

Supporting Information for

Confinement of a bioinspired nonheme Fe(II) complex in 2D hexagonal mesoporous silica with metal site isolation.

Véronique Jollet,^a Belén Albela,^b Katell Sénéchal-David,^a Pascale Jégou,^c Emilie Kolodziej,^a
5 Joëlle Sainton,^a Laurent Bonneviot,^{b,*} and Frédéric Banse.^{a,*}

^a *Institut de Chimie Moléculaire et des Matériaux d'Orsay, Laboratoire de Chimie Inorganique, Université Paris Sud, F-91405 Orsay Cedex*

^b *Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, Institut de Chimie de Lyon, Université de
10 Lyon, 46 allée d'Italie, F-69364 Lyon cedex 07.*

^c *CEA Saclay, CEA DRECAM, F-91191 Gif Sur Yvette.*

Detailed experimental procedures.

15 Formulae for the calculation of the molar fractions of grafted functions.

Table S1. XPS data for the supported complexes.

Figure S1. Experimental and theoretical ESI-MS feature of $[(L_5^2USi)Fe^{II}Cl]^+$.

Figure S2. N₂ adsorption-desorption isotherms of 1a and 2a at different steps of their elaboration.

Figure S3. Solid state UV-visible spectra of SiO₂-L-PS-Fe (2b) and SiO₂-LFe-PS (**1b**).

20 **Figure S4.** N 1s and Fe 2p_{3/2} XPS spectra and deconvolution of the complex $[(L_5^2USi)FeCl]Cl$.

Physical Measurements.

¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer (at 300.13 MHz for ¹H and 75.47 MHz for ¹³C).

Elemental analyses were carried out by the “Service Central d’Analyse du CNRS de Solaize”.

Solution UV-visible spectra were recorded on a Varian CARY 50 in 1 cm pathlength quartz cuvettes.

Solid state UV-visible spectra were recorded on a Varian CARY 5000 from aluminium cells with quartz windows.

Low-angle X-ray powder diffraction experiments have been carried out with a Bruker (Siemens) D5005 diffractometer using Cu K_α monochromatic radiation.

Infrared spectra were recorded from KBr pellets using a Perkin Elmer Spectrum 1000 FTIR spectrometer. For the sake of quantitative monitoring of the IR spectra, peak intensities were normalized with respect to the band at 460 cm⁻¹ as an internal reference (bending mode of the SiO₄ tetrahedral units).

Nitrogen adsorption-desorption isotherms at 77 K were determined with a volume device Micromeritics ASAP 2010M. Adsorbed volumes are reported in standard temperature and pressure (STP) of gas equivalent on figures and in liquid equivalent corresponding to real volume in the text. *TGA* measurements were collected from Al₂O₃ crucibles on a SDT Q600 instrument under air (100 mL/min), with a 298-1273K (10 K / min) temperature increase.

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Analytical Axis Ultra DLD spectrometer with monochromatized Al K_α X-ray (hν = 1486.6eV), hemispherical analyzer and channel plates detector. The pressure in the analysis chamber was less than 2 10⁻⁹Torr. The spectrometer was calibrated with Au 4f core level at a binding energy of 84 eV. Spectra were recorded at a take-off angle of 90° with a 700 μm × 300 μm slot aperture. The pass energy was set to 160 eV for survey and 20 eV for core level giving an energy resolution of 0.38eV. XPS is a quantitative chemical surface analysis. After decomposition of the core level spectra we measured the relative atomic concentrations (at.%) of the different species and their chemical states present on the surface. Deconvolution of the spectra were made using a Gaussian/Lorentzian (70/30) peak shape.

Gas chromatography was performed on a Varian 430-GC equipped with a PDMS VF-1ms column (15 m). Temperature program was 50°C (1 min) up to 250°C at 10°C/min.

Potentiometric analyses of chloride was performed using a chloride ion selective electrode (Bioblock Scientific). Standard NaCl solutions were used for calibration before analysis.

Materials.

Hexadecyltrimethylammonium-p-toluene-sulfonate (CTATos) (>99% Merck), hexamethyldisilazane (HMDSA) (98% Acros), Ludox HS-40 (40% SiO₂ Aldrich), and 3-isocyanatopropyltriethoxysilane (95% Aldrich) were used as received. The fumed silica was purchased from Evonik Industries (AEROSIL 200, surface area 200 m².g⁻¹, particle size *ca.* 12 nm). Toluene and absolute ethanol were stored with molecular sieves under argon. All other chemicals were purchased from Acros and used without further purification, unless noted in the text. Fe^{II} complexes were synthesized under an argon atmosphere.

