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Ultrafast nonlinear optical properties of dye-doped PMMA discs irradiated by 40 fs laser pulses

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ABSTRACT

The two-photon absorption (TPA) characteristics of PMMA discs doped with three different dyes were studied using an fs-pulsed Ti-Sapphire laser as the pump source, and employing the open-aperture *Z*-scan technique. TPA cross-sections obtained for PMMA doped with the dyes PM597, DCM and rhodamine 6G–rhodamine B (co-doped) were found to be equal to 24.7, 33.3 and 32.3 GM, respectively ($1\,GM = 10^{-50}\,cm^4\,s\,phot^{-1}\,mol^{-1}$). Furthermore, two-photon fluorescence was measured for the samples containing DCM and rhodamine 6G–rhodamine B (co-doped). Compared to the one-photon fluorescence spectrum, the peaks in the two-photon fluorescence spectrum were red shifted and the extent of red shift increased with increasing doping concentration. We have also observed that the red shift in the two-photon fluorescence peak of the samples in the solid form is much larger than that in the solution state. This phenomenon could be explained by a twisted intra-molecular charge transfer model.

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1. Introduction

Organic dye solutions have been widely used in tunable lasers as well as for laser pulse shaping through Q-switching and mode-locking techniques. More recently, solid-state dye lasers, wherein an organic dye is doped into a suitable solid matrix, have attracted much attention [1–4]. Such lasing materials have the advantage of the broad tuning range and high efficiency associated with organic dyes. In such applications the host materials must be highly transparent and the scattering losses must be reduced. Moreover, it should be possible to achieve high doping concentrations without the formation of dye aggregates and the doped solid material must have high optical damage threshold. Another important requirement is that the material must have high resistance to photo-degradation and good thermal properties so that it could be used in high repetition rate lasers. In the past, several glasses, polymers and organic–inorganic composites have been examined for this purpose and the search for better materials continues. Polymers have distinct advantages over glasses due to the better solubility of dyes in polymers which ensure very good optical homogeneity. It is also possible to alter the molecular structure of the polymer to suit a particular application. Polymeric materials are easy to fabricate in any desired shape for devices. However, polymers have the disadvantage of rather low optical damage threshold and high thermal degradation under laser irradiation, which result in a lower operational lifetime of the optical devices. Thus, it is very important to study the thermo-optic properties of the polymer host before using it to form the lasing medium for high repetition rate lasers.

With the development of Ti-Sapphire lasers, the generation of laser pulses of a few 10 s of femtosecond duration has become a routine affair. These fs pulses have sufficiently high peak power to induce nonlinear effects in the medium in which they propagate. One of the most important nonlinearities is two-photon absorption (TPA), which corresponds to the third-order optical nonlinearity. The *Z*-scan technique has become a standard method to determine the third-order nonlinear optical properties of a large variety of materials. This technique is simple to implement and yields not only the values of the nonlinear parameters, but also indicates the nature of the nonlinearity. However, the *Z*-scan technique does not give accurate results if the laser pulse repetition rate is high or the pulse duration is long. The results are reliable only if the laser is operated in single-shot mode and a time gap is maintained between successive measurements. Very recently, Gnoli et al. [5] have reported a simple method to take into account the cumulative thermal effects in *Z*-scan

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measurements using high repetition rate lasers. In their paper they have shown how to disentangle the cumulative thermal lens effect from other contributions to nonlinear refractive index variation.

Open-aperture *Z*-scan is a direct method for measuring nonlinear absorption of substances, in particular, to calculate the TPA cross sections. Chunosova et al. [6] have determined TPA cross sections of three different dicyanomethylene-pyrane DCM dye solutions by the open-aperture *Z*-scan using fs laser pulses from a Ti-Sapphire laser. Reinhardt et al. [7] obtained very high TPA cross-section values of 11560, 9700 and 3900 GM for some new asymmetric dyes, named as AF-50, AF-60 and AF-70. Sharma et al. [8] obtained TPA coefficient of 0.010 cm/MW in the sample based on PMMA doped with rhodamine 6G using single-beam *Z*-scan technique under excitation by the second harmonic of Nd:YAG laser beam (532 nm). Shettigar et al. [9] obtained TPA cross section of 48300 GM in the Sydnone-doped PMMA using nano second *Z*-scan at 532 nm.

