Pyrene Fluorophore in Halogenated Solvents

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Pyrene chromophore has been widely used as a probe because of i) its considerably long singlet lifetime (> 100 ns) and the information that can be obtained from its fluorescence emission (I/I, ratio, the excimer-to-monomer ratio, and the polarization value, ii) its long-lived pyrene radical cation (microsecond scale), and iii) its absorption (strength) features. Thus, this chromophore has been applied as a probe to acquire information about the structure and dynamics of macromolecular systems, surface properties, and adsorption sites; it has also been used in fluorescent chemosensors that can recognize selectively chemical species (ions, oxygen, explosives, ...) in potential analytical applications.

Pyrene undergoes a significant photodegradation in several media (adsorbed onto cellulose and silica, or dissolved in methanol, acetic acid, among others), that can have drastic effects on the accuracy of the analysis under consideration. In this respect, there is special concern about the use of this fluorophore in halogenated solvents. Yamada et al. have performed gas chromatography-mass spectrometry analyses of photolysates resulting from illumination of an mM pyrene chloroform solution using UV-A and sun-light. The formation of two isomeric pyrenecarboxaldehydes (one of them identified as 1-pyrenecarboxaldehyde), 1-chloropyrene, and a monoxygenated adduct of chloropyrene (whose structure is unknown) was reported. Pyrene showed less photostability in the presence of oxygen than in nitrogen, leading to a greater formation of aldehydes. In spite of that, pyrene chromophore is still used in chloroform for applications related to its fluorescent properties, because of its good solubility properties.

Interestingly, though pyrene quickly transforms into stable photoproducts (whose structure was not studied) when irradiated (λexc = 338 nm) in CCl4, its photodegradation quantum yield in dichloromethane under UV light (λexc = 311 nm) is similar to that in water (1.8 x 10-3 vs 2.1 x 10-3). The photochemical reaction in halogenated solvents is believed to occur via pyrene singlet electron transfer to the solvent, followed by the reaction of the pyrene radical cation with the fragmentation products of the radical anion of the haloalkane. In water, it has been suggested that the first step involves an electron transfer from the excited singlet state of pyrene to molecular oxygen in a contact charge-transfer pair, followed by the reaction of the pyrene radical cation with water, leading to 1-hydroxy pyrene as the initial photoproduct. A similar mechanism has been suggested for the photodegradation of pyrene on silica surfaces in the presence of oxygen (under simulated laboratory irradiation conditions and solar irradiation), where 1-hydroxy pyrene is generated via the reaction of the pyrene radical cation with physisorbed water.

There is relatively little known about the nature of pyrene photoproducts in chloroform which makes further investigation into the photostability of pyrene-functionalised nanodevices in this solvent of interest. Such investigation will give information on the photodegradation process so that it can be avoided when possible.

![Pyrene, pyrene analogues, and preparation of a QD-pyrene nanohybrid](image)

In this communication, we will present studies on a quantum dot-pyrene nanohybrid and analyze its stability under UV-A illumination in chloroform. The influence of the nanoparticle on the outcome will be analyzed by comparing the results of illuminating the nanohybrid with outcomes from pyrene and pyrene analogues under the same reaction conditions. In addition, the photostability of
the pyrene systems in chloroform will be compared with that in dichloromethane. These studies have been performed to gain information about the actual photodegradation process of pyrene in halogenated solvents.

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References