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Supporting information for article:

Unusual flash cooling-induced phase in silanol crystal Ph₃SiOH

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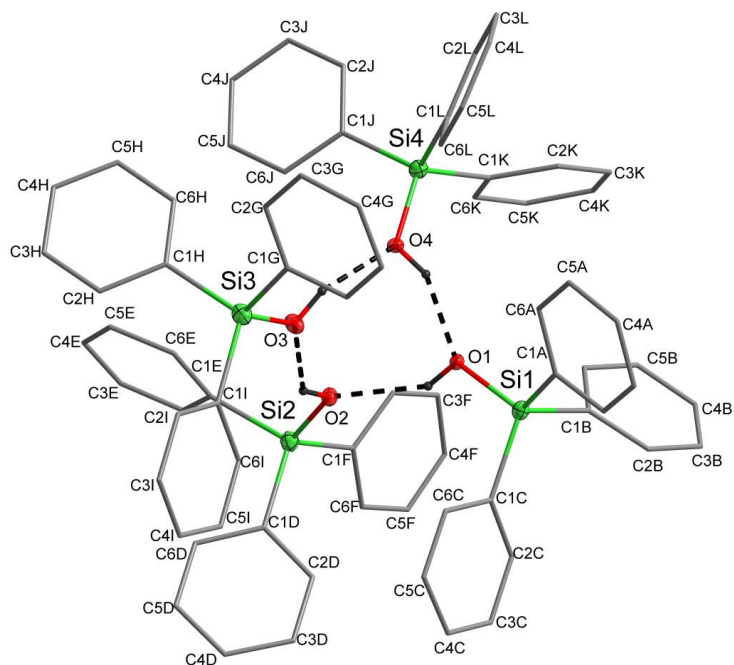
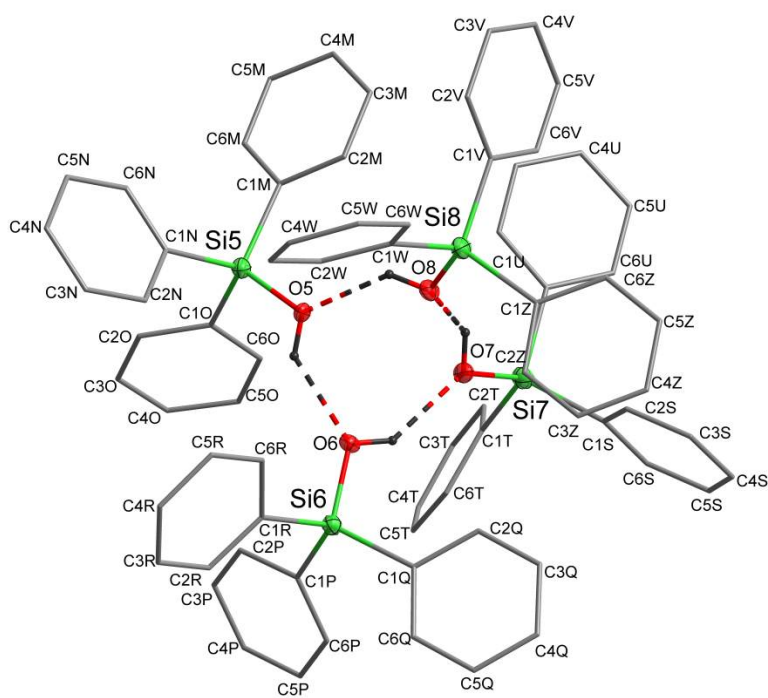
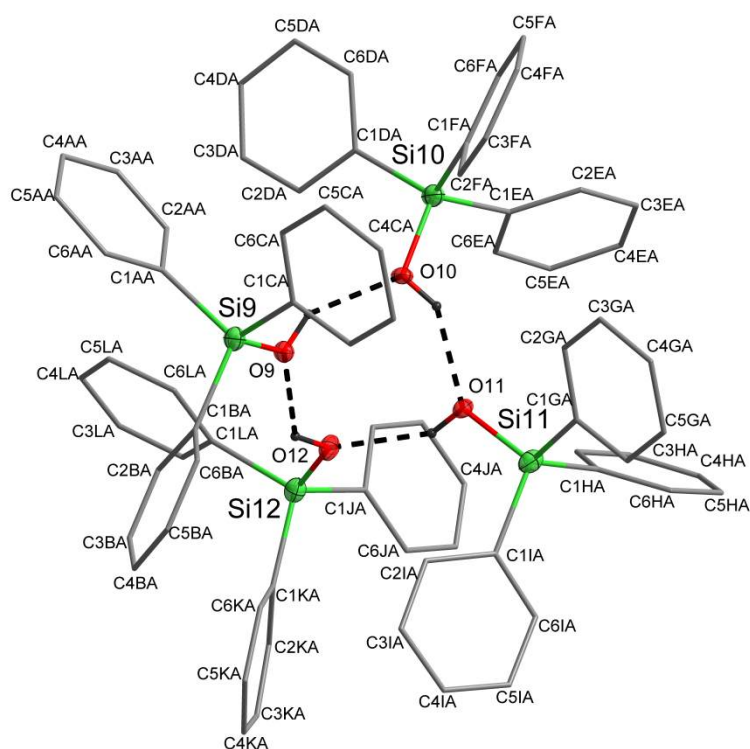
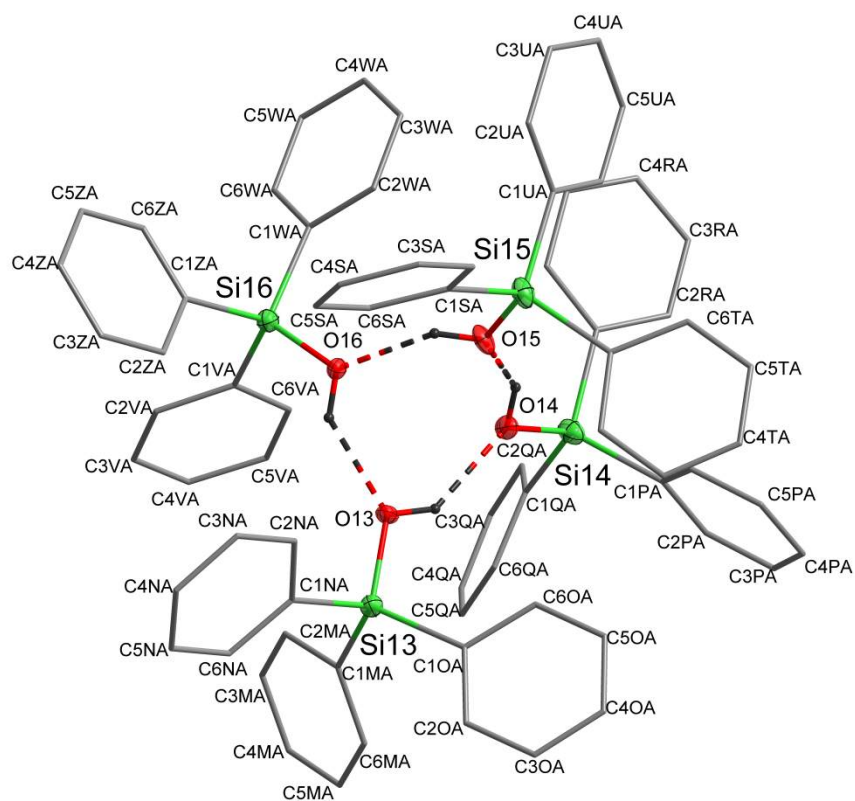
S1. Atom-numbering schemes for tetramers in the phase II**Figure S1.** Atom-numbering scheme for the tetramer *T1* in the phase II at 80 K.

