Supporting Information

The Power of One-pot: A Hexa-component System Containing π-π stacking, Ugi reaction and RAFT polymerization for Simple Polymer-conjugation on Carbon Nanotube

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Experimental Section

1. Materials

Multi-walled carbon nanotube (CNT) with diameter 20-30 nm was purchased from Timenano (Chengdu, China) and used without further treatment. Aniline (Aladdin, 98%), cyclohexyl isocyanide (J&K, 98%), α-Cyclodextrin (J&K, 98%), and 1-pyrenecarboxaldehyde (J&K, 98%) were used as purchased. 2,2'-Azobis(2-methylpropionitrile) (AIBN, J&K, 99.9%) was recrystalized twice from acetone prior

to use. N-isopropylacrylamide (NIPAAm) (J&K, 98%) was recrystalized from n-hexane prior to use.

Amino terminated methoxypolyethylene glycol (mPEG-NH_2, M_n ~ 5150)[1], and 2-(2-(((ethylthio)carbonothioyl)thio)propanamido)acetic acid[1] were synthesized as previous literatures.

2. Instrumental Analysis

^1H NMR spectra were obtained using a JEOL JNM-ECA400 (400MHz) spectrometer for all samples. The Fourier transform infrared (FT-IR) spectra were obtained in a transmission mode on a Perkin-Elmer spectrum 100 spectrometer (Waltham, MA, USA). Typically, 4 scans at a resolution of 1 cm^{-1} were accumulated to obtain one spectrum. Thermal gravimetric analysis (TGA) was conducted on a TA instrument Q50 with a heating rate of 20 °C/min. Samples weighing between 2 and 5 mg were heated from 25 to 600 °C in air flow (60 mL/min), N_2 as the balance gas (40 mL/min). Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 kV; the TEM specimens were made by placing a drop of the nanoparticle ethanol suspension on a carbon-coated copper grid.

3. Method

3.1. Preparation of CNT-PNIPAAm:

CNT (150 mg), 1-pyrenecarboxaldehyde (30 mg, 0.13 mmol), aniline (30 mg, 0.32 mmol), 2-(2-(((ethylthio)carbonothioyl)thio)propanamido)acetic acid (40 mg, 0.15 mmol), cyclohexyl isocyanide (30 mg, 0.27 mmol), NIPAAm (1.0 g, 8.8 mmol), AIBN (13 mg, 0.08 mmol) was dissolved in 3 mL of methanol in a Schlenk tube. The tube was then sealed with a rubber septum and purged by nitrogen flow for 20 min. The tube was then put into an oil bath maintained at 65 °C for 20 h. The CNT-PNIPAAm complex can be easily purified by washing with methanol and isolated by centrifugation (20000 rpm, 30 min, 5 times). Several characterizations were then

taken to further analyze the CNT-PNIPAAm complex, including ^{1}H NMR, FT-IR, TEM, and TGA.

3.2. Preparation of CNT-copolymer:

CNT (150 mg), 1-pyrenecarboxaldehyde (30 mg, 0.13 mmol), mPEG-NH_2 (1.0 g, 0.19 mmol), 2-(2-(((ethylthio)carbonothioyl)thio)propanamido)acetic acid (40 mg, 0.15 mmol), cyclohexyl isocyanide (30 mg, 0.27 mmol), NIPAAm (1.0 g, 8.8 mmol), AIBN (13 mg, 0.08 mmol) was dissolved in 3 mL of methanol in a Schlenk tube. The tube was then sealed with a rubber septum and purged by nitrogen flow for 20 min. The tube was then put into an oil bath maintained at 65 °C for 20 h. The CNT-copolymer complex can be easily purified by washing with methanol and isolated by centrifugation (20000 rpm, 30 min, 5 times). Several characterizations were then taken to further analyze the CNT-copolymer complex, including ^{1}H NMR, FT-IR, TEM, and TGA.

3.3. Preparation of CNT supermolecular hydrogel:

CNT-copolymer (10 mg) was dispersed in water (300 μL), and then mixed with saturated α-CD solution (300 μL). The combined solution was kept under ultrasonic oscillations at 40 °C for 15 min, and then cooled down to 25 °C to generate the supermolecular hydrogel.

Two control experiments were carried out using CNT-PNIPAAm to mix with α-CD or direct using CNT-copolymer without α-CD. No hydrogel formed in both cases.

Supporting Data

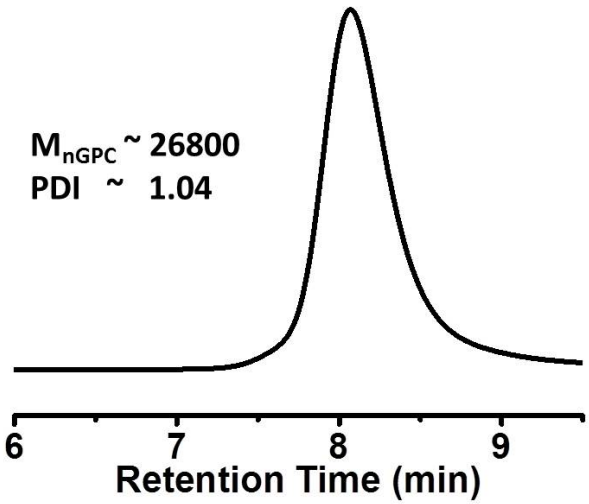

Figure S1. GPC spectrum of the unconjugated polymers in the methanol solution of the one-pot system.

