Cu^{o}-loaded organo-montmorillonite with improved affinity towards hydrogen-an insight in matrice-metal and non-contact hydrogen-metal interactions

Radia Sennour et al, …..Abdelkrim Azzouz*

Supporting Information

1. *NMR details for product identification*

In NMR spectra, proton and carbon chemical shifts (δ) are reported in ppm relative to the chemical shift of residual acetone which was set at 2.05 ppm (^{1}H) and 29.8 ppm (^{13}C); the residual CD_3OD, which was set at 3.30 ppm (^{1}H) and 49.0 ppm (^{13}C); the residual DMSO, which was set at 2.49 ppm (^{1}H) and 39.5 ppm (^{13}C). Coupling constants (*J*) are reported in Hertz (Hz), and the following abbreviations are used for peak multiplicities: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet with equal coupling constants (t_{ap}), triplet (t), multiplet (m).

2. *Detailed synthesis procedures*

2.1. Preparation of N-[4-(Prop-2-ynyloxy) phenyl] acetamide (2)

Propargylation of 4-acetamidophenol 1 (10.00 g, 66.16 mmol, 1.0 equiv.) was done following literature procedure,[31] using potassium carbonate (18.29 g, 132.32 mmol, 2.0 equiv.) and propargyl bromide solution (80% in toluene, 6.93 mL, 1.2 equiv.) in dry acetone (100 mL), which was heated under reflux for 3 h (Scheme 1). The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The organic layer was washed with brine several times. The residue was purified by silica gel chromatography (DCM-MeOH 96:4) which, after solvent evaporation, afforded propargylated compound 2 as a white solid (11.27 g, 59.54 mmol, 90%). $R_f = 0.29$, 96:4 CH_2Cl_2-MeOH; ^{1}H NMR (acetone-d6) δ 9.11 (s, 1H, NH), 7.56 (d, 2H, $J_{H,H} = 9.0$ Hz, H-arom.), 6.92 (d, 2H, $J_{H,H} = 9.0$ Hz, H-arom), 4.72 (d, 2H, $J_{CH2,H} = 2.5$ Hz, OCH_2), 3.04 (t, 1H, $J_{CH2,H} = 2.5$ Hz, C≡CH), 2.05 ppm (s, 3H, CH_3); ^{13}C NMR (acetone-d6) δ 168.6 (CO), 154.5 (C_q-arom.), 134.3 (C_q-arom.), 121.4, 115.7 (CH-arom.), 79.9 (C≡CH), 76.8 (C≡CH), 56.5 (OCH_2), 24.1 ppm (CH_3) (**Fig. S1**).

2.2. Preparation of N-(4-(2,3-bis(2,3-dihydroxypropylthio) propoxy)phenyl)acetamide (3)

Compound **2** (378 mg, 2.0 mmol, 1.0 equiv.), 1-thioglycerol (519 µL, 6.0 mmol, 3.0 equiv.) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 5 mg, 0.02 mmol, 0.01 equiv.) were solubilized in THF/MeOH (2:1, 3 mL) in a photometer cell which was stirred at room temperature with irradiation at 365 nm for 15 min. The mixture was diluted with MeOH and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (DCM-MeOH 9:1) to afford compound **3** (mixture of diastereoisomers) as a pale yellow oil (655 mg, 1.62 mmol, 81%). $R_f = 0.15$, 9:1 CH_2Cl_2-MeOH; ^{1}H NMR (CD_3OD) δ 7.32 (d, 2H, $J_{H,H} = 9.0$ Hz, *H*-arom.), 6.79 (d, 2H, $J_{H,H} = 9.0$ Hz, *H*-arom), 4.13 (dd, 1H, $J_{H,H} = 9.8$ Hz, $J_{H,H} = 5.1$ Hz, *H*-g), 4.04 (dd, 1H, $J_{H,H} = 9.8$ Hz, $J_{H,H} = 5.9$ Hz, *H*-g), 3.76-3.60 (m, 2H, *H*-k and *H*-n), 3.55-3.37 (m, 4H, *H*-l and *H*-o), 3.16 (m, 1H, *H*-h), 2.89 (m, 2H, *H*-i), 2.74, 2.63, 2.52 (3 x m, 4H, *H*-j and *H*-m), 1.99 ppm (s, 3H, CH_3); ^{13}C NMR (CD_3OD) δ 171.3 (*C*O), 156.6 (C_q-arom-d.), 133.0 (C_q-arom-c.), 123.0 (*C*H-arom-b), 115.8 (*C*H-arom-a), 73.1 (*C**-k), 72.8 (*C**-n), 70.9 (*C*-g), 65.8 (*C*-l and *C*-o), 47.1 (*C**-h), 37.2 (*C*-j/m), 36.2 (*C*-i), 35.8 (*C*-j/m) and 23.6 ppm (*C*H_3). ^{13}C NMR (D_2O+acetone): ESI$^+$-HRMS: $[M+Na]^+$ calculated for $C_{17}H_{28}NO_6S_2$, 406.1353; found, 406.1361 (**Fig. S2-S3**).

