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New triethoxysilylated 10-vertex closo-decaborate clusters. Synthesis and controlled immobilization into mesoporous silica.

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Novel silylated hydroborate clusters comprising the closo-decaborate cage were prepared and characterized by ^1H, ^{13}C, ^{11}B, ^{29}Si NMR and mass spectroscopy ESI. The synthesis of such silylated clusters was achieved by using reactive derivatives of $[B_{10}H_{10}]^{2-}$, $[1-B_{10}H_9N_2]^-$ and $[2-B_{10}H_9CO]^-$. These silylated decaborate clusters constitute a new class of precursors that can be covalently anchored onto various silica supports without any prior surface modification. As a proof of concept, the synthesized precursors were successfully anchored on mesoporous silica, SBA-15 type, in different percentages where the mesoporous material retained its structure. All materials modified with closo-decaborate were characterized by ^{11}B and ^{29}Si solid state NMR, XRD, TEM and Nitrogen sorption.
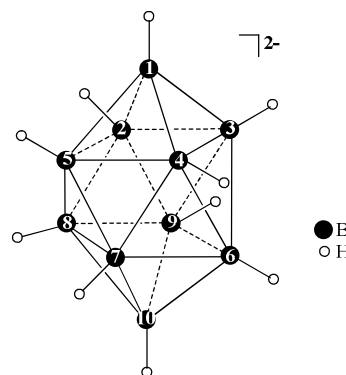
Introduction

The chemistry of the closo-decaborate anion has been well developed[1,2] owing to its atypical oxidative, hydrolytic and thermal properties.[3] These properties are governed by the 3-dimensional aromaticity and electron deficient nature which renders the exo-B-H systems susceptible to nucleophilic, electrophilic and radical substitution.[4] Nowadays, literature concerning these clusters focused on the decaborate reactivity, particularly on the activation of the B-H bond, apical and equatorial positions. The high stability and low toxicity of the closo-decaborate anion and its derivatives render these clusters to be excellent candidates for Boron Neutron Capture Therapy (BNCT),[5,6] among several other applications such as extraction,[7] catalysis,[8] material science[9] and nuclear wastes treatment.[10]

Interest in closo-decahydrodecaborate anion $[B_{10}H_{10}]^{2-}$ (Scheme 1) has been slowly receding in comparison to its higher polyhedral borate sister $[B_{12}H_{12}]^{2-}$, mainly due to the higher cost. Nevertheless, a number of exo-polyhedral substitution reactions of the $[B_{10}H_{10}]^{2-}$ anion have been recently investigated.[3] For example, monoanions such as $[1-B_{10}H_9NH(C_6H_5)_2]^-$, $[1-B_{10}H_9N(C_6H_5CH_2)(C_6H_5)_2]^-$ and $[1-B_{10}H_9P(OH)(C_6H_5)_2]^-$ were prepared from the diazonium derivative of $[B_{10}H_{10}]^{2-}$ and used for the extraction of radioactive Cs^+ cations.[7,11,12]

In addition, hetero-disubstituted derivatives of the closo-decaborate anion such as 1-(4-pentyloxypyridinyl)-10-(4-pentyl-1-thiacyclohexyl)-closo-decaborane were prepared as

structural elements for quadrupolar liquid crystals following a sequential introduction of the oxonium fragments at the apical positions of the closo-decaborate cluster.[11] Here again the diazonium derivative $[1-B_{10}H_9N_2]^-$ was used as the reactive intermediate in the synthesis.

Scheme 1. schematic representation of the anion $[B_{10}H_{10}]^{2-}$

Furthermore, oxonium derivatives of $[B_{10}H_{10}]^{2-}$, which constitute a useful intermediate for the preparation of novel derivatives, were synthesized by the reaction of the closo-decaborate anion with cyclic ethers in the presence of CF_3COOH, dry hydrogen halides or Lewis acids as initiators.[12,13]

Silicon-openborane clusters such as $6,9-(CH_3SiCH=CH)_2-B_{10}H_{12}$ and $(CH_3)_3Si(CH_2)_3-B_{10}H_{13}$ were reported for the open

cage decaborane $B_{10}H_{14}$.[14,15] The 6,9-derivative was prepared by reacting $B_{10}H_{14}$ with trimethylsilylacetylene through an iridium $[Cp*IrCl_2]_2$ catalyzed hydroboration. The monosilylated derivative $(CH_3)_3Si(CH_2)_3-B_{10}H_{13}$ was prepared by the reaction of $B_{10}H_{14}$ with allyltrimethylsilane catalyzed by $Cp_2Ti(CO)_2$. However, alkoxy silylated closo-decaborate clusters $((RO_3)_3Si\text{-linker-}B_{10}H_9)$, comprising the closo-decaborate cage $[B_{10}H_{10}]^{2-}$, were never reported and are unprecedented. The difficulties and challenges which were faced during the synthesis of such clusters are outweighed by the important potential applications.

For instance, the covalent anchoring of such deca-borate bearing silica precursors on silica matrices holds interest in the production of boron-silica based matrices (silica, glass, silicon substrate, silica nanoparticles...) ever since the latter has gained notice in the field of medicine as drug carriers and probes.[16] Theoretically, the notion of incorporating the $[B_{10}H_{10}]^{2-}$ cluster into a biologically compatible luminescent silica-based drug carrier can facilitate the imaging process of tumours and their treatment by BNCT.[17] Since its appearance, BNCT has been plagued with the lack of suitable drug carriers. The success rate of this phenomenon depends on the preferential accumulation of the Boron enriched source in tumour cells. Hence, such silylated boron clusters provide a novel method for the production of boron enriched silica matrices for biological application.

In order to achieve such silylated clusters, one needs to explore the wide variety of reactions which $[B_{10}H_{10}]^{2-}$ undergo to produce substituted derivatives. Recent studies[18] have focused on the reaction of $(NH_4)_2B_{10}H_{10}$ with solvents containing nucleophilic functional groups such as nitriles, alcohols, thiols and amines. These solvents can play the role of a ligand thereby producing polysubstituted derivatives in the form of $[B_{10}H_9L]^{n-}$, $[B_{10}H_8L_2]^{n-}$, $[B_{10}H_7L_3]^{n-}$, etc… (L is a solvent molecule). The mechanism suggested for the synthesis of such derivatives is an electrophile-induced nucleophilic substitution, where the electrophile acts as an initiator.[3] Unfortunately, these reactions are often accompanied with the production of isomers. To avoid such occurrences, other routes were investigated.

Considered to be the most useful among all substituents to give monosubstituted decaborates is the diazonium derivative $(CH_3)_4N[1-B_{10}H_9N_2]$ which can be obtained through the diazotation of $K_2B_{10}H_{10}$.[19,20,21] Another important precursor for substituted derivatives of $[B_{10}H_{10}]^{2-}$ is the carbonyl derivative $PPh_4[2-B_{10}H_9CO]$ reported by Hawthorne et al.,[22] facilitating the production of new derivatives through the reaction of the carbonyl group with diverse nucleophiles.

