Supporting Information

Postfunctionalization of periodic mesoporous silica SBA-1 with magnesium and iron(II) silylamides

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Synthesis Procedures

Materials.

SBA-1 1: C_{18}TEABr (5.70 g, 13.08 mmol), concentrated HCl (37 wt %, 362.9 g, 3.18 mol), and distilled water (598.5 g, 33.23 mol) were combined, and the resulting mixture was vigorously stirred until a homogeneous solution formed (ca. 30 minutes). The solution was cooled to 0 °C in an ice bath and 13.68 g (65.67 mmol) of TEOS was slowly added. Stirring was continued for 4 h at 0 °C, and then the reaction mixture was heated in a polypropylene bottle to 100 °C and maintained there for n hours without stirring (n =1; 6). The solid product was recovered by filtration (without washing) and dried at ambient temperature. The as-synthesized material was calcined at 540 °C (air, 5 h) and dehydrated in vacuo (270 °C, 10^{-4} Torr, 8 h). The molar composition of the synthesis gel was 1:5:280:3500 C_{18}TEABr:TEOS:HCl:H_2O.

Grafting Precursors.

$[Mg\{N(SiHMe_2)_2\}_2]_2$ (2). To a solution of 1.87 g $HN(SiHMe_2)_2$ (14.00 mmol) in 5 mL hexane a 1M $Mg(n\text{-}Bu)_2$ solution in heptane (7 ml, 7.00 mmol) was added slowly. The solution was stirred for 4 h at ambient temperature during which gas evolution was observed (*n*-butane). Afterwards, the solvent was removed in vaccuo. Two times subsequent crystallization in *n*-hexane at –35 °C yielded 1.80 g (6.23 mmol, 89% yield) colourless crystals of the pure compound. Analysis calculated for $C_8H_{28}N_2Si_4Mg$ (wt%): C, 33.25; H, 9.77; N, 9.69. Found: C, 33.64; H, 9.04; N, 9.51. DRIFT (KBr, KBr, cm^{-1}): 2953s, 2897w, 2078s, 2047s, 1781w, 1428w, 1410w, 1259s, 1247s, 1058s, 957s, 889s, 843s, 793s, 775s, 765s, 737w, 709w, 692w, 683w, 634w, 619w, 488m, 408w.

$[Mg\{N(SiMe_3)_2\}_2]_2$ (3). To a solution of 2.26 g $HN(SiMe_3)_2$ (14.00 mmol) in 5 mL hexane a 1M $Mg(n\text{-}Bu)_2$ solution in heptane (7 ml, 7.00 mmol) was added slowly. The solution was

stirred for 4 hours at ambient temperature during which gas evolution was observed (*n*-butane). Afterwards, the solvent was removed in vaccuo. Two times subsequent crystallization in *n*-hexane at -35°C yielded 2.11 g (6.11 mmol, 87% yield) colourless crystals of the pure compound. Analysis calculated for $C_{12}H_{36}N_2Si_4Mg$ (wt%): C, 41.77; H, 10.52; N, 7.04. Found: C, 41.51; H, 11.14; N, 7.77. DRIFT (KBr, KBr, cm^{-1}): 2946s, 2897m, 1462w, 1450w, 1429w, 1391w, 1316w, 1296w, 1251m, 1239s, 1184w, 1025m, 986s, 876s, 841s, 826s, 780m, 747m, 712w, 664m, 621w, 610m, 435w.

$[Fe^{II}\{N(SiHMe_2)_2\}_2]_2$ (5). A solution of 4.40 g $LiN(SiHMe_2)_2$ (31.56 mmol) in 5 mL THF was added slowly (highly exothermic reaction) to a milky solution of 2.04 g $FeCl_2$ (15.78 mmol) in 5 mL THF. The solution turned dark brown immediately. After one hour of stirring at ambient temperature, the solvent was removed. Centrifugation and three times washing of the remaining solid with *n*-hexane led to a dark green/black solution. The washing fractions were collected and *n*-hexane was removed. Extraction with *n*-hexane and two times subsequent crystallization in *n*-hexane at –35 °C yielded 3.06 g (9.56 mmol, 61% yield) green crystals of the pure compound. Analysis calculated for $C_8H_{28}N_2Si_4Fe$ (wt%): C, 29.98; H, 8.81; N, 8.74. Found: C, 29.49; H, 9.01; N, 8.46. DRIFT (KBr, KBr, cm^{-1}): 2949s, 2899m,2116s, 2083s, 1418w, 1250s, 1001m, 889s, 839s, 804m, 788m, 773m, 727w, 628w, 604w 472w.

