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The photophysical properties of monomeric and dimeric ruthenium polypyridyl complexes immobilized in sol-gel matrices

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Abstract

The temperature dependence of the emission properties of the compounds $[Ru(phen)_2(3Mptr)]^+$ (**1**), $[Ru(bpy)_2(bpt)]^+$ (**2**), $[Ru(bpy)_2(bpzt)]^+$ (**3**), $[\{Ru(bpy)_2\}_2(bpt)]^{3+}$ (**4**) and $[\{Ru(bpy)_2\}_2(bpzt)]^{3+}$ (**5**) in solution and in tetraethylorthosilicate xerogels is reported. It is shown that the excited state parameters of the compounds are strongly affected by the matrix and are dependent on the initial pH of the gel.

Keywords: Photophysical; Polypyridyl complexes; Sol-gel matrices

1. Introduction

In the last two decades, there has been increasing interest in the investigation of the properties of ruthenium (II) polypyridyl complexes immobilized in solid matrices. This interest is motivated by the possible application of such modified glasses as sensors for oxygen [1] and as a result, an extensive chemistry dealing with the immobilization of Ru(II) polypyridyl complexes in sol-gel derived glasses, Vycor glass and other solid matrices has emerged [2]. Because of this proliferation of practical applications of such solid state materials the study of the photophysics of solid matrices is becoming more and more important. However, the study of the photophysical pathways of Ru(II) polypyridyl complexes in solids has progressed at a slow pace and studies have mostly concentrated on complexes of the type $[Ru(L)_3]^{2+}$, where L stands for polypyridyl ligands such as 2,2′-bipyridyl and 4,7-diphenyl-1,10-phenanthroline [3]. The photophysical aspects of such materials are by no means straightforward. In contrast to solution based systems, solid supports are frequently heterogeneous on a microscopic scale, giving rise to complex characterized decay kinetics. This heterogeneity makes the analysis of photophysical data much more complex than in fluid systems. In an earlier study we reported on the temperature dependence of the photophysical properties of a series mixed ligand Ru(II) complexes of 2,2′-bipyridyl (bpy) and 4,7-diphenyl-1,10-phenanthroline (dpp). These studies found that the photophysical properties were substantially changed upon incorporation into a solid state matrix. For 2,2′-bipyridyl containing complexes no population of the ^3MC level was perceived. For the tris(dpp) complex on the other hand this process was still observed [4].

In the present study we wish to extend our investigations to mixed ligand Ru(II) compounds with intrinsic acid–base properties and to dinuclear compounds. Towards this end mononuclear ruthenium compounds $[Ru(phen)_2(3Mptr)]^+$ (**1**), where H3Mptr is 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole and phen is 1,10-phenanthroline, $[Ru(bpy)_2(bpt)]^+$ (**2**), where Hbpt is 3,5-bis(pyridin-2-yl)-1,2,4-triazole and $[Ru(bpy)_2(bpzt)]^+$ (**3**), where Hbpzt is 3,5-bis(pyrazin-2-yl)-1,2,4-triazole were incorporated into the sol-gel matrix and their excited-state decay behaviour was investigated as a function of temperature and of the nature of the sol-gel. The dinuclear complexes $[\{Ru(bpy)_2\}_2(bpt)]^{3+}$ (**4**) and $[\{Ru(bpy)_2\}_2(bpzt)]^{3+}$ (**5**) have also been studied. For ligand structures see Fig. 1. The photophysical properties of these complexes in solution are well understood [5]. Compounds **1–3** have well defined acid–base properties which lead to significantly different behavior in the temperature dependent luminescent lifetimes for the protonated and deprotonated complexes [6]. It is of interest to examine whether the acid base properties of these compounds are modified by the sol-gel. For the dinuclear compounds it has been established that in **4** the emitting state is based on the bipyridyl ligands, while for **5** the emitting state is based on the bridging ligand [5]. This gives us the opportunity to investigate whether the location of the excited state effects the photophysical properties of the immobilized species in the xerogel.

