

## Solid-state dynamics and single-crystal to single-crystal structural transformations in octakis(3-chloropropyl)octasilsesquioxane and octavinyl octasilsesquioxane.

A. Kowalewska, M. Nowacka, M. Włodarska, B. Zgardzińska, R. Zaleski, M. Oszejca, J. Krajenta and S. Kaźmierski

### Electronic Supplementary Information

#### 1. Experimental

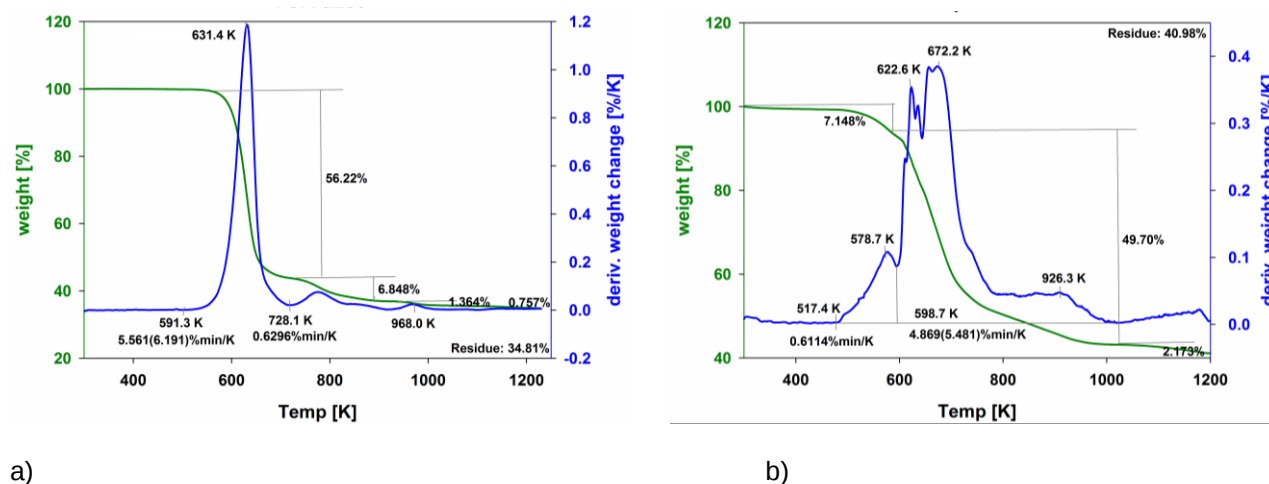
##### 1.1. Materials:

Octavinyl octasilsesquioxane [ $T_8(CH=CH_2)_8$ ] was purchased from Hybrid Plastics. It is fine-crystalline material (<1 mm). Octakis(3-chloropropyl)octasilsesquioxane [ $T_8(CH_2CH_2CH_2Cl)_8$ ] was prepared using the procedure applied earlier by us for the synthesis of octakis(3-mercaptopropyl)octasilsesquioxane [1]. Crystals of about 3-5 mm size were grown at room temperature using the vapour diffusion technique using  $CH_2Cl_2$  as the solvent and pentane as the precipitant. All reagents used for the synthesis were of “pure for analysis” grade. All solvents used were purified according to the literature procedures [2].

##### 1.2. Instrumentation:

##### Thermal analysis:

Thermogravimetric measurements were performed using a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) in the atmosphere nitrogen or air (heating rate 10 K /min, resolution 3, sensitivity 3).



**Figure ESI-1.** Thermal stability of  $T_8(CH_2CH_2CH_2Cl)_8$  in the atmosphere of  $N_2$  (a) and air (b) (TGA, heating rate 10 K/min).

Phase transitions of  $T_8(CH=CH_2)_8$  and  $T_8(CH_2CH_2CH_2Cl)_8$  were studied under nitrogen flow by differential scanning calorimetry (DSC) technique using an indium calibrated DSC apparatus (TA Q20, TA Instruments). Thermograms were taken for samples of total mass of 6–8 mg sealed in aluminum pans and pressed slightly in order to ensure good contact with the DSC cell surface. Samples of  $T_8(CH=CH_2)_8$  and  $T_8(CH_2CH_2CH_2Cl)_8$  were heated at 10 K/min as indicated in Table ESI-1.

