SUPPORTING INFORMATION

HUISGEN CYCLOADDITION WITH ACETYLENE GAS BY USING AN AMPHIPHILIC SELF-ASSEMBLED POLYMERIC COPPER CATALYST

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General Information

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (396 MHz for ^{1}H NMR, 99 MHz for ^{13}C NMR) or JEOL-AL300 spectrometer (300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR). The ^{1}H-NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). GC-MS was measured by an Agilent 7860A/JEOL JMS-T100GC equipped with a capillary column (IL-60, 0.25 mm i.d. × 30 m). ESI-MS was measured by a Bruker MicrOTOF QIII. TLC analysis was performed on Merck silica gel 60 F254. Column chromatography was carried out on silica gel (Wako gel C-200). XAFS spectra of Cu K-edge (9.0 keV) were measured in transmission mode with Si(111) double-crystal monochromator at BL14B2 beamline in SPring-8 (JASRI), Japan. The catalyst samples for XAFS were pressed into 10 mm diameter disks using BN under Ar atmosphere. XAFS data processing was performed using Demeter software package[8] and FEFF6 code[9]. Quantum chemical calculations were performed using Firefly QC package,[10] which is partially based on the GAMESS (US)[11] source code. The optimized geometries were confirmed to have no imaginary frequencies by vibrational calculations at the same level of theory used for geometry optimizations. All basis sets have been downloaded[12] from EMSL Basis Set Exchange[13,14].

Material

Reagents and solvents except water were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system as a Milli-Q grade. *t*-BuOH and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. Copper(II) sulfate pentahydrate, sodium azide and sodium ascorbate were purchased from Wako Pure Chemical Industries, Ltd. Dissolved acetylene was purchased from Kanto Acetylene Industry Co. Ltd.

Preparation of MPPI-Cu:

MPPI-Cu was prepared in accordance with our reported procedure.[1]

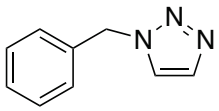
Preparation of Organic Azides 4:

Organic azides except benzyl azide were prepared by the following procedure. Sodium azide (1.1-1.3 mol equiv) was dissolved in dry DMSO (0.5 M). Commercially available benzylic/aliphatic bromide (1 mol equiv) was added to the solution, and the reaction mixture was stirred at 25 °C. After the reaction was completed, water was added and the product was extracted with Et_2O. The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel gave the corresponding azide **4**.

General Procedure for the Two-component [3+2] Cycloaddition:

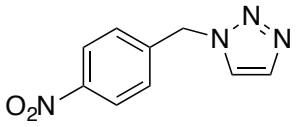
A Schlenk flask was charged with MPPI-Cu **3** (3 mg, 0.25 mol%), an organic azide **4** (0.5 mmol), sodium ascorbate (10 mg, 10 mol%) in water and *t*-BuOH (1.5/0.5 mL each). The Schlenk flask was purged with acetylene gas and the reaction mixture was stirred under an acetylene atmosphere with a balloon at 50 ℃ for 4.5 h. After the reaction was completed, the reaction mixture was diluted with water and EtOAc. The supernatant was transferred to a separatory funnel, and the recovered catalyst in the Schlenk flask was dried *in vacuo*. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel gave the corresponding 1*H*-1,2,3-triazole **6**. The recovered catalyst was reused for further reactions.

Product Data



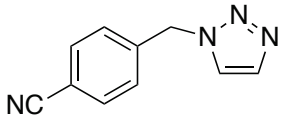
1-Benzyl-1*H*-1,2,3-triazole (6a): CAS: 4368-68-7, White solid, 94 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.70 (s, 1H), 7.48 (s, 1H), 7.40-7.33 (m, 3H), 7.29-7.24 (m, 2H), 5.57 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 134.7, 134.2, 129.1, 128.7, 128.0, 123.3, 53.9; EI-MS *m/z* = 160 $(M+H)^+$.

NMR data are in accordance with those reported in the literature.[2]



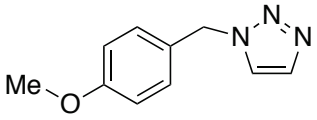
1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole (6b): CAS: 99590-25-7, Pale yellow solid, 95 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.25-8.22 (m, 2H), 7.79 (s, 1H), 7.58 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 5.70 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 148.1, 141.7, 134.7, 128.5, 124.3, 123.6, 52.9; ESI-MS *m/z* = 205 $(M+H)^+$.

