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A Programmable Molecular Diode Driven by Charge-Induced Conformational Changes

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Molecules several orders of magnitude smaller than semiconductor-based devices can complement, enhance, or replace them.¹ In a possible scenario for molecular electronics, molecules are interconnected to metal clusters,² which partially isolate the molecules preserving their electrical properties. Because of their small size, molecules cannot be individually addressed in a molecular circuit. Rather, molecules and metal clusters may be self-assembled on a chip, forming randomly interconnected networks that can only be externally addressed; this arrangement is known as the nanocell,² and it needs to be programmed to perform as a functional unit. The lack of addressability of the individual components must be compensated by the ability of programming, thus requiring molecules to have highly nonlinear current–voltage (I – V) characteristics, which lead to a multivalued response of a molecular circuit when a bias voltage is applied.³ For other molecular electronics scenarios the reader is referred to the corresponding literature.⁴

Among others, two main mechanisms for switching have been identified in molecules, driven by conformational changes and by charging.⁵ In this work, we identify a two-pyridine-substituted molecule, 3-nitro-2-(3'-nitro-2'-ethynylpyridine)-5-pyridinethiol (DNPD), showing charge-induced relative rotation of the two rings (Figure 1).

We analyze the molecule using our combined Density Functional–Green Function approach.⁶ The molecule and its ions are extended with two Au atoms at each end, resembling some experiments,⁷ and are fully optimized using Gaussian 98⁸ at the B3PW91/LANL2DZ level of theory.⁹ The Au contacts are also fully optimized using a procedure specialized for periodic systems with the crystalline structure of Au bulk, using CRYSTAL 98¹⁰ with the PW91/SBKJC-VDZ level of theory.¹¹ Both methods use Gaussian basis sets, and they yield similar results when swapped. Several initial conformations with coplanar and rotated rings are tested for the neutral and anions; in all cases, the final geometry is perpendicular for the neutral and coplanar for the anions. For the neutral, the dihedral (the angle between the two pyridine rings, with 0° corresponding to the cis conformation of the two-pyridinic N) is 82°, and for the anion and dianion the dihedrals are 180°. The geometries of the three charge states correspond to minimum energy conformations since all the eigenvalues of their Hessian matrixes are positive. The anion and dianion are stable with respect to the neutral and anion and yield adiabatic electron affinities of 3.35 and 0.08 eV, respectively. The strong conformational difference between the neutral and the ions is due to the strong resonance of the neutral rings that induces a very strong sp^2 character in the pyridinic N, leading to repulsion between its lone electron pairs and those of the O on the opposite ring, yielding a perpendicular conformation. However, for the anions, the resonance is weakened by the presence of the extra electrons, which adds a stronger sp^3 character to the pyridinic N, leading to its rehybridization, weakening the repulsion between lone pairs, and thus allowing the coplanar conformation.

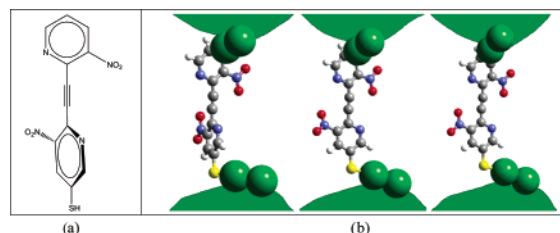


Figure 1. (a) Molecular structure of DNPD. (b) Attached to Au atoms and extended by Au continua: neutral (left), anion (center), and dianion (right). Au (green), C (gray), H (white), N (blue), O (red), and S (yellow).

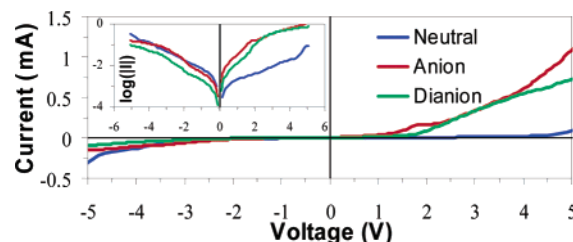


Figure 2. I – V characteristics for the DNPD: neutral (blue), anion (red), and dianion (green). The inset shows $\log(|I|)$ vs V .

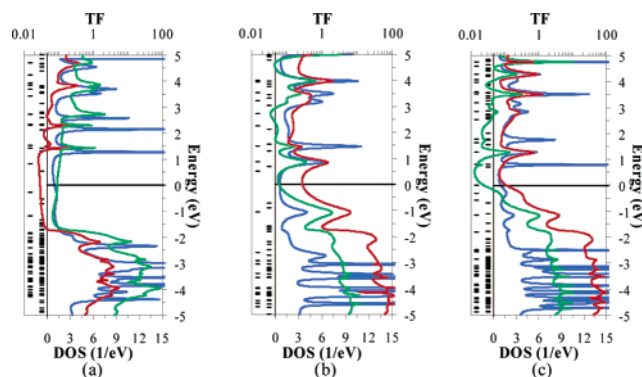


Figure 3. DOS (blue) and TF for positive (red) and negative (green) bias for DNPD: (a) neutral, (b) anion, and (c) dianion. The Fermi level (black) is set to zero. The two sets of bars on the left of each plot represent the position of the MOs with (left) and without (right) the effect of contacts.

of the two rings. The resonance is weaker on the top ring due to changes in the hybridization of the top C, which feels the presence of the Au atoms. Notice that the coplanar conformation is always the minimum of energy one when phenyl rings are present;¹² thus, the functionality foreseen for this molecule is not possible on phenyl-based molecules.

