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Luminescence and Time-Resolved Infrared Study of Dyads Containing (Diimine)Ru(4,4′-diethylamido-2,2′-bipyridine)$_2$ and (Diimine)Ru(CN)$_4$ Moieties: Solvent-Induced Reversal of the Direction of Photoinduced Energy-Transfer

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The exploitation of the dramatic negative solvatochromism of the [Ru(bipy)(CN)$_4$] moiety (bipy = 2,2′-bipyridine) allows a change in solvent to reverse the direction of photoinduced energy transfer (PEnT) in two related dinuclear complexes. Both dyads consist of a [Ru(bpyam)$_2$L^n]$^{2+}$ (**Ru-bpyam**) unit (bpyam = 4,4′-diethylamido-2,2′-bipyridine; L^n = bis-bipyridyl-based bridging ligand) and a [Ru(L^n)(CN)$_4$]$^{2-}$ (**Ru-CN**) unit. Both termini have IR-active spectroscopic handles (amide carbonyl or cyanide, respectively) allowing the excited-state dynamics to be studied by time-resolved IR (TRIR) spectroscopy. One dyad (**1**) contains a relatively rigid exoditopic macrocyclic bis-bipyridyl bridging ligand (L^1) and the other (**2**) contains a more flexible bis-bipyridyl bridging ligand with only one covalent linkage between the two bipyridyl binding sites (L^2). The conformational effects on PEnT rates in these dyads are probed using a combination of luminescence and TRIR studies. In both **1** and **2** in D$_2$O it is demonstrated that **Ru-CN** → **Ru-bpyam** PEnT occurs (PEnT time scales were in the range 10 ps−3 ns) because the ^{3}MLCT energy of the **Ru-CN** terminus is higher than that of the **Ru-bpyam** terminus. Changing the solvent from D$_2$O to CH$_3$CN results in lowering the ^{3}MLCT energy of the **Ru-CN** unit below that of the **Ru-bpyam** unit such that in both dyads a reversal in the direction of PEnT to **Ru-bpyam** → **Ru-CN** (time scales of 10 ps−2 ns) occurs. Complex kinetic behavior results from the presence of a dark ^{3}MLCT excited state formulated as $\{(\text{bpyam})_2\text{Ru}^{3+}(\text{L}^{n\bullet-})\}$ and by the presence of multiple conformers in solution which have different Ru···Ru separations giving rise to different energy transfer rates.

Introduction

Photoinduced energy transfer (PEnT) and electron transfer (PET) have been widely exploited in the area of supramolecular photochemistry.[1] PEnT is an extensively studied phenomenon[2] because of its importance in photosynthesis and photosynthetic model compounds,[3] artificial light harvesting antenna systems for solar energy conversion,[4] sensing and imaging,[5] display devices[6] and, potentially, in molecular electronic devices, whereby excitation energy is used as information which can be transferred from one point to another.[7] At the molecular level such devices use energy transfer over long distances and/or along predetermined

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directions usually utilizing metal coordination compounds consisting of an energy donating unit and an energy accepting unit.[8] The level of sophistication of these "molecular wires" is increasing, and in this context the design, synthesis, characterization, and understanding of molecules in which the direction of PEnT can be controlled is an area of great interest.[7,8] However, the construction of multimetallic systems for such complex functions has been mostly based on the covalent linkage of the photoresponsive units and involves construction of sophisticated molecular architectures and considerable synthetic effort.

There is interest in being able to control and switch energy transfer more simply. For example, Pikramenou, DeCola, and co-workers have tried to overcome the synthetic complexity of producing such systems by constructing dyad and triad assemblies based on cyclodextrin receptors which form metal-containing donor−acceptor systems in water. In one example they demonstrated[9] that the direction of energy transfer can be switched from or to a Ru(II) center appended to a cyclodextrin by the choice of the metalloguest, Os(II) or Ir(III), bound in the cyclodextrin cavity. In a second example they showed[10] that a unidirectional two-step photoinduced energy transfer process takes place by using a self-assembled junction formed by selective binding of three different photoactive components.

In this paper we investigate in detail the use of the solvatochromic $[Ru(bipy)CN)_4]^{2-}$ unit[11] in switching the direction of energy transfer in simple dyads simply by changing the nature of the solvent. The energy of the ^{3}MLCT state of $[Ru(bipy)(CN)_4]^{2-}$ is strongly affected by interaction of the cyanide lone pairs with hydrogen-bond donor solvents, such that the ^{3}MLCT state is low in energy in solvents such as MeCN and CH_2Cl_2 (with very weak luminescence at around 800 nm) but much higher in energy in water, displaying strong, long-lived luminescence at around 600 nm.[11] This property has been exploited in some simple dyads in which the flow of energy between a $[Ru(bipy)CN)_4]^{2-}$ unit and an additional chromophore could be controlled by changing the solvent composition: these systems were studied by luminescence methods only.[12]

Two recent pieces of work from our groups provide the platform for this new study.[13] First, we performed a luminescence- and TRIR-based study into the photophysics of the dyad **RuL^{2}Re** (Chart 1) containing $\{Re(bipy)(CO)_3Cl\}$ and $\{Ru(bipy)(bpyam)_2\}^{2+}$ termini, with a particular focus on Re → Ru photoinduced energy-transfer.[13a] TRIR studies, which were facilitated by the presence of IR-active functional groups at both termini, revealed the presence of at least three distinct Re → Ru energy-transfer processes, with lifetimes of about 20 ps, 1 and 13 ns. This was ascribed to a combination of (i) two different Ru-based ^{3}MLCT states (Ru → L^2 and Ru → bpyam) with different spatial localizations, and (ii) the presence of different conformers with different Re···Ru separations arising from the flexible ethylene spacer of the bridging ligand L^2. The combination of these effects gives a range of distances for interchromophore Re → Ru energy-transfer, from which we could isolate three different energy-transfer rate constants; and it was notable that the TRIR studies provided much more information about the kinetic behavior of the faster events than did the luminescence measurements.

Second, we studied the dyad **2** (Chart 1) based on the same bridging ligand but containing a different combination of chromophores: a $\{Ru(bipy)(bpyam)_2\}^{2+}$ terminus (as before) whose MLCT energy levels are approximately independent of solvent, and a $\{Ru(CN)_4(bipy)\}$ terminus whose ^{3}MLCT energy could be varied substantially by either changing the solvent polarity (solvatochromism) or, more unusually, adding metal cations to interact with the cyanide lone pairs (metallochromism).[13b] In this dyad the direction of intercomponent energy-transfer could be reversed by adding Ba^{2+} ions to the solvent. In MeCN the $\{Ru(bipy)(bpyam)_2\}^{2+}$ terminus has a higher-energy ^{3}MLCT state than does the $\{Ru(CN)_4(bpy)\}^{2-}$ terminus, leading to conventional **RuBpy → Ru-CN** energy-transfer and quenching of the **RuBpy** luminescence. Addition of Ba^{2+} ions, which coordinate to

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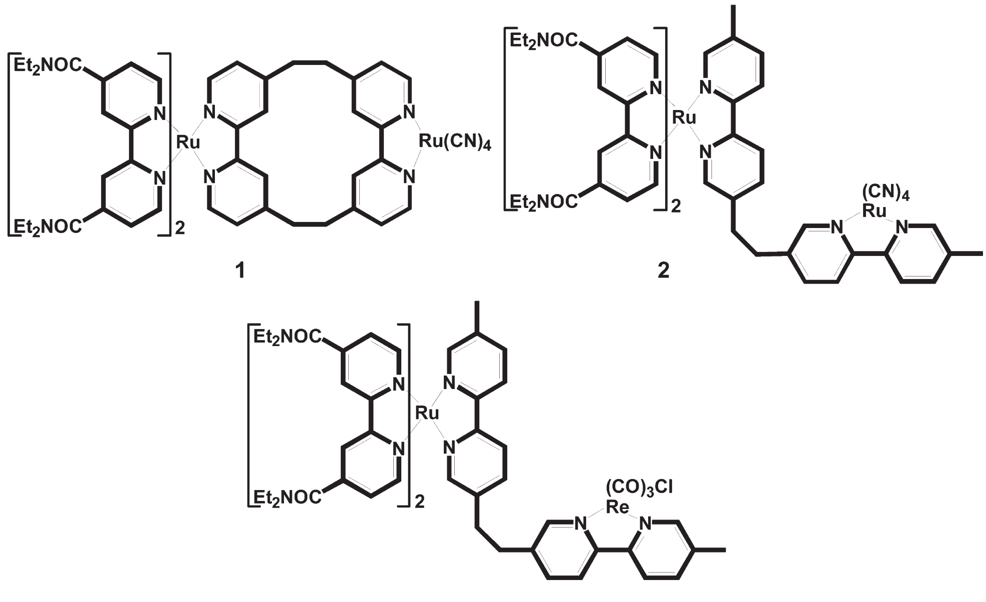
Chart 1



ReL^{2}Ru

the cyanide groups, raises the ^{3}MLCT energy of the $\{Ru(CN)_4(bipy)\}^{2-}$ terminus to the extent that it lies higher in energy than the $\{Ru(bipy)(bpyam)_2\}^{2+}$ terminus, leading to **Ru-CN** → **RuBpy** energy-transfer and the restoration of the strong **RuBpy** luminescence. Addition of dibenzo-18-crown-6 to the mixture, which sequestrates the Ba^{2+} ions, reverses the effect, allowing the direction of energy-transfer to be switched back and forth between the two chromophores.

