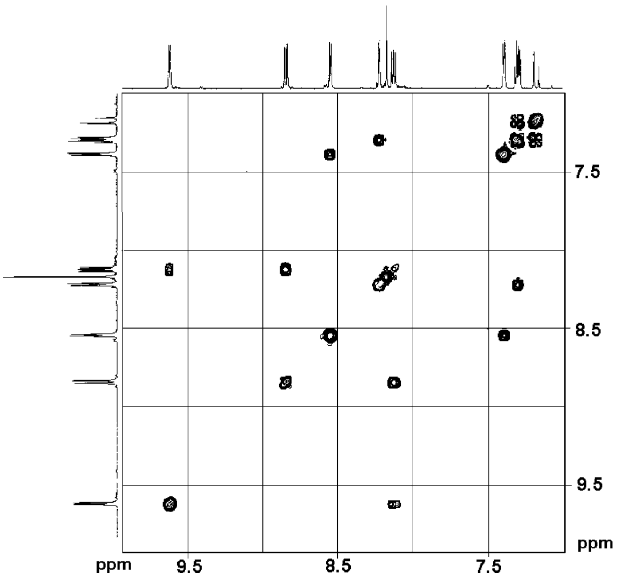


Fig. 2. 500 MHz COSY NMR spectra of *fac*-$[Re(CO)_3$(phen)(*trans*-bpe)]$^+$ in CD_3CN.

Table 2
^{1}H NMR data of *fac*-[Re(CO)$_3$(NN)(L)]$^+$ and the free ligands L

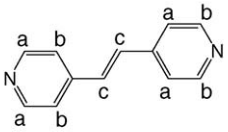
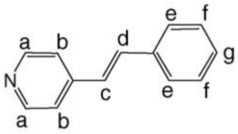
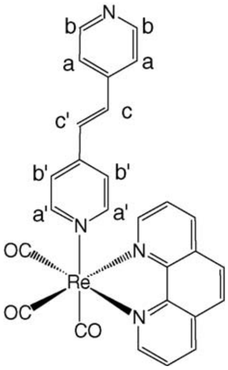
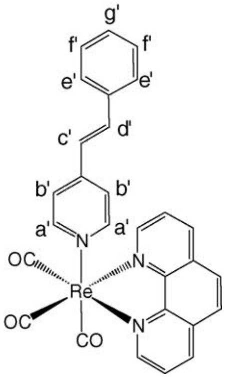
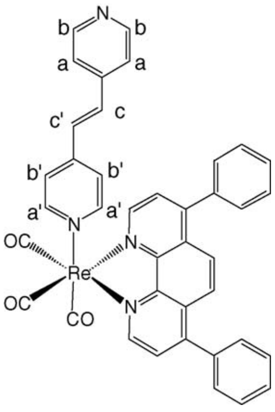
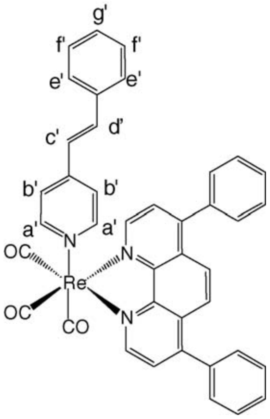
Compounds	Proton type	δ (ppm)	*J* (Hz)
trans-bpe 	H_a	8.58 (d, 4H)	4.49
	H_b	7.50 (d, 4H)	4.51
	H_c	7.39 (s, 2H)	
trans-stpy 	H_a	8.53 (d, 2H)	6.15
	H_b	7.47 (d, 2H)	8.80
	H_c	7.17 (d, 1H)	16.40
	H_d	7.41 (d, 1H)	16.70
	H_e	7.62 (d, 2H)	6.32
	H_f	7.41 (t, 2H)	7.30
	H_g	7.34 (t, 1H)	7.33
fac-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ 	H_a	8.54 (dd, 2H)	4.60
	H_b	7.39 (dd, 2H)	4.66
	H_c	7.30 (d, 1H)	16.40
	$H_{a'}$	8.22 (dd, 2H)	5.38
	$H_{b'}$	7.30 (dd, 2H)	4.01
	$H_{c'}$	7.18 (d, 1H)	16.46
fac-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ 	$H_{a'}$	8.16 (d, 2H)	6.38
	$H_{b'}$	7.26 (d, 2H)	6.97
	$H_{c'}$	6.97 (d, 1H)	16.4
	$H_{d'}$	7.37 (d, 1H)	16.2
	$H_{e'}$	7.52 (dd, 2H)	8.25
	$H_{f'}$	7.35 (m, 2H)	
	$H_{g'}$	7.35 (m, 1H)	
fac-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ 	H_a	8.55 (dd, 2H)	1.63; 4.57
	H_b	7.40 (dd, 2H)	1.63; 11.33
	H_c	7.34 (d, 1H)	16.03
	$H_{a'}$	8.31 (dd, 2H)	1.47; 5.32
	$H_{b'}$	7.36 (dd, 2H)	1.52; 5.10
	$H_{c'}$	7.23 (d, 1H)	16.45

Table 2 (*Continued*)

