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High sensitivity fluorescence up-conversion spectroscopy of $^3\text{MLCT}$ emission of metal-organic complexes

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Abstract. We demonstrate the implementation of a broadband fluorescence up-conversion set-up with high signal-to-noise ratio and dynamic range allowing for the detection of weak luminescence from triplet states in Fe(II) NHC complexes. Based on the experimentally determined radiative rates and the emission spectra, these states have dominant MLCT character.

1 Context

Since very recently, metallo-organic Fe(II) complexes with N-heterocyclic carbene (NHC) ligands are designed with the aim of increasing the ligand field splitting and thereby avoiding the ultrafast spin crossover (SCO) into quintuplet states [1-3]. This opens the way to use these Fe(II)-NHC complexes as photo-sensitizers with excited state lifetimes beyond 20 ps. Indeed, it was shown by femtosecond broadband transient absorption (TA) spectroscopy that the excited $^1\text{MLCT}$ (metal-to-ligand charge transfer) state relaxes within less than 100 fs into a triplet state, which, depending on the ligands, display lifetimes of up to 530 ps [3]. However, the exact nature of this state, a $^3\text{MLCT}$ or a metal-centred triplet state (^3MC), is still controversial. Since the stimulated emission of this state is quasi spin-forbidden and therefore too weak to be detected in TA, it would be extremely valuable to detect the luminescence directly in a background-free experiment in order to determine its energy shift and radiative rate.

Earlier attempts to detect $^3\text{MLCT}$ emission by broadband fluorescence up-conversion spectroscopy (FLUPS) in Ru complexes were only partly successful, since only the initial sub-ps portion was detected and the longer-lived emission from the electronically and structurally relaxed $^3\text{MLCT}$ was buried in the noise floor [4]. We therefore implemented a broadband FLUPS experiment with a sufficiently high dynamic range and sensitivity that

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allows to determine both the triplet emission energy and its radiative rate relative to the $^1\text{MLCT}$ emission.

Broadband FLUPS capable of measuring full emission spectra for fixed delay times was introduced more than 20 years ago [5], and significantly improved in recent years in terms of sensitivity, bandwidth and time resolution [6,7]. Following these works, we implemented in the present approach a non-collinear type II sum frequency generation (SFG), enhancing the spectral acceptance bandwidth. However, given the relatively long-lived emission signal to be detected a compromise between sensitivity and time resolution led us to use a slightly thicker 400- μm BBO crystal as SFG medium, entailing a 190-fs time resolution estimated from the solvent Raman emission. Since the absorption spectrum due to the $^1\text{MLCT}$ transition of the complexes have their maximum at 510 nm (fig. 2, [2]), the pump was set as 515 nm, with ~ 60 fs pulses, produced by an optical parametric amplifier (TOPAS Prime, Light conversion) at 5 kHz. The excitation energy was 0.4 μJ . Gate pulses at 1420 nm were produced by the same OPA. The fluorescence was collected by a pair of 3-inch parabolic mirrors, then focused and overlapped with the gate beam in spots of 0.4-0.5 mm diameter in the BBO crystal. The BBO phase matching angle is fixed and centred for highest SFG efficiency with 630-640 nm fluorescence. The up-converted fluorescence was detected with a SP-2300i spectrometer and a LN_2 -cooled CCD camera. The measurements consisted of 5 scans with 15 s exposure at each time delay. The samples were placed in a 1-mm cuvette with an absorbance at the excitation wavelength of $\text{OD}=1.0$.

2 Results and discussion

Figure 1 displays the results obtained for a Fe(II)-NHC complexes in acetonitrile with four carbene bonds and two COOH groups attached to the central bi-pyridine moieties (inset, fig. 1B). The time- and wavelength resolved data (fig. 1A) show Raman replica of the chirped excitation pulses at 570-630 nm, and a broad intense fluorescence due to the $^1\text{MLCT}$ state ranging from 580 to beyond 720 nm. This signal is temporally unresolved and followed by a weaker emission band in the 630 to 720 nm range, slowly decaying on a 20-ps timescale (figs. 1 B&C). The high dynamic range of FLUPS (here 4 orders of magnitude) allows these weak components to be observed. A multi-exponential fit of the decay kinetics averaged over 660 to 705 nm, shows the $^1\text{MLCT}$ fluorescence at $t=0$, followed by a $\tau_1=0.45$ ps, a $\tau_2=17.5\pm 2.0$ ps component, and weak non-decaying background (fig. 1 B).

