Two-photon induced amplified spontaneous emission from needlelike triphenylamine-containing derivative crystals with low threshold

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Two-photon induced amplified spontaneous emission (ASE) characteristics of a needlelike crystal were studied. Under two-photon excitation, the upconverted light emission was confined within the crystal and self-waveguided along the needle axis then radiated from the needle tips. The full width at half maximum of the two-photon excited fluorescence reaches 6.5 nm and ASE threshold is as low as 0.29 mJ pulse^{-1} cm^{-2} for the *N*-(4-(4-(4-(diphenylamino)styryl)styryl)phenyl)-*N*-phenylbenzene amine crystal, comparable with those achieved by single-photon pumping. The needlelike crystal is shown to be a promising candidate for frequency up-converted organic semiconductor microlasers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3142383]

Over recent years, two-photon pumped frequency upconversion lasing[1–4] has been become interesting and promising not only because the gain material can be pumped at a longer wavelength than the that for lasing but also no phase-matching condition is required compared with other commonly used approaches such as sum frequency or second harmonic generation. Different with cascaded two-step one-photon processes, two-photon absorption (TPA) is the simultaneous absorption of two photons in order to excite a molecule from one state (usually the ground state) to a higher energy electronic state.[5] In the past years, a sizable number of novel organic chromophores have been developed, which can be used as highly efficient two-photon-pumped (TPP) lasing dyes. Experimentally, TPP lasing behaviors have been reported in solutions of organic dyes,[4] dye-doped molecular solids,[6] and organic crystals. It is well known that crystals are the suitable materials from the viewpoint of the achievement of lasing. To induce population inversion, the organic crystal must survive under the high pump energy. However, considering that the two-photon excitation cross section is much smaller than the corresponding one-photon cross section, even for a strong TPA medium, higher pump intensity is required for TPP lasing purposes. A major challenge in developing organic-molecule-based photonic devices is the high intensity threshold required for inducing optical nonlinearities.[7] A low pumping energy could make the degradation process slower and prolong the lifetime of devices. It is necessary to develop high quality crystal with low threshold energy for upconversion lasing. In this letter, we report two-photon induced frequency upconverted amplified spontaneous emission (ASE) from needlelike crystals of *N*-(4-(4-(4-(diphenylamino)styryl)styryl)phenyl)-*N*-phenylbenzene amine (Ph-TPA2). The upconverted mirrorless lasing was observed. Furthermore, excitation power dependence of emission intensity showed a rising edge at ~0.29 mJ pulse^{-1} cm^{-2}.

Ph-TPA2 is a well known compound with a rigid and planar structure [Fig. 1(a)], a strong tendency to form crystals, and a large TPA cross section in solution.[8] Figure 1(a) shows the absorption (solid line) and photoluminescence (PL) spectra of Ph-TPA2 in solution (dashed line) and crystal (dotted line). The energy bandgap (E_g) of 2.7 eV was determined from the UV-visible absorption threshold, and the refractive index is about 1.8 for the organic crystal. The TPA spectra were determined by using laser pulses (~100 fs

