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Summers, Peter A. and Calladine, James A. and Ibrahim, Nasiru and Kusumo, Kennedy P. and Clark, Charlotte A. and Sun, Xue-Z. and Hamilton, Michelle L. and Towrie, Michael and McMaster, Jonathan and Schröder, Martin and George, Michael W. (2017) Probing the use of long lived intra-ligand π-π * excited states for photocatalytic systems: a study of the photophysics and photochemistry of [ReCl(CO)3(dppz-(CH3)2)]. Polyhedron, 123 . pp. 259-264. ISSN 0277-5387

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Probing the use of long lived intra-ligand π-π * excited states for photocatalytic systems:

A study of the photophysics and photochemistry of [ReCl(CO)₃(dppz-(CH₃)₂)]

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Keywords: Rhenium, time-resolved IR, photophysics, photochemistry, dppz, intra-ligand excited state, reductive quenching

Abbreviations:

MLCT = metal-to-ligand charge transfer,

FTIR = Fourier transform infrared,

TRIR = time-resolved infrared,

IL = intra-ligand,

LUMO = lowest unoccupied molecular orbital

DNA = deoxyribonucleic acid

bpy = 2,2'-bipyridine,

dppz = dipyrido[3,2-a:2',3'-c]phenazine,

dppz-$(CH_3)_2$ = 11,12-dimethyl-dipyrido[3,2-a:2',3'-c]phenazine,

[$NiFe_2$] = [Ni'S_4'$Fe_2(CO)_6$] cluster ('S_4' = $(CH_3C_6H_3S_2)_2(CH_2)_3$),

i-Pr-PyCa = pyridine-2-carbaldehyde N-isopropylimine,

dapa = 2,6-diacetylpyridine bis(anil),

dpp = 2,3-di(2-pyridylpyrazine),

abpy = azo-2,2'-bipyridine.

Abstract

We report the excited state photophysics and photochemistry of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (dppz-(CH$_3$)$_2$ = 11,12-dimethyl-dipyrido[3,2-a:2',3'-c]phenazine) in CH$_3$CN using time-resolved infrared (TRIR) and Fourier transform infrared (FTIR) spectroscopy. Excitation of the [1]MLCT (metal-to-ligand charge transfer) band of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] populates a [3]MLCT excited state which rapidly interconverts on a timescale < 1 ns to a long lived IL (intra-ligand) π-π* excited state with a lifetime of 190 (± 5) ns. In the presence of an electron donor (NEt$_3$), the IL excited state of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] can be reductively quenched to [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ with the radical in the latter localised on the distal phenazine (phz) portion of the dppz ligand. The phz based electron in [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ has minimal interaction with the rhenium metal centre which increases the stability of the photosensitiser in its reduced form. In non-dried, non-degassed CH$_3$CN (1 M NEt$_3$), [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ shows no significant change in the carbonyl region of the IR spectrum for at least 2 hours during continuous photolysis. In addition, we investigate the use of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ to reduce the previously studied catalyst [NiFe$_2$], with facile electron transfer from [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ to form [NiFe$_2$]$^-$.

