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## Pump–probe XAS investigation of the triplet state of an Ir photosensitizer with chromenopyridinone ligands†

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The triplet excited state of a new Ir-based photosensitizer with two chromenopyridinone and one bipyridine-based ligands has been studied by pump–probe X-ray absorption near edge structure (XANES) spectroscopy coupled with DFT calculations. The excited state has a lifetime of 0.5  $\mu$ s in acetonitrile and is characterized by very small changes of the local atomic structure with an average metal–ligand bond length change of less than 0.01 Å. DFT-based calculations allow the interpretation of the XANES in the energy range of  $\sim$ 50 eV around the absorption edge. The observed transient XANES signal arises from an additional metal-centered Ir 5d vacancy in the excited state which appears as a result of electron transfer from the metal to the ligand. The overall energy shift of the excited state spectrum originates from the shift of 2p and unoccupied states induced by screening effects. The approach for the analysis of time-resolved spectra of 5d metal complexes is quite general and can also be used if excited and ground state structures are significantly different.

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## Introduction

The development of pump-and-probe X-ray absorption spectroscopy (XAS) has been rapid during the last decade as a time-resolved technique to study the electronic and local atomic structures of materials.<sup>1–3</sup> Initially, this method was proposed in the hard X-ray range for experiments with 100 ps resolution in the picosecond–nanosecond time range.<sup>4,5</sup> Later, the efficiency of such measurements has increased due to the development of powerful high repetition rate lasers.<sup>6,7</sup> Furthermore, the technique evolved in the direction of ultra-fast experiments with sub-picosecond resolution<sup>8–10</sup> and slower experiments in the microsecond range.<sup>11–13</sup> The sub-picosecond range is explored now with X-ray free electron lasers.<sup>14–17</sup> The focus of our efforts at the SLS synchrotron is on processes that occur in the 100 ns to 100  $\mu$ s time range.

This time interval is especially relevant for photocatalysis.<sup>18,19</sup> The approach that we have realized in the pump-sequential-probe setup allows us to measure simultaneously the whole kinetics with 30 ns resolution and XAS spectra. Previously we have used this method in the microsecond range to study Co catalysts and have determined the structure of Co(i) catalytic intermediates.<sup>11,19</sup> In the present article, we demonstrate for the first time such an approach in the nanosecond range to investigate the excited state of a photosensitizer.

Photosensitizers are probably the most popular systems for pump–probe XAS investigations due to their applications in light harvesting, dye-sensitized solar cells and photocatalysis. A common feature of all these compounds is the fast electron transfer, most often from the metal to the ligand. Classical photosensitizers are complexes of 4d and 5d metals, which are efficient due to strong spin–orbit coupling and typically small structural rearrangements in the excited state. An attractive alternative is complexes of 3d metals, of which some were studied by pump–probe XAS.<sup>20–22</sup> In spite of the tendency to significantly rearrange the metal environment in the excited state, they were recently engineered to have a long-lived metal-to-ligand charge transfer (MLCT) state<sup>23</sup> with a lifetime comparable to Ru-based benchmarks. Knowledge about the excited state structure of related complexes obtained using time-resolved X-ray spectroscopy<sup>21</sup> is important for such development. Ru photosensitizers have been investigated at K- and L

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absorption edges. These studies do not look only at dissolved complexes,<sup>4</sup> but also at photosensitizers assembled on semiconductor nanoparticles.<sup>24,25</sup>

