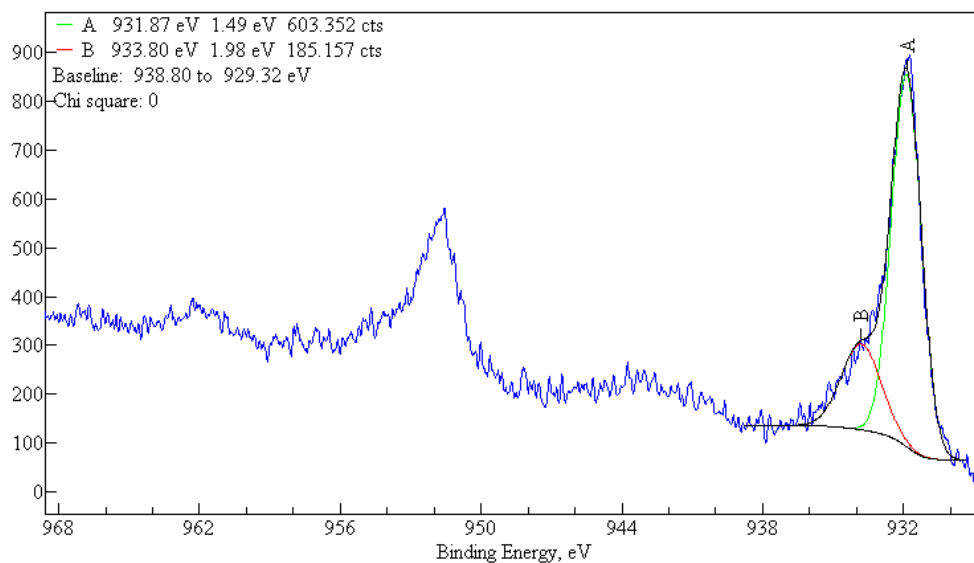


Experimental Section

Nanoparticle synthesis. Copper nanoparticles were synthesized by thermal decomposition of copper(II) acetylacetonate in neat oleylamine. A solution of 0.52 g (2.0 mmol) of copper(II) acetylacetonate in 19.7 ml (60.0 mmol) of oleylamine was slowly heated (2 °C/min) to 230 °C under vigorous stirring in argon atmosphere. After 6 hours at 230 °C, the reaction crude was allowed to cool and hexane (10 ml) was added. After separating the insoluble residue by centrifugation (6000 rpm, 5 min), ethanol (90 ml) was added and the NPs collected by centrifugation. The NPs were re-dispersed in toluene (8 ml). Centrifugation of the toluene dispersion gave a clear, brown-violet dispersion and a minor residue. The above procedure was carried out either by carefully deaerating all solvents and vessels with argon or not.

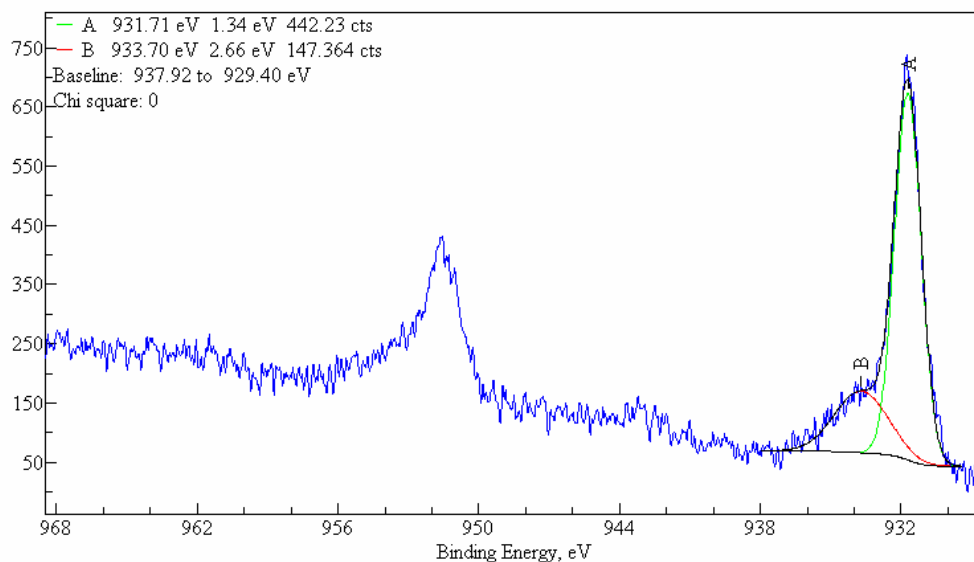
Nanoparticle characterization. For TEM characterization, the NP dispersion was diluted 1:10 v/v with *n*-octane and a drop was placed on a formvar/carbon coated copper grid and dried under argon. The sample was examined by an EFTEM LEO 912AB 120 kV microscope. For XRD measurements, the NP dispersion was deposited on a background-free silica sample holder, dried and sealed by a Mylar film. The spectrum of the air-exposed sample has been collected using a Philips PW 1820, CuK α radiation, graphite monochromator on diffracted beam, scintillation counter. The spectrum of the air-protected sample has been collected on a Bruker D8, MoK α radiation, SOL-X energy discriminating solid state detector. Rietveld analysis has been performed using the TOPAS package. For XPS experiments, freshly precipitated NPs were quickly transferred into the vacuum chamber. XPS spectra were collected in an M-probe apparatus (Surface Science Instruments). The source was monochromatic AlK radiation (1486.6 eV). A spot size of 200 x 750 μ m and a pass energy of 25 eV were used. When required, sample preparation was carried out under argon using deaerated solvents and vessels. The XPS spectra of air-exposed and air-protected NPs can be found below along with the peak assignment. The Cu(II):[Cu(I)+Cu(0)] atomic ratio has been obtained from the area of the corresponding XPS peaks at ~934 and ~932 eV, respectively. The Cu(0):Cu(I) atomic ratio has been obtained from Auger data.