2.3. Preparation of 4-(Prop-2-ynyloxy)aniline hydrochloride (PBA) (4)[32]

A solution of HCl in MeOH (4M, 10 mL) was added into a solution of propargylated **2** (1.89 g, 10.0 mmol, 1.0 equiv.) in ethanol (15 mL) and the mixture was stirred at 60°C for 3 h. After cooling to room temperature, product **3** was isolated by filtration and washed with ethyl acetate (1.40 g, 7.7 mmol, 77%). ^{1}H NMR (DMSO-*d*6) δ 10.30 (s, 1H, N*H*), 7.33 (d, 2H, $J_{H,H} = 9.0$ Hz, *H*-arom.), 7.07 (d, 2H, $J_{H,H} = 9.0$ Hz, *H*-arom), 4.81 (d, 2H, $J_{CH2,H} = 2.5$ Hz, OCH_2), 3.59 ppm (t, 1H, $J_{CH2,H} = 2.5$ Hz, C≡C*H*); ^{13}C NMR (DMSO-*d*6) δ 156.5 (C_q-arom.), 124.9 (C_q-arom.), 124.4, 115.8 (*C*H-arom.), 78.8 (*C*≡CH), 78.4 (C≡*C*H), 55.7 ppm (O*C*H_2) (**Fig. S4**).

3. NMR patterns of the synthesized organic compounds

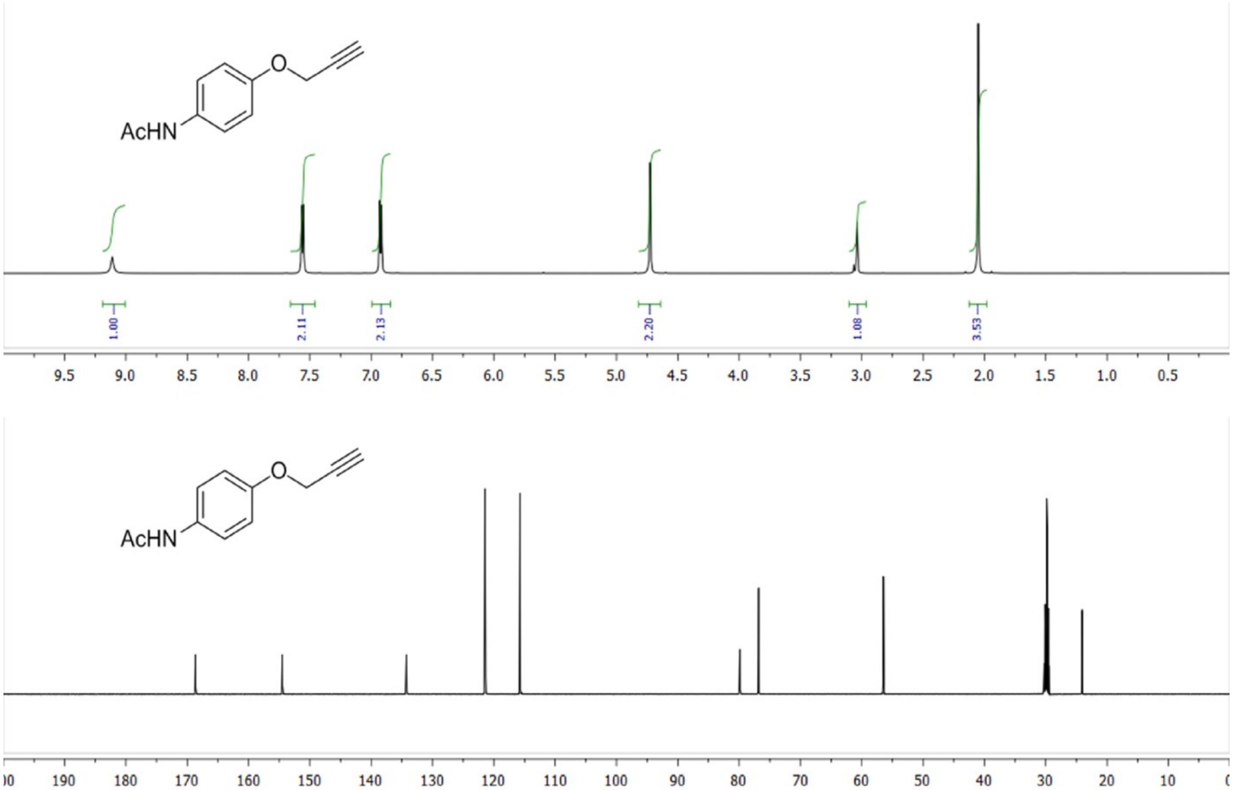


Figure S1. ^{1}H and ^{13}C NMR spectrum (600 and 125 MHz, acetone-*d*6) of compound **2**.

