

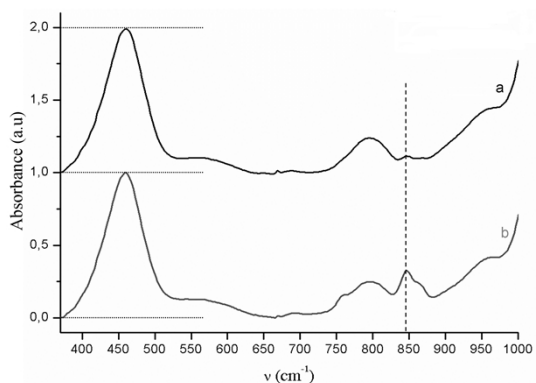
## Electronic Supporting Information

### Site isolation and coordination control of a transition metal ion by molecular surface engineering in mesoporous silica: case of a bio-inspired copper-polyamine grafted complex

5 Sébastien Abry, Ping Zhang,<sup>‡</sup> Belén Albela\* and Laurent Bonneviot\*

10

#### 1. Figures

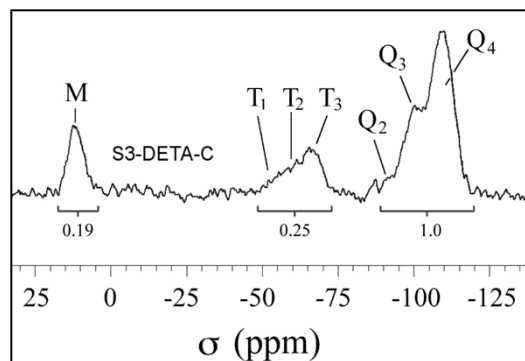


15 **Fig. S1** Typical IR spectra used for quantification of the trimethylsilyl functions (TMS) present in the mesoporous silica: **(a)** S2-L, **(b)** S2-L-C. Each spectrum was previously normalized using the peak at 459 cm<sup>-1</sup> on the left hand side of the figure (SiO<sub>2</sub> bending of the silicon framework), and baseline was corrected using a straight line drawn using two points at 670 and 1500 cm<sup>-1</sup> on all the spectra. Then TMS was quantified by measuring the height of the peak at 846 cm<sup>-1</sup> which corresponds to the Si-C stretching band of O-Si-(CH<sub>3</sub>)<sub>3</sub> entities. The calculation of the TMS loading was obtained using as reference the non silylated LUS and the fully silylated LUS for 0 and 100 % surface coverage, respectively.

