Experiment Report Form

	Experiment title: Probing aurophilicity in stimuli-responsive dimer complexes: the role of “host-guest” interactions	**Experiment number**: CH 5623
Beamline: ID09	**Date of experiment**: from:03 October 2018 at 08:00 to: 08 October 2018 at 08:00	**Date of report**: ***12.09.2023*** *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Dr. Matteo Levantino	

Names and affiliations of applicants (* indicates experimentalists):

Laboratory European XFEL Scientific Instrument FXE Holzkoppel 4 DE - 22869 SCHENEFELD

Dr. Dmitry Khakhulin*, Tae Kyu Choi*, Dr. Frederico Alves Lima*, Dr. Wojciech Gawelda, Prof. Christian Bressler, Dr. Serguei Molodtsov

Laboratory A.E. Arbuzov IOPC - subdivision of FIC KazSC Organoelement and coordination compounds Kazan, Arbuzov-str, 8 RU - 420088 KAZAN
Dr. Igor Strelnik*

Laboratory St Petersburg State University Institute of Chemistry Old Peterhof RU - 198904 ST PETERSBURG
Dr. Elena Gracheva*

Report:

The experiment was successfully performed using the standard pump-probe WAXS setup at ID09 and 266 nm or 320 nm excitation from the picosecond laser system. Since the experiment was done before the EBS upgrade, and the pink beam spectrum was asymmetric with a low energy tail, the pink beam was conditioned with a multilayer monochromator (1.7 % relative bandwidth). Single X-ray pulses isolated by the high-speed chopper at 1 kHz were used to scatter from a flat liquid jet (300 um) and the scattering patterns were collected using a Rayonix detector. Scattering images for each pump-probe delay were collected multiple times (typically a few hundred for each) with a reference point at a negative delay of -3 ns in between to correct for the background drifts and long-term instabilities. Typical exposure time was on the order of 1-3 s per image depending on the signal strength. Images were azimuthally integrated to produce 1D S(q) curves, sorted according to the delay and averaged, then the difference curves were produced by subtractive the respective curve at -3 ns delay. The following sections present a summary of results collected throughout the beamtime.

According to the plan of studying metallophilic interactions in dimeric complexes the beamtime was started measuring two silver and gold-based compounds namely $[Ag\text{-}Ag(dcpm)_2]^{2+}$ (dcpm =

bis(dicyclohexylphosphino)methane) [1] and $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ (L= 1,5-bis(ptolyl)−3,7-bis(pyridine-2-yl)−1,5-diaza-3,7-diphosphacyclooctane) [2] in acetonitrile (MeCN) and dichloromethane (DCM) solvents, respectively. Since the main optical absorption band of the molecules is centred in the UV at 260 nm, we first used the third harmonic of the Ti:Sapphire laser radiation (266 nm) for excitation. The silver complex could only be dissolved to low concentration of 1 mM due to the solubility limit and has not produced sufficient difference scattering signal above the usual solvent heating response. The additional complication was that the solvent heating was always present event in neat solvent due to UV absorption.

The gold-dimer sample $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ could be dissolved in DCM to 2 mM concentration, however the high evaporation rate of the DCM itself limited the total time for data collection with one sample batch. Although the difference signals looked healthy at the first glance with strong oscillations in the high-q indicating the expected Au-Au distance shortening in the excited state, the solvent heating response, collected on the neat solvent directly after the sample measurement, exhibited similar oscillations (see Fig. 1) making DCM solvent hardly suitable for scattering studies in such systems at least with the 266 nm excitation.

