Numerical Investigation of a Molecular Switch Based on Conformational Change, with the Inclusion of Contacts

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Implementing switch functionality at the molecular scale

■ Modulation of transport properties via field effect

As discussed by Damle, Rakshit, Paulsson and Datta [IEEE Trans. on Nanotechnology 1, 145 (2002)] controlling the current through a molecular field effect device poses the same challenges as in the case of nanoscale MOS devices, with the only advantage of a reduced permittivity with respect to that of silicon.

To be effective, a lateral control gate electrode should be separated from the molecule by a distance smaller than the separation between the source and drain electrodes between which the molecule is connected (usually about 1 nm).

■ Modulation of transport properties via conformational changes

Molecules, however, have a further degree of freedom with respect to bulk silicon: their conformation can be changed and this may lead to a significant variation of their transport properties.

We investigate how a transverse electric field can act upon the mutual angular position of molecular fragments and how this affects the energy barrier for electron transport.
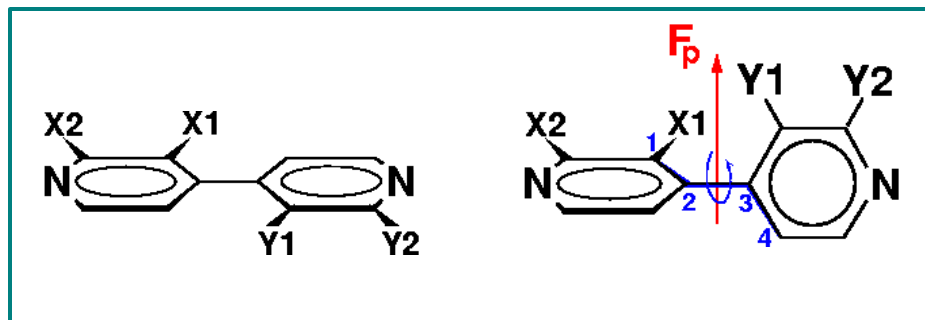
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Model and initial molecular prototypes

MOLECULAR SWITCH FUNCTIONALITY
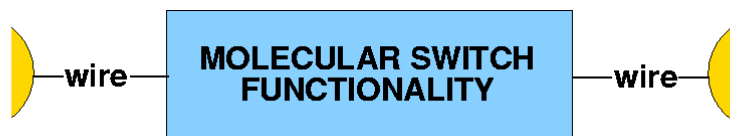
- Longitudinal conduction is controlled as a function of the transverse electric field by the molecular switch included in a longer conductive chain contacted to a pair of metallic electrodes
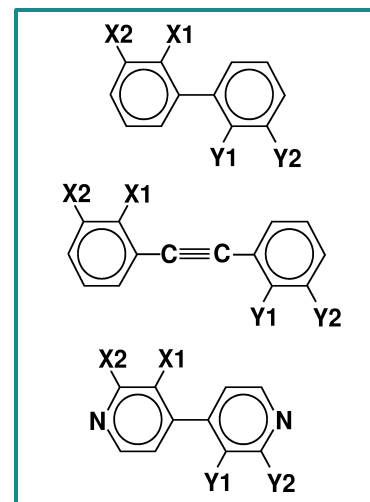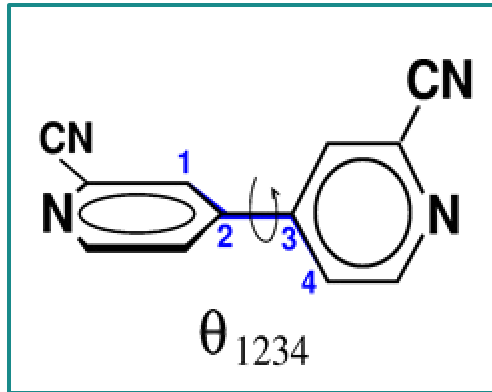
Action of a transverse electric field on a model molecule

