Computational Discovery of Stable Conjugated Biradicals

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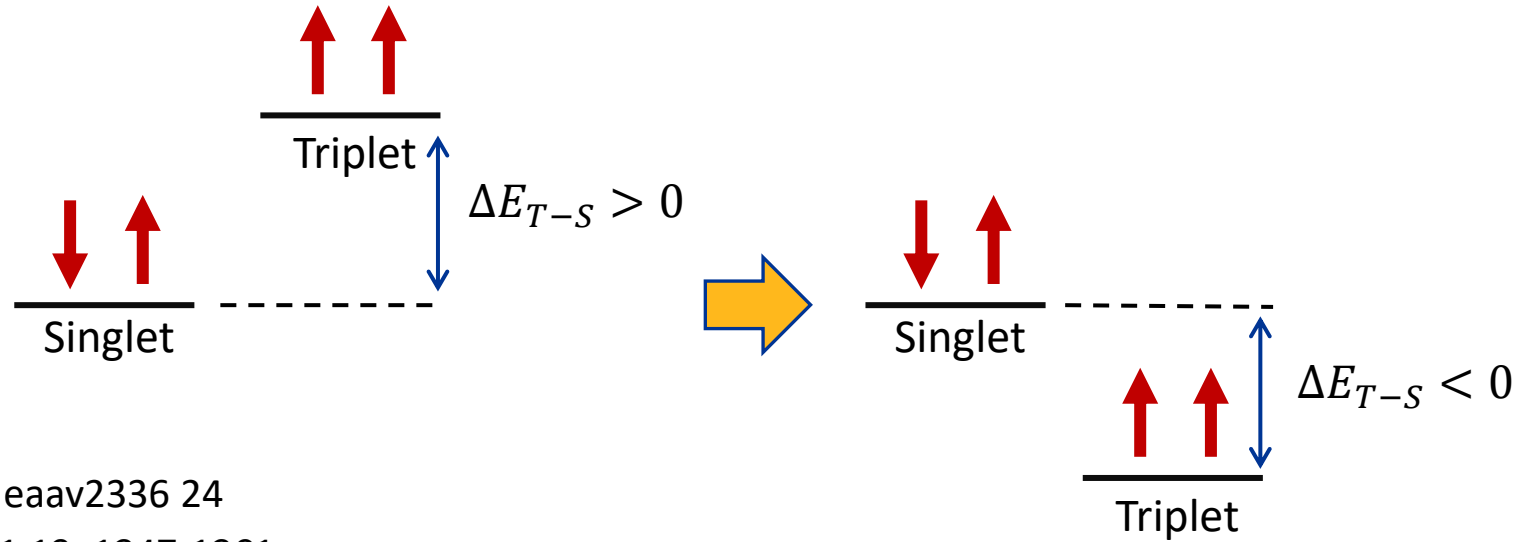
AUGUST 21, 2022

Conjugated Biradicals

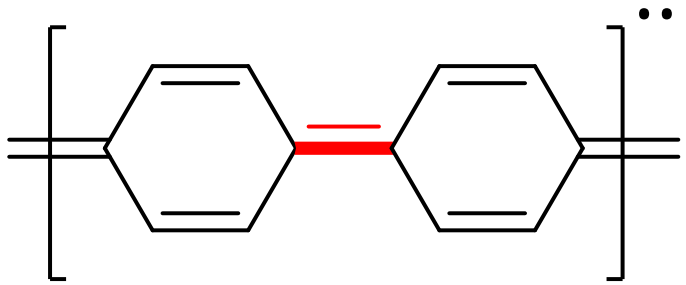
- Organic polymers with a stable triplet ground state
- Unique properties & potential uses
- Made from alternating donor-acceptor monomers



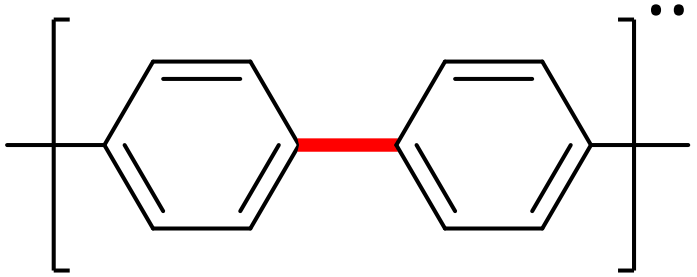
London et al., Sci. Adv. 2019;5 : eaav2336 24
Fang et al., Polym. Chem., 2021,12, 1347-1361

Why Are They Stable?

