Supplementary Information

Mesostructured fatty acid-tethered silicas: Sustaining the order by co-templating with bulky precursors

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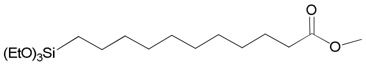
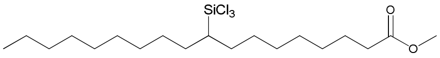
S1 - *Synthesis* and NMR spectra of the starting precursors:

Synthesis of methyl 11-(triethoxysilyl)undecanoate (SiFA$_1$):



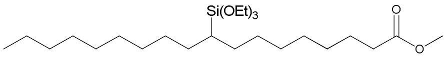
A mixture of methyl 10-undecenoate (1.50 g, 7.57 mmol) and triethoxysilane (1.86 g, 11.35 mmol) was heated in a Carius tube in presence of Karstedt's catalyst [Pt^0] at 60 °C for 6 h. Distillation of the residue under reduced pressure gave 2.63 g of SiFA$_1$. Yield: 96%. b.p. 142°C/0.07 mmHg. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.48-0.54 (m, 2H, CH_2Si); 1.11 (t, ^3J (H,H) = 7.0 Hz, 9H, $OCH_2C\mathit{H}_3$); 1.16 (s.br, 12H, $(CH_2)_6$); 1.24-1.34 (m, 2H, $C\mathit{H}_2$-CH_2-CH_2CO); 1.42-1.57 (m, 2H, $C\mathit{H}_2$-CH_2CO); 2.19 (t, ^3J (H,H) = 7.5 Hz, 2H, CH_2CO); 3.55 (s, 3H, OCH_3); 3.70 (q, ^3J (H,H) = 7.0 Hz, 6H, $OC\mathit{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 10.32 (CH_2Si), 18.23 ($OCH_2\mathit{C}H_3$), 22.70, 24.90, 29.09, 29.16, 29.19, 29.39, 33.11 ($(CH_2)_8$), 34.03 ($\mathit{C}H_2CO$), 51.32 (OCH_3), 58.21 ($O\mathit{C}H_2CH_3$), 174.22 (CO). ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ = -44.58. IR (pure): ν = 1162 cm^{-1} (C-O-C). MS (EI): m/z (%) = 363 (4) [M+1], 331 (5) [M – OCH_3], 316 (4) [M − (EtOH)], 163 (100) [$Si(OEt)_3$]. Elemental analysis (%) calcd. for $C_{18}H_{38}O_5Si$ (362.25): C, 59.63; H, 10.56. Found: C, 59.60; H, 10.49.

Synthesis of methyl 10-(trichlorosilyl)octadecanoate FA$_2$-Cl:



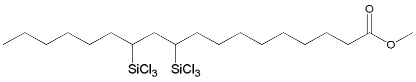
A mixture of methyl oleate (2.60 g, 8.77 mmol) and trichlorosilane (1.77 g, 13.14 mmol) was heated in a Carius tube from 20 °C to 150 °C under RIS conditions for 45 h). Distillation of the residue under reduced pressure gave 3.40 g of FA$_2$-Cl. Yield: 90%. b.p. 165°C/ 0.05 mmHg. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.86 (t, ^3J (H,H) = 6.5 Hz, 3H; CH_3), 1.26-1.81 (m, 29H; $(C\mathit{H}_2)_7$-$C\mathit{H}Si$-$(C\mathit{H}_2)_7$), 2.28 (t, ^3J (H,H) = 7.4 Hz, 2H; CH_2CO), 3.64 (s, 3H; OCH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71, 24.94, 28.09, 29.03, 29.15, 29.24, 29.35, 29.53, 29.62, 29.73, 31.94 ($(\mathit{C}H_2)_7$-$CHSi$-$(\mathit{C}H_2)_8$), 33.64 ($\mathit{C}HSi$), 34.15 ($\mathit{C}H_2CO$), 51.43 (OCH_3), 174.22 (CO). ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ = 14.42. IR (pure): ν = 1171 cm^{-1} (C-O-C), 1741 cm^{-1} (C=O). MS (EI): m/z (%) = 432 (6) [M$^+$], 401 (3) [M − (OCH_3)], 297 (40) [M − (Cl_3Si)], 317 (16) [$(CH(SiCl_3)(CH_2)_8COOCH_3)^+$], 74 (100) [$(CH_2{=}C(OH)OCH_3)^+$]

Synthesis of methyl 10-(triethoxysilyl)octadecanoate (SiFA$_2$):



To a solution of methyl 10-(trichlorosilyl) octadecanoate FA$_2$-Cl (3.40 g, 7.90 mmol) in pentane (25 mL) was added a solution of triethylamine in large excess (37 mL) in ethanol (15mL) at -40 °C. After 1 h, the mixture was warmed to room temperature and stirred overnight. After filtration, the solvent was removed and distillation under reduced pressure yielded 2.91 g of compound SiFA$_2$ as a colorless liquid. Yield: 80%. b.p. 182°C/ 0.08 mmHg. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.80 (t, ^3J (H,H) = 6.5 Hz, 2H; CH_3); 1.14 (t, ^3J (H,H) = 7.0 Hz, 9H, $OCH_2C\mathit{H}_3$); 1.19 (s.br, 25H, $(C\mathit{H}_2)_7$-$C\mathit{H}Si$-$(C\mathit{H}_2)_5$)); 1.35-1.48 (m, 2H, $C\mathit{H}_2$-CH_2-CH_2CO); 1.48-1.62 (m, 2H, $C\mathit{H}_2$-CH_2CO); 2.22 (t, ^3J (H,H) = 7.5 Hz, 2H, CH_2CO); 3.58 (s, 3H, OCH_3); 3.74 (q, ^3J (H,H) = 7.0 Hz, 6H, $OC\mathit{H}_2CH_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.00 (CH_3), 18.25 ($OCH_2\mathit{C}H_3$), 22.66 (CHSi), 22.62, 24.90, 28.63, 28.66, 28.70, 29.02, 29.12, 29.21, 29.30, 29.51, 29.55, 29.59, 29.76, 29.89, 29.97, 31.87 ($(\mathit{C}H_2)_7$-$CHSi$-$(\mathit{C}H_2)_8$), 34.01 ($\mathit{C}H_2CO$), 51.24 (OCH_3), 58.25 ($O\mathit{C}H_2CH_3$), 174.12 (CO). ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ = -46.87. IR (pure): ν = 1168 cm^{-1} (C-O-C), 1743 cm^{-1} (C=O). MS (EI): m/z (%) = 461 (3) [M$^+$], 430 (9) [M − (OCH_3)], 415 (13) [M − (EtOH)], 347 (21) [$(CH(Si(OEt)_3(CH_2)_8COOCH_3)^+$], 163 (100) [$Si(OEt)_3$]; Elemental analysis calc. for $C_{25}H_{52}O_5Si$ (460.36): C, 65.16; H, 11.38, found: C, 65.61; H, 11.51.

