Electronic Supplementary Material (ESI) for Nanoscale.


# Inclusion of Cu Nano-cluster 1D Arrays inside a $C_3$- Symmetric Artificial Oligopeptide via Co-assembly

**Ruiying Gong, Fei Li, Chunpeng Yang, Xiaobo Wan ***

## Supporting Information

## Table of Contents

**Gel Preparation:**

In a typical experiment, oligopeptide **3** (0.01g, 0.006 mmol) was dissolved in DMF/MeOH (120 μL, 5:1 volume ratio) at 65°C and then incubated at 36°C for 30 days to form stable gel. Here we identify this gel as gel@ BTA-$C_3$-GVGVOMe.

In a typical co-assembly of Cu Nano-cluster arrays and a BTA-$C_3$-GVGVOMe experiment, BTA-$C_3$-GVGVOMe **3** (0.1 g, 0.06 mmol), ascorbic acid (3.1 mg, 0.018 mmol) and $CuSO_4$•$5H_2O$ (2.2 mg, 0.009 mmol) were dissolved in DMF (2 mL) at ambient condition for 3 days under magnetic stirring. Subsequently, the resultant mixture was precipitated in $Et_2O$ to remove ascorbic acid and dried under reduced pressure at room temperature. The dried precipitate (10.0 mg) was heated at 65°C until the solid was completely dissolved in a mixture of DMF (100 μL) and methanol (20 μL) and then incubated at 36°C for more than 30 days. Here we identify this gel as gel@ BTA-$C_3$-GVGVOMe &Cu. Gelation was considered to have occurred when a homogeneous solid-like material was obtained that exhibited no gravitational flow.

**General Methods for Characterization:**

*Scanning Electron Microscopy (SEM).* The morphologies of the xerogels were characterized by SEM (HitachiS-4800) equipped with an energy dispersive spectrometer (EDS) (7593-H, HORIBA, Japan) at an accelerating voltage of 3 kV or 20 kV. The prepared organogel was casted on a freshly cleaved mica sheets, dried under reduced pressure for 6 days at 50°C to remove the solvent, and then used for characterizations of SEM. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination. EDS was carried out in 6 μm scanning region at 20 kV.

*X-ray photoelectron spectroscopy (XPS).* XPS measurement was performed using a Thermo Fisher ESCALAB250Xi system with a monochromatic aluminum K-alpha X-rays source. A disk-shaped sample holder made of stainless steel was filled with a size of 3×3 mm xerogel sample casted on a mica sheet, and kept for several hours in an ultra high vacuum (UHV) XPS chamber before measurements. For xerogel preparation, the prepared organogel was casted on a freshly cleaved mica sheet, dried under reduced pressure for 6 days at 50°C, The energy spectra of photoelectrons were observed at normal emission. The spectrometer pass energy was set to be 1 eV for the survey spectra and 0.05 eV for high resolution spectra.

*Fourier Transform Infrared (FTIR) Spectroscopy.* FTIR spectra were recorded on Nicolet 6700 FT-IR Spectrometer. The spectra were taken in the region between 500 and 2000 $cm^{-1}$ with a resolution of 1 $cm^{-1}$ and average over 20 scans. For xerogel measurements, the prepared organogel was casted on KBr crystal flakes, dried under reduced pressure for 6 days at 50°C, and then used for characterizations of FTIR.

*Transmission Electron Microscopy (TEM)*. Transmission electron microscopy (TEM) images were captured using a HITACH IH-7650 transmission electron microscope operating at 100 kV fitted with Catan 830 camera. The carbon film was touched onto the gel surface for 3 s and blotted down using filter paper. Each sample was allowed to dry afterward for 6 days at 50°C in a dust-free environment, and the dried specimens were then imaged using the microscope.

## Preparation of BTA-$C_3$-GVGVOMe

*Preparation of N, N', N''-tris- propargyl benzene-1,3,5-tricarboxamide **2**:*

Anhydrous triethylamine (TEA, 0.7 mL, 5 mmol) was added to an ice-cooled solution of propargylamine (0.2 mL, 3 mmol) in anhydrous $CH_2Cl_2$ (25 mL) and the mixture was stirred for 20 minutes. 1,3,5-Tris(chlorocarbonyl) benzene (0.265 g, 1 mmol) dissolved in anhydrous $CH_2Cl_2$ (50 mL) was added dropwise over a period of 15 minutes and the mixture was stirred for 24 h. The solvent was evaporated and the residue obtained was dissolved in distilled ethyl acetate (50 mL), and washed with 2 M aqueous HCl, water and saturated aqueous $NaHCO_3$ solution. The organic layer was dried with $Na_2SO_4$ and the solvent evaporated to yield 0.20 g of **2**. Yield 62%; $^1$H NMR (d-acetone, 600 MHz): δ = 2.85 (s, 3 H), 4.26 (d, J = 2.6 Hz, 6 H), 8.41 (s, 3 H), 8.5 (s, 3 H), ppm.

