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Review

Transient spectroscopy of dipyridophenazine metal complexes which undergo photo-induced electron transfer with DNA

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ABSTRACT

This review considers transient spectroscopic studies of electron transfer reactions between nucleic acids and the excited states of transition metal complexes containing dipyridophenazine or related ligands and focuses mainly on complexes of ruthenium, chromium and rhenium. Particular emphasis is placed on systems where transient UV/visible and/or infrared absorption spectroscopy have been employed.

1. Introduction

The photosensitised oxidation of DNA continues to attract wide attention both because of its inherent importance as a major route to the damage of DNA in living organisms [1] and because it provides an excellent method for probing the conduction properties of nucleic acids [2–4]. A complete understanding therefore requires that we investigate the ultrafast chemistry that follows the excitation of the photosensitiser and in particular monitor the transient species that are formed during these processes. Transient absorption spectroscopy methods are particularly valuable for this purpose as they allow the detection of both the excited states involved and the products of the electron transfer. Most such studies have been carried out by measuring the transient species in the ultraviolet or visible region of the spectrum (laser flash photolysis), but more recently the value of the insights to be gained from probing vibrational spectra in the mid-IR has been recognised [5]. The main focus of the current article is the study of the photo-induced electron transfer reactions of transition metal complexes and in particular those containing the ligand dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine), its derivatives and related molecules (see Fig. 1). However for comparison we

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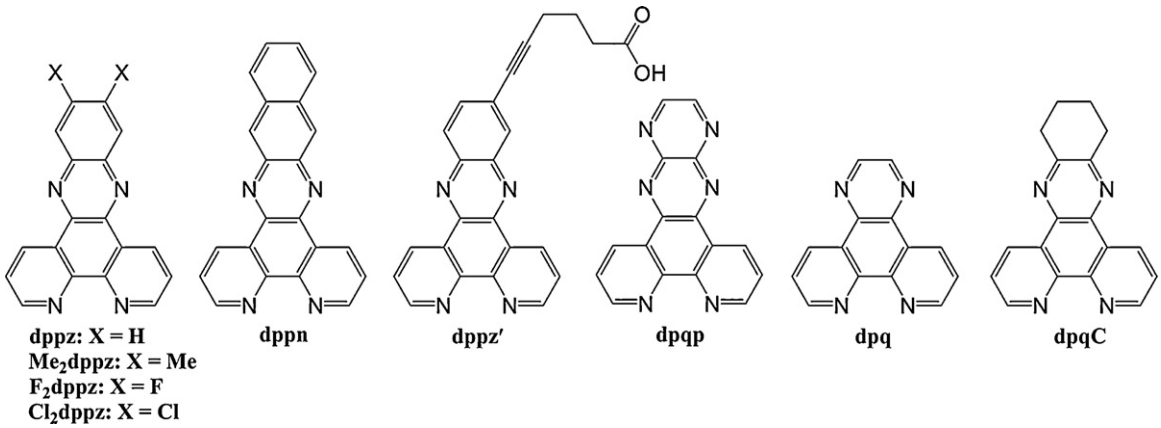


Fig. 1. dppz and related ligands referred to in this review.

initially briefly highlight some studies which use solely organic systems.

2. Selected organic systems

It has been known for many years that the fluorescence of many molecules (such as dyes) is strongly quenched when they bind to DNA and that this is due to photo-induced electron transfer. This phenomenon has been studied in detail for a number of classes of molecules, including methylene blue, thionine and related dyes [6–9], naphthalimides [10–14], anthraquinones [15–18], and stilbenes [19–21]. We briefly consider two of these types of photosensitisers below.

In the case of thionine (Fig. 2), which intercalates between the base-pairs of DNA, it has been shown from stimulated emission and transient absorption measurements that the forward electron transfer from the singlet excited state proceeds very rapidly when the dye is bound to guanine-containing DNA [6–8].

In the case of double-stranded $[poly(dG–dC)]_2$, where every dye is in contact with a guanine, the lifetime for the electron transfer from the guanine to the thionine excited state is 260 fs. Interestingly the back reaction also proceeds rapidly and in the case of thionine and $[poly(dG–dC)]_2$ the lifetime for the reduced dye was found to be only 760 fs.

$$Th^{+*}: G \rightarrow Th^{\bullet} : G^{\bullet+} \rightarrow Th^{+}: G \quad (1)$$

By contrast when the dye was intercalated into $[poly(dA–dT)]_2$ the lifetime was 110 ps (only slightly less than that of the dye free in aqueous solution, 320 ps), indicating that as expected the rate of electron transfer is much faster for guanine than for the other nucleic acid bases. Measurements with a range of related dyes and nucleic acids showed that the variation of the rates of the forward and reverse reactions with the driving force of the reaction conformed well to the behaviour predicted by Marcus theory with electronic coupling energy of ca. 330 cm^{-1}, and reorganization energy of ca. 8070 cm^{-1} for both the forward and reverse reactions.

Another class of organic photosensitisers that has been studied for direct oxidation of guanine in DNA are the naphthalimides (Fig. 3). Such work has been carried out with mononucleotides [22], polynucleotides [23] and oligonucleotides (consisting of short double-stranded defined sequence DNA molecules) [24]. The effect of non-covalent binding of the molecule on the efficiency of the electron transfer reaction was nicely shown by Majima and co-workers [24] using nanosecond laser flash photolysis and three substituted naphthalimides (**3a**–**3c**) with differently charged substituents. It was found that the reduced form of the naphthalimide is clearly observable with the negatively charged compound **3a** and to a lesser extent with neutral **3b**. However this is not the case for the positively charged species **3c**—a fact attributed to the forward and back electron transfer (involving the singlet state) proceeding in the sub-nanosecond range for the strongly bound (and probably intercalated) **3c**. By contrast with **3a**, where ground state binding is much weaker because of repulsion by the negatively charged nucleic acid, the observed activity is attributed to the triplet state. The role of intervening A–T sequences in controlling the rate of charge separation and subsequent charge recombination has recently been demonstrated using the series of compounds **3d** [10]. It was found that the maximum yield occurred for $n = 4$ or 5.

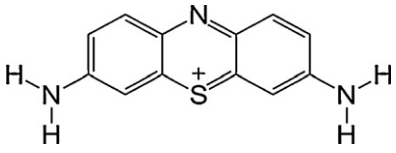


Fig. 2. Structure of thionine.

It can be seen from the above examples that intercalating organic photosensitisers have been successfully used to promote direct oxidation of nucleic acids. Complementing these studies are experiments involving transition metal diimine complexes. Such compounds are particularly useful for this purpose as they have a rich photochemistry and it has been shown that the nature of the excited state and its redox properties can be tuned by modifying the metal, diimine and ancillary ligands [25–30]. The interaction of complexes of ruthenium, chromium and rhenium with nucleic acids has been studied by our groups and others and the results of these investigations are reported below.

