

Supporting Information

Experimental Section

1. Rhizofiltration

E. crassipes was bought in a garden center. The plants were placed in an outdoor pool, with water during 6 months without additional fertilizer.

1.1. Rhizofiltration of effluents for the preparation of EcoCu₁

After 6 months in the pool, *E. crassipes* was exposed to an aqueous HNO₃ solution (2L, pH = 3) containing 40 mg/L of copper. Cu(NO₃)₂·3H₂O was used (1.25 mmol, 302.5 mg). The accumulation occurred outside (the plants suffered necrosis quickly in inside pool), for 6 days.

1.2 Rhizofiltration from aqueous layer for ecological recycling of EcoCu₁ and the preparation of EcoCu₂

After CuAAC reaction performed with EcoCu₁ (371.25 mg of EcoCu₁), the combined aqueous layers (70 mL) were diluted with an aqueous HNO₃ solution (pH = 3) to 2 L. *E. crassipes* was exposed to this solution ([Cu] = 7.4 mg/L). The accumulation occurred outside for 6 days.

2. CuAAC reaction

Reagents and methods

Reagents and solvents were purchased from Sigma-Aldrich, and were used without further purification. Flash column chromatography was performed using Chromagel Carlo Erba Reactifs SDS silica 60 Å CC 35-70 µm. NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature, ¹H frequency is at 300 MHz and ¹³C frequency is at 75.5 MHz. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode. GC-MS analyses were performed on a Shimadzu QP2010SE apparatus, equipped with a 30 m × 0.25 mm × 0.25 µm ZB-5MSi Guardian column (Phenomenex®) with hydrogen as carrier gas. LC-MS analyses were performed on a Waters Alliance 2695 coupled to a Photodiode Array Detector Waters 996 PDA and a Micromass Quattro Micro API. Non commercially available azide derivatives were prepared according to the literature procedures^[28] from halogenated reagents. All known compounds synthesized were fully characterized and found to be in agreement with the literature data: (3b, 3c)^[29], (3a, 3e, 3f, 3g, 3h, 3i)^[28], 3j^[30].

2.1. Preparation of EcoCu₁

EcoCu₁ was prepared from roots of *Eichhornia crassipes*, after six days of rhizofiltration of aqueous media enriched with Cu(II). The roots (5.8 g) were dried at 80 °C for 6 h. The obtained solid (2.6 g) was calcined at 550 °C for 6 h and the resulting ashes (84 mg) were added to 20 mL of concentrated HCl (37%). The yellow solution was stirred for 4 h at 90 °C. The reaction mixture was then filtered on a celite pad. The resulting yellow solution, composed of different metal chlorides, was concentrated under vacuum, yielding the ecocatalyst EcoCu₁ as an ochre powder (104 mg). EcoCu₁ was stored in a desiccator.

2.2. Fourier transform infrared spectroscopy characterization of adsorbed pyridine on catalysts

FTIR measurements were carried out using pyridine as a probe. Excess pyridine was adsorbed, then the samples were degassed for 15 min at 25 °C (4 mbar) and a first spectrum was recorded. The samples were then degassed for 40 min at 150 °C (4 mbar) to eliminate the physisorbed pyridine and a second spectrum was recorded.

2.3. Nitrogen sorption measurements

Nitrogen sorption isotherms were obtained at 77 K using a Micromeritics Tristar 3000 apparatus. Prior to the measurement, the samples were degassed for 18 hours at 100 °C. The surface areas (S_{BET}) were determined from BET treatment at P/P₀ values < 0.3 and assuming a surface coverage of the nitrogen molecule estimated to be 13.5 Å². Pore size distributions were calculated from the adsorption branch of the isotherms using the BJH method. The pore width was estimated at the maximum of the pore size distribution. The pore volume was calculated from the nitrogen uptake at the relative pressure P/P₀ of 0.995.

2.4. CuAAC reaction: general procedure with EcoCu₁

To a solution of EcoCu₁ (265 µmol of Cu) in degassed deionized water (25 mL) were sequentially added azide **1** (5.31 mmol), alkyne **2** (5.31 mmol) and finally sodium ascorbate (105 mg, 531 µmol). The resulting mixture was stirred at room temperature. The mixture was stirred at room temperature for 2 h. The reaction was then checked for completion by GC-MS.

Aqueous 0.1 N HCl (50 mL) and Me-THF (75 mL) were added and the emulsion stirred at RT for 30 min to ensure complete dissolution of all salts. The 2 layers were then separated; the organic layer washed one time by aqueous 0.1 N

HCl (20 mL). The organic phase was analyzed by GC-MS with hexadecane as internal standard and then evaporated to dryness to give the desired triazole as a pale yellow solid.