Among the 5d metal complexes, pump-probe XAS investigations have been performed for bi-platinum complexes in which electron transfer from antibonding orbitals has induced significant contraction of the Pt-Pt distance.<sup>26,27</sup> For W and Re halide complexes, the photo-induced structural changes are smaller.<sup>28,29</sup> Finally, complexes with a 5d<sup>6</sup> central atom ground state electron configuration as well N or C in the first coordination sphere display only minor changes in their local structure ( $\sim 0.02$  Å) upon photoexcitation and the X-ray absorption spectra in the near-edge region (XANES) became sensitive to the electronic structure only. Os photosensitizers were the first examples in this category<sup>30,31</sup> and the interest for Ir has increased since then.<sup>32–34</sup> Here we will demonstrate the use of pump-probe XAS on a novel organometallic Ir complex with chromenopyridinone ligands [Ir(Chp)<sub>2</sub>(dtbbpy)]PF<sub>6</sub>, where Chp is 3-methyl-6-oxo-6H-isochromeno[4,3-b]pyridin-10-ide and dtbbpy is 4,4'-di-*tert*-butyl-2,2'-bipyridine (Fig. 1). Chromenopyridines and chromenopyridinones are well-known for their pharmacological properties,<sup>35</sup> but to our knowledge, they have not yet been utilized for organometallic complexes.

## Experimental methods

Experiments have been performed at the SuperXAS beamline of the Swiss Light Source (SLS), Villigen, Switzerland. The storage ring was run in the top-up mode with an average current of 400 mA. The X-ray beam was collimated by using a Si-coated mirror and the energy has been scanned by using a channel-cut Si(111) monochromator. A toroidal mirror with Rh coating next to the monochromator was employed to focus the incident X-rays to a spot size of  $100 \times 100 \mu\text{m}^2$  on the sample. The photon flux at the sample was found to be  $3.3 \times 10^{11}$  photons per s. Excitation was performed at the second harmonic (395 nm) of a Wyvern 500 femtosecond laser amplifier (KM labs). The repetition rate of the laser was 50 kHz, with a pulse duration of  $\sim 80$  fs and an output power of 0.8 W. The size of the laser spot at the sample was  $200 \times 300 \mu\text{m}^2$ .

The synthesis of the complex and its characterization by 1D <sup>1</sup>H- and <sup>13</sup>C-NMR, 2D <sup>1</sup>H/<sup>13</sup>C-HMBC and -HSQC, and MS are

described in the ESI.† For the X-ray measurements, the complex was dissolved in anhydrous acetonitrile to a concentration of 1 mM. Approximately 70 mL of the sample was circulated in a closed-cycle flow-system with the laser and X-ray beams focused on the round jet of the sample with a diameter of 750  $\mu\text{m}$ . The sample was kept under an N<sub>2</sub> atmosphere. The linear speed of the sample flow was  $\sim 10 \text{ m s}^{-1}$  at the point of the interaction of both beams. Since the expected excited state lifetime is significantly lower than the period between two laser pulses, molecules which were excited by a previous laser pulse have sufficient time to fully recover to the ground state and therefore can be re-excited.

The pump-sequential-probe method has been used for time-resolved Ir L<sub>3</sub> edge XAS measurements. Within this approach the full kinetic information is obtained without any scan of the delay time. A time-tagged single photon counting method is used as described previously.<sup>11</sup> The setup is based on a multichannel digital X-ray processor XIA XMAP running in the 'list mapping' mode with signals in all channels sampled with a 20 ns step. As detectors for incoming and fluorescence X-ray radiation, we used large area avalanche photodiodes (APD) (Advanced Photonix Inc, model 630-70-72-500, sensitive surface area 200 mm<sup>2</sup>) coupled to a charge sensitive preamplifier (fastComTec, model CSP10). We used custom-made Soller slits with conical walls and a Z-1 filter (Zn foil with absorption edge jump 4.5) to reduce the background noise caused due to the elastic scattering. The overall time resolution of the setup, which takes into account the contribution from detectors, amplifiers, the data acquisition system and synchronization jitters, is around 30 ns. In comparison with the setup, described previously,<sup>11</sup> a new laser system, which has higher repetition rates and shorter pulses, has been used. It has allowed us to increase the efficiency of the setup for short-lived species. The flow system for the sample has also been optimized with the goal to refresh the sample in the probed area during the time between two laser pulses. The optimization of the nozzle that forms the open jet is essential to obtain a stable flow. The long tip at the end of the nozzle with an almost constant diameter influences negatively on the jet stability,<sup>36</sup> therefore, we have developed a glass nozzle with a contraction angle of more than 30° and a very short tip.

