

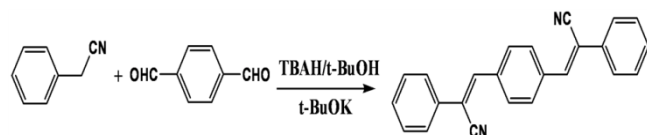
Supplementary Information:

Supramolecular Interaction-induced Self-assembly of Organic Molecules into Ultra-long Tubular Crystal with Wave Guiding and Amplified Spontaneous Emission

Yuanxiang Xu, Houyu Zhang, Feng Li, Fangzhong Shen, Huan Wang, Xianjie Li, Yang Yu and Yuguang Ma*

* State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun, 130012, P. R. China. Fax: (+86) 431-85168480; Tel: +86 431-85168480; E-mail: ygma@jlu.edu.cn

Synthesis of BCPEB



Scheme S1. The synthetic scheme

BCPEB was synthesized according to the procedure shown in Scheme S1.^[1] All chemicals were purchased commercially, and used without further purification. The mixture of Benzylcyanide (201 mg, 1.5 mmol) and Terephthalaldehyde (0.345 mL, 3 mmol) in tert-butyl alcohol (10 mL) was stirred at 46 °C for 30 min. Then, potassium tert-butoxide (1 M solution in tetrahydrofuran, 0.25 mL) and Tetrabutylammonium hydroxide (TBAH, 1 M solution in methanol, 0.25 mL) were added, and stirred for 20 minutes. The resulting precipitate was filtered and purified by column chromatography using dichloromethane. BCPEB powder (348 mg) was obtained in yield of 70% by evaporated the solvent. ¹H NMR (CDCl₃) δ [ppm]: 8.01 (s, 4H, Ar-H), 7.72 – 7.71 (d, 4H, Ar-H), 7.56 (s, 2H, Vinyl-H), 7.49 – 7.46 (t, 4H, Ar-H), 7.44 – 7.43 (t, 2H, Ar-H).

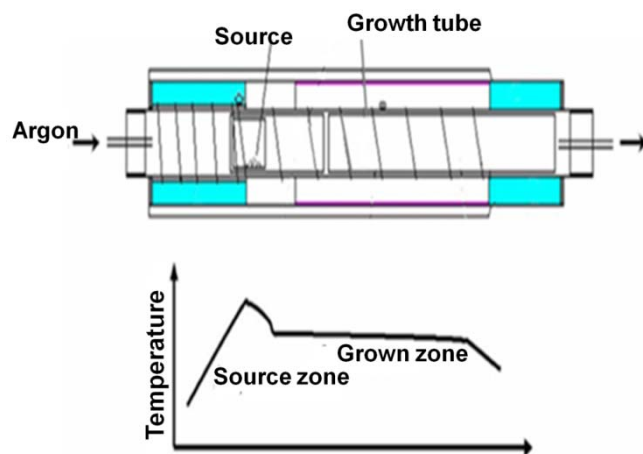


Figure S1. Schematics of the crystal growth apparatus for physical vapor transport method, and the temperature gradient in experiment.

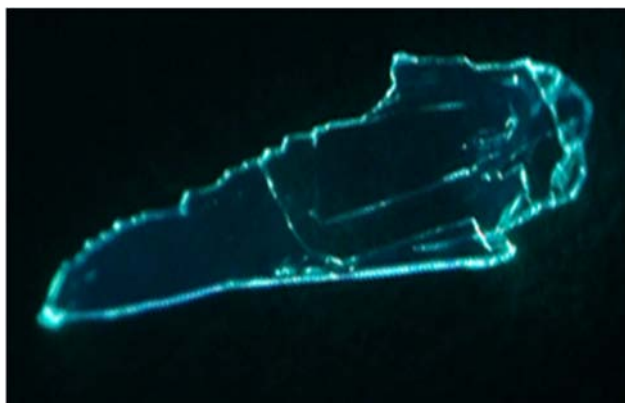


Figure S2. Image of a slice-like crystal under UV light (365 nm).

