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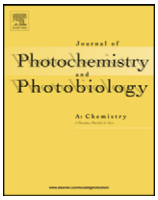

Solvent effects on the absorption and emission of $[Re(R_2bpy)(CO)_3X]$ complexes and their sensitivity to CO_2 in solution

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ABSTRACT

The solvatochromic properties of a series of rhenium(I) organometallic compounds have been studied. For this goal, their absorption and emission spectra have been undertaken in a wide range of solvents with different polarity.

Kamlet–Taft multiparametric equation and DFT calculations have been used to explain the solvent effect in the MLCT transition of the $[Re(R_2bpy)(CO)_3X]$ (R = H, *t*-Bu; X = Cl^-, OTf^-, C≡CpyRe$(R_2bpy)(CO)_3$) complexes.

Polarity/polarizability is observed to play an important role in the solvatochromism of the compounds. In spite of this, in general, the splitting of the solvent contributions shows that this effect is not the solely responsible for the observed variations in the energy of this transition and solvent coordination also affects the observed solvatochromism.

Compounds with a labile position in the coordination sphere of the metal atom have also been explored in sensorial applications for CO_2 detection in solution by means of reversible changes in the recorded emission spectra intensity. The solvent effect on the sensing process is discussed.

1. Introduction

From decades, there has been a continuous interest in the phenomenon of solvatochromism [1–10] and it is still a very promising research area nowadays [11–16]. The studies in the field of inorganic and organometallic chemistry are related with efforts to control the photo and electrochemical behaviour of complexes with metal-to-ligand charge transfer (MLCT) transitions and to get insight on the solvent effect on the properties of complexes. Interesting studies of solvent sensitivity for charge transfer transitions have been reported for square–planar transition metal complexes or monomeric octahedral coordination complexes that exhibit specific solute–solvent interactions, such as Ni(S(CN)C=C(Ph)S)phen [17], $Pt(bpy)X_2$ (X = Cl, Br) [18], $Os(fppz)_2(CO)(L)$ [19], $M(CO)_4L_2$ [5,20–23] and $M(CO)_5L$ (M = Cr, Mo, W) [24,25]. Photochemical and photophysical properties of several classes of groups 6 and 7 metal carbonyl compounds have been investigated with respect to solvatochromism [5,7,20–22,24,26–29] and for many of them the electronic transitions have shown to be solvent sensitive. Usually, the observed effect is a negative solvatochromism in the absorption, i.e., the hypsochromic shift of the MLCT absorption bands in polar solvents which is explained by assuming that the transfer of the charge in the MLCT excited state occurs antiparallel to the ground state dipole moment [1,30] (the excited state has a lower dipole moment than the ground state). The higher transition energy in more polar solvents may thus be attributed to the ground state stabilization prevailing with respect to the excited state stabilization during the transition. This picture could be an oversimplification in some cases, as solvatochromic properties can also be exhibited by compounds with no ground state dipole moment, such as centrosymmetric complexes [20], while other factors (e.g. H-bonds, solvent coordination, etc.) shall also be taken into account.

Several empirical solvent polarity parameters have been proposed to characterize quantitatively solute–solvent interactions [3,31,32], being the multiparametric method of Kamlet and Taft [33], in which UV–vis absorption and emission energies are correlated with different solvent properties according to equation (1), one of the most extensively applied [34–39]:

$$\bar{\nu} = \bar{\nu}_0 + a\alpha + b\beta + p(\pi^* + d\delta) \qquad (1)$$

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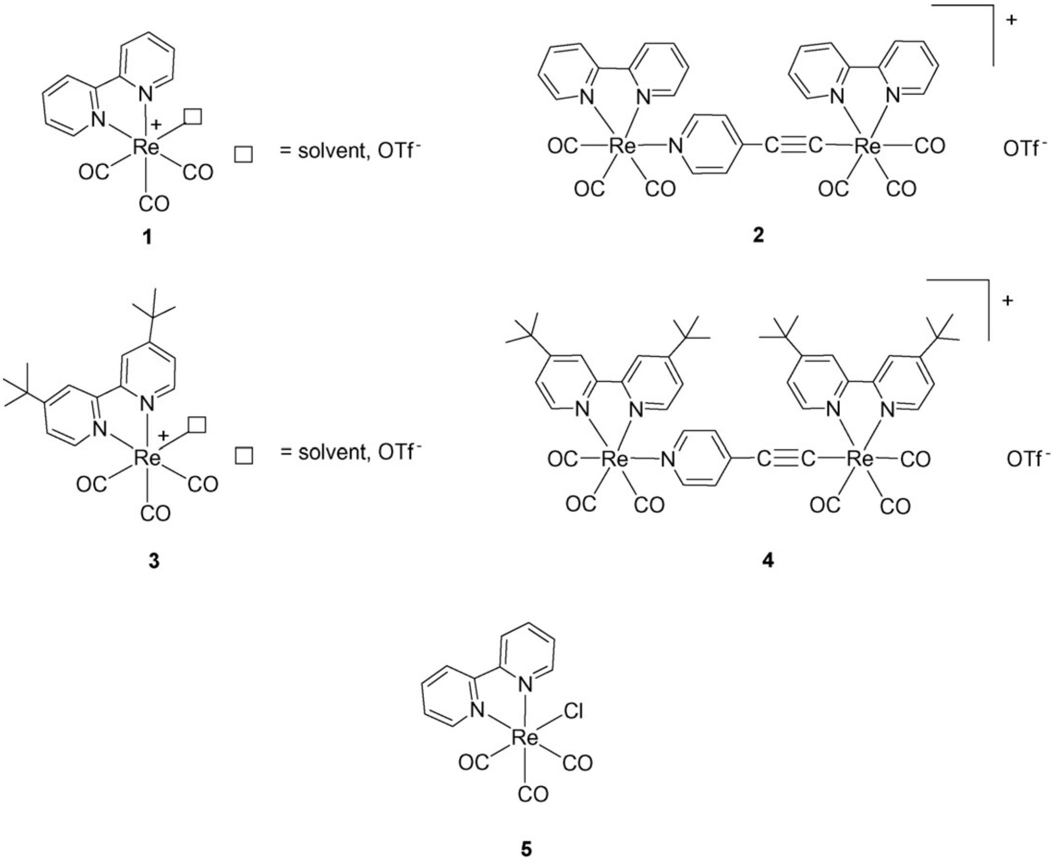


Scheme 1.

