Two-Photon Pumped Amplified Spontaneous Emission from Cyano-Substituted Oligo(p-phenylenevinylene) Crystals with Aggregation-Induced Emission Enhancement

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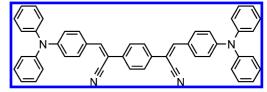
We report the effective two-photon absorption-induced upconversion amplified spontaneous emission (ASE) in the cyano-substituted oligo(p-phenylenevinylene) 1,4-bis[1-cyano-2-(4-(diphenylamino)phenyl)vinyl]benzene (TPCNDSB) organic crystals. The material shows enhanced emission in the solid state (31% quantum yield in crystal) and efficient two-photon absorption. The ASE under the one-photon and two-photon excitation were observed. It is demonstrated that the organic crystals of TPCNDSB might be practically used as fluorescent materials for potential upconversion laser applications.

1. Introduction

Over the past few years, there has been great interest in two-photon absorption materials[1,2] for their promising applications such as optical limiting,[3,4] microfabrication,[5−7] bioimaging,[8] and two-photon pumped (TPP) up-converted lasing.[9−12] TPP lasing is of increasing interest for making novel light source, which allows pumping at red or near-infrared wavelengths. In addition, it releases the phase-match condition compared with second harmonic generation. Up to now, TPP lasing in organic small molecules has been demonstrated in the past in dye-doped organogels[13] as well as dye-doped films[14] and dye solution,[15,16] whereas the reports on TPP lasing from the crystals are seldom. Many chromophoric organics and polymers are highly emissive in their dilute solutions; they become only weakly luminescent when the concentration is high, especially in the solid state. Crystallization can aggravate the situation by further lowering the quantum yields of fluorescence. This is believed to be caused by the formation of less emissive species such as excimers or delocalized excitons according to the aggregation of lumino-phores, leading to a reduction in the luminescence efficiency. This quenching effect may be one of factors that is responsible for the scarce number of organic crystals with TPP fluorescence,[2,9,17] especially TPP lasing.

Very recently, intriguing processes of aggregation-induced emission enhancement (AIEE) and crystallization-enhanced emission (CEE),[18−23] which enhance emission from the aggregate or crystal, have been discovered. Lots of novel materials with AIEE have been developed, such as carbazole-based fluorophores[24] and benzene-cored luminophors.[25] This special class of organic semiconductor, showing potential application for organic light emitted device or laser, has attracted increasing attention.[26]

SCHEME 1: Molecule Structure of TPCNDSB

In this work, we reported cyano-substituted oligo(p-phenylenevinylene) 1,4-bis[1-cyano-2-(4-(diphenylamino)phenyl)vinyl]benzene (TPCNDSB) organic crystals The photoluminscence properties and long fluorescence lifetime were obtained for the sample in an aggregate state as compared with the sample in solution. The materials possess enhanced solid emission in the crystalline state. Restricted intramolecular motion and intramolecular charge transfer state has been suggested for the reason. Then, the one-photon pumped amplified spontaneous emission (ASE, sometimes called mirrorless lasing) was observed in the crystals. Furthermore, the nonlinear absorption and ASE induced by TPA were demonstrated.

2. Experimental Section

Scheme 1 shows chemical structure of TPCNDSB. The crystals were prepared by solvent-exchange process at room temperature under rigorous exclusion of light. Absorption spectra of solution were measured by a Shimadzu UV-1700 spectrophotometer. Emission spectra were recorded with an AvaSpec 2048-UA-50-AF spectrometer. Crystalline state photoluminescence (PL) efficiencies were measured in an integrating sphere.

For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (Hamamatsu H5783p), which is connected to a time-correlated single-photon counting (TCSPC) board (Becker & Hickel SPC-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) is ∼220 ps. The PL signals were measured near the emission peak.

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The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo Kα and control software using RAPID AUTO at 293 (2) °C. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs, respectively.

