Electronic Supplementary Information

Preparation of Well-defined Fibrous Hydrogels *via* Electrospinning and *In-Situ* "Click Chemistry"

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1. Synthesis of 1-azido-3-aminopropane

3-Bromopropylamine hydrobromide (3.2 g, 15 mmol) was added into a 150 mL round-bottom flask containing 100 mL of deionized water. Sodium azide (3.2 g, 50 mmol) were added into the solution. After stirring the reaction mixture at 80 ^{o}C for 16 h, about two-thirds of the solvent was removed by vacuum distillation. The flask was then immersed into an ice-water bath, and potassium hydroxide (4 g) was slowly added into the above solution. The solution was extracted with 50 mL of diethyl ether for three times. The organic phase was combined, dried over anhydrous K_2CO_3 overnight, and filtrated. 1-Azido-3-aminopropane was obtained without further purification, after removing diethyl ether by rotary evaporation and drying under reduced pressure.

2. Synthesis of azido-pendant linear functional PEG derivatives ($(PEG_n(N_3))_m$)

Linear functional PEG derivatives having pendant azido groups were synthesized via the epoxide-amine reaction of PEGDGE and 1-azido-3-aminopropane. 1-Azido-3-aminopropane (1.0 g, 8.143 mmol) and PEGDGE (5.0 g, 8.143 mmol) were added into a round-bottom flask containing 5 mL of methanol. The reaction mixture was then stirred with the mechanical stirrer at room temperature. After stirring for 7 days, the reaction mixture was dialyzed against deionized water for 72 h. $(PEG_{11}(N_3))_{19}$ was obtained by removing the solvent using rotary evaporation and drying under reduced pressure.

3. Synthesis of alkynyl-pendant linear functional PEG derivatives ($(PEG_n(C\equiv CH))_m$)

Linear functional PEG derivatives having pendant alkynyl groups were synthesized via the epoxide-amine reaction of PEGDGE and propargylamine. Propargylamine (0.12 g, 8.143 mmol) and PEGDGE (5.0 g, 8.143 mmol) were added into a round-bottom flask containing 5 mL of methanol. The reaction mixture was then stirred with the mechanical stirrer at room temperature. After stirring for 4 days, the reaction mixture was dialyzed against deionized water for 72 h. $(PEG_{11}(C\equiv C))_{28}$ was obtained by removing the solvent using rotary evaporation and drying under reduced pressure.

4. Synthesis of benzyl azide

Benzyl chloride (12.60 g, 0.1 mol) and sodium azide (9.75 g, 0.15 mol) were mixed in 50 mL of acetone. The reaction was carried out at 80 °C for 24 h. After that, the reaction mixture was poured into deionized water (50 mL). The solution was extracted with 20 mL of dichloromethane and dried with anhydrous Na_2SO_4. The Na_2SO_4 was filtered off, and dichloromethane was removed by rotary evaporation. The product was obtained as a liquid.

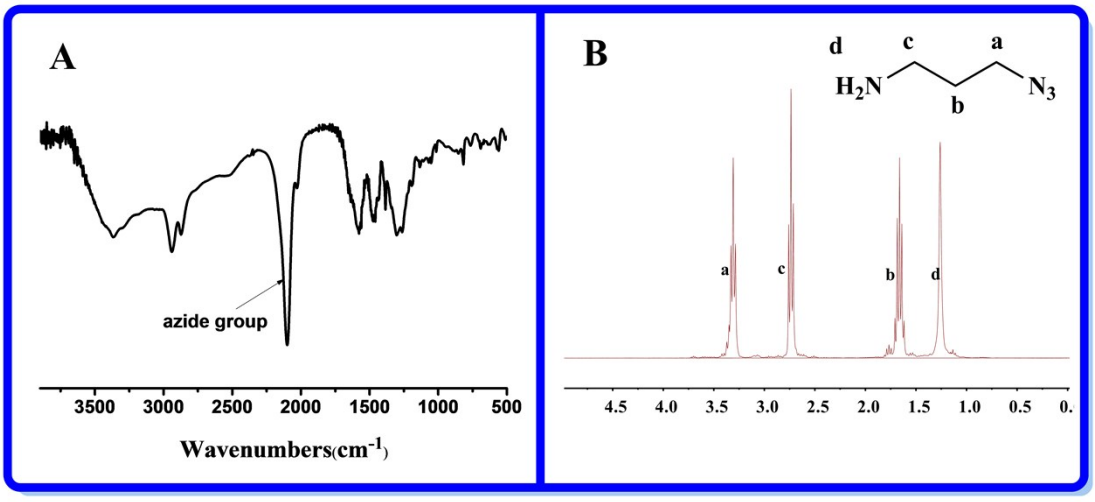

Figure S1. FT-IR spectrum (A) and ^{1}H NMR spectrum (B) of 1-azido-3-aminopropane