3. Ruthenium complexes

It has been known for many years that ruthenium polypyridyl complexes are able to photosensitise damage to DNA [31–35]. In most cases these reactions involve reactive oxygen species which are produced by interaction of the ^{3}MLCT excited state of the complexes with molecular oxygen (Type 2 oxidation) [36]. However the excited states of complexes which contain ligands such as 1,4,5,8-tetraazaphenanthrene (TAP), 1,4,5,8,9,12-hexaazatriphenylene (HAT) or 2,2′-bipyrazine (bpz) (see Fig. 4 for structures of non-dppz ligands) are much more oxidising than those of complexes such as $[Ru(bpy)_3]^{2+}$ {bpy = 2,2′-bipyridine} and may directly oxidise the guanine in both mononucleotides and polynucleotides including double-stranded DNA [33,37–39]. This photo-oxidation process can lead to direct strand breaks, alkali-sensitive sites and photo-adducts [33,37,40–45]. The biological

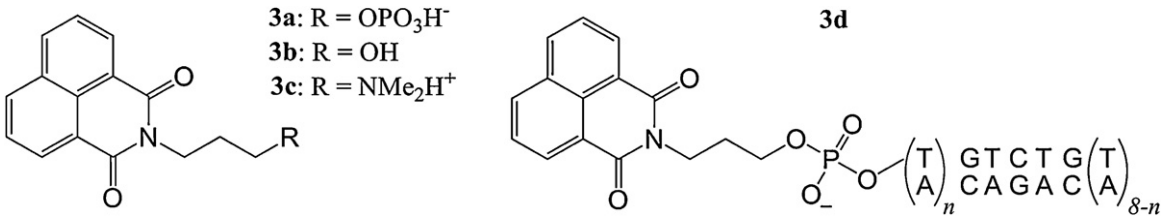


Fig. 3. Structures of naphthalimides discussed in the text.

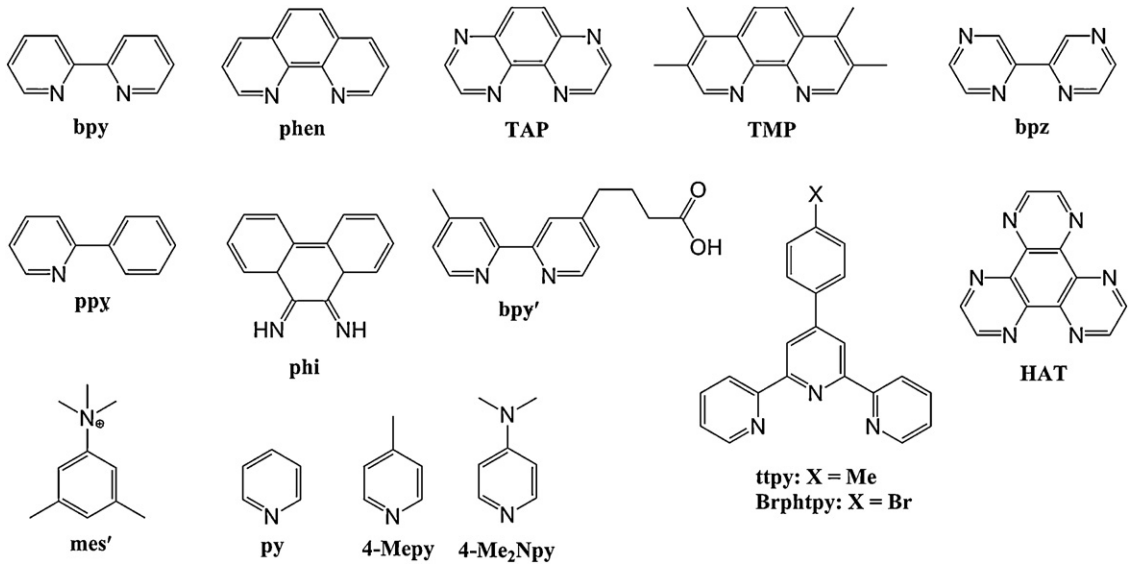


Fig. 4. Structures of other ligands discussed in this review.

applications of this have recently been reviewed by Elias and Kirsch-De Mesmaeker [46] and by Moucheron [47]. The mechanism of this process was partially elucidated by Lecomte et al. [38] who used nanosecond flash photolysis studies of $[Ru(TAP)_3]^{2+}$ and 5′-guanosine monophosphate (5′-GMP) to propose the following mechanism:-

$$[Ru(TAP)_3]^{2+*} + G \rightarrow [Ru(TAP)_2(TAP^{\bullet-})]^{+} + G^{\bullet+} \quad (2)$$

$$G^{\bullet+} \rightarrow G(-H)^{\bullet} + H^{+} \quad (3)$$

$$[Ru(TAP)_2(TAP^{\bullet-})]^{+} + G(-H)^{\bullet} + H^{+} \rightarrow [Ru(TAP)_3]^{2+} + G \quad (4)$$

$$[Ru(TAP)_2(TAP^{\bullet-})]^{+} + H^{+} \rightarrow [Ru(TAP)_2(TAPH^{\bullet})]^{2+} \quad (5)$$

$$[Ru(TAP)_2(TAPH^{\bullet})]^{2+} + G(-H)^{\bullet} \rightarrow [Ru(TAP)_3]^{2+} + G \quad (6)$$

These studies showed that the relatively long-lived ^{3}ML(TAP)CT state of $[Ru(TAP)_3]^{2+}$ was efficiently quenched by the 5′-GMP. It was expected that this led to the guanine radical cation ($G^{\bullet+}$), which is known to deprotonate at neutral pH (pKa = 3.9), giving the guanine radical $G(-H)^{\bullet}$ (Eq. (3)). At pH >7 this radical is subsequently rapidly reduced by $[Ru(TAP)_2(TAP^{\bullet-})]^{+}$ ($k_q = 1.5 \times 10^9\ M^{-1}\ s^{-1}$). However as at lower pH the reduced ruthenium complex protonates ($pK_a = 7.6$) back reaction (6) then dominates. Similar experiments were also carried out with complexes of the type $[Ru(L)_2(phen)]^{2+}$ (L = TAP, HAT; phen = 1,10-phenanthroline) [37]. The reaction of the radicals was suggested as leading to the formation of adducts [43,44] and this has recently been confirmed by CIDNP studies [48,49].

In contrast to what was observed for GMP, nanosecond laser flash photolysis experiments with $[Ru(TAP)_3]^{2+}$ in the presence of double-stranded DNA gave only low yields of transient species [50]. This was attributed to there being significant static quenching as most of the complex would be bound to the DNA and a further investigation would require picosecond measurements. However for such studies it would be desirable to be able to work with complexes in which the geometry of the bound photosensitising metal complex is well defined. In this regard $[Ru(TAP)_3]^{2+}$ is not ideal, as like its analogue $[Ru(phen)_3]^{2+}$ it is expected that the ligand is only partially intercalated between the base-pairs of the double-stranded polynucleotide [51–53]. By contrast it is well established that dppz complexes of the type $[Ru(L)_2(dppz)]^{2+}$ bind very much more strongly to DNA because the dppz ligand is inserted between the base-pair. This makes the system ideal for transient spectroscopic studies as the relative orientation of the electron acceptor (the metal complex) and the electron donor (guanine) is well-defined.