## Theoretical methods

XANES calculations have been performed using the approach developed previously<sup>37</sup> on the basis of Slater-type orbitals obtained self-consistently using the ADF2016 package.<sup>38,39</sup> In all calculations, we have taken into account the C<sub>2</sub> symmetry of the complex. All electrons were taken into account during self-consistent field (SCF) cycles. Relativistic spin-unrestricted calculations within one-component ZORA formalism<sup>40</sup> for singlet and triplet states of the complex were performed. A quadruple- $\zeta$  basis set of the Slater-type with four polarization functions was used. The intensities of 2p-to-unoccupied state transitions were obtained by integration of dipole transition

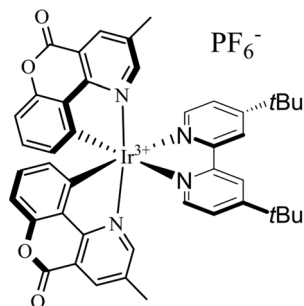


Fig. 1 [Ir(Chp)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> complex.

matrix elements between 2p-originated MOs and unoccupied MOs. The integration has been performed on a 3D spatial cubic grid in close proximity to the absorbing Ir atom with 132 651 points and a 0.01 Å step size in each direction. The simulation of the XANES spectral region (~50 eV) requires integration for ~1000 lowest unoccupied MOs. Because of the very weak influence of the distant alkyl groups on the XANES spectra, a simplified Ir complex with 5-oxo-5*H*-chromeno[4,3-*b*]pyridin-10-ide and 2,2'-bipyridine was used for simulations. Finally, Lorentzian broadening of this discrete spectrum was performed using the energy-dependent arctangent model. This accounted for the finite mean free path of the photoelectron, the core hole lifetime broadening, and the monochromator resolution. The exchange–correlation potential with parameterization by Vosko, Wilk, and Nusair<sup>41</sup> calculated within the local density approximation (LDA) was used. Geometrical optimization was performed using the GGA: BLYP exchange–correlation functional,<sup>42,43</sup> within the one-component ZORA formalism using the triple- $\zeta$  basis set with two polarization functions.

## Results and discussion

To characterize the excited state of  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]\text{PF}_6$  we have performed time-resolved Ir  $L_3$  edge X-ray Absorption Near Edge Structure (XANES) spectroscopy using the pump-sequential-probe method.<sup>11</sup> The experimental spectrum of the Ir  $L_3$  XANES for  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]\text{PF}_6$  in the ground state is shown as a solid line on the top part of Fig. 2, while the experimental transient spectrum corresponding to the formation of the photo-excited state is shown as a solid line on the bottom panel. The pump-sequential-probe setup allows simultaneous measurements of many XANES spectra for different delays between the laser pump and the X-ray probe, providing the possibility of monitoring the excited state kinetics. Our setup allowed us to measure more than 500 points with 20 ns time steps. Principal component analysis (PCA) of this spectral series was subsequently performed using a previously described method.<sup>44</sup> The PCA indicated two statistically significant components, one of them corresponds to the ground state, while the other one is a long-lived excited state. The kinetics of the excited state component can be fitted as a mono-exponential decay with a lifetime of 0.5  $\mu\text{s}$  (Fig. 3).