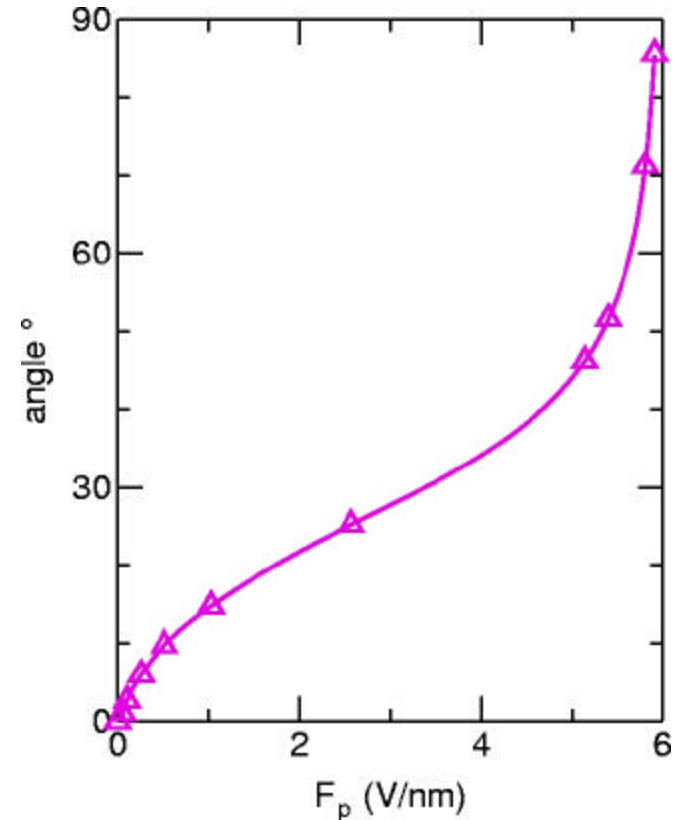- X1, X2, Y1, Y2 electron-acceptor (or donor) groups

Pyridine based molecules

Fp (90) ~ 6 V/nm

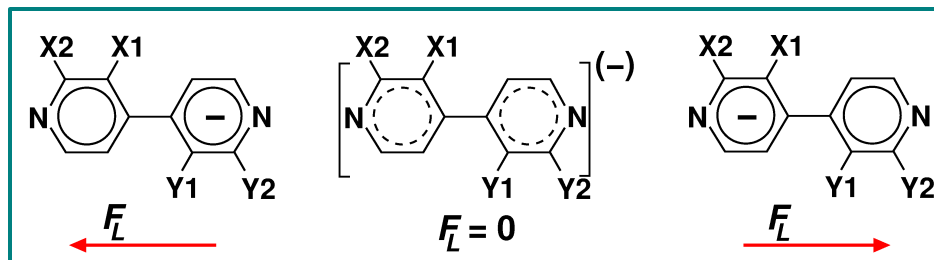exceeds by far the threshold for dielectric breakdown in commonly used materials
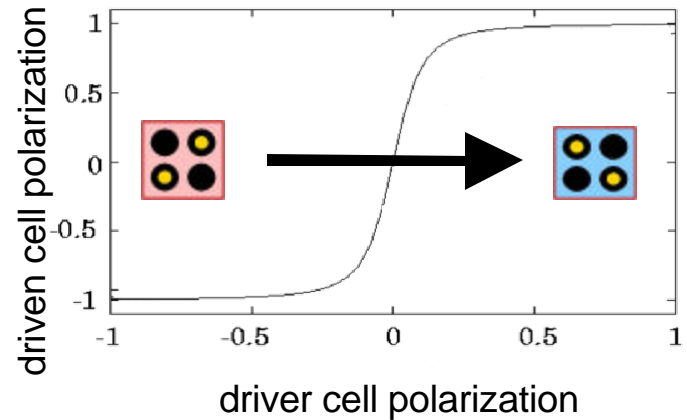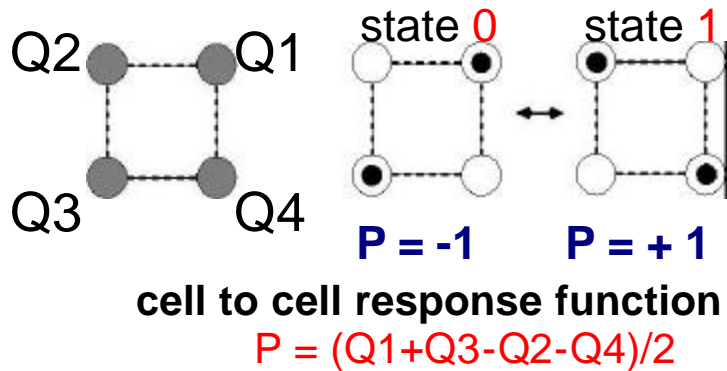
Electron transfer simulation

