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Review

$[Ru(bipy)(CN)_4]^{2-}$ and its derivatives: Photophysical properties and its use in photoactive supramolecular assemblies

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Contents

Abstract

This review describes the intriguing properties of the complex anion $[Ru(bipy)(CN)_4]^{2-}$, whose redox and photophysical properties are strongly solvent-dependent. This complex and its analogues and derivatives are proving to be of particular value as components of polynuclear assemblies because of the ease with which they associate with other species by either hydrogen-bonding via the cyanides, or by direct ligation of the cyanide ligands to other metal ions. The strong solvatochromism means that the ability of the complex to act as an energy or electron donor in its ^{3}MLCT excited state can be switched over a wide range, a feature which has so far only been exploited in a few instances.

Keywords: Photophysical properties; Solvatochromism; Polynuclear assemblies; Bipyridyl complexes; Ruthenium

1. Introduction

The study of the photophysical properties of d^6 transition metal complexes with polypyridine ligands has been one of the most fertile areas of research in inorganic chemistry for the last 20 years. Complexes of Ru(II), Os(II), Re(I), Ir(III) [and also the d^8 metal Pt(II)] with, principally, 2,2′-bipyridine (bipy) and its analogues have provided insights into basic photophysical processes such as photoinduced energy and electron transfer as well as useful applications such as luminescent sensors, solar cells, and materials for use in OLED displays [1–4].

Against this backdrop, the complex $[Ru(bipy)(CN)_4]^{2-}$ stands out as having received relatively little attention, especially when compared to its ubiquitous cousin $[Ru(bipy)_3]^{2+}$. Although it is a relatively new compound – first described by Scandola and co-workers in 1986 [5] – it has still received less attention than its intriguing properties deserve, with a relatively limited number of recent papers devoted to its photophysical properties and its use as a component of polynuclear assemblies. This is odd when one considers the many particular advantages that it offers compared to $[Ru(bipy)_3]^{2+}$ in the general field of molecular and supramolecular photochemistry. These may be summarized as follows:

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- Like $[Ru(bipy)_3]^{2+}$, $[Ru(bipy)(CN)_4]^{2-}$ has a luminescent ^{3}MLCT Ru → bipy excited state. However, instead of being more or less fixed in its properties, the energies of its frontier orbitals are highly solvent-dependent, resulting in considerable variation in its ^{3}MLCT excited state energy, and its ground state and excited state redox potentials, in different solvents. Changing the solvent accordingly provides a simple means of *tuning* the redox and photophysical properties of $[Ru(bipy)(CN)_4]^{2-}$, and hence its ability to act as an energy donor or an electron donor or acceptor in its excited state.
- It is far more versatile in the way in which it can be incorporated into polynuclear assemblies. $[Ru(bipy)_3]^{2+}$ can only be linked to other molecules or components via covalent attachments on one of the bipy ligands. This route is also available to $[Ru(bipy)(CN)_4]^{2-}$. However, the externally directed lone pairs on the N atoms of the cyanide ligands of $[Ru(bipy)(CN)_4]^{2-}$ are capable of acting as hydrogen-bond acceptors, allowing the complex to act as a component of hydrogen-bonded assemblies; and the lone pairs can also coordinate to additional metal cations, allowing formation of polynuclear complexes via Ru–CN–M linkages.
- Finally, the CN ligands provide a convenient infrared spectroscopic handle to monitor the excited state, as the positions of the CN vibrations are highly sensitive to changes in the electron distribution in the complex. This allows the excited state to be interrogated by monitoring changes in the ν(CN) vibrations using time-resolved infrared spectroscopy.

This review provides a brief summary of the photophysical and redox properties of $[Ru(bipy)(CN)_4]^{2-}$, and then discusses recent work in which it and its relatives have been used in covalently bonded dyads, and in supramolecular assemblies. These supramolecular assemblies are based on participation of the cyanide groups in either hydrogen-bonding interactions, or coordination to other metal ions to give coordination networks and polymers.

2. Synthesis and isolation of $[Ru(bipy)(CN)_4]^{2-}$ and its relatives

The first communication concerning $[Ru(bipy)(CN)_4]^{2-}$ described its synthesis in ≈30% yield from $K_4[Ru(CN)_6]$ and bipy by a photochemical method, using irradiation with 254 nm light for 16 h in aqueous methanol, followed by chromatographic purification [5]. A more convenient and high-yielding (80%) synthesis was subsequently described, which we and others have

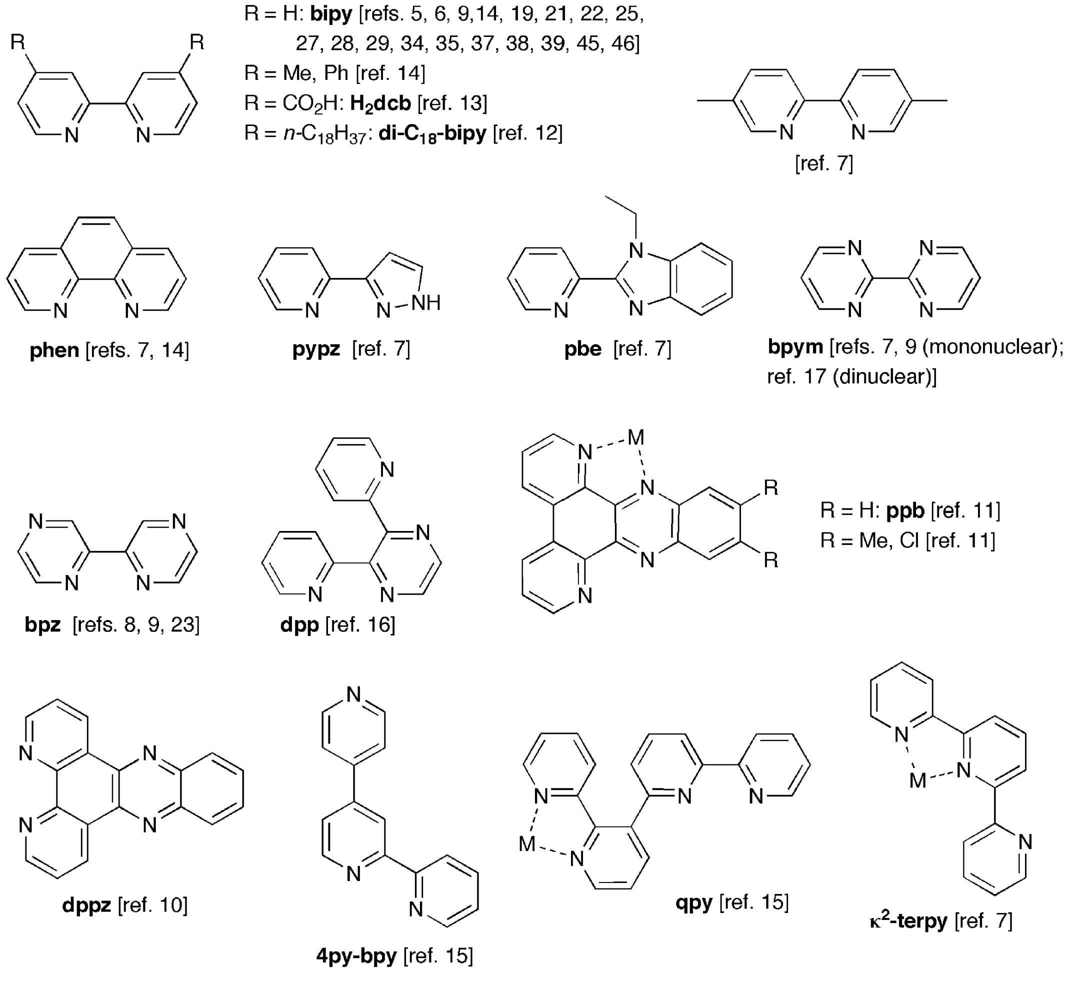

Fig. 1. Ligands that have been used to make complexes $[Ru(diimine)(CN)_4]^{2-}$. For those that are referred to in the main text, abbreviations are given. When there is any ambiguity, the site of metal coordination is indicated.

exploited; this dispenses with the photolysis and just requires reaction of $K_4[Ru(CN)_6]$ with bipy at reflux in aqueous acid (or aqueous acid/MeOH mixtures) at a pH of 3–4 [6]. This yields the complex as its potassium salt which is conveniently purified by precipitation from aqueous solution using acetone, followed if necessary by either gel-filtration or ion-exchange chromatography on different forms of Sephadex. These synthetic methods have been applied to complexes with a wide range of other diimines such as those in Fig. 1 [7–17]. Use of potentially bridging ligands such as 2,3-bis(2-pyridyl)pyrazine [16] and 2,2′-bipyrimidine [17] affords a mixture of mononuclear and dinuclear complexes, which are readily separated by ion-exchange chromatography on Sephadex eluting with aqueous KI.

Interestingly, reaction of $K_4[Ru(CN)_6]$ with terpy in aqueous acid this way does not give $K[Ru(terpy)(CN)_3]$ with a terdentate terpy ligand, but affords instead $K_2[Ru(\kappa^2\text{-terpy})(CN)_4]$ in which the terpy ligand is only bidentate [7]. This is a shame as $K[Ru(terpy)(CN)_3]$ is in itself an interesting compound [18,19] whose only reported syntheses so far requires $[Ru(terpy)Cl_3]$ and $[Et_4N]CN$ [19].