The properties of the two photon absorption and two-photon emission have been studied by femtosecond pulse laser experiments in dichloromethane solution at a concentration of 10^{-5} mol L^{-1}. The TPA cross section (δ) has been determined by the two-photon fluorescence method.[27] The reference standards (r) used in the measurement were fluorescein (in water, pH 11) and rhodamine B (in methanol), whose two-photon properties have been well characterized in the literature. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon-induced emission. A 100 fs, 82 MHz pulse train from mode-locked Ti/sapphire laser (Spectra-Physics, Tsunami) was used for the measurement.

In the stimulated emission experiment, a regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti/sapphire laser (Tsunami, Spectra Physics) that generated laser pulses of ~120 fs at wavelength of 800 nm was used for the two-photon pump, and the second harmonic generation was used as the single-photon pump. The energy of excited pulse can be controlled by neutral density filters, and the beam of excite laser was focused with a cylindrical lens into a strip that covered the crystal under experiment. The sample was glued on the quartz substrate parallel to the long axis of stripe. The light emitted from the crystal was collected along the directions parallel and perpendicular to the long crystal axis. The emitted light was detected by the optical fiber and then dispersed to the spectrometer connected to CCD, which is time-gated triggered by the electrical pulse. We observed no significant degradation in the lasing characteristics during the measurement period.

3. Results and Discussion

3.1. Molecular Stacking Features. The crystal structure of TPCNDAB was found to be triclinic with space group $P\bar{1}$ ($a = 9.504$ Å, $b = 9.873$ Å, $c = 19.355$ Å; $\alpha = 81.09°$, $\beta = 81.08°$, $\gamma = 89.47°$) containing two molecules (Figure 1a). The analysis of the crystal structures demonstrates that they have a nonplanar conformation and twisted structure in their crystals. Two types of C−H···N interactions, which are shorter than the van der Waals distance of ~2.75 Å, exist between TPCNDSB molecules. As is shown in the Figure 1b, the distance for one type is 2.523 Å, and the C−H···N angle is 143.66°. The distance for the other type of C−H···N interactions is 2.692 Å, with angle 160.77°. Two aromatic CH/π hydrogen bonds are formed between two molecules with interaction distance of 2.899 Å and angle of 161.01° (Figure 1c), making the end of triphenylamine of the two molecules connected to each other, are not free. Each TPCNDSB molecule connects to three adjacent molecules through aromatic C−H···N interactions and CH/π hydrogen bonds. Both of the strong supramolecular interactions not only make the molecule more rigid and stable in the crystal lattice but also induce tight intermolecular packing, and as a result, the molecules assemble themselves together and prevent the free twisting motions around the double bonds.

3.2. Optical Properties and Excited-State Lifetime. The absorption and fluorescence spectra are shown in Figure 2. The linear absorption of TPCNDSB (in methylene dichloride) with a maximum at 380 nm and the low-energy tail extends to ~500 nm. For the PL spectra, one can find that the peak is at 554 nm
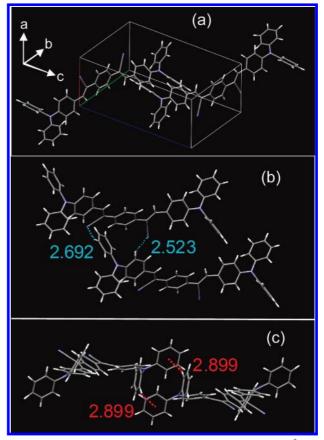

Figure 1. (a) Crystal structure of TPCNDSB with $a = 9.504$ Å, $b = 9.873$ Å, $c = 19.355$ Å; $\alpha = 81.09°$, $\beta = 81.08°$, $\gamma = 89.47°$. (b) Two types (the distances are 2.523 and 2.692 Å) of C−H···N interaction between the adjacent molecules. (c) CH/π interaction in the crystal. The interaction distance and angle of C−H···π center are 2.899 and 161.01°.
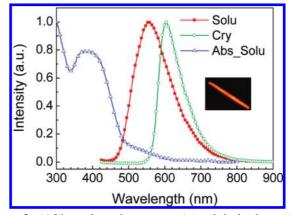

