

New analysis tools for excited-state quantum chemistry: Turning numbers in to chemical insight

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Loughborough
University

Introduction

Design of functional molecules

→ Light sources, photovoltaics, probes, sensors

▶ Synthesis

😊 Ever more intricate structures

▶ Spectroscopy

😊 Time-resolved, high-resolution, ...

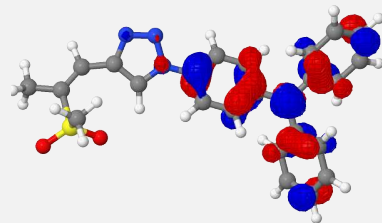
▶ Computation

😊 Quantum chem. methods / Environment / Algorithms + faster computers

❓ How do we put it all together

→ **Chemical Insight**

😞 **Look at some blobs of colour**



Motivation

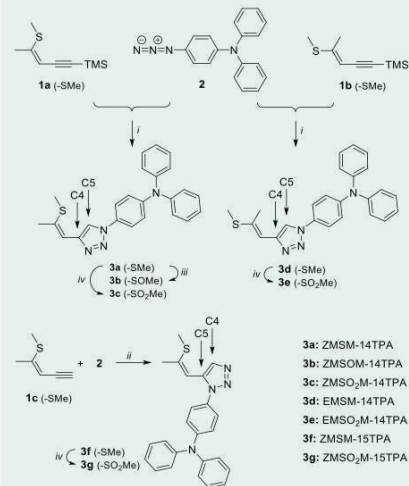
- ① Can we assign **excited-state character** in a **completely automated** way
 - Save time and analyse **larger data sets**
 - Remove **personal bias**
- Detailed analysis of **structure-property relationships** in functional molecules

- ② Can we learn about physics **beyond the MO picture**
 - Cross-links to other models
- Exciton theory
- Valence-bond theory

Push-pull systems

- Synthesis of push-pull chromophores
- Triphenylamine / triazole / alkene + sulphur
 - Different **isomers**
 - Different oxidation states of **sulphur**

Synthesis



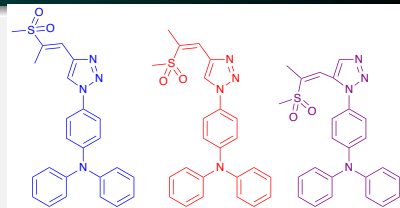
¹P. Kautny, F. Glöcklhofer, T. Kader, J.-M. Mewes, B. Stöger, J. Fröhlich, D. Lumpi, FP, *PCCP* **2017**, 19, 18055.

Optical spectra

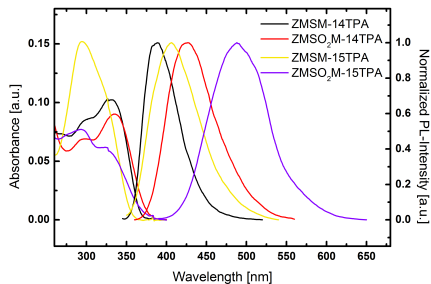
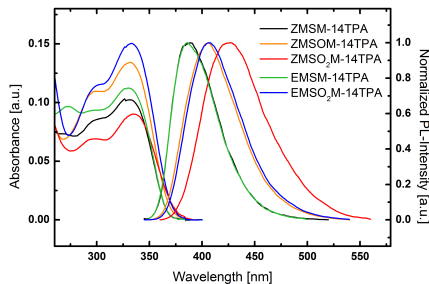
► Strongly different emission energy for **sulfoxides**

- $\text{EMSO}_2\text{M-14TPA}$ > $\text{ZMSO}_2\text{M-14TPA}$ > $\text{ZMSO}_2\text{M-15TPA}$

⑦ Why



UV/Vis spectra



► Ab initio **electronic structure** computations

→ ADC(2)

► High-level **solvation model**

→ State-specific PCM

J.-M. Mewes, et al., *J. Phys. Chem. A* **2015**, 119, 5446.

