View Online

Downloaded by Technische Universitat Braunschweig on 21 October 2010
Published on 17 March 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00741E

Influence of the alkyl linker in the structuring of bridged silsesquioxanes obtained by self-recognition properties

G. Arrachart, A. Bendjerriou, C. Carcel, J. J. E. Moreau and M. Wong Chi Man*

Received (in Montpellier, France) 9th December 2009, Accepted 2nd February 2010
First published as an Advance Article on the web 17th March 2010
DOI: 10.1039/b9nj00741e

A bridged silsesquioxane was obtained from a monosilylated precursor derivative of ureidopyrimidinone, which combines self-assembling properties and hydrophobic interaction of a long alkyl linker (10 carbons). The formation of the organic bridge was promoted through dimerisation *via* the 4 H-bonds of the ureidopyrimidinone functionality. The association of the organic bridge was brought by the hydrophobic interactions of the long alkylene chains between the organic bridges and the terminal hydrolysable trialkoxysilyl functionality. The self-assembling and structuring of the molecular precursor was transcribed to the resulting hybrid bridged silsesquioxanes after hydrolysis–condensation in aqueous acidic conditions as shown by a set of spectroscopic methods. The long hydrocarbon chain greatly influences the structuring and the morphology of the hybrid material.

Introduction

Organo-bridged silsesquioxanes are a family of hybrid organic–inorganic materials prepared by sol–gel process of molecular precursors containing an organic bridging group covalently bonded to two hydrolysable trialkoxysilyl or trichlorosilyl groups.

Due to the stability of the Si–C bond towards the hydrolysis and condensation, bridged silsesquioxanes can be prepared with a broad range of organic bridging groups incorporated as an integral part of the network.[1–3] The ability to control the structure of materials on the nanoscale is of great interest for the design and improvement of material properties. In this field, utilization of surfactant as an external structuring agent represents a way to form periodic mesoporous hybrid materials.[4–8] Recently, the self-directed assembly through intermolecular interactions (hydrogen-bonding, π–π, and/or hydrophobic interactions) between the organic bridging fragments has been used to generate ordered hybrid silicates in the absence of a templating agent.[9–14] In all cases, these organo-bridged silsesquioxanes were obtained from bis-silylated organic precursors $(RO)_3Si–X–Si(OR)_3$, (X = organic bridging fragment).

The construction of bridged silsesquioxanes from two distinct monosilylated precursors $(EtO)_3SiR–R'(SiOEt)_3$ (R–R′ representing the organic bridging unit with R connected to R′ through H-bonding) represents an interesting route to: (i) direct the hierarchical structuring of the materials,[15,16] (ii) to introduce multifunctionalities from the starting mixture of the precursors[17] and (iii) to consequently have the possibility to adjust and optimise the properties of the hybrids.

We developed this new concept to prepare such organo-bridged silsesquioxanes starting from monosilylated precursors capable of forming the bridging unit by molecular recognition properties (Table 1).

We recently reported two different systems, the first being a system starting from two different monosilylated precursors, in which the two different organic fragments can interact with each other *via* a complementary H-bond to form the bridging unit (Table 1 – complementary system). Organo-bridged silsesquioxanes from adenine (A)–thymine (T) base pairs (2 complementary hydrogen bonds) have been synthesized.[13] The characterization of the H-bond networks, in both homo- and hetero-assemblies, has been emphasized by using ^1H solid-state NMR and FT-IR spectroscopy.[18] In this context we have also exploited the molecular recognition properties of the melamine (M)–cyanuric acid (CA) couple (two faces with 3 complementary hydrogen bonds) which gave access to bridged silsesquioxane, when both complementary precursors are silylated, or to imprinted hybrid silica with non-silylated melamine.[19]

A second system using only one monosilylated precursor with self-recognition properties has been studied (Table 1 – self-recognition system). This precursor consists of a silyl derivative of ureidopyrimidinone which dimerises through a 4 H-bonding fragment, thus forming a bis-silylated dimer.[20] This study was focused on the utilization of a short chain linker (3 carbons) between a silicon atom and the main organic fragments. In this case we have demonstrated the transcription of the self-assembly as a dimer from the precursor to the resulting bridged silsesquioxane.

