Molecular switch adressed by chemical stimuli

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Conception of a new class of conformational memories

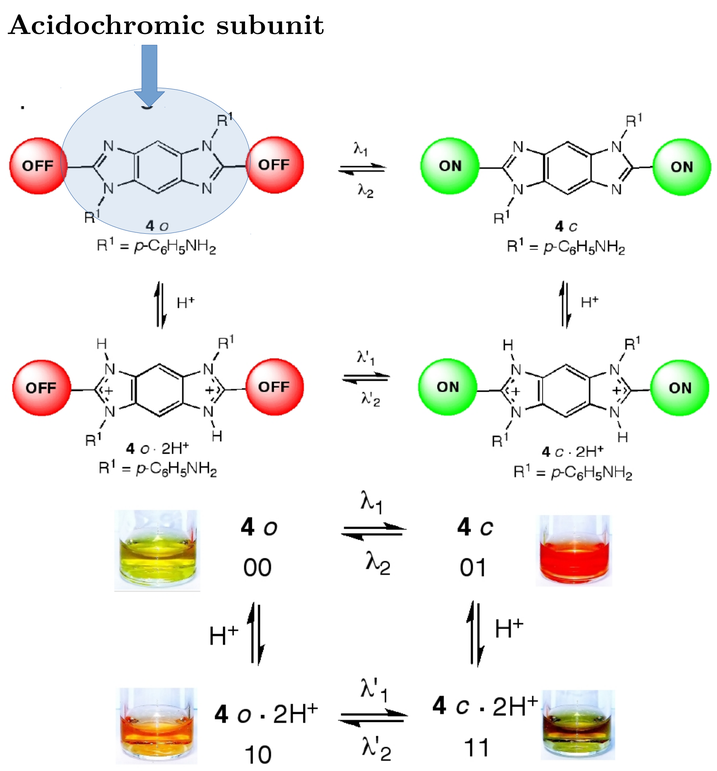
Built around 2 adressable subunits :

-benzo-bis(imidazole): acidochrome adressed by a chemical stimuli

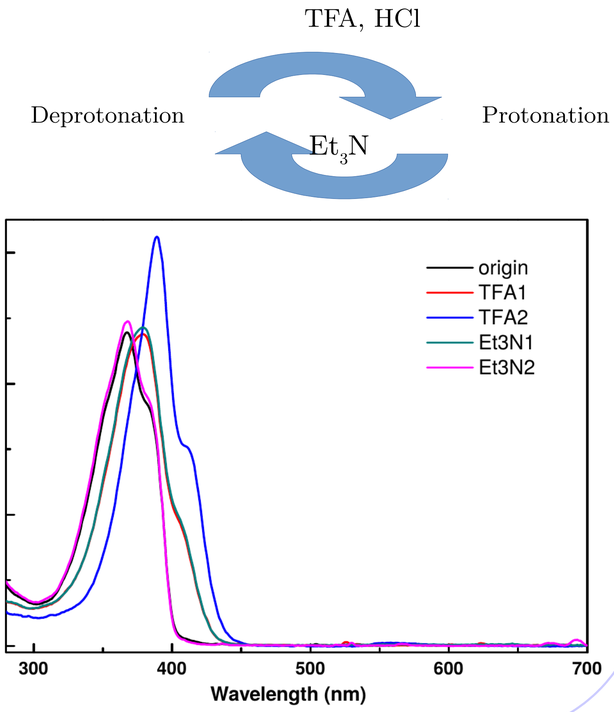
-diarylethene : photochrome adressed by light stimuli

This molecule can undergo conformational changes upon Irradiation and/or protonation

Expected to present four different electronic states

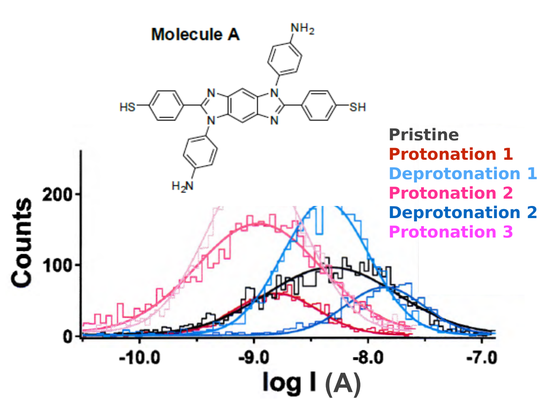


Reversible switching upon protonation / deprotonation
In solution

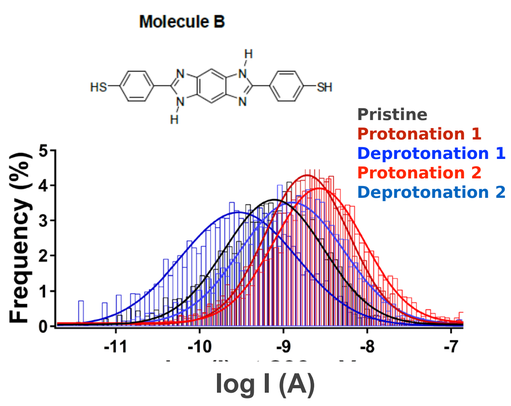


Conductance measurements on the acidochromic subunit
Reversible conductance switching on self-assembled monolayers
Compared to measurements at the single molecule scale using a Mechanically Controlled Break Junction (MCBJ)

