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Review

Ultrafast ligand-to-ligand electron and energy transfer in the complexes *fac*-$[\mathrm{Re^I(L)(CO)_3(bpy)}]^{n+}$

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This article is dedicated to the memory of Prof. D.J. Stufkens (University of Amsterdam) whose work has much contributed to our knowledge and understanding of organometallic photophysics and photochemistry.

Contents

Abstract

Depending on the ligands L and N,N (=polypyridine, α-diimine), the complexes $[\mathrm{Re(L)(CO)_3(N,N)}]^{n+}$ undergo different photophysical and photochemical processes. Herein, we compare the behavior of complexes with an electron-accepting ligand L = *N*-methyl-4,4′-bipyridinium ($\mathrm{MQ^+}$), isomerizable ligand L = *trans*-4-styrylpyridine (*t*-stpy), and L = *trans*-*N*-methyl-4,4′-dipyridiniumethylene ($\mathrm{Medpe^+}$), which can undergo either reduction, or isomerization, or both. In particular, we discuss the dynamics and mechanisms of (i) $\mathrm{NN^{\bullet-}} \rightarrow \mathrm{MQ^+}$ interligand electron transfer (*ILET*) from a ^{3}MLCT state of $[\mathrm{Re^I(MQ^+)(CO)_3(dmb)}]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine), (ii) intramolecular energy transfer from a ^{3}MLCT state of the $\mathrm{Re(CO)_3(bpy)}$ unit of $[\mathrm{Re}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$ to the intraligand ^{3}IL $\pi\pi^*$ state of the axial ligand *t*-stpy and its subsequent isomerization, and (iii) competition between charge and energy transfer/isomerization in $[\mathrm{Re^I(Medpe^+)(CO)_3(dmb)}]^{2+}$.

Optical excitation of $[\mathrm{Re^I(MQ^+)(CO)_3(dmb)}]^{2+}$ populates a Re → dmb ^{3}MLCT excited state $[\mathrm{Re^{II}(MQ^+)(CO)_3(dmb^{\bullet-})}]^{2+}$. Ultrafast $\mathrm{dmb^{\bullet-}} \rightarrow \mathrm{MQ^+}$ *ILET* follows, producing a Re → $\mathrm{MQ^+}$ MLCT excited state $[\mathrm{Re^{II}(MQ^\bullet)(CO)_3(dmb)}]^{2+}$. The *ILET* rate (8–18 ps, depending on the solvent) is much faster than predicted by conventional electron-transfer theories, being accelerated by a combination of large (ca. 130 cm^{-1}) electronic coupling through the $\mathrm{Re^{II}}$ atom and vibrational excitation of the ^{3}MLCT(dmb) precursor state. Irradiation of $[\mathrm{Re^I}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$ populates a Re → bpy ^{3}MLCT excited state, which converts into a ^{3}IL state of the *t*-stpy ligand with a 3.5 ps time constant. This ^{3}MLCT → ^{3}IL conversion amounts to an intramolecular energy transfer from the electronically excited chromophore $\mathrm{Re(CO)_3(bpy)^+}$ to the *t*-stpy ligand. The *t*-stpy ligand in the ^{3}IL state undergoes a 12 ps twist around the C═C bond to the perpendicular geometry, followed by further 18 ns twist to the ground state and the *cis* isomer. The same isomerization mechanism operates for $[\mathrm{Re^I(Cl)(CO)_3}(t\text{-stpy})_2]^+$ whose ^{3}IL state is populated directly. Excitation of $[\mathrm{Re^I(Medpe^+)(CO)_3(bpy)}]^{2+}$ leads to both Re → bpy and Re → $\mathrm{Medpe^+}$ MLCT states. A ps energy transfer to a ^{3}IL state follows, triggering rotation around the C═C bond. In contrast, the electron-acceptor character of the $\mathrm{Medpe^+}$ ligand prevails in $[\mathrm{Re^I(Cl)(CO)_3(Medpe^+)_2}]^{2+}$, where only a Re → $\mathrm{Medpe^+}$ ^{3}MLCT state is populated, which decays to the ground state with ca. 100 ps lifetime by a $\mathrm{Medpe^\bullet} \rightarrow \mathrm{Re^{II}}$ electron transfer.

Keywords: Rhenium; Carbonyl; Bipyridine; Charge transfer; Isomerization; Excited state; Photochemistry; Energy transfer; ILET; MLCT

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1. Introduction

The combination of diverse and tunable photoactivity with chemical stability and synthetic flexibility makes the complexes $[\mathrm{Re^{I}(L)(CO)_3(N,N)}]^{n+}$ (N,N = polypyridines, α-diimines) very attractive photosensitizers and probes, Fig. 1. They can be attached to proteins, incorporated into conductive polymers and molecular wires, liquid crystals, DNA, or linked with specific substrate-binding units either through the axial ligand L or by a judicious modification of the α-diimine ligand.

