Direct synthesis of ordered mesoporous silica containing iodopropyl groups. A useful function for chemical modifications

Johan Alauzun, Ahmad Mehdi,* Catherine Reyé and Robert Corriu*

Received (in Montpellier, France) 1st March 2007, Accepted 13th March 2007
First published as an Advance Article on the web 30th March 2007
DOI: 10.1039/b703155f

In this paper, we report a clever approach permitting, in one step, the synthesis of ordered (hexagonal phase) mesoporous silica functionalized with iodopropyl groups [$I(CH_2)_3$] located in the pore channels. This material was obtained by the hydrolysis and co-condensation of tetraethylorthosilicate (TEOS) and iodopropyltriethoxysilane ($I(CH_2)_3Si(OEt)_3$) in the presence of P123 as a non-ionic structure-directing agent and hydrogen iodide as an acid catalyst. All materials were characterised by X-ray diffraction measurements, transmission electron spectroscopy, nitrogen adsorption analyses, elemental analyses, and solid-state ^{13}C and ^{29}Si NMR spectroscopy. The accessibility and reactivity of this functional group was investigated, showing the advantage of the iodo group for the introduction of bulky or hydrophilic groups.

Introduction

Ordered mesoporous *organo*silicas constitute a very interesting class of materials due to their potential applications,[1] such as in separation,[2] catalysis,[3] encapsulation[4] and chemical sensing.[5] Such materials have often been prepared by post-synthetic grafting of an organotrialkoxysilane, $RSi(OR')_3$, onto the pore surface of ordered mesoporous silica.[5a,6a,b] This post-synthetic process has allowed the anchoring of a large number of organic groups, including bulky ones.[6c–e] However, this very practical method does not allow control of the loading, and has led to inhomogeneous distributions of the functional groups on the inner pore surfaces.[7] One alternative approach consisted of the introduction of organic groups during the synthesis of the material by the co-condensation of tetraethylorthosilicate (TEOS) and an organotriethoxysilane $RSi(OEt)_3$ in the presence of a structure-directing agent.[8] In this case, the functional groups of the resulting materials were regularly distributed on the pore surfaces.[9]

Though this method overcomes the main drawbacks of the grafting method, it has, however, its own limitations. Indeed, this method requires that the R-group be sufficiently hydrophobic to enter the core of the micelle and not be too bulky so as to avoid perturbation.[10] This means that the introduction of bulky or hydrophilic groups cannot be achieved by this route. Therefore, post-modification of the functionalized mesoporous materials by direct synthesis could be an alternative to obtaining ordered mesoporous materials with large and/or hydrophilic functional groups regularly distributed. Indeed, use of the post-modification method could avoid the design and synthesis of new organosilane precursors and reduce the difficulty in obtaining ordered mesoporous materials containing large and/or hydrophilic functional groups.

The iodopropyl pendant group could be a particularly useful candidate for subsequent modification since iodo is a very good leaving group in nucleophilic displacement and a much better one than chloro, which was previously introduced into **SBA-15** mesoporous silica.[11]

In the present paper, we report a direct synthesis of ordered mesoporous silicas containing iodopropyl groups located in the pore channels. The ability of these materials to immobilise various species is shown and compared to that of ordered mesoporous silicas containing chloropropyl groups.

Experimental

General procedures

Triblock copolymer ($EO_{20}PO_{70}EO_{20}$ with PEO = poly(ethylene oxide) and PPO = poly(propylene oxide)) Pluronic P123, 3-chloropropyltriethoxysilane, tetraethylorthosilicate (TEOS), sodium fluoride (NaF), hydrogen iodide (HI), triethylphosphite, ethylenediamine, dipropylenetriamine and ephedrin were purchased from Sigma-Aldrich and used as supplied. Tris(2-cyanoethyl)phosphine was purchased from Sterm Chemicals. 1,4,8,11-tetraazacyclotetradecane (cyclam) was purchased from Chematech. 3-Iodopropyltriethoxysilane was prepared by a halogen exchange reaction between 3-chloropropyltriethoxysilane and NaI according to a previously described procedure.[12]

CP-MAS ^{29}Si and ^{13}C solid-state NMR spectra were recorded on a BRUKER FTAM 300, in the latter case using the TOSS technique. The repetition time was 5 s for ^{13}C and 10 s for ^{29}Si, with contact times of 3 ms for ^{13}C and 5 ms for ^{29}Si. The duration of the ^{1}H pulse was 4.2 μs for ^{13}C and 4.5 μs for ^{29}Si, and the MAS rate was 10 kHz for ^{13}C and 5 kHz for ^{29}Si. Chemical shifts (δ/ppm) were referenced to Me_4Si (^{13}C and ^{29}Si).

Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2010 analyser (using 74 points and starting from 0.01 as the

---

Institut Charles Gerhardt, UMR 5253 CNRS, Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Place E. Bataillon, F-34095 Montpellier Cedex 5, France. E-mail: ahmad.mehdi@univ-montp2.fr; Fax: +33 4 6714 3852; Tel: +33 4 6714 3038

value for the relative pressure). The average pore diameters were calculated by the BJH method.

Powder X-ray diffraction experiments were carried out using a high resolution Bonse–Hart camera with two germanium channel cuts for very small q values. The wavelength used was 1.542 Å (Cu-K$_\alpha$ radiation).

Transmission Electron Microscopy (TEM) images were gathered at 100 kV on a JEOL 1200 EXII microscope. Samples for TEM measurements were prepared using ultramicrotomy techniques and then deposited on copper grids.

Yields of substitution were determined by the elemental analyses of introduced N and P atoms, and the residual Cl and I atoms. Elemental analyses of Si, C, N, P, Cl and I were performed by the Service Central d'Analyse (CNRS, Vernaison, France).

Syntheses

Preparation of SBA$_x$-Cl (x = 19 and 30). **SBA$_x$-Cl** was prepared according to the procedure previously described.[11]

Preparation of SBA$_x$-I (x = 19 and 30). **SBA$_x$-I** was prepared according to the same procedure. The preparation of **SBA$_{19}$-I** is given as an example.

SBA$_{19}$-I. 4.0 g of P123 ($EO_{20}PO_{70}EO_{20}$) was dissolved in an aqueous HI solution (160 mL, pH ≈ 1.5). This solution was poured into a mixture of TEOS (8.85 g, 42.56 mmol) and 3-iodopropyltriethoxysilane (**1**) (0.74 g, 2.24 mmol) at ambient temperature. The mixture was stirred for 90 min, giving rise to a microemulsion. After heating this perfectly transparent solution at 60 °C, a small amount of NaF (80 mg) was added with stirring to induce polycondensation. The molar composition of the reaction mixture was $0.04\ F^- : 1\ TEOS : 0.05\ \mathbf{1} : 0.02\ P123 : 0.12\ HI : 220\ H_2O$. The mixture was left for 72 h at 60 °C with stirring. The resulting solid was filtered and washed with acetone. The surfactant was removed by hot ethanol extraction in a Soxhlet apparatus over 24 h. After filtration and drying at 120 °C under vacuum, 2.75 g (2.02 mmol, 90%) of **SBA$_{19}$-I** was obtained as a white solid.

Modification of SBA$_{19}$-I

SBA$_{19}$-cyc. To a solution of cyclam (0.45 g, 2.20 mmol) in acetonitrile (90 mL) and triethylamine (0.48 g, 4.74 mmol) as base was added 2.15 g of **SBA$_{19}$-I** (1.58 mmol) at room temperature. The resulting mixture was stirred and heated under reflux for 1 h. The solid was recovered by filtration and washed 3 times with hot chloroform and 3 times with hot ethanol to remove the excess cyclam. After drying at 120 °C overnight under vacuum, 2.05 g (91%) of **SBA$_{19}$-cyc** was obtained as a white powder.

SBA$_{19}$-tria. To a solution of dipropylenetriamine (0.11 g, 0.84 mmol) in toluene (15 mL) and triethylamine (0.13 g, 1.32 mmol) as base was added 0.60 g of **SBA$_{19}$-I** (0.44 mmol) at room temperature. The resulting mixture was stirred and heated under reflux for 4 h. The solid was recovered by filtration and washed twice with toluene. After drying at 120 °C overnight under vacuum, 0.58 g (97%) of **SBA$_{19}$-tria** was obtained as a white powder.

SBA$_{19}$-dia. To a solution of ethylenediamine (50.1 mg, 0.84 mmol) in toluene (15 mL) and triethylamine (0.13 g, 1.32 mmol) as base was added 0.60 g of **SBA$_{19}$-I** (0.44 mmol) at room temperature. The resulting mixture was stirred and heated under reflux for 8 h. The solid was recovered by filtration and washed twice with toluene. After drying at 120 °C overnight under vacuum, 0.61 g (98%) of **SBA$_{19}$-dia** was obtained as a white powder.

