Computational Discovery of Stable Conjugated Biradicals

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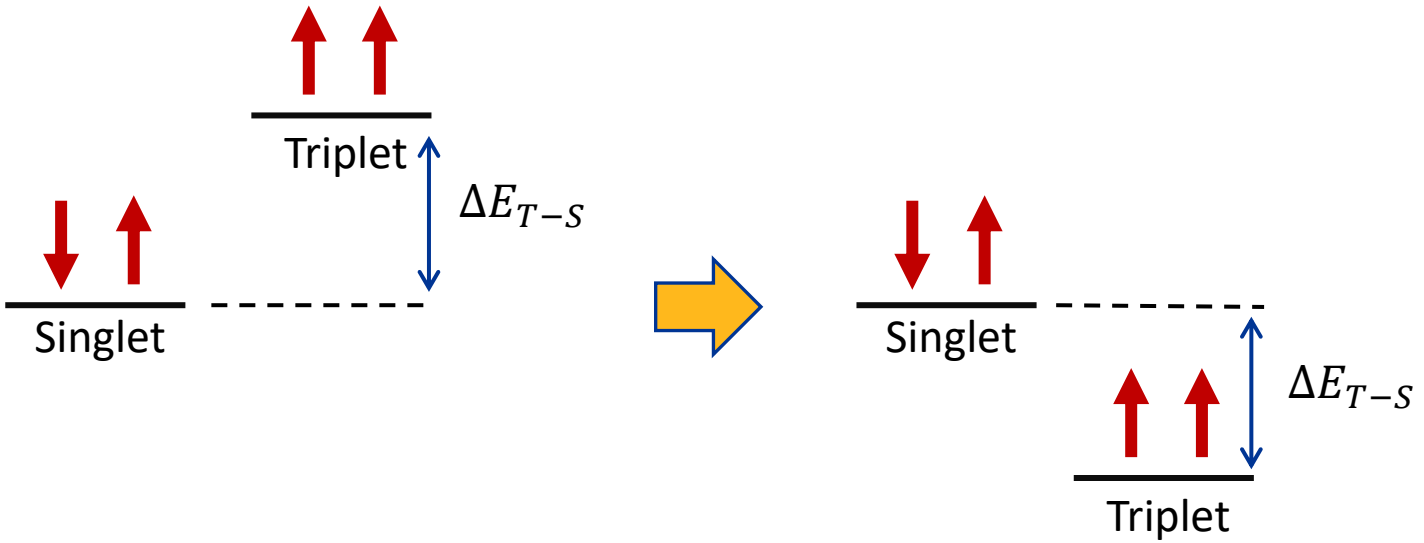
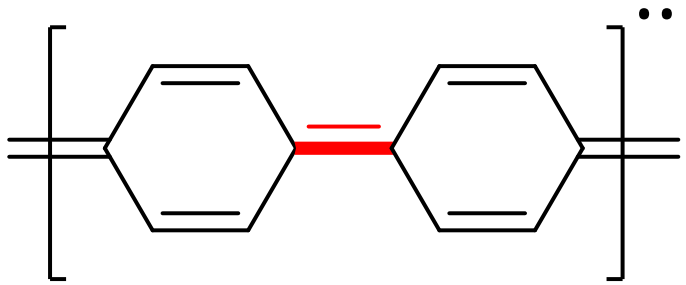
Conjugated Biradicals

- Organic polymers with a stable triplet ground state
- Unique properties & potential uses
- Made from alternating donor-acceptor monomers

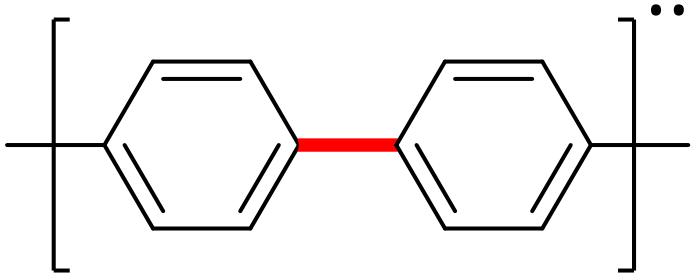


Why are they Stable?