Figure S2. Atom-numbering scheme for the tetramer *T2* in the phase II at 80 K.**Figure S3.** Atom-numbering scheme for the tetramer *T3* in the phase II at 80 K.**Figure S4.** Atom-numbering scheme for the tetramer *T4* in the phase II at 80 K.

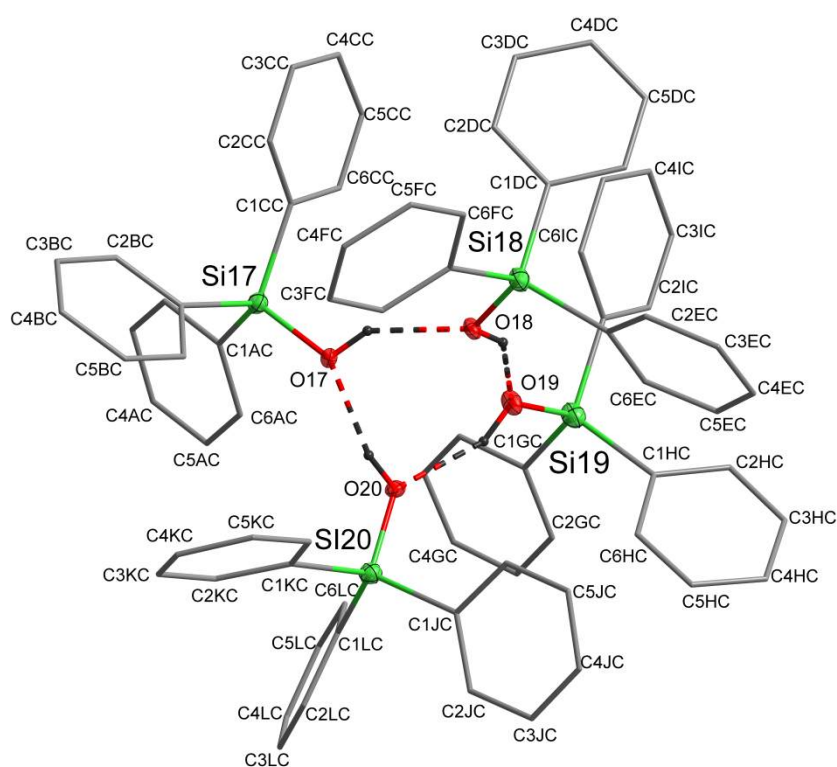


Figure S5. Atom-numbering scheme for the tetramer *T5* in the phase II at 80 K.

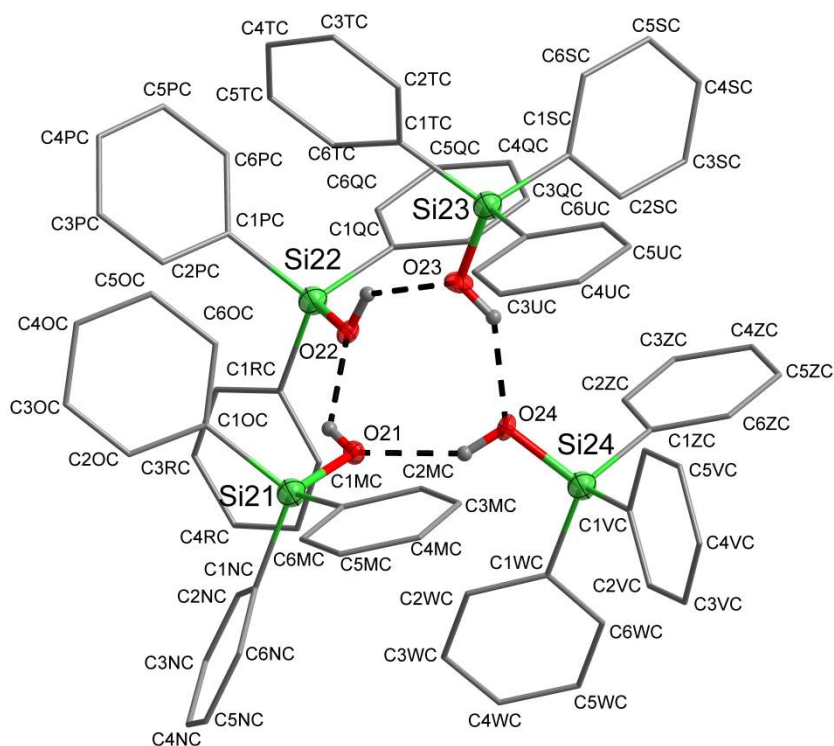


Figure S6. Atom-numbering scheme for the tetramer *T6* in the phase II at 80 K.

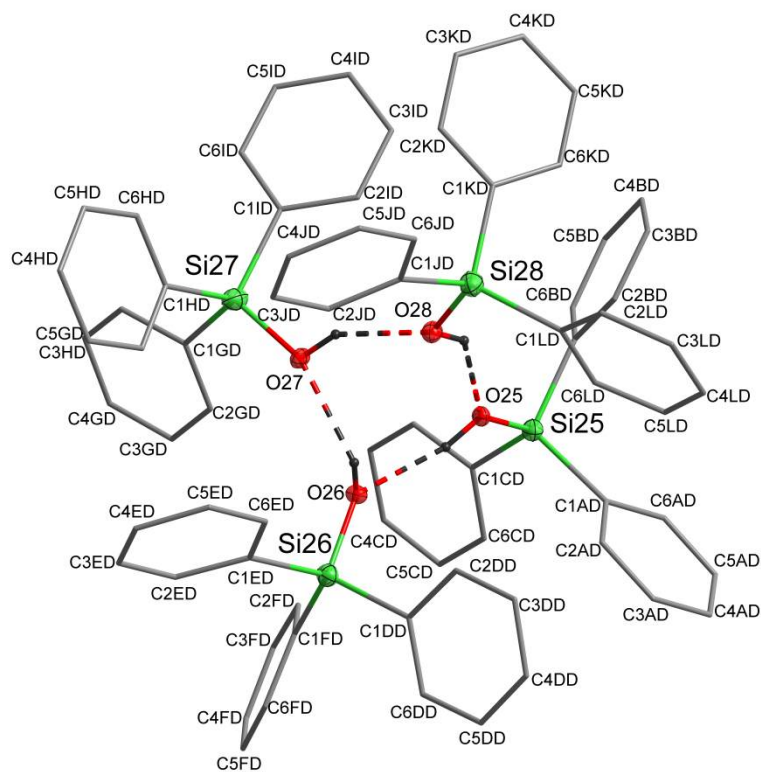


Figure S7. Atom-numbering scheme for the tetramer *T7* in the phase II at 80 K.

