J. Am. Chem. Soc. **2001,** *123,* 1509−1510

New Hybrid Organic−Inorganic Solids with Helical Morphology via H-Bond Mediated Sol−Gel Hydrolysis of Silyl Derivatives of Chiral (*R*,*R*)- or (*S*,*S*)-Diureidocyclohexane

Joël J. E. Moreau,* Luc Vellutini, Michel Wong Chi Man, and Catherine Bied

Laboratoire de Chimie Organométallique, UMR CNRS 5076
Ecole Nationale Supérieure de Chimie de Montpellier
34296 Montpellier Cedex 05, France

Received November 1, 2000

Hybrid materials[1] have attracted the attention of chemists and material scientists due to commercial interest in their applications as well as scientific interest in the challenges posed by their synthesis. Even though major strides have been made in the past decade, the goal of the synthesis of materials and the tailoring of their properties by design from molecules remains largely elusive.

In this context, silsesquioxane hybrids,[2−4] with well-defined composition and resulting from the sol−gel hydrolysis condensation of functionalized organic molecules, constitute an interesting class of materials for study. The combination of organic and inorganic substructures offers unique possibilities for designing new synthetic routes. However, the tailoring of these materials is complicated by the fact that they are metastable products made under kinetic rather than thermodynamic control, and many factors influence the structure of the synthetic materials. The morphology of the solid varies according to the nature of the organic molecules and according to the experimental conditions of the synthesis.[3a,4a−6] Also, weak intermolecular interactions have been shown to influence the kinetic parameters, to modify the texture and to generate anisotropy in the resulting hybrid materials.[5b,7] Clear examples of templating and structure-directing have also been demonstrated. The use of the silicas templating agents: molecular assemblies,[8] organogelators,[9] has been recently extended to the creation of porous hybrids with well-ordered mesostructures.[10] The control of the pore structure is certainly of great importance in the preparation of catalytic materials. However, for potential applications such as electronic, optic, advanced catalysis the control of the structure at macroscopic and nanoscopic level is also important. Efforts have been made to control the macroscopic morphology of silicas using surfactant-mediated fabrication; interesting helical silica structures were produced using chiral gelators as templates.[11] Regarding porous hybrids, a surfactant-mediated approach was only recently used to generate a cubic crystal with decaoctahedral shape.[12]

In all of the above cases, the structure of the material was controlled by the addition of an external organic template which directs the organization of the inorganic phase. Silsesquioxane hybrids offer much larger potentialities and seem very interesting because, owing to the covalent bond between the organic and the inorganic fragments, the auto-assembly of the organic substructure can control the formation of the inorganic silicate components and eventually direct the structure at the meso- or macroscopic level. A judicious choice of the organic substructure in the precursor may lead to auto-organized solids upon simple hydrolysis. We wanted to test the use of intermolecular H-bond interactions between precursor molecules during the solid formation, as a mean to control the three-dimensional structure of the hybrid network.

Our current interest in the design of chiral hybrids containing (*R*,*R*)- or (*S*,*S*)-diamino-cyclohexane units and of new enantioselective catalytic materials[13] has led us to study the use of chiral organic substructures capable of auto-association. Here we report the creation of a hybrid with helical morphology via H-bond-mediated hydrolysis of a single precursor. A left- or right-handed helix is auto-generated, according to the configuration of the organic substructure.

Diureido derivatives, which are low-molecular weight gelators, were chosen because of their ability to auto-associate through H-bonds.[14] Compound (*R*,*R*)-**2**, $[\alpha]_D$ +4.3 ($c = 3$, $CHCl_3$), was obtained from *trans*-(1*R*,2*R*)-diaminocyclohexane (*R*,*R*)-**1** upon reaction with γ-isocyanatopropyl-triethoxysilane as shown in Scheme 1. Despite the absence of a long hydrocarbon chain substituent[14] in compound **2**, it easily auto-associates by H-bonds in solution and was found to form organogel upon dissolution in organic solvents such as cyclohexane or mesitylene, at ∼3−5

