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Probing inter-ligand excited state interaction in homo and heteroleptic ruthenium(II) polypyridyl complexes using selective deuteriation

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Dedicated to professor Vincenzo Balzani.

Abstract

The effect of deuteriation on the photophysical properties of two series of regioselectively deuteriated Ru(II) complexes ($[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$, where $x = 0$–3 and ph_2phen is 4,7-diphenyl-1,10-phenanthroline and $[Ru(bipy)_2(dcbipy^{2-})]$, where $H_2dcbipy$ is 4,4′-dicarboxy-2,2′-bipyridyl) is reported. Although overall, deuteriation results in an increase in emission lifetime for all complexes, the effect of substitution of hydrogen for deuterium shows strong regioselectivity both in terms of the ligand and the position on individual ligands that are exchanged.

Keywords: Ruthenium; Polypyridyl; Deuteriation; Luminescence; Lifetime; Resonance Raman

1. Introduction

Since the 1st report of room temperature luminescence from $[Ru(bipy)_3]^{2+}$ by Paris and Brandt [1], Ru(II) tris–diimine complexes have served as a mainstay of inorganic photochemistry and photophysics [2]. However, despite the intensive studies of this simple compound and a myriad of its derivatives and analogues, the excited state structure of $[Ru(bipy)_3]^{2+}$ continues to attract considerable attention and debate [3]. Both with regard to the relaxation processes from the Franck–Condon state to the thermally equilibrated excited (THEXI) state [4] and the nature of the THEXI state itself, vis-a-vis the localisation/delocalisation of the lowest excited state over all three bipy ligands and of the interaction between ligands in heteroleptic complexes [5–7].

Strommen, Kincaid and co-workers have carried out extensive resonance Raman studies on $[Ru(bipy)_3]^{2+}$, and its selectively deuteriated isotopologues [8,9]. These studies lead to the conclusion that the excited state of $[Ru(bipy)_3]^{2+}$ is best described, at least on the vibrational timescale, as being spatially localised on a single bipy ligand rather than over all three bipy ligands [8]. The primary basis for this conclusion rested in the excited state resonance Raman spectrum of the complex, which presents features very similar to neutral bipy and that of

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the 2,2′-bipyridyl anion radical ($Li^{+}bipy^{-*}$). However, the resonance Raman technique provides information with regard to delocalisation of the THEXI state/s on the vibrational timescale. In contrast, luminescence spectroscopy allows for probing of the interaction between the ligands over the lifetime of the excited state. The effect of deuteriation on the vibrationally coupled deactivation of electronically excited states of $[Ru(bipy)_3]^{2+}$ was first reported by Van Houten and Watts in 1975 [10]. For the free ligand, 2,2′-bipy, a 100% increase in emission lifetime values was observed upon deuteriation while for $[Ru(bipy)_3]^{2+}$ a more modest 20% increase was observed. This study demonstrated that although C–H vibrational modes are less important towards mediating vibrational relaxation in the complex than in the free ligand, deuteriation is still a useful probe of the THEXI state [11]. Indeed selective deuteriation has been employed as a spectroscopic probe in several subsequent studies. Krausz et al. have shown that sequential deuteriation of one, two and all three bipy ligands resulted in a statistical decrease in the observed radiative rate constant at 298 K [12]. That study provides considerable evidence in support of the excited state model for $[Ru(bipy)_3]^{2+}$, in which the excited state is localised on the vibrational timescale on an individual ligand but 'hops' between ligands much faster than the rate of deactivation of the THEXI state. The emission decay from all three differently deuteriated complexes was mono-exponential and hence the observed excited state decay rate (k_{obs}) is a sum of the radiative and non-radiative decay rates from states localised on each of the three ligands (i.e. $k_{obs} = \Sigma_i(k_{r,i}+k_{nr,i})$ where $i = 1$–3). Since the radiative rate (k_r) is much lower than the non-radiative rate (k_{nr}) the effect of deuteriation is to reducing the vibrational component of k_{nr}. The linear dependence of the k_{obs} on deuteriation indicates that $k_{nr}(D)$ is only marginally slower than $k_{nr}(H)$.

Kincaid and co-workers have taken a different approach to that of Krausz et al. in examining the effect of selective deuteriation [21]. Their results again indicate that the increase in the observed emission lifetime depends on the number of deuterons introduced, however, an additional observation is that deuteriation at the C3 and C4 positions of the bipy ring has relatively little effect, except when all other positions are deuteriated. No explanation for this anomaly was proposed, however, the study highlighted the fact that although deuteriation can be viewed as an innocent probe in terms of overall electronic structure, its effect on vibrational modes is not restricted to the overlap integrals between ground and excited states but may affect the vibrational structure itself [13].

One aspect of these studies is somewhat perplexing. For $[Ru(bipy)_3]^{2+}$ the effect of deuteriation, although discernable, is nevertheless small in comparison with its effect on the excited state lifetimes of rare earth ions and organic compounds [11]. The process of non-radiative deactivation by vibrational relaxation involves the vibrionic adiabatic coupling between excited state promoter modes and ground state acceptor modes [8c]. It has been determined from low temperature high resolution emission spectra and from the absence of C–H stretching vibrations in the excited state resonance Raman spectrum of $[Ru(bipy)_3]^{2+}$ that the principle acceptor modes for non-radiative vibrationally coupled deactivation are totally symmetric skeletal modes and not C–H symmetric stretching vibrations [11]. Comparison of experimentally determined non-radiative rate constants and the calculated vibrational modes (which are potential promoter modes) shows that the most important modes are non-totally symmetric in plane C–C–C and C–C–H bending motions of the bipy ligand. In summary, it is most likely that for $[Ru(bipy)_3]^{2+}$ the origin of the deuteriation effect may not be in inhibiting the dissipation of electronic energy as vibrational heat, as is the case with lanthanide photophysics, but rather in reducing the vibrionic coupling between the excited state promoter vibrionic modes and the ground state acceptor vibrionic modes.

