Organometallic optoelectronically active magnetic molecules for logic and memory

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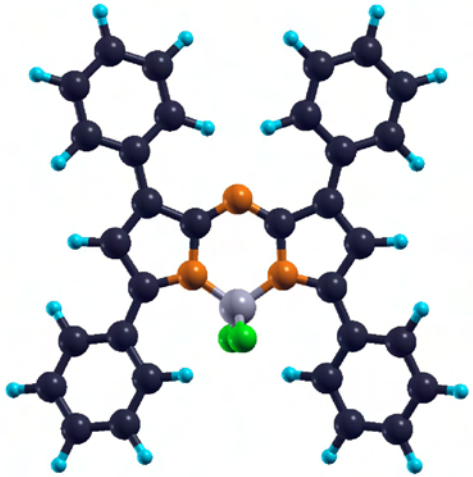
Outline

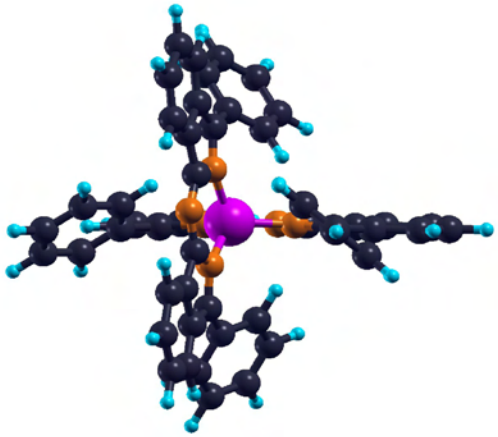
- Introduction
- Results: interaction with substrate
- Results: interaction with electric field
- Applications: logic and memory
- Conclusions, outlook and acknowledgments

Introduction

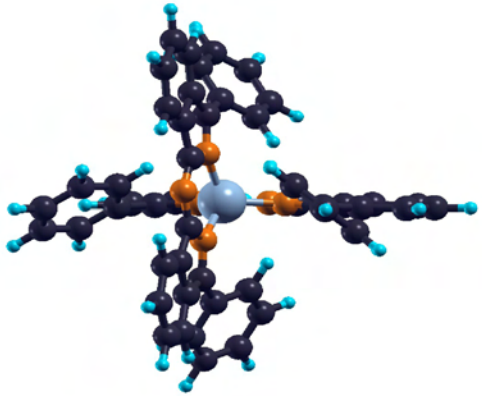
Aza-bodipy molecules



B central atom

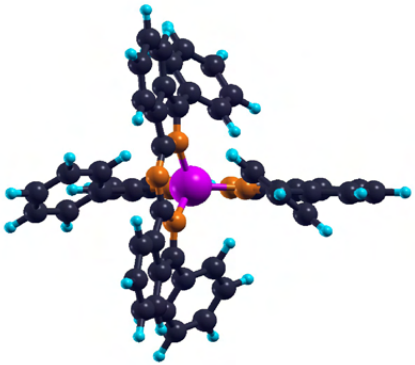


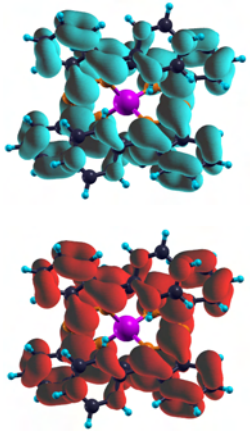
Zn central atom



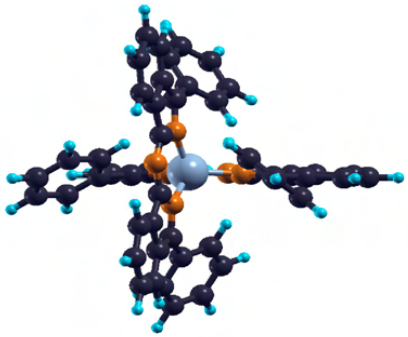
Co central atom

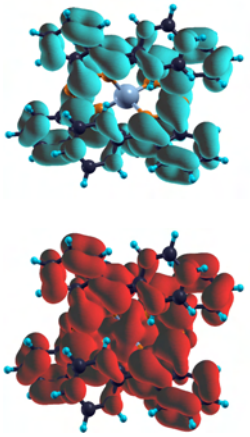
- Aza-bodipy molecule is infra-red absorber
- Used as electron donor in organic solar cells
- STM investigation of interaction with Au(111) published in:
  J. Meyer, A. Wadewitz, Lokamani, C. Toher, R. Gresser, K. Leo, M. Riede, F. Moresco, G. Cuniberti, Phys. Chem. Chem. Phys. **13**, 14421 (2011).