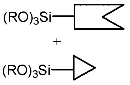
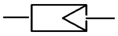
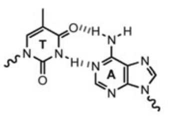
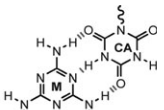
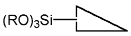
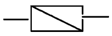
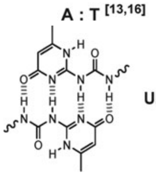
Herein, we report an extension of this latter concept by increasing the length of the linker. In this case, the properties of self-recognition of the organic fragment are combined with the hydrophobic interactions of the linker (10 carbons). Such hydrophobic properties of the long alkyl chains (van der Waals interaction) are expected to play a cooperative role or directly induce the structuring of the resulting bridged silsesquioxane, as already shown by previous studies, on typical bridged silsesquioxanes obtained from single organobridged precursors.[21]

Architectures Moléculaires et Matériaux Nanostructurés, ICG Montpellier (UMR 5253) UMII-CNRS-ENSCM-UMI, 8 rue de l'école, 34296 Montpellier Cedex 05, France. E-mail: michel.wong-chi-man@enscm.fr; Fax: +33 467 144 353; Tel: +33 467 147 219

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2010

View Online

Table 1 Systems involved in the preparation of organo-bridged silsesquioxanes by molecular recognition properties

Precursors capable of molecular recognition	Bridging unit	Systems studied
	Complementary system 	 A : T [13,16]  M : CA [17]
	Self-recognition system 	 UPY [18]

Our aim was to investigate the effect of such hydrophobic interactions in the dimerisation process of the ureidopyrimidinone and in the structural evolution of the precursor and the resulting hybrid material prepared by hydrolytic condensation under acidic conditions.

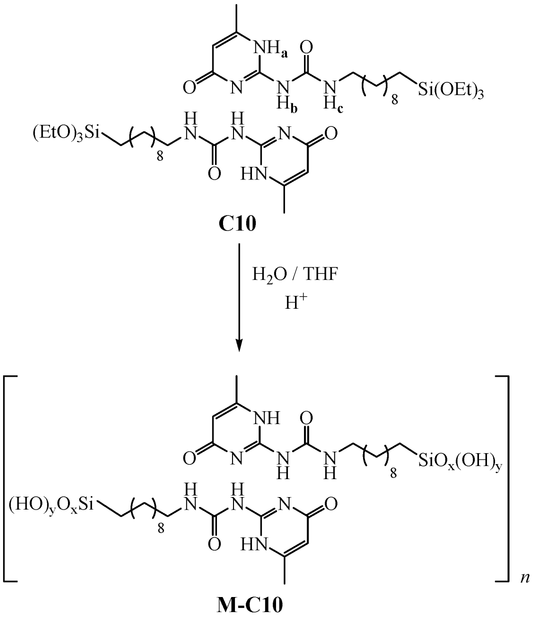
Results and discussion

Ureidopyrimidinone derivatives exist as dimers of 4[1*H*]-pyrimidinone (keto) and pyrimidinol (enol) tautomeric forms.[22] The formation of dimers *via* a DDAA array from the keto form as well as *via* a DADA array from the enol form are possible due to four linear hydrogen bonds preorganized by an intramolecular hydrogen bond. In the case of the silylated molecular precursor with a short chain linker **C3** we have demonstrated that the dimerization takes place *via* the DDAA array.[20]

In the present work we synthesized the corresponding **C10** molecular precursor in one step in high yield by reaction of 6-methylisocytosine with 1.2 molar equivalents of isocyanatoundecenytriethoxysilane. The addition of lipophilic interactions of the long alkyl carbon chains did not affect the dimerisation of the ureidopyrimidinone functionality; precursor **C10** was found to form quadruple hydrogen-bonded DDAA dimers similarly to **C3** (Scheme 1), both in the solid state and in solution, as evidenced by FT-IR and NMR spectroscopies.

