Benchmarking and Design of BN-Doped [6]Helicenes for TADF Applications

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Carles Alcaide, Sílvia Simon, and Miquel Solà

Institut de Química Computacional i Catàlisi (IQCC)
Universitat de Girona, Girona, Catalunya, Spain
Contact: carles.alcaide@udg.edu

OBJECTIVES

1. Establish a robust computational protocol by evaluating density functionals and the TDA approximation to accurately describe states in TADF materials.
2. Apply the optimal method to a library of 37 hexabenzenoids, and use strategic BN-pair doping on the [6]helicene scaffold to minimize the energy gap (ΔE_{ST}) and identify new TADF emitters.

BACKGROUND

Thermally Activated Delayed Fluorescence (TADF) has emerged as a cornerstone strategy to overcome the efficiency limitations of third-generation Organic Light-Emitting Diodes (OLEDs). The performance of these materials critically depends on achieving a minimal energy gap between the first excited singlet and triplet states (ΔE_{ST}). However, the accurate theoretical description of these states remains a significant challenge due to the inherent charge-transfer nature of the transitions.

- TADF mechanism: achieves 100% internal quantum efficiency by harvesting dark triplet excitons via thermally activated reverse intersystem crossing (RISC).
- Molecular design: in general uses donor-acceptor (D-A) architectures to spatially separate frontier molecular orbitals, minimizing the singlet-triplet energy gap (ΔE_{ST}).
- Theoretical challenge: RISC efficiency depends on a delicate interplay between charge transfer (CT) and locally excited (LE) states. Accurate electronic structure methods are crucial for modeling ΔE_{ST} and spin-orbit coupling (SOC) to guide the rational design of novel organic emitters.

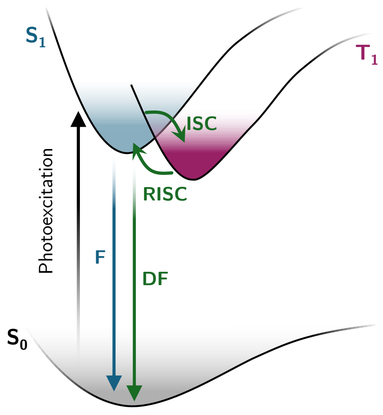


Figure 1. Schematic mechanism of TADF[1].

