

## Supporting Information

### Stimuli-responsive hydrogels prepared by simultaneous “Click Chemistry” and metal-ligand coordination

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### **Synthesis of 4-(prop-2-ynoxy)benzaldehyde**

According to the method reported,<sup>1</sup> 4-hydroxy-benzaldehyde (15.14 g, 0.124 mol), KOH (10.42 g, 0.186 mol), and propargyl bromide (22.13 g, 0.186 mol) were weighed into a 100 mL round-bottom flask, and the mixture was dissolved in 60 mL of ethanol and mixed thoroughly. The solution was heated under reflux at 80 °C for 20 h, and then cooled down to the room temperature. Solvent and unreacted propargyl bromide was removed under high vacuum to give rise to a dark brown solid. The solid was mixed with water (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic fraction was subsequently dried with anhydrous MgSO<sub>4</sub> and filtered. The solvent was later removed under high vacuum. The recovered solids were crystallized in ethanol, yielding brown crystals (yield: 68%, 10.3 g).

### **Synthesis of Diepoxy End-Functionalized PEG<sub>45</sub> ( $\alpha$ , $\omega$ -diepoxy PEG<sub>45</sub>) (DEP<sub>45</sub>)**

DEP<sub>45</sub> was prepared from PEG according to the method reported in the literature.<sup>2</sup> PEG ( $M_n = 2000$  g/mol, 10 g, 5 mmol) and 150 mL of anhydrous THF were added to a dry 250 mL flask under nitrogen. After the complete solvation of PEG, NaH (0.264 g, 11 mmol) was added in excess. The solution was stirred at room temperature under a nitrogen atmosphere for 12 h. Then epichlorohydrin (4 mL) was added to the mixture and the reaction mixture was left stirring for another 24 h and then passed through a neutral alumina column to remove salt and byproducts. After that, the filtrate was concentrated via a rotary evaporator and slowly precipitated into cold diethyl ether. The precipitate was then filtered and washed with diethyl ether three times. After precipitation, the filtered product was dried in vacuum at room temperature and then stored in a refrigerator (yield: 96%).

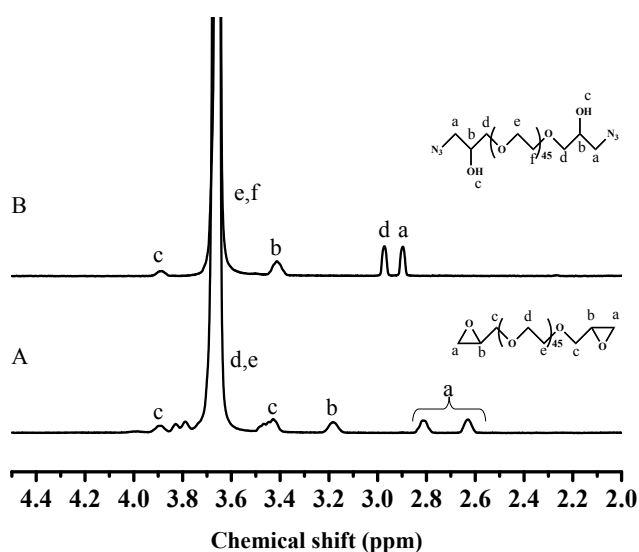
### **Synthesis of $\alpha$ , $\omega$ -diazide/hydroxyl PEG<sub>45</sub> (PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub>)**

PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> was synthesized according to the method reported.<sup>3</sup> The prepared  $\alpha$ ,  $\omega$ -diepoxy PEG<sub>45</sub> (5 g, 2.5 mmol) was dissolved in the mixture of water and dimethylformamide (DMF) (50 mL, V/V = 1 : 1). Sodium azide (3.25 g, 50 mmol) and ammonium chloride (0.27 g, 5 mmol) were then added into the above mixture,