Compounds	Proton type	δ (ppm)	J (Hz)
fac-[Re(CO)$_3$(ph$_2$phen)(*trans*-stpy)]$^+$ 	$H_{a'}$	8.26 (dd, 2H)	1.47; 5.34
	$H_{b'}$	7.33 (dd, 2H)	1.52; 5.37
	$H_{c'}$	7.02 (d, 1H)	16.41
	$H_{d'}$	7.41 (d, 1H)	16.43
	$H_{e'}$	7.54 (dd, 2H)	1.66; 7.79
	$H_{f'}$	7.37 (m, 2H)	
	$H_{g'}$	7.37 (m, 1H)	

literature [44,45]. The same behavior is observed for polypyridyl protons in *fac*-[ClRe(CO)$_3$(ph$_2$phen)] and other complexes.

For monometallic *fac*-[Re(CO)$_3$(NN)(*trans*-bpe)]$^+$, NN = phen or ph$_2$phen, the coordination to the metal center lowers the symmetry of the *trans*-bpe moiety and removes the degeneracy of each pair of protons, Table 2. This behavior is reported for *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ and for other rhenium polypyridyl complexes [26,40]. The attachment of a second *fac*-[Re(CO)$_3$(NN)]$^+$ fragment restores the symmetry of the bridging ligand for the binuclear complex. Thus, the NMR spectrum of [(CO)$_3$(phen)Re(*trans*-bpe)Re(phen)(CO)$_3$]$^{2+}$ exhibits a simplified pattern, similar to that found for the free ligand.

For *fac*-[Re(CO)$_3$(NN)(*trans*-bpe)]$^+$ the influence of electronic perturbation is higher for proton signals of the bound pyridyl ring, since the coordinated pyridyl group of *trans*-bpe is shielded upfield in comparison to its unbound pyridyl ring, Table 2. The proton signals of L in the *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$ complexes are shifted upfield upon coordination due to the anisotropic effect of the diimine ligand [46,47].

3. Photoinduced isomerization in fluid solution

Photolyses of stilbene-like compounds lead to changes in absorption spectra assigned to *trans*-to-*cis* isomerization with a characteristic spectral variation, Fig. 3. Quantum yields, for 313 nm excitation, are in the range of 0.003–0.25 for *trans*-1,2-bis(4-pyridyl)ethylene [26,48–51] and 0.37–0.46 for *trans*-4-styrylpyridine [20,48,51,52], depending on the polarity of the solvent, Table 3. After protonation, the absorption band red-shifts and allows irradiation up to 334 nm. For instance, the quantum yields for isomerization of *trans*-bpe in methanolic solution are 0.17 ± 0.03 for the non protonated ligand under 313 nm irradiation, and 0.19 ± 0.02 and 0.15 ± 0.01 for the protonated ligand, respectively, for 313 and 334 nm excitation [26].

The red-shifted absorption band can also be achieved by coordinating stilbene-like ligands, *trans*-L, in the *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$ complexes, NN = phen, ph$_2$phen, Cl-phen or dppz, and L = bpe or stpy. Therefore, coordination is

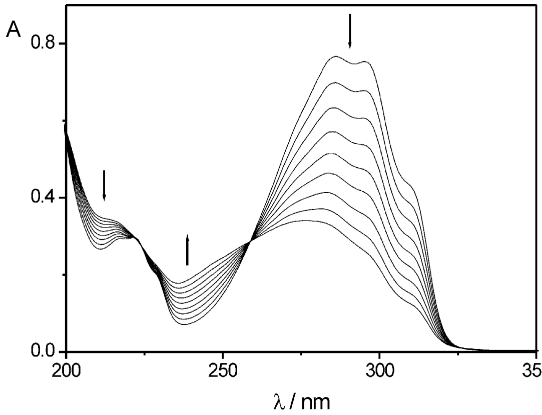


Fig. 3. Spectral changes of free *trans*-bpe in CH$_3$CN upon irradiation at 313 nm (Δt = 4 s).

Table 3
Quantum yields of *trans–cis* isomerization for *trans*-bpe and *trans*-stpy upon 313 nm excitation

Compounds	Solvent	Φ_{313}	Refs.
trans-bpe	Benzene	0.003	[49,50]
	Methyl-cyclohexane	0.005	[49,50]
	n-Hexane	0.03	[51]
	2-Propanol	0.04	[49,50]
	tert-Butyl alcohol	0.08	[50]
	Methanol	0.17	[26]
	Acetonitrile/water[a]	0.25	[49,50]
	Benzene[b]	0.39	[48]
trans-stpy	*n*-Hexane	0.37	[51]
	Benzene	0.37	[51]
	Dichloromethane	0.38	[20]
	Benzene[b]	0.40	[48]
	Acetonitrile/water[a]	0.44	[52]
	Acetonitrile[c]	0.46	[51]

[a] 70% Acetonitrile by volume.

[b] Benzophenone sensitized.

[c] λ_{irr} = 320 nm.