In this equation, $\bar{\nu}_0$ is the value of the absorption and/or emission energies in a reference solvent (cyclohexane; $\alpha = \beta = \pi^* = 0$), α is an index of the solvent's ability to act as a hydrogen-bond donor (or electron pair acceptor) toward a solute and β is a measure of the ability of a bulk solvent to act as a hydrogen-bond acceptor (or electron-pair donor), π^* is an index of the solvent polarity/polarizability which measures the solvent's ability to stabilize a neighbouring charge or dipole through non-specific dielectric interactions and δ is polarizability correction for different types of solvent (aliphatic, aromatic or halogenated). Often, the contribution of δ is negligible leading to the simplified equation (2), from which the parameters a, b and p (corresponding to the responses of the appropriate solute molecular property to the relevant solvent property) can be retrieved through a multiparametric fitting on various solvents:

$$\bar{\nu} = \bar{\nu}_0 + a\alpha + b\beta + p\pi^* \quad (2)$$

In the present paper we have studied the MLCT band solvent sensitivity of a series of [Re(R_2bpy)(CO)$_3$X] (R = H, *t*-Bu; X = Cl^-, OTf^-, C≡CpyRe(R_2bpy)(CO)$_3$) [40–42] complexes (Scheme 1).

The effect of the labile position (X = OTf^-) on the solvent sensitivity of the absorption and emission spectra of these compounds has been studied in representative solvents which cover a large polarity range, as well as the effect of an electron donating group in the bipyridyl ligand (R = *t*-Bu).

Interestingly, compounds that present a labile position (**1** and **3**) show emission solvatochromism while compounds **2**, **4** and **5** do not.

Since rhenium(I) diimine compounds are known to coordinate CO_2 and have been shown to act as photocatalysts and/or electrocatalysts for CO_2 reduction to CO [43,44], the luminescence of **1** and **3** has been explored towards CO_2 detection. Quenching assays show that the emission of **1** and **3** exhibits good sensitivity to the presence of dissolved CO_2 in acetonitrile.

2. Experimental methods

2.1. Materials

Compounds **1** [40], **2** [41], **3** [40], **4** [41] and **5** [42] (Scheme 1) were synthesized as described previously in the literature. Dichloromethane (Fluka, p.a. grade), dimethylformamide (Riedel, >99.5%, p.a. grade), methanol (Riedel, >99.8%, p.a. grade), dimethylsulfoxide (Riedel, >99%), carbon tetrachloride (Merck, >99.7%), cyclohexane (Panreac, >99.9%), chloroform (Riedel, >99%), tetrahydrofurane (Merck, >99.7%), ethyl acetate (Merck, >99.7%) and 1,4-dioxane (Riedel, >99.5%) were used as received. Acetonitrile (Riedel, >99.5%) was dried over CaH_2 and distilled under nitrogen atmosphere.

2.2. Apparatus

Absorption spectra were recorded on a Shimadzu UV-2510 PC, UV–vis recording spectrophotometer. Emission spectra were recorded on a SPEX Jobin–Yvon Fluorolog 3 spectrofluorimeter. Volumes smaller than 1 ml were measured with microliter pipettes Pipetman (Gilson).

2.3. Solution preparations

Complexes **1**–**5** were prepared in dichloromethane, in a 10^{-3} M concentration. 500 μl (for compounds **1**, **3** and **5**) or 100 μl (for compounds **2** and **4**) were introduced in a 10 ml flask and concentrated to dryness under vacuum for 1 h. The resulting solid was dissolved

Table 1
α, β, π^* parameters for the solvents used [1].

Solvent	α	β	π^*	ε_r	n
Dichloromethane	0.3	0	0.82	8.93	1.4242
Carbon tetrachloride	0	0	0.28	2.24	1.4602
Chloroform	0.44	0	0.58	4.89	1.4459
Methanol	0.93	0.62	0.60	32.66	1.3284
Acetonitrile	0.19	0.31	0.75	35.94	1.3441
Dimethylformamide	0	0.69	0.88	36.71	1.4305
Tetrahydrofuran	0	0.55	0.55	7.58	1.4072
1,4-Dioxane	0	0.37	0.55	2.21	1.4224
Ethyl Acetate	0	0.45	0.55	6.02	1.3724
Cyclohexane	0	0	0	2.02	1.4262
Dimethylsulfoxide	0	0.76	1	46.45	1.4793
Toluene	0	0.11	0.54	2.38	1.4969
Benzene	0	0.1	0.59	2.27	1.5011

in the corresponding organic solvent to obtain 5×10^{-5} M solutions for compounds **1**, **3** and **5** and 1×10^{-5} M for compounds **2** and **4**.

Final absorbances under 0.2 of the MLCT band (wavelength excitation band for emission spectra acquisition) were obtained.

2.4. Measurements

The absorption spectra were recorded with 1 nm resolution for all cases. The wavelength of the MLCT transition was determined both by a peak detection algorithm of Origin 7.0 Professional from Microcal and by visual confirmation.

2.5. DFT calculations

Ground state electronic structure calculations of rhenium(I) organometallic compounds **1–5** have been performed using density functional theory (DFT) [45] methods employing the Gaussian 03 software package [46]. Ground state geometries were obtained in the gas phase by full geometry optimization. The optimum structures, located as saddle points on the potential energy surfaces, were verified by the absence of imaginary frequencies. The basis set used throughout this study was the LANL2DZ basis functions together with the corresponding effective core potential for Re atom and the basis set 6-31G** for the C, N, O, Cl and H atoms. In order to estimate the response of the electronic structure to solvation, the solvent was modelled using the polarizable continuum model (single point PCM) as implemented in Gaussian 03. The singlet excited states of the closed shell complexes were calculated with the TDDFT formalism [47–50]. Moreover, non-equilibrium single point TDDFT/PCM calculations, as implemented in Gaussian 03, were employed in order to reproduce the solvation of the excited states. The polarizability of the excited states was computed using the polar = ENONLY input to Gaussian03 which requests double numerical differentiation of energies to produce polarizabilities.

