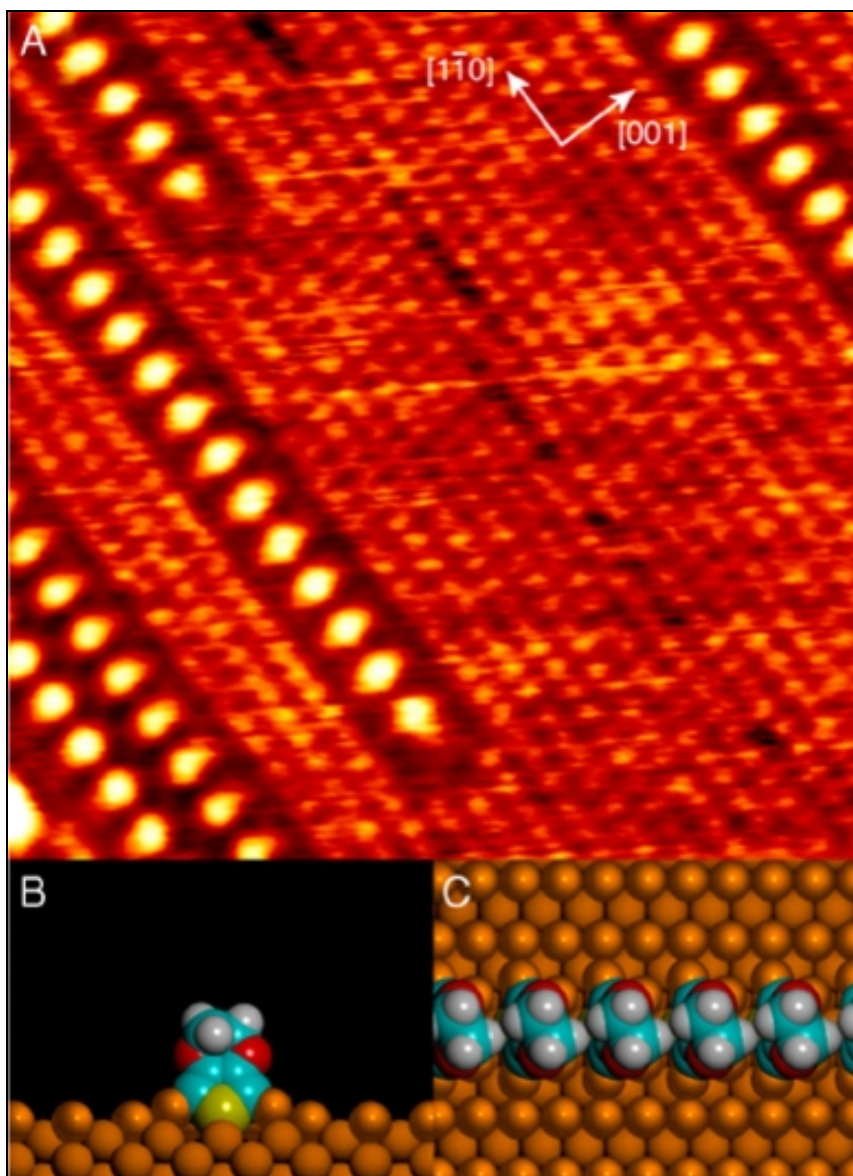
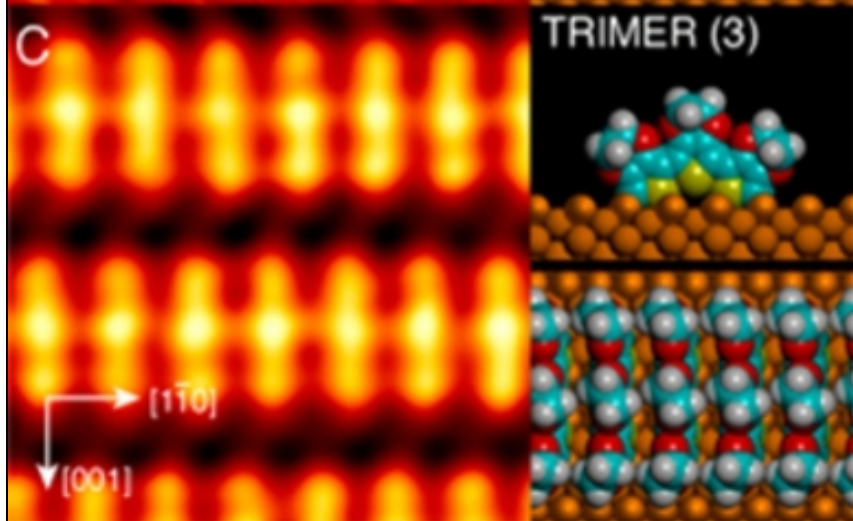
