SUPPLEMENTARY INFORMATION (SI)

EXPERIMENTAL METHODS

Materials

Tris(2,2'-bipyridine)iron(II) chloride hexahydrate ($[Fe(2,2'\text{-bipyridine})]_3Cl_2 \times 6H_2O$) was synthesized according to Ref. [1]. Deionized water was used as the solvent. Room temperature solutions of $[Fe^{II}(bpy)_3]^{2+}$ were used in both transient absorption (1-10 mM) and fluorescence up-conversion (1 mM) experiments at 20^o C. Static UV-VIS absorption spectra of the samples were measured using a Perkin-Elmer LAMBDA-35 spectrophotometer (or Shimadzu).

Fluorescence Up-Conversion Setup

We used the broadband femtosecond fluorescence up-conversion set-up described in Refs [2, 3] to capture the early relaxation processes of the ^{1}MLCT state of $[Fe^{II}(bpy)_3]^{2+}$ in the 440-690 nm range, with a resolution of 110±10 fs. The sample is excited at 400 nm by means of pulses with a typical width of ~40 fs, a power of 40-80 nJ/pulse, in a focal spot of 50 μm (FWHM), and a repetition rate of 250 Hz. The luminescence, collected in forward scattering geometry, is up-converted in a 250 μm thick Beta Barium Borate (BBO) crystal by mixing with a pulse at 800 nm (so called gate pulse). The up-converted signal is spatially filtered and detected with a spectrograph and a liquid-N_2 cooled CCD camera in polychromatic mode.

Color filters were used to attenuate the remaining 400 nm and 800 nm light, which greatly improve the signal-to-noise ratio, but limit the detectable spectral range to the 440-690 nm region. Time zero was determined by detecting the up-converted Raman line of water. The aqueous solution of $[Fe^{II}(bpy)_3]^{2+}$ was flown in a 0.2 mm thick quartz flow cell at a speed of 2 m/s to avoid photodegradation. With the above experimental conditions, the 400 nm pulse hits the same spot ~5 times. However, since the lifetime of the lowest excited state (here the quintet $^5T_2$ state) is about 650 ps, all excited molecules relax to the ground state between two adjacent pump pulses.

The collected luminescence signal was corrected for the Group Velocity Dispersion (GVD) over the entire detection range (the blue-most component is delayed by ~400 fs with respect to the red-most component).

We measured it by recording a white light pulse signal generated in a neat water solution at the same experimental conditions. The reported emission spectra are corrected for both

colour filters present in the beam. Neither the spectral response of the CCD camera nor the dependence on the BBO acceptance angle was corrected. However, since these corrections are slowly varying functions of the wavelength, they are not critical for the evaluation of the peak position and of the intensity distribution of the spectra. Finally, an additional source of spectral distortion originates from re-absorption since the blue tail of the emission band overlaps the red tail of the absorption band. We checked this in a study as a function of concentration and of flow-cell thickness, and found no changes.

Transient Absorption Setup

The transient absorption (TA) spectrometer is based on a 1 kHz Ti:sapphire pumped regenerative amplifier system producing ~100 fs, 0.8 mJ pulses centered at ~800 nm. Briefly, a white-light continuum (WLC) probe beam was generated by focusing a small part of the fundamental output into a 2 mm thick CaF_2 window. Excitation at 400 nm with pulse energies up to ca. 100 μJ were obtained by frequency doubling 90% of the fundamental 800 nm output. The pump and probe beam diameters were fixed to 180 μm and 65 μm, respectively. The relative polarization of the excitation and probe electric field vectors were orthogonal to each other. The pump beam was chopped at the repetition rate of 500 Hz, whereas the probe beam was detected at the nominal frequency of the laser (1 kHz). The sample was a 0.1 mm-thick free jet, in order to refresh it after each pair of pump and probe laser pulses. We recorded adjacent pairs of pumped and unpumped spectra for each laser shot and after subtraction we obtained transient spectra for each pair of pulses. After the sample, the probe beam was re-collimated and focused on the entrance slit of a double grating monochromator coupled with a 512 pixel diode array. The detector can be read out at 1 kHz and yields corresponding pumped and unpumped spectra for each probe laser shot. The spectral response and the energy calibration were measured, either using an Hg line emission lamp or by recording a steady-state spectrum of the sample with the WLC. The monochromator grating of 150 l/mm was used in order to cover a broad spectral range between 340-650 nm.

The GVD of the WLC beam was measured in a neat water jet exploiting two-photon absorption and cross-phase modulation signals around time zero. A strong emission feature (FWHM duration 140 ± 15 fs) at 450-460 nm in liquid water due to the Raman-active symmetric stretch mode of H_2O (ν_1 = 3490 cm^{-1}) delivered a cross-correlation signal between pump and probe pulses.

