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Supporting Information

Transition from Polythiophene-based One-Dimensional Nanofibers to Spherical Clusters in Ultrafiltration

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Experimental conditions:

Atomic force microscopy (AFM) was performed at ambient conditions by a commercial AFM, using a Digital Instruments MultiMode IV in the tapping mode. The dry samples were mounted on a sample stage which was three-dimensionally driven by a piezo tube scanner. Both height and phase images were recorded simultaneously. Thin polymer films were prepared by spin-coating the P3BT-*b*-P3DDT anisole solutions onto the silicon wafers with a layer of SiO_x (~ 2 nm thick from ellipsometry) at 2000 rpm for 60 s. Prior to spin-coating, the wafers were cleaned with a 70/30 v/v solution of 98% H_2SO_4/ 30% H_2O_2 at 80 °C for 30 min, and then thoroughly rinsed with deionized water and dried.

Transmission electron microscopy (TEM) was taken on a Tecnai G^2 20, FEI electron microscope operated at 200 kV. For the TEM measurements, a drop of P3BT-*b*-P3DDT anisole solution was placed on a carbon-coated copper grid, and dried at room temperature. The cryo-TEM was performed with a drop of P3BT-*b*-P3DDT anisole solution transferred to cryogrid. They were plunged into liquid ethane at its freezing point using the Vitrobot™ (Vitrification Robot) device.

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The grid was transferred on a Gatan 626 cryoholder using a cryo-transfer device. Direct imaging was carried out at a temperature of approxiamately - 170 °C, using the images acquired with a Gatan 894 CCD.

Dynamic laser light scattering (DLLS) was taken to detect the nanostructures in the P3BT-*b*-P3DDT anisole solution. An ALV 5022F spectrometer equipped with a time correlator and a He-Ne laser (632.8 nm, 22 mW) was used. The angle of detecting scattering signal was fixed at 90°, and the hydrodynamic radius distribution $f(R_h)$ could be obtained from each measured intensity-intensity correlation function. In our experiment, Each $f(R_h)$ curve was measured twice.

UV-vis spectroscopy was carried out with a Perkin-Elmer Lambda 35 equipment.

The viscosity was measured by digital viscometer (SNB-2，Shanghai Nirun Intelligent Technology Co. Ltd.).

The commercial nylon membrane was purchased from Jinteng experiment equipment Co. Ltd., (Tianjin, China) and the nanopore diameter was given by the company. The diameter and thickness of membrane were measured by using vernier caliper.