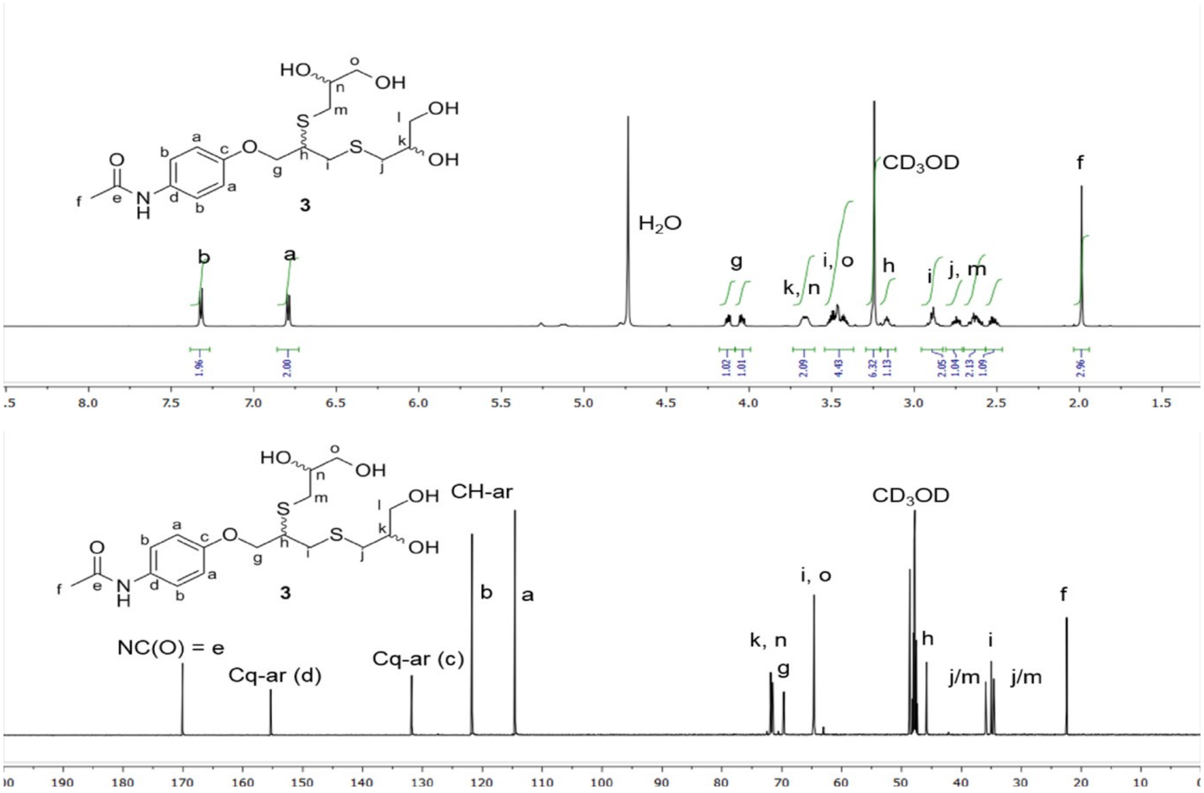


Figure S2. ^{1}H and ^{13}C NMR spectrum (600 and 125 MHz, CD$_3$OD) of compound **3**.

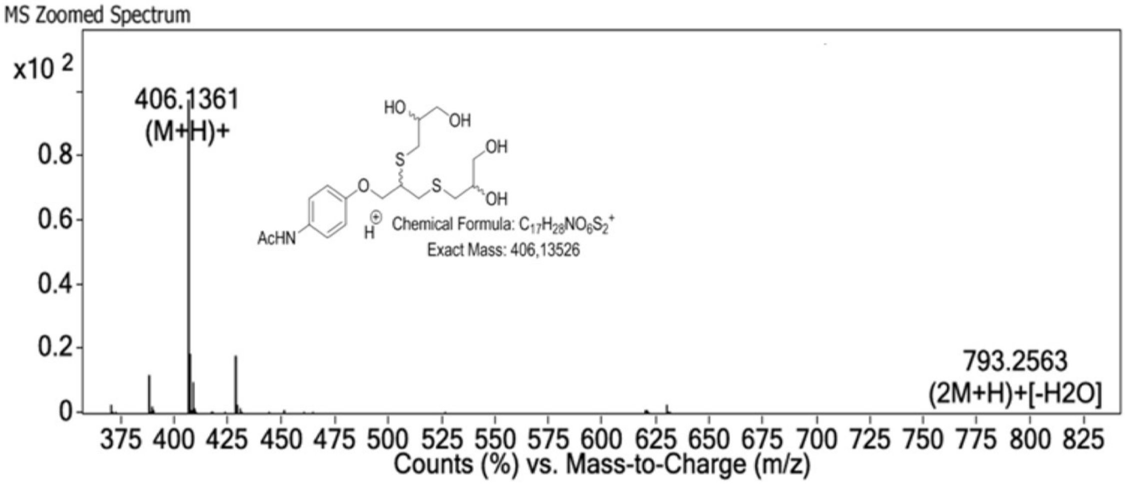


Figure S3. HRMS spectrum of compound **3**.

