Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

The effect of 1D- and 2D-polymorphs on organic single-crystal optoelectronic devices: lasers and field effect transistors

By Qing Liao*†, Zhen Wang†, Qinggang Gao†, Zhaoyi Zhang†, Jiahuan Ren†, Jianbo De†, Xiaosen Zhang†, Zhenzhen Xu†, and Hongbing Fu*†‡

[†] Department of Chemistry, Capital Normal University, Beijing, 100048, P. R. China. Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing, 100048, P. R. China

[‡] Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Sciences, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

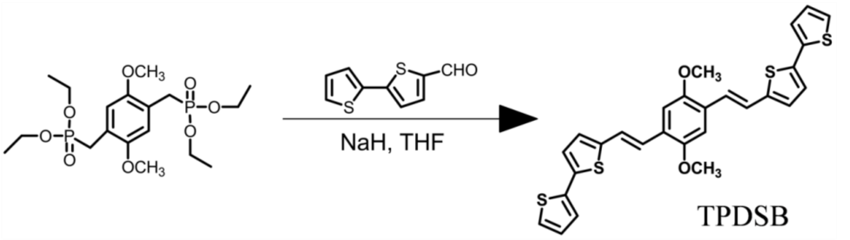
*E-mail: hbfu@cnu.edu.cn; liaoqing@cnu.edu.cn

Keywords: organic microcrystal optoelectronics, polymorph, molecular-stacking arrangement, laser, transistor

Experimental details

1. Synthetic procedure of TPDSB

The compound used in our work, 1, 4-dimethoxy-2, 5-di [bithiophenestyryl] benzene (TPDSB) was synthesized according to Horner-Wadsworth-Emmons reaction (Xu *et. al*, Adv. Mater. 2012, 24, OP216-OP220.). All starting materials were purchased from Sigma-Aldrich and used as received without further purification. The tetrahydrofuran (THF, HPLC grade) and hexane were purchased from Beijing Chemical Agent Ltd., China. Ultrapure water with a resistance of 18.2 MΩ·cm^{-1}, produced by using a Milli-Q apparatus (Millipore), were used in all experiments.



Scheme S1. The synthetic route of (TPDSB).

Without water and oxygen, a mixture of 2,5-bismethoxy-1,4-xylene-bis(diethyl phosphonate) (500mg, 1.14mmol) and catalyzer NaH (54.72mg, 2.28mmol) in tetrahydrofuran (THF) solution was cooled in an ice bath at 0 °C during a 30 min period. Then the 2, 2'-Bithiophene-5-carboxaldehyde (509.38 mg, 2.62mmol)/THF solution inject reaction bulb. And the reaction mixture was stirred at room temperature for 3 hour and subsequently poured into a little water. The phase was extracted with CH_2Cl_2. The pooled organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by chromatography on silica gel by means of CH_2Cl_2/petroleum ether (1:4). Finally orange powder was obtained as the compound (425.2 mg, 0.82 mmol) in 72% yield. 1H NMR (400 MHz, $CDCl_3$): δ 7.19 - 7.23 (m, 8 H), 7.08 - 7.09 (d, 2 H), 7.01 - 7.04 (m, 4 H), 6.97 - 6.99 (d, 2 H), 3.93(s, 6 H); MS (MALDI - TOF): 518.0.

2. Synthesis of 1D-MWs and 2D-MDs.

In our experiment, 1D-MWs and 2D-MDs were prepared by a facile solution self-assembly method. Typically, 100 μL of stock TPDSB dichloromethane (DCM) solution (1mM) was dropped onto the glass substrate, which was placed in a little beaker sealed by a porous Parafilm (3M) in order to control the evaporation rate of solution. When the beaker was posited under the high temperature (30 °C), 1D-MWs were obtained finally. While the beaker was posited under the low temperature (2 °C), 2D-MDs were obtained finally.

