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Supramolecular interaction-induced self-assembly of organic molecules into ultra-long tubular crystals with wave guiding and amplified spontaneous emission[†]

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Ultra-long tubular crystals (length up to 10 mm and diameter of 70 μ m) of a small organic functional molecule, 1,4-bis(2-cyano-2-phenylethenyl)benzene (BCPEB), are successfully prepared through a physical vapor transport (PVT) method. On the basis of crystal structural analysis and density functional theory calculations, we show that the formation of such tubular crystals is drawn by the branched hydrogen bonds between the BCPEB molecules. High crystalline quality, highly ordered molecular orientation, and hollow-like topological structure enable the crystal to exhibit optical wave guided emission behaviors with low optical loss (3 dB mm⁻¹) and highly polarized emission (the polarized ratio is about 20). Amplified spontaneous emission (ASE) characteristics of the tubular crystals were also studied; the net gain coefficients at the peak wavelength and the threshold are 91.7 cm⁻¹ and 36 kW cm⁻², respectively.

Introduction

Organic crystals constructed of π -conjugated molecules have attracted great attention in the field of organic optoelectronic materials.1 The advantages of organic crystal materials lie in their definite structures, which provide a model for the deep understanding of basic interactions between the molecules (supramolecular interactions), and structure-property relationships between the molecular packing arrangement and optoelectronic properties (luminescence and carrier mobility).² The academic motivation in hunting for organic crystals with desired high thermal stability, highly ordered structures and high carrier mobility is due to their potential application in optoelectronic devices such as optically pumped lasers,3 field-effect transistors,4 electroluminescence,5 and photovoltaic cells.6 Different from crystalline inorganic semiconductors, which are constructed of atoms joined by strong chemical bonds (bond energy 100-400 kJ mol⁻¹), organic crystals are built from molecules connected by weak intermolecular interactions, such as van der Waals interactions, $\pi - \pi$ stacking interactions, and hydrogen bonding (interaction energy 10-65 kJ mol⁻¹).7 This gives rise to the diversities of organic crystal structures (polymorphs and topologies) and complexities for the controlled growth of organic crystals.⁸ Recently organic crystals with topological structures, in the shape of *e.g.* hollow tubes, have attracted much attention due to potential applications in fields such as optics and electronics.⁹ Artificial preparation of high quality, long range order and regular shaped crystal tubes according to the requirements of function and device is of great importance. This, however, remains a challenge because of the difficulty in controlling the growth and directionality of organic molecules on a large scale under the driving forces of weak intermolecular interactions. On the basis of investigation of crystal growth, characterization of crystal structure and optical property measurements, we describe here a example of ultra-long organic crystal tubules from the π -conjugated molecule 1,4-bis(2-cyano-2-phenylethenyl)benzene



Fig. 1 (a) The chemical structure of a single BCPEB molecule. (b) Image of a single tube under UV light (365 nm). (c) SEM image of the BCPEB tube. (d) Confocal fluorescence microscopy image of the BCPEB tube's cross-section.

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(BCPEB, see Fig. 1a) through the physical vapor transport (PVT) method (see Fig. S1, ESI[†]).¹⁰ In the PVT environment, high energy BCPEB molecules in vapor are cooled to a relatively low temperature, thus they aggregate slowly through the self-assembly process driven by supramolecular interactions. In principle, the growth of a one dimensional (1D) structure requires a directional interaction, which has dominance in interaction energy over other intermolecular interactions. In BCPEB molecules, the directional interaction is branched hydrogen bonds between N (from the cyano-segment) and two H atoms (from the aromatic segment and double bond).

Experimental section

Materials and synthesis

All chemicals were purchased commercially, and used without further purification. The synthetic procedures and characterization data are described in the ESI.[†]

Measurements

NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with chloroform-d as solvent and tetramethylsilane (TMS) as internal standard. The morphology and size of the samples were measured by field emission scanning electron microscopy (SEM) on a JSM-6700F electron microscope (JEOL, Japan). Ultraviolet-visible absorption and fluorescence spectra were recorded on UV-3100 and RF-5301 PC spectrophotometers, respectively. The X-ray diffraction experiment was performed on a Bruker D8 with GADDS X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) at 40 KV and 20 mA. The diffractometer is equipped with a graphite monochromator. The wall of the tubular BCPEB crystal was selected randomly as a sample for X-ray crystallography test and crystallographic data were collected at a temperature of 20 ± 2 °C on a Bruker ApexII CCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ A). Data processing was accomplished with the SAINT processing program.11 The structure was solved by direct refinement with a full-matrix least-squares technique using the SHELXTL-97.12 Experimental details for the structural determination are described in Table S2, ESI.† The confocal fluorescence microscopy images were taken on an OLYMPUS FLUOVIEW FV1000. For details of amplified spontaneous emission (ASE), optical waveguide and polarization tests see the ESI.†

