### Synthesis and Catalytic Properties of Hybrid Mesoporous Materials Assembled from Polyhedral and Bridged Silsesquioxane Monomers

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Abstract: A family of hybrid mesoporous materials with high temperature stability was obtained by the suitable covalent combination of two types of siloxane precursors. Specifically, cubic T<sub>8</sub> polyhedral oligomeric (POSS) and aryl bridged silsesquioxane monomers (1,4-bis(triethoxysilyl)benzene, BTEB) play the role of nanobuilders. An optimal molar ratio of the two precursors (5-25 mol% of total silicon content

from the BTEB disilane) generated a homogenous, highly accessible, and well-defined mesoporous material with hexagonal symmetry and narrow poresize distribution. Physicochemical, tex-

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### Introduction

The synthesis of hybrid organic-inorganic materials is one of the most attractive and emerging fields in the area of nanomaterials preparation, with potential applications in advanced materials.[1-3]

Traditionally, the simplest approach to obtaining stable hybrid materials involve the incorporation of organic molecules into inorganic structures, such as the encapsulation of organic compounds inside an inorganic matrix by non-covalent interactions (van der Waals forces, hydrogen-, or ionicbonding interactions); these methods typically afford hybrid solids in which the functionality from the organic counterpart can remain active for a long time. Representative examples of this type of hybrid material include organic functional molecules that were occluded or prepared in situ (ship-in-a-bottle method) inside the cavities of microporous silicates or zeolites.<sup>[4,5]</sup> Alternatively, the incorporation-and stabilization-of organic moieties into the interlayer space of lamellar inorganic systems is another example of this family of organic-inorganic solids that are based on weak chemical interactions between the different components of the materials.<sup>[6]</sup> In general, these hybrid materials have been termed as Class I in various reviews on the subject.<sup>[7]</sup> Although the stability of the organic components increased when they were occluded inside the inorganic voids, the weak chemical connections lessened the potential for coop-

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tural, and spectroscopic analysis corroborated the effective integration and preservation of the two different nanoprecursors, thereby confirming the framework of the mesoporous hybrid materials. A post-synthesis amination treatment allowed the effective incorporation of amino groups onto the aryl linkers, thereby obtaining a stable and recyclable basic catalyst for use in C-C bond-formation processes.

erative effects between the organic host and the inorganic network. Moreover, leaching, deactivation, and the desorption of active organic moieties from inorganic matrixes are important limitations of these types of hybrid solids.<sup>[8,9]</sup> Therefore, advanced hybrid materials have been prepared that avoided the limitations described above by introducing strong covalent interactions between the organic and inorganic fragments that held the framework together on the nanometer scale (Class II hybrids).[10] In this way, various materials have been produced in which different organic functions were isolated and integrated into the hybrid framework.<sup>[11]</sup> The organic counterparts in these solids were more stable than the isolated organic molecules. Moreover, the presence of organic fragments in the walls of the solids favours the homogenous distribution of the organic active sites along the channels of the porous material without blocking them, unlike the materials that contained organic groups anchored on the walls that reached into the pore system.[12-15]

The use of suitable monomers as precursors for the synthesis of Class II materials, in which organic and inorganic units were pre-reacted together, is vital for affording effective transfer of this hybrid combination into the final nanometer-scale materials, whilst generating structures that were comprised from structural sub-units that arose from the starting precursors. This methodology has been used in the synthesis of hybrid materials that showed the high mechanical, structural, and hydrothermal stability that are characteristic of inorganic materials, together with the flexibility and functionality that are typical of organic compounds.[16,17] Bridged silsesquioxanes  $((R'O)_3Si-R-Si(OR')_3)$  can be easily integrated into solid frameworks owing to the high reactivity of their terminal siloxane groups.<sup>[18,19]</sup> This type of disilanes has typically been used in the one-pot sol-gel syn-

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thesis of ordered- and non-ordered hybrid materials with various textural properties that depended on the rigidity or flexibility of the starting silsesquioxane and on the reaction conditions.<sup>[20]</sup> Specifically, the use of self-assembling micellar routes has favored the preparation of periodic mesoporous materials (PMOs) with applications in catalytic or technological fields.<sup>[21]</sup>

Another attractive route for the preparation of stable hybrid materials is the direct assembly of individual building blocks in which it is possible to effectively combine suitable preformed organic and inorganic species that remain intact in the final material without losing their initial properties. This approach allows the simplest construction of two or more active precursors to generate multifunctional hybrid materials.<sup>[22]</sup> Examples of these types of hybrid systems include metallic nanoclusters that were surface-functionalized with reactive organic groups and inorganic layered materials that were pillared with specific bridged silsesquioxanes.<sup>[23,24]</sup>

Of the silsesquioxane monomers, polyhedral oligomeric silsesquioxanes (POSS) could be ideal as nanoscale building blocks for the generation of structured hybrid materials. Various POSS units are shown in Scheme 1, in which, for example, double four-membered rings are present in the  $T_8$  POSS structure; these units have also been used as secon-

dary building units in many crystalline micro- and mesoporous zeolite-type materials.<sup>[25–27]</sup>

During the preparation of these oligosilsesquioxanes, it would be possible to incorporate functional organic substituents or metallic species that were projected outward from the corners of the cube-type POSS, thereby shielding the siloxane core.<sup>[28]</sup> The integration of these active building blocks into different organized frameworks could generate attractive hybrid materials that have potential catalytic properties. Alternatively, the use of POSS units as precursors may afford ordered hybrid materials owing to their ability to act as structural nodes and to react covalently with another organic-inorganic building block (Scheme 2). Despite the interesting features of POSS, attempts to use them as effective precursor units have normally led to non-crystalline polymers or compact dendrimers. The lack of porosity of these prepared materials has limited their applications owing to the



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Scheme 1. Structures of various POSS units.[25]

poor accessibility of the functional groups. Only recently, Kuroda and co-workers and van Santen and co-workers have used POSS that consisted of double-four-memberedring (D4R) units, which was functionalized with mono-, di-, and trialkoxysilyl or vinyl groups, as nanobuilding blocks to obtain robust mesostructured silica materials by using amiphilic triblock copolymer surfactants as structure-directing



Scheme 2. Synthesis of the hybrid mesoporous materials and the structure of an organic–inorganic framework that was composed of  $T_8$  POSS and aryl linkers that were obtained from their respective silsesquioxane precursors.

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agents. The high surface area (960 m<sup>2</sup>g<sup>-1</sup>) and improved hydrothermal stability that were exhibited by porous hybrid materials that were derived from octavinyl-POSS units have increased the potential use of these materials in a variety of applications.<sup>[29–32]</sup>

Taking into account the possibility that the bridged and polyhedral silsesquioxane monomers can act as effective building blocks for the generation of porous and organized hybrid materials, we have obtained the first hybrid materials that were formed from the combination of T<sub>8</sub> POSS units and 1,4-bis(triethoxysilyl)benzene (BTEB). These materials were prepared by an acidic self-assembly micellar route in the presence of surfactants as structure-directing agents. The resulting hybrid frameworks were composed of the two starting precursors and the amount of each silsesquioxane that was incorporated into the structure was controlled by changing different synthesis variables. The presence and stability of double four-membered rings (D4R), from the T<sub>8</sub> POSS units, which were covalently assembled with aryl bridged fragments, afforded a highly stable and robust mesoporous hybrid network. The introduction of different active functional groups, both in the POSS and in the bridged silsesquioxane units, would allow the generation of multifunctional hybrid porous materials with potential catalytic applications. Herein, amino groups were incorporated onto the aryl building blocks, thereby generating basic catalysts for C-C bond-formation processes. Therefore, herein, we report a new strategy for the synthesis of strong hybrid materials; this strategy involved the assembly of functional silsesquioxane monomers that acted as effective nanobuilding blocks.

