Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

Transition of Chemically Modified Diphenylalanine Peptide Assemblies Revealed by Atomic Force Microscopy

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EXPERIMANTAL SECTION

Self-assembly of PPA nanospheres. PPA was dissolved in HFIP at 0.5 mg/mL or 0.25 mg/mL and drop-casted or spin-coated on mica. For the spin-coating, the spin speed was 3000 rpm and spin time was 2 min. In order to prevent aggregation in HFIP, solutions were stocked at 4 °C for no more than 1 week.

Solvent induced transition to nanofibers. A 5 μL drop of water was added to PPA nanospheres on mica surface and air dried. The drop usually dried within 5 min. For prolonged treatment, a 15 μL drop was added and the drying out time was about 10 min.

Atomic force microscopy. AFM measurements were conducted on a Multimode® 8 atomic force microscope (Bruker Nano Inc., Santa Barbara, CA, USA). Topographical images were recorded in air with tapping mode, using OMCL-AC160TS (Olympus) cantilevers with nominal spring constant of 42 N/m. For PeakForce QNM, Cantilevers with spring constants of 5.5 N/m (TAP150A) and 26.2 N/m (RTESPA) from Bruker were used. Measurements were carried out on the same cantilever when difference sample were to be compared.

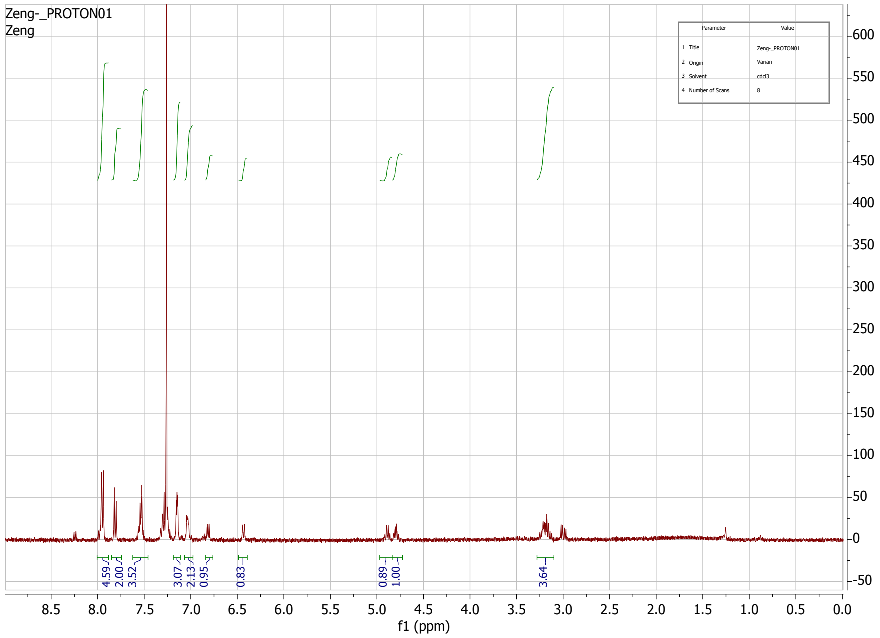
Transmission electron microscopy. TEM images were captured on Philips CM20 at 200 kV acceleration voltage. For the sample preparation, carbon films suspended on copper grids were cleaned by glow discharge with PELCO easiGlowtm (Ted Pella, Redding, CA, USA) to make them more hydrophilic. A 5 μL drop of 0.25 mg/mL PPA in HFIP was added on the carbon film and dried in air. To prepare nanofibers, another 5 μL drop of water was added subsequently and dried in air. Samples were observed under TEM without staining.

S1. Supplementary methods: synthesis of Azobenzene-Phe-Phe-OH (PPA)

All purchased chemicals were used as received without further purification. H-Phe-Phe-OH (0.4 mmol) was added to 1.5 mL of water and 0.15 mL of 10 M NaOH. To this solution was added 4-[(E)-phenyldiazenyl]benzoyl chloride at 0°C in small portions with vigorous stirring over a period of 3 min.

