



AFM-Raman

c-AFM and in operando TERS & µRaman Characterization of Molecular Switching in Organic Memristors



Note Organic Memories

AFM19

Application

#### Sreetosh Goswami<sup>1</sup>, Sreebrata Goswami<sup>2</sup>, Thirumalai Venkatesan<sup>1</sup>, Agnès Tempez<sup>3</sup>, Marc Chaigneau<sup>3</sup>

<sup>1</sup>National University of Singapore, Singapore, <sup>2</sup>Indian Association for the Cultivation of Science, Kolkata, <sup>3</sup>HORIBA FRANCE SAS, Palaiseau, France.

**Abstract :** Memristive elements are believed to be one of the most promising components for the next generation of electronics for artificial intelligence (AI) and internet of things (IoT). One of the biggest problems with existing memristors is that their switching is non-uniform (filamentary) and stochastic which accounts for their lack of reproducibility and device-to-device consistency. This application note reports on the demonstration of a 100% uniform molecular switching mechanism in memristors based on Ru-complexes of azo-aromatic ligands using concurrent nanoscale mapping of the conductance by c-AFM and of the chemical signature by in operando TERS.

**Keywords :** Conductive AFM, memristor, in operando Tip-enhanced Raman spectroscopy, transition metal complex, uniformity.

#### **Context and issues**

The word memristor is the contraction of memory and resistance; a memristor is an electrical two-terminal device whose resistance depends on the history of the applied voltage. Memristors are non-volatile memories predicted to be the component of the future for high density data storage and brain inspired ultralow energy computing. Of different material systems used to realize memristive devices, oxide based devices are close to a commercial deployment. Among other genres, a lot of research effort has also been put in organic memristors because of their nonstochastic and more uniform switching as well as their cheap fabrication cost. However, emergence of organic memristors has been hindered by poor reproducibility, endurance stability scalability and low switching speed. Knowing the primary driving



Fig. 1. From microscale to molecular scale.

mechanism at the molecular scale will be the key to improve the robustness and reliability of such organic based devices. Deterministic tracking of molecular mechanisms necessitates nanoscale in-situ spectroscopy in tandem with nanoscopic current measurement that can correlate molecular changes with the current response. Such a measurement remains long awaited yet elusive. The article by Goswami *et.al.,* in Advanced Materials achieves this using a concurrent cAFM and TERS measurement [1].

#### Potential/ Input from technique

TERS has emerged as a powerful analytical technique providing high chemical sensitivity for surface molecular mapping with nanoscale spatial resolution. In operando TERS and concurrent conductive AFM will allow to characterize the chemical fingerprints of the molecular switching mechanism: as voltage across the memristive layer between the AFM tip and a bottom conductive layer is applied Raman spectra are acquired and plasmonic enhancement permits nanoresolution at the contact point of the tip. In addition,  $\mu$ Raman comes in play to confirm the switching mechanism up to the microscale.

#### Starting point, what is known?

A device based on a ruthenium complex with an azo-aromatic ligand has been reported as giving great performance: stable (tested over hundreds of devices), enduring ( $\approx 10^{12}$  write/erase cycles), fast (<30 ns), and ultralow energy ( $\approx 1.5$  fJ) memristive switching properties [2-5]. Its switching

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mechanism has been studied using in situ  $\mu$ Raman and UV-vis spectroscopies. The role of the ligand in the molecular redox transition has been determined and confirmed by quantum chemical calculations. As schematically depicted in Fig. 1, chemical fingerprints obtained in  $\mu$ Raman will be compared with the molecular changes probed by in-operando TERS to establish areal switching uniformity[1].

## Description of sample and measurement

The memristive organic layers are prepared from solutions of the two precursor azo-aromatic complexes in acetonitrile (Fig. 2): (i) system-A,  $[Ru(L_1)_3]$  (PF<sub>6</sub>)<sub>2</sub> (L<sub>1</sub> = 2(phenylazo)pyridine) and (ii) system-B,  $[Ru(L_2)_2]$  (PF<sub>6</sub>)<sub>2</sub> (L<sub>2</sub> = 2,6-bis(phenylazo) pyridine). The test devices comprise a layer of these materials off-centred spin coated (thickness ≈15-70 nm) on an epitaxial indium tin oxide (ITO) film of ≈60 nm thickness grown via pulsed laser deposition (PLD) on an annealed yttria-stabilised zirconia (YSZ) substrate. The ITO thin film serves as the bottom electrode and the conductive c-AFM/ TERS tip as the top electrode. The use of an atomically flat ITO bottom electrode (RMS roughness of ≈0.5 nm over 25 × 25 µm<sup>2</sup>) facilitates the formation of an ultrasmooth spin-coated film with RMS roughness ≈1.5 nm over 25 × 25 µm<sup>2</sup>. After deposition, the samples were stored inside a vacuum chamber with a pressure of about 10<sup>-8</sup> Torr for 12 h.

