Supporting Information

From molecular germanates to microporous Ge@C via twin polymerization

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Analyses

A1 NMR spectroscopy of the germanates 1 - 4



Figure S1 ¹H NMR spectrum of compound **1** in CDCl₃. Resonance signals and the integral ratios (determined value is depicted in red) are assigned to the species that are assumed to be present in solution. The asterisk (*) mark resonance signals of residual solvents and silicon grease.



Figure S2 ¹H NMR spectrum of compound **2** in CDCI₃. Resonance signals and the integral ratios (determined value is depicted in red) are assigned to the species that are assumed to be present in solution. The asterisk (*) mark resonance signals of residual solvents and silicon grease.

The integral ratios of the dimethylammonium cationic methylene groups that are assigned to the hexacoordinated dianionic germanate of **1** and **2** gave lower values (80 % for **1** and 83 % for **2**) than expected (Figure S1 - S2). This might be a result of the dynamic equilibrium between a dimethylammonium cation and a dimethyl amine molecule that is a prerequisite for the conversion of the hexacoordinated dianionic germanates (compounds **1** and **2**) into the pentacoordinated species (compounds **1a** and **2a**).



Figure S3 ¹H NMR spectra of compound **1** recorded at -40 °C (blue line), 25 °C (black line) and 55 °C (red line) in CDCl₃. The inlet magnifies the resonance signals of the methylene group protons. The integral ratios of these methylene group protons are given to illustrate the equilibrium between the species (germanate **1** and compound **1a**) that are assumed to be present in solution. The asterisk (*) mark resonance signals of residual solvents and silicon grease.



Figure S4 ¹H NMR spectra of compound **1** in CDCl₃ before (black line) and after addition of an equimolar amount of HNMe₂ (red line) by addition of a 2 M NHMe₂ THF solution to the former solution. The inlet magnifies the resonance signals of the methylene group protons. The integral ratios of these methylene group protons are given to illustrate the equilibrium between the species (germanate **1** and compound **1a**) that are assumed to be present in solution. The asterisk (*) mark resonance signals of residual solvents and silicon grease.



Figure S5 ¹H NMR spectrum of compound **3** [D₈]THF. Resonance signals and the integral ratios (determined value is depicted in red) are assigned to the species that are assumed to be present in solution. The asterisk (*) mark resonance signals of residual solvents and silicon grease.



Figure S6 ¹H NMR spectrum of compound **4** in CDCI₃. Assignment of the resonance signals and the integral ratios are given. The asterisk (*) mark resonance signals of residual solvents and silicon grease.

A2 IR spectroscopy of the germanates 1 - 4



Figure S7 ATR-FT-IR spectra of the germanates a) 1, b) 2, c) 3 and d) 4.



Figure S8 Molecular structure of the dianion of **2** $[\Delta - (C_{24}H_{24}O_6Ge)^2]$ exhibiting Δ configuration in the solid state together with four hydrogen bonded $[H_2NMe_2]^+$ cations. Thermal ellipsoids are drawn with 50% probability. All hydrogen atoms (ball and stick style) that are bonded to carbon atoms have been omitted for clarity. The intermolecular hydrogen bonding motifs $C_2^2(5)$ (orange) and $R_1^2(4)$ (green) are depicted as dashed lines. Symmetry transformations used to generate equivalent atoms: "" denotes -x + 1, -y + 1, -z + 1.



 $\cdots \Delta - [\text{Ge1}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot [\text{H}_2\text{NMe}_2]^+ \cdots \Delta - [\text{Ge4}({}^{\text{Me}}\text{Sal})_3]^2 \cdots [\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - [\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot [\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - [\text{Ge2}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot [\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - [\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot [\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - (\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot [\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - (\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot (\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - (\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot (\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - (\text{Ge3}({}^{\text{Me}}\text{Sal})_3]^2 \cdots 3 \cdot (\text{H}_2\text{NMe}_2]^+ \cdots \Lambda - (\text{H}_2\text{NMe}_2]^+$

Figure S9 Illustration of the hydrogen bonded network observed in the chains that are formed by dimethylammonium cations and germanate dianions of compound **2** in the solid state. Thermal ellipsoids for oxygen, nitrogen and germanium are drawn with 50% probability and carbon atoms are given in wireframe style. All hydrogen atoms (ball and stick style) that are bonded to carbon atoms have been omitted for clarity. The connectivity pattern of the Δ -[Ge1(^{Me}Sal)₃]²⁻, the Δ -[Ge4(^{Me}Sal)3]²⁻ (left), the Λ -[Ge2(^{Me}Sal)₃]²⁻ and Λ -[Ge3(^{Me}Sal)₃]²⁻ (right) moieties is simplified in a formula (bottom). The H atoms of the NH2 groups are depicted in ball and stick style. The intermolecular hydrogen bonding motifs $C_2^2(5)$ (orange) and $R_1^2(4)$ (green) are depicted as dashed lines. Symmetry transformations used to generate equivalent atoms: ' denotes *x*, *y* - 1, *z* + 1; " denotes *x* - 1, -*y*, -*z* + 2.



