

Unlocking Inverted Singlet-Triplet Gap in Alternant Hydrocarbons with Heteroatoms



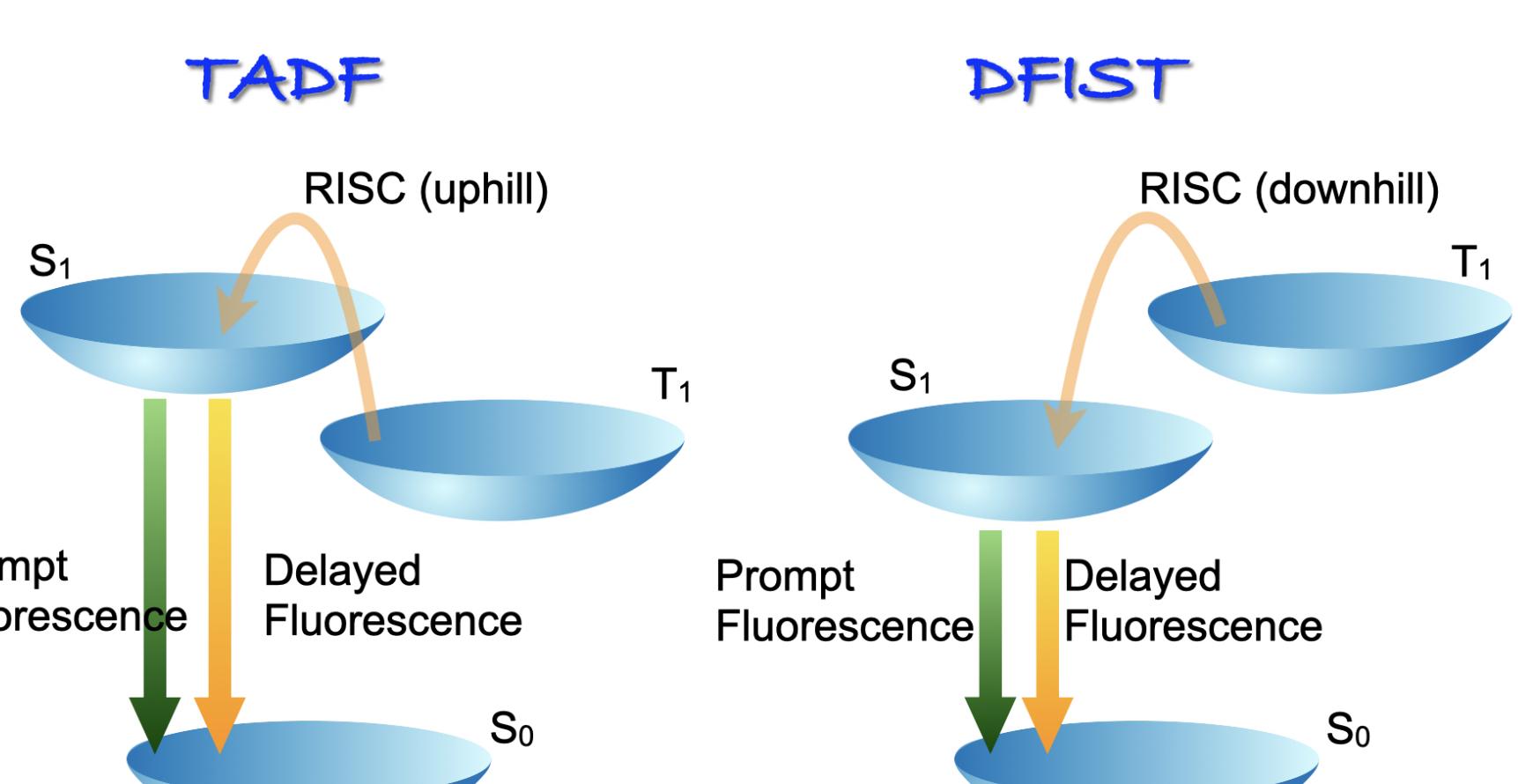
Atreyee Majumdar & Raghunathan Ramakrishnan

Tata Institute of Fundamental Research, Hyderabad 500046, India

atreyeem@tiffrh.res.in

AOSC-2025

INTRODUCTION



This poster presents results that show heteroatoms substituted polycyclic aromatic hydrocarbons can be considered as candidates for fifth generation organic light emitting diodes (OLEDs). [1]

