COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Revealing the photophysics of *fac*-[(dppz-12-NO_2)Re$(CO)_3$(4-Me_2Npy)]$^+$: a picosecond time-resolved IR study†

Joanne Dyer,[a] David C. Grills,[a] Pavel Matousek,[b] Anthony W. Parker,[b] Michael Towrie,[b] Julia A. Weinstein[a] and Michael W. George*[a]

[a] *School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD*

[b] *Central Laser Facility, Chilton, Didcot, Oxon, UK OX11 0QX. E-mail: mike.george@nottingham.ac.uk*

Received (in Cambridge, UK) 18th January 2002, Accepted 12th March 2002

First published as an Advance Article on the web 22nd March 2002

DOI: 10.1039/b200586g

The photophysics of *fac*-[(dppz-12-NO_2)Re$(CO)_3$(4-Me_2Npy)]$^+$ in CH_3CN have been investigated using picosecond time-resolved IR (ps-TRIR) spectroscopy, to reveal the first example of a Re(I)–dppz complex with a charge separated lowest-lying excited state.

In recent times, a great deal of attention has been focused on the structural features and electron transfer processes which occur along the DNA helix and the role of both of these factors in DNA damage. This has resulted in the creation of a wide range of complexes designed to provide an insight into the mechanism of this damage and aid the development of novel diagnostic and chemotherapeutic tools.[1]

Transition metal complexes of Ru(II), Rh(III) and Cu(I) with polypyridine ligands, which interact strongly with DNA, have been at the forefront of such investigations.[1] The majority of such complexes have long been known to possess low-lying charge separated metal-to-ligand charge transfer (MLCT) excited states.[2] This property heightens the sensitivity of these complexes to their electronic environment and renders them as efficient reporters of their surroundings. Perhaps the most ubiquitous class of complexes of this type with respect to DNA interactions, are those typified by $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2'-bipyridine, dppz = dipyrido[3,2*a*:2′,3′*c*]phenazine). The latter, termed a molecular 'light switch' for DNA, is non-emissive in aqueous buffer solution, but displays an enhancement of luminescence in the presence of DNA. The interaction is intercalative with the extended planar dppz ligand stacking into the double helix of appropriate chirality.[3] The strong similarities between such systems and complexes of the type *fac*-[α-diimine)Re$(CO)_3$(L)]$^+$ (L = ligand) have made these natural candidates for use in the study of DNA. Typically, these complexes also feature a moderately long-lived and strongly luminescent lowest-lying excited state, which is based on the dπ(Re) → π*(α-diimine) MLCT transition.[4] However, despite the well documented photophysics and photochemistry arising from this property, reports of the interactions of Re(I)–dppz complexes with DNA have been limited. The reason for this may be the complex photophysics arising from the inclusion of the strongly accepting dppz ligand, which in the cases reported has resulted in close-lying ligand-centred (π → π*) and MLCT lowest excited states.[5]

The complex dynamics of Re(I)–dppz species on excitation has fuelled our interest in the factors which govern the energetics of these excited states. The objectives underpinning this interest have been twofold. First, to develop a methodology which allows the more facile study of the photophysics of these complexes. To this end, we have invoked the inherent spectroscopic handle offered by the tricarbonyl moiety. Transient IR spectroscopy has long been known to be of value in the study of the excited states of metal complexes containing CO ligands.[6] This is due to the high oscillator strength of ν(CO) stretching vibrations and the sensitivity of their energy and bandwidth to electronic and molecular structure. As a result, photoexcitation produces significant changes in the transient IR absorption, which are characteristic of the changes in electronic structure between states. The second aim is to use the understanding gained from this study in the rational design of Re(I)–dppz complexes with tuneable excited states, which would allow the more widespread use of these as DNA probes.

The starting point for our investigations was *fac*-[(dppz)Re$(CO)_3$(py)]$^+$ (py = pyridine) (**1**). Previous studies of this complex have led to the assignment of the lowest-lying excited state as being ligand-centred (π → π*) in nature.[5] The effects of ligand substitution, by electron-withdrawing groups on dppz and electron-donating groups on py, on the excited state energetics have been explored and will appear in a forthcoming publication.[7] The object was to create an environment around the metal centre, which stabilised the formation of positive charge at the latter and lowered the energy involved in an MLCT transition. Here we report the photophysics of a complex which fulfils the criteria.

fac-[(dppz-12-NO_2)Re$(CO)_3$(4-Me_2Npy)]$^+$ (**2**) (4-Me_2Npy = 4-(dimethyl)aminopyridine) was prepared by modification of the procedure used for *fac*-[(α-diimine)Re$(CO)_3$(L)]$^+$ complexes (see ESI†). The product obtained was characterized by ^{1}H NMR, positive ion FAB-MS and elemental analysis (see ESI†).[8]