In this paper, we have studied the TPA in solid PMMA doped with three different dyes, viz. PM597, DCM and rhodamine 6G–rhodamine B, irradiated by femtosecond laser pulses produced by a commercial Ti-Sapphire laser. We have obtained TPA cross sections for the solid samples by the open-aperture *Z*-scan method. Two-photon fluorescence characteristics of the samples have also been investigated (Fig. 1).

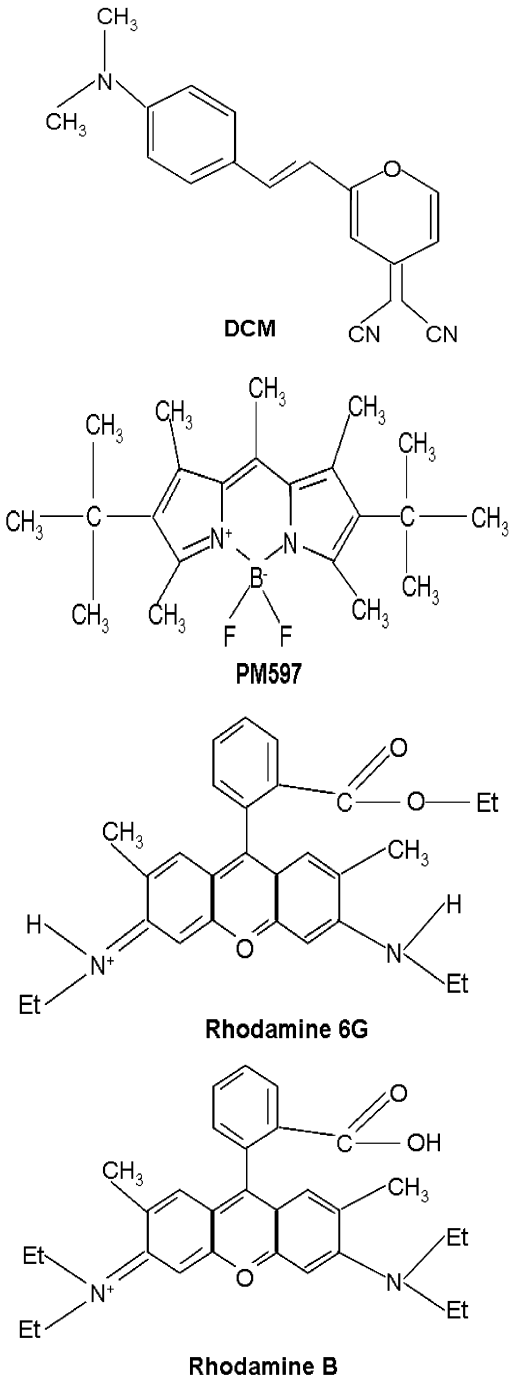

Fig. 1. Structural formulae of the dyes studied in our experiments.

2. Sample preparation and open-aperture *Z*-scan experiment

The solid samples of PMMA doped with the dye materials were prepared by the following procedure. An appropriate quantity of a laser dye (such as PM 597, DCM rhodamine series) was dissolved in purified methyl-methacrylate, by sonication technique. A thermal initiator α-azoisobutyronitrile (AIBN) was added, and the mixture was again sonicated. The resulting solution was filtered into cylindrical moulds, and then sealed. Polymerization was performed in the dark in a thermostatic bath at 40–45 °C until solidification (at least 5 days). The sample was cut into cylindrical discs of desired thickness and their ends were polished to obtain reasonably flat, smooth, glass-like surfaces. Fig. 2 shows the samples of PMMA doped with rhodamine 6G–rhodamine B (left) and DCM (right) in the form of discs.

The open-aperture *Z*-scan experiments were performed using a commercial Ti-sapphire laser ("Legend" Laser from Coherent Inc., USA) that produces 40 fs pulses at 808 nm wavelength with repetition rate 1 kHz. Laser beam from the Legend amplifier was focused by a spherical lens of focal length 200 mm. The Laser beam intensity was controlled by an attenuator. In our experiment, the energy of the incident fs laser is 3.9 mW with peak intensity $I = 7\,\mathrm{TW/cm^2}$ for PM 597 and DCM, while the energy of the laser beam is 2.1 mW, peak intensity $I = 4\,\mathrm{TW/cm^2}$ for Rh 6G+B. The sample is mounted on a computer-controlled motorized translation stage to move the sample along the Z-axis. The average power transmitted by the dye-doped disc sample was measured using EPM2000 power meter (Molectron Inc., USA) interfaced to a computer for data acquisition and analysis. Detailed descriptions of this method and apparatus can also be found in some Refs. [6,7,10].