Thermally activated delayed fluorescence (TADF)

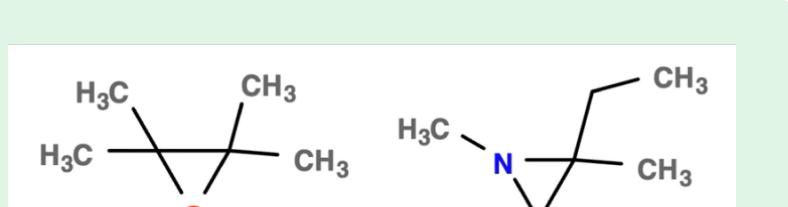
Endothermic reverse intersystem crossing (RISC).

Delayed fluorescence from inverted singlet and triplet states (DFIST)

Violates the Hund's Rule and shows exothermic RISC.

Past Studies

A comprehensive search in 12,880 prototypical small molecules using high-level, accurate electronic structure methods such as TD-DFT with double-hybrid functionals and ADC(2) revealed no evidence of Hund's rule violation with negative singlet-triplet gap (STG). [2]

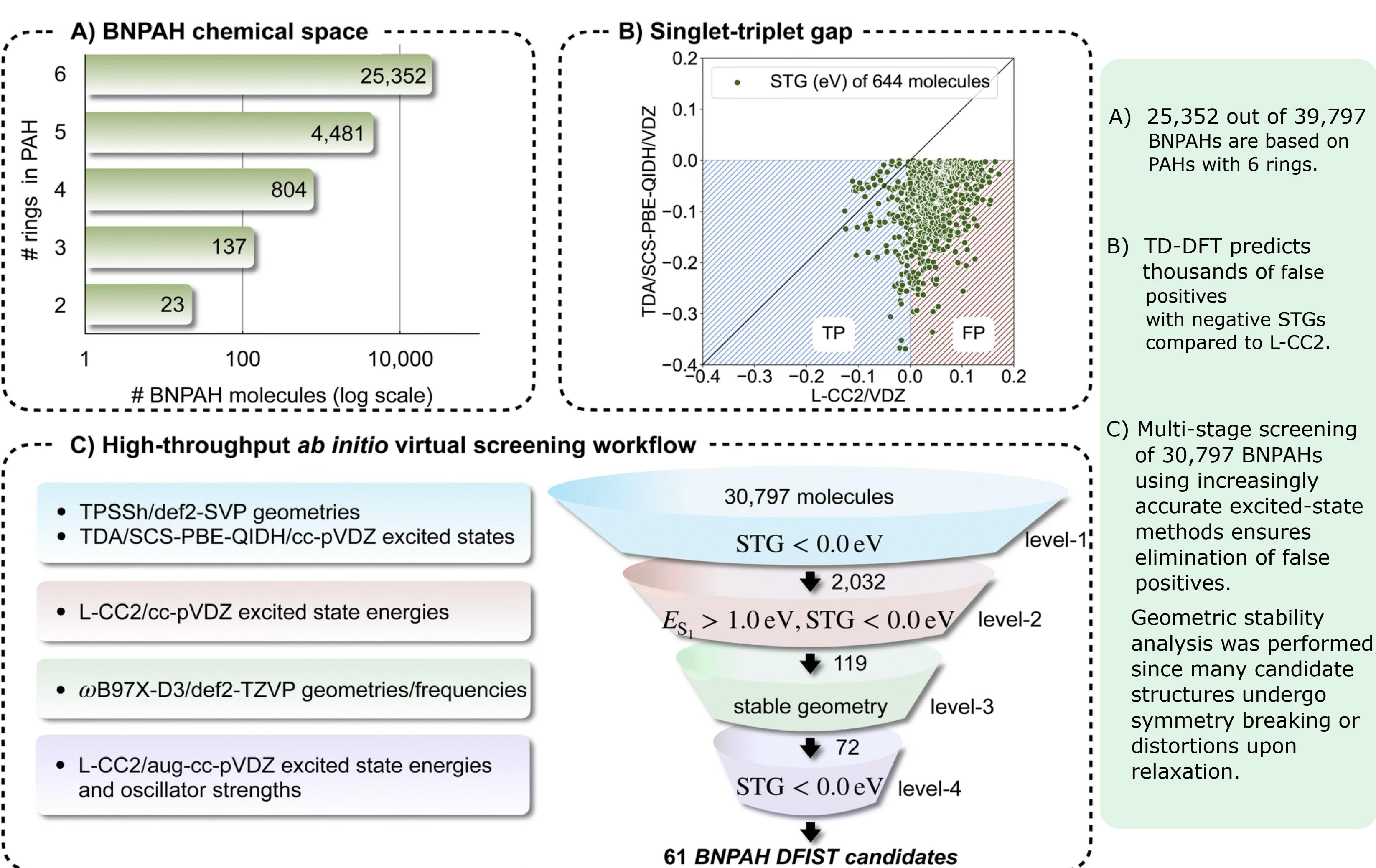


Some azaphenalenes show negative STG, but geometric stability must be considered, as symmetry breaking often results in a positive gap at the true minima. [3,4,5,6,7]

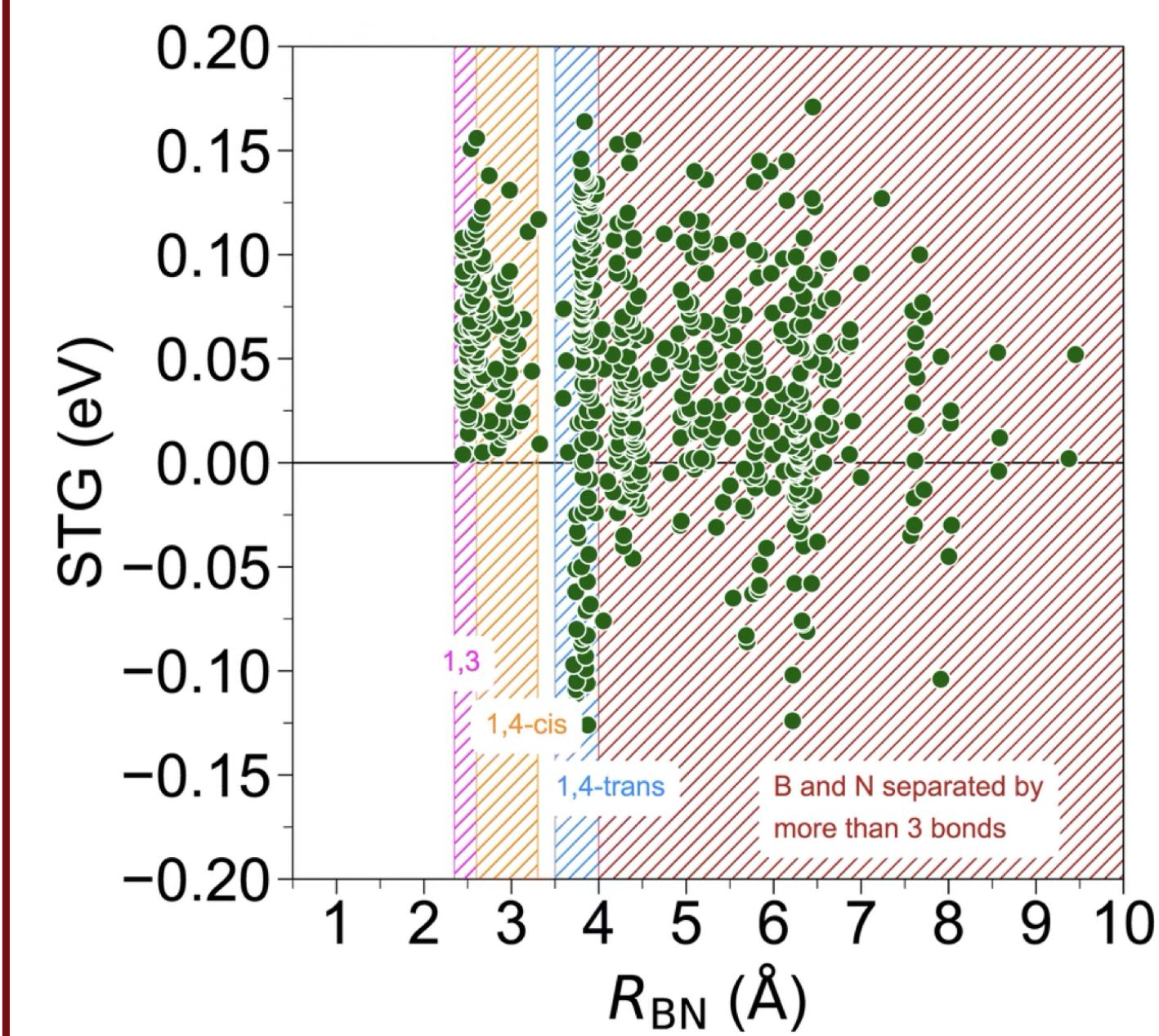
Highly accurate negative STGs can be predicted for large organic molecules with L-CC2 and L-ADC(2). [8]

