Theoretical Study of Molecular Quantum Dot Cellular Automata

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Molecular quantum-dot cellular automata (QCA) is an alternative paradigm for molecular electronics. Each single molecule acts as a QCA cell and binary information is encoded in the configuration of charge among redox-active molecular sites. Coulomb interaction between neighboring molecules provides information transport from one molecule to another, so the heat dissipation is low because no current through molecular circuits is needed.

Recent experiments suggest that mixed-valence complex be possible molecular QCA candidates. Trans-$Ru(dppm)_2(C\equiv CFc)(NCCH_2CH_2NH_2)$ dication is synthesized and attached on the surface of a Si substrate. The measurement of capacitance as a function of external electric field suggests the existence of two redox-active centers inside the candidate molecule and the mobile electrons be driven to move between them. More recent experiment synthesized the molecule of $\{\eta^5\text{-}C_5H_5\}Fe(\eta^5\text{-}C_5H_4)\}_4(\eta^4\text{-}C_4)Co(\eta^5\text{-}C_5H_5)$, which contains four ferrocene groups expected as four redox-active centers. Oxidation of the molecule gives the 1+, 2+, and 3+ ions. 2+ ion has a 2-electron, 2-hole mixed-valence state and thus is suitable for QCA operation.

In this paper, we present a quantum-chemistry *ab initio* analysis of these two QCA candidates. For Trans-$Ru(dppm)_2(C\equiv CFc)(NCCH_2CH_2NH_2)$ dication, our calculation confirms a bistable charge configuration in which the binary information can be encoded. The ferrocence and $Ru(dppm)_2$ groups are two natural quantum dots in the molecule. The carbon-carbon triple bond connecting these two dots provides the tunneling junction for a mobile electron. Driven by an external electric field, the mobile electron can move from one dot to the other, resulting in an abrupt change of dipole moment. The critical driven field is determined by the energy difference of the bistable states and the effect of counterions as well. Our calculations qualitatively explain the experimental observations.

For $\{\eta^5\text{-}C_5H_5\}Fe(\eta^5\text{-}C_5H_4)\}_4(\eta^4\text{-}C_4)Co(\eta^5\text{-}C_5H_5)$ dication, our studies are focused on the planar, 4-fold symmetrical structure, while the geometries of each functional group are optimized separately. The orbital analysis shows that two ferrocenium groups occupy the antipodal positions of a square structure to minimize the total energy, and two mobile electrons can tunnel through $(\eta^4\text{-}C_4)Co(\eta^5\text{-}C_5H_5)$ group between two ferrocene-ferrocenium pairs when driven by a point quadrupole driver or neighboring molecule. Our studies also show this molecular QCA cell is error tolerant when the 4-fold symmetry is broken up.

Reference:
(1) Lent, C. S.; Isaksen, B.; Lieberman, M. *J.Am.Chem.Soc.* 2003,125,1056.
(2) Qi, H.; Sharma, S.; Li, Z., Snider, G. L.; Orlov, A. O.; Lent, C. S.; Fehlner, T. P. *J.Am.Chem.Soc.* 2003,125,15250.
(3) Jiao, J.; Long, G. J.; Grandjean, F. G.; Beatty, A. M.; Fehlner, T. P. *J.Am.Chem.Soc.* 2003,125,7522.
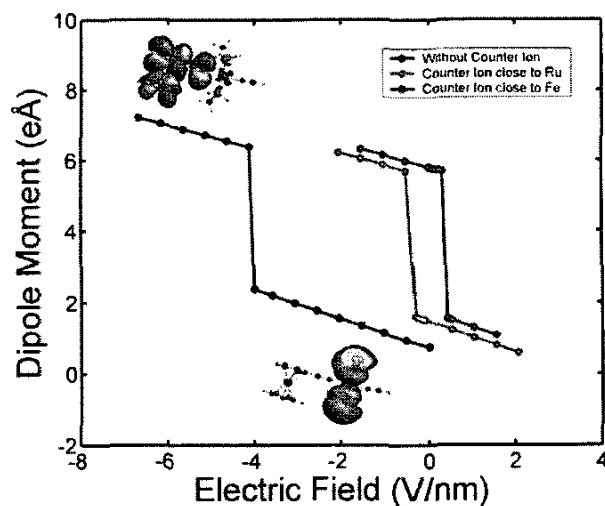
Figure 1: The response function of Trans-Ru(dppm)$_2$(C≡CFc)(NCCH$_2$CH$_2$NH$_2$) dication driven by an external electric field. For each field, the induced molecular dipole moment is calculated. Black curve (without counterion). Blue and Red curves (with counterion).
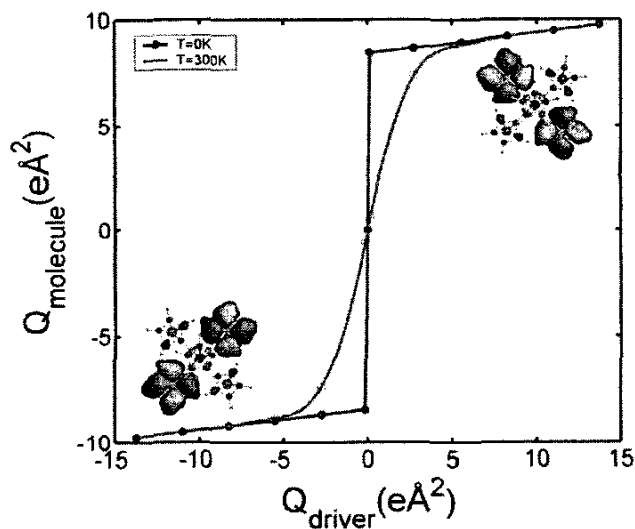

Figure 2: The response function of {η^5-C$_5$H$_5$}Fe(η^5-C$_5$H$_4$)}$_4$(η^4-C$_4$)Co(η^5-C$_5$H$_5$) dication when driven by a quadrupole driver. For each dirver quadrupole moment the induced molecular quadrupole moment is calculated. Blue (T = 0 K). Red (T = 300 K).