2. Experimental

2.1. Materials

The compounds $[\mathrm{Ru(phen)_2\ (3Mept)}]^{+}$ (**1**), $[\mathrm{Ru(bpy)_2(bpt)}]^{+}$ (**2**), $[\mathrm{Ru(bpy)_2(bpzt)}]^{+}$ (**3**), $[\{\mathrm{Ru(bpy)_2}\}_2\mathrm{(bpt)}]^{3+}$ (**4**) $[\{\mathrm{Ru(bpy)_2}\}_2\mathrm{(bpzt)}]^{3+}$ (**5**) were available from earlier studies [5].

2.2. Sol-gel preparations

Monolithic sol-gel samples were prepared by the hydrolysis and condensation of tetraethoxysilane (TEOS) in an ethanol solution. A water:TEOS ratio of 4:1 was used. To a mixture of 3.6 g (0.2 mol) of water (adjusted to the appropriate pH using conc. HCl) and 13.8 g (0.3 mol) of ethanol (containing the desired dopant complex), 10.4 g (0.05 mol) of TEOS was added dropwise. The mixture was stirred for 1 h in a sealed beaker before pouring into a plastic cell suitable for spectroscopic measurements. The plastic cell was covered to allow gelation and ageing to occur in a closed environment at a temperature of 50°C. The initial concentration of the complexes in the sols was 10^{-5} M. After ageing (500 h) the sample lid was pierced to allow the evaporation of excess solvent for 300 h. Throughout the sol-gel

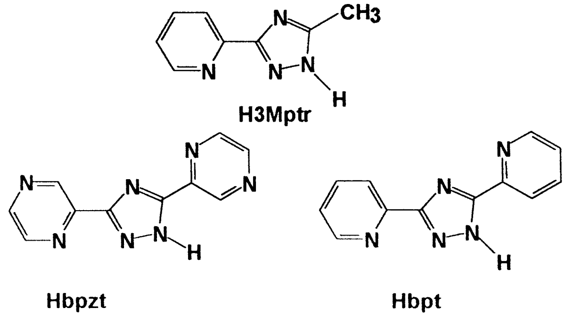


Fig. 1. Structure of the ligands 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (H3Mptr), 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (Hbpzt), and 3,5-bis(pyridyn-2-yl)-1,2,4-triazole (Hbpt).

process samples were stored at 50°C. The time required to reach the gel point was found to depend greatly on the initial pH employed. At pH 1 gelation times were typically 350 h, while at pH 5 a period of 50 h was sufficient [7]. The undoped gels display high optical transparency in the visible region.

2.3. Instrumentation

UV–vis spectra were obtained using a Shimadzu 3100 UV–vis/NIR spectrophotometer. Solid sol-gel sample measurements were obtained using diffuse reflectance.

Emission spectra were carried out with an LS50B spectrometer fitted with a Hamamatsu R928 red-sensitive detector. The spectra were not corrected for photomultiplier response. Emission spectra were determined as a function of temperature with a custom built quartz sample holder in combination with an Oxford Instruments variable temperature liquid nitrogen cryostat PE1704 equipped with a Thor 3030 temperature controller. Samples were degassed for 30 min under nitrogen prior to analysis. The absolute error on the temperature is estimated at ± 2 K. Emission lifetime measurements were carried out using a Q-switched Nd-YAG laser system (Quanta-Ray GCR2, pulse width 9 ns). The emission decay curves were analyzed as single and double exponentials using the standard methods reported previously [4].