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



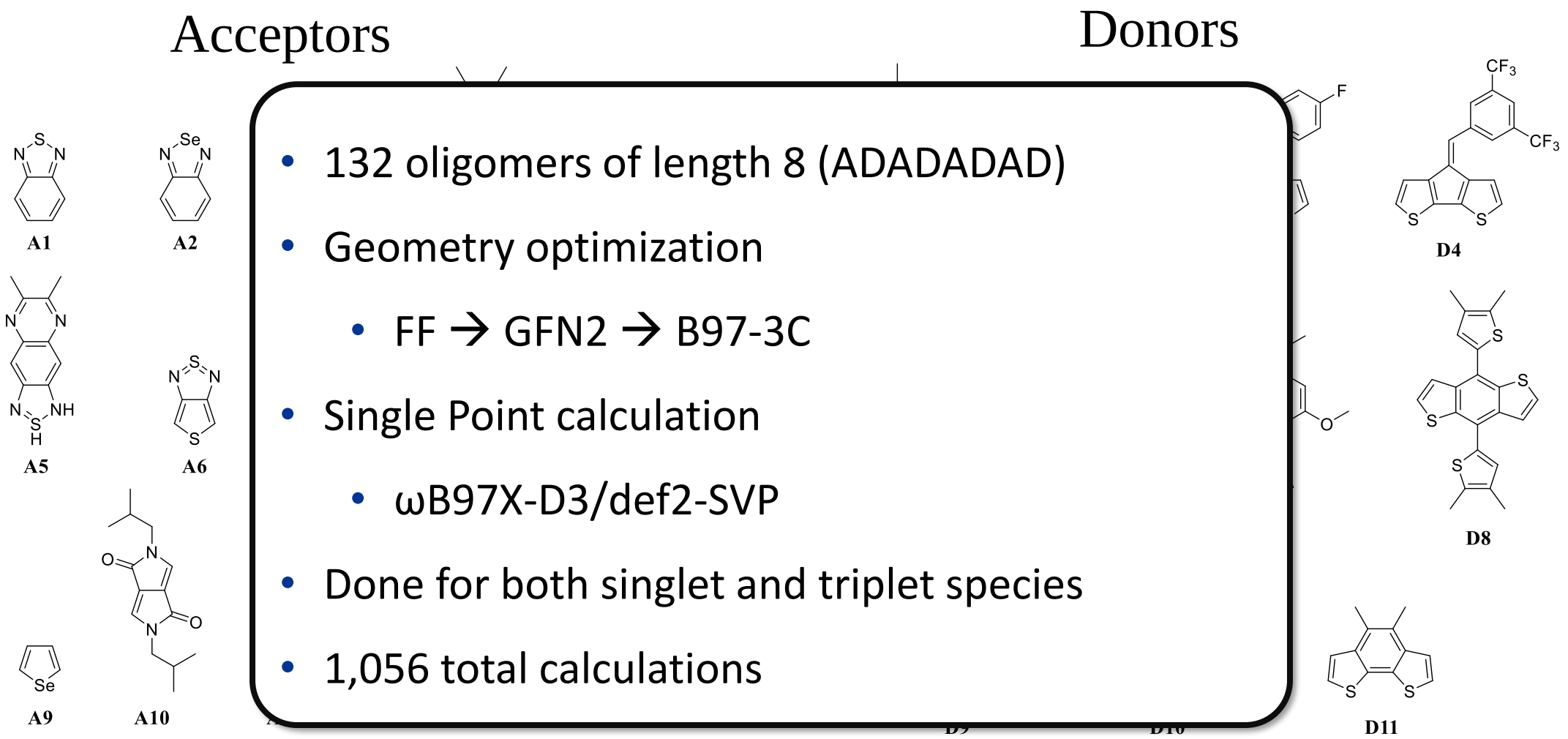
Quinoidal



Aromatic

London et al., Sci. Adv. 2019;5 : eaav2336 24
Fang et al., Polym. Chem., 2021,12, 1347-1361