Taken together, these two recent studies have allowed us to investigate the effects of conformational flexibility of the bridging ligand, and the ability to modify the ^{3}MLCT energy of one component selectively, on the energy-transfer processes in the two dyads. One of the aims of this new work is to use the combination of TRIR and luminescence techniques to study in detail the interchromophore energy-transfer processes occurring in the related pair of dyads **1** and **2** (Chart 1), both comprising a $\{Ru(CN)_4(bipy)\}^{2-}$ terminus (hereafter **Ru-CN**) connected by a saturated ethylene spacer to a $\{Ru(bipy)(bpyam)_2\}^{2+}$ (bpyam = 4,4′-diethylamide-2,2′-bipyridine) terminus (hereafter **Ru-bpyam**), via use of the bis-bipyridyl bridging ligands L^1 and L^2. Our investigations focus on two particular features of these complexes. First, the comparison between **1** and **2** will allow us to probe the extent to which rigidification of the bridging ligand affects the energy-transfer kinetics. This will potentially simplify the possible processes that are occurring by restricting the conformational flexibility of the complexes and hence the range of interchromophore distances available in different conformations. Second, the use of different solvents will allow us to exploit the solvatochromism of the **Ru-CN** termini and examine whether it is possible to switch the direction of energy-transfer between the metal complex units simply by changing the solvent, in a similar manner to that reported in studies using emission analysis methods.[12]

The mononuclear complexes $[Ru(bpyam)_2(L^1)]^{2+}$ (**RuL^1**), $[Ru(bpyam)_2(L^2)]^{2+}$ (**RuL^2**) and $[Ru(CN)_4(bipy)]^{2-}$ [**Ru-CN**] were also investigated as model complexes for comparison purposes. The diethylamide substituents on **RuL^1** and **RuL^2** serve two useful purposes by (i) greatly improving the solubility of these complexes, and (ii) providing convenient IR-active reporters, the amide carbonyl groups, which can be a sensitive probe of changes in electron distribution upon MLCT excited state formation.[13a] The saturated spacers in the dinuclear complexes mean that the **Ru-CN** and **Ru-bpyam** chromophores can be considered as electronically isolated such that their individual properties can be accurately estimated by using the mononuclear model complexes.

Results and Discussion

The dinuclear complexes **1** and **2** are shown in Chart 1. The latter is conformationally highly flexible with a single ethylene spacer separating the two chromophores, whereas the former is more rigid due to the cyclic structure of the ligand L^1 with two tethers between the bipyridyl binding sites. Both were prepared in a stepwise manner, by reacting the bridging ligand with 1 equiv. of $[Ru(bpyam)_2Cl_2]$ to add a $\{Ru(bpyam)_2\}^{2+}$ fragment to one terminus, followed by reaction with $K_4Ru(CN)_6$ to attach the $\{Ru(CN)_4\}^{2-}$ fragment to the second terminus. The combination of 2+ and 2− metal complex termini means that the complexes are neutral but zwitterionic in character.

UV/vis and Emission Measurements. The UV/vis absorption spectra of **1** and **2** in both D_2O and CH_3CN are shown in Figure 1 and summarized in Table 1. The main low-energy features of both dyads (whose spectra are very similar to one another) in CH_3CN are two ^{1}MLCT absorptions at around 450 nm associated with the **Ru-bpyam** terminus, and the lowest-energy ^{1}MLCT absorption of the **Ru-CN** terminus, which is apparent as a less intense shoulder at ~530 nm. For the **Ru-bpyam** terminus, the two ^{1}MLCT absorptions (at about 480 and 430 nm) can be ascribed to (bpyam)Ru → bpyam and (bpyam)Ru → L^n transitions respectively.[13,14] These bands are associated with the two different types of bipyridyl ligand and the ligand having the lower-energy lowest unoccupied molecular orbital (LUMO; bpyam) will give rise to the lower-energy ^{1}MLCT absorption. The mononuclear model complexes **RuL^1** and **RuL^2** show similar behavior.

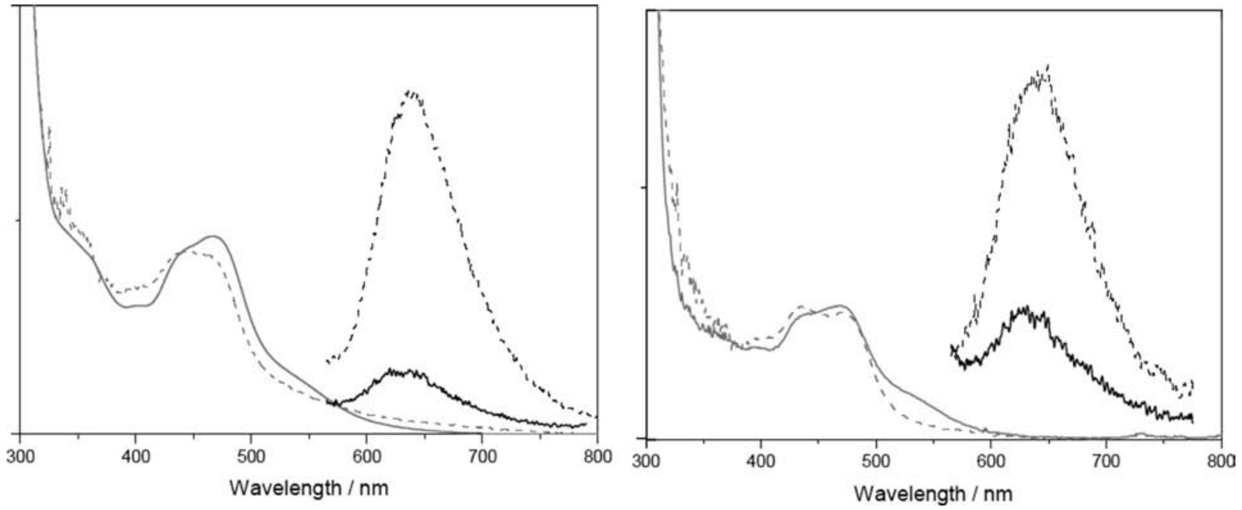


Figure 1. Absorption (*gray*) and emission (*black*) (excitation wavelength λ_{ex} = 400 nm) spectra of **1** (*left*) and **2** (*right*) in D_2O (*dashed*) and CH_3CN (*solid*).

Two ^{1}MLCT absorptions are expected for a **Ru-CN** chromophore in CH_3CN,[11] of which the ~530 nm shoulder is the lower in energy of the two; the higher-energy one is expected at about 370 nm but is obscured under the much more intense absorption of the **Ru-bpyam** terminus. In D_2O, the 530 nm shoulder is blue-shifted because of the solvatochromism of the **Ru-CN** unit, and disappears under the more intense **Ru-bpyam**-based absorptions, resulting in an increase in absorbance around 430 nm where the ^{1}MLCT absorptions for both termini now overlap.

The luminescence spectra of the two complexes show significant differences between the two solvents, associated with the solvent sensitivity of the ^{3}MLCT energy of the **Ru-CN** terminus.[11] Excitation into any of the absorption bands for either dyad in D_2O results in broad emission at about 655 nm. This is similar to the luminescence shown by the respective mononuclear model complexes **RuL^1** and **RuL^2**, and is associated with an emission from a Ru → bpyam ^{3}MLCT state.[14a,b] However, the luminescence from **1** and **2** is much weaker (by an order of magnitude) than that from **RuL^1** and **RuL^2**, indicating that the additional **Ru-CN** terminus in the dinuclear complexes partially quenches the **Ru-bpyam** based ^{3}MLCT state in each case, either by acting as an energy-acceptor or by providing new non-radiative quenching pathways. Time-resolved measurements show that this **Ru-bpyam** based emission is multiexponential for both **1** and **2**. We ascribe this to the presence of multiple conformers of the dinuclear complexes in solution, each of which will result in a different degree of quenching of the **Ru-bpyam** excited state by the **Ru-CN** terminus. The fact that some **Ru-bpyam** based luminescence still persists means that any **Ru-bpyam** → **Ru-CN** energy transfer is incomplete because either (i) the gradient is small (i.e., the two chromophores have similar ^{3}MLCT energies), and/or (ii) the distance is too great in some conformations for energy-transfer to complete with radiative deactivation of the **Ru-bpyam** terminus, even if it is thermodynamically favorable. We return to this later.

In CH_3CN the emission from both **1** and **2** undergoes two changes compared with the situation in D_2O. The major change is a significant reduction in intensity (by ≈ 80%), associated with additional quenching of the **Ru-bpyam** based ^{3}MLCT state. The minor change is a slight shift of the remaining luminescence to higher energy. The additional quenching of the **Ru-bpyam** based ^{3}MLCT state of both **1** and **2** in MeCN compared to D_2O can be ascribed to the reduction in energy of the ^{3}MLCT state of the **Ru-CN** unit (cf. the absorption spectrum), which increases the thermodynamic gradient for **Ru-bpyam** → **Ru-CN** energy transfer, as shown previously.[13b] (We note that any emission in the 750−800 nm region from the **Ru-CN** unit, either by direct excitation or following **Ru-bpyam** → **Ru-CN** energy transfer, is expected to be very weak and short-lived in MeCN such that it will not be detectable over the much stronger residual **Ru-bpyam** emission).[11a] The slight blue-shift of the weak residual **Ru-bpyam** emission on moving from D_2O to MeCN can be ascribed to slight *positive* solvatochromism of that terminus.[15] Again the lifetime of the residual **Ru-bpyam** emission is multiexponential in both complexes, similarly ascribable to the presence of multiple conformers.