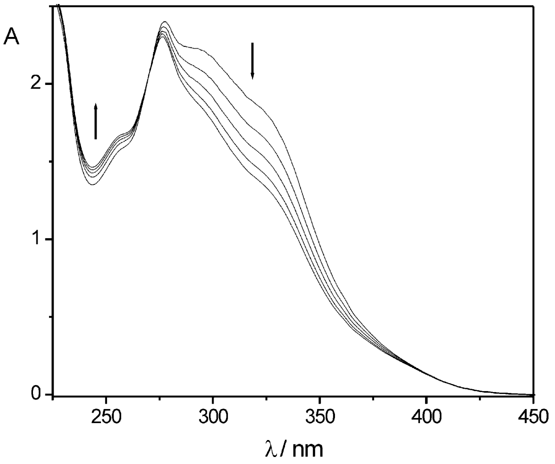
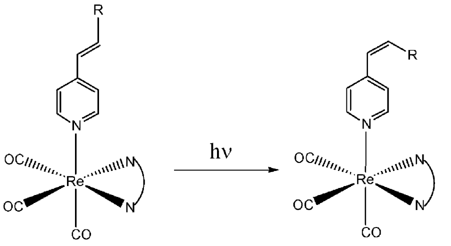


Fig. 4. Spectral changes of *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ in CH$_3$CN upon irradiation at 365 nm ($\Delta t = 5$ s).

another approach to allow photoassisted isomerization under irradiation in a lower energy region, where the free ligand does not absorb. Irradiation of *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$ complexes in solution results in spectral changes assigned to *trans–cis* isomerization of the coordinated stilbene-like ligand, such as *trans*-bpe or *trans*-stpy, Eq. (1). Photoinduced isomerization of the coordinated *trans*-bpe in *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ shows spectral changes with clear isosbestic point at 270 nm, Fig. 4.



(1)

The photoisomerization quantum yields determined for rhenium(I) complexes, *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$, L = bpe or stpy, under irradiation at 313, 334 or 365 nm, based on the absorption spectral changes, are listed in Tables 4 and 5. These results show an efficient sensitization since the isomerization can be achieved even at 365 nm excitation, where the ligand itself does not absorb.

Table 4
Quantum yields of *trans–cis* isomerization in *fac*-[Re(CO)$_3$(NN)(*trans*-bpe)]$^+$ in acetonitrile solution

NN	$\Phi_{313\,\mathrm{nm}}$	$\Phi_{334\,\mathrm{nm}}$	$\Phi_{365\,\mathrm{nm}}$
phen	0.41 ± 0.02	–	0.39 ± 0.02
Cl-phen	0.31 ± 0.02	0.31 ± 0.03	0.30 ± 0.02
ph$_2$phen	0.19 ± 0.02	0.18 ± 0.01	0.17 ± 0.01
dppz	0.15 ± 0.03	–	0.12 ± 0.02

Table 5
Quantum yields of *trans–cis* isomerization in *fac*-[Re(CO)$_3$(NN)(*trans*-stpy)]$^+$ in acetonitrile solution

NN	$\Phi_{313\,\mathrm{nm}}$	$\Phi_{334\,\mathrm{nm}}$	$\Phi_{365\,\mathrm{nm}}$
phen	0.35 ± 0.02	0.36 ± 0.02	0.31 ± 0.02
ph$_2$phen	0.27 ± 0.03	0.33 ± 0.02	0.32 ± 0.05

Moreover, the data demonstrate that the efficiency of the photoisomerization process can be modulated by the polypyridinic ligand (NN) and the isomerizable ligand (L). By changing NN and/or L ligands, the energy of the MLCT and/or IL excited states can be tuned. For instance, the lower quantum yields observed for isomerization of *fac*-[Re(CO)$_3$(dppz)(*trans*-bpe)]$^+$ in comparison to *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ show a less efficient sensitization of the *trans*-bpe ^{3}IL excited state in dppz complex. The isomerization quantum yields for *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ are higher when compared to *fac*-[Re(CO)$_3$(phen)(*trans*-stpy)]$^+$ [32], showing that the sensitization of ^{3}IL excited state is more efficient in the *trans*-bpe complex.

Photoisomerization of the coordinated ligand can even occur in binuclear complexes in spite of the bulk groups attached to the bridging ligand [25,37]. Irradiation of [(CO)$_3$(phen)Re(*trans*-bpe)Re(phen)(CO)$_3$]$^{2+}$ leads to spectral changes with clear and well defined isosbestic points due to the *trans–cis* isomerization of coordinated bpe [16,26,27,37]. On the other hand, no photoreaction was observed for the bimetallic [(phen)Re(CO)$_3$(*trans*-bpe)Os(trpy)(bpy)]$^{3+}$ complex [16]. The absence of isomerization is assigned to the presence of the low lying MLCT state of the osmium unit that quenches the chemical reaction. For the same reason, the ligand isomerization is inhibited by competitive intramolecular energy transfer for the binuclear [(phen)Re(CO)$_3$(*trans*-bpe)Fe(CN)$_5$]$^{2-}$ complex due to the low lying MLCT$_{\mathrm{Fe}\rightarrow trans\text{-bpe}}$ state [53].

