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Selection of Two Optional Covalent Bonds by Electric Stimuli: Dual Catalytic Switching of Redox-Active Copper

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Supporting Information

Materials and Equipments:

Phenylacetylene(**E$_B$**), tetramethylethylenediamine(TMEDA), $CuCl_2$, *o*-terphenyl were used as purchased without further purification. Commercial tetra-*n*-butylammonium hexafluorophosphate($^nBu_4NPF_6$) was recrystallized from methanol-water before use. $CuCl_2$(tmeda)[1], ethynylferrocene(**E$_F$**)[2], benzylazide(**A$_B$**)[3], azidomethylferrocene[4], 4-nitrophenylazide[5], 4-(*N*,*N*-dimethylamino)phenylazide(**A$_N$**)[6], 4-(triisopropylsilyl)ethynylbenzenediazonium tetrafluoroborate (TIPS-Eth-$N_2 \cdot BF_4$)[7] were prepared according to literature methods. All organic solvents were distilled with appropriate drying reagents (CaH_2, Mg or Na) and stored under N_2.

A terminal alkyne modified glassy carbon electrode (**E$_s$**) was prepared by cathodic grafting of TIPS-Eth-$N_2 \cdot BF_4$ followed by a deprotection with $^nBu_4NF$, according to the literature procedure[7]. A 3 mmϕ glassy carbon rod (Tokai Carbon) was embedded in a glass tube, and the cross section was polished with an aluminum powder (50 nm) and used as a base electrode.

A stock solution of catalyst containing Cu(tmeda)Cl_2 (0.12 molL^{-1}) and TMEDA (0.11 molL^{-1}) were prepared and used in the surface electromodification experiment.

Electrochemical measurements were operated with ALS 600D electroanalyzer. A simultaneous potential application to two electrodes was operated with ALS 600D electroanalyzer and HOKUTO HAB-101 potentiostat. An Ag/Ag$^+$ reference electrode ($\Delta E_{1/2} = 0.089$ V for ferrocene/ferrocenium in 0.1 M $^nBu_4NPF_6$ in MeCN) and a Pt wire as a counter electrode were immersed in an unseparated electrochemical cell with the working electrode. The amounts of immobilized species were quantified by an area calculation of a cyclic voltammogram recorded at 10 Vs^{-1}, in which 1-electron oxidation waves of ferrocenyl(**E$_S$-E$_F$**) and diemthylaminophenyl(**E$_S$-A$_N$**) were fitted with Gaussian-Lorenzian curves with linear baseline correction (Igor Pro. 6.22J) . Gas chromatography(GC) was carried out with Shimadzu GC-2014 equipped with J&W Scientific DB-35MS capillary column at 300 °C. High-pressure liquid chromatography (HPLC) was carried out with JASCO LC system equipped with COSMOSIL Cholester packed column eluted with methanol at 40 °C.

Experimental Procedures:

Selective reaction of one-pot ethynyl/azide solution by N_2/O_2 replacement

Under a nitrogen atmosphere, $CuCl_2$(tmeda) (9.2 mg, 36 μmol) and *o*-terphenyl (85 mg, 370 μmol, as a GC standard) were mixed in MeOH-DME (1:1 v/v, 6 mL) in a Schlenk tube. Oxygen gas was bubbled through the solution and phenyl acetylene ($\mathbf{E_B}$, 480 μL, 4.4 mmol) and benzyl azide($\mathbf{A_B}$, 400 μL, 3.2 mmol) were added. The atmosphere was replaced by alternate 30sec bubblings of N_2 or O_2 through the reaction solution, and the products were monitored by a gas chromatography.

Anodic electrolysis of phenylacetylene with Cu catalyst

A two-compartment cell was equipped with a platinum mesh electrode (as a working electrode), an Ag/$AgNO_3$ reference electrode, and a platinum wire (as a counter electrode in the separated compartment). $^{n}Bu_4NPF_6$ (0.7g, 1.8 mmol), $CuCl_2$(tmeda) (27 mg, 0.11 mmol), phenylacetylene (1.44 mL, 13 mmol) and *o*-terpheyl(255 mg, 1.1 mmol, as a standard) were dissolved in MeOH-DME(1:1 v/v, 18 mL). Anodic potential (+0.4 V *vs*. Ag^+/Ag) was applied just after the addition of TMEDA(15 *μ*L, 0.10mmol), and the reaction was monitored by HPLC. An additional portion of TMEDA was added to the solution when the product formation ceased by the consumption of TMEDA with protonation.