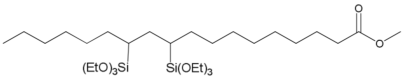
Synthesis of methyl 10,12-bis(trichlorosilyl)octadecanoate FA$_3$-Cl:



A mixture of methyl linoleate (3.00 g, 10.20 mmol) and trichlorosilane (8.29 g, 61.69 mmol) was heated in a Carius tube from 20 °C until 150 °C under RIS conditions for 72 h. Distillation of residue under reduced pressure yielded 4.30 g of FA$_3$-Cl. Yield: 75%. b.p. 196°C/ 0.03mm Hg. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.88 (t, ^3J (H,H) = 6.5 Hz, 3H, CH_3); 1.29-1.64 (m, 28H, $(C\mathit{H}_2)_5$-$C\mathit{H}Si$-$C\mathit{H}_2$-$C\mathit{H}Si$-$C\mathit{H}_2)_7$); 2.29 (t, ^3J (H,H) = 7.5 Hz, 2H, CH_2CO); 3.65 (s, 3H, OCH_3). ^{13}C NMR

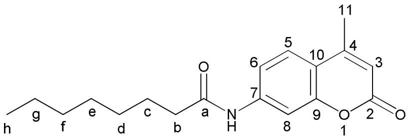
(75.48 MHz, $CDCl_3$): δ = 14.00 (CH_3), 22.25, 22.28, 25.00, 26.42, 27.00, 28.36, 28.52, 29.07, 29.33, 29.79, 30.43, 30.54, 31.11, 31.34, 31.72, 32.41 ($(CH_2)_5$-CHSi-CH_2-CHSi-$(CH_2)_7$), 33.32, 33.46 (CHSi), 34.00 (CH_2CO), 51.44 (OCH_3), 174.23 (CO). ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ = 13.78, 14.12. IR (pure): ν = 1175 cm^{-1} (C-O-C), 1740 cm^{-1} (C=O). MS (EI): m/z (%) = 562 (3) [M$^+$], 531 (5) [M − (OCH_3)], 429 (11) [M − ($SiCl_3$)], 231 (13) [(CH_3-$(CH_2)_4$-CH_2-$CHSiCl_3$)$^+$], 331 (4) [M − (CH_3-$(CH_2)_4$-CH_2-$CHSiCl_3$)], 245 (27) [(Cl_3SiCH- $(CH_2)_8$-$COOCH_3$)$^+$], 133 (100) [$SiCl_3$].

Synthesis of methyl 10,12-bis(triethoxysilyl)octadecanoate (SiFA$_3$):

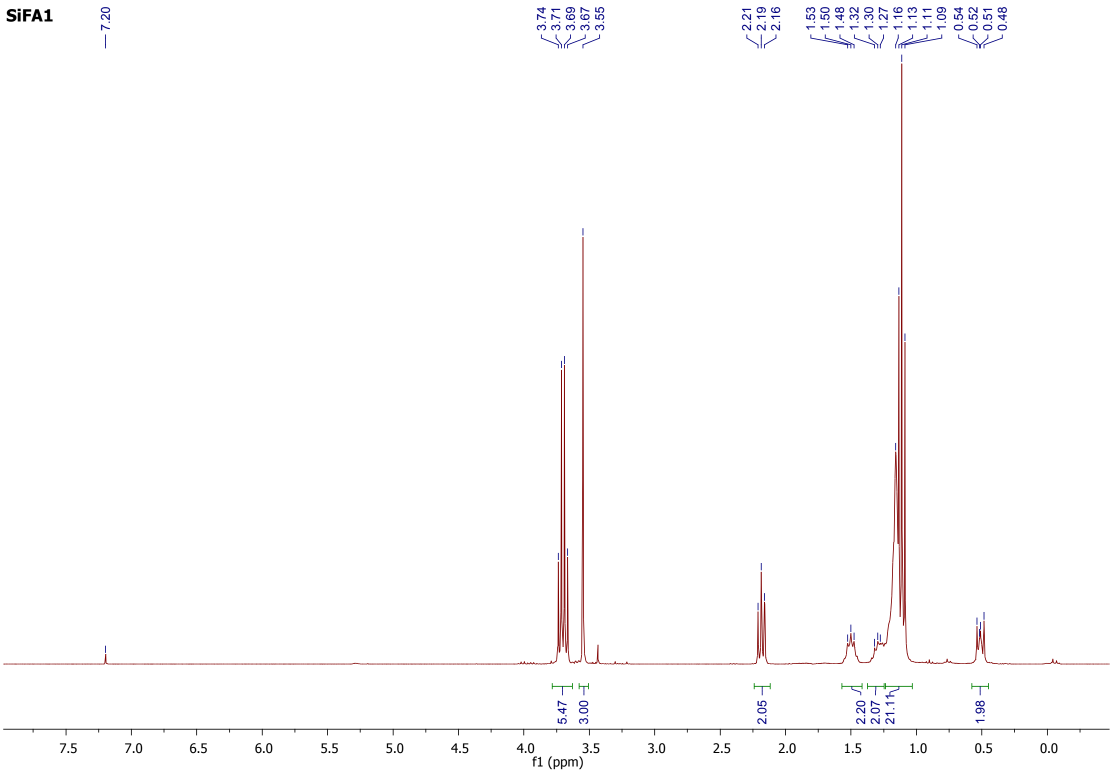


A solution of triethylamine (64 mL) in ethanol (26 mL) was added dropwise to a solution of methyl 10,12-bis(trichlorosilyl) octadecanoate FA$_3$-Cl (4.30 g, 7.65 mmol) in pentane (30 mL) at -40°C. The mixture was warmed to room temperature and stirred overnight. After filtration of the chlorhydrate, the solvent was removed and distillation under reduced pressure yielded 3.57 g of SiFA$_3$ as a colorless and viscous liquid. Yield 75%. b.p. 222°C/ 0.02 mmHg. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.87 (t, ^3J (H,H) = 6.5 Hz, 2H, CH_3); 1.22 (t, ^3J (H,H) = 6.8 Hz, 18H, OCH_2CH_3); 1.24-1.37 (m, 24H, $(CH_2)_5$-CHSi-CH_2-CHSi-$(CH_2)_6$)); 1.45-1.53 (m, 2H, CH_2-CH_2CO); 1.56-1.66 (m, 2H, CHSi); 2.31 (t, ^3J (H,H) = 7.4 Hz, 2H, CH_2CO); 3.67 (s, 3H, OCH_3); 3.83 (q, ^3J (H,H) = 7.0 Hz, 12H, OCH_2CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 14.20 (CH_3), 18.29 (OCH_2CH_3), 22.64, 22.72 (CHSi), 22.58, 22.97, 23.29, 24.95, 26.39, 27.91, 28.38, 28.69, 29.07, 29.15, 29.65, 29.99, 31.82, 31.89, 32.26 ($(CH_2)_5$-CHSi-CH_2-CHSi-$(CH_2)_7$), 34.08 (CH_2CO), 51.33 (OCH_3), 58.28 (OCH_2CH_3), 174.21 (CO). ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ = -48.07. IR (pure): ν = 1166 cm^{-1} (C-O-C), 1732 cm^{-1} (C=O). MS (EI): m/z (%) = 622 (10) [M$^+$], 576 (25) [M − (EtOH)], 563 (13) [M − ($COOCH_3$)], 459 (13) [M − $(SiOEt)_3$], 361 (14) [M − (CH_3-$(CH_2)_5$-$CHSi(OEt)_3$)], 275 (30) [M − ($CHSi(OEt)_3$-$(CH_2)_8$-$COOCH_3$)], 163 (100) [$Si(OEt)_3$].