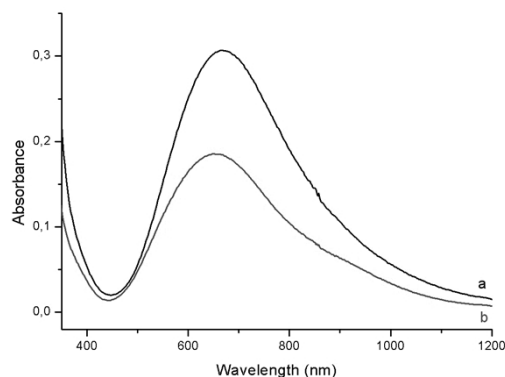
20

25

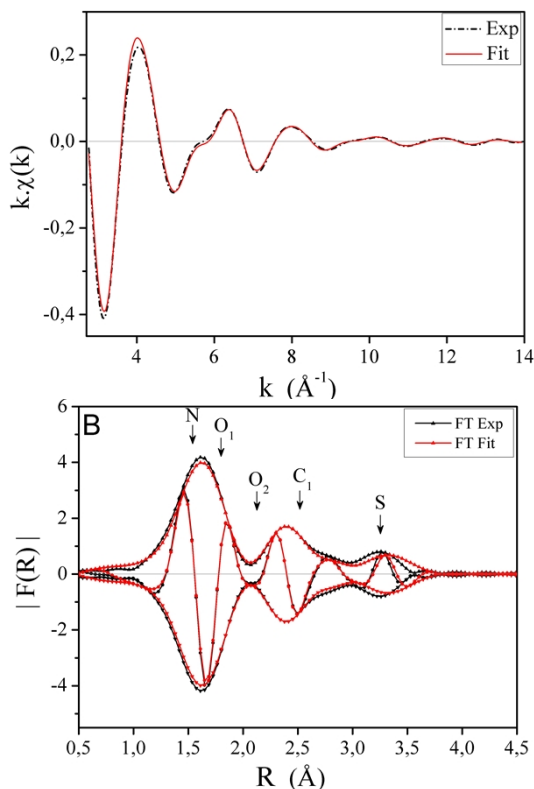
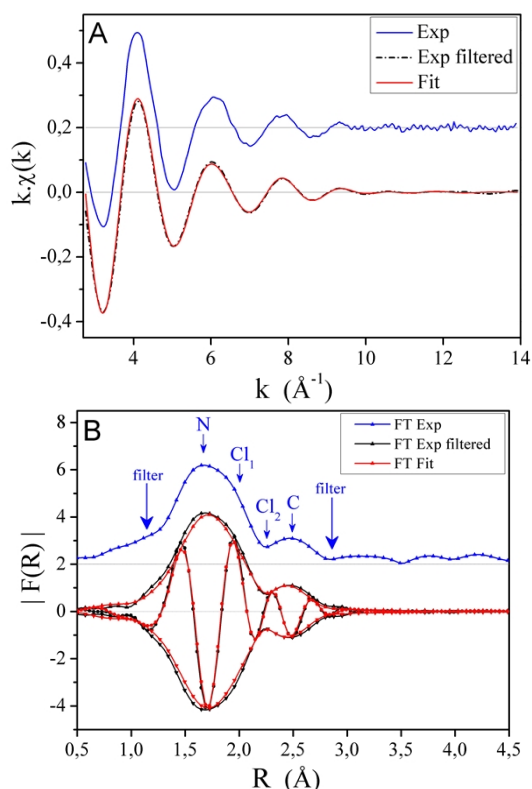
30



35 **Fig. S2** Typical solid state MAS <sup>29</sup>Si-NMR at 298 K of a material after the grafting of the ligand L measured here for S3-L-C. M is reminiscent of the silicon atom of a monografted trimethylsilyl moieties while T<sub>1</sub> (weak shoulder), T<sub>2</sub> (strong shoulder) and T<sub>3</sub> (dominant signal of this massif around -60 ppm) are the fingerprint of the mono- (< 10%), di- (ca. 30%) and tri-grafted (ca. 60 %) DETA-propylsilyl moieties.

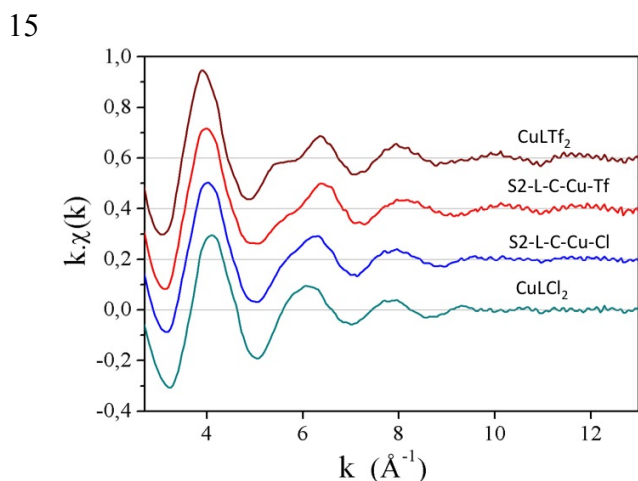


40 **Fig. S3.** Solid DR UV-visible spectra (Kubelka-Munk) of copper grafted complexes on LUS: **(a)** S3-L-C-Cu-Cl, **(b)** S3-L-C-Cu-Tf.