Reaction of alkyne-modified electrode

Under a nitrogen atmosphere, two-compartment cell or an undivided cell was equipped with an Ag/$AgNO_3$ reference electrode, and a platinum wire as a counter electrode. The electrolyte solution containing 0.1 M $^{n}Bu_4NPF_6$ in MeOH-DME(1:1 v/v) was charged in the cell, and both or one of the substrates (37 mM ethynylferrocene and 37 mM 4-(*N*,*N*-dimethylamino)phenylazide) were added. A portion of a stock solution of the catalyst was added to be 6.0 mM Cu(tmeda)Cl_2 and 5.6 mM TMEDA. After a brief stirring of the solution, terminal alkyne modified electrode was immersed in the solution followed by an immediate electric potential application. After a certain duration of the potential application, the electrode was rinsed with acetone and hexane, and thoroughly washed (20 min) and sonicated (5 min) in dichloromethane. For the detection of immobilized redox species, the modified electrodes were immersed in an undivided cell containing 0.1 M $^{n}Bu_4NPF_6$ acetonitrile solution, and electrochemical measurements were operated with an Ag/$AgNO_3$ reference electrode, and a platinum wire as a counter electrode. For a reaction monitoring, the modified electrode was immersed back into the substrate solution again, and the same procedure was repeated.

