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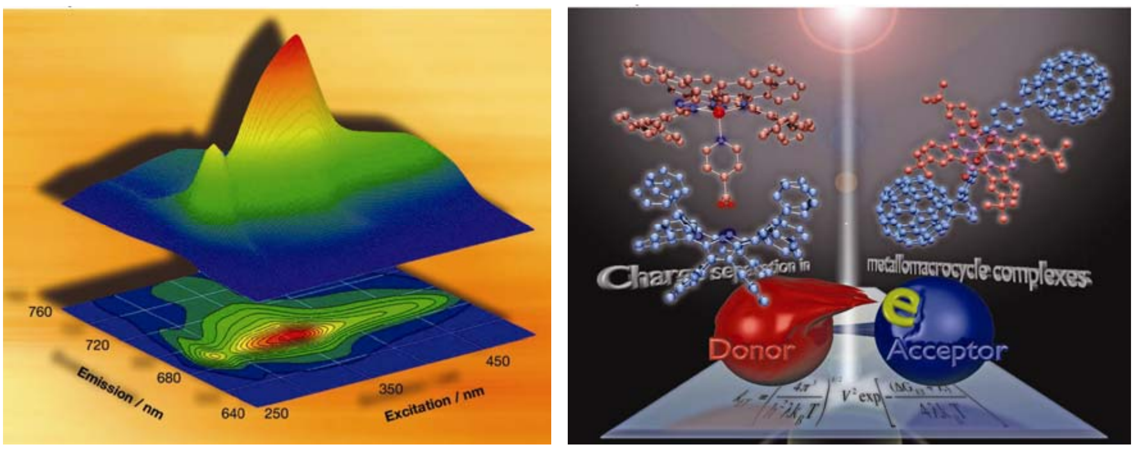

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Excited-state relaxation dynamics of Re(I) tricarbonyl complexes with macrocyclic phenanthroline ligands studied by time-resolved IR spectroscopy†

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Two sets of supramolecular rhenium carbonyl-phenanthroline complexes were prepared: *fac*-[Re(Cl)$(CO)_3$(N,N)] and *fac*-[Re(Etpy)$(CO)_3$(N,N)]$^+$, where N,N is 2,9-di-anisyl-1,10-phenanthroline (dap) or two related macrocyclic ligands, where the two anisyl groups are connected by a polyether chain of different length and rigidity (m27, m30), which wraps around and above the equatorial Re$(CO)_2$ group. The excited-state character and relaxation dynamics of these complexes were investigated by picosecond time-resolved IR spectroscopy in the spectral region of C≡O stretching vibrations, ν(CO). The results were interpreted with the aid of DFT and TD-DFT calculations of the molecular structures and electron-density redistribution upon excitation. [Re(Cl)$(CO)_3$(phen-macrocycle)] in CH_2Cl_2 have the same type of lowest excited state as analogous acyclic phen or bpy complexes, that is a mixed Re$(CO)_3$→phen and Cl→phen MLCT/XLCT, together with some ππ*(phen) IL character. Its relaxation dynamics are qualitatively similar to those of phen or bpy complexes. However, relaxation of [Re(Cl)$(CO)_3$(m30)] shows a slow kinetics component (~22 ps) which arises from confined local solvent molecules and/or from conformational movements of the flexible m30 polyether ring. In contrast, attaching anisyl groups at the 2 and 9 phen positions in [Re(Etpy)$(CO)_3$(phen-macrocycle)]$^+$ effectively "freezes" excited-state relaxation in MeCN, regardless of the presence of the macrocyclic ring. The lowest excited triplet state has a mixed MLCT/IL character. Restricting the solvent access to the excited chromophore clearly affects both the character and dynamics of the lowest excited state.

Introduction

Macrocyclic polypyridine ligands form interesting metal complexes in which a polyether ring wraps around a metal center, affecting its electrochemical and photochemical behavior.[1–5] Ligands of this type were used to construct various metal catenanes and rotaxanes. Some of them act as "molecular motors" in which mechanical movement is accomplished electrochemically or photochemically by changing the oxidation or electronic state of the metal center, respectively.[1–3] Wrapping the polyether ring of a macrocyclic polypyridine ligand ring around Ru(II)-containing chromophores was found to change their photoreactivity. Generally, the metal center is stabilized against photosubstitution by solvent. Instead, irradiation leads to intriguing photoisomerizations and rearrangements.[4] In mixed-polypyridine Ru(II) complexes, the sterically demanding macrocyclic ligand is least amenable to photodissociation.

Recently, it was found that excited-state relaxation of Re(I) carbonyl-polypyridyl complexes *fac*-[Re(L)$(CO)_3$(N,N)]$^{n+}$ (L = halide, n = 0; L = 4-Et-pyridine (Etpy), imidazole, n = 1; N,N = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) depends sensitively on the nature of the surrounding medium and its dynamical properties.[6–11] While investigating relaxation dynamics of Re$(CO)_3$(phen) chromophores attached to proteins, we have realized that Re(I) carbonyl-diimines can be employed as probes reporting on solvation, flexibility and dynamics of binding sites of biomolecules and other complex molecular systems.[10] However, the nature of the medium motions involved and the mechanism whereby they are coupled with the relaxation dynamics of the excited state of the molecular probe are far from understood.