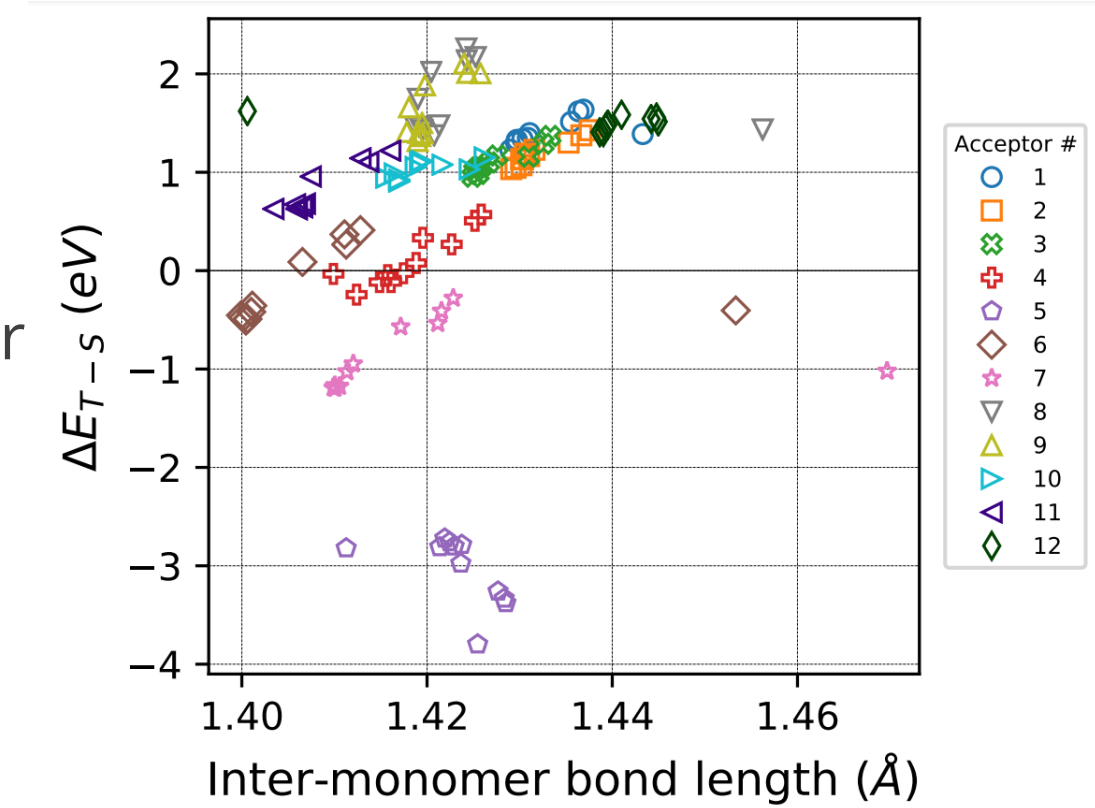
Computational Study



- 132 oligomers of length 8 (ADADADAD)
- Geometry optimization
  - FF → GFN2 → B97-3C
- Single Point calculation
  - ωB97X-D3/def2-SVP
- Done for both singlet and triplet species
- 1,056 total calculations

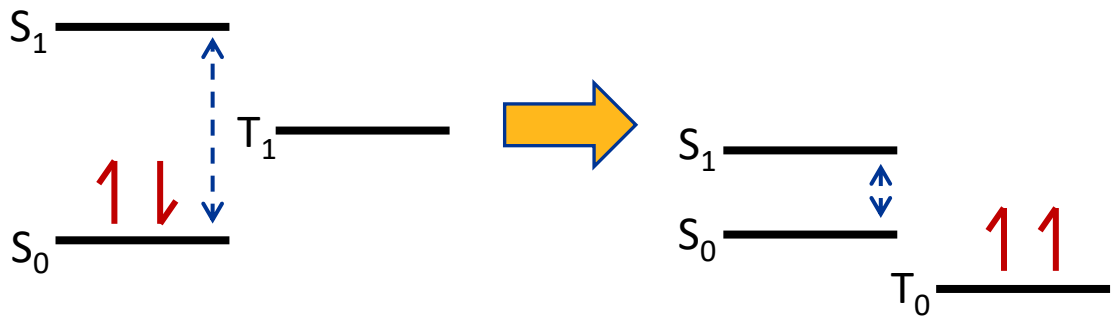
Inter-Monomer Bond Length

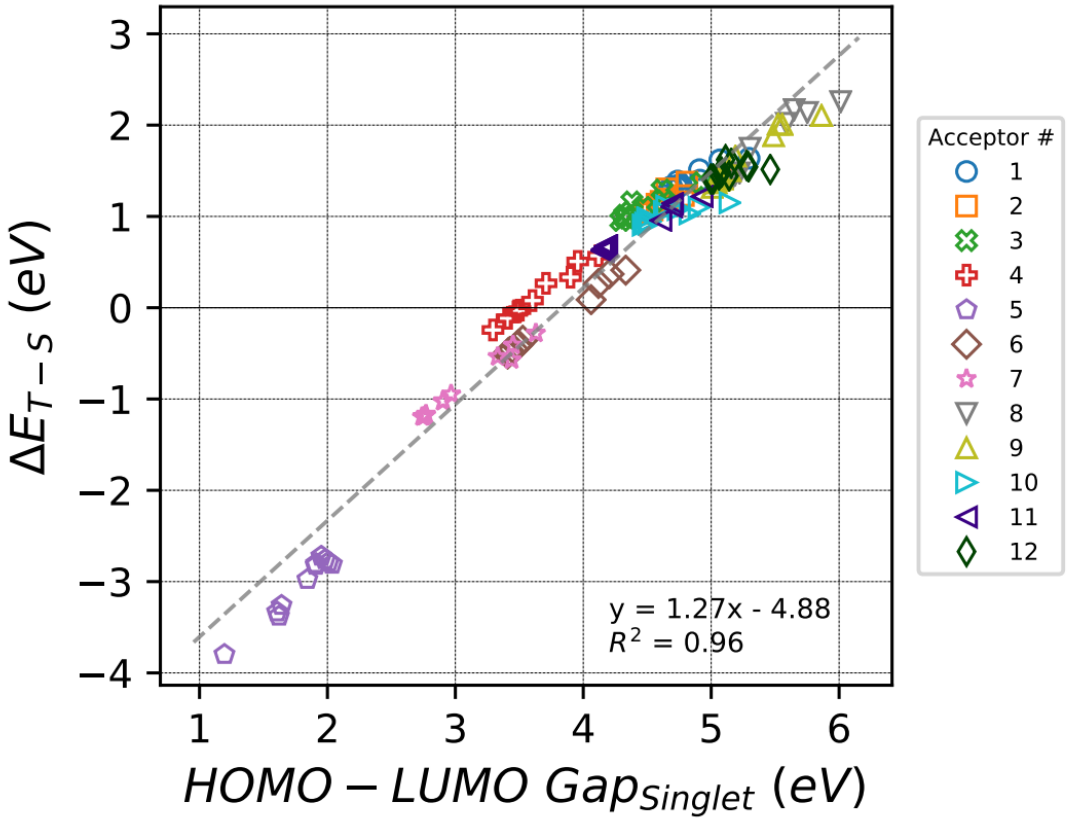
- If the quinoidal hypothesis is correct
  - Bond lengths should be smaller as the triplet stability increases
  - This is not the case…
- Bonding structure is not a global predictor
  - What is?



