PRF# 56595-ND6
Project Title Pressure Response of Organic Photonic Materials at the Nano- and Mesoscale
P.I. Name, Affiliation Dr. J. Mathias Weber, JILA and Department of Chemistry, University of Colorado at Boulder

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Work was performed throughout the year, although the graduate student mainly working on the project (James Curtis Beimborn II) was only available full-time for this project in the fall of 2017 and in the summer of 2018.

Experiments on cibalackrot

We have continued our studies on the effects of pressure on the photoluminescence (PL) of the indigo derivative cibalackrot (7,14-diphenyl-diindolo[3,2,1-de;3',2',1'-ij][1,5]naphthyridine-6,13-dione), which shows promise as a singlet fission material. After our first experiments in the previous report period, we moved into the mesoscale, studying thin film (TF) samples of cibalackrot prepared by vapor deposition by the group of Prof. Josef Michl. AFM characterization of the TF samples show that they are 40-60 nm thick. The photoluminescence spectra of the TF samples show a vibronic progression with a spacing of ca. 1300 cm^{-1} (see Figure 1).

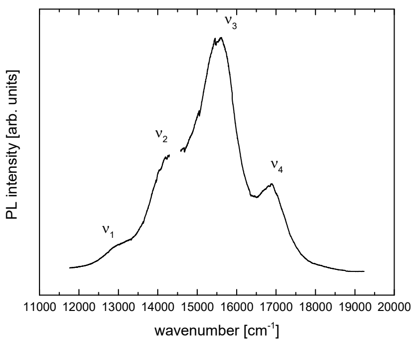

Figure 1: Experimental PL spectrum of cibalackrot. The break in the spectrum is to remove the PL of the ruby pressure gauge.

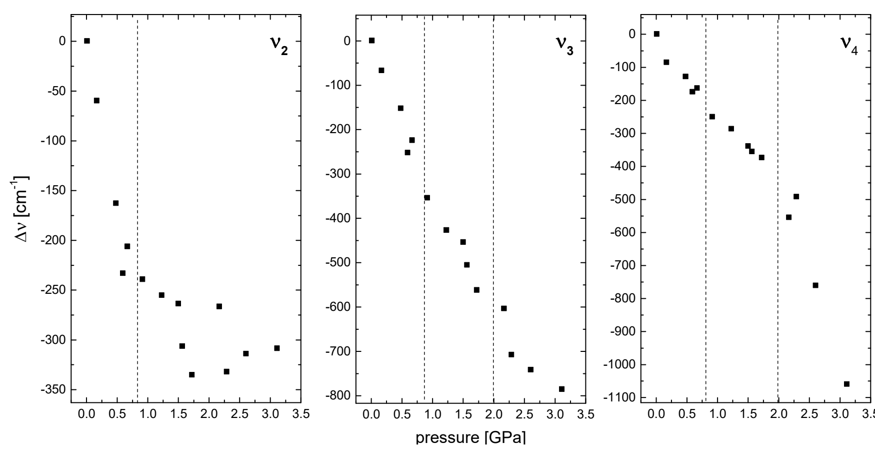

Figure 2: Pressure dependent shifts of the three most intense vibronic features in the cibalackrot PL spectrum.

The three most intense features show very different pressure behavior (see Figure 2), with apparent changes in the pressure dependent shifts at ca. 0.7 GPa and 2.0 GPa. These changes may be indicative for structural phase changes, but the details need to be explored further. Based on experiments with different polarizations, the vibronic peaks do not show any significant Davydov splitting, but instead are likely in a J-aggregate configuration, consistent with the red-shift in PL energy as a function of pressure.

