Excited state dynamics of metal-bipyrimidine complexes studied by Time-Resolved Infrared spectroscopy

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Introduction

Controlling photoinduced energy and electron transfer within polynuclear systems is an area of growing interest because it will facilitate the design of switchable multicomponent systems on a molecular scale. We have prepared dinuclear complexes with an extremely short metal-metal distance (*ca.* 550 nm) across a polypyridyl ligand in which transfer of excitation energy can be mediated by synthetic changes and external stimuli.

Rebpm   RuCNbpm
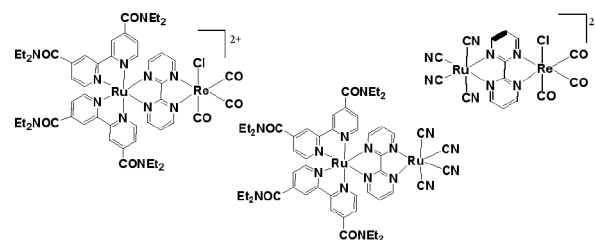
bpyamRubpm
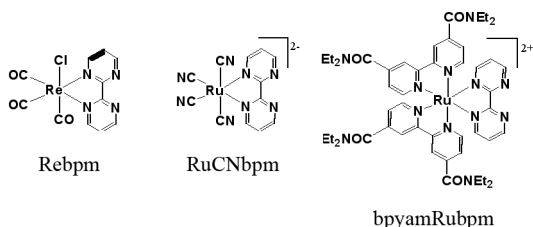
Mononuclear model complexes

The three mononuclear complexes above can be used as modular building blocks to make three homodinuclear and three heterodinuclear bipyrimidine (bpm) bridged complexes. All of these complexes are weakly emissive and have been prepared with IR reporters to allow direct monitoring of the excited state dynamics by Time-Resolved Infrared (TRIR) spectroscopy; these are metal carbonyls, amide carbonyls (bpyam ligand) and metal cyanides.
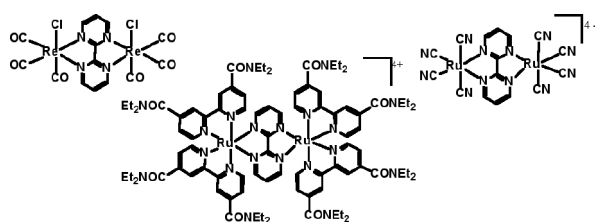
Homodinuclear complexes

Our aim was to investigate the electronic structure of the excited states formed after laser excitation; absorption of light results in a metal-to-ligand charge-transfer (^{3}MLCT) excited state which can either be 'localised' on one half of the system or 'delocalised' over both metals and the bpm bridge.[1,2] If localised, then excitation into one of the higher energy chromophores could result in energy transfer (PEnT) to the lowest energy excited state.

In all of these complexes, the initially formed ^{1}MLCT state undergoes intersystem crossing (isc) to the ^{3}MLCT on a sub-picosecond timescale. The **bpyamRubpm** unit has additional chromophores corresponding to Ru → bpyam ^{1}MLCT absorptions.

Heterodinuclear complexes

Model complexes

The **Rebpm** unit has a higher energy ^{3}MLCT excited state than **bpyamRubpm**, and the strong *negative* solvatochromism of the **RuCNbpm** unit offers a readily accessible ^{3}MLCT excited state whose energy can be varied over a wide range simply by altering the solvent.

Using the PIRATE spectrometer, photoexcitation in CH$_3$CN or D$_2$O gives ps- and ns-TRIR spectra for the mononuclear complexes, shown in Fig 1. In both the **Rebpm** and **RuCNbpm** systems the ground state bands are bleached and transients appear to higher energy, indicative of the M → bpm ^{3}MLCT excited state[3]. In the **bpyamRubpm** complex, the ν(CO)$_{amide}$ parent band (*ca.* 1610 cm^{-1}) is bleached and, in contrast to the analogous experiment with **bpyamRubpy** (bpy = 2,2'-bipyridine), a transient to *higher* energy is seen, also indicative of the M → bpm ^{3}MLCT excited state; the shift to higher energy corresponds to the transient oxidation of the Ru centre by electron transfer *away* from the bpyam ligands and onto the bpm ligand. This is further supported by the observed bleach of a ring-breathing mode of bpm (*ca.* 1580 cm^{-1})
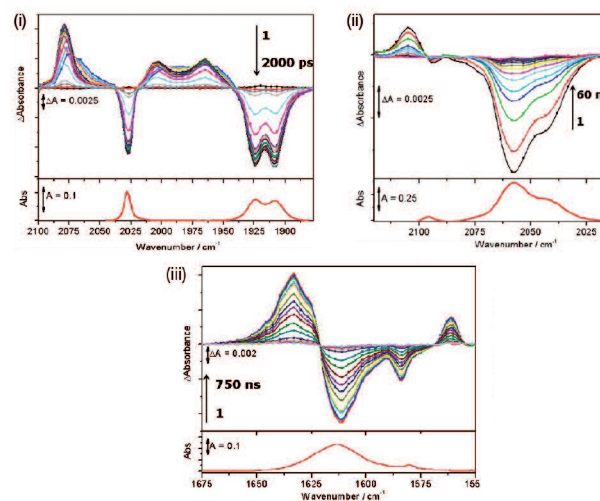