Control of pH during the reaction is important, as too strongly acidic conditions will result in loss of HCN, liberating a coordination site at the Ru(II) centre which allows formation of oligomeric materials via coordination of a cyanide group from another $[Ru(\mathbf{NN})(CN)_4]^{2-}$ (where **NN** denotes a diimine ligand) to fill the vacancy. This results in a minor dark-coloured fraction appearing during chromatographic purification which is usually discarded as containing ‘unidentified polymeric impurities’ [6]; however, recent evidence suggests that these could be interesting materials in their own right. During attempts to crystallize the Sm(III) salt of $[Ru(bipy)(CN)_4]^{2-}$ using a batch that had been prepared under too-acidic conditions and not purified properly before use, crystals of the Sm(III) salt of $[Ru_2(bipy)_2(CN)_7]^{3-}$ were isolated [20]. The complex anion contains a bridging cyanide ligand and can be written as $[(NC)_3(bipy)Ru(\mu\text{-}CN)Ru(bipy)(CN)_3]^{3-}$; the crystal structure of the Sm(III) salt (Fig. 2) is interesting, being a one-dimensional coordination network containing a sequence of alternating square and hexagonal macro-rings based on Ru–CN–Sm interactions. This presages some of the coordination networks of $[Ru(diimine)(CN)_4]^{2-}$ units with lanthanide ions that will be discussed later. The dinuclear complex $[Ru_2(bipy)_2(CN)_7]^{3-}$, if it can be isolated in significant quantities, should have interesting electrochemical and photophysical properties in its own right, but its occurrence here is a nice illustration of the importance of both pH control during the synthesis of $[Ru(bipy)(CN)_4]^{2-}$, and careful chromatographic purification subsequently.

The K^+ complexes prepared in this way are water-soluble but, unless they bear hydrophobic substituents such as alkyl groups, are essentially insoluble in organic solvents. For electrochemical and spectroscopic studies in other solvents (which is an important issue, given the solvatochromism of the complexes, as described below) cation metathesis is required. Cation exchange from K^+ to Bu_4N^+ affords salts which are highly soluble in organic solvents, although they can in our experience be hygroscopic. More recently Mann et al. proposed the use of the bulky cation $[Ph_3P{=}N{=}PPh_3]^+$(PPN), and this is very convenient [21]; simply mixing hot aqueous solutions of $K_2[Ru(\mathbf{NN})(CN)_4]$ and PPNCl generally affords a precipitate of clean, crystalline $(PPN)_2[Ru(\mathbf{NN})(CN)_4]$ which is soluble in polar organic solvents such as MeCN, acetone and dmf.

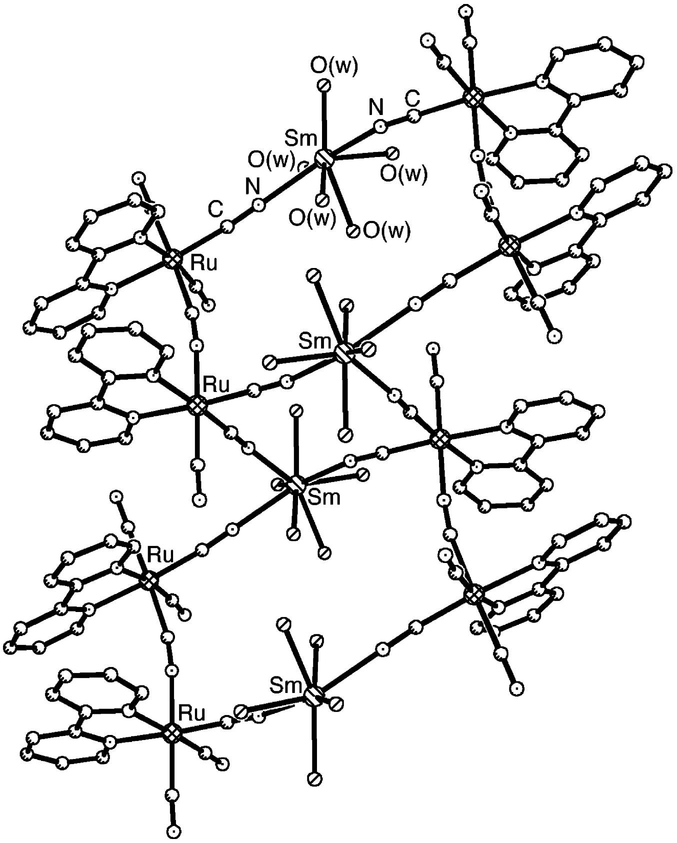

Fig. 2. Part of the one-dimensional coordination polymer $\{[Sm(H_2O)_5][(NC)_3(bipy)Ru(\mu\text{-}CN)Ru(bipy)(CN)_3]\cdot 11H_2O\}_\infty$ showing the alternation of hexagonal $Ru_3Sm_3(\mu\text{-}CN)_6$ and square $Ru_2Sm_2(\mu\text{-}CN)_4$ rings (O(w) denotes an oxygen atom from a coordinated water ligand). See ref. [20].

3. Photophysical and electrochemical properties in solution: solvatochromism

The presence of a single bipyridyl ligand in $[Ru(bipy)(CN)_4]^{2-}$ makes the complex an appealing target for the detailed study of MLCT excited states, as the presence of only one diimine ligands means that, in contrast to $[Ru(bipy)_3]^{2+}$, questions as to whether the excited electron is localized on one ligand or delocalized over several do not arise [22]. The strong-field cyanide ligands mimic the strong ligand-field environment provided by the bipy ligands in $[Ru(bipy)_3]^{2+}$, but without being able to participate in MLCT transitions. From a combination of electrochemical and spectroelectrochemical studies, it is clear that the oxidation at positive potential is a Ru(II)/Ru(III) couple, and the reduction at high negative potential is ligand-centred [5,9,23]; consequently, the lowest excited state has MLCT character, with the absorption generating the ^{1}MLCT state and

Table 1
Compilation of photophysical data for mononuclear [Ru(**NN**)(CN)$_4$]$^{2-}$ complexes

Ligand **NN**	Solvent	Temperature	λ_{max} (nm) (10^{-3} ε (M^{-1} cm^{-1}))[a]	λ_{em} (nm) (τ (ns))	Ref.
bipy	Water	rt	400	610 (101)	[5]
	dmf	rt	562	813 (≈4)	[5]
	9 M aqueous LiCl	77 K		521 (6800)	[5]
	dmf:CH_2Cl_2 (9:1)	77 K		610 (2000)	[5]
bipy	Water	rt	404 (4.1)	640	[19]
	dmf	rt	559 (4.6)	818	[19]
bipy	Water	rt	404 (4.1)	624 (100)	[26]
	Dmso	rt	550 (5.4)	806	[26]
	Dmso	77 K		590 (2000)	[26]
bipy	Water	rt	400	629 (120)	[14]
	D_2O	rt	400	629 (364)	[14]
	EtOH/MeOH	77 K		560	[14]
bipy	MeOH	rt	445	640 (62)	[30]
	MeOD	rt	445	640 (156)	[30]
bipy	MeCN	rt	535	790 (7)	[34]
	[32-Ane-N_8·8H]$^{8+}$/MeCN	rt	415	640 (330)	[34]
bipy	Solid state, 100% humidity	rt	458	655	[21]
	Solid state, under dry N_2	rt	571	815	[21]
phen	Water	rt	385	610 (590)	[14]
	D_2O	rt	385	610 (1940)	[14]
	EtOH/MeOH	77 K		571	[14]
4,4′-Me_2bipy	Water	rt	395	621 (113)	[14]
	D_2O	rt	395	621 (355)	[14]
	EtOH/MeOH	77 K		562	[14]
4,4′-Me_2bipy	Water	rt	392	600 (115)	[33]
	MeCN	rt	530	780 (7)	[33]
4,4′-Ph_2bipy	Water	rt	417	645 (145)	[14]
	D_2O	rt	417	645 (450)	[14]
	EtOH/MeOH	77 K		588	[14]
5,5′-Me_2bipy	D_2O	rt	393 (2.1)	621 (370)	[7]
	MeCN	rt	514	758 (36)	[7]
bpym	D_2O	rt	437 (2.2)	– (3.4)[b]	[7]
	MeCN	rt	575	– (0.25)[b]	[7]
pbe	D_2O	rt	404 (3.6)	665 (471)	[7]
	dmf	rt		– (4.5)	[7]
pypz	D_2O	rt	353 (6.9)	554 (17)	[7]
κ^2-terpy	D_2O	rt	411 (2.7)	647 (106)	[7]
bpz	Water	rt	465 (5.7)	704 (5)	[8]
	Acetone	rt	599 (5.0)		[8]
	9 M aqueous LiCl	77 K		599	[8]
	EtOH/MeOH	77 K		659	[8]
bpz	dmf	rt	601		[23]
	MeCN	rt	554		[23]
dpp	Water	rt	447 (≈5)	652	[16]
ppb	Water	rt	524	– (<5)[b]	[11]
Me_2ppb	Water	rt	524	– (<5)[b]	[11]
dppz	Water	rt	390		[10]
	Dmso	rt	520		[10]
	EtOH	77 K		600	[10]
4py-bpy	MeCN/water	rt	448 (4.6)	684 (60)	[15]
qpy	MeCN/water	rt	440 (3.0)	680 (30)	[15]
H_2dcb	MeCN	rt	515	750	[13]
	dmf	rt	535	770	[13]

[a] Lowest-energy MLCT absorption maximum.