The chemical nature and bonding properties of the axial ligand L determine the character of the lowest excited state(s) of these complexes and, hence, their photochemical and photophysical properties [1]. Usually, the lowest excited state contains a predominant contribution from Re → N,N metal to ligand charge transfer (MLCT), which can mix with a L → N,N ligand-to-ligand charge transfer (LLCT), if L is a π-donor ($\mathrm{NCS^-}$, halides) [1–4]. On the other hand, axial ligands bound to Re by a strong σ-bond (alkyls, metal fragments) introduce a sigma-bond-to-ligand charge transfer (^{3}SBLCT) lowest excited state, which involves transfer of electron density from a Re-L σ-bonding orbital to the π^*(N,N) orbital [1,5–15]. For highly delocalized, large polypyridines N,N (some phenanthroline derivatives, dppz) and/or strongly electron-accepting L (isonitriles), the lowest allowed transition can be of a $\pi\pi^*$(N,N) intraligand, IL(N,N), character [1]. In rare cases, two of which will be discussed below, the lowest excited state is localized on the ligand L.

The axial ligand L can perform various chemical functions upon optical excitation of the $\mathrm{Re^{I}(CO)_3(N,N)}$ chromophore, whose MLCT excited state can be formulated as $\mathrm{Re^{II}(CO)_3(N,N^{\bullet-})}$. Thus, reducing ligands L (phenothiazine, tryptophane) can act as electron donors toward the $\mathrm{Re^{II}}$ atom, effectively quenching the ^{3}MLCT excited state [16–23]. Electron transfer from the $\mathrm{N,N^{\bullet-}}$ ligand to the ligand L, or energy transfer from the MLCT-excited $\mathrm{Re(CO)_3(N,N)}$ chromophore to a $\pi\pi^*$(L) state are also possible. These two processes, which can result in the reduction or isomerization of the axial ligand, respectively, are discussed herein and their mechanisms and dynamics compared. To this effect, we have investigated ultrafast excited state dynamics of three complexes of the type $[\mathrm{Re^{I}(L)(CO)_3(bpy)}]^{n+}$ where L is an electron acceptor *N*-methyl-4,4′-bipyridinium ($\mathrm{MQ^+}$), an isomerizable ligand *trans*-4-styryl-pyridine (*t*-stpy) or a ligand which combines both functions, *trans*-*N*-methyl-4,4′-bipyridiniumethylene $\mathrm{Medpe^+}$, see Fig. 2.

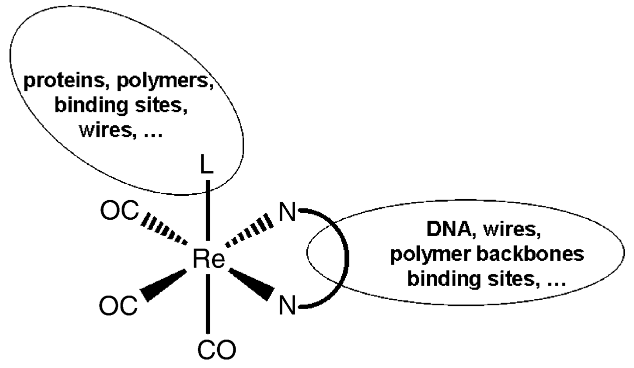

Fig. 1. Schematic structure of the $[\mathrm{Re^{I}(L)(CO)_3(N,N)}]^{n+}$ complexes. These structural units can be attached to biomolecules or incorporated into molecular devices through the axial ligand L or the equatorial α-diimine ligand N,N.

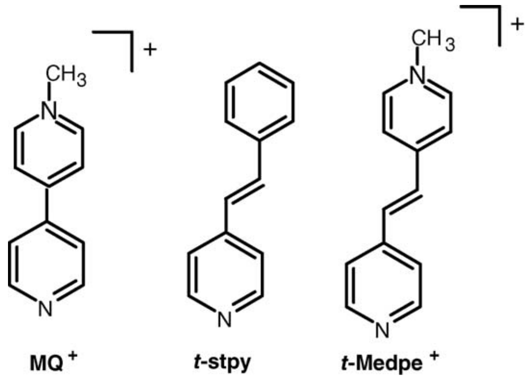

Fig. 2. Formulas of the ligands L used in this study.

2. Interligand electron transfer, ILET. The case of $[\mathrm{Re^{I}(MQ^+)(CO)_3(N,N)}]^{2+}$

Optical excitation (400 or 355 nm) of the complexes $[\mathrm{Re^{I}(MQ^+)(CO)_3(N,N)}]^{2+}$ (N,N = bpy, 4,4′-Me$_2$-2,2′-bpy (dmb), 4,4′-(NH$_2$)$_2$-2,2′-bpy) populates a Re → N,N ^{3}MLCT excited state (^{3}MLCT(dmb)), which can be formulated as $^*[\mathrm{Re^{II}(MQ^+)(CO)_3(N,N^{\bullet-})}]^{2+}$. A picosecond $\mathrm{N,N^{\bullet-}} \rightarrow \mathrm{MQ^+}$ electron transfer follows, producing $^*[\mathrm{Re^{II}(MQ^{\bullet})(CO)_3(N,N)}]^{2+}$. This species can be viewed as another ^{3}MLCT state originating in a Re → $\mathrm{MQ^+}$ charge transfer, further denoted ^{3}MLCT($\mathrm{MQ^+}$). The photo-behavior of $[\mathrm{Re^{I}(MQ^+)(CO)_3(dmb)}]^{2+}$, which has been studied in detail [24–29], is depicted in Fig. 3. Time-resolved visible absorption spectroscopy [28,29] has shown that *ILET* is an ultrafast process, whose rate has a surprisingly small solvent dependence [29], apparently only because of small driving-force ($-\Delta G^0$) variations with the solvent. The *ILET* time constant values range from 8 ps in MeCN to 18 ps in diglyme ($\mathrm{MeOCH_2CH_2OMe}$), where the driving-force values of 0.47 eV and 0.33 eV, respectively, were determined electrochemically. No correlation between the *ILET* rate and solvent reorganization energy or through-solvent electronic coupling was found. This effectively excludes the possibility that the electron transfer is mediated by solvent molecules placed between the two ligands. Instead, a superexchange mechanism, whereby the two ligands $\mathrm{MQ^+}$ and $\mathrm{dmb^{\bullet-}}$ are electronically coupled by $\mathrm{Re^{II}}$, was proposed, with a coupling constant of $\sim$130 cm^{-1} [29]. Importantly, *ILET* rates do not correlate with solvent relaxation times. Actually, in several of the solvents studied, the *ILET* rate considerably exceeds the solvent-controlled adiabatic limit. A simple analysis in terms of Marcus and Jortner–Bixon theories concluded that *ILET* in $[\mathrm{Re^{I}(MQ^+)(CO)_3(dmb)}]^{2+}$ is a (partly) adiabatic process, which is driven by intramolecular vibrations that are faster than solvent fluctuations [29]. This mechanism requires that the *ILET* precursor, that is the ^{3}MLCT(dmb) excited state,

