Laboratoire PPSM - UMR CNRS 8531



Photochimie et Photophysique Supramoléculaires et Macromoléculaires

Séminaire PPSM

Mardi 19 décembre 2017 - 10h30

Auditorium D. Chemla - Bâtiment IDA

Jan Patrick DeLa Cruz CALUPITAN

Nara Institute of Science and Technology, Japon

Invité par : Clémence Allain, Rémi Métivier

«Highly-sensitive terarylenes: synthesis, switching and STM studies»

Diarylethenes, and their terarylene derivatives, are promising for next generation optoelectronic devices due to their excellent photoswitching properties. For such applications, it is necessary (1) to develop derivatives highly sensitive to switching; (2) to modify them for studies on 2D surfaces; and (3) to eventually study them at the nanoscale on 2D by scanning tunneling microscopy(STM).

Although terarylenes can display photocyclization quantum yields near 100 %, that of cycloreversion remains low so an alternative route, through an oxidative chain-reaction process, was sought. The first part presents how this reaction may be controlled by attachment of aromatic groups on reactive carbons.² In the second part, these molecules were functionalized with tert-butyl and chloride groups. Experimental data and DFT calculations demonstrated that these substituents preserve the excellent photochemical properties of terarylenes. At the same time, tert-butyl groups improve STM image contrasts.³ In the third part, two sets of STM data are presented. At 77 K, a new bottom-up approach for forming reproducible terarylene assemblies was developed.⁴ Meanwhile, at 5 K, the terarylene functionalized with tert-butyl groups present different forms on Ag(111). With the aid of DFT calculations, we assign different conformations of the molecule on the surface. Direct visualization of occupied and unoccupied states could also be achieved on NaCl/Ag(111).⁵

Thus, molecular design principles are presented in order to maximize the sensitivity of terarylenes to switching and make them viable for STM investigations. These STM studies on 2D surfaces under ultra-high vacuum conditions uncovered new properties and phenomena previously unobserved in solution chemistry.

<u>References</u>

- 1. M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 2014, 114, 12174-12277.
- 2. J.P.D.C. Calupitan, T. Nakashima, Y. Hashimoto, T. Kawai, Chem. Eur. J. 2016, 29, 10002-10008.
- 3. J.P.D.C. Calupitan, O. Galangau, O. Guillermet, R. Coratger, T. Nakashima, G. Rapenne, T. Kawai, *Eur. J. Org. Chem.* **2017**, *17*, 2451-2461.
- 4. J.P.D.C. Calupitan, O. Galangau, O. Guillermet, R. Coratger, T. Nakashima, G. Rapenne, T. Kawai, *J. Phys. Chem. C* **2017**, *121*, 25384-25389.
- 5. J.P.D.C. Calupitan, O. Guillermet, O. Galangau, J. Echeverria, X. Bouju, J. Echeverria, R. Coratger, T. Nakashima, G. Rapenne, T. Kawai, *Manuscript under revision*.

PPSM

ENS Cachan – 61 avenue du Président Wilson 94235 Cachan Cedex – France **Tél**: +33 1 47 40 53 38 – **Fax**: +33 1 47 40 24 54 **e-mail**: ahusson@ppsm.ens-cachan fr

e-mail: ahusson@ppsm.ens-cachan.fr site web: http://www.ppsm.ens-cachan.fr



