Novel Layered Organic−Inorganic Hybrid Materials with Bridged Silsesquioxanes as Pillars

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Layered organic−inorganic hybrid materials were synthesized by pillaring with viologen and nitroaniline compounds which are intercalated between magadiite layers. The bridged silsesquioxanes, 4,4′-bis-(trimethoxysilylpropyl)viologen and 4-nitro-*N*,*N*′-bis(3-trimethoxysilyl)propylaniline react with the surface silanol groups of the inorganic layers of silicate, bonding covalently with them. The preparation process was followed by DRX, and the pillarization was corroborated using chemical and thermogravimetrical analyses. The presence of viologen and nitroaniline organic linkers covalently bonded to inorganic layers was confirmed by ^{13}C and ^{29}Si NMR spectroscopy. UV−visible diffuse reflectance permitted to observe the high stabilization achieved by the intercalated organic fragments. Micro- and mesoporosity were also generated because of the existence of interlayer galleries conformed by homogenously distributed organic linkers into the interlayer space. The layered organic−inorganic hybrids exhibited a thermally stable network, and the organic spacers remained after elimination of the swelling agents by acid extraction. The resultant materials can be of interest as sensors and for nonlinear optics.

Introduction

Porous nanostructured organic−inorganic hybrid materials have attracted considerable attention from the point of view of fundamental chemistry as well as for their technological applications.[1−5] Hybrid composite materials are formed when at least two different components are mixed to form their structural network. The overall properties of a hybrid material are established not only by the individual components but also by the global phase and interfacial properties favored by structuration at the nanometric length scale.[6,7]

In this sense, layered silicate nanolayers can be used as alternative inorganic components for the construction of nanostructured organic−inorganic hybrid composites.[8] The alkali-metal-ion forms of this family of layered silicate include as components kanemite, makatite, octosilicate, magadiite, and kenyaite. The detailed crystal structure of these layered materials is still unknown, except for makatite.[9] But, it is generally accepted that their structure is built up of one or more sheets of SiO_4 tetrahedra therefore contain a large number of hydroxyl groups on the layered surface.[10−12]

The layers of alkali-metal silicates contain silicon sites in which the terminal oxygen is compensated by alkali ions and/or protons that are easily exchangeable, whereas the interlayer space can be occupied by different organic molecules.[13,14] Although a large number of organic compounds have been intercalated into layered silicic acid derivatives, the stability of the confined organic groups was poor.[15] Nevertheless, the rich intercalation chemistry of these layered silicates can be used to prepare different types of organic−inorganic hybrid materials by intercalation of interesting organic molecules.[16,17]

One approach to this would involve the use of bridged silsesquioxanes precursors $(R'O)_3Si-R-Si(OR')_3$ as intercalation agents.[18−20] The high reactivity of their terminal alkoxy groups allows interaction with the layered surface Si−OH groups, favoring the covalent introduction of bridged organic−inorganic units as pillars into the interlayer space. This procedure maximizes interfacial contact between the

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organic and inorganic phases,[21,22] and the surface and framework of these materials can be tuned by changing the bridging organic linkers incorporated during the synthesis process. So, the apparent structural order of these nanohybrids is directly related to their ability to perform the desired function for a specific application.[23]

Following this, a few pillared layered hybrid materals using bridged silsesquioxanes and layered silicic acid have been reported.[24,25] However, the organic linkers intercalated up to now into the interlayer space have low stability and little interest for catalysis and nanotechnology.

In this paper, we have synthesized a series of porous hybrid materials formed by magadiite as the inorganic crystalline layer silicate and two specific types of bridged silsesquioxanes, 4,4′-bis(trimethoxysilylpropyl)viologen (BTMPVi) and 4-nitro-*N*,*N*′-bis(3-trimethoxysilyl)propylaniline (BTMPNA), which have been intercalated as pillars into the interlayer space. The resultant porous materials are thermally highly stable and can be of interest because of the unique electron transfer ability of the viologen units to generate radical cations and their possible use as thermal or luminiscence sensors.[26,27] Moreover, the nitroaniline groups are very active as chromophores, improving second-order nonlinear optical (NLO) properties.[28,29]

We will show here that in the prepared materials there is a perfect covalent intercalation of organic groups distributed homogenously in the interlayer space, generating porosity and high free porous volume, whereas the pillared organic−inorganic hybrid materials synthesized are highly stable.

Experimental Section

Reagents. Na-Magadiite was synthesized with Ludox AS-40 (DuPont), NaOH (Aldrich), and trans-4-aminocyclohexanol (Fluka) as structure-directing agent.[30] The swelling process was carried out using cetyltrimethylammonium bromide (Aldrich) exchanged with Amberlite IRN-78 ionic resin (Supelco). The bridged silsesquioxanes with viologen or nitroaniline units as organic linkers between two Si atoms were obtained following the procedure described below. HCl (Aldrich, 37 wt %) and ethanol (Scharlau) were employed during the extraction of swelling molecules to obtain the final pillared products.

Preparation of 4,4′-Bis(trimethoxysilylpropyl)viologen (BTMPVi). Silylated derivative of viologen was prepared using 5.02 g (32.14 mmol) of 4,4′-bipyridine disolved in 200 mL of anhydrous CH_3CN under N_2. Next, 100 mL (0.511 mol) of 3-iodopropyltrimethoxysilane was added to this solution. The mixture was then heated under reflux for 24 h. The orange precipitate obtained was filtered under a vacuum and washed with CH_3CN, providing 18.53 g (78%) of the desired product. ^1H NMR (300 MHz, D_2O): δ 9.0 (d, $J = 7$ Hz, 4H), 8.5 (d, $J = 7$ Hz, 4H), 4.6 (t, $J = 7$ Hz, 4H), 3.5 (s, 18H), 2.1 (m, 4H), 0.8 (m, 4H). Anal. Calcd for $C_{22}H_{38}I_2N_2O_6Si_2$: C, 35.88; H, 5.20; N, 3.80. Found: C, 35.18; H, 5.23; N, 3.79.