[b] Emission maximum either not measured or too weak to detect under the conditions used; lifetimes were determined from transient IR or Raman spectroscopy.

emission coming from the ^{3}MLCT state [22], exactly as with $[Ru(bipy)_3]^{2+}$ and other d^6 metal–polypyridyl complexes.

In contrast to other d^6 metal–polypyridyl complexes, however, $[Ru(bipy)(CN)_4]^{2-}$ is remarkably solvatochromic, with the redox properties, ^{1}MLCT absorption and ^{3}MLCT emission maxima all varying substantially as a function of solvent. This solvatochromism of $[Ru(bipy)(CN)_4]^{2-}$ and its relatives arises from two effects: (i) a dipolar interaction between the complex anion and the solvent and (ii) the interaction of the lone pairs of electrons on the cyanide ligands with solvents which have the ability to act as electron acceptors, principally by containing δ^+ H atoms which act as hydrogen-bond donors [5–8,10,19,22]. This electron-accepting characteristic of the solvent is quantified by the Gutmann acceptor number, a measure determined by NMR experiments of the ability of each solvent to accept a pair of electrons [24]. Values for some common solvents are: water, 54.8; MeOH, 41.3; CH_2Cl_2, 20.4; MeCN, 19.3; dmf, 16.0; acetone, 12.5; thf, 8.0. It will be seen that water is in a class by itself as an electron acceptor, with alcohols next, and solvents such as MeCN, chlorinated solvents, dmf and dmso all being poor electron acceptors. The reasonably good basicity of the cyanide N-termini of $[Ru(bipy)(CN)_4]^{2-}$ is shown by the pK_a value of 1.8 for the first protonation of a cyanide group [8].

The dipole of $[Ru(bipy)(CN)_4]^{2-}$, which lies along the C_2 axis, is stabilized by a dipolar interaction with strongly polar solvents. This effect is diminished in the ^{3}MLCT excited state because the direction of the Ru → bipy charge transfer reduces the dipole moment. Consequently, the energy gap between ground and MLCT excited states is higher in polar solvents. In addition, the occurrence of Ru–CN···H–X hydrogen-bonding interactions with protic solvents (as shown by X-ray diffraction studies in both the solid state [21] and in aqueous solution [25]) results in removal of electron density from the cyanide ligand and increases its ability to act as a π-acceptor, thereby increasing its ligand field strength and lowering the Ru-d(π) orbitals in energy, as shown by redox potential measurements (see below). Since the bipy π^* orbital energy is relatively insensitive to solvent effects [6], this means that the effect of hydrogen bonding is to increase the energy gap between ground and MLCT excited states in hydrogen-bond-accepting solvents. These two quite distinct effects tend to act in concert because solvents which are strong hydrogen-bond donors also tend to be polar.

This solvatochromism has several consequences. In the electronic spectrum, the energy of the lowest-energy absorption, the Ru[d(π)] → bipy(π^*) ^{1}MLCT transition, is blue-shifted in higher polarity and more strongly hydrogen-bonding solvents; likewise, the ^{3}MLCT emission maximum is blue-shifted and, following the energy-gap law which states that higher-energy excited states are less susceptible to quenching by low-energy vibrations, the emission becomes more intense and longer lived [5–8,19,22]. The effect is substantial: changing from dmso to water, for example, results in the ^{1}MLCT absorption of $[Ru(bipy)(CN)_4]^{2-}$ moving from 550 to 400 nm (see Table 1 for a compilation of spectroscopic and photophysical data), with a consequent colour change in the complex from purple to yellow [19]; the associated ^{3}MLCT luminescence moves from 805 nm (barely detectable) to 624 nm, with a lifetime in water of 100–120 ns (different papers report slightly different values in this range) [5,14,26]. The change in absorption and luminescence spectral properties of $[Ru(bipy)(CN)_4]^{2-}$ as the solvent composition is varied between pure water and pure dmso is shown in Fig. 3. It will be apparent that the shift in energy in the ^{3}MLCT emission maxima between these two solvents ($\approx$3600 cm^{-1}) is much less that the shift in energy between the ^{1}MLCT absorption maxima ($\approx$6600 cm^{-1}), which is because of the weaker interaction between the cyanide lone pairs and the solvent molecules in the excited state. Transient oxidation of the metal centre in the ^{3}MLCT state reduces the electron density on the cyanide N atoms, thereby making them less basic and reducing their hydrogen-bonding capability; it has been calculated that the N···H hydrogen bonds lengthen by 0.05 Å in the excited state, in the gas phase [25]. Likewise, the reduced dipole moment in the excited state lowers the dipolar interaction with the solvent. The result is that the emission maxima are less solvent-dependent than the absorption maxima [27–29]. In MeOH/EtOH mixtures at temperatures just above the freezing point, where the solvent is viscous, excitation of $[Ru(bipy)(CN)_4]^{2-}$ results in emission whose wavelength increases with time over a few microseconds as the solvent reorganizes to stabilize the excited state [22].

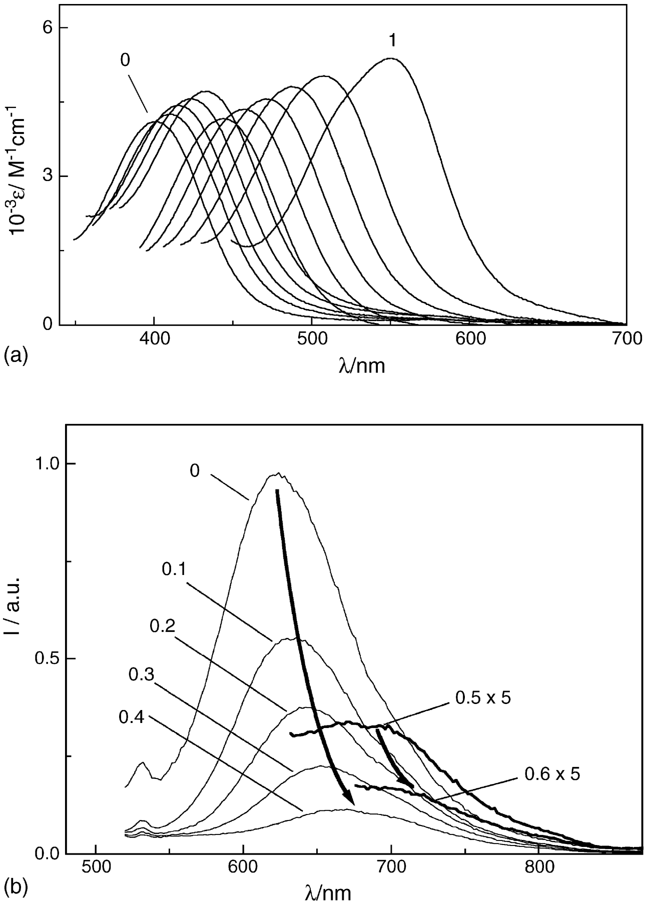

Fig. 3. Solvent dependence of (a) the ^{1}MLCT absorption and (b) ^{3}MLCT emission, of $K_2[Ru(bipy)(CN)_4]$ in water/dmso mixtures of varying composition (‘0’ denotes pure water, ‘1’ denotes pure dmso). See ref. [26].

Other members of the $[Ru(\mathbf{NN})(CN)_4]^{2-}$ series show the same behaviour [7,8,10]: for example, the lowest-energy

^{1}MLCT absorption of $[Ru(bpym)(CN)_4]^{2-}$ moves from 437 nm in water to 575 nm in MeCN, and the ^{3}MLCT excited state lifetime decreases from 3.4 to 0.25 ns [7]. Of the complexes prepared so far, $[Ru(pypz)(CN)_4]^{2-}$ has the highest ^{3}MLCT energy with an emission maximum in water of 554 nm; however its lifetime is relatively short (18 ns) [7]. The longest excited state lifetime is shown by $[Ru(phen)(CN)_4]^{2-}$ (590 ns in water at 298 K) because the rigidity of the phen ligand compared to bipy prevents some of the non-radiative deactivation pathways [14]. Using D_2O as solvent instead of H_2O increases the lifetimes and quantum yields further, not because of changes in the energy levels concerned (which are the same in H_2O and D_2O) but, again, because use of D_2O decreases the non-radiative decay rate constant. Thus, the emission lifetime of $[Ru(phen)(CN)_4]^{2-}$ in D_2O is nearly 2 μs, and for $[Ru(bipy)(CN)_4]^{2-}$ the ^{3}MLCT lifetime increases from 120 to 364 ns from H_2O to D_2O [14,30]. Similar effects have been observed on comparison of the photophysical properties of $[Ru(bipy)(CN)_4]^{2-}$ between normal and deuterated alcoholic solvents, with significant increases in luminescence lifetimes and quantum yields detected in the deuterated alcohols [30].