- Two hypotheses from the stability of the triplet ground-state
  - Quinoidal vs. Aromatic bonding structure



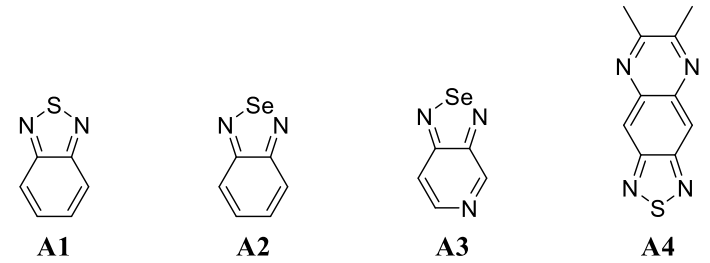
Quinoidal



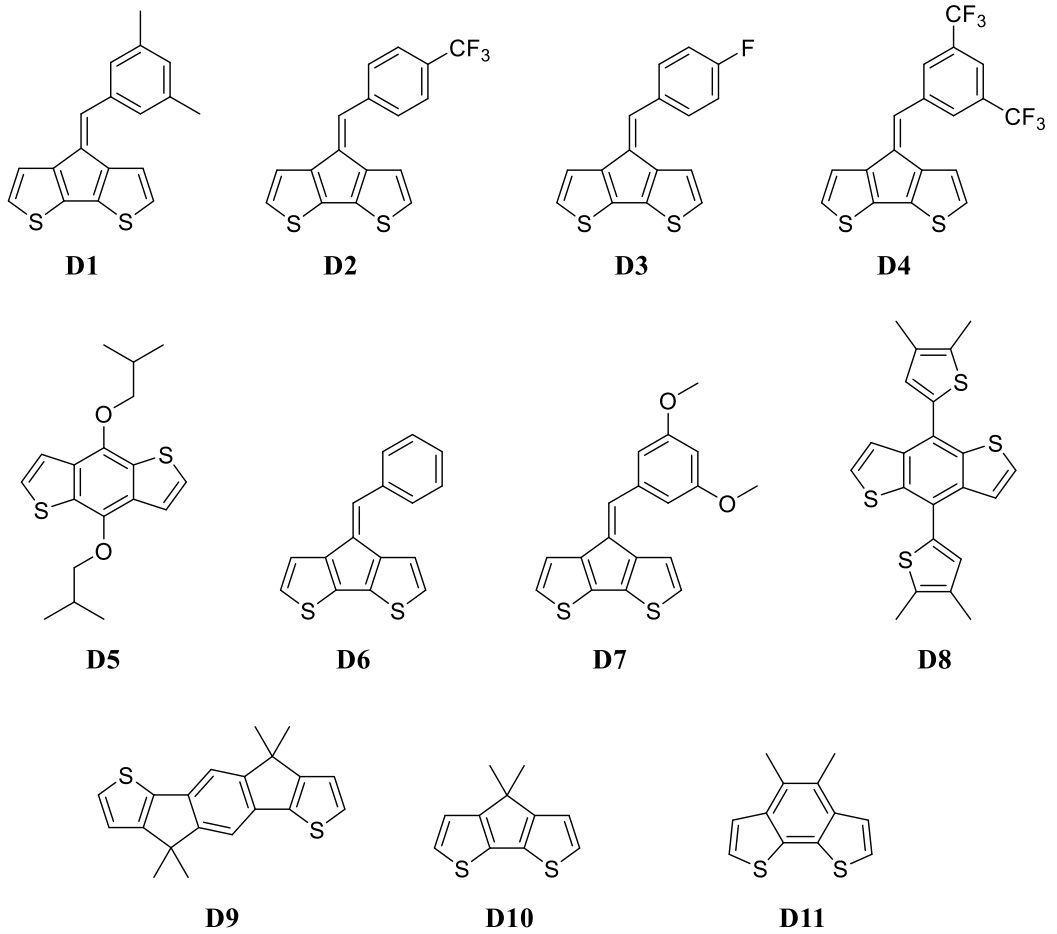
Aromatic

Computational Study

Acceptors



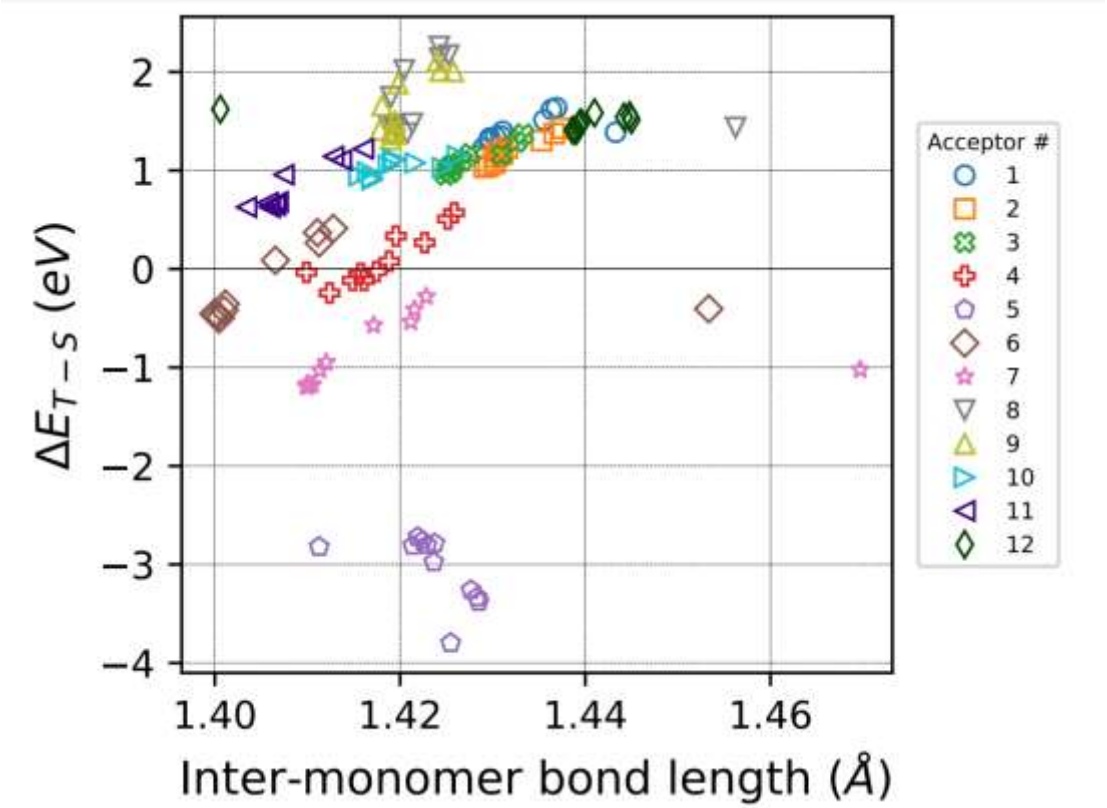
Donors



