

Mechanism of the Stoddart–Heath Bistable Rotaxane Molecular Switch

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Molecular-scale electronics is developing rapidly¹ because of advances in the synthesis of suitably tailored organic structures, bringing us closer to the ultimate miniaturization of nanoelectronic devices.^{2,3} In a recent success, the Stoddart and Heath groups designed rotaxanes (which have a ring molecule encircling the dumbbell-shaped molecule in Scheme 1) that function as a programmable electronic switch.^{4–9} There are two likely sites for the ring molecule to localize: the tetrathiafulvalene group (TTF) in the left half and the 1,5-dioxynaphthalene group (DNP) in the right half. The experiments showed conclusive evidence of two distinct states (one with a resistance 10–100 times that of the other) and that the system could be switched from one state to the other by applying a sharp address voltage or applying a suitable oxidant or reductant. It is assumed that the switching behavior arises from the difference in conductivity between the two states. However, the atomistic-level mechanism of the switch is still unknown.

To provide the molecular-level understanding necessary to design and optimize such nanoelectronic devices, we initiated theoretical studies of the switching mechanism for the bistable [2]rotaxane shown in Scheme 1, which is based on formula I in Figure 3 of ref 8, but without the stoppers at each end. The detailed simulation procedures are given in the Supportive Information.

The calculation of electric conductivity at the atomic level is now well established.^{10–14} The I – V curves calculated by combination of quantum mechanics^{15–19} and Green's function theory^{12–14} for the two states of the rotaxane molecule are shown in Figure 1. Current flow through the state with the ring on the DNP group (R-DNP) increases almost linearly to 1.5 nA from 0 to 0.25 V bias and reach its maximum of 1.8 nA after 0.3 V. However, current through the state with the ring molecule on the TTF group (R-TTF) increases only to 0.05 nA at range from 0 to 0.5 V, shown in Figure 1b. The calculation results show large different conductivities between the R-DNP and R-TTF states. For applied bias from 0.01 to 0.2 V, the calculated ON/OFF ratio increases from 37 to 58 and decreases to 39 from 0.2 to 0.5 V applied bias. This ON/OFF ratio is comparable to experimental values⁷ of 10–100. This suggests that the simulation has captured the essence of the experimental system. In particular, we find that the switch is OFF when the ring is on the TTF group (R-TTF) and ON when the ring is on the DNP group (R-DNP). Exactly this same assignment was previously proposed.^{4,8}

Next we examine the orbital basis for the switching behavior. The frontier MOs, including highest occupied molecular orbital (HOMO), lowest occupied MO (LUMO), and nearby orbitals of the R-DNP and R-TTF states, are shown in Figure 2, respectively. More MOs can be found in the Supporting Information. These MOs contain contributions from four groups of atoms: Au electrode atoms at each end, the TTF group, the DNP group, and the ring group. We find two states with distinct I – V differences:

- R-DNP state (ON): The HOMO is delocalized over the TTF and ring groups. The LUMO and LUMO+1 (0.1 eV above the

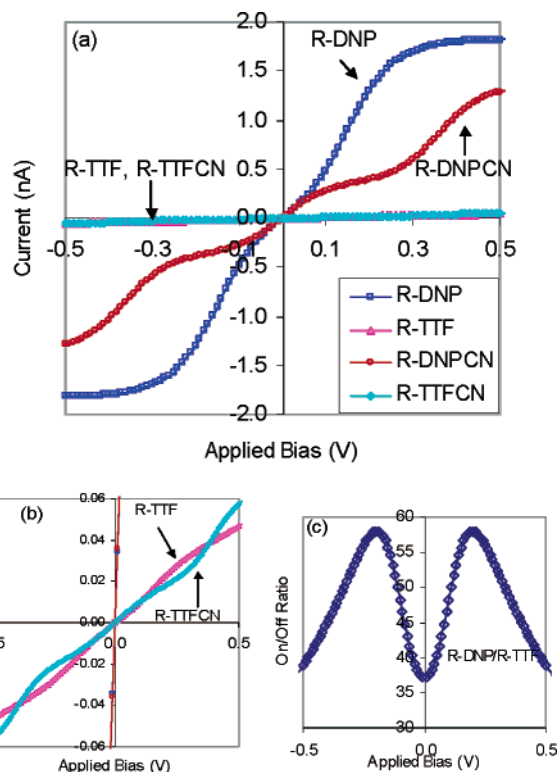
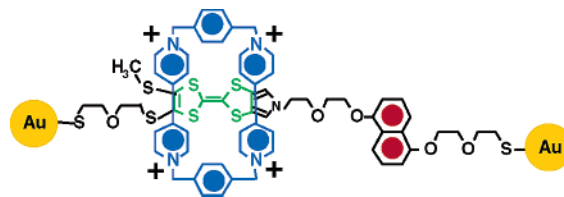


Figure 1. I – V curve of Au–rotaxane–Au switch. (a) The four I – V curves correspond to ring on DNP (R-DNP), on TTF (R-TTF), and for the modified version of the rotaxane bearing a CN group substituted on the DNP unit, R-DNPCN, and R-TTFCN states. (b) Small-scale I – V curve of R-TTF and R-TTFCN. (c). The voltage-dependent ON/OFF ratio.

Scheme 1. Rotaxane Molecule Used in Our Simulation (Each Au Electrode Includes Three Au Atoms)



LUMO) are delocalized over the TTF and ring-DNP groups. HOMO–1 is localized near the upper Au electrode.

- R-TTF state (OFF): HOMO–2 is localized at DNP; LUMO and LUMO+1 are localized at the TTF. HOMO–1 and HOMO are mostly localized at the electrodes.

Since the transmission function determines the electrical properties of the system, we establish a correspondence between the molecular MOs with the peaks in the transmission function. The correlation is shown in Figure 3. The frontier MOs exactly match the peaks in the transmission function (except for the MOs localized on Au, which do not contribute to conductivity). For the R-DNP/ON state, HOMO, LUMO, and LUMO+1 correspond to the three