Figure 2. (a) Linear absorption spectrum (△) and single-photon- (405 nm pump) induced fluorescence spectrum in dichloromethane (□) and crystal (○). Inset: fluorescence photograph of the crystal.

and slightly broadened in the solution. Remarkably, the main emission peak is red-shifted (~50 nm) in the crystal. The fluorescence yield of TPCNDSB is ~18% in methylene dichloride solution. Compared with emission efficiency of their solution, the crystals exhibit stronger fluorescence (quantum yield: 31%). Restricted intramolecular motion and intramolecular charge transfer state have been suggested to be the possible mechanism of AIEE,[28,29] considering that vibrational/torsional motion of the molecule can drastically affect the radiative/nonradiative recombination processes of the excited state. The enhanced fluorescence in the crystal also showed corresponding
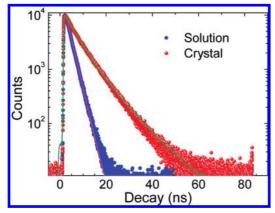
Figure 3. Time-resolved fluorescence curves in solution (pentagon) and crystal (sphere). The fitted fluorescence lifetime in solution is ~2.4 ns and 9.7 ns in crystal.

dramatic changes in emission lifetime, as illustrated by the time-resolved fluorescence curves in Figure 3. The fitted fluorescence lifetime in solution is ~2.4 ns, whereas it is much longer in the crystal (9.7 ns). The results are very similar to the reported molecules CNDPASDB with aggregation-induced emission;[29] that is, the transition time in solution is very fast, resulting in a low fluorescence quantum yield, whereas in crystal, the intramolecular torsion is restricted, and the intramolecular charge transfer state is eliminated. Furthermore, the twisted structure of TPCNDSB in the crystal prevents face-to-face $\pi-\pi$ interactions, which generally quench fluorescence. Therefore, the strong supramolecular interactions enhance the rigidity of molecular skeleton and the tightness of their packing. This, together with the fact that no parallel molecular stacking is present, makes the crystals show strong fluorescence.

3.3. Stimulated Emission in the Crystal. ASE is a powerful tool for the evaluation of the optical gain of the materials.[30,31] The fluorescence emission of TPCNDSB crystal by one photon excitation was investigated first. Figure 4a shows the spectrum taken at different pump intensity. The spectrum obtained with low pump energy is initially broad (>70 nm). As the incident laser fluency is increased, the emission peak intensities exponentially grow, accompanied by the narrowing, which are typical characteristics indicating that stimulated emission occurred (Figure 4b). And the full width at half-maximum (fwhm) was narrowed to be 10 nm. The threshold could be easily concluded from the relationship between the PL intensity and the pump fluence, which is 0.15 mJ pulse^{-1} cm^{-2}. This proved the potential as gain media for laser device.

3.4. Two-Photon Absorption and Upconversion Stimulated Emission. A direct measurement of TPA cross section of the crystals apparently helps to evaluate the two-photon absorptive capability. This, however, as an open problem in the field of nonlinear optics, is technically challenging. Therefore, TPCNDSB solution was measured instead as an approximation of the crystal property. The measured TPA spectra for the chromophore are shown in Figure 5. This shows that TPCNDSB exhibits high two-photon absorption cross section (620 GM at 800 nm, 1 GM = 10^{-50} cm^4/(photon/s) or simply cm^4 s).