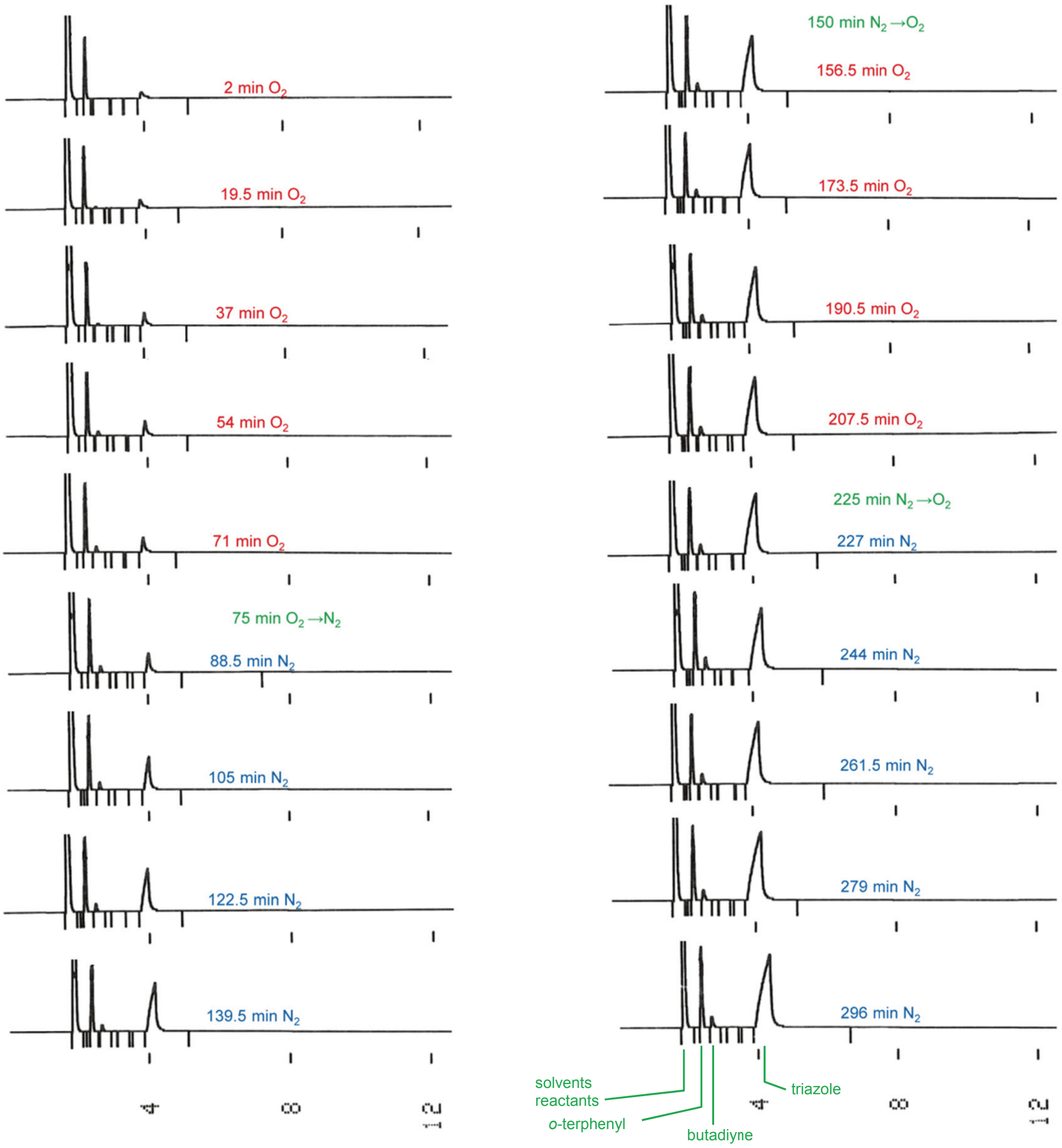

Figure S1. Gas-chromatograph changes of one-pot Glaser-Hay/CuAAC solution with alternate O_2/N_2 replacement. The starting solution was composed of $\mathbf{E_B}$ (4.3 mmol), $\mathbf{A_B}$ (3.2 mmol), $CuCl_2$(tmeda) (0.035 mmol) and TMEDA(0.035 mmol) in 10 ml MeOH-DME(1:1 v/v).

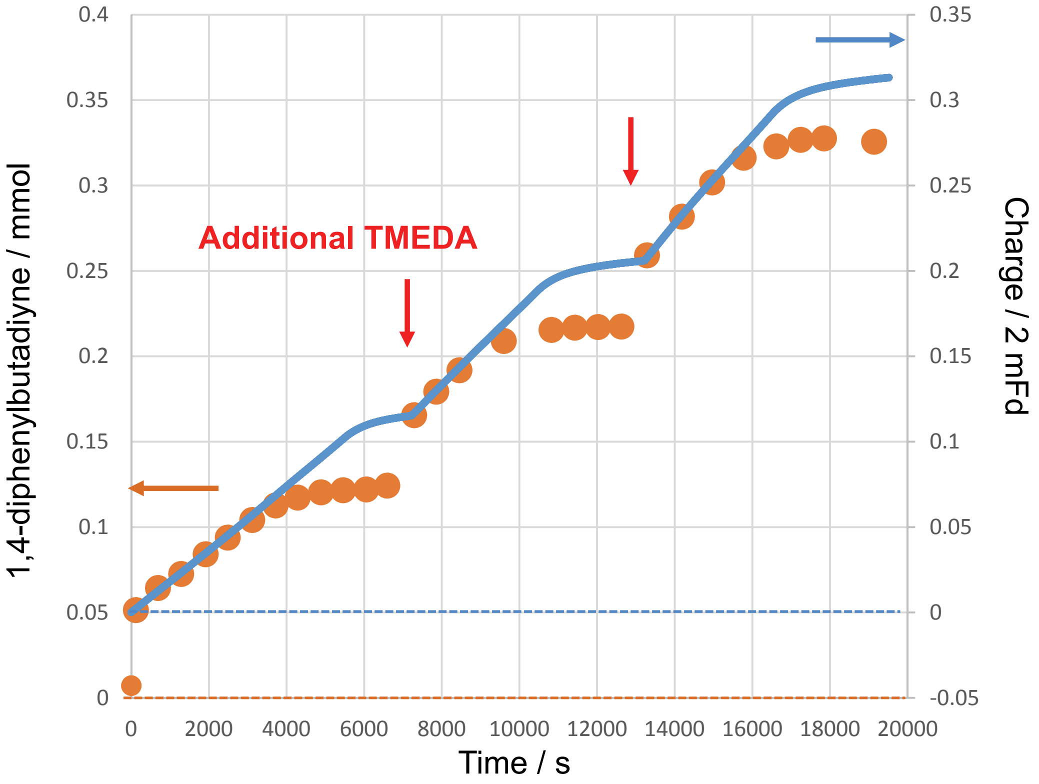

Figure S2. Time-course-dependent formation of 1,4-diphenylbutadiyne from phenylacetylene by the anodic Glaser-Hay coupling. Additional portions of TMEDA (1equiv. to Cu) were added at the time indicated with arrows. Half of the anodic charge profile is also shown with a 0.055 mmol offset, counting that the initial Cu(II) state of the catalyst.