3. Structural and photoelectric characterization

The 1D-MWs and 2D-MDs samples were characterized by field emission scanning electron microscopy (S-4800, Hitachi) by dropping on a silicon wafer. The height of microcrystals was measured by atomic force microscopy (AFM, Santa Barbara, CA). Samples examined by transmission electron microscopy (TEM) (JEM-1011, JEOL) were obtained by one drop of the solution being dropped on a carbon-coated copper grid and evaporated. TEM measurement was performed at room temperature at an accelerating voltage of 100 kV. The X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54050$ Å) operated in the 2θ range from 3 to 30°, by using the samples on a cleaned glass slide.

The diffused reflection absorption and emission spectra were measured on Shimidazu UV-3600 UV-VIS-NIR and Horiba FluoroMax-4-NIR spectrophotometers, respectively. Φ of monomer solution in DCM measured through a relative method by using Rhodamine 6G as a standard and Φ of 1D-MWs and 2D-MDs measured through an absolute method by using an integration sphere.

The isolated single TPDSB was characterized by using a homemade optical microscope equipped with a 50 × 0.9 NA objective (Figure S9). The second harmonic (λ = 400 nm, pulse width 150 fs) of a 1 kHz Ti: sapphire regenerative amplifier was focused to a 50 μm diameter spot to excite the middle part of the selected single TPDSB on a 2D movable table. Spatially resolved PL spectra were collected underneath by using a 3D-movable objective coupled to an optical fiber and detected using a liquid-nitrogen cooled charge-coupled device (CCD).

For electronic characterization, we used highly n-doped (100) Si wafers (0.05–0.2 U·cm) with a 300 nm SiO_2 as a dielectric layer (10 nF/cm^2). The SiO_2/Si substrates were first washed with acetone, ethanol, deionized water and hot sulfuric acid : hydrogen peroxide = 7 : 3 solution and dried using a N_2 gun. 1D-MWs and 2D-MDs were fabricated by directly dropping the TPDSB/DCM solution onto the silicon wafers, using the same procedure as for the glass substrate. The crystals were further annealed (90°C) in a vacuum oven for at least 2h to remove the solvent. A top-contact/bottom-gate configuration was used to fabricate the TPDSB-crystal-based OFET device. The source and drain electrodes (Au, 50 nm thick) were evaporated and copper grids were used as the mask. The current–voltage (I–V) curves were recorded with a Keithley 4200 SCS analyzer. All measurements were performed at room temperature in air.

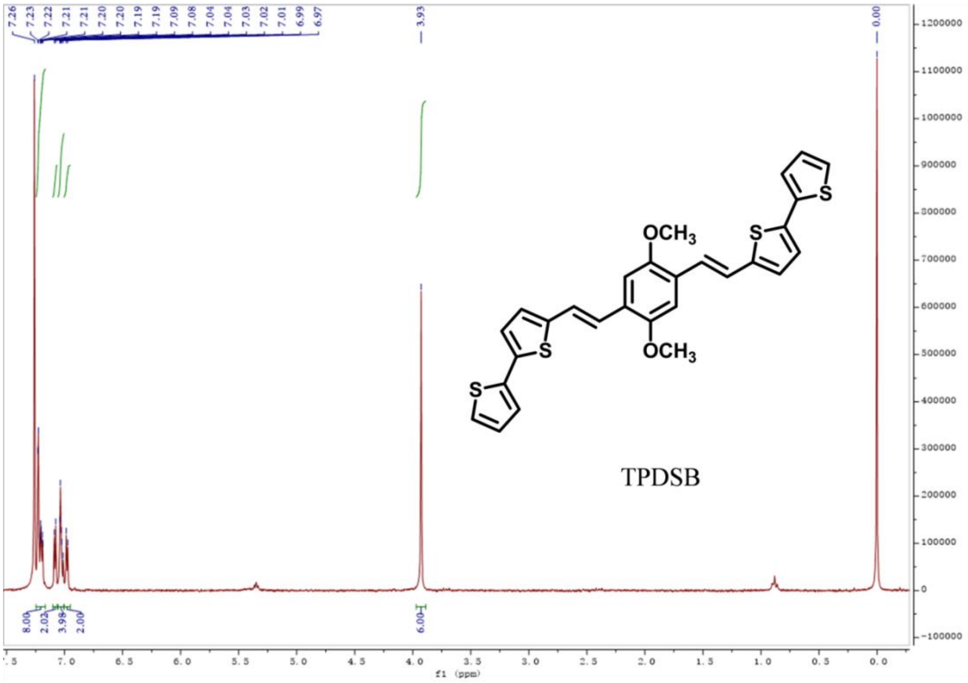


Figure S1. ^{1}H Nuclear magnetic resonance（NMR) spectrum of TPDSB.

