Theory and Modeling of Organic Semiconductor (Spintronic) Devices:
From Organic Molecular Junctions and Spin Valves to Ionic Liquid Gated FETs

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❖ Background and Goals

Spintronics is a relatively new field of research that refers to spin-based electronics. Information is stored and manipulated through the spin polarization of mobile electrons or holes rather than their charge. This offers opportunities for a new generation of devices combining nano-scale electronics with spin-dependent effects arising from the interaction between the spins of the carriers their environment. The potential advantages of spintronic devices include increased data processing speed, decreased electric power consumption, and enhanced integration densities. **Organic semiconductors** (OSs) have intriguing potential for spintronic devices because of their compatibility with a wide range of magnetic materials and because their intrinsic nature, being composed almost exclusively of light atoms, allows mobile carriers to have very long spin coherence times. In recent years these properties have given rise to a field of research that has become known as **organic spintronics**.

I am pursuing two parallel paths in organic spintronic device research: 1) **Non-magnetic Organic Molecular Tunnel Junctions,** and 2) **Organic Semiconductor Spin Valves**. The efforts of integrating the concepts of quantum mechanics, semiconductor physics, electronics, and material science seek to understand the fundamentals of organic spintronics, such as spin injection and extraction efficiencies and spin transport, the detection of spin polarization, and to develop a deeper understanding of fundamental spin interactions in organic materials.

❖ Contributions to the Field

1) Non-magnetic Molecular Tunnel Junctions

Certain molecules, such as oligophenylene thiols, bond in oriented fashion to gold substrates and lend themselves to the formation of well-defined self-assembled monolayers (SAMs). Contacting the exposed face of the SAM allows for the application of a small voltage across the molecules and the measurement of the resulting tunneling current. Experiments have led to the observation of surprisingly large, room-temperature magnetoresistance (MR) at low applied magnetic fields. The experimental observations are attributable to the interaction between tunneling charge carriers and unpaired charge carriers in the molecules, which originate from the charge transfer in the chemisorption of aromatic thiols on metals. More details of significant achievements are listed below.

i. Analytical model for the electron transport in the Au-Molecule-Au device. The system composed of the metal contacts and the molecule is modeled with the aid of a one-dimensional chain of interacting localized states. The incident tunneling electron together with the unpaired electron populating a contact-molecule interface state form singlet and triplets states. The Coulomb interaction between the electrons causes the tunnel barriers to be different for different states. Singlet and triplet pairing thus correspond to separate conduction channels with different transmission probabilities.

ii. Investigating the function of spin relaxation on the electron transmission process. The tunneling model essentially defines four parallel transmission channels for the four possible spin configurations in the initial state. Singlet and triplet initial states are nearly degenerate and weak mechanisms between electrons in the injecting metal contact and electrons in the molecule can produce spin relaxation. This enables spin flips and transitions between the transmission channels, and it therefore tends to maximize the tunneling current for a given applied bias.

iii. Identifying the role of the applied magnetic field in MR. A small-applied magnetic field lifts the singlet and triplets energy degeneracy of the initial states through the Zeeman interaction and therefore suppresses the transitions between singlet and triplet channels, giving rise to different total current with and without the magnetic field. Thus, it generates strong MR.

2) Organic Semiconductor Spin Valves

The spin valves discussed here consist of organic semiconductors sandwiched between ferromagnetic metallic electrodes (FM/OS/FM). The theoretical work focuses on the electron transport through metal/OS interfaces and in the bulk semiconductor, and a connection is built to integrate the two processes that involve very different length scales. This research aims at a fundamental understanding of the physical mechanisms governing OS spin valves, and to explore their dependence on material properties.

i. Modeling tunneling process enabling spin-polarized injection. Spin-polarized tunnel injection into an OS is envisioned as a process that involves localized states in the OS band gap. It is demonstrated that the tunneling current is determined by three factors: the tunneling matrix element, the Fermi function and the OS density of states (DOS). Tunneling predominantly involves organic molecular levels near the metal Fermi energy, and therefore usually in the tail of the OS band that supports carrier transport. Thus, a wide bandwidth, i.e. strong disorder, can benefit spin injection from a FM electrode.

ii. Developing a physical model for FM/OS/FM structures. This model contains three parts: spin injection, transport and extraction. Spin injection at OS/FM interfaces was studied in detail as briefly discussed above and extraction is the reverse process of injection. Transport occurs essentially via carrier hopping between neighboring molecules. In a device model, it is described by macroscopic carrier mobilities following a Poole-Frenkel model. This type of model in integrated with the microscopic injection/extraction model.

iii. Investigating OS disorder and the electric field's significance on current polarization. My work showed how the current spin-polarization depends on the distribution of OS molecular states involved in the tunneling process. Spin current increases with the OS DOS width and decreases with the mean energy of the DOS relative to the FM Fermi level. For large applied electric field, the injecting contact becomes dominant, and the relative polarization of the collecting contact is less relevant, which explains MR results published by several experimental groups.

❖ Additional Current and Possible Future Projects

In addition, I also research a closely related field: **flexible organic electronics**, specifically an approach that uses ionic liquids (ILs) instead of traditional dielectrics as gate insulators for OS field effect transistors. ILs have found use as excellent high-capacitance 'dielectrics' for electronic devices. At the high induced charge carrier densities that can be reached with ILs, unique phenomena such as insulator-to-metal transitions and field-effect induced superconductivity may occur. But the dynamics of the IL capacitors themselves require a deeper understanding than is the current state-of-the-art.

Dynamical characteristics of ILs investigated. As part of my close collaboration with experimentalists, I recently developed an equivalent circuit model for the frequency dependent impedance and time dependent current vs. voltage characteristics. The analysis of the experimental data indicates that the dynamics of ILs are characterized by a wide distribution of relaxation times.

Future Directions. Research in OS devices is a challenging interdisciplinary field with many opportunities for significant advances. Building directly on my past work, an exploration of the Molecular Tunnel Junction with FM contacts would be very exciting, particularly if it is coupled to an experimental effort, as has been the fortunate case for much of my work thus far. For the IL FET exploration, the development of a two- or three-dimensional model appears to be of critical importance. First steps in this direction are part of my current work, but significant challenges – and rewards – remain.