Syntheses.

preparation of partially silylated silica (LUS-PS-E) has already been described elsewhere.¹ Two different samples of LUS-PS-E (denoted LUS1-PS-E and LUS2-PS-E) containing different amounts of trimethylsilyl groups were used in this work for the grafting of the Fe complex. Anal. found: LUS2-PS-E C 8.22, H 2.31, N < 0.1; weight loss at 1273 K 9.70 %. LUS1-PS-E found C 7.59, H 2.12, N < 0.1; weight loss at 1273 K 7.90 %.

Synthesis of N,N,N'-tris(2-pyridylmethyl)-ethane-1,2-diamine (*trispicen*) reagent was performed according to a previously reported method.²

N,N,N'-tris(2-pyridylmethyl)-N'-ethylamine-ethane-1,2-diamine (L₅²NH₂). To 1 g (3.00 mmol) of *trispicen* dissolved in acetonitrile was added 0.835 g (3.28 mmol) of N-(2-bromoethyl)-phthalimide, 3.12 g of potassium carbonate and 5 mg of potassium iodide. The reaction mixture was stirred under reflux for 16 h. Then, the solution was filtered and the solvent removed under reduced pressure. The residue was purified via neutral alumina gel chromatography using Et₂O to elute unreacted N-(2-bromoethyl)-phthalimide. Then, the protected product was isolated with CH₃CN. The oil obtained was added to 1 eq of hydrazine monohydrate in EtOH. The mixture was stirred at reflux temperature for 2 h. After cooling, 20 eq of 37% aqueous HCl solution (6.00 10⁻² mol) was added and the mixture was further refluxed for 30 minutes. After filtration, the filtrate was concentrated and the pH was adjusted to 9 with aqueous NaOH solution. The aqueous layer was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, then filtered and concentrated under reduced pressure. The product was obtained as a brown oil (yield 46%, C₂₂H₂₈N₆ M=376.5). ¹H NMR (360.13 MHz, CDCl₃): 8.41 (d, 4.7 Hz, 2H), 8.36 (d, 4.7 Hz, 1H), 7.49 (m, 2H), 7.44 (m, 1H), 7.34 (d, 7.9 Hz, 2H), 7.23 (m, 1H), 6.99 (m, 3H), 3.70 (s, 2H), 3.59 (s, 4H), 2.61 (s, 4H), 2.57 (t, 6.1 Hz, 2H), 2.40 (t, 6.1 Hz, 2H), 1.5 (s, 2H); ¹³C NMR (90.56 MHz ; CDCl₃): 159.9, 159.6, 149.0, 148.9, 136.3, 136.2, 122.8, 122.7, 121.8, 121.7, 61.0, 60.7, 57.8, 52.5, 52.3, 39.7. ESI-MS (CH₂Cl₂) *m/z* 377.25 ([M+H]⁺).

L₅²USi ligand. As a preamble, 1g (2.65 mmol) of L₅²NH₂ dissolved in distilled MeOH was passed

through a pad of neutral alumina. Then, MeOH was removed and the resulting oil was dissolved in 30 mL of distilled dichloromethane. To this solution was added 6.56 μL (2.65 mmol) of 3-isocyanatopropyltriethoxysilane under an argon atmosphere. The reaction mixture was then refluxed at 313 K overnight. The solvent was removed under vacuum and a light brown oil was obtained (yield 97%, $\text{C}_{32}\text{H}_{49}\text{N}_7\text{O}_4\text{Si}$ $M=623.9$). ^1H NMR (250.13 MHz, CDCl_3): 8.44 (d, 5.0 Hz, 2H), 8.34 (d, 5.0 Hz, 1H), 7.54 (m, 2H), 7.33 (m, 3H), 7.03 (m, 4H), 6.19 (s, 1H), 6.02 (t, 5.5 Hz, 1H), 3.70 (m, 10H), 3.55 (s, 2H), 3.20 (t, 4.7 Hz, 2H), 3.10 (quad., 6.6 Hz, 2H), 2.54 (m, 6H), 1.51 (quint., 7.7 Hz, 2H), 1.09 (t, 7.0 Hz, 9H), 0.52 (m, 2H).