Preparation of 4-Nitro-N,N′-bis(3-trimethoxysilyl)propylaniline (BTMPNA). Bridged silsesquioxane containing *p*-nitroaniline groups as organic linker was obtained using 1.38 g (10 mmol) of 4-nitroaniline disolved in 50 mL of methanol solution of MeONa (0.5 M) under a N_2 atmosphere. Next, 6.38 (22 mmol) g of 3-iodopropropyltrimethoxysilane was added to the solution, and the slurry was heated at 313 K under reflux for 4 days. The methanol excess in the mixture was removed in a rotavapor. The brown solid precipitate was washed with CH_3Cl, providing 3.57 g (80%) of the desired product. ^1H NMR (300 MHz, D_2O): δ 8.0 (d. $J = 7$ Hz, 2H), 6.7 (d, $J = 7$ Hz, 2H), 3.5 (s, 18H), 3.0 (t, $J = 7$ Hz 4H), 1.7 (m, 4H) and 0.7 (m, 4H). Anal. Calcd for $C_{18}H_{34}N_2O_7Si_2$: C, 48.43; H, 7.62; N, 6.28. Found: C, 48.05; H, 7.18; N, 6.15

Synthesis. *(i) Preparation of the Layered Silicate: Na-Magadiite (MAG).* Na-Magadiite was obtained by preparing a synthesis gel with $1SiO_2$:0.2NaOH:0.5*trans*-4-aminocyclohexanol:$15H_2O$ as molar ratio. After stirring, the gel was transferred to a Teflon-lined autoclave and heated at 423 K for 3 days. The Magadiite product was filtered, washed with deionized water, and dried to 333 K overnight.

(ii) Swelling of Na-Magadiite (MAG-CTMA). To prepare the swollen Magadiite, we dispersed 10 g of the lamellar precursor in 40 g of H_2O milliQ, and 200 g of a cetyltrimethylammonium hidroxide solution (CTMA, 25 wt %, 50% exchanged Br/OH) was added, with a final pH of 12.5. The resultant mixture was refluxed at 353 K, stirring vigorously, for 16 h in order to facilitate the swelling of the layers of the precursor material. At this point, the swollen material was recovered by centrifugation, washed with distilled water, and dried at 333 K for 12 h.

(iii) Pillaring of Swollen Magadiite (MAG-CTMA-BTMPVi and MAG-CTMA-BTMPNA). The swollen Magadiite (0.5 g) was vigorously stirred with an aqueous solution (60 mL) of pillaring agents, BTMPVi (0.5 g) or BTMPNA (0.5 g), for 5 days at 333 K. This process was realized under an inert atmosphere (N_2). An orange or brown solid was recovered from the suspension by centrifugation. The compounds were then air-dried for 7 days at room temperature.

(iv) Pillared Organic−Inorganic hybrid materials (MAG-BTMPVi and MAG-BTMPNA). To remove the CTMA employed as swollen agents, we suspended the pillared compounds (0.5 g) and refluxed them in 50 mL of 1 M HCl ethanol solution for 3 days at 343 K. The pillared final products were recovered after filtration with distilled water and were air-dried at 333 K overnight.

Characterization. XRD analysis was carried out with a Philips X'PERT diffractometer equipped with a proportional detector and a secondary graphite monochromator. Data were collected stepwise over the $2° \leq 2\theta \leq 40°$ angular region, with steps of 0.02° 2θ, 20 s/step accumulation time, and Cu Kα ($\lambda = 1.54178$ Å) radiation. Textural properties were determined by nitrogen isotherms at liquid N_2 temperature using a Micromeritics ASAP 2010 apparatus (static volumetric technique). Samples (∼0.2 g) were first outgassed overnight at 373 K under a vacuum. Chemical analysis (C, N, H) was carried out by combustion using a Perkin-Elmer analyzer. The NMR spectra were recorded at room temperature under magic-angle spinning (MAS) on a Bruker AV400 spectrometer. The single pulse ^{29}Si spectra were acquired using pulses of 3.5 μs corresponding to a flip angle of $3/4\pi$ radians and a recycle delay of 240 s. The ^1H to ^{13}C cross-polarization (CP) spectra were acquired by using a 90° pulse for ^1H of 5 μs, a contact time of 5 ms, and a

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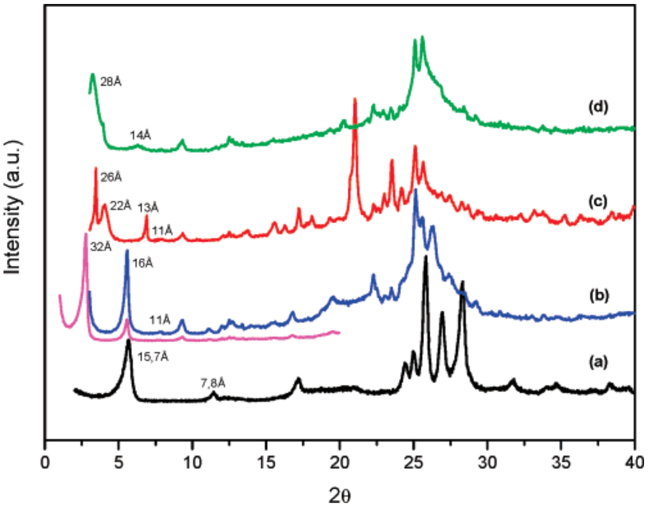

Figure 1. Powder X-ray diffraction patterns of (a) Na-MAG, (b) MAG-CTMA, (c) MAG-CTMA-BTMPVi, and (d) MAG-BTMPVi.