The highest occupied molecular orbital (HOMO) for the ground state is a mixture of Ir d-orbitals with p-orbitals of C localized on the phenyl groups of the Chp ligand (Fig. 4). The lowest unoccupied molecular orbital (LUMO) is distributed over the neutral bpy-unit with a weak Ir 5d contribution. In the triplet state, an electron from the HOMO is excited to the LUMO and changes its spin. Both these orbitals have non-bonding character between Ir and the ligand. Small structural differences between the lowest singlet and the triplet excited state are therefore expected. Indeed, optimization of the local structure using the DFT-based approach (coordinates are reported in the ESI†) has indicated a change of <0.01 Å in the average Ir-ligand bond length that accompanies the transition

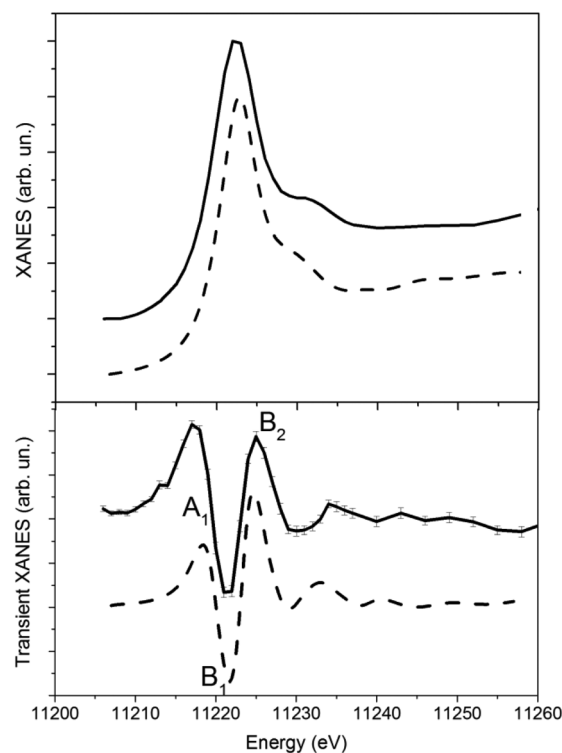


Fig. 2 Top: Ir  $L_3$  XANES spectra of  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]^+$  in the ground state obtained experimentally (solid line) and using DFT-based theoretical calculations (dashed line). Bottom: Transient XANES spectra obtained experimentally (solid line) for a 1  $\mu\text{s}$  time window and using DFT based calculations (dashed line).

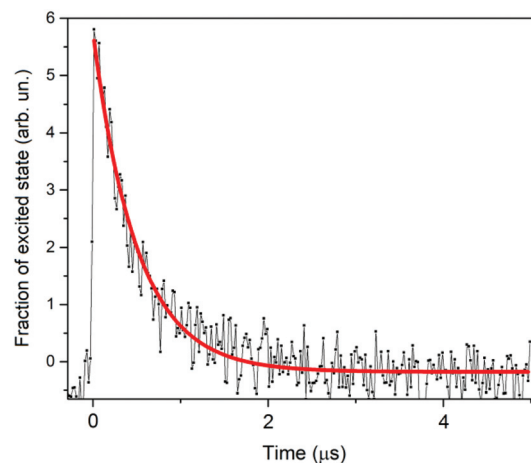


Fig. 3 Kinetics obtained using principal component analysis of experimental time-resolved Ir  $L_3$  XANES spectra (black line) and mono-exponential fit with lifetime 0.5  $\mu\text{s}$ .

from the ground singlet to the photo-excited triplet state. The Ir–C distances in the ground and excited states are 2.056 Å and 2.030 Å, respectively. Ir–N distances for the Chp ligand are 2.106 Å (ground) and 2.108 Å (excited), while for dtbbpy, these are 2.206 Å (ground) and 2.207 Å (excited).

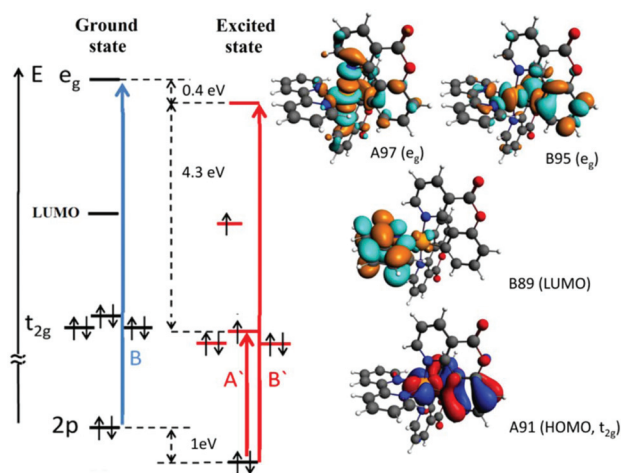


Fig. 4 Energy level diagram and some important molecular orbitals which are relevant to explain the transient Ir  $L_3$  XANES spectra.

