Supporting Information

Molecular engineering excited-state process for multicolor microcrystalline lasers

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Materials and experimental details

1. Materials:

Three compounds, including 4,4'-bis(2-thienylvinyl)biphenyl (BPVT), 4,4'-bis(2-bithienylvinyl)biphenyl (BBTVB), 4,4'-bis(2-terthienyl-vinyl)biphenyl (BTTVB), have been synthesized through the Horner-Wadsworth-Emmons reaction (detailed synthetic route in **Scheme S1**) and purified by sublimation. All reagents for organic systhsis were commercially available.



Scheme S1. The synthetic route of BPVT, BBTVB, and BTTVB. The molar ratio of reactants is about 1:2. The reaction is carried out in a N_2 atmosphere and stirred at room temperature for about 12 h. The reaction mixture was washed and recrystallized many times due to the limited solubility in most organic solvent. Then the compounds were obtained in 75% yield.

2. Preparation of the microstructures of three organic compounds

In a typical synthesis, three molecules were put into a quartz boat, which were then placed into a quartz tube inserted in a horizontal tube furnace, respectively. A stream of nitrogen gas flow was introduced into the system at a rate of 30 sccm to purge oxygen from the tube and carry the vapor to the low-temperature zone. The ITO substrates were placed at the downstream side of the flowing N_2 to collect the products. Set different temperature and holding time in high temperature zone and low temperature zone, after the furnace was naturally cooled to the room temperature, the raw materials were physically deposited onto the substrates to form the microsheets or bulk crystals. The detailed deposition condition of BPVT, BBTVB, and BTTVB microcrystals were shown in **Table S1**.

Bulk crystals were also cultivated from the method of PVD by increasing time and raw materials as well as different substrates in order to obtain single crystal data.

3. Structural and morphological characterization

The compound was confirmed by High resolution mass spectroscopy (MAIDI-MS) and ¹³C-NMR (600MHz, 295K). Due to the limitation of the material solubility, the CHS element analysis were recorded by Thermo Flash Smart aimed to prove purity. Thermal gravimetric analysis (TGA) was performed on a STA 409 PC thermogravimeter in air at a heating rate of 10 °C min⁻¹. The crystals samples were characterized by transmission electron microscopy (TEM, JEM-1011, JEOL) were obtained by transferring two samples on a carbon-coated copper grid. TEM measurement was performed at room temperature at an accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54050$ Å) operated in the 2 θ range from 5 to 40°, by using the samples on a cleaned quartz substrates. Samples examined by field emission scanning electron microscopy (SEM, S-4800, Hitachi) were obtained by dropping on a silicon wafer. The height of microcrystals was measured by atomic force microscopy (AFM, Bruker MultiMode 8-HR). Crystallographic data (excluding structure factors) for the structure of BPVT, BBTVB and BTTVB reported in this paper were deposited in the Cambridge Crystallographic Data Centre (CCDC: 796660, 2052458 and 2052459).

4. Optical measurements

The fluorescence and absorption spectra were obtained by a fluorescence spectrometer (Hitachi F-4600) and an ultraviolet-visible spectrophotometer (Hitachi U-3900H) respectively; The absolute fluorescence quantum yields were measured by using the Edinburgh FLS1000 with an integrating sphere; The fluorescence lifetimes were measured based on universal streak

camera C10910; Bright-field optical images and fluorescence microscopy images were taken by a home-made optical microscopy equipped with a 50×0.9 NA excitation objective and a charge couple device (CCD, Olympus DP-73, Tokyo, Japan) at room temperature in air, the excitation source is a Xenon lamp equipped with a band-pass filter ($330 \sim 380$ nm for UV-light) and the samples were deposited onto a quartz slide. The second harmonic (400 nm, 150 fs, 1 kHz) of a regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) was used to pump the crystals.

