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Review

Photophysical properties and applications of Re(I) and Re(I)–Ru(II) carbonyl polypyridyl complexes

Anthony Coleman, Claire Brennan, Johannes G. Vos, Mary T. Pryce*

School of Chemical Sciences, SFI SRC for Solar Energy Conversion, Dublin City University, Dublin 9, Ireland

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ABSTRACT

This review focuses on the photophysical properties of rhenium(I) tricarbonyl moieties of the type [Re(CO)$_3$(NN)L] (where NN = polypyridyl ligand and L = chloride or nitrogen donor atom) and their importance to the area of inorganic chemistry. Processes such as electron transfer, energy transfer and photodissociation are also highlighted. The second aspect of this review highlights the photophysical properties of dinuclear ruthenium(II)–rhenium(I) complexes, with particular emphasis on the importance of the electronic properties of the bridging ligand between the metal centres. Applications of such complexes include CO$_2$ reduction, DNA cleavage, and biological labels for various therapeutic, diagnostic, and mechanistic applications.

1. Introduction

The spectroscopic, photochemical and photophysical properties of rhenium(I) tricarbonyl complexes of the type *fac*-[Re(CO)$_3$(NN)L], continue to attract much attention ever since their interesting excited state properties, which are similar to those of the Ru(II) polypyridyl analogues, were first recognized in the 1970s [1]. Later work by Meyer and co-workers helped elucidate the relationship in these systems between the nature of the chloride and/or polypyridyl ligand and the character of the photophysical properties observed [2]. The low energy excited state of these rhenium(I) polypyridyl systems is mixed in character involving low lying metal-to-ligand charge transfer (MLCT) states and intraligand (IL) $^3\pi$–π^* excited states [3]. As a result of strong spin-orbit coupling, resulting in enhanced singlet–triplet mixing this class of chelated metal carbonyl complex are strong phosphorescent emitters possessing long-lived excited states [4]. Such systems easily lend themselves to the design of luminescent sensors and materials for supramolecular devices. It is therefore very important to understand their electronic structure and correctly assign their low-lying electronic transitions. Their excited states have also demonstrated the potential to act as active catalytic species in the photo- and electrocatalytic reduction of CO$_2$ to CO [5], and as labelling reagents for biomolecules [6,7,23]. The photophysical and photochemical properties of these systems can be tuned by varying the ligand coordinated to the rhenium(I) tricarbonyl moiety. Furthermore, it has been shown that rhenium(I) complexes of this type can display

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* Corresponding author. Tel.: +353 17008005; fax: +353 17005503.
E-mail address: mary.pryce@dcu.ie (M.T. Pryce).

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two-photon excitation (at 705 nm or at longer wavelengths), as the emission intensity depended on the square of the laser power. [8] Complexes that undergo multi-photon process have potential applications as probes in multi-photon microscopy or in tissues.

2. Mononuclear rhenium(I) tricarbonyl complexes

2.1. Preparation of complexes of the type fac-[Re(CO)$_3$(NN)L]

Rhenium(I) tricarbonyl complexes of the type [Re(CO)$_3$(NN)Cl], can be readily synthesized by reacting the appropriate N-donor ligand (NN), such as 2,2′-bipyridine, under an inert argon atmosphere with an equimolar amount of [Re(CO)$_5$Cl] in a non-polar solvent such as hexane or toluene, although the latter is more commonly used [9]. The desired [Re(CO)$_3$(NN)Cl] product often precipitates from solution on cooling, allowing easy isolation and further purification.

The chloride ligand may also be substituted with a nitrogen donor ligand such as pyridine to form complexes of the type [Re(CO)$_3$(bpy)(py)]$^+$, where bpy = 2,2′-bipyridine and py = pyridine. Two methods have been developed for the substitution of the chloride ligand with an N-donor ligand [10–12]. These involve either reacting [Re(CO)$_3$(bpy)Cl] with triflic acid (CF_3SO_3H) in room temperature dichloromethane or refluxing the former with silver triflate ($AgCF_3SO_3$) in THF, the method used being dependent on the electron donating abilities of the coordinating N-donor ligand. In both cases the triflate salt [Re(CO)$_3$(bpy)(O$_3$SCF$_3$)] is formed, which is subsequently reacted with the N-donor ligand to yield the desired products, such as [Re(CO)$_3$(bpy)(py)](CF$_3$SO$_3$).

2.1.1. Photophysical properties of fac-[Re(CO)$_3$(NN)L]

Rhenium tricarbonyl complexes of the type [Re(CO)$_3$(NN)L], where NN = polypyridine ligand and X = Cl or PPh$_3$, typically possess C_s geometry with three IR active vibrational modes [$A'(1) + A'(2) + A''$], corresponding to three carbonyl ligands in a facial arrangement [1,13,14]. When the ancillary Cl or PPh$_3$ ligand is an N-donor ligand the local coordination around the Re metal centre possesses pseudo-C_{3v} symmetry, resulting in the observance of only two IR active bands; the higher energy band assigned to an A$_1$ vibrational mode while the broad lower energy (E) band is a convolution of the previously mentioned $A'(2) + A''$ bands. For the complex *fac*-[Re(CO)$_3$(bpy)Cl], the ν_{CO} bands are observed at 2024, 1917 and 1900 cm^{-1} in CH_3CN solution [15]. The position of these carbonyl bands is greatly affected by the d_π electron density of the rhenium centre as a result of π-back donation and the π-acceptor capabilities of the coordinated polypyridyl ligand. By varying the coordinating polypyridyl ligand, the electronic properties of the system studied may also be fine-tuned. The electronic absorption spectrum of *fac*-[Re(CO)$_3$(bpy)Cl] typically exhibits a number of high energy absorption bands. A high energy feature at ~295 nm is associated with a bipyridyl based π–π^* transition [1]. A lower energy band observed at ~390 nm is associated with a Re → π^* (bpy) MLCT transition and Cl → bpy LLCT (LLCT = ligand-to-ligand charge transfer) transition [16]. This assignment was later confirmed with density functional theory (DFT) calculations [17]. The MLCT transition exhibits solvatochromism [18] and is also sensitive to the electron-donating/-withdrawing nature of any substituents on the bipy ligand. Recently, the *meridonal* isomer, *mer*-[Re(CO)$_3$(bpy)Cl], was synthesized, and isolated for the first time [19]. The *mer* isomer was obtained following irradiation of the corresponding *fac* isomer at 313 nm in THF solution. Large differences are observed in the spectral data, for instance, in the ^{1}H NMR spectra, only four proton signals are observed for *fac*-[Re(CO)$_3$(bpy)Cl], whereas eight proton signals are observed for *mer*-[Re(CO)$_3$(bpy)Cl]. In the UV–vis spectra the MLCT absorption bands are red-shifted by 50–100 nm when compared to *fac*-[Re(CO)$_3$(bpy)Cl], and furthermore the *mer* isomer does not emit at room temperature, in contrast to the *fac* isomer.