In the present contribution, two sets of selectively deuteriated Ru(II) complexes are examined in an attempt to further our understanding of the nature of the THEXI state of heteroleptic complexes and in particular to answer two key questions. Firstly, is the small increase in emission lifetime observed for $[Ru(bipy)_3]^{2+}$ upon deuteriation also observed for complexes of the type $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ (where $x = 0$–3 and ph_2phen is 4,7-diphenyl-1,10-phenanthroline). Secondly, can partial deuteriation provide information as to the localisation of the lowest lying emissive state on a particular ligand or ligand component. Recently we suggested the use of partial deuteriation [14] as a way to determine the localisation of the emitting state in mixed ligand complexes using emission lifetime measurements. In this contribution we attempt to develop this approach further by investigating the emission lifetimes of selective deuteriation of the ph_2phen on the photophysical properties of properties $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ and also of compounds of the type $[Ru(bipy)_2(dcbipy^{2-})]$, where $H_2dcbipy$ is 4,4′-dicarboxy-2,2′-bipyridyl.

2. Results and discussion

2.1. Synthesis and characterization

The preparation of several of the regioselectively deuteriated ph_2phen ligands employed in the present study is reported elsewhere [14]. Nevertheless, a brief discussion of the preparation of the various isotopologues is warranted. As was observed previously for 2,2′-bipyridine, facile $^1H/^2H$ exchange at the C2/C9 positions of ph_2phen is observed in neutral aqueous solution (at 200 °C). In basic solution exchange at all positions is observed, however the rate of exchange decreases in the order of C2/9,

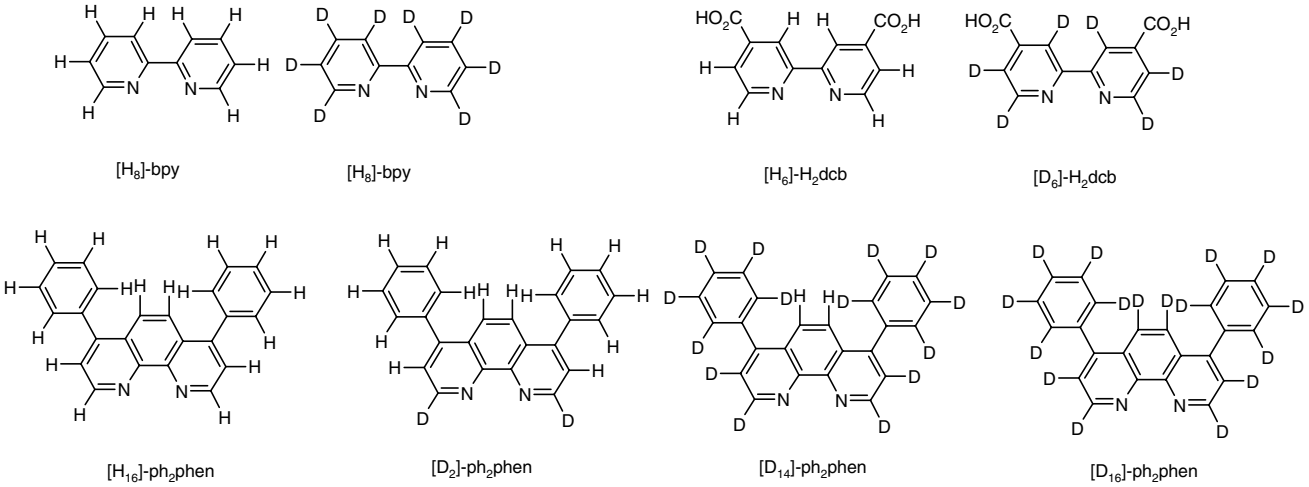

Fig. 1. Structure formulas of the ligands of the Ru(II) complexes examined.

C3/C8 > C5/C6 ≫ phenyl. Ph_2phen shows a reactivity similar to that observed for 1,10-phenanthroline in the presence of Pd/C catalyst [14], with the exception of the C5/C6 position where exchange is not observed. This is unexpected because for 1,10-phenanthroline no such selectivity is observed with deuteriation occurring readily at the C5/C6 position [14]. Such selectivity suggests that whilst exchange in basic media, and at the C2/C9 positions in neutral media, occurs via acid/base reactions, in neutral media in the presence of Pd/C catalyst exchange at the C3/C8 and phenyl positions occurs via an arene type interaction of the palladium. For the C5/C6 position, the reduced aromatic character of the ring results in the positions behaving as an alkene rather than an aromatic group. Hence, although for the unsubstituted phenanthroline exchange in the presence of the Pd/C catalyst occurs readily, in the substituted diphenyl-phenanthroline such interactions are sterically unfavourable due to the interference of the phenyl groups. The synthesis of the $[H_6]$–H_2dcbipy and $[D_6]$–H_2dcbipy was achieved, as outlined in the Section 3.1, by oxidation of $[H_{12}]$-4,4′-dimethyl-2,2-bipyridine and $[D_{12}]$-4,4′-dimethyl-2,2-bipyridine, respectively. The extent of deuteriation on the pyridyl rings was unaffected by oxidation of the methyl groups (See Fig. 1).

The non-deuteriated complexes of the type $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ and $[Ru(bipy)_2(dcb)]$ have been prepared previously and have been the focus of several detailed studies. The latter compound has been employed extensively in solar cell applications [6,15,16]. The ^{1}H NMR spectra of the complexes of type $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ are relatively simple due to the high symmetry of the complexes ($\sim C_{2v}$). Deuteriation allows for confirmation of assignments, which are readily made by ^{1}H COSY NMR spectroscopy. The electronic spectroscopic properties of the complexes are already described extensively [2] and will only be discussed briefly in relation to trends observed.

