ACS PRF # 57897-UNI12

Design and Synthesis of Persistent Luminescent Organic Radicals and Investigation of Doublet-State Photophysics

Graham T. Sazama, Department of Chemistry, Lawrence University

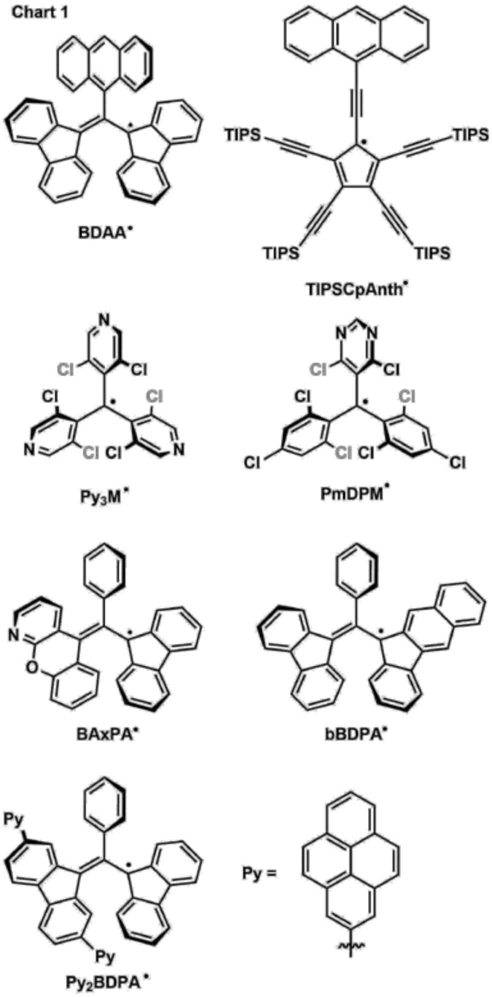
This project is an investigation into whether or not persistent radical compounds are capable of luminescence from a doublet ground state. There are two sequential goals to this project; first, incorporation of chromophore moieties into known persistent radical scaffolds with the goal of creating persistent ground state radicals with the potential to luminesce; and second, investigation of the targeted compounds as to their luminescent properties to develop our understanding of ground state doublet photophysics. 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, seven 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. Key findings from our work are highlighted here.

We successfully synthesized bis(diphenylene)-9’-anthracenylallyl (BDAA$^{\bullet}$) using a modification of the synthetic strategy for accessing the well-known radical bis(diphenylene)-9’-phenylallyl (BDPA$^{\bullet}$, Koelsch’s radical). Radical persistence lifetimes have been measured for BDAA$^{\bullet}$, with a half-life of 26 days in degassed toluene solution, stored at room temperature in the dark. Efforts to purify quantities large enough for spectroscopic analysis continue.

Our initial computational investigations into the electronic structure of BDPA$^{\bullet}$-based radicals suggests very little radical spin density on the chromophoric anthracene group of BDAA$^{\bullet}$, 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

Chart 1



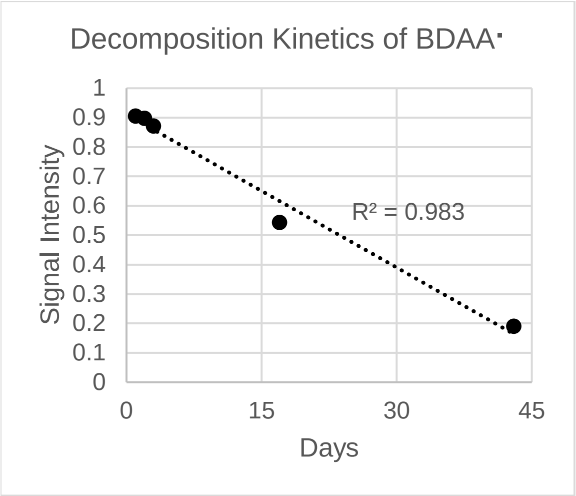


Figure 2. Plot of quantitative EPR signal vs. time in days for the BDAA radical. The first-order decomposition half-life of the radical in deoxygenated toluene solution is 26 days.

