

Solvent-based switching of photophysical properties of polynuclear complexes

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Introduction

Controlling the direction of photoinduced energy and electron transfer within polynuclear systems is an area of growing interest because it will allow the design of switchable multicomponent systems on a molecular scale. We have designed dinuclear systems which feature two chromophores; one whose MLCT energy varies as a function of the solvent and one whose MLCT energy is solvent-independent¹. Electronic excitation of the system is expected to result in photoinduced energy transfer (PEnt) to the lowest energy emissive state with subsequent radiative decay. Switching of the location of this state from one chromophore to the other by variation of the solvent will result in switching of the direction of PEnt (Figure 1).

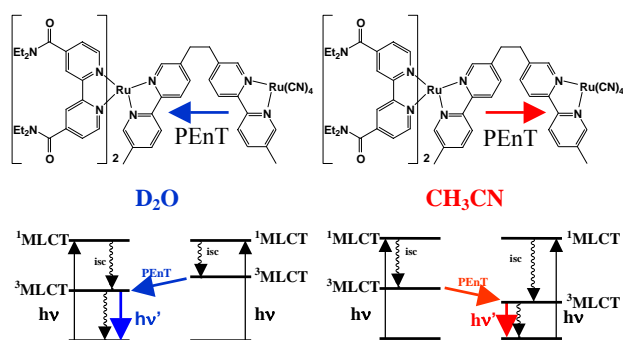
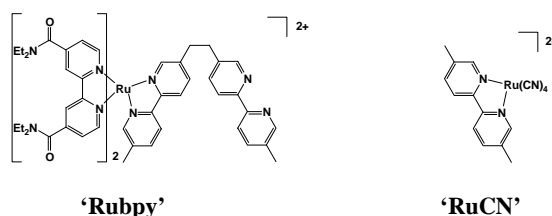


Figure 1. Schematic showing the solvent-dependent switching of PEnt in the 'Ruby-RuCN' dinuclear complex.

Our dinuclear complex **Ruby-RuCN** is composed of two components. The first (**Ruby**) utilises the photophysical properties of the $[\text{Ru}(\text{bpy})_3]^{2+}$ moiety (bpy = 2,2'-bipyridine), which have been extensively studied. These properties, combined with facile synthesis and easy manipulation of its electronic structure by addition of substituents to the polypyridyl ligands, make it ideal as the 'fixed' energy chromophore. Specifically, amide substituents act as IR reporters to allow monitoring of the excited state dynamics by Time-Resolved Infrared (TRIR) spectroscopy.



The strong *negative* solvatochromism of the $[\text{Ru}(\text{CN})_4(\text{bpy})]^{2-}$ moiety (**RuCN**) offers a readily accessible metal-to-ligand charge-transfer (³MLCT) excited state whose energy can be varied over a wide range with respect to the ground state simply by altering the solvent². This range, from *ca.* 12000 to 16000 cm^{-1} between CH_3CN and H_2O respectively, encompasses the ³MLCT excited state energy of the **Ruby** unit at $\approx 15000 \text{ cm}^{-1}$ and forms the basis of the solvent switch. The cyanide groups act as reporters for TRIR spectroscopy. The

solvatochromism is a result of the electronic interaction with solvent of the outwardly-directed CN: lone pairs.

Our aim was to directly monitor PEnt using TRIR for the first time and to demonstrate the ability to reverse the direction of PEnt by changing solvent.

Ruby model complex

Photoexcitation at 400 nm in the PIRATE system gives ps- TRIR as in Figure 2. The parent band of the amide $\nu(\text{CO})$ is bleached and a transient at lower energy is observed.