Introduction

There is increased interest in the direct use of solar energy as an attractive and renewable alternative to fossil fuels. The use of light to drive the photochemistry required to split water to produce H_2, or the reduction of CO_2 to produce solar fuels, has attracted considerable interest and there are many approaches to achieve this goal.[1, 2] Generally however, homogeneous systems have utilised a photosensitiser that mediates electron transfer to or from a multi-electron catalyst. A key parameter for such catalytic systems is the reductive/oxidative quenching of a short-lived photo-excited state that is typically MLCT-based (metal-to-ligand charge transfer) for metal diimine photosensitisers used in such cycles. We focus herein on photosensitisers that undergo reductive quenching to generate radical anions. For this processes, the absorption of a photon by the photosensitiser needs to generate a long-lived excited state, which is reductively quenched by an electron donor to generate the reduced photosensitiser, which can either reduce a catalyst [Scheme 1 (a)] or act as a catalyst itself. For MLCT excited states the lifetime can directly affect the efficiency of such cycles. Example systems of this type are extensive; their applications for the reduction of CO_2,[3, 4] and/or H^+[5-8] have been reviewed recently.
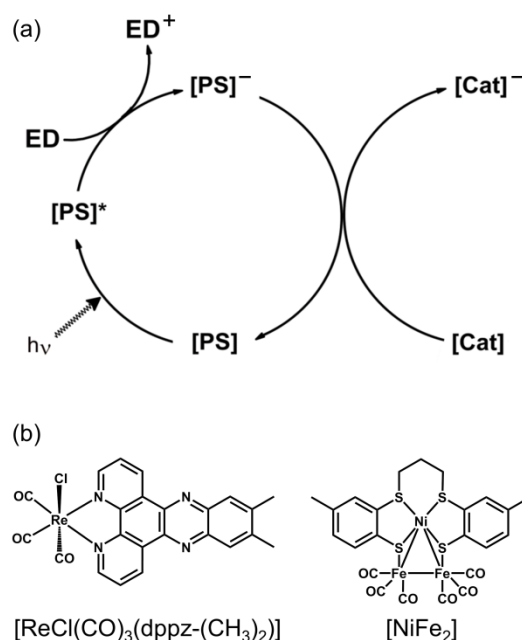
Scheme 1. (a) Simplified schematic of the one-electron reduction of a catalyst ([Cat]) by a photosensitiser ([PS]) proceeding *via* the reductive quenching of [PS]* by an electron donor ([ED]). (b) Structures of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] and [NiFe2].

For the successful implementation of a photocatalytic cycle, such as that in Scheme 1 (a), it is essential that all components remain robust under the catalytic conditions employed, and as a result there is interest in developing photo-stable components with high turn-over numbers (TON). In recent studies, heterogeneous photosensitisers have shown remarkable stabilities under continuous photolysis. Thus, CdSe quantum dots have maintained activity for weeks, with TONs of 600000 or more.[8, 9] Homogeneous systems generally do not show such long-lived stability, and often require rigorous purification and degassing of solvents. However, homogeneous systems still attract attention since their properties may be tuned, and they may be easier to study and are atom efficient in their design when compared to heterogeneous catalysts. In such homogeneous systems, the reduced form of the photosensitiser may undergo competing side-reactions rather than those associated with the intended catalytic cycle.[5, 8, 10, 11] For example, rhodamine dyes have been studied as a photosensitiser in the reduction of a Co^{III} H_2-evolving catalyst.[12] Concentration dependent studies reveal that as the concentration of the Co^{III} catalyst decreases, the rate of decomposition of the reduced photosensitiser increased. Fast time-resolved IR has proven to be extremely useful for examining complex catalytic systems,[13] and we have recently used IR spectroscopy to probe catalytic systems for the photochemical production of H_2. These systems employ [ReCl(CO)$_3$(bpy)] (bpy = 2,2'-bipyridine) based photosensitisers and a synthetic catalyst [NiFe$_2$] [Figure 1(b)] with a structure inspired by the nature of the active site of [NiFe] hydrogenases.[14, 15] In our previous studies we noted that the catalytic efficacy of these systems is compromised by the decomposition of the photosensitiser during turnover and the catalyst decomposition on photolysis, complicating the mechanistic study of [NiFe$_2$]. Indeed, the rapid dissociation of Cl$^-$ from [ReCl(CO)$_3$(bpy)]$^-$ in solution has been well documented.[16-18] The chemistry of a range complexes of type [ReX(CO)$_3$(diimine)]$^{0/+}$ (diimine = bpy , i-Pr-PyCa, dapa, dpp, abpy; X = Cl$^-$, Br$^-$, I$^-$ OTf$^-$, donor solvent, n-PrCN, PR$_3$, P(OMe)$_3$; i-Pr-PyCa = pyridine-2-carbaldehyde N-isopropylimine; dapa = 2,6-diacetylpyridine bis(anil); dpp = 2,3-di(2-pyridylpyrazine); abpy = azo-2,2'-bipyridine) have been studied following their one-electron reduction.[16] The stability of the Re-X bond appears to be related to the ability of the complex to