2.1.2. Charge transfer excited states

Rhenium(I) tricarbonyl complexes are one of the few classes of metal carbonyl complexes to emit in fluid solution. They are thus important candidates for electron and energy transfer systems. Many examples [20] exist of rhenium(I) tricarbonyl complexes, which exhibit ^{3}MLCT emission at both room temperature and 77 K. The presence of the halide in the axial position of complexes of the type [Re(CO)$_3$(NN)L] allows great synthetic freedom and with this, manipulation of the excited state behaviour is possible. *fac*-[Re(CO)$_3$(bpy)Cl] exhibits a broad structureless emission band with a λ_{max} at 610 nm in solution at 298 K [1]. In a 77 K 4:1 EtOH:MeOH glass this emission band is blue shifted to 535 nm. This rigidochromic effect is characteristic of the ^{3}MLCT origin of the emissive state of this complex. Furthermore, on cooling to 77 K the excited state lifetime increases from 51 ns to 2.68 μs. This is a consequence of the immobility of the solvent dipoles on the timescales involved, resulting in an inability to respond to the change in electronic configuration. The excited state lifetime is further extended in a frozen glass as non-radiative decay pathways such as vibronic coupling, solvent interactions and possible oxygen diffusion are all significantly reduced [21]. A further example of the significant importance of the nature of the axial ligand L, where L = halide is evident in the studies by Stufkens and co-workers [16] on *fac*-[Re(L)(CO)$_3$(α-diimine)] complexes, where L = Cl, Br, I and α-diimine = bpy, pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa) and *N*,*N*′-di-isopropyl-1,4-diaza-1,3-butadiene (*i*Pr-DAB). Time resolved absorption and infrared studies suggest that the character of the lowest lying excited state transition of *fac*-[Re(L)(CO)$_3$(α-diimine)] is determined by the halide present and that the excited state character changes from predominantly ^{3}MLCT (Re → α-diimine) when L = Cl to predominately LLCT (halide L → (α-diimine) when L = Br. This is attributed to the increased level of mixing between the Re(d_π) and L(p_π) orbitals as the L(p_π) orbital energy increases in going from Cl → Br → I. Furthermore, with increased halide character the excited state lifetime is increased due to a decreased rate of non-radiative decay. The emission maxima of such systems at room temperature or at 77 K are also sensitive to the nature of the polypyridine ligand (NN), and to any substituent on the polypyridyl ligand. For instance, for complexes of the type [Re(CO)$_3$(4,4′-X$_2$-bpy)Cl], where X is an electron-withdrawing/or -donating group there is a considerable shift in the emission λ_{max}. When X = NEt$_2$, the λ_{max} is observed at 575 nm at 295 K (501 nm at 77 K), whereas on changing X to the electron-withdrawing group –NO$_2$, the emission λ_{max} is observed at 780 nm at 295 K (670 nm at 77 K) [22]. Computational studies employing DFT have shown that this emission arises from a mixed ^{3}MLCT and ^{3}LLCT (Re to bpy and Cl to bpy) excited state and that the nature of the axial ligand L has a profound effect on both the absorption and emission spectra due to changes in the HOMO–LUMO energy gap depending on the electron-withdrawing/donating abilities of the ligand [23]. Hence, the energy band gap ($|\Delta A$(HOMO–LUMO)$|$) increases in the order [Re(CO)$_3$(4,4′-(CH$_3$)$_2$–bpy)Cl] > [Re(CO)$_3$(bpy)Cl] > [Re(CO)$_3$(5,5′-Br$_2$–bpy)Cl] > [Re(CO)$_3$(4,4′-2COOCH$_3$–bpy)Cl]. Similarly, for a series of rhenium(I) polypyridine isothiocyanate and maleimide complexes, electron-donating substituents on the polypyridine ligand result in emission at higher energies than those containing electron-withdrawing moieties [6,24]. [Re(phen)(CO)$_3$(py-3-NCS)](CF$_3$SO$_3$) was found to emit at 530 nm in CH$_2$Cl$_2$ solution, while substitution with a more electron withdrawing moiety

Table 1
Photophysical data of selected rhenium(I) tricarbonyl complexes

Complex	Medium	λ_{em} (nm)	τ_0 (μs) (Φ_{em})
$Re(CO)_3(bpy)Cl$[a]	CH_2Cl_2	387	–
	CH_3CN	370	–
$Re(CO)_3(bpm)(Cl)$[a]	CH_3CN	365	–
$[Re(CO)_3(dppt)Cl]$[b]	CH_2Cl_2	449	–
$[Re(CO)_3(bpm)(py)]^+$[c]	CH_3CN	364	–
$Re(dppz)(CO)_3(py–CH_2–NH–biotin)(PF_6)$[d]	CH_2Cl_2	558, 601(sh.)	4.90 [0.0049]
	CH_3CN	556, 559 (sh.)	7.12 [0.0016]
$Re(dppn)(CO)_3(py–CH_2–NH–biotin)(PF_6)$[d]	CH_2Cl_2	587	17.88 [0.20]
	CH_3CN	595	31.47 [0.13]

[a] Ref. [15].
[b] Ref. [26].
[c] Ref. [27].
[d] Ref. [6a].

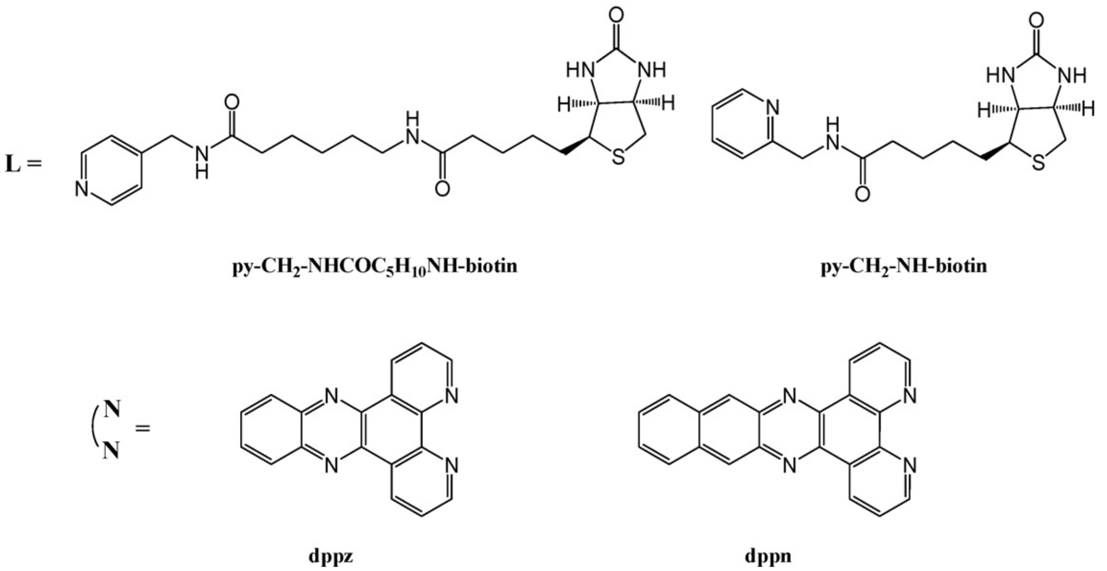


Fig. 1. Structures of biotin ligands (L) and selected polypyridyl ligands (N–N) [25].

$[Re(biq)(CO)_3(py\text{-}3\text{-}NCS)](CF_3SO_3)$ (biq = 2,2′-biquinolinyl) blue shifts the emission maximum to 642 nm, which suggests a ^{3}MLCT Re(d) → π* (polypyridine ligand) state [6].

A series of rhenium(I) tricarbonyl systems incorporating an Avidin–Biotin protein system (Table 1) have also been investigated for use in bioanalytical applications [6,25]. As indicated in Table 1 these rhenium(I) tricarbonyl–biotin complexes exhibit intense long-lived ^{3}MLCT-based emission. Interestingly, titrations of the rhenium(I) tricarbonyl–biotin complex in the presence of avidin was found to result in an enhancement of up to 300% of the emission intensity, with a concomitant increase in the triplet lifetime. This increase in emission intensity has been credited to the binding of the complex to the biotin binding sites of avidin. Although emission quenching is often observed following formation of fluorophore–biotin conjugates, in this case there is negligible overlap between the absorption and emission spectra of the rhenium(I) tricarbonyl–biotin complex.

Furthermore, it is speculated that this emission enhancement may also be partially due to the hydrophobicity of the avidin moiety as well as the observed increase in the rigidity of the molecule following avidin binding, which is believed to result in a decrease in the efficacy of non-radiative decay processes. Subsequent coordination of planar extended polypyridyl ligands (N–N) such as dipyrido-[3,2-*a*:2′,3′-*c*]-phenazine (dppz) and benzo[*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppn) (see Table 1 and Fig. 1) were shown to further extend both the triplet emission intensity and the excited state lifetime.

Recently, Perutz and co-workers [28] have studied Zn and Mg-tetraphenylporphyrins (Zn-TPP and Mg-TPP) linked covalently to a $[Re(CO)_3(bpy)(pic)]$ (pic = picoline) unit via an amide bond (Fig. 2). The electron-donating picoline moiety was introduced as previous efforts [29,30] with $[Re(CO)_3(bpy)Br\text{-}MTPP]$ (M = Zn or Mg), indicated that with the Br axial ligand no photoinduced reactions with

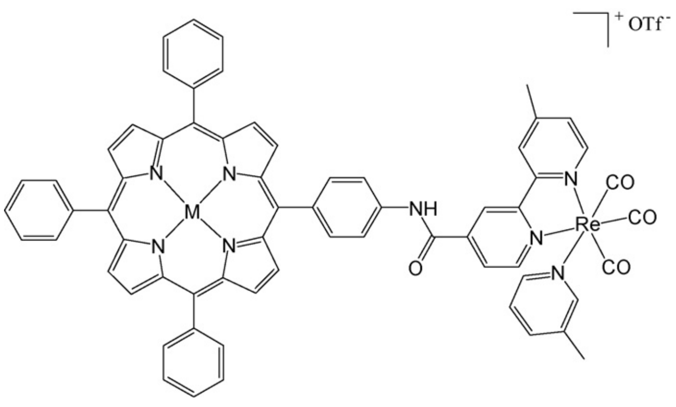


Fig. 2. Structure of $[Re(CO)_3(pic)(bpy)\text{-}MTPP][OTf]$ [28].

intermolecular electron donors occur and that the solubility was very low in common organic solvents.

