



Supplementary Materials for

Long-range extended chains arising from polymerization-driven spontaneous assembly

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The PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 to S31
Tables S1 to S6
References

Table of Contents

1. Materials and Methods

• Materials.....	4
• Nanoribbon fabrication/synthesis.....	4
• AFM characterization.....	4
• 4D-STEM and HRTEM characterization.....	4
• Variable-temperature ¹ H solid-state NMR characterization.....	5
• GIWAXS, solution-WAXS, solution-SAXS characterization.....	5
• ¹ H NMR, ESI-MS, UV-vis-NIR characterization.....	6
• Nano-confined n-PBDF nanoribbons thin film fabrication.....	7
• Electrical conductivity measurement.....	8
• Polarized Raman Measurements.....	8
• TDS-THz measurement.....	9

2. Supplementary Text

• The stabilization of the n-PBDF nanoribbons.....	9
• The generality of PSA.....	10

3. Characterization for individual n-PBDF nanoribbon

• Fig. S1. Cryo-TEM bright-field image of n-PBDF nanoribbons frozen in DMSO.....	11
• Fig. S2. Fast Fourier Transform (FFT) of the HRTEM.....	12
• Fig. S3. HRTEM of the long nanoribbon-like structure.....	13
• Fig. S4. Electron diffraction pattern.....	14
• Fig. S5. The π - π orientation map of 4D-STEM mapping of nanoribbons.....	15
• Fig. S6. 4D-STEM data set collecting and analysis.....	16

4. Structural analysis of n-PBDF nanoribbons

• Fig. S7. GIWAXS of stacked n-PBDF nanoribbons.....	17
• Fig. S8. Varied nanoribbon thickness.....	18
• Fig. S9. Structural characteristics of the nanoribbon in the thickness direction.	19
• Fig. S10. Doping level of n-PBDF nanoribbons estimated from XPS.....	20
• Fig. S11. ¹ H NMR solid-state NMR (ssNMR) spectra of the n-PBDF	21
• Fig. S12. Thermodynamically preferred packing motifs of n-PBDF nanoribbon.....	22
• Fig. S13. Packing motifs of n-PBDF nanoribbons.....	23
• Fig. S14. The chain arrangement of n-PBDF nanoribbon with base treatment.....	24
• Table. S1. Diffraction peak assignment in 2D-GIWAXS.....	43
• Table. S2. Calculated lattice parameters of packing motif of n-PBDF nanoribbon.....	44

5. Nanoribbon formed via polymerization-driving spontaneous assembly mechanism

• Fig. S15. AFM image of n-PBDF nanoribbon prepared with different conditions.....	25
• Fig. S16. Spontaneous formation of n-PBDF nanoribbons with long-range order.....	26

• Fig. S17. Explanation for solution SAXS data.....	27
• Fig. S18. Salting-out of n-PBDF nanoribbon.....	28
• Fig. S19. Nanoribbon morphology evolution with reaction time	29
• Fig. S20. UV-vis-NIR spectra of BDF doping neutral PBDF.....	30
• Fig. S21. ¹ H NMR spectra of PBDF promoting polymerization of BDF.....	31
• Fig. S22. ¹ H NMR spectrum and UV-vis-NIR spectrum of BDF in DMSO-d ₆	32
• Fig. S23. Negative ion EIS-MS of the mixtures of BDF and dedoped n-PBDF.	33
• Fig. S24. Schematic of nanoribbon formation.....	34
• Fig. S25. Schematic illustration of nanoribbon stacking.....	35
• Table S3. Processing conditions of nanoribbons.	45
• Table S4. Synthesis conditions of nanoribbons.	46
6. Preparation and electrical performance of oriented n-PBDF nanoribbon	
• Fig. S26. Preparation process of oriented n-PBDF nanoribbon thin film.	36
• Fig. S27. Polarized optical micrographs aligned nano-confined n-PBDF films.	37
• Fig. S28. Schematic illustration of the four-probe conductivity measurement	38
• Fig. S29. Electrical conductivity of nano-confined n-PBDF nanoribbons.	39
• Fig. S30. AFM images of aligned n-PBDF nanoribbons.....	41
• Fig. S31. Fitting of the temperature-dependent electrical conductivity of n-PBDF.....	42
• Table S5. Conductivity of aligned nanoribbons... ..	47
• Table S6. Samples conditions for all nanoribbon characterizations.....	48
7. Reference	

Materials and Methods

Materials

3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (BDF) monomer was synthesized according to previous report.⁽³³⁾ All reagents and solvents for the synthesis and analysis were purchased from Sigma-Aldrich, Alfa Aesar, Thermo Fisher, and TCI and were used without further purification, unless otherwise mentioned.

Nanoribbon fabrication/synthesis

The n-doped poly(benzodifurandione) (n-PBDF) nanoribbon suspension can be synthesized via multiple reaction systems (varied concentrations, temperatures, oxidants/catalyst, solvents) using BDF as the precursor under a nitrogen atmosphere. The representative reaction systems include: (i) 10 mg mL⁻¹ BDF in DMSO with 2 equivalents of duroquinone (TMQ(8)) as an oxidant, heated at 105 °C for approximately 3 hours. (ii) 15 mg mL⁻¹ BDF in DMSO with 0.1 equivalent of selenium dioxide (SeO₂(24)) as a catalyst, heated at 100 °C for 24 hours. (iii) 5 mg mL⁻¹ BDF in DMSO with 0.001 equivalent of molybdenum trioxide (MoO₃(25)) as a catalyst, heated at 100 °C for 16 hours. (iv) 10 mg mL⁻¹ BDF in N,N-Dimethylformamide (DMF) with 2 equivalents of TMQ as an oxidant, heated at 105 °C for approximately 6 hours. More synthesis conditions are provided in **Table S4** and **Fig. S15**. The samples for various characterization techniques are clarified and summarized in **Table S6**.

AFM characterization

The dispersed nanoribbons on substrate are characterized via atomic force microscopy (AFM). The n-PBDF nanoribbon suspension in DMSO (4-15 mg mL⁻¹) was diluted to 0.0025-0.05 mg mL⁻¹ using DMSO, methanol, or acetone as the diluent. The diluted suspension was then spin-coated onto mica substrates at 2000 rpm for 60 seconds, followed by drying under vacuum at 25 °C or 60 °C to remove residual solvent. The AFM images were collected via Oxford Cypher ES operating in tapping mode, with AFM probes having a force constant of 3 N m⁻¹. Detailed processing conditions are provided in **Table S3** and **Fig. S15**.

4D-STEM and HRTEM characterization

Four-dimensional scanning transmission electron microscopy (4D-STEM) samples were prepared via drop-casting 0.5 mg mL⁻¹ n-PBDF nanoribbon DMSO suspension on TEM copper grids with ultrathin carbon film (< 3 nm) on lacey carbon support. High-resolution transmission

electron microscopy (HRTEM) samples were prepared via drop-casting 0.01 mg mL⁻¹ n-PBDF nanoribbon DMSO suspension on TEM copper grids with single-layer graphene support films.

4D-STEM datasets were acquired using an electron microscope pixel array detector (EMPAD), a high-dynamic-range direct electron detector, on a ThermoFisher Scientific Spectra 300 microscope operated at 300 kV in STEM mode. Datasets were collected with a small convergence semi-angle of 150 μ rad, a beam current of 18 pA, a scan step of 1.9 nm, an exposure time of 1 ms and a nominal camera length of 1.44 m, yielding an electron dose of ~ 311 e/ $\text{\AA}^2$. The pseudocolor annular dark-field (ADF) image (Right panel of **Fig. S4**) was generated by integrating the diffraction intensity over 2.6 to 3.2 nm⁻¹ (the π - π stacking signals). The orientation map is determined by the azimuth of the π - π stacking diffraction points, indexed as (010).

HRTEM images were acquired using an OneView camera with an electron dose of ~ 111 e/ $\text{\AA}^2$, on a ThermoFisher Scientific Spectra 300 microscope operated at 300 kV in TEM mode.

Variable-temperature ¹H solid-state NMR characterization

Solid-state NMR sample of n-PBDF were prepared via precipitating n-PBDF nanoribbon suspension in a CHCl₃/hexane mixed solvent (v/v = 3:1). The precipitate was filtered, dried under vacuum at 100 °C, and finely ground to yield n-PBDF powder.

The variable-temperature solid-state ¹H NMR spectra of the n-PBDF sample were measured on a Bruker Avance Neo 600 MHz / 395 GHz dynamic nuclear polarization (DNP) nuclear magnetic resonance (NMR) spectrometer. The solid-state NMR spectrometer is a Bruker Avance Neo wide-bore model, with an operating frequency of 599.99 MHz (¹H Larmor frequency). Although the spectrometer is equipped with a microwave source, this component was not used in the present experiment. It is also equipped with a broadband triple-resonance 3.2 mm low-temperature magic-angle spinning (MAS) DNP probe. During data acquisition, the sample was subjected to a variable-temperature range of 140 K-297 K. Under all variable-temperature conditions, the MAS frequency was maintained consistently at 30 kHz. All spectra were acquired using a one-pulse sequence, with an excitation pulse length of 2.5 μ s at 20 W. The recycle delay was 3 s. The ¹H chemical shifts were referenced to adamantane powder ($\delta(^1\text{H}) = 1.91$ ppm). Phase adjustment of all NMR data was performed and analyzed using Bruker TopSpin software (Version 4.3.0).

GIWAXS, solution-WAXS, solution-SAXS characterization

2D GIWAXS and solution SAXS measurements were performed in beamline 12-ID-B of the Advanced Photon Source at Argonne National Laboratory. For GIWAXS, the 13.3 keV X-ray beam was incident at a grazing angle of about 0.08 degrees with an exposure time of 0.7 seconds. For solution SAXS, the n-PBDF suspension and pure DMSO were loaded into quartz capillaries.

The X-ray beam was directed through the center of the capillaries with an exposure time of 0.2 seconds. The scattered X-ray were detected using PerkinElmer detector (XRpad 4343F) for GIWAXS and Eiger2 9Mdetector for SAXS.

For the in-situ SAXS measurements, 10 mg mL⁻¹ BDF and 2eq TMQ were dissolved in DMSO under a nitrogen atmosphere at 40 °C for 30 min. The resulting solution was loaded into quartz capillaries with a diameter of 0.15 cm and sealed with epoxy under nitrogen in a glovebox. The sealed capillaries were mounted in a heating stage on the X-ray beamline. The stage was heated to 100 °C at a rate of 10 °C/min, and SAXS data collection was initiated once the temperature reached 100 °C. Data were recorded every 10 minutes. A quartz capillary filled with pure DMSO was used as background reference. An automated translation stage was employed to switch between the pre-set positions of the reaction and reference capillaries, enabling simultaneous collection of reaction and reference SAXS data. The background scattering from DMSO in the reaction capillaries was subtracted during data processing.

The solution WAXS were performed in beamline 11-BM of National Synchrotron Light Source II at Brookhaven National Laboratory. For the solution WAXS, the 13.5 keV X-ray was transmitted through the quartz capillary containing 15 mg mL⁻¹ n-PBDF/DMSO suspension or pure DMSO solvent with 1 s exposing time.

¹H NMR, ESI-MS, UV-vis-NIR characterization

¹H NMR spectra were recorded on Bruker NEO 300 (300 MHz). All chemical shifts were reported in parts per million (ppm). ¹H NMR chemical shifts were referenced to DMSO-*d*₆ (2.50 ppm).

Dedoped n-PBDF (PBDF) powder was prepared following the procedure described below. As the n-PBDF can be effectively dedoped by Magic Blue(15), the n-PBDF powder (50 mg, 0.27 mmol repeated unit) were mixed with 2eq Magic Blue (438 mg, 0.54 mmol) in 100 mL acetonitrile (ACN), stirring for 30 min at room temperature. The solution remained blue after the reaction, indicating an excess of Magic Blue. The mixture was then filtered and washed with ACN 10 times to ensure the complete removal of Magic Blue and get the dedoped n-PBDF powder.

To investigate the products of BDF doping n-PBDF via ESI-MS, BDF in DMSO (1 mg mL⁻¹, 1 mL, 0.0053 mmol) were mixed with 5eq dedoped n-PBDF powder (5 mg, 0.027 mmol), stirring at 100 °C for 3 hours in N₂ glovebox. The samples containing only dedoped n-PBDF or only BDF, keeping all other conditions the same, were used as the control. After the reaction, the mixtures are filtered with 0.22 μm PTFE filter and filtrates were diluted with ACN (0.2 mL filtrate and 0.8 mL ACN) for the ESI-MS measurements.

ESI-MS measurements were carried out on an Agilent 6560 Ion Mobility Quadrupole Time-of-Flight (IM Q-TOF) mass spectrometer (Santa Clara, CA, USA) equipped with a custom-

built ESI source. Sample solutions ($\approx 100 \mu\text{mol/L}$) prepared in acetonitrile/DMSO (80:20, v/v) were introduced into the instrument through a fused-silica capillary (50 μm ID, 150 μm OD) at a flow rate of 1 $\mu\text{L/min}$ using a syringe pump and ionized using spray voltage of -4.5 kV and an inlet temperature of 325 $^{\circ}\text{C}$. All mass spectra were acquired in negative ion mode within the m/z range of 50 to 3200 and mass resolving power ($m/\Delta m$) of 21,000.

The promoting effect of dedoped n-PBDF on BDF polymerization was investigated by monitoring the consumption of BDF using NMR spectroscopy. BDF were dissolved in DMSO- d_6 with a concentration of 10 mg mL^{-1} . 1,2,4,5-Tetramethylbenzene (TMB) were added as the reference. Four experimental groups were set up. (1) BDF/DMSO- d_6 heating at 100 $^{\circ}\text{C}$ for 36 h in N_2 glovebox. (2) BDF/DMSO- d_6 mixed with 0.1 eq dedoped n-PBDF powder heating at 100 $^{\circ}\text{C}$ for 36 h in N_2 glovebox. (3) BDF/DMSO- d_6 heating at 100 $^{\circ}\text{C}$ for 36 h in Air. (4) BDF/DMSO- d_6 mixed with 0.1 eq dedoped n-PBDF powder heating at 100 $^{\circ}\text{C}$ for 36 h in Air. After the reaction, UV-vis-NIR spectrum were measured via diluting 20 μL aliquot of each reaction with 3 mL DMSO to determine whether n-PBDF was formed. And 600 μL aliquot of each reaction are used for the NMR to determine whether BDF was consumed.

The ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were measured with an Agilent Technologies (Cary 5000/6000i) Cary Win UV-vis-NIR spectrophotometer. Solution UV-vis-NIR spectra were recorded with a wavelength between 300 to 1650 nm in a quartz cuvette with a 1 cm path length. Spectra beyond 1650 nm were not collected for solution samples because DMSO exhibits a strong absorption peak around 1700 nm, which exceeds the instrumental detection limit. Thin film UV-vis-NIR spectra were recorded with a wavelength range of 300 to 2500 nm.

Nano-confined n-PBDF nanoribbons thin film fabrication

Polydimethylsiloxanes (PDMS) precursor and cross-linker (Sylgard 184, Dow Corning) were mixed in a mass ratio of 10:1, followed by degassing under vacuum to remove any entrapped air bubbles. Subsequently, the mixture liquid was cast onto a silicon master mold and covered with a flexible supporting film (polyimide, $\sim 500 \mu\text{m}$ thickness). To facilitate demolding, the silicon master mold was first surface-modified with perfluorodecyltrichlorosilane (Specifically, the mold underwent oxygen plasma treatment followed by vapor-phase deposition in a vacuum oven at 120 $^{\circ}\text{C}$ for 180 min). After heat curing (80 $^{\circ}\text{C}$ for 2 hours), the solidified PDMS replica was readily separated from the silicon master mold. A n-PBDF solution (2 μL) was drop-cast onto substrate and subsequently laminated by a grating-patterned PDMS mold ($\sim 1 \text{ cm} \times 1 \text{ cm}$). The lamination pressure was regulated using weights of varying masses. Subsequently, the substrate was transferred to a vacuum oven and kept under vacuum overnight to ensure complete solvent removal. The nanowire array was obtained after separating the PDMS mold.

Electrical conductivity measurement

The as-prepared oriented nanoribbon thin films were first patterned using a pre-cut PDMS stencil to protect the target region, while the exposed areas were removed by O₂ plasma etching. Subsequently, Au/Cr electrodes (30 nm Au and 5 nm Cr) were thermally evaporated onto the film surface, with their long axis aligned either perpendicular or parallel to the nano-confined channel direction, thereby enabling measurement of the parallel and perpendicular conductivities. A four-probe configuration was then employed to measure the electrical conductivity, in which the test channel was connected to the pads of a Physical Property Measurement System (PPMS). The channel length and width were approximately 500 μm and 3500 μm, respectively. By applying different current levels (0-100 μA in 10 μA steps), the channel voltage difference was recorded and the channel resistance was extracted. The temperature-dependent electrical conductivity was also measured using the PPMS system over a temperature range of 2 to 300 K.