- **In order to analyze the effect of relative rotation of the molecular fragments, we compute the bistability properties of the molecule, based on the polarization response to a longitudinal electrical field: the molecule is considered to be globally negative, with the presence of an excess electron that moves from one end to the other as a result of the external field.**
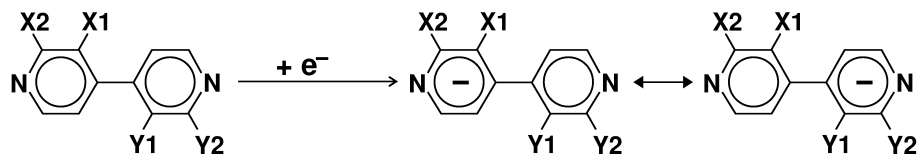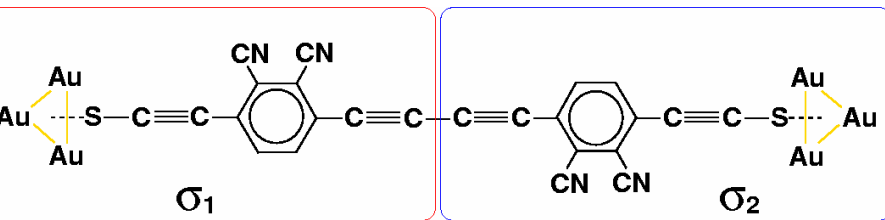

- **The longitudinal bias can be simulated with a spatially constant electric field**

Bistable behavior

Q2 Q1

Q3 Q4

state 0   state 1

P = -1   P = +1

cell to cell response function
P = (Q1+Q3-Q2-Q4)/2

driven cell polarization

driver cell polarization

For a molecule:

σ_1 σ_2

Electron occupancies of the two fragments (σ_1 and σ_2) are computed from the integration of the electron densities (r) over the two regions

Polarization: $$\Delta\rho = \frac{\sum_{\sigma_1}\rho - \sum_{\sigma_2}\rho}{e}$$

We analyze the dependence on the magnitude of the driving charge

Model molecule

SWITCH FUNCTIONALITY
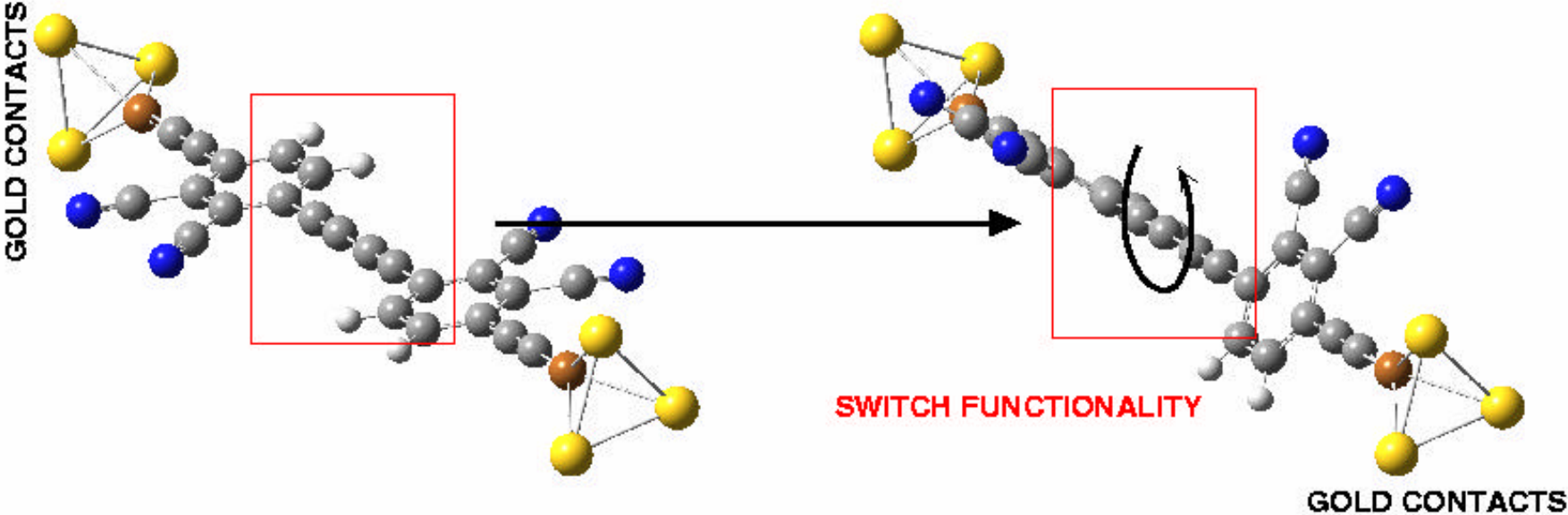
Computational details

