Exploring the excited state character of nitroarylcarbazole derivatives using wavefunction analysis

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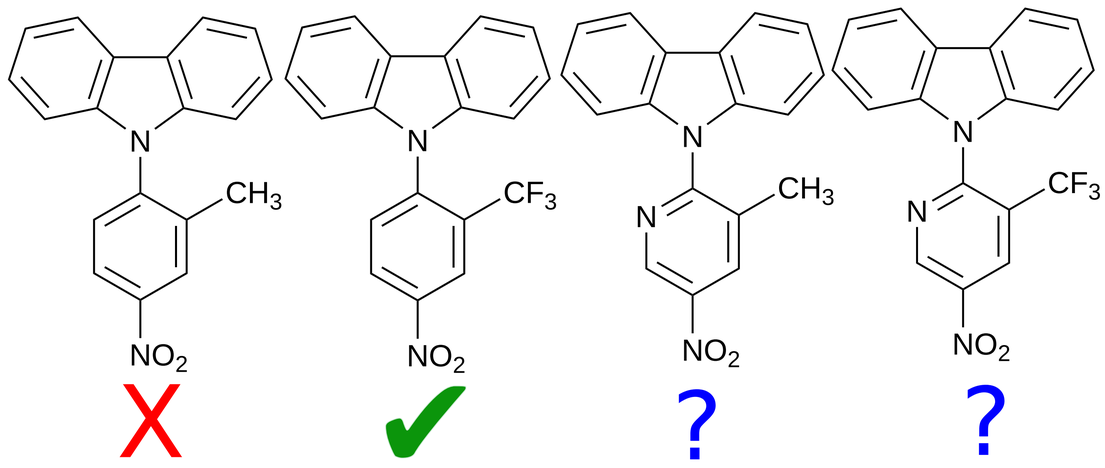
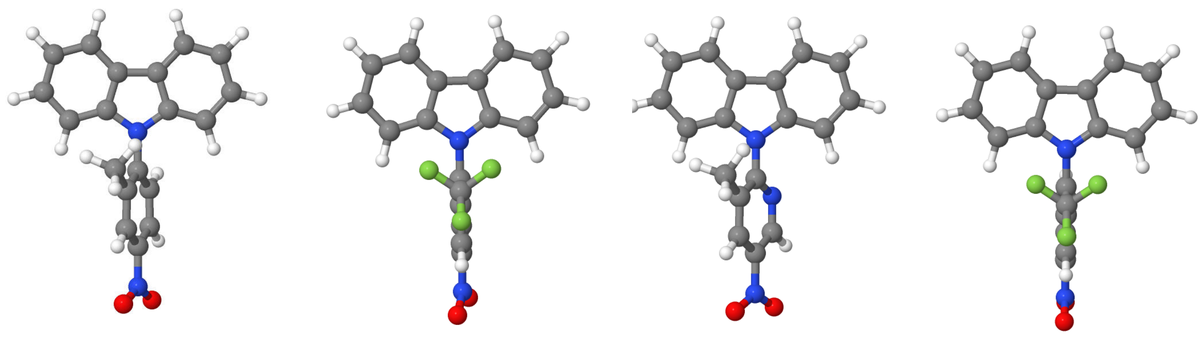
Introduction

- Nitroarylcarbazoles can display aggregation induced emission behaviour[1]
- Can we understand this behaviour in terms of the electronic transitions which occur on excitation?

Solid state emissive?