The redox potentials of these complexes are similarly solvent-dependent, for the same reasons. The Ru(II)/Ru(III) redox potential of $[Ru(bipy)(CN)_4]^{2-}$ becomes much more positive in H-bond donating solvents such as alcohols and water, because the stabilization of the d(π) orbitals makes removing an electron more difficult. In the original paper describing the first synthesis of $[Ru(bipy)(CN)_4]^{2-}$, Scandola and co-workers report the Ru(II)/Ru(III) couples as +0.78 V in water and +0.20 V in dmf, both versus SCE, a swing of 580 mV [5]. In a later paper, Timpson et al. report the Ru(II)/Ru(III) couples in these same solvents to be +0.77 V in water and −0.28 V in dmf, versus ferrocene/ferrocenium as internal reference, a much larger swing of 1.05 V [19]; these potentials translate to +1.08 and +0.03 V versus SCE using the conversion factor given in the paper. This is a substantial discrepancy. A possible reason for this is the use of different supporting electrolytes. Bignozzi et al. report using $[Et_4N][ClO_4]$ as base electrolyte [5]; Timpson et al., however, do not report what base electrolyte was used. Given the particular sensitivity of $[Ru(bipy)(CN)_4]^{2-}$ to interactions with its environment, we may speculate that the redox potential of $[Ru(bipy)(CN)_4]^{2-}$ is particularly affected by the nature and concentration of other solutes used as electrolytes. Murphy and co-workers report that the presence of different cations in solution (e.g. alkali metal ions versus tetraalkylammonium ions) results in changes to the electronic spectra of complexes of this type [10]. We found the Ru(II)/Ru(III) redox potential of $K_2[Ru(bipy)(CN)_4]$ to be +0.89 V versus Ag/AgCl in water containing 0.1 M KCl [7]. Table 2 contains a compilation of electrochemical data from the literature.

The combination of the effects of solvent on the ^{3}MLCT energy and the ground state redox potential mean that the excited state redox potentials of $[Ru(bipy)(CN)_4]^{2-}$ will also be strongly solvent-dependent. In its excited state, $^*[Ru(bipy)(CN)_4]^{2-}$ is a considerably stronger reductant than $^*[Ru(bipy)_3]^{2+}$ {the potential of the $[Ru(bipy)_3]^{3+}/^*[Ru(bipy)_3]^{2+}$ couple is only −0.86 V versus NHE in water [1a]} because less of the excited state energy is required to oxidize the metal to Ru(III), to an extent depending on the solvent. For example, protonation of the pendant pyridyl residues of $[Ru(qpy)(CN)_4]^{2-}$ and [Ru(4py-

Table 2
Compilation of electrochemical data for mononuclear $[Ru(\mathbf{NN})(CN)_4]^{2-}$ complexes

Ligand **NN**	Ru(III)/Ru(II) redox potential	Ligand-centred redox potential	Conditions	Ref.
bipy	+0.78 V vs. SCE		Water/TEAP[a]	[5]
	+0.20 V vs. SCE	−1.95 V vs. SCE	dmf/TEAP	[5]
bipy	+0.77 V vs. Fc/Fc$^+$		Water	[19]
	−0.14 V vs. Fc/Fc$^+$		MeCN	[19]
	−0.28 V vs. Fc/Fc$^+$		dmf	[19]
bipy		−2.46 V vs. Fc/Fc$^+$	dmf/TBAF[b]	[9]
bipy	+0.89 V vs. Ag/AgCl		Water/KCl	[7]
bipy	+0.80 V vs. SCE		Water	[34]
	+0.27 V vs. SCE	−1.95 V vs. SCE	MeCN/TBAF	[34]
	+1.0 V vs. SCE	−1.58 V vs. SCE	MeCN/TBAF/[32-ane-$N_8{\cdot}8H]^{8+}$ (Fig. 7)	[34]
5,5′-Me_2bipy	+0.85 V vs. Ag/AgCl		Water/KCl	[7]
pbe	+0.79 V vs. Ag/AgCl		Water/KCl	[7]
pypz	+0.83 V vs. Ag/AgCl		Water/KCl	[7]
bpym	+1.05 V vs. Ag/AgCl		Water/KCl	[7]
bpym		−2.09 V vs. Fc/Fc$^+$	dmf/TBAF	[9]
bpz		−2.00 V vs. Fc/Fc$^+$	dmf/TBAF	[9]
bpz	+1.00 V vs. SSCE		Water	[8]
	+0.50 V vs. SSCE	−1.48 V vs. SSCE	dmf/TBAF	[8]
bpz	+0.50 V vs. Ag/AgCl	−1.48 V vs. Ag/AgCl	dmf/TBAF	[23]
dpp	+0.44 V vs. Ag/AgCl	−1.59 V vs. Ag/AgCl	MeCN/TBAF	[16]

[a] TEAP, tetraethylammonium perchlorate.

[b] TBAF, tetrabutylammonium hexafluorophosphate (also called TBAH in some papers).

bpy)$(CN)_4]^{2-}$ results in quenching of the luminescence, presumably by photoinduced electron-transfer (the pendant pyridyl groups are more basic than the cyanide groups, with pK_a values of 3.13 and 3.19, so protonation occurs preferentially at the pyridyl groups) [15].

Using the redox potentials reported in ref. [5], Bignozzi et al. estimated the potentials of the $[Ru^{III}(bipy)(CN)_4]^-/^*[Ru(bipy)(CN)_4]^{2-}$ couple as somewhere between −1.6 and −1.28 V in water, and somewhere between −1.83 and −1.32 V (versus SCE) in dmf [31]. Thus, although the ^{3}MLCT excited state of $[Ru^{II}(bipy)(CN)_4]^{2-}$ has a higher energy content in water, it is a better electron donor in dmf (and other aprotic solvents) as a consequence of the much greater ease of formation of the Ru(III) form in these solvents. This represents an intriguing potential use of this (and related) complexes, viz. as energy- or electron-transfer agents whose properties can be controlled with a high degree of precision by varying the solvent.

On the basis of the larger redox potential swing of >1 V for the Ru(II)/Ru(III) couple of ground state $[Ru(bipy)(CN)_4]^{2-}$ between different water and dmf reported in ref. [9], it should be possible to alter the potential of the $[Ru^{III}(bipy)(CN)_4]^-/^*[Ru(bipy)(CN)_4]^{2-}$ couple over a much wider range than that suggested in ref. [5], with the complex becoming an extremely strong excited-state reductant in aprotic solvents. The possibility to switch on/off photoinduced electron transfer by changing the solvent is an intriguing one for the development of molecular electronic devices. Clearly, a detailed study of the electrochemistry of $[Ru(bipy)(CN)_4]^{2-}$, not only in different solvents but in the presence of different electrolytes – and the consequent effects on the excited state redox potentials – would be very useful. Examples of polynuclear assemblies in which the ability of $[Ru(bipy)(CN)_4]^{2-}$ to act as an energy-donor is controlled by changing the solvent are discussed in a later section.

4. Time-resolved infrared spectroscopy of $[Ru(bipy)(CN)_4]^{2-}$ and its relatives

In the ground state, four CN vibrational modes are expected for these complexes. These are all resolved in solid state spectra, with three strong peaks closely spaced in the 2030–2060 cm^{-1} range and a weaker peak at around 2090 cm^{-1}; in aqueous solution the peaks are less well resolved [7,15]. In the ^{3}MLCT excited state, the loss of electron density from the metal, which becomes (formally) Ru(III), should result in a reduction in Ru-$d(\pi) \rightarrow CN(\pi^*)$ back-bonding and hence an increase in the CN stretching frequency. An exactly similar effect is well-established in $[Re(bipy)(CO)_3Cl]$ and its derivatives, where the CO bands move to higher energy in the ^{3}MLCT excited state [32].

A typical example is shown in Fig. 4, which shows the IR difference spectrum of $[Ru(bpym)(CN)_4]^{2-}$ in D_2O, 100 ps shortly after excitation at 400 nm [7]. The main feature on the low-energy end of the spectrum corresponds to a bleach (reduction in intensity) of the ground state C–N vibrational manifold as the ground state is depopulated. The weaker upward-going feature to the left is the new C–N vibration of the excited state, and it is shifted higher in energy by ≈50 cm^{-1} with respect to the ground state. Since this is the most intense feature in the vibrational spectrum of the excited state it is assumed to correspond to the main bleach in the ground state spectrum. The weakness of this C–N vibrational band in the excited state is consistent with the expected diminution of the C–N dipole moment in the excited state. Since cyanide formally carries a negative charge at the C atom, transient oxidation of the metal centre to Ru(III) will reduce this and result in lower intensity C–N vibrations in the excited state. A range of different mononuclear complexes in this series gave similar results [7,15], with a shift of ≈50 cm^{-1} to higher energy in the principal C–N vibration when the ^{3}MLCT state forms. The rate of disappearance of the transient peak, and the reappearance of the bleached ground state signal, allowed determination of ^{3}MLCT lifetimes for those complexes whose emission was too weak or short-lived to measure, e.g. 3.4 ns for $[Ru(bpym)(CN)_4]^{2-}$ in D_2O (from the data in Fig. 4), and 250 ps for the same complex in MeCN [7]. This method has obvious promise for examining fast photoinduced energy or electron transfer in polynuclear complexes; such studies are being carried out in the author's group.

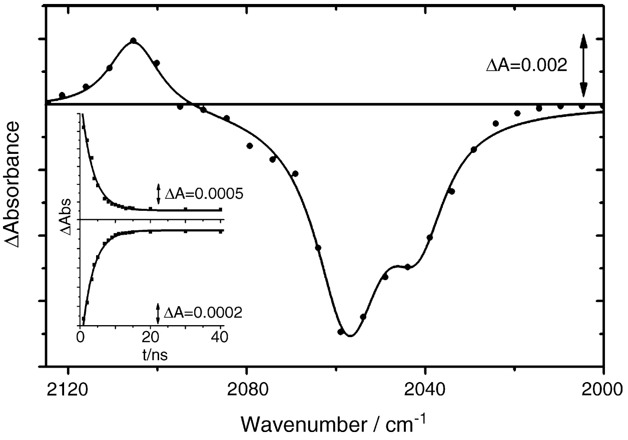

Fig. 4. IR difference spectrum of $K_2[Ru(bpym)(CN_4)]$ in D_2O obtained 100 ps after 400 nm excitation into the ^{1}MLCT absorption manifold. *Inset*: Kinetic traces showing decay of the transient (top) and recovery of the bleach (below) from which excited state lifetimes were derived.