accommodate the radical electron in the π*-LUMO (lowest unoccupied molecular orbital) localised on the diimine unit; the stability of the Re-X bond follows the order bpy < i-Pr-PyCa < dapa < dpp < abpy. Studies on similar systems have concluded that there is orbital contribution between the π*-LUMO in the diimine ligand and the σ(Re-X) antibonding orbital.[19] Thus, population of the π*-LUMO weakens the Re-X bond, which can result in the reversible dissociation of the axial ligand [Figure 1]. Consequently, for the development of an effective photosensitiser based on a [ReCl(CO)₃(diimine)] unit the design elements of the diimine ligand are crucial, with a key consideration being to localise the π*-LUMO away from the metal centre.
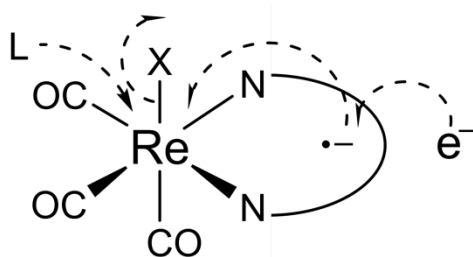

Figure 1. Substitution mechanism of the axial ligand X in [ReCl(CO)₃X(diimine)], promoted by the delocalised electron on the diimine ligand. Adapted from reference [19].

Transition metal complexes containing ligands based on dppz (dppz = dipyrido[3,2-a:2′,3′-c]phenazine) have been used widely as intercalating probes for DNA (deoxyribonucleic acid) and the study of DNA-mediated electron transfer and DNA damage.[20-22] However, the photophysical properties of complexes containing dppz-type ligands still remain ambiguous, partly due to the nature of the dppz ligand that can be described as a fusion of two moieties, phenanthroline (phen) and phenazine (phz), both of which contain localized π* acceptor orbitals.[23] This leads to the possibility of four low-lying triplet excited states in dppz-containing metal complexes, involving MLCT or IL (intra-ligand) π-π* transitions to orbitals localised on either the phen or phz moieties of the ligand, where the LUMO lies on the phz moiety. The first reduction process for [ReCl(CO)₃(bpy)] occurs at −1.74 V *vs.* Fc⁺/Fc in DMF.[19] However, as the phz localised [ReCl(CO)₃(dppz)] LUMO is lower in energy than the [ReCl(CO)₃(bpy)] LUMO, the first reduction process for [ReCl(CO)₃(dppz)] occurs at −1.42 V *vs.* Fc⁺/Fc in

CH$_3$CN.[24] Indeed, the one-electron reduction of [ReCl(CO)$_3$(dppz)] results in a relatively small shift in v(CO) band positions (*ca.* 7 cm^{-1} in CH$_2$Cl$_2$), evidence that the phz based electron does not interact significantly with the Re centre.[24] In this paper we investigate the photophysics and subsequent photochemistry of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (dppz-(CH$_3$)$_2$ = 11,12-dimethyl-dipyrido[3,2-a:2',3'-c]phenazine) in CH$_3$CN. [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] has the potential to be used as a photosensitiser that is more robust under the reducing conditions of continuous photocatalysis than commonly used chromophores such as [ReCl(CO)$_3$(bpy)]. We chose to study [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] rather than [ReCl(CO)$_3$(dppz)] because addition of methyl groups at the C11 and C12 positions of the dppz ligand simplifies the observed excited state photophysics in CH$_3$CN on the ns timescale (see below) and the reduced [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] photosensitiser (−1.48 V *vs.* Fc$^+$/Fc in CH$_2$Cl$_2$) possesses a more negative reduction potential than [ReCl(CO)$_3$(dppz)].[24] In addition, [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] has a long-lived π-π* excited state and the use of such IL excited states have not been exploited extensively in photocatalytic applications.[24]

Experimental

Materials: For TRIR (time-resolved infrared) experiments, CH$_3$CN (99.9%, Merck) and NEt$_3$ (> 99.5%, Sigma-Aldrich) were distilled under an inert atmosphere of Ar from calcium hydride. High-purity Ar was obtained from BOC gasses. For steady state FTIR measurements, CH$_3$CN and NEt$_3$ were used as received. [ReCl(CO)$_3$(bpy)],[25] [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)],[24, 26] and [NiFe$_2$],[27] were prepared according to adapted literature methods.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra were recorded in solution cells (Harrick Scientific Products, Inc.) with CaF$_2$ windows using a ThermoFisher Nicolet iS10 or Bruker Vertex 70 FTIR spectrometer, typically at 2 cm^{-1} resolution and a path length of 0.63 or 0.67 mm. Steady state photolysis was performed using a light emitting diode

(THORLABS, 420 nm, 12 nm FWHM bandwidth) operated at 200 mA, 2.5 cm from the sample.