1. Ground state optimised structures

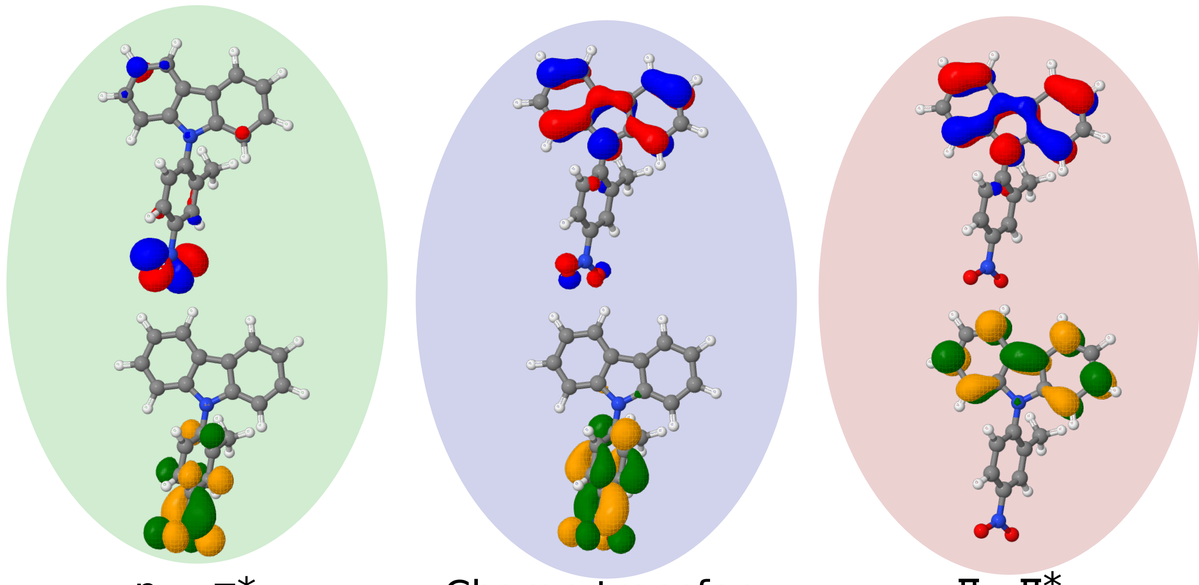


Methyl containing aryl groups → twisted

Trifluoro containing aryl groups → orthogonal

Calculate vertical excitations and use fragment decomposition to analyse the excited states

2. Excited state characterisation



$n_{NO2}\pi^*$

Charge transfer

π - π^*
(Local excitation)

