# Numerical investigation of a molecular switch based on conformational change, with the inclusion of contacts

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Although very significant difficulties have so far prevented their usage in practical applications, single-molecule devices are still considered the ultimate step in the scaling-down process of electronic circuits. One of the possible, proposed approaches to molecular-scale electronics consists in replicating the classical architecture based on three-terminal devices, which has so far been so successful with CMOS technology. However, it has been shown that modulation of molecular conductance via a purely electrostatic effect (such as in field-effect transistors) is not viable [P. Damle *et al.* IEEE Trans. on Nanotechnology **1**, 145 (2002)], and that, in order to obtain a reasonable modulation of conductance, either mechanical deformation of otherwise induced conformational changes are necessary.

In this contribution, we present our investigation of this latter approach, focusing on a class of molecules that may allow the implementation of switching functionalities. Switching is obtained by means of the action of a transverse electric field which induces a conformational change, thereby altering the transparency of intramolecular barriers and, as a result, the conduction state of the molecule.

The molecules that we shall discuss are substantially made up of two aromatic rings bridged by an acetylene unit. The two rings have electron acceptor substituents on their opposite sides (Fig. 1) and are contacted on each side with acetylene wires and thiol to gold electrodes, modelled with three-atom clusters (Fig. 2). The electron acceptor groups on the two rings give rise to an opposite dipole moment perpendicular to the inter-ring axis, which can be exploited for the purpose of applying a torque between the two rings by means of a transverse electric field.

The relative rotation of the rings leads to a variation in the conjugation of the current carrying orbitals, altering the potential barrier between the two rings. This results in a variation of electron localization on the two sides of the barrier: as the barrier is raised, electrons are more strongly localized on the two sides, and transport across the molecule is suppressed. Without performing a full conductance calculation, we can estimate the amount of electron localization (and therefore the corresponding reduction in barrier transparency for transport), by computing the response of molecular polarization to a longitudinal electric field, assuming that the molecule is instantaneously charged with one excess electron.

After geometry optimization at the DFT (density functional theory) level performed in the absence of a longitudinal electric field, calculations have been performed with the Complete Active Space Multi Configuration Self Consistent Field (CASSCF) approach, including 12 electrons in the active space.

An example of the difference in the Mulliken population of the two moieties as a function of the longitudinal electric field, obtained by means of CAS calculations at different values of the transverse field is shown in Fig. 3 for a simplified case without gold contacts. It is apparent that, even for this relatively optimized structure, the field required for switching is extremely large, of the order of 1 V/nm, which represents a serious drawback. However, we have observed that, increasing the length of the strucure and tuning the choice of the substituents, there is some room for further reduction of such a field, as we discuss in our paper.
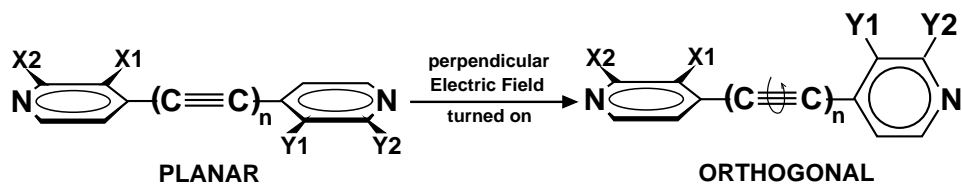
Fig. 1: Switching functionality: the action of the perpendicular field forces the rings into an orthogonal conformation.
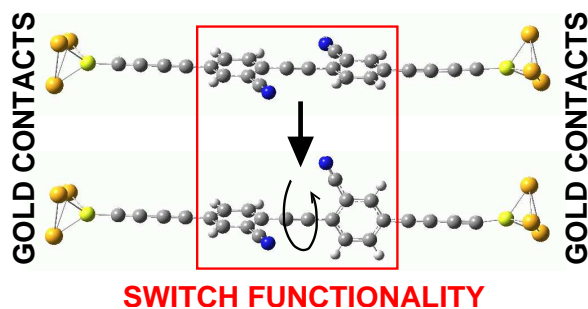


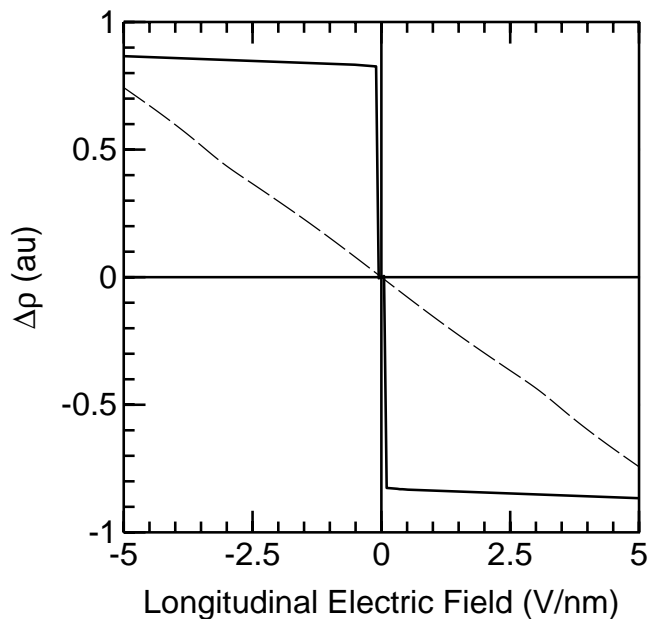Fig. 2: Molecular structure with gold contacts.



Fig. 3: Response of the bridged anion (Fig. 1) to the longitudinal electric field for the planar (dashed line) and the orthogonal conformation (continuos line).