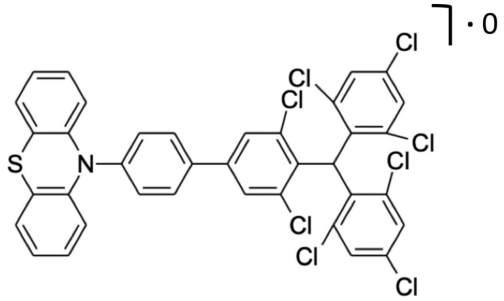
Gregor Lauter | 07.06.2024

SOMO/HOMO inversion (SHI)

The unpaired molecular orbital associated with the radical character of the system lies energetically below one or several paired molecular orbitals.

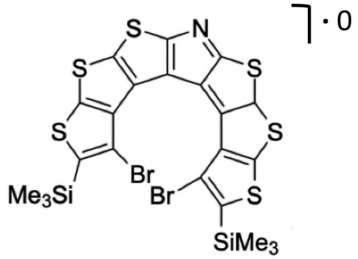
SHI radical formation[1]

Scenario 1: Spatially Disjoint Orbitals
Example: TTM-PPTA System



Initial closed-shell state:
- HOMO localised on TTM fragment
- HOMO-1 localised on PPTA fragment
- Minimal overlap leads to weak Coulomb repulsion between them

Scenario 2: Nearly Degenerate Orbitals
Example: ATH System



Initial closed-shell state:
- HOMO and HOMO-1 quasi degenerate.
- Significant overlap between the HOMO and HOMO-1
- strong 'self-Coulomb' repulsion

Upon ionisation:
- electron removed from the HOMO
- significant reduction in Coulomb repulsion in the HOMO
- SOMO (formerly HOMO) energy drops significantly

Result:
- SOMO energy stabilises below the HOMO-1

Design strategies

- choosing appropriate molecular fragments to ensure spatial disjointness of frontier orbitals
- tuning of the SOMO−HOMO energy gap in a multifragment SHI radical *via* optimisation of the HOMO energies of the precursor molecules
- weak electrostatic repulsion between the HOMO and other occupied frontier MOs (small energy drop of other MO upon ionisation)

- strong repulsion between the α and β spin components in HOMO ('self-Coulomb' repulsion) of the closed-shell parent compound (large energy drop of other MO upon ionisation)

- computational prescreening and "big data" machine-learning approaches

HOMO and HOMO-1 of the CS spatially disjoint (minimal overlap) and quasi degenerate (effectively the same energy levels)

Applications

- organic luminescent emitters light-emitting diodes (OLEDs) devices
- increased photostability of SHI radicals versus non-SHI radicals[2]

Methodology

- spin-(un)restricted KS DFT
- PBE0-D3/def2-SV(P)
- solvent corrections (PCM) for several solvents

Reference: [1] *Chem. Mater.* **2021**, *33*, 3678-3691. 2] *Nat. Mater.* **2019**, *18*, 977-984.