The bands observed in the FT-IR spectra (Fig. 1) in the solid state (KBr) and in solution ($CDCl_3$) were consistent with the formation of DDAA dimers in the pyrimidinone tautomer. The bands at 3217 and 3150 cm^{-1} were assigned to hydrogen-bonded NH groups and the stretching vibration of the keto form was found at 1701 cm^{-1}. Bands of free NH groups corresponding to the pyrimidinol tautomer at 2500 cm^{-1} (H-bonded OH groups) were not observed.[23]

The existence of the DDAA arrangement was confirmed by liquid NMR studies. In the ^1H NMR spectrum of **C10** (in $CDCl_3$) the NH proton Ha, Hb and Hc signals were found, at 13, 11.7, and 10.1 ppm respectively, indicating the hydrogen bonding of the array.[23] The presence of the pyrimidinone tautomer was also shown by the presence of the peak at 172 ppm corresponding to the carbonyl carbon of the keto form.



Scheme 1 Preparation of hybrid material **M-C10**.

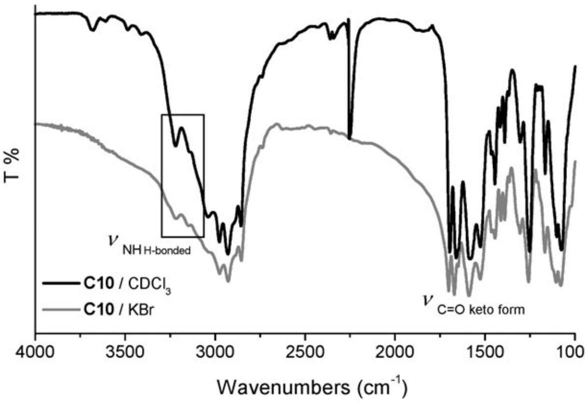


Fig. 1 FT-IR spectra of **C10** in KBr and $CDCl_3$.

X-ray diffraction of **C10** showed a long-range ordered organization, with up to fifth-order reflection of the 001 plane being observed (Fig. 2a). Indeed, the assigned peaks (001, 002, 003 and 005) correspond to the X-ray reflections of a family of reticular planes indicating that the structure of C10 is mainly characterized by a lamellar periodicity in one direction.

Downloaded by Technische Universitat Braunschweig on 21 October 2010
Published on 17 March 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00741E

View Online

Downloaded by Technische Universitat Braunschweig on 21 October 2010
Published on 17 March 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00741E

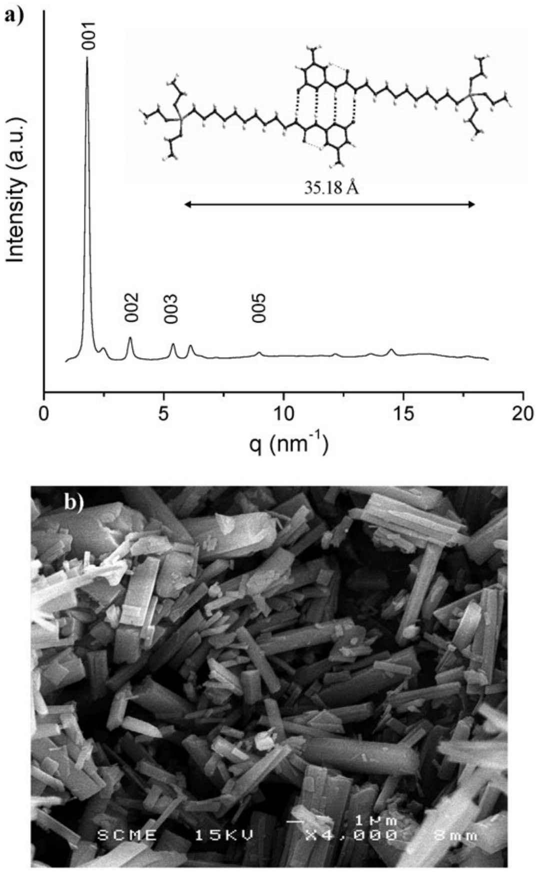


Fig. 2 (a) PXRD and Hyperchem (Mm+) model of **C10**; (b) SEM image of **C10**.

