Spokesperson: Jane Great

Analyzing Chalcogen and Metal Variation in Microcrystalline Metal-Organic Chalcogenolates via Small-Molecule Serial Femtosecond X-Ray Diffraction

Abstract: The lack of structural solutions for radiation-sensitive microcrystalline materials is a key bottleneck in the process of hypothesis-driven nanomaterials design. Small-molecule serial femtosecond X-ray diffraction (smSFX) is a key advance in serial crystallography that results in single-crystal quality structures from microcrystalline powders without radiation damage. This advance has allowed for in-depth analysis in structural variation in a class of hybrid materials: metal-organic chalcogenolates (MOChas). The structural versatility of MOChas allows for a wide range of metal, chalcogen, and ligand combinations. These materials have attracted recent interest as promising materials for catalysis and semiconducting materials due to their structural robustness and unique optoelectronic properties. The structures provided from beamtime, if awarded, will provide critical insight into the influences of metallophilic and metal-ligand interactions on the structures and optoelectronic properties of these materials.

Scientific Case: Metal–organic chalcogenolates (MOChas) are self-assembling 3-dimensional crystalline arrays composed of semiconducting 1D and 2D nanostructured wires or sheets electronically isolated by ordered organic ligands. These compounds have a general formula $(M_x(ER)_y)\infty$, where M is a metal, E is a chalcogen and R signifies any organic functional group[1]. Luminescent compounds in this family have been identified that exhibit strongly bound anisotropic excitons and recent studies show evidence of strongly coupled polaronic states. These recent discoveries make MOChas especially relevant for potential use in dispersion engineering in devices and as stable platforms for studying fundamental quantum photonic phenomena[23]. The triality of compositional flexibility *via* exchange of the coordination metal, chalcogen and organic ligand enables dimensionality and bandgap tunability of the inorganic semiconducting sublattice through crystal engineering. Ease-of-synthesis by leveraging the self-assembly characteristics of the coinage metals (Cu, Ag, Au) have made it straightforward to synthesize entire libraries of this class of materials with varying properties. Prior to the development of smSFX as a technique, structural characterization was limited, as the synthetic strategies that allow for easy crystal engineering also favor microcrystalline powders as opposed to single crystal growth. Their radiation sensitivity also made alternative methods for structure determination from small crystallites, like micro-electron diffraction not compatible. The use of smSFX has allowed MOCHa chemists to move into the realm of rational synthetic design, identifying differences in argentophilic (Ag-Ag) bonding in silver benzenchalcogenolate MOChas that led to notable differences in photoemissive properties[4] and unveiling the presence of supramolecular patterns known as synthons in MOChas with organofluorine bonds[5]. We expect that continued use of the smSFX technique will continue to advance knowledge of MOCHa chemistry and aid in the rational synthetic design of this emerging class of semiconducting materials.

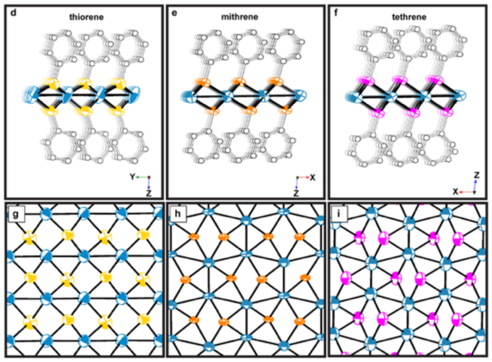

Figure 1: Side and top views of crystal structures from smSFX for thiorene (**d**), mithrene (**e**) and tethrene (**f**). Thermal ellipsoids for Ag (blue), S (yellow), Se (orange) and Te (magenta) are drawn at the 50% probability level. Hydrogen atoms and one position of disordered C_6H_5 (for mithrene) are omitted for clarity. **g–i**, Models of thiorene (**g**), mithrene (**h**) and tethrene (**i**) with the view oriented down the *c* axis of the unit cell, with the carbon and hydrogen atoms omitted, displaying the divergence in the thiorene Ag–Ag bonding environment compared to that in mithrene and tethrene[1].

