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Photophysical, photochemical and laser behavior of some diolefinic laser dyes in sol–gel and methyl methacrylate/2-hydroxyethyl methacrylate copolymer matrices

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ABSTRACT

The photophysical properties such as singlet absorption, molar absorptivity, fluorescence spectra, dipole moment, fluorescence quantum yields, fluorescence lifetimes and laser activity of 1,4-bis (β-Pyridyl-2-Vinyl) Benzene (P_2VB), 2,5-distyryl-pyrazine (DSP) and 1,4-bis(2-methylstyryl)benzene(MSB) diolefineic laser dyes have been measured in different restricted hosts. (P_2VB), (DSP) and (MSB) are embedded in transparent sol–gel glass and a copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) media. The absorption and fluorescence properties of these laser dyes in sol–gel glass matrices are compared with their respective properties in copolymer host. The photostability of these laser dyes in sol–gel glass and (MMA/HEMA) copolymer samples are measured in terms of half-life method (using nitrogen laser 337.1 nm in pumping), as the number of pulses necessary to reduce the dye laser intensity to 50% of its original value. The gel laser materials show improved photostability upon pumping by nitrogen laser compared with those in organic polymeric host matrix.

1. Introduction

Liquid solutions of organic laser dye molecules have been widely used as good laser gain media from the near UV to the near IR regions of the spectrum [1]. There are several disadvantages in using liquid dye lasers like poor thermal stability of dye solutions, requirement of large volume of solutions and need of significant maintenance, etc [2–5]. These difficulties can be overcome by doping stable laser dye molecules into restricted host matrices like polymers, silica gels, xerogels and sol–gel glasses [4–8]. Solid-state dye laser presents some advantages, e.g. they do not contain volatile solvents, they are non-flammable, nontoxic, compact in size and mechanically and thermally more stable [2,3]. The possibility and applications of incorporating a dye in a gel was first illustrated by Avnir and coworkers in 1984 [2]. The effect of drying control chemical additives (DCCA) on the optical and lasing properties of pyrromethene (PM) dye-doped sol–gel and organically-modified silicates (ormosils) has been reported [9]. Moreover, DCCA can control the hydrolysis and the condensation rate that strongly influences the dye molecule in sol–gel matrix [10]. In this sense, silica xerogel matrix would be a good host for these dyes due to its transparency, chemical inertness and the possibility to disperse the dye at molecular level [2,11,12]. However, polymeric host materials have been shown to be inherently lacking in mechanical and thermal properties and photostability [13,14].

The sol–gel method is a method for incorporation of organic dye molecules into an inorganic silica host [15]. Incorporation of the laser dyes into sol–gel matrices by doping method was reported by several authors [2,4,5]. A simple classification, based on the nature of the links and interactions that the organic and inorganic components exchange, has been proposed for hybrid materials. Two main classes have been defined. Class I corresponds to all the systems where there are no covalent or iono-covalent bonds between the organic and the inorganic components. In such materials, the various components only exchange interactions such as van der Waals forces, hydrogen bonding or electrostatic forces. On the contrary, in class II materials, at least parts of the organic and inorganic components are linked through strong chemical bonds (covalent or iono-covalent) [16]. In dope method, dyes are mixed at the sol stage and drying is carried out afterward. Sol–gel shows some advantages, e.g. its reaction can be controlled easily by chemical methods. It allows introducing permanent organic groups to form inorganic–organic hybrid materials [17] and the process takes place at low temperature [18]. High porous

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material was prepared in which the matrix is chemically inert and possesses low poisoning [19]. It has exultant optical low intrinsic fluorescence. The higher thermal conductivity of silica in comparison with that of polymer materials allows heat dissipation and minimizes both photo degradation and thermal lensing effect which causes laser beam divergence [20]. The process provides good flexibility during polymerization steps [21] with ability to be functionalized before or after polymerization. Hence sol–gel host provides a more suitable surrounding for the dye molecules compared to polymeric hosts.

