

# **Prevention of Aerobic Oxidation of Copper Nanoparticles by Anti-Galvanic Alloying: Gold versus Silver**

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## 1. General data

All commercial materials were used without further purification, unless indicated. <sup>1</sup>H NMR was recorded on a Bruker Avance 300 FT (<sup>1</sup>H: 300MHz, <sup>13</sup>C: 75.3MHz) spectrometer. The chemical shifts for the NMR spectra are reported in ppm relative to the solvent residual peak.<sup>1</sup> Coupling constants J are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; st, sextet; m, multiplet; br, broad; dd, doublet of doublet. Yields refer to isolated material determined to be pure by NMR spectroscopy and thin-layer chromatography (TLC), unless specified in the text. Flash chromatography was performed on Fluka Silica Gel 60 Å, 40-63 μm.

UV-vis. absorption spectra were measured with a Perkin-Elmer Lambda 19 Uv-vis. spectrometer.

Transmission Electron Microscopy (TEM) images of nanoparticles were obtained on a JEOL JEM 1400 (120 kV) microscope. The TEM samples were prepared by deposition of the nanoparticle suspension (10μL) onto a carbon-coated microscopy copper grid. Samples were left to dry in vacuum prior to insertion into TEM microscope.

Scanning-Transmission Electron microscopy (STEM) images were recorded by FEI TITAN Low-base equipped with a CESCOR Cs-probe corrector (CEOS, Heidelberg, Germany) in high angle annular dark field.

Energy Dispersive X-Ray Spectroscopy (EDX) spectra are recorded with an energy resolution of 0.14 eV using Gatan Energy Filter Tridiem 866 ERS and a monochromator at 300 kV.

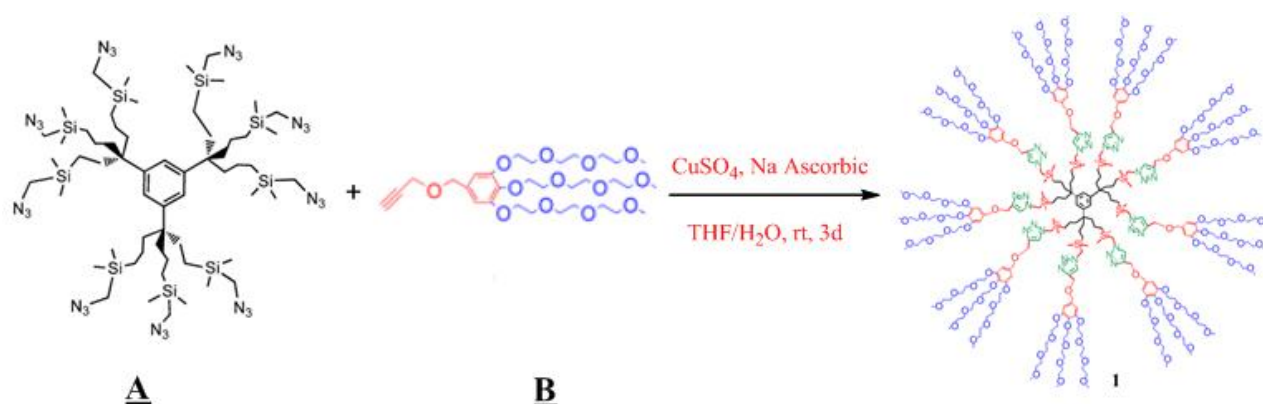
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<sup>1</sup> Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

### **X-ray Photoelectron Spectroscopy (XPS)**

Surface analysis by XPS was performed in a SPECS SAGE HR 100 system spectrometer in an ultra-high vacuum (UHV) chamber. The X-ray sources employed for this analysis were a non-monochromatic Mg K $\alpha$  (1253.6 eV) and 250 W or Al K $\alpha$  operated at 1.25 kV and 300W, calibrated using the 3d $_{5/2}$  line of Ag with a full width at half maximum (FWHM) of 1.1 eV. The take-off angle was fixed at 90° and the analysis was conducted at a pressure of  $\sim 10^{-6}$  Pa. Samples were dispersed onto glass, silicon or titanium surfaces, dry and inserted into the XPS. The selected resolution for the spectra was 30 eV of Pass Energy and 0.5 eV/step for the general survey spectra and 15 eV of Pass Energy and 0.15 eV/step for the detailed spectra of Cu 2p, Ag 3d and Au 4f photoelectron lines. Spectra were analyzed with the CasaXPS 2.3.15dev87 software. The analysis consisted of satellite removal, Shirley background subtraction, calibration of the binding energies related to the C 1s C-C peak at 285 eV, and peak fitting with Gaussian-Lorentzian line shapes where the FWHM of the peaks were constrained while the peak positions and areas were set free.

