

# Solvent dependent photophysics of *fac*-[Re(CO)<sub>3</sub>(11,12-X<sub>2</sub>dppz)(py)]<sup>+</sup> (X = H, F or Me)

Joanne Dyer,<sup>a</sup> Caitriona M. Creely,<sup>b</sup> J. Carlos Penedo,<sup>b</sup> David C. Grills,<sup>a</sup> Sarah Hudson,<sup>b</sup> Pavel Matousek,<sup>c</sup> Anthony W. Parker,<sup>c</sup> Michael Towrie,<sup>c</sup> John M. Kelly<sup>\*b</sup> and Michael W. George<sup>\*a</sup>

Received 21st December 2006, Accepted 2nd April 2007

First published as an Advance Article on the web 8th May 2007

DOI: 10.1039/b618651c

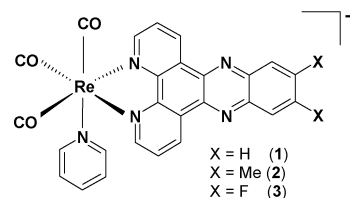
The photophysical properties of [Re(CO)<sub>3</sub>(dppz)(py)]<sup>+</sup> (dppz = dipyrido-[3,2-*a*:2',3'-*c*] phenazine) (**1**) and its 11,12 substituted derivatives [Re(CO)<sub>3</sub>(dppzMe<sub>2</sub>)(py)]<sup>+</sup> (**2**) and [Re(CO)<sub>3</sub>(dppzF<sub>2</sub>)(py)]<sup>+</sup> (**3**) have been examined in organic and aqueous environments using phosphorescence and picosecond transient visible and infrared absorption spectroscopic methods. The roles of the intraligand IL( $\pi$ - $\pi^*$ ) and metal-to-ligand charge transfer MLCT(phz) excited states are evaluated and used to explain the major effect of difluoro-substitution, which is particularly remarkable in water, where the excited state of [Re(CO)<sub>3</sub>(dppzF<sub>2</sub>)(py)]<sup>+</sup> (**3**) is strongly quenched.

## Introduction

It has been amply demonstrated over the last few years that the photophysical and photochemical properties of metal polypyridyl complexes make them suitable for a wide range of applications, ranging from energy conversion and storage<sup>1</sup> to optoelectronic devices<sup>2</sup> and sensors.<sup>3</sup> Complexes containing dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) and its derivatives have been widely studied particularly because of their interesting applications with DNA. The discovery that the excited state properties of [Ru(diimine)<sub>2</sub>(dppz)]<sup>2+</sup> (diimine = phen (1,10-phenanthroline) or bpy (2,2'-bipyridyl)) are very different in water than in an organic environment (such as when intercalated into DNA) has stimulated considerable interest in understanding the water-induced switching of the excited state properties.<sup>4</sup> The dppz ligand can be considered as a fusion of two ring systems: a phenanthroline (phen) system and a phenazine (phz) system.<sup>5</sup> The current model, based on a study of the temperature-dependence of the emission, holds that there is a bright state (with the electron based on the bpy or phen moiety of the dppz ligand) and a dark state (where the electron is located mainly on the phenazine portion of the ligand).<sup>6,7</sup> The importance of entropic factors due to the H-bonding of water to the phenazine-N atoms has been emphasised. Evidence for the possible roles for intra-ligand  $\pi$ - $\pi^*$  (dppz) states (IL( $\pi$ - $\pi^*$ )) has also been given from theoretical support.<sup>8</sup>

The properties of related dppz complexes containing the Re(CO)<sub>3</sub> moiety have attracted much less attention than the analogous Ru and Os compounds. The vibrational signatures of *fac*-[Re(CO)<sub>3</sub>(dppz)(PPh<sub>3</sub>)]<sup>+</sup> (Ph = phenyl) were reported<sup>9</sup> and the IR spectrum of the excited states of these and related complexes showed that the lowest-lying excited state is IL( $\pi$ - $\pi^*$ ) in character. [Re(CO)<sub>3</sub>(dppz)(py)]<sup>+</sup> has been shown to interact with DNA and

photophysical investigations led to the assignment of the lowest-lying excited state as being IL( $\pi$ - $\pi^*$ ) in nature.<sup>10,11</sup> To elucidate the nature and dynamics of the excited state it is necessary to carry out ultrafast time-resolved spectroscopic studies. We have already performed a detailed investigation<sup>12</sup> of the photophysical properties of *fac*-[Re(CO)<sub>3</sub>(dppz)(py)]<sup>+</sup> (**1**) using both picosecond and nanosecond time-resolved visible and infrared absorption and resonance Raman spectroscopy where it was found that a IL( $\pi$ - $\pi^*$ ) state was initially formed followed by partial decay to a relaxed equilibrium of <sup>3</sup>IL( $\pi$ - $\pi^*$ ) and <sup>3</sup>MLCT(phz) excited states which then decayed with the same rate. The time-resolved IR measurements were particularly useful in distinguishing between MLCT states involving either phen or phenazine based orbitals since the  $\nu$ (CO) band positions are diagnostic of each state. Thus, the IR spectrum of the phz-based MLCT states showed these bands were shifted to higher wavenumber relative to the phen-based states reflecting the lower electron density on the metal centre in these states.



Time resolved resonance Raman measurements have been used to probe *fac*-[Re(CO)<sub>3</sub>(dppz-X,Y)Cl] (dppz-X,Y = 11-X,12-Y-dppz with X,Y = Me, Me,<sup>13</sup> Br, H,<sup>14</sup> CO<sub>2</sub>Et, H<sup>14</sup>) and have shown that the nature of the lowest excited state can vary depending upon X and Y. The emission spectra of *fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)(L)]<sup>0,+</sup> (L = Cl, 4-ethylpyridine (4-Etpy), 4,4'-bipyridine (4,4'-bpy)); with the dppz-X<sub>2</sub> = 11,12-dppz-X<sub>2</sub> with X = CH<sub>3</sub> or Cl) have been studied both in dichloroethane solution at room temperature and in a MeTHF glass.<sup>15</sup> From the emission spectra and room temperature lifetime measurements for the Etpy and 4,4'-bpy complexes it was concluded that their emitting states are dppz-localized, while the appearance of broad structureless emission at room temperature and greatly shortened lifetimes in *fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)Cl],

<sup>a</sup>School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

<sup>b</sup>School of Chemistry and School of Physics, University of Dublin, Trinity College, Dublin 2, Ireland

<sup>c</sup>Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK OX11 0QX. E-mail: Mike.George@nottingham.ac.uk; Fax: +44 (0)115-9513563; Tel: +44(0)115-9513512

(X = CH<sub>3</sub>, Cl) points to the MLCT states being lowest lying for these complexes. A TRIR study on [Re(dppz-Cl<sub>2</sub>)(CO)<sub>3</sub>(L)]<sup>n+</sup> (L = Cl (*n* = 0), py (*n* = 1) and (4-dimethylamino)pyridine (*n* = 1)) in CH<sub>3</sub>CN showed only evidence for a <sup>3</sup>IL ππ\* excited state for L = Cl but two sets of ν(CO) bands were observed arising from IL ππ\* and Re-phenazine MLCT states for L = 4-Me<sub>2</sub>Npy. In the TRIR spectrum of *fac*-[Re(dppz-Cl<sub>2</sub>)(CO)<sub>3</sub>Cl] there was evidence for only a phenazine-localised MLCT.<sup>16</sup> A generalised energy level diagram has been proposed to account for the photophysics of Re-dppz carbonyl complexes which is similar to that previously reported<sup>12</sup> for *fac*-[Re(CO)<sub>3</sub>(dppz)(py)], with rapid interconversion between MLCT and ππ\* states, which are in facile equilibrium. In this paper we develop this work further to examine the photophysical properties of *fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)(py)]<sup>+</sup> (X = H, Me or F) using fluorescence, transient absorption and infrared spectroscopy in a range of solvents. In particular the remarkable effect that fluoro-substitution of the ligand has on the photophysical properties of the complex, which is most evident in water, is reported.