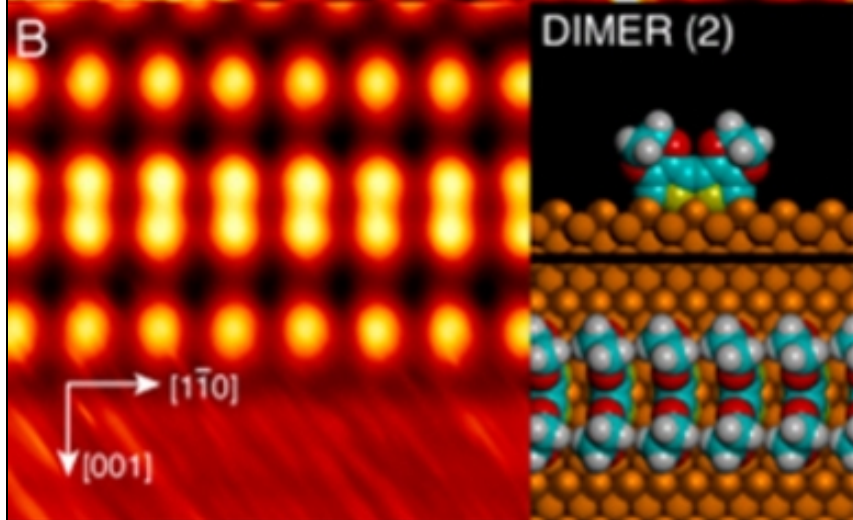
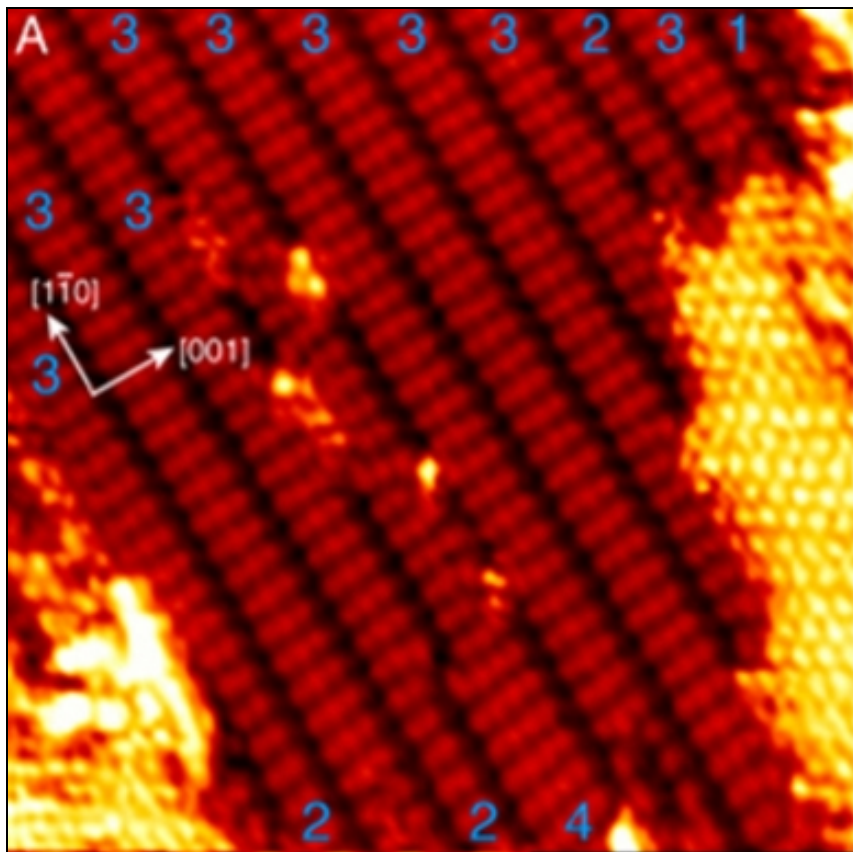