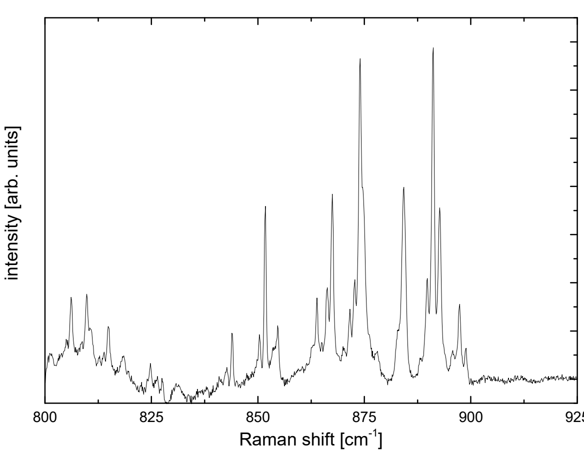

Figure 3: Ambient pressure Raman spectrum of cibalackrot powder.

Over the past year, we have put together a home built, fiber coupled 785 nm external cavity diode laser, which we can use to take Raman spectra of materials. Cibalackrot has strong PL under 532 nm excitation, so up until this point, we have not been able to perform Raman spectroscopy of the TF samples as a function of pressure. With the new laser setup, this will now be possible. Figure 3 shows a Raman spectrum of cibalackrot powder taken with our new system. We plan to use this new technology to measure the Raman spectra as a function of pressure to test our hypothesis of pressure-induced phase changes. We anticipate publication of results in 2019/20.

Experiments on rubrene

The orthorhombic crystalline polymorph of rubrene has been shown to exhibit up-converted PL (UCPL) without the use of a sensitizing molecule in recent work by Bardeen and coworkers. The upconversion efficiency may be dependent on the spacing between adjacent molecules in the crystal, which means applying high pressure should tune the efficiency. We used our 785 nm ECDL to excite the powder sample. The UCPL spectrum of rubrene powder (Aldrich, sublimed grade, 99.99% trace metals basis, used without further purification) at ambient pressure is shown in Figure 4. We are presently working on measuring the pressure dependent integrated UCPL intensity, PL spectrum, and Raman spectrum of rubrene. We expect to publish our results on UCPL in rubrene in 2019/20.

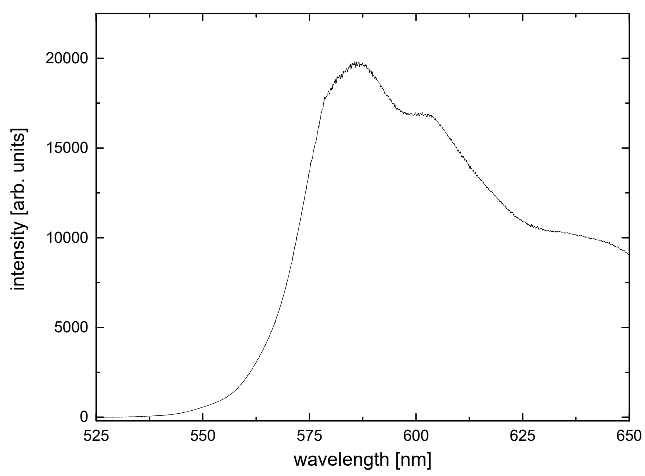

Figure 4: UCPL spectrum of rubrene powder excited with a 785 nm CW laser at ambient pressure.

Project impact

We expect that the outcome of this project will contribute to our understanding of how intermolecular distances and solid-solid phase transitions affect exciton formation and decay in molecular organic semiconductors. This in turn impacts our understanding of the chemical physics of effects such as singlet fission and upconversion in such materials.

This project has been instrumental for the support of J. Curtis Beimborn, the graduate student supported on this grant. The results from this project will constitute a large part of his doctoral thesis. I anticipate that he will graduate in 2020.

The project has been very important for gaining experience in high-pressure chemical physics of materials, and it has significantly contributed to the improvement of experimental capabilities in my group. For example, a new apparatus capable of producing pressures up to 700 MPa with high levels of pressure control resolution using a hydraulic setup has been partially supported from this grant. In addition, we have built a 785 nm external cavity stabilized diode laser, which has expanded our tool set for collecting Raman spectra and studying upconversion has been supported by this grant. As a result, we have now multiple avenues for demonstrating our ability to perform high-pressure research on materials, and we will use them to attract federal funding for this research area in the coming years.