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Ultrafast excited-state dynamics of photoisomerizing complexes fac-[Re(Cl)(CO)₃(papy)₂] and fac-[Re(papy)(CO)₃(bpy)]⁺ (papy = trans-4-phenylazopyridine)

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Dedicated to Vincenzo Balzani.

Abstract

The character and dynamics of low-lying electronic excited states of the complexes fac-[Re(Cl)(CO)₃(papy)₂] and fac-[Re(papy)- $(CO)_3(bpy)^{\dagger}$ (papy = trans-4-phenylazopyridine) were investigated using stationary (UV-Vis absorption, resonance Raman) and ultrafast time-resolved (visible, IR absorption) spectroscopic methods. Excitation of $[Re(Cl)(CO)_3(papy)_2]$ at 400 nm is directed to $\frac{1}{\pi}\pi^*(papy)$ and Re \rightarrow papy ¹MLCT excited states. Ultrafast (\ll 1.4 ps) intersystem crossing (ISC) to ³n π^* (papy) follows. Excitation of [Re(papy)- $(CO)_3(bpy)]^+$ is directed to ${}^1\pi\pi^*(papy)$, ${}^1MLCT(papy)$ and ${}^1MLCT(bpy)$. The states ${}^3n\pi^*(papy)$ and ${}^3MLCT(bpy)$ are then populated simultaneously in less then 0.8 ps. The ³MLCT(bpy) state decays to $^{3}n\pi^{*}(papy)$ with a 3 ps time constant. $^{3}n\pi^{*}(papy)$ is the lowest excited state for both complexes. It undergoes vibrational cooling and partial rotation around the -N=N- bond, to form an intermediate with a nonplanar papy ligand in less than 40 ps. This species then undergoes ISC to the ground state potential energy surface, on which the *trans* and cis isomers are formed by reverse and forward intraligand papy rotation, respectively. This process occurs with a time constant of 120 and 100 ps for $[Re(Cl)(CO)_3(papy)_2]$ and $[Re(papy)(CO)_3(byy)]^+$, respectively. It is concluded that coordination of papy to the Re center accelerates the ISC, switching the photochemistry from singlet to triplet excited states. Comparison with analogous 4-styrylpyridine complexes (M. Busby, P. Matousek, M. Towrie, A. Vlček Jr., J. Phys. Chem. A 109 (2005) 3000) reveals similarities of the decay mechanism of excited states of Re complexes with ligands containing -N=N- and -C=C- bonds. Both involve sub-picosecond ISC to triplets, partial rotation around the double bond and slower ISC to the trans or cis ground state. This process is about 200 times faster for the -N=N- bonded papy ligand. The intramolecular energy transfer from the ³MLCT-excited *Re(CO)₃(bpy) chromophore to the intraligand state of the axial ligand occurs for both L = stpy and papy with a comparable rate of a few ps. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

trans-Azobenzene, Ph–N=N–Ph, is one of the most studied photoresponsive molecules and an active component of photonic devices. It undergoes efficient *trans-cis*

isomerization upon irradiation with UV or blue light, which takes place on a sub-picosecond time scale. Isomerization can be reversed either photochemically or thermally. The high photoisomerization yield, its ultrafast rate, reversibility and stability of the azobenzene chromophore open the way for its applications in optical switches, photochemical memories or optically controlled molecular triggers [1]. This is shown schematically in Scheme 1, where the gray spheres represent polypeptide chains, supramolecular entities, metal complexes or nanoparticles. Photoisomerization of such

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Scheme 1. Photoisomerization of azobenzene – containing molecular assemblies.

assemblies profoundly changes their size, conformation, shape and optical properties. Thus, for example, laser-pulse irradiation of polypeptides with an inserted azobenzene unit triggers conformational changes and induces folding [2–4]. Photoinduced shape changes in azobenzene-containing molecular assemblies or liquid-crystal films were proposed as an operational principle of high-density molecular memories [1,5,6]. Several transition metal complexes containing azobenzene-type ligands show a "light-switch" effect, whereby luminescence is switched on by irradiation of a non-emissive *trans*-isomer [7,8]. Other systems show pronounced photochromism.

Photoactive azobenzene-type metal complexes are often designed by attaching an azobenzene unit -p-C₆H₄-N=N-Ph or an azo group -N=N- to a polypyridine and coordinating the resulting ligands to a transition-metal atom [8-11,13–15]. Thus, Re^I, Pt^{II}, Rh^{III}, Ru^{II}, Fe^{II} or Co^{II,III} complexes containing terpyridine or 2,2'-bipyridine ligands with appended azobenzene group(s) have been prepared and their electrochemistry, spectroscopy and photochemistry studied. Some of these complexes show photochromism [15] or luminescence switching [7,8] upon irradiation. Photoisomerization quantum yields are generally much lower than for free azobenzene; 10^{-4} – 10^{-3} . They show interesting dependencies on the metal, its oxidation state, viscosity and polarity of the solvent, as well as on the nature of the counter-anion. Isomerization is assumed to take place from intraligand excited states localized on the azobenzene unit. The photoisomerization is suppressed in Fe^{II} and Ru^{II} complexes, presumably by energy transfer from the reactive azobenzene-localized intraligand (IL) state to low-lying MLCT states. On the other hand, the lack of reactivity seen for Co^{III} was attributed [13,14] to electron transfer from excited the azobenzene unit to Co^{III} and to efficient reverse $cis \rightarrow trans$ isomerization. Much more efficient photoisomerization was reported [13,14] for analogous Co^{II} complexes.

trans-4-Phenylazopyridine, Ph–N=N–py, is the closest analogue of azobenzene, which can be directly coordinated

to a metal atom through the pyridine ring, see Fig. 1. Herein, it will be abbreviated papy. The complex $[Re(papy)-(CO)_3(bpy)]^+$ has been shown [7] to undergo efficient *trans* - *cis* isomerization upon irradiation with near UV light. Only the *cis* isomer being emissive, the complex behaves as an optically controlled switch, whose emission is switched on by photoisomerization.

