The Physical Organic Chemistry of Molecular Conductance

C. Daniel Frisbie
Department of Chemical Engineering & Materials Science, University of Minnesota

This talk will describe fundamental measurements in my laboratory aimed at understanding the conductance of molecules connected between metal electrodes. We explore conductance in two regimes: the tunneling regime, applicable to short molecules, and the polaron hopping regime, which pertains to longer molecules. In the tunneling regime, quantitative analysis of current-voltage (I-V) characteristics is aided greatly by application of the analytical single level model (developed by Ioan Baldea of Heidelberg University), which allows extraction of the molecular orbital (e.g. HOMO or LUMO) offset from the Fermi level, ε, and the metal molecule coupling, Γ. We show that the single level model applies extremely well to common molecular junctions and we are able to relate the junction parameters ε and Γ to molecular structure and the nature of the metal-molecule contacts. Our experiments in the polaron hopping regime rely on high yield click-like chemistry to build pi-conjugated molecular wires up to 10 nm in length from metal substrates. We probe the conductance and I-V behavior as a function of wire length and we observe a clear transition from tunneling to hopping near 4 nm. Transport for long wires > 4 nm is thermally activated and we have recently observed a very strong kinetic isotope effect, which we believe will allow us to understand transition states and polaron localization effects for intramolecular conductance along pi-conjugated chains. In general, there are many opportunities to understand the kinetics of electrical conduction in molecules in much the same way the kinetics of reactions are explored in classical physical organic chemistry.

Biography of the Speaker:

C. Daniel Frisbie is Distinguished McKnight University Professor and Head of Chemical Engineering and Materials Science at the University of Minnesota. A physical chemist by training, he obtained a PhD from MIT in 1993 and was an NSF Postdoctoral Fellow in Chemistry at Harvard. His research focuses on materials for printed electronics, including organic semiconductors and their applications in devices such as transistors and electrochromic displays. He also has a long-standing program in molecular electronics. Research themes include the synthesis of novel organic semiconductors, structure-property relationships, device physics, and the application of scanning probe techniques. New efforts also include manufacturing approaches for flexible electronics and strategies for electrocatalysis. From 2002-2014, Frisbie led a multi-investigator effort in Organic Semiconductors at the University of Minnesota, sponsored by the Materials Research Science and Engineering Center (MRSEC) program of the NSF. He was the lead investigator on a Multi-University Research Initiative (MURI) grant funded by the Office of Naval Research from 2011-2017 for development of a roll-to-roll printed electronics manufacturing platform.