

Supplementary Information for

**Five- and sixfold coordinated silicon in silicodiphosphonates: short range order investigation by solid-state NMR spectroscopy**

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## 1. Synthesis of silicophosphates from diphosphonic acids

**SiOP\_H1:** HEDP (1.00 g, 4.85 mmol) was dissolved in THF (140 mL) in the boiling heat. TEOS (1.01 g, 4.85 mmol) was added under cooling to the solution. After the complete addition the reaction mixture was stored in the fridge for several days. Yielding 1.06 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:2.6.  $^1\text{H}$  MAS NMR (400.30 MHz):  $\delta$  = 1.4 ( $\text{CH}_3$ ), 3.9 ( $\text{CH}_2$ ), 10.5 (P-OH) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta$  = 17.1 ( $\text{CH}_3$ ), 26.0 ( $\text{CH}_2$ -THF), 60.2 (Si-O- $\text{CH}_2$ ), 69.3 (O- $\text{CH}_2$ -THF or P-C(OSi)-P) ppm.  $^{31}\text{P}$  MAS NMR (162.04 MHz):  $\delta$  = 10.5 (C-P(O)(OSi) $_2$ ) ppm.  $^{29}\text{Si}$  MAS NMR (79.52 MHz):  $\delta$  = -104.5, -111.3 ( $\text{SiO}_4$ ), -210.6 (Si(OP) $_6$ ) ppm.

**SiOP\_H2:** HEDP (1.00 g, 4.85 mmol) was dissolved in THF (140 mL) in the boiling heat. TEOS (4.05 g, 19.41 mmol) was dropped under cooling to the solution. The reaction mixture was stored in the fridge for some days. Yielding 1.57 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:1.7.  $^1\text{H}$  MAS NMR (400.30 MHz):  $\delta$  = 1.2 ( $\text{CH}_3$ ), 3.8 ( $\text{CH}_2$ ), ~13 (P-OH) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta$  = 16.9, 18.0 ( $\text{CH}_3$ ), 25.9 ( $\text{CH}_2$ -THF), 60.4 (Si-O- $\text{CH}_2$ ), 69.0 (O- $\text{CH}_2$ -THF or P-C(OSi)-P) ppm.  $^{31}\text{P}$  MAS NMR (162.04 MHz):  $\delta$  = 7.7 (C-P(O)(OSi) $_2$ ) ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta$  = -88.8, -98.0 ( $\text{SiO}_4$ ), -131.8 ( $\text{SiO}_5$ ), -196.0 ( $\text{SiO}_6$ ), -210.4 (Si(OP) $_6$ ) ppm.  $^{29}\text{Si}$  MAS NMR (79.52 MHz):  $\delta$  = -89.3, -98.0 ( $\text{SiO}_4$ ), -211.2 (Si(OP) $_6$ ) ppm.

**SiOP\_M1:** MDP (0.25 g, 1.42 mmol) was dissolved in DMF (10 mL) at room temperature. TEOS (0.30 g, 1.42 mmol) was dropped under cooling to the solution. The reaction mixture was stored in the fridge for several days. Yielding 0.41 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:2.6.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta$  = -95.6, -102.0 ( $\text{SiO}_4$ ), -207.6 (Si(OP) $_6$ ) ppm.

**SiOP\_M2:** TEOS (1.18 g, 5.68 mmol) was added under cooling in a 4:1 molar ratio to a solution of MDP (0.25 g, 1.42 mmol) in DMF (10 mL). Previously, MDP was dissolved in DMF at room temperature. The reaction mixture was stored in the fridge for some days. Yielding 0.33 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:2.3.  $^1\text{H}$  MAS NMR (400.30 MHz):  $\delta$  = 1.1 ( $\text{CH}_3$ ), 2.8 ( $\text{CH}_3$ -DMF), 3.8 ( $\text{CH}_2$ ), 8.1 (CH-DMF) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta$  = 18.2 ( $\text{CH}_3$ ), 26.2 ( $\text{CH}_3$ ), 31.9 ( $\text{CH}_3$ -DMF), 35.1 ( $\text{CH}_3$ -DMF), 37.4 ( $\text{CH}_2$ ), 40.2 ( $\text{CH}_2$ ), 60.2 (Si/P-O- $\text{CH}_2$ ), 164.2 (CH-DMF) ppm.  $^{31}\text{P}$  MAS NMR (162.04 MHz):  $\delta$  = 4.9 ( $\text{CH}_2$ -P(O)(OSi) $_2$ ) ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta$  = -88.6, -96.8, -104.5, -108 ( $\text{SiO}_4$ ), -206.6 (Si(OP) $_6$ ) ppm.  $^{29}\text{Si}$  MAS NMR (79.52 MHz):  $\delta$  = -88.2, -95.7 ( $\text{SiO}_4$ ), -207.5 (Si(OP) $_6$ ) ppm.

**SiOP\_E1:** EDP (0.25 g, 1.32 mmol) was dissolved in DMF (10 mL) in the boiling heat. TEOS (0.27 g, 1.32 mmol) was also added in the boiling heat. After the complete addition the reaction mixture was cooled to room temperature and then stored in the fridge for some days. Yielding 0.26 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:5.7.  $^{31}\text{P}$  CP MAS NMR (162.04 MHz):  $\delta$  = 28.5 (EDP), 18.3 (( $\text{CH}_2$ )P(O)(OSi)OH), 4.0 (( $\text{CH}_2$ )P(O)(OSi) $_2$ ), ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta$  = -101.4, -110.3 ( $\text{SiO}_4$ ), -206.3, -210.1 (Si(OP) $_6$ ) ppm.