3. Results and discussion

For compounds **1–3**, a well-defined acid–base behavior has been observed in solution. The triazole ring of these complexes can be reversibly protonated/deprotonated and this leads to an extensive ground-state and excited-state acid–base chemistry [5b,e,f, 6]. A summary of the relevant parameters is given in Table 1. This table highlights the significant differences between the absorption and emission maxima for the different species. All compounds exhibit intense absorption bands in the visible region of the spectrum, which have been assigned as metal-to-ligand charge-transfer (^{1}MLCT) bands and the emission signals originate from a ^{3}MLCT state [5,8]. This table shows that the ground state pK_a values for these compounds are between 2 and 5 and that, in agreement with earlier observations for pyridyltriazoles [5a], **1** and **2** are more acidic in the excited state. This observation suggests that in these compounds the excited state is based on the polypyridyl ligands [6,9]. The spectroscopic properties of **1** and **2** can be presented as shown in Scheme 1 for compound **1**. For compound **3** the situation is more complex. It has been shown previously that for mononuclear pyrazinetriazole based complexes the excited state is located on the bpy when the triazole is deprotonated and is pyrazine based for protonated triazole complexes [5h,i, 6c]. The small shift in absorption and emission maxima are unfortunately not indicative for the protonation state of the species.

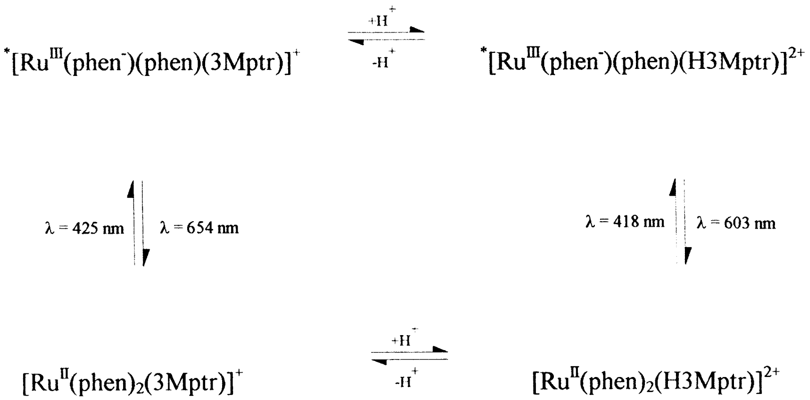
Table 1
Acid-base properties of compounds **1**–**3**

Compounds	pH 1		pH 7		pK_a	pK_a[a]
	Absorption (nm)	Emission (nm)	Absorption (nm)	Emission (nm)		
$[Ru(phen)_2(3Mptr)]^+$ (**1**)	418	606	425	654	5.0	2.7
$[Ru(bpy)_2(bpt)]^+$ (**2**)[a]	429	645	475	678	4.2	3.7
$[Ru(bpy)_2(bpzt)]^+$ (**3**)[a]	453	662	446	675	2.0	2.8

[a] Data obtained from Ref. [5b,e,f]. All measurements carried out in aqueous Britton-Robinson buffer. Excited state values, pK_a^*, estimated using the Förster equation. (T. Förster, Z. Electrochem. 54 (1950) 273). All values ± 0.2.

3.1. Electronic properties of immobilized compounds

The emission properties of the final xerogels containing **1–5** are listed in Table 2. The emission decays could not be analyzed using a single exponential approach. This has been observed previously and has been attributed to the presence of different sites in the sol-gel matrix. Various methods have been utilized to address this issue [3,10]. In our approach we have analyzed the data using a double exponential model. With this method satisfactory fits for the experimental data were obtained for all xerogels. With this model two different lifetimes are obtained for all samples; a longer component with a contribution at about 70–80% and a smaller contribution of a shorter lifetime. Both components are affected by the



Scheme 1. Absorption and emission properties of **1** in aqueous solution.