Figure 1. The ps and ns-TRIR of mononuclear complexes i) Rebpm (CH$_3$CN), ii) RuCNbpm (D$_2$O) and iii) bpyamRubpm (D$_2$O) after photoexcitation at 355 or 400 nm.

and corresponding transient to lower energy as electron density on the ligand increases in the excited state.

The combinations of these units may afford control over PEnT in dinuclear systems by tuning the thermodynamic driving force through synthetic changes and solvent variation (in RuCN-containing systems).

Homodinuclear complexes

These systems have been studied to gain insight into the more complicated behaviour of dinuclear complexes with conjugated bridges. It has been shown that complexation of a second metal centre lowers the π^* LUMO energy of bpm[1], which consequently affects the photoinduced excited state properties.

The **RebpmRe** complex is a good example of these systems – Figure 2 shows the ps-TRIR after 400 nm excitation in which in addition to the three higher energy excited state transient bands (blue) also seen in the mononuclear model complex, three transient bands to *lower* energy (red) are formed. All six transient bands decay iso-kinetically with the recovery of the parent bleaches with a lifetime of 46 ps, suggesting they are due to a single excited state.
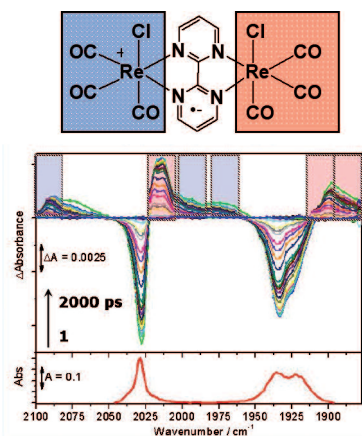

Figure 2. ps-TRIR of Cl(CO)$_3$RebpmRe(CO)$_3$Cl in CH$_3$CN

If this excited state were delocalised across the molecule on the timescale of the experiment only a single set of transient bands to *higher* energy would be seen, with a band shift approximately half of that observed in the mononuclear complex. The presence of these six bands therefore indicates that the excited state is localised, the three higher energy bands caused by the MLCT transition originating from the transiently oxidised terminus and the three *lower* energy transient bands being caused by the 'spectating' Re centre experiencing an increase in electron density on the bridging ligand.

Similarly, transient bands to higher *and* lower energy are detected for the **RuCNbpmRuCN** dinuclear, indicating a localised (CN)$_4$Ru^{III}bpm$^{•-}$–Ru^{II}(CN)$_4$ excited state is formed, which decays with a lifetime of 67 ps.

The ps-TRIR of the dinuclear **bpyamRubpmRubpyam** complex shows predominantly a higher energy transient band for the ν(CO)$_{amide}$ which grows in over 8 ps and then decays with the parent bleach recovery with a lifetime of 6 ns. We believe this to be due to initial formation of the Ru → bpyam ^{1}MLCT undergoing isc to the ^{3}MLCT state (sub-ps) and subsequently internally converting to the

Ru → bpm ^{3}MLCT state on a timescale of ca. 8 ps before decaying back to the ground state.
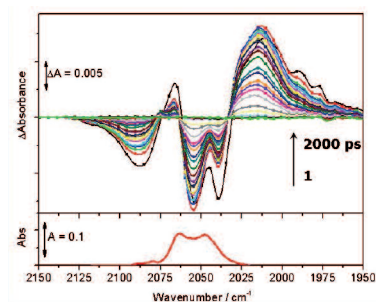

Figure 3. ps-TRIR of [(CN)$_4$RubpmRu(CN)$_4$]$^{4-}$ in CH$_3$CN

The conclusion of these experiments is that the triplet excited state formed is localised on one metal centre and the bridging ligand on the timescale of these experiments. The study was extended to heterodinuclear systems to determine if excitation leads to PEnT from one side of the molecule to the other as predicted by our model. Lifetimes quoted are ± 10 %.