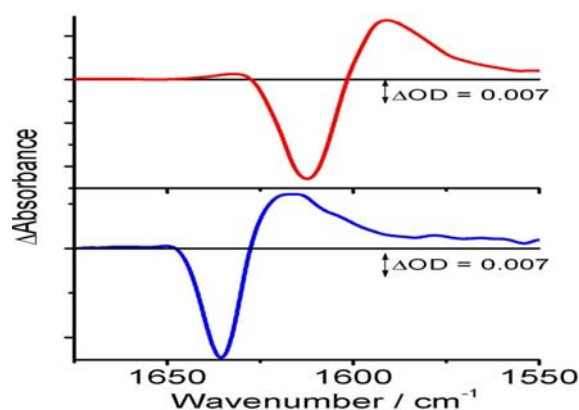


Figure 2. TRIR of 'Ruby' amide $\nu(\text{CO})$ 50 ps after photoexcitation at 400 nm.

The presence of a single lower energy transient is indicative of the ³MLCT excited state being localised on an amide-substituted bpy ligand, $[(\text{bpyam})\text{bpyamRu}^{\text{III}}\text{L}_1]^{2+}$, increasing electron density on that ligand. Initial excitation to the ¹MLCT state undergoes intersystem crossing to the ³MLCT on a sub-picosecond timescale.

Solvent	λ_{abs} (nm)	λ_{em} (nm)	τ_{LUM} (ns)	τ_{TRIR} (ns)	ϕ
H_2O	436 479	652	367	>300	0.022
CH_3CN	432 471	641	341	>300	0.014

Table 1. Photophysical properties of 'Ruby' (τ_{LUM} and τ_{TRIR} = lifetimes obtained from luminescence and TRIR).

RuCN model complex

The TRIR spectrum of **RuCN** 50 ps after photoexcitation at 400 nm is shown in Figure 3. The parent $\nu(\text{CN})$ bands are bleached and a transient at higher energy is observed. This is due to MLCT excitation away from the cyanide ligands to form $[(\text{bpy}\cdot\text{-})\text{Ru}^{\text{III}}(\text{CN})_4]^{2-}$, reducing electron density on the metal centre and increasing the $\nu(\text{CN})$ energy. This shift in electron density also results in a reduced electronic interaction between the cyanides and the solvent. It can be seen that the parent bands are more solvent dependent than the transient, which in both D_2O and CH_3CN is at *ca.* 2110 cm^{-1} .

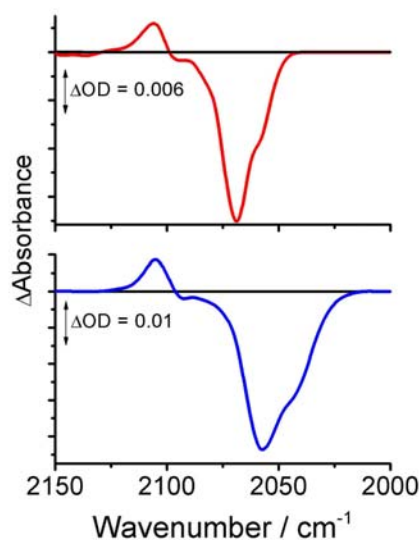


Figure 5. TRIR of 'RuCN' $\nu(\text{CN})$ 50 ps after excitation at 400 nm.

Solvent	λ_{abs} (nm)	λ_{em} (nm)	τ_{LUM} (ns)	τ_{TRIR} (ns)	ϕ
D ₂ O	395	614	1250	810	0.053
H ₂ O	395	614	430		0.021
CH ₃ OH	431	649	135		0.016
CH ₃ CN	483	692	49	43	0.005

Table 2. Photophysical properties of 'RuCN'.

Rubpy-RuCN dinuclear complex

Emission studies on analogous systems suggested a progressive quenching of the **Rubpy** ³MLCT excited state by the lower energy ³MLCT excited state of the **RuCN** terminus as the solvent mixture was changed from H₂O to CH₃CN.

TRIR allows both the initial formation of the ³MLCT excited states and subsequent energy transfer to be monitored on the ps and ns timescales. The energy donor chromophore, **RuCN** in D₂O and **Rubpy** in CH₃CN, is rapidly quenched (<1 ns) and the energy acceptor terminus shows long excited state lifetimes. Figures 7 and 8 show spectra at 2 ps and 2 ns after excitation in both solvents.