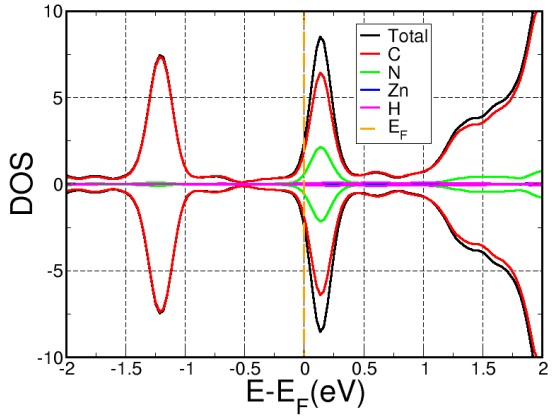


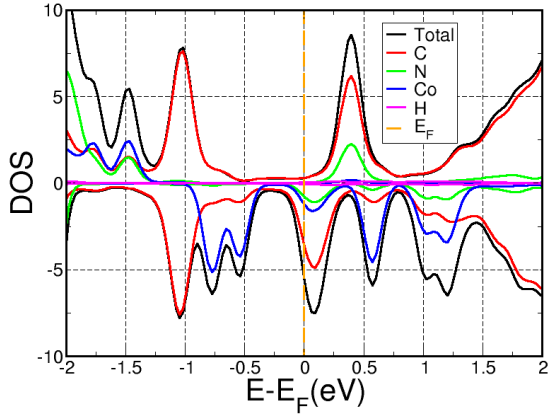
Zn central atom



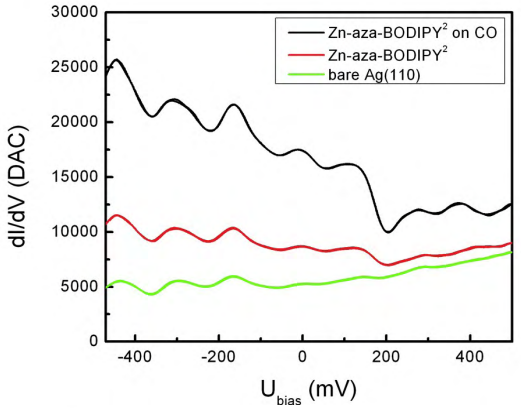


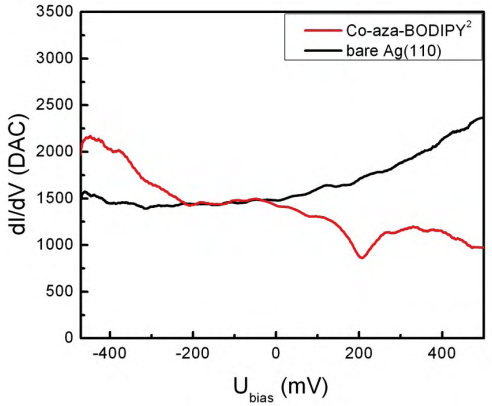
Co central atom





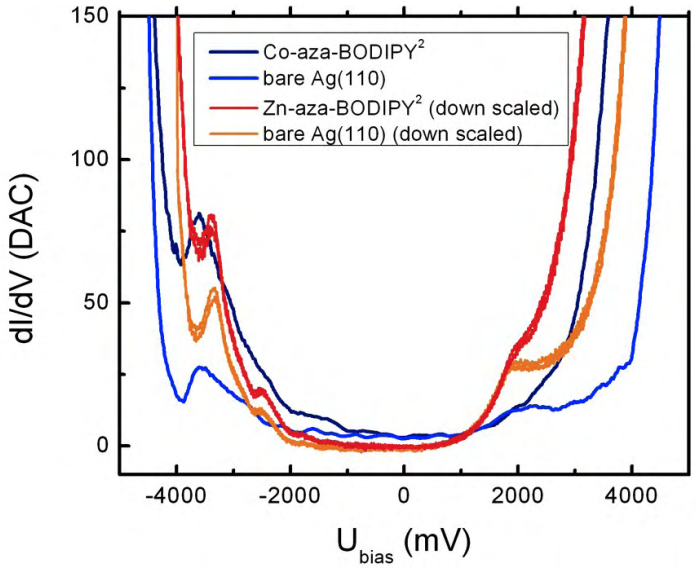
DOS: DFT



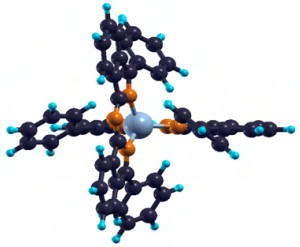


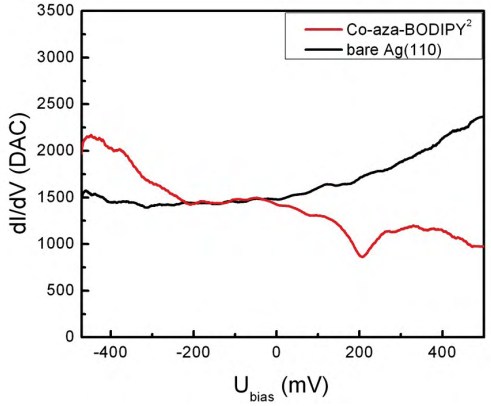
dI/dV: STM

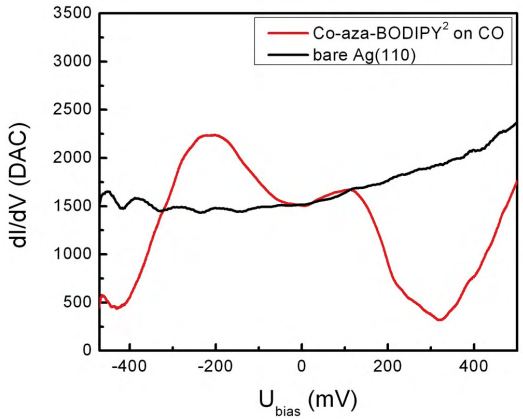
STM dI/dV spectra



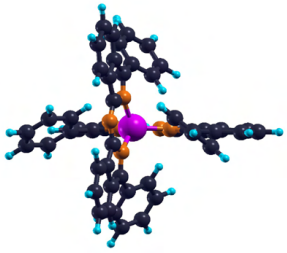
Co central atom

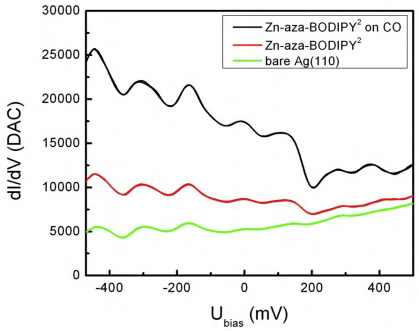






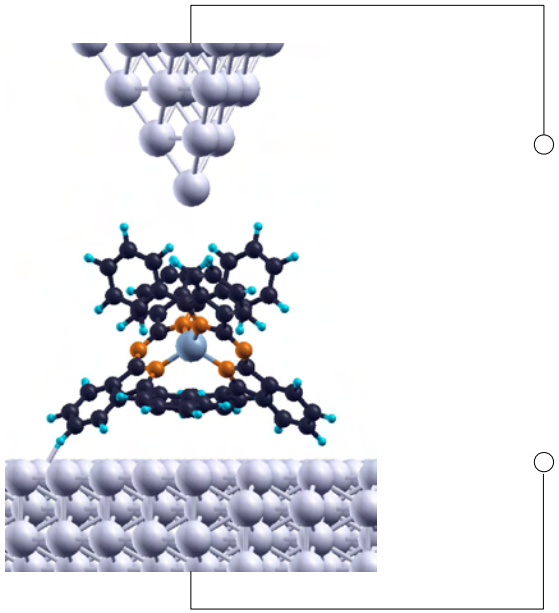
