Supplementary Information (SI) for Materials Horizons.
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Supporting Information

Highly polarized single-crystal organic light-emitting devices with low turn-on voltage and high brightness

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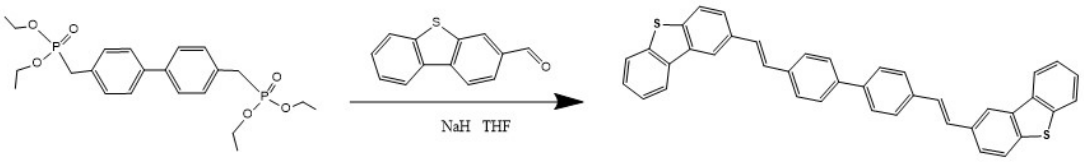
Supplementary Materials and Methods

Synthesis of DBTVB molecule. Tetraethyl ([1,1'-biphenyl]-4,4'-diylbis(methylene)) bis(phosphonate) (400 mg, 0.88 mmol) and NaH (80 mg, 3.3 mmol) were dissolved and activated in 20 ml anhydrous tetrahydrofuran (THF) into a 100 ml reaction flask under an argon atmosphere and ice-water bath for 1 hour. Then the THF solution of dibenzothiophene-2-carboxaldehyde (374 mg, 1.76 mmol) was fast injected into the reaction mixture. After being stirred overnight, add water to quench the reaction. The whole reaction process is under the room temperature. The precipitate was obtained via filter washing multiple times and was then further purified by sublimation twice. [All reagents were used as received from Bei Jing Tong Guang Fine Chemicals]



Scheme S1. Synthesis of 4,4'-bis(2-dibenzothiophenyl-vinyl) biphenyl (DBTVB).

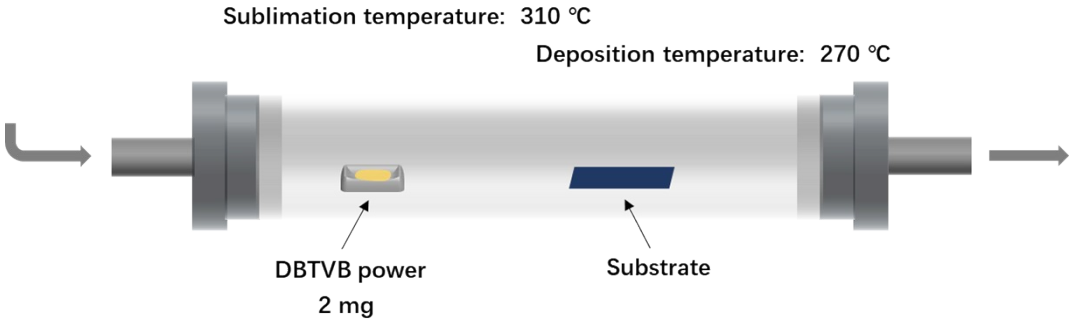
Characterization techniques. The target compound was characterized using elemental analysis and high-resolution mass spectroscopy (MS) after the sublimation purification. The results of the measurement are following [F. Yin, *et al.*, *Nano Lett*. 2022, **22**, 5803-5809.]:

HRMS (MALDI-MS) m/z: 570.15 [M+];

Elemental analysis: Anal. calculated for $C_{40}H_{26}S_2$ (%): C: 84.21, H: 4.56, S: 11.23. Experimental: C: 84.06, H: 4.55, S: 11.50.

Preparation of the single crystal. In our experiment, DBTVB single crystals were fabricated using a facile PVT method. A quartz boat carrying 2 mg DBTVB was then placed in the center of a quartz tube which was inserted into a horizontal tube furnace. The pre-prepared substrates were placed on the downstream side of the argon flow for product collection and the furnace was heated to the sublimation temperature of DBTVB (at temperature region of ~ 310 °C), upon which it was physically deposited onto the pre-prepared substrates at temperature region of ~ 270 °C for 15 hours.

[CCDC 2115005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]



Scheme S2. PVT system for the growth of DBTVB single crystals. PVT system for the growth of hexagonal DBTVB single crystals and large-sized DBTVB single crystals.