The conductivity measurement was based on ~11-nm-thick nanoribbon film produced via nano-confinement growth using a PDMS template with a 130 nm line width. It should be noted that under this template dimension, a thin underlying n-PBDF layer that is not nano-confined remains beneath the nanoribbon array. Therefore, a parallel conduction model was applied to extract the intrinsic conductivity of the nano-confined n-PBDF region. Specifically, assuming the cross-sectional areas of the bottom unconfined layer and the top nano-confined region are S_1 and S_2 , respectively, the total resistance satisfies $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$, where $R_1 = \frac{L}{\sigma_1 S_1}$, and $R_2 = \frac{L}{\sigma_2 S_2}$. From this relationship, the conductivity of the nano-confined region (σ_2) can be determined. The averaged value of σ_2 for six devices achieve $10,198 \pm 175 \text{ S cm}^{-1}$ when the conductive pathway is parallel to the nano-confined channel.

Polarized Raman Measurements

Polarized Raman measurements were performed using a LabRAM HR Evolution confocal Raman microscope (Horiba). A solid-state laser with an excitation wavelength of 532 nm was employed as the excitation source. The laser beam was focused onto the sample surface through a 50× objective lens (NA = 0.50). To avoid laser-induced heating or damage to the sample, the laser power was attenuated to 5% using a neutral density (ND) filter. The acquisition time for each spectrum was set to 10 s with 2 accumulations to ensure a high signal-to-noise ratio. The measurements were conducted in backscattering geometry. We investigated two specific polarization configurations relative to the nanowire orientation: the “parallel” configuration, where both incident and scattered light polarizations were parallel to the nanowire axis; and the “perpendicular” configuration, where both polarizations were parallel to each other but

perpendicular to the nanowire axis. In both cases, the analyzer was kept parallel to the incident polarization.

TDS-THz measurement

THz-TDS measurements were performed using a commercial Z3 THz time-domain spectrometer (Zomega Terahertz Corp., U.S.A.). Terahertz pulses were generated by a photoconductive antenna and detected using an electro-optic crystal. The excitation source was a mode-locked Ti:sapphire laser (Spectra Physics, U.S.A.) operating at a central wavelength of 800 nm with a pulse duration of 100 fs. During data acquisition, the optical path was purged with high-purity nitrogen (99.999%) to suppress absorption by water vapor. The recorded time-domain signals were converted into frequency-domain spectra in the range of 0.2-1.6 THz by Fourier transformation. The complex conductivity spectra $\sigma(\omega)$ were obtained from the measured transmission ratio $E_s(\omega)/E_r(\omega)$ using a standard air/film/substrate optical model that includes multiple internal reflections in the film. The frequency-dependent $\sigma(\omega)$ was then fitted with a Drude-Smith model to extract the relevant charge-transport parameters.

Supplementary Text

The stabilization of the n-PBDF nanoribbons

In the absence of mechanisms that suppress van der Waal attractions between nanoparticles, their high surface energy renders dispersed nanoparticles thermodynamically prone to further aggregation and eventual precipitation from solution. Here, we find that n-PBDF nanoribbons directly obtained from polymerization at a concentration over 10 mg mL⁻¹ can remain stably dispersed in solution for several months, even up to half a year, with almost no obvious aggregation. This suggests that there are inherent mechanisms that prevent aggregation between the nanoribbons, effectively counteracting the van der Waals attractions between the nanoparticles. The obvious peak in the solution SAXS implies the presence of short-range correlations among the nanoparticles dispersed in solution. Furthermore, the peak position (q_{max}) shows a dependence on nanoribbon concentration (c) following $q_{max} \propto c^{0.37}$ (**Fig. 2B**). This behavior is characteristic of polyelectrolyte solutions, in which the correlation peak arises from electrostatic repulsion, leading to a coherently repeated center-to-center distance between neighboring objects. The polyelectrolyte-like behavior exhibited by the n-PBDF nanoribbon dispersion indicates that the suppression of aggregation between the nanoribbons is most likely governed by electrostatic repulsion between the nanoribbons. To further verify this mechanism, we investigated the salting-out behavior of the nanoribbons (**Fig. S18**). The salting-out behavior further proves that there is electric double layer formed at the nanoribbon surface, characterized by the n-PBDF nanoribbon with negative charge surrounded by positive counter-ion (proton) near the surface.

The generality of PSA

From a design perspective, PSA is expected to be applicable to conjugated polymer systems that combine (i) sufficiently specific interactions between monomers and growing polymer chains to promote ordered assembly, (ii) a controlled-growth polymerization chemistry in which controlled chain-growth can occur through the activation of monomer and polymer chain front, and (iii) electronic structures that permit charge transfer or doping during growth. Under such conditions, polymerization and assembly may become coupled, enabling spontaneous formation of extended, ordered conjugated backbones.

From an application perspective, the spontaneous and solution-processable nature of PSA may enable the incorporation of highly conductive ordered polymer structures into diverse soft-material platforms, including hydrogels and biological environments.

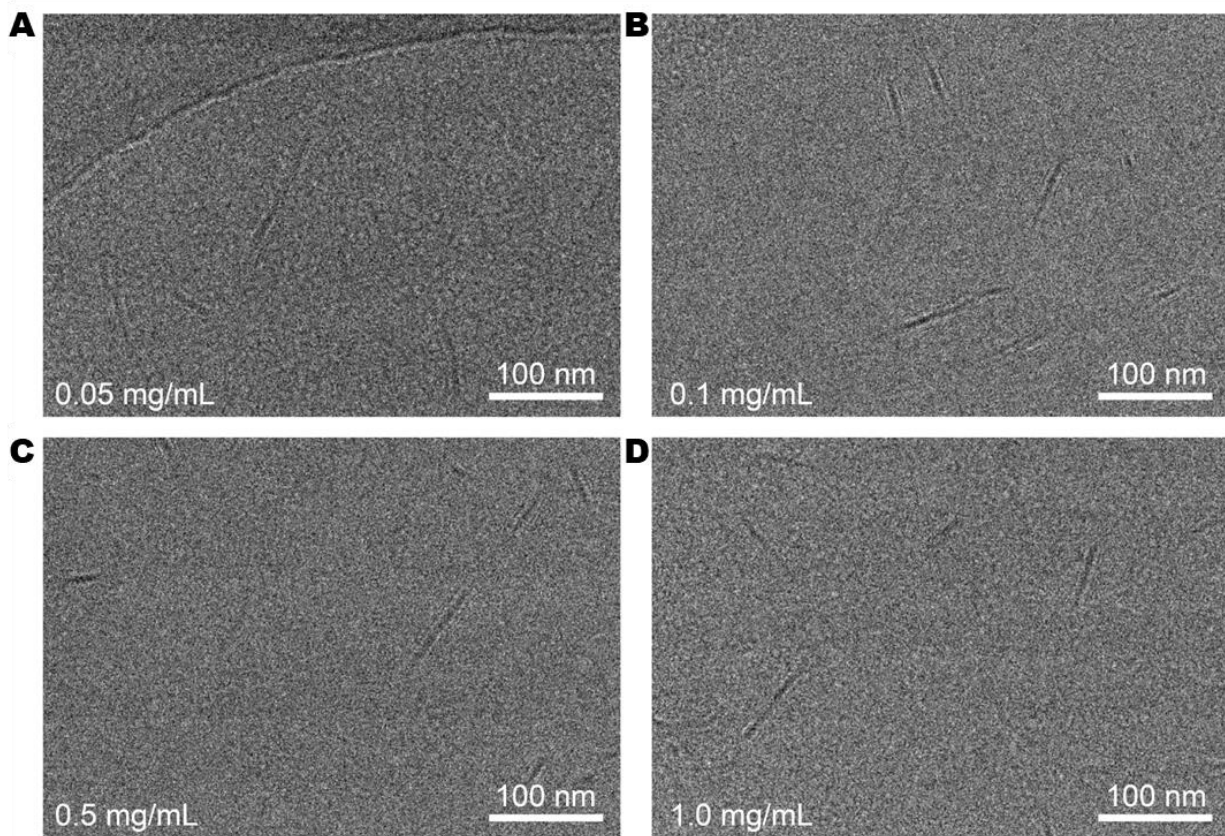


Fig. S1. Cryo-TEM bright-field image of n-PBDF nanoribbons frozen in DMSO. Upon freezing dilute n-PBDF nanoribbon DMSO suspension to low temperatures, ribbon-like structures exhibiting dark contrast and lengths ranging from tens to hundreds of nanometers were observed in the TEM bright-field images.

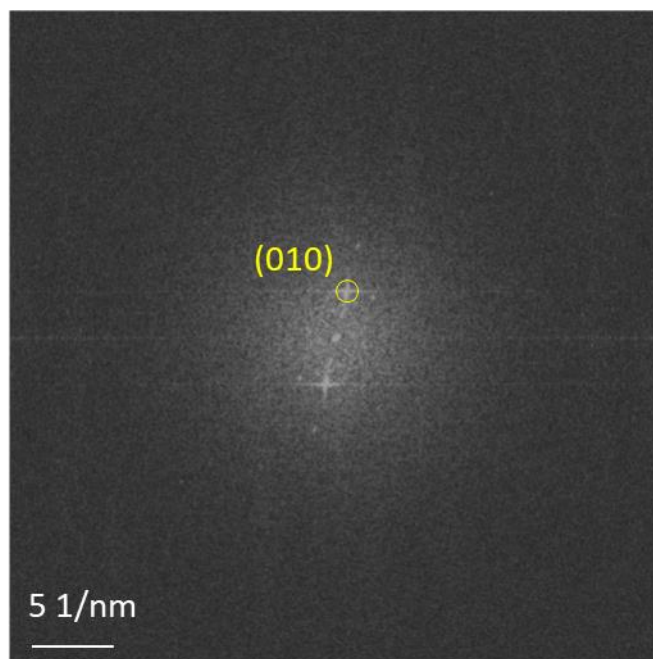


Fig. S2. Fast Fourier Transform (FFT) of the HRTEM image in Fig. 1C. Sharp diffraction spot corresponds to the π - π stacking distance ($d_{(010)}$), 0.34 nm.

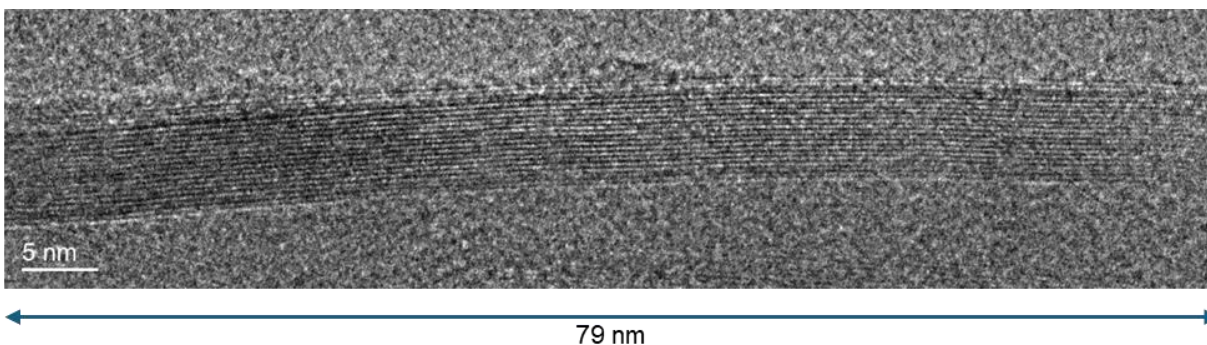


Fig. S3. HRTEM of the long nanoribbon-like structure supported by single layer graphene TEM grid. All of them show clear lattice fringes extending perpendicular to the long axis of the nanoribbon, with an interplanar spacing of 0.34 nm, corresponding to the π - π stacking distance.

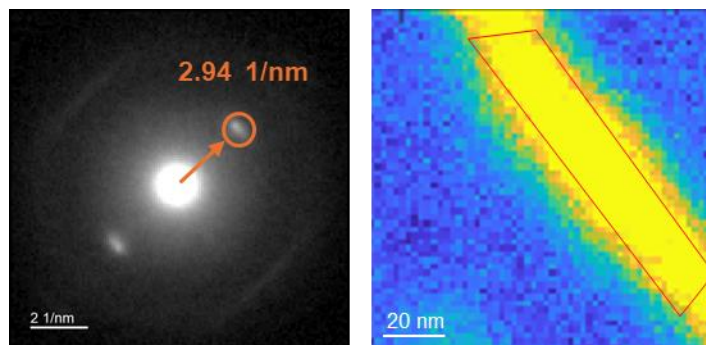


Fig. S4. Electron diffraction pattern collected from the red box region in the right image reconstructed from the diffraction signals in the range of $2.6\text{--}3.2\text{ nm}^{-1}$ via 4D-STEM

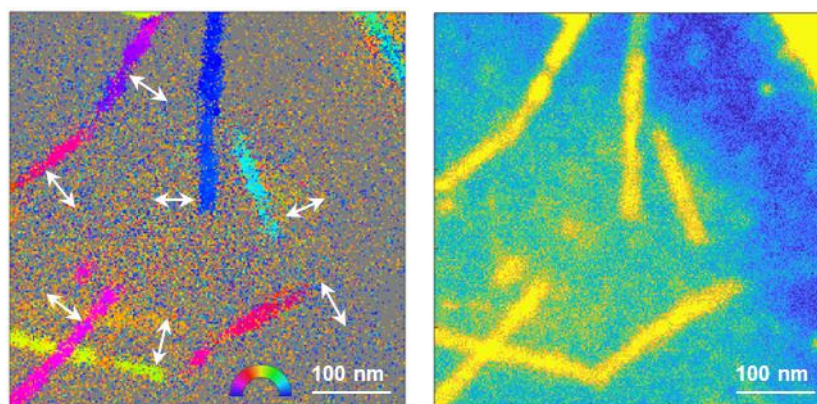


Fig. S5. The π - π orientation map of larger scale 4D-STEM mapping image of nanoribbons.

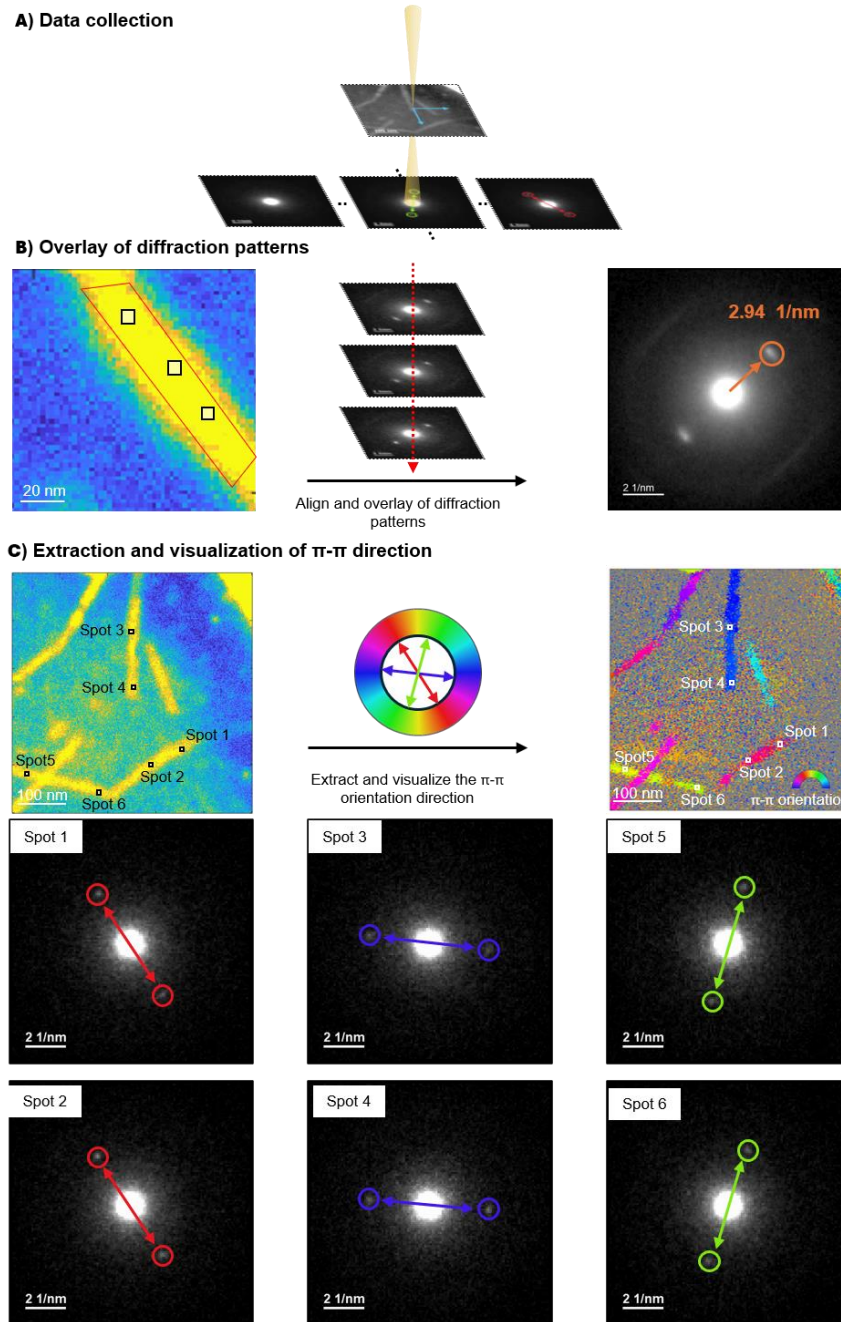


Fig. S6. 4D-STEM data set collecting and analysis. (A) Schematic of 4D-STEM acquisition, which records a diffraction pattern at each scanning position. (B) Schematic of data analysis of 4D-STEM. All diffraction patterns are aligned using the central spot. Then, the diffraction patterns from the red box are summed up to get the overall diffraction of the selected nanoribbon. (C) Schematic of data analysis of 4D-STEM. The chain orientation of each pixel is determined from the π - π diffraction spots and visualized by the color mapping, where each color corresponds to a specific direction according to the color wheel.