3. Results of *Z*-scan measurements

We have studied three different kinds of solid-state dye materials doped into PMMA at different concentrations: PM567 in PMMA, DCM in PMMA and rhodamine 6G–rhodamine B co-doped in PMMA. Fig. 3 shows the experimental results of the *Z*-scan measurements for different doping concentrations of the dyes in PMMA.

Following Refs. [6,11,12], the TPA cross section can be written as

$$\sigma_2 = \frac{h\omega\beta}{2\pi N} \tag{1}$$

where N is the concentration of molecules in $\mathrm{cm^{-3}}$ and $h\omega/2\pi$ is the fs laser photon energy. β is the TPA coefficient and it can be obtained from the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$. From the open-aperture *Z*-scan data, we can evaluate the β values by fitting the transmittance curves.

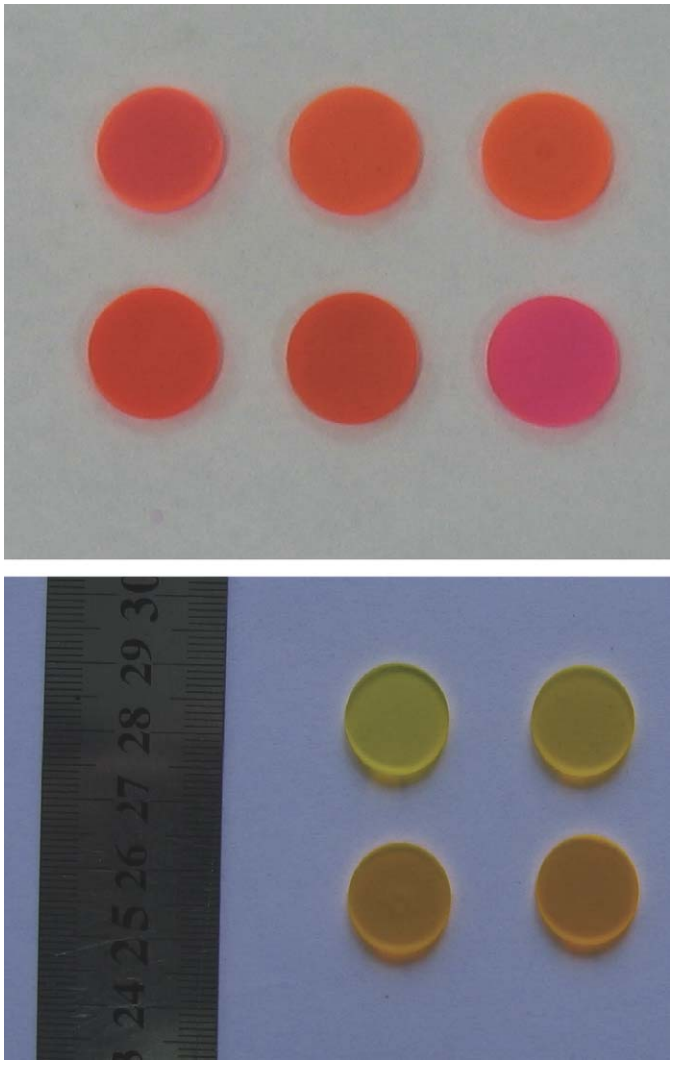

Fig. 2. Pictures of some solid PMMA samples doped with Rh6G+B (top) and DCM (bottom).

Table 1 indicates that solid samples of PMMA doped with DCM dye have high TPA cross sections at the 808 nm wavelength, which implies that this material has greater potential applications in solid-state lasers. It is also seen that the TPA cross sections of the solid dye samples based on PMMA are higher than that of these dyes in the solution form [6,13,14].

