

Two-Photon Absorption and Spectral-Narrowed Light Source

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Abstract—This paper reports the two-photon absorption (TPA) and the spectral-narrowed light emission (SNLE) from the crystals of 9,10-distyrylanthracene (DSA) derivatives. The results obtained by the Z-scan method show that the tested molecules possess high TPA cross sections. Upon near-IR excitation, strong two-photon-excited fluorescence could be observed in the crystals of four types of materials. Furthermore, SNLE with low threshold occurs in three of the four crystals under pumping with the second harmonic generated in the amplifier. Single crystals of the DSA derivatives exhibit unique photonic properties, including strong solid-state fluorescence, large TPA cross section, and stimulated emission. The results demonstrate that these are potential candidates for compact and practical solid-state laser applications.

Index Terms—Light source, organic crystal, spectral-narrowed, two-photon absorption, upconversion.

I. INTRODUCTION

COMPACT upconversion lasers [1]–[3] have been extensively studied because of their wide variety of applications in the fields of high-density optical data storage, lithography, and optical communication. As an effective route for realizing the upconverted lasing, two-photon absorption (TPA) has attracted much attention in recent years [4]–[12]. Unlike in second-harmonic generation (SHG), no phase-matching condition is required in the TPA-induced lasing process, rendering the implementation of upconverted lasers with a variety of gain media and resonator configurations. A large number of papers on two-photon [7], [13]–[19], even three-photon [20], [21] or four-photon [22] pumped lasing phenomena have been published, such as two-photon-pumped lasing in a solution of stilbene-type chromophores [14], substituted (*p*-aminostyryl)-1-(3-sulfoxypropyl) pyridinium inner salts [19], first-generation bisfluorene dendrimers

[6], symmetrical fluorene derivatives [17], and hybrids of inorganic polymers and organic chromophores [23]. Most of the TPA-induced lasing is reported in solution, which is not convenient for constructing a compact laser. Recently, attention has been focused on crystalline materials owing to their high purity, rigorously defined structure, and thermal and photochemical stability, which make them promising candidates for realizing compact solid-state lasers [24]–[29]. Moreover, organic crystal can have large TPA properties. Zhao *et al.* [30] have reported two-photon-pumped spectroscopy from Troger's base crystal. Subsequently, two-photon-pumped amplified spontaneous emissions (ASE) from organic crystals have been observed by Sun's group [31]–[35]. In addition, Gao *et al.* also reported the strong two-photon-excited fluorescence and stimulated emission from an thiomethyl-terminated oligo(phenylenevinylene) [36]. Nevertheless, reports on two-photon-pumped lasing from organic crystals remain scarce, when compared to those on amorphous materials, because of the difficulty to obtain high-quality crystals. A number of molecules with large TPA cross-section are very large in size, such as dendrimers [36], [37], [37]–[39] and cyclic oligomers [40], [41], which are not very suitable for crystal growth, while materials that possess very efficient TPA properties and can be used for crystal growth are small in number. Thus, finding new high-quality materials is one of the urgent tasks to be accomplished for realizing practical compact upconversion lasers.

In this paper, we report the TPA properties and their spectral-narrowed light emission (SNLE) from 9,10-distyrylanthracene (DSA) and its derivatives, including 9,10-bis(4-methoxystyryl)anthracene (BMOSA), 9,10-bis(4-butoxystyryl)anthracene (B-4-BOSA), and 9,10-bis(2-butoxystyryl)anthracene (B-2-BOSA) (their molecular structures are shown in Fig. 1). Strong two-photon-excited fluorescence and SNLE were observed from the crystals of the derivatives. Experimental results revealed that these compounds have the potential applications for use in compact and practical solid-state laser.

II. EXPERIMENTAL

A. Materials, Linear Properties, and Time-Resolved Emission

The synthesis of DSA derivatives has been described elsewhere [42], while their structures and fluorescence photographs are shown in Fig. 1. Single crystals of all DSA derivatives were prepared by slow evaporation from mixed solvents of chloroform and ethanol at room temperature.

