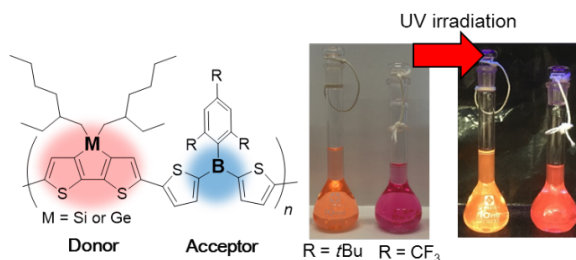
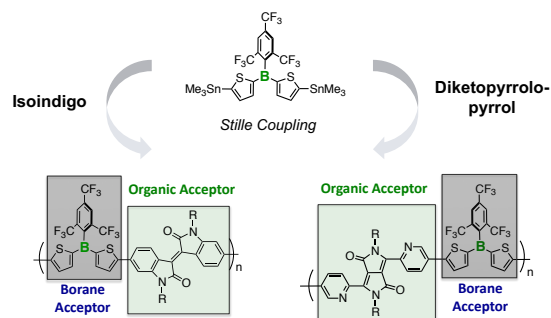


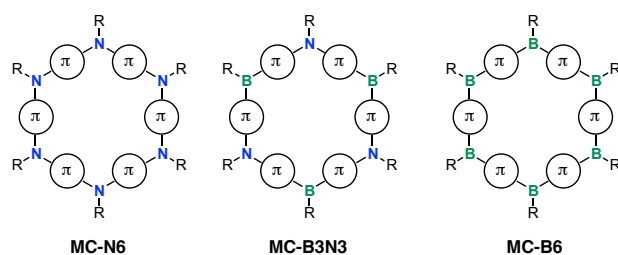
Luminescent Materials



Acceptors for all-polymer Solar Cells



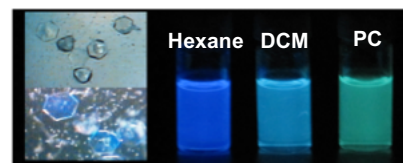
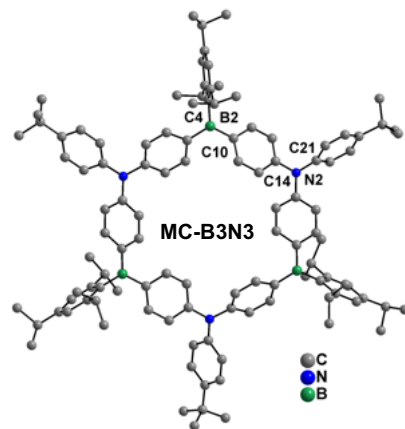
2) Conjugated Organoborane Macrocycles [A12-A14]. We have introduced a new class of conjugated macrocycles that incorporate electron-deficient organoborane moieties. These macrocycles are interesting



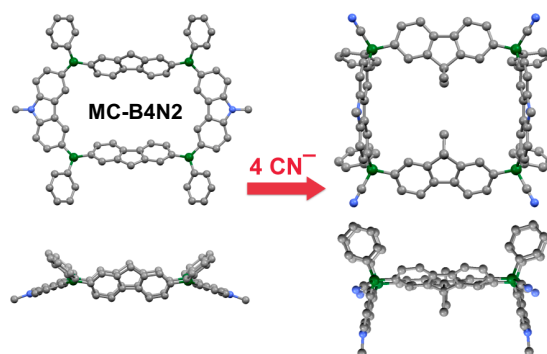
from a fundamental point of view due to the absence of end groups that can influence the photophysical and electronic characteristics of conjugated oligomers and polymers. The high rigidity also makes them useful as hosts for guest molecules and promotes formation of well-defined porous supramolecular materials. Another attractive aspect is the potential for self-assembly into highly symmetric arrays upon deposition on surfaces.

Electron-rich macrocyclic species are abundant, and crown ethers and cryptands have been widely explored in molecular recognition. Among conjugated systems porphyrins and phthalocyanines are noteworthy as they play a major role in photosynthesis and as dyes in various industrial processes. Most relevant to the discussions here is a 2010 report by Ito and Tanaka, in which they described the preparation of the first hexa-aza-paracyclophane (**MC-N6**, $\pi = 1,4$ -phenylene, $R = \text{anisyl}$). **MC-N6** proved to exhibit very interesting electronic properties upon partial oxidation of the electron-rich arylamine moieties. Similarly intriguing electronic structures can be expected for conjugated macrocycles that feature highly electron-deficient borane groups as an integral part of the ring system. In 2011, we introduced the first example of an electron-deficient conjugated macrocyclic organoborane, **MC-B6**, which contains 6 Lewis acidic borane moieties alternating with fluorenes as the π -system, a feat that attracted much interest in the community and was highlighted in C&E News.

Expanding upon this discovery, more recently we prepared the ambipolar macrocycle, **MC-B3N3**, which contains N as donor and B as acceptor sites, bridged by phenylene groups. This new type of macrocycle may be viewed as a π -expanded borazine; however, introduction of the phenylene bridges results in remarkably different properties compared to borazine: The macrocycle forms colorless crystals that are blue-emissive when exposed to UV light. Photoexcitation in solution gives rise to an intense emission, which experiences a pronounced red shift with increasing solvent polarity. This solvatochromic effect in the emission, but not the absorption, points to a highly polarized excited state, a phenomenon that is consistent with ICT in a D- π -A system.