Table 2
Emission properties of the complexes in solution and in sol-gel matrix

Complex	Medium	λ_{max} (nm)[a]	λ_{max} (nm)[b]	τ (ns)[a]	τ (ns)[b]
$[Ru(bpy)_3]^{2+}$	Solution	611	580	700 (280)[c]	4500
	pH 1 gel	598	579	1100(70), 470(30)[d]	4490(75), 1590(25)[d]
	pH 5 gel	588	576	2100(80), 660(20)[d]	4450(85), 1800(15)[d]
$[Ru(phen)_2(3Mptr)]^{+}$	Solution	654	606	90 (55)[c]	7200
$[Ru(phen)_2(H3Mptr)]^{2+}$	Solution	606	568	–[e]	9800
	pH 1 gel	598	566	350(85), 60(15)[d]	9450(80), 2150(20)[d]
	pH 5 gel	585	568	1920(80), 480(20)[d]	9650(70), 2460(30)[d]
$[Ru(bpy)_2(bpt)]^{+}$	Solution	660	624	355 (160)[c]	5500
$[Ru(bpy)_2(Hbpt)]^{2+}$	Solution	640	612	100 (40)[c]	4200
	pH 1 gel	618	606	320(65), 80(35)[d]	4170(70), 1630(30)[d]
	pH 5 gel	612	600	765(75), 170(25)[d]	4300(80), 1500(20)[d]
$[(Ru(bpy)_2)_2(bpt)]^{3+}$	Solution	642	603	85 (50)[c]	4160
	pH 1 gel	616	599	140(85), 40(15)[d]	4030(80), 1550(20)[d]
	pH 5 gel	611	600	760 (70), 190(30)[d]	4010(75), 1455(25)[d]
$[Ru(bpy)_2(bpzt)]^{+}$	Solution	662	610	100 (60)[c]	6400
$[Ru(bpy)_2(Hbpzt)]^{2+}$	Solution	675	612	120 (75)[c]	4970
	pH 1 gel	640	613	180(85), 40(15)[d]	4900(75), 1030(25)[d]
	pH 5 gel	627	612	615(70), 110(30)[d]	4850(80), 1150(20)[d]
$[(Ru(bpy)_2)_2(bpzt)]^{3+}$	Solution	671	617	105 (70)[c]	7030
	pH 1 gel	668	615	180(70), 40(30)[d]	6900(75), 1400(25)[d]
	pH 5 gel	665	612	830(75), 200(25)[d]	7300(75), 1700(25)[d]

[a] Room temperature measurements were degassed by purging with argon. Sol-gel samples were not degassed.

[b] These measurements were carried out at 77 K. For solution values, the solvent employed was ethanol/methanol 4/1 v/v.

[c] Value in parentheses indicates lifetime of the complex in aerated ethanol solution.

[d] Values in parentheses are the lifetime components pre-exponential factor given in percent.

[e] This value was outside the range of the instrumentation (i.e. <20 ns).

presence of oxygen. In our further analysis we only discuss the main component. The minor component behaves in a similar way however.

At pH 1 the emission maxima observed for **1–3** are significantly higher in energy than in solution. It has been proposed that this shift to higher energy upon immobilization is due to the destabilization of the ^{3}MLCT state [11]. For **1–3** the emission wavelengths obtained are in agreement with the presence of a protonated species in the xerogel. And this is indeed expected from the pK_a values in Table 1. Surprisingly, the emission wavelengths observed for **1** and **2** in pH 5 xero-gels are also indicative for the presence of protonated species. This observation is supported by absorption measurements, which show that in pH 5 gels the absorption maximum of **1** shifts from 425 to 417 nm during the gelation process. The intense shoulder observed at ca. 470 nm in the deprotonated species is also absent in the final gel. This suggests that the compounds become less acidic upon immobilization in the TEOS matrix. This has been observed before for other acidic dyes immobilized in sol-gel matrices [2f] The data obtained obtained from the pH 5 gel do not allow us to discriminate between the protonated state of compound **3**. However, based on the pK_a values we expect this compound to be protonated as well.

The energy of the luminescence peak of **5** is only slightly altered upon incorporation into the sol-gel matrix. This behavior is very different from that observed for **4** (see Table 3). This is possibly explained by the fact that **4**, has a bpy based emitting state, whereas for **5** the excited electron resides on the central bridging unit [5,12]. As such, the excited state of the bpzt$^-$ dimeric species may be shielded by the $Ru(bpy)_2$ units and the effect of the gel matrix will be less.