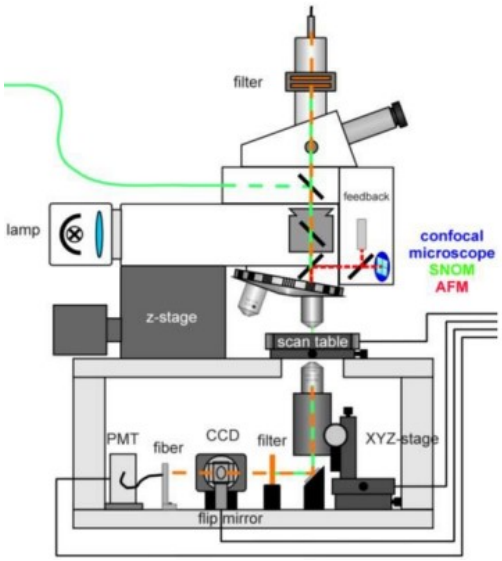
Preparation of DBTVB OLEDs. Thin single crystals of DBTVB were prepared by the physical vapor transport method, with a thickness of 58.3 nm. The uniform and smooth surface of DBTVB Organic single crystals with a roughness about 0.2 nm pave the way for fabricating microcavity OLEDs. The detailed preparation steps are as follows. First, transfer the cleaned silicon wafer into the vapor deposition chamber for vacuum deposition of a total reflection mirror silver film with a thickness of 100 nm. After the electrode is evaporated, a hole transport layer MoO_3 is deposited with a thickness of 2 nm. After the evaporation is completed, take out the evaporated device. As-prepared organic single crystals of DBTVB were then transferred on the 100 nm Ag/ 2 nm MoO_3 film predeposited on silicon wafer through electrostatic adsorption. Finally, 1.5 nm CsF/ 5 nm Ca/ 20 nm Ag films were vacuum deposited sequentially through a mesh-mask, giving rise to an array of microcavity OLEDs on the surface of thin organic single crystals. OLED arrays are in 40 × 40 μm^2 and separated by 20 μm to avoid cross-talk and short circuit.

Turn-on voltage. The voltage of the device is at its brightness of 1cd/m^2. This method is extensively used by the previous literatures (*Nat. Photon.* 2019, 13, 765-769. & *Adv. Opt. Mater.* 2021, 9, 2101149. & *Adv. Mater.* 2023, 35, 2300574).

Theoretical calculation for transition dipole moment. All the geometrical and electronic structures of ground state are calculated at B3LYP/6-31G(d) level in Guassian09 Program. The excited state electronic structures are calculated at the B3LYP/6-31G(d) level. The geometrical

and electronic structures of all investigated systems are firstly calculated in the gas phase. The electronic couplings are evaluated at B3LYP/6-31G(d) level by Guassian09 Program.

Methods. DBTVB 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 Kα radiation (λ = 1.54050 Å) operated in the 2θ range from 5 to 35°, by using the samples on a cleaned quartz substrate. The height of microcrystals was measured by atomic force microscopy (AFM, Bruker Multi-Mode 8-HR). The photoluminescence spectrum of the device was characterized by using a homemade optical microscope equipped with a 50 × 0.9 NA objective. The fluorescence micrograph was measured on Olympus IX71. The photoluminescence spectra of DBTVB single crystals in microcavity was characterized by using a homemade optical microscope equipped with a 50 × 0.9 NA objective (Scheme S3).



Scheme S3. Schematic demonstration of the experimental setup for the optical characterization: the near-field scanning optical microscopy.

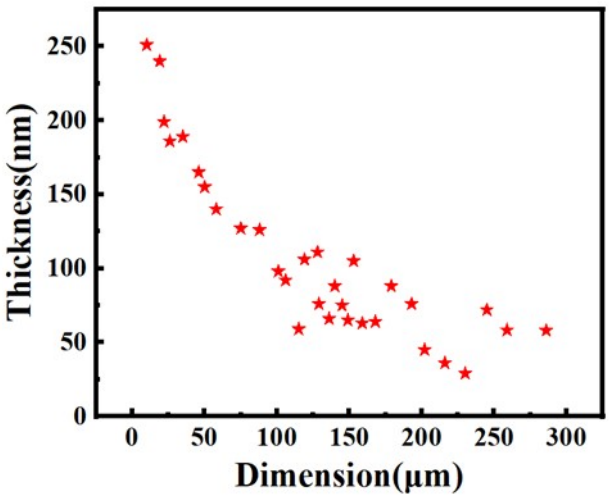


Figure S1. The distribution of thickness and dimension by random measurement of 30 samples.