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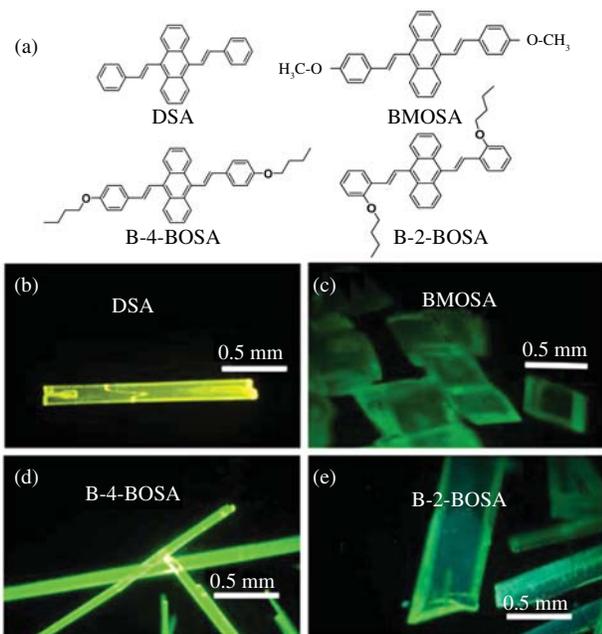


Fig. 1. (a) Chemical structures of DSA derivatives. Fluorescence photograph under the microscope of the crystals for (b) DSA, (c) BMOSA, (d) B-4-BOSA, and (e) B-2-BOSA.

Fluorescence microscopy measurements were performed using an IBE2000 inverted fluorescent microscope. The absorption spectra were measured by a Shimadzu UV-1700 spectrophotometer. The steady-state fluorescence spectra were obtained with an AvaSpec 2048-UA-50-AF spectrometer. The photoluminescence (PL) efficiencies of crystals were recorded using an integrating sphere. Time-resolved fluorescence measurements were performed on the time-correlated single-photon counting (TCSPC) system. The fluorescence signals were collimated and focused onto the entrance slit of a monochromator, with the output plane equipped with a photomultiplier tube (Hamamat-suH5783p), which is connected to a board (Becker & HickelSPC-130). A 405-nm picosecond diode laser (Edinburgh Instruments EPL-405, repetition rate 10 MHz) was used to excite the samples. The time constant of the instrument response function (IRF) was about 220 ps. The time-resolved fluorescence decay was measured near the emission peak position. The fluorescence lifetime was fitted to single exponential functions, and was convoluted with the system response function by fixing the long lifetime obtained from TCSPC measurement.

B. TPA Measurement

An open-aperture Z -scan system was used to measure the nonlinear absorption cross section, where the transmittance of the sample was monitored as it was scanned along the beam axis through the focal region while the energy was held constant. Through a lens ($f = 150$ mm), the 4-mm diameter pump beam was focused vertically onto the center of a 1-mm path quartz cell that was filled with the solution sample. A regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics), which generated laser pulses of about 120 fs at the