**Table ESI-1.** DSC parameters for experiments carried out with  $T_8(\text{CH}=\text{CH}_2)_8$  and  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$ . (heating rate 10 K/min)

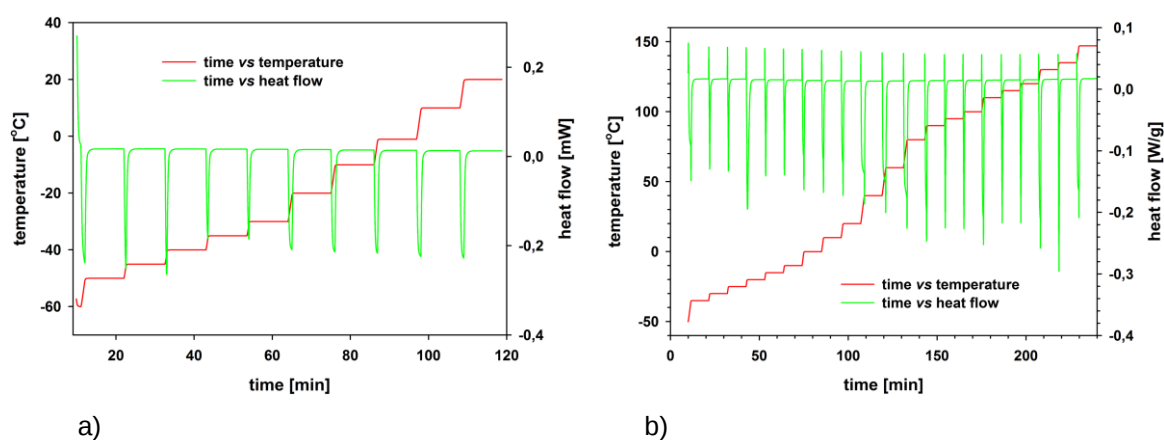
| run                                                 | a [K] | b [K] | c [K] |
|-----------------------------------------------------|-------|-------|-------|
| $T_8(\text{CH}=\text{CH}_2)_8$                      |       |       |       |
| 1 <sup>st</sup> heating                             | RT    | 373   | 373   |
| 1 <sup>st</sup> cooling                             | 373   | 173   | 173   |
| 2 <sup>nd</sup> heating                             | 173   | 373   | 373   |
| 2 <sup>nd</sup> cooling                             | 373   | 173   | 173   |
| 3 <sup>rd</sup> heating                             | 173   | 373   | -     |
| $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$ |       |       |       |
| 1 <sup>st</sup> cooling                             | RT    | 173   | 173   |
| 1 <sup>st</sup> heating                             | 173   | 523   | 523   |
| 2 <sup>nd</sup> cooling                             | 523   | 173   | 173   |
| 2 <sup>nd</sup> heating                             | 173   | 523   | 523   |
| 3 <sup>rd</sup> cooling                             | 523   | 223   | -     |

a - starting temperature

b - final temperature

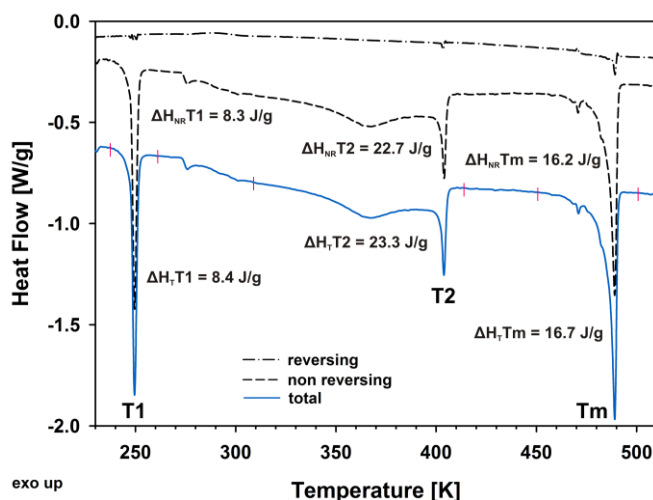
c – temperature of isotherm (1 min) at the end of the run

Another type of heating programming was applied for the studies on the relative changes of heat capacity ( $\Delta C_p$ ).  $T_8(\text{CH}=\text{CH}_2)_8$  was cooled down from RT to 213 K (kept for 1 minute isotherm) and then heated at 10 K/min up to 293 K with several isotherm stops (10 min each at 223 K, 228 K, 233 K, 238 K, 243 K, 253 K, 263 K, 272 K, 283 K, 293 K). Analogously,  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  was cooled down from RT to 223 K (kept for 1 minute isotherm) and then heated at 10 K/min up to 523 K with several isotherm stops (10 min each at 238 K, 243 K, 248 K, 253 K, 258 K, 263 K, 273 K, 283 K, 293 K, 313 K, 333 K, 353 K, 363 K, 368 K, 373 K, 383 K, 388 K, 393 K, 403 K, 408 K, 413 K, 423 K, 433 K, 453 K, 473 K, 483 K, 493 K, 523 K) and cooled down to 453 K. The relative heat capacity change was measured as the heat flow measured for the intervals between the isotherms (Figure ESI-2).



**Figure ESI-2.** Changes in the heat flow during DSC experiment with a mixed 10 K/min ramp and 10 min isothermal intervals for a)  $T_8(\text{CH}=\text{CH}_2)_8$  and b)  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$ .

