Efficient Two-Photon Excited Amplified Spontaneous Emission from Organic Single Crystals

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E, E-1, 4-bis[4′-(*N,N*-dibutylamino)styryl]-2,5-dimethoxy-benzene (DBASDMB) organic crystals with high crystalline quality, large size and excellent optical properties are prepared. The linear and nonlinear properties in the crystal are comparatively studied. The relaxation dynamics pumped by two-photon are very similar with that pumped by one-photon. The crystal exhibits very strong two-photon excited fluorescence and amplified spontaneous emission. Efficient two-photon absorption, reasonably high fluorescent quantum efficiency, and high crystal quality together with stimulated emission make organic crystals ideal for the application in frequency upconversion and other optoelectronic fields.

1. Introduction

Organic materials that exhibit strong two-photon absorption and efficient two-photon fluorescence are attractive for applications such as data storage,[1] optical limiting,[2] two-photon photopolymerization,[3–5] fluorescence microscopy,[6] two photon absorption (TPA) photoconductors[7] and two-photon pumped (TPP) lasing.[8–12] TPP lasing is currently of considerable interest for upconversion lasers, as the gain medium can be pumped at red or near-infrared wavelengths, for which laser diodes are inexpensive and need no phase matching. So far, two-photon pumped lasing has been achieved with dye solutions,[11] conjugated polymers[12] and dye-doped solids[13] as gain media. On account of their high purity and their rigorously defined structure, high-quality single crystals are more advantageous than polymer films and solutions.[14] Crystal materials[15–18] possess higher thermo-stability compared with amorphous materials, which are in thermodynamically metastable phases and tend to transit to a more stable phase at low temperature (glass transition temperature, T_g). Unlike solution-processed thin films, single crystals do not display grain boundary defects that may serve as carrier traps. Furthermore, a single crystal is excellent in optical properties, typically the low light propagation loss due to less light scattering and naturally formed crystal facet cavities with molecular-scale flatness.[19]

Herein, we report strong solid fluorescence and amplified spontaneous emission (ASE) induced by absorption of two photons from π-conjugated *E, E*-1, 4-bis[4′-(*N,N*-dibutylamino)-styryl]-2,5-dimethoxy-benzene (DBASDMB) organic crystals, which represent a new avenue in pursuit of wavelength shorting by means upconversion lasing.

2. Results and Discussion

Figure 1a shows the structure of a symmetric D-π-D conjugated-donor molecule *E, E*-1, 4-bis[4′-(*N,N*-dibutylamino)styryl]-2,5-dimethoxy-benzene (DBASDMB), initially designed as a high efficiency photoinitiator for laser micro-nanofabrication based on two-photon photopolymerization. The molecule is synthesized by the Witting reaction of [(2,5-Dimethoxy-1,4-phenylene)]bis-(methylene)bistriphenylphosphonium dichloride and 4-(*N,N*-di-n-butylamino) benzaldehyde.

2.1. Descriptions of the Crystal Structures

The transparent slab-like crystals with clear and sharp crystal faces of DBASDMB (Figure 2a) can be easily obtained by vaporizing a solution of DBASDMB in dichlorometrane at room temperature. The unit cell of DBASDMB is triclinic, space group $P-1$, containing eight molecule snippets with $a = 9.303$ Å, $b = 9.625$ Å, $c = 10.442$ Å, and $\alpha = 81.493°$, $\beta = 78.387°$, $\gamma = 87.876°$. Crystal structure reveals that two double bonds of DBASDMB molecule preserve trans-conformation. According to meticulous analysis of the DBASDMB crystal structure, we found supramolecular interactions existing in two-dimensional direc-

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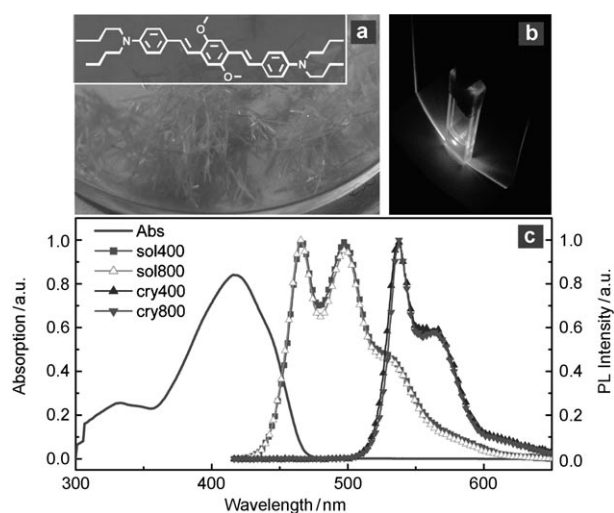Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201000142.

