Synthesis of Chiral Periodic Mesoporous Silicas (ChiMO) of MCM-41 Type with Binaphthyl and Cyclohexadiyl Groups Incorporated in the Framework and Direct Measurement of Their Optical Activity

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A series of periodic mesoporous silicas of MCM-41 type containing varying amounts (5−50%) of chiral binaphthyl and cyclohexadiyl moieties occupying framework positions have been synthesized, and their characteristic MCM-41 features were observed by powder XRD and porosity measurements. The covalent bonding of the organics to the silicate framework was confirmed by ^{1}H and ^{29}Si MAS NMR experiments. Direct measurement of the optical activity demonstrates that the solids are able to rotate the angle of plane-polarized light. Also, a certain degree of chiral discrimination has been observed for the asymmetric enhancement of the binaphthyl fluorescence by adding enantiomerically pure 1,2-cyclohexadiamine.

Introduction

Since the initial reports on the surfactant-mediated synthesis of inorganic mesoporous structures such as MCM-41 there has been considerable interest in modifying the inorganic material by introducing organic moieties that could impart some functionality to the solid.[1−6] Although there have been numerous reports on the synthesis of such inorganic/organic hybrid structures, in all of them the organic groups are hanging in the void space of the mesopores.[7−12] Recent reports, however, have described the synthesis of periodic mesoporous organosilicas (PMO) with the organic groups directly integrated to the silica framework by means of two terminal silyl groups.[13−18] Although these seminal contributions proved the principle with simple organic groups such as methylene, ethylene, phenylene, and others, the synthetic methodology can serve equally well to introduce a variety of organic groups, thus making it possible to produce new structured materials with interesting chemical, electronic, or optical properties. Herein, we describe the synthesis of new periodic mesoporous silicas with "*chiral*" binaphthyl and cyclohexadiyl units in the structure imparting chirality to the resultant solid. The search for a solid silicate exhibiting chirality has been long pursued given the enormous potential for its use in chromatography and enantioselective catalysis.[4] Some progress in this direction has been achieved by introducing chiral organic molecules attached to the MCM-41 walls and occupying the solid mesopores[17,19,20] and also in the synthesis of microporous silica with chiral templates.[21] Our contribution is a step forward by incorporating the organic chiral inductor during the synthesis of the material within the solid walls leaving the internal pore volume free. And most significantly, the solids display remarkable optical activity by rotating the plane of polarized light and exhibit enantioselective discrimination.

Experimental Section

Synthesis. Silylated binaphthyl (Si−BN−Si) precursors were synthesized by slow addition of a solution of 3-iodopropyltrimethoxysilane in an excess of potassium carbonate (BN1) or 3-isocyanatepropyltrimethoxy silane (BN2) in 10 mL of

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acetonitrile to a hot solution of *R*-(+)- or (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine in dry acetonitrile under inert atmosphere. Silylated cyclohexadiyl (Si−CH−Si) precursor was synthesized by slow addition of a solution of 3-isocyanate propyltrimethoxysilane in 10 mL of acetonitrile to a solution of 1*R*,2*R*-(−)- or 1*S*,2*S*-(+)-1,2 diaminocyclohexane in dry acetonitrile under inert atmosphere. The mixture was then refluxed for 4 days in the case of Si−BN1−Si or stirred at room temperature for Si−BN2−Si. The yellow oily liquids obtained were washed with hexane. Si−BN1−Si, Si−BN2−Si, and Si−CH−Si were characterized by analytical and spectroscopic data. *Si−BN1−Si*. ^{1}H NMR ($CDCl_3$): δ 0.49, 1.50, 3.42, 3.54 (s), 6.94, 7.01−7.23 and 7.72−7.88. ^{13}C NMR ($CDCl_3$): δ_C 12.03, 21.87, 54.43, 69.63, 120.50, 121.00, 126.00, 127.60, 127.82, 128.60, and 156.00. *Si−BN2−Si*. ^{1}H NMR ($CDCl_3$): δ 0.48, 1.12 (t), 1.45, 2.88, 3.41, 3.80 (q), 7.31 (t), 7.74−7.83 and 8.35−8.44. *Si−CH−Si*. ^{1}H NMR ($CDCl_3$): δ 0.57, 1.2, 1.22, 3.67, 3.71, 3.78. ^{13}C NMR ($CDCl_3$): δ 18.26, 42.98, 158.99.

Periodic mesoporous silica materials were synthesized by mixing the reactants to get a uniform white gel. TEOS and silylated chiral organic precursors were used as the silicon source, and hexadecyltrimethylammonium bromide (CTABr) was the structure-directing agent. The typical molar composition of the gel was 1.00:0.12:8.0:114:8−10 Si/CTABr/NH_3(20%)/H_2O/EtOH. Amounts of TEOS and organic silica precursor were varied to obtain atomic ratios of the two different silicon sources from 50:50 to 95:5. After mixing the reactants, the resulting clear gel was transferred to a polyethylene container and heated at 90 °C in static conditions for 4 days. The solid obtained was washed thoroughly with water and dried in air at 60 °C. The structure-directing agent was removed by extracting the solid with 0.05 M ethanolic HCl acid solution at 50 °C for 5 h (20 mL of 0.05 M ethanolic HCl for 0.5 g of solid).