BENCHMARK

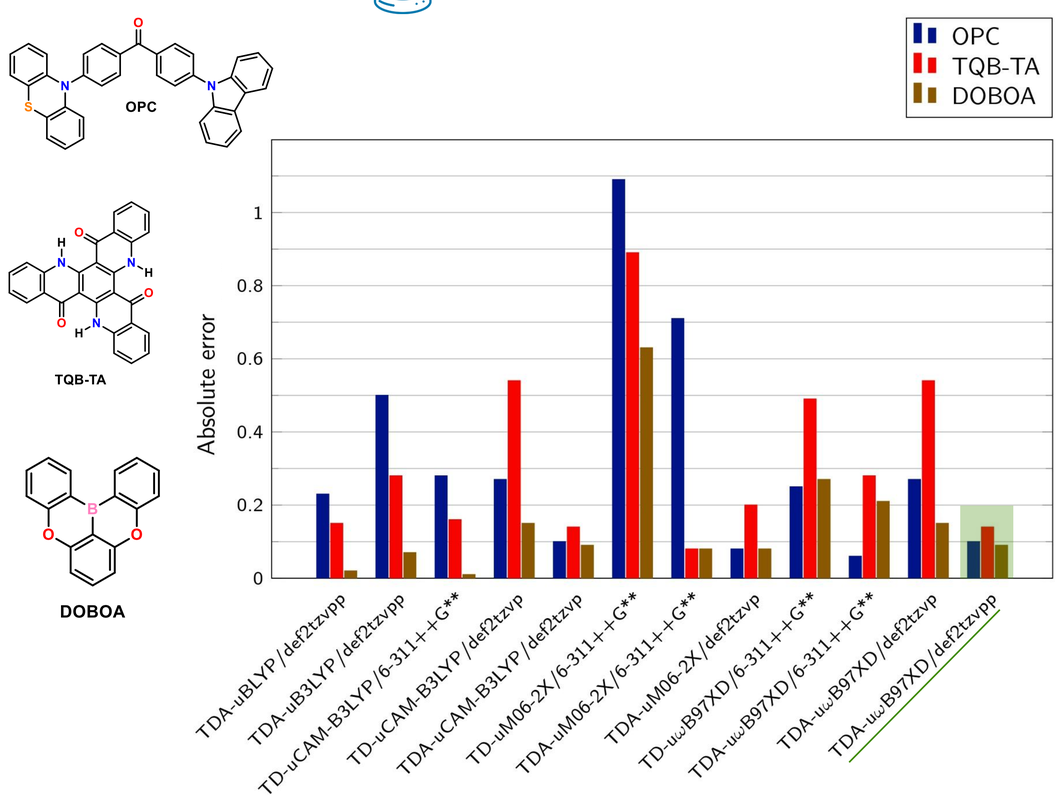
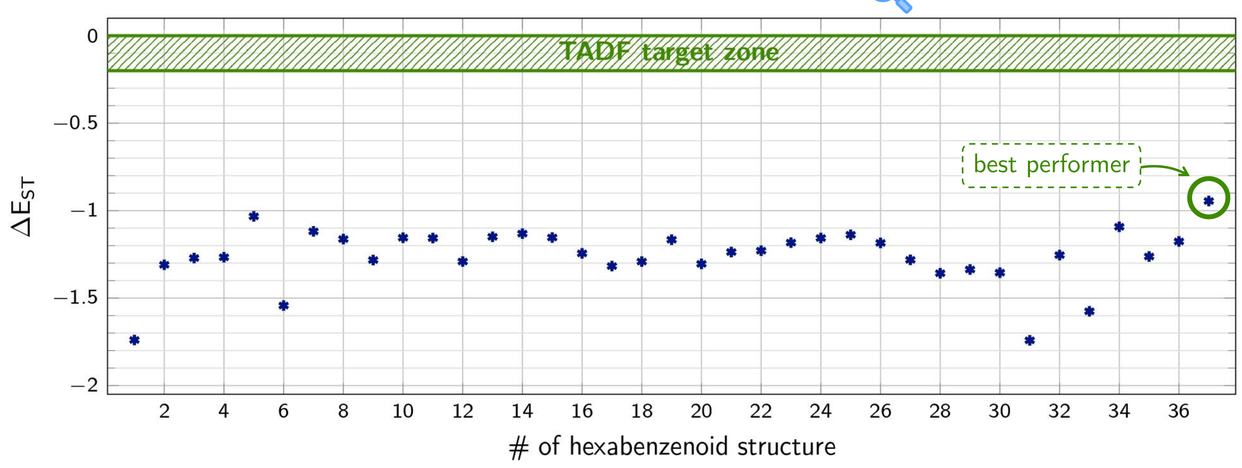
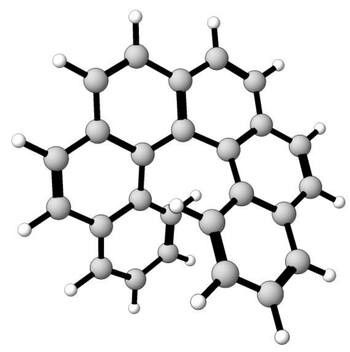


Figure 2. Absolute errors in singlet-triplet energy gaps (ΔE_{ST}(calc) - ΔE_{ST}(ref)) for benchmark TADF emitters across evaluated density functionals, comparing standard TD-DFT and TDA-DFT against reference data[1], highlighting the TDA-uωB97xd/def2tzvpp level of theory as the most favorable protocol. The absolute error values are in eV.

SCREENING AND OPTIMIZATION



Structure 37



- Lowest ΔE_{ST} (-0.95 eV)
- The helical core minimizes HOMO-LUMO overlap
- **Prime candidate for BN-doping!**

Figure 3. Screening of the singlet-triplet energy gap for all 37 catacondensed hexabenzenoid isomers[2]. Values were obtained using the validated TDA-DFT/uωB97X-D/def2-TZVPP protocol. The horizontal zone indicates the target threshold for viable TADF applications (≈0.2 eV), highlighting the [6]helicene scaffold as the most favorable structural starting point prior to BN-doping. The energy values are in eV.

