Bistable [2]Rotaxane Based Molecular Electronics: Fundamentals and Applications

Thesis by

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Dedicated with Love and Gratitude

To Dami, Justin and Alexis

And to my dearest parents, Kyungwon Choi and Kisoon Lee

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Chapter 3 is taken in part from "A 160 kilobit molecular electronic crossbar memory circuit patterned at 10^{11} Bits per square centimeter," *Nature*, 2007, 445, 414-417. Copyright 2007 Nature Publishing Group.

Abstract

Bistable [2]rotaxanes are a unique class of supramolecules that have two constitutional isomers. Upon sandwiched between two electrodes, these two isomeric states show different conducting states, thus behaving as molecular switches. In this thesis, I describe how the bistable [2]rotaxanes have been investigated to ensure that the switching characteristics in solid-state devices are those of the bistable [2]rotaxanes and not those of extraneous elements. In addition, integration of these molecules onto ultra-dense nanowire arrays to constitute a memory circuit is presented.

The bistable [2]rotaxanes have been examined in various environments to study kinetics and ground-state thermodynamics between both isomeric states. In the kinetic study, as molecules are embedded in more viscous environments (solution→polymer gel→solid-state device), a key step in switching cycle slows down significantly, thus reflecting the environments where the molecules are surrounded. In thermodynamic study, one of the major units in the molecular structure was modified and then equilibrium population ratio between both isomeric states was monitored at various temperatures. In both solution and solid-state devices, the population ratio of the modified [2]rotaxane was more sensitive to temperature. This result is very critical in that the properties of devices can be tailored by manipulating the structure of molecular components.

The bistable [2]rotaxanes were integrated into crossbar nanowire arrays to constitute a memory circuit. Ultra-dense nanowire arrays used as electrodes are generated by superlattice nanowire pattern transfer (SNAP) method. Due to extremely narrow pitch (~33 nm) of the SNAP nanowire arrays, the device sets a remarkable record in memory density (~10^{11} Bits/cm^2). Although the circuits were found to have large

numbers of defects, those defects were identified through electronic testing and the working bits were configured to form a fully functional random access memory for storing and retrieving information.

Finally, nanofluidic devices have been developed by utilizing the SNAP method. Due to small channel dimensions (< Debye screening length), passage of ions was modulated by electrostatic interactions between the ions and the nanochannel walls. Devices are being developed to quantify isoelectric points of peptides so that ultimately, the device could function as a protein identifier at a single molecule level.

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