The absorption and emission spectroscopy provides initial evidence that changing solvent from D_2O to MeCN increases the **Ru-bpyam** → **Ru-CN** energy transfer following a reduction in energy of the ^{3}MLCT state of the **Ru-CN** terminus. The excitation at 400 nm is, however, non-selective, so luminescence spectroscopy alone does not offer definitive evidence of energy transfer since both chromophores are excited simultaneously (in a ratio of ca. 2:1 **Ru-bpyam**/**Ru-CN** from the extinction coefficients above). It is therefore not possible to be sure which emission components arise from direct excitation of the **Ru-bpyam** chromophore and which arise, for example,

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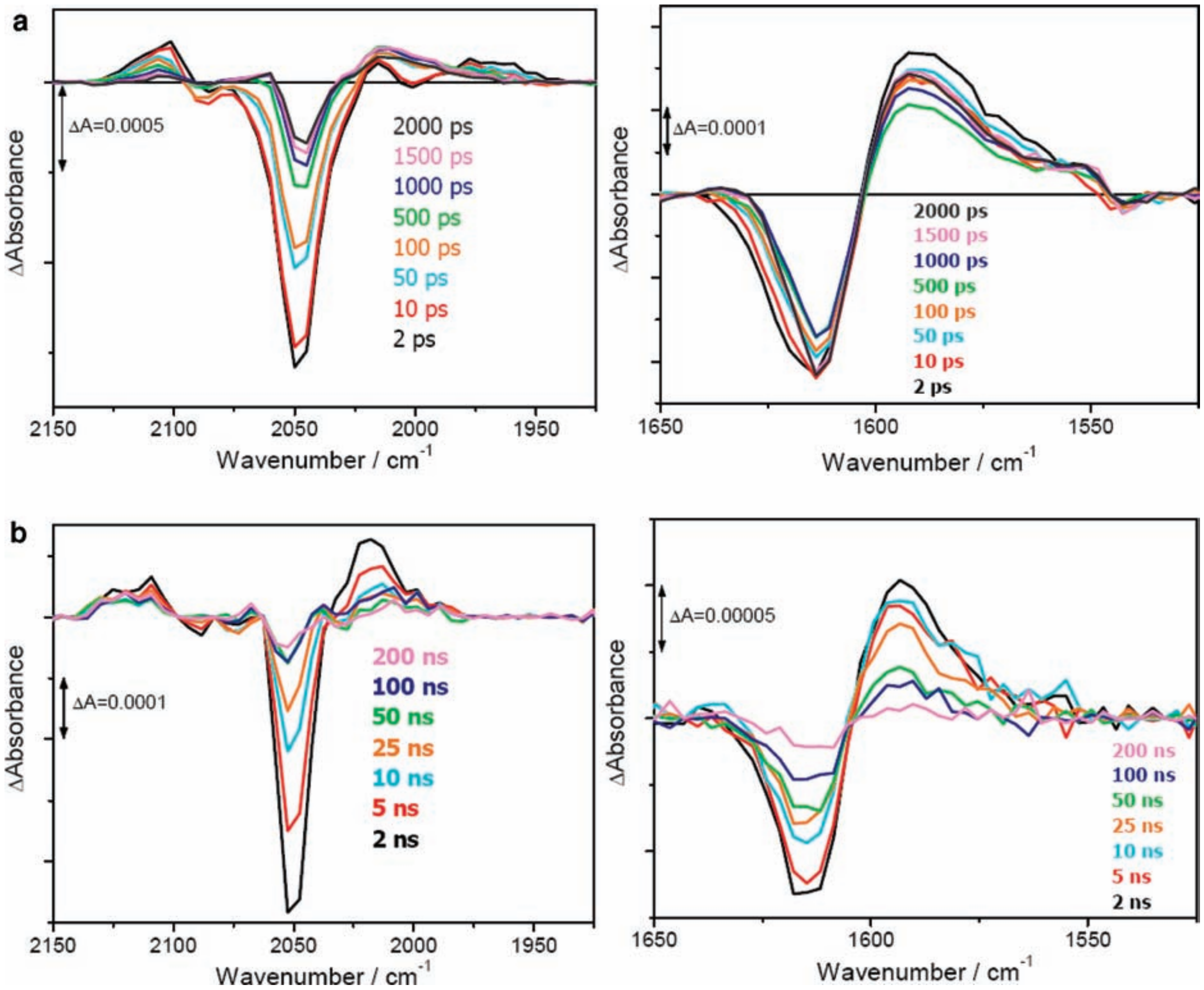

Figure 2. (a) ps-TRIR spectra of **1** in D_2O. ν(CN) spectra (*left*) and $\nu(CO)_{amide}$ spectra (*right*). Excitation λ = 400 nm. (b) ns-TRIR spectra of **1** in D_2O. ν(CN) spectra (*left*) and $\nu(CO)_{amide}$ spectra (*right*). Excitation λ = 355 nm.

from sensitized **Ru-CN** → **Ru-bpyam** energy-transfer which may be possible in water in which the ^{3}MLCT level of **Ru-CN** is high.

For the **Ru-CN** → **Ru-bpyam** energy-transfer to be thermodynamically favorable, the ^{3}MLCT energy of the **Ru-CN** chromophore must be sufficiently high in D_2O that it lies far enough above the ^{3}MLCT energy of the **Ru-bpyam** chromophore to prevent any back energy-transfer. $[Ru(CN)_4(dmb)]^{2-}$ (dmb = 5,5′-dimethyl-2,2′-bipyridine) can be considered a reasonable model for the **Ru-CN** terminus of the dyads because they bear two alkyl substituents attached to the $[Ru(CN)_4(bipy)]^{2-}$ core. In D_2O the luminescence maximum of $[Ru(CN)_4(dmb)]^{2-}$ is at 621 nm,[11b] implying that its ^{3}MLCT state lies above the lowest energy ^{3}MLCT state of both **1** (656 nm) and **2** (657 nm). To establish if PEnT is indeed reversing direction on changing solvent, we need to monitor the non-emissive states of these dyads as well as the emissive states. To do this, we have employed time-resolved Infrared (TRIR) spectroscopy to investigate the photophysics of **1** and **2** allowing us to interrogate the ^{3}MLCT excited states associated with (CN)Ru → L^n; (bpyam)Ru → L^n, and (bpyam)Ru → bpyam charge transfer processes. Since the TRIR experiments are performed at much higher concentrations than the emission measurements, we have checked for possible intermolecular aggregation in the ground state by recording FTIR spectra of **1** and **2** at a range of concentrations and find no evidence for aggregation.

TRIR Studies of 1

The picosecond and nanosecond TRIR spectra were obtained in the metal–cyanide and amide regions following excitation into the ^{1}MLCT absorption manifold of **1** in D_2O using either 400 nm (picosecond-time scale experiments) or 355 nm (nanosecond-time scale experiments) excitation, Figure 2. This allows each end of the dyads to be monitored independently as the cyanide and carbonyl stretching vibrations are in different regions of the IR spectrum. The ν(CN) bands of the **Ru-CN** moiety (2091, 2051, 2032, and 1995 cm^{-1}) are clearly bleached and weak new bands to both higher (2105 cm^{-1}) and lower (2015 cm^{-1}) energy are produced.

Parent band positions are quoted from ground-state FTIR spectra and transient band positions are estimated by peak fitting using Lorentzian line-shapes.

The IR band positions are summarized in Tables 2. The v(CN) band to higher energy is characteristic of a $\{(CN)_4Ru\}$ → diimine ^{3}MLCT excited state, in which the Ru^{II} center is transiently oxidized and the CN bonds are therefore strengthened because of the reduction in $\{Ru(d\pi)\}$ → $CN(\pi^*)$ back-bonding.[11b,16] This higher-energy ν(CN) transient shows

Table 1. Absorption and Emission Properties of Mono- and Dinuclear Complexes in D_2O and CH_3CN[a]

complex	solvent	AN	$\lambda_{abs}{}^1$ (nm)	$\lambda_{abs}{}^2$ (nm)	$\lambda_{abs}{}^3$ (nm)	$\lambda_{abs}{}^4$ (nm)	$\lambda_{em}{}^b$ (nm)	τ (ns)	ϕ^c
$(bpyam)_2Ru(L^1)$	H_2O	54.8	353	437	471		636	551 ± 5	0.041
	CH_3CN	19.3	350	435	496		615	501 ± 5	0.096
$(bpyam)_2Ru(L^2)$	H_2O	54.8	369	436	479		652	367 ± 40	0.069
	CH_3CN	19.3	367	432	471		641	341 ± 10	0.041
$(bpyam)_2Ru(L^1)Ru\text{-}CN$	D_2O	54.8	290	424	469		657	[e]	0.0031
	CH_3CN	19.3	290	437	473	~530[d]	651	[e]	0.0006
$(bpyam)_2Ru(L^2)Ru\text{-}CN$	D_2O	54.8	296	435	473		656	[e]	0.0023
	CH_3CN	19.3	296	434	476	~530[d]	640	[e]	0.0006

[a] All complexes have a $\pi-\pi^*$ ligand absorption at about 300 nm which is solvent invariant. [b] Sample concentrations were 1×10^{-5} M. Emission maxima and quantum yields are from corrected spectra. [c] Measured against a $[Ru(bpy)_3]^{2+}$ standard solution (±10%), excitation wavelength $\lambda_{ex} = \lambda_{abs}{}^2$. [d] Shoulder, position approximate. [e] Lifetimes are multiexponential, see text.