**SiOP\_E2:** TEOS (1.09 g, 5.26 mmol) was dropped in the boiling heat to a solution of EDP (0.25 g, 1.32 mmol) in DMF (10 mL). Previously, EDP was dissolved in DMF in the boiling heat. The reaction mixture was stored in the fridge for several days. Yielding 0.33 g of a white solid after drying in vacuo. ICP-OES: Si/P = 1:1.7.  $^1\text{H}$  MAS NMR (400.30 MHz):  $\delta$  = 1.1 ( $\text{CH}_3$ ), 2.8 ( $\text{CH}_3$ -DMF), 2.9 ( $\text{CH}_3$ -DMF), 3.8 ( $\text{CH}_2$ ), 8.0 (CH-DMF), ~15 (P-OH) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta$  = 18.2 ( $\text{CH}_3$ ), 20.8 ( $\text{CH}_3$ ), 31.3 ( $\text{CH}_3$ -DMF), 35.0 ( $\text{CH}_3$ -DMF), 36.6 ( $\text{CH}_2$ ), 39.9 ( $\text{CH}_2$ ), 60.2 (Si/P-O- $\text{CH}_2$ ), 163.3 (CH-DMF) ppm.  $^{31}\text{P}$  CP MAS NMR (162.04 MHz):  $\delta$  = 14.6 ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta$  = -89.5, -97.2, -106.0 ( $\text{SiO}_4$ ), -209.8 (Si(OP) $_6$ ) ppm.

## 2. Silylation of 1-hydroxyethylidene-1,1-diphosphonic acid and diphosphoric acid

**Pentakis(O-trimethylsilyl)hydroxyethylidene diphosphonic acid – Si-HEDP:** The synthesis was performed according to the literature.<sup>1</sup> Hexamethyldisilazane (4.03 g, 25 mmol) was added in a 1:1 molar ratio to HEDP (5.15 g, 25 mmol) to start the reaction. The mixture was heated and the liberation of ammonia gas was observable. After that, the mixture was heated with continuous addition of HMDS (12.10 g, 75 mmol) until a 1:4 molar ratio was reached. The mixture was heated under reflux for one hour. The obtained product was a yellow oil.  $^{31}\text{P}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.06 (Si-HEDP), -19.05 ppm.  $^{29}\text{Si}$  (99.36 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.9 (( $\text{CH}_3$ ) $_3$ SiOSi( $\text{CH}_3$ ) $_3$ ), 15.8 (t,  $^3\text{J}(\text{SiP})$  = 5.4 Hz, COSi( $\text{CH}_3$ ) $_3$ ), 20.7 (t,  $^2\text{J}(\text{SiP})$  = 4.8 Hz, POSi( $\text{CH}_3$ ) $_3$ ), 21.1 (t,  $^2\text{J}(\text{SiP})$  = 4.5 Hz, POSi( $\text{CH}_3$ ) $_3$ ) ppm.

**Tetrakis(trimethylsilyl) diphosphate – Si-POP:** The synthesis was performed according to the literature.<sup>2</sup> A dry Schlenk-tube was loaded with dihydrogen disodium diphosphate (10.10 g, 45 mmol) and formamide (30 mL). Trimethylsilyl chloride (19.98 g, 184 mmol) was dropped under cooling and stirring over 45 minutes to the suspension. After the addition was completed, the mixture was warmed up to room temperature, and petrol ether

(100 mL) was added. After one hour of stirring the clear top layer was separated into a dry Schlenk tube. Petrol ether and remaining trimethylsilyl chloride were removed under reduced pressure. The obtained product was a colourless liquid (18 g)  $^{31}\text{P}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta = -20.72$  ([HO/(CH<sub>3</sub>)<sub>3</sub>SiO(O)POP]), -25.89 (OP[OSi(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>), -31.56 (Si-POP), -31.81 (P[OP(O)(OSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]), -31.96 (d,  $^2J(\text{PP}) = 11.1$  Hz, (P[OP(O)(OSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]), -37.11 (t,  $^2J(\text{PP}) = 11.1$  Hz, [PO(PO(OSi(CH<sub>3</sub>)<sub>3</sub>)OP)] ppm.  $^{29}\text{Si}$  (99.36 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.2$  ((CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub>), 21.0 (OP(OSi(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>), 24.5 (Si-POP), 25.3, 25.6 ppm.

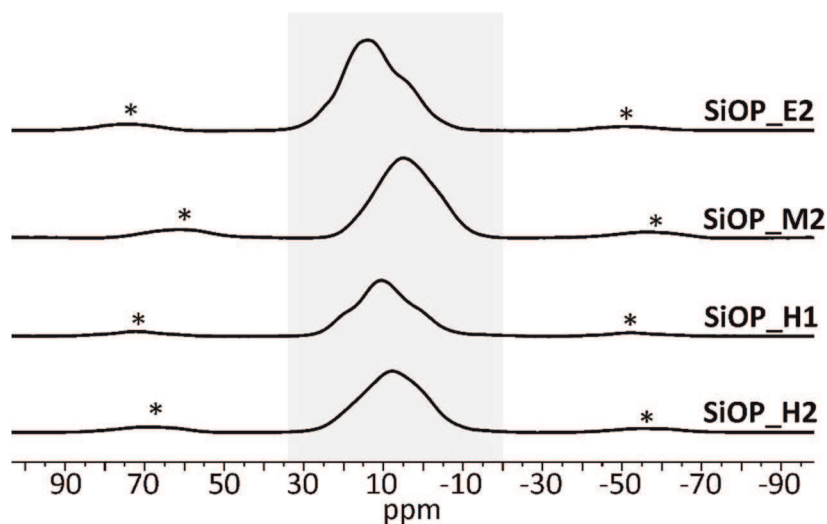
### 3. Synthesis of a) silicophosphates and b) silicodiphosphonates via transsilylation

**a) Si-POP** (1.28 g, 2.7 mmol) was dissolved in toluene (30 mL). Tetramethoxysilane (1.63 g, 11 mmol) was added to the solution. A turbidity was observed. The reaction mixture was warmed up under vacuum (0.6 kPa) for one hour to remove methoxy(trimethyl)silane. After that the solvent was removed under reduced pressure. The obtained white solid was suspended in hexane (15 mL) and separated via filtration yielding 0.55 g after drying in vacuo.

