# **Electronic Supplementary Information**

Precise Surface Structure of Nanofibres with Nearly Atomic-Level Precision

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# S1. Materials.

Poly(ethylene glycol) monomethyl ether (PEG<sub>113</sub>-OH,  $M_n$  = 5000 g/mol) was purchased from Sigma-Aldrich (USA) and dried under vacuum before use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd (China), dried over CaH<sub>2</sub> and purified by distillation. Tetrahydrofuran (THF) was purchased from Sinopharm Chemical Reagent Co., Ltd (China) and purified by distillation over sodium. CuCl was purchased from Sinopharm Chemical Reagent Co., Ltd (China), purified by precipitating the concentrated hydrochloric acid solution of CuCl into excess water. The precipitate was then washed with acetic acid and diethyl ether, correspondingly. 4-Vinylpyridine (4-VP) was purchased from Sigma-Aldrich (USA), dried over CaH<sub>2</sub> and distilled under reduced pressure. 2-bromoisobutyryl 2-Chloropropionyl chloride, bromide, 4-toluenesulfonylchloride and 5-hydroxy-2-nitrobenzaldehyde were purchased from Sigma-Aldrich (USA). Sodium borohydride, sodium hydride, and 4-dimethylaminopyridine (DMAP) were purchased from TCI (Japan). Basic alumina and neutral alumina were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Circular plasmid DNA, pcDNA3.1/myc-His(-) A (5522 bp, Invitrogen, USA) and pcDNA3.1/myc-His(-)/lacZ (8592 bp, Invitrogen, USA) were extracted from Escherichia coli using the alkaline lysis method. DNA primers, PCR kits, EcoR I and T4 DNA ligase were purchased from Sangon Biotech (China). HS-PEG<sub>44</sub>-N<sub>3</sub> ( $M_{n, PEG}$  = 2000 g/mol) was purchased from ToYong Bio (China). Other reagents and solvents were used as received.

#### S2. Characterization.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained using a 400 MHz Bruker instrument (Germany) and analysed with Bruker Topspin

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software (Germany) using tetramethylsilane (TMS) as a reference. Gel permeation chromatography (GPC) was carried out on a Waters-Wyatt system (USA) comprising a Waters 1515 HPLC pump, Waters 2414 refractive index detector, TOSOH TSK gel  $\alpha$ -3000 and  $\alpha$ -2500 columns in series with dimethylformamide (DMF) (0.2% LiBr, w/w) as the elution solvent. Molecular weights were determined with Astra software (USA) calibrated using the polyethylene oxide calibration standard kit. Dynamic light scattering (DLS) was performed on an ALV-5000 laser light-scattering spectrometer (Germany). All the sample solutions were filtered through 0.45-µm Millipore filters (Millex-LCR hydrophilic PTFE, USA) to remove dust. Transmission electron microscopy (TEM) observations were conducted using a Philips CM120 electron microscope (Netherland) at an acceleration voltage of 60 kV and a FEI Tecnai G2 20 TWIN electron microscope (USA) at an accelerating voltage of 200 kV. Steady-state fluorescence emission spectra (FLS) were recorded using a QM40 fluorescence spectrometer (PTI, USA) from 500 nm to 800 nm at an excitation wavelength of 482 nm. UV-vis spectra were collected on a SHIMADZU-2550 spectrophotometer (Japan). Gel electrophoresis was performed using CSL-RVMSCHOICETRIO gel electrophoresis equipment (UK) at a voltage of 90 V and a current of 60 mA for 50 min.

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# S3. Synthesis of PEG-ONB-P4VP (7) by atom transfer radical polymerization (ATRP).

PEG-ONB-P4VP (7) was synthesized by ATRP, as shown in Scheme S1.



Scheme S1. Synthesis of PEG-ONB-P4VP.