The importance of organic-inorganic materials has escalated after the development of the sol-gel process in 1930, in particular, silica-organic based composites.[23] So far these composites have been extensively studied. Indeed, silica based hybrid materials obtained through the sol-gel process[24] "*chimie douce*" constitute an interesting class of materials which combine the properties of organic moieties and inorganic

matrices.[25,26,27] Hybrid organosilsesquioxanes materials (R-$SiO_{1.5}$) and bridged polysilsesquioxanes ($_{1.5}OSi\text{-}R\text{-}SiO_{1.5}$) with a large variety of spacers *R* comprising functional organic units can be obtained starting respectively from mono[28,29] or bis-silylated[30,31] precursors. One of the classes of silica based hybrid materials are the ordered mesoporous silica.

Since their discovery, ordered mesoporous silica[32,33] has fascinated and continues to attract a number of research groups due to their large surface areas, as well as controllable pore sizes and arrangements.[27] The modification of such materials, which holds significant importance in the field of biomedical science, can be achieved through covalently grafting of organic moieties[34] or by direct copolymerization of the silica precursor (TEOS) with an organotrialkoxysilane $RSi(OR')_3$ bearing the desired functionality.[35]

In this study, we report the preparation of the first triethoxysilylated closo-decaborate clusters and their immobilization into the pores of mesoporous silica by grafting or by direct synthesis.

Experimental procedure

Chemicals and Characterization

All synthetic reactions were performed under Argon atmosphere using vacuum line and Schlenk-techniques. All solvents were dried and distilled unless stated otherwise. $(NH_4)_2[B_{10}H_{10}]$ was purchased from Katchem Ltd., Prague; it was dried under vacuum for 24 hours at 80 °C prior to use. 3-Aminopropyltriethoxysilane, 3-isocyanopropyltriethoxysilane, 3-cyanopropyltriethoxysilane and tetraethylorthosilicate $Si(OEt)_4$ were purchased from Sigma-Aldrich and used as received. Oxalyl chloride was obtained as 2.0 M solution in CH_2Cl_2 from Aldrich. The salt $(PPh_4)_2B_{10}H_{10}$ was precipitated from an aqueous $(NH_4)_2B_{10}H_{10}$ and recrystallized from Acetonitrile/Et_2O mixture.

The nitrogen adsorption isotherms were measured at N_2 liquid temperature (77 K) using a Micromeritics Tristar 3000 analyzer. The samples were degassed under vacuum for 12 h at 80 °C prior to analysis. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method using 74 points and starting from 0.01 as the value of the relative pressure and the pore size distributions were determined by the BJH method applied to the adsorption branch. Elemental analyses of C, H and N were performed on a FLASH EA 1112 CHNS analyzer. Solution ^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR, ^{31}P-NMR and ^{29}Si-NMR spectra were recorded using an AMX 400 Bruker spectrometer operating respectively at 400 MHz, 100 MHz, 128 MHz, 162 MHz and 80 MHz. Chemical shifts were externally calibrated to TMS for ^{1}H, ^{13}C, and ^{29}Si nucleus, H_3PO_4 (85%) for ^{31}P nuclei and $EtO_2.BF_3$ for ^{11}B nuclei. Deuterated chloroform and acetonitrile were used as solvents. Powder X-ray diffraction patterns were measured on a Bruker D5000 diffractometer equipped with a rotating anode. The wavelength used was 1.542 Å (Cu Kα radiation). Mass Spectrometry measurements were performed by negative

Electrospray Ionization method (ESI). Transmission Electron Microscopy (TEM) observations were carried out at 100 kV on a JEOL 1200 EXII microscope. Si and B content were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) following this procedure: 5 mg of material, 1,5 g of NaOH pellet and 1,5 g of KNO_3 were mixed in Nickel crucible. After thermal treatment at 650°C for 10 hours, the crucible was cooled at room temperature and the obtained pearl was dissolved in 10 mL of distilled water. After filtration, the solution was recovered in Teflon flask and analyzed by ICP-AES on Perkin Elmer Optima 2100 DV spectrometer. Scanning Electron Microscopy (SEM) images were obtained with FEI Quanta 200 FEG microscope. EDX analyses were measured on X-Max^N silicon drift detector. Solid state NMR spectra for ^{29}Si, ^{11}B, ^{31}P and ^{13}C were recorded on a Varian VNMRS 300 solid spectrometer with a magnetic field strength of 7.05 T equipped with 7.5 mm MAS probe at 5 kHz as a spinning rate.

Synthesis of silylated boron clusters

[Me$_4$N][1-B$_{10}$H$_9$N$_2$] **(1)**
Compound **1** was prepared as described in the literature.[20]
^{11}B (^{1}H) NMR (δ ppm, 128 MHz, CD$_3$CN): 21.50 (d, 1 B, J_{B-H} = 151 Hz), -13.5 (s, 1 B), -17.4 (d, 4 B, J_{B-H} = 138 Hz) and -25.1 (d, 4 B, J_{B-H} = 137 Hz).

[PPh$_4$][1-B$_{10}$H$_9$NH$_2$CH$_2$CH$_2$NH$_2$] **(2)**
2.00 g (9.13 mmol) of **1** were mixed with 30 mL of ethylenediamine under argon and heated at 120 °C for 24 hrs. After cooling to ambient temperature the mixture was filtered and passed through a silica gel column 2.5 x 30 cm, eluted with CH$_2$Cl$_2$:CH$_3$CN gradient mixture as described in literature.[36] The dark red solid was precipitated as the tetraphenylphosphonium salt and recrystallized from CH$_3$CN:CH$_2$Cl$_2$ to give compound **2** as dark red solid with 71% yield.
^{11}B (^{1}H) NMR (δ ppm, 128 MHz, CD$_3$CN): 10.3 (s, 1 B), -2.4 (d, 1 B, J_{B-H} = 138 Hz), -28.4 (d, 4 B, J_{B-H} = 119 Hz) and -30.1 (d, 4 B, J_{B-H} = 127 Hz).

[PPh$_4$][2-B$_{10}$H$_9$CO] **(3)**
[PPh$_4$][2-B$_{10}$H$_9$CO] was prepared according to literature[22] with 74% yield after crystallization from CH$_2$Cl$_2$:Et$_2$O.
^{11}B (^{1}H) NMR (δ ppm, 128 MHz, CDCl$_3$): 5.3 (d, 2 B, J_{B-H} = 141 Hz), -18.7 (d, 1 B, J_{B-H} = 128 Hz), -26.8 (d, 2 B, J_{B-H} = 145 Hz), -28.1 (d, 2 B, J_{B-H} = 110 Hz), -29.8 (d, 2 B, J_{B-H} = 120 Hz), -44.7 (s, 1 B).

