Harnessing electric-field driven tautomerizations in porphyrins for electric devices

Yenni P. Ortiz, Arnau Cortés Llamas, Jordi Ribas and Stefan Bromley

iqtc

UNIVERSITAT DE BARCELONA

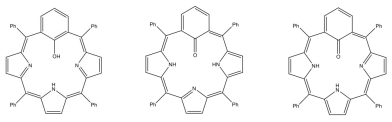
Introduction

Free-metal porphyrins offer a versatile platform in quantum transport research for exploring electron flow at the molecular scale . In his study we aim to design a coherent way to use these molecules in molecular wires and transistors.

Objectives

- Apply Electric field to our systems for a tautomeric exchange.
- Study the quantum electron transport properties for each tautomer.

System



(a) (b) (c)

Figure 1. Image with the different used porphyrin's tautomers for the study. (a)Tautomer 1, (b) tautomer 2, and (c) tautomer 3.

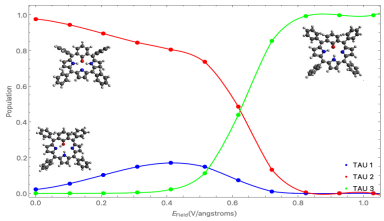
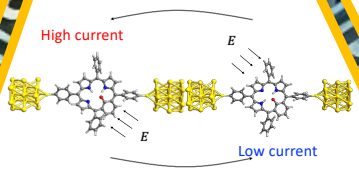


Figure 2. Graphic representing the canonic ensemble populations for each tautomer at every E-field step. The blue line indicates the population for Tautomer one, while the green represents Tautomer three and the red line represents Tautomer two.

Schematic Representation of Device Structure



The diagram illustrates the reversible tautomerization of porphyrin, highlighting the transition between Tautomer 2 and Tautomer 3 forms, both induced by an in-plane electric field. The electric field is applied parallel to the molecular plane, with arrows indicating its direction in each case. The schematic also emphasizes the symmetry of the system and how the structural reorganization can be reversed when the field is altered.

Methods

Electric-field control of porphyrin tautomerization

Density functional theory (DFT) was used to investigate the activation of a tautomer exchange under an electric field (E-field) as shown in Figure 1. By optimizing E-field values in Gaussian 16 [1] up to 1 V/Å, we analyzed tautomer populations within the canonical ensemble. The PBE0 functional with Grimmer dispersion and a 6-311G(d,p) basis set were used for these calculations.

Quantum electron transport calculations

The current calculations combine Kohn-Sham density functional theory (DFT – PBE1PBE/6-311G(d,p)) for the electronic structure of the molecular junction with the nonequilibrium Green's function (NEGF) method [2, 3, 4] for electron transport. On the basis LANL2DZ, the current flow is calculated as implemented in the ARTAIOS software [5].

- Transmission functions were calculated through the Green's function,

$$T = 4\mathrm{Tr}\left(\mathrm{Im}\left(\Sigma_S\right) G \mathrm{Im}\left(\Sigma_D\right) G^{\dagger}\right)$$

$$G(E) = (E\,S - H - \Sigma_S - \Sigma_D)^{-1}$$

- Current

$$I(V) = \frac{2e}{h}\int_{E_F-\frac{eV}{2}}^{E_F+\frac{eV}{2}} dE\; T(E,V)$$

Two-states switch

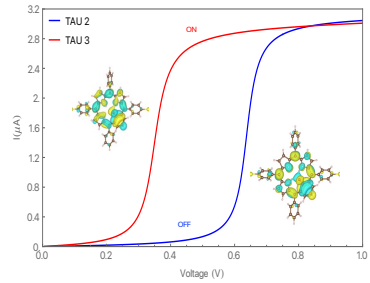


Figure 3. (a) Calculated current in porphyrin's tautomer 2 (blue curve) and 3 (red curve).

Results

Tautomerization

Tautomers 2 and 3 were identified as the most stable. Applying an E-field in the Y direction caused no molecular deformation, with population exchange observed at 0.7 V/Å. This tautomeric exchange may alter conjugation patterns, potentially impacting conductivity.

Electron Transport Study and the Proposal for a Molecular Switch

Here we propose a switch made of tautomerizable free metal porphyrin conductance controlled by an external electric field applied.

Multi-state switches

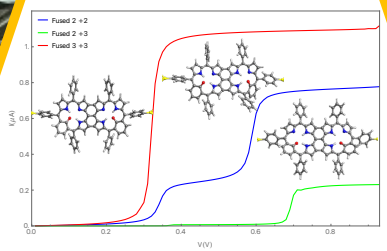
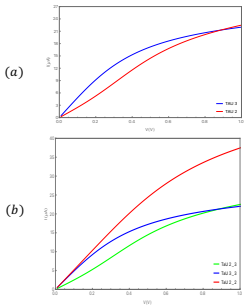


Figure 4. Calculated current in porphyrin's tautomer 2 fused with 2 (green line), 2 fused with 3 (black line) and 3 fused with 3 (orange line).

Molecular wire



(a)

(b)

Figure 5. Calculated current in case II, (a) single cases. porphyrin's tautomer 2 (red curve) and 3 (blue curve). (b) Fused tautomers.

Conclusions

Our calculations have demonstrated the potential of electric-field driven tautomerizations in asymmetric porphyrins as a new mechanism for electrical single-molecule switches.

References

[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, et al., Gaussian, Inc. Wallingford CT, 2016.
[2] Supriyo Datta, Nanoscale device modeling: the Green's function method. Superlattices and Microstructures, 28, 4 (2000).
[3] Camsari, K.Y., Chowdhury, S., Datta, S. The Nonequilibrium Green Function (NEGF) Method. In: Rudan, M., Brunetti, R., Reggiani, S., Springer Handbook of Semiconductor Devices
[4] Gao, F., Menchón, R.E., Garcia-Lekue, A., Brandbyge, M. Tunable spin and conductance in porphyrin-graphene nanoribbon hybrids. Commun Phys 6, 115 (2023).
[5] M. Deffner, L. Groß, T. Steenbock, B. A. Voigt, G. C. Solomon, and C. Herrmann, ARTAIOS, a code for postprocessing quantum chemical electronic structure calculations, https://www.chemie.uni-hamburg.de/institute/ac/arbeitsgruppen/herrmann/software/artaios.html

Financiado por la Unión Europea NextGenerationEU

Ayuda PRE2022-101336 financiada por MICIU/AEI /10.13039/501100011033 y por FSE invierte en tu futuro.