**Synthesis of 3-hydroxymethyl-4-nitrophenol (2).** According to the literature,<sup>[1]</sup> 5-hydroxy-2-nitrobenzaldehyde (1) (1.4 g, 8.4 mmol) was dissolved in 50 mL of MeOH in a flask in an ice bath. Then, sodium borohydride (1.0 g, 26.5 mmol) was slowly added to the solution. The mixture was stirred in an ice bath for 5 h. Then, 35 mL of 10% HCl solution was added to the solution to quench the reaction. The solution was dried under vacuum and redissolved in water. Then, the solution was extracted with EtOAc (50 mL×4). The combined EtOAc solution was washed with saturated brine, dried with anhydrous MgSO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by flash column chromatography with hexane/EtOAc (1:1) to obtain a yellow solid (1.2 g, 86% yield).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, *δ*): 10.90 (s, 1H), 8.07 (d, 1H), 7.26 (s, 1H), 6.81 (d, 1H), 5.52 (s, 1H), 4.83 (s, 2H).

<sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, *δ*): 163.53, 143.39, 138.41, 128.28, 114.33, 114.28, 60.79.

Synthesis of PEG-OTs (4). According to the literature,<sup>[2]</sup> PEG-OH (3) (10.0 g, 2 mmol) and 4-toluenesulfonylchloride (4.0 g, 20.8 mmol) were completely dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) in an ice bath. Triethylamine (3.0 ml, 21.6 mmol) was added dropwise to the above solution; the resulting solution was stirred in an ice bath for 3 h, followed by stirring for an additional 48 h at room temperature. The reaction solution was precipitated in cold diethyl ether and dried under vacuum at 30 °C to obtain PEG-OTs (9.5 g, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.45 (s, 3H), 3.38 (s, 3H), 3.47 (t, 2H), 3.55(t,

2H), 3.64 (s, 450H), 3.82 (t, 2H), 4.16 (t, 2H), 7.35 (d, 2H), 7.80 (d, 2H).

**Synthesis of PEG-ONB-OH (5).** According to the literature,<sup>[1]</sup> sodium hydride (288 mg, 7.2 mmol, 60% in mineral oil) was added to dried THF (10 mL) in an ice bath. 5-Dydroxy-2-nitrobenzyl alcohol (2) (1.2 g, 7.2 mmol) in dry THF (10 mL) was slowly added to the above solution over 30 min. After stirring in an ice bath for 30 min, PEG-OTs (4) (9.0 g, 1.8 mmol) in THF (100 mL) was added to the mixture solution. The solution was reacted at 70 °C for 48 h. The reaction was quenched by distilled water (2.5 mL). The solution was filtered through basic alumina and precipitated in cold diethyl ether to obtain PEG-ONB-OH (8.5 g, 94% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*): 8.18 (d, 1H), 7.36 (s, 1H), 6.91 (d, 1H), 5.01 (s, 2H), 4.27 (t, 2H), 3.64 (s, 450H), 3.38 (s, 3H).

**Synthesis of PEG-ONB-Br (6).** According to the literature,<sup>[1]</sup> in a 250-mL round-bottomed flask, PEG-ONB-OH (5) (9.0 g, 1.8 mmol), DMAP (20 mg, 0.16 mmol), TEA (4.5 mL, 32.4 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) were added sequentially. 2-Bromo-2-methylpropanoyl bromide (1 mL, 8 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added dropwise to the above solution over 30 min in an ice bath. The resulting solution was stirred in an ice bath for 3 h and then reacted

at room temperature for an extra 48 h. The reaction was quenched by methanol (5.0 mL). The solution was filtered through basic alumina, concentrated under vacuum and precipitated in cold diethyl ether to obtain PEG-ONB-Br (7 g, 78% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*): 8.22 (d, 1H), 7.21 (s, 1H), 6.96 (dd, 1H), 5.66 (s, 2H), 4.24 (t, 2H), 3.64 (s, 450H), 3.38 (s, 3H), 2.01 (s, 6H).