Conductance measurements on self-assembled monolayers on ^{TS}Au surfaces conductive AFM



$G_{depro} > G_{pro}$
a factor ~ 10



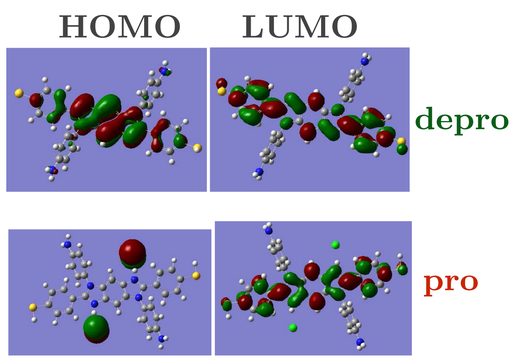
$G_{pro} > G_{depro}$
a factor ~ 5-10

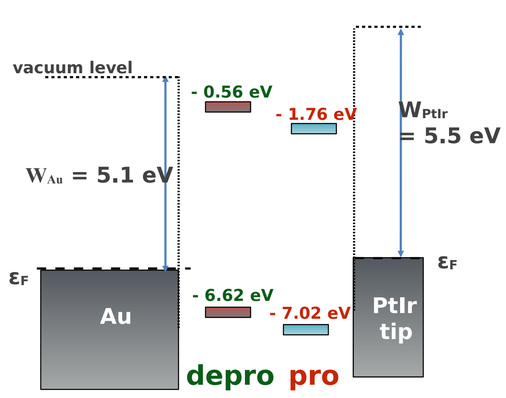
– protonation : exposed to HCl (35%) or CF_3COOH vapors, ca. 1 min
– deprotonation : exposed to triethylamine (99.5%) vapor, ca. 1 min

C-AFM at 5 nN & 200 mV, 800-1000 measurements

Theoritical calculations on molecule A

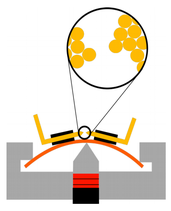
Gaussian03 (B3LYP,6-311g)



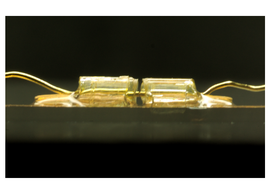


Pro : localized HOMO, deeper HOMO
in agreement with $G_{pro} < G_{depro}$ for molecule A

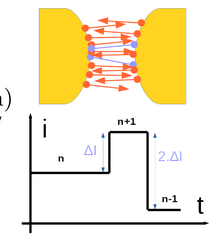
Single molecule conductance measurements using a MCBJ



Mechanically controlled Break Junction
Excellent thermal & mechanical stability
Sub-picometer resolution of electrode positionning

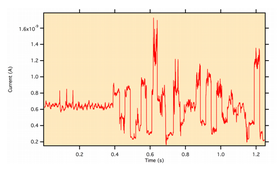


A metal / molecules / metal contacts is allowed to fluctuate (thermal motion)
We record the current and track the jumps related to molecules connexion / deconexion events
The magnitude of these jumps is related to single molecule conductance

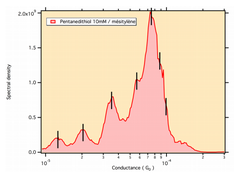


Validation for octanedithiols

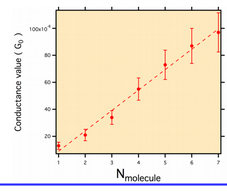
Recording of molecular events



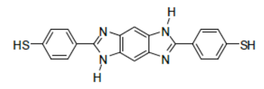
Current histogram



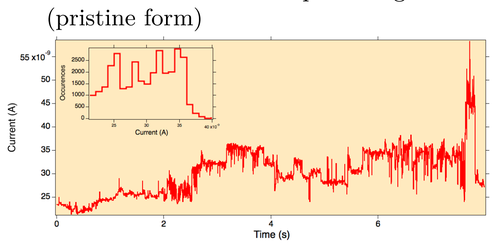
Conductance vs N_{MOL}



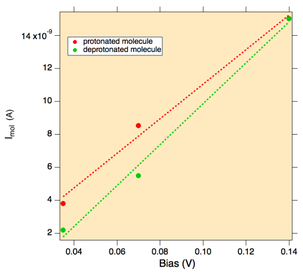
Measurements on



Molecular events & sample histogram (pristine form)



Deprotonated and protonated (Hcl) vs Bias



$G_{PRO} > G_{DEPRO}$
Similar results for ex-situ & in-situ protonation
In agreement with SAMs measurements for molecule B

Reversible conductance switching is measured on self-assembled monolayers on ^{TS}Au surfaces, and is compared to measurements at the single molecule scale
Both approaches give results in quantitative agreement : Conductance of molecule A is lower in protonated form
The result is inverted for molecule B

Results for molecule A are supported by theoritical calculations
Calculations for molecule B are in progress

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