2.2. $[Ru(bpy)_x(ph_2phen)_{3-x}]^{2+}$ ($x = 1$–3) complexes

The UV/Vis absorption and emission spectra of all complexes were found to be independent of the level of deuteriation to within the resolution of the spectra available.[2] The absorption and emission spectra of the complexes $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ are shown in Fig. 2. A progressive hypochromic in the absorption maximum is observed on successive substitution of bipy with ph_2phen, suggesting the lowering of the energy of the ^{1}MLCT bands of the complex by ph_2phen substitution, in agreement with the trend observed in the emission spectra. In addition the ^{1}MLCT absorption bands broaden considerably with increasing substitution of bipy with ph_2phen.

The shift to the red in the emission λ_{max} on increasing substitution of bipy with ph_2phen is also observed, which is as would be expected, considering that the MLCT excited states of ph_2phen are slightly lower in energy than that of bipy [2]. A minor but progressive decrease in the emission full width at half maximum (FWHM) is observed with increasing substitution of bipy for ph_2phen. This can be attributed to the change in vibrational fine structure resulting from the increased rigidity of the ph_2phen ligand.

2.3. Isotope effects on emission lifetime

$[Ru(bipy)_n(ph_2phen)_{3-n}]^{2+}$ complexes (where $n = 0$–3). The emission lifetime data for all complexes examined at 298 K are shown in Table 1. The effect of increasing substitution of bipy by ph_2phen on the emission lifetime is readily accounted for by two factors. Firstly the increased structural rigidity of the ligand and loss of C–H oscillators in the order bipy < ph_2phen, makes vibrationally coupled

[2] This is not unexpected as although deuteriation affects the vibrational fine structure of emission and absorption spectra, these differences are only observed at very low temperatures (<10 K) with high-resolution emission spectroscopic techniques. See, for example, Ref. [3].

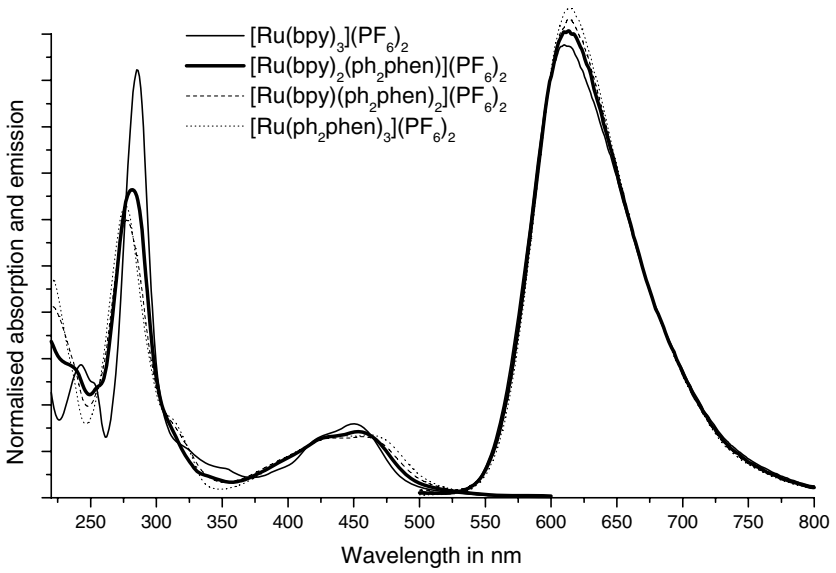

Fig. 2. Absorption and emission spectra (aerated acetonitrile solutions, 298 K) of the four per-protio-Ru(II) complexes. (The spectral abs./intensity are adjusted for clarity).

Table 1
Luminescence data of the differently deuteriated $[Ru(bpy)_x(ph_2phen)_{3-x}]^{2+}(x = 1–3)$ complexes [a,b]

	τ (μs)[b,c]	k_{obs} (10^6 s^{-1})	ϕ
$[Ru(bipy)_3]^{2+}$	1.0[d]	1.00	0.06[d]
$[Ru([D_8]\text{-bipy})_3]^{2+}$	1.1	0.91	
$[Ru(bipy)_2(ph_2phen)]^{2+}$	2.5	0.40	0.14
$[Ru([D_8]\text{-bipy})_2(ph_2phen)]^{2+}$	3.1	0.32	0.17
$[Ru(bipy)_2([D_{16}]\text{-}ph_2phen)]^{2+}$	2.6	0.38	0.15
$[Ru([D_8]\text{-bipy})_2([D_{16}]\text{-}ph_2phen)]^{2+}$	3.3	0.30	0.15
$[Ru(bipy)(ph_2phen)_2]^{2+}$	4.6	0.22	0.16
$[Ru([D_8]\text{-bipy})(ph_2phen)_2]^{2+}$	4.4	0.23	0.15
$[Ru(bipy)([D_{16}]\text{-}ph_2phen)_2]^{2+}$	5.0	0.20	0.20
$[Ru([D_8]\text{-bipy})([D_{16}]\text{-}ph_2phen)_2]^{2+}$	5.4	0.185	0.18
$[Ru(ph_2phen)_3]^{2+}$	6.3	0.16	0.25
$[Ru([D_2]\text{-}ph_2phen)_3]^{2+}$	7.5	0.13	
$[Ru([D_{14}]\text{-}ph_2phen)_3]^{2+}$	8.0	0.125	
$[Ru([D_{16}]\text{-}ph_2phen)_3]^{2+}$	8.2	0.12	

[a] Measurements in degassed (freeze-pump-thaw 4 cycles) acetonitrile solutions at 298 K.
[b] All values assumed to have ±2.5% uncertainty.
[c] The lifetime of all complexes in aerated solution is 170 (±6) ns.
[d] Literature value.

deactivation via skeletal modes less important to the overall non-radiative rate constant k_{nr} [11]. Secondly, the increased size of the ligand in the same order results in an increased spatial delocalisation of the excited electron and the excited state geometry of the complex is less distorted compared with the ground state making low frequency vibrational modes less important towards deactivation [11]. In addition, the decreased excited state distortion (S, the Huang–Rhys factor is reduced) results in a relative increase in the importance of high energy C–H stretching modes towards non-radiative deactivation and an increased deuteriation effect would be anticipated.

