Supporting Information

Controllable Synthesis of Organic 1D Microcrystals for Efficient Optical Waveguide Applications

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Experimental details

1. Materials

2,5-bismethoxy-1,4-xylene-bis(diethyl phosphonate), isonicotinaldehyde, NaH, 2,4,5-tetrafluoro-3,6-diiodobenzene (98%) was purchased from Sigma-Aldrich. The tetrahydrofuran (THF, HPLC grade) and hexane were purchased from Beijing Chemical Agent Ltd., China. Ultrapure water with a resistance of 18.2 $M\Omega \cdot cm^{-1}$, produced by using a Milli-Q apparatus (Millipore), were used in all experiments. The chloroform ($CHCl_3$, analysis grade) solvent was purchased from Beijing Chemical Agent Ltd., China. In addition, all compounds and solvents were used without further treatment. Alumina membranes with a pore size of 20 nm and polytetrafluoroethylene filters (PTFE, Puradisc 25 TF, 0.1um) were bought from Whatman International Ltd.

2. Synthesis procedure of 4,4'-((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dipyridine (DPEpe)

A mixture of 2,5-bismethoxy-1,4-xylene-bis(diethyl phosphonate) (1.01 g, 2.26 mmol) and the isonicotinaldehyde (0.48 g, 4.52 mmol) in THF cooled in an ice bath was added 2 eq. NaH in small portions during a 30 min period. The reaction mixture was stirred at room temperature for 3 h and poured into 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 flash chromatography on silica gel by means of CH_2Cl_2/petroleum ether (1:4). And DPEpe was obtained as a mixture of three isomers. Then the mixed product was dissolved in the minimum amount of a boiling solution containing iodine in toluene (0.1 mM) and

refluxed for 12 h. After gentle removal of solvent in vacuum the green residue was further purified by flash chromatography on silica gel by means of CH_2Cl_2/petroleum ether (1:4). Finally a highly fluorescent yellow powder was obtained as the title compound (0.655 g, 1.82 mmol) in 81% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (d, J = 5.4 Hz, 4H), 7.70 (s, 1H), 7.66 (s, 1H), 7.54 (d, J = 5.5 Hz, 4H), 7.41 (s, 3H), 7.36 (s, 1H), 3.92 (s, 6H).

3. Preparation of Organic Microcrystals

Typically, 0.2 mmol (6.8 mg) DPEpe and 0.2 mmol (8.0 mg) F_4DIB were dissolved in 20 ml dichloromethane (DCM), resulting in a green pellucid solution. Then the green pellucid solution was directly dropped onto the quartz substrate at room temperature in the air, and the 1D single-crystal microrods were obtained after the solvent evaporated totally. Similarly, 0.2 mmol (6.8 mg) DPEpe and 0.2 mmol (8.0 mg) F_4DIB were dissolved in 20 ml mixture solvent of DCM and ethanol (EtOH) with the volume ratio of 2:1, resulting in a green pellucid solution. Then the green pellucid solution was directly dropped onto the quartz substrate at room temperature in the air, and the 1D single-crystal microtubes were obtained after the solvent evaporated totally.

4. Characterizations:

The morphology and size of micro/nanostructures were examined by emission scanning electron microscopy (FESEM, Carl Zeiss, Supra 55, Germany) dropping on an indium tin oxide (ITO) coated glass. TEM images were obtained by a transmission electron microscopy (TEM, FEI company, Tecnai G2 F20, United States). One drop of the solution was 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 (λ = 1.54050 Å) operated in the 2θ range from 5° to 30°, by using the samples on the quartz. Fluorescence images were recorded using an fluorescence optical microscope (Leica, DM4000M, Germany) with a spot-enhanced charge couple device (Diagnostic Instrument, Inc.). The excitation source is a mercury lamp equipped with a band-pass filter (330-380 nm for UV-light). The samples were prepared by placing a drop of solution onto a cleaned quartz, and then evaporated at room temperature. Microarea photoluminescence (μ-PL) spectra were collected on a homemade optical microscopy as shown in the Figure S8. To measure the PL spectra of individual microplate, the plate was excited locally with a 375 nm laser focused down to the diffraction limit. The excitation laser was filtered with a 375 nm notch filter. The light was subsequently coupled to a grating spectrometer (Princeton Instrument, ARC-SP-2356) and recorded by a thermal-electrically cooled CCD (Princeton Instruments, PIX-256E). PL microscopy images were taken with an inverted microscope (Olympus, BX43).