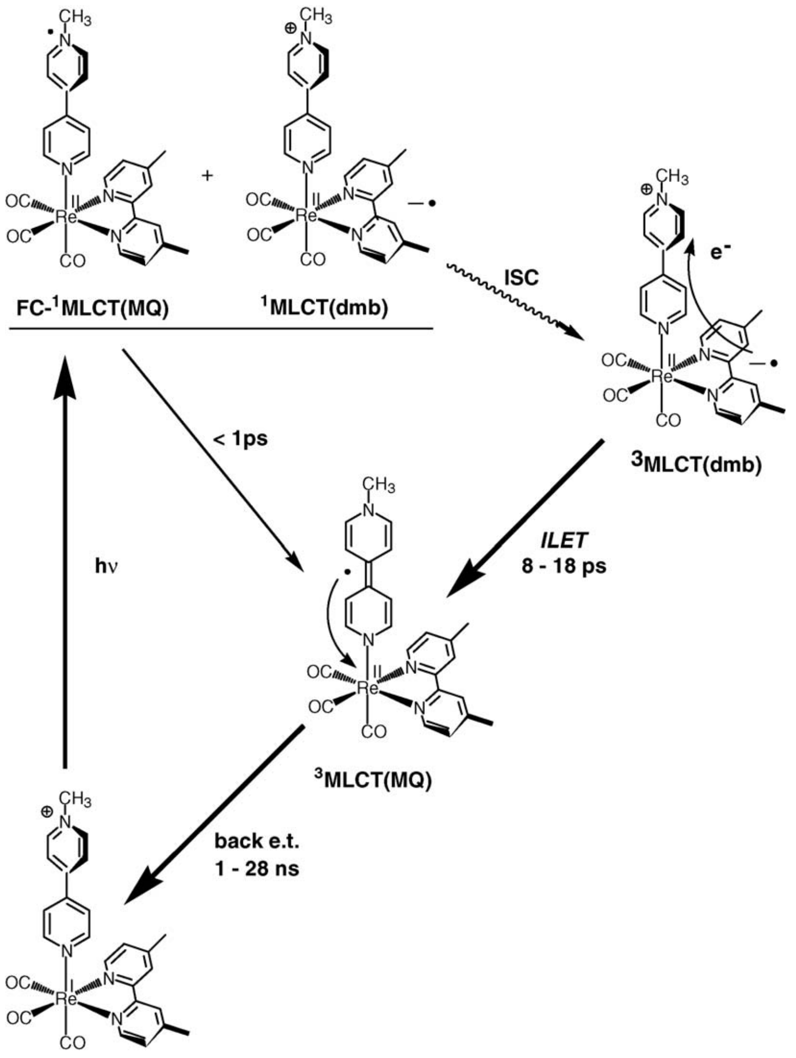

Fig. 3. Excited state dynamics of $[Re^I(MQ^+)(CO)_3(dmb)]^{2+}$. Optical excitation (400 nm) populates Franck–Condon ^{1}MLCT(MQ^+) and ^{1}MLCT(dmb) states, which both undergo intersystem crossing to the corresponding triplets. *ILET* occurs from ^{3}MLCT(dmb). It is a Marcus-normal process, accelerated by relatively strong electronic coupling through Re^{II} and by vibrational excitation of the precursor ^{3}MLCT(dmb) state [29]. The back reaction occurs as a $MQ^\bullet \rightarrow Re^{II}$ electron transfer. The time constant depends moderately on the solvent, in the range 1–28 ns. It is a Marcus-inverted process, accelerated by vibrational excitation of the product, that is the ground state $[Re^I(MQ^+)(CO)_3(dmb)]^{2+}$ [31].

is formed vibrationally excited. This vibrational excitation is provided by the energy released during intersystem crossing (ISC) from the optically populated ^{1}MLCT state to the ^{3}MLCT state. Irradiation at 400 nm excites a $[Re^I(MQ^+)(CO)_3(dmb)]^{2+}$ molecule 6000–7000 cm^{-1} above the zero-point energy of the ^{3}MLCT(dmb) state. This extra energy is released during the ISC and deposited into low-frequency, large-amplitude vibrational modes of the ^{3}MLCT(dmb) state. Activation of these modes, together with relatively strong electronic coupling, accelerates *ILET* into the ultrafast (picosecond) regime. (The initial vibrational excitation of the ^{3}MLCT state persisting for some 30 ps, was clearly demonstrated [30] for a model complex $[Re(4\text{-}Etpy)(CO)_3(dmb)]^+$ by observation of a time-dependent shift of excited state ν(CO) IR bands to higher frequencies, and an intensity increase of excited state Raman and near-UV absorption bands).