Postsynthetic anchoring of the silylated precursor to calcined MCM-41 support was done by stirring 1 g of thermally dehydrated template-free MCM-41 silica with a solution of 0.5 g of Si−CH−Si precursor in 10 mL of dry toluene and refluxing for 24 h. The solid was extracted exhausively with CH_2Cl_2 for 72 h and finally dried in air at 60 °C.

Characterization. Powder X-ray diffraction (PXRD) patterns of the solids were recorded on a Philips X'pert diffractometer using nickel filtered Cu Kα radiation with $\lambda = 1.54178$ Å operating at 40 KV and 35 mA. Infrared and diffuse reflectance UV−vis spectra were measured on Jasco 460 Plus and Shimadzu DT-2101 spectrophotometers, respectively. Carbon and nitrogen contents of the solids were determined by combustion analysis in a Fisons EA 1108 elemental analyzer. Specific surface area and pore size distribution of the catalysts were measured by recording the nitrogen adsorption/desorption isotherms at liquid N_2 temperature using a Micromeritics ASAP 2010 system. Before measurements, the samples were outgassed at 150 °C under vacuum (10^{-3} Torr) for 6 h to remove any adsorbed species. Pore size distribution was determined from the desorption branch of the isotherm by the Barrett−Joyner−Halenda (BJH) method using the Halsey equation. Solid-state ^{1}H and ^{29}Si MAS NMR spectra were recorded on a Bruker 400 spectrometer with samples packed in zirconia rotors spinning at 30 and 5.5 kHz, respectively. Optical activity of the solids was measured in a Jasco Polarimeter (P1030) using Na emission (589 nm). A 5−8-mg portion of the solid was suspended in 10 mL of dichloroethane. Correction for the solvent was made before measuring the optical rotation values for periodic mesoporous silica solids. Photoluminescence measurements were carried out in a PTI spectrophotometer using septum-capped quartz cells purged with N_2. For measurements with solids, cells of 3 × 7 mm were used (Luzchem Ltd) with a front-face arrangement using cutoff filters to prevent the excitation wavelength from reaching the detector. Quenching experiments were performed by the addition of a known amount of the quencher diluted in CH_2Cl_2 to the solids and allowing the solvent to evaporate.

Results and Discussion

Preparation of the chiral MCM-41 type solid containing binaphthyldiamine (BNDA) or cyclohexyldiamine (CHDA) units was accomplished following a procedure similar to that described earlier for the preparation of simpler organic-incorporated mesoporous silicas having methylene groups in the walls.[15,16] In this strategy, trimethoxysilylpropyl groups were attached to the N atoms of chiral *R*-(+) or *S*-(−) BNDA or CHDA following two different procedures as shown in Scheme 1. Subsequently, the silylated chiral precursors, Si−BN−Si or Si−CH−Si, were used in combination with TEOS in the synthesis of chiral MCM-41, using cetyltrimethylammonium bromide (CTABr) as the structure-directing agent. Concerning the hydrophobic−hydrophilic balance of the precursors, they contain 1 or 3 N plus O heteroatoms for every 13 carbons in the case of Si−BN−Si precursors or 3 N plus O atoms for every seven in the case of Si−CH−Si. Moreover, it is well-known that, because of the polarity introduced by the π bonds, naphthalene and other aromatics are considerable more hydrophilic than saturated analogues. Therefore, despite the relatively large molecular size of Si−BN2−Si precursors, they fulfill the right hydrophilic/hydrophobic balance between C and heteroatoms. A series of solids was prepared in which the chiral moiety, Si−BN−Si or Si−CH−Si, was covalently attached through an amine or urea functionality. The TEOS/Si−BN−Si or TEOS/Si−CH−Si molar ratios were varied from 95:5 to 50:50. It was noted that with higher amounts of the silylated precursor in the synthesis gel the resulting solids obtained were mostly amorphous in nature. Table 1 summarizes some physical properties of the well-structured samples prepared in this work.

The periodic structure of the as-synthesized and template-free mesoporous solids was determined by powder XRD. Presence of a sharp reflection appearing at about $2\theta = 2°$ corresponding to the d_{100} basal plane of MCM-41 type solids confirms the formation of mesoporous structure for those solids in which the TEOS/Si−BN−Si (or Si−CH−Si) ratio was 85:15 or higher (Figure 1). XRD patterns of the acid-extracted solids are also shown in the figure for comparison. It was observed that when the organic content in the gel was higher, a significant decrease in periodicity of the solids was observed. It can be seen from Figure 1 that at a TEOS/Si−X−Si ratio of 90:10 or 95:5 very-well-structured organic-incorporated mesoporous MCM-41 silica could be obtained with BN1, BN2, and CH silylated precursors. It can also be seen from Figure 1 that these materials mostly retain their mesoporous structure even after the acid-extraction process. When the TEOS/Si−X−Si ratio was lower than 90:10 the materials obtained were poorly crystalline and collapsed partially or completely during the acid-extraction process. This observed decrease of periodicity in the solids, as the percentage of Si−BN−Si or Si−CH−Si in the synthesis gel increases, was most likely due to the perturbation introduced in the sol by the size and geometry of the organic precursors during crystallization of the solids. Thus, solids obtained with a gel having a TEOS/Si−BN−Si (or Si−CH−Si) ratio lower than 85:15 showed less-ordered amorphous-like materials. Nevertheless, when