## Experimental

### Materials and sample handling

*fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)(py)]<sup>+</sup> (X = H, Me or F) was prepared by adapting published procedures,<sup>11</sup> initially as the PF<sub>6</sub><sup>-</sup> salt from which the water soluble Cl<sup>-</sup> compounds were prepared by ion-exchange using a methanol solution of the PF<sub>6</sub><sup>-</sup> salt and a Dowex IX2-110 anion exchange resin and methanol. Spectrophotometric grade CH<sub>3</sub>CN, EtOH, CH<sub>2</sub>Cl<sub>2</sub> and D<sub>2</sub>O (Aldrich) were used as received. The samples for ns studies were degassed. Those for ps studies were not, as the diffusion of oxygen will not affect processes on this time-scale.

### UV-visible absorption and emission measurements

UV-visible absorption spectra were obtained using a Perkin Elmer Lambda 5 spectrophotometer. Emission measurements were performed on an Edinburgh Instruments FLS920 fluorimeter. Samples in acetonitrile were degassed in specially modified 1 × 1 cm quartz cuvettes and the optical density was adjusted to *ca.* 0.2 at the excitation wavelength. Corrected steady-state emission spectra were obtained with a xenon arc lamp as the excitation source. Quantum yields are reported relative to [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in degassed aqueous solution ( $\phi_{\text{em}} = 0.042$ )<sup>17</sup> and for the samples measured in acetonitrile the values are corrected for the difference in refractive index between acetonitrile and water.

### Picosecond transient visible absorption experiments

The samples were pumped at 400 nm (pulse energy *ca.* 10 μJ) and probed from 450 to 700 nm. The laser source was a Ti-Sapphire oscillator/regenerative amplifier system (Spectra Physics Tsunami/Spitfire), producing *ca.* 150 fs fundamental pulses at 800 nm. The pulse train was split in the ratio 1 : 3, the first part being frequency doubled by an SHG crystal to give the pump pulses and the other part used to generate the white light continuum probe in a 10 mm water flow cell. The continuum beam was split to give a probe and a parallel reference beam, which did not pass through the sample. The pump beam was sent along a delay line before being passed through the sample cuvette,

intersecting the white light beam at a small angle. The probe and reference beams were dispersed by a diffraction grating across a pair of diode arrays, which were connected to a PC for signal detection and processing. A more complete description of the experimental set up can be found elsewhere.<sup>18</sup> The diode arrays were calibrated daily from pixel to wavelength using bandpass filters at 460 and 660 nm. Samples (typically 1.5–3 × 10<sup>-4</sup> M) were contained in a 5 × 5 mm cell and agitated by a magnetic stirrer bar. UV-visible spectra taken before and after irradiation, indicated that decomposition of the sample was minimal.

### Nanosecond step-scan FTIR experiments

Time-resolved step-scan FTIR (s<sup>2</sup>-FTIR) experiments were conducted using a combination of a Nicolet Magna 860 Interferometer and a Nd:YAG laser (Spectra Physics GCR-12).<sup>19</sup> Synchronisation of the laser with data collection was achieved using a pulse generator (Stanford DG535). The interferometer was equipped with both an internal 100 kHz 16-bit digitiser and an external 100 MHz 12-bit digitiser (GAGE 8012A). In these experiments a 1 mm photovoltaic HgCdTe (MCT) detector was used with a 20 MHz preamplifier. This detector has AC and DC outputs, which are digitised simultaneously to ensure proper phase matching. The AC signal was amplified by an external pre-amplifier (Stanford SR 560) to use the full dynamic range of the digitiser. Single sided interferograms were obtained using one laser pulse at each mirror position. An external optical bench (Nicolet-TOM<sup>®</sup>) was used in these experiments.<sup>19</sup>

### Picosecond time-resolved infrared (ps-TRIR) experiments

The ps-TRIR experiments were carried out at the Central Laser Facility of the Rutherford Appleton Laboratory. This apparatus has been described in detail previously.<sup>20</sup> Briefly, part of the output from a 1 kHz, 800 nm, 150 fs, 2 mJ Ti-Sapphire oscillator/regenerative amplifier (Spectra Physics Tsunami/Spitfire) was used to pump a white light continuum seeded β-barium borate (BBO) OPA. The signal and idler produced by this OPA were difference frequency mixed in a type I AgGaS<sub>2</sub> crystal to generate tunable broadband mid-infrared pulses (*ca.* 150 cm<sup>-1</sup> FWHM, 1 μJ), which were split to give probe and reference pulses. The probe pulses were focused into the sample and imaged onto the input slit of a spectrograph (150 lines mm<sup>-1</sup>). The reference pulses followed a similar optical path but were transmitted through a cell containing only the solvent and then imaged into a second spectrograph. Second harmonic generation of the residual 800 nm light provided 400 nm pump pulses, which were sent along a delay line before exciting the sample. Both the pump and probe pulses were focused to a diameter of 200–300 μm at the sample. Changes in infrared absorption at various pump–probe time delays were recorded by normalising the outputs from a pair of 64-element HgCdTe (MCT) infrared linear array detectors on a shot-by-shot basis at 1 kHz. Data were collected in pump-on/pump-off pairs in order to minimize the effect of long-term drift in the laser intensity.

Samples were probed in a standard IR solution cell equipped with CaF<sub>2</sub> windows (Harrick Scientific Corp.). For experiments in CH<sub>3</sub>CN a closed Ar-flushed, re-circulating flow system was used while for D<sub>2</sub>O, samples were contained in a sealed IR cell (pathlength 50–100 μm). In both cases the cell was rapidly oscillated in the plane perpendicular to the direction of the

laser beams in order to minimise the potential build-up of decomposition products on the windows. For the flowing samples, a second IR cell in the flow system was placed in the sample compartment of an FTIR spectrometer for online monitoring of sample decomposition during the measurements. Static samples were monitored following each experiment.

## Results and discussion

The luminescence of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})](\text{PF}_6)$  (**1**),  $[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})](\text{PF}_6)$  (**2**) and  $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})](\text{PF}_6)$  (**3**) have been studied in a number of organic solvents of different polarity. Examples are given in Fig. 1. As can be observed, the spectra of the parent complex (**1**) and its dimethyl-derivative (**2**) in  $\text{CH}_2\text{Cl}_2$  are dominated by sharp peaks at 559 nm for **1** and 570 nm for **2**, each with a shoulder at *ca.* 600 nm. Upon moving to the more polar solvents, the spectra are only slightly changed. Such behaviour is expected for an  $\text{IL}(\pi-\pi^*)$  excited state.