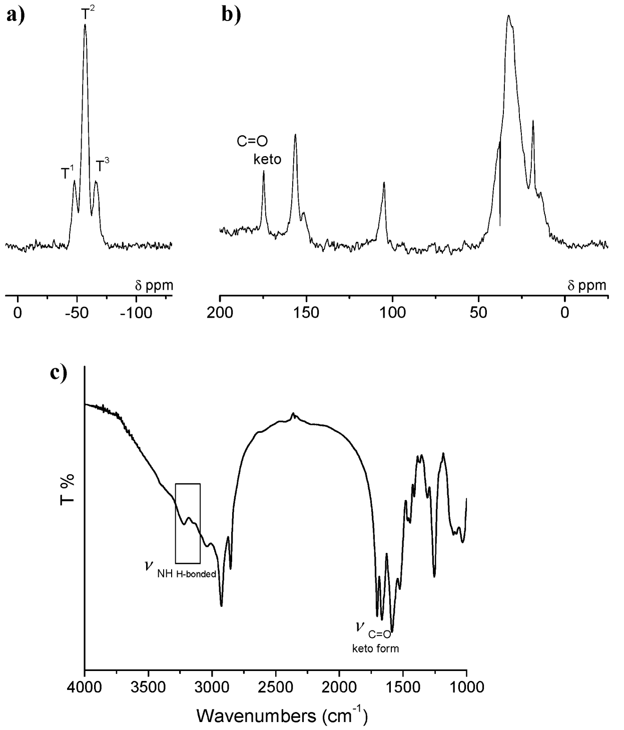


Fig. 3 Characterisation of **M-C10** (a) ^{29}Si NMR spectrum; (b) ^{13}C NMR spectrum; (c) FT-IR spectrum.

Additional reflections might be due to periodicity in another direction, which cannot currently be attributed. The first sharp and intense signal with a distance of 35.1 Å can be assigned to the length of the organic dimer. Indeed, a Hyperchem simulation suggests a length of 35.18 Å separating the two silicon atoms in the dimer. This different structure of the **C10** precursor, in contrast to the hexagonal structure found for the precursor with a short chain linker **C3**,[20] is mainly due to the predominant self-assembling properties of long alkyl chain linkers which tend to arrange into lamellar forms.[24,25]

Interestingly, a hierarchical structure was confirmed by SEM, which showed that the molecular precursor **C10** consists of thin plates (Fig. 2b) instead of the hexagonal rods obtained for **C3**.[20] The morphologies were found to be closely associated to the structure of the precursor.[10*e*]

The self-assembled molecular precursor **C10** was subjected to hydrolysis–condensation with an acidic catalyst in a mixture of water and THF. The precursor was totally dissolved and after a few minutes, a white precipitate appeared in the medium. After 3.5 days without stirring at 65 °C, the material **M-C10** was isolated as a white powder (Scheme 1). The mixture of THF–water at 65 °C facilitates the dissolution of the precursor, but because at room temperature, the reaction was too slow to obtain the hybrid material in a reasonable time.

Solid-state NMR and FT-IR spectroscopies show that the organic fragments were completely retained in the solid (Fig. 3). The ^{29}Si NMR spectrum (Fig. 3a) exhibits a major T^2 (82%) peak at −56.9 ppm and minor T^1 (8%) and T^3 (10%) peaks at respectively −47.9 and −65.8 ppm. This clearly shows that the hybrid **M-C10** is moderately condensed and that no C–Si cleavage occurred during the hydrolysis. In the ^{13}C NMR spectrum (Fig. 3b), the peak at 174.6 ppm indicates the presence of the keto form in the solid. This means that the DDAA array structure has been transcribed to the hybrid **M-C10**.

This was confirmed by the FT-IR spectrum which shows the characteristic bands of the DDAA array: NH bands at 3220 and 3147 cm^{-1} and stretching vibration of the keto form at 1703 cm^{-1}. As for the precursor, no signal corresponding to the pyrimidinol tautomer was observed (Fig. 3c).