Figure 1. a) The optical microscopic image of DBASDMB single crystals. Inset: molecular structure. b) The lasing image of DBASDMB in solution of 6×10^{-2} M, pumped by 400 nm. c) The optical properties of DBASDMB. Abbreviations denotes: Sol: solution of hexane (10^{-4} mol L^{-1}), Cry: Crystal, excitation wavelengths of femtosecond laser are 400 nm and 800 nm. The three sets of figures are the absorption of DBASDMB solution (left), photoluminescence from solution (middle) and from the single crystal (right).
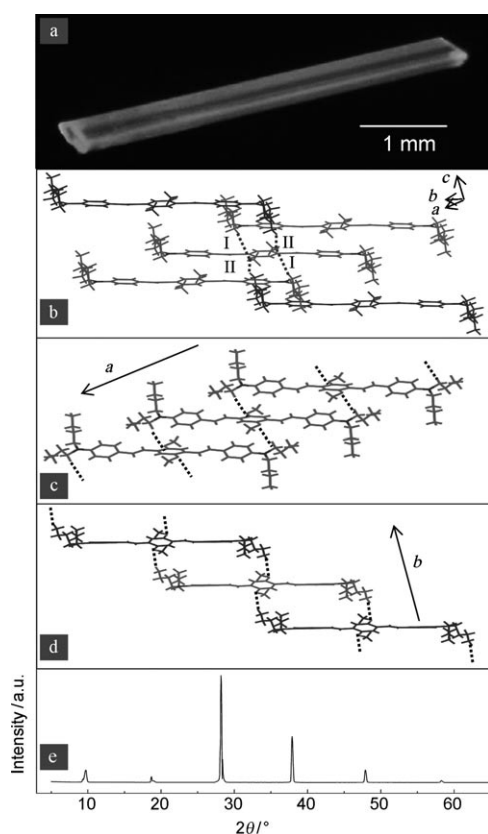

Figure 2. a) The fluorescence microscopic image of a DBASDMB single crystal. b), c) the crystal structure of a DBASDMB molecule. d) The nearest aromatic C–C distance of two DBASDMB molecules. e) Wide-angle X-ray diffraction pattern of crystal.

tion that induce DBASDMB molecules to assemble themselves into like-strip shape and J-aggregation molecular stacking mode. As shown in Figure 2 b, two types of short H···O distances exist between the methoxy groups on DBASDMB molecules and the hydrogen atoms of the neighboring molecules, which are shorter than the van der Waals distance of about 2.9 Å. The presence of these two types of hydrogen bonds (C−H···O) are labeled as interactions I and II. For type I, two hydrogen bonds exist between the two oxygen atoms in one molecule and two hydrogen atoms in butyl group of the two neighboring molecules along OA orientation. The H···O distances of two hydrogen bonds are 2.991 Å and C−H···O angle is 136.697°. As shown in Figure 2 c the C−H···O interaction networks of type I connect the DBASDMB molecular clusters along the axis. For the type II interactions, there are also two hydrogen bonds. These are between the two oxygen atoms in one molecule and the two hydrogen atoms on the end of the alkyl group of the two neighboring molecules. The H···O distances of the two hydrogen bonds are 2.940 Å and C−H···O angle is 158.153°. As Figure 1 d shows the C−H···O interaction networks of type II connect the DBASDMB molecular clusters along the alternate *b* axis. The intermolecular interaction could cause a "brick wall" motif J-aggregate molecular stacking mode. The wide-angle X-ray diffraction pattern of the slab-like DBASDMB crystal shows the diffraction peak at 9.75° corresponds to (001) crystal plane, and other equivalent periodic diffraction peaks at 18.7°, 28.2°, 37.9°, 47.9°, and 58.25°. The diffraction results indicate that the *ab*-plane is parallel to the crystal surface of DBASDMB.