#### **Results and Discussion**

**Synthesis and characterization**: The preparation of hybrid mesoporous materials was carried out by condensing two different polyhedral and bridged silsesquioxane monomers, which acted as building blocks, in the presence of surfactant molecules in acidic medium (Scheme 2). The porous solids were formed from cube-type POSS units that were linked through bridging aryl groups on the bis-silylated BTEB precursors. The presence of polyhedral silsesquioxanes as small cages of double four-membered rings, which were connected through functional organic linkers and constituted the "walls" of the solids, should allow the preparation of robust, stable, and functional mesoporous materials with catalytic applications.

Several hybrid materials were prepared by using various amounts of the two types of silsesquioxane precursors: mesoporous materials that were obtained from  $T_8$  POSS (HYB-100P) alone, BTEB (HYB-100B) alone, as well as intermediate materials that were synthesized from a combination of the two nanobuilding blocks in different silicon molar ratios (HYB-xP-yB, with x and y between 0 and 100), were studied. These materials were analyzed by XRD and the results showed that the initial ratio of the two silsesquioxanes



Figure 1. X-ray patterns of as-synthesized mesoporous materials that were obtained from  $T_8$  POSS and/or BTEB silsesquioxanes: a) HYB-100P, b) HYB-50P-50B, c) HYB-25P-75B, d) HYB-100B, e) HYB-95P-5B, and f) HYB-75P-25B.

was crucial for obtaining homogeneous mesoporous materials with long-range order (Figure 1). In fact, the solid that was prepared from T<sub>8</sub> POSS alone did not exhibit much homogeneous structural order, as deduced from the low intensity and broadness of the low-angle diffraction band that is characteristic of mesoporous materials. On the contrary, when BTEB was introduced into the material (5 mol% and 25 mol% of the total silicon content), the homogeneity in the mesoporous materials improved markedly, as indicated by the XRD patterns in which the bands that were associated with the (110) and (200) reflections, which corresponded to a mesoporous solid with a conventional hexagonal M41S topology, were also visible in the HYB-95P-5B material.<sup>[33]</sup> The porous homogeneity and structural regularity decreased in the materials that had a higher amount of BTEB bis-silvlated precursor (50, 75, and 100 mol% of the total silicon content), as indicated by the low-angle X-ray patterns

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(Figure 1). Therefore, it was possible to prepare well-structured mesoporous materials with M41S topology by combining T<sub>8</sub> POSS and BTEB nanobuilding blocks. However, well-ordered materials were better obtained when the amount of BTEB-bridged silsesquioxane was between 5 and 25 mol% of the total silicon content. Under these conditions, the aryl fragments from the BTEB monomers acted as linkers of the POSS cubic units, thereby facilitating the optimal structure-formation and good distribution of the organic and inorganic building blocks, thereby yielding homogenous mesoporous hybrid materials with P6mm symmetry. Crystalline hybrid materials with only BTEB as silicon a source, which were synthesized in strongly alkaline media, have been described previously.<sup>[34,35]</sup> However, those conditions were not suitable for the preparation of hybrid materials that contained both T<sub>8</sub> POSS and BTEB. The synthesis of mesoporous materials from two precursors was only successful under acidic conditions (see the Experimental Section).

The XRD patterns of the hybrid samples after calcination at 400 °C (Figure 2) showed intense low-angle bands of the as-synthesized solids when the amount of BTEB was between 5–25 mol% of the total silicon content, thereby confirming that the mesoporous order remained, even after removal of the surfactant molecules that were used as structure-directing agents. In the case of the samples with higher BTEB content, the calcination step partially improved the mesoporous order of the respective as-synthesized samples, as deduced from the presence of low-angle diffraction bands, although they were broad and less intense.

TEM analysis (Figure 3) supported the XRD results. More specifically, the hybrid samples in which 5 and 25 mol% of the total silicon content came from the BTEBbridged silsesquioxane precursors (HYB-95P-5B and HYB-75P-25B) exhibited a well-ordered and homogeneous distribution of the porous channels, with a diameter of about 3 nm (Figure 3 b,c). Thus, by using the equation  $a = 2d_{100}/2$  $\sqrt{3}$ <sup>[36]</sup> the *d*-spacing for the (100) reflection band from the X-ray diffractograms, and the mean pore diameter that was estimated from the TEM images, we calculated that the pore-wall thickness in the hybrid mesoporous materials was about 1.8 nm; this result would be consistent with an assembly of four POSS monomers that were organized as consecutive layers to construct the walls of the porous solids (Scheme 3). On the contrary, the materials that were prepared from polyhedral POSS silsesquioxane alone and, above all, those that were prepared by combining the cubic silsesquioxane units with high amounts of BTEB (> 25 mol% of the total silicon content) exhibited inhomogeneous mesoporous distribution with poorer structural organization (Figure 3a, d, e); this result was also deduced from the X-ray patterns. After the amination process (see the Experimental Section), in which amino groups were covalently bonded onto the aryl fragments to form HYB-75P-25B-NH<sub>2</sub>, the obtained diffractogram was practically the same as that of the calcined sample, thereby confirming that the post-synthesis treatment had no effect on the organization of the mesoporous structures (Figure 2).



Figure 2. X-ray patterns of calcined mesoporous materials that were obtained from  $T_8$  POSS and/or BTEB silsesquioxanes: a) HYB-100P, b) HYB-50P-50B, c) HYB-25P-75B, d) HYB-100B, e) HYB-95P-5B, f) HYB-75P-25B, and g) HYB-75P-25B-NH<sub>2</sub>.



Figure 3. TEM micrographs of hybrid materials that were obtained from  $T_8$  POSS and/or BTEB silsesquioxanes: a) HYB-100P, b) HYB-95P-5B, c) HYB-75P-25B, d) HYB-50P-50B, and e) HYB-100B. The scale bars correspond to 100 nm in (a)–(c) and 200 nm in (d) and (e).



Scheme 3. Structures of the mesoporous materials that were synthesized from  $T_8$  polyhedral silsesquioxanes (POSS) as silicon precursors.

Elemental analysis of as-synthesized-, calcined-, and samples of HYB-100P and HYB-75P-25B after the post-synthesis amination process is listed in Table 1. These results indicated that, in the as-synthesized samples, during the micellar route, the C<sub>18</sub>TMA surfactant molecules were incorporated into the mesoporous channels (Table 1, entry 1). Indeed, the experimental C/N molar ratio in the sample that was obtained when using T<sub>8</sub> POSS as the sole silicon source (22) was close to the theoretical value (21), owing to the presence of C<sub>18</sub>TMA. This result confirmed that almost all TMA<sup>+</sup> ions, which were compensating for the anionic T<sub>8</sub> POSS monomers, were not present in the final as-synthesized hybrid materials because the theoretical C/N molar ratio of the TMA ions (4) was too far from the experimental ratio (C/N = 22.0).

When the synthesis was performed in the presence of bridged silsesquioxane molecules (HYB-75P-25B), the organic content increased (Table 1, entry 3) owing to the incorporation of additional BTEB aromatic groups into the hybrid framework. This result was clearly confirmed after calcination and the elimination of  $C_{18}$ TMA, because then the carbon content corresponded exclusively to the benzylic fragments (Table 1, entry 4). The analytical results also corroborated the effectiveness of the calcination method in completely removing the surfactant molecules (Table 1, entry 2 and 4); the 18 wt.% in the final hybrid samples corresponded to the aryl groups that presumably had been incorporated into the structure and linked to the siloxane cubic units (see below). After the amination process (HYB-75P-25B-NH<sub>2</sub>), the carbon content decreased slightly compared with the calcined sample, presumably owing to the partial removal of some of the benzylic fragments during the strong-acid treatment that was used to incorporate the amino groups (Table 1, entry 5). However, the presence of some nitrogen content (2.5 wt.%) after this process confirmed that basic sites had been effectively introduced into the material.