^{13}C NMR (62.90 MHz ; CDCl_3): 159.5, 158.9, 148.8, 148.6, 136.4, 136.1, 123.4, 123.0, 122.0, 121.8, 60.5, 60.3, 58.1, 53.4, 52.0, 51.3, 42.7, 37.9, 23.8, 18.1, 7.6. ESI-MS ($\text{CH}_3\text{CH}_2\text{OH}$) m/z 646.39 (53.5%) ($[\text{M}+\text{Na}]^+$), 624.41 (100%) ($[\text{M}+\text{H}]^+$).

$[(\text{L}_5^2\text{USi})\text{FeCl}]\text{PF}_6$ complex. This synthesis was performed in a glovebox. Anhydrous iron chloride (0.203 mg, 1.60 mmol) dissolved in 10 mL of a mixture of absolute ethanol/ CH_2Cl_2 (2/1 v/v) was added dropwise to 1 g of L_5^2USi (1.60 mmol) in 30 mL of the same solvent mixture. After stirring for 1 hour, 270 mg (1.60 mmol, 1 equiv.) of sodium hexafluorophosphate dissolved in ethanol was added. Upon addition of methyl *tert*-butyl ether, a greenish precipitate was formed and isolated by filtration. (yield 52%, $\text{C}_{32}\text{H}_{49}\text{ClN}_7\text{O}_4\text{FeSiPF}_6$ $M=860.1$). Anal. calcd for $\text{C}_{30}\text{H}_{45}\text{N}_7\text{O}_4\text{F}_6\text{ClPSiFe}$: C 43.3, H 5.5, N 11.8, Cl 4.3; found: C 43.9, H 5.9, N 12.1, Cl 5.2. ESI-MS m/z 714.26 (100%) ($[\text{M}-\text{PF}_6]^+$, calculated 714.26), m/z 594.19 (25.2%) ($[\text{M}-\text{PF}_6-\text{Cl}-3(\text{CH}_2\text{CH}_3)+2\text{H}]^+$, calculated 594.19); UV-vis (CH_3CN): λ_{max} (ϵ , $\text{L.mol}^{-1}.\text{cm}^{-1}$) = 388 nm (2000), 258 nm (12000); (CH_2Cl_2): λ_{max} (ϵ , $\text{L.mol}^{-1}.\text{cm}^{-1}$) = 400 nm (1550), 260 nm (13000).

Grafting of L_5^2USi ligand on LUS2-PS-E : LUS2-PS- L_5^2USi . In a round-bottom, two-neck flask, LUS-PS-E (1 g) was heated at 403 K for 1 h under an argon flow, then 5 h under vacuum. After cooling down to RT under argon, the solid was stirred with 30 mL of dry toluene. To this mixture, 2.23 g of L_5^2USi (3.58 mmol, ca. 10 equiv. vs. SiOH sites) dissolved in 10 mL of distilled acetonitrile were added. The mixture was stirred at room temperature for 1 h and refluxed for 16 h. After filtration, the solid was washed with toluene (3 \times 30 mL), technical ethanol (3 \times 30 mL), acetone (3 \times 30 mL), and then dried in vacuum overnight, leading to around 1 g of product. Weight loss at 1273 K: 27.50 %.

Metallation of LUS2-PS- L_5^2USi by Fe^{II} : LUS2-PS- $\text{L}_5^2\text{USi-Fe}$ (2a). 100 mg of LUS2-PS- L_5^2USi dried at 333 K for 1.5 h under an argon flow and then 2 h under vacuum was suspended in 5 mL of methanol. A solution of 43.0 mg of anhydrous FeCl_2 (0.34 mmol, 1 equiv. vs L_5^2USi) in 5 mL of MeOH was added to the suspension of silica. The reaction mixture was stirred under reflux for 2 h.

After filtration, the resulting solid was washed with MeOH, technical ethanol and acetone (3 × 30 mL each) and then dried under vacuum overnight. Around 90 mg of a yellow powder was obtained. Anal. found: C 11.19, H 2.18, N 1.39, Cl 0.71, Fe 0.89. Weight loss at 1273 K: 26.01 %.

