Electronic Supplementary Information

of

Interface self-assembly to construct vertical peptide nanorods on quartz template

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1. Materials

1-Pyrene methanol was purchased from ACROS (USA) and used without further purification. *N*-Fluorenyl-9-methoxycarbonyl (FMOC) protected glycine, 2-chlorotrityl chloride resin (100-200 mesh, loading: 1.32 mmol/g), *N*-hydroxybenzotriazole (HOBt), benzotriazole-*N,N,N',N'*-tetramethyluroniumhexafluorophosphate (HBTU) and piperdine were purchased from GL Biochem (Shanghai) Ltd. (China) and used as received. 2,2,2-Trifluoroethanol, acetate acid and dichloromethane (DCM) were provided by Shanghai Reagent Chemical Co. (China) and used directly. Dimethylformamide (DMF), diisopropylethylamine (DiEA) and 1,4-dioxane were obtained from Shanghai Reagent Chemical Co. (China) and distilled prior to use. All other reagents and solvents were of analytical grade and used directly.

2. Synthesis of 4-Oxo-4-(pyren-2-ylmethoxy) Butanoic Acid

1-Pyrenyl methanol (4.64 g, 0.02 mol), succinic anhydride (2.6 g, 0.026 mol), pyridine (2.1 mL, 0.026 mol) and triethylamine (2.5 mL, 0.026 mol) were dissolved in 150 mL dry 1,4-dioxane. In dark, the mixture was stirred at room temperature for 24 h and then evaporated under vacuum. The crude product was dissolved in CH_2Cl_2 and then cold 1 M HCl was added to precipitate the product. The purified product was collected after repeated washing the precipitation using distilled water and drying under vacuum (Yield: 79.2%). ^{1}H-NMR (300 MHz, CDCl3, δ ppm): 11.76 (1H, -COO*H*), 8.34-8.06 (9H, $C_{16}H_9$-CH_2O-), 5.73 (2H, $C_{16}H_9$-C*H*$_2$O-), 2.51 (2H, $C_{16}H_9$-CH_2OC=OCH_2CH_2COOH), 2.43 (2H, $C_{16}H_9$-CH_2OC=OCH_2CH_2COOH).

3. Synthesis of Glycyl-glycine Derivative (Pyrene-CH_2O-succinyl-Gly-Gly)

The dipeptide building block was synthesized manually in 1.98 mmol scale on the 2-chlorotrityl chloride resin employing a standard FMOC solid phase peptide synthesis

(SPPS) method. Before the reaction, the resin was washed with DCM (three times) and DMF (three times) and then immersed in DMF for 30 min. After draining off DMF solution, a DMF solution of the mixture of FMOC protected glycine (4 equiv relative to resin loading) and DiEA (6 equiv) was added to the resin and shaken for 2 h at room temperature. After removing the reaction solution, the resin was washed with DMF (three times). Subsequently, 20% piperdine/DMF (V/V) solution was introduced to the resin to remove the FMOC protected groups. After shaking for 30 min at room temperature, the reaction solution was drained off and the resin was washed with DMF (three times). The presence of free amino groups was indicated by a blue color in the Kaiser test. Thereafter, a DMF solution of the mixture of FMOC protected glycine (4 equiv), HBTU (4 equiv), HOBt (4 equiv) and DiEA (6 equiv) was added. After shaking at room temperature for 1.5 h, the reaction solution was drained off and the resin was washed with DMF (three times). The absence of free amino groups was indicated by a yellow color in the Kaiser test. After the deprotection and washing, a DMF solution of the mixture of 4-oxo-4-(pyren-2-ylmethoxy) butanoic acid (4 equiv), HBTU (4 equiv), HOBt (4 equiv) and DiEA (6 equiv) was added. After shaking at room temperature for 1.5 h, the resin was washed with DMF (three times) and DCM (three times). Cleavage of the aromatic peptide from the resin was performed using a mixture of 2,2,2-trifluoroethanol, acetate acid and DCM in the ratio of 2:1:7. After 2 h shaking at room temperature, the cleavage mixture and DCM washing were collected. The combined solution was concentrated to a viscous solution by rotary evaporation. Thereafter, cold ether was added to precipitate the product. After washing with cold ether (five times), the glycyl-glycine derivative (pyrene-CH_2O-succinyl-Gly-Gly) was obtained after drying the precipitation under vacuum for 24 h. Purity (Fig. S1A): 99.1% determined by high-pressure liquid chromatography (HPLC) with a C18 column and using a linear gradient of acetonitrile and DI water containing 0.1% NH_4OH. Element analysis: ($C_{25}H_{22}N_2O_6$): Calcd. C 67.26, N 6.27, H 4.97; Found C 67.02, N 6.57, H 5.06. ^{1}H-NMR (Fig. S1B, 300 MHz, DMSO-d_6, δ ppm):

