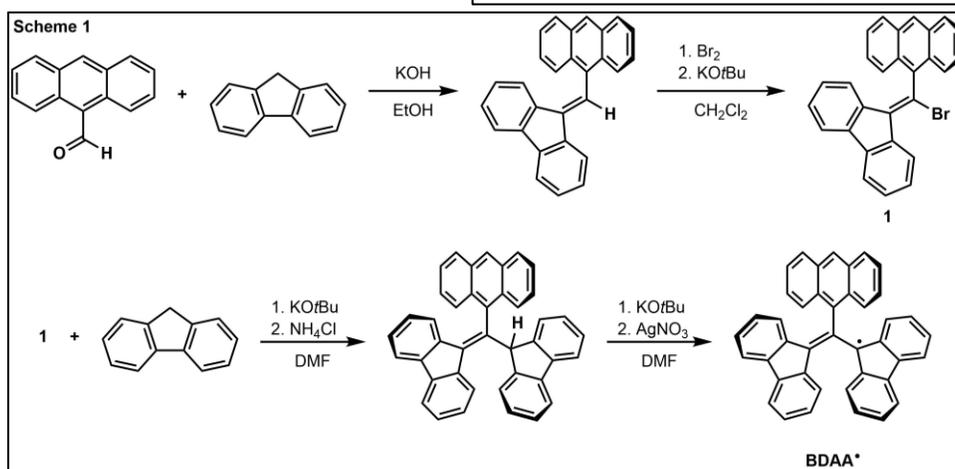
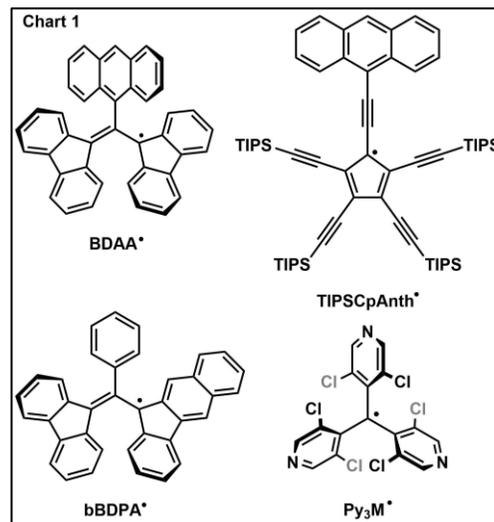


This project is an investigation into whether or not persistent radical compounds are capable of luminescence from a doublet ground state. There are two sequential goals to this project; first, design and synthesis of compounds which are persistent ground state radicals with the potential to luminescence by incorporating chromophore moieties into known persistent radical scaffolds; and second, investigation of the targeted compounds as to their luminescent properties. The properties we plan on investigating include: persistence lifetime under irradiation; HOMO-LUMO gap energies; luminescence lifetime of doublet states; and electronic structure investigations to determine the luminescent electronic manifold (i.e. which states and molecular orbitals are involved in the luminescence processes).

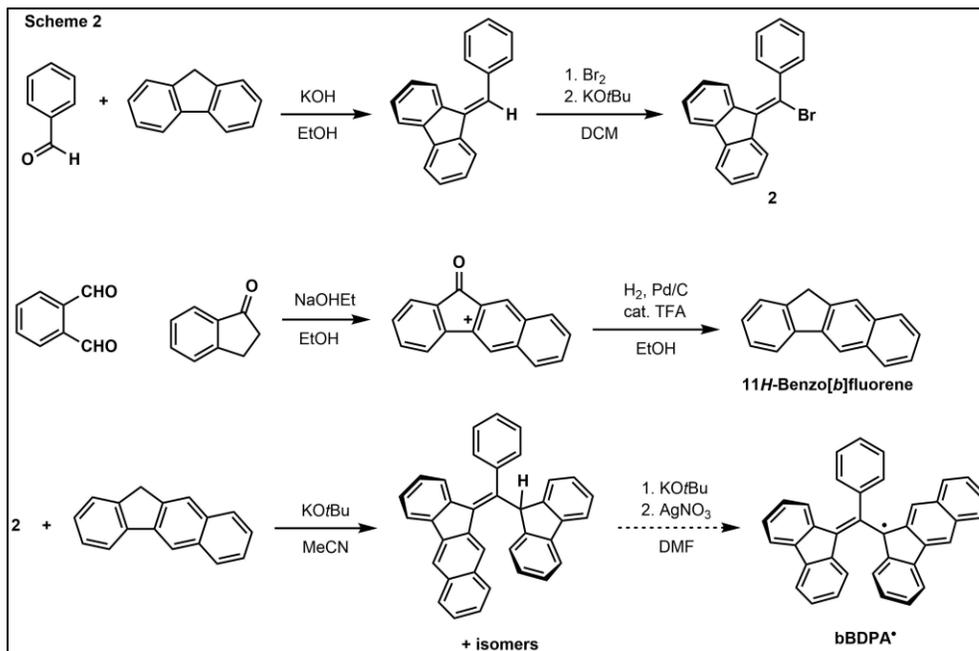
To date, four of our five undergraduate researchers have designed their own candidate molecules (Chart 1), based on known persistent radical frameworks, but incorporating chromophores into the scaffold. The students have then each spent a ten-week summer period making progress toward the synthesis of their radical.