For $[Ru(bipy)_2(ph_2phen)]^{2+}$ and $[Ru(bipy)(ph_2phen)_2]^{2+}$ a decrease of 25% and 17% in k_{obs} is observed upon complete deuteriation, which is in line with the 20% increase observed by Van Houten and Watts for $[Ru(bipy)_3]^{2+}$ [10]. Hence for both the homo- and hetero-leptic complexes upon complete deuteriation the homoleptic and mixed ligand complexes behave similarly. Also of interest here are the results obtained for the partially deuteriated $[Ru(ph_2phen)_3]^{2+}$ complexes. The data show that deuteriation at the C2/C9 positions has a major effect on k_{obs} of the complex while further deuteriation of the ligands results in a much smaller decrease. This suggests that as for the H6/H6′ protons of $[Ru(bipy)_3]^{2+}$, the vibrational modes associated with the H2/H9 protons are important in the deactivation process.

The results obtained for the partial deuteriation of the mixed ligand compounds are less clear. For the $[Ru(bipy)_2(ph_2phen)]^{2+}$ complexes deuteriation of the bipy ligand results in a decrease in k_{obs} of ~20–25%, whereas deuteriation of the ph_2phen ligand has no significant effect (~5%). However for $[Ru(bipy)(ph_2phen)_2]^{2+}$ the opposite is observed and deuteriation of bipy has no effect on k_{obs}, whereas deuteriation of the ph_2phen ligands results in 8% decrease. This effect of deuteriation is unexpected because the overall rate of decay is additive over the component decay rates and hence as for the homoleptic complexes the difference in k_{obs} from single ligand deuteriation to full deuteriation should be the same as the increase found on deuteriation of two ligands. This indicates that although each ligand contributes to some extent to the overall decay rate, the contribution is dependent on the number of ligands deuteriated more than the nature of the ligands deuteriated. The results for this series of complexes show no clear evidence for the localisation of the emitting excited state on either bipy or ph_2phen.

The results of resonance Raman studies demonstrate the intricate nature of Ru(II) polypyridyl photophysics and the importance of environment to electronic excited state struc-

ture. Turro and co-workers have reported several studies of the ground and excited state resonance Raman spectra of mixed ligand Ru(II) complexes $[Ru(bipy)_x(ph_2phen)_{3-x}]^{2+}$ (where $x = 1$ or 2) [7]. For the heteroleptic complexes both $bipy^{*-}$ and ph_2phen^{*-} modes are observed in the excited state resonance Raman spectra, confirming that both bipy and ph_2phen based ^{3}MLCT excited states are populated significantly. For $[Ru(bipy)_2(ph_2phen)]^{2+}$ in aqueous media the excited state is localised on the vibrational timescale on both the bipy and ph_2phen ligands. However, localisation exclusively on one or other ligand may be achieved readily by changing the solvent environment, or by the presence of surfactants, which serve to selectively stabilise either bipy or ph_2phen [7]. The results obtained in this contribution are therefore in agreement with rR results obtained by Turro et al. [7c].

2.4. $[Ru(bpy)_2(dcb^{2-})]$ and $[Ru(bpy)_2(H_2dcb)]^{2+}$ complexes

In the second example the effect of deuteration on the 4,4′dicarboxy-2,2′-bipyridyl (dcb^{2-}) complex $[Ru(bipy)_2(dcb)]$ is investigated as a function of protonation state. For the complex $[Ru(bipy)_2(dcb^{2-})]$ and its isotopologues, protonation results in a large red shift in the emission λ_{max} from 641 to 679 nm (see Table 2). In both cases the effect of protonation is to stabilise the lowest emissive state relative to the ground state. This is expected and is attributable to destabilisation of the ground state (due to a reduction in the σ-donor strength of the ligand and hence reduction in CFSE) and to the stabilization of the ligand based π^* orbitals involved in the ^{3}MLCT excited state.

The resonance Raman spectra recorded at 457.5 nm show bands at 1564, 1492, 1425 and 1319 cm^{-1} (assigned to bipy based vibrational modes), 1619, 1563, 1477, 1269 and 1255 cm^{-1} (assigned to H_2dcb based vibrational modes) and 1615, 1542, 1477, 1294 and 1270 and 1256 cm^{-1} (assigned to dcb^{2-} based vibrational modes). Assignments of vibrational bands to individual ligands is facilitated by the effect of deuteration on the resonance Raman spectra (Fig. 3). The increase in energy of the vibrational modes of the dcb^{2-} ligand in the region 1450–1650 cm^{-1} upon protonation is in agreement with the expected decrease in electron density of the pyridyl rings identified by UV–Vis spectroscopy.

Table 2
Luminescence data for the differently deuteriated $[Ru(bpy)_2(dcb^{2-})]$and $[Ru(bpy)_2(H_2dcb)]^{2+}$ complexes[a]

	Lum. λ_{max} (nm)	$\tau_{298\ K}$ (ns)	k_{obs} ($^*10^6$) {Δ%}
$[Ru(bipy)_2(dcb)]$	641	562	1.78
$[Ru(bipy)_2([D_6]\text{-}dcb)]$	641	633	1.58 {10%}
$[Ru([D_8]\text{-}bipy)_2(dcb)]$	641	573	1.75 {2%}
$[Ru([D_8]\text{-}bipy)_2([D_6]\text{-}dcb)]$	641	679	1.47 {17%}
$[Ru(bipy)_2(H_2dcb)]^{2+}$	679	292	0.342
$[Ru(bipy)_2([D_6]\text{–}H_2dcb)]^{2+}$	679	330	0.303 {11%}
$[Ru([D_8]\text{-}bipy)_2(H_2dcb)]^{2+}$	679	299	0.334 {2%}
$[Ru([D_8]\text{-}bipy)_2([D_6]\text{–}H_2dcb)]^{2+}$	679	348	0.287 {16%}

[a] In degassed (argon purged) Britton–Robinson aqueous buffer at 298 K. All values assumed to have ±2.5% error. {Δ%} indicates % decrease in radiative rate constant relative to the per-protio complex.

