Electronic Supplementary Information

Copper nitride nanoparticles supported on a superparamagnetic mesoporous microsphere for toxic-free click chemistry

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Methods

Characterization of Inorganic Materials. Powder X-ray diffraction patterns were recorded with a Rigaku DMAX 2500 diffractometer (Cu Kα) operating at 40 kV and 150 mA. High resolution scanning electron microscope (HR-SEM) analyses were carried out using a Hitachi s-5500. Samples for HR-SEM were prepared by dropping the diluted sample in ethanol on a lacey grid. Transmission electron microscope (TEM) analyses were carried out on a JEOL JEM-2100F. Samples were also subjected to chemical microanalysis with an Oxford Instruments INCA TEM 300 system for energy dispersive X-ray analysis. Specimens for TEM examination were prepared by dispersing finely-ground powders in high purity ethanol, then allowing a drop of the suspension to evaporate on a 400 mesh carbon-coated grid. The field-dependent magnetization measurements were measured at 10 and 300 K with a Quantum Design MPMS-5 SQUID magnetometer. The X-ray photoelectron spectroscopy experiments were carried out in an ultrahigh vacuum analysis chamber which was connected to a preparation chamber where all deposition processes took place *in situ*. Spectra were recorded on AXIS-NOVA using an Al K_α (1486.6 eV) source. The base pressure of the chamber was 4.2×10^{-9} Torr. The dwell time was 100 ms, the settle time was 500 ms, and the line delay was 500 ms. Each spectral scan range was 20 eV, with a step energy of 0.05 eV and a 100 ms acquisition time. High-resolution spectra were resolved by fitting each peak with a Guassian-Lorentzian function after subtracting the background by a Shirley method.

Organic Experiments. All chemicals were obtained from commercial suppliers and were used without further purification unless otherwise stated. Both azide and acetylene compounds in Table 2 were prepared by well-established one or two-step synthesis. Column chromatography was carried out using Merck silica gel 60 (230-400 mesh) and eluting with ethyl acetate/hexanes or methanol/dichloromethane.

^{1}H and ^{13}C NMR spectra were recorded using either a Varian 400MR (400 MHz) or an INOVA-500 (500 MHz) and calibrated using residual undeuterated solvent as an internal reference. High performance liquid chromatography (HPLC) was conducted for reaction optimization (Table 1) and recycle study by using Varian 920-LC and Varian Pursuit XRs column (5 μm, RP C18, 4.6 mm x 250 mm). Low-resolution mass spectra were obtained using Electrospray Ionization (ESI, Varian 500-MS) and Electron Ionization (EI, Agilent-5973N).

Synthesis of Superparamagnetic Mesoporous Silica Microspheres $Fe_3N@SiO_2$. Mesoporous silica (SiO_2) spheres composed of mesoporous shell and solid core with average diameter of about 500 nm are prepared by slight modification of the Unger procedure. For the synthesis of superparamagnetic microspheres containing iron nitride nanoparticles (NPs), mesoporous silica (SiO_2, 1.0 g) was added into a 10 mL of ethanol with vigorous stirring, which was then sonicated to disperse the silica microspheres completely. To the solution 0.2705 g of $Fe(NO_3)_3{\cdot}9H_2O$ (98+%, Aldrich) was added. After complete dissolution of the Fe precursor, 20 mL of dioctyl ether (99%, Aldrich) and 1 mL of Igepal CO-520 (Aldrich) were added into the mixed solution, followed by stirring and sonicating for 10 min. The reaction mixture was heated to 90 °C with stirring until ethanol was almost completely evaporated. The resultant colloidal microspheres with yellow color were separated by centrifugation (2,800 rpm), which was dried in an oven at 80 °C for 24 h. The as-prepared microspheres containing iron precursors were annealed at 700 °C in a mixed NH_3 atmosphere (NH_3:N_2=7:3) for 6 h. Hereafter we denote the resulting microsphere as $Fe_3N@SiO_2$.