Herein, we have set out to investigate the dynamics of a system where solvation is restricted by a bulky ring-shaped ligand (Fig. 1) which partly shields the Re$(CO)_3$ group. To this effect, we prepared a series of complexes [Re(Cl)$(CO)_3$(N,N)] and [Re(Etpy)$(CO)_3$(N,N)]$^+$ with N,N = 2,9-macrocycle-1,10-phenanthroline ligands (phen-macrocycle), and investigated their excited-state relaxation dynamics employing picosecond time resolved IR spectroscopy (TRIR) in the spectral region of C≡O stretching vibrations, ν(CO). If the macrocycle surrounding the Re$(CO)_3$ moiety induces constraints on the solvation mechanism, or its own motions couple with the relaxation of the ^{3}MLCT lowest excited state of the Re$(CO)_3$(phen) moiety, it should be possible to follow these effects by means of time-dependent shifts of excited-state ν(CO) bands in TRIR spectra.[8–10]

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† Electronic supplementary information (ESI) available: Additional experimental details and Fig. S1–S4. See DOI: 10.1039/b820748h

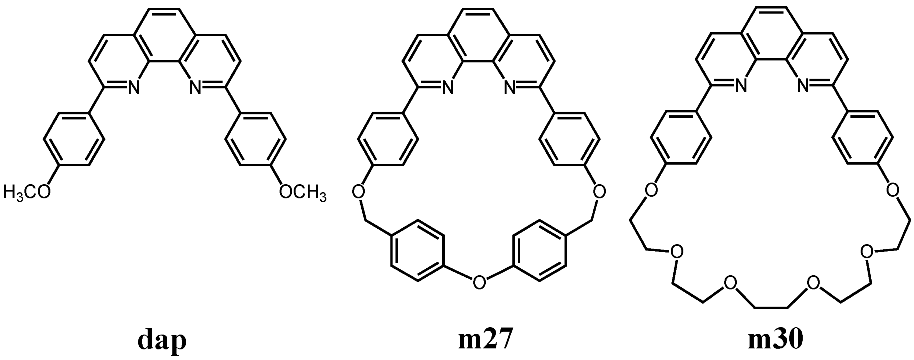

Fig. 1 Schematic structures of the 2,9-macrocycle-1,10-phenanthroline ligands (phen-macrocycle). The ligands m27 and m30 differ in the ring size and flexibility, while dap was chosen as an open-ring reference.

Experimental

Materials

MeCN and CH_2Cl_2 solvents (spectroscopic quality) and $Re(CO)_5Cl$ were used as obtained from Aldrich. The ligands dap, m27 and m30 (Fig. 1) were synthesized and characterized as described previously.[12,13]

The $[Re(Cl)(CO)_3(\text{phen-macrocycle})]$ and $[Re(Etpy)(CO)_3(\text{phen-macrocycle})]^+$ complexes were synthesized by a well-established route, known[9,14–18] to selectively produce the desired tricarbonyl-polypyridine complexes. $[Re(Cl)(CO)_3(\text{phen-macrocycle})]$ was obtained by refluxing the phen-macrocycle ligand with $[Re(Cl)(CO)_5]$ for 4 h in toluene, followed by filtration and repeated washing with hexane. To make the $[Re(Etpy)(CO)_3(\text{N,N-macrocycle})]PF_6$ complexes, the corresponding $[Re(Cl)(CO)_3(\text{phen-macrocycle})]$ was first converted to $[Re(OTf)(CO)_3(\text{phen-macrocycle})]$ by stirring 1.88 mmol with $Ag(CF_3SO_3)$ (1.3 m. eq.) in dry THF (~20 mL) for 4–5 h. The mixture was filtered through Celite, and its volume doubled with petroleum spirits (60–80 °C). The solvent was removed to a minimum volume and the precipitate formed was filtered and dried *in vacuo*. The product was immediately used for the next synthetic step, whereby it was reacted with 4-ethyl-pyridine (Etpy) (1.1 m. eqv.) in THF for 12 h. The mixture was filtered hot and the solvent was removed *in vacuo*. The solid was dissolved in the minimum amount of methanol and a saturated solution of NH_4PF_6 in methanol (~3 mL) was added. Water was added to form a precipitate, which was then filtered and repeatedly recrystallized from methanol. The products were characterized as single-species tricarbonyls by FTIR, ^{1}H-NMR and MS, Table 1 and electronic supplementary information, ESI.†

Spectroscopic measurements. Time resolved IR (TRIR) spectra were measured using the equipment and procedures described in detail previously.[17,19–24] In short, the sample solution was excited (pumped) at 400 nm, using frequency-doubled pulses from a titanium sapphire laser of ~150 fs duration (FWHM). TRIR spectra were probed with IR pulses (~150 fs) obtained by difference-frequency generation. The IR probe pulses cover a spectral range *ca.* 200 cm^{-1} wide, tunable from 1000 to 5000 cm^{-1} (*i.e.*, 2–10 μm). The cell was rapidly oscillated in the plane perpendicular to the direction of the laser beams in order to minimise the potential build-up of decomposition products on the windows. The sample integrity was checked by FTIR spectra measured before and after each experiment. All spectral fitting procedures were performed using Microcal Origin 7 software.

DFT and TDDFT calculations. The electronic structures were calculated by density functional theory (DFT) methods using the Gaussian 03[25] program package. For H, C, N, O and Cl atoms 6-31G* polarized valence double - ζ basis sets[26] were used, together with quasirelativistic effective core pseudopotentials and corresponding optimized set of basis functions for Re.[27]

Table 1 Ground- and excited-state ν(CO) energies of $[Re(Cl)(CO)_3(\text{phen-macrocycle})]$ and $[Re(Etpy)(CO)_3(\text{phen-macrocyle})]^+$ measured in CH_2Cl_2 and MeCN, respectively. Excited-state A″ and A′(2) energies are estimated from spectra measured at 1 ns. A′(1) energies are extrapolated to an infinite time delay (ν(∞)). Band assignment is based on ref. 34–36

	Ground state			Excited state (extrapolated to $t = \infty$)					
	A′(2)	A″	A′(1)	A″	A′(2)	A′(1)	Δν A″	Δν A′(2)	Δν A′(1)
$[Re(Cl)(CO)_3(dap)]$, exp.	1884	1924	2022	~1960 sh	~1972	2050	~36	~88	28
$[Re(Cl)(CO)_3(dap)]$, calc.[b]	1888	1920	2022	1951	1978	2043	31	90	21
$[Re(Cl)(CO)_3(m27)]$	1884	1927	2023	1953	1973	2049	26	89	26
$[Re(Cl)(CO)_3(m30)]$	1885	1924	2022	1950–1980[a]		2049	—	—	27
$[Re(Etpy)(CO)_3(dap)]^+$	1923	1923	2029	1961	~2010	<2041	38	~87	<12
$[Re(Etpy)(CO)_3(m27)]^+$	1924	1924	2029	1968	~2010	<2042	44	~86	<13
$[Re(Etpy)(CO)_3(m30)]^+$	1921	1921	2028	1958	~2010	<2045	37	~89	<17

[a] Broad unresolved band. [b] UKS (B3LYP, CPCM for CH_2Cl_2) Calculated energies scaled by 0.973.

