

Mesoporous hybrid materials containing two transition metal ions, one in the framework, the other in the channel pores†

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Mesoporous hybrid materials containing bridged metal–cyclam moieties in the silicate framework were synthesized by using triblock copolymer F127 as template and SiH_3 as hydrolysable terminal groups; grafting of a metal–cyclam precursor in the channel pores led to materials containing two different strongly chelated transition metal ions in two steps.

The recent use of bridged silsesquioxane molecules as precursors for the synthesis of periodic mesoporous organosilicates (PMOs) is a remarkable advance in mesoporous hybrid materials.^{1–4} Indeed, these materials are novel in that the organic groups are integrated to the silicate framework by means of two or more terminal silyl groups, leaving the channel pores unoccupied. This last point renders this class of materials of particular interest as it can lead to bifunctional hybrid materials *via* the functionalisation of both the channel pores and the framework.^{5–7}

Until now, most of the mesoporous hybrid materials prepared by sol–gel process have been formed in order to exhibit one property (for example, catalysis, optic, magnetism, biosensor...). Therefore, it is a challenge for chemists to find the routes which permit them to control the introduction of two functions, which might involve interactive properties. Materials coupling photoluminescence and magnetism or photoluminescence and non-linear optics can be imagined, for example.

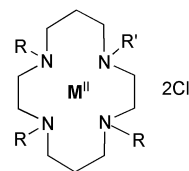
We previously described the preparation of nanostructured hybrid materials containing one transition metal salt strongly chelated⁸ using the cyclam derivative **1**⁹ (cyclam = 1,4,8,11-tetraazacyclotetradecane), cyclam and cyclam derivatives being well-known for their remarkable binding ability towards transition metal ions.^{10,11} These ions were introduced by two routes, which were demonstrated to be non equivalent (hydrolysis polycondensation of **1** followed by the quantitative incorporation of a transition metal salt or gelation of the complex **1**[M]).⁸

We now focus our efforts on the selective introduction of two different transition metal ions into mesoporous hybrid materials, one in the channel pores, the other in the framework, all these ions having potential physical properties (optic, magnetic...).

In this paper, we describe a chemical way allowing the introduction in two steps of two strongly chelated transition metal ions, using an original neutral templating approach.

Co-hydrolysis and polycondensation of the precursor **1**[Cu] with terminal triethoxysilyl groups and tetraethylorthosilicate (TEOS), in the presence of the triblock copolymer Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as structure-directing agent failed whatever the couple solvent/co-solvent and the catalyst used (acid, basic or nucleophilic). Therefore, we prepared the metal–cyclam complexes **2**[Cu] and **2**[Co] with terminal trihydrosilyl groups. Indeed, the hydrolysis and polycondensation of organohydrosilanes in the presence of fluoride ions as catalyst was proved to be an alternative route to organosilsesquioxane leading to well condensed materials.¹² Nevertheless, a very

poor yield of solid was obtained by co-hydrolysis and polycondensation of **2**[Cu] or **2**[Co] and TEOS in aqueous solution at pH 1.5 using P123 as structure-directing agent and NaF as catalyst. As CH_3OH was the only polar solvent in which **2**[Cu] and **2**[Co] were soluble, we decided to use the hydrophilic Pluronic triblock copolymer F127 ($\text{EO}_{77}\text{PO}_{29}\text{EO}_{77}$),¹³ well soluble in CH_3OH instead of P123. These novel experimental conditions allowed the co-condensation of **2**[Cu] or **2**[Co] and TEOS in high yield.



- 1** : R = R' = $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, M = Φ
1[M] : R = R' = $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, M = Cu or Co
2[M] : R = R' = $-(\text{CH}_2)_3\text{SiH}_3$, M = Cu or Co
3 : R = H, R' = $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, M = Φ
3[M] : R = H, R' = $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, M = Cu or Co

In a typical synthesis, a mixture of F127 (2.94 g, 0.35 mmol), CH_3OH (77.8 mL), H_2O (1.21 g, 64.40 mmol) and decane (32 mg, 0.35 mmol) placed in a 100 mL flask, was stirred until the dissolution of the surfactant. This solution was then added to a mixture of TEOS (3.62 g, 17.44 mmol) and **2**[Cu] (680 mg, 1.09 mmol). The emulsion was vigorously and regularly stirred for 3 h at room temperature. The resulting brown transparent microemulsion was heated at 60 °C then 0.57 mL (0.57 mmol) of a 1 M THF solution of tetrabutylammonium fluoride (TBAF) was injected. The mixture was heated at 60 °C under stirring for 3 days. The purple resulting solid was recovered by filtration and washed three times with EtOH. The template was removed from the as-synthesized material by Soxhlet extraction with ethanol heated under reflux for 24 h. The solid was again recovered by filtration, washed with EtOH, acetone and ether then dried under vacuum at 120 °C for 12 h to give the solid **XCu** as a purple powder (1.10 g, 91%). The xerogel obtained from **2**[Co] in a similar way was named **XCo**.

