First organic–inorganic hybrid materials with controlled porosity incorporating cyclam units

Géraud Dubois,[a] Robert J. P. Corriu,*[a] Catherine Reyé,[a] Stéphane Brandès,[b] Franck Denat[b] and Roger Guilard*[b]

[a] *Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637 CNRS, Université de Montpellier II, Sciences et Techniques du Languedoc, Place E. Bataillon, F-34095 France. E-mail: corriu@crit.univ-montp2.fr*
[b] *Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz (LIMSAG), UMR 5633, Université de Bourgogne, 6, Boulevard Gabriel, 21100 Dijon, France. E-mail: limsag@u-bourgogne.fr*

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The sol-gel process has been used to prepare new organic–inorganic hybrid materials with various textures from cyclam derivatives bearing four hydrolysable SiX_3 groups (X = OEt, H) as well as from the corresponding Cu^{II} and Co^{II} complexes of the cyclam derivative (X = OEt).

It is a challenge to prepare materials able to incorporate strongly chelated metal cations which remain chemically accessible. In order to do that, it is necessary to include a good chelating ligand within the solid and to control the texture as well as the structure of the material. Since saturated polyazamacrocycles and especially 1,4,8,11-tetraazacyclotetradecane (cyclam) have long been known for their remarkable binding ability towards transition metal cations,[1,2] we set out to incorporate cyclam units within silica matrices by using the sol-gel process. Indeed the hydrolysis and polycondensation of molecular precursors substituted by more than one hydrolysable groups such as $Si(OR)_3$ allow the preparation of nanostructured hybrid materials.[3–6] This new class of monophasic materials constitutes an expanding area of research in materials science. In this way, the silica matrix is built around the organic moiety during the hydrolytic polycondensation. Silica gel was recently used for the immobilization of polyazacycloalkanes including cyclam, by using a grafting process.[7] However, though this method of attachment of organic groups at the silica surface produced highly effective adsorbents[8,9] and catalysts,[10,11] it presents some drawbacks especially as the loading of the macrocycles is often low (< 0.4 mmol g^{-1}) and is uncontrolled.

Nanocomposite materials incorporating tetraazamacrocycles within silica matrices have been made[12] by the sol-gel process. Here we report the first preparation of monophasic hybrid materials with various textures obtained from isolated cyclam derivatives bearing four hydrolysable SiX_3 groups (X = OEt, H). The hydrolysis of the Cu^{II} and Co^{II} complexes of the cyclam derivative (X = OEt) is also described.

Tetrasilylated cyclam derivative **1** was prepared by reaction of 4 equiv. of 3-iodopropyltriethoxysilane with cyclam under basic conditions;† the corresponding hydrosilylated derivative **2** was obtained by $LiAlH_4$ reduction of **1**.[13] Complexation of Cu^{2+} and Co^{2+} by the tetrasilylated macrocycle **1** was performed in the presence of 1 equiv. of $CuCl_2$ or $CoCl_2$ in THF heated under reflux to afford respectively the complexes **3a** and **3b** in high yield [eqn. (1)]. Sol-gel polycondensation of **1**, **2**, **3a** and **3b** was achieved in the presence of a stoichiometric amount of water (6 equiv.) and under different experimental conditions to yield respectively xerogels **X1a–e**, **X2** and **X3a–b** (Table 1). All the gels were allowed to age for five days at room temperature before being powdered, washed twice with EtOH followed by Et_2O, and finally dried (120 °C at 20 mm Hg for 12 h). It is important to note that after this processing, metal cations were quantitatively retained within the xerogels (measured by elemental analysis and X-ray fluorescence). We had previously observed that 95% of Na^+ and 96% of K^+ was retained within the xerogels obtained by hydrolysis and polycondensation of Na^+ or K^+ complexes of bisilylated dibenzo-18-crown-6.[14] The solid state ^{13}C NMR spectra of the xerogels displayed the

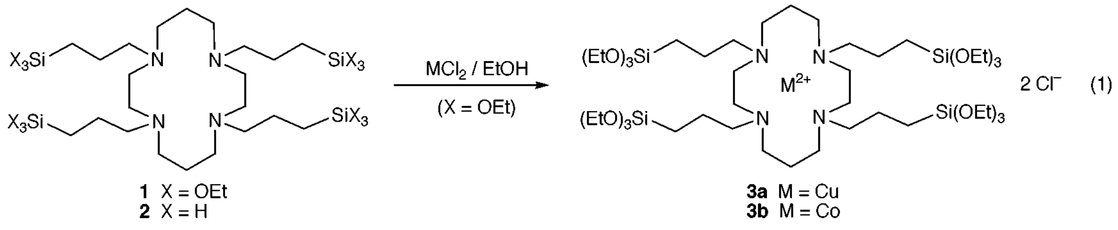

Table 1 Hydrolysis and polycondensation of 1 M solution of **1** and **2**, 0.5 M solution of **3a** and 0.25 M solution of **3b** in the presence of a stoichiometric amount of water. BET surface area and mean pore diameters[a] of xerogels