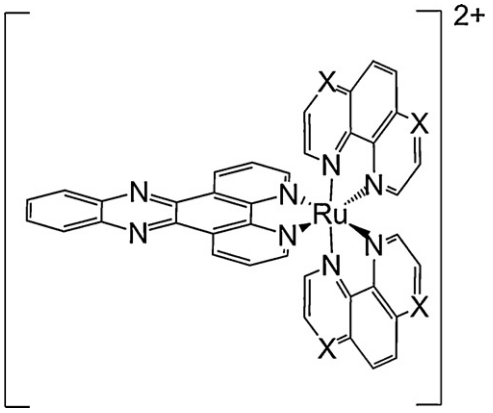
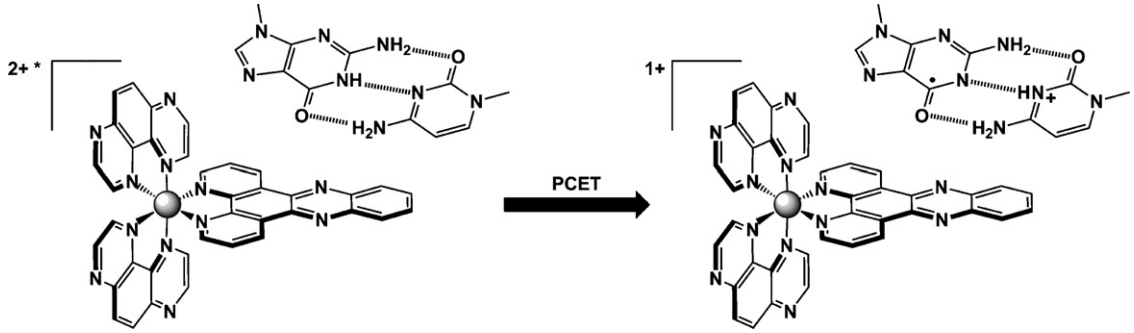


Fig. 5. Structure of $[Ru(L)_2(dppz)]^{2+}$. For L = phen, X = C–H; for L = TAP, X = N.



Scheme 1. Proposed mechanism of the proton-coupled electron transfer (PCET) between $[poly(dG–dC)]_2$ and excited $[Ru(TAP)_2dppz]^{2+}$. Photooxidation of the guanine proceeds with a simultaneous proton transfer from the N1 atom of the guanine to the N3 atom of the cytosine.

The complex $[Ru(phen)_2(dppz)]^{2+}$ (Fig. 5) has been very well studied, largely arising from the well-publicised '*light switching*' properties of the complex. This originates from the fact that the complex is very weakly emitting in aqueous solution (lifetime 250 ps), but is luminescent when bound to DNA. There have been a number of papers dealing with the photophysics of this complex [54–61]. The effect was initially explained by state reversal when the dppz ligand was removed from water and sandwiched into the nonaqueous environment of the stacked base-pairs. However later experiments by Brennaman et al. [57,62] and Lincoln and co-workers [56,63,64] showed that the situation is more involved and in particular that entropic effects play a major role. It was proposed that a key role was played by the binding of one or two water molecules to the N-atoms on the phenazine ligands.

From the above considerations the complex $[Ru(TAP)_2(dppz)]^{2+}$ (Fig. 5) should be an excellent molecule for the study of the photo-induced electron transfer behaviour. This was indeed shown to be the case [45,65]. The photophysical properties in water are quite different from those of $[Ru(phen)_2(dppz)]^{2+}$ in that the complex is luminescent in water (lifetime = 1090 ns). This is attributed to the electron in the lowest MLCT excited state being localised on the TAP ligand rather than on the dppz ligand. This assignment was verified by time resolved resonance Raman experiments [66]. The excited state interactions of $[Ru(TAP)_2(dppz)]^{2+}$ with a range of nucleic acids have been studied. With GMP the excited state is efficiently quenched (with a rate constant $k_q = 1.70 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, which is higher than that for the less oxidising excited state of $[Ru(TAP)_2(phen)]^{2+}$—$0.98 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$). Interestingly the rate constant for quenching was approximately halved when the experiment was carried out in D_2O. Nanosecond laser flash photolysis experiments demonstrated that the quenching produced both the reduced ruthenium complex and also the guanine radical, which is the stable species at neutral pH.

$$[Ru(TAP)_2(dppz)]^{2+*} + G \rightarrow [Ru(TAP)(TAP^{\bullet -})(dppz)]^{+} + G(-H)^{\bullet} + H^{+} \quad (7)$$

The observed isotope effect led to the suggestion that the process involves proton-coupled electron transfer (PCET) and this would also be consistent with the energetics of the system as the $E^{\circ}(Ru^{II}/Ru^{I}) = 1.44$ V vs NHE, if a value of $E^{\circ}(G^{\bullet +}/G) = 1.58$ V [8] based on pulse radiolysis data is assumed [67]. {In discussions on the oxidation of guanine, a value of $E^{\circ}(G_{ox}/G) =$ ca. 1.3 V, at pH = 7, is often employed [68,69]. However at this pH the oxidised species will be the guanine radical rather than the cation, as the pKa for deprotonation of $G^{\bullet +}$ (Eq. (2)) is 3.9. When account is taken of this deprotonation (ca. 60 mV per pH decade), the higher value is estimated.} The rate constants for the reverse reaction were also determined by flash photolysis methods and an isotope effect of 2.1 was observed (1.13×10^6 and $0.53 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$), again consistent with PCET. However in both the forward and reverse reactions it is not clear which proton is being transferred.

When $[Ru(TAP)_2(dppz)]^{2+}$ binds to guanine-containing DNA the emission is strongly quenched. {In the case of natural DNA containing 42% G-C base-pairs the quenching is ca. 80%; with double-stranded poly(dG–dC) 98%. By contrast with double-stranded poly(dA–dT) the emission is enhanced by a factor of 100%.} Picosecond transient visible absorption spectroscopy (ps-TA) revealed that when bound to $[poly(dG–dC)]_2$ the forward electron transfer proceeded with a rate constant of $1/506\ ps^{-1}$ (in H_2O buffered solution) and of $1/680\ ps^{-1}$ (in D_2O buffered solution). The back reaction was slower with rate constants of $1/8850\ ps^{-1}$ (in H_2O buffered solution) and of $1/14{,}000\ ps^{-1}$ (in D_2O buffered solution). The k_H/k_D isotope effects (of 1.3 and 1.6) were somewhat

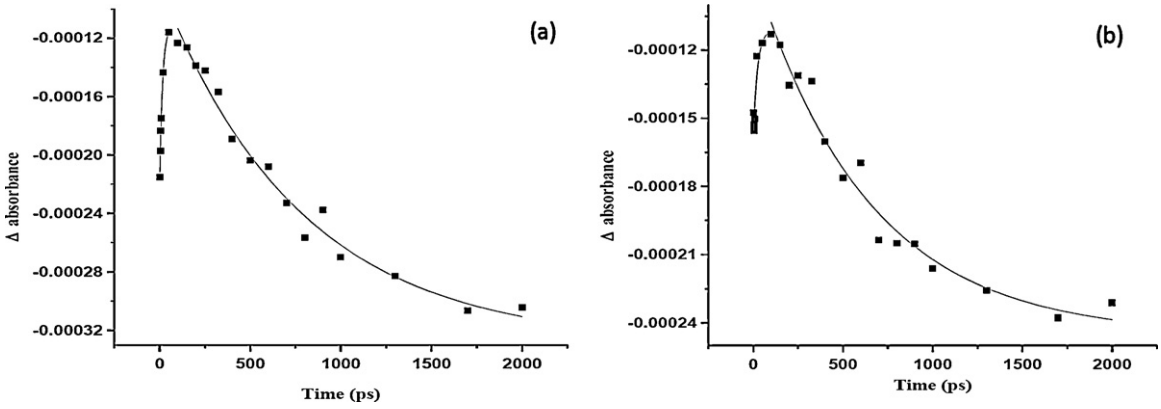


Fig. 6. Kinetic traces at G depletion ($1690\ cm^{-1}$; left) and C depletion ($1656\ cm^{-1}$; right), derived from ps-TRIR spectra of $[poly(dG–dC)]_2$ (1.7×10^{-2} M) in the presence of $[Ru(TAP)_2(dppz)]^{2+}$ (8×10^{-4} M) following a 400 nm laser excitation [65].

lower than that observed for the nucleotides. It was speculated that the proton involved was that initially bound to the N1 atom of guanine (Scheme 1).

