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Spectroscopic properties and amplified spontaneous emission of fluorescein laser dye in ionic liquids as green media

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ABSTRACT

The use of ionic liquids (ILs) as milieu materials for laser dyes is a promising field and quite competitive with volatile organic solvents and solid state-dye laser systems. This paper investigates some photophysical parameters of fluorescein dye incorporated into ionic liquids; 1-Butyl-3-methylimidazolium chloride (BMIM Cl), 1-Butyl-3-methylimidazolium tetrachloroaluminate (BMIM $AlCl_4$) and 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4) as promising host matrix in addition to ethanol as reference. These parameters are: absorption and emission cross-sections, fluorescence lifetime and quantum yield, in addition to the transition dipole moment, the attenuation length and oscillator strength were also investigated. Lasing characteristics such as amplified spontaneous emission (ASE), the gain, and the photostability of fluorescein laser dye dissolved in different host materials were assessed. The composition and properties of the matrix of ILs were found that it has great interest in optimizing the laser performance and photostability of the investigated laser dye. Under transverse pumping of fluorescein dye by blue laser diode (450 nm) of (400 mW), the initial ASE for dye dissolved in BMIM $AlCl_4$ and ethanol were decreased to 39% and 36% respectively as time progressed 132 min. Relatively high efficiency and high fluorescence quantum yield (11.8% and 0.82% respectively) were obtained with good photostability in case of fluorescein in BMIM BF_4 that was decreased to ~56% of the initial ASE after continuously pumping with 400 mW for 132 min.

1. Introduction

The surrounding medium for laser dye probe plays an important role when defining physical properties and potential hazards for dye laser. The lasing wavelength may be tunable for some dyes by varying the laser cavity parameters, the dye concentration, the solvent (polarity and PH) and also temperature [1]. In dye laser media, an organic solvent such as ethanol which has a good solubility to organic dyes is usually used as a proper solvent. However, a dye laser has many kinds of problems caused by the organic solvent. For example, high volatility of organic solvents results from the dye concentration changes as time progresses. In addition, bubbles generated in the strong excitation, may cause stable oscillation difficulties. Furthermore, most organic solvents are flammable and this makes its use associated with the risk of an explosion and it thus always requires a cooling circulating unit. For these reasons, ionic liquids are used as the laser dye solvents. The field of ionic liquid is continuously growing as the practical alternative of conventional organic solvents in dye laser systems. An ideal host matrix should possess good optical transparency in the region of absorption and emission of the dissolvent dye. It should not have chemical and photo-physical interaction with the dye. It should possess thermal and mechanical stability and time durability (longevity). Using of ionic liquids combines thermal stability, lower thermal expansion and better thermal coefficient of refractive index. Ionic liquids are organic salts composed entirely of anions and cations, and remain in the liquid state at ambient conditions. Recently, ionic liquids have been extensively studied as possible “green substitutes” for volatile organic solvents [2]. Due to their unique chemical and physical properties, such as thermal stability, low vapor pressure, and the surface properties [3,4], ionic liquids have also been used for electrochemical applications, solar batteries and biopolymers [5]. Furthermore, many dyes are known to be soluble in different ionic liquids, and the photophysical properties of the dyes in ionic liquids are expected to be interesting. For example, as the solvation of dye molecules in ionic

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liquids is expected to have properties different from those in usual solvents. It is necessary to know and understand the effect of various host matrices on the various properties including, photostability, photophysical properties as well as laser efficiency. Photophysical properties provide basic information about the lasing behavior of the material [6]. Fluorescein dye is well known as a good laser medium in the visible region and is notable for its moderate fluorescence quantum yield and photostability.

In this paper a comparison and description of the spectroscopic and photophysical properties of fluorescein dye probe dissolved in different ionic liquids and ethanol as reference were assessed.

2. Experimental parts

2.1. Materials

The chemical materials which are used in this work were; fluorescein, 1-Butyl-3-methylimidazolium chloride (BMIM Cl), 1-Butyl-3-methylimidazolium tetrachloroaluminate (BMIM $AlCl_4$), 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4), (cf. Fig. 1) and ethanol. All chemicals were used as received without further purification. Fluorescein laser dye dissolved into three types of ILs (BMIM Cl, BMIM $AlCl_4$, BMIM BF_4) and ethanol as reference with different dye concentrations. Pre-cleaned amber measuring flasks were used to prepare the required amounts of appropriate different dye concentrations. Fluorescein dissolved in (BMIM $AlCl_4$), with concentrations of (1×10^{-3}, 7×10^{-4}, 3.5×10^{-4}, 1×10^{-4}, 7×10^{-5}, 2×10^{-5}) M, in (BMIM BF_4), with concentrations of (1×10^{-3}, 7×10^{-4}, 3.5×10^{-4}, 1×10^{-4}, 7×10^{-5}) and in (BMIM Cl, ethanol), with concentrations of (1×10^{-2}, 8×10^{-3}, 6×10^{-3}, 2×10^{-3}, 1×10^{-3}, 7×10^{-4}, 3.5×10^{-4}, 1×10^{-4}, 7×10^{-5}, 2×10^{-5}) M. Above 1×10^{-2} M of fluorescein, we noticed the aggregation of dye in ethanol.