Entry	Precursor	Catalyst	Solvent	T/°C	Xerogel	S_{BET}/m^2 g^{-1}	Mean pore diameter/Å
1	**1**	No catalyst	EtOH	24	**X1a**	< 10	—
2	**1**	NH_3[b]	EtOH	22	**X1b**	< 10	—
3	**1**	TBAF (1%)	formamide	22	**X1c**	< 10	—
4	**1**	TBAF (1%)	EtOH	24	**X1d**	370	< 30
5	**1**	TBAF (1%)	EtOH	110[c]	**X1e**	800	20–50
6	**2**	No catalyst	THF	0	**X2**	320	20–60
7	**3a**	TBAF (1%)	THF	22	**X3a**	< 10	—
8	**3b**	TBAF (1%)	THF	26	**X3b**	< 10	—

[a] Calculated by the BJH method. [b] Molar ratio of NH_3/precursor: 158/100. [c] Sealed tube.

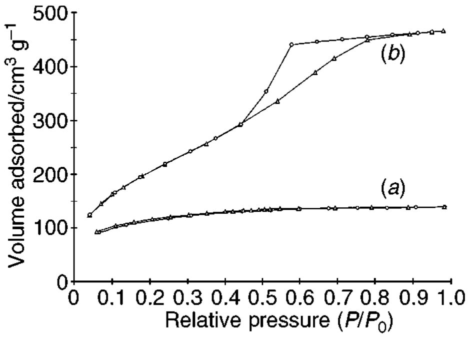

Fig. 1 Sorption isotherms (N_2) for xerogels (*a*) **X1d** and (*b*) **X1e** (Δ = adsorption, ○ = desorption).

signals which characterise the cyclam moieties. Solid state ^{29}Si NMR spectroscopy showed that there was no Si–C bond cleavage during the sol-gel process (absence of any signal corresponding to SiO_4 substructures). All the ^{29}Si NMR spectra display one major resonance centred at δ −65 (substructure T^3 [C–Si(OSi)$_3$]) except for **X1a** and **X1c** which were not well condensed (major substructure T^0 [C-Si(OR)$_3$]). The BET surface areas of the xerogels were determined by N_2 adsorption–desorption measurements and the average pore diameter by the BJH method.[15]

Overall the results reported in Table 1 show that it is possible to obtain materials with various textures by changing the experimental conditions of gelification. The following parameters appear to be of importance.

(1) *Nature of the hydrolysable SiX$_3$ group* (entries 1 and 6): in the absence of catalyst, the hydrosilane **2** was much more readily hydrolyzed than the corresponding alkoxysilane **1**. Thus, gel formation of **2** took less than 1 min at 0 °C giving rise to the mesoporous xerogel **X2** while that of **1** occurred within 36 h affording the non-porous xerogel **X1a**.

(2) *Nature of the catalyst* (entries 1, 2 and 4): hydrolysis and polycondensation of **1** without catalyst, or in presence of base, yielded respectively the non-porous xerogels **X1a** and **X1b** while hydrolysis of **1** in the presence of 1% TBAF afforded the essentially microporous xerogel **X1d** with a rather large surface area.

(3) *Effect of solvent and of the concentration of the precursor*: all the results reported in Table 1 have been obtained using molar solutions of precursor. We observed that increasing the concentration of the precursor up to 3 M affected neither the specific area nor the pore diameter. In contrast, the nature of the solvent is of importance. Thus, running the hydrolysis in EtOH, THF or CH_2Cl_2 did not change significantly the material, while using formamide as the solvent yielded a material without specific surface area (compare entries 3 and 4).