A recent study on heteroatom-doped PAHs, reported significantly reduced singlet-triplet gaps relevant for TADF applications; however, none of these systems exhibited genuine gap inversion. [9]

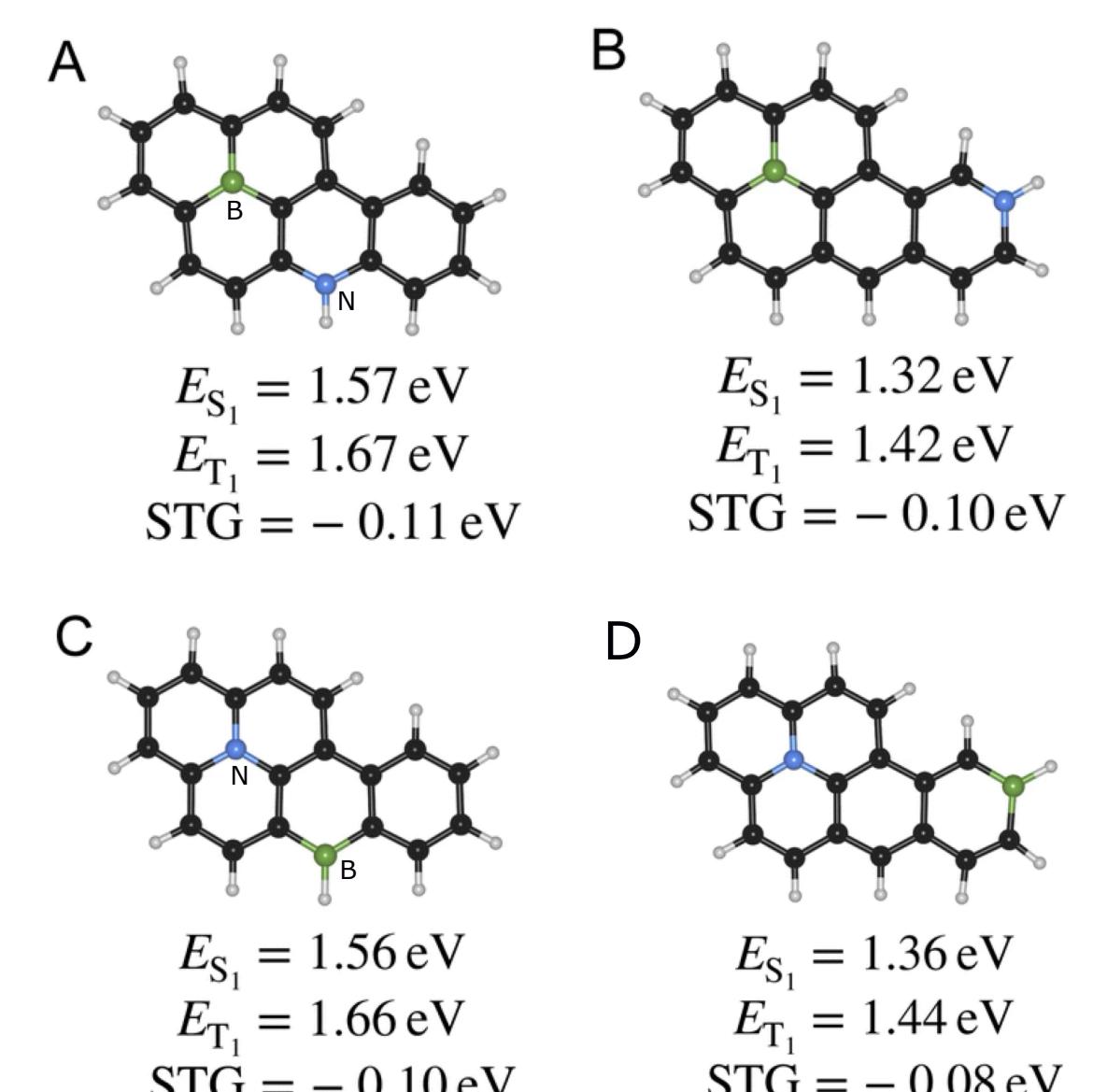
DATA GENERATION WORKFLOW AND DATA QUALITY