2.6. Kamlet–Taft parameters

The solvents used in this work together with their respective solvent parameters (α, β, π^*) employed in the correlations are presented in Table 1.

2.7. Determination of saturation concentration of CO_2 in acetonitrile and dimethylformamide

30 ml of either acetonitrile or dimethylformamide were introduced in a Shlenck and several cycles of freeze–pump–thaw were performed until the solvent was fully degassed (no bubbles observed during thaw process). The degassed solution was weighted in an analytical balance. Then the Shlenck was connected to a CO_2 bottle and a flow of CO_2 was passed through the solution at atmospheric pressure after pre-saturation with the corresponding solvent in order to avoid solvent evaporation of the degassed solution. The Shlenck was then weighted and the CO_2 concentration calculated by difference. Several measurements were made until the CO_2 concentration become stabilized.

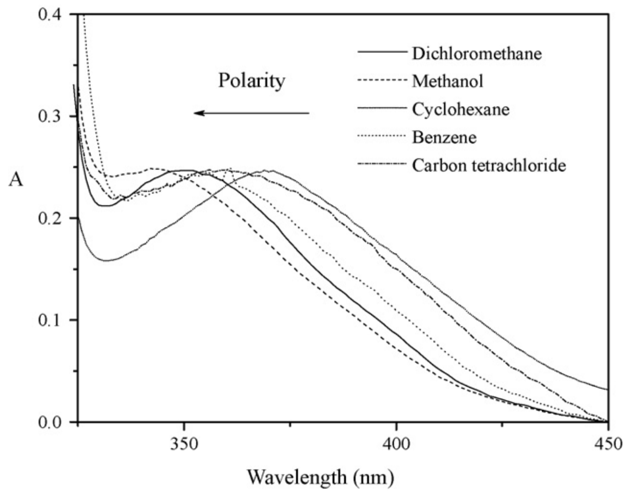


Fig. 1. Normalized absorption spectra for compound **3** in different solvents.

3. Results and discussion

3.1. Solvent effect on the absorption spectrum

The solvent effect on the absorption spectra of compounds **1**–**5** has been investigated. In all cases a blue shift (negative solvatochromism) is observed in the lowest energy electronic transition on going to solvents with increasing polarity as illustrated in Fig. 1, where absorption spectra of compound **3** are shown in different solvents.

In general trends, the results show that absorption spectra of mononuclear compounds are more affected with solvent polarity than binuclear complexes. While energy changes on absorption spectra for compounds **1**, **3** and **5** can be as large as 2000–3000 cm^{-1} over the full polarity range studied, for binuclear complexes the observed changes are roughly half that value (~1400 cm^{-1}, see Table 2). The greatest solvatochromic effect is displayed by compound **3** (2974 cm^{-1}) which is on the order of that reported for other organometallic carbonyl derivatives [21].

The presence of electrodonating groups in the bipyridine ligand increases the solvent sensitivity of the transition with respect to their analogue non-substituted bipyridine derivatives. Thus, absorption solvatochromism of compound **3** is larger than that **1** ($\Delta\bar{\nu}$ (**3–1**) ~1000 cm^{-1}) over the polarity range studied. The same trend is observed between compounds **4** and **2** although the difference is very small in this case ($\Delta\bar{\nu}$ (**4–2**) ~100 cm^{-1}).

It is known that substituents affect the position of the absorption maxima since they perturb the HOMO–LUMO energies [51]. Electron donor groups shift the absorption maximum to lower wavelength, while the electron withdrawing groups act in the reverse way. This is observed in the mononuclear compounds used in this work which differ in the substituents on the bipyridine ligand (**1** and **3**, see Table 2), while the same trend is not observed for the binuclear compounds **2** and **4**.

Ground state electronic structure calculations of compounds **1**–**5** have been performed using density functional theory (DFT) [45] models. Table 3 describes the orbitals involved in the lowest energy singlet electronic transitions of the compounds. The transitions with the highest oscillator strength are marked in bold and

Table 2
Experimental values for the energy of the MLCT absorption band (nm and cm^{-1}) of compounds **1**–**5**.

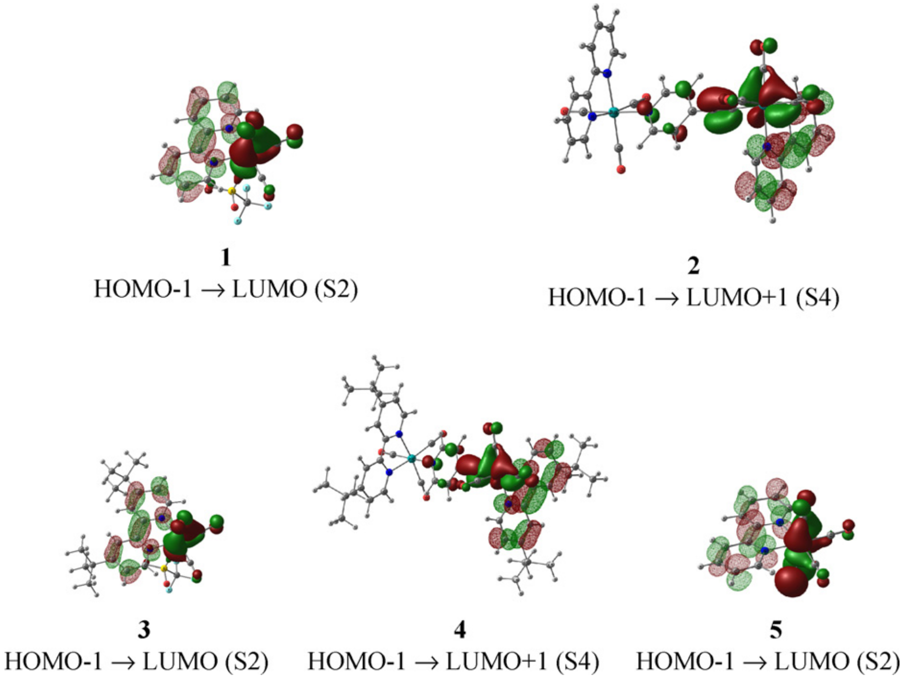
Solvent	λ (**1**), nm (cm^{-1})	λ (**2**), nm (cm^{-1})	λ (**3**), nm (cm^{-1})	λ (**4**), nm (cm^{-1})	λ (**5**), nm (cm^{-1})
Dichloromethane	357 (28,011)	357 (28,011)	350 (28,571)	359 (27,855)	385 (25,974)
Carbon tetrachloride	366 (27,322)	363[a] (27,548)	364 (27,473)	363 (27,548)	[b]
Chloroform	358 (27,933)	357 (28,011)	351 (28,490)	358 (27,933)	391 (25,575)
Methanol	350 (28,571)	350 (28,571)	344 (29,070)	353 (28,329)	364 (27,473)
Acetonitrile	334[a] (29,940)	351 (28,490)	328[a] (30,488)	351 (28,490)	372 (26,882)
Dimethylformamide	354 (28,249)	349 (28,653)	336[a] (29,762)	350 (28,571)	370 (27,027)
Tetrahydrofurane	349 (28,653)	354 (28,249)	341[a] (29,326)	354 (28,249)	387 (25,840)
Dioxane	354 (28,249)	353 (28,329)	336[a] (29,762)	356 (28,090)	392 (25,510)
Ethyl Acetate	356 (28,090)	353 (28,329)	341 (29,326)	353 (28,329)	386 (25,907)
Cyclohexane	368[a] (27,174)	367[a] (27,248)	369 (27,100)	366 (27,322)	[b]
Dimethylsulfoxide	343[a] (29,155)	349 (28,653)	339 (29,499)	349 (28,653)	367 (27,248)
Toluene	360 (27,778)	362 (27,624)	358 (27,933)	360 (27,778)	399 (25,063)
Benzene	363 (27,548)	359 (27,855)	356 (28,090)	359 (27,855)	398 (25,126)