Inter-Monomer Bond Length

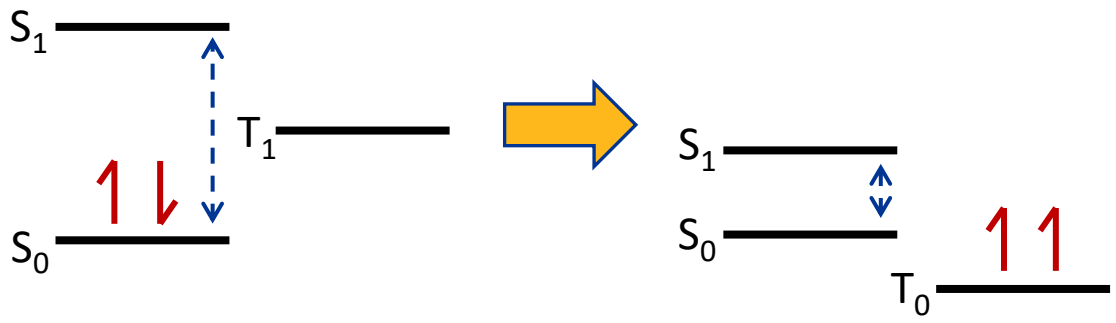
- If the quinoidal hypothesis is correct
  - Bond lengths should be smaller as the triplet stability increases
  - This is not the case…

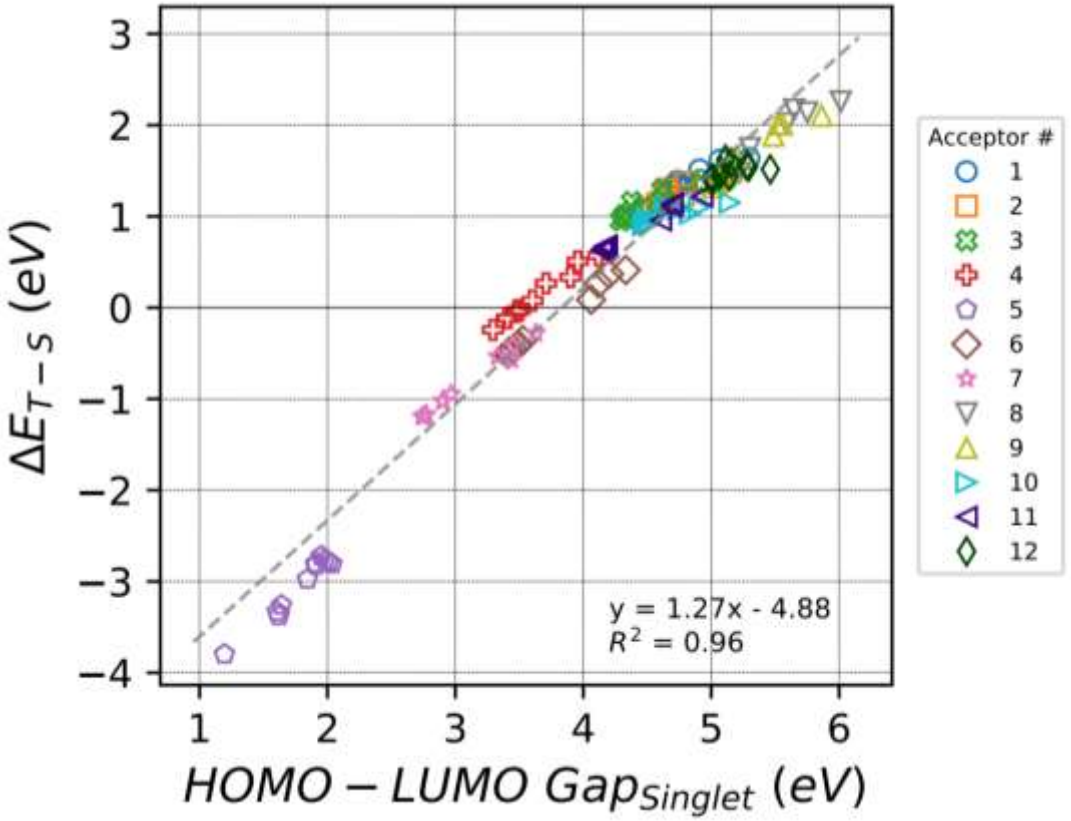
- Bonding structure is not a good predictor
  - What is?