It is also interesting to examine the influence of the ligands on *ILET*. Variations in the diimine ligand N,N affect *ILET* mostly by changing the relative energetic positions of the ^{3}MLCT(N,N) and ^{3}MLCT(MQ^+) states. Thus, *ILET* was seen for N,N = dmb (8.3 ps in MeCN), bpy (~15 ps) or 4,4′-$(NH_2)_2$-2,2′-bpy (no rate reported) [25,28,29,32]. It does not occur in complexes with strongly electron accepting N,N ligands 4,4′-$(COOEt)_2$-2,2′-bpy [25] or $Pr^iN=CHCH=NPr^i$ (iPr-DAB) [32], whose presence stabilizes ^{3}MLCT(N,N) below ^{3}MLCT(MQ^+) [25,32]. Similarly, no *ILET* was seen for $[Re^I(4\text{-benzoylpyridine})(CO)_3(bpy)]^+$, whose Re → benzoylpyridine ^{3}MLCT state lies too high in energy [33]. Replacing the MQ^+ ligand by an analogous ligand PQ^+ has only a small effect. The complex $[Re^I(PQ^+)(CO)_3(bpy)]^{2+}$ (PQ^+ = *N*-phenyl-4,4′-bipyridinium undergoes *ILET* from its ^{3}MLCT excited state with a time constant of about 3 ps [32].

To undergo *ILET* upon excitation, the $[Re(L)(CO)_3(N,N)]^{n+}$ complex has to posses two distinct MLCT states originating in Re → L and Re → N,N CT excitations, denoted MLCT(L) and MLCT(N,N), respectively. Electronic coupling between the two ligands has to be strong enough to allow for fast electron transfer, but still relatively weak to keep the excited electron localized. The relaxed ^{3}MLCT(L) state has to lie energetically below the optically populated ^{1}MLCT(N,N) state and the corresponding ^{3}MLCT(N,N) state. To make *ILET* experimentally observable, it is advantageous if the optical transition to the ^{1}MLCT(L) state has a smaller oscillator strength and/or lies at higher energy than the transition to ^{1}MLCT(N,N). In the particular case of $[\mathrm{Re^I(MQ^+)(CO)_3(dmb)}]^{2+}$, the oscillator strengths of the transitions to ^{1}MLCT(MQ$^+$) and ^{1}MLCT(dmb) are comparable, the former occurring at a slightly higher energy [28]. The extensive structural reorganization of the MQ$^+$ ligand upon reduction, whereby the twisted MQ$^+$ ligand [34] changes into a planar quinoidal MQ$^\bullet$ radical (Fig. 3), stabilizes the relaxed ^{3}MLCT state well below the ^{1}MLCT(dmb) and ^{3}MLCT(dmb) states, making *ILET* energetically downhill.

3. Intraligand *trans* → *cis* isomerization upon Re → bpy MLCT excitation. The case of $[\mathrm{Re^I}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$

Trans-styrylpyridine (*t*-stpy, Fig. 2) is a stilbene-like ligand that undergoes photochemical *trans* → *cis* isomerization upon UV irradiation into its $\pi\pi^*$ absorption band. This photoreactivity is retained upon coordination to the Re atom in the complexes $[\mathrm{Re^I(Cl)(CO)_3}(t\text{-stpy})_2]$ or $[\mathrm{Re^I}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$ and their analogues [35–42]. A combined femto/picosecond time-resolved visible absorption, resonance Raman and IR spectroscopic study [42] of $[\mathrm{Re^I(Cl)(CO)_3}(t\text{-stpy})_2]$ has revealed that ligand photoisomerization occurs from a *t*-stpy localized ^{3}IL state of a $^3\pi\pi^*$ character. This contrasts photoisomerization of the free ligand [43], which occurs on a singlet $^1\pi\pi^*$ potential energy surface, similarly to the stilbene isomerization [44–47]. This switching from the singlet to triplet photoisomerization mechanism upon coordination to the Re center is caused by the heavy-atom effect of Re, which strongly accelerates the $^1\mathrm{IL} \rightarrow {}^3\mathrm{IL}$ ISC through large spin-orbit coupling.

Picosecond time-resolved IR (TRIR) spectra measured immediately after optical excitation of $[\mathrm{Re^I(Cl)(CO)_3}(t\text{-stpy})_2]$ show the A′(1) ν(CO) band of the ^{3}IL state shifted by ~10 cm^{-1} lower from the corresponding ground state band, see Chart 1 (top (a)) [42]. The ^{3}IL state subsequently undergoes a 12 ps conversion to another ^{3}IL state, whose A′(1) IR band is downshifted by only ~5 cm^{-1} from the ground state position. This conversion is interpreted as rotation of a stpy ligand around the C=C bond to achieve a near-perpendicular geometry [42]. The resultant state is denoted $^3\mathrm{IL_p}$. Isomerization to the *cis* form and return to the ground state follows on a much slower time scale, ~17 ns [48] by further ~90° rotation in the forward or backward direction, respectively. The excited state behavior of $[\mathrm{Re^I(Cl)(CO)_3}(t\text{-stpy})_2]$ is shown in Fig. 4.