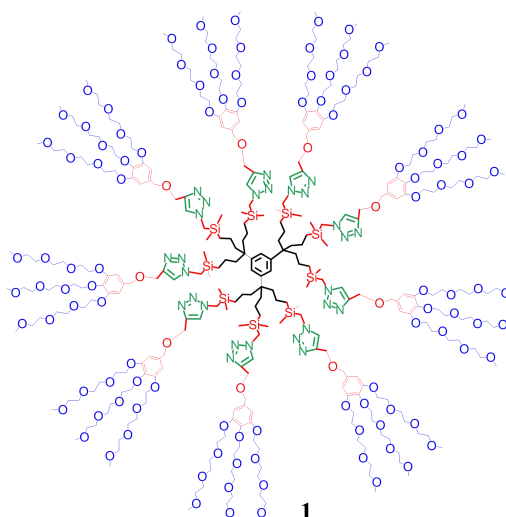
## 2. Preparation of dendrimer (1)



**Scheme 1.** The synthesis of dendrimer **1**.

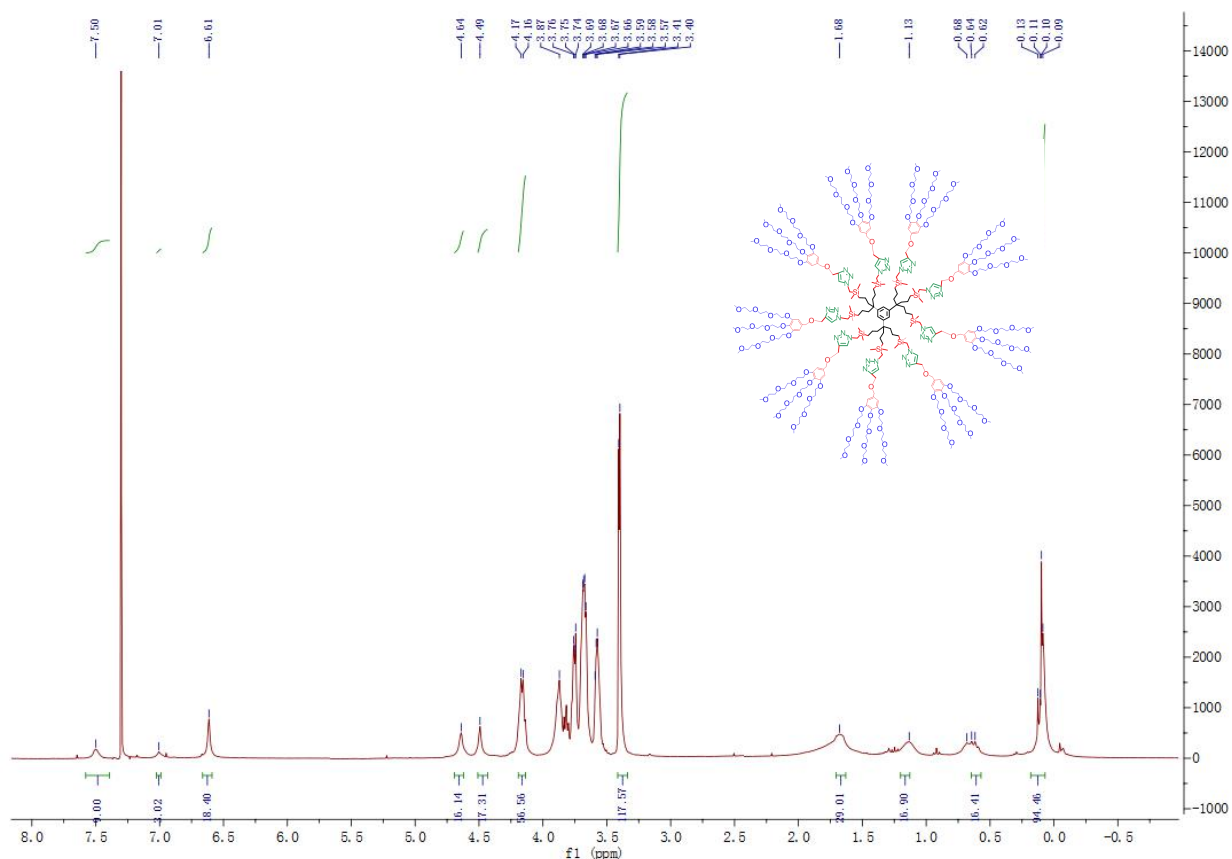
### Procedure for the preparation of dendrimer **1**.