HOMO-LUMO Gap

- Triplet stability comes from a small HOMO-LUMO gap





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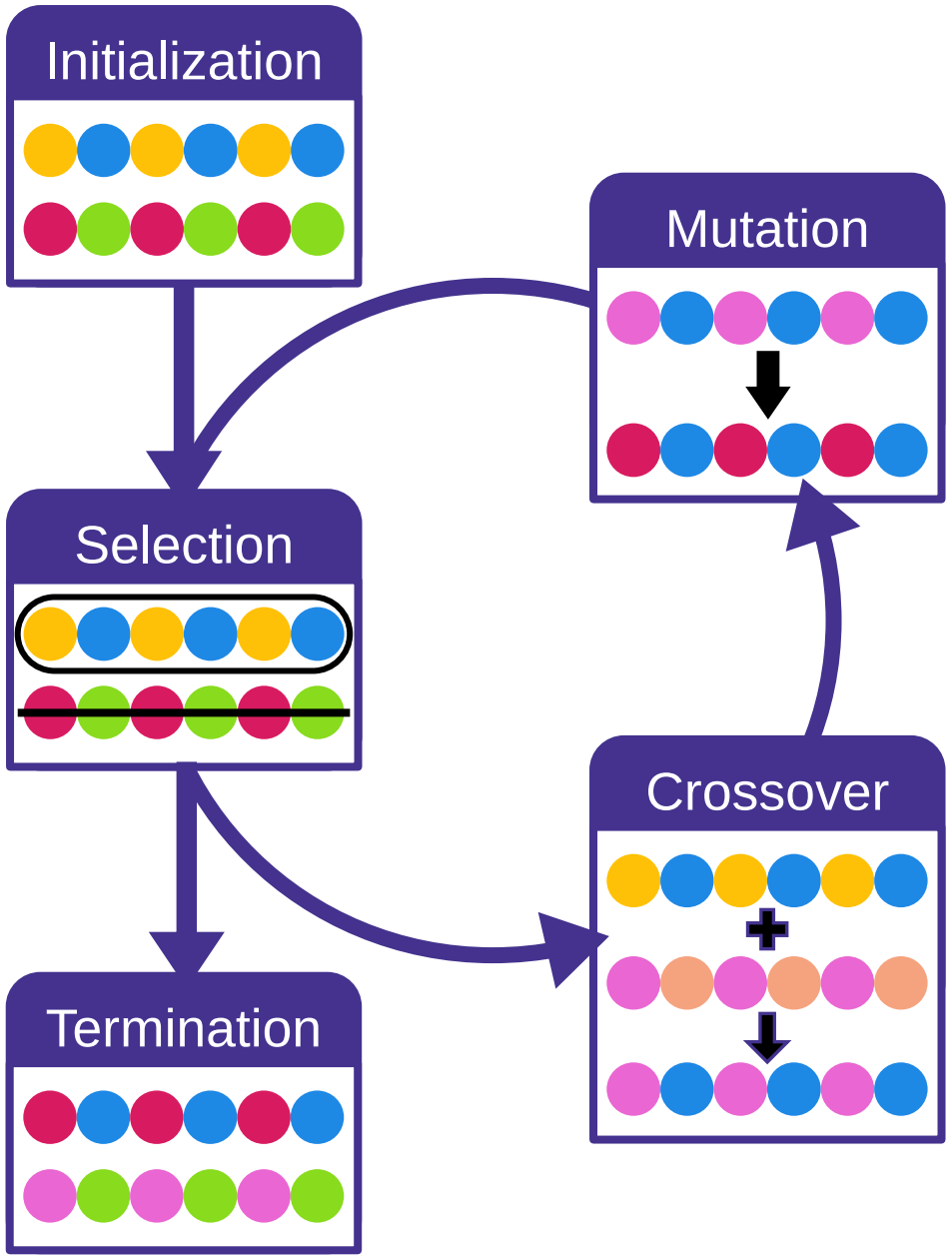
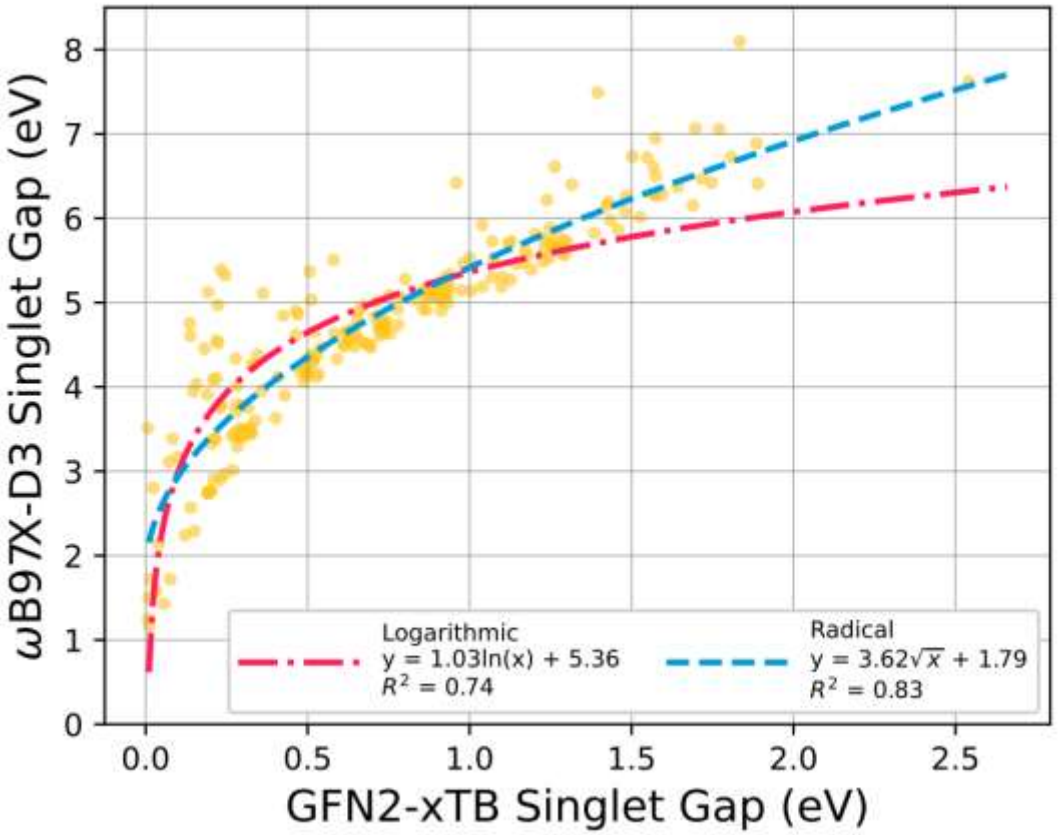
Genetic Algorithm