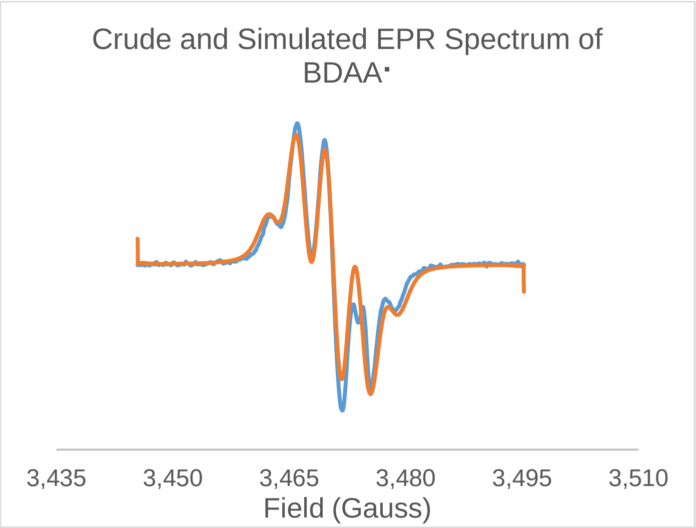


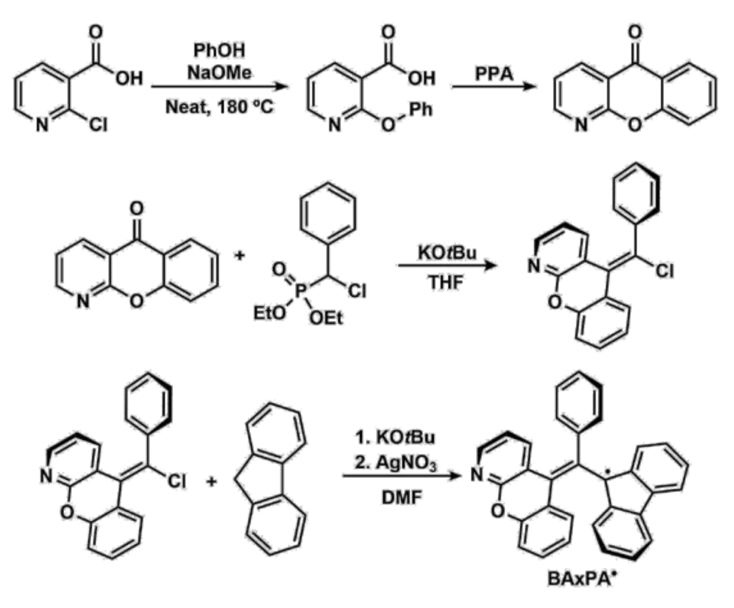
Figure 3. Crude room-temperature EPR spectrum (blue) overlaid with simulated spectrum (orange) of BDAA$^{\bullet}$ in toluene solution.

data to elucidate the photophysical processes involved in luminescence from the BDAA$^{\bullet}$ radical.

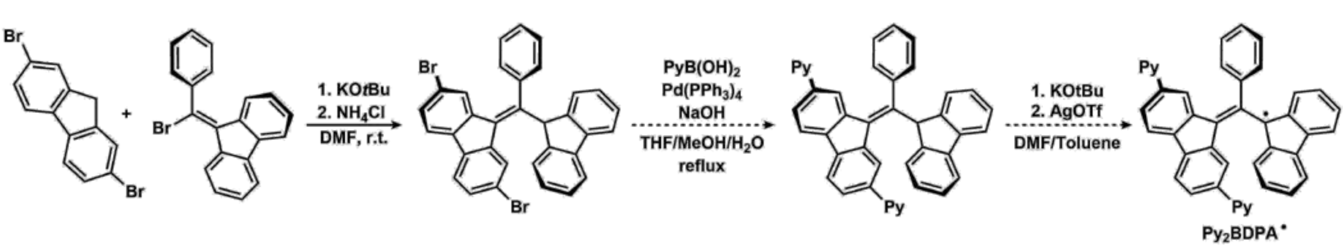
In addition to continuing our research on BDAA$^{\bullet}$, we have initiated the synthesis of three newly designed radicals as well. We have successfully synthesized a BDPA$^{\bullet}$ derivative incorporating the potential chromophore 4-azaxanthone in place of one fluorene wing of the BDPA scaffold (Chart 1, BAxPA$^{\bullet}$; Scheme 2). Incorporation of the chromophore in different places around the BDPA scaffold will allow us to elucidate the positional dependence of the chromophore on radical luminescence. Preliminary results show persistence lifetime of BAxPA$^{\bullet}$ on the order of days, and the radical color is significantly blue shifted from other radical species (typically orange); purification is needed in order to acquire fluorescence data, and is forthcoming.

A third strategy to potentially engender luminescent behavior on persistent radicals is to append a chromophore external to the aromatic radical π-structure of the molecule. To this end, a student has pursued the synthesis of a dibrominated BDPA, allowing for modular modification of the radical (Chart 1, Scheme 2). Our first efforts involve installation of pyrenyl groups, commonly employed chromophores, via Pd-catalyzed cross coupling reactions to form Py$_2$BDPA (Py = pyrenyl), and are underway currently.

Scheme 1



Scheme 2



PRF support has enabled the pursuit of seven novel persistent radicals with the potential for luminescence. Four of the target molecules have been successfully synthesized and characterized by EPR spectroscopy. Electronic absorption and luminescence spectroscopy is currently underway for the successfully synthesized species. Results from these studies and computational electronic structure investigations will guide further design of next-generation radical emitters.

In total, seven different undergraduate students have contributed to this research project thanks to the support of this ACS PRF grant. Two students attended the Spring 2019 ACS national meeting in Orlando, FL and presented posters of their research, one student presented work at the November 2018 Midstates Consortium Undergraduate Research Symposia and a second student plans to present at the 2019 symposia, and all presented during our Lawrence University Summer Research Symposia. The support from PRF has greatly enabled me to establish a strong research culture in my research group. Publication of our results is forthcoming.