Electronic Supplementary Material (ESI) for CrystEngComm.

Self-assembly of Fluoride-encapsulated Polyhedral Oligomeric Silsesquioxane (POSS) nanocrystals

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Contents

1. Isothermal crystallization DSC thermograms

Figure S1A and 1B, show the DSC thermograms of the isothermally crystallized crownC_6 and crownC_8, respectively. At all isothermal crystallization temperatures, the isothermal crystallization thermograms are flat, which indicates that no obvious re-ordering or crystallization has occurred at these temperatures for both samples. Hence, the re-ordering of the POSS cages is a very slow process, occurring when samples have been left at room temperature for a several days.

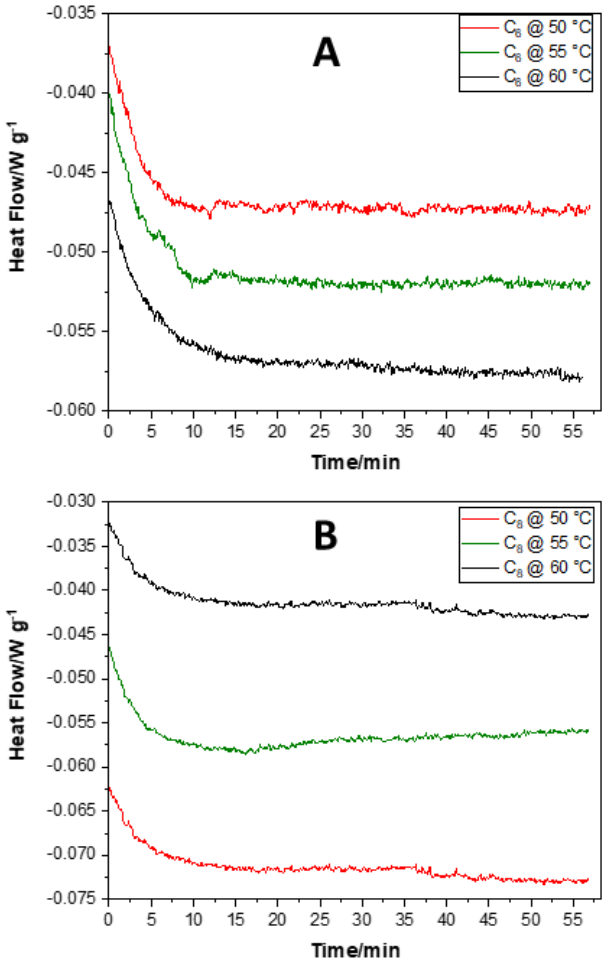

Figure S1: Isothermal crystallization DSC thermograms at 50, 55 and 60 °C of A: crownC_6 and B: crownC_8 samples.

2. 2D SAXS/WAXS patterns of samples at 30 ºC

Figure S2 shows the individual 2D SAXS/WAXS data from all samples tested. The SAXS data presented for the TBAF and crown compounds with increasing fluorinated alkyl arm length, shows distinct rings indicating crystalline ordering and regular packing of the molecules. However, this is not observed in the SAXS for the compounds without F^- on encapsulation (no F). Similarly, the WAXS for TBAF and crown compounds shows many scattering rings, which is indicative of a complex unit cell lattice system. Note that in some cases (TBAF and crown samples), there is evidence of some orientation of the crystallites in the compounds, which is highlighted from the concentration of the rings into arcs in the 2D SAXS/WAXS patterns. This orientation of crystallites arises from the compression process during the preparation of the samples in the DSC pans used in the X-ray scattering experiments.