Zn central atom

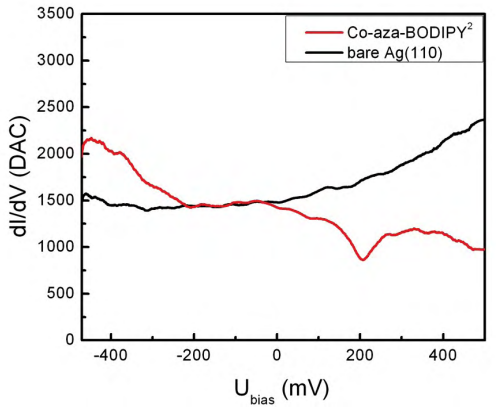


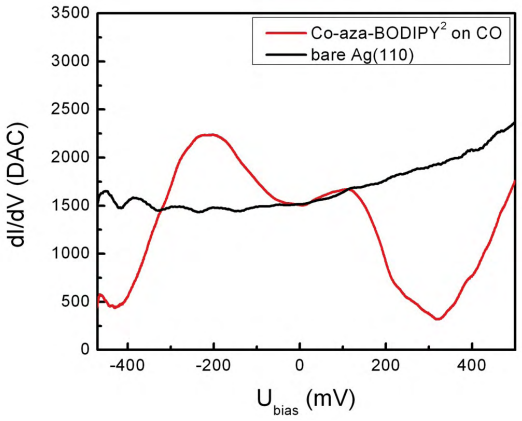


- With Co central atom, two different spectra are observed
- Molecule appears to switch between two different conductance states when bias is applied

Molecular magnetic switch



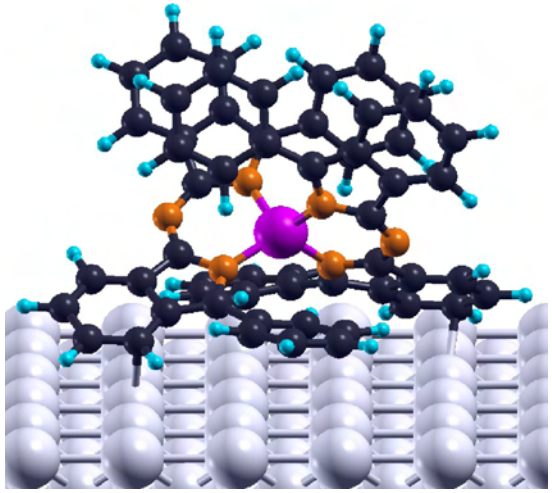


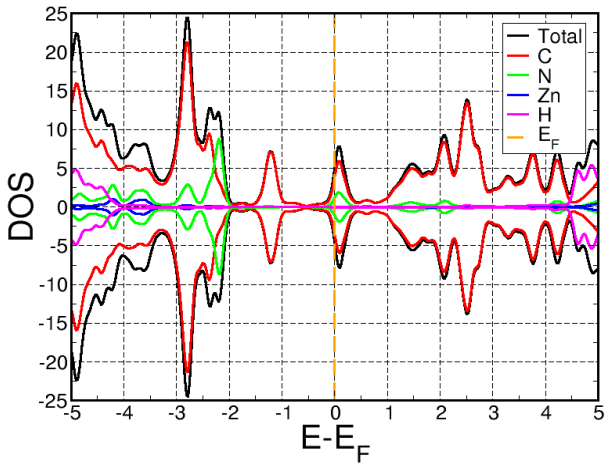


- Applying bias changes electronic structure and conductance
- Applications in logic and memory
- First need to understand physical mechanism responsible for switching