[PPh$_4$][1-B$_{10}$H$_9$NH$_2$CH$_2$CH$_2$NHCONH(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$] **(4)**
1.00 g (4.32 mmol) of 3-Isocyanatopropyltriethoxysilane was slowly added to a mixture of **2** (1.00 g, 1.93 mmol) in 20 mL of dry acetonitrile under argon. After stirring under reflux for 24 hours, the mixture was cooled to room temperature and the solvent was reduced to 5 ml under vacuum. Excess of 3-isocyanatopropyltriethoxysilane were eliminated by washing

with pentane followed by drying at 80 °C to yield 1.20 g of compound **4** (81%).
^{1}H NMR (δ ppm, 400 MHz, CD$_3$CN): 0.60 (2 H, t, CH$_2$), 1.12 (9 H, t, CH$_3$), 1.65 (2 H, quin, CH$_2$), 2.11 (2 H, s, NH$_2$), 2.21 (3 H, m, BH), 2.35 (2 H, m, CH$_2$), 3.07 (6 H, m, BH), 3.13 (2 H, m, CH$_2$), 3.57 (2 H, q, CH$_2$), 3.76 (6 H, q, CH$_2$), 5.72 (1 H, s, NH), 5.76 (1 H, s, NH), 7.68-7.97 (22 H, m, Ph). ^{11}B (^{1}H) NMR (δ ppm, 128 MHz, CD$_3$CN): 7.5 (s, 1 B), -1.2 (d, 1 B, J_{B-H} = 140 Hz), -27.6 (d, 4 B, J_{B-H} = 129 Hz), -29.4 (d, 4 B, J_{B-H} = 132 Hz). ^{29}Si NMR (δ ppm, 80 MHz, CD$_3$CN): -45.16 (s). ^{13}C NMR (δ ppm, 100 MHz, CH$_3$CN): 160.00, 135.45, 134.74, 130.41, 118.72, 117.34, 58.09, 52.54, 42.71, 39.28, 23.52, 17.78, 7.26. ^{31}P NMR (δ ppm, 162 MHz, CH$_3$CN): 22.88 (s). IR (ATR, ν, cm^{-1}): 2560 (B-H ap.), 2462 (B-H eq.), 1101 (B-H deformed), 878 (B-B), 1549-1660 (NH-CO-NH), 2926-2981 (CH$_3$), 1210-840-723 (OSiC). MS/ESI = 423.74 (m/z theoretical = 423.36). *Anal*. Calc. for C$_{36}$H$_{58}$B$_{10}$O$_4$N$_3$PSi: C, 56.61, H, 7.60, B, 14.15, N, 5.50, Si, 3.66. Found: C, 56.90, H, 7.94, B, 14.23, N, 5.44, Si, 3.65.

[PPh$_4$][(^{i}pr)$_2$(Et)NH][2-B$_{10}$H$_9$CONH(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$] **(5)**
450 mg (2.06 mmol) of 3-Aminopropyltriethoxysilane were added to a mixture of **3** (1.00 g, 2.06 mmol) in 20 mL of dry CH$_2$Cl$_2$ under argon and refluxed for 4 hours in the presence of excess di-isopropylethylamine (1.00 mL). The solvent was reduced to 5 mL and excess of 3-aminopropyltriethoxysilane was removed by washing with pentane. The viscous light yellow solid obtained was further washed by diethyl ether. After drying under vacuum at 80 °C for 6 hours; 1.57 g (1.88 mmol, 92%) of **5** were obtained as pale yellow solid.
^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$): -0.50-1.5 (5 H, broad, m, BH), 0.50 (2 H, t, CH$_2$), 1.18 (9 H, t, CH$_3$), 1.37 (15 H, m, CH$_3$), 2.95 (2 H, quin, CH$_2$), 3.12 (2 H, q, CH$_2$), 3.55 (2 H, q, CH$_2$), 3.42-4.73 (4H, broad, m, BH), 3.68 (2 H, s, CH$_2$), 3.79 (6 H, q, CH$_2$), 6.04 (1 H, s, NH), 7.69-7.98 (20 H, m, Ph). ^{11}B (^{1}H) NMR (δ, ppm, 128 MHz, CDCl$_3$): 0.4 (d, 1 B, J_{B-H} = 110 Hz), -1.7 (d, 1 B, J_{B-H} = 130 Hz), -24.8 (s, 1 B), -27.6 to -29.7 (m, broad, 7 B). ^{29}Si NMR (δ ppm, 80 MHz, CDCl$_3$): -45.06 (s). ^{13}C NMR (δ ppm, 100 MHz, CDCl$_3$): 161.20, 135.82, 134.33, 130.92, 117.77, 116.81, 58.45, 42.97, 22.88, 18.36, 7.52, ^{31}P NMR (δ ppm, 162 MHz, CDCl$_3$): 22.85 (s). IR (ATR, ν, cm^{-1}): 2540 (B-H ap.), 2462 (B-H eq.), 1100 (B-H deformed), 890 (B-B), 1550 (CON), 1190-860-717 (OSiC).MS/ESI = 365.45 (m/z theoretical = 365.50). *Anal*. Calc. for C$_{42}$H$_{71}$B$_{10}$O$_4$N$_2$PSi: C, 60.43, H, 8.51, B, 12.94, N, 3.35, Si, 3.35. Found: C, 60.21, H, 8.49, B, 12.80, N, 3.34, Si, 3.30.

[NH$_4$][2-B$_{10}$H$_9$NC(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$] **(6)**
In a Schlenk tube, 5 mL of 3-cyanopropyltriethoxysilane were mixed with (NH$_4$)$_2$B$_{10}$H$_{10}$ (0.50 g, 3.2 mmol) and heated at 140 °C under argon for 48 hours. Excess of 3-cyanopropyltriethoxysilane was eliminated by washing with pentane to yield a viscous yellow solid, which was further copiously washed with diethyl ether and dried at 80 °C for 24 hours to yield a light yellow viscous solid.

^{11}B (^{1}H) NMR (δ ppm, CD$_3$CN): -1.2 (d, 2 B), -30.1 (d, 8 B) corresponding to the initial reactant (NH$_4$)$_2$B$_{10}$H$_{10}$, 1.0 (d, 1B), -4.5 (d, 1B), -14.4 (s, 1B), -25.5 (d, 4B), -29.0 (d, 3B) corresponding to compound **6** and another product believed to be the di-silylated cluster 2,6-*B$_{10}$H$_8$[NC(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_2$*. Attempts to separate these 3 derivatives were unsuccessful.

Grafting of silylated closo-decaborate clusters on SBA-15

SBA-15 was prepared through the traditional sol-gel process according to literature.[37] 4.00 g (0.067 mmol) of the triblock polymer HO(CH$_2$CH$_2$O)$_{20}$(CH$_2$CH(CH$_3$)O)$_{70}$(CH$_2$CH$_2$O)$_{20}$H (P123) were dissolved in 160 mL of an acidic aqueous solution of pH~1.5. To the obtained clear solution, 9.30 g (44.8 mmol) of TEOS were added and the resulting mixture was vigorously stirred at room temperature until a homogenous solution is evident, then 76 mg of NaF were added to the mixture to initiate polymerization and the setup was immediately placed in an oil bath at 60 °C for 3 days. Afterwards, the resulting material was filtered and the surfactant was selectively removed with Soxhlet extraction over ethanol. The mesoporous silica SBA-15 was obtained quantitatively as white powder after drying under vacuum at 120 °C for 24 hours.

Grafting of **4** on mesoporous silica SBA-15 (**SBA@4**)

1.0 g (16.6 mmol) of SBA-15 was dispersed in 20 mL of acetonitrile, a solution 10 % by mole of **4** (1.30 g, 1.7 mmol) in 5 mL of acetonitrile was added. The resulting mixture was refluxed overnight. After cooling to room temperature and filtration, the solid was copiously washed with acetonitrile to remove any adsorbed compounds and dried for 4 hours at 80 °C to obtain the material **SBA@4** as pale orange powder.

^{11}B CP-MAS NMR: 5 (B$_1$), -1 (B$_{10}$), -10 to -25 ppm (B$_{2-9}$). ^{29}Si CP-MAS NMR: -57 (T^2), -67 (T^3), -92 (Q^2), -105 (Q^3) and -112 ppm (Q^4). ^{31}P CP-MAS NMR: 24 ppm. ^{13}C CP-MAS NMR: 159 (C=O), 100-140 (Pph$_4$), 72, 61, 45, 24, 13 ppm (ammonium salt and propyl spacer).