The UV-visible absorption spectra of **1** and **2** shown in Fig. 1 are in contrast to the broad and featureless absorption bands which characterise *fac*-[(α-diimine)Re$(CO)_3$(L)]$^+$ complexes (where α-diimine = 2,2'-bipyridine or 1,10-phenanthroline). The latter are assigned solely to dπ(Re) → π*(α-diimine) MLCT transitions. However, deconvolution of the absorption spectra of **1** and **2** confirms that these are the result of both π → π*(dppz) and dπ(Re) → π*(dppz) MLCT transitions. In **1** the proximity in energy of the excited states is apparent (363 and 381 nm for π → π* and 372 nm for MLCT), however in **2** the influence of the substituents is manifested in a considerable shift to lower energy of the band associated with the dπ(Re) → π*(dppz) MLCT transition (432 nm). This is confirmed by the emission spectrum of **2** in CH_3CN (Fig. 1), which appears as a broad, structureless band with λ_{max} = 573 nm and is indicative of emission from this complex as being from the dπ(Re) →

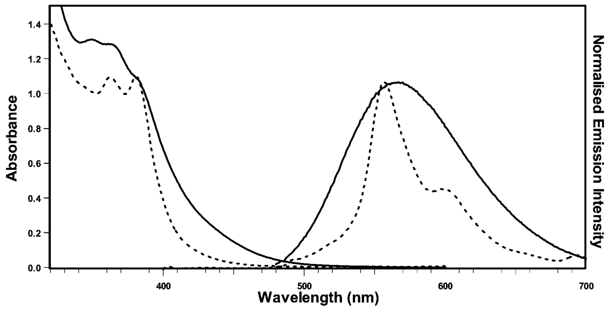

Fig. 1 UV-visible absorption spectra (left axis) and emission spectra (right axis) of **1** (dashed line) and **2** (solid line) in CH_3CN. Note that the *y*-scale for the emission spectra is arbitrary; the relative quantum yield for emission from **2** measured *vs.* $[Ru(bpy)_3]Cl_2$ is 0.0006.

---

† Electronic supplementary information (ESI) available: synthetic procedures, product characterization and brief descripion of ps-TSIR experiments. See http://www.rsc.org/suppdata/cc/b2/b200586g/

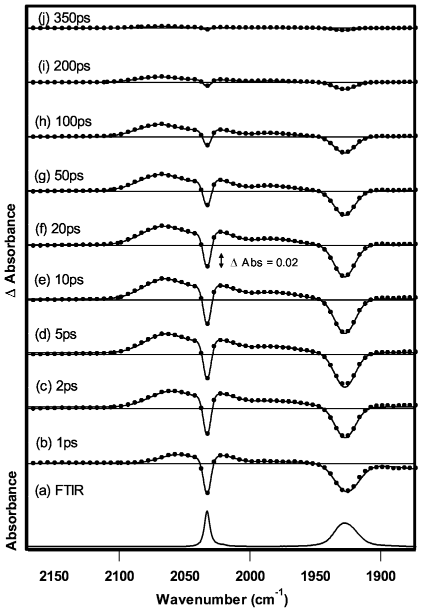

Fig. 2 (a) FTIR of *fac*-[(dppz-12-NO$_2$)Re(CO)$_3$(4-Me$_2$Npy)]$^+$ in CH$_3$CN. (b–j) ps-TRIR spectra obtained following 400 nm excitation.

π*(dppz) MLCT excited state. The contrast with the emission from **1** (Fig. 1), which exhibits vibrational structure characteristic of emission from a ligand-centred state, is noteworthy.

The properties of **2** discussed suggest that the lowest-lying excited state of this complex is MLCT in nature. This is unequivocally confirmed by our ps-TRIR study (see ESI†). Fig. 2(a) shows the ground state FTIR spectrum of **1** in CH$_3$CN with two bands in the CO stretching region at 2033 and 1928 cm^{-1} (due to local C_{3v} symmetry; a$_1$ and e, respectively). The ps-TRIR spectra obtained at a series of time delays after UV photolysis (400 nm) of the solution are shown in Fig. 2(b)–(j). Several conclusions can be drawn from these data:

(i) At Δt (pump–probe delay time) = 1 ps the parent IR absorptions at 2033 and 1928 cm^{-1} are bleached. The latter splits and shifts to higher energy producing two new broad absorption bands centred at *ca.* 2024 and 1968 cm^{1}. This splitting is a consequence of a reduction of the local symmetry ($C_{3v} \rightarrow C_s$) in the excited state species.[8] The higher energy parent band shifts to give a broad absorption band at *ca.* 2059 cm^{-1}.