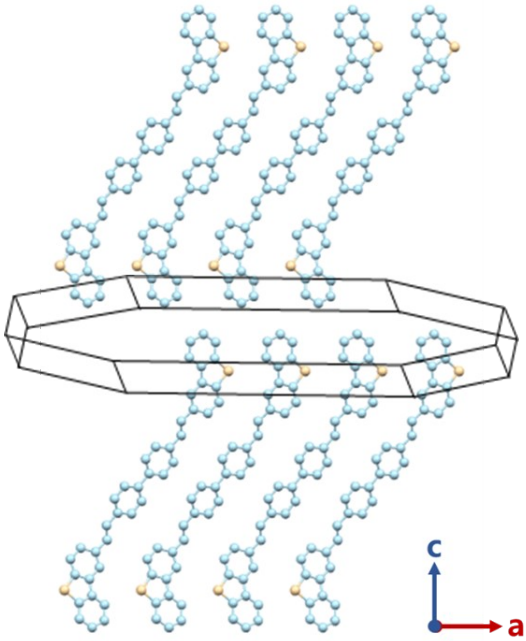


Figure S2. Schematic diagram of DBTVB molecule arrangement in the *ac*-plane.

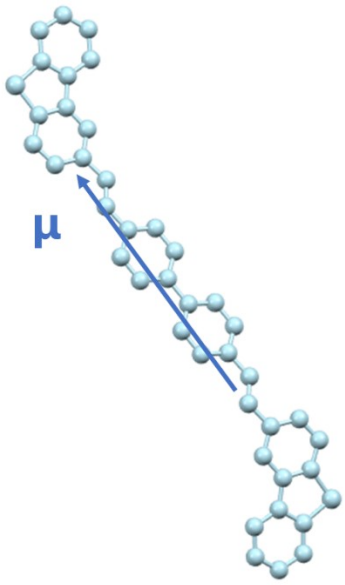


Figure S3. Schematic diagram of transition dipole moment direction. The transition dipole moment of DBTVB is oriented parallel to the molecular long axis according to the results of theoretical calculation.

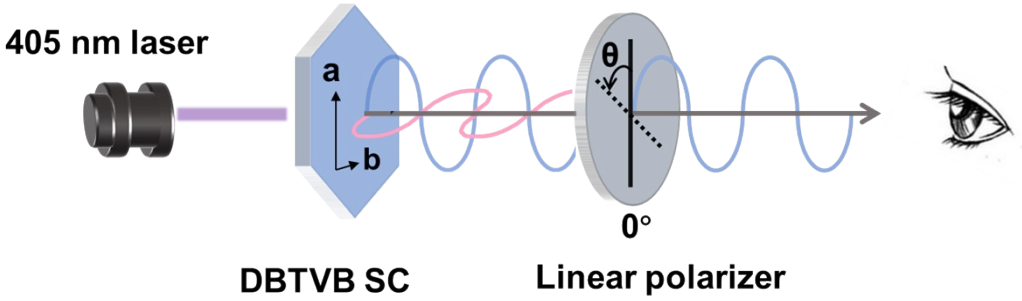


Figure S4. Schematic diagram of the relationship between the polarized light and the angle of the crystal *a*-axis.

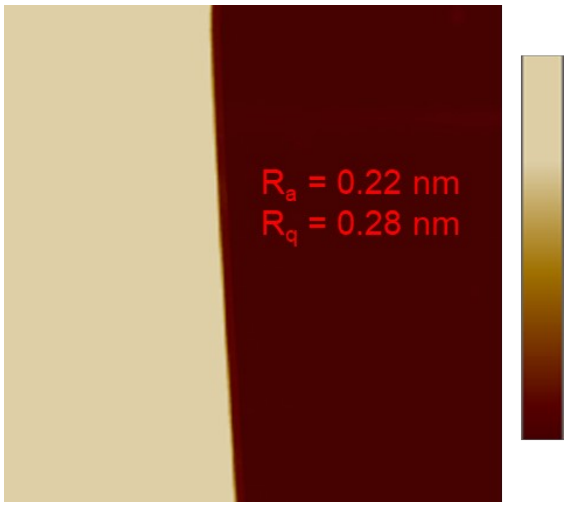


Figure S5. AFM image of DBTVB crystal with surface roughness parameters R_a and R_q of 0.22 and 0.28 nm.

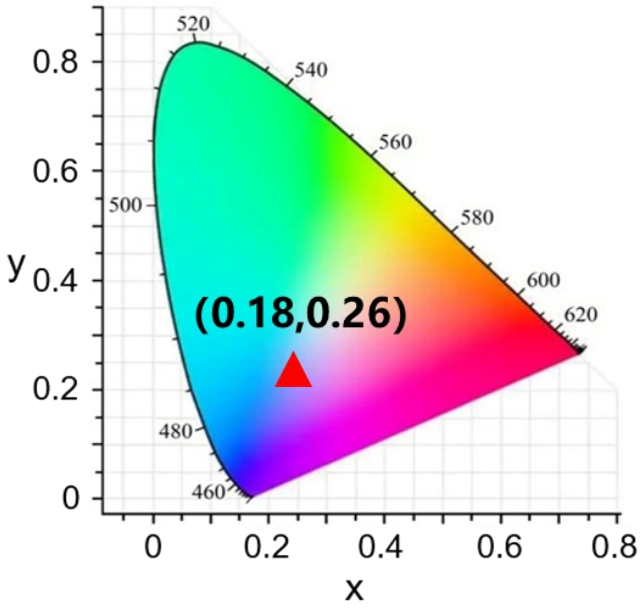


Figure S6. The illustration corresponds to the CIE chromaticity diagram for EL.

