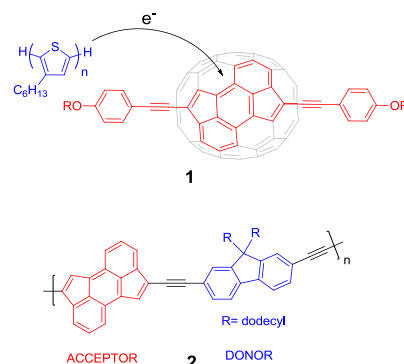


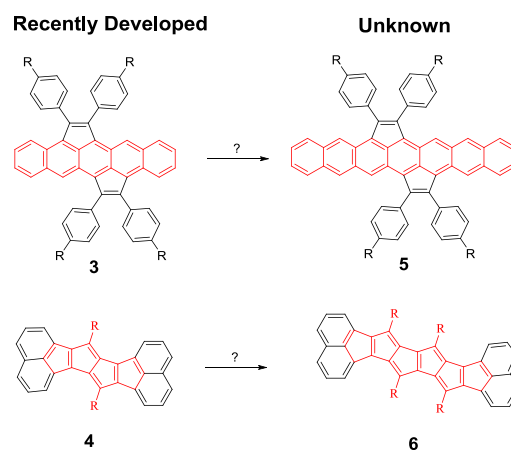
**Significance / Broader Impact:** The design of new electron acceptors is important to a range of energy related fields including n-type organic field effect transistors, non-fullerene based organic photovoltaics, and reversibly charging polymers for supercapacitor storage devices. Our lab is interested in the synthesis and application of new materials to better these technologies.

**Previous Results:** Although cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) have been synthesized for many decades to provide compounds useful to elucidate PAH aromaticity or to create geodesic structures, very few CP-PAHs have been utilized as active components in electronic devices (*SynLett.*, SYNFACTS article, **2013**, 24, 898-902). Our group is interested in developing new synthetic methods to access the scalable synthesis of novel CP-PAHs that possess unique photochemical and electrochemical properties. The defining feature of these materials is their ability to accept electrons owing to the formation of cyclopentadienyl anion-like substructures upon reduction. Our recent work (*J. Am. Chem. Soc.* **2012**, 134, 15783-15789, *Org. Lett.* **2013**, 15, 1202-1205, *J. Mater. Chem. C.*, **2016**, 4, 3963-3969) utilizes a palladium-catalyzed cyclopentannulation transformations to access small molecule electron acceptors based on functionalizable cyclopenta[hi]aceanthrylenes **1** and dicyclopenta[de,mn]tetracenes. The synthetic pathways are straightforward and allow functionalization of the CP-PAHs on either the 5-membered rings or the 6-membered rings to access differing electrochemical properties. We have further utilized these CP-PAH based electron acceptors in donor-acceptor copolymers **2** (*Angew. Chem. Int. Ed.*, **2012**, 51, 12321-12324) and have accessed low band gap (~1.3 eV) materials that are amazingly low for an all hydrocarbon framework.

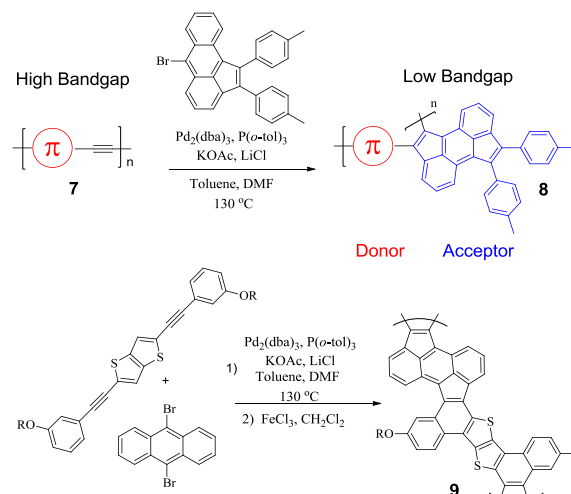
This new cyclopentannulation chemistry has opened many new opportunities in my lab to access unique molecular architectures. For example, we now have methods to prepare 1,2,8,9-tetraaryldicyclopenta-[fg,qr]pentacenes **3** (*Angew. Chem. Int. Ed.*, 2015, 54, 15762-15766) and diacenaphthylpentalenes **4** (*J. Org. Chem.* 2016, 81, 8312-8318), which are unusually photo-stabilized pentacene and unsaturated tetraquinane (four 5-membered rings fused together) derivatives (Figure 2). Owing to their remarkable stability, we are now looking into their properties in electronic devices (OFETs and OPVs) as well as applying the newly developed chemistry to new molecular scaffolds based on heptacenes **5** and unknown hexaquinanes **6**. In a unique application of the cyclopentannulation reactions condition, we have converted high band gap poly(arylene ethynylene)s into low band donor-acceptor copolymers in an efficient manner with the optical band gaps decreasing from ~2.6 eV to 1.5 eV upon functionalization (*Macromolecules*, **2016**, 49, 127-133). This new method opens the door to new materials for absorbers for OPVs. The remarkable efficiency of our new chemistry has led us to develop a new palladium-catalysed cyclopentannulation polymerization that can create unique ladder-polymers **9** (*J. Am. Chem. Soc.*, 2017, 139, 5801-5807). The major benefit of this system is the contorted nature of the polymer backbone that provides added solubility compared to traditional ladder polymers.



**Figure 1.** Previously prepared small molecule acceptors and donor-acceptor copolymers from cyclopenta[hi]aceanthrylenes.



**Figure 2.** Future adaptation of stabilized higher acenes and quinanes.



**Figure 3.** Unique donor-acceptor and ladder polymers from cyclopentannulations.

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