Nitrogen sorption (adsorption branch): S$_{BET}$ (m^2/g): 358; Vp (cm^3/g): 0.71 and Dp: 75 Å

Atomic ratio Si/N: 13.6.

Anal. Calc.: Si, 37.53, B, 3.57. Found: Si, 38.01, B, 3.49.

Grafting of **5** on SBA-15 (**SBA@5**)

1.00 g of SBA-15 was dispersed in 20 mL of DMF, a solution of 10 % by mole of **5** (1.40 g, 1.7 mmol) dissolved in 5 mL DMF was added to the resulting mixture and heated at 90 °C over night. After cooling, filtration, and washing extensively with DMF and acetonitrile, the resulting pale yellow powder **SBA@5** was dried at 80°C for 4 hours.

^{11}B CP-MAS NMR: -0.5 (B$_{1,10}$), -10 to -25 ppm (B$_{2-9}$). ^{29}Si CP-MAS NMR: -57 (T^2), -68 (T^3), -92 (Q^2), -102 (Q^3) and -110 ppm (Q^4).

Nitrogen sorption (adsorption branch): S$_{BET}$ (m^2/g): 446; Vp (cm^3/g): 0.76 and Dp: 72 Å.

Atomic ratio Si/N: 10.5.

Anal. Calc.: Si, 30.07, B, 5.80. Found: Si, 30.45, B, 5.50.

Anchoring of **3** on **SBA-NH$_2$**

Direct synthesis of SBA-15 functionalized with 10% NH$_2$ was prepared according to published literature.[38]

Nitrogen sorption (adsorption branch): S$_{BET}$ (m^2/g): 600; Vp (cm^3/g): 0.98 and Dp: 62 Å.

Atomic ratio Si/N: 15.6.

0.50 g (0.769 mmol) of **SBA-NH$_2$** was dispersed in 20 ml of dichloromethane where a solution of cluster **3** (0.25 g, 0.516 mmol in 5 mL of dichloromethane) was added with 1.00 mL of diisopropylethylamine. The resulting mixture was refluxed overnight where 0.64 g of a pale yellow powder **SBA-NH$_2$@3** was isolated after filtration and drying.

^{11}B CP-MAS NMR: -0.7 (B$_{1,10}$), -10 to -28 ppm (B$_{2-9}$). ^{29}Si CP-MAS NMR: -56 (T^2), -68 (T^3), -92 (Q^2), -101 (Q^3) and -110 ppm (Q^4).

Nitrogen sorption (adsorption branch): S$_{BET}$ (m^2/g): 360; Vp (cm^3/g): 0.65 and Dp: 59 Å.

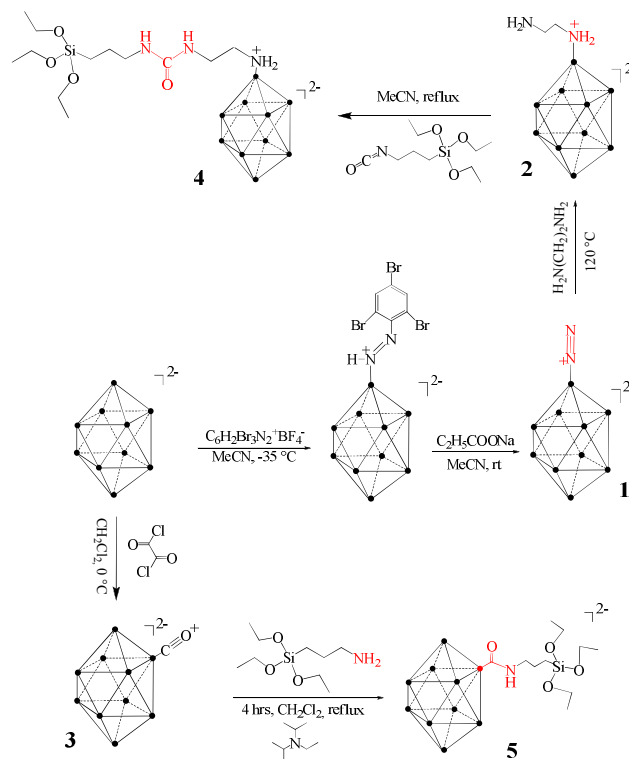Atomic ratio Si/N: 13.7.

Results and Discussion

Silylated closo-decaborate clusters

The anchoring approach of the triethoxysilyl group on (NH$_4$)$_2$B$_{10}$H$_{10}$ was investigated and several silylated clusters were prepared following scheme 2 where only the quantitative products are attributed.
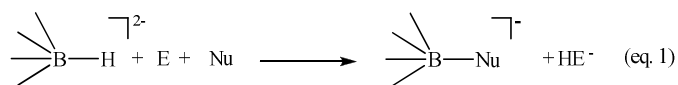
Before approaching the silylated closo-decaborate clusters, it is worth mentioning that the attempt to directly synthesize silylated clusters starting from (NH$_4$)$_2$B$_{10}$H$_{10}$ were unsuccessful
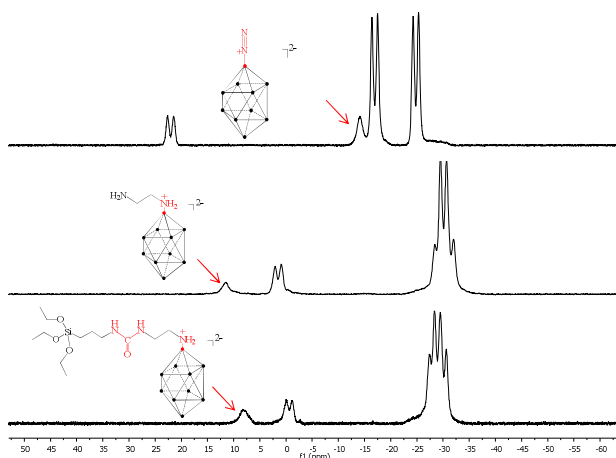

Scheme 2. General pathway for the preparation of quantitative silylated decaborate clusters **4** and **5**.

due to the lack of a suitable electrophile to initiate the reaction. Also, some successful reactions were plagued with either isomerisation or very low yields or both. For example, the reaction involving $(NH_4)_2B_{10}H_{10}$ with 3-cyanopropyltriethoxysilane was not efficient because attempts to separate the two obtained products $NH_4[2-B_{10}H_9NC(CH_2)_3Si(OC_2H_5)_3]$, $2,6-B_{10}H_8[NC(CH_2)_3Si(OC_2H_5)_3]_2$ and the initial reactant $(NH_4)_2B_{10}H_{10}$ were unsuccessful (see experimental part, cluster **6**).