Figure 4 shows the TGA and DTA curves of a sample that were synthesized from T<sub>8</sub> POSS as the only silicon source (HYB-100P) and a mixed sample with BTEBbridged silsesquioxane (HYB-75P-25B). These results confirmed the presence and hydrothermal stability of the different organic compounds (C18TMA surfactant molecules and aryl fragments) in the hybrid materials. More specifically, in the as-synthesized HYB-100P sample, a main weight loss was observed between 200 °C and 400 °C, named as I, which was attributed to the surfactant molecules. The DTA curves showed three bands: two in weight-loss region I (Figure 4a) and a third band between 500 °C and 700 °C (region II). The two bands in region I corresponded to C<sub>18</sub>TMA and indicated that there were two types of surfactant molecules (presumably neutral and cationic) with different modes of attachment or stabilities. Weight loss II was around 3% (Table 1) and could be related to water that was formed by dehydroxylation in the sample that was obtained from only the POSS monomers. This water was produced from the condensation of surface silanol groups at high temperatures. The effectiveness of the calcination process at 400°C to completely remove the occluded surfactant molecules was confirmed from the TGA and DTA curves of the calcined HYB-100P (Figure 4b) in which weight loss I was not observed.

The presence of benzylic fragments in sample HYB-75P-25B would be consistent with the marked increase in weight loss II (Table 1, Figure 4c) compared with the sample without BTEB, because we estimated that approximately 16% of the total weight of the hybrid materials may have come from the aryl fragments (after deduction of the dehydroxy-lated water that was formed at high temperatures). This organic content, which was associated with the benzyl groups, was practically the same as that determined by elemental analysis (Table 1) because the structural aromatic fragments were hydrothermally stable up to 650°C; this result was in agreement with the high stability of previously reported

Table 1. Organic content of hybrid samples that were prepared from the T<sub>8</sub> POSS and BTEB monomers.<sup>[a]</sup>

	Elemental Analysis					TGA				
Sample	C [%]	N [%]	C/N <sup>[b]</sup>	Organic content [%]	Loss I (200–400 °C) [%]	Loss II (500–700 °C) [%]	Organic content [%] <sup>[c]</sup>	Aryl units [mmol g <sup>-1</sup> SiO <sub>2</sub> ] <sup>[d]</sup>		
HYB-100P	26.3	1.4	22.0	33.3	28.2	2.5	30.7	_		
HYB-100P-Calc.	0.1	0	_	1.4	0	3.1	3.1	-		
HYB-75P-25B	30.7	1.0	35.8	38.3	20.5	15.2	35.7	3.28		
HYB-75P-25B-Calc.	17.0	0	-	18.5	0	18.8	18.8	3.22		
HYB-75P-25B-NH <sub>2</sub>	13.0	2.5	6.1	17.6	0	15.5	15.5	2.55		

[a] Organic content was obtained by elemental- and thermogravimetric analyses. [b] C/N molar ratio was determined by elemental analysis. [c] Organic content was determined by TGA without considering the hydration water. [d] Determined from loss II in the TGA and assigned to aryl fragments by considering the pure-silica content.

Chem. Eur. J. 2012, 00, 0-0

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Figure 4. TGA and DTA curves of hybrid samples that were obtained from  $T_8$  POSS and/or BTEB silsesquioxanes: a) as-synthesized HYB-100P, b) calcined HYB-100P, c) as-synthesized HYB-75P-25B, d) calcined HYB-75P-25B, and e) aminated HYB-75P-25B-NH<sub>2</sub>.

benzene periodic mesoporous organosilicon compounds.<sup>[37]</sup> In addition, weight loss I, which was due to the presence of surfactant molecules, was observed within the same temperature range as the HYB-100P sample, although the amount of  $C_{18}$ TMA molecules that were finally occluded in the POSS hybrid samples that were obtained with BTEB was lower (about 20 wt.%) than that in absence of this bridged silsesquioxane (28 wt.%, Table 1).

When sample HYB-75P-25B was calcined (Figure 4d), weight loss I disappeared, thereby confirming the complete elimination of surfactant molecules. Meanwhile, weight loss II, which was assigned to the aryl fragments, remained the

same when compared with the sample before calcination (19 wt.%, Table 1). This result confirmed that the benzyl units and the hybrid network were hydrothermally stable at quite high temperatures after removing the structure-directing agent.

Finally, after the amination process, the TGA and DTA curves for sample HYB-75P-25B-NH<sub>2</sub> (Figure 4e) were similar to those of the calcined hybrid material, thus indicating that the aryl fragments were preserved after the incorporation of the amino groups by post-synthesis treatment. Only a slight decrease in the organic content was observed (Table 1), probably owing to the strong-acid method used during the amination step. This treatment may have caused the partial decomposition of some of the aryl units, as also deduced from elemental analysis.

**Spectroscopic characterization**: It should be possible to confirm the presence of cubic siloxane and aryl moieties, and hence the mesoporous framework of hybrid materials, by using IR spectroscopy. Figure 5 shows the IR spectrum of



Figure 5. IR spectra of mesoporous materials that were based on the  $T_8$  POSS and BTEB monomers: a) HYB-100P, b) HYB-75P-25B, and c) HYB-100P-25B- NH<sub>2</sub>.

the HYB-75P-25B hybrid material. This spectrum showed additional bands at about 1390, 1510, 1600, 3010 and  $3060 \text{ cm}^{-1}$  compared with HYB-100P, which were associated to the asymmetric silicon–phenyl stretching vibrations, thereby indicating the presence of aryl units in the material (Figure 5b). Only a residual amount of hydrocarbon fragments from the surfactant molecules that were used during the self-assembly process were detected after the calcination step, as indicated by the presence of small bands at about 2860 and 2980 cm<sup>-1</sup>. Moreover, the characteristic intense band at 3730 cm<sup>-1</sup>, which was due to the silanol groups and is commonly found in conventional mesoporous materials,

was also observed in the calcined HYB-100P material (Figure 5a), although this band was partially shifted (about  $3650 \text{ cm}^{-1}$ ) owing to the incorporation of the aryl fragments into the hybrid network (Figure 5b). This displacement in the silanol band was probably due to the spatial proximity between the  $\equiv$ Si–OH and the structural silyl–aromatic groups.<sup>[38]</sup>

When the post-synthesis amination process was carried out on the calcined HYB-75P-25B hybrid material, the IR spectrum exhibited additional bands at 1350, 1540, and 1630 cm<sup>-1</sup>, which corresponded to  $\delta$ -(NH<sub>2</sub>) bending vibrations, as well as the characteristic bands between 3350– 3500 cm<sup>-1</sup>, which were due to  $\nu$ -(NH<sub>2</sub>) stretching vibrations. These results supported the hypothesis that the amino groups were covalently incorporated onto the aryl groups (Figure 5 c). Importantly, the presence of bands owing to the aromatic units in the spectrum of the aminated solid clearly confirmed that the aryl moieties were preserved during the amination step. All of these results confirmed that the aryland aminoaryl groups were present in the mesoporous hybrid materials.

On the other hand, from the IR spectroscopic study, we identified the presence of cubic units that were incorporated into the mesoporous framework, both in the solids that were solely obtained from polyhedral  $T_8$  POSS monomers and in the hybrid materials from the combination with the BTEB-bridged silsesquioxane molecules; these cubic units were preserved during the calcination and post-amination processes (Figure 6). The assignment of vibrational bands to the



Figure 6. IR spectra in the double-four-membered-ring (D4R) skeletal-vibration range for different porous materials that were based on highly siliceous frameworks: a) HYB-75P-25B, b) HYB-75P-25B-NH<sub>2</sub>, c) MCM-41, and d) zeolite A.