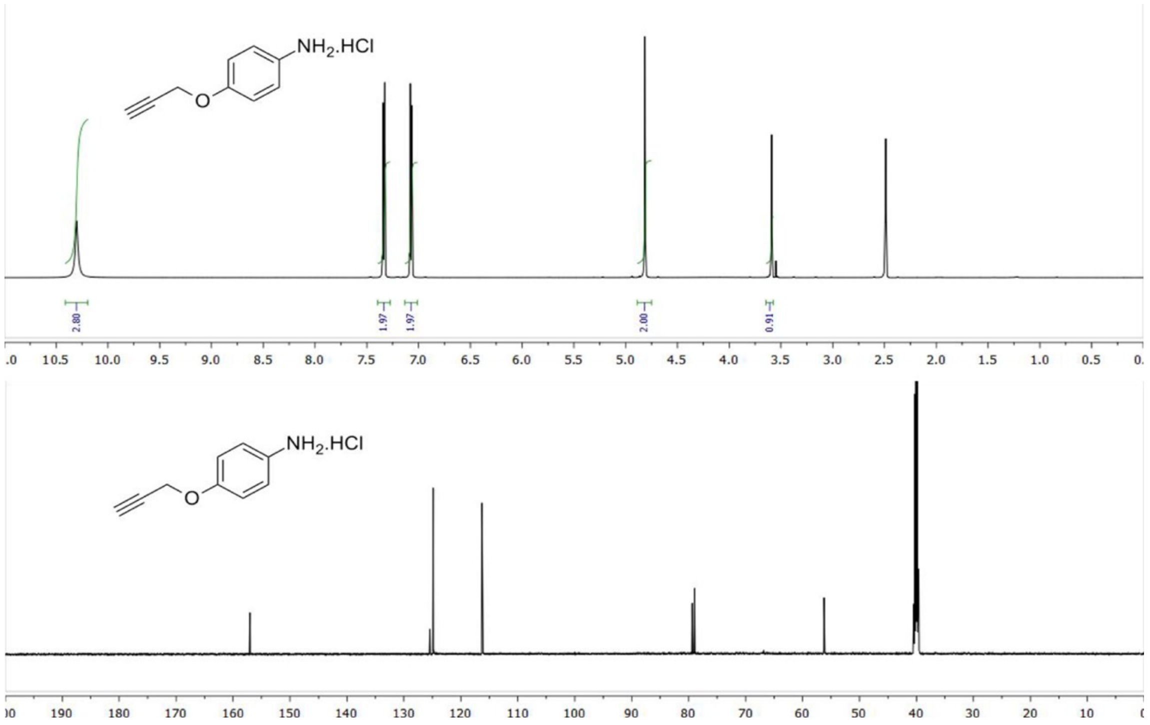


Figure S4. ^{1}H and ^{13}C NMR spectrum (600 and 125 MHz, DMSO-*d*6) of compound **4**.

4. ***BJH assessment of the pore size distribution***

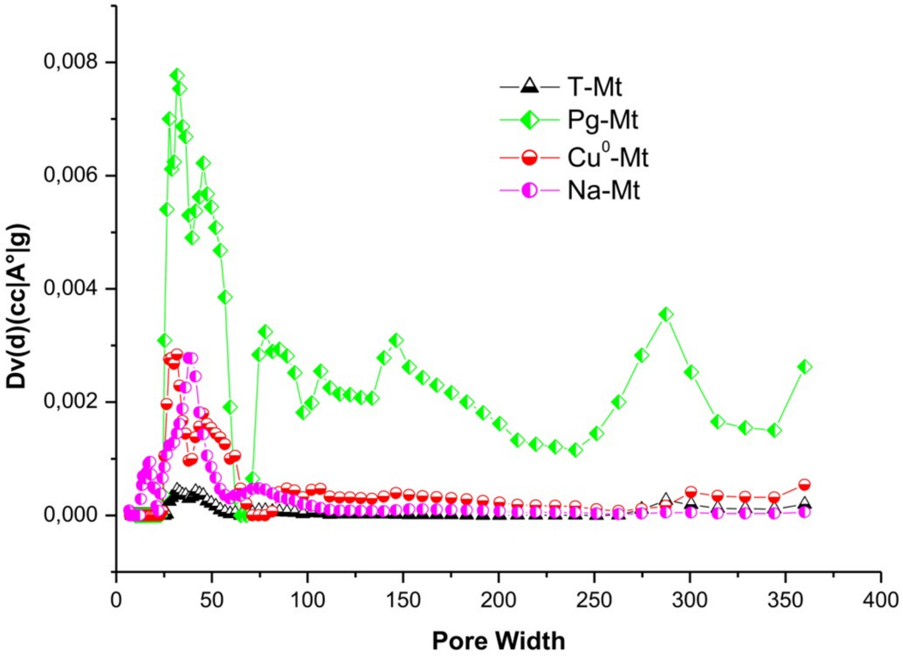


Figure S5. Pore size distribution using adsorption-desorption of nitrogen, after outgassing 4h at 100°C for T-Mt and for Cu/T-Mt, 80°C for Pg-Mt and 120°C for NaMt.