In the past, we reported a number of studies on 1,4-Bis (β-Pyridyl-2-Vinyl) Benzene (P_2VB) [22–27], 2,5-distyryl-pyrazine (DSP) [22–27] and 1,4-bis(2-methylstyryl)benzene (MSB) [28–30], as new laser dyes having the advantage of laser emission in the UV- blue spectral region. In the present paper, we report the behavior of these diolefinic laser dyes in silica sol–gel solid as well as in a copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) media in a trial to improve the quality of laser action. The plasticity of the material was internally increased by copolymerization of methyl methacrylate (MMA) with 2-hydroxyethyl methacrylate (HEMA). The presence of HEMA increases the plasticity of the material while maintaining its transparency. It also ensures a good solubility of dyes such as Rh6G due to the polar character of HEMA [31].

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 [1]. With this objective, sol–gel host samples were prepared by HCl acid catalyzed hydrolysis of tetraethylorthosilicate (TEOS). The absorption and emission properties of these laser dyes in sol–gel glass matrices are compared with their respective properties in copolymer host matrices. The data are also compared with those in free solutions.

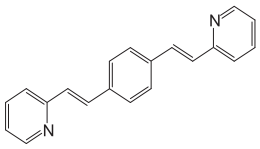
Laser dye life-time is a key performance parameter which limits a laser dye application. Intensive research efforts have been made to explore the mechanism of photodegradation of laser dyes. It has been demonstrated that the mechanism of photodegradation occurs by the interaction of the dye molecules in the excited state with other species such as impurities, other dye molecules and singlet oxygen. Through the process of doping laser dyes into a solid medium, the photochemical pathways including bimolecular reactions can be suppressed by caging or trapping the dyes within a solid host, and the photostability of the dye molecules doped in the solid host is improved as compared with the dye molecules in a liquid solvent [32].

The improved photostability of the dye within solid hosts has been attributed to caging and immobilizing the dye molecules, thereby minimizing excited-state interaction with other species including molecular oxygen. So in a solid host, the photodegradation of the laser dye depends on the nature of dye molecule, the composition and structure of the host, and the impurities present in the host. In order to further improve the photostability and decrease photodegradation of the laser dye, control of the surroundings of the dye molecules becomes the most critical issue for the solid-state dye laser.

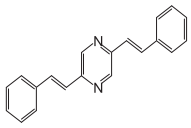
Sol–gel derived glasses have many advantages e. g. thermally stability much beyond the range of temperatures which are of relevance for polymeric matrices, they do not photodegrade and, in the case of SiO_2 matrices, are not involved in light induced reactions with the matrix. Sol–gel matrices are transparent well into the UV region down to ~250 nm for SiO_2 and are thus highly suitable for optical applications. These are major advantages of silicate matrices compared with organic polymeric ones.

Another possible factor that may explain the reduced rate of degradation in the more rigid matrices may be that the dye molecules are more tightly confined within the pores of the matrix, limiting rotational and translational freedom. A mobile molecule, as in solution, will be more likely to encounter an oxygen molecule and undergo degradation. Less freedom, as defined by the restrictive pores of the matrix, may make the dye molecule less likely to interact with molecular oxygen leading to photodegradation or fluorescence quenching. Molecular oxygen is a well-known fluorescence quencher due to its paramagnetic nature [32].

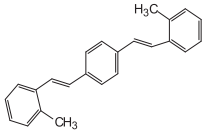
In the present communication we report lasing, photostability, and a number of photophysical characteristics of three UV-blue diolefinic laser dyes in sol–gel and polymeric matrices. A number of advantages of sol–gel matrix over the copolymer are highlighted.



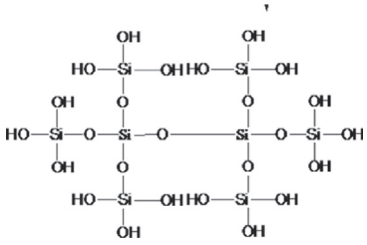
1, 4-bis (β-pyridyl-2-vinyl) benzene (P_2VB)



2, 5 distyrylpyrazine (DSP)



1, 4bis (2-methylstyryl) benzene (MSB)



Sol-gel network

2. Experimental

Sol–gel materials were prepared by the hydrolysis of silicon alkoxide followed by polycondensation. Dye is incorporated into the matrix by doping method. The sol–gel matrix was prepared using HCl as a catalyst and glycerol as DCCA to reduce the cracking of monoliths during drying [33]. This method involves the