In  $\text{CH}_2\text{Cl}_2$  the spectrum of  $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})](\text{PF}_6)$  (**3**) is similar to that of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})](\text{PF}_6)$  (**1**) in the same solvent, although it is somewhat broader and is shifted to shorter wavelengths ( $\lambda_{\text{max}} = 535$  nm) with a more pronounced long-wavelength shoulder (at *ca.* 574 nm). It is likely therefore that this luminescent state is also  $\text{IL}(\pi-\pi^*)$ . However, unlike what is found with **1** there is a very obvious shift in the spectra of **3** in the more polar solvents. For example in  $\text{CH}_3\text{CN}$   $\lambda_{\text{max}}$  is located at 583 nm with a pronounced shoulder at *ca.* 540 nm. This behaviour is consistent with a change of the nature of the emitting excited state, so that in polar solvents we postulate for  $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})](\text{PF}_6)$  (**3**) that the excited state has some MLCT character. In agreement with this assignment the excited state lifetime in degassed acetonitrile solution was determined to be 180  $\mu\text{s}$  for **1**, but much shorter (5  $\mu\text{s}$ ) for **3**.

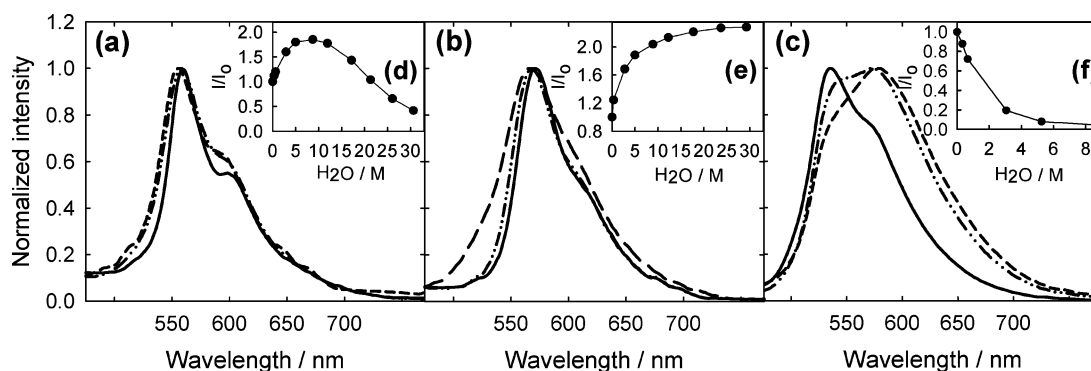
A particularly striking effect is observed when water is added to solutions of the three complexes in deaerated  $\text{CH}_3\text{CN}$ . For  $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})](\text{PF}_6)$  (**3**) (Fig. 1(c)) it is observed that water strongly quenches the emission, with the quantum yield for the complex in water being less than 1% of the value of that in  $\text{CH}_3\text{CN}$ . It is possible that in  $\text{CH}_3\text{CN}$  the MLCT state is at a slightly higher energy than the  $\text{IL}(\pi-\pi^*)$  state and it is expected that in water this state will be further stabilised. Furthermore, it appears that in water the lowest MLCT state formed is non-emissive, in

a fashion similar to the well-studied  $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$ .<sup>6,7</sup> In contrast to this behaviour, addition of water (up to a final concentration of 30 M) to deaerated  $\text{CH}_3\text{CN}$  solutions of  $[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})](\text{PF}_6)$  (**2**) causes the emission to continually intensify (Fig. 1(b)). This behaviour is consistent with the  $\text{IL}(\pi-\pi^*)$  state being lowest under all conditions. For the unsubstituted complex (**1**), as previously reported,<sup>11</sup> the emission intensity initially increases up to a concentration of 9 M, before then decreasing as the proportion of water is increased (Fig. 1(d)). In this case it would appear that the lowest excited state is also  $\text{IL}(\pi-\pi^*)$  in aqueous  $\text{CH}_3\text{CN}$  until the water concentration exceeds 9 M. Increasing concentrations of water will stabilise the MLCT state so that a point is reached at which it provides an effective deactivation pathway.

It is clear that changing the solvent from  $\text{CH}_3\text{CN}$  to  $\text{H}_2\text{O}$  has a dramatic effect on the photophysics of  $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$ . The similarities in the spectral shape between the UV-visible absorption measurements recorded in  $\text{CH}_3\text{CN}$  and water (not shown) suggest that the nature of the Franck-Condon excited states populated immediately following photoexcitation are not significantly altered. In general, near-UV excitation of *fac*- $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$  in both  $\text{CH}_3\text{CN}$  and  $\text{D}_2\text{O}$  results in the population of both  $\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{phen})$   $^1\text{MLCT}(\text{phen})$  and  $^1\text{IL}(\pi,\pi^*)$  excited states. However, it is also apparent that the development of this excited state population with time is markedly different in each solvent. In order to probe these effects further we have undertaken transient absorption experiments.

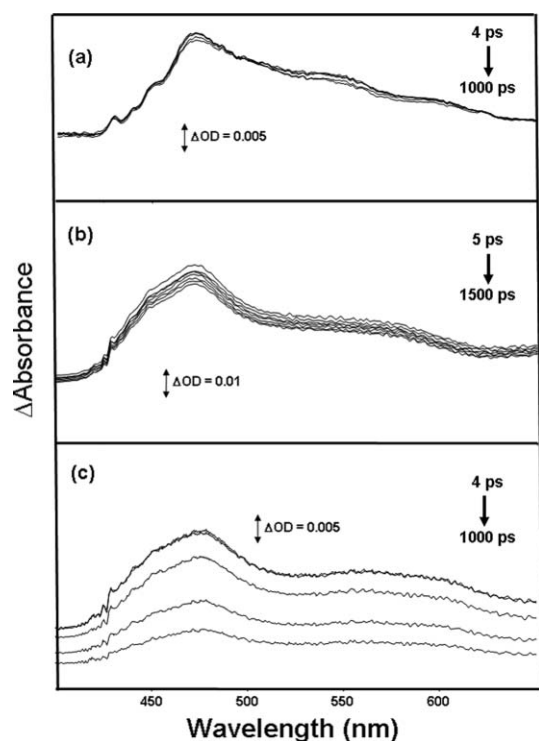
### Picosecond transient absorption spectroscopy

Initially we carried out picosecond spectroscopic studies of **1** and **3** in both  $\text{CH}_3\text{CN}$  and water using a sub-picosecond 400 nm excitation pulse and probing throughout the visible spectrum. The transient absorption spectra of **3** in  $\text{CH}_3\text{CN}$  (Fig. 2(a)) are shown at delay times ranging from 4 to 1000 ps and appear as broad absorptions with a maximum at *ca.* 475 nm and shoulders at *ca.* 540 and 595 nm. A slight increase in intensity (*ca.* 5%) at the maximum is observed over the first 100 ps, with equally small changes occurring elsewhere. Similar behaviour is found for **1**.<sup>12</sup> However, in water, transient methods show that the photophysical behaviour of **1** and **3** are quite different. Fig. 2(b) shows the transient spectra of **1** in buffered  $\text{D}_2\text{O}$  with a maximum at 470 nm. The spectrum decays only slightly over the first 100 ps and the



**Fig. 1** Phosphorescence spectra of (a)  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})](\text{PF}_6)$  (**1**), (b)  $[\text{Re}(\text{CO})_3(\text{dppzMe}_2)(\text{py})](\text{PF}_6)$  (**2**) and (c)  $[\text{Re}(\text{CO})_3(\text{dppzF}_2)(\text{py})](\text{PF}_6)$  (**3**) in (i) dichloromethane (—), (ii) ethanol (---) and (iii) acetonitrile (· · ·). Insets: variation of emission intensity upon addition of water to acetonitrile solutions of complexes (d) **1**, (e) **2**, (f) **3**.