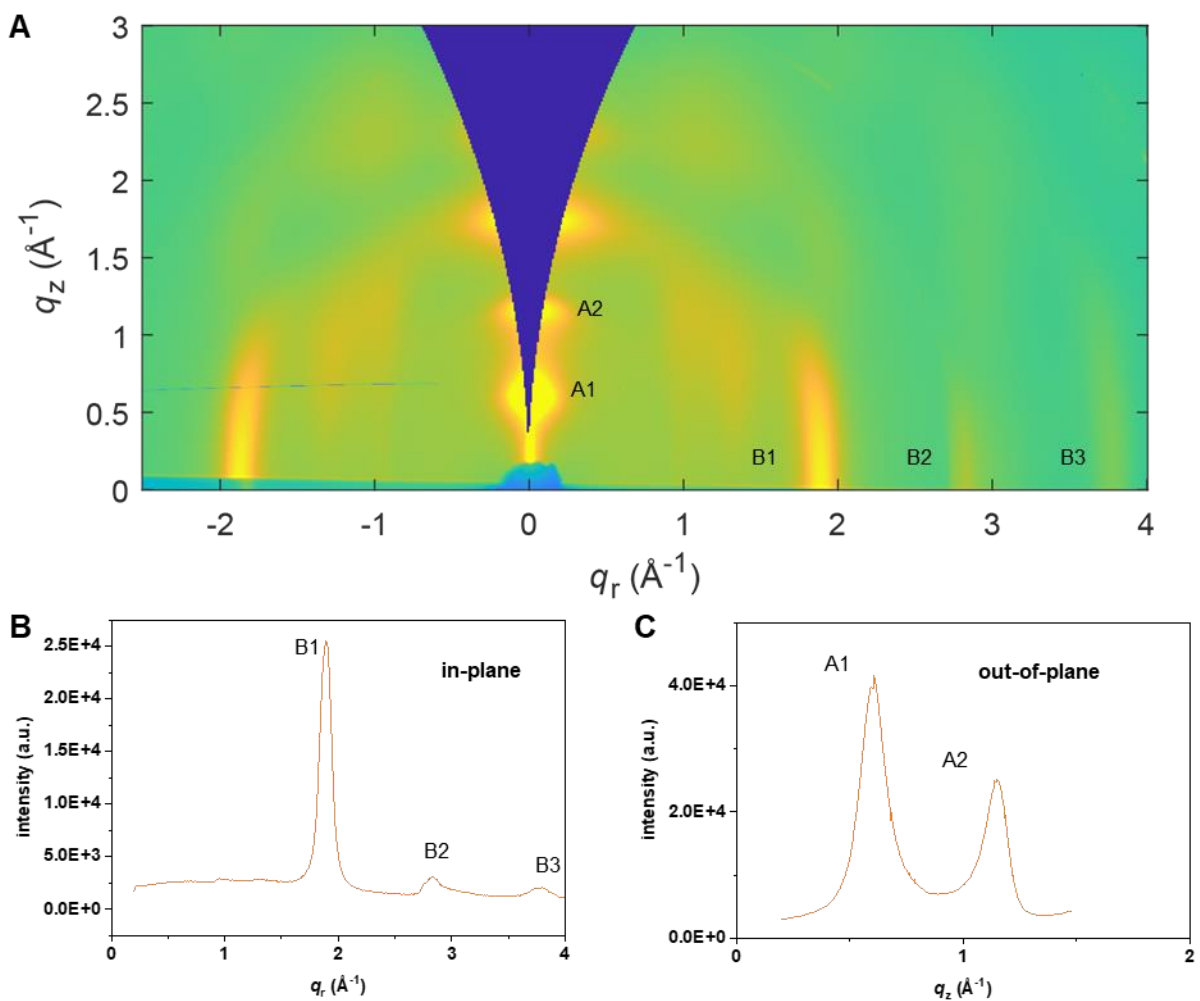


Fig. S7. GIWAXS of n-PBDF thin films composed of stacked nanoribbons formed by spin-coating with about 50 nm thickness. (A) 2D GIWAXS. (B) The out-of-plane profile. (C) The in-plane profile.

The d -spacings and corresponding hkl assignments for the diffraction peaks are summarized in Table S1.

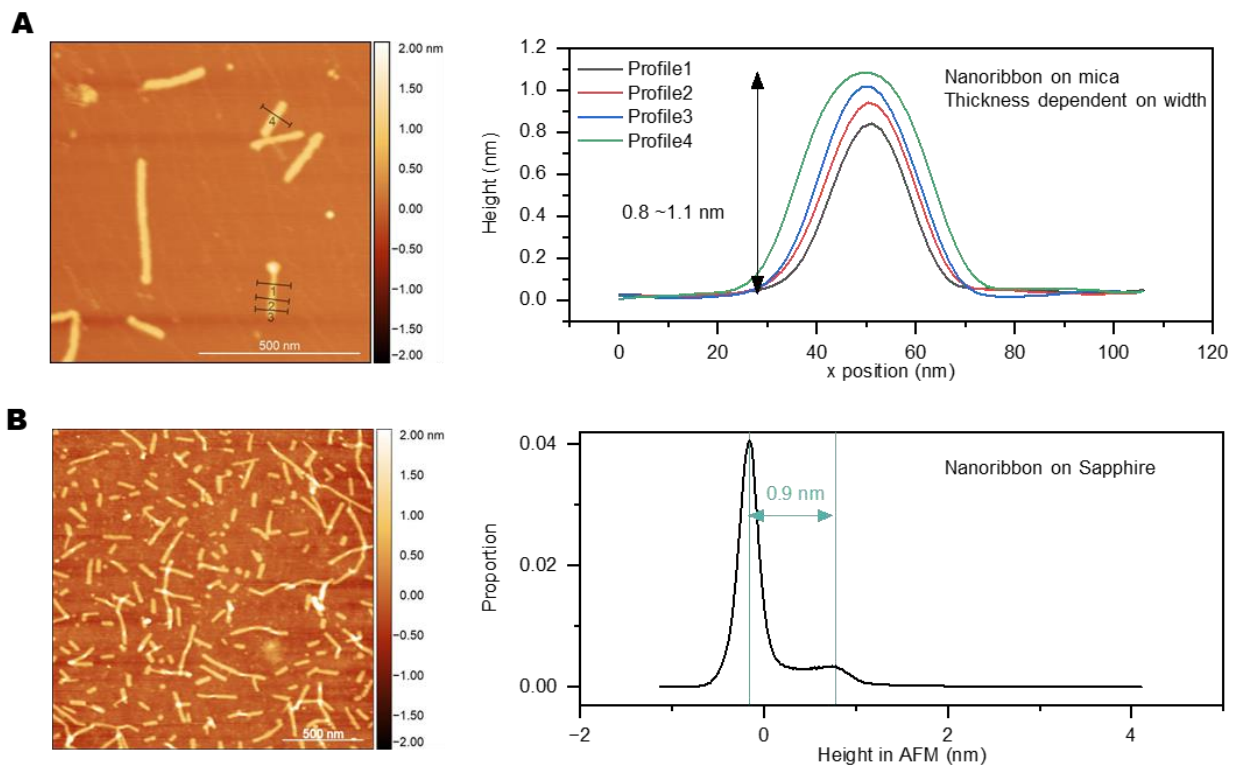
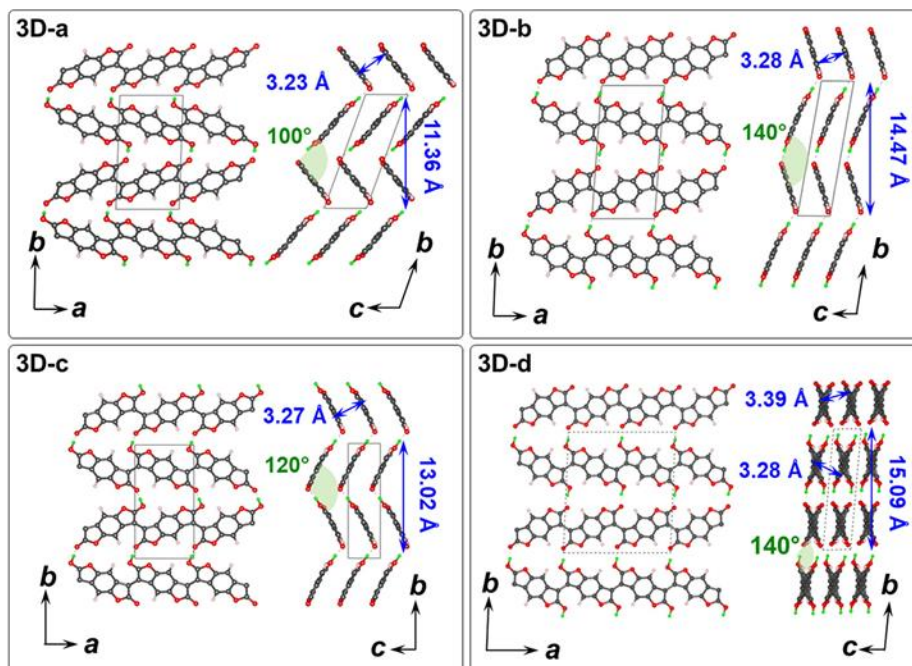


Fig. S8. Varied nanoribbon thicknesses with different widths and on different substrates. (a) Nanoribbons on mica with different widths show different thicknesses, varied from 0.8 nm to 1.1 nm. (b) Nanoribbons on sapphire substrate show average thickness around 0.9 nm.

A Simulated lattice parameter of n-PBDF in literature



B GIWAXS revealed lamellar thickness of n-PBDF nanoribbon

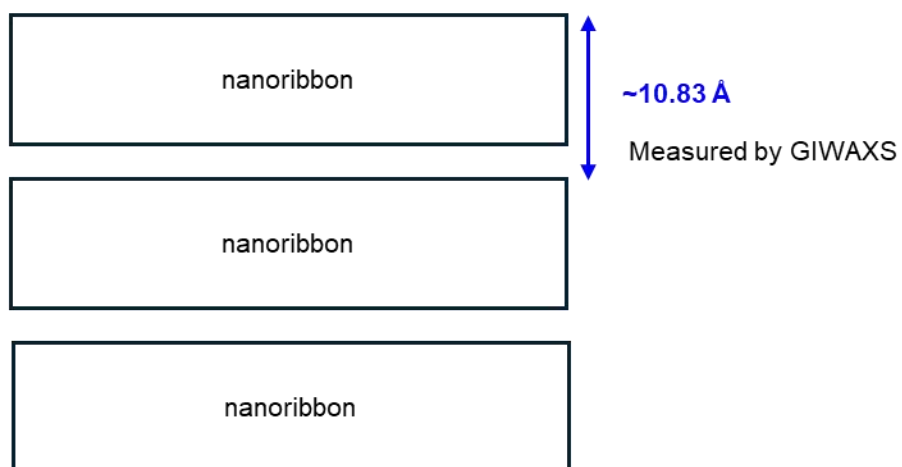


Fig. S9. Structural characteristics of the nanoribbon in the thickness direction. (A) Calculated lattice parameter of n-PBDF in 3D structure reported in literature.⁽¹³⁾ The lamellar packing distance composed of two chains ranges from 11.30 to 15.10 Å. (B) Measured packing distance of nanoribbon in lamellar direction via GIWAXS.

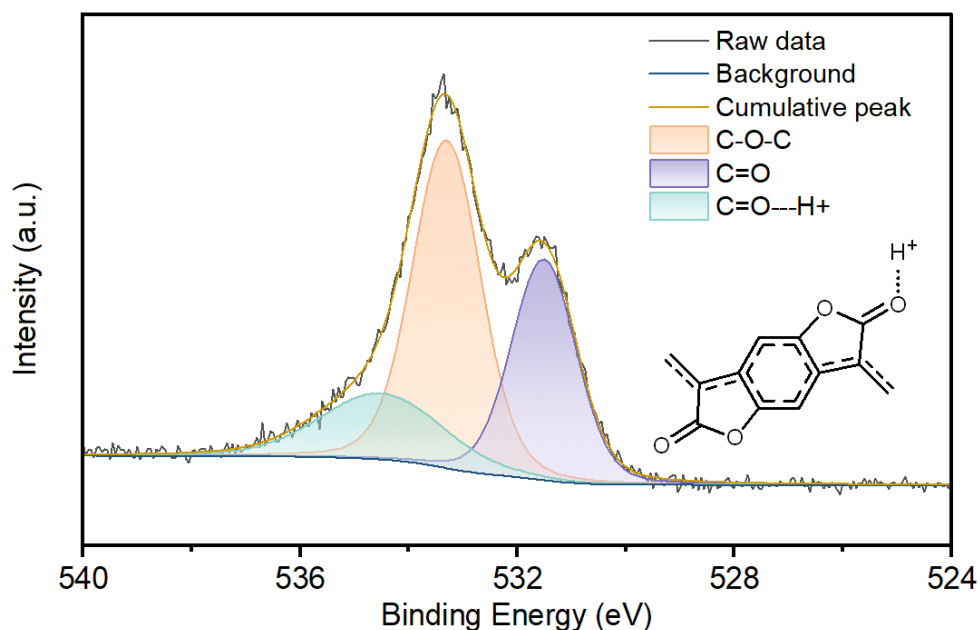


Fig. S10. Doping level of n-PBDF nanoribbons assessed from X-ray photoelectron spectroscopy (XPS). The doping level is estimated to be 73%, derived from the O 1s XPS spectrum by deconvoluting the peaks into different chemical states, including C–O–C (533.3 eV), C=O (531.5 eV), and protonated carbonyl (C=O···H⁺) (534.5 eV). The area of the protonated carbonyl peak corresponds to the number of doped repeat units. The combined area of the carbonyl-related peaks (C=O + C=O···H⁺) is approximately equal to that of the C–O–C peak, half of either of these contributions represents the total number of repeat units. The doping level is then defined as the ratio between the doped repeat units and the total number of repeat units.

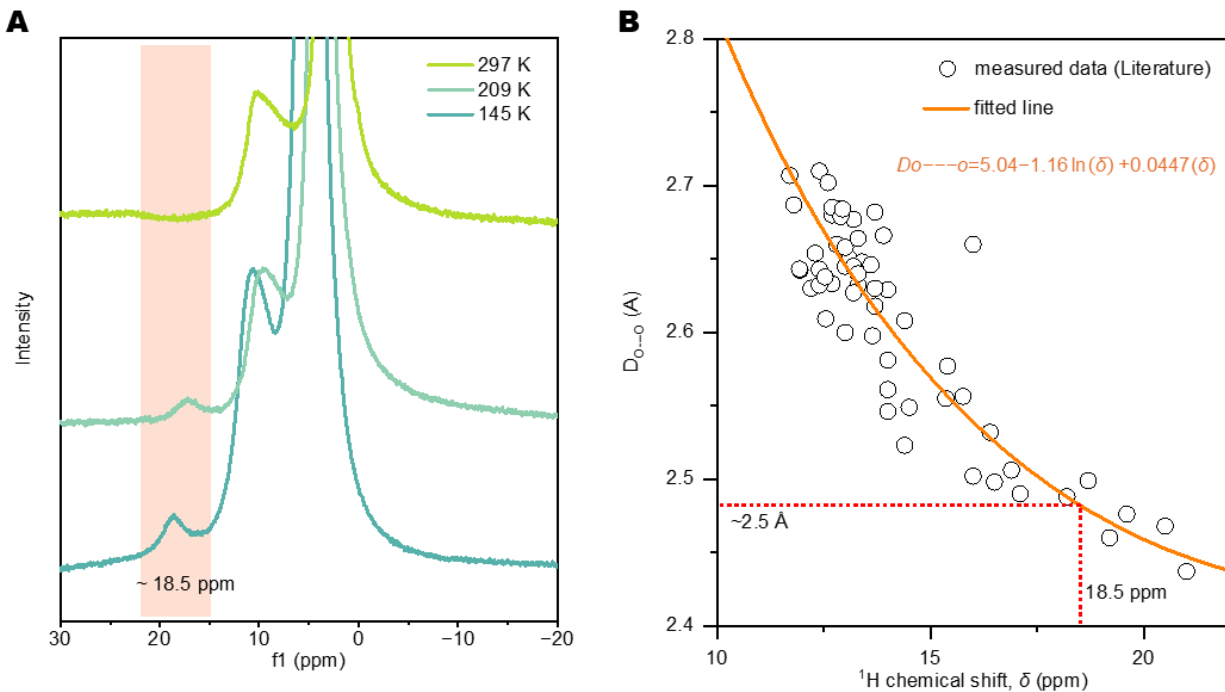


Fig. S11. Temperature varied ^1H solid-state NMR (ssNMR) spectra of the n-PBDF and the analysis of the H-bonding length. (A) ^1H ssNMR spectra of n-PBDF under 145 K, 209 K, 297 K. (B) Unfilled circles show ^1H chemical shifts (δ) from ssNMR and O-H...O H-bonding distances ($D_{\text{O}\cdots\text{O}}$) from X-ray diffraction (Data are from reference (17, 34)). The orange curve is fitted equation from reference (16, 35).