Synthesis of PEG-ONB-P4VP (7). The ATRP reaction was conducted in a Schlenk flask; PEG-ONB-Br (6) (1.0 g, 0.2 mmol), CuCl (25 mg, 0.25 mmol), Me<sub>6</sub>TREN (92  $\mu$ L, 0.33 mmol), 4-VP (8.0 mL, 74.6 mmol) and butanone/2-propanol (8.0 mL, v/v = 7:3) were added sequentially. After three freeze-thaw cycles, the mixture was reacted at 40 °C for 10 h. After the reaction was quenched by liquid nitrogen, the solution was exposed to air. The solution was filtered through neutral alumina, concentrated under vacuum and precipitated in cold diethyl ether to obtain PEG-ONB-P4VP (2.0 g, 22% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.30 (br, aromatic H), 6.36 (br, aromatic H), 3.66 (br, -CH<sub>2</sub>CH<sub>2</sub>O-), 1.40 (br, -CH<sub>2</sub>CH-).

The degree of polymerization of P4VP is 54; the obtained polymer is PEG<sub>113</sub>-ONB-P4VP<sub>54</sub>.  $M_n$  (GPC) = 11.5 kg/mol,  $M_w/M_n$  = 1.24.

# S4. Photocleavage of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> by UV irradiation.

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Scheme S2. Photocleavage of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub>.

The *ortho*-nitrobenzyl (ONB) group in PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> is photocleavable under UV irradiation (365 nm), as shown in Scheme S2. When the ONB group is photocleaved, the absorption peak of ONB at 308 nm will disappear.<sup>[3]</sup> Solutions of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mg/mL) were irradiated under 365-nm UV light. The intensity of the peak at 308 nm decreased stepwise with an absorption tail appearing, which indicated that the nitro-aromatic moiety of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> disappeared (Figure S8). Correspondingly, the colour of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> in CH<sub>2</sub>Cl<sub>2</sub> changed from colourless to light yellow under UV irradiation (Figure S9). GPC analysis confirmed that PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> (2 mg/mL in DMF) was photocleaved after 4 h of UV irradiation (Figure S10).<sup>[1]</sup>

#### S5. Synthesis of PEG-*b*-P4VP by ATRP.

PEG-*b*-P4VP was synthesized as previously described.<sup>[4]</sup> In brief, PEG-*b*-P4VP was synthesized using PEG-CI as the macroinitiator and 4-VP as the monomer, as shown in Scheme S3. The <sup>1</sup>H NMR spectra and GPC curves of the polymers are shown in Figures S11-S13.



#### Scheme S3. Synthesis of PEG-b-P4VP.

**Synthesis of PEG-CI.** PEG-OH (10 g, 2 mmol), TEA (1.1 mL, 8 mmol) and 30 mL of dry CH<sub>2</sub>Cl<sub>2</sub> were dissolved in a 100-mL round-bottomed flask. Then, 2-chloropropionyl chloride (0.58 mL, 6 mmol) in 5.0 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the mixture over 30 min. After the mixture was reacted at room temperature for 48 h, it was precipitated in cold diethyl ether to obtain PEG-CI (9.0 g, 90% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*): 4.43 (m, 1H), 4.32 (t, 2H), 3.64 (s, 450H), 3.37 (s, 3H), 1.70 (d, 3H).

**Synthesis of PEG-***b***-P4VP.** PEG-Cl (1.0 g, 0.2 mmol), CuCl (25 mg, 0.25 mmol), Me<sub>6</sub>TREN (135 μL, 0.50 mmol), 4-VP (8.0 mL, 73.6 mmol), and

isopropanol (8.0 mL) were added sequentially to a Schlenk flask. After three freeze-thaw cycles, the mixture was reacted at 45 °C for 40 min. After the reaction was quenched by liquid nitrogen, the mixture was exposed to air. The product was filtered through neutral alumina, concentrated under vacuum and precipitated in cold diethyl ether to obtain PEG-*b*-P4VP (2.2 g, 24% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*): 8.33 (br, aromatic H), 6.38 (br, aromatic H), 3.65 (br, -CH<sub>2</sub>CH<sub>2</sub>O-), 1.45 (br, -CH<sub>2</sub>CH-).

The degree of polymerization of P4VP is 58; the obtained polymer is PEG<sub>113</sub>-*b*-P4VP<sub>58</sub>.  $M_n$  (GPC) = 13.0 kg/mol,  $M_w/M_n$  = 1.25.

