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ChemComm
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Mesoporous hybrid materials containing functional organic groups inside both the framework and the channel pores†

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Received (in Cambridge, UK) 1st March 2002, Accepted 15th May 2002
First published as an Advance Article on the web 27th May 2002

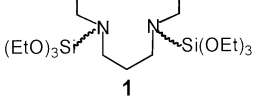
DOI: 10.1039/b202179j

Mesoporous hybrid materials containing cyclam moieties inside the framework have been obtained by using a neutral templating route; these materials with large pores and narrow pore size distribution are shown to be particularly suitable for grafting functional organic groups inside the channel pores giving rise to bifunctional hybrid materials.

In 1999, several groups independently reported the preparation of a new class of hybrid materials.[1–4] These materials are formed by the hydrolysis and polycondensation of bis(trialkoxysilyl) organic precursors in the presence of a surfactant template.[5,6] These periodic mesoporous organosilicas (PMOs) are novel in that the organic fragments and the inorganic oxide are homogeneously distributed within the framework in which they are covalently linked. This class of hybrid materials is of considerable interest and opens up an extraordinary field of investigation, as the properties of the framework (optical, electronic, magnetic) may be modified by changing the bridging organic group. This would be possible provided that the right experimental conditions for the introduction of the appropriate organic group inside the framework could be found. It is worth noting that very few examples of PMOs incorporating functional organic groups have been prepared up to now.[2,4,6,7]

Our interest in hybrid materials able to strongly chelate metal cations led us to incorporate within a silica matrix 1,4,8,11-tetraazacyclotetradecane[8] (cyclam), well known for its remarkable binding ability toward transition metals.[9,10] This was done by hydrolysis and polycondensation of the precursor **1** in the absence of surfactant.[8] Since such systems can give rise to materials presenting interesting physical properties, as a function of the nature of the chelated salt, we have also investigated the preparation of cyclam-containing hybrid materials in the presence of a surfactant template with the aim of locating the cyclam moieties inside the framework.

In this communication, we report an original synthesis of mesoporous cyclam-containing hybrid materials in high yield, with a narrow pore size distribution, using a neutral templating route. We show that the surface of the pores of such materials is particularly suitable for grafting functional organic groups inside the channel pores giving rise to bifunctional hybrid materials.



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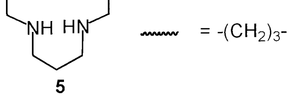

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We have adopted a self-assembly strategy avoiding the use of an acid at any stage of the preparation. Indeed, the protonation of the tetraazamacrocycle could greatly modify the arrangement of the organic moieties.[11] Therefore, we first chose the triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as structure directing agent, this surfactant having been widely used in the synthesis of ordered mesoporous materials with large pores.[12,13]

In a typical synthesis, a mixture of Pluronic 123 (2.36 g, 0.40 mmol), H_2O (51.7 g, 2.87 mol), ethanol (5.70 g, 124.0 mmol) and decane (0.04 g, 0.28 mmol) was vigorously stirred in a 100 mL flask until a transparent solution was obtained. This solution was then added to a mixture of TEOS (3.36 g, 16.2 mmol) and **1** (1.82 g, 1.80 mmol). The emulsion was vigorously and regularly stirred for 3 h at room temperature. It was then heated at 60 °C with stirring. The nucleophilic catalyst NaF (0.97 mmol, 41 mg) was then added. The molar ratio of the mixture was: **1**:TEOS:P123:H_2O:ethanol:decane:NaF = 1:9:0.23:1596:69:0.16:0.54. After ageing with regular stirring for 3 days at 60 °C, the solid product was recovered by filtration, washed three times with EtOH then three times with acetone. The template was completely removed (as indicated by the ^{13}C CP MAS NMR spectroscopy) from the as-synthesized material by Soxhlet extraction with ethanol heated under reflux for 24 h. The solid was again recovered by filtration and dried under vacuum at 120 °C for 12 h to give the solid **2** as a white powder (2.01 g, 97%).

The N_2 adsorption–desorption isotherm for the sample **2** showed a type IV isotherm, characteristic of mesoporous materials with a BET surface area of 420 $m^2\ g^{-1}$, a total pore volume of 0.79 $cm^3\ g^{-1}$ and a narrow pore size distribution centred at 80 Å. It is worth noting that the solid **2′** obtained under the same experimental conditions, in the absence of surfactant is mesoporous but with a very large pore size distribution.