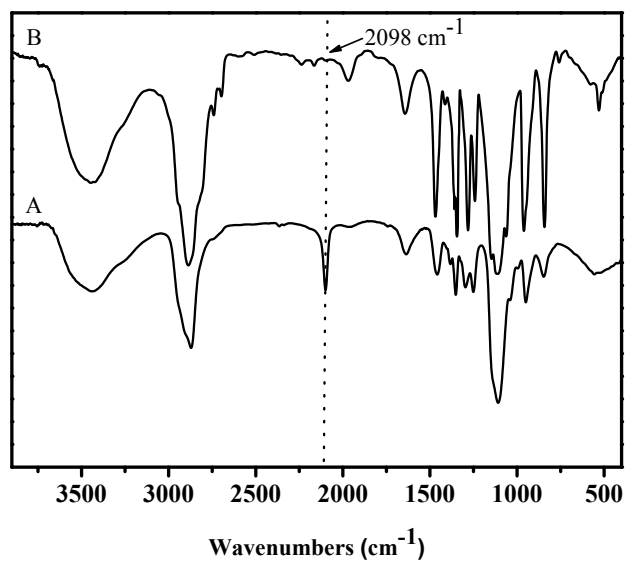
and the reaction was carried out at 50 °C under stirring for 72 h. The product was then filtered and transferred to a separatory funnel. The resulting solution was extracted with methylene chloride three times (50 mL each), and then the combined organic extracts were allowed to pass through a neutral alumina column to remove residue reactants and dried over anhydrous MgSO<sub>4</sub> overnight. After removal of the solvent by distillation under reduced pressure, the product was purified by precipitation in an excess amount of cold diethyl ether. The resulting product was obtained by filtration and dried in vacuum overnight (yield: 84%).

### Preparation of polymer extracts from simultaneous “click chemistry” and metal coordination chemistry in a one-pot process

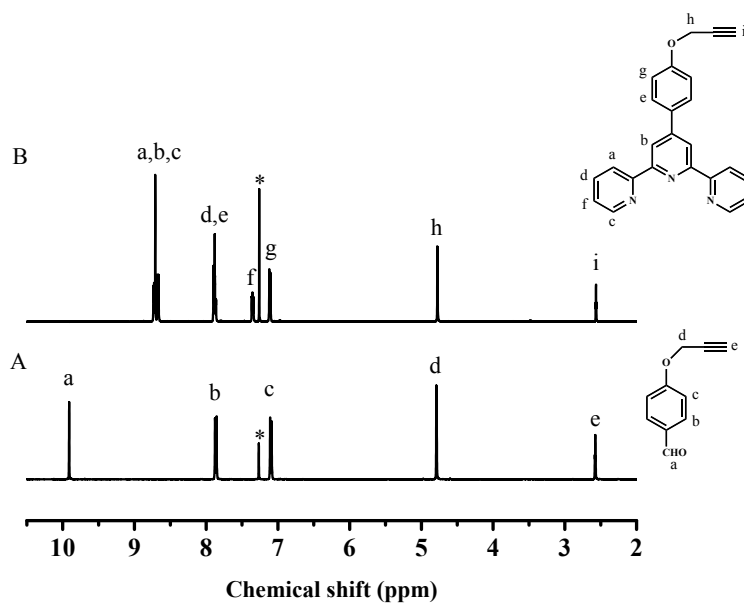
PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> and Terpy- $\phi$ -CH<sub>2</sub>C $\equiv$ CH (molar ratio: 1 : 2) were dissolved in 2 mL of DMF-CHCl<sub>3</sub> mixture in a nitrogen-purged vial. Then CuBr (2 equiv) was quickly added into the above vial under ultrasonic agitation. After the specified time, the polymer solution was diluted in dichloromethane and passed through basic alumina column to remove copper salts. Next, the mixture was evaporated in vacuum and the residue was precipitated in excess of cold diethyl ether. The desired polymer was collected by filtration and vacuum-dried at room temperature overnight.