Dendrimer **1** has been synthesized following reference **14** of the main text. 9-azido core (**A**) (0.012 mmol) and the alkyne tris TEG dendron (**B**) (0.13 mmol, 1.2 equiv. per branch) are dissolved in THF. CuSO<sub>4</sub>·5H<sub>2</sub>O is added (0.032 g, 0.13 mmol, 1 equiv. per branch, 1M in aqueous solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (0.051 g, 0.26 mmol, 2 equiv. per branch, 1M in water solution) in order to set a 1:1 THF/water ratio. The reaction mixture is stirred for 3 days at 25°C under N<sub>2</sub>. After removing THF in vacuo, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and an aqueous ammonia solution (2.0 M, 50 mL) are successively added. The mixture is allowed to stir for 10 minutes in order to remove all the Cu<sup>II</sup> trapped inside the dendrimer as [Cu(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [SO<sub>4</sub>]. The organic phase is washed twice with water, then this operation is repeated three more times to ensure complete removal of copper ions. The organic phase is dried with sodium sulfate, and the solvent is removed in vacuo. The product is washed with 50 mL diethyl ether several times in order to remove the excess of the dendron. Dendrimer **1** is obtained (in 68 % yield)



**Dendrimer 1**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : ppm: 7.50 (CH-triazole), 7.00 (CH-arom. intern), 6.61 (CH- arom. extern), 4.54 (triazole- $\text{CH}_2\text{-O}$ ), 4.40 (O- $\text{CH}_2\text{-arom.}$  extern), 4.04-4.09 ( $\text{CH}_2\text{O-arom.}$  extern), 3.90 (Si- $\text{CH}_2\text{-triazole}$ ), 3.51-3.78 (O $\text{CH}_2\text{CH}_2\text{O}$ ), 3.49-3.42 ( $\text{CH}_3\text{O}$ ), 1.68 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 1.13 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.62 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.09 ( $\text{Si}(\text{CH}_3)_2$ ).



**Figure S1:**  $^1\text{H}$  NMR spectrum of dendrimer **1** in  $\text{CDCl}_3$ .

### 3. Preparation of Ag/Cu BNPs and Au/Cu BNPs

$3.6 \times 10^{-4}$  mmol of dendrimer **1** (2.59 mg) is dissolved in 1.1 mL of water in a Schlenk flask, and a colorless solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  ( $3.2 \times 10^{-3}$  mmol in 1.1 mL water) is added to the solution of the dendrimer. 30 mL of water is added, and the solution is stirred for 1 h. The concentration of  $\text{AuCl}_4^-$  is 0.1 mM. A 1 mL aqueous solution containing  $3.2 \times 10^{-2}$  mmol of  $\text{NaBH}_4$  is added dropwise, provoking the formation of a violet color corresponding to the reduction of  $\text{AuCl}_4^-$  to  $\text{Au}(0)$  and formation of AuNP. The dendrimer **1**-encapsulated AuNP solution is purged with  $\text{N}_2$  continuously from 15 min prior to addition of  $\text{NaBH}_4$  until 2 h after reduction. A borohydride destruction procedure follows by addition of aqueous  $\text{HCl}$ , the pH of the resulting 0.1 mM AuNP solution being adjusted to 3. Then a colorless solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ( $3.2 \times 10^{-3}$  mmol in 1.1 mL water) is added dropwise to the solution of the dendrimer-**1**, and the solution is stirred for 1 h. A 1 mL aqueous solution containing  $3.2 \times 10^{-2}$  mmol of  $\text{NaBH}_4$  is added dropwise. Au/Cu BNPs is formed. The preparation of Ag/Cu BNPs is carried out as above process.