**Step-by-step growth of epitaxially aligned polythiophene by surface-confined oligomerization
(Result of the month 07/2010)**

One of the great challenges in surface chemistry is to assemble aromatic building blocks into ordered structures that are mechanically robust and electronically interlinked i.e., are held together by covalent bonds. We demonstrate the surface-confined growth of ordered arrays of poly(3,4-ethylenedioxythiophene) (PEDOT) chains, by using the substrate (the 110 facet of copper) simultaneously as template and catalyst for polymerization. Copper acts as promoter for the Ullmann coupling reaction, whereas the inherent anisotropy of the fcc 110 facet confines growth to a single dimension. High resolution scanning tunneling microscopy performed under ultrahigh vacuum conditions allows us to simultaneously image PEDOT oligomers and the copper lattice with atomic resolution. Density functional theory calculations confirm an unexpected adsorption geometry of the PEDOT oligomers, which stand on the sulfur atom of the thiophene ring rather than lying flat. This polymerization approach can be extended to many other halogen-terminated molecules to produce epitaxially aligned conjugated polymers. Such systems might be of central importance to develop future electronic and optoelectronic devices with high quality active materials, besides representing model systems for basic science investigations.



Low-coverage EDOT molecules on Cu(110) self-organize into stacks. (A) STM image showing stacks of EDOT molecules on Cu(110) subsequent to a five-minute DIEDOT exposure [$V = -365$ mV, $I = 1.0$ nA, $(8.9 \text{ nm})^2$]. The surrounding bare regions of the Cu(110) substrate exhibit a (1×1) symmetry. The positions of the molecules in the stack are shown, as calculated by DFT viewed from (B) the front and (C) the top. The model shows Cu atoms lifted out of the top substrate layer to participate in bonding to the EDOT molecule.



Higher coverages of EDOT results in the formation of a well-organized oligomer overlayer. (A) STM image of this higher-coverage surface reveals doubling and tripling of the stack elements [$V = -1.06$ V, $I = 1.1$ nA, $(14.4$ nm) 2]. In this image we observe monomer (1), dimer (2), trimer (3), and tetramer (4) stacks, surrounded by a (brighter) region of species in a (2×2) reconstruction in a layer above. High resolution STM data and DFT calculated structures are shown for (B) dimer and (C) trimer stacks.

Authors:

J. A. Lipton-Duffin ^(1,2), J. A. Miwaa,^b M. Kondratenko ^(2,3), F. Cicoiraa ⁽²⁾, B. G. Sumpter^d ⁽⁴⁾, V. Meunier^d ⁽¹⁾, D. F. Perepichk ^(1,2,3) and F. Rosej ^(1,2)

⁽¹⁾ INRS-ÉMT, Université du Québec, 1650 Boulevard Lionel-Boulet, Varennes, QC J3X 1S2 Canada;

⁽²⁾ Center for Self-Assembled Chemical Structures and

⁽³⁾ Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montréal, QC, H3A 2K6 Canada;

⁽⁴⁾ Oak Ridge National Laboratory, P.O. Box 2008 MS6367, Oak Ridge, TN 37831-636

Institute web-pages:

<http://www.nanofemtolab.qc.ca/>

<http://www.emt.inrs.ca>

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This result has been obtained with : **OMICRON Variable Temperature UHV SPM**