*Preparation of BTA-$C_3$-GVGVOMe **3**:*

To a stirred solution of tetrapeptide $N_3$-GVGV-OMe (0.15 g, 0.329mmol) in dry DMF (5 mL), were added **2** (0.035 g, 0.11mmol), $CuSO_4 \cdot 5H_2O$ (4.4 mg, 0.0176 mmol) and ascorbic acid (5.8 mg, 0.033 mmol) at room temperature under nitrogen for 3 days. The reaction was monitored by TLC. After the reaction finished, the mixture was concentrated. The resulting product was precipitated with $Et_2O$ and collected by filtration. The crude was re-dissolved in DMF and purified by precipitation one more time. The yield of the BTA-$C_3$-GVGVOMe is around 90%. $^1$H NMR (*d*-DMF, 600 MHz): δ= 0.956 (m, 36 H), 2.17 (m, 12 H), 2.32 (m, 6 H), 3.7 (s, 9 H), 3.95 (t, 12 H), 4.31 (t, 6 H), 4.49 (t, 6 H), 4.69 (s, 6 H), 7.83~9.16 (21 H) ppm.

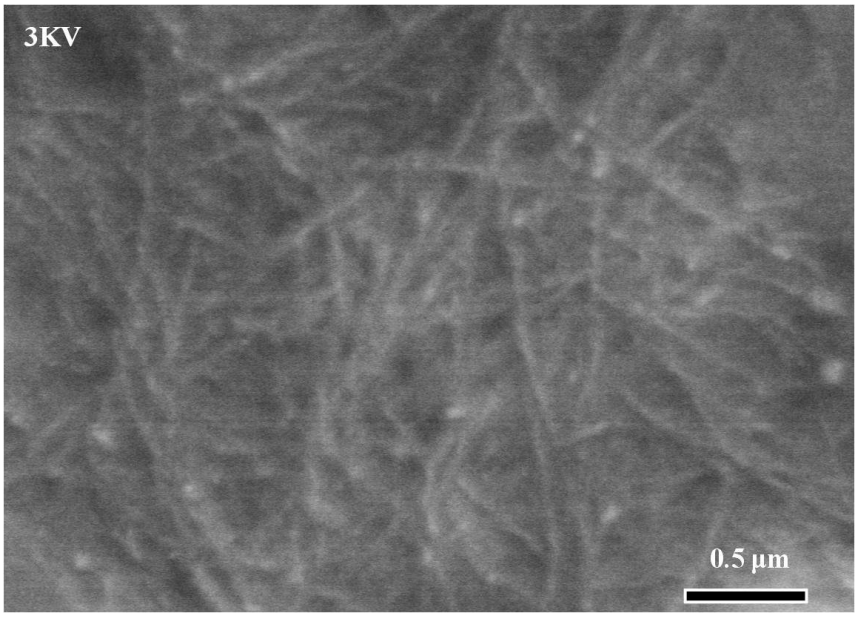


**Figure S1** SEM image of the assembly morphology of gel@ BTA-$C_3$-GVGVOMe

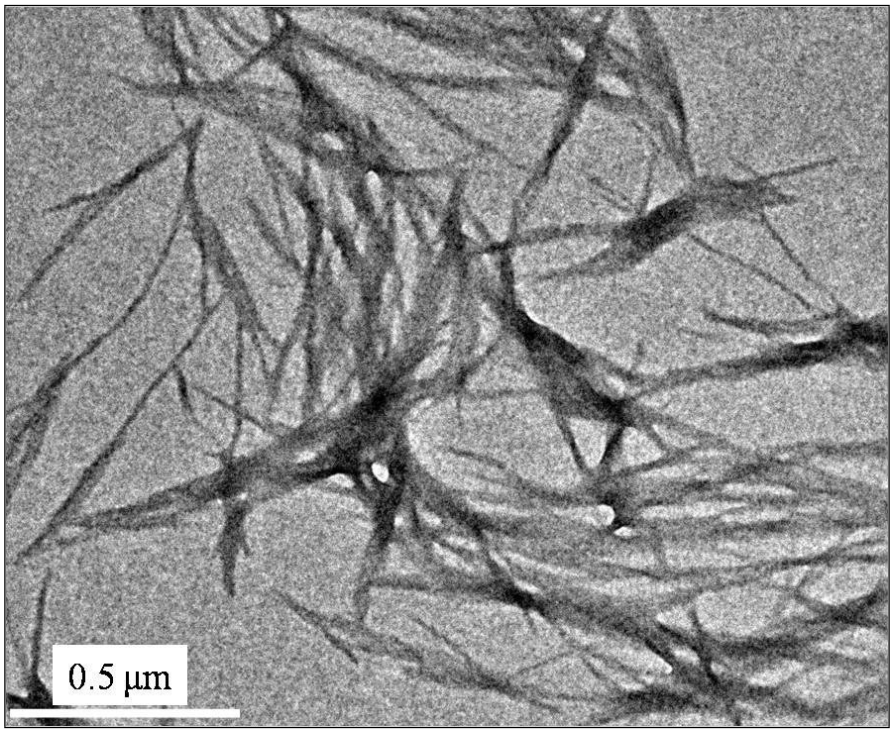


**Figure S2** TEM image of the assembly morphology of gel@ BTA-$C_3$-GVGVOMe

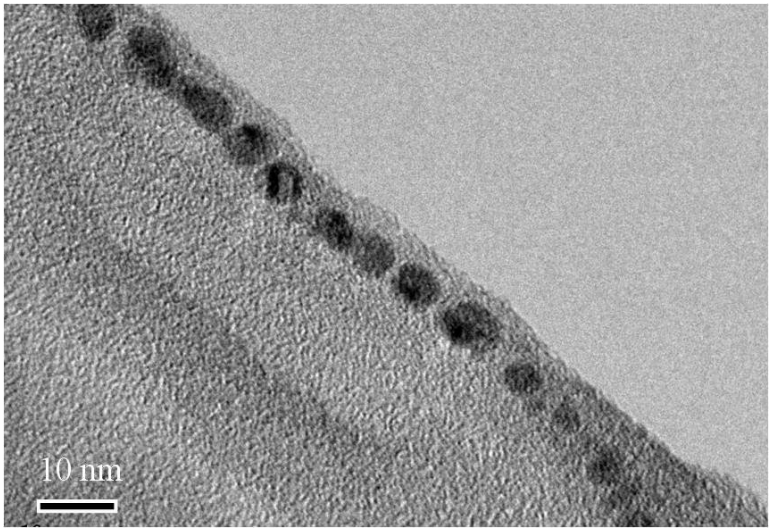