4. Two-photon fluorescence spectrum of solid-state dyes in PMMA by fs laser pulses

The Ti-Sapphire fs laser beam was focused by a spherical lens with a focal length of 200 mm on the dye-doped disc samples as shown in Fig. 2. The laser power into the samples could be adjusted by a neutral density filter. The emission fluorescent spectrum was detected by Ocean Optics HR4000 Fiber-Optic Spectrometer.

Fig. 4 shows the fluorescence spectrum of PMMA (polymeric host) irradiated by 808 nm, 40 fs laser pulses. It is clear that no wavelength other than the 808 nm pump laser exists in the spectrum. It can be seen that the fluorescence is too weak to be detected or there is no TPA generation, so PMMA matrix can be considered to have no influence on the measurement of the TPA of

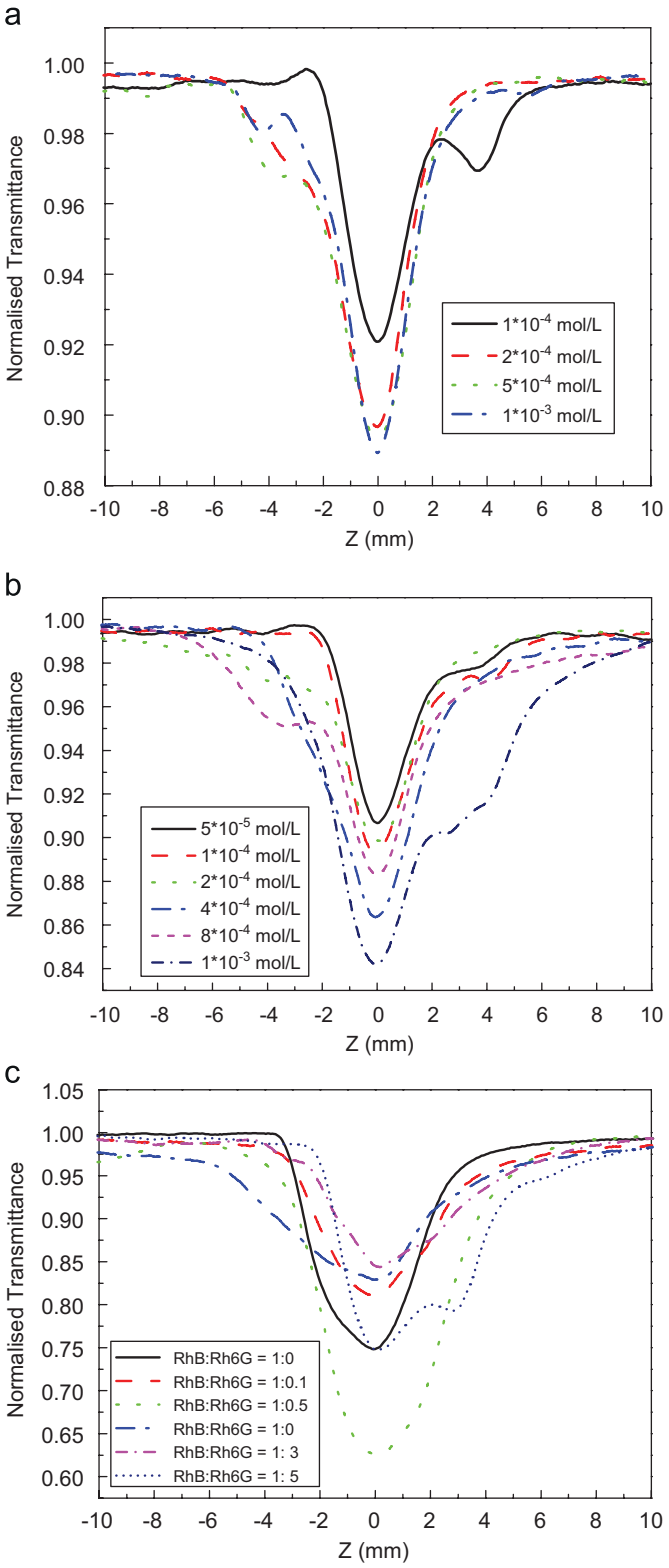

Fig. 3. Dependence of the normalized transmittance T of different solid-state dye-doped discs on the sample position 'z' relative to the focal point. (a) Z-scan profiles for PM597-doped samples at different concentrations. (b) Z-scan profiles for DCM-doped samples at different concentrations. (c) Z-scan profiles for Rh6G+B-doped samples at different concentrations when the concentration of RhB is 1×10^{-3} mol/L.

dye-doped polymer samples. Fig. 5 shows the fluorescence spectrum of DCM, (a) in solid-state PMMA and (b) in alcohol solution, when irradiated by 808 nm, 40 fs laser pulses.