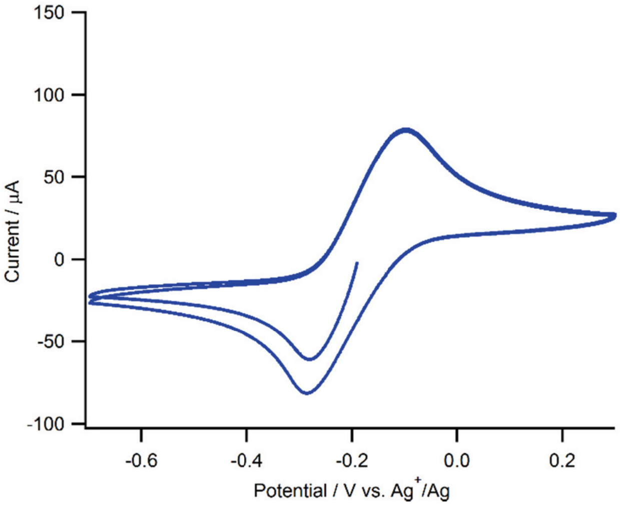

Figure S3. A cyclic voltammogram of Cu(tmeda)Cl_2 in 0.1 M $^{n}Bu_4NPF_6$-MeOH/DME (1:1 v/v). Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag^+/Ag.

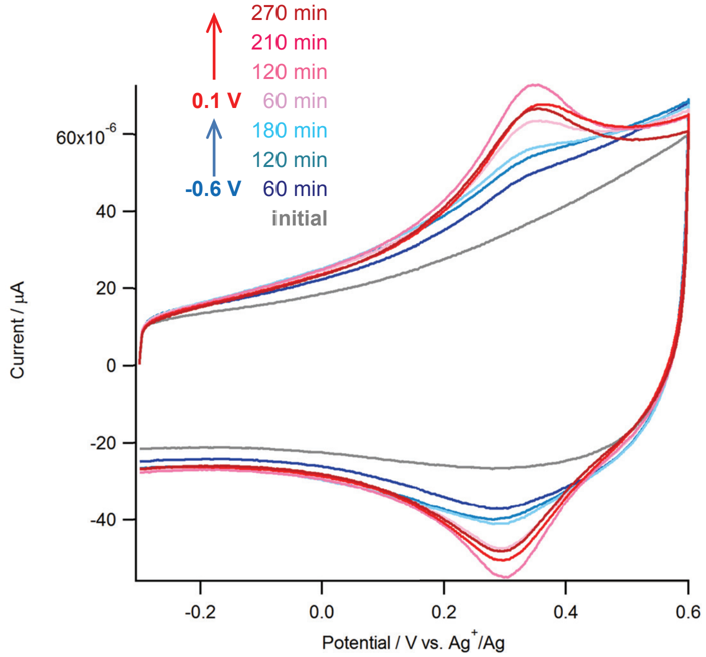

Figure S4. Cyclic voltammograms of terminal alkyne-modified glassy carbon electrode ($\mathbf{E_S}$) reacted upon potential change at the electrode. The reaction solution was composed of $\mathbf{E_F}$ (37 mM in), CuCl$_2$(tmeda) (6.0 mM) and TMEDA(5.5 mM) in 0.1M ^{n}Bu$_4$NPF$_6$-MeOH-DME(1:1 v/v). The voltammograms were recorded in 0.1 M ^{n}Bu$_4$NPF$_6$–MeCN after rinsing the reaction solution. Counter electrode: Pt wire, reference electrode: Ag$^+$/Ag.