**Figure S3** High-resolution TEM image of Cu clusters

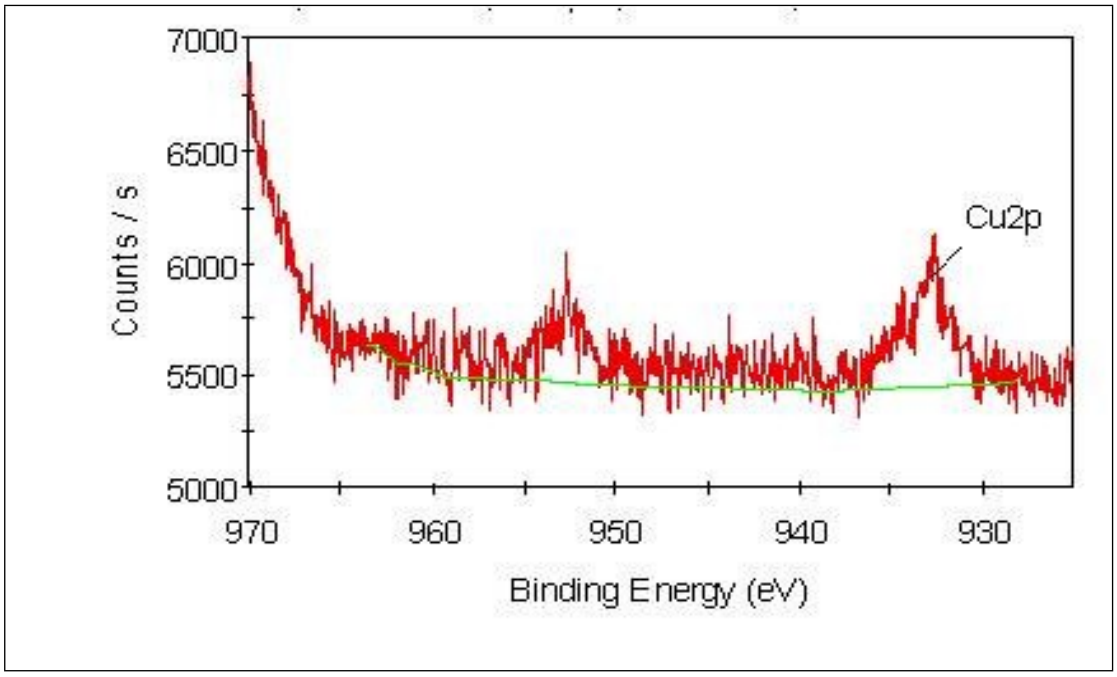


**Figure S4** X-ray spectroscopy by Cu2p scan

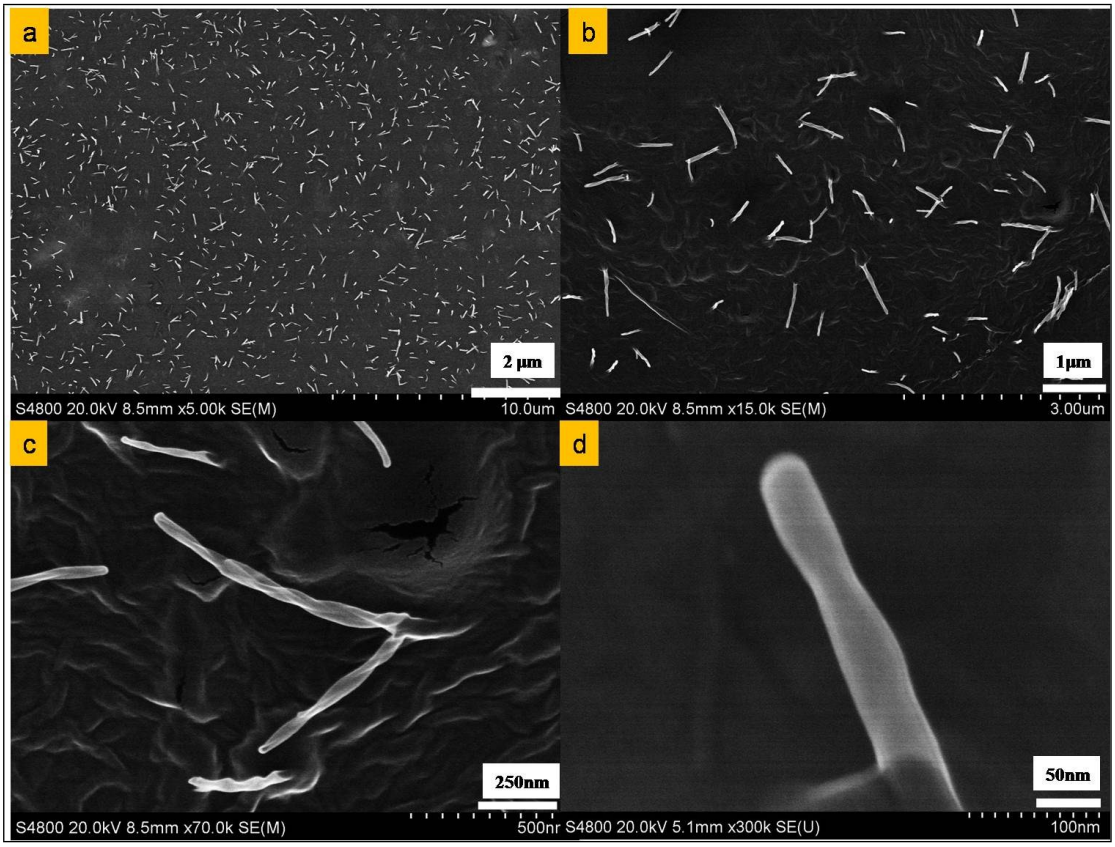


**Figure S5** SEM images of the assembly morphology of gel@ BTA-$C_3$-GVGVOMe &Cu at different scale bar (at 20 KV scanning voltage)

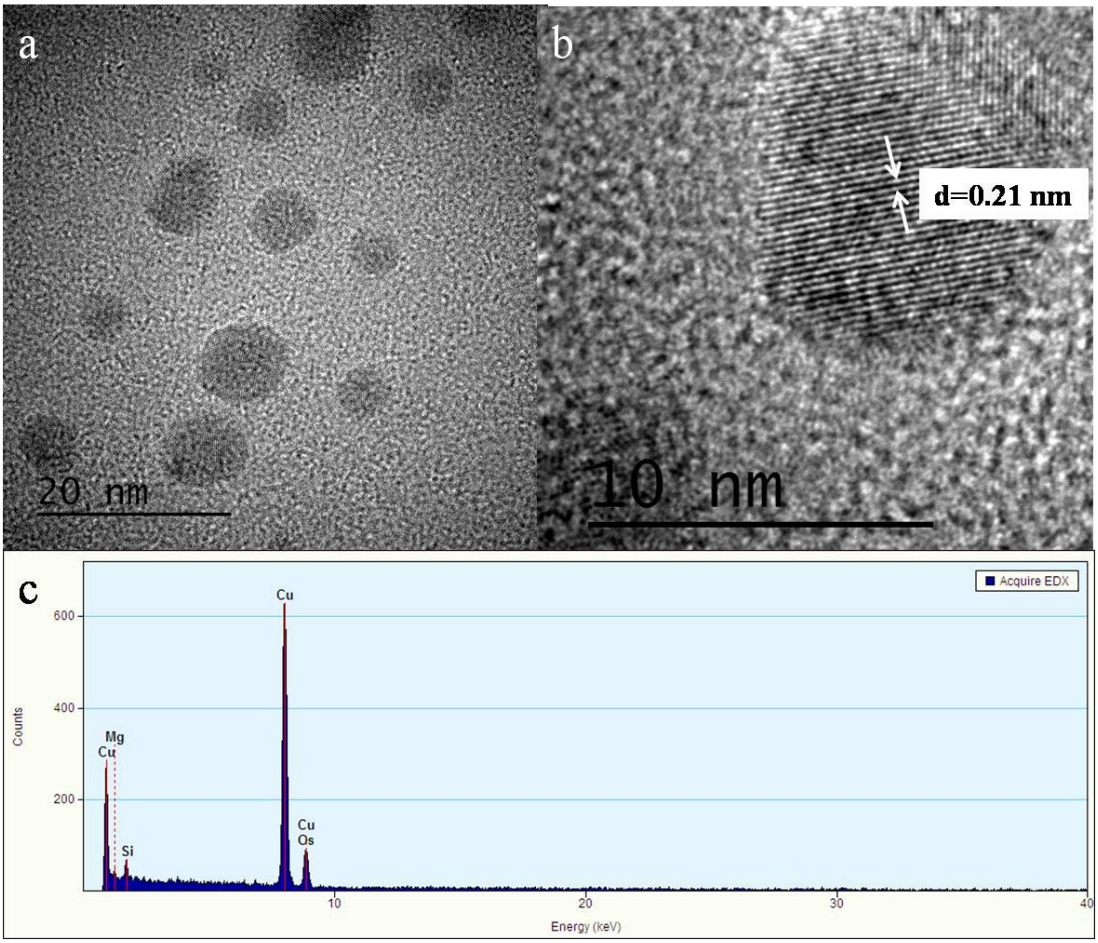


**Figure S6** High-resolution TEM image of Cu clusters of the assembly morphology of gel@ BTA-$C_3$-GVGVOMe &Cu stored at ambient temperature for almost two years