The lifetime values obtained for the perprotio complexes are in agreement with previously reported values [17]. The attribution of the emissive state as being dcb^{2-}/H_2dcb localised, was based on the increased basicity in the excited state. For both the fully protonated and fully deprotonated complex, deuteriation of the bipy ligand results in no significant increase in emission lifetime, whilst deuteriation of the H_2dcb/dcb^{2-} ligand results in a relatively large increase (compared to 5% for $[Ru(bipy)_2([D_8]\text{-}bipy)]^{2+}$) [12]. The absence of an appreciable effect of deuteriation of the bipy ligand strongly supports this assignment of

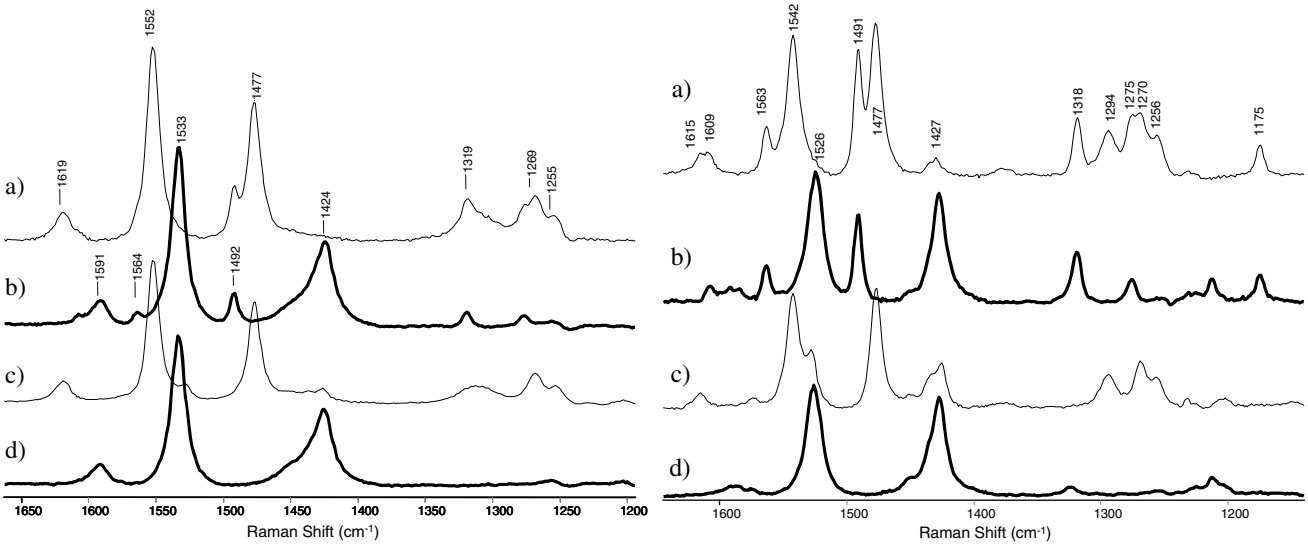

Fig. 3. Luminescence data for the differently deuteriated: (a) $[Ru([H_8]\text{-}bpy)2([H_6]\text{–}H_2dcb)]^{2+}$; (b) $[Ru([H_6]\text{-}bipy)2([D_6]\text{-}H_2dcb)]^{2+}$; (c) $[Ru([D_6]\text{-}bpy)2([H_6]\text{–}H_2dcb)]^{2+}$ and (d) $[Ru([D_6]\text{-}bpy)2([D_6]\text{-}H_2dcb)]^{2+}$ in left: HCl(aq) (pH 1.5) and right NaOH(aq) (pH 9).

the emissive state as being localised almost entirely on the dcb^{2-}/H_2dcb ligand. It should be noted that complete deuteriation results in an additional increase in the observed emission lifetime. This is not unusual and has been observed by Kincaid et al. also in studies on the positional dependence of the effects of deuteriation of $[Ru(bipy)_3]^{2+}$ (vide supra) [8c].

In contrast to the previous examples of heteroleptic complexes of bipy and ph_2phen, in this case deuteriation provides strong evidence for the localisation of the excited state on a particular ligand. It should be noted that the relative energy difference between the bipy and dcb^{2-}/H_2dcb localised ^{3}MLCT states are considerably larger than in the previous system.

3. Conclusions

The application of deuteriation as a probe in electronic spectroscopy of Ru(II) polypyridyl complexes is demonstrated in the studies described here. Together with the methodology for the preparation of deuteriated ligands in useful quantities, the further development of isotopic perturbation as a general and commonplace technique has been brought closer to realisation. The general conclusions reached from this study of effect of deuteriation on emission lifetime values, and consequently on k_{obs} of emission, are in full agreement with the results obtained with other techniques (in particular excited state rR).

For heteroleptic bipy/ph_2phen complexes, the relative contribution of each ligand to the overall observed radiative decay rate is clearly not equivalent. On the other hand, for the H_2dcb compounds the effect of deuteriation is clear in that it convincingly identifies the location of the emitting state. The difference of the ph_2phen and H_2dcb complexes are related to the energy differences between the excited states localised on these ligands compared with bipy localised excited states. For complexes containing H_2dcb ligand these differences are considerable larger. However, it is also apparent that although the THEXI state may be assigned to a particular ligand, the role of 'spectator' ligands in the deactivation of THEXI cannot be ignored. This is demonstrated clearly by the effect of deuteriation of the bipy ligands in the $[Ru(bipy)_2(H_ndcb)]^{n+}$ (where $n = 0$ or 2) complexes, which is more apparent in the $[D_6]$-dcb complexes than the $[H_6]$-dcb complexes (Table 2).