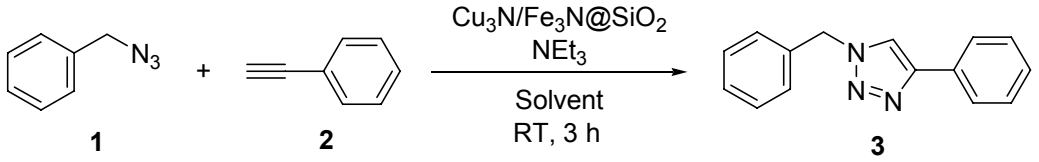
Synthesis of $Cu_3N/Fe_3N@SiO_2$. For the synthesis of Cu_3N NPs embedded within mesoporous shells of $Fe_3N@SiO_2$, $Fe_3N@SiO_2$ (1.0 g) was added into a 10 mL of methanol with vigorous stirring, which was then sonicated to disperse completely. To the solution 0.2 g of $Cu(OAc)_2{\cdot}H_2O$ (98+%, Aldrich) were added. After complete dissolution of the Cu precursor, 15 mL of octane (Aldrich) and 0.45 g of CTAB (Aldrich) were added into the mixed solution, followed by stirring and sonicating for 10 min. Then, 0.45 mL of 1-butanol (>99.4%, Aldrich) was added into the solution. The reaction mixture was heated to 80 °C with stirring until methanol was almost completely evaporated. The resultant colloidal microspheres were separated by centrifugation (2,800 rpm), which was dried in an oven at 80 °C for 24 h. The as-prepared microspheres containing Cu precursors were annealed at 250 °C in a mixed NH_3 atmosphere (NH_3:N_2=7:3) for 6 h. Hereafter we denote the resulting microsphere as $Cu_3N/Fe_3N@SiO_2$.

Quantitative Analysis of Cu and Fe Contents in $Cu_3N/Fe_3N@SiO_2$ by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). $Cu_3N/Fe_3N@SiO_2$ (0.0005 g) was weighed and transferred into

a vessel for microwave acid digestion. Then, HF (2 mL), H_2SO_4 (2 mL), and HNO_3 (5 mL) were added into the vessel, followed by the programmed procedure for the digestion. The solution containing the digested sample was cooled to room temperature, which was delivered into a 100 mL volumetric flask. After the solution was properly diluted, the Cu and Fe contents in the solution were determined by ICP-MS. The weight percentages of Cu_3N and Fe_3N were determined to be 3.05 % and 0.52 %, respectively.

Typical Procedure for the Synthesis of 1,2,3-Triazoles in Table S1 and Table S2. To a suspension of benzyl azide (**1**, 0.1 mmol), phenylacetylene (**2**, 0.1 mmol), and $Cu_3N/Fe_3N@SiO_2$ (5 mg) in solvent (0.5 mL) was added amine (0.3 mmol) at room temperature. The mixture suspension was vortexed at a speed of 300 r.p.m. for 3 h. The solution was carefully decanted and separated from the reaction mixture using a permanent magnet, in which the $Cu_3N/Fe_3N@SiO_2$ microspheres were stuck on the bottom of reaction vessel by a magnetic block. Conversion ratio (%) was determined by HPLC analysis. HPLC conditions: acetonitrile/water (55:45, isocratic), flow 1 mL min^{-1}, detection UV (λ = 254 nm), injection loop 20 μL → 10.0 min (triazole, **3**), 11.8 min (phenylacetylene, **2**).

Table S1 Reaction of benzyl azide (1) with phenylacetylene (2) in the presence of $Cu_3N/Fe_3N@SiO_2$ and various organic solvents.[a]

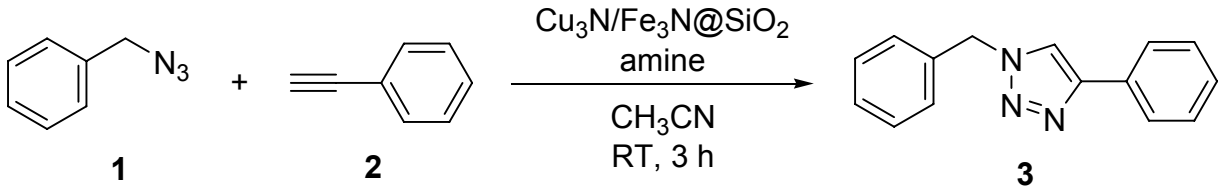


Entry	Solvent	Conversion (%)[b]
1	CH_3CN	80
2	CH_2Cl_2	77
3	THF	48
4	MeOH	18
5	EtOH	32
6	*t*-BuOH	18
7	acetone	36
8	DMF	22
9	DMSO	23

[a] All reactions were carried out using the same scale and procedure as in Table 1.