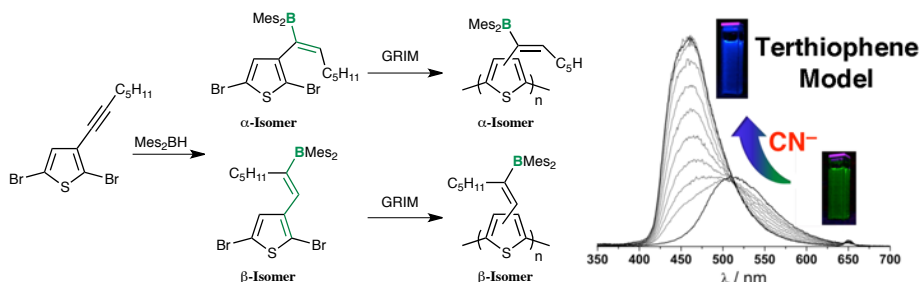


Electrochemical studies revealed reversible oxidation and reduction events at moderate potentials, suggesting possible utility as ambipolar materials in OLEDs. More general routes to these types of macrocycles with different shapes and functional building blocks have recently been developed. An example is the macrocycle **MC-B4N2**, which features carbazoles as bridging units that provide for a more compact structure than that of **MC-B6**. Interestingly, cyanide anion binding allows for controlled changes in the shape of the macrocycle as the trigonal borane moieties are converted to tetrahedral organoborates with much more acute endocyclic C-B-C angles.

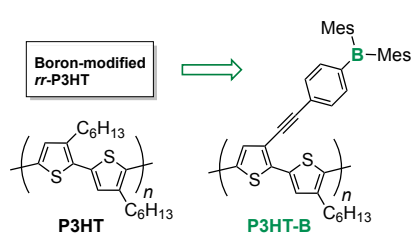


3) Side Chain Functionalization of Conjugated Polymers [A15-A20]. An alternative approach to conjugated boron polymers is to functionalize the side chains of conjugated organic building blocks that can be polymerized in a controlled fashion. A major challenge is to develop controlled polymerization procedures that lead to regioregular polythiophenes and ultimately allow for preparation of rod-coil block copolymers that feature organoborane groups attached to the conjugated block segments. To this end, we studied the Kumada CTP of 2,5-dibromo-3-heptynyl-thiophene and then introduced dimesitylborane groups into the polymer side chains via hydroboration with Mes_2BH . We also explored the direct polymerization of 3-vinylborane-functionalized thiophene monomers, which were readily prepared by hydroboration of the respective alkynyl-functionalized precursor (see Scheme). Reaction with Mes_2BH led to almost equal amounts of two different vinylborane isomers, the α - and β -borylation products. The isomers were separated by reverse-phase column chromatography and then polymerized individually.

We further investigated the effect of borane substitution on the electronic structure and optical properties of the isomeric polythiophenes and terthiophene model systems by a combination of

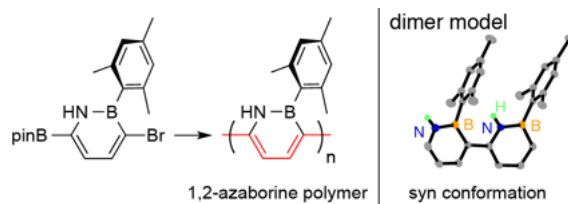


experimental methods and DFT calculations. Our studies demonstrate that the position of the tricoordinate boron centers has a direct influence on the photophysical properties. Another interesting aspect is that strong fluorescence enhancement is observed upon exposure to anions. This phenomenon is most pronounced for the β -isomer, resulting in a dramatic change of the emission color from green to blue with a 4-fold increase in intensity.



More recently, we prepared dibromothiophene monomers that are equipped with dimesitylborylphenylethynyl groups. We discovered that selective activation of one of the bromo substituents is possible, but polymerization control could not be achieved, possibly due to interaction of the catalyst with the alkynyl group at the chain end. However, the selective functionalization in 2-position enabled us to prepare unsymmetric AB-type mono- and bithiophene monomers, which were converted to regioregular polymers using Stille-type polycondensation. The photophysical properties, electrochemical characteristics, and anion binding behavior of these borylated P3HT analogues were examined in detail.

4) Other Related Collaborative Efforts [A21-A25]. We also enjoyed a number of fruitful collaborations on the borane functionalization of conjugated polymers over the past several years. Polymers that incorporate ferrocenylborane and diboraanthracene moieties have been explored in a collaborative effort with Professor Wagner at the University of Frankfurt. On the other hand, ADMET techniques have been applied for the first time to boron-containing conjugated polymers in a collaborative effort with Professor Peetz at CUNY Staten Island. Finally, in a collaboration with Prof. Liu at Boston College we are currently exploring azaborines as new building blocks for polymeric materials. Our results indicate that the azaborine analog of poly(para-phenylene) (PPP) adopts an unusual *syn*-conformation and exhibits electronic characteristics that are more reminiscent of a polyacetylene derivative.



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