Polarization dependent two-photon properties in an organic crystal

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The dependence of the fluorescence on the excitation beam polarization under two-photon excitation was studied in a 1,4-bis(R-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene organic crystal. The crystal shows strong response to the polarization, especially when the pump intensity was increased. The polarization plays an important role on the threshold of amplified spontaneous emission (ASE) and the ΔG_{ASE} under two-photon excitation (TPE). Moreover, the polarization distribution between the TPE (800 nm) and one-photon excitation (400 nm) are very different. The former generates a $\cos^4 \theta$ distribution, while the later gives rise to $\cos^2 \theta$ distribution in different orientation. © *2010 American Institute of Physics*. [doi:10.1063/1.3486683]

There has been a great interest in the past years in organic two-photon materials for their applications in optoelectronics and photonics. Two-photon absorption (TPA) induced lasing is one of the currently active researches.[1–3] The release of phase-matching condition make them convenient to realize the upconverted lasing. It has been demonstrated in many systems, such as dyes solution,[4] spin-coated film,[5] and quantum dot doped waveguide.[3] Recently, organic crystals have attracted attentions for their high purity, good thermostability, large molecule density, and excellence in optical properties, such as low light propagation loss due to less light scattering.[6,7] In addition, the properties of the building molecules can be specially designed and tailored. Two-photon pumped fluorescence and amplified spontaneous emissions have been reported in the past in the organic crystals, such as oligothiophenes,[8] Troger's base,[9] and oligo(PhenyleneVinylene).[10–13]

Single crystals inherently possess long-range structural ordering and may exhibit a remarkable optical anisotropy.[14] It has been experimentally and theoretically shown that linear optical phenomena (absorption, emission, etc.) in organic crystals demonstrate a strong dependence of optical characteristics on the polarization of exciting light.[15,16] This is caused by the anisotropic packing of the molecules in organic single crystals, resulting in an orientation-dependent optical absorption or emission in the materials. Thus, the probability of optical transitions strongly depends on the crystal orientation with respect to polarization of the excitation light. Also, it is natural to expect such polarization dependence for two-photon properties in crystals. Moreover, the degree of anisotropy in this case may be higher than that for linear effects because the TPA is square dependent on the power of the optical electric field. Since the TPA excitation is essential to such applications as up-conversion lasers, the polarization dependence must be more thoroughly understood and taken into account. The present paper is devoted to

the relationship between the anisotropic macroscopic two-photon properties and molecule packing structure in the organic crystals. For this purpose, we performed experimental investigations of the two-photon properties in an organic crystal for different angles between the polarization vector of exciting light and the crystal axis.

The organic crystal used here is 1,4-bis(R-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (CNDPASDB),[6] whose molecular geometry in the crystals is shown in Fig. 1(a). It is nonplanar and has the trans conformation with the point group of C_{2h}. For the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital
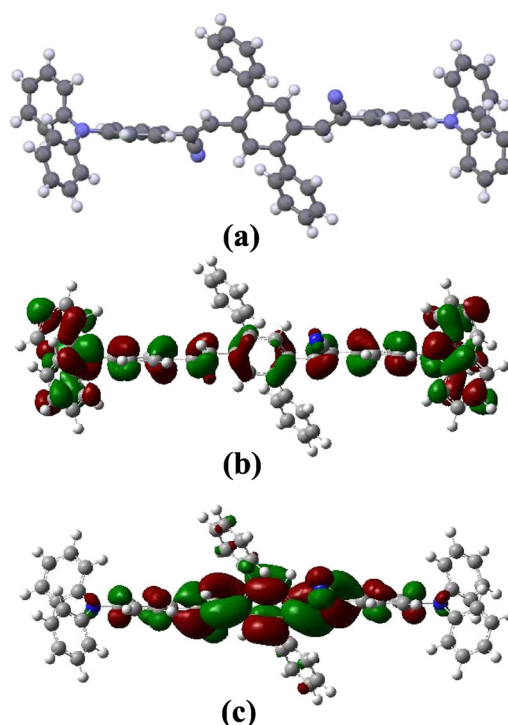

FIG. 1. (Color online) (a) Molecular geometry of CNDPASDB in the crystals. The calculated HOMO (b) and LUMO (c).