HOMO-LUMO Gap

- Triplet stability comes from a small HOMO-LUMO gap





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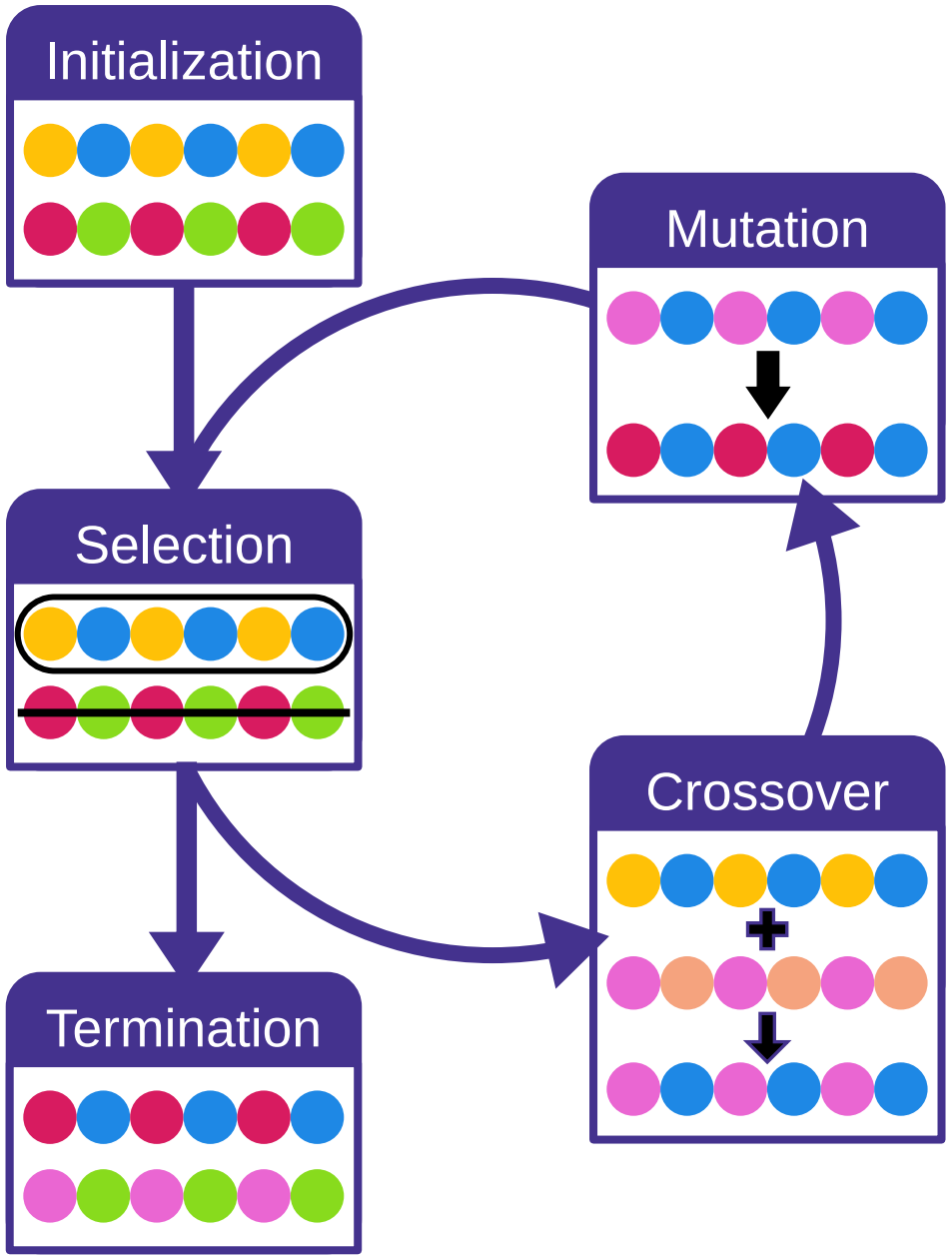
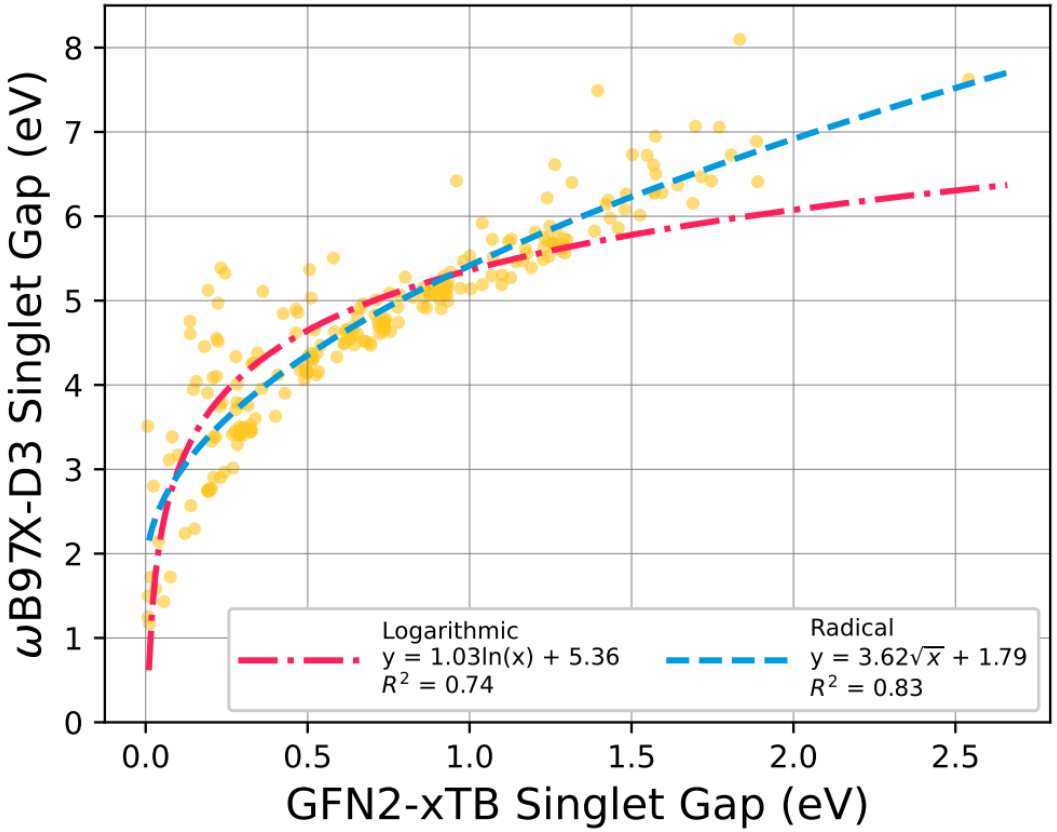
Genetic Algorithm