#### 4. Microscopy images of Au/Cu and Ag/Cu.

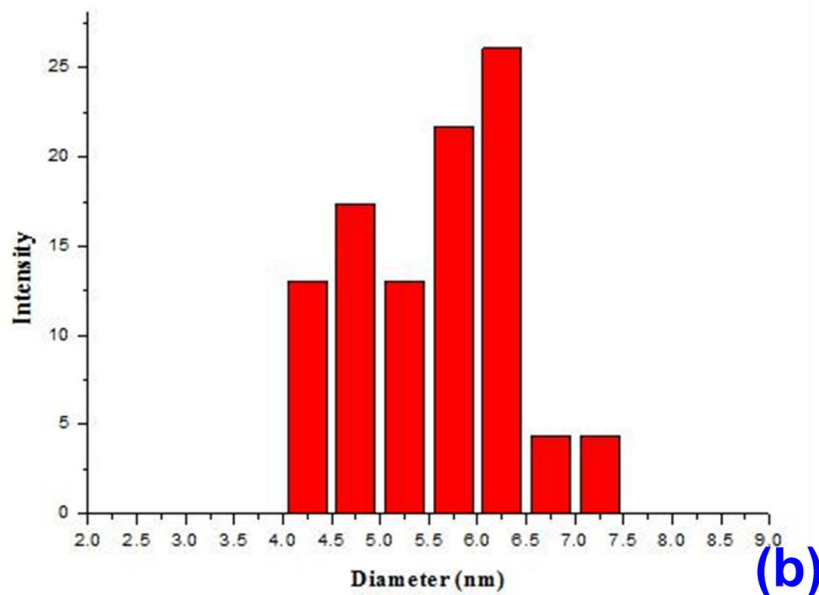