IR spectroelectrochemical studies of $[Re(CO)_3(pic)bpy\text{-}ZnTPP]^+$ were undertaken in room temperature PrCN, and new bands at 2012 and 1902 cm^{-1} were assigned to the radical species $[Re^+(CO)_3(pic)bpy^{\bullet -}$ ZnTPP]. Cyclic voltammetry studies confirmed that no significant exchange of picoline with PrCN occurs. Both the $[Re(CO)_3(pic)bpy\text{-}ZnTPP]^+$ and $[Re(CO)_3(pic)bpy\text{-}MgTPP]^+$ complexes were studied using steady-state emission spectroscopy, which revealed solvent dependent quenching of the porphyrin emission, on irradiation of the porphyrin (560 nm). The emission spectrum of $[Re(CO)_3(pic)bpy\text{-}ZnTPP][OTf]$ was similar to that of the bpy-ZnTPP, however the emission spectrum of the Re–porphyrin complex is substantially reduced in intensity (by 85%). Further reductions in emission intensity were observed in THF. A similar trend was observed for the bpy-MgTPP analogue, with a reduction in emission intensity to only 2.5% of bpy-MgTPP. No evidence was obtained for the Re MLCT emission. At 77 K however, both rhenium–porphyrin complexes emit with a similar intensity to that of the Re(I) free system, indicating a possible electron-transfer process. Overall, these systems demonstrate a solvent-dependent quenching of the porphyrin-based emission on irradiation into the porphyrin Q bands. Furthermore, irradiation of these systems at low energies (560 nm) in TR-VIS studies results in spectral features indicative of a typical porphyrin S_1 state, with an absorption at 460 nm and stimulated emission at 610 nm. This S_1 state decays over 17 ps for $[Re(CO)_3(pic)bpy\text{-}MgTPP][OTf]$ and 24 ps for $[Re(CO)_3(pic)bpy\text{-}ZnTPP][OTf]$ in PrCN, with the transient species being strongly solvent dependent. TRIR studies led to the generation of bands at 2028, 2008, 1900 cm^{-1}, following excitation of $[Re(CO)_3(pic)bpy\text{-}MgTPP][OTf]$ (ν_{CO} 2033, 1931 cm^{-1}) at 600 nm. These bands are consistent with those obtained in the IR spectroelectrochemical studies, and are assigned to a charge separated (CS) excited state in which the Re(bpy)moiety is converted from a cation to a radical, and the metalloporphyrin is converted to a radical cation, $[Re^+(CO)_3(pic)bpy^{\bullet -}$ MgTPP]. The CS state decays to a vibrationally hot ground state species. Vibrational and electronic relaxation then occurs over 25–55 ps. It is suggested that this process occurs *via* a rapid charge separation mechanism and back electron transfer process resulting in solvent dependent quenching of the porphyrin emission.

2.1.3. Mixed charge transfer and ligand localized excited states

Rhenium(I) carbonyl systems may also exhibit ligand localized $^3\pi–\pi^*/^3$IL and ^{3}MLCT excited state character. Systems, which emit from both ^{3}MLCT and ^{3}IL states were first reported by Wrighton and co-workers [31] for the series of complexes $[Re(CO)_3(3\text{-bopy})_2L]$ and $[Re(CO)_3(4\text{-bopy})_2L]$, where bopy = 3-benzoylpyridine or 4-benzoylpyridine and L = Cl. Excitation of $[Re(CO)_3(3\text{-bopy})_2Cl]$ and $[Re(CO)_3(4\text{-bopy})_2Cl]$ at room temperature, resulted in broad structureless emission bands at 546 and 600 nm respectively which are assigned to a ^{3}MLCT state. For the 4-bopy derivative, lowering the temperature to 77 K results in a blue shift of the emission maxima, an increase in emission intensity and an increase in the excited state lifetime. Furthermore, the emission band was resolved into two components, with lifetimes of 18 and 1400 μs. The short-lived component was assigned to a ^{3}MLCT state, while the longer lived component was attributed to a ^{3}IL state of the 3-bopy ligand. The analogous systems $[Re(CO)_3(4\text{-bopy})_2Cl]$ and $Re(CO)_3(bpy)(4\text{-bopy})]^+$ have also been recently studied [32]. The lowest lying excited state of $[Re(CO)_3(4\text{-bopy})_2Cl]$ was assigned as ^{3}MLCT (Re(d) → π*(4-bopy) in character based on time-resolved visible absorption (TA) and time-resolved resonance Raman (TR^3) studies. While, the lowest lying excited state of $[Re(CO)_3(bpy)(4\text{-bopy})]^+$ was also found to be ^{3}MLCT in character, time-resolved infrared (TRIR) studies suggest that the excited electron density remains localized on the bpy ligand with no involvement of the 4-bopy ligand, thus giving an excited state with Re(d) → π*(bpy) character. More recently, the analogous 2-benzoylpyridine complex *fac*-$[Re(CO)_3(2\text{-bopy})Cl]^+$ has also been studied by UV–vis spectroscopy and density functional theory calculations [33]. Time-dependent density functional theory calculations show that the low energy absorption band at 466 nm, originates largely from the HOMO-1 → LUMO transition, with the HOMO-1 delocalized on the $Re(CO)_3Cl$ moiety, and the LUMO centred on the bopy ligand. Hence the HOMO-1 → LUMO transition has mixed Re → bopy (MLCT) and Cl → bopy (LLCT) character. Many systems of the type $[Re(CO)_3(s\text{-phen})Cl]$, where *s*-phen represents a methyl substituted 1,10-phenanthroline ligand, have been extensively studied [34]. In room temperature solution complexes of this type emit from a ^{3}MLCT state. However, in 77 K glasses some display a single emission band while others display dual emission. Where the latter is the case the two emitting states are often energetically similar and show extensive vibrational structure on the high-energy side of each band. The extent of the vibrational structure is dependent on the nature of the phenanthroline ligand. At 77 K the excited state lifetimes of all of the methyl substituted phenanthroline complexes studied displayed biexponential decays as shown in Table 2. The long-lived component is very similar to the $^3\pi–\pi^*$ emission characteristic of the uncoordinated phenanthroline ligand and a $^3\pi–\pi^*$ band observed for the similar $[Rh(s\text{-phen})_3]^{3+}$ species [35]. The long-lived component is temperature and solvent independent while the shorter lived component is dependent on temperature, solvent polarity and the nature of the polypyridyl ligand. The $^3\pi–\pi^*$ decay times are *ca.* four orders of magnitude shorter than those of the protonated ligands. This decrease is attributed to mixing with a ^{1}MLCT state through spin-orbit coupling.

Table 2
Measured decay times of the emissive states of $Re(CO)_3(s\text{-phen})Cl$ complexes at 77 K

Ligand	τ (μs)	
	$^3\pi–\pi^*$	^{3}MLCT
4,7-Me_2phen	135	12.8
Me_4phen	175	13.2
5,6-Me_2phen	279	9.1

The photophysical properties of acetylide and gold(I) acetylide derivatives of a $[Re(CO)_3(phen)Cl]$ complex possessing mixed ^{3}MLCT and ^{3}IL excited state character have also been investigated [36]. The complexes $[Re(phen–C≡C–AuPPh_3)(CO)_3Cl]$ and $[Re(phen–C≡C–AuH(CO)_3Cl]$ have been studied using transient absorption, room temperature and 77 K time-resolved photoluminescence, and time-resolved infrared (TRIR) spectroscopy. The room temperature excited state decay of $[Re(phen–C≡C–H(CO)_3Cl]$ was found to be MLCT in character, while on cooling to 77 K a lower lying excited state with ^{3}IL character, localized on the polypyridyl ligand, was observed. In contrast, the Au coordinated analogue exhibited more complex excited state behaviour with a mixed MLCT (Re-phen) and ^{3}IL excited state decay character observed at room temperature. However, as previously observed for $[Re(phen–C≡C–H(CO)_3Cl]$ at 77 K the excited state is predominantly ^{3}IL in character. Furthermore, time resolved infrared studies carried out on $[Re(phen–C≡C–AuPPh_3(CO)_3Cl]$ in $CHCl_3$, indicate formation of a transient species at higher energy than the parent complex, which typically suggests a Re-based MLCT excited state process. The authors suggest that further weaker transient absorption, also observed, may be due to a ^{3}IL excited state. Similarly, for $[Re(phen–C≡C–H(CO)_3Cl]$, irradiation at 355 nm resulted in the formation of a red-shifted transient species indicative of a Re-based MLCT state. These results confirm that the excited state behaviour of these complexes consists of both MLCT and ^{3}IL excited states in thermal equilibrium.