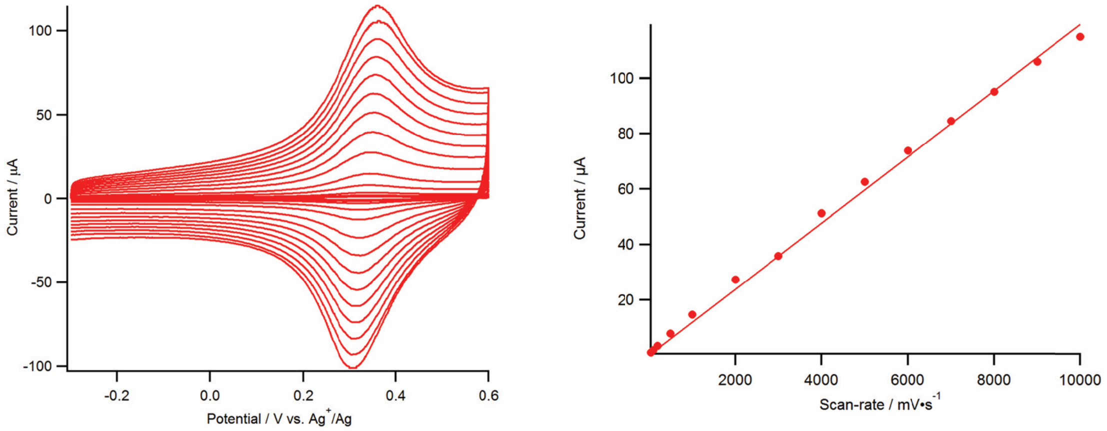

Figure S5. (a) Cyclic voltammograms of $\mathbf{E_S}$-$\mathbf{E_F}$ modified electrode with various scan rates in 0.1 M ^{n}Bu$_4$NPF$_6$-acetonitrile. (b) Scan rate dependence of the anodic peak current.

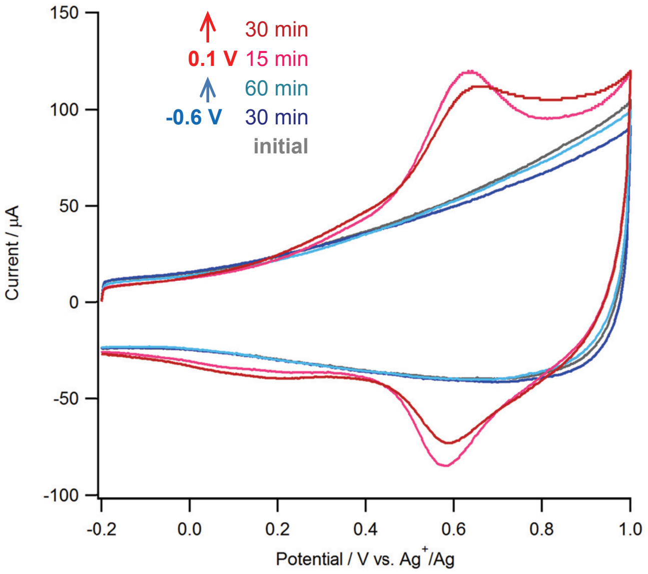

Figure S6. Cyclic voltammograms of terminal alkyne-modified glassy carbon electrode (**E$_S$**) reacted upon potential change at the electrode. The reaction solution was composed of **A$_N$** (37 mM), CuCl$_2$(tmeda) (6.0 mM) and TMEDA(5.5 mM) in 0.1M ^{n}Bu$_4$NPF$_6$-MeOH-DME(1:1 v/v). The voltammograms were recorded in 0.1 M ^{n}Bu$_4$NPF$_6$–MeCN after rinsing the reaction solution. Counter electrode: Pt wire, reference electrode: Ag$^+$/Ag.

