

Department of Chemistry

Graduate Student Seminar – Summer 2020

**Fluorescence spectra study of sterically strained isomers of  $C_{24}H_{14}$  Polycyclic aromatic hydrocarbons (PAHs) & Characterization of a bio-sourced, fluorescent, ratiometric pH indicator with Alkaline pKa**

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The work in this study divided into two independent projects: the goal of the first project is to evaluate the ability of time-dependent density functional theory to predict fluorescence spectra for polycyclic aromatic hydrocarbons (PAHs) isomers of  $C_{24}H_{14}$ . The PAHs studied including dibenzo[a,j]fluoranthene, dibenzo[a,k]fluoranthene and dibenzo[a,l]fluoranthene. These isomers differ in the placement of one of six aromatic rings and in the amount each molecule deviates from planarity. Spectra are calculated at the CAM-B3LYP/cc-pVDZ level and include solvent. Theoretical spectra are compared to vibronically resolved experimental data obtained at cryogenic temperatures. Computed spectra for dibenzo[a,j]fluoranthene and dibenzo[a,k]fluoranthene are blue shifted versus experiment by 24.5 nm in the  $S_{1,0} \rightarrow S_{0,0}$  transition and exhibit a wavelength range that is overestimated by 30.8 %. Conversely, the computed  $S_{1,0} \rightarrow S_{0,0}$  transition of dibenzo[a,l]fluoranthene is red shifted by 51 nm. This difference is attributed to steric interactions in dibenzo[a,l]fluoranthene that creates a deviation from planarity of  $35.2^\circ$ . The second project focus on utilizing organisms as sources of fluorophores relieves the demand for petroleum feedstock in organic synthesis of fluorescent products, and endophytic fungi provide a promising vein for natural fluorescent products. We report the characterization of a pH-responsive fluorophore from an endophytic fungus isolated from sand pine. The endogenous fluorescence of the live organism was measured using fluorescence microscopy. Computational interpretation of the spectra was accomplished with time-dependent density functional-theory methods. The combined use of experimental and theoretically predicted spectra revealed the pH equilibria and photo-excited tautomerization of the natural product, 5-methylmellein. This product shows promise both as a stand-alone pH-indicating fluorophore, with alkaline pKa, and as "green" feedstock for synthesis of custom fluorophores.