

Supplementary Information

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1 Experimental details

1.1 Chemicals and Reagents

HPLC-grade methanol was purchased from Fisher Scientific (Pittsburgh, PA, USA). HPLC-grade dichloromethane was purchased from Kemiou Chemical Reagent Company (Tianjin, China). Pure water was purchased from Wahaha Company (Hangzhou, Zhejiang, China). Phenylacetylene, benzyl azide solution (0.5 M in dichloromethane), 1-(azidomethyl)-4-chlorobenzene solution (0.5 M in dichloromethane), Copper (I) acetate (CuOAc), neocuproine, CuSO₄, Na ascorbate, H₂O₂, chloroform-*d* were obtained from Sigma Aldrich (St. Louis, MO, USA), which were of AP-grade or higher. All chemicals were used as received without further purification. 1-benzyl-4-phenyl triazole was synthesized according to the literature¹. ¹H NMR (500 MHz, CDCl₃) δ=7.79 (d, *J* = 7.4 Hz, 2H), 7.66 (s, 1H), 7.44 – 7.22 (m, 5H), 5.54 (s, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ=148.23, 134.73, 130.59, 129.14, 128.80, 128.76, 128.15, 128.05, 125.71, 119.58, 54.21 ppm, which were consistent with previous data¹.

The gold and the silicon sample plates, respectively, were obtained from department of microelectronics in Peking University (Beijing, China). The gold plate was fabricated by sputtering a layer of gold (1600 Å) on a silicon substrate. These two kind of plates (Si and Au) were ultra-sonicated in 1:1 methanol/water before use. The iron and copper plates, respectively, were purchased from Alfa Aesar. Before use, these two kind of plates (Fe and Cu) were first polished with abrasive paper (grit 240–360) and then ultra-sonicated in 1:1 methanol/water for several minutes.

1.2 ESI-(tandem) MS

ESI-(tandem) MS was done using a Thermo Finnigan LCQ Advantage MAX ion trap mass spectrometer (San Jose, CA, USA). The main experimental parameters used were as follows: spray voltage 5.5 kV, capillary voltage 4.0 V, tube lens offset -50.0 V, heated capillary temperature 250 °C and nebulizing gas (N₂) pressure 0.4 mPa. In MS/MS mode, isolation width was set at 5 Th. All mass spectra were acquired in positive mode with 3 microscans and were recorded by the instrument software (Xcalibur version 1.4 SR1).

1.3 High Resolution MS

The high resolution electrospray ionization mass spectrometry (HR-ESI-MS) measurement was done on an Agilent 6510 Q-TOF mass spectrometer (Santa Clara, CA, USA) at a flow rate of 10 μL/min. The spray solution was methanol and water (v/v 1:1). The typical positive mode Q-TOF-MS conditions were as follows. The ion source temperature was 325 °C. The ESI and the skimmer voltage were set to 3.5 kV and 65 V, respectively. The fragmentor voltage was set to 400 V. The drying gas (N₂) flow rate was 4 L/min.

Control click reactions were catalyzed by either CuSO₄/Na ascorbate or CuOAc. The concentrations of phenylacetylene and benzyl azide were 5 mM each, the same as those in in-source click reaction. The catalyst loading is 0.8% equivalent. Reaction solutions (Conditions A to D) were sampled at different reaction time points and diluted 100 times for analyses. To quantify the signal intensities of *m/z* 236, 2% H₂O₂ was added.

1.4 UV-vis Measurement

A thermo nanodrop 2000C (San Jose, CA, USA) UV-vis photometer was used. All the experiments were done in NaOAc and HOAc buffer (pH = 4.50). The absorbance was detected at 454 nm. The concentration of neocuproine was 0.5 mmol/L, the concentration of Na ascorbate was 0.5 mmol/L. CuSO_4 (0.010-0.200 mmol/L) was added as copper source. When the detection of the in-source sample, Na ascorbate was not added.