[b] Determined by HPLC.

Table S2 HDC reaction of benzyl azide (1) with phenylacetylene (2) in the presence of $Cu_3N/Fe_3N@SiO_2$ and various amines.[a]



Entry	Amine	Conversion (%)[b]
1	-	4
2	NEt_3	80
3	DIPEA	62
4	DMEDA[c]	<1
5	TMEDA[d]	42

[a] All reactions were performed with a 0.1 mmol scale of **1** and **2** in 0.5 mL of CH_3CN, using 5 mg of $Cu_3N/Fe_3N@SiO_2$ and 0.3 equiv of amine. [b] Determined by HPLC [c] *N,N'*-dimethylethyleneamine. [d] *N,N,N',N'*-tetramethylethylene-diamine.

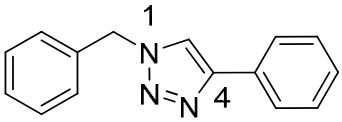
Catalyst Reusability. Triethylamine (0.3 mmol) was added to a suspension of benzyl azide (**1**, 1.0 mmol), phenylacetylene (**2**, 1.1 mmol), and $Cu_3N/Fe_3N@SiO_2$ (20 mg) in acetonitrile (3.0 mL) at room temperature. The suspension was vortexed at a speed of 300 r.p.m. for 24 h. The solution was carefully decanted and separated from the reaction mixture using a permanent magnet, in which the $Cu_3N/Fe_3N@SiO_2$ microspheres were stuck on the bottom of reaction vessel by a magnetic block. The decanted solution was characterized by HPLC and ICP-AES analysis. The residual $Cu_3N/Fe_3N@SiO_2$ microspheres were recovered by rinsing with acetonitrile (3.0 mL) three times and drying under reduced pressure for the next run. This procedure was repeated to use the recovered $Cu_3N/Fe_3N@SiO_2$ catalyst up to five runs. HPLC profile data of the reaction products using the recycled catalyst showed almost 100% conversion yield until the 4th run. Negligible amount of decrease in conversion yield was observed in the 5th run, which is found to be 99.8%.

General Procedure for the Synthesis of 1,2,3-Triazoles in Table 1. To a suspension of alkyne (1.0 mmol), azide (1.1 mmol), and $Cu_3N/Fe_3N@SiO_2$ (20 mg) in CH_3CN (4.0 mL) was added triethylamine (0.3 mmol) at room temperature. The mixture suspension was vortexed at a speed of 300 r.p.m. at room

temperature. Each reaction was carefully monitored by TLC and maintained at room temperature until alkyne disappeared on TLC. The solution was carefully decanted and separated from the reaction mixture using a permanent magnet, in which the $Cu_3N/Fe_3N@SiO_2$ microspheres were stuck on the bottom of reaction vessel by a magnetic block. The residual $Cu_3N/Fe_3N@SiO_2$ microsphere was rinsed with CH_3CN (4.0 mL) three times and dried under reduced pressure for reuse. The combined CH_3CN solution was concentrated under vacuum. The product was purified by column chromatography and re-crystallized with a combination of ethyl acetate, methanol, and *n*-hexane.

Characterization of 1,2,3-Triazole Compounds in Table 1

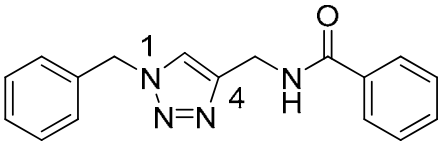
1-Benzyl-4-phenyl-*1H*-1,2,3-triazole (3, 1st column, 1st line).



Registry number: 108717-96-0.