To explain the mechanism of the -N=N- trans-cis photoisomerization, one has to consider that azobenzene and its derivatives have two kinds of low-lying excited states: $\pi\pi^*$ and $n\pi^*$, which are manifested in the azobenzene absorption spectrum by a strong UV band at about 315 nm and a very weak, broad visible absorption at \sim 445 nm, respectively [12,16]. The presence of a low-lying $n\pi^*$ state makes azo compounds spectroscopically and photochemically very different from stilbene (Ph-C=C-Ph) and other molecules that undergo isomerization of a C=C bond. The quantum yield of *trans* \rightarrow *cis* photoisomerization of azobenzene in hexane increases from 0.12 to 0.24 upon changing the excitation wavelength from the $\pi\pi^*$ to the $n\pi^*$ transition [17]. Photoisomerization mechanism of azobenzene and its derivatives has been studied by a variety of laser spectroscopic and theoretical techniques. Generally, it seems that, regardless the excitation wavelength, isomerization occurs from the lowest singlet state, ${}^{1}n\pi^{*}$ (S₁). Two pathways are possible, namely rotation (torsion) around the N=N bond and inversion at one nitrogen atom, see Scheme 2. The relative importance of these two pathways depends on the particular compound, the medium and the initial excess of energy. After many years of controversy, both experimental [18,19] and theoretical [16,20] evidence was amassed to support the rotation mechanism, which, however, can be coupled with some changes in the NNC angle, i.e. with movement along the inversion coordinate. It follows that the two mechanisms are limiting cases, which cannot be clearly separated. The inversion mechanism, which maintains planarity of the azobenzene unit throughout the reaction, seems to be preferred in viscous media and spatially restricted environments, such as supramolecules, proteins or molecular assemblies, provided that the molecule is excited with a sufficient excess of energy



Fig. 1. Schematic structures of fac-[Re(Cl)(CO)₃(papy)₂] (left) and fac-[Re(papy)(CO)₃(bpy)]⁺(right). The prefix fac- will be hereinafter omitted for brevity. The two complexes will be known as Re(papy)₂ and Re(papy)(bpy), respectively.



Scheme 2. Two proposed mechanisms of azobenzene photoisomerization.

[16,18]. Very little is known about the lowest triplet state, which was calculated as ${}^{3}n\pi^{*}$ [16,20]. Energy transfer experiments with triplet sensitizers have estimated [21] its energy to be quite low, 1.52 eV (=12240 cm⁻¹). Sensitization experiments indicate a negligible yield of *trans* \rightarrow *cis* isomerization from the ${}^{3}n\pi^{*}$ triplet state, but an efficient reverse reaction [17,22]. Because of its very short lifetime, the azobenzene ${}^{3}n\pi^{*}$ state have eluded spectroscopic characterization.

Photoisomerization of azobenzene-appended polypyridine ligands in metal complexes is usually assumed to take place from an intraligand ${}^{1}n\pi^{*}$ excited state of the azobenzene unit, following the same mechanism as free azobenzene. Time-resolved visible absorption spectra were measured for the Co [13,14], Fe [13], Pt [8] and Ru [10] complexes. They show broad transient bands, which afford very little structural information. Nevertheless, the transigned to the ${}^{1}\pi\pi^{*}$ (rapidly decaying) and ${}^{1}n\pi^{*}$ states of the azobenzene unit. The signal attributed to the latter decays within a few hundreds of picoseconds, that is much more slowly than for the free ligands. Interestingly, *trans* \rightarrow *cis* isomerization of an azo group can also occur upon MLCT excitation, provided that it is directed into the π^* N=N orbital. This is the case of azaferocene [9] or a Ru^{II} complex with an azo-bpy ligand [15].

Photochemistry of azobenzene and its metal complexes clearly presents a mechanistic challenge and a great opportunity for the development of photoresponsive functional molecules and optically controlled switches. Herein, we have focused on the excited state dynamics of two photoisomerizing complexes, fac-[Re(Cl)(CO)₃(papy)₂] and fac-[Re(papy)(CO)₃(bpy)]⁺, hereinafter abbreviated as Re(papy)₂ and Re(papy)(bpy), respectively. Their schematic structures are shown in Fig. 1. We proceed from the characterization of their allowed electronic transitions by UV–Vis absorption and resonance Raman spectra to dynamic studies using time-resolved visible and infrared absorption spectroscopy. This research complements our investigations [23,24] of -C=C- photoisomerization in fac-[Re(Cl)(CO)₃(stpy)₂] and fac-[Re(stpy)(CO)₃(bpy)₂]⁺, whose photochemistry involves $\pi\pi^*$ IL excited states (stpy = *trans*-4-styryl-pyridine = Ph–C=C–py).

It is shown that coordination of papy to the Re atom changes the photoisomerization mechanism from singlet to triplet $n\pi^*$ states, slowing the reaction down to about 100 ps, that is 100 times. Nevertheless, the decay to the ground state and -N=N- bond photoisomerization from a ${}^3n\pi^*$ state of papy is about 170 times faster than for the ${}^3\pi\pi^*$ state stpy ligand [23]. To our knowledge, this is the first study of triplet-state isomerization of an azobenzenetype molecule. Moreover, an ultrafast intramolecular energy transfer from the 3MLCT state of the Re(CO)₃(bpy) chromophore is established as an alternative pathway to populate the reactive ${}^3n\pi^*$ (papy) state of Re(papy)(bpy) upon low-energy irradiation.

2. Experimental

2.1. Materials

Starting materials were purchased from Aldrich. Solvents of spectroscopic quality were used as obtained. The metal complexes were synthesized by modified literature procedures and the products were identified by FTIR, NMR and electrospray mass spectroscopy.

trans-4-Phenylazopyridine (papy) was synthesized following a modified literature procedure [25]: 4-Aminopyridine (4.44 g, 47.2 mmol) was dissolved in a stirred mixture of 15 ml of pyridine and 25 ml of 50% aqueous NaOH, and heated to 80 °C. Nitrosobenzene (6.0 g, 57.7 mmol) was added over 45 min and then kept at 80 °C for further 45 min. The reaction mixture was cooled and the organic layer was extracted with 3×50 ml of toluene, which was then removed in vacuo. The crude orange solid was further purified via column chromatography [neutral alumina, toluene/ethanol, 99/1]. The pure compound was obtained after crystallization from petrolether (60–80 °C). 55% yield. Characterization: ¹H NMR CDCl₃ 270 MHz: 7.55 (3H, m, aromatic CH), 7.73 (2H, d, J 6.2, aromatic CH), 7.95 (2H, m, aromatic CH), 8.82 (2H, d, J 6.0, aromatic CH).

fac-[Re(OTf)(CO)₃(bpy)]; OTf = triflate [26]: [Re(Cl)-(CO)₃(bpy)] (1.88 mmol) was stirred with AgOTf (0.6 g, 2.35 mmol) in dry THF for 6 h. The mixture was then filtered through celite, and its volume doubled with petrole-ther (60–80 °C). The solvent was then removed to a minimum. The precipitate was filtered and dried in vacuo.

fac-[Re(Cl)(CO)₃(papy)₂] was synthesized by a standard procedure: [Re(Cl)(CO)₅] (0.52 g, 1.44 mmol) and papy (3.2 mmol) were refluxed in dry toluene for 12 h. The solution was cooled and the volume reduced to a minimum. The precipitate was filtered under suction and washed with petrolether (60–80 °C) to remove any excess of free ligand. 81% yield. Characterization: FTIR (DCM) $v_{CO} = 2027(s)$, 1926(m), 1891(m) cm⁻¹; ¹H NMR CDCl₃ 270 MHz: 7.57 (6H, m, aromatic CH), 7.72 (4H, d, J 5.4, aromatic CH), 7.96 (4H, d, *J* 9.4, aromatic CH), 8.96 (4H, d, *J* 7.0, aromatic CH); ES-MS *m*/*z* 856.4, 690.3, 637.2.