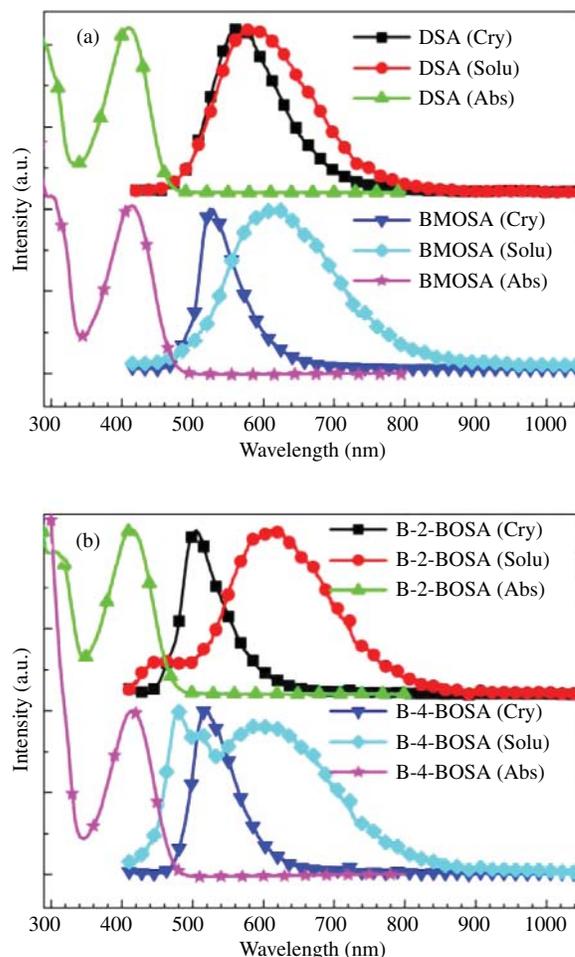


Fig. 2. (a) UV-vis absorption spectra of DSA (\blacktriangle) and BMOSA (\blackstar) in toluene, and the normalized emission spectra of DSA in toluene solution (\bullet) and crystal (\blacksquare) BMOSA in solution (\blacklozenge) and crystal (\blacktriangledown). (b) UV-vis absorption spectra of B-2-BOSA (\blacktriangle) and B-4-BOSA (\blackstar) in toluene, and the normalized emission spectra of B-2-BOSA in toluene solution (\bullet) and crystal (\blacksquare) and B-4-BOSA in solution (\blacklozenge) and crystal (\blacktriangledown).

wavelength of 800 nm, was used as an excitation source. A toluene solution with around 10^{-3} mol/l was used in the experiment. The Z -scan traces with open aperture were symmetric with respect to the focus ($Z = 0$). Subsequently, the TPA coefficient (β) was determined from the transmittance curves by fitting the experimental results with a self-compiled program.

The TPA-induced upconversion fluorescence spectra of the crystals were investigated by a Spectra-Physics Tsunami Mode-locked Ti:sapphire laser with 82-MHz repetition rate as pump source and an Avantes fiber optic spectroscopy as recorder. Before entry into the slit of the spectrometer, the scattered pump light was filtered by a dichroic mirror (DIM 50S-RED).

C. SNLE

The single crystals were optically pumped by the SHG from the Ti:sapphire regenerative amplifier. The crystals were glued onto a quartz substrate and the excitation beam was directed onto the crystal with focusing normally to the

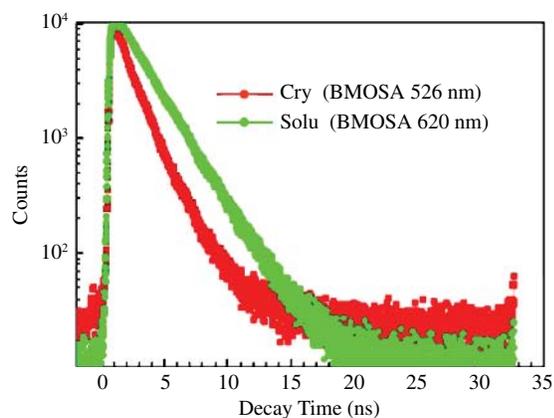


Fig. 3. Fluorescence decay in crystal and solution for the BMOSA measured by TCSPC.

TABLE I
LIFETIME OF THE DSA DERIVATIVES IN TOLUENE SOLUTION
AND CRYSTALLINE STATE

Molecule		Detected Wavelength (nm)	Lifetime (ns)
DSA	Solution	580	4.6
	Crystal	575	5.2
BMOSA	Solution	620	2.4
	Crystal	526	1.5
B-2-BOSA	Solution	450	3.2
	Crystal	620	3.0
B-4-BOSA	Crystal	500	1.1
	Solution	475	1.1
	Crystal	600	2.2
Crystal		515	2.2

substrate. The near-Gaussian beam diameter of the pump laser was 4 mm and the excitation area of the crystals was adjusted by the slit. Emitted light from the crystals was collected with a lens and then collimated and focused into the entrance slit of a 300-mm monochromator/spectrograph (SR-3031-A, Andor). The spectrogram of the emission was recorded using a charge coupled device (iDus, Andor). The intensity of the pump beam was controlled by neutral density filters.