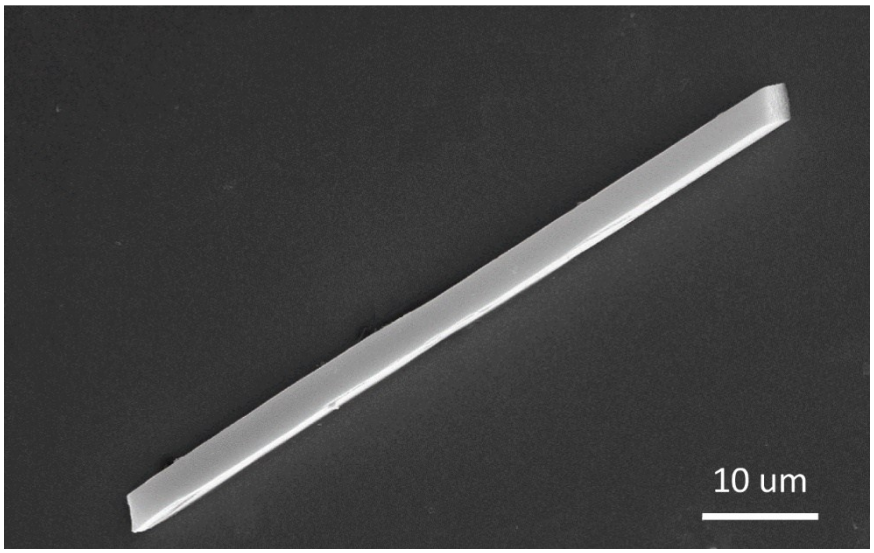

Figure S1. The SEM image of the individual DPEpe-F_4DIB cocrystal microrod with the scale bar of 10 um.

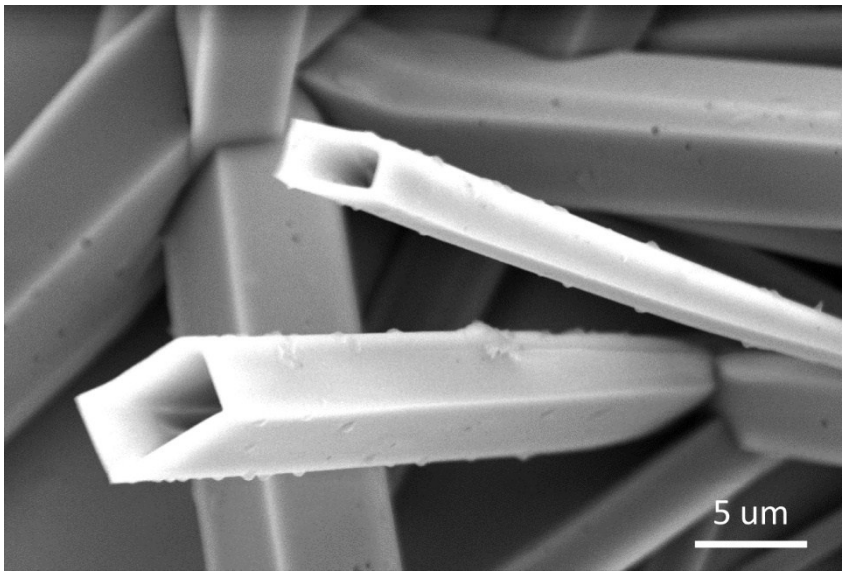

Figure S2. The high resolution SEM image of the DPEpe-F_4DIB cocrystal tube from different viewing angles and resolution with the scale bar of 2 um.