Results and discussion

Fabrication and structural characterization of tubular BCPEB crystals

The PVT growth of BCPEB crystals was carried out in a temperature-controlled quartz tube. The BCPEB powder (about 10 mg) was placed into the source zone at a predetermined temperature. Ultrapure argon was used as carrier gas and protection gas to prevent the BCPEB from being oxidized at high temperature during the PVT process.^{10,13} The crystal grows in a growth zone at relatively low temperature. After several hours, club-shaped crystals as well as slice-like crystals were found hanging inside the wall of the growth tube (see Fig. S2, ESI[†]). Fig. 1b shows the photograph of the club-shaped crystals under ultraviolet (UV) light (365 nm), which depicts a single club of uniform size. The clubs have a length of up to 10 mm and diameter of 70 μ m. Very strong blue fluorescence is emitted from the ends of the club. The scanning electron microscopy (SEM) and confocal fluorescence microscopy images (Fig. 1c and Fig. 1d) demonstrate that the club-shaped crystals have a hollow pentagonal cross section (see Fig. S3, ESI[†]).

X-ray crystallography indicates the ultra-long tube is a high quality crystal.[‡] The crystal structure is triclinic with space group $P\bar{1}$, the molecule is on the center of symmetry (inversion center) and half of the molecule is crystallographically independent. The ORTEP drawing of BCPEB is shown in the ESI.[†] The perspective view of molecular alignment in the BCPEB crystal from the top of the *bc* plane (along the *a* axis) is shown in Fig. 2a. It indicates that all BCPEB molecules are in a parallel alignment with identical conformation in the crystalline tube and exhibit very regular uniaxially oriented packing. As shown in Fig. 2b, along the *a* axis in the crystal molecules are bound by two types of N…H–C hydrogen bond, I and II (the distance of H to N and angle of the hydrogen bonds are summarized in Table 1). Driven



Fig. 2 (a) Uniaxially oriented alignment of BCPEB molecules in the crystal. (b) C–H···N hydrogen bonds I and II viewed along the *a* axis. (c) CH/ π interactions III and IV between adjacent molecules.

Table 1 Hydrogen bonds in the BCPEB crystal

Hydrogen bond	I: C(8)–H(8)····N(1) ^{<i>a</i>}	II: C(10)–H(10)····N(1) ^a
D…A distances (Å)	3.42(3)	3.59(7)
H…A distances (Å)	2.49(7)	2.73(3)
D–H…A angle (°)	155(4)	147(1)

^{*a*} Symmetry transformations used to generate equivalent atoms: -1+x, y, z.

‡ Crystal data for BCPEB: C₂₄H₁₆N₂, M = 332.39, triclinic, a = 6.737(2)Å, b = 8.541(3) Å, c = 8.965(3) Å, $\alpha = 79.742(7)^{\circ}$, $\beta = 68.025(7)^{\circ}$, $\gamma = 67.714(7)^{\circ}$, V = 442.2(3) Å ³, T = 293(2)K, space group $P\bar{1}$, Z = 1, 2845 reflections measured, 1824 independent reflections ($R_{int} = 0.0394$). The final R_1 values were 0.0563 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1176 ($I > 2\sigma(I)$). The final R_1 values were 0.1574 (all data). The goodness of fit on F^2 was 0.946.

Table 2 Aromatic CH/ π interactions in the	BCPEB crystal
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Hydrogen bond	III: C11–H(11)…ring1[C1/C6]	IV: C4–H(4)…ring2[C9/C11a]
H…ring distances (Å)	3.02(1)	2.94(3)
C…ring distances (Å)	3.72(2)	3.75(2)
C–H…ring angle (°)	129(5)	136(2)

by these branched hydrogen bonds, as described above, a molecular layer formed. In the *bc* plane, molecules are stacked in a parallel displaced manner along the *c* axis in length of a phenylene vinylene moiety. The interconnections between two stacked molecules are aromatic CH/π interactions III and IV (the distance from H to the central point of the phenyl ring and angle of the CH/π ring are summarized in Table 2), as shown in Fig. 2c.

The detailed formation of tubular crystals with pentagonal topological structure is so far not very clear. In principle, the tubular crystal growth is related to the intermolecular interactions and the growth conditions.14 As described above, the BCPEB molecules were mainly affected by N…H-C hydrogen bonds and CH/ π interactions in the tubular crystal. To determine the dominant direction of crystal growth with the larger energy among these intermolecular interactions, a computational study of the interaction energy has been carried out by density functional theory. By a supermolecular approach, the calculated interaction energy is 27.7 kJ mol⁻¹ for a hydrogen bonded dimer along the *a* axis, while the interaction energies are 18.5 kJ mol⁻¹ and 9.5 kJ mol⁻¹ for CH/ π interactions in the two configurations, respectively (see ESI[†]). This indicates that the branched hydrogen bonds are the directional driving forces, which make the BCPEB molecules arrange along the same direction leading to the formation of 1D straight crystals.