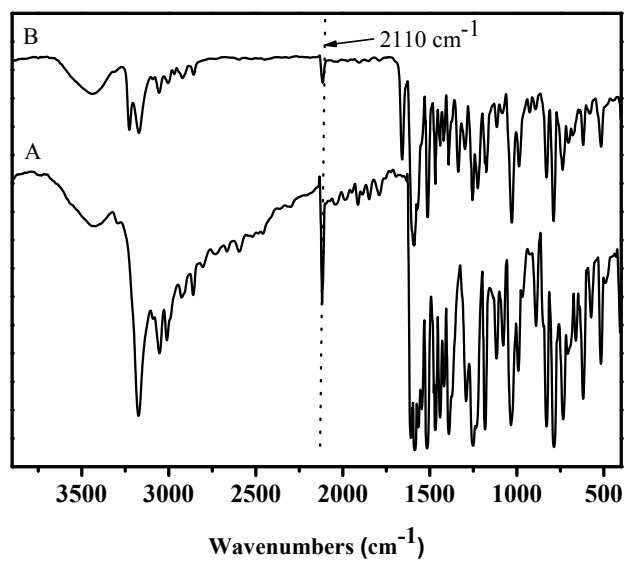
**Figure S1.** <sup>1</sup>H NMR spectra of DEP<sub>45</sub> (A) and PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> (B) in CDCl<sub>3</sub>-d.



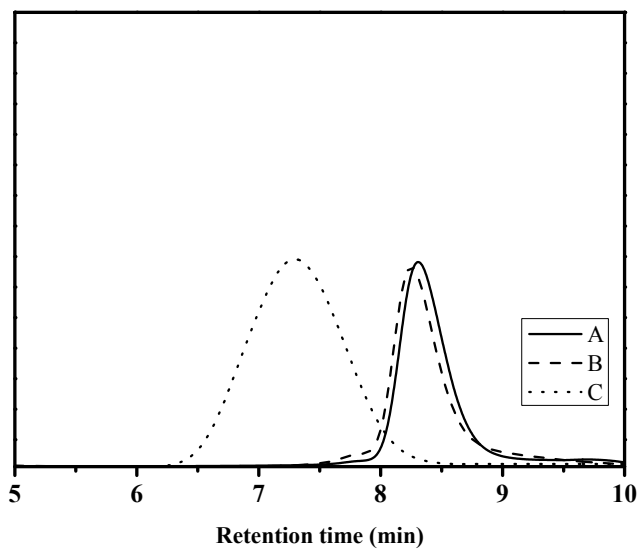
**Figure S2.** FT-IR spectra of PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> (A) and DEP<sub>45</sub> (B).



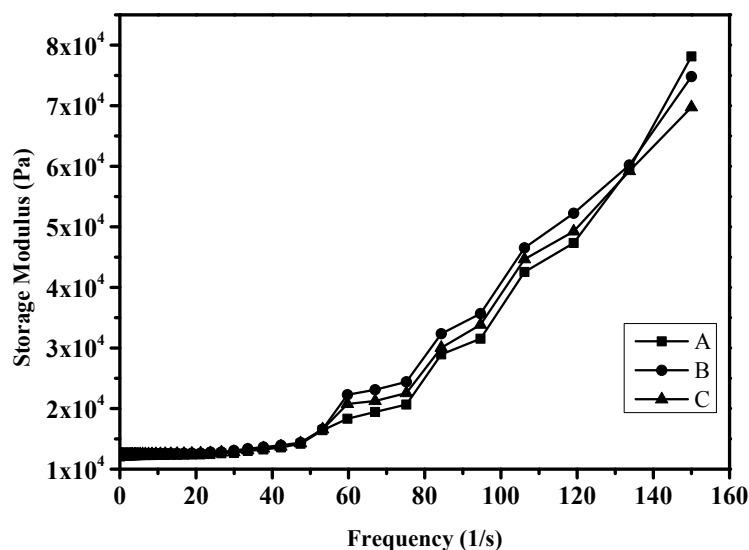
**Figure S3.** <sup>1</sup>H NMR spectra of 4-(prop-2-ynoxy)benzaldehyde (A) and Terpy-φ-CH<sub>2</sub>C≡CH (B) in CDCl<sub>3</sub>-d.



