Design of an azo-based molecular switch controlled by light

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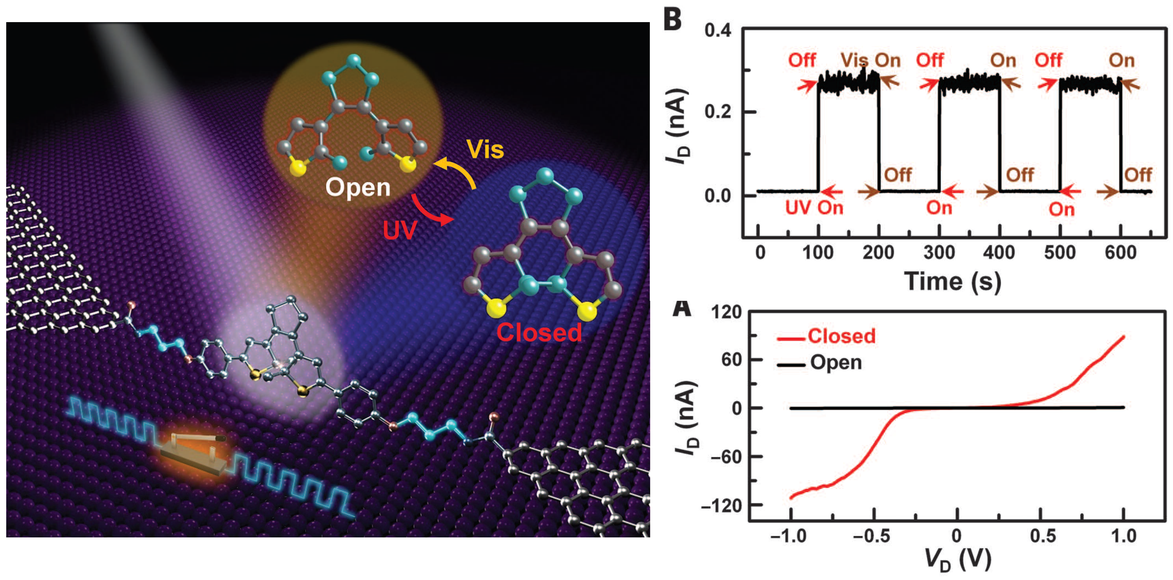
Introduction

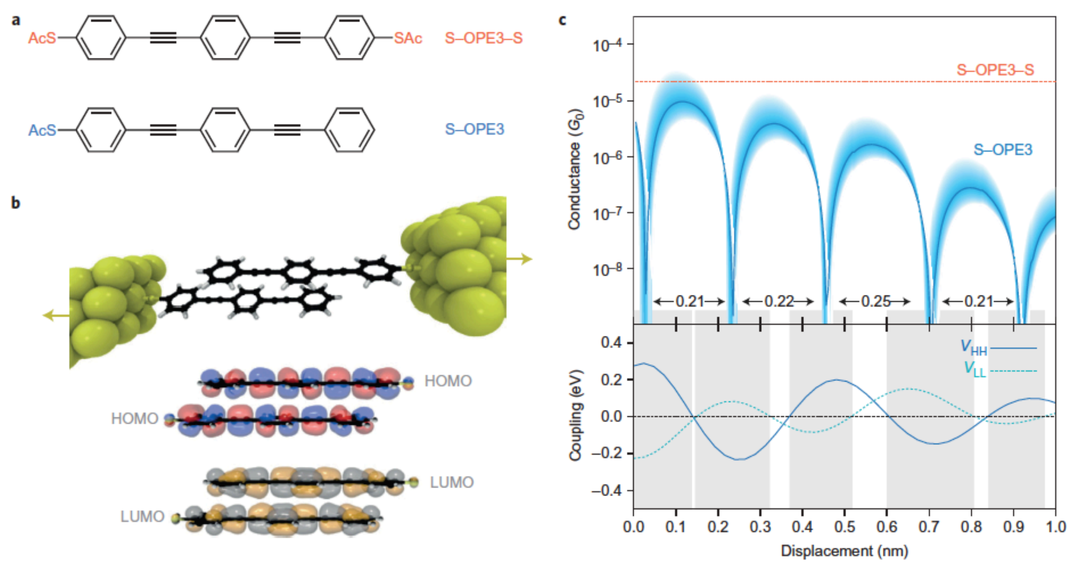
One of the greatest challenges of nanotechnology is the design of molecular devices that could be integrated in more complex systems. Some working switches controlled by light at very low temperature have been reported. In the present work we have designed a light controlled molecular switch at room temperature using π-stacked dimers. For this purpose, 4-(phenyldiazenyl)benzenethiol is a promising molecule according to our theoretical calculations.

