

Investigating the photophysical dynamics of anthracene and acridine derivatives using time-resolved spectroscopy

PhD Seminar

Sophia Tiano
Department of Chemistry
University of Rhode Island

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Anthracenes and acridines are among the simplest visible light absorbing polycyclic aromatic chromophores and as such, have been studied extensively for applications such as LEDs, dye-sensitized solar cells, fluorescent sensors and photochemistry. These dyes are typically covalently linked into assemblies for these applications through a carbon on the central ring (the 9-position). Because of this, understanding how substitutions at the 9-position of these molecules affect photophysical processes such as intersystem crossing, fluorescence and internal conversion is vital for optimizing the molecular design of these assemblies. The fluorescence and phosphorescence lifetimes of some 9-substituted anthracenes and acridines have been studied in the past using time-resolved photoluminescence. However, this technique can only quantify radiative decay processes, and instrumental limitations of the 1960s and 1970s only allowed for quantification of processes on the order of 5-10 ns or longer. Transient absorption spectroscopy is a more robust time-resolved technique that can more precisely track and quantify both radiative and nonradiative photophysical processes. With shorter pulse widths and higher resolution detectors, our instrumental capabilities allow the measurement of time delays as short as 200 fs and as long as 45 μ s. Using a visible light probe ranging from 380 nm to 750 nm allows for the observation of the intersystem crossing in acridines and anthracenes which have a distinct triplet-triplet absorption peak within that range. Transient absorption spectroscopy allows us to directly measure the kinetics of the formation and decay of this peak.

In this talk I will discuss the results of the transient absorption spectroscopy conducted for the 9-substituted hydroxymethyl, methyl and carboxaldehyde derivatives of anthracene and acridine. These derivatives were chosen to pave the way for studies on the photophysics of reactions involving alcohol and aldehyde groups, which are ubiquitous in synthesis. We have quantified the intersystem crossing rates and triplet excited state lifetimes for each compound to compare and contrast the effect that different 9-position substituents have on these values. It was found that the intersystem crossing rates of acridines regardless of substituent are significantly faster than those of anthracenes due to the presence of a nitrogen heteroatom on the central ring of acridine. A similar effect is seen for the hydroxymethyl substituent of anthracene, which has faster intersystem crossing than the methyl-substituted derivative, due to the presence of an oxygen heteroatom on the substituents. These results indicate that the primary factor that accelerates intersystem crossing rates in anthracenes and acridines is the presence of a heteroatom, particularly if it is within the ring infrastructure of the molecule.