

The first polymer with a fluorosilicate backbone and a non-polar shell

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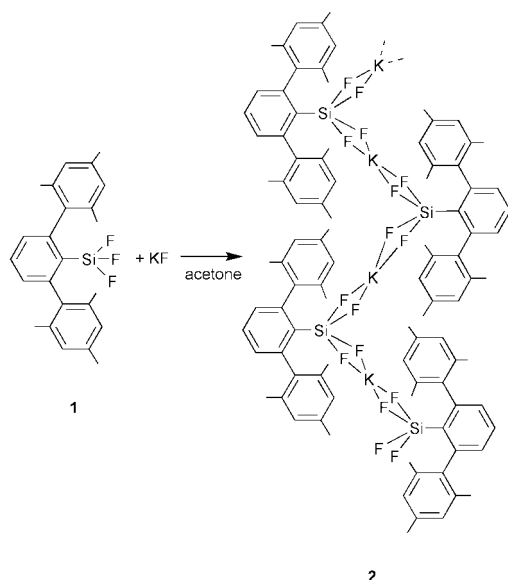
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A novel type of linear inorganic–organic hybridic polymer is presented in which terphenyl ligands are covering the inorganic backbone, providing it with a non-polar coating.

Over recent years coordination polymers have attracted considerable interest.¹ Besides their properties and potential application,² controlling the self organisation of the monomeric units to build one or higher dimensional frameworks has been a major achievement in this fascinating research area.³ Most of these inorganic–organic hybrid materials are constructed from metal cations connected by organic ligands, forming a hybrid inorganic–organic backbone.⁴ There are also examples of coordination polymers with a completely inorganic backbone showing a wealth of different coordination modes.⁵

Several examples of crystal structures of organo-tetrafluorosilicates are known to date.^{6–8} In all of these structures the anions show no direct interaction with more than one counter-cation. Organofluorosilicates with a potassium counter-cation are usually destabilized due to potassium–fluorine interactions. These interactions can be minimised by complexation of the cation with 18-crown-6⁷ or completely removed with [2,2,2]-cryptand.⁸

Earlier we reported⁹ a globular-terphenyl substituted fluoro-silicate in which both tetra- and penta-fluoro silicate units are interconnected in a network built together by the counter-cation interaction. Herein we report the first inorganic fluorosilicate based coordination polymer enveloped by a non-polar organic shell, starting from a multidentate ligand site offering steric control. In order to investigate the balance between electrophilicity and steric protection of the silicon centre in such compounds, we allowed 2,6-dimesitylphenyl trifluorosilane **1** to react with an excess of KF. We exclusively observed the formation of the terphenyl tetrafluorosilicate **2** (Scheme 1) and the product adopts a one dimensional polymeric structure in the solid state (see Fig. 1). To our knowledge this is the first



Scheme 1 Synthesis of **2**.

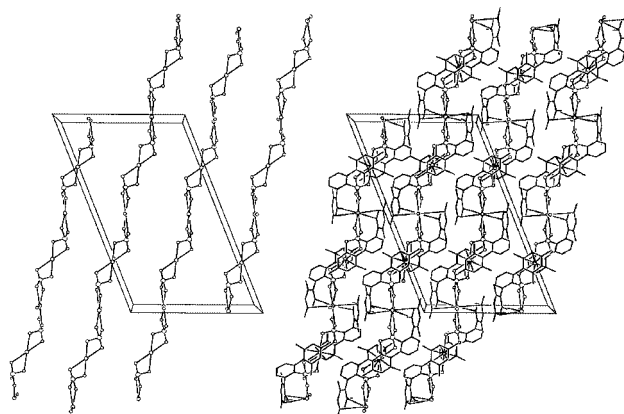


Fig. 1 Inorganic backbone of **2** with (right) and without (left) ligand shell.

structurally characterised potassium organo-tetrafluorosilicate polymer. The interaction of the counter ions leads to association forming a K–F–Si–F–K type of a linear coordination polymer.

Under stoichiometric conditions 2,6-dimesitylphenyl tetrafluorosilicate **2** can be readily synthesised† from the corresponding trifluorosilane **1** and KF. It is a one dimensional coordination polymer the structure of which has been established by X-ray diffraction analysis (see Fig. 2).‡ Polymer **2** is built by organo-tetrafluorosilicate units each of which acts as a bidentate ligand towards two potassium ions. The potassium cations are surrounded by fluorine atoms forming a square planar coordination environment. The axial positions above and below the potassium are occupied by the mesityl substituent of the organic ligand. Additionally one molecule of acetone is present in the coordination sphere of every second potassium ion.

The inorganic backbone consists of four membered SiF₂K rings which are spiro connected at the silicon and the potassium centres. The zig-zag arrangement of the inorganic backbone is shielded by the organic terphenyl ligands attached to each silicon atom. The bulky aryl ligands prevent extensive coordination of solvent to the potassium centres, which instead interact with the π -systems of the mesityl rings of the terphenyl system. This interaction of the cation with the organic shell

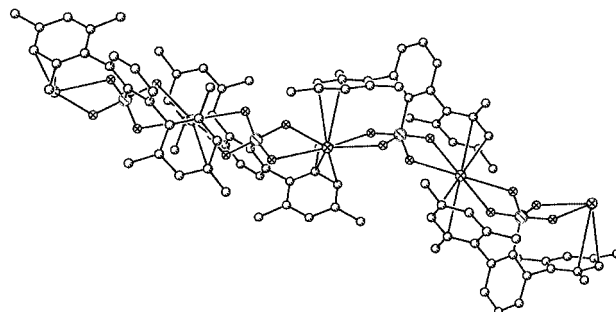


Fig. 2 Detail of the structure of **2**.