$^1\text{H}$  MAS NMR (400.30 MHz):  $\delta = 0.3$  (Si(CH<sub>3</sub>)<sub>3</sub>), 1.3, 3.6 (CH<sub>3</sub>), 7.1 (CH-toluene), 15.1 (P-OH) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta = 0.2$  (Si(CH<sub>3</sub>)<sub>3</sub>), 51.7 (OCH<sub>3</sub>) ppm.  $^{31}\text{P}$  MAS NMR (162.04 MHz):  $\delta = -9.2, -20.9, -32.7$  ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta = 25.0$  (POSi(CH<sub>3</sub>)<sub>3</sub>), -85.3, -87.0, -95.3, -104.0 (SiO<sub>4</sub>), -212.4 (Si(OP)<sub>6</sub>) ppm.

**b) Tetramethoxysilane** (1.37 g, 9.01 mmol) was added to a solution of **Si-HEDP** in toluene (30 mL). A turbidity was observed. The reaction mixture was warmed up. Toluene was removed under reduced pressure. A yellow oil was obtained. Hexane (10 mL) was added and the obtained white solid was separated via filtration yielding 0.59 g after drying in vacuo.  $^1\text{H}$  MAS NMR (400.30 MHz):  $\delta = 0.3$  (Si(CH<sub>3</sub>)<sub>3</sub>), 1.7 (CH<sub>3</sub>), 3.5 (OCH<sub>3</sub>), 16.4 (P-OH) ppm.  $^{13}\text{C}$  CP MAS NMR (100.67 MHz):  $\delta = 0.9$  (Si(CH<sub>3</sub>)<sub>3</sub>), 20.2 (C-CH<sub>3</sub>), 51.3 (O-CH<sub>3</sub>), 71.5 (-COSi(CH<sub>3</sub>)<sub>3</sub>) ppm.  $^{31}\text{P}$  CP MAS NMR (162.04 MHz):  $\delta = 0.6, 7.4$  ppm.  $^{29}\text{Si}$  CP MAS NMR (79.52 MHz):  $\delta = 25.1$  (POSi(CH<sub>3</sub>)<sub>3</sub>), -85.4, -93.7, -102.1 (SiO<sub>4</sub>), -195.4, -211.1 (Si(OP)<sub>6</sub>) ppm.

### 4. Supplementary figures



**Fig. S1:**  $^{31}\text{P}$  SP MAS NMR spectra of **SiOP\_E2**, **SiOP\_M2**, **SiOP\_H1**, and **SiOP\_H2**. The broad NMR signals at around 10 ppm indicate the survival of the diphosphonic structures in the Si-O-P materials independent of molar ratio (\* represents the spinning side bands).

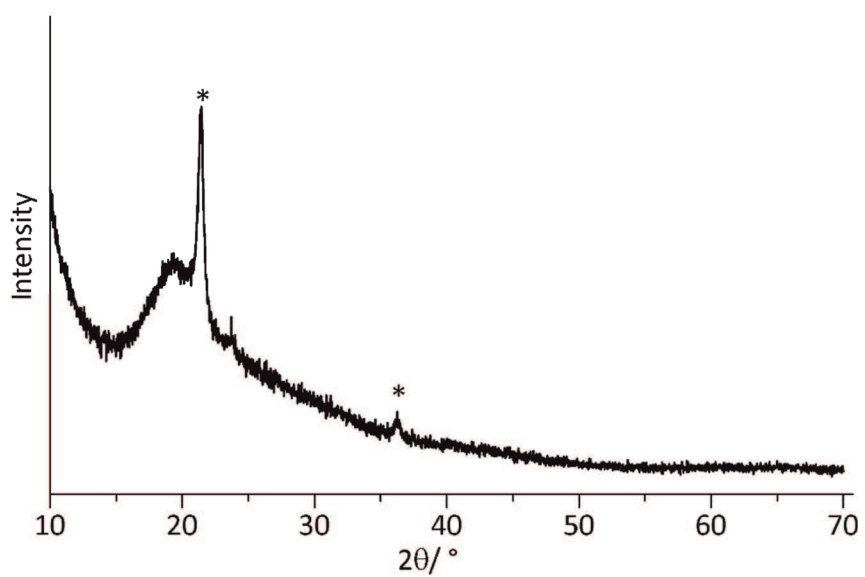


Fig. S2: Powder X-ray diffraction pattern of SiOP\_H2 (\* represents the used cover foil).