Table 2 shows that in pH 1 xero-gels the emission lifetimes show a significantly smaller increase from the solution value than for the pH 5 materials. This effect was

Table 3
Excited state decay parameters of **1–5** in solution (4/1 ethanol/methanol, v/v) and in sol-gel matrices[a]

Complex	Medium	k_0 (s^{-1})	A_i (s^{-1})[b]	ΔE_i (cm^{-1})[b]
$[Ru(bpy)_3]^{2+}$	Solution[b]	4.50×10^5	1.4×10^{14}	3900
	pH 1 gel[b]	2.30×10^5	1.2×10^7	740
	pH 5 gel[b]	3.00×10^5	9.1×10^6	660
$[Ru(phen)_2(3Mptr)]^+$	Solution	1.38×10^5	2.9×10^7	320
$[Ru(phen)_2(H3Mptr)]^{2+}$	Solution	1.60×10^5	2.0×10^{13}	3006
	pH 1 gel	1.56×10^5	6.36×10^{12}	2655
	pH 5 gel	1.22×10^5	1.44×10^7	800
$[Ru(bpy)_2(bpt)]^+$	Solution[c]	2.41×10^5	3.8×10^8	1127
$[Ru(bpy)_2(Hbpt)]^{2+}$	Solution[c]	2.33×10^5	8.55×10^{14}	3600
	pH 1 gel	3.75×10^5	5.45×10^{14}	3525
	pH 5 gel	3.48×10^5	7.28×10^7	900
$[\{Ru(bpy)_2\}_2(bpt)]^{3+}$	Solution[c]	2.40×10^5	5.3×10^{15}	4061
	pH 1 gel	4.92×10^5	2.84×10^{14}	3600
	pH 5 gel	3.64×10^5	4.63×10^7	800
$[Ru(bpy)_2(bpzt)]^+$	Solution[c]	1.6×10^5	2.9×10^9	1370
$[Ru(bpy)_2(Hbpzt)]^{2+}$	Solution[c]	1.4×10^5	1.66×10^{13}	3100
	pH 1 gel	3.19×10^5	2.42×10^{13}	3225
	pH 5 gel	3.21×10^5	3.84×10^8	1000
$[\{Ru(bpy)_2\}_2(bpzt)]^{3+}$	Solution[c]	1.4×10^5	9.9×10^{13}	3735
	pH 1 gel	4.11×10^5	1.26×10^{13}	3020
	pH 5 gel	2.37×10^5	1.46×10^{11}	2500

[a] All samples were degassed prior to measurements.

[b] From Ref. [4].

[c] From Ref. [8].

noticed previously for those gels doped with $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ [2,4,7]. This is possibly caused by the charge of the sol-gel surface, since a negatively charged surface would diminish the non-radiative decay of the Ru(II) pyridyltriazole cation to a greater extent than a positively charged one. In effect, the SiO^- groups present at pH 5 would inhibit the molecular motion of the dopant more effectively than the positively charged $SiOH_2^+$ groups which are thought to be present on the surface of the gels below the isoelectric point of the xero-gel of 2.2 [11a].

3.2. Temperature dependent emission studies

Temperature dependent emission lifetime (τ) experiments were carried out for all xero-gels. As described in the literature, high temperature data have been fitted by assuming that the excited state decay consists of a temperature independent intrinsic decay from the ^{3}MLCT state and a single thermally activated non-radiative decay process [8]. The activation energies (ΔE) and pre-exponential parameters A as obtained from the equation:

$$\frac{1}{\tau} = k_0 + A \exp\left(\frac{-\Delta E}{RT}\right)$$

are given in Table 3 together with some relevant solution data. Some typical $\ln(1/\tau)$ versus $1/T$ plots are shown in Figs. 2 and 3. The analysis of the temperature dependent lifetime of the immobilized complexes was restricted to only the longer lived, most dominant lifetime component. The results obtained for the other component were similar and are not further discussed.