Column chromatography with 30% ethyl acetate/*n*-hexane gave a 81% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 128-129 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.50 (s, 2H), 7.37-7.23 (m, 8H), 7.77 (s, 1H), 7.80-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 54.0, 119.5, 125.5, 127.9, 128.56, 128.64, 128.9, 130.4, 134.6, 148.0. HRMS (EI) *m/z* $C_{15}H_{13}N_3$ $[M]^+$ calcd 235.1109, found 235.1105.

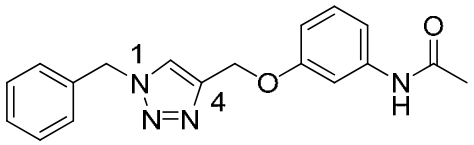
4-(Benzamido)methyl-1-benzyl-*1H*-1,2,3-triazole (1st column, 2nd line).



Registry number: 907563-53-5 (*Tetrahedron Lett*. **2006**, 47, 5105-5109.)

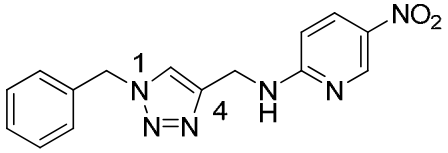
Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 89% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, J = 5.6 Hz, 2H), 5.45 (s, 2H), 7.22–7.24 (m, 2H), 7.31–7.37 (m, 5H), 7.42–7.46 (m, 2H), 7.56 (s, 1H), 7.77 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.5, 54.4, 122.8, 127.3, 128.4, 128.7, 129.0, 129.4, 131.8, 134.2, 134.7, 145.4, 176.6; MS (EI) m/z: 292 (M^+), 187, 173.

4-[3-(*N*-Acetamido)phenoxy]methyl-1-benzyl-*1H*-1,2,3-triazole (1st column, 3rd line).



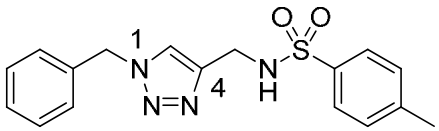
Column chromatography with 80% ethyl acetate/*n*-hexane gave a 79% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 149.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H), 5.13 (s, 2H), 5.51 (s, 2H), 6.67 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.25-7.27 (m, 2H), 7.30 (s, 1H), 7.34-7.39 (m, 3H), 7.56 (s, 1H), 7.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.8, 54.4, 62.1, 106.7, 110.9, 112.8, 123.1, 128.3, 129.0, 129.3, 129.9, 134.6, 139.4, 144.5, 158.8, 168.7; MS (ESI) m/z: 345 $[M+Na]^+$, 323 $[M+H]^+$. Anal. Calcd for $C_{18}H_{18}N_4O_2$: C, 67.07; H, 5.63; N, 17.38. Found: C, 67.09; H, 5.48; N, 17.24.

1-Benzyl-4-[(5-nitropyridin-2-yl)amino]methyl-*1H*-1,2,3-triazole (1st column, 4th line).



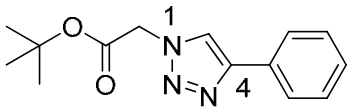
Filtration of precipitate gave a 89% of yield as a yellow solid, and re-crystallized with CH_3OH: m.p. 229.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.63 (s, 2H), 5.55 (s, 2H), 6.60 (d, *J* = 9.2 Hz, 1H), 7.28-7.34 (m, 5H), 8.07-8.12 (m, 2H), 8.53 (s, 1H), 8.92 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 37.0, 53.4, 109.3, 124.0, 128.6, 128.8, 129.4, 132.6, 135.3, 136.8, 145.2, 147.4, 161.6; MS (ESI) m/z: 309 $[M-H]^-$. Anal. Calcd for $C_{15}H_{14}N_6O_2$: C, 58.06; H, 4.55; N, 27.08. Found: C, 58.19; H, 4.57; N, 26.97.

1-Benzyl-4-(*p*-toluenesulfonamido)methyl-*1H*-1,2,3-triazole (1st column, 5th line).



Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 91% of yield as a white solid, and re-crystallized with ethyl acetate/n-hexane: m.p. 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.19 (d, *J* = 6.4 Hz, 2H), 5.30 (br s, 1H), 5.42 (s, 2H), 7.19–7.24 (m, 4H), 7.33–7.35 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 38.9, 54.4, 122.4, 127.4, 128.3, 129.1, 129.39, 130.0, 134.5, 136.7, 143.9, 144.3; MS (ESI) m/z: 365 $[M+Na]^+$. Anal. Calcd for $C_{17}H_{18}N_4O_2S$: C, 59.63; H, 5.30; N, 16.36; S, 9.36. Found: C, 59.53; H, 5.32; N, 16.43; S, 9.35.

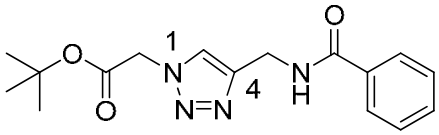
1-(*tert*-Butyloxycarbonyl)methyl-4-phenyl-*1H*-1,2,3-triazole (2nd column, 1st line).



(*Angew. Chem. Int. Ed*. **2007**, 46**,** 3649-3651.)

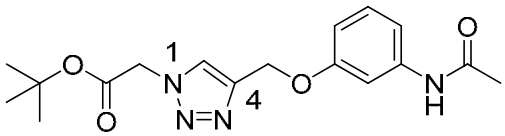
Column chromatography with 50% ethyl acetate/*n*-hexane gave a 82% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 112.0 °C (decomposed); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 9H), 5.11 (s, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 51.8, 84.1, 121.1, 126.0, 128.4, 129.0, 130.7, 148.3, 165.5; MS (EI) m/z 259 (M^+), 203, 175, 116.

4-(Benzamido)methyl-1-(*tert*-butyloxycarbonyl)methyl-*1H*-1,2,3-triazole (2nd column, 2nd line).



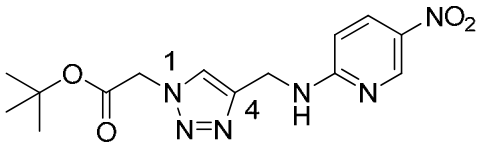
Column chromatography with 50% ethyl acetate/*n*-hexane gave a 79% of yield as an ivory solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 140.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 9H), 4.72 (d, *J* = 6.0 Hz, 2H), 5.03 (s, 2H), 7.12 (br s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.74 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 35.6, 51.7, 84.1, 124.1, 127.2, 128.7, 131.8, 134.2, 145.1, 165.4, 167.6; MS (EI) m/z: 316 (M^+), 301, 260, 187, 105, 77. Anal. Calcd for $C_{16}H_{20}N_4O_3$: C, 60.75; H, 6.37; N, 17.71. Found: C, 60.80; H, 6.42; N, 17.82.

4-(3-Acetamidophenoxy)methyl-1-(*tert*-butyloxycarbonyl)methyl-*1H*-1,2,3-triazole (2nd column, 3rd line).



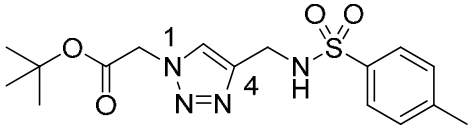
Column chromatography with 50% ethyl acetate/*n*-hexane gave a 82% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 110.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.14 (s, 3H), 5.06 (s, 2H), 5.18 (s, 2H), 6.70 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.3 Hz, 1H), 7.28 (s, 1H), 7.69 (s, 1H), 7.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.8, 28.1, 51.8, 62.0, 84.1, 106.7, 111.0, 112.8, 124.6, 129.9, 139.4, 144.5, 158.7, 165.4, 168.7; MS (ESI) m/z: 369 $[M+Na]^+$, 347 $[M+H]^+$. Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.40; N, 16.17. Found: C, 59.00; H, 6.36; N, 16.09.

1-(*tert*-Butyloxycarbonyl)methyl-4-[(5-nitropyridin-2-yl)amino]methyl-*1H*-1,2,3-triazole (2nd column, 4th line).