Thermal characteristics of  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  were also taken using thermally modulated DSC (TMDSC) method. Measurements were performed with a “heating only profile” at a ramp of 3 K/min within the temperature range 223–523 K [modulation period (P) of 20 s and modulation temperature amplitude (A) of 0.159 K] (Figure ESI-3). Similar measurements were performed separately within 223–273 K (ramp 1 K/min; P = 20s; A = 0.053 K) and 413–513 K (ramp 1 K/min; P = 50; A = 0.133). Temperatures of phase transitions and melting were calculated from the total and reversing signals; respective enthalpies  $\Delta H$  were assessed from the endotherms corresponding to solid state transitions and melting within the indicated temperature ranges of the total ( $\Delta H_T$ ) and non-reversing ( $\Delta H_{NR}$ ) heat flow.



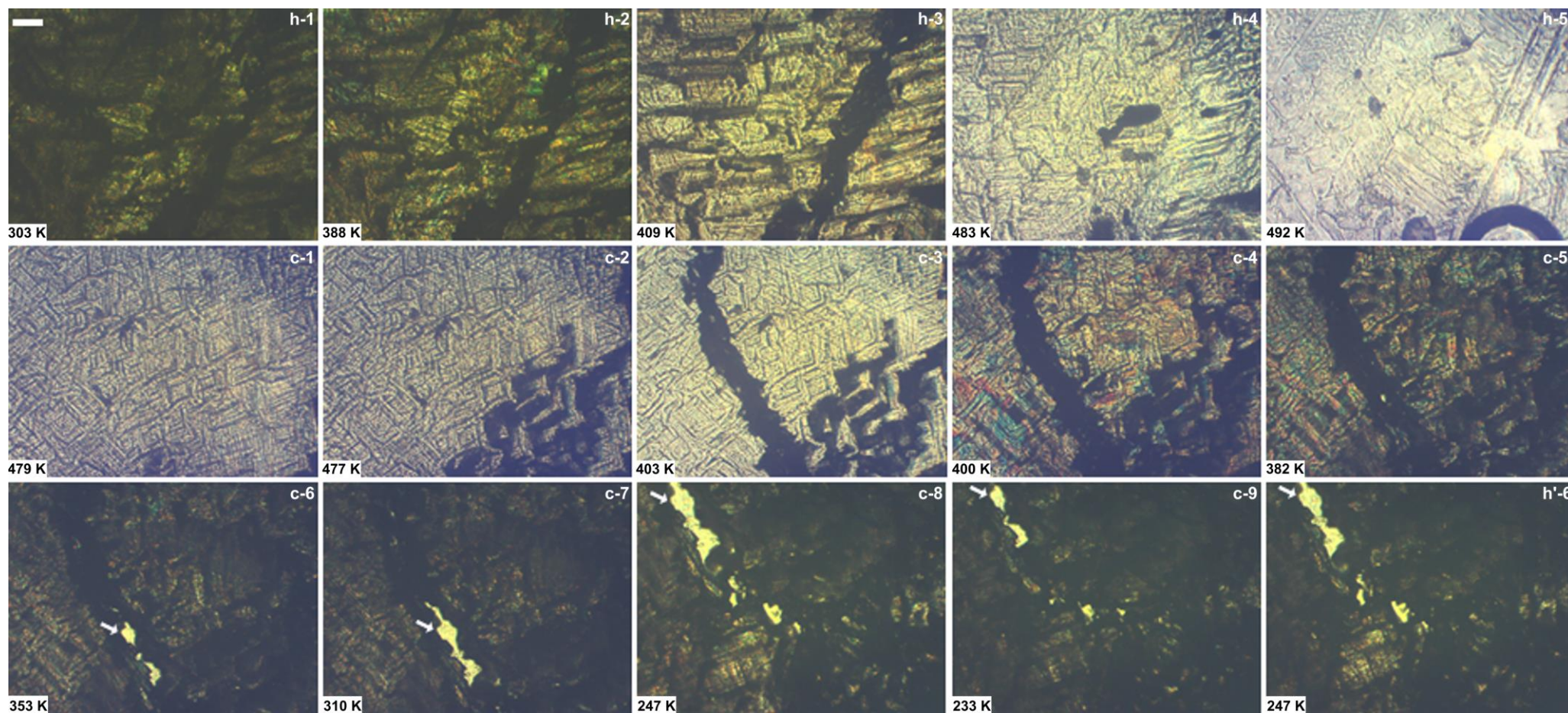
**Figure ESI-3.** TMDSC thermograms recorded for  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  (ramp 3 K/min; P = 20; A = 0.159) – separation of total heat flow on the reversing and non-reversing signals.