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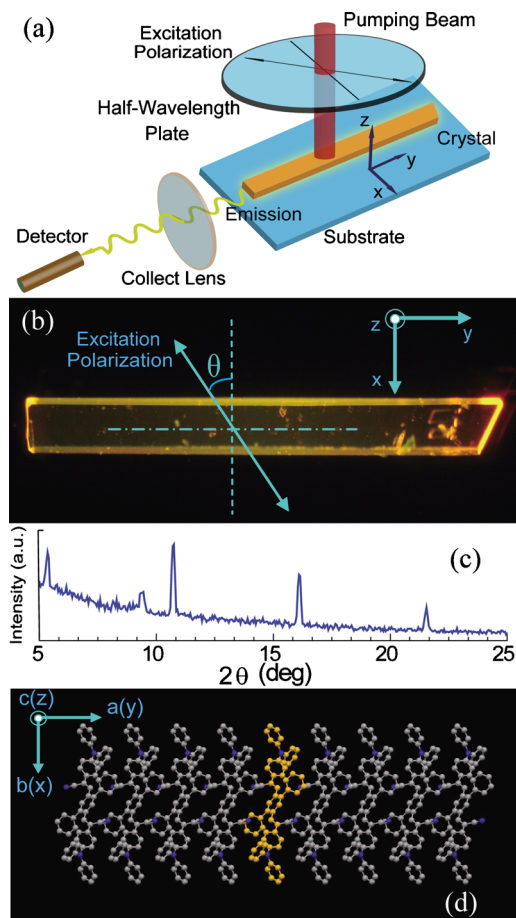
FIG. 2. (Color online) (a) The representation of the experimental setup. (b) The schematic diagram of the measurement geometry for one crystal. (c) X-ray diffraction patterns of the crystal of CNDPASDB. (d) The molecular arrangement view down reciprocal cell axis c*.
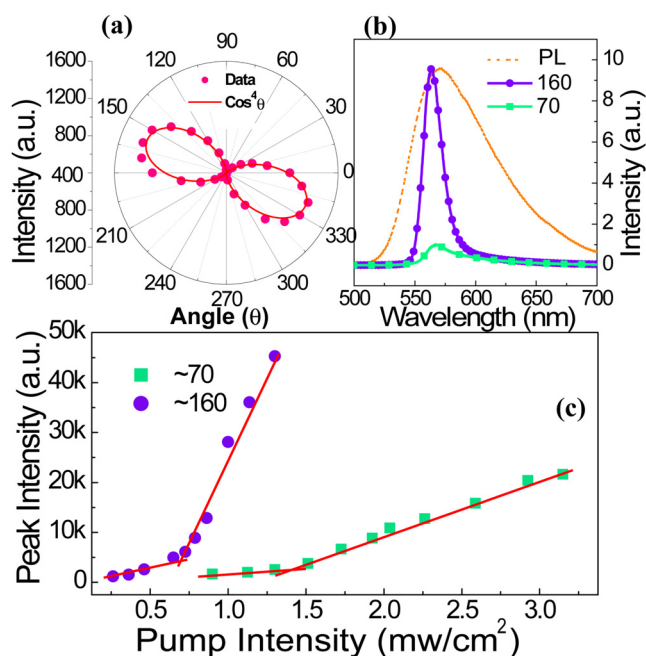

FIG. 3. (Color online) (a) The photoluminescence intensity of the crystal with respect to the polarization of the pump laser at excitation wavelength of $\lambda_{ex}=800$ nm (pump intensity is 0.2 mw/cm^2). (b) The fluorescence spectrum excited at two different polarizations, $\theta=160°$ and $\theta=70°$ (pump intensity is 1.3 mw/cm^2), and the linear fluorescence spectrum of the crystal. (c) The emission intensity vs pump intensity at two $\theta=160°$ and $\theta=70°$ (pump intensity is 1.3 mw/cm^2).

(LUMO), density functional theory calculations were performed using RB3LYP/6-31G*. The calculated results are shown in Figs. 1(b) and 1(c), respectively. The orientation of the S_0-S_1 transition dipole moment of CNDPASDB against the molecular long axis is predicted to be ~13°. Electronic absorption corresponding to this HOMO–LUMO transition occurs in the ultraviolet (UV) region and the fluorescence from the singlet excited state exhibits a yellow light emission band.

For the two-photon excitation (TPE), a beam from the chirped-pulse Ti:sapphire regenerative amplifier (Spitfire Pro) (with pulse ~120 fs, 800 nm, and 1 KHz) was employed. With a half-wave plate, the polarization vector of exciting light was subsequently rotated and the pump intensity per pulse can be varied from 0 to 1 mw with neutral density filters. The fluorescence emitted from the crystal was collected along the direction parallel to the long crystal axis, and then dispersed to the spectrometer equipped with charge coupled device (CCD). The schematic diagram of the measurement geometry for one crystal is shown in Figs. 2(a) and 2(b). We stepwise rotated the half-wave plate and measured the emission from the end of the crystal, while the pump intensity was kept constant.

Figure 3(a) shows the photoluminescence (PL) intensity of the crystal with respect to the polarization of the impinging laser at excitation wavelength of $\lambda_{ex}=800$ nm (TPE) under the excitation intensity of 0.2 mw/cm^2. As expected, the

fluorescence intensity shows very strong dependence on the polarization of the incidence light. The ratio of emission intensities between the maximum and the minimum can reach to be 3.7. The distribution function for the linear polarization TPE in this crystal [Fig. 3(a)] can be well fitted by a cosine biquadratic function ($\cos^4 \theta$). The orientation with maximum intensity was obtained at $\theta \approx 160°$. This means that for 800 nm excitation, the CNDPASDB crystal is most efficiently coupled with the laser electrical field in this orientation.