5. *XPS evidence of the role of sulfur and oxygen atom in Cu^oNP stabilization*

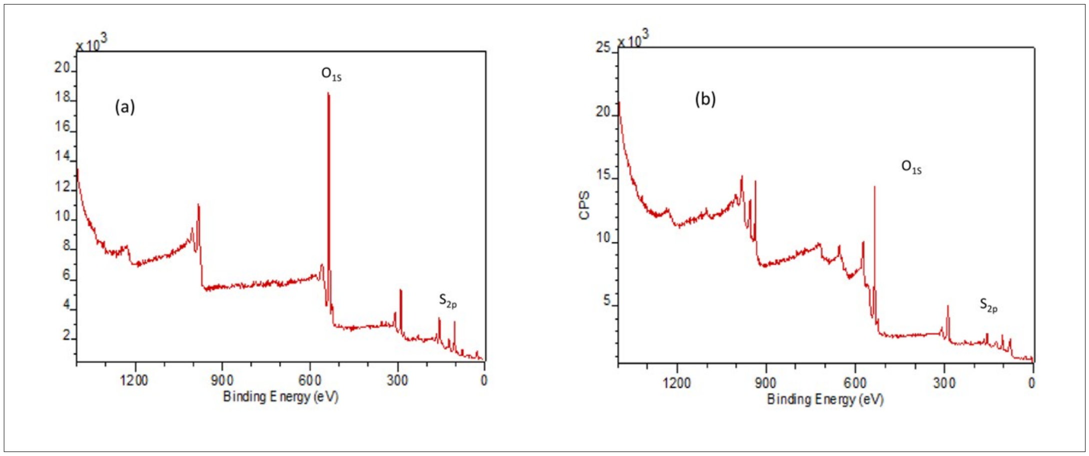


Figure S6. XPS spectra of T-Mt (a) and Cu/T-Mt (b)

Table S1. Electron binding energies in the structure of T-Mt

Electron assignation	Binding energy (eV)	FWHM	Area	At%
O1s	532.22	3.447	51702.89	40.52
C1s	285.00	3.622	12130.71	27.85
S2p	164.19	2.740	1605.87	2.19
Si2p	102.59	3.341	7913.57	22.24
Al2p	75.39	2.976	1683.74	7.20

Table S2. Electron binding energies in the structure of Cu/T-Mt.

Name	Binding energy (eV)	FWHM	Area	At%
O1s	531.42	3.447	40534.33	30.85
C1s	285.00	3.654	10942.12	24.4
S2p	163.39	2.626	869.93	1.15
Si2p	102.59	3.275	4438.42	29.60
Al2p	75.39	2.976	7128.00	12.12
Cu2p	932.24	3.545	21291.58	1.87

6. ***NMR evidence for Cu^o stabilization in the organo-montmorillonite matrice.***

Table S3. Change in the chemical shift in ^{13}C- NMR (in D_2O) of Compound **3** before and after incorporation of Cu^{2+} or Cu^0.

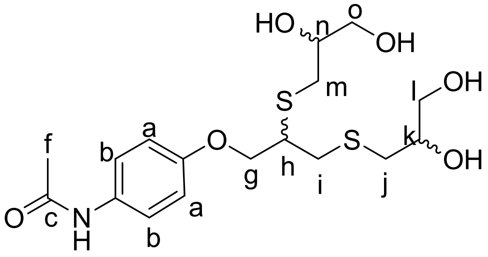
Atom location in the structure of compound 3	^{13}C-NMR assignments	Compound 3	Compound 3 with Cu^{2+}	Compound 3 with Cu^0
	e	172.3	172.3	172.3
	d	155.0	154.9	154.5
	c	130.4	130.1	130.6
	b	123.4	123.4	123.3
	a	115.0	114.9	115.0
	n/k*	70.8	70.7	70.5
	n/k*	70.7	70.4	70.3
	n/k*	70.5	69.4	70.0
	n/k*	70.4	69.4	70.0
	g*	69.2	69.2	69.8/69.7
	l and o	63.9	63.8	64.0/63.9/63.8
	h*	44.8	44.7	48.9
	h*	44.8	44.7	48.9
	h*	44.7	44.5	48.6/48.5
	j/m*	35.0	34.8	36.2/36.1/35.9/35.7
	i*	34.0	33.8	38.1/38.0
	j/m*	33.5	33.3	36.2/36.1/35.9/35.7
	f	22.3	22.1	22.3

Table S4. Chemical shift in ^{1}H-NMR (in D_2O) of compound **3** before and after incorporation of Cu^{2+}.

Assigned carbon atom	^{1}H-NMR chemical shifts (ppm) for compound 3	
	Before	After Cu^{2+} incorporation
b	7.21	7.21
a	6.81	6.89
g	4.03	4.15