Accelerate the search for new high-spin conjugated polymers



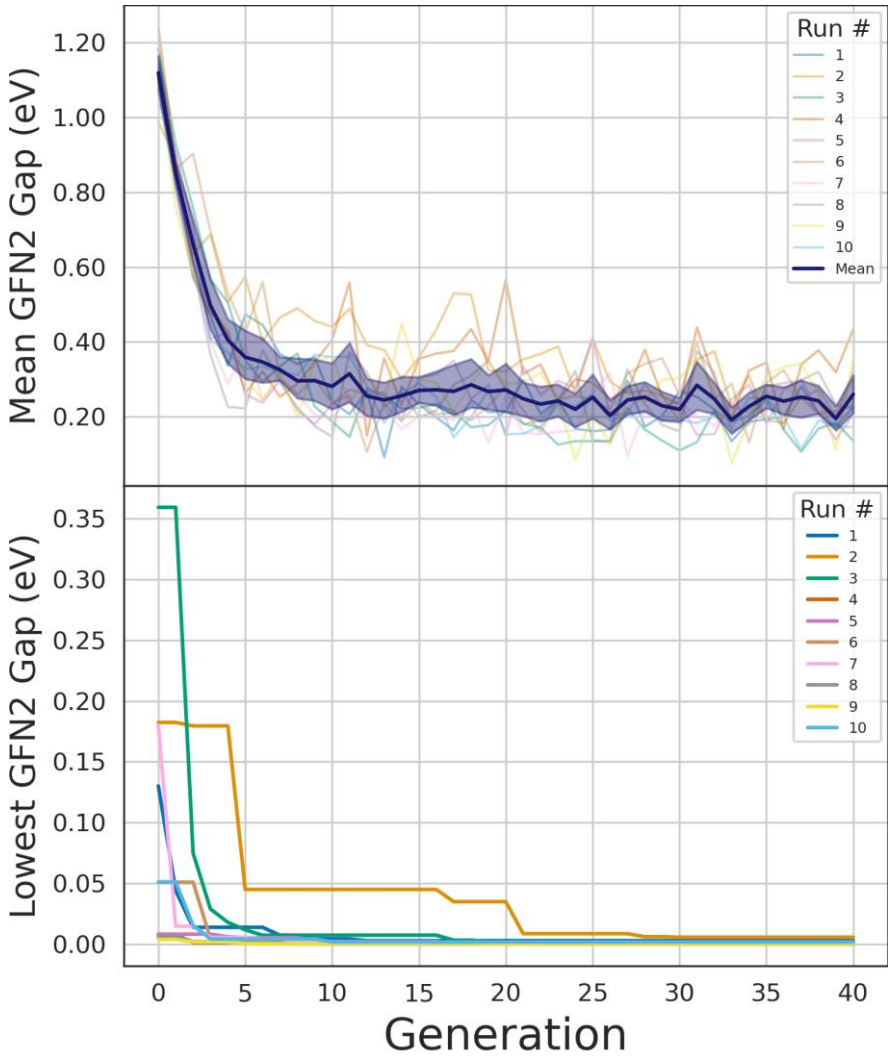
DFT Surrogate

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



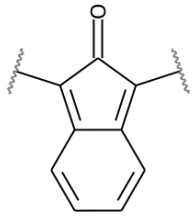
Genetic Algorithm

- Minimize the GFN2 HOMO-LUMO gap
- 1225 monomers
  - ~1.5 million combinations
- 10 runs, 40 generations each

