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Supporting Information

Ion-Conduction Pathways in Self-Organized Ureidoarene-Heteropolysiloxane Hybrid Membranes**

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Materials and methods

3-isocyanatopropyltriethoxysilane, aniline, 5-aminoindole, 4-aminophenol, p-anisidine and 4-aminobenzyl alcohol were purchased from Aldrich and used as received. All other reagents were obtained from commercial suppliers and used without further purification. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). ^{1}H and ^{13}C NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$ with the use of the residual solvent peak as reference. Solid state NMR was performed on a Brucker ASX400 spectrometer. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform 2+). Samples were dissolved in acetonitrile and were continuously introduced into the mass spectrometer at a flow rate of 10 mL/min through a Waters 616HPLC pump. The temperature (60°C), the extraction cone voltage (V_c=30V) was usually set to avoid fragmentations. X-ray powder diffraction measurements were performed with Cu-Ka radiation at 20°C using a Philips X'Pert Diffractometer equipped with a Xcelerator detector. SEM images were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5-30 kV.

General procedure for synthesis of compounds 1-5: **1-5** were prepared by adding 3-isocyanatopropyltriethoxysilane to corresponding amino derivative in chloroform and reaction was stirred and refluxed for 5 h. After removal of the solvent, the residue was subjected to purification by flash column chromatography on silica gel (eluent $CHCl_3$/MeOH 9:1) to give products **1,2,4,5** or recrystallization from hexane for **3**.

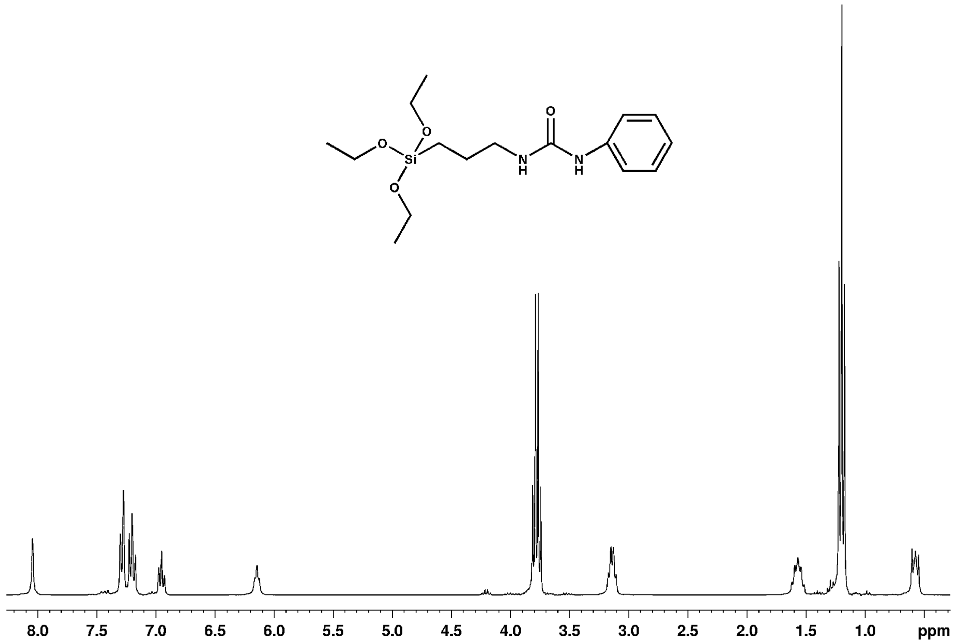
1-(3-(triethoxysilyl)propyl)-3-phenyl urea , 1: aniline (1.13 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added and the mixture was stirred and heated at 80° C for 5 h.Yield **1** (4.05 g , 11.9 mmol, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): *d* (ppm) = 0.57 (t, *J* = 8.4 Hz, 2H), 1.2 (t, *J* = 7.05Hz, 9H), 1,57 (m, *J* = 7.65 Hz, 2H), 3.14 (q, *J* = 6.6 Hz, 2H), 3.79 (q, *J* = 7 Hz, 6H), 6.14 (t, *J* = 5.25 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.95 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 8.04 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): *d* (ppm) = 8.1, 18.2, 23.6, 42.7, 58.2, 119.7, 122.6, 128.83, 139.4, 156.9. ^{29}Si NMR (59.6 MHz, $CDCl_3$) *d* (ppm) = -45.7; T^0 [C-Si-$(OR)_3$]; MS (ESI): m/z (%): 341.1 (30V) $[M+H]^+$; calcd. for $C_{18}H_{28}N_20_4Si$: C 56.44, H 8.29, N 8.23, O 18,80 ; found C 55.61, H 8.59, N 9.11, O 10.21.

1-(3-(triethoxysilyl)propyl)-3-(1H-indol-5-yl)urea, 2: 5-aminoindole (1.60 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added and the mixture was stirred and heated at 80° C for 5 h.Yield **2** (4.1 g , 10.8 mmol, 89 %).^{1}H RMN (300 MHz,$CDCl_3$) : *d* (ppm) = 0.61 (t, *J* = 8.4 Hz, 2 H), 1.22 (t, *J* = 7.1 Hz, 9H), 1.61 (m, *J* = 7.6 Hz, 2H), 3.24 (q, *J* = 6.6 Hz, 2H), 3.79 (q, *J* = 7 Hz, 6H), 4.80 (t, *J* = 5.2 Hz, 1H), 6.12 (t, *J* = 7.2 Hz, 1H), 6.56 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* =7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 8.32 (s, 1H).^{13}C RMN (75 MHz,$CDCl_3$): *d* (ppm) = 8.1, 18.2, 23.6, 42.7, 58.2, 102.2, 111.6, 115.4, 119.1, 125.6, 128.3, 130.2, 133.7, 158.1. ^{29}Si NMR (59.6 MHz,$CDCl_3$) *d* (ppm) = -45.1; T^0 [C-Si-$(OR)_3$]; MS (ESI): m/z (%): 379.19 (30V) $[M+H]^+$; calcd. for $C_{18}H_{29}N_30_4Si$: C 56.96, H 7.70, N 11.07, O 16.86 ; found C 56.47 , H 7.91 , N 12.31 , O 9.49 .

1-(3-(triethoxysilyl)propyl)-3-(4-hydroxyphenyl)urea, **3**: 4-aminophenol (1.32 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added and the mixture was stirred and heated at 80° C for 5 h.Yield **3** (4.1 g , 11.5 mmol, 95 %) .^{1}H RMN (300 MHz,$CDCl_3$) : *d* (ppm) = 0.52 (t, *J* = 8.1Hz, 2 H), 1.14 (t, *J* = 7.1 Hz , 9H), 1.47 (m, *J* = 7.8 Hz, 2H), 3.06 (q, *J* = 6.5 Hz, 2H), 3.72 (q, *J* = 5.9 Hz, 6H), 5.2 (t, *J* = 5.5 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 1H), 6.81 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.8-8 (s, 1H).^{13}C RMN (75 MHz,$CDCl_3$): *d* (ppm) = 7.5, 18.2, 23.5, 42.7, 58.5, 116.1, 125, 129.9, 154.1, 157.6 .^{29}Si NMR (59.6 MHz,$CDCl_3$) *d* (ppm) = -45.3 ; T^0 [C-Si-$(OR)_3$];MS (ESI): m/z (%): 357.2 (30V) $[M+H]^+$ .calcd. for $C_{16}H_{28}N_20_5Si$: C 53.91, H 7.92, N 7.86, O 22.44 ; found C 52.73, H 8.16, N 8.76, O 14.57.