5. Applications associated with solvatochromism

The solvent-dependent absorption spectral behaviour of $[Ru(bipy)(CN)_4]^{2-}$ has been exploited by Evju and Mann as a simple crystalline humidity sensor. The crystal structure of $(PPN)_2[Ru(bipy)(CN)_4]$ revealed large channels in the structure occupied by solvent molecules which could interact with the cyanide groups of the complex anion. The anhydrous material is purple, but on exposure to moist air it turns yellow as water molecules enter the channels and solvate the complex anion. The change is reversible on heating, with the degree of change in the absorption (and emission) behaviour of the solid related to the extent of water uptake; up to 15 molecules of water per $[Ru(bipy)(CN)_4]^{2-}$ could be absorbed, with the cyanide ligands *trans* to the bipy ligand being the first to be solvated on the basis of FTIR studies [21].

Another simple way to exploit the solvent-dependent properties of these complexes has been demonstrated by Bignozzi and co-workers using the complex $[Ru(dcb)(CN)_4]^{4-}$ (dcb is the dianion of 2,2′-bipyridine-4,4′-dicarboxylic acid). This complex anchors to nanocrystalline films of TiO_2 in the usual way and acts as a sensitizer in a regenerative solar cell, with the added refinement that changing the solvent modifies both the light-harvesting behaviour of the dye (related to its absorption spectrum) and the efficiency with which injected electrons are converted into current (indirectly related to the redox potential of the dye). The highest IPCE (incident photon-to-current conversion efficiency) value obtained was 40% at 510 nm using thf as solvent [13].

Two examples of the solvent-based switching of photoinduced energy-transfer in dyad systems based on $[Ru(bipy)(CN)_4]^{2-}$ chromophores have been described. Fig. 5 shows the complexes involved. In complex **A**, the energy of the ^{3}MLCT state of the $[Ru(bipy)_3]^{2+}$ terminus is essentially solvent-invariant. In contrast, the ^{3}MLCT energy of the $[Ru(bipy)(CN)_4]^{2-}$ terminus varies such that in water it is approximately equal to that of $[Ru(bipy)_3]^{2+}$, whereas in dmso it is lower by >3500 cm^{-1}, as shown by studies on mononuclear model complexes [26]. Accordingly, we expect a situation where as the solvent composition is changed from pure H_2O to water/dmso mixtures, the steady drop in energy of the $[Ru(bipy)(CN)_4]^{2-}$ ^{3}MLCT state makes it more effective at acting as an energy-acceptor from the $[Ru(bipy)_3]^{2+}$ terminus whose luminescence should therefore become quenched. This is illustrated in Fig. 6, which shows the emission intensity of the $[Ru(bipy)_3]^{2+}$ unit as a function of solvent composition: quenching of this luminescence as energy-transfer to the $[Ru(bipy)(CN)_4]^{2-}$ unit becomes endergonic is clear. In principle, sensitized luminescence from the $[Ru(bipy)(CN)_4]^{2-}$ terminus should become apparent, but in dmso this is inherently very weak and presumably lost in the tail of the residual $[Ru(bipy)_3]^{2+}$-based luminescence. At 77 K, the reverse happens: the ^{3}MLCT level of the $[Ru(bipy)(CN)_4]^{2-}$ unit is blue-shifted more than that of the $[Ru(bipy)_3]^{2+}$ unit, even in dmso, such that $[Ru(bipy)(CN)_4]^{2-} \rightarrow [Ru(bipy)_3]^{2+}$ energy-transfer occurs and sensitized emission from the $[Ru(bipy)_3]^{2+}$ terminus is seen [26].

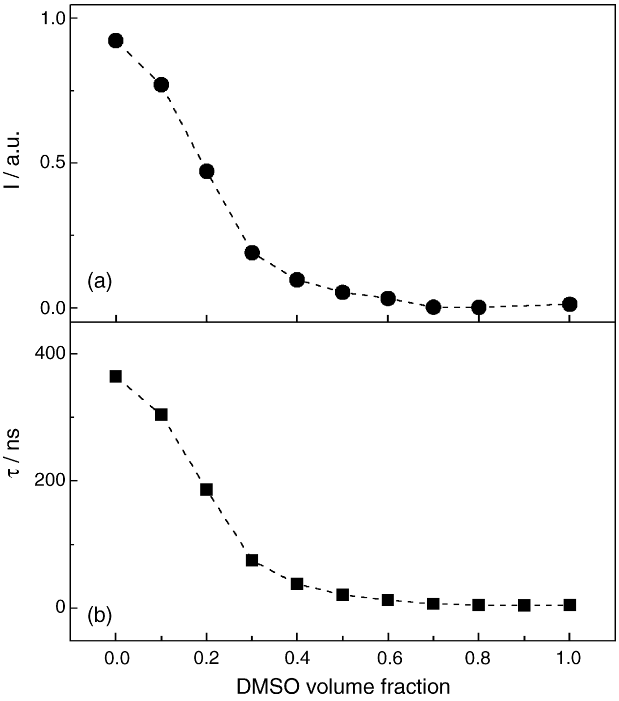

Fig. 6. Effect of changing the dmso/water proportions on (a) the luminescence intensity and (b) the luminescence lifetime, of the $[Ru(bipy)_3]^{2+}$ unit of complex **A** (measured at 620 nm). See ref. [26].

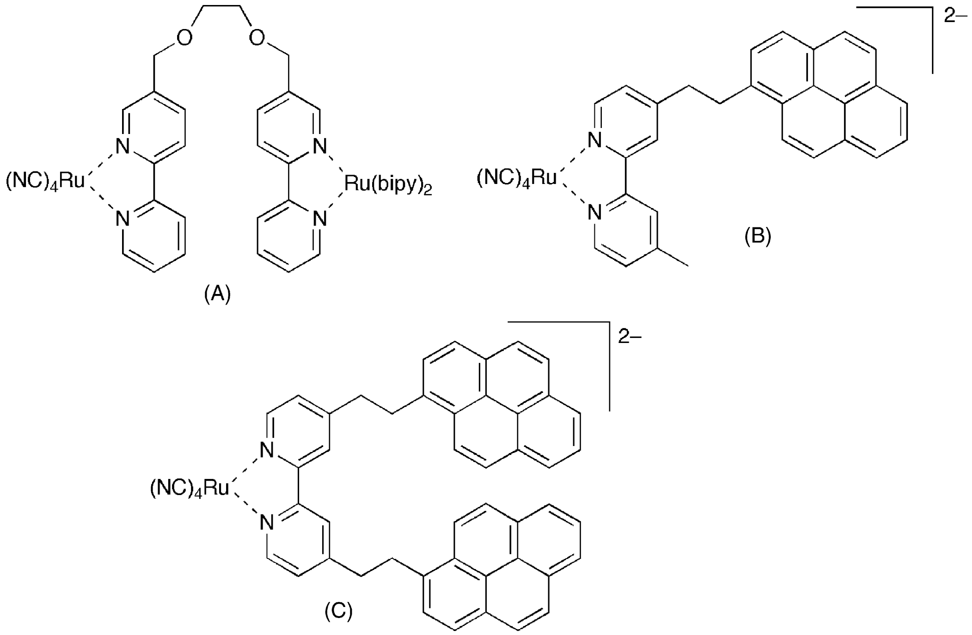

Fig. 5. Structural formulae of complexes **A**–**C** in which energy-transfer between the $[Ru(bipy)(CN)_4]^{2-}$ unit and the other component is controlled by changing the solvent.

In complexes **B** and **C** [33], energy-transfer between the covalently-linked $[Ru(bipy)(CN)_4]^{2-}$ and pyrene units is controlled in the same way. In water, the high ^{3}MLCT energy of the Ru unit is 1900 cm^{-1} above the pyrene $^3\pi-\pi^*$ level, resulting in fast Ru → pyrene energy-transfer and complete quenching of Ru-centred luminescence. In contrast, in MeCN, the Ru-based ^{3}MLCT state is now 1100 cm^{-1} *below* the pyrene triplet level, such that energy-transfer cannot occur and the normal weak emission characteristic of $[Ru(bipy)(CN)_4]^{2-}$ occurs. In MeOH, however, a particularly interesting situation arises, with the energies of the Ru-based ^{3}MLCT and the pyrene-based $^3\pi-\pi^*$ levels being very similar such that energy-transfer between the two states is *reversible* and the two excited states are in thermal equilibrium. The consequence of this is a remarkable lengthening of the emission lifetime (to 260 ns, cf. 30 ns for mononuclear $[Ru(Me_2bipy)(CN)_4]^{2-}$ under the same conditions). The emission has the characteristics of arising from the Ru-based ^{3}MLCT state, whose deactivation is inherently much faster than that of the pyrene triplet state, but it has the same lifetime as the pyrene triplet state as shown by transient absorption measurements. Thus, by altering the solvent, it has been demonstrated that the $[Ru(bipy)(CN)_4]^{2-}$ ^{3}MLCT can lie above, below, or in equilibrium with the pyrene $^3\pi-\pi^*$ state.

