

In situ Infrared Spectroscopic Studies of Molecular Behavior in Nanoelectronic Devices

Tony Jun Huang¹, Amar Flood², Chih-Wei Chu³, Seogshin Kang², Tzung-Fang Guo³, Tohru Yamamoto², Hsian-Rong Tseng², Bi-Dan Yu¹, Yang Yang³, J. Fraser Stoddart², Chih-Ming Ho¹

¹Mechanical and Aerospace Engineering Department,

²Department of Chemistry and Biochemistry,

³Department of Materials Science and Engineering,

University of California, Los Angeles
Los Angeles, CA 90095 USA

Abstract: An *in situ* Fourier-transform infrared (FTIR) spectroscopic technique has been developed to monitor molecular behavior in single-molecule thick nanoelectronic devices. This approach is applicable to a range of molecular-based devices and has the potential to provide researchers in the field with a tool to understand the molecular behavior that contributes to device performance.

Keywords: *in situ* spectroscopy; molecular electronic devices; rotaxanes; structure / function relationships

I. INTRODUCTION

During the past four decades, microelectronics has been growing at an extremely fast rate. The complementary logic metal-oxide semiconductor (CMOS)-based integrated circuits have evolved from a small number of transistors to millions of transistors on a chip. However, fundamental physical limitations, as well as increasingly prohibitive costs, hinder miniaturization of electronic devices using the current technology [1]. In order to attain the reduction of the length scale down to the nanometer range, different fabrication methods have to be introduced. This end of the roadmap problem may be resolved by employing a “bottom-up” approach, using some of the smallest building blocks of all, namely molecules, to fabricate electronic devices [2].

Recent developments in the field of molecular electronics over the past few years have raised peoples’ expectations to a level where they believe that this bottom-up technology may one day replace the traditional CMOS-based top-down technology. Perhaps, more likely, it will be a hybrid top-down, bottom-up (HTDBU) technology, which will provide future generations of ultrasmall, ultrafast and low power electronic devices. However, it is widely believed that this field is in its infancy [3]. One major barrier facing researchers is the absence of an effective tool to monitor the molecules’ behavior within device settings. Most molecular electronic devices have similar structures – molecules are sandwiched between two metal

electrodes. Once the molecules are incorporated into these devices, hardly any information about the molecular behavior, other than current-voltage (I/V) characteristics, can be obtained. A recent article on “nanoelectronics” [4] featured a major advance in the area of molectronics. The point was also made, however, that “researchers in the field do not yet understand the maneuverings that change the molecules’ resistance”. The fundamental mechanism of conduction in these devices is just one of the many properties as yet not understood. Until an effective tool is developed to monitor molecular behavior in an operating device, researchers will face difficulties to build up molecular structure / device function relationships, which are routinely used as a guide for molecular design, ultimately allowing for device optimization.

Switchable rotaxanes [5] have been successfully implemented [6,7] in molecular-switch tunnel junctions (MSTJs). In this paper, we describe experiments that have been designed to provide IR spectroscopic proof of the role that switchable rotaxanes play in MSTJ devices. Our preliminary results have shown that IR radiation can penetrate and exit through thin top electrodes, which give us the opportunity to monitor the molecular behavior *in situ* while the devices are operating. In order to provide an unambiguous spectroscopic signature of molecular behavior upon electrical stimulation, we have designed and synthesized rotaxanes with vibrational sensors which are very sensitive to changes in the ring positions, allowing the rotaxane’s influence on the device’s switching properties to be established. Our experiments will (1) build up semi-empirical molecular structure / device function relationships, (2) provide an explanation of device mechanisms, (3) help design molecules rationally to optimize device performance, and, (4) measure the time constant of the molecular switching process within solid-state devices. Potentially, the technique developed here can be used in a range of molecular electronic devices, thus providing researchers in this area with a tool to understand the maneuverings that alter device characteristics at the molecular level.

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II. EXPERIMENTAL

A. Molecules

This study focuses on a rotaxane ($1 \cdot 4PF_6$, Fig. 1.) that shows electrical switching behavior when integrated into MSTJ devices [6]. This molecule consists of a tetracationic ring component, and a linear rod-like section, which contains two constitutionally different recognition sites, a tetrathiafulvalene (TTF) and a dioxynaphthalene (DNP) unit. A hydrophilic (light blue) and a hydrophobic (black) stopper are incorporated at each end of the rod, thus enabling the molecule to form Langmuir-Blodgett (LB) monolayers. As originally designed, the ground state (1^{4+} , Fig. 1B) of this bistable rotaxane has the TTF unit encircled by the ring component. Upon oxidation, the TTF unit becomes doubly oxidized (TTF^{2+}), and the Coulombic repulsion between TTF^{2+} and the tetracationic ring component causes the ring to slide to the DNP unit, forming the switched version of the molecule.