Laser Flash Photolysis: TRIR spectra were obtained using purpose-built equipment based on a pump-probe approach both at the University of Nottingham (without NEt$_3$) and the Rutherford Appleton Laboratory (with NEt$_3$). Details of the equipment and methods used for the TRIR studies have been described previously;[28, 29] a brief description of both systems are given below. The University of Nottingham apparatus: The pump beam (355 nm, *ca.* 600 ps) was provided by a Q-switched Nd:YVO laser (Advanced Optical Technology ACE) and the probe (180 cm^{-1} spectral band width, *ca.* 150 fs) generated from a commercial Ti:sapphire oscillator (MaiTai)/regenerative amplifier system (Spitfire Pro, Spectra Physics). The mid-IR probe was detected using a 128-element HgCdTe array detector (Infrared Associates). The Rutherford Appleton Laboratory apparatus: A seeded dual titanium sapphire chirped pulse amplifier was used to generate 10 kHz, 40-80 fs, 0.8 mJ pulses at 800 nm. The beam was focused, and a part was used to pump a computer controlled OPA (Optical Parametric Amplifiers) generating a mid-IR probe beam. Once through the sample the infrared beam was collimated and focused onto a spectrograph and detected using a 128-element HgCdTe array detector. Access to the nanosecond to microsecond time delays was provided by a nanosecond laser system generating 1064 nm pulses (10 kHz, 1 ns, 0.05 mJ). The 355 nm harmonic was used, typically delivering 1 μJ pulse energy at the sample, synchronised to the probe beam described above. For all samples, a path length of 0.5 or 1 mm was used and solutions were prepared under an inert atmosphere, degassed by three freeze-pump-thaw cycles and put under 1.5 atm of Ar. Samples were recirculated using a peristaltic pump as the sample was rastered in the x- and y-planes in order to minimise cumulative photo-damage to both the sample and window during repeated photolysis.

Results and Discussion

TRIR spectroscopic studies: The complex photophysics of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] in CH$_3$CN at short time delays after excitation (< 1 ns) have been investigated previously using ps-TRIR spectroscopy (λ_{ex} = 400 nm).[24] Bands originating from an IL π-π* excited state associated with dppz-(CH$_3$)$_2$ ligand were observed and at very early time delays (< 100 ps) and a short lived ^{3}MLCT excited state could also be observed.[24] This complex excited state photophysics results in the population of an IL π-π* excited state on the ns timescale after excitation with diagnostic ν(CO) bands reported at 2020, 1913 and 1890 cm^{-1}. Thus, a ns-TRIR study should not be complicated by the photophysics exhibited by [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] at early time delays. The ns-TRIR experiments have not been previously reported and we have performed these measurements as the starting point of our studies.
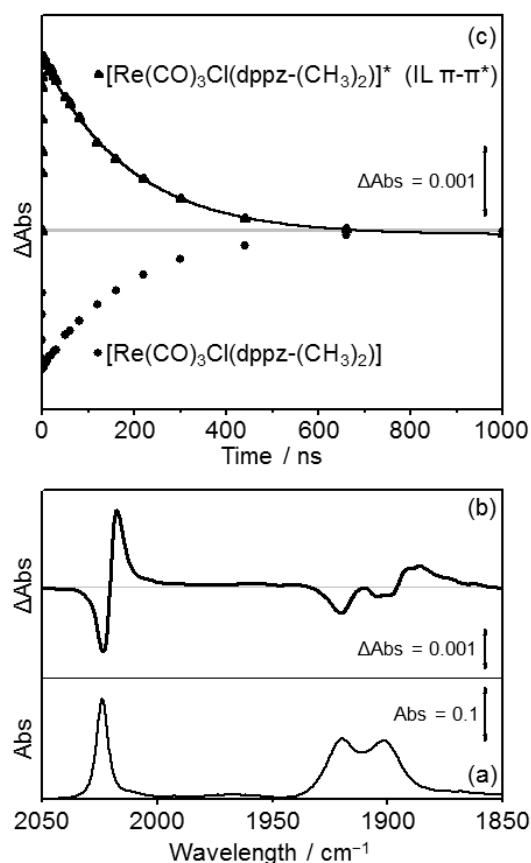

Figure 2. FTIR and ns-TRIR spectra of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) in CH$_3$CN. (a) FTIR ground state spectrum. (b) ns-TRIR difference spectra taken 1 ns after excitation. (c) ns-TRIR single point kinetic traces for the decay of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]*

(IL π-π*) (▲, 2019 cm^{-1}) and the re-growth of the ground state complex [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (●, 2024 cm^{-1}).