 $fac-[Re(papy)(CO)_3(bpy)](PF_6)$ [7]: [Re(OTf)(CO)_3-(NN)] (2.06 mmol) and papy (2.26 mmol) were refluxed in 30 ml of dry THF for 12 h. The mixture was filtered hot and the solvent was then removed in vacuo. The solid was dissolved in 30 ml of methanol and a saturated solution of methanol containing 1g of NH₄PF₆ was added to form a precipitate, which was then filtered and repeatedly recrystallized from methanol. 49% yield. Characterization: FTIR (DCM) $v_{CO} = 2036(s)$, 1937 (br) cm⁻¹; ¹H NMR CD₃CN 250 MHz: 7.67 (5H, m, aromatic CH), 7.88 (2H, dd, J 7.5, aromatic CH), 7.98 (2H, d, J 6.4, aromatic CH), 8.34 (2H, dd, J 7.8, aromatic CH), 8.45 (2H, d, J 6.4, aromatic CH), 8.49 (2H, d, J 6.9, aromatic CH), 9.32 (2H, d, J 6.9, aromatic CH); ¹³C NMR CD₃CN 67.9 MHz: 118.54, 123.53, 124.97, 128.96, 129.92, 133.74, 141.02, 152.19, 153.72, 154.16, 155.73, 158.32, 191.55 (CO), 196.03 (CO).

2.2. Instrumentation

Ground-state resonance Raman spectra were obtained using a Coherent Innova 90-5 UV argon-ion laser, with a power output of ca. 50 mW at 457.9 nm and 30 mW at 351.1 nm. The Raman spectra were recorded using 2 mm quartz flow tubes and the scattered light was collected at 90° from the excitation beam passed through a Spex Triplemate 187 Series monochromator and dispersed across a Princeton Instruments LN/CCD-1024 CCD camera. Spectra were calibrated and solvent bands subtracted using CSMA CCD Spectrometric Multichannel Analysis Software, version 2.4a, Princeton Instruments Inc. program.

Time-resolved visible absorption spectra were measured using the experimental setup at the Rutherford Appleton Laboratory using ~150 fs, 400 nm pulses and a white-light continuum generated with 800 nm fundamental in D₂O flowing through a quartz cell [27,28]. The spectra were detected on 512 pixel diode arrays. The instrument time resolution was 400–500 fs. The sample solutions were circulated through a 2 mm quartz cell.

Time-resolved IR (TRIR) spectra were obtained using the equipment and procedures described previously [27– 29]. In short, the sample solution was excited (pumped) at 400 nm, using frequency-doubled pulses from a Ti:Sapphire laser of ~150 fs duration (FWHM). TRIR spectra were probed at selected time delays with IR (~150 fs) pulses obtained by difference-frequency generation. The IR probe pulses cover spectral range ca. 200 cm⁻¹ wide and are tunable from 1000 to 5000 cm⁻¹. The sample solutions were flown through a 0.5 mm CaF₂ raster-scanned cell.

TA and TRIR spectra are presented in the difference mode, whereby the ground-state spectrum is always subtracted from the spectrum generated by the pump pulse.

All spectral and kinetic fitting was performed using Microcal Origin 7 software.

3. Results

3.1. Photochemistry

Continuous irradiation of Re(papy)₂ in a CH₂Cl₂ solution with a 405 nm monochromatic light or a polychromatic light of a medium-pressure Hg lamp passed through a ~350 nm UV cut-off filter causes a small (~6%) decrease of the absorbance at the maximum and the red-side of the 325 nm absorption band. Its maximum shifts to 323 nm upon irradiation. The blue side of this band and the 235 nm band were affected much less. A very small rise in the absorbance was seen between 255 and 270 nm. These spectral changes are reversible and the original spectrum is fully restored after 15 min in dark. This behavior shows [2,7,11] that Re(papy)₂ undergoes a thermally reversible photoisomerization:

$$\operatorname{Re}(\operatorname{Cl})(\operatorname{CO})_{3}(t\operatorname{-papy})_{2} \stackrel{hv}{\underset{\Delta}{\leftrightarrow}} \operatorname{Re}(\operatorname{Cl})(\operatorname{CO})_{3}(t\operatorname{-papy})(c\operatorname{-papy})$$
(1)

The thermal back reaction renders the complex essentially photostable, at least under low-intensity continuous irradiation. The photoisomerization is not manifested in the IR spectrum.

Re(papy)(bpy) has been reported [7] to undergo a lowyield *trans* \rightarrow *cis* photoisomerization of the papy ligand under continuous irradiation with a $\lambda > 350$ nm polychromatic light. Notably, isomerization is accompanied by emergence of emission, presumably from a ³MLCT(bpy) state of the *cis* isomer [7]. In our experiments, 3 h irradiation with the $\lambda > 350$ nm light caused only negligible change in the UV–Vis spectrum and no change in the IR spectrum. Much faster reaction, which was not studied further, occurs under polychromatic UV irradiation.

Qualitatively, it appears that the initial photoisomerization quantum yield is higher for $\text{Re}(\text{papy})_2$ than Re(papy)(bpy), but the thermal back reaction shifts the photostationary state of the former species toward the *trans* isomer. No information is available on the occurrence of a reverse $cis \rightarrow trans$ photoisomerization at 400 nm, which (if present) can shift the photostationary state to the *trans* isomer.

3.2. UV–Vis absorption

UV–Vis spectra of free papy, Re(papy)₂ and Re(papy)-(bpy), shown in Fig. 2, are rather similar, exhibiting a strong UV band between 300 and 330 nm. In particular, free papy shows a strong band at 310 nm ($\varepsilon = 16300 \text{ M}^{-1} \text{ cm}^{-1}$) and a much weaker band at 450 nm ($\varepsilon = 360 \text{ M}^{-1} \text{ cm}^{-1}$). These features are attributed to ${}^{1}\pi\pi^{*}$ and ${}^{1}n\pi^{*}$ transitions, respectively, by comparison with the azobenzene spectrum [12,16]. (Note that $n\pi^{*}$ transitions involve excitation of a nonbonding electron from the nitrogen lone pairs of the –N=N– group.) Re(papy)₂ shows an intense, broad band at 323 nm ($\varepsilon = 38100 \text{ M}^{-1} \text{ cm}^{-1}$).



Fig. 2. UV–Vis absorption spectra, of papy (doted line) in CH₃CN; [Re(Cl)(CO)₃(papy)₂] (dashed line) in CH₂Cl₂ and [Re(papy)(CO)₃(bpy)]⁺ (solid line) in CH₃CN. The inset shows the $n\pi^*$ absorption band of free papy.