In the FT-IR spectrum, the strong absorbance peak at about 2098 cm^{-1} is belonging to the azido moieties in 1-azido-3-aminopropane. The peak assignments in the ^{1}H NMR spectrum are consistent with the chemical structure of 1-azido-3-aminopropane.

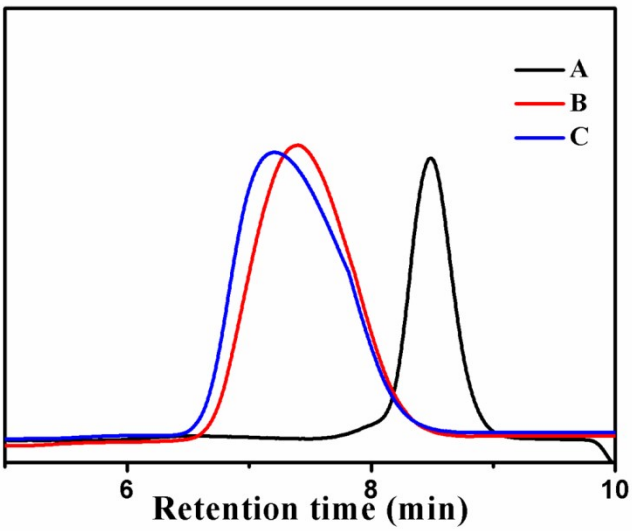

Figure S2. GPC traces of (A) PEGDGE, (B) $((PEG_{11}(N_3))_{19})$ and (C) $((PEG_{11}(C{\equiv}CH))_{28})$ using THF as the eluent