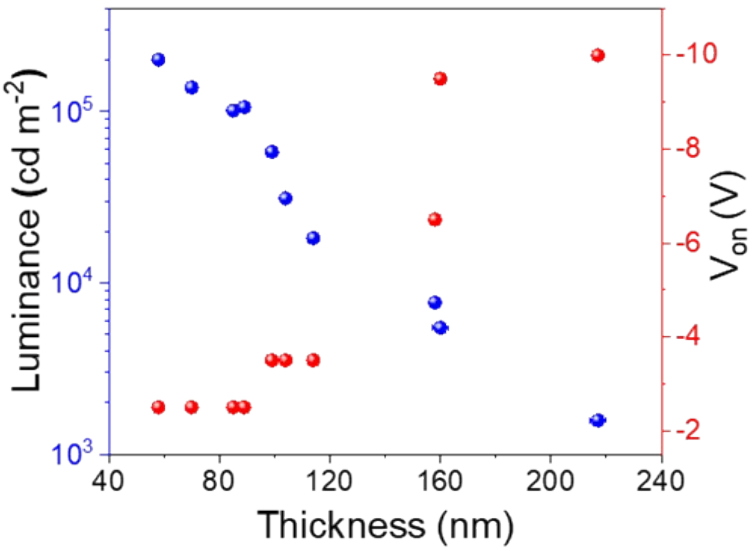


Figure S7. Statistical chart of the influence of crystal thickness on device performance.

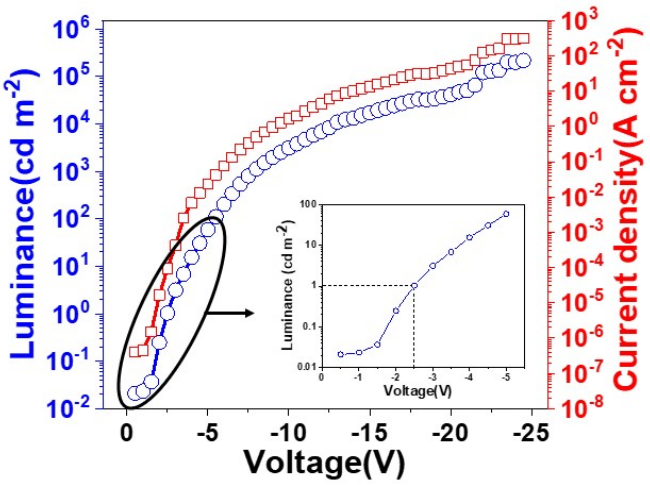


Figure S8. The J-V-L curve of OLED. Inset: the magnification figure at the range of -0.5 V to -5.0 V.

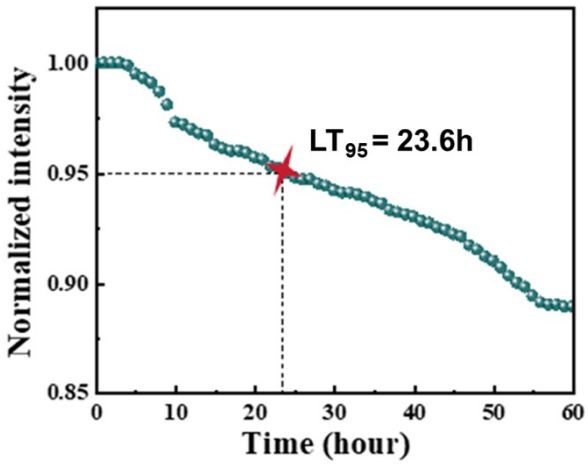


Figure S9. Lifetime curve of the devices at initial brightness of 1000 cd/m^2.

The statistical table：

Year	Molecule	Luminance (cd m^{-2})	DOP	V_{on} (V)	Current density (A cm^{-2})
2014	BP2T	16.87	0.81	--	1933
2015	BP3T	5	--	6	--
2022	BP1T	290	0.81	--	--
2022	BP1T-CN	6122	0.98	--	--
2023	DPA	2427	0.74	--	--
2024	DBTVB	200000	0.95	2.5	400

Table S1. Summary of OLED performance based on single crystals.