Compared with the free ligand spectrum, this band is redshifted and much broader on its long-wavelength side. Moreover, a low-energy shoulder stretches into the visible, beyond 500 nm. By comparison with the free ligand, the main band is assigned as an IL ${}^{1}\pi\pi^{*}$ transition. Re \rightarrow papy ¹MLCT and ¹n π^* IL transitions are thought to contribute to the broad low-energy side of the band and to its long tail, respectively. The molar absorptivity of the main band is about twice that of free papy, in accordance with the presence of two papy ligands in the molecule. Re(papy)-(bpy) shows an intense ${}^{1}\pi\pi^{*}$ IL(papy) band between 315 and 335 nm, which overlaps with a sharp band at 320 nm that is due to a ${}^{1}\pi\pi^{*}$ IL(bpy) transition ($\varepsilon =$ $32700 \text{ M}^{-1} \text{ cm}^{-1}$). As for Re(papy)₂, the band is broadened on its long-wavelength side, with a shoulder that stretches well into the visible region, possibly due to Re \rightarrow papy, Re \rightarrow bpy MLCT and $^{1}n\pi^{*}$ transitions.

3.3. Resonance Raman spectroscopy

The (pre)resonance Raman (rR) spectrum of free papy, Fig. 3a, was measured in acetonitrile upon excitation at 351.1 nm that is directed into the low-energy onset of the $\pi\pi^*$ absorption band. The highest band, which seems to be composed of two, is seen at 1590 cm⁻¹. It is rather weak in intensity. A detailed vibrational analysis of the generic compound azobenzene shows [30] that this band corresponds to an aromatic v(CC) vibration of the phenyl ring. At lower wavenumbers, strong bands are seen at 1483(s), 1468(s) and 1446(s) cm⁻¹ that are all thought to contain significant v(N=N) character [30]. Their large enhancements indicate a strong coupling of the v(N=N) vibration to the $\pi\pi^*$ electronic transition. The only other bands of significant intensity occur at 1167(m) and 1147(m) cm⁻¹. They are assigned to N–Ph/py stretches, as for azobenzene [30].

The (pre)resonance Raman spectrum of $\text{Re}(\text{papy})_2$ (Fig. 3b) was measured using excitation at 457.9 nm, direc-



Fig. 3. Resonance Raman spectra of: (a) papy in CH₃CN, excited at 351.1 nm; (b) $[\text{Re}(\text{Cl})(\text{CO})_3(\text{papy})_2]$ in CH₃CN, excited at 457.9 nm, and (c) $[\text{Re}(\text{papy})(\text{CO})_3(\text{bpy})]^+$ in CH₃CN, excited at 457.9 nm. * Indicates uncompensated solvent subtraction.

ted into the onset of the lowest absorption band. A Raman band due to the A'(1) in-phase C \equiv O stretching vibration, v(CO), is clearly seen at 2027 cm⁻¹. Its intensity enhancement indicates a contribution from a $Re \rightarrow papy$ MLCT transition, hereinafter denoted MLCT(papy). A strongly enhanced band at 1609 cm^{-1} replaces the weak broad 1590 cm^{-1} band seen in the free papy spectrum. It shows a shoulder at ~ 1594 cm⁻¹. Tentatively, we assign [31] the main maximum at 1609 cm⁻¹ and the \sim 1594 cm⁻¹ shoulder to aromatic v(CC) stretching vibrations of the pyridine and phenyl rings, respectively. A new band appears at 1027(m) cm⁻¹, which is also thought [31] to correspond to a pyridyl-localized mode. It is resonantly enhanced only in the spectrum of the complex, but not of the free ligand. These differences and enhancement of Raman bands due to pyridine-based vibrations suggest a MLCT(papy) contribution. The rest of the spectrum is similar to that of unbound papy ligand, supporting the assignment of the 323 nm band to a ${}^{1}\pi\pi^{*}$ transition. In particular, a well-resolved triplet is seen at 1493(m), 1468(s) and 1446(vs) cm⁻¹. As for the free ligand, it originates in vibrations involving the v(N=N)stretch. N-Ph/py stretches are manifested by bands at 1174(m) and 1149(m) cm⁻¹.

Re(papy)(bpy), when excited in the visible at 457.9 nm, displays a weakly enhanced A'(1) v(CO) band at 2036(w) cm⁻¹, as well as papy-based bands at 1611(m), 1494(m), 1467(s), 1446(vs), 1174(m), 1148(m) and 1027(m) cm⁻¹. The spectrum is very similar to that of Re(papy)₂, see Fig. 3c. The only evidence for bands pertaining to the bpy moiety [31,32] are very weak bands at 1631, 1566 and 1315 cm⁻¹. This spectral pattern indicates that the main resonant electronic transition has a $\pi\pi^*$ (papy) character. A smaller contribution arises from MLCT(papy). The MLCT(bpy) contributes even less, if at all. Resonance Raman spectrum of an analogous complex $[\text{Re}(t\text{-stpy})-(\text{CO})_3(\text{bpy})]^+$, reported previously [23], shows a similar pattern, the bpy-based bands being enhanced only very weakly.

3.4. Time-resolved visible absorption spectroscopy (TR-Vis)

Time-resolved absorption spectrum of free papy (Fig. 4a) was measured after 400 nm excitation into its $n\pi^*$ absorption band. The transient absorption consists of a broad band between 500 and 700 nm with a maximum at 570-620 nm. The signal decays monoexponentially, with a lifetime of 1.0 ± 0.1 ps, as measured at 560 nm. The decay proceeds straight to the ground state, without any intermediate. The broad transient absorption was therefore attributed to the lowest ${}^{1}n\pi^{*}$ singlet state of papy. Its decay kinetics are comparable with the 2.6 ps decay seen for the $n\pi^*$ state of *t*-azobenzene, which also shows a broad absorption band around 550 nm [12]. By analogy with azobenzene [18], the 1.0 ps time constant is mostly associated with the rotational movement around the -N=N- bond, that leads to conical intersection with the ground-state potential energy surface and, then, to the ground state and the cis isomer.

The transient absorption of $\text{Re}(\text{papy})_2$, measured after 400 nm excitation, covers the whole visible spectral region, without any prominent bands. Compared with free papy, it shows additional absorption at shorter wavelengths, between 450 and 500 nm, while the maximum at 570–



Fig. 4. Difference time-resolved visible absorption spectra of: (a) papy in CH_3CN , measured at 2, 2.25, 2.75, and 4 ps after excitation at 400 nm; (b) $Re(papy)_2$ in CH_2Cl_2 , measured at 2, 3, 8, 50, and 200 ps after excitation at 400 nm, (c) Re(papy)(bpy) in CH_3CN , measured at 2, 3, 10, and 100 ps after excitation at 400. The spectra decrease in intensity with time as indicated by the arrows. The spectra measured at 2 ps are skewed above ca. 580 nm by uncorrected spectral chirp. The drop in intensity at short wavelengths is caused by the subtracted ground-state absorption.