Calculations employed the hybrid functional B3LYP.[28] The solvent was described by the polarizable conductor calculation model (CPCM).[29] Geometry optimizations were performed without any symmetry constraints. The unrestricted Kohn–Sham approach (UKS) was used to optimize the lowest triplet states. Calculations of the vibrational frequencies for ground and lowest triplet states $[Re(Cl)(CO)_3(dap)]$ and $[Re(py)(CO)_3(dap)]^+$ were performed at the corresponding optimized geometries. Low-lying singlet and triplet excited states were calculated by time-dependent DFT (TD-DFT) at the ground-state geometry. The difference density plots were drawn using the GaussView software.

Results

Ground-state structures and spectra

Ground-state structures of $[Re(Cl)(CO)_3$(phen-macrocycle)] (Fig. 2) and $[Re(Etpy)(CO)_3(dap)]^+$ (Fig. 3) in vacuum were calculated by DFT. It can be seen that the two anisyl groups at the 2 and 9 positions of the phen ligand lie nearly perpendicular to the equatorial $Re(CO)_2$ plane, twisted toward the axial ligand, *i.e.* Cl or Etpy. The phen ligand is tilted below the equatorial $Re(CO)_2$ plane, unlike in other Re tricarbonyl-diimine complexes, where the $(N,N)Re(CO)_2$ moiety is planar.[17,18,30–32] The bulky anisyl groups in $[Re(py)(CO)_3(dap)]^+$ force the pyridine ligand to adopt a highly unusual configuration in the symmetry plane of the molecule, *i.e.* bisecting the plane of the phen ligand (Fig. 3), in contrast with analogous Re complexes[17,18,30,31] where the pyridine plane always lies perpendicularly to the symmetry plane, bisecting the equatorial OC–Re–N(diimine) angles. Macrocyclic rings in m27 and m30 are partly wrapped around the equatorial $Re(CO)_2$ group. They are folded above the equatorial plane, in the direction of the axial ligand. DFT calculations have found at least three stable conformations of $[Re(Cl)(CO)_3(m30)]$, which differ only in the polyether chain folding, to occur within a 0.1 eV energy range. This indicates a considerable flexibility of the m30

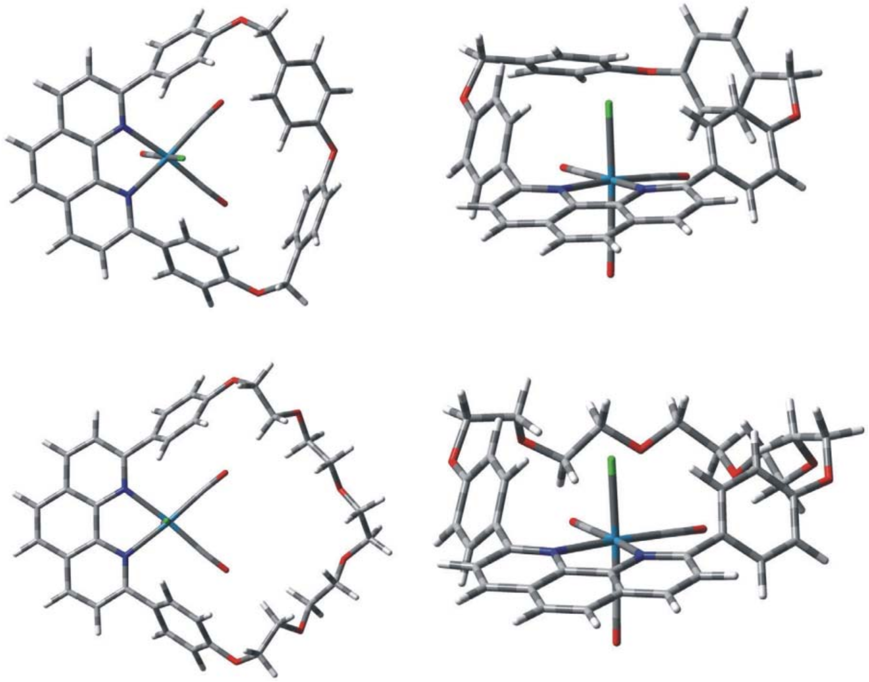

Fig. 2 Two different views of optimized structures of $[Re(Cl)(CO)_3(m27)]$ (top) and $[Re(Cl)(CO)_3(m30)]$ (bottom) in vacuum. Left: the Cl ligand points towards the viewer. Right: the Cl ligand points up and phen points toward the viewer. Calculated by DFT (G03/B3LYP).