6. Interaction of $[Ru(bipy)(CN)_4]^{2-}$ with protonated aza-crown macrocycles: hydrogen-bonded assemblies

Protonated aza-crown macrocycles such as $[24\text{-ane-}N_6\cdot 6H]^{6+}$ and $[32\text{-ane-}N_8\cdot 8H]^{8+}$ act as effective hydrogen-bonding partners for $[Ru(bipy)(CN)_4]^{2-}$, by formation of $Ru–CN\cdots HN^+$ charge-assisted hydrogen bonds [34–36]. In this way the polyammonium species mimic the behaviour of strongly hydrogen-bonding solvents, such that when $[32\text{-ane-}N_8\cdot 8H]^{8+}$ is added to $[Ru(bipy)(CN)_4]^{2-}$ in MeCN, the spectroscopic properties of the complex anion immediately change to those normally associated with highly protic environments, viz. a colour change from purple to yellow, and a corresponding blue-shift and increased lifetime for the ^{3}MLCT luminescence [34]. Thus, the weak emission of $[Ru(bipy)(CN)_4]^{2-}$ in MeCN (790 nm, 7 ns) shifts to 640 nm with a lifetime of 330 ns after addition of $[32\text{-ane-}N_8\cdot 8H]^{8+}$; the Ru(II)/Ru(III) redox potential also undergoes a substantial positive shift. In water the spectroscopic shifts are less obvious because the change in environment is not so great – the cyanides were already involved in hydrogen-bonding interactions – but NMR experiments show that a strong adduct with $[32\text{-ane-}N_8\cdot 8H]^{8+}$ forms even in water. A proposed structure for this 'supercomplex' is shown in Fig. 7. Surprisingly, despite the fact that the $[Ru(bipy)(CN)_4]^{2-}/[32\text{-ane-}N_8\cdot 8H]^{8+}$ adduct should be a good reductant in its excited state (see earlier), electrostatic association with potential electron-acceptors carrying a negative charge {e.g. $[Rh(dcb)_3]^{3-}$, whose pendant carboxylates also form hydrogen bonds with the protonated amines of the macrocycle} does not result in luminescence quenching even though it should be endergonic. It is proposed that the macrocyclic surround acts as an insulator preventing electronic interactions between excited $^*[Ru(bipy)(CN)_4]^{2-}$ and the potential electron-acceptor [34].

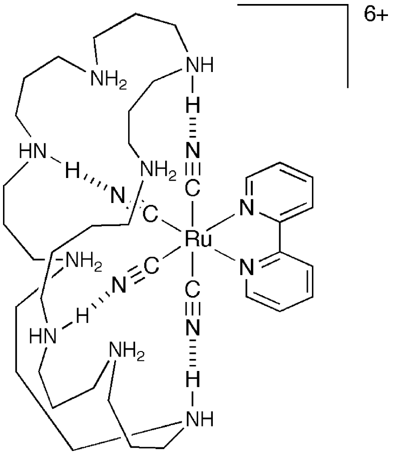

Fig. 7. Proposed structure for the hydrogen-bonded supercomplex $\{[Ru(bipy)(CN)_4]\cdot[32\text{-ane-}N_8\cdot 8H]\}^{6+}$; hydrogen-bonds are indicated by thick black lines.

Additional consequences of supercomplex formation with protonated amine macrocycles are that the complex anion is rigidified, and the number of energy-accepting vibrational modes provided by closely associated solvent molecules is reduced (several independent water molecules are replaced by one macrocycle). Thus, although replacement of the coordinating shell of water molecules by a protonated polyamine macrocycle does not change the *energy* of the ^{3}MLCT state, its *lifetime* is substantially lengthened due to a reduction in the non-radiative decay rate. A related consequence is that the volume increase following excitation to the ^{3}MLCT state (due to the weakening of the hydrogen bonds to the cyanide groups) is much less: ca. 15 cm^3 mol^{-1} for $[Ru(bipy)(CN)_4]^{2-}$ in water but 5 cm^3 mol^{-1} for the supercomplex with $[32\text{-ane-}N_8\cdot 8H]^{8+}$, because of the greater rigidity of the macrocyclic cavity [35].

The strong hydrogen-bond interaction between protonated aza-crowns and $[Ru(bipy)(CN)_4]^{2-}$ has been exploited as a way of combining photoactive components in supramolecular assemblies (Fig. 8). Complex **D** contains a $[Ru(bipy)_3]^{2+}$ core with a pendant diprotonated 14-ane-N_4 (cyclam) macrocyclic unit to which, in a non-competitive solvent like MeCN, one molecule of $[Ru(bipy)(CN)_4]^{2-}$ can associate, resulting in the expected blue-shift in its absorption and emission maxima. This adduct formation results in quenching of the luminescence of the $[Ru(bipy)_3]^{2+}$ unit by Förster energy-transfer to the associated $[Ru(bipy)(CN)_4]^{2-}$ unit whose ^{3}MLCT level is slightly lower in energy; the energy-transfer rate constant is 3.8×10^7 s^{-1}, allowing estimation of the inter-chromophore separation of 11.5 Å [37]. In a similar vein, complex **E** contains four $[Ru(bipy)_3]^{2+}$ units pendant from a di-protonated cyclam core. In MeCN, a $[Ru(bipy)(CN)_4]^{2-}$ fragment associates to the two protonated sites of the macrocycle and quenches the emission of the $[Ru(bipy)_3]^{2+}$ units by energy-transfer, with an energy-transfer rate constant of 5.8×10^7 s^{-1}. Accordingly, this system behaves as an 'energy-trap' with the four $[Ru(bipy)_3]^{2+}$-type chromophores funneling their excited state energy to a single centre, in the manner of natural photosynthetic systems [38].

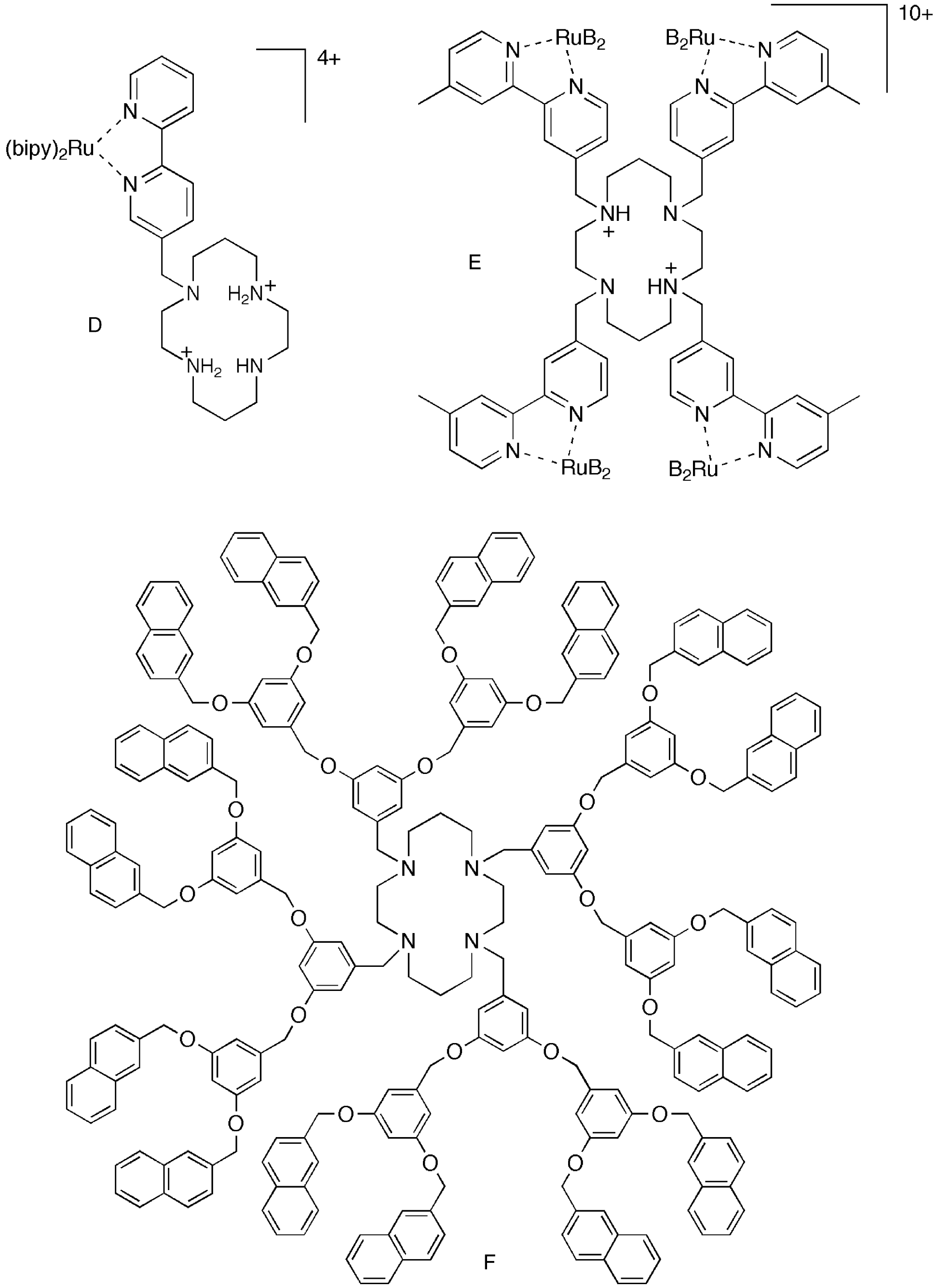

Fig. 8. Substituted cylam derivatives used to form hydrogen-bonded assemblies with $[Ru(bipy)(CN)_4]^{2-}$ (for complex **E**; ‘B’ denotes 2,2′-bipyridine).

