

# Two-photon excited highly polarized and directional upconversion emission from slab organic crystals

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Effective upconversion emission from an organic crystal of cyano-substituted oligo (*p*-phenylenevinylene) (CNDPASDB) based on two-photon absorption is presented. Frequency upconverted cavityless lasing, or amplified spontaneous emission, from the crystal pumped by a femtosecond laser of 800 nm was observed when the excitation energy exceeded the threshold of  $1.3 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ . Its polarization contrast was estimated to be  $\sim 0.93$ . This large ratio is due to the unified unidirectional configuration of the molecular long axis in crystal, beneficial to the stimulated emission with a low threshold. These results indicate that the present CNDPASDB crystal has a potential for upconversion laser device application. © 2010 Optical Society of America

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Studies on two-photon excitation of organic molecule are of interest for applications including fluorescence microscopy [1], microfabrication [2], and upconversion lasing [3,4]. The nonlinear nature of the excitation process enables materials to be pumped by wavelengths longer than the materials' emission. The frequency upconversion, together with the tunability of the lasing wavelength within a quite broad spectral range and the elimination of the phase-matching requirement, makes two-photon excitation a promising approach toward novel short-wavelength light sources. So far, two-photon pumped (TPP) lasing has been achieved from solutions and dye-doped solid matrices of various geometries like films [5], fibers [6] and microdroplets [7]. However, practical applications are hindered by the high lasing thresholds, which arises from the low density of chromophores because of their low solubility, or from the efficiency loss due to intermolecular quenching and thermal deactivation in amorphous materials. Enlightened by work on single-photon pumped amplified spontaneous emission (ASE) of organic crystals, which exclude impurities and possess high-density molecules, TPP cavityless lasing, or TPP ASE of organic single crystals has recently been reported [8,9]. In a crystal, molecules are orderly bonded via van der Waals forces, and their lasing properties are not only related to the emission ability of primitive building blocks, molecules, but also closely associated with the crystal structure. An obvious example is the intrinsic polarization of the laser output, which reflects the molecular arrangement in a crystal and in the meantime is an important index of the laser beam quality. Such an important issue, although critical for laser device design, remains untouched. In this Letter, we reported efficient TPP upconverted emission with high polarization contrast (0.93), realized in cyano-

substituted oligo(*p*-phenylenevinylene) organic crystals with a threshold of  $1.3 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ , implying the potential to reach high gain as a laser medium.

The molecule used here is 1,4-bis( $\alpha$ -cyano-4-diphenylaminostyryl)-2,5-diphenyl benzene (CNDPASDB, inset of Fig. 1) [10]. Crystals were obtained by vaporizing the solution of CNDPASDB in mixture of dichloromethane and methanol under exclusion of light. The solution containing crystals (about 3 mm in length and 0.5 mm in width, unpolished), was dispersed in ethanol and drop cast onto the quartz plate and subsequently dried. X-ray diffraction analysis indicates the CNDPASDB crystallizes in the  $P\bar{1}$  space group with uniaxially oriented molecular arrangement.

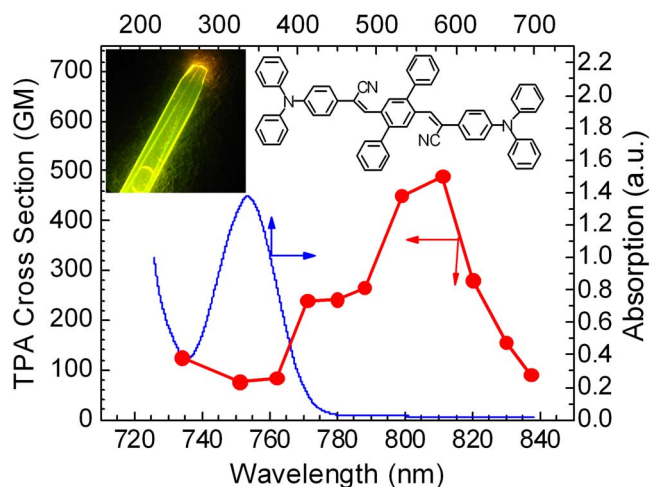


Fig. 1. (Color online) Linear absorption (solid curve) and two-photon absorption spectra for femtosecond pump pulse. Inset, molecular structure of CNDPASDB and fluorescence photographs of CNDPASDB organic crystal.