Scheme 1

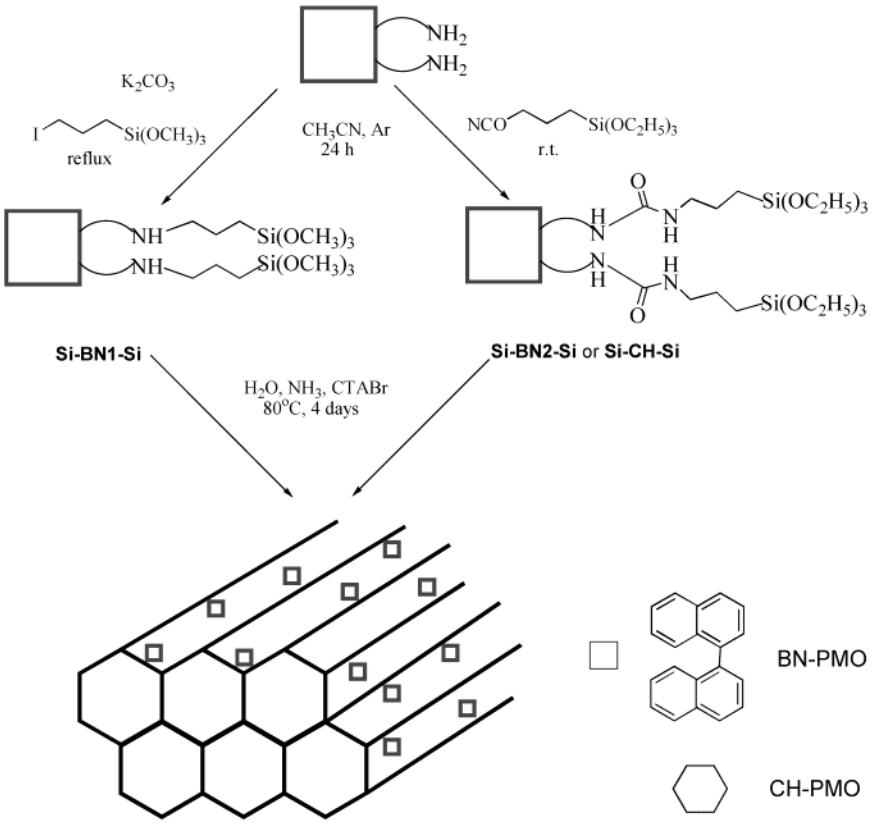


Table 1. Physical Properties of the Chiral Mesoporous Solids Incorporated with Organic Moiety

sample	precursor used	TEOS/Si-X-Si (molar ratio in gel)	X/Si (molar ratio in solid	crystallinity[a]	C and N content[b] C (wt %)	N (wt %)	C/N
BN1−1	Si−BN1−Si	90:10	5:100	high	19.2	1.7	13.0
BN1−2	Si−BN1−Si	85:15	6.8:100	medium	24.6	2.2	12.9
BN2−1	Si−BN2−Si	95:5	2.7:100	very high	12.5	2.1	6.8
BN2−2	Si−BN2−Si	90:10	4.9:100	high	20.3	3.3	7.1
BN2−3	Si−BN2−Si	85:15		medium			
CH-1	Si−CH−Si	95:5	3:100	very high	74.	2.2	4.0
CH-2	Si−CH−Si	90:10	6:100	high	13.1	3.3	4.7
CH-3	Si−CH−Si	85:15		poor			
CH-ps[c]	Si−CH−Si	90:10	6:100	good	12.9	3.2	4.7

[a] From XRD patterns. [b] From chemical analysis of acid-extracted samples. [c] Postsynthetically anchored sample.

harsher extraction conditions were applied periodicity of all the solids were significantly damaged.

Chemical analysis of the as-synthesized and acid-extracted solids was performed to determine the final organic content in these materials. Table 1 shows that the values of carbon to nitrogen (C/N) ratio of the acid-extracted solids were very close to those for the precursor used, 13 for BN1, 7 for BN2, and 3.5 for CH. For as-synthesized solids the value was higher because ofthe presence of the template molecules in the channels of the solids.

IR spectra of the as-synthesized BN1−MCM-41 solids show two peaks at 2925 and 2853 cm^{-1} characteristic of asymmetric and symmetric stretching vibrations of $-CH_2-$ groups (Figure 2a). Another less intense peak at 1480 cm^{-1} corresponds to the bending vibration of $-CH_2-$ groups. Because the $-CH_2-$ groups in the as−synthesized mesoporous silicas are predominantly due to CTA^+, after acid extraction the intensity of these peaks decreases dramatically. In the case of BN1−MCM-41, the characteristic bands of binaphthyl in the aromatic region are considerably less intense than those of CH_2 groups of CTABr, but they remain unaltered after extraction (inset Figure 2). The fact that BN1 units were bound to the solid walls and not removed during the template extraction procedure was also evidenced by chemical analysis of the surfactant-free solids (see Table 1).