620 nm is not apparent. No feature attributable to papy⁻ is seen, excluding the possibility that a MLCT(papy) state is populated. (A strong sharp band at about 430 nm would be expected for papy⁻, by analogy with the azobenzene radical anion [33].) The whole broad transient absorption of Re(papy)₂ is assigned to an IL excited state. The transient absorption decays biexponentially, with time constants of 1.4 ± 0.1 ps (80%) and 119 ± 26 ps (20%), as measured at 570 nm. The decay kinetics are, within the experimental error, independent of the probe wavelength. The long-lived (\sim 120 ps) decay component is incomparably longer than any transient seen for azobenzene or its derivatives. Hence, we attribute the broad, long-lived signal to the lowest triplet IL excited state of a ${}^{3}n\pi^{*}$ origin. The fast decay component (\sim 1.4 ps) can correspond either to decay of a strongly absorbing $\pi\pi^*(\text{papy})$ IL state, or it could reflect early relaxation of the ${}^{3}n\pi^{*}$ IL state.

Re(bpy)(papy) also shows a broad transient absorption extending over the visible spectral region. At time delays of 4 ps and shorter, the spectra show two weak bands at 460–470 nm and \sim 675 nm, which indicate population of a ³MLCT(bpy) excited state [31]. They are superimposed on a broad absorption that is very similar to that of Re(papy)₂. The two maxima disappear at longer time delays ($\geq 10 \text{ ps}$) and the transient spectrum becomes virtually identical to that of Re(papy)₂, attributed to ${}^{3}n\pi^{*}(papy)$. The transient absorption decays biexponentially, with time constants of 2.5 ± 0.4 (70%) and 101 ± 15 ps (30%) at 470 nm, in the region of the combined ³MLCT and ³n π^* absorption, and 0.8 ± 0.1 (88%) and 95 ± 11 ps (12%) at 560 nm, where only the ${}^{3}n\pi^{*}$ state absorbs. (Note that the 0.8 ps lifetime has been obtained without deconvolution of the instrument function.) These kinetics suggest that the ${}^{3}n\pi^{*}(papy)$ IL state is populated from a ³MLCT(bpy) state with a time constant of ~ 2.5 ps. The 0.8 ps probably corresponds to the decay of higher-lying singlet or triplet $\pi\pi^*(\text{papy})$ states, or to vibrational cooling, as for Re(papy)₂. The ${}^{3}n\pi^{*}(papy)$ IL state of Re(bpy)(papy) decays with a lifetime of ca. 100 ps, leaving no absorption in the visible.

3.5. Time-resolved infrared spectroscopy (TRIR)

The TRIR spectrum of Re(papy)₂ (Fig. 5) measured at 2 ps after excitation shows negative bleach bands at 2027 (B1), 1926 (B2) and 1890 (B3) cm⁻¹, which mirror the ground-state FTIR spectrum. The bleach bands are due to the depleted ground-state population. In addition, three bands due to photogenerated transient species are seen at ca. 2011 (A), 1910 (D) and 1872 (E) cm⁻¹. These bands are shifted to lower wavenumbers relative to the corresponding ground-state bands. Such small downward shift is characteristic of intraligand excited states [23,34] and allows us to assign the photoproduced species as the lowest ³IL(papy) excited state, most probably ³nπ^{*}.

The TRIR spectra show rather complicated temporal evolution, which is displayed in Fig. 6 for the highest A'(1) v(CO) band. At early times (3–4 ps), the IR absorp-



Fig. 5. (Top) Difference time-resolved IR spectra of $[Re(Cl)(CO)_3(papy)_2]$ in CH₂Cl₂, measured at 2 (black), 10 (red), 30 (green), 100 (blue) and 1000 (cyan) ps after 400 nm excitation. The spectrum evolves in the direction of the arrows. Separation between experimental points is 4–5 cm⁻¹. (Bottom) Ground-state FTIR spectrum.

tion is dominated by a broad absorption between ca. 1998 and 2017 cm⁻¹ which encompasses the band A at ~2004 cm⁻¹ and a much weaker broad band C at ~2013 cm⁻¹. (The presence of two bands was revealed by Gaussian analysis of the band shape.) The band A rapidly decays and narrows, while the band C grows and shifts to higher wavenumbers, into the region of the negative bleach band B1. The band C becomes clearly apparent at ~10 ps. At 15 ps, the spectrum shows the band C at ca. 2019 cm⁻¹,



Fig. 6. High-resolution difference time-resolved IR spectra of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{papy})_2]$ in CH_2Cl_2 shown in the region of the highest A'(1) v(CO) bands, measured at 3 (black), 4 (red), 6 (green), 10 (blue), 15 (cyan), 20 (magenta), 30 (yellow), 50 (brown), 70 (navy), 100 (purple), 200 (wine) and 1000 (olive) ps after excitation at 400 nm. The spectrum evolves in the direction of the arrows. Separation between experimental points is ca. 2.5 cm⁻¹. Decay lifetimes (ps) at selected probe wavenumbers are inserted.

with a shoulder due to A at about 2004 cm^{-1} . This process continues at longer time delays. For example, at 70 ps, the band C peaks at 2021 cm^{-1} with a very weak shoulder A at 2004 cm^{-1} . These spectral changes occur alongside an overall decay of the spectral intensity, which is caused by the decay of the transient itself (documented by TR-Vis spectra) and by increasing overlap between the positive transient band C and the negative bleach band B at 2027 cm⁻¹. Convolution of all these processes (shift of C and its increasing overlap with B1, narrowing of A and C, conversion $A \rightarrow C$, overall decay) is manifested by the dependence of the decay kinetics on the probe wavenumber (Fig. 6). It prevents us from determining the time-constants of the individual processes. Similar, although less pronounced, behavior is seen in the lower spectral region, $1850-1950 \text{ cm}^{-1}$, where the transient (E, D) and bleach (B2, B3) bands decay with a similar time constant of 38 ± 4 ps. This spectral evolution indicates a structural reorganization of the ${}^{3}n\pi^{*}$ state. A very weak signal persists even at 1000 ps, which is tentatively attributed to the *cis* isomer. Its weakness indicates that the isomerization quantum yield is very low.

The TRIR spectrum of Re(papy)(bpy) (Fig. 7) measured at 1.5 ps shows negative bleach bands at 2037 (B4) and 1936 (B5) cm^{-1} , which mirror the ground-state FTIR spectrum. Three transient bands, which are upshifted from the corresponding ground-state positions, occur at 2055 (K), 2002 (L) and ~1965 (M) cm⁻¹. In addition, the 2 ps spectrum shows two downshifted bands at 2027 cm⁻¹ (N, strong, sharp) and 1911 (O) cm^{-1} . The upward shift of the spectral pattern K + L + M is characteristic of a ³MLCT state. The magnitude of the shift of the highest band K from the corresponding bleach B3 can be estimated from the 6 ps spectrum as $+26 \text{ cm}^{-1}$. This value is typical for ³MLCT(bpy) states [23,24,28,31,34–41], but much smaller than the shifts seen for $Re \rightarrow L^{3}MLCT$ states of analogous complexes $[\operatorname{Re}(L)(\operatorname{CO})_3(\operatorname{bpy})]^{2+}$; for example $+62 \text{ cm}^{-1}$ for L =N-methyl-4,4'-bipyridinium [24,28] and $+51 \text{ cm}^{-1}$ for L = trans-N-methyl-4,4'-dipyridiniumethylene [24,42]. Hence, we attribute the spectral bands K, L and M to the ³MLCT(bpy) excited state, instead of ³MLCT(papy). The downshifted bands N and O are, by analogy with Re(papy)₂, attributed to the ${}^{3}n\pi^{*}$ ${}^{3}IL(papy)$ state. The MLCT bands K+L+M rapidly decay with a lifetime of $3.0\pm0.1~\text{ps},$ as measured at 2061 cm⁻¹. At the same time, the band K moves to $\sim 2063 \text{ cm}^{-1}$ at 4–6 ps, due to vibrational relaxation [31]. The ³IL bands N and O grow in intensity by ca. 30% between 2 and 8 ps. Since this growth occurs concurrently with the MLCT(bpy) decay, both processes are thought to be linked. At longer time delays, both ³IL bands N and O shift to higher wavenumbers and decay in intensity, due to increasing overlap with the negative bleach bands and the overall decay to the ground state, evidenced by TR-Vis spectra. Detailed, high-resolution, spectrum (Fig. 8), reveals that the upward shift of the band N actually results from its conversion to the band P, which overlaps with the bleach B4. The maximum of the band P appears