Hybrid Materials.

$SiHMe_2$@SBA-1 (1a). Dehydrated SBA-1 (**1**) (100 mg) was suspended in 5 ml of *n*-hexane. Under stirring, 200 mg (1.50 mmol) of $HN(SiHMe_2)_2$ was added. The suspension was stirred for 18 h at ambient temperature and nonreacted silazane separated via combined *n*-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded the hybrid material (81 mg). Analysis found (wt%): C, 7.36; H, 1.90; N, 0.02.

Si(vinyl)Me$_2$@[Mg{N(SiHMe$_2$)$_2$}$_2$]$_2$@SBA-1 (1j). A suspension of 56 mg of the hybrid material **1i** in 5 ml *n*-hexane was prepared. Under stirring, 200 mg (1.08 mmol) of HN[Si(vinyl)Me$_2$]$_2$ was added. After stirring the suspension overnight at ambient temperature, nonreacted silazane was separated via combined *n*-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded a slightly yellowish hybrid material (65 mg). Analysis found (wt%): C, 8.99; H, 2.08; N, 0.19; Mg, n.d..

Si(vinyl)Me$_2$@SBA-1 (1k). A suspension of 96 mg of the SBA-1 material (**1**) in 5 ml *n*-hexane was prepared. Under stirring, 500 mg (2.70 mmol) of HN[Si(vinyl)Me$_2$]$_2$ was added. After stirring the suspension overnight at ambient temperature, nonreacted silazane was separated via combined *n*-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded a white hybrid material (80.7 mg). Analysis found (wt%): C, 12.65; H, 2.57; N, 0.01.

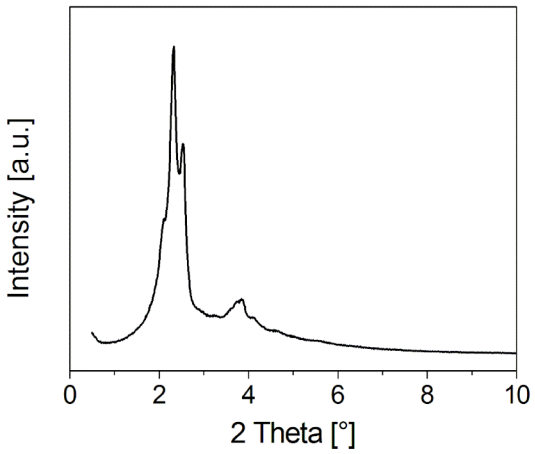

Figure S1. PXRD of SBA-1 **1**.

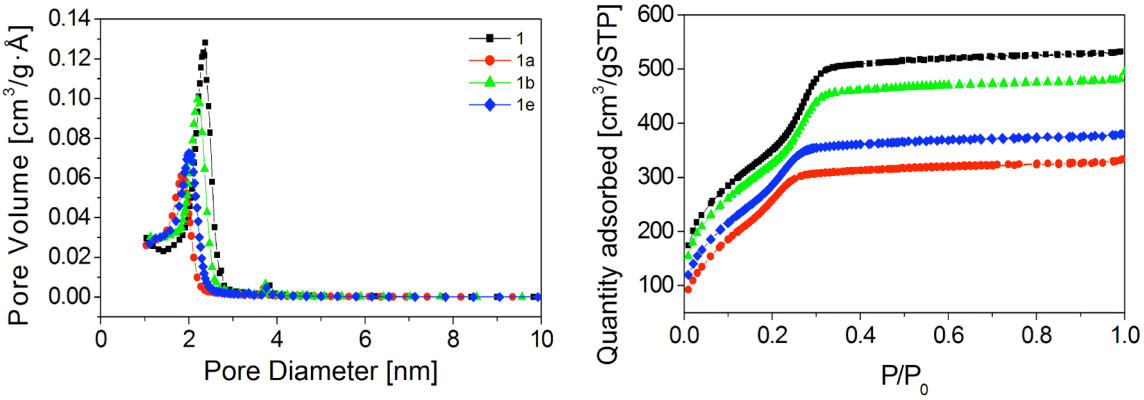

Figure S2. Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1b**) (□) after 18 h grafting and $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1e**) (□) after 4d grafting.