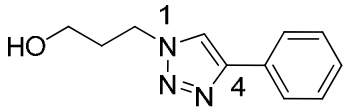
Column chromatography with 50% ethyl acetate/*n*-hexane gave a 60% of yield as a yellow solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 176.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.39 (s, 9H), 4.65 (s, 2H), 5.21 (s, 2H), 6.63 (d, J = 9.2 Hz, 1H), 7.99 (s, 1H), 8.12 (d, J = 8.0, 1H), 8.60 (s, 1H), 8.93 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 28.28, 36.82, 51.54, 82.96, 109.41, 125.21, 132.63, 135.33, 144.92, 147.38, 161.67, 166.95; MS (ESI) m/z: 333 $[M-H]^-$. Anal. Calcd for $C_{14}H_{18}N_6O_4$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.35; H, 5.49; N, 25.24.

1-(*tert*-Butyloxycarbonyl)methyl-4-(*p*-toluenesulfonamido)methyl-*1H*-1,2,3-triazole (2nd column, 5th line).



Column chromatography with 50% ethyl acetate/*n*-hexane gave a 90% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 117.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.43 (s, 3H), 4.26 (d, J = 6.0 Hz, 2H), 5.00 (s, 2H), 5.30 (t, J = 5.75 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.59 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 28.1, 38.9, 51.7, 84.2, 123.9, 127.4, 130.0, 136.8, 143.8, 144.2, 165.3; MS (EI) m/z: 203 (M^+), 130, 117, 102, 90; MS (ESI) m/z: 389 $[M+Na]^+$, 367 $[M+H]^+$. Anal. Calcd for $C_{16}H_{22}N_4O_4S$: C, 52.44; H, 6.05; N, 15.29; S, 8.75. Found: C, 52.33; H, 6.13; N, 15.21; S, 8.37.

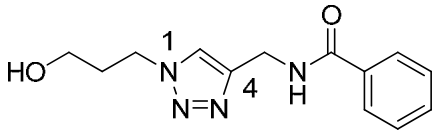
1-(3-Hydroxy-*n*-propyl)-4-phenyl-*1H*-1,2,3-triazole (3rd column, 1st line).



Registry number: 1034194-27-8 (*Chem. Commun*. **2008**, 39, 4747-4749.); *QSAR Comb. Sci*. **2007**, 26, 1274-1279.)

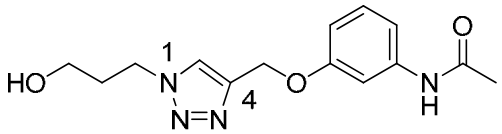
Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 76% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (quintet, J = 6.3 Hz, 2H), 2.72 (s, 1H), 3.66 (t, J = 5.4 Hz, 2H), 4.54 (t, J = 6.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.37–7.41 (m, 2H), 7.77–7.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9, 47.2, 58.8, 120.5, 125.9, 128.4, 129.1, 130.7, 147.9; MS (EI) m/z: 203 (M^+), 130, 117, 102, 90.

1-(3-Hydroxy-*n*-propyl)-4-(benzamido)methyl-*1H*-1,2,3-triazole (3rd column, 2nd line).



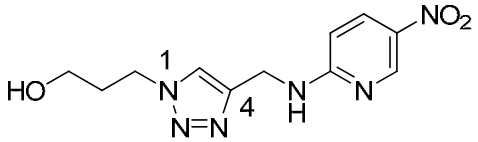
Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 72% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (quintet, J = 6.3 Hz, 2H), 2.85 (t, J = 5.0 Hz, 1H), 3.61 (q, J = 5.6 Hz, 2H), 4.47 (t, J = 6.6 Hz, 2H), 4.66 (d, J = 5.6 Hz, 2H), 7.35–7.39 (m, 3H), 7.44-7.48 (m, 1H), 7.68 (s, 1H), 7.77 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 35.5, 47.2, 58.8, 123.4, 127.3, 128.8, 131.9, 134.1, 144.9, 167.8; MS (EI) m/z: 260 (M^+), 231, 187, 155. Anal. Calcd for $C_{13}H_{16}N_4O_2$: C, 59.99; H, 6.20; N, 21.52. Found: C, 60.00; H, 5.97; N, 21.39.