Another major point was to see if the lamellar structure from the precursor could be kept in the resulting material. According to the arrangement of the hydrolysable alkoxy groups in the hexagonal structure of precursor **C3**, it appeared that this structure could not be retained after its hydrolysis to yield the resulting material **M-C3**, as demonstrated by the powder X-ray diffractogram of the latter. Indeed, a quite complex structure, which has yet to be solved, was obtained.[20] Considering the lamellar arrangement of the molecules of the precursor **C10**, and the similarity to already described organo-bridged precursors with long alkyl chains,[10*b*,*e*,21] it is likely that the siloxane bond (Si–O–Si) formation is favoured, taking into account the proximity of the hydrolysable functionalities to create the silica network with slight distortion of the flexible alkyl groups.[26] The transcription to the resulting material of the original lamellar structure from the precursor is hence favourable. This is confirmed by the PXR diffractogram of **M-C10** (Fig. 4a) which exhibits three diffraction peaks centred

View Online

Downloaded by Technische Universitat Braunschweig on 21 October 2010
Published on 17 March 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00741E

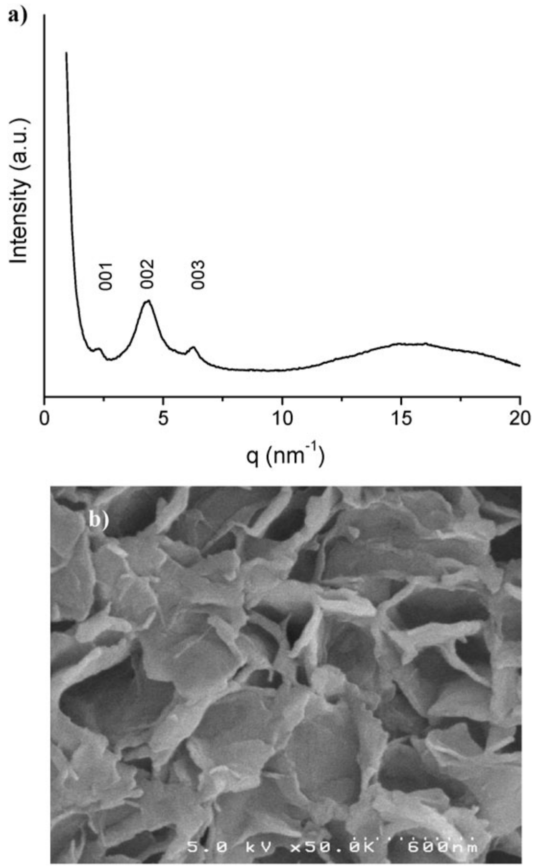


Fig. 4 (a) PXRD of **M-C10**; (b) SEM image of **M-C10**.

at *d* values of 28.9, 14.3 and 9.8 Å respectively, corresponding to the first three harmonic peaks of a lamellar arrangement. Peak broadening and also the decrease of the interlayer spacing observed in the hybrid material results from the reorganization of the material during the formation of the Si–O–Si framework.[27] These may be a consequence of the reversible order–disorder phase transition of the flexible alkylene chain in the all-*trans* and the all-*trans*/gauche configurations.[25,26]

Finally, the SEM images (Fig. 4b) of **M-C10** showed a solid consisting of petal-like structures formed by interconnected thin plates. These are more flexible than the corresponding **C10** precursor, corroborating a less organized structure in the hybrid material.[10*b*,*e*]

Conclusions

We have shown that a novel molecular precursor, ureidopyrimidinone silyl derivative **C10**, forms a stable dimer *via* quadruple hydrogen bonds in the solid state as well as in solution, and demonstrated the preparation of bridged silsesquioxane formed by self-assembly of this dimer. For both the precursor and resulting hybrid material, the DDAA array was observed for the dimers as evidenced by the NMR analyses and IR studies. In contrast to the hexagonal structure from the precursor with a short linker, the molecular precursor adopts a lamellar structure due to the combination of self-recognition properties of the organic fragment and the cooperative properties provided by van der Waals interactions from the long alkyl chain linker. In this case, the original DDAA array and lamellar structure of the precursor has been transcribed to the resulting hybrid material **M-C10**. This result shows the potential of a specifically designed molecular precursor for the development of self-assembled hybrid materials.