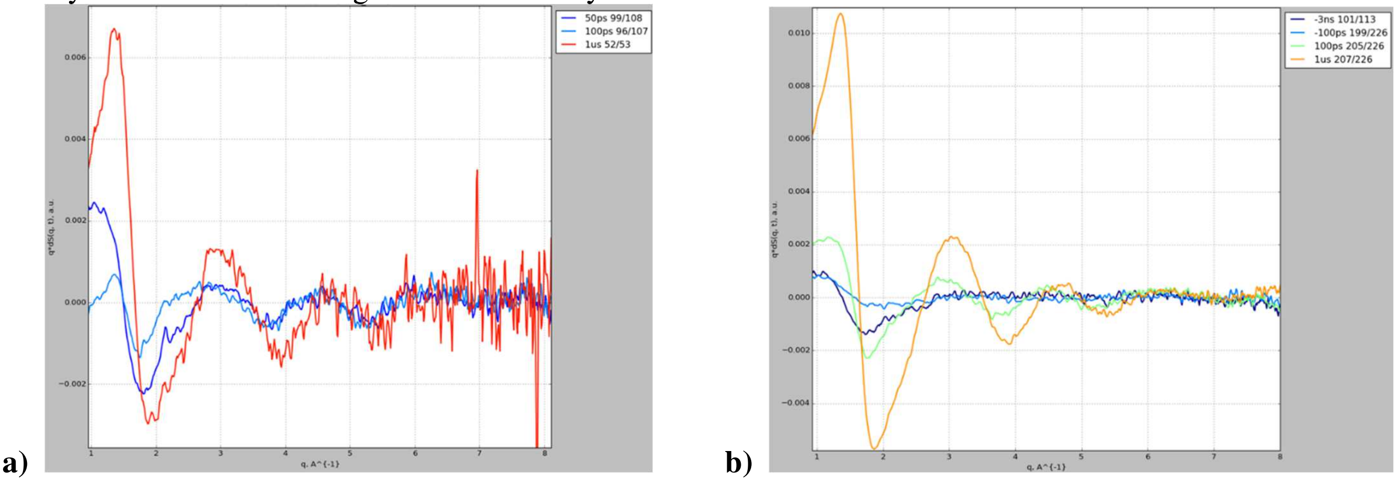

Figure 1. *(a) Example pump-probe scattering data for the* $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ *solution in DCM; (b) difference scattering in neat DCM solvent.*

The next molecule of chose for 266 nm excitation in MeCN was the relatively well-known gold-based $[Au\text{-}Au(dcpm)_2]^{2+}$ complex [3] (Fig. 2a). Despite the low concentration of 2.4 mM, the achieved S/N ratio allowed resolving the high-q oscillatory signals (Fig. 2b) in scattering corresponding to the Au-Au bond shortening by 0.3-0.4 Å due to the aurophilic interaction that agrees with simulations and previous reports. It was confirmed that the high-q oscillations are not present in the solvent heating response of MeCN, so they are due to the structural change in the solute molecule. However, the excitation at 266 nm has led to a gradual sample degradation, so the amount of data collected was limited, although of suitable quality.

