Enhanced laser action of Perylene-Red doped polymeric materials

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Abstract: The laser action of Perylene-Red doped in linear, crosslinked, fluorinated and sililated polymeric materials is reported. The purity of dye was found to be a key factor to enhance its solid-state laser behaviour. The samples were transversely pumped at 532 nm, with 5.5 mJ/pulse and 10 Hz repetition rate. Perylene-Red doped copolymers of methyl methacrylate with a 10 vol% proportion of 2,2,2-trifluoroethyl-methacrylate exhibited a lasing efficiency of 26% with a high photostability since the dye laser output remained at the same level after 100,000 pump pulses in the same position of the sample. This lasing behaviour is, to the best of our knowledge, the highest achieved to date for organic, inorganic, and hybrid materials doped with Perylene-Red.

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References and links

1. Introduction

Solid-state dye lasers with tunable emission at the red-edge spectral region could replace their liquid phase counterparts finding a niche in optical and optoelectronic applications provided the laser behaviour of the as yet reported systems is improved. Dyes derived from perylene di-imides have particularly attractive optical properties [1–3] due to an exceptional chemical, thermal, and photochemical stability with high fluorescence quantum yield close to unity [4–6]. One of these red-emitting dyes which has been adapted to solid-state hosts is the non-ionic and nonpolar dye commercially named Perylene-Red (Per-Red, Fig. 1) [7–10]. Surprisingly, in spite of its good photophysical and photochemical properties, few reports have appeared on the lasing behaviour Per-Red doped solid-state materials [11–18]. A number of reasons could justify this scarcity of studies, mainly the insolvency of this dye in common organic solvents, which probably led to Per-Red dye being one of the first dyes to be incorporated into sol-gel hybrid materials [19,20], in spite of some serious limitations exhibited by these materials (complex and lengthy synthesis process, fragility which results in difficult mechanization of the final material, and most important, frequent optical inhomogeneity caused by refractive index mismatch between organic and inorganic parts). These early experimental studies revealed that this dye lases in the 610-640 nm range with a photostability much higher than that of the rhodamine family dyes, which are well known to be fairly stable [21], albeit with a much lower lasing efficiency [13].
To attempt producing a solid-state laser in the red–spectral region with a rather high lasing efficiency while retaining high photostability, and taking into account that the best dye/host combination is specific for each dye molecule and that there is no universal material which can optimize the lasing properties of all different dyes [22], we proceeded to incorporate the Per-Red laser dye into a number of organic polymeric matrices, which actual composition was decided in the light of the information obtained in our previous studies on the solid-state lasing properties of PM567 [23–26].

In this work, we report on the solid-state laser action of Per-Red dye doped organic linear and crosslinked matrices, since the rigidity of the matrix is of utmost importance, once caging and immobilizing the chromophores reduces, consequently, the dynamic interactions with other species (i.e. oxygen, other dyes molecules and free radicals) avoiding early photobleaching of the dye. Taking into account that hybrid organic-inorganic materials have been used with good results to improve the thermal resistance of the host without losing the benefits provided by polymers [15,16,27], the dye was also dissolved in silicon-modified organic matrices. The presence of monomers containing silicon atoms in their backbone avoids the problems related to the sol-gel hybrid organic-inorganic matrices while maintaining its organic character, which means good dye solubility, plasticity and easy synthesis, but with improved thermal properties [25]. Although, up to date, no attention has been paid to the influence that the purity of the commercial Per-Red dye has on its laser action, this work reveals it to be a key factor to enhance its lasing properties.

2. Experimental

2.1 Materials

Perylene-Red (BASF Lumogen Red 305) was first used as received with a purity of only 90% (checked by spectroscopic and chromatographic methods). Thus, the dye purity was improved up to a 99% through a flash column chromatography based on silica with hexane/ethyl acetate 95/5 v/v proportion as eluent, to remove the N-methyl-2-pyrrolidone, identified by NMR-\textsuperscript{1}H as the principal impurity. Solvents for laser studies were of spectroscopic grade (Merck, Aldrich or Sigma) and were used without purification. Linear copolymers were obtained by copolymerization of methyl methacrylate (MMA) with different volumetric proportions of the siliilated monomer 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) as well as the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFMA). Crosslinked matrices were obtained by copolymerization of MMA with di-, tri- and tetra-functionalized comonomers, such as ethyleneglycol dimethacrylate (EGDMA), pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETRA), respectively. All monomers were purchased from Aldrich and were used as received. Figure 1 shows the molecular structures of these monomers.