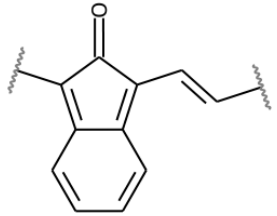


Top Oligomers

- 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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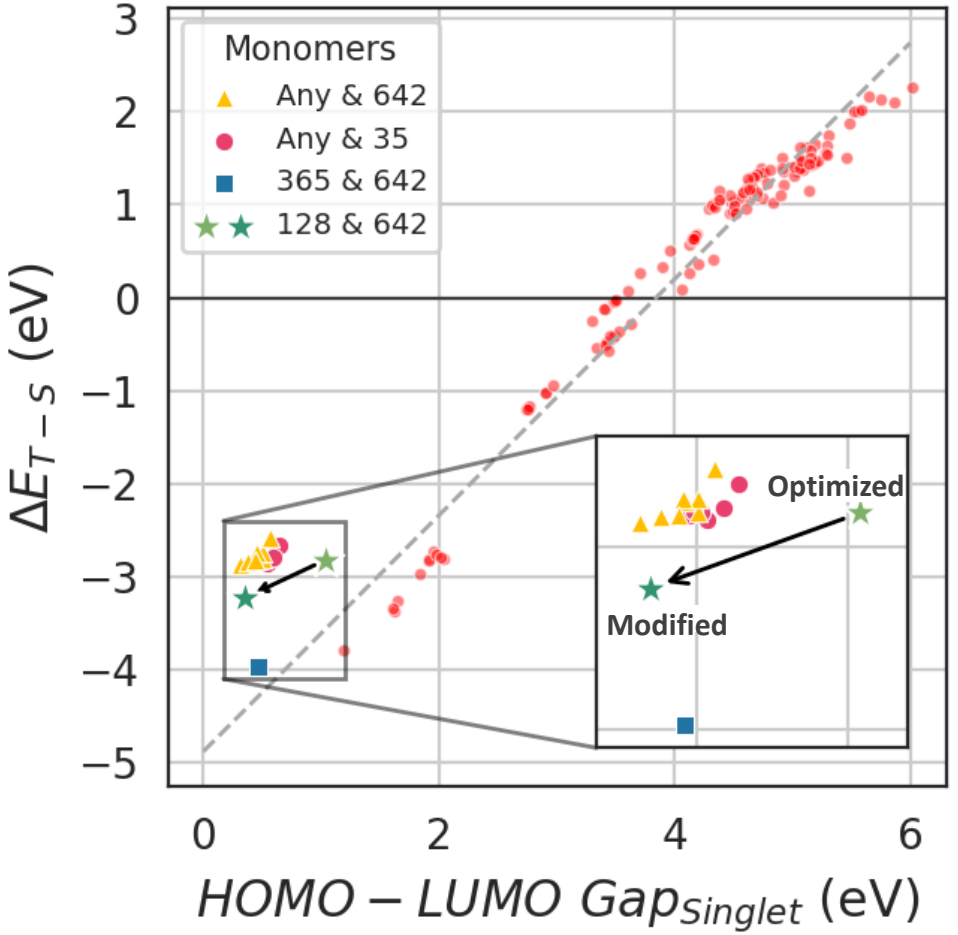
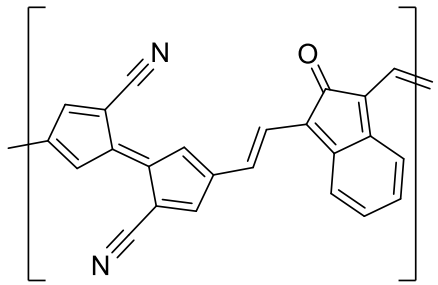