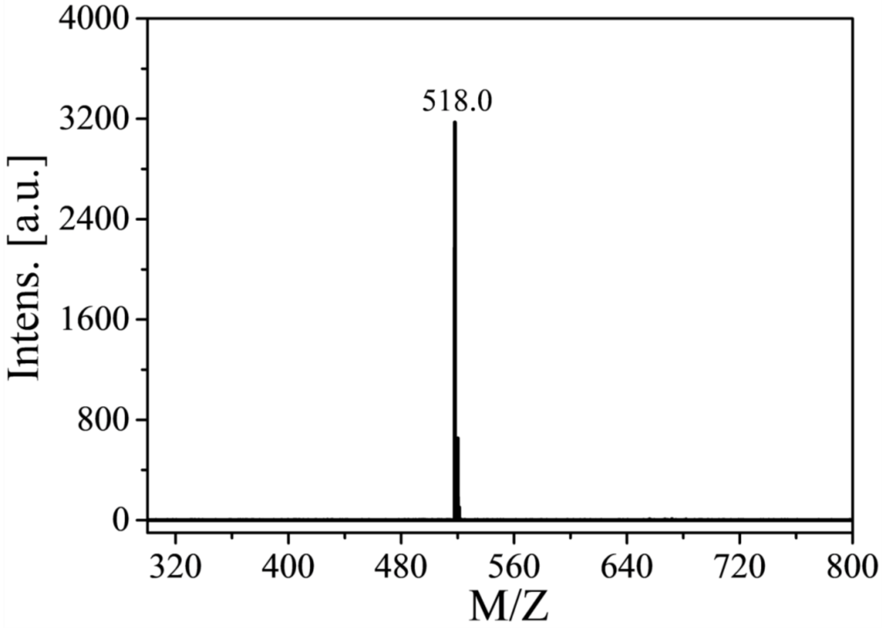


Figure S2. MALDI-MS spectrum of TPDSB.

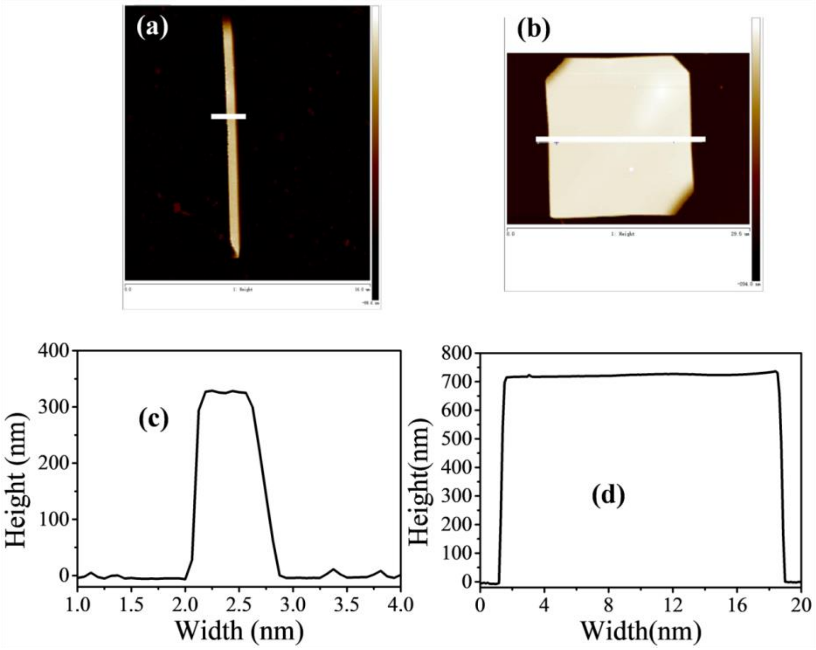


Figure S3. (a) AFM image of a single 1D-MWs. (b) AFM image of an individual 2D-MDs. The corresponding height profiles of 1D-MW (c) and 2D-MD (d), respectively.