A difficulty in using deuteriation as a probe of excited state properties has been encountered in this study. In the presence of a very efficient deactivation channel such as oxygen quenching and population of strongly coupled short lived excited states (i.e. ^{3}MC state), the observation of less competitive routes such as those due to vibrationally coupled deactivation (e.g. C–H, N–H and O–H modes) is not possible. Nevertheless, given that contributing factors can be eliminated or accounted for then the effect of deuteriation provides a powerful and under-exploited probe of the excited state properties of inorganic systems.

3.1. Experimental

Materials. All solvents employed were of HPLC grade or better and used as received unless otherwise stated. For all spectroscopic measurements Uvasol (Merck) grade solvents were employed. All reagents employed in synthetic procedures were of reagent grade or better. *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ [18], *cis*-$[Ru([D_8]\text{-bipy})_2Cl_2]\cdot 2H_2O$ [18], *cis*-$[Ru(ph_2phen)_2Cl_2]\cdot 2H_2O$, *cis*-$[Ru([D_{16}]\text{-}ph_2phen)_2Cl_2]\cdot 2H_2O$ were prepared by previously reported procedures. The ligands $[D_8]$-bipy, $[D_2]$-ph_2phen, $[D_{14}]$-ph_2phen, and $[D_{16}]$-ph_2phen were available from earlier studies [14].

$[Ru(bipy)_3](PF_6)_2$. 350 mg (2.24 mmol) of bipy and 670 mg (1.2 mmol) *cis*-$[Ru(bipy)_2Cl_2]$ were dissolved in 50/50 v/v/ethanol/water. The solution (purple) was refluxed for 4 h. Ethanol was removed under reduced pressure. The product was precipitated with saturated ammonium hexafluorophosphate solution filtered and air-dried for 3 h. The deep red product was recrystallised from acetone/water 5/1. Yield 690 mg (0.75 mmol, 62%).^{1}H NMR (400 MHz) in CD_3CN; 8.415 (6H, d, H3), 7.97 (6H, dd, H4), 6.50 (6H, d, H6), 7.31 (6H, dd, H5). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{30}H_{24}$: C, 41.91; H, 2.79; N, 9.78. Found: C, 41.90; H, 2.69; N, 9.65%.

$[Ru([D_8]\text{-}bipy)_3](PF_6)_2$. As for $[Ru(bipy)_3](PF_6)_2$ except 200 mg (1.2 mmol) of d_8-bipy and 350 mg (1.0 mmol) *cis*-$[Ru([D_8]\text{-bipy})_2Cl_2]$. Yield 460 mg (0.52 mmol, 52%). ^{1}H NMR (400 MHz) in CD_3CN; 8.41 (*resid.* s. H3), 7.965 (*resid.* s, H4), 6.49 (*resid.* s, H6), 7.30 (*resid.* s, H5).

$[Ru(ph_2phen)_3](PF_6)_2\cdot H_2O$. As for $[Ru(bipy)_3](PF_6)_2$ except 100 mg (0.3 mmol) of ph_2phen and 160 mg (0.18 mmol) *cis*-$[Ru(ph_2phen)_2Cl_2]$. Yield 210 mg (0.15 mmol, 83%). ^{1}H NMR (400 MHz) in CD_3CN; 8.32 (d, 2H), 8.26 (s, 2H), 7.69 (d, 2H), 7.66 (m, 10H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{72}H_{48}\cdot H_2O$: C, 61.49; H, 3.49; N, 5.98. Found: C, 60.91; H, 3.36; N, 5.86%.

$[Ru(bipy)_2(ph_2phen)](PF_6)_2\cdot H_2O$. As for $[Ru(bipy)_3](PF_6)_2$ except 200 mg (0.6 mmol) of ph_2phen and 350 mg (0.67 mmol) of *cis*-$[Ru(bipy)_2Cl_2]$. Yield 340 mg (0.33 mmol, 49%).^{1}H NMR (400 MHz) in CD_3CN; 8.6 (1H, d), 8.57 (1H, d), 8.215 (s, 1H), 8.18 (d, 1H), 8.14 (dd, 1H), 8.07 (dd, 1H), 7.92 (d, 1H), 7.73 (dd, 2H), 7.65 (m, 5H), 7.50 (dd, 1H), 7.33 (dd, 1H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{44}H_{32}\cdot H_2O$: C, 50.14; H, 3.13; N, 7.98. Found: C, 51.08; H, 3.13; N, 7.64%.

$[Ru([D_8]\text{-}bipy)_2(ph_2phen)](PF_6)_2\cdot 2(CH_3)_2CO$. As for $[Ru(bipy)_3](PF_6)_2$ except 100 mg (0.3 mmol) of ph_2phen and 140 mg (0.26 mmol) of *cis*-$[Ru([D_8]\text{-bipy})_2Cl_2]$. Yield 190 mg (0.18 mmol, 69%). ^{1}H NMR (400 MHz) in CD_3CN; 8.57 (1H, d), 8.215 (s, 1H), 7.73 (dd, 2H), 7.65 (m, 5H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{44}H_{16}D_{16}\cdot 2(CH_3)_2CO$: C, 51.41; H, 3.77; N, 7.20. Found: C, 51.78; H, 3.01; N, 7.11%.

$[Ru(bipy)_2([D_{16}]\text{-}ph_2phen)](PF_6)_2\cdot (CH_3)_2CO$. As for $[Ru(bipy)_3](PF_6)_2$ except 100 mg (0.29 mmol) of $[D_{16}]$-ph_2phen and 130 mg (0.25 mmol) of *cis*-$[Ru(bipy)_2Cl_2]$.

Yield 230 mg (0.22 mmol 88%).^{1}H NMR (400 MHz) in CD_3CN; 8.6 (1H, d), 8.18 (d, 1H), 8.14 (dd, 1H), 8.07 (dd, 1H), 7.92 (d, 1H), 7.73 (dd, 2H), 7.33 (dd, 1H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{42}H_{16}D_{16}$. $(CH_3)_2CO$: C, 50.86; H, 3.43; N, 7.57. Found: C, 50.81; H; 3.23; N, 7.54%.