Numerous fabrication experiments indicated the formation of tubular crystals is controllable and repeatable. The length and diameter of the BCPEB tubes can be readily controlled by adjusting the experimental conditions, such as growth time and temperature of the growth zone. Longer tubes can be obtained by prolonging the growth period. For example, at a fixed growth temperature of 248 °C, the final lengths of the tubes were 3 mm, 5 mm, and 10 mm at growth periods of 8, 16 and 24 h, respectively. Tubes of different average thickness have also been obtained at various temperatures. For example, when 238, 243 and 248 °C were adopted at a fixed growth time of 16 h, we obtained tubular walls with an average thickness of 8.1, 15.8 and 17.4 μ m respectively (see Fig. S6, ESI†). When the temperature of the growth zone was below 238 or above 248 °C, the tubular crystals were not obtained.

Optical waveguide and polarized emission properties

Under UV light, the tubes exhibit blue emission with very bright luminescence spots observed from the ends of each tube and a weaker emission observed from the bulk surface of tube, as shown in Fig. 1b. If excited with a focused laser ($\lambda = 355$ nm) at different positions along the tube, stronger emission from both tips than from the body was also found (see Fig. S7, ESI†). It indicates that the light emitted at the excited region was confined inside the crystal and propagated along the tube axis, then radiated from the tips.^{3,15,16} In order to elucidate this self-waveguided mode of light emission in the tubular crystals, the orientation of the BCPEB molecules in the crystal was determined. We have tested five faces of each tubular crystal and found them to have the same XRD pattern. Fig. 3a is an X-ray diffraction pattern of the crystal tube (bottom) and X-ray diffraction pattern predicted for BCPEB based on single crystal data (top). By comparing the two curves, the diffraction spacing is determined and it is assigned to the $(0\ 2\ -1)$ plane of the BCPEB crystal. In the $(0\ 2\ -1)$ plane, the



Fig. 3 (a) X-ray diffraction pattern of BCPEB tubular crystals obtained by prediction based on single crystal data (top) and experimental test (bottom). Inset: BCPEB molecules lay in the (0 2 -1) plane. (b) Fluorescence spectra taken with polarizations of E_{\parallel} and E_{\perp} . Inset: dependence of the output intensity at $\lambda = 482$ nm on polarization of angle, where θ denote the angles of the polarization plane of the emitted light with respect to the excited surface.

BCPEB molecules interact with each other through the branched hydrogen bonds in a uniaxial orientation (see the inset in Fig. 3a). This means that the transition dipoles of BCPEB molecules in the crystal are uniaxially aligned (the calculation results show that the orientation of the S0–S1 transition dipole moment of BCPEB



Fig. 4 Schematic representation of molecular arrangement in the tubular BCPEB crystal and configuration of the polarized emission from the crystal.



Fig. 5 (a) PL spectra of BCPEB crystal tube as a function of the pump laser energy. (b) Dependence of the peak intensity and FWHM of emission spectra on the pump laser energy.

is along the molecular long axis, see Fig. S10, ESI[†]), so the emission light from the tips may be polarized,^{3,17} which can be proved by polarization experiments. Polarization-dependent fluorescence spectra are shown in Fig. 3b, and a schematic illustration of spectra obtained parallel (E_{\parallel}) and perpendicular (E_{\perp}) to the excited surface of the tube is shown in Fig. 4. The maximum and minimum intensity of spectra correspond to the E_{\parallel} and E_{\perp} , respectively, with a ratio of about 20. This result indicates that the self-waveguided emitted light is polarized parallel to the excited surface of the tube.^{3,17,18} Thus the self-waveguided mode of light emission in the tubular crystals is clear, schematically shown in Fig. 4.

Further, we measured the value of its optical loss as 3 dB mm⁻¹ at 482 nm (for a detailed description of the optical waveguide and optical loss test see the ESI[†]). Compared with the many organic nanowires/nanofibes and films that have been reported (>100 dB mm⁻¹),¹⁹ the propagation loss of the BCPEB tube is much lower; approximately that of subwavelength-diameter silica wires (about 1.7 dB mm⁻¹).²⁰ This can be attributed to the following reasons. Firstly, its low self-absorption due to well separated absorption and emission bands of the BCPEB tube^{19,21} (the absorption and emission spectra of BCPEB are in Fig. S9, ESI[†]). Secondly, the smooth surface and uniform diameter (as shown in Fig. 1b) are beneficial for decreasing the optical loss due to the reduction of light scattering.^{15a,18} Thirdly, photons are spatially confined in two dimensions in the thin tubular wall due to the air medium inside the tubes. Such confinement of the light decreases the interaction of the light reflected from the internal waveguiding surface with the substrate, which gives rise to lower propagation losses.16,19

Amplified spontaneous emission (ASE) properties

Generally, waveguided propagation of emission is thought to be one prerequisite for lasing or amplified spontaneous emission (ASE),²² and the uniaxially oriented molecules should be a suitable configuration to amplify emitted light and achieve the



Fig. 6 Peak intensity of PL spectra as a function of the pump stripe length.