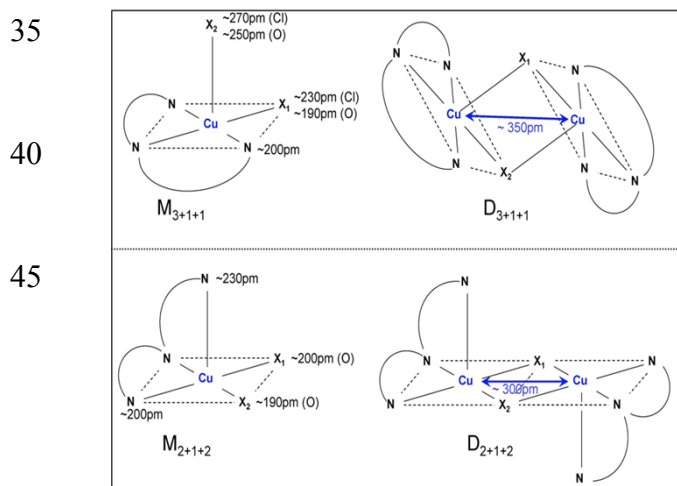


**Fig. S4** EXAFS of  $\text{CuLCl}_2$ : (A) EXAFS oscillations between 0.28 and 1.4  $\text{nm}^{-1}$  (top, noise = 0.01) and superposition of filtered signal between 107 and 286 pm (bottom, dotted line) and the simulation (plain line). (B) Fourier transforms ( $k \cdot \chi(k)$ ): experimental values after Kaiser windowing ( $\tau = 3.0$ , top) and superposition of FT filtered EXAFS signal provided in (A) and the simulated FT using Roundmidnight<sup>1</sup> software with  $d_{\text{Cu-N}}$ ,  $d_{\text{Cu-Cl1}}$ ,  $d_{\text{Cu-Cl2}}$  and  $d_{\text{Cu-C}}$  equal to 204, 228, 264 et 297 pm, respectively (bottom).

**Fig. S5** EXAFS of  $\text{CuLTf}_2$ : (A) EXAFS oscillations between 0.28 and 1.4  $\text{nm}^{-1}$  with a filter between 107 and 361 pm (dotted line) and the corresponding simulation (plain line). (B) Fourier transforms  $k \cdot \chi(k)$  after Kaiser windowing ( $\tau = 3.0$ ) of the filtered EXAFS signal provided in (A) and the simulated FT with  $d_{\text{Cu-N}}$ ,  $d_{\text{Cu-O1}}$ ,  $d_{\text{Cu-O2}}$ ,  $d_{\text{Cu-Cl1}}$ ,  $d_{\text{Cu-C2}}$  et  $d_{\text{Cu-S}}$  equal to 204.2, 222, 244 et 291, 306 et 370 pm, respectively.



**Fig. S6.** EXAFS spectrum of materials S2-L-C-Cu-Cl and S2-L-C-Cu-Tf and the molecular analogues  $\text{CuLCl}_2$  and  $\text{CuLTf}_2$ .



**Fig. S7** Possible geometries for  $\text{Cu-L-X}_1\text{X}_2$  complexes grafted in the silica ( $\text{X}_1, \text{X}_2 = \text{O}, \text{Cl}$ ).

## 2. Tables

**Table S1.** Textural analysis: BET specific surface area, total pore volume and pore diameter using the Broekhoff and de Boer (BdB) method.

