

Observation of the Photoinduced Phase Transition in $\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$ by Femtosecond Electron Diffraction

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Abstract: Femtosecond electron diffraction has been used to probe the photoinduced phase transition in the strongly-correlated system, $\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$, revealing molecular motions involved in this process and breaking new ground in terms of chemical complexity.

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1. Introduction

The technique of femtosecond electron diffraction (FED) has been evolving over the last decade from the first successful experiment with sub-picosecond resolution on the melting of aluminum [1] to dynamics of semiconductors such as silicon, and suppression of charge-density waves in TaS_2 [2]. Recently, the first molecular system to be studied by FED was published; $(\text{EDO-TTF})_2\text{PF}_6$, [3] and it was found that it was possible to model the changes of diffraction intensities using just three real-space reaction coordinates. These advances can be summarized as increasing the sample complexity that can be studied, however, theoretical considerations of the coherence length of electron bunches produced by table-top electron sources indicate that we are approaching the physical limit in terms of molecular size that can be studied using this technology. Nevertheless, it is of interest to experimentally test the limits of the technique by investigating even larger systems and determine the practical limitations.

$\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$ [4] provides an interesting test bed for investigating these limits as its crystal structure has a much larger unit cell ($a = 2.9$ nm, $b = 1.26$ nm, $c = 3.7$ nm at 100 K) than any other compound previously studied by FED, for instance, the dimensions of $(\text{EDO-TTF})_2\text{PF}_6$ are: $a = 0.98$ nm, $b = 1.48$ nm, $c = 1.15$ nm. $\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$ also exhibits an intriguing structural phase transition induced by charge-ordering in $\text{Pt}(\text{dmit})_2$ dimers below the critical temperature of 215 K. In the low-temperature (LT) phase of $\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$, two types of dimers with different intermolecular spacings are spatially ordered. This phase is known as a charge-separated phase and can be classified as a structure-charge coupled ordering mediated by the interaction of frontier molecular orbitals. Optical pump-probe time-resolved spectroscopy have suggested a photoinduced phase transition (PIPT) due to the intra-dimer photoexcitation resembling the results reported on the analogous $\text{Pd}(\text{dmit})_2$ salt [5]. These results indicate the occurrence of a large structural change triggered by the optical excitation which, based on considerations of the molecular orbitals involved, is anticipated to be associated with a change of the intermolecular spacing. Application of FED to this problem can unveil the precise atomic motions involved in the generation of the PIPT of this unique electron-lattice strongly-correlated system, help to resolve the nature of the photoinduced state, improve our understanding of the interplay between the molecular structure changes and charge transfer, and provide new insight into the mechanism of energy transfer from excitation centers to the crystal lattice responsible for the PIPT.

2. FED Instrument Development

A new compact electron diffraction apparatus has been constructed that operates at voltages of up to 140 kV,

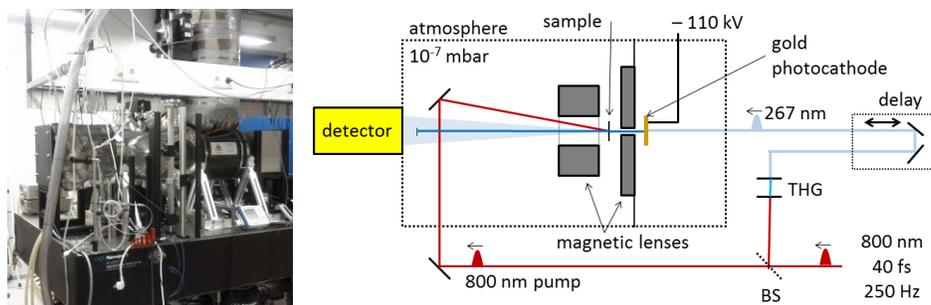


Figure 1. Table-top FED apparatus (left) and schematic representation of the important features (right).

allowing high temporal and spatial resolution to be achieved as well as providing stable operating conditions for the duration of the data collection process. The experimental setup is shown in Figure 1 and is based on a similar design to previous generations of FED setups developed at the University of Toronto, the main differences being an additional electron lens after the sample and higher electron energy (the previous maximum being 100 keV), leading to improved time resolution and source brightness and enabling the study of thicker samples.

3. Preliminary FED data and outlook

A typical electron diffraction pattern of $\text{Me}_4\text{P} [\text{Pt}(\text{dmit})_2]_2$ in the LT phase (80 K) is shown in Fig. 2a. The diffraction quality is remarkable, given the size of the unit cell, and preliminary analysis indicates that the current limitation in terms of molecular size is the crystallinity of the sample after preparation for the FED experiment, rather than the coherence length of the source. The diffraction pattern of the high temperature (HT) phase (225 K) was also recorded and the difference pattern for the HT–LT phase is shown Fig. 2b. The difference pattern observed 100 ps after photoexcitation of the LT phase is also shown in Fig. 2c. In the case of the thermal phase transition, local structure changes are accompanied by mesoscopic modifications of the unit cell and crystal size, resulting in small changes in diffraction peak positions as well as intensities. In contrast, in the PIPT there is insufficient time for such large-scale re-arrangements required for changes in unit cell parameters, so only changes in intensity are observed, although these intensity changes are qualitatively similar to those observed in the thermal phase transition indicating, that there is a close relationship between the atomic scale structure changes involved.

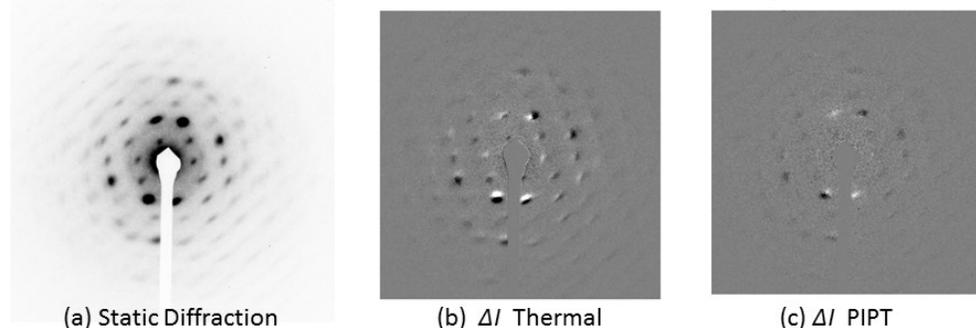


Figure 2. (a) Electron diffraction pattern of the LT phase without excitation. (b) Intensity differences between the diffraction patterns of the HT and LT phases. (c) Diffraction intensity changes after laser excitation

These data represent a snapshot of the structural modifications that occur on the timescale of many picoseconds, after establishment of the photoinduced phase. Additional, data collected on the ultrafast timescale show clear features that are consistent with all-optical pump-probe measurements, including the direct observation of the coherently excited optical phonon mode implicated in directing the structural phase transition.

These results represent the current state-of-the-art in FED experiments with compact electron sources. The associated increase in sample complexity necessitates the development of robust protocols for data analysis and interpretation. In this regard, a new reconstruction method for time-resolved molecular structure in real space is giving a very detailed picture of the key modes directing the charge separation in $\text{Pt}(\text{dmit})_2$. This is an important step towards atomically resolved dynamics of macromolecular and biological systems.

4. References

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