Of particular relevance to this study is the case of $[Ru(bpy)_3]^{2+}$ in a rigid cellulose acetate matrix [2g]. While in fluid solution the temperature dependent lifetime data for the complex are apparently dominated by the participation of the ^{3}MC state ($A_i = 4 \times 10^{12}$ s^{-1} and $\Delta E_i = 3275$ cm^{-1}), upon incorporation into the rigid matrix the data yielded values of $A_i = 1.7 \times 10^7$ s^{-1} and $\Delta E_i = 810$ cm^{-1}. This behavior was interpreted by Kober and Meyer [8,13] to indicate that the ^{3}MC state is destabilized by the rigid matrix, to the extent that it becomes inaccessible over the temperature range investigated. In this situation, participation of the so-called fourth MLCT state becomes evident. The same complex immobilized in a sol-gel yielded a comparable set of parameters ($A_i = 1.2 \times 10^7$ s^{-1} and $\Delta E = 740$ cm^{-1})[4] indicating similar changes in the photophysics of the compound.

Returning to the present study, in solution the protonated complexes **1–3** and compounds **4** and **5** exhibit a steep decrease in lifetime above 220 K resulting in a high activation energy and pre-factor. As is the case with $[Ru(bpy)_3]^{2+}$ an activated surface crossing to a ^{3}MC excited state is occurring with rapid deactivation via this metal-centred state [8]. On the other hand, the deprotonated complexes **1–3** show a low pre-factor and a small activation energy. As mentioned above, this activated process corresponds to the population of a fourth ^{3}MLCT state, which is slightly higher in energy than the emitting state [8,13]. In these compounds population of the ^{3}MC level is not observed.