Table 3 Comparison of the ASE performance of different organic crystals

Crystal	Threshold value ^{<i>a</i>}			
	$(\mu J \text{ cm}^{-2})$	$(kW \text{ cm}^{-2})$	Net gain coefficient ^{D} (cm ^{-1})	Reference
BCPEB	360 (10 ns)	36	91.7 (180 kW cm ⁻²)	This work
DPDSB	7000 (10 ns)	700		27
CNDPASDB	305 (10 ns)	30.5	55 (1900 kW cm ⁻²)	18
CNDPDSB	395 (10 ns)	39.5	$33(375 \text{ kW cm}^{-2})$	24
BP1T	400 (30 ns)	13.3	57.1 (620 kW cm ⁻²)	28
BP2T	355 (500 ps)	710		23
BC4	50 (500 ps)	100	_	23
AC5	560 (16 ns)	35	75 (61.3 kW cm ⁻²)	29

^{*a*} For changing μ J cm⁻² into kW cm⁻², the pulse durations were given in brackets. ^{*b*} Net gain coefficient: these parameters were obtained at the corresponding excitation energies in the brackets.

organic crystal laser with low energy threshold. This is because the light emission of organic materials is from excitons localized on a single molecule, and dipole moments with the same configuration can easily interact into a certain phase with respect to the optical field, which should induce the coherent emission and the light amplification.¹⁸ To study the ASE property, an isolated single BCPEB tube was excited with a pulsed laser ($\lambda =$ 355 nm) and PL emissions were subsequently collected from the tip area.^{23,24} As the pump energy increased, a gain-narrowed peak rises out of the broad emission spectrum (Fig. 5a). Fig. 5b represents dependence of the peak intensity and full widths at half-maximum (FWHM) of emission spectra on the pump laser energy. The relationship between the peak intensity and the pump energy is nonlinear. This is characterized as the ASE caused by stimulated emission.²⁵ The slope of the peak intensity versus pump energy curve changes at 36 kW cm⁻², which should be the threshold value of ASE. Fig. 6 shows the peak intensity (482 nm) of PL spectra as a function of pump stripe length at pump energy of 150 kW cm⁻² (for the experimental process see the ESI[†]). The peak intensity increases exponentially with increasing pump stripe length. The solid curves are fits to the data using the following equation:

$$I(\lambda) = \frac{A(\lambda)P_0}{g(\lambda)} \left(e^{g(\lambda)l} - 1 \right) \tag{1}$$

where A is a parameter proportional to the PL quantum yield, P_0 is the pump intensity, g is the net gain coefficient (subtract loss from gain), and l is the length of the pump stripe.²⁶ The net gain coefficients at the peak can reach 91.7 cm⁻¹ under a pump energy of 150 kW cm⁻². We have also tested the threshold value and the net gain coefficients of the slice-like BCPEB crystal, which are 340 kW cm⁻² and 21.8 cm⁻¹ under a pump energy of 150 kW cm⁻², respectively. The ASE performance of the slice-like crystal is much worse than that of the tubular crystal. This result can be explained thus: the hollow structure confines the photons in the thin tubular wall and reduces the light scattering, which results in low optical loss.^{18,19}

In order to highlight the advantages and limitations of the tubular crystal studied here, its ASE performance was compared to that of various representative organic crystals studied in the literature (see Table 3). By comparing, it is clear that the threshold value for the tubular BCPEB crystal is among the lowest values, and the net gain coefficient is among the

highest values. The comparison indicates that the high quality tubular BCPEB crystal with regular uniaxially oriented molecules is suitable to amplify emitted light and achieve the laser with low threshold.

Conclusions

By means of supramolecular assembly in the gas phase, tubular crystals with a hollow pentagonal cross section were prepared *via* PVT. It is found that BCPEB molecules in the tubes are uniaxially orientated, which is verified by characterization of crystal structure by X-ray diffraction, and polarized emission measurements. The unique morphology and molecular arrangement give tubular BCPEB crystals possible applications as optical waveguides with low optical loss and organic lasers with low threshold. Directional non-covalent interactions such as π - π interactions and hydrogen bonds could be utilized to build well controlled structures.

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