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presence of double four-membered rings (D4R) in the framework of different zeolite materials has been discussed in several publications and, in general, such an assignment is still a controversial topic.<sup>[39,40]</sup> However, it is accepted that it is possible to detect the bands that are due to the skeletal vibration of D4R units (550-600 cm<sup>-1</sup>).<sup>[41,42]</sup> More specifically, theoretical models of pure silica zeolite structures have estimated that the ring-opening vibration frequency for D4R units is centered at 581 cm<sup>-1</sup>.<sup>[43]</sup> In our case, the mesoporous materials that were based on POSS blocks showed vibrational bands at around 580 cm<sup>-1</sup>, which would confirm that silsesquioxane double four-member rings (D4R) were present in the framework of the hybrid materials, even in the presence of aryl building blocks (Figure 6a). This characteristic peak was also observed in HYB-75P-25B-NH<sub>2</sub>, thereby indicating that the D4R units were preserved after the strong-acid post-amination process, thereby confirming the high stability of the mesoporous network (Figure 6b).

We have compared the above IR spectra with those of a conventional M41S mesoporous material and a siliceous zeolite  $A^{[44]}$  (Figure 6c,d, respectively). M41S was composed of amorphous silica and the vibrational IR band owing to D4R units was not observed. On the contrary, in the case of pure-silica zeolite A, which contained D4R secondary building units, an intense band at about 580 cm<sup>-1</sup> was clearly visible, as in the hybrid materials studied herein.<sup>[45,46]</sup> This matter corroborated the presence and preservation of cubic silsesquioxanes in the hybrid materials synthesized herein.

In addition, by using NMR spectroscopy we confirmed the presence and integrity of the aryl fragments in the framework of the mesoporous materials and their effective covalent interactions with the cubic siloxane building blocks. More specifically, the <sup>13</sup>C NMR spectrum of the as-synthesized HYB-75P-25B sample showed characteristic bands of aromatic rings that were bonded to siloxane groups (centered at  $\delta = 133$  ppm), thereby supporting the existence of carbon atoms that were directly linked to siloxane groups (Figure 7 a). Moreover, we observed intense bands that were due to surfactant molecules that were used during the selfassembly process (Figure 7, inset). After calcination to remove the structure-directing molecules, the bands that were attributed to surfactant molecules completely disappeared, thus corroborating the effectiveness of surfactant removal at high temperatures (400 °C) without destroying the aryl fragments, as shown by the retention of characteristic bands after the calcination step (Figure 7b). Moreover, the presence of amino groups, which were incorporated onto the benzene fragments during the amination process, was also confirmed by <sup>13</sup>C NMR spectroscopy. Indeed, splitting of the characteristic NMR shift of aromatic carbons ( $\delta =$ 133 ppm) into three broad NMR signals was observed, owing to the covalent interactions between the aryl building blocks and the NH<sub>2</sub> groups that were introduced during the post-synthesis amination process (Figure 7c). Specifically, the band at about  $\delta = 150$  ppm was assigned to a carbon atom that was directly linked to an amino group (Figure 7 c).



Figure 7. CP/MAS <sup>13</sup>C NMR spectra of hybrid mesoporous materials that were based on  $T_8$  POSS cubic siloxanes that were linked through aryl fragments: a) as-synthesized HYB-75P-25B, b) calcined HYB-75P-25B, and c) aminated HYB-75P-25B-NH<sub>2</sub>.

 $^{13}$ C NMR spectroscopy was used to confirm the presence, integrity, and preservation of aryl fragments during the synthesis and modification of the mesoporous materials. However,  $^{29}$ Si NMR spectroscopy was required to ascertain the effective covalent interaction between the different nanobuilding blocks (BTEB and T<sub>8</sub> POSS), which determined the network structure of the solids. The  $^{29}$ Si NMR spectrum of HYB-75P-25B (Figure 8) showed the presence of Q-type



Figure 8. BD/MAS  $^{29}Si$  NMR spectra of hybrid mesoporous materials that were based on  $T_8$  POSS cubic siloxanes that were linked through aryl fragments: a) HYB-75P-25B, b) aminated HYB-75P-25B-NH<sub>2</sub>, c) HYB-100P, and d) pure BTEB.

NMR bands, at around  $\delta = -95/-110$  ppm, which are typical of highly siliceous mesoporous materials, and which were associated to tetrahedrally coordinated silicon atoms (Q<sup>4</sup>: Si- $(OSi)_4$ , Q<sup>3</sup>: Si(OH)(OSi)<sub>3</sub>, and Q<sup>2</sup>: Si(OH)<sub>2</sub>(OSi)<sub>2</sub>), together with T-silicon bands that were attributed to the existence of Si-C covalent bonds from the effective incorporation of aryl groups on the BTEB precursors within the framework (Figure 8a). Indeed, in the T-silicon species, it was possible to identify the bands that corresponded to the T<sup>3</sup> (SiC(OSi)<sub>3</sub>) and T<sup>2</sup> (SiC(OH)(OSi)<sub>2</sub>) silicon atoms at  $\delta = -78$  and -71 ppm, respectively. The absence of T<sup>1</sup> (SiC(OH)<sub>2</sub>(OSi)) silicon atoms in the <sup>29</sup>Si NMR spectrum of HYB-75P-25B (Figure 8), together with the absence of carbon signals that were attributed to terminal ethoxide groups (Figure 7), confirmed that almost all of the terminal alkoxide groups from the aryl-bridged silsesquioxane molecules (BTEB) were involved in the structural formation of the T<sub>8</sub> POSS mesoporous materials. Another additional confirmation of the effective covalent integration of benzene fragments into the framework of the hybrid solids came from the marked displacements in the NMR shifts of the T-silicon bands when the spectra of the hybrid materials was compared with that of the pure-BTEB-bridged silsesquioxane as the starting silicon precursor. In the case of the pure disilane (Figure 8d), the silicon signal ( $\delta = -59 \text{ ppm}$ ) was shifted from  $\delta =$ -60 ppm to  $\delta = -80$  ppm when the silsesquioxane was effectively integrated into the hybrid framework (Figure 8a).<sup>[47]</sup> Moreover, from the integration of the T-silicon bands in the <sup>29</sup>Si NMR spectrum of HYB-75P-25B, as well as by considering the T/(Q+T) ratio, we calculated that 3.1 mmol of the aryl fragments per gram of SiO<sub>2</sub> were incorporated into the material, which was in very good agreement with the value that was estimated from TGA (3.2; Table 1).

After the amination process, most of the Si-C species were preserved because the T-silicon bands remained practi-

cally unchanged, thereby confirming the integrity and high stability of the hybrid networks that were held by covalent interactions between the aryl and POSS nanobuilding blocks. However, the acid treatment that was used for the amination process probably resulted in a certain loss of crystallinity in the organic–inorganic mesoporous materials, as was deduced from the lower resolution of the Q-type silicon bands (Figure 8b).

**Textural properties**: The nitrogen-adsorption isotherms of the mesoporous materials that were obtained from several POSS/BTEB silsesquioxanes molar ratios are shown in Figure 9. In addition, Table 2 shows the values of specific surface area

and pore volume that were calculated from the isotherms. These results clearly showed that the amount of aryl fragments that were inserted into the hybrid framework was vital for obtaining well-structured materials with a homogenous mesoporous distribution. Specifically, the materials that were prepared by incorporating 5% and 25% of the total silicon content from the BTEB precursor monomers



Figure 9. Nitrogen-adsorption isotherms of mesoporous hybrid materials that were based on the covalent combination of cubic- and aryl-siloxane building blocks.

Table 2. Mean textural properties of calcined hybrid mesoporous organic-inorganic materials that were obtained from nitrogen-adsorption isotherms.