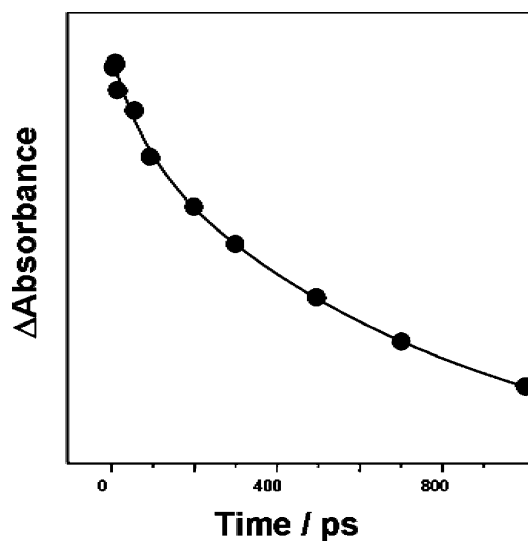


**Fig. 2** Transient absorption spectra at room temperature taken at various delay times on the ps time-scale following 400 nm laser excitation of (a) *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> (4, 10, 100, 500 and 1000 ps) in CH<sub>3</sub>CN, (b) *fac*-[Re(CO)<sub>3</sub>(dppz)(py)]<sup>+</sup> (5, 10, 45, 500, 1000 and 1500 ps) in D<sub>2</sub>O and (c) *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> (4, 10, 100, 500 and 1000 ps) in D<sub>2</sub>O.

spectral profile is similar to that found in CH<sub>3</sub>CN.<sup>12</sup> By contrast for **3** in buffered water, careful analysis shows that although there is an absorption maximum at *ca.* 475 nm there is clear evidence for extra absorbance at 450 nm and the very broad feature centred at *ca.* 565 nm, replaces those at *ca.* 540 and 595 nm. Most strikingly, greater than 80% of the intensity of the entire absorption decays on the time-scale of the experiment. This decay was monitored at a number of wavelengths between 470 and 570 nm (Fig. 3(a)) and is best represented by fitting to a double exponential function, which gives the two components having the same decay parameters ( $\tau = 73 (\pm 19)$  ps and  $810 (\pm 200)$  ps) within error in buffered H<sub>2</sub>O or D<sub>2</sub>O.

The similar transient absorption characteristics of **1**, **2** (not shown) and **3** in CH<sub>3</sub>CN suggest in all cases the IL( $\pi$ - $\pi^*$ ) excited state is the dominant species. In D<sub>2</sub>O, the similarity of the transient absorption data for **1** indicates that the IL( $\pi$ - $\pi^*$ ) excited state is present and that no other low lying state strongly perturbs the kinetic behaviour on the picosecond time-scale. By contrast, the transient absorption data and the rapid decay kinetics for the difluoro analogue **3** in water are consistent with the involvement of another excited species.

The differences at early times in the features in D<sub>2</sub>O, with respect to those observed in CH<sub>3</sub>CN, suggest that absorption due to an additional excited state species is present. The increased signal at *ca.* 600 nm is particularly significant here as this is the region where the radical anion of Re-bound dppz is expected to absorb with the electron localized on the phenazine moiety.<sup>21</sup> The UV-visible spectrum of the reduced form of **3** has a clear absorption



**Fig. 3** Kinetic traces obtained by monitoring at 470 nm, following 400 nm excitation of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> in D<sub>2</sub>O.

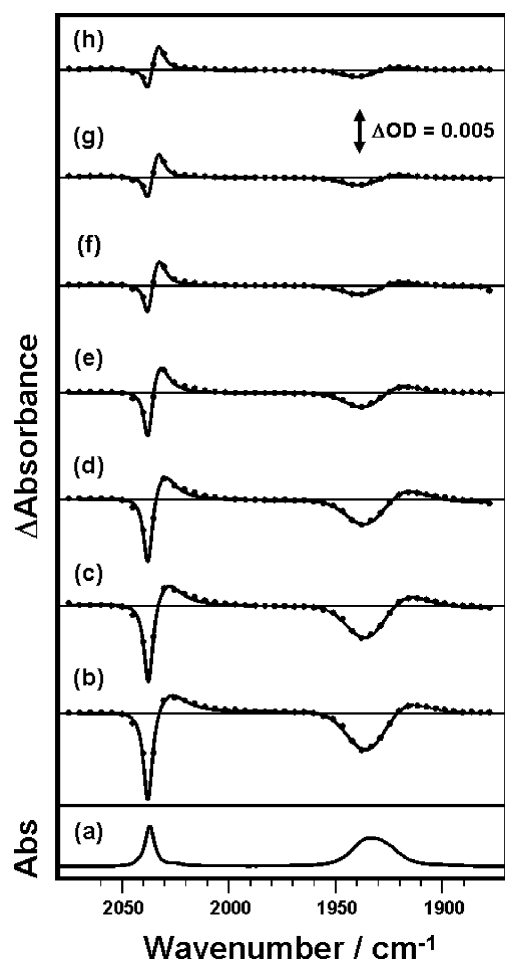
maximum at 604 nm (not shown) and we use this result to interpret the transient absorption spectra in water. The extra absorption at *ca.* 600 nm is tentatively assigned to the presence of a <sup>3</sup>MLCT(phz) excited state. However, sufficient similarities to the spectra of the complex in CH<sub>3</sub>CN are present to indicate that the IL( $\pi$ - $\pi^*$ ) excited state is also present. The rapid decay of **3** in water is consistent with an enhanced rate of quenching provided by the MLCT excited state.

#### Picosecond and nanosecond time-resolved infrared spectroscopy

The investigations into the photophysics of these complexes considered in the previous sections have provided evidence for differences in their photophysical behaviour, particularly for **3** in CH<sub>3</sub>CN vs. D<sub>2</sub>O. We now employ TRIR spectroscopy to probe further the identity of the excited state species involved.

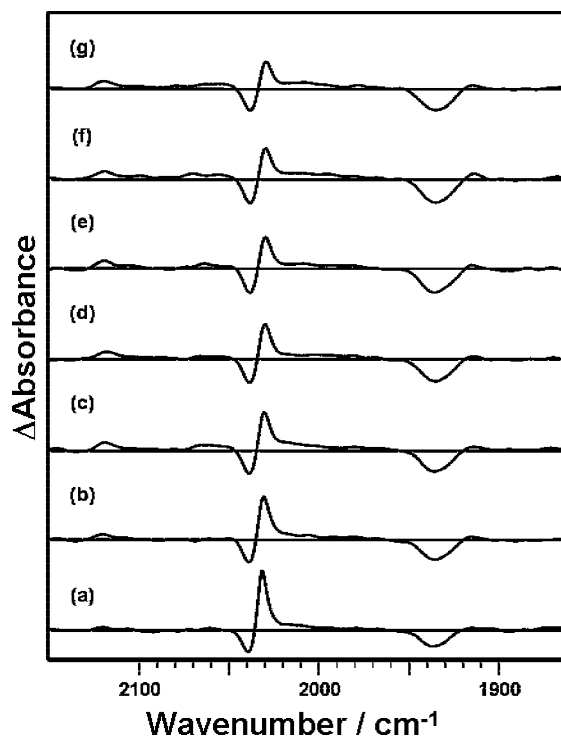
**Non-protic solvents.** The ps-TRIR spectra of **3** in CH<sub>3</sub>CN, shown in Fig. 4, reveal similar photophysics to that of **1**, which we previously demonstrated is dominated by an IL( $\pi$ - $\pi^*$ ) excited state on this time-scale.<sup>12</sup> The shift of the excited state bands to lower wavenumber with respect to the parent absorptions clearly differentiates between MLCT and IL( $\pi$ - $\pi^*$ ) excited states.<sup>12</sup> At early times ( $\Delta t$  is increased from 2–50 ps) the excited state bands narrow and shift to slightly higher wavenumber consistent with relaxation from a vibrationally excited state of the newly formed species. The apparent recovery of the ground state is attributed to this cooling process due to appreciable overlap of the cooled IL( $\pi$ - $\pi^*$ ) bands with those of the ground state. The alternative explanation of rapid decay to the ground state is considered unlikely given that there are no significant changes in the visible absorption, Fig. 2(a). The thermally-equilibrated IL( $\pi$ - $\pi^*$ ) excited state does not decay appreciably up to the longest time measured on this time-scale (1000 ps).