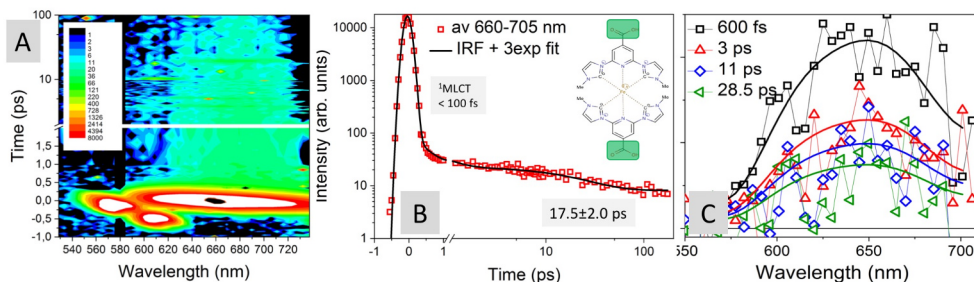


Figure 1: Emission data of the Fe(II)-NHC complex in $\text{C}_2\text{H}_3\text{N}$ (inset fig. 1B) measured by the high-sensitivity FLUPS experiment. (A): 2D map of time- and wavelength-resolved data. (B) Kinetic trace of the emission obtained by integrating the intensity over 660 to 705 nm. (C) Time-resolved emission spectra for the delays indicated. Solid lines are guide-to-the-eye.

This is in good agreement with excited state decay times determined from TA on the same compounds, 130 fs and 16.5 ps, respectively for vibrational relaxation and excited state decay of the long-lived triplet state [8]. We therefore conclude that this triplet state is

weakly emissive, with a radiative rate roughly 500-1000 times smaller than the $^1\text{MLCT}$ state, as determined from the fitted amplitudes of the emission components.

Figure 2 compares the normalized, time-resolved emission spectra recorded with FLUPS (dotted lines) and with a streak camera (SC, full lines) under 515 nm excitation. With an 8-10 ps time resolution (IRF), the SC spectrum at 15 ps is still dominated by the much more intense $^1\text{MLCT}$ fluorescence peaking at 550 nm. Comparison of the SC and FLUPS spectrum of the $^1\text{MLCT}$ fluorescence at 300 fs (green dashed line) indicates that the latter is limited by the acceptance bandwidth of the FLUPS set-up, which is not more than 80 nm wide in the present case. The triplet emission “filtered” by this SFG bandwidth appears to have its maximum at 685-695 nm (blue line, fig.2), almost 0.5 eV red-shifted with respect to the $^1\text{MLCT}$ fluorescence.

In conclusion, the triplet emission is characterized by a ≥ 400 meV red-shift, and a 500-1000 times weaker radiative rate than the $^1\text{MLCT}$ transition. This allows us to assign this long-lived state to the $^3\text{MLCT}$ transition rather than to ^3MC , since emission from the latter is expected to be further red-shifted (> 1 eV) in the structurally relaxed state [9], and to have an even weaker radiative rate, since it is double forbidden due to spin and symmetry selection rules in the Fe(II) octahedral geometry.

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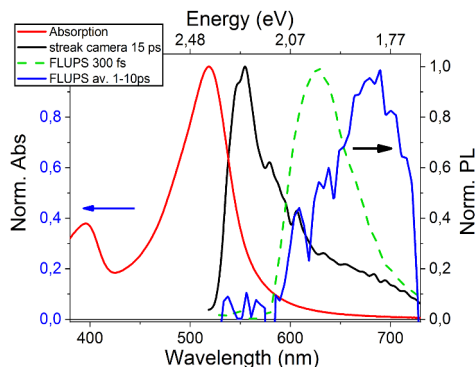


Figure 2: Normalized absorption and time-resolved spectra of the Fe(II) complex presented in fig. 1. Black: $^1\text{MLCT}$ spectrum measured with a SC; Green: $^1\text{MLCT}$ emission through the acc. bandwidth filter of FLUPS; Blue: $^3\text{MLCT}$ emission spectrum averaged 1-10 ps.