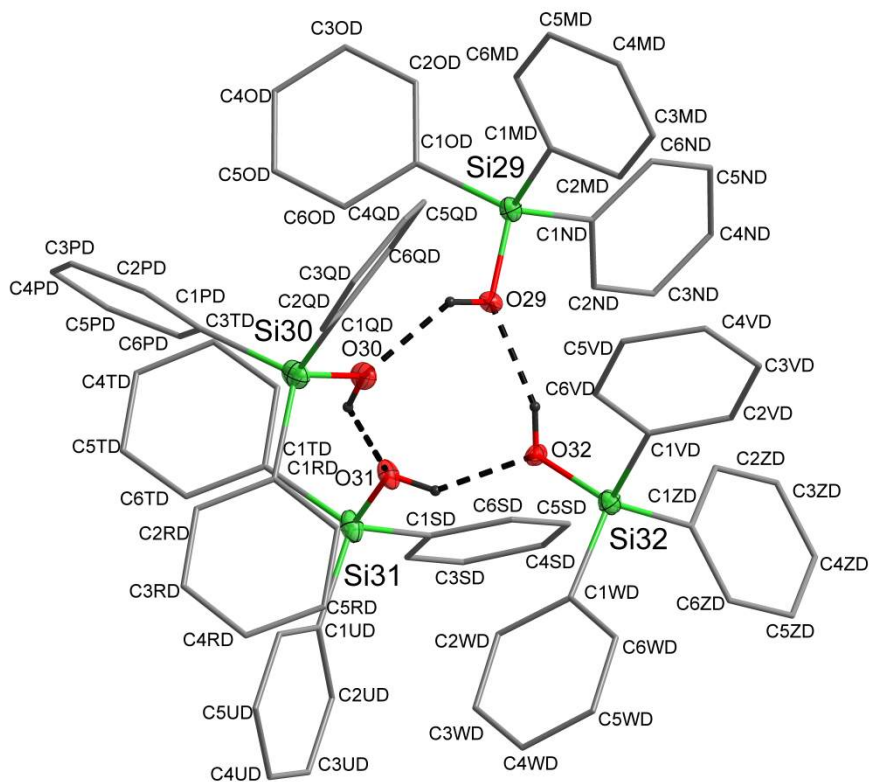


Figure S8. Atom-numbering scheme for the tetramer *T8* in the phase II at 80 K.

Crystal size (mm)	0.21 × 0.12 × 0.09	0.21 × 0.12 × 0.09	0.18 × 0.13 × 0.05	0.18 × 0.13 × 0.05	0.20 × 0.10 × 0.07	0.20 × 0.10 × 0.07	0.40 × 0.34 × 0.22
Crystal colour	colourless	colourless	colourless	colourless	colourless	colourless	colourless
Crystal form	plate	plate	plate	plate	plate	plate	plate
Θ range (°)	2.00 – 74.06	2.00 – 74.06	2.85 – 75.65	2.85 – 75.65	2.11 – 75.31	2.11 – 75.31	3.39 – 28.28
h, k, l range	-27 ≤ h ≤ 27	-27 ≤ h ≤ 27	-27 ≤ h ≤ 27	-27 ≤ h ≤ 27	-18 ≤ h ≤ 18	-18 ≤ h ≤ 18	-20 ≤ h ≤ 20
	-30 ≤ k ≤ 30	-30 ≤ k ≤ 30	-29 ≤ k ≤ 30	-29 ≤ k ≤ 30	-24 ≤ k ≤ 24	-24 ≤ k ≤ 24	-25 ≤ k ≤ 25
	-30 ≤ l ≤ 30	-30 ≤ l ≤ 30	-31 ≤ l ≤ 31	-31 ≤ l ≤ 31	-25 ≤ l ≤ 28	-25 ≤ l ≤ 28	-31 ≤ l ≤ 30
Data collection							
Diffractometer	XtaLAB Synergy R, DW system HyPix-Arc 150	XtaLAB Synergy R, DW system HyPix-Arc 150	XtaLAB Synergy R, DW system HyPix-Arc 150	XtaLAB Synergy R, DW system HyPix-Arc 150	XtaLAB Synergy R, DW system HyPix-Arc 150	XtaLAB Synergy R, DW system HyPix-Arc 150	Xcalibur Gemini Ultra with the CCD Ruby detector
Tmin/Tmax	0.829/0.925	0.829/0.925	0.849/0.943	0.849/0.943	0.859/0.937	0.859/0.937	0.699/0.820
No. of measured, independent and observed ($I > 2\sigma(I)$) reflections	397556, 87781, 82971	397556 , 46617, 44838	223133, 71611, 66316	220935, 47333, 44713	213840, 45079, 40603	213840, 23804, 21872	60840, 27604, 19043
R_{int}	0.026	0.031	0.047	0.049	0.029	0.036	0.035
$(\sin\theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.624	0.624	0.630	0.619	0.629	0.629	0.680

Refinement on	F^2	F^2	F^2	F^2	F^2	F^2	F^2
Data/restraints/ parameters	87781/3/5781	46617/0/2916	71611/3/5781	47333/0/2947	45079/3/2936	23804/0/1517	27604/0/1504
$R[F^2 > 2\sigma(F^2)]$	0.040	0.119	0.066	0.136	0.048	0.055	0.055
$wR(F^2)$	0.114	0.252	0.191	0.289	0.143	0.158	0.143
Goof = S	1.06	1.22	1.02	1.21	1.12	1.03	1.02
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (\AA^{-3})	0.62/ -0.44	0.68/ -0.78	1.33/ -0.78	0.93/ -0.82	0.66 / -0.52	0.98 / -0.52	0.50 / -0.58
Absolute structure parameter	0.318(9)	-	0.359(16)		0.47(2)	-	-