NMR data are in accordance with those reported in the literature.[2]



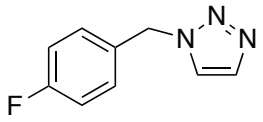
1-(4-Cyanobenzyl)-1*H*-1,2,3-triazole (6c): CAS: 118618-40-9, White solid, 90 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.77 (s, 1H), 7.68-7.66 (m, 2H), 7.56 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.9, 134.6, 132.8, 128.2, 123.6, 118.1, 112.7, 53.1; ESI-MS *m/z* = 185 $(M+H)^+$.

^{1}H NMR data are in accordance with those reported in the literature.[3]



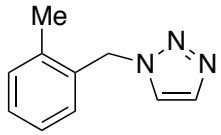
1-(4-Methoxybenzyl)-1*H*-1,2,3-triazole (6d): CAS: 31794-11-3, White solid, 95 %, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.69 (s, 1H), 7.43 (s, 1H), 7.24-7.20 (m, 2H), 6.92-6.87 (m, 2H), 5.50 (s, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.9, 134.1, 129.6, 126.6, 123.0, 114.4, 55.3, 53.1; EI-MS *m/z* = 189 $(M)^+$.

NMR data are in accordance with those reported in the literature.[4]



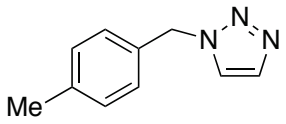
1-(4-Fluorobenzyl)-1*H*-1,2,3-triazole (6e): CAS: 76508-47-9, Colorless oil, 85 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.71 (s, 1H), 7.48 (s, 1H), 7.28-7.24 (m, 2H), 7.09-7.03 (m, 2H), 5.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.8 (d, *J* = 248.5 Hz), 134.3, 130.5 (d, *J* = 3.3 Hz), 130.0 (d, *J* = 8.3 Hz), 123.2, 116.1 (d, *J* = 22.3 Hz), 53.2; EI-MS *m/z* = 177 $(M)^+$.

NMR data are in accordance with those reported in the literature.[5]



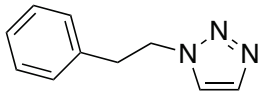
1-(2-Methylbenzyl)-1*H*-1,2,3-triazole (6f): CAS: 63777-98-0, White solid, 96 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.69 (s, 1H), 7.36 (s, 1H), 7.31-7.13 (m, 4H), 5.57 (s, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 136.9, 134.0, 132.5, 131.0, 129.3, 129.1, 126.6, 123.1, 52.1, 18.9; EI-MS *m/z* = 174 $(M+H)^+$.

NMR data are in accordance with those reported in the literature.[4]



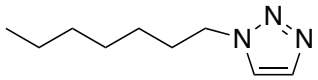
1-(4-Methylbenzyl)-1*H*-1,2,3-triazole (6g): CAS: 123799-83-7, Pale yellow solid, 95 %, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.69 (s, 1H), 7.45 (s, 1H), 7.21-7.12 (m, 4H), 5.52 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 138.6, 134.1, 131.6, 129.7, 128.0, 123.1, 53.7, 21.1; EI-MS *m/z* = 173 $(M)^+$.

NMR data are in accordance with those reported in the literature.[4]



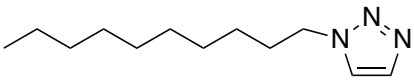
1-Phenethyl-1*H*-1,2,3-triazole (6h): CAS: 63777-90-2, Colorless oil, 83 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.61 (s, 1H), 7.30-7.22 (m, 4H), 7.10-7.08 (m, 2H), 4.62 (t, *J* = 7.4 Hz, 2H), 3.21 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 136.9, 133.4, 128.7, 128.6, 127.0, 123.6, 51.4, 36.7; EI-MS *m/z* = 174 $(M+H)^+$.

^{1}H NMR data are in accordance with those reported in the literature.[6]



1-Heptyl-1*H*-1,2,3-triazole (6i): CAS: 63777-80-0, Pale yellow oil, 76 %, ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.70 (d, *J* = 1.2 Hz, 1H), 7.54 (d, J = 0.8 Hz, 1H), 4.39 (t, *J* = 7.4 Hz, 2H), 1.95-1.88 (m, 2H), 1.33-1.26 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 133.6, 123.1, 50.1, 31.4, 30.2, 28.5, 26.3, 22.4, 13.9; EI-MS *m/z* = 168 $(M+H)^+$

^{1}H NMR data are in accordance with those reported in the literature.[3]