[a] Absorption shoulder; extrapolated value.

[b] Compound not soluble enough in this solvent.

Table 3
Selected TDDFT calculated composition of the lowest energy singlet excited states (Sn) of compounds **1**–**5**, $Sn \leftarrow S0$ oscillator strengths and transition energies (eV). Entries in bold represent the transition with highest oscillator strength shown in Fig. 2.

Compound	Singlet transition							
	S1		S2		S3		S4	
1	$\Delta E = 3.369$ $f = 0.0143$	LUMO ↑ HOMO − 1	$\Delta E = 3.474$ $f = 0.0352$	**LUMO** ↑ **HOMO** − 1	$\Delta E = 3.763$ $f = 0.0009$	LUMO ↑ HOMO − 2	–	
2	$\Delta E = 2.258$ $f = 0.0034$	LUMO ↑ HOMO − 1	$\Delta E = 2.310$ $f = 0.0010$	LUMO ↑ HOMO − 1	$\Delta E = 3.041$ $f = 0.0017$	LUMO + 1 ↑ HOMO	$\Delta E = 3.092$ $f = 0.0572$	**LUMO** + 1 ↑ **HOMO** − 1
3	$\Delta E = 3.534$ $f = 0.0210$	LUMO ↑ HOMO − 1	$\Delta E = 3.628$ $f = 0.0441$	**LUMO** ↑ **HOMO** − 1	$\Delta E = 3.917$ $f = 0.0010$	LUMO ↑ HOMO − 2	–	
4	$\Delta E = 2.499$ $f = 0.02042$	LUMO ↑ HOMO − 1	$\Delta E = .542$ $f = 0.0009$	LUMO ↑ HOMO − 1	$\Delta E = 3.216$ $f = 0.0025$	LUMO + 1 ↑ HOMO	$\Delta E = 3.258$ $f = 0.0740$	**LUMO** + 1 ↑ **HOMO** − 1
5	$\Delta E = 2.880$ $f = 0.0013$	LUMO ↑ HOMO − 1	$\Delta E = 2.957$ $f = 0.0328$	**LUMO** ↑ **HOMO** − 1	$\Delta E = 3.625$ $f = 0.0003$	LUMO ↑ HOMO − 1	–	



1
HOMO-1 → LUMO (S2)

2
HOMO-1 → LUMO+1 (S4)

3
HOMO-1 → LUMO (S2)

4
HOMO-1 → LUMO+1 (S4)

5
HOMO-1 → LUMO (S2)

Fig. 2. Representation of the B3LYP/6-31G** isosurfaces 0.045 e^{-} au^{-3} of the orbitals involved in the dominant electronic transition. Occupied orbital is coloured opaque while unoccupied orbital is coloured transparent. (**1**) HOMO − 1 → LUMO (S2). (**2**) HOMO − 1 → LUMO + 1 (S4). (**3**) HOMO − 1 → LUMO (S2). (**4**) HOMO − 1 → LUMO + 1 (S4). (**5**) HOMO − 1 → LUMO (S2).

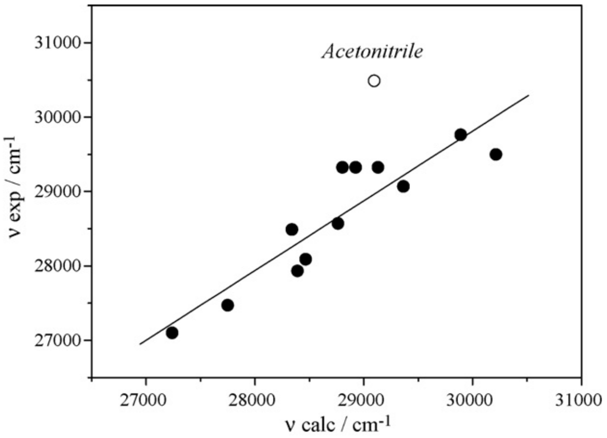


Fig. 3. Plot of $\bar{\nu}_{\text{exp}}$ vs. $\bar{\nu}_{\text{calc}}$ for absorption data of compound **3**.

Table 4
$\bar{\nu}_0$, a, b and p-values, in cm^{-1}, as well as slope and correlation coefficients obtained from Kamlet–Taft multiparametric fitting of the absorption data.