Grafting of [(L₅²USi)FeCl]PF₆ complex on LUS1-PS-E : LUS1-PS-L₅²USiFe (1a). In a round-bottom, two-neck flask, LUS1-PS-E (100 mg) was heated at 403 K for 1.5 h under an argon flow and then 2 h under vacuum. The solid was suspended in 5 mL of dry toluene. [(L₅²USi)FeCl]PF₆ (25.4 mg, 2.95 × 10⁻⁵ mol, 1.1 equiv. vs. SiOH sites), was dissolved in 5 mL of dimethylformamide under argon, and then added to the suspension. The mixture was stirred at room temperature for 1 h and refluxed for 16 h. After filtration, the product was washed with toluene (3 × 5 mL), technical ethanol (3 × 5 mL), and acetone (3 × 5 mL). The bifunctionalized silica was dried in vacuum overnight, leading to around 90 mg of a greenish powder. Anal. found for C 10.20, H 2.12, N 0.88, Cl 0.60, Fe 0.64. Weight loss at 1273 K 12.20 %.

Grafting of L₅²USi ligand on fumed silica : SiO₂-L₅²USi. The mole number n_x of ligand or complex used was calculated as follows : $n_x = \frac{1}{2} \times \frac{S_{\text{SiO}_2} \times N_{\text{OH}} \times m_{\text{SiO}_2}}{3 \times N_A}$, where S_{SiO₂} is the surface area (200 m²/g), m_{SiO₂} the mass of fumed silica, N_{OH} the density of surface silanol groups (3.10¹⁸ /m²) and 3 is the maximum number of surface SiOH capped by ligand or complex. Fumed silica (1 g) was placed in a round-bottom, two-neck flask and heated at 403 K for 1 h under argon, then 5 h under vacuum. After cooling down to RT under argon, the solid was stirred with 20 mL of dry toluene. The L₅²USi ligand (1.06 g, 1.71 mmol, ca. 0.5 equiv. vs SiOH sites) dissolved in 10 mL of distilled acetonitrile was added and the mixture was stirred at room temperature for 1 h and then refluxed for 16 h. After filtration, the solid was washed with toluene (3 × 30 mL), technical ethanol (3 × 30 mL), acetone (3 × 30 mL), and then dried in vacuum overnight. All the manipulations caused some loss of product, yielding finally to around 1 g of product. Weight loss at 1273 K: 6.29 %.

Silylation of SiO₂-L₅²USi : SiO₂-L₅²USi-PS. 1 g of SiO₂-L₅²USi was heated at 333 K under vacuum for 5h. After cooling down to RT under argon, 40 mL of dry cyclohexane and 3.53 mL of HMDSA (1.62 × 10⁻² mol, 100 equiv. vs SiOH sites) was added to the solid. The mixture was stirred at room temperature for 1 h and refluxed for 16 h at 353 K. The solid was finally filtered and washed with cyclohexane, acetone and ethanol (3 × 30 mL of each) and dried under vacuum overnight to give 900 mg of yellow solid. Weight loss at 1273 K, 6.18 %.

Metallation of SiO₂-L₅²USi-PS by Fe^{II} : SiO₂-L₅²USi-PS-Fe (2b). 500 mg of SiO₂-L₅²USi heated at 333 K for 1.5 h under argon and then 2 h under vacuum was suspended in 15 mL of distilled methanol. A solution of 59.5 mg of anhydrous FeCl₂ (0.47 mmol, 1 eq vs L₅²USi) in 5 mL of distilled MeOH was added to this suspension. The reaction mixture was stirred under reflux for 2 h, then filtered. The solid was washed with MeOH, technical ethanol and acetone (3 × 30 mL of each) before being dried under vacuum overnight. Around 450 mg of a yellow powder was obtained. Anal. found: C 4.20, H 0.69, N 0.40, Fe 0.82. Weight loss at 1273 K: 7.44 %.

Grafting of [(L₅²USi)FeCl]PF₆ complex on fumed silica : SiO₂-(L₅²USi)Fe. Fumed silica (100 mg) was placed in a round-bottom, two-neck flask and heated at 403 K for 1.5 h under argon and then 2 h under a vacuum. Then, the solid was suspended in 5 mL of dry toluene. [(L₅²USi)FeCl]PF₆ (24.6 mg, 2.86 × 10⁻⁵ mol, 1.1 eq vs SiOH sites) was stirred in 5 mL of dimethylformamide until complete dissolution, and then added under argon to this suspension. The resulting mixture was stirred at room temperature for 1 h and refluxed for 16 h. The product was filtered and washed with toluene (3 × 5 mL), technical ethanol (3 × 5 mL), and acetone (3 × 5 mL). The solid was dried in vacuum overnight, leading to around 90 mg of yellow powder. Anal. found: C 3.42, H 0.40, N 0.92, Cl 0.48, Fe 0.42. Weight loss at 1273 K 11.14 %.