1-(3-(triethoxysilyl)propyl)-3-(4-methoxyphenyl)urea, 4: p-anisidine (1.49 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added and the mixture was stirred and heated at 80° C for 5 h.Yield **4** (4.17 g , 11.3 mmol, 93 %) ^{1}H RMN (300 MHz,$CDCl_3$) : *d* (ppm) = 0.57 (t, *J* = 8.2Hz, 2 H), 1.19 (t, *J* = 7.1 Hz, 9H), 1.58 (m, *J* = 7.7 Hz, 2H), 3.14 (q, *J* = 6.6 Hz, 2H), 3.7 (s,1H), 3.77 (q, *J* = 5.9 Hz,6H), 5.65 (t, *J* = 5.7 Hz,1H), 6.76 (d, *J* = 4.5 Hz,2H), 7.14 (d, *J*= 4.5 Hz,2H), 7.4 (s, 1H).^{13}C RMN (75 MHz,$CDCl_3$): *d* (ppm) = 8.1, 18.2, 23.6, 42.7, 55.4, 58 .4, 114.2, 122.6, 132.1, 156, 157.4.^{29}Si NMR (59.6 MHz,$CDCl_3$) *d* (ppm) = -45.2 ; T^0 [C-Si-$(OR)_3$];MS (ESI): m/z (%): 371.22 (30V) $[M+H]^+$ .calcd. for $C_{17}H_{30}N_20_5Si$: C 55.11 , H 8.16, N 7.56, O 21.59; found C 54.89, H 8.26, N 8.34, O 13.94 .

1-(3-(triethoxysilyl)propyl)-3-(4-hydroxymethyl)phenyl)urea, 5: 4-aminobenzyl alcohol (1.49 g, 12.1 mmol) was dissolved in $CHCl_3$ and 3-isocyanatopropyltriethoxysilane (3 g, 12.1 mmol) was slowly added and the mixture was stirred and heated at 80° C for 5 h.Yield **5** (3.5 g , 9.5 mmol, 78%).^{1}H RMN (300 MHz,$CDCl_3$) : *d* (ppm) = 0.54 (t, *J* = 8.4Hz, 2 H), 1.16 (t, *J* = 6.9 Hz, 9H), 1.49 (m, *J* = 7.65 Hz, 2H), 3.08 (q, *J* = 6.5 Hz, 2H), 3.75 (q, *J* = 7 Hz, 6H), 4.1 (s , 1H), 4.42 (s, 2H), 5.90 (t, *J* = 5.4 Hz, 1H), 7.06 (t, *J* = 9.3 Hz, 4H), 7.79 (s, 1H).^{13}C RMN (75 MHz,$CDCl_3$): *d* (ppm) = 7.6, 18.2, 23.2, 42.6, 58.4, 64.3, 120.3, 127.7, 135.1, 138.5, 156.7 .^{29}Si NMR (300 MHz,$CDCl_3$) *d* (ppm) = -45.5 ; T^0 [C-Si-$(OR)_3$] MS (ESI): m/z (%): 371.22 (30V) $[M+H]^+$ .calcd. for $C_{17}H_{30}N_20_5Si$: C 55.11, H 8.16, N 7.56, O 21.59 ; found C 55.5, H 8.08, N 7.08, O 13.87 .



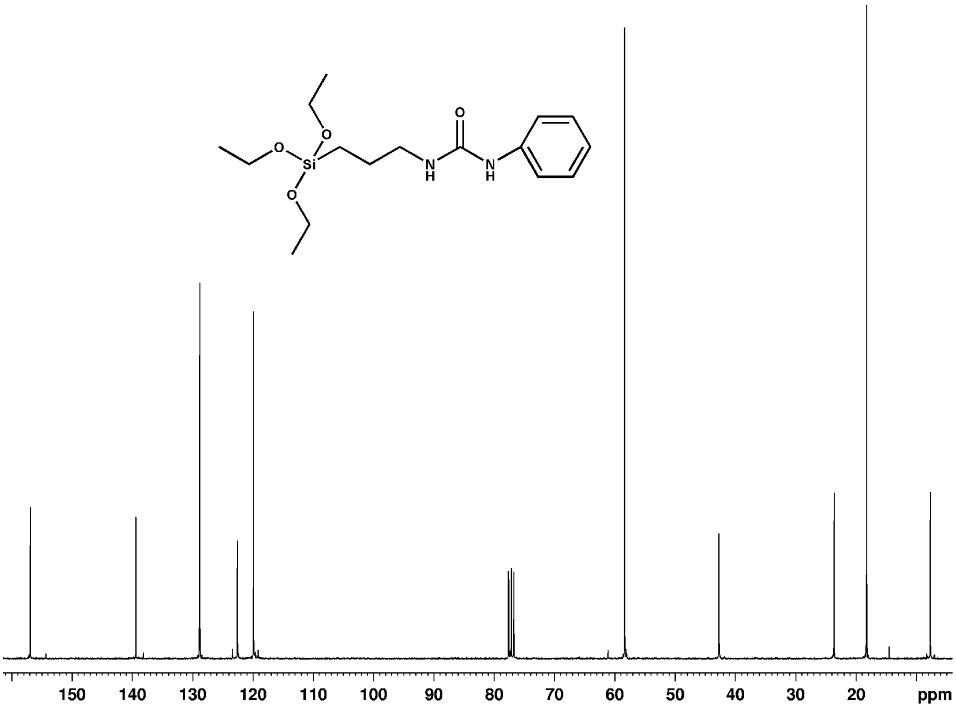
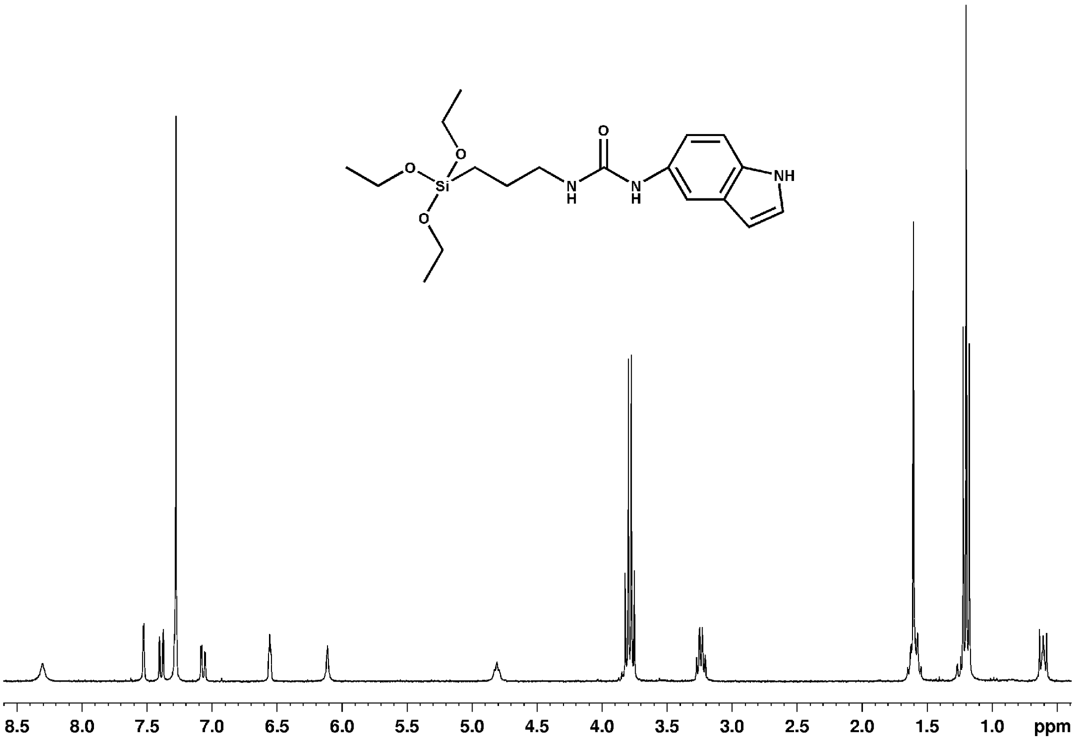