Quantum yields of photochemical reactions are usually determined following the process spectrophotometrically. However, when both the photoproduct and reactant absorb in the same spectral region, variations in absorption spectra are not the best technique for quantum yield determination. Quantum yields for *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$ determined based on spectral variation are apparent, since both the reactants and their photoproducts absorb in the same spectral region. In this case, the photoisomerization process of *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$ has also been monitored by ^{1}H NMR spectroscopy following both the chemical shifts and coupling constants. These parameters, especially for the olefinic protons, are observed in fairly different regions for the two isomers. Therefore, ^{1}H NMR spectroscopy gives more accurate quantum yields for the isomerization process of coordinated ligands.

Upon irradiation of *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$, the signals of the *trans*-isomer at 7.30 and 7.18 ppm decrease, while the *cis*-isomer signals at 6.80 and 6.50 ppm gradually build up in intensity, as can be observed in Fig. 5. The characteristics ^{1}H NMR coupling constants for both the *trans*-isomer (16 Hz) and the *cis* form (12 Hz) are also observed. Much higher quantum yields, the true ones, are determined by ^{1}H NMR experiments resulting in 0.70 for *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ and 0.40 for *fac*-[Re(CO)$_3$(ph$_2$phen)(*trans*-bpe)]$^+$ [42,54,55]. ^{1}H NMR spectroscopy has also been employed by Yam et al. [25] to follow the isomerization process in *trans*-NO$_2$-stpy rhenium complexes. Wenger et al. reported quite similar quantum yields

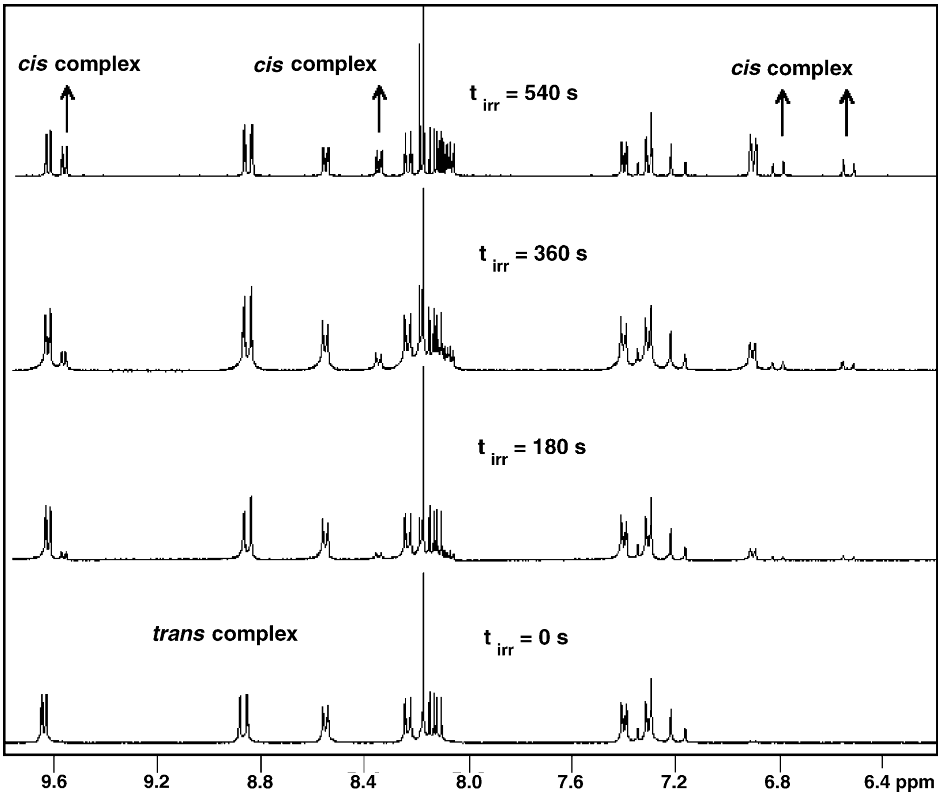


Fig. 5. ^{1}H NMR spectra of *fac*-[Re(CO)$_3$(phen)(bpe)]$^+$ in CD$_3$CN upon photolyses at 313 nm.

in *trans*-bpe rhenium complexes determined both by UV–vis and by ^{1}H NMR spectroscopy [31].

The *cis–trans* back-reaction process has been reported [28,31] under 250 nm irradiation in few cases. However, some photodecomposition is also observed which does not allow for reliable determination of quantum yields.

The photoisomerization process can also be monitored following luminescence upon formation of the *cis*-isomer complex, Fig. 6. While the *trans* isomer does not emit, the *cis*-complex exhibits a broad and non-structured band characteristic of rhenium(I) complex emission from ^{3}MLCT.