(ii) As Δt is increased from 1 to 20 ps, these bands narrow and shift to slightly higher wavenumber, consistent with a vibrational cooling of the newly formed species. Assuming an exponential form for the narrowing[9] of these bands, the vibrational relaxation time is estimated to be 10 ps.

The vibrationally relaxed bands for the excited state species are observed at 1983, 2027 and 2070 cm^{-1}. The shifts to higher energy are consistent with an oxidation of the metal centre and the formation of an MLCT excited state.[6] The internal conversion from ^{1}MLCT to ^{3}MLCT states has been shown to occur on the femtosecond timescale for Ru(II)–α-diimine complexes,[10] and as a result the excited state species observed has been assigned as being ^{3}MLCT in nature.

(iii) The kinetic traces shown in Fig. 3 illustrate that from Δt = 20 to 350 ps, the vibrationally relaxed ^{3}MLCT excited state species decays with a lifetime, $\tau \approx 120\ (\pm 20)$ ps. The ground state species is observed to reform on the same time scale. No further species were observed at later delay times.

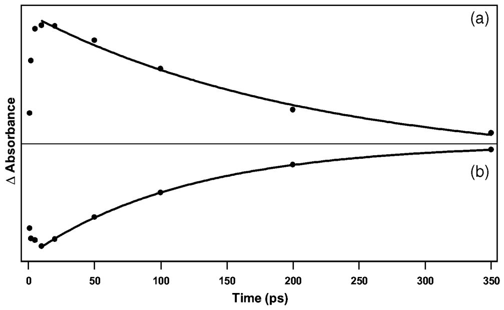

Fig. 3 Kinetic decay traces for *fac*-[(dppz-12-NO$_2$)Re(CO)$_3$(4-Me$_2$Npy)]$^+$ in CH$_3$CN following 400 nm excitation. The traces are obtained from the curve fitted peak areas of (a) the high frequency transient and (b) the low frequency bleach.

In summary, the shift of the CO stretches to higher wavenumber on excitation and the similarity of these shifts to those of previously studied species,[11] confirms the assignment of the lowest lying excited state of *fac*-[(dppz-12-NO$_2$)Re(CO)$_3$(4-Me$_2$Npy)]$^+$ as being ^{3}MLCT in nature. This state is formed by the excitation of an electron from the Re(dπ) to a π* MO of the dppz-12-NO$_2$ ligand. To date this is the only example of a complex of the type *fac*-[(dppz)Re(CO)$_3$(L)]$^+$ with a charge separated lowest-lying excited state, making this a suitable candidate as the first IR probe of DNA.

The authors thank the EPSRC (GR/M40486), the University of Nottingham and the Government of Gibraltar for funding this work. We also thank Professor J. M. Kelly for helpful discussions.

Notes and references

1 K. E. Erkkila, D. T. Odom and J. K. Barton, *Chem. Rev.*, 1999, **99**, 2777.
2 K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic, London, 1992.
3 A. E. Friedman, J. C. Chambron, J. P. Sauvage, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc.*, 1990, **112**, 4960; R. M. Hartshorn and J. K. Barton, *J. Am. Chem. Soc.*, 1992, **114**, 5919.
4 K. S. Schanze, D. B. Macqueen, T. A. Perkins and L. A. Cabana, *Coord. Chem. Rev.*, 1993, **122**, 63; L. A. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1990, **29**, 4335; L. A. Worl, R. Duesing, P. Chen, L. Della Ciana and T. J. Meyer, *J. Chem. Soc., Dalton Trans.*, 1991, 849.
5 H. D. Stoeffler, N. B. Thornton, S. L. Temkin and K. S. Schanze, *J. Am. Chem. Soc.*, 1995, **117**, 7119; V. W. W. Yam, K. K. W. Lo, K. K. Cheung and R. Y. C. Kong, *J. Chem. Soc., Dalton Trans.*, 1997, 2067.
6 M. W. George and J. J. Turner, *Coord. Chem. Rev.*, 1998, **177**, 201.
7 J. Dyer, D. C. Grills, P. Matousek, A. W. Parker, M. Towrie, J. A. Weinstein, S. Hudson, J. M. Kelly and M. W. George, in preparation.
8 J. R. Schoonover, K. C. Gordon, R. Argazzi, C. A. Bignozzi, R. B. Dyer and T. J. Meyer, *J. Am. Chem. Soc.*, 1993, **115**, 10996.
9 T. P. Dougherty and E. J. Heilweil, *J. Chem. Phys.*, 1994, **100**, 4006.
10 N. H. Damrauer and J. K. McCusker, *J. Phys. Chem. A*, 1999, **103**, 8440.
11 J. R. Schoonover, G. F. Strouse, R. B. Dyer, W. D. Bates, P. Chen and T. J. Meyer, *Inorg. Chem.*, 1996, **35**, 273.