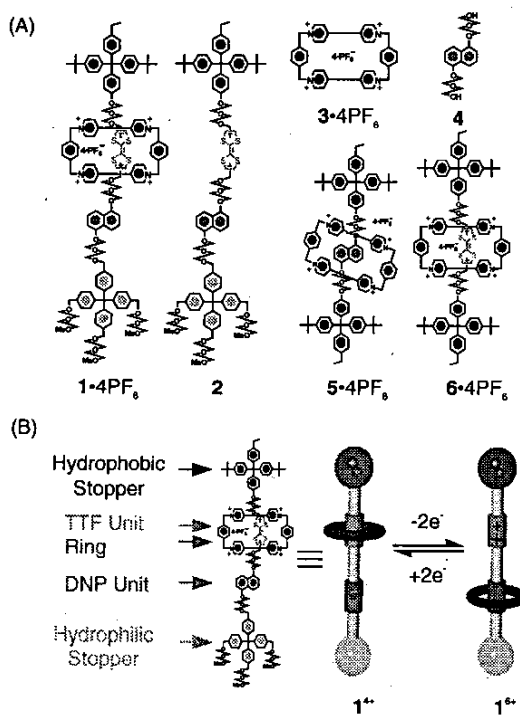


Fig. 1. (A) Structural formulas of an amphiphilic bistable rotaxane $1 \cdot 4PF_6$, its dumbbell 2 , the tetracationic ring $3 \cdot 4PF_6$ and dioxynaphthalene (DNP) thread 4 components, and the model, single-station DNP $5 \cdot 4PF_6$ and tetrathiafulvalene (TTF) $6 \cdot 4PF_6$ rotaxanes, used in this work. (B) Graphic representation of the rotaxane $1 \cdot 4PF_6$, with all the active components labeled, showing its redox-controllable mechanical ring movement.

B. Device Fabrication

Fig. 2 shows a schematic drawing of the experimental setup of a rotaxane-based crossbar junction device. The devices were prepared by (1) evaporating 100 nm-thick aluminum onto silicon nitride substrates, through a contact shadow mask, (2) transferring monolayers of the rotaxane to the substrate using LB techniques [8], and (3) evaporating a semi-transparent top electrode, consisting of a thin layer of Ti (2 nm), followed by a thicker layer of Al (4–6 nm) through a contact shadow mask. Bias voltages are applied to the Al bottom electrode and the Ti/Al top electrode is connected to ground through a current amplifier. The semi-transparent Ti/Al top electrode allows most of the incident and reflected IR beam to pass through to the rotaxane LB films, allowing their molecular signatures to be recorded.

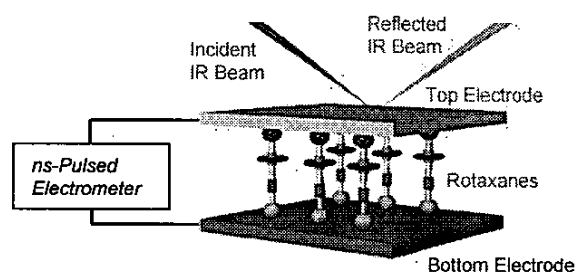


Fig. 2. Schematic diagram for the experimental setup, which consists of a rotaxane-based crossbar device, a nanosecond-pulsed electrometer, an infrared (IR) spectrometer and an IR microscope (not shown in the figure).

C. Experimental Setup

The experimental setup (Fig. 2) consists of a rotaxane-based crossbar junction device, a nanosecond-pulsed electrometer, an IR spectrometer and an IR microscope. Before carrying out any IR spectroscopic experiments, I/V characteristics of each crossbar junction device were measured to ensure that an electrical short circuit did not occur. The IR spectra of the rotaxane mono/multi layers were recorded simultaneously on a Bruker EQUINOX 55 spectrometer, equipped with a Hyperion 1000 IR microscope, while the electrometer was used to apply voltages across the device. The IR microscope was used to focus the incident IR beam onto the crossbar junction device.

Not only is the experiment designed in order to record molecular behavior within an operating device, but it is also intended to quantify the response time for rotaxanes' switching from one state to another. The time constant determines the operation speeds and thus the practical value and future impact of rotaxane-based electronic devices. In these studies, we will use the Bruker EQUINOX 55 spectrometer, along with a time-resolved step-scan IR (TR-S²-IR) detection system.

III. RESULTS AND DISCUSSION

A. IR Spectroscopic Signature in Crossbar Devices

Devices illustrated in Fig. 2 have been fabricated and their IR spectra have been recorded. Fig. 3 shows the IR spectra of the ground-state rotaxanes (1) in an LB trilayer and (2) in a monolayer on an Al electrode, as well as (3) of a monolayer sandwiched between two electrodes. It has been observed that, when the thicknesses of the Ti/Al electrodes are 2/6 nm, the IR spectra obtained are still the same as those without the top electrode, i.e., the top electrode is transparent to the incident and reflected IR beam and we can record the IR spectra of rotaxanes faithfully within operating devices.