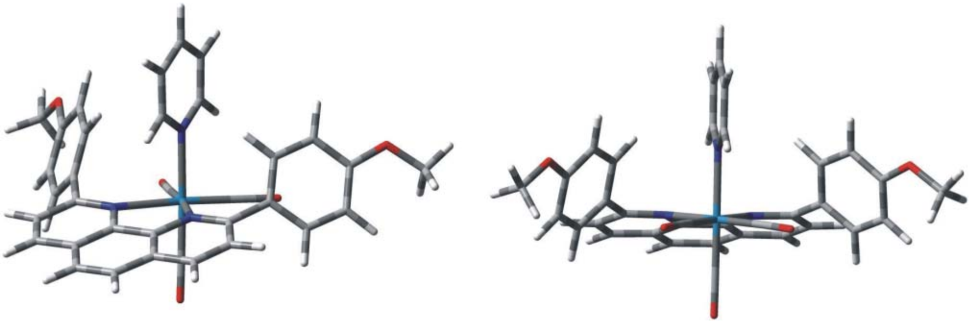

Fig. 3 Two different views of the optimized structure of $[Re(py)(CO)_3(dap)]^+$ in vacuum. Left, right: phen and equatorial CO ligands point toward the viewer, respectively. Calculated by DFT (G03/B3LYP, CPCM).

polyether ring. On the other hand, the m27 ring appears rather rigid.

FTIR spectra measured in the region of C≡O stretching vibrations, ν(CO), are shown in Fig. 4 and the IR band energies are summarized in Table 1. The chloro complexes show the characteristic splitting of the low-energy A″ and A′(2) bands, caused[33] by different values of stretching force constants of the axial and equatorial CO ligands. These two vibrations merge into a single band in the case of the Etpy complexes, indicating that the local symmetry of the Re(CO)$_3$ unit approaches C_{3v}. The spectra of the dap and cyclic complexes being essentially identical, it follows that wrapping by the macrocyclic ligand does not significantly affect the Re(CO)$_3$ geometry. The shape of the A′(1) band is predominantly Lorentzian with a smaller Gaussian contribution.

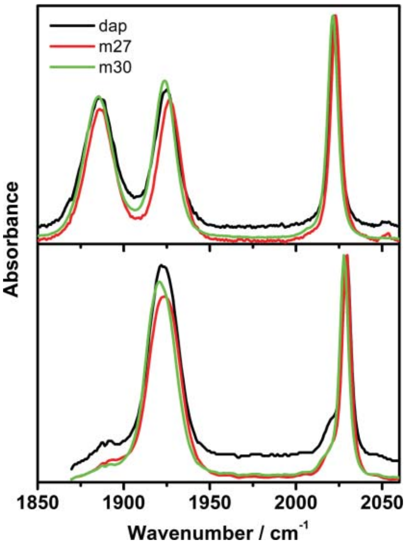

Fig. 4 Ground-state FTIR spectra of [Re(Cl)(CO)$_3$(phen-macrocyle)] (top) and [Re(Etpy)(CO)$_3$(phen-macrocyle)]$^+$ (bottom) measured in CH$_2$Cl$_2$ and MeCN, respectively.

UV-vis spectra of [Re(Cl)(CO)$_3$(phen-macrocyle)] are typical[37,38] of Re^I tricarbonyl-phen complexes. The lowest absorption band of the chloro complexes occurs as a shoulder at about 400 nm while the cationic Etpy complexes show a lowest-lying band (shoulder) at about 330 nm, tailing to ~440 nm.

Picosecond Time-Resolved IR spectroscopy, TRIR. TRIR spectra were obtained at selected time delays after excitation with 400 nm, ~150 fs laser pulses. They are presented as differences of the spectra obtained after and before excitation. Positive and negative features in the spectra thus correspond to photoproduced transients and depleted ground-state population, respectively. Chromophore reorientation effects on the spectra were excluded by setting the polarization directions of the optical pump and IR probe beams at the magic angle. Excitation was directed into the onset of the metal to ligand charge transfer (MLCT) absorption band.

Excited-state IR bands of [Re(Cl)(CO)$_3$(phen-macrocycle)] (Fig. 5) occur at higher energies than their ground-state counterparts, as is typical[8,19,35,36,39–41] for a Re→polypyridine ^{3}MLCT excited state. The constant signal intensity over the 500 ps time range is in accord with the expected[37,42] long excited-state lifetime. A large dynamic upward shift of the A′(1) excited-state band accompanied by a much smaller A′(2) shift is the only time-evolution seen in the spectra. To quantify this effect, the

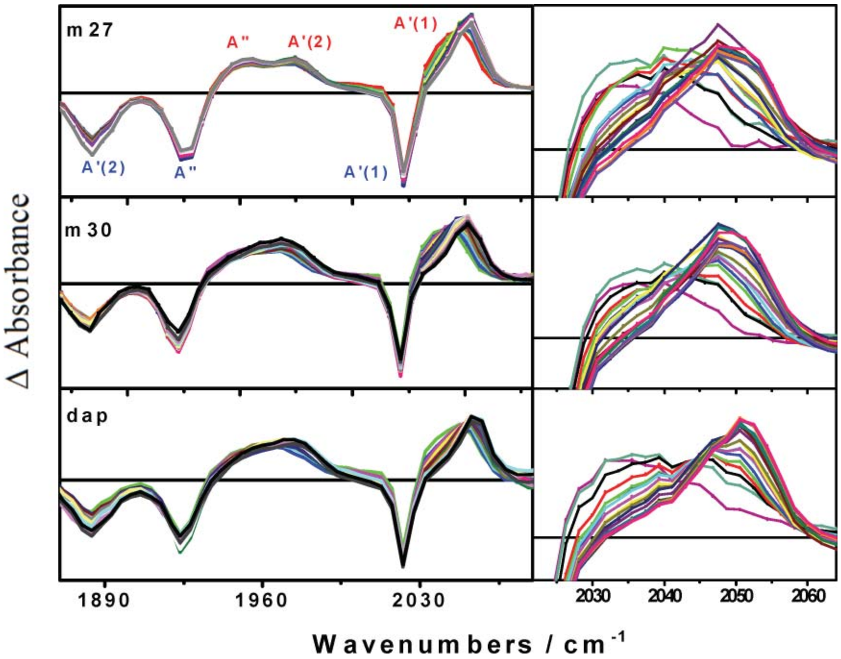

Fig. 5 Difference TRIR spectra of [Re(Cl)(CO)$_3$(phen-macrocycle)] in CH$_2$Cl$_2$, excited at 400 nm, ~150 fs FWHM. Left: full spectra measured over a 1–500 ps time range. Experimental points are separated by 4–5 cm^{-1}. Right: high-resolution spectra of the A′(1) band measured over a 1–30 ps time range. Experimental points are separated by ~2 cm^{-1}. IR band assignment[34] is shown in the top left spectrum in blue and red for the electronic ground and excited state, respectively.

region of the A′(1) band was investigated with a higher spectral resolution, Fig. 5-right. The energy of the A′(1) band maximum as a function of time was determined by Gaussian fitting, as shown in Fig. 6. Very good Gaussian fits were obtained despite the small asymmetry of the A′(1) band. To exclude any drifts in the fitted values, exactly the same fitting procedure was applied to the spectra obtained at each time-delay and for each sample investigated.

