Electronic Supplementary Information

Ultra-long ionic nanofibrils in aqueous: imitate the amyloid fibril from molecular self-assembly to fibrous self-arranging

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1. Experimental Methods

1.1. Fourier Transform Infrared Spectra (FT-IR)

FT-IR spectra were recorded with a TENSOR 27 apparatus (Bruker) at room temperature. (MCT detector, 64 scans, 4 cm^{-1}).

1.2. Nuclear Magnetic Resonance Spectra (NMR)

The 300 MHz ^{1}H NMR and 75 MHz ^{13}C NMR measurements were performed on a Bruker Avance 300 spectrometer using TMS as an internal reference.

1.3. Elemental Analysis

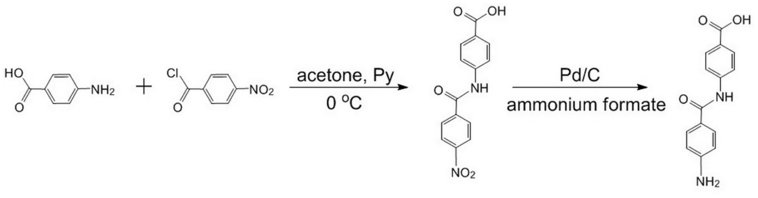
Elemental analysis was taken on an Elementar Vario EL cube (Elementar, Hanau, Germany). Oxidation and reduction temperatures are 950 and 500 °C respectively.

2. $P_7(COONa)_3$ Synthesis

2.1. Materials

1,3,5-Benzenetricarboxylic acid, *p*-nitrobenzoyl chloride, Pd/C catalyst and 4-aminobenzoic acid was purchased from Aladdin-Reagent, Shanghai. All the other chemicals were purchased from Sinopharm Chemical Reagent co., Ltd, China. 1,3,5-Benzenetricarboxylic acid and 4-aminobenzoic acid were recrystallized in water and deep dried before reaction. N,N-dimethylacetamide (DMAc) and pyridine (Py) was dehydrated with CaH_2 overnight and then distilled under reduced pressure before reaction. Acetone was dehydrated with $CaCl_2$ overnight and then distilled before reaction. Other chemicals were used as received.

2.2. Synthesis Procedure



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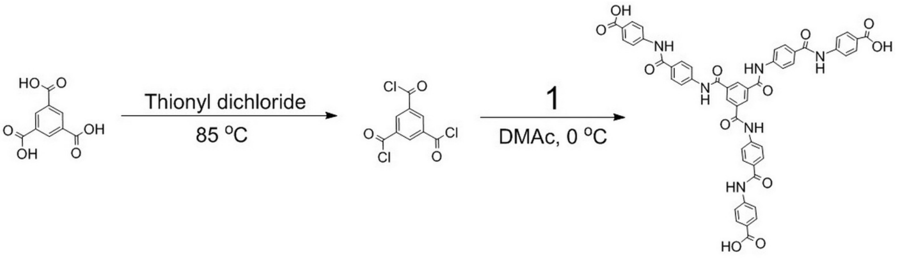
In a two-necked flask equipped with a constant pressure dropping funnel, 4-aminobenzoic acid (2.40 g, 17.5 mmol) was dissolved in anhydrous acetone (20 mL), and pyridine (3 mL) was added as acid-acceptor. Under nitrogen atmosphere, the flask was placed in ice water, and then *p*-nitrobenzoyl chloride (3.60 g, 19.3 mmol, dissolved in 20 mL acetone) was fed dropwise. The mixture was stirred at ambient temperature for additional one hour to complete the reaction. After filtration, the obtained yellow powder was washed with acetone and water. The obtained 4-(4-nitrobenzamido)benzoic acid was directly added in a flask equipped with a condenser pipe. The flask was placed in ice water and DMAc (20 mL), methanol (130 mL), ammonium formate (13.0 g) and Pd/C catalyst (0.30 g) were fed under nitrogen atmosphere. The mixture was stirred at 30 ºC overnight to complete the reaction. After filtration, the solution was concentrated using a rotary evaporator, and then precipitated in water. The solid residue was washed with deionized water and deep dried under vacuum to give 4-(4-aminobenzamido)benzoic acid **(1)** as white powder (3.60 g, 14.05 mmol, 80% yield). ^{1}H NMR δ_{H} (300 MHz, DMSO-*d*6): 5.84 (2H, s), 6.60 (2H, d), 7.73 (2H, d), 7.89 (4H, s), 10.05 (1H, s), 12.69 (1H, s) ppm. ^{13}C NMR δ_{C} (75 MHz, DMSO-*d*6): 113.1, 119.7, 121.1, 125.2, 130.1, 130.6, 144.5, 152.9, 166.1, 167.6 ppm.