#### Polarized light imaging:

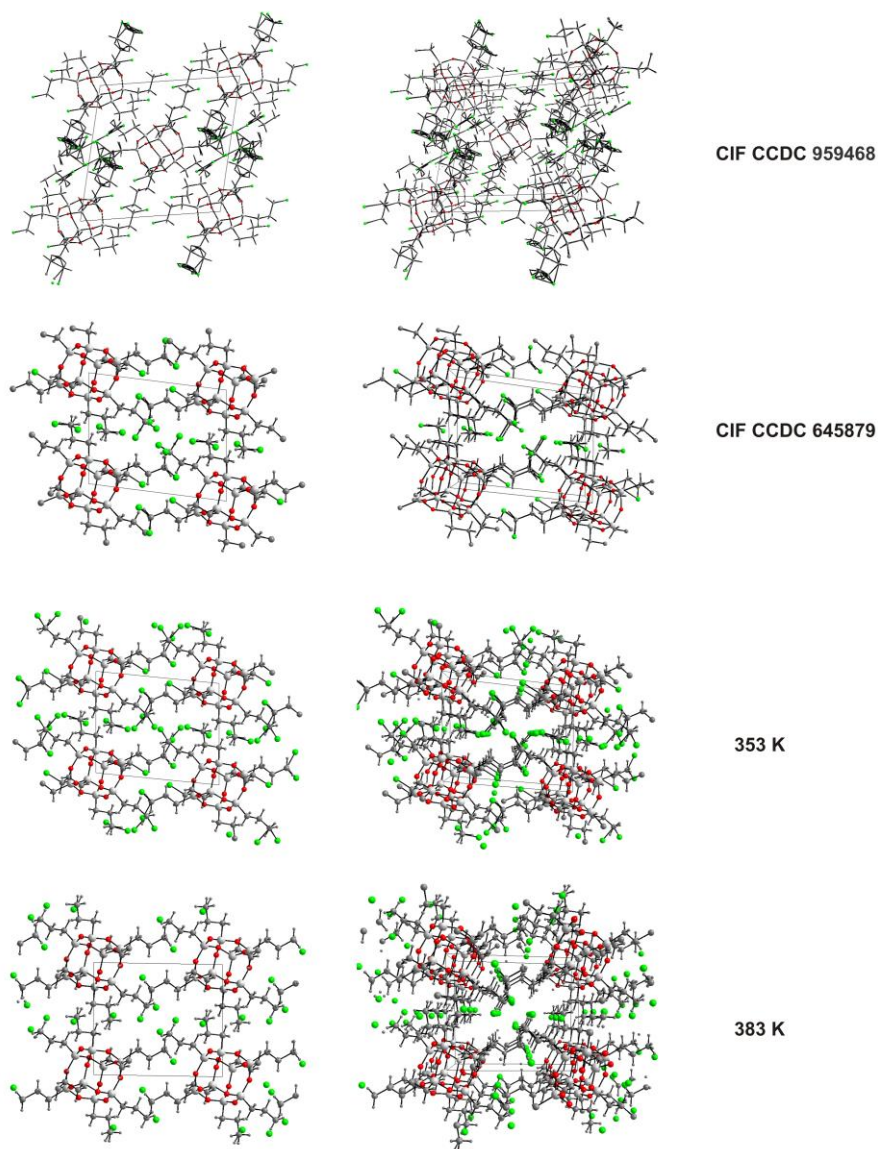
Textures of the compounds in polarized light were observed through a microscope (PZO 25328, with an additional polarizer) in cross-polarized arrangement. A nitrogen-cooled Linkam HFS600E-PB4 hot stage was used to carry out the observations in a wide range of temperatures (173–543 K). Micrographs of the textures were taken with a digital camera. Samples were prepared by placing the material between two parallel plain-glass plates.