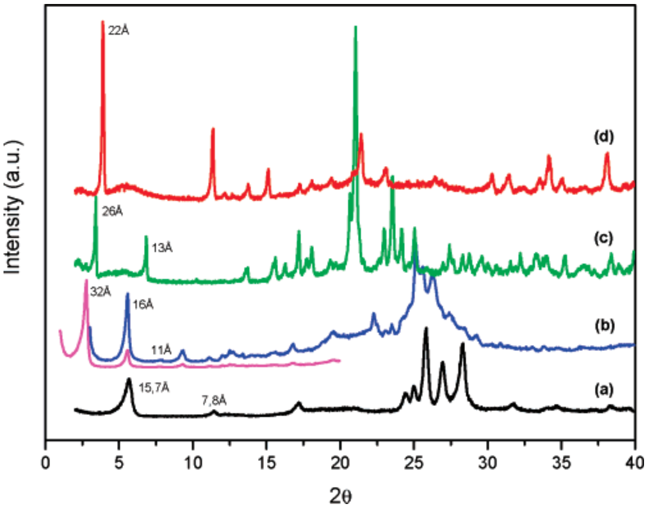

Figure 2. Powder X-ray diffraction patterns of (a) Na-MAG, (b) MAG-CTMA, (c) MAG-CTMA-BTMPNA, and (d) MAG-BTMPNA.

recycle of 3 s. All spectra were recorded with a 7 mm Bruker BL-7 probe and at a sample spinning rate of 5 kHz. The ^{29}Si spectra were referred to tetramethylsilane (TMS) and the ^{13}C to adamantane. Thermogravimetric and differential thermal analyses (TGA-DTA) were conducted in an air stream with a Metler Toledo TGA/SDTA 851E analyzer. A Cary 5 spectrometer equipped with a diffuse reflectance accessory was used for UV measurements.

Results and Discussion

Different experiments were performed using bridged silsesquioxanes (BTMPVi or BTMPNA) as pillaring agents to synthesize different hybrid layered materials. In these materials, the organic linkers (viologen or nitroaniline) present in the initial organosilanes could be incorporated into the interlayer space of layered silicates, covalently bonded to surface of magadiite-type inorganic layers. Indeed, XRD patterns of Na-, swollen-, and pillared-magadiite shown in Figure 1 and 2exhibit *00l* reflections corresponding, in the case of Na-Magadiite, to a basal spacing of 15.7 Å due to the presence of sodium cations and water molecules present between the magadiite layers whose thickness is ~9.5 Å, whereas after the swelling process, the basal spacing increases to 32 Å because of the effective intercalation of CTMA$^+$ molecules in the interlayer space. When the pillaring step was realized with BTMPVi as pillar, the basal spacing reduces to 28 Å in the final material (Figure 1d). Taking into account the thickness (9.5 Å) of the magadiite layers, the space occupied by the bridged silsesquioxane corresponds to 18.5 Å, which closely matches the molecular length of the BTMPVi molecule (Figure 3a). This fact confirms that the organic−inorganic precursor was successfully intercalated into the interlayer space with the viologen units perpendicularly oriented to the silicate layer. The diffraction pattern of pillared sample before acid extraction (Figure 1c) also shows one additional basal spacing of 22 Å, which disappears after the swelling molecules are removed. This second type of ordering could be explained by the intercalation of bridged silsesquioxane molecules of BTMPVi, which are not covalently bonded with the silanol groups present on the surface of the silicate layers and are eliminated during the extraction process.

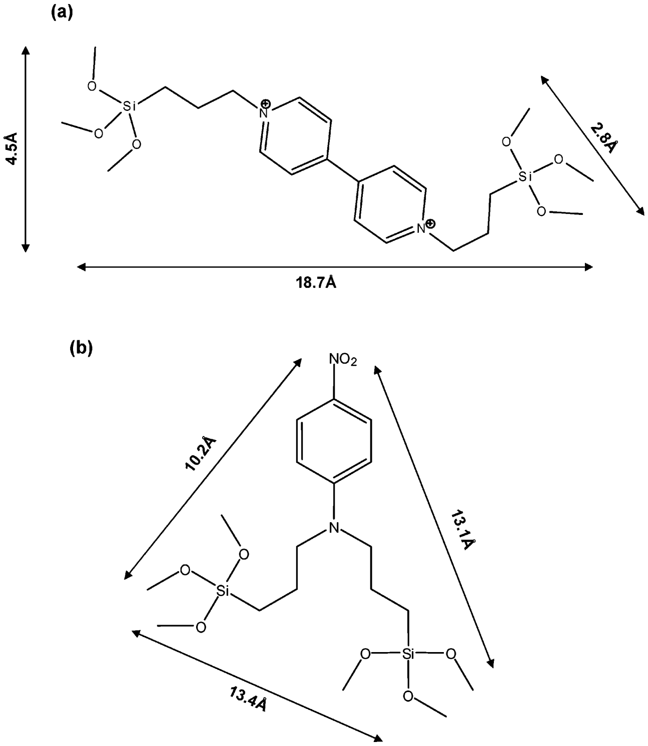

Figure 3. Molecular representation of bridged silsesquioxanes used as pillaring agents: (a) BTMPVi and (b) BTMPNA.

The diffraction patterns showed in Figure 2 confirm that the organic−inorganic BTMPNA molecules are also perpendicularly intercalated into the interlayer space between the magadiite layers (Figure 2d). In this case, the basal spacing in the pillared hybrid is of 22 Å, corroborating that the bridged silsesquioxanes of ~13.4 Å of length (Figure 3b) is intercalated between the silicate layers.

