

Excited-state interconversion between emissive MLCT levels in a dinuclear Ru(II) complex containing a bridging ligand with an extended π system

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For a diruthenium complex, charge migration between different moieties of a bridging ligand with extended conjugation is directly monitored for the first time by using time-resolved emission and absorption spectroscopy.

In recent years, luminescent Ru(II) complexes containing bpy-like polypyridine ligands with extended conjugation have received extensive attention because of their possible use as building blocks for multicomponent systems. These include stereochemically pure metallo-dendrimers,¹ molecular wires,^{2–4} topologically controlled dyads and triads,⁵ and compounds designed to behave as luminescent DNA probes.^{6–11}

During the progress of these studies, some interesting and somewhat unexpected results have been obtained, in particular: (i) a dramatic effect of solvent or microenvironment on the luminescence properties of these species, which led to the so-called ‘light-switching’ behaviour of some of these species with respect to DNA interactions;^{6,7,10} (ii) a relatively small electronic coupling between metal-based chromophores connected by large and conjugated planar bridges,^{1–4} implying relatively slow photoinduced electron and energy transfers across the bridges.

Recent investigations^{1,10} pointed out that most of these results could be rationalised by taking into account the presence of multiple metal-to-ligand charge-transfer (MLCT) excited states (Fig. 1). According to this view, these states are localised on different moieties of the polypyridine ligands with extended conjugation, with their relative energy ordering and interconversion rates subject to the influence of the microenvironment. This assumption however relies on dynamics of interconversion between states which have been only marginally addressed.^{10,11}

Here, we present direct evidence for the excited state interconversion between luminescent MLCT levels involving the tetrapyrrodo[3,2-*a*:2',3'-*c*3'',2''-*h*:2''',3'''-*j*]phenazine bridging ligand (tpphz). The interplay of these MLCT levels is responsible for the photophysical properties of the dinuclear complex [(phen)₂Ru(μ -tpphz)Ru(phen)₂](PF₆)₄ **1** (phen = 1,10-phenanthroline; the structural formula of **1** is shown in Fig. 2),¹ and the dynamics of the process are described on the basis of the results obtained from time-resolved absorption and luminescence spectroscopy.

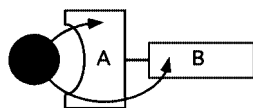


Fig. 1 Schematic representation of the MLCT transitions (arrows) from a metal M (solid circle) to a planar ligand A–B with extended conjugation, which give rise to multiple MLCT excited states. To underline the different localization of the two ligand orbitals involved in the transitions, the ligand A–B is represented as a segmented species, in which A and B are different moieties. Additional ligands and complex charges are neglected. M-to-A CT may convert into M-to-B CT by an A-to-B electron-transfer process.

The redox behavior, ground state absorption spectra, and steady-state luminescence spectra of **1** in acetonitrile fluid solution at room temperature and in a MeOH–EtOH (4:1, v/v) rigid matrix at 77 K have been previously reported.¹ The results are consistent with the following description. Direct irradiation first leads to population of the singlet Ru \rightarrow tpphz CT state involving the phenanthroline moiety of the tpphz ligand, which very rapidly decays to the corresponding triplet state. At 77 K in rigid matrix, this latter state deactivates to the ground state, giving rise to a ³MLCT luminescence peaking at 585 nm. By contrast, in fluid solution at room temperature a charge reorganization process occurs within the (formally) reduced tpphz bridging ligand. Here, the extra electron initially localized on the phen moiety migrates towards the central, pyrazine-based part of the bridge. Thus, the charge-reorganization process leads to population of a triplet Ru \rightarrow tpphz CT state involving the pyrazine moiety of tpphz, which is the lowest energy excited state of **1**.¹ In turn, this level deactivates to the ground state ($\lambda_{em}^{max} = 710$ nm, $\tau = 100$ ns; data in argon-purged acetonitrile).

In an attempt to study in further detail the dynamics of the excited-state interconversion taking place in **1**, we have performed time-resolved studies in different solvents.¹² In acetonitrile solution at room temperature the shape of the luminescence spectrum, as registered at the end of a 35 ps laser pulse, is constant in a time window of 7 ns, and essentially similar to that obtained from steady-state experiments. A possible explanation can be sought in the rate constant of the process, which could be faster than our experimental resolution time (30 ps). If this is the case, the interconversion process has to be slowed down to be detectable. For this reason, we decided to perform the experiments in dichloromethane because in this low-polarity solvent, CT levels are expected to be destabilized with respect to what happens in acetonitrile. Because of the different donor–acceptor separation in the two possible MLCT states involving the large bridging ligand, the extent of this effect should be larger for the final, lower-lying MLCT level (with reference to Fig. 1, this level could be described as a M-to-B CT state) than for the upper-lying MLCT state initially populated (which may be described as M-to-A CT, Fig. 1). As a consequence, in dichloromethane and with respect to acetonitrile, the lower-lying MLCT level should be destabilized (or less

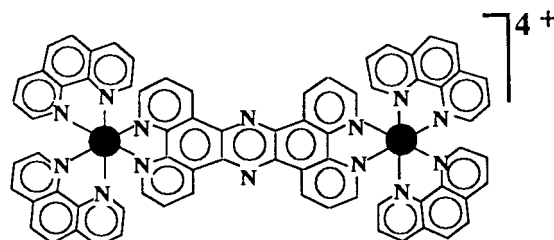


Fig. 2 Structural formula of **1**.

stabilized) with respect to the upper-lying level, so that the driving force of the interconversion process between the two MLCT states is expected to be less favourable and the related rate constant slower and accessible to the time resolution of our equipment.