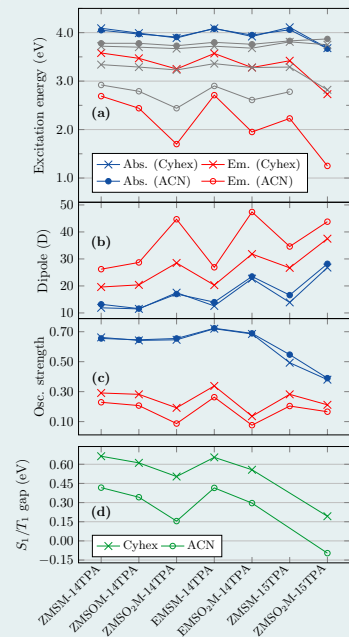
► Emission energies

☺ Trends reproduced

❓ So what

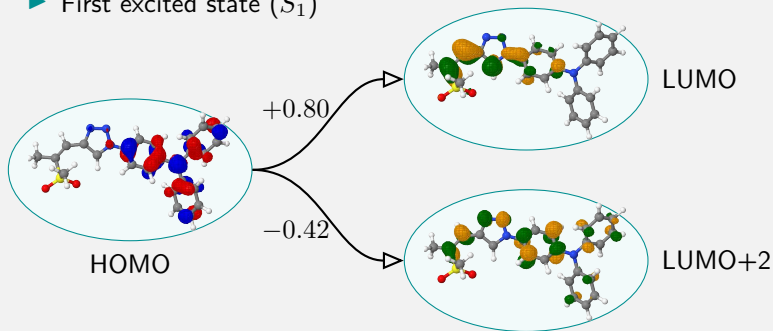
► Dipole moments, oscillator strengths

→ not the whole story



ZMSO₂M-TPA

- ▶ Frontier orbitals
- ▶ First excited state (S_1)



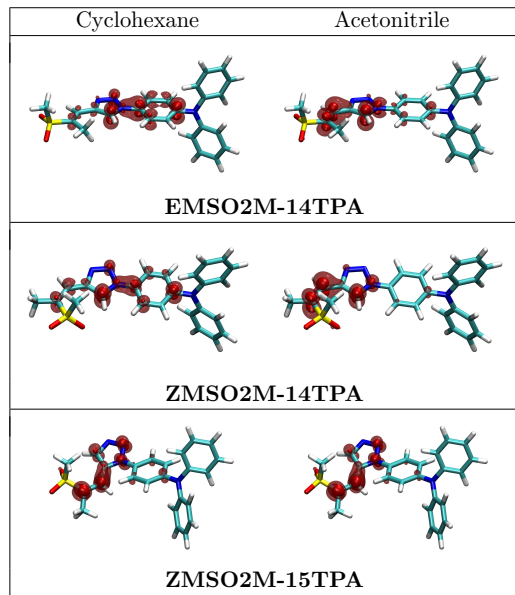
- ❗ Frontier orbitals do not tell the whole story
- ❓ How do we move beyond?

Electron-hole densities

- ▶ Summation over all the **occupied** and **virtual** orbitals involved in the transition
 - Density of the excitation **hole**
 - Density of the excited **electron**
- ▶ *Alternative*: Natural transition orbitals

- ▶ Densities of the **excited electron**
 - **Hole** always on triphenyl amine
- ▶ Solvent
 - **Wavefunction altered** by solvent
- Acetonitrile pulls stronger than cyclohexane
- ▶ E vs Z
 - Curved structure for Z
- Larger **dipole moment** for E
- ▶ 1,4 vs 1,5
 - **Conjugation** break

Excited-electron densities



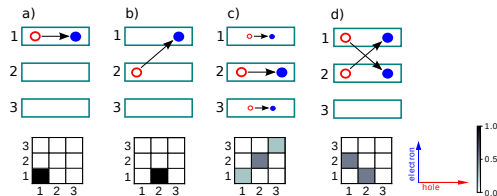
Electron-hole densities

- ▶ Electron-hole densities
- 😊 Compact graphical representation
- 😞 Still looking at blobs of colour

Charge-transfer numbers

- ▶ Excited state interpreted as a correlated **electron-hole** pair
 - Molecule divided into **fragments**
- ▶ Analysis of the **mutual** probability distribution of **electron** and **hole**
- **Charge-transfer numbers** Ω_{AB}
 - Ω_{AB} – probability of $A \rightarrow B$ charge transfer
 - Ω_{AA} – probability of local excitation on fragment A

Fragment decomposition



- a) Local excitation
- b) Charge-transfer state
- c) Delocalised exciton
- d) Charge-resonance state

¹A. V. Luzanov and O. A. Zhikol, *IJQC* **2010**, 110, 902.

²FP, H. Lischka, *JCTC* **2012**, 8, 2777.

³FP, *JCP* **2020**, 152, 084108.