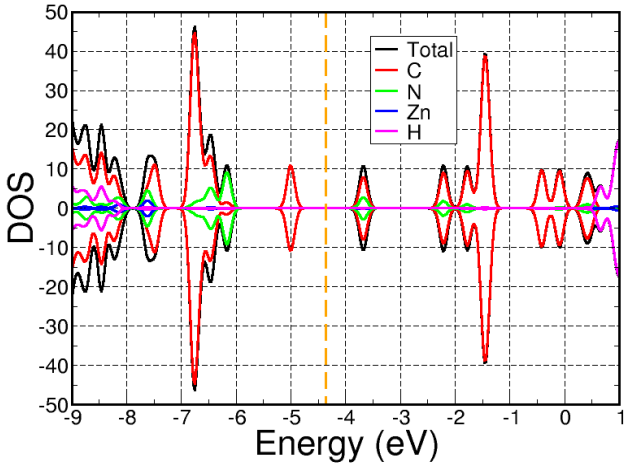
Results:
Interaction with substrate

Interaction with substrate





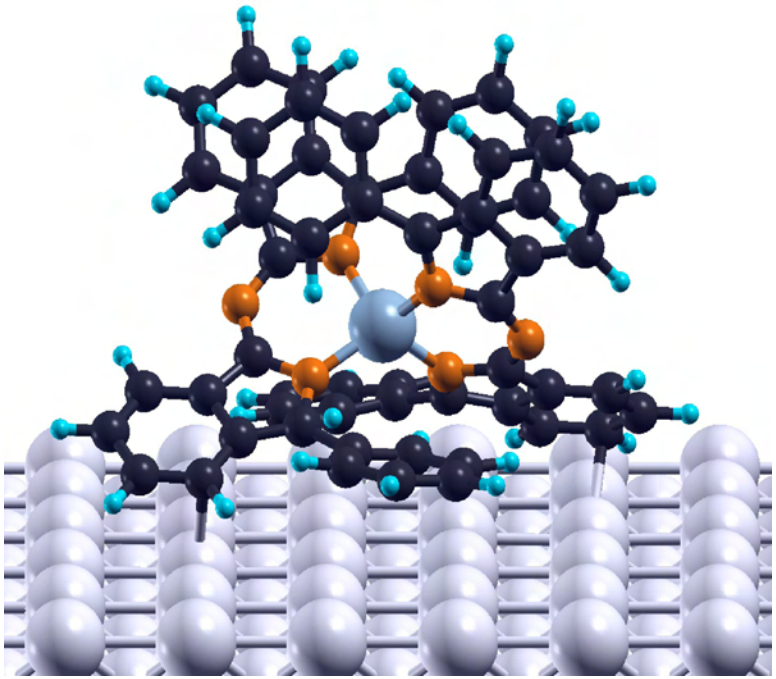
Molecule on substrate

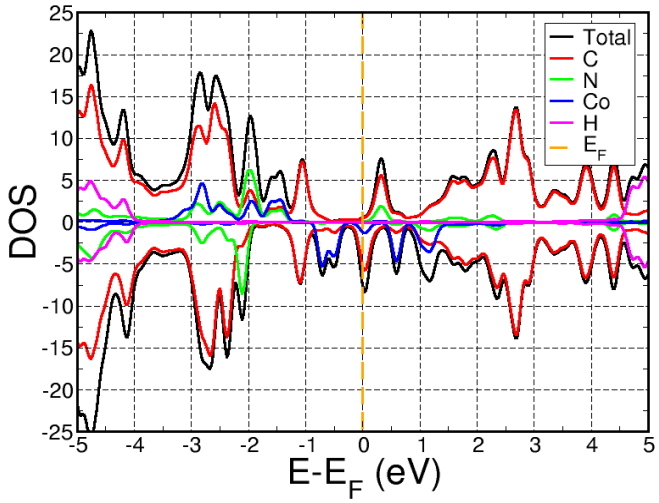


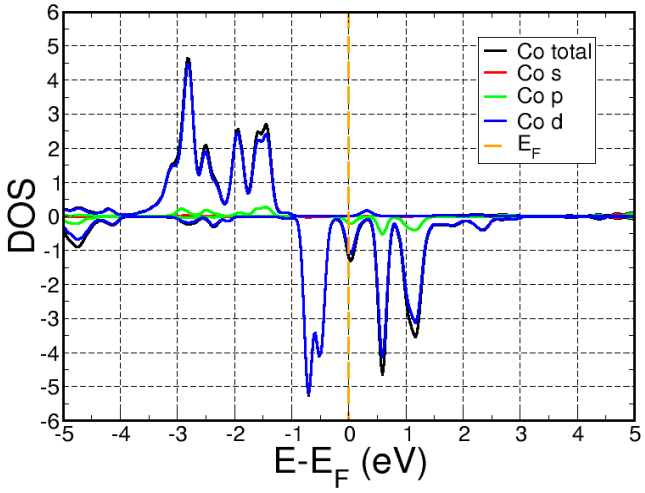
Gas phase molecule

- Molecule on Ag(110)
- DOS similar to gas phase, charge transfer is small
- Interaction with this substrate is relatively weak

