# Time and Spin-resolved Photoluminescence of Crystalline Organic Semiconductors

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## Introduction

The presence of unpaired electrons in ***d***-orbitals of the metal-center of MPcs and the delocalized ***π***-orbitals of metal free $H_2Pc$ can play a crucial role on the ***d-d*** spin exchange and spin polarization mechanisms. In this experiment, specific ratio mixed solution of metal (M) and metal-free ($H_2$) phthalocyanines (Pc) are engineered to realize an RKKY-like mechanism. Time and spin-resolved photoluminescence were performed to further understand the exchange interaction between πand the magnetic ion spins.

## Experimental

The back scattering photoluminescence experiment set up in the Helix Magnet at NHMFL Tallahassee employed the 86 MHz, 50 fs pulses of a Coherent Vitesse Ti-Sapphire Oscillator as the source of excitation. A two-prism pulse stretcher configuration increased the pulse duration to approximately 1.5 ps while maintaining good beam collimation and offering a narrower spectral bandwidth required for this experiment. The Vitesse output was tuned at 745nm for a quasi-resonant excitation energetically close to the band edge exciton of the organic semiconductor. The experiment was conducted up to 25T at 14K for crystalline thin films of metal/metal free mixtures with different ratios.

## Results and Discussion

Figure 1 illustrates results of these experiments. The left hand side panel (Fig 1(a)) shows a summary plot of 25T luminescence spectra from a selection of mixed/alloyed metal/meta-free Pc crystalline thin films, dominated by the band-gap exciton radiative recombination. Typical exciton radiative lifetimes are less than 1 ns in this materials. Our experimental setup enables us to resolve differences in radiative lifetimes between various components of the luminescence spectrum, as evidenced by the PL decay data shown in Fig 1 (b). Finally, Fig 1(d) summarizes the evolution of luminescence polarization with magnetic field that represents unequivocal evidence of the existence of spin-polarized bandgap excitons. The spin polarization originates in the exchange between d-shell electrons of Mn and the delocalized π-electrons.

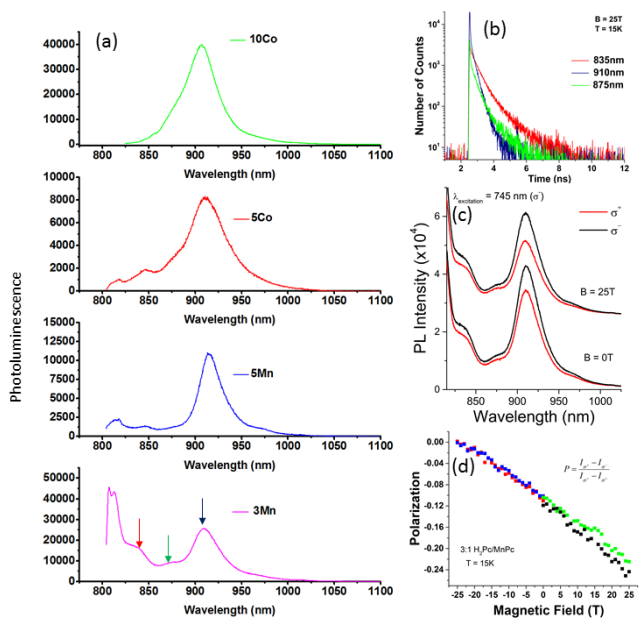


***Figure 1.*** *(a) Photoluminescence spectra from $H_2Pc$/MPc crystalline thin films. (b) Radiative decay measured at different wavelengths across the PL spectrum of the 3:1 $H_2Pc$/MnPc film. (c) Polarization resolved PL spectra of the 3:1 $H_2Pc$/MnPc film measured at 0T and 25T. (d) Excitonic PL Polarization vs magnetic field for the same sample measured at 15K.*

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