Photoisomerization of a *trans*-stpy ligand occurs also in the bpy complex $[\mathrm{Re^I}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$. An intriguing question arises, whether the MLCT(bpy) excited state is involved, and how. Chart 1 (top (b)) shows the picosecond TRIR spectra of $[\mathrm{Re^I}(t\text{-stpy})\mathrm{(CO)_3(bpy)}]^+$ measured after 400 nm laser pulse irradiation, which populates predominantly the ^{1}MLCT(bpy) state. Immediately after excitation, we can see negative bands (bleach) due to depleted ground state population at 1932 cm^{-1} (A′(2) + A″) and 2034 cm^{-1} (A′(1)) and three transient bands at higher wave numbers: 1963, 1995 and 2061 cm^{-1}, see Chart 1 (top (b)). Such a spectral pattern is characteristic of a ^{3}MLCT(bpy) excited state, as was observed before for $[\mathrm{Re^I(4\text{-}Etpy)(CO)_3(bpy)}]^+$ and other complexes [30,33,49–54]. These ^{3}MLCT(bpy) spectral features essentially disappear within the first 6–10 ps. Decay of the ^{3}MLCT bands is accompanied by growth of a sharp transient band at 2027 cm^{-1} and a broad absorption between 1910 and 1960 cm^{-1}. The latter strongly overlaps with the A′(2) + A″ negative bleach bands, nearly canceling absorption in this spectral region. This secondary transient IR spectrum is characteristic of a ^{3}IL excited state. It closely resembles the initial IR spectral pattern seen

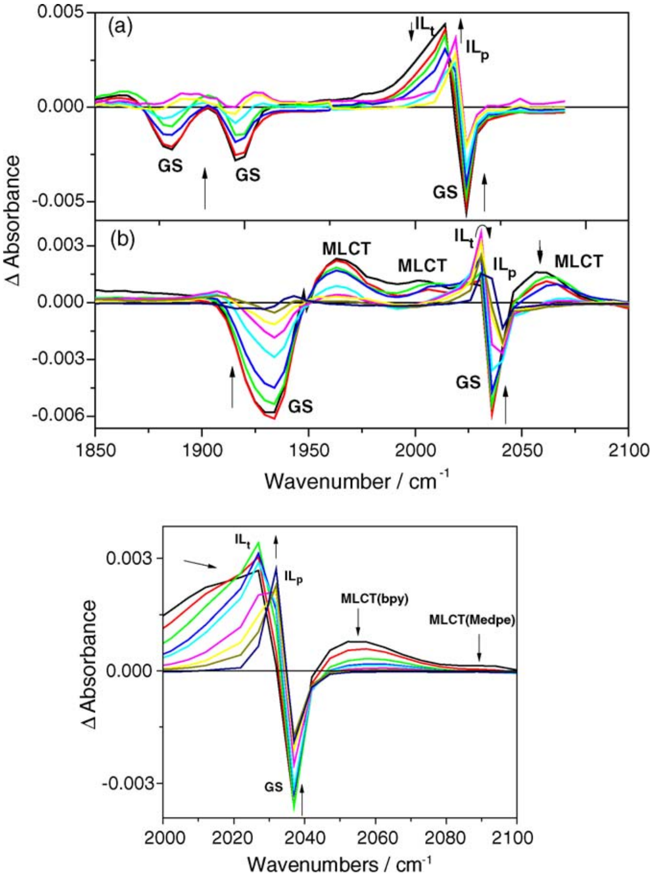

Chart 1. Top: Difference time-resolved infrared spectra of (a) $[\mathrm{Re^I(Cl)(CO)_3(stpy)_2}]$ in $\mathrm{CH_2Cl_2}$. Spectra shown at 2 ps (black), 6 ps (red), 10 ps (green), 20 ps (blue), 50 ps (cyan), 100 ps (magenta) and 1000 ps (yellow). (b) $[\mathrm{Re^I(stpy)(CO)_3(bpy)}]^+$ in $\mathrm{CH_2Cl_2}$. Spectra shown at 1 ps (black), 1.5 ps (red), 2 ps (green), 3 ps (blue), 6 ps (cyan), 10 ps (magenta), 20 ps (yellow), 30 ps (brown) and 1000 ps (navy). Measured after 400 nm excitation. Experimental points are separated by 4–5 cm^{-1}. From Ref. [42]. Negative and positive bands correspond to the depleted ground state and photoproduced transients, respectively.
Bottom: Difference time-resolved infrared spectra of $[\mathrm{Re^I(Medpe)(CO)_3(bpy)}]^{2+}$ in $\mathrm{CH_2Cl_2}$. Spectra shown at 2 ps (black), 3 ps (red), 5 ps (green), 8 ps (blue), 10 ps (cyan), 20 ps (magenta), 30 ps (yellow), 50 ps (brown) and 1000 ps (navy). Measured after 400 nm excitation. Experimental points are separated by 4–5 cm^{-1}. Negative and positive bands correspond to the depleted ground state and photoproduced transients, respectively.