S2. Dependence of unit-cell volume of temperature

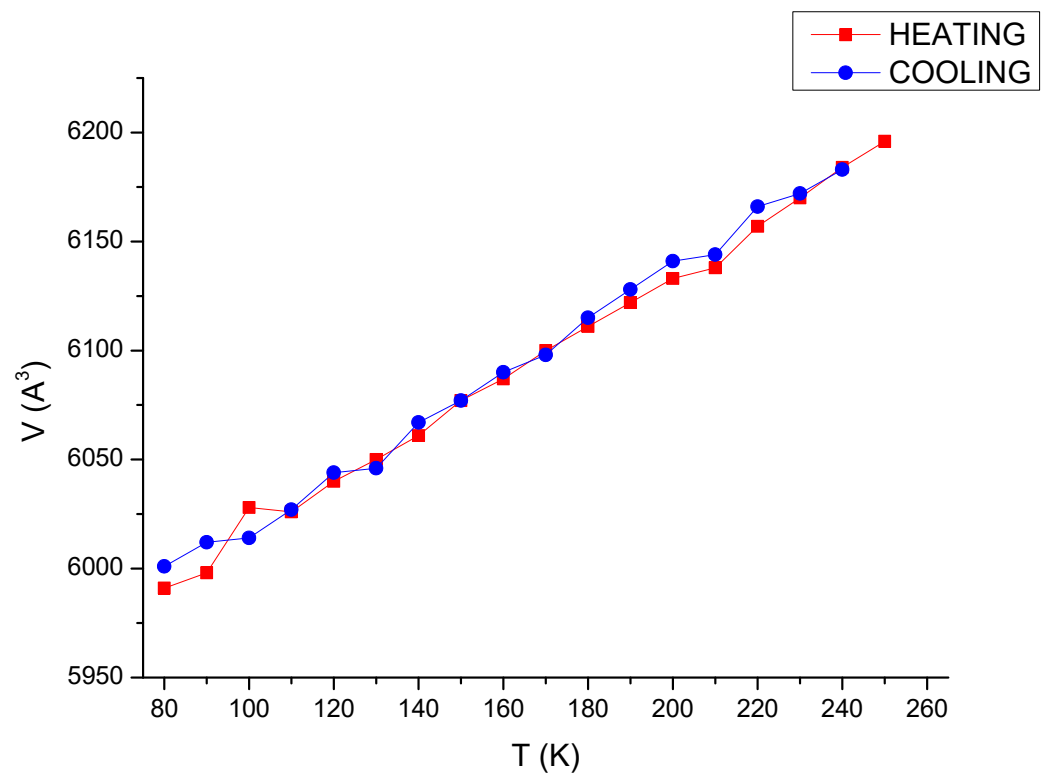


Figure S9. Plot of dependence of the unit-cell volume of temperature upon heating and cooling cycle. The unit-cell for both experiments is assumed as in the phase I.

S3. Refinement

Phase II (model in space group $P\bar{1}$) at 80 and 100 K

After the refinement on the difference Fourier map the additional maxima close to C atoms were observed, which were interpreted as partially disordered phenyl rings and introduced mainly with restraint for the C—C distance of 1.39 Å by means of AFIX 66 command. The disorder of aromatic rings was modelled over two, usually equal or three positions, using PART commands. The components of disordered phenyl rings modelled over three positions were refined isotropically. In the case of displacement parameters of some C atoms the EADP instructions were applied. It is to note, that the structure solution in $P\bar{1}$ is not preferred due to the high R -factors equalled 0.136 and 0.119, respectively.

Phase II (model in space group $P1$) at 80 and 100 K

The preliminary atomic coordinates of O, Si and C atoms were taken from the structure solution of the phase II in the $P\bar{1}$ space group. In the solution the instructions LATT -1 and 'MOVE 1 1 1 -1' and L.S. equalled 1 (1 cycles full-matrix least-squares) were introduced. After the refinement new atomic coordinates were obtained. Afterwards, the atomic coordinates for O, Si, C atoms from the solution in the $P\bar{1}$ space group were introduced to the new solution. Upon refinement, the Fourier difference map did not reveal any high maxima close to C atoms. Uniquely, the structures of phase II in $P1$ space group at 80 K and 100 K are fully ordered with the R -factors significantly lower, viz. 0.066 and 0.040, respectively, compared to the structure solutions in $P\bar{1}$. Therefore this unambiguously proved that the structure solution for the phase II in the $P1$ space group is strongly preferred.

Phase I (model in space group $P\bar{1}$) at 80 and 150 K

In the crystal structure solutions determined at 80 K and 150 K preliminary atomic coordinates of Si, O and C atoms were taken from the crystal data reported by Bowes *et al.* (CSD refcode JIPTIL02; 2002), deposited in the Cambridge Structural Database and refined with reflections collected at 80 K. After the refinement of the positions of all atoms on the difference Fourier map the additional maxima appeared. These peaks were located close to carbon atoms and were interpreted as a partial disorder of phenyl rings as follows.

In the structure solution at 80 K three phenyl rings were disordered. In each of aromatic rings the disorder was modelled over two positions using PART commands, with occupancies of 0.662(3), 0.338(3) (phenyl rings: C1D/C2D/C3D/C4D/C5D/C6D, C1DA/C2DA/C3DA/ C4DA/C5DA/C6DA and

C1F/C2F/C3F/C4F/C5F/C6F, C1FA/C2FA/C3FA/C4FA/C5FA/C6FA). The third phenyl ring was modelled over two positions, with s.o.f. equalled: 0.812(4), 0.188(4) (C1G/C2G/C3G/C4G/C5G/C6G, C1GA/C2GA/C3GA/C4GA/C5GA/C6GA).

In the structure solution at 150 K two phenyl rings were disordered over two positions, with occupancies of 0.758(3) and 0.242(3) (phenyl rings: C1D/C2D/C3D/C4D/C5D/C6D, C1DA/C2DA/C3DA/C4DA/C5DA/C6DA and C1F/C2F/C3F/C4F/C5F/C6F, C1FA/C2FA/C3FA/C4FA/C5FA/C6FA).

In both structures for displacement parameters of some C atoms the EADP instructions were also applied. Moreover, the restraints for the C—C distance of 1.39 Å were applied by means of AFIX 66 command.

Phase I (model in space group *P*1) at 80 K

In the crystal structure solution determined at 80 K preliminary atomic coordinates of Si, O and C atoms were taken from the crystal data in the *P* $\bar{1}$ space group reported by Nieger *et al.* (CSD refcode JIPTIL01; Nieger, 2001), deposited in the Cambridge Structural Database and refined with reflections collected at 80 K. In the structure solution the instructions: LATT -1, 'MOVE 1 1 1 -1' and L.S. equalled 1 (1 cycles full-matrix least-squares) were introduced. After the refinement new atomic coordinates were obtained. Afterwards, the atomic coordinates for O, Si, C atoms from the structure solution in the *P* $\bar{1}$ space group were introduced to the new solution. Upon the refinement the final difference Fourier map revealed additional maxima close to C atoms, which were introduced as carbon atoms of partially disordered phenyl rings.