Table S1. Crystal date and structure refinement for TPDSB.

Name	1D-MWs (CCDC no. 1556955)	2D-MDs (CCDC no. 1556956)
Empirical formula	$C_{28} H_{22} O_2 S_4$	$C_{28} H_{22} O_2 S_4$
Formula weight	518.69	518.69
Temperature	293(2) K	173.1500 K
Wavelength	0.71073 Å	0.710747 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 1 21/c 1	P 1 21/c 1
Cell Lengths (Å)	a = 10.771(2) Å	a = 14.239(3) Å
	b = 5.5138(11) Å	b = 9.3938(19) Å
	c = 20.877(4) Å	c = 9.0364(18) Å
Cell Angles (º)	a= 90°	a= 90°
	b= 98.08(3)°	b= 102.22(3)°
	c = 90°	c = 90°
Volume	1227.5(4) Å^3	1181.3(4) Å^3
Z	2	2
Density (calculated)	1.403 Mg/m^3	1.458 Mg/m^3
Absorption coefficient	0.412 mm^{-1}	0.428 mm^{-1}
F(000)	540	540
Theta range for data collection	1.910 to 27.482°.	1.463 to 27.484°.
Index ranges	-13<=h<=13, -7<=k<=7, -27<=l<=26	-18<=h<=18, -11<=k<=12, -10<=l<=11
Reflections collected	9749	8165
Independent reflections	2787 [R(int) = 0.0463]	2689 [R(int) = 0.0632]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2787 / 0 / 155	2689 / 44 / 174
Goodness-of-fit on F^2	1.116	1.105
Final R indices [I>2sigma(I)]	R1 = 0.0612, wR2 = 0.1423	R1 = 0.0510, wR2 = 0.1210
R indices (all data)	R1 = 0.0678, wR2 = 0.1465	R1 = 0.0586, wR2 = 0.1264
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.457 and -0.320 e.Å^{-3}	0.334 and -0.361 e.Å^{-3}

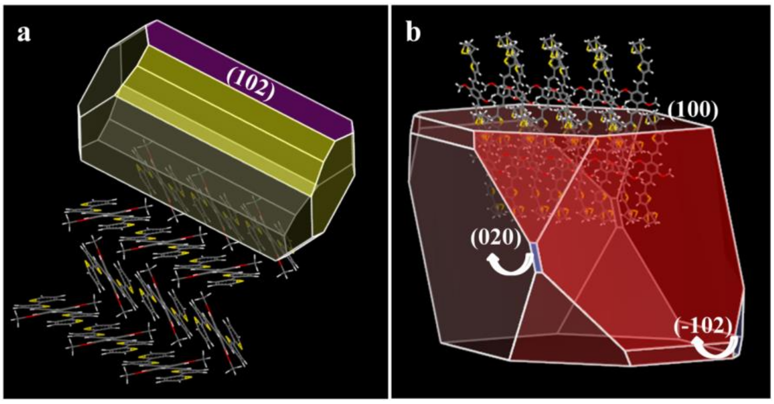


Figure S4. The simulated growth morphologies of 1D-MWs (a) and 2D-MDs (b), respectively, using Materials Studio package. For the type-I monoclinic crystals, the flat face of (102) is also the most-abundant face in prediction (Figure S4a), and the preferential growth along b-axis is also the main stacking direction predicted, which is agreement with the results of 1D-MWs (Figure 2g). For the type-II monoclinic crystals, the prediction morphology (Figure S4b) remarkably matches with the observed disk-like morphology, and that the crystal is mainly bounded by (100), (020), (102) and their symmetric faces. These results reveal that the external morphologies of 1D-MWs and 2D-MWs are mainly governed by their crystal structures. Besides, according to the calculation of Materials Studio (Table S2), the lattice energy of 1D-MW is -104.2 kcal/mol with two molecules per unit cell, while the lattice energy of 2D-MD is -89.2 kcal/mol with two molecules per unit cell. This means that the Gibbs energy of 1D-MW is 15.0 kcal lower than that of 2D-MD every two mol of molecules. That is, 1D-MW phase should be more thermodynamically stable than 2D-MD phase.