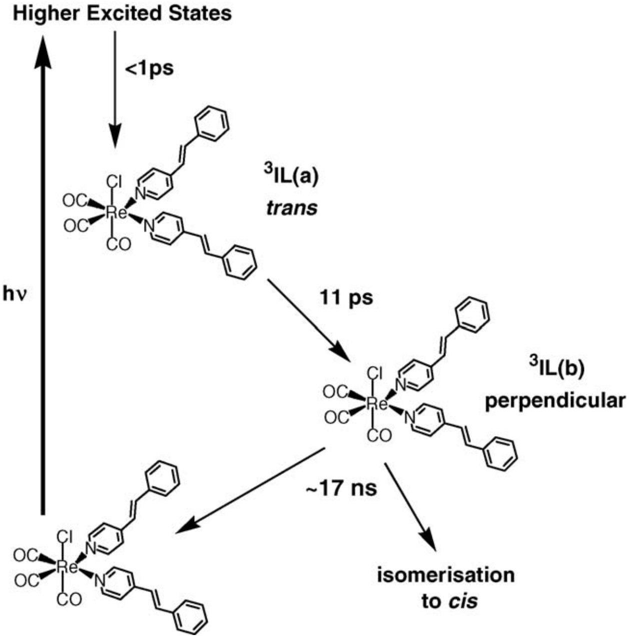

Fig. 4. Photochemistry of [Re^I(Cl)(CO)$_3$(*t*-stpy)$_2$]. The time constants shown were determined by time-resolved visible and IR absorption spectroscopy. The mechanism is also supported by picosecond time-resolved resonance Raman experiments. See Ref. [42] for details.

for [Re^I(Cl)(CO)$_3$(stpy)$_2$]. Hence, it is attributed to the same stpy–localized ^{3}IL$_t$ excited state. The 2027 cm^{-1} band is most prominent between 10 and 15 ps. It subsequently decays, being replaced by another band at ca. 2031 cm^{-1}, which is attributed to the ^{3}IL$_p$ excited state, with perpendicular orientation of the phenyl and pyridine rings of the stpy ligand. This is the key photoisomerization intermediate. The 2031 cm^{-1} band then decays with a ∼17 ns time constant by concurrent conversion to the *cis* form and decay to the ground state.

The photochemical mechanism of [Re^I(*t*-stpy)(CO)$_3$(bpy)]$^+$ is shown in Fig. 5. Optical excitation first prepares the ^{3}MLCT(bpy) state. Then, a picosecond conversion to the ^{3}IL$_t$ state of the *t*-stpy ligand occurs. This state has a $^3\pi\pi^*$ character and undergoes ∼90° rotation to the perpendicular form ^{3}IL$_p$, from which the *cis* isomer or the ground state are produced with a 17 ns time constant by further ∼90° rotation in a forward or backward direction, respectively [37,48]. As far as we are aware, this is the first direct observation of intramolecular triplet energy transfer from ^{3}MLCT-excited Re(CO)$_3$(bpy) fragment to a ^{3}IL $\pi\pi^*$ state of the axial ligand. The occurrence of such process has been proposed earlier to explain photophysics of other systems [55–57], albeit without a firm evidence. Another type of interaction and conversion between MLCT and IL states was described in detail for a series of [Re(Cl)(CO)$_3$(Me$_n$-phen)] complexes (Me$_n$-phen = phen and its methylated derivatives) [58]. In these compounds, the ^{1,3}IL $\pi\pi^*$ states are localized on the same ligand (i.e. Me$_n$-phen) which accommodates the excited electron in the MLCT state.

4. Electron or energy transfer? The case of [Re^I(*t*-Medpe$^+$)(CO)$_3$(bpy)]$^{2+}$

The *t*-Medpe$^+$ ligand (Fig. 2) combines both functionalities: it can undergo a photoinduced *ILET* to the pyridinium ring or isomerization of the C=C bond. The actual photoreactivity will depend on the relative energies of the ^{3}MLCT(Medpe) and ^{3}IL(Medpe) excited states and on the rates of their population by electron (*ILET*) or energy transfer from ^{3}MLCT(bpy), respectively. Chart 1 (bottom) shows the time-dependent changes of the A′(1) ν(CO) band after 400 nm excitation of [Re^I(*t*-Medpe)(CO)$_3$(bpy)]$^{2+}$. A rather complicated situation emerges, whereby several transients are seen immediately after excitation: (i) ^{3}MLCT(bpy) characterized by a broad band

