Journal of Photochemistry and Photobiology A: Chemistry 298 (2015) 9–16

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Studies on the photochemical stabilities of some fluorescent films based on pyrene and pyrenyl derivatives

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ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 6 October 2014
Accepted 10 October 2014
Available online 18 October 2014

Keywords:
Fluorescent film sensors
Pyrene
Pyrenyl derivatives
Photo-bleaching
Photo-stability

ABSTRACT

Photo-degradation is one of the most challenging problems to limit the re-usability of fluorescent film sensors, and thereby, it is a necessity to evaluate the photochemical stability of a fluorescent film before it is put into practical uses. Accordingly, the photochemical stability of some widely used pyrene and its derivatives-based fluorescent films were studied under mild conditions (i.e., in air and at room temperature) with ultraviolet (UV) or visible light as the light source. It was found that the fluorophores based films fabricated in physical ways are all un-stable to the irritation of light, in particular when UV is employed as a light source. ^{1}H NMR, FTIR and high-resolution MS studies revealed that ring-opening and oxidation of the saturated carbon next to pyrenyl structure are two of the important results of the photochemical degradation of the fluorophores tested. But it is to be noted that photo-chemically pyrene is much more stable than its derivatives no matter what kind of substituent is introduced. Furthermore, the films are only sensitive to the illumination of UV light rather than visible light. Mechanism studies revealed that the pyrene and pyrene derivatives-based films decomposed via two channels under light irritation. One is the photo-decomposition without the participation of other chemicals, and the other is photo-degradation via reaction with the chemicals. Kinetic study demonstrated that the films lost their fluorescence mainly via the second channel. It is believed that this finding is of interest to the development of novel pyrenyl derivatives-based fluorescent film sensors.

1. Introduction

The design and fabrication of fluorescent sensors with high sensitivity and selectivity have attracted extensive attention during the last few decades since they have been playing a great role in environmental monitoring, medical diagnosis, forensic analysis, and in particular explosive detection [1,2]. Among them, sensors in film state are particularly attractive owing to their advantages in re-usability and contamination free, at least in theory, when used in solution phase [3–5]. However, as found in using organic dyes, photo-bleaching or photo-degradation of fluorophores has become one of the most challenging problems in fluorescent film sensing [6]. This is because if the films were to fulfill a leading role in real-life uses their stability under mild conditions (i.e., air and room temperature) and UV–vis light illumination for prolonged periods would have to be high [7–9]. Therefore, it is of great importance to evaluate the photochemical stability of a fluorescent sensing film before it is put into practical uses.

As it is known, photo-bleaching is a dynamic process. During the process, organic fluorophores, in particular polycyclic aromatic hydrocarbons (PAHs), take place photo-induced chemical degradation upon exposure to light, resulting in irreversible loss of emitters which may lead to unexpected results and thereby affect the performances of the dyes-based devices or products [7]. Of course, as a coin has its two sides, photo-bleaching is not always negative, and it also has its own positive side. For example, it is the basis of fluorescence recovery, an important method for studying molecular diffusion within solid matrices [7,8,10,11].

Practically, fluorophores could be inorganic compounds or organic compounds, of which, generally speaking, the organic ones

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http://dx.doi.org/10.1016/j.jphotochem.2014.10.008
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are more likely to suffer from photo-bleaching. Pyrene is almost the most known organic fluorophore, since it possesses a number of unique photophysical properties such as high fluorescence quantum yield, long fluorescence lifetime, great tendency to form an excimer, and high polarity dependence of its monomer emission. It is the properties that makes pyrene and its derivatives have been widely used as a polarity probe in solution and as sensing fluorophores in the design of a variety of fluorescent sensors [12–14]. For example, over the past decade, a series of mono-layer chemistry-based and pyrene functionalized fluorescent films have been designed and prepared in our laboratory [15–23]. The films as created have been used for the sensing of dicarboxylic acids, organic copper (II) salts, sodium nitrite, nitrobenzene, picric acid, etc., in solution phase, and also used for quantifying the composition of water–ethanol mixtures and checking the purity of water. Furthermore, the films as aforementioned can be also used for sensing of nitro-aromatics, acetic acid and some volatile organic compounds (VOCs) in gaseous state [19]. In addition to the films fabricated in a chemical way, the fluorescent films fabricated in spin-coating, dip-coating, curtain-coating, and/or other physical ways are also widely adopted for sensing [24–28].