Table S2. Calculation results of lattice energy for two crystals, performed by Materials Studio under the COMPASS force field.

	Lattice energy (*k*cal/mol)	Van der Waal contribution (*k*cal/mol)	Electrostatic contribution (*k*cal/mol)	Molecular number per unit cell
1D-MWs	-104.179	-96.181	-7.998	2
2D-MDs	-89.217	-96.427	7.210	2

Table S3. Calculated energy level of 1D-MWs and 2D-MDs.

	Energe/a.u.	HOMO/eV	LUMO/eV	Eg/eV
1D-MWs	-2823.43333796	-4.94	-2.22	2.72
2D-MDs	-2823.47906853	-4.93	-2.28	2.65

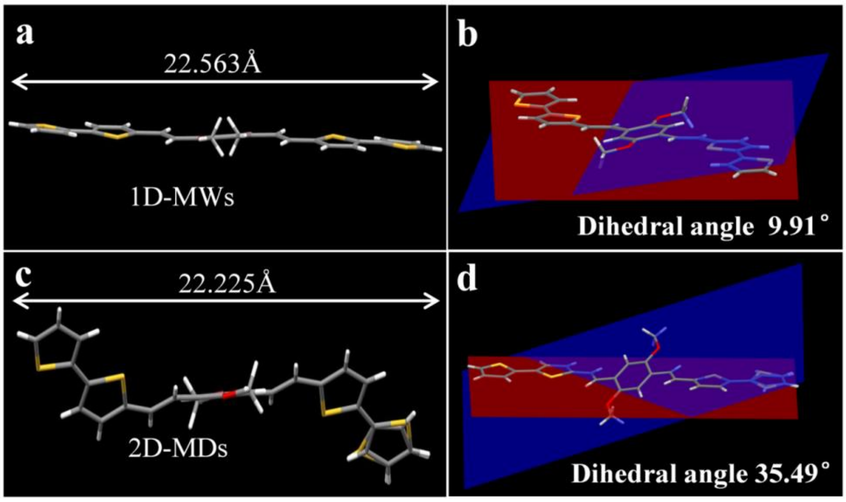


Figure S5. (a) and (b) display side view of 1D-MWs molecular length and angle. (c) and (d) display side view of 2D-MDs molecular length and angle.

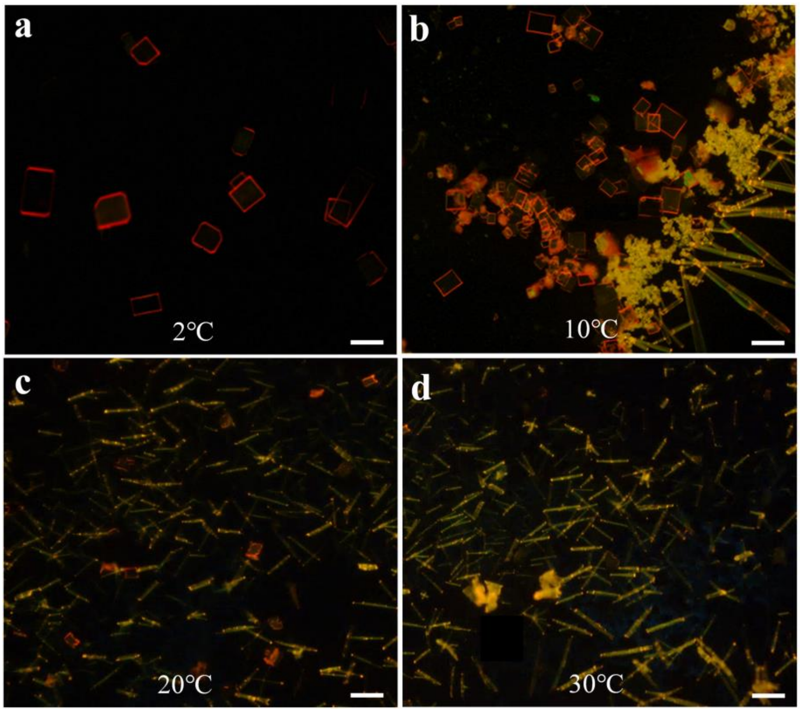


Figure S6. PL microscopy images of the as-prepared polymorphisms placed on a substrate under the different temperatures for the nucleation and growth process. It is clearly seen that 2D-MDs are dominant under the condition of the low temperature (2 °C). As the rise of the reaction temperature, the quantities of 1D-MWs gradually increase. All of as-prepared polymorphs are almost 1D-MWs under the temperature of 30 °C. All scale bars are 20 μm.