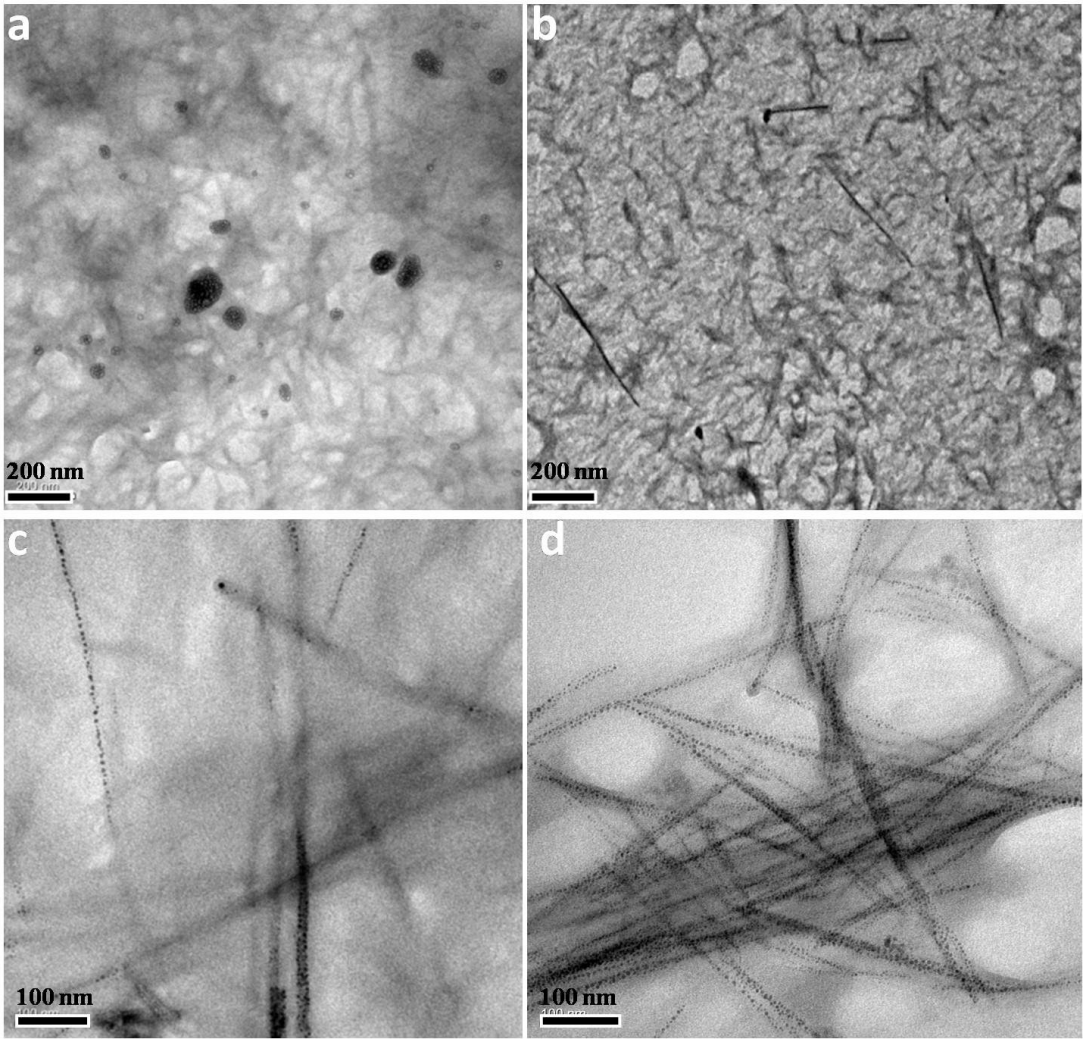


**Figure S7** The TEM images of the evolution of Cu naoparticle existential state with different gelation time. (a): 1 days (11℃); (b): 6 days (17℃); (c): 12 days (at 22℃); (d): 29 days(at 36℃);