2.2. Measurements

Absorption and excitation–emission spectra were measured by Camspec M501 UV–Vis Spectrophotometer and PF-6300 Spectrofluorometer respectively. Fluorescence quantum yields φ_f were obtained by applying a comparative method [7]. Optimum concentration of the dye as linear fluorescence in ethanol was detected from its absorption and emission spectra. The fluorescence lifetime (τ_f), was measured by using Nitrogen laser (laser photonics LN1000) of pulse duration of 800 ps and wavelength 337.1 nm. The maximum energy per pulse was 2 mJ. The fluorescence signal registration with a fast phototube (Hamamatsu R1328U-03) through optical fiber. The fast phototube (+H.V) powered by power supply at 750 V and connected to the 300 MHz εZ-digital oscilloscope (DS-1530) attached to the computer processing unit for processing the spectrum. The dye samples were contained in 1 cm optical-path quartz cells that were transversely pumped by blue laser diode (450 nm). The exciting beam was directed toward the surface of cell sample with a combination of concave lens (f = 10 cm) and a cylindrical lens forming a line shape of 1 cm. The pumping energy (input energy) was measured via a beam splitter (4%) and the Gentec power meter (ModelQE50) detector head. The ASE output was focused by convex lens (f = 15 cm) onto Oplenic spectrophotometer which was connected to a computer unit for processing the spectrum. The samples were transversely pumped and were allowed to emit in the super radiant mode without employing a cavity mirror, since optical feedback were provided by reflection at host material air interface.

3. Results and discussion

The study of the photophysics of fluorescein dye in different environments provides useful informations on the potential of the different ionic liquids herein studied as laser media. Absorption spectra of (1×10^{-4} M) of fluorescein dissolved in different solvents with 2 mm path length cuvette are presented in Fig. 2. The absorption profile of fluorescein was dependent on the host material and their PH value since fluorescein dye has different

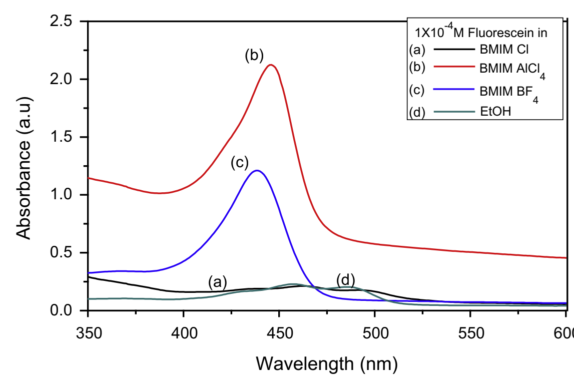

Fig. 2. Absorption spectra of fluorescein in different host materials with 2 mm path length cuvette.

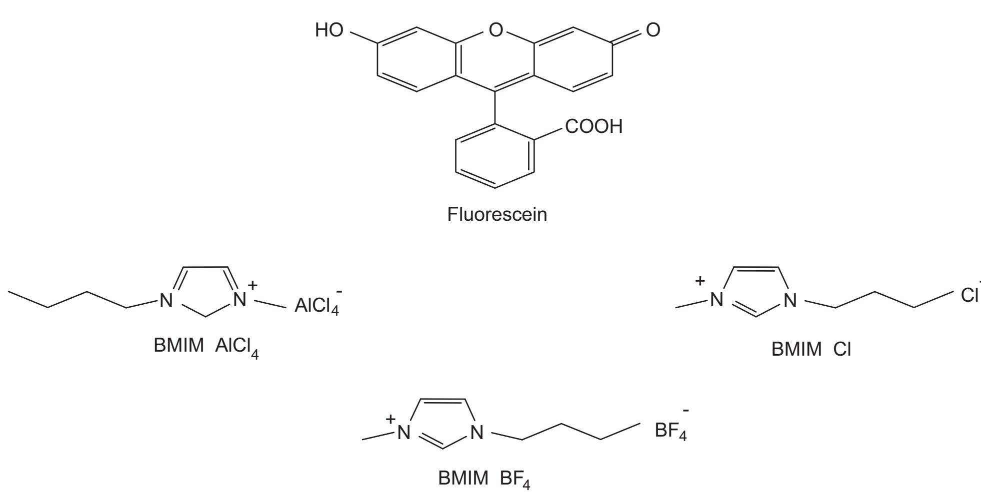

Fig. 1. Molecular structure of laser dye (fluorescein) and ionic liquids.