We checked the linearity of our measurements by recording the pump wavelength dependence of the ground state bleach signal, and found a linear dependence up to 80 mJ/cm^2. In addition our results were found independent of concentration.

GLOBAL ANALYSIS PROCEDURE

The transient absorption results presented in this work were analyzed by means of the global analysis (GA) approach[4]. The GA term refers to simultaneous analysis of all measurements contained in a multivariable data set[5]. The time-resolved transient absorption spectra recorded in these experiments are a typical example of 2-variable measurements, where the independently measured variables are the wavelengths and time (or more precisely the time delay between the pump and the probe pulses). A representative set of transient absorption data measured with our setup is shown in Fig. 3 of the article. The data is sorted into M x N matrix, where M defines the wavelength dimension (in this case there are 512 discrete wavelength measurements each corresponding to a diode pixel) and N corresponds to discrete time steps over the entire time delay measured in the experiments (In Fig. 3 the time step was ca. 67 fs and the total time delay measured was 20 ps, which means we have measured this delay with 299 time steps). With data set as shown in Fig. 3, the GA allows for simultaneous analysis of the dynamical information across the entire spectral and temporal range by fitting the data with just one model scenario.

In addition, the global techniques permit to separate the physically-relevant information from the stochastically-distributed additive noise present in the data set by means of singular value decomposition (SVD)[6]. In principle, the SVD procedure allows determining the rank of an arbitrary matrix corrupted by random noise. In data analysis, it translates into a powerful technique of data reduction and noise suppression[4]. It allows reducing the data dimensionality and permits performing a nonlinear least square global fit on the reduced data, without losing any relevant information contained in the data.

Singular Value Decomposition (SVD)

We assume that the data matrix of the TA experiment is defined as follows:

$$A(\lambda_i, t_k) \equiv A = \widetilde{A} + \Xi \qquad \text{(SI.1)}$$

where $A(\lambda_i, t_k)$ is the M x N matrix composed of discrete sets of wavelengths λ_i and time delay t_k, and the noise present in the data is additive. The $\widetilde{A}$ matrix contains all the

information about the spectral evolution of the system, whereas the Ξ matrix represents the stochastic normally-distributed noise with zero mean value. The SVD procedure allows decomposing the A matrix into a product of 3 components according the formula:

$$A = USV^T \tag{SI.2}$$

where U and V^T stand for orthogonal matrices of M x M and N x N dimensions, respectively. Their columns contain the left and right singular vectors. In the case of TA absorption data, the SVD approach yields U and V^T matrices, which we can identify as basis spectra and basis kinetics (time traces), as shown in previous works [7-10]. The diagonal elements of S matrix yield the singular values $S_{ii}=s_i$.[11] The outcome of the SVD transformation it to reduce significantly the number of relevant kinetic and spectral components required to describe the entire spectral and temporal evolution of the system.

In our case, we assume a sequential kinetic scheme[4], in which the temporal evolution of the system is described by a sequence of events with specific first-order decay rates k_i and corresponding lifetimes τ_i, so that the kinetic response can be modeled by a sum of N model functions. The TA absorption kinetics are modeled as a sum of exponential functions convoluted with the instrument response function (IRF). The IRF is approximated with a Gaussian function of FWHM equal to the cross-correlation function of the experiment (i.e. 145(15) fs). The analytical function is given by [4]:

$$\Delta A(t) = e^{-k_i \cdot t} \otimes IRF(t) = \frac{1}{2}\sum_{i=1}^{N} a_i \exp\left[k_i(\mu - t) + \frac{(k_i\sigma)^2}{2} \right]\left[1 + erf\left(\frac{t - (\mu + k_i\sigma^2)}{\sqrt{2}\sigma} \right) \right]. \tag{SI.3}$$

where a_i if the amplitude of i^{th} decay, μ describes the time origin of the IRF function (time-zero) and σ its width. FWHM is then defined as $FWHM = 2\sigma \cdot \sqrt{2\ln 2}$.

