Coursework

Class Number & Title	**Grade**
Texas A & M University	
CHEM 610 – Organic Reactions & Mechanisms	B
CHEM 615 – Organic Synthesis	B
CHEM 646 – Physical Organic Chemistry	B
CHEM 647 – Spectra of Organic Compounds	A
CHEM 686 – Ethics in Chemical Research	A
CHEM 697 – Methods of Teaching Chemistry Laboratory (Organic Chemistry I Laboratory)	A
CHEM 697 – Methods of Teaching Chemistry Laboratory (Organic Chemistry II Laboratory)	A
University of Southern California	
CHEM 516 – Reactivity & Mechanism in Inorganic & Organometallic Chemistry	In Progress

Electron Transport Materials Based on Cyclodiborazane

Sean Owen Clancy

Advisor: Aaron W. Harper

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Outline

- History
- Background
- Synthesis
- Characterization
- Applications

History

- MacDiarmid, Heeger, and Shirakawa (1977) – Electrically Conductive Polymers
- Burroughes et al. (1990) – Electroluminescence (EL) in Conjugated Polymers
- Chujo et al. (1992) – Development of purportedly π-electron-deficient n-type π-conjugated polycyclodiborazane

Background

- Advantages / Disadvantages of PLEDs versus Conventional Inorganic LEDs
- Charge Transport
- Limitations of Electron Transport Materials
- Cyclodiborazane
- Single-Layer Device
- Triple-Layer Device

Advantages/Disadvantages of PLEDs vs. Inorganic LEDs

Advantages

- Cost
- Flexible substrate
- Size

Disadvantages

- Lifetime
- Stability
- Phase segregation

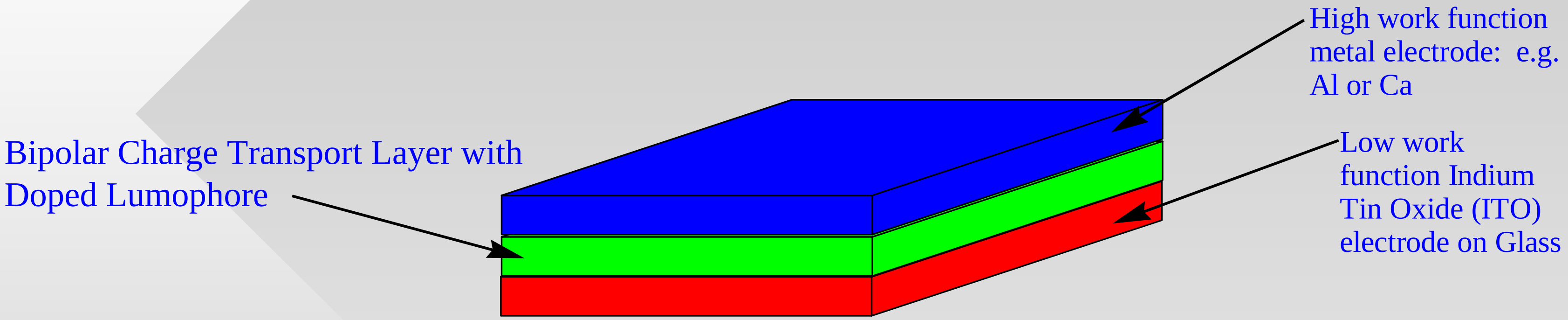
Charge Transport

– Background:

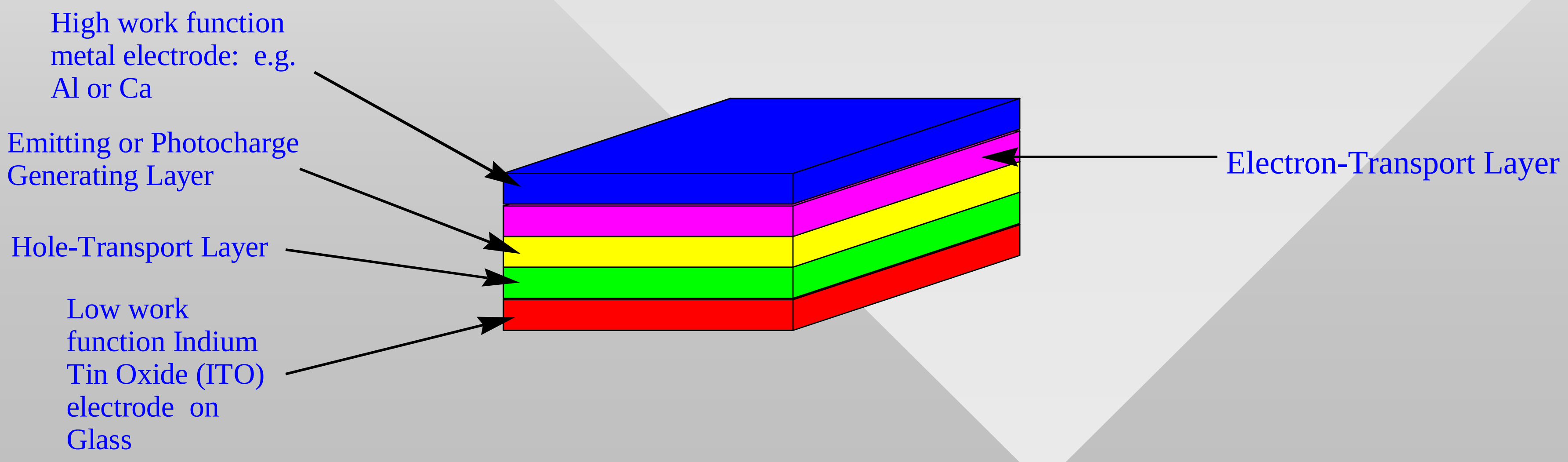
- The band gap is a region where no formal energy levels reside.
- All states below the gap are occupied and form the "π band," a.k.a. the valence band.
- States above the band are empty and form the "π^* band," a.k.a. the conduction band.
- The top of the "π band" is called the HOMO.
- The bottom of the "π^* band" is called the LUMO.