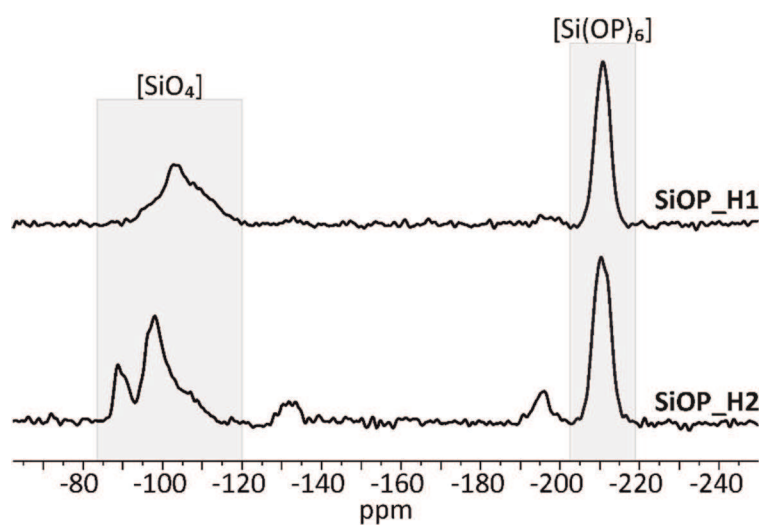
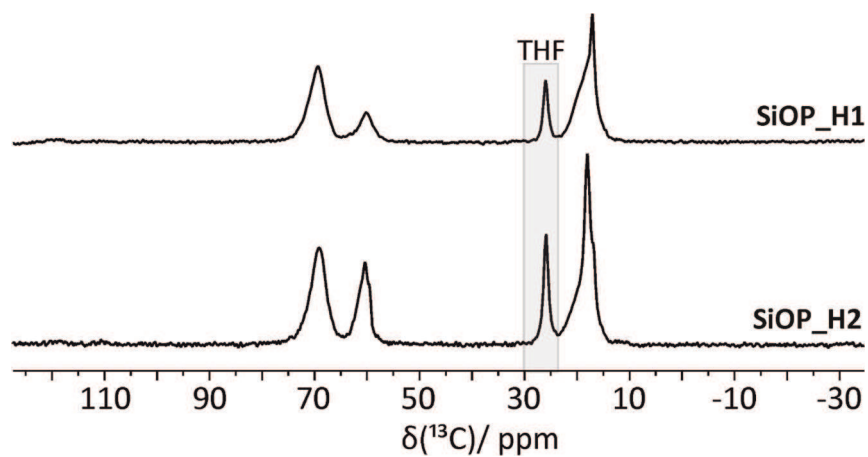
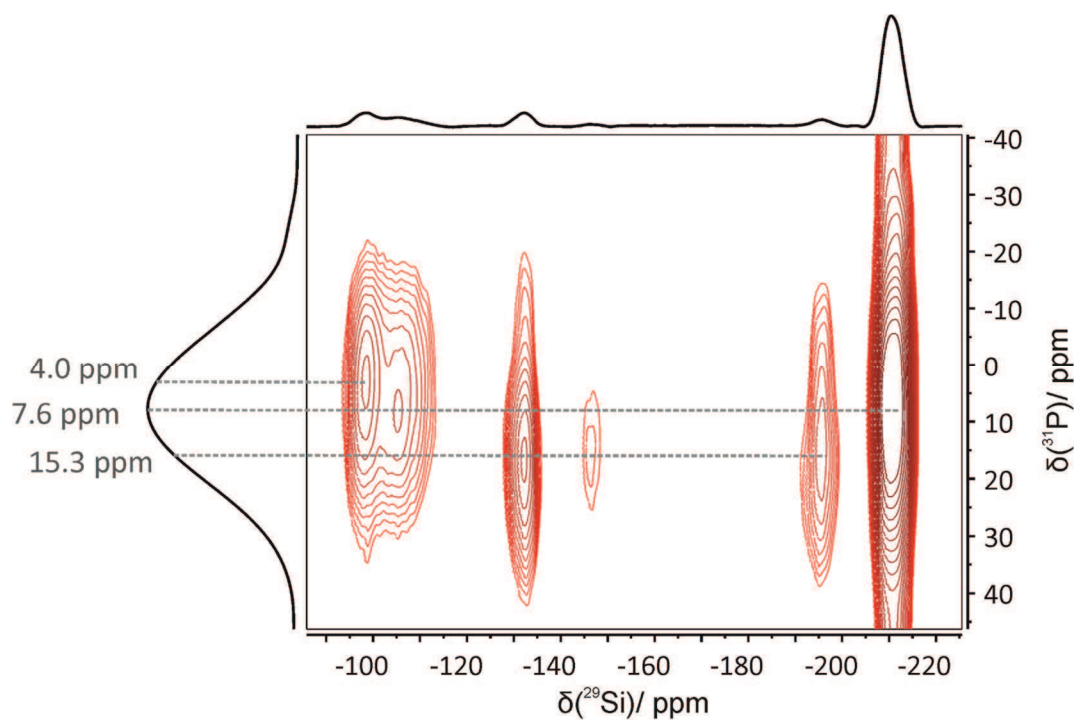


Fig. S3:  $^{29}\text{Si}$  CP MAS NMR spectra of SiOP\_H1 and SiOP\_H2.



**Fig. S4:**  $^{13}\text{C}$  CP MAS NMR spectra of **SiOP\_H1** and **SiOP\_H2**;  $^{13}\text{C}$  resonance at 25.9 ppm represents methylene group of THF (marked in grey colour); second  $^{13}\text{C}$  signal of THF at 68.0 ppm overlaps with the chemical shift of the bridging carbon of HEDP.



**Fig. S5:**  $^{31}\text{P}$ - $^{29}\text{Si}$  correlation NMR spectrum via  $^1\text{H}$ - $^{31}\text{P}$ - $^{29}\text{Si}$  double CP experiment of **SiOP\_H2**.

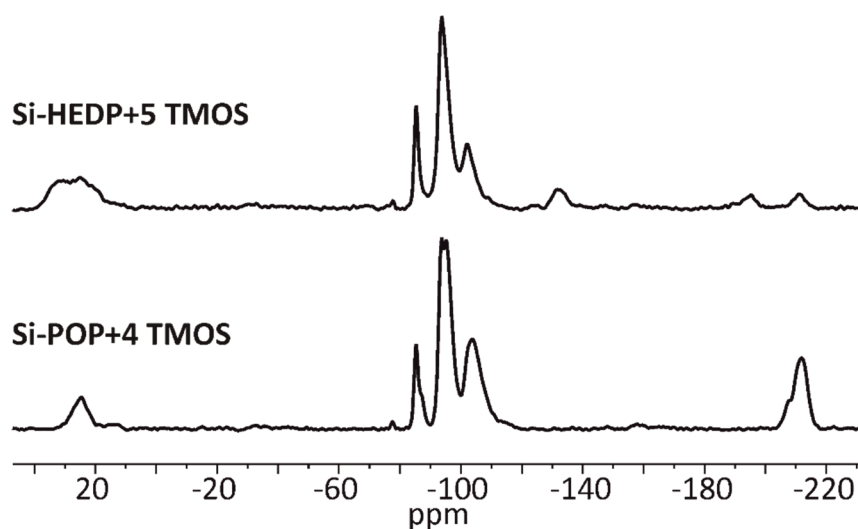
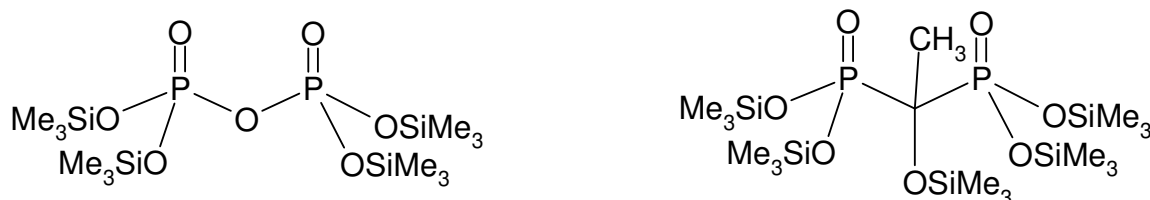


Fig. S6:  $^{29}\text{Si}$  CP MAS NMR spectra of Si-O-P materials synthesized via transsilylation.