2.2 Preparation of solid polymeric samples

Per-Red was incorporated into the different solid matrices following the procedure previously described [23], and rendering materials named as COP(MMA/monomer). The solid monolith laser samples were cast in a cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A cut was made parallel to the axis of cylinder to obtain a lateral flat surface of \( \approx 6 \times 10 \) mm. This surface as well as the ends of the laser rods were prepared for lasing experiments by using a grinding and polishing machine (Phoenix Beta 4000, Buehler) until optical-grade finished.
Fig. 1. Molecular structures of Perylene-Red (Per-Red) dye as well as the monomers selected in this work: methyl methacrylate (MMA), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), 2,2,2-trifluoroethyl-methacrylate (TFMA), ethylene glycol dimethacrylate (EGDMA), pentaerythritol triacrylate (PETA), and pentaerythritol tetraacrylate (PETRA).

2.3 Methods

Liquid solutions of dyes were contained in 1 cm optical-path quartz cells that were carefully sealed to avoid solvent evaporation during experiments. Both the liquid cells and the solid samples were transversely pumped at 532 nm with 5.5 mJ, 6 ns FWHM pulses from a frequency-doubled Q-switched Nd:YAG laser (Monocrom OPL-10) at a repetition rate of up to 10 Hz. Details of the experimental system can be found elsewhere [23,25,26].

Narrow-line-width laser emission and tuning ranges of dye solutions were obtained by placing the samples in a home-made Shoshan-type oscillator [28], consisting of full-reflecting aluminium back and tuning mirrors and a 2400-lines mm\(^{-1}\) holographic grating in grazing incidence, with outcoupling via the grating zero order. Wavelength tuning was accomplished by rotation of the tuning mirror. Tuning mirror and grating (both from Optometrics) were 5 cm wide and the angle of incidence on the grating was 88.5°. Laser line width was measured with a Fabry-Perot etalon (IC Optical Systems) with a free spectral range of 15.9 GHz.

Absorption and fluorescence (after excitation at 532 nm) spectra of the dyes were recorded on a fibre optic spectrophotometer (Ocean Optics USB2000) and on a spectrofluorimeter (Perkin Elmer LS-50B), respectively, for diluted (5x10\(^{-4}\) M) and concentrated (1x10\(^{-3}\) M) dye solutions in ethyl acetate contained in 0.01 cm optical path length quartz cuvettes.

3. Results and discussion

A systematic analysis of the laser behaviour of the dye in liquid phase was previously carried out as a guide to develop polymeric materials enhancing its laser action in solid-state. Under
the selected experimental conditions, a concentration of $5 \times 10^{-4}$ M, corresponding to an optical density (for a 1 cm path length at 532 nm) of 16, in ethyl acetate optimized the lasing efficiency (21%) of the dye when used as received. The purification process of the dye increased this conversion efficiency up to 26% although, when compared with other laser dyes pumped under the same experimental conditions, Per-Red is the least efficient because of its high excited-state absorption impairing the conversion efficiency [29]. In order to analyze the influence of the dye purity on the laser photostability, solutions of both pure and non-purified Per-Red were irradiated under experimental conditions identical to those selected to irradiate the fluorophores when doped into solid polymeric matrices. Because the irradiated volume in solid samples was estimated to be 8 $\mu$L, capillary tubes into which ethyl acetate solutions ($5 \times 10^{-4}$ M) of dyes were incorporated offer the best geometry to reproduce the area irradiated in the solid samples, thus maintaining the same laser pump conditions in both cases. Although the low optical quality of the capillary prevents laser emission from the dyes, information about photostabilities can be obtained by monitoring the decrease in laser-induced fluorescence intensity, excited transversally to the capillary, as a function of the number of pump pulses. The fluorescence emission was monitored perpendicular to the exciting beam, and its collection and analysis was carried out with the same set-up selected to characterize the laser emission from dyes incorporated into solid samples. From the results obtained (Fig. 2) it can be concluded, for the first time to the best of our knowledge that the Per-Red photostability depends strongly on the purity of the chromophore since the presence of impurities in the commercial dye impairs drastically its laser action.