The GA consists of simultaneous fitting of all significant V_i^T traces with a number of $\Delta A_k(t)$ functions[4]:

$$V_i^T = \sum_{k=1}^{K} a_{i,k} \cdot \Delta A_k(t) \tag{SI.4}$$

The coefficients $a_{i,k}$ obtained in the fit can be used to calculate the corresponding decay-associated spectra (DAS) of the involved kinetics by using the set of properly weighted U_i spectral SVD components via[4]:

$$DAS_k = \sum_{i=1}^{N} a_{i,k} \cdot s_i \cdot U_i \tag{SI.5}$$

The obtained DAS contain the contribution of corresponding lifetime decays τ^i in the spectral evolution of the system. In some cases, the decay-associated spectra can be directly attributed to the species-associated spectra (SAS), which describe their corresponding absorption spectra. In our case, as described in the article, the DAS cannot be assigned to SAS due to the strongly overlapping transient absorption spectra of the photochemical species involved in subsequent steps of the relaxation processes.

SVD Results

In order to analyze the results presented in Fig. 3 of the article, we have employed the approach discussed above. The analysis consisted of the SVD decomposition of the TA data sets according to Eq. SI.2 . Next to it, it was followed by the global fitting of the kinetic V_i^T components retained after the transformation using the global fit function, defined in Eq. SI.3, using Eq. SI.4. Once all the SVD kinetic components are fitted, using the extracted pre-exponential coefficients $a_{i,k}$, we have constructed the decay-associated spectra (DAS) corresponding to the characteristic lifetimes τ_i used in the fit (see Eq. SI.4). In addition, we assume the absence of the spectral diffusion in our TA data. This approach was be applied to the results obtained in 3 different time windows, namely 5 ps, 20 ps and 1 ns for the aqueous solution of 9 mM $[Fe^{II}(bpy)_3]^{2+}$.

For the long-time TA data (time delay up to 1.2 ns) and as expected, we find a single singular value with a lifetime is τ_1 = 665±45 ps, and a DAS that reflects the ground state absorption. For the short time data (5 ps time window), we have applied the SVD transformation and panels a) through d) of Fig. S1 present the singular values retained in the analysis, their corresponding spectral U_i and temporal V_i^T basis sets together with the fit functions using the aforementioned kinetic model and the selected single-wavelength kinetic traces of the unreduced data set fitted using the same kinetic model. The choice of the wavelengths is supported by the fact that they cover the most relevant spectral regions (see article), where significant excited-state absorption changes are observed on the very fast timescales (i.e. the ESA at 370 nm and 630 nm described in Figs. 4 and 5b in the article) and the very subtle rise time observed on the ground-state bleach signal (i.e. at 523 nm).