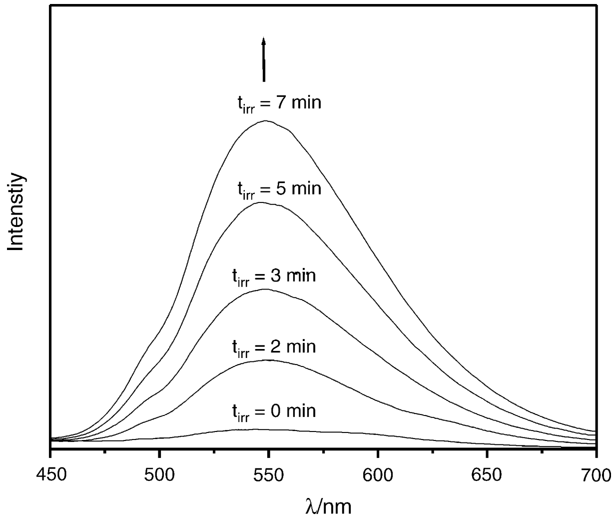


Fig. 6. Enhancement in emission intensity upon 313 nm irradiation of *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ in acetonitrile solution.

The photosensitized isomerization process has been further investigated by time-resolved infrared (TRIR) spectroscopy of *fac*-[Re(CO)$_3$(phen)(bpe)]$^+$, analyzing the ν(CO) and ν(C=C) regions [29]. These measurements have provided, for the first time, direct evidence for a photochemical transient for *trans–cis* isomerization of the coordinated ligand. Both the direction and the magnitude of the ν(CO) shifts between the ground and excited states can be associated with the nature of the lowest lying excited state. Small and negative shifts have been assigned to an IL ($\pi\pi^*$) excited state, while large and positive ones, due to partial oxidation at rhenium(I) and loss of dπRe → π^*(CO) back-bonding, have been assigned to a MLCT excited state. The observed shifts of −6 and −7 cm^{-1}, and ν(CO) appearing at 1927 and 2029 cm^{-1}, for *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ [29] are comparable to those for *fac*-[Re(CO)$_3$(dppz)(PPh$_3$)]$^+$. Based on these data that lead to a dppz-localized excited state, ^{3}IL ($^3\pi\pi^*$) [56,57], the lowest lying excited state in *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ is *trans*-bpe localized, which is responsible for the *trans–cis* isomerization process. The ^{3}IL state is in the nanosecond domain and decays to the ^{3}p* excited state of the *trans*-bpe ligand, in which the rings are approximately perpendicularly oriented to each other and it is the immediate precursor of the *trans–cis* isomerization. The ^{3}p* excited state formed by intramolecular sensitization ^{1}MLCT, ^{1}IL → ^{3}MLCT → ^{3}IL → ^{3}p* [29] has also been reported for other polypyridyl rhenium complexes with photoisomerizable ligands [38,58]. Large and positive shifts (+40, +31

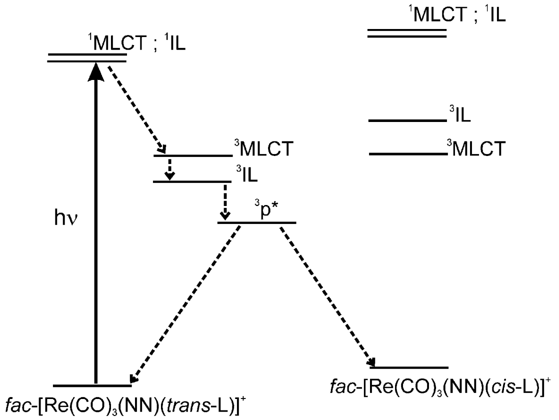


Fig. 7. Simplified energy diagram proposed for *fac*-[Re(CO)$_3$(NN)(L)]$^+$.

and +83 cm^{-1}) observed for *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ are ascribed to MLCT excited states. The energy diagram proposed for *fac*-[Re(CO)$_3$(NN)(L)]$^+$ complexes is shown in Fig. 7.

The proposed ^{1,3}MLCT sensitization of ^{3}IL for photoisomerization as well as luminescence properties of other rhenium(I) carbonyl complexes have recently been confirmed by Daniel et al. [59,60] in theoretical analysis.

4. Photoinduced isomerization in rigid medium

Investigations of the photoassisted isomerization of *fac*-[Re(CO)$_3$(phen)(*trans*-L)]$^+$, L = bpe or stpy ligands, in rigid medium have also been carried out in poly(methyl methacrylate), PMMA, films. The spectral changes, similar to those observed in fluid solutions, have been ascribed to *trans*–*cis* isomerization of the coordinated ligand [27,32,37]. Spectral changes due to photoinduced *trans*–*cis* isomerization of the coordinated ligand in *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ in PMMA exhibit clear isosbestic points, Fig. 8.

Photoisomerization in rigid medium exhibits lower photolysis percentages in the photostationary state than those determined for fluid solutions [27,32]. This photoisomerization inhibition is due to a relatively smaller free volume in the solid matrix in comparison to fluid solutions [27,32,37] and has also been reported for other compounds, such as the *trans*–*cis* isomerization of azobenzene in organic–inorganic polymer hybrids [61].