Fig. 7. (Top) Difference time-resolved IR spectra of $[\text{Re(papy)}(\text{CO})_3(\text{bpy})]^+$ in CH₂Cl₂ (b), spectra shown at 1.5 (black), 2 (red), 4 (green), 6 (blue), 10 (cyan), 20 (magenta), 80 (yellow) and 1000 (brown) ps after 400 nm excitation. The spectrum evolves in the direction of the arrows. Separation between experimental points is $4-5 \text{ cm}^{-1}$. (Bottom) Ground-state FTIR spectrum.

at ~2031 cm⁻¹, but the real maximum probably occurs deeper in the bleach region, at 2033–2034 cm⁻¹. The dynamic shift of the band P into the bleach region is largely responsible for the decay of the B4 bleach band, whose time constant was determined as 40 ± 2 ps, that is faster than the transient decay seen in TR-Vis spectra. In fact, the B4 decay kinetics is determined more by the dynamic shift of the band P than by the bleach recovery. The very weak residual signal still present at 1000 ps is again tentatively attributed to the *cis* isomer.



Fig. 8. High-resolution difference time-resolved IR spectra of $[\text{Re(papy)}(\text{CO})_3(\text{bpy})]^+$ in CH₂Cl₂ shown in the region of the highest A'(1) v(CO) bands, measured at 3 (black), 4 (red), 6 (green), 8 (blue), 20 (cyan), 30 (magenta), 50 (yellow), 70 (brown), 100 (navy), 200 (purple) and 1000 (wine) ps after excitation at 400 nm. The spectra evolve in the direction of the arrows. Separation between experimental points is ca. 2.5 cm⁻¹.

4. Discussion

4.1. Franck–Condon transitions and UV–Vis absorption spectra

UV-Vis absorption and (pre)resonance Raman spectra clearly show that the lowest intense absorption band, which occurs for both Re(papy)₂ and Re(papy)(bpy) at 320–340 nm, is dominated by an intraligand ${}^{1}\pi\pi^{*}$ transition localized at the papy ligand. ¹MLCT(papy) is another contributor. For Re(papy)(bpy), the ¹MLCT(bpy) absorption band is expected between 330 and 350 nm, based on comparison with [Re(stpy)(CO)₃(bpy)]⁺ and [Re(Etpy)(CO)₃-(bpy)⁺ [23,31]. However, its contribution to the resonance Raman enhancement is very low. In this respect, we should note that the papy ligand is a strong electron acceptor, owing to the presence of the electron-withdrawing -N=N-Ph group. In fact, the electrochemical reduction of the papy ligand in Re(papy)(bpy) occurs some 360 mV more positively than the bpy-localized reduction [7]. Hence, the ¹MLCT(papy) transition is expected to occur at lower energy than ¹MLCT(bpy), contributing thus more strongly to the resonance Raman enhancement. In addition to these, spectrally manifested transitions, the very weak ${}^{1}n\pi^{*}$ absorption, seen in the free-ligand spectrum, is supposed to contribute to the red side of the main absorption band of both complexes. It follows that the 400 nm irradiation, used in the time-resolved experiments, excites all the allowed transitions: mostly ${}^{1}\pi\pi^{*}$, and, to a lesser extent, ¹MLCT(papy) and ¹n π^* (papy). For Re(papy)(bpy), ¹MLCT(bpy) is excited as well.

4.2. Excited-state dynamics and the photochemical mechanism

Time-resolved visible and IR spectroscopy demonstrate that the lowest excited state is the same for both $Re(papy)_2$ and Re(papy)(bpy) and undergoes a complicated dynamical evolution on a ca. 100 ps time scale. To reveal the nature of the lowest state, we have to consider both its spectroscopic characteristics and lifetime. TR-Vis spectra of both complexes show a broad, structureless absorption, which is different from the ${}^{1}n\pi^{*}$ excited-state spectrum of either free papy (Fig. 3a) or azobenzene [12]. Its lifetime, 100–120 ps, is far too long for a singlet excited state of this type of molecules, suggesting that it corresponds to a spintriplet excited state. The shift of v(CO) bands to lower wavenumbers relative to their ground-state positions is caused by population of a ligand π^* orbital in the excited state, which is not accompanied by depopulation of Relocalized orbitals [34]. This downward shift is thus a clear evidence for an IL(papy) character of the lowest excited state, either ${}^{3}\pi\pi^{*}$ or ${}^{3}n\pi^{*}$. By analogy with azobenzene [16,20], we assign the lowest excited state of both $Re(papy)_2$ and Re(papy)(bpy) as the ${}^{3}n\pi^{*}$ IL state of the papy ligand.

Although the character of the lowest excited state is the same for $Re(papy)_2$ and Re(papy)(bpy), the mechanisms of

its population after optical excitation are quite different. In the case of $Re(papy)_2$, the 400 nm excitation prepares the ${}^{1}\pi\pi^{*}(\text{papy})$ and ${}^{1}MLCT(\text{papy})$ excited states, which both undergo ultrafast intersystem crossing (ISC) to the ${}^{3}n\pi^{*}$ state. The 1.4 ps time constant, estimated from TR-Vis. should be regarded as an upper limit, the actual ISC rate being probably a few hundreds of femtoseconds, at most. (The 1.4 ps value is affected by other dynamical processes such as vibrational relaxation.) The ultrafast rate of ISC is not surprising. ISC between singlet and triplet MLCT states of Re^I or Ru^{II} diimine complexes occurs [43-45] in tens of femtoseconds, while a ~ 200 fs time constant was estimated for ISC between $^{1,3}\pi\pi^*$ intraligand and MLCT states of $[\text{Re(stpy)(CO)}_3(\text{bpy})]^+$ [23]. It is interesting to note that no evidence was seen for the population of ³MLCT(papy). It appears that ³MLCT(papy) is bypassed by much faster ${}^{1}\pi\pi^* \rightarrow {}^{3}n\pi$ and ${}^{1}MLCT(papy) \rightarrow {}^{3}n\pi^*$ ISC. It is also possible that ³MLCT(papy), if populated, decays to the lowest ${}^{3}n\pi^{*}$ too fast to be detected spectroscopically. We may thus conclude that the lowest ${}^{3}n\pi^{*}$ excited state of $Re(papy)_2$ is populated directly from the optically prepared states on a sub-picosecond timescale $(\tau < 1.4 \text{ ps}).$