In general, the synthesis of closo-decaborate derivatives involves the abstraction of an exo-polyhedral hydride ion (eq. 1) through electrophile-induced nucleophilic substitution (EINS). EINS reactions require the presence of an electrophile such as Bronsted acids, Lewis acids, carbocations, organometallic catalysts, or gaseous hydrogen halide. The context of the current work was limited by this criterion since the ethoxy groups in the silica precursors are highly sensitive to acids, bases, and humidity.

$$\cdots B\!-\!H \ + \ E \ + \ Nu \ \longrightarrow \ \cdots B\!-\!Nu \ + HE^- \qquad (eq. 1)$$

Moreover, recent unpublished results[18] have revealed $(NH_4)_2B_{10}H_{10}$ predisposition to react solely with polar protic/aprotic solvents to yield mono, di, and polysubstituted derivatives (isomerisation). This predisposition was later determined to be a result of the NH_4^+ counter cation of the cluster $[B_{10}H_{10}]^{2-}$ already present in the medium.[18] Hence, any direct synthesis starting from $[B_{10}H_{10}]^{2-}$ leads to mono and polysubstituted isomers where the separation attempts while trying to conserve the ethoxy chemical group were unsuccessful. Subsequently, the silylation often resulted in two mono-substituted major products, $[B_{10}H_9L]^{n-}$ and to several poly-substituted products where L is either the silicon precursor or a solvent molecule. Consequently, silica precursors were anchored on reactive derivatives of the closo-decaborate cage which are: the diazo-derivative[19] $[1-B_{10}H_9N_2]^-$ and the carbonyl derivative $[2-B_{10}H_9CO]^-$.[22]

Compounds **1**[19], **2**[36] and **3**[22] were prepared following described methods. The reaction between silane precursors and the highly reactive diazonium derivative $[1-B_{10}H_9N{\equiv}N]^-$ was accompanied with the production of multiple isomers in the form of $[1-B_{10}H_9L]^{n-}$ where L is either a solvent molecule or the silane precursor, since $[1-B_{10}H_9N{\equiv}N]^-$ is highly reactive towards certain solvents at higher temperature. Under rigorous conditions, the reaction proceeds with an insignificant yield where a considerable percentage of $[1-B_{10}H_9N{\equiv}N]^-$ reverted to the unmodified cluster $[B_{10}H_{10}]^{2-}$. Therefore, the diazonium derivative was further functionalized with ethylenediamine to give $[1-B_{10}H_9NH_2CH_2CH_2NH_2]^-$ (**2**).

The synthesis of **4** involved the reaction of the peripheral amine on the cluster with –N=C=O group present in 3-isocyanatopropyltriethoxysilane. The ^{11}B NMR of cluster **4** (Figure 1) is virtually the same as that of compound **2** since the reaction occurred at a distance from the substitution site (apical position) of $[1-B_{10}H_9NH_2CH_2CH_2NH_2]^-$, an insignificant shift in the chemical shift (ppm) from **2** was observed. However evidence of the reaction was observed in ^{1}H NMR, ^{29}Si NMR and IR (ATR) where two unique absorption at 1540 and 1650 cm^{-1} relevant to the urea group were now evident.

The ^{1}H NMR spectrum contains a triplet at 1.12 ppm and a quadruplet at 3.76 ppm corresponding to the ethoxy groups (CH_3CH_2O-) attached to the silicon atom, a triplet at 0.60 ppm corresponding to the $-CH_2$ adjacent to the silicon atom and 2 singlets at 5.72 and 5.76 ppm relevant to the hydrogen's of urea units ($-NH-CO-NH-$) can also be seen. ^{29}Si NMR spectrum revealed a peak at -45.16 ppm characteristic for $-Si(OEt)_3$ group. ^{13}C NMR clearly exhibited a signal at 160.00 ppm corresponding to the carbonyl group and an additional one at 7.26 ppm corresponding to the $-CH_2$ adjacent to the silicon atom. In addition, compound **4** was verified by mass spectroscopy ESI to be 423.74 (m/z theoretical = 423.36).

Figure 2. ^{11}B (^{1}H) NMR spectra of clusters **3** (top) and **5** (bottom); the arrows indicate the peaks of the corresponding substituted boron atom (equatorial position).
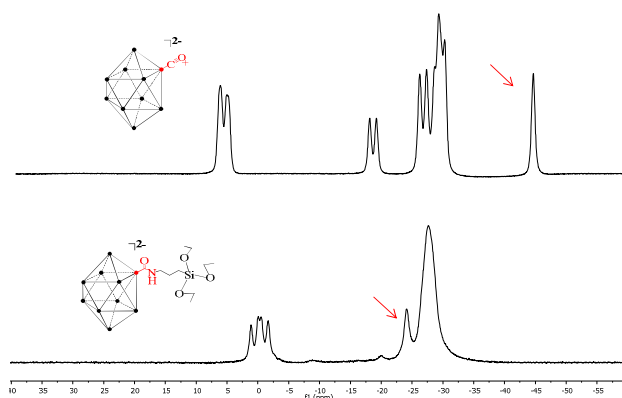

Figure 1. ^{11}B (^{1}H) NMR spectra of clusters **1**(top), **2** (middle) and **4** (bottom); the arrows indicate the peaks of the corresponding substituted boron atom (apical position).

The synthesis of **5** involved the reaction of $-C{\equiv}O$ with 3-aminopropyltriethoxysilane in the presence of a base; the
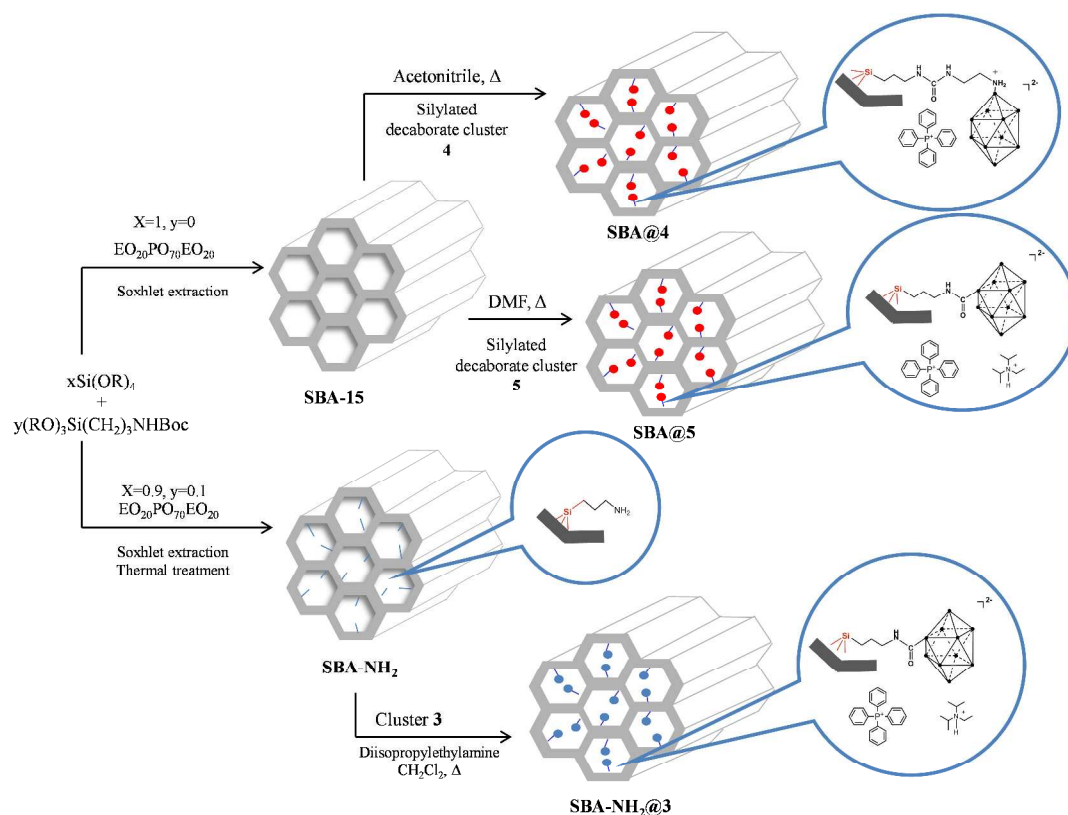
product analyzed caused a shift of the singlet in ^{11}B NMR characteristic of —B–C≡O$^+$ from -44.76 ppm to -24.89 ppm at the equatorial position (Figure 2). The two apical boron atoms B_1 and B_{10} appear as a triplet (two overlapping doublets) at 0.41 and -1.74 ppm, and the 7 remaining equatorial Boron atoms B_3 to B_7 appear as a broad peak between -27.0 and -33.0 ppm, this is in agreement with published literature[22] which state that the remaining equatorial peaks are indiscernible in the spectrum. ^{29}Si NMR also exhibited a signal at -45.06 ppm relevant to Si(OEt)$_3$ and the MS/ESI = 365.4 (m/z theoretical = 365.5). Initially, the preceding reaction was performed in the absence of a base and an excess of 3-aminopropyltriethoxysilane, the amine group NH$_2$ present in the silane precursor played the role of a base and abstracted a H-atom to produce (EtO)$_3$Si(CH$_2$)$_3$NH$_3^+$ which was evident in ^{1}H and ^{29}Si NMR. ^{29}Si NMR revealed the presence of two silicon types, the desired product **5** and the protonated derivative seen as two signals at -45.04 and -46.10 ppm while the product retained a viscous nature. When triethylamine was used as the base, two major products were observed, the silylated cluster [(EtO)$_3$Si(CH$_2$)$_3$NHCO-B$_{10}$H$_9$]$^{2-}$ and the triethylamine derivative [(Et$_3$)NCO-B$_{10}$H$_9$]$^-$. As a consequence, it is best to use a more basic less nucleophilic base. Indeed, di-isopropyl ethylamine proved to be successful when utilized in excess, and the reaction yielded a quantitative product when the two reactants were used in equivalent ratios. Note that attempts to crystallize these two clusters (**4** and **5**) were unsuccessful.

