Design and Synthesis of Functionalized Organic Semiconductors

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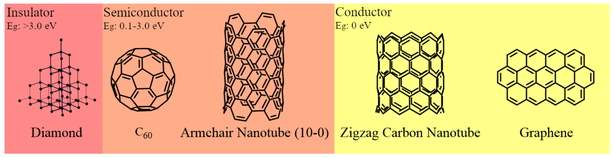
Intro & Background

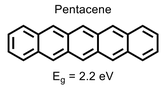
Allotropes of Carbon Have Varying Conductivities



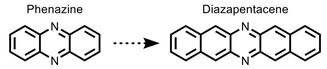
Molecules with the same molecular formula but different structures can have very different physical and electronic properties. Synthesis can be used to fine-tune these properties.

Organic Semiconductors (OSCs):

Organic (carbon containing) semiconductors (materials with conductive and insulative properties) have promising potential in the fields of nanotechnology and solar cells; however, due to instability and low charge carrier mobility, their commercialization has been hindered. An example of an unstable semiconductor is pentacene.



Pentacene is a great semiconductor but is unstable due to oxidation.



Diazapentacene, a phenazine derivative, is more stable than pentacene but has lower charge carrier mobility.

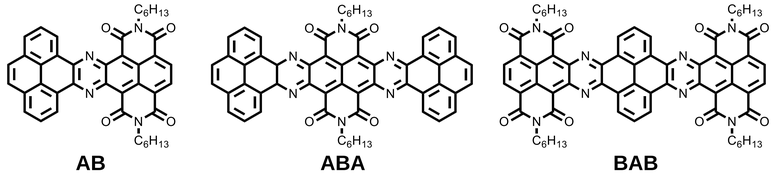
Objective:

Design and functionalize new phenazine derivatives to target new semiconductor candidates and understand how structure and functionality impact optical and electrical properties.

Specific Targets:

Phenazine derivatives of NDI, a great π-conjugated, electron accepting n-type semiconductor.

Target Phenazines:



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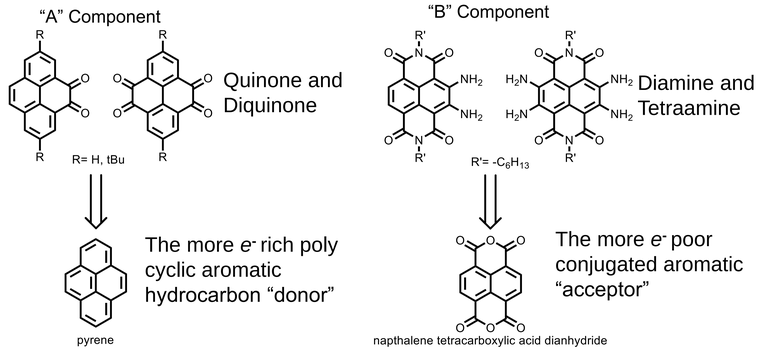
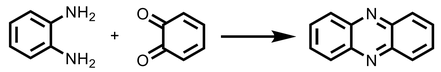
Synthetic Plan & Components

Target Precursors:



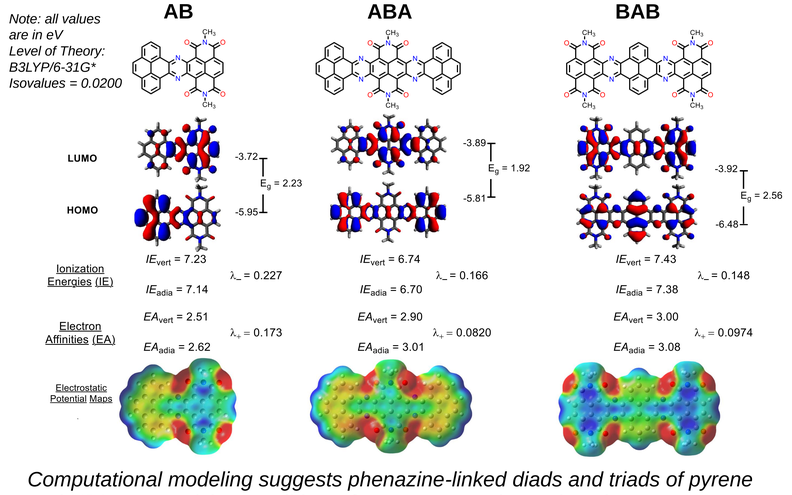
How does the arrangement of donor and acceptor units impact properties?

