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On the photophysics of *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ complexes: a theoretical/experimental study

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Abstract

The influence of polypyridyl ligand on the photophysics of *fac*-$[Re(CO)_3(NN)(bpa)]^+$, bpa = 1,2-bis-(4-pyridyl)ethane and NN = 1,10-phenanthroline (phen), pyrazino[2,3-f][1,10]-phenanthroline (dpq), dipyrido[3,2-a:2'3'-c]phenazine (dppz) has been investigated by steady state and time-resolved emission spectroscopy combined with theoretical calculations using time-dependent density function theory (TD-DFT). The *fac*-$[Re(CO)_3(phen)(bpa)]^+$ is a typical MLCT emitter in acetonitrile with $\phi = 0.11$ and $\tau = 970$ ns. Emission lifetime and quantum yield decrease significantly in *fac*-$[Re(CO)_3(dpq)(bpa)]^+$ ($\phi = 0.05$; $\tau = 375$ ns) due to the presence of a close lying dark charge transfer state locate at the pyrazine ring of dpq, as indicated by TD-DFT data. The luminescence of these complexes is quenched by hydroquinone with $k_q = (2.9 \pm 0.1)\text{x}10^9$ and $(2.6 \pm 0.1)\text{x}10^9$ L mol^{-1} s^{-1}, respectively for NN = phen or dpq. These values are increased respectively to $(4.6 \pm 0.1)\text{x}10^9$ and $(4.2 \pm 0.1)\text{x}10^9$ L mol^{-1} s^{-1} in 1:1 H_2O/CH_3CN mixture. In this medium Stern-Volmer constants determined by steady-state and time-resolved measurements differ from each other, which is a indicative of static quenching, *i.e.* the pre-association of hydroquinone and the complexes through a hydrogen bonding between the remote N-atom in the bpa ligand ($K_A \cong 1\text{-}2\text{x}10^1$ L mol^{-1}), followed by a concerted proton-electron transfer. In contrast to other investigated complexes, *fac*-$[Re(CO)_3(dppz)(bpa)]^+$ is weakly emissive in acetonitrile at room temperature ($\phi \cong 10^{-4}$) and do not exhibit rigidochromic effect. This photophysical behaviour as well as TD-DFT data indicate that the lowest lying triplet excited state can be described as $^3IL_{dppz}$. The results provide additional

insights on the role of polypyridyl ligand on the photophysical properties of Re(I) complexes.

Introduction

The influence of the coordination sphere on the photophysical and photochemical properties of transition metal complexes has been subject to intense research [1-6], due the direct application of these species in light emitting devices [7-10], electron transfer reactions [11-14], DNA probes [15, 16], among others. Particularly, Re(I) tricarbonyl complexes have been widely studied due to their interesting emissive properties, facile preparation and tunable ground and excited states redox properties [17-24].

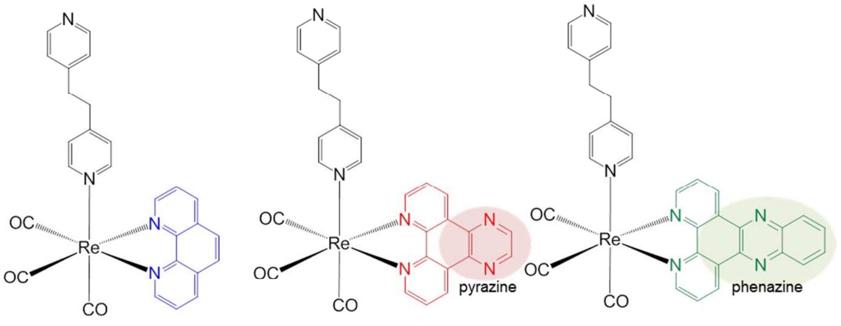
Several studies have investigated the influence of the polypyridyl ligand on the excited state dynamics of metal complexes, with considerable attention to those involving the dipyrido[3,2-a:2'3'-c]phenazine (dppz) ligand [25-32]. Its coordination to the metal center turns the excited state manifold more complicated with several states close in energy, which makes difficult the assignment of the lowest lying excited states. Moreover, Ru(II), Os(II) and Re(I) complexes with the dppz ligand exhibit the so-called light switch effect when intercalated into DNA double helix [33]. This effect is attributed to the presence of three close lying excited states: triplet intraligand ($^3IL_{dppz}$) and two metal-to-ligand excited states that differ in relation to the acceptor orbitals, $MLCT_{phen}$ and $MLCT_{pz}$. The $MLCT_{phen}$ excited state is emissive and the charge is transferred to orbitals located in the 1,10-phenanthroline portion of the dppz ligand. $MLCT_{pz}$ is non-emissive and the charge is transferred to orbitals in the phenazine unit of dppz. For $[Ru(bpy)_2(dppz)]^{2+}$, bpy = 2,2'-bipyridine, it has been shown that the population of the bright and dark states are controlled by enthalpic and entropic factors [34].

Other authors have explored the influence of polypyridyl ligand on the excited state manifold to tune photoinduced energy/electron transfer processes, with direct application on the development of catalysts for CO_2 reduction [35-37], water oxidation [38-41] and other key reactions for solar fuel production.

In this work, we have extended the studies on the influence of polypyridyl ligand on the photophysics of Re(I) complexes by investigating three complexes of general formula *fac*-$[Re(CO)_3(NN)(bpa)]PF_6$, bpa = 1,2-bis-(4-pyridyl)ethane and NN = 1,10-phenanthroline (phen), pyrazino[2,3-f][1,10]-phenanthroline (dpq), dipyrido[3,2-a:2'3'-c]phenazine (dppz), Scheme 1. The influence of introduction of pyrazine (dpq) or phenazine (dppz) units to the polypyridyl ligand on the photophysical properties was systematically investigated by steady-state and time-resolved emission spectroscopy. The results were combined with calculations using time-dependent density function theory (TD-DFT) to describe the excited state manifold of the complexes.

Furthermore, emission quenching experiments in the presence of hydroquinone (H_2Q) were performed and evidenced the role of the ancillary bpa ligand on the photoinduced electron transfer process. This ligand contains an additional protonatable nitrogen atom which may be involved in photoinduced proton-coupled electron transfer reactions (PCET) in the presence of phenols, as observed for other Re(I) complexes with 1,4-pyrazine [42] or 4,4-bipyridine [43] as ancillary ligands. Excited-state PCET chemistry plays a key role on photosynthesis and other biological processes, and such investigations has direct implications on catalysis and energy conversion [13, 44-47].