Two phenyl rings were disordered over two positions, with occupancies of 0.651(5) and 0.349(5) (phenyl rings: C1T/C2T/C3T/C4T/C5T/C6T, C1TR/C2TR/C3TR/C4TR/C5TR/C6TR and C1U/C2U/C3U/C4U/C5U/C6U, C1UR/C2UR/C3UR/C4UR/C5UR/C6UR). The disorder of another two phenyl rings was modelled over two positions with s.o.f. equalled 0.555(3) and 0.445(3) (C1W/C2W/C3W/C4W/C5W/C6W, C1WW/C2WW/C3TWW/C4WW/C5WW/C6TR and C1Z/C2Z/C3Z/C4Z/C5Z/C6Z, C1ZZ/C2ZZ/C3ZZ/C4ZZ/C5ZZ/C6ZZ). Moreover, the EADP instructions were applied for displacement parameters of some C atoms as well as restraints for the C—C distance of 1.39 Å were applied by means of AFIX 66 command.

Table S2. Geometry of O—H \cdots O hydrogen bonds in the phase II.

O–H···O	D–H (Å)	H···A (Å)	D···A (Å)	<(D–H···A) (°)
O1–H1···O2	0.84	1.95	2.66193)	142
O2–H2···O3	0.84	1.97	2.647(3)	137
O3–H3···O3	0.84	1.91	2.663(3)	149
O4–H4···O1	0.84	1.86	2.640(3)	154
O5–H5···O6	0.84	1.98	2.657(4)	137
O6–H6···O7	0.84	1.96	2.668(3)	142
O7–H7···O8	0.84	2.00	2.657(3)	135
O8–H8···O5	0.84	1.97	2.636(3)	135
O9–H9···O10	0.84	1.95	2.688(3)	147
O10–H10···O11	0.84	1.96	2.687(3)	145
O11–H11···O12	0.84	1.94	2.689(4)	147
O12–H12···O9	0.84	2.05	2.693(3)	132
O13–H13···O14	0.84	1.98	2.672(3)	140
O14–H14···O15	0.84	1.95	2.648(4)	140
O15–H15···O16	0.84	1.93	2.651(3)	144
O16–H16···O13	0.84	1.95	2.651(3)	140
O17–H17···O18	0.84	1.93	2.673(3)	146
O18–H18···O19	0.84	1.96	2.683(3)	144

O19–H19···O20	0.84	1.93	2.680(3)	148
O20–H20···O17	0.84	1.85	2.643(3)	156
O21–H21···O22	0.84	1.94	2.659(3)	144
O22–H22···O23	0.84	2.01	2.662(3)	134
O23–H23···O24	0.84	1.91	2.615(3)	141
O24–H24···O21	0.84	1.90	2.642(3)	146
O22–H22···O23	0.84	1.88	2.681(3)	160
O25–H25···O26	0.84	1.12	2.660(3)	122
O26–H26···O27	0.84	1.94	2.701(3)	151
O27–H27···O28	0.84	1.94	2.701(3)	151
O28–H28···O25	0.84	2.04	2.723(3)	138
O29–H29···O30	0.84	1.97	2.663(4)	139
O30–H30···O31	0.84	1.93	2.642(4)	142
O31–H31···O32	0.84	1.91	2.628(3)	142
O32–H32···O29	0.84	1.89	2.648(3)	149

Table S3. Values of selected geometrical parameters (Å) in phases I and II.

Phase, space group, temperature (K)	II, P1, 80(2) K	II, P1, 100(2) K	I, P1, 80(2) K
Si1–O1	1.640(2)	1.637(3)	1.653(4)
Si2–O2	1.643(2)	1.645(4)	1.643(5)
Si3–O3	1.650(2)	1.649(4)	1.635(5)
Si4–O4	1.651(2)	1.651(3)	1.648(4)
Si5–O5	1.645(2)	1.641(4)	1.648(4)
Si6–O6	1.649(2)	1.647(4)	1.640(4)
Si7–O7	1.643(3)	1.639(4)	1.657(5)
Si8–O8	1.646(2)	1.652(4)	1.651(5)
Si9–O9	1.655(2)	1.654(4)	1.643(4)
Si10–O10	1.651(2)	1.646(4)	1.647(5)
Si11–O11	1.637(2)	1.632(4)	1.658(5)
Si12–O12	1.641(3)	1.638(4)	1.635(4)
Si13–O13	1.645(2)	1.649(4)	1.647(4)
Si14–O14	1.639(2)	1.635(4)	1.652(4)
Si15–O15	1.647(2)	1.650(4)	1.625(5)
Si16–O16	1.644(2)	1.645(4)	1.642(5)
Si17–O17	1.645(2)	1.641(3)	
Si18–O18	1.649(2)	1.646(4)	
Si19–O19	1.644(2)	1.641(4)	
Si20–O20	1.642(2)	1.642(3)	
Si21–O21	1.646(2)	1.643(4)	
Si22–O22	1.645(2)	1.641(4)	
Si23–O23	1.651(3)	1.651(4)	
Si24–O24	1.647(2)	1.647(4)	
Si25–O25	1.654(2)	1.650(4)	
Si26–O26	1.644(2)	1.648(3)	

Si27–O27	1.644(2)	1.643(4)
Si28–O28	1.658(2)	1.665(4)
Si29–O29	1.645(2)	1.640(4)
Si30–O30	1.650(3)	1.651(4)
Si31–O31	1.648(2)	1.646(4)
Si32–O32	1.646(2)	1.641(4)

Table S4. Geometry of C–H $\cdots\pi$ interactions in the phase II.

C–H $\cdots\pi$	H \cdots Cg (Å)	C \cdots Cg (Å)	\angle (C–H \cdots Cg) (°)	T \cdots T contacts
C2D–H2D \cdots Cg3	2.97	3.63	127	T1 \cdots T1
C2I–H2I \cdots Cg92 ⁱⁱⁱ	2.93	3.64	132	T1 \cdots T8 ⁱⁱⁱ
C4B–H4B \cdots Cg16 ⁱ	2.78	3.57	141	T1 \cdots T2 ⁱ
C4L–H4L \cdots Cg39 ^{iv}	2.78	3.55	143	T1 \cdots T4 ^{iv}
C3V–H3V \cdots Cg61 ⁱⁱⁱ	2.99	3.68	131	T2 \cdots T6 ⁱⁱⁱ
C5T–H5T \cdots Cg16	2.96	3.71	137	T2 \cdots T2
C3BA–H3BA \cdots Cg57 ^v	2.81	3.51	131	T3 \cdots T5 ^v
C6BA–H6BA \cdots Cg72 ⁱⁱⁱ	2.97	3.68	133	T3 \cdots T6 ⁱⁱⁱ
C4FA–H4FA \cdots Cg17 ⁱ	2.90	3.68	140	T3 \cdots T2 ⁱ
C3KA–H3KA \cdots Cg81	2.82	3.67	149	T3 \cdots T7
C2MA–H2MA \cdots Cg46	2.89	3.72	148	T4 \cdots T4
C5QA–H5QA \cdots Cg37	2.94	3.64	131	T4 \cdots T4
C4BC–H4BC \cdots Cg64 ^{vi}	2.70	3.49	140	T5 \cdots T6 ^{vi}
C6BC–H6BC \cdots Cg59	2.96	3.66	132	T5 \cdots T5
C3CC–H3CC \cdots Cg4 ^{vii}	2.91	3.72	144	T5 \cdots T1 ^{vii}
C4LC–H4LC \cdots Cg87 ^{viii}	2.79	3.54	137	T5 \cdots T8 ^{viii}
C5TC–H5TC \cdots Cg64	3.00	3.81	144	T6 \cdots T6
C4AD–H4AD \cdots Cg46	2.86	3.70	149	T7 \cdots T4