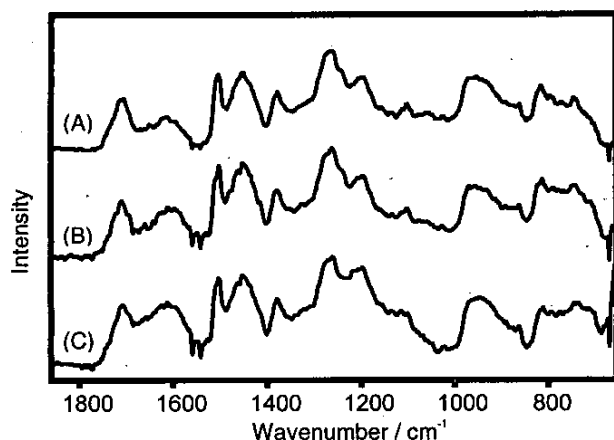


Fig. 3. Grazing angle reflection-absorption IR spectra of the rotaxane $1\cdot 4PF_6$, recorded using an IR microscope (0° polarization, fast accumulation) of (A) an LB trilayer on an Al electrode, (B) an LB monolayer on an Al electrode, and (C) an LB monolayer, sandwiched between two electrodes.

B. IR Analysis

The IR spectra (Fig. 4) of the rotaxane $1\cdot 4PF_6$ and its constituent components were recorded as KBr pellet preparations. All of the spectra of the molecular subsystems leading to the construction of the rotaxane have been analyzed and assigned in terms of their smaller component parts. A number of results obtained from this analysis bear directly on the ability to reveal the molecular behavior in crossbar junction devices. The spectra are constituted by many overlapping vibrational bands, which have been assigned to almost every component, thus leading to complex data that are not easy to deconvolute. This situation is simplified by taking two observations into consideration. They are – (1) The approximate IR band positions and intensities are a simple linear combination of the component parts, with a couple of exceptions. (2) Of the key electronically-active components, from which the rotaxanes are believed to derive both their switching and conduction properties, the TTF signature is too

weak for even the most intense marker bands to be identified. The DNP-based signature is marked by the presence of bands at 1505 and 1268 cm^{-1} , and the tetracationic ring, a strong IR absorber, displays characteristic marker bands at 1633 , 1555 and 639 cm^{-1} . In order to distinguish between the two switching states (Fig. 1B), the marker bands of these key components must appear at sufficiently different positions. The bands for the ring component display energy shifts (Table 1), compared to the free ring, when complexed with either TTF or DNP units. Overall, the vibrational bands of the tetracationic ring shift to lower energies, indicating the presence of modestly weaker and longer bonds. These shifts arise from the charge-transfer mixing of the TTF- or DNP-based HOMO(s) with the ring-based antibonding LUMOs. However, these shifts do not lead to significantly different band positions that would allow the location of the ring along the dumbbell to be exclusively identified.

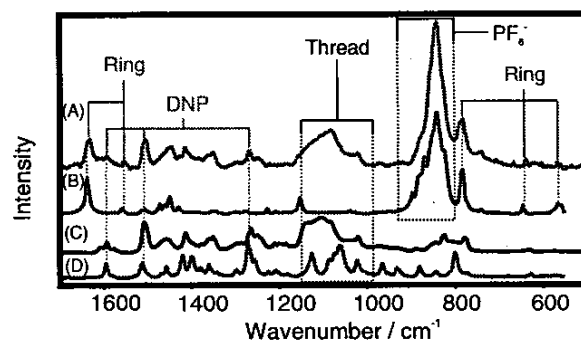


Fig. 4. Assignments of the FTIR spectra of (A) the rotaxane $1\cdot 4PF_6$, based on the band positions of (B) the ring $3\cdot 4PF_6$ and (C) the dumbbell $2\cdot 4PF_6$, and (D) the DNP-thread 4 components.

Table 1. Comparison of the ring-based ($3\cdot 4PF_6$) IR band positions and their spectroscopic shifts when complexed to the single-station model DNP ($5\cdot 4PF_6$) and TTF ($6\cdot 4PF_6$) rotaxanes, and the two-station rotaxane $1\cdot 4PF_6$.^a

IR Band Positions and Shifts / cm^{-1}						
$3\cdot 4PF_6$	$5\cdot 4PF_6$	Shift	$6\cdot 4PF_6$	Shift	$1\cdot 4PF_6$	Shift
644	644	0	639	-5	639	-5
741	739	-2	740	-1	740	-1
782			790	+8	781,789	
1153	1154	+1	1155	+2	1155	+2
1227	1223	-4			1222	-5
1355			1357	+2		
1429	1426	-3	1425	-4	1426	-3
1449	1446	-3	1446	-3		
1558	1557	-1	1556	-2	1555	-3
1638	1633	-5	1633	-5	1633	-5

^a IR Data recorded as KBr pellets with 4 cm^{-1} resolution.