8.34-8.12 (9H, $C_{16}\boldsymbol{H}_9$-CH_2O-), 5.82 (2H, $C_{16}H_9$-$C\boldsymbol{H}_2O$-), 3.69-3.71 (4H of Gly), 2.57-2.59 (4H, $C_{16}H_9$-CH_2OC=$OC\boldsymbol{H}_2C\boldsymbol{H}_2C$=O). ^{13}C-NMR (Fig. S1C, 300 MHz, DMSO-d_6, δ ppm): 173.1-169.9 ($C_{16}H_9$-$CH_2O\boldsymbol{C}$=$OCH_2CH_2\boldsymbol{C}$=O and $\boldsymbol{C}$=O of Gly), 131.7-123.9 ($\boldsymbol{C}_{16}H_9$-CH_2O-), 64.8 ($C_{16}H_9$-$\boldsymbol{C}H_2O$-), 42.7 and 41.3 ($\boldsymbol{C}H_2$ of Gly), 30.2 and 29.6 ($C_{16}H_9$-CH_2OC=$O\boldsymbol{C}H_2CH_2\boldsymbol{C}$=O); FT-IR: ~3465 cm^{-1} amide A band, ~1735 cm^{-1} stretching vibration of ester bond, ~1655 cm^{-1} amide I band, ~1557 cm^{-1} amide II band; ESI-MS: 231.1 $(M\text{-Pyrene methyl})^+$.