fsTA Spectroscopy. A Ti: sapphire femtosecond laser system provided laser pulses for the femtosecond transient absorption measurements. A regenerative amplifier (Spectra Physics, Spitfire) seeded with a mode-locked Ti: sapphire laser (Spectra Physics, Tsunami) delivered laser pulses at 800 nm (120 fs, 1 kHz), which were then divided into two components by using a 9:1 beam splitter. The major component was sent to an optical parametric amplifier (Spectra Physics, OPA-800CF) to generate the pump pulses (480 & 650 nm, 130 fs, 1 kHz). The minor component was further attenuated and focused into a 3-mm sapphire plate to generate the probe pulses. A short-pass filter (SPF-750, CVI) was inserted into the probe beam to select visible probe (420-750 nm). The time delay between the pump and probe beams were regulated through a computer-controlled motorized translation stage in the pump beam. The temporal resolution between the pump and theprobe pulses was determined to be 150 fs (FWHM). The transmitted light was detected by a CMOS linear image sensor (S8377-512Q, Hamamatsu). Thin films are excited with sufficiently low pump energies (~ 10 µJ) to minimize signal contributions from singlet-singlet annihilation and photoinduced heating effects. The absorbance at the excitation wavelength was about 0.4-0.8. All the spectroscopic measurements were carried out at room temperature.

Supporting Figures



Figure S1. ¹³C Nuclear Magnetic Resonance (NMR) spectra. ¹³C NMR (15 kHz, solid)

- (a) BPVT: δ 144.84, 143.60, 135.69, 131.85, 130.69, 128.71, 125.18, 123.07, 121.72.
- (b) BBTVB: δ 143.04, 140.39, 139.44, 137.70, 136.29, 132.83, 130.47, 128.52, 125.82, 124.84, 123.14.
- (c) BTTVB: δ 141.66, 140.56, 138.22, 135.89, 132.03, 130.27, 128.81, 125.06.



Figure S2. HR-MS (MAIDI-MS) of BPVT (a), BBTVB (b), BTTVB (c) and element analysis.

BPVT: m/z: 370.08 calcd for $C_{24}H_{18}S_2$; found, 370.084. Elem Anal. calcd for $C_{24}H_{18}S_2$: C 77.84, H 4.86, S 17.30; found: C 76.89, H 4.88, S 17.24.

BBTVB: m/z: 534.06 calcd for $C_{32}H_{22}S_4$; found, 534.059. Elem Anal. calcd for $C_{32}H_{22}S_4$: C 71.91, H 4.12, S 23.97; found: C 71.01, H 4.29, S 23.04.

BTTVB: m/z: 698.04 calcd for $C_{40}H_{26}S_6$; found, 698.034. Elem Anal. calcd for $C_{40}H_{26}S_6$: C 68.77, H 3.72, S 27.51; found: C 66.98, H 3.48, S 24.85.

Material	The first zone	Low-temperature zone	Substrate	Heating time (h)
BPVT	270 °C	170 °C	Si/SiO ₂	2
BBTVB	300 °C	240 °C	Quartz plate	3
BTTVB	340 °C	290 °C	ITO	6

 Table S1. The deposition conditions of BPVT, BBTVB, and BTTVB microcrystals.



Figure S3. Thermal gravimetric analysis (TGA) of BPVT (a), BBTVB (b), and BTTVB (c), respectively.



Figure S4. Atomic force microscopy images of a single BPVT (a), BBTVB (b), and BTTVB (c) microcrystals and their corresponding thickness, respectively. The thickness is both between 600-700 nm.

	BPVT	BBTVB	BTTVB
CCDC	796660	2052458	2052459
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_l/n$
a/Å	6.0725(7)	5.89390(10)	6.07960(10)
b/Å	7.4958(10)	7.3958(2)	7.7710(2)
c/Å	19.872(3)	29.0039(6)	68.0504(16)
α/°	90.00	90	90
β/°	90.00	92.309	90.547(2)
$\gamma/^{\circ}$	90.00	90	90
volume/Å ³	904.5(2)	1263.26(5)	3214.87(12)
Z factor	2	2	4
$v/z/Å^3$	452.25	631.63	
$ ho_{calc}/{ m g~cm^{-3}}$	1.360	1.406	1.444
Final D indexes [I>-2-(I)]	$R_1 = 0.0346,$	$R_1 = 0.0346,$	$R_1 = 0.0922,$
Final K indexes $[1 \ge -20(1)]$	$wR_2 = 0.0855$	$wR_2 = 0.1006$	$wR_2 = 0.2578$
Final D index [all data]	$R_1 = 0.0401,$	$R_1 = 0.0358,$	$R_1 = 0.1152,$
rmark muex [an uata]	$wR_2 = 0.0882$	$wR_2 = 0.1015$	$wR_2 = 0.2843$
GOF ^C	1.002	1.059	1.052

Table S2. Crystal data and structure refinement for BPVT, BBTVB, and BTTVB.