Interaction with substrate

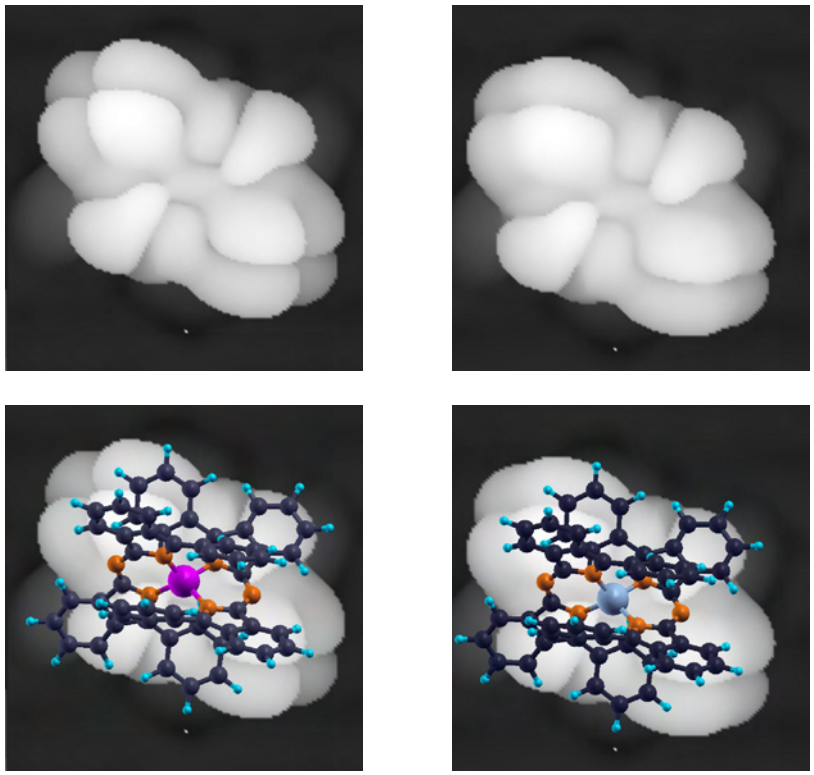






- Molecule on Ag(110)
- DOS similar to gas phase
- Spin-polarization preserved

STM images



Zn central atom Co central atom

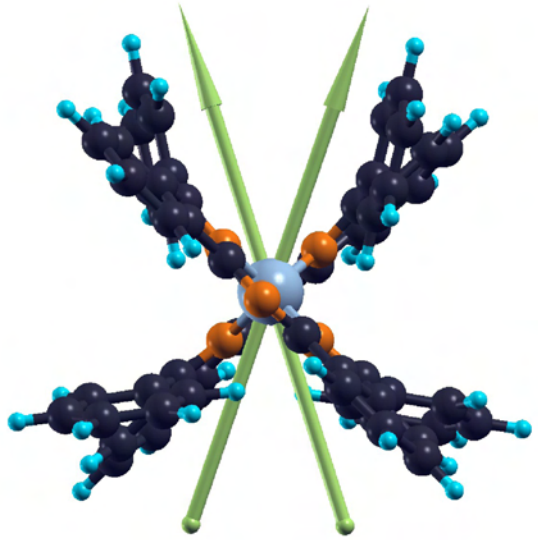
Simulated images

Experimental STM images

- Both experimental and simulated images relatively featureless
- Difficult to image in STM due to 3D geometry of molecule

Results:
Interaction with electric field

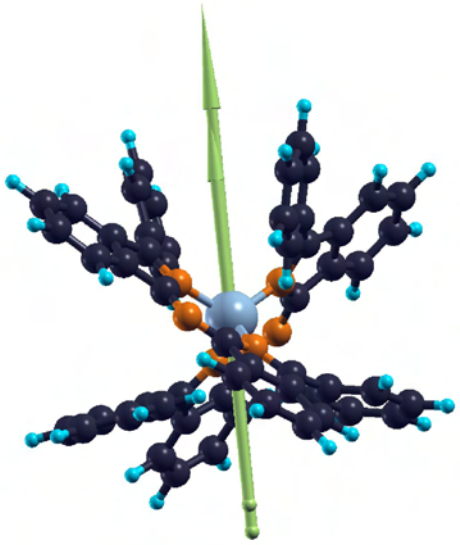
Electrostatic spin cross-over effect



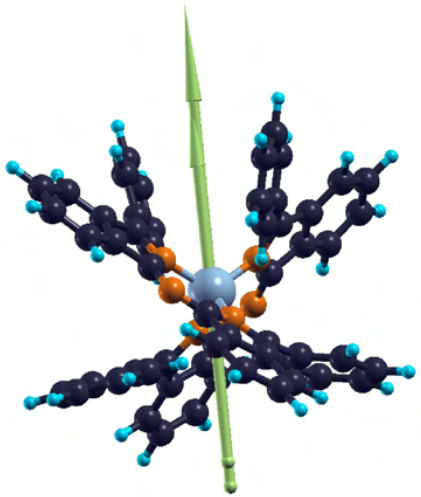
- Different spin configurations have different electric dipole moments
- Applying electric field along direction of one electric dipole moment can switch molecule to corresponding spin configuration
- N. Baadji et. al., Nature Materials **8**, 194 (2009)
- Alernatively, can also force non-magnetic molecule into magnetic state
- M. Diefenbach and K. S. Kim, Angew. Chem. Int. Ed. **46**, 7640 (2007)