- **Geometry optimization of the molecular anion at the DFT (B3LYP) level in the presence of a perpendicular Electric Field FP**

- **Large basis sets for C, H, N and S**

- **Effective core potential for Au**

- **Geometry constraint arise from the presence of the contacts**

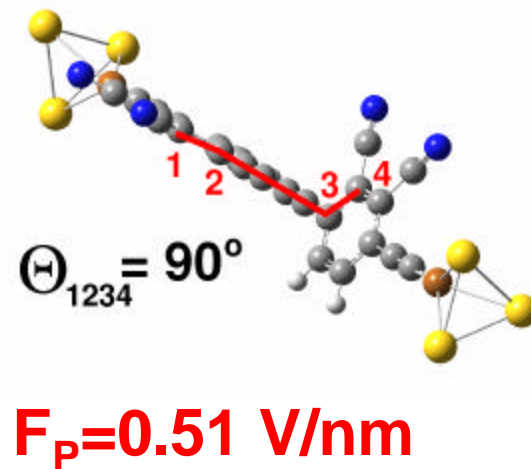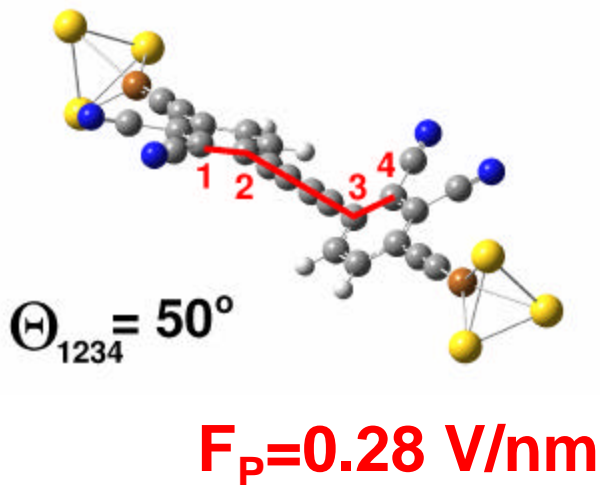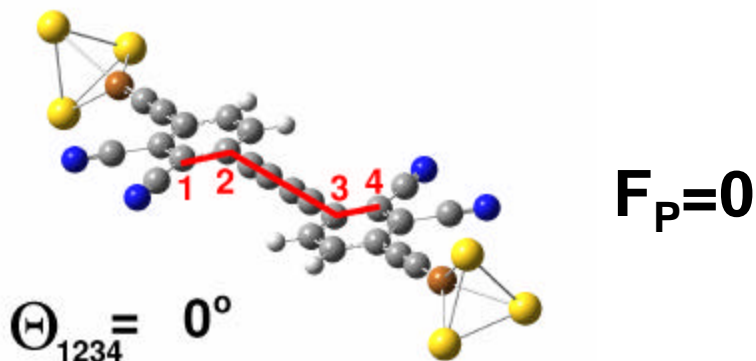- **Mulliken population analysis from Hartree-Fock wave functions**

