Dye-Doped Organogels: A New Medium for Two-Photon Pumped Lasing and Other Optical Applications

M. Lal, S. Pakatchi, G. S. He, K. S. Kim, and
P. N. Prasad*

Photonics Research Laboratory, Departments of Chemistry and Physics, State University of New York at Buffalo, Buffalo, New York 14260

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Water-in-oil microemulsions are made up of nanometer-sized droplets of water, coated by a monomolecular layer of surfactant molecules and dispersed in an oil-rich continuous phase.[1,2] Recently it was observed that under certain conditions, when hydrophilic molecules such as gelatin are solubilized in the water pools (characterized by W_O, the water−surfactant molar ratio) of microemulsion, formation of a clear isotropic gel takes place.[3−5] Since the major component of the gel is a hydrocarbon, sometimes these gels are also referred to as “hydrocarbon gels”[6] or “organogels”. This sol−gel transition takes place above a small threshold of the solubilizate concentration.[7] It is to be noted that a very small amount of water is needed for gelation (as opposed to pure gelatine gels[8]) and no guest polymer is needed for gelation.[9,10] The formation of gel is interpreted in terms of the formation of an extensive network of rigid rods of water and gelatin surrounded by a shell of surfactant.[11,12]

In this communication we have compared the lasing performance in dye-doped aqueous gelatin gels that in dye-doped organogels and have demonstrated that the organogels are more efficient and highly suitable media for lasing applications. Until recently, polymeric materials are the most common substitute for inorganic glasses as solid materials in the development of solid-state lasers.[13] Besides the obvious technical advantages offered by solid-state lasers such as compactness, absence of toxic solutions, suppression of flow fluctuation, etc., polymeric materials facilitate the design of solid laser systems as they are inexpensive and easy to fabricate.[13] However, the polymer-based systems have several shortcomings, mainly due to poor heat conduction resulting in a low damage threshold[14] and short lasing lifetime. It has also been reported that the polymeric matrix undergoes photodegradation due to direct photolysis of the polymer.[15]

In the present work, we have obtained stable and efficient two-photon lasing from organogels containing a two-photon up-converting dye DAST (4-(dimethylamino)-*N*-methylstilbazoliumtosylate) that has been extensively studied as a second-order nonlinear material. Two-photon-pumped (TPP) lasing offers distinct merits; some of these are[16] (i) frequency upconversion without the restriction of phase matching, (ii) use of a long interaction length, and (iii) minimization of local thermal damage because of weaker absorption. The two main requirements for TPP lasing are to maintain high concentration of the dye and high optical quality of the bulk. The polymer systems have a limitation on doping in high concentrations as it leads to phase separation, thereby affecting the optical quality of the system. The organogels have a distinct advantage since they arise from an organized ternary system which offers an optically isotropic transparent system containing hydrophilic and hydrophobic domains well-separated from each other. The aim of our work was to examine the lasing lifetime and damage threshold of organogels and to investigate the application of organogels as an alternate medium for optics applications.

The dye-doped organogels were prepared by introducing the dye (DAST) in the solid form to the microemulsion system having a fixed droplet size, $W_O = 35$ ($W_O =$ [H_2O]/[surfactant]). Sodium bis(2-ethylhexyl sulfosuccinate) or AOT is the commonly used surfactant[2] for forming reverse microemulsions. In a typical preparation of lasing sample, the dye in the powder form [2.0×10^{-2}M] was added to a 0.5 M AOT/isooctane/water reverse micellar solution with a fixed droplet size $W_O = 35$ (obtained by adding water). This dye-doped micellar solution was heated to 45 °C while stirring in an oil bath. Solid gelatin (11% w/v) was then added to the hot microemulsion mixture with vigorous stirring. The system was maintained at 45 °C in an oil bath under stirring until the gelatin had completly dissolved and a clear viscous mixture was obtained. This transparent homogeneous mixture was then poured into a glass cuvette and allowed to cool at room temperature. Upon cooling, entrapped air bubbles were released and an optically transparent homogeneous bulk gel was formed. These gels were then sealed with epoxy to prevent meniscus formation arising due to the evaporation of the solvent. Dye-doped organogels appeared to be indefinitely stable in closed containers. To make gelatin films, the homogeneous mixture was poured or spin coated on slides prior to cooling.[3] The films were first dried at room temperature and then under vacuum

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(1) Towey, T. F.; Lodhi, A. K.; Robinson, B. H. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (22), 3757−3762.