In the the ^1H NMR spectra, three peaks are observed. The peak at ~ 3.5 ppm can be attributed to residual DMSO or adsorbed water. The peak at ~ 10 ppm is likely associated with protons on the backbone, where intramolecular hydrogen bonding induces a low-field shift to approximately 10 ppm. And the peak at ~ 18.5 ppm corresponds to the proton sandwiched between carbonyl oxygens on two adjacent chains. From the empirical equation of δ and $D_{\text{O}\cdots\text{O}}$:

$$D_{\text{O}\cdots\text{O}} = 5.04 - 1.16 \ln(\delta) + 0.0447(\delta)$$

the chemical shift of 18.5 ppm measured in ^1H NMR of n-PBDF should relate to a 2.5 Å O-H $\cdots$ O distance.

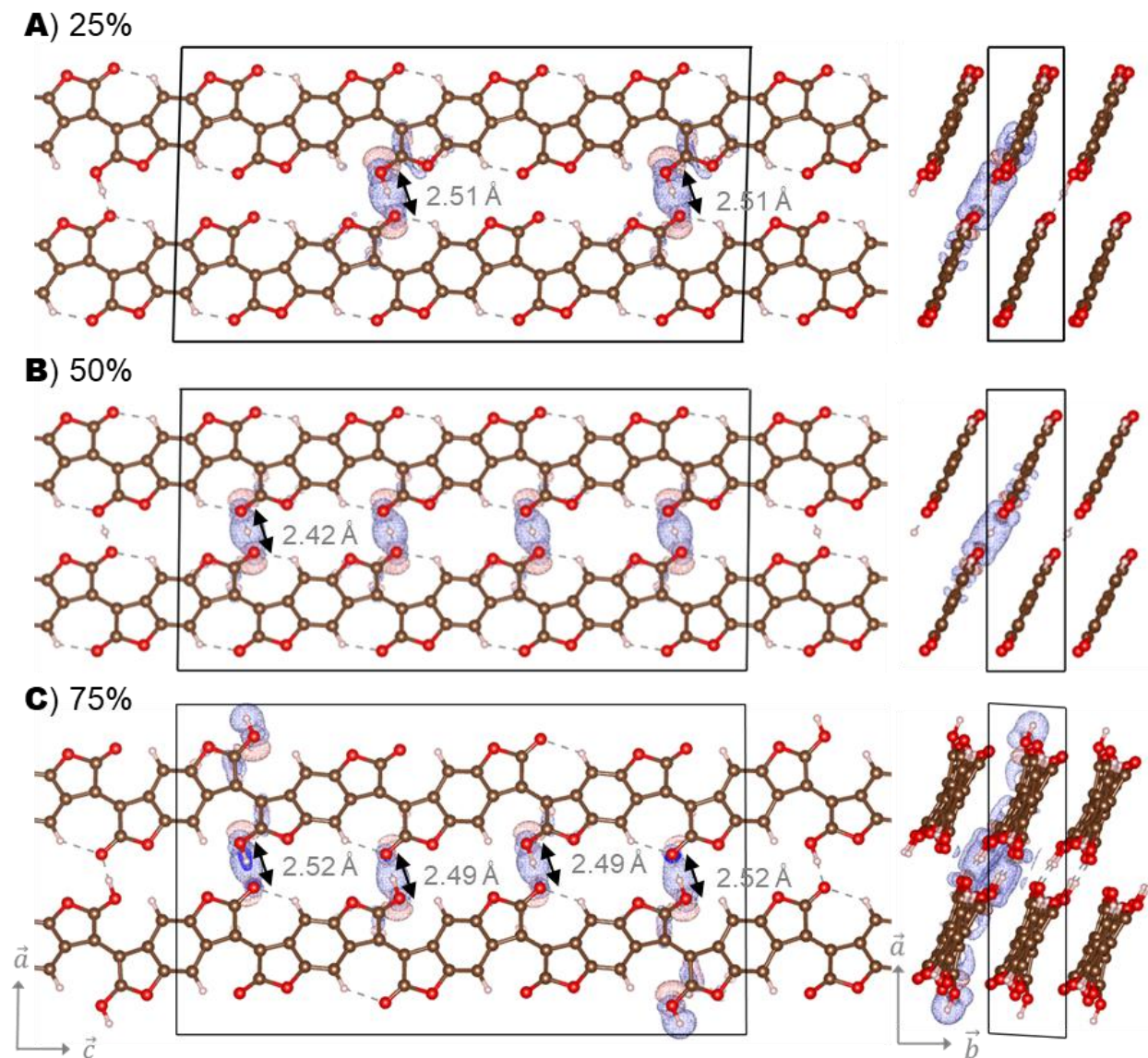


Fig. S12. Thermodynamically preferred packing motifs of n-PBDF nanoribbon at doping levels of (A) 25%, (B) 50% and (C) 75%. The isosurfaces display the charge density difference ascribed to protonation, where isovalue of $0.004 \text{ e}/\text{\AA}^3$ is taken. Purple and pink colors denote electron accumulation and depletion, respectively. The distances correspond to hydrogen bond donor-acceptor distance.

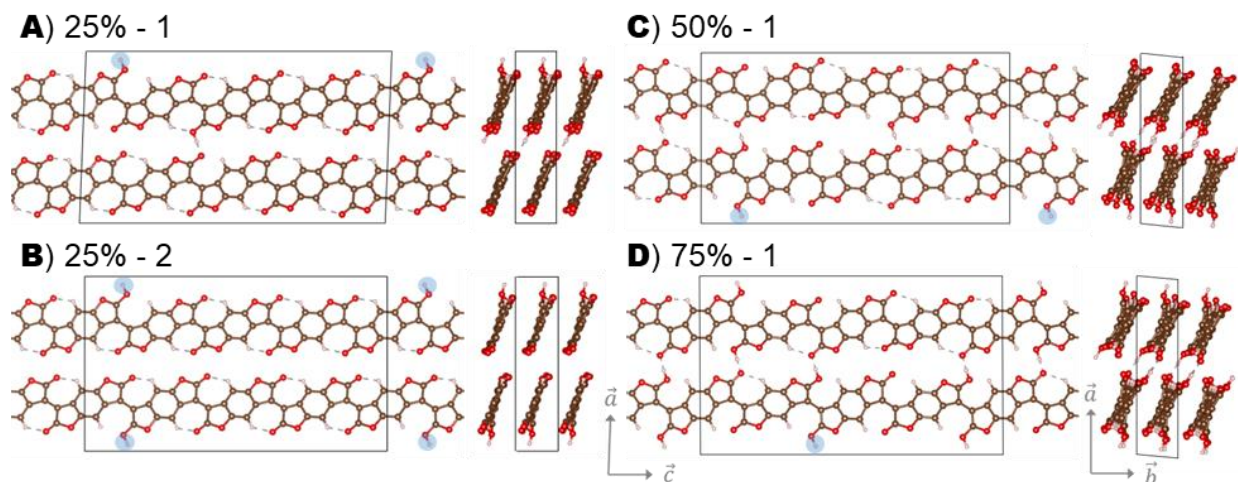


Fig. S13. Packing motifs of n-PBDF at doping levels of (A-B) 25%, (C) 50% and (D) 75%, where one or two protons are artificially moved to the external sides. Blue shaded regions highlight the protonation distribution change against packing motifs shown in Fig. S12.

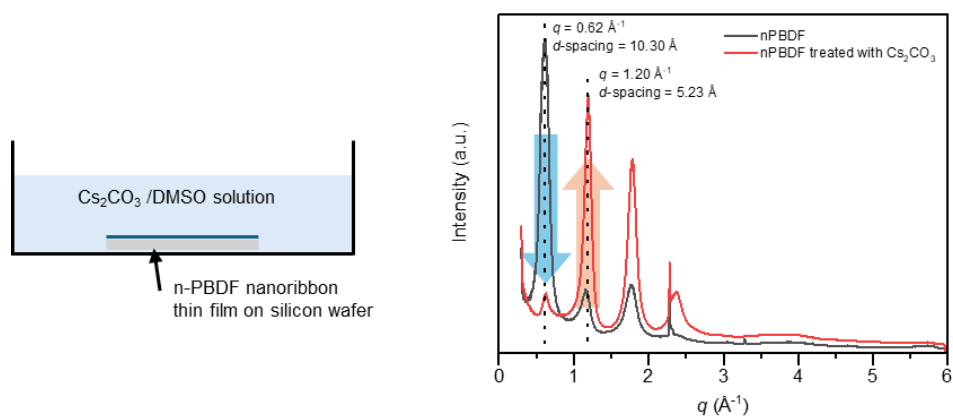


Fig. S14. The chain arrangement of n-PBDF nanoribbon with base treatment. The out-of-plane GIWAXS profiles of n-PBDF thin films before and after treatment with a Cs_2CO_3 /DMSO solution show that the scattering peak corresponding to a d -spacing of $10.30 \text{ \AA}$ (representing the nanoribbon thickness, d_{100}) becomes weaker, accompanied by an enhancement of the peak corresponding to approximately half of that spacing ($5.23 \text{ \AA}$, d_{200}), indicating the structural arrangement in the duplex unit cell. The unit cell symmetry changes drive by base treatment suggests that the repeated unit of the nanoribbon thin films should be composed of at least two chains, thus supporting the H-bonded duplex as the basic unit of the nanoribbon.

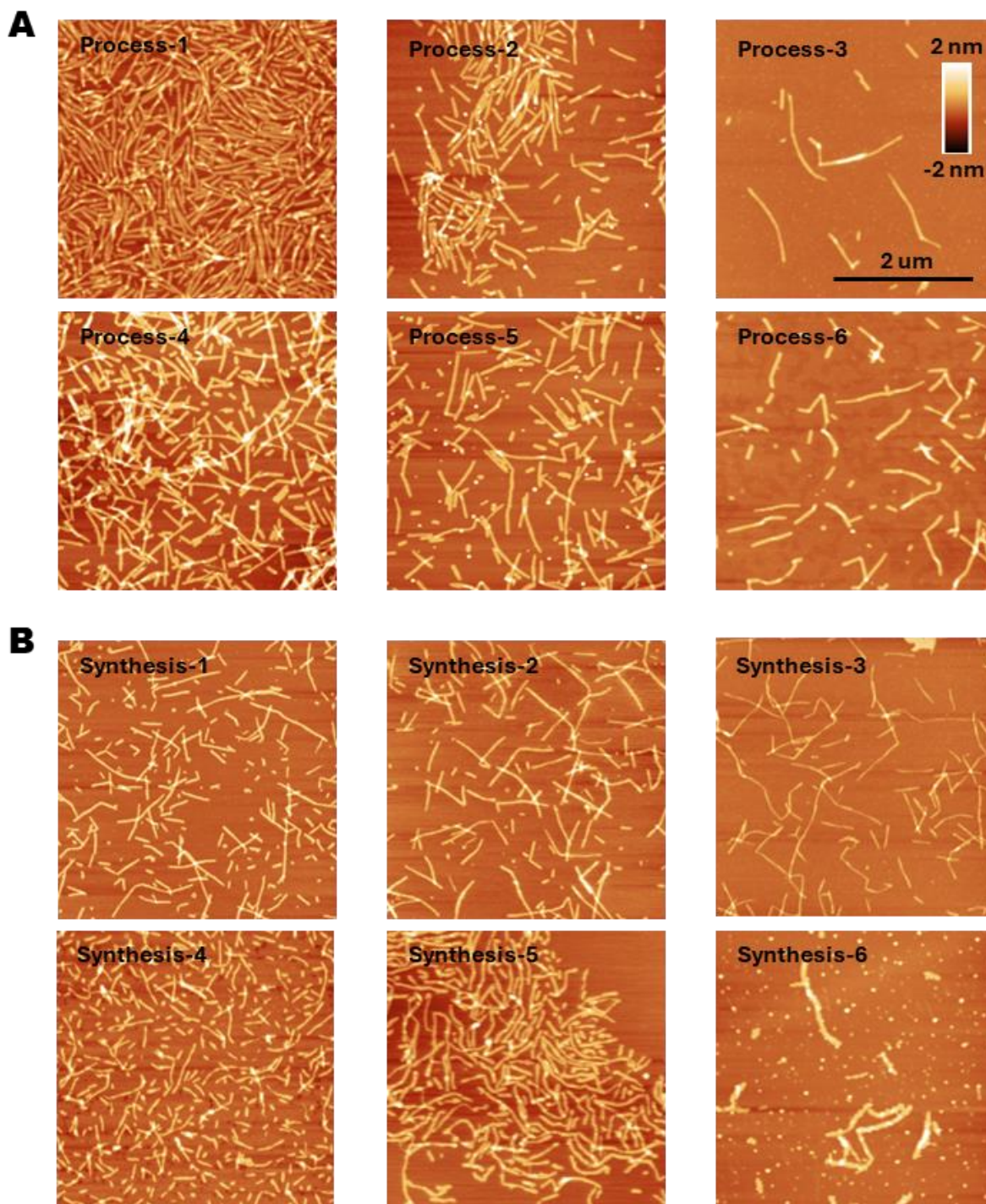


Fig. S15. AFM image of n-PBDF nanoribbon prepared with different conditions. (A) AFM images of n-PBDF nanoribbon prepared via different processing conditions corresponding to Table S3. (B) AFM images of n-PBDF nanoribbon prepared via different synthesis conditions corresponding to Table S4.

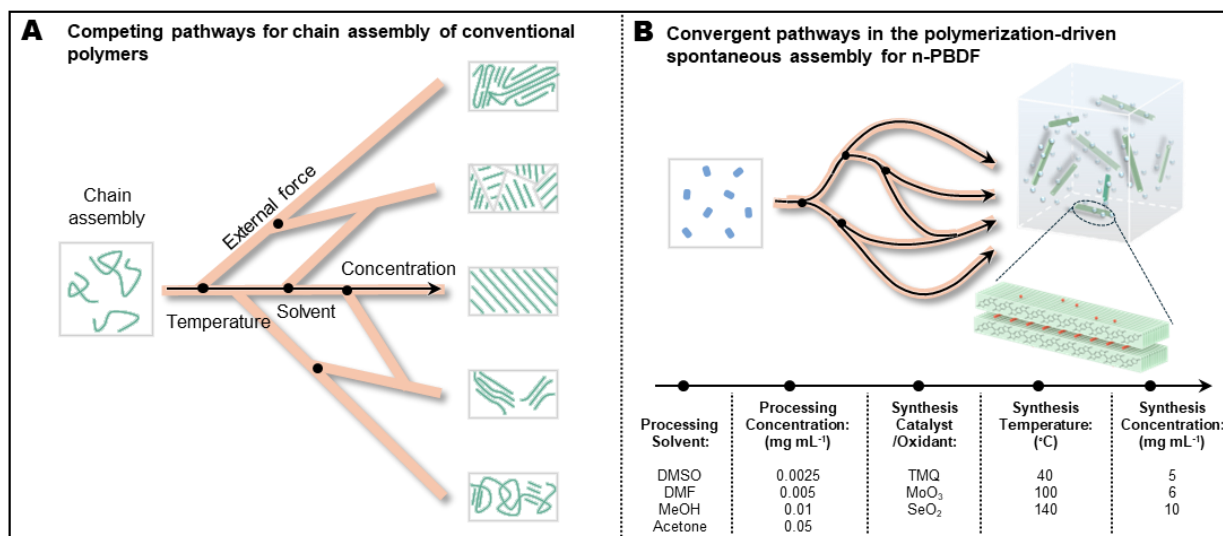
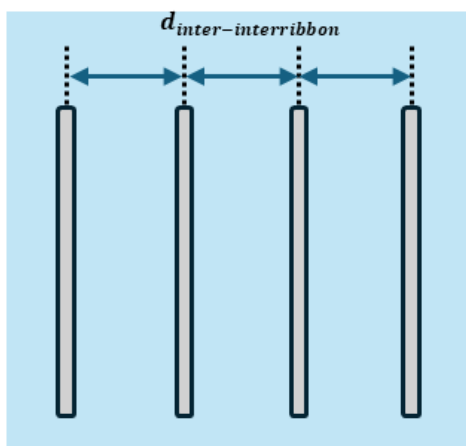


Fig. S16. Spontaneous formation of n-PBDF nanoribbons with long-range order. (A) Competing pathway for conventional polymer to form ordered structure. (B) Spontaneous pathway for n-PBDF to form long-range ordered structure. In conventional polymer systems, the formation of long-range ordered structures is typically highly sensitive to processing conditions and often limited to a narrow experimental window. In contrast, n-PBDF nanoribbons formed consistently across all conditions examined in Fig. S16, highlighting the robust and spontaneous nature of the PSA process.

❑ **Scattering peak in SAXS**



Electrostatic repulsion lead to the nanoribbons to disperse at a certain 'inter-ribbon' distance

$$d_{inter-ribbon} = \frac{2\pi}{q_{max}}$$

❑ **Concentration dependence**

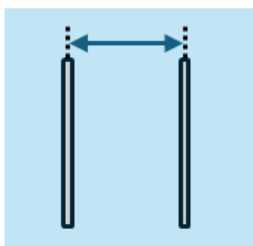
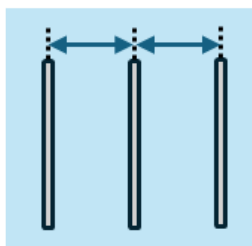
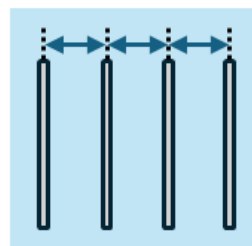


Fig. S17. Explanation for solution SAXS data. In a polyelectrolyte solution or suspension, the ions associated with the polyelectrolyte chains can become solvated, forming charged polymer chains or nanoparticles surrounded by solvation shells of oppositely charged counterions. Electrostatic correlations (repulsive interactions) between these solvation shells lead to the formation of a characteristic correlation distance (d) between them. This distance gives rise to a characteristic scattering peak in SAXS, where the position of the peak max (q_{max}) satisfies the relation $q_{max} = 2\pi/d$. As the concentration of the polyelectrolyte increases, meaning a greater number of chains or nanoparticles are present in the solution, d decreases, resulting in a shift of q_{max} toward larger values.