XPS spectrum of air-exposed NPs



Peak	Cu at. %	Assignment
A	77%	Cu(I)
B	23%	Cu(II)

XPS spectrum of air-protected NPs



Peak	Cu at. %	Assignment
A	35%	Cu(0)
A	40%	Cu(I)
B	25%	Cu(II)

Cycloaddition between arylazides 1 and acetylenic dipolarophiles 2: General procedure. A solution of **1** (0.85 mmol), **2** (0.85 mmol), and toluene NP dispersion (1.0 ml) in dry toluene (1.0 ml) was stirred at room temperature for the time indicated in Table 1 of the main text. The mixture was filtered through a celite pad, which retained the NP catalyst. The solvent was evaporated under reduced pressure, and the residue was crystallized from diisopropyl ether giving analytically pure 4-substituted-1,2,3-triazoles **3**.

Compounds **3a**, **3b**, **3c**, **3d**, **3h**, **3j** and **3k** are known in the literature.

3a, **3h**, **3j**: G. Molteni, A. Ponti *Chem. Eur. J.* 2003, 9, 2770-2774. **3b**: O. Tsuge, K. Ueno, A. Inaba *Heterocycles* 1976, 4, 1-7. **3c**: G. Rembarz, B. Kirchoff, G. Dongowski *J. Prakt. Chem.* 1966, 33, 199-205. **3d** and **3k**: G. L'Abbe, M. Bruynseels, P. Delbecke, S. Toppet *J. Heterocycl. Chem.* 1990, 27, 2021-2027.

Compound **3e**: White solid, m.p. 107°C; ¹H NMR (300 MHz, CDCl₃): δ 1.70-2.27 (5H, m), 3.82 3.88 (2H, t, *J* 7.3), 3.69 (2H, t, *J* 7.3), 7.28 (1H, s), 7.4-7.8 (5H, m); IR (Nujol): ν_{\max} 3280 cm⁻¹; MS: *m/z*: 217 [M⁺]; Elemental analysis calcd (%) for C₁₂H₁₅N₃O: C 66.34, H 6.96, N 19.34; found: C 66.38, H 6.99, N 19.40.

Compound **3f**: White solid, m.p. 122°C; ¹H NMR (300 MHz, CDCl₃): δ 3.20 (1H, br s), 6.13 (1H, s), 7.2-7.7 (10H, m), 7.85 (1H, s); IR (Nujol): ν_{\max} 3265 cm⁻¹; MS: *m/z*: 251 [M⁺]; Elemental analysis calcd (%) for C₁₅H₁₃N₃O: C 71.70, H 5.21, N 16.72; found: C 71.74, H 5.18, N 16.79.

Compound **3g**: Pale yellow solid, m.p. 97°C; ¹H NMR (300 MHz, CDCl₃): δ 3.40 (2H, s), 4.70 (2H, br s), 7.4-8.0 (5H, m), 8.05 (1H, s); IR (Nujol): ν_{\max} 3320, 3300, 3275 cm⁻¹; MS: *m/z*: 175 [M⁺]; Elemental analysis calcd (%) for C₉H₁₀N₄: C 62.05, H 5.79, N 32.16; found: C 62.08, H 5.83, N 32.23.)

Compound **3i**: White solid, m.p. 114°C; ¹H NMR (300 MHz, CDCl₃): δ 3.48 (3H, s), 4.36 (2H, s), 7.0-7.4 (4H, m), 7.56 (1H, s); IR (Nujol): ν_{\max} 3270 cm⁻¹; MS: *m/z*: 205

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[M⁺]; Elemental analysis calcd (%) for C₁₀H₁₁N₃O₂: C 58.53, H 5.40, N 20.48; found: C 58.57, H 5.37, N 20.53.