Figure 1Sa. ^{1}H NMR(300MHz, $CDCl_3$) and ^{13}C NMR(75 MHz,$CDCl_3$) of compound **1**



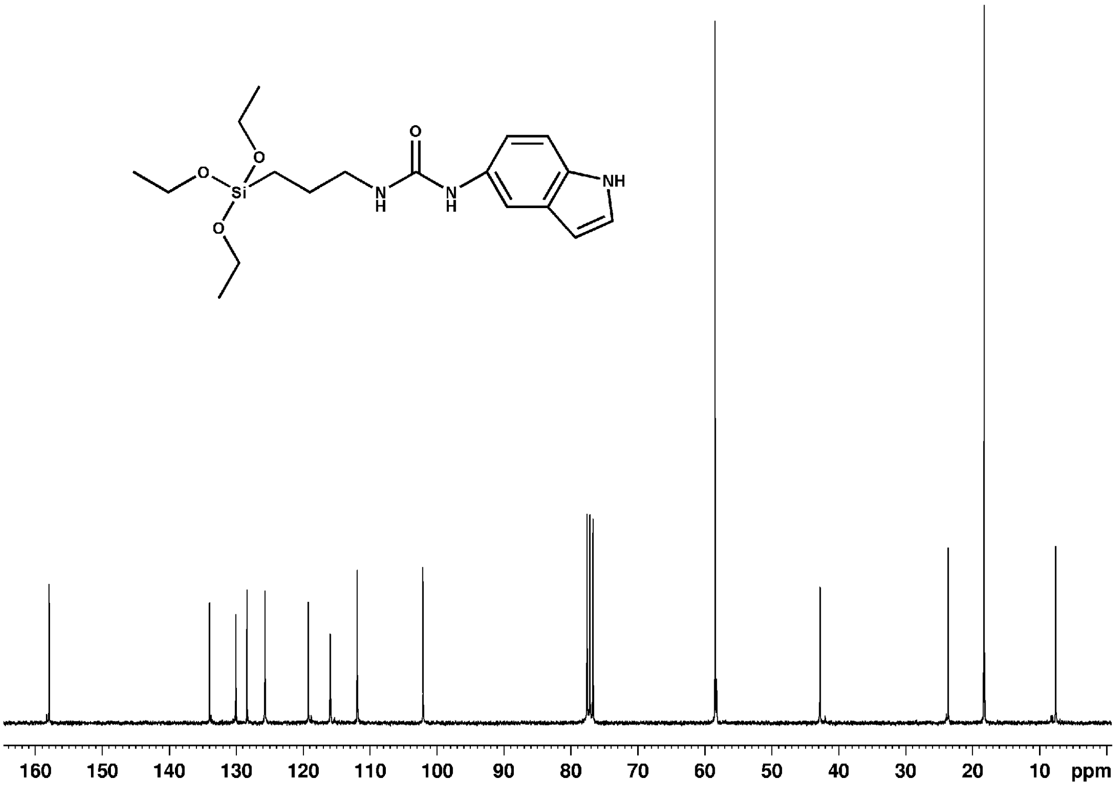
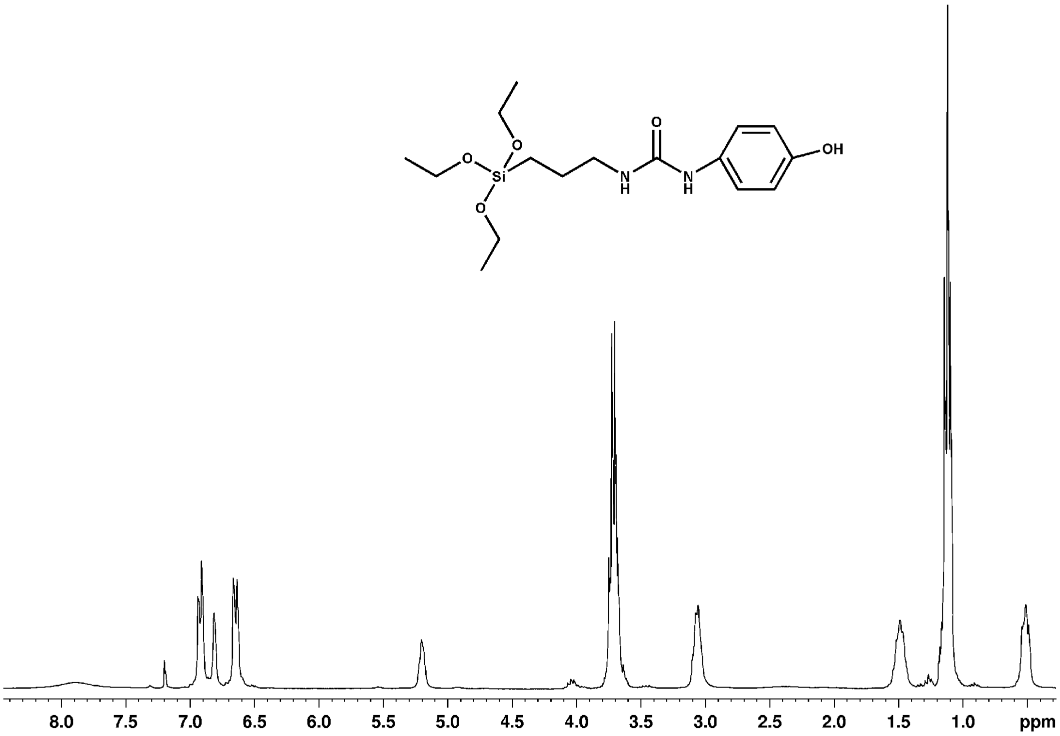