Compound	$\bar{\nu}_0$	a	b	p	Slope	r^2
1	27,080	388	970	1352	0.95	0.81
2	27,386	209	827	676	1.16	0.93
3	27,240	97	1517	1822	0.93	0.87
4	27,385	68	826	757	0.99	0.90
5	23,512	1450	1740	2637	1.00	0.93

are also represented in Fig. 2 as electron isodensity surface plots of the principal orbitals populated and depopulated upon excitation.

In all cases the HOMO, HOMO − 1 and HOMO − 2 orbitals involved are metal centred orbitals and the LUMO and LUMO + 1 orbitals are centred at the bipyridine ligand, i.e., all the transitions are MLCT in character, as it is known in literature [52–55]. TDDFT calculations show that in the mononuclear compounds the most important transition is S2 ← S0 while in the binuclear compounds **2** and **4** the most important transition is S4 ← S0.

Multiparametric fitting of the Kamlet–Taft equation (Eq. (2)) to the observed MLCT absorption energies in 13 different solvents have been performed (see list of solvents in Table 1). With this treatment, linear plots of $\bar{\nu}_{\text{exp}}$ versus $\bar{\nu}_{\text{calc}}$, like the exemplified for compound **3** (Fig. 3), have been obtained for all compounds and the fitted parameters ($\bar{\nu}_0$, a, b and p), as well as slope and correlation coefficients are presented in Table 4.

Plots of $\bar{\nu}_{\text{exp}}$ versus $\bar{\nu}_{\text{calc}}$ yield slopes that are close to 1 and reasonable correlation coefficients are obtained in all cases.

Solvatochromism in the absorption of compounds **1**–**4** is essentially reflected in p and b solute parameters (see Table 4), i.e., higher sensitivity to the polarity/polarizability of the solvent and to the H-bond acceptor (or electron donor) strength of the solvents. On the other hand, chloride derivative (**5**) presents a significantly higher a parameter which means that the energy of the observed transition in **5** is also affected by the acceptance of hydrogen bonds from (or donation of electron pairs to) the solvent.

A point to retain is that acetonitrile does not correlate in the fitting of the mononuclear compounds **1** and **3**, where a labile coordination site occupied by a triflate ion exists. This must reflect a change in the coordination sphere (e.g. ion pair separation or solvent coordination) which cannot be justified by the solvation terms included in the Kamlet–Taft treatment. Acetonitrile correlates well in the linear plots of **2**, **4** and **5** where no labile position exists.

3.2. DFT predictions of the solvent polarity/polarizability effect

Ground state dipole moments and polarizabilities were calculated and confirm that substitution with the t-butyl groups increases both the polarizability and ground state dipole moment of the molecule (Table 5) which is compatible with the higher p values obtained for **3** and **4** with respect to **1** and **2**, respectively (Table 4).

Ground state dipole moments have also been calculated according to the McRae–Bayliss model of solvatochromism which is directly evolved from of Onsager's reaction field theory [1] where the electronic transition from the ground to the excited state of a solvatochromic solute is given by the following equation:

$$\bar{\nu}_{\text{eg}} = \bar{\nu}_{0,\text{eg}} - x(F_1 - F_2) - yF_2 \tag{3}$$

where $x = ((\bar{\nu}_{\text{g}}\bar{\nu}_{\text{e}}\cos\phi - \bar{\nu}_{\text{g}}^2)1/a^3)$, $y = ((\bar{\nu}_{\text{g}}^2 - \bar{\nu}_{\text{g}}^2)1/a^3)$, $F_1 = 2(\varepsilon_{\text{r}} - 1)/(2\varepsilon_{\text{r}} + 1)$ and $F_2 = 2(n^2 - 1)/(2n^2 + 1)$ and ε_{r} and n are the permitivity constant of the solvent and the corresponding diffraction index, respectively (see Table 1). The values obtained with this treatment (see Table 6) are in reasonable agreement with the ground state dipole moments calculated by DFT (Table 5).

The dipole moment shift of compound **5**, when going from the ground state to the excited state, has been studied previously, using both experimental and theoretical (semi-empirical) approaches [29]. Experimental values were 7.7 and 3.0 D for ground (gs) and excited (es) states, respectively, while the semi-empirical method used afforded 12.0 D for the gs (no excited states were calculated). Our calculated values, in gas phase, afforded 10.6 and 1.9 D for ground and excited states, respectively, which are in good agreement with the experimental ones [29].

Table 5
Ground state dipole moment (μ_{gs}) and excited state dipole moment (μ_{es}). Polarizability of the ground state α_{gs} and excited state (α_{es}). α_{es} calculated as $1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$.

Compound	Solvent	μ_{gs} (D)	α_{gs} (a.u.)	μ_{es} (D)	α_{es} (a.u.)	Transition	E_{TDDFT} (eV)	λ (nm)	*Oscillator strength*
1	Gas phase	10.385	233.76	5.953	219.02	**LUMO** ↑ **HOMO** − 1	2.7331	453.64	0.0353
	DMSO	15.142	322.83	8.457	401.41		3.3566	369.38	0.0841
2	Gas phase	4.867	528.68	16.930	641.62	**LUMO** + 1 ↑ **HOMO** − 1	2.4994	496.05	0.0572
	DMSO	9.940	722.38	19.698	892.20		2.9152	425.30	0.0457
3	Gas phase	12.032	331.71	5.496	327.69	**LUMO** ↑ **HOMO** − 1	2.8915	428.79	0.0441
	DMSO	16.910	437.65	9.054	526.12		3.4028	364.35	0.1014
4	Gas phase	5.349	723.10	18.203	–	**LUMO** + 1 ↑ **HOMO** − 1	2.6552	466.95	0.0740
	DMSO	–	–	–	–		–	–	–
5	Gas phase	10.579	213.94	1.906	234.61	**LUMO** ↑ **HOMO** − 1	2.2948	540.29	0.0328
	DMSO	14.914	297.80	4.281	390.51		3.2105	386.18	0.0753

Table 6
Ground state dipolar moments obtained through the application of the Onsager equation to the experimental values.