VARIATION OF STG WITH B,N SEPARATION

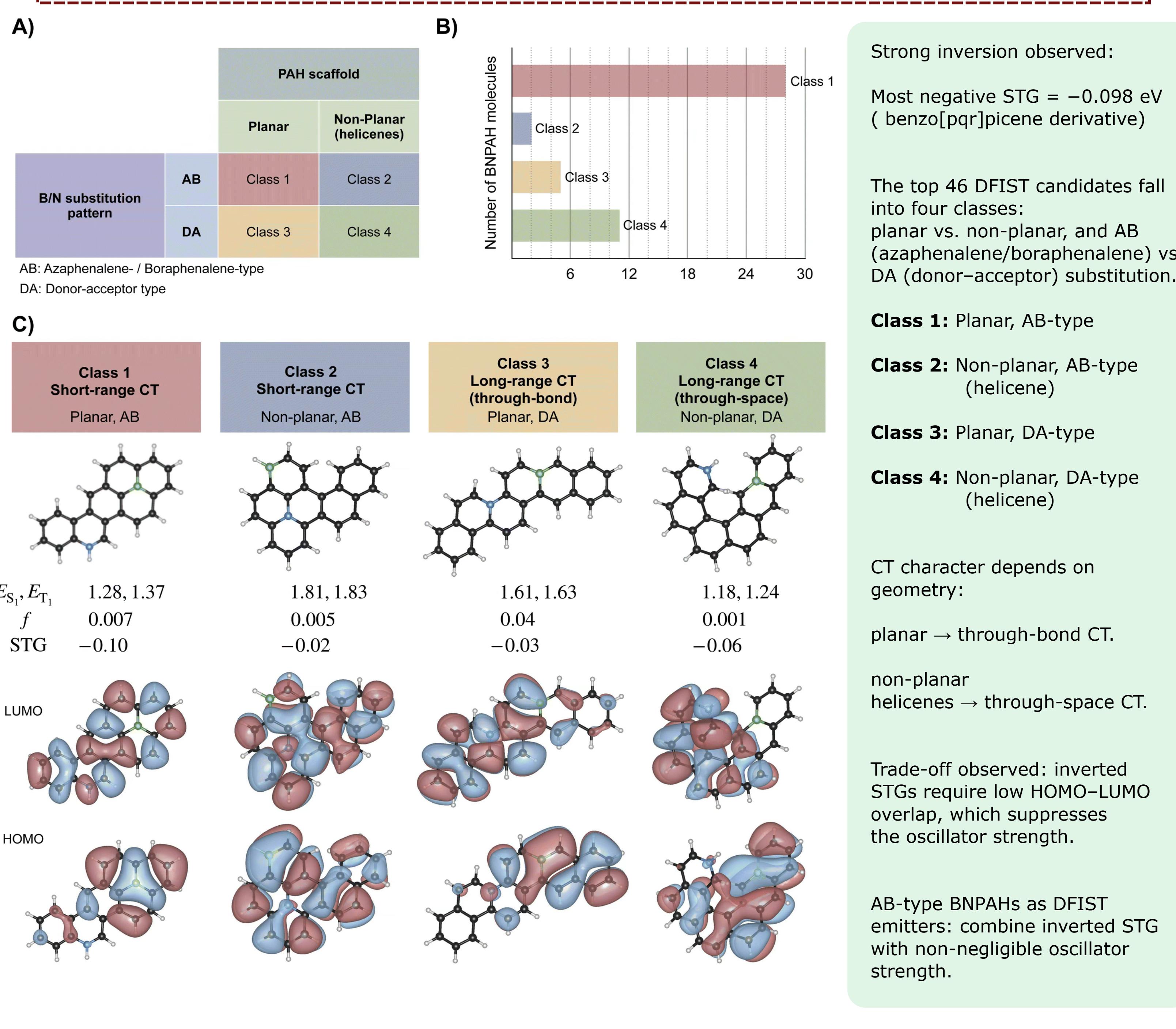


1,3 and 1,4-cis B-N arrangements (two-bond separations) consistently show STG > 0 eV.
For the 1,4-trans configuration, several molecules exhibit negative STGs.
No clear trend of negative STG is observed for B-N distances > 4 Å.