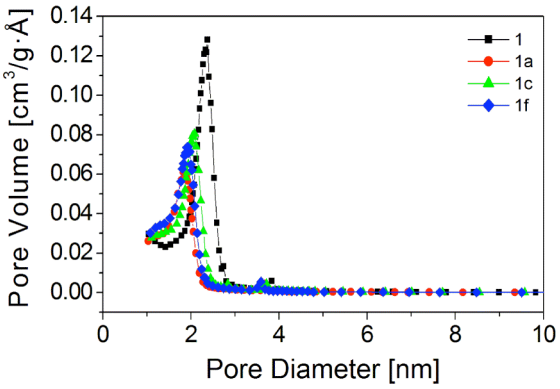

Figure S3. BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), $[Mg\{N(SiMe_3)_2\}_2]_2$@SBA-1 (**1c**) (□) after 18 h grafting and $[Mg\{N(SiMe_3)_2\}_2]_2$@SBA-1 (**1f**) (□) after 4 d grafting.

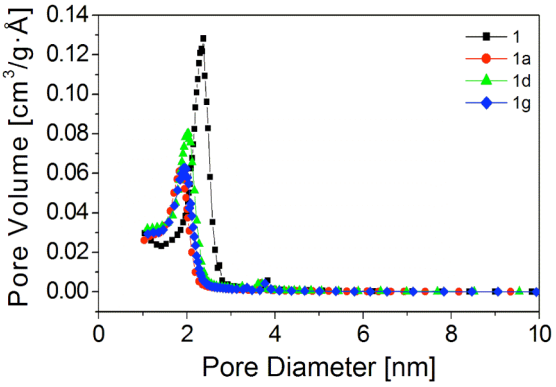

Figure S4. BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), $Mg[N(SiPhMe_2)_2]_2$@SBA-1 (**1d**) (□) after 18 h grafting and $Mg[N(SiPhMe_2)_2]_2$@SBA-1 (**1g**) (□) after 4 d grafting.

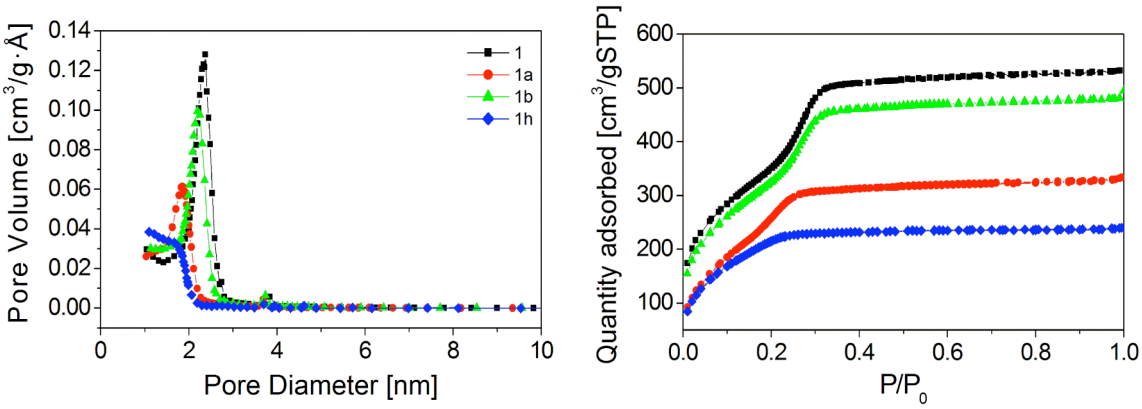

Figure S5. Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1b**) (□) after 18 h grafting and $[Fe^{II}\{N(SiHMe_2)_2\}_2]_2$@$[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1h**) (□) after 4 d grafting.