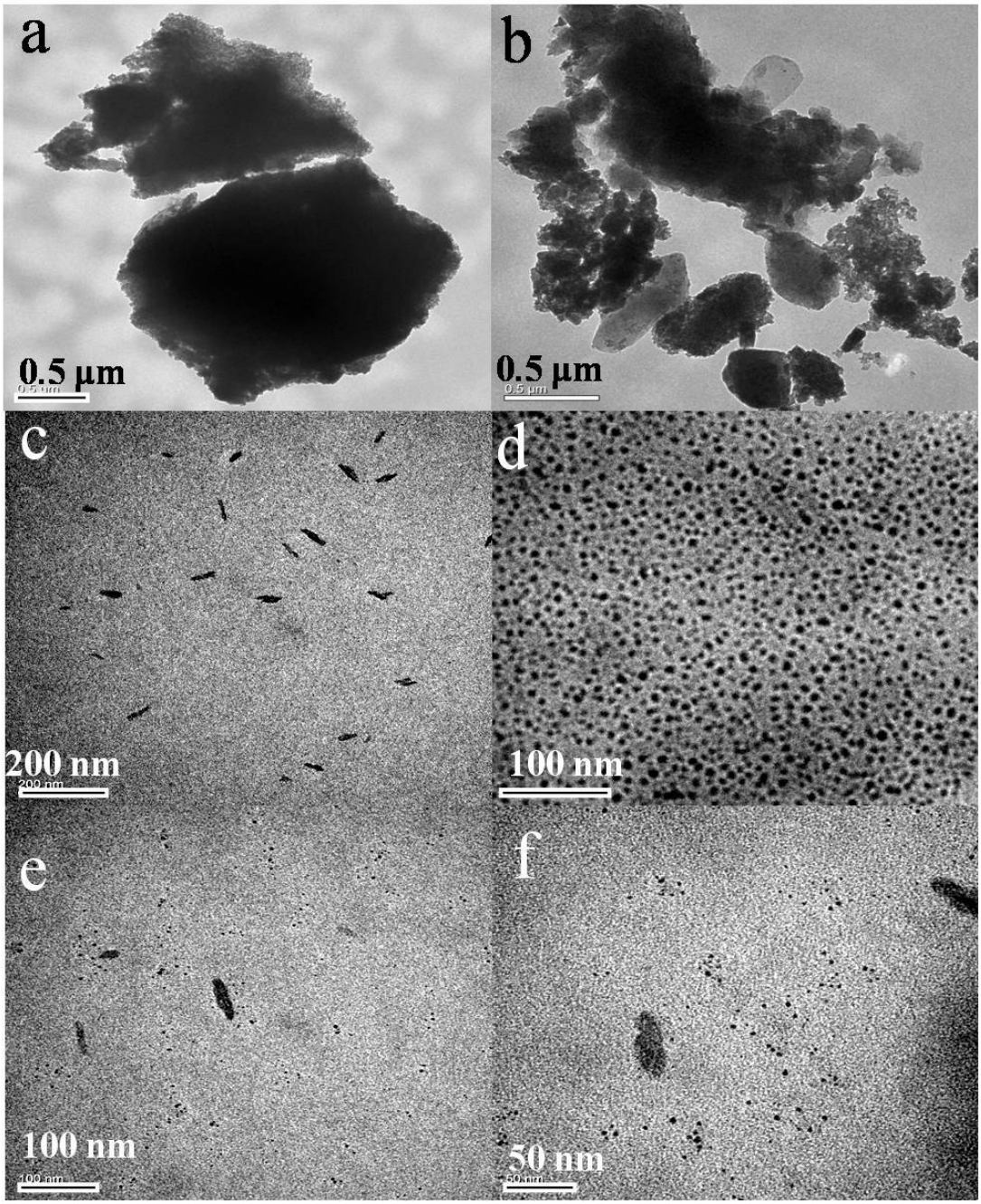


**Figure S8** The TEM images of the evolution of Cu naoparticle existential state in DMF/MeOH. Here the concentration of $CuSO_4 \cdot 5H_2O$ is 8.8 mmol/mL, and the molar content of the ascorbic acid is twice as much as that of $CuSO_4 \cdot 5H_2O$.