## 5. Analysis of scalar couplings in diphosphonate and diphosphate $^{31}\text{P}$ - $^{29}\text{Si}$ spin systems

Scheme S1 shows the molecules under discussion. The trimethylsilyl groups in **Si-POP** are all chemically but not magnetically equivalent. A related situation holds for **Si-HEDP** with the difference that the two trimethylsilyl groups in the phosphonate group are not chemically equivalent. The molecules can therefore be considered as an  $A_2A_2'XX'$  spin system and an  $A_2B_2'MXX'$  spin system, respectively, with A, B, M =  $^{29}\text{Si}$  and X =  $^{31}\text{P}$ .

Due to the low natural abundance of  $^{29}\text{Si}$ , the spin systems of the phosphate and phosphonate moieties can be reduced to an  $AXX'$  system for simulation.



Scheme S1: Tetrakis(trimethylsilyl)diphosphate (**Si-POP**) and pentakis(*O*-trimethylsilyl)hydroxyethylidene diphosphonate (**Si-HEDP**).

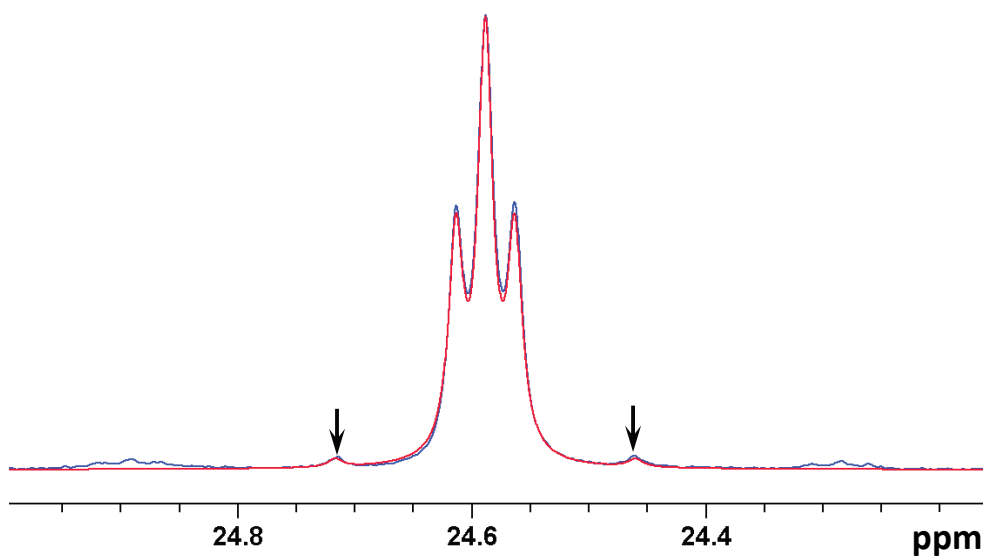
### 5.1 Tetrakis(trimethylsilyl)diphosphate (Si-POP)

A comparison of the experimental spectrum with a calculated one using the literature data and with our higher order coupling analysis is given in Fig. 6 of the main article.

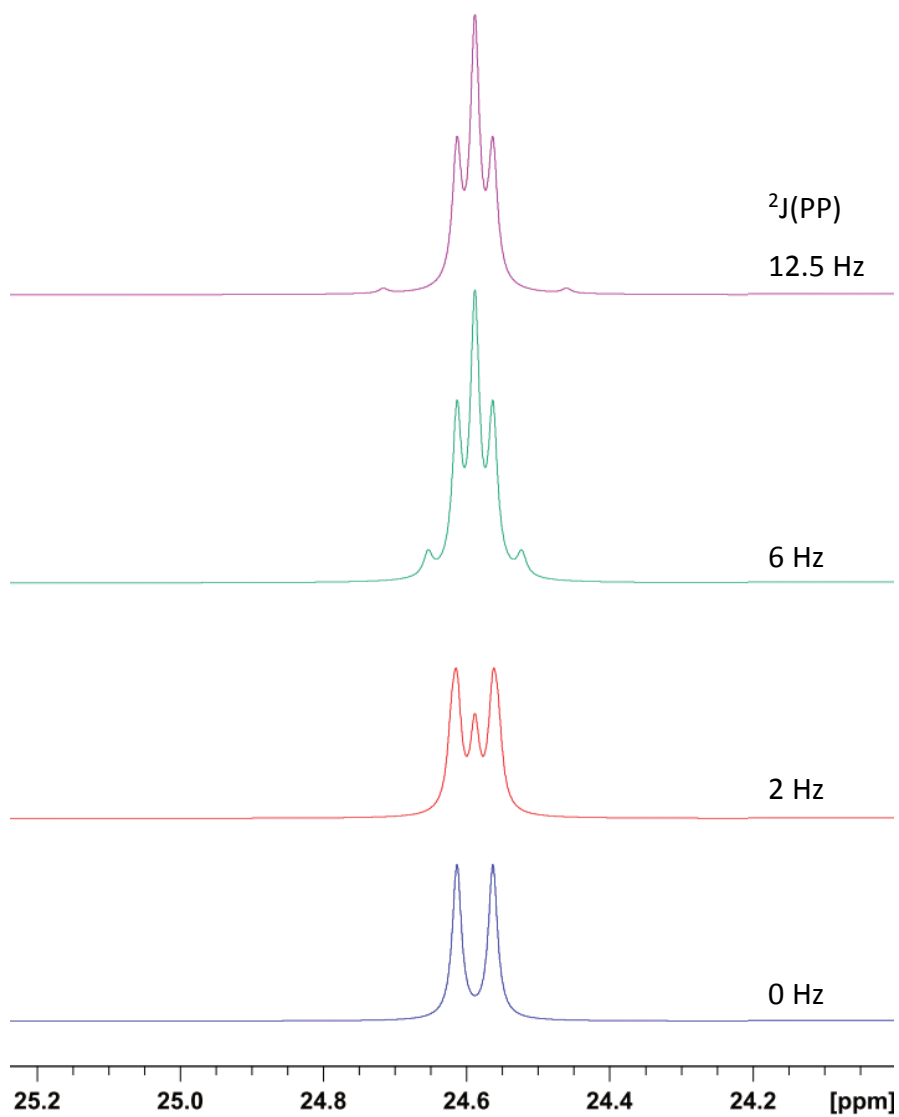
For clarity, the experimental spectrum and the calculated spectrum are shown in Fig. S7 again.

