Magneto-Photoluminescence from Platinum Porphyrin in n-octane Crystals

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Organic semiconductors are attractive candidates for the active layer in spintronic devices because they are expected to have much longer spin lifetimes than inorganic semiconductors due to their weak spin-orbit interaction, which is the principal spin de-phasing mechanism in these materials. However, spin-orbit coupling is also responsible for selection rules that allow optical generation/detection of polarized electron spin distributions. Optical injection and detection was essential in the development of electrical spin injection in inorganic semiconductors, and will provide a powerful tool in the development of organic spintronics. To inject/detect spin optically in organic semiconductors we are investigating incorporating heavy metal containing metal-organic molecules, which introduce a strong spin-orbit interaction.

The metal-porphyrins are a well studied class of metal organic molecules. We have previously studied the magneto-photoluminescence properties of one particular solution processabble porphyrin, Platinum(II) oactaethyl porphyrin (PtOEP), in a polymer matrix, where the polymer was poly(9,9-dioctylfluorenyl-2,7-diyl) [PFO]. In this system the zero phonon peak at 643 nm goes away as the temperature is lowered from 20K to 2K, and the application of a magnetic field restores this peak.

The PFO/PtOEP system consists of an amorphous matrix, where the peaks are broadened by disorder in the system. Many porphyrins can be oriented in frozen n-alkane Shpolskii hosts [1]. These systems have sharp optical spectra which enable a better understanding of the detailed physical processes. Here we measured PtOEP and PtP n-alkane crystals. The PtP molecule lacks the 8 ethyl side groups which improve the solubility of PtOEP. These side groups can also act to break the symmetry of the molecule, as they distort in a matrix.

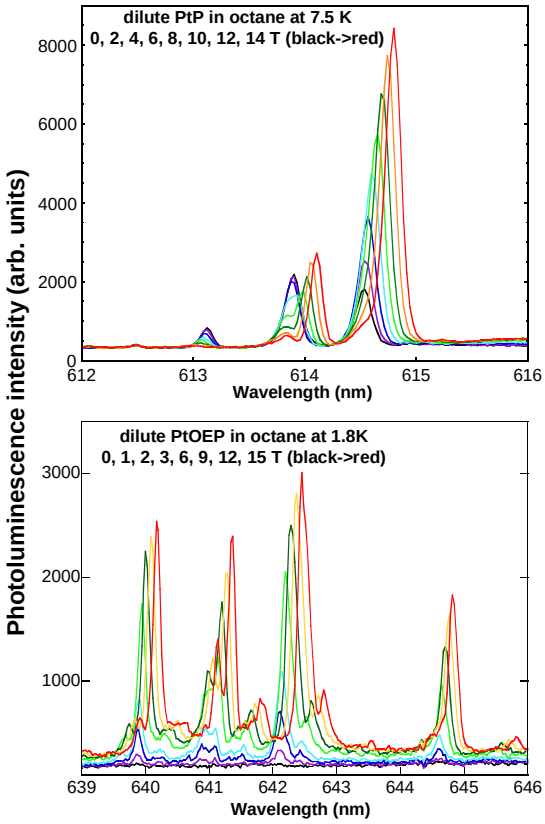

Figure 1: Low-temperature magneto-PL on dilute PtP (upper) and PtOEP (lower) porphyrins frozen in an n-octane crystal matrix.

Figure 1 shows the magneto-PL spectra of PtP (upper) and PtOEP. The PtOEP spectra are consistent with the previous data, application of a magnetic field restores the zero phonon peaks at 643 nm which are suppressed as temperature was lowered. The richness of the spectra are likely due to disorder introduced by distortions of the ethyl side groups. The PtP spectra is cleaner and shows some different behavior. While the peak at 615 nm is restored with magnetic field, the peak at 613 nm is suppressed, and the double peak at 614 nm show transfer of intensity from a high energy to a low energy component.

Hybrid density functional theory was used to provide quantitative predictions of equilibrium geometries, infrared and Raman spectra, and optical spectra of platinum poryphyrin (PtP) and the octaethylporphrin derivative (PtOEP). The optical transitions investigated as a spin interrogation probe involve transitions to doubly degenerate electronic states that are subject to Jahn-Teller distortions. The potential energy surface (PES) associated with the Jahn-Teller problem was determined by hybrid DFT calculations. Extrema on the PES were characterized as either minima or transition states through the explicit calculation of the vibrational frequencies. The latter also allows us to determine vibrational Huang-Rhys factors for comparison with optical spectra. By explicit calculation of the intrinsic reaction path connecting the stationary points, we can develop an effective 1-dimensional PES for the pseudo-rotation. This, in combination with the spin-orbit coupling, was used to define an effective vibronic Hamiltonian combining the effects of the JT interaction, the spin-orbit coupling, and the magnetic field. The calculated PL spectra were in good agreement with experiment.

[1] G. Jansen, et al., *Molecular Physics* **39**, 865 (1980).