Experimental

Synthesis of C10: 2-(3-(triethoxysilyl)decylureido)-6-methyl-4[1*H*]pyrimidone

3-Isocyanatodecyltriethoxysilane[28] (3.32 g, 9.6 mmol) was added under a nitrogen atmosphere to a suspension of 6-methylisocytosine (1 g, 8 mmol) in dry pyridine (15 mL) in a Schlenk tube. The suspension was heated under reflux for 4–5 h, giving a clear solution. The solvent was evaporated and the white precipitate obtained was washed several times with pentane. After filtration the white powder was dried under vacuum.

Yield: 80%. m.p. 86 °C. ^{1}H NMR (δ, ppm, $CDCl_3$): 0.6 (CH_2Si, 2H, t), 1.1–1.3 (CH_3CH_2O and $(CH_2)_8$, 25H, m), 2.2 (CH_3, 3H, s), 3.2 (NCH_2, 2H, q), 3.8 (OCH_2, 6H, qd), 5.7 (=CH, 1H, s), 10.1 (CH_2NH, 1H, s), 11.7 (N=C–NH, 2H, s), 13 ((CH_3)C–NH, 1H, s). ^{13}C NMR (δ, ppm, $CDCl_3$): 10 (CH_2Si), 18 (CH_3CH_2O), 19 (CH_3), 23 (CH_2), 27 (CH_2), 29 (4 CH_2), 33 (CH_2), 40 (CH_2N), 58 (CH_2O), 106 (CH=C), 148 (C=CH), 154 (CO), 156 (C=N), 172 (CO). ^{29}Si NMR (δ, ppm, $CDCl_3$): −44.5. IR (KBr, cm^{-1}): 3217, 3150, 2975, 2927, 2855, 1701, 1669, 1640, 1530, 1259, 1100–1080. MS (FAB+): *m*/*z* (%): 471 (18). Anal. Calcd for $C_{22}H_{42}N_4O_5Si$ (%):C 56.14 H 8.99 N 11.90; Found: C 55.28 H 8.93 N 12.27.

Preparation of hybrid material M-C10

Compound **C10** (177 mg, 0.375 mmol) was completely dissolved in THF (1.2 mL) and water (1.2 mL). Then a solution of HCl (1 M, 37.5 μL) was added and the mixture heated at 65 °C. Precipitation occurred after 5 min. The mixture was filtered after 3.5 days and the resulting solid washed successively with water, ethanol and acetone. After drying under vacuum, **M-C10** was obtained as a white powder (120 mg).

^{13}C CP-MAS NMR (δ, ppm): 14, 18.5, 32.6, 104.9, 151.4, 156.2, 174.6. ^{29}Si CP-MAS NMR (δ, ppm): −47.9, −56.9, −65.8 (T^1, T^2 and T^3 units). IR (KBr, cm^{-1}): 3220, 3147, 3040, 2926, 2854, 1703, 1665, 1590, 1559, 1525, 1251, 1108, 1038.

Acknowledgements

The funding from the CNRS, the French Ministry of Research and the NoE FAME-EMMI are gratefully acknowledged.

References

1 (*a*) K. J. Shea, D. A. Loy and O. W. Webster, *J. Am. Chem. Soc.*, 1992, **114**, 6700; (*b*) D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431; (*c*) K. J. Shea and D. A. Loy, *Chem. Mater.*, 2001, **13**, 3306.
2 (*a*) R. J. P. Corriu, J. J. E. Moreau, P. Thépot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217; (*b*) R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420.

Downloaded by Technische Universitat Braunschweig on 21 October 2010
Published on 17 March 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00741E

3 K. J. Shea, J. J. E. Moreau, D. A. Loy, R. J. P. Corriu and B. Boury, in *Functional Hybrid Materials*, ed. P. Gomez-Romero and C. Sanchez, Wiley-VCH, Weinheim, 2004, p. 50.

4 (*a*) S. Guan, S. Inagaki, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 5660; (*b*) S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, **416**, 304.

5 (*a*) T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867; (*b*) M. J. MacLachlan, T. Asefa and G. A. Ozin, *Chem.–Eur. J.*, 2000, **6**, 2507; (*c*) T. Asefa, C. Yoshina-Ishii, M. J. MacLachlan and G. A. Ozin, *J. Mater. Chem.*, 2000, **10**, 1751.