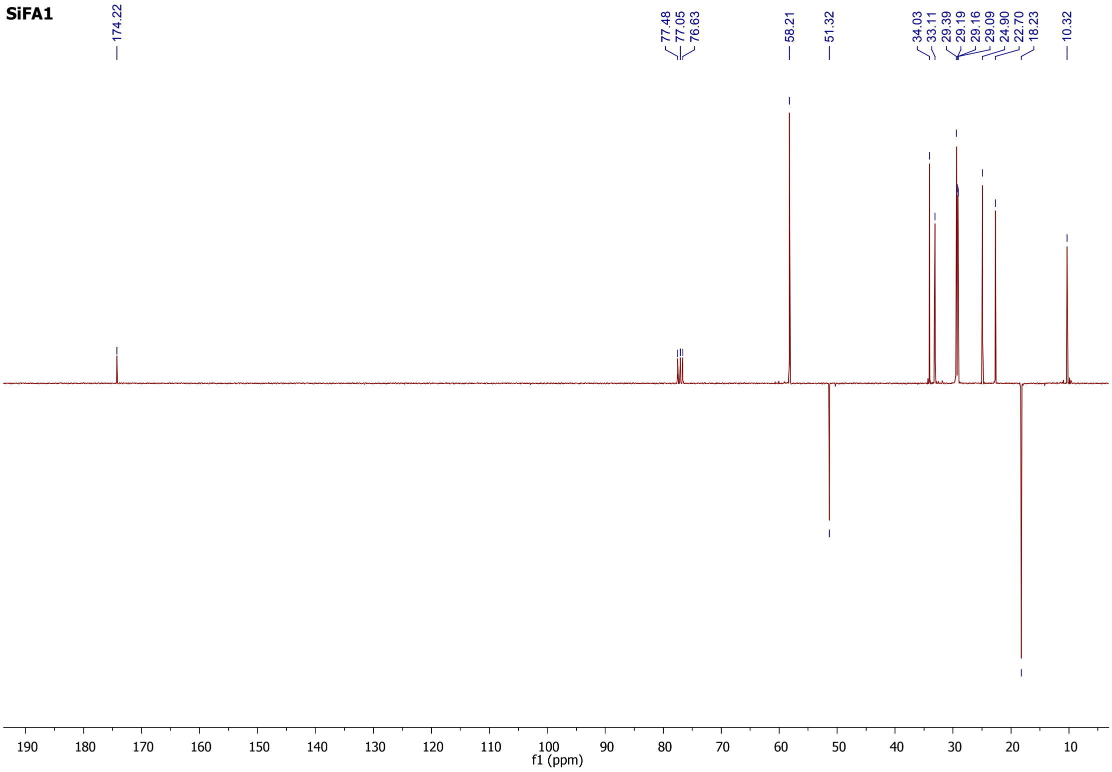
Synthesis of N-7(4-methylcoumarin)octanamide.



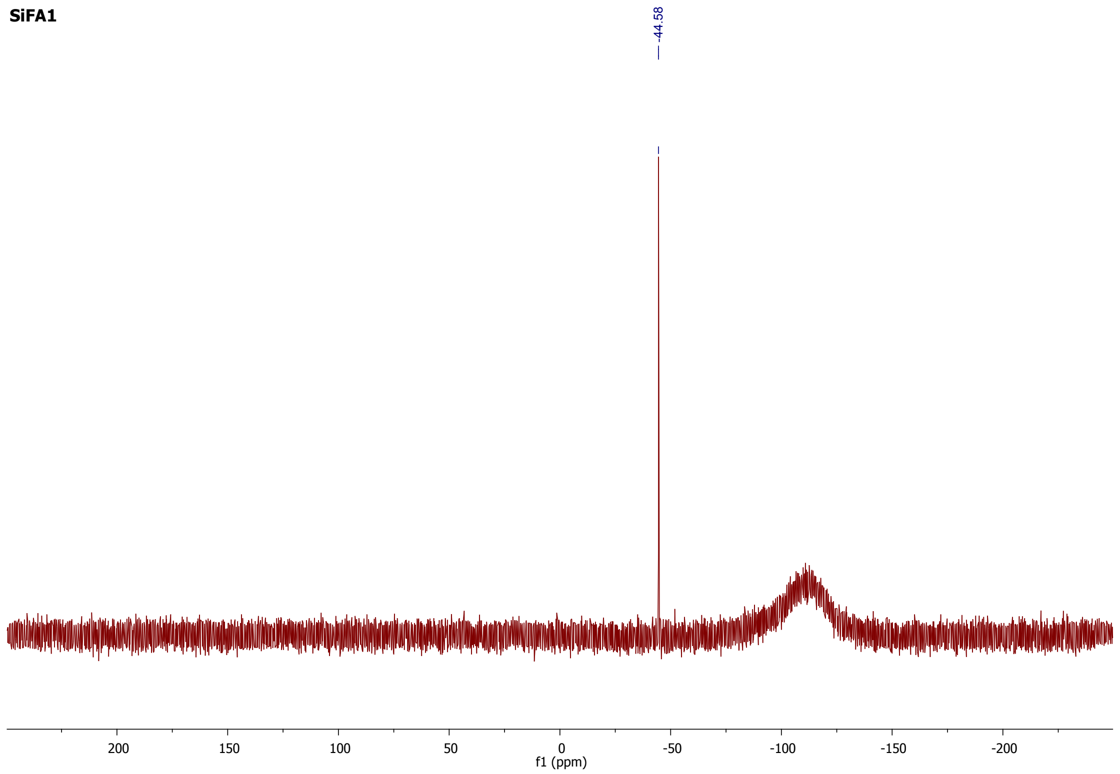
According to Selve et *al.*,[38] *N*-Methyl morpholine (0.25 g, 2.50 mmol) is added under argon to a solution of octanoïc acid (0.36 g, 2.50 mmol) in dimethyl formamide (DMF) (20 mL). After cooling the solution to -10 °C, a mixture of isopropenyl chloroformiate (0.30 g, 2.50 mmol) and 7-amino-4-methylcoumarin (0.44 g, 2.50 mmol) in DMF (5 mL) is introduced into the reaction vessel. The solution is then heated to 30 °C for 2 h. After evaporation of DMF under reduced pressure, the residue is dissolved into dichloromethane and washed successively with water, sodium carbonate solution, acidic solution and water. Then, the organic phase is dried with $MgSO_4$ and the solvent evaporated. The product is crystallised from a mixture of CH_2Cl_2/acetone. ^{13}C NMR (75.48 MHz, $CDCl_3$) δ: 13.0 (C_h), 17.5 (C_{11}), 21.6 (C_g), 24.5 (C_f), 28.0, 28.2 (C_d, C_e), 30.7 (C_c), 36.7 (C_b), 105.8 (C_8), 112.0 (C_3), 114.9 (C_6), 120.0 (C_{10}), 124.7 (C_5), 141.1 (C_7), 151.7 (C_9), 153.2 (C_4), 160.4 (C_2), 171.2 (C_a). IR (pure): ν = 1520 and 3413 cm^{-1} (NH), 1625 cm^{-1} (CO amide), 1724 cm^{-1} (CO lactone). MS (EI): m/z (%) = 301 [M$^+$], 175 (100) [M-(CH_3-$(CH_2)_6$-CONH].