The physical characteristics of the material can be further tuned by changing the parameters of the experimental procedure. Thus, by using *n*-butanol as co-surfactant[14] in place of ethanol, the pore volume and the specific surface of the resulting material **3** were increased (Table 1). The material **4** was prepared in the presence of tergitol 15-S-12 [$C_{15}H_{31}O(CH_2CH_2O)_{12}H$] in place of P123. The pore volume was found to be even larger, as well as the mean pore diameter, the latter

Table 1 Some relevant data of mesoporous hybrid materials prepared from **1** and TEOS in a 1:9 ratio, in H_2O–ROH

Surfactant	ROH	Final material	Organic group:SiO_2[a]	$S_{BET}/m^2\ g^{-1}$	$V_p/cm^3\ g^{-1}$	D_p[b]/Å
P123	EtOH	**2**	1:8	420	0.79	80
P123	*n*-Butanol	**3**	1:8 (1:8.6)	695	0.94	51
Tergitol 15S-12	*n*-Butanol	**4**	1:9.2 (1:8.9)	703	1.46	87

[a] The molar ratio organic group:SiO_2 of the final material was determined from elemental analyses and by TGA analyses (in parentheses). [b] Calculated from the desorption branch by using the BJH method.

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† Electronic supplementary information (ESI) available: ^{29}Si CP MAS NMR spectrum of a representative hybrid material. See http://www.rsc.org/suppdata/cc/b2/b202179j/

Table 2 Grafting of functional organic groups onto the pores of hybrid materials **3** and **4**. Comparison with grafting on silica in parentheses

	3				**4**			
$ZSi(OR)_3$	S_{BET}/m^2 g^{-1}	V_p/cm^3 g^{-1}	$D_p{}^a$/Å	Z group : $SiO_2{}^b$	S_{BET}/m^2 g^{-1}	V_p/cm^3 g^{-1}	$D_p{}^a$/Å	Z group : $SiO_2{}^b$
$Cl(CH_2)_3Si(OMe)_3$	342	0.45	44	1 : 10 (1 : 22)^c	385	0.77	74	1 : 5
$(EtO)_2PO(CH_2)_3Si(OMe)_3$	—	—	—	1 : 11	368	0.71	75	1 : 5
5	266	0.37	43	1 : 13 (1 : 23)^c	300	0.62	73	1 : 6

[a] Calculated from the desorption branch by using the BJH method. [b] Molar ratio inferred from elemental analyses. [c] In parentheses, the molar ratio grafting species : silica prepared from TEOS and under the same conditions as for **3**

attaining the value of 87 Å (Table 1). Both materials **3** and **4** are also mesoporous with a narrow pore size distribution (Fig. 1).

The ^{29}Si CP MAS NMR spectra of different samples display a broad signal at −66.0 ppm attributed to T^3 substructures in addition to two other signals at −100.6 and −108.2 ppm attributed to Q^3 and Q^4 substructures, respectively.

The composition of the final materials was inferred from the results of elemental analysis of Si and N. They were found to be close to those for the original mixtures as indicated in Table 1. These data were corroborated by thermogravimetric analysis (Table 1), (weight loss of the organic group between 250 and 700 °C). A SAXS analysis of samples has shown the presence of channels of smooth surface (POROD-type).[15]

In order to prove the location of the cyclam moieties inside the framework, grafting of functional groups onto the pores was attempted (Scheme 1). For this purpose, samples **3** and **4** were chosen because of their notable difference of pore volumes (Table 1). Functionalised monomers $ZSi(OR)_3$ that were grafted were 3-chloropropyltrimethoxysilane, trimethoxysilylpropyldiethylphosphonate[16] and *N*-triethoxysilylpropylcyclam **5**,[17] all of them allowing subsequent chemical transformation. Treatment of **3** and **4** with a toluene solution of $ZSi(OR)_3$ afforded the corresponding bifunctional materials (Scheme 1), the textural characteristics of which are given in Table 2. The N_2 adsorption–desorption isotherms of hybrid materials after grafting of different functional groups are of type IV, with a narrow pore size distribution. The surface area, pore volume and mean pore diameter decreased significantly after grafting (*cf.* data in Tables 1 and 2). These observations are consistent with the presence of an important quantity of grafted species attached inside the channel pores of the material as confirmed by the results of elemental analysis for the organic groups (Table 2). It is worth noting that the content of grafted species on the hybrid material **4** is notably higher than this grafted on **3** with narrower mean pore diameters. Furthermore, the amount of grafting species on a silica (pore size centred around 200 Å) prepared from TEOS and under the same conditions as for **3** is much less than that obtained from **3** giving a further proof of the location of cyclam moieties inside the framework.