Scheme 1. Chemical structures of Re(I) polypyridyl complexes investigated.



fac-[Re(CO)$_3$(phen)(bpa)]$^+$ *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$ *fac*-[Re(CO)$_3$(dppz)(bpa)]$^+$

Experimental Methods

All solvents employed were HPLC grade. [ClRe(CO)$_5$], 1,10-phenantroline (phen), 1,2-bis-(4-pyridyl)ethane (bpa), trifluoromethanesulfonic acid and poly(methyl methacrylate), PMMA, (M_w = 110000 g mol^{-1}) were purchased from Aldrich and used as received. The ligands, pyrazino[2,3-f][1,10]-phenanthroline (dpq) and dipyrido[3,2-a:2'3'-c]phenazine (dppz) were synthesized as described previously[48-51].

The *fac*-[Re(CO)$_3$(NN)(bpa)]PF$_6$ complexes (NN = phen, dpq and dppz) were prepared following the procedures described elsewhere[19, 24, 52]. Briefly, [ClRe(CO)$_5$] and an excess of the polypyridyl ligand were refluxed in toluene for 5-7 h to yield a yellow solid, *fac*-[ClRe(CO)$_3$(NN)]. The products were collected by filtration and recrystallized from CH_2Cl_2 solutions by slow addition of *n*-pentane. Then, *fac*-[ClRe(CO)$_3$(NN)] were suspended in argon-saturated CH_2Cl_2 and trifluoromethanesulfonic acid was added to yield the respective intermediates *fac*-[Re(CO)$_3$(NN)(CF$_3$SO$_3$)], which were precipitated by slow addition of ethyl ether. Finally, an excess of the bpa ligand was added to *fac*-[Re(CO)$_3$(NN)(CF$_3$SO$_3$)] in methanol and the mixture was kept in reflux under argon atmosphere during 8-9 h. After cooling, the final products were precipitated by addition of NH_4PF_6. The solids were separated by filtration, washed with water, to remove the NH_4PF_6 excess, and then, ethyl ether.

For *fac*-$[Re(CO)_3(phen)(bpa)]PF_6$, yield was 45%. Anal. Calcd. for $ReC_{27}H_{20}N_4O_3PF_6$: C, 42,20%; N, 7,03%; H, 3,01%; *Found:* C, 42,49%; N, 6,95%; H, 2,51%. ^{1}H RMN (CD_3CN δ / ppm): 9,58 (dd, 2H); 8,84 (dd, 2H); 8,30 (dd, 2H); 8,17 (s, 2H); 8,10 (dd, 2H); 8,09 (d, 2H); 6,98 (dd, 2H); 6,93 (d, 2H); 2,78 (m, 2H); 2,72 (m, 2H).

For *fac*-$[Re(CO)_3(dpq)(bpa)]PF_6$, yield was 35%. anal. Calcd. for $ReC_{29}H_{20}N_6O_3PF_6$: C, 41,87%; N, 10,10%; H, 2,41%; *Found:* C, 41,86%; N, 10,00%; H, 2,19%. ^{1}H RMN (CD_3CN δ / ppm): 9,78 (dd, 2H); 9,66 (dd, 2H); 9,21 (s, 2H); 8,26 (d, 2H); 8,24 (dd, 2H); 8,13 (dd, 2H); 7,01 (dd, 2H); 6,94 (dd, 2H); 2,79 (m, 2H); 2,71 (m, 2H).

For *fac*-$[Re(CO)_3(dppz)(bpa)]PF_6$, yield was 43%. Anal. Calcd. for $ReC_{33}H_{22}N_6O_3PF_6$: C, 44,93%; N, 9,53%; H, 2,50%; *Found:* C, 44,18%; N, 9,35%; H, 2,77%. ^{1}H RMN (CD_3CN δ / ppm): 9,88 (dd, 2H); 9,64 (dd, 2H); 8,45 (dd, 2H); 8,26 (dd, 2H); 8,24 (d, 2H); 8,17 (dd, 2H); 8,13 (dd, 2H); 7,04 (dd, 2H); 6,94(dd, 2H); 2,78 (m, 2H); 2,72 (m, 2H).

PMMA films of the complexes were prepared as described previously [53] by dissolving 5.0 mg of the complex and 250 mg of PMMA (M_w = 110000 g mol^{-1}) in 7.0 mL of acetonitrile (Aldrich), and then left to dry in absence of light and humidity.

^{1}H NMR spectra were recorded on a DRX-500 (500 MHz) Brüker Avance spectrometer using CD_3CN (Cambridge) as solvent. Steady state emission experiments were performed by using a Hitachi F4500 spectrofluorometer. Room temperature measurements were performed in degassed acetonitrile

(Aldrich) solutions in a 1.000 cm quartz cuvette. Typical concentrations employed in the experiments were between $1x10^{-5}$ and $5x10^{-5}$ mol L^{-1}. Emission quantum yields were determined as described elsewhere [54], using *fac*-$[ClRe(CO)_3(phen)]$, phen = 1,10-phenanthroline, as standard (ϕ_{em} = 0.018 in CH_3CN, 298 K). Low temperature steady state measurements were obtained in an ethanol/methanol mixture (4:1, v/v) at 77 K using a quartz tube placed in a Dewar flask filled with liquid nitrogen.

Emission lifetimes were obtained by using the third harmonic (355 nm) of an Nd:YAG pulsed laser (Quantel Brio, 5ns FWHM; 20 Hz repetition rate). Emission decays were monitored at 90° with a Thorlabs silicon photodetector model DET10A coupled to a Tektronix BPO 4104 oscilloscope. Appropriate cut-off filters were used to avoid the detection of laser scattering. Reported lifetimes are the averaged result of 500 decay traces probed at the respective emission maxima. The measurements were performed in argon degassed acetonitrile or 1:1 CH_3CN/H_2O solutions placed in a 1.000 cm quartz cuvette. Emission decays in PMMA films were recorded in air with the samples at 45° with respect to the laser beam. Quenching experiments were carried out in acetonitrile or 1:1 CH_3CN/H_2O mixture in the presence of hydroquinone (VETEC) with concentrations ranging from 10^{-4} to 10^{-2} mol L^{-1}. The absorbance of the Re(I) complexes at the excitation wavelength was typically between 0.1 and 0.3, which correspond to molar concentrations between $1x10^{-5}$ and $3x10^{-5}$ mol L^{-1}.