6 (*a*) B. J. Melde, B. T. Holland, C. F. Blanford and A. Stein, *Chem. Mater.*, 1999, **11**, 3302; (*b*) A. Stein, B. T. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403.

7 (*a*) A. Sayari, S. Hamoudi, Y. Yang, I. L. Moudrakovski and J. R. Ripmeester, *Chem. Mater.*, 2000, **12**, 3857; (*b*) A. Sayari and S. Hamoudi, *Chem. Mater.*, 2001, **13**, 3151; (*c*) W. Wang, W. Zhou and A. Sayari, *Chem. Mater.*, 2003, **15**, 4886.

8 (*a*) 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; (*b*) J. Pang, L. Yang, D. A. Loy, H. Peng, H. S. Ashbaugh, J. Mague, C. J. Brinker and Y. Lu, *Chem. Commun.*, 2006, 1545.

9 (*a*) B. Boury, R. J. P. Corriu, V. Le Strat, P. Delord and M. Nobili, *Angew. Chem., Int. Ed.*, 1999, **38**, 3172; (*b*) B. Boury, F. Ben and R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2001, **40**, 2853; (*c*) B. Boury and R. J. P. Corriu, *Chem. Commun.*, 2002, 795; (*d*) H. Muramatsu, R. J. P. Corriu and B. Boury, *J. Am. Chem. Soc.*, 2003, **125**, 854.

10 (*a*) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man and C. Bied, *J. Am. Chem. Soc.*, 2001, **123**, 1509; (*b*) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man and C. Bied, *Chem.–Eur. J.*, 2003, **9**, 1594; (*c*) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, *J. Am. Chem. Soc.*, 2001, **123**, 7957; (*d*) J. J. E. Moreau, B. P. Pichon, M. Wong Chi Man, C. Bied, H. Pritzkow, J.-L. Bantignies, P. Dieudonné and J.-L. Sauvajol, *Angew. Chem., Int. Ed.*, 2004, **43**, 203; (*e*) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, P. Dieudonné, J.-L. Bantignies and J.-L. Sauvajol, *Chem.–Eur. J.*, 2005, **11**, 1527.

11 (*a*) F. Lerouge, G. Cerveau and R. J. P. Corriu, *New J. Chem.*, 2006, **30**, 1364; (*b*) J. Alauzun, A. Mehdi, R. Mouawia, C. Reyé and R. J. P. Corriu, *J. Sol-Gel Sci. Technol.*, 2008, **46**, 383.

12 (*a*) N. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y.-B. Jiang and C. J. Brinker, *J. Am. Chem. Soc.*, 2002, **124**, 14540; (*b*) N. Liu, D. R. Dunphy, M. A. Rodriguez, S. Singer and C. J. Brinker, *Chem. Commun.*, 2003, 1144.

13 X. Zhang, P. Xie, Z. Shen, J. Jiang, C. Zhu, H. Li, T. Zhang, C. C. Han, L. Wan, S. Yan and R. Zhang, *Angew. Chem., Int. Ed.*, 2006, **45**, 3112.

14 L. Yang, H. Peng, K. Huang, J. T. Mague, H. Li and Y. Lu, *Adv. Funct. Mater.*, 2008, **18**, 1526.

15 (*a*) J. J. E. Moreau, B. P. Pichon, G. Arrachart, M. Wong Chi Man and C. Bied, *New J. Chem.*, 2005, **29**, 653; (*b*) G. Arrachart, C. Carcel, J. J. E Moreau and M. Wong Chi Man, *Materials Forum*, 2007, **31**, 128.

16 (*a*) C. Arnal-Hérault, A. Banu, M. Barboiu, M. Michau and A. Van der Lee, *Angew. Chem., Int. Ed.*, 2007, **46**, 4268; (*b*) C. Arnal-Hérault, M. Barboiu, A. Pasc, M. Michau, P. Perriat and A. Van der Lee, *Chem.–Eur. J.*, 2007, **13**, 6792.