Table 2. Infrared Band Positions (cm^{-1}) of Ground and ^{3}MLCT Excited States of Mono- and Dinuclear Complexes in D_2O and CH_3CN

complex	solvent	ground state	(CN)Ru → L ^{3}MLCT	(bpyam)Ru → L ^{3}MLCT	(bpyam)Ru → bpyam ^{3}MLCT
$(bpyam)_2Ru(\mathbf{L^1})Ru\text{-}CN$	D_2O	2091, 2051, 2032, 1995, 1615	2105	2016, 1627	1589
	CH_3CN	2086, 2069, 2058, 1989, 1637	2105	2012	1616
$(bpyam)_2Ru(\mathbf{L^2})Ru\text{-}CN$	D_2O	2094, 2061, 2051, 2034, 1612	2096	[a]	1590
	CH_2Cl_2	2081, 2055, 2045, 2035, 1635	2103	[a]	1615
	CH_3CN	2090, 2060, 2045, 2035, 1636	2102	[a]	1621

[a] No detectable signal was observed corresponding to this excited state.

complicated decay kinetics, and these data can be fitted to at least four exponential decay components affording lifetimes of about 10–30 ps, 450 ps, 3 and 15 ns (a large error was associated with the fitting of the early ps component).

Comparison with the behavior of the mononuclear model complexes in D_2O leads us to expect that the **Ru-CN**-based ^{3}MLCT excited state of **1** will be slightly higher in energy than the **Ru-bpyam** based ^{3}MLCT state (cf. the luminescence results above), and hence it is likely that the ^{3}MLCT state of the **Ru-CN** terminus is primarily quenched by **Ru-CN** → **Ru-bpyam** energy-transfer. The observed multiexponential nature of the quenching could be ascribed to either (i) multiple conformers in solution resulting in more than one interchromophoric separation and hence multiple energy transfer rates and/or (ii) the presence of more than one energy-accepting state at the **Ru-bpyam** terminus. Evidence for the latter is provided by the new transient band seen to *lower* energy than the parent ν(CN) bands in the TRIR spectra, implying an increase in electron density at the Ru(II) center of the **Ru-CN** terminus. This may indicate the formation of a (bpyam)Ru → L^1 ^{3}MLCT state following the energy-transfer, that is, a higher ^{3}MLCT state of the **Ru-bpyam** terminus in which the excited electron goes to the bipy fragment of the bridging ligand L^1, and not to a bpyam ligand which has a low-energy LUMO because of the electron-withdrawing amide substituents. This increase in electron density on to the bridging ligand will increase the electron density on the "spectating" **Ru-CN** terminus, resulting in a lower-energy ν(CN) transient.[16] This is perhaps surprising given the saturated linker but may indicate some orbital overlap in a folded conformation between the bipyridine rings of the bridging ligand.

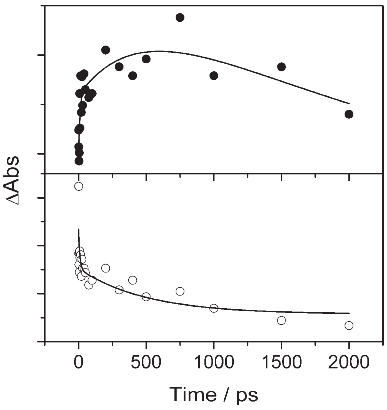

Figure 3. Kinetics of **1** in D_2O measured by ps-TRIR at 2106 cm^{-1} (*hollow circles*) and 2015 cm^{-1} (*solid circles*).

The ^{3}MLCT energy of this (bpyam)Ru → L^1 excited state is not known directly since it cannot be detected by luminescence (the luminescence of **1** and **RuL^1** is assumed to come from the lowest-lying (bpyam)Ru → bpyam state of the **Ru-bpyam** terminus). If this ordering is correct for the ^{3}MLCT states which are monitored by TRIR, then the (CN)Ru → L^1 state is indeed the highest in energy and can act as an energy donor to both **Ru-bpyam**-based ^{3}MLCT states. Further evidence for this is given by the TRIR decay kinetics of the lower-energy ν(CN) transient: it *grows in* biexponentially on the picosecond-time scale with time constants that approximately match the two fastest decay components of the (CN)Ru → L^1 ^{3}MLCT state (Figure 3), implying that it is populated as a result of energy-transfer from the **Ru-CN** ^{3}MLCT state. This (bpyam)Ru → L^1 state then decays on the nanosecond-time scale with lifetimes of 1 and 7 ns, presumably to the lowest-lying (bpyam)Ru → bpyam ^{3}MLCT state which is emissive. A similar conclusion is reached from the nanosecond-time scale TRIR measurements: the lower-energy ν(CN) transient dominates the spectrum in this region and is at a maximum at about 1 ns, which again suggests that the (CN)Ru → L^1 ^{3}MLCT state is decaying to this non-emissive (bpyam)Ru → L^1 state via PEnT.

Further evidence for the intermediate "dark" (bpyam)-Ru → L^1 ^{3}MLCT state is found in the ν(CO) region of the TRIR spectra, which reports on events at the **Ru-bpyam** terminus. The parent ν(CO) band (1615 cm^{-1}) in D_2O is

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(16) Alsindi, W. Z.; Easun, T. L.; Sun, X.-Z.; Ronayne, K. L.; Towrie, M.; Herrera, J.-M.; George, M. W.; Ward, M. D. *Inorg. Chem.* **2007**, *46*, 3696.

relatively broad and featureless and is bleached on laser excitation. Transient bands are formed both to higher (1630 cm^{-1}) and lower (1590 cm^{-1}) energy, indicating formation of two excited states. The transient band to higher energy is relatively weak and heavily overlaps with the parent ν(CO) bleach band, but its presence is notable for the time-dependent band shape changes it imposes on the parent band. This weak high-energy transient band is consistent with the presence of the (bpyam)Ru → L^1 ^{3}MLCT state, in which Ru(II) is transiently oxidized but the bpyam ligands are *not* transiently reduced, and has previously been reported on a related dyad which incorporated a **Ru-bpyam** unit.[13a] The early time kinetic behavior of this band can satisfactorily be fitted to a biexponential increase in magnitude (grow-in) with time constants of 10 (±4) ps and 530 (±160) ps. These correlate within error to the two components of the biexponential grow-in of the low-energy ν(CN) transient band [assigned to the same (bpyam)Ru → L^1 ^{3}MLCT state], and also to the biexponential decay [ca. 10 −30 and 450 (±70) ps] of the higher energy (CN)Ru → L^1 ^{3}MLCT state, assigned as the energy-donor state which populates the lower-lying (bpyam)Ru → L^1 state by energy-transfer. The error associated with fitting the kinetics of this 1627 cm^{-1} transient ν(CO) band data is significantly lower, and this gives a time constant of about 10 ps for the fast energy transfer component. The longer-time kinetics are less clear because of the significant overlap with the recovery of the parent band but it appears to decay on a time scale of about 1 ns. This is also in keeping with the 1 ns decay of the lower-energy ν(CN) transient band at 2015 cm^{-1} which monitors the same state.

The new ν(CO) transient band shifted to lower energy (at 1590 cm^{-1}) is typical of the formation of the (bpyam)-Ru → bpyam ^{3}MLCT state in which a bpyam ligand is reduced, weakening the CO bond by population of a bpyam-based antibonding orbital.[16,17] As with the upshifted ν(CN) band, and the parent bleach bands, it is instantaneously formed on (non-selective) laser excitation of **1**. Overlap with the parent ν(CO) bleach band results in a small *apparent* decay of about 500 ps in the transient which we interpret as further bleaching of the overlapping parent band as the intermediate (bpyam)Ru → L^1 ^{3}MLCT state grows in following energy-transfer from the higher-energy (CN)Ru → L^1 state (see above). The ps-TRIR experiment then shows a small grow-in of the 1590 cm^{-1} downshifted ν(CO) band as the intermediate (bpyam)Ru → L^1 ^{3}MLCT state decays into the lowest energy (bpyam)Ru→bpyam ^{3}MLCT state on a time scale of about 1 ns, correlating with the observed decay of the intermediate state and affording further evidence of energy transfer from (bpyam)Ru → L^1 to (bpyam)Ru → bpyam. Finally, the downshifted ν(CO) band decays on the nanosecond-time scale with lifetimes of 2 and 50 ns (major component). The presence of the 15 ns decay component of the higher energy ν(CN) transient band is either a slow energy transfer process which is not observed elsewhere or a weak residual decay by luminescence in a conformation where energy transfer is only partially complete, therefore correlating with the minor lifetime component fitted in the emission spectrum as 10 ns.

Simple molecular mechanics calculations[18] have been performed to investigate the conformational flexibility of **1** in the gas phase to examine the possible structures that may contribute to the excited state processes described above. Two main conformers were identified (Supporting Information). The first of these conformers corresponds to a "roofed" structure in which both bipyridyl termini are on the same side of the partly folded bridging ligand; the second corresponds to a more open structure. This is in keeping with the crystallographic identification of a similar pair of conformers for a related RuL^{1}Ru dyad described by Hosseini et al.[19] Given that two rapid energy transfer lifetimes were reported on the picosecond-time scale (10−30 ps and ca. 500 ps) these may correspond to PEnT from the (CN)Ru → L^1 ^{3}MLCT state to the (bpyam)Ru → L^1 ^{3}MLCT state in two conformers. The subsequent decay of the (bpyam)Ru → L^1 ^{3}MLCT state into the lowest energy (bpyam)Ru → bpyam ^{3}MLCT state is unlikely to be significantly affected by conformational changes in the bridging ligand since it is effectively an internal conversion at a single chromophoric center and not dependent on the position of the **Ru-CN** unit. We have calculated the Förster critical distances using observed experimental rates of PEnT in CH_3CN (17.1 Å) and D_2O (20.7 Å), and the range of internuclear separations obtained from the molecular mechanics calculations are significantly less than these values for all conformers.

