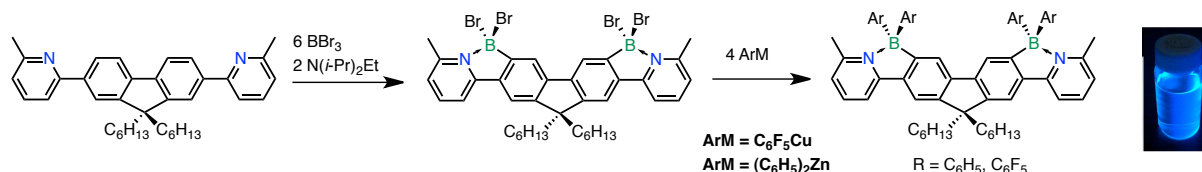


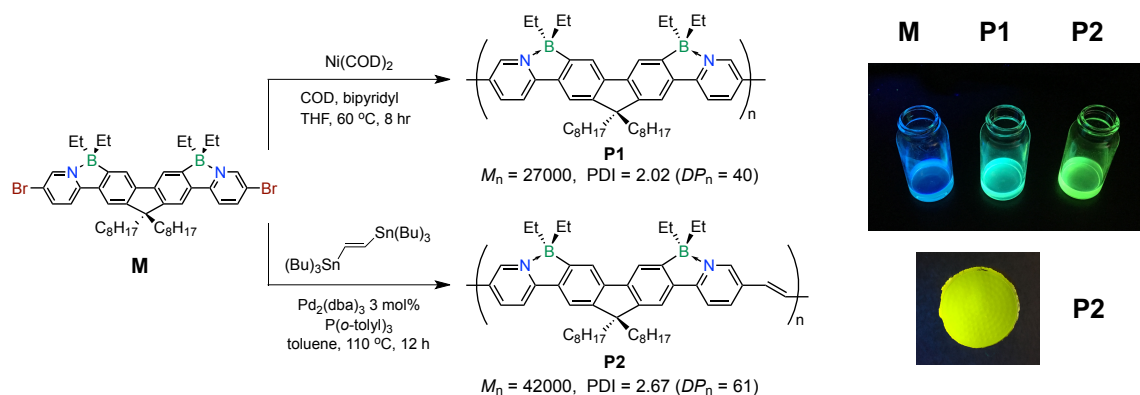
Project B: Lewis Pair Functionalization of Polycyclic Aromatic Hydrocarbons

Four-coordinate organoboron compounds with rigid π -conjugated structures have emerged as very attractive materials for various applications, including organic light-emitting diodes, organic field-effect transistors, photovoltaics, sensory and biological imaging materials, photo and mechanoresponsive materials and memory devices. To construct these 4-coordinate boranes, chelate ligands with π -electrons are coordinated to B via the vacant p-orbitals. A key role of the B atom is to stabilize the ligand by coordination and to allow intramolecular electron delocalization, thereby enhancing the π -conjugation. Such ring-fused structures often enhance the electron affinity by lowering the lowest unoccupied molecular orbital (LUMO), which makes four-coordinate boron compounds attractive as electron-transport materials. Recent research has also shown that four-coordinate boron compounds with an N,C-chelate backbone are capable of undergoing facile reversible photothermal isomerization, which has opened exciting opportunities to use these compounds as a new class of photo-responsive materials.

Methods for the synthesis of π -conjugated materials based on B-N chelates include sequential lithiation-borylation reactions, direct metal-catalyzed borylations, and metal-free electrophilic borylations. We are pursuing the B-N Lewis pair functionalization of larger PAHs through directed electrophilic borylation reactions as a means to tune the electronic properties and develop new applications.