SBA$_{19}$-eph. To a solution of ephedrine (90.8 mg, 0.55 mmol) in toluene (20 mL) and triethylamine (86 mg, 0.87 mmol) as base was added 0.40 g of **SBA$_{19}$-I** (0.29 mmol) at room temperature. The resulting mixture was stirred and heated under reflux for 24 h. The solid was recovered by filtration and washed twice with toluene. After drying at 120 °C overnight under vacuum, 0.38 g (93%) of **SBA$_{19}$-eph** was obtained as a white powder.

SBA$_{19}$-Pho. A mixture of triethylphosphite (20 mL) and 0.30 g of **SBA$_{19}$-I** (0.22 mmol) was stirred and heated under reflux for 4 h. The solid was recovered by filtration and washed twice with acetone. After drying at 120 °C overnight under vacuum, 0.30 g (97%) of **SBA$_x$-Pho** was obtained as a white powder.

SBA$_{19}$-P$^+$. To a solution of tris(2-cyanoethyl)phosphine (0.64 g, 0.84 mmol) in acetonitrile (50 mL) was added 0.60 g of **SBA$_{19}$-I** (0.44 mmol) at room temperature. The resulting mixture was stirred and heated under reflux for 4 h. The solid was recovered by filtration and washed twice with acetonitrile. After drying at 120 °C overnight under vacuum, 0.56 g (58%) of **SBA$_x$-P$^+$** was obtained as a white powder.

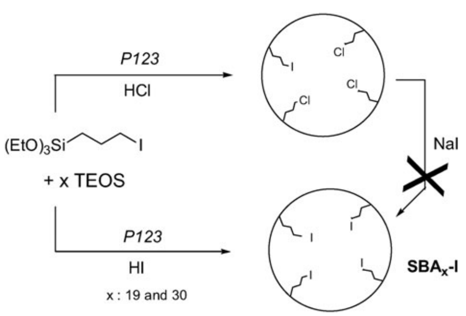
Results and discussion

Preparation and characterization of ordered iodopropyl-functionalized mesoporous silica

Ordered mesoporous silicas containing variable quantities of iodopropyl groups were synthesized by the co-condensation of a mixture of iodopropyltriethoxysilane ($I(CH_2)_3Si(OEt)_3$) and tetraethylorthosilicate (TEOS), in the presence of P123 as a structure-directing agent in a low acidity (HI) medium (see the Experimental section). The functionalized materials obtained after removal of the surfactant were named **SBA$_x$-I**, x indicating the number of molar equivalents of TEOS *per* iodopropyl group in the initial mixture.

The key step in the synthetic procedure was the use of HI instead of HCl as the catalyst. Indeed, when HCl was used, the co-condensation of 3-iodopropyltriethoxysilane and TEOS, in the presence of P123, gave rise to an ordered mesoporous silica containing mostly chloropropyl groups (70%), in addition to some iodopropyl groups. Furthermore, it is worth noting that no exchange reaction occurred when ordered mesoporous silica containing chloropropyl groups[11] was treated with NaI in excess (Scheme 1).

Table 1 summarizes the physicochemical and textural properties of materials **SBA$_x$-I** and **SBA$_x$-Cl**. The composition of the final materials was inferred from the results of Si, C, I and Cl elemental analyses. These were found to be close



Scheme 1 Preparation of **SBA$_x$-I** materials.

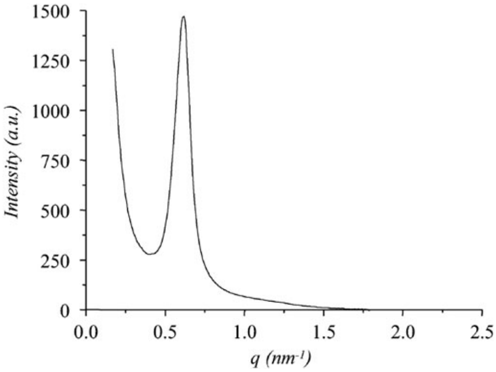


Fig. 1 XRD pattern of **SBA$_{19}$-I**.

to those for the original mixtures, thus showing that the chloro and iodo groups survived under the experimental conditions.