Experimental Procedure: To perform this experiment, we request access to the MFX instrument using the fast fixed-target sample delivery system with a helium flow environment. We request access to the Jungfrau 16M detector positioned at a 50 mm distance from the interaction point and a photon energy of 15 keV to achieve 0.8 Å overall resolution datasets. In anticipation of the impending downtime for MFX at the end of Run 26, we request the XCS instrument as a secondary instrument, as the ambient conditions required for this experiment can be accommodated there as well. Although most microcrystalline powders are made up of majority 5-10 μm microcrystals, in some samples, due to the synthetic strategies employed, larger outliers appear. These crystals produce very bright Bragg peaks, which then causes pixel saturation on the detector, to handle this we will be using the Jungfrau 16M detector in gain-switching mode. We request access to the XRT spectrometer during our experiment to measure the per-pulse energy spectrum which is critical for our data processing pipeline and the TXI DCCM to calibrate the XRT spectrometer.

Technical Feasibility: This experiment is part of the LCLS mail-in small molecule SFX program, all collaborators and LCLS staff supporting this program have extensive experience developing and performing smSFX experiments at multiple XFEL facilities. The MFX instrument has already been used successfully for smSFX experiments using the fast-fixed target sample delivery system. The automated nature of sample delivery for the mail-in smSFX reduces the impact on sample delivery staff at LCLS. Our data processing pipeline using *cctbx.small_cell_process* has been used successfully to solve 55 structures from small-molecule microcrystals. The recent introduction of new unit cell determination software will drastically improve the number of structures solved during an individual beamtime by overcoming prior unit cell determination challenges we had using conventional software. Our data processing team is well-equipped to handle the volume of data we expect to produce during this experiment using both LCLS computing resources and NERSC.

If this proposal is accepted, we will provide optical/scanning electron microscopy to demonstrate that the samples are 1 to 20 μm in size along at least two dimensions and powder X-ray diffraction patterns showing sharp diffraction peaks. Additionally, we will provide the necessary safety documents requested by the LCLS staff. These documents will allow the LCLS staff to do an assessment of the feasibility/safety of our samples to see if they can participate in the program.

Sample/Material Class: *Hybrid Materials*

Experimental team:

Name	email	Project Role	Position
Prof. I.M. Good[1]	imgood@email.com	PI	Professor
Jane Great[2]	jgreat@slac.stanford.edu	Spokesperson	Postdoc

(1) Institute of Materials Science, University of Connecticut, Storrs, CT, 06269, USA
(2) Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA

Additional Questions	Yes/No
If our samples are too large (>20 μm) to participate in the beamtime at LCLS, we wish to be considered for the data collection at the Gemini MX beamline at the Advanced Light Source.	*Yes*
We do not have access to a pXRD instrument and request support from the powder X-ray diffraction program (BL2-1) at the Stanford Synchrotron Radiation Light source.	*No*
We agree to submit all requested feasibility and safety documents to the LCLS staff a minimum of month prior to beamtime or our samples will not be accepted.	*Yes*
We agree that no unapproved samples will be shipped to LCLS and that non-compliance will result in disqualification from future submissions.	*Yes*
We have read and agree with the "experimental procedure" and "technical feasibility" sections of this proposal.	*Yes*
If our data results in publication we agree to acknowledge LCLS.	*Yes*

Funding: DOE-BES, NIH

References:

1. Schriber, E. A. *et al.* Mithrene Is a Self-Assembling Robustly Blue Luminescent Metal–Organic Chalcogenolate Assembly for 2D Optoelectronic Applications. *ACS Appl. Nano Mater.* **1**, 3498–3508 (2018).
2. Aleksich, M. *et al.* Ligand-Mediated Quantum Yield Enhancement in 1-D Silver Organothiolate Metal–Organic Chalcogenolates. *Adv. Funct. Mater.* **35**, 2414914 (2025).
3. Anantharaman, S. B. *et al.* Ultrastrong light–matter coupling in two-dimensional metal–organic chalcogenolates. *Nat. Photonics* 1–7 (2025) doi:10.1038/s41566-024-01590-0.
4. Schriber, E. A. *et al.* Chemical crystallography by serial femtosecond X-ray diffraction. *Nature* **601**, 360–365 (2022).
5. Kotei, P. A. *et al.* Engineering Supramolecular Hybrid Architectures with Directional Organofluorine Bonds. *Small Sci.* **4**, 2300110 (2024).