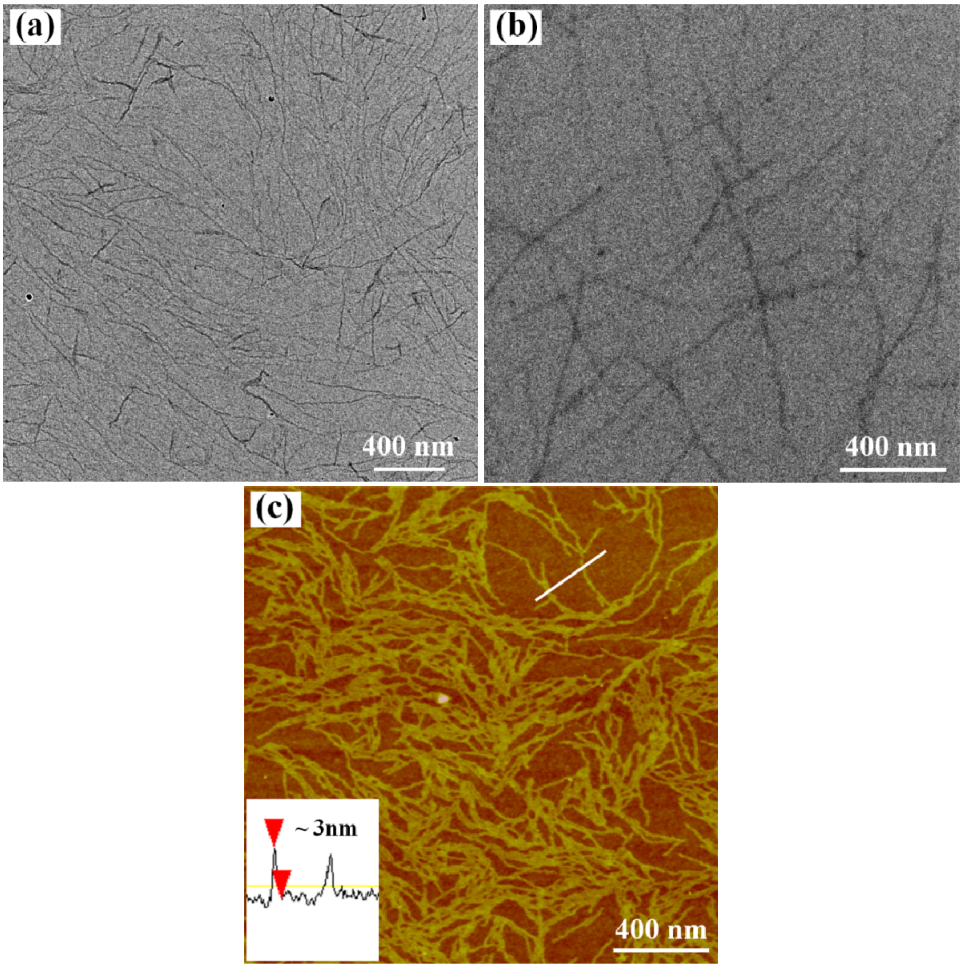

Figure S1. (a) TEM, (b) cryo-TEM and (c) AFM images of the nanofibers formed in the initial 0.2 mg/mL P3BT-*b*-P3DDT solution. Cross-sectional analysis of the nanofibers is shown in the inset of (c).

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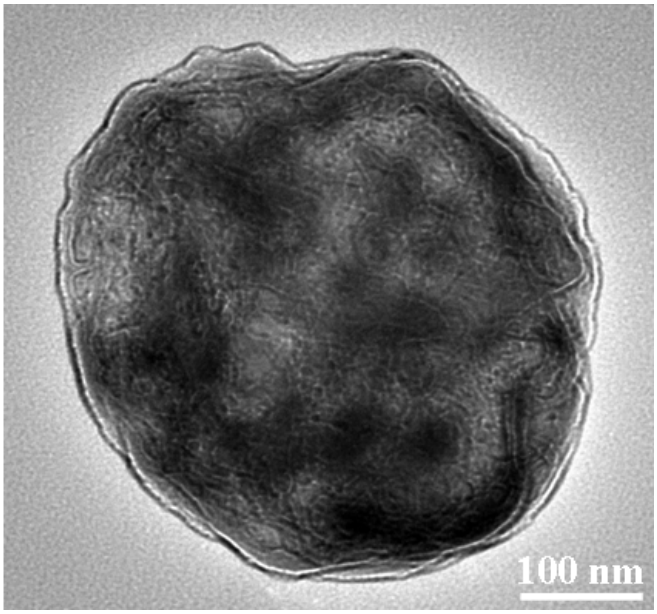
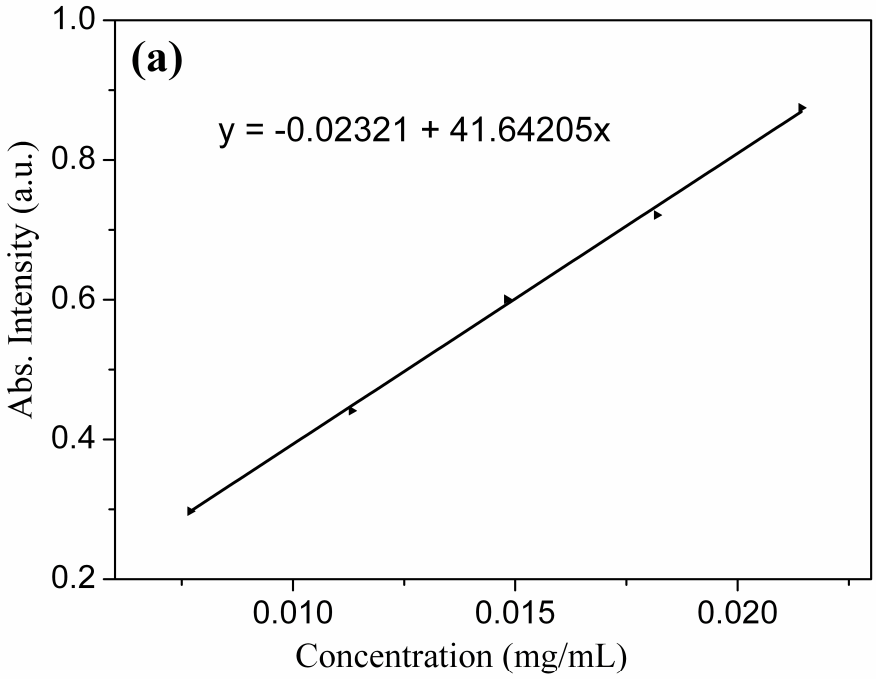


Figure S2. A magnified TEM image of the inset in Figure 1(c).