Powder X-ray diffraction patterns of the samples exhibited an intense diffraction peak corresponding to the d_{100} spacing. The XRD pattern of sample **SBA$_{19}$-I** is reported as an example in Fig. 1. Although no reflections higher than d_{100} have been clearly resolved, Pinnavaia *et al.* have shown that similar single reflection materials can still exhibit local hexagonal symmetry.[13] The identification of the first Bragg peak as a reflection on the (100) scattering planes of the hexagonal structure allows the determination of the hexagonal lattice parameter a_0 (see Table 1).

The transmission electron microscopy (TEM) micrograph shown in Fig. 2 confirms that the material exhibits local hexagonal symmetry.

The N_2 adsorption–desorption isotherm of material **SBA$_{19}$-I** is of type IV, characteristic of mesoporous materials with a narrow pore size distribution (Fig. 3). Numerical data for these materials is given in Table 1. It is worth noting that the S_{BET} of these materials are high (800 to 900 $m^2\ g^{-1}$) with large pore volumes (0.8 to 1 $cm^3\ g^{-1}$).

The incorporation of iodopropyl groups into the mesoporous materials and the removal of the surfactant were confirmed by solid-state NMR spectroscopy. ^{13}C CP-MAS NMR spectra of **SBA$_x$-I** revealed that the organic groups remained intact, as shown by the signals at 27.1 (CH_2–I), 16.4 (CH_2–CH_2–CH_2) and 8.1 ppm (CH_2–Si). A typical ^{29}Si CP-MAS NMR spectrum displayed signals at −92.2, −101.0 and −110.1 ppm, attributed to Q^2, Q^3 and Q^4 substructures, respectively, denoting high cross-linking of the species. An additional signal at −65.5 ppm, assigned to a T^3 substructure, revealed fully cross-linked organosilsesquioxane species.

Reactivity of iodopropyl groups immobilized on SBA-15 mesoporous silica

We studied the accessibility and reactivity of iodo groups located within the channel pores of materials **SBA$_{19}$-I** and compared them to those of chloro groups within **SBA$_{19}$-Cl**. All the results are reported in Table 2 and Scheme 2.

Firstly, the nucleophilic displacement of iodo groups by cyclam moieties was investigated. Indeed, we have previously shown that cyclam moieties located within the pore channels of mesoporous silica allow the chelation of different transition metal ions[11] and even europium ions.[14] This post-modification was achieved by treating **SBA$_{19}$-I** with 1.4 equiv. of cyclam in acetonitrile under reflux. 95% iodo substitution was obtained after 1 h under reflux while, using the same experimental conditions, 32 h were necessary to obtain 90% chloro substitution within **SBA$_{19}$-Cl**. As shown previously,[11] textural properties are maintained after chemical modification. Thus, the N_2 adsorption–desorption isotherm of **SBA$_{19}$-cyc** (Fig. 3) is type IV, characteristic of mesoporous materials, and very similar to that of **SBA$_{19}$-I**. In addition, the powder X-ray diffraction pattern of **SBA$_{19}$-cyc** is also very similar to that of **SBA$_{19}$-I**, indicating that the structure was maintained even after post-modification of the material.

Mesoporous silicas have often been successfully employed as supports for various chiral catalysts. For that purpose, chloropropyl groups grafted onto mesoporous silica were one of the linkers used for the subsequent introduction of chiral ligands.[15] We show here that ephedrine can be easily introduced into ordered mesoporous silica thanks to the iodopropyl group, and with a much better yield than *via* the chloropropyl linker. The incorporation of ephedrine in the resulting

Table 1 Physicochemical characteristics of functionalized mesoporous silica[a]

	SBA$_{19}$-I	**SBA$_{30}$-I**	**SBA$_{19}$-Cl**	**SBA$_{30}$-Cl**
$S_{BET}/m^2\ g^{-1}$	908	811	866	919
$V_p/cm^3\ g^{-1}$	1.00	0.77	0.96	1.02
D_p[b]/nm	5.8	5.6	6.1	6.2
a_0/nm	11.2	11.8	11.9	12.1
Wall thickness[c]/nm	5.3	6.2	5.8	5.9
Organic groups content[d]/ mmol g^{-1}	0.65 (0.73)	0.47 (0.49)	0.72 (0.78)	0.50 (0.52)

[a] S_{BET} = BET surface area; V_p = pore volume; D_p = pore diameter. [b] Estimated from the BET surface area. [c] From $a_0 - D_p$ with $a_0 = 2d_{100}/3^{0.5}$. [d] Calculated from the elemental analysis; theoretical values are in parentheses.