(2) Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 6961.

(3) Haering, G.; Luisi, P. L. *J. Phys. Chem.* **1986**, *90*, 5892−5895.

(4) Quellet, C.; Eicke, H. F. *Chimia* **1986**, *40*, 233.

(5) Howe, A. M.; Katsikides, A.; Robinson, B. H.; Chadwick, A. V.; Al-Mudaris, A. *Prog. Colloid Polym. Sci.* **1988**, *266*, 211.

(6) Daum, U.; Wei, G.; Luisi, P. L. *Colloid Polym. Sci.* **1988**, *266*, 657−662.

(7) Luisi, P. L.; Scartazzini, R.; Haering, G.; Schurtenberger, P. *Colloid Polym. Sci.* **1990**, *268*, 356−374.

(8) Veis, A. *The Macromolecular Chemistry of Gelatin*: Academic: New York, 1964.

(9) Gay, L. R.; Schlott, J. R.; Burroghs, E. J. U.S. Patent; *Chem. Abstr*. 90-074182/10.

(10) Akira, I.; Mitsuru, T.; Kikuo, T.; Yasumasa, H. Japanese Patent; *Chem. Abstr.* 86-092993/14.

(11) Atkinson, P. J.; Grimson, M. J.; Heenan, R. K.; Howe, A. M.; Robinson, B. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1807.

(12) Capitani, D.; Segre, A. L.; Haering, G.; Luisi, P. L. *J. Phys. Chem.* **1988**, *92*, 3500.

(13) Zhao, C. F.; He, G. S.; Bhawalkar, J. D.; Park, C. K.; Prasad, P. N. *Chem. Mater.* **1995**, *7*, 1979−1983.

(14) Kaminow, I. P.; Stulz, L. W.; Chandross, E. A.; Pryde, C. A. *Appl. Opt.* **1972**, *11*, 1563.

(15) Itagaki, H. *J. Photopolym. Sci. Technol.* **1991**, *4*, 187.

(16) Zhao, C. F.; Gvishi, R.; Narang, U.; Ruland, G.; Prasad, P. N. *J. Phys. Chem.* **1996**, *100*, 4526−4532.

10.1021/cm990199i CCC: $18.00

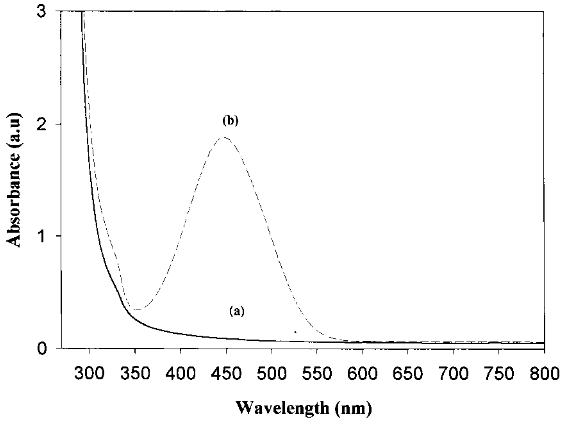

Figure 1. UV−vis spectra of (a) blank (undoped) gel and (b) dye (DAST)-doped gel derived from water-in-oil microemulsion system at droplet size, $W_O = 35$.

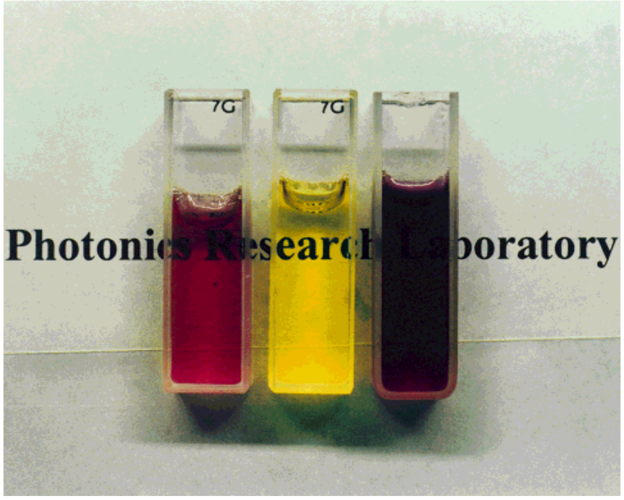

Figure 2. Photograph of various dye-doped gels (in a open cuvette) derived from the water-in-oil microemulsion at droplet size, $W_O = 35$.

at 60 °C for 24 h. It was also observed that gelation of the dye-doped microemulsions occurred even with AOT/toluene/water system and AOT/benzene/water.