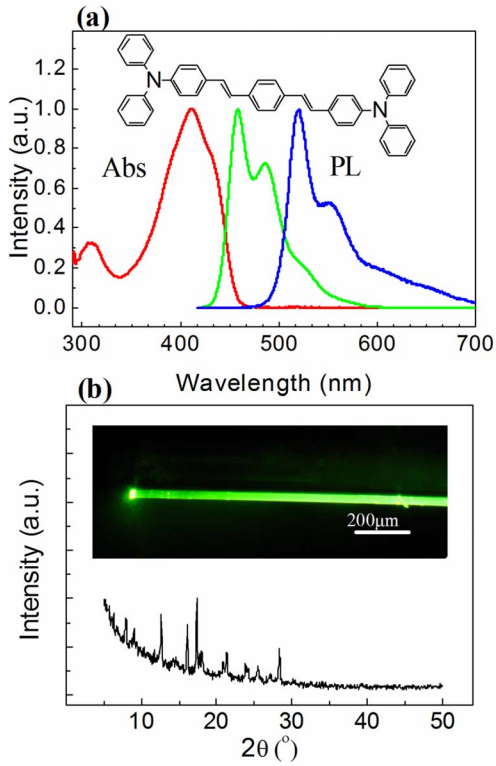

FIG. 1. (Color online) (a) The absorption (left line) and PL spectra of Ph-TPA2 in solution (middle line) and crystal (right line). Inset: The chemical structure of Ph-TPA2. (b) X-ray powder diffraction pattern of the Ph-TPA2 crystal. Inset: The photograph of the crystal under fluorescence microscope.

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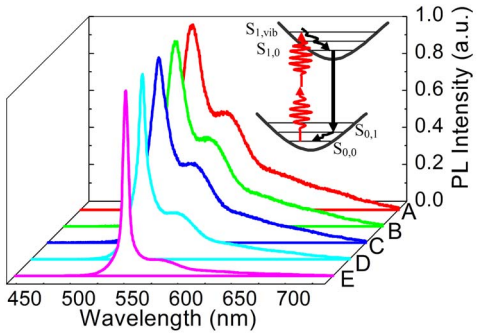

FIG. 2. (Color online) Normalized light emission spectra of Ph-TPA2 crystals at five different the intensity of the incident laser light (A) 0.22 mJ pulse^{-1} cm^{-2}, (B) 0.29 mJ pulse^{-1} cm^{-2}, (C) 0.33 mJ pulse^{-1} cm^{-2}, (D) 0.44 mJ pulse^{-1} cm^{-2}, (E) 0.92 mJ pulse^{-1} cm^{-2}. Inset: Scheme of four-level mechanism including vibration sublevels.

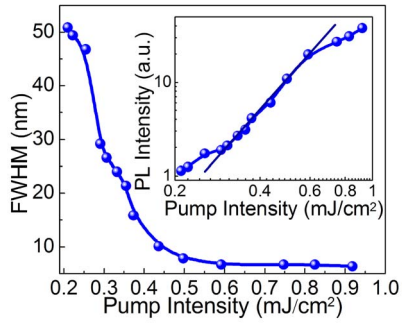

FIG. 3. (Color online) FWHM and PL peak intensity (inset) of self-waveguided light emission of a Ph-TPA2 single crystal as a function of the incident laser energy intensity.

duration, 82 MHz repetition rate) from 710 to 840 nm generated by a mode locked Ti:sapphire laser (Spectra-Physics). A fiber-coupled spectrometer was used to monitor the excitation wavelength. All data were taken by two-photon-excited fluorescence method with fluorescein (in water, *p*H =11) as reference. The TPA cross section at 800 nm is about 200 GM [1 GM=10^{-50} cm^4(photon s)] in the chloroform solution. The crystal was prepared by vaporizing mixed solvents of chloroform and methanol slowly at room temperature under rigorous exclusion of light. The Ph-TPA2 crystals grow in a linear needlelike morphology with a 1–2 mm length and a width of several tens of microns. Green light emission of the crystals under UV excitation is confined within the crystal and waveguided along the needle axis. According to x-ray diffraction analysis, the single crystal belongs to the triclinic system and $P-1$ space group. Powder x-ray diffraction analysis in Fig. 1(b) shows a series of very sharp peaks, which confirms the crystalline nature for Ph-TPA2 crystal. The inset of Fig. 1(b) shows crystal under UV light excitation using a conventional inverse fluorescence microscopy.

For the ASE measurements, the excitation source is from a Ti:sapphire regenerative amplifier with laser pulses of 800 nm, ~100 fs pulses duration and 1 kHz repetition rate. The pulse energy was controlled using neutral density filters. An adjustable slit and a cylindrical lens were used before the beam splitter in order to shape the beam into a narrow stripe with a continuously varied length on the crystal. The laser energy is measured by an optical power meter (Newport). The light from the crystal was collected by a lens and introduced to an Andor iDus charge-coupled device camera connected with a spectrometer. In this configuration, the fluorescent light is collected in the direction parallel to the needle axes of the crystal.

