Transition from Direct to Inverted Marcus Regions in Highly Efficient Molecular Diodes

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The mechanisms of charge transport can be, generally speaking, described by two theories: activationless coherent tunnelling processes which can be described by the Landauer theory [1], or thermally-activated charge transfer which can be described by the Marcus theory [2]. In molecular junctions with redox-active molecules, the mechanism of charge transport may be in between these two extremes [3]. For example, low activation energies are frequently observed in molecular junctions but cannot be readily explained, and activationless transport has been reported for very long molecules [4].

We have been studying the mechanisms of charge transport across molecular diodes inside EGaIn junctions based on self-assembled monolayers of with redox-active ferrocenyl (Fc) groups [5]. This system has been well-characterized and yields molecular diodes with exceptionally large rectification ratios [6]. Here, the Fc units oxidize only in one direction of bias and the Fc^+ interaction with the negatively charged top-electrode is much stronger than in opposite bias when the Fc units are neutral. This bias dependent change in the electrostatic interaction results in highly efficient molecular diodes with rectification ratios of nearly 10^6. We used this system to demonstrate experimentally the transition from the Marcus to the inverted Marcus region via intra-molecular orbital gating [7]. In the inverted Marcus region, charge transport is incoherent yet virtually independent of temperature; these findings fit well to a theoretical model that combines Landauer and Marcus theories [3]. As a group, these findings demonstrate that molecular junctions can operate in the grey zone in between pure electrochemical and tunnelling extremes which can be used in the future design of molecular junctions.

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