Figure 2 shows I – V characteristics for the three charge states, and Figure 3 shows the density of states (DOS) and transmission function (TF) for both positive and negative bias. The two sets of bars on the left are the energy levels in the extended molecule (left) and the energy levels in the molecule embedded in the contacts (right).

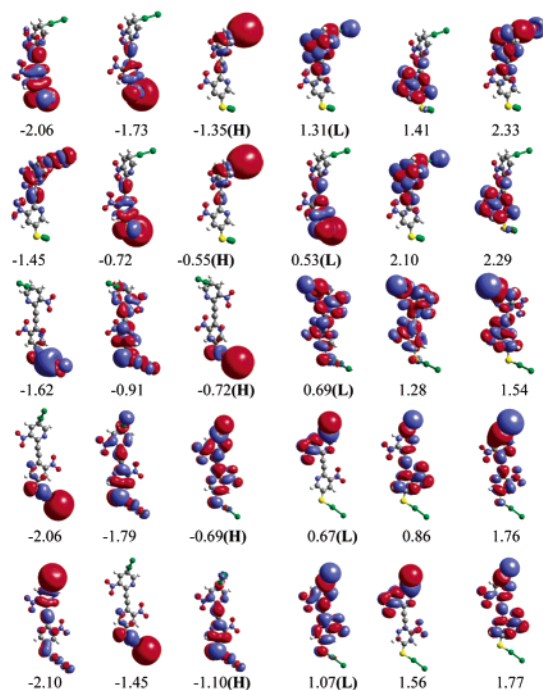


Figure 4. MOs and their relative energies (eV) with respect to the Fermi level for DNNDP. First and second row correspond to the neutral α and β , respectively, third row to the anion, and the last two rows to the dianion α and β , respectively. The HOMO and LUMO are indicated by H and L, respectively.

For positive bias (the top end of the molecule is positive with respect to the bottom S-ended side), the neutral state shows lower conductance than the anion (Figure 2) due to the misalignment between its rings. The dianion shows an intermediate conductance between the neutral and anion, except from 2.5 to 4 V where both charged species conduct similarly. For negative bias, the conduction is weak for all charge states. The anion and dianion have clear rectifying characteristics which are due to the asymmetric coupling to the contacts, as also found on phenylethylene oligomers (PEO).¹² However, the neutral also shows diode characteristics but with reverse polarities than the anions, as shown by the inset of Figure 2. The current ratio at positive and negative bias shows a maximum of 7 at 3.95 V, 14 at 1.75 V, and 19 at 2.52 V for neutral, anion, and dianion, respectively. This molecule is a controlled diode whose connectivity can be reverted by the state of charge. At the high-bias operation, the neutral can be considered an OFF diode while the anion is an ON diode, i.e., resembling diodes in field programmable gate arrays where diodes are burned (OFF) or left there (ON) to design logic. ON–OFF ratios (anion to neutral) are 15, 39, and 12 for 1, 3, and 5 V, respectively. Both high and low bias operation of this new device provides versatile characteristics for the new paradigm of molecular electronics with no counterpart in present microelectronics devices. These interesting features can be tracked down from the TF shown in Figure 3 where the TF at the Fermi level (E_F) for the neutral is lower than that of the anions. The anion shows the largest TF, thus having larger current than the dianion at low bias.

Figure 4 shows a few molecular orbitals (MO) near the HOMO and LUMO energies. The perpendicular rings in the neutral localize its MOs in one of the rings, leaving no clear path for electron conduction. Anion MOs are fully delocalized along the molecule

and the Au atoms, except for the HOMO and HOMO–2. Similar characteristics are observed for the dianion MOs.

The shape and energies of the MOs change and shift, respectively, due to applied bias; our calculations explicitly consider these effects by calculating the electronic structure of the molecule under the whole range of applied bias voltages.

The DNNDP shows rectifying behavior with a charge-induced controllable switching. It can be used as a memory by inducing its charging with an external field able to rotate one ring by interacting with its local dipole. Alternatively, DNNDP can be used as a nano-actuator externally controlling the rotation by charging the molecule with a bias voltage.

Temperature-induced rotation can affect performance; however, the rotational barrier is almost 4 kcal/mol, 4 times larger than the typical barrier for the popular PEOs. Nevertheless, the finding of this molecular device is a profound advance. The coplanar conformation is always the minimum energy when phenyl rings are present, and thus for the first time we have found a complementary PEO system.

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