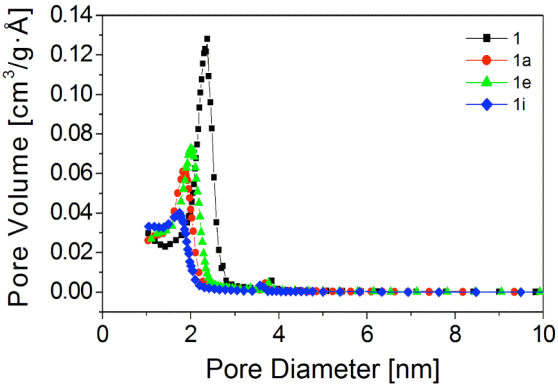

Figure S6. BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1e**) (□) after 4 d grafting and $[Fe^{II}\{N(SiHMe_2)_2\}_2]_2$@$[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1i**) (□) after 4 d grafting.

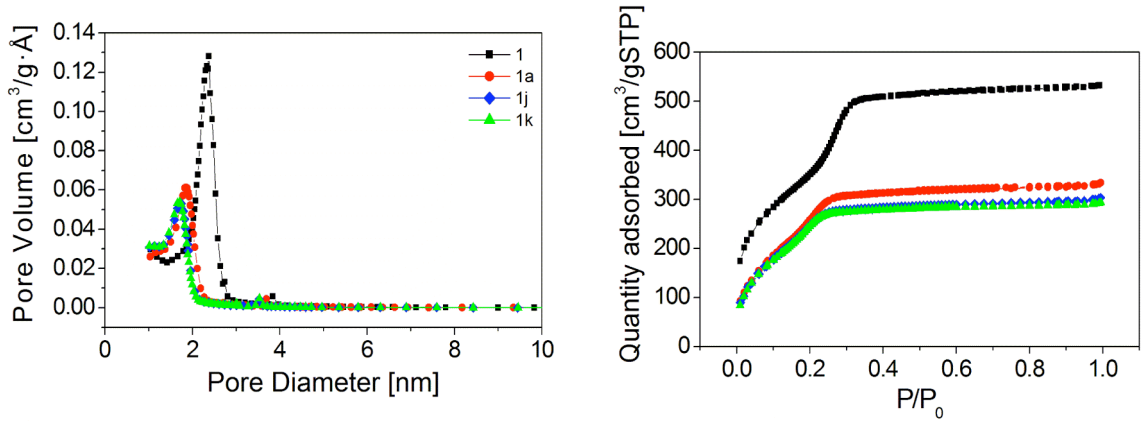

Figure S7. Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (**1**) (□), $SiHMe_2$@SBA-1 (**1a**) (□), Si(vinyl)Me_2@[$Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1j**) (□) and Si(vinyl)Me_2@SBA-1 (**1k**) (□).

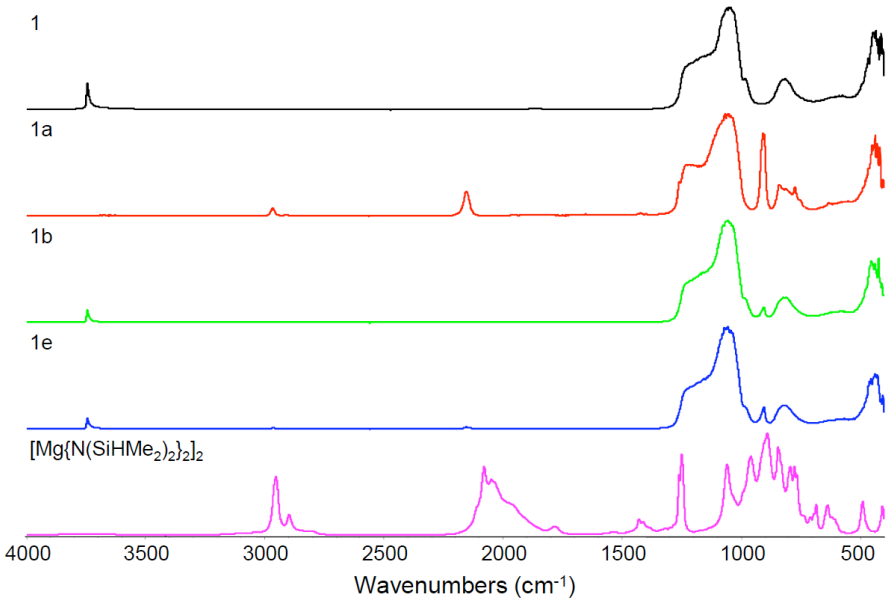

Figure S8. IR spectra (DRIFT) of mesoporous silica SBA-1 (**1**) and hybrid materials $SiHMe_2$@SBA-1 (**1a**), $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1b**) and $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1e**) and precursor $[Mg\{N(SiHMe_2)_2\}_2]_2$ (**2**) in the range of 400-4000 cm^{-1}.