### S6. Nanofibre preparation with PEG-ONB-P4VP and DNA.

Typically, for the preparation of DNA/PEG-ONB-P4VP nanofibres, 8.0 mL of CO<sub>2</sub> saturated water was first added to 2.0 mL of PEG-ONB-P4VP diblock copolymer solution in methanol at 2.0 mg/mL to prepare micelles under gentle magnetic stirring. Then, 1.0 mL of monodisperse DNA at 0.2 mg/mL was added. After 72 h of incubation, 2.0 µL of pure 1,4-dibromobutane was added to crosslink the core of the nanofibres to obtain a stable structure. The crosslinking mechanism was the quaternization between the pyridine groups of P4VP and 1,4-dibromobutane (Scheme S4). DNA/PEG-*b*-P4VP nanofibres were fabricated by similar assembly procedures.



**Scheme S4.** Schematic illustration of the structure of the P4VP core crosslinked by 1,4-dibromobutane (DBB) as the crosslinker through quaternization reaction between the pyridine groups and DBB.

# S7. Preparation of DNA with functional groups (DBCO) at different sites.

(a) Preparation of different DNA sequences by PCR

*Templates:* Circular plasmid DNA, pcDNA3.1/myc-His(-) A (5522 bp, Invitrogen, USA)

The different DNA primers are shown below:

1) DNA (1516 bp) with a single DBCO group on the end (DNA-S-DBCO): Sense primer: /5'Phos/ GCCAGATATACGCGTTGACATTGATTAT 3' G: G-DBCO

Anti-sense primer: /5'Phos/ TAGACCGAGATAGGGTTGAGTGTTGTTC 3'

2) DNA (760 bp) with an enzyme site and one DBCO group (760-EN-DBCO):
 Sense primer: /5'Phos/ TATGAATTCT TATCCGCTCACAATTCCA 3' T: T-DBCO
 Anti-sense primer: /5'Phos/ ATACCTCGCTCTGCTAATC 3'

The ligation product of 760-EN-DBCO is 1516 bp DNA with two neighbouring DBCO groups in the midpoint (DNA-M-DBCO). The two neighbouring DBCO groups in the midpoint are considered as a DBCO group (see the explanation in S7b).

3) DNA (1516 bp) with a single DBCO group on each end (DNA-D-DBCO):
Sense primer: /5'Phos/ GCCAGATATACGCGTTGACATTGATTAT 3' G: G-DBCO
Anti-sense primer: /5'Phos/ TAGACCGAGATAGGGTTGAGTGTTGTTC 3' T: T-DBCO
4) DNA (760 bp) with an enzyme site and two DBCO groups (DBCO-760-EN-DBCO):

Sense primer: /5'Phos/ TATGAATTCTTATCCGCTCACAATTCCA 3' T: T-DBCO Anti-sense primer: /5'Phos/ ATACCTCGCTCTGCTAATC 3' A: A-DBCO The ligation product of DBCO-760-EN-DBCO is 1516 bp DNA with two neighbouring DBCO groups in the midpoint and one DBCO group on each end (DNA-T-DBCO). The two neighbouring DBCO groups in the midpoint are considered as a DBCO group (see the explanation in S7b).

*PCR protocol for 1516 bp DNA:* 94 °C 3 min, [94 °C 30 s, 64 °C 30 s, 72 °C 90 s] 30×, 72 °C 10 min.

*PCR protocol for 760 bp DNA:* 94 °C 3 min, [94 °C 30 s, 46 °C 30 s, 72 °C 90 s] 30×, 72 °C 10 min.

Reagents	Concentration	Volume (µL)
Plasmid template	25 mg/L	1.0
Sense primer	10 µM	1.0
Anti-sense primer	10 µM	1.0
Taq DNA polymerase	5 U/µL	0.5
dNTP	2 mM	5.0
Buffer solution	10×Taq Buffer with (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	5.0
MgCl <sub>2</sub>	25 mM	3.0
ddH <sub>2</sub> O		33.5

 Table S1. Ingredients for each PCR tube.

(b) Explanation of the midpoint modification of DNA with a DBCO group.