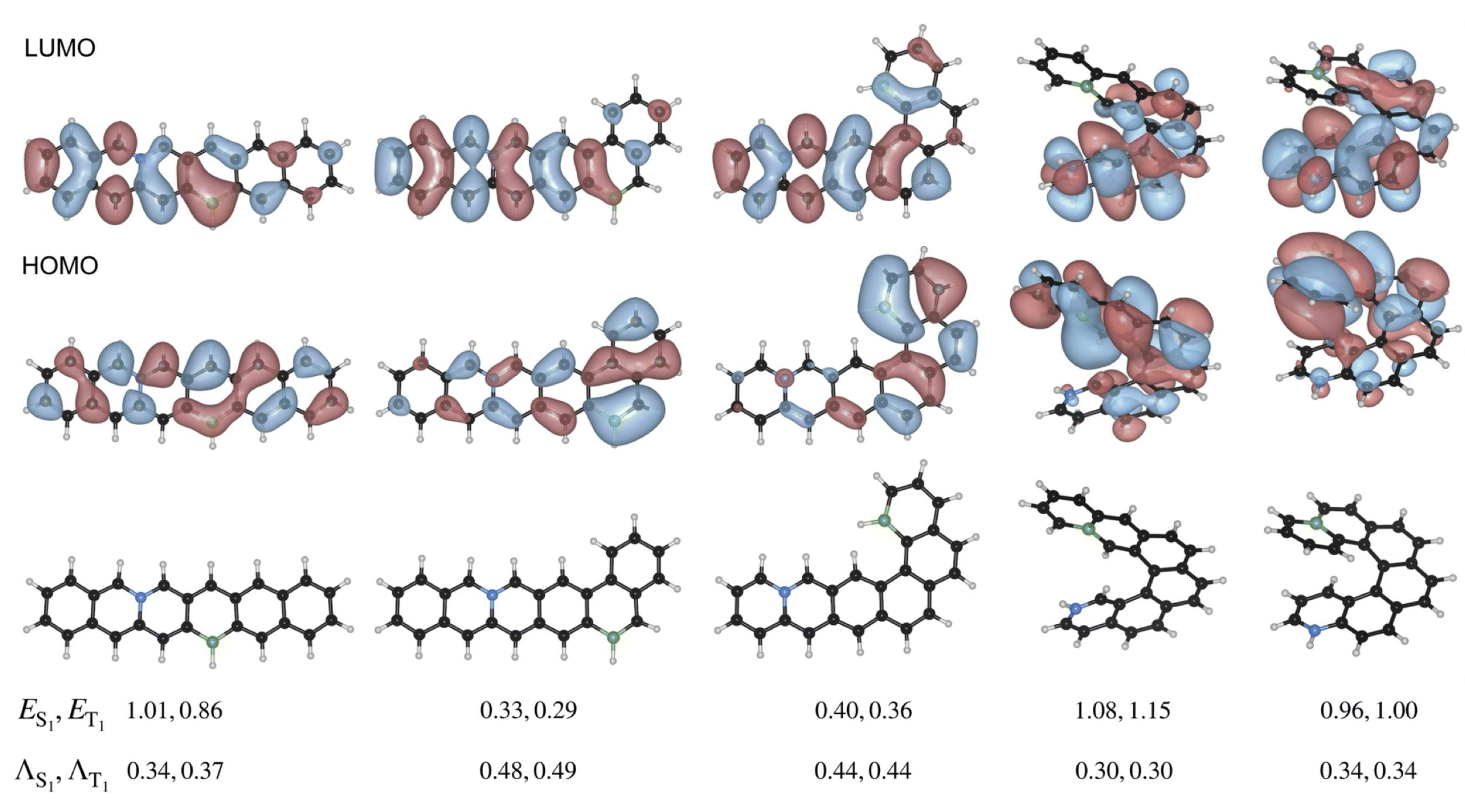


DFIST-BNPAH CANDIDATES

72 stable BNPAHs identified after ω B97X-D3/def2-TZVP optimization/frequency analysis; 61 exhibit negative STGs.
46 robust DFIST candidates shortlisted (STG < -0.015 eV, L-CC2's mean error).