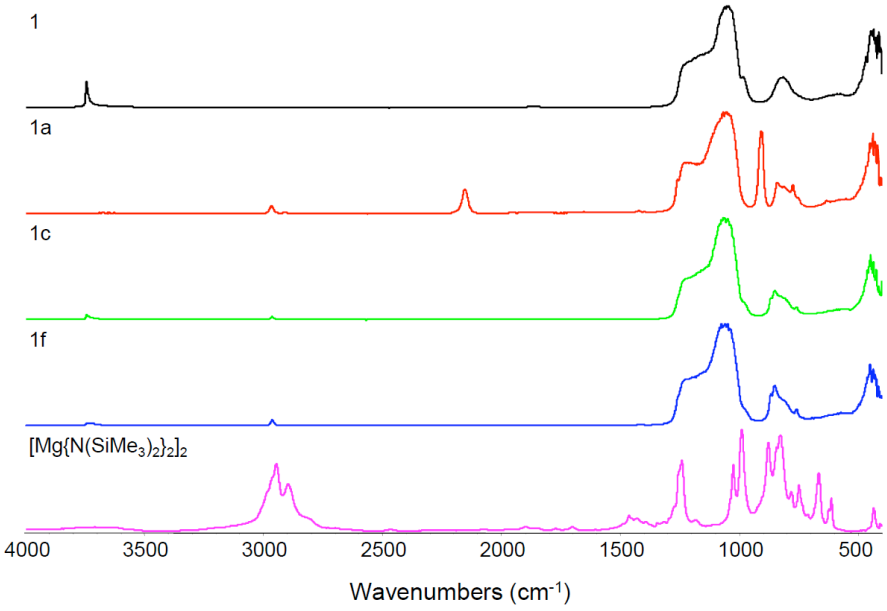

Figure S9. IR spectra (DRIFT) of mesoporous silica SBA-1 (**1**) and hybrid materials $SiHMe_2$@SBA-1 (**1a**), $[Mg\{N(SiMe_3)_2\}_2]_2$@SBA-1 (**1c**) and $[Mg\{N(SiHMe_2)_2\}_2]_2$@SBA-1 (**1f**) and precursor $[Mg\{N(SiMe_3)_2\}_2]_2$ (**3**) in the range of 400-4000 cm^{-1}.

