Novel Mechanisms to Tune Electronic Characteristics in Small-Molecule Organic Semiconductors

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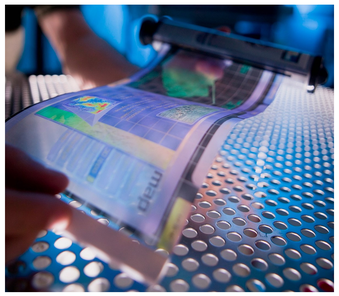
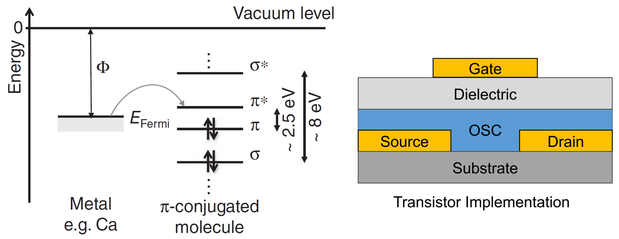
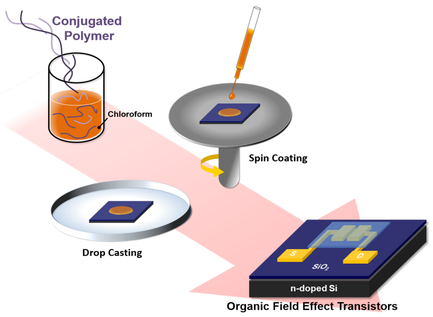
Promise of Organic Semiconductors



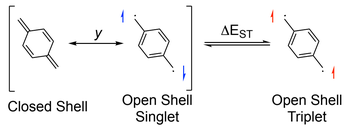


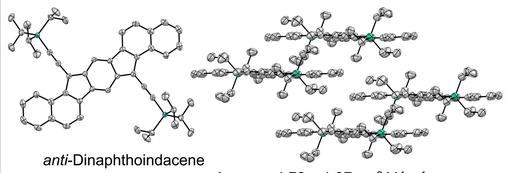


- Organic semiconductors possess inherent advantages over their current inorganic counterparts.
- Manufacture is much less energetically harsh, and high solubility enables unique processing techniques.
- Solution processing and roll-to-roll printing promise easier device fabrication.
- Bottom-up synthesis of small molecule semiconductors allows for high modularity to tailor specific electronic applications.
- Tuning these systems modulates important electronic properties such as frontier molecular orbitals.
- Establishing structure-property relationships will be important for optimizing these molecules for application in electronic devices.

Köhler, A.; Bässler, H. *Electronic Processes in Organic Semiconductors,* 1st Ed.; Wiley-VCH Verlag GmbH; Weinheim, 2015.

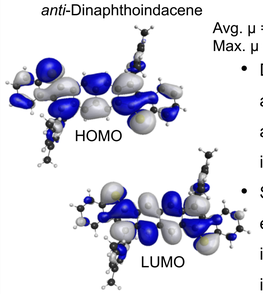
Ideal Characteristics





anti-Dinaphthoindacene

Avg. μ = 4.72 ± 1.97 $cm^2\ V^{-1}\ s^{-1}$
Max. μ = 7.12 $cm^2\ V^{-1}\ s^{-1}$



***LC-RBLYP/6–311G(d)**

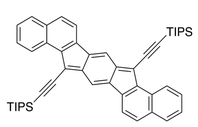
- Degree to which molecule exists as a diradical in favor of aromatizing its core is known as its diradical character index, y_0.
- Slip-stacking in the solid state enhances conductivity through increased orbital overlap, which is crucial for electron mobility.
- Magnetic properties, governed by ΔE_{ST}, allow for access of desirable electronic states.

Dressler, J. J.; et al. *Nat. Chem.* **2018**, *10*, 1134-1140.

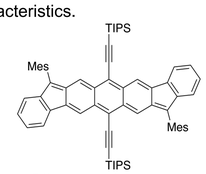
Project Diradical

Indeno[1,2-b]fluorene

- Diradical character is defined as molecular possession of two unpaired electrons, which interact to produce a single spin state.
- Increased diradical character leads to favorable characteristics such as decreased HOMO-LUMO energy gaps.
- Many diradical molecules are known, but this phenomenon still is not well understood.
- Our lab has since aimed to build a library of analogues to further optimize electronic characteristics.