Under weak incident intensities pumped by the femtosecond laser of 800 nm (Figure 6a), the emission spectra (including the conventional PL spectra) for TPCNDSB crystal exhibited a broad feature, which was identical to the spontaneous emission excited by single photon. This implies that the same emission processes in the crystal from the one-photon and two-photon excited states to the ground state are involved. A sharp PL spectrum centered at ~600 nm is observed when the pump is
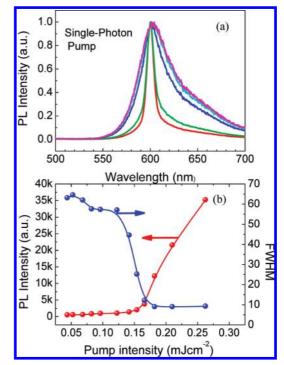

Figure 4. (a) Normalized PL emission spectra from crystal of TPCNDSB under different incident laser fluences pumped by single photon (400 nm). (b) Light emission peak intensity and their full widths at half-maximum (fwhm) as a function of the incident laser fluence.
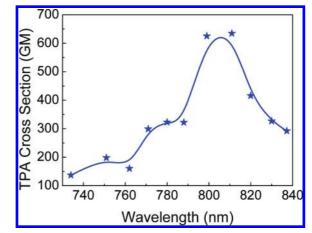

Figure 5. Two-photon absorption cross section at different wavelength for the TPCNDSB molecules in the solution.

high enough and the fwhm is ~10 nm. Figure 6b represents the light emission peak intensity and its fwhm as a function of the incident laser fluency. As the pump increased, the PL peak abruptly increased; only the gain-narrowed peak survives, whereas the broad tails of the PL are completely suppressed, and we can easily conclude the threshold E_{th} from the change of slope in the pump intensity dependence at 3.5 mJ pulse^{-1} cm^{-2}, which is not very high compared with that pumped by one photon. In addition, the fwhm of the emission spectrum was dramatically reduced from 75 to 10 nm at the neighborhood of threshold. Upon further increasing the pump energy, gain narrowing is halted and the fwhm changes no more. The reported ASE threshold of the TPCNDSB crystals is not very low but comparable to some value of lasing threshold of polymers or dendrimers.[32,33] The large fwhm in TPCNDSB crystals is not very beneficial to lower ASE threshold. It is believed that confining the light into the high gain materials reduces the lasing threshold. Lasing in the distributed feedback
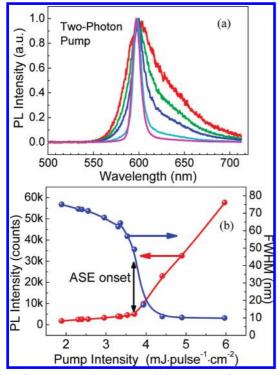
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Figure 6. (a) Normalized PL emission spectra from crystal of TPCNDSB under different incident laser fluences pumped by two-photon (800 nm). (b) Light emission peak intensity and their full widths at half-maximum (fwhm) as a function of the incident laser fluences.

(DFB) or microcavities such as Fabry–Pérot cavities and rings have been demonstrated in the inorganic or organic semiconductor. Microcavities can provide a strong coupling of stimulated emission into lasing modes and lead to lower lasing thresholds.[34−36] If the organic crystals are equipped with feedback structure, for example, by laser micronanomachining, then it can be predicted that a narrower fwhm would be obtained, and the threshold can be further reduced.

4. Conclusions

In summary, we have demonstrated up-converted ASE behavior in crystal with simultaneously enhanced solid-state emission and high two-photon absorption cross section. Suppressed intramolecular motions through strong supramolecular interactions in packing make the TPCNDSB crystal emit brightly under photopumping. Two-photon optical properties in the crystal and lasing characteristics induced by one- and two-photon were investigated. With larger two-photon absorption cross section and high PL efficiency (benefit from the property of AIEE), TPP lasing was observed in the crystals of TPCNDSB, with threshold only one order larger compared with SPP lasing. We note that there are seldom reports of two-photon-induced upconversion lasing in organic crystals. Our current results demonstrate the great potential for using organic crystals with enhanced solid-state emission as the gain medium in upconversion lasers.

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