The situation is different for Re(papy)(bpy), where the lowest ${}^{3}n\pi^{*}$ state is populated by two pathways. The optically prepared Franck–Condon states ($^{1}\pi\pi^{*}(\text{papy})$, ¹MLCT(papy) and, probably, also ¹MLCT(bpy)) undergo branched intersystem crossing populating simultaneously the ${}^{3}n\pi^{*}$ and ${}^{3}MLCT(bpy)$ states with a time constant shorter than 0.8 ps. Their spectral signals are fully developed already at the earliest time delays investigated, 1-2 ps. The direct pathway to ${}^{3}n\pi^{*}$ is analogous to the ISC of Re(papy)₂, discussed above. The ³MLCT(bpy) state is initially formed vibrationally excited and in an unequilibrated solvent arrangement [31]. This is evidenced by the shift of the A'(1) v(CO) band K of the ${}^{3}MLCT(bpv)$ state from 2055 to 2063 cm⁻¹, which occurs between 1.5 and 6 ps. This dynamic evolution is caused by cooling and solvent relaxation [31]. In addition, ³MLCT(bpy) undergoes conversion to the ${}^{3}n\pi^{*}(papy)$ state with a time constant of \sim 3 ps, as is clearly manifested by the decay and rise of the corresponding IR spectral patterns K + L + M and O + N, respectively, see Figs. 7 and 8. This process amounts to an intramolecular energy transfer from the MLCTexcited $Re(CO)_3(bpy)$ unit to the axial papy ligand. It is comparable to the \sim 3 ps conversion of the ³MLCT(bpy) state of $[\text{Re(stpy)(CO)}_3(\text{bpy})]^+$ to the ${}^3\pi\pi^*$ IL state of the axial stpy ligand [23]. No evidence for the population of ³MLCT(papy) was found, even if it is expected (on electrochemical grounds [7]) to lie about 0.36 eV below ³MLCT(bpy). In principle, ³MLCT(papy) could be populated from the ³MLCT(bpy) state by an interligand electron transfer (ILET) bpy⁻ \rightarrow papy. Such a reaction would be similar to the bpy⁻⁻ \rightarrow *N*-methyl-4,4'-bipyridinium (MQ⁺) ILET in $[Re(MQ^+)(CO)_3(bpy)]^{2+}$, which occurs with a comparable driving force [28,46]. By comparison, a rate constant of $(15-20 \text{ ps})^{-1}$ can be expected for the bpy \rightarrow papy ILET in Re(papy)(bpy), which would be much slower than the $(3 \text{ ps})^{-1}$ rate constant of the energy transfer to the ${}^{3}n\pi^{*}$ state. It follows that ILET to ${}^{3}MLCT(papy)$ is not kinetically competitive with the energy transfer to ${}^{3}n\pi^{*}$. (In fact, we cannot entirely exclude the possibility that ${}^{3}n\pi^{*}$ is populated via ${}^{3}MLCT(papy)$, which is extremely short-lived. However, this is unlikely by comparison with the [Re(stpy)(CO)₃(bpy)]⁺, where the ${}^{3}MLCT(bpy) \rightarrow {}^{3}\pi\pi^{*}$ energy transfer occurs with a comparable rate [23] even in the absence of any ${}^{3}MLCT(stpy)$ state.)

The ${}^{3}n\pi^{*}$ excited state of either complex undergoes a complicated temporal evolution, which is manifested by spectral changes in the region of the highest v(CO) band (Figs. 6 and 8). In particular, the ${}^{3}n\pi^{*}$ band A of Re(papy)₂ narrows and shifts with time to higher wavenumbers, forming the band C, which is apparent at longer time delays (Fig. 6). Both bands keep moving to higher wavenumbers with increasing time delay. The ${}^{3}n\pi^{*}$ IR spectrum of Re(papy)(bpy) shows less narrowing of the initial band N, but its conversion to the higher-lying new band P is more pronounced (Figs. 7 and 8). This spectral evolution can be rationalized by structural changes of the excited papy ligand, namely by rotation around the N=N bond and a large-amplitude movement on a shallow ${}^{3}n\pi^{*}$ potential energy surface. Rotation destroys the planarity and decouples the electronically excited -N=N-Ph group from the $(-pyridine)Re(CO)_3(bpy)$ moiety. The IR v(CO) bands then shift closer to their ground-state positions. Such internal rotation of the papy ligand will eventually lead to the ground state in a twisted geometry, followed by return to the parent trans isomer or, with smaller probability, by isomerization to the *cis* form. This proposed mechanism is fully in line with the rotation mechanism of azobenzene isomerization, predicted by recent high-level theoretical studies of azobenzene [16,20]. Much smaller changes in the v(CO) spectrum would be expected for the alternative inversion mechanism, which preserves the planarity of the papy ligand and, hence, the electronic coupling with the Re center. The initial broadness and continuous shift of the IR bands seen for Re(papy)₂ shows that ${}^{3}n\pi^{*}$ is initially highly vibrationally excited and cools down in parallel with the intraligand rotation in a few tens of picoseconds. The initial high energy excess originates in the molecule being excited at 400 nm (=25000 cm⁻¹), that is ca. 12760 cm^{-1} above the ${}^{3}n\pi^{*}$ state, which occurs at ~12240 cm⁻¹ (estimated from azobenzene [21]). This behavior agrees with the release of a large amount of energy observed after azobenzene excitation, whose dissipation occurs in several steps ranging from 0.32 to 13 ps [47]. The much smaller degree of vibrational cooling seen for the ${}^{3}n\pi^{*}$ state of Re(bpy)(papy) can be explained by dissipation of the excess vibrational energy from the intermediate MLCT state(s), before the ${}^{3}n\pi^{*}$ level is reached. Finally, we should note that the actual structures of the initially populated and "relaxed" ${}^{3}n\pi^{*}$ states are not exactly known. The assumed parallel and twisted (perpendicular) configurations of the papy ligand, respectively, are necessary idealizations. As far as we know,

there is no experimental information available on the dynamics of azobenzene triplet states. Theoretical calculations [16,20] predict multiple crossings between the ${}^{3}n\pi^{*}$ and singlet ground-state (¹GS) potential energy surfaces along the rotation and inversion coordinates of free azobenzene. These crossings, when combined with strong electronic interaction between ${}^{3}n\pi^{*}$ (papy) and 1 GS induced by Re spin-orbit coupling, can lead to several broad local minima on the ${}^{3}n\pi^{*}$ (papy) potential energy surface. The low photoisomerization yield of both Re complexes, observed herein and in a previous study [7], is in agreement with the proposed triplet mechanism and with the older observation of a negligible efficiency of triplet-sensitized *trans* \rightarrow *cis* isomerization of azobenzene [17,22].