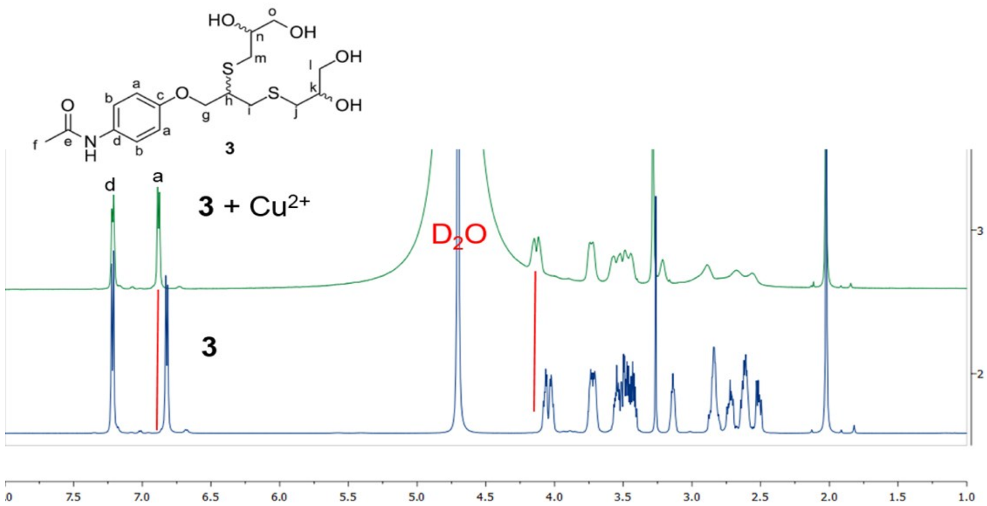


Figure S7. ^{1}H NMR spectra of N-(4-(2,3 bis((dihydroxypropyl)thio)propoxy)phenyl)acetamide before (A) and after incorporation of Cu^{2+} cations (B) in D_2O (20 mg of BPA in 0,4 mL solvent).

7. *Cu^{o}NP dispersion and particle size assessment*

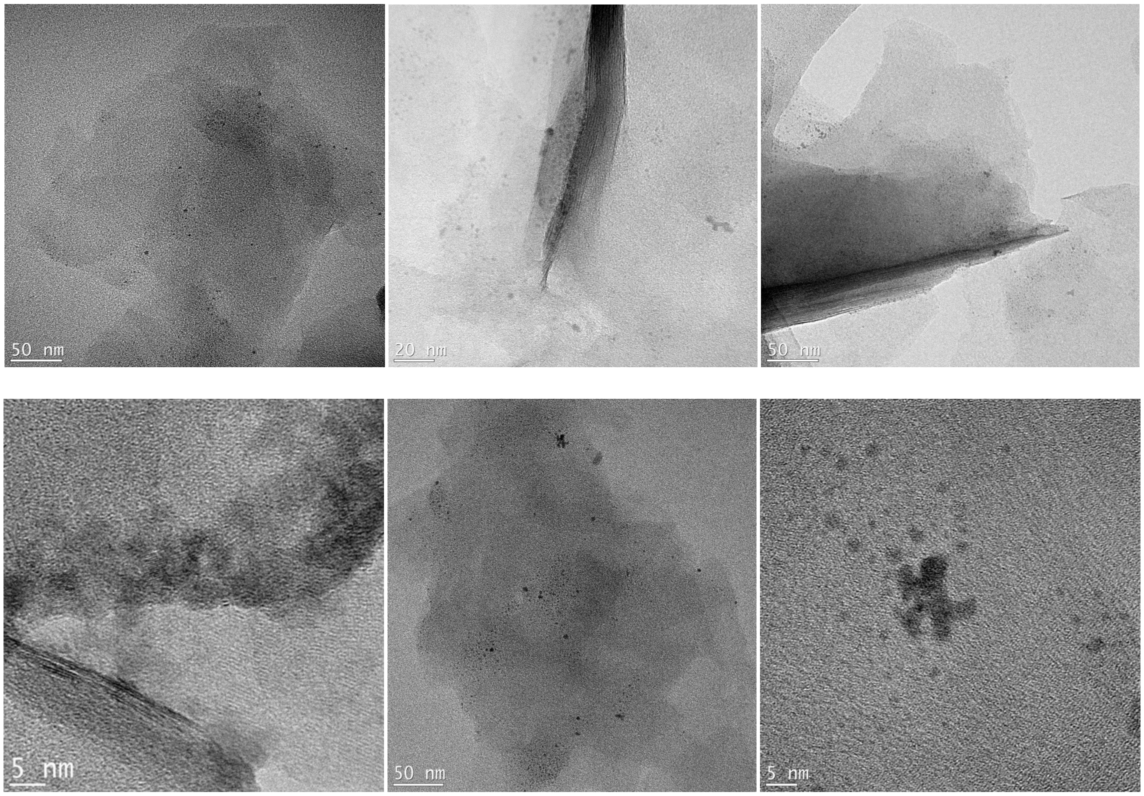


Figure S8. TEM images of of Cu/T-Mt materials. Here, Cu/T-Mt material was obtained by Cu^{0} insertion and stabilization in the T-Mt sample (see Table S1). The Si, Al, O, C, S, Mg and Fe rays are due to the clay mineral and organic moiety grafted. The Ni X-rays are due to the sample support of the MET instrument.