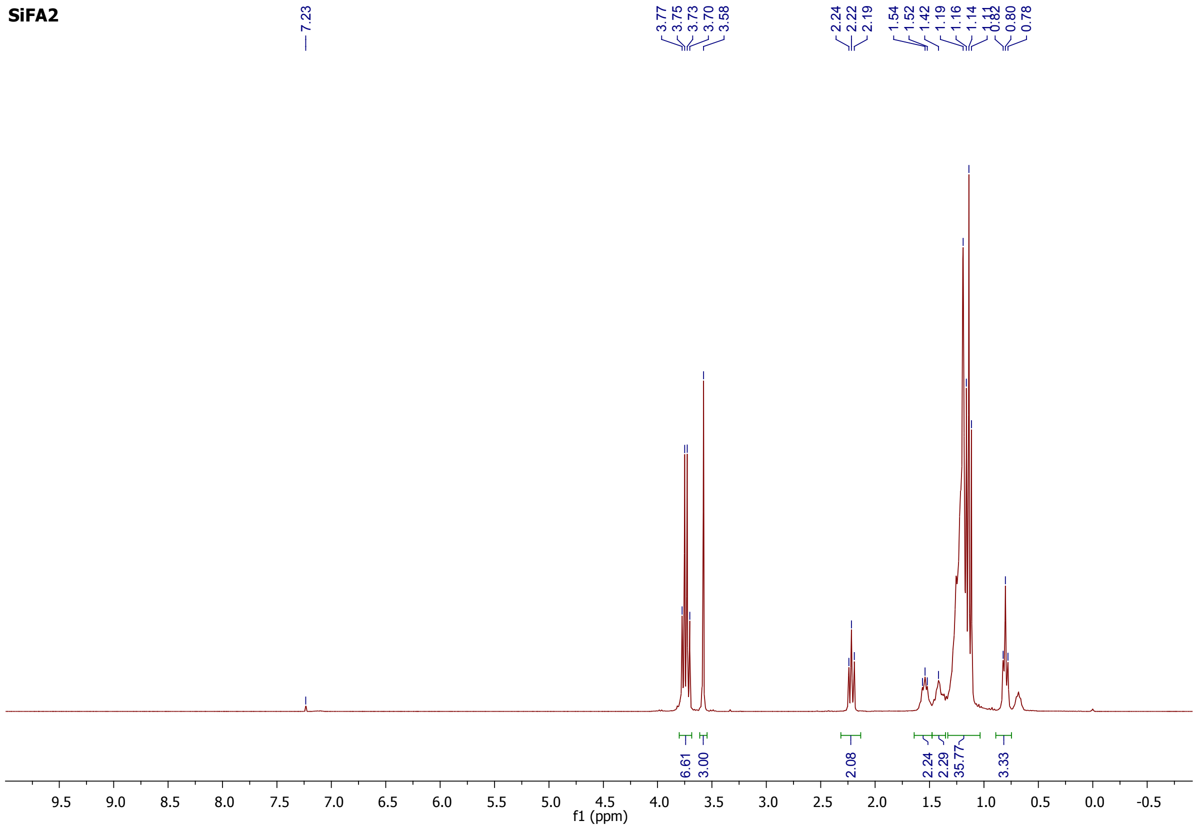
^{1}H NMR of SiFA$_1$



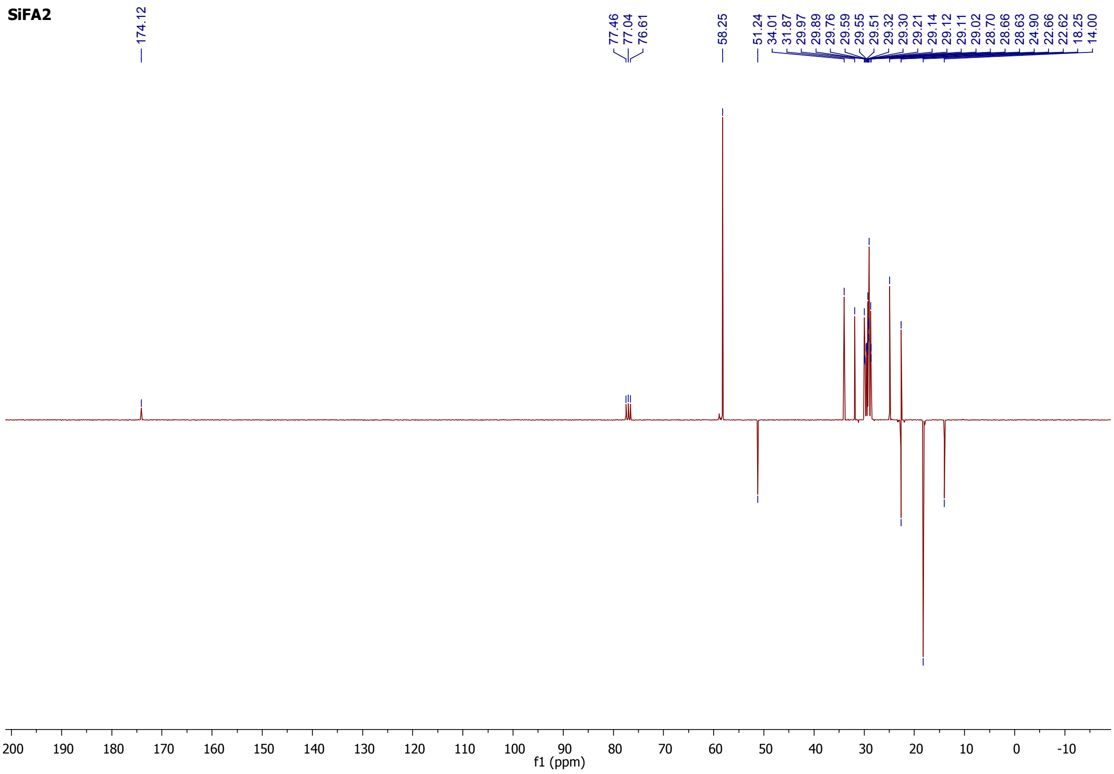
^{13}C NMR of SiFA$_1$



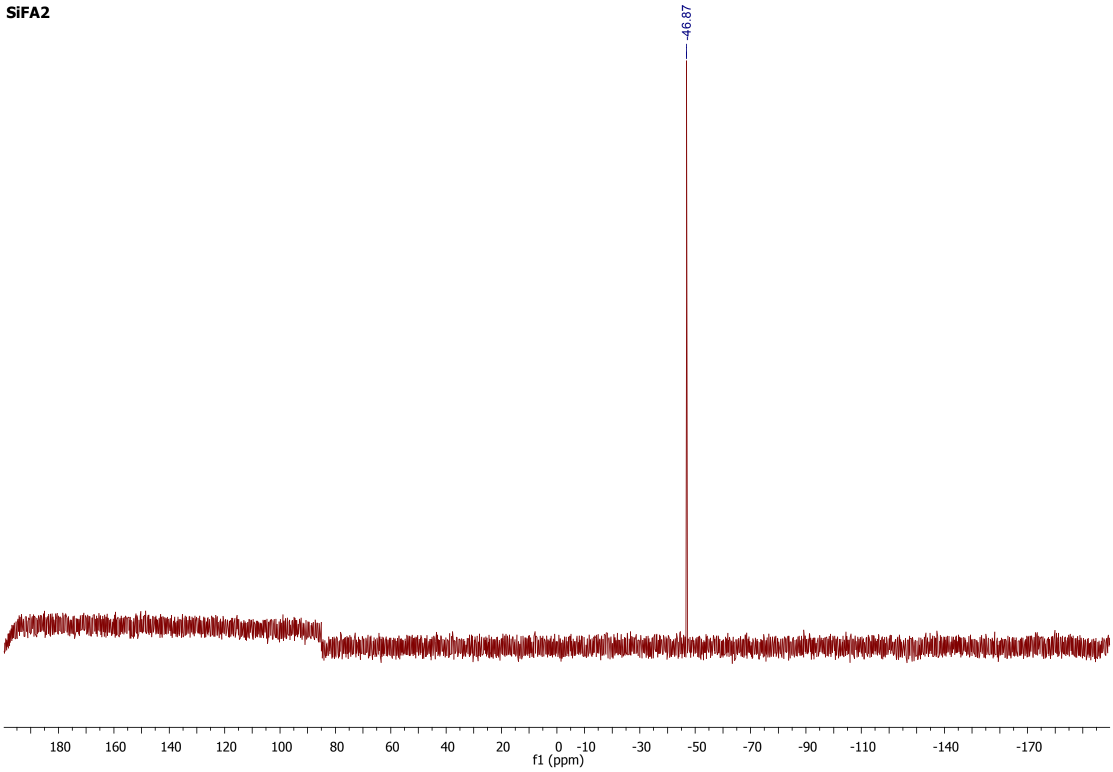
^{29}Si NMR of SiFA$_1$