![Graph](image)

Fig. 2. Normalized laser-induced fluorescence emission as a function of the number of pump pulses at 10 Hz repetition rate for (a) pure and (b) impure Perylene-Red dye in ethyl acetate solutions.

The influence of both composition and structure of solid matrix on the laser action of Per-Red was analyzed, in a systematic way, for the purified dye dissolved at a $5 \times 10^{-4}$ M concentration in a number of copolymeric formulations with different compositions and/or degree of crosslinked based on MMA, since this is the monomer which mimics the ethyl acetate solvent.

Broad-line-width laser emission in a simple plane-plane non-tunable resonator with a single peak centred at the wavelength of $\approx$620 nm, beam divergence of $\approx$5 mrad, and pulse duration of $\approx$5 ns FWHM, was obtained from all the materials under study. The tuning capability of the dye-doped solid matrices, one of the most important features of dye lasers, was determined placing the samples in a grazing-incidence grating cavity in Shoshan...
configuration. Tunable laser emission with line width of the order of 0.15 cm$^{-1}$ was obtained, with a tuning range of 50 nm, from 605 to 655 nm.

A summary of the results obtained is shown in Table 1, where data on lasing efficiency, peak of the laser emission and intensity of the laser output (referred to initial intensity) after 100,000 pump pulses in the same position of the sample are included. For the sake of clarity, the evolution of the lasing photostability with the number of pump pulses is shown in Fig. 3 for some of these optical materials. Lasing efficiencies up to 21% were obtained depending on the matrix composition, which are only slightly lower than those registered in liquid phase, in spite of the polishing surface of the solid samples relevant to laser operation not being laser grade, which results in higher losses in the optical cavity.

Table 1. Laser parameters for Perylene-Red dye in linear, crosslinked, fluorinated and silicon-containing organic matrices. Nd:YAG laser (second harmonic) pump energy and repetition rate: 5.5 mJ/pulse and 10 Hz, respectively. Dye concentration: 5x10$^{-4}$ M.

<table>
<thead>
<tr>
<th>Material</th>
<th>vol/vol prop.</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Eff (%)</th>
<th>$I_{100,000}$ (%)</th>
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<td>90/10</td>
<td>616</td>
<td>16</td>
<td>87</td>
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<tr>
<td>COP(MMA/EGDMA)</td>
<td>80/20</td>
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<td>16</td>
<td>77</td>
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<tr>
<td></td>
<td>70/30</td>
<td>620</td>
<td>15</td>
<td>72</td>
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<tr>
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<td>92</td>
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<tr>
<td>COP(MMA/PETA)</td>
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<td>74</td>
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<tr>
<td></td>
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<tr>
<td>COP(MMA/PETRA)</td>
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<tr>
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<td>100</td>
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<tr>
<td></td>
<td>70/30</td>
<td>618</td>
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<td>96</td>
</tr>
</tbody>
</table>

* Eff: energy conversion efficiency; $\lambda_{\text{max}}$: peak wavelength of the laser emission. Intensity of the dye laser output after 100,000 pump pulses in the same position of the sample referred to the initial intensity $I_0$, $I_n(\%) = (I_n/I_0)\times 100$. 

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The lasing photostabilities of Per-Red doped in the studied materials depend strongly on the actual composition of the matrix. Thus, for each functionalized monomer, low crosslinking degrees in the matrix enhance lasing photostability, which points out the importance of proper adjustment of the material’s rigidity in the laser performance of the dye. The results obtained with Per-Red dye incorporated into crosslinked matrices do not show a significant enhancement of the lasing action with respect to that reached in the PMMA homopolymer. Although no single cause is expected to fully explain the mechanism at work, a factor such as the molecular size of the dye should play a key role in its photodegradation process, probably related to its partial exclusion from the shrinking free volume, and the resulting formation of aggregates, with the deleterious effect on the laser operation. In accordance with these criteria, the Per-Red dye was found to reach high photostabilities in linear matrices. Contrary to the general trend exhibited by pyromethene dyes, the presence of a silicon-containing monomer such as TMSPMA enhancing the thermal properties of the final material, does not improve the lasing photostabilities. Taking into account that perylene diimide dye photo-oxidation is an important photodegradation mechanism [18], high silicon contents could accelerate this processes, as a consequence of the higher oxygen permeability in sililated materials, and the longer lifetime of singlet molecular oxygen in these media [30].