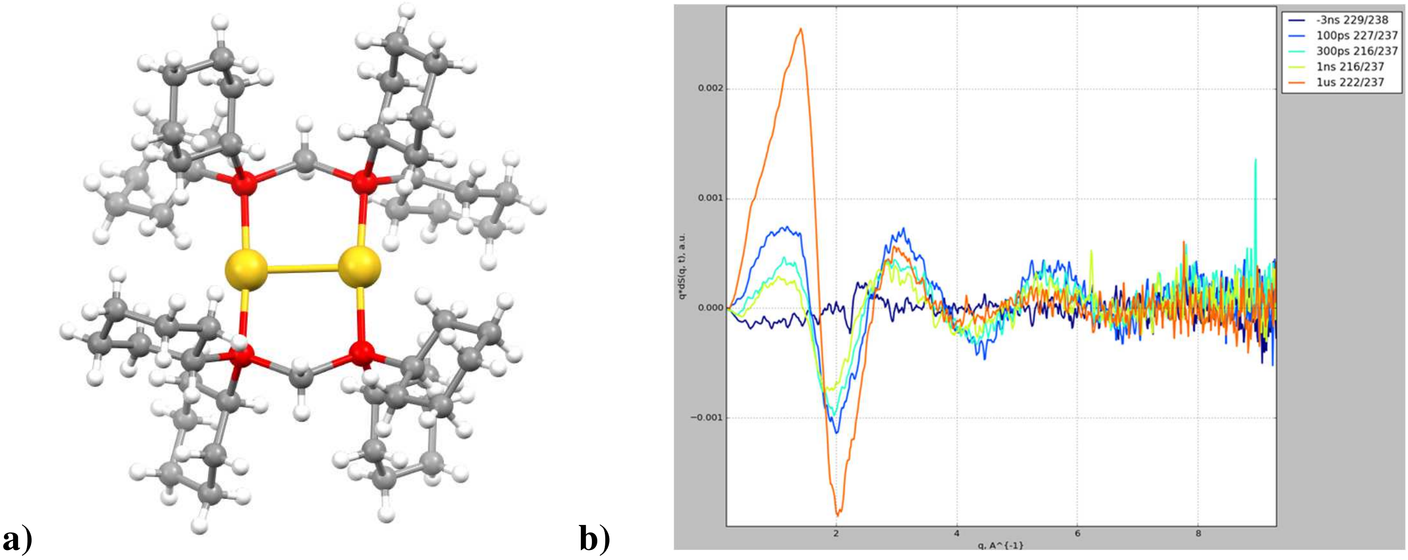

Figure 2. *(a) Structure of* $[Au\text{-}Au(dcpm)_2]^{2+}$ *complex and (b) the respective difference signals acquired with 266 nm excitaion.*

In order to mitigate the risk of direct absorption in the solvent itself it was decided to continue with 320 nm excitation from the TOPAS system, which then limited the selection of sample to the two gold dimers based on the PNNP ligand (L = 1,5-bis(ptolyl)−3,7-bis(pyridine-2-yl)−1,5-diaza-3,7-diphosphacyclooctane), namely $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ [2] and $[(Au\text{-}AuL_2)Cl_2]^{2+}$ [4] (Fig. 3A,B). The two complexes exhibit an additional absorption peak around 320 nm representing the mixed intraligand and ligand-to-metal charge transfer states (Fig. 3C), which appears to enhance the efficiency of the aurophilic triplet state formation.

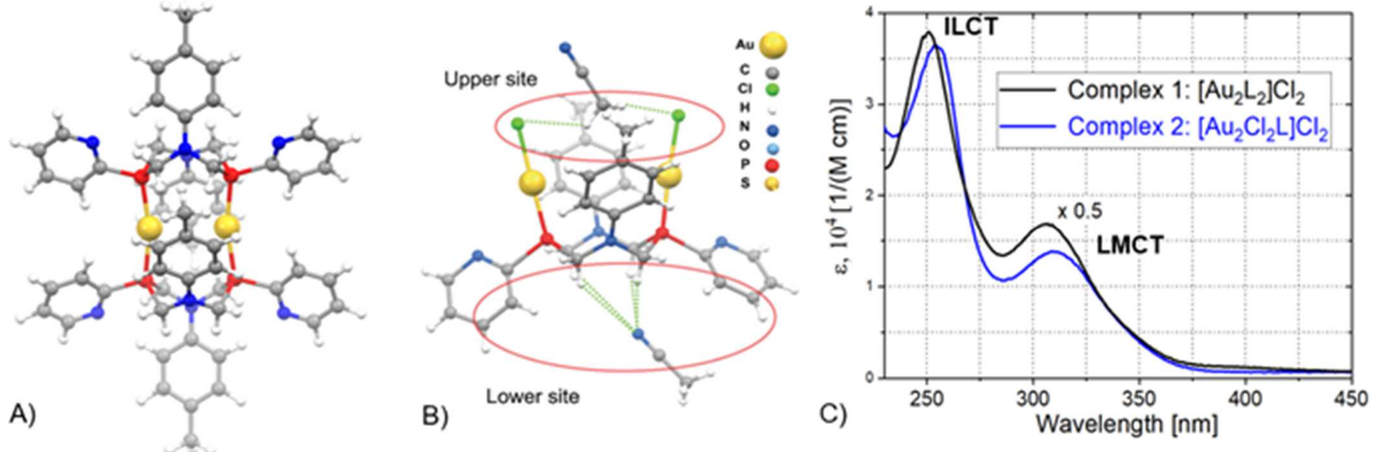

Figure 3. *(A) Stuctures of $[(Au\text{-}AuL_2)Cl_2]^{2+}$ and (B) $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ complexes and their absorption spectra (C).*