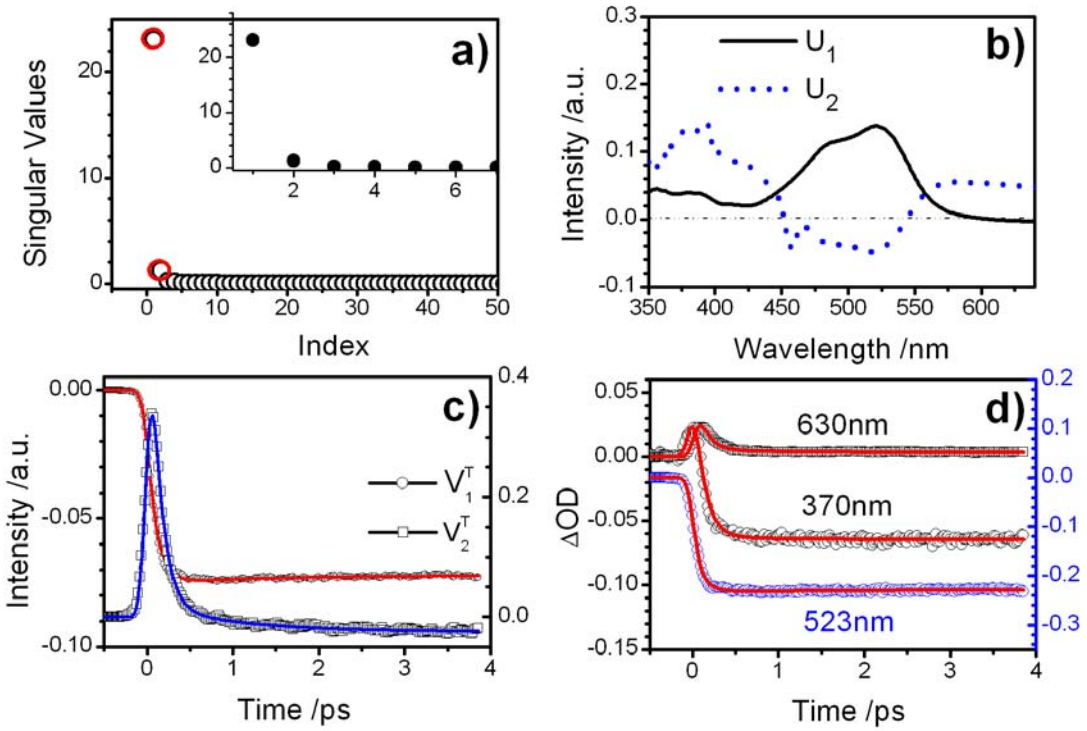

Figure S1: SVD decomposition of the transient absorption data of a 9mM aqueous solution of $[Fe^{II}(bpy)_3]^{2+}$ upon 35 mJ/cm^2 excitation fluence. Panel (a): singular values as obtained upon the decomposition (circles indicate the retained values), where the inset zooms into the initial 7 values to show better the noise cut-off of the singular values. Panels (b)-(c): spectral (U_i) and temporal (V_i^T) basis vectors used in the data reconstruction. In addition, panel (c) presents the global fit results of the SVD kinetics. In (d) the kinetic traces at 3 selected wavelengths are displayed together with their fit functions using a global fit model (see Fig. 6 of the article)

The analysis resulted in 2 dominant SVD components. Their kinetic parts are shown in Fig. S1c. Clearly, they account for the ESA absorption found at the blue-most and red-most parts of the transient absorption spectra (V_2^T) and the GSB signal (V_1^T). The spectral parts, U_1 and U_2 in Fig. S1b, can be associated with the ground state absorption spectrum and the reported spectrum of the reduced bipyridine (bpy^-) ligand. Indeed, the U_2 spectrum resembles very much the steady-state spectrum of the reduced $[Fe^{II}(bpy)_3]^{1+}$ complex reported in Ref. [12] (see article). In the kinetic model used here, we assume the existence of three relaxation rate constants, which are linked to only two spectral components. Therefore we cannot directly link the U_2 spectrum to the ^{3}MLCT species, although it contains a major fraction of its absorption band. On contrary, the U_1 component remains unchanged both in 5 ps and 1 ns time windows and thus we interpret its spectral components as directly linked to the species-associated spectrum (SAS) of the ground state species.

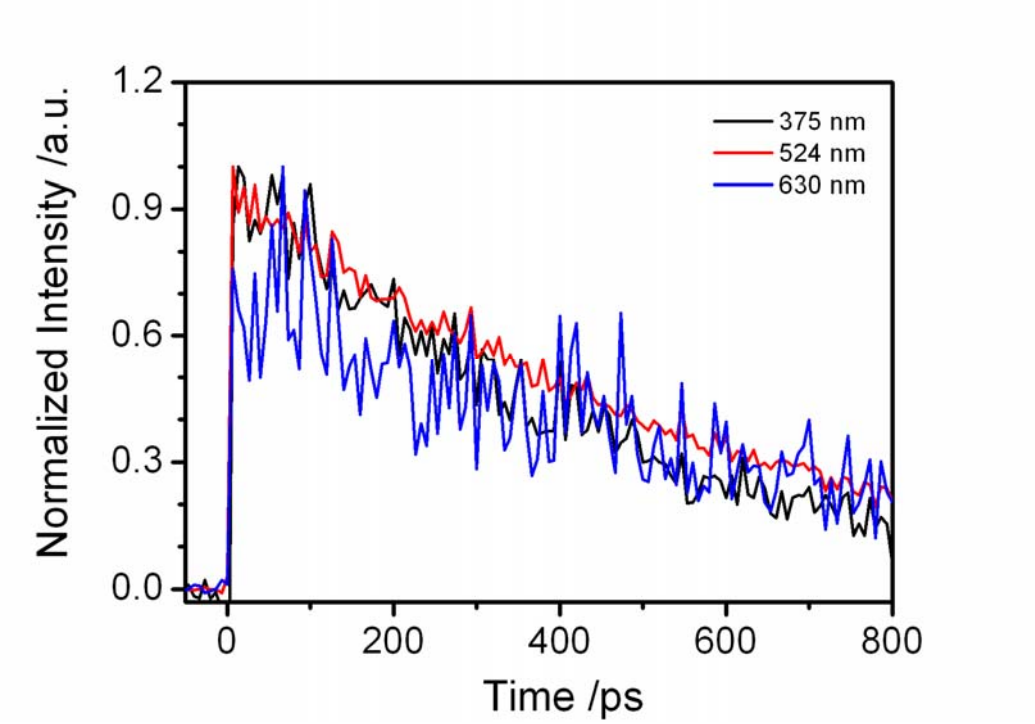

Figure S2: Long-time kinetics of $[Fe^{II}(bpy)_3]^{2+}$ at characteristic wavelengths. The bleach traces at 375 nm and 524 nm have been inverted and normalized to the 630 nm excited state absorption trace.

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