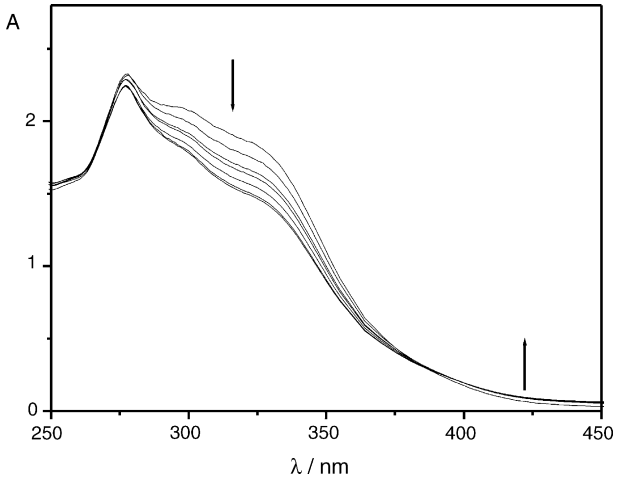


Fig. 8. Spectral changes of *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ in PMMA upon irradiation at 365 nm (Δ*t* = 2 s).

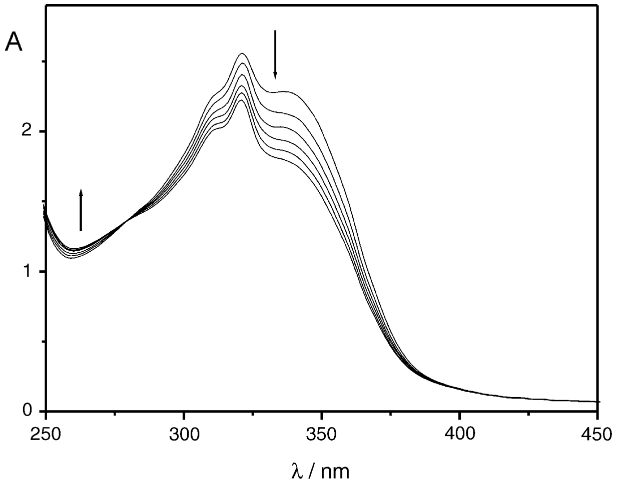


Fig. 9. Spectral changes of *fac*-[Re(CO)$_3$(bpy)(*trans*-stpy)]$^+$ in PMMA upon irradiation at 365 nm (Δ*t* = 2 s).

The investigation has been extended to a series of *fac*-[Re(CO)$_3$(bpy)(*trans*-L)]$^+$. The photoisomerization of *fac*-[Re(CO)$_3$(bpy)(*trans*-stpy)]$^+$ takes place in PMMA (Fig. 9; [62]) contrary to what has been recently reported for this complex and for *fac*-[ClRe(CO)$_3$(*trans*-stpy)$_2$] using TRIR [38]. Further investigations are in progress to better elucidate the process.

The formation of the *cis*-isomer complex in rigid medium has also resulted in an increase in luminescence as a function of the photolysis time. This behavior is observed for all rhenium(I) carbonyl polypyridyl complexes and Fig. 10 shows the spectral changes for [(CO)$_3$(phen)Re(*trans*-bpe)Re(phen)(CO)$_3$]$^{2+}$ in PMMA matrix [37] upon irradiation at 365 nm. The ^{3}MLCT

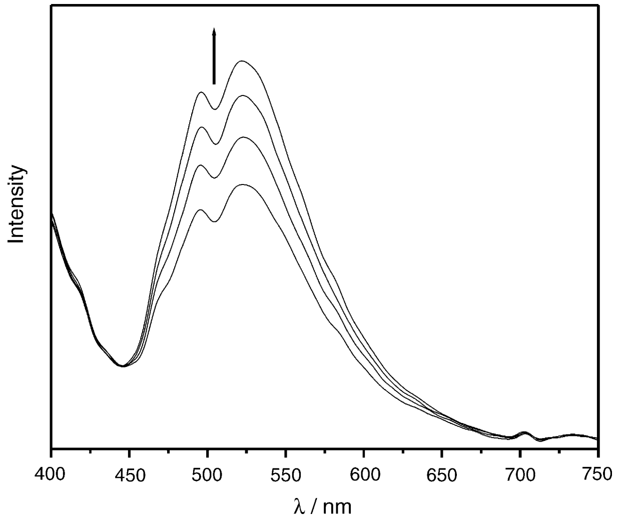


Fig. 10. Enhancement in emission intensity upon 365 nm irradiation of [(CO)$_3$(phen)Re(*trans*-bpe)Re(phen)(CO)$_3$]$^{2+}$ in PMMA (Δ*t* = 40 s).

excited state is the lowest lying one for the *cis*-photoproduct and is the responsible for the intense emission observed, both in fluid and in rigid medium, as has been previously discussed for fluid solutions.

5. Luminescence properties of *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$

There was no measurable luminescence of *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$, NN = phen, bpy or ph$_2$phen and L = bpe or stpy. This can be rationalized in terms of the main pathway of the excited state deactivation of the *trans*-isomer complex being photoisomerization from the ^{3}IL lowest lying excited state. On the other hand, ^{3}MLCT, responsible for the intense luminescence observed, is the lowest lying excited state in *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$ complexes and exhibits characteristic broad and non-structured emission [33,34,36,63–65].