Compound	μ_{gs} (D)
1	7.83
2	6.90
3	10.25
4	4.57
5	9.21

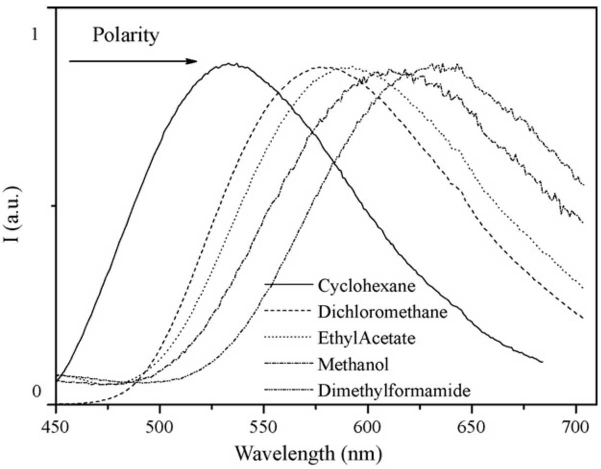


Fig. 5. Normalized emission spectra for compound **1** in different solvents.

A stabilization of a strong dipolar ground state in polar solvents would have some influence for the observed negative solvatochromism. The ground state (*gs*) dipole moment calculated for compound **1** is similar to the calculated for **5** and double in magnitude with respect to the calculated dipolar moment of binuclear compounds **2** and **4**. The corresponding value calculated for **3** is higher. This is compatible with the larger negative solvatochromism showed by compound **3** with respect to their analogues mononuclear compounds.

The theoretical data obtained in solvent ($\varepsilon = 46.7$, DMSO) has also been calculated (see Fig. 4). We have not been able, due to computational limitations, to calculate the solvated excited state of compound **4**.

Energetic stabilizations of all ground states are observed in the presence of solvent, with similar variations for compounds **1** and **5**. Compound **3** is predicted to be less stabilized, in spite of having larger dipolar moment (12.0 D).

The comparison of the excited states shows quite different behaviours. The *es* of compound **1** is stabilized in 0.26 eV, while the es of compound **3** is stabilized only in 0.16 eV and the es of compound **5** is not stabilized at all, or even destabilized (0.001 eV). This means that the strong negative solvatochromism of compound **5** depends, in some extent, on the solvent stabilization of the *gs* and does not depend on the relative stability of its *es* in solvents of various polarities as happens for compounds **1** and **3**. Nevertheless, specific interactions with the solvent, like hydrogen bonding, not accounted in a continuum solvation model, can also have a significant impact on the solvatochromism of **5**.

The bimetallic compounds **2** and **4** exhibit quite different behaviour, relatively to the mono-metallic complexes, and must be discussed separately. Although we have not values for the solvated excited state of compound **4**, we will assume that it should not behave much different that compound **2**, considering the similarities of their ground states. In spite of having a considerably lower dipolar moment in gas phase (4.9 D, Table 5), compound **2** has the strongest energetic stabilization due to solvation (2.28 eV) as shown in Fig. 4. This value, which is more than the double of that calculated for compound **5** (0.91 eV) cannot be solely explained on the basis of the ground state dipolar moment. Nevertheless, a justification can be found if the polarizabilities of compound **2** are compared with those of **1**–**3** and **5**. Compound **2** has a considerably larger value, which allows for a stronger stabilization due to solvation. Based on this observation, one could expect a strong blue shift of its absorption spectra in polar solvents. Nevertheless, this is not observed, neither experimentally nor theoretically, implying that the excited state has also to suffer a strong solvent stabilization. This indeed can be observed in Fig. 4 and can be justified on the basis of two different reasons. On one hand the solvated excited state of compound **2** has also a large polarizability value. On the other hand, the relative dipolar directions, between the ground and excited states (Fig. S1, supporting information) are quite similar, meaning that the solvent shell calculated for the ground state is also efficient on the stabilization of the dipolar moment of the excited state. Due to these contributions, the solvated excited state of compound **2** is only slightly less stabilized in solvent (1.86 eV) than its ground state (2.28 eV), and quite more stabilized than the excited states of all the other studied structures. This is compatible with the less solvatochromic effect observed in absorption for binuclear compounds.

3.3. Emission solvatochromic behaviour

Emission spectra have also been recorded in different solvents (Table 7), and a red shift of the emission from the ^{3}MLCT state is observed with increasing solvent polarity (positive solvatochromism), as shown in Fig. 5 where emission spectra of compound **1** are shown in different solvents.

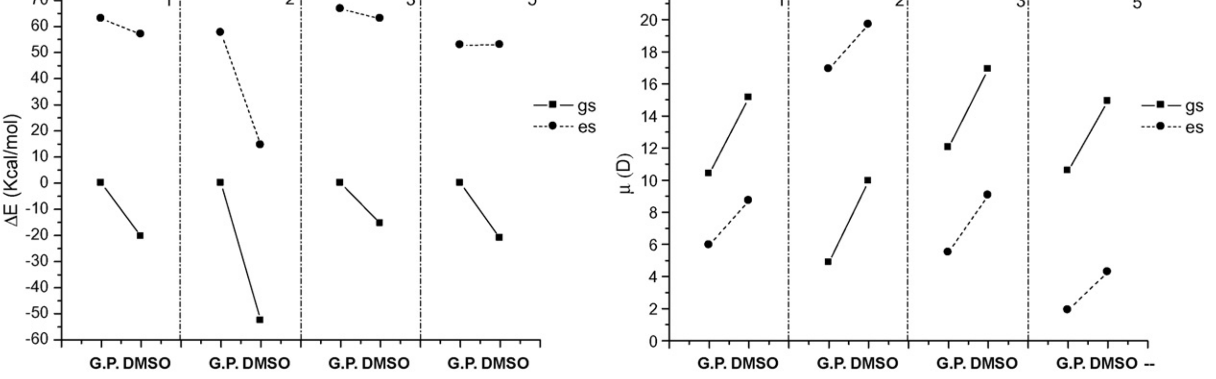


Fig. 4. Plot of ΔE shifts (left) and dipole moment shifts (right) of compounds **1**–**3** and **5**, when going from gas phase to a polar solvent (DMSO).

Table 7
Experimental values for the MLCT emission energy band (nm and cm^{-1}) of compounds **1**–**5**.