For the two neighbouring DBCO groups in the midpoint of 1516 bp DNA, they are considered as a DBCO group. The distance between the two neighbouring DBCO groups is only 2.0 nm, while the size of the AuNP-N<sub>3</sub> is  $14.4 \pm 1.9$  nm with the surface modified with the PEG<sub>44</sub> chain of a contour length of 16.5 nm. Once one AuNP connects to the DBCO group in the middle of DNA chain, it is very difficult to connect the second AuNP due to the steric hindrance effect. Therefore, it is reasonable to consider that the two neighbouring DBCO groups in the midpoint of 1516 bp DNA are equivalent to a DBCO group.

(c) Typical EcoR I restriction and ligation reaction for 760 bp DNA.<sup>[5]</sup>

1) EcoR I restriction: 760 bp DNA (40  $\mu$ L) was incubated for 3 h at 37 °C in a water bath with EcoR I (4  $\mu$ L, 10 U/ $\mu$ L) in the appropriate buffer (5  $\mu$ L, 10×EcoR I buffer: 500 mM Tris-HCI, pH 7.5, 100 mM MgCl<sub>2</sub>, 1 M NaCl, 0.2% Triton X-100, 1 mg/ml bovine serum albumin) and then inactivated at 65 °C for 20 min.

2) Ligation reaction: The solution resulting from EcoR I restriction without purification (49  $\mu$ L) was incubated with T4 DNA ligase (2  $\mu$ L, 10 U/ $\mu$ L) at 22 °C for 3 h in the appropriate buffer (4  $\mu$ L, 10×T4 DNA ligase buffer: 400 mM Tris-HCl, 100 mM MgCl<sub>2</sub>, 100 mM DTT, 5 mM ATP, pH 7.8, 25 °C) and then incubated at 65 °C for 20 min to denature the T4 DNA ligase. The resulting solution was purified with PCR purification kits obtained from Sangon Biotech (China).

# S8. Preparation of positively charged HS-PEG<sub>44</sub>-N<sub>3</sub>-modified gold nanoparticles (AuNPs-N<sub>3</sub>) (Scheme S5).

Positively charged AuNPs were prepared as previously described.<sup>[6]</sup> Then, 30 mg of HS-PEG<sub>44</sub>-N<sub>3</sub> in 3.0 mL of DMF was slowly added to 10 mL of AuNP aqueous solution at 30 °C over 1.5 h; the mixture was continuously stirred at 30 °C for 72 h to achieve sufficient ligand exchange. Subsequently, HS-PEG<sub>44</sub>-N<sub>3</sub>-modified AuNPs were washed with water by centrifugation 4 times and redispersed in water.

In brief, the HS-PEG<sub>44</sub>-N<sub>3</sub>-modified AuNPs are 14.4  $\pm$  1.9 nm in size and positively charged with a zeta potential of +78.0 mV at pH 6.5.<sup>1</sup>H NMR and Fourier-transform infrared spectroscopy (FTIR) experiments demonstrated the successful modification of AuNPs with HS-PEG<sub>44</sub>-N<sub>3</sub> (Figures S18 and S19).



**Scheme S5.** The illustration of HS-PEG<sub>44</sub>-N<sub>3</sub>-modified gold nanoparticles (AuNPs-N<sub>3</sub>).



**Figure S1**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) spectrum of 3-hydroxymethyl-4-nitrophenol (2).



Figure S2. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) spectrum of 3-hydroxymethyl-4-nitrophenol (2).



Figure S3. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PEG-OTs (4).



Figure S4. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PEG-ONB-OH (5).



Figure S5. <sup>1</sup>H NMR (CDCI<sub>3</sub>) spectrum of PEG-ONB-Br (6).



Figure S6. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PEG-ONB-P4VP (7).



Figure S7. GPC curves of PEG-ONB-Br (6) and PEG-ONB-P4VP (7) in DMF.



**Figure S8**. UV-vis spectra of 2 mg/mL PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> in CH<sub>2</sub>Cl<sub>2</sub> recorded after different UV (365 nm) irradiation times. The intensity of the peak at 308 nm decreased stepwise with the appearance of an absorption tail, which indicated that the nitro-aromatic moiety of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> disappeared.