#### X-ray powder diffraction (XRD):

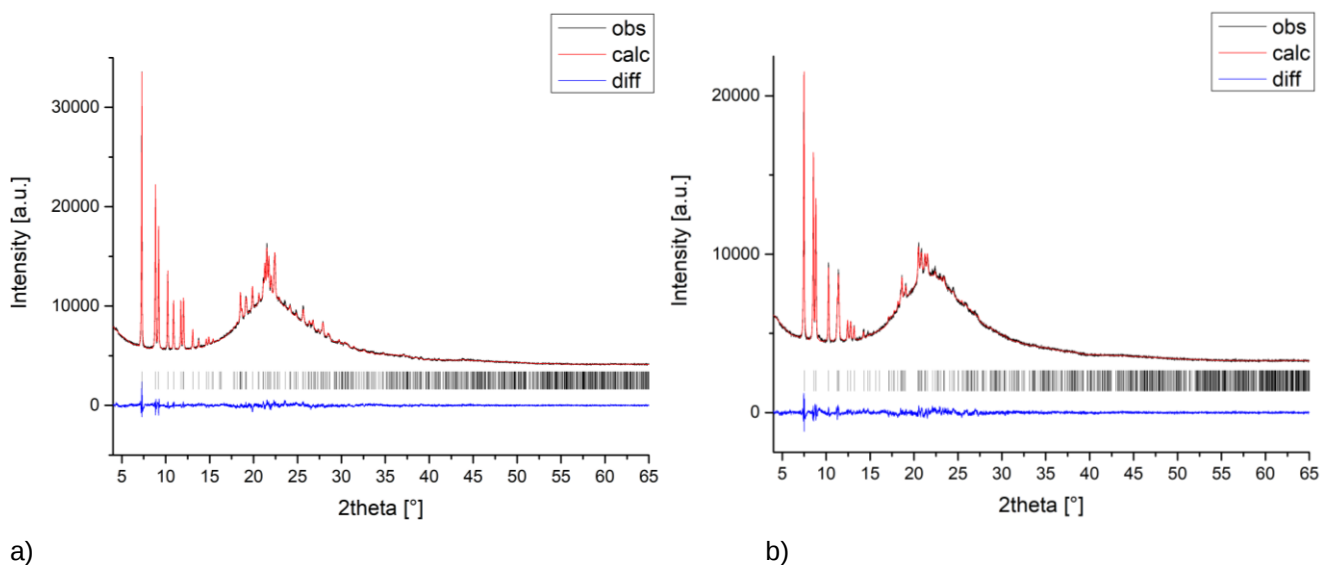
X-ray powder diffraction experiments were performed using a PANalytical X'Pert PRO powder diffractometer equipped with a Cu LFF X-ray source. Since the samples contained relatively light atoms the observed intensities decayed relatively rapidly with increasing diffraction angle. This led to a decision to select the experimental range between  $4^\circ$  and  $65^\circ$  of  $2\theta$  angle according to the preliminary data collected on a diffractometer. Based on the information from the DSC experiments a number of experimental temperatures were selected for the preliminary temperature-dependent diffraction measurements. These revealed that the studied compound reacts with oxygen from residual air present in the heating chamber instead of undergoing a reversible phase transition at higher temperatures. Due to this the sample was packed inside a borosilicate capillary for the remainder of the studies. Heating of the samples during the experiments was accomplished using an OxfordCryosystems Cryostream 700 Plus.



**Figure ESI-4.** Textures of  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  crystals on heating from 303 K (h-1) to 492 K (h-5, melting), cooling to 233 K (c-9) and second heating (h'-6) (nonpolarized light); h-heating, c-cooling run, white bar = 100  $\mu\text{m}$ .



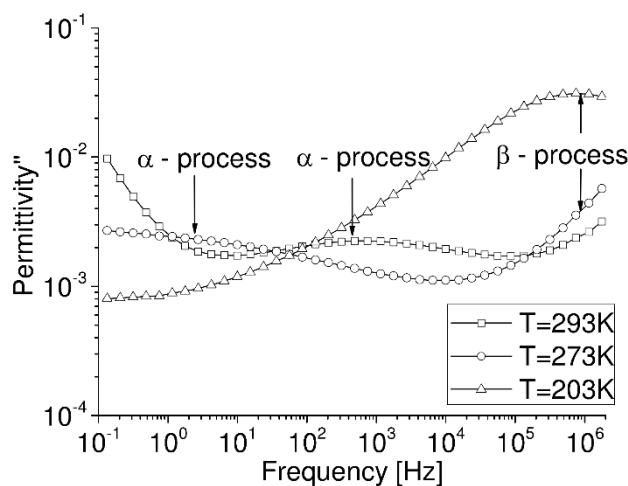
**Figure ESI-5.** Crystal structure of  $T_8(CH_2CH_2CH_2Cl)_8$ : phase A at 200 K [3], phase B at 293 K [4], 353 K (CCDC 1565522) and 383 K (CCDC 1565523).



**Figure ESI-6.** Differential Rietveld curves for  $T_8(CH_2CH_2CH_2Cl)_8$  at 353 K (a) and 383 K (b).

### Dielectric Relaxation Spectroscopy (DRS):

The complex permittivity  $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ , where  $f$  is the frequency and  $\varepsilon'$ ,  $\varepsilon''$  are the real and imaginary components, was recorded in a frequency range of  $10^0$ – $10^6$  Hz using a Novocontrol system comprising an Alpha high-resolution dielectric analyzer and a Quatro cryosystem. The temperature controller provided thermal stabilization of the samples with accuracy better than 0.1 K. Isothermal frequency sweeps at different temperatures were made in the cooling route starting from isotropization temperature for  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$ , and in the heating route for  $T_8(\text{CH}=\text{CH}_2)_8$ . Samples were prepared in a sandwich arrangement between parallel metal electrodes with 10 mm diameter, using 50  $\mu\text{m}$  silica spacers to avoid a short circuit. The amplitude of the measuring AC signal was 1 V. The static dielectric constant was determined at the frequency of 20 kHz.



**Figure ESI-7.** Exemplary dielectric response of  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  at three selected temperatures where relaxation processes  $\alpha$  and  $\beta$  are visible.