Sample	$S_{\rm BET}$	$S_{\rm Micro}$	S <sub>Ext</sub> <sup>[a]</sup>	$V_{\rm TOT}$	$V_{ m Micro}$	$V_{\rm BJH}$	$d_{\rm BJH}^{[b]}$
	$[m^2g^{-1}]$	$[m^2g^{-1}]$	$[m^2g^{-1}]$	$[cm^{3}g^{-1}]$	$[cm^{3}g^{-1}]$	$[cm^{3}g^{-1}]$	[Å]
HYB-100P	832	0	832	0.845	0	0.505	25
HYB-95P-5B	1149	0	1149	0.941	0	0.552	30
HYB-75P-25B	721	0	721	0.785	0	0.344	30
HYB-50P-50B	584	201	383	0.536	0.106	0.103	mp <sup>[c]</sup>
HYB-25P-75B	602	267	335	0.686	0.131	0.131	mp <sup>[c]</sup>
HYB-100B	514	193	321	0.564	0.100	0.045	mp <sup>[c]</sup>
HYB-75P-25B-NH <sub>2</sub>	735	0	735	0.732	0	0.321	30

[a]  $S_{\text{Ext}} = (S_{\text{BET}} - S_{\text{Micro}})$  from the *t*-plot method. [b] BJH mean pore diameter. [c] Porediameter distribution was in the microporous (mp) range.

(HYB-95P-5B and HYB75P-25B) exhibited the classical type IV isotherm of structured mesoporous materials with hexagonal symmetry, such as in M41S solids (Figure 9, bottom),<sup>[48]</sup> with a marked shift towards high relative pressures in the inflexion point of the isotherms ( $p/p_0 > 0.3$ ). This effect was especially clear in HYB-95P-5B owing to the good structural integrity and high regularity that was ach-

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ieved when suitable amount of aryl units were incorporated as linker fragments, by optimally connecting the T<sub>8</sub> POSS building groups to generate homogeneous mesoporous materials. In this case, the BET surface area was above  $1100 \text{ m}^2 \text{g}^{-1}$ , which was completely due to the mesoporous structure. In the case of HYB-75P-25B, the N<sub>2</sub>-adsorption isotherm was similar to that of HYB-95P-5B, which corresponded to hexagonal M41S-type materials, although the total surface area and mesoporous volume were smaller (S<sub>BET</sub>  $\approx$  700 m<sup>2</sup>g<sup>-1</sup>), presumably owing to a loss of uniformity in the mesoporous distribution. In both materials, the pore size was about 30 Å (Figure 10), which agreed with the pore diameters that were observed by TEM (Figure 3).



Figure 10. BJH pore-size distribution of mesoporous hybrid materials that were based on the covalent combination of cubic- and aryl-siloxane building blocks.

On the contrary, the porous materials that were synthesized by using POSS silsesquioxane monomers alone or combined with higher amounts (>25%) of BTEB precursor showed adsorption isotherms that were different from conventional hexagonal mesoporous materials (Figure 9, top); these isotherms were more similar to those of porous materials that had non-ordered structural organization, which agreed with the XRD and TEM results.<sup>[49]</sup> In these cases, the shift in the isotherm inflexion point was observed at lower relative pressures ( $p/p_0 < 0.2$ ), which was indicative of the presence of smaller pores. In fact, the specific surface area and pore volume of samples HYB50P-50B and HYB25P-75B (Table 2) clearly showed that these hybrid materials contained an appreciable microporous component, with a wide pore-size distribution in the mesoporous range (Figure 10).

The hybrid materials that were obtained after the amination process maintained the textural properties that were characteristic of hexagonal mesoporous materials, thereby showing a nitrogen-adsorption isotherm, surface area, and pore volume that were similar to pristine mesoporous HYB-75P-25B (Figure 9, bottom; Figure 10, bottom; and Table 2).

Catalytic activity: The Knoevenagel condensation of carbonyl compounds with active methylenic groups is a commonly used synthetic route for the preparation of alkene derivatives. These compounds are of interest as end-products and intermediates in the production of fine chemicals and commodities (perfumes, pharmaceuticals, polymers, etc.).<sup>[50,51]</sup> The kinetics of the Knoevenagel reactions have been widely studied, and the process follows first-order kinetics with respect to each reactant and catalyst.<sup>[52-54]</sup> Moreover, Knoevenagel reactions have been used as test reactions to determine the number and strength of basic sites. Thus, we performed the Knoevenagel condensation between benzaldehyde and substrates with different  $pK_a$  values (with distinct activated methylenic groups), such as malononitrile ( $pK_a$ )  $\approx$ 7), ethyl cyanoacetate (p $K_a \approx$ 9), and ethyl acetoacetate  $(pK_a \approx 11)$ , in the presence of the hybrid mesoporous material HYB-75P-25B (Table 3). This study was useful to evaluate the strength and effectiveness of the basic sites in the hybrid catalyst. From the kinetic results, we confirmed the presence, accessibility, and activity of basic groups, and 99% yield of benzylidene malononitrile and ethyl cinnamate were achieved after reaction times of 10 and 3.5 h, respec-

Table 3. Knoevenagel condensation of benzaldehyde with substrates that contained various activated methylene groups (that is, with different  $pK_a$  values), by using mesoporous hybrid catalyst HYB-75P-25B.<sup>[a]</sup>

		+		•		ý,	+ H <sub>2</sub> O
Entry	Х	Y	Т [°С]	N [mol %]	<i>t</i> [h]	Yield [%]	Selectivity [%]
1	CN	CN	30	2.1	10	99 <sup>[b]</sup>	>99
2	CN	COOEt	60	3.4	3.5	99 <sup>[c]</sup>	>99
3	COCH <sub>3</sub>	COOEt	80	3.4	24	66 <sup>[d]</sup>	92.5

[a] Reaction conditions: The reactions were carried out in a closed conic vessel under a nitrogen atmosphere with magnetic stirring. [b] Molar ratio benzaldehyde (4.8 mmol)/malononitrile (3.3 mmol)=1.45, MeCN (1 mL). [c] Molar ratio benzaldehyde (3 mmol)/ethyl-cyanoacetate (2.1 mmol)=1.43, EtOH (1 mL). [d] Molar ratio benzaldehyde (3 mmol)/ ethyl-acetoacetate (2.1 mmol)=1.43, EtOH (1 mL).

tively, with close to 100% selectivity in both cases. When a substrate with a higher  $pK_a$  value was used, such as ethyl acetoacetate, the yield of ethyl-2-benzylideneacetoacetate after 24 h was 66% (Table 3, Figure 11), thereby indicating that the amino groups that were introduced into the hybrid material were able to catalyze reactions that required relatively weak basic sites.



Figure 11. Yields of benzylidene malononitrile ( $\blacksquare$ ), ethyl benzylidene cyanocinnamate ( $\blacklozenge$ ), and ethyl 2-benzylidene acetoacetate ( $\blacklozenge$ ) versus time for the Knoevenagel reactions in the presence of hybrid material HYB-75P-25B.

HYB-75P-25B was recycled three times in the reaction and, after each run, the catalyst was filtered, washed with EtOH, and dried at 373 K for 12 h. Figure 12 shows that the catalyst could be reused in three successive cycles without any loss in activity, thereby showing the high stability of HYB-75P-25B as a catalyst.