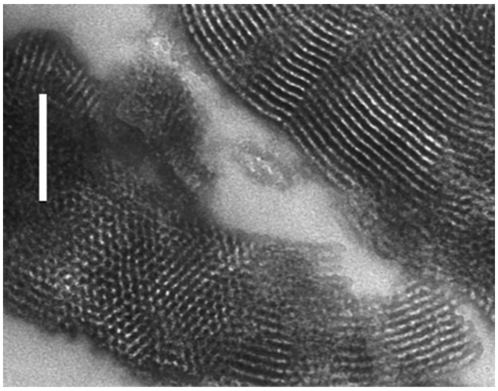


Fig. 2 TEM micrograph of **SBA$_{19}$-I**. Scale bar = 100 nm.

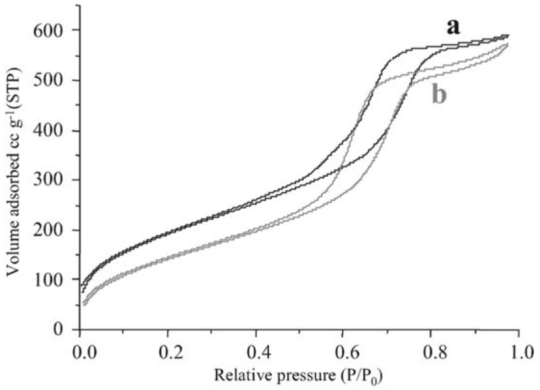


Fig. 3 Nitrogen adsorption–desorption isotherms of (a) **SBA$_{19}$-I** and (b) **SBA$_{19}$-cyc**.

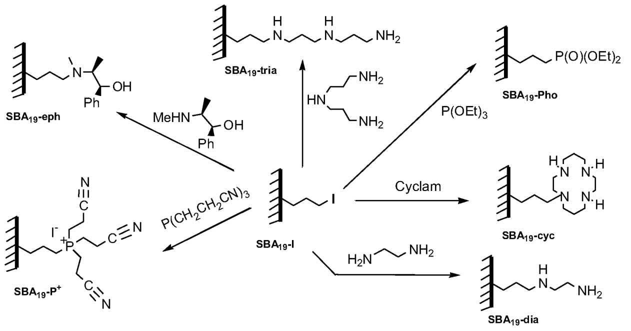
material was confirmed by solid-state NMR spectroscopy. The ^{13}C CP-MAS spectrum of **SBA$_{19}$-eph** displayed three signals at 141.3, 125.9 and 115.2 ppm, attributed to the aromatic group, and two additional signals at 74.3 and 57.4 ppm, assigned, respectively, to *C*H–O and *C*H–N carbon atoms. It also exhibited a broad signal between 11.3 and 18.7 ppm, attributed to CH$_2$ and CH$_3$ groups.

As ethylenediamine and dipropylenetriamine are considered very efficient for the chelation of transition metal salts,[16] their anchoring within **SBA$_{19}$-I** was attempted. We found that 100% displacement of iodo groups was achieved after 8 and 4 h of treatment with ethylenediamine and dipropylenetriamine, respectively (see the Experimental section). In contrast, a 48 h reaction was necessary under the same experimental conditions for the quantitative substitution of chloro groups within **SBA$_{19}$-Cl** by dipropylenetriamine. Furthermore, from N, I and Cl elemental analyses, it can be concluded that the anchoring of diamine and triamine occurs essentially by monosubstitution. It is worth noting that neither hydrophilic group can be introduced into the channel pores of mesoporous silica by direct synthesis, especially in acidic media.[16c]

Table 2 Chemical modifications of **SBA$_{19}$-I** and **SBA$_{19}$-Cl**

	SBA$_{19}$-I		**SBA$_{19}$-Cl**	
Reagents	Yield (%)^a	Time/h	Yield (%)^a	Time/h
Cyclam	95	1	90	32
Ephedrine	91	24	62	48
Diamine	100	8	—	—
Triamine	100	4	100	48
Triethylphosphite	100	4	20	72
Phosphine	58	24	8	48

^{a} Substitution yields calculated by elemental analysis.



Scheme 2 Post-modification of **SBA$_{19}$-I**.