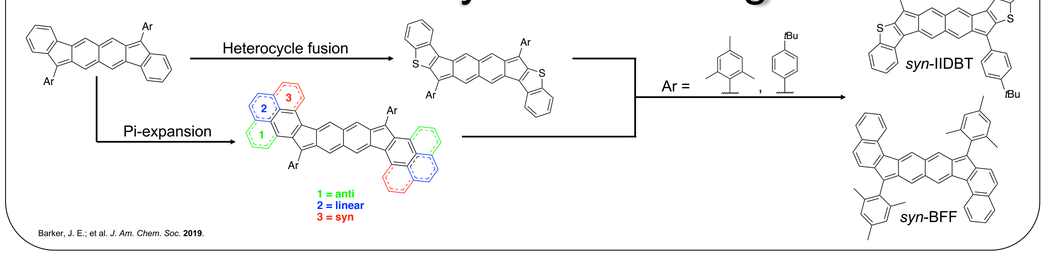
Dinaphthoindacene



Diindenoanthracene

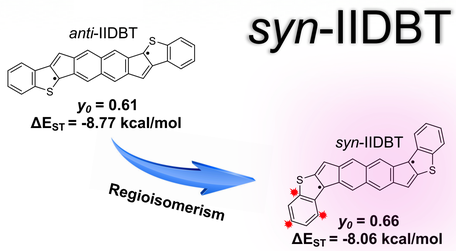
Chase, D. T.; et al. *Angew. Chem. Int. Ed.* **2011**, *50*, 1127-1130.
Frederickson, C. K.; et al. *J. Am. Chem. Soc.* **2016**, *138*, 16827-16838.
Rudebusch, G. E.; et al. *Nat. Chem.* **2016**, *8*, 753-759.

Modular Synthetic Tuning



Barker, J. E.; et al. *J. Am. Chem. Soc.* **2019**.

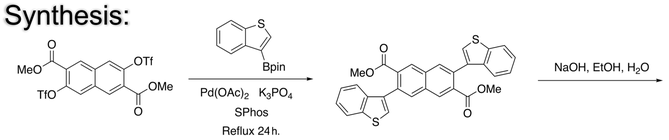
syn-IIDBT

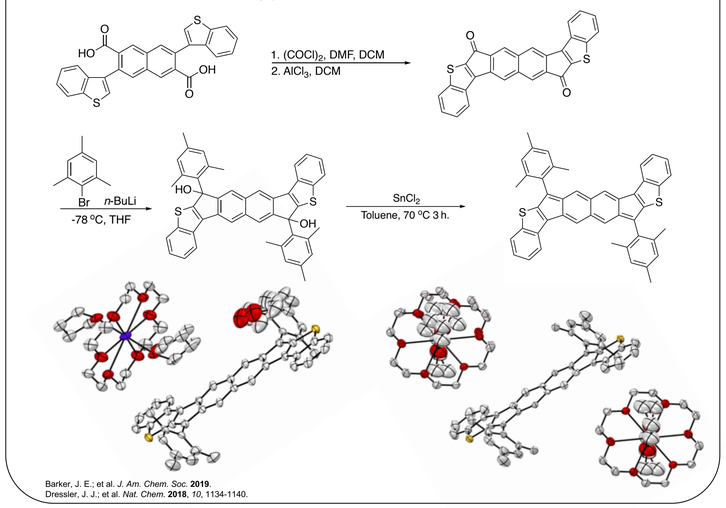


y_0: PUHF/6-311G*
ΔE_{ST}: (SF-NC-)TDDFT PBE50/6-311G*

- Reported in 2018, *anti*-IIDBT showed high diradical character with a relatively high singlet-triplet energy gap (ΔE_{ST}).
- Modulating the direction of fusion of terminal benzothiophene units was expected to increase electron delocalization around the core system.
- This in turn increases diradical character, as denoted by calculated y_0 values, and lowers the singlet-triplet energy gap.