**Figure S9**. Images of 2 mg/mL PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> in CH<sub>2</sub>Cl<sub>2</sub> (a) before and (b) after UV irradiation at 365 nm for 4 h. The solution colour changed from colourless to light yellow, indicating that the nitro-aromatic moiety of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> disappeared while a nitroso compound appeared.



**Figure S10.** GPC curves of 2 mg/mL PEG<sub>113</sub>-ONB-Br and 2 mg/mL PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> in DMF recorded after different UV (365 nm) irradiation times. After 4 h of UV irradiation (365 nm), two new peaks appeared, meaning that the ONB groups of PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> were photocleaved.



Figure S11. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PEG-Cl.



Figure S12. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PEG-*b*-P4VP.



Figure S13. GPC curves of PEG-CI and PEG-b-P4VP in DMF.



**Figure S14.** Fluorescence spectra of ethidium bromide (EB) and EB with 8592 bp DNA, non-crosslinked 8592 bp DNA/PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> nanofibres, and PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> micelles at pH 6.3. The molar ratio of EB/DNA base pairs is fixed at 1:6. The relative intensity of the EB/8592 bp DNA mixture is almost identical to that of EB/8592 bp DNA/PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> nanofibres (non-crosslinked) mixture, indicating the DNA in the nanofibres is fully accessible to EB intercalation. Thus, DNA is on the surface of the core instead of embedded in the core.<sup>[7]</sup> Moreover, the zeta potential of non-crosslinked nanofibres is negatively charged (–45.5 mV) at pH 6.3.



**Figure S15.** UV-vis spectra of P4VP core-crosslinked 8592 bp DNA/PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> nanofibres before (black line) and after (red line) irradiation at 365 nm for 6 h. The P4VP core-crosslinked 8592 bp DNA/PEG<sub>113</sub>-*b*-PVP<sub>58</sub> nanofibre suspension at the same concentration was used as a reference. The concentration of the nanofibre suspension in methanol/water (v/v = 2:9) was fixed at 0.36 mg/mL. After UV irradiation, the peak at 308 nm disappeared, meaning that the PEG shell was photocleaved from the nanofibres.



**Figure S16**. Gel electrophoresis images of 1516 bp DNA (1), 760-EN-DBCO (2) and ligation products (DNA-M-DBCO, 2'), DNA-D-DBCO (3), and DBCO-760-EN-DBCO (4) and ligation products (DNA-T-DBCO, 4'). M represents the DNA marker, and the bands represent DNA with 100, 250, 500, 750, 1000, 1500, 2000, 3000, and 5000 base pairs from the bottom to the top.



**Figure S17.** TEM images of (a) DNA-S-DBCO/PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> nanofibres before UV irradiation, and (b) DNA-S-DBCO/PEG<sub>113</sub>-ONB-P4VP<sub>54</sub> nanofibres after UV irradiation. The details of P4VP core-crosslinking reaction and PEG shell removal photocleavage reaction can be seen in S4 and S6 in ESI.







**Figure S19.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectra of HS-PEG<sub>44</sub>-N<sub>3</sub> polymer and HS-PEG<sub>44</sub>-N<sub>3</sub>-modified AuNPs (AuNPs-N<sub>3</sub>). The PEG signals confirmed the successful modification of AuNPs with HS-PEG<sub>44</sub>-N<sub>3</sub>.



**Figure S20.** FTIR spectra of HS-PEG<sub>44</sub>-N<sub>3</sub> and HS-PEG<sub>44</sub>-N<sub>3</sub>-modified AuNPs (AuNPs-N<sub>3</sub>). The peak of the azide groups (N<sub>3</sub>) confirmed the successful modification of AuNPs with HS-PEG<sub>44</sub>-N<sub>3</sub>. However, there was a slight shift in the azide peak because of the interaction with the AuNPs.<sup>[8]</sup>



**Figure S21.** TEM image of nanofibres specifically modified with a single  $AuNP-N_3$  at one end. TEM samples were prepared via lyophilization.

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