17 (*a*) F. Gelman, J. Blum and D. Avnir, *Angew. Chem., Int. Ed.*, 2001, **40**, 3647; (*b*) F. Gelman, J. Blum and D. Avnir, *New J. Chem.*, 2003, **27**, 205.

18 (*a*) M. Wong Chi Man, G. Arrachart, C. Carcel, J. J. E. Moreau, C. Bonhomme, B. Alonso, F. Babonneau, G. Creff, J.-L. Bantignies, P. Dieudonné, C. Blanc and J.-L. Sauvajol, *Mater. Res. Symp.*, 2007, **1007**, S02–03; (*b*) G. Arrachart, C. Carcel, J. J. E. Moreau, G. Hartmeyer, B. Alonso, D. Massiot, G. Creff, J.-L. Bantignies, P. Dieudonné, M. Wong Chi Man, G. Althoff, F. Babonneau and C. Bonhomme, *J. Mater. Chem.*, 2008, **18**, 392.

19 G. Arrachart, C. Carcel, P. Trens, J. J. E Moreau and M. Wong Chi Man, *Chem.–Eur. J.*, 2009, **15**, 6279.

20 G. Arrachart, G. Creff, H. Wadepohl, C. Blanc, C. Bonhomme, F. Babonneau, B. Alonso, J.-L. Bantignies, C. Carcel, J. J. E. Moreau, P. Dieudonné, J.-L. Sauvajol, D. Massiot and M. Wong Chi Man, *Chem.–Eur. J.*, 2009, **15**, 5002.

21 (*a*) J. J. E. Moreau, B. P. Pichon, C. Bied and M. Wong Chi Man, *J. Mater. Chem.*, 2005, **15**, 3929; (*b*) J. Alauzun, A. Mehdi, C. Reyé and R. J. P. Corriu, *J. Mater. Chem.*, 2005, **15**, 841.

22 (*a*) F. H. Beijer, H. Kooijman, A. L. Spek, R. P. Sijbesma and E. W. Meijer, *Angew. Chem., Int. Ed.*, 1998, **37**, 75; (*b*) F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 6761.

23 (*a*) K. J. H. K. Hirschberg, F. H. Beijer, H. A. Van Aert, P. C. M. M. Magusin, R. P. Sijbesma and E. W. Meijer, *Macromolecules*, 1999, **32**, 2696; (*b*) J. T. Han, D. H. Lee, C. Y. Ryu and K. Cho, *J. Am. Chem. Soc.*, 2004, **126**, 4796.

24 A. Shimojima and K. Kuroda, *Chem. Rec.*, 2006, **6**, 53.

25 L. D. Carlos, V. D. Bermudez, V. S. Amaral, S. C. Nunes, N. J. O. Silva, R. A. S. Ferreira, J. Rocha, C. V. Santilli and D. Ostrovskii, *Adv. Mater.*, 2007, **19**, 341.

26 (*a*) J. J. E. Moreau, L. Vellutini, P. Dieudonné, M. Wong Chi Man, J.-L. Bantignies, J.-L. Sauvajol and C. Bied, *J. Mater. Chem.*, 2005, **15**, 4943; (*b*) J.-L. Bantignies, L. Vellutini, J.-L. Sauvajol, D. Maurin, M. Wong Chi Man, P. Dieudonné and J. J. E. Moreau, *J. Non-Cryst. Solids*, 2004, **345–346**, 605; (*c*) J.-L. Bantignies, L. Vellutini, D. Maurin, P. Hermet, P. Dieudonné, M. Wong Chi Man, J. R. Bartlett, C. Bied, J.-L. Sauvajol and J. J. E. Moreau, *J. Phys. Chem. B*, 2006, **110**, 15797.

27 P. Dieudonné, M. Wong Chi Man, B. P. Pichon, L. Vellutini, J.-L. Bantignies, C. Blanc, G. Creff, S. Finet, J.-L. Sauvajol, C. Bied and J. J. E. Moreau, *Small*, 2009, **5**, 503.

28 X. Qinghong, J. J. E. Moreau and M. Wong Chi Man, *J. Sol-Gel Sci. Technol.*, 2004, **32**, 111.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2010