Heterodinuclear complexes

Laser excitation at 400 nm results in unselective excitation of all MLCT chromophores in all the heterodinuclear complexes. The ps- and ns-TRIR spectra for **RebpmRuCN** are shown in Figure 4. The overlapping ν(CO) and ν(CN) bands make assignment difficult but comparison of the early (<2 ns) and late (>2 ns) spectra with the homodinuclear analogues demonstrates several key points. The early time spectra show a large transient band *ca.* 2000 cm^{-1} *cf.* the broad low energy transient of **RuCNbpmRuCN** (Fig 3) due to the spectating Ru centre. Also in the early time spectra are the two low energy bands *ca.* 1850 cm^{-1} *cf.* the low energy transient bands of **RebpmRe** (Fig 2) due to the spectating Re centre. The later time spectra are significantly different and resemble a combination of the low energy ν(CO) transient bands due to a spectating Re centre and a higher energy ν(CN) transient band due to a transiently oxidised Ru centre.

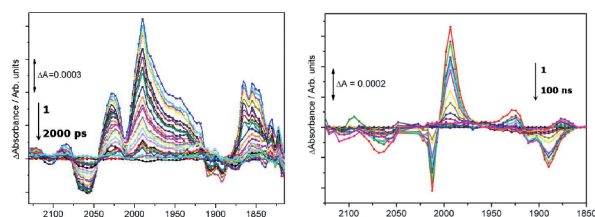**Figure 4. ps-TRIR (left) and ns-TRIR (right) spectra of RebpmRuCN in CH$_3$CN**

It appears that at early time both the [Cl(CO)$_3$Re^{II}bpm$^{•-}$-Ru^{II}(CN)$_4$]$^{2-}$ and the [Cl(CO)$_3$Re^{I}bpm$^{•-}$-Ru^{III}(CN)$_4$]$^{2-}$ ^{3}MLCT states are formed, and that at later time only the longer-lived and lower energy [Cl(CO)$_3$Re^{I}bpm$^{•-}$-Ru^{III}(CN)$_4$]$^{2-}$ state remains.

The **RebpmRubpyam** dinuclear complex in CH$_3$CN displays a grow-in of the higher energy ν(CO)$_{amide}$ transient band (*ca.* 20 ps) and subsequent decay iso-kinetically with *low* energy ν(CO)$_{Re}$ transient bands, both of which imply that the Re-based excited state formed initally decays into the ultimate excited state,

$[Cl(CO)_3Re^I bpm^{•-}Ru^{III}(bpyam)_2]^{2+}$. As expected the behaviour of the **bpyamRubpmRuCN** dinuclear complex is solvent dependent and has not yet been conclusively deconvoluted. There is evidence for 'PEnT' from the higher energy Ru → bpyam MLCT to the lower energy Ru_{CN} → bpm MLCT in CH_3CN on a timescale of *ca.* 10 ps in the form of a rapidly decaying *lower* energy $\nu(CO)_{amide}$ transient band and a concurrent short time component for the $\nu(CN)$ parent bleach followed by longer (*ca.* 90 ps) recovery of that bleach. In D_2O the ultimate excited state can be identified as $(bpyam)_2Ru^{III}bpm^{•-}Ru^{II}(CN)_4$ by the persistence of a higher energy $\nu(CN)$ transient band not seen in CH_3CN. We conclude from this that the location of the ultimate excited state has been switched from a Ru_{CN} → bpm ^{3}MLCT state in CH_3CN to a Ru_{amide} → bpm ^{3}MLCT state in D_2O.

Conclusions

The location of the final excited state in dinuclear bipyrimidine-bridged complexes has been shown to be localised on one metal centre and the bridging ligand on the timescale of the PIRATE experiments. The location of this ultimate excited state can be altered by synthetic variation of the metal units and, in the case of **bpyamRubpmRuCN** can be switched from one terminus to the other by variation of solvent.

References

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2. W. Kaim and S. Kohlmann, *Inorg. Chem.,* **29**, 2909, (1990)
3. H. Adams, W. Z. Alsindi, G. M. Davies, M. B. Duriska, T. L. Easun, H. E. Fenton, J.-M. Herrera, M. W. George, K. L. Ronayne, X.-Z. Sun, M. Towrie and M. D. Ward, *J. Chem. Soc.,* Dalton Trans., **39**, (2006)