Electric dipole moments

LDA (SIESTA):
Spin 3/2 : 1.0782 Debye
Spin 1/2 : 1.2309 Debye

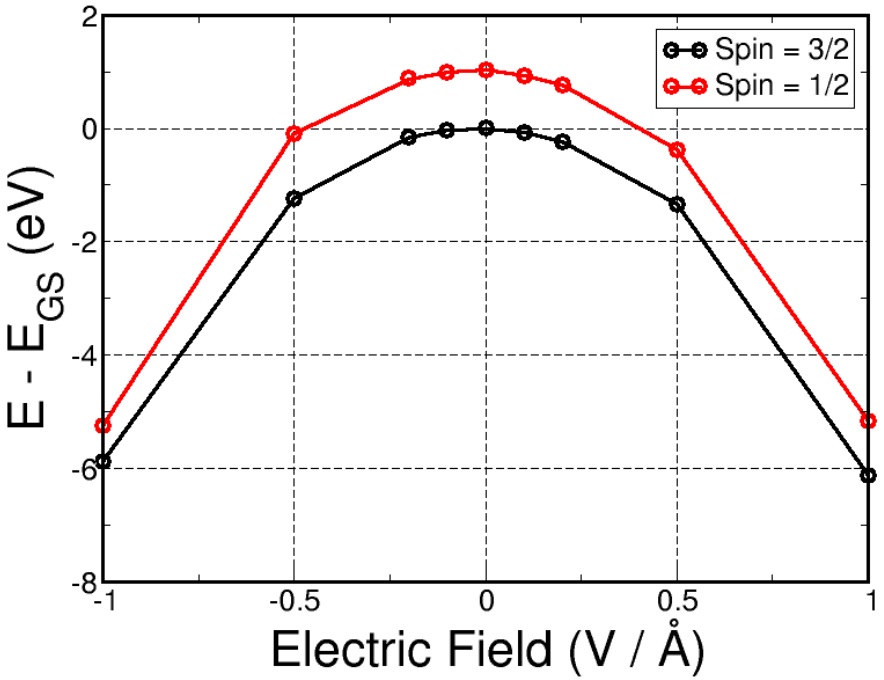


GGA (SIESTA, PBE):
Spin 3/2 : 1.0298 Debye
Spin 1/2 : 1.3501 Debye



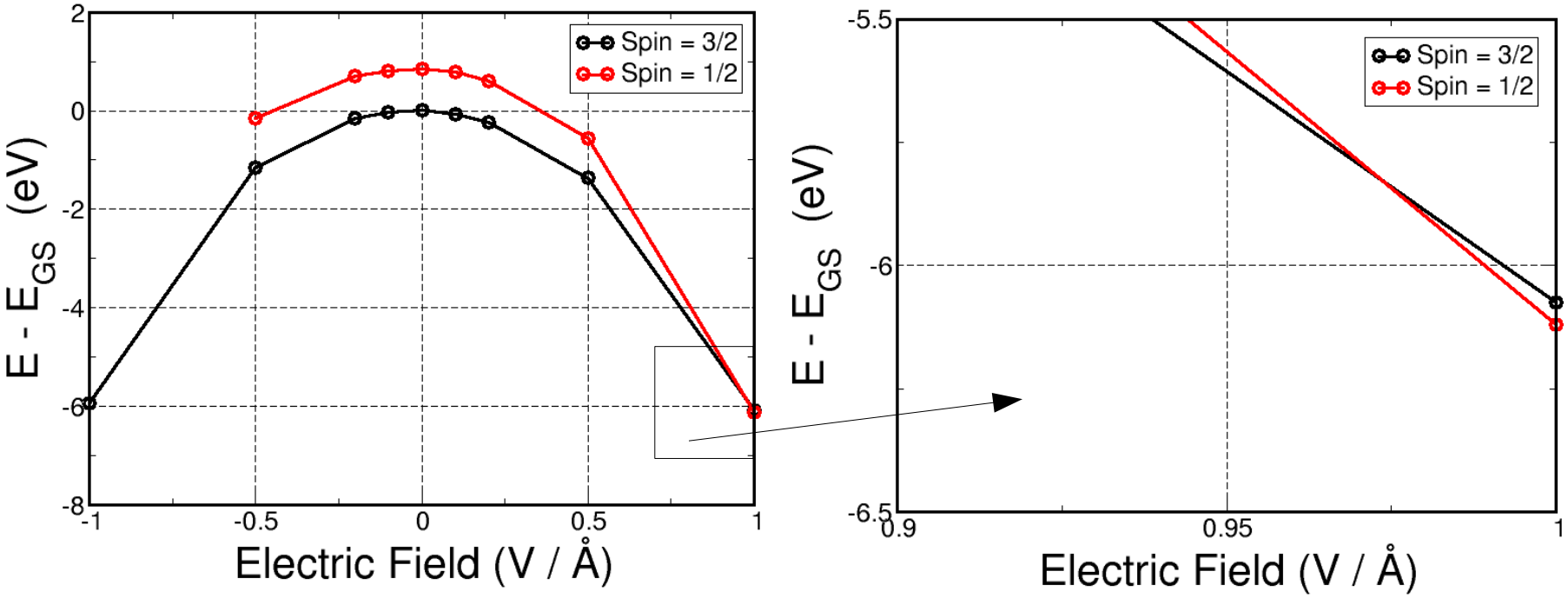
B3LYP (Gaussian):
Spin 3/2 : 1.3274 Debye