5

Samples	$A_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	$\phi_{\text{BdB}}$ (nm)	C value
LUS	$970 \pm 50$	$0.86 \pm 0.02$	$3.7 \pm 0.1$	105
S3	$930 \pm 50$	$0.78 \pm 0.02$	$3.4 \pm 0.1$	43
S3-L-C	$600 \pm 30$	$0.49 \pm 0.02$	$2.9 \pm 0.1$	10
S3-L-C-Cu-Cl	$540 \pm 30$	$0.38 \pm 0.02$	$3.0 \pm 0.1$	31

Note that the Broekhoff and de Boer method (BdB) leads to pore size values close within 0.1 nm to those obtained from DFT and both techniques are more reliable methods than commonly used Barrett, Joyner, and Halenda (BJH), which provides values about 0.7 nm smaller, *i. e.*, between 3.0 and 3.2 nm often reported for MCM-41 templated by cetyltrimethylbromide, CTAB. For smaller values the difference increases, for instance 2.2 nm (BJH) for 3.0 nm (BdB).

10

**Table S2.** Quantification of grafted species from elemental analysis, weight loss from TGA experiments and quantitative IR spectroscopy.

Sample	$L^a$ ( $\text{mmol}\cdot\text{g}^{-1}$ )	$L/\text{Si}_{\text{inorg}}^{a,b}$	L coverage <sup>c</sup> (%)	$\text{TMS}/\text{Si}_{\text{inorg}}^{a,b}$	TMS coverage <sup>c</sup> (%)	total cov <sup>c</sup> (%)
S1				0.04	15	15
S2				0.08	34	34
S3				0.12	52	52
S1-L	1.45	0.12	50	0.01	5	55
S2-L	1.40	0.12	49	0.04	16	65
S3-L	1.12	0.09	37	0.07	32	69
S1-L-C	1.33	0.14	58	0.09	40	98
S2-L-C	1.26	0.13	54	0.10	42	96
S3-L-C	1.10	0.11	45	0.12	52	97
S1-L-C-Cu-Cl	1.02	0.14	59	0.05	20	79
S2-L-C-Cu-Cl	0.98	0.15	62	0.06	24	86
S3-L-C-Cu-Cl	0.95	0.12	50	0.09	39	89
S1-L-C-Cu-Tf	0.79	0.12	50	0.07	29	79
S2-L-C-Cu-Tf	0.95	0.15	61	0.07	32	93
S3-L-C-Cu-Tf	0.86	0.12	48	0.10	42	90

S1, S2, S3 stand for increasing silylation level coverage, respectively, L = DETA for diethylenetriamine, C for capped with TMS groups, Cl for chloride and Tf for trifluoromethanesulfonate counterion. **a)** L (= EDTA) quantification from N elemental analyses (10% error) and TMS quantification from IR spectroscopy (5% error, see S1 Fig. 1); **b)** all the amounts are given in molecular ratio related to silicon of the silica framework, which is called inorganic silicon ( $\text{Si}_{\text{inorg}}$ ),  $\text{Si}_{\text{inorg}} = \text{Si}_{\text{total}} - \text{Si}_{\text{org}}$ ,  $\text{TMS} = \text{Si}_{\text{org}} \text{C}_3$  and  $\text{DETA} = \text{Si}_{\text{org}} \text{C}_7\text{N}_3$ ; **c)** a total coverage corresponding to  $\text{TMS}/\text{Si}_{\text{inorg}} = 0.23$  was considered.<sup>2</sup>

15

5 **Table S3.** Quantification of Cu and counterions (Cl<sup>-</sup> and Tf<sup>-</sup>) from chemical analyses.

Sample	Molar ratio <sup>a</sup>		
	L/Cu	Cl/Cu	Tf/Cu
S1-L-C-Cu-Cl	1.0 ± 0.1	1.9 ± 0.2	
S1-L-C-Cu-Tf	1.4 ± 0.1		1.4 ± 0.1
S2-L-C-Cu-Cl	1.1 ± 0.1	1.8 ± 0.2	
S2-L-C-Cu-Tf	1.6 ± 0.2		1.4 ± 0.1
S3-L-C-Cu-Cl	1.7 ± 0.2	2.1 ± 0.2	
S3-L-C-Cu-Tf	1.9 ± 0.2		1.4 ± 0.1

S1, S2, S3 stand for increasing silylation level coverage, respectively, L = DETA for diethylenetriamine, C for capped with TMS groups, Cl for chloride and Tf for trifluoromethanesulfonate counterion; <sup>a</sup>) calculated on nitrogen, copper and sulfur elemental analysis for each specific case.