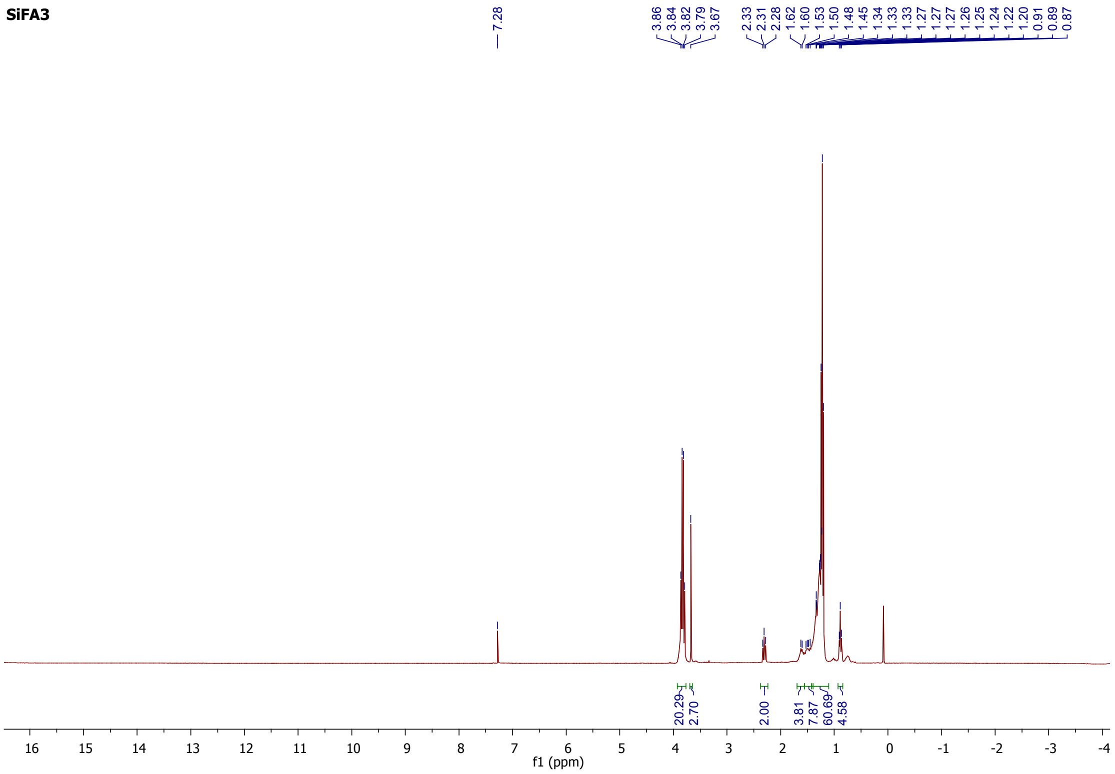
^{1}H NMR of SiFA$_2$



^{13}C NMR of SiFA$_2$



^{29}Si NMR of SiFA$_2$



^{1}H NMR of SiFA$_3$

S2 – Solid state ^{13}C NMR spectra of hybrid materials.