The fluorescence spectrum of solid DCM-doped PMMA ranged from 545 to 630 nm; the bandwidth of the fluorescence spectrum was about 85 nm. The fluorescence spectrum showed a red shift which increased with increasing concentration of the dye in PMMA. At higher concentration of the dye in PMMA the attenuation of the shorter wavelength part of the fluorescence spectrum is stronger. Fig. 5 shows that the effect of the small change in DCM concentration on the two-photon fluorescence spectrum is much stronger in the solid-doped PMMA sample than that in liquid form. Another interesting phenomenon is that the peaks (about 570 nm) in the fluorescence spectrum of the solid sample occurred at much shorter wavelengths compared with the peak values (about 630 nm) for DCM in liquid form. These phenomena can be explained by the TICT (Twisted Intramolecular Charge Transfer) theory. The formation of the TICT state is strongly dependent on the polarity of the medium. In polar solvent such as ethanol, the transition to TICT state completed very quickly, no fluorescence from the locally excited state is observed and only the large red-shifted emission from the TICT state is detected [15–17]. But in the medium such as PMMA, the rotation around the nitrogen-aromatic carbon is hindered and the TICT state that caused red shift of fluorescence is not formed.

We have also compared the two-photon fluorescence spectrum with the single photon fluorescence spectrum for Rh6G+RhB dye embedded in PMMA experimentally. The single photon fluorescence spectrum was obtained by using the frequency-doubled Nd:YAG laser output at 532 nm as the pump source.

Fig. 6 (left) shows the one-photon fluorescence spectrum of rhodamine B co-doped with rhodamine 6G in PMMA. Rhodamine B acts as an electron acceptor and rhodamine 6G as a donor. The peaks in one-photon fluorescence spectrum ranged from 587 to 604 nm and the bandwidth was about 35 nm. The peak values of the two-photon fluorescence spectrum of rhodamine B alone in PMMA were around 603 nm and the addition of rhodamine 6G

Table 1
The TPA coefficient and TPA cross section of different solid-state dye materials in PMMA irradiated by 40 fs laser pulses.

Solid-state dye	Concentrations (mol/L)	β (cm/TW)	σ_2 (GM)
PM597 in PMMA	1×10^{-4}	0.060 ± 0.003	25 ± 1
DCM in PMMA	1×10^{-4}	0.081 ± 0.004	33 ± 1
Rh6G+B in PMMA	1×10^{-3}	0.78 ± 0.03	32 ± 1

Noteβ is the TPA coefficient and σ_2 is the TPA cross section.

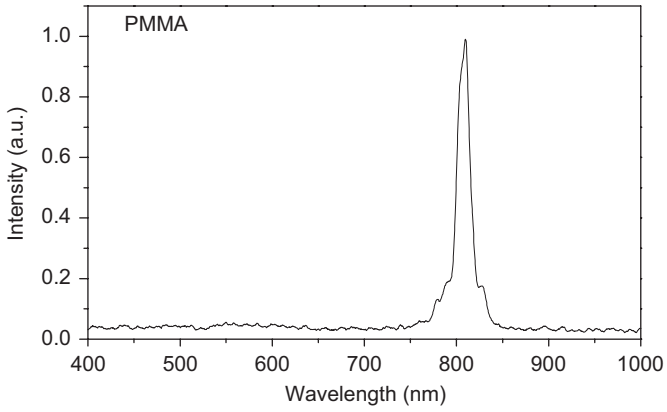

Fig. 4. The fluorescence spectrum of polymeric host-PMMA.