Figure 2b shows the IR spectra of BN2−MCM-41 and CH−MCM-41 solids. For CH−MCM-41 the characteristic IR bands corresponding to the cyclohexane ring fall in the same region as the $-CH_2-$ groups of CTA^+, and therefore, the IR spectra were less informative. However, IR spectra of the two samples after acid extraction show the presence of the urea units that should bridge the chiral binaphthyl and cyclohexadiyl moieties to the alkylsiloxy groups. Presence of the doublet at 1640 and 1610 cm^{-1} in the IR spectra firmly proves the presence of urea units in the BN2−MCM-41and CH−MCM-41 solids. In addition, combustion chemical analysis shows

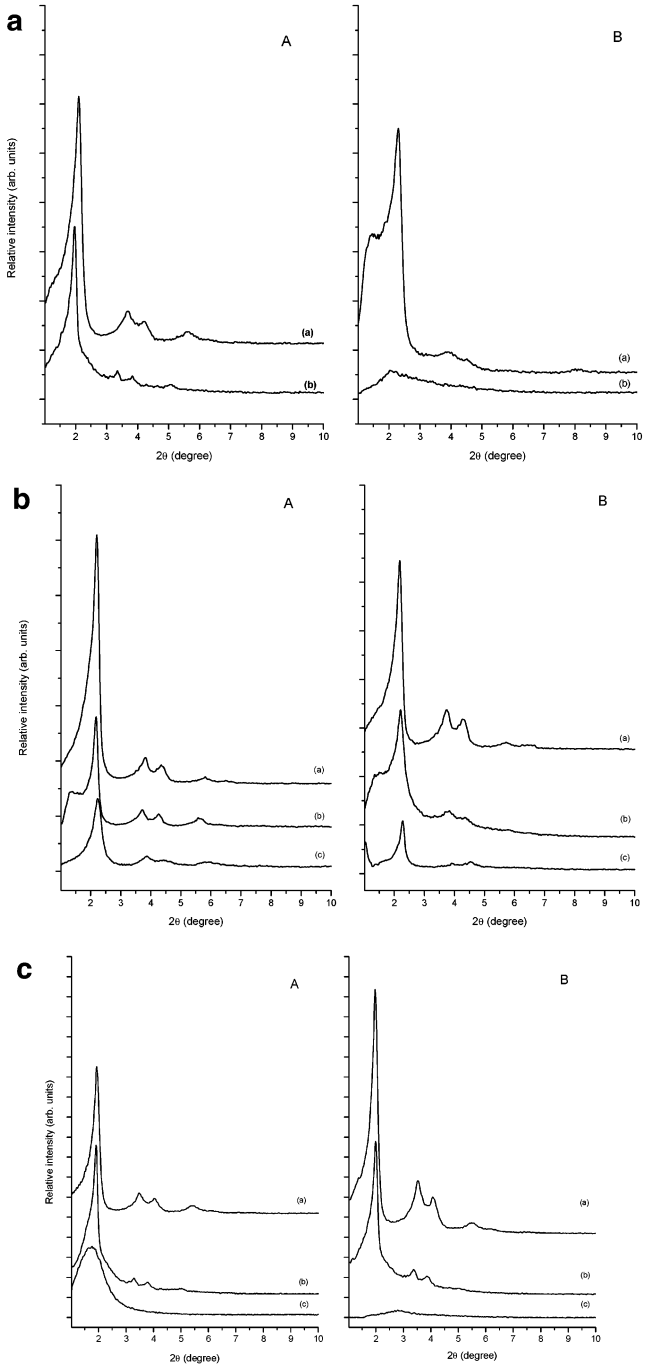


Figure 1. (a) XRD patterns of as-synthesized (A) and template-extracted (B) BN1−MCM-41 solids. TEOS/Si−BN1−Si: trace (a) 90:10, and trace (b) 85:15. (b) XRD patterns of as-synthesized (A) and template-extracted (B) BN2−MCM-41 solids. TEOS/Si−CH−Si: trace (a) 95:5, trace (b) 90:10, and trace (c) 85:15. (c) XRD patterns of as-synthesized (A) and template-extracted (B) CH−MCM-41 solids. TEOS/Si−CH−Si: trace (a) 95:5, trace (b) 90:10, and trace (c) 85:15.

the presence of residual organic materials compatible with the presence of grafted BN2 and CH units as shown by the values of C/N ratios (Table 1).

For BN1−MCM-41 or BN2−MCM-41 the presence of binaphthyl units in the structure was also apparent from diffuse reflectance UV−vis spectroscopy (Figure 3). The UV−vis spectrum of the as-synthesized sample showed a sharp peak at 230 nm along with two broad bands at about 300 and 365 nm. Pure BNDA and Si−BN−Si compounds also showed similar bands at 285