Extending this principle even further, compound **F** comprises a dendrimeric array of 16 naphthalene units around a central 14-ane-N_4 core. Whilst **F** is neutral there is no association with $[Ru(bipy)(CN)_4]^{2-}$ in $MeCN/CH_2Cl_2$, however; addition of acid protonates two of the amine groups, immediately allowing $[Ru(bipy)(CN)_4]^{2-}$ to associate via two hydrogen bonds and resulting in strong quenching of the naphthalene luminescence by energy transfer to the $[Ru(bipy)(CN)_4]^{2-}$ unit. Addition of base removes the protons and separates the two components; also, addition of *excess* acid protonates the cyanides of $[Ru(bipy)(CN)_4]^{2-}$ and similarly disrupts the assembly. Thus, the system **F**/$[Ru(bipy)(CN)_4]^{2-}$ exhibits one of two different luminescence outputs (naphthalene-based or Ru-based) depending on the presence of acid or base, and can function as either an XOR or an XNOR logic gate depending on which luminescent output is read [39].

7. Coordination networks of $[Ru(diimine)(CN)_4]^{2-}$ anions with K^+ and lanthanides

Until recently, the only crystal structure determination of a member of this family was $(PPN)_2[Ru(bipy)(CN)_4]\cdot 2H_2O\cdot 2MeCN\cdot 2Et_2O$ by Mann and co-workers [21]; this was proposed as a humidity sensor on the basis of the

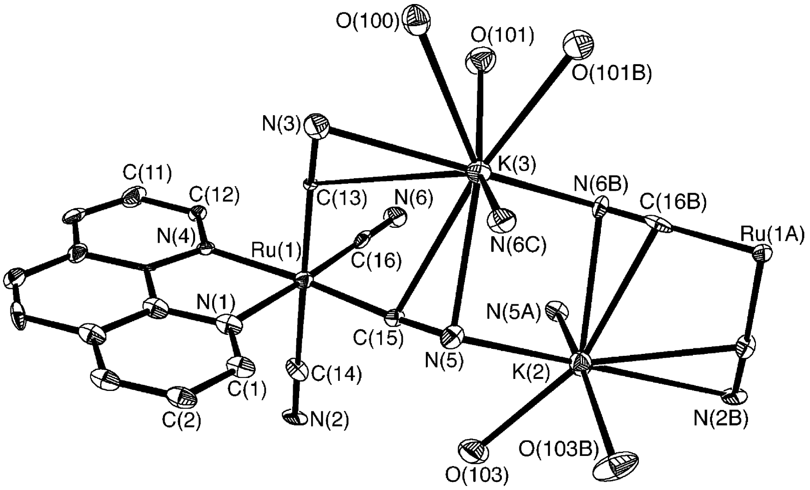

Fig. 9. ORTEP diagram of the asymmetric unit of $K_2[Ru(phen)(CN)_4]\cdot4H_2O$, with some additional symmetry-equivalent atoms included to complete the coordination spheres around the metal atoms. Note, in particular, the side-on interactions of cyanide ligands with K^+ ions. See ref. [7].

reversible uptake of water into the solvent channels in the structure, leading to a yellow–purple colour change (see Section 5, above).

Our fortuitous isolation of crystals of $[Ru_2(bipy)_2(CN)_7]^{3-}$ as its Sm(III) salt [20] prompted us to embark on a more systematic study of the structural chemistry of $[Ru(bipy)(CN)_4]^{2-}$ and its derivatives, with two aims in mind. Formation of Ru–CN–M bridges should lead to formation of coordination networks and polymers in the manner well known with other cyanometallate anions. However, these should have the added interest that the solid materials would be photophysically active. Given the sensitivity of the complexes to interaction of the cyanides with Lewis acids such as protic solvents or aza-crown macrocycles, coordination of metal ions to the cyanides would provide an additional mechanism for modifying the properties of the chromophore; further, the possibility of photoinduced energy and/or electron transfer to the counter-ions M^{n+} is also available.

X-ray diffraction studies of the K^+ salts of $[Ru(phen)(CN)_4]^{2-}$, $[Ru(\kappa^2\text{-terpy})(CN)_4]^{2-}$ and $[Ru(bpym)(CN)_4]^{2-}$ revealed formation of coordination networks based on complicated arrays of Ru–CN–K interactions, but with (in every case) the unexpected formation of 'side-on' interactions between cyanide ligands and K^+ ions in addition to the expected 'end-on' Ru–CN–K interactions [7]. There are a few examples of such side-on interactions between cyanide ions and alkali metal cations in the literature, from the work of Rauchfuss and co-workers [40–42], but they are surprisingly rare given the extensive structural chemistry of other cyanometallate anions. These interactions, presumably arising from weak electrostatic attraction of the K^+ centres to the electron density in the triple bond, are characterized by approximately equal K···C and K···N separations and, as shown in Figs. 9 and 10, are part of complicated coordination network structures. It is noticeable how some cyanide ions manage to interact with four metal cations, being C-bound to Ru(II), end-on N-bound to K^+, and side-on interacting with two further K^+ ions.

In contrast, salts of $[Ru(bipy)(CN)_4]^{2-}$ with hard lanthanide(III) cations are based exclusively on end-on Ru–CN–Ln bridges, with the lanthanide(III) cations also coordinated by water molecules [7,17,43,44]. Thus, $[\{Ru(bipy)(CN)_4\}_3\{Ln(H_2O)_4\}_2]\cdot xH_2O$ (Ln = Gd, Nd) have a two-dimensional layer structure based on fused $Ru_2Ln_2(\mu\text{-CN})_4$ squares, with bipy ligands above and below the central metal cyanide layer (Fig. 11) and each Ru centre being involved in either two or three Ru–CN–Ln bridges. $[\{Ru(bipy)(CN)_4\}_2\{Pr(H_2O)_7\}\{K(H_2O)_2\}]\cdot10H_2O$ contains both Pr^{3+} and K^+ cations, and forms discrete tetranuclear units in which two $[Ru(bipy)(CN)_4]^{2-}$ units each coordinate one cyanide ligand to the central lanthanide(III) cation, and the K^+ ion lies neatly in the central cavity described by four cyanide ligands and is side-on coordinated to all of them (Fig. 12). Yb(III) and Er(III) afford networks of the same stoichiometry but with the K^+ ions in a different position [44]. Other structural types formed by related complexes include a one-dimensional chain of corner-sharing $Ru_2Er_2(\mu\text{-CN})_4$ diamondoid units displayed by $KEr[Ru(pbe)(CN)_4]_2\cdot10H_2O$, and a helical one-dimensional chain formed by $[Eu(NO_3)(H_2O)_5][Ru(bpym)(CN)_4]$ [7]. The

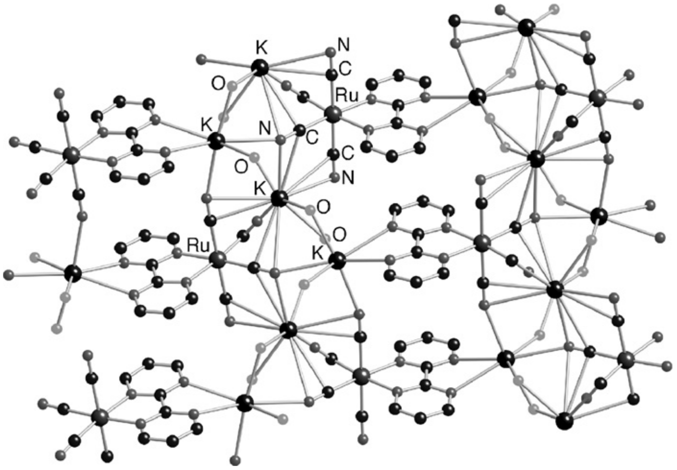

Fig. 10. View of the two-dimensional sheet structure of $K_2[Ru(bpym)(CN)_4]\cdot3H_2O$. See ref. [7].

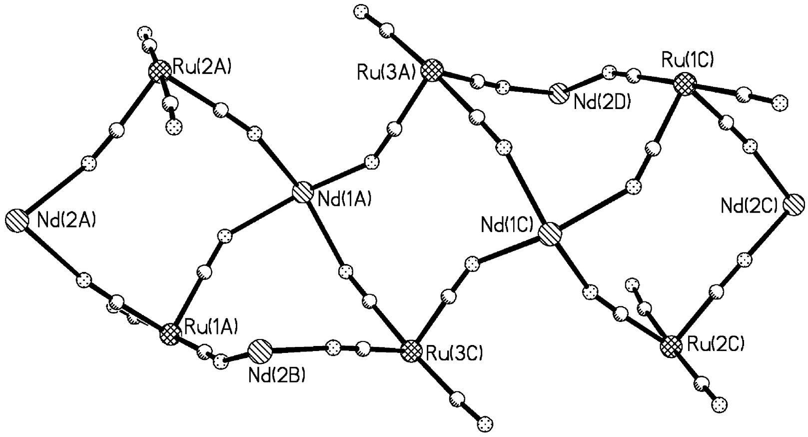

Fig. 11. Part of the two-dimensional sheet structure in $[\{Ru(bipy)(CN)_4\}_3\{Nd(H_2O)_4\}_2]\cdot 11H_2O$, showing only the metal ions and the cyanide bridging ligands. See ref. [44].

dinuclear complex $[\{Ru(CN)_4\}_2(\mu\text{-bpym})]^{4-}$, which has a connectivity of potentially eight via its cyanide groups, actually uses six of the cyanides to bind to lanthanides in the cubic structure of $[\{Ru(CN)_4\}_2(\mu\text{-bpym})][Gd(hfac)(H_2O)_4]_2\cdot 10H_2O$ (Fig. 13) [17]. The structural properties of complexes based on $[Ru(bipy)(CN)_4]^{2-}$ and related anions is clearly an area worth pursuing further.