2.2. Optical Properties

The linear absorption of DBASDMB (10^{-4} mol L^{-1} in hexane) peaks at wavelength $\lambda = 417$ nm, ranging from 360 nm to 470 nm, beyond which there is no absorption in the visible-to-near infrared range (Figure 1 c). Excited by either by 400 nm and 800 nm wavelength, 100 fs width and 82 MHz repetition rate laser, identical PL spectra appear, peaking at 467 nm accompanied by two shoulders. For the crystal, the situation is similar but the PL peaks move to 532 nm (Figure 1 c). To obtain further information on the nature of the excited state, the fluorescence lifetime was measured by time-correlated single photon counting (TCSPC). The fluorescence decay (see Figure S1, Supporting Information) of the crystal at 535 nm ($\tau_{cry} = 0.36$ ns) is relatively faster than that of the THF solution at 495 nm ($\tau_{solu} = 1.29$ ns), which is consistent with the formation of J-aggregates.[20, 21]

In the solution or crystal, there are negligible differences in the shape and peak positions of the PL spectra excited by one- and two-photons, revealing that the emission stems from the same excited state. Furthermore, time-resolved investigations (femtosecond fluorescence upconversion experiments) are employed to study the dynamic properties of one- and two-photon excited molecular transitions and relaxation in solution and crystals. Figures 3 a and b show the temporal kinetics for the normal emission in THF solution and in the crystal, respectively, excited by 400 and 800 nm. The time (several pi-
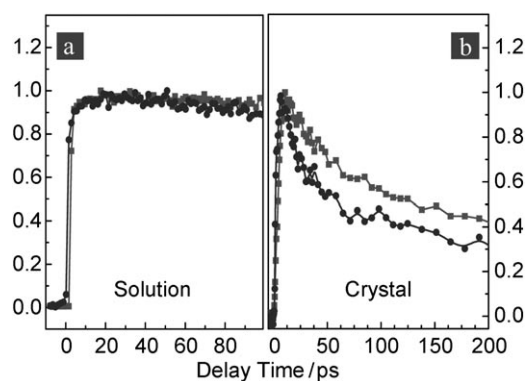
Figure 3. a) Temporal profiles of the fluorescence decay in the first 100 ps pumped by 400 nm (circle) and 800 nm (square) in solution. b) Temporal profiles of the fluorescence decay in the first 100 ps pumped by 400 nm (circle) and 800 nm (square) in the crystal.

Figure 4. Single-photon pumping of the DBASDMB single crystal under 400 nm wavelength femtosecond laser. a) Photoluminescence spectra, and b) PL intensity and FWHM versus pumping intensity. Letters denote pumping energy density of (A) 75, (B) 110, (C) 160, (D) 230 and (E) 260 $\mu J\, cm^{-2}\, pulse^{-1}$, respectively.

coseconds) for the fluorescence to reach their maximum intensity is almost same for excitation at 400 and 800 nm. The two-photon pumped spontaneous emission spectrum is virtually identical to the emission excited by a one-photon process. This suggests that the emission stems from the same excited odd numbered state as the case of one-photon excitation. The most likely scenario to describe the relaxation is: After excitation into the density of two-photon accessible even (grade) states (mA_g), an ultrafast relaxation to the excited ungerade $1B_u$ state takes place. The $1B_u$ state can either decay radiatively or separate to form a geminate pair.

The two-photon absorption cross-section of DBASDMB in solution was previously studied. It has large TPA cross sections: $\delta = 900 \times 10^{-50}\, cm^4 s^{-1} photon^{-1}$.[22] However, the TPA properties may be different due to the arrangement of the molecules in the crystal and the concomitant strong molecular interactions. The two-photon absorption in the slab crystal is investigated by nonlinear transmission (NLT) method.[23]

When the laser polarization is along the long axis, the measured two-photon absorption is about 588.7 GM (see Figure S3, Supporting Information), which is slightly smaller than that in solution. The TPA properties maybe closely connected with crystal structure and the optical properties of excited states, as there are more non-radiative processes in the crystal. Further experiments are needed to study the relationship between the two-photon properties and molecule aggregate state. On the other hand, the crystal exhibits very strong anisotropic properties. The fluorescence intensity (see Figure S4, Supporting Information) is significantly more intense when the crystal is excited with polarization of the laser perpendicular to the long axis, which suggests highly anisotropic molecular packing.

