Progress Toward Synthesis of Contorted Covalent Organic Polygons

Sally Landon Tepper and Brian H. Northrop

Department of Chemistry, Wesleyan University, Middletown, CT 06459

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Introduction and Background

Aggregate Induced Emission

Aggregation induced emitting luminogens (AIEs) are a new and exciting type of material being developed, having wide variety of uses, from environmental toxicity monitors to biomedical probes. Most luminescent molecules are highly conjugated, which often results in them having planer geometries. Planer, π-conjugated molecules π-stack which allows the molecules to dissipate energy vibrationally due to the decrease in the HOMO LUMO gap instead of dissipating energy photochemically. This phenomenon is called quenching. In contrast, AIEs do not fluoresce as single molecules or in low concentrations, but when many come together in high concentration, the result is a luminescent substance. AIEs characteristically have bulky 3-D geometries and extended π-conjugation. When excited by light, they can thermally release energy by rotating or vibrating but when squished together in high concentrations, that movement is restricted so the only option to release energy is photochemical.

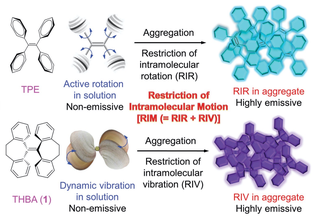
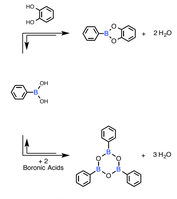


Figure 1: Explanation for aggregate induced emission.[1]

Boronate Ester Self Assembled Polygons

Dynamic Covalent Chemistry: thermodynamically reversible covalent bond forming reactions



Nanoporous Framework Materials made from boronate ester self assembly

In low concentrations, these frameworks are florescent but in high concentrations, the florescence is quenched due to pi stacking forces. π-stacking is allowed because of the planer geometry. High concentrations become a problem due to poor solubility of some frameworks or when a solid is required for application.

Figure 2: Boronate ester dynamic covalent chemistry can lead to nanoporous frameworks

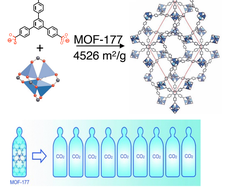
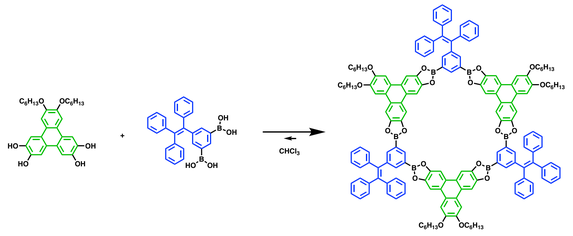


Figure 3: Physisorption of gases is the noncovalent binding of different gases (H_2, N_2, CH_4, CO_2, SO_2, etc.) to the interior walls of MOFs.

Millward, A. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 17998

Goal

The Northrop lab has extensive experience using dynamic covalent boronate ester condensation to self-assemble π-conjugated nanoporous covalent organic polygons. To date, however, all these nanoporous polygons have been fluorescent in solution but undergo aggregation induced quenching that limits or prevents their fluorescence in condensed phases. This project aims to explore whether the use of AIE luminogens as components in boronate ester self-assembly will enable highly fluorescent nanoporous covalent organic polygons to be prepared, with likely applications as sensors and optical materials.[2] In order to answer this question, we first are working to find an efficient synthesis to make covalent organic hexagons. Successful boronate ester self-assembly will involve linking tetraphenylethylene bis(boronic acids), which are AIE luminogens, with π-conjugated triphenylene tetraols. This summer has been focused on the synthetic steps that will lead to these target molecules.



Scheme 1: Boronate ester self assembly of twisted [3+3] covalent organic hexagon that is predicted to show florescent properties.

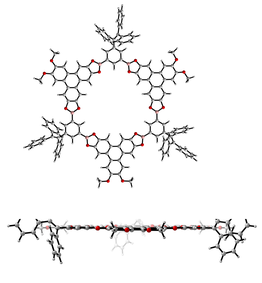
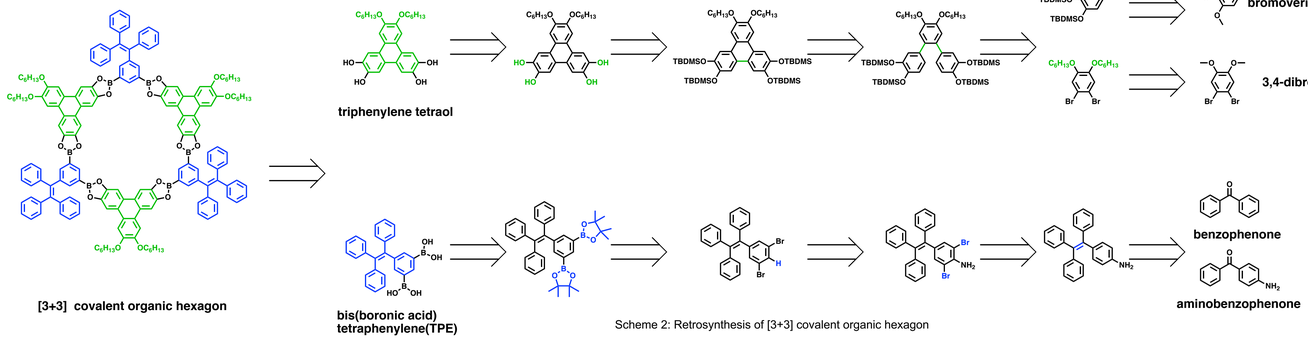


Figure 4: Front and Side view of [3+3] covalent organic hexagon generated by Gaussian.