**Figure S4.** FT-IR spectra of Terpy- $\phi$ -CH<sub>2</sub>C $\equiv$ CH (A) and 4-(prop-2-ynoxy)benzaldehyde (B).



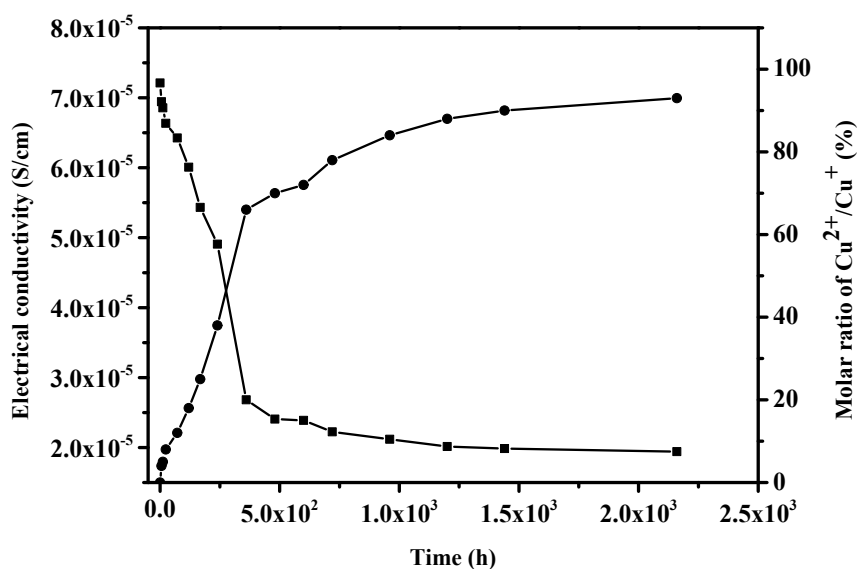
**Figure S5.** GPC curves of PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> (A), Terpy-terminated PEG derivative (B), and a linear polymer by chain extension of di-alkyne terminated PEG<sub>45</sub> with PEG<sub>45</sub>(N<sub>3</sub>)<sub>2</sub> via CuAAC (C) using THF as the eluent.



**Figure S6.** Storage modulus as a function of frequency (Hz) for Gel-1 exposed to the atmospheric oxygen (A), Gel-2 ( $[\text{Cu}^{2+}] : [\text{Terpy-terminated PEG derivative}] = 2 : 1$ ) (B) and Gel-3 ( $[\text{Cu}^{2+}] : [\text{Terpy-terminated PEG derivative}] = 2.2 : 1$ ) (C).

### Ionic conductivity

The variation in ionic conductivity and content of  $\text{Cu}^{2+}$  of PEG-based  $\text{Cu}^+$ -MCPG when being exposed to the humidified air were shown in Figure S7, revealing gradual oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ . There was a remarkable decrease in conductivity with the increase in content of  $\text{Cu}^{2+}$  from 6 h to 2160 h. It was evident from Figure S7 that the dramatic reduction in ionic conductivity was occurred within the first 360 h of oxidation, as only about 37% of the original conductivity was remained at this time point. After that, the reduction slowed down gradually and a nearly steady-state value of around  $2 \times 10^{-5}$  S/cm was reached. The ionic conductivity of PEG-based MCPG was most probably attributed to the presence of mobile charge carriers, such as copper ions, within its network. The concentration and mobility of these ionic species then determined the degree of electrical conductivity of the gel. According to the above data, it seemed that the concentration and mobility of ionic species decreased with time if the gel was exposed to the humidified air.

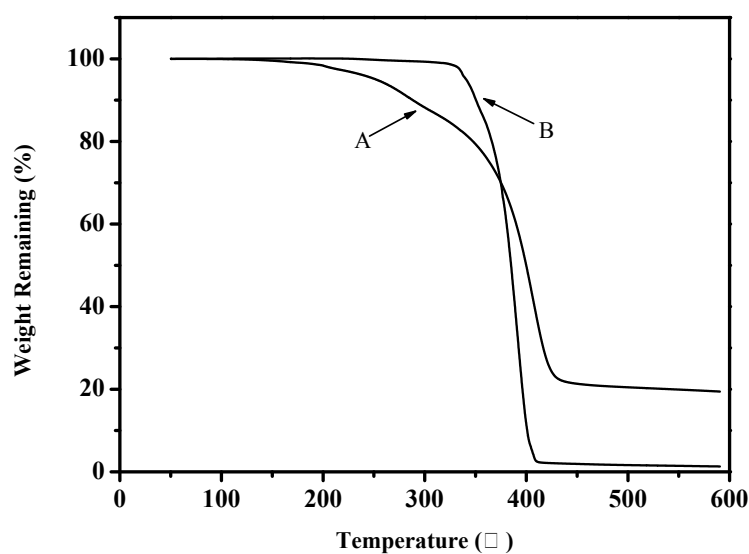


**Figure S7.** Ionic conductivity of PEG-based Cu<sup>+</sup>-MCPG (squares) and content of Cu<sup>2+</sup> in MCPG (circles) as a function of time over a slow oxidation process via exposure to the humidified air.