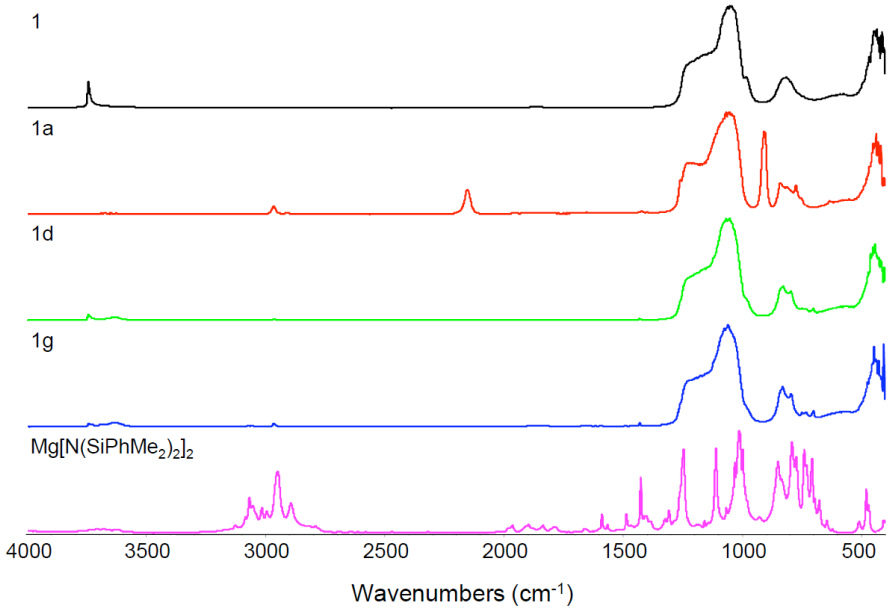

Figure S10. IR spectra (DRIFT) of mesoporous silica SBA-1 (**1**) and hybrid materials $SiHMe_2$@SBA-1 (**1a**), $Mg[N(SiPhMe_2)_2]_2$@SBA-1 (**1d**) and $Mg[N(SiPhMe_2)_2]_2$@SBA-1 (**1g**) and precursor $Mg[N(SiPhMe_2)_2]_2$ (**4**) in the range of 400-4000 cm^{-1}.

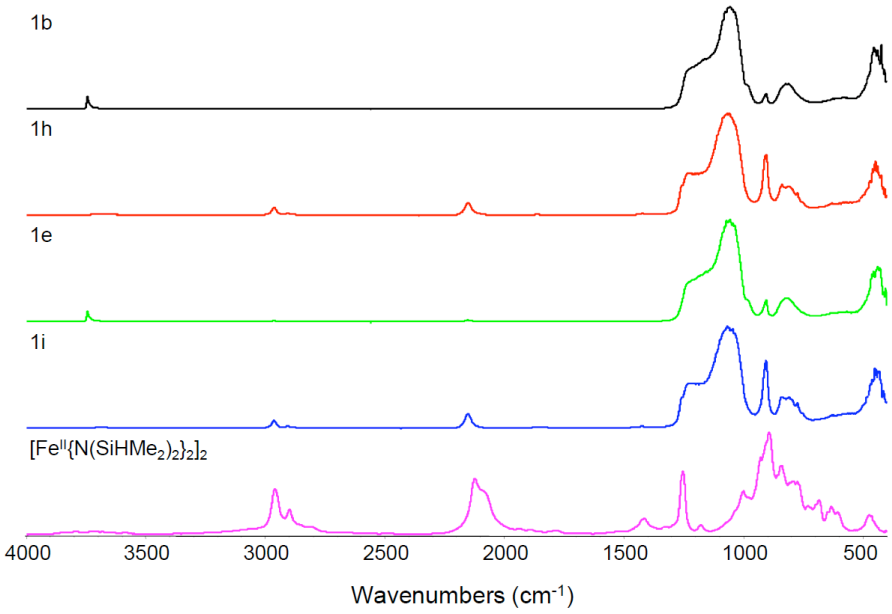

Figure S11. IR spectra (DRIFT) of mesoporous silica SBA-1 (**1**) and hybrid materials [Mg{N(SiHMe$_2$)$_2$}$_2$]$_2$@SBA-1 (**1b**), [Fe^{II}{N(SiHMe$_2$)$_2$}$_2$]$_2$@[Mg{N(SiHMe$_2$)$_2$}$_2$]$_2$@SBA-1 (**1h**), [Mg{N(SiHMe$_2$)$_2$}$_2$]$_2$@SBA-1 (**1e**) and [Fe^{II}{N(SiHMe$_2$)$_2$}$_2$]$_2$@[Mg{N(SiHMe$_2$)$_2$}$_2$]$_2$@SBA-1 (**1i**) and precursor [Fe^{II}{N(SiHMe$_2$)$_2$}$_2$]$_2$ (**5**) in the range of 400-4000 cm^{-1}.

