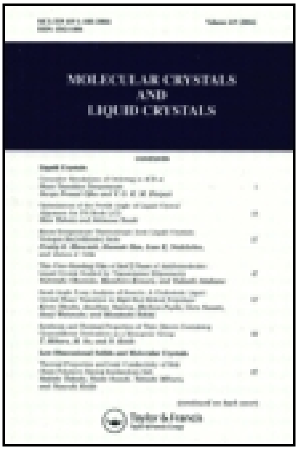

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Two-Photon Excitation of Dye-Doped Liquid Crystal by a CW-Laser Irradiation

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We report on excitation of photoluminescence via two-photon absorption (2PA) in dye-doped liquid crystal droplets using tightly focused cw-laser illumination at 1064 nm wavelength. The photoluminescence of the 2PA dye $C_{40}H_{54}N_2O_2$ (MBAPB) dispersed inside the 7CB liquid crystal host increases as square of the laser tweezers' irradiance. The 2PA cross-section of MBAPB was measured by femtosecond Z-scan method. The polarization and temperature dependence of the photoluminescence corroborated the presence on the dye's molecular alignment inside the nonpolar liquid crystal host. The molecular alignment via the host-dye interaction can be used for the laser manipulation of micro-objects (e.g., doped liquid crystal droplets) in micro-fluidic/mechanical applications.

Keywords: laser trapping; liquid crystals; molecular ordering; photo-luminescence; two-photon absorption

1. INTRODUCTION

The multi-photon absorption allows spatial localization of light and is a key requirement for the three dimensional (3D) and confocal microscopies, also, for optical terra-bit memory [1], photonic crystal applications [2–4], and nano-structuring approaching molecular resolution [5]. In order to achieve high irradiance necessary for excitation of two (or multi) photon absorption pulsed lasers are typically

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employed. A cw-laser excitation of the multi-photon absorption would be useful solution [6] provided strongly absorbing nonlinear dyes are available [7]. The dye molecules oriented in a host matrix become more efficient absorbers, e.g., perfectly aligned dipoles produce strongest absorption which is five times larger than that of isotropic random orientation [8] (see, ref. [9] for the review on enhancement of light-matter interaction). Liquid crystals are prospective dyes' hosts for molecular ordering since they are hydrophobic as many of dyes. Hence, the dye-doped liquid crystals can be in principle used in water solutions where they forms self-contained particles [10–12] and could be used as micro-light sources, micro-lasers, or effective orbital/angular momentum receivers in micro-mechanical applications and light-to-mechanical energy converters.

Here, we show that a strong two-photon absorbing dye MBAPB can be excited by a tightly focused cw-laser radiation using laser tweezers. The two-photon absorption (2PA) mechanism of the dye excitation is demonstrated at the laser trapping wavelength of 1064 nm, which is far from the 2PA maximum at 740 ± 30 nm.

2. EXPERIMENTAL

The hydrophobic two-photon absorbing dye $C_{40}H_{54}N_2O_2$ (MBAPB; molar weight 580.4 g/M, the molecular structure shown in the inset of Figure 1) synthesized by the reported method [13] was doped into nonpolar 7CB (Aldrich) nematic liquid crystal by ratio 1.5 mg to 20 μl (molar concentration 129 mM/l) at 60°C, at which 7CB is isotropic (phase transition temperature from nematic to isotropic: $T_{NI} = 43$°C). °C). At this temperature the dye was uniformly dispersed in an isotropic phase of 7CB. Then, the dye-doped 7CB was dispersed into D_2O (20 ml) under ultrasonic bath shaker conditions and droplets

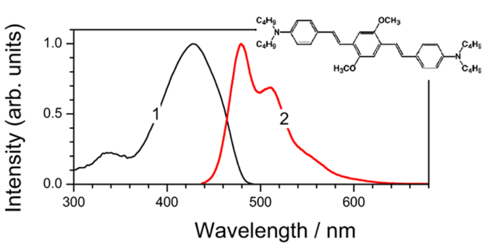

FIGURE 1 The normalized spectral profiles of absorption (1) and emission (2) of MBAPB in toluene. The molecular MBAPB structure [13] is schematically shown in the inset.

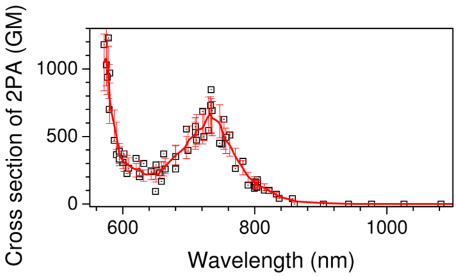

FIGURE 2 Spectral dependence of the two-photon absorption (2PA) cross section of $C_{40}H_{54}N_2O_2$ (MBAPB) dye measured by Z-scan in toluene solution (1 GM $= 10^{-50}$ cm^{4}s). Error bars are at 20%.