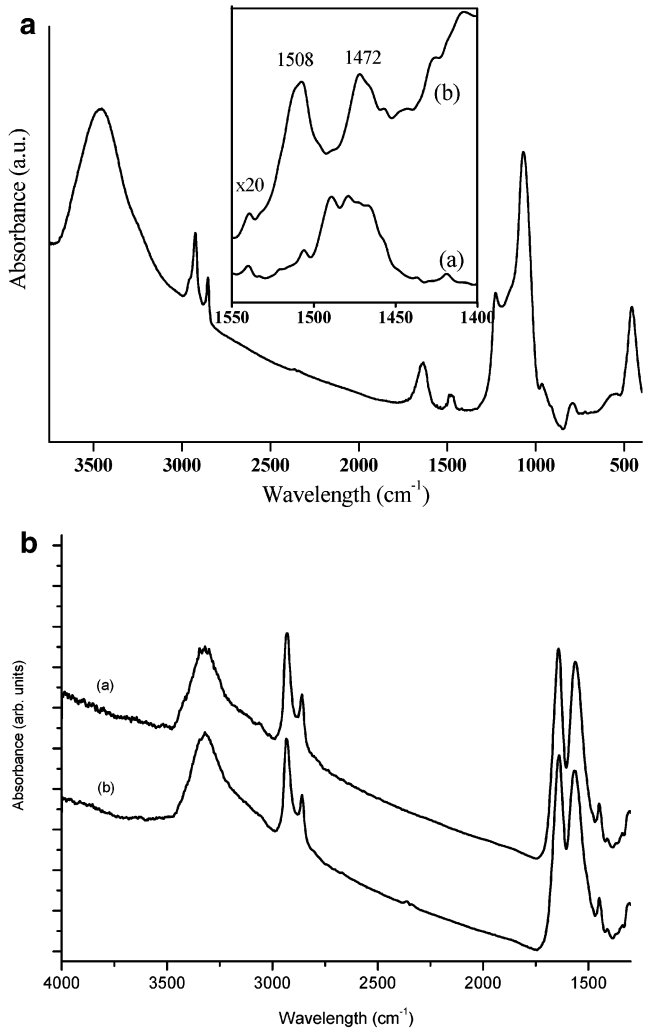


Figure 2. (a) IR spectrum of as-synthesized BN1−MCM-41 (TEOS/Si−BN1−Si = 90:10) solid. Inset: enlarged part of the same spectrum, trace (a) before, and trace (b) after acid-extraction. (b) IR spectra of trace (a) BN2−MCM-41 (TEOS/Si−BN2−Si = 90:10) and trace (b) CH−MCM-41 (TEOS/Si−CH−Si = 90:10) solids.

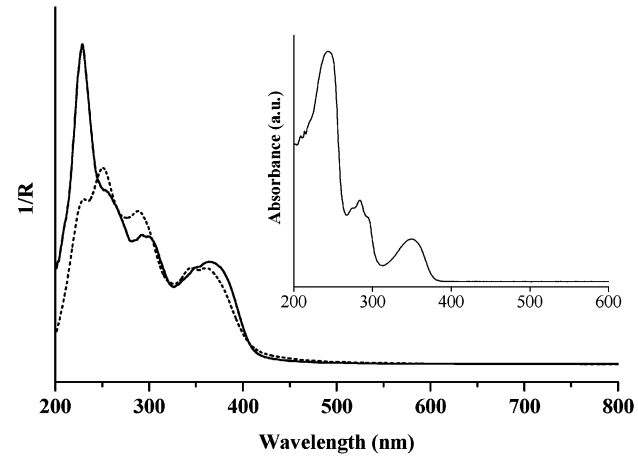


Figure 3. DR UV−Vis spectra of as-synthesized and acid-extracted (dotted line) BN1−MCM-41 (TEOS/Si−BN1−Si = 90:10); (inset) UV−vis spectrum of pure BNDA.

and 350 nm. These absorption bands are totally absent in pure MCM-41 and they are due to the $\pi \rightarrow \pi^*$ transitions of the organic aromatic compound. The intensity of the peaks in the UV−vis spectrum of the

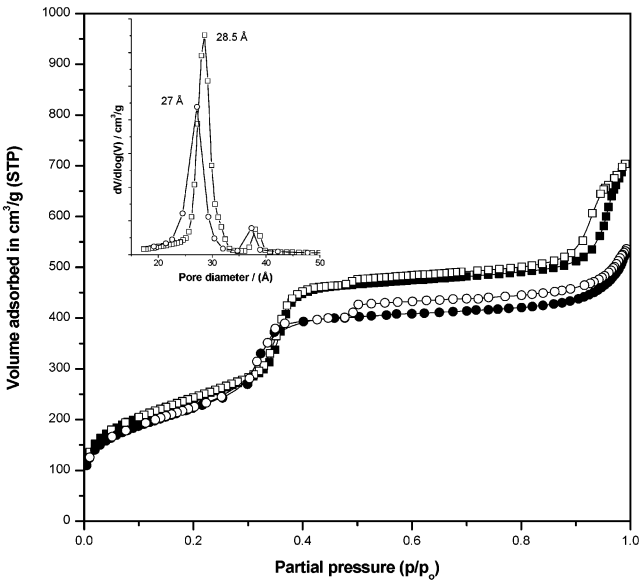


Figure 4. Isothermal N_2 adsorption−desorption isotherms for the acid-extracted mesoporous silicas CH−MCM-41 (TEOS/Si−CH−Si = 90:10) (■, □) and BN-1−MCM-41 (TEOS/Si−BN1−Si = 90:10) (●, ○). The inset shows the pore size distributions for these two samples.

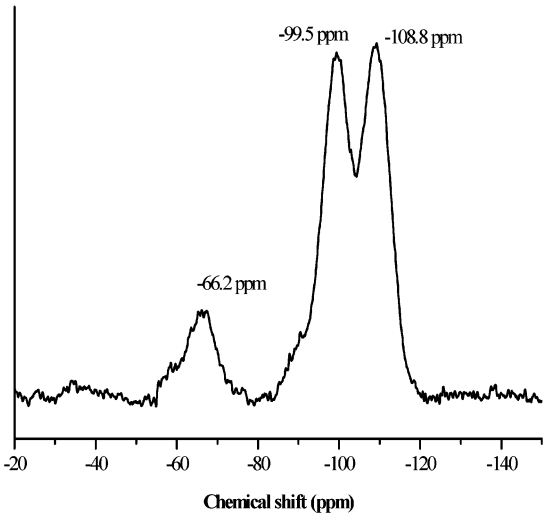
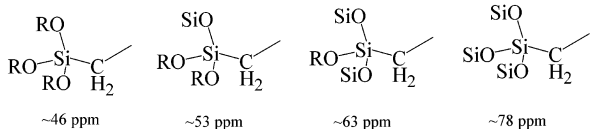


Figure 5. ^{29}Si MAS NMR spectrum of acid-extracted CH−MCM-41 solid (TEOS/Si−CH−Si = 90:10).