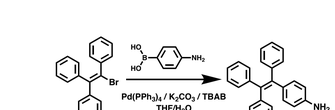
Methods and Results

Synthetic Approach



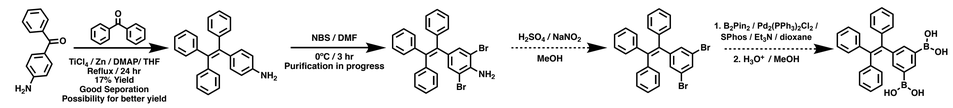
Scheme 2: Retrosynthesis of [3+3] covalent organic hexagon

Synthetic Progress [3-7]

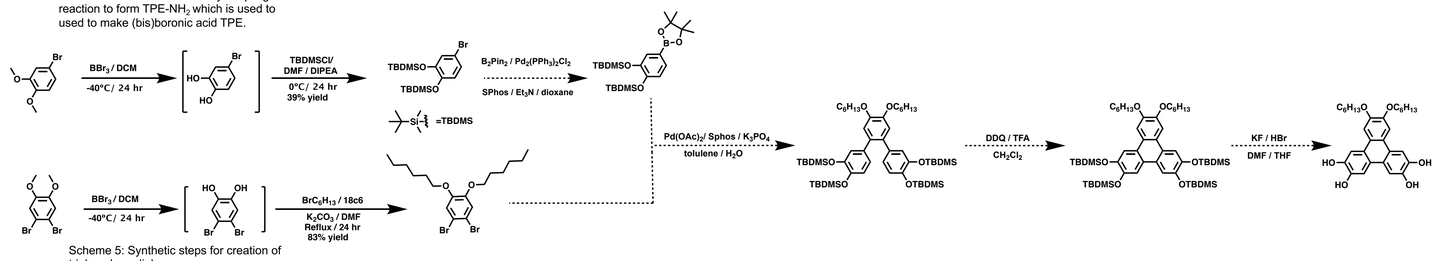


Scheme 3: Failed Suzuki coupling reaction to form TPE-NH_2

We first tried a Suzuki coupling reaction but even using multiple solvents, a phase catalyst and different periods of time, the yield was not ideal. We turned to a McMurry coupling reaction as a second option and received much better results. Although the yield was only 17%, we believe a much higher yield can be achieved with a few changes to the work up and purification solvent systems.



Scheme 4: Successful McMurry coupling reaction to form TPE-NH_2 which is used to used to make (bis)boronic acid TPE.



Scheme 5: Synthetic steps for creation of triphenylene diol.

Future Directions

The next steps in this project will be to complete the synthesis of the triphenylene diol and the bis(boronic) acid tetraphenylene. As the bis(boronic) acid tetraphenylene has no literature precedent, we anticipate having to workshop the conditions for the deamination and palladium cross coupling reactions. When the [3+3] hexagon is built, we plan on characterizing its properties, especially its florescence. We also plan on going back and improving synthetic yields.

References

1. Mei, J.; Hong, Y.; Lam, J. W. Y.; Qin, A.; Tang, Y.; Tang, B. Z., Aggregation-Induced Emission: The Whole Is More Brilliant than the Parts. Advanced Materials 2014, 26 (31), 5429-5479.
2. Dalapati, S.; Jin, E.; Addicoat, M.; Heine, T.; Jiang, D., Highly Emissive Covalent Organic Frameworks. Journal of the American Chemical Society 2016, 138 (18), 5797-5800.
3. Chen, W.; Zhang, C.; Han, X.; Liu, S. H.; Tan, Y.; Yin, J., Fluorophore-Labeling Tetraphenylethene Dyes Ranging from Visible to Near-Infrared Region: AIE Behavior, Performance in Solid State, and Bioimaging in Living Cells. J Org Chem 2019, 84 (22), 14498-14507.
4. Duan, X. F.; Zeng, J.; Lü, J. W.; Zhang, Z. B., Insights into the General and Efficient Cross McMurry Reactions Between Ketones. J Org Chem 2006, 71 (26), 9873-6.
5. Luo, M.; Zhou, X.; Chi, Z.; Liu, S.; Zhang, Y.; Xu, J., Fluorescence-Enhanced Organogelators with Mesomorphic and Piezofluorochromic Properties based on Tetraphenylethylene and Gallic Acid Derivatives. Dyes and Pigments 2014, 101, 74-84.
6. Smith, M. K.; Powers-Riggs, N. E.; Northrop, B. H., Rational Synthesis of Bis(hexyloxy)-tetra(hydroxy)-triphenylenes and Their Derivatives. RSC Advances 2014, 4 (72), 38281-38292.
7. YI, Z.; ZHUXIN, Z.; TINGTING, Y.; YUE, M.; JIARUI, X.; SIWEI, L.; ZHENGUO, C. Diamine Compound with Aggregation-Induced Emission Groups, and Preparation Method and Application Thereof 2017.

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