2–20 µm in diameter were formed. The dye was not washed out into water due to its hydrophobicity. The droplets appeared bipolar in polariscope imaging as the undoped 7CB droplets. At room temperature, the liquid crystal particles changed from nematic into solid phase (the nematic-to-crystalline transition occurs at $T_{NC} = 30$°C in undoped 7CB); some of the droplets were freely moving in water while some were attached to a cover glass.

The absorption and emission spectra of MBAPB in toluene are shown in Figure 1. There were no linear absorption at the wavelength of laser trapping at 1064 nm. Figure 2 shows spectral dependence of the 2PA cross section of MBAPB measured by femtosecond Z-scan in toluene. These data were close to the originally reported 2PA cross-sections [13]. The smallest cross section reliably determined was approximately 25 GM at our experimental conditions, i.e., the actual 2PA cross-section is not reliably measured at the wavelength of laser trapping. An increase of 2PA cross-section at the shorter wavelengths (Fig. 2) is due to the resonant 2PA [14].

Figure 3 shows the crystalline phases of undoped and MBAPB-doped 7CB crystals obtained by casting on a slide glass (without dispersing in D_2O). It shows that the dye was incorporated into the liquid crystal. This mixture was used in laser trapping experiments after its dispersion in heavy water where it formed bipolar micro-droplets (Fig. 3(c)).

Liquid crystal samples were kept on a transparent hot-plate which temperature was changed from 25 to 75°C to explore molecular orientation in different crystalline, nematic, and isotropic phases. Imaging of liquid crystals was carried out in a polariscope mode. Laser trapping of the dye-doped droplets was carried out with tightly focussed (the numerical aperture of an objective lens was $NA = 1.3$)

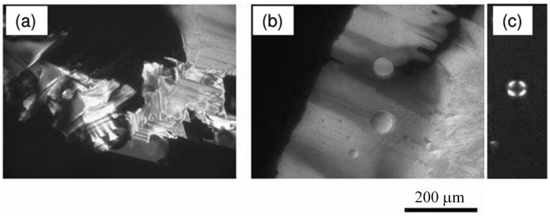

FIGURE 3 Polariscope images of (a) nematic liquid crystal 7CB and MBAPB-doped 7CB film on a slide glass (b) at room temperature. (c) The self-formed droplet of a MBAPB-doped 7CB of the bipolar structure; diameter 7 μm. The nematic-to-crystalline transition occurs at $T_{NC} = 30°C$.

laser tweezers at 1064 nm wavelength (see, refs. [15,10,12,16,17] for details on setup and laser manipulation).

3. RESULTS AND DISCUSSION

3.1. 2PA at Tight Focusing

Since the MBAPB is a strong two-photon absorber at around 740 nm wavelength (2PA cross section is $\sim$1000 GM), we explored a possibility to excite this dye at longer wavelengths. Even out of 2PA optimum wavelength the 2PA cross section is comparatively large and can exceed that of efficient dyes such as rhodamine with typical cross-sections of 100 GM at the maximum. If molecular alignment is present, as expected in dye-doped liquid crystals, an additional enhancement is expected [9]. Figure 4 shows a visible fluorescence of MBAPB from the focal region, which has lateral cross-section comparable with the wavelength $\lambda = 1064$ nm (a numerical aperture of the objective lens was $NA = 1.3$). The excitation mechanism of this emission is focus of this study. A recognizable emission was observed when laser power was larger than 0.1 W. It should be noted, that there is a negligible absorption of 7CB and D_2O at this wavelength. No visible emission was observed from 7CB nor D_2O at the same conditions of focusing. Hence, the observed PL originated from the MBAPB dye. Figure 5 shows the spectrum collected from the entire particle. It is consistent with PL of MBAPB (Fig. 1) which has slightly different spectrum in environments of different polarity.