On the nanosecond time-scale it was previously shown that the <sup>3</sup>IL( $\pi$ - $\pi^*$ ) excited state of **1** partially decays to a relaxed equilibrium of <sup>3</sup>IL( $\pi$ - $\pi^*$ ) and <sup>3</sup>MLCT(phz) excited states.<sup>12</sup> In order to establish whether a similar behaviour is found for **3**, we have recorded ns-step-scan FTIR spectra of **3** in CH<sub>3</sub>CN,

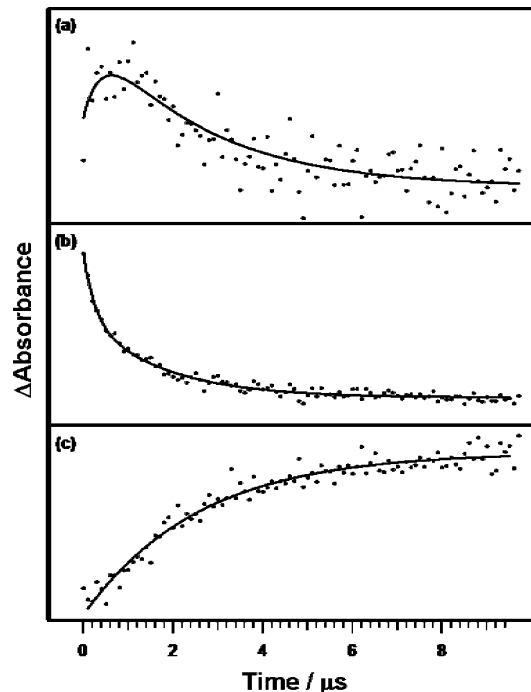


**Fig. 4** (a) FTIR spectrum of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> in CH<sub>3</sub>CN, at room temperature and ps-TRIR spectra obtained (b) 2 ps, (c) 5 ps, (d) 10 ps, (e) 25 ps, (f) 50 ps, (g) 100 ps and (h) 500 ps following 400 nm excitation of this solution.

obtained at a series of time delays between 250 and 850 ns, following 355 nm excitation, Fig. 5. The spectrum obtained at 250 ns shows a depletion of the  $\nu(\text{CO})$  ground state bands at 2037 and 1934  $\text{cm}^{-1}$  and the formation of two transient bands associated with the  ${}^3\text{IL}(\pi-\pi^*)$  excited state at 2031 and 1930  $\text{cm}^{-1}$ , similar to those observed at the limit of the ps-TRIR experiment. However, there are also indications of three transient  $\nu(\text{CO})$  bands (2120, 2057 and 2014  $\text{cm}^{-1}$ ) associated with a  ${}^3\text{MLCT}(\text{phz})$  excited state species. These bands become more prominent over the following 600 ns. The TRIR kinetic traces over 10  $\mu\text{s}$  are shown in Fig. 6 and reveal that the  ${}^3\text{MLCT}(\text{phz})$  excited state of **3** grows in with a time constant,  $\tau = 400 (\pm 40)$  ns and decays exponentially with a lifetime,  $\tau = 2.5 (\pm 0.1)$   $\mu\text{s}$ . The bands due to the  ${}^3\text{IL}(\pi-\pi^*)$  excited state species are present immediately after excitation on the nanosecond time-scale but decay *via* a double exponential function  $\{\tau = 430 (\pm 40)$  ns and  $2.3 (\pm 0.3)$   $\mu\text{s}\}$ . These results are consistent with the  ${}^3\text{IL}(\pi-\pi^*)$  state decaying to a relaxed equilibrium of  ${}^3\text{IL}(\pi-\pi^*)$  and  ${}^3\text{MLCT}(\text{phz})$  excited states which then reforms the parent. Similar behaviour was observed for [Re(CO)<sub>3</sub>dppz-Me<sub>2</sub>](py)<sup>+</sup> (**2**) except that the  ${}^3\text{MLCT}$  bands are not as prominent as they were for **1** and **3** in the early spectra (not shown). The bands attributed



**Fig. 5** A series of step-scan FTIR spectra of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> in CH<sub>3</sub>CN at room temperature, obtained (a) 250 ns, (b) 350 ns, (c) 450 ns, (d) 550 ns, (e) 650 ns, (f) 750 ns and (g) 850 ns following 355 nm excitation.



**Fig. 6** TRIR kinetic decay traces generated from the areas of the  $\nu(\text{CO})$  bands in the step-scan FTIR of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> in CH<sub>3</sub>CN at room temperature, following 355 nm excitation; (a) grow in and decay of the band at 2120  $\text{cm}^{-1}$  assigned to the  ${}^3\text{MLCT}(\text{phz})$  species; (b) decay of the band at 2031  $\text{cm}^{-1}$  assigned to the  ${}^3\text{IL}(\pi-\pi^*)$  excited state species and (c) recovery of the parent band at 2037  $\text{cm}^{-1}$ . The TRIR traces have been autoscaled.

to the  $^3\text{MLCT}(\text{phz})$  excited state of  $[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})]^+$  in  $\text{CH}_3\text{CN}$  grow in with a time constant,  $\tau = 850 (\pm 20)$  ns and decay monoexponentially with a lifetime,  $\tau = 6.0 (\pm 0.4)$   $\mu\text{s}$  while the  $^3\text{IL}(\pi-\pi^*)$  excited state of  $[\text{Re}(\text{CO})_3(\text{dppzMe}_2)(\text{py})]^+$  is present immediately after excitation, and decays *via* a double exponential function  $\{\tau = 870 (\pm 20)$  ns and  $5.6 (\pm 0.6)$   $\mu\text{s}\}$ . The formation of less  $^3\text{MLCT}$  in the case of  $[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})]^+$  reflects the equilibrium between the two states lying more towards the  $^3\text{IL}(\pi-\pi^*)$  excited state. The shorter excited state lifetimes obtained from the TRIR experiments are probably due to quenching which results from the use of higher parent concentration in these experiments, an effect which is often observed in such experiments.<sup>23</sup>

We have previously investigated the photophysics of **1** in 77 K PrCN–BuCN (5 : 4 v/v) glasses using TRIR<sup>12</sup> and observed only the  $^3\text{IL}(\pi-\pi^*)$  excited state, as the MLCT states should be raised in energy significantly in the 77 K glass<sup>22</sup> while the  $^3\text{IL}(\pi-\pi^*)$  state is expected to be much less affected. The TRIR spectra obtained for **2** and **3** at 77 K show only the presence of the  $^3\text{IL}(\pi-\pi^*)$  excited state, Table 1.