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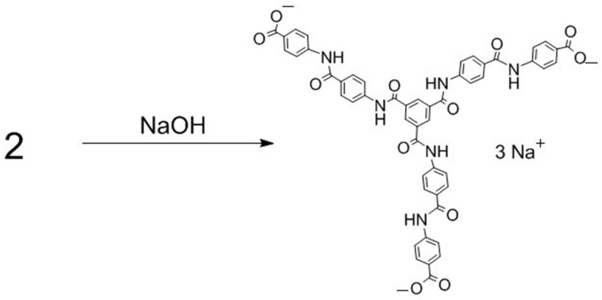
In a flask equipped with a condenser pipe, 1,3,5-benzenetricarboxylic acid (0.94 g, 4.47 mmol) was refluxed together with thionyl chloride (15 mL, add a drop of N,N-dimethylformamide) for 3 hours at 85 ºC to get a glassy yellow solution. Excess thionyl chloride was distilled at reduced pressure leaving the benzenetricarboxylic acid chloride. In a two-necked flask equipped with a constant pressure dropping funnel, 4-(4-aminobenzamido)benzoic acid **(1)** (3.50 g, 13.68 mmol) was dissolved in anhydrous DMAc (20 mL). Under nitrogen atmosphere, the flask was placed in ice water, and then the above obtained benzenetricarboxylic acid chloride in 10 mL DMAc was fed dropwise. The mixture was stirred at ambient temperature for an additional two hours to complete the reaction then precipitated in water. After filtration, the solid residue was washed with methanol and acetone and then dried under vacuum to give (**2)** as white powder (3.89 g, 4.21 mmol, 94% yield). ^{1}H NMR δ_H (300 MHz, DMSO-*d6*): 8.17-7.77 (24H, m), 8.81 (3H, s), 10.48 (3H, s), 10.92 (3H, s), 12.74(3H, s) ppm. ^{13}C NMR δ_C (75 MHz, DMSO-*d6*): 119.4, 119.6, 125.4, 128.7, 129.6, 130.2, 135.2, 142.2, 143.4, 164.7, 165.2, 166.9 ppm. Elemental analysis calcd (%) for C51H36N6O12: C, 66.23%; H, 3.92%; N, 9.09%. found: C, 63.75%; H, 4.50%; N, 9.12%.



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$P_7(COONa)_3$

In a flask equipped with a condenser pipe, sample 2 was reacted with 3.3 eq. NaOH in water at 90 ºC, the solution was concentrated using a rotary evaporator, and then precipitated in alcohol. After filtration, the solid residue was washed with alcohol and then dried under vacuum to give the P7(COONa)3 (**3).**