When the system was studied by ps-TRIR spectroscopy it was observed that as expected the guanine ground state bands depleted at the same rate as that found by ps-TA for the metal complex reduction. A weak IR band was also detected at ca. 1700 cm^{-1} and such a signal has previously been identified as arising from oxidised guanine following photoionisation of guanine derivatives using high energy UV irradiation [70,71]. Interestingly the cytosine-localised vibration bands also depleted at the same rate (Fig. 6). This would be expected if the process is indeed proton coupled electron transfer. However formation of the guanine radical in the base-pair would also be expected to exert a major influence on the frequency of the cytosine carbonyl vibration.

A number of complexes have been designed with derivatives of the dppz ligand intended to capitalise on the high intercalative binding affinity of the ligand while at the same time tuning the photophysical properties of the system. $[Ru(bpy)_2(dpqp)]^{2+}$ {dpqp is a ligand resembling dppz but with an additional pair of aza nitrogens on the distal ring (see Fig. 1)}, differs from the traditional light-switch system in that it is quite emissive in water [72]. Transient absorption experiments have revealed a ^{3}MLCT excited state with a lifetime in excess of 920 ns capable of initiating photocleavage via $^1O_2$ generation with a greater efficiency than the analogous dppz complex. Similarly efficient photocleavage was achieved using $[Ru(bpy)_2(dppn)]^{2+}$ [73,74]. The complex was found to possess an emissive, highly reactive ^{3}MLCT excited state (~1.64 V vs NHE) for the direct oxidation of guanine, as well as a long-lived (>30 μs in CH_3CN) non-emissive dppn-localised $^3\pi\pi^*$ state through which to sensitise $^1O_2$. Transient absorption measurements demonstrate that intersystem crossing results in a mixed population of the two states: a peak at 536 nm corresponding to the $^3\pi\pi^*$ state grows in over 2 ps and remains unchanged out to 2 ns, while the ^{3}MLCT signal at 370 nm remains constant from 1 ps to 20 ps, before decreasing slightly out to 1 ns as the state decays away [73].

Intercalated DNA-binding complexes with excited-state potentials insufficient for *direct* oxidation of guanine have been employed as probes of DNA oxidative damage using the flash/quench technique. An intercalated Ru(II) complex is oxidised to Ru(III) via a photoinduced electron transfer to a weakly bound quencher. The Ru(III) species generated in situ is a powerful ground-state oxidiser, abstracting an electron from guanine to yield the original Ru(II) species and a neutral guanine radical. The guanine radical subsequently returns to its original state by reacting with reduced quencher, or undergoes further irreversible reaction(s) to yield oxidative products [75]. Flash/quench studies involving $[Ru(bpy)_2(L)]^{2+}$ {where L is an intercalating ligand: dpq = dipyridoquinoxaline, dpqC = dipyrido-6,7,8,9-tetrahydrophenazine, dppz, or Me_2dppz} revealed a direct correlation between the intercalative strength of a complex and the extent of guanine oxidation via DNA-mediated charge transport [76].

As mentioned in the introduction, oxidative damage has itself been employed as a convenient means by which to probe charge transport through DNA. The ability of planar intercalative ligands such as dppz to couple with the π-stacked array of bases in DNA makes complexes featuring such moieties useful tools by which to initiate charge migration through the double helix [2,4,77]. In a number of such studies cyclopropylamine-modified nucleobases (e.g. ^{CP}G and ^{CP}C) have been used as hole traps, with fast, irreversible ring-openings (10^{11} s^{-1}) used to monitor oxidative reactions in oligonucleotides. For instance, oxidative decomposition of ^{CP}G was observed using $[Ru(phen)(dppz)(bpy')]^{3+}$ {bpy′ = 4-(4′-methyl-2,2′-bipyridyl)butanoic acid—Fig. 1} generated via the flash/quench technique [78]. (In the same investigation $[Rh(phi)_2(bpy)]^{3+}$ {phi = phenanthrenequinone diimine}, having an excited state potential in excess of 1.9 V, was found to directly decompose both ^{CP}G and ^{CP}C}. Further flash/quench studies with this ruthenium complex have used transient absorption measurements to monitor the oxidative generation of methylindole radical cations [79]. The complex was tethered to an oligonucleotide such that it intercalated within the duplex several residues away from the methylindole. The flashed *Ru(II) complex excited state was found to decay biexponentially with lifetimes of τ_1 = 71 ns (76%) and τ_2 = 279 ns (24%) when bound to a sequence predominantly AT in nature but with the central methylindole flanked by guanines. The growth of a peak in the transient absorption spectra of the system at 600 nm has been attributed to the formation of the methylindole radical cation (with a rate of 4×10^7 s^{-1}). Concurrent with this is the disappearance of an MLCT-based bleach at 440 nm, demonstrating the conversion from *Ru(II) to Ru(III). The methylindole radical peak was seen to decay at a rate of approximately 1×10^6 s^{-1} in this oligonucleotide; however the 600 nm peak lingered in other more guanine-rich sequences, perhaps due to the subsequent generation of the guanine radical [79].

4. Chromium complexes

Chromium(III) complexes are a class of putative DNA-binding photooxidants that have, to date, received comparatively little attention relative to analogous Ru(II) and Re(I) species. This neglect may arise in part from the somewhat more difficult synthetic chemistry of polypyridyl Cr(III) complexes, with efficient means to produce heteroleptic complexes only afforded by recently published methodologies [80,81].

Like their Ru(II) counterparts, $[Cr(diimine)_3]^{3+}$ species typically exhibit a long-lived room-temperature luminescence. However in Cr(III) complexes this emission arises from the radiative decay of a doublet metal-centred excited state rather than a triplet charge-transfer state. This $^2E_g \rightarrow {}^4A_{2g}$ (O_h) transition gives rise to a characteristic phosphorescence signal at approximately 730 nm in aqueous solution, with a lifetime in excess of 50 μs–much longer than comparable Ru(II) species. Furthermore, the oxidative power of the chromium ^{2}MC excited state is considerably higher than that of the ^{3}MLCT state of analogous ruthenium complexes as the energetic cost of reducing the Cr(III) complex is significantly less than that required for Ru(II) analogue. Thus, polypyridyl Cr(III) complexes are potentially more powerful photooxidative agents than Ru(II) species.

In 1975 Bolletta et al. first reported evidence of $[Cr(bpy)_3]^{3+}$ being a strong one-electron photooxidant [82], and bimolecular electron-transfer reactions have subsequently been demonstrated for a variety of substrates, including biomolecules. Seminal investigations by Kane-Maguire and co-workers found that the emission of $[Cr(phen)_3]^{3+}$ was rapidly and dynamically quenched by dGMP with a bimolecular rate constant of 2.2×10^9 M^{-1} s^{-1}, close to the diffusion-controlled limit previously measured for Ru(II) complexes of HAT or TAP [83]. In contrast, no bimolecular quenching was observed in the presence of the less readily oxidisable dAMP, dCMP or dTMP nucleotides. Both the synthetic polynucleotide $[poly(dG–dC)]_2$ and calf thymus DNA were found to induce quenching with a bimolecular rate constant of 1.1×10^8 M^{-1} s^{-1}, with a significant *static* quenching component attributable to the formation of non-emissive ion pairs between the complex and double-helical DNA. $[Poly(dA–dT)]_2$, however, yielded only small reductions in emission intensity and lifetime. This evidence is indicative of notable quenching only in the presence of guanine; indeed, the excited state potentials of $[Cr(phen)_3]^{3+}$ and $[Cr(bpy)_3]^{3+}$ are ca. 1.4 V vs NHE, in excess of the 1.3 V necessary for oxidation of guanine at pH 7. $[Cr(TMP)_3]^{3+}$ {TMP = 3,4,7,