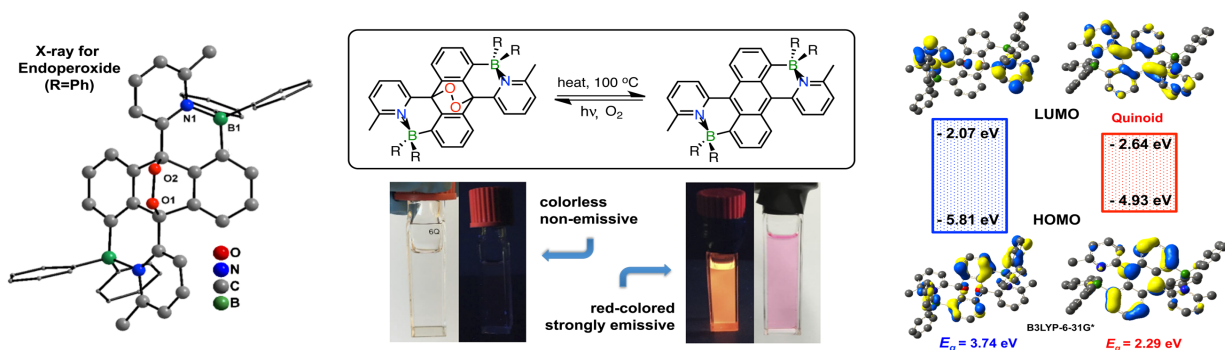
1) Fluorene Ladder Systems [B1-B2]. In our first foray we prepared a series of luminescence ladder compounds by Lewis base-directed electrophilic borylation. Dipyrindylfluorene was prepared and treated with BBr_3 in the presence of a bulky amine as a base. The products were then reacted with $\text{C}_6\text{F}_5\text{Cu}$ and $(\text{C}_6\text{H}_5)_2\text{Zn}$ respectively, to produce the targeted air and moisture-stable BN ladder compounds. Single crystal X-ray analyses revealed an essentially planar conjugated structure that includes the BN heterocycles. Photophysical studies demonstrated that these molecules are strongly blue luminescent with high quantum efficiencies. They undergo multi-step reversible reduction and oxidation processes. Fluorination of the pendant aryl groups lowers both the HOMO and LUMO levels as confirmed by electrochemical studies and DFT methods. Ongoing efforts at extending our approach to larger PAHs suggest that the properties of PAHs can be dramatically influenced by this borylative annulation approach.



The incorporation of these ladder compounds into polymers was also achieved. UV-Vis absorption and fluorescence measurements showed significant bathochromic shifts for the polymers with respect to the monomer. As a result of extended π -conjugation the absorption maximum of **P1** experiences a

bathochromic shift to 458 nm, and a strong blue-green emission is observed with a maximum at 472 nm and a shoulder at 503 nm. In comparison, the copolymer **P2** exhibits a longer wavelength maximum absorption at 485 nm and maximum emission at 495 nm with a shoulder at 529 nm. The additional bathochromic shifts for **P2** compared with **P1** are consistent with better coplanarity of the conjugated building blocks and therefore improved extension of π -conjugation. A further red-shift was detected in the absorption and emission spectra of polymer films relative to the spectra in solution, attributed to π - π stacking interactions in the solid state. A manuscript on this work is in progress and to be submitted within the next few weeks.

2) Anthracene-Based Systems [B3-B4]. In late 2017, we published a communication in *J. Am. Chem. Soc.* describing a new class of BN-substituted PAHs with unique structural features and electronic properties, based on a Lewis pair functionalization approach. We demonstrated that the formation of B-N Lewis pairs in the periphery of anthracene leads to severe distortions (buckling) due to steric strain. Detailed variable temperature NMR and theoretical studies suggested that these materials are dynamic, involving reversible formation of the Lewis acid-base interactions (“flexible Lewis pairs”). Secondly, we found that the formal “BN” Lewis pair functionalization results in substantially decreased LUMO energy levels, due to stabilization of a “quinoid”-like structure. This finding was further ascertained by comparison with the all-carbon analogs using computational methods. As a result, these materials exhibit large bathochromic shifts in the absorption relative to all-carbon analogs and strong low energy emissions. Finally, we discovered that the intensely red colored BN-functionalized anthracenes rapidly react with O₂ in the presence of light with selective and reversible formation of the corresponding endoperoxides. This occurs without the need for an external photosensitizer. Triplet state calculations suggested that intersystem crossing to T1 results in even more severe distortions, thus further enhancing the reactivity. This B-N Lewis pair functionalization of polycyclic aromatic hydrocarbons presents a new approach to conjugated materials development, in particular the preparation of structurally distorted systems. The ensuing desirable photophysical and electronic properties are promising for optoelectronic materials development, while the facile reactivity with O₂ suggests potential in O₂ capture/release applications and possibly the broader field of small molecule activation.



We are currently extending this approach to the functionalization of other, even larger PAH systems. We are also exploring applications in singlet oxygen sensitization, triplet-triplet annihilation and singlet fission processes.

CORRESPONDING REFERENCES:

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