Figure S10 Illustration of the hydrogen bonded network observed in the chains that are formed by dimethylammonium cations and germanate dianions of compound **1** in the solid state. Thermal ellipsoids for oxygen, nitrogen and germanium are drawn with 50% probability and carbon atoms are given in wireframe style. All hydrogen atoms (ball and stick style) that are bonded to carbon atoms are omitted for clarity. The connectivity pattern of the Δ -[Ge1(Sal)₃]²⁻ (left) and Λ -[Ge2(Sal)₃]²⁻ (right) moieties is simplified in a formula (bottom). The intermolecular hydrogen bonding motifs C₂²(5) (orange) and R₁²(4) (green)^[1] are depicted as dashed lines. Symmetry transformations used to generate equivalent atoms: ' denotes -x + 0.5, *y*, -z + 1; " = -x - 0.5, *y*, -z.

Table S1 Selected bond lengths [Å] and bond angles [°] of the compounds 1, 2 and 4.				
	1	2	4	
Ge1-O1	1.889(2)	1.891(2)	1.8435(11)	
Ge1-O2	1.897(2)	1.882(2)	1.8025(11)	
Ge1-O3	1.879(2)	1.898(2)	1.7766(12)	
Ge1-O4	1.900(2)	1.874(2)	1.8846(11)	
Ge1-O5	1.895(2)	1.902(3)	1.7969(12)	
Ge1-O6	1.911(2)	1.878(2)	-	
01-Ge1-O2	93.53(10)	92.85(10)	93.79(5)	
O1-Ge1-O3	87.07(10)	84.67(11)	86.13(5)	
O1-Ge1-O4	179.47(10)	92.60(11)	173.87(5)	
O1-Ge1-O5	87.57(10)	87.14(11)	85.80(5)	
O1-Ge1-O6	92.70(10)	177.88(10)	-	
O2-Ge1-O3	95.12(10)	176.26(11)	114.87(6)	
O2-Ge1-O4	86.55(10)	89.83(11)	91.45(5)	
O2-Ge1-O5	176.60(10)	91.67(11)	122.27(5)	
O2-Ge1-O6	84.91(10)	89.27(10)	-	
O3-Ge1-O4	93.45(10)	93.07(11)	94.56(5)	
O3-Ge1-O5	88.14(10)	85.42(11)	122.65(5)	
O3-Ge1-O6	179.77(11)	93.21(10)	-	
O4-Ge1-O5	92.31(10)	178.49(10)	88.71(5)	
O4-Ge1-O6	86.78(10)	87.49(11)	-	
O5-Ge1-O6	91.83(10)	92.71(11)	-	

Table S2 Selected bond lengths and bond angles of hydrogen bonds of compound 1.				
D-H…A	D…A [Å]	D-H…A [°]		
N1-H1N…O1	2.808(3)	168(4)		
N1-H1N…O3	3.036(4)	120(3)		
N2-H3N…O12	2.795(4)	159(3)		
N2-H4N…O6	2.818(4)	159(3)		
N3-H5N…O3	2.773(4)	176(3)		
N3-H5N…O5	3.069(4)	113(2)		
N3-H6N…O5'	2.820(4)	175(3)		
N4-H9N…O7	2.813(4)	170(3)		
N4-H9N…O9	3.004(4)	118(3)		
N4-H10N…O11	2.781(4)	167(4)		
N5-H8N…O9	2.761(4)	174(3)		
Symmetry transformation used to generate equivalent atoms: ' denotes $-x + 0.5$, $y, -z + 1$				

Table S3 Selected bond lengths and bond angles of hydrogen bonds of compound 2.				
D-H…A	D…A [Å]	D-H…A [°]		
N1'-H1B'···O3'	2.872(4)	140		
N1-H1A…O9	2.828(4)	145		
N2-H2A…O10	2.731(4)	171		
N2-H2B…O16	3.049(4)	121		
N2-H2B…O18	2.770(4)	164		
N3-H3B…O12	2.745(4)	171		
N3-H3A…O16	2.746(4)	173		
N4-H4B…O8	2.756(4)	170		
N4-H4A…O14	2.790(4)	169		
N5"-H5B"…O13	3.002(4)	134		
N5"-H5B"…O15	2.928(4)	141		
N5"-H5A"-O21"	2.849(4)	146		
N6"-H6B"-O2'	3.041(4)	120		
N6"-H6B"-O6'	2.769(4)	165		
N6"-H6A"-O22"	2.730(4)	172		
N7"-H7A"-O2'	2.737(4)	175		
N7"-H7B"-O24"	2.773(4)	170		
N8"-H8B"-O4'	2.816(4)	168		
N8"-H8A"-O20"	2.756(4)	169		
Symmetry transformation used to generate equivalent atoms: ' denotes $x, y - 1, z + 1$;				
" denotes x - 1, $-y$, $-z$ + 2.				