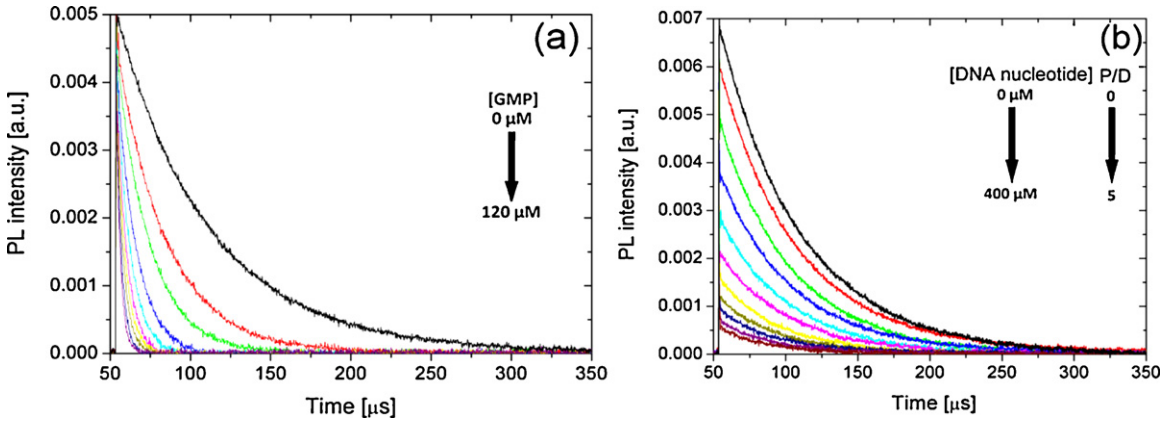


Fig. 7. Phosphorescence lifetime quenching of an air-saturated, phosphate (100 mM) buffered solution of $[Cr(phen)_2(F_2dppz)]^{3+}$ in the presence of increasing amounts of (a) GMP ([Cr] = 45 μM) and (b) CT-DNA ([Cr] = 80 μM). P/D = nucleotide/Cr. λ_{ex} = 308 nm. Figure adapted from Wojdyla et al. [87].

8-tetramethyl-1,10-phenanthroline} on the other hand has an excited state oxidising power of only 1.1 V, insufficient to oxidise guanine, and thus no quenching of this complex was observed in the presence of GMP.

Vaidyanathan and colleagues have examined a series of polypyridyl Cr(III) complexes featuring terpyridine-based ligands [84]. These complexes were found to possess very high excited-state potentials: +1.65 V vs NHE for $[Cr(ttpy)_2]^{3+}$ {ttpy = *p*-tolylterpyridine} and +1.85 V vs NHE for $[Cr(Brphtpy)_2]^{3+}$ {Brphtpy = (*p*-bromophenyl)terpyridine}. Despite being non-intercalators, the emissions of both of these complexes were quenched by DNA. Furthermore, $[Cr(ttpy)_2]^{3+}$ was found to be quenched by both GMP and AMP, while $[Cr(Brphtpy)_2]^{3+}$ was reportedly quenched by *all four* deoxymononucleotides (GMP, AMP, TMP and CMP). Both of the complexes demonstrated efficient photonuclease activity, cleaving plasmid DNA upon irradiation. Again, an electron transfer mechanism is proposed as the DNA cleavage is unaffected by the presence of the $^1O_2$-scavenger NaN_3.

The DNA-binding affinities of such largely electrostatically binding species were found to be relatively small, so subsequent studies turned to the intercalative derivative $[Cr(phen)_2(dppz)]^{3+}$ (an intercalative binding mode has been confirmed by means of UV/vis titrations, linear dichroism and viscosity measurements, with a binding constant of greater than $10^5\ M^{-1}$) [85,86]. As with the homoleptic $[Cr(diimine)_3]^{3+}$ complexes, $[Cr(phen)_2(dppz)]^{3+}$ exhibits ^{2}MC phosphorescence in aqueous solution. However, upon intercalation of the dppz moiety into double-stranded DNA, the ^{2}MC emission is quenched [85,86], so that in contrast to the archetypical Ru(II) analogue $[Ru(phen)_2(dppz)]^{2+}$, but similar to $[Ru(TAP)_2(dppz)]^{2+}$, the Cr(III) species acts as a *reverse* light-switch.

The quenching of the ^{2}MC phosphorescence of $[Cr(phen)_2(dppz)]^{3+}$ complex and also its derivatives $[Cr(phen)_2(Me_2dppz)]^{3+}$ and $[Cr(phen)_2(F_2dppz)]^{3+}$ by monononucleotides has been studied in detail [85,87]. Comparison of Stern–Volmer plots based on the lifetime traces (e.g. Fig. 7a) and of the steady state data emission-quenching data reveal *dynamic* lifetime quenching for GMP, consistent with collisional deactivation of emissive Cr(III) complexes in solution with bimolecular rate constants in the range of $2.3–2.8 \times 10^9\ M^{-1}\ s^{-1}$. The potentials of the excited states of these complexes (1.52, 1.49 and 1.62 V vs NHE for H_2, Me_2 and F_2, respectively) are all in excess of those values reported for one-electron oxidation of guanine (see above). AMP was found to quench inefficiently, with a rate constant some two orders of magnitude less than GMP, attributable to the higher thermodynamic driving forces required to oxidise adenine. To probe for the expected electron transfer products transient absorption spectra of $[Cr(phen)_2(dppz)]^{3+}$ and its analogues in the presence of GMP were recorded using laser flash photolysis on the nanosecond timescale [87]. The excited states of these complexes absorb strongly in the visible spectral region with each exhibiting a broad band centred at approximately 500 nm with a wide shoulder extending out past 700 nm, properties reminiscent of those obtained from other $[Cr(diimine)_3]^{3+}$ species [88,89]. The lifetime of the excited state (60–70 μs) is shortened in the presence of GMP in good agreement with the transient absorption data. However no new transient species were detectable. This suggests that the initial oxidation of the nucleotide must be followed by back electron transfer (Eq. (9)) on a timescale shorter than the microsecond domain of the decay of the excited state. This behaviour contrasts to that observed in similar experiments performed with $[Ru(TAP)_2(dppz)]^{2+}$ [45], where the oxidised guanine and the reduced metal complex were observed, and where a proton-coupled electron transfer process (PCET, see Eq. (7) above) is proposed. Whether this differing behaviour is a consequence of the nature of the excited state (^{3}ML(TAP)CT vs ^{2}MC), differing mechanism (direct electron transfer vs PCET) or different timescales (nanosecond or microsecond) remains to be elucidated.

$$[Cr(phen)_2(dppz)]^{3+*} + G \rightarrow [Cr(phen)_2(dppz)]^{2+} + G^{\bullet+} \quad (8)$$

$$[Cr(phen)_2(dppz)]^{2+} + G^{\bullet+} \rightarrow [Cr(phen)_2(dppz)]^{3+} + G \quad (9)$$