10

**Table S4.** Data from DR UV-visible and EPR spectroscopies.

Sample	$\lambda$ (nm)	$g_1$	$g_2$	$g_3$	$g_{iso}$	$A_1$ (G)	Orthorhombicity factor $\delta$
S1-L-C-Cu	680				2.104		
S1-L-C-Cu-Tf	633	2.235	2.066	2.001	2.101*	175	0.72
S2-L-C-Cu	677				2.101		
S2-L-C-Cu-Tf	638	2.232	2.066	2.001	2.100*	176	0.72
S3-L-Cu	668	2.244	2.081	2.015	2.113*	165	0.71
S3-L-C-Cu	669	2.249	2.083	2.022	2.118*	159	0.73
S3-L-C-Cu-Tf	655	2.233	2.062	2.000	2.098*	182	0.73

$\lambda$  corresponds to the maximum of the absorption peak measured on the DR UV-visible spectrum, ( $\pm 1$  nm). ( $g_1$ ,  $g_2$ ,  $g_3$ ) parameters and the hyperfine coupling constant  $A_1$  values were deduced from the EPR spectra recorded at room temperature at 9.4 GHz as shown in Fig. 3. Accuracy for  $g_i$  is  $\pm 0.002$  and for  $A_1$   $\pm 2$  G. \*:  $g_{iso}$  is calculated from  $g_{iso} = 1/3 * (g_1 + g_2 + g_3)$ . Orthorhombicity factor  $\delta$  is defined as  $\delta = (g_1 - g_2) / (g_1 - g_3)$ .

15

**Table S5.** Simulation parameters of the Cu K-edge EXAFS for copper model complexes with DETA ligand (L).

Samples	Structural Parameters				Simulation characteristics
	X <sup>a</sup>	N <sub>x</sub>	d <sub>x</sub> (pm)	σ <sub>x</sub> (pm <sup>2</sup> )	
CuLCl <sub>2</sub>	N	3	204 ± 1	87 ± 15	QF = 0.80 ν = 6 ΔE <sub>0</sub> = 2.2 ± 0.7
	Cl <sup>1</sup>	1	228 ± 3		
	Cl <sup>2</sup>	1	264 ± 3		
	C	6	297 ± 3	196 ± 45	
	Cl <sup>1</sup>	1	225 ± 3	255 ± 61	
	Cl <sup>2</sup>	1	262 ± 3		
CuLTf <sub>2</sub>	N	3	204.2 ± 0.6	29 ± 6	QF = 0.66 ν = 7 ΔE <sub>0</sub> = 3.3 ± 0.5
	O <sup>1</sup>	1	222 ± 2	60 ± 21	
	O <sup>2</sup>	1	244 ± 3		
	C <sup>1</sup>	4	291 ± 1		
	C <sup>2</sup>	2	306 ± 4		
S	2	370 ± 57	267 ± 100		
CuL <sub>2</sub> Cl <sub>2</sub> .nH <sub>2</sub> O	N <sup>1</sup>	3	203.6 ± 0.6	47 ± 7	QF = 0.72 ν = 7 ΔE <sub>0</sub> = 2.4 ± 0.7
	N <sup>2</sup>	1	230 ± 3	86 ± 73	
	N <sup>3</sup>	1	245 ± 4		
	N <sup>4</sup>	1	260 ± 6		
	C <sup>1</sup>	5	288 ± 1	65 ± 29	
	C <sup>2</sup>	3	302 ± 3		
Cu	1	347 ± 5	182 ± 79		

(a) X = scattering atom, N for nitrogen, Cl<sup>n</sup> for chlorine with n = 1 for pseudo-equatorial position in pseudo square pyramidal symmetry, and n = 2 for apical position, O<sup>n</sup> for oxygen (same meaning for n).