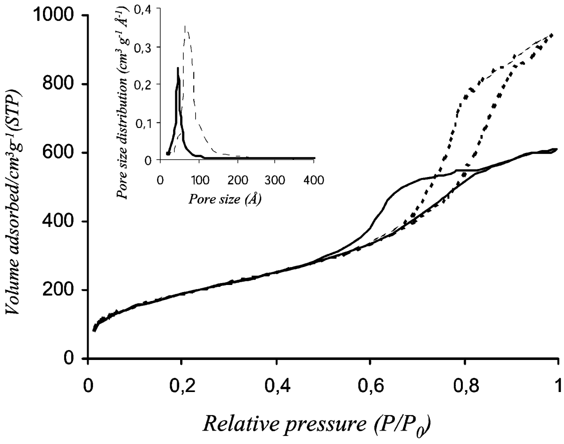
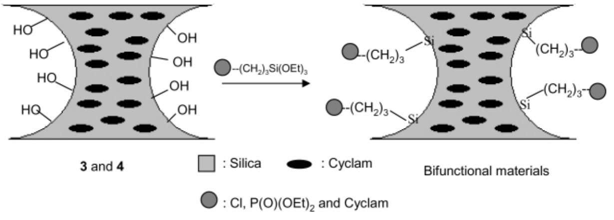


Fig. 1 Nitrogen adsorption–desorption isotherms and pore size distribution plot (inset) of **3** (—) and **4** (---).



Scheme 1 Grafting of functional organic groups onto the pores surface.

In conclusion, we have described a neutral templating route to mesoporous hybrid materials containing cyclam moieties inside the framework. We have shown that the textural characteristics of these materials with a narrow pore size distribution can be modified by changing the experimental conditions. The immobilisation of this large chelating group allows the grafting of functional groups inside channel pores, considerably extending the potential applications of these materials. Thus, the preparation of bimetallic materials with control of the coordination both in the framework and in the pores is in progress.

Notes and references

1 S. Inagaki, S. Guan, Y. Fukushima, T. Oshuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611.
2 B. J. Melde, B. T. Holland, C. F. Blanford and A. Stein, *Chem. Mater.*, 1999, **11**, 3302.
3 T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867.
4 C. Yoshina-Ishii, T. Asefa, N. Coombs, M. J. MacLachlan and G. A. Ozin, *Chem. Commun.*, 1999, 2539.
5 T. Asefa, M. J. MacLachlan, H. Grondey, N. Coombs and G. A. Ozin, *Angew. Chem., Int. Ed.*, 2000, **39**, 1808.
6 Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. Lavan and C. J. Brinker, *J. Am. Chem. Soc.*, 2000, **122**, 5258.
7 M. Alvaro, B. Ferrer, V. Fornès and H. Garcia, *Chem. Commun.*, 2001, 2546.
8 G. Dubois, R. J. P. Corriu, C. Reyé, S. Brandès, F. Denat and R. Guilard, *Chem. Commun.*, 1999, 2283.
9 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.
10 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
11 G. Dubois, C. Reyé, R. J. P. Corriu, S. Brandès, F. Denat and R. Guilard, *Angew. Chem., Int. Ed.*, 2001, **40**, 1087.
12 O. Muth, C. Schellbach and M. Froba, *Chem. Commun.*, 2001, 2032.
13 H. Zhu, D. J. Jones, J. Zajac, J. Rozière and R. Dutartre, *Chem. Commun.*, 2001, 2568.
14 P. Feng, X. Bu and D. J. Pine, *Langmuir*, 2000, **16**, 5304.
15 G. Porod, *Small Angle X-ray Scattering of X-rays*, John Wiley, New York, 1995.
16 R. J. P. Corriu, L. Datas, Y. Guari, A. Mehdi, C. Reyé and C. Thieuleux, *Chem. Commun.*, 2001, 2568.
17 A. Mehdi, F. Denat, F. Barbette, R. Guilard and G. Lagrange, *World Pat.*, WO 9937399, 1999.