Table S4. Factors controlling the shape of prepared 1D-MWs and 2D-MDs.

T	**Shape**	**percentage**
2℃	2D-MDs	100%
10℃	2D-MDs/1D-MWs	80%
20℃	2D-MDs/1D-MWs	15%
30℃	1D-MWs	100%

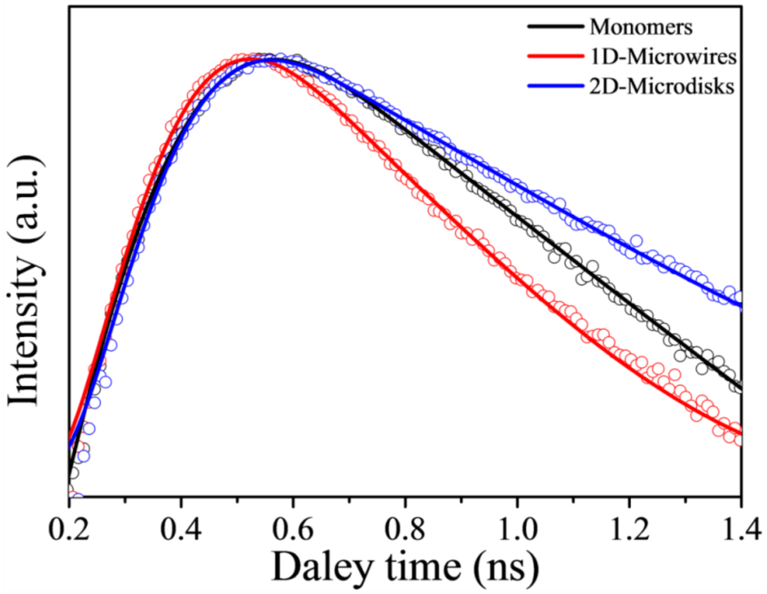


Figure S7. PL decay and fitted curves of TPDSB monomeric solution in THF (black line), yellow 1D-MWs (red line) and red 2D-MDs (blue line) on quartz plate, respectively.

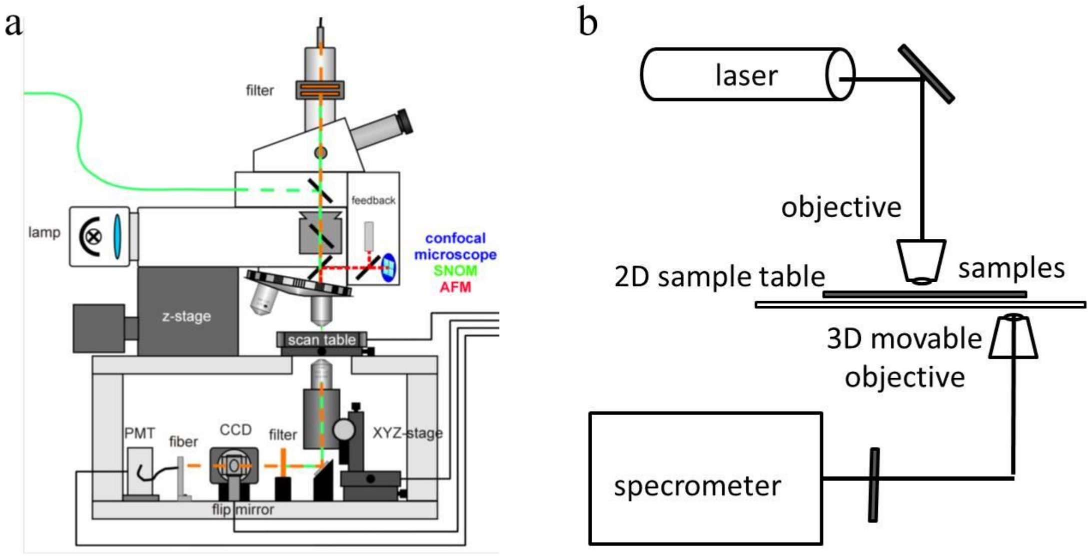


Figure S8. Schematic demonstration of the experimental setup for the optical characterization: (a) the near-field scanning optical microscopy, and (b) the transmittance optical path for the waveguide measurements.