A schematic model of the prepared layered organic−inorganic hybrid materials is represented in Figure 4, where the viologen and nitroaniline groups are homogenously distributed in the interlayer space.

The organic content present in the swollen and pillared materials was obtained by C, H, N chemical analyses and results are shown in Table 1, with the integrity of the organic molecules being present in the interlayer space confirmed

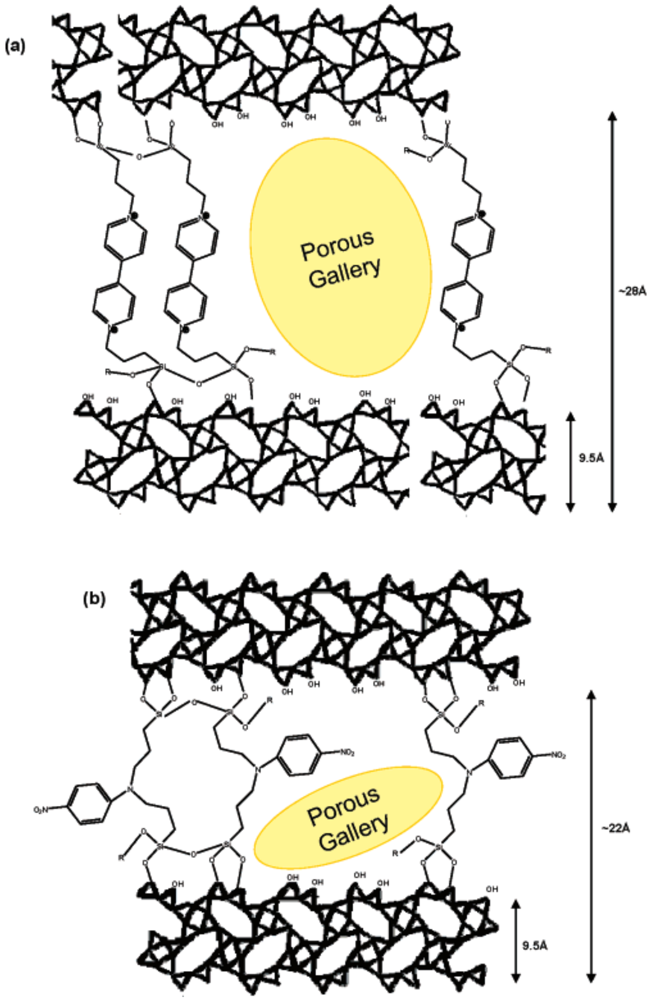

Figure 4. Schematic representation of layered hybrid organic−inorganic materials with (a) viologen and (b) nitroaniline units in the interlayer space.

from the calculated C/N ratios. In the case of the swollen magadiite (MAG-CTMA), the results show that the experimental carbon content (28.3 wt %) is similar to the estimated theoretically (26.3 wt %), which confirms that the CTMA molecules used as swollen agents are effectively introduced, separating the layers between them. When the swollen sample is pillared with viologen units (MAG-CTMA-BTMPVi), the CHN results show that the experimental C/N ratio (12.7) is higher than the theoretical (10.0), which could be explained by the presence of some CTMA molecules in the interlayer space together with bridged silsesquioxanes of BTMPVi. Finally, when the swollen molecules are extracted, both the theoretically estimated (13.2 wt % and 6.9) and experimentally measured (12.9 wt % and 7.2) carbon content and C/N ratio are very close, confirming that the viologen units are successfully intercalated into the interlayer space.

In the case of hybrids pillared with nitroaniline groups, the theoretical and experimental results are also co-incident. Before extraction (MAG-CTMA-BTMPNA), part of the CTMA molecules used during the swollen process remain together with BTMPNA molecules used as pillars (Table 1). After the extraction process, practically the totality of the swollen molecules is removed and the C/N ratio of the pillared hybrid is co-incident with the C/N ratio of BTMPNA molecule. Therefore, the results obtained for the final solid (MAG-BTMPNA) indicate that when it is pillared with BTMPNA, the theoretical carbon content and C/N ratios calculated (10.6 wt % and 5.1) are very similar to experimental results (10.8 wt % and 5.4), confirming that nitroaniline groups are intercalated between the magadiite layers.

So, considering these CHN experimental results, it is possible to confirm that 0.033 mol of BTMPVi and 0.037 mol of BTMPNA are incorporated as pillars per mole of layered silicate type magadiite.

The thermal stability and the presence of organic fragments into the interlayer space of magadiite layered precursor are clearly shown using thermogravimetrical (TGA) and thermodiferential (DTA) analyses for different samples obtained during the pillarization process (Figure 5). In the case of Na-magadiite (Figure 5a), the only weight loss observed corresponds to adsorbed water. When the swollen step is carried out, the CTMA molecules (22.3 wt %) are removed at ∼500 K (loss named I in Figure 5b). Following with the pillarization process, when BTMPVi or BTMPNA are employed as pillaring agents, it is possible to deduce from the TGA curves (panels c and e in Figure 5) the presence of bridged silsesquioxanes units (loss II) together with CTMA molecules that remain from the swelling step (loss I). Then, considering the weight loss with the temperature, it is possible to consider that the viologen and nitroaniline organic pillars (12.2 and 10.5 wt %, respectively) are still stable at temperatures close to 600 K (Table 1). This is confirmed from the TGA and DTA analyses obtained for the pillared hybrids after the acid extraction in which only the weight loss at 600 K (loss II) due to organic pillars is observed (panels d and f in Figure 5). The total absence of CTMA (loss I) in the TGA, together with elemental analyses, for final layered hybrids confirm that acid extraction was very effective in removing any organic employed as swelling agent. Moreover, it is important to remark that the weight loss due to viologen and nitroaniline groups contained in the final pillared hybrid materials (12.3 and 10.9 wt %, respectively) is very similar to the organic content calculated from CHN analyses (12.9 and 10.8 wt %, respectively). This comparison is shown in Table 1.