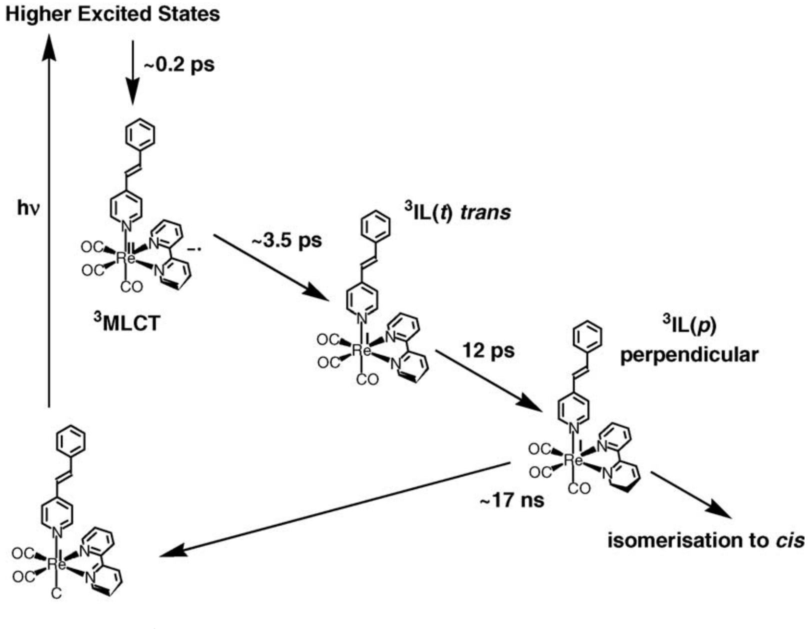

Fig. 5. Photochemistry of [Re^I(*t*-stpy)(CO)$_3$(bpy)]$^+$. The time constants shown were determined by time-resolved visible and IR absorption spectroscopy. The mechanism is also supported by picosecond time-resolved resonance Raman experiments. See Ref. [42] for details.

at 2057 cm^{-1} (+20 cm^{-1}), (ii) a very weak band due to the ^{3}MLCT(Medpe) state at ∼2088 cm^{-1} (+51 cm^{-1}), and (iii) a ^{3}IL$_t$ state at 2027 cm^{-1} (−10 cm^{-1}) (the numbers in parentheses show the shifts from the ground state position of the A′(1) band). Both ^{3}MLCT states are populated by ISC after optical excitation of the corresponding ^{1}MLCT states. The same can be partly true for the ^{3}IL state, since the ^{1}IL transition also contributes to the lowest absorption band. The IR bands of the ^{3}MLCT(Medpe) and ^{3}MLCT(bpy) states decay very rapidly, with the time constants of ∼0.6 and 11 ps, respectively. The ^{3}IL$_t$ band increases concomitantly, reaching maximum intensity at about 5 ps. A picosecond rotation around the C=C bond follows, being manifested by an isosbestic conversion of the ^{3}IL$_t$ band into a band at 2032 cm^{-1} (−5 cm^{-1}), attributed to the perpendicular state ^{3}IL$_p$.

It follows that ^{3}IL$_t$ of the Medpe$^+$ ligand is the lowest excited state of [Re^I(*t*-Medpe)(CO)$_3$(bpy)]$^{2+}$. It is populated upon optical excitation from the corresponding ^{1}IL$_t$ state, by intramolecular energy transfer from the ^{3}MLCT(bpy) excited state, and by an internal conversion from the ^{3}MLCT(Medpe) state, see Fig. 6. *Trans* → *cis* photoisomerization of the Medpe$^+$ ligand in [Re^I(*t*-Medpe$^+$)(CO)$_3$(bpy)]$^{2+}$ follows the same mechanism as that of *t*-stpy in [Re^I(*t*-stpy)(CO)$_3$(bpy)]$^+$. No evidence for bpy$^{\bullet-}$ → Medpe$^+$ *ILET* from the ^{3}MLCT(bpy) state has been found.

By comparison, 400 nm excitation of [Re^I(Cl)(CO)$_3$(*t*-Medpe$^+$)$_2$]$^{2+}$ leads only to a ^{3}MLCT(Medpe) state, which decays on a picosecond timescale [59]. Obviously, the energy balance between different excited states strongly depends on the nature of the ancillary ligands present in the coordination sphere. The electron-donating chloride ligand appears to stabilize the ^{3}MLCT(Medpe) state below ^{3}IL, whose energy is much less sensitive to the composition of the Re coordination sphere.

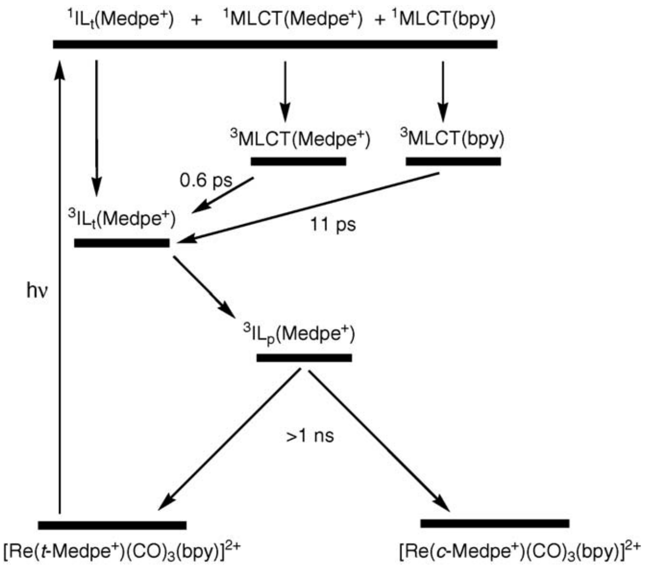

Fig. 6. Photochemistry of [Re^I(*t*-Medpe$^+$)(CO)$_3$(bpy)]$^{2+}$. The time constants shown were determined by time-resolved visible and IR absorption spectroscopy. The mechanism is further supported by TR^3 spectroscopic experiments [59].