Computational Details

Optimizations, vertical absorption spectra and state diagram for the solvent-non-relaxed states (TD-DFT) were computed using the density functional theory (DFT) Minnesota 2006 (M06) functional,[55] the segmented all-electron relativistically contracted combined to the Douglas-Kroll-Hess (SARC-DKH) atomic basis to describe Re[56, 57], and Def2-TZVPP (orbitals with effective core potential) for the other elements [57, 58]. All calculations were done using the Gaussian09 revision D.01 software package [59] considering the species solvated in acetonitrile. Solvent effect corrections were performed by using the IEFPCM model [60].

The SARC basis sets are loosely contracted, offering computational advantages compared to other generally contracted relativistic basis sets. The relatively small size of this kind of basis sets allows it to be used in place of effective core potentials (ECPs) for routine studies of molecules [56]. Practical assessments of the SARC basis sets in DFT calculations of physical and molecular properties confirm that this basis sets yield accurate and reliable results, providing a balanced description of core and valence electron densities.

Def2-TZVPP is a triple zeta valence quality Gaussian basis set, defined for H–Rn [58], recommended, at the DFT level, to obtain results that are not too far from the DFT basis set limit.

Results and Discussion

Electronic structure and UV-Vis absorption spectra

DFT optimized structures exhibit a distorted octahedral geometry, in agreement with previous calculations and also with crystallographic data for similar complexes[28, 61 62]. In all complexes, the Re(I) metal center is coplanar to the aromatic rings of the polypyridyl ligand, with N-Re-N bond angles between 74.37º and 76.19º. As expected, the polypyridyl ligand is closer to the metal center than bpa in c.a. 0.05 Å.

The *fac*-[Re(CO)$_3$(NN)(bpa)]PF$_6$ complexes were characterized by UV-Vis absorption spectroscopy. The complex *fac*-[Re(CO)$_3$(phen)(bpa)]PF$_{6,}$ previously described by Argazzi et al.[63], was taken as a reference for the description of spectral properties of the new species with dpq and dppz. The experimental and theoretical UV-Vis spectra of the complexes in acetonitrile are shown in Figure 1. Their spectral parameters, as well as those for the free polypyridyl ligands and the respective chloro complexes, are listed in Table 1.

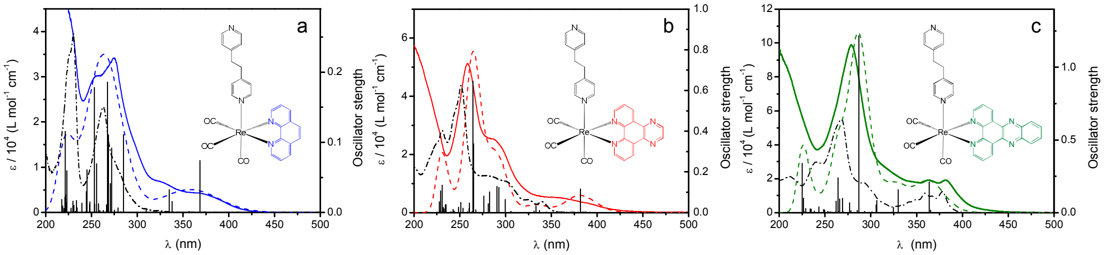


Figure 1. Theoretical (----) and experimental (——) electronic spectra of *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ in acetonitrile, NN = phen (a), dpq (b) and dppz (c) along with the spectra of the respective free polypyridyl ligands (—·—).

Table 1. Experimental spectral parameters of Re(I) complexes and the free ligands in acetonitrile

Compound	**λ_{max} (nm) (ε / 10^4 L mol^{-1} cm^{-1})**
bpa	256 (0.74)
phen	230 (3.9), 263 (2.3)
dpq	230 (2.8), 251 (4.3), 278 (1.2), 299 (1.0), 324 (0.4)
dppz	241 (1.9), 268 (3.4), 292 (1.2), 359 (0.7), 367 (0.6), 378 (0.8)
fac-[ClRe(CO)$_3$(phen)]	216 (4.4), 265 (2.6), 365 (0.34)
fac-[Re(CO)$_3$(phen)(bpa)]$^+$	254 (3.0), 275 (3.4), 360 (0.44)
fac-[ClRe(CO)$_3$(dpq)]	257(4.7), 291(1.9), 380 (0.3)
fac-[Re(CO)$_3$(dpq)(bpa)]$^+$	258 (5.1), 286 (2.5), 360 (0.5)
fac-[ClRe(CO)$_3$(dppz)]	276 (7.1), 318 (1.6), 360 (1.3), 379 (1.1)
fac-[Re(CO)$_3$(dppz)(bpa)]$^+$	278 (9.8), 363 (1.9), 381(1.9)

The *fac*-$[Re(CO)_3(phen)(bpa)]^+$ ion exhibits typical absorption trends observed for Re(I) tricarbonyl polypyridyl complexes [22, 54, 64]. At high energy region (200-300 nm), intense bands ascribed to completely allowed ligand centered (IL) electronic transitions are observed. The lowest energy band with λ_{max} = 360 nm is also observed in the spectrum of the precursor *fac*-$[ClRe(CO)_3(phen)]$ being assigned to the charge transfer from the metal to 1,10-phenanthroline, $MLCT_{Re\rightarrow phen}$. The attributions are consistent with the results of TD-DFT calculations, Table 2. As expected, the nature of the highest energy bands is mainly $\pi\pi^*$(phen) with some contribution of the metal to bpa charge transfer at 4.3 eV (285 nm). The dominant excitation for the lowest lying absorption band is the HOMO-1→LUMO transition, corresponding to the charge transfer from Re(I) d-orbitals to the π^* ones in the phen ligand. As shown in Figure 2, there is also some contribution of the π^*(CO) and π(bpa) orbitals to the HOMO-1 state. The TD-DFT simulations pointed out that the HOMO state in *fac*-$[Re(CO)_3(phen)(bpa)]^+$ is localized in the N-lone pairs and in the π^* orbitals of the pyridine ring of bpa non-coordinated to the Re(I) center. This state is only 0.01 eV higher in energy than the metal centered HOMO-1 one, and does not contribute for any low lying electronic transition.

Table 2. Solvent corrected (acetonitrile) major transition energies to the excited states of *fac*-$[Re(CO)_3(NN)(bpa)]^+$ with their contributing excitations (%), oscillator strengths (f) and associated wavelengths (λ).