We have also investigated the effect of changing the solvent from D_2O to CH_3CN to examine whether altering the relative energies of the MLCT states can affect the energy cascade process. The TRIR spectra in CH_3CN show that the ν(CN) bands of the **Ru-CN** moiety are clearly bleached after excitation, and weak new transient bands to both higher (2105 cm^{-1}) and lower (2012 cm^{-1}) energy are produced on the picosecond-time scale, Figure 4. The upshifted ν(CN) band corresponding to the (CN)Ru → L^1 ^{3}MLCT state grows-in with a lifetime of 12 (±8) ps before decaying biexponentially with lifetimes of 85 (±50) ps (Figure 5) and about 1 (±0.2) ns (this latter figure is in agreement with the known very weak emission of $[Ru(bipy)(CN)_4]^{2-}$ in MeCN which occurs on the time scale of a few ns).[12b] The (CN)Ru → L^1 ^{3}MLCT state is expected to be the lowest energy excited state in CH_3CN and therefore to act as the ultimate energy acceptor in this solvent.

The other ν(CN) transient band, shifted to *lower* energy than the parent band, is indicative of the (bpyam)Ru → L^1 ^{3}MLCT state discussed above which is now the highest in energy of the three possible ^{3}MLCT states. This band displays decay lifetimes of 140 ps and about 2 ns when measured by the picosecond-time scale experiment. At first glance, the ns-TRIR experiment appears to be dominated by this (bpyam)Ru → L^1 ^{3}MLCT state since the parent ν(CN) band at 2058 cm^{-1} is bleached and a downshifted transient band at 2012 cm^{-1} is formed. The apparent longevity of this high-lying (bpyam)Ru → L^1 ^{3}MLCT state is perhaps surprising as the lowest energy state is expected to be the (CN)Ru → L^1 ^{3}MLCT, which is characterized by a weak upshifted transient band at 2105 cm^{-1} There are several factors which contribute

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(17) Butler, J. M.; George, M. W.; Schoonover, J. R.; Dattelbaum, D. M.; Meyer, T. J. *Coord. Chem. Rev.* **2007**, *251*, 492.

(18) Molecular mechanics calculations have been performed using the SPARTAN02 Computational Suite Wavefunction Inc.: Irvine, CA, 2001.

(19) (a) Lagref, J.-J.; Hosseini, M. W.; Planeix, J.-M.; De Cian, A.; Fischer, J. *Chem. Commun.* **1999**, *21*, 2155. (b) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 920. (c) Kaes, C.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Tetrahedron Lett.* **1997**, *38*, 4389. (d) Kaes, C.; Hosseini, M. W.; Ruppert, R.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1995**, *14*, 1445.

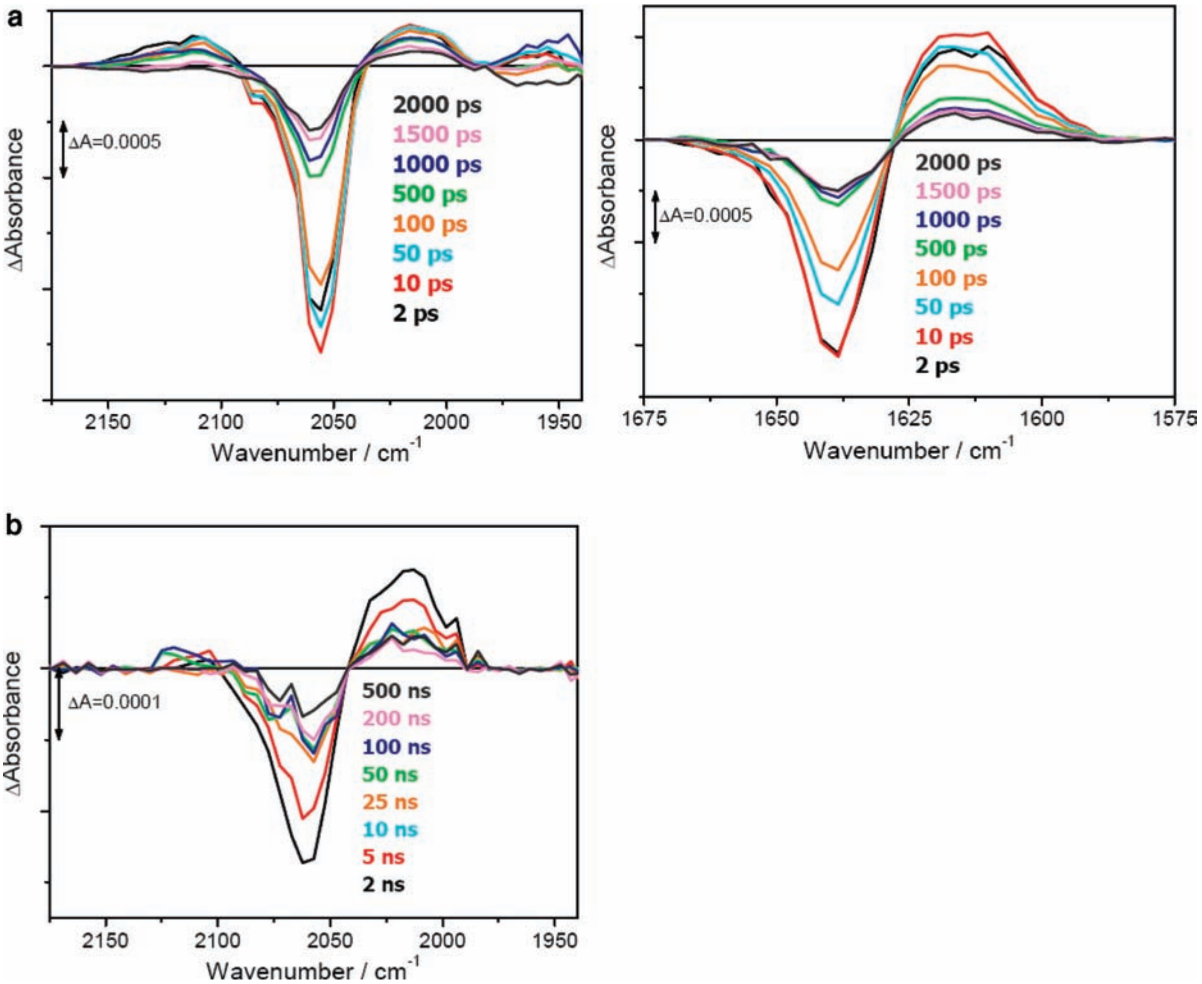

Figure 4. (a) ps-TRIR spectra of **1** in CH_3CN. ν(CN) spectra (*left*) and $\nu(CO)_{amide}$ spectra (*right*). Excitation λ = 400 nm. (b) ns-TRIR spectra of **1** in CH_3CN. ν(CN) spectra. Excitation λ = 355 nm.

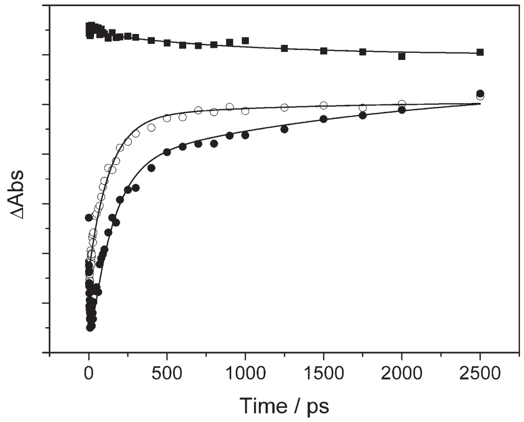

Figure 5. Kinetics of **1** in CH_3CN measured by ps-TRIR at 2107 cm^{-1} (*solid squares*), 2056 cm^{-1} (*solid circles*), and 1638 cm^{-1} (*hollow circles*).

to this observation. The relative intensity of the downshifted ν(CN) band is inherently greater (for the same concentration) than either the parent bleach band or the expected weak upshifted ν(CN) band,[16] and hence it is visually particularly prominent. The ns-TRIR experiment uses higher energy excitation wavelength (355 nm) compared with the ps-TRIR experiments and will almost exclusively populate the (bpyam)Ru → L^1 ^{1}MLCT state on excitation. The downshifted transient band and parent bleach band recover with a 2 ns lifetime, which corresponds to data from the ps-experiment, and is notably similar to the decay lifetime of the same state in D_2O. The relative energies of the two $[Ru(diimine)_3]^{2+}$ ^{3}MLCT states do not vary greatly with solvent, and we conclude that the decay of the (bpyam)-Ru → L^1 ^{3}MLCT state into the (bpyam)Ru → bpyam state occurs on a similar time scale (1−2 ns) in both solvents.

No new transient ν(CO) band can be seen at higher energy than the bleach of the ν(CO) parent band at 1637 cm^{-1} on the picosecond-time scale. Such a high-energy transient would be indicative of a (bpyam)Ru → L^1 ^{3}MLCT state (cf. the behavior in D_2O). However a *down*shifted transient band, associated with the lower-energy (bpyam)Ru → bpyam ^{3}MLCT state, is formed at 1616 cm^{-1}. The parent ν(CO) bleach demonstrates a small recovery component with a lifetime of about 4 ps which may be due to PEnT from the (bpyam)-Ru → L^1 ^{3}MLCT state to the lowest energy (CN)Ru → L^1 ^{3}MLCT, correlating with the rapid 12 ps growth seen for that species in the ν(CN) ps-TRIR experiment. The ν(CO) parent bleach and low-energy transient band then recover with biexponential kinetics with lifetimes of 130 and 1200 ps. These two decays correlate well with the 140 ps and 2 ns decay components observed for the (CN)Ru → L^1 ^{3}MLCT state. No ν(CO) signal could be detected on the nanosecond-time scale experiment, which is consistent with the rapid quenching of both the (bpyam)Ru → L^1 and (bpyam)Ru → bpyam

^{3}MLCT excited states by the lower-lying (CN)Ru → L^1 ^{3}MLCT state.