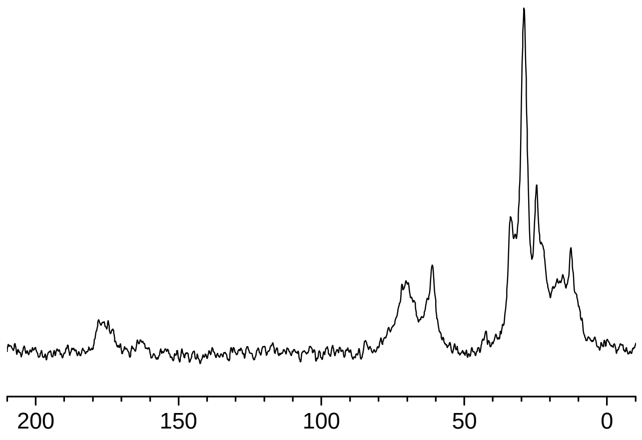


Figure S2a. CP MAS ^{13}C NMR of **SBA-FA$_1$**

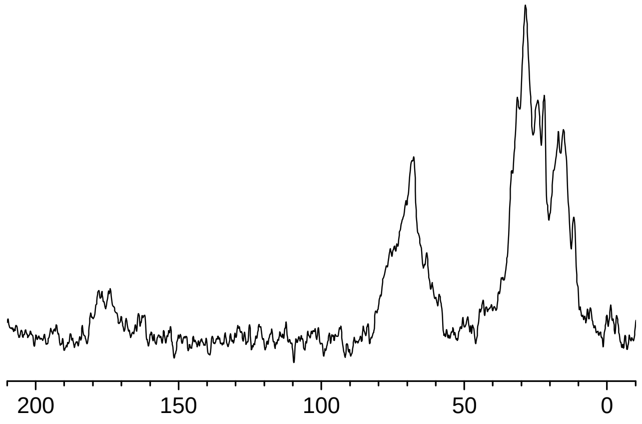


Figure S2b. CP MAS ^{13}C NMR of **SBA-FA$_3$**

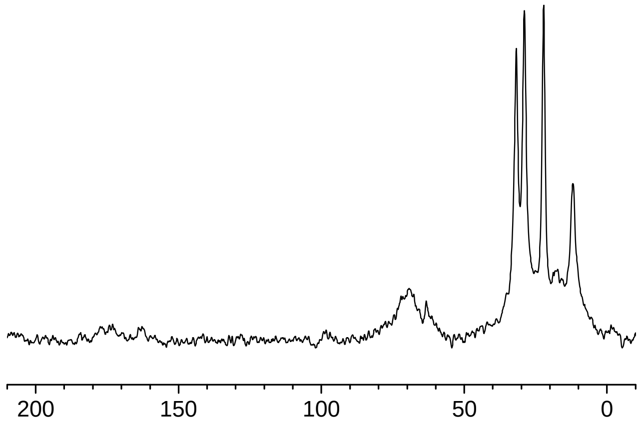


Figure S2c. CP MAS ^{13}C NMR of **SBA-FA$_0$**

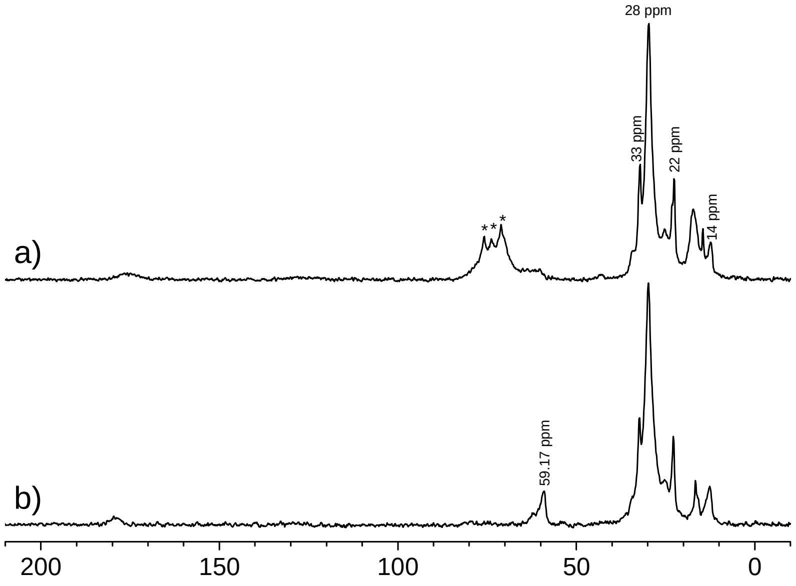


Figure S2d. ^{13}C CP-MAS spectra of a) **SBA-FA$_2$** and b) **MCM-FA$_2$**

S3 – Solid state ^{29}Si NMR spectra of hybrid materials and spectral decomposition

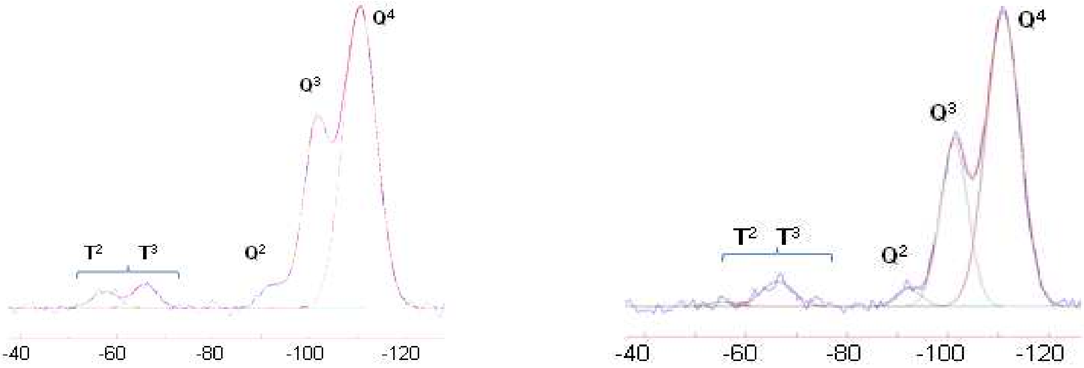
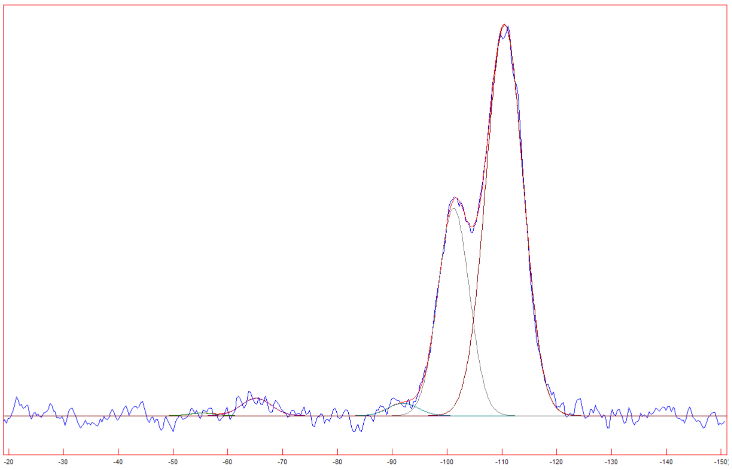


Figure S3c. ^{29}Si One Pulse MAS NMR spectra of materials **SBA-FA$_2$** (left) and **MCM-FA$_2$** (right).

SBA-FA$_1$
Nucleus : ^{29}Si. Peak Model : Gaussian



Fit results:

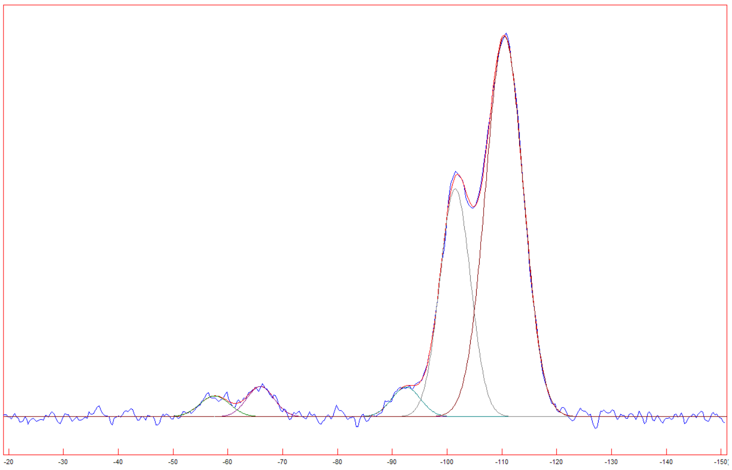
Peak	Amplitud	Position (ppm)	Width (ppm)
1	0.93	-55.28	5.45
2	6.19	-65.17	6.41
3	4.42	-91.96	6.46
4	73.35	-101.22	6.71
5	138.23	-110.49	7.98

Model Integration: sum of T-sites (0.31+2.38)%=2.69%

Peak	%
1	0.31
2	2.38
3	1.71
4	29.50
5	66.10

SBA-FA$_2$

Nucleus : ^{29}Si. Peak Model : Gaussian



Fit results:

Peak	Amplitutde	Position (ppm)	Width (ppm)
1	7.42	-57.59	6.45
2	10.78	-65.95	5.83
3	10.56	-92.52	6.17
4	81.34	-101.49	6.55
5	135.71	-110.47	8.08