---

(1) (a) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 989−1007. (b) Laine, R. M.; Sanchez, C.; Brinker, C. J.; Giannelis, E., Eds. *Organic/Inorganic Hybrid Materials, MRS Symp. Vol. 519,* **1998**. (c) Klein, L.; DeGuire, M.; Lorraine, F.; Mark, J. Eds. *Organic/Inorganic Hybrid Materials II, MRS Symp. Vol. 576,* **1999**. (d) Laine, R. M.; Sanchez, C.; Brinker, C. J., Eds. *Organic/Inorganic Hybrid Materials III*; Materials Research Society symposium proceedings; Materials Research Society: Warrendale, PA, 2000, Vol. 628.

(2) (a) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102,* 199−236. (b) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95,* 1409−1430.

(3) (a) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 4, 6700−6710. (b) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431−1442 and references therein.

(4) (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*,1217−1224. (b) Corriu R. J. P.; Moreau J. J. E.; Thépot P.; Wong Chi Man M. *Chem. Mater.* **1996**, *8*, 100−106. (c) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420−1436 and references therein.

(5) (a) Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Myers, S. A.; Assink, R. A.; Shea, K. J. *Chem. Mater.* **1996**, *8*, 656−663. (b) Myers, S. A.; Assink, R. A.; Loy, D.A.; Shea, K. J. *J. Chem. Soc., Perkin Trans. 2* **2000**, 545−549.

(6) (a) Cerveau G.; Corriu, R. J. P.; Lepeytre, C.; Mutin, P. H. *J. Mater. Chem.* **1998**, *8*, 2707−2713. (b) Cerveau G.; Corriu, R. J. P.; Framery, E. *J. Chem. Soc., Chem. Commun.* **1999**, 2081−2082.

(7) (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *J. Mater. Chem.* **1994**, *4*,987−988. (b) Corriu, R. J. P.; Moreau, J. J. E.; Chorro, C.; Lère-Porte, J.-P.; Sauvagol, J.-L.; Thépot P.; Wong Chi Man, M.; *Chem. Mater.* **1994**, *6*, 640−649. (c) Boury, B.; Corriu, R. J. P.: Le Strat, V.; Delord, P.; Nobili, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3172−3175. (d) Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376−1398.

(8) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartulli, J.C.; Beck, J. S. *Nature* **1992**, *359*, 710−712. (b) Beck, J. S.; Vartulli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D., Chu, C. T−W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc*. **1992**, *114*, 10834−10843. (c) Qisheng Huo; Margolese, D. I.; Ciesla, U.; Pingyun Feng; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317−321. (d) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500−503.

(9) Clavier, G. M.; Pozzo, J. L.; Bouas-laurent, H.; Liere, C.; Roux, C.; Sanchez, C. *J. Mater. Chem.* **2000**, *10*, 1725−1730.

(10) (a) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611−9614. (b) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302−3308. (c) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867−871. (d) Yoshina-Ishii, C.; Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Chem. Commun.* **1999**, 2539−2540. (e) MacLachlan, M. J.; Asefa, T.; Ozin, G. A. *Chem. Eur. J.* **2000**, 2507−2511 (f) Asefa, T.; Yoshina-Ishii, C.; MacLachlan, M. J.; Ozin, G. A. *J. Mater. Chem.* **2000**, *10*, 1751−1755.

(11) (a) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *Chem. Lett.* **1999**, 1119−1120. (b) Jong Hwa Jung; Ono, Y.; Shinkai, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1862−1865. (c) Jong Hwa Jung; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008−5009 and references therein.

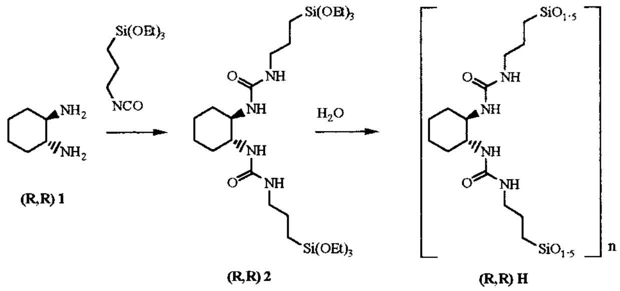
(12) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660−5661.