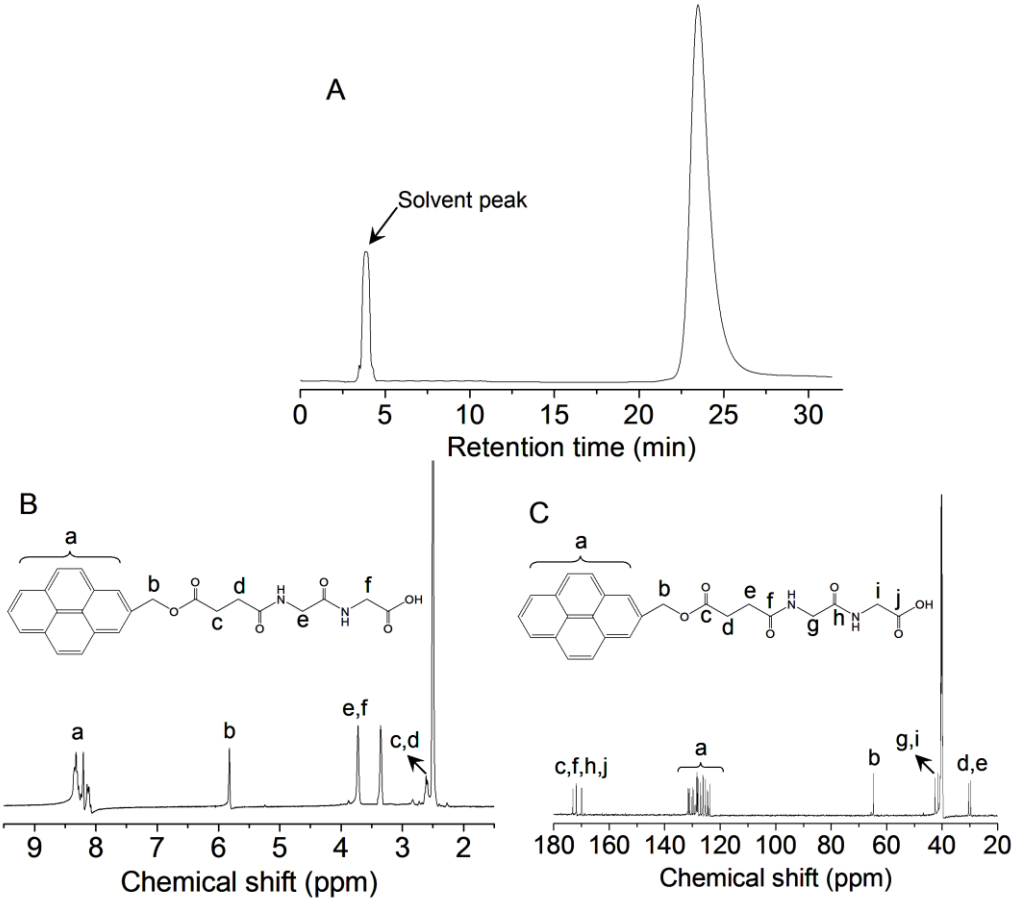

Fig. S1. (A): HPLC profile of the glycyl-glycine derivative, pyrene-CH_2O-succinyl-Gly-Gly; (B) ^{1}H-NMR spectrum of the glycyl-glycine derivative, pyrene-CH_2O-succinyl-Gly-Gly; (C) ^{13}C-NMR spectrum of the glycyl-glycine derivative, pyrene-CH_2O-succinyl-Gly-Gly.

4. Functionalization of Quartz Template

The blank quartz template (2×0.8×0.1 cm^3) was ultrasonically cleaned with deionized water,

ethanol, and dichloromethane for 30 min, respectively. Then the template was dried at nitrogen atmosphere and subsequently immersed into a piranha solution (30% hydrogen peroxide /concentrated sulfuric acid, v/v) at 110 ^{o}C for 1 h. After repeated rinsing with deionized water, the template was dried at nitrogen atmosphere. To perform amino-functionalization, the dried blank quartz template was placed into a dried toluene containing 1% APTES at 60 ^{o}C for 15 min. Thereafter, the template was rinsed with dried toluene for five times and dried at nitrogen atmosphere. To chemically bind the glycyl-glycine derivative onto the surface of the template, the amino-functionalized quartz template was immersed into a 2 mL DMF solution containing 15 mg dipeptide, 8 mg HOBt and 10 μL DIC for 48 h, followed by repeated washing with DMF, ethanol, deionized water, ethanol, respectively and drying at nitrogen atmosphere.

5. Interface Self-Assembly

The aqueous solution of the dipeptide with different concentration (0.5, 1.1 and 1.6 mg/mL) was first prepared by dissolving the required amount of the dipeptide in distilled water at a pH of ~10. Then, the peptide-bound quartz template was placed into this solution. Thereafter, the solution pH was adjusted to 2.5 using HCl vapor to trigger the interface self-assembly of the dipeptide. At predetermined time, the quartz template was taken out, followed by repeated rinsing with distilled water at a pH of 4 for five times (20 mL×5) and drying at nitrogen atmosphere for characterizations. The control experiment was performed by immersing the amino-functionalized quartz template into the dipeptide aqueous solution (1.6 mg/mL) and allowing the self-assembly for 2 h via adjusting the solution pH to 2.5.

6. Water Contact Angle (CA)

CA of the quartz template was examined on a Dataphysics OCA20 (German) equipment. A droplet of deionized water (2 μL) which was formed at the end of the needle was dropped

onto the surface of the quartz template and CA was measured within twenty seconds. The detailed CA profile of the quartz template is shown Fig. S2.

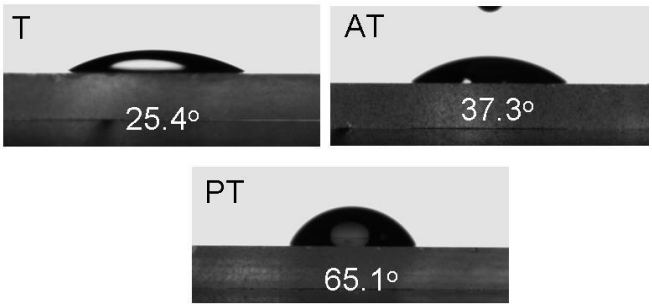

Fig. S2. CA values of the blank, amino-functionalized and dipeptide-bound quartz templates. (T: blank quartz template; AT: amino-functionalized quartz template; PT: dipeptide bound-quartz template)

7. Atomic Force Microscopy (AFM)

The surface morphology of the quart template was examined on a Picoscan atomic force microscope (Molecular Imaging, Tempe, AZ). The AFM images of the blank, amino-functionalized and dipeptide-bound quartz templates are exhibited in Fig. S3. And the surface roughness of the blank, amino-functionalized and peptide-bound quartz templates are 0.5, 2.1 and 2.6, respectively.