3. Nuclear Magnetic Resonance Spectra

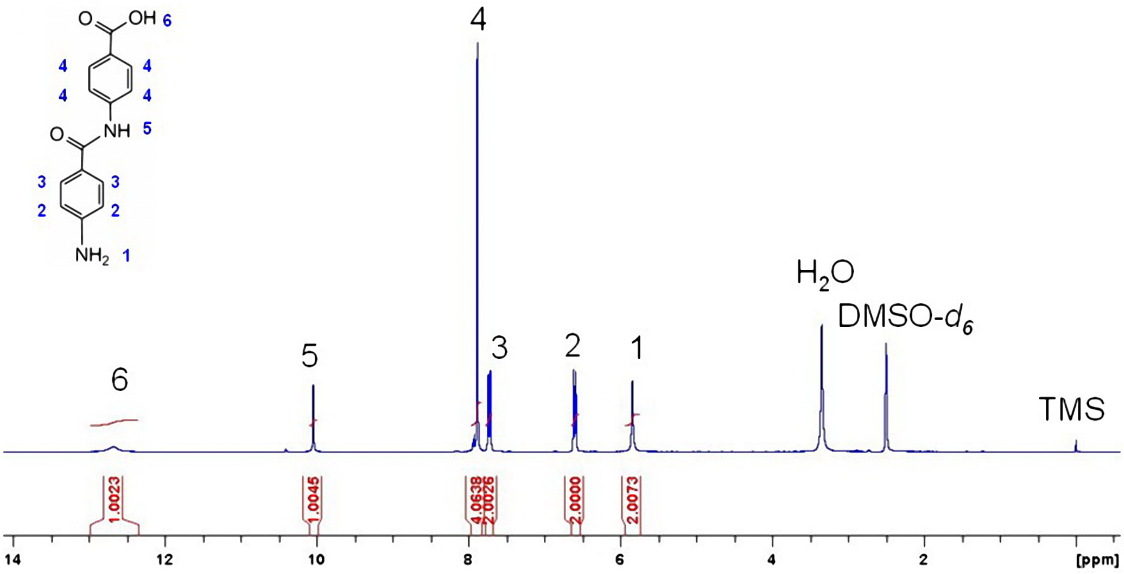

Fig. S1. ^{1}H NMR spectrum of **1** in DMSO-*d6* (300 MHz) at 25 ºC.

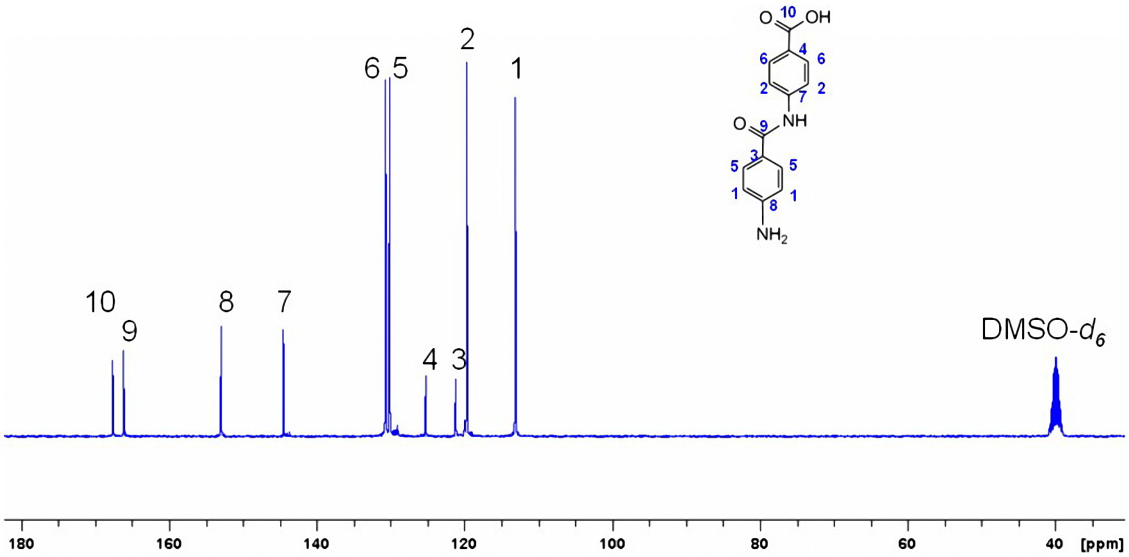

Fig. S2. ^{13}C NMR spectrum of **1** in DMSO-*d6* (75 MHz) at 25 ºC.