Electric field effect: DFT-LDA



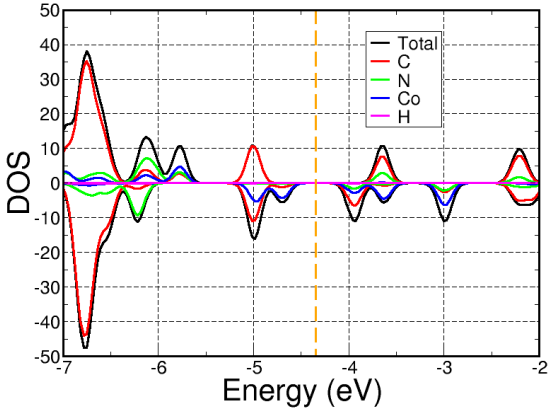
- Electric field is applied parallel to dipole moment of molecule in spin = 1/2 configuration
- No spin cross-over effect observed for this range of field strength

Electric field effect: DFT-GGA (PBE)

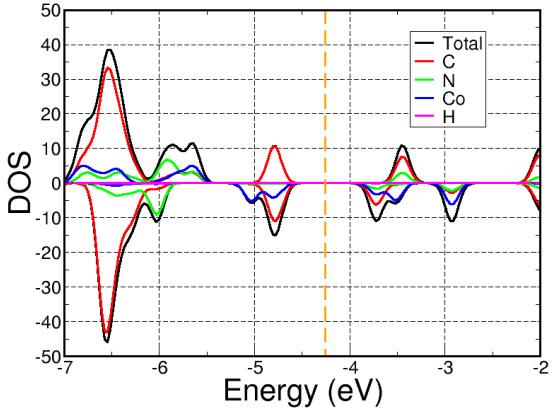


- Electric field is applied parallel to dipole moment of molecule in spin = 1/2 configuration
- Spin cross-over effect observed for field of ~ 1V/Ang

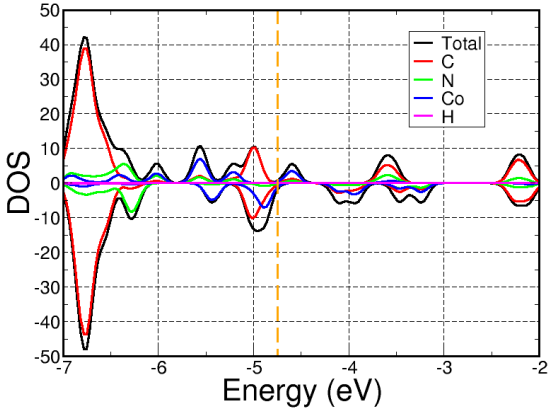
DOS for different spin configurations



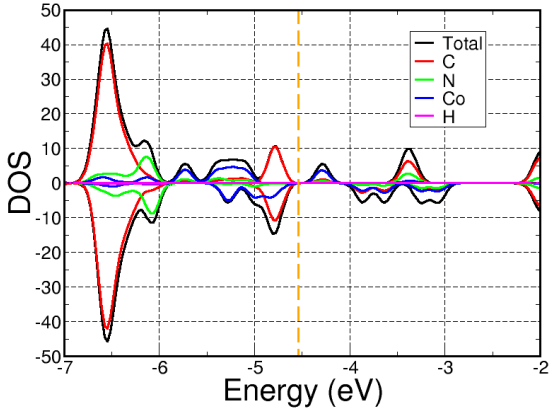
DFT-LDA: Spin = 3/2



DFT-GGA: Spin = 3/2



DFT-LDA: Spin = 1/2

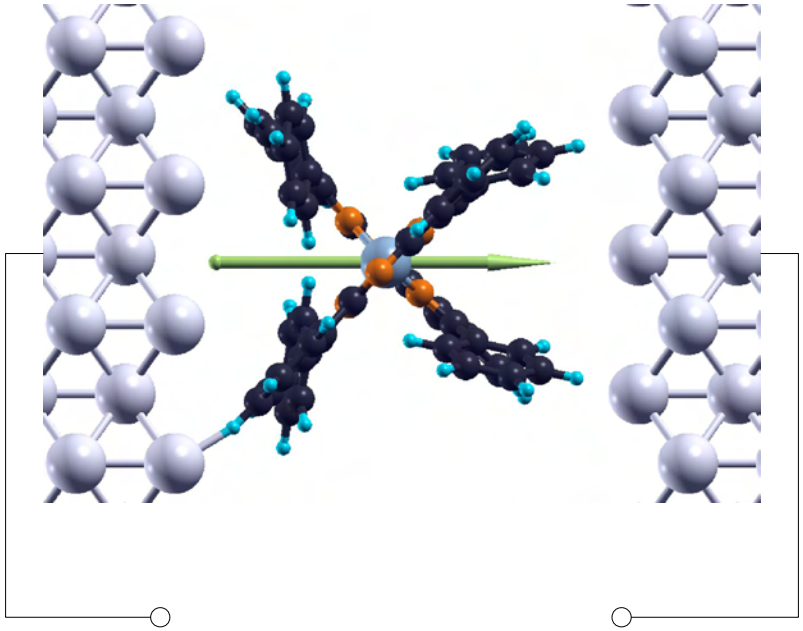


DFT-GGA: Spin = 1/2

- Different spin configurations have noticeably different DOS around HOMO-LUMO gap
- Thus the spin-crossover would result in significant changes to DOS and conductance, as seen in STM experiments