The results of the experiments in CH_3CN can be fit by the following model. The highest energy (bpyam)Ru → L^1 ^{3}MLCT state decays into the (bpyam)Ru → bpyam ^{3}MLCT state on a time scale of 1−2 ns, as also seen in D_2O. In a different conformation, probably with a shorter interchromophore distance, the same (bpyam)Ru → L^1 ^{3}MLCT state undergoes PEnT to the (CN)Ru → L^1 ^{3}MLCT state on a time scale of 4−12 ps. The (bpyam)Ru → bpyam ^{3}MLCT state decays with two lifetimes (corresponding to two conformers, a long and a short) of about 140 ps and 2 ns into the (CN)Ru → L^1 ^{3}MLCT state. The (CN)Ru → L^1 ^{3}MLCT state then decays back to the ground state with a lifetime of 85 ps, with the longer decay components observed being a result of it being continually repopulated on the slower time scales of 140 ps and 2 ns. This model therefore calls for two primary conformers in solution, which are likely to be as modeled above, the "roofed" and the open conformers obtained from the molecular mechanics calculations.

The question remains as to why there are no long-lived excited-state species observed in the ns-TRIR experiments but there are in the luminescence measurements in CH_3CN. It should be noted that the total emission in CH_3CN is very weak. The long-lived luminescence has a lifetime of about 680 ns which is comparable to the luminescence lifetime of the $[Ru(bpyam)_2(L^1)]^{2+}$ complex in CH_3CN (551 ns). It may be the result of incomplete quenching of the (bpyam)-Ru → bpyam excited state, perhaps in an extended conformation. Another quite likely possibility is that trace amounts of water are preferentially solvating the cyanide ligands at the **Ru-CN** termini of some of the molecules in solution. This phenomenon has been previously described[13b] and allows simple $[Ru(bipy)(CN)_4]^{2-}$ complexes to behave as sensitive luminescent sensors of moisture in "dry" solvents. In our case, it will have the effect of raising the energy of the **Ru-CN** terminus MLCT states in those molecules affected, such that the direction of PEnT in the dyad is reversed in a similar manner to dissolving the complex in D_2O, generating emission from the (bpyam)Ru termini in a small fraction of the molecules. As the concentration used for the luminescence experiments is considerably lower than that of the TRIR experiments (1×10^{-5} M vs 1×10^{-3} M), small amounts of water in the solvent will have a more significant effect on the luminescence, whereas in the TRIR experiments water-solvated dyads would constitute a much smaller proportion of the total molecules (100-fold less assuming constant concentration of water in both experiments).

To summarize the results of these experiments with **1**, in D_2O excited-state energy transfer is clearly observed from the **Ru-CN** terminus to the **Rubpyam** terminus of the dyad, that is, from the highest-lying (CN)Ru → L^1 ^{3}MLCT state, via the intermediate (bpyam)Ru → L^1 ^{3}MLCT state to the lowest-lying (bpyam)Ru → bpyam ^{3}MLCT state. In CH_3CN, the direction of excited-state energy transfer is reversed, making the **Rubpyam** terminus the energy donor and the **Ru-CN** terminus the energy acceptor. In both cases, the presence of at least two primary conformers in solution was identified from the kinetic analysis.

TRIR Studies of 2

The dyad **2** is much more conformationally flexible than **1**, thus allowing us to investigate further the conclusions we have obtained from the experiments on **1**. On the picosecond-time scale in D_2O the ν(CN) bands of the **Ru-CN** moiety are bleached after excitation, and a weak new band to higher (2096 cm^{-1}) energy is produced, Figure 6, Table 2. No new transient band to lower energy is observed. This is in contrast to the TRIR results for **1**, and we interpret this to indicate that the conformational freedom of the **L^2** bridging ligand means that it is less likely that a major conformer will involve the necessary alignment of the excited-state dipole of the (bpyam)Ru → L^n ^{3}MLCT state with that of the **Ru-CN** moiety which is necessary for PEnT to occur. In essence the **Ru-CN** terminus of **2** no longer acts as a spectator which reports on the other terminus: it is likely to be too distant and misaligned with the (bpyam)Ru → bpyam chromophore to be affected by formation of MLCT states at the Ru(bpyam) terminus and provide a downshifted ν(CN) transient in the TRIR spectrum.

The transient ν(CN) band to higher energy corresponds to the (CN)Ru → **L^2** ^{3}MLCT excited state in the usual way. This decays with lifetimes of 13 and 375 ps (Figure 7), and both parent bleach and transient band have returned to the baseline by 2 ns. There is no signal on the ns-TRIR experiment, further indicating that the (CN)Ru → **L^2** ^{3}MLCT excited state has been rapidly quenched (cf. the lifetime of mononuclear $[Ru(CN)_4(dmb)]^{2-}$ in D_2O of 370 ns),[11b] presumably by PEnT to the (bpyam)Ru terminus as before.

The ν(CO) region of the spectrum displays the typical bleach of the parent band, and a new transient band to lower energy (1590 cm^{-1}), associated with the formation of the (bpyam)Ru → bpyam ^{3}MLCT state. Both transient and parent bands continue to grow-in with a lifetime of 7 ps, subsequently decaying with lifetimes that can be fitted to 440 ps (ps-experiment) and 7, 28 and 100 ns (ns-experiment), with the major component being 28 ns. The observed grow-in correlates with the 13 ps decay of the higher energy (CN)Ru → L^2 ^{3}MLCT state and is possibly due to PEnT to the (bpyam)Ru → bpyam ^{3}MLCT state, which then returns to the ground state.

No transient ν(CO) band to higher energy is apparent in either the ps- or ns-TRIR experiments on **2**, which may be a consequence of the competition at the excitation wavelength in D_2O between absorption into the (bpyam)Ru → L^2 ^{1}MLCT state and absorption by the **Ru-CN** terminus. As with dyad **1**, simple molecular mechanics calculations in the gas phase were performed to investigate the conformational flexibility of **2** (Supporting Information). We have again calculated the Förster critical distances using observed experimental rates of PEnT in CH_3CN (14.6 Å) and D_2O (15.7 Å), and the range of internuclear separations obtained from the molecular mechanics calculations are well within these values for all calculated conformers meaning that Förster PEnT, the most likely mechanism given the saturated linkages, is perfectly possible.

In D_2O it is clear that **2** has multiple possible conformations. The kinetic data outlined above are consistent with the (CN)Ru → L^2 ^{3}MLCT state decaying to the Ru → bpyam ^{3}MLCT state on two time scales; fast (7−13 ps) and slow (~ 400 ps), probably due to two major conformations. The Ru → bpyam ^{3}MLCT state then decays back to the ground state with multiple lifetimes [7 ns, 28 ns, long (100 ns)] observed both in the TRIR and the luminescence data. Additionally, the "open" ligand conformation changes the interaction between the centers when compared with the