In the ground state, Ir has a low spin  $5d^6$  electron configuration and the qualitative interpretation of Ir  $L$  edge XANES can be performed within the model of the octahedral environment. An intense white line is observed at 11 222 eV, which is due to the transition of an electron from Ir 2p to unoccupied 5d states with  $e_g$  symmetry. The ground state spectrum does not have visible shoulders on the low energy side of the white line because the  $t_{2g}$  states of Ir are fully occupied. A more precise description of the XANES spectra is based on molecular orbital calculations. The obtained ground state spectrum is shown in Fig. 2 (dashed line).

Fig. 4 schematically represents the most important transitions. The two most important orbitals that contribute to peak B in the spectrum (Fig. 5) have  $\sigma^*$  anti-bonding character between the Ir 5d states with the orbitals of the nearest ligands. Orbital A97 has a significant contribution of p-states of N atoms of Chp groups, while the B95 orbital is localized at

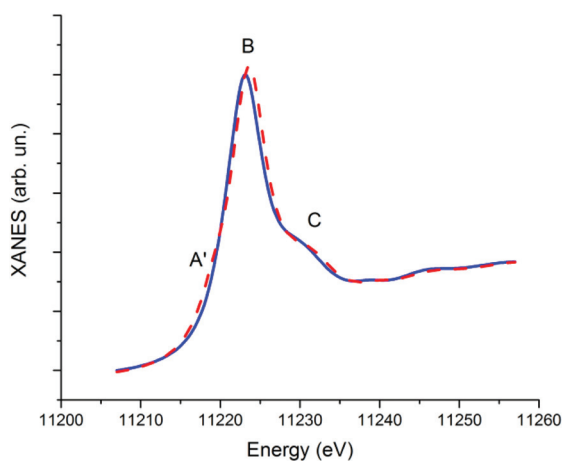


Fig. 5 Theoretical Ir  $L_3$  XANES spectra calculated for the ground state (singlet) – blue line and excited state (triplet with the lowest energy) – red dashed line.

the Ir and phenyl groups. There are a few unoccupied molecular orbitals with an energy lower than the  $e_g$  states. In particular, the LUMO has a relative energy of  $-6.8$  eV, while those of the  $e_g$  states range from  $-4.2$  eV to  $-3.4$  eV. Nevertheless, these states are localized mainly at the ligands and therefore contribute only very weakly to the Ir  $L$  edge XANES spectra.

The experimental transient spectrum is compared with the calculations in Fig. 2 (bottom). The theoretical XANES spectra for the ground and excited states are shown in Fig. 5. Since the structural differences between the singlet and triplet states are very small, the spectral changes are mainly induced by the modification of the electronic structure of the complex after photo-excitation. The theoretical spectrum of the excited state has an additional shoulder A' which is absent in the ground state. This feature arises from the transition to an Ir  $t_{2g}$  state, since an unoccupied state of such symmetry should appear after the electron transfer to the ligand. In the transient XANES spectrum shown in Fig. 2 (bottom), this feature appears as peak  $A_1$ .

The shift in the XANES white line maximum towards higher energies is also seen when the excited state spectrum is compared to the one of the ground state (Fig. 5). It leads to the appearance of minimum  $B_1$  and positive peak  $B_2$  in the transient spectrum (Fig. 2). DFT calculations show that both the Ir 5d  $e_g$  and 2p states move towards lower energies after photo-excitation. This is due to the change in their screening by the 5d electrons after the electron transfer to the ligand. The shift of the 2p levels is more significant than the shift of the 5d and therefore the energy of the overall XANES white line maximum moves up. These results are schematically summarized in Fig. 4.