The FTIR and ns-TRIR spectra of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] in CH$_3$CN are shown in Figure 2. At 1 ns after excitation the ground state IR bands have been lost (2024, 1920 and 1901 cm^{-1}) and the only clear transient formed is the IL π-π* excited state (2019 and 1907 and 1888 cm^{-1}) consistent with previous ps-TRIR studies on [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (2020 and 1913 and 1890 cm^{-1}).[24] This excited state decays [τ = 190 (± 5) ns] as the parent bands of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] recover and no other transients are observed over the timescale of the experiment (10 μs). The lifetime of the IL π-π* excited state is longer than that reported (τ = 4.7 ± 0.5 ns).[24] This is because the previous lifetime was extrapolated from a slight decay in a small number of time delays from a ps-TRIR experiment. A weak band at 2005 cm$^-$ can also be observed in the TRIR spectra at early time delays. This feature, red shifted from the main IL π-π * excited state band, is common in the TRIR experiments and has been observed previously for similar compounds.[30, 31] However, due to the low intensity and rapid depletion of this peak its precise origin could not be determined and was not investigated further. Quenching of the relatively long-lived IL excited state for potential use in a catalytic cycle was investigated. Figure 3 shows the ns-TRIR spectra of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] in a solution of NEt$_3$ (1 M) and CH$_3$CN.
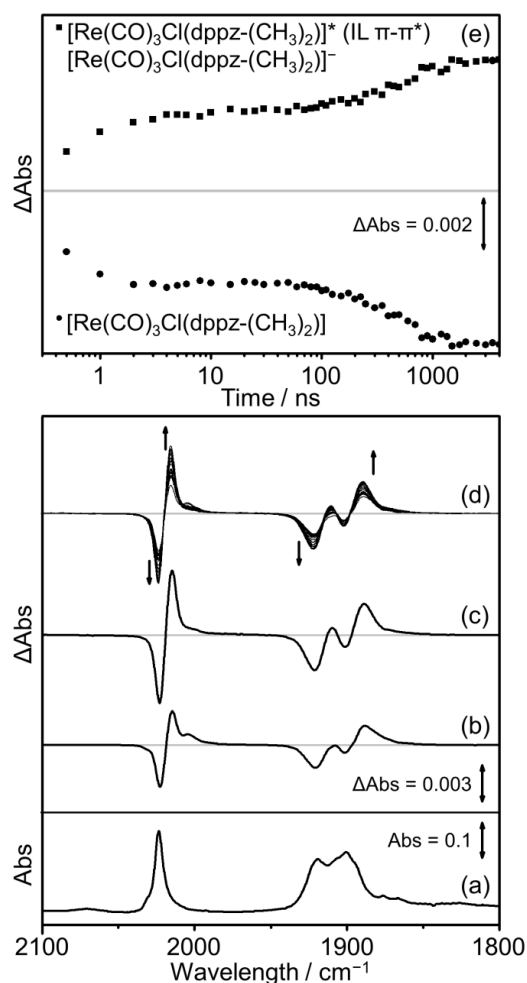
Figure 3. FTIR and ns-TRIR spectra of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) in a solution of NEt$_3$ (1 M) and CH$_3$CN. (a) FTIR ground state spectrum. ns-TRIR difference spectra taken (b) 2 ns, (c) 4000 ns and (d) a series of ns-TRIR spectra between 1 and 50 μs, after excitation. (e) ns-TRIR single point kinetic traces for the growth of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]* (IL π-π*) /[ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ (■, 2016 cm^{-1}) and the depletion of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (●, 2023 cm^{-1}).