TERS measurements were performed using a NanoRaman system from HORIBA Scientific integrating an atomic force



Fig. 2. Left: Azo-aromatic molecules of system-A:  $[Ru(L_{\gamma})] (PF_{\vartheta_2}) (L_{\gamma} = 2(phenylazo)pyridine) and system-B:, <math>[Ru(L_{\gamma})] (PF_{\vartheta}) (L_{\gamma} = 2, 6-bis(phenylazo)pyridine)$ , Right: schematic diagram of the test device.

microscope (OmegaScope, based on SmartSPM) and a Raman microscope (XploRA) with a 100× WD objective tilted by 60° with respect to the sample plane. A 638 nm *p*-polarized laser (80  $\mu$ W) was focused onto the cantileverbased gold coated AFM-TERS tip (OMNI TERS-SNC-Au, App Nano). This probe was conductive and thereby suitable to apply a voltage and acquire Raman spectra at any voltage. After recording an AFM topography image in AC mode (2 × 2  $\mu$ m<sup>2</sup>), the tip was positioned on a spot of interest, potential voltage was applied on the tip, and a Raman spectrum was

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Fig. 3. (a) System-A: TER (left) and µRaman (right) spectra measured in operando for two states (b) System-B: TER (left) and µRaman (right) spectra measured in operando for three conductance states. (c) and (d) Intensity color plots of spectral voltage dependence in TERS (left) and µRaman (right) of system-A and system-B for forward (top) and reverse (bottom) voltage sweeps.

acquired for 50 s with the tip in contact with sample surface with a typical interaction of 2–10 nN. It had been checked that the spectrum acquired with the tip few nm away from the sample, which is the far-field or  $\mu$ Raman contribution, was background spectrum without Raman signature. As a result, the "in contact" spectrum was pure near-field contribution generated from the nanoregion under the tip. Fig. 3 compares the Raman spectra obtained in  $\mu$ Raman and in TERS for both systems A and B in their ON and OFF states and also



Fig. 4. Areal uniformity in TERS mapping: **a)** In situ TER spectra measured in ON and OFF states of system-A. The blue frame in spectra (a) represents the range (1320–1400 cm<sup>-1</sup>) integrated in the TERS maps presented in panels (b) and (c). **b)** A 2 × 2  $\mu$ m<sup>2</sup> TERS map in the ON and OFF states. **c)** A 200 × 200 nm<sup>2</sup> TERS map of ON and OFF states with the same spectral range as in (b). **d–f)** Same as (a)–(c) for the three states of system-B.

in the intermediate state for system B. In both scale Raman spectroscopies, the changes in the azo-stretching modes are identical. The molecular redox process induces spectral weight transfer, from a dominant  $E_{_{DA}}$  (unreduced) mode in the ON state to a dominant  $E_{_{1A}}$  (singly reduced ligand) in the OFF state in the reduction process for system-A (Fig. 3b). For system-B, the Raman spectrum features a higher  $E_{_{2B}}$  (triply reduced ligand state) mode in the ON state, higher  $E_{_{1B}}$  (singly reduced ligand state) in the intermediate state and dominant  $E_{_{0B}}$  (unreduced ligand state) in the OFF state (Fig. 3c). The plots featuring color coded intensity  $\mu$ Raman and TERS spectra collected for voltages from -0.3 V to +0.3 V (forward sweep) and from +0.3 V to -0.3 V also indicate the very close voltage dependence behavior for both devices A&B at the micro and

nanoscales. Another way to show the areal uniformity of the switching mechanism is to record TERS maps and monitor intensity of characteristic ON/Intermediate/OFF state Raman bands. Fig. 4b and 4c show the variation of intensity in the range of 1330-1400 cm<sup>-1</sup> for device A for scan area of 2 × 2  $\mu$ m<sup>2</sup> (pixel size = 50 nm) and 200 × 200 nm<sup>2</sup> (pixel size = 7 nm), respectively in both ON and OFF conductance states of device A. Standard deviations (A(2\sigma)/Amean) in the spectral distributions in all states are <10%. In Fig. 4d–f, we show uniform TERS response for device B. The integration spectral range is 1250–1380 cm<sup>-1</sup> and the spectral weights in different states (i.e., OFF, intermediate and ON) are different but spatially uniform for each conductance state.

### **Conclusion and perspectives**

This note shows how TERS mapping realized in operando in a memristive device brings the key demonstration of the homogeneity of the molecular redox transition mechanism between conductance states with a sub-10 nm spatial resolution. With the complementary µRaman study a uniform 100% switching of an entire device area has been proved. Knowing that the molecular switching process scale from nanoscale to macroscale is a significant and long awaited achievement in organic memristors and molecular resistance switches. This paves the way for robust devices and implementation in ultralow energy digital electronics. This in operando characterization method could be applied to a wide variety of molecule-enabled electronic devices and systems, such as molecular diodes, organic light emitters, and collectors.

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## info.sci@horiba.com

USA: +1 732 494 8660 UK: +44 (0)1604 542 500 China: +86 (0)21 6289 6060 Taiwan: +886 3 5600606 
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 Italy:
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