1.5 In-Flask Click Reaction Catalyzed by the Crystallized Dimer

5 mM phenylacetylene and 5 mM 4-chloro-benzyl azide were dissolved in 1:1 MeOH/H₂O, and 0.04 mM CuL_2BF_4 (L= 1-benzyl-4-phenyl triazole) was added as the catalyst. The reaction solution was sampled at different time points for ESI-(tandem) MS analyses to monitor the changes of dimer analogs.

2 Additional Results

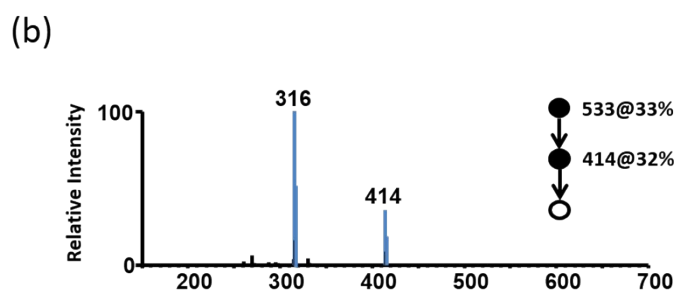
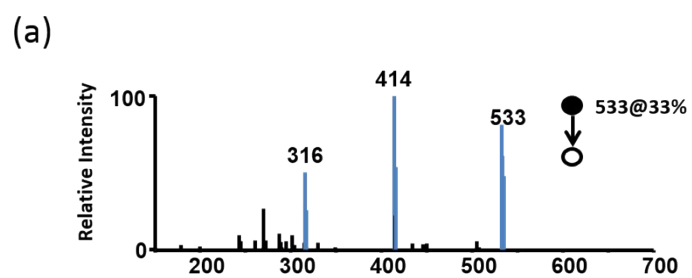


Fig S1 (a) HALDI-MS/MS analysis of the copper(I) triazole dimer in the in-source reaction. (b) HALDI-MS³ analysis of the same cation.

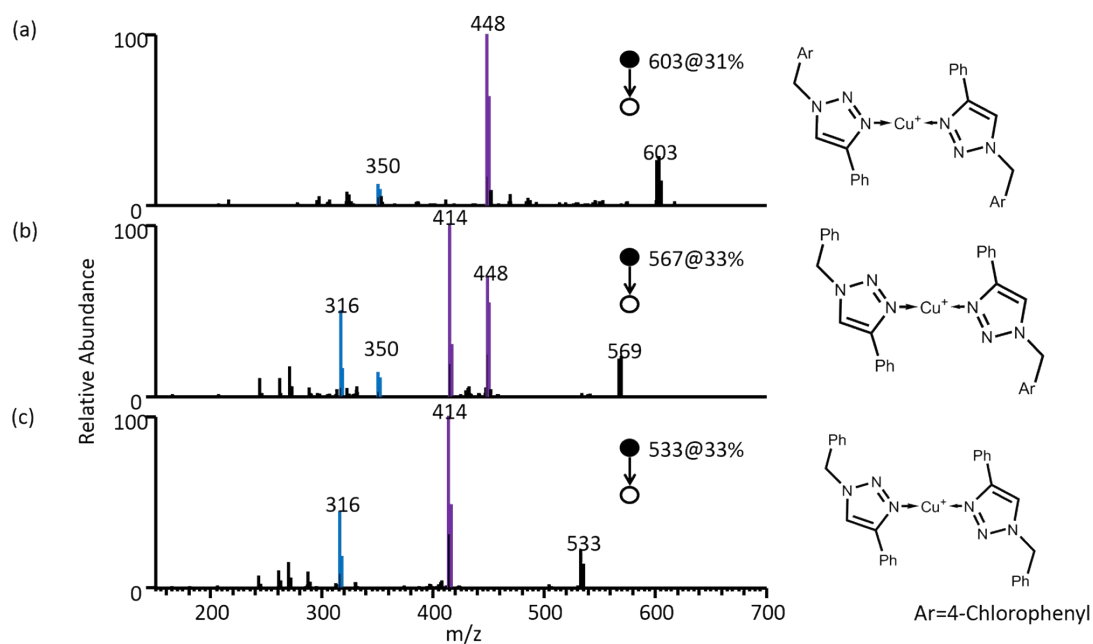


Fig S2 (a-c) ESI-MS/MS analysis of the copper(I) triazole dimer analogs. Purple peaks denoted the retro [3+2] fragments, while blue peaks denoted the water-triazole ligand exchange fragments. Fragmentation pathways could be seen in Fig 4e.