The emission maxima of *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$ are dependent on the NN as well as on the *cis*-L ligands, Table 6. The ^{3}MLCT excited state energy is affected mainly by the NN ligands. Polypyridinic ligands having electron withdrawing groups shift the emission maximum to a lower energy region. The evidence of ^{3}MLCT stabilization can be observed by the emission maximum for *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ at 548 nm, while for *fac*-[Re(CO)$_3$(Cl-phen)(*cis*-bpe)]$^+$ it is centered at 560 nm. The opposite effect is observed by comparison of the shifts of emission maximum of *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ at 548 nm and *fac*-[Re(CO)$_3$(Me$_4$phen)(*cis*-bpe)]$^+$ at 525 nm due to the destabilization ^{3}MLCT caused by the electron donor groups.

6. Luminescence rigidochromic effect

Emissive properties of the *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ complex have been investigated both in PMMA and in acetonitrile solution at 298 K to investigate the luminescence rigidochromic effect. The emission spectrum of the complex in a PMMA film is blue shifted in comparison to a fluid solution and two maxima can be observed. In a more constrained medium, such as glassy EPA (77 K), this shift is enhanced with a more structured spectrum, Fig. 11a.

The shifts in emission spectra of the *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$ complexes are a result of changes in solvation environment and the rigidity of the polymer matrix/solvent medium. In a relaxed ^{3}MLCT excited state, the dipole moment is reversed in a comparison to the ground state and the surrounding solvent molecules are promptly capable of reorienting themselves around the complex to best accommodate its dipole moment in fluid solution. This relaxation process takes place readily in fluid solution, but is considerably restrained in a more rigid environment and destabilizes the excited state. Therefore, the energy of the ^{3}MLCT state is increased as the rigidity of the medium increases [2,10,13,37].

Table 6
Emission maxima of *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$ in different environments

Complex	Environment	λ_{max} (nm)	Refs.
fac-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$	CH$_3$CN, 298 K	548	[26]
	PMMA, 298 K	495, 520	[27,37]
	EPA, 77 K	470, 490	[27,37]
fac-[Re(CO)$_3$(Cl-phen)(*cis*-bpe)]$^+$	CH$_3$CN, 298 K	560	[62]
	PMMA, 298 K	524	[62]
	EPA, 77 K	475, 500	[62]
fac-[Re(CO)$_3$(Me$_4$phen)(*cis*-bpe)]$^+$	CH$_2$Cl$_2$, 298 K	525	[31]
fac-[Re(CO)$_3$(ph$_2$phen)(*cis*-bpe)]$^+$	CH$_3$CN, 298 K	555	[41]
	PMMA, 298 K	530	[66]
	EPA, 77 K	494, 520	[66]
fac-[Re(CO)$_3$(phen)(*cis*-stpy)]$^+$	CH$_3$CN, 298 K	540	[25]
	CH$_2$Cl$_2$, 298 K	548	[25]
	CH$_3$CN, 298 K	555	[32]
	PMMA, 298 K	490, 515	[32]
	EtOH/MeOH, 77 K	475, 490	[32]
fac-[Re(CO)$_3$(ph$_2$phen)(*cis*-stpy)]$^+$	CH$_3$CN, 298 K	555	[43]
	PMMA, 298 K	535	[62]
	EPA, 77 K	500, 530	[62]
fac-[Re(CO)$_3$(bpy)(*cis*-bpe)]$^+$	CH$_2$Cl$_2$, 298 K	568	[31]
fac-[Re(CO)$_3$(Me$_2$bpy)(*cis*-bpe)]$^+$	CH$_2$Cl$_2$, 298 K	558	[31]
fac-[Re(CO)$_3$(bpy)(*cis*-stpy)]$^+$	CH$_3$CN, 298 K	540	[25]
fac-[(CO)$_3$(phen)Re(*cis*-bpe)Re(phen)(CO)$_3$]$^{2+}$	CH$_3$CN, 298 K	548	[37]
	PMMA, 298 K	510	[37]
	EtOH/MeOH, 298 K	548	[53]
	EtOH/MeOH, 77 K	506	[53]

