

## ABSTRACT

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Title: Control of Structure and Charge Transport in Polymer Active Layers of Organic Electronic Device

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Organic electronics have been heavily researched due to their promise for lightweight, ease of processing, and mechanical flexibility. However, there are still a number of critical demands for various applications including organic photovoltaics (OPVs), organic memory devices and organic field effect transistors (OFETs). Above all, the structure of active layers of organic electronics plays a crucial role in improving and optimizing devices. Particularly, the phase separated nano-structures of blended active layer have a great impact on the performance of heterojunction-based organic devices (*e.g.*, OPVs and organic ferroelectric diodes (OFEDs)). Furthermore, the control of interfacial properties in the active layer also leads significant advances for OFETs. Especially, a new class of conductive material, radical polymers show a great promise in providing new potentials of chemical designs and diverse functionalities as well as improving the OFET performance.

Here, we present how the structure of active layers affects the performance of organic electronics and demonstrate how to control and optimize it to improve the charge transport of devices. In the first of these efforts, I focused on polymer-based memory devices. Organic non-volatile memory devices with phase-separated blends of semiconducting and ferroelectric polymers have been rapidly developed as one of the most competitive avenues of research in the realm of flexible organic electronic memory devices.

In these thin films, the ferroelectric phase serves as the memory retention medium while the semiconducting phase acts as the pathway to read out the memory in a non-destructive manner. Therefore, controlling the nanoscale structure (i.e., the phase separated and percolating networks of each polymer phase) of these active layers plays an important role in the device performance and its lifetime stability. In order to systematically evaluate this structure-property relationship, we fabricated ordered OFeDs through common lithographic techniques to establish the impact of nanoscale structure on the macroscopic performance. In addition, we demonstrate that there is an optimal domain size (~400 nm) for the interpenetrating networks, and show that the ordered device provides a significant increase in ON/OFF current ratio relative to the blended device using standard techniques.

As demonstrated in the case of organic memory devices, interfacial control of structures is a key process of organic electronics to achieve high performance and durability. This is because the main charge transfer events occur at interfaces, and they are closely interlinked with the properties of interfacial materials. While the first effort in my research focused on controlling organic-organic interfaces, modifying the interface between the active channel layer and the metal electrodes (i.e., an organic-metal interface) of organic field-effect transistors (OFETs) also significantly influences the device performance. In this effort, we firstly introduce open-shell oxidation-reduction-active (redox-active) macromolecules, namely radical polymers (i.e., macromolecules composed of non-conjugated backbones with stable unpaired electrons on the pendant groups of the materials), in order to serve as organic-metal interfacial modifiers in pentacene-based OFETs. By implementing the specific radical polymer, poly(2,2,6,6-tetramethylpiperidine-1-oxyl methacrylate) (PTMA), the charge transport energy level of the interfacial layer is

tuned to provide facile charge exchange between the pentacene active layer and the gold source and drain electrodes. That is, the insertion of the radical polymer between the active layer and contacts considerably reduces the contact resistance, which initially arose from the mismatch of the work function of gold and the transport level of pentacene. In addition, we prove that the amorphous radical polymer film allows for the stable growth of pentacene grains relative to the pristine gold substrate. As a result, the inclusion of this radical polymer interlayer leads to bottom-contact OFETs with substantially enhanced hole mobility values and ON/OFF current ratios relative to pristine (i.e., without the radical polymer interlayer being present) OFETs.

Finally, as an extension of investigating this new class of non-conjugated redox-active polymer as an active polymer layer, we illustrate an organic electrochemical transistor (OECT) using a radical polymer as the active component layer for the first time in the third research effort. The charge transport mechanism of a model radical polymer, PTMA, is established for the first time through the introduction of an electrochemically-gated organic thin film transistor. In this system, the ion gel gate allows for electrochemical ion (cation or anion) diffusion into the main channel PTMA layer through the application of a gate bias. Furthermore, the rapid electron transfer of non-conjugated PTMA through oxidation or reduction provides a transparent transistor with ambipolar characteristics by applying a positive or negative gate bias. We investigate that the ion gel-activated charge mobility and conductivity values of PTMA are on the same order of magnitude as common conjugated semiconducting polymers at low gate biases ( $V_g = \pm 2$  V). Additionally, electrochemical doping of the PTMA layer increases the conductivities by a factor of 100 – 1,000 as well as produces ON/OFF current ratios of  $\sim 10^4$ . As such, we believe these

works make a great contribution to control of nanostructure in active layers and utilization of radical polymers for a myriad of solid-state organic electronic applications.