Accelerate the search for new high-spin conjugated polymers



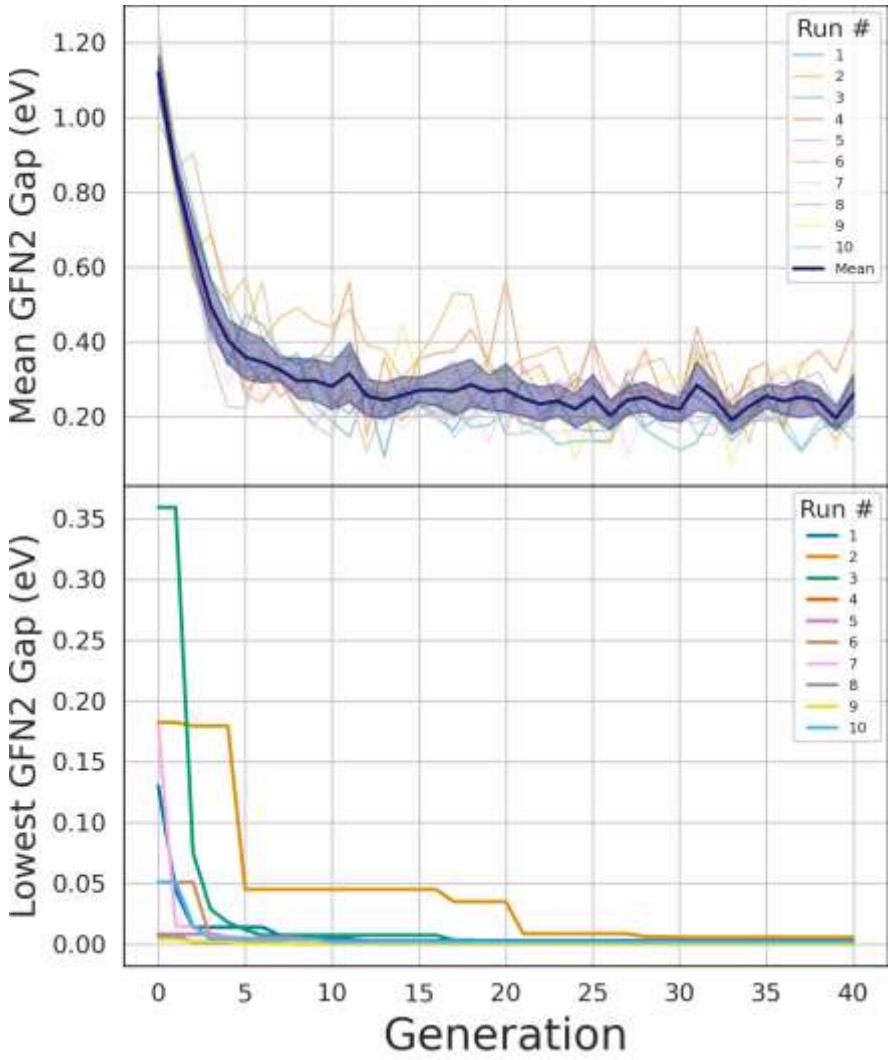
DFT Surrogate

- GFN2 can act as a surrogate for DFT
  - Faster
  - Correlates with DFT HOMO-LUMO gaps



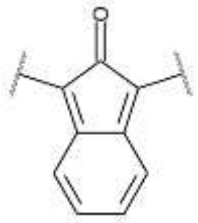
Genetic Algorithm

- Minimize the GFN2 HOMO-LUMO gap
- 1226 monomers
- 10 runs, 40 generations each