[Ru([D$_8$]-bipy)$_2$([D$_{16}$]-ph$_2$phen)](PF$_6$)$_2$ · H$_2$O. As for $[Ru(bipy)_3](PF_6)_2$ except 119 mg (0.34 mmol) of [D_{16}]-ph_2phen and 140 mg (0.26 mmol) of *cis*-[Ru([D_8]-$bipy)_2Cl_2$]. Yield 220 mg (0.21 mmol, 80%). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{42}D_{32} \cdot H_2O$: C, 48.66; H, 3.04; N, 7.74. Found: C, 48.94; H, 3.01; N, 7.69%.

[Ru(bipy)(ph$_2$phen)$_2$](PF$_6$)$_2$ · 2H$_2$O. As for $[Ru(bipy)_3](PF_6)_2$ except 200 mg (1.28 mmol) of bipy and 350 mg (40 mmol) of *cis*-[Ru($ph_2phen)_2Cl_2$]. Yield 390 mg (0.33 mmol,82%). ^{1}H NMR (400 MHz) in CD_3CN; 8.39 (1H, d), 8.095 (1H, d), 8.00 (s, 1H), 7.99 (s, 1H), 7.90 (m, 2H), 7.67 (s, 1H), 7.55 (d, 1H), 7.40 (m, 11H), 7.17 (dd, 1H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{58}H_{40} \cdot 2H_2O$: C, 55.81; H, 3.37; N, 6.74. Found: C, 56.07; H, 2.42; N, 5.66%.

[Ru(bipy)([D$_{16}$]-ph$_2$phen)$_2$](PF$_6$)$_2$ · H$_2$O · CH$_3$CN. As for $[Ru(bipy)_3](PF_6)_2$ except 105 mg (0.67 mmol) of bipy and 300 mg (0.33 mmol) of *cis*-[Ru([D_{16}]-$ph_2phen)_2Cl_2$]. Further purification by flash precipitation from acetonitrile into diethylether was carried out. Yield 350 mg (0.29 mmol 87%). ^{1}H NMR (400 MHz) in CD_3CN; 8.39 (1H, d), 7.90 (dd, 1H), 7.67 (s, 1H), 7.17 (dd, 1H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{58}H_8D_{32} \cdot H_2O \cdot CH_3CN$: C, 55.21; H, 3.37; N, 7.52. Found: C, 54.32; H, 3.13; N, 7.43%.

[Ru([D$_8$]-bipy)(ph$_2$phen)$_2$](PF$_6$)$_2$ · 2H$_2$O. As for $[Ru(bipy)_3](PF_6)_2$ except 103 mg (0.63 mmol) of [D_8]-bipy and 350 mg (40 mmol) of *cis*-[Ru($ph_2phen)_2Cl_2$]. Yield 400 mg (0.34 mmol 85%). ^{1}H NMR (400 MHz) in CD_3CN; 8.095 (1H, d), 8.00 (s, 1H), 7.99 (s, 1H), 7.90 (d, 1H), 7.55 (d, 1H), 7.40 (m, 11H). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{58}H_{32}D_8 \cdot 2H_2O$: C, 55.46; H, 3.35; N, 6.69. Found: C, 54.13; H, 3.17; N, 6.98%.

[Ru([D$_8$]-bipy)([D$_{16}$]-ph$_2$phen)$_2$](PF$_6$)$_2$. As for $[Ru(bipy)_3](PF_6)_2$ except 110 mg (0.67 mmole) of [D_8]-bipy and 370 mg (0.4 mmole) *cis*-[Ru([D_{16}]-$ph_2phen)_2Cl_2$]. Yield 420 mg (0.34 mmole, 85%). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{58}D_{40}$: C, 55.64; H, 3.20; N, 6.71. Found: C, 55.29; H, 3.15; N, 7.07%.

[D$_6$]-2,2′-bipyridine-4,4′-dicarboxylic acid [19]. 4.5 g (23 mmol) of [D_{12}]-4,4′-dimethyl-2,2′-bipyridine was added slowly to 120 cm^3 of 98% H_2SO_4, followed by 24 g of sodium dichromate (92 mmol). The reaction temperature was maintained at 70 °C for 3 h followed by cooling to 20 °C. The reaction mixture was poured over 800 g of ice, stirred for 20 min and the yellow [D_6]-2,2′-bipyridine-4,4′-dicarboxylic acid collected by vacuum filtration. The crude product was suspended in 120 cm^3 of 50% nitric acid and heated to reflux for 4 h. After cooling the solution to room temperature it was added to 200g of ice and 500 cm^3 of water. On cooling to 5 °C a white precipitate formed. This was collected under vacuum and air-dried. Yield 4.2 g (16 mmol, 70%).^{1}H NMR ([D_6]-DMSO): 8.92 (*resid*. s), 8.85 (*resid*. s), 7.92 (*resid*. s)

[Ru(bipy)$_2$(4,4′-dcb)](PF$_6$)$_2$ · 3H$_2$O 260 mg (0.5 mmol) of *cis*-[Ru($[bipy)_2Cl_2$] and 122 mg (0.5 mmol) of H_2dcb were heated at reflux in 50 cm^3 of EtOH/H_2O 50/50 v/v for 4 h. The reaction mixture was cooled to room temperature and 2 cm^3 of saturated aqueous NH_4PF_6 solution were added. The solution was acidified to pH 2 and the precipitate collected by vacuum filtration and washed with diethyl ether. The product was recrystallised from methanol/water (pH 1) Yield 300 mg (0.31 mmol, 62%) ^{1}H NMR in [D_6]-DMSO/NaOD: 8.84 (1H, s), 8.70 (2H, d), 8.09 (2H, dd), 7.73 (4H, m), 7.48 (2H, m).^{13}C NMR [D_6]-DMSO/NaOD: 166.44, 156.78, 156.73, 156.70, 151.375, 148.45, 138.25, 128.09, 127.07, 124.60, 123.25. CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{32}H_{24}O_4 \cdot 3H_2O$: C, 38.36; H, 2.70; N, 8.18. Found: C, 38.33; H, 2.53; N, 8.18%.