1-Decyl-1*H*-1,2,3-triazole (6j): CAS: 1456603-53-4, White solid, 92 %, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.70 (s, 1H), 7.53 (s, 1H), 4.38 (t, *J* = 7.4 Hz, 2H), 1.94-1.89 (m, 2H), 1.32-1.25 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 133.7, 123.1, 50.2, 31.8, 30.3, 29.4, 29.3, 29.2, 29.0, 26.4, 22.6, 14.1; EI-MS *m/z* = 210$(M+H)^+$

^{1}H NMR data are in accordance with those reported in the literature.[7]

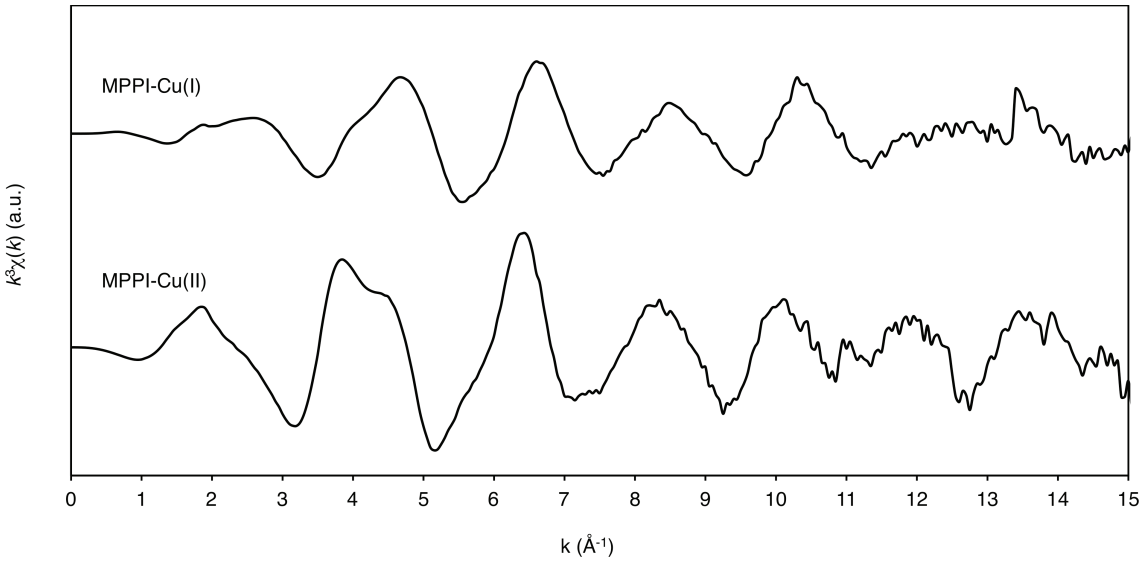


Figure S1. EXAFS in *k*-space of MPPI-Cu(I) and -Cu(II)

Optimized geometry of $[Cu^{I}(1\text{-methylimidazole})_2]^{+}$

CU	0.0000000000	0.0000000000	0.0257214448
N	-3.0569969030	2.6581686570	-0.4125060161
N	3.0569969030	-2.6581686570	-0.4125060161
N	-1.5821673128	1.0672629203	0.0377517400
N	1.5821673128	-1.0672629203	0.0377517400
C	-3.6279980870	1.8487894390	0.5530149822
C	3.6279980870	-1.8487894390	0.5530149822
C	-2.7046052686	0.8628448951	0.8269396169
C	2.7046052686	-0.8628448951	0.8269396169
C	-1.8297161733	2.1593102147	-0.6975474362
C	1.8297161733	-2.1593102147	-0.6975474362
C	-3.6745036090	3.8413110290	-1.0148207516
C	3.6745036090	-3.8413110290	-1.0148207516
H	-4.6242362255	2.0429609792	0.9535985001
H	4.6242362255	-2.0429609792	0.9535985001
H	-2.7755388796	0.0324105608	1.5318300943
H	2.7755388796	-0.0324105608	1.5318300943
H	-1.1569104564	2.6086762371	-1.4311493695
H	1.1569104564	-2.6086762371	-1.4311493695
H	-4.6099289526	3.5562175433	-1.5287315493
H	4.6099289526	-3.5562175433	-1.5287315493
H	-2.9752060263	4.2782564198	-1.7465360098
H	2.9752060263	-4.2782564198	-1.7465360098
H	-3.8971446741	4.5879877933	-0.2317287472
H	3.8971446741	-4.5879877933	-0.2317287472

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