

Investigation of Charge Transport in Organic Photoconductors



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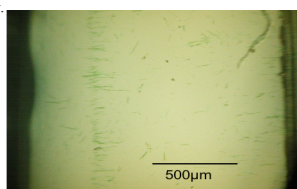
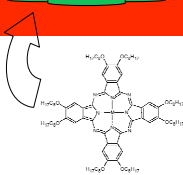
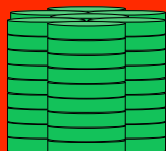


1. Introduction

Organic photoconductors are useful for their application in organic electronics and optoelectronics which are said to be safer, cheaper and lighter than conventional electronics. A notorious problem amongst these materials is their low photoconductivity when compared to other non-organic materials. A proposed solution to this problem is to use semiconducting discotic liquid crystalline materials whose columnar phase creates nano-wires with good mobility along the column axis. One such family of liquid crystals is the Metal Phthalocyanines (MPes), disk-like molecules with a rigid metal containing core surrounded by long hydrocarbon chains. An investigation of the carrier dynamics of MPes is necessary for assessment of their performance as photoconductors and is of fundamental importance to our knowledge of carrier properties in organic semiconductors. Here we consider ZnPc as a model system and will attempt to describe its carrier dynamics using optical techniques: optical pump-optical probe spectroscopy.

2. Material

ZnPc (shown left) is a discotic liquid crystalline material having a columnar phase where individual molecules align in ordered stacks as represented by the figure to the left. It is an attractive candidate for a commercial organic photoconductor due to its good axis mobility, thermal stability and large absorption in the visible. We have demonstrated that a solution of aggregate ZnPc in butanol will self assemble into individual stacks or "fibers" of 50-100um in length when cooled from temperatures above 100°C. Since these fibers have good conductivity along the column axis (due to the electron dense metalated core) and poor conductivity orthogonal to this axis (due to the long hydrocarbon substituents) they can be aligned using an electric field. A sample of aligned ZnPc fibers was formed using a sample cell made from etched ITO. A photo of this sample cell is shown below.

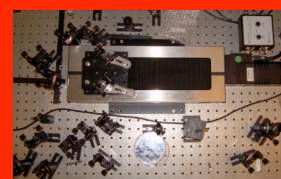


3. Method

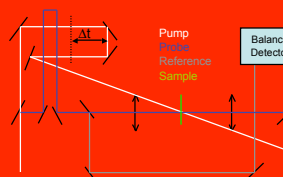
When struck with optical radiation ZnPc will absorb energy via electronic transitions. These electronic transitions will create excitons which are bound states of electrons and electron holes (positively charged band vacancies.) To better understand the photoconduction properties of ZnPc we wish to characterize the transport properties of these excitons and examine their relaxation from the excited state. To do this we wish to have a time resolved look at the absorption spectrum of ZnPc at times following optical excitation. So we excite excitons in the material and measure the absorption spectrum for a few picoseconds after this excitation. This is accomplished using ultra-short pulses of laser radiation and a technique known as Optical Pump-Probe spectroscopy. To generate these ultra-short pulses we use an Nd:Yag pump laser (4.2W power) coupled into an oscillator cavity with a Ti:Sapphire lasing medium. From this we generate ~500mW of ~50fs mode-locked pulses which are spectrally centered about 800nm.

Optical Pump/Probe Spectroscopy:

1. Oscillator output split into two beams, pump (high power) and probe (low power).
2. A reference is split from the probe pulse and both go into a two channel balance detector.
3. Pump pulse goes through a variable delay.
4. At time zero pump pulse strikes and excites sample.
5. At time t=0 probe pulse strikes sample and the transmission is measured.
6. The delay of the pump pulse is shortened and the process repeated.
7. From this a time resolved absorption spectrum is obtained.



Photograph of Optical pump optical probe spectroscopy experiment.



Photograph of Optical pump optical probe spectroscopy experiment.

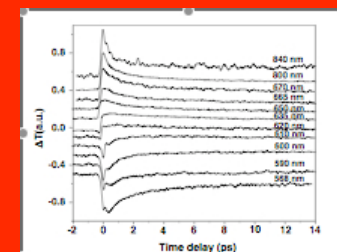
4. Exciton Relaxation Mechanisms

In principle there are four mechanisms to consider when analyzing the relaxation of excitons in obtained data. They are:

- EXCITON - EXCITON ANNIHILATION- Not expected, estimated carrier density is too low for our setup
Rate: $\frac{dn}{dt} = -kn^2$
- EXCITON - PHONON ANNIHILATION- Expected to be the primary contributor.
Rate: $\frac{dn}{dt} = -kn$
- TRAPPING-Expected to contribute significantly on long time scales (after several picoseconds).
- FLOURESCENSE- No fluorescence is observed, this mechanism is not expected to contribute.

5. Expected Results

Thus far due to experimental difficulties the transient absorption of the ZnPC nano-wires has not been obtained. Below I have given a representation of what we expect the results will be similar to. This data was obtained by J. Zhou et al as was published in the Journal of Optical Materials (Volume 7.) This result (shown below) is obtained by the same techniques proposed here but is of a different sample (titanylphthalocyanine) and the pump power is much higher implying the importance of the exciton-exciton annihilation mechanism.



Here J.Zhou measured the differential optical transmission as a function of delay time. Note that some decay curves have the appearance of a fast decay followed by a slower decay. These are the curves which correspond to wave lengths having high enough absorption to have a large density of photoexcited excitons large enough for exciton-exciton annihilation. The curve corresponding to 635nm is expected to be similar in shape to the results we will obtain for ZnPc in our setup. Our pump power is not large enough to allow for exciton annihilation so the predominate decay mechanism is the slower one, exciton phonon coupling.

6. Acknowledgements

I would like to thank the three graduate students in my lab B. Kubera, C. Ryan and C.Xia for their discussions on concepts and help in the lab. Also, I would like to thank V. Duzhko for his guidance in purifying the aggregate ZnPc and forming the fibers.