**Aqueous solutions.** The ps-TRIR spectra obtained at a series of time delays following 400 nm excitation of **1** and **3** in  $\text{D}_2\text{O}$  are shown in Fig. 7. For **1** we find that on the picosecond time-scale the  $^3\text{IL}(\pi-\pi^*)$  excited state is the only excited state species observed and there is an apparent decay (14 ( $\pm 2$ ) ps) due to relaxation from an initially formed vibrationally excited species similar to that described above for **3** in  $\text{CH}_3\text{CN}$ . By contrast, for **3**, as well as the  $^3\text{IL}(\pi-\pi^*)$  excited state, three new broad absorption bands due to formation of a MLCT state are present. The high frequency band centred at 2105  $\text{cm}^{-1}$  may be assigned to a  $^3\text{MLCT}(\text{phz})$  excited state consistent with the earlier visible absorption results, Fig. 2(c). Thus both  $^3\text{IL}(\pi-\pi^*)$  excited state and  $^3\text{MLCT}(\text{phz})$  excited states are formed rapidly in water (<20 ps) unlike what is observed in  $\text{CH}_3\text{CN}$  ( $\approx 400$  ns). We have already seen that the nature of the substituent on dppz can have an effect on the rate of conversion from the IL to the MLCT(phz) states in  $\text{CH}_3\text{CN}$  where the rate decreases in the order  $\text{dppzF}_2$  (400 ns) >  $\text{dppz}$  (*ca.* 500 ns) >  $\text{dppzMe}_2$  (800 ns). In water, we exclude that direct excitation at 400 nm of **3** favours the production of the MLCT(phz) in water but not in acetonitrile, since the transition probability will be very low irrespective of the solvent, so other factors must be involved (see later).

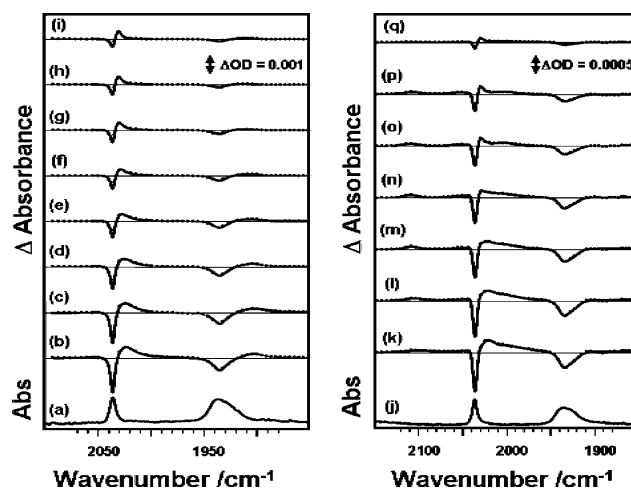


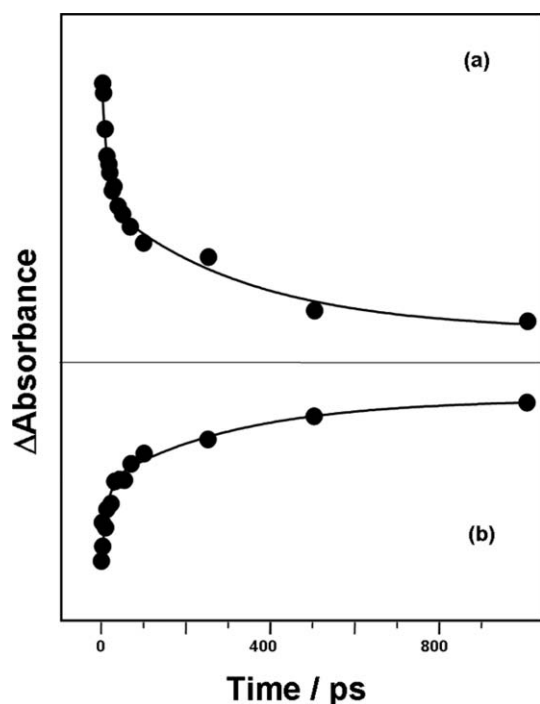
Fig. 7 (a) FTIR spectrum of *fac*- $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$  in  $\text{D}_2\text{O}$  at room temperature and ps-TRIR spectra obtained of this solution after (b) 2 ps, (c) 4 ps, (d) 10 ps, (e) 20 ps, (f) 30 ps, (g) 50 ps, (h) 100 ps and (i) 1000 ps. (j) FTIR spectrum of *fac*- $[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$  in  $\text{D}_2\text{O}$  and ps-TRIR spectra obtained of this solution after (k) 2 ps, (l) 4 ps, (m) 10 ps, (n) 20 ps, (o) 50 ps, (p) 100 ps and (q) 1000 ps.

Analysis of the TRIR kinetics of **3** in  $\text{D}_2\text{O}$  reveals that the decay must be fitted by a multi-exponential function, Fig. 8. Using a double exponential, the shorter component has a lifetime of 14 ( $\pm 2$ ) ps similar to that of **1** and is likewise attributed to relaxation from a vibrationally excited state. No comparable short-lived decay was observed using visible transient absorption and the kinetic traces were fitted with a double-exponential decay ( $\tau = 73 (\pm 19)$  ps and 810 ( $\pm 200$ ) ps) (*vide supra*). The transient absorption (TA) and TRIR results both show a longer-lived signal (TRIR:  $\tau = 732$  ps ( $\pm 200$ ) ps) and TA (810 ( $\pm 200$ ) ps). Unfortunately, the signal-to-noise ratio of this TRIR signal is insufficient to warrant subjecting the experimental data to a three exponential analysis. We interpret the values for these decay rates to mean that there may actually be three processes that are occurring: vibrational relaxation (observed in the TRIR kinetics), interconversion between excited states (seen in visible absorption kinetics) *e.g.* formation of IL/MLCT equilibrium and decay of the relaxed excited states (present in both data). Further studies are underway to try to unravel the complexity of this system.

Table 1 IR  $\nu(\text{CO})$  band positions ( $\text{cm}^{-1}$ ) of Re-dppz complexes under different conditions. The excited state assignments are also given

Complex	Solvent	Temperature/K	$\nu(\text{CO})$ ground state	$\nu(\text{CO})$ excited state	Excited state assignment
$[\text{Re}(\text{CO})_3(\text{phen})(\text{py})]^+$	$\text{CH}_3\text{CN}$ <sup>12</sup>	298	2036, 1931	2064, 2011, 1969	$^3\text{MLCT}(\text{phen})$
$[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$	$\text{CH}_3\text{CN}$ <sup>12</sup>	298	2037, 1933	2029, 1917 2120, 2060, 2016	$^3\pi\pi^*$ $^3\text{MLCT}(\text{phz})$
$[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$	PrCN–BuCN (5 : 4 v/v) <sup>12</sup>	77	2036, 1935	2029, 1914	$^3\pi\pi^*$
$[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$	$\text{D}_2\text{O}$	298	2036, 1937	2032, 1918	$^3\pi\pi^*$
$[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})]^+$ <sup>a</sup>	$\text{CH}_3\text{CN}$	298	2036, 1932	2032, 1921 2120, 2059, 2011	$^3\pi\pi^*$ $^3\text{MLCT}(\text{phz})$
$[\text{Re}(\text{CO})_3(\text{dppz-Me}_2)(\text{py})]^+$	PrCN–BuCN (5 : 4 v/v)	77	2035, 1936	2028, 1910	$^3\pi\pi^*$
$[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$	$\text{CH}_3\text{CN}$	298	2037, 1934	2031, 1930 2120, 2057, 2014	$^3\pi\pi^*$ $^3\text{MLCT}(\text{phz})$
$[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$	PrCN–BuCN (5 : 4 v/v)	77	2034, 1933	2029, 1912	$^3\pi\pi^*$
$[\text{Re}(\text{CO})_3(\text{dppz-F}_2)(\text{py})]^+$	$\text{D}_2\text{O}$	298	2036, 1935	2029, 1924 2108, 2047, 2003	$^3\pi\pi^*$ $^3\text{MLCT}(\text{phz})$

<sup>a</sup> Ref. 12.