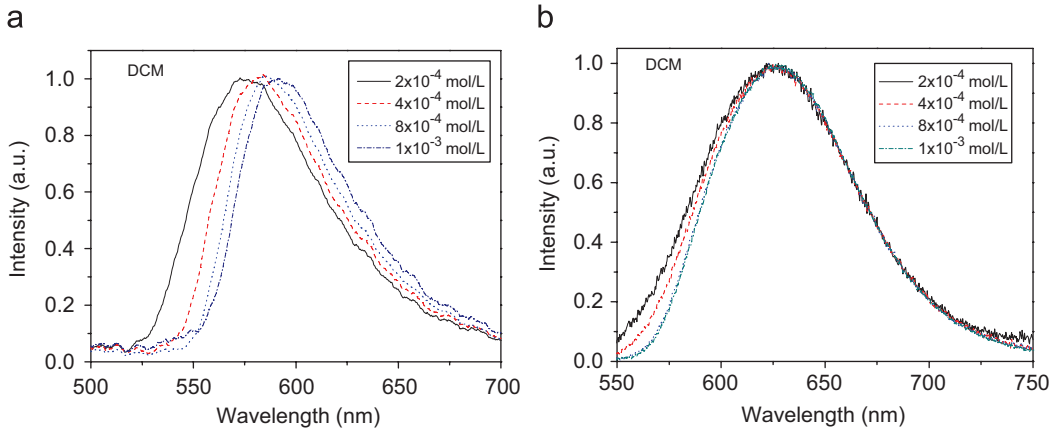

Fig. 5. Two-photon fluorescence spectrum of DCM (a) in solid-state PMMA and (b) in alcohol solution taken in 2 mm Cuvette.

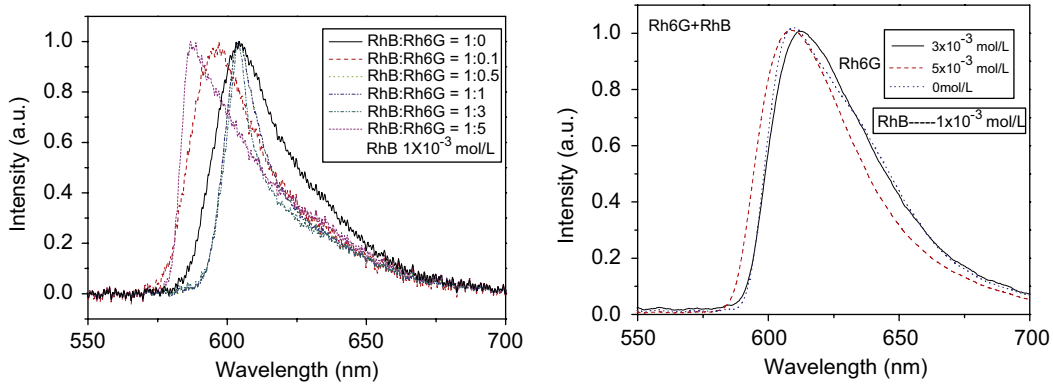

Fig. 6. The one-photon (left) and two-photon (right) fluorescence spectrum of rhodamine 6G–rhodamine B co-doped in PMMA.

into it resulted in blue shifts of the peaks. Compared to one-photon fluorescence spectrum, the two-photon fluorescence spectrum has larger red shifts due to the re-absorption. One-photon absorption could occur at the front face of the sample and the fluorescence can be easily emitted, while TPA could only occur in the middle of the sample and the fluorescence can be re-absorbed. In general, the fluorescence spectrum of the dyes doped in PMMA retains the characteristic broad spectrum in both solid and in liquid form. Therefore, the dye doped PMMA in the solid state should be suitable for applications to tunable lasers as well as that in the solution form.

5. Conclusions

Dyes embedded in PMMA in the solid state are useful materials for broad band tunable lasers and have several advantages such as ease of handling, low cost, compactness and absence of toxicity. To assess any new material for applications in lasers, the investigation of the physical properties, especially their nonlinear optical properties, is very essential. We have used *Z*-scan technique, in the fs time scale, to study the TPA characteristic of the solid-state dye materials and measured the TPA cross-sections of some solid-state dyes. We have also studied the two-photon fluorescence spectrum of DCM in solid state PMMA and in alcohol solutions and compared the two-photon fluorescence spectrum with the one-photon fluorescence spectrum in rhodamine 6G–rhodamine B co-doped in PMMA. The applications of solid-state dye devices in laser systems will be the subject of our future investigations.

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