Scheme 2



acid-extracted solid does not vary with respect to that of the as-synthesized solid, this observation being compatible with the assumption that binaphthyl units are covalently attached to the solid and also in good agreement with the IR results.

Isothermal nitrogen adsorption measurements were carried out to determine the surface area and pore size distribution of the chiral mesoporous MCM-41 solids. Figure 4 shows the adsorption−desorption isotherms for two highly crystalline and well-structured samples containing binaphthyl and cyclohexadiyl groups. These measurements indicate that the mesoporous silicas, CH−MCM-41 (90:10) and BN2−MCM-41 (90:10), possess specific surface areas of 878 and 816 $m^2 \cdot g^{-1}$, respectively. The inset in Figure 4 also shows the pore size distribution of these samples. The corresponding average pore sizes were found to be 28.5 and 27 Å, respectively. These values are typical of well-structured MCM-41 type materials and demonstrate that the channel systems of the mesoporous silicas containing binaphthyl or cyclohexadiyl units are not blocked by the organic units.

Although in the case of CH−MCM-41 infrared spectra confirms the presence of urea units in the acid-extracted samples, the anchoring of the CHDA units cannot be detected by either UV−vis diffuse reflectance or IR spectroscopy because this chromophore does not have any absorption band above 250 nm and the CH vibrations are coincident with those arising from CTA^+. Also in the case of BN1− or BN2−MCM-41, optical and IR spectroscopy demonstrate the presence of binaphthyl units in the solid; however, they do not directly demonstrate the covalent anchoring of Si−BN−Si on the silica walls. Direct evidence that the organic moiety is covalently bound to the inorganic silicate framework can be obtained, however, from solid-state ^{29}Si NMR spectroscopy. Thus, ^{29}Si MAS NMR spectra of a CH−MCM-41 (90:10) sample after CTA^+ removal shows presence of Q_4 and Q_3 silicon species, corresponding to Si atoms attached to 4 or 3 neighboring other Si atoms, as observed in normal MCM-41 samples. No Q_2 or Q_1 species were detected, but a weak signal at ∼−66 ppm was barely observable from the background. This weak signal is in the chemical shift range expected for Si atoms of Si−CH−Si moieties. To support this, CP spectrum from ^{1}H to ^{29}Si was performed. Under these conditions, the peak at −66 ppm was clearly observable (Figure 5). The chemical shifts of siloxanes and partially condensed siloxanes in solution are well-known.[20,21] It has been measured that $Si-CH_2$ having three alkoxy or hydroxy groups appear at around −45 ppm, while the chemical shift gradually shifts toward higher field with the number of Si atoms bonded to second coordination sphere (Scheme 2). Also, the chemical shift of framework bonded $Si-C_6H_4-Si$ has been reported at −72 ppm.[20] Therefore, the signal at −66 ppm clearly matches that of an Si atom covalently bonded to carbon atoms of T^2 configuration C(OR)**Si**$(OSi)_2$ (Scheme 2). The observed CP effect and the chemical shift, combined with the infrared spectroscopy results showing the presence of urea groups, strongly support the presence of Si−CH−Si units forming part of the silica framework. Also, the CP ^{29}Si NMR rules out the possibility that some Si−BN−Si or Si−CH−Si precursors were grafted by a single terminal Si instead of the two, as the signal corresponding to T° Si atoms of the triethoxysilyl or trihydroxysilyl groups at about −45 ppm is below the detection limit. However, the presence of some population of CH_2**Si**$(OSi)_3$ cannot be ruled out because its chemical shift would most probably overlap with Q_3 signals of the silicate. In addition, solid state ^{1}H MAS NMR (Figure 6) of CH−MCM-41 (TEOS/X = 50:50) also confirms the presence of CHDA groups as shown by the presence of a broad and intense peak at about 1 ppm, accompanied with the $Si-CH_2$ at 0 ppm, −CO−NH−C*H* between 3 and 2 ppm, and coadsorbed water at ∼6 ppm. Attempts to remove adsorbed water molecules

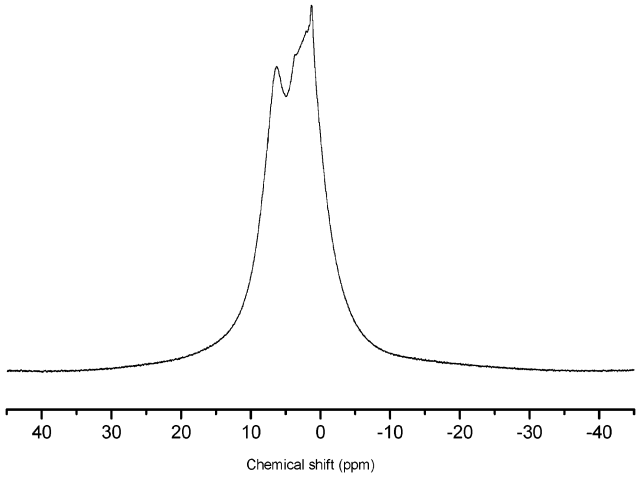


Figure 6. MAS ^{1}H NMR spectrum of acid-extracted CH−MCM-41 solid (TEOS/Si−CH−Si = 50:50).

completely by thermal treatment were not very successful due to thermal instability of the organic moiety which decomposed at elevated temperatures.