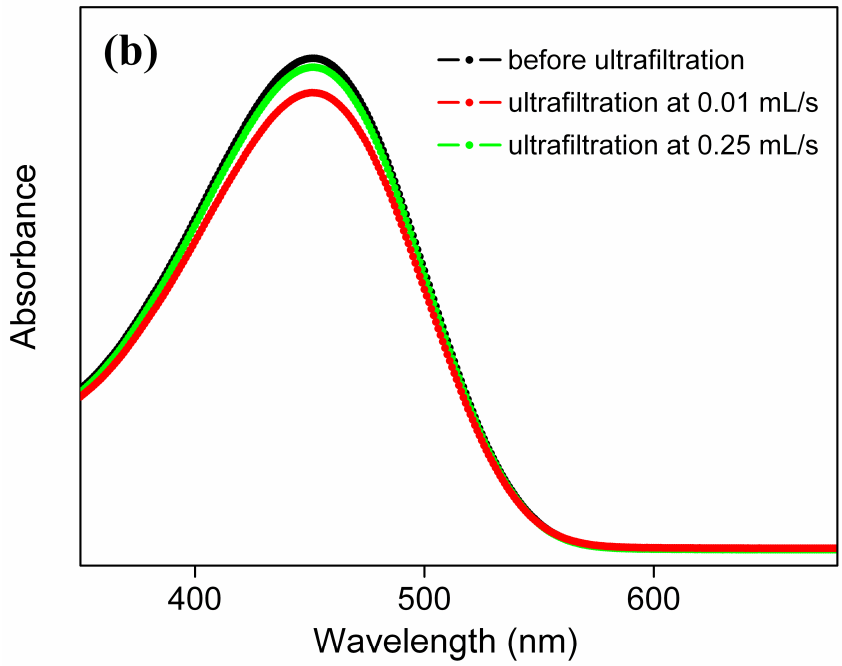


Figure S3. (a) The linear dependence of the absorption intensity on the P3BT-*b*-P3DDT solution concentration, as determined by UV-vis spectroscopy. (b) UV-vis absorption spectra of 0.2 mg/mL P3BT-*b*-P3DDT solution before and after ultrafiltration at $Q_s \approx 0.01$ mL/s and $Q_f \approx 0.25$ mL/s, respectively.

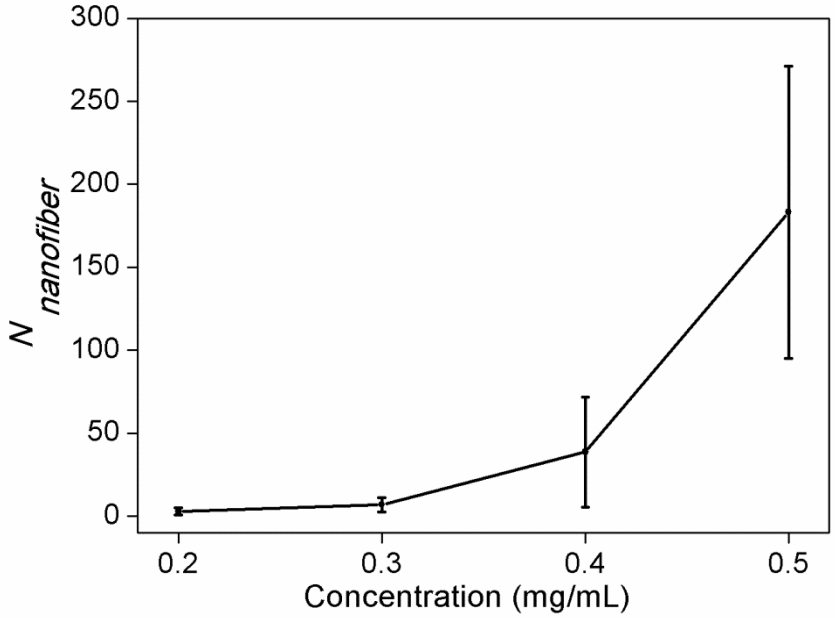


Figure S4. The dependence of the nanofiber number compacted in one cluster on the P3BT-*b*-P3DDT solution concentration.

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Calculations:

1. Estimation of the interpenetrating degree of nanofibers

The interpenetrating degree can be directly estimated by comparing the average distance of the mass center of nanofibers in solutions, d, with the size of undisturbed single nanofiber, i.e., the effective radius of gyration of a free nanofiber, R_g. When d is obviously smaller than R_g in concentrated nanofiber solutions, the nanofibers are strongly interpenetrated, and they perform collective behaviors. In the opposite situation, each nanofiber behaves nearly independently.