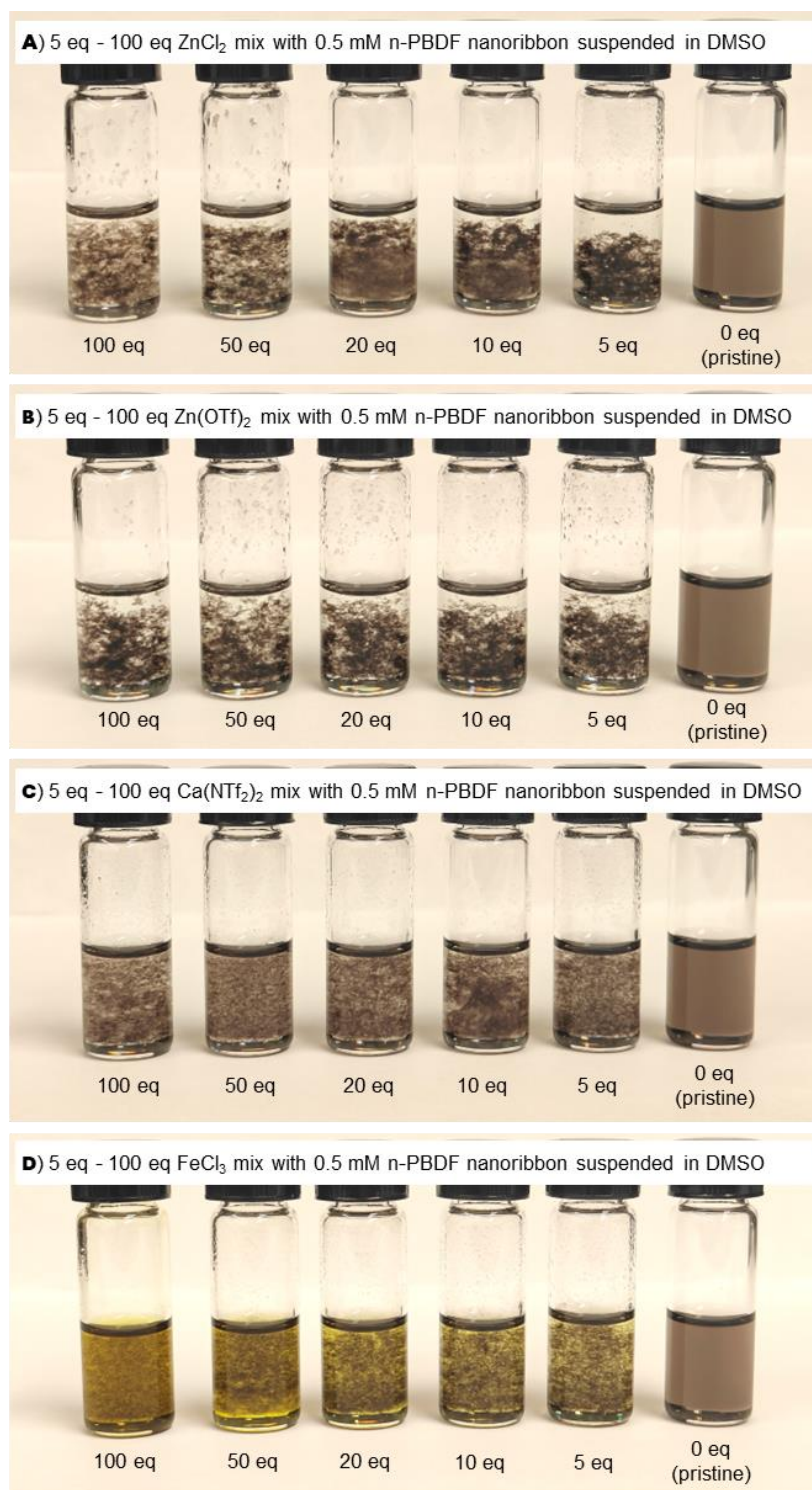


Fig. S18. Salting-out of n-PBDF nanoribbon by mixing with (A) Zinc chloride (ZnCl_2), (B) Zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$), (C) Calcium(II) bis(trifluoromethanesulfonimide) ($\text{Ca}(\text{NTf}_2)_2$), (D) Iron(III) chloride (FeCl_3) in DMSO.

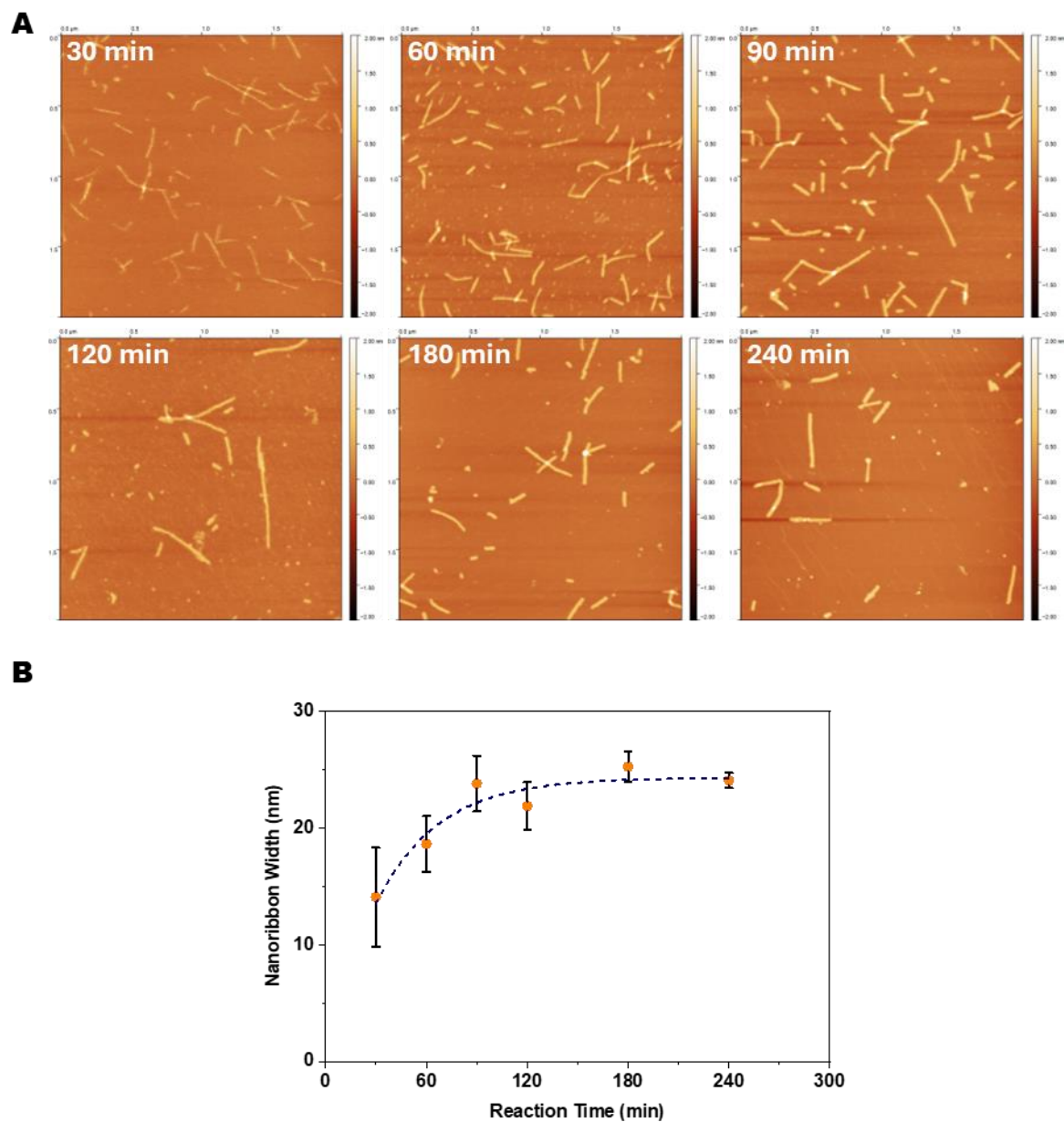


Fig. S19. Nanoribbon morphology evolution with reaction time (Conditions: 10 mg mL⁻¹ BDF in DMSO, 2eq TMQ, 100 °C, sealed in N₂). (A) AFM images of nanoribbons sampled at different reaction times (30, 60, 90, 120, 180, 240 min). (B) Evolution of averaged nanoribbon width with reaction times.

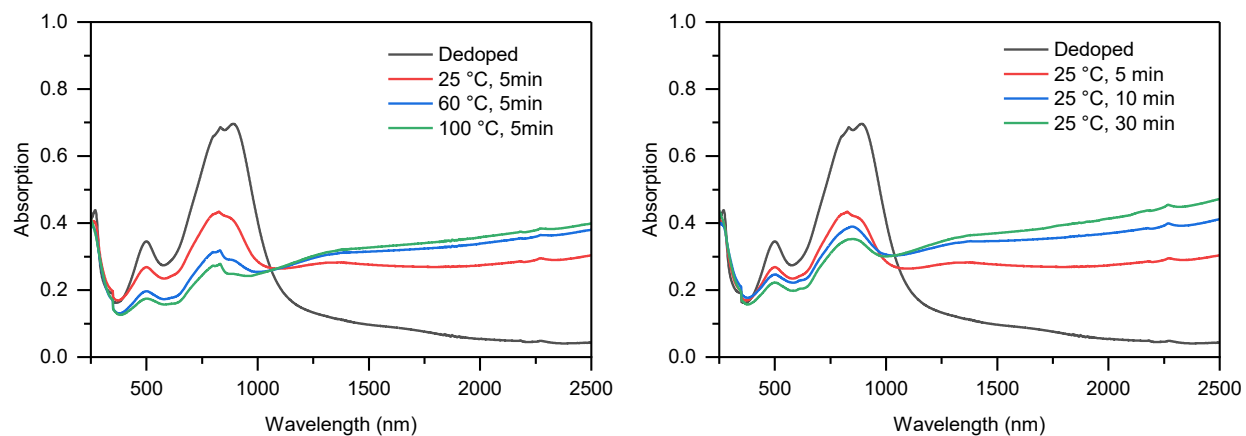


Fig. S20. UV-vis-NIR spectra of dedoped n-PBDF (neutral) thin film before and after treated with 15 mg mL^{-1} BDF/DMSO solution under different temperatures and treating times. The doping effect of BDF on dedoped n-PBDF becomes more pronounced with increasing time or elevated temperature.

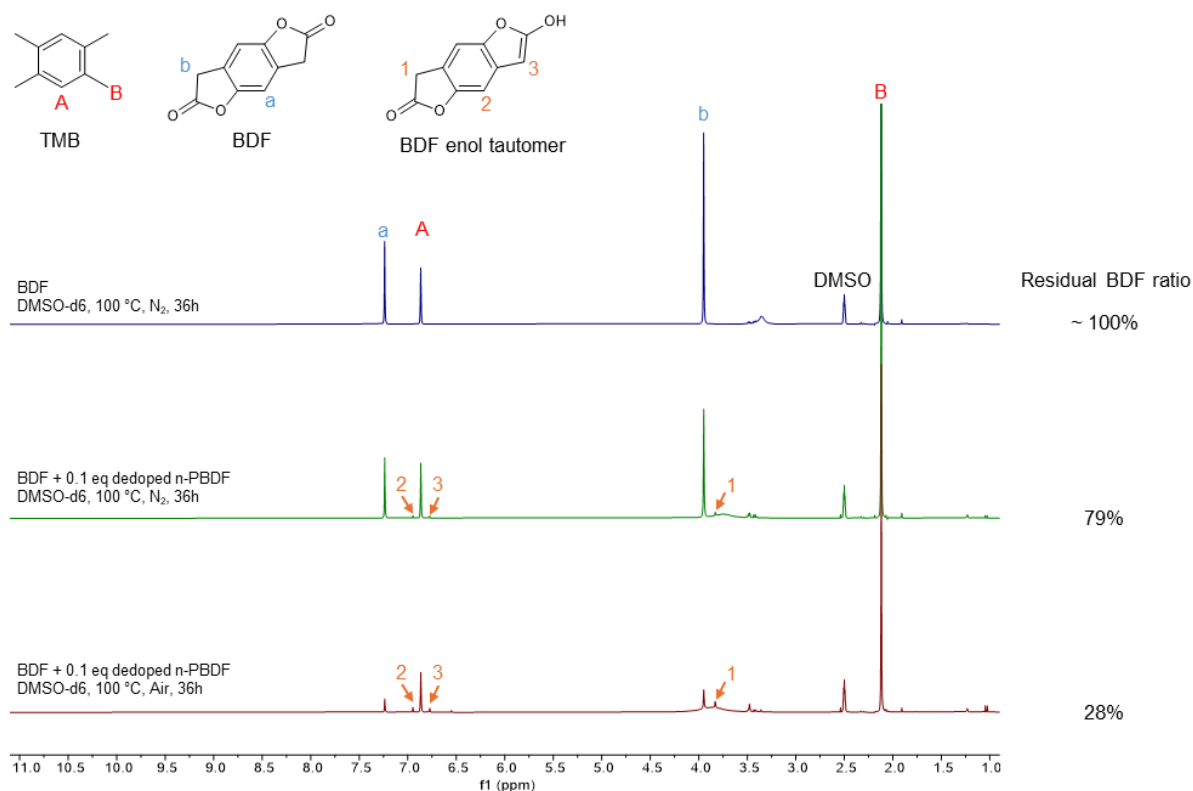


Fig. S21. ¹H NMR spectra of the mixture of BDF and dedoped n-PBDF in DMSO-d₆, heating at 100 °C in N₂ or Air for 36h.

The consumption of BDF upon mixing with dedoped n-PBDF and heating at 100 °C was confirmed by the ¹H NMR spectrum. When a BDF/DMSO-d₆ solution was mixed with 0.1 eq dedoped n-PBDF powder and heating at 100 °C for 36 h in N₂ glovebox, the residual BDF ratio decreased to 79%. Together with the enhanced absorption in the NIR region of the UV-vis-NIR spectrum (Fig. 3F, this result indicates the conversion of BDF into n-PBDF. When the reaction was carried out in air, where O₂ may act as oxidant and facilitate the oxidative polymerization process, the residual BDF further decreased to 28%, accompanied by a stronger NIR absorption in UV-vis-NIR spectrum.

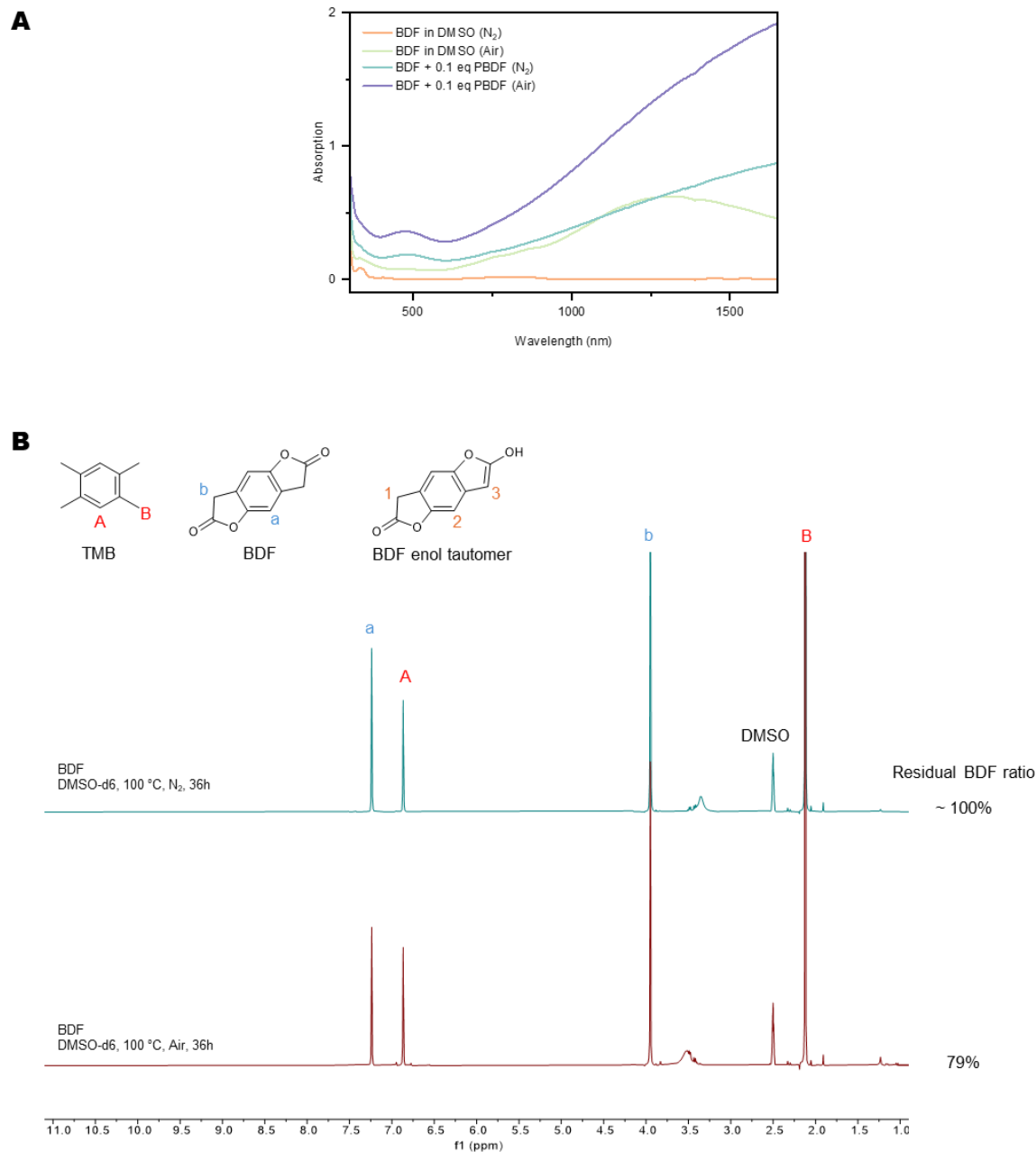


Fig. S22. ^1H NMR spectrum and UV-vis-NIR spectrum of BDF in DMSO- d_6 , heating at 100 °C in Air for 36h.