NN	Transition*	f	Energy (eV)	λ (nm)	Character
phen	H-3 – L	0.0008	3.31	374	$MLCT_{d(Re)\rightarrow\pi^*(phen)}$
	H-1 – L	0.0741	3.37	368	$MLCT_{d(Re)\rightarrow\pi^*(phen)}$
	H-3 – L+1	0.0325	3.70	335	$MLCT_{d(Re)\rightarrow\pi^*(phen)}$
	H-1 – L+2 (54%) H – L+2 (20%)	0.1111	4.35	285	$MLCT_{d(Re)\rightarrow\pi^*(bpa)}/IL_{(bpa)}$
	H-7 – L (30%) H-6 – L+1 (28%) H-4 – L+5 (26%)	0.1858	4.64	267	$IL_{(phen)}$
	H-3 – L+3 (27%) H-1 – L+4 (10%)	0.1778	4.90	253	$MLCT_{d(Re)\rightarrow\pi^*(phen)}/IL_{(phen)}$
dpq	H – L	0.1153	3.25	382	$MLCT_{d(Re)\rightarrow\pi^*(dpq)}$
	H – L+2	0.0106	3.67	337	$MLCT_{d(Re)\rightarrow\pi^*(dpq)}$
	H-1 – L+2 (59%) H – L+1(41%)	0.0345	3.72	333	$MLCT_{d(Re)\rightarrow\pi^*(dpq)}$/ $IL_{(dpq)}$
	H-7 – L	0.0639	4.14	299	$IL_{(dpq)}$
	H – L+3	0.1242	4.23	292	$MLCT_{d(Re)\rightarrow\pi^*(bpa)}$
	H-5 – L+1	0.1282	4.26	290	$IL_{(dpq)}$
	H-7 – L+1	0.1020	4.38	282	$IL_{(dpq)}$
	H-5 – L+2 (33%) H-7 – L+1 (36%)	0.3368	4.67	265	$IL_{(dpq)}$
	H-7 – L+2	0.6454	4.68	264	$IL_{(dpq)}$
dppz	H-3 – L	0.0012	3.25	380	$MLCT_{d(Re)\rightarrow\pi^*(dppz)}$
	H-2 – L (83%) H – L+1 (17%)	0.0160	3.40	365	$IL_{(dppz)}/MLCT_{d(Re)\rightarrow\pi^*(dppz)}$
	H – L (54%) H – L+1 (36%)	0.2116	3.41	363	$IL_{(dppz)}/MLCT_{d(Re)\rightarrow\pi^*(dppz)}$
	H-4 – L (71%) H-2 – L+2 (29%)	0.1578	3.76	330	$IL_{(dppz)}$
	H-2 – L+1 (48%) H – L+2 (22%)	0.0342	3.81	325	$IL_{(dppz)}$
	H-4 – L+1 (39%) H-1 – L+2 (31%)	0.0840	4.04	307	$IL_{(dppz)}$
	H – L+2	0.0532	4.06	305	$MLCT_{d(Re)\rightarrow\pi^*(dppz)}$
	H-2 – L+2	1.2157	4.3	287	$IL_{(dppz)}$
	H-1 – L+4 (31%) H – L+3 (37%)	0.0982	4.6	269	$IL_{(dppz)}/IL_{(bpa)}$

* H = HOMO; L = LUMO

For the *fac*-$[Re(CO)_3(dpq)(bpa)]^+$ complex, the HOMO → LUMO transition is the dominant excitation at low energy and can be described as a charge transfer from the Re(I) d-orbitals to the π* orbitals of the phenanthroline moiety of dpq ligand, Figure 2, similar to the observed for *fac*-$[Re(CO)_3(phen)(bpa)]^+$. Other major transitions include HOMO→LUMO+2 and HOMO-1→LUMO that can also be described as $MLCT_{Re\rightarrow dpq}$. Nevertheless, it is noteworthy to observe some contribution of π orbitals of dpq to the HOMO and HOMO-1 states, Figure 2. The contribution of π_{dpq} orbitals to the lowest energy absorption band is expected since the pyrazine ring tends to stabilize $\pi\pi^*$ transitions. Such a stabilization is evidenced by the bathochromic shift observed in the spectrum of the free dpq ligand relative to the spectrum of 1,10-phenhantroline.

Differently to the complexes with phen and dpq, the coordination of dppz to the Re(I) center does not lead to appearance of new absorption bands. The spectrum of *fac*-$[Re(CO)_3(dppz)(bpa)]^+$ resembles the dppz one, but with higher molar absorptivities. The calculations indicate that the lowest lying electronic transition at 380 nm involves HOMO-3→LUMO orbitals, which can be described as $MLCT_{Re\rightarrow dppz}$. However, the oscillator strength for this transition is considerably low (f = 0.0012). Higher oscillator strengths are found at 365 and 363 nm, in which the excitations HOMO-2→LUMO, HOMO → LUMO and HOMO→LUMO+1 are involved. As shown in Figure 2, the electron density in the HOMO is distributed between Re(I) d orbitals and dppz π ones, while in HOMO-2, the electron density is completely located at π orbitals of the polypyridyl ligand. Therefore, the absorption bands at low energy region can be described as a mixture between $IL_{\pi\pi^*}$ and $MLCT_{Re\rightarrow dppz}$ excitations. This overlap between transitions that behave differently to the surround medium makes difficult a better match between the calculated and the experimental spectra, due to the presence of trace amounts of water and other contaminants in the solvent.

