10th International Conference on Molecular Electronics
November 29 - December 2, 2021

On-surface photoswitch from different AZO and DAE derivatives studied by scanning tunneling microscope

L. Guan[1], I. Hind[1], F. Denis[1,2], F. Lafolet[1], S. Cobo[3], F. Maurel[1], J. C. Lacroix*[1], X. Sun*[1]

[1]*Université de Paris, ITODYS, CNRS-UMR 7086, 15 rue J-A. de Baïf, F-75013 Paris, France.*

[2]*Université Lyon, ENS de Lyon, CNRS-UMR 5182, Laboratoire de Chimie, F69342 Lyon, France.*

[3]*Université Grenoble Alpes, CNRS, DCM, F-38000 Grenoble, France*

guanlihao666@gmail.com

Abstract:

Scanning tunneling microscope (STM) is a powerful technique to investigate topographic as well as electronic properties on functional organic molecules down to sub-molecular or atomic scale.[1] We have recently designed and studied ditopic ligands consisting of bipyridine (bpy) terminal groups linked through photochromic central moieties including azobenzene (AZO) or diarylethene (DAE). These molecules exhibit multi-switchable properties by different triggers such as protonation and light illumination.[2,3] Bpy-AZO-bpy and bpy-DAE-bpy molecules have been allowed to first self-organize on surface then have been photo-switched in situ. The different conformers or configurations from both systems, before and after switching, were evidenced by STM at a sub-molecular level at the solid/liquid interface.

The bpy-AZO-bpy molecules were first self-assembled with the AZO center in their flat TRANS confirmation (Figure a).[4] The orientation of the two bipyridine terminals can be modified by protonation, where "U" shape cis conformers are transformed into the "S" shape trans conformers. After UV irradiation, individual AZO units switch out of plane to their CIS conformation and are observed by STM as shown in Figure b.

The DAE photochromic center, from bpy-DAE-bpy molecule, can switch reversibly between its open- (OF) and closed forms (CF) upon visible and UV light irradiation, respectively.[5] The CF molecules show two kinds of density of states (DOS) patterns, (Figure 1c and d) representing the HOMO and LUMO, respectively. Reversible CF/OF photo-switches are evidenced on the LUMO images at a sub-molecular level. The observed images are attributed to a combined electronic DOS as well as topographic contrasts. Density function theory calculation provides a theoretical comprehension to the observed HOMO/LUMO images and the DAE switches. (Figure 2c and d). As an exciting result, the bpy-DAE-bpy molecules show a clear cooperative photo-switch.

These observations demonstrate on surface multi-functional switches at a sub-molecular level.

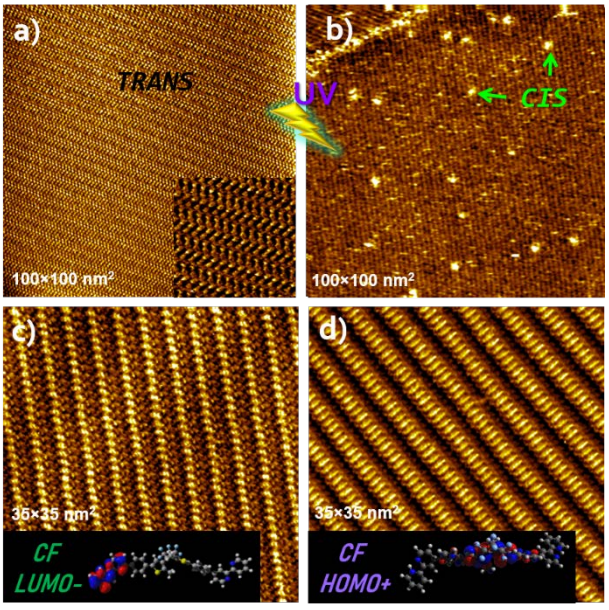

Figure 1 – STM images showing the self-organizations from bpy-AZO-bpy and bpy-DAE-bpy, respectively.

References:

[1] X. Sun*, X. Yao, G. Trippé-Allard, J. C. Lacroix*, *J. Phys. Chem. C* 2021, 125, 1, 957–963.

[2] X. Sun*, F. Lafolet*, G. Lemercier, F. Maurel, J. C. Lacroix, *J. Phys. Chem. C* 2017, 121, 20925−20930.

[3] X. Sun*, X. L. Yao, D. Frath, F. Lafolet, G. Lemercier, J. C. Lacroix*, *J. Phys. Chem. Lett.* 2019, 10, 15, 4164

[4] I. Hnid, X. Sun*, D. Frath, F. Lafolet*, J. C. Lacroix. *Nanoscale* 2019,11, 23042-23048.

[5] I. Hnid, **L. Guan**, E. Chatir, S. Cobo, F. Lafolet, F. Maurel, J. C. Lacroix*, X. Sun*. Topographic Contrasts on Cooperatively Switched Diarylethene-Bridged Ditopic ligand, *Submitted*