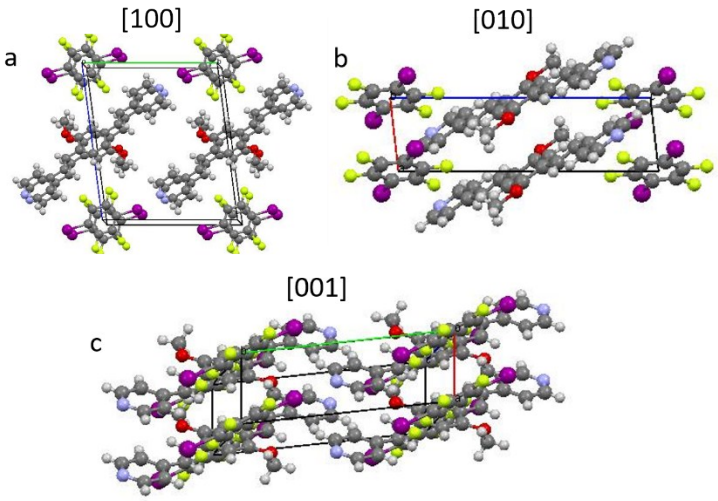

Figure S3. Molecular packing structure of the DPEpe-F4DIB cocrystal along (a) [100], (b) [010] and (c) [001] directions.

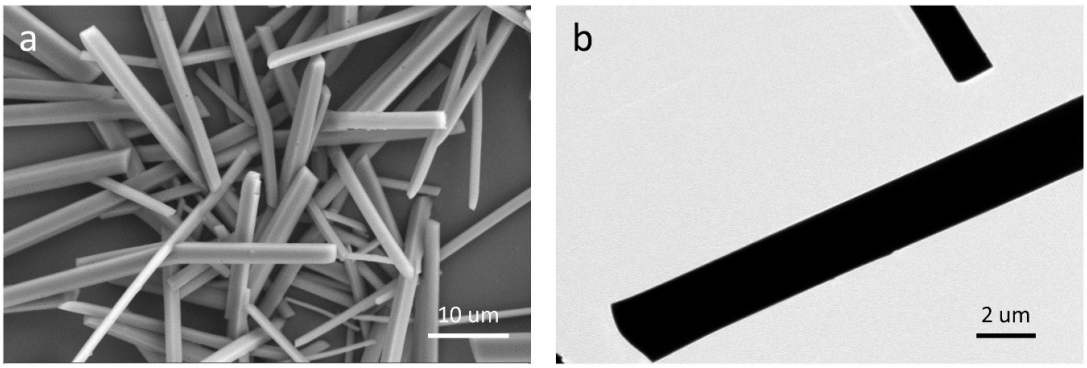

Figure S4. (a) The SEM image of the DPEpe-F_4DIB cocrystal microros pereared based on the mixture solvent systems of DCM and n-hexane with the volume ratio of 2:1. The scale bar is 10 um. (b) The TEM image of the DPEpe-F_4DIB cocrystal microros pereared based on the mixture solvent systems of DCM and n-hexane with the volume ratio of 2:1. The scale bar is 2 um.

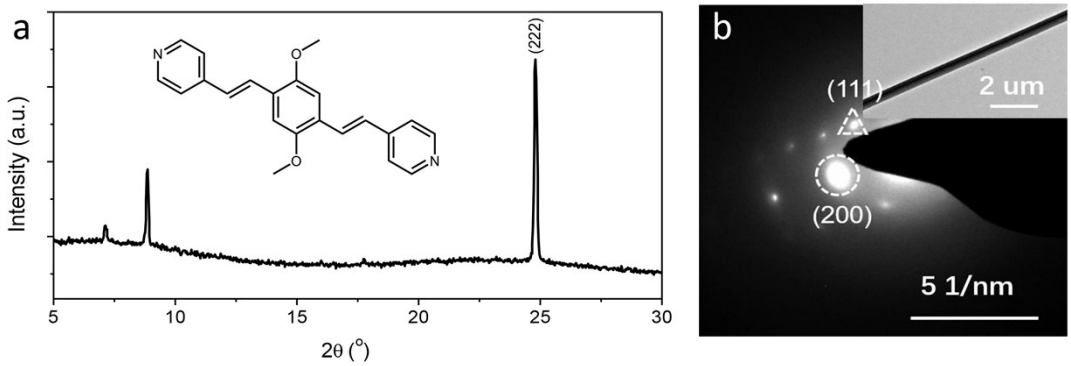

Figure S5. (a) The X-ray diffraction patterns of DPEpe crystals. (b) SAED patterns of one typical DPEpe organic nanowire. The inset: TEM image of the corresponding organic microrods. Based on the crystal data, the SAED pattern of the DPEpe crystal with measured d-spacing values of 7.1 Å, 4.3 Å and intersection angle of 42.8° can be assigned to (111) and (200), respectively. It is greatly different from that of the DPEpe-F4DIB cocrystal.