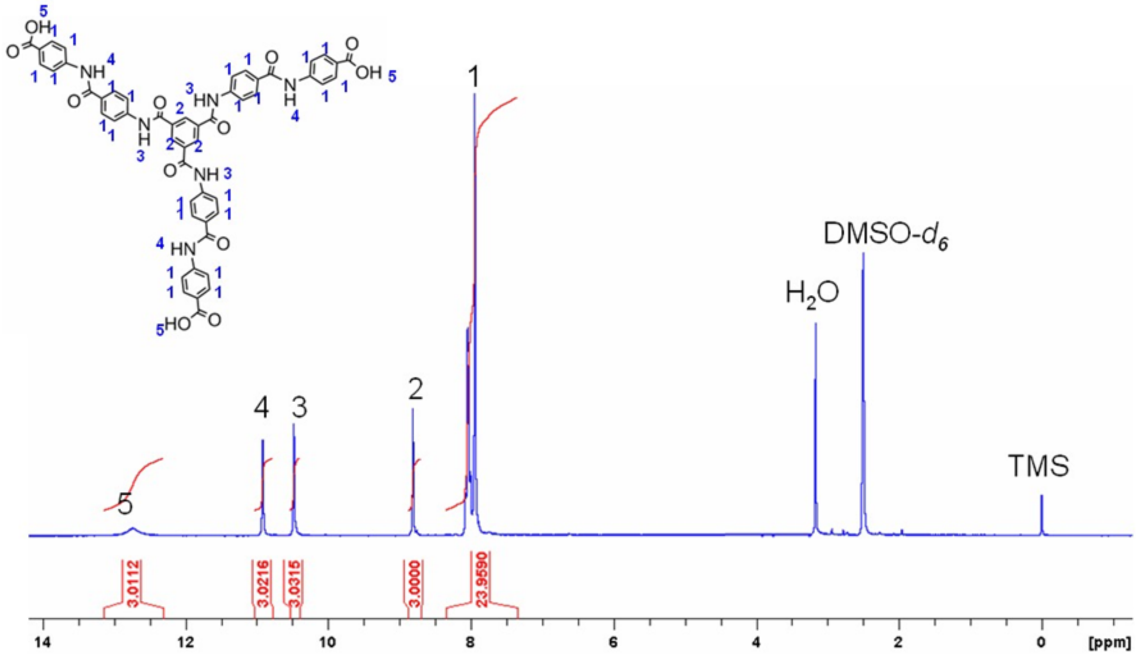

Fig. S3. ^{1}H NMR spectrum of **2** in DMSO-*d6* (300 MHz) at 25 ºC.