### Positron Annihilation Lifetime Spectroscopy (PALS):

A sample with positron source ( $^{22}\text{Na}$ , activity of 0.8 MBq in the Kapton<sup>®</sup> envelope with the thickness of 0.8  $\mu\text{m}$ ), was placed in a vacuum chamber in the sample-source-sample sandwich configuration. Temperature in the chamber was regulated in the range  $133 \div 473$  K using the combination of a heating coil and liquid nitrogen cooling. The temperature was measured by a thermocouple, and controlled by the Shimaden FP21 unit with the accuracy of  $\pm 0.1$  K. The positron annihilation lifetime spectra (PALS) were measured using a standard fast-slow delayed coincidence spectrometer with the resolving time better than 0.23 ns, FWHM. The time of spectrum acquisition was 2 h (six times longer for the selected high-statistics spectra) and at least  $10^6$  counts per spectrum was collected. The spectra were processed by LT 9.2 program [5] assuming three or four exponential components, convoluted with the instrumental resolution curve approximated by a single Gaussian. The correction for positron annihilation in the Kapton<sup>®</sup> was also applied (10%, 382 ps). The high-statistic spectra were additionally analyzed by the MELT program [6, 7] - the obtained results are consistent with the analysis by LT 9.2 program. The exponential components were ascribed to *para*-positronium decay (p-Ps,  $\tau_1 \approx 0.16$  ns), annihilation of free positrons ( $\tau_2 \approx 0.4 \div 0.5$  ns) and to *ortho*-positronium decay (o-Ps, one or two components with lifetimes over 1 ns).

During the measurements, the sample was cooled down from room temperature to 133 K, then heated and cooled again to room temperature. The cycle was repeated to verify the reproducibility of results and verify if the temperature changes of the sample structure are reversible.

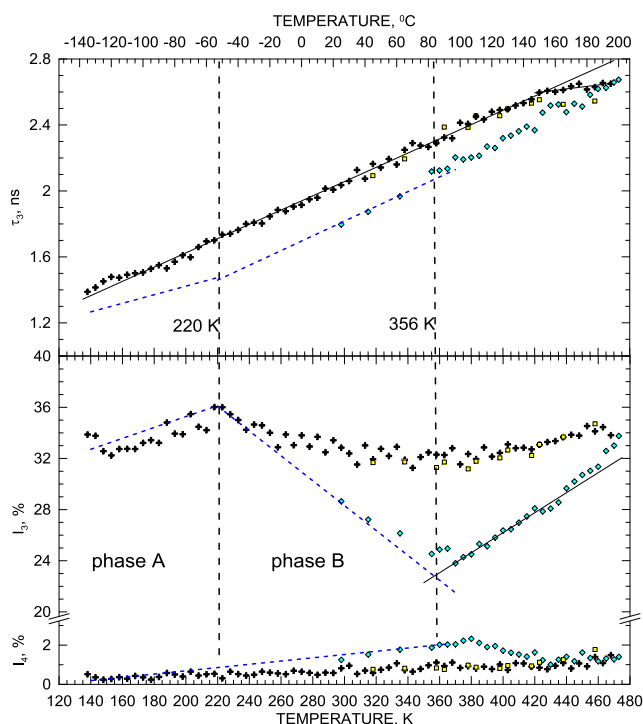
The o-Ps lifetimes ( $\tau_{o-ps}$ ) was used to determine the sizes of free-volume – the radius ( $R$ ) of spherical free volume was calculated using the Tao-Eldrup model [8, 9]:

$$\tau_{o-ps} = \frac{1}{2} \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R} \right]^{-1}$$

where  $\Delta=0.166$  nm is an empirical parameter. The volume of free voids  $V_f = 4/3 \pi R^3$  (expressed in  $\text{\AA}^3$ ) was used in calculation of fractional free volume (expressed in %):

$$f_v = C \cdot V_f \cdot I_{o-ps},$$

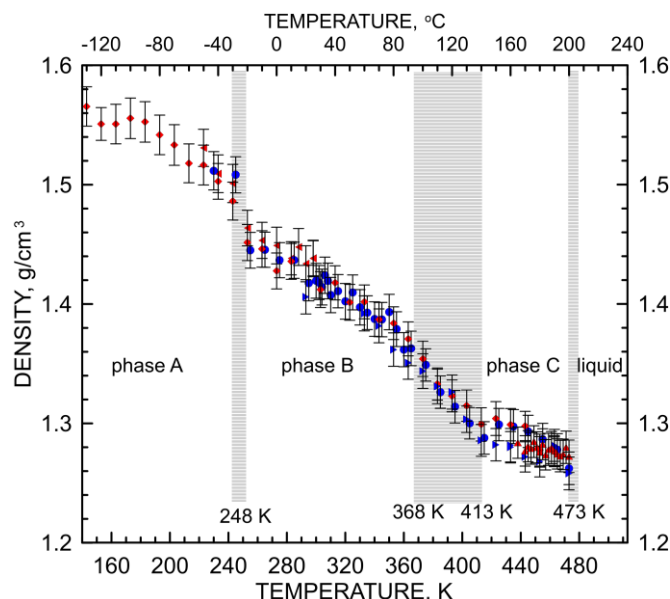
where  $C=0.0018$  is an empirically determined parameter [10, 11] and  $I_{o-ps}$  is the o-Ps intensity (in %).