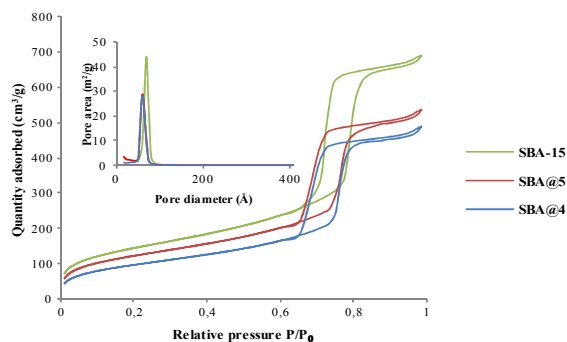### Grafting of 4 and 5 on SBA-15

The triethoxysilylated borate clusters **4** and **5** were grafted directly onto the pore surfaces of SBA-15 (Scheme 3). This covalent linking was realized by the treatment of the silica (1 eq.) with a solution of **4** (0.1 eq) in acetonitrile or **5** (0.1 eq) in DMF. Acids were not utilized in this process since acid presence might induce the production of [B$_{10}$H$_9$L]$^{n-}$ where L is a solvent molecule. It is noteworthy to mention that closo-decaborate functionalized SBA material was not achieved directly through sol-gel process due to the hydrophobicity of the silylated clusters (insolubility in acidic water).

The functionalized hybrid materials were characterized by elemental analyses, N$_2$ adsorption/desorption, solid state NMR, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Nitrogen sorption isotherms at 77 k (Figure 3) of SBA-15, **SBA@4** and **SBA@5** show type IV isotherms with a clear H1-type hysteresis loop at high pressure, characteristic of mesoporous material. The isotherms exhibit a sharp inflection in the P/P$_0$ region at ~0.63 characteristic of capillary condensation and uniform pore size distribution. All isotherms are quite similar in the overall trend; however they differ in a notable shift of the hysteresis position towards lower P/P$_0$ for **SBA@4** and **SBA@5** plus a significant decrease in overall nitrogen adsorption. An evident decrease in surface area can be noticed from 520 m^2/g relevant to SBA-15 to 358 m^2/g and 446 m^2/g for **SBA@4** and **SBA@5** respectively. Another decrease can also be observed for pore volume (1.00 cm^3/g for SBA-15, to 0.71 cm^3/g for **SBA@4** and 0.76 cm^3/g for **SBA@5**) which

Scheme 3. General pathway for the preparation of the closo-decaborate functionalized mesoporous silica.
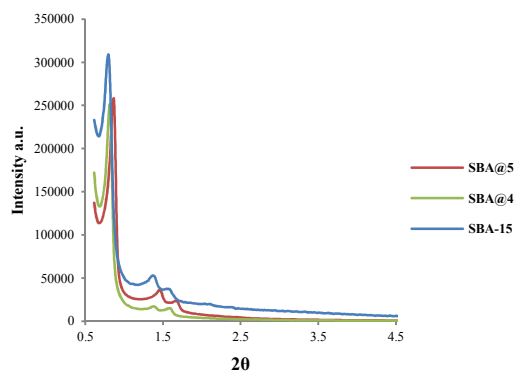
indicates that the grafted precursors are located inside the mesoporous pores, hence reducing the pore dimension in comparison with the unmodified SBA-15. Based on nitrogen, boron and silicon % determined from elemental analyses and EDS, the estimated molar percentage of grafted precursors are 2.6 % for **SBA@4** and 5.2 % for **SBA@5**.
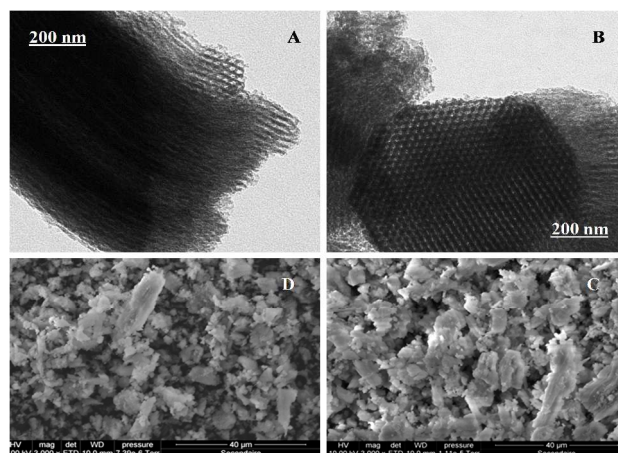

Figure 3. Nitrogen adsorption/desorption isotherms of SBA-15, **SBA@4** and **SBA@5**. The inset represents BJH pore-size distributions calculated from adsorption branch for SBA-15, **SBA@4** and **SBA@5**.