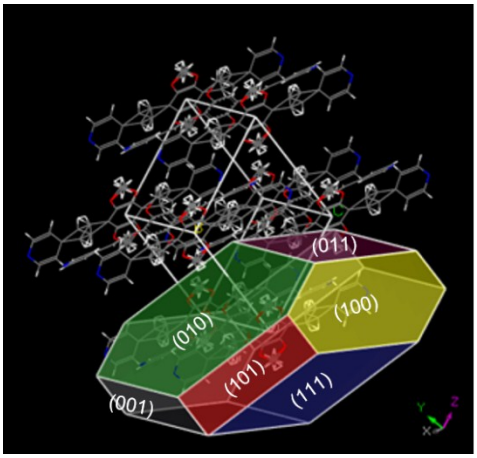

Figure S6. The simulated growth morphology of DPEpe molecules based on the attachment energies using the Materials Studio software package.

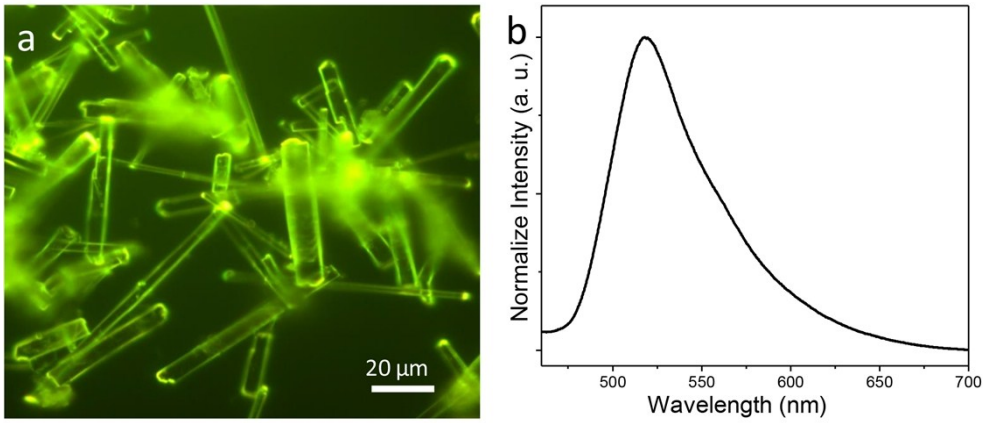

Figure S7. (a) The simulated growth morphology of DPEpe-HCl molecules based on the attachment energies using the Materials Studio software package. (b) The photoluminescence (PL) spectra of DPEpe microcrystals.

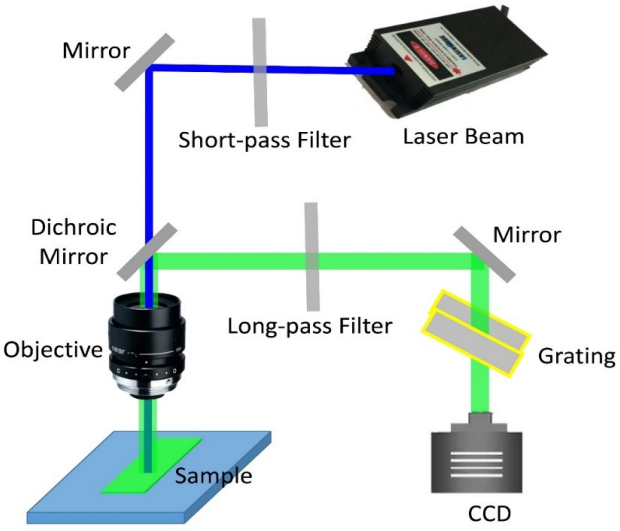

Figure S8. Schematic demonstration of the experimental setup for the optical characterization. PL microscopy images were taken with an inverted microscope (Olympus, BX43). To measure the PL spectra of the 2D cocrystals, the samples were excited locally with a 375 nm laser with a focused beam (*d*~2μm) through an objective (Nikon CFLU Plan, 50×, N.A. = 0.8). The power at the input was altered by the neutral density filters. The emissions from the distal ends of 2D cocrystals were dispersed with a grating (150 G/mm) and recorded with a thermal-electrically cooled CCD (Princeton Instruments, PIX-256E).