Combination use of synthetic technology developed in molecular chemistry and self-assembly techniques developed in supramolecular chemistry has been becoming a well-recognized strategy in the development of novel fluorescent films with superior sensing performances [29–32]. Recently, Liu et al. developed a pyrene-terthiophene (Py-3T)-based fluorescent film and realized sensitive detection of nitrobenzene in gaseous phase [33]. The film had been fabricated by immobilizing a fluorophore, Py-3T, onto a supramolecular gel network supported on a glass plate surface. The “synthesis + assembly” strategy may also be put into practice via purposive design and direct use of fluorescent compounds. As an example, a butterfly-shaped pyrene derivative of cholesterol was specially designed and prepared by Zhao et al. of which the design is believed to embody an effort of combining the probing advantages of pyrene and the assembling superiority of cholesterol into one [12]. As expected, the compound as obtained shows strong tendency to form a variety of supra-molecular assemblies, and the emissions from the assemblies are sensitive to the variation of the polarity and viscosity of the medium, a property very different from that of pyrene. Far beyond our imagination, the compound, in specific its assemblies, is photochemically un-stable when it is immobilized onto a glass plate surface as indicated by the fact that the fluorescence emission of the film decreases continuously under irritation of UV light.

To have a deeper understanding of the photo-chemical stability of fluorescent films, raise useful information for the proper use of fluorescent films, and develop more sophisticated film sensors, the factors affecting the photochemical stabilities of the films, of which pyrene and pyrenyl derivatives-based films were taken as representatives, were studied systematically. This paper reports the details.

2. Materials and methods

2.1. Materials

Pyrenesulfonyl chloride, ploydimethylsiloxane (PDMS) (Sylgard 184, A:B = 1:10), and **5**–**7** (c.f. Fig. 1) were synthesized according to relevant literature methods [12,34–36]. Pyrene (**1**), tert-butyl phenyl carbonate, diethylenetriamine, 1-pyrenemethanol (**2**) and cholesteryl chloroformate were purchased from Sigma–Aldrich. Organic liquids used throughout were of analytical grade and used as received, or dried to eliminate any water residue if necessary. Other reagents, excepting those specified, were of analytical grade and used without further purification. Water used in this work was acquired from a Milli-Q reference system.

2.2. Fluorescence measurements

Fluorescence measurements were performed at room temperature on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) with a front-face

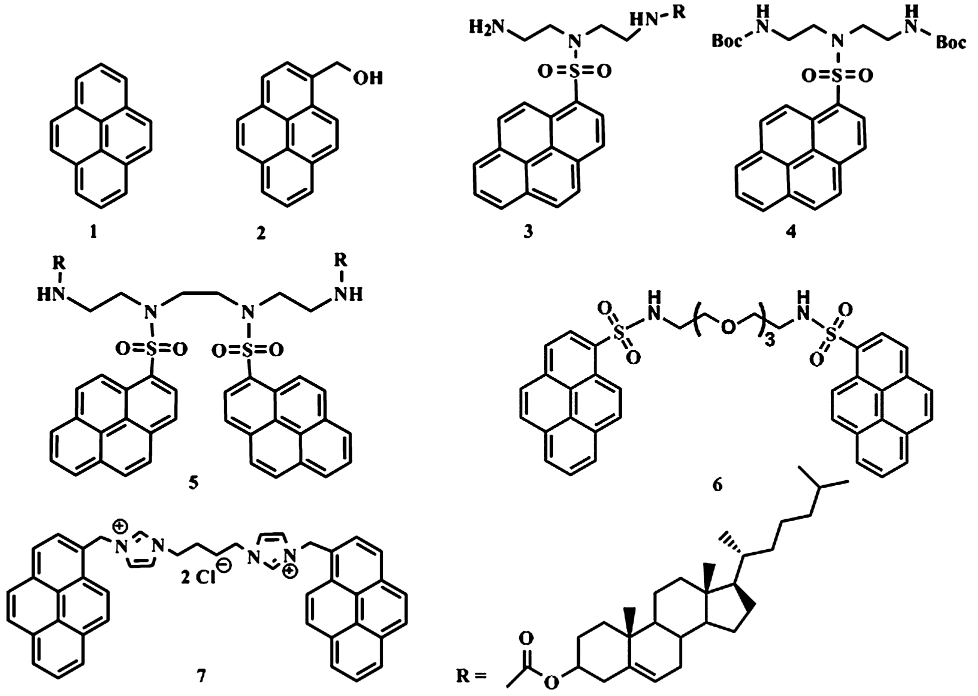

Fig. 1. The chemical structures of pyrene and pyrenyl derivatives.