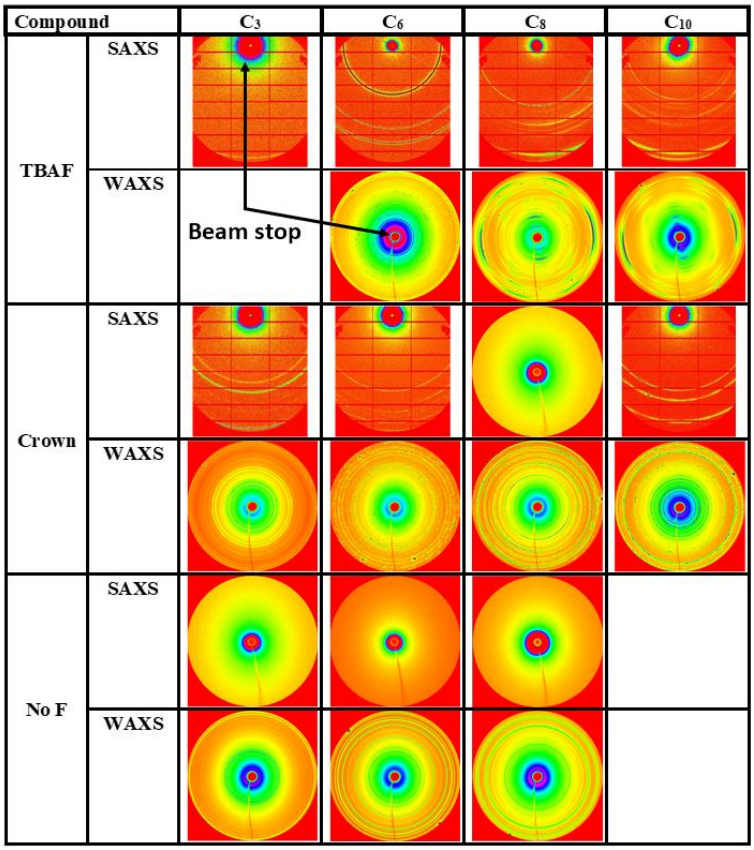

Figure S2. 2D SAXS/WAXS patterns of samples at 30 ºC. The beam stop is situated at the top or centre of the detector as labelled. High scattering intensity is coloured yellow to green and low intensity is red.

3. Major SAXS and WAXS peak positions from 1D SAXS profiles

Table S1. Major SAXS and WAXS peak positions from 1D SAXS profiles. **Bold numbers** correspond to single crystal analysis[S1, S2] unit cell dimensions duplicated in the SAXS/WAXS.

Compounds	**Major SAXS peaks/Å**	**Major WAXS peaks/Å**
$TBAFC_3$	**13.5**	Single crystal structure obtained[23]
$TBAFC_6$	31.2; **18.3**; 15.5	**32.5**; 17.4; 15.5; **12.5**; 4.6
$TBAFC_8$	25.1; 19.0;17.9;16.8;13.8	25.1; 19.2; 17.7; 16.7; 13.9; 12.9; 4.9
$TBAFC_{10}$	28.4;19.2; 14.1;13.4	27.5; 20.6; 14.0; 4.9
$CrownC_3$	**22.6**; 19.7; **17.2 15.7**; **13.4**	19.5; **13.5**; 11.3; 10.5; 4.9
$CrownC_6$	**20.1**; **16.8**; 15.3; **14.9; 14.5** 13.2	**20.2**; **16.9**; **14.2**; **8.9**; 7.3; 4.9
$CrownC_8$	-	15.5;12.9; 9.0; 6.6; 4.9
$CrownC_{10}$	20.0;17.7;14.2	20.2;17.9;14.4;11.3;10.2;6.4;4.6
C_3	-	13.7; 11.3; 10.4; 4.8; 4.6
C_6	-	15.8; 11.4; 7.3; 5.6; 4.9
C_8	-	13.0; 11.5; 8.8; 5.7; 4.9

4. Example unit cell projections on molecular packing diagrams

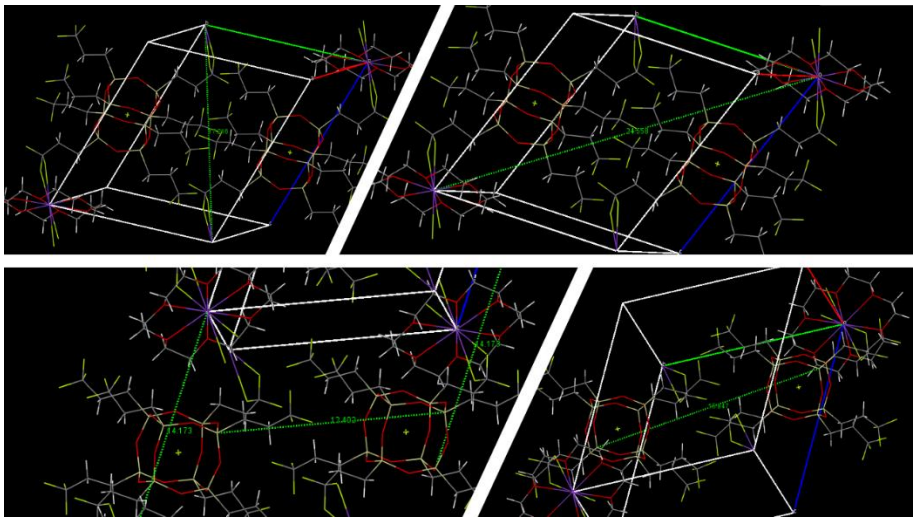

Figure S3: unit cell projection on crownC_3 packing.