Charge Transport

Structure of a Single-Layer Device:



Structure of a Triple-Layer Device:



Charge Transport

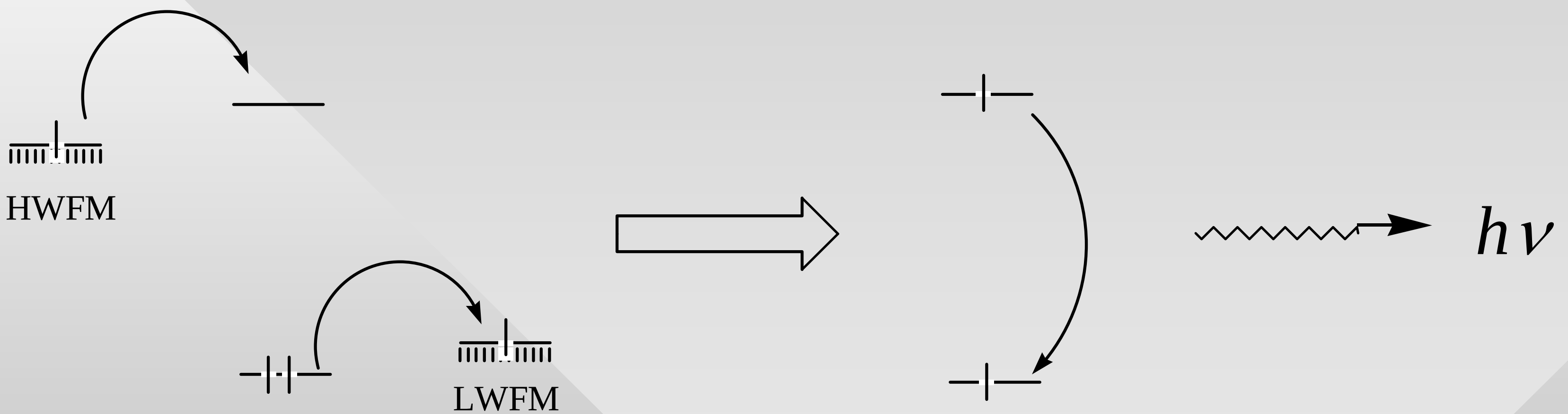
- When voltage is applied, a radical anion is formed in the ETL when the HWFM injects an electron into the ETL.
- This radical anion species travels through the π-conjugation of the ETL towards the positive electrode / LWFM.
- A radical cation is formed in the HTL when the LWFM removes an electron from the HTL.
- This radical cation species travels through the π-conjugation of the HTL towards the negative electrode / HWFM.

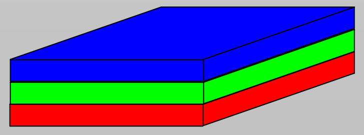
Charge Transport

- Charge recombination and formation of exciton.
- Formation of singlet and triplet excited states.
- A photon is released when the singlet state relaxes.

Charge Transport

– Single-Layer Device:

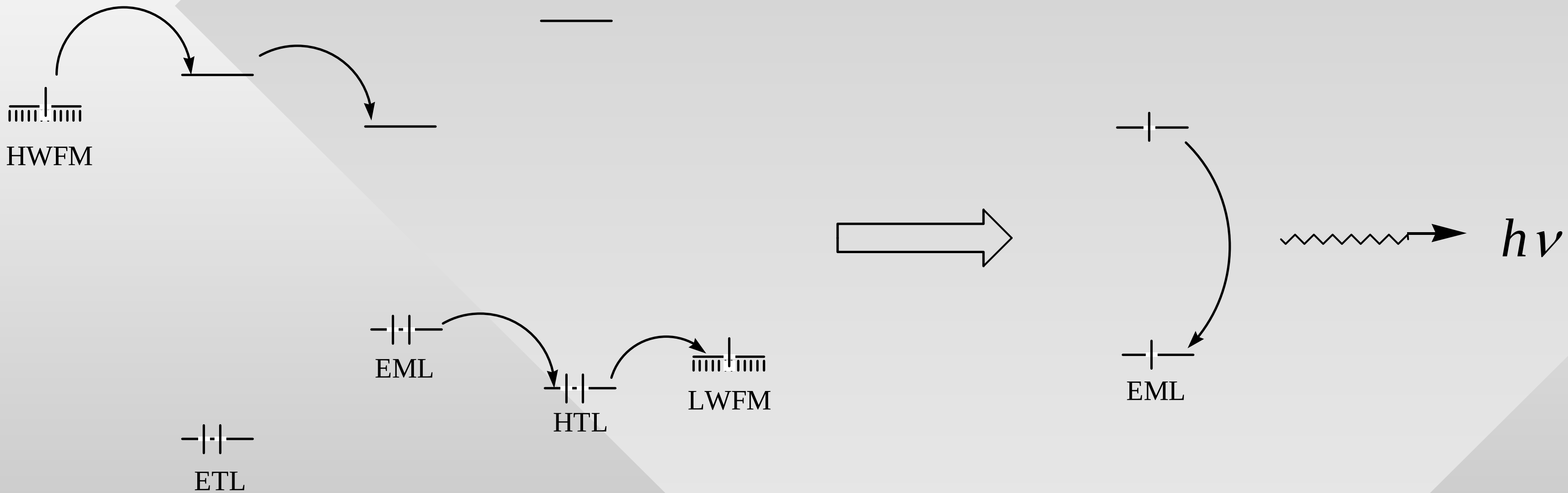


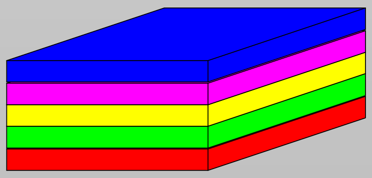


Legend:
HWFM = High Work Function Metal, e.g. Al or Ca
ETL = Electron Transport Layer
EML = Emissive Layer
HTL = Hole Transport Layer
LWFM = Low Work Function Metal, e.g. ITO (Indium-Tin Oxide)

Charge Transport

– Triple-Layer Device:





Legend:
HWFM = High Work Function Metal, e.g. Al or Ca
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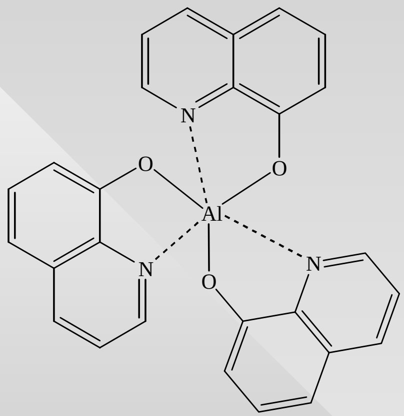
Other Electron Transport Materials

Material | Deficiencies

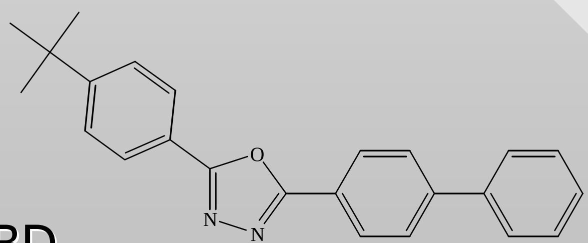
Tris(8-hydroxyquinolinato)aluminum



Alq_3

- Presence of charge traps.
- Quenching of EL by crystallization of amorphous Alq3.

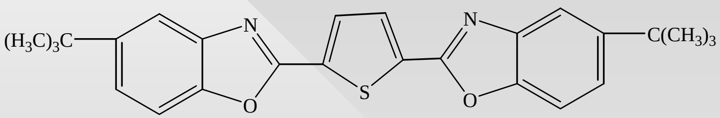
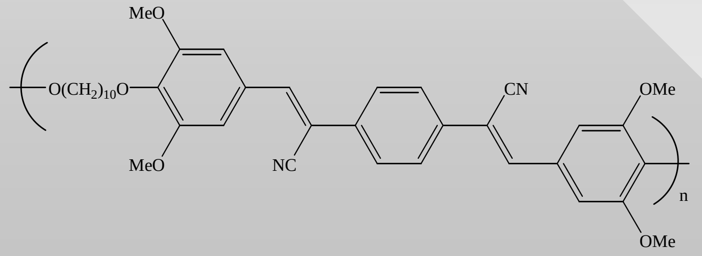
Oxadiazoles



PBD

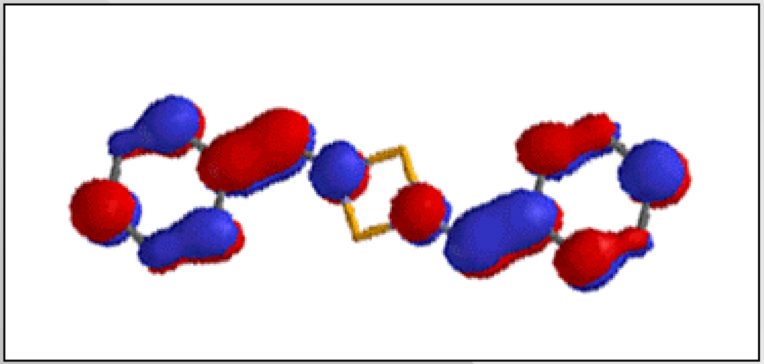
- Can undergo irreversible redox reactions.

Other Electron Transport Materials

Material	Deficiencies
Thiophenes	• Electronic properties are temperature dependent.
 BBOT	
PPVs with electron-withdrawing groups	• Conjugation shortened to make polymer easier to process. • Chemically reactive.
 PC10	

Cyclodiborazane

- Contains electron deficient boron in the π-system.
- Boron in conjugation delocalizes electron deficiency rather than providing an electron sink/trap.
- Semi-empirical calculations (AM1 level, Spartan MOPAC program) of a model compound showed a LUMO that suggests that the electron deficiency is effectively delocalized.

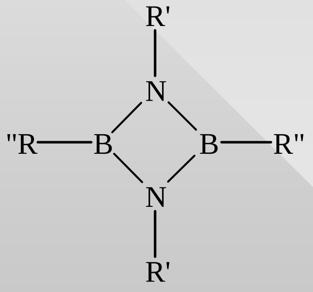


- Lobes at ends of the model suggest that conjugation can be extended.