(13) (a) Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *J. Mater. Chem.* **1997**, *7*, 2331−2333. (b) Moreau, J. J. E.; Wong Chi Man, M. *Coord. Chem. Rev.* **1998**, *178−180*, 1073−1084 and references therein. (c) Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *Chirality* **2000**, *12*, 411−420. (d) Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2000**, *11*, 2183-2194.

(14) (a) Van Esch, J.; Schoonbeek, F.; De Loos, M.; Kooijman, H.; Spek, A. L.; Kellogg, R. M.; Feringa, B. L. *Chem. Eur. J.* **1999**, *5*, 937−980. (b) Schoonbeek, F.; Van Esch, J.; Wegewijs, B.; Rep, D. B. A.; De Haas, M. P.; Klapwijk, T. M.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1393−1397. (c) Van Esch, J.; De Feyter, S.; Kellogg, R. M.; De Schryver, F.; Feringa, B. L. *Chem. Eur. J.* **1997**, *3*, 1238−1243. (d) Jadzyn, J.; Stockhauser, M.; Zywucki, B. *J. Phys. Chem.* **1987**, *91*, 754−757.

10.1021/ja003843z CCC: $20.00

Scheme 1



mg·mL^{-1}. This indicates that quite facile and stable auto-association of molecules of **2** by H-bonds occurs. Evidence for H-bond association was obtained from the FTIR spectrum: at low concentration (6 mg·mL^{-1} $CHCl_3$), (*R*,*R*)-**2** shows single absorption in the NH stretch region (3368 cm^{-1}) and in the amide I and II regions (1656 and 1550 cm^{-1}) characteristic for the presence of non-hydrogen-bonded urea groups and at higher concentration or in the organogel, shifts are observed toward shorter wavenumbers for the NH and amide I (respectively 3330 and 1630 cm^{-1}) and toward higher wavenumbers for the amide II (1572 cm^{-1}) in agreement with strong association of the urea groups.[14]

The hybrid gel (*R*,*R*)-**H** was then synthesized under acidic hydrolysis in a purely aqueous medium. In a typical synthesis, a mixture containing molar ratio of (*R*,*R*)-**2**:1, H_2O:600, HCl:0.2 was vigorously stirred in an oil-bath at 80 °C for 2 h and then allowed to stand for 2 days at the same temperature. The resulting white slurry solution was filtered and washed with water until neutral pH was attained and again washed with ethanol. Careful drying at 110 °C of the gel led to a white solid (*R*,*R*)-**H**. The precursor (*S*,*S*)-**2**,$[\alpha]_D$ −4.8 ($c = 3.1$, $CHCl_3$), and hybrid gel (*S*,*S*)-**H** were similarly obtained from *trans*-(1*S*,2*S*)-diaminocyclohexane (*S*,*S*)-**1**. For both hybrids, the ^{29}Si CP-MAS NMR spectra exhibit two signals at −58 and −67 ppm assigned to $\underline{Si}C(OH)(OSi)_2$ (T^2) and $\underline{Si}C(OSi)_3$ (T^3). Consistent with the existence of covalent Si−C bonding between the organic diureido structure and the silicate units, no signal corresponding to SiO_4 (Q) substructures was detected. The ^{13}C solid-state spectra show a peak at 160 ppm attributed to the C=O signal in addition to the different sp^3 carbon atoms at 55, 43, 34, 25, and 10 ppm. The FTIR spectrum showed vibrations at 3344, 1636, and 1576 cm^{-1}; these values, close to those observed in the organogel gave evidence for H-bonded urea groups within the solid.