III. RESULTS AND DISCUSSION

A. Linear Photophysical Properties and Excited-State Lifetime

Fig. 2 shows the steady-state absorbance and emission spectra of the DSA derivatives in toluene solution and in the crystalline state. The absorption bands located 415 nm in all the four chromophores can be attributed to the $\pi - \pi^*$ transition [42], while the bands near the 300 nm can be attributed to the phenyl group. However, this is strongly affected by the substitutional group and its positions, especially in B-4-BOSA. Because of the different substitutional groups, the absorption near 300 nm increases from DSA to B-4-BOSA. The substituent positions may also play a role. The absorption of the B-2-BOSA near 300 nm is much lower than that of B-4-BOSA. The substituents in the ortho and para positions lead to different conjugates of the molecules, which results in different absorption spectra [43]. For the emission, all of them exhibit a broad orange emission in toluene solution, while it

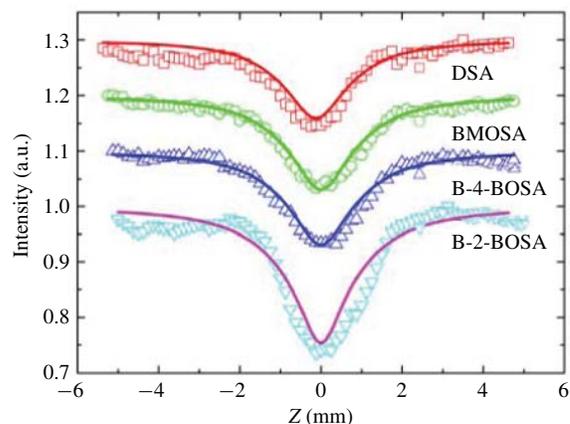


Fig. 4. Normalized open-aperture Z-scan transmittance of the four compounds in toluene solution at 800 nm.

was relatively narrow and blue-shifted in crystals. As shown in Fig. 1, the emission was yellow-green in the crystals of DSA, green in the BMOSA and B-4-BOSA, and more blue-shifted in B-2-BOSA under the fluorescence microscope, which is believed to be due to the strongly distorted conformation of the molecules in the crystal. All four molecules have a nonplanar conformation in crystals, which can be attributed to the CH/π hydrogen bonds leading to relatively tight packing and rigid molecules [44], [45]. The large torsion angle of the molecules in the crystal may also be the reason for the high absolute quantum yield of 50.8% for DSA, and 40.5, 31.2, and 18.7% for BMOSA, B-4-BOSA, and B-2-BOSA, respectively, which are higher than those of the most reported fluorescent organic crystals.

To gain insight into the nature of the excited state of the DSA derivatives, fluorescence lifetimes were measured in the solution and solid state. Fig. 3 shows the fluorescence decay in the solution and the crystalline state for the BMOSA (the results for the other materials are listed in Table I). The measured lifetimes for the DSA derivatives in the toluene solution were all in the order of several nanoseconds. In the crystalline state, it was noted that the lifetime for DSA was the longest, about 5.2 ns, while it was only 1–2 ns for the other materials.

B. TPA Properties

TPA cross sections of the compounds were measured by Z-scan using a Ti:sapphire laser as the excitation source (at 800 nm). For the measurement, low-frequency (1 kHz) femtosecond laser pulses were used and, consequently, the contribution from the excited-state absorption was eliminated totally, and the nonlinear transmission was mainly induced by TPA of the sample molecules. Fig. 4 shows a typical Z-scan trace for the four materials dissolved in toluene. The sharp dip of the trace is an evident sign for the nonlinear absorption, which is due to two-photon resonance. This procedure generates an absorption signature, and the magnitude of the TPA process can be extracted from it. The open-aperture Z-scan transmittance change can be found by recording the