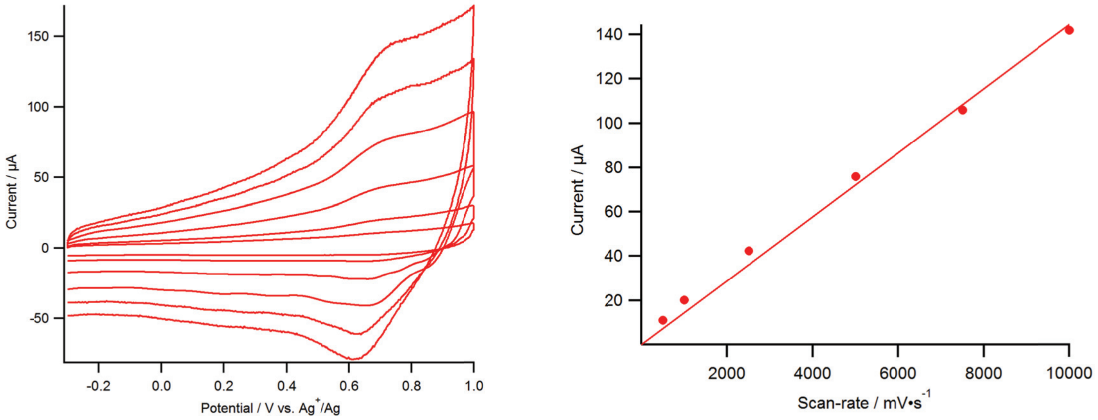

Figure S7. (a) Cyclic voltammograms of **E$_S$-A$_N$** modified electrode with various scan rates in 0.1 M ^{n}Bu$_4$NPF$_6$-acetonitrile. (b) Scan rate dependence of the anodic peak current.

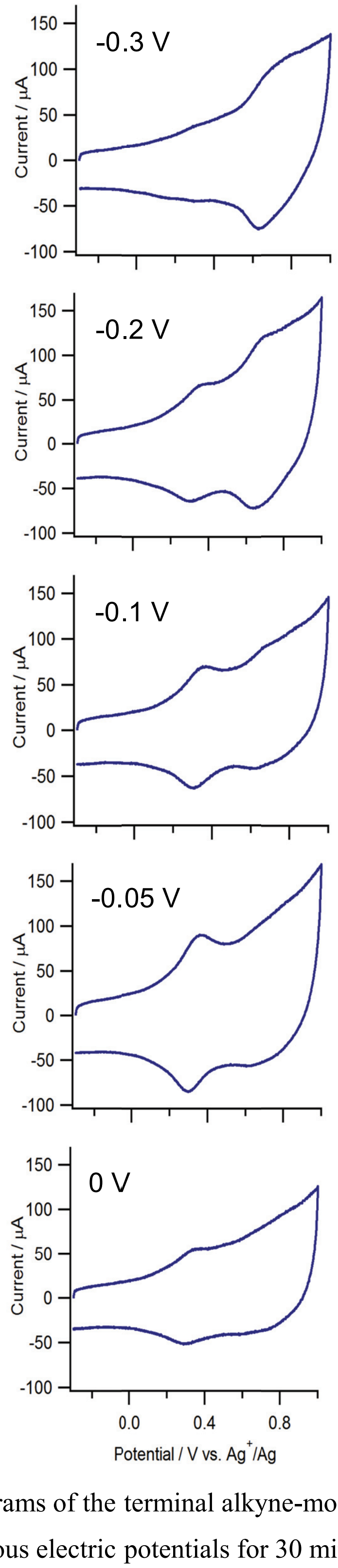

Figure S8. Cyclic voltammograms of the terminal alkyne-modified glassy carbon electrode reacted upon application of various electric potentials for 30 min. The reaction solution was composed of $\mathbf{E_F}$ (37 mM), $\mathbf{A_N}$ (37 mM), $CuCl_2$(tmeda) (6.0 mM), and TMEDA (5.5 mM) in 0.1M $^nBu_4NPF_6$-MeOH-DME (1:1 v/v). Voltammograms were recorded in 0.1 M $^nBu_4NPF_6$–MeCN after rinsing the reaction solution. Counter electrode: Pt wire, reference electrode: Ag^+/Ag.