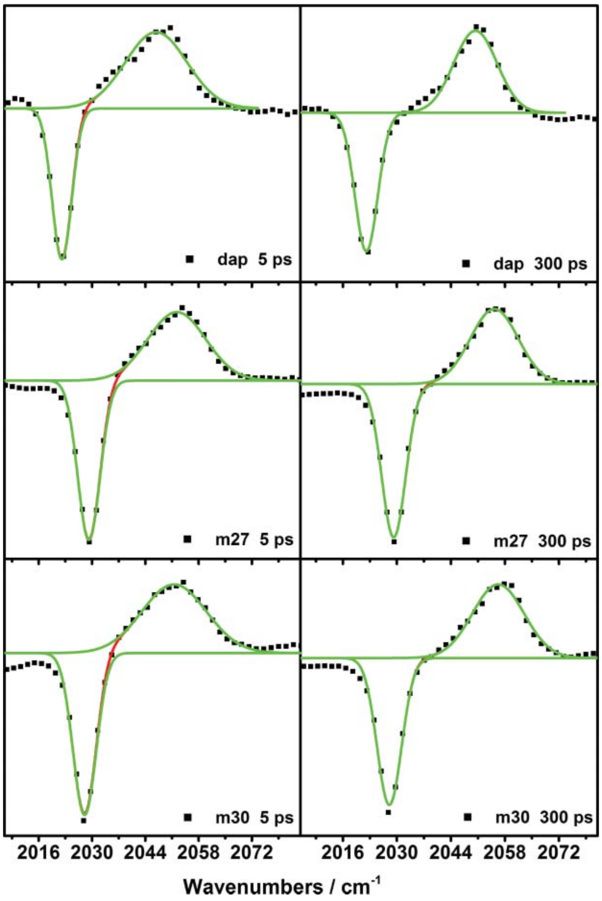

Fig. 6 Typical fits of the high resolution TRIR spectra of [Re(Cl)(CO)$_3$(phen-macrocycle)] in CH_2Cl_2, measured at 5 ps (left) and at 300 ps (right). The macrocyclic ligand is specified in the legend. Black: experimental points. Green: individual Gaussian bands. Red: final simulated spectrum that in most cases overlaps with the green curve. Top to bottom: dap, m27, m30.

Table 2 IR spectral shift parameters[a] of the A′(1) peak energy of [Re(Cl)(CO)$_3$(phen-macrocycle)] and [Re(Cl)(CO)$_3$(phen)] in CH_2Cl_2 at 21 °C. Fitted from 2 ps

	phen	dap	m27	m30
ν_{GS}, cm^{-1}	2023.7	2022.1	2023.1	2021.6
$\nu_{(\infty)}$, cm^{-1}	2054.1	2050.4	2049.1	2049.4
Total shift, cm^{-1}	30.4	28.3	26.0	27.8
Inst. shift, cm^{-1}	21.2	10.9	12.0	12.6
Dyn. shift, cm^{-1}	9.2	17.4	14.0	15.2
A_s, cm^{-1}	2.4 ± 0.04	5.1 ± 0.3	2.7 ± 0.4	3.5 ± 0.3
A_f, cm^{-1}	6.8 ± 0.1	12.3 ± 1.6	11.3 ± 0.7	11.7 ± 0.7
τ_s, ps	11.2 ± 0.2	10.0 ± 0.6	13.4 ± 2.2	22.0 ± 2.9
τ_f, ps	1.4 ± 0.03	1.4 ± 0.2	2.1 ± 0.2	2.5 ± 0.2

[a] Total shift = Inst. shift + Dyn. shift. $A_s + A_f$ = Dyn. shift.

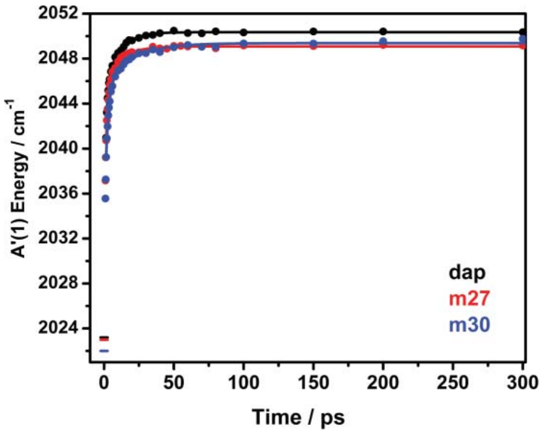

Fig. 7 Time dependences of the peak energy of the excited-state A′(1) ν(CO) band of [Re(Cl)(CO)$_3$(phen-macrocycle)] in CH_2Cl_2. The curves show the bi-exponential fits. The horizontal lines at a zero time delay correspond to the ground-state positions of the A′(1) band. Experimental data are shown from $t = 1$ ps, biexponential fitting starts at 2 ps because of poorly defined band shapes at earlier time delays.

