

Self-assembly of oligothiophenecarboxylic acid monolayer by Scanning Tunneling Microscope (STM)

Chaoying Fu¹, Oleksandr Ivasenko¹, Jennifer M. Macleod^{2#}, Tyler Taerum¹, Dmitrii F. Perepichka¹ and Federico Rosei²

¹Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montréal, QC, Canada H3A 2K6

²INRS-ÉMT, Université du Québec, 1650 Boulevard Lionel-Boulet, Varennes, QC J3X 1S2 Canada

[#]Current address: Dipartimento di Fisica, Università degli Studi di Trieste, Trieste, Italy
chaoying.fu@mail.mcgill.ca

Thiophene-containing molecules and polymers comprise a very important class of electronic materials. Among various candidates, fullerene/polythiophene have shown the best performance in solar cell applications. However, the difficulties arise from significantly uncontrolled morphologies; namely, polydispersity of polythiophenes and uncontrolled agglomeration of fullerenes. In this work, H-bonding has been used to control the self-organization of oligothiophene semiconductors. By means of Scanning Tunneling Microscopy (STM), the study has demonstrated formation of highly ordered 2D networks of the COOH-substituted oligothiophene TTBTA (**Figure Ia**) and TTATA (**Figure II**) as well as monolayers of oligothiophene and fullerene molecular semiconductors (**Figure Ib**). Thus, the results have revealed details of the molecular-scale phase separation and ordering with potential implications for the design of organic electronic devices, in particular future bulk heterojunction solar cells.

Oligothiophenecarboxylic acid (TTBTA and TTATA) self-assembles at the solution/graphite interface into either a porous network linked by dimeric hydrogen bonding associations of COOH groups (R_2^2 (8)) or a close-packed network linked in a novel hexameric (R_6^6 (24)) or tetrameric (R_4^4 (12)) hydrogen binding motifs. Analysis of high-resolution STM images shows that the pore cavities can efficiently host C60 molecules, which form ordered domains with number of fullerenes per cavity varying from one to four. The observed monodisperse filling and long-range co-alignment of fullerenes is described in terms of a combination of an electrostatic effect and the commensurability between the graphite and molecular network, which leads to differentiation of otherwise identical adsorption sites in the pores.

References

- 1) J.M. MacLeod, O. Ivasenko, C. Fu, T. Taerum, F. Rosei, and D.F. Perepichka, *J.Am.Chem.Soc.* **2009**,131(46), 16844.
- 2) T. Taerum, O. Lukoyanova, R. Wylie, D. F. Perepichka, *Org. Lett.* **2009**, 11(15), 3230.
- 3) J. L. Brusso, O. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei, D. F. Perepichka, *Chem. Mater.* **2008**, 20, 2484.
- 4) D. F. Perepichka, F. Rosei, *Science* **2009**, 323, 216.

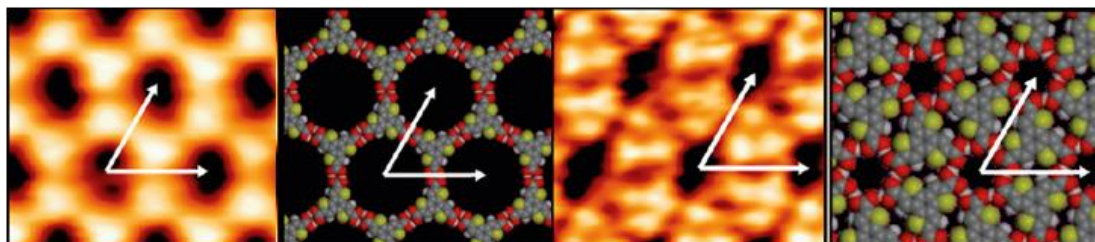


Figure 1a STM image and model of the TTBTA chicken wire and close-packed structures, formed at the HOPG/heptanoic acid interface. Lattice vectors are indicated in white.

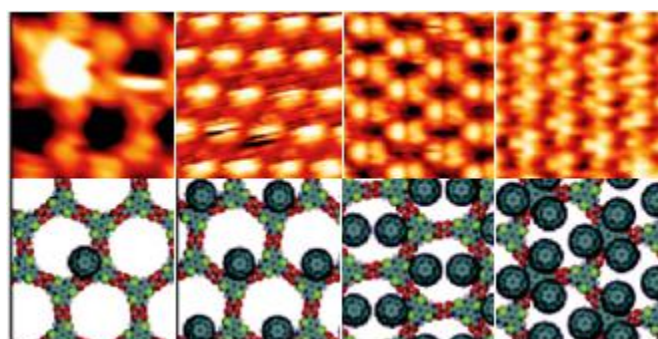


Figure 1b STM image and model of the TTBTA-C60 chicken wire host-guest architectures with sparse fullerene coverage and one, two, and three fullerenes per chicken wire unit cell.

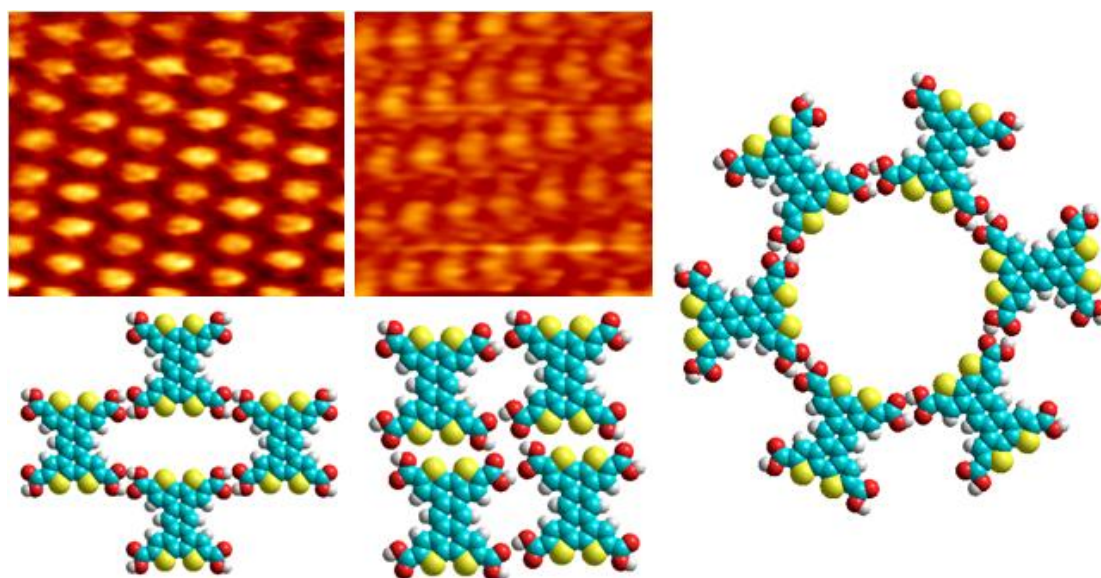


Figure 2 STM image and model of the TTATA rectangular and close-packed structures, formed at the HOPG/Octanoic acid/Trichlorobenzene interface. The last model of Kagome structure is purely theoretically modeled but waiting for experimental observation in near future.