A prerequisite of the upconversion emission is the high two-photon absorption ability of a material. We mapped the two-photon absorption and the corresponding photoluminescence (PL) spectra of dispersed molecules as a function of pumping wavelengths by the two-photon fluorescence method in dichloromethane solution with fluorescein (in water, pH 11) and Rhodamine B (in methanol) as standards, whose two-photon properties have been well characterized [11]. The measurements were conducted under femtosecond laser excitation (100 fs, 82 MHz) and in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation. The collected two-photon excitation cross sections along with the linear absorption are shown in Fig. 1. The measured TPA cross section centered at 810 nm is about 500 GM.

For the convenience of the TPP ASE test, laser from the ultrafast amplifier system (800 nm) was chosen as the pump light. The energy of the excited pulse was controlled by neutral-density filters, and the laser beam was focused with a cylindrical lens into a slab crystal. The light emitted from the crystal was collected along the directions parallel and perpendicular to the long crystal axis and was detected by the optical fiber spectrometer connected with a CCD. Bright light emits from the crystals under two-photon excitation. Under weak incident intensities, the emission spectra exhibited a broad feature [Fig. 2(a)]. On the other hand, a sharp PL peak centered at about 561 nm with FWHM  $\sim 15$  nm was observed at high pump intensity. Figure 2(b) represents the light emission peak intensity and FWHM as a function of the incident laser fluency. As the pump level rose, the PL peak abruptly increased; only the gain-narrowed peak survived, while the broad tails of the PL were completely suppressed. We can therefore deduce the threshold  $E_{th}$  from the change of slope in the pump intensity dependence at  $1.3 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ . The FWHM of the emission spectrum is dramatically reduced from 63 to 15 nm in the neighborhood of threshold. Upon further increasing the pump energy, gain narrowing is halted, and the FWHM did not change any more. The intensity dependence of the PL peak changed in slope when the excitation exceeded  $4.4 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ , which may come from the exciton–exciton annihilation. Interestingly, we observed that when the pump intensity increased, a yellowish-green and highly directional emission [Fig. 3(a)] was produced in the direction parallel to the

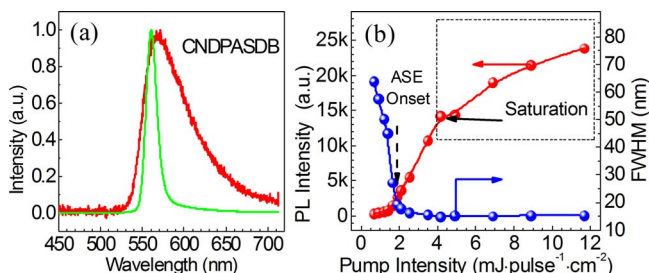


Fig. 2. (Color online) (a) Upconverted normalized spontaneous emission and ASE spectra. (b) PL intensity and FWHM as function of the incident laser fluence.

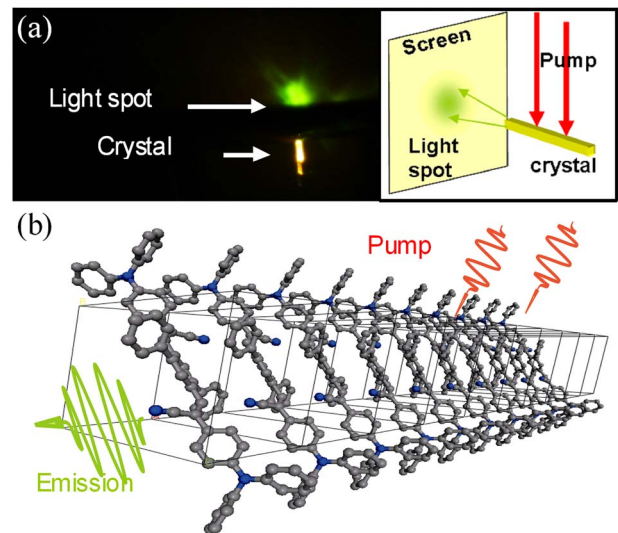


Fig. 3. (Color online) (a) Photograph of a yellowish-green light spot from the CNDPASDB crystal. Inset, schematic representation of relative orientation for recording the PL spectra. (b) Molecular arrangement and configuration of the polarized emission from the crystals.

long crystal axis pumped, provided that the excitation was higher than a certain threshold. No light spot was found on the opposite side, implying the excellent property of the CNDPASDB slab crystal for upconversion laser or amplifier. The net conversion efficiency measured from the absorbed pump energy (two photon) to the lasing output is  $\eta = 1.3\%$  (sum of the two sides of the crystal) when pump at  $2.1 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ . This is not very high. But we believe the efficiency could be higher if the pump energy is increased or introduces resonant feedback.