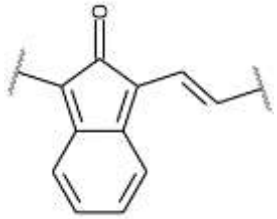


Top Oligomers

- Top 20 oligomers with low GFN2 gap
  - All show a very stable triplet ground-state
- All share either monomer 35 or 642



35



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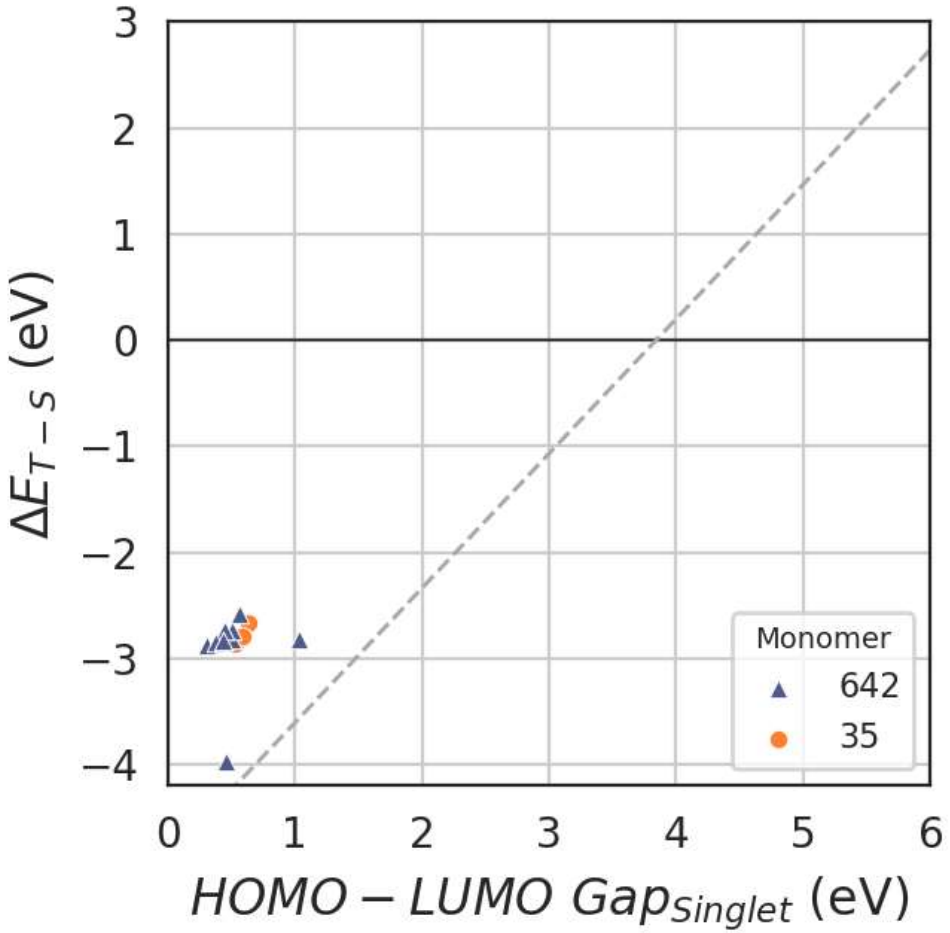
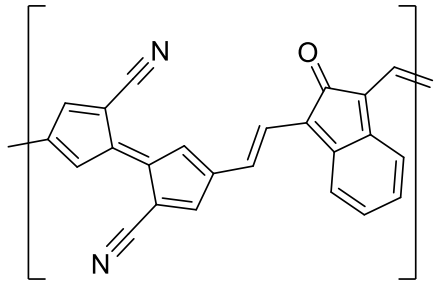