The Arbuzov reaction can be achieved by the treatment of **SBA$_{19}$-I** with triethylphosphite, giving rise to **SBA$_{19}$-pho** functionalized with phosphonate groups (Scheme 2, Table 2). After 4 h under reflux, the reaction was found to be quantitative. The solid-state ^{31}P NMR spectrum of **SBA$_{19}$-pho** displayed a single resonance at 31.6 ppm, characteristic of phosphonate groups. In contrast, treatment of **SBA$_{19}$-Cl** under the same conditions afforded only 7% **SBA$_{19}$-pho** and about 20% conversion after 72 h (Table 2). It is worth noting that it is the first time that such a chemical transformation has been achieved within such a material, thus avoiding the tedious preparation of a trialkoxysilylalkyldiethylphosphonate. Phosphonate groups can be useful for many purposes, including the stabilization of metal or metal oxide nanoparticles within functionalized ordered mesoporous silica.[17]

Finally, the attachment of tris(2-cyanoethyl)phosphine, thanks to the iodopropyl group, was also realized, giving rise to **SBA$_{19}$-P$^+$** in 58% yield after 24 h (Scheme 2). The moderate yield obtained in this case could be due to steric hindrance of the ligand. The solid-state ^{31}P NMR spectrum of **SBA$_{19}$-P$^+$** displayed a single resonance at 36.5 ppm, characteristic of a phosphonium salt. It is worth noting that no more than 8% attachment of this same phosphine was achieved starting from **SBA$_{19}$-Cl**. This ligand is of great interest to us. Indeed, it can be easily hydrolysed to the tris(2-carboxyethyl) phosphonium salt, becoming a very efficient multidentate complexing ligand for transition metal salts[18] or lanthanides, similar to the corresponding nitrilotriacetic salt.[19]

Conclusions

We have described an adapted route allowing the direct synthesis of ordered mesoporous silica containing iodopropyl pendant groups. By comparison with the chloropropyl group, we have shown that the iodo group allows easier and faster chemical transformations, giving rise quantitatively to a variety of mesoporous materials with large and/or hydrophilic functional groups located within the channel pores that are difficult or impossible to obtain by other routes.

Acknowledgements

The authors thank Dr Philippe Dieudonné (GDPC, Université Montpellier II, France) for SAXS measurements, and the CNRS and the Université Montpellier II for financial support.

References

1 C. Sanchez, B. Julian, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559.

2 (*a*) K. W. Gallis, J. T. Araujo, K. J. Duff, J. G. Moore and C. C. Landry, *Adv. Mater.*, 1999, **11**, 1452; (*b*) T. Salesch, S. Bachmann, S. Brugger, R. Rabelo-Schaefer, K. Albert, S. Steinbrecher, E. Plies, A. Mehdi, C. Reyé, R. J. P. Corriu and E. Lindner, *Adv. Funct. Mater.*, 2002, **2**, 134; (*c*) J. Zhao, F. Gao, Y. Fu, W. Jin, P. Yang and D. Zhao, *Chem. Commun.*, 2002, 752; (*d*) M. Mesa, L. Siera, B. Lopez, A. Ramirez and J.-L. Guth, *Solid State Sci.*, 2003, **5**, 1303; (*e*) T. Martin, A. Galarneau, F. DiRenzo, D. Brunel and F. Fajula, *Chem. Mater.*, 2004, **16**, 1725.

3 (*a*) M. Benitez, G. Bringmann, M. Dreyer, H. Garcia, H. Ihmels, M. Waidelich and K. Wissel, *J. Org. Chem.*, 2005, **70**, 2315; (*b*) F. Hoffman, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216.

4 H. Djojoputro, X. F. Zhou, S. Z. Qiao, L. Z. Wang, C. Z. Yu and G. Q. Lu, *J. Am. Chem. Soc.*, 2006, **128**, 6320.

5 (*a*) L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, 1997, **9**, 500; (*b*) X. Feng, G. E. Fryxxell, L. Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923; (*c*) B. Johnson-White, M. Zeinali, K. Shaffer, C. Patterson, P. Charles and M. Markowitz, *Biosens. Bioelectron.*, 2007, **22**, 1154.

