Organic Materials for Electronic Devices

by

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To my family

CURRICULUM VITAE

Lichang Zeng was born in 1978 in Fujian, China. In 2001, he received a Bachelors of Engineering degree in Polymer Materials from Zhejiang University, Hangzhou, China. He continued on at Zhejiang University receiving his Master of Science degree in 2004. He then moved to the University of Rochester to pursue his doctorate in Chemical Engineering under the joint supervision of Professors Shaw H. Chen and Ching W. Tang, receiving a Master of Science degree in 2009. His field of research was in organic electronic materials and devices.

Selected Publications in Referee Journals

1. Zeng, L. C.; Tang, C. W.; Chen, S. H. “Effects of Active Layer Thickness and Thermal Annealing on Polythiophene:Fullerene Bulk Heterojunction Photovoltaic Cells.” *Applied Physics Letters*, **2010**, *97*, 053305.
2. Zeng, L. C.; Blanton, T. N.; Chen, S. H. “Modulation of Phase Separation between Spherical and Rod-Like Molecules Using Geometric Surfactancy.” *Langmuir* **2010**, *26*, 12877.
3. Zeng, L. C.; Lee, T. Y. S.; Merkel, P. B.; Chen, S. H. “A New Class of Non-Conjugated Bipolar Hybrid Hosts for Phosphorescent Organic Light-Emitting Diodes.” *Journal of Materials Chemistry* **2009**, *19*, 8772.
4. Zeng, L. C.; Yan, F.; Wei, S. K. H.; Culligan, S. W.; Chen, S. H. “Synthesis and Processing OF Conjugated Oligomers Into Monodomain Films by

Thermal and Solvent-Vapor Annealing." *Advanced Functional Materials* **2009**, *19*, 1978.

5. Chen, A. C. A.; Wallace, J. U.; Wei, S. K. H.; Zeng, L. C.; Chen, S. H. "Light-Emitting Organic Materials with Variable Charge Injection and Transport Properties." *Chemistry of Materials* **2006**, *18*, 204 and 6083.

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ABSTRACT

Through light absorption and emission as well as charge carrier generation, transport and recombination, π-conjugated molecules are central to electronic devices including organic field-effect transistors, organic light-emitting diodes, and organic solar cells. This thesis reports on materials development via molecular design, material synthesis and processing, device fabrication and characterization. Major accomplishments are summarized as follows.

A series of oligo(fluorene-*co*-bithiophene)s, **OF2Ts**, have been synthesized and characterized for an investigation of the effects of oligomer length and pendant aliphatic structure on thermotropic properties, light absorption and emission, and anisotropic field-effect mobilities. Solvent-vapor annealing at room temperature was shown to be capable of orienting **OF2Ts** into monodomain glassy-nematic films with an orientational order parameter emulating that achieved with conventional thermal annealing on a rubbed polyimide alignment layer.

Comprising hole- and electron-transporting moieties with flexible linkages, non-conjugated bipolar compounds have been developed for use as hosts for electrophosphorescence. These materials are characterized by an elevated glass transition temperature, morphological stability against crystallization, LUMO and

HOMO levels unaffected by chemical bonding, and triplet energy unconstrained by the electrochemical energy gap. Phosphorescent OLEDs containing solution-processed emitting layers were fabricated with **TRZ-3Cz(MP)2**, **TRZ-1Cz(MP)2** and **Cz(MP)2** hosting $Ir(mppy)_3$ for an illustration of how chemical composition and hence charge transport properties affect device performance.

Bulk heterojunction organic solar cells comprising an active layer of **P3HT**:**PCBM** blend at a 1:1 mass ratio with thickness from 130 to 1200 nm have been fabricated and characterized before and after thermal annealing. Before thermal annealing, both short circuit current density and power conversion efficiency decrease with an increasing film thickness, resulting in an inverse spectral response for thick-film devices. Thermal annealing decreases the thin-film device efficiency but substantially increases that of the thick-film devices while eliminating the inverse character of spectral response therefrom.

A conjugated oligomer-C_{60} **Dyad** has been synthesized to demonstrate its ability to modulate the extent of phase separation between rod-like **OFTB** and spherical **PCBM**. While thermal annealing of the **OFTB:PCBM** at a 1:1 mass ratio results in a eutectic mixture, **OFTB:Dyad:PCBM** film at a 9:2:9 mass ratio undergoes phase separation into interspersed 30-nm amorphous domains at approximately equal fractions upon thermal annealing. Geometric surfactancy is

inferred by analogy to the widely reported formation of microemulsions in traditional oil-surfactant-water systems and ternary polymer blends.

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FORWORD

This thesis summarizes my PhD research in collaboration with my advisers, my fellow students, and scientists within and outside the University of Rochester. My participation and contributions to the research are as what follows.

Chapter 1 of my thesis is to introduce the background information pertinent to the researches discussed in the following chapters. I did the literature study and wrote this chapter.

I'm the leading author of Chapter 2 and have collaborated with Professor Shaw H. Chen, Feng Yan, Sean W. Culligan, and Simon K. H. Wei. Feng Yan synthesized compound **OF2T-1**, **-2**, **-3**, **-4**, **-5**, and **-7**. Sean W. Culligan measured the hole mobilities for **OF2T-4** and **-5.** This chapter has been published in *Advanced Functional Materials* **2009**, *19*, 1978

Chapter 3 of my thesis was co-authored with Professor Shaw H. Chen, Thomas Y. H. Lee, and Paul B. Merkel. The low-temperature phosphorescence spectra were collected by Paul B. Merkel. I'm the leading author for this chapter published in the *Journal of Materials Chemistry* **2009**, *19*, 8772

Chapter 4 of my thesis originates in the joint efforts with Professor Ching W. Tang and Professor Shaw H. Chen. I carried out all the experiments reported in this chapter, and it has been published in *Applied Physics Letters* **2010**, *97*, 053305.

Chapter 5 of my thesis was co-authored with Professor Shaw H. Chen, and

Thomas N. Blanton of the Eastman Kodak Company. All the X-ray diffraction data were collected by Blanton, and I'm responsible for all other data. This chapter has been published in *Langmuir* **2010**, *26*, 12877.