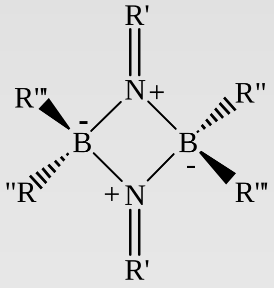
Cyclodiborazane

- More structural studies have been done on a related molecule, 1,3-diaza-2,4-diboretidine.
- Anti-aromaticity is not an issue since the ring is puckered, and parallel bonds are of different lengths than the perpendicular bonds.

N = pyramidal
B = planar



1,3-diaza-2,4-diboretidine



cyclodiborazane

N = planar
B = pyramidal

- Coordinative nature of the 4-center-4-electron bonding lends to the stability of the molecule.

Cyclodiborazane

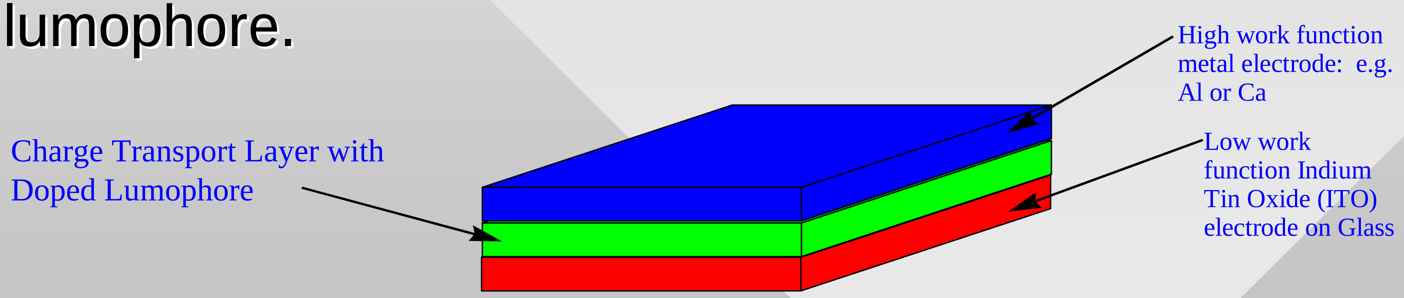
- Chujo has developed the synthesis of polycyclodiborazanes and has shown their stability towards air and moisture.
- Expectations are that polycyclodiborazanes should be good electron transport materials but no studies have been done to date.
- Polycyclodiborazane has an innate fluorescence in which the maxima are affected by solvation.

Single-Layer Device

- Polymer with electron-deficient and electron-rich moieties in the repeat unit to balance the electron- and hole-transport properties.

- Balancing of electron- and hole-transport properties by use of electron-deficient monomer copolymerized with an electron-rich monomer.

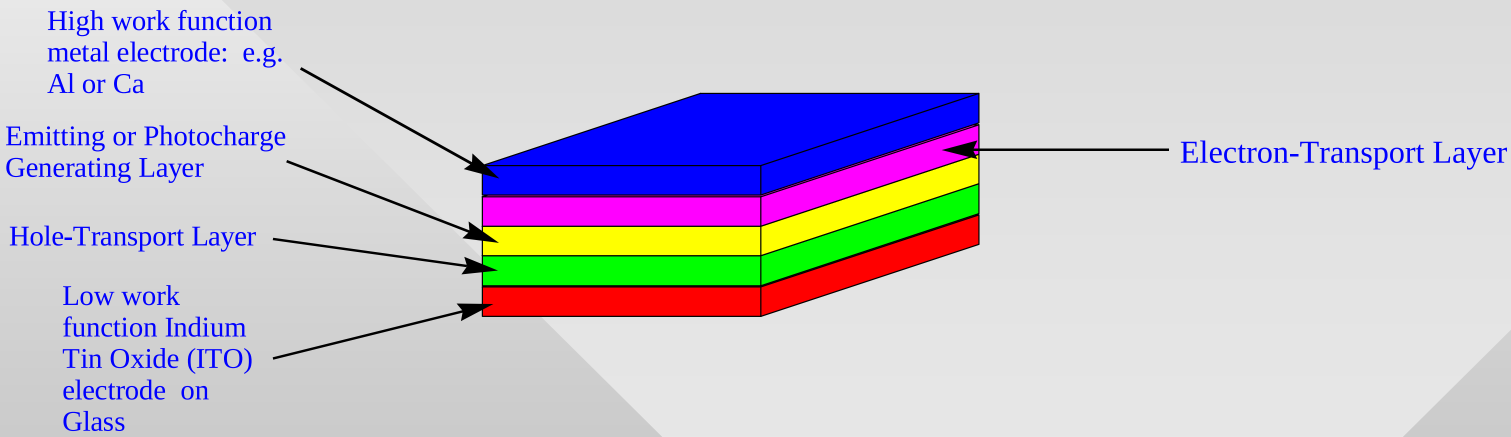
- Applications in single-layer devices, when doped with a lumophore.



- Properties can be tailored by using other divinylaromatics.

Triple-Layer Device

- The cyclodiborazane heterocycle in the repeat unit of this polymer allows for an electron-deficiency, which can be exploited for use as an electron-transport layer (ETL) in a multi-layer device.