2.3. Amplified Spontaneous Emission Experiments

When a DBASDMB crystal is excited at 400 nm, a highly directional coherent green emission is produced along the long crystal axis, with the increase of the pumping laser power. In the meantime, the full width at half maximum (FWHM) of the spectra reduces rapidly: from 40 nm at pumping intensity of
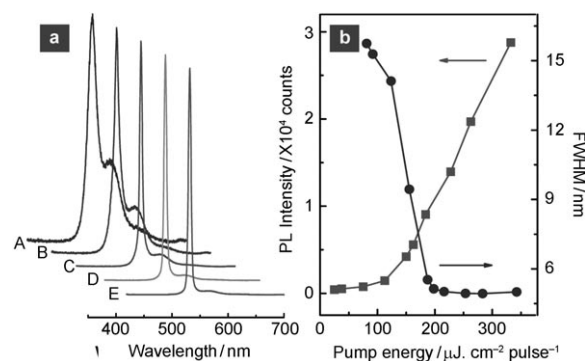
75 $\mu J\, cm^{-2}\, pulse^{-1}$ to 5 nm at 260 $\mu J\, cm^{-2}\, pulse^{-1}$ (Figure 4a). The spectral narrowing is accompanied with a simultaneous output jump (Figure 4b) indicating a typical amplified spontaneous emission. The same behavior has been observed in TPP for the same crystal excited with the fundamental wavelength 800 nm of the femtosecond laser (Figures 5b and d). In this case, 58 nm width of the 532 nm photoluminescence spectrum at low pump energy, 0.32 $mJ\, cm^{-2}\, pulse^{-1}$ was shortened to 5 nm at a high pump energy 2.82 $mJ\, cm^{-2}\, pulse^{-1}$, and the threshold of TPP lasing is measured to 1.68 $mJ\, cm^{-2}\, pulse^{-1}$. The time-resolved emission profiles above the ASE threshold obtained by the upconversion technique shows that the ASE occurs in tens of picoseconds (see Figure S5, Supporting Information). Furthermore, the light intensity in the parallel direction (Figure 5e) changes faster than that in the vertical direction (Figure 5c) with a lower threshold and different spectra (Figure 5f). It's the evidence that self-waveguide effect is playing an important role in the amplified spontaneous emission.[24]

Notice the TPP lasing threshold is 15 times larger than that by single-photon pumping. Considering the chain of lasing processes, the first is the absorption of photons by electrons in crystal, upon which excited singlet states are generated. As long as the excitation wavelength, or equivalent wavelength in case of TPP, is in the spectral region of the $S_{0,0} \rightarrow S_{1,vib}$ transition, vibrationally excited Franck–Condon states are generated. The light absorption is described by one- and two-photon absorption coefficients, α and β as shown in Equation (1):

$$\frac{dI}{dz} = -\alpha I - \beta I^2 \tag{1}$$

where I is the intensity of the incident beam propagating along the z-axis. In the case where linear absorption is negligible, that is when DBASDMB is pumped by 800 nm laser, Equation (1) is rewritten as Equation (2):

$$\frac{dI}{dz} = -\beta I^2 \tag{2}$$

3. Conclusions

TPP amplified spontaneous emission of organic crystals has been observed. The large two-photon absorption cross-section, reasonably high fluorescent quantum efficiency and good crystal quality together with stimulated emission make these organic crystals suitable for the application of frequency conversion in lasers.

Experimental Section

All samples were characterized by ^{1}H NMR spectroscopy on a Varian Mercury-300 NMR spectrometer using solvent signals as internal reference. DBASDMB: ^{1}H NMR (300 MHz, CDCl$_3$) δ [ppm]: 7.39 (d, 4 H, $J = 8.73$ Hz; phenyl), 7.22 (d, 2 H, $J = 16.5$ Hz; vinyl), 7.10 (s, 2 H; phenyl), 7.03 (d, 2 H, $J = 16.5$ Hz, vinyl-), 6.61 (d, 4 H, 8.70 Hz, phenyl-), 3.91 (s, 6 H; OMe), 3.29 (t, 8 H, $J = 7.56$ Hz; NCH2), 1.58(quintet, 8 H, $J = 7.43$ Hz; CH2), 1.35 (sextet, 8 H, $J = 7.50$ Hz; CH2), 0.96 (t, 12 H, $J = 7.20$ Hz; CH3).

Single-crystal X-ray diffraction data were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo Kα and Control Software using RAPID AUTO. The structures were solved with direct methods and refined with a full-matrix leastsquares technique using the SHELXS v. 5.1 programs, respectively. Wide-angle X-ray diffraction was detected using a Rigaku X-ray diffractometer (D/Max-γA, with Cu Kα radiation of wavelength 1.542 A°).

UV/Vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence was measured with a RF-5301PC spectrofluorimeter. Quantum yields in solution were measured using sulfate quinine as the reference standard. Fluorescence microscope measurements were performed using an IBE2000 Inverted fluorescent microscope. The nonlinear absorption coefficient in the crystal is experimentally measured by nonlinear transmission (NLT) method.

In the time-correlated single photon counting (TCSPC) system, a 405 nm picosecond diode laser was used to excite the sample. The emission was detected by a photomultiplier tube (Hamamatsu H5783p) and a TCSPC board (Becker&Hickel SPC-130). The instrument response function (IRF) is about 220 ps. In the upconversion method All the measurements were done at room temperature, a Ti:sapphire oscillator was used to seed a regenerative amplifier. The amplifier produced excitation pulses centered at 800 nm with a repetition rate of 1 kHz, and a temporal FWHM of 120 fs. A portion of the 800 nm compressor output was used as the upconversion gate beam. The instrument response function (IRF) is about 200 fs.