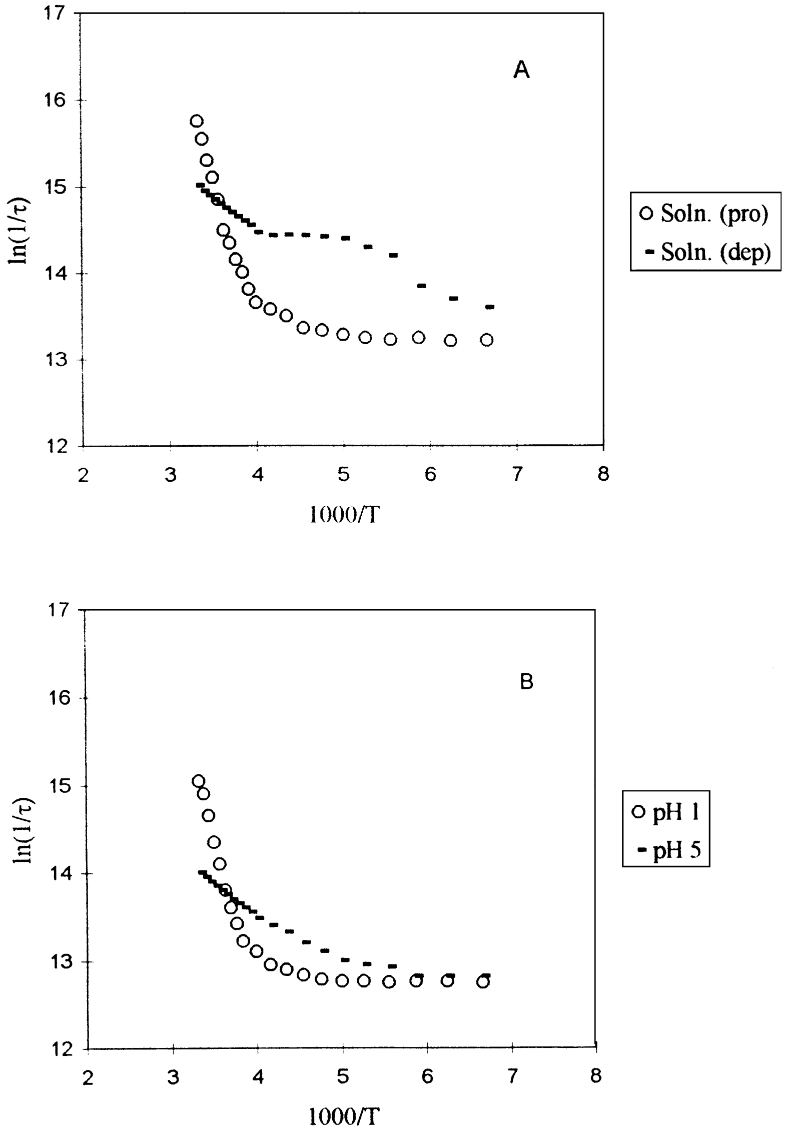


Fig. 2. (A) Temperature dependence for the luminescent lifetime of **2** in 4:1 ethanol/methanol temperature range 150–300 K. O, protonated form; —, deprotonated; and (B) Temperature dependence for the luminescent lifetime of **2** in O, pH 1 sol-gel; —, pH 5 sol-gel.

3.3. Sol-gel measurements

In our earlier studies on bpy and mixed bpy/dpp complexes the pre-factors and activation energies observed indicated that population of the ^{3}MC state was not occurring for bpy containing compounds irrespective of the initial pH of the sol-gel

[4]. The temperature dependent behavior of the immobilized complexes **1–4** does, however, depend greatly on the initial pH of the sol-gel. In pH 1 gels high activation energies indicate population of the ^{3}MC state, while low activation energies indicate that this state is not populated in pH 5 gels (see Fig. 2). For pH 5 gels it could be argued that the low kinetic parameters suggest the presence of the deprotonated form of complexes **1–3**. However, although we cannot rule out this possibility, for the reasons outlined in the previous section, we suggest that the protonated forms are present. The data obtained at pH 1 for **1–3** are clearly indicative for the presence of protonated species. The temperature dependence observed for these compounds is significantly different from that discussed above for the tris(bpy) complex.

Fig. 3 illustrates the $\ln(1/\tau)$ versus $1000/T$ plots **5** in solution and in the sol-gel matrices. For the gel prepared at pH 1 a steep rise in the temperature-dependent lifetime plots is observed indicating that at pH 1 an activated surface crossing to the ^{3}MC states followed by deactivation is occurring. The kinetic parameters obtained for **5** in a pH 5 gel indicate surface crossing to a ^{3}MC state under conditions where these two states are in equilibrium [8]. Overall the behavior observed for **5** in sol-gels is quite similar to that observed in solution· For **4** a more profound change in the kinetic decay parameters is observed for gels prepared at pH 5. In this case the temperature dependent lifetime analysis of this species revealed a low pre-factor and a small activation barrier (see Table 3).

To explain the observed effects for the temperature dependent behavior of the lifetime of the immobilized complexes a number of possibilities have been proposed. One possible explanation involves the argument that the location of the dd states

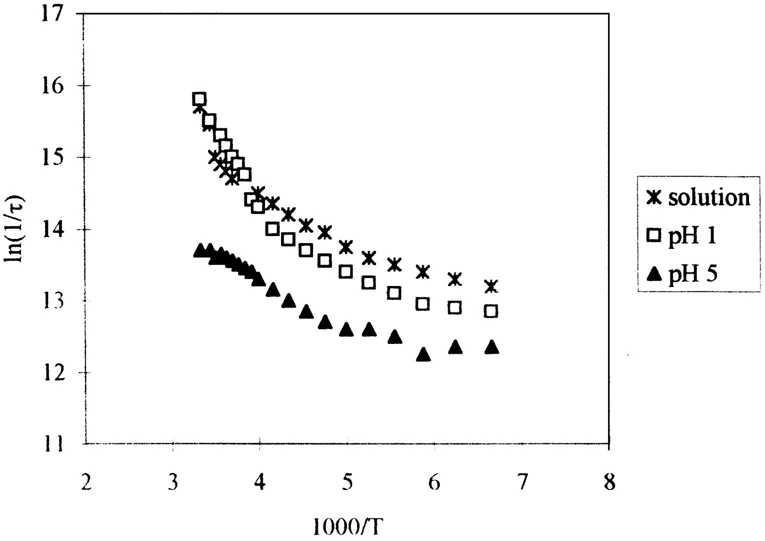


Fig. 3. Temperature dependence for the luminescent lifetime of **5** in *, 4:1 ethanol/methanol; □, pH 1 sol-gel; ▲, pH 5 sol-gel in the temperature range 150–300 K.