Figure S5. Typical herringbone arrangements (a, c, e) and pitch angles (b, d, f) of BPVT, BBTVB, and BTTVB crystals. Therefore, all three EHMSs are determined to H-aggregation according to their pitch angles of 57.6°, 72.5°, and 60.7°, respectively.



Figure S6. We calculate the coupling energy at the B3LYP/6-31G(d) level by the Gaussian16 package for BPVT (a), BBTVB (b), and BTTVB (c), respectively. All calculated values are positive, which also supports the conclusion of H-aggregation in three EHMSs.



Figure S7. Approximate energy level schemes for H-aggregation crystals. Due to the fact that the 0-0 fluorescence transition is optically forbidden in H-aggregates, the optically allowed 0-1 transitions naturally provide a four-level system. An effective stimulated process from the reservoir of $|10\rangle$ excitons to the $|01\rangle$ state.



Figure S8. Normalized absorption and PL spectra of 120-nm films.



Figure S9. Theoretically predicted S_1 emission cross sections (black solid) and $T_1 \rightarrow T_n$ absorption cross sections (red dot-dashed). We plot emission cross section of S_1 and triplet absorption cross section according to

$$\sigma_{em}(\lambda) = \frac{e^2 \lambda^2}{4\varepsilon_0 m_e c_0^2 n_F} g(\lambda) f_{em} \qquad \sigma_{abs}^{T_1 - T_n}(\lambda) = \frac{e^2 \lambda^2}{4\varepsilon_0 m_e c_0^2 n_F} g(\lambda) f_{abs}^{T_1 - T_n}, \quad \text{where} \quad f_{em} \quad \text{and} \quad f_{abs}^{T_1 - T_n}$$

corresponds to stimulated emission oscillator strength and triplet absorption oscillator strength which is calculated by combining Gaussian09 [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *et al.* Gaussian 09, Gaussian, Inc., Wallingford, CT, **2009**.] and Multiwfn [T. Lu, F. W. Chen, *J. Comput. Chem.* **2012**, 33, 580-592.]. For three investigated systems, a Gaussian broadening with a the full-width-half-maximum (fwhm) of 75 nm is applied to $S_0 \rightarrow S_1$ absorption, while a Gaussian broadening with a 125 nm fwhm is applied triplet absorption processes due to their broadened nature. Each parameter is shown in the table below.

	f _{em}	$f_{abs}^{T_1 - T_n}$	σ_{em}	$\sigma_{abs}^{T_1 - T_n}$
BPVT	2.30	0.13	3.88×10-16	2.53×10 ⁻²³
BBTVB	2.92	2.72	6.88×10 ⁻¹⁶	1.40×10 ⁻¹⁶
BTTVB	3.58	3.20	1.03×10 ⁻¹⁵	3.15×10 ⁻¹⁶



Figure S10. (a) Schematic illustration of homemade confocal microphotoluminescence system. (b) Schematic diagram of the optical path.



Figure S11. To further understand the cavity mode and the relationship of the mode spacing $\Delta \lambda$ between two adjacent resonance peaks and the WGM cavity, the following equation is given

$$\Delta \lambda = \frac{\lambda^2}{L[n - \lambda(dn/d\lambda)]}$$

where *L* is the optical path length in the resonator, $[n - \lambda(dn/d\lambda)]$ is the group refractive index. Corresponding high-resolution PL spectra of laser emission recorded above threshold for BPVT (a), BBTVB (b), and BTTVB (c) crystals with different cavity length.



Figure S12. Threshold values of crystals as a function of the cavity length for BPVT (a), BBTVB (b), and BTTVB (c), respectively.