C3BD–H3BD...Cg9 ^{vii}	2.78	3.53	136	$T7 \cdots T1^{vii}$
C6BD–H6BD...Cg24 ⁱⁱ	2.99	3.67	130	$T7 \cdots T2^{ii}$
C4FD–H4FD...Cg65 ^{vi}	2.85	3.60	137	$T7 \cdots T6^{vi}$
C4HD–H4HD...Cg77	2.85	3.67	145	$T7 \cdots T7$

Symbol T – kind of tetramer: $T1, T2, \dots, T8$. Symmetry codes: (i) = $x, y+1, z$; (ii) = $x-1, y, z$; (iii) = $x+1, y, z$; (iv) = $x+1, y+2, z+1$; (v) = $x+1, y+1, z+1$; (vi) = $x, y-1, z$; (vii) = $x-1, y-1, z-1$; (viii) = $x-1, y-2, z-1$. Centres of aromatic rings (Cg): Cg3 [C1C/C2C/C3C/C4C/C5C/C6C]; Cg4 [C1D/C2D/C3D/C4D/C5D/C6D]; Cg9 [C1I/C2I/C3I/C4I/C5I/C6I]; Cg16 [C1P/C2P/C3P/C4P/C5P/C6P]; Cg17 [C1Q/C2Q/C3Q/C4Q/C5Q/C6Q]; Cg24 [C1Z/C2Z/C3Z/C4Z/C5Z/C6Z]; Cg37 [C1MA/C2MA/C3MA/C4MA/C5MA/C6MA]; Cg39 [C1OA/C2OA/C3OA/C4OA/C5OA/C6OA]; Cg46 [C1VA/C2VA/C3VA/C4VA/C5VA/C6VA]; Cg57 [C1IC/C2IC/C3IC/C4IC/C5IC/C6IC]; Cg59 [C1KC/C2KC/C3KC/C4KC/C5KC/C6KC]; Cg61 [C1MC/C2MC/C3MC/C4MC/C5MC/C6MC]; Cg64 [C1PC/C2PC/C3PC/C4PC/C5PC/C6PC]; Cg65 [C1QC/C2QC/C3QC/C4QC/C5QC/C6QC]; Cg72 [C1ZC/C2ZC/C3ZC/C4ZC/C5ZC/C6ZC]; Cg77 [C1ED/C2ED/C3ED/C4ED/C5ED/C6ED]; Cg81 [C1ID/C2ID/C3ID/C4ID/C5ID/C6ID]; Cg87 [C1OD/C2OD/C3OD/C4OD/C5OD/C6OD]; Cg92 [C1TD/C2TD/C3TD/C4TD/C5TD/C6TD].

S4. C–H... π interactions in the phase I

Table S5. Geometry of C–H... π interactions in the phase I in $P\bar{1}$ space group.

C–H... π	H...Cg (Å)	C...Cg (Å)	\angle (C–H...Cg) (°)	$T \cdots T$ contacts
C2D–H2D...Cg25	2.86	3.60	135	$T1 \cdots T3$
C3B–H3B...Cg19 ^x	3.00	3.77	140	$T1 \cdots T2^x$
C3K–H3K...Cg6	2.85	3.71	150	$T1 \cdots T1$
C4C–H4C...Cg20 ^{ix}	2.83	3.61	140	$T1 \cdots T2^{ix}$
C4F–H4F...Cg18 ^{vi}	2.99	3.82	147	$T1 \cdots T2^{vi}$
C4J–H4J...Cg21 ^x	2.80	3.59	141	$T1 \cdots T2^x$
C6J–H6J...Cg11	2.94	3.63	130	$T1 \cdots T1$

Symbol $T1, T2$ – kind of tetramer

Symmetry codes: (vi) = $x, y-1, z$; (ix) = $-x+2, -y+1, -z+1$; (x) = $-x+1, -y+1, -z+1$;

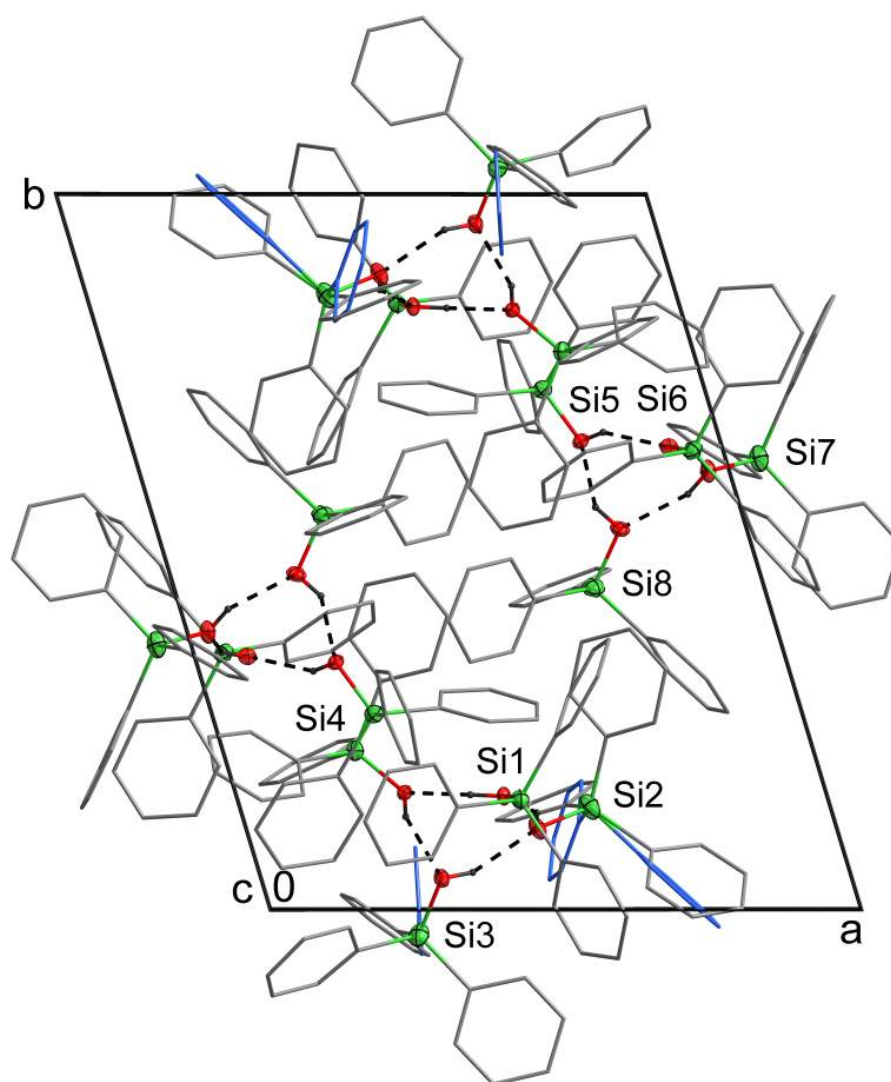
S5. Crystal structure of PPh_3SiOH_5 in $P\bar{1}$ space group in the phase I at 80 K.