The emission of $[Cr(phen)_2(dppz)]^{3+}$ is greater than 98% quenched when the complex is bound to calf thymus DNA. By contrast with what is found with GMP, the quenching by natural polymeric DNA is predominantly *static* in nature, as is clearly shown by the time-resolved excited state decays (e.g. Fig. 7b). This implies that the DNA-bound state for the Cr(III) species is essentially non-emissive. There is also a small dynamic quenching component by CT-DNA with rate constants of between 1 and $3 \times 10^7\ M^{-1}\ s^{-1}$, presumably due to unbound metal complex (or possibly to complex bound in a non-intercalative mode). The efficient static quenching may be presumed to proceed via direct oxidation of the guanine base in the DNA by the excited state of the intercalated metal complex. It may be noted that the efficiency of quenching upon binding to this natural mixed sequence DNA is much higher than that observed for $[Ru(TAP)_2(dppz)]^{2+}$. Whether this is due to specificity of binding to a particular site on the DNA or to a different mechanism of quenching (direct electron transfer vs proton-coupled electron transfer) remains to be elucidated. This will require the use of femtosecond/picosecond experiments. The importance of Type 1 processes with $[Cr(phen)_2(dppz)]^{3+}$ is further demonstrated by recent plasmid DNA photocleavage experiments performed by

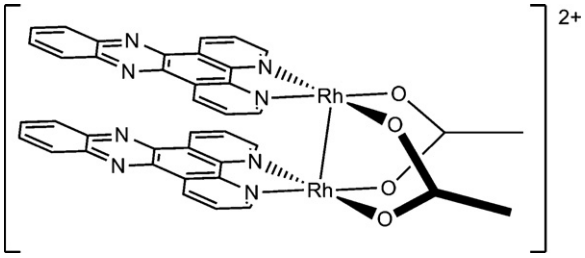


Fig. 8. A representative dirhodium species, *cis*-$[Rh_2(\mu\text{-}O_2CCH_3)_2(dppz)_2]^{2+}$.

Toneatto et al. who observed more efficient photocleavage in the absence of oxygen than in aerated solution [90].

5. Other platinum group metal complexes

While ruthenium, chromium and rhenium have received the most attention, dppz-based complexes of numerous other transition metal complexes have been explored with regards to their DNA-binding and oxidative capabilities. Perhaps most abundant amongst these are the dirhodium(II,II) lantern-type complexes (Fig. 8). While the DNA photocleavage activity of such species has been extensively investigated, there have been few transient spectroscopy-based studies of these reactions. Initial studies looked at tetraacetate species of the form $Rh_2(O_2CCH_3)_4(L)_2$ {where L = alcohol, py, PPh_3, THF or H_2O} with excited states having lifetimes of up to 5 μs [91,92]. Such species induce oxidative damage only in the presence of an electron acceptor, by which the oxidative mixed-valence Rh_2(II,III) complex is generated. Subsequent studies introduced intercalative dppz moieties in order to enhance binding affinity. *cis*-$[Rh_2(\mu\text{-}O_2CCH_3)_2(dppz)(\eta^1\text{-}O_2CCH_3)(CH_3OH)]^+$ and *cis*-$[Rh_2(\mu\text{-}O_2CCH_3)_2(dppz)_2]^{2+}$ (see Fig. 8) were found to induce DNA photocleavage via both oxygen-dependent and independent mechanisms [93]. Transient absorption studies performed on the analogous dirhodium species featuring dppn ligands revealed non-emissive $^3\pi\pi^*$ dppn-centred excited states with lifetimes of 2.4–4.1 μs [94]. These complexes induced DNA photocleavage through the generation of reactive oxygen species.

The Pt(II) complex $[(dppz)Pt(mes')_2]^{2+}$ {mes′ = *N*,*N*,*N*,3,5-pentamethylaniline} was found to initiate photooxidative ring-opening of ^{CP}G through the DNA stack [95], while the covalently tethered, cyclometallated Ir(III) complex $[Ir(ppy)_2(dppz')]^+$ {dppz′ = dppz moiety tethered via the 11-position} was shown to induce *either* photooxidative or reductive damage to cyclopropylated bases in an oligonucleotide depending upon the flanking sequence of the base [96].

A variety of osmium(II)-dppz complexes have also been investigated. These possess high binding affinities and demonstrate light-switch effects (a red emission with a lifetime in the range of 10 ns) similar to their Ru(II) counterparts, however they possess significantly lower excited-state oxidation potentials (0.76 V vs NHE for $[Os(phen)_2(dppz)]^{2+}$, for instance) which hampers their direct photooxidative capabilities [97–99].

6. Rhenium complexes

The results mentioned above for $[Ru(TAP)_2(dppz)]^{2+}$ illustrate the potential for using IR spectroscopy for interrogation of the photophysical/photochemical processes of metal-dppz complexes intercalated into DNA, since this technique provides a direct structural probe of these ultrafast processes, including a direct marker band for formation of the oxidised guanine species at ca. 1700 cm^{-1} [65,70,71]. However, the IR fingerprint region where key processes

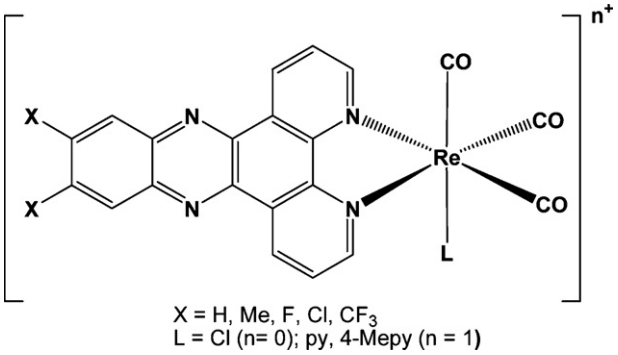


Fig. 9. Generalised structure of the *fac*-$[Re(CO)_3(X_2dppz)(L)]^{n+}$-type complex.

in the DNA can be monitored is very congested and complex photophysical processes can be difficult to untangle. Ideally, we would like transient IR signals associated with the metal complex to correlate with signals obtained from the DNA, so that both the reduction of the metal complex ion excited state and the oxidation of the guanine can be monitored simultaneously. Although there should be IR signatures of the excited state associated with the dppz ligand, these bands are not ideal as they are also in the fingerprint region. Metal carbonyls on the other hand are potentially ideal reporters of photo-induced electron transfer reactions of DNA-bound metal complexes since the frequencies of ν(CO) IR bands are sensitive to electronic structure. These ligands therefore may act as probes of electron distribution in the excited state and may also directly monitor the oxidising and reducing products formed from that excited state [100–102]. $[Re(CO)_3(dppz)(L)]^{n+}$ complexes of the type shown in Fig. 9 are ideal for this purpose. From a spectroscopic perspective these complexes also have the advantage that since only one chromophoric ligand is present there is no ambiguity with respect to the acceptor ligand, so that it should be easier to identify the roles of ^{3}IL(π,π^*), ^{3}MLCT (phen) or ^{3}MLCT (phz) states in photochemical processes (Fig. 10).