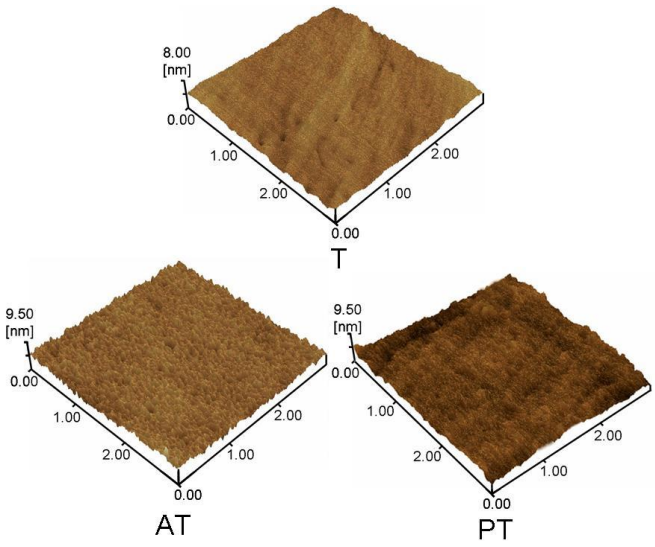

Fig. S3. AFM images of the blank, amino-functionalized and peptide-bound quartz templates.

(T: blank quartz template; AT: amino-functionalized quartz template; PT: peptide bound-quartz template)

8. X-ray Photoelectron Spectroscopy (XPS)

The chemical properties of the surface of the quartz template was examined on an X-650 (HITACHI, Japan) using a monochromated beam from a magnesium source run at FRR analyzer mode.

9. Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) measurements were made using a SOPRA GES-5E spectroscopic ellipsometer over a typical wavelength range of 300-800 nm to obtain ellipsometric angles, Ψ and Δ. The experimental data were fitted using a classical Lorentz oscillator model to calculate thickness of the film on the quartz template.

10. Fluorescence Spectroscopy

Fluorescence emission spectrum of the quartz template was recorded on a LS55 luminescence spectrometry (Perkin-Elmer) with excitation at 330 nm and emission data range between 340 and 750 nm.

11. 2D Planar AFM images of Surface Morphology of the Quartz Template

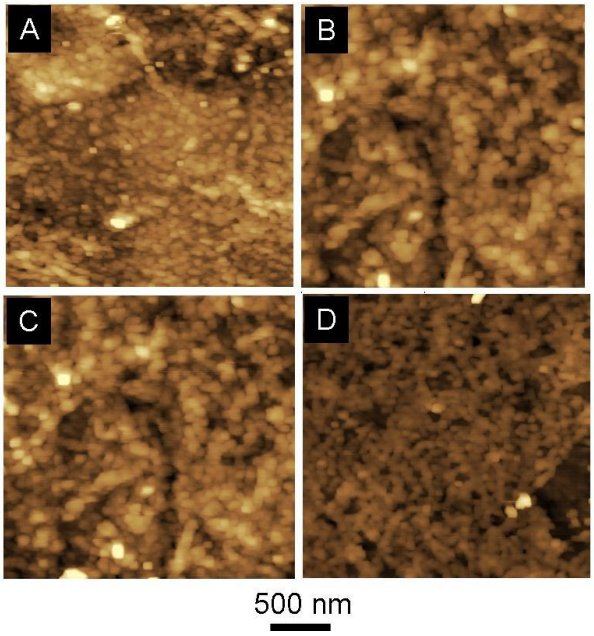

Figure S4. 2D planar AFM images of surface morphology of the quartz template. (A): Peptide-bound quartz template obtained after immersing into the dipeptide solution (1.1 mg/mL) and then allowing the interface self-assembly for 2 h; (B): Peptide-bound quartz template obtained after immersing into the dipeptide solution (1.1 mg/mL) and then allowing the interface self-assembly for 4 h; (C): Peptide-bound quartz template obtained after immersing into the dipeptide solution (1.1 mg/mL) and then allowing the interface self-assembly for 6 h; D: Peptide-bound quartz template obtained after immersing into the dipeptide solution (1.6 mg/mL) and then allowing the interface self-assembly for 1 h.