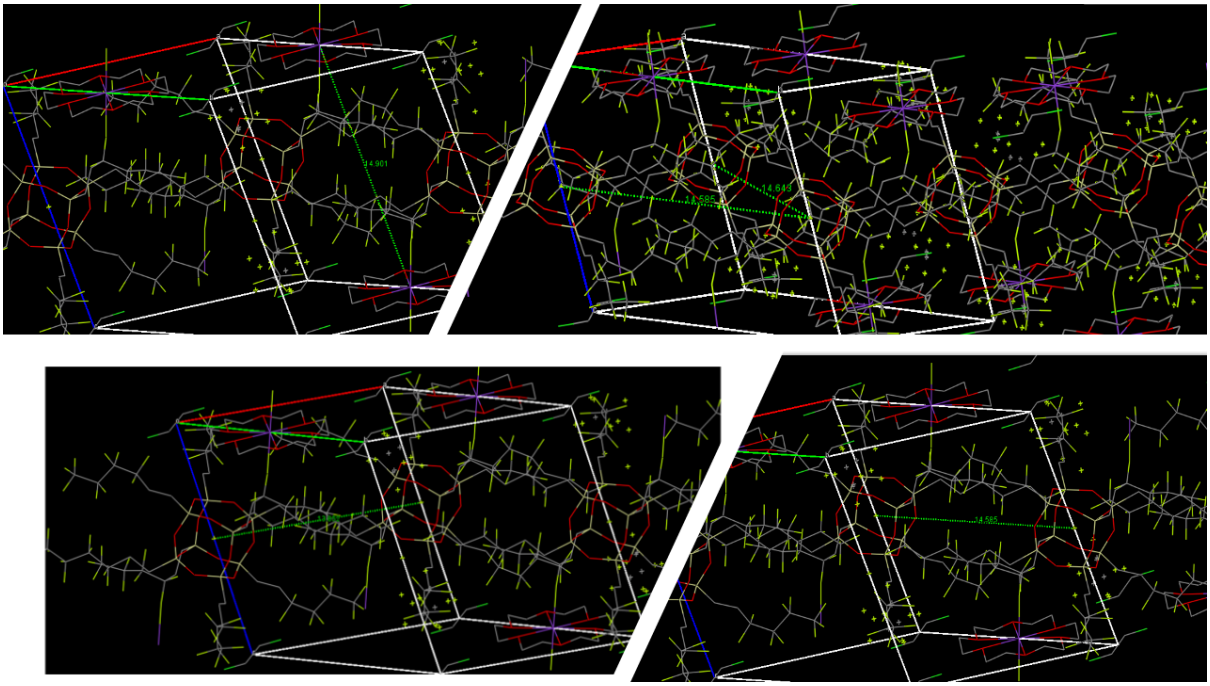

Figure S4: unit cell projection on crownC_6 packing.

Figures S3 and S4 show examples of the unit cell projection on the on the molecular packing diagrams for crownC_3 and crownC_6 compounds, obtained from single crystal X-ray analysis.[S1,S2]

5. Dynamic 1D SAXS/WAXS heat-cool

CrownC_3

Figure S5 shows the main 1D SAXS profiles during the heat-cool of crownC_3. Peaks disappear completely at 80 ^{o}C (T_m = 78.9 ^{o}C). On cooling peaks return by 64 ^{o}C.

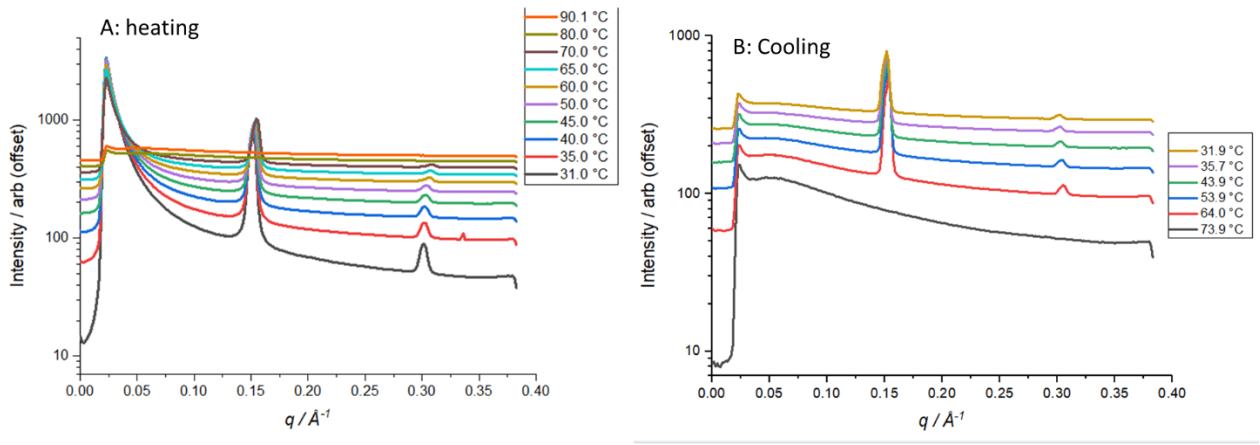

Figure S5: 1D SAXS profiles during heating and cooling of crownC_3.

$TBAFC_6$

Figure S6 shows the 1D SAXS profiles during the heating and cooling of $TBAFC_6$. The