Condensation of Diamines and Quinones, eg:



"A" and "B" components will be joined together via a condensation reaction.

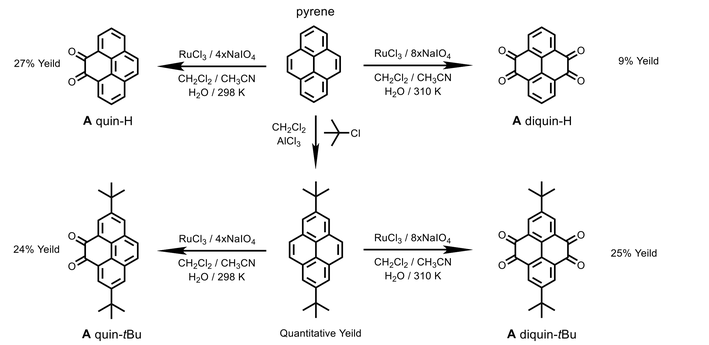
Computational Modeling Results



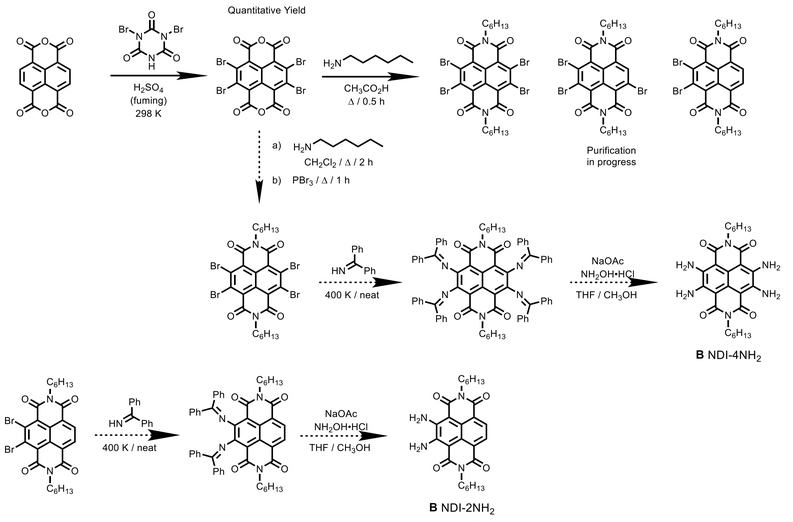
Computational modeling suggests phenazine-linked diads and triads of pyrene and NDI are promising candidates for n-type organic semiconductors:

- As predicted, pyrene acts as the more e^- rich "donor" while NDI behaves as the more e^- poor "acceptor" as observed by HOMO, LUMO, and electrostatic potential plots
- HOMO-LUMO gaps are all predicted to be < 3.0 eV
  - Range: 1.92-2.56, Pentacene: 2.21 eV
- The desired electron affinity (EA) for n-type semiconductors is 3.0 < EA < 4.0 eV, which is predicted for triads ABA and BAB
- Reorganization energies ($\lambda_{+/-}$) below 0.20 eV are desired for efficient electron transfer, which also is predicted for the triads
  - Pentacene: λ_+ = 0.093, λ_- = 0.132 eV

Synthesis Results



Synthesis and purification of the pyrene components has been successful. In addition to the default di and mono-quinones, tertbutyl versions have been created.



Synthesis of the di and tetra-amines is on going. Currently the amination reaction is being troubleshooted.

Conclusions & Future Work

Since the computational modeling showed promising semiconductive properties of the triads, synthesis will be continued. While the computational work showed slightly less promise for the diad, its synthesis will be carried through in order to understand how molecule length impacts electronic properties. Next steps involve the completion of the NDI components as well as the condensation reactions between them and the pyrene derivatives. Once the target molecules have been purified, their electronic properties will be compared to the computational predictions. Finally, further functionalization will be repeated in hope of fine tuning electronic and/or optical properties.

Acknowledgements

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