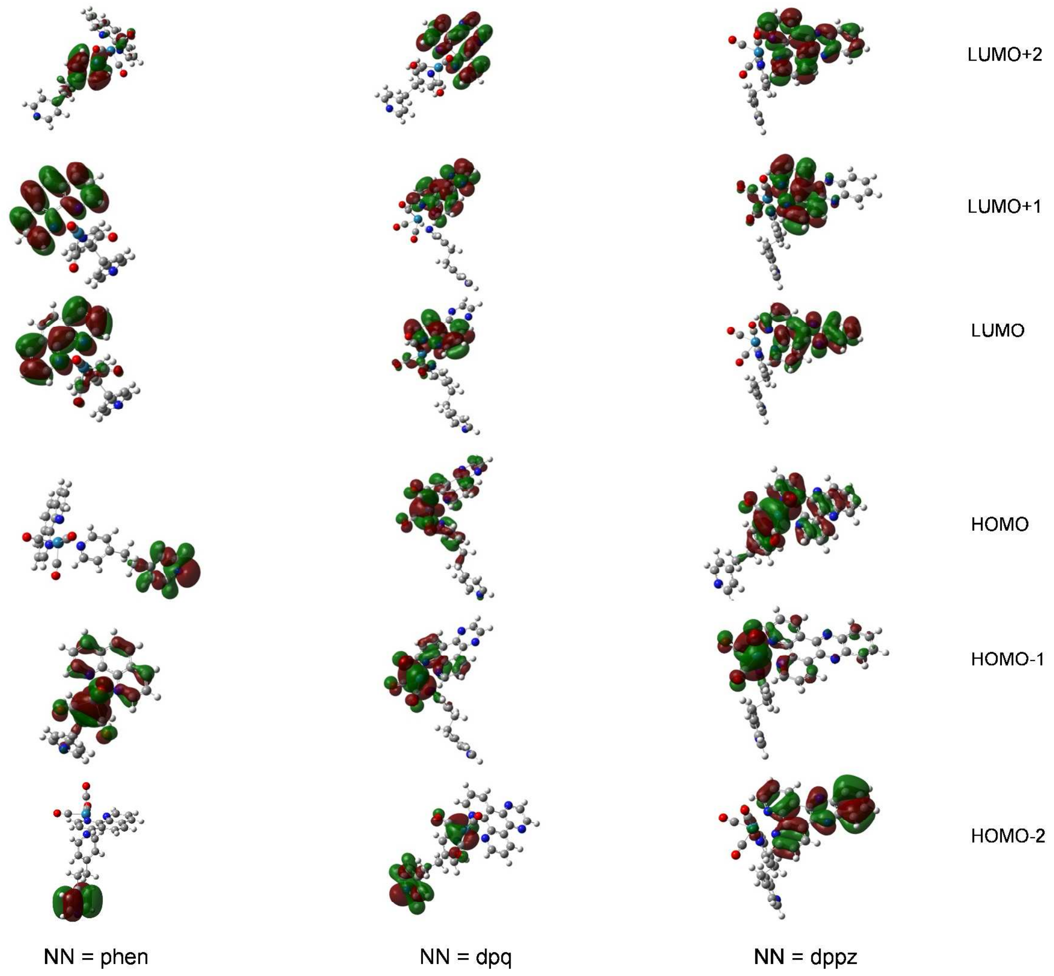


Figure 2. Isosurface plots of frontier orbitals of *fac*-$[Re(CO)_3(NN)(bpa)]^+$ in CH_3CN.

The TD-DFT data also show that, for *fac*-$[Re(CO)_3(dppz)(bpa)]^+$, the lowest lying Franck Condon MLCT state is distributed all over the π^* orbitals of dppz with a significant contribution of the orbitals located in the phenazine portion of the dppz ligand. This state is only 0.01 eV lower in energy than π^* orbitals located only at phen moiety (LUMO+1). The results are in accordance with previous calculations done for other Re(I) complexes having dppz as polypyridyl complexes, such as *fac*-$[Re(CO)_3(dppz)(py)]^+$ [65], py = pyridine, and *fac*-$[ClRe(CO)_3(dppz)]$ [28].

From spectral data and TD-DFT calculations, it can be concluded that the substitution of phen ligand by dpq and dppz, does not change substantially the energy of the MLCT$_{Re \rightarrow NN}$ transition, that remains around 360-370 nm. However, the presence of pyrazine (dpq) or phenazine (dppz) moieties increases the contribution of the π orbitals to the highest energy occupied orbitals. As a consequence, the lowest lying transitions in *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$ and mainly in *fac*-[Re(CO)$_3$(dppz)(bpa)]$^+$ have a significant IL$_{NN(\pi\pi^*)}$ character.

Emissive properties

The introduction of pyrazine or phenazine moieties in the polypyridyl ligand of *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ complexes also lead to profound changes in their photophysical properties. All complexes exhibit some luminescence in fluid solution at room temperature, but with distinct quantum yields and lifetimes. In Table 3 is presented the photophysical data of the complexes in acetonitrile along with those obtained in PMMA films at 298 K and in EtOH:MeOH (4:1) at 77 K. Normalized emission spectra in the different media are shown in Figure 3. The emission decay curves in acetonitrile and in PMMA can be found at supplementary information (Fig S1 and S2, respectively).

Table 3. Emission maxima, quantum yields and lifetimes for *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ in different media.

NN	Media					
	Acetonitrile (298 K)			PMMA (298 K)		EtOH/MetOH (77 K)
	λ_{max} (nm)	ϕ_{em}	τ (ns)	$\lambda_{máx}$ (nm)	τ (μs)	$\lambda_{máx}$ (nm)
phen	553	0.11	970	507	4.8	493
dpq	555	0.05	375	510	2.4	505
dppz	553	10^{-4}	——	546	2.0	544

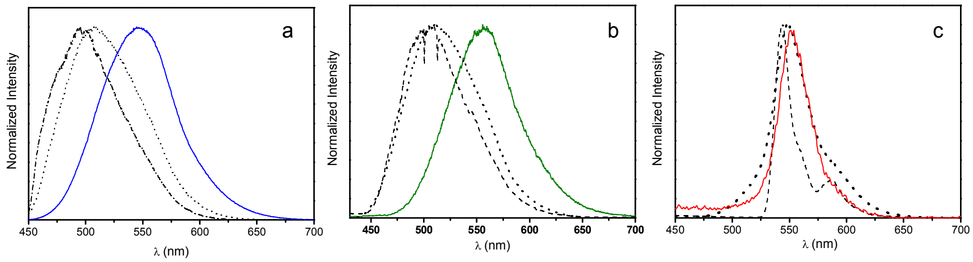


Figure 3. Emission spectra of *fac*-[Re(CO)$_3$(NN)(bpa)]PF$_6$ in CH$_3$CN (—), in PMMA at 298 K (·····) and in EtOH:MeOH (4:1) at 77 K (-----);NN = phen (a), dpq (b) and dppz (c); λ_{exc} = 365 nm.

The *fac*-[Re(CO)$_3$(phen)(bpa)]PF$_6$ complex is a typical ^{3}MLCT emitter [18, 63]. It exhibits a broad and non-structured emission band in acetonitrile, with relatively high emission quantum yield and rate constant of *c.a.* 10^6 s^{-1}. As the medium rigidity increases, the emission is blue-shifted due to the so-called rigidochromic effect, which is associated to the frozen nature of the surrounding medium dipoles that increase the excited-to-ground state energy gap and consequently the emission energy[66-68]. ^{3}MLCT states are very sensitive to the medium rigidity, while the energy of ligand-centered excited states remains almost unchanged.