***Isoelectric substitution* (BN-doping)**

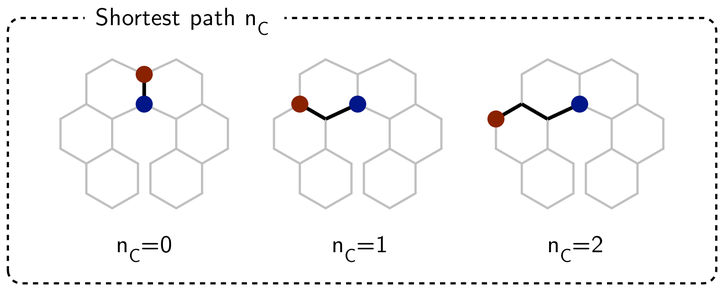


Figure 4. Heteroatom substitution scheme adapted from literature[3,4]. All possible regioisomers are generated by pairing one inner-rim atom with one outer-rim atom, indexed by the number of intervening carbon atoms along the shortest path (n_C = 0, 1, 2). Blue and red circles denote N and B atoms, respectively.

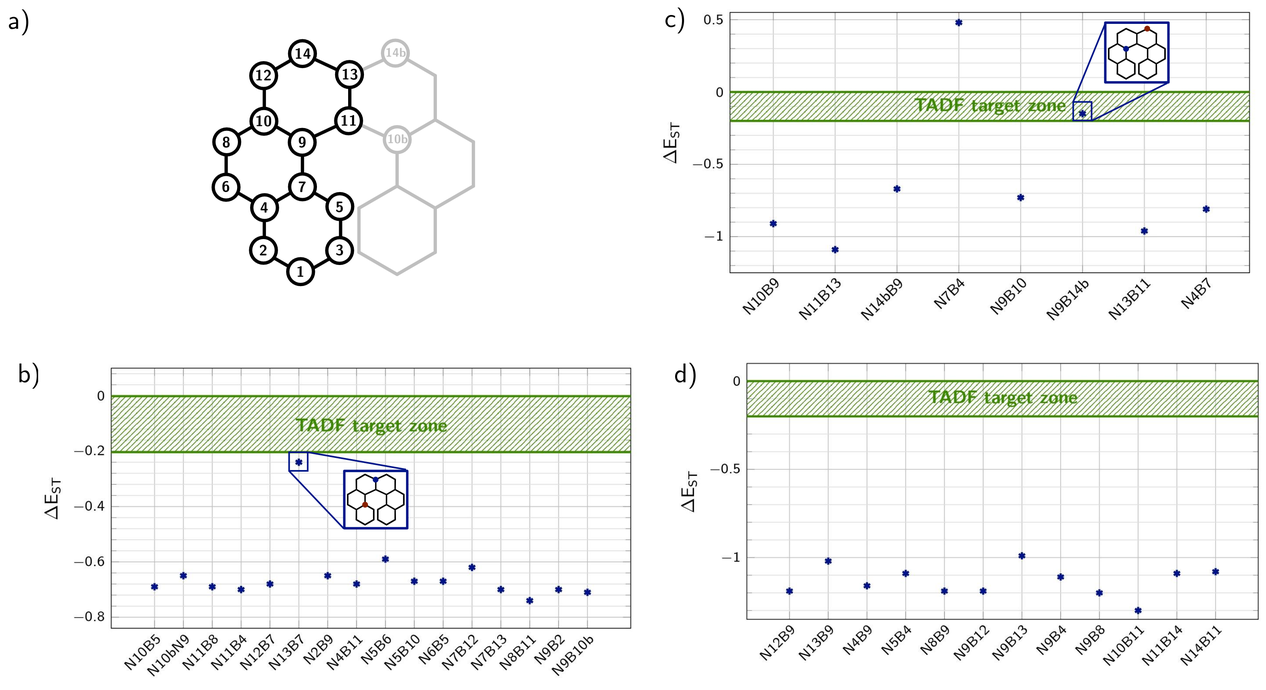


Figure 5. Reference atom numbering corresponding to the x-axis nomenclature (a), and computed ΔE_{ST} values for BN-doped regioisomers grouped by heteroatom separation distance: b) n_C = 0, c) n_C = 1, and d) n_C = 2. Optimal TADF candidates fall within the shaded green target zone. The reported energy values are in eV.

CONCLUSIONS

- ✓The TDA-DFT approach, paired with the ωB97X-D/def2-TZVPP protocol, is the most reliable methodology for accurately describing TADF transitions.
- ✓While pure hydrocarbon hexabenzenoids do not exhibit ideal TADF behavior, [6]helicene emerges as the most favorable structural starting point.
- ✓Strategic BN-pair substitution on the [6]helicene core successfully minimizes the singlet-triplet energy gap (ΔE_{ST}), yielding highly promising candidates for TADF applications.

REFERENCES

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