Figure 1Sb. ^{1}H NMR(300MHz, CDCl$_3$) and ^{13}C NMR(75 MHz,CDCl$_3$) of compound **2**



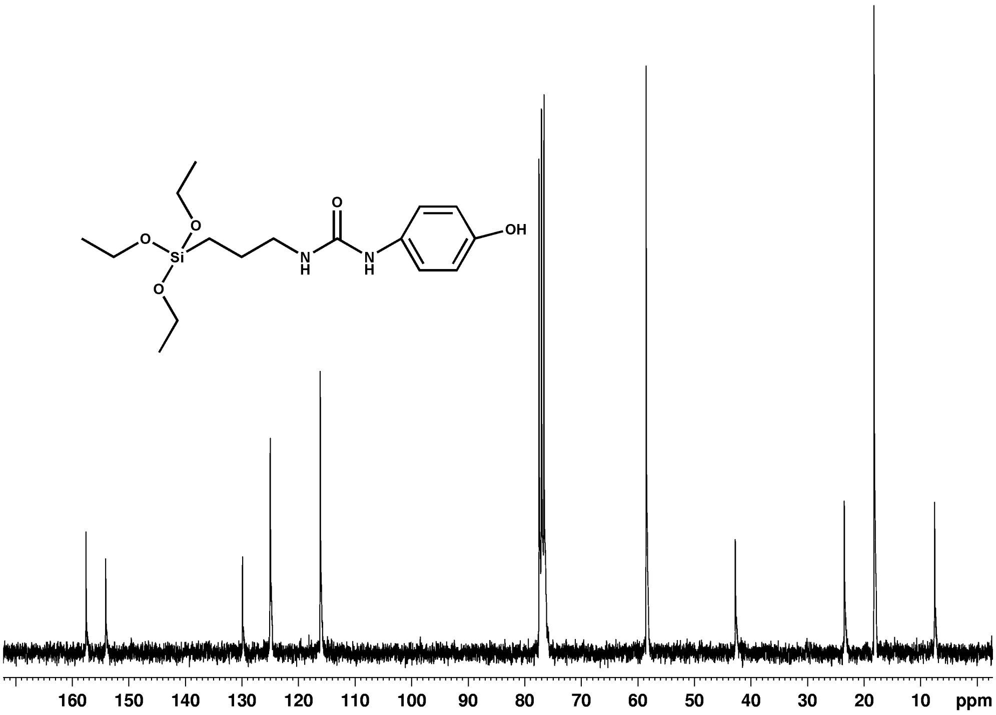
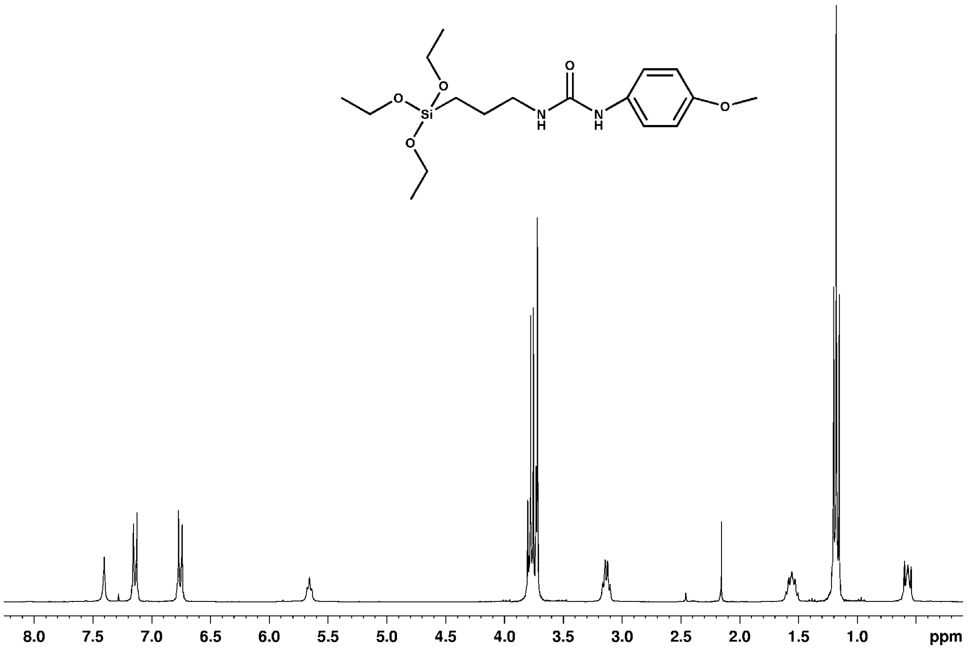


Figure 1Sc ^{1}H NMR(300MHz, $CDCl_3$) and ^{13}C NMR(75 MHz,$CDCl_3$) of compound **3**