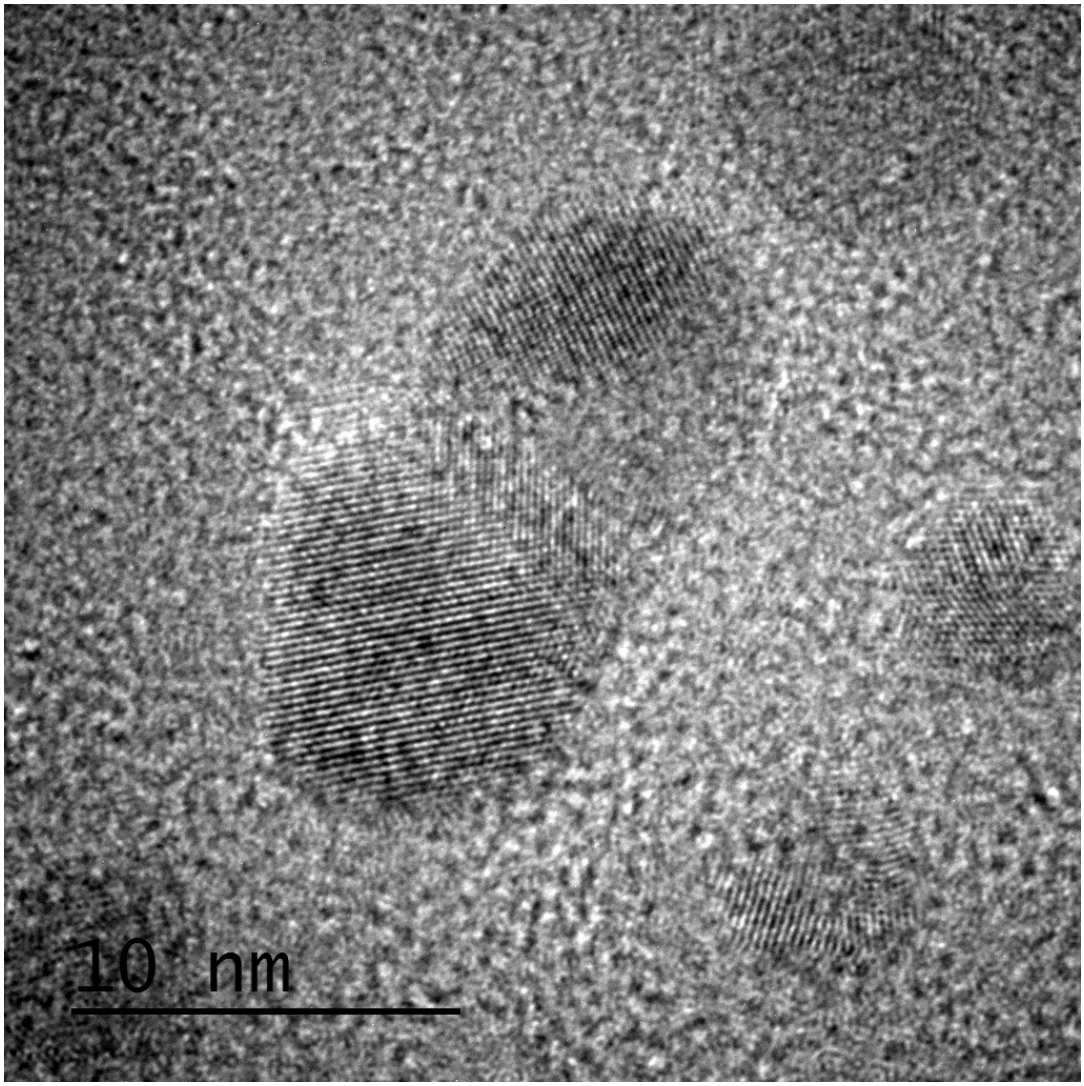


**Figure S9** High-resolution TEM image of Cu naoparticle existential state in DMF/MeOH. Here the concentration of $CuSO_4 \cdot 5H_2O$ is 8.8 mmol/mL, and the molar content of the ascorbic acid is twice as much as that of $CuSO_4 \cdot 5H_2O$.

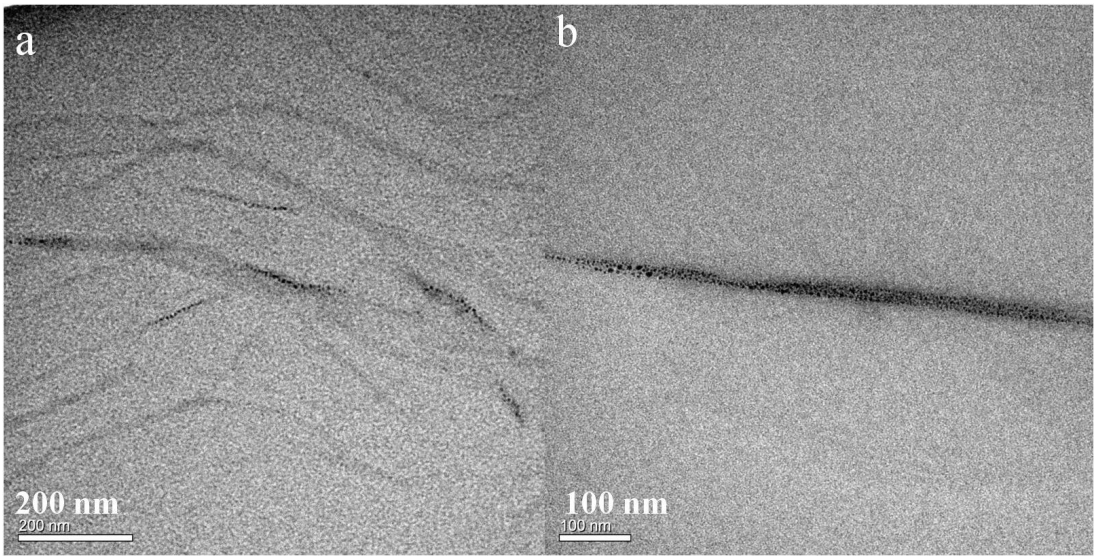


**Figure S10** The TEM images of Cu clusters of the assembly morphology of gel@ BTA-$C_3$-GVGVOMe in a re-synthesized Cu cluster.