Figure 1 shows the linear (one-photon) absorption spectra of the dye (DAST)-doped organogel versus the blank undoped gel (inside a 1-cm glass cuvette). As seen from the figure, the undoped gel has no absorption in the visible region. Figure 2 shows a photograph of various (different structures) two-photon dye-doped organogels derived from water-in-oil (w/o) microemulsion system. As seen from the picture, the gels obtained are transparent and of high optical quality. Figure 3 shows the one-photon-induced fluorescence spectra of the dye-doped aqueous gelatin gel and the dye-doped microemulsion based organogel recorded using a RF5000U spectrofluorometer from Shimadzu. The dopant (DAST) concentration in both the gelatin gel and the organogel was 2×10^{-4} M. The single photon excitation wavelength was 512 nm, and the spectral resolution was ~5 nm. From Figure 3, it is observed that the relative fluorescence yield of the DAST organogel is easily ~300 times greater than that of the aqueous gelatin gel. This behavior may be due to the difference in polarity of the microenvironment inside the aqueous core of the microemulsion system versus the bulk aqueous dye-doped gel based on a twisted intramolecular charge-transfer model (TICT).[17] According to the TICT model, the excited dye molecules initially form a moderately polar state with a geometry similar to that in the ground state. Subsequently, these excited molecules undergo an intramolecular transfer of an electron from a donor to an acceptor which is accompanied by a twist around the bond joining the donor and the acceptor.[18] The rate of this process is strongly dependent on the polarity of the solvent, i.e., the activation barrier for the TICT process decreases with an increase in the solvent polarity. As a result, with an increase in the polarity, the TICT state becomes less emissive due to nonradiative transitions, thereby resulting in marked decrease in the fluorescence yield.[19] This effect has also been observed in the previous work from our group.[20] Our experimental results, as seen from Figure 3, are in agreement with this model. In the AOT/isooctane/water microemulsion system, initially (before adding the gelatin), the dye is in a hydrophilic environment surrounded by water molecules in the aqueous core. However, during gelation the gelatin molecules push the water outside the aqueous core causing connectivity between neighboring droplets and thereby reducing the polarity of the microenvironment around the dye. As a result the polarity around the dye molecules becomes considerably reduced, leading to enhancement in emission as seen in Figure 3. In the aqueous gelatin gels, doped with DAST (~2×10^{-4}M), as seen from Figure 3, there is no increase in emission of the dye after gelation. In dye-doped pure gelatin gels which contain water as the bulk phase, even after gelation, the dye is in a highly polar environment. As a result, there is a marked decrease in the fluorescence yield due to nonradiative transitions.

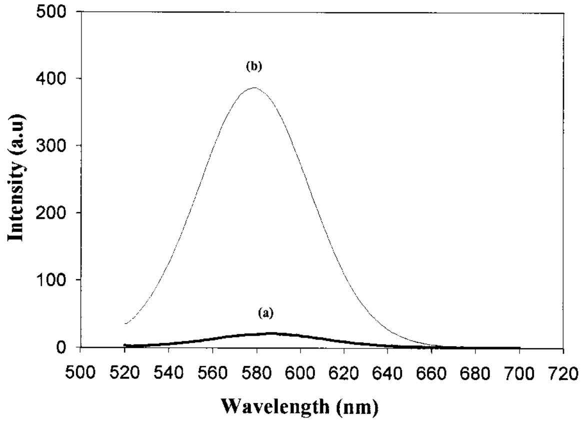

Figure 3. One-photon-induced fluorescence emission of (a) dye (DAST)-doped aqueous gelatin gel and (b) dye (DAST)-doped organogel, where [DAST] = 0.0002 mol/L.

To determine the applicability of these organogels as an alternate medium for optics applications, we investigated the two-photon-pumped (TPP) lasing properties of these dye (DAST)-doped organogels. The experimental setup for TPP lasing measurements is basically the same as described in an earlier work from our group.[21] In the present work, the DAST-doped gelatin organogel

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[17] Simon, J. D.; Su, S. G. *J. Chem. Phys.* **1987**, *87*, 7016.