Recently, the photoinduced structural changes in *fac*-$[Re(CO)_3(phen)(stpy)]^+$, where stpy is 4-styrylpyridine, have been investigated both in solution and solid films [37]. Irradiation at 365 nm of *fac*-$[Re(CO)_3(phen)(stpy)]^+$ in CH_3CN solution and in a PMMA (poly(methyl methacrylate)) polymer film resulted in both cases in approximately 50% *trans*–*cis* isomerization of the coordinated styrylpyridine moiety with concomitant intense emission. This emission observed on formation of the *cis*-isomer is due to a change in the lowest lying excited state character to a ^{3}MLCT state. Conversely for the *trans*-isomer $[Re(CO)_3(phen)(t\text{-}stpy)]^+$, the ^{3}IL state responsible for isomerization is lower in energy than the ^{3}MLCT state, thus deactivation to the ground state takes place via the ^{3}IL isomerization pathway. The low dihedral angle in the *trans*-styrylpyridine ligand, allows for significant π interactions between the pyridyl and benzyl rings. However, in the *cis*-isomer this is severely reduced. As a result of the destabilization of the $^3IL_{c\text{-stpy}}$ state the $^3IL_{t\text{-stpy}}$ state is higher in energy than the emissive ^{3}MLCT state. The assignment of this ^{3}MLCT state as a Re(d) → π* (phen) state is based on comparison with the results obtained in analogous studies on *fac*-[Re(CO)$_3$(phen)(TFMS)] (TFMS = trifluoromethanesulfonic acid) under similar conditions. As a consequence of the rigidochromic effect the energy of the ^{3}MLCT state increased as the rigidity of the system increased. In particular, the emission spectrum of *fac*-$[Re(CO)_3(phen)(c\text{-}stpy)]^+$ recorded in EPA (diethyl ether–isopentane–ethanol, 5:5:2) at 77 K resembles the phenanthroline ligand in a rigid medium. This suggests that under these conditions of temperature and rigidity the $^3IL_{phen}$ and ^{3}MLCT state may become energetically similar or that complete population inversion may have occurred resulting in the previously higher energy ^{3}IL state becoming the lowest lying excited state. This effect, which has been previously observed [38], may have potential uses in the development of photochemical optical devices [39]. The ultrafast excited state dynamics of the 2,2′-bipyridyl analogues, *fac*-$[Re(CO)_3(t\text{-}stpy)(bpy)]^+$ and *fac*-$[Re(CO)_3(t\text{-}stpy)_2]$, have also been recently studied and found to possess both ^{3}MLCT and ^{3}IL character [40]. Optical excitation of the ^{1}MLCT absorption band of *fac*-$[Re(CO)_3(t\text{-}stpy)(bpy)]^+$ results in population *via* intersystem crossing over *ca.* 0.2 ps to a vibrationally hot Re(d) → bpy(π*) ^{3}MLCT excited state. This vibrationally hot triplet state, which is characterized by broad carbonyl bands, cools and decays over 3.5 ps *via* an intramolecular energy transfer process to form a ^{3}IL with a *trans*-stpy geometry. The fast decay rate suggests complete conversion from the ^{3}MLCT state to the ^{3}IL state. The IL state undergoes a ∼90° rotation about the C═C bond (11 ps), to form an excited state species with perpendicular orientation of the pyridine and phenyl rings. This state decays to the ground state, and isomerizes on the ns timescale as previously observed for $[Re(CO)_3(bpe)(bpy)]^+$[41], (bpe = 2-bis(4-pyridyl)ethylene)[41]. Thus coordination of the *trans*-4-styrylpyridine moiety allows for population of the reactive ^{3}IL state via ISC from the initially formed ^{3}MLCT state. The excited state dynamics of a similar system, *fac*-$[Re(CO)_3(papy)(bpy)]^+$, where the *trans*-4-styrylpyridine unit has been replaced by a *trans*-4-phenylazopyridine (papy) unit has also been reported [42]. The structure of *fac*-$[Re(CO)_3(papy)(bpy)]^+$ and the *trans*-4-strylpyridine analogue *fac*-$[Re(CO)_3(stpy)(bpy)]^+$ are shown in Fig. 3.

Irradiation of the analogous system *fac*-$[Re(papy)(CO)_3(bpy)]^+$ at 350 nm results in *trans* → *cis* isomerization of the papy ligand [42,43]. As is observed in many stilbene systems, isomerization to form the *cis*-isomer also switches on the emission, presumably *via* a ^{3}MLCT state. TRIR spectroscopic studies of *fac*-$[Re(CO)_3(papy)_2Cl]$ and *fac*-$[Re(papy)(CO)_3(bpy)]^+$ indicate that both complexes share a common lowest lying excited state, which are populated by two very different mechanisms. As indicated in Scheme 1 visible irradiation of *fac*-$[(Re(CO)_3(papy)_2(Cl)]$ populates both the ^{1}ππ* (papy) and ^{1}MLCT (papy) states, which rapidly undergo ISC to the ^{3}nπ* state. This is in contrast to previous studies on similar complexes where the ^{3}MLCT state was populated following ISC from the ^{1}ππ* and ^{1}MLCT states [44,45]. It may be the case that, either the ^{1}MLCT (papy) state is in fact populated, but decays too quickly to be measured, or that population of this state is circumvented by faster ISC to populate the ^{3}nπ* state *via* the ^{1}ππ* and ^{1}MLCT states. In the case of *fac*-$[Re(CO)_3(papy)(bpy)]^+$, irradiation results in population of the ^{1}ππ* (papy), ^{1}MLCT (papy) and ^{1}MLCT (bpy) states, which then undergo ISC to populate both the ^{3}nπ* and ^{3}MLCT state (Scheme 2). This is similar to the mechanism observed for *fac*-$[(Re(CO)_3(papy)_2)(Cl)]$. However, the ^{3}MLCT state, also populated by ISC, is formed vibrationally "hot".

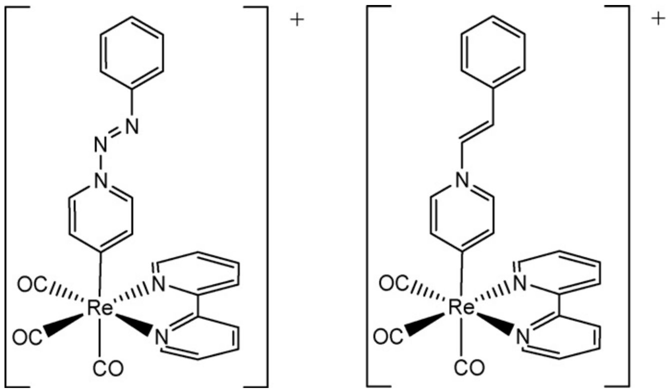
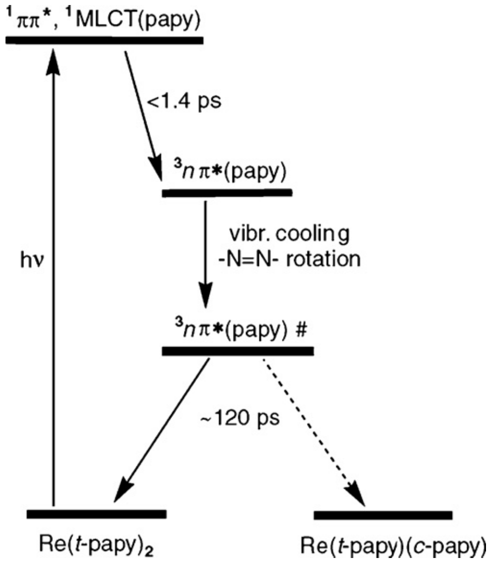
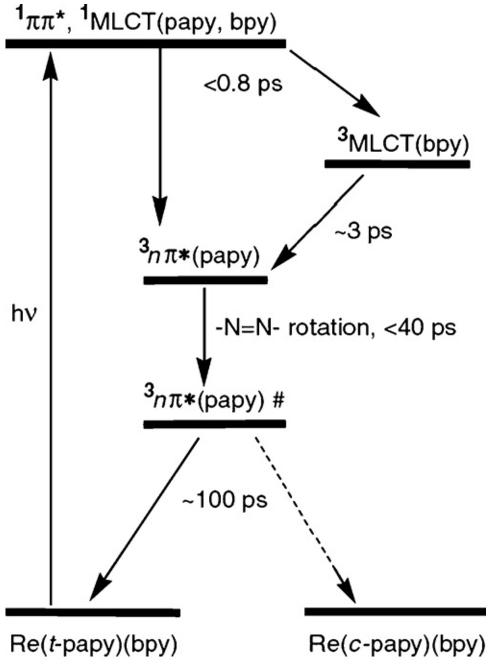


Fig. 3. Structures of *fac*-$[Re(CO)_3(papy)(bpy)]^+$ and *fac*-$[Re(CO)_3(stpy)(bpy)]^+$ [40,42].