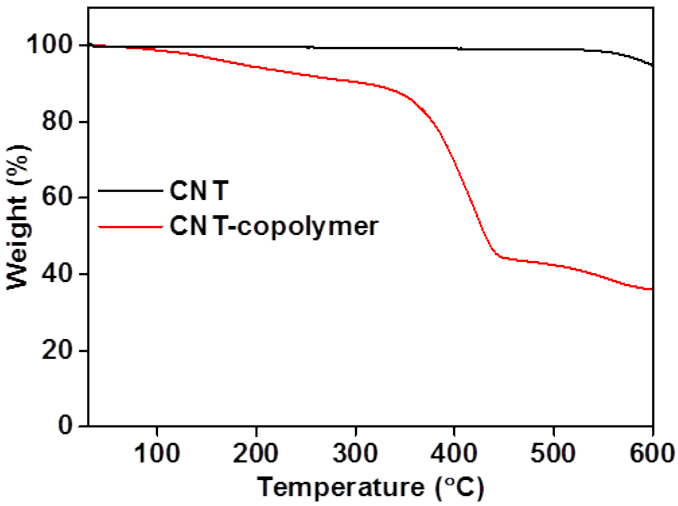

Figure S2. TGA image of pristine CNT and CNT-copolymer.

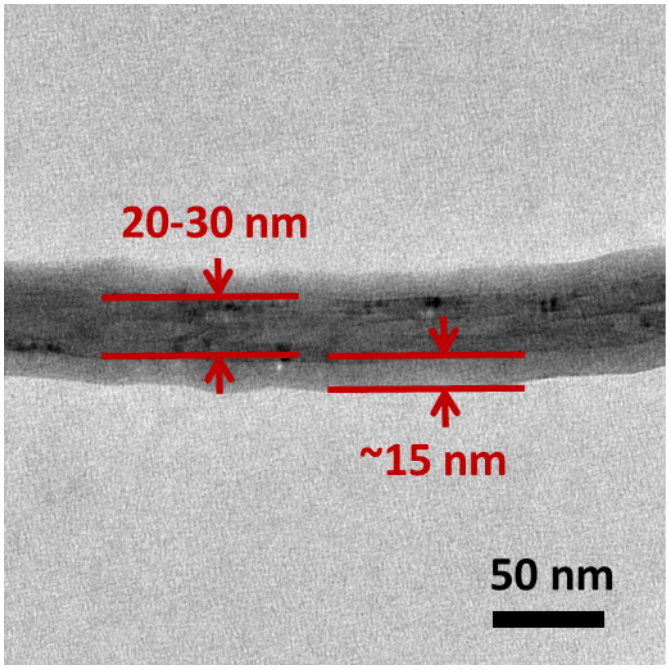

Figure S3. TEM image of CNT-copolymer.

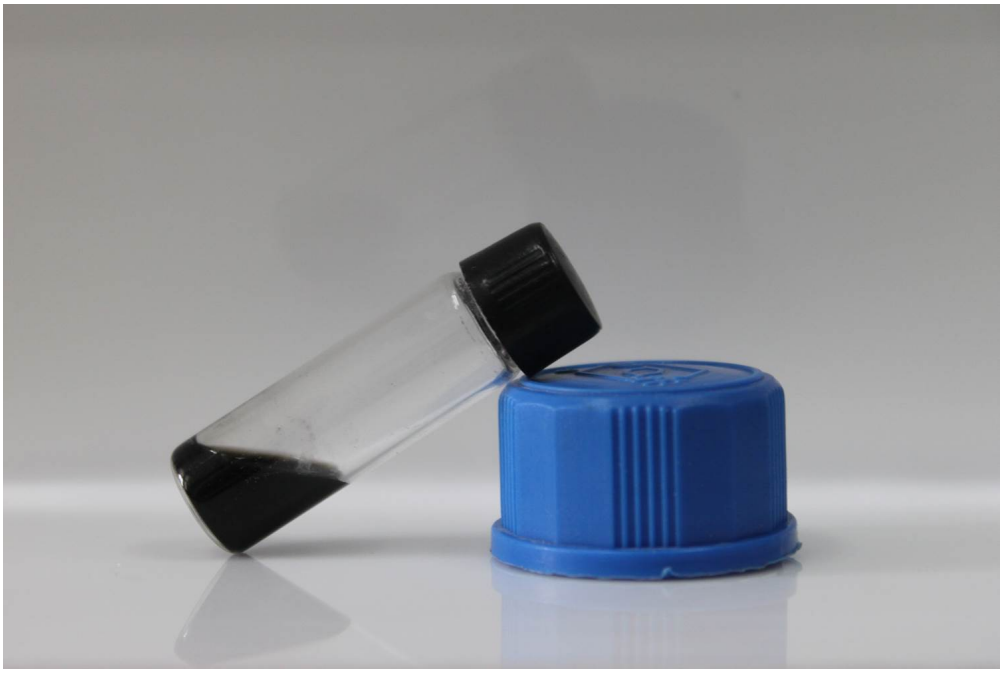

Figure S4. Photograph of control group (CNT-PNIPAAm with α-CD).

Figure S5. Photograph of control group (CNT-copolymer without α-CD).

Reference

[1] B. Yang, Y. Zhao, C. Fu, C. Zhu, Y. Zhang, S. Wang, Y. Wei, L. Tao, *Polym. Chem.* **2014**, *5*, 2704-2708.