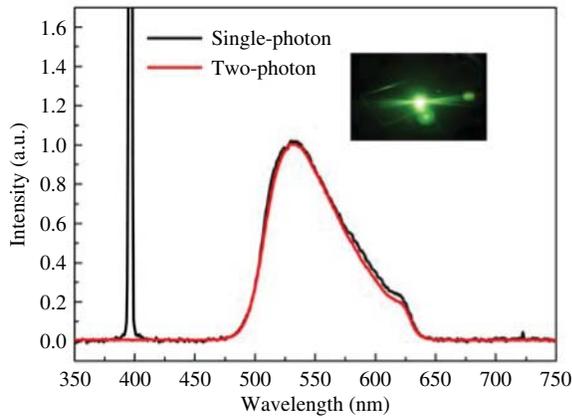


Fig. 5. Fluorescence spectra of B-2-BOSA crystal excited by a single photon and two photons. Inset: Photograph of the B-2-BOSA crystal pumped by 800 nm.

transmitted power to give the normalized energy transmittance, assuming a Gaussian pulse [46].

$$T = \frac{1}{\sqrt{x}q_0(z, 0)} \int_{-\infty}^{+\infty} \ln \left[1 + q_0(z, 0)e^{-\tau^2} \right] d\tau \quad (1)$$

where

$$q_0(z, 0) = \beta I_0(t) L \left(\frac{1 + z^2}{z_0^2} \right)^{-1} \quad (2)$$

and L is the sample thickness, z_0 is the Rayleigh length, z is the sample position, and I_0 is the pulse irradiance. The macroscopic TPA coefficients β (in units of cm/GM) were measured at several different values of laser irradiance. Subsequently, it was evaluated from a fit of the experimental trace according to the equation mentioned earlier. By knowing the β value, the TPA cross section for a given molecule was determined by the following relationship [47]:

$$\sigma = \frac{h\nu\beta}{N_A d_0 \times 10^{-3}} \quad (3)$$

where σ is the molecular TPA cross section in units of $\text{cm}^4/(\text{photon/s})$, N_A is Avogadro's number, and d_0 is the molar concentration of the absorbing molecules in units of M, and $h\nu$ is the photon energy of the input light beam. In the experiment, all the DSA derivatives showed effective TPA properties. The calculated TPA cross section for DSA was about 95 GM, and for BOMSA, B-2-BOSA, and B-4-BOSA it was 88, 143, and 112 GM, respectively.

The studied crystals in this paper showed strong TPA-induced fluorescence emission. Fig. 5 depicts the measured one- and two-photon-excited fluorescence spectra of the B-2-BOSA crystal. The fluorescence spectral shape remained the same as that obtained by the one-photon absorption, that is, the same emission processes from the one- and two-photon-excited states to the ground state are involved. As further evidence, the two-photon-excited fluorescence intensity as a function of the incident energy is in good agreement with the best fitting curve following the square dependence, which implies that the upconverted emission indeed stems from the TPA processes. Under TP excitation at 800 nm, the crystals strongly emitted broadband fluorescence (as shown in the

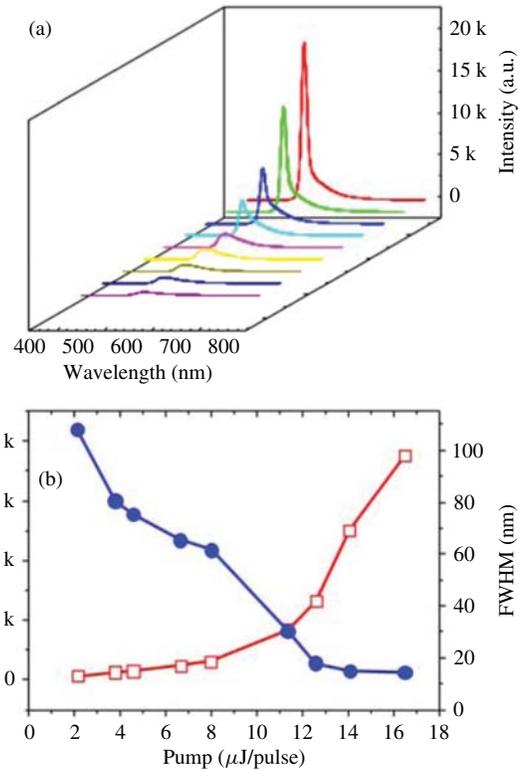


Fig. 6. (a) Light-emission spectra of BMOSA crystals at different intensities of the incident laser light. (b) FWHM and PL peak intensity of light emission of a BMOSA single crystal as a function of the incident laser energy.

inset of Fig. 5), implying great potential for upconversion applications.