Calculations of dimer interaction energies

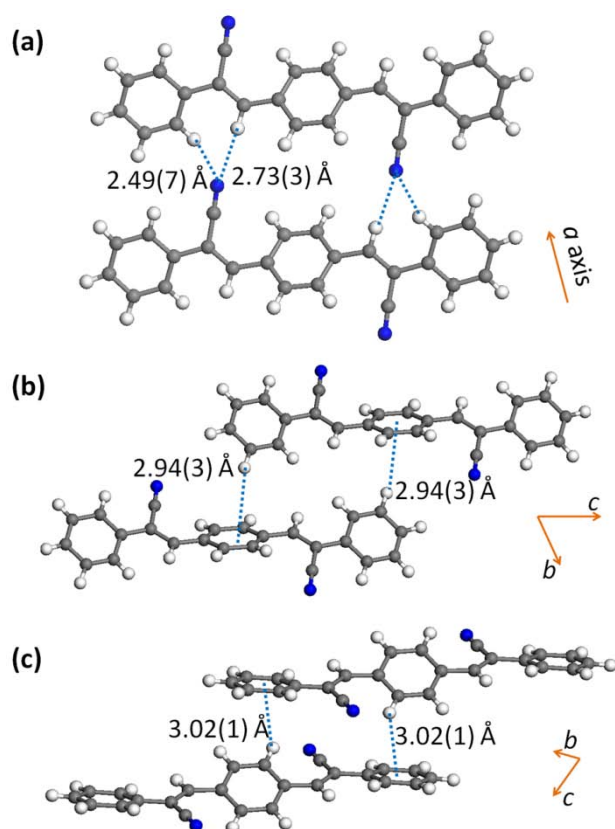


Figure S5. (a) dimer alone *a* axis; (b) and (c) two dimer configurations for CH/π interaction.

We employ the density functional theory method with MPWB1K functional to calculate the interaction energies of dimer along *a* axis (direction for hydrogen bonding interaction) and dimer for CH/π interactions. The exchange-correlation functional MPWB1K was tested for describing stacking and hydrogen bonding interactions in nucleic acid bases.² By supermolecular approach, the interaction energy can be calculated as follows: $E_{\text{interaction}}(A,B)=E(AB)-E(A)-E(B)$. At the MPWB1K/6-311++G** level, the calculated the interaction energy is 27.7 kJ mol⁻¹ for hydrogen bonding dimer along *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, seen in Figure S3. Hence by theoretical calculation, we know that *a* axis is the dominant crystal growth direction due to larger intermolecular interaction. All calculations are performed using Gaussian 09 package.

BCPEB crystals obtained in various growth conditions

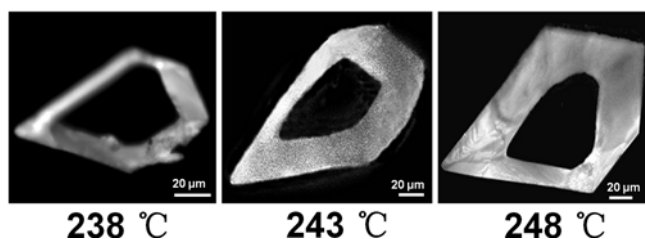


Figure S6. Confocal fluorescence microscopy images of the cross-section of the tubes fabricated at different temperature.

Table S1: The average thickness of the tube' wall obtained at different temperature.

Temperature (/°C)	Average thickness (/μm)	Average aperture (/μm)
238	8.1	40
243	15.8	35
248	17.4	33

Detailed description on the optical waveguide and optical loss test

In order to describe the waveguiding behavior of the tube in detail, the microarea photoluminescence (PL) microscopy images (as shown in Figure S7) were taken by confocal fluorescence microscopy and the distance dependent photoluminescence spectra showing propagation of light through single tubes were measured (with the setup as shown in Figure S11). Figure S8a shows the spatially resolved PL spectra of the excited position and out-couples light by excitation at a distance of 0~4 mm from the end tube. The dependence of the peak intensity (482 nm) of waveguided PL out-coupled at the tip of the tube on propagation length is shown in Figure S8b. The peak intensity of the spectra decreases almost exponentially following the increase of propagation length.

To evaluate the efficiency of the tube, the optical loss coefficient of guided light was obtained by the equation:

$$\alpha = -10 \times \log(I_{\text{tip}}/I_{\text{body}}) \times L^{-1} \quad (1)$$

where I_{tip} and I_{body} are the PL intensity measured at the tube tip and the excitation spot, respectively. Accordingly, the loss coefficient at 482nm is 3 dB mm^{-1} .