Actually, the luminescence properties of **1** are time-dependent in dichloromethane solution at room temperature (Fig. 3). In this solvent, the luminescence spectrum registered within the time gate 0–250 ps peaks at ca. 610 nm, while the spectrum registered within the time interval 1200–1450 ps is significantly red-shifted, peaking at ca. 630 nm (this spectrum is substantially similar to the steady-state emission spectrum in dichloromethane). These results suggest that at least two excited states contribute to the emission of **1** in dichloromethane at room temperature. The kinetic analysis of the streak image in the high- and low-energy wavelength regions of the emission spectra clearly indicates that the lower-energy emissive state is produced from the excited state responsible for the higher-energy emission. Actually, this latter emission decays with a lifetime of 220 ps, whereas the lower-energy emission exhibits a risetime of 200 ps, Fig. 3. Further evidence for the two-state interconversion comes from transient absorption spectroscopy, Fig. 4. Here we see that the absorption spectrum which is present at the end of the laser pulse, exhibiting a maximum

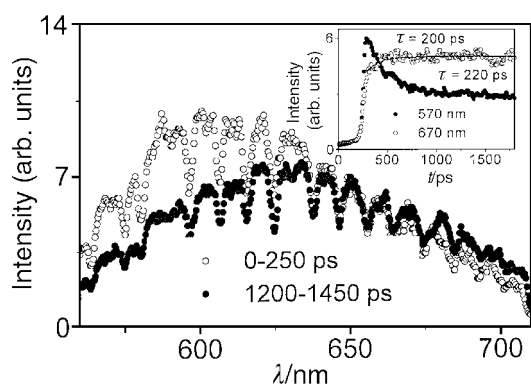


Fig. 3 Time-resolved luminescence spectra of **1** in CH_2Cl_2 following a 35 ps laser pulse (355 nm, 4 mJ); (○) integrated spectrum in the time interval 0–250 ps after the laser pulse; (●) integrated spectrum in the time interval 1200–1450 ps after the laser pulse. The inset shows the luminescence time profiles at 570 nm (●) and 670 nm (○) with the fitted exponential functions.

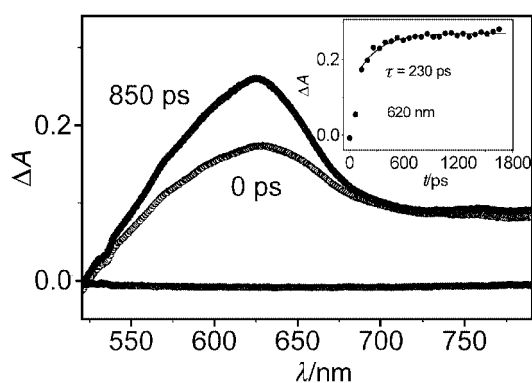


Fig. 4 Time resolved absorption spectra of **1** in CH_2Cl_2 following a 35 ps laser pulse (532 nm, 7 mJ); absorbance at the end of the laser pulse (○) and at 850 ps after the laser pulse (●). The inset shows the time evolution of the absorbance at 620 nm with the fitted exponential function.

around 625 nm, evolves to a new spectrum with a slightly blue shifted maximum, 620 nm, and a higher extinction coefficient. The rate of formation of the new species is 230 ps, see inset of Fig. 4, in good agreement with the luminescence results.

On the basis of the spectroscopic results as observed for the time windows of Fig. 3 and 4, we assign the detected process to formation of the $\text{Ru} \rightarrow \text{tpphz}$ CT state involving the pyrazine moiety of the tpphz bridging ligand (MLCT_0) from the initially produced $\text{Ru} \rightarrow \text{tpphz}$ CT level involving the phenanthroline moiety of tpphz (MLCT_1). Over longer timescales, subsequent decay of the MLCT_0 state to the ground state takes place (not shown in the Figures). From the time evolution of the spectra the rate constant for the charge-migration process leading the interconversion from MLCT_1 to MLCT_0 is found to be $5 \times 10^9 \text{ s}^{-1}$. Given that rate constants of the order of 10^{12} – 10^{13} s^{-1} might be expected for an intramolecular conversion step between states of the same multiplicity, this suggests that a non-negligible energy barrier exists.

In conclusion, we have reported on the experimental observation of the interconversion dynamics of two MLCT excited states localised on the tpphz ligand, a bridge with an extended conjugation incorporated within a $\text{Ru}(\text{II})$ dinuclear species. We believe that our results may provide a useful basis for studies concerned with photoinduced intramolecular energy and electron transfer processes occurring in multinuclear species and across large-sized ligands.

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- The system for time-resolved luminescence experiments is based on a Nd:YAG laser (PY62-10 Continuum, 35 ps pulse) and a streak camera (C1587 Hamamatsu). Excitation was performed at 355 nm, and the absorbance of the solutions at the excitation wavelength was around 1. Time-resolved absorption spectra were detected by a pump and probe system based on the same 35 ps laser and an OMA. Excitation was performed at 532 nm and the absorbance of the solutions at the excitation wavelength was 0.2. For further details see ref. 13.
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