The time-dependences of the A′(1) peak energy for individual complexes are shown in Fig. 7. Experimental data can be fitted to biexponential kinetics, eqn (1):

$$\tilde{\nu}(t) = \tilde{\nu}(\infty) - A_f \exp(-t/\tau_f) - A_s \exp(-t/\tau_s) \qquad (1)$$

Herein, $\tilde{\nu}(t)$ is the time-dependent A′(1) peak energy (in cm^{-1}), $\tilde{\nu}(\infty)$ is the A′(1) energy extrapolated to $t = \infty$ that corresponds to a fully relaxed excited state, τ_f and τ_s are the "fast" and "slow" relaxation times, while A_f and A_s are the corresponding amplitudes. In addition, we can define the total spectral shift on excitation $\tilde{\nu}(\infty)$–$\tilde{\nu}$(GS), the "instantaneous" shift $\tilde{\nu}(0)$–$\tilde{\nu}$(GS), which occurs within the experimental time resolution, and the dynamic shift $A_f + A_s$. $\tilde{\nu}(0)$ is the A′(1) energy extrapolated to $t = 0$, *i.e.* $\tilde{\nu}(0) = \tilde{\nu}(\infty) - (A_f + A_s)$. The fitted curves are shown in Fig. 7 and all the shift parameters are summarized in Table 2. The dynamic band shift is accompanied by narrowing. Widths (fwhm) of the excited-state A′(1) band of the three [Re(Cl)(CO)$_3$(phen-macrocycle)] complexes increase sharply between 1 and 2 ps and then decay single-exponentially with a lifetime of *ca.* 10 ps, see Fig. S1–S3 in the ESI.† The A′(1) width of [Re(Cl)(CO)$_3$(phen)] only decays monotonically with lifetimes of 2.0 ± 0.2 and 10.6 ± 1.6 ps, without showing any rise, Fig. S4.†

TRIR spectra of the complexes [Re(Etpy)(CO)$_3$(phen-macrocycle)]$^+$ (Fig. 8) point to a very different excited-state behavior. While the overall excited-state IR pattern is still typical of a ^{3}MLCT excited state, the highest A′(1) band is upshifted upon excitation by an unusually small amount, *ca.* 10 cm^{-1}, partly overlapping with the bleach. The A′(1) band is rather broad and neither narrowing nor a dynamic shift occur over the time range investigated. Overall, the spectral shape observed is unprecedented for [Re(L)(CO)$_3$(N,N)]^n complexes in solution, as can be seen from the comparison with the spectrum of [Re(Etpy)(CO)$_3$(phen)]$^+$ in MeCN, shown in Fig. 9-left. The unusual excited-state band shape, small shift and lack of dynamic evolution are reminiscent of the behavior of cationic [Re(Etpy)(CO)$_3$(N,N)]$^+$ complexes in PMMA polymer matrices, see Fig. 9-right.

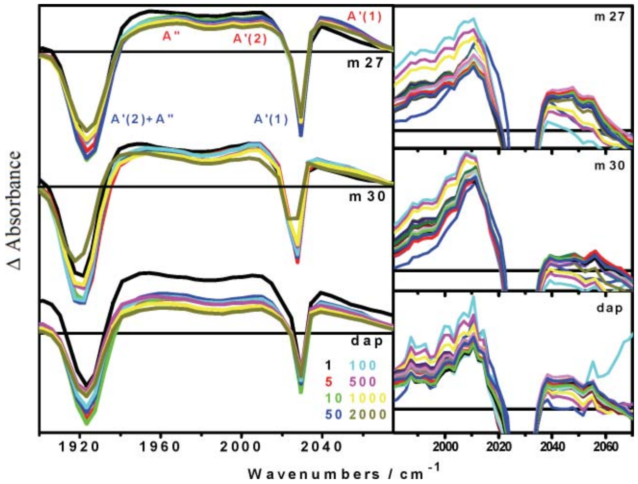

Fig. 8 Difference TRIR spectra of the [Re(Etpy)(CO)$_3$(macrocycle)]$^+$ complexes in MeCN, excited at 400 nm, ~150 fs FWHM. Left: full spectra, experimental points separated by 4–5 cm^{-1}. Right: high-resolution spectra of the A′(2) and A′(1) bands, measured over a 1.5–2000 ps time range. Experimental points are separated by ~2 cm^{-1}. IR band assignment[34] is shown in the top left spectrum in blue and red for the electronic ground and excited state, respectively. The small intensity drop at longer time delays is an instrumental artifact caused by decreasing overlap between pump and probe pulses.

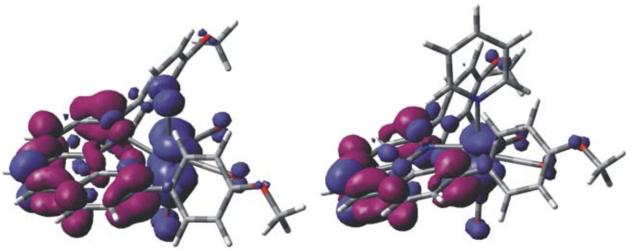

Fig. 10 Electron density difference between the lowest triplet state and the ground state calculated by TD-DFT (B3LYP/CPCM) for [Re(Cl)(CO)$_3$(dap)] in CH$_2$Cl$_2$ (left) and [Re(py)(CO)$_3$(dap)]$^+$ in MeCN (right). The axial ligands Cl and py point up.

DFT characterization of the lowest ^{3}MLCT state

The lowest triplet excited states of [Re(Cl)(CO)$_3$(dap)] and [Re(py)(CO)$_3$(dap)]$^+$ at the ground-state geometry were identified by TD-DFT calculations as a^{3}A″ and characterized by electron-density difference plots, Fig. 10. The lowest triplet state of [Re(Cl)(CO)$_3$(dap)] involves a charge transfer from the Re(Cl)(CO)$_3$ unit to phen combined with a minor electron density reorganization on phen. This is a predominantly MLLCT[41] (or MLCT/XLCT in another terminology;[43] X = Cl) state, with an admixture of a ππ* intraligand (IL) character. The same excited-state description is obtained by an UKS (B3LYP, CPCM for CH$_2$Cl$_2$) structural optimization of the lowest triplet, which was validated by an excellent match between the calculated and experimental excited-state IR spectra, Table 1. The lowest triplet state of [Re(py)(CO)$_3$(dap)]$^+$ (Fig. 10-right) is predominantly ππ* IL localized on phen, with a minor Re(CO)$_3$→phen MLCT contribution. UKS optimization of the lowest triplet state failed because of a close energetic proximity of another triplet of A″ symmetry. Excited states of both complexes show a minor charge transfer from the anysil groups to phen, which is more extensive for [Re(py)(CO)$_3$(dap)]$^+$.