This state cools and undergoes solvent relaxation as suggested by a shift in the IR spectrum. This ^{3}MLCT (bpy) state then undergoes interconversion (IC) to the ^{3}nπ* state. Overall, this may be viewed as charge transfer from the $^*Re(CO)_3(bpy)$ moiety to the papy ligand. For both complexes, the populated ^{3}nπ* state results in narrowing and a red-shift of the higher energy CO band over time. This change in CO band position is rationalized in terms of rotation about the



Scheme 1. Proposed excited state behaviour of *fac*-$[(Re(CO)_3(papy)_2(Cl)]$. Reproduced from [42] with permission.



Scheme 2. Proposed excited state dynamics of *fac*-[Re(CO)$_3$(papy)(bpy)]$^+$. Reproduced from [42] with permission.

central N=N bond, which removes the planarity of the complex and decouples the excited N=N–Ph unit. This is then expected to lead to a twisted ground state geometry, which will then return to either the *trans* and/or the *cis* isomer. This process occurs in 120 ps for *fac*-[(Re(CO)$_3$(papy)$_2$Cl] and 100 ps for *fac*-[Re(CO)$_3$(papy)(bpy)]$^+$, and is similar to that observed for similar styrylpyridine systems [37] where sub-ps ISC from the singlet excited state to the triplet state occurs, and is followed by the formation of an intermediate *via* partial rotation about the N=N bond and then slower ISC to either the *cis*- or *trans*-ground state geometry. However, in the case of the papy systems this process occurs approximately 200 times faster.

A recent review by Murakami-Iha and co-workers [44] has focused on further examples of photo-induced *trans* → *cis* isomerization reactions of rhenium complexes of the type, *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$. Irradiation of complexes of the type *fac*-[Re(CO)$_3$(NN)(*trans*-L)]$^+$, where NN = 1,10-phenanthroline, 5-chloro-1,10-phenanthroline (Cl-Phen), 4,7-diphenyl-1,10-phenanthroline (ph$_2$phen) or dipyrido[3,2-*a*:2′,3′-*c*]phenazine and L = 2-bis(4-pyridyl)ethylene (bpe) or 4-styrylpyridine, in acetonitrile solution results in spectral changes in the UV–vis spectrum, which are assigned to photoinduced *trans* → *cis* isomerization. The nature of either the bidentate or L ligand used has a profound effect on the quantum yield for isomerization. Following irradiation at 313 nm of a *trans*-bpe complex where NN = phen, the quantum yield, $\Phi_{313\,\mathrm{nm}} = 0.41$ while it is reduced to 0.19 where NN = dppz. This shows a less efficient sensitization of the *trans*-bpe triplet IL excited state in the dppz complex compared to the phen complex. This fact has been used to modulate the energy of the MLCT or intraligand excited states. Further monitoring of the photoinduced isomerization of *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ has been undertaken using TRIR spectroscopy [45]. This study shows that in *fac*-[Re(CO)$_3$(phen)(*trans*-bpe)]$^+$ the lowest lying excited state is characterized by a ^{3}IL ($^3\pi \rightarrow \pi^*$) transition, with electron density localized on the *trans*-bpe ligand. It is this excited state which is responsible for *trans*–*cis* isomerization. This ^{3}IL state decays to the parallel triplet excited state (^{3}p*) [46] of the *trans*-bpe ligand with a lifetime (τ) of 28 ± 1 ns, at a rate (k) of $3.6 \times 10^7\ \mathrm{s}^{-1}$. This suggests that the ^{3}p* excited state is formed by intramolecular sensitization ^{1}MLCT, ^{1}IL → ^{3}MLCT → ^{3}IL → ^{3}p* and that it is the ^{3}IL state which is the immediate precursor leading to *trans*–*cis* isomerization [40].

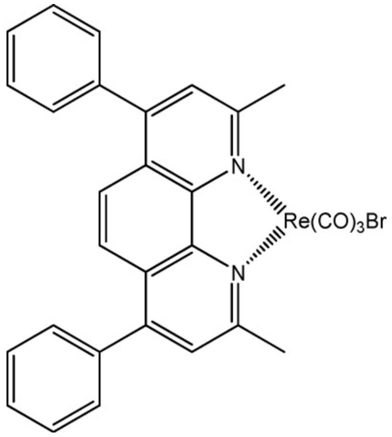


Fig. 4. Molecular structure of Re[(DDPA)(CO)$_3$Br] [47].

Recently Li et al. demonstrated that Re(CO)$_3$–phenanthroline complexes show great promise as potential materials for high-efficiency organic light emitting diodes (OLED's) [47]. The Re(I) bipyridyl complex [Re(CO)$_3$(DDPA)Br], where DDPA = 2,9-dimethyl-4,7-diphenyl-1,10-phenathroline) was employed in a 4,4′-*N*,*N*′-dicarbazole-biphenyl host matrix as an emissive dopant for the fabrication of OLED devices. This system demonstrated high electroluminescence efficiency (21–8 cd/A and luminescence 8315 cd/cm^2). The authors attribute this high performance to the structure (Fig. 4) of the [Re(CO)$_3$(DDPA)Br], complex and the high electron mobility of the complex.

The luminescence properties of the systems [Re(CO)$_3$(N–N)(btpz)] (N–N = bpy or phen, and btpz = 1,2-bis(tetrazol-1-yl)propane) were studied in both CH$_2$Cl$_2$ and CH$_3$CN solution as well as in thin films [4]. As shown in Table 3 excitation of either system, in CH$_2$Cl$_2$ or CH$_3$CN solution, of the π–π* or MLCT absorption bands produced emission bands at 571 and 568 nm, while in the solid state these emission maxima are blue shifted to 525 and 544 nm, respectively. These bands are assigned as arising from ^{3}MLCT phosphorescence based on favourable comparison with the parent halide complexes [Re(CO)$_3$(phen)Br] and [Re(CO)$_3$(bpy)Br], where ^{3}MLCT bands were observed in the range 620–640 nm [48]. The observed blue shift of the emission maximum compared to the halide parent systems is due to the presence of the btpz ligand, which reduces the Re(d$_\pi$) orbital energy, thereby producing a higher energy MLCT transition. The blue shift of the emission maxima observed for solid-state phosphorescence suggests a rigidochromic effect [1]. The excitation spectra for both [Re(CO)$_3$(N–N)(btpz)] systems are also superimposable with the recorded absorption spectra, suggesting that the major emitting state (^{3}MLCT) originates from the corresponding

Table 3
Photophysical data of [Re(CO)$_3$(N–N)(btpz)] [4]

Complex	Medium	λ_{em} (nm)	Φ_{em} (air)	Φ_{em} (deaerated)
N–N=bpy	CH$_2$Cl$_2$	571	1.9×10^{-3}	3.3×10^{-3}
	CH$_3$CN	573	2.8×10^{-3}	3.8×10^{-3}
	Solid	525	–	–
N–N=phen	CH$_2$Cl$_2$	568	4.1×10^{-3}	2.2×10^{-2}
	CH$_3$CN	571	1.1×10^{-2}	4.1×10^{-2}
	Solid	544	–	–

electronic excited state. Furthermore, the heavy atom effect of the Re atom allows efficient relaxation, *via* ISC, of the upper excited state to efficiently relax to the emitting spin-forbidden ^{3}MLCT state.

The excited state lifetimes of both systems also suggests an emissive excited state possessing ^{3}MLCT character. [Re(CO)$_3$(bpy)(btpz)] exhibits dual emission with two exponential decays of lifetimes of 1.56 μs (92%) and 0.51 μs (8%). Similarly [Re(CO)$_3$(phen)(btpz)] also exhibits a biexponential decay with lifetimes of 1.39 μs (87%) and 0.44 μs (13%). Such multi-exponential decay kinetics indicates the existence of two emissive excited states with comparable energies [49].