Direct heating of BDF in air also leads to its consumption. According to the absorption spectra, it is converted into species exhibiting absorption in the 1000–1650 nm range, although the effect is much less pronounced than that observed in the presence of dedoped n-PBDF.

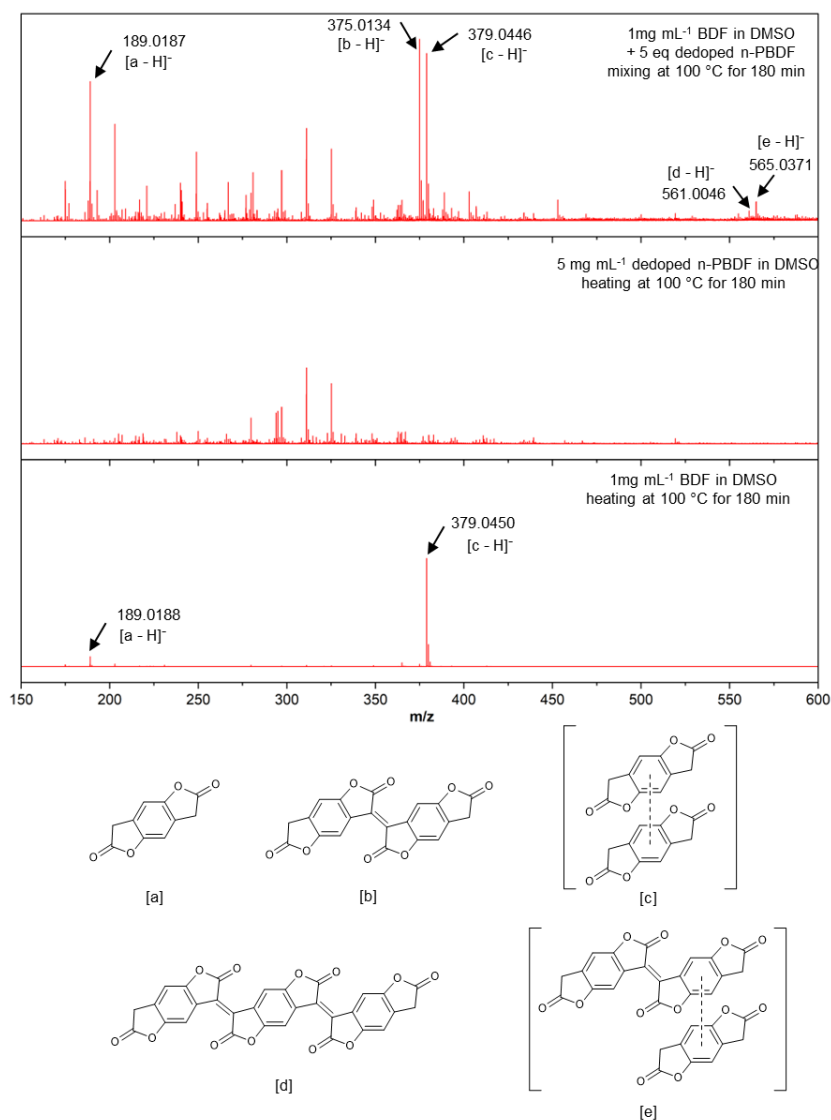


Fig. S23. Negative ion EIS-MS of the mixtures of BDF and dedoped n-PBDF.

The ion products with m/z of 375.0134, 379.0446, 561.0046, 565.0371 formed in BDF and dedoped n-PBDF mixture imply the formation of BDF dimer, charge transfer complex (CTC) of two BDF monomers, BDF trimer, and CTC of BDF monomer and BDF dimer, respectively. In the control group containing only dedoped n-PBDF, these ion products were barely observed, indicating that their formation was not induced by dedoped n-PBDF. In the control group containing only BDF, a strong CTC of two BDF monomers was observed. The difference between the products of the BDF /dedoped n-PBDF mixture and those of pure BDF suggests that BDF have a strong tendency to form CTCs with BDF itself or its oligomer. The presence of dedoped n-PBDF can promote the oligomerization of BDF, such as the formation of dimers and trimers.

Ordered structure formation pathway

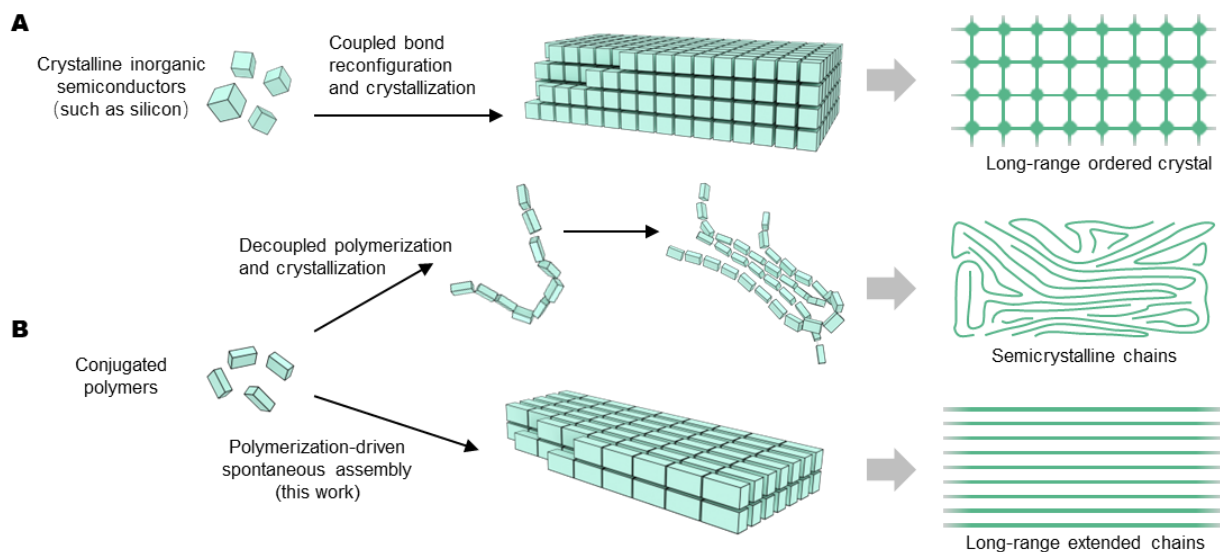


Fig. S24. Schematic of structural order formation of crystalline inorganic semiconductors and conjugated polymers. (A) The formation of long-range crystalline state of inorganic semiconductors such as silicon. (B) The two-step formation of semicrystalline states (top) and one-step synthesis of long-range crystalline states (bottom, this work) of conjugated polymers.

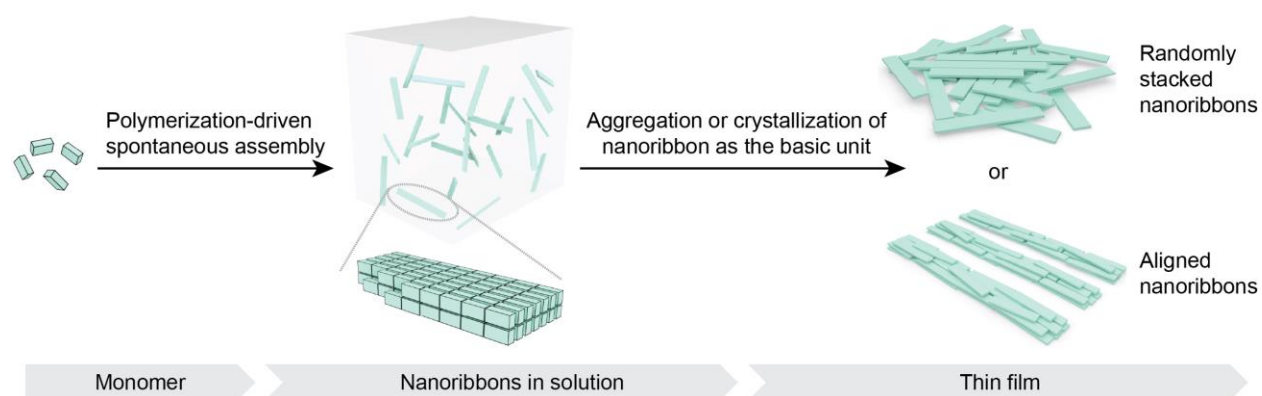


Fig. S25. Schematic illustration of the two-level aggregations for nanoribbon formation and the stacking of nanoribbons. Notably, unlike many polymer nanowires or nanoribbons, where the fast growth direction is typically along the interchain stacking direction, while the fast growth direction of n-PBDF nanoribbons in the PSA process corresponds to the chain axis.

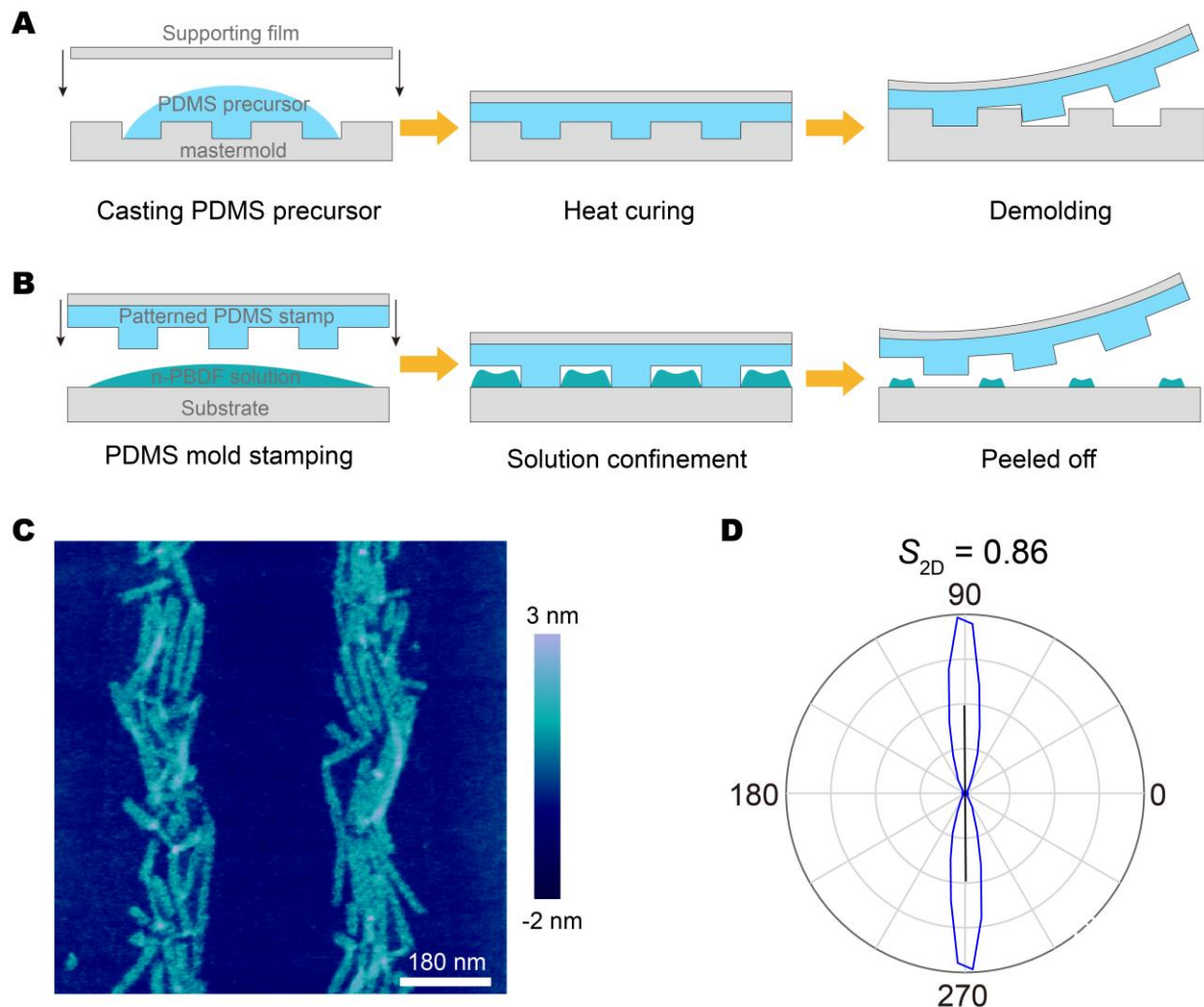


Fig. S26. Preparation process of oriented n-PBDF nanoribbon thin film. (A) Schematic illustration of the fabrication process for PDMS templates. (B) Schematic illustration of oriented n-PBDF nanoribbons thin film fabricated using a PDMS-templated nano-confinement method. (C) Orientation distribution extracted from the AFM image. The radial axis represents the number of pixels corresponding to a given orientation. The black diametrical line marks the average orientation, and the full-frame orientational order parameter (S_{2D}) is displayed at the top.

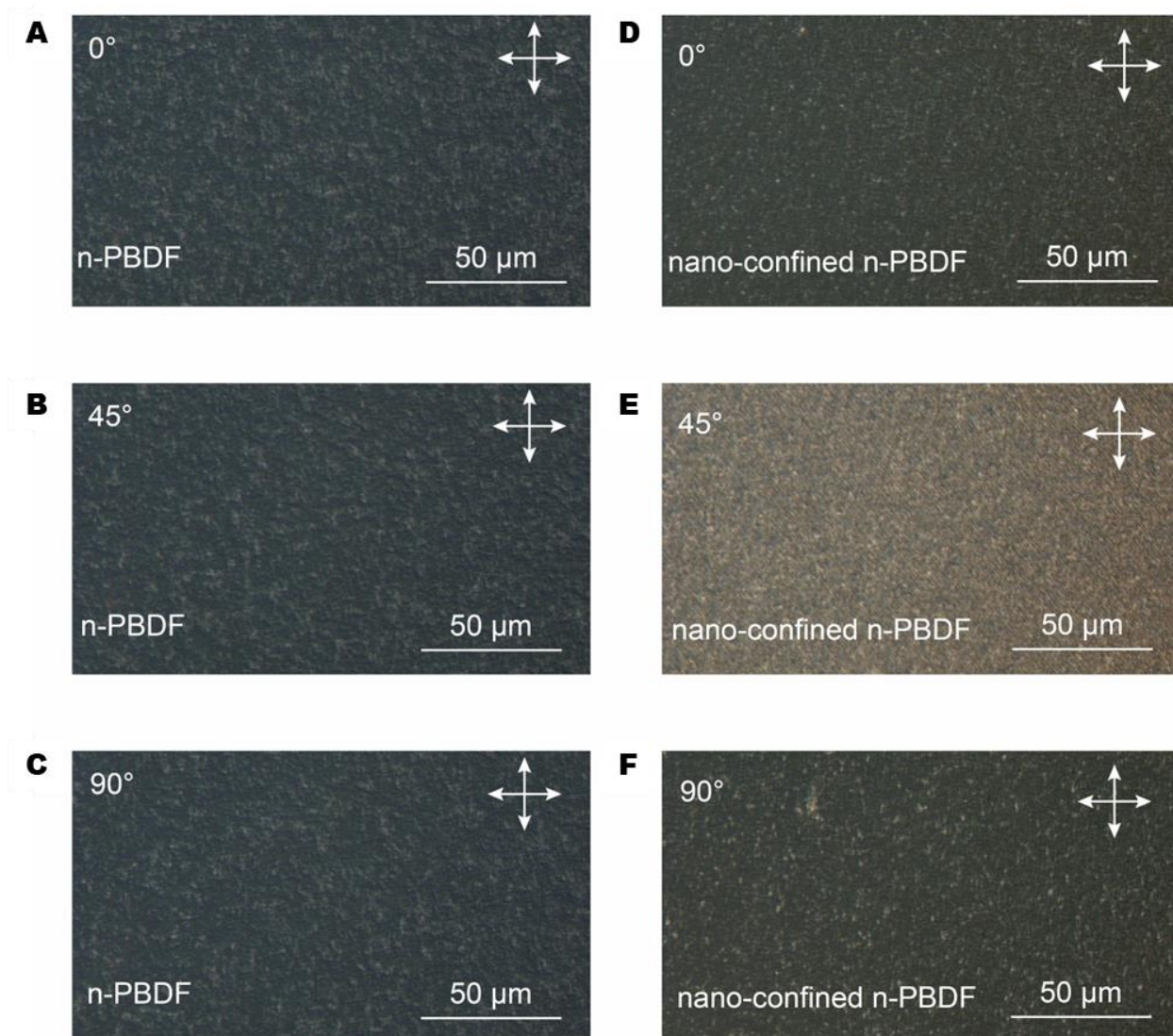


Fig. S27. Polarized optical micrographs of n-PBDF and aligned nano-confined n-PBDF films. (A–C) Polarized optical micrographs of spin-coated n-PBDF films recorded at 0°, 45°, and 90°, showing nearly identical brightness in all orientations, indicative of isotropic morphology. (D–F) Polarized optical micrographs of aligned nano-confined n-PBDF films prepared via the templated confinement method. The films appear dark at 0° and 90°, while enhanced brightness and fine stripe features are observed at 45°, confirming anisotropic alignment. Scale bar: 50 μm .