12. AFM images of the Concentration Dependence of Chemically Bound Vertically Aligned Nanorods on the Surface of Quartz Template

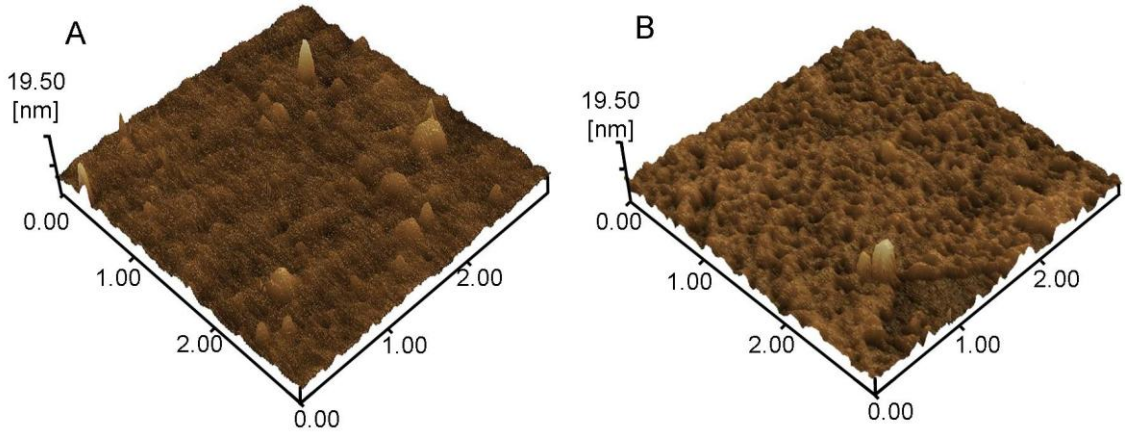

Fig. S5. AFM images of the chemically bound vertically aligned nanorods (CBVANs) on the surface of the quartz template formed via the interface self-assembly of the dipeptide at a concentration of 0.5 mg/mL (A) and 1.6 mg/mL (B) for 1 h.

13. AFM Image and Fluorescent Emission Spectrum of Amino-Functionalized Quartz Template Immersed into the Self-Assembled Peptide Aqueous Solution

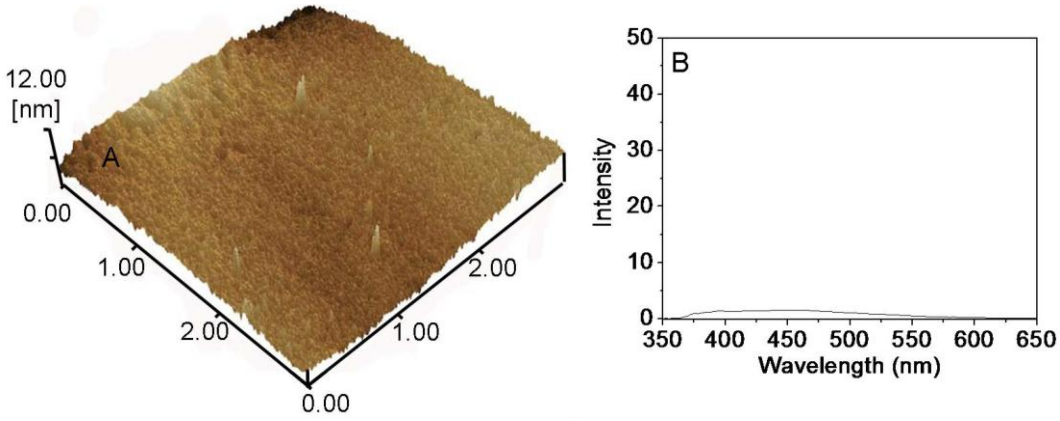

Fig. S6. AFM image (A) and fluorescent emission spectrum (B) of amino-functionalized quartz template obtained after immersing into the dipeptide aqueous solution (1.6 mg/mL) and then allowing the self-assembly for 2 h.

14. AFM Image of the Surface Morphology of UV Light (365 nm) Irradiated Quartz Template with CBVANs

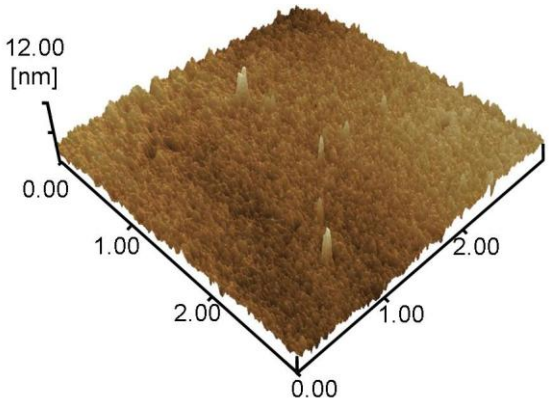

Fig. S7. AFM image of the UV light irradiated quartz template with CBVANs obtained after placing the peptide-bound quartz template into the dipeptide aqueous solution (1.1 mg/mL) and then allowing the self-assembly for 2 h.