8. Photophysical properties of coordination networks: energy-transfer to lanthanides and sensitized near-infrared luminescence

As a microcrystalline solid, $K_2[Ru(bipy)(CN)_4]\cdot 3H_2O$ shows ^{3}MLCT luminescence with the emission maximum at 570 nm [43]. This is at higher energy than the luminescence observed in water, partly because of the lack of solvent repolarisation in the excited state, and partly because coordination of a cyanide ligand to a K^+ ion has an even stronger electron-withdrawing effect than does interaction with a δ+ proton of water. The lifetime is much longer than in solution, with two components being observed at 750 ns (major component) and 2955 nm (minor component). The presence of two components may be ascribed to the facts that (i) not all complex molecules in the crystal may be in the same environment, but there may be crystallographically independent units which interact with different numbers of K^+ ions/water molecules and/or (ii) the crystal necessarily is imperfect with molecules at the surface or at defect sites being in a different environment from those in the interior.

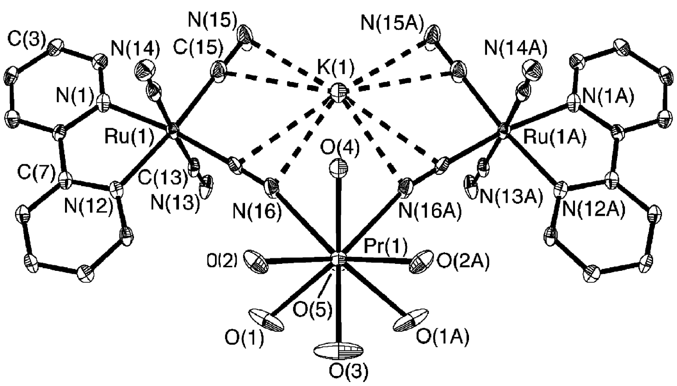

Fig. 12. ORTEP diagram of the molecular structure of $[\{Ru(bipy)(CN)_4\}_2\{Pr(H_2O)_7\}\{K(H_2O)_2\}]\cdot 10H_2O$.

In the lanthanide salts, energy-transfer is possible to those lanthanide(III) ions which have f–f levels significantly below the ^{3}MLCT level of the $[Ru(bipy)(CN)_4]^{2-}$ unit, which allows the strongly-absorbing d-block fragment to act as an antenna and provide sensitized luminescence from f-block ions which cannot easily be excited directly because of the weakness of the f–f transitions. We used Pr, Nd, Er and Yb for this purpose since all of them display near-infrared luminescence from low-lying f–f states [44]. In these networks, the combination of (i) reduced

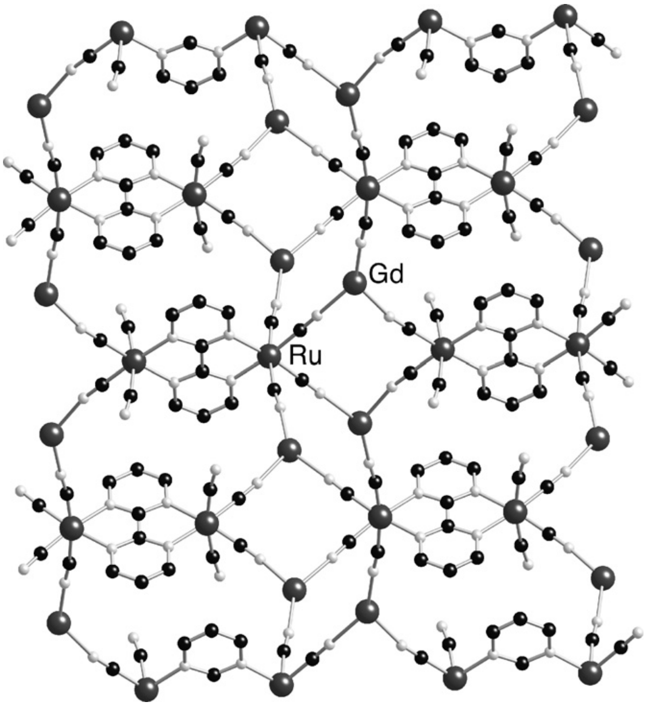

Fig. 13. A view of the three-dimensional lattice in $[\{Ru(CN)_4\}_2(\mu\text{-bpym})][Gd(hfac)(H_2O)_4]_2\cdot 10H_2O$, showing only the Ru, Gd, bipyrimidine and cyanide atoms. See ref. [17]

intensity and lifetime for the Ru-centred emission and (ii) the appearance of the characteristic near-IR lanthanide emission bands following excitation of the Ru centre (e.g. Yb, 980 nm; Nd, 880 and 1060 nm; Er, 1550 nm; Pr, 840 and 1010 nm), proved that Ru → Ln energy-transfer had occurred. Although the coordination networks in this series are not isostructural, Ru → Ln energy-transfer will be dominated by the closest Ru···Ln separations which are about the same in every case and not dependent on the bulk structure.

Time-resolved measurements on the residual ^{3}MLCT Ru-based emission allowed calculation of the rate of Ru → Ln energy-transfer in these networks, which varied over approximately two orders of magnitude, from $2 \times 10^8\ s^{-1}$ (for Ru → Nd energy-transfer) to $3 \times 10^6\ s^{-1}$ (for Ru → Yb energy-transfer). These energy-transfer rates correlate well with the availability of f–f excited states of the appropriate energy on the lanthanide centre, which will determine the spectroscopic overlap integral between Ru-based emission and lanthanide-based absorption. Nd(III) has many f–f absorptions in the visible region, overlapping with the emission envelope of the $[Ru(bipy)(CN)_4]^{2-}$ unit; in contrast, Yb(III) has a single f–f absorption at 980 nm which only just overlaps with the low-energy tail of the Ru-based emission. Thus, the rates of energy-transfer are clearly highly dependent on the donor/acceptor spectral overlap between the Ru energy-donor and the lanthanide energy-acceptor [44].

9. Miscellaneous other work

Derivatives of $[Ru(bipy)(CN)_4]^{2-}$ have attracted interest in other fields. The amphiphile $[Ru(di\text{-}C_{18}\text{-}bipy)(CN)_4]^{2-}$, with two C_{18} alkyl chains attached to the bipy ligand, was used to prepare monolayers which reacted with Fe^{3+} ions to form a two-dimensional Prussian-Blue type Langmuir–Blodgett film [12].

Soaking a Cd-plated electrode in a solution of $K_2[Ru(bipy)(CN)_4]$ affords a layer of $Cd[Ru(bipy)(CN)_4]$ on the electrode surface; this layer is luminescent, emitting at 590 nm, but when the layer is oxidized [Ru(II) → Ru(III)] by application of a positive potential the luminescence disappears [45]. The luminescence reappears only slowly when the potential is reversed, because of slow electron-transfer kinetics, however, this problem can be ameliorated by the presence of a $[CdFe(CN)_6]^{2-/-}$ layer on the electrode surface which speeds up the heterogeneous charge-transfer rate.

The dinuclear complex $[\{Ru(CN)_4\}_2(\mu\text{-}dpp)]^{4-}$, with two metal centres connected by a pyrazine bridge, displays a separation of 230 mV between the successive Ru(II)/Ru(III) couples in aqueous solution; the mixed-valence Ru(II)–Ru(III) state displays an inter-valence charge-transfer band at 1100 nm, from which a rather weak metal–metal coupling V_{ab} of $550\ cm^{-1}$ was calculated, consistent with a weakly interacting valence-localized (Robin and Day class II) species [16].

$[Ru(CN)_4(dppz)]^{2-}$ shows unusual dual emission behaviour, with very weak green dppz-centred emission in fluid solution which reverts to the expected red emission of the ^{3}MLCT chromophore at 77 K. This implies a thermal equilibrium between ligand-centred and ^{3}MLCT levels which is not possible at 77 K [10]. Transient resonance Raman spectra of $[Ru(CN)_4(ppb)]^{2-}$ reveal little change in geometry of the ppb ligand when it is transiently reduced to its radical anion, in agreement with DFT calculations [11].

The effects of an external magnetic field on the rates of photoinduced electron transfer from $[Ru(bipy)(CN)_4]^{2-}$ to methylviologen were studied to generate information on the rates of back electron-transfer, spin-relaxation in the photogenerated radical pair, and the rate of cage escape. For example, the $[Ru^{III}(bipy)(CN)_4]^-/MV^{\bullet+}$ radical pair dissociates particularly slowly, possibly because of a specific ion-pairing effect which is absent in (for example) the $[Ru^{III}(bipy)_3]^{3+}/MV^{\bullet+}$ radical ion pair [46].

10. Conclusions

It will be clear from the above examples that $[Ru(bipy)(CN)_4]^{2-}$ and its analogues offer unique advantages for the preparation of photoactive supramolecular assemblies, due to a combination of tunable redox and photophysical properties, the presence of IR-active spectroscopic handles, and the ability of the complexes to participate in supramolecular assemblies by both hydrogen-bonding and coordination to additional metal ions. Despite these useful characteristics, this complex has so far received relatively little attention compared to $[Ru(bipy)_3]^{2+}$ and is deserving of much more extensive study.

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