To investigate the polarization properties of the slab waveguide, we measured the polarization state of the ASE emission and calculated the polarization contrast  $C$  [12], defined as

$$C = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min}), \quad (1)$$

where  $I_{\max}$  and  $I_{\min}$  are the maximal and minimal polarization components of the PL emission, respectively. The maximal/minimal intensity ratio ( $I_{\max}/I_{\min}$ ) below the threshold [Fig. 4(a)] is about 2. The origin for this polarized emission should be from the uniaxially oriented packing of the molecules in

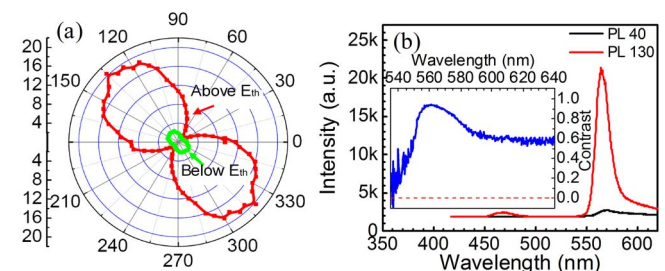


Fig. 4. (Color online) (a) Relationship between the PL intensity and the polarization angle below and above the threshold. (b) Fluorescence spectra taken with maximal and minimal intensity. Inset, polarization contrast  $C$  spectra of the CNDPASDB pumped at  $2.1 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ .

the crystals [13]. Further increasing the pump to  $3.1 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$  (above the threshold) led to significantly narrowed spectra of emission. In this case, the emissions are strongly polarized. For example, at the angle  $\varphi=130^\circ$  ( $\varphi$  denotes the angle of the polarization plane of the emitted light with respect to the horizontal orientation), PL reached the maximum, consistent with spontaneous emission [Fig. 4(a)]. The ratio ( $I_{\text{max}}/I_{\text{min}}$ ) as detected in Fig. 4(a) was about 20, producing a polarization factor,  $C$ , of  $\sim 93\%$ . The high polarization contrast means that the emission at 560 nm is nearly perfect linearly polarized. The spectroscopy at  $\varphi=130^\circ$  and  $\varphi=40^\circ$  was plotted in Fig. 4(b) along with the polarization contrast spectrum [inset of Fig. 4(b)].

The crystal structure reveals that all of the CNDPASDB molecules array parallel with an identical conformation and orientation in the crystal, and they exhibit regularly uniaxially oriented packing, in contrast to a herringbone packing motif (where the molecules are packed more or less edge-to-face in two-dimensional layers), commonly adopted by conjugated molecules. The x-ray diffraction measurements of the crystal indicate the (001) plane parallels the crystals' surface, and the angle of the orientation of the molecule against the horizontal plane is  $\sim 40^\circ$ , corresponding to the polarization direction. The results show us that the polarization of light pumped by two-photon is parallel to the transition dipole, the same as that induced by single-photon [10]. Because the electronic transition dipoles are along the molecular axis [14]. This explains why a highly directional emission [Fig. 3(b)] is produced in the direction parallel to the long crystal axis. On the other hand, because of the intrinsic order present in the crystal, the transition dipole moments of the molecules exhibit an optimal configuration with regard to the absorption and emission of light. This facilitates stimulated photon emission from the inverted population because the seed photons have been synchronized in the polarization. Light polarized parallel to the molecular dipole direction is enhanced and the lasing threshold is reduced when the photons are waveguided in the uniaxially oriented molecular crystals, while uniaxial polarization of the emitted light is often obstructed in the crystals with bidirectional molecular packing [15,16]. If the shape of the crystal can be properly controlled, we believe that the crystals of CNDPASDB would be of great interest for polarization applications. The question is that whether the polarization is always polarized in this orientation. The polarization state of the output under different conditions (with varied polarization of

the pump) is investigated. PL reached the maximum at the angle  $\varphi=130^\circ$  all the time. This suggests that the polarization of output is due to the intrinsic molecular packing, which is independent of the pump.

In conclusion, we reported efficient two-photon pumped upconversion lasing with high polarization contrast, realized in cyano-substituted oligo(*p*-phenylenevinylene) organic crystals. The emission from the crystal is of almost linear polarization and highly directional without the help of any resonator. The present results give a very favorable implication for the use of CNDPASDB as upconversion organic laser material.

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