**Fig. 8** Kinetic traces from the TRIR of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> in D<sub>2</sub>O at room temperature following 400 nm excitation, corresponding to (a) the sum of the curve-fitted excited state IR ν(CO) band areas and (b) the curve-fitted band area of the high frequency IR ν(CO) bleach.

## Conclusions

The combination of techniques used in this study and especially the spectroscopic ‘handles’ provided by the carbonyl group, has allowed us to partially reveal the complex photophysics involved in these *fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)(py)]<sup>+</sup> compounds and to demonstrate that these depend strongly on the nature of the substituent (X = H, Me or F). This is particularly evident for the difluoro-compound **3** dissolved in aqueous solvents.

In acetonitrile all complexes **1–3** behave similarly in the ps range and we assign the dominant species present after rapid vibrational relaxation to the triplet <sup>3</sup>IL(π–π\*) excited state. At much longer times (hundreds of nanoseconds) this excited state species transforms to an equilibrium mixture of <sup>3</sup>IL(π–π\*) and <sup>3</sup>MLCT(phz) states, this process being somewhat faster for the complex with the more electron-withdrawing substituents. Luminescence measurements reveal that in most organic solvents the deactivation of the excited states to ground state proceeds through the <sup>3</sup>IL(π–π\*) state. However in the case of *fac*-[Re(CO)<sub>3</sub>(dppz-F<sub>2</sub>)(py)]<sup>+</sup> (**3**) in polar solvents such as acetonitrile a <sup>3</sup>MLCT state appears to be favoured.

The most striking differences between the complexes were, however, observed in aqueous solution. Thus while the ps and luminescence studies show that the <sup>3</sup>IL(π–π\*) is the dominant species for parent complex **1** and its dimethyl derivative **2**, the situation is quite different for **3**, where the complex is essentially non-emissive in water. The ps studies of **3** in this solvent reveal that after initial vibrational relaxation (in contrast to what is found for **1** and **2**) a mixture of <sup>3</sup>IL(π–π\*) and <sup>3</sup>MLCT(phz) states exists. This decays rapidly by a process which is substantially independent of the deuteration of the solvent and we propose that

the deactivation mechanism of **3** in water involves the H-bonding of the water to the basic nitrogen atoms in the phenazine ring in the <sup>3</sup>MLCT(phz) state, in a fashion similar to that proposed for [Ru(diimine)<sub>2</sub>(dppz)]<sup>2+</sup>.<sup>6,7</sup>

The reasons for the rapid formation of the <sup>3</sup>MLCT(phz) excited state in water but not in CH<sub>3</sub>CN are unclear. One hypothesis we have considered is that conversion from the <sup>3</sup>IL(π–π\*) to <sup>3</sup>MLCT(phz) cannot rapidly take place directly, but rather proceeds through another state *e.g.* <sup>3</sup>MLCT(phen) state. It is possible that in the case where the energies of the states lie in the order <sup>3</sup>IL(π–π\*) < <sup>3</sup>MLCT(phen) > <sup>3</sup>MLCT(phz) then the formation of the <sup>3</sup>MLCT(phz) will be very slow, as is the case for CH<sub>3</sub>CN solutions. On the other hand if the energies of the states are in the order <sup>3</sup>IL(π–π\*) ≥ <sup>3</sup>MLCT(phen) ≥ <sup>3</sup>MLCT(phz), then the transition could be fast, and this may be the case in aqueous solutions. A full elucidation of this tentative hypothesis will require a range of detailed experimental and theoretical studies such as those used for the Ru-derivatives.<sup>6,7</sup> Finally we note that the photophysics of *fac*-[Re(CO)<sub>3</sub>(dppz-X<sub>2</sub>)(py)]<sup>+</sup> make it a versatile molecule for probing DNA and similar biomolecules, as both UV-visible and IR spectroscopy can be employed.

## Acknowledgements

We thank EPSRC (GR/M40486) (MWG, AWP, MT and PM), University of Nottingham and the Government of Gibraltar (JD), HEA PRTLI (CMC) Enterprise Ireland (EI/98/332) (JMK/SH), EUTMR (ERBFMRXCT980226) (JCP/JMK) for financial support. We are also grateful to the EU access programme of the Rutherford Appleton Laboratory (JMK) which allowed some of these measurements to be made. We thank Dr J. A. Weinstein for help with some of the luminescence measurements.

## References

- (a) See *Coord. Chem. Rev.*, 2004, **248**, pp. 1161–1530, special issue dedicated to Dye Sensitized Solar Cells; (b) M. Grätzel, *Nature*, 2001, **414**, 338; (c) R. J. Forster, T. E. Keyes and J. G. Vos, *Interfacial Supramolecular Assemblies*, Wiley, London and New York, 2003, ch. 6.
- (a) J.-M. Lehn, *Supramolecular Chemistry. Concept and Perspectives*, VCH, New York, 1995, ch. 8; (b) V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003; (c) V. Balzani, P. Ceroni, M. Maestri, C. Saudan and V. Vicinelli, *Light-harvesting dendrimers*, *Top. Curr. Chem.*, 2003, **228**, 159.
- (a) K. E. Erkkilä, D. T. Odom and J. K. Barton, Recognition and reaction of metallointercalators with DNA, *Chem. Rev.*, 1999, **99**, 2777; (b) C. Moucheron, A. Kirsch-De Mesmaeker and J. M. Kelly, Photophysics and Photochemistry of Metal Polypyridyl and Related Complexes with Nucleic Acids, *Struct. Bonding*, 1998, **92**, 163; (c) B. Nordén, P. Lincoln, B. Åkerman and E. Tuite, DNA interactions with substitution-inert transition metal ion complexes, *Metal Ions Biol. Syst.*, 1996, **33**, 177; (d) C. Metcalfe and J. A. Thomas, Kinetically inert transition metal complexes that reversibly bind to DNA, *Chem. Soc. Rev.*, 2003, **32**, 215; (e) M. J. Clarke, *Coord. Chem. Rev.*, 2003, **236**, 209.
- A. E. Friedman, J. C. Chambron, J. P. Sauvage, N. J. Turro and J. K. Barton, Molecular light switch for DNA-Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup>, *J. Am. Chem. Soc.*, 1990, **112**, 4960.
- J. Fees, W. Kaim, M. Moscherosch, W. Matheis, J. Klima, M. Krejčík and S. Zalis, Electronic structure of the molecular light switch [Ru(bpy)<sub>2</sub>(dppz)]<sup>2+</sup> (dppz = dipyrido[3,2-A-2',3'-C]phenazine)-cyclic voltametric, UV Vis and EPR ENDOR study of multiply reduced complexes and ligands, *Inorg. Chem.*, 1993, **32**, 166.
- M. K. Brennaman, J. H. Alstrum-Acevedo, C. N. Fleming, P. Jang, T. J. Meyer and J. M. Papanikolas, Turning the [Ru(bpy)<sub>2</sub>dppz]<sup>2+</sup>