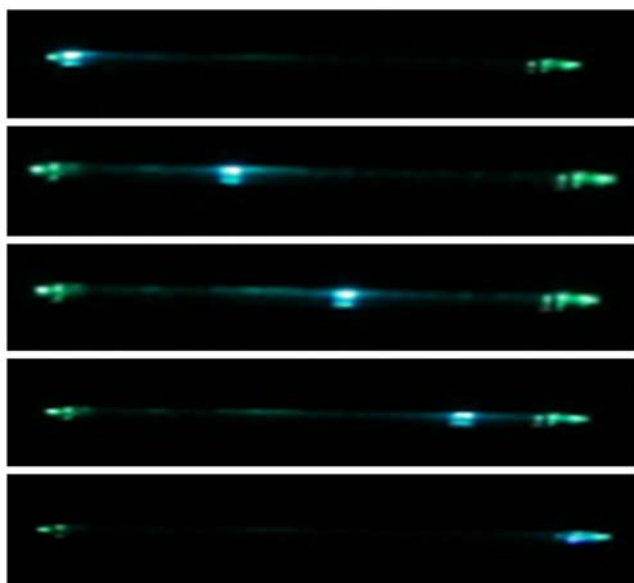


Figure S7. PL images obtained by exciting identical tubes at different positions.

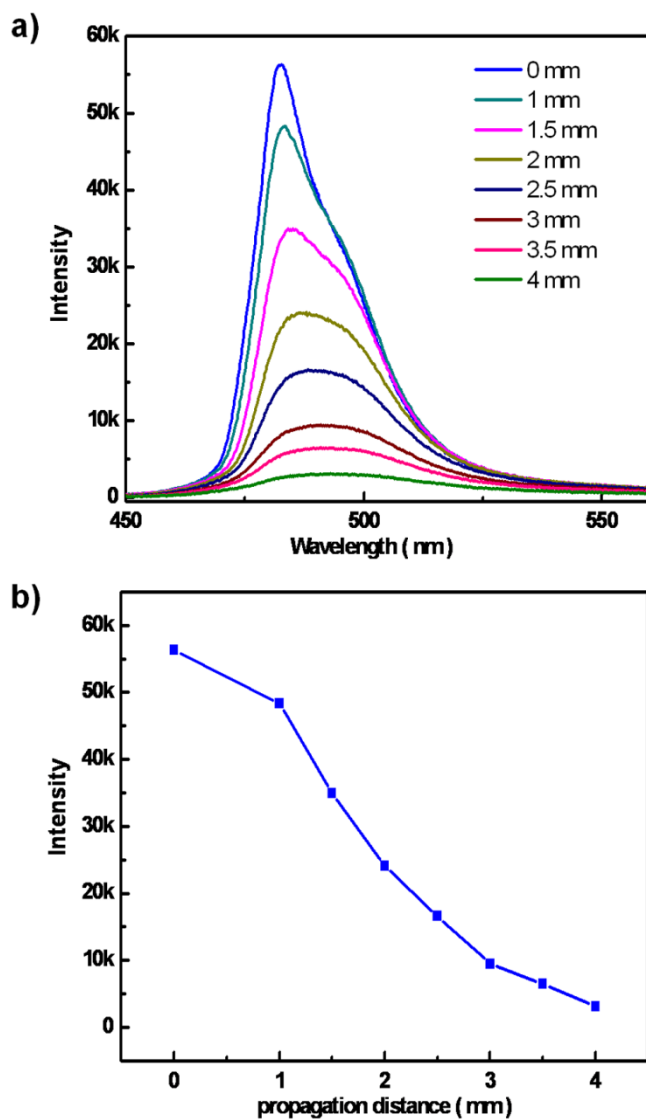


Figure S8. a) Spectra of the emission that is out-coupled at the tip of a single tube from a distance of 0 ~ 4 mm from the tip. b) Maximum intensity versus excitation position for the PL spectra.

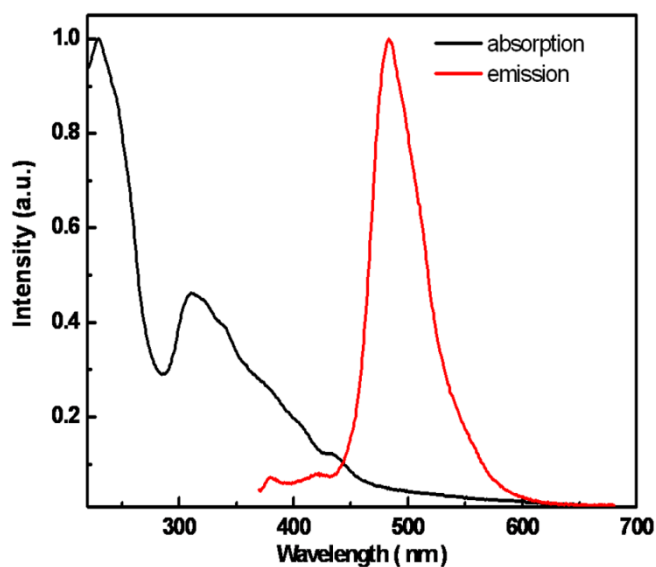


Figure S9. Absorption spectrum of BCPEB vacuum-deposited thin film with quartz substrate and emission spectrum of tubular BCPEB crystal.