Figure 2 shows the emission spectra of a crystal detected from the sample tip at five different pump energy densities. At 0.22 mJ pulse^{-1} cm^{-2}, the PL spectrum, which consists of two main broad bands (520 and 550 nm), is weak and featureless and reflects a nature of a spontaneous emission. As the excitation density increases, the spectroscopic profiles dramatically change. At pump energies higher than 0.3 up to 1 mJ pulse^{-1} cm^{-2}, the broad PL band at 520 nm is progressively gain narrowed down to a line width of 6.5 nm full width at half maximum (FWHM).

The line at 520 nm coincides with the maximum of the broad PL spectrum and would then corresponds to the transition from the vibrational ground level of the S_1 excited state to the first vibrational level of the fundamental state S_0.[9] Amplified spontaneous emission or traveling wave lasing can be interpreted according to the basic principles of stimulated emission (SE).[10] In the quasistationary pumping regime, we can then obtain the population rate equation for the S_0 ground state and S_1 excited state of each pulse. In a weak population rate regime and for single-pass amplification, the SE intensity I_{SE} can be written as

$$I_{SE} = I_0 \exp(\sigma_{1-0} N_y I_p / I_{p,sat}), \quad (1)$$

where I_0 is I_{SE} at $y=0$, N is the density of molecules, σ_{1-0} is the SE cross section, y is the gain length, I_p is the pump intensity, and is $I_{p,sat}$ the pump intensity at saturation.

FWHM and PL intensity of fluorescence emission of a Ph-TPA2 single crystal as a function of the incident laser energy intensity were shown in Fig. 3. To determine the threshold value for ASE, the width of the ASE band at 520 nm was extracted from a Gaussian fit to the ASE bands and plotted versus the pump energy intensity. Finally, the threshold value was extracted from the incident laser intensity as halfway point from fluorescence to the completely narrowed ASE.[11] The value deduced by this method corresponds well with the value obtained from the change of slope in the pump intensity dependence at a low threshold of 0.29 mJ pulse^{-1} cm^{-2} for the onset of ASE in crystal.[12] This threshold is extremely low compared with other results reported (see Table I).[13–15] The low threshold value and the observed ASE peak intensity dependence on pump energy density were confirmed by repeating the ASE experiment. The photodegradation of the crystal did not occur under the experiment.

Since waveguided propagation of the emission is a prerequisite for lasing or ASE,[16,17] a self-waveguide effect is

TABLE I. Threshold of ASE for different crystals (a) pumped by two-photon (800 nm) and (b) single photon.

Sample no.	Threshold (μJ/cm^{-2})	Pulse duration	Reference
Ph-TPA2	290(a)	120 fs	This work
CN-DPDSB	395(b)	10 ns	12
BP1T	77(b)	200 fs	13
p–6P	855(b)	7 ns	14
p–6P	110(b)	120 fs	14