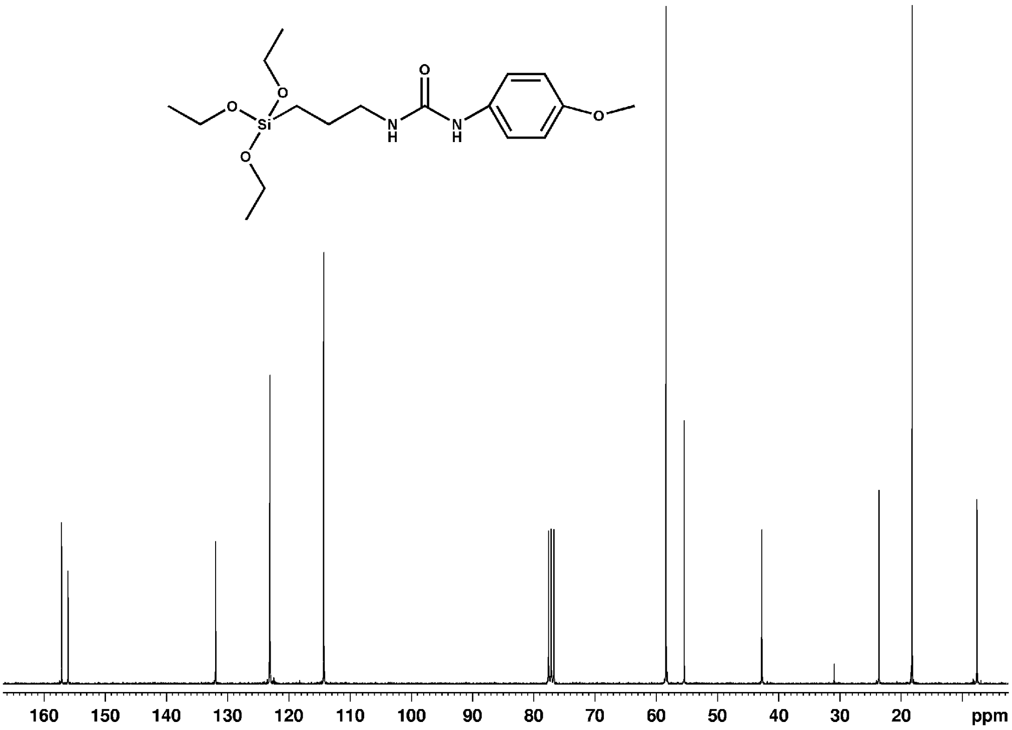
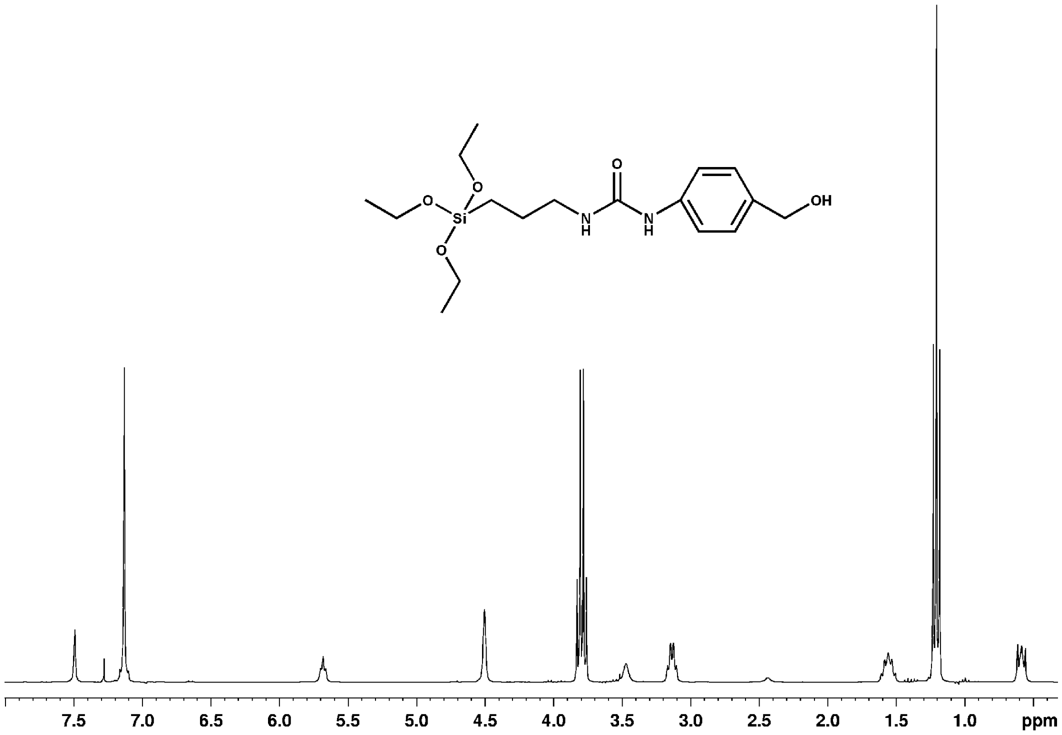


Figure 1Sd.^{1}H NMR(300MHz, CDCl$_3$) and ^{13}C NMR(75 MHz,CDCl$_3$) of compound **4**



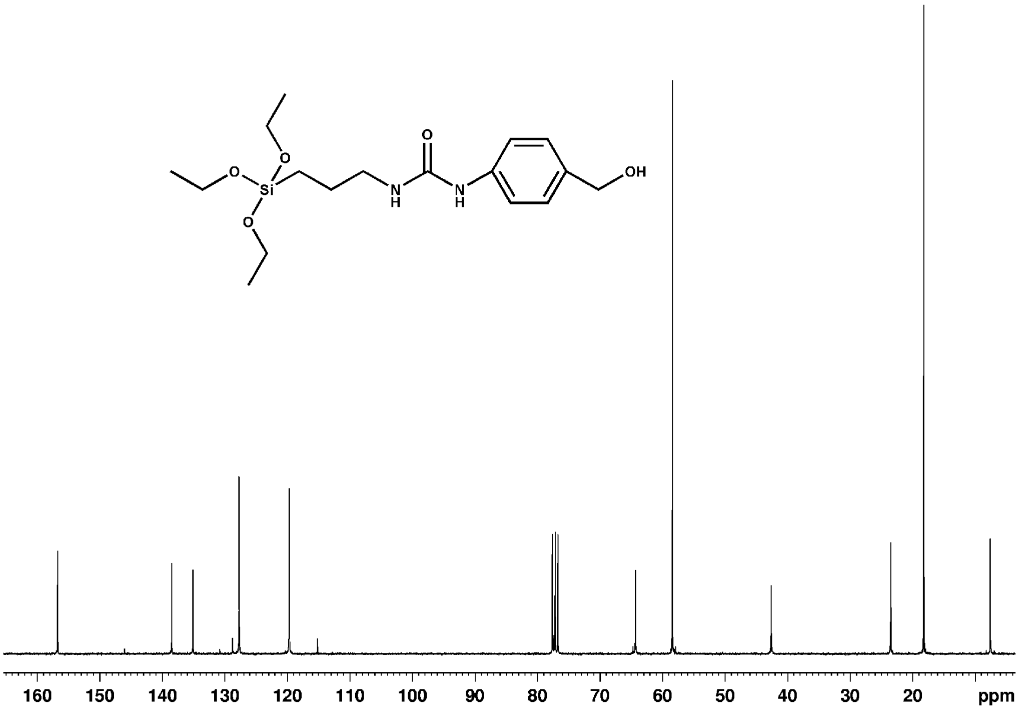


Figure 1Se. ^{1}H NMR(300MHz, CDCl$_3$) and ^{13}C NMR(75 MHz,CDCl$_3$) of compound **5**

X-ray Single Crystal Diffraction Data: Crystals suitable for X-ray structure determination were obtained after a few days in acetone (C=0.1 g/ml) at -10 °C. The diffraction intensities for **1-5** were collected at the joint X-ray Scattering Service of the Institut Charles Gerhardt and the Institut Européen des Membranes of the University of Montpellier II, France, at 175 K using an Oxford Diffraction Xcalibur-I and a Gemini-S diffractometer. The crystal-to-detector distance was 50 mm for all five measurements. The structures were solved by direct methods using SIR2002[1s] or by ab-initio (charge-flipping) methods using SUPERFLIP[2s] and refined by least-squares methods on F using CRYSTALS.[3s] Only very poor crystals could be obtained and so that in a number of cases restraints were used to optimise the geometries of especially Oeth groups and to stabilise the refinements. CCDC 636357-636361 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

1, $C_{17}H_{28}N_2O_4Si$, crystal dimensions: 0.06x0.16x0.25mm, cell dimensions: *a*=9.032(2)Å, *b*=8.933(2)Å, *c*=23.900(5)Å, *a*=90°, *b*=93.99(2)°, *g*=90°, V=1923.6(7)Å^3, monoclinic, space group $P2_1/n$, Z=4, ρ_{calcd}=1.176 gcm^{-3}, μ=0.142 mm^{-1}. 35919 measured reflections, 6376 unique, 401 with $I>2\sigma(I)$. Final *R* factors R_1=0.0676 and wR_2=0.0654; 98 parameters, 4 restraints, maximal residual electron density is 0.38 eÅ^{-3}.