Initial measurements were performed in the “rigid” $[(Au\text{-}AuL_2)Cl_2]^{2+}$ complex that should demonstrate a stronger structural difference signal in high-q due to well-defined but different Au-Au distances in the singlet ground and the triplet excited states. A pulse energy of ~30 uJ/pulse was used for the excitation at 320 nm and the samples were studies in both DMSO and MeCN solvents with 3 mM concentrations, while the direct pink beam with asymmetric spectrum (without the monochromator) was used for probing in this case to increase the incoming flux and shorten the collection time. The initial results for $[(Au\text{-}AuL_2)Cl_2]^{2+}$ are presented in Fig. 4 and allow making preliminary conclusions on the amount of the structural change, excitation fraction and even the relevant timescales of the transitions. However, within the limited time left after acquiring the solvent responses in this beamtime, it was not possible to perform careful investigation as a function of excitation fluence and to achieve sufficient statistics at short delays for both solvents, while using symmetric X-ray beam spectrum (important for structural refinement). Moreover, the key comparison to the “flexible” single-ligand $[(Au\text{-}AuCl_2L)Cl_2]^{2+}$ complex (Fig. 3B) could not be done. The “flexible” geometry of the complex is responsible for interaction with solvent molecules and for shortening of the lifetime to ca. 150 ps as confirmed by the optical spectroscopy, thus presenting a particular interest in comparison to the “rigid” variant (Fig. 3A).

Further investigation potentially including electronically sensitive X-ray absorption measurements will be proposed to complete the study in the future, taking advantage of the higher performance after the EBS upgrade (brigher and more symmetric spectrum of “pink” beam) and keeping in mind the lessons learned from the initial beamtime.

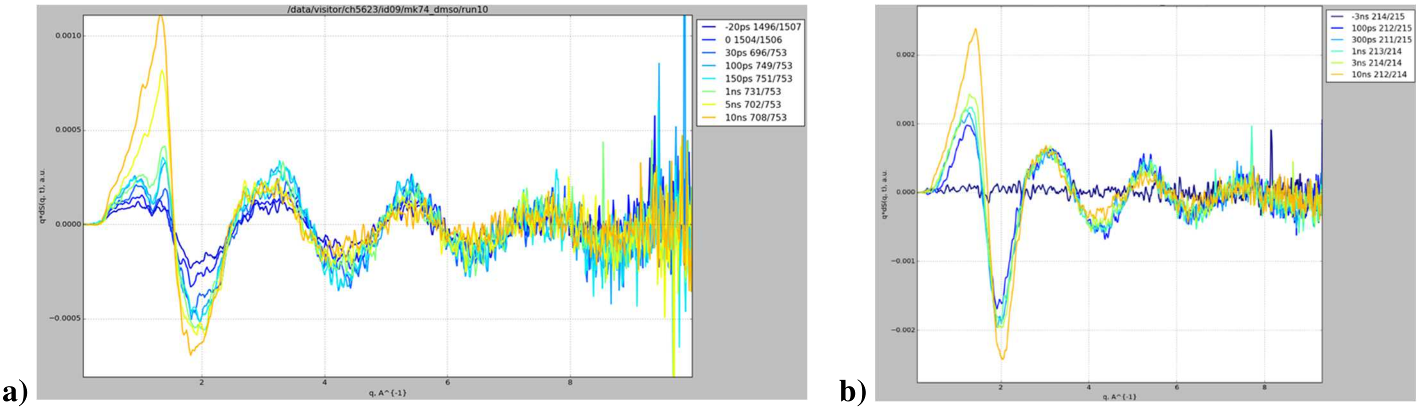

Figure 4. *Difference scattering of the $[(Au\text{-}AuL_2)Cl_2]^{2+}$ complex in DMSO (a) and MeCN (b) solvents.*

References

[1] S. V. Kruppa *et al., PCCP.*, **19**, 22785 (2017)
[2] N. A. Shamsutdinova *et al., New J. Chem.*, **40**, 9853 (2016)
[3] D. L. Phillips *et al., Coord. Chem. Rev.*, **249**, 1476 (2005)
[4] J. Elistratova *et al., J. Lumin.*, **196**, 485–491 (2018)