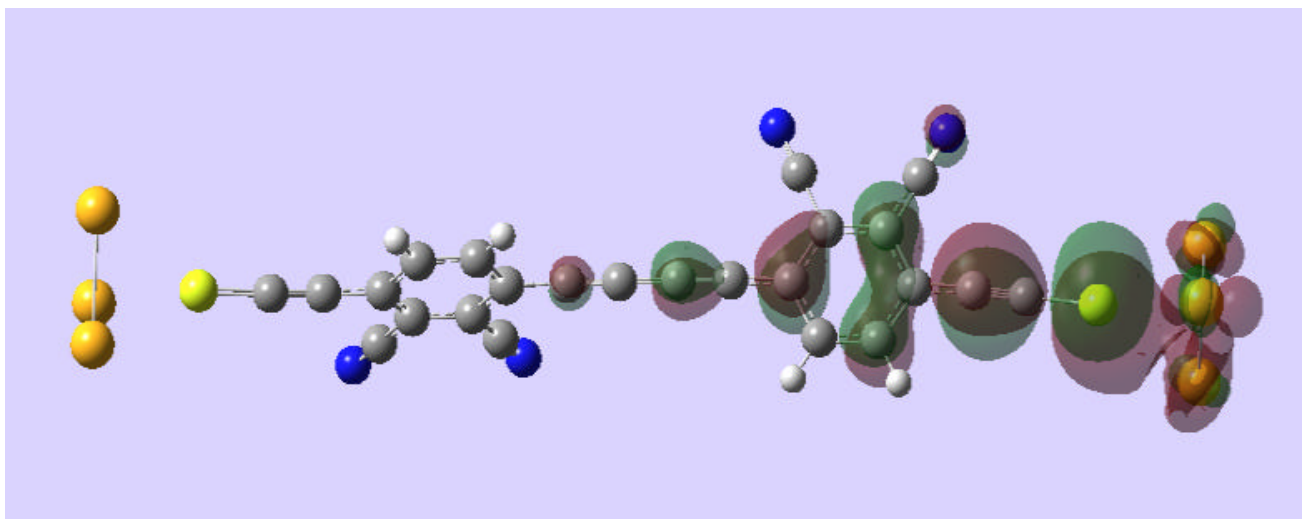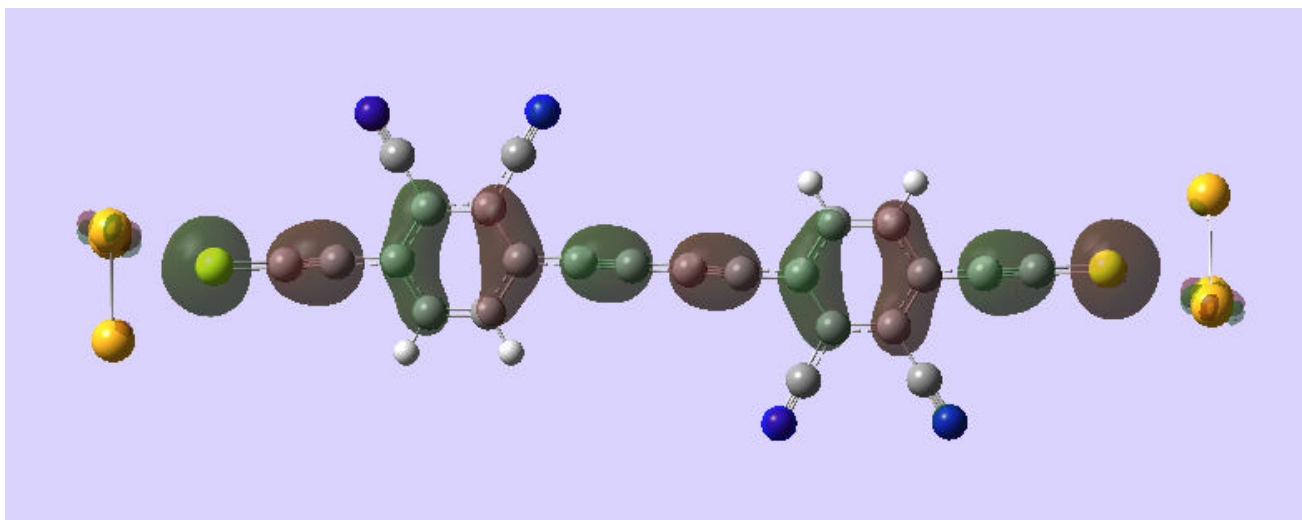# Constrains arising from the contacts