Nitrogen adsorption isotherms of pillared materials are shown in Figures 6 and 7. In the case of layered materials with intercalated viologen units, a classical mesoporous type IV isotherm is observed (Figure 6a), with a BET specific surface area and pore volume of 635 m^2 g^{-1} and 0.354 cm^3 g^{-1}, respectively. On the contrary, when nitroaniline groups are intercalated into the interlayer space, a conventional microporous type I isotherm is observed (Figure 7a), with a BET surface area of 563 m^2 g^{-1} and pore volume of 0.247 cm^3 g^{-1}. The different isotherms obtained with BTMPVi and BTMPNA could be explained by the viologen units being placed into the interlayer space more linearly than BTMPNA, generating mesoporous between viologen pillars. In the case of BTMPNA, the occupied volume for nitroaniline groups is higher, decreasing the free space between the pillars and generating microporosity. The pore distribution for hybrid materials (Figure 8) confirmed this hypothesis, showing a pore distribution centered at ∼20 Å for the MAG-BTMPVi material, whereas the pore size for the MAG-BTMPNA

Table 1. Chemical Analyses and Organic Content Contained in the Samples Obtained during the Pillarization Process

	%C		%C/%N		%organic, exp[b]		
sample	theor	exp[a]	theor	exp[a]	weight loss	CTMA (~**500 K**)	disilane (~**600 K**)
MAG−CTMA	28.3	26.3	16.3	15.5	25.7	22.3	
MAG−CTMA−BTMPVi	41.5	33.2	10.0	12.7	39.8	20.3	12.2
MAG−BTMPVi	13.2	12.9	6.9	7.2	14.7		12.3
MAG−CTMA−BTMPNA	38.9	24.8	8.9	10.8	21.2	8.2	10.5
MAG−BTMPNA	10.6	10.8	5.1	5.4	15.8		10.9

[a] Carbon and nitrogen content estimated by C, H, N chemical analyses. [b] Organic content estimated by thermogravimetrical analyses. Adsorbed water was not considered.

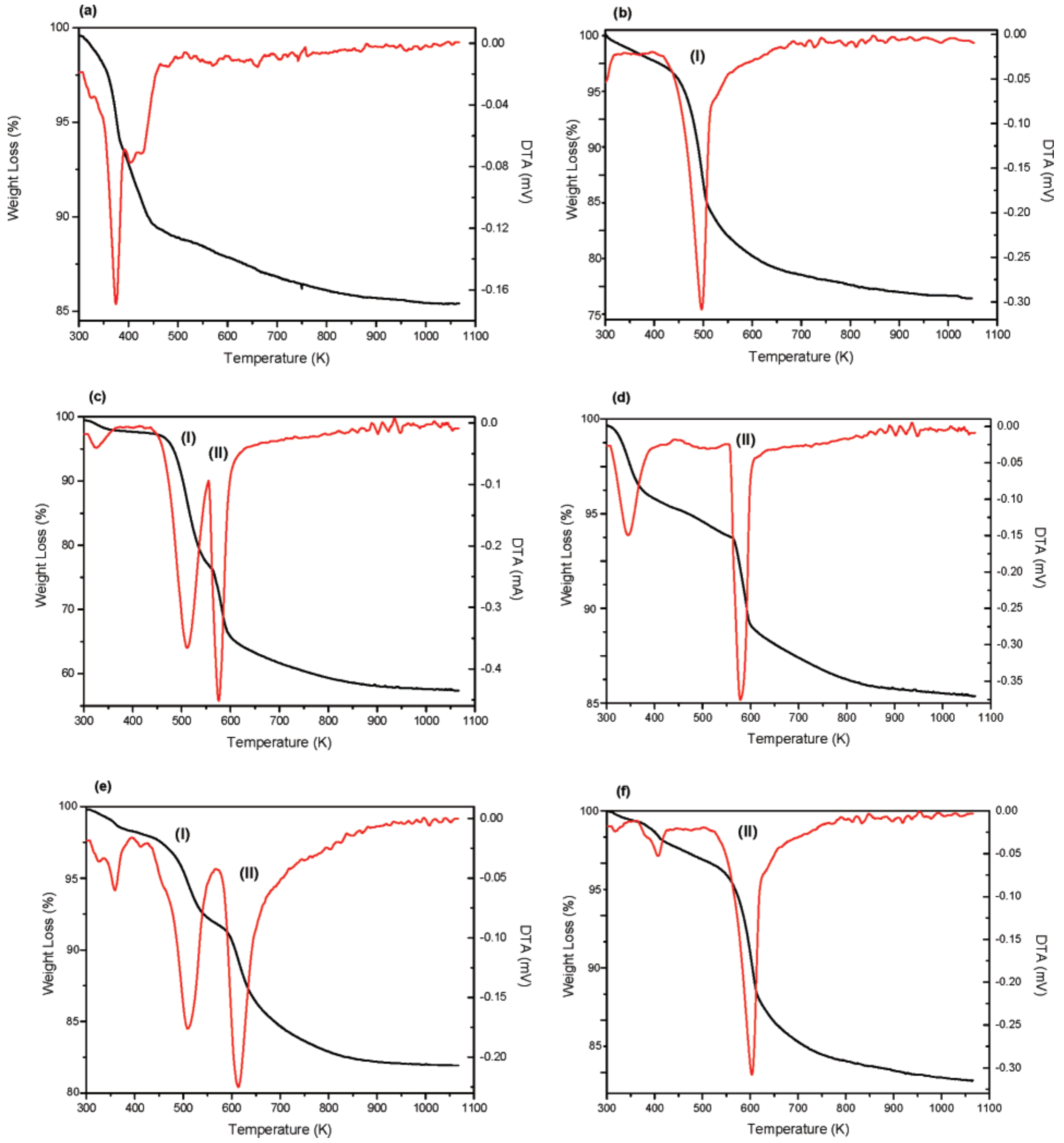

Figure 5. DTA and TGA curves of (a) Na-MAG, (b) MAG-CTMA, (c) MAG-CTMA-BTMPVi, (d) MAG-BTMPVi, (e) MAG-CTMA-BTMPNA, and (f) MAG-BTMPNA.

distribution is centered at ~10 Å. The schematic representation of the free porous space presents into the pillared hybrid materials is shown in Figure 4.