8. *Determination of Cu lattice characteristics*

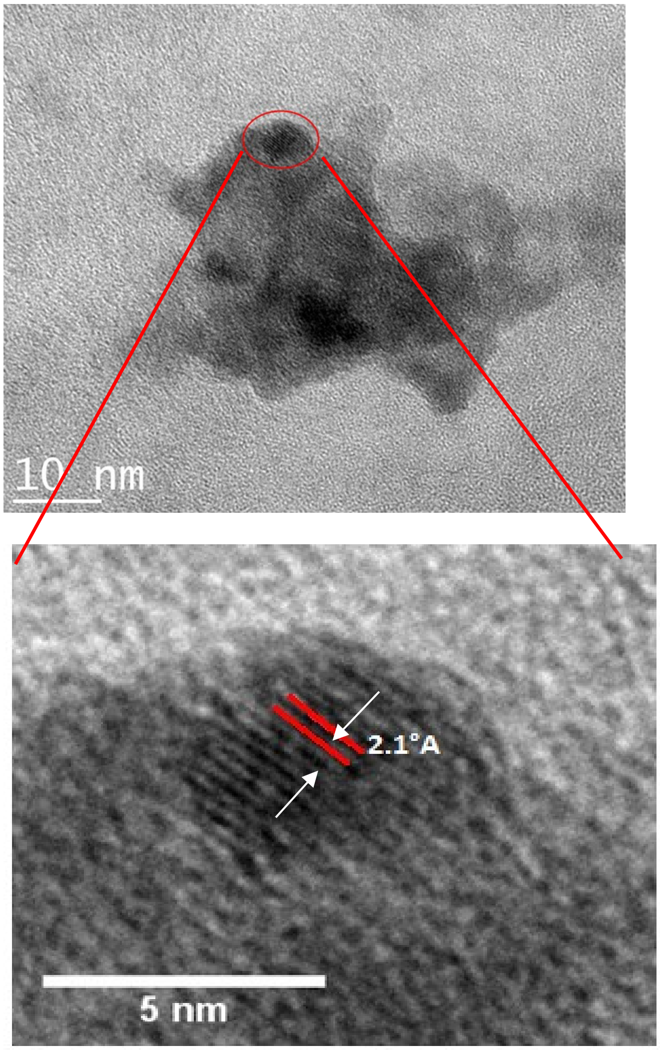


Figure S9. TEM image of Cu/T-Mt with a close-up on a CuNP.

The measured value of d= 0.21 nm = 2.1 °A (Calculated from the image using the Imagej soft) gave a cell unit size of 3.62 °A. The latter agrees with an atomic radius= 1.28nm, close to that of copper atom, as calculated using the model for face-centered cubic symmetry of copper (fcc) ($a = \frac{4\,R}{\sqrt{2}}$). The measured distance accounts for the interreticular distance between two of the 111 plane family.

9. ***Energy dispersion X-ray fluorescence measurements of the chemical composition***

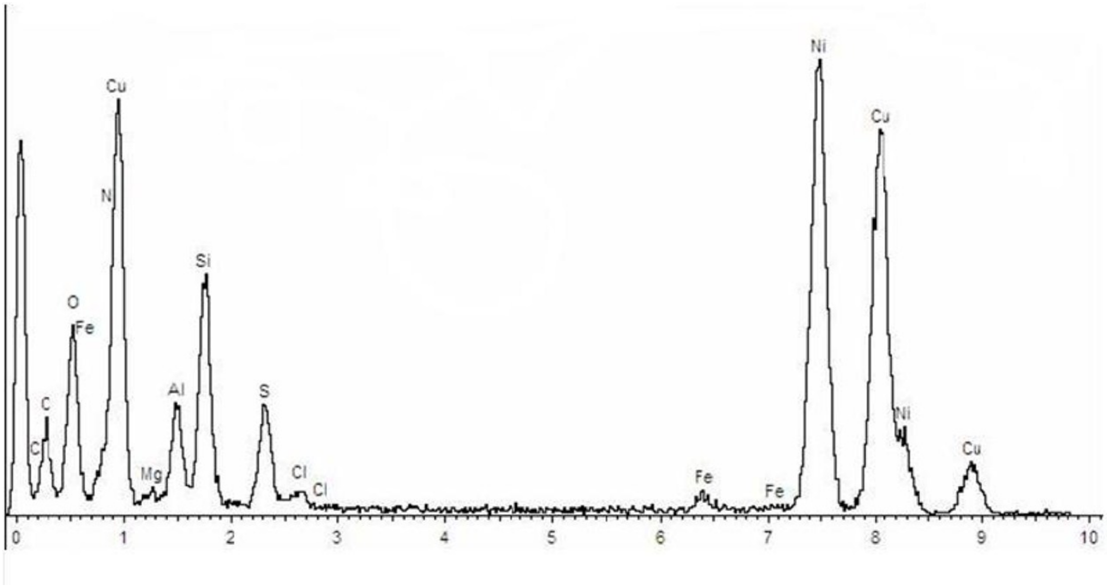


Figure S10. Chemical composition through XRF-EDS analysis of Cu/T-Mt.

10. DSC measurements of the desorption heat for hydrogen-saturated samples.

Table S5. Retention capacity and desorption heat for H_2-saturated organo-montmorillonites

Samples[1]	$T_{\text{Desorption peak}}$[2]	Desorption heat[3]		Mass loss[4]	Differential mass loss[5]	ΔH[6]
	(°C)	(cal.g^{-1})	(cal.g^{-1})	wt.%	(mmol.g^{-1})	(kcal,mol^{-1})
NaMt	95	0.0023	28.308	1.875	0.00	-
NaMt-H_2	102	28.31		2.217		
T-Mt	-	0.308	95.382	2.645	3.53	72.5
T-Mt-H_2	65-70 (flat)	95.69		3.692		
Cu/T-Mt	-	0.006	903.99	1.997	13.10	44.0
Cu/T-Mt-H_2	90	904		5.317		

[1] For DSC measurements. the different adsorbents were previously saturated by dry pure H_2 overnight in static mod. without carrier gas at ambient temperature and pressure.