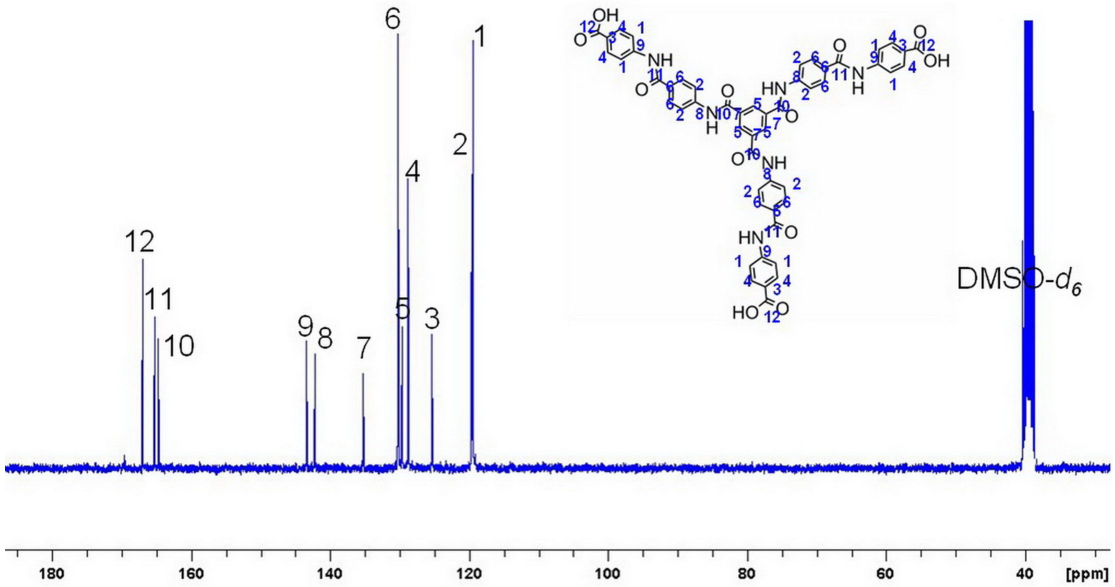

Fig. S4. ^{13}C NMR spectrum of **2** in DMSO-*d6* (75 MHz) at 25 ºC.

4. Optical Microscope

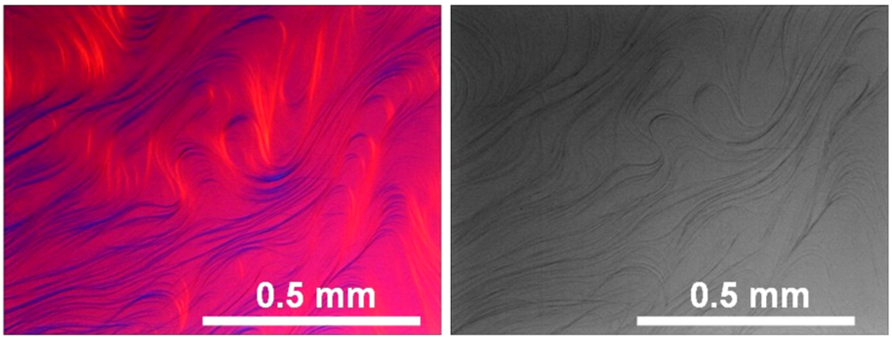

Fig. S5. Polarized optical microscope (left) and optical microscope (right) imagines of aqueous sample with *w* = 3.4 wt%. The apparent length of microfiber exceeds one millimeter and endless fibers were detected under the visual field.

5. Fourier Transform Infrared Spectra

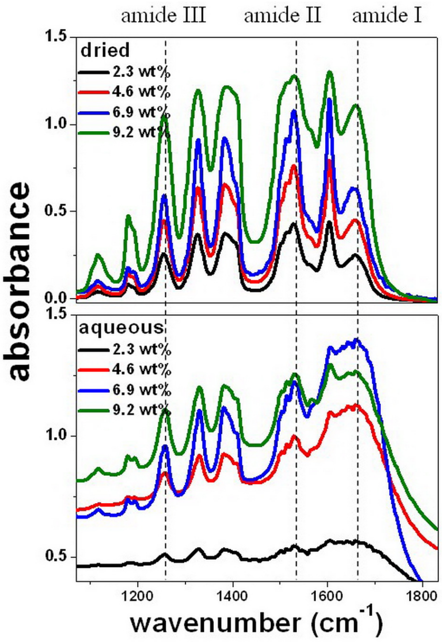

Fig. S6. FT-IR spectra of aqueous (down) and dried (up) samples with different *w*, where the absorption peak positions of amide bond are marked by dash line (**amide I**, C=O st, 1661 cm^{-1}; **amide II**, N-C=O st, 1530 cm^{-1}; **amide III**, N-H and C-N st, 1254 cm^{-1}).

6. SAXS Peak-position Data

hk *w*	10	01	11/20	21	30	12	22/40	41
2.3 wt%	**0.264**	**0.468**	**0.535**	**0.706**		**0.962**	**1.073**	**1.156**
4.6 wt%	**0.271**	**0.487**	**0.556**	**0.740**		**1.010**		
6.9 wt%	**0.278**	**0.488**	**0.557**	**0.760**	**0.843**	**0.982**		
9.2 wt%	**0.293**	**0.531**	**0.611**	**0.805**	**0.898**	**1.049**		

Tab. S1. SAXS peak positions (*q* values of each peak with unit of nm^{-1}) in main text Fig. 3.