Discussion

Excited-state IR spectra presented above provide information on the excited-state character, *i.e.* the extent of charge transfer upon excitation. Their dynamic evolution reports on the inner- and outer-sphere relaxation dynamics, involving structural reorganization of the excited chromophore and its environment, respectively.[8–10]

Concerning the excited-state relaxation dynamics, two experimental observations deserve further discussion:

– [Re(Cl)(CO)$_3$(phen-macrocycle)] in CH$_2$Cl$_2$ show qualitatively the same type of relaxation that was observed for analogous phen or bpy complexes, however, with important macrocycle-dependent quantitative differences.

– Attaching anisyl groups at the 2 and 9 phen positions in [Re(Etpy)(CO)$_3$(phen-macrocycle)]$^+$ effectively "freezes" excited-state relaxation.

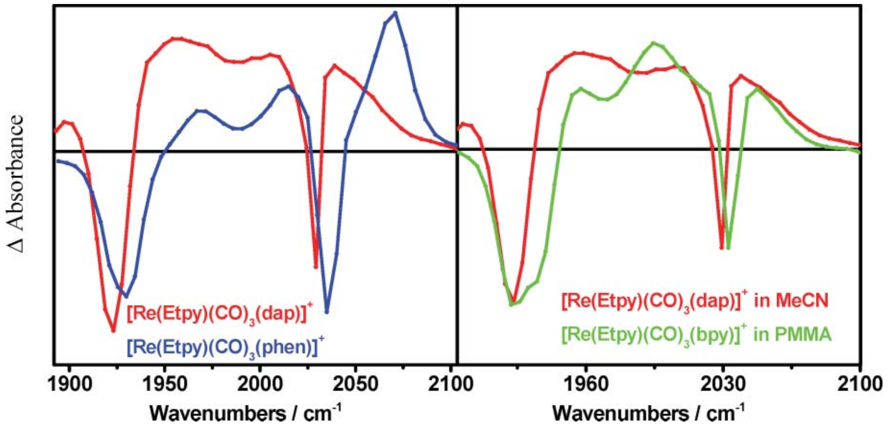

Fig. 9 Left: Comparison of TRIR spectra of [Re(Etpy)(CO)$_3$(dap)]$^+$ (red) and [Re(Etpy)(CO)$_3$(phen)]$^+$ (blue) in MeCN, shown at 500 and 1000 ps respectively. Right: Comparison of TRIR spectra of [Re(Etpy)(CO)$_3$(dap)]$^+$ in MeCN (red) and [Re(Etpy)(CO)$_3$(bpy)]$^+$ in a PMMA film (green), shown at 500 ps.

TRIR spectra as well as DFT and TD-DFT calculations of [Re(Cl)(CO)$_3$(phen-macrocycle)] clearly show that the lowest triplet excited state has a MLCT/XLCT/IL character consisting of a predominant Re(Cl)(CO)$_3$$\rightarrow$phen and minor $\pi\pi^*$ IL(phen) contributions. This is typical[32,41,43–45] for [Re(Cl)(CO)$_3$(N,N)] complexes. Total A′(1) spectral shifts observed for [Re(Cl)(CO)$_3$(phen-macrocycle)] upon excitation (Tabs. 1, 2) are smaller than those observed for analogous species such as [Re(Cl)(CO)$_3$(4,4′-bpy)],[46] [Re(Cl)(CO)$_3$(bpy)],[39] or [Re(Cl)(CO)$_3$(phen)] (Table 2) in CH_2Cl_2. This is due to a slightly larger admixture of an IL character and/or restricted solvent reorganization by the anisyl groups and the macrocycle.

Electronic and structural changes observed upon excitation of [Re(Cl)(CO)$_3$(phen-macrocycle)] occur on three different timescales, manifested by the bi-exponential character of the IR shift dynamics and the rather large values of the instantaneous shift, Fig. 7 and Table 2. These relaxation dynamics can be explained by considering a "supermolecule" or a solute-solvent complex {[Re(Cl)(CO)$_3$(phen-macrocycle)](local solvent)}, which includes ordered solvent molecules that intercalate into the chromophore structure and interact specifically with individual ligands. This "local solvent" is assumed to have very different dynamics from the usual[47] dielectric relaxation. The supermolecule is solvated by bulk CH_2Cl_2 in the usual way and feels its electrostatic field, so called reaction field.[47]

The instantaneous shift, which occurs within the experimental time resolution, accounts for about 40–45% of the total shift. It encompasses several processes such as electron-density redistribution upon Franck–Condon excitation and intersystem crossing,[45] intramolecular vibrational redistribution (IVR), as well as the inertial and part of the collective reorientational relaxation of bulk CH_2Cl_2, which are known[47] to occur with lifetimes of 0.14 ps (52%) and 1.0 ps (48%), respectively.