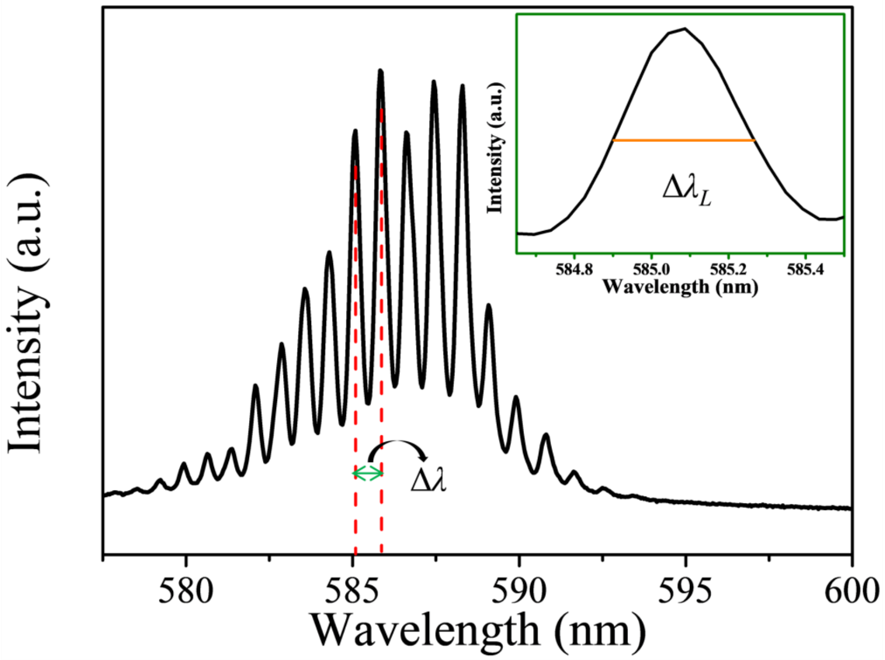


Figure S9. The PL spectra (black curve) and peak-separation-fitting spectra (red curve) of 1D-MWs. Inset: The $\Delta\lambda_L$ is the line-width of the peak around 585 nm.

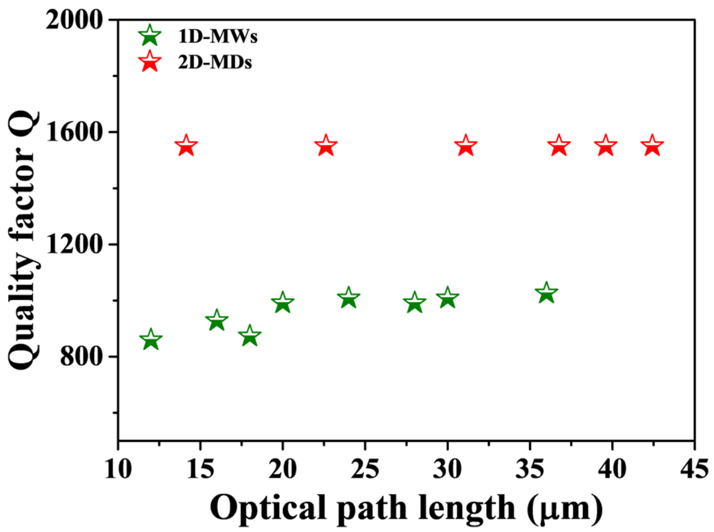


Figure S10. Quality factor (Q) corresponding to 1D-MWs (stars) and 2D-MDs (squares) with different sizes, respectively.