Spin Density

- Spin density plot show delocalization of the unpaired electrons

630-642



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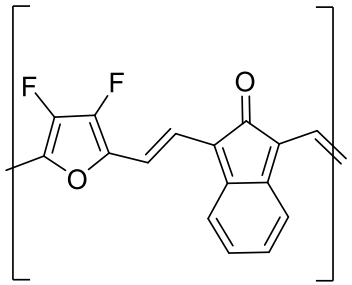
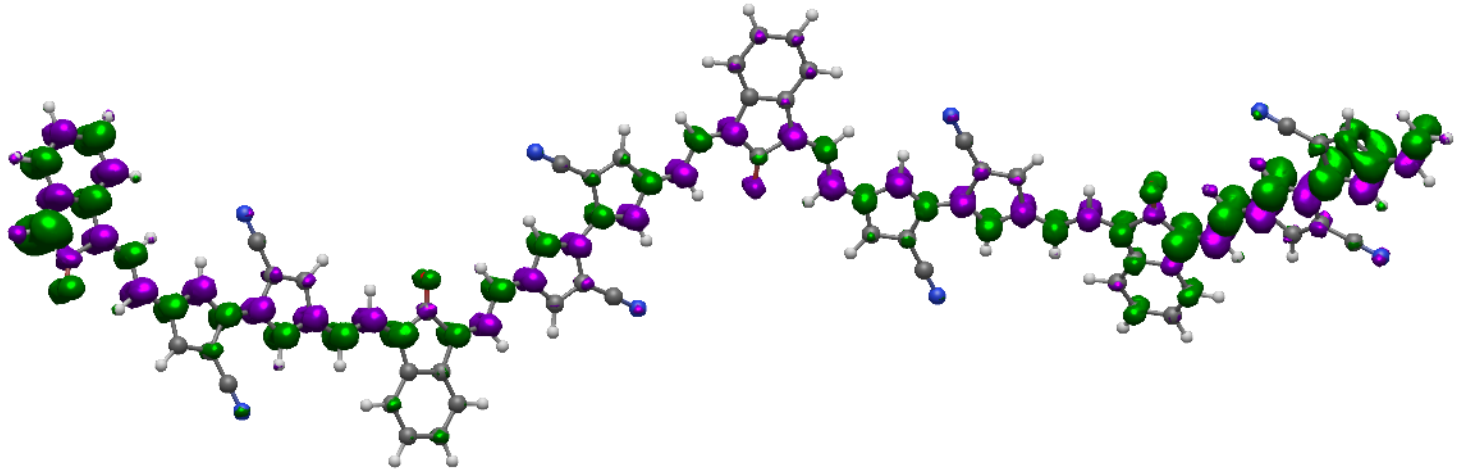
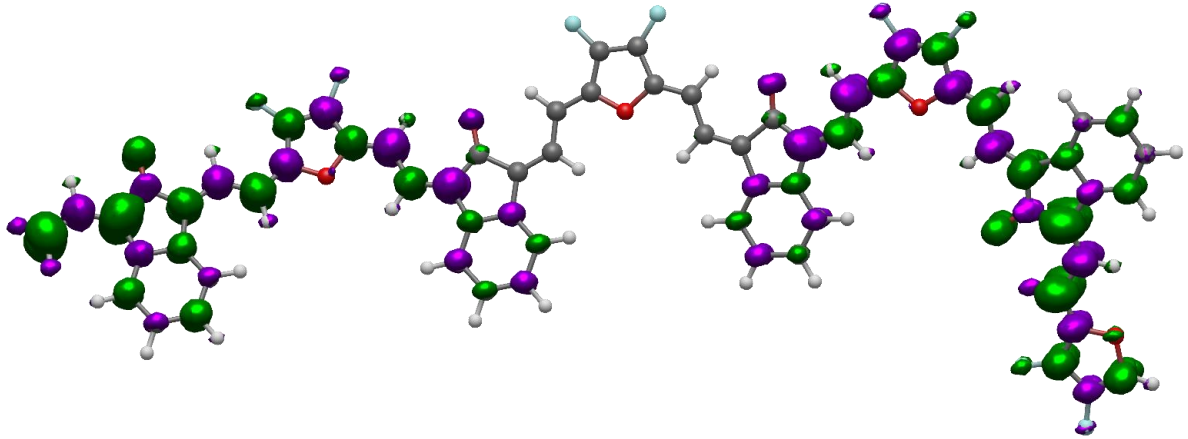
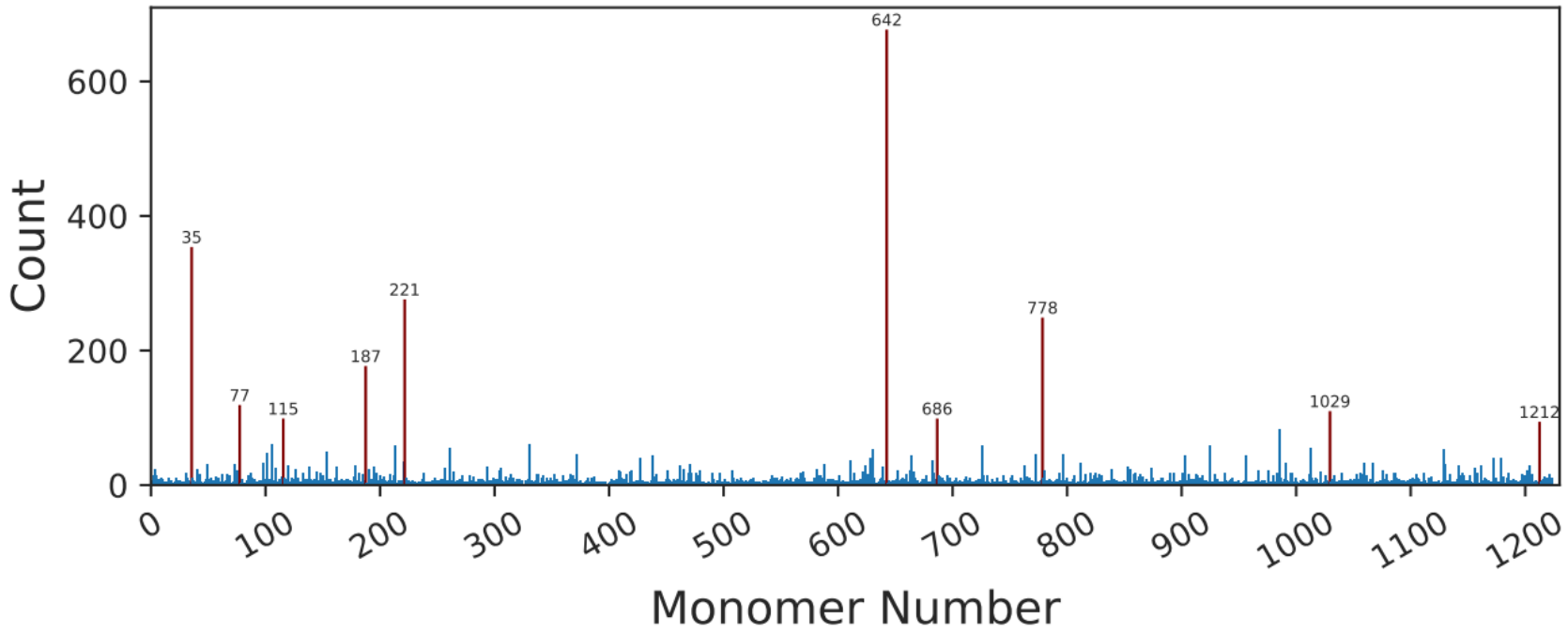
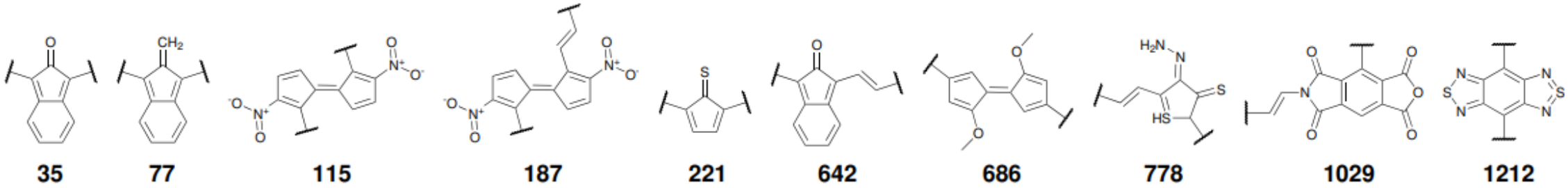