Light control



C. Jia, *et al. Science.* **2016**, *352*, 1443-1445

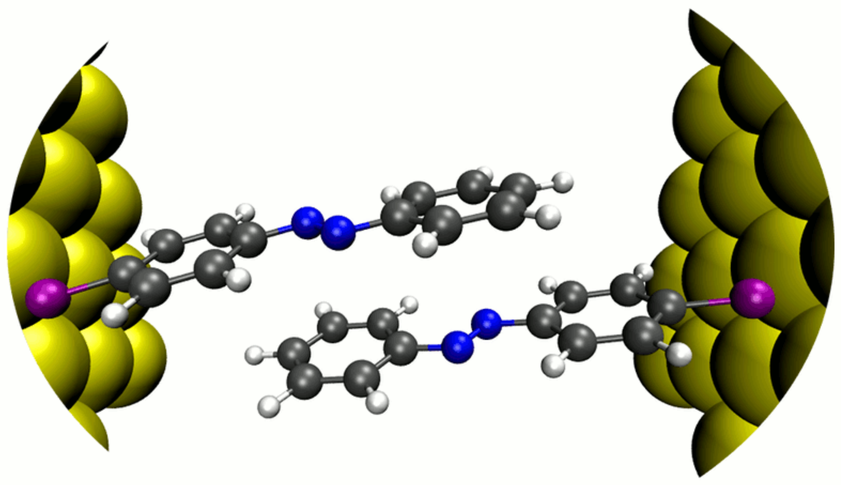
π-stacking



R. Frisenda, *et al. Nat. Chem.* **2016**, *8*, 1099-1104

Merging ideas: A new switch

ON

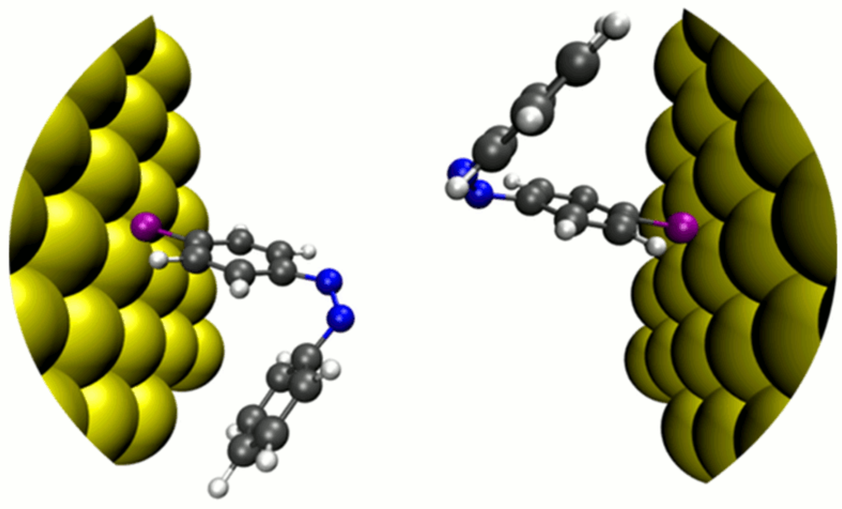


***trans* N=N**

UV
310 - 350 nm

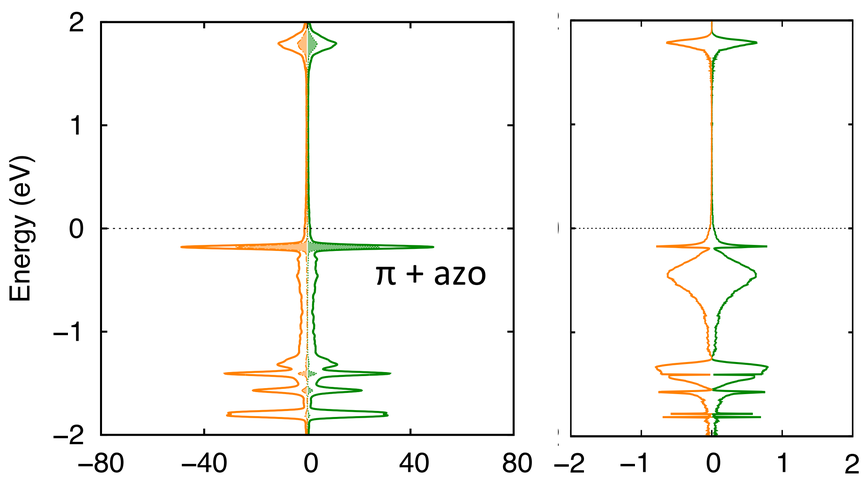
Visible
450 nm , **Δ**

OFF



***cis* N=N**

(E)-4-(phenyldiazenyl)benzenethiol



DFT: PBE, DZP, corepseudopotential
Transport properties: EGF

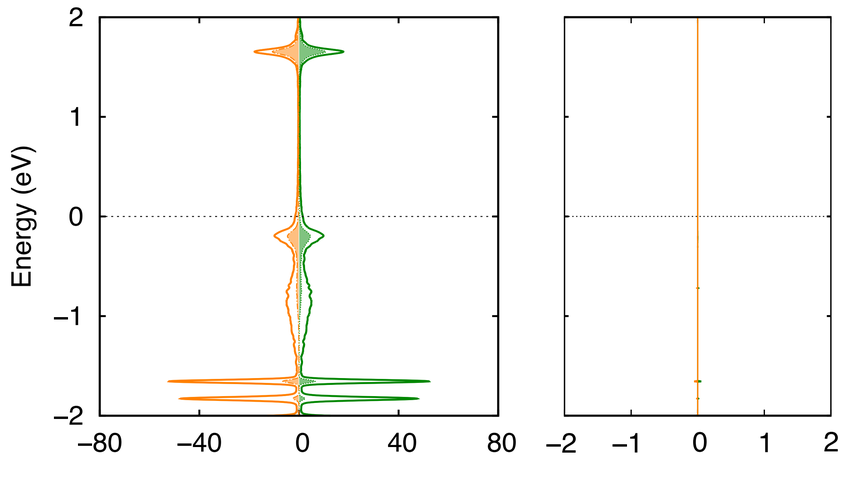
-SH anchoring

$G_{ON} = 7.2 \cdot 10^{-2}\ G_0$

$G_{OFF} = 3.6 \cdot 10^{-5}\ G_0$

ON/OFF = 10^3

(Z)-4-(phenyldiazenyl)benzenethiol



Avoiding –SH polymerisation

-SCH_3 anchoring

$G_{ON} = 1.8 \cdot 10^{-4}\ G_0$

$G_{OFF} = 6.8 \cdot 10^{-8}\ G_0$

ON/OFF = 10^3

-NO_2 anchoring

$G_{ON} = 7.4 \cdot 10^{-5}\ G_0$

$G_{OFF} = 1.0 \cdot 10^{-8}\ G_0$

ON/OFF = 10^4

Conclusions

- Abrupt opening of the circuit in the *cis* conformation leads to very high ON/OFF ratios and a strictly increasing ratio with voltage.
- The system is suitable to work at room temperature.
- –SH anchoring group offers a large conductance but may polimerise. –SCH3 and –NO2 anchoring groups solve the problem with the same ON/OFF ratio and good conductance values.
- Length and width of the aromatic system can be easily modified to overcome possible experimental problems.