6 (*a*) A. Cauvel, G. Renard and D. Brunel, *J. Org. Chem.*, 1997, **62**, 749; (*b*) P. M. Price, J. H. Clark and D. J. Macquarrie, *J. Chem. Soc., Dalton Trans.*, 2000, 101; (*c*) S.-G. Shyu, S.-W. Cheng and D.-L. Tzou, *Chem. Commun.*, 1999, 2337; (*d*) C. M. Crudden, D. Allen, M. D. Mikoluk and J. Sun, *Chem. Commun.*, 2001, 1154; (*e*) C. Gonzalez-Arellano, A. Corma, M. Iglesias and F. Sanchez, *Adv. Synth. Catal.*, 2004, **346**, 1758.

7 (*a*) D. J. Macquarrie, D. B. Jackson, J. E. J. Mdoe and J. H. Clark, *New J. Chem.*, 1999, **23**, 539; (*b*) A. Walcarius and C. Delacôte, *Chem. Mater.*, 2003, **15**, 4181.

8 (*a*) S. L. Burkett, S. D. Sims and S. Mann, *Chem. Commun.*, 1996, 1367; (*b*) D. J. Macquarrie, *Chem. Commun.*, 1996, 1961; (*c*) M. H. Lim, C. F. Blanford and A. Stein, *J. Am. Chem. Soc.*, 1997, **119**, 4090; (*d*) L. Mercier and T. J. Pinnavaia, *Chem. Mater.*, 2000, **12**, 188.

9 (*a*) M. H. Lim and A. Stein, *Chem. Mater.*, 1999, **11**, 3285; (*b*) R. J. P. Corriu, C. Hoarau, A. Mehdi and C. Reyé, *Chem. Commun.*, 2000, 71; (*c*) R. J. P. Corriu, F. Embert, Y. Guari, A. Mehdi and C. Reyé, *Chem. Commun.*, 2001, 1116; (*d*) R. Mouawia, A. Mehdi, C. Reyé and R. J. P. Corriu, *New J. Chem.*, 2006, **1**, 1077.

10 A. Mehdi, C. Reyé, S. Brandès, R. Guilard and R. J. P. Corriu, *New J. Chem.*, 2005, **29**, 965.

11 R. J. P. Corriu, A. Mehdi, C. Reyé and C. Thieuleux, *Chem. Mater.*, 2004, **16**, 159.

12 V. Matsura, Y. Guari, J. Larionova, C. Guerin, A. Caneschi, C. Sangregorio, E. Lancelle-Beltran, A. Mehdi and R. J. P. Corriu, *J. Mater. Chem.*, 2004, **14**, 3026.

13 (*a*) P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865; (*b*) P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.

14 R. J. P. Corriu, A. Mehdi, C. Reyé, C. Thieuleux, A. Frenkel and A. Gibaud, *New J. Chem.*, 2004, **28**, 156.

15 (*a*) P. Sutra and D. Brunel, *Chem. Commun.*, 1996, 2485; (*b*) S. J. Bae, S.-W. Kim, T. Hyeon and B. Moon Kim, *Chem. Commun.*, 2000, 31; (*c*) S. Abramson, M. Laspéras, A. Galarneau, D. Desplantier-Giscard and D. Brunel, *Chem. Commun.*, 2000, 1773; (*d*) H. M. Lee, S.-W. Kim, T. Hyeon and B. M. Kim, *Tetrahedron: Asymmetry*, 2001, **12**, 1537; (*e*) A. Lee, W. Kim, J. Lee, T. Hyeon and B. M. Kim, *Tetrahedron: Asymmetry*, 2004, **15**, 2595.

16 (*a*) M. C. Burleigh, M. A. Markowitz, M. S. Spector and B. P. Gaber, *Chem. Mater.*, 2001, **13**, 4760; (*b*) M. C. Burleigh, S. Dai, E. W. Hagaman and J. S. Lin, *Chem. Mater.*, 2001, **13**, 2537; (*c*) T. Yokoi, H. Yoshitake and T. Tatsumi, *J. Mater. Chem.*, 2004, **14**, 951.

17 Y. Guari, K. Soulantica, K. Philippot, C. Thieuleux, A. Mehdi, C. Reyé, B. Chaudret and R. J. P. Corriu, *New J. Chem.*, 2003, **7**, 1029.

18 A. Krezel, R. Latajka, G. D. Bujacz and W. Bal, *Inorg. Chem.*, 2003, **42**, 1994.

19 W. Li, R. Wang, S. Si and Y. Li, *J. Mol. Struct.*, 2004, **27**, 694.