Solvent	λ (**1**), nm (cm^{-1})	λ (**2**), nm (cm^{-1})	λ (**3**), nm (cm^{-1})	λ (**4**), nm (cm^{-1})	λ (**5**), nm (cm^{-1})
Dichloromethane	582 (17,182)	639 (15,649)	566 (17,667)	603 (16,583)	627 (15,948)
Carbon tetrachloride	550 (18,181)	596 (16,778)	532 (18,796)	616 (16,233)	562 (17,794)
Chloroform	586 (17,065)	631 (15,848)	571 (17,513)	609 (16,420)	626 (15,974)
Methanol	619 (16,155)	641 (15,601)	600 (16,667)	620 (16,129)	629 (15,898)
Acetonitrile	560 (17,857)	645 (15,504)	549 (18,215)	629 (15,898)	635 (15,748)
Dimethylformamide	632 (15,823)	647 (15,456)	600 (16,667)	628 (15,926)	633 (15,798)
Tetrahydrofurane	591 (16,920)	644 (15,528)	580 (17,241)	616 (16,234)	635 (15,748)
Dioxane	591 (16,920)	635 (15,748)	581 (17,212)	630 (15,873)	634 (15,773)
Ethyl Acetate	590 (16,949)	639 (15,649)	586 (17,065)	620 (16,129)	636 (15,723)
Cyclohexane	538 (18,587)	587 (17,036)	519 (19,268)	618 (16,181)	560 (17,857)
Dimethylsulfoxide	638 (15,674)	646 (15,480)	619 (16,155)	626 (15,974)	634 (15,773)
Toluene	581 (17,212)	605 (16,529)	573 (17,452)	625 (16,000)	626 (15,974)
Benzene	586 (17,065)	618 (16,181)	571 (17,513)	623 (16,051)	622 (16,077)

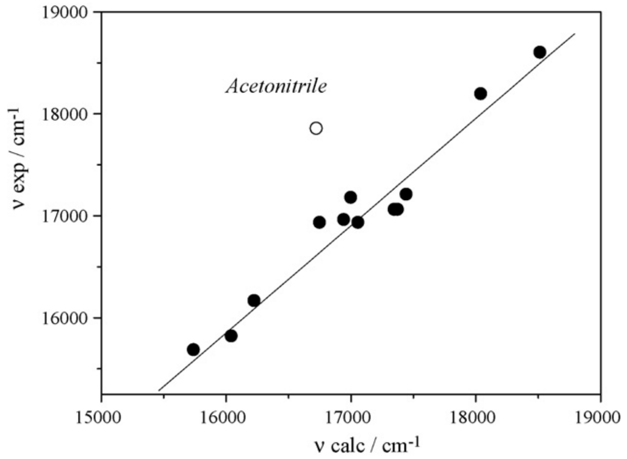


Fig. 6. Plot of $\bar{\nu}_{exp}$ vs. $\bar{\nu}_{calc}$ for emission data of compound **1**.

Since solvent shells optimized for the excited states shall be less efficient on the stabilization of the ground states, the net result will be a stronger stabilization of the excited states, with the consequent emission red shift. This is due to changes in directions and scalar values of ground and excited states dipolar moments as well as to changes in polarizability.

The multiparametric fitting of the Kamlet–Taft equation has also been applied to the emission maxima of compounds **1**–**3** and **5**. Linear plots were only obtained for both **1** and **3** which are the compounds that display significant solvatochromic effect in emission (see Fig. 6). Compound **4** does not show any significant change with solvent polarity, and the solvatochromism of **2** and **5** is not linear and can only differentiate between the most apolar solvents (cyclohexane and carbon tetrachloride) and the others (see plot for compound **5** in Fig. S2, supporting information).

The solute parameters, $\bar{\nu}_0$, *a*, *b* and *p*, slope and correlation coefficients obtained from the fitting of emission data are presented in Table 8. The solvatochromic effect is essentially an effect of the polarity/polarizability of the solvent (*p* parameter) and the H-bond acceptor (or electron donor) strength of the solvents (*b* parameter), as seen in the absorption data.

Table 8
$\bar{\nu}_0$, *a*, *b* and *p*-values, in cm^{-1}, as well as slope and correlation coefficients obtained from Kamlet–Taft multiparametric fitting of the emission data.

Compound	$\bar{\nu}_0$	*a*	*b*	*p*	Slope	r^2
1	18,507	−403	−1498	−1583	1	0.95
2	16,934	–	–	–	–	–
3	18,977	−349	−1462	−1640	1	0.90
5	17,556	–	–	–	–	–

Acetonitrile must be excluded from the correlation in order to obtain good fittings for compounds **1** and **3**, as occurred in the absorption.

Another point to retain is the different behaviour exhibited by the complexes although their similar structural characteristics. While compounds **1** and **3** show linear dependence on solvent polarity that allow a confident treatment with the Kamlet–Taft equation, similar work with compounds **2**, **5** and **4** yield no correlation with solvent polarity. The labile position in **1** and **3** seems to be important in the observed emission solvatochromism. Moreover, only in the case of acetonitrile a significant change in the coordination sphere seems to occur, as can be reflected in the off-correlation shown only by this solvent.

3.4. CO_2 detection studies

Rhenium(I) diimine compounds have been shown to act as photocatalysts and/or electrocatalysts for CO_2 reduction to CO [43,44]. Due to the known CO_2 coordination to rhenium atoms, the use of compounds **1** and **3** in CO_2 detection studies seemed an interesting way to inspect the availability of their labile coordination site by means of changes in their absorption and/or emission spectra upon saturation with this gas.

The experiments were carried out in acetonitrile and dimethylformamide in order to test the sensitivity to CO_2 in two solvents with different behaviour with respect to solvatochromic trends. Solutions of compounds **1** and **3** were saturated with argon in order to minimize the quenching by the oxygen present in air. Then, CO_2 and argon have been alternately bubbled into the samples and the corresponding absorption and emission spectra have been recorded at each point. Clear reversible changes have been recorded in emission in both solvents (acetonitrile and dimethylformamide) and for both compounds (**1** and **3**). While only a *ca.* 10% quenching effect is observed in dimethylformamide, the saturation of deaerated acetonitrile solutions with CO_2 leads to a decrease in emission of *ca.* 50% (see Fig. 7). Absorption spectra did not show noticeable changes in either case.