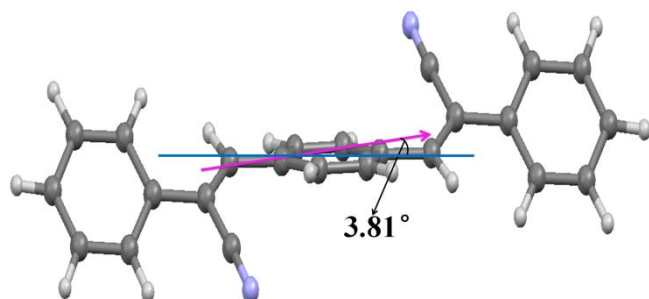


Figure S10. The orientation of the S₀-S₁ transition dipole moment of BCPEB (pink line with arrow). The transition dipole moment was calculated using Gaussian 09 package. The orientation of the S₀-S₁ transition dipole moment of BCPEB (pink line with arrow) against the molecular long axis (blue line) is predicted to be ~3.81°.

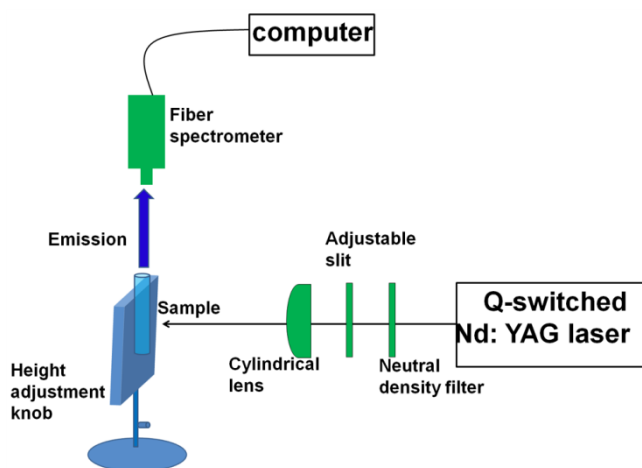


Figure S11. Schematic illustration of the transmittance optical path for the waveguide measurements.
(YAG: yttrium aluminum-garnet.)

Amplified Spontaneous Emission (ASE) Experiment.

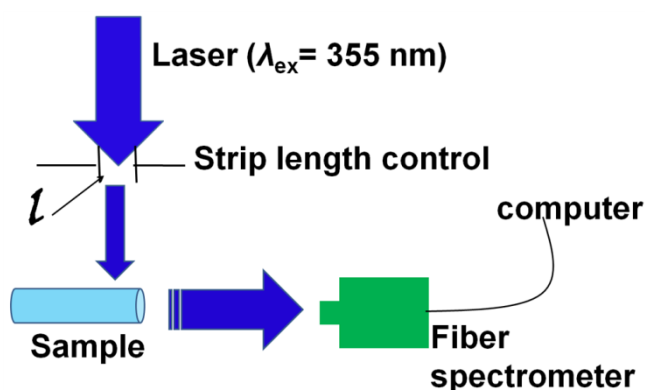


Figure S12. Schematic illustration of ASE experiment. The strip length can be adjusted by the strip length control.

The tube was optically pumped with Nd:YAG (yttrium aluminum-garnet) laser ($\lambda_{ex} = 355$ nm, pulse duration 10 ns, repetition rate 10 Hz). The energy of pumping laser was adjusted using calibrated neutral density filters. The beam was focused by using a cylindrical lens into a strip whose shape was 2.5×0.5 mm² and was perpendicular to the long axis of this crystal which was glued on the quartz substrate. The emission from the tip of crystal was detected using a fiber spectrometer (Maya2000-pro, Ocean Optics). The polarization of light emitted from the tip of BCPEB crystal was measured by rotating a polarizer in front of the optical fiber spectrometer.

References

- 1 F. J. Lange, M. Leuze, M. Hanack, *J. Phys. Org. Chem.* **2001**, *14*, 474.
- 2 A. Dkhissi, R. Blossey, *Chem. Phys. Lett.* **2007**, *439*, 35.