It is known that complexes of the type [Re(CO)$_3$(NN)L] typically possess an excited state with ^{3}MLCT or mixed ^{3}MLCT/^{3}ILCT character. Recently, Vlček and co-workers [50] have synthesized a number of phosphido- and amido-based rhenium complexes [Re(CO)$_3$(ER$_2$)(bpy)], where ER$_2$ = NHPh, NTol$_2$ or PPh$_2$ (Tol = 4-methylphenyl). The electronic absorption spectra of these systems in THF display a weak broad absorption band in the range 590–720 nm. DFT studies suggest this electronic absorption band is solely due to a HOMO–LUMO transition, ER$_2$ → bpy LLCT. These systems are substantially different from typical Re(I) systems containing halide or N-donor ligands as charge transfer occurs from a largely ligand-based molecular orbital rather than the Re-L–π antibonding which is typically observed. TRIR studies of these systems in THF solution further suggest a largely ligand-based LLCT excited state, as only a very minor shift in the position of the ν_{CO} frequencies is observed. A large shift typically indicating a significant involvement of a MLCT excited state. Furthermore, these studies indicate population of this ^{3}LLCT state on the femtosecond timescale by ISC from the initially populated (within 2 ps of excitation) ^{1}LLCT and ^{1}LLCT/MLCT states. The ^{3}LLCT state is formed initially "vibrationally hot", with the excess energy dissipated *via* internal and solvent relaxation pathways. The "relaxation" is evident in the shift of the ν_{CO} frequencies following relaxation and the dependence of the excited state lifetime on the probe wavenumber. This "vibrational cooling" is however notably slower than that typically observed for other Re(I) complexes, and the authors infer that an intramolecular conformational change is involved. It is suggested that this ^{3}LLCT state consists of a coordinated aminyl or phosphonyl radical cation ^{3}[Re(ER$_2^{\bullet+}$)(CO)$_3$(bpy$^{\bullet-}$)].

The chelating ligand N–N refers to polypyridine ligands in this review, however, novel chelating ligands based on the 4-(2-pyridyl)-1,2,3-triazole motif have been recently developed by Obata et al. [51]. A number of 4-(2-pyridyl)-1,2,3-triazole derivatives (Fig. 5) were synthesized *via* the well known "click chemistry" involving Cu(I)-catalysed 1,3-dipolar cycloaddition reactions between an azide and a terminal alkyne developed by Sharpless and co-workers [52]. This method has also been previously used to introduce a binding site into biomolecules for rhenium or technetium coordination [53]. The corresponding [Re(CO)$_3$Cl] complexes were synthesized and their photophysical properties studied. The complex [Re(CO)$_3$Cl(Bn-pyta)] (Bn-pyta = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole) was found to be highly emissive, possessing an emission band at 633 nm in CH$_3$CN solution, blue shifted by almost 100 nm compared to [Re(CO)$_3$Cl(bpy)]. At 77 K in MeTHF the excited state lifetime of [Re(CO)$_3$Cl(Bn-pyta)] (τ = 8.90 μs) is also considerably longer than that observed for [Re(CO)$_3$Cl(bpy)] (τ = 3.17 μs) under the same conditions.

Overall, the blue shifted absorption and luminescence spectra, high fluorescence quantum yield and excited state lifetime demonstrates that Bn-pyta acts as an electron-rich bipyridine mimic. Such luminescence properties may allow for the employment of Re-pyta complexes in time-gated imaging.

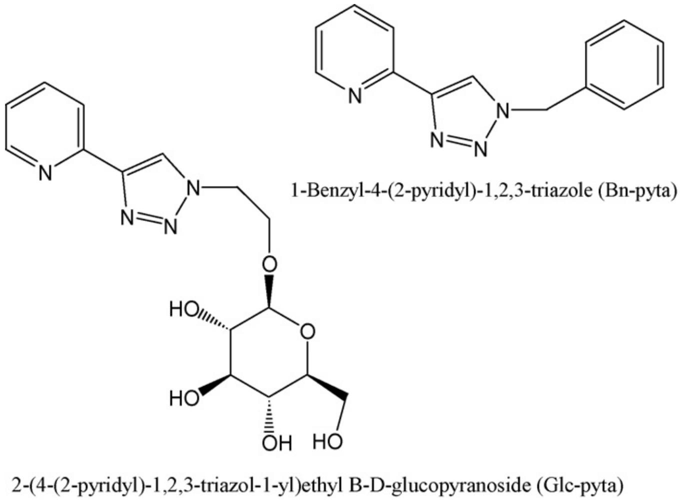


Fig. 5. Structures of selected 4-(2-pyridyl)-1,2,3-triazole derivatives synthesized [5].

3. Dinuclear ruthenium(II)–rhenium(I) complexes

3.1. Photophysical properties and applications

Control of the photophysical, photochemical, and electrochemical properties, of transition metal complexes has attracted much interest because of the applications of these complexes in molecular devices, photonics, artificial photosynthesis, or in photocatalysis. There has been considerable interest in the study of photoinduced electron and energy transfer between components in supramolecular systems due to the potential development of devices capable of performing light-induced functions. [54] This section focuses on the photophysical properties of heteronuclear systems based on Ru(II)/Re(I), and their applications, such as CO$_2$ reduction. The synthesis of the compounds discussed in this section is similar to that discussed previously for the mononuclear rhenium(I) carbonyl compounds.

In each of the complexes in Fig. 6, the bridging ligand is a conjugated system with a relatively small intermetallic distance between the metal centres. The photophysical and electrochemical

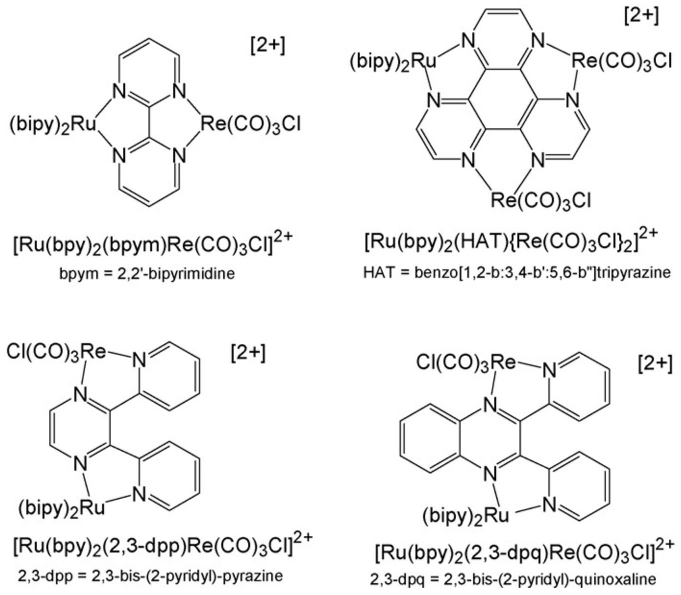


Fig. 6. Examples of Ru(II)/Re(I) heteronuclear complexes [55–57].

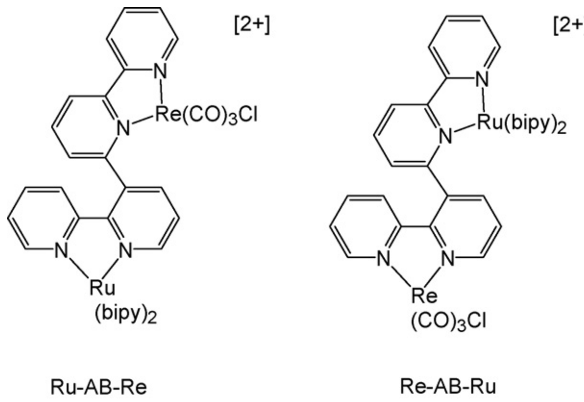


Fig. 7. Heterodinuclear Ru(II)/Re(I) complexes of the asymmetric quaterpyridine ligand, AB [58].

properties of the heteronuclear complexes shown have been studied [55–57]. For each of these complexes, the lifetime obtained, indicates that the emission originates from a ruthenium charge transfer excited state.