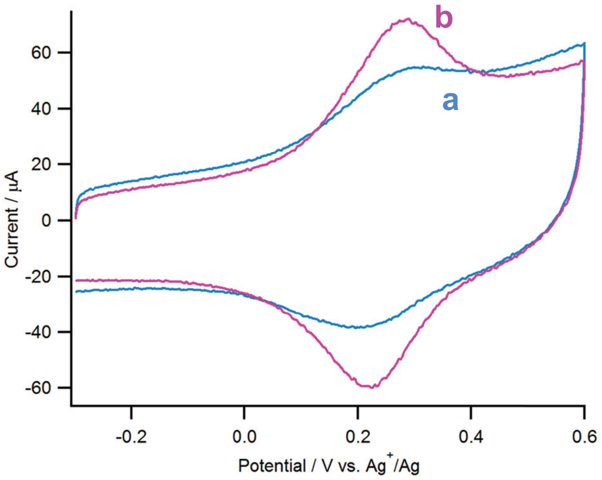

Figure S9. Cyclic voltammograms of immobilized species recorded in 0.1 M $^{n}Bu_4NPF_6$-acetonitrile upon successive application of -0.05 V (60 min, a) and -0.3 V (30 min, b) on a terminal alkyne immobilized electrode. The reaction solution was composed of $\mathbf{E_F}$ (37 mM), ferrocenylmethyazide (37 mM), Cu(tmeda)Cl_2 (6.0 mM) and TMEDA (5.6 mM) in 0.1M $^{n}Bu_4NPF_6$ -MeOH-DME (1:1 v/v).

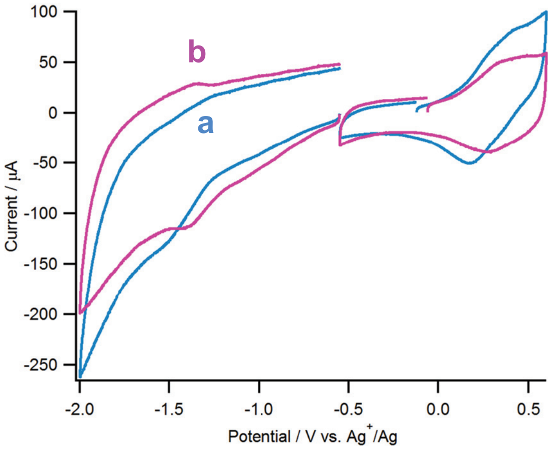

Figure S10. Cyclic voltammograms of immobilized species recorded in 0.1 M $^{n}Bu_4NPF_6$-acetonitrile upon successive application of -0.05 V (30 min, a) and -0.3 V (30 min, b) on a terminal alkyne immobilized electrode. The reaction solution was composed of $\mathbf{E_F}$ (37 mM), 4-nitrophenylazide (37 mM), Cu(tmeda)Cl_2 (6.0 mM) and TMEDA (5.6 mM) in 0.1M $^{n}Bu_4NPF_6$ -MeOH-DME (1:1 v/v).

References

[1] Margraf, G.; Bats, J. W.; Wagner, M.; Lerner, H. W., *Inorganica Chimica Acta* **2005**, 358, 1193-1203.

[2] (a) Tappe, K.; Knochel, P., *Tetrahedron: Asymmetry*, 2004, 15, 91–102. (b) Angelica Aguilar-Aguilar, Annette D. Allen, Eduardo Pen a Cabrera, Andrei Fedorov, Nanyan Fu, Huda Henry-Riyad, Jo¨rg Leuninger, Ulrich Schmid, Thomas T. Tidwell, and Rishi Verma, *J. Org. Chem.* **2005**, 70, 9556-9561. [3] Alvarez, S.G.; Alvarez, M.T., Synthesis 1997, 413-414

[4] Choi, I.; Kim, Y. K.; Min, D. H.; Lee, S. W.; Yeo, W. S., *J. Am. Chem. Soc.* **2011**, 133, 16718-16721

[5] Katti, K.V.; Raghuraman, K.; Pillarsetty, N.; Karra,S. R.; Gulotty, R. J.; Mark A. Chartier, M. A.; Langhoff, C. A., *Chem. Mater.* **2002**, 14, 2436-2438.

[6] (a) Das, B.; Venkateswarlu, K.; Majhi, A.; Siddaiah, V.; Reddy, K. R., *Journal of Molecular Catalysis A: Chemical* **2007**, 267, 30–33. (b) Baron, A.; Herrero, C.; Quaranta, A.; Charlot, M. F.; Leibl, W.; Vauzeilles, B.; Aukauloo, A., *Inorg. Chem.* **2012**, 51, 5985−5987.

[7] (a) Leroux, Y. R.; Hapiot, P., *Chem. Mater.* **2013**, 25, 489−495. (b) Leroux, Y. R.; Fei, H.; Noel, J. M.; Roux, C.; Hapiot, P., *J. Am. Chem. Soc.* **2010**, 132 14039-14041.