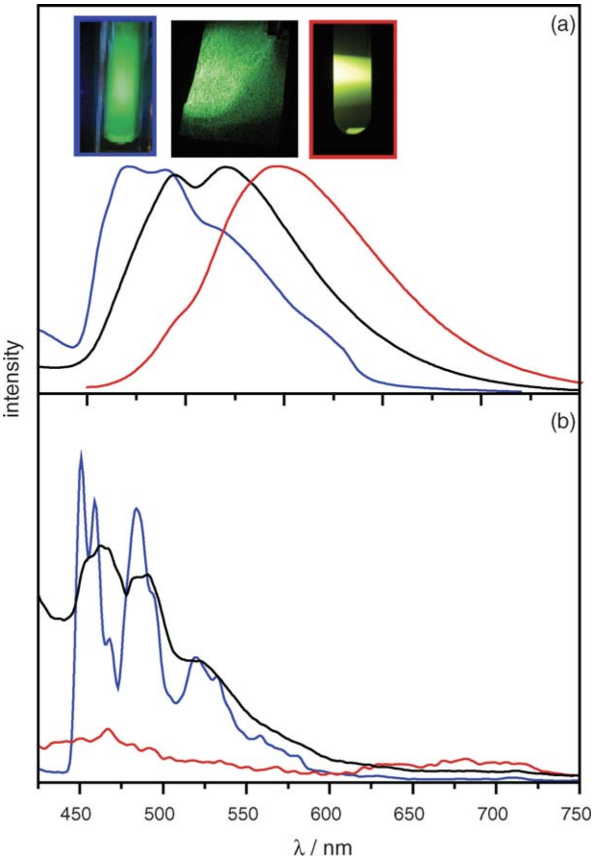


Fig. 11. Emission spectra of *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ (a) and 1,10 phenanthroline (b) in PMMA (black line) or fluid solution (red line) at 298 K, and in EPA (blue line) at 77 K (*inset:* emission of the complex according to the environment).

A structured spectrum observed for *fac*-[Re(CO)$_3$(phen)(*cis*-bpe)]$^+$ in rigid media can be explained by comparison with the spectrum of the complex and that of 1,10-phenanthroline, recorded under the same conditions, Fig. 11b. In the 510–700 nm region, the 1,10-phenanthroline ligand does not exhibit luminescence in acetonitrile. In this medium, only its fluorescence can be observed in the higher energy region (300–400 nm). In PMMA matrix, the intersystem crossing is enhanced and, as a consequence, its phosphorescence can also be observed in the 430–650 nm region. In EPA (77 K), the phosphorescence is enhanced both by the medium rigidity as well as by the temperature effect, due to a decrease in the rate of non-radiative processes [2,27,32,37]. The emission spectrum of the complex resembles that of the ligand, showing the existence of a contribution of the ^{3}IL excited state to the ^{3}MLCT emission. Following the sequence acetonitrile, PMMA and EPA, hypsochromic shifts indicate the increase in the ^{3}MLCT energy as a function of the medium rigidity, Fig. 12.

The rigidity of PMMA can be considered an intermediary situation between fluid solution and glassy EPA. Two maxima observed for most of *fac*-[Re(CO)$_3$(NN)(*cis*-L)]$^+$ result from dual or mixed emission with contributions from both the ^{3}IL$_{NN}$ and blue shifted ^{3}MLCT states, a typical behavior expected for the rhenium(I) complexes with the lowest lying ^{3}MLCT excited state. The existence of dual or mixed emissions can often be discerned by wavelength dependence lifetime measurements [37] and further studies are in progress.

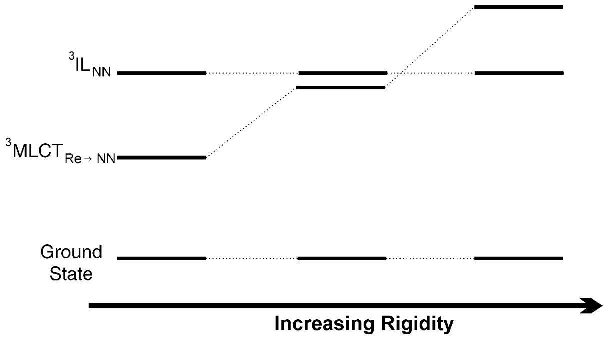


Fig. 12. Changes in energy levels as a function of medium rigidity.

7. Final remarks

Our investigation has shown that the Re chromophore in rhenium(I) tricarbonyl polypyridyl complexes with a photoisomerizable stilbene-like ligand allows for a lower energy photoisomerization of the coordinated organic substrates due to an efficient intramolecular triplet energy transfer sensitization.

Actually, the triplet manifold reached by coordinating the stilbene-like ligands in transition metal complexes based on rhenium tricarbonyl polypyridyl depends on the ^{3}MLCT energy, which can be conveniently tuned by substitution of the polypyridyl ligand through molecular engineering.

Different approaches to characterizing excited state electronic structure were taken, and the dynamics of the light driven photoisomerization have been investigated by TRIR, mapping excited states in rhenium tricarbonyl polypyridinic complexes by their ground-to-excited state shifts in ν(CO). Investigations of the dynamics of sensitized ligand isomerization by TRIR and the quenching of the isomerization by the formation of selected binuclear complexes with low lying MLCT excited states were essential tools in determining the nature of excited states.

The photoisomerization of the coordinated ligand resulted in a change of lowest excited state energy, from ^{3}IL to ^{3}MLCT, leading a non emissive complex to an emissive one. Therefore, *fac*-[Re(CO)$_3$(NN)(L)]$^+$ complexes, where L = photoisomerizable ligands, hold promise as a light activated photochromic switch of emission intensity. Moreover, to this luminescence change, emission from ^{3}MLCT, lowest excited state of the *cis*-complex photoproduct, is highly sensitive to changes in the rigidity of the medium. Developing a comprehensive understanding of molecules in rigid environments is essential to using these materials in device applications. The hipsochromic shift as the rigidity increases (rigidochromic effect) allows sensing applications such as asset to the control of polymerization processes.

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