We have pursued a synthesis (Scheme 1) of bis(diphenylene)-9'-anthracenylallyl (BDAA[•]) using a modification of the synthetic strategy for accessing the well-known radical bis(diphenylene)-9'-phenylallyl (BDPA[•]; Koelsch's radical). We can install the anthracenyl chromophore by using 9-anthracenecarboxaldehyde in place of benzaldehyde in the first step, a Knoevenagel condensation reaction. Subsequent bromination and elimination of hydrobromic acid yields the acceptor molecule, **1**. Finally, coupling of fluorene to acceptor **1** provides access to the protonated BDAAH, which can be purified, deprotonated and oxidized to form the BDAA[•] radical species. Preliminary investigations of degassed toluene solutions of BDAA[•] show persistent radical character on the order of days when stored in the dark, and these solutions also show blue luminescence. We are currently running control experiments to rigorously determine whether the BDAA[•] radical is indeed the luminescent species in solution and exclude the possibility of contamination by a secondary luminescent species.

Our initial computational investigations into the electronic structure of BDPA[•]-based radicals suggests very little radical spin density on the chromophoric anthracene group of BDAA[•], due to the majority of electron spin being delocalized about the two fluorene "wings" of the radical species. We are currently pursuing detailed computational studies on the candidate radicals to further elucidate the amount of electron spin involved in the luminescence process. It is our intention to correlate theoretical predictions and experimental data to elucidate the photophysical processes involved in luminescence from the BDAA[•] radical.



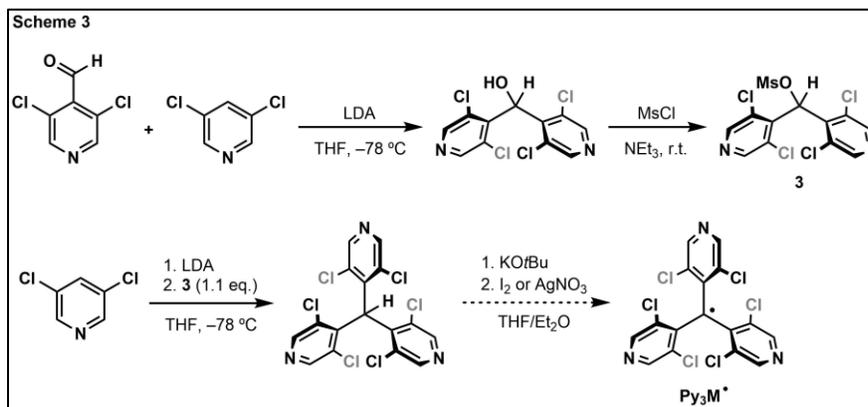
A second radical design based on BDPA[•] features a benzannulated fluorene group, which has been shown to luminesce with an emission peak at 379 nm. The chromophore 11*H*-Benzo[*b*]fluorene was synthesized from the previously reported aldol condensation of 1,2-benzenedicarboxaldehyde with indanone, followed by reduction of the product ketone. 11*H*-Benzo[*b*]fluorene was then coupled to acceptor 2, which was synthesized using literature methods, followed by deprotonation and oxidation to form a singly benzannulated BDPA[•] radical derivative (bBDPA[•]). The protonated precursor bBDPAH can also be isolated and purified, which will prove an important step in the process of assigning the luminescent behavior to the bBDPA[•] radical species itself.



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This second radical design, bBDPA[•], features a chromophore in the location on the molecule with the largest contribution to radical spin density. Upon confirmation of luminescence from the radical species, computational investigations will help elucidate the electronic structure of the luminescence manifold and distinguish whether the singly-occupied molecular orbital (SOMO) is indeed responsible for the luminescence, or whether the luminescence occurs from the next-highest occupied molecular orbital (NHOMO). Further synthetic work includes synthesis of the symmetrical bis(monobenzannulated)BDPA[•], as well as other elaborations on the fluorene subunits present in the molecule.

Two more undergraduate researchers are pursuing the synthesis of two disparate candidate designs for luminescent radicals. Based on persistent radical scaffolds other than BDPA, these designs will allow us to probe the design criteria for inducing luminescence in radicals. Synthesis of each of these compounds is ongoing, and the proposed synthetic pathway for one, hexachlorotripyridylmethanyl radical (Py₃M[•]) is outlined in scheme 3.



Five different undergraduate students have contributed to the research in this project, three of whom have been directly supported by this grant for a ten-week summer research program. Of the three students supported by ACS last summer, one continued his research during Lawrence University's new December-Term program, which occurs over two weeks of the university's winter break. The support from PRF has greatly enabled me to establish a strong research culture in my research group. Several of these students will be joining me at upcoming conferences during the 2018-2019 academic year in order to showcase their work, and we intend to publish these results upon conclusion of our studies.