C. SNLE

Under the ultraviolet excitation, the light emitted from the edges of all the tested crystals was much stronger than that from the body surface, indicating that self-waveguide emission occurs in the crystals. Waveguide propagation of the emission is thought to be a prerequisite for lasing. In the spectral-narrowed emission experiment, the crystals were placed on quartz substrates. First, we examined the emission characteristics of the crystals of BMOSA. Fig. 6(a) shows the emission spectra of a crystal of BMOSA detected from the edge at several different pump energy densities. At the pump energy of 2 μJ per pulse, the PL, which consisted of a broad band, reflected the nature of spontaneous emission. As the excitation density increased, the spectroscopic profiles changed dramatically. At pump energies between 10 and 17 μJ per pulse, the broad PL band at 532 nm progressively gain-narrowed from about 100 nm down to 16 nm full-width-at-half-maximum (FWHM). The obvious change in the spectra at high excitation intensity suggests that the PL confined in the single crystal is under resonance and gives out the stimulated emission. It is important to note that the existence of gain results in not only a narrowing of the emission spectra at certain pump intensity but also a considerable increase in the output intensity. This is illustrated in Fig. 6(b), where the output intensity at the maximum wavelength of the emission spectrum has been represented as a function of pump intensity

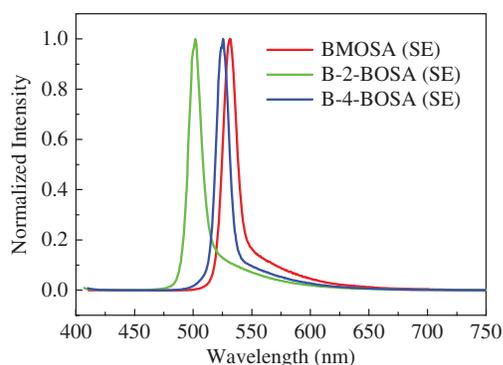


Fig. 7. Normalized ASE spectra for the crystals of BMOSA, B-2-BOSA, and B-4-BOSA.

for BMOSA crystal. As observed, the intensity grows linearly with the pump intensity, and shows a clear collapse at higher pump power densities into a single emission peak, which coincides with the 0–1 transition of the fluorescence spectrum. This has been generally found in the case of SNLE, and can be interpreted in terms of a four-level laser system, where the maximum gain can be expected from the 0–1 vibronic transition. Similarly, the B-2-BOSA and B-4-BOSA exhibited pronounced SNLEs centered at 501 and 526 nm with a low threshold of 12.8 and 1.0 μJ per pulse, respectively (Fig. 7). However, we did not observe the SNLE in the DSA crystals, although they exhibited high quantum efficiency. The underlying reason may be related to the material's photophysical properties. The stimulated emission cross section is essential for the expected performance, because it determines the relationship between the gain and the energy stored, while it is inversely proportional to fluorescent lifetime and fluorescent line width [48]. As mentioned earlier, the lifetime in the DSA crystals is much longer than that of the others, and the FWHM of the fluorescence of spontaneous emission is larger.

IV. CONCLUSION

In summary, the TPA properties and SNLE of a number of small-molecule organic single crystals of symmetrical DSA derivatives were comprehensively examined. The TPA cross sections were obtained by open-aperture Z-scan method. The results showed that the derivatives exhibit large TPA, and also strong two-photon-excited fluorescence in the crystals. Moreover, SNLE from the crystals of DSA, B-2-BOSA, and B-4-BOSA was observed. Considering their TPA cross section and high crystalline-state PL, the novel DSA derivative crystals are expected to be attractive for the implementation of alternative optical pumping schemes toward compact and practical solid-state laser applications.

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