Scanning electron microscopy (SEM) images reveal that the whole materials have a fiber-like structure and (*R*,*R*)-**H** (Figure 1a,b) and (*S*,*S*)-**H** (Figure 1c,d) are essentially composed of helical fiber-like structures assembled in bundles within the range of 0.3−1 μm width and up to 15 μm length. The helices were always right-handed for the materials obtained from the (*R*,*R*)-**2** and left-handed in the case of those arising from the (*S*,*S*)-**2**. TEM images confirm the fiber-like structure of the materials, the average width of a fiber being approximately 2−5 nm.

It represents the first example of the creation of a chiral morphology in hybrids. It was not observed in the case of the sol−gel condensation of related chiral diaminocyclohexane precursors not possessing auto-association properties,[13] therefore providing here evidence for the role of self-association by H-bonds during the solid synthesis.

Nitrogen sorption experiments of (*R*,*R*)-**H** revealed a type II adsorption−desorption isotherm and a BET surface area of 120 m^2·g^{-1}. It showed a broad distribution of pore size in the mesopore domain, ranging from 5 to 50 nm. The voids of the fibrous structure may account for the observed porosity.

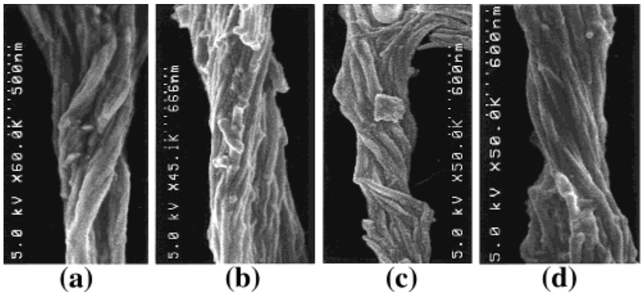


Figure 1. SEM images of hybrid silicas made from (a, b) precursor (*R*,*R*)-**2**, and from (c, d) (*S*,*S*)-**2**.

Supramolecular polymeric architectures with helical morphologies have been obtained by the auto-association of chiral structures on the basis of H-bonding interactions.[15] H-bonds also lead to the auto-association of organic molecules to form organogels,[16] and recently chiral low-molecular weight gelators were used as templates in the sol−gel hydrolysis of TEOS and interestingly led to the creation of helical silica structures.[11]

The present results show the first example of self-organized chiral hybrid material. The nature of the intermolecular interaction between molecules of precursor **2** and the structure of the organic assembly before hydrolysis are probably similar to those of related nonsilylated molecular gelators.[14] However, further studies are necessary to clarify the mechanistic pathway leading from **2** to **H** and how the large-scale nanostucture relates to the structure of organogels. It is interesting to note that the formation of strong siloxane bonds during the polycondensation of compounds **2**, to some extent, can be controlled by weak intermolecular H-bonds between chiral monomeric units or growing oligomers, creating chirality in the entire hybrid material. However, the formation of siloxane bridges seemed to influence the arrangement of the organic substructures and lead to some variability in the structure of the material. Despite an overall rope-like morphology, varying pitches appeared, and the spirals range from about 0.5 to 1 μm.

The self-assembly properties which can be assigned to the organic units, offer possibilities for achieving a structure control at different scales. Material with chiral morphology and properties are of great interest for heterogeneous catalysis. Whereas in solution, very efficient and highly enantioselective molecular catalytic species have been obtained by designing the coordination sphere of transition metal complexes,[17] the design of heterogenised catalyst with activity and enantioselectivity similar to those of homogeneous species remains a challenge.[18] We already showed that enhanced enantioselectivity can result from supramolecular effect in an amorphous chiral hybrid host matrix.[13] Controlled formation of the three-dimensional chiral network in hybrid silicas may permit a tailoring of the environment around the immobilized species analogous to that of molecular species. This may lead in the future to a rational design of chiral hybrid catalyst.

Acknowledgment. Support from the “Ministère de la Recherche” and CNRS is gratefully acknowledged.

JA003843Z

---

(15) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304−1319 and references therein.

(16) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133−3159 and references therein.

(17) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley-Interscience: New York, 1994 and references therein.

(18) Blaser, H. U. *Chem. Rev.* **1992**, *92*, 935−952.