EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Polymorphism of the Luminescent Gold(I) Compounds Under Pressure	**Experiment number:** CH-6630
Beamline: ID15B	**Date of experiment:** from: 01 Mar 2023 to: 03 Mar 2023	**Date of report:** 26 Apr 2023
Shifts: 6	**Local contact(s):** Tomasz Poreba (email: tomasz.poreba@esrf.fr)	*Received at ESRF:*

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Report:

The main objective of the study was to correlate photoluminescence with structure in 1-(pyren-1-yl)-prop-2-yn-1-onyl)-(triethylphosphine)-gold(I) (**1P**), which combines two distinct luminophores: linear Au(I) aggregates and pyrene moieties stacked in the crystal structure. Its sensitivity to pressure and polymorphism offer a unique opportunity to analyze the evolution of the elusive Au···Au metalophilic interactions and to pinpoint their impact on various physicochemical properties. Starting with a new, structurally challenging, highly luminescent and modulated triclinic **β** polymorph, we intended to track changes leading to phase transition around 0.6GPa, describe its mechanism and investigate structures of high-pressure modulated phases coexisting as domains of an initially single crystal up to 6 GPa.

The first data series covered four single crystals of **1P**: 2 specimens of the title triclinic **β** polymorph and 2 specimens of monoclinic **γ** polymorph, placed in a standard membrane DAC loaded with He gas as a pressure-transmitting medium and initially pressurized to 0.2 GPa. Diffraction data were collected in 0.5° steps in ±32° ω-scans. Several test scans have been performed in order to establish optimum data collection conditions for collecting both Bragg and satellite reflections (i.e. undulator settings, exposure time) and to asses the extent of radiation damage caused on the sample, which appeared to be considerable. The satellite reflections in both of the modulated structures, esp. **γ** polymorph, have been observed and could be indexed, but yielded very weak signals ($I/\sigma < 3$). Subsequently, of two crystal specimens for each polymorph, one was dedicated for satellite data collection with 2s exposure time and another to Bragg reflections data collection with exposure time of 0.5s. The pressure in a DAC was then increased to 0.6 GPa, 0.8 GPa, 1.1 GPa and higher, covering a total of 17 pressure points up to 9.5 GPa. At each pressure point, diffraction data were collected from a different spot on the crystal surface, to avid the effects of radiation damage.
In the applied experimental conditions (i.e. gaseous, highly hydrostatic medium and relatively fast pressure increases) the triclinic **β** polymorph did not undergo the expected split at above 0.6 GPa; however, a distinct

change in the modulation vector, from the initial q = [0.333,0.666,0.666] to q = [0.4,0.2,0.8] took place at 1 GPa, followed by a substantial improvement in the satellite reflections' intensities. Preliminary R_{int} statistics for the data were 0.06 with the 1-st order satellite reflections included and 0.08 for the 2-nd order satellite reflections included. These statistics improved with increasing pressure, reaching 0.03 or the 2-nd order satellite reflections included at 2.5 GPa. At above 3.0 GPa both crystals of the triclinic **β** polymorph split into several pieces. These pieces retained their crystallinity, therefore we continued to collect data for the triclinic **β** polymorph in order to reconstruct powder diffraction patterns and further track the variations in the modulation vector. Crystal structure refinements with restraints will be possible for data collected in 0.8 – 2.5 GPa range.
Both crystals of the monoclinic **γ** polymorph retained monocrystallinity up to 9.5 GPa. Notably, the relative intensities of the satellites with respect to the main reflections improved continuously as the pressure was increased. In the case of this polymorph, the initial modulation vector q = [0,0.41,0.0] has been roughly retained, though showed a slight variation (e.g.: q = [0,0.35,0.0] at 1.5 GPa). However, the 2-nd order satellites began to be clearly observable above 2.5 GPa. Additionally, doubling of the a unit cell constant from ~ 16 to ~32Å took place at 2.5 GPa. Merged data from two single crystals should provide enough coverage for a structure refinement with restraints in the whole investigated pressure range.

In order to increase the chance of structure solution at certain pressures for low symmetry **1P β** and **γ** polymorphs, we next attempted data collection for samples enclosed a DACOne20 diamond anvil cell with 52° opening angle, using Daphne oil as a pressure medium. Diffraction data were collected in 0.5° steps in ±52° ω-scans with 2s exposure times.
In the case of the title **1P** triclinic **β** polymorph, 3 single crystals in distinct orientations were placed in such a DAC. Unfortunately, the crystals splintered into several domains each immediately after increasing pressure up to 0.6 GPa, making further data collection impracticable.
On the other hand, three differently oriented single crystals of **1P** monoclinic **γ** polymorph placed in such a DAC endured pressure increases and resulted in single-crystal data collection at 6 pressure points from 0.5 GPa to 3.0 GPa. Satellite reflections were indexed, and the modulation vectors analogous to the ones observed in the membrane DAC (e.g.: q = [0,0.36,0.0] at 1.6 GPa) were found.

In addition, preliminary diffraction studies have been conducted for three other compounds analogous to 1P, in which 1-(pyren-1-yl) moiety has been replaced with ferrocenyl, methoxyphenyl and tiophene moieties accordingly. For the ferrocenyl derivative, 4 single crystals were placed in a standard membrane DAC loaded with He gas as a pressure-transmitting medium and initially pressurized to 0.39 GPa. Diffraction data were collected in 0.5° steps in ±32° ω-scans with 1s exposure at the total of 9 pressure points. Out of 4 single crystals, 3 yielded diffraction data suitable for structure solution and refinement in the investigated pressure range, with R_{int} statistics below 0.06.
For the methoxyphenyl and tiophene derivatives, data were collected in Merrill-Basset DAC-s with 39° opening angle, using Daphne oil as a pressure medium. Diffraction data were collected in 0.5° steps in ±39° ω-scans with 1s and 0.5 exposure times accordingly.
4 distinctly oriented single crystals of methoxyphenyl derivative yielded interpretable structural data with the total coverage of over 90% at 5 pressure points ranging from 1.6 to 3.3 GPa, while 2 distinctly oriented crystals of tiophene derivative yielded interpretable structural data with the total coverage of about 70% at 5 pressure points ranging from 1.6 to 3.0 GPa.