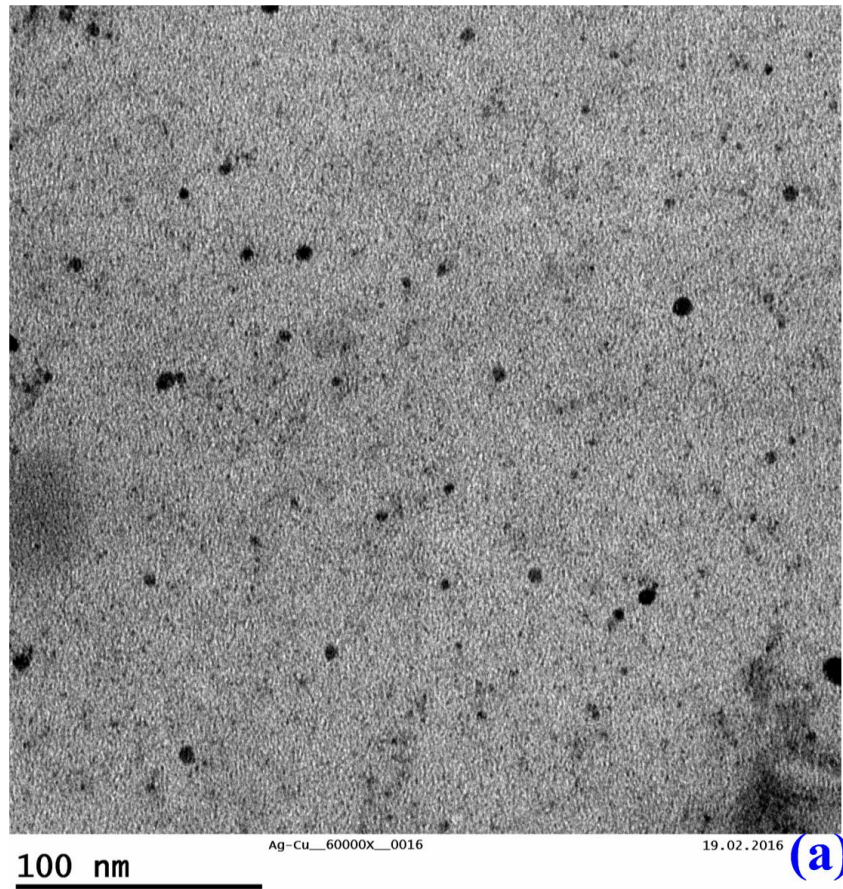
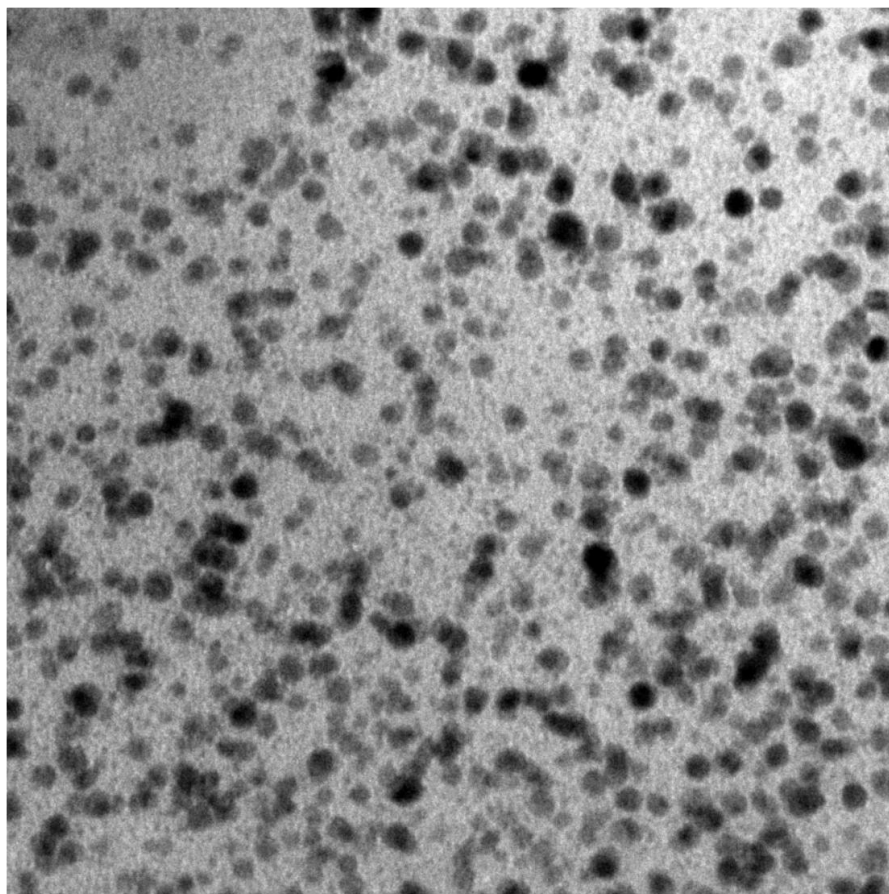