For comparison purposes, two amorphous hybrid materials were synthesized that supported bridged silsesquioxane precursors over amorphous silica.[31] The nitrogen adsorption isotherms for these solids (Figures 6b and 7b) show practically no porosity (12 m^2 g^{-1} for BTMPVi and 33 m^2 g^{-1} for

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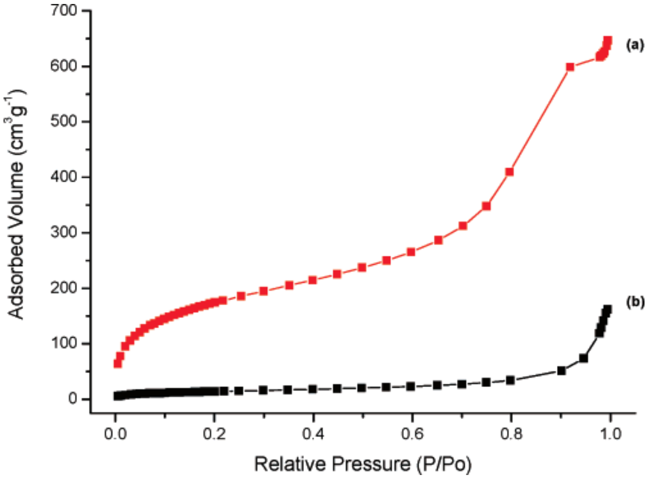

Figure 6. Nitrogen adsorption isotherms of (a) MAG-BTMPVi and (b) amorphous-BTMPVi.

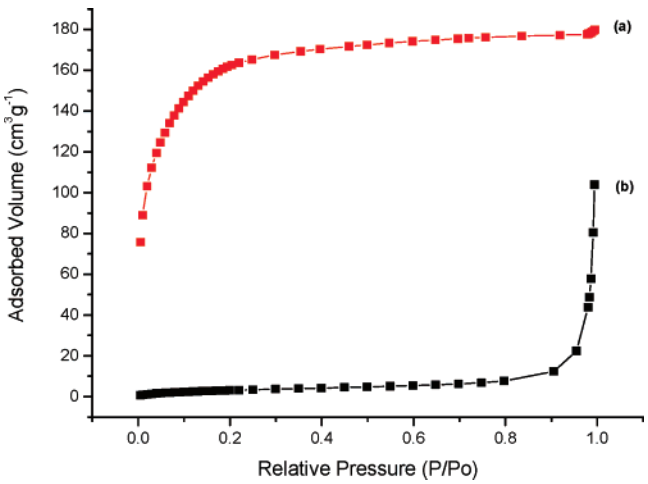

Figure 7. Nitrogen adsorption isotherms of (a) MAG-BTMPNA and (b) amorphous-BTMPNA.

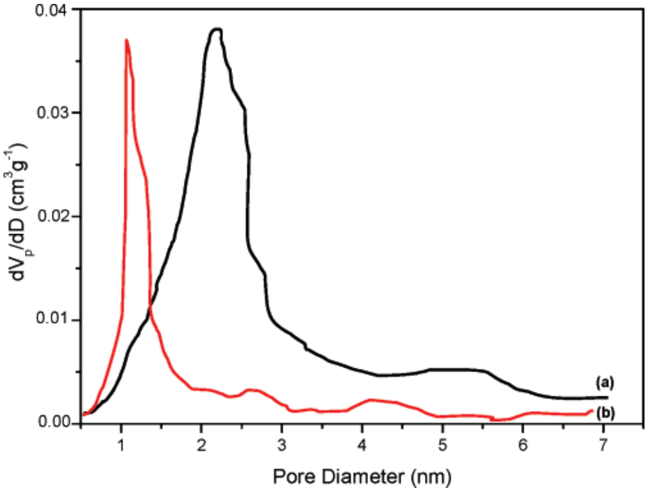

Figure 8. Pore distributions of (a) MAG-BTMPVi and (b) MAG-BTMPNA using the Horwath−Kawazoe method.

BTMPNA), corroborating that no structural order was achieved in the amorphous silica because of the presence of bridged organic−inorganic molecules.

The ^{13}C CP/MAS NMR spectra of the organic−inorganic materials are shown in Figure 9. In all cases, it is possible to observe a peak around 0 ppm that can be assigned to carbon species propylviologen (Figure 9a) and propylnitroaniline (Figure 9b) that are directly bonded to Si atoms.[32] This fact confirms that organic fragments remain intact as in the initial bridged silsesquioxane reagents, indicating the incorporation of Si-bonded carbon species derived from the silicon sources into the interlayer space. The total integrity of organic linkers is completely confirmed because all their carbon atoms are univocally assigned in the ^{13}C NMR spectra (see the inset in Figure 9). Moreover, the absence of a peak around 52 ppm, assigned to methoxy groups, is an indication of the covalent interaction of silanol species, placed in the surface of silicate layers, with the reactive alcoxy groups present in the bridged silsesquioxanes used as pillars. No peak assigned to CTMA molecules, used as swelling agents, was observed, showing the high effectivity of the acid extraction process to remove CTMA.