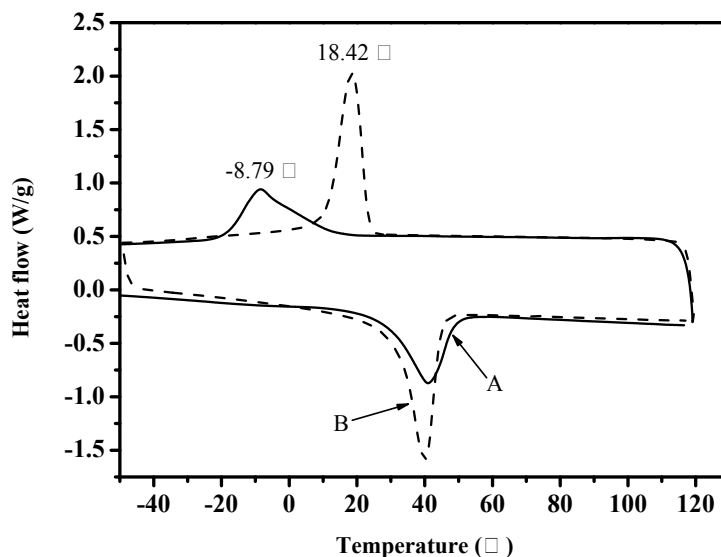
### Thermal properties

The thermal properties of PEG-based MCPGs were studied by DSC and TGA. TGA results of Cu<sup>2+</sup>-MCPG and TPOM-PEG hydrogel networks were shown in Figure S8. The major weight loss of PEG-based Cu<sup>2+</sup>-MCPG commenced at around 250 °C, which was associated with the decomposition of terpyridine groups. The main weight residue (noncombustible inorganic component) of Cu<sup>2+</sup>-MCPG at 500 °C was copper ions with a weight content of about 19%. TPOM-PEG hydrogel exhibited improved thermal stability with a rapid weight loss commenced at about 337 °C, which was much higher than that of Cu<sup>2+</sup>-MCPG. Hence, the thermal decomposition of Cu<sup>2+</sup>-MCPG was initiated at the “weak links” by depropagation, leading to the formation of Terpys and short chain oligomers. The volatilization of these small molecules resulted in the weight loss and reduced the thermal stability of PEG-based MCPG networks. The DSC heating and cooling curves of Cu<sup>2+</sup>-MCPG and TPOM-PEG hydrogel networks from -50 to 120 °C were shown in Figure S9. An exothermic peak at -8.79 °C in the cooling process and an endothermic one at 41.27 °C in the heating process were observed, which were associated with the crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of PEG network, respectively. The  $T_m$  of Cu<sup>2+</sup>-MCPG

network was higher than that (40.03 °C) of TPOM-PEG hydrogel network. The increase in the  $T_m$  of PEG network in  $\text{Cu}^{2+}$ -MCPG could be accounted for the fact that the attachment of Terpy segments and the formation of metal complexes raised the crystallinity of PEG networks.



**Figure S8.** Thermogravimetric analysis of PEG-based  $\text{Cu}^{2+}$ -MCPG (A) and TPOM-PEG hydrogel (B) with a heating rate of 10 °C/min under a nitrogen atmosphere.



**Figure S9.** DSC curves of dried PEG-based  $\text{Cu}^{2+}$ -MCPG (A) and TPOM-PEG hydrogel (B).

## References



1. E. H. Wong, M. H. Stenzel, T. Junkers and C. Barner-Kowollik, *Macromolecules*, 2010, 43, 3785-3793.
2. R. Laine, S. Kim, J. Rush, R. Tamaki, E. Wong, M. Mollan, H.-J. Sun and M. Lodaya, *Macromolecules*, 2004, 37, 4525-4532.
3. G. D. Fu, H. Jiang, F. Yao, L. Q. Xu, J. Ling and E. T. Kang, *Macromolecular rapid communications*, 2012, 33, 1523-1527.