Spin Density

- Spin density plot show delocalization of the unpaired electrons



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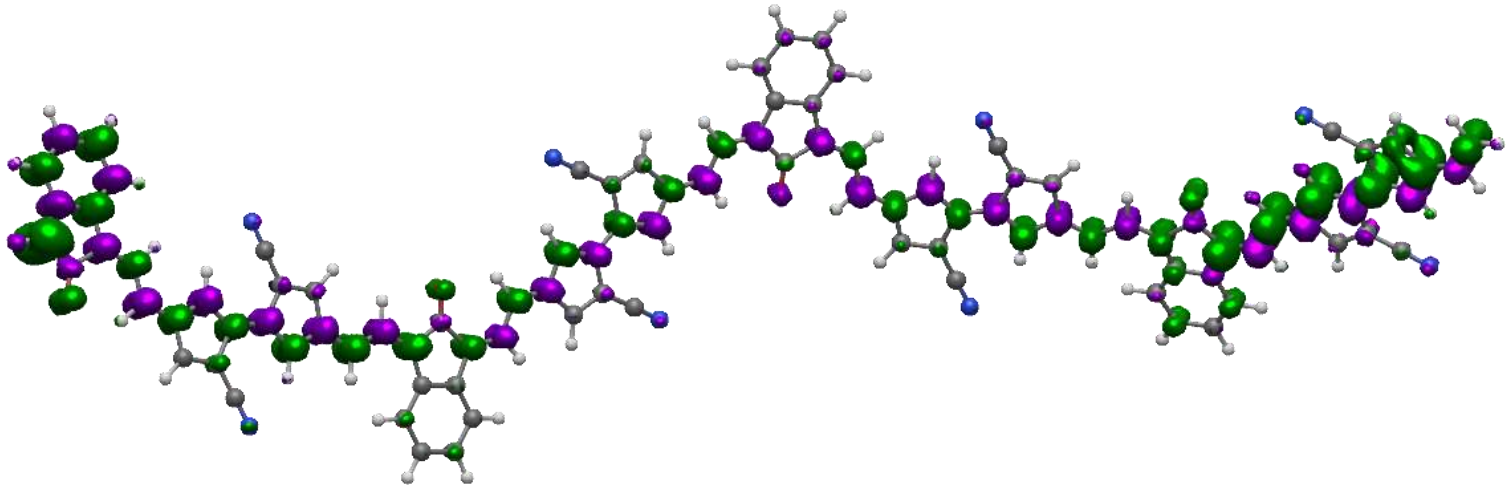
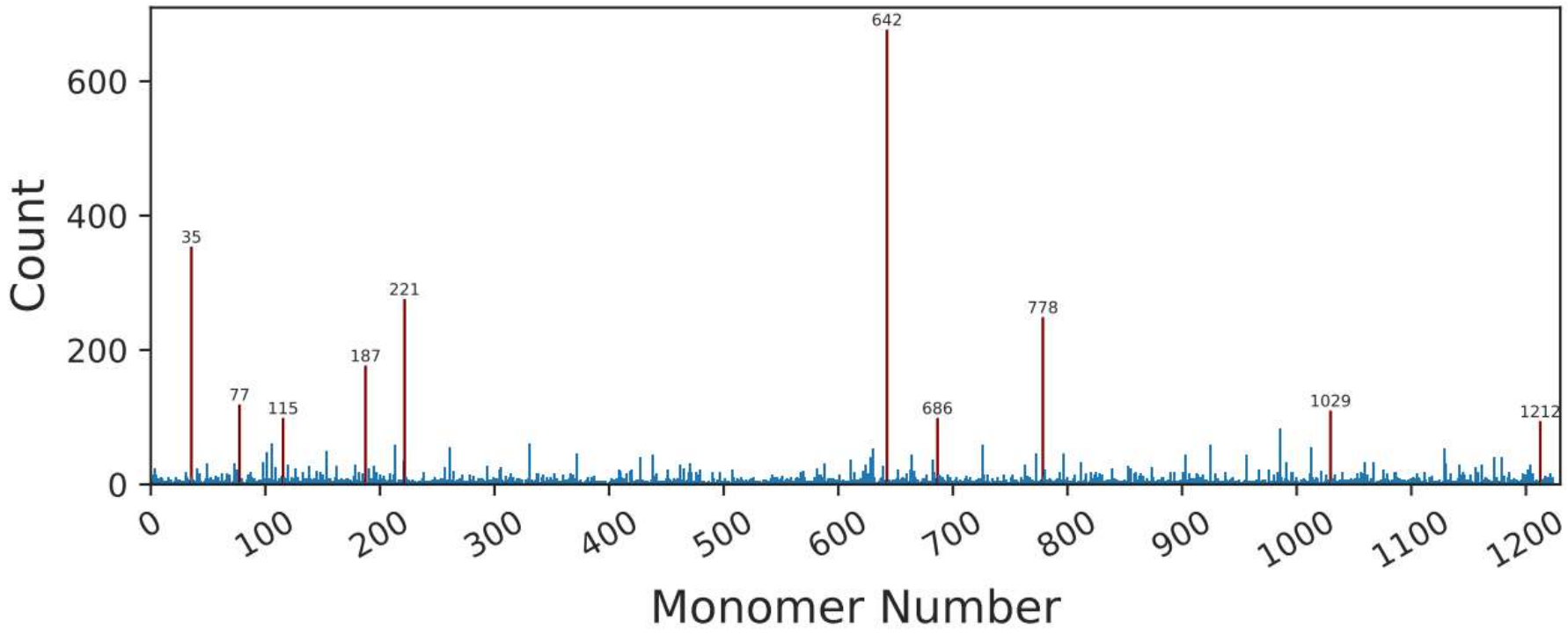
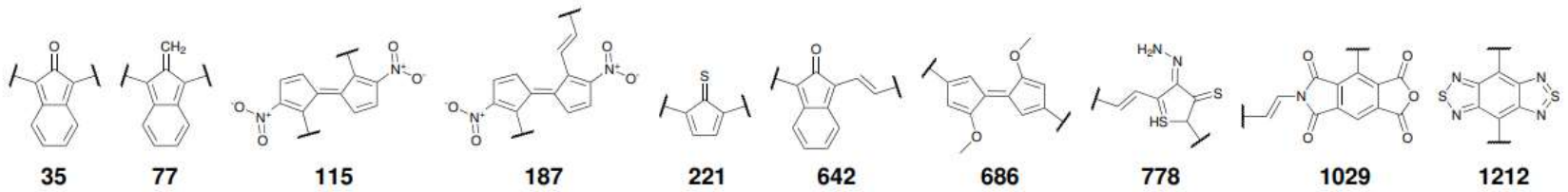