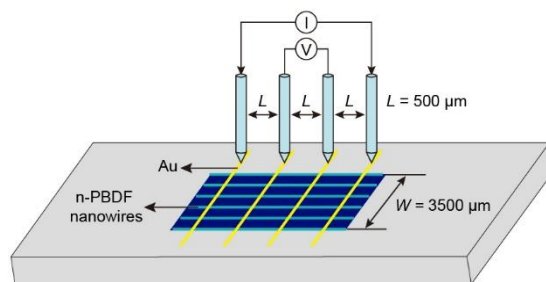


Fig. S28. Schematic illustration of the four-probe conductivity measurement on aligned n-PBDF nanowire films. Aligned n-PBDF nanowires are patterned between Au electrodes, forming a conducting channel with length $L=500\ \mu\text{m}$ and width $W=3500\ \mu\text{m}$. Four collinear probes are placed with equal spacing in a symmetric same-side configuration. Current is sourced through the outer probes, while the voltage drop is measured between the two inner probes.

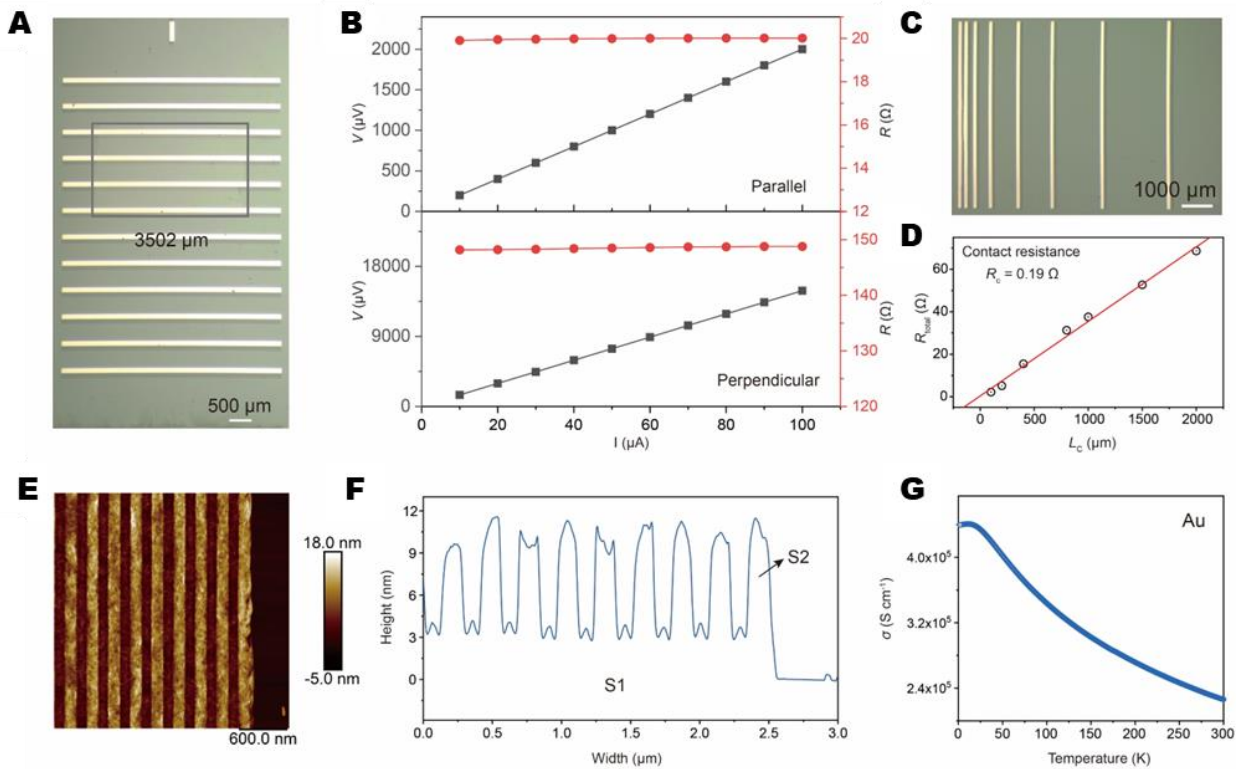


Fig. S29. Four-probe measurement of the electrical conductivity of nano-confined n-PBDF nanoribbons. (A) Optical image of the patterned nano-confined n-PBDF thin film (in the rectangular frame) with deposited Au electrodes. (B) Resistance of the n-PBDF nanoribbon film measured under different applied currents, with the conductive pathways oriented parallel and perpendicular to the nanoconfined channel orientation. (C) Optical image of the device used for contact-resistance measurements via the transmission line method (TLM). The TLM measurements were conducted to estimate the metal/film contact resistance. The contact resistance (R_C) between the Au electrodes and the polymer film was extracted using the relation: $R_{total} = R_{channel} + 2R_C = \frac{L_C}{\sigma d W_C} + 2R_C$, where L_C is the channel length, d is the film thickness, and W_C is the channel width. (D) Linear fitting yields a contact resistance of 0.19 Ω, which is much smaller than the channel resistance, ensuring the accuracy of the conductivity measurements. (E) AFM image of the nano-confined n-PBDF nanoribbons. (F) Line-cut profile corresponding to the AFM image in panel E. To ensure intimate contact between nanoribbons within the conductive channel, the total film thickness was maintained at ~11 nm due to experimental limitations. Under this template dimension, a thin unconfined n-PBDF base layer remains beneath the nano-confined nanoribbon array. The base layer appears nearly isotropic in-plane, whereas the nano-confined nanoribbons form continuous transport pathways predominantly along the channel direction. Accordingly, a parallel-resistor model was applied to separate the electrical contributions from the base layer and the nano-confined nanoribbon layer. Specifically, assuming the cross-sectional

areas of the bottom unconfined layer and the top nano-confined region are S_1 and S_2 , respectively, the total resistance satisfies $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$, where $R_1 = \frac{L}{\sigma_1 S_1}$, and $R_2 = \frac{L}{\sigma_2 S_2}$. In this model, the base layer contributes isotropically to in-plane transport, while the nano-confined nanoribbons contribute primarily along the channel direction. The conductivity of the base layer (σ_1) is determined to be $1,800 \pm 100 \text{ S cm}^{-1}$, from the perpendicular conductivity measurement. From this relationship, the conductivity of the nano-confined region (σ_2) can be determined. The averaged value of σ_2 for six devices achieve $10,200 \pm 200 \text{ S cm}^{-1}$ when the conductive pathway is parallel to the nano-confined channel. (G) Temperature-dependent conductivity of the Au electrodes from 300 K to 2 K. To exclude the possibility of short-circuiting during measurements, the conductivity and temperature dependence of the Au electrodes were examined. The electrodes exhibit a conductivity of $\sim 2.3 \times 10^5 \text{ S cm}^{-1}$ at room temperature, far higher than that of the n-PBDF film, and their temperature dependence differs completely from that of the polymer, further confirming the reliability of the measurements.

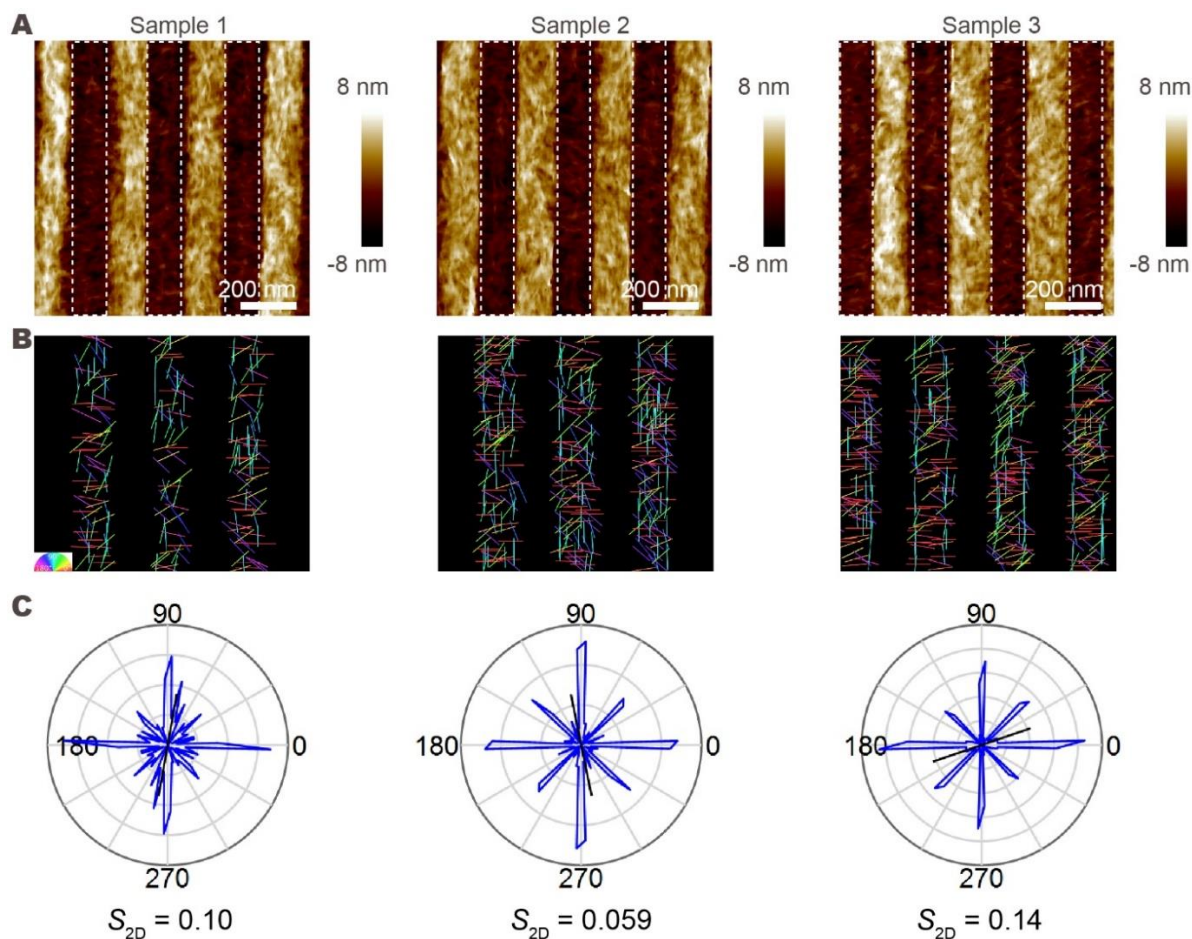


Fig. S30. (A) AFM image of an aligned n-PBDF film prepared by a nanoconfinement-assisted method using an n-PBDF solution with a concentration of 10 mg mL^{-1} . The residual base-layer film is highlighted by the white dashed box. (B) False-color orientation map extracted from the residual base-layer region in (A). The orientation of each pixel is encoded according to the attached color wheel. (C) Orientation distribution extracted from the orientation map in (B). The radial axis represents the pixel count for a given orientation. The diametrical black line indicates the average orientation, and the corresponding S_{2D} value is shown at the bottom.

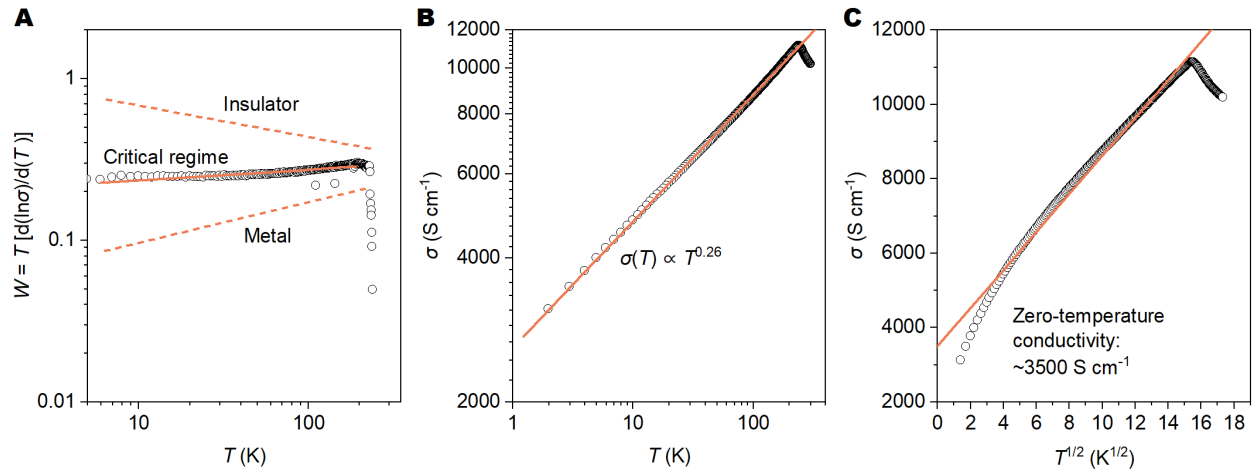


Fig. S31. (A) Log-log plot of $W(T)$ versus temperature for n-PBDF films. The dashed lines show the characteristics of the insulator and metal. (B) Power-law fit of conductivity vs temperature, yielding $\sigma(T) \propto T^{0.26}$. (C) Temperature-dependent electrical conductivity measured from 2 K to 300 K. The data in the range of 2-240 K are fitted using the $\sigma-T^{1/2}$ approximation. The horizontal axis scale and zero-temperature extrapolation follow the relationship with the $\sigma-T^{1/2}$ approximation. The extrapolated zero-temperature conductivity of the aligned n-PBDF films is approximately 3500 S cm⁻¹. These experimental results suggest that the transport behavior in n-PBDF nanoribbon thin film is metal-like transport. (36, 37)

Table S1. Diffraction peak assignment in 2D-GIWAXS (Fig. S7).

Peak	orientation	q ($\text{\AA}^{-1}$)	d-spacing ($\text{\AA}$)	hkl assign
A1	out-of-plane	0.58	10.83	100
A2	out-of-plane	1.15	5.46	200
B1	in-plane	1.89	3.29	010 + 002
B2	in-plane	2.83	2.23	003
B3	in-plane	3.78	1.63	020

Table S2. Lattice parameters of packing motifs of n-PBDF nanoribbon and relative formation energy due to protonation distribution change against packing motifs shown in Fig. S12 and S13.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	$\Delta E/\text{proton}$ (eV)
25%	14.23	3.66	27.11	84.51	89.73	85.70	0
50%	13.50	3.73	27.37	85.76	89.27	89.51	0
75%	13.91	3.63	27.29	80.30	88.13	89.70	0
25%-1	14.28	3.68	27.22	75.52	87.43	89.42	+0.55
25%-2	14.14	3.67	27.24	79.55	90.26	90.49	+0.65
50%-1	14.06	3.67	27.04	83.78	89.41	84.33	+0.29
75%-2	14.30	3.70	27.01	83.42	89.75	85.71	+0.44

Table S3. Processing conditions of nanoribbons.

Process Number	Raw Material	Concentration (mg mL ⁻¹)	Solvent	Processing Method	Temperature (°C)	Outcome
1	n-PBDF ink	0.05	DMSO	Spin-coating	60	n-PBDF nanoribbon
2	n-PBDF ink	0.01	DMSO	Spin-coating	60	n-PBDF nanoribbon
3	n-PBDF ink	0.0025	DMSO	Spin-coating	60	n-PBDF nanoribbon
4	n-PBDF ink	0.01	MeOH	Spin-coating	25	n-PBDF nanoribbon
5	n-PBDF ink	0.01	Acetone	Spin-coating	25	n-PBDF nanoribbon
6	n-PBDF ink	0.005	DMF	Spin-coating	60	n-PBDF nanoribbon

Table S4. Synthesis conditions of nanoribbons.