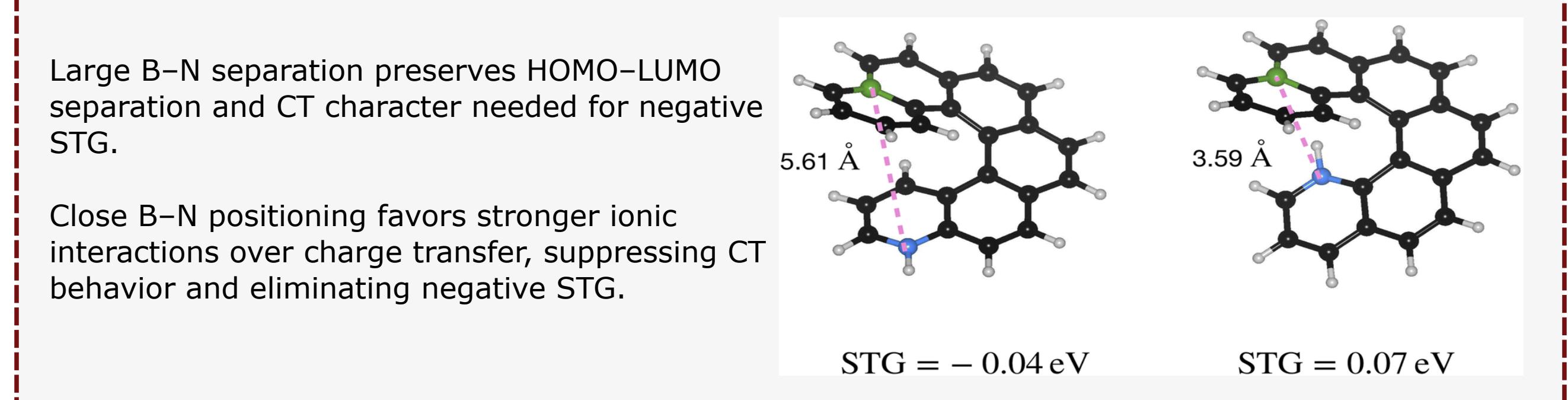
BN-HELICENE MOLECULES



Homo density lies near the boron donor end and the LUMO density is localized around the nitrogen acceptor end showing an intramolecular CT.

Large B-N separation prevents bond formation upon relaxation, maintaining CT-type S_1/T_1 states.

The spatially separated HOMO-LUMO regions indicate a through-space CT interaction driving the negative STG.



CONCLUSIONS

- A multi-level high-throughput virtual screening workflow was developed to minimize false positives in negative STG predictions.
- From 30,797 BNPAHs (single B,N substitutions in 77 PAHs), 61 molecules with negative STG and 46 with STG < -0.015 eV were identified.
- Low-symmetry BNPAHs show non-vanishing oscillator strengths for $S_0 \rightarrow S_1$, making them spectroscopically identifiable DFIST candidates.
- The top 46 DFIST candidates fall into four categories: planar vs. non-planar, and AB (azaphenalen/boraphenalen) vs DA (donor-acceptor) substitution.
- Small unstable cores (e.g., 1BP) can be stabilized within larger PAHs, retaining negative STG properties.
- BN-helicenes emerge as DFIST candidates due to through-space charge transfer, though limited stacking may hinder solid-state efficiency.
- The full BNPAH space (~7.4 trillion molecules) requires ML and evolutionary approaches; top-46 candidates are concrete DFIST candidates.

REFERENCES

- A. Majumdar et al., *Chem. Sci.*, 2025, 16, 14392.
- A. Majumdar et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 14505.
- A. Majumdar et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 26723.
- J. Ehrmaier et al., *J. Phys. Chem. A*, 2019, 123, 8099.
- K. D. Wilson et al., *J. Am. Chem. Soc.*, 2024, 146, 15688.
- N. Aizawa et al., *Nature*, 2022, 609, 502.
- P.-F. Loos et al., *J. Phys. Chem. Lett.*, 2023, 14, 11069.
- A. Majumdar et al., *J. Comput. Chem.*, 2025.
- R. Walia et al., *Nat. Mater.*, 2025, 1–8.

THANK YOU



We acknowledge Surajit Das for various discussions.