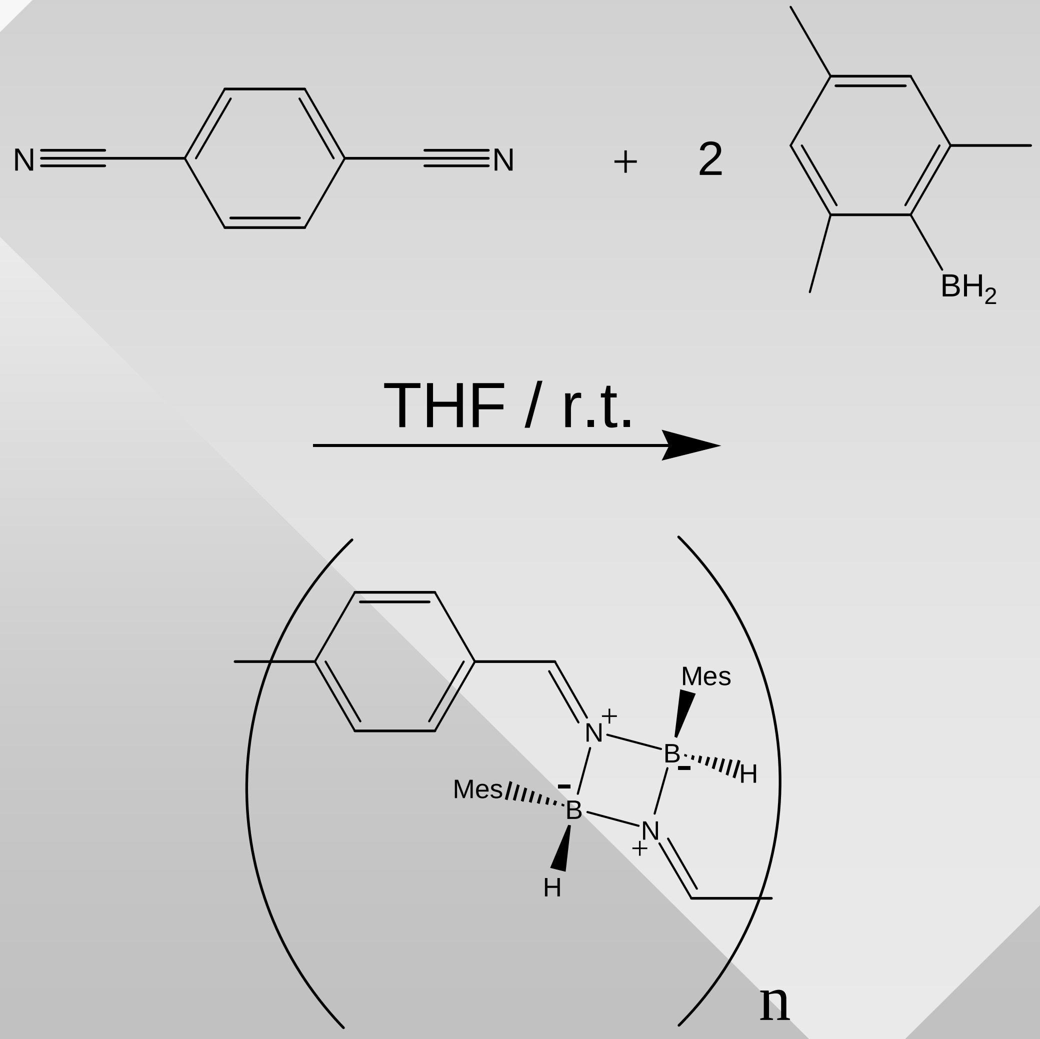
- Properties are varied by using other dicyanoaromatics and arylboranes.

- Triple-layer device desirable for photovoltaics in order to minimize recombination.