- light-switch on and off with temperature, *J. Am. Chem. Soc.*, 2002, **124**, 15094; M. K. Brennaman, T. J. Meyer and J. M. Papanikolas, [Ru(bpy)<sub>2</sub>dppz]<sup>2+</sup> light-switch mechanism in protic solvents as studied through temperature-dependent lifetime measurements, *J. Phys. Chem.*, 2004, **108**, 9938.
- 7 J. Olofsson, B. Onfelt and P. Lincoln, Three-state light switch of [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup>: Distinct excited-state species with two, one, or no hydrogen bonds from solvent, *J. Phys. Chem. A*, 2004, **108**, 4391; B. Onfelt, J. Olofsson, P. Lincoln and B. Norden, Picosecond, and steady-state emission of [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup> in glycerol: Anomalous temperature dependence, *J. Phys. Chem. A*, 2003, **107**, 1000; J. Olofsson, L. M. Wilhelmsson and P. Lincoln, Effects of methyl substitution on radiative and solvent quenching rate constants of [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup> in polyol solvents and bound to DNA, *J. Am. Chem. Soc.*, 2004, **126**, 15458.
- 8 G. Pourtois, D. Beljonne, C. Moucheron, S. Schumm, A. Kirsch-De Mesmaeker, R. Lazzaroni and J. L. Bredas, Photophysical properties of ruthenium(II) polyaaromatic compounds: A theoretical insight, *J. Am. Chem. Soc.*, 2004, **126**, 683.
- 9 J. R. Schoonover, G. F. Strouse, P. Y. Chen, W. D. Bates and T. J. Meyer, Application of time-resolved resonance Raman spectroscopy to intramolecular electron transfer, *Inorg. Chem.*, 1993, **32**, 2618; J. R. Schoonover, G. F. Strouse, R. B. Dyer, W. D. Bates, P. Y. Chen and T. J. Meyer, Application of time-resolved, step-scan Fourier transform infrared spectroscopy to excited-state electronic structure in polypyridyl complexes of rhenium(I), *Inorg. Chem.*, 1996, **35**, 273.
- 10 V. W. W. Yam, K. K. W. Lo, K. K. Cheung and R. Y. C. Kong, Synthesis, photophysical properties and DNA binding studies of novel luminescent rhenium(I) complexes-X-ray crystal structure of [Re(dppn)(CO)<sub>3</sub>(py)](OTf), *J. Chem. Soc., Chem. Commun.*, 1995, 1191; K. K. W. Lo and K. H. K. Tsang, Bifunctional luminescent rhenium(I) complexes containing an extended planar diimine ligand and a biotin moiety, *Organometallics*, 2004, **23**, 3062.
- 11 H. D. Stoeffler, N. B. Thornton, S. L. Temkin and K. S. Schanze, Unusual photophysics of a rhenium(I) dipyrrophenazine complex in homogeneous solution and bound to DNA, *J. Am. Chem. Soc.*, 1995, **117**, 7119.
- 12 J. Dyer, W. J. Blau, C. G. Coates, C. M. Creely, J. D. Gavey, M. W. George, D. C. Grills, S. Hudson, J. M. Kelly, P. Matousek, J. J. McGarvey, J. McMaster, A. W. Parker, M. Towrie and J. A. Weinstein, The photophysics of fac-[Re(CO)<sub>3</sub>(dppz)(py)]<sup>+</sup> in CH<sub>3</sub>CN: a comparative picosecond flash photolysis, transient infrared, transient resonance Raman and density functional theoretical study, *Photochem. Photobiol. Sci.*, 2003, **2**, 542.
- 13 M. R. Waterland and K. C. Gordon, Electronic absorption, resonance Raman and excited-state resonance Raman spectroscopy of rhenium(I) and copper(I) complexes, with substituted dipyrido[3,2-*a*:2',3'-*c*]phenazine ligands, and their electron reduced product, *J. Raman Spectrosc.*, 2000, **31**, 243; A. Flood, R. B. Girling, K. C. Gordon, R. E. Hester, J. N. Moore and M. I. J. Polson, Revealing the chromophoric composition of multichromophoric polypyridyl complexes of Re(I) and Os(II): a resonance Raman study, *J. Raman Spectrosc.*, 2002, **33**, 434.
- 14 N. J. Lundin, P. J. Walsh, S. L. Howell, J. J. McGarvey, A. G. Blackman and K. C. Gordon, Complexes of functionalized dipyrido[3,2-*a*:2',3'-*c*]phenazine: A synthetic, spectroscopic, structural, and density functional theory study, *Inorg. Chem.*, 2005, **44**, 3551; P. J. Walsh, K. C. Gordon, N. J. Lundin and A. G. Blackman, Photoexcitation in Cu(I) and Re(I) complexes containing substituted dipyrido[3,2-*a*:2',3'-*c*]phenazine: A spectroscopic and density functional theoretical study, *J. Phys. Chem. A*, 2005, **109**, 5933.
- 15 R. López, B. Loeb, D. Striplin, M. Devenney, K. Omberg and T. J. Meyer, Tuning the excited states in fac-[Re(X<sub>2</sub>dppz)(CO)<sub>3</sub>](L): Intraligand, charge transfer or both?, *J. Chil. Chem. Soc.*, 2004, **49**, 149.
- 16 M. K. Kuimova, W. Z. Alindi, J. Dyer, D. C. Grills, O. S. Jina, P. Matousek, A. W. Parker, P. Portius, X. Z. Sun, M. Towrie, C. Wilson, J. Yang and M. W. George, Using picosecond and nanosecond time-resolved infrared spectroscopy for the investigation of excited states and reaction intermediates of inorganic systems, *Dalton Trans.*, 2003, 3996.
- 17 J. V. Caspar and T. J. Meyer, Photochemistry of Ru(bpy)<sub>3</sub><sup>2+</sup>-solvent effects, *J. Am. Chem. Soc.*, 1983, **105**, 5583.
- 18 W. M. Kwok, C. Ma, D. Phillips, P. Matousek, A. W. Parker and M. Towrie, Picosecond time-resolved study of 4-dimethylaminobenzonitrile in polar and nonpolar solvents, *J. Phys. Chem. A*, 2000, **104**, 4188.
- 19 X. Z. Sun, S. M. Nikiforov, J. Yang, C. S. Colley and M. W. George, Nanosecond Time-Resolved Step-Scan FT-IR Spectroscopy in Conventional and Supercritical Fluids Using a Four-Window Infrared Cell, *Appl. Spectrosc.*, 2002, **55**, 31.
- 20 M. Towrie, D. C. Grills, J. Dyer, J. A. Weinstein, P. Matousek, R. Barton, P. D. Bailey, N. Sabramaniam, W. M. Kwok, C. Ma, D. Phillips, A. W. Parker and M. W. George, Development of a broadband picosecond infrared spectrometer and its incorporation into an existing ultrafast time-resolved resonance Raman, UV-visible, and fluorescence spectroscopic apparatus, *Appl. Spectrosc.*, 2003, **57**, 367.
- 21 J. Fees, M. Ketterle, A. Klein, J. Fiedler and W. Kaim, Electrochemical, spectroscopic and EPR study of transition metal complexes of dipyrido[3,2-*a*:2',3'-*c*]phenazine, *J. Chem. Soc., Dalton Trans.*, 1999, 2595.
- 22 M. S. Wrighton and D. L. Morse, Nature of lowest excited-state in tricarbonylchloro-1,10-phenanthroline rhenium(I) and related complexes, *J. Am. Chem. Soc.*, 1974, **96**, 998.
- 23 P. Glyn, M. W. George, P. M. Hodges and J. J. Turner, Fast Time-resolved IR Studies of the Excited States of Co-ordination Compounds: Direct Observation of Intramolecular Charge Transfer, *J. Chem. Soc., Chem. Commun.*, 1989, 1655.