The substitution of the phen ligand by dpq causes a small (13 nm) bathochromic shift in the emission band in acetonitrile that remains broad and non-structured, *i.e.* *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$ is also a ^{3}MLCT emitter. The emission quantum yield and lifetime are considerable decreased, which indicates an enhancement in the contribution of non-radiative excited state deactivation pathways.

In *fac*-[Re(CO)$_3$(dppz)(bpa)]PF$_6$, the emission quantum yield is much lower than that observed for the other complexes, which did not allow a precise determination of the emission lifetime in fluid solution using the experimental setup available. Moreover, the complex did not exhibit rigidochromic effect. The emission maxima remain almost constant in all investigated media and the band becomes more structured as the medium rigidity increases. It is also noteworthy to observe the similarity between the emission spectrum of the complex with the spectrum of free dppz ligand in glassy medium (supplementary information, Fig S3).

TD-DFT calculations were employed to calculate the energy and the nature of emissive states. In Table 4 are shown the data for the three lowest lying non-relaxed triplet excited states for each complex in acetonitrile, along with their respective attributions.

Table 4. TD-DFT calculated singlet-triplet energies for *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ in acetonitrile (non-relaxed).

NN	State	Energy (eV)	Transitions	Character[a]
phen	T_1	2.76	H-3→L (42%) H-1→L+1 (48%)	$^3MLCT_{phen}$
	T_2	3.00	H-1→L (88%)	$^3MLCT_{phen}$
	T_3	3.22	H-3→L (58%) H-1→L+1 (42%)	$^3MLCT_{phen}$
dpq	T_1	2.78	H-1→L (63%)	$^3MLCT_{phen}$
	T_2	2.94	H→L (78%)	$^3MLCT_{phen}$
	T_3	3.17	H→L+2 (62%)	$^3MLCT_{pz}$
dppz	T_1	2.39	H-2→L (85%)	$^3IL_{dppz}$
	T_2	2.91	H→L (89%)	$^3MLCT_{pz}$/$^3IL_{dppz}$
	T_3	3.04	H-1→L+1(76%)	$^3MLCT_{phen}$

In the Table 4, the MLCT excited states are labeled as function of the acceptor orbital position. In *fac*-[Re(CO)$_3$(phen)(bpa)]$^+$, the lowest lying triplet excited states correspond to metal-to-ligand charge transfer to the 1,10-phenanthroline ligand (MLCT$_{phen}$), which agrees with the luminescent properties observed in fluid solution. Similar situation is found for the first and second lowest lying triplet states of *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$, in which the acceptor orbital is the LUMO, located in the phenanthroline moiety of dpq. However, the T$_3$ state refers to the population of LUMO+2 that includes π* orbitals and N-lone pairs of the pyrazine ring in dpq (MLCT$_{pz}$). This state is non-emissive [31, 34] and can be thermally populated. The low energy gap between the T$_3$ (^{3}MLCT$_{pz}$) and the emissive ^{3}MLCT$_{phen}$ states is probably the main cause of the significant decrease in the emission quantum yield as the polypyridyl ligand is changed from phen to dpq.

TD-DFT calculations also point out that for *fac*-[Re(CO)$_3$(dppz)(bpa)]$^+$ the lowest lying triplet excited state in acetonitrile is ^{3}IL$_{dppz}$, which corroborates with the lack of observation of the rigidochromic effect on the luminescence properties. This result is in principle different to the ones previously obtained by Dyer and co-workers for the complex *fac*-[Re(CO)$_3$(dppz)(py)]$^+$ in a solvent with relative permittivity equal to 37.5 [65]. The authors found that the T$_1$ state is ^{3}MLCT$_{pz}$ and it is in equilibrium with ^{3}IL$_{dppz}$, *c.a.* 0.3 eV higher in energy. However, considering the approximations taken for the calculations, the number of electrons involved and the small energy difference, it is reasonable to considerer both results qualitatively similar. In both cases, the ^{3}MLCT$_{pz}$ and ^{3}IL$_{dppz}$ states are lower in energy than the ^{3}MLCT$_{phen}$ and tend to dominate the deactivation pathways at room temperature. As a result, *fac*-[Re(CO)$_3$(dppz)(bpa)]$^+$ exhibits very weak luminescence with a strong intra-ligand character.

Quenching experiments

Emission quenching experiments were performed with *fac*-[Re(CO)$_3$(phen)(bpa)]$^+$ and *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$ in the presence of hydroquinone (H_2Q) as quencher. The experiments were carried out in acetonitrile and in a 1:1 acetonitrile/water mixture. Changes in the emission intensity and lifetime were monitored as a function of the hydroquinone concentration, Figure 4, and the data was fitted to the Stern-Volmer model (equation 1), Figure 5. The rate constants for the bimolecular excited state quenching (k_q) for both complexes in the different media are shown in Table 5.

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \left(1 + k_q \tau_0 [H_2Q]\right) \qquad (1)$$

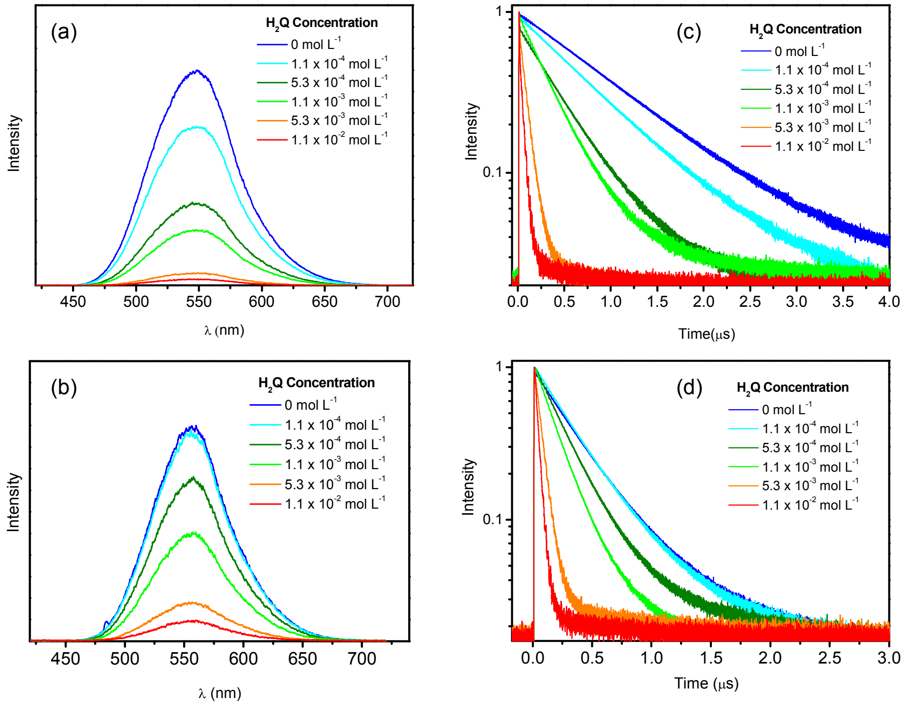


Figure 4. Emission spectra and luminescence decays of *fac*-[Re(CO)$_3$(phen)(bpa)]$^+$ (a, c) and *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$ (b, d) in acetonitrile solutions of hydroquinone at different concentrations (T = 298 K).