Although some MCM-41 solids having attached chiral groups inside the channels have been previously reported,[19] as far as we know direct evidence of the optical activity of the solids by measurement of the rotation angle of the plane-polarized light has never been reported. The reason for this is that typical measurements of the optical activity require transparent solutions. Herein the confirmatory proof for the presence of chiral units in the solid was obtained by observing the behavior of the solid toward plane polarized light. For these measurements small amounts of the solid particles were suspended in dichloroethane and optical rotation of the transparent suspension was measured in a conventional polarimeter using the yellow Na emission. A related precedent of this methodology consists of the use of transmission techniques to record optical spectra of suspended zeolite particles.[22−24] Likewise, the success of our optical activity measurements relies on the fact that suspensions of mesoporous silicas are sufficiently transparent and the sedimentation time is satisfactorily slow to permit such experiments. Not surprisingly the solids exhibited chiral properties by rotating the plane of polarized light with an estimated specific rotation of 38° × g^{-1} for BN-1−MCM-41 (90:10), 33° × g^{-1} for BN-2−MCM-41 (90:10), and 52° × g^{-1} for CH−MCM-41 (90:10). Blank controls using nonchiral solids do not exhibit optical activity, thus, reinforcing that our measurements are not an artifact but are really testing the chirality of the transparent suspension. However, comparison of the optical activity of the as-synthesized mesoporous silicas before and after acid extraction reveals a significant decrease of the optical activity after the extraction procedure. This apparent decrease of the optical activity can be attributed to several reasons including: (i) removal of the excess of binaphthyl moieties not covalently bonded to the framework during the extraction, (ii) changes in the refraction index as a consequence of the removal of the surfactant within the pores, (iii) partial protonation of N atoms of the organic structures due to the acid utilized for the extraction, and (iv) racemization during template extraction. The latter possibility seems unlikely given the mild conditions in which the surfactant is removed and that racemization in solution requires prolonged heating and higher temperatures. On the other hand, protonation seems more likely for the CHDA derivative than for the BN solid due to the difference in pK_b of the aromatic amines. The importance of direct optical activity measurement is evident when we consider that in some cases samples that initially exhibited optical activity completely lost their activity after the extraction was done with stronger acidic media, or at higher temperatures, or if a longer extraction time were used. Therefore, assumptions based on the chiral activity of the precursors without direct determination may be erroneous because loss of optical activity can occur during different stages of solid preparation and template removal steps. Also, by using the opposite Si−BN−Si or Si−CH−Si enantiomers, the optical rotation was found to be opposite with a specific rotation value similar to that of the other enantiomer.

To provide a comparison of the optical activity of mesoporous silica prepared in this work, a postsynthetically grafted sample was also prepared by anchoring the **Si**−CH−**Si** organic precursor on calcined purely siliceous MCM-41 silica. The final solid, represented as CH-ps, contained slightly higher amounts of the organics than those prepared by direct synthesis. The specific rotation value was found to be 66° × g^{-1}, which is very close to that obtained for silicas prepared by direct synthesis. This is not surprising in view of the structural similarity between the materials obtained by direct synthesis or by postsynthetic anchoring.

Chirality introduced by BNDA on the mesoporous silica solids is also reflected on the occurrence of enatioselective fluorescence enhancement by the addition of enantiomerically pure *1R,2R*-(−)- or *1S,2S*-(+)-isomers of 1,2-diaminocyclohexane. It is well-known that naphthalene derivatives in general, and binaphthyls in particular, emit fluorescence upon excitation at absorption λ_{max}. Figure 7 shows the excitation and emission spectra (in acetonitrile solution) of the parent BNDA compound, structurally related to the photolumophore present in BN1−MCM-41 solids. Upon addition of increasing amounts of *1R,2R*-(−)- or *1S,2S*-(+)-1,2-diaminocyclohexane, the emission is quenched with different quenching constants for each of the enantiomers. The difference in the quenching constants reflects the level of chiral discrimination of the emission quenching.

When the same type of photoluminescence measurement was carried out with the BN1−MCM-41 solids, the emission intensity was much weaker (Figure 8). But upon addition of *1R,2R*-(−)- or *1S,2S*-(+)-1,2-diaminocyclohexane an enhancement of the luminescence intensity was observed. Importantly, the observed enhancement in intensity was different for the two enantiomers, reflecting again a certain degree of chiral recognition. In blank experiments performed under similar conditions but in the absence of 1,2-diaminocyclohexane no enhancement was observed. A series of measurements has been undertaken to demonstrate that the observed