The exquisite sensitivity of the TRIR spectrum of the $Re(CO)_3$(diimine) complexes to changes in substituent and medium is well illustrated by the compounds *fac*-$[Re(CO)_3(X_2dppz)Cl]$ (X = Me, H, F, Cl, CF_3) [103]. The lowest excited state may be ^{3}IL(π,π^*), ^{3}MLCT (phen) or ^{3}MLCT (phz) depending on the substituent and/or solvent. Fig. 11 shows this behaviour for the

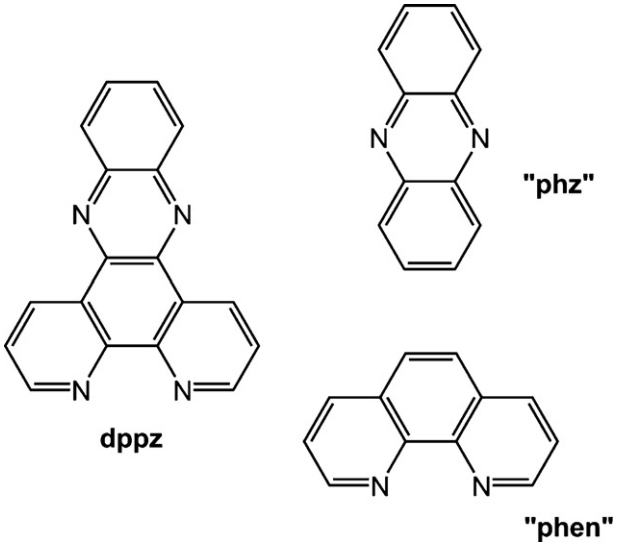


Fig. 10. The structural components of the dppz ligand that give rise to the different localised ^{3}MLCT (phen) or ^{3}MLCT (phz) states.

complexes in dichloromethane solvent. For example, the ^{3}IL(π,π^*) (formed in the Me derivative) shows no high frequency CO stretch band, whereas in the ^{3}MLCT (phen) this vibration is ca. 40 cm^{-1} displaced from the parent's and for the ^{3}MLCT (phz) (e.g. in the CF_3 complex) about a further ca. 20 cm^{-1} to higher wavenumber.

The binding of dppz-rhenium complexes to DNA was first reported independently by Yam, Schanze and their co-workers [104–106]. Yam showed that when *fac*-[Re(CO)$_3$(dppz)(py)]$^+$ was bound to poly(dA)·poly(dT) there was a 15-fold enhancement in emission, whereas with poly(dG)·poly(dC), the emission intensity was hardly affected. The dppn analogue gave strong enhancement with the A–T polymer, and an actual quenching with poly(dG)·poly(dC)—behaviour similar to that observed with the ruthenium TAP compounds (see earlier section). Schanze and co-workers [106] compared the emission properties of *fac*-[Re(CO)$_3$(dppz)(4-Mepy)]$^+$ in methanol solution and when bound to DNA and assigned the structured band with two vibronic components at λ_{max} = 556 and 598 nm to emission from a IL $\pi\pi^*$ triplet state in both cases. By contrast the complex in degassed aqueous buffered solution shows no luminescence so that it acts as a 'DNA light switch' in a manner similar to that of [Ru(phen)$_2$(dppz)]$^{2+}$. The role of the ^{3}IL($\pi\pi^*$) state when the complex is bound to DNA was confirmed using nanosecond flash photolysis, as this state has a strong absorption band at ca. 470 nm.

In order to try and clarify the ambiguity of the photophysics of *fac*-[Re(CO)$_3$(dppz)(py)]$^+$, our groups employed a range of time-resolved spectroscopic methods so as to establish the photophysical behaviour in CH_3CN [107,108] (see Fig. 12 for an overview of this behaviour). As mentioned above, the luminescence and nanosecond-TA spectra of *fac*-[Re(CO)$_3$(dppz)(py)]$^+$ in organic solvents are consistent with the presence of an IL(π,π^*) excited state. Picosecond–TA measurements of *fac*-[Re(CO)$_3$(dppz)(py)]$^+$ in CH_3CN showed that the IL(π,π^*) excited state was present shortly after excitation, and demonstrated that any initially formed MLCT

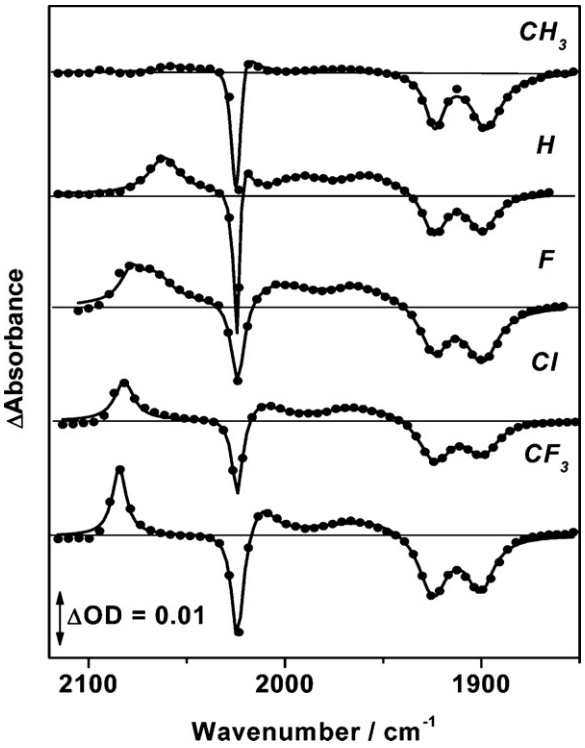


Fig. 11. TRIR spectra of *fac*-[Re(CO)$_3$(X$_2$dppz)Cl] {X = CH_3, H, F, Cl, or CF_3} obtained 100 ps after 400 nm excitation of CH_2Cl_2 solutions at room temperature (•) with the multicurve Lorentzian fit (line) [103].

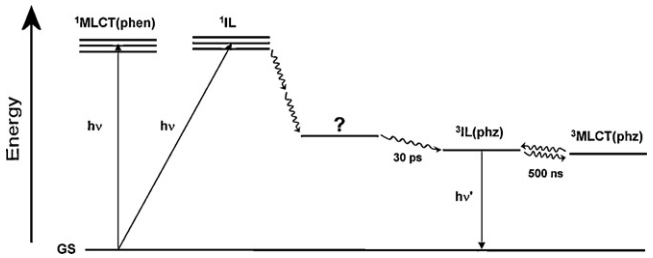


Fig. 12. Proposed Jablonski diagram describing the observed photophysics of *fac*-[Re(CO)$_3$(dppz)(py)]$^+$ in CH_3CN [107].

excited states must convert to the IL(π,π^*) excited state on a sub-picosecond timescale. Picosecond and nanosecond resonance Raman spectroscopy (TR^3) were also able to provide evidence for the IL(π,π^*) excited state being produced within the first 30 ps, but perhaps the clearest evidence came from the ps-TRIR measurements. The transient excited state possesses ν(CO) bands which are shifted to slightly lower wavenumber relative to the parent bands, as expected for the formation of a IL(π,π^*) excited state. In the first few picoseconds the peaks due to the IL(π,π^*) excited state bands are initially broad but with time these bands narrow and shift to slightly higher wavenumber which is consistent with vibrational relaxation. It was noted, however, that any interconversion between different IL(π,π^*) excited states on this timescale may be difficult to monitor by ps-TRIR. On the nanosecond timescale the ν(CO) bands partially decay (ca. 500 ns) to form a new species with ν(CO) bands shifted to higher wavenumber than the parent bands and assigned to the formation of a ^{3}MLCT state (see Fig. 12). This upward shift in the ν(CO) bands of this MLCT excited state was higher than that observed in other Re-phen and Re-bpy complexes and was interpreted as showing that the excited state was localised on an orbital which is further from the Re centre (e.g. the phz-localised molecular orbital). Interestingly the bands of the $\pi\pi^*$ IL and MLCT excited states decay at the same rate, consistent with them being in equilibrium. This study shows the need to use a combination of transient spectroscopic methods to fully unravel the complexities of the photophysics of such Re-dppz carbonyl complexes.