The PL of MBAPB was observed originating from the focal volume as well as from the locations of the largest curvature. Figures 4(c), (d) shows separation of excitation and emission in the case of an elliptical droplet fixed on the cover glass. Due to fixation, it was possible to

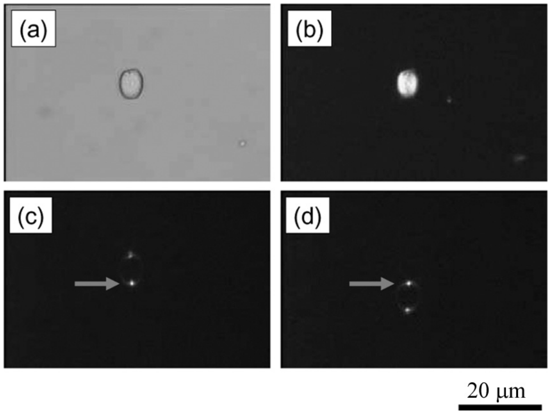

FIGURE 4 Microscope (a) and polariscope (b) images of a 7CB droplet doped by MBAPB dispersed in D_2O. (The droplet is on a cover glass). (c), (d) The same droplet irradiated at two different locations (the poles of droplet marked by arrows) by a focused laser beam of 0.4 W without condenser illumination.

illuminate rim of the droplet without centering of the droplet as it occurs in the case of free-moving droplets (Fig. 3(c)). The opposite end of the ellipsoidal particle (to the one illuminated) showed PL of MBAPB (Figs. 4(c), (d)). Such emission is a result of leaky modes of an ellipsoidal cavity defined by the shape of the droplet [18,19].

Let us estimate the difference in cross-sections of two- and three-photon absorption (2|3PA). Such scaling can be estimated from the typical one-photon absorption cross-section, σ_1, which is approximately equal to the geometrical cross section of absorbing molecules,

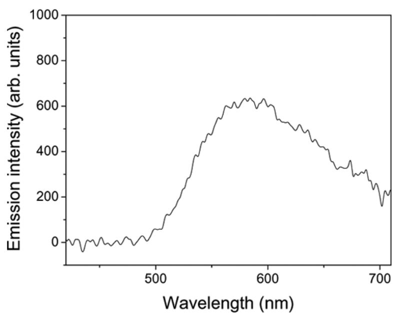

FIGURE 5 Spectrum of photoluminescence from a dye-doped 7CB droplet shown in Figure 4. The spectrum was measured within a 20 μm radius with a central focus on the droplet.

$\Delta S \simeq 10^{-16}\,\mathrm{cm}^{-2}$, and lifetime of the virtual state, $\tau = 10^{-16}\,\mathrm{s}$ (estimation based on the uncertainty principle). Then a N-photon absorption cross-section is given by $\sigma_N = \sigma_1^N \tau^{N-1}$ $[\mathrm{cm}^{2N} \cdot \mathrm{s}^{N-1}]$ [20]. The ratio of probabilities of 3PA and 2PA is $\sigma_1 \tau \simeq 10^{-32}\,\mathrm{cm}^2\mathrm{s}$.

Usually 3PA becomes significant at a $100\,\mathrm{GW/cm}^2$ or higher intensity, when the optical density $OD \equiv \alpha d \sim 1$, here α is the absorption coefficient and d is the thickness of the sample. In the case of 2PA and 3PA, the absorption coefficient $\alpha = \alpha_0 + \alpha_2 I + \alpha_3 I^2$, where $\alpha_{2,3}$ are the 2PA ([cm/W]) and 3PA ($[\mathrm{cm}^3/\mathrm{W}^2]$) coefficients, respectively, I the irradiance/intensity, and α_0 the linear absorption coefficient. The nonlinear absorption coefficients can be expressed via the corresponding absorption cross-sections:

$$\alpha_2[\mathrm{cm/W}] = \frac{\sigma_2[\mathrm{cm}^4\mathrm{s}] N_A d_0 \times 10^{-3}}{\hbar\omega}, \tag{1}$$

where N_A is the Avogadro number, d_0 is the molar concentration (mol/l), and $\hbar\omega$ the photon energy. Similarly, the evaluation of 3PA coefficient is then:

$$\alpha_3[\mathrm{cm}^3/\mathrm{W}^2] \simeq \frac{(\sigma_2[\mathrm{cm}^4\mathrm{s}] \times 10^{-32}[\mathrm{cm}^2\mathrm{s}]) N_A d_0 \times 10^{-3}}{(\hbar\omega)^2}. \tag{2}$$

In our experiments, the irradiance corresponding to the 0.5 W power focused by a $NA = 1.3$ objective lens was $\sim 60\,\mathrm{MW/cm}^2$; here a diffraction-limited focal spot of diameter $d = 1.22\lambda/NA$ is considered. The threshold value at which fluorescence of MBAPB was observed in terms of power was approximately 80 mW. This irradiance value is an upper-bound estimate, since we assume a diffraction-limited focusing, however, the actual intensity distribution inside the droplet is more complicated [21]. The 3PA is highly improbable at such irradiance as one can find from Eq. (2).