2, $C_{16}H_{28}N_2O_5Si$, crystal dimensions: 0.10x0.17x0.40mm, cell dimensions: *a*=16.9710(10)Å, *b*=9.0970(10)Å, *c*=25.877(3)Å, *a*=90°, *b*=105.780(10)°, *g*=90°, V=3844.5(7)Å^3, monoclinic, space group $P2_1/n$, Z=8, ρ_{calcd}=1.230 gcm^{-3}, μ=0.148 mm^{-1}. 70975 measured reflections, 12735 unique, 1308 with $I>2\sigma(I)$. Final *R* factors R_1=0.1099 and wR_2=0.0827; 203 parameters, 4 restraints, maximal residual electron density is 0.60 eÅ^{-3}.

3, $C_{17}H_{30}N_2O_5Si$, crystal dimensions: 0.23x0.35x0.50mm, cell dimensions: *a*=9.0280(10)Å, *b*=13.589(2)Å, *c*=16.989(2)Å, *a*=90°, *b*=90°, *g*=90°, V=2084.2(5) Å^3, orthorhombic, space group $P2_12_12_1$, Z=4, ρ_{calcd}=1.181 gcm^{-3}, μ=0.139 mm^{-1}. 40018 measured reflections, 6849 unique, 1867 with $I>2\sigma(I)$. Final *R* factors R_1=0.0685 and wR_2=0.0681; 227 parameters, maximal residual electron density is -0.260 eÅ^{-3}.

4, $C_{18}H_{29}N_3O_4Si$, crystal dimensions: 0.12x0.15x0.30mm, cell dimensions: *a*=11.2494(5)Å, *b*=9.2335(4)Å, *c*=19.5030(10)Å, *a*=90°, *b*=90.731(5)°, *g*=90°, V=2025.64(16) Å^3, monoclinic, space group $P2_1/c$, Z=4, ρ_{calcd}=1.244 gcm^{-3}, μ=0.143 mm^{-1}. 26344 measured reflections, 6657 unique, 1197 with $I>2\sigma(I)$. Final *R* factors R_1=0.1190 and wR_2=0.0834; 114 parameters, 11 restraints, maximal residual electron density is 0.760 eÅ^{-3}.

5, $C_{17}H_{30}N_2O_5Si$, crystal dimensions: 0.10x0.50x0.50mm, cell dimensions: *a*=8.9840(10)Å, *b*=14.0600(10)Å, *c*=16.022(2)Å, *a*=90°, *b*=90°, *g*=90°, V=2023.8(4) Å^3, orthorhombic, space group $P2_12_12_1$, Z=4, ρ_{calcd}=1.216 gcm^{-3}, μ=0.143 mm^{-1}. 39138 measured reflections, 3829 unique, 1089 with $I>2\sigma(I)$. Final *R* factors R_1=0.0800 and wR_2=0.0532; 110 parameters, , maximal residual electron density is -0.540 eÅ^{-3}

[1S] M. C. Burla, M. B. Camalli, G. L. Carrozzini, R. Cascarano, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, **2003**, *36*, 1103.

[2S] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D.J. Watkin, *J. Appl. Crystallogr.*, **2003**, *36*, 1487.

[3S] L. Palatinus. and G. Chapuis, G. (2006). *Superflip - a computer program for solution of crystal structures by charge flipping in arbitrary dimensions* (http://superspace.epfl.ch/superflip).

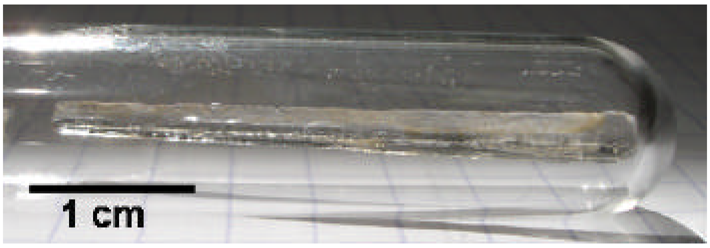


Figure 2S: Photography of single-crystal of **4.**

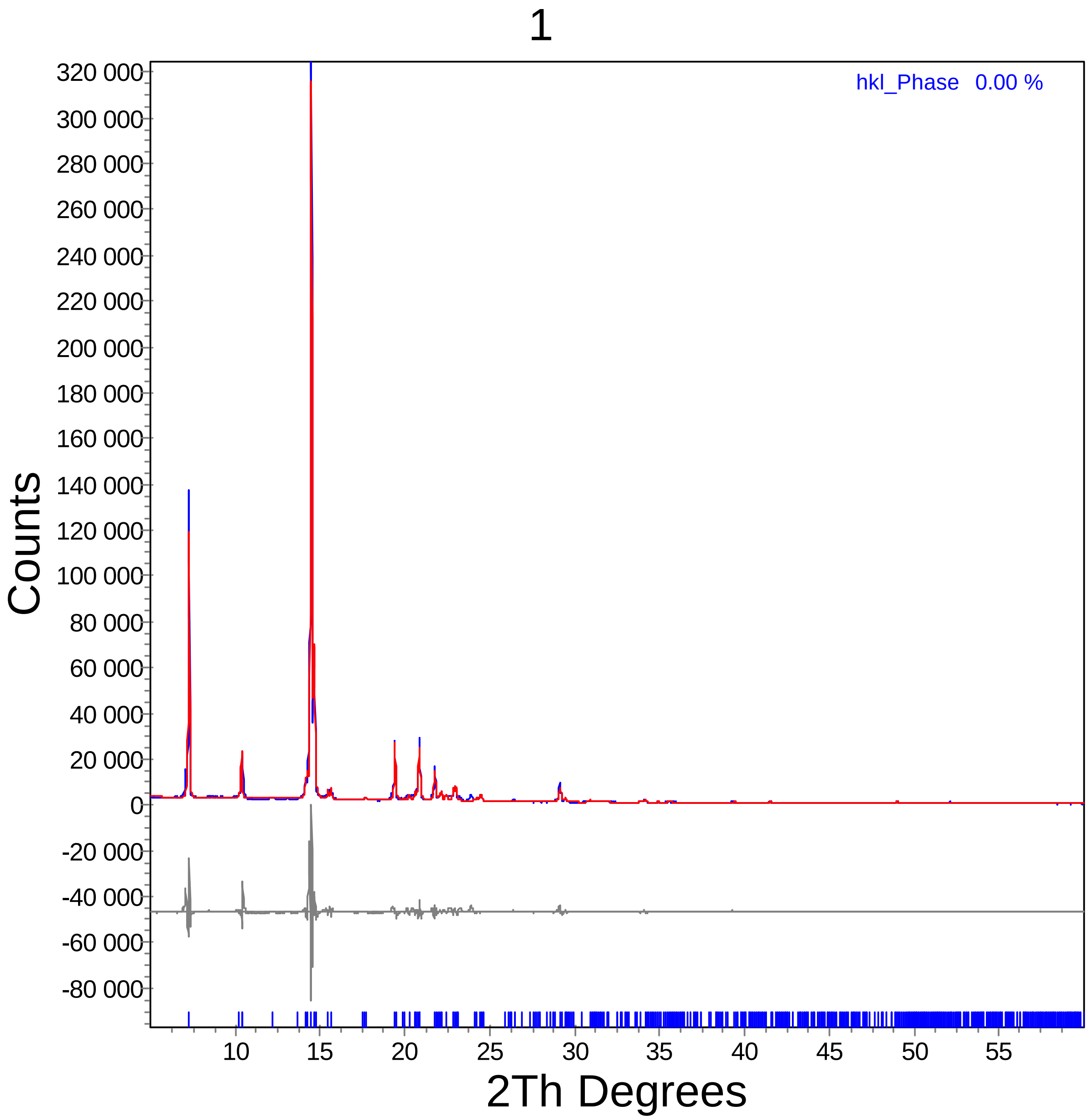


Figure 3Sa : Le Bail profile fit for precursor **1**.