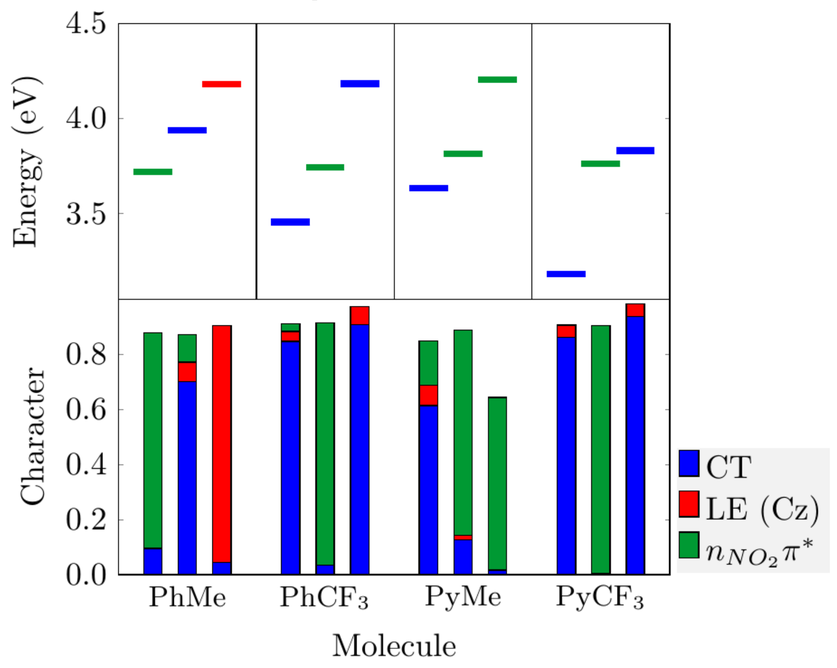
4. $PhCF_3$ - a closer look

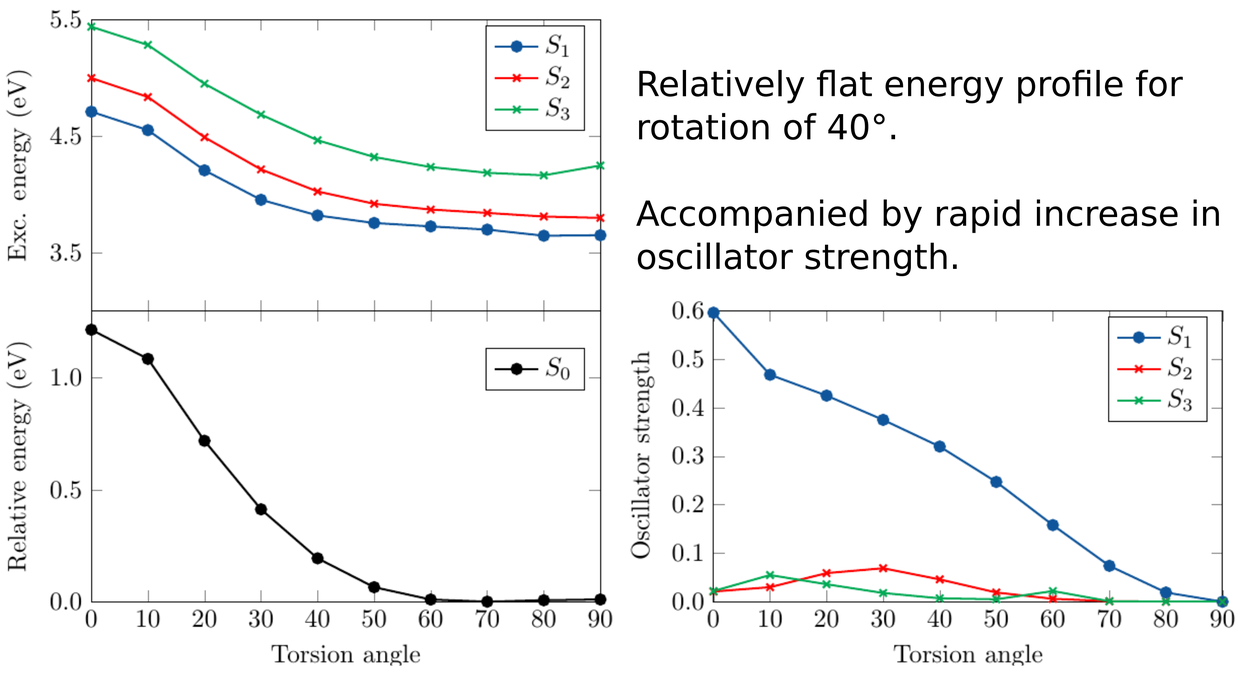
State	ΔE(eV)	f	CT	Character
S_1	3.455	0.000	0.887	CT
S_2	3.744	0.000	0.045	$n_{NO_2}\pi^*$
S_3	4.183	0.000	0.932	CT

Zero oscillator strength but solid state emissive - how?

Rotation from the orthogonal conformation to a planar one.

3. Bar representation





Relatively flat energy profile for rotation of 40°.

Accompanied by rapid increase in oscillator strength.

5. Conclusions

We propose that provided:

1. The barrier to reach a conformation with appreciable oscillator strength is small
2. The first excited state is a charge transfer state

The molecule will be solid state emissive.

Computational details

Turbomole 7.4 using MP2/def2-SV(P) for geometry optimisations and ADC(2)/def2-SV(P) for vertical excitations.

TheoDORE 2.0.2 for wavefunction analysis and decomposition of excited states.[2]

REFERENCES

1. Mater. Chem. Front., 2017,1, 1125-1129. DOI: 10.1039/C6QM00343E

2. F. Plasser, TheoDORE: a package for theoretical density, orbital relaxation and exciton analysis; available from http://theodore-qc.sourceforge.net/

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