Discussion of the solid state structure of 1

The one-dimensional, infinite hydrogen bonded networks as-determined for compound **1** in the solid state can be described as follows. Four dimethylammonium cations bind by hydrogen bonds of moderate strength^[2] to the germanate dianion. While three of them are bonded to the benzylic oxygen atoms {N1-O1 2.808(3) Å, N1-O3 3.036(4) Å, N3-O3 2.773(4) Å, N3-O5 3.069(4) Å, N3'-O5 2.820(4) Å for Δ -[Ge1(Sal)₃]²⁻ and N4-O7 2.813(4) Å, N4-O9 3.004(4) Å, N4"-O11 2.781(4) Å, N5-O9 2.761(4) Å for Λ -[Ge2(Sal)₃]²⁻}, one dimethylammonium cation is bonded to a phenolic oxygen atom {N2-O6 2.818(4) Å for Δ -[Ge1(Sal)₃]²⁻ and N2-O12 2.795(4) Å for Λ -[Ge2(Sal)₃]²⁻} at the opposite face of the germanate dianion. Thus, the dimethylammonium cations interconnect the germanate dianions forming a one-dimensional, infinite hydrogen bonded network of dimethylammonium germanate chains with the repeating motif as illustrated in Figure S10. The intermolecular hydrogen bonding motif of the dimethylammonium cation (N2) bridging two phenolic oxygen atoms of two germanate moieties Δ -[Ge1(Sal)₃]²⁻ and Λ -[Ge2(Sal)₃]²⁻ is C²₂(5) (O6•••H4N-N2-H3N•••O12) corresponding to the assignment of Etter, whereas the dimethylammonium

cations bridging the benzylic oxygen atoms of two crystallographic equivalent germanate moieties exhibit additional $R_1^2(4)$ motifs {e.g. (O3-Ge1-O5•••H5N•••) for Δ -[Ge1(Sal)₃]²⁻ and (O7-Ge2-O9•••H9N•••) for Λ -[Ge2(Sal)₃]²⁻}.^[1] A similar one-dimensional, infinite hydrogen bonded network exhibiting a $R_1^2(5)$ hydrogen bonding motif formed by dimethylammonium cations and germanate dianions that show alternating configurations (Δ -and Λ -configuration) within the chains was reported for dimethylammonium *fac*-tris[benzohydroximato(2-)]germanate-CH₃OH.^[3]



A4 TGA/DSC analyses

Figure S11 Differential scanning calorimetry measurement of a) germanate 1 (black curve), b) 2 (red curve), c) 3 (blue curve) and d) 4 (violet curve).



Figure S12 Thermal gravimetric analysis of the germanates a) 1, b) 2, c) 3 and d) 4.





Figure S13 ATR-FT-IR spectra of a) HM-1, b) C-1 and c) Ox-1.



Figure S14 N₂ physisorption isotherms of a) C-1 and b) Ox-1.





Figure S15 X-ray powder diffraction pattern of a) **C-1** and b) **Ox-1**. The red bars in a) and b) display the standard diffraction pattern of cubic Ge (ICDD no. C03-065-0333) and of hexagonal GeO₂ (ICDD no. C00-036-1463), respectively. Determination of the crystalline Ge and GeO₂ particle sizes by applying the Scherrer equation were based on the (220) and (101) reflection marked in a) and b), respectively.



Figure S16 Raman spectra of C-1 at selected surfaces of the samples.

Raman spectroscopy revealed that surface 1 exhibit a high carbon but low germanium content as indicated by the low intensity of the absorption band at 300 cm^{-1} (Ge-Ge vibrations) and the high intensities of the carbon D (~ 1300 cm^{-1}) and G (~ 1600 cm^{-1}) bands. Surface 2 possesses a low carbon but high germanium content as indicated by the intensities of inverse order for the Ge-Ge vibrations and the carbon D and G bands.

References:

- [1] M. C. Etter, Acc. Chem. Res. **1990**, 23, 120-126.
- [2] T. Steiner, Angew. Chem., Int. Ed. 2002, 41, 48-76.
- [3] A. Biller, C. Burschka, M. Penka, R. Tacke, *Inorg. Chem.* **2002**, *41*, 3901-3908.