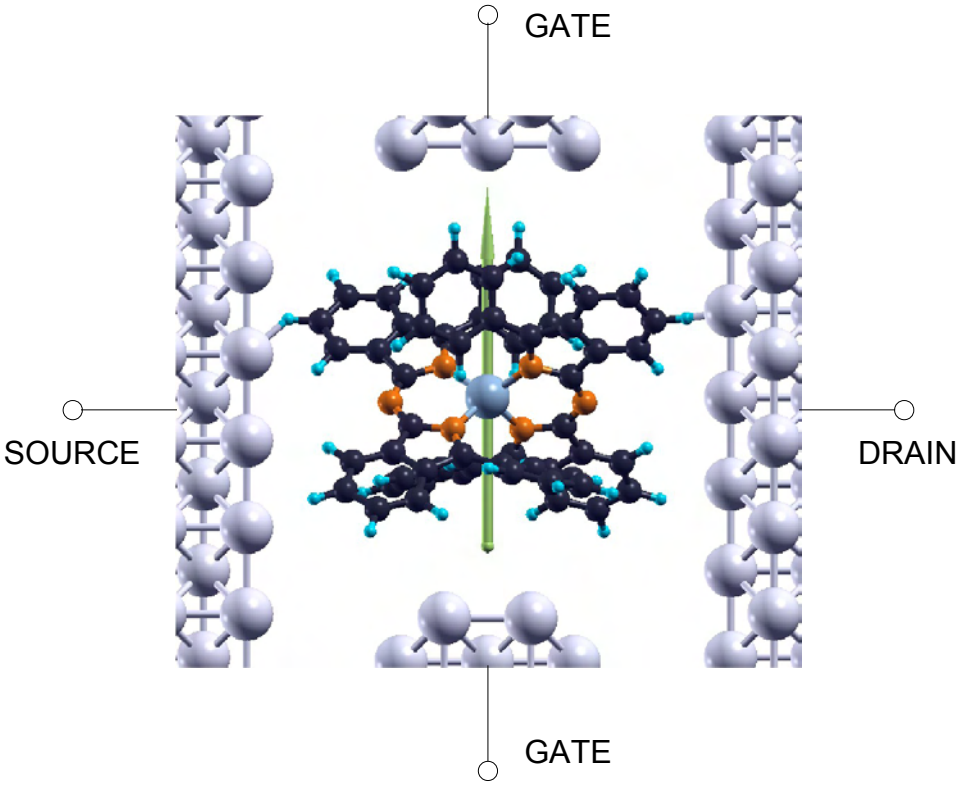
Applications:
Logic and memory

Application: memory element



- Two-terminal device: apply electric field parallel to dipole moment
- Write operation: high bias
- Read operation: low bias

Application: transistor/logic element



- Three/four-terminal device:
- Control spin state using gate field applied parallel to dipole moment
- Read spin state by applying bias perpendicular to electric dipole moment

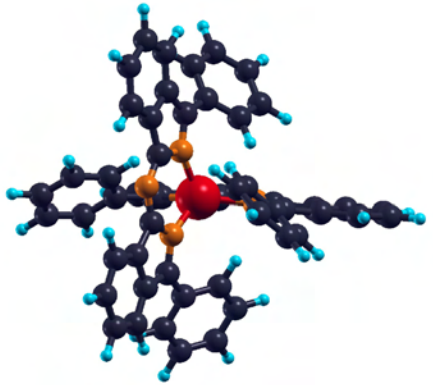
Conclusions, outlook and acknowledgments

Conclusions

- STM measurements indicate switching between two different conductance states for Co-aza-bodipy molecule when a bias is applied
- DFT-LDA, DFT-GGA and B3LYP all indicate that Co-aza-bodipy molecule has strong electric dipole moment
- DFT-GGA calculations for gas phase molecule suggest that Co-aza-bodipy may experience spin-crossover effect for high electric fields
- Thus, calculations and STM measurements suggest that the conductance state of this molecule can be controlled using electric fields
- This has applications for molecular memory, single molecule logic, etc.

Outlook

- Higher level calculations (e.g. B3LYP) required to confirm presence of spin-crossover effect, to estimate value of magnetic anistropy energy barrier, etc.
- STM measurements to determine exact switching conditions, stability of two configurations, etc.
- Investigation of how interaction with substrate and charge transfer affects spin-crossover effect
- Replacing central Co atom by other metallic atoms, e.g. Fe



Acknowledgments

TECHNISCHE UNIVERSITÄT DRESDEN
complex nano materials

Collaborators

- Molecule synthesis: R. Gresser, M. Riede, K. Leo; Institute for Applied Photophysics, TU Dresden
- Useful discussions: S. Avdoshenko, D. Nozaki, T. Brumme, Lokamani

MAX BERGMANN center of biomaterials dresden

Institut für Angewandte Photophysik

Computing methods and resources

- SIESTA: J. Phys. Cond. Matter 14, 2745 (2002)
- Gaussian 09: www.gaussian.com
- Computational facilities: Zentrum für Informationdienste und Hochleistungsrechnen (ZIH), TU Dresden

siesta

ZIH
Zentrum für Informationsdienste und Hochleistungsrechnen

Acknowledgments

Funding

- ECEMP: European Center for Emerging Materials and Processes, Dresden, Project A2.
- Atmol: Atomic scale and single molecule logic gate technologies