[2] Temperature of the desorption peak;

[3] Heat amount during the gas desorption as assessed by DSC in the temperature range 20-100^{o}C. This temperature range was imposed by the thermal stability threshold as determined by thermal gravimetry

[4] Mass loss corresponding to the amount of thermally desorbed gas;

[5] The differential mass loss allows calculating the absolute hydrogen retention capacity (HRC), expressed in terms of mmol H_2 desorbed per 1 gram of adsorbent, between 20 and 100^{o}C, assuming that T-Mt does not display affinity towards hydrogen.

[6] ΔH is the enthalpy of the gas desorption in the same temperature range.

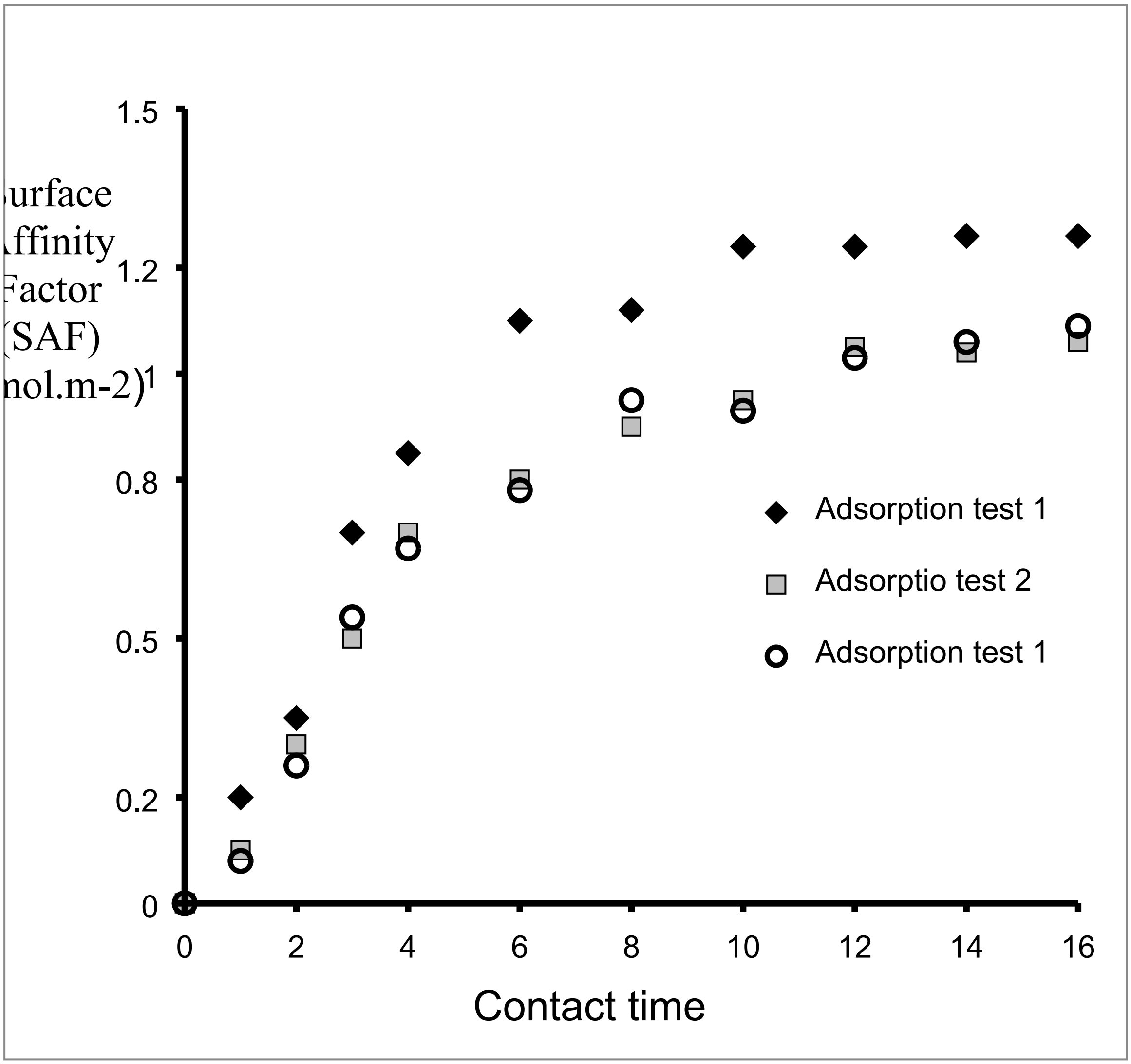


Fig. S11. Triplicate adsorption test of hydrogen on Cu/T-Mt at ambient temperature and pressure. Test 1 was achieved with the as-synthesized Cu/T-Mt after air drying at 30°C in sealed enclosure containing dry nitrogen and NaOH pills. Tests 2 and 3 were carried out after thermal regeneration up to 80°C without rehydration and re-saturation with dry hydrogen in sealed enclosure.