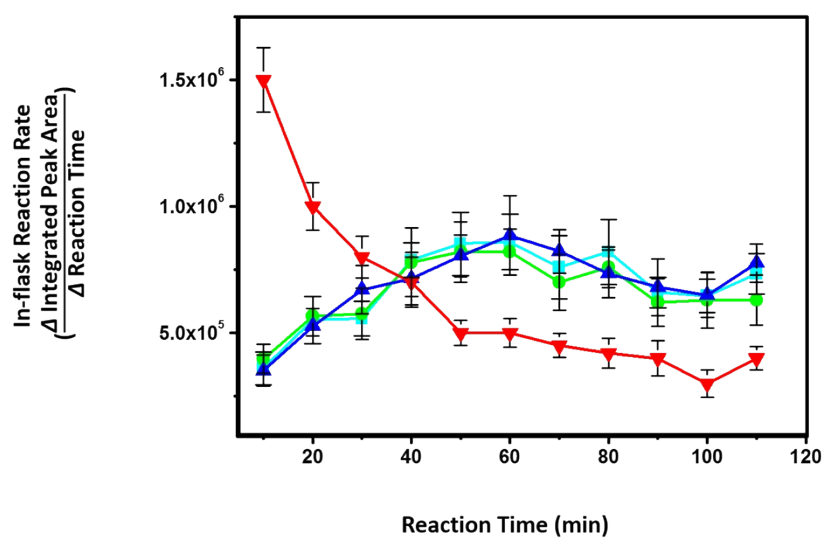


Fig S3 Rate comparison of the in-flask click ratios detected by high resolution MS. (Red: condition A', green: condition B', blue: condition C, Cyan: condition D)

Crystal Data:

Synthesis from 4 mM 1-benzyl-4-phenyl-triazole and 2 mM $\text{Cu}(\text{MeCN})_4\text{BF}_4$, which were dissolved in 10 mL dichloromethane, and the solution was layered with hexane. After 2 days for crystallization, approximately 7 mg colorless crystal could be got (~ 70% yield). CCDC number: 1016871, melting point: 278 °C. Elemental Analysis: Cal. C 58.03 H 4.22 N 13.53, Det. C 58.04 H 4.20 N 13.51.

Identification code	
Empirical formula	$\text{C}_{30}\text{H}_{26}\text{CuN}_6\text{BF}_4$
Formula weight	620.92
Temperature/K	180.01(10)
Crystal system	monoclinic
Space group	$I2/c$
a/Å	24.8641(12)
b/Å	6.0228(3)
c/Å	18.6609(10)
α /°	90
β /°	97.811(5)
γ /°	90
Volume/Å ³	2768.6(3)
Z	4
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.490
μ/mm^{-1}	0.848
F(000)	1272.0
Crystal size/ mm^3	$0.2 \times 0.1 \times 0.1$
2 θ range for data collection	6.616 to 52.042°
Index ranges	$-24 \leq h \leq 30, -7 \leq k \leq 6, -14 \leq l \leq 23$
Reflections collected	4768
Independent reflections	2681 [R(int) = 0.0225]
Data/restraints/parameters	2681/0/192
Goodness-of-fit on F^2	1.037
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0561, wR_2 = 0.1369$
Final R indexes [all data]	$R_1 = 0.0717, wR_2 = 0.1482$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.02/-0.95

References

- 1 C. W. Shao, G. L. Cheng, D. Y. Su, J. M. Xu, X. Y. Wang, Y. F. Hu, *Adv. Synth. Catal.* **2010**, *352*, 1587-1592.