**Table S6.** Simulation parameters of the Cu K-edge EXAFS for materials containing the DETA ligand (L).

Sample	Structural Parameters				Simulation Characteristics
	X	N <sub>x</sub>	d <sub>x</sub> (pm)	σ <sub>x</sub> (pm <sup>2</sup> )	
S1-L-C-Cu-Tf	N	3	201 ± 1	47 ± 14	QF = 0.83 ν = 5 ΔE <sub>0</sub> = 3.0 ± 1.1
	O <sup>1</sup>	1	211 ± 5	136 ± 200	
	O <sup>2</sup>	1	237 ± 6		
	C	4	292 ± 3		
S2-L-C-Cu-Tf	N	3	200 ± 1	42 ± 13	QF = 0.46 ν = 5 ΔE <sub>0</sub> = 2.3 ± 1.3
	O <sup>1</sup>	1	215 ± 6	172 ± 420	
	O <sup>2</sup>	1	240 ± 10		
	C	4	292 ± 3		
S3-L-C-Cu-Tf	N	3	202 ± 1	41 ± 12	QF = 0.32 ν = 5 ΔE <sub>0</sub> = 3.9 ± 0.6
	O <sup>1</sup>	1	217 ± 15	69 ± 65	
	O <sup>2</sup>	1	238 ± 3		
	C	4	294 ± 2		
S1-L-Cu-Cl	N	3	202 ± 1	57 ± 10	QF = 0.59 ν = 5 ΔE <sub>0</sub> = 3.6 ± 0.7
	O <sup>1</sup>	1	212 ± 25		
	O <sup>2</sup>	1	250 ± 3	85 ± 32	
	C	4	291 ± 2		
	Cu	0.46	307 ± 5		
S1-L-C-Cu-Cl	N	3	203 ± 1	57 ± 10	QF = 0.82 ν = 5 ΔE <sub>0</sub> = 4.2 ± 0.7
	O <sup>1</sup>	1	212 ± 18		
	O <sup>2</sup>	1	250 ± 4	120 ± 50	
	C	4	293 ± 3		
	Cu	0.35	310 ± 8		
S2-L-Cu-Cl	N	3	203 ± 1	44 ± 15	QF = 0.45 ν = 5 ΔE <sub>0</sub> = 3.2 ± 0.8
	O <sup>1</sup>	1	215 ± 3		
	O <sup>2</sup>	1	248 ± 4	80 ± 29	
	C	4	291 ± 2		
	Cu	0.38	307 ± 6		
S2-L-C-Cu-Cl	N	3	203 ± 1	47 ± 17	QF = 0.70 ν = 5 ΔE <sub>0</sub> = 3.9 ± 0.8
	O <sup>1</sup>	1	215 ± 3		
	O <sup>2</sup>	1	249 ± 4	103 ± 41	
	C	4	292 ± 3		
	Cu	0.32	310 ± 7		
S3-L-Cu-Cl	N	3	202.8 ± 0.8	40 ± 14	QF = 0.67 ν = 6 ΔE <sub>0</sub> = 5.6 ± 0.9
	O <sup>1</sup>	1	214 ± 2		
	O <sup>2</sup>	1	238 ± 5	95 ± 26	
	C	4	295 ± 2		
S3-L-C-Cu-Cl	N	3	202 ± 1	47 ± 19	QF = 0.71 ν = 5 ΔE <sub>0</sub> = 4.1 ± 1.1
	O <sup>1</sup>	1	213 ± 3		
	O <sup>2</sup>	1	241 ± 4	95 ± 27	
	C	4	293 ± 2		

---

## Notes and references

‡Present address of P. Zhang: Key Laboratory of Inorganic Synthesis Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, China.

5

1. A. Michalowicz, ed. *L. p. I. chimie*, Société Française de Chimie, Paris, 1991.
2. S. Abry, B. Albel and L. Bonneviot, *C. R. Chim.*, 2005, **8**, 741-752.

10