Ward and co-workers have synthesized a number of Ru(II)/Re(I) complexes containing the asymmetric ligand 2,2′:3′,2″:6″,2‴-quaterpyridine (AB) [58]. This quaterpyridine ligand is a binucleating ligand with two bpy-type binding sites, A and B. The interesting feature of this ligand is that these sites, A and B, are both sterically and electronically inequivalent. Chelating site B is more sterically hindered when compared to site A. The structures of two of the complexes synthesized are shown in Fig. 7. In both cases the first metal fragment is preferentially coordinated to the sterically less hindered site (labelled A). When one equivalent of the metal is reacted with the ligand, the metal only binds to site A, only and under more extreme conditions, does a second metal co-ordinate at site B. In both Ru–AB–Re and Re–AB–Ru, the metal fragments are photochemically and redox active. Both complexes exhibit site-dependent absorption, luminescence and electrochemical properties. The luminescence state of the Ru–AB–Re complex at room temperature is Ru-based (i.e. Re → Ru energy transfer), as the emission and photochemical properties are similar to the Ru–AB and Ru–AB–Ru systems studied. However, in the Re–AB–Ru complex, luminescence is centred on the Re moiety (i.e. Ru → Re energy transfer), based on the similarity of the lifetimes to those of the Re–AB and Re–AB–Re complexes.

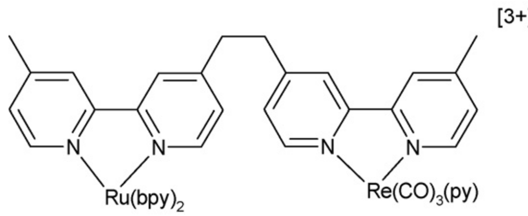


Fig. 8. The mixed-metal complex $[Ru(bpy)_2(bpyen)Re(CO)_3(py)]^{3+}$, where bpyen = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane [59].

When the mixed-metal complex $[Ru(bpy)_2(bpyen)Re(CO)_3(py)]^{3+}$ (Fig. 8) was excited at 355 nm in dichloromethane, the complex was found to emit at both 610 nm (Ru) and 540 nm (Re) [59]. The emissions observed at these wavelengths were assigned as ^{3}MLCT in origin. Communication *via* the bridging ligand, bpyen was poor, but was sufficient to allow Ru → Re energy transfer between the metal centres. The dual emission observed in $[Ru(bpy)_2(bpyen)Re(CO)_3(py)]^{3+}$ differs from the pre-

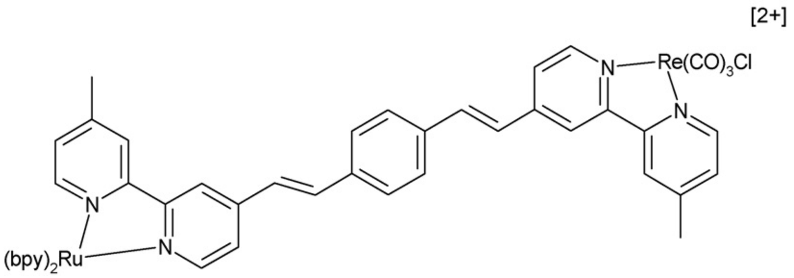


Fig. 9. The heteronuclear Ru(II)/Re(I) complex $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$, where dstyb is the bridging ligand 1,4-bis[2-(4′-methyl-2,2′-bipyridyl-4-yl)ethenyl]benzene [60].

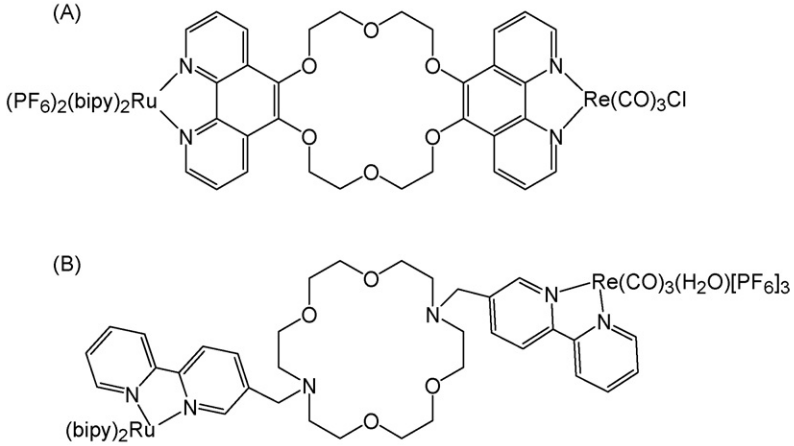


Fig. 10. The heteronuclear Ru(II)/Re(I) complexes with bridging ligands 18-crown-6 bridge (A) and diaza-18 crown-6 (B) macrocyles [61].

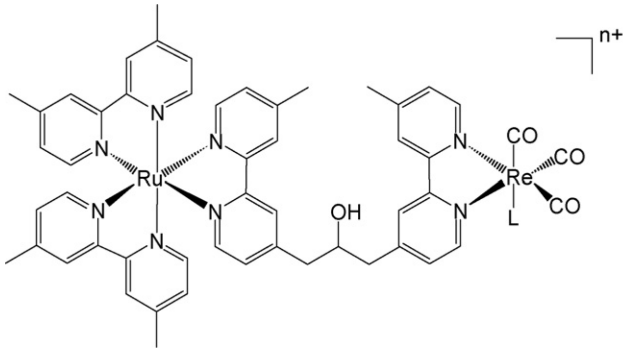


Fig. 11. Structure of the photocatalysts for CO_2 reduction based on Ru(II)–Re(I) binuclear complexes (L = $P(OEt)_3$ or Cl^-) [64].

vious examples of heteronuclear Ru(II)/Re(I) complexes as all these complexes exhibited emission originating from a single metal centre.

Encinas et al. have also reported dual emission, in this case for $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$ (Fig. 9) [60]. The luminescence spectrum of this compound at room temperature shows two distinct emission features at 621 and 695 nm. The band maximum at 621 nm is attributed to emission from the ^{3}Ru → dstyb MLCT excited state, while the band at 695 nm is assigned to an intraligand transition (^{3}IL) from the bridging ligand, dstyb. Fast deactivation of the ^{3}MLCT is attributed to lack of rhenium(I)-based emission. By comparing the excitation spectrum of $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$ with the absorption spectra of $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$ and the mononuclear ruthenium complex $[Ru(bpy)_2(dstyb)]^{2+}$, at 77 K the authors established the relaxation pathways in the heteronuclear complex. Emission from the ^{3}IL(dstyb) state is sensitized by the rhenium-based absorption, and the ^{3}Ru → LCT emission is not directly sensitized by the rhenium-based absorption. They concluded that some of the light absorbed by the rhenium-based chromophore of $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$ is firstly transferred to the bridging ligand and then redistributed between the ^{3}IL(dstyb) and ^{3}Ru → dstyb CT levels. The overall excitation process of $[Ru(bpy)_2(dstyb)Re(CO)_3Cl]^{2+}$ involves an indirect Re → Ru energy transfer process mediated by the bridging ligand.

Photoinduced energy transfer has been reported by Ward and co-workers [61] for a complex which incorporates $[Re(bipy)(CO)_3Cl]$ and $[Ru(bipy)_3]^{2+}$ separated by an 18-crown-6 bridge (Fig. 10). Based on photophysical studies, and associated mononuclear complexes, photoinduced energy transfer from Re → Ru occurs with a rate constant of $1.9 \times 10^8\ s^{-1}$. This results in almost complete quenching of the Re(I)-based luminescence. At 77 K no luminescence from the Re(I)-based centre was detected. Both K^+ and Ba^{2+} salts were added to solutions of the Re–Ru dinuclear complex, with no effect on the photophysical properties, which is attributed to low association constants. The energy transfer rate in this study is of the same order of magnitude to that previously reported, for other dinuclear Re–Ru chromophores linked by diaza-18 crown-6 macrocyles [62]. At 77 K only Re → Ru energy transfer occurs with, $k_{en} = 2 \times 10^8\ s^{-1}$ in the absence of Ba^{2+}, whereas this value decreases to $7 \times 10^6\ s^{-1}$ in the presence of Ba^{2+}. In contrast at room temperature, no photoinduced energy transfer was observed, however electron transfer with $k_{el} = 1.2 \times 10^{10}\ s^{-1}$