Silylation of SiO₂-(L₅²USi)Fe : SiO₂-(L₅²USi)Fe-PS (1b). SiO₂-(L₅²USi)Fe (1g) was dried at 333 K under vacuum overnight and then let to cool down under argon. Dry cyclohexane (40 mL) and hexamethyldisilazane (0.7 mL, 3.36 mmol, 10 eq. vs. SiOH) were added. The mixture was stirred at room temperature for 1 h and then at 80°C for 16 h. Finally, the solid was filtered, washed with cyclohexane, acetone and ethanol (3 × 30 mL each) and dried overnight to afford a greenish powder (900 mg). Anal. found: C 5.10, H 0.93, N 0.76, Cl 0.59, Fe 0.53. Weight loss at 1273 K 6.63 %.

Catalysis.

Catalytic oxidation of trichlorophenols.

The reaction mixtures were Fe / H₂O₂ / 2,3,6-TCP or 2,4,6-TCP : 1 / 200 / 20, under vigorous magnetic stirring in water. The quantity of supported catalyst used for each sample was calculated for a putative 1 mM concentration in Fe. After catalytic run, the aqueous phase was either directly used for potentiometric analysis of Cl⁻ or extracted thrice with ether. The organic phases were combined and

analyzed by GC. Selectivity for chlorine mineralization is defined as $\frac{\%_{\text{released Cl}^-}}{\%_{\text{TCP degradation}}} \times 3$.

Catalytic oxidation of anisole.

molar ratio Fe / H₂O₂ / anisole : 1 / 20 / 9200, without any other additive, reaction time of 2h at room temperature. The mass of catalyst used accounted for a 1 mM concentration in Fe.

Molecular Fractions of grafted functions.

5 For the sake of comparison, all the molar percentages were divided by the molar percentage of bulk

silica : $\%n_{\text{Si}_{\text{inorg}}} = \frac{\%m_{\text{SiO}_2}}{M_{\text{SiO}_2}} - \%n_{\text{TMS}} - \%n_{\text{ligand}}$, where $\%m_{\text{SiO}_2}$ is the total percentage of SiO₂

deduced from the weight loss at high temperature measured by TGA, and $\%n_{\text{TMS}}$ and $\%m_{\text{ligand}}$ are the molar percentages of TMS and ligand, respectively. This value is, therefore, the total SiO₂ corrected from SiO₂ formed upon calcination of TMS and ligand or complex. The molar percentages of TMS

10 and ligand are obtained with the equations: $\%n_{\text{ligand}} = \frac{\%m_{\text{N}}}{7 \times M_{\text{N}}}$ and

$\%n_{\text{TMS}} = \frac{\%m_{\text{C}} / M_{\text{C}} - 4 \times \%n_{\text{TMA}} - 26 \times \%n_{\text{ligand}}}{3}$. The quantities $\%m_{\text{N}}$ and $\%m_{\text{C}}$ are obtained from

elemental analyses, 7 is the number of N atoms in the L₅²USi ligand and 26 represents the number of C atoms of the grafted ligand (provided all alkoxy functions have been hydrolyzed). In the last equation, $\%n_{\text{TMA}}$ stands for the molar percentage of TMA masking agent that is present in the pores for early
15 stages of the supported catalyst elaboration (before introduction of the ligand or complex). It is deduced from the N elemental analysis.

- 20 1. K. Zhang, B. Albela, M. Y. He, Y. M. Wang and L. Bonneviot, *Physical Chemistry Chemical Physics*, 2009, **11**, 2912-2921.
2. P. Mialane, A. Novorokjine, G. Pratviel, L. Azéma, M. Slany, F. Godde, A. Simaan, F. Banse, T. Kargar-Grisel, G. Bouchoux, J. Sainton, O. Horner, J. Guilhem, L. Tchertanova, B. Meunier and J. J. Girerd, *Inorg. Chem.*, 1999, **38**, 1085-1092.