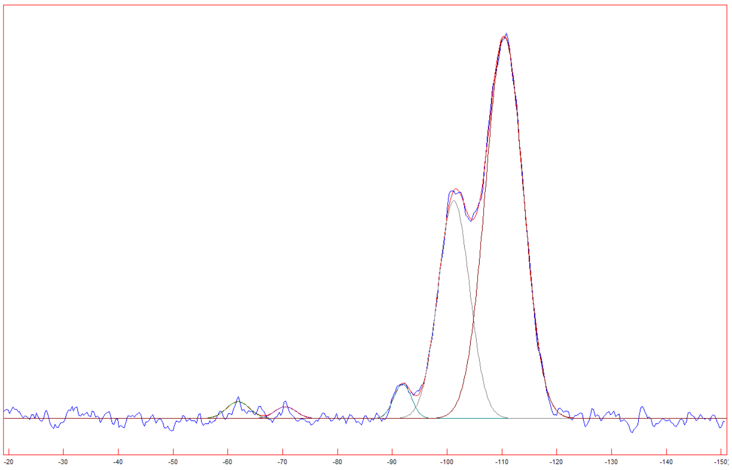
Model Integration :

sum of T-sites : (2.65+3.48)%= 6.13%

#	%
1	2.65
2	3.48
3	3.61
4	29.52
5	60.73

SBA-FA$_3$

Nucleus : ^{29}Si. Peak Model : Gaussian



Fit results:

Peak	Amplitutde	Position (ppm)	Width (ppm)
1	6.0	-61.87	5.0
2	4.26	-70.49	4.58
3	12.26	-91.89	3.81
4	77.69	-101.24	6.74
5	136.10	-110.45	8.08

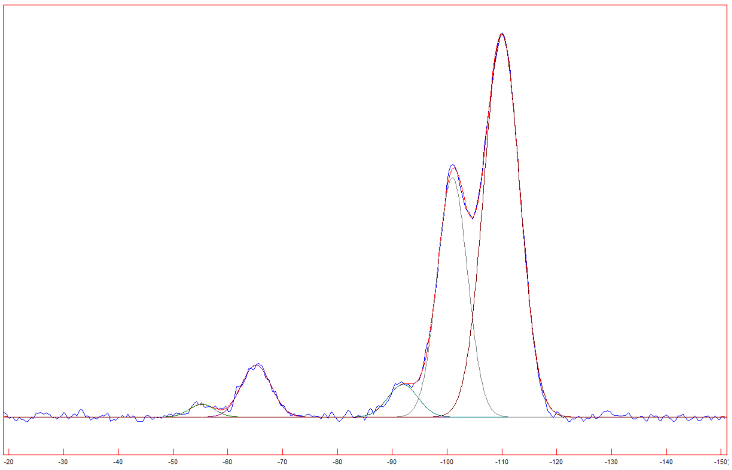
Model Integration :

sum of T-sites : (1.74+1.13)%= 2.87%

Peak	%
1	1.74
2	1.13
3	2.72
4	30.42
5	63.98

SBA-FA$_0$

Nucleus : ^{29}Si. Peak Model : Gaussian



Fit results:

Peak	Amplitutde	Position (ppm)	Width (ppm)
1	4.57	-55.28	5.45
2	18.56	-65.17	6.41
3	11.55	-91.96	6.46
4	85.42	-100.98	6.45
5	136.39	-109.98	7.70

Model Integration :

sum of T-sites : (1.37+6.54)%=7.91%

Peak	%
1	1.37
2	6.54
3	4.10
4	30.29
5	57.70

S4– Method of calculation of the fatty acid loading content.

1/ by elemental analysis.

Elemental analysis of the hybrid materials

Materials	Si %	C %
MCM-FA$_0$	34.10	8.70
MCM-FA$_1$	33.76	13.30
MCM-FA$_2$	33.32	13.91
MCM-FA$_3$	32.05	15.87
SBA-FA$_0$	34.91	13.79
SBA-FA$_1$	30.03	7.17
SBA-FA$_2$	28.02	22.81
SBA-FA$_3$	36.74	7.05

The chemical composition of each sample determined from its elemental analysis was calculated from the following equation taking into account the C% and Si% (elemental analysis data)

$$\mathbf{N\ (mmol.g\ SiO_2^{-1}) = C\%\ x\ 28\ /\ (Si\%\ x\ c\ x\ 60\ )\ x\ 10^3}$$

where c corresponds to the number of carbon in the anchored fatty acid molecule, 28 and 60 being the molar mass of Si and SiO_2 respectively.

For example for **SBA-FA$_2$**:

$$N\ (mmol.g_{SiO2}{}^{-1}) = 22.81x\ 28\ /\ (28.02\ x\ 12\ x\ 18\ x\ 60)\ 10^3 = 1.75$$

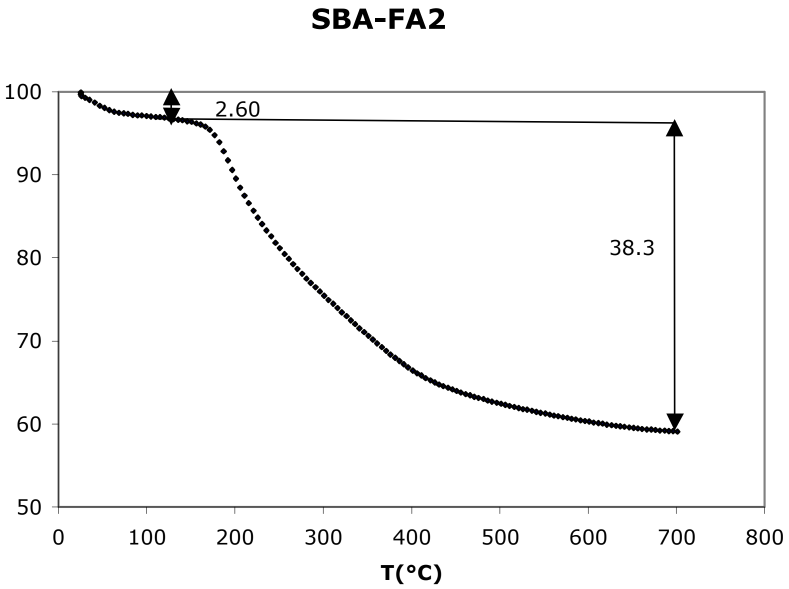
2/ by thermo-gravimetric analysis (TGA).

When the organic content was estimated from TGA measurements, decomposed weight / residual SiO_2 weight at 700 °C stems from organic amounts on silica corresponding to amount based on 1 g of pure silica. The formula used for this calculation was as follows:

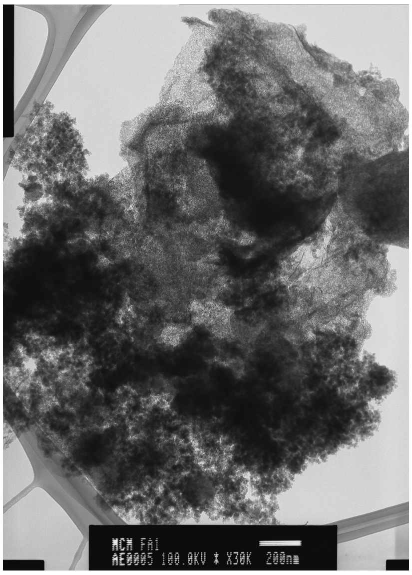
$$\mathbf{N\ (mmol.g\ SiO_2^{-1}) = (org\ wt\ \%\ /\ [100 - (org\ wt\ \%\ -\ H_2O\ wt\ \%)\ x\ (M_{SiFA} - 17n)])\ x\ 10^3}$$

where org wt % is the weight fraction of the organic part per SiO_2, 17n corresponds to the molecular mass loss during the oxidative thermal decomposition of the anchored organic moieties leading to an additional Si-OH mineral surface for each Si-C bond oxidized, n being the number of Si atom in the precursor.