Figure S10. The structure of the phase I at 80 K ($P\bar{1}$ space group); minor components of disordered phenyl rings were depicted in blue colour. H atoms of aromatic rings were removed for clarity.

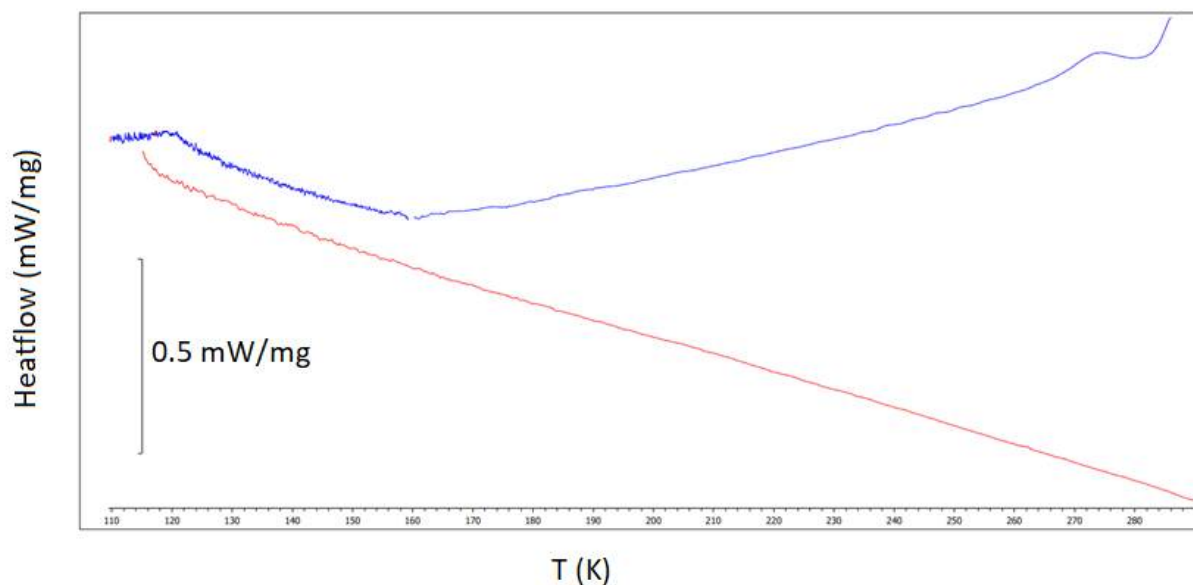
S6. DSC and heat capacity.

Figure S11. Temperature dependence of the heat flow for the crystal of Ph_3SiOH . Blue curve – cooling of the crystal at the rate of 10 K min^{-1} down to 160 K and than at the rate 2 K min^{-1} ; red curve – heating of the crystal at the rate of 10 K min^{-1} .

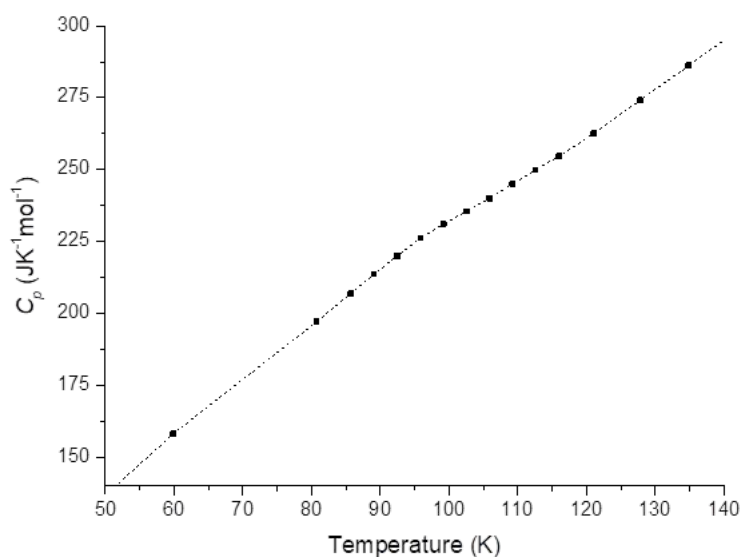


Figure S12. Temperature dependence of the specific heat C_p on gradual cooling shown in the temperature range 50 - 140 K.

