

## Demonstration of terahertz molecular switches

Imen HNID,<sup>1</sup> David GUÉRIN,<sup>1</sup> Ali YASSIN,<sup>2</sup> Lionel SANGUINET,<sup>2</sup> Philippe BLANCHARD,<sup>2</sup> Stéphane LENFANT,<sup>1,\*</sup> and Dominique VUILLAUME,<sup>1,\*</sup>

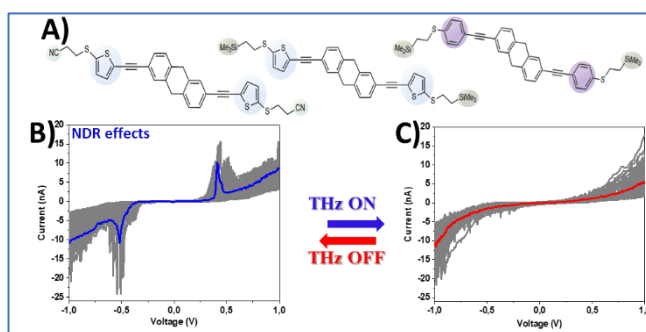
<sup>1</sup> IEMN, CNRS, Univ. Lille, Av. Poincaré, F-59652 Villeneuve d'Ascq, France.

<sup>2</sup> MOLTECH-Anjou, CNRS, Univ. Angers, F-49045 Angers, France.

\* [stephane.lenfant@iemn.fr](mailto:stephane.lenfant@iemn.fr) and [dominique.vuillaume@iemn.fr](mailto:dominique.vuillaume@iemn.fr)

We study the electron transport properties under a terahertz (THz) irradiation of three molecules that consist of two conjugated parts that are coupled through a non-conjugated linker (Fig. 1A). Due to this non-conjugated linker, each molecule can be seen as two weakly coupled sites in series and a resonant transport occurs only when the energy of the two sites are aligned leading to negative differential resistance (NDR) behaviors<sup>[1]</sup>. Moreover, it has been theoretically suggested that switching in such systems, between different current states in transport through molecules, is possible and may be triggered by a passing electromagnetic pulse in the THz range<sup>[2]</sup>. This mechanism relies on a THz-induced resonant electron transfer between the pair of neighboring subunits. As a consequence, the energy of the two sites are misaligned and therefore, the passage of current is turned off by the irradiation pulse and the NDR behaviors are eliminated.

Three molecules that differ by the spacer (phenyl vs. thiophene) and the anchor group (thiol vs. cyanide) – Fig. 1A were synthesized and SAMs were formed on very flat template-stripped gold electrodes (RMS<0.5nm). Solid-state molecular junctions (MJs), in which a C-AFM (Conducting-Atomic Force Microscopy) tip in Pt/Ir is used as the top electrode, were formed. The electronic properties of the resulting MJs were investigated under an in-situ THz irradiation (30THz) and will be presented for the three molecules. When the THz irradiation is OFF, NDR behaviors at the nanoscale (few tens of molecules) were observed (Fig. 1B) with an unprecedented large peak-to-valley ratios (up to ca. 500 compared to ca. 15 in the MCBJ experiments<sup>[1]</sup>). The energy of the molecular orbitals involved in the NDR effect are determined by fitting and analytical model. When the THz irradiation is ON, the junction is immediately switched and the NDR behaviors are completely suppressed (Fig. 1C). These phenomena were reproducibly and reversibly observed for all three molecular junctions, whatever the nature of the spacer and anchoring group, and will be presented and discussed.



**Fig. 1. A)** Molecular structures of all three studied molecules. **B)** and **C)** Experimental I-V characteristics obtained from the junctions metal-molecule-metal of the first molecule shown in A under THz irradiation. The blue and red curves approximate an average of several curves (gray) over a few positions on the samples using C-AFM set-up, showing NDR behaviors at the OFF state.

### References

- [1] M. L. Perrin, R. Frisenda, M. Koole, J. S. Seldenthuis, J. A. C. Gil, H. Valkenier, J. C. Hummelen, N. Renaud, F. C. Grozema, J. M. Thijssen, D. Dulić and H. S. J. Van Der Zant, *Nat. Nanotechnol.*, 2014, 9, 830.
- [2] P. Orellana and F. Claro. *Phys. Rev. Lett.* 2003, 90, 4.

We acknowledge J.F. Lampin for the loan of the 30 THz laser and help with its set-up. Financial support by ANR (project EVOLMONET, #ANR-20-CE30-0002).