5. Concluding remarks

MLCT excited states of the Re^I(CO)$_3$(N,N) chromophore in the complexes [Re^I(L)(CO)$_3$(N,N)]$^{n+}$ can act as electron or energy donors toward the axial ligand L. These processes are conceptually similar, involving one- or two-electron exchange, respectively, see Fig. 7. They are surprisingly fast, occurring on the timescale of picoseconds. These ultrafast rates indicate that the electronic coupling, which is in both cases provided by the Re^{II} atom of the ^{3}MLCT state, is relatively large, while still preserving the distinct characters and localizations of the excited states in question. In this respect, it is interesting to note that the π systems of the N,N and L ligands interact with the same Re 5d$_\pi$ orbital. Strong electronic coupling can make both the electron and energy transfer partly adiabatic, driven by intramolecular and/or solvent vibrations. Notably, the time scale of the processes studied herein is comparable with that of vibrational relaxation and cooling. It is thus suggested that intramolecular vibrations play a crucial role and that vibrational excitation of the initial ^{3}MLCT(N,N) state provides the necessary acceleration, making both *ILET* and energy transfer processes ultrafast.

Switching of the photoisomerization reaction from the singlet ππ* to the corresponding triplet potential energy surface is another interesting phenomenon. *Trans*-stilbene and its derivatives undergo ca. 100 ps isomerization from the ^{1}ππ excited state, upon overcoming an energy barrier between the *trans* and perpendicular configurations [44–47]. A time constant of ca. 60 ns has been estimated for the *trans* → *cis* isomerization of the ^{3}ππ* state of *t*-stilbene using sensitizers [60–63]. For both Re-stpy complexes, it appears that the triplet state ^{3}IL is trapped near the perpendicular geometry, from which it decays back to the *trans* ground state and, in part, to the *cis* product with a 17 ns lifetime. Such a situation may arise from a crossing between the ^{3}IL and ground state potential energy surfaces along the isomerization coordinate, as shown schematically in Fig. 8 [44,64].

Both electron and energy transfer from an excited Re^I(CO)$_3$(bpy) chromophore to the axial ligand is relevant to possible applications of [Re^I(L)(CO)$_3$(N,N)]$^{n+}$ complexes in molecular devices. For example, if the Re complex is incorporated into a molecular wire or a conductive polymer, *ILET* could

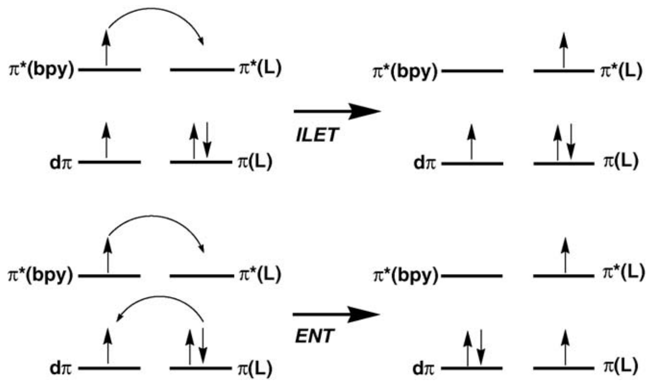

Fig. 7. Comparison of *ILET* (top) and intramolecular energy transfer processes (bottom) from ^{3}MLCT(bpy) excited state of [Re^I(L)(CO)$_3$(bpy)]$^+$.

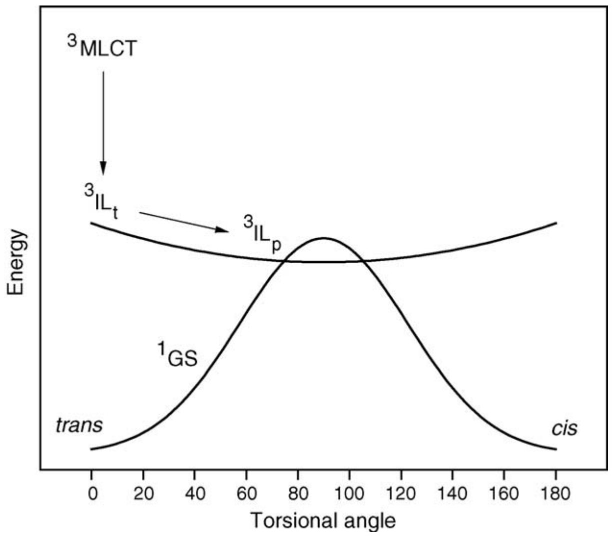

Fig. 8. Idealized potential energy curves of the ground state and the ^{3}IL excited state of $[\mathrm{Re^I(L)(CO)_3(bpy)}]^+$ as functions of the torsional angle between the phenyl an pyridine rings of the stpy ligand. The $^3\mathrm{IL_p}$ state adopts a geometry close to that of the crossing between the two surfaces, slightly less then 90°. Decay to the ground state and isomerization occurs by intersystem crossing to the ground state curve. The asymmetry of the crossing region, which is approached only from the left, accounts for the fact that the isomerization quantum yield is much smaller than 0.5.

be used to switch electron conduction or to route an electronic signal between "wires" attached to the diimine and axial ligands. In photosensitizer-type applications, *ILET* could be detrimental to photoinjection through the diimine ligand, e.g. in photoelectrochemical applications. Energy transfer is directly relevant to the use of isomerizable $[\mathrm{Re^I(L)(CO)_3(N,N)}]^{n+}$ complexes (L = stpy or 1,2-di-pyridyl-ethylene) as reversible luminophores, which can be switched on and off by irradiation with 400 and 265 nm light, respectively [38–40]. Energy transfer from the $\mathrm{Re^I(CO)_3(bpy)}$ chromophore to the isomerizable ligand L leads to *trans* → *cis* ligand isomerization, making the complex strongly emissive.

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