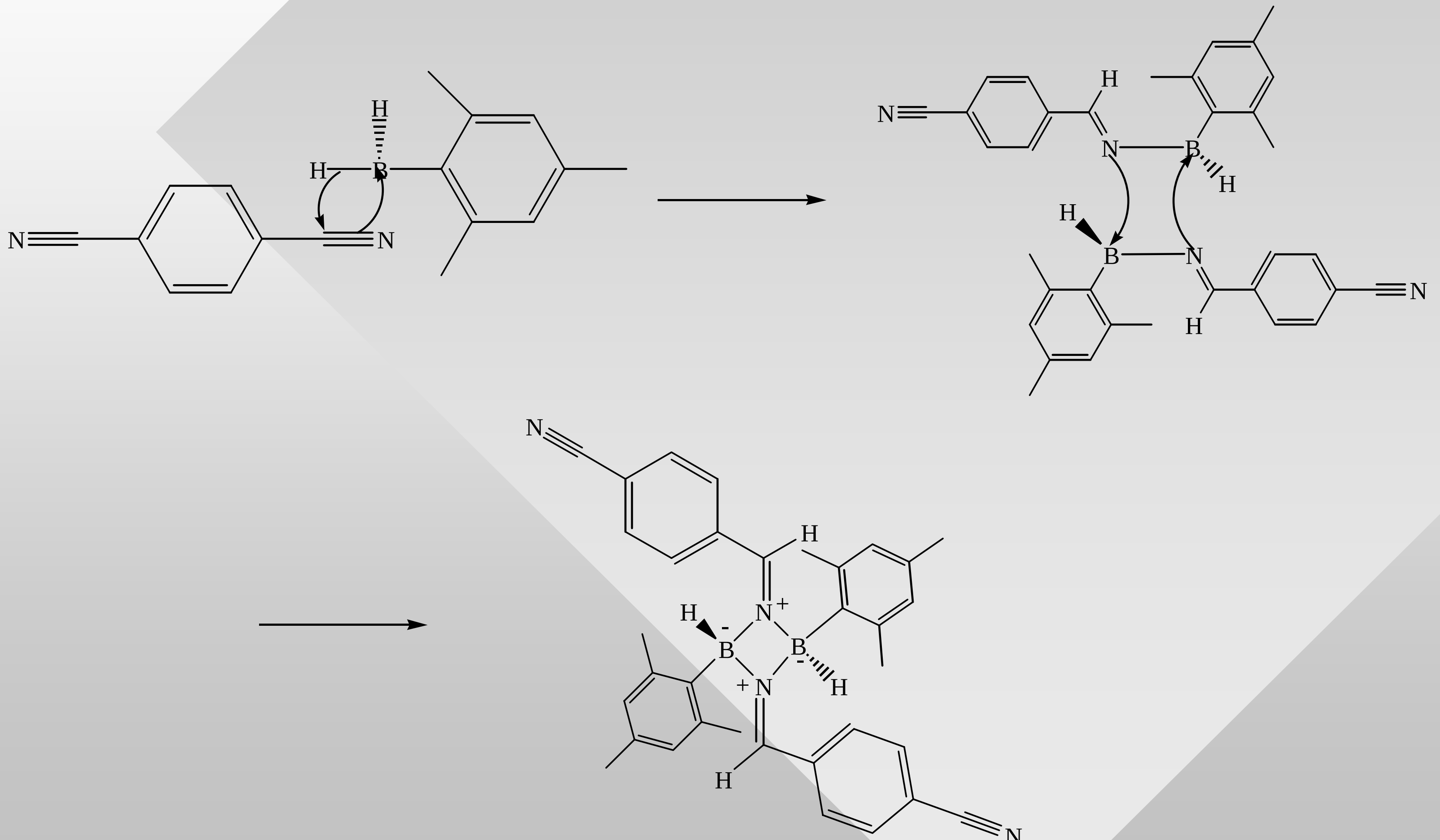
Synthesis

- Electron Deficient Polymers for Triple-Layer Devices
- Balanced Charge Transport Polymers for Single-Layer Devices
- Varying Charge Mobilities by Varying Starting Materials

Electron Deficient Polymer for Electron Transport Layer

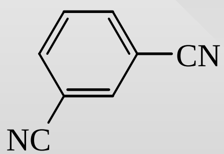


Hydroboration Polymerization

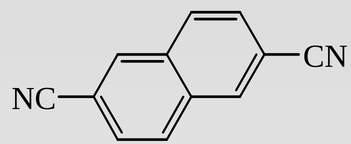


Tailoring Charge Mobilities by Varying Starting Materials

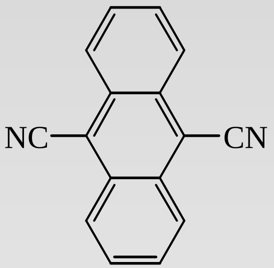
- Use other dicyanoaromatics to make cyclodiborazanes.