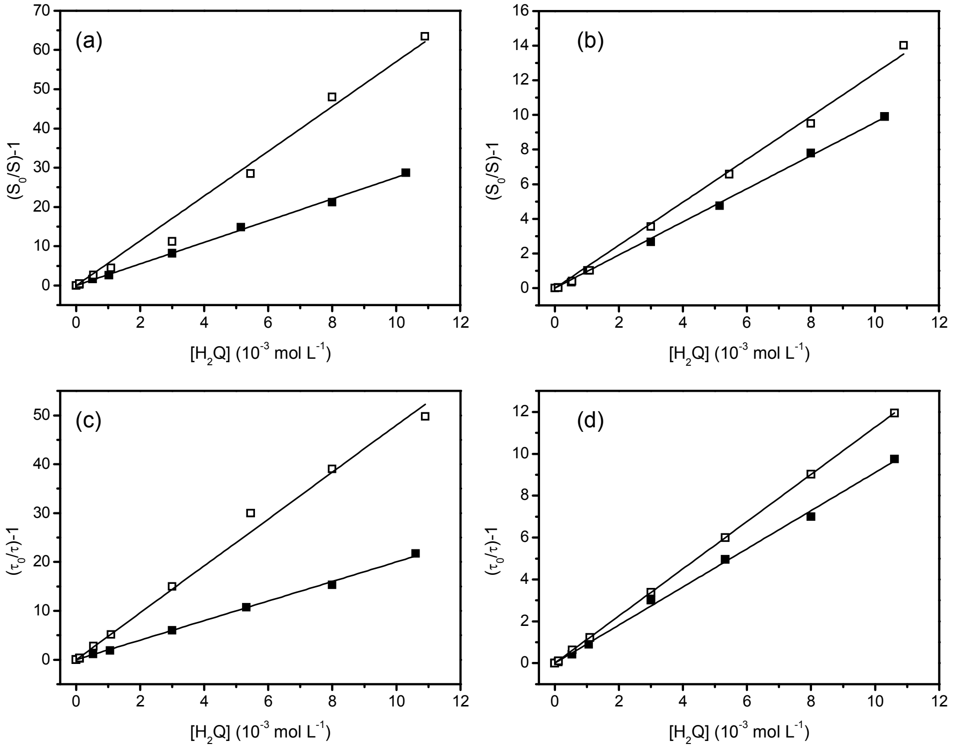


Figure 5. Stern-Volmer plots based on luminescence intensity and lifetime of *fac*-$[Re(CO)_3(phen)(bpa)]^+$ (a, c) and *fac*-$[Re(CO)_3(dpq)(bpa)]^+$ (b, d) in CH_3CN (■) or 1:1 H_2O/CH_3CN (□) solutions of hydroquinone at different concentrations.

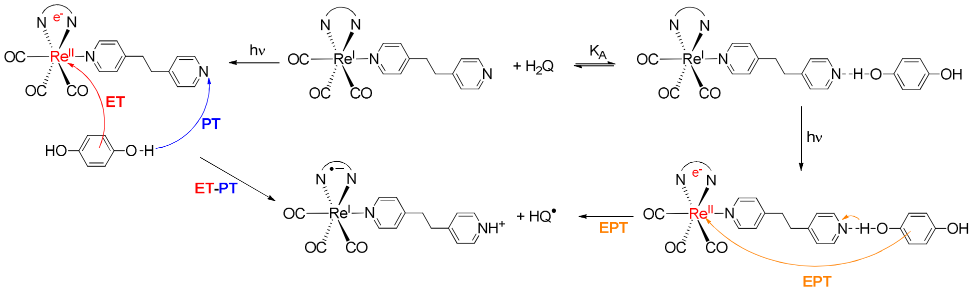
Table 5. Rate constants for bimolecular excited-state quenching for *fac*-$[Re(CO)_3(phen)(bpa)]^+$ and *fac*-$[Re(CO)_3(dpq)(bpa)]^+$ in the presence of hydroquinone as determined from emission intensities and lifetimes in CH_3CN and 1:1 $CH_3CN:H_2O$

NN	medium	τ_0 (ns)	Data	k_q (10^9 L mol^{-1} s^{-1})
phen	CH_3CN	969	intensity	2.9 ± 0.1
			lifetime	2.5 ± 0.1
	1:1 CH_3CN/H_2O	1300	intensity	4.6 ± 0.1
			lifetime	3.6 ± 0.1
dpq	CH_3CN	375	intensity	2.6 ± 0.1
			lifetime	2.5 ± 0.1
	1:1 CH_3CN/H_2O	300	intensity	4.2 ± 0.1
			lifetime	3.6 ± 0.1

The luminescence quenching is associated to the electron transfer (ET) from H_2Q to the Re^{II} center, probably followed by a proton loss by $H_2Q^{\bullet +}$ radical (pKa ≅ -1[39]), Scheme 2. In neat acetonitrile, the values of k_q determined for both complexes by monitoring the emission intensities and lifetimes are experimentally similar, which is consistent to a dynamic emission quenching mechanism [69-71]. The decrease of the emission lifetime due to the substitution of the phen ligand by dpq does not influence substantially the quenching rate constant, suggesting the effectiveness of the quenching process.

As the solvent is changed to 1:1 v/v $CH_3CN{:}H_2O$, the excited-state quenching rate constants are enhanced. In this medium, the k_q values determined by probing the changes in the emission intensity are about 27% (NN = phen) and 17% (NN = dpq) higher than those determined by lifetime measurements. The emission decay curves for both complexes in this medium can be found at supplementary information (Fig. S4), as well as changes in the emission intensity as a function of H_2Q concentration (Fig. S5). The mismatch between the k_q values determined by steady-state and time-resolved emission measurements is consistent with an additional excited state deactivation pathway, probably involving a static quenching process, *i.e.* the pre-association of hydroquinone and the complexes through a hydrogen bonding between the remote N-atom in the bpa ligand, Scheme 2. From Stern-Volmer plots, it is clear that the additional static quenching process becomes more effective at high H_2Q concentrations ($>5\times10^{-3}$ mol L^{-1}). In the static quenching, excitation of the adduct leads to population of the $^3MLCT_{NN}$ excited state, followed by electron transfer from the associated H_2Q to the Re^{II} center.