Figure S2: (a) TEM image of Ag/Cu; (b) Diameter histogram distribution of Ag/Cu.

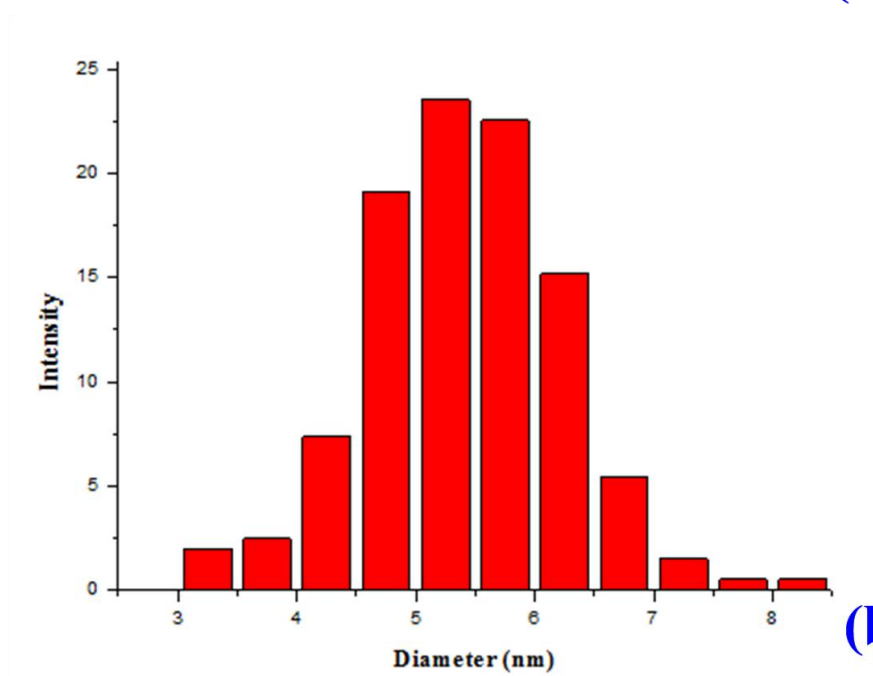


50 nm

Au-Cu\_100000X\_0021

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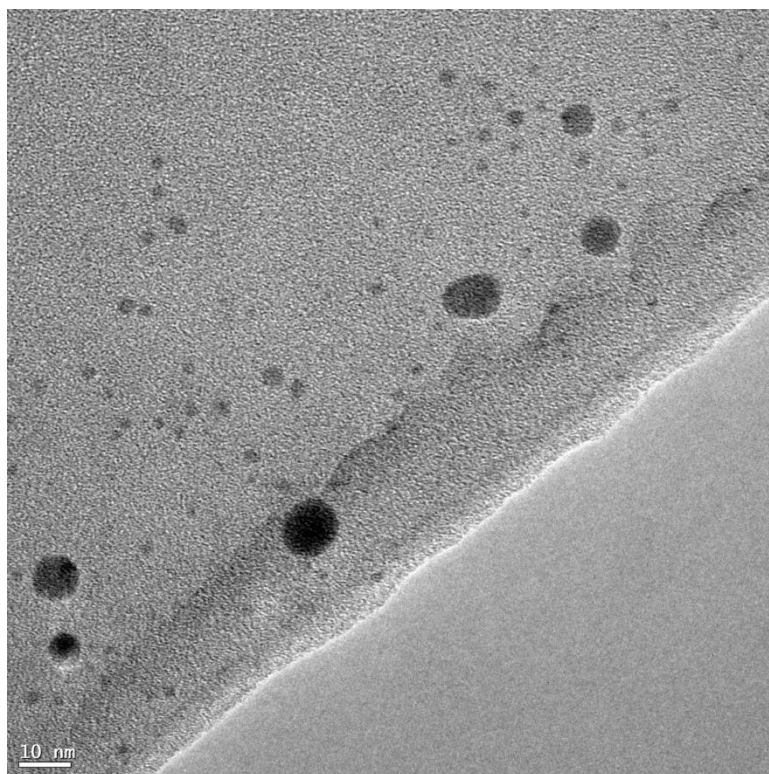
(a)



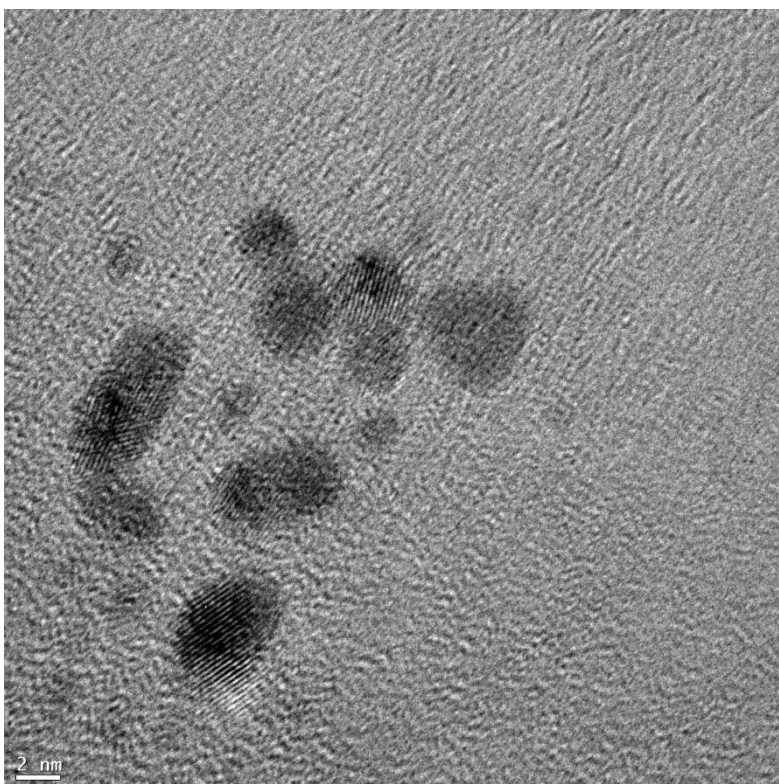
(b)