4-(3-Acetamidophenoxy)methyl-1-(3-hydroxy-*n*-propyl)-*1H*-1,2,3-triazole (3rd column, 3rd line).



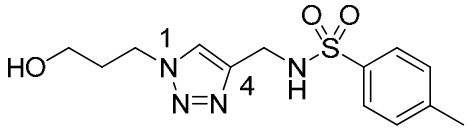
Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 89% of yield as a yellow solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 120.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.89-1.96 (m, 2H), 1.99 (s, 3H), 3.33-3.38 (m, 2H), 4.38 (t, J = 7.2 Hz, 2H), 4.65 (t, J = 4.8 Hz, 1H), 5.04 (s, 2H), 6.69 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.2 Hz, 1H), 7.30 (s, 1H), 8.18 (s, 1H), 9.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 33.6, 47.4, 58.1, 61.7, 106.4, 109.5, 112.3, 125.2, 130.2, 141.1, 143.2, 158.1, 169.0; MS (EI) m/z: 290 (M^+), 144. Anal. Calcd for $C_{14}H_{18}N_4O_3$: C, 57.92; H, 6.25; N, 19.30. Found: C, 59.95; H, 6.38; N, 19.39.

1-(3-Hydroxy-*n*-propyl)-4-[(5-nitropyridin-2-yl)amino]methyl-*1H*-1,2,3-triazole (3rd column, 4th line).



Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 84% of yield as a yellow solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 124.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.91 (quintet, J = 6.4 Hz, 2H), 3.34-3.38 (m, 2H), 4.35 (t, J = 7.0 Hz, 2H), 4.62-4.66 (m, 3H), 6.61 (d, J = 9.2 Hz, 1H), 8.00 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.54 (s, 1H), 8.93 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 33.7, 36.9, 47.3, 58.1, 109.4, 123.9, 132.6, 135.3, 144.7, 147.4, 161.6; MS (ESI) m/z: 277 $[M-H]^-$. Anal. Calcd for $C_{11}H_{14}N_6O_3$: C, 47.48; H, 5.07; N, 30.20. Found: C, 47.09; H, 5.33; N, 29.67.

1-(3-Hydroxy-*n*-propyl)-4-(*p*-toluenesulfonamido)methyl-*1H*-1,2,3-triazole (3rd column, 5th line).



Column chromatography with 5% CH_3OH/CH_2Cl_2 gave a 82% of yield as a white solid, and re-crystallized with ethyl acetate/*n*-hexane: m.p. 112.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99-2.05 (m, 3H), 2.39 (s, 3H), 3.51-3.55 (m, 2H), 4.19 (d, *J* = 6.0 Hz, 2H), 4.41 (t, *J* = 6.6 Hz, 2H), 5.97 (t, *J* = 6.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.76, 32.60, 38.80, 47.20, 58.65, 123.25, 127.37, 129.99, 136.77, 143.87, 143.96; MS (ESI) m/z: 333 $[M+Na]^+$, 311 $[M+H]^+$. Anal. Calcd for $C_{13}H_{18}N_4O_3S$: C, 50.31; H, 5.85; N, 18.05; S. 10.33. Found: C, 50.50; H, 5.78; N, 17.93; S. 10.50.