► **Automatic assignment** of state character

→ Localisation and charge transfer

- Comparison to *natural transition orbitals*

► Brightest state: S_1

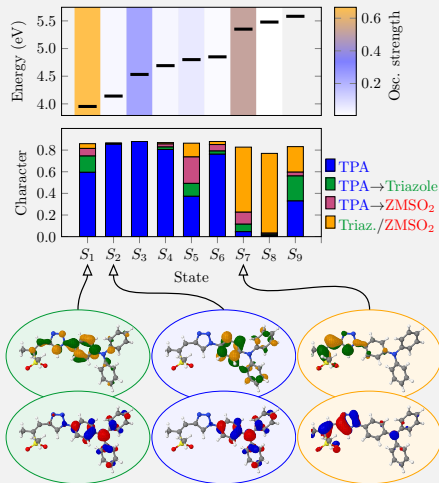
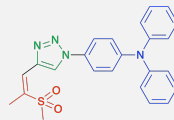
- Some CT character

► Next band

- TPA centred

😊 States assigned automatically

→ Use to analyse trends among molecules



Transition metal complexes

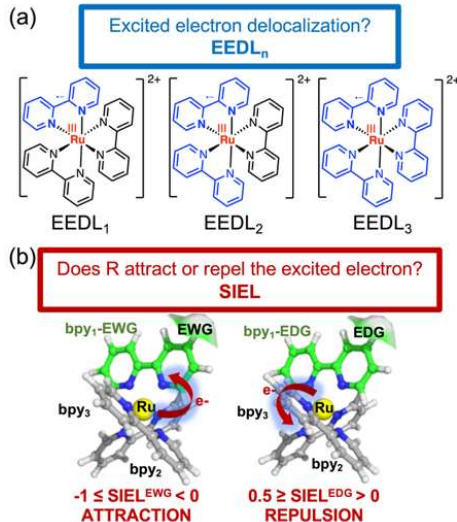
► Ruthenium complexes - $\text{Ru}(\text{bpy})_3$

① How are the excited states affected by different substituents

→ Excited electron delocalisation (EEDL)

→ Substituent induced electron localisation (SIEL)

Ru complexes

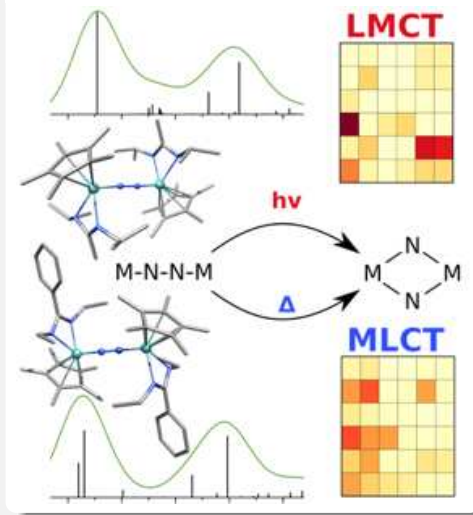


¹P. A. Sánchez-Murcia, J. J. Nogueira, FP, L. González, *Chem. Sci.* **2020**, 331, 195–199.

N₂ splitting

- Binuclear complexes
- Used for N₂ splitting
- Assign excited-state character
 - Ligand-to-metal charge transfer (**LMCT**)
 - Metal-to-ligand charge transfer (**MLCT**)

Binuclear complexes



¹S. Rupp, FP, V. Krewald, *Eur. J. Inorg. Chem* **2020**, 2020, 1506.

Conclusions

- ▶ Extended *wavefunction analysis toolbox* for excited states and open shells
- ▶ **Automated assignment** of excited-state character
 - Push-pull systems
 - Transition metal complexes
 - Multichromophoric systems
 - Rydberg *vs* valence states
 - Single *vs* double excitations
- Use for *dynamics, extended sampling, method comparison*
- ▶ Deeper **physical insight**
 - **Valence-bond** picture: ionic/covalent (+/−) states
 - **Excitons** in conjugated polymers

Further reading

► Intro for practical computations¹

- User friendly analysis tools
- Plotting
- Rigorous and **quantitative** analysis of trends

► Chemical theory²

- Learn about nature and/or quantum chemical methods
- New **qualitative** insight
- Understanding of excitation energies via *partial densities* and their *ESPs*

¹FP, *JCP* **2020**, 152, 084108.

²P. Kimber, FP, *PCCP* **2020**, 22, 6058.

Software

Extended *wavefunction analysis toolbox*.

TheoDORE - **T**heoretical **D**ensity, **O**rbital **R**elaxation and **E**xciton analysis¹

- ▶ Program package for wavefunction analysis
- ▶ Interfaces to various quantum chemistry programs:
Columbus, Turbomole, Orca, GAMESS, Gaussian, ADF, Terachem
- ▶ Open-source

libwfa - An open-source wavefunction analysis tool library²

- ▶ **Q-Chem**: ADC, EOM-CC, TDDFT
- ▶ **MOLCAS**: CASSCF, MS-CASPT2
- ▶ **CFOUR**

¹<http://theodore-qc.sourceforge.net>

²<https://github.com/libwfa/libwfa>

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Slides available at: <https://fplasser.sci-public.lboro.ac.uk>