Table S1. XPS data for the supported catalysts obtained via different methods and the molecular complex. Binding energy in eV, the percentage obtained from deconvolution and full width at half maximum in parenthesis

	LUS2-PS-L-Fe (2a)	LUS1-PS-LFe (1a)	SiO ₂ -L-PS-Fe (2b)	SiO ₂ -LFe-PS (1b)	[(L ₅ ² USi)FeCl]Cl
Fe (2p_{3/2}) eV (%; fwhm)	709.2	709.5	709.8	710.0	709.3
	(46.7; 1.50)	(40.3; 1.45)	(35.6; 1.50)	(30.4; 1.50)	(43.1; 1.38)
	710.5	710.8	711.2	711.2	710.6
	(34.6; 1.55)	(39.1; 1.60)	(41.3; 1.60)	(38.0; 1.60)	(37.5; 1.55)
	711.8	712.2	712.8	712.6	711.9
	(18.7; 1.75)	(20.6; 1.75)	(23.1; 1.70)	(31.6; 1.75)	(19.4; 1.70)
N (1s) eV (%; fwhm)		399.3	399.6	399.8	
		(9.5; 1.39)	(19.3; 1.50)	(25.8; 1.40)	
	400.0	400.4	400.5	400.8	400.15
	(100.0; 1.52)	(73.0; 1.39)	(58.5; 1.50)	(55.0; 1.40)	(100.0; 1.39)
		401.1	401.5	401.8	
	(17.5; 1.39)	(22.2; 1.50)	(19.2; 1.40)		

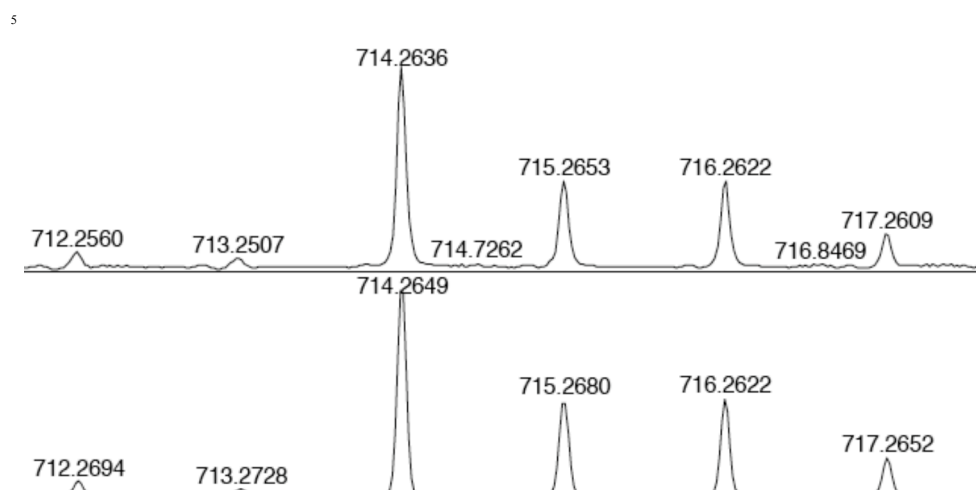


Figure S1. Electrospray ionization mass spectrometry of [(L₅²USi)Fe^{II}Cl]PF₆ in acetonitrile focusing on the [(L₅²USi)Fe^{II}Cl]⁺ isotopic distribution (top). The theoretical distribution for [(L₅²USi)Fe^{II}Cl]⁺ is shown on the bottom.