Characterization of excited-states of $Re(papy)_2$ and Re(papy)(bpy) and elucidation of their dynamics, discussed above, allows us to propose photochemical mechanisms for both complexes, which are shown in Schemes 3 and 4.

Excited-state dynamics of Re(papy)₂ and Re(papy)(bpy) show remarkable similarities with those of Re(stpy)₂ and Re(stpy)(bpy), which react from the ${}^{3}\pi\pi^{*}(stpy)$ state [23]. Coordination to Re makes the ISC to either ${}^{3}n\pi^{*}(papy)$ or ${}^{3}\pi\pi^{*}(stpy)$ much faster than any evolution on singlet potential energy surfaces, switching the isomerization mechanism to the triplets. Intramolecular energy transfer from ${}^{3}MLCT(bpy)$ occurs with a comparable rate regardless the nature of the terminal state; ${}^{3}n\pi^{*}(papy)$ or ${}^{3}\pi\pi^{*}(stpy)$. Their following dynamics are slightly different: ${}^{3}\pi\pi^{*}(stpy)$ undergoes a clean conversion from planar to



Scheme 3. Excited-state behavior of fac-[Re(Cl)(CO)₃(*t*-papy)₂]. Excitation at 400 nm populates singlet Franck–Condon states ${}^{1}\pi\pi^{*}$ (papy) and ${}^{1}MLCT$ (papy). Ultrafast (subpicosecond) ISC to the ${}^{3}n\pi^{*}$ (papy) state follows. Other low-lying states, such as ${}^{3}\pi\pi^{*}$ (papy) and ${}^{3}MLCT$ (papy) are bypassed. The ${}^{3}n\pi^{*}$ state undergoes vibrational cooling and partial rotation around the -N=N- bond, to form an intermediate ${}^{3}n\pi^{*}$ # with a nonplanar papy ligand, which undergoes ISC to the ground state potential energy surface. The *trans* and *cis* isomers are then formed by reverse or forward intraligand papy rotation, respectively.



Scheme 4. Excited-state behavior of fac-[Re(t-papy)(CO)₃(bpy)]⁺. Excitation at 400 nm populates singlet Franck–Condon states ${}^{1}\pi\pi^{*}$ (papy), ${}^{1}MLCT$ (papy) and ${}^{1}MLCT$ (bpy). Ultrafast (subpicosecond) ISC to the lowest ${}^{3}n\pi^{*}$ (papy) and ${}^{3}MLCT$ (bpy) states follows. Other low-lying states, namely ${}^{3}\pi\pi^{*}$ (papy) and ${}^{3}MLCT$ (papy) are bypassed. ${}^{3}MLCT$ (by) decays with a 3 ps time constant to ${}^{3}n\pi^{*}$ (papy), which undergoes partial rotation around the -N=N- bond, to form an intermediate ${}^{3}n\pi^{*}\#$ with a nonplanar papy ligand in about 40 ps. This species undergoes ISC to the ground state potential energy surface. The *trans* and *cis* isomers are then formed by reverse or forward intraligand papy rotation, respectively.



Scheme 5. Idealized potential energy curves of the ground state and the ³IL excited states of Re complexes with stpy and papy ligands as functions of the torsional angle between the phenyl and pyridine rings. The potential energy surface of the ³ $\pi\pi^*$ state of stypy complexes crosses with the ground-state surface at rather high energy, close to the perpendicular geometry [23,24]. The perpendicular state, abbreviated ³IL_p [23,24], decays to the ground-state potential energy surface. Further evolution leads either to the parent *trans* or to the *cis* isomer. For the ³ $\pi\pi^*$ states of papy complexes, the crossing occurs at a much lower energy and, hence, at smaller torsion angle. Return to the *trans* parent is thus more probable than isomerization.

twisted (perpendicular) form, with only little signs of accompanying energy dissipation. In contrast, large-amplitude motions on a shallow potential energy surface and cooling occur for ${}^{3}n\pi^{*}$ (papy). The rates of the return to the ground state and accompanying isomerization are also different. The perpendicular ${}^{3}\pi\pi^{*}$ configuration of stpy complexes (${}^{3}IL_{t}$) decays to the ground-state *trans* and *cis* isomers with a ~17 ns time constant [23,24,48]. This process is much faster for the twisted ${}^{3}n\pi^{*}$ #(papy) state; 100–120 ps. Moreover, isomerization from the ${}^{3}n\pi^{*}$ states of stpy complexes is more efficient than for ${}^{3}n\pi^{*}$ (papy). This could be caused by the lower energy of the latter state, as is qualitatively explained in Scheme 5.

The conclusions of the present work present some implications for the photoisomerization mechanism of other metal complexes containing azobenzene-type ligands. Namely, the possibility of the triplet mechanism should be considered in the cases of Rh^{III} or Pt^{II} complexes with azobenzene-appended polypyridine ligands, for which transients lived for hundreds of picoseconds have been observed [8,10].

5. Conclusions

Coordination of an azobenzene-like ligand, *trans*-4phenylazopyridine, to a Re^I center in the complexes *fac*-[Re(Cl)(CO)₃(papy)₂] and *fac*-[Re(papy)(CO)₃(bpy)]⁺ accelerates singlet \rightarrow triplet intersystem crossing from optically prepared Franck–Condon states (${}^{1}\pi\pi^{*}$, ${}^{1}MLCT$ and ${}^{1}n\pi^{*}$) to the femtosecond time domain, switching thus the *trans–cis* isomerization mechanism to the triplet ${}^{3}n\pi^{*}$ potential energy surface. The Re^I moiety acts as an intramolecular triplet sensitizer.

The ³MLCT(bpy) state of *fac*-[Re(papy)(CO)₃(bpy)]⁺ undergoes a 3 ps conversion to the reactive intraligand ${}^{3}n\pi^{*}$ excited state. This process amounts to an intraligand energy transfer from the Re^I(CO)₃(bpy) to the papy ligand.

Dynamical evolution of the ${}^{3}n\pi^{*}$ state of the papy ligands involves a large-amplitude motion that includes partial rotation around the N=N bond and (mostly for Re(papy)₂) energy dissipation to the medium. These structural changes take place in ca. 40 ps or less. Conversion to the ground-state *trans* and, less, *cis* isomers follows with a time constant of 100–120 ps. This process is about 200 times faster than isomerization of a -C=C- bond from a ${}^{3}\pi\pi^{*}$ state of analogous Re styrylpyridine complexes.

Azobenzene-type metal complexes are attractive as active components of optically operated molecular devices, although the low photoisomerization yields might be a problem. Excited-state dynamics of Re(papy)(bpy), a known [7] luminescence switch, demonstrate the possibility to sensitize papy isomerization by intramolecular energy transfer.

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