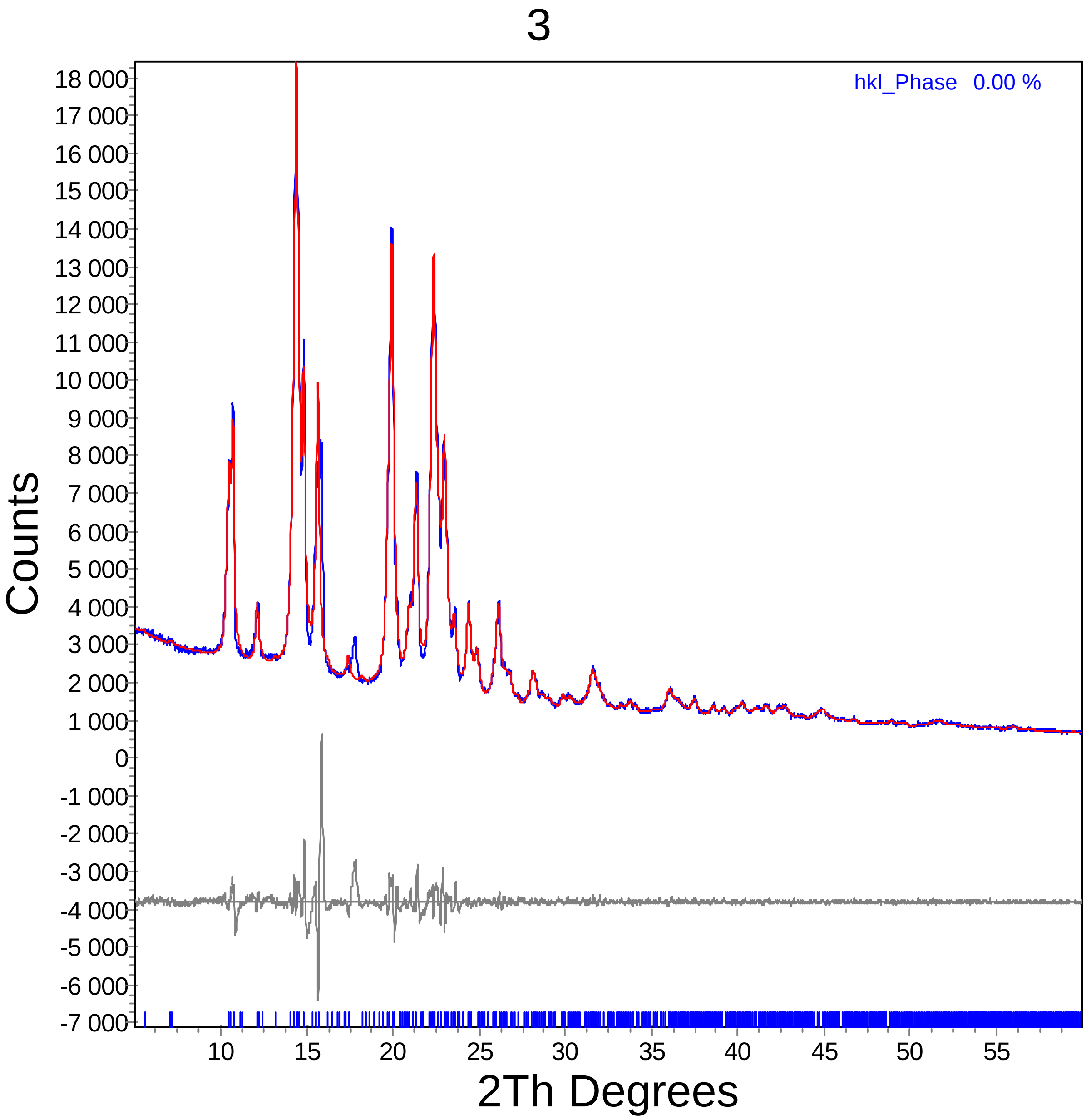


Figure 3Sb: Le Bail profile fit for precursor **3**.