Synthesis Number	Monomer	Concentration (mg mL ⁻¹)	Solvent	Catalyst/Oxidant	Temperature (°C)	Outcome
1	BDF	6	DMSO	TMQ (2eq)	140	n-PBDF nanoribbon
2	BDF	10	DMSO	TMQ (2eq)	140	n-PBDF nanoribbon
3	BDF	10	DMSO	TMQ (2eq)	40	n-PBDF nanoribbon
4	BDF	10	DMF	TMQ (2eq)	100	n-PBDF nanoribbon
5	BDF	5	DMSO	MoO ₃ (0.001 eq)	100	n-PBDF nanoribbon
6	BDF	15	DMSO	SeO ₂ (0.1 eq)	100	n-PBDF nanoribbon

Table S5. σ of template-grown n-PBDF films measured along the parallel and perpendicular directions at room temperature. Considering that the films consist of nanoconfined ribbons and a residual unconfined layer, the parallel conductivity of the nanoconfined ribbons was estimated using a parallel-resistor model detailed in Fig. S29. Data represents six independent samples.

Device	$\sigma_{\text{parallel}} (\text{S cm}^{-1})$	$\sigma_{\text{perpendicular}} (\text{S cm}^{-1})$
1	9933	1820
2	10153	1715
3	10388	1975
4	10452	1680
5	10170	1838
6	10094	1709

Table S6. Summarize of the samples conditions for all the nanoribbon characterizations.

Characterization	Sample description	Related data
AFM	Individual nanoribbons on mica	Fig. 1A, S8A, S15, S19
	Individual nanoribbons on Sapphire	Fig. S8B
Cryo-TEM	Frozen n-PBDF nanoribbon DMSO suspension (0.05 - 1 mg mL ⁻¹)	Fig. S1
HRTEM	Free standing individual nanoribbons	Fig. 1C, Fig. S2
	Individual nanoribbons on graphene TEM grid	Fig. S3
4D-STEM	Individual nanoribbons on TEM grid with ultrathin carbon supporting film	Fig. S4 to 6
GIWAXS	~50 nm n-PBDF thin film composed of multilayer nanoribbons	Fig. S7 and S14
XPS	~50 nm n-PBDF thin film composed of multilayer nanoribbons	Fig. S10
ssNMR	n-PBDF powders composed of multiple nanoribbons	Fig. S11
Solution-SAXS	n-PBDF nanoribbon suspended in DMSO (2, 4, 6, 8 mg mL ⁻¹)	Fig. 2B
Solution-WAXS	n-PBDF nanoribbon suspended in DMSO (15 mg mL ⁻¹)	Fig. 2A
In-situ solution SAXS	DMSO solution of 10 mg mL ⁻¹ BDF monomer and 2 eq TMQ	Fig. 2C
AFM of aligned nanoribbons	1 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. 4A
	10 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. 4B
POM	10 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. S27
Raman	10 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. 4C
Electrical Conductivity	10 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. 4D and S29, S30
THz	10 mg mL ⁻¹ n-PBDF nanoribbon solution dried under nanoconfinement	Fig. 4E and F

References and Notes

1. A. J. Heeger, Semiconducting and metallic polymers: The fourth generation of polymeric materials (Nobel lecture). *Angew. Chem. Int. Ed.* **40**, 2591–2611 (2001). [doi:10.1002/1521-3773\(20010716\)40:14<2591:AID-ANIE2591>3.0.CO;2-0](https://doi.org/10.1002/1521-3773(20010716)40:14<2591:AID-ANIE2591>3.0.CO;2-0)
2. R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* **12**, 1038–1044 (2013). [doi:10.1038/nmat3722](https://doi.org/10.1038/nmat3722) [Medline](#)
3. A. Khasbaatar, Z. Xu, J.-H. Lee, G. Campillo-Alvarado, C. Hwang, B. N. Onusaitis, Y. Diao, From Solution to Thin Film: Molecular Assembly of π -Conjugated Systems and Impact on (Opto)electronic Properties. *Chem. Rev.* **123**, 8395–8487 (2023). [doi:10.1021/acs.chemrev.2c00905](https://doi.org/10.1021/acs.chemrev.2c00905) [Medline](#)
4. P. J. Flory, Thermodynamics of crystallization in high polymers. IV. A theory of crystalline states and fusion in polymers, copolymers, and their mixtures with diluents. *J. Chem. Phys.* **17**, 223–240 (1949). [doi:10.1063/1.1747230](https://doi.org/10.1063/1.1747230)
5. A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, Solitons in conducting polymers. *Rev. Mod. Phys.* **60**, 781–850 (1988). [doi:10.1103/RevModPhys.60.781](https://doi.org/10.1103/RevModPhys.60.781)
6. K. Kang, S. Watanabe, K. Broch, A. Sepe, A. Brown, I. Nasrallah, M. Nikolka, Z. Fei, M. Heeney, D. Matsumoto, K. Marumoto, H. Tanaka, S. Kuroda, H. Sirringhaus, 2D coherent charge transport in highly ordered conducting polymers doped by solid state diffusion. *Nat. Mater.* **15**, 896–902 (2016). [doi:10.1038/nmat4634](https://doi.org/10.1038/nmat4634) [Medline](#)
7. Y. Lu, Z.-D. Yu, Y. Liu, Y.-F. Ding, C.-Y. Yang, Z.-F. Yao, Z.-Y. Wang, H.-Y. You, X.-F. Cheng, B. Tang, J.-Y. Wang, J. Pei, The Critical Role of Dopant Cations in Electrical Conductivity and Thermoelectric Performance of n-Doped Polymers. *J. Am. Chem. Soc.* **142**, 15340–15348 (2020). [doi:10.1021/jacs.0c05699](https://doi.org/10.1021/jacs.0c05699) [Medline](#)
8. H. Tang, Y. Liang, C. Liu, Z. Hu, Y. Deng, H. Guo, Z. Yu, A. Song, H. Zhao, D. Zhao, Y. Zhang, X. Guo, J. Pei, Y. Ma, Y. Cao, F. Huang, A solution-processed n-type conducting polymer with ultrahigh conductivity. *Nature* **611**, 271–277 (2022). [doi:10.1038/s41586-022-05295-8](https://doi.org/10.1038/s41586-022-05295-8) [Medline](#)
9. Z. Ke, A. Abtahi, J. Hwang, K. Chen, J. Chaudhary, I. Song, K. Perera, L. You, K. N. Baustert, K. R. Graham, J. Mei, Highly Conductive and Solution-Processable n-Doped Transparent Organic Conductor. *J. Am. Chem. Soc.* **145**, 3706–3715 (2023). [doi:10.1021/jacs.2c13051](https://doi.org/10.1021/jacs.2c13051) [Medline](#)
10. R. Sarabia-Riquelme, L. E. Noble, P. Alarcon Espejo, Z. Ke, K. R. Graham, J. Mei, A. F. Paterson, M. C. Weisenberger, Highly conductive n-type polymer fibers from the wet-spinning of n-doped PBDF and their application in thermoelectric textiles. *Adv. Funct. Mater.* **34**, 2311379 (2024). [doi:10.1002/adfm.202311379](https://doi.org/10.1002/adfm.202311379)
11. I. Sanjuán, D. Franco, Q.-G. Chen, C.-C. Chueh, W.-Y. Lee, A. Guerrero, Proton migration-modulated n-doped poly(benzodifurandione) organic electrochemical transistors used for neuromorphic computing applications. *ACS Energy Lett.* **10**, 5209–5217 (2025). [doi:10.1021/acsenerylett.5c02076](https://doi.org/10.1021/acsenerylett.5c02076) [Medline](#)

12. I. Song, W.-J. Lee, Z. Ke, L. You, K. Chen, S. Naskar, P. Mehra, J. Mei, An n-doped capacitive transparent conductor for all-polymer electrochromic displays. *Nat. Electron.* **7**, 1158–1169 (2024). [doi:10.1038/s41928-024-01293-y](https://doi.org/10.1038/s41928-024-01293-y)
13. X. Ni, H. Li, V. Coropceanu, J.-L. Brédas, Dimensionality-Dependent Electronic Properties of the Highly Conducting n-Type Polymer, Poly(benzodifurandione). *ACS Mater. Lett.* **6**, 2569–2576 (2024). [doi:10.1021/acsmaterialslett.4c00624](https://doi.org/10.1021/acsmaterialslett.4c00624)
14. C. Chen, M. Chen, X. Guo, C. Yang, J. Liu, D. Lei, H. Li, Y. Zhu, Elucidating the hierarchical architecture of polymer spherulites via 4D scanning transmission electron microscopy. *Small* **22**, e13905 (2026). [doi:10.1002/sml.202513905](https://doi.org/10.1002/sml.202513905) [Medline](#)
15. Z. Ke, J. Chaudhary, L. Q. Flag, K. N. Baustert, A. O. Yusuf, G. Liu, L. You, K. R. Graham, D. M. DeLongchamp, J. Mei, Controlled Dedoping and Redoping of N-Doped Poly(benzodifurandione) (n-PBDF). *Adv. Funct. Mater.* **34**, 2400255 (2024). [doi:10.1002/adfm.202400255](https://doi.org/10.1002/adfm.202400255)
16. T. K. Harris, Q. Zhao, A. S. Mildvan, NMR studies of strong hydrogen bonds in enzymes and in a model compound. *J. Mol. Struct.* **552**, 97–109 (2000). [doi:10.1016/S0022-2860\(00\)00469-5](https://doi.org/10.1016/S0022-2860(00)00469-5)
17. T. Steiner, The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.* **41**, 49–76 (2002). [doi:10.1002/1521-3773\(20020104\)41:1<48:AID-ANIE48>3.0.CO;2-U](https://doi.org/10.1002/1521-3773(20020104)41:1<48:AID-ANIE48>3.0.CO;2-U) [Medline](#)
18. X. Yi, W. Chen, Y. Xiao, F. Liu, X. Yu, A. Zheng, Spectroscopically visualizing the evolution of hydrogen-bonding interactions. *J. Am. Chem. Soc.* **145**, 27471–27479 (2023). [doi:10.1021/jacs.3c08723](https://doi.org/10.1021/jacs.3c08723) [Medline](#)
19. J. Huang, S. Virji, B. H. Weiller, R. B. Kaner, Polyaniline nanofibers: Facile synthesis and chemical sensors. *J. Am. Chem. Soc.* **125**, 314–315 (2003). [doi:10.1021/ja028371y](https://doi.org/10.1021/ja028371y) [Medline](#)
20. C. Zhao, X. Lai, D. Liu, X. Guo, J. Tian, Z. Dong, S. Luo, D. Zhou, L. Jiang, R. Huang, M. He, Molecular-dipole oriented universal growth of conjugated polymers into semiconducting single-crystal thin films. *Nat. Commun.* **16**, 1509 (2025). [doi:10.1038/s41467-025-56757-2](https://doi.org/10.1038/s41467-025-56757-2) [Medline](#)
21. K. Rahimi, I. Botiz, N. Stingelin, N. Kayunkid, M. Sommer, F. P. V. Koch, H. Nguyen, O. Coulembier, P. Dubois, M. Brinkmann, G. Reiter, Controllable processes for generating large single crystals of poly(3-hexylthiophene). *Angew. Chem. Int. Ed.* **51**, 11131–11135 (2012). [doi:10.1002/anie.201205653](https://doi.org/10.1002/anie.201205653)
22. H. Dong, S. Jiang, L. Jiang, Y. Liu, H. Li, W. Hu, E. Wang, S. Yan, Z. Wei, W. Xu, X. Gong, Nanowire crystals of a rigid rod conjugated polymer. *J. Am. Chem. Soc.* **131**, 17315–17320 (2009). [doi:10.1021/ja907015p](https://doi.org/10.1021/ja907015p) [Medline](#)
23. T. Zhang, S. Chen, P. S. Petkov, P. Zhang, H. Qi, N. N. Nguyen, W. Zhang, J. Yoon, P. Li, T. Brumme, A. Alfonsov, Z. Liao, M. Hambsch, S. Xu, L. Mester, V. Kataev, B. Büchner, S. C. B. Mannsfeld, E. Zschech, S. S. P. Parkin, U. Kaiser, T. Heine, R. Dong, R. Hillenbrand, X. Feng, Two-dimensional polyaniline crystal with metallic out-of-plane conductivity. *Nature* **638**, 411–417 (2025). [doi:10.1038/s41586-024-08387-9](https://doi.org/10.1038/s41586-024-08387-9) [Medline](#)

24. G. Liu, H.-H. Hsu, S. Samal, W.-J. Lee, Z. Ke, L. You, B. M. Savoie, J. Mei, Selenium dioxide catalyzed polymerization of N-doped poly(benzodifurandione) (n-PBDF) and its derivatives. *Angew. Chem. Int. Ed.* **64**, e202418668 (2025). [doi:10.1002/ange.202418668](https://doi.org/10.1002/ange.202418668) [Medline](#)
25. G. Liu, U. Pal, S. Samal, M. F. Espenship, Y. Li, W.-J. Lee, L. A. Ogunfowora, L. You, J. Laskin, J. Mei, Catalytic polymerization of n-doped poly(benzodifurandione) (n-PBDF) using parts per million (ppm) levels of molybdenum trioxide. *Angew. Chem. Int. Ed.* **64**, e202510411 (2025). [doi:10.1002/anie.202510411](https://doi.org/10.1002/anie.202510411) [Medline](#)
26. A. V. Dobrynin, R. H. Colby, M. Rubinstein, Scaling theory of polyelectrolyte solutions. *Macromolecules* **28**, 1859–1871 (1995). [doi:10.1021/ma00110a021](https://doi.org/10.1021/ma00110a021)
27. M. Nierlich, C. E. Williams, F. Boué, J. P. Cotton, M. Daoud, B. Famoux, G. Jannink, C. Picot, M. Moan, C. Wolff, M. Rinaudo, P. G. de Gennes, Small angle neutron scattering by semi-dilute solutions of polyelectrolyte. *J. Phys. France* **40**, 701–704 (1979). [doi:10.1051/jphys:01979004007070100](https://doi.org/10.1051/jphys:01979004007070100)
28. J. Hwang, Q. Zhao, M. Ahmed, A. C. Yakisan, M. F. Espenship, J. Laskin, B. M. Savoie, J. Mei, Reductive Doping Inhibits the Formation of Isomerization-Derived Structural Defects in N-doped Poly(benzodifurandione) (n-PBDF). *Angew. Chem. Int. Ed.* **63**, e202401465 (2024). [doi:10.1002/anie.202401465](https://doi.org/10.1002/anie.202401465) [Medline](#)
29. M. H. V. Huynh, T. J. Meyer, Proton-coupled electron transfer. *Chem. Rev.* **107**, 5004–5064 (2007). [doi:10.1021/cr0500030](https://doi.org/10.1021/cr0500030) [Medline](#)
30. Y. Yao, H. Dong, F. Liu, T. P. Russell, W. Hu, Approaching intra- and interchain charge transport of conjugated polymers facily by topochemical polymerized single crystals. *Adv. Mater.* **29**, 1701251 (2017). [doi:10.1002/adma.201701251](https://doi.org/10.1002/adma.201701251) [Medline](#)
31. S. Fratini, M. Nikolka, A. Salleo, G. Schweicher, H. Sirringhaus, Charge transport in high-mobility conjugated polymers and molecular semiconductors. *Nat. Mater.* **19**, 491–502 (2020). [doi:10.1038/s41563-020-0647-2](https://doi.org/10.1038/s41563-020-0647-2) [Medline](#)
32. M. Chen, D. Wang, Y. Zou, C. Chen, X. Yang, L. Niu, G. Sheng, J. Wang, L. Q. Flagg, L. J. Richter, B. A. Phillips, B. Xiao, G. Liu, L. You, J. Laskin, D. M. DeLongchamp, K. Zhao, Y. Zhu, C. Di, J. Mei, Long-range extended chains arising from polymerization-driven spontaneous assembly. Zenodo (2026). [doi:10.5281/zenodo.18749621](https://doi.org/10.5281/zenodo.18749621)
33. T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang, J. Pei, Electron-deficient poly(*p*-phenylene vinylene) provides electron mobility over 1 cm² V⁻¹ s⁻¹ under ambient conditions. *J. Am. Chem. Soc.* **135**, 12168–12171 (2013). [doi:10.1021/ja403624a](https://doi.org/10.1021/ja403624a) [Medline](#)
34. R. K. Harris, P. Jackson, L. H. Merwin, B. J. Say, G. Hägele, Perspectives in high-resolution solid-state nuclear magnetic resonance, with emphasis on combined rotation and multiple-pulse spectroscopy. *J. Chem. Soc., Faraday Trans. I* **84**, 3649–3672 (1988). [doi:10.1039/f19888403649](https://doi.org/10.1039/f19888403649)
35. Q. Zhao, C. Abeygunawardana, A. G. Gittis, A. S. Mildvan, Hydrogen bonding at the active site of Δ^5 -3-ketosteroid isomerase. *Biochemistry* **36**, 14616–14626 (1997). [doi:10.1021/bi971549m](https://doi.org/10.1021/bi971549m) [Medline](#)

36. M. Ahlskog, M. Reghu, A. J. Heeger, The temperature dependence of the conductivity in the critical regime of the metal - Insulator transition in conducting polymers. *J. Phys. Condens. Matter* **9**, 4145–4156 (1997). [doi:10.1088/0953-8984/9/20/014](https://doi.org/10.1088/0953-8984/9/20/014)
37. S. Zanettini, J. F. Dayen, C. Etrillard, N. Leclerc, M. V. Kamalakar, B. Doudin, Magnetoconductance anisotropy of a polymer thin film at the onset of metallicity. *Appl. Phys. Lett.* **106**, 063303 (2015). [doi:10.1063/1.4908526](https://doi.org/10.1063/1.4908526)