**Figure ESI-8.** Changes of o-Ps lifetime and intensities as a function of temperature in  $T_8(\text{CH}=\text{CH}_2)_8$  (blue dashed lines correspond to the course of the PALS parameter changes shown in Figure 9, vertical dashed lines – phase transition temperatures). Point shapes correspond to the direction of temperature changes: UP  $\blacklozenge$  DOWN  $+$ , 2<sup>nd</sup> UP  $\bullet$ .

The sample  $T_8(\text{CH}=\text{CH}_2)_8$  was also investigated in an extended temperature range. Exceeding 356 K leads to irreversible structural changes in the sample (Figure ESI-8). Above this temperature the o-Ps intensity  $I_3$  increases up to 34% at 473 K. Further measurements as a function of decreasing temperature show that the changes of PALS parameters no longer reproduce the course observed in the virgin sample (not heated above 356 K). The o-Ps intensity remains at the level of 32-36% and the o-Ps lifetime is longer by about 0.2 ns. The heating affects also the

second o-Ps component ( $\tau_4=16$  ns). First, its intensity  $I_4$  increases with temperature until it reaches maximum at 380 K. Then it decreases until its value is one percent or less at  $\sim 430$  K. During the decrease and the second increase of temperature the  $I_4$  is consistently below one percent. The altered structure of the heated sample is characterized by the larger free volumes and the higher probability of the o-Ps formation.



**Figure ESI-9.** Changes of density in  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  in the course of the PALS analysis.

#### Solid-state NMR Spectroscopy:

All solid-state CP MAS experiments were performed on BRUKER Avance III 400 spectrometer operating at 400.13 for  $^1\text{H}$ , 100.61 for  $^{13}\text{C}$  and 79.495 MHz for  $^{29}\text{Si}$ . Dual channel ( $^1\text{H}/\text{BB}$ ) 4 mm DVT MAS probe head working with 4 mm  $\text{ZrO}_2$  rotors was used. During the measurements the sample were spun at 8000 MAS frequency.

For  $^{13}\text{C}$ , a sample of glycine was used for setting the Hartmann-Hahn condition, and adamantane was used as a secondary chemical shift reference; resonances at  $\delta = 38.48$  ppm and 29.46 ppm from the external TMS [12].  $^{13}\text{C}$  CP MAS spectra were accumulated with proton  $90^\circ$  pulse of 5.0  $\mu\text{s}$  in length and a contact time of 2 ms. The repetition delay was 4 s, and the spectral width was 21.5 kHz. The FIDs were accumulated with a time domain size of 2 K data points 64 scans each and a SPINAL sequence was applied for  $^1\text{H}$  decoupling [13].

For  $^{29}\text{Si}$  a sample of  $\text{Q}_8\text{M}_8$  was used both for setting the Hartmann-Hahn condition and as a chemical shift reference ( $\delta = 0.00$  ppm) [14].  $^{29}\text{Si}$  CP MAS spectra were accumulated with proton  $90^\circ$  pulse of 6.0  $\mu\text{s}$  in length and a contact time of 5 ms. The repetition delay was 4 s, and the spectral width was 48 kHz. The FIDs were accumulated with a time domain size of 4 K data points 32 scans each and a SPINAL sequence was applied for  $^1\text{H}$  decoupling.