Figure 4 depicts XRD patterns obtained for unmodified SBA-15 and the decaborate functionalized SBA materials. X-ray of the hybrid materials exhibited three low-angle reflections characteristic of a hexagonal symmetry of space group *p6m* with an intense diffraction peak corresponding to d_{100} spacing (10.47 nm) as well as weak and broad peaks at d_{110} and d_{200} reflection. The similarity of the XRD patterns of **SBA@4** and **SBA@5** to the unmodified SBA-15 clearly indicates the preservation of the hexagonal symmetry and structure. Further evidence of the hexagonal structure was provided by TEM images (Figure 5).
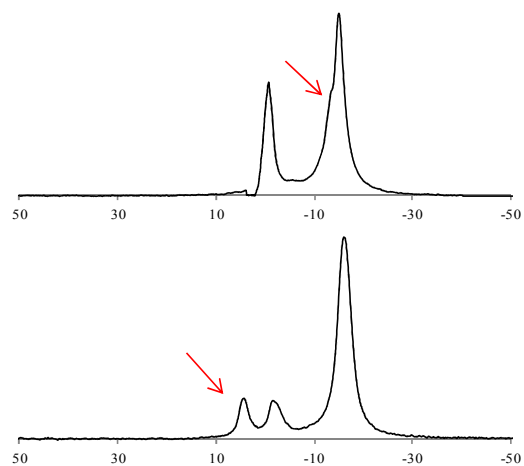

Figure 4. Powder X-ray diffraction patterns of SBA-15, **SBA@4**, and **SBA@5**.

The ^{11}B CP/MAS NMR of **SBA@4** and **SBA@5** and ^{29}Si CP/MAS NMR spectra of the **SBA@4** and SBA-15 materials are shown in figures 6 and 7 respectively. ^{11}B NMR of **4** and **5** (Figure 6) is in general consistent with that of liquid NMR but with a varying fluctuation in chemical shifts. The ^{11}B NMR of

Figure 5. TEM images of **SBA@4** (A), **SBA@5** (B) and SEM images of **SBA@4** (D), **SBA@5** (C).

SBA@4 reveals a peak at ~5 ppm (7.5 ppm in liquid NMR) corresponding to the substituted B_1 atom position, another peak at ~ -1 ppm (-1.2 ppm) for B_{10} atom position and a broad peak between -10 to -25 ppm for the remaining 8 equatorial B atoms (-27 to -32 ppm). The ^{11}B NMR of **SBA@5** reveals a peak at ~ -0.5 ppm for $B_{1,10}$ (seen as 2 adjacent peaks in liquid NMR at 0.4 and -1.7 ppm) and a broad peak between -10 and -25 ppm

Figure 6. Solid state ^{11}B CP/MAS NMR spectra of **SBA@5** (top) and **SBA@4** (bottom); arrows are to indicate the peaks corresponding to the substituted boron atom for **SBA@5** (equatorial position) and **SBA@4** (apical position.)

where the substituted boron peak at position 2 is overlapped with the remaining B_{3-8} peaks.

The ^{29}Si shows resonance peaks at -92, -105 and -112 ppm originating from the structural units of SBA-15 corresponding respectively to Q^2, Q^3 and Q^4 substructures. After the modification of SBA-15 material with silylated clusters, the

intensities of Q^2 and Q^3 peaks are reduced with respect to that of SBA-15 while the intensity for the Q^4 increases and two new peaks appear at -57 and -67 ppm corresponding respectively to T^2 and T^3 substructures characteristic for anchored silylated decaborate clusters.

Figure 7. ^{29}Si CP/MAS NMR spectra of SBA-15 (top) and **SBA@4** (bottom).

In order to verify the integrity of grafted precursors, ^{31}P and ^{13}C NMR were realised for SBA@4 material. 31P spectrum shows a board signal at 24 ppm which characterizes the phosphonium ion. ^{13}C spectrum revealed a peak at 159 corresponding to C=O group, several peaks between 100 and 140 for the phosphonium cation (PPh$_4$) and at 72, 61, 45, 24, 13 ppm attributed to ammonium salt and propyl spacer. These chemical shifts being similar to those observed in solution for **4** and confirm that the organic moieties are intact within the material.

Finally, as previously mentioned, the direct copolymerization of silylated decaborate clusters with TEOS to obtain decaborate functionalized SBA material was unsuccessful because of clusters **4** and **5** insolubility in water (pH = 1.5). As such, **SBA-NH$_2$** (Scheme 3) containing 6% molar of –NH$_2$ groups regularly distributed in the pores, was synthesized according to published procedures.[38] The carbonyl derivative **3** of closo-decaborate was covalently anchored to the –NH$_2$ in the presence of diisopropylethyl amine in order to control the percentage of grafting where the obtained pale yellow solid was characterized with N$_2$ adsorption-desorption. As expected, a decrease in surface area from 600 m^2/g for **SBA-NH$_2$** to 360 m^2/g for **SBA-NH$_2$@3**, and in pore volume from 0.98 cm^3/g to 0.65 cm^3/g were observed. The powder small-angle X-ray pattern for **SBA-NH$_2$@3** also exhibits a diffraction peak corresponding to d_{100} spacing , in addition to solid ^{11}B and ^{29}Si NMR where the results were similar to that of **SBA@5** (Figures 6 and 7). From elemental analysis and EDS, anchoring rate for **3** was estimated to be 2.0 % by mole. This incomplete anchoring can be attributed to two factors, the bulkiness of the

cluster PPh$_4$[B$_{10}$H$_9$CO] or/and the competition between the species present in the medium, since [B$_{10}$H$_9$CO]$^-$ reacts with the amine in **SBA-NH$_2$** to obtain **SBA-NH$_2$@3** and with the base di-isopropylethylamine to give [B$_{10}$H$_9$N(^{i}pr)$_2$(Et)]$^-$.

Conclusion

New mono-silylated decaborate clusters were prepared starting from the [B$_{10}$H$_{10}$]$^{2-}$ derivatives such as [1-B$_{10}$H$_9$N$_2$]$^-$ and [2-B$_{10}$H$_9$CO]$^-$ in quantitative yields through a general approach without the use of catalysts. These derivatives were prepared following reported procedures through the replacement of an exo-polyhedral hydrogen atom with the diazonium or the carbonyl functional group, and then additionally modified with nucleophilic substituents to obtain silylated clusters.

As a proof of concept, these clusters were successfully grafted on mesoporous silica SBA-15 with molar percentage between 2.6 and 5.2 %. The hexagonal symmetry and mesoporosity of SBA-15 were retained after modification as seen in nitrogen sorption and XRD studies.

The importance of this family of precursors is their ease to be covalently anchored on any silica matrices, glass, silicon surface and specially on metal oxide nanoparticles, hence facilitating the tracing of the closo-decaborate drug pathway in BNCT. In other terms, the design of such precursors containing hydrolysable alkoxy groups would be favourable since it allows the incorporation of a closo-decaborate cluster into a biologically compatible luminescent silica-based drug carrier; thereby opening a broad venue to optical and biomedical applications. In the near future, multifunctionalized luminescent nanoparticles will be prepared through the introduction of silylated decaborate clusters into the luminescent silica nanoparticles either through grafting or through one pot synthesis for controlled vectorization.

Acknowledgements

Notes and references

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1 I. Sivaev, A. V. Prikaznov and D. Naoufal, Coll. Czech. Chem. Commun., 2010, 75, 1149.