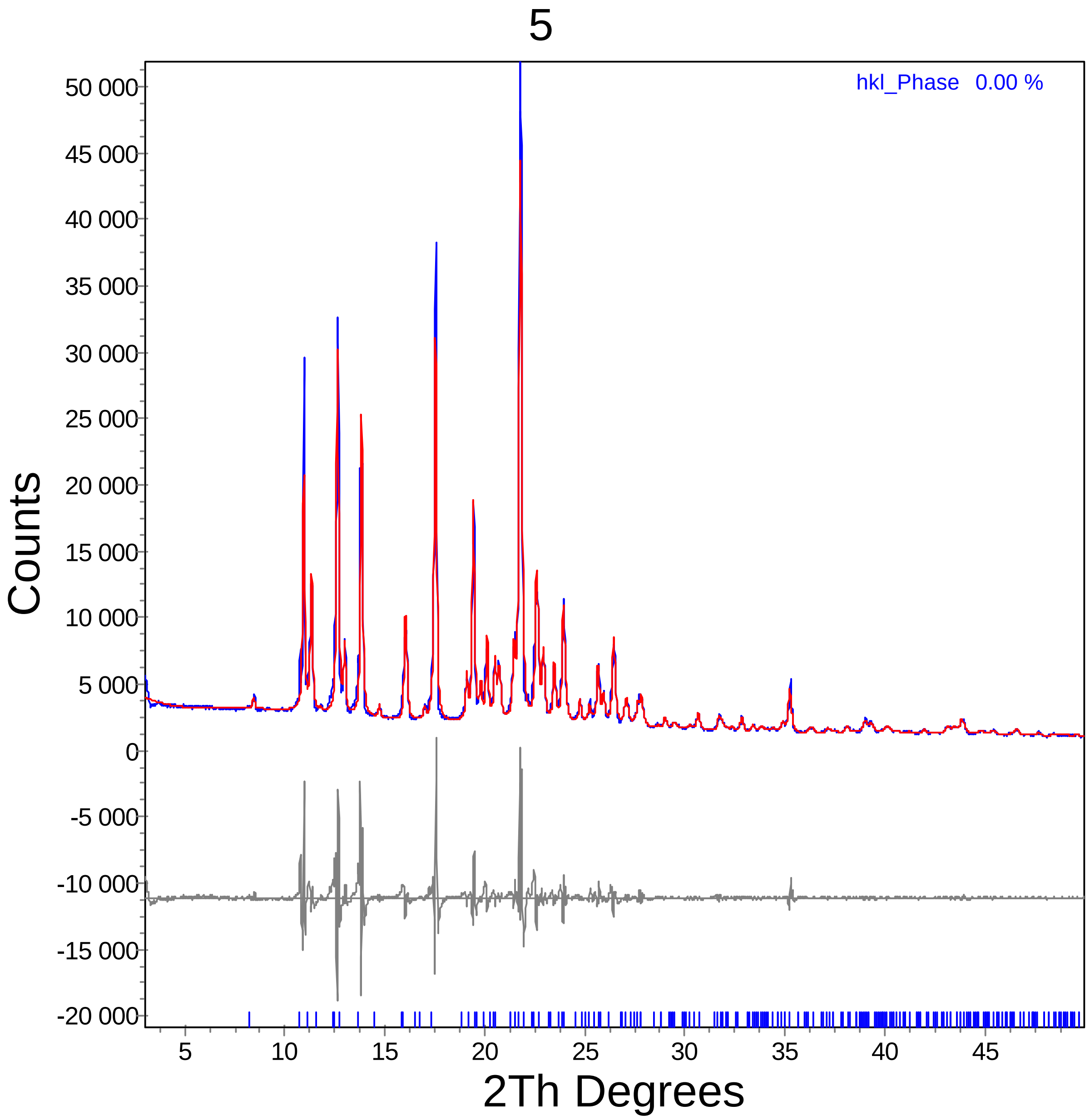


Figure 3Sc : Le Bail profile fit for precursor **5**.

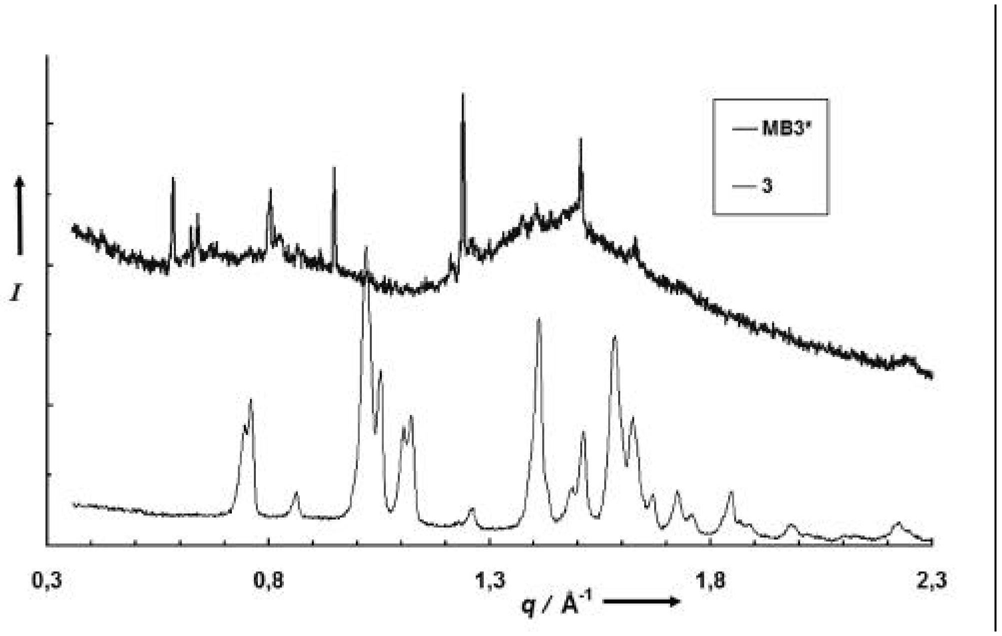


Figure 4S X-ray powder diffractogram for precursor **3** and for the corresponding hybrid membrane **MB3*** made under organic catalysis.

General procedure for synthesis of hybrid materials: Hybrid siloxane materials **M1-M4** were prepared from acetone (**1**,**3**,**4**) or chloroformic (**2**) solutions or organogels (C≥1M) of compounds **1-4** using HCl or Diphenyldichlorosilane as catalysts. The synthesis of dense and homogeneous membranes prepared from compound **5** failed**.** The sols were briefly stirred and allowed to react at room temperature under static conditions for at least 2 days. Then, the sols were deposited by tape-casting onto polyvinylidenefluoride (PVDF) support, dried 24 h at room temperature and 5-6 h at 40 °C to give the thin layer hybrid membranes.

The ^{29}Si MAS NMR spectroscopic experiments on membranes materials agree with partial condensed hybrid materials (rate of condensation about 70%), mostly composed of T^1 [C-Si(OSi)(OH)$_2$] (about 3 to 15%), T^2 [C-Si(OSi)$_2$(OH)] (about 60 to 66 %) and T^3 units [C-Si(OSi)$_3$] (about 15 to 30%) according with a predominant two-dimensional arrangement and with a low percent of cross linked species.

Typical synthesis under acid catalysis: Precursor **1** (340 mg, 1 mmol) was dissolved in acetone (1ml) and a solution of HCl (0.1 M, 300µL) was added .The mixture was then briefly stirred and allowed to react at room temperature under static conditions for 2 days. The gel was then deposited by tape casting onto polyvinylidenefluoride support (PVDF) and dried 24 h at room temperature and 5-6 h at 40 °C. We obtained the corresponding **MB1** hybrid membrane with a thickness about 1.6 µm. **MB1** : ^{29}Si MAS NMR: *d* (ppm) = –49.1 (T^1, 8%) ; -58.4 (T^2 , 65%) ; -66.5 (T^3, 27%).

Typical synthesis under organic catalysis: Precursor **3** (357 mg, 1 mmol) was dissolved in acetone (1ml) and a solution of Diphenyldichlorosilane in acetone (5 mg, 0.02mmol) was added. The mixture was then briefly stirred and allowed to react at room temperature under static conditions for 2 days. The gel was then deposited by tape casting onto polyvinylidenefluoride support (PVDF) and dried 24 h at room temperature and 5-6 h at 40 °C. We obtained the corresponding **MB3*** hybrid membrane with a thickness about 1.5 µm. **MB3***: ^{29}Si MAS NMR: *d* (ppm) = -50.3 (T^1, 4%); -59.2 (T^2, 67%); -67.1 (T^3,29%). We can also notice the presence of a low percent of D^2 units [Ph-Si($OSi)_2$-Ph] (1%).

Membrane transport experiments: were performed with a bi-compartmental device, magnetically stirred at room temperature. It consists of two PTFE cell device separated by the solid membrane oriented with the active dense film to the feed phase. Nitrogen permeation measurements were performed to ensure that they were dense and defect free. The feed phase was either an aqueous solution at pH= 1 for the proton transport experiments, a 10^{-1}M NaCl or a 10^{-1}M KCl solution for cation single transport experiments and a 10^{-1}M (NaCl + KCl) solution for the competitive cation transport experiments. The membrane consisted of supported hybrid dense material (S=5.32 cm^2) while the receiving phase consisted of 50ml of deionized water. The Na^+ and K^+ concentrations were monitored at different time intervals using the atomic absorption spectrophotometry. The permeabilities *P*, have been determined from experimental concentration versus time profiles using the solution-diffusion model.[20]