The size of the triplet splitting results from  $\frac{1}{2}[^2J(\text{SiP})+^4J(\text{SiP})]$ .

The position of the arrow marked satellite signals is given by the size of  $^2J(\text{PP})$ , as the simulation for different  $^2J(\text{PP})$  shows in Fig. S8. They can be observed at  $\Delta\nu = ^2J(\text{PP})$  with respect to the main signal, but only if  $^2J(\text{SiP}) \neq ^4J(\text{SiP})$ . The sign of  $^2J(\text{PP})$  has no influence on the splitting pattern. The intensity of the satellites enhances with increasing difference between  $^2J$  and  $^4J$  and matches the experimental spectrum best for  $^2J(\text{SiP}) = 4.9$  Hz,  $^4J(\text{SiP}) = 0.1$  Hz, and  $^2J(\text{PP}) = 12.5$  Hz.



**Fig. S7:**  $^{29}\text{Si}$  refocused INEPT spectrum at 20 °C (blue) and calculated spectrum with  $^2J(\text{SiP}) = 4.9$  Hz,  $^4J(\text{SiP}) = 0.1$  Hz,  $^2J(\text{PP}) = 12.5$  Hz (red).

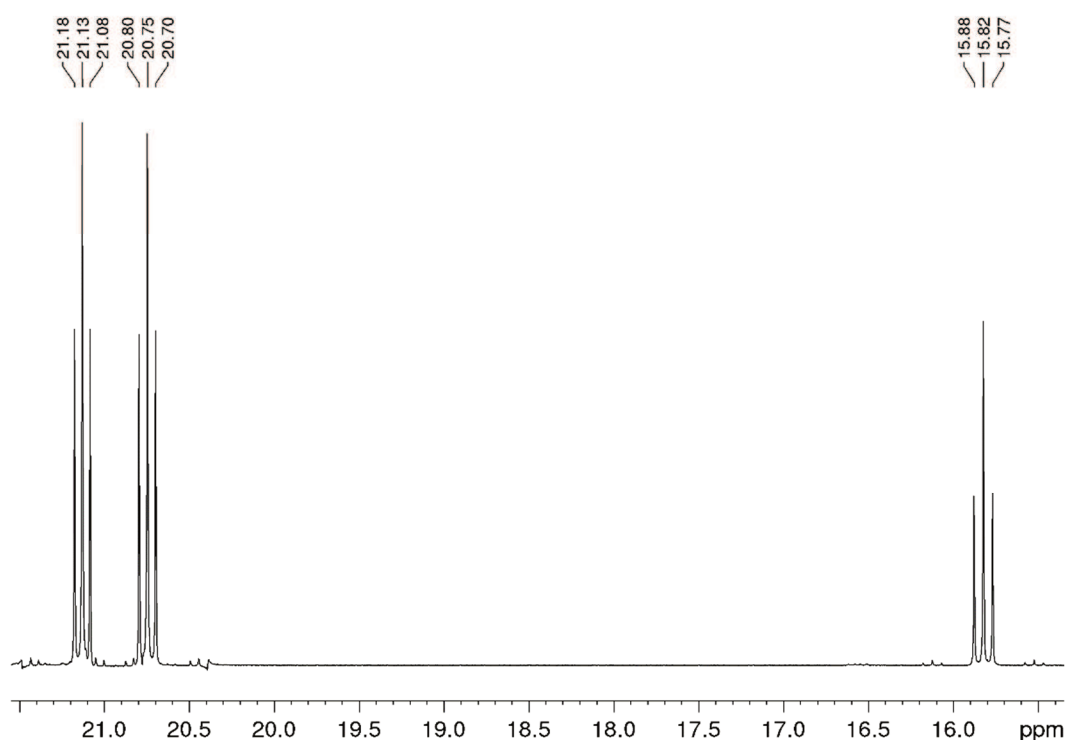


**Fig. S8:** Calculated  $^{29}\text{Si}$  spectra of Si-POP with  $^2J(\text{SiP}) = 4.9$  Hz,  $^4J(\text{SiP}) = 0.1$  Hz, and varying  $^2J(\text{PP})$ .

In principle, the  ${}^2J(\text{SiP})$  coupling should also be observable in the  ${}^{31}\text{P}$  NMR spectra as  ${}^{29}\text{Si}$  satellite signals with an intensity according to the natural abundance of  ${}^{29}\text{Si}$ . Due to the comparatively small coupling constant the satellites are not resolved for **Si-POP** and will therefore be discussed for **Si-HEDP**.

## 5.2 Pentakis(*O*-trimethylsilyl)hydroxyethylidenediphosphonate (Si-HEDP)

Fig. S9 shows the  ${}^{29}\text{Si}$  NMR spectrum of compound **Si-HEDP**. At 15.82 ppm the trimethylsilyl group at the methylene bridge can be observed ( ${}^3J(\text{SiP}) = 5.4$  Hz). The signals at 21.13 and 20.75 ppm represent the two chemically not equivalent  $\text{Me}_3\text{SiO}^-$  groups at the phosphorus with a triplet splitting of 4.55 Hz and 4.85 Hz, respectively.