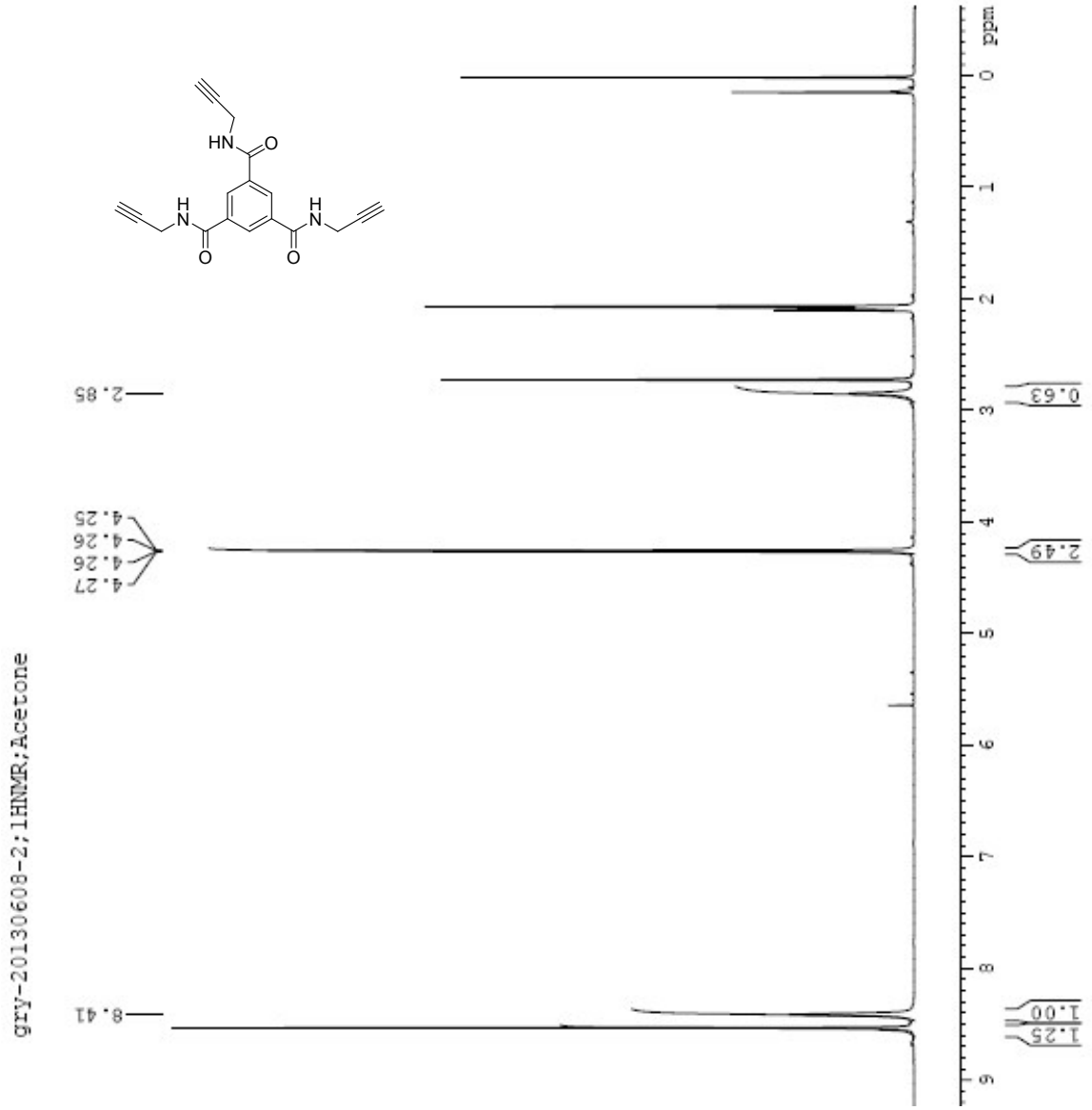


**Figure S11** [1]H NMR spectrum of N, N', N''-tris-propargyl benzene-1,3,5-tricarboxamide **2**

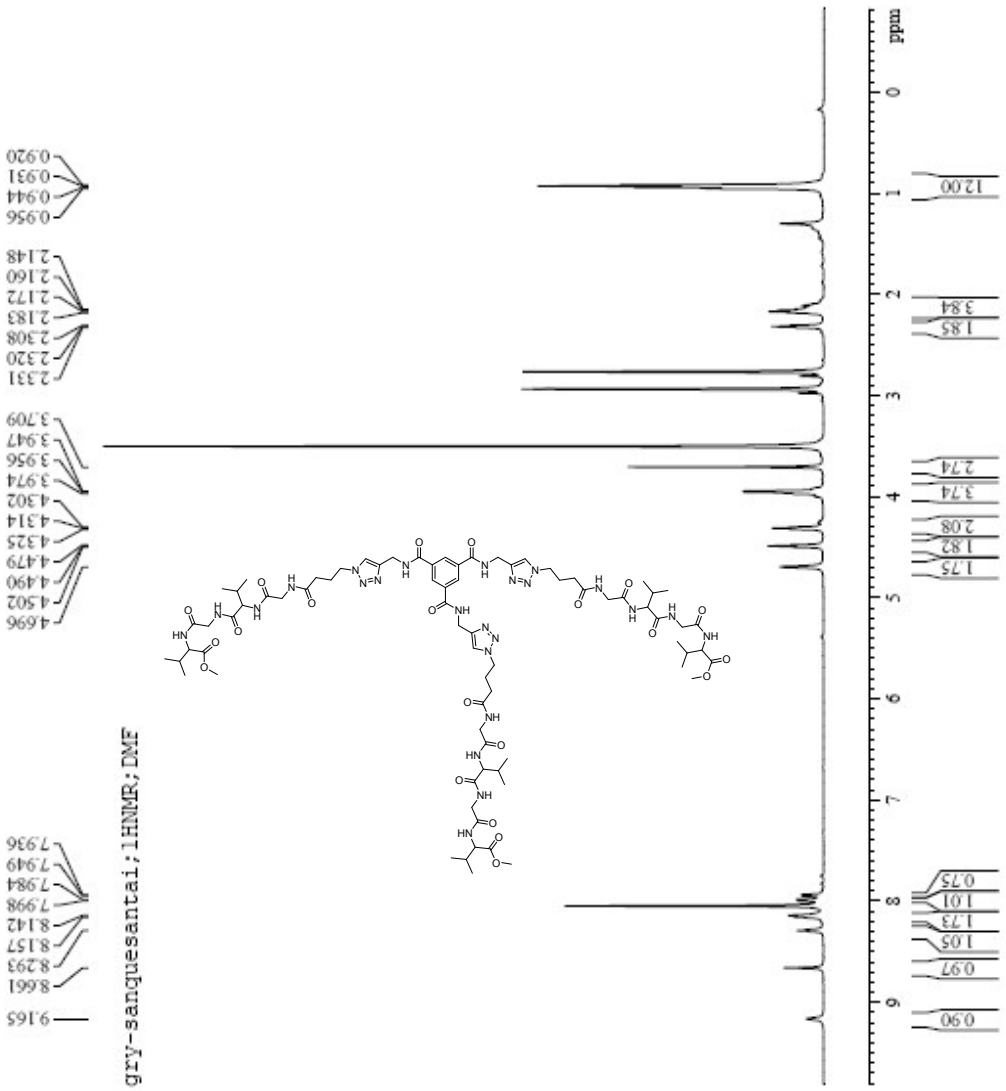


**Figure S12** $^{1}$H NMR spectrum of BTA-$C_3$-GVGVOMe **3**