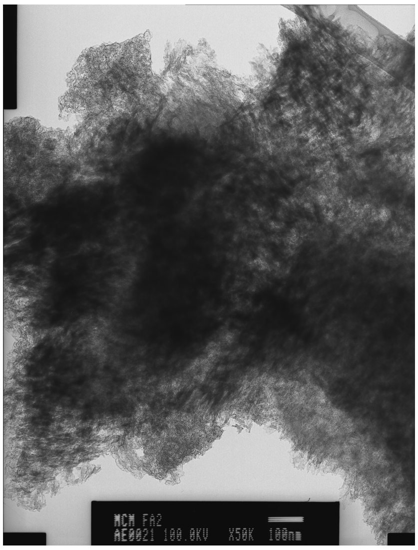
For example for **SBA-FA$_2$** : N (mmol.gSiO_2^{-1}) = (38.3 / [(100-38.3-2.60) x (283-17)]) x 10^3 = 2.44



S5 – Transmission electronic microscopy of hybrid MCM-41-type materials.



MCM-FA$_1$



MCM-FA$_2$

MCM-FA$_3$

S6 – DRIFT study.

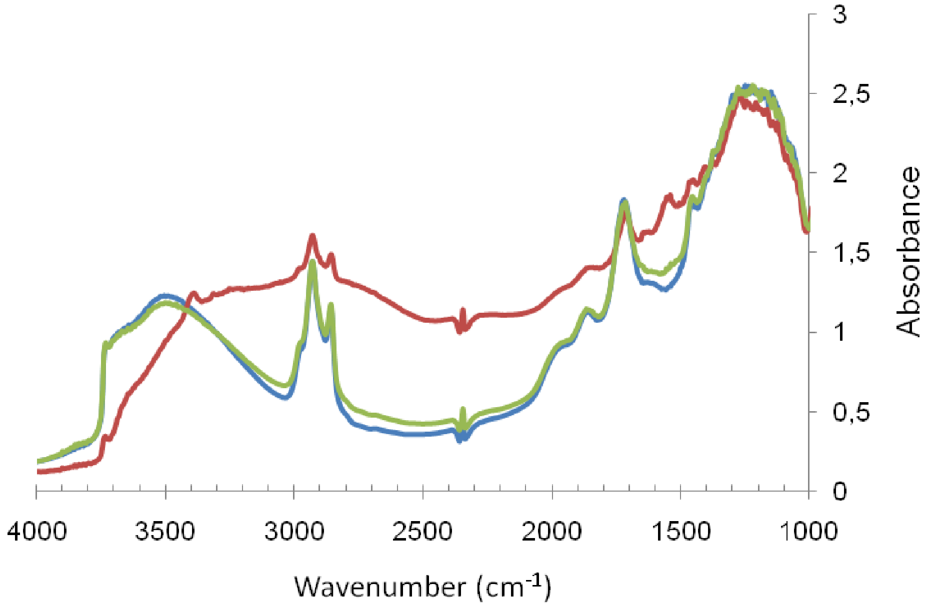


Figure S6a. DRIFT spectra of **SBA-FA$_1$** after heating at 120°C for 3h (—), after contacting with an NH$_3$ gas stream for 2h (—), and after purging under argon at 120°C for 30min (—).

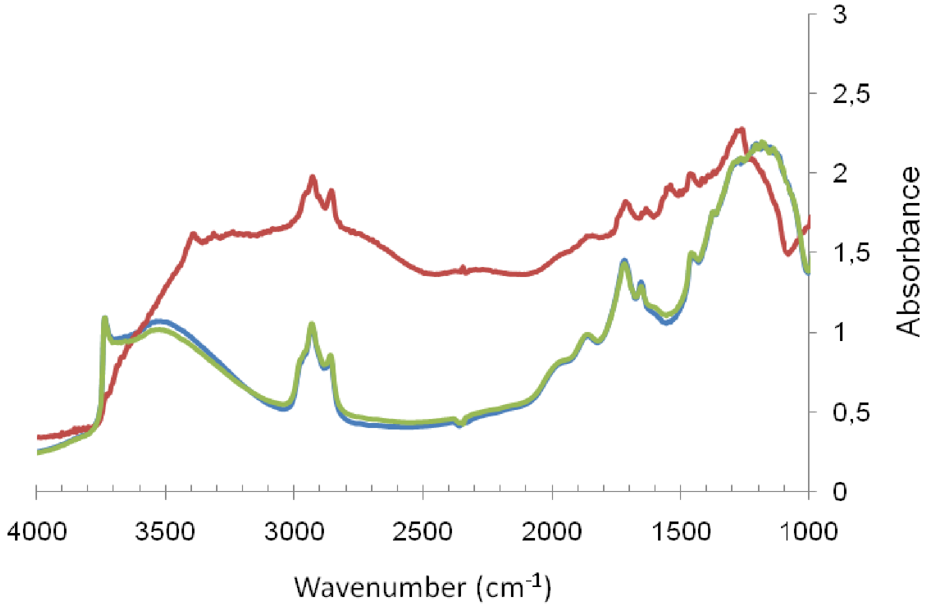


Figure S6b. DRIFT spectra of **SBA-FA$_3$** after heating at 120°C for 3h (—), after contacting with an NH$_3$ gas stream for 2h (—), and after purging under argon at 120°C for 30min (—).

S7- DRIFT of peptide coupling between carboxy-silicates and coumarine.

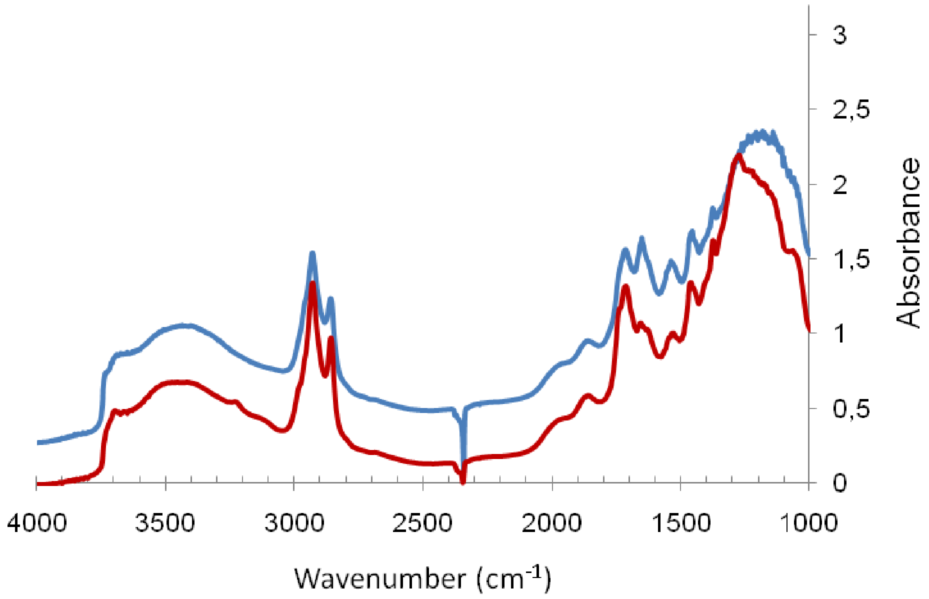


Figure S7. DRIFT spectra of **SBA-FA$_1$-amide** (—) and **MCM-FA$_1$-amide** (—) after heating at 120°C under an argon stream