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**Si–C attachment points during sol–gel synthesis of organosilicas from 2,8-bis-silylated Tröger's base as building block precursor†**

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The porous organosilica framework containing Tröger's base (TB) prepared by mild sol–gel synthesis from 2,8-bis-silylated TB precursor contains a mixture of two point attached TB and one point attached TB units, resulting from unexpected partial Si–C bond cleavage as demonstrated by  $^{29}\text{Si}$  MAS NMR spectroscopy and by selective chemo-desorption of the anchored organic part of the hybrid material.

**Introduction**

The field of organosilicas *via* self-condensation of bridged organosilanes as organic building blocks has witnessed a tremendous growth during the last decades since the pioneering works of Loy *et al.*<sup>1</sup> and Corriu *et al.*<sup>2</sup> Then, this type of hybrid organic–inorganic materials have been extended to periodic mesoporous organosilicas independently by Inagaki *et al.*,<sup>3</sup> Ozin *et al.*,<sup>4</sup> and Stein *et al.*,<sup>5</sup> using additional structure-directing surfactants to provide well-ordered structure with a homogeneous distribution of organic fragments. This family was furthermore intensively developed when functionalities were integrated either in the building block precursor molecule or by post-synthesis modification of the framework organic counterpart endowing these materials with unique physico-chemical properties.<sup>6</sup>

Recently, we have investigated the preparation of mesoporous organosilica containing different contents of Tröger's base (TB) as builder moieties aiming to obtain disordered hybrid materials that exhibit highest organic–inorganic framework flexibility in contrast to those featuring well-ordered structure, for catalytic applications.<sup>7</sup> In this respect the bis-silyl TB building block was incorporated in the silic framework using two different sol–gel processes in the presence of various amounts of TEOS: (i) through polycondensation using fluoride anion as sol–gel catalyst, at neutral pH and low temperature

in the absence of structural directing agents (SDAs); (ii) by auto-assembly in the presence of long-chain amines to obtain HMS-type structure through micellar route.

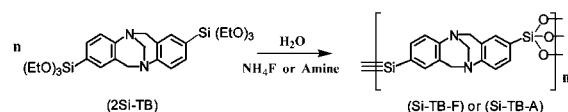
The presence and the content of TB moieties in the framework structure were determined by various complementary physico-chemical methods. However, the values of TB loadings obtained considering  $^{29}\text{Si}$  One Pulse MAS NMR, using the relation: TB loading ( $\text{mol g}^{-1}\text{SiO}_2$ ) =  $(T/T + Q)/2/M_{\text{SiO}_2}$ , were always lower than those obtained by elemental and thermogravimetric analyses. We have supposed that this slight discrepancy results from a partial Si–C bond cleavage occurring during the synthesis processes, though aromatic carbon–silicon hydrolysis have never been observed in the literature under mild synthetic conditions.<sup>2a,b,6c,8–11</sup> Now, the Si–C hydrolysis was actually observed during the phenylene-bridged material preparation when the sol–gel reaction required drastic conditions such as strongly basic<sup>4a</sup> or acidic<sup>12</sup> conditions, hydrothermal procedures<sup>13</sup> or when the PMOS was treated at very high temperatures.<sup>4c,14</sup> On the other hand, cleavage of Si–C bond was observed during the preparation of hybrid materials under soft conditions using ammonium fluoride in aqueous methanol, only when the polysilylated precursors specifically contained acetylenic groups linked to the silicon atoms.<sup>15</sup>

In this work, we investigated the possible Si–C linkage during the preparation of TB-bridged organosilicas from Tröger's base bis-silylated at the 2,8-positions of the aromatic nucleus as pure precursor albeit mild synthetic conditions were used, either in the presence of catalytic amount of fluoride anion (Si–TB–F) or using long chain amine as templating agent (Si–TB–A) (Scheme 1).

The hydrolytic Si–C bond cleavage leading to a transient formation of  $\equiv\text{Si–OH}$  groups entails the formation of  $\equiv\text{Si–O–Si}\equiv$  units through condensation reaction and easily identifiable as  $Q'$  silicon species in the hybrid material framework. Hence, the presence of such silicon nucleus type is prone to univocally evidence the Si–C bond cleavage. Moreover, it was of importance to determine the subsequent structural and composition of the final material network.