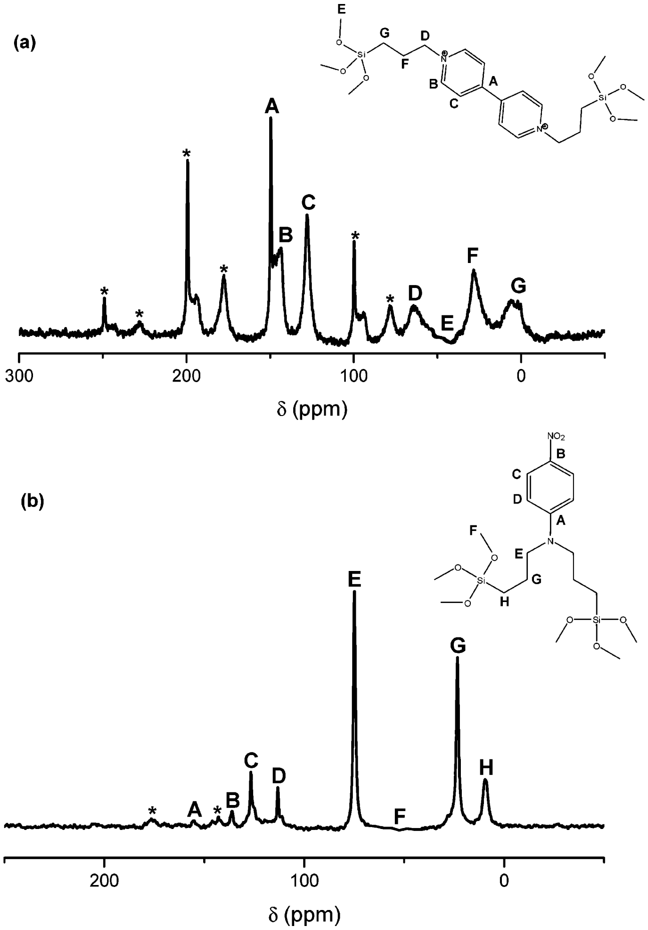

Figure 9. ^{13}C CP/MAS NMR spectra of (a) MAG-BTMPVi and (b) MAG-BTMPNA. Asterisks (*) correspond to spinning bands.

Although ^{13}C NMR was able to confirm that organic fragments preserve their integrity during the pillarization processes, ^{29}Si MAS NMR was required to confirm that the organic groups not only remain intact but are also incorporated covalently into the free interlayer space, bonded to inorganic magadiite layers. Figure 10 shows the ^{29}Si CP/MAS NMR spectra of Na-Magadiite and viologen and nitroaniline pillared hybrids. The spectra of hybrid silicates exhibit characteristic bands around −60 ppm (Figures 10b and 10c) assigned to T-type silicon species, namely, silicon

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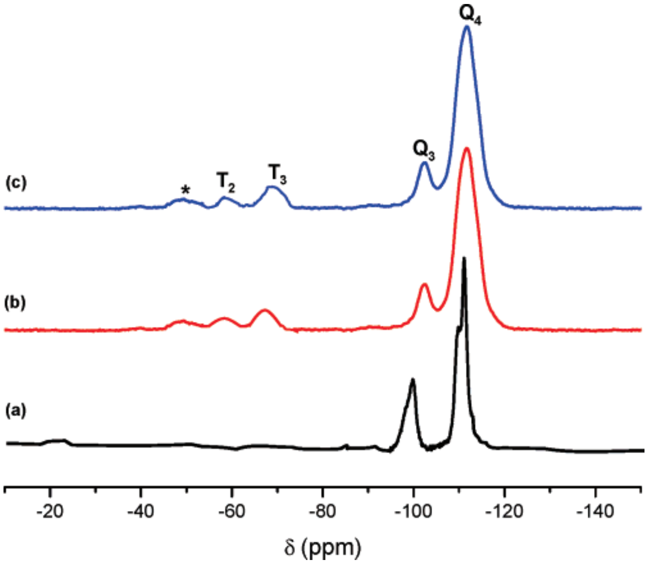

Figure 10. ^{29}Si BD/MAS NMR spectra of (a) Na-Magadiite, (b) MAG-BTMPVi, and (c) MAG-BTMPNA. Asterisks correspond to spinning bands.

species having a Si−C bond.[33] More specifically, it is possible to appreciate two bands at −58 and −67 ppm corresponding to T^2 (C−Si(OH)(OSi)$_2$) and T^3 (C−Si(OSi)$_3$), respectively. This fact definitively confirms the presence of viologen or nitroaniline modified silicon species bonded to the layers in these materials. The existence of T^2 and T^3 atoms results from successful hydrolysis and policondensation of BTMPVi and BTMPNA reagents, because the molecules have three methoxy groups on the Si atoms bonded to each end of the organic linkers.

All ^{29}Si MAS NMR spectra show two peaks at −100 and −110 ppm assigned to Q^3 (Si(OH)(OSi)$_3$) and Q^4 (Si(OSi)$_4$) units, respectively, that originate from the magadiite layer, which consists of tetrahedral SiO$_4$ units and silanol groups (Figure 10a). The Q^3/Q^4 ratio of magadiite is approximately 0.5, whereas the ratio of pillared hybrid materials is lower (∼0.2) because of the decrease in the silanol groups on the surface of silicate layers (graphs b and c in Figure 10). These results suggest the effective condensation of silanol groups from the layers with alkoxy groups in the bridged silsesquioxane molecules. It is important to remark that some of the BTMNPVi and BTMPNA molecules probably react with each other along the direction parallel to that formed by the organic linkers into the interlayer space. This could result in additional formation of the siloxane bonds with the generation of dimers, which might yield to the connection between the layers through the siloxane bond of each bridged silsesquioxane in the dimer (Figure 4). Thus, silanol groups present at the surface might be deduced from the condensation phenomenon because of dimer generation. However, these types of additional siloxane bonds have not been identified by ^{29}Si NMR studies, probably because the signal corresponding to these silicon species are included inside of broad T^2 and T^3 bands.