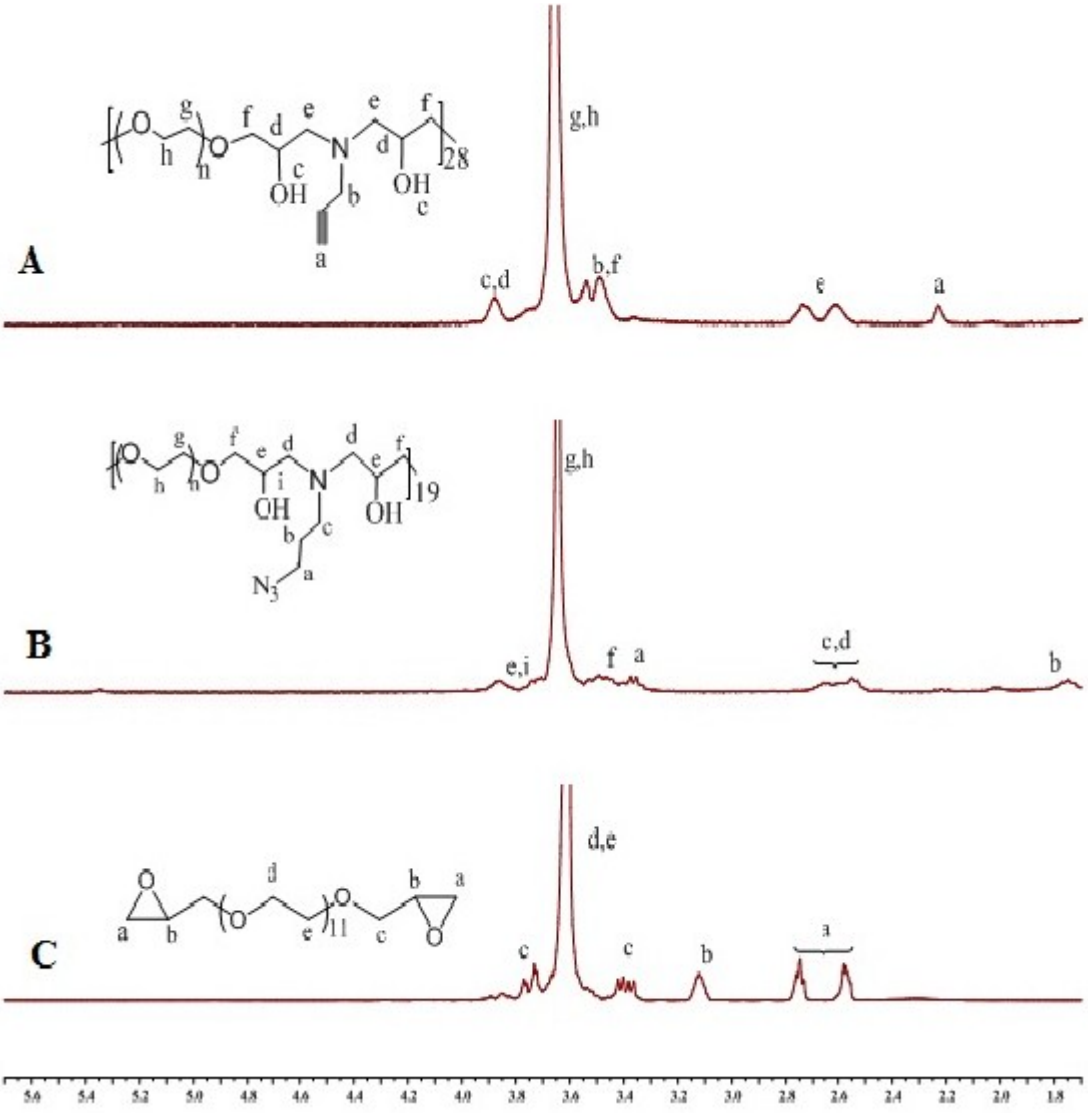

Figure S3. ^{1}H NMR spectra of (A) $(PEG_{11}(C{\equiv}CH))_{28}$, (B) $PEG_{11}(N_3)_{19}$ and (C) PEGDGE in $CDCl_3$-*d*