The "fast" relaxation component τ_f accounts for most of the dynamic shift. It involves the later stages of IVR and of the collective reorientational relaxation of CH_2Cl_2. Within the present model, IVR includes redistribution of vibrational energy between the modes of the chromophore and the local solvent molecules. Interestingly, τ_f slightly increases in the order dap < m27 < m30. This order could reflect the decreasing access of the local as well as bulk solvent to the chromophore, see Fig. 2. By and large, however, the observed τ_f values are similar to those seen for analogous "small" Re complexes in other dipolar solvents such as MeCN,[8,9,48] D_2O,[10] or MeOH,[6,7,48] indicating that they are mostly due to the chromophore itself. The occurrence of IVR on this timescale is further supported by the observation of a major 1.6 ps shift of IR bands of vibrationally excited electronic ground state of *p*-nitroaniline in MeOH, which is also accompanied by initial IR band broadening.[49]

The "slow" relaxation component τ_s does not have any counterpart in solvent dielectric relaxation dynamics measured by time-dependent fluorescence Stokes shift.[47] Even the fastest process observed herein, 10 ps, is about 10-times slower than the slowest kinetics component of CH_2Cl_2 dielectric relaxation.[47] Time constants of 10–15 ps are generally considered as typical of vibrational energy relaxation in dipolar solvents. Similar times were observed by TRIR or time-resolved resonance Raman for analogous[6–10,48] acyclic Re complexes including [Re(Cl)(CO)$_3$(phen)] (Table 2), *t*-stilbenes[50–53] aromatic cations,[54] and hot *p*-nitroaniline,[49] as well as in UV-vis spectra of several excited transition metal complexes. The observation[8] that the excited-state UV band at ~380 nm and excited-state Raman bands due to bpy$^{\bullet-}$ vibrations of [Re(Etpy)(CO)$_3$(4,4′-Me$_2$-bpy)]$^+$ and [Re(Cl)(CO)$_3$(bpy)] grow in intensity within the first 20 ps after excitation shows that the underlying processes affect electronic structure of the excited chromophore. Therefore, we can hardly attribute this process only to a simple transfer of vibrational energy from excited Re(Cl)(CO)$_3$(phen) moiety to collective vibrations of the bulk solvent. Instead, we propose vibrational relaxation of the whole supermolecule {[Re(Cl)(CO)$_3$(phen-macrocycle)](local solvent)}, which involves restructuring of the "intercalated" local solvent, whose molecules adopt new orientations and enter new interactions with the ligands, befit the excited-state structure and electron density distribution. The "slow" relaxation lifetime τ_s increases in the order dap < m27 << m30. While the values of 10 and 13 ps measured for dap and m27, respectively, are in the range expected for Re carbonyl-polypyridines in solution, the 22 ps relaxation time of m30 is distinctively slower. The increase of τ_s on going to the m30 complex is not paralleled by an increase in the band-narrowing time, which stays at *ca.* 10 ps for all three complexes. We propose that the relatively slow relaxation rate of [Re(Cl)(CO)$_3$(m30)] is caused either by slow reorganization of a few local CH_2Cl_2 molecules whose movement is hampered by their confinement inside the folded polyether ring, or by conformational motions of the polyether ring itself, which create a time-dependent field acting on the equatorial CO groups. In reality, the slow solvent- and conformational motions can be coupled, as has been proposed for protein relaxations.[55,56] The proposed active role of m30 polyether ring motions in the excited-state dynamics is supported by the DFT-calculated conformational flexibility. Analogous structural fluctuations are not expected for the much more rigid m27 ring. Notably, relatively slow (206 ps) solvation/conformational dynamics has been reported[57] for free 4,13-diaza-18-crown-6, which accelerates to 22 ps upon complexation with K$^+$.

[Re(Etpy)(CO)$_3$(phen-macrocycle)]$^+$ shows completely different TRIR spectra. The shifts and splitting of the two lower-lying A″ and A′(2) bands are typical[8,9,35,36,40,48] of a ^{3}MLCT state, while the highest A′(1) band is shifted unusually little and does not show any dynamic evolution. In fact, the total A′(1) shift is *ca.* 3-times smaller than that of [Re(Etpy)(CO)$_3$(phen)]$^+$ in MeCN (Fig. 8), which shows the usual relaxation dynamics (τ_f = 1.5 ps, A_f = 12.6 cm^{-1}, τ_s = 13 ps, A_s = 3.1 cm^{-1}, total shift = 32 cm^{-1}) The unusual excited-state behavior of [Re(Etpy)(CO)$_3$(phen-macrocycle)]$^+$ cannot be attributed to wrapping the chromophore by the macrocyclic ring, since it is the same (Fig. 8) for the open-ring [Re(Etpy)(CO)$_3$(dap)]$^+$ and its cyclic m27 and m30 congeners. The nature of the excited state is affected by the presence of the anisyl groups. Interestingly, fixing [Re(Etpy)(CO)$_3$(bpy)]$^+$ in a PMMA film has a very similar effect on the TRIR spectrum, Fig. 8. The DFT-optimized structure of [Re(py)(CO)$_3$(dap)]$^+$ shows (Fig. 3) that the pyridine ligand together with tilted anisyl groups effectively block solvent access to the equatorial CO ligands from the top and the sides. Any rotational movement or out-of-plane vibrations of the py ligand are also hindered. Ensuing steric restrictions on solvent and conformational dynamics would prevent restructuring of the local solvent and fix the excited state structure and charge distribution in a configuration similar to that present in freely relaxing media at very early time delays after excitation, just after the "instantaneous" shift. Indeed, the A′(1) ν(CO) band of most Re carbonyl-diimines at the onset of the dynamic relaxation is shifted only by about 15–20 cm^{-1}. In the case of [Re(py)(CO)$_3$(dap)]$^+$, this shift is even smaller because of a large IL admixture to the lowest triplet state, revealed by TD-DFT, see Fig. 10-right.

In conclusion, it follows that shielding the CO ligands in organometallic molecules with a supramolecular ligand affects both the excited-state character and its relaxation processes, that is the dynamic coupling with the solvent. It is proposed that a small number of ordered solvent molecules, a "local solvent", plays an important role in excited-state relaxation of the solute. In addition, evidence has been obtained indicating a dynamic coupling between excited-state relaxation of the chromophore and conformational movements of its supramolecular surroundings, that is the polyether chain.

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