2 E. A Malinina, V. V. Avdeeva, L. V. Goeva, and N. T. Kuznetsov, Russ. J. Inorg. Chem., 2010, 55, 2148.

3 K. Yu. Zhizhin, A. P. Zhdanov, and N. T. Kuznetsov, Russ. J. Inorg. Chem., 2010, 55, 14, 2089.

4 R. Dobrott and W. Lipscomb, J. Chem. Phys., 1962, 37, 1779.

5 D. Gabel, S. Mai and O. Perleberg, J. Organomet. Chem., 1999, 581, 45.

6 I. B. Sivaev, N.A. Votinova, V. I. Bragin, Z.A. Starikova, L. V. Goeva, V. I. Bregadze and S. Sjoberg, J. Organomet. Chem., 2002, 657, 163; V. I. Bregadze, I. B. Sivaev and S. A. Glazun, Anti-Cancer Agents Med. Chem., 2006, 6, 75.

7 D. Naoufal, B. Grüner, P. Selucký, B. Bonnetot and H. Mongeot, J. Radioanal. Nucl.Chem., 2005, 266, 145.

8 P. Kaszynski, Coll. Czech. Chem. Commun.,, 1999, 64, 895; O. N. Kazheva, A. N. Chekhlov, G. G. Alexandrov, L. I. Buravov, A. V. Kravchenko, V. A. Starodub, I. B. Sivaev, V. I. Bregadze and O. A. Dyachenko, J. Organomet. Chem., 2006, 691, 4225; M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer and D. Neuhauser, Science, 2004, 303, 1849.

9 M. F. Hawthorne, Advances on Boron and the Boranes, ed. J. F. Liebman, A. Greenberg and R. E. Williams, VCH Publishers, New York, 1988, 225; A. Demonceau, E. Saive, Y. de Froidmont, A. F. Noels, A. J. Hubert, I. T. Chizhevsky, I. A. Lobanova and V. I. Bregadze, Tetrahedron Lett., 1992, 33, 2009.

10 V. N. Romanovskiy, I. V. Smirnov, V. A. Babain, T. A. Todd, J. D. Law, R. S. Herbst and K. N. Brewer, Solvent Extr. Ion Exch., 2001, 19, 1; J. F. Dozol, M. Dozol and R. M. Macias, J. Inclusion Phenom. Macrocyclic Chem., 2000, 38, 1; J. Rais and B. Grüner, Solvent Extr. Ion Exch, ed. Y. Marcus and A. K. Sengupra, CRC Press, Boston, 2004, 17, 243.

11 A. Jankowiak, A. Balinski, J. E. Harvey, K. Mason, A. Januszko, P. Kaszynski, V. G. Young Jr., and A. Persoons, J. Mater. Chem. C, 2013, 1, 1144.

12 K. Yu. Zhizhin, V. N. Mustyatsa, E. A. Malinina, N. A. Votinova, E. Yu. Matveev, L. V. Goeva, I. N. Polyakova and N. T. Kuznetsov, Russ. J. Inorg. Chem., 2004, 49, 221.

13 S. S. Akimov, E. Yu. Matveev, G. A. Razgonyaeva, L. I. Ochertyanova, N. A. Votinova, K. Yu. Zhizhin, and N. T. Kuznetsov, Russ. Chem. Bull., Int. Ed., 2010, 59, 371.

14 S. Chatterjee, P. J. Carroll, and L. G. Sneddon, Inorg. Chem., 2013, 52, 9119.

15 Mark J. Pender, Patrick J. Carroll, and Larry G. Sneddon, J. Am. Chem. Soc., 2001, 123, 12222.

16 D. M. Webster, P. Sundaram and M. E. Byrne, European Journal of Pharmaceutics and Biopharmaceutics, 2013, 84, 1.

17 A. H. Soloway, W. Tjarks, B. A. Barnum, F. Rong, R. F. Barth, I. M. Codogni and J. Gerald Wilson, Chem. Rev., 1998, 98, 1515.

18 D. Naoufal et al, Unpublished results.

19 R. N. Leyden and M. F. Hawthorne; Inorg. Chem., 1975, 14, 2444.

20 R. N. Leyden and M. F. Hawthorne J. Am. Chem. Soc., 1973, 95, 2032.

21 L. L. Ng, B. K. Ng, K. Shelly, C. B. Knobler and M. F. Hawthorne, Inorg. Chem., 1991, 30, 4278.

22 K. Shelly, C. B. Knobler, and M. F. Hawthorne; Inorg. Chem., 1992, 31, 2889.

23 B. Lin, F. Chu, N. Yuan, H. Shang, Y. Ren, Z. Gu, J. Ding, Y. Wei and X. Yu, J. Power Sources, 2014, 252, 270; I. Saana Amiinu, X. Liang, Z. Tu, H. Zhang, J. Feng, Z. Wan and M. Pan, ACS Appl. Mater. Interfaces, 2013, 5, 11535; C. Laberty-Robert, K. Valle, F. Pereira and C. Sanchez, Chem. Soc. Rev., 2011, 40, 961; B. P. Tripathi and V. K. Shahi, Prog. Polym. Sci., 2011, 36, 945.

24 C. J. Brinker and G. W. Scherrer, Sol-Gel Science, 1990: the physics and chemistry of sol-gel processing, 1st ed.; Academic Press: San Diego.

25 C. Sanchez, B. Julian, P. Belleville and M. Popall, J. Mater. Chem., 2005, 15, 3559.

26 G. Kickelbick, Hybrid Materials, 2006, Wiley-VCH, Weinheim.

27 A. Mehdi, C. Reye and R. J. P. Corriu, Chem. Soc. Rev., 2011, 40, 563.

28 C. O. Turrin, V. Maraval, A. Mehdi, C. Reye, A. M. Caminade and J. P. Majoral, Chem. Mater., 2000, 12, 3848.

29 S. Dourdain, J.-F. Bardeau, M. Colas, B. Smarsly, A. Mehdi, B. M. Ocko and A. Gibaud, Appl. Phys. Lett., 2005, 86, 113108.

30 J. Alauzun, A. Mehdi, C. Reye and R. J. P. Corriu, J. Am. Chem. Soc., 2005, 32, 11204.

31 E. Besson, A. Mehdi, D. A. Lerner, C. Reye, and R. J. P. Corriu, J. Mater. Chem., 2005, 15, 803.

32 T. Yanagisawa, C. Yokoyama, K. Kuroda and C. Kato, Bull. Chem. Soc. Jpn., 1990, 63, 47.

33 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, Nature, 1992, 359, 710.

34 G. Subra, A. Mehdi, C. Enjalbal, M. Amblard, L. Brunel, R. J. P. Corriu and J. Martinez, J. Mater. Chem., 2011, 21, 6321; S. Jebors, C. Enjalbal, M. Amblard, G. Subra, A. Mehdi and J. Martinez, J. Mater. Chem. B, 2013, 23, 2921.

35 R. Mouawia, A. Mehdi, C. Reye and R. J. P. Corriu, J. Mater. Chem., 2008, 18, 2028.

36 D. Naoufal, Z. Assi, E. Abdelhai, G. Ibrahim, O. Yazbeck, A. Hachem, H. Abdallah and M. El Masri, Inorganica Chimica Acta, 2012, 383, 33.

37 R. J. P. Corriu, E. Lancelle-Beltran, A. Mehdi, C. Reyé, S. Brandès and R. Guilard, J. Mater. Chem., 2002, 12, 1355.

38 A. Mehdi, C. Reye, S. Brandes, R. Guilard and R. J. P. Corriu, New J. Chem., 2005, 29, 965.

<div align="center">**Graphical Abstract**</div>

Triethoxysilyalted borate clusters comprising the closo-decaborate cage were synthesized and immobilized into the pores of SBA-15 mesoporous silica.