The effect of substitution of the dppz ligand on the photophysical properties of this class of compound is demonstrated by the behaviour of *fac*-[Re(CO)$_3$(X$_2$dppz)(py)]$^+$ (X = Me, H or F) [108]. All compounds emit strongly (from the ^{3}IL(π,π^*) state) in acetonitrile, but show very different behaviour when water is added to this solution. In the case of the methyl-derivative the emission is enhanced by the addition of water, whereas for the fluoro-subsituted analogue the emission is strongly quenched. (For the parent compound the emission is initially enhanced by addition of small quantities of water and quenched when larger quantities are present.) In agreement with this finding ps-TA studies show that the average lifetime of *fac*-[Re(CO)$_3$(F$_2$dppz)(py)]$^+$ is ca. 450 ps in aqueous solution, compared to >5 μs in acetonitrile.

Subsequent transient spectroscopy experiments with *fac*-[Re(CO)$_3$(F$_2$dppz)(py)]$^+$ in the presence of polynucleotides have been carried out [109]. Picosecond-scale transient absorption spectra obtained with *fac*-[Re (CO)$_3$(F$_2$dppz)(py)]$^+$ in the presence of [poly(dA–dT)]$_2$ after excitation at 400 nm were reminiscent of spectra obtained in CH_3CN (transient maxima at ca. 475 and 575 nm), consistent with the ^{3}IL(π,π^*) excited state of the metal complex. Interestingly observation of the DNA region of the TRIR spectrum of [poly(dA–dT)]$_2$ showed that excitation of the complex induced strong bleaching of the adenine and thymine bands which recovered with the same kinetics as the decay of the ^{3}IL(π,π^*) excited state {which could also be readily be monitored by its ν(CO)}. For the first time this provides structural information

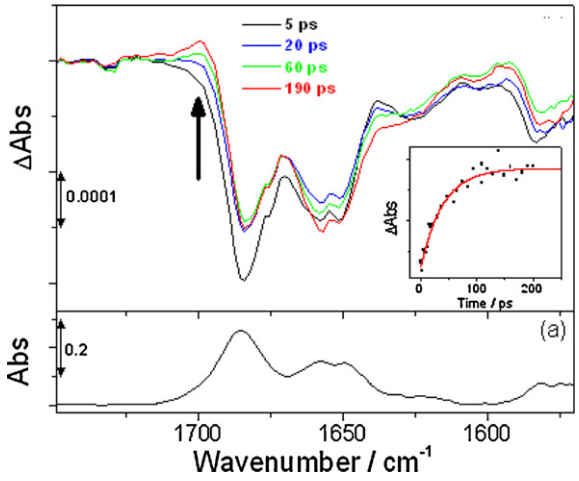


Fig. 13. (a) Ground state FTIR and (b) ps-TRIR DNA-region difference spectra of *fac*-$[Re(CO)_3(F_2dppz)(py)]^+$ in buffered D_2O in the presence of $[poly(dG–dC)]_2$ ([nucleotide]:[Re] = 20:1) after 400 nm excitation [109]. Inset shows the absorbance change at 1695 cm^{-1}.

about the perturbation of base-pair binding site upon formation of an intercalated excited state. Markedly different behaviour is observed upon excitation of *fac*-$[Re(CO)_3(F_2dppz)(py)]^+$ bound to $[poly(dG–dC)]_2$. In this case strong, broad transients at 470 and ca. 600 nm are observed at short times (e.g. 2 ps) after the laser pulse. However, over the next 200 ps absorbance at 470 nm decreases while the longer wavelength absorption sharpens to a peak at ca. 580 nm which persists beyond the timescale of the experiment (>2 ns). This long wavelength band is assigned to the reduced metal complex formed by electron transfer quenching of the rhenium excited state. This process occurs on two timescales: <1 ps (66%) and 34 ps (34%). In ps-TRIR measurements monitoring in the metal-carbonyl region showed the formation of the reduced rhenium complex in the presence of $[poly(dG–dC)]_2$, while in the DNA region bleaching of guanine and cytosine bands was observed along with the appearance of a new transient at 1695 cm^{-1} (see Fig. 13), at a wavenumber similar to that expected for the oxidised guanine species [65,71]. This transient grows in over a period of 39 ± 5 ps, with an initial intensity (at $\tau = 2$ ps) that was approximately 64% of its final intensity (at $\tau = 200$ ps), in concurrence with the values obtained via ps-TA. The occurrence of the electron transfer over two very different timescales is intriguing. It is significant that the fast process proceeds in less than a picosecond and therefore is comparable with the rates previously observed by Reid et al. for the singlet excited state of thionine [7,8]. The other process may be of an electron transfer originating from another excited state.

Foxon et al. [110] have reported a heterometallic dinuclear Re^{I}-Ru^{II} dppz species $[\{Ru(tpm)(dppz)\}\{\mu\text{-py-}(CH_2)_5\text{-py}\}$ *fac*-$(CO)_3Re(dppz)\}]^{3+}$ {tpm = tris(1-pyrazoyl)methane} which acts as a dual-function light-switch and cleavage agent and potentially provides a DNA-targeting compound with a unique combination of photophysical properties. The complex is non-luminescent in water and TRIR experiments show evidence for a short-lived dppz-centred IL (π,π^*) excited state. The short lifetime is explained by deactivation via energy transfer to the Ru^{II} centre and subsequent formation of an extremely short-lived $Ru(d\pi) \rightarrow dppz(\pi^*)$ ^{3}MLCT state. Upon addition to DNA the dinuclear complex exhibits a strong luminescence, with a biexponential decay having lifetimes (τ_{em} = 36 and 117 ns) similar to those observed for the analogous mononuclear ruthenium species $[Ru(tpm)(dppz)(py\text{-}(CH_2)_5\text{-}py)]^{2+}$ (32 and 102 ns). This is consistent with the "light-switch effect" of the complex arising from intercalation of the Ru^{II}-dppz moiety. Although irradiation of the complex in the presence of plasmid DNA leads to nicking and eventual cleavage of the DNA, it is not clear whether this is caused by direct electron transfer.

The measurements performed with complexes of the type *fac*-$[Re(CO)_3(X_2dppz)(py)]^+$ not only show the versatility of this class of metal complexes as nucleic acid probes but also confirm our expectation that using TRIR and UV/visible TA techniques in tandem can provide insights about photo-oxidation of nucleic acids that is not possible using solely one of the techniques.

7. General conclusions

The studies reviewed in this short article demonstrate that metal complexes of dppz and similar ligands are not only valuable as light switches for nucleic acids but have potential as tools for sensitising the direct oxidation of DNA. Although it should be possible to prepare metal dppz-type complexes that are be able to oxidise adenine, in the vast majority of cases so far it is only guanine which is oxidised efficiently. An open question is still what factors for particular complexes determine whether this oxidation proceeds by direct oxidation or proton-coupled electron transfer. More studies will also have to be carried out to see how the rates of the reaction depend on the thermodynamic driving force for the forward reaction. While it is apparent that with some compounds the rate of the back reaction can be very rapid indeed (sub-picoseond), in others (e.g. $[Ru(TAP)_2(dppz)]^{2+}$ or *fac*-$[Re(CO)_3(F_2dppz)(py)]^+$) it is much slower (in the nanosecond domain). From a perspective of designing systems to initiate Type 1 photooxidation of DNA, it will be helpful to also be able to predict the rate of this reaction, as the lifetime of the transient oxidised nucleobase (whether as the radical cation or its deprotonated product) will certainly affect the efficiency of subsequent DNA damage.

Acknowledgements

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