relative to the luminescent excited states [13] (i.e. the ^{3}MLCT–^{3}MC energy gap) in the pH 5 matrix is significantly altered upon incorporation. This interpretation maintains that the negatively charged surface destabilizes the crystal field levels, which are populated in fluid media near room temperature, to such an extent that that population of the ^{3}MC state from the ^{3}MLCT is no longer possible at ambient temperatures.

These results can be also be accounted for in terms of a rigid matrix perturbation of the potential wells. A general discussion of the phenomenology of solvent matrix spectroscopic effects has been presented by Dellinger and Kasha [14a]. Their report suggests that the potential wells are made steeper by the viscosity of the rigid matrices formed at 77 K and/or a change in the equilibrium distance (ΔQ_e). Watts and Missimer [14b] report an application of rigid matrix perturbations of molecular potentials to an interpretation of the luminescence rigidochromic effect. With regard to the present study, under the influence of a rigid matrix perturbation caused by the sol-gel, steepening of potential wells would in turn lead to an increase in the activation energy. This explanation suggests that the perturbation varies according to the surface charge of the sol-gel matrix. As such, those species experiencing a large rigid matrix perturbation populate the ^{3}MLCT level only, while those experiencing a small perturbation may populate the ^{3}MC state at ambient temperatures.

Finally, small changes in the equilibrium distance ΔQ_e between the ^{3}MLCT and the ^{3}MC state, or between the ^{3}MC state and the ground state upon immobilisation of the complexes may occur [15]. This in turn would influence vibrational overlap of the potential surfaces.

At present there are not sufficient data to allow us to be specific on which of these models is appropriate. Taking into account our earlier resonance Raman work on the bpy/dpp systems [4] we favor at present the interpretation that the sol-gel environment is imposing some restrictions on ligand distortion modes and that as a result population of the various excited state levels by vibrational processes is affected in some subtle manner. The matrix might also change the shape and position of the levels involved and further affect changes in the photophysical properties of the immobilized species. If we assume that a deviation from the solution behavior is indicative for a stronger interaction with the xero-gel matrix then we have to conclude that interaction is stronger on pH 5 gels. This is not unexpected since at that pH the surface is negatively charged. Compound **5** seems less affected by immobilization. This might be explained by the fact that for this compound the excited state is localized on the bpzt bridging ligand. Since this ligand is positioned in the center of the complex. Modes for interaction with the matrix are more limited.

4. Conclusion

In this contribution, mono- and dinuclear Ru(II) complexes containing pyridyltriazole ligands were successfully incorporated into the sol-gel matrix and their photophysical properties were examined. With the exception of the bpzt$^-$ dimer, all of the complexes exhibited a blue shift in the emission energy upon immobilization into the sol-gel matrix. This shift has been attributed to dipole reorientation with the excited state being energetically destabilized in the gel with respect to solution. For the bpzt$^-$ dinuclear molecule, the lowest π*-level is based on the bridging ligand and the excited state of the bpzt$^-$ dimeric species appears to be shielded to an extent by the $Ru(bpy)_2$ units.

The pH at which the sol-gels were prepared was found to significantly alter the kinetic parameters obtained from the temperature dependent lifetime analysis of these immobilized complexes. The pH plays an important role in determining both the surface charge of the matrix and also the evolution of the gel structure. It would appear that the negatively charged surface of the sol-gel samples prepared at pH 5 distorts the excited states of the immobilized complex to a greater extent than when the surface is positively charged (i.e. at pH 1). It is important to remember however that for the bpy/dpp complexes investigated earlier such behavior was not observed. The interaction between the xero-gel matrix and the ruthenium complex therefore appears to be very specific and at this stage no general explanation can be put forward to explain the behavior observed.

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