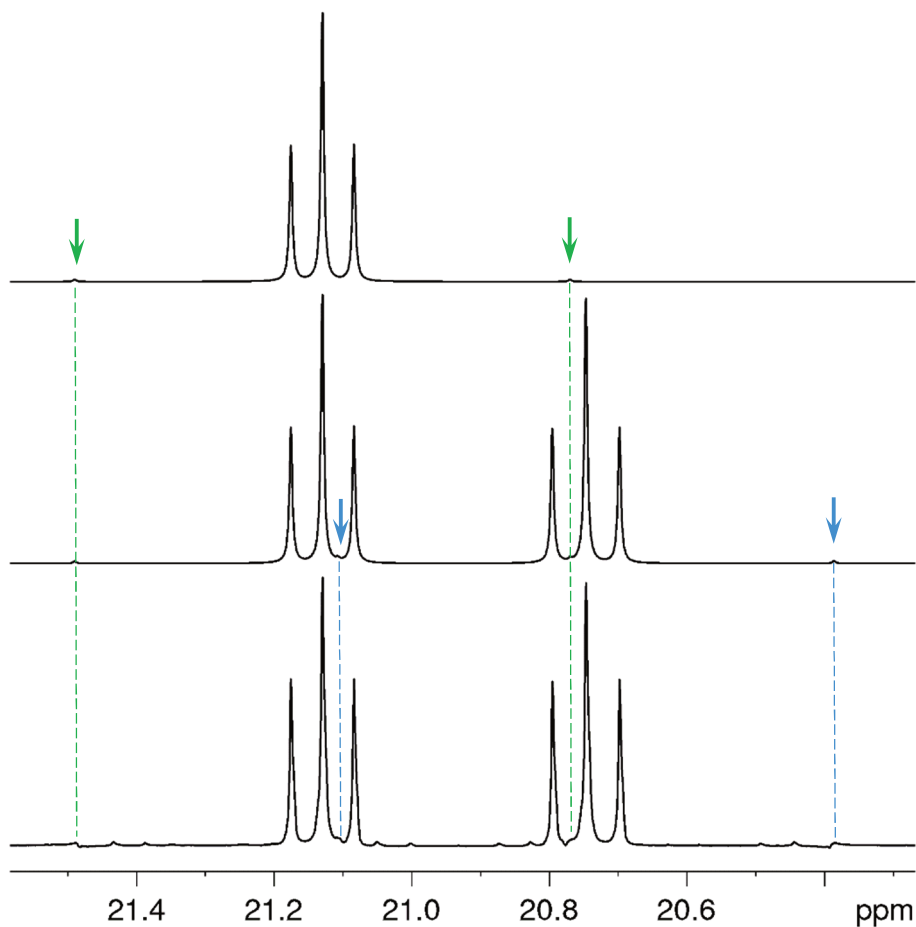
**Fig. S9:**  ${}^{29}\text{Si}$  refocused INEPT NMR spectrum of **Si-HEDP**.

The coupling pattern for the  $\text{Me}_3\text{SiO}^-$  groups at phosphorus arise from the same situation as discussed for **Si-POP** with the difference that the  ${}^2J(\text{SiP})$  and  ${}^2J(\text{PP})$  coupling constants are significantly larger. Table S1 summarizes the values used to calculate the spectra. Fig. S10 shows the experimental spectrum compared to the calculated. Note again that the small satellite signals marked by arrows, which again can only be observed for  ${}^2J(\text{SiP}) \neq {}^4J(\text{SiP})$  and under consideration of  ${}^2J(\text{PP})$ .

**Table S1:** NMR parameter used for the calculation of the Si-P coupling patterns for **Si-POP** and **Si-HEDP**. A linewidth of 0.4-0.6 Hz was applied.

compound	$\delta({}^{29}\text{Si})$ / ppm	${}^2J(\text{SiP})$ / Hz	${}^4J(\text{SiP})$ / Hz	${}^2J(\text{PP})$ / Hz	Additional data
<b>Si-POP</b>	24.59	4.9	0.1	12.5	
<b>Si-HEDP</b>	15.82				${}^3J(\text{SiP}) = 5.4$ Hz
	20.75	9.6	0.1	35.0	${}^1J(\text{PC}) = 171.3$ Hz
	21.13	9.0	0.1	35.0	$\delta({}^{31}\text{P}) = 3.056$ ppm



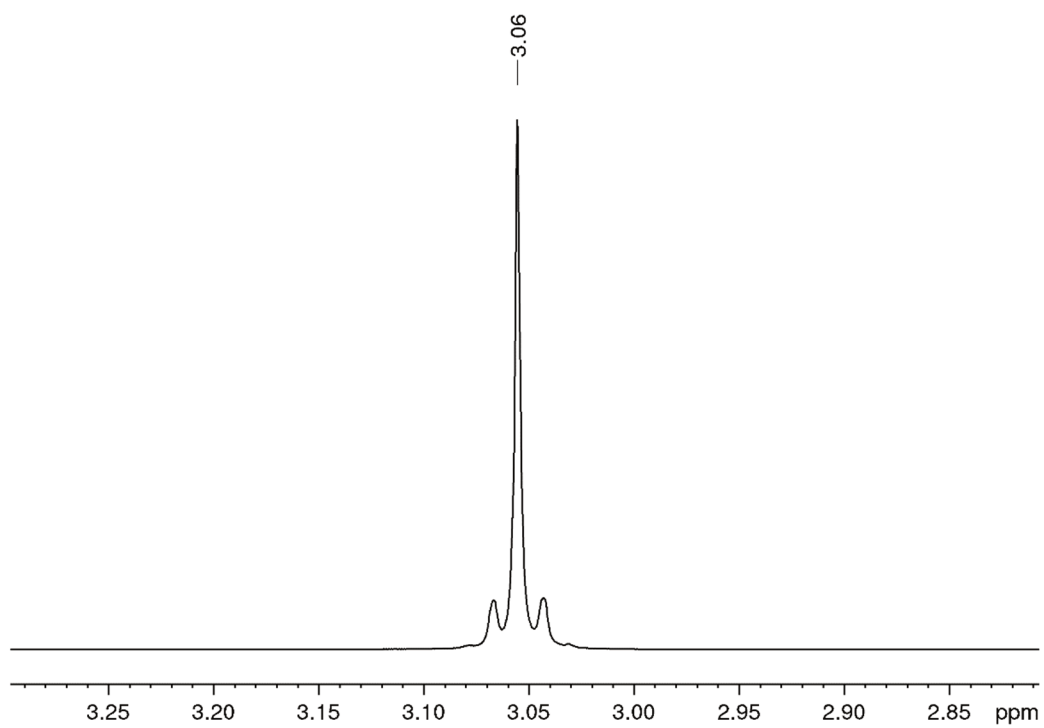


**Fig. S10:** Section of experimental  $^{29}\text{Si}$  refocused INEPT NMR spectrum of compound **Si-HEDP** (bottom) together with simulated  $A_2XX'$  spectra for both trimethylsilyl groups at phosphonate (middle) and only one group (top).