The spectrum taken 2 ns after photolysis [2016, 1909 and 1889 cm^{-1}, Figure 3(b)] shows formation of an IL π-π* excited state consistent with results performed without NEt$_3$ [Figure 2(b)]. The difference in wavenumber (*ca.* 3 cm^{-1} for the high energy band) is likely due to a variation in calibration and instrument resolution between the different apparatus used for each experiment and a difference in polarity of the solvent on addition of NEt$_3$. When NEt$_3$ is absent from the solution containing [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)], the IL π-π* excited state decays with a lifetime of τ = 190 (± 5) ns and is accompanied by the

re-formation of the parent complex. However, in the presence of NEt$_3$, the bands at 2016, 1909 and 1889 cm^{-1} increase in intensity. This is assigned to reductive quenching of the IL π-π* excited state of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] by NEt$_3$ to form [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$, where the electron is localised on the phz moiety of the ligand as evidenced by the ν(CO) band positions [Figure 3(c)]. The bands associated with the formation of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ are consistent with those reported in CH$_2$Cl$_2$,[24] and are unfortunately in a similar position to the bands of the IL π-π* excited states of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]. The rise in the intensities of the bands associated with [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$/[ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]* (IL π-π*) occur over two distinct timescales [Figure 3(e)]. The initial rise (0-10 ns) represents about 60 % of the final band intensity and the second rise (10-4000 ns) accounts for the remaining 40%. This complicated kinetics is a consequence of the overlapping depletion of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]* (IL π-π*) and the concomitant formation of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$. In addition, [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ will not only be formed through reductive quenching of the IL π-π* excited state, but also through direct reduction of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] to [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ by a strongly reducing C-centred radical (CH$_3$C$^•$HNEt$_2$) formed from the decomposition of the oxidised electron donor ($^•$NEt$_3$$^+$).[14, 32-34]. This dark reduction process explains the continued growth of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ at time delays after the decay of the IL π-π* excited state. However, our experiments could not distinguish between these different reduction processes. Decomposition of the oxidized electron donor also results in the rapid release of a proton, and the possibility that this interacts with the pyridyl nitrogen atoms in the dppz-(CH$_3$)$_2$ ligand cannot be excluded.[35] The excited state photochemistry of [ReCl(CO)$_3$(diimine)] complexes are predominantly controlled by the formation of MLCT and/or IL excited states,[31, 36, 37] where MLCT excited states can be reductively quenched by electron donors to promote further chemical reactions.[38] Our experiments demonstrate that IL π-π* excited states can also be reductively quenched to produce the intermediates required for photochemical reduction processes.

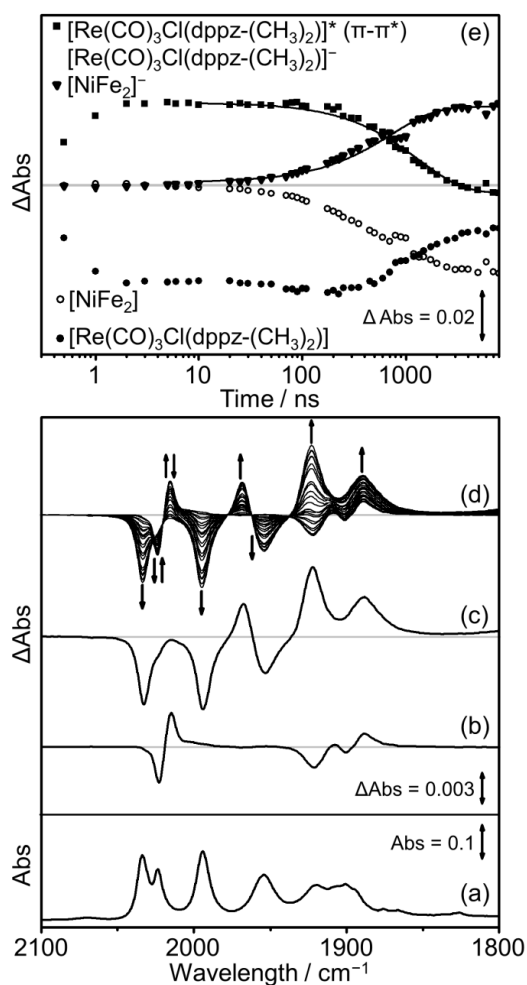**Figure 4.** FTIR and ns-TRIR spectra of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) and [NiFe$_2$] (0.5 mM) in a solution of NEt$_3$ (1 M) and CH$_3$CN. (a) FTIR ground state spectrum. ns-TRIR difference spectra taken (b) 2 ns, (c) 8000 ns, and (d) a series of spectra between 2 and 8000 ns, after flash photolysis at 355 nm. (e) single point kinetic traces for growth and decay of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]* (IL π-π*) /[ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ (■, 2014 cm^{-1}), the loss and recovery of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (●, 2023 cm^{-1}), the formation of [NiFe$_2$]$^-$ (▼, 1967 cm^{-1}) and the loss of [NiFe$_2$] (○, 1953 cm^{-1}). The solid lines are mono-exponential best-fits of the data.