[Ru(bipy)$_2$([D$_6$]-4,4′-dcb)](PF$_6$)$_2$ · 2H$_2$O. As for $[Ru(bipy)_2(4,4'\text{-dcb})](PF_6)_2$ except 260 mg (0.5 mmol) of *cis*-[Ru($[bipy)_2Cl_2$] and 125 mg (0.5 mmol) of [D_6]-H_2dcb were heated at reflux in 50 cm^3 of EtOH/H_2O 50/50 v/v for 4 h. Yield 280 mg (0.29 mmol, 58%)^{1}H NMR in [D_6]-DMSO/NaOD: 8.84 (*resid*. s), 8.70 (2H, d), 8.09 (2H, dd), 7.73 (2H, dd), 7.48 (2H, m). ^{13}C NMR [D_6]-DMSO/NaOD: 166.01, 156.70, 156.73, 156.67, 151.41, 148.75, 138.22, 127.07, 124.65. CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{32}H_{18}D_6O_4 \cdot 2H_2O$: C, 38.83; H, 2.86; N, 8.49. Found: C, 38.52; H, 2.56; N, 8.25%.

[Ru([D$_8$]-bipy)$_2$(4,4′-dcb)](PF$_6$)$_2$ · 3H$_2$O. As for $[Ru([H_8]\text{-bipy})_2([H_6]\text{-4,4′-dcb})](PF_6)_2$ except 260 mg (0.485 mmol) of *cis*-[Ru($[D_8]$-$bipy)_2Cl_2$] and 125 mg (0.51 mmol) of H_2dcb were heated at reflux in 50 cm^3 of EtOH/H_2O 50/50 v/v for 4 h. Yield 290 mg (0.30 mmol, 60%) ^{1}H NMR in [D_6]-DMSO/NaOD: 8.825 (1H, s), 8.75 (2*resid* s), 8.12 (2*resid*. s), 7.73 (4H, d), 7.685 (1H, d), 7.49 (*resid*. s).^{13}C NMR [D_6]-DMSO/NaOD: 166.44, 156.73, 151.19, 149.04, 127.09, 123.24. CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{32}H_8D_{16}O_4 \cdot 3H_2O$: C, 37.76; H, 2.65; N, 8.26. Found: C, 37.75; H, 2.48; N, 8.15%.

[Ru([D$_8$]-bipy)$_2$([D$_6$]-4,4′-dcb)](PF$_6$)$_2$ · 2H$_2$O. As for $[Ru([D_8]\text{-bipy})_2([H_6]\text{-4,4′-dcb})](PF_6)_2$ except 260 mg (0.485 mmol) of *cis*-[Ru($[D_8]$-$bipy)_2Cl_2$] and 125 mg (0.5 mmol) of [D_6]-H_2dcb were heated at reflux in 50 cm^3 of EtOH/H_2O 50/50 v/v for 4 h. Yield 310 mg (0.32 mmol, 64 %)^{1}H NMR in [D_6]-DMSO/NaOD: 8.82 (*resid* s), 8.77 (*resid*. s), 8.765 (*resid*. s), 8.127 (*resid*. s), 8.116 (*resid*. s), 7.73 (3*resid*. s), 7.686 (*resid* s), 7.50 (*resid*. s). ^{13}C NMR [D_6]-DMSO/NaOD: 165.67, 156.76 (2 peaks). CHN *Anal.* Calc. for $RuP_2F_{12}N_6C_{32}H_2D_{22}O_4 \cdot H_2O$: C, 38.21; H, 2.59; N, 8.36. Found: C, 38.36; H, 2.49; N, 8.19%.

3.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) NMR Spectrometer. All measurements were carried out in [D_6]DMSO or [D_1]chloroform for ligands [D_6]acetone for complexes. Peak positions are relative to residual solvent peaks. UV/Vis absorption spectra

(accuracy ± 2 nm) were recorded on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV/Vis data manager. Molar absorption coefficients are ±10% – Emission spectra (accuracy ± 2 nm) were recorded at 298 K using a LS50B luminescence spectrofluorimeter, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin–Elmer Fl WinLab custom built software. Emission and excitation slit widths were 10 nm. Emission spectra are uncorrected for photomultiplier response. Ten millimeters path length quartz cells were used for recording spectra.

Luminescence lifetime measurements were obtained using an Edinburgh analytical instruments (EAI) time-correlated single-photon counting apparatus (TCSPC) as described previously [20]. Samples were deaerated for 20 min using Ar gas before measurements were carried out, followed by repeated deaeration to ensure complete oxygen exclusion. Lifetime measurements of Ru(II) polypyridyl complexes reported in this contribution are, as expected [15], particularly sensitive to oxygen. For some of the Ru(II) complexes displacement of O_2 by N_2 or Ar by gas purge was found to be insufficient to eliminate the quenching effect of oxygen and hence several freeze-pump-thaw cycles were carried out before sample lifetimes were measured. In several cases the measurements were repeated employing fresh solutions. Emission lifetimes were calculated using a single exponential fitting function; Levenberg–Marquardt algorithm with iterative reconvolution (Edinburgh instruments F900 software) and are + 2.5%. The reduced χ^2 and residual plots were used to judge the quality of the fits.

Ground state resonance Raman spectra of the complexes were recorded at 457.9 nm using an Argon ion laser (Spectra Physics model 2050) as the excitation source. The laser power at the sample was typically 30–40 mW. The Raman backscatter was focused onto the entrance slit of a single stage spectrograph (JY Horiba HR640), which was coupled to a CCD detector (Andor Technology DV420-OE). A 50:50 (v/v) mixture of acetonitrile and toluene was used as the calibration solution [21].

Elemental analysis has been carried out at the Microanalytical Laboratory at University College Dublin.

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