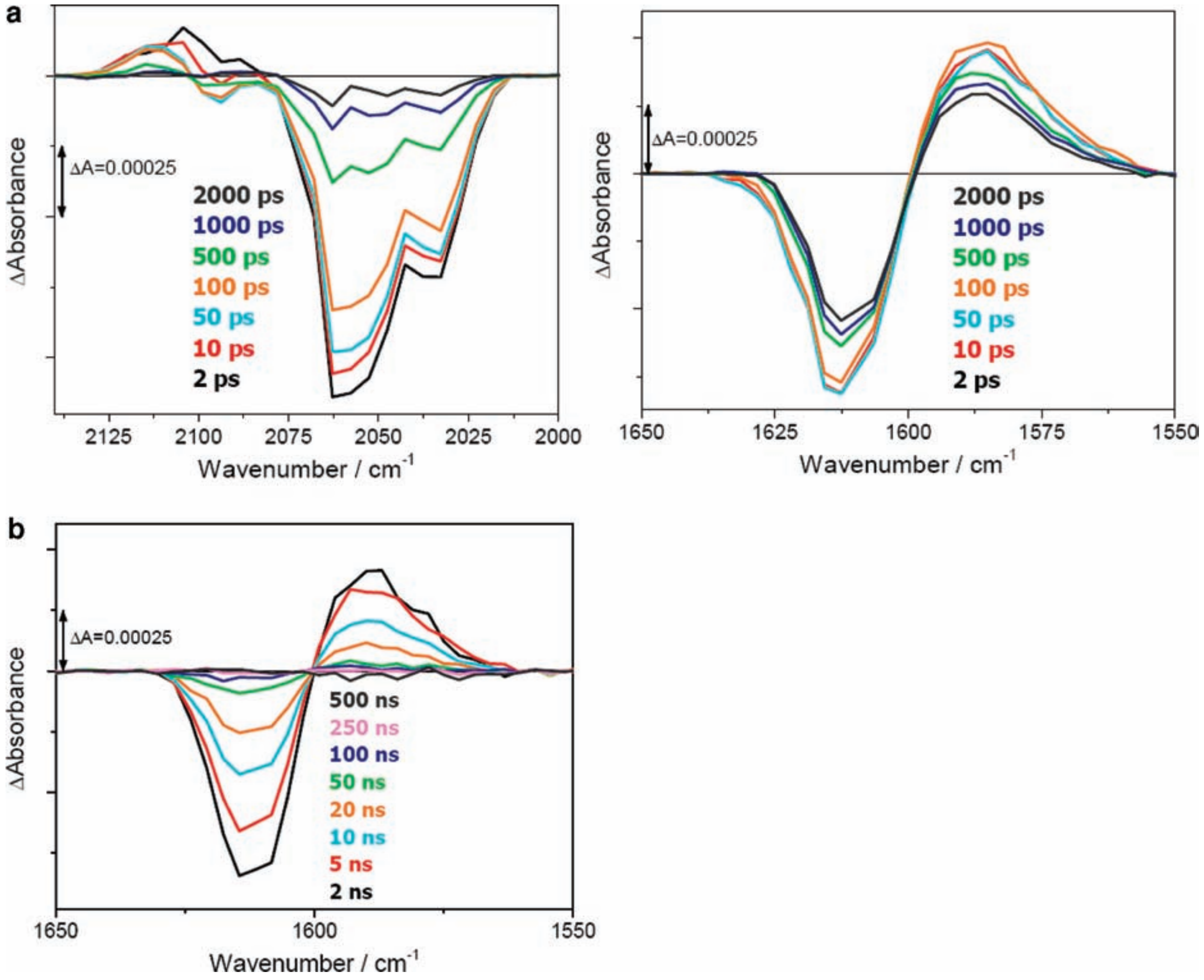

Figure 6. (a) ps-TRIR of **2** in D_2O; ν(CN) spectra (*left*) and $\nu(CO)_{amide}$ spectra (*right*). Excitation λ = 400 nm. (b) ns-TRIR of **2** in D_2O; $\nu(CO)_{amide}$ spectra. Excitation λ = 355 nm.

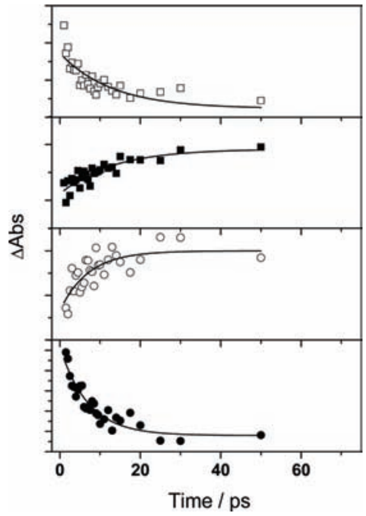

Figure 7. Early time kinetics of **2** in D_2O measured by ps-TRIR at 2084 cm^{-1} (*hollow squares*), 2039 cm^{-1} (*solid squares*), 1590 cm^{-1} (*hollow circles*), and 1612 cm^{-1} (*solid circles*). Lines denote exponential fitting of the fastest decay/growth.

more rigid dyad **1**: the presence of a (bpyam)Ru → L^2 state is not signaled by transient changes in the ν(CN) terminus of **2** because the two bpy ligands of the bridging ligand L^n are no longer spatially constrained relative to each other.

We have also investigated the photophysics of **2** in CH_3CN, Figure 8. On the picosecond time scale, the ν(CN) bands of the **Ru-CN** moiety are bleached after excitation and a weak new band to higher (2102 cm^{-1}) energy is produced. As in D_2O, no new transient band to lower energy is apparent. The 2102 cm^{-1} band corresponds to the (CN)-Ru → **L^2** ^{3}MLCT excited state and displays a grow-in with a lifetime of 12 (±4) ps (Figure 9), subsequently decaying with lifetimes of 275 ps (±20), 3 (±1) ns and 68 (±8) ns. Similar to the behavior of **1** in MeCN, the (CN)Ru → L^2 ^{3}MLCT state is expected to be the lowest energy excited state for **2** and is expected to act as an energy acceptor, which is supported by the rapid grow-in on the picosecond-time scale. There was no transient ν(CO) signal recorded on the nanosecond-time scale, consistent with the **Ru-bpyam** terminus acting as an excited-state energy donor to the **Ru-CN** terminus in CH_3CN and being rapidly quenched. On the picosecond time scale the parent ν(CO) band is bleached on excitation, and a new transient band to lower energy (1621 cm^{-1}) is formed, characteristic of the (bpyam)Ru→ bpyam ^{3}MLCT state in which a bpyam ligand is transiently reduced. Both parent and transient ν(CO) bands return to the ground-state on the same time scale, with lifetimes of about 10 and 300 ps. The faster of these decay components corresponds well with the 12 ps grow-in of the upshifted ν(CN) transient band of the (CN)-Ru → **L^2** ^{3}MLCT state. The slower decay component may be

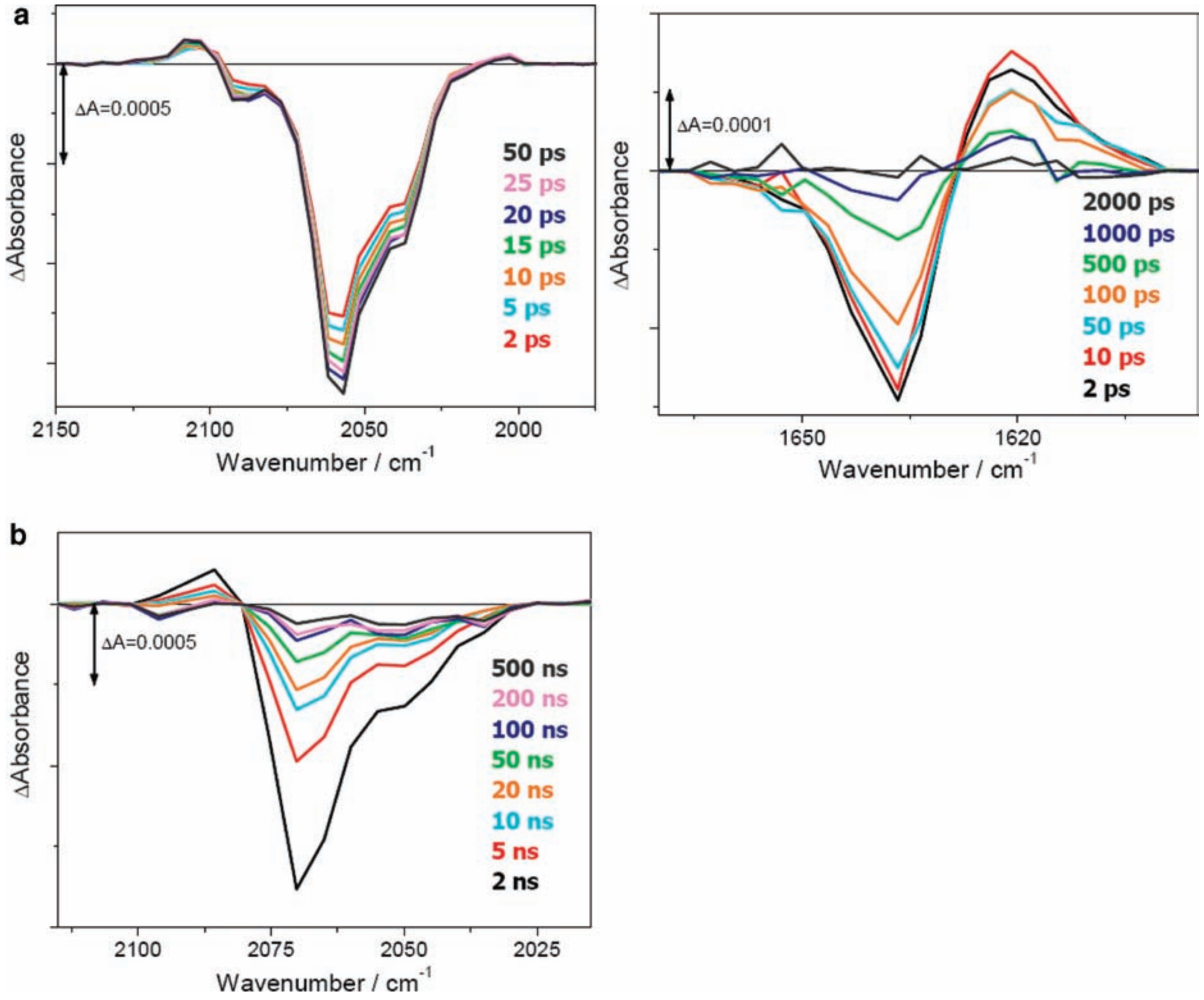

Figure 8. (a) ps-TRIR of **2** in CH_3CN; ν(CN) spectra (*left*) and $\nu(CO)_{amide}$ spectra (*right*). Excitation $\lambda = 400$ nm. (b) ns-TRIR of **2** in CH_3CN; ν(CN) spectra. Excitation $\lambda = 355$ nm.

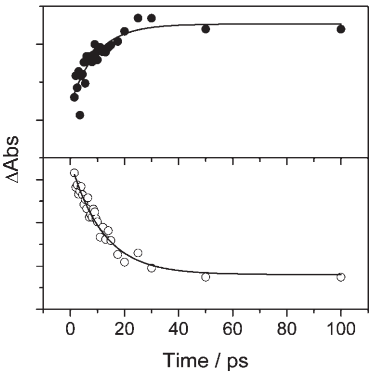

Figure 9. Early time kinetics of **2** in CH_3CN measured by ps-TRIR at 2103 cm^{-1} (*solid circles*) and 2042 cm^{-1} (*hollow circles*).

due to PEnT quenching in a more extended conformation. The ν(CO) parent bleach band and transient band have returned fully to the baseline by 2 ns.