■ **S Hollow on a 3-atom gold cluster**
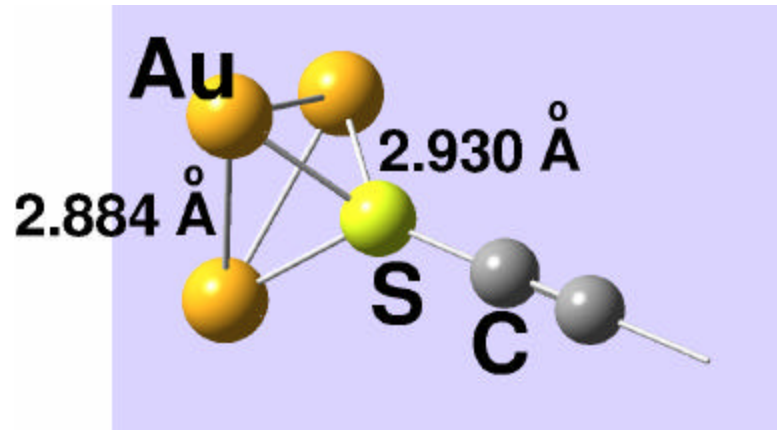
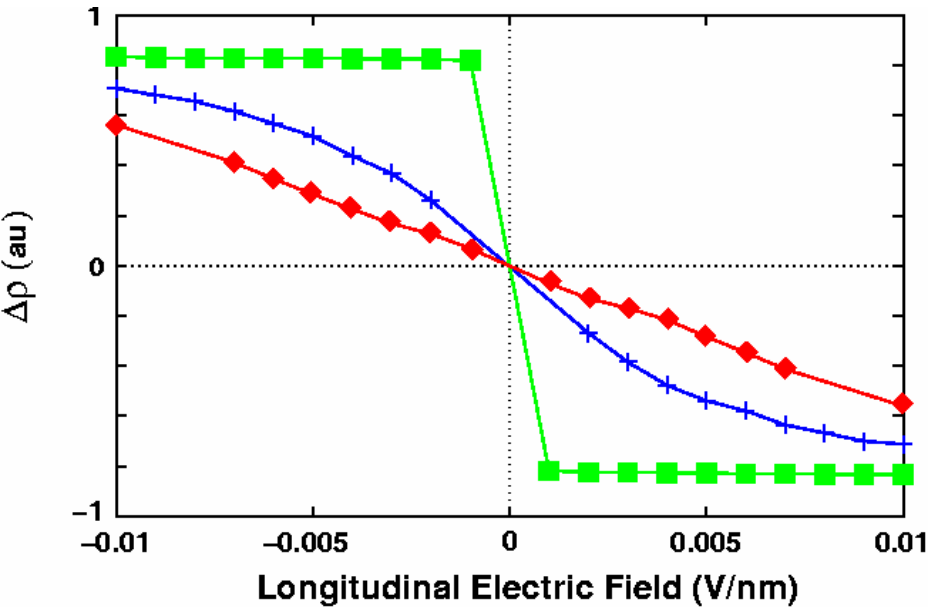■ **Au_3S- units frozen to the values optimized for $F_P=0$**

Effect of the transverse electric field

$F_P=0$

$\Theta_{1234} = 0°$

$\Theta_{1234} = 50°$

$F_P=0.28$ V/nm

$\Theta_{1234} = 90°$

$F_P=0.51$ V/nm

HOMO orbital for planar and orthogonal conformation

Response analysis

F_P=0.00 V/nm φ_I=0°

F_P=0.28 V/nm φ_I=52°

F_P=0.51 V/nm φ_I=89°

Conclusions

- **We have investigated the behavior of a molecular structure based on two aromatic rings, connected to gold contacts, in response to a transverse electric field**

- **Relative rotation of the two rings to an orthogonal configuration is achieved for a transverse field that is large, but in principle achievable in an experiment**

- **The variation of the intramolecular barrier is analyzed by looking at the response of the electron density to a longitudinal electric field**

- **Future work also includes a detailed evaluation of the conductance of the structure as a function of the transverse electric field**