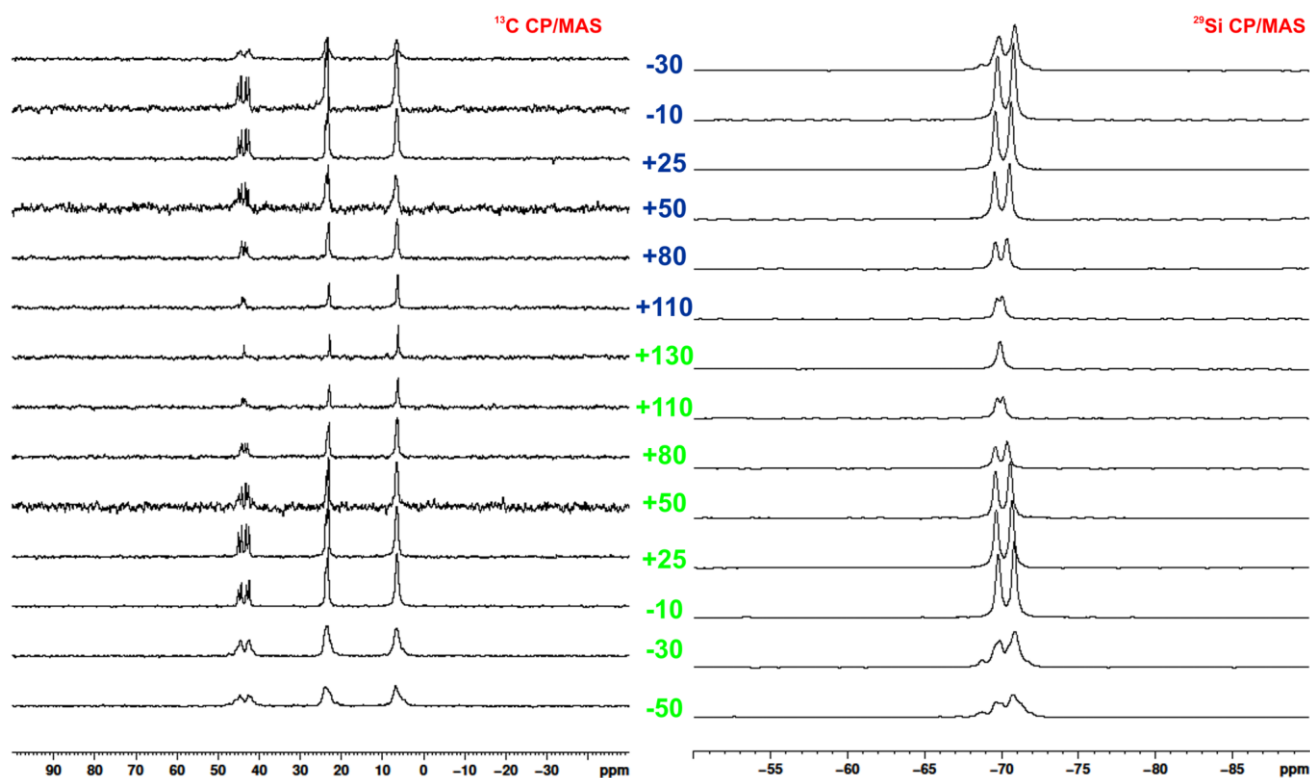
For variable temperature measurements, as cooling/heating medium, the dried air was utilized. The air was cooled down in LN2 heat exchanger (Bruker). The temperature was controlled and stabilized with BVT3200 unit. Before the acquisition sample was conditioned at desired temperature for at least 10 minutes.

All spectra were acquired and processed using Bruker TopSpin 2.1 software running on HP XW4400 Work Station under Windows XP Professional operating system.

thermal history:

heating from 223 K to 403 K (10 K/min, 10 min isotherm at selected temperatures)

cooling from 403 K to 223 K (10 K/min, 10 min isotherm at selected temperatures)



**Figure ESI-10.** CP MAS NMR spectra of  $T_8(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_8$  recorded at selected temperatures (thermal history involves cooling from room temperature to 223 K at 10 K/min, then heating and second cooling at 10 K/min with 10 min isotherms at selected temperatures).

#### References:

1. A. Kowalewska, M. Nowacka and W. Maniukiewicz, *J. Organomet. Chem.*, 2016, **810**, 15-24.
2. W. L. F. Armarego and Ch. L. L. Chai, *Purification of laboratory chemicals*, 5th edn. (2003) Elsevier Science.
3. A.-M.-C. Dumitriu, M. Balan, A. Bargan, S. Shova, C.-D. Varganici and M. Cazacu, *J. Molec. Struct.*, 2016, **1110**, 150-155.
4. B. Marciniak, M. Dutkiewicz, H. Maciejewski, M. Kubicki, *Organometallics*, 2008, **27**, 793-794.
5. J. Kany, *Nucl. Instrum. Methods Phys. Res. A*, 1996, **373**, 235-244.
6. A. Shukla, M. Peter and I. Hofman, *Nucl. Instrum. Methods Phys. Res. A*, 1993, **335**, 310-317.
7. R. Zaleski, *Acta Phys. Polon. A*, 2006, **110**, 729-738.
8. S. J. Tao, *J. Chem. Phys.*, 1972, **56**, 5499-5510.
9. M. Eldrup, D. Lighbody and J. N. Sherwood, *Chem. Phys.*, 1981, **63**, 51-58.
10. C. Jean, *Microchem. J.*, 1990, **42**, 72-102.
11. Y. Y. Wang, H. Nakanishi, Y. C. Jean and T. C. Sandreczki, *J. Polym. Sci., Part B: Polym. Phys.*, 1990, **28**, 1431-1441.
12. C. R. Morcombe and K. W. Zilm, *J. Magn. Reson.*, 2003, **162**, 479-486.

13. B. M. Fung, A. K. Khitrin and K. Ermolaev, *J. Magn. Reson.*, 2000, **142**, 97–101.
14. E. Lippmaa, M. Maegi, A. Samoson, M. Tarmak and G. Engelhardt, *J. Am. Chem. Soc.*, 1981, **103**, 4992–4996.