The TRIR spectra obtained for **2** on the nanoscond time scale showed only weak signals, indicating that the primary photoprocesses were all occurring on the picosecond-time scale in CH_3CN. The multiexponential decay of the (CN)-Ru → L^2 ^{3}MLCT state suggests again the presence of more than one conformer. There is direct evidence of a rapid about 10 ps PEnT process from the (bpyam)Ru → bpyam ^{3}MLCT state to the (CN)Ru → L^2 ^{3}MLCT state, which then decays back to the ground state. This energy transfer process is in the opposite direction to that observed in D_2O. Considering the very low quantum yield of the luminescence recorded in CH_3CN, it is probable that the major decay pathway is non-emissive. We also repeated these experiments on **2** in CH_2Cl_2 (a solvent with a similar lack of ability to MeCN to act as a hydrogen-bond donor and which therefore engenders similar properties in the **Ru-CN** chromophore) and found similar results, with the (bpyam)Ru → bpyam ^{3}MLCT state decaying to form the (CN)Ru → L^2 ^{3}MLCT state (25 ± 4 ps), providing evidence for the predicted intercomponent PEnT process from **Ru-bpyam** to **Ru-CN** occurring in both CH_2Cl_2 and CH_3CN, in the opposite direction to that observed in D_2O.

Conclusions

Although use of the solvatochromic **Ru-CN** chromophore as a solvent-dependent energy donor/acceptor in simple dyads has been previously demonstrated by luminescence methods, the use of TRIR spectroscopy provides a far more detailed picture of the complex series of events in **1** and **2** following initial excitation. Luminescence spectra of both **1** and **2** in CH_3CN offer evidence of **Ru-bpyam** → **Ru-CN** PEnT on the basis of quenching of the normal luminescence of the

Ru-bpyam unit. In D_2O we would expect the direction of PEnT to be reversed, that is, to be in the sense **Ru-CN** → **Ru-bpyam**, following the substantial increase in energy of the **Ru-CN** ^{3}MLCT state in D_2O. However, luminescence spectroscopy alone in D_2O is not completely unambiguous since the excitation is non-selective and can directly excite both acceptor and donor states. This leads to emission from the lowest energy (bpyam)Ru → bpyam ^{3}MLCT state independently of any energy transfer from the higher energy (CN)-Ru → L ^{3}MLCT state.

The additional use of time-resolved infrared spectroscopy, however, has shown that, for both dyads, we can directly observe the switching of the direction of photoinduced energy transfer by changing from a high acceptor number (good H-bond donor) solvent (D_2O) to a lower acceptor number solvent (poor H-bond donor; CH_2Cl_2 or CH_3CN) which results in the ^{3}MLCT energy of the **Ru-CN** unit moving from *above* the **Ru-bpyam** ^{3}MLCT state to *below* it. The TRIR measurements directly highlight the importance of an additional dark (non-emissive) (bpyam)Ru → L ^{3}MLCT state in the excited-state decay pathways, a state which cannot be observed by luminescence experiments. The multiexponential decays observed in the luminescence spectra suggest some of the complexity of the photoprocesses in these complexes, but do not elucidate them completely. The TRIR measurements also clearly show the presence of multiple conformers in solution for both complexes and go some way toward providing insight into the internuclear separations of those conformers which control the PEnT rates.

Experimental Section

General Details. The following compounds were available from previous work: **RuL^2**, **2** and $[Ru(bpyam)_2Cl_2]$.[13b] Ruthenium salts $RuCl_3 \cdot 3H_2O$ and $K_4[Ru(CN)_6]$ were kindly provided on loan from Johnson Matthey plc. ^{1}H NMR spectra were recorded on Bruker AC-250 or AMX2−400 spectrometers. Electrospray mass spectra were recorded on a Waters-LCT time-of-flight spectrometer. UV/vis spectra were measured on a Cary-50 instrument. Details of equipment and methods used for the luminescence studies have been described previously.[16] The equipment used for TRIR measurements has been described in detail previously.[20] IR spectra were probed with IR pulses generated by difference-frequency generation (ca. 200 cm^{-1} wide). The sample solution was excited in the ps-TRIR at 400 nm, using frequency-doubled pulses from a 1 kHz Ti:sapphire laser (~150 fs). The delay between pump and probe in these experiments was achieved using an optical delay. On the nanosecond time scale pumping was achieved using 1 kHz 355 nm pulses (1 ns), and the time delay between the pump and probe pulses was achieved using a electronic delay.

Synthesis of Exoditopic Macrocyclic Bridging Ligand L^1. A sample of (*i*-Pr)$_2$NH (3.56 mL, 25 mmol) was dried over KOH and distilled under N_2. After dissolving in dry THF (10 mL) and cooling to −80 °C, a solution of BuLi (15.63 mL, 1.6 M in hexanes, 25 mmol) was added dropwise. The combined solution was allowed to warm to room temperature, stirred for 30 min then cooled to 0 °C. 4,4′-Dimethyl-2,2′-bipyridine (1.84 g, 10 mmol) was dissolved in dry, degassed THF (170 mL) and cooled to −80 °C. This solution was added dropwise via a cannula to the fresh LDA solution, an orange color formed, and the solution stirred at 0 °C under N_2 for 1 h. A sample of $BrCH_2CH_2Br$ (1 mL, 11.6 mmol) was dried by passing through a Pasteur pipette containing active alumina and dissolved in dry THF (200 mL). The two solutions were then added simultaneously dropwise via cannulae and under N_2 over a period of 5 h to a vigorously stirred (mechanical stirrer) 3-neck flask containing dry room temperature THF (500 mL), and the resulting mixture turned opaque gray-green. H_2O (10 mL) was added to quench any remaining LDA, generating a white precipitate, and the solution filtered. The solid was washed with $CHCl_3$ (4 × 100 mL), the organic phases recombined and evaporated to dryness. The resulting solid was redissolved in $CHCl_3$ (300 mL), mixed with H_2O (200 mL) and the product extracted with further $CHCl_3$ (4 × 100 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated to dryness. The white product was purified by column chromatography (alumina, $CHCl_3$:AcOEt 1:1) and recrystallized from $CHCl_3$/hexane to yield a white powder (450 mg, 25%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.85 (8 H, s, $-CH_2-$), 6.25 (4 H, s, bpy H$^{3,3'}$), 7.15 (4 H, dd, bpy H$^{4,4'}$), 8.48 (4 H, dd, bpy H$^{6,6'}$).

Synthesis of [(bpyam)$_2$Ru(L^1)]Cl$_2$ (RuL^1). In EtOH (100 mL), $[Ru(bpyam)_2Cl_2]$ (561 mg, 0.64 mmol) and silver nitrate (216 mg, 1.28 mmol) were combined and refluxed for 30 min. The white AgCl precipitate was filtered off and **L^1** (244 mg, 0.67 mmol) dissolved in EtOH (25 mL) was added to the filtrate. The reaction mixture was refluxed with stirring overnight and then the solvent removed in vacuo. Purification of the crude reaction product was achieved by column chromatography on Sephadex SP C-25 with increasing concentration of aqueous NaCl solution (0−0.2 M) as eluent. This afforded a dark red product which was recrystallized from $CHCl_3$/hexane to yield the red powdery product (505 mg, 63%). ESMS: *m*/*z* 587 $[M - 2Cl]^{2+}$. Calcd for $[(bpyam)_2Ru(L^1)]Cl_2 \cdot 5H_2O$: C, 57.56; H, 6.19; N, 12.58%. Found: C, 57.33; H, 6.51; N, 12.37%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.05−1.42 (24 H, m, $-CH_3$), 3.13 and 3.15 (8 H, s, bpy-CH_2-CH_2-bpy), 3.30−3.75 (16 H, m, −CON-[**CH$_2$**-CH$_3$]$_2$), 7.02 (2 H, d, **L^1**), 7.20 (2 H, d, **L^1**), 7.39 (2 H, s, **L^1**), 7.48 (2 H, d, **L^1**), 7.57 (2 H, d, **L^1**), 8.20−8.30 (10 H, m, 2 × **L^1**, 4 × bpyam), 8.41 (4 H, d, bpyam).

Synthesis of [(bpyam)$_2$Ru(L^1)Ru(CN)$_4$] (1). A mixture of **RuL^1** (250 mg, 0.20 mmol) and $K_2[Ru(CN)_6] \cdot 3H_2O$ (103 mg, 0.22 mmol) was combined in H_2O:MeOH (1:1, 50 mL, pH 3.5 with H_2SO_4) and refluxed with stirring for 36 h to form a red solution. After cooling, the solution was neutralized with K_2CO_3 and the solvent evaporated in vacuo. The residue was redissolved in CH_2Cl_2 and filtered through Celite to remove unreacted $K_4[Ru(CN)_6]$ yielding a dark red-black powder. The product was purified by passing through a short Sephadex SP C-25 column with water as the eluent. The neutral product is washed straight through and the charged impurities are retained on the column. Evaporation of water followed by recrystallization from CH_2Cl_2/acetone afforded pure red-black product (200 mg, 72%). IR (solid state ATR): ν(CN) 2048(s), 1990(m) cm^{-1}; ν(CO) 1610 cm^{-1}. ^{1}H NMR spectra were broadened because of paramagnetism (traces of aerial oxidation of the **Ru-CN** terminus to Ru^{III}). ESMS: *m*/*z* 713 $[M + 2Na]^{2+}$. Calcd for $[(bpyam)_2Ru(L^1)Ru(CN)_4] \cdot 8H_2O$: C, 53.6; H, 5.8; N, 14.7%. Found: C, 53.1; H, 6.3; N, 14.7%.

Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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