In order to check if the observed quenching was due to the existence of coordination complexes with CO_2 or simply due to collisional quenching, resulting from encounters between the excited complex and a CO_2 molecule, the decay times were measured in degassed solutions of several solvents and the results are presented in Table 9. All the recorded decays are fitted with a single exponential, which is in agreement with the presence of a single emitting species in solution, *i.e.*, in case of the presence of solvent coordination, the equilibrium is fully shifted toward the solvent coordinated complex.

In the majority of the solvents the decay times of **1** are in the range ∼100–200 ns, except in dimethylformamide, dimethylsulfoxide and methanol, where the decays are significantly shorter

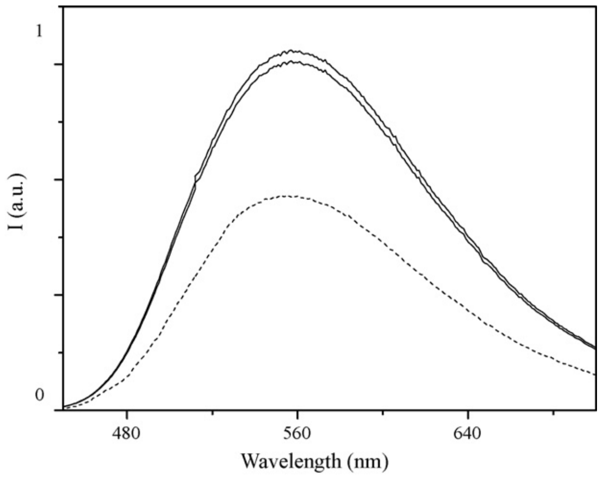


Fig. 7. Emission spectra of 1×10^{-5} M solution of compound **1** in acetonitrile (λ_{exc} = 358 nm) with different saturation cycles with argon (solid line) and carbon dioxide (dashed line).

(~10–30 ns), and acetonitrile where the decay is much longer (458 ns), in the same order of the values previously observed for similar compounds in acetonitrile [56]. The same trend is observed for compound **3**. The longer decay time in acetonitrile, as well as the significantly shorter decay times in dimethylformamide, dimethylsulfoxide and methanol, are indicative of solvent interactions which are present in these solvents and absent (or present in much less extent) in the case of the remaining solvents. The opposite effect of these solvents in the decay times could be related with the different nature of the metal–solvent coordinating bond (Re–O in the case of shorter decay times and Re–N in the case of longer decay times).

The longer decay time observed in acetonitrile could explain the higher quenching observed in this solvent without the need of considering the presence of coordination of CO_2 to the complex. However, a more careful analysis of the data indicates otherwise. Solutions of **1** in acetonitrile, saturated with CO_2, have an emission decay time of 140 ns. The saturation concentration of CO_2 in acetonitrile at 1 atm and 40 °C (0.57 M) can be extrapolated from the linear part of the *Px* diagrams (low Pression region) [57]. There are no published data for the saturation concentration of CO_2 in acetonitrile at 25 °C and 1 atm, but weighting measurements performed by us give a value in accordance (0.6 M). A Stern–Volmer analysis of the observed quenching in CO_2 saturated acetonitrile solutions of **1** yields a quenching rate constant much lower than expected for diffusional quenching ($k_q = 8.6 \times 10^6\ s^{-1}$), which implies some chemical rate limiting step for the observed quenching. The analysis of the data obtained in dimethylformamide, where the extrapolated concentration saturation of CO_2 is lower (0.14 M) [58] yields a quenching rate constant of the same order ($4.7 \times 10^7\ s^{-1}$). In conclusion, the fact that a much higher quenching effect is observed in acetonitrile has two origins: (1) CO_2 is more soluble in MeCN and (2) the decay time in MeCN (without CO_2) is higher, probably due to the coordination of the solvent through the nitrogen atom. At the same time, the fact that the observed quenching rate constants are similar in both solvents and their orders of magnitude below that of diffusion, suggests that in both cases the quenching involves solvent substitution by CO_2. Based on these results we must conclude that, despite we have no strong evidence for the complexation of CO_2 with either **1** or **3**, we cannot account for the value of the quenching rate constants without assuming it.

Table 9
Emission decay times of compound **1**, collected at room temperature.

Solvent	τ (1) (ns)	τ (3) (ns)
Dichloromethane	189	239
Carbon tetrachloride	117	70
Chloroform	117	107
Methanol	11	30
Acetonitrile	458	566
Dimethylformamide	33	56
Tetrahydrofurane	92	36
Dioxane	107	110
Ethyl Acetate	87	97
Cyclohexane	61	60
Dimethylsulfoxide	10	13
Toluene	162	138
Benzene	176	78

4. Conclusions

Kamlet–Taft multiparametric equation and DFT calculations have been used to explain the solvent effect in the MLCT transition band of a series of mono and bimetallic rhenium(I) complexes. DFT calculated values of dipolar moments and polarizabilities and calculated solvent effects in the ground and excited states, offer a rationale that contributes to understand the observed solvatochromic behaviour in general terms.

In summary, there are two facts to retain. Firstly, substituents in the bipyridine ligand affect the solvatochromism of the absorption band, leading to greater solvent sensitivity when the chelate ligand is substituted by electrodonating groups. Secondly, only compounds that possess a labile coordination position in the coordination sphere of the metal exhibit interesting solvatochromism in emission. These compounds show linear dependence on solvent parameters that allow a confident treatment with Kamlet–Taft equation for all solvents except acetonitrile, which could be related with changes in the coordination sphere occurring in it. At the same time, a significant quenching of the emission is observed in acetonitrile when the solutions are saturated with CO_2, when compared with deaerated solutions. The effect of CO_2 is much less important in dimethylformamide. Nevertheless, the similar values calculated for the quenching rate constants in both solvents, that are some orders of magnitude below diffusion, suggest that in both cases the quenching involves solvent substitution by CO_2.

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Appendix A. Supporting information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.03.022.

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