Figure S3: (a) TEM image of Au/Cu; (b) Diameter histogram distribution of Au/Cu

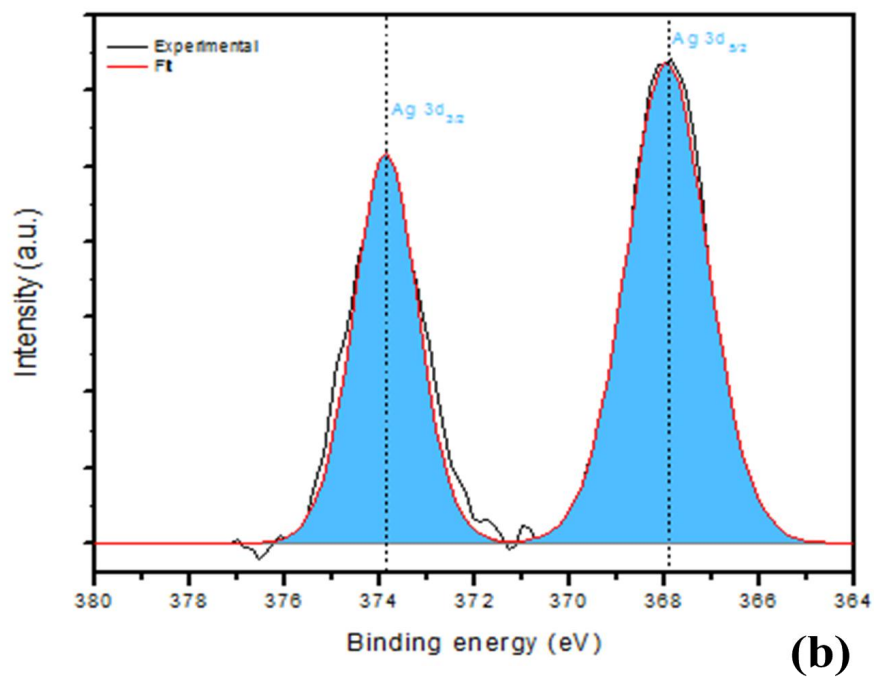
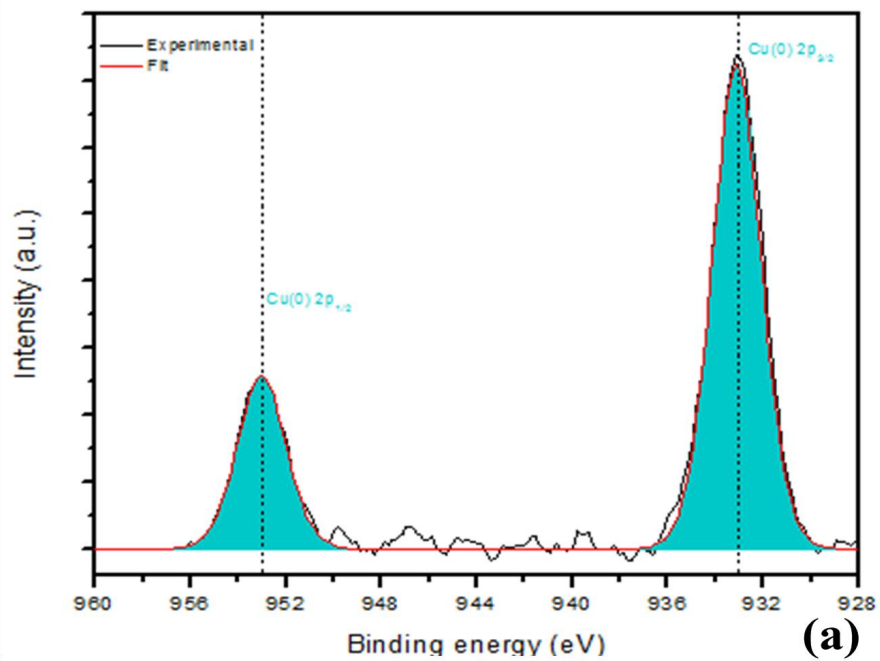