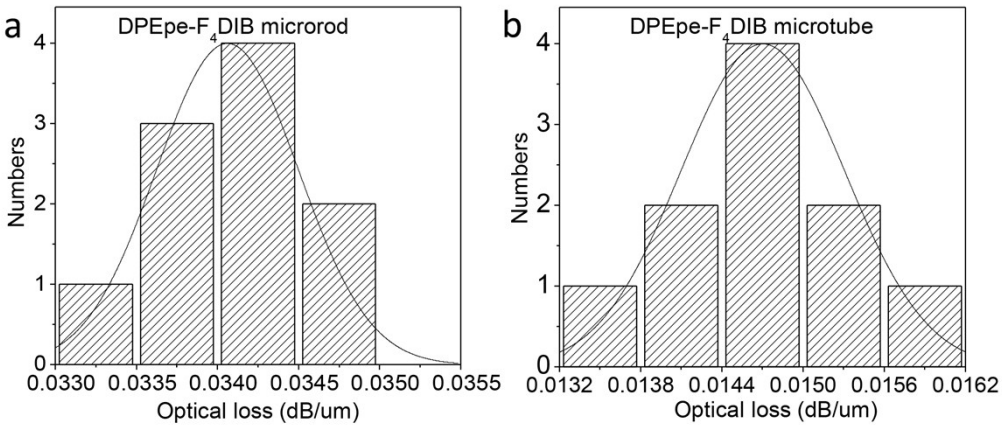

Figure S9. Histogram of optical loss measured from 10 samples for (a) DPEpe-F_4DIB microrod and (b) DPEpe-F_4DIB microtube.

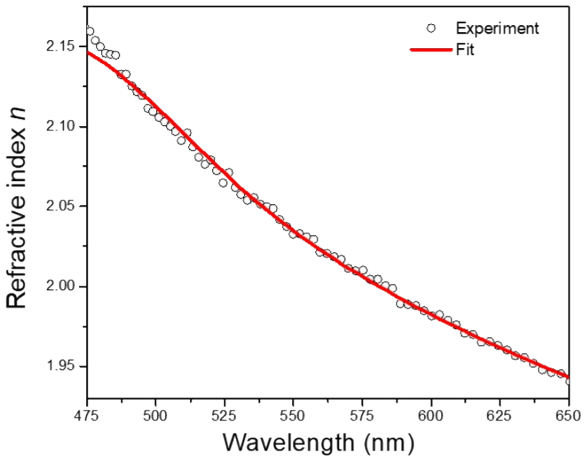

Figure S10. The wavelength-dependent refractive index of cocrystals measured by ellipsometry. The refractive index of 2D cocrystals at 524 nm is about 2.

Table S1. Crystal data and structure refinement for DPEpe-F_4DIB (CCDC No. 1838524).

Name	DPEpe-F_4DIB
Empirical formula	$C_{28}H_{20}F_4I_2N_2O_2$
Formula weight	746.26
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space Group	*P*-1
Cell Lengths (Å)	*a*=4.0465(2), *b*=12.3742(6) *c*=14.4568(8)
Cell Angle (°)	*α*=82.585(2), *β*=82.769(2), *γ*=83.758(2)
Cell Volume (Å^3)	719.22
Z: 4 Z': 0	*Z*: 1 *Z′*: 0
R-Factor (%)	1.62

Table S2. Crystal data and structure refinement for DPEpe (CCDC No. 1861142).

Name	DPEpe
Empirical formula	$C_{22}H_{18}N_2O_2$
Formula weight	343.39
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space Group	*P*-1
Cell Lengths (Å)	*a*=9.2040(9), *b*=9.5032(11) *c*=11.0300(12)
Cell Angle (°)	*α*=74.062(3), *β*=74.517(3), *γ*=72.833(3)
Cell Volume (Å^3)	868.02(16)
Z: 4 Z': 0	*Z*: 2 *Z′*: 0
R-Factor (%)	1.042