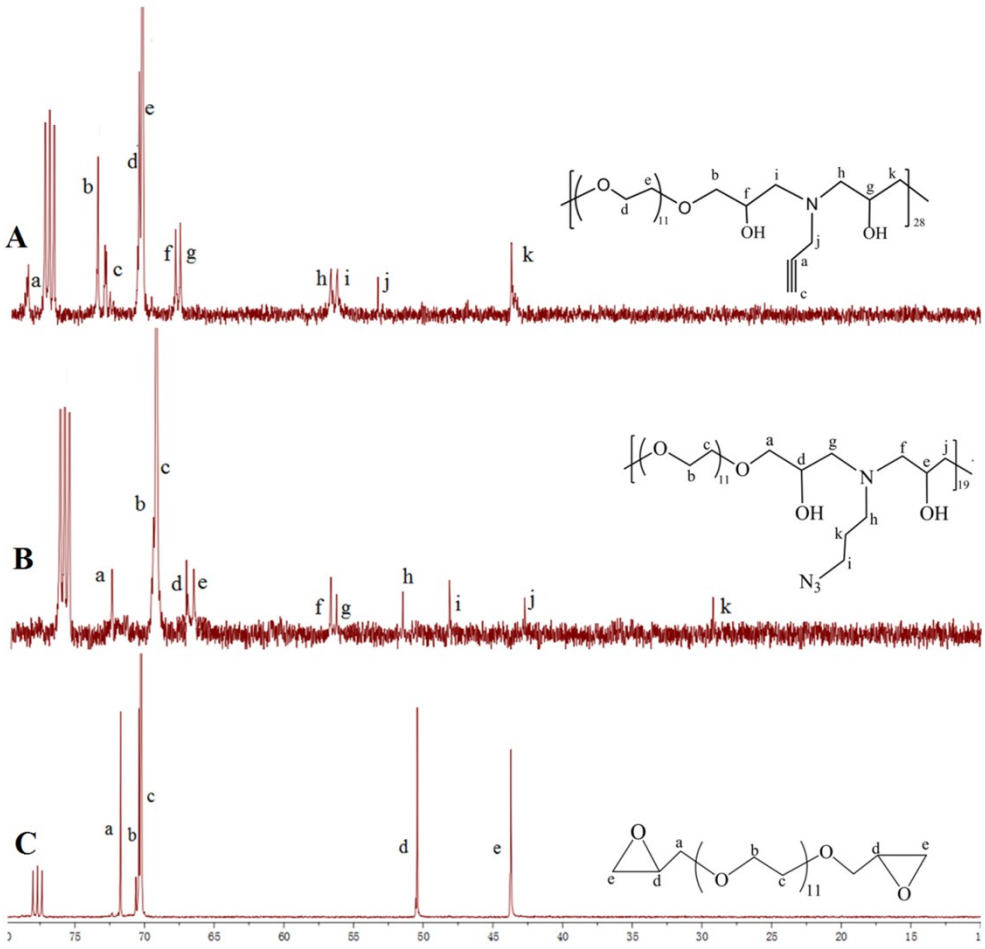

Figure S4. ^{13}C NMR spectra of (A) $(PEG_{11}(C{\equiv}CH))_{28}$, (B)$(PEG_{11}(N_3))_{19}$ and (C) PEGDGE in $CDCl_3$-*d*

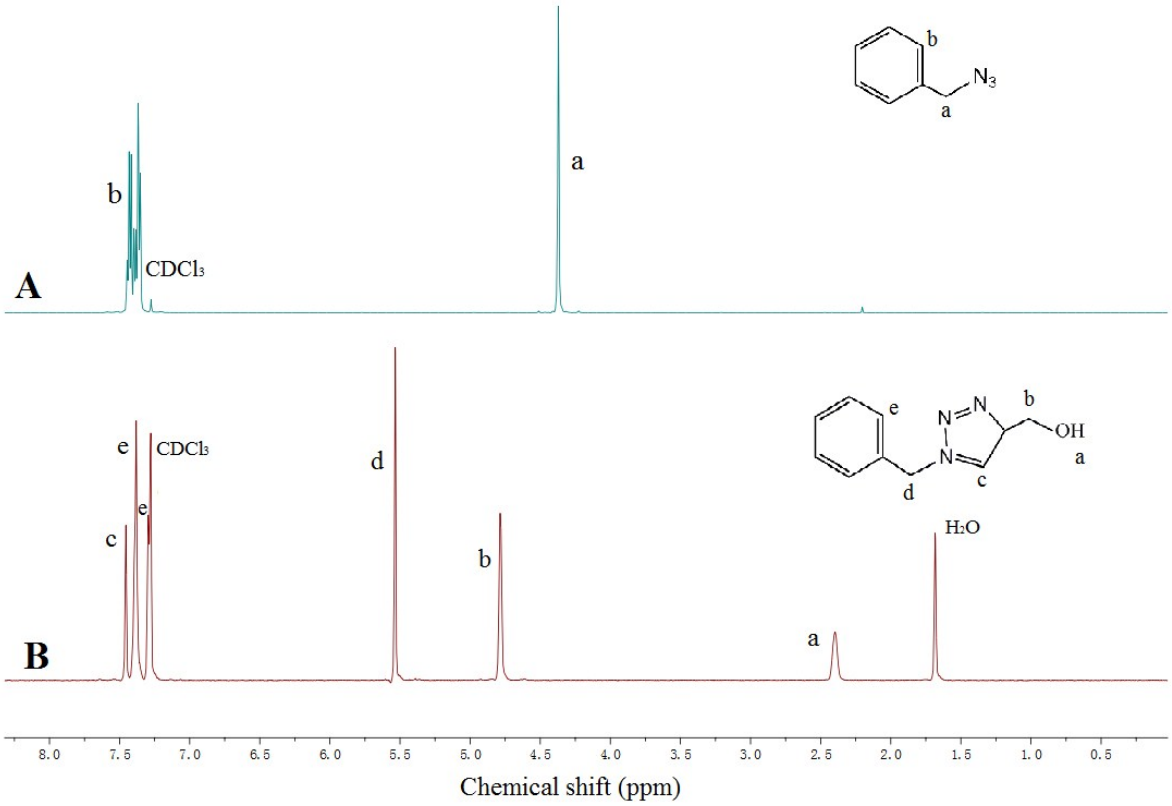

Figure S5. ^{1}H NMR spectra of (A) benzyl azide and (B) 1,2,3-triazole product in $CDCl_3$-*d*

Table 1. The time-dependent yields of 1,2,3-triazole product in the CuAAC reaction catalyzed by the copper nanoparticles-encapsulated $FH_{0.3}$ and $MH_{0.3}$

Reaction time (min)	**2**	**5**	**10**	**15**	**25**	**40**	**720**
$FH_{0.3}$	6.78	74.64	91.22	93.67	95.82	96.51	96.62
$MH_{0.3}$	1.23	17.02	63.31	87.85	93.88	96.21	-