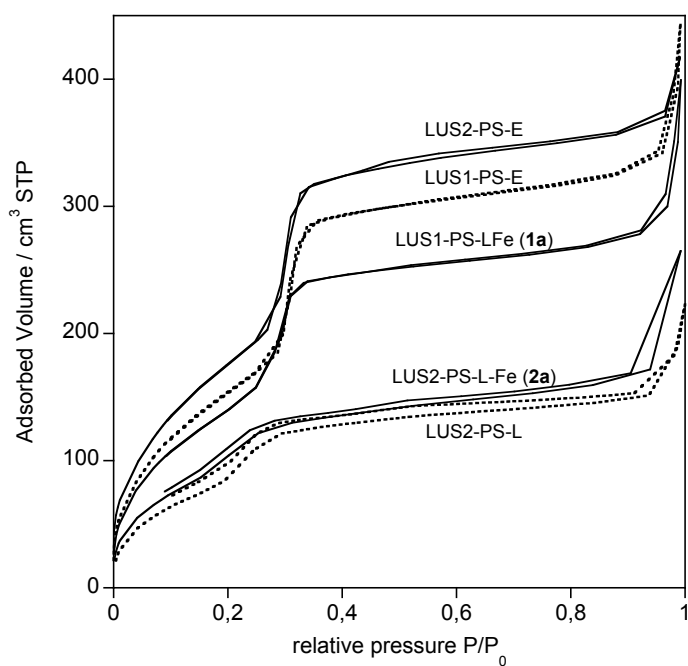


Figure S2. N₂ adsorption-desorption isotherms at 77K of the supported catalysts **1a** and **2a** at different steps of their elaboration.

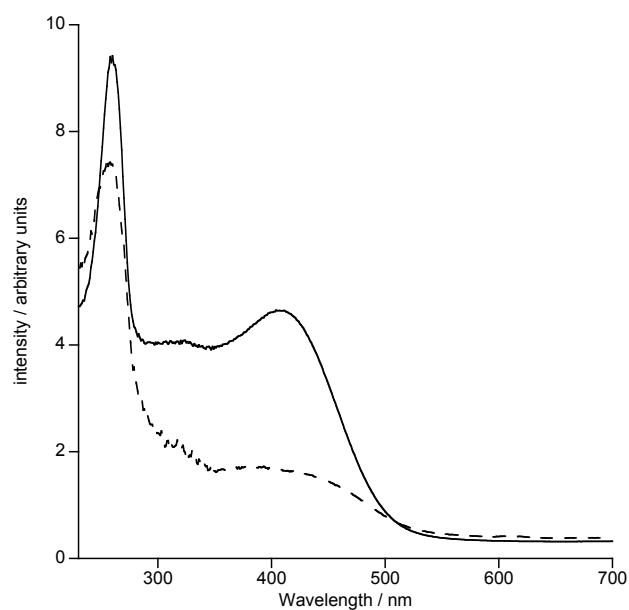


Figure S3. Solid state UV-visible spectra of SiO₂-L-PS-Fe (**2b**) (plain line), and SiO₂-LFe-PS (**1b**) (dashed line).

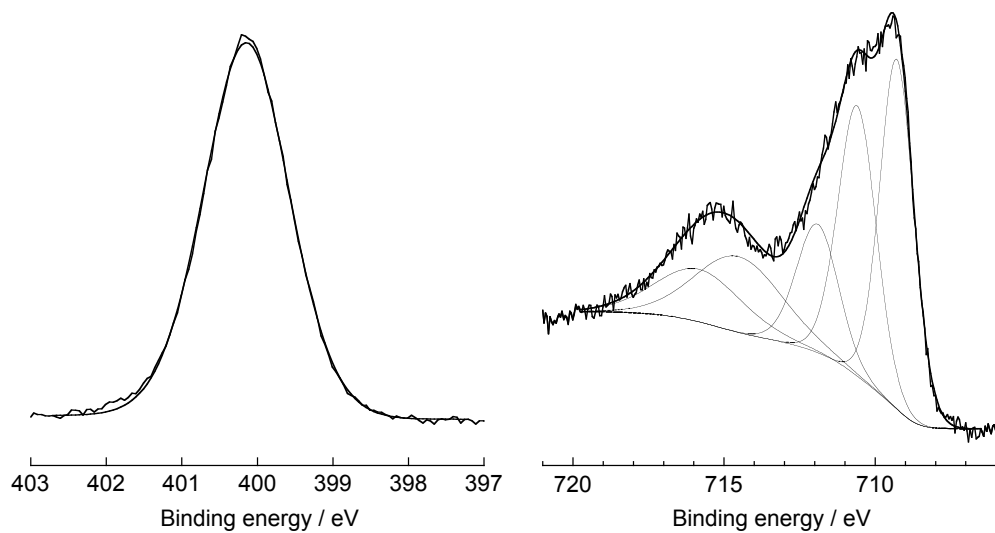


Figure S4. N 1s (left) and Fe 2p_{3/2} (right) XPS spectra and deconvolution of the complex [(L₅²USi)FeCl]Cl.