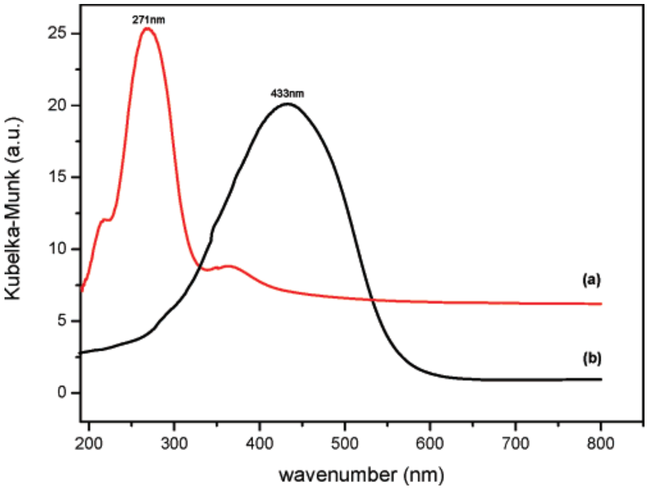

Figure 11. Diffuse reflection absorption spectra of (a) MAG-BTMPVi and (b) amorphous-BTMPVi.

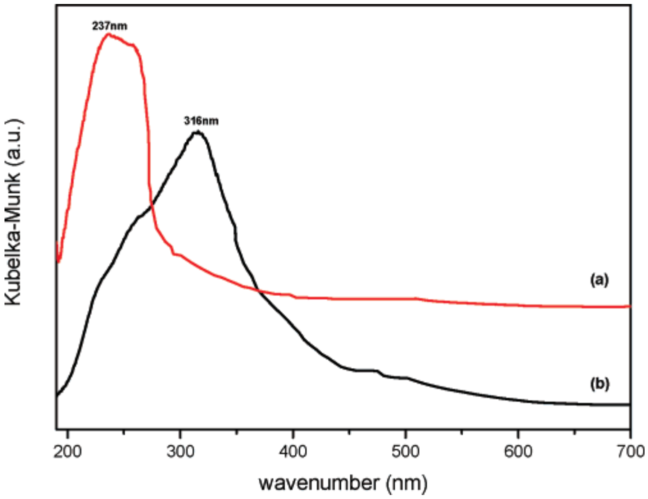

Figure 12. Diffuse reflection absorption spectra of (a) MAG-BTMPNA and (b) amorphous-BTMPNA.

The UV−visible diffuse reflectance absorption spectra of MAG-BMPNVi and MAG-BTMPNA pillared materials are showed in Figures 11 and 12. The viologen and nitroaniline groups, when they are supported over amorphous silica, show absorption characteristic bands whose peaks of maximal intensity are placed approximately at 433 nm (Figure 11b) and 316 nm (Figure 12b), respectively. When these organic linkers are intercalated into the interlayer space, the more intense bands are centered at lower wavenumbers, more specifically at 271 nm (Figure 11a) and 237 nm (Figure 12a) for viologen and nitraniline units, respectively. The shift observed suggests that organic pillars are effectively stabilized into the interlayer space,[34] making the interactions between organic linkers in the free interlayer space possible.

Conclusions

Novel porous organic−inorganic hybrid materials have been successfully prepared from the layered silicates magadiite using bridged silsesquioxanes as pillars. The intercalation of viologen or nitroaniline groups into the interlayer space was confirmed by X-ray diffraction, making it possible to control the different steps followed during the synthesis

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(33) Yamamoto, K.; Sakata, Y.; Nohara, Y.; Takahashi, Y.; Tatsumi, T. *Science* **2003**, *300*, 470.

(34) Hobson, S. T.; Zieba, J.; Prasad, P. N.; Shea, K. J. *Mater. Res. Soc. Symp. Proc.* **1999**, *561*, 21.

method: swelling, pillarization, and acid extraction. The galleries formed between the magadiite layers because of intercalated organic pillars exhibited pores of ∼20 and ∼10 Å diameters for viologen and nitroaniline units, respectively, generating a large free microporous and mesoporous volume into the interlayer space ($S_{BET} \approx 500-650$ m^2 g^{-1} and $V_{TOT} \approx 0.25-0.35$ cm^3 g^{-1}). The presence of organic linkers between the silicate layers was corroborated by thermogravimetric and chemical analyses, and the final pillared materials contain ∼11−12 wt % organic fragments into the interlayer space. These results have also confirmed that the pillared hybrid materials are stable up to 600 K. On the other hand, the integrity of organic linkers has been shown by NMR studies, confirming that viologen and nitroaniline groups are convalently bonded to the surface of magadiite layers. Additionally, the UV−visible results showed that organic pillars present in the free interlayer space are stabilized by the silicate layers.

Stabilized viologen and nitroaniline groups are potentially interesting from a sensoring and optical device standpoint. More specifically, viologen hybrids could be used as excellent sensors because of their ability to accept electrons in a variety of electron-transfer processes, generating detectable radical cationic species. On the other hand, hybrids with intercalated chromophore groups such as nitroaniline could exhibit a large macroscopic second-order susceptibility, making them excellent nonlinear optical (NLO) materials. We are now investigating these possibilities.

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