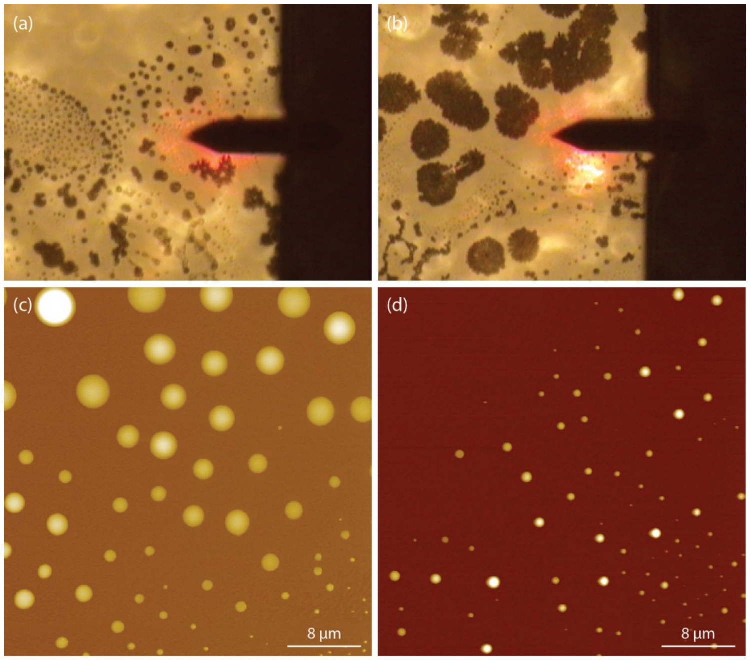
The reaction mixture was stirred for another 10 min. The solution was acidified with 6 M HCl. The light yellow precipitate was washed with water and recrystallized from CH_2Cl_2. After removing the solvent, the product was dried on the high vacuum.

^{1}H NMR spectra were recorded at 400 MHz on a Varian Mercury 400 spectrometer. The chemical shifts of the NMR spectra are reported in parts per million (ppm) relative to the solvent residual peak.[1] NMR spectra are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, m = multiplet, b = broad, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets). ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.95 (d, J = 8.0 Hz, 4H), 7.81 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 7.6 Hz, 3H), 7.31-7.25 (m, 6H), 7.15-7.14 (m, 3H), 7.05-7.01 (m, 2H), 6.81 (d, J = 7.6 Hz, 1H), 6.43 (d, J = 7.2 Hz, 1H), 4.89 (q, J = 7.2 Hz, 1H), 4.79 (q, J = 6.0 Hz, 1H), 3.26-3.12 (m, 4H).



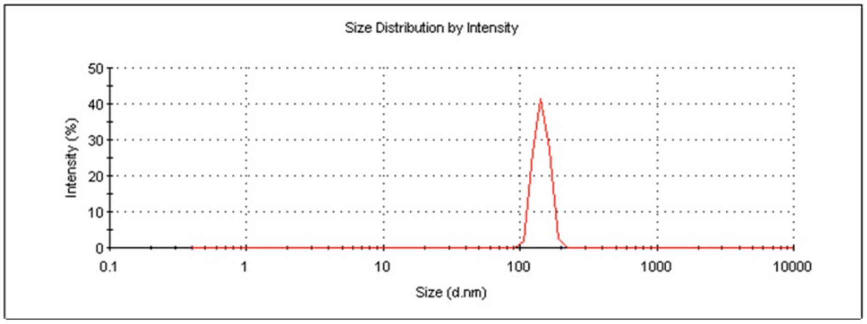
Supplementary Figure 1. ^{1}H NMR spectrum of PPA.