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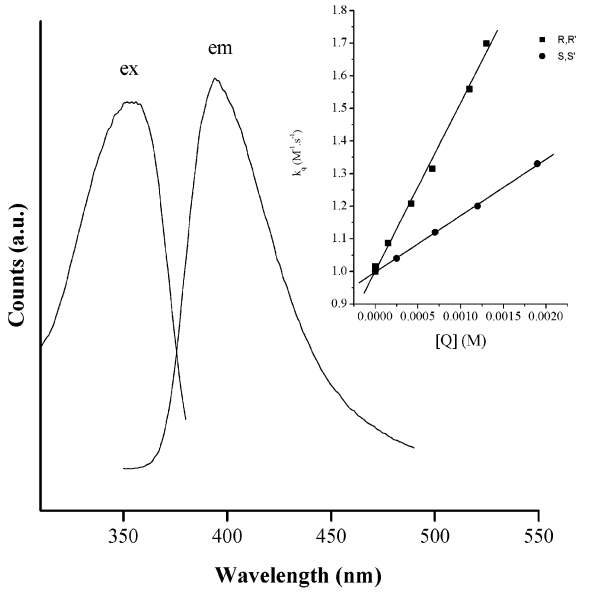

Figure 7. Excitation (ex) and emission (em) spectra of BNDA in acetonitrile solution in nitrogen atmosphere; (inset) quenching experiment with enantiomeric quenchers.

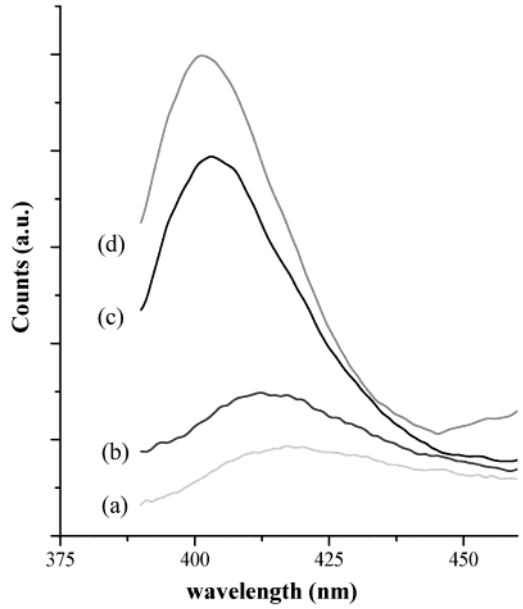

Figure 8. Emission spectra of (a) extracted BN1−MCM-41 solid with solvent only, (b) BN1−silica with *S,S′*-1,2-diaminocyclohexane, (c) BN1−silica with *R,R′*-1,2-diaminocyclohexane, (d) BN1−MCM-41with *S,S′*-1,2-diaminocyclohexane, and (e) BN1−MCM-41 with *R,R′*-1,2 cyclohexylamine. The amount of diaminocyclohexane was 5 mg·g $^{-1}$ in all cases.

difference in the response with the addition of *1R,2R*-(−)- or *1S,2S*-(+)-1,2-diaminocyclohexane was reproducible and consistent. A possible explanation of this effect is that the characteristic emission in solution of the BN lumophore is somehow quenched in the BN1−MCM-41 solid, most probably by interaction with the −OH groups present in the silica matrix. Upon addition of diaminocyclohexane, the hydrogen bonding of the diamine groups would be disrupted, partly restoring to some extent the original emission observed in solution. The strength of this interaction would be different for each enantiomer. Although their interaction occurs either in solution or in the solid the results will be opposite. When in the initial situation BN emits (as observed in solution), the interaction with diaminocyclohexane decreases the emission. But, when in the initial state BN does not emit (as in the case of BN−MCM-41 solid) then the interaction leads to an enhancement of the photoluminescence.

Photoluminescence measurements can also be used to support the structure of BN1−MCM-41, in particular, the predominant internal location of the organic BN moiety covalently grafted to the channel walls. For this purpose, two controlled experiments were undertaken. First, a quenching experiment with enantiomeric pure 1,2-diaminocyclohexane (as described earlier) was performed on as-synthesized BN1−MCM-41 containing the structure-directing template molecules inside the channels. No significant enhancement of the photoluminescence was observed, supporting our proposed model that BN moiety is mostly located inside the channels. Thus, in as-synthesized samples the chiral BN moieties are not accessible to the 1,2-diaminocyclohexane molecules. For another controlled experiment, an amorphous BN1−silica sample was prepared by using the same precursor as for BN1−MCM-41 but in the absence of any structure-directing templates. The solid obtained was amorphous in nature and in photoluminescence experiments showed minor enhancement upon the addition of 1,2-diaminocyclohexane (see Figure 8). The observed enhancement was found to be only $^1/_3$ of that observed in the case of BN1−MCM-41. The results indicate that in the case of an amorphous solid only a small fraction of the organic BN lumophores is accessible to the quencher molecules. This contrasts with the behavior of the periodic mesoporous silicas containing BN1, where a larger fraction of BN1 moieties present inside the channels can interact with the quencher molecules.

In conclusion, we have shown a simple methodology to synthesize "*chiral*" mesoporous silicas by using disilylated chiral binaphthyl or cyclohexadiyl precursor units. These chiral MCM-41 solids exhibit the fingerprint of chirality by rotating the plane of polarized light to a significant degree. The direct measurement of the optical activity has revealed that caution has to be exercised as racemization can occur in various steps during the preparation and handling of the solids. On the other hand, chiral discrimination has also been demonstrated by measuring the photoluminescence of the chiral organosilicas in the presence of enantiomerically pure quenchers. Further improvements are, however, necessary to introduce larger quantities of the chiral organics in the solid (above 15%) or the selection of appropriate precursors to minimize the structural stress introduced by the presence of the organic moiety in the silicate framework.

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