C. Design and Synthesis of Molecules with Vibrational Sensor

As indicated in Section B (IR analysis), the changes in the positions of the peaks assigned to the ring component are not sufficient enough for us to distinguish between the two molecular states, the ground-state 1^{4+} and the switched one 1^{6+} . In order to obtain a clear molecular spectroscopic signature, which will allow the molecular switching behavior to be revealed, some functional groups will be introduced (Fig. 5) into the molecular structure of the ring component. These attached functional groups, or so-called vibrational sensors, involve esters and nitriles that are electronically coupled to the π -electron system [9,10]. These vibrational sensors should satisfy the following requirements: (1) Intense bands are displayed in their IR spectra. (2) The bands for the sensors are positioned in regions of the spectrum uncongested from other features. Switchable rotaxanes encircled with the most ideally modified ring will be incorporated into crossbar junction devices for *in situ* IR studies.

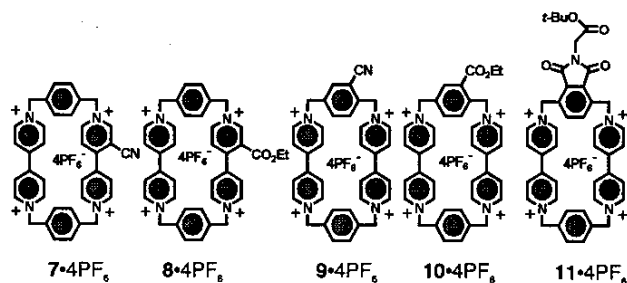


Fig. 5. Schematic formulas of rings $7\cdot 4PF_6 - 11\cdot 4PF_6$ where one of the paraquat units and one of the phenylene units have been modified with additional functional groups.

IV. CONCLUSION

In summary, we are developing a spectroscopic technique to monitor *in situ* molecular signatures in rotaxane-based crossbar junction devices. Preliminary results have shown that IR radiation can penetrate and exit through thin top electrodes. Thus, IR spectra of rotaxanes can be faithfully recorded within operating devices. Since the current rotaxane molecules used don't have discriminatory band shifts for the ring component, it

is challenging to obtain an unambiguous change of the molecular spectroscopic signature in response to electrical stimuli. To solve this problem, we have designed and synthesized molecules with vibrational sensors, which are very sensitive to the ring's position. Our experiments will (1) build up semi-empirical molecular structure / device function relationships, (2) provide an explanation of device behaviors, (3) help rationally design molecules to optimize the device performance, and, (4) measure the time constant of the molecular switching process within solid-state devices. The approach that we are advocating here promises to provide researchers with an effective tool to study molecular behavior in operating molecular devices, and thus, to help advance the field to the next level.

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REFERENCES

- [1] M. Riordan and L. Hoddeson, *Crystal Fire: The Birth of the Computer Age*. NY: W. W. Norton & Company, 1997.
- [2] A. Aviram and M. Ratner, "Molecular rectifiers", *Chem. Phys. Lett.*, vol. 29, pp. 277-283, 1974.
- [3] C. Joachim, J.K. Gimzewski, A. Aviram, "Electronics using hybrid-molecular and mono-molecular devices", *Nature*, vol. 408, pp. 541-548, 2000.
- [4] "Nanoelectronics", *The Economist*, pp. 76-77, September 14th, 2002.
- [5] V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, "Artificial molecular machines", *Angew. Chem. Int. Ed.*, vol. 39, pp. 3348-3391, 2000.
- [6] Y. Luo *et al.*, "Two-dimensional molecular electronic circuit," *ChemPhysChem*, vol. 3, pp. 519-525, 2002.
- [7] C.P. Collier *et al.*, "Electronically configurable molecular-based logic gates," *Science*, vol. 285, pp. 391-394, 1999.
- [8] A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*. Academic Press, Boston, MA, 1991.
- [9] P. Chen, R.A. Palmer, "Ten-nanosecond step-scan FT-IR absorption difference time-resolved spectroscopy: applications to excited states of transition metal complexes," *Appl. Spectrosc.*, vol. 51, pp. 580-583, 1997.
- [10] J.R. Schoonover, C.A. Bignozzi, T.J. Meyer, "Application of transient vibrational spectroscopies to the excited states of metal polypyridyl complexes," *Coord. Chem. Rev.*, vol. 165, pp. 239-266, 1997.