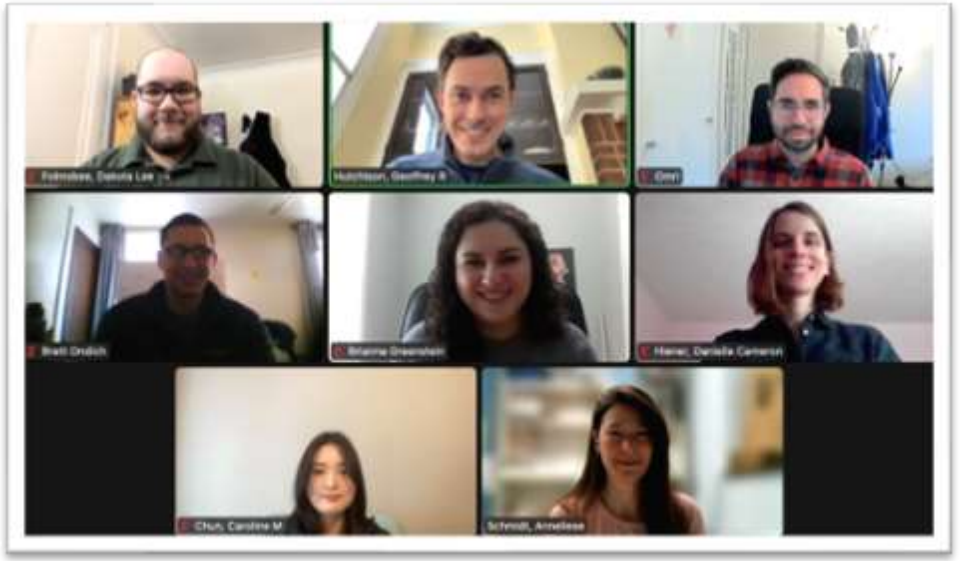
Common Monomers





Conclusions

- Smaller gap ➔ more stable triplet ground state
- The genetic algorithm works
  - New polymers with stable triplet ground-state
- Some monomers are better at inducing smaller gap
  - But the monomer combination is important



Thank You

QUESTIONS?

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