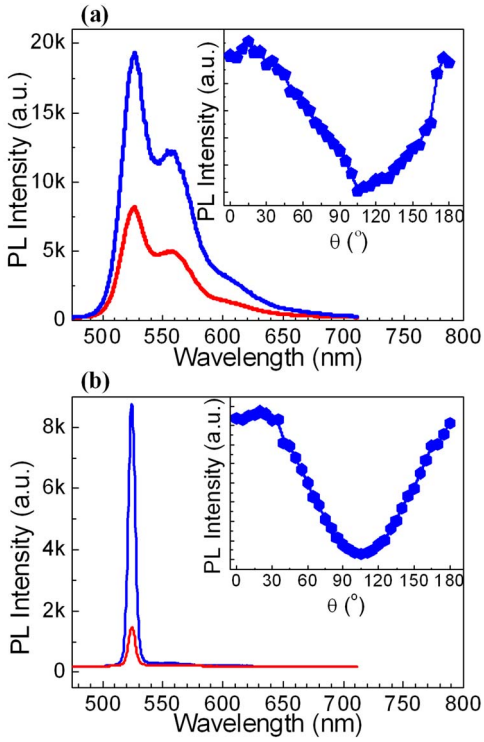

FIG. 4. (Color online) (a) Fluorescence spectra taken under the polarizer with the polarization of θ=20 and 110 pumped at 0.1 mJ pulse^{-1} cm^{-2}. Inset: dependence of the output intensity at peak position on polarization of angle. (b) Fluorescence spectra taken with the polarization of θ=20 and 110 pumped at 0.8 mJ pulse^{-1} cm^{-2}. Inset: dependence of the output intensity at peak position on polarization of angle.

another important factor besides large TPA cross section and high PL efficiency for low threshold upconverted lasing, especially in the crystal with needlelike morphology. The light emitted at the excited region is confined inside the crystal and propagated along the needle axis, then radiated from the tip, just as showed in Fig. 1(b). In order to prove this self-waveguided mode of the light emission in the needlelike crystals, the polarization of the emitted light was observed by changing a linear polarizer before the detector at the energy of pumping laser about both 0.1 and 0.8 mJ pulse^{-1} cm^{-2}. Figures 4(a) and 4(b) (inset) show the angular dependences of light emission intensity at peak position pumped at 0.1 and 0.8 mJ pulse^{-1} cm^{-2}, respectively, where θ denote the angles of the polarization plane of the emitted light with respect to the horizontal orientation. Emission spectra taken at both polarizations with θ=20 (maximum) and θ=110 (minimum) were shown in Figs. 4(a) and 4(b), pumped at 0.1 and 0.8 mJ pulse^{-1} cm^{-2}, respectively. The fluorescence intensity is much higher for at polarization with θ=20, as is expected from the spatial distribution of the light emitted from the orientation of the transition dipoles of the Ph-TPA2 molecules in the crystals. The angular-resolved polarized fluorescence intensity indicates that the propagation of polarized light emitted from the molecules with uniaxial orientation. The polarization $P=(I_{max}-I_{min})/(I_{max}+I_{min})$ about 0.74 at the energies of 0.8 mJ pulse^{-1} cm^{-2} is large than 0.41 at the energies of 0.1 mJ pulse^{-1} cm^{-2}. All these behaviors support the above-mentioned self-waveguided effect of the light emission in the needlelike crystals. The low threshold demonstrated of the crystal reflects the high quality and transparency encompassing in the whole crystal, and is a consequence of an efficient confinement of self-waveguided lights. One-dimensional needlelike morphology is a very suitable configuration to amplify the emitted light along the needle axis.[17] If the shape of the needle tips can be properly controlled, we believe that the needlelike crystals of Ph-TPA2 would be of great interest for a resonant self-cavity effect and a good candidate for upconverted laser. However, there is a need for further evaluation of the morphology effect on lasing characteristics and the quality of the self-waveguide mode in each single needle.

In conclusion, we have demonstrated two-photon induced amplified spontaneous emission of light (520 nm) using microneedlelike crystal. The FWHM of the two-photon excited fluorescence reaches 6.5 nm when the pumping energy is 0.8 mJ pulse^{-1} cm^{-2}. The organic crystal exhibits a low threshold value of 0.29 mJ pulse^{-1} cm^{-2} for ASE, which can compared with some crystals pumped by single photon. Furthermore, the crystal exhibits an excellent stability against photodegradation even at high pump energy densities under ambient conditions. The observed ASE is also highly polarized. Our results show that the needlelike crystals may be very attractive material as gain media for frequency upconverted organic microlasers and light amplifiers due to their very low threshold values for ASE.

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