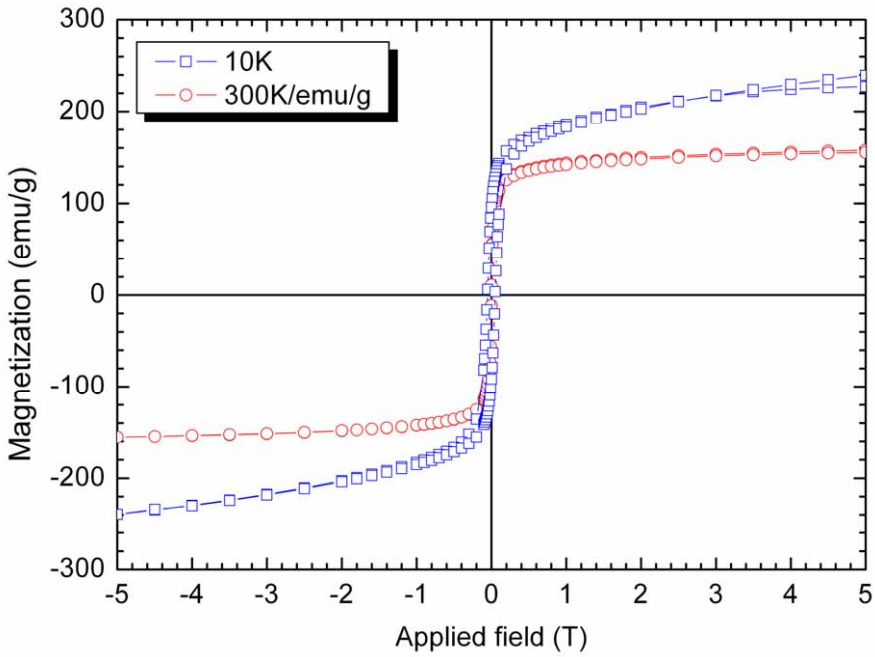


Fig. S1 Field-dependent magnetization curves of the $Cu_3N/Fe_3N@SiO_2$ microspheres. Open square and sphere symbols represent magnetization data collected at 10 and 300 K, respectively.

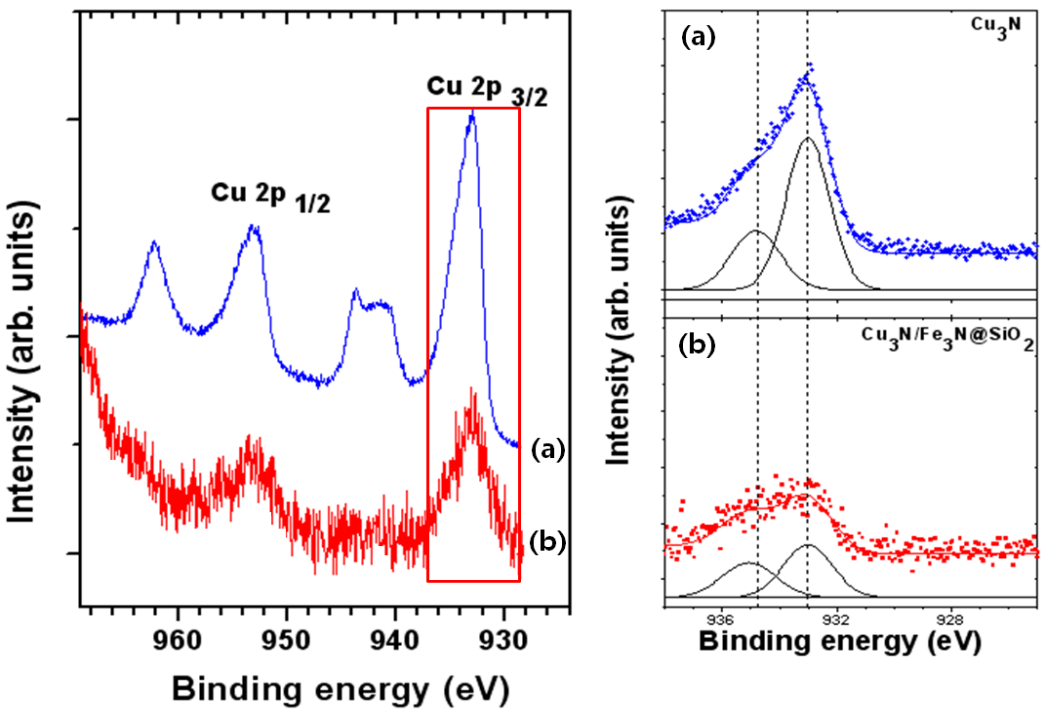


Fig. S2 Cu 2*p* X-ray photoemission spectra of (a) Cu_3N bulk powders and (b) $Cu_3N/Fe_3N@SiO_2$ microspheres. The right panels show the expanded regions, which include the Cu $2p_{3/2}$ core level shifts of corresponding samples. In curve fitting results, points represent real data and continuous lines correspond to their fits composed of two components.