[18] Sarkar, N.; Das, K.; Nath, D. N.; Bhattacharyya, K. *Langmuir* **1994**, *10*, 326.

[19] Narang, U.; Zhao, C. F.; Bhawalkar, J. D.; Bright, F. V.; Prasad, P. N. *J. Chem. Phys.* **1996**, *100*, 4526.

[20] He, G. S.; Yuan, L.; Cui, Y.; Li, M.; Prasad, P. N. *J. Appl. Phys.* **1997**, *81* (6), 2529−2537.

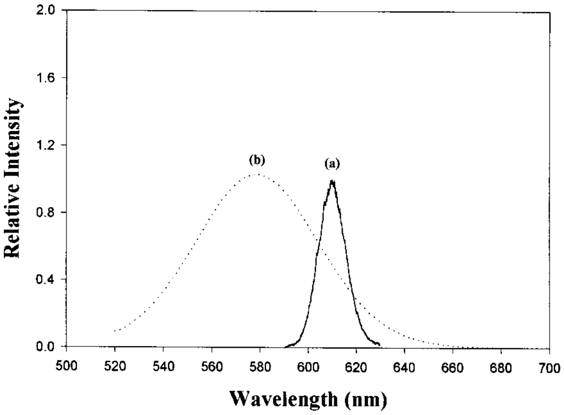

Figure 4. Relative spectral distribution for (a) TPP lasing from dye (DAST)-doped organogel in a 1-cm optical length glass cuvette, excited with 1.06 μm source, and (b) single-photon-induced fluorescence from dye (DAST)-doped organogel.

sample was formed in a 1-cm optical length glass cuvette. The pump source was a Q-switched Nd:YAG pulsed laser with the output wavelength of 1.06 μm, beam size of ~2 mm, divergence angle of ~1 mrad, and a repetition rate of 3 Hz. The IR pump beam was focused by a $f = 20$ cm lens on the sample. The two parallel windows of the cuvette formed a cavity when the pump beam was incident along the normal direction of these two windows. When the pump beam intensity was higher than a certain threshold value (~600 MW/cm^2), a strong highly directional forward and backward frequency up-converted visible lasing could be easily observed. The typical TPP lasing spectrum is shown in Figure 4b, which was obtained by using a grating spectrograph (SPEX; Triplemate) in conjuction with an optical multichannel analyzer (OMA-III) system. For comparison, the one-photon-excited fluorescence spectrum of a low concentration sample is shown in Figure 4a. One can see that the lasing spectral width (~13 nm) is obviously narrower than the corresponding bandwidth (~60 nm) of the fluorescence spectrum. Another feature is a remarkable red-shift of the peak position of the lasing spectrum relative to that of the one-photon-excited fluorescence spectrum. This red-shift effect is due to the linear self-absorption effect.[21]

The TPP lasing lifetime is defined as the output lasing pulse number before the power level drops to 15% of its initial value. In our experiment, the lasing lifetime attained was higher than 6.5×10^4 pulses without any cooling requirement and sample movement. The measured pump power for damage threshold was higher than 600–700 MW/cm^2. The previously reported TPP lasing lifetime and pump beam damage threshold (defined as the minimum pump intensity or energy level that causes the surface or internal mechanical damage of the gain medium) for dye-doped solid rod systems were 4×10^4 pulses and 350–450 MW/cm^2 respectively.[21] After the lasing output dropped to below 15%, we blocked the pump beam for a period of ~12 h. When the sample was again exposed to the pump beam, the lasing output had recovered to ~80% of the original value, indicating a self-healing process. This behavior maybe due to sufficient fluidity (structural flexibility) of the gel microenvironment. This will be another very attractive feature of a gel-based optical medium. Another useful optical application of these organogels will be for optical power limiting, which we are currently exploring.

In conclusion, we have demonstrated that microemulsion-based organogels offer a suitable medium for optics applications. Since the lasing output in glass and polymer bulk samples is limited by dye decomposition and localized heating of the matrix, organogels offer an advantage due to their thermoreversibility and flexibility leading to a longer optical lifetime and higher damage threshold in organogels in comparison to dye-doped polymer and sol–gel glass systems.

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(21) He, G. S.; Bhawalkar, J. D.; Zhao, C. F.; Prasad, P. N. *IEEE J. Quantum Electron.* **1996**, *32*, 749.