The characteristic yellow emission of the MBAPB (Fig. 4) was clearly recognizable from the focal volume of laser tweezers. This demonstrates that MBAPB can be used for two-photon microscopy even out of the most favorable wavelengths of excitation where the 2PA has its maximum. The MBAPB has still a large 2PA cross-section out of its resonance and can be excited at $\sim 10^2\,\mathrm{MW/cm}^2$ irradiance which is accessible using cw-lasers under tight focusing. The 2PA mechanism of PL excitation has been proven by numerically integrating the PL emission images at different laser powers. The confocal aperture was fully opened and entire PL was recorded on a CCD camera. The results are shown in Figure 6 which follow a second order power dependence as would be expected in the case of 2PA.

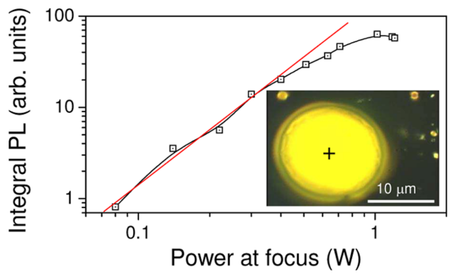

FIGURE 6 The integrated back-ground-subtracted PL over an approximately $5 \times 5\mu$ m^2 area around the focus at different irradiation powers; line represents a second order slope. The inset shows the actual liquid crystal droplet at room temperature imaged in a condensor illumination. The cross marks the location of the focus of laser tweezers.

3.2. Molecular Ordering

The liquid crystal host can act as a medium which enforces molecular alignment on the dispersed dyes or can experience an optical alignment torque from the photo-excited dye [22,23]. Usually, a molecular ordering increases the absorption cross section. The orientational average of dipoles oriented at angle θ with the chosen direction (e.g., a linear light polarization) depends on a factor [8]:

$$\gamma_I \equiv \langle \cos(\theta)^4 \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \cos(\theta)^4 \sin(\theta) d\theta d\varphi, \tag{3}$$

where θ, φ are the angles of spherical coordinates. The fully linearly ordered dipoles result in the strongest absorption according to $\gamma_I = 1$, which can be considered as a 1D ordering. In a plane (2D ordering) of randomly oriented dipoles the average is $\gamma_I = 3/8$, yet even smaller for a fully 3D disordered case with $\gamma_I = 1/5$ [8].

Figure 7 shows the dependence of PL emission from the focal region at different polarization of laser tweezers. The focal volume was placed inside the dark region (as imaged in polariscope (a)) where an average director alignment of liquid crystal molecules was present. Once polarization of laser light was aligned with the local director, the PL intensity was larger than that at circular polarization. This corroborates the presence of a molecular alignment of MBAPB dye in the host of nonpolar 7CB.

We have also measured a temperature dependence of PL at room temperature, where 7CB is crystalline (Fig. 3(a)) and at 50°C where it is isotropic under linearly polarized laser excitation at 1064 nm wavelength. The integral PL intensity was about 10–15% lower at the high

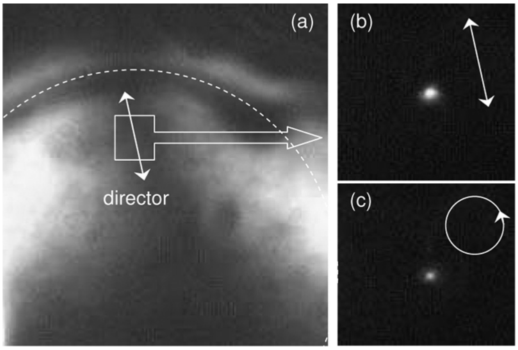

FIGURE 7 (a) Poliariscope image of the MBAPB-doped 7CB liquid crystal droplet (the dashed lines marks the edge of a 20-μm-diameter droplet). The PL images of the focal region (marked in (a)) at linear (b) and circular (c) polarized excitation of approximately 1 W power.

temperature and the PL intensity was restored after cooling down to 25°C. This observation is consistent with the dye alignment [8] imposed by a molecular order of the liquid crystal host but not vice versa.

It is noteworthy, that the laser trapping of bipolar dye-doped 7CB droplets using a circularly polarized light in heavy water caused their rotation as was earlier observed in the case of other nematic liquid crystal droplets [10,12,16,24]. In addition, complex visco-elastic flows and molecular reorientation patterns were observed in polariscope under circular and elliptical polarization of laser tweezers [25]; the complex molecular rotations are expected at such conditions [26,27].

4. CONCLUSIONS

We demonstrated a possibility of nonlinear 2PA using tightly focused cw-laser emission in laser tweezers geometry. The microspheres of dye-doped liquid crystals were laser trapped, manipulated, and the PL was excited inside the droplets. This principle can be utilized for micro-light sources which can be manipulated by laser tweezers. The molecular alignment of dye molecules inside the liquid crystal host was corroborated by polarization and temperature dependence of the PL.

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