Supporting Information

Highly accurate excited-state structure of $[Os(bpy)_2dcbpy]^{2+}$ determined by X-ray transient absorption spectroscopy

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1. X-ray transient absorption (XTA) measurement

The XTA measurements were carried out at 11ID-D of the APS at Argonne National Laboratory. The laser pump pulse was the second harmonic output of a Nd:YLF regenerative amplified laser at 527 nm, 1.6 kHz repetition rate, 5 ps FWHM (full width half maximum). The experiment was carried out under a hybrid timing mode where an intense X-ray pulse with 16% of the total average photon flux was separated in time from other weak X-ray pulses. The intense X-ray pulse with 160 ps FWHM and 271.5 kHz repetition rate was used as the probe. OsL_2L' dissolved in methanol (0.8 mM) was flowed through a stainless steel tube and formed a free jet of 550 μm in diameter. Two avalanche photodiodes (APDs) positioned at 90˚ angle on both sides of the incident X-ray beam collected the X-ray fluorescence signals. A soller slits/Zn filter combination, which was custom-designed for the specific sample chamber configuration and the distance between the sample and the detector, was inserted between the sample fluid jet and the APD detectors.

The outputs of the APDs were sent to two fast analyzer cards (Agilent) that were triggered by a signal at 1.6 kHz from the scattered laser light collected by a photo diode. The card digitized the X-ray fluorescence signals as a function of time at 1ns/point after each trigger and averaged repeated measurements at a 4s integration time. The fluorescence from the synchronized X-ray pulse at 400 ps after the laser excitation was used for building the excited state spectrum and the ground state spectrum was obtained by averaging the intense X-ray pulses in the previous 50 synchrotron ring cycles.

2. XANES data analysis

The Os L_{III}-edge XANES spectra of the ground and the ^{3}MLCT excited state are fitted with a sum of an Arctangent function for the edge jump absorption, and several pseudo-Voigts functions to represent the transition bands. The ionization potential is fixed at 10884.9 eV and 10886.8 eV for the GS and ^{3}MLCT respectively based on the EXAFS data analysis. The peak positions extracted from the fitting are listed in Table 1S.

Table 1S. Peak positions of transition bands in OsL_2L' XANES specta extracted from XTA measurements.

	$^1A_1$ (eV)	^{3}MLCT (eV)	$\Delta(^3\text{MLCT} - {}^1A_1)$ (eV)
IP	10884.9 ± 1.1	10886.2 ± 1.2	1.3
A'(B')		10870.7± 0.05	
B(B')	10874.7 ± 0.02	10875.3 ± 0.02	0.6
C(C')	10882.0± 0.1	10882.5 ± 0.2	0.5

3. EXAFS data analysis

The Athena program is used to process experimental XAS data to extract the normalized oscillation amplitude $\chi^{exp}(k)$ and the photoelectron wave number k is defined by $k = \sqrt{2m(E-E_0)/\hbar}$, where E_0 is the absorption edge energy. The theoretical calculated $\chi^{th}(k)$ is given by EXAFS equation,

$$\chi^{th}(k) = \sum_j \frac{S_0^2 N_j f_j(k)}{kR_j^2} e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda(k)} \sin[2kR_j + \delta_j(k, r_j)]$$

where j indicates a shell with identical backscatters, N_j is the coordination number of jth shell, f_j is the backscattering amplitude, R_j is the average distance, σ_j is the mean square variation, δ_j is the scattering phase shift, λ is the effective mean free path and S_0^2 is the amplitude reduction factor.

FEFF6 is used to calculate f_j, δ_j and λ. Fitting to the experimental data to refine the structure parameters S_0^2, N_j, R_j, σ_j^2 is done using the Artemis program. Crystal structure of $Os(bpy)_3(PF_6)_2$ from X-ray diffraction (XRD) measurement (CSD code: KAZXUE) is used as the starting structure for fitting of both $^1A_1$ and ^{3}MLCT states. The contributions from all the paths in the first two scattering shells Os-N, Os-$C_{\alpha,\beta}$, were included in the fitting. Each shell shares a common σ_i^2 and distance changes from the input structure. All paths share a common S_0^2 and E_0.

The change of the average Os-N bond-length from the $^1A_1$ state to the ^{3}MLCT state is 0.010 ± 0.008) Å. Assuming a normal distribution in the analysis of our results, such change refers to an 89.4% probability of a positive difference. Therefore, there is an increase in Os-N average bond-length after laser excitation within the statistical frame.

4. XANES calculations using Density functional theory (DFT)

The XANES calculations have been performed using the approach developed previously[1] on the basis of Slater-type orbitals calculated self-consistently using ADF2010 package. All electrons were taken into account during SCF cycles. Relativistic spin-unrestricted calculations

within one-component ZORA formalism[2] for singlet and triplet states of the complex were performed. A triple-ζ basis set of the Slater-type with one polarization function was used. Intensities of 2p-to-unoccupied states transitions were calculated by integration of dipole transition 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 Os atom with 132651 points and 0.01 Å step size in each direction. Simulation of the XANES spectral region (~50 eV) requires integration for ~1000 lowest unoccupied MOs. 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[3] calculated within local density approximation (LDA) was used.

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[2] E. van Lenthe, E.J. Baerends and J.G. Snijders, J.Chem. Phys. **101**, 9783 (1994)
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