We investigated the potential application of the photochemistry of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] in a catalytic cycle through an examination of the effect of adding a known proton reduction catalyst [NiFe$_2$] (0.5 mM) to the solution of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) and NEt$_3$ (1 M) in CH$_3$CN [Figure 4]. At 2 ns after photolysis the spectral features are the same as those observed above when [NiFe$_2$] was

not present, assigned to the formation of $[ReCl(CO)_3(dppz-(CH_3)_2)]^*$ (IL $\pi-\pi^*$) and/or $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ [Figures 2 (b) and 3 (b)]. At this early time there is no change in the energies of the $\nu(CO)$ bands associated with the $[NiFe_2]$ catalyst. A previous TRIR study on $[NiFe_2]$ has been reported and although $[NiFe_2]$ exhibits its own photophysics following excitation, these processes have ceased after 300 ps and do not interfere with the experiment on the ns timescale.[14] In the presence of NEt_3, the IL $\pi-\pi^*$ excited state $[ReCl(CO)_3(dppz-(CH_3)_2)]^*$ is reductively quenched to form the one-electron reduced photosensitiser $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$. On a longer nanosecond timescale the bands of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ decay as the $\nu(CO)$ bands of the $[NiFe_2]$ moiety are concomitantly bleached as $[NiFe_2]$ is reduced to $[NiFe_2]^-$, with $\nu(CO)$ bands at 1968, 1922 and 1889 cm^{-1} [Figure 4(c)]. These bands are consistent with previous spectroelectrochemical FTIR and TRIR experiments on $[NiFe_2]$.[14] The single point ns-TRIR kinetics of the electron transfer process described above are shown in Figure 4(e). The IL $\pi-\pi^*$ excited state is formed within the timescale of the experiment. The formation of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ obscures the decay of the excited state as they fall in the same spectral region and is represented by a rise in the peak at 2014 cm^{-1} [Figure 4(e)]. This is mirrored in the kinetics associated with the ground state complex $[ReCl(CO)_3(dppz-(CH_3)_2)]$ [Figure 4(e)]. On a longer timescale (10-4000 ns) the bands of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ decay [$\tau = 1300\ (\pm 100)$ ns] and $[ReCl(CO)_3(dppz-(CH_3)_2)]$ reforms. At the same time the bands of $[NiFe_2]$ are lost [Figure 4(e), $\tau = 750\ (\pm 50)$ ns] and $[NiFe_2]^-$ is formed such that the ns-TRIR spectrum obtained after 8000 ns is dominated by $[NiFe_2]^-$. The difference between the lifetime of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ decay and the growth of $[NiFe_2]^-$ is potentially due to the production of a second reducing equivalent, formed from the decomposition of $^{\bullet}NEt_3^+$ (observed in experiments above without $[NiFe_2]$), which could accelerate the formation of $[NiFe_2]^-$ or retard the decay of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$. In the control experiment in the absence of NEt_3, the was no interaction between the excited state of

[ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] and [NiFe$_2$], and the formation [NiFe$_2$]$^-$ was not observed. The second order rate constant for electron transfer between [ReCl(CO)$_3$(bpy)]$^-$ and [NiFe$_2$] in CH$_3$CN is $k_{inter} = 6.6 \pm 0.5 \times 10^9$ M^{-1} s^{-1}.[14] From the exponential decay of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$, k_{inter} can be estimated to be $8.0 \pm 1.0 \times 10^8$ M^{-1} s^{-1}. However, it should be noted that this calculation ignores any influence from the decomposition of the oxidised electron donor.
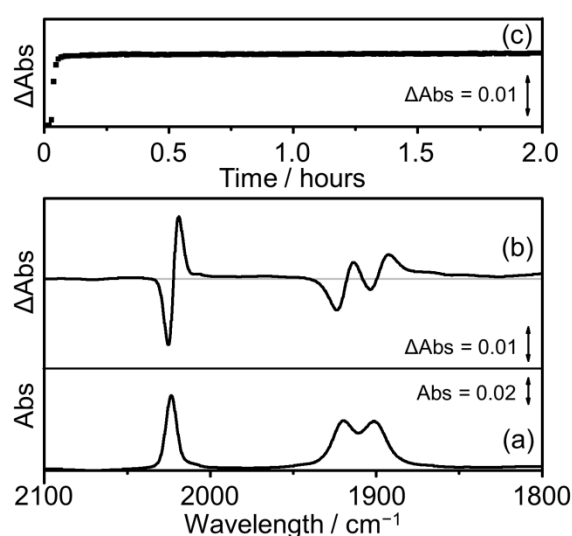
FTIR studies:

Figure 5. (a) FTIR ground state spectrum of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) in a solution of NEt$_3$ (1 M) and CH$_3$CN. (b) FTIR difference spectrum taken 0.5 hr after continuous photolysis at 420 nm. (c) Steady state photolysis kinetic trace for the formation of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ recorded at 2019 cm^{-1}.

The photo-induced formation of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ was probed by FTIR spectroscopy using *in situ* irradiation from a LED (light emitting diode) light source (420 nm). Solutions were prepared in non-dried, non-degassed solvents under atmospheric conditions. The FTIR spectrum of [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)] (0.5 mM) in a solution of NEt$_3$ (1 M) and CH$_3$CN obtained 0.5 hr after continued photolysis [Figure 5(b)] clearly shows the presence of bands assigned to [ReCl(CO)$_3$(dppz-(CH$_3$)$_2$)]$^-$ (2019, 1914 and 1893 cm^{-1}) and is similar to the TRIR spectra obtained after 4000 ns [Figure 3(c)].

The kinetic evolution of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ during continuous photolysis is shown in Figure 5(c). Once formed there are only minor changes in the spectral features over 2 hr of irradiation. Control experiments, in which NEt_3 or the light source were absent from the test solution lead to no significant changes in the FTIR spectrum after photolysis. When $[ReCl(CO)_3(dppz-(CH_3)_2)]$ was replaced with $[ReCl(CO)_3(bpy)]$, the characteristic band associated with the formation of $[ReCl(CO)_3(bpy)]^-$ at 1998 cm^{-1},[17] was only observed as a very weak band at early photolysis times.

Conclusions

We have investigated the excited state photophysics and photochemistry of the homogeneous photosensitiser $[ReCl(CO)_3(dppz-(CH_3)_2)]$ using TRIR and FTIR spectroscopies. Excitation forms a long-lived ligand-based (IL π-π*) excited state is observed [τ = 190 ($\pm$ 5) ns] on the ns timescale in CH_3CN. Following a photochemical mechanism usually observed with MLCT excited states, this IL π-π* excited state can be reductively quenched by NEt_3 to form $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$, which can subsequently reduce a suitable proton reduction catalyst ($[NiFe_2]$ in this study). Steady state photolysis shows that $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ is stable during continuous photolysis (420 nm) for more than 2 hr with no other bands observed in the metal carbonyl region of the IR spectrum. This increase in apparent robustness of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$ when compared to $[ReCl(CO)_3(bpy)]^-$ may result from the localisation of the radical electron in a phz-based molecular orbital that is considerably more distant from the Re metal centre than in $[ReCl(CO)_3(bpy)]^-$, as evidenced in a small red shift of the ν(CO) bands upon reduction. The alternative photochemistry exhibited by $[ReCl(CO)_3(dppz-(CH_3)_2)]$ and the relative stability of $[ReCl(CO)_3(dppz-(CH_3)_2)]^-$, provides an interesting possibility of its use in place of more commonly used photosensitisers such as $[ReCl(CO)_3(bpy)]$ in photochemical catalytic cycles.

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