The single crystal was photo-pumped by Ti:sapphire laser with 100 fs pulses at a repetition rare of 1 kHz, (wavelength $\lambda = 800$ nm, $\lambda = 400$ nm by BBO double frequency). The crystal was glued on
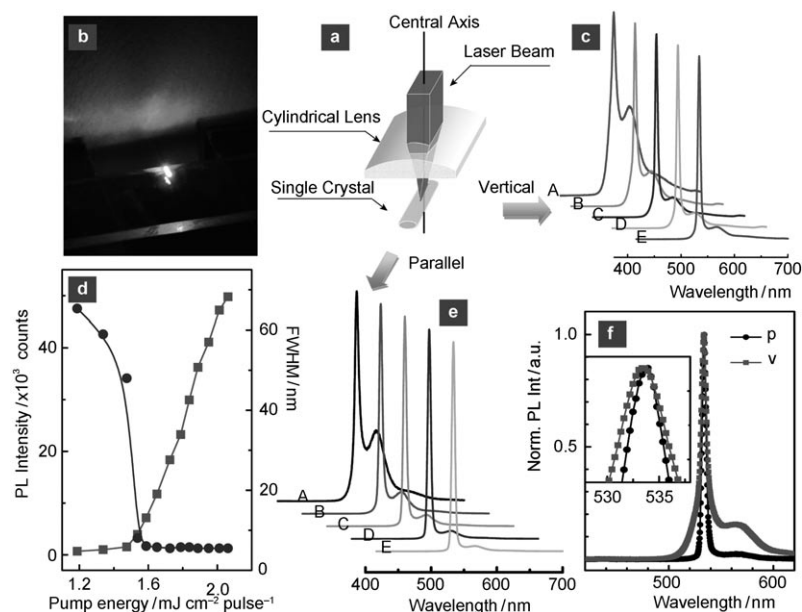

Figure 5. Two-photon pumping of the DBASDMB single crystal under 800 nm wavelength femtosecond laser. a) The pumping system setup. b) The image of the laser spot. c) The photoluminescence spectra measured in the vertical polarization, and in the parallel direction (e), as well as their magnification (f). d) The photoluminescence intensity and FWHM versus pumping intensity. Letters denote pumping energy density of (A) 0.88, (B) 1.48, (C) 2.26, (D) 2.82 and (E) 3.26 mJ cm^{-2} pulse^{-1}.

The parameter β can be further expressed as Equation (3):

$$\beta = \frac{\delta N_A d_0 10^{-3}}{h\nu} \qquad (3)$$

where δ is the molecular TPA cross section in units of cm^4 s photon^{-1}, N_A is Avogadro's number, and d_0 is the molar concentration of the absorbing molecules in units of M, $h\nu$ is the photon energy of the input light beam. For a 100 fs pulse at 1 kHz repetition rate, the threshold 1.68 mJ cm^{-2} pulse^{-1} corresponds to a pulse intensity of 16.8 GW cm^{-2}. Comparing the one photon absorption coefficients α with βI, one can easily deduce that the TPP lasing threshold is 2 orders larger, which is higher than results of the experiment. However, the two photon absorption allows the pump light deep into the inside of the sample, while the light penetration depth is very short for single photon excitation. It is envisaged that, there are more molecules inside of the crystals are excited, while only the molecules near the surface of the crystals contributed to stimulated emission in single-photon condition. This explained why the experimental value is lower than the calculated.

The net gain, an important parameter, was measured with a variable stripe-length technique.[25] Positive value of g produces an exponential increase in output intensity. The exponential term indicates that small change in g would produce appreciable variation in the output. From the pump-length dependence of edge output intensity, the net gains at the peak wavelength of 532 nm are 37 cm^{-1} under 2.3 mJ cm^{-2} pulse^{-1} and 45 cm^{-1} at 4 mJ cm^{-2} pulse^{-1}. The result reveals that the current geometry and quality of the DBASDMB single crystal is very suitable for applications as solid-state lasers.

the quartz substrate and the excitation beam was perpendicular to the glass plane, directed onto the crystal with focusing. The near-Gaussian beam diameter of the pump laser was 5 mm and the excited area of the crystals was about 3 mm × 0.3 mm, adjusted by a slit. Emitted light was collected by the optical fiber and then dispersed by omni-λ300 monochromator/spectrograph spectrometer.

Acknowledgements

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