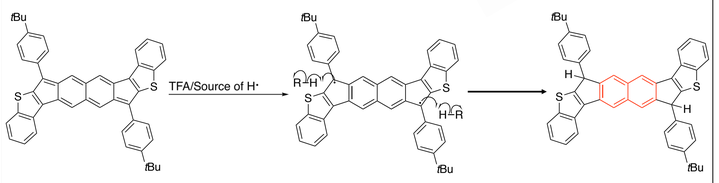
Synthesis:

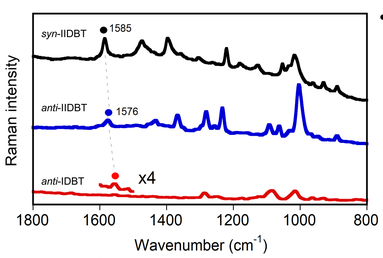




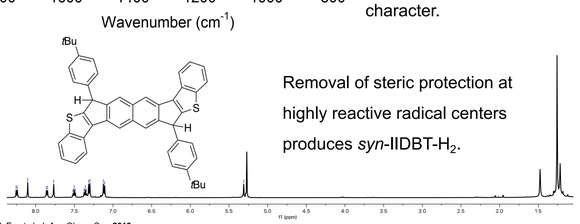
Barker, J. E.; et al. *J. Am. Chem. Soc.* **2019**.
Dressler, J. J.; et al. *Nat. Chem.* **2018**, *10*, 1134-1140.

Characterization





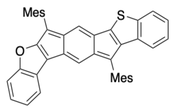
- Shifted Raman spectrum, red-shifted UV-VIS absorbance, and easier population of the triplet state in HT-SQUID measurements corroborate that *syn*-IIDBT possesses a lower ΔE_{ST} than *anti*-IIDBT and exhibits higher diradical character.

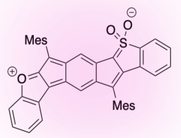


Removal of steric protection at highly reactive radical centers produces *syn*-IIDBT-H_2.

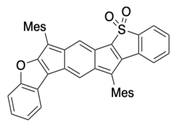
Barker, J. E.; et al. *J. Am. Chem. Soc.* **2019**.
Dressler, J. J.; et al. *Nat. Chem.* **2018**, *10*, 1134-1140.

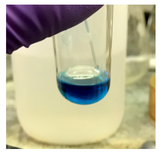
syn, anti-IBFBT





syn, anti-IBFBT-sulfone

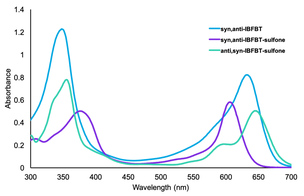


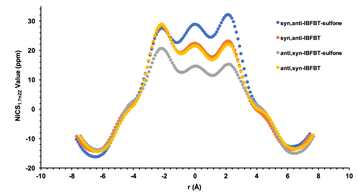


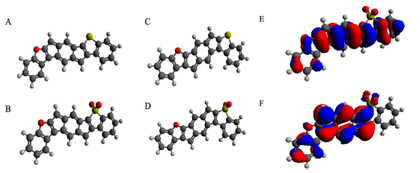
- Asymmetric scaffold incorporating heteroatoms and sulfonation locations around the *s*-indacene core has yet to be explored.
- IBFBT lacks symmetry on three fronts: fusion directions, heteroatom incorporation, and sulfonation.
- Intriguingly, IBFBT may act as a donor-acceptor system and exhibit ”push-pull” characteristics which may further act as a mechanism to tune electronic characteristics.

Strand, E. T.; *Manuscript in preparation.* **2020**.

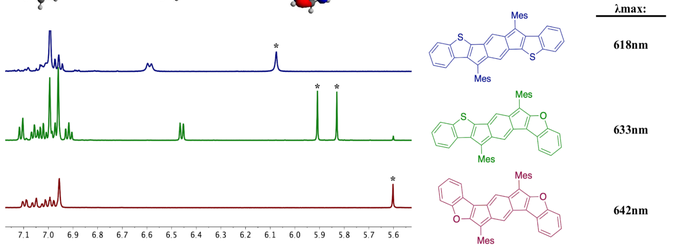
Late-Stage Modification Tunes Molecular Orbitals







	HOMO (eV)	LUMO (eV)	Gap (eV)
A	-5.291	-3.436	1.855
B	-5.692	-4.017	1.675
(flipped)	-5.659	-4.015	1.644
C	-5.258	-3.416	1.842
D	-5.868	-3.844	2.024



- Our future plans include continued work toward the synthesis of a wide variety of analogues to better identify properties for optimization of organic semiconductors.

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