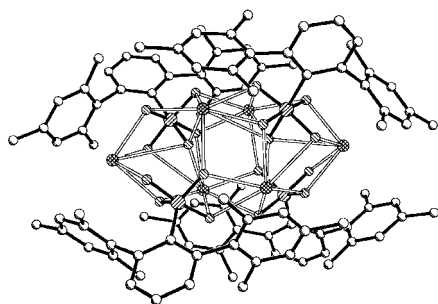


Fig. 3 Crystal structure of **3**.⁹

seems to be crucial for the stability of the polymer, and despite some effort we have not been able to observe similar structures with smaller alkali metal ions.

These findings are in good accordance with previous observations that, due to their preference for increased coordination numbers, the larger alkali metal cations have a tendency to participate in the formation of higher aggregates than smaller alkali metal cations,¹⁰ even though the cation π -system stabilisation energies are smaller for potassium than those observed for lithium.^{11,12} The K–C distances in **2** (3.1–3.5 Å) fall in the normal range of such interactions.⁶

The linear polymer **2** is somewhat related to a structural isomer **3** which however shows no polymeric structure but does start a fluorosilicate network in which a globular inorganic core is covered by a shell of organic terphenyl ligands (see Fig. 3).⁹ This globular adduct is formed under different kinetic conditions than **2**. The chain **2** forms when both starting materials, dimesitylphenyl trifluorosilane and potassium fluoride, are present in equal concentration in the reaction mixture. In contrast the formation of the globular system **3** is characterised by a large excess of the bulky trifluorosilane in the presence of a small concentration of potassium fluoride. The latter is continuously formed in the course of a slow reductive process.⁹ This illustrates how delicately the reaction parameters control the resulting architecture of the polymer. Starting with identical components and controlling reaction conditions globular **3** or linear arrangement **2** can be obtained.

The structure of **2** is not retained in solution as indicated by NMR studies. In acetone solution the coordination polymer dissociates into two species as indicated by ¹⁹F-NMR. The main signal at –113.3 ppm is sharp and shows ²⁹Si satellites (214 Hz), while a minor signal at –127.3 ppm is relatively broad ($\nu_{1/2}$ = 30 Hz) probably due to chemical exchange. Simple ²⁹Si-NMR experiments are hampered by the fact that the expected fluorosilicates show their resonance in the same region as the broad resonance of the glass peak of the NMR tube. Moreover the Si–H coupling constants and the number of protons that are close enough to be used for INEPT or DEPT experiments are too small for this purpose. However, with ¹H{²⁹Si}-2D-HMQC experiments we have been able to observe ²⁹Si spectra and to assign the data to the respective dissociation products. The predominant species shows a ²⁹Si signal at –123 ppm (¹J_{SiF} = 214 Hz) and can be assigned to the monomeric Mes₂C₆H₃SiF₄[–] ion. For comparison PhSiF₄[–] shows a ²⁹Si resonance at –126 ppm. The ²⁹Si resonance of the other dissociation product appears at –59 ppm (¹J_{SiF} = 249 Hz), but due to the low signal intensity the multiplet cannot be unambiguously assigned. It should be mentioned that the dissociation process in solution is reversible and the linear polymer **2** forms again on evaporation of the solvent.

For similar reasons as in solution the presence of proton and fluorine nuclei and their dipolar interaction with the silicon nucleus interferes with conventional CP-MAS NMR techniques. More sophisticated experiments with observation of ²⁹Si with simultaneous decoupling of ¹⁹F and ¹H are in progress. Due to the complexity of these experiments, their results will be reported in context with monomeric organofluorosilanes elsewhere in the future.

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Notes and references

† Synthesis of **2**: Mes₂C₆H₃SiF₅⁹ (0.80 g, 2 mmol) is dissolved in acetone (10 mL) and potassium fluoride (0.12 g, 2 mmol) is added to this solution at room temperature. The mixture is heated to reflux giving a clear solution. After cooling to room temperature the solvent is slowly evaporated and **2** is obtained as colourless crystals which can be separated by filtration (0.76 g, 82.6%). Elemental analysis calc. (%) for C₅₁H₅₆F₈K₂OSi₂: C: 63.06, H: 5.81; found: C: 63.29, H: 5.54. ¹⁹F-NMR (acetone-d₆): –113.3 ppm, ²⁹Si-NMR (acetone-d₆): –123 ppm (¹J_{SiF} = 214 Hz).

‡ Crystal data for **2**: Formula = C₅₁H₅₆F₈K₂OSi₂, *M* = 971.34, monoclinic, space group C2/c; *a* = 27.63(2) Å; *b* = 11.432(12) Å; *c* = 17.03(2) Å; β = 111.50(4)°; *V* = 5005(10) Å³; *Z* = 8; *D*_c = 1.289 Mg m^{–3}; λ = 0.71073 Å; reflections collected/unique 12806/4429; *R*₁ = 0.0556, *wR*₂ = 0.1121.

CCDC reference number 164463. See <http://www.rsc.org/suppdata/cc/b1/b102853g> for crystallographic data in CIF or other electronic format.

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