The anisotropy is more evident when it was excited under relatively high intensity (1.3 mw/cm^2). The ratio of emission intensities between the maximum and the minimum can reach to be 15, as shown in Fig. 3(b). Besides the peak intensity, the full width at half maximum (FWHM) also varied at high pump intensity. The FWHM for the high one is 18 nm and apparent narrower than that of the low one (52 nm). This narrowed spectral emission strongly suggested stimulated emission occurs. We measured the pump power dependent PL spectrum at following two different excitation polarizations: one is at $\theta=160°$ and the other is at $\theta=70°$. Figure 3(c) shows the PL intensity versus excitation intensity, where the nonlinear increase in PL intensity indeed implies the amplified spontaneous emission (ASE) occurs. Obviously, the threshold for the nearly parallel polarization excitation ($\theta=160°$) is 2 times lower than the other one. Moreover, the ASE gain, defined as the slope of the curve obtained by plotting the emission intensity versus the pump power; ΔG_{ASE}, in the former direction is 5.7 times higher than the later one. Therefore, for the optimization of the optically pumped up-conversion laser, one needs to determine the most efficient pump polarization.

In a randomly oriented molecular system, such as in the solution, the two-photon absorptivity is orientation-averaged.
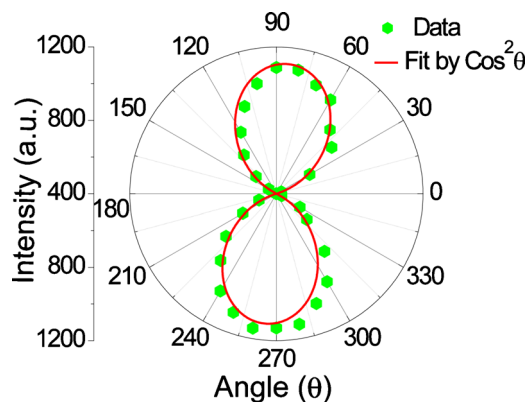
FIG. 4. (Color online) The photoluminescence intensity of the crystal with respect to the polarization of the pump laser at excitation wavelength of $\lambda_{ex}=400$ nm.

Different with these homogeneous systems, in the organic crystals, the molecules are "frozen" with definite orientations and high orderly packed. These may underline the intrinsic anisotropic optical properties in the crystals. So it is important to connect polarization with the molecule orientation. The XRD measurements [Fig. 2(c)] of the crystal indicate that the xy-plane has (001) refractions and the ab-plane is parallel to the xy-plane. Figure 2(d) shows the molecule arrangement view down reciprocal cell axis c*, i.e., perpendicular to the ab-plane. Combined this with the polarization-dependent measurement of two-photon excited emission, we can conclude that it is much easier for excitation when the polarization of the 800 nm pump light is nearly parallel to the molecular long axis.

Furthermore, we employed the 400 nm (one-photon excitation, from the second harmonic generation of the 800 nm, frequency doubled by a nonlinear optical crystal of β-barium borate) femtosecond laser to excite the crystal. As well as in the 800 nm (two-photon) excitation case, the emission shows distinctive polarization-dependent [Fig. 4]. However, the story is very different for the one-photon case. The most efficient polarization for 400 nm is nearly perpendicular to molecular long axis, while it is almost parallel in 800 nm condition. This indicates that this transition is not caused by the π-π^* absorption in CNDPASDB molecules. Moreover, the distribution is also very different in shape. One-photon (400 nm) here looks fatter and generates a $\cos^2\theta$ distribution, while TPE gives rise to sharper distribution and can be fitted $\cos^4\theta$ very well.

The unit cell for the crystal is triclinic, space group $P\bar{1}$, containing one discrete molecule.[6] The molecule preserve transconformation in the crystal and has a crystallographically imposed center of inversion, and the asymmetric unit contains one-half molecule. All of the CNDPASDB molecules array parallel with the identical conformation and orientation in the crystal and exhibit very regular uniaxially oriented packing. This is a system with centrosymmetric, for which the selection rules for one-photon and two-photon ab-

sorption is very different, and the symmetry of their initial and final singlet states for the two conditions may be inversely. This would make the TPA properties show a very different polarization with that under one-photon case. The distinctive results of the PL spectra and the polarization features reveal that the mixed electronic energy states of the CNDPASDB are involved under 400 nm (one-photon) and 800 nm (two-photon) excitations and the TPE reach the one-photon forbidden states.

In conclusion, we have experimentally investigated the polarization dependent emission excited by two-photon absorption from an organic crystal. The crystal shows very strong anisotropic effect in TPE and one-photon absorption, which is associated with the alignment of the high orderly CNDPASDB molecules in the crystal and the coupling efficiency with the electric field of the polarized excitation source. Meanwhile, the TPE can reach the one-photon forbidden states and to determine the symmetries of excited states. This may help us for better understanding the intrinsic optical properties of molecules and optimization of the two-photon induced up-conversion laser.

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