1,3-benzenedicarbonitrile



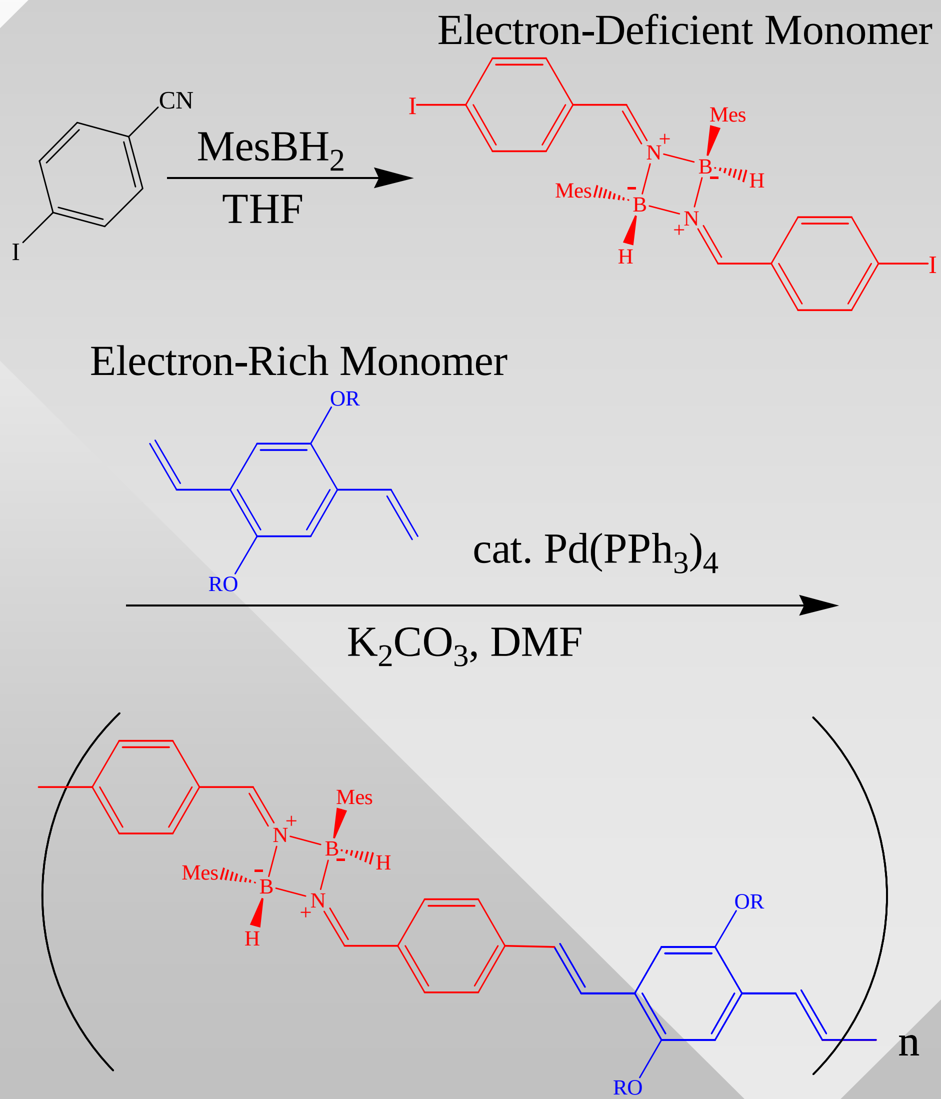
2,6-naphthalenedicarbonitrile



9,10-anthracenedicarbonitrile

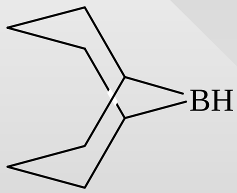
- Variations on the above.
- Copolymerization with aromatic dicyanoheterocycles, e.g.: pyrrole, thiophene, etc.

Polymer for Bipolar Charge Transport Layer

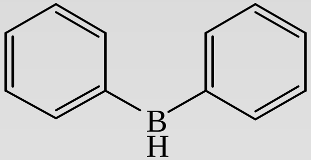


Tailoring Charge Mobilities by Varying Starting Materials

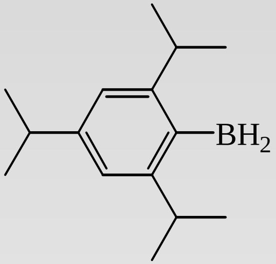
- Use other boranes to make cyclodiboranzanes.



9-borabicyclo[3.3.1]nonane; "9-BBN"

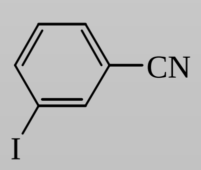


diphenylborane

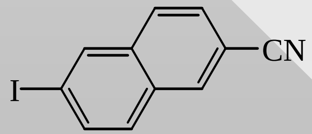


2,4,6-tris(1-methylethyl)phenylborane; "tripylborane"

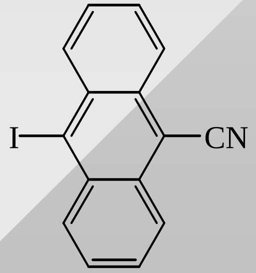
- Use other halocyanoaromatics.



3-iodobenzonitrile



6-iodo-2-naphthalenecarbonitrile



10-iodo-9-anthracenecarbonitrile

Characterization

- ^{1}H and ^{11}B NMR Spectroscopy
- Gel Permeation Chromatography
- Fluorescence and UV-Vis Spectroscopy
- Cyclic Voltammetry & Electrical Conductivity
- Photoelectron Spectroscopy (Ionization Potential)
- Time of Flight (Electron Mobilities)
- Thermal Analysis (DSC, TGA, DTA)

Applications

- PLEDs
- Photovoltaic Devices
- Other Organic Microelectronic Devices, e.g.:
  - Field-Effect Transistors (FETs)
  - Thin-Film Transistors (TFTs)

Summary

- Polycyclodiborazanes are potentially useful for electron and bipolar charge transport materials.
  - Electron deficiency is delocalized throughout the π-framework.
  - Stable towards oxidation, hydrolysis and photolysis.
  - The properties can be manipulated by several means: mainly copolymerization with comonomers of varying electron demand in the bipolar charge transport polymers, and incorporation of various dicyanoaromatics in the electron transport polymers.