**Figure S4:** HRTEM image of Ag/Cu BNP



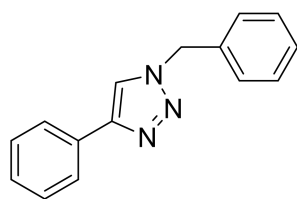
**Figure S5:** HRTEM image of Au/Cu BNP



**Figure S6:** (a) XPS of CuNP in Ag/Cu BNPs, (b) XPS of AgNP in Ag/Cu BNPs.

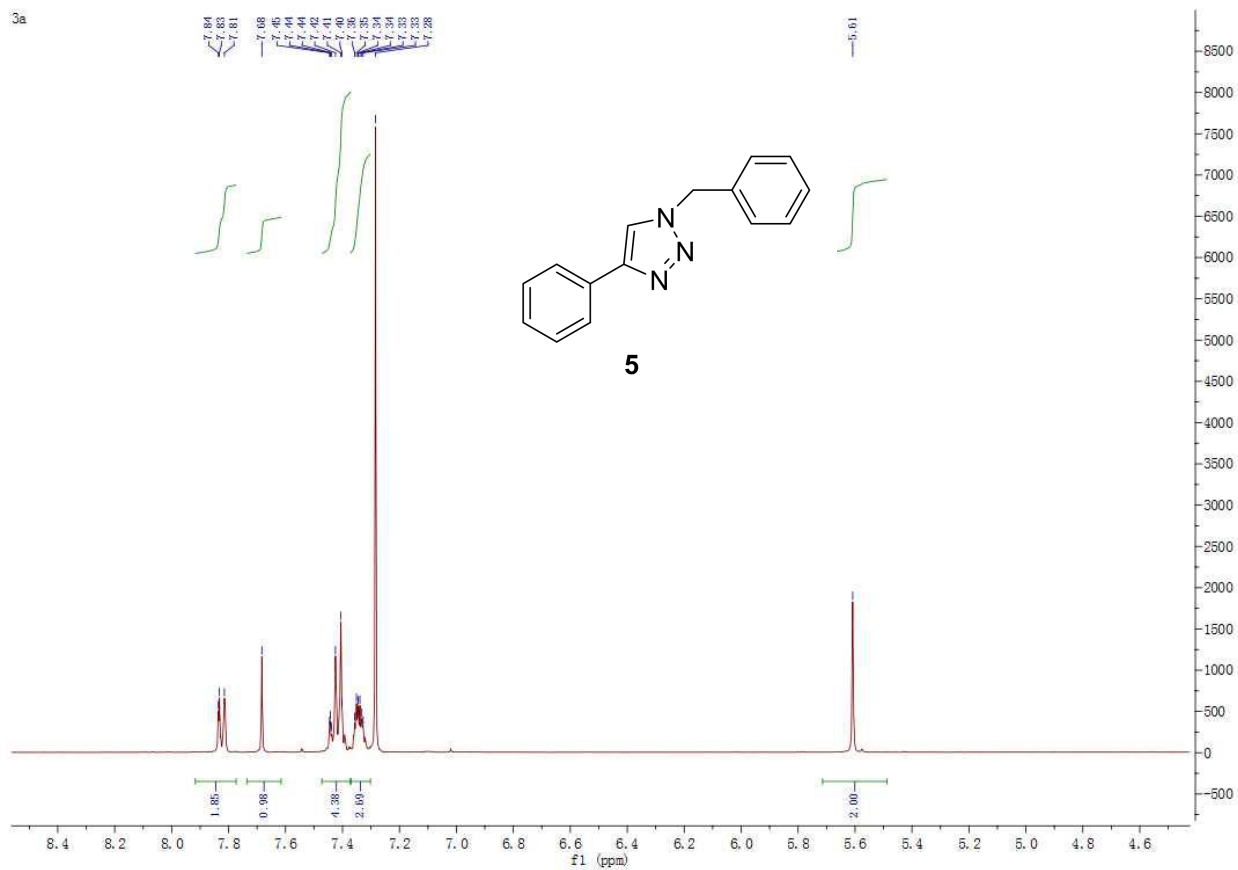
#### 4. Procedure for the preparation of 5

Azidomethylbenzene (**3**) 0.5 mmol, ethynylbenzene (**4**) 0.55 mmol, Ag/Cu (200pm) and 2ml H<sub>2</sub>O were taken in a round bottom flask equipped with stirrer. The resulting mixture was stirred for 24 h at 35°C under Air. After cooling to rt, water (2 mL) was added to the reaction mixture, and the latter was extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (2×5 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was subjected to flash column chromatography with hexanes/EtOAc (v/v = 5/1) as eluent to obtain the desired 1-benzyl-4-phenyl-1H-1,2,3-triazole (**5**) as white solid (98% yield).



**5**

1-benzyl-4-phenyl-1H-1,2,3-triazole (**5**) was purified by flash chromatography (hexane-EtOAc, v/v=5/1) as white solid (yield: 98 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ: 7.81-7.84 (d, J=6Hz, 2H), 7.68 (s, 1H), 7.40-7.45 (m, 5H), 7.275-7.36 (m, 3H), 5.61 (s, 2H).



**Figure S7:**  $^1\text{H}$  NMR spectrum of **5** in  $\text{CDCl}_3$