Scheme 2. Possible mechanisms for the reductive quenching of *fac*-$[Re(CO)_3(NN)(bpa)]^+$ by hydroquinone



The occurrence of both dynamic and static luminescence quenching in the presence of hydroquinone have been observed previously by Stewart et al. [43] with the complex *fac*-$[Re(CO)_3(bpy)(4,4'\text{-bpy})]^+$, bpy = 2,2'-bipyridine, 4,4'-bpy = 4,4'-bipyridine. Nanosecond transient absorption measurements have shown that in the adduct, the quenching process occurs via a concerted electron-proton transfer (EPT) with an H-atom being transferred to the non-coordinated N-atom in 4,4'-bpy. The authors reported an increase of k_q from $(1.8 \pm 0.2)\times10^9$ L mol^{-1} s^{-1} in CH_3CN to $(3.04 \pm 0.09)\times10^9$ L mol^{-1} s^{-1} in 1:1 v/v CH_3CN/H_2O. Similar mechanism is proposed by Bronner and Wenger for *fac*-$[Re(CO)_3(bpy)(pz)]^+$, pz = 1,4-pyrazine using 4-cyanophenol as quencher [42].

In the data presented here, there is no direct evidence of concerted electron-proton transfer. However, given the similarity of the results found with those previously reported [43], it is reasonable to assume that the EPT pathway is probably responsible for the increase of the quenching rate constants in 1:1 CH_3CN/H_2O mixture with high H_2Q concentrations. Such a mechanism plays a role on the redox chemistry of quinone/hydroquinone couple [39] and also on several biological processes [13, 44, 72].

Considering the occurrence of dynamic and static quenching in 1:1 CH_3CN/H_2O, the changes in the emission intensity (S_0/S) can be correlated to the hydroquinone concentration through the quadratic relationship shown in the equation 2, where K_A is the association constant related to the formation of the adduct between hydroquinone and the complexes and k_q is the bimolecular quenching rate constant determined by lifetime measurements.

$$\frac{S_0}{S} = \left(1 + k_q\tau_0[H_2Q]\right)(1 + K_A[H_2Q]) \qquad (2)$$

The values of K_A estimated from the fits of the experimental data (Fig. S6) to the equation 2 are $(2.4 \pm 0.3)\times10^1$ L mol^{-1} and $(1.3 \pm 0.2)\times10^1$ L mol^{-1}, respectively for *fac*-[Re(CO)$_3$(phen)(bpa)]$^+$ and *fac*-[Re(CO)$_3$(dpq)(bpa)]$^+$. The values evidence that the dynamic quenching is the major process and static quenching only plays a role at high hydroquinone concentrations.

Summary of the photophysical properties of *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$

The photophysical behavior of the *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ complexes, NN = phen, dpq and dppz can be summarized in the energy diagram shown in Figure 6.

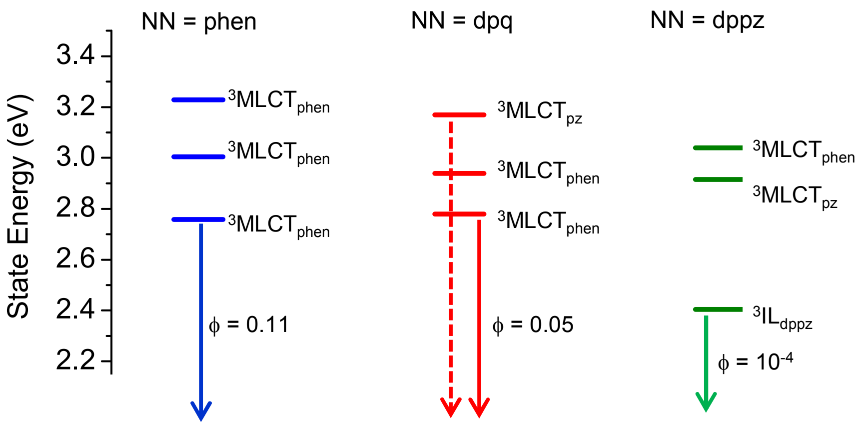


Figure 6. Energy level diagram for non-relaxed lowest lying triplet excited states for *fac*-[Re(CO)$_3$(NN)(bpa)]$^+$ in acetonitrile.

The complexes with 1,10-phenanthroline (phen) and pyrazino[2,3-f][1,10]-phenanthroline (dpq) exhibit emission properties characteristic to the radiative decay of triplet $MLCT_{phen}$ excited states, such as the rigidochromic effect. The presence of the pyrazine ring in the dpq ligand introduces a dark charge transfer state ($^3MLCT_{pz}$) energetically closer to the emissive $^3MLCT_{phen}$ one. As a result the luminescence quantum yield and lifetime in *fac*-$[Re(CO)_3(dpq)(bpa)]^+$ are much lower than in *fac*-$[Re(CO)_3(phen)(bpa)]^+$. The radiative decay of both complexes is reductively quenched in the presence of hydroquinone with similar rate constants as evidenced by Stern-Volmer analysis. In 1:1 CH_3CN/H_2O, the quenching rate constants are enhanced, possibly due to the occurrence of static quenching involving the pre-association of hydroquinone with the protonatable site in the bpa ligand prior to the photoinduced electron transfer.

The *fac*-$[Re(CO)_3(dppz)(bpa)]^+$ ion exhibits distinct photophysical properties in relation to those observed for the complexes with phen or dpq. Experimental and theoretical data indicate that the lowest lying triplet excited state is $^3IL_{dppz}$ in nature as a result of the stabilization of π orbitals due to the introduction of phenazine moiety. Additionally, the dark $^3MLCT_{pz}$ excited state is lower in energy than the bright $^3MLCT_{phen}$ one. As a result, the complex exhibit very low emission quantum yield in acetonitrile and the luminescence energy is independent on the medium rigidity. The results presented here extend the understanding about the influence of the polypyridyl ligand on the photophysical properties of Re(I) complexes and can be conveniently used in the development of DNA probes and photossensors, as well as in electron transfer studies.

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