(4) *Effect of the temperature*: if we compare the results of entries 4 and 5, it is clear that both the surface area and the porosity are strongly dependent on the temperature. The higher the temperature, the larger the surface area and the average pore diameters. The difference between the textures of the xerogels X**1d** and X**1e** appears clearly in Figs. 1 and 2. The adsorption isotherm of **X1d** is typical of a microporous solid [type I of BDDT classification,[15] Fig. 1(*a*)] while that of **X1e** shows a type IV isotherm, characteristic for mesoporous materials [Fig. 1(*b*)]. It is also to be noted that the pore distribution in **X1e** is rather narrow [Fig.2(*b*)], which is not the case for the microporous solid **X1d** [Fig. 2(*a*)]. Another interesting feature of these materials is that they contain up to 1.4 mmol of cyclam per gram of solid (based on nitrogen elemental analyses), which is notably more than the silica gel-supported cyclam.[7]

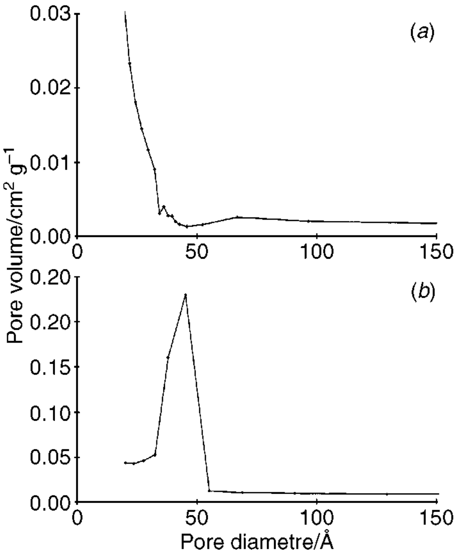

Fig. 2 Pore size distribution curves for (*a*) **X1d** and (*b*) **X1e**.

We have described the preparation of monophasic hybrid materials with various textures from well defined cyclam precursors bearing four hydrolysable SiX$_3$ groups (X = OEt, H). These materials are fundamentally different from those previously described including cyclam units[7,12] due to the mode of their preparation. We have also shown that the complexation of metal cations by **1** survives the sol-gel process which indicates that, in spite of the high degree of condensation of the network observed in most of the cases, the tetraazamacrocycle is flexible enough to maintain the complexation during the polycondensation. The study of the binding properties of this new class of materials is currently in progress.

Notes and references

† *Experimental procedure*: for **1** A mixture of 2 g (10 mmol) of cyclam, 12.41 g (90 mmol) of K_2CO_3 and 13.27 g (40 mmol) of 3-iodopropyltriethoxysilane in 100 ml of MeCN was heated under reflux for 12 h under an argon atmosphere. The solvent was removed *in vacuo* and 100 ml of pentane was added to precipitate the salts. The precipitate was filtered and washed with pentane (2 × 30 ml). Evaporation of pentane gave 9.85 g (9.7 mmol, 97%) of **1** as a colorless oil: δ_H 0.58 (m, 8H, CH_2), 1.23 (t, 36H, CH_3), 1.55 (m, 12H, CH_2), 2.39 (m, 8H, CH_2), 2.51 (m, 8H, CH_2), 2.54 (s, 8H, CH_2), 3.83 (q, 24H, CH_2); δ_C 7.0 (CH_2Si), 17.3 (CH_3), 19.6, 21.9 (CH_2), 49.5, 50.4 (CH_2N), 57.3 (CH_2O), 57.9 (CH_2N); δ_{Si} −44.6. (calc. for $C_{46}H_{104}N_4O_{12}Si_4$. C, 54.33; H, 10.24; N, 5.51. Found: C, 53.90; H, 9.93; N, 5.89%).

1 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, CUP, Cambridge, 1989.

2 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.

3 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431 and references therein.

4 U. Schubert, N. Hüsing and A. Lorenz, *Chem. Mater.*, 1995, **7**, 2010.

5 R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420 and references therein.

6 G. Cerveau and R. J. P. Corriu, *Coord. Chem. Rev.*, 1998, **178–180**, 1051.

7 C. Gros, F. Rabiet, F. Denat, S. Brandès, H. Chollet and R. Guilard, *J. Chem. Soc., Dalton Trans.*, 1996, 1209.

8 L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, 1997, **9**, 500.

9 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923.

10 A. Cauvel, G. Renard and D. Brunel, *J. Org. Chem.*, 1997, **62**, 749.

11 J. H. Clark and D. J. Macquarrie, *Chem. Commun.*, 1998, 853.

12 T. Tsuda and T. Fujiwara, *J. Chem. Soc., Chem. Commun.*, 1992, 1659.

13 R. Corriu, C. Reyé, A. Medhi, G. Dubois, C. Chuit, F. Denat, B. Roux-Fouillet, R. Guilard and G. Lagrange, *Fr. Pat.*, 9800785, 1998.

14 C. Chuit, R. J. P. Corriu, G. Dubois and C. Reyé, *Chem. Commun.*, 1999, 723.

15 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd edn., Academic Press, New York, 1982.

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