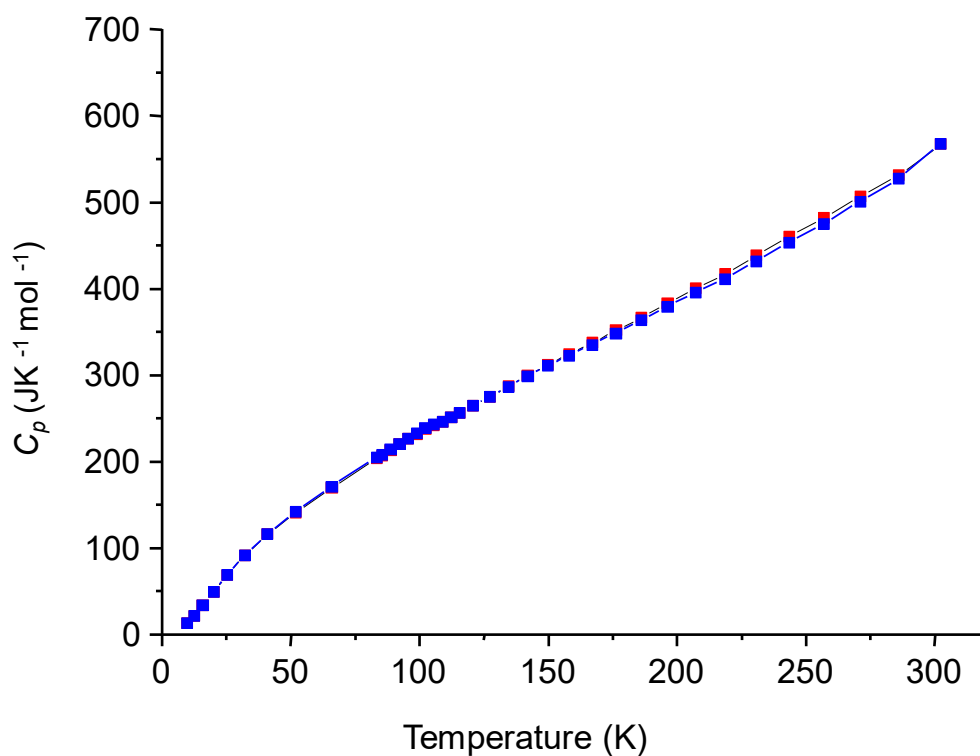


Figure S13. Temperature dependence of the specific heat C_p on gradual cooling from 300 K down to 10 K (blue points and curve) and on gradual heating from 10 K up to 300 K (red points and curve).

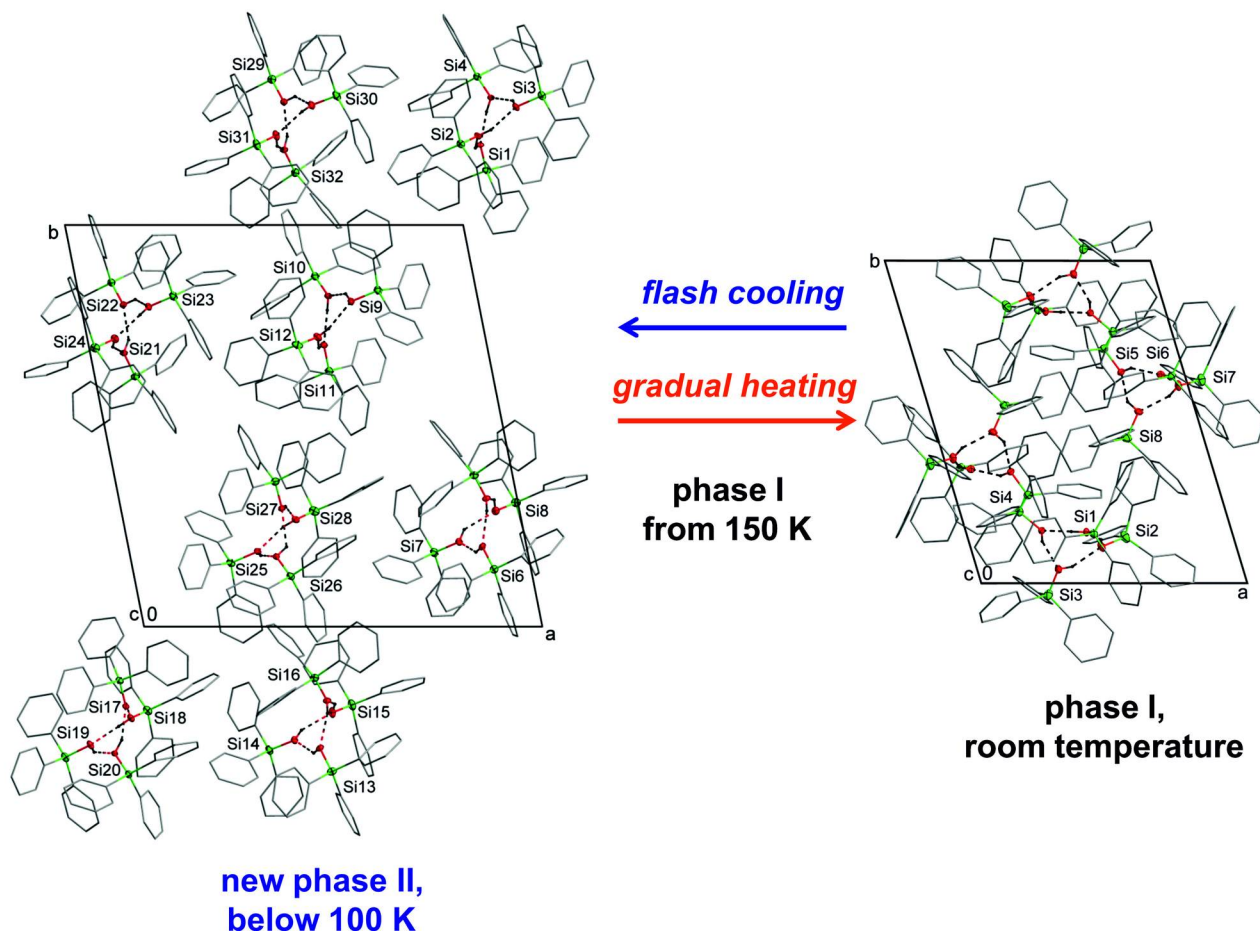


Figure S14. A diagram presented the occurrence of the phases I and II. The reappearance of the phase I was observed during gradual heating to ~ 150 K (viz. ~ 3.3 K min^{-1}). The structure of the phase I was obtained at 80 K ($P\bar{1}$ space group); minor components of disordered phenyl rings and H atoms of aromatic rings were removed for clarity. The unit cell in the phase I was presented in another projection than in the Figure 1.

Hamilton's R-factor test

Hamilton's *R*-ratio test confirmed the choice of *P1* space group, which was performed according to Hamilton (1965). The following hypothesis was tested.

H_0 : $P\bar{1}$ is the correct space group.

The crystal structure solutions at 80 K in *P1* and $P\bar{1}$ space groups are compared.

For the test weighted *R* factors $wR(F^2)$ for the structure solutions in *P1* and $P\bar{1}$ space groups were used.

The value of the experimental *R*-factor ratio denoted as *F* equals:

$$F = \frac{wR(F^2, P\bar{1})}{wR(F^2, P1)} = \frac{0.252}{0.114} = 2.21$$

Experimental *F* value exceeds the value $F_{b,n-m,\alpha}$ for which: $P[F > F_{b,n-m,\alpha}] = \alpha = 0.05$

(degrees of freedom: $b = 2865$; $n-m = 82000$)

For the significance level $\alpha = 0.05$ the critical value equals $F_{2865,82000,0.05} = 0.9499993 \approx 0.95$.

Therefore, the hypothesis H_0 is rejected at the significance level 0.05. The correct space group is *P1*.

The critical value has been established using R computer package (2020).

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <https://www.R-project.org/>.