Cyclometalated Ir complexes, in particular,  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$  have been studied using pump-probe X-ray absorption spectroscopy by other groups, while  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]^+$  is investigated for the first time. The trends in the transient XAS spectra observed for different Ir $^{3+}$  complexes in the pseudo-octahedral environment are similar though. This can be explained by the dominant effect of electronic structure modifications and the rather small photo-induced structural rearrangements of these complexes. Such small structural changes are confirmed by our DFT calculations and desirable for some applications. For example, a rigid geometry is desired to minimize non-radiative energy losses in OLED (Organic Light Emitting Diode) materials. Other groups perform experiments at undulator beamlines, in particular, at P11 of PETRA III,<sup>32</sup> Sector 7 of APS<sup>34</sup> and MicroXAS of SLS.<sup>33</sup> We have obtained time-resolved spectra of similar quality at the bending magnet beamline SuperXAS, characterized by a significantly lower X-ray flux. This became possible due to the combination of an efficient time-tagged photon-counting data acquisition system<sup>11</sup> and a high repetition rate (50 kHz) laser system. A promising direction in the time-resolved measurements of 5d transition metal systems is a combination of XAS and X-ray emission spectrometers<sup>45,46</sup> to measure XANES with a resolution higher than the core-hole lifetime broadening, time-resolved HERFD (High Energy Resolution Fluorescence-Detected) XAS.<sup>34</sup> Nevertheless,

for Ir photosensitizers, which have insignificant structural changes, such an improvement only allows a slight improvement in the precision of the energy splitting determination for the 5d levels. For complexes that undergo significant structural changes, such an improvement of XANES energy resolution can potentially be important to allow local structure investigations, assuming that approaches to analyze such spectra are sufficiently developed.

A few different approaches for the analysis of time-resolved XAS spectra of 5d transition metal complexes, Ir photosensitizers in particular, exist. Decomposition of the spectrum into peaks can be used to determine the energy splitting of the 5d levels.<sup>31,34</sup> Alternatively, TD-DFT calculations using Gaussian-type orbitals<sup>47</sup> have been applied to predict the shape of the XAS white line.<sup>33</sup> Yet, this approach does not allow XANES analysis for energies above the white line. For TDDFT, this is mainly due to the computational costs, since the application of this method to hundreds of molecular orbitals is very challenging. We use a simplified approach with a direct calculation of the transition matrix elements between the core and the unoccupied levels and, as one can see from Fig. 2, such an approach is in good agreement with experiments in a relatively wide energy range (~50 eV). Direct coupling of DFT calculations with XANES analysis can thus be very useful, for example, for the investigation of Ir compounds applied for water splitting, which significantly change both in electronic and local atomic structures.<sup>48</sup> Alternative methods of XANES simulations, like the full multiple scattering theory<sup>49</sup> and the finite difference method,<sup>50</sup> allow us to calculate the shape of the spectrum after the white line, while they lack predictive power in the low energy part of XANES. In contrast to MO-based approaches, the occupancy of different levels is not defined in these methods and therefore the shape and intensity of the white line strongly depend on the parameter defining the splitting of filled and unoccupied states. Thus the approach that we present in this article uniquely combines the possibility of calculating the whole XANES spectrum of 5d elements directly taking into account the charge and spin of the complex and its local atomic structure.

## Conclusions

We have demonstrated that the pump-sequential-probe setup at the SuperXAS beamline of the SLS is efficient in the nanosecond time range, in addition to the microsecond range explored earlier.<sup>11</sup> DFT calculations are directly coupled to the XANES interpretation reproducing the spectral changes, as induced by the electronic structure changes. This methodology is promising for studying processes with additional local structural rearrangements.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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