As the nanofiber is composed of crystallized P3AT chains, it should have some rigidity. Therefore we use a semiflexible chain to describe it. Mathematically, the radius of gyration of a free fiber, R_g, can be roughly estimated by $N^v a$, where v is a pseudo-Flory exponent, N and a are the effective number and size of segment. For the semiflexible fiber, v depends on its rigidity, and its value is between the two limit cases of ideal flexible chain (v = 0.6) in good solvent and totally rigid rod (v = 1). Without loss of generality, we take an intermediate value of v = 0.8 during our calculations. The value of a is chosen as the width of the nanofiber, which is measured by AFM as about 15 nm. N is computed by dividing the average nanofiber length, L, by a. Then we obtain $R_g \sim 1$ μm.

With the average length and the average area of the cross-section of nanofibers by AFM measurement, the average volume of each nanofiber is estimated as $\sim 1\times10^5$ nm^3. For a given nanofiber concentration, we can determine the number density of nanofiber (the nanofiber density is approximated as 1 g/cm^3). Then the average

distance, d, is directly given by the number density. For the 0.1 mg/ml and 0.2 mg/ml solutions, d is about 1 μm and 0.79 μm, respectively.

The comparison of R_g and d suggests that there is no obvious interpenetration among nanofibers in the solution of 0.1 mg/ml, and the interpenetrating degree becomes higher and higher as the concentration increases.

2. The critical macroscopic flow rate Q_c.

The hydrodynamic driving force (F_h) is given by $3\pi\eta(q/D^2)L_e$, where η, q and D are the solvent viscosity, the microscopic flow rate and the pore diameter, respectively. L_e is the effective length along the flow direction. Using nondraining model, $L_e = D$.

The Stokes drag force (F_s), experienced by the nanofiber outside the nanopores, is simply given by $6\pi\eta R\cdot v = 6\pi\eta R_g\cdot R_g/\tau$, where τ is the passing time of the nanofiber in a R_g region and can be estimated as $4\pi R_g^3/3q$.

F_c, from the confinement of the nanopore, is estimated as k_BT/D, where k_B is the Boltzmann constant and T is the absolute temperature.

For the typical values of parameters in our experiments，$R_g \sim 1$ μm, $L_e = D = 220$ nm, $\eta = 0.82\times10^{-3}$ Pa·s, $T = 293$ k, the equation of $F_h = F_s + F_c$ gives the critical microscopic flow rate $q_c \approx 5.5\times10^{-13}$ mL/s.

Finally the critical macroscopic flow rate is given as $Q_c = q_c\times N_{nanopore} = 5.5\times10^{-13}$ mL/s$\times2\times10^8 = 1.1\times10^{-4}$ mL/s.

In fact, the confined nanofibers are draining, which tends to decrease the critical flow rate further.

3. Estimation of the force exerted by flow and the force needed to break the nanofiber.

The nanofibers consist of many parallel stacks of the extended polymer backbones along the nanofiber long axis and of several laminated layers of the polymer backbones separated by alkyl side chains. The force needed to break the nanofiber F_{break} can be given by $E_{break}/d_{\pi\text{-}\pi}$, where E_{break} is the energy needed to break the nanofiber and $d_{\pi\text{-}\pi}$ is the distance between two neighbored polymer backbones at π-π interaction direction. E_{break} can be given by $n_{chain} \cdot N \cdot E_{\pi\text{-}\pi}$, where n_{chain} is the number of laminated layer perpendicular to the long axis of the nanofibers, and N is the monomer units. According to the nanofiber dimension and the molecular weight of P3BT-*b*-P3DDT, n_{chain} is ~ 3, N is ~ 42 and $d_{\pi\text{-}\pi}$ is ~ 0.38 nm. If we take $E_{\pi\text{-}\pi}$ as 20 kJ/mol, then we get $F_{break} \sim 1.1 \times 10^{-8}$ N.

On the other hand, the force exerted on the nanofiber is the hydrodynamic driving force, F_h, and can be given by $F_h = 3\pi\eta(q/D^2)L_e \sim 3\pi\eta q/D$. Substituting typical values, we get $F_h \sim 4.4 \times 10^{-11}$ N.

Based on the above calculation, the force exerted by flow is much lower than the force needed to break the nanofiber. Therefore, the fibers would not be broken during ultrafiltration.

4. Estimation of the effective number of pores in the membrane.

The macroscopic flow rate Q increases linearly with the pressure P applied on the

syringe with the network-like membrane. According to Hagen-Poiseuille equation, $Q = \pi P r_p^4 / 8\eta L \cdot N$, where r_p is the radius of nanopore, η is the viscosity of the solution, L is the thickness of the membrane and N is the number of the nanopores. Therefore, we can estimate the effective number of pores in the network-like membrane. For the typical values of parameters in our experiments, Q = 0.01 mL/s, $P = 7.7 \times 10^4$ Pa, r_p = 110 nm, $\eta = 0.82 \times 10^{-3}$ Pa·s, L = 110 μm, the equation gives the effective number of pores to be ~ 2×10^8.

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