Acknowledgements

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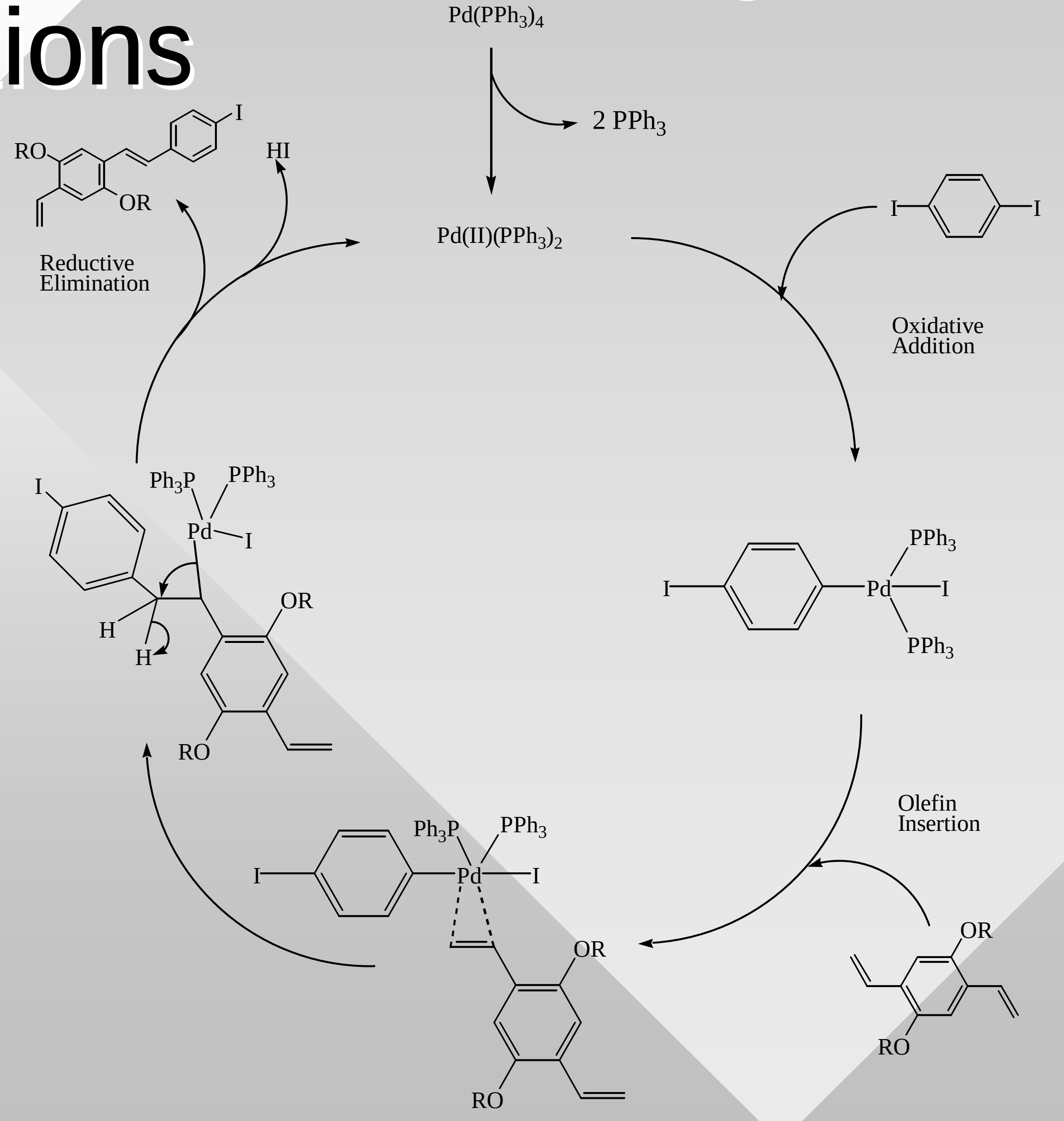
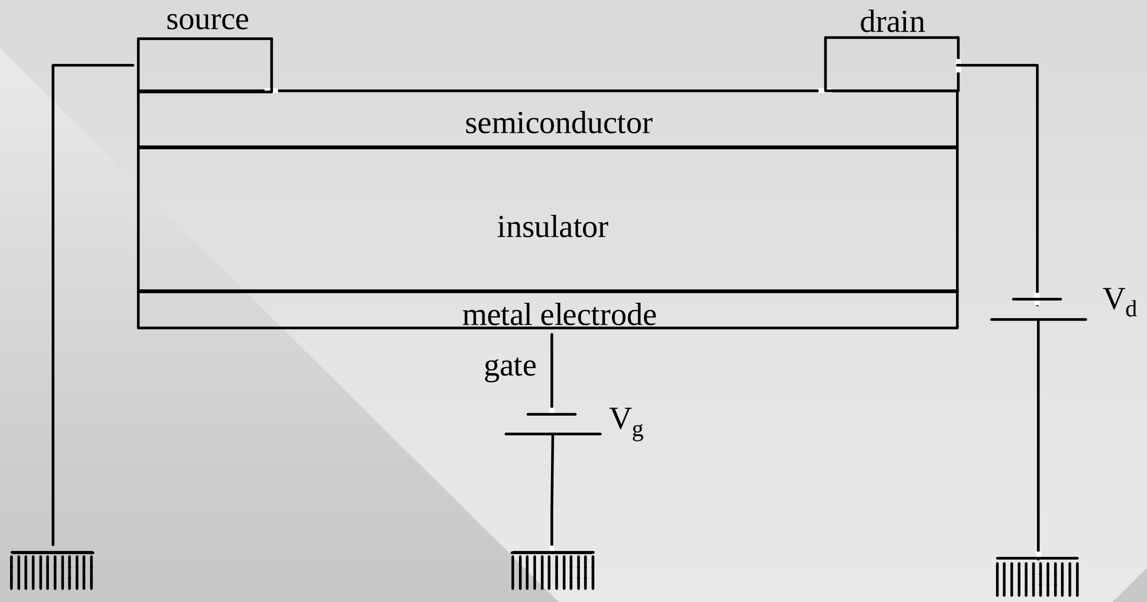
  - Jeremy Collette
  - Michael Julian
  - Cory Miller
  - Asanga Padmaperuma

Polymerization through Heck Reactions



Transistors

- Field-Effect Transistors (FETs)



Schematic of the TFT structure used in an Organic FET.

Transistors

- Field-Effect Transistors (FETs)
  - Two independent voltages drive a FET:
    - First voltage is applied across the insulator serves to create charges at the insulator/semiconductor interface.
    - Second bias is applied between source and drain that drives the charges induced by the first bias.
  - Device behaves as a variable resistance that can be modulated by the voltage applied the gate electrode.
- Thin-Film Transistors (TFTs)
  - A TFT is an insulated gate FET.

Electron Deficient Polymer for Electron Transport Layer

– Mechanism: Hydroboration Polymerization

- The boron-hydrogen bond of the borane overlaps the carbon-nitrogen bond of the nitrile.
- Sequential transfer of electrons forms borazane.
- Attack of nitrogen’s lone pair of electrons on a neighboring boron form a dicycloborazane unit.
- Process repeats for para-cyano group and free boranes.

Polymer for Charge Transport Layer

- Mechanism: Polymerization through Heck Reactions

- The boron-hydrogen bond of the borane overlaps the carbon-nitrogen bond of the nitrile.
- Dimerization of two borane-nitrile complexes (borazanes) form a dicycloborazane unit.
- Palladium organometallic mechanistic cycle, with halogen and alkene.