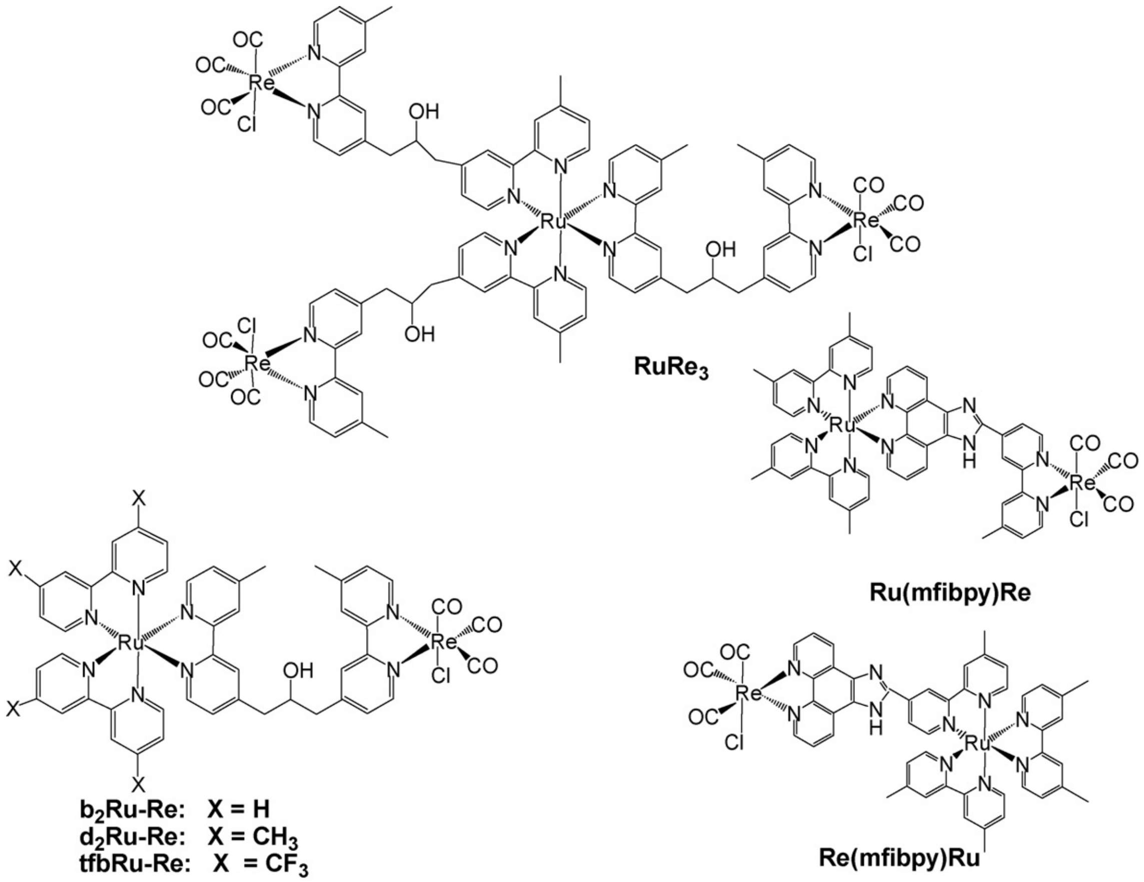


Fig. 12. Structure of the photocatalysts for CO_2 reduction based on Ru(II)–Re(I) bi- and tetranuclear complexes [65].

occurs in the absence of Ba^{2+}. Addition of Ba^{2+} to the solution inhibits electron transfer.

Sun and co-workers have prepared and investigated the photophysics of a freebase and zinc porphyrin-based triad with ruthenium bipyridyl and $[Re(CO)_3(bpy)Cl]$ units covalently attached [63]. A combination of electrochemical and photochemical studies indicated very weak electronic interactions in both the freebase and Zn-metallated multi-component system. The transient absorption spectra obtained following 532 nm excitation were typical of the porphyrin $^3(\pi-\pi^*)$ excited states with an intense absorption at 480 nm. A feature at 780 nm for the Zn-metallated porphyrin triad is attributed to mixing of the porphyrin $^3(\pi-\pi^*)$ excited states and the charge separated excited state from the porphyrin (π) to bpy (π^*). Emission from both the freebase and zinc–porphyrin triads, were reduced significantly when compared to tetraphenyl porphyrin (14-fold and 62-fold, respectively). This quenching is mainly attributed to electron transfer to the ruthenium unit as energy transfer is not thermodynamically feasible.

Ishitani and Furue recently reported an efficient photocatalyst for CO_2 reduction based on a Ru(II)–Re(I) binuclear complex, where metal centres are bridged using 1,3-bis(4-methyl-[2,2]bipyridinyl-4-yl)-propan-2-ol (see Fig. 11). The reaction is driven using visible light, with quantum yields (ϕ_{CO}) for CO formation of 0.21, and a turnover number (TN_{CO}) for CO production of 232, when one of the ligands coordinated to the rhenium site is $P(OEt)_3$ [64,65]. On replacing $P(OEt)_3$, with Cl^- the values decrease with values for $\phi_{CO} = 0.21$ and $TN_{CO} = 160$. A comparison of the absorption spectra of the dinuclear complexes with their mononuclear analogues, indicates that there is no strong interaction between the Ru(II) and Re(I) metal centres. The first reduction observed were those for the bridge in the range 1.59–1.78 V *vs.* $Ag/AgNO_3$, followed by reduction at the Ru site with $E_{1/2} = \sim 1.77$ V.

Previously the photocatalysts for CO_2 reduction based on Ru(II)–Re(I) bi- and tetra-nuclear complexes were reported [65]. Good photocatalytic activity was obtained for the tetra- and bi-Ru–Re complexes, with quantum yields of 0.120 and 0.093, respectively for CO formation, and turnover numbers of 170 and 240 for CO formation (Fig. 12). The photocatalytic properties of the supramolecules were influenced by both the bridging and peripheral ligands. In the absorption spectra for the mfibpy complexes (where the bridging ligand mfibpy = 4-methyl-4′-[1,10]phenanthroline-[5,6-*d*]imidazol-2-yl)bipyridine) weak bands were assigned to the bridging ligand, which indicates communication between the metal centres. These complexes demonstrated lower photocatalytic activity however, as did the peripheral bipy ligands with CF_3 attached. In contrast there is little communication across the 1,3-bis(4′-methyl-[2,2′]bipyridinyl-4-yl)propan-2-ol bridge for the bi- and tetra-complexes studied, but relatively high quantum yields and large turnover numbers for CO production were observed. The good photocatalytic activity for the $RuRe_3$ is attributed to intramolecular electron transfer from the one electron reduced species to the rhenium moiety.

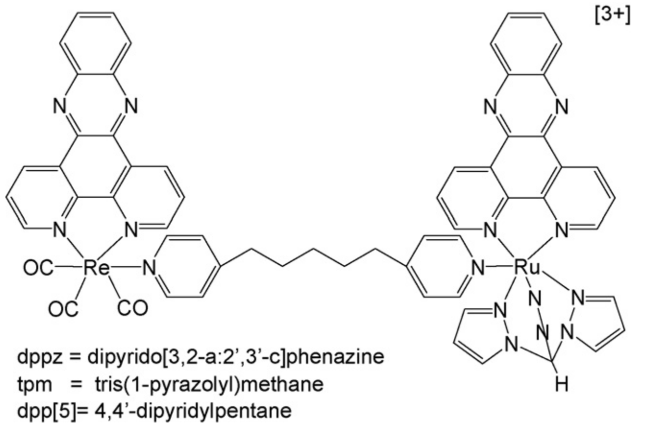


Fig. 13. Structure of the heterobimetallic Ru–Re dipyridophenazine complex [66].

Polypyridyl-based transition metal cations have proven to be excellent probes for the physical properties of DNA. Recently the DNA binding and cleavage properties of a hetero-dinuclear [66] complex $[\{Ru(tpm)(dppz)\}(\mu\text{-}dpp[5])\{fac\text{-}(CO)_3Re(dppz)\}]^{3+}$ (where dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine, tpm = tris(1-pyrazolyl)methane, dpp[5] = 4,4′-dipyridylpentane) have been reported (Fig. 13). The excited states of both metal centres were monitored independently, with the ns-TRIR and emission studies clearly demonstrating energy transfer from the Re(I) to Ru(II) centre. The complex binds to the DNA duplex, and displays DNA light switch and cleavage properties. The {Ru(dppz)} unit supplies the light-switch function and enhances the binding affinity of the {Re(dppz)} unit.

4. Conclusions

Rhenium(I) tricarbonyl complexes have been widely studied due to their luminescence properties and excited state reactivities. The rhenium(I) complexes discussed here have been studied for their energy and electron transfer properties, and it is the manipulation of the energy and electron transfer rate constants, between various states, that determines the suitability of the rhenium complexes for functions such as luminescent sensing, materials for supramolecular or optical devices, or in photoisomerization. Rhenium(I) tricarbonyl complexes with stilbene type ligands attached, undergo lower energy photoisomerization of the coordinated substrate due to efficient energy transfer sensitization. In recent years, dinuclear systems based on Re–Ru have grown in interest because of their photocatalytic properties and applications in the design of materials capable of carrying out light induced functions. It is clear that the choice of bridging ligand between the metal centres is critical to the application of the chosen system.

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