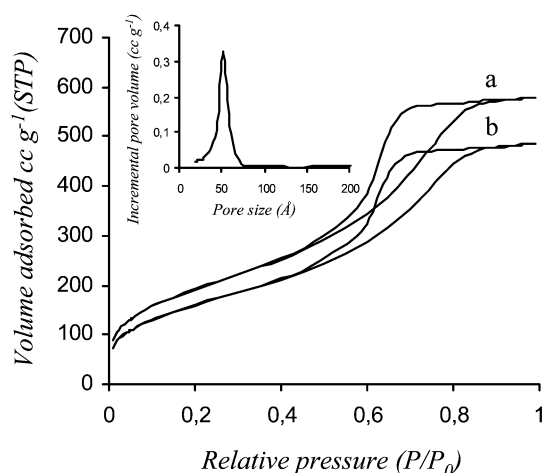
A SAXS analysis of **XCu** and **XCo** revealed the absence of a Bragg peak. However, the diffractogram presents a linear part of q^{-1} slope, characteristic of channels non-correlated¹⁴ but of similar size (see supplementary information†). In both cases, the N_2 adsorption–desorption isotherms showed a type IV isotherm, characteristic of mesoporous materials with narrow pore size distribution (Fig. 1). BET surface area and pore volumes are large as well as the pore sizes,^{15,16} calculated from the desorption branch using the BJH method (Table 1). The concentration in cyclam moieties and in transition metal ion (Table 1) were inferred from the results of elemental analysis of Si, N, and metal. They were found to be very close to those of the original mixture for both materials, showing thus that no carbon–silicon bond cleavage occurred during the synthesis and that the complexation survived the synthesis and washing. It is worth noting that, when the molar ratio TEOS/precursor was in between 9 and 17, the materials were found to be mesoporous.

† Electronic supplementary information (ESI) available: SAXA pattern of **XCu**. See <http://www.rsc.org/suppdata/cc/b3/b303492p/>

Table 1 Some relevant characteristics for the mesoporous materials **XCu**, **XCo**, **XCu[Co]** and **XCo[Cu]**

Material designation	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_p/\text{cm}^3 \text{g}^{-1}$	$D_p/\text{\AA}^a$	[cyclam] ^b / mmol g ⁻¹	[M] _{framework} ^b / mmol g ⁻¹	[M'] _{pores} ^b / mmol g ⁻¹
XCu	680	1.13	75	0.53 (0.60) ^c	0.52	0
XCo	700	0.90	71	0.50 (0.60) ^c	0.48	0
XCu[Co]	590	0.75	52	0.74	0.38(Cu)	0.36(Co)
XCo[Cu]	470	0.74	51	0.70	0.40(Co)	0.30(Cu)

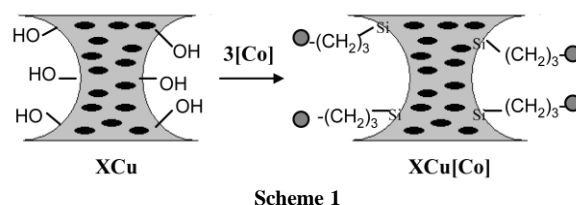
^a Calculated from the desorption branch by using the BJH method. ^b Values inferred from the results of elemental analysis. ^c Theoretical values.

**Fig. 1** Nitrogen adsorption–desorption isotherms of **XCo** (a), **XCo[Cu]** (b) and pore size distribution plot (inset) of **XCo[Cu]**.

When the ratio was 4, the solid was microporous while the solid was macroporous for a ratio of 30. Thus, there exists an ideal range for which the surfactant can be really a structure-directing agent leading to mesoporous materials with narrow pore size distribution.

As cyclam is a stronger chelating ligand than the tetra-N-substituted cyclam derivatives, we attempted the decomplexation of **XCu** by washing it with an acetonitrile solution containing a large excess of cyclam. Surprisingly, no decomplexation occurred even after several hours under reflux while quantitative decomplexation took place for the nanostructured hybrid material resulting from the gelation of **1[Cu]** accomplished without surfactant. This result shows how stable the bridged metal/cyclam complex is located in the framework and the importance of the surfactant in the structuring of **XCu**.

In order to incorporate into the channel pores of **XCu** and **XCo** another strongly chelated transition metal salt, grafting of **3[Co]** and **3[Cu]** was achieved (**3[Co]** and **3[Cu]** were obtained quantitatively by reaction of N-triethoxysilylpropylcyclam **3**¹⁷ with a stoichiometric amount of CoCl_2 or CuCl_2). Treatment of **XCu** with a toluene solution of **3[Co]** heated under reflux for 24 h gave rise to **XCu[Co]** (XM to recall the starting material and [M'] to recall the metal ion originating in the grafting (Scheme 1)). Grafting of **3[Cu]** onto **XCo** under the same conditions led to **XCo[Cu]**. Some relevant characteristics of these materials are given in Table 1. The N_2 adsorption–desorption isotherms of both materials revealed that the mesoporosity of materials was maintained as well as a narrow pore size distribution (Fig. 1). It is worth noting that grafting the complexes **3[Cu]** and **3[Co]** produced a decrease of textural data of the materials, as expected after grafting.¹⁸ Results of elemental analyses of Si, N, Cu and Co allowed the determination of the content of chelated



metal in the channel pores and in the framework showing thus that we succeeded to introduce specifically one metal salt in the framework and another in the channel pores.

In summary, we described the preparation in two steps of materials containing one transition metal salt strongly chelated in the framework and another in the channel pores. That was possible thanks to the hydrolysable SiH_3 groups in place of $\text{Si}(\text{OEt})_3$, which shows how versatile the sol–gel process is. This method, which can be extended to any other transition metal ions, could open the route to materials coupling physical properties.

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