S2. Supplementary figure: optical and AFM images of drop-casted PPA particles



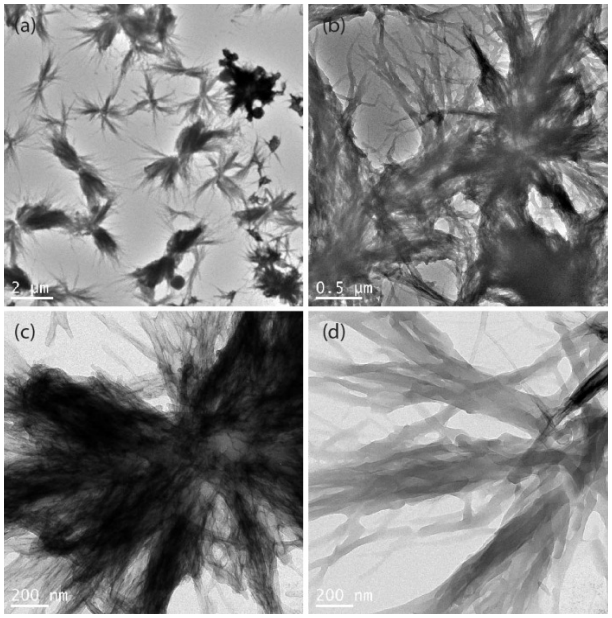
Supplementary Figure 2. Optical and AFM images of PPA particles drop-casted from 0.25 mg/mL HFIP solution. (a) and (c) refer to one location with micrometer particles. (b) and (d) refer to another location with several to tens of nanometers particles.

S3. Supplementary figure: DLS measurement of PPA nanospheres in HFIP



Supplementary Figure 3. Dynamic light scattering (DLS) measurement of PPA nanospheres in HFIP. The experiment was performed at 25 °C. The diameter of nanospheres formed by PPA in HFIP solution was characterized by DLS using a Malvern Zetasizer Nano (Malvern Instruments Ltd., Worcestershire, UK). All measurements were performed at an angle of 173°. The size distributions were analyzed by using the Malvern Dispersion Software (V5.10, www.zetasizer.com), which gives a diameter of 143 ± 18 nm and polydispersity index (PDI) of 0.432.

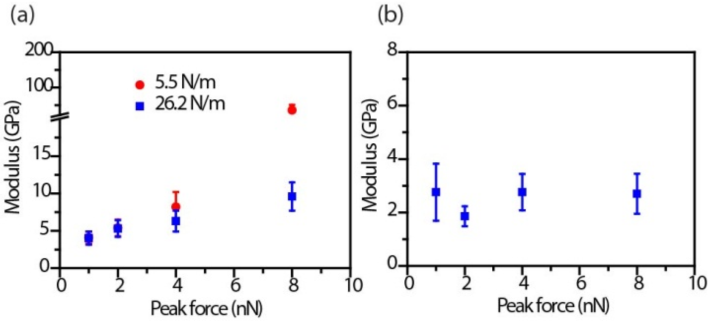
S4. Supplementary figure: TEM images of PPA nanofibers



Supplementary Figure 4. TEM images of PPA nanofibers made by drop-casting from 0.5 mg/mL solution followed by water treatment.

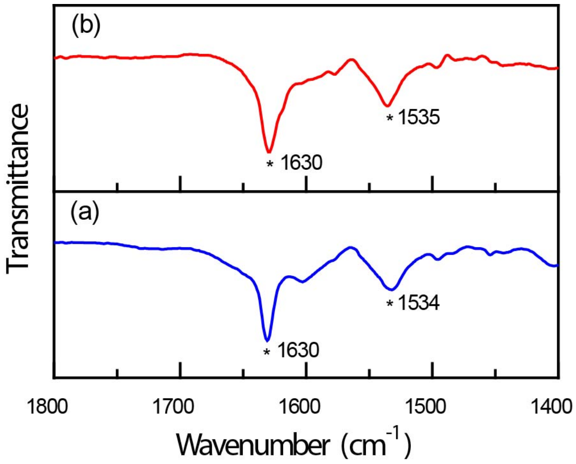
S5. Supplementary figure: the selection of cantilevers and peak force for stiffness measurement.

In order to determine the optimal conditions to measure the stiffness of nanospheres and nanofibers, cantilevers with different spring constant were tested at different peak force set points. The Yong's moduli of the nanofibers were determined by performing Gaussian fits on the modulus distributions in the same region of fiber films. As shown in supporting information Fig. S6a, two cantilevers with spring constants of 5.5 N/m and 26.2 N/m gave similar results at 1 nN, 2 nN and 4 nN peak force set points, while at 8 nN set point, the 5.5 N/m cantilever gave an unreasonably large modulus value, which means that 8 nN peak force is out of the linear region of the 5.5 N/m cantilever. Therefore, 26.2 N/m cantilever was used for further measurements.