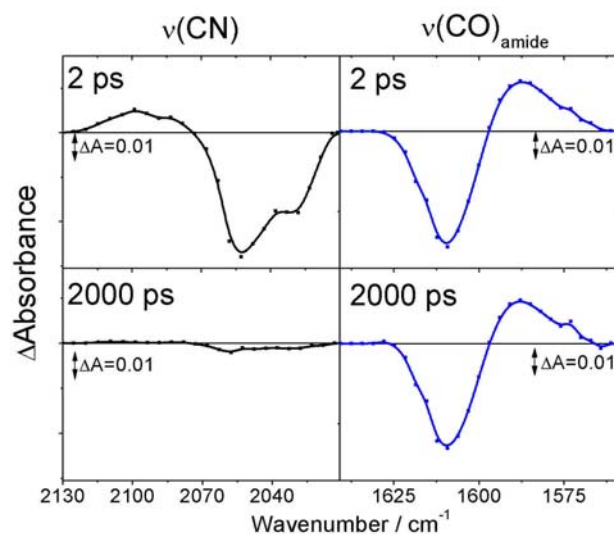


Figure 7. TRIR of 'Rubpy-RuCN' after excitation at 400 nm in D₂O.

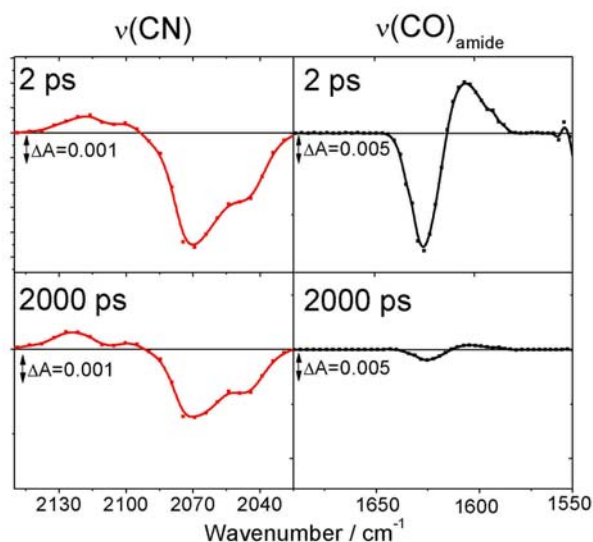


Figure 8. TRIR of 'Rubpy-RuCN' after excitation at 400 nm in CH₃CN.

Monitoring the <50 ps kinetics of the acceptor terminus shows the 'grow-in' behaviour expected for PE_nT to the lower energy terminus. In D₂O the $\nu(\text{CO})$ bleach indicates PE_nT to **Rubpy** with $\tau = 6 \pm 1$ ps; in CH₃CN the $\nu(\text{CN})$ bleach indicates PE_nT to **RuCN** with $\tau = 14 \pm 1$ ps. In both cases these termini then display slow decay of a long-lived excited state.

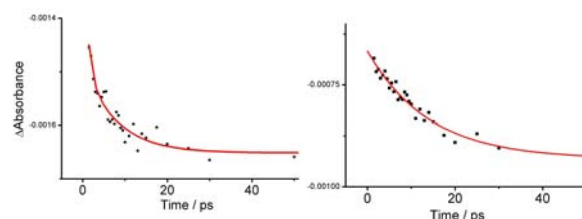


Figure 9. Ultrafast kinetics of parent $\nu(\text{CO})$ and: $\nu(\text{CN})$ to monitor PE_nT in D₂O (left) and CH₃CN (right) respectively.

Conclusions

We have demonstrated reversal of the direction of PE_nT in this dyad by varying the solvent. TRIR has allowed us to observe intercomponent PE_nT directly. However, we do observe complex multi-exponential kinetics on longer timescale and further investigation are in progress and will elucidate the role of conformational freedom in these systems.

Acknowledgements

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