An application of Knoevenagel type-reaction is the synthesis of coumarins, which are in the benzopyrone chemical class of compounds, and are found in many plants. Coumarins have found various applications as additives in foods and cosmetics, optical brightening agents, dispersed fluorescent and laser dyes, and in medicines for the production of anticoagulants.<sup>[55–57]</sup> 3-Cyanocoumarin was selectively prepared at 40°C in the presence of HYB-75P-25B from the reaction between 2-hydroxibenzaldehyde (salicylaldehyde) and ethyl cyanoacetate (Scheme 4). The vields of 3-cvanocoumarin and ethyl cyanoacetate versus time are plotted in Figure 13. 3-Cya-



Figure 12. Catalytic activity of basic hybrid material HYB-75P-25B for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in EtOH (1 mL) over three consecutive cycles; molar ratio benzaldehyde (3 mmol)/ethyl-cyanoacetate (2.1 mmol) = 1.43.



Figure 13. Yields of 3-cyanocoumarin (**n**) and ethyl cyanoacetate ( $\bullet$ ) versus time in the presence of the basic hybrid material HYB-75P-25B. Reaction conditions: molar ratio salicylaldehyde (1.3 mmol)/ethyl-cyanoacetate (1.2 mmol)=1.08, EtOH (1 mL), 40 °C.



Scheme 4. Knoevenagel condensation between 2-hydroxibenzaldehyde and ethyl cyanoacetate.

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nocoumarin was successfully obtained in 94% yield with complete consumption of ethyl cyanoacetate.

In addition, when the reaction was carried out at 80 °C in the presence of water and EtOH, it was possible to convert 3-cyanocoumarin into ethyl-3-coumarincarboxylate

(Scheme 4). Complete conversion of ethyl cyanoacetate after 4 h afforded the latter compound in 89% yield with other coumarin side-products (Figure 14). The post-conver-



Figure 14. Yields of 3-cyanocoumarin (**n**), ethyl-3-coumarincarboxylate ( $\blacktriangle$ ), and ethyl cyanoacetate ( $\blacklozenge$ ) versus time in the presence of basic hybrid material HYB-75P-25B. Reaction conditions: molar ratio salicylal-dehyde (1.3 mmol)/ethyl-cyanoacetate (1.2 mmol)=1.08, EtOH (1 mL) and water (0.6 mL), 80 °C.

sion of 3-cyanocoumarin into ethyl-3-coumarin carboxylate constituted an alternative route for its preparation from the Knoevenagel condensation between diethylmalonate and salicyladehyde. Indeed, diethyl malonate had a higher  $pK_a$  value (close to 13) and we showed that, above that value, HYB-75P-25B contained weakly basic sites and was unable to perform the reaction with  $pK_a > 11$ .

The validity of these hybrid mesoporous materials as basic catalysts could be extended to other more-specific C– C bond-formation processes, such as the Henry reaction (also referred to as the nitro-aldol reaction) between a nitroalkane and an aldehyde or ketone in the presence of a basic catalyst to form  $\beta$ -nitroalcohols.<sup>[58,59]</sup> The Henry reaction is a useful process in organic chemistry owing to the synthetic utility of its corresponding products. In fact, they can be easily converted into other useful synthetic intermediates. These conversions include subsequent dehydration to yield nitroalkenes, oxidation of the secondary alcohol to yield  $\beta$ amino alcohols. Many of these uses have been exemplified in the syntheses of various pharmaceutical compounds, including antibiotics.<sup>[60]</sup> Herein, we reacted benzaldehyde and



Scheme 5. Henry reaction between benzaldehyde and nitromethane.

nitromethane (p $K_a \approx 10.2$ ), with HYB-75P-25B as catalyst (Scheme 5).

After a reaction time of 14 h, 98% yield of nitrostyrene was achieved (Figure 15). During the reaction, the final



Figure 15. Yields of benzaldehyde ( $\Box$ ), 1,3-dinitro-2-phenylpropane ( $\times$ ), and nitrostyrene ( $\bullet$ ) versus reaction time. Reaction conditions: benzaldehyde (1.9 mmol), nitromethane (14 mmol), 373 K, under an inert atmosphere (N<sub>2</sub>), catalyst (40 mg, that is, 3.7 mol% of N).

product was the nitroalkene (99% selectivity) owing to the consecutive dehydration of the nitroalcohol intermediate. 1,3-Dinitro-2-phenylpropane, which is a sub-product of the 1,2 addition of nitromethane onto nitrostyrene, was detected in very low concentrations in the reaction medium (<1%).

Importantly, by comparing the catalytic performances of these hybrid materials in promoting the Henry and condensation reactions with conventional amine-type catalysts,<sup>[61,62]</sup> these results showed clear advantages that were associated to the high activity and selectivity of the aniline-type building blocks, together with the higher stability and reusability of the hybrid catalysts.

#### Conclusion

A family of hybrid mesoporous materials was synthesized based on the structural combination of two types of silsesquioxane buildering blocks, that is, cubic  $T_8$  POSS and aryl units. By using TGA, DTA, MAS NMR and IR spectroscopy, XRD, TEM, and N<sub>2</sub> adsorption techniques, we confirmed that the two silsesquioxane building blocks formed the walls

of the resulting mesoporous materials. Excellent crystallinity and narrow pore distribution, exclusively in the mesoporous region, were only achieved for  $T_8$  POSS/BTEB silicon molar ratios of 5–25%. The resultant organic–inorganic materials were very stable and could be heated at 650°C without any structural modification. It was possible to functionalize these mesoporous materials by using post-synthesis treatments, even if strong-acid treatments were required. Thus, amino groups were covalently incorporated onto the aryl linkers within the crystalline framework. The resultant hybrid organic–inorganic materials with the amino groups were active and selective catalysts for performing base-catalyzed C–C bond-forming reactions, such as Knoevenagel condensations and Henry-type reactions.

#### **Experimental Section**

Synthesis of the hybrid mesoporous materials (HYB-POSS-BTEB): Ordered porous hybrid materials were synthesized from polyhedral oligomeric silsesquioxanes, also called T<sub>8</sub> POSS, as the main building blocks, with an appropriate amount of disilane, (R'O)<sub>3</sub>Si–R–Si(OR')<sub>3</sub>, as the bridging silsesquioxane. Organic linkers were conformed by silyl-aryl units from 1,4-bis(triethoxysilyl)benzene (BTEB), which reacted with cubic POSS siloxane groups. The final reaction mixture had the molar composition: SiO<sub>2</sub>/C<sub>18</sub>TMABr/HCl/H<sub>2</sub>O, 1:0.33:0:133.

The first step of the synthesis involved the preparation of a gel by mixing HCl (37%, 14.7 g), distilled water (30.5 g), and octadecyltrimethylammonium bromide (2.15 g,  $C_{18}$ TMABr, Aldrich). Next, a solution of the appropriated amount of T<sub>8</sub> POSS (octakis(tetramethylammonium)silsesquioxane, ABCR) and BTEB (Aldrich) in EtOH was added and the resultant mixture was vigorously stirred for 2 h at RT. After that, the mixture was left to stand in a polypropylene flask for 2 days at 373 K. The mesoporous material was recovered by filtration, washed with hot distilled water until the pH value of the washings reached pH 7, and dried in air at 333 K for 18 h. The surfactant was removed from the synthesized material by calcination under a nitrogen atmosphere (2.5 mLs<sup>-1</sup>) in a quartz reactor; the material was heated from RT to 400°C over 3 h at a rate of 2.1°Cmin<sup>-1</sup>, and maintained at 400°C for 1 h. Afterwards, a flow rate of 2.5 mLs<sup>-1</sup> of air was applied for 4 h.

The samples were termed HYB-xP-yB, where x and y were the number of moles of silicon in the starting gel that originated from T<sub>8</sub> POSS and BTEB silsesquioxanes, respectively.

Post-synthesis incorporation of amino (NH<sub>2</sub>) groups into the mesoporous hybrid materials (HYB-POSS-BTEB-NH<sub>2</sub>): To incorporate amino groups onto the bridged benzene groups, which formed the linkers between the building blocks, HYB-POSS-BTEB (0.5 g) was suspended in H<sub>2</sub>SO<sub>4</sub> (15.2 g, 98%, Aldrich) and HNO<sub>3</sub> (3.47 g, 65%, Panreac) for 3 d at RT. The acid mixture was pre-prepared and slowly added over the solid. Then, cold distilled water (300 mL) was added and the resultant solution was stirred for 4 h at RT. The pale-yellow solid was recovered by filtration, washed with distilled water, and dried in air at 333 K for 8 h. The dried solid was suspended in a pre-prepared solution of HCl (15 mL, 37%, Aldrich) and SnCl<sub>2</sub> (1.59 g, 98%, Aldrich) and stirring was maintained for an additional 3 d at RT. Next, distilled water (300 mL) was added into the solution and stirring was continued for a further 4 h. The yellow sample was recovered by filtration and washed with distilled water and EtOH. Finally, the amino-substituted solid was dried in air at 333 K for 8 h.

**Characterization techniques:** XRD analysis was carried out on a Philips X'PERT diffractometer that was equipped with a proportional detector and a secondary graphite monochromator. The data were collected stepwise over the range  $2\theta = 2-20^{\circ}$ , at steps of 0.02°, an accumulation time of 20 s/step, and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). TEM micrographs were

obtained with a JEOL 1200X electron microscope operating at 120 keV. The samples were prepared directly by dispersing the powders over carbon copper grids. Elemental analysis was determined on a Carlo Erba 1106 elemental analyzer, whilst the Al content was determined by atomic absorption spectroscopy (Spectra AA 10 Plus, Varian). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted in a stream of air on a Metler Toledo TGA/SDTA 851E analyzer. IR spectra were obtained in a Nicolet 710 spectrometer (resolution: 4 cm<sup>-1</sup>) by using a conventional grease-less cell. Wafers of 10 mg cm<sup>-2</sup> were outgassed at 100°C overnight.

Nitrogen-adsorption isotherms were measured at 77 and 87.3 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, the samples were degassed for 12 h at 100 °C. The BET specific surface area<sup>[63]</sup> was calculated from the nitrogen-adsorption data in the relative pressure range 0.04–0.2. The total pore volume<sup>[64]</sup> was obtained from the amount of N<sub>2</sub> that was adsorbed at a relative pressure of about 0.99. External surface area and micropore volume were estimated by using the *t*-plot method in the range t=3.5-5. The pore diameter and pore-size distribution were calculated by using the Barret–Joyner–Halenda (BJH) method<sup>[65]</sup> on the adsorption branch of the nitrogen isotherms.

Solid-state MAS NMR spectra were recorded at RT under magic angle spinning (MAS) on a Bruker AV-400 spectrometer. The single-pulse  $^{29}$ Si NMR spectra were acquired at 79.5 MHz with a 7 mm Bruker BL-7 probe by using pulses of 3.5  $\mu$ s, which corresponded to a flip angle of 3/4  $\pi$  radians and a recycle delay of 240 s. The <sup>1</sup>H to <sup>13</sup>C cross-polarization (CP) spectra were acquired by using a 90° pulse for <sup>1</sup>H nuclei of 5  $\mu$ s, a contact time of 5 ms, and a recycle time of 3 ms. The <sup>13</sup>C NMR spectra were recorded with a 7 mm Bruker BL-7 probe and at a sample spinning rate of 5 kHz. The <sup>13</sup>C NMR and <sup>29</sup>Si NMR spectra were referenced to adamantine and tetramethylsilane, respectively.

**Catalytic tests**: Knoevenagel reactions were carried out in a closed conic vessel under a nitrogen atmosphere and magnetic stirring.

*Benzylidene malononitrile.* A mixture of benzaldehyde (4.8 mmol) and malononitrile (3.3 mmol) was magnetically stirred at 303 K under a nitrogen atmosphere and the catalyst (40 mg, 2.1 mol % N) was added. MeCN (1 mL) was used as the solvent.

*Ethyl cyanocinnamate.* A mixture of benzaldehyde (3 mmol) and ethyl cyanoacetate (2.1 mmol) was magnetically stirred at 333 K under a nitrogen atmosphere and the catalyst (40 mg, 3.4 mol % N) was added. EtOH (1 mL) was used as the solvent.

*Ethyl-2-benzylideneacetoacetate.* A mixture of benzaldehyde (3 mmol) and ethyl acetoacetate (2.1 mmol) was magnetically stirred at 353 K under a nitrogen atmosphere and the catalyst (40 mg,  $3.4 \mod \%$  N) was added. EtOH (1 mL) was used as the solvent.

The synthesis of cyanocoumarin was carried out in a closed conic vessel under a nitrogen atmosphere and magnetic stirring.

A mixture of salicylaldehyde (1.3 mmol) and ethyl cyanoacetate (1.2 mmol) at 353 K was magnetically stirred under a nitrogen atmosphere and the catalyst (40 mg, 6.2 mol % N) was added.

The Henry reaction was carried out in a closed conic vessel under a nitrogen atmosphere and magnetic stirring.

*Nitrostyrene*. A mixture of benzaldehyde (1.9 mmol) and nitromethane (14 mmol) was magnetically stirred at 373 K under a nitrogen atmosphere and the catalyst (40 mg, 3.7 mol% N) was added.

In all of these reactions, samples were taken periodically during the reaction and analyzed by GC (HP-5 column,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$ ) with an FID detector. The temperature program was: 80 °C for 2 min, heating to 300 °C at a rate of 30 °C min<sup>-1</sup>, then at that temperature for 5 min.

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- G. Kickelbick in *Hybrid Materials* (Ed.: G. Kickelbick), Wiley-VCH, Weinheim, 2007, pp. 1–46.
- [2] C. Sanchez, B. Julián, P. Belleville, M. Popall, J. Mater. Chem. 2005, 15, 3559–3592.
- [3] G. Férey, Chem. Soc. Rev. 2008, 37, 191–214.
- [4] A. Corma, H. García, Eur. J. Inorg. Chem. 2004, 2004, 1143-1164.
- [5] A. Corma, C. del Pino, M. Iglesias, F. Sánchez, J. Chem. Soc. Chem. Commun. 1991, 1253–1255.
- [6] E. Ruiz-Hitzky, J. M. Rojo, *Nature* **1980**, *287*, 28–30.
- [7] C. Sanchez, F. Ribot, New J. Chem. 1994, 18, 1007–1047.
- [8] G. Alberti, E. Giontella, S. Murcia-Mascarós, *Inorg. Chem.* 1997, 36, 2844–2849.
- [9] V. Srivastava, K. Gaubert, M. Pucheault, M. Vaultier, *ChemCatCh-em* 2009, 1, 94–98.
- [10] K. Yamamoto, Y. Sakata, Y. Nohara, Y. Takahashi, T. Tatsumi, *Science* 2003, 300, 470–472.
- [11] M. Boronat, M. J. Climent, A. Corma, S. Iborra, R. Montón, M. J. Sabater, *Chem. Eur. J.* 2010, 16, 1221–1231.
- [12] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 1999, 121, 9611–9614.
- [13] T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* 1999, 402, 867–871.
- [14] B. J. Melde, B. T. Holland, C. F. Blandford, A. Stein, *Chem. Mater.* 1999, 11, 3302–3308.
- [15] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* 2002, 416, 304– 307.
- [16] U. Díaz, T. García, A. Velty, A. Corma, J. Mater. Chem. 2009, 19, 5970–5979.
- [17] R. J. P. Corriu, A. Mehdi, C. Reyé, C. Thieuleux, *Chem. Mater.* 2004, 16, 159–166.
- [18] G. Cerveau, R. J. P. Corriu, B. Dabiens, J. L. Bideau, Angew. Chem. 2000, 112, 4707–4711; Angew. Chem. Int. Ed. 2000, 39, 4533–4537.
- [19] K. J. Shea, D. A. Loy, O. Webster, J. Am. Chem. Soc. 1992, 114, 6700-6710.
- [20] J. Alauzun, A. Mehdi, C. Reyé, R. J. P. Corriu, J. Am. Chem. Soc. 2006, 128, 8718–8719.
- [21] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem. 2006, 118, 3290–3328; Angew. Chem. Int. Ed. 2006, 45, 3216–3251.
- [22] B. D. Hatton, K. Landskron, W. J. Hunks, M. R. Bennet, D. Shukaris, D. Perovic, G. A. Ozin, *Mater. Today* 2006, 9, 22–31.
- [23] G. Budroni, A. Corma, Angew. Chem. 2006, 118, 3406–3409;
   Angew. Chem. Int. Ed. 2006, 45, 3328–3331; Angew. Chem. Int. Ed. 2006, 45, 3328–3331.
- [24] A. Corma, U. Díaz, T. García, G. Sastre, A. Velty, J. Am. Chem. Soc. 2010, 132, 15011–15021.
- [25] P. A. Agaskar, Inorg. Chem. 1991, 30, 2707-2708.
- [26] J. Jiang, J. Yu, A. Corma, Angew. Chem. 2010, 122, 3186–3212; Angew. Chem. Int. Ed. 2010, 49, 3120–3145.
- [27] J. Jiang, J. L. Jordá, J. Yu, L. Baumes, E. Mugnaioli, M. J. Díaz-Cabañas, U. Kolb, A. Corma, *Science* **2011**, *333*, 1131–1134.
- [28] S. Sulaiman, R. Guda, A. Bhaskar, T. Goodson, J. Zhang, R. M. Laine, *Chem. Mater.* 2008, 20, 5563–5573.
- [29] Y. Hagiwara, A. Shimojima, K. Kuroda, Chem. Mater. 2008, 20, 1147–1153.
- [30] A. Shimojima, R. Goto, N. Atsumi, K. Kuroda, Chem. Eur. J. 2008, 14, 8500–8506.
- [31] L. Zhang, H. C. L. Abbenhuis, Q. Yang, Y. M. Wang, P. C. M. M. Magusin, B. Mezari, R. A. van Santen, C. Li, *Angew. Chem.* 2007, *119*, 5091–5094; *Angew. Chem. Int. Ed.* 2007, *46*, 5003–5006.

- [32] L. Zhang, Q. Yang, H. Yang, J. Liu, H. Xin, B. Mezari, P. C. M. M. Magusin, H. C. L. Abbenhuis, R. A. van Santen, C. Li, *J. Mater. Chem.* 2008, 18, 450–457.
- [33] C. Kresge, M. Leonowicz, W. Roth, C. Vartuli, S. Beck, *Nature* 1992, 359, 710–712.
- [34] N. Bion, P. Ferreira, A. Valente, I. S. Gonçalves, J. Rocha, J. Mater. Chem. 2003, 13, 1910–1913.
- [35] S. Fujita, S. Inagaki, Chem. Mater. 2008, 20, 891–908.
- [36] M. Jaroniec, L. A. Solovyov, *Langmuir* **2006**, *22*, 6757–6760.
- [37] M. P. Kapoor, S. Inagaki, *Bull. Chem. Soc. Jpn.* 2006, 79, 1463–1475.
  [38] J. Sauer, P. Ugliengo, E. Garrone, V. R. Saunders, *Chem. Rev.* 1994, 94, 2095–2160.
- [39] R. A. van Santen, D. L. Vogel, Adv. Solid-State Chem. 1989, 1, 151– 224.
- [40] A. J. M. de Man, R. A. van Santen, Zeolites 1992, 12, 269-279.
- [41] M. Baertsch, P. Bornhauser, G. Calzaferri, R. Imhof, J. Phys. Chem. 1994, 98, 2817–2831.
- [42] C. Marcolli, P. Lainé, R. Bühler, G. Calzaferri, J. Tomkinson, J. Phys. Chem. B 1997, 101, 1171–1179.
- [43] L. A. Villaescusa, F. M. Márquez, C. Zicovich-Wilson, M. A. Camblor, J. Phys. Chem. B. 2002, 106, 2796–2800.
- [44] A. Corma, F. Rey, J. Rius, M. J. Sabater, S. Valencia, *Nature* 2004, 431, 287–290.
- [45] Y. Huang, Z. Jiang, Microporous Mater. 1997, 12, 341-345.
- [46] W. Mozgawa, W. Jastrzebski, M. Handke, J. Mol. Struct. 2005, 744– 747, 663–670.
- [47] U. Díaz-Morales, G. Bellussi, A. Carati. R. Millini, W. O. Parker, C. Rizzo, *Microporous Mesoporous Mater.* 2006, 87, 185–191.
- [48] C. G. Wu, T. Bein, Chem. Commun. 1996, 925-926.
- [49] D. A. Loy, J. V. Beach, B. M. Baugher, R. A. Assink, K. J. Shea, J. Tran, J. H. Small, *Chem. Mater.* **1999**, *11*, 3333–3341.
- [50] I. Rodriguez, S. Iborra, F. Rey, A. Corma, Appl. Catal. A 2000, 194– 195, 241–252.
- [51] M. J. Climent, A. Corma, S. Iborra, K. Epping, A. Velty, J. Catal. 2004, 225, 316–326.
- [52] F. S. Prout, U. D. Beaucaire, G. R. Dyrkarcz, W. M. Koppes, R. E. Kuznicki, T. A. Marlewski, J. A. Pienkowski, J. M. Puda, *J. Org. Chem.* **1973**, *38*, 1512–1517.
- [53] G. Jones, Org. React. 1967, 15, 204–599.
- [54] J. Guyot, A. Kergomard, Tetrahedron 1983, 39, 1167-1179.
- [55] G. Keating, R. O'Kennedy in *Coumarins: Biology, Applications and Mode of Action* (Eds.: R. O'Kennedy, R. D. Thornes), Wiley & Sons, Chichester, **1997**, pp. 23–66.
- [56] M. Zahradnik, The Production and Application of Fluorescent Brightening Agents, Wiley & Sons, Chichester, 1992.
- [57] M. Maeda, Laser Dyes, Academic Press, New York, 1994.
- [58] L. Kurti, B. Czako, Strategic Applications of Named Reactions in Organic Synthesis, Elsevier Academic Press, Burlington, 2005, pp. 202– 203.
- [59] O. Noboru, *The Nitro Group in Organic Synthesis* Wiley-VCH, New York, 2001, pp. 30–69.
- [60] F. A. Luzzio, Tetrahedron 2001, 57, 915-945.
- [61] I. Morao, F. P. Cossio, Tetrahedron Lett. 1997, 38, 6461-6464.
- [62] K. Motokura, M. Tomita, M. Tada, Y. Iwasawa, Chem. Eur. J. 2008, 14, 4017–4027.
- [63] S. J. Gregg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982, pp. 111–190.
- [64] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 1985, 57, 603–619.
- [65] E. P. Barrett, L. G. Joyner, P. P. Halenda, J. Am. Chem. Soc. 1951, 73, 373–380.

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ganic mesoporous materials were synthesized by the suitable combination of T<sub>8</sub> polyhedral oligomeric (POSS) and arylic-bridged (BTEB) silsesquioxane precursors. The post-synthesis amination treatment has allowed the incorporation of amino groups, generating efficient basic catalysts for C-C bond-forming reactions (see figure).

### **Mesoporous Materials -**

U. Díaz, T. García, A. Velty, 

Synthesis and Catalytic Properties of Hybrid Mesoporous Materials Assembled from Polyhedral and Bridged **Silsesquioxane Monomers** 