Supplementary Figure 5. (a) Young's moduli of the PPA nanofiber films measured with two cantilevers with spring constants of 5.5 N/m and 26.2 N/m at different peak force set points. (b) Young's moduli of the PPA nanospheres measured with a 26.2 N/m cantilever at different peak force set points.

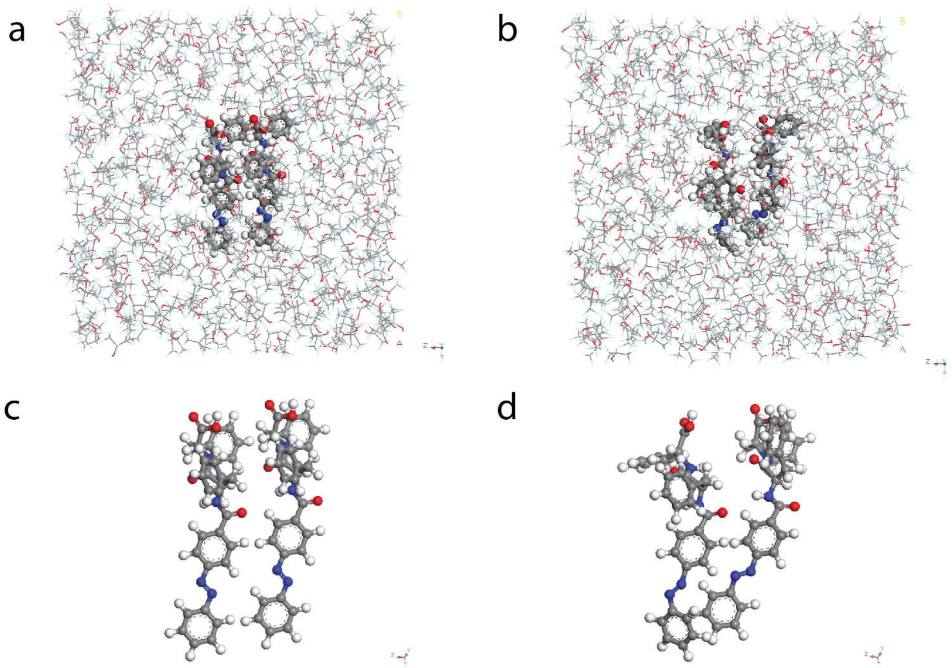
S6. Supplementary figure: FT-IR spectra of PPA nanospheres and nanofibers.



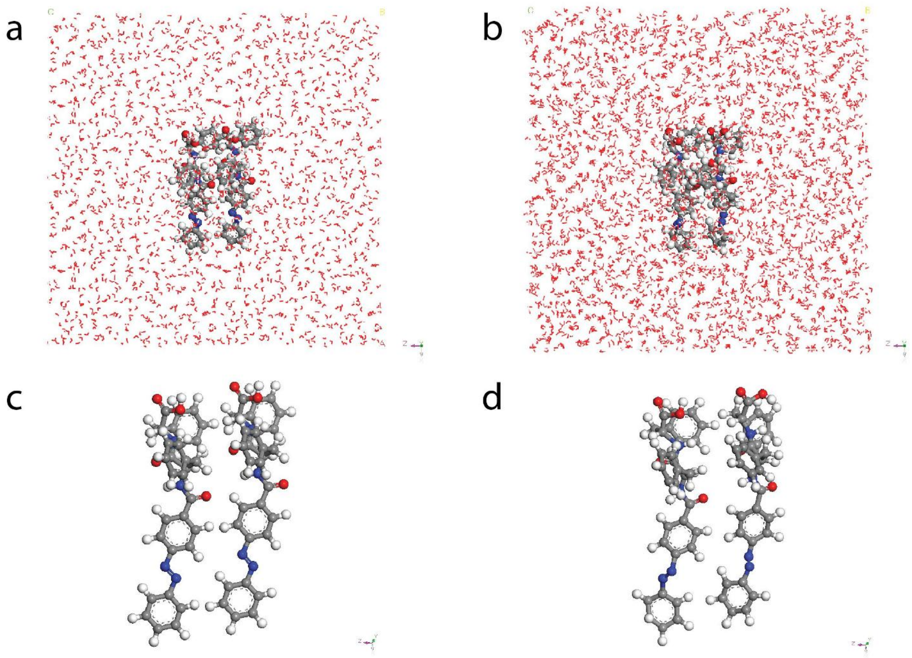
Supplementary Figure 6. FT-IR spectra of PPA nanosheres (a) and nanofibers (b). FT-IR spectra were recorded on Spetrum Two with UATR (Single Reflection Diamond) accessory (PerkinElmer, Waltham, MA, USA). Spectra were obtained from 32 scans at 4 cm^{-1} resolution. The procedure of sample preparation was the same with that of TEM measurements.

