Summer Summary

The main goals of my research this summer were focused on the synthesis and characterization of three perylene-3,4-dicarboximide (PMI)-based trefoil molecules. I had the additional goal of expanding my synthetic and analytical toolbox to include several new types of reactions and a number of new instruments. While I was only successful in the synthesis of one of the targets, the synthesis and initial characterization of which is included in this report, I have prepared the necessary precursors and learned techniques necessary for completing the synthetic goals in the future. In terms of instrumentation, I was trained on MALDI-TOF mass spectrometry and NMR techniques that are used to determine the presence and purity of a reaction product. I was trained to use the glovebox used to store the air-sensitive ruthenium catalyst needed for headland substitution reactions. I learned how to use both analytical and preparatory scale HPLC for difficult purifications. I also used steady-state UV-visible spectroscopy and fluorescence spectroscopy to characterize the target molecule that was synthesized.

Synthesis:

All compounds were characterized using H^1 NMR on a Varian 500 MHz system and a Bruker MALDI-TOF mass spectrometer.

Target 1 (Scheme 1): N-(2-ethylhexyl) PMI was previously synthesized in a one-pot imide condensation and decarboxylation reaction that yielded compound 1. The PMI was selectively brominated at the 9 position using bromine in refluxing dichloromethane (DCM). Compound 2 was reacted with 3-methylhex-1-yn in a Sonogashira cross-coupling reaction to afford compound 3. Compound 3 was hydrogenated under a hydrogen atmosphere over 10% palladium on carbon in a Parr Shaker to give compound 4. This material was divided into three portions to synthesize each of the three target systems. To achieve the first target molecule, a C-H insertion reaction catalyzed by Ru(H_2)CO(PPh_3) was used to insert t-butylstyrene to yield compound 5, a PMI with t-butylphenethyl groups substituted in the 2 and 5 positions. The imide was hydrolyzed using KOH, and the resulting anhydride, compound 6, was condensed onto previously synthesized 1,3,5-tris(4'-aminophenyl)benzene to give the target molecule, compound 7.

Target 2 (Scheme 2): A portion of compound 4 from the previous scheme was subjected to similar C-H insertion conditions with dodec-2-ene to yield compound 8.

Target 3 (Scheme 3): A portion of compound 4 was selectively brominated in the 1 and 6 positions in refluxing chloroform to yield compound 11.

Steady-State Spectroscopy:

UV-visible spectra was taken of compound 7 in tetrahydrofuran (THF) and methylcyclohexane (MCH). The spectrum in THF looks like a characteristic PMI spectrum in terms of vibronic structure with a maximum absorption at 484 nm. In MCH, however, the spectrum shows stronger absorption in the blue range of the spectrum with an absorption maximum at 479 nm, indicative of face-to-face interactions of PMIs. Fluorescence spectra of compound 7 in THF and MCH at low concentrations displayed broad spectra.
Discussion and Future work:

There were several issues encountered during the synthesis. A low yield of 24% was achieved for the Sonogashira reaction due to the dominance of a side product. The hydrogenation reaction initially also produced a low yield despite the reaction typically being quantitative. The Pd/C was suspected to be poisoned after others who had used the catalyst from the same bottle reported similar problems. Repeating the reaction using catalyst from a new container resulted in a quantitative yield. The air-free reaction using the Ru(H₂)CO(PPh₃)₃ catalyst also suffered many difficulties. During the first attempt, oversized glassware was used, and the reaction mixture was left open to air after purging. One of the Schlenk lines that connected the reaction vessel to a nitrogen atmosphere may not have been properly set. Further, the catalyst used for this reaction had not been properly stored, and thus may not have been active. For the subsequent runs, I took greater care to maintain air-free conditions and was trained to obtain fresh catalyst from the glovebox. The dibromination reaction with compound 4 showed significant tribromination. In the future, this reaction can be subjected to milder conditions, either a fewer equivalents of bromine, a shorter reaction time or both. Careful monitoring by thin layer chromatography and mass spectrometry will ensure that minimal side products are generated. Due to low reaction yield of compound 5, Charusheela Ramanan’s donated her crude product of the anhydride of the 4-tertbutylstyrene disubstituted PMI, compound 6. After her product was purified using, the target molecule was synthesized.

Moving forward, the reactions that offered poor yield need to be adjusted, perhaps by analyzing the side products and determining what aspects of the reaction conditions would reduce the favorability of those side products. The reactions then would be taken to a larger scale. Preliminary steady-state results indicate that the molecules will aggregate in low-polarity solvents. The aggregation of the products can be studied in different solvents and at different concentrations or in solid-state via films. Analyses that were unable to be run this summer would be used, such as electrochemistry, small- and wide- angle X-ray scattering, and electron paramagnetic resonance techniques.