Lasing efficiency and photostability optimizes in the matrix with fluorinated composition. Polymers that contain atomic fluorine in or along the backbone possess many desirable physical properties, mainly due to high thermal stability, high optical damage threshold, and enhanced chemical resistance when compared to their non-fluorinated analogues [31]. In addition, the fluoropolymers increase the rigidity of the matrix enhancing, at the same time, the fractional free volume (FFV) that, estimated from the polymer specific volume and the specific van der Walls volume [32], can be up to 1.87 times higher than that obtained in sililated matrices with the same monomer proportion. As was discussed for the crosslinked matrices, the free volume available within the polymeric matrix could control, at least to some extent, the photodegradation process of the dye. Consequently, and taking into account the molecular size of Per-Red, the fluorinated matrices could be defining a protecting “polymer cage” so that the free volume is completely occupied by the dye reducing the photobleaching rate. In order to lend support to this tentative conclusion, a more detailed study of free volume holes and their distribution inside the matrix is currently in progress.

Fig. 3. Normalized laser output as a function of the number of pump pulses for Perylene-Red dye dissolved in (a) COP(MMA/TFMA 7/3), (b) silicon-containing copolymer COP(MMA/TMSPMA 9/1) and (c) crosslinked copolymer COP(MMA/PETRA 7/3). Dye concentration: 5x10^{-4} M. Pump energy and repetition rate: 5.5 mJ/pulse and 10 Hz, respectively.
To the best of our knowledge, this laser action is the highest achieved up to date for solid-state dye laser based on Perylene-Red doped organic, inorganic and hybrid matrices under less efficient and more demanding transversal pumping selected in the present work, without rotating or translating the sample to distribute the thermal load over a large volume, even as our resonator cavity was non-optimized.

It has to be remarked that proper comparison of the laser action in our studies with that reported by different authors is a difficult task because of the substantial differences in experimental conditions, such as pumping configuration, optimization of oscillator cavity or repetition rate, which can strongly affect the efficiency and longevity of the solid samples. Thus, the best lasing efficiency exhibited by Perylene-Red in xerogel (20%) was recorded under longitudinal pumping and in an optimized cavity [12]. In the same way, the best previous lifetime was obtained with a sample of Perylene-Red in a vinyl-triethoxysilane ORMOSIL, where the laser output dropped by 50% after just 40,000 pulses under longitudinally pumping and low repetition rate (2 Hz) [11,16]. When these samples were synthesized under oxygen-free conditions the photostability was optimized, and the laser output dropped by 50% after 250,000 pulses under longitudinal pumping, with pulses of 1 mJ at 5 Hz repetition rate [12].

Although the laser photostability of dyes is strongly conditioned by their photophysical and photochemical properties the laser performance of Per-Red can also be compared with that of other good laser dyes in the red-edge spectral region such as Rhodamine 6G or Pyromethene 650 under the same experimental conditions. Thus, purified Rh6G ($4 \times 10^{-4}$ M) incorporated into some of linear copolymers synthesized in the present work such as COP(HEMA/TMSPMA 70/30) exhibited lower photostability (its laser emission drops to 50% of the initial value after 100000 pump pulses at 10 Hz repetition rate) than the Per-Red. Pyromethene 650 resulted to be highly unstable when incorporated into solid polymeric matrices since, with independence of the composition and structure of the final material, the dye experienced a continuous and irreversible photodegradation process under the selected pumping conditions, with the disappearance of the laser emission. This degradation is related to the dye fragmentation with the result of losing the 8-cyano substituent.

In conclusion, the results presented in this work indicate that the laser action of the nonpolar and non-ionic Perylene-Red dye is greatly enhanced in polymeric matrices by properly incorporating fluorine atoms into the structure of the organic monomers. Reasonable lasing efficiencies for laser operation under transversal pumping in non-optimized cavities were recorded with a long stable lifetime operation, with only a slight degradation in the laser output after 100,000 pump pulses in a static sample at 10 Hz repetition rate. These new laser materials that exhibit important advantages with respect to the sol-gel hybrid matrices since they remain organic, have the potential to be used as active media in highly processible, reproducible, versatile, and easy to handle solid-state dye lasers and to substitute existing commercially available dye lasers in liquid phase impelling the applications of this new technology into optoelectronic fields.

The materials described in this work and their utilization in solid-state dye lasers are covered by Spanish Patent No. P200802558 filed on September 2008.

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