S7, S8. Supplementary figures and table: MD simulations

Molecular dynamics (MD) simulations were implemented using the DISCOVER code in Materials Studio. All the MD simulations were performed in periodic boundary conditions in the range of 150 × 150 × 150 Å 3 at 300 K. PPA molecules were put into the solution surroundings (HFIP and water) and implemented by using a constant-pressure/constant-temperature dynamics (NPT) ensemble simulation with the time step of 0.1 fs in the initial. After that the system is simulated in a constant-volume/constant-temperature dynamics (NVT) ensemble simulation with the time step of 1 fs. The data are collected at intervals of 1 ps and then the full-precision trajectory was then recorded and the results were analyzed.



Supplementary Figure 7. The MD simulation results of PPA dimer conformation in HFIP. (a), (c): Initial conformation of PPA dimer in HFIP. (b), (d): Final conformation of PPA dimer in HFIP after stabilization.

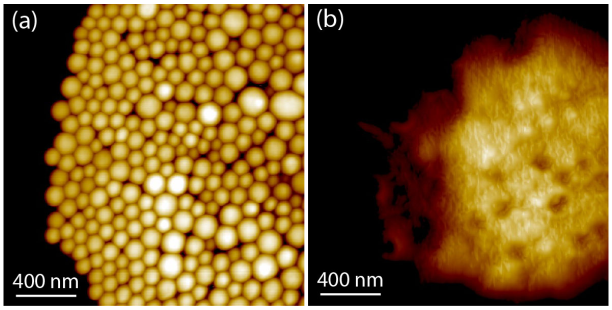


Supplementary Figure 8. The MD simulation results of PPA dimer conformation in water. (a), (c): Initial conformation of PPA dimer in water. (b), (d): Final conformation of PPA dimer in water after stabilization.

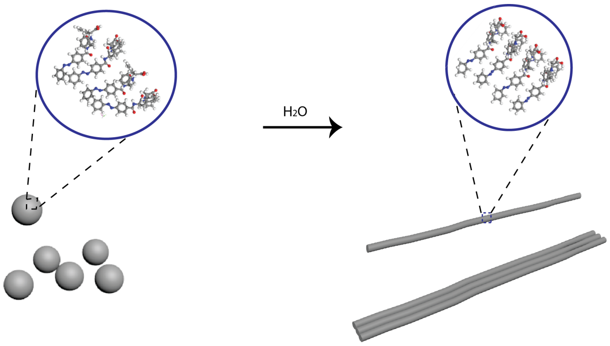
Table 1: The variation of conformation of PPA dimer in different solvents

	Initial conformation	**Final conformation**
PPA dimer molecule in HFIP	Parallel	V shape
PPA dimer molecule in water	Parallel	Parallel

S9. Supplementary figure: PPA structures formed after UV irradiation



Supplementary Figure 9. Structures formed by spin-coating of 0.25 mg/mL PPA in HFIP without (a) and with (b) UV irradiation for 2 h.



Supplementary Figure S10. The scheme of proposed mechanism of PPA nanostructure transition.

References

1 Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. Organometallics, 29, 2176 (2010).