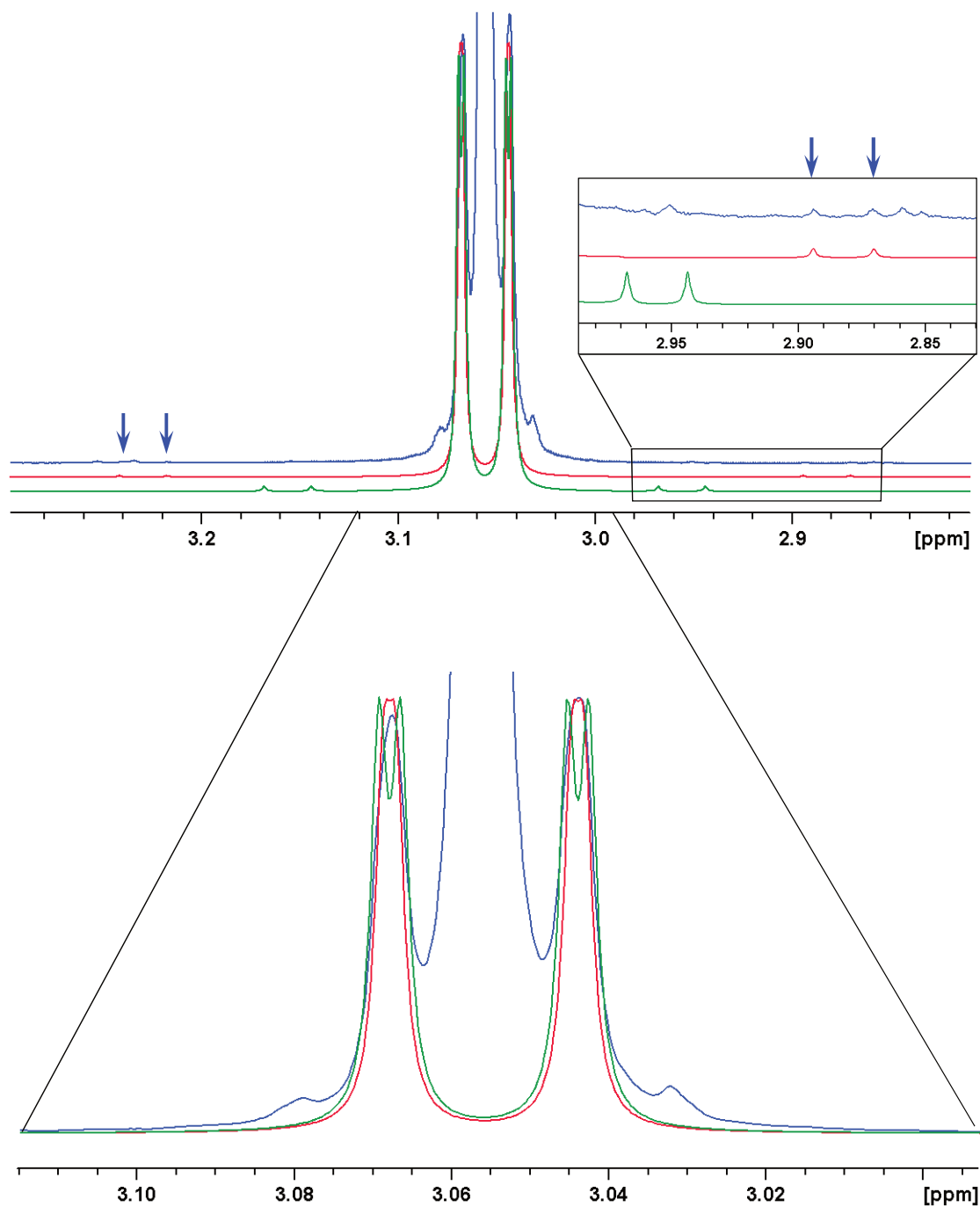
For **Si-HEDP** the  $^{29}\text{Si}$  satellites are resolved in the  $^{31}\text{P}$  spectrum as shown in Fig. S11. Their linewidth is noticeable larger than those of the parent signal. This can be due to the slightly different  $^2J(\text{SiP})$  coupling constants of the two different  $\text{Me}_3\text{SiO-}$  groups. But it is also caused by the coupling pattern, as the calculation showed. Fig. S12 gives the experimental spectrum and calculated spectra for two different  $^2J(\text{PP})$ . In addition, it demonstrates that the intensity and position of the two small satellite doublets (see arrows) again depends mainly on the size of  $^2J(\text{PP})$ .

The experimental  $^{31}\text{P}$  spectrum cannot be completely described using an  $A_2XX'$ - system, as the small satellite signals on both sides of the main signal show in Fig. S12 (intensity less than 1%). Regarding the high number of  $\text{Me}_3\text{SiO-}$  groups in the molecule, the probability of having more than one  $^{29}\text{Si}$  nucleus in the molecule is about 1%, which leads to an even more complex coupling pattern and may be the reason for these satellites.

In principle, the situation discussed above for silicon and phosphorus also holds for the methyl groups in the  $^{13}\text{C}$  spectra. Again, triplets can be observed not only for  $\text{Me}_3\text{SiO-}$  at the PCP- bridge with  $^4J(\text{CP}) = 0.8$  Hz but also for  $\text{Me}_3\text{SiO-}$  at phosphorus with  $^3J(\text{CP}) = 1.3$  Hz.



**Fig. S11:** Section of the  $^{31}\text{P}$  NMR spectrum of **Si-HEDP**.



**Fig. S12:** Section of the  $^{31}\text{P}$  NMR spectrum of Si-HEDP (blue) and calculated spectra using:  
 red: the values for the  $\text{Me}_3\text{SiO-}$  moiety with  $\delta(^{29}\text{Si}) = 21.13$  ppm from Table S1 green: the same but  $^2J(\text{PP}) = 20$  Hz

## References

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