Common Monomers



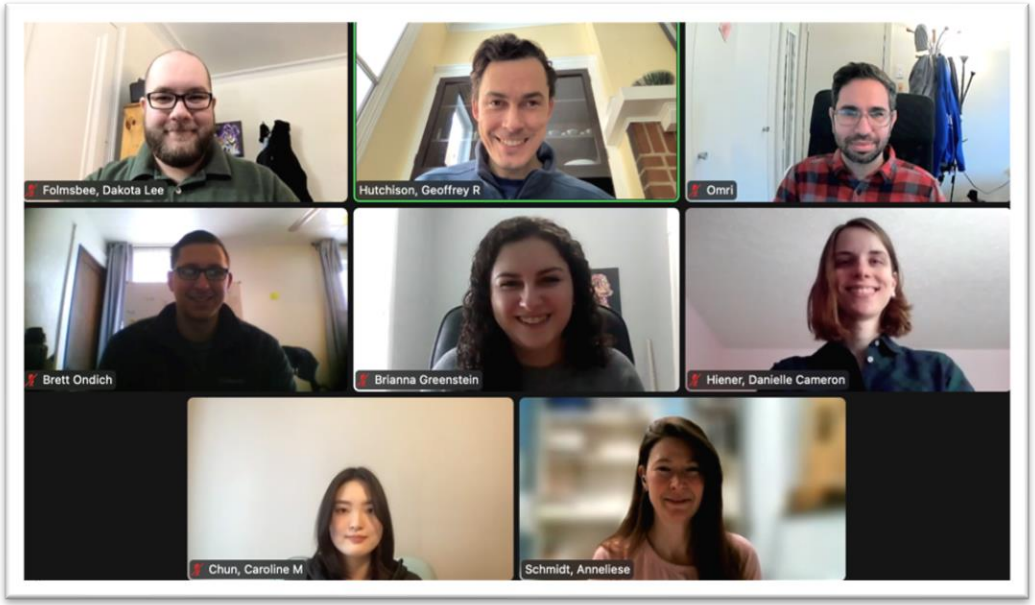


Conclusions

- Bonding structure is not a global predictor
- Smaller gap leads to a more stable triplet ground state
- Searching for low gap oligomers is a good design strategy
- Some monomers are better at inducing smaller gap
  - But the monomer combination is more important
- **We have found new polymer candidates**

https://doi.org/10.1021/acs.jpclett.2c00509

https://doi.org/10.26434/chemrxiv-2022-g5qfr



Thank You

QUESTIONS?

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