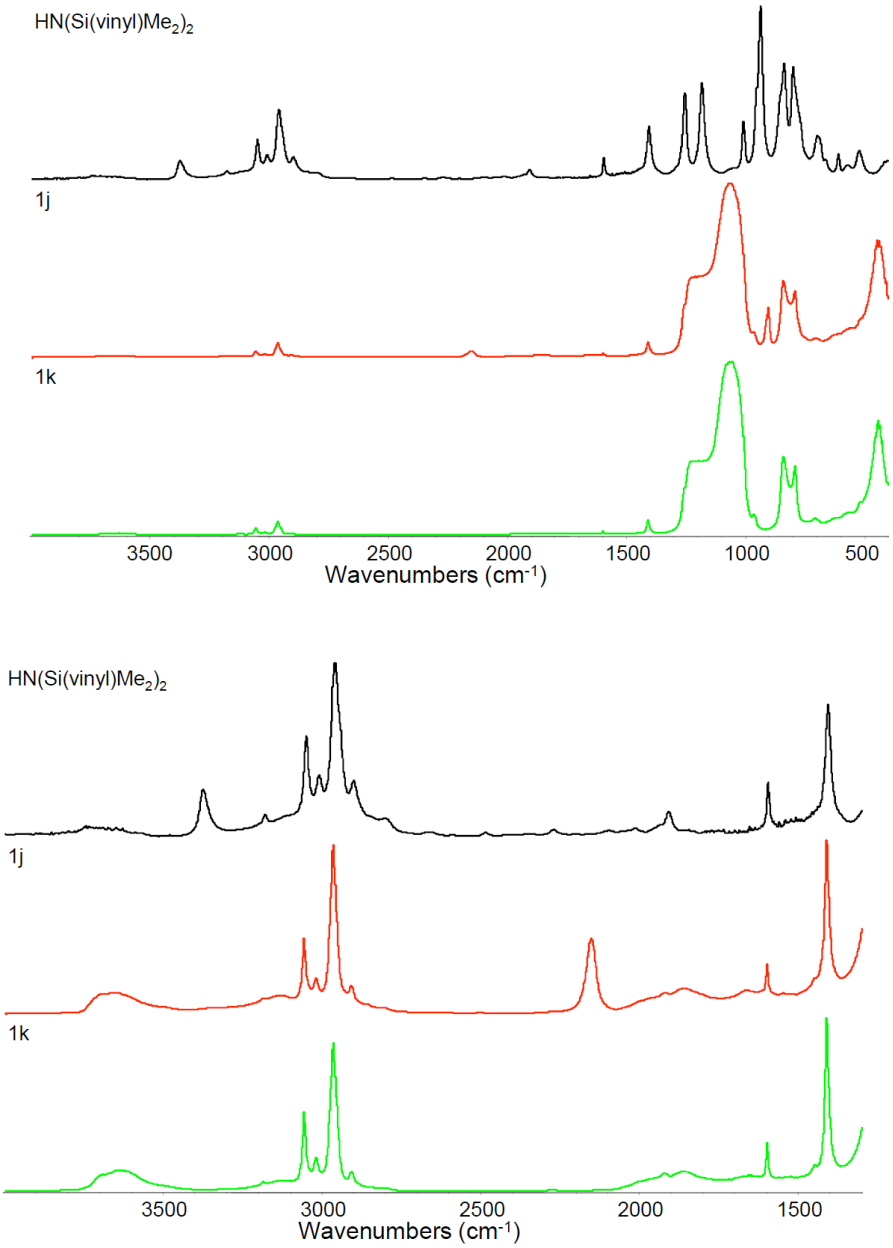

Figure S12. IR spectra (DRIFT) of the silazane HN[Si(vinyl)Me_2]$_2$ and the hybrid materials Si(vinyl)Me_2@[Mg{N(SiHMe_2)$_2$}$_2$]$_2$@SBA-1 (**1j**), Si(vinyl)Me_2@SBA-1 (**1k**).

Table S1. Analytical data of the vinyl-functionalized materials

	Sample/Precursor	a_S[m^2/g][a]	D_{me}[nm][b]	V_p[cm^3/g][c]	C [wt%][d]	N [wt%][d]
1	SBA-1 (a = 8.50 nm)	1320	4.5	0.82	-	-
1a	$SiHMe_2$@SBA-1	1110	4.2	0.51	6.61	0.11
1j	Si(vinyl)Me_2@Mg[$N(SiHMe_2)_2]_x$@SBA-1	960	4.2	0.46	8.99	0.19
1k	Si(vinyl)Me_2@SBA-1	950	4.2	0.45	12.65	0.01

[a] Specific BET surface area. [b] Pore diameter calculated according to Ravikovich and Neimark;[7] all samples were pretreated at 250 °C (parent materials), 100 °C (silylated samples) and 25 °C (grafted samples) respectively *in vacuo* until the pressure was $<10^{-3}$ Torr. [c] Pore volume determined at the relative pressure $p/p_0 = 0.975$. [d] Elemental analysis obtained after treatment at 100 °C *in vacuo* ($<10^{-3}$ Torr).