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† Electronic supplementary information (ESI) available: Tables S1 and S2 depict the composition of the various silicon nucleus species resulting from the signal decompositions. Fig. S3 shows the  $^1\text{H}$  NMR of the collected products resulting from the oxidative treatment of Si–TB–F sample. S4 indicates the estimation method of the contribution of the one-point attachment (O) content. See DOI: 10.1039/c1jm10426h



**Scheme 1** Preparation of mesoporous organosilica containing Tröger's base as building-block.

## Results and discussion

The preparation of the ( $\pm$ )-2,8-bis(triethoxysilyl)-6*H*,12*H*-5,11-methanodibenzo-*[b,f]*[1,5]diazocine (2SiTB) precursor and the sol-gel synthesis of the materials (Si-TB-F) and (Si-TB-A) were performed according to same experimental conditions as in ref. 7. Here, the molar compositions of the reaction mixture were: 1 (2SiTB) : 4 MeOH : 4 H<sub>2</sub>O :  $2.35 \times 10^{-4}$  NH<sub>4</sub>F and 1 (2SiTB) : 0.125 hexadecylamine : 1.02 iPrOH : 3.42 EtOH : 11.1 H<sub>2</sub>O for the preparation of (Si-TB-F) and (Si-TB-A), respectively, and the textural characteristics and the chemical composition of the resulting evacuated materials after ethanol, then ethyl ether washings are given in Tables 1 and 2.

As depicted in Table 1 (Si-TB-F) and (Si-TB-A) samples exhibit surface areas close to 150 and 360 m<sup>2</sup> g<sup>-1</sup> and total pore volumes of 0.12 and 0.22 mL g<sup>-1</sup>, and estimated pore size of less than 32 Å and around 24 Å, respectively. These materials, obtained only with the precursor, feature textural characteristics with lower mesoscopic structured order than those of samples obtained in the presence of TEOS,<sup>7</sup> according to the usual trends observed with the most sophisticated building blocks.

The organic content of the materials was also estimated from elemental analyses (Table 2).

The experimental N/C molar ratio is close to the theoretical molar ratio obtained for the Tröger-base units (N/C = 0.13) for both hybrid materials confirming that the organic fragments are preserved during the synthesis processes. Moreover, the molar ratio N/C found for the ordered sample Si-TB-A obtained after the removal of the structure directing surfactant molecules corresponds to the theoretical value. This result demonstrates the effectiveness of the alcohol extraction step to completely remove the structure directing agents.

Interestingly, when One Pulse <sup>29</sup>Si MAS NMR analyses of the two hybrid structures were carried out, results in Fig. 1 clearly show the presence of Q<sup>n</sup>-type species, though no tetraalkoxysilane was used for the preparation of Si-TB-F or Si-TB-A samples.

This implies that Si-C bond cleavage occurs during the sol-gel synthesis by bond hydrolysis due to nucleophilic assistance by fluoride or amine at the silicon atom on the basis of previous mechanistic studies in homogeneous conditions.<sup>17,18</sup>

**Table 1** Textural characteristics of the Tröger's base (TB) hybrid materials

Sample	Surface area/m <sup>2</sup> g <sup>-1</sup>	V <sub>p</sub> /mL g <sup>-1</sup>	Mean pore diameter <sup>a</sup> /Å
Si-TB-F	149	0.12	<32
Si-TB-A	363	0.22 (μV: 0.15) <sup>b</sup>	24

<sup>a</sup> Determined by 4 V S<sup>-1</sup> according to a cylindrical pore model. <sup>b</sup> μV microporous volume determined by *t*-plot method.

**Table 2** Chemical composition of the hybrid materials<sup>b</sup>

Sample	EA molar N/C <sup>a</sup>	EA TB/mmol g <sup>-1</sup> hybrid (TB/mmol g <sup>-1</sup> SiO <sub>2</sub> )	TGA TB/mmol g <sup>-1</sup> hybrid (TB/mmol g <sup>-1</sup> SiO <sub>2</sub> )	Solid NMR T/T + Q (TB/mmol g <sup>-1</sup> SiO <sub>2</sub> )
Si-TB-F	0.14	2.64 (6.00)	2.92 (6.60)	0.59 (4.95)
Si-TB-A	0.13	2.47 (5.25)	2.98 (6.35)	0.62 (5.20)

<sup>a</sup> Theoretical molar N/C ratio 0.13. <sup>b</sup> Determined by elemental analysis (N% and C%) considering dry sample (or pure silica content).

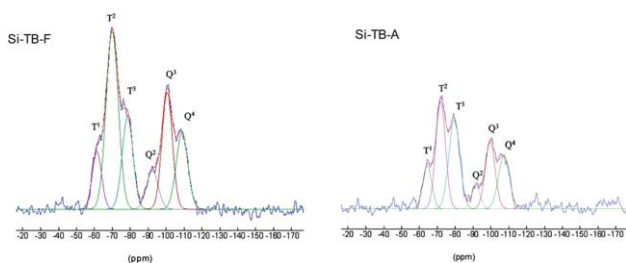
Actually, the values for the ratio  $\Sigma Q^n / \Sigma Q^n + \Sigma T^n$  determined from the signal modelling (Tables S1 and S2 in the ESI†) are 0.41 and 0.36, for samples Si-TB-F and Si-TB-A, respectively. Moreover, the condensation degrees for both T<sup>n</sup> and Q<sup>n</sup> nucleus were slightly smaller for sample Si-100-F (T<sup>5</sup> : T<sup>2</sup> : T<sup>1</sup> ratio = 1 : 2.1 : 0.5 and Q<sup>4</sup> : Q<sup>3</sup> : Q<sup>2</sup> ratio = 1 : 1.4 : 0.5) than for sample Si-TB-A (T<sup>n</sup> ratio = 1 : 1.1 : 0.4 and Q<sup>4</sup> : Q<sup>3</sup> : Q<sup>2</sup> ratio = 1 : 1.14 : 0.3) in line with the lower framework organization achieved in the former sample.

Since hydrolysis at the Si-C can occur during the sol-gel reaction, we could confirm this by evidencing the loss of one or two silyl substituents in the immobilized TB molecule, which should then be replaced by one or two hydrogen atoms (Scheme 2). In the case of a bis-Si-C bond cleavage, the resulting 2,8-hydrogeno-TB base being only physisorbed would be eliminated during the sample washing treatment.

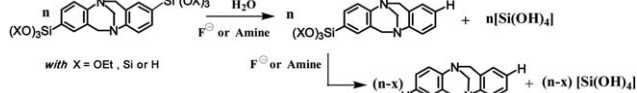
At this point and in order to determine the organic moieties anchored on silica, in the final hybrid materials, we have carried out an oxidative treatment on the sample Si-TB-F (see Scheme 3). Indeed, the selective cleavage of the covalent C-Si anchoring bond under mild condition has been previously reported in the literature through oxidative treatment of stationary chromatography phases by hydrogen peroxide in the presence of fluoride, the recovered molecule bearing a C-OH group instead of the C-Si≡ junction.<sup>19</sup> This methodology, based on the pioneering work of Tamao *et al.*<sup>20</sup> and a theoretical mechanism reported,<sup>21</sup> has been more recently applied for homogeneous organoarylsilane oxidation, leading to one-step hydroxylated aromatics with functional group-tolerance.<sup>22</sup> Further mechanistic investigation on the reaction pathway of the fluoride-catalyzed rearrangement around silicon when hydrogen peroxide was used as oxidant suggested that the reaction probably proceeds *via* anionic penta-coordinate silicate species by attack of HOO<sup>-</sup> followed by migration of an alkyl group with simultaneous loss of hydroxide or by formation and rearrangement of a hexavalent di-fluoride intermediate.<sup>22</sup>

In our case, we have performed the oxidative treatment of Si-TB-F by adding potassium bicarbonate (8 eq./TB precursor), ammonium fluoride (8 eq.) and hydrogen peroxide 30% (12 eq.) in a mixture of THF/methanol (1/1). The extracted product, collected after refluxing the reaction mixture (12 h) and separation from insoluble material products, was analyzed by <sup>1</sup>H NMR spectroscopy.

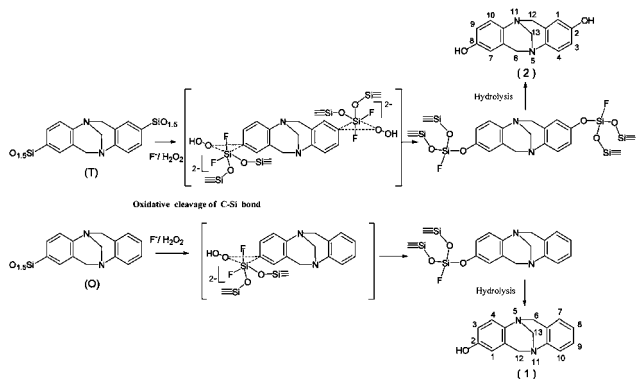
The <sup>1</sup>H NMR spectra (see ESI, Fig. S3†) of the recovered organics after neutralisation and dissolution in deuterated methanol are consistent with a mixture of 2- and 2,8-di-hydroxy TB, named (1) and (2) respectively in Scheme 3. The spectrum exhibits, in the aromatic signal range 6.4–8 ppm, a multiplet (dd) that can be assigned to H<sub>4</sub> of (1) and H<sub>4,10</sub> of (2), a multiplet (ddd) at 6.9 ppm corresponding to the proton H<sub>10</sub> of (1), a multiplet (dd) at 7.2 ppm and 7.22 ppm characteristic of H<sub>3</sub> of (1) and H<sub>3,9</sub> of (2) and, a multiplet around 7.3 ppm corresponding to the H<sub>1</sub> of (1) and H<sub>1,7</sub> of (2), and three multiplets at



**Fig. 1**  $^{29}\text{Si}$  One Pulse MAS NMR spectra of Si-TB-F and Si-TB-A in blue and the signals modeling using the Dmfit program.<sup>16</sup>



**Scheme 2** Hydrolytic cleavage of aromatic carbon-silicon bond by nucleophilic assistance in the presence of fluoride or long chain amine.



**Scheme 3** Extraction of the tethered Tröger's base by selective oxidative cleavage of Si-C bond according to ref. 21 and 22.

7.3–7.4, 7.4 and 7.90 ppm, which would correspond to the  $\text{H}_7$ ,  $\text{H}_8$ , and  $\text{H}_9$  of (I). These authentic samples have been never described in the literature, and are hardly accessible, even from 2,8-di-methoxy and 2-methoxy-TB, due to the cleavage of the methano-bridge under the drastic OH deprotection conditions.<sup>23,24</sup>

The data obtained by  $^{29}\text{Si}$  NMR spectroscopy may give only a qualitative information on the nature of the mixed mode of TB: one-point attached (O) and two-point-attached (T) species integrated into the structure of the hybrid materials, because the quantifiable  $\Sigma Q^n/\Sigma Q^n + \Sigma T^n$  ratio cannot strictly reflect the true ratio between bis- and mono-anchoring modes. Indeed, this latter can be possibly governed by the kinetics of the condensation between the various silicate species present in the reaction mixture. Those species were formed through one and two C-Si bond hydrolysis giving additional tetrasilicates that are more reactive in the condensation process. Then, a more valuable estimation of such anchoring-type composition could be made by considering the loading through the two different methodologies (Table 2). The average pure organic TB part content was determined either from TGA and elemental analyses whatever the point attachment type, or from the anchored-Si bonding content evaluated from  $\Sigma T^n/\Sigma Q^n + \Sigma T^n$  ratio assuming a two-point attachment (T) only. Hence, the differences observed

between these two values of molecular TB loading are indicative of the contribution of one-point attachment (O) that under-estimates the TB content in the case of estimation from  $^{29}\text{Si}$  One Pulse MAS NMR data (see ESI, S4†). According to this determination method, the contribution of (O) would be about 43% of the total mode in the case of Si-TB-F and around 21% for Si-TB-A. Now, the ratios  $\Sigma Q^n/\Sigma Q^n + \Sigma T^n$  for Si-TB-F and Si-TB-A determined from the direct signal modelling are 41 and 36%, respectively, which indicates a better fitting between the two determination methods for the material prepared in the presence of fluoride anion as catalyst than for the materials synthesized using long chain amine.

In this work, we have demonstrated that organosilica materials containing Tröger's base units synthesized by sol-gel procedure from bis-silylated Tröger's base as building blocks in mild conditions using either fluoride anion as catalyst or long chain amine as templating agent contain the Tröger's base fragment as a two point-attached building block into the framework. However, one-point attached Tröger's base units in addition with generation of oligosilicates are also detected, demonstrating some Si-C cleavage during the sol-gel synthesis. These results are in line with the recent theoretical studies reported by Inagaki *et al.* by molecular orbital theory calculations considering the proton affinity of the carbon atom at the *ipso*-position versus the cleaved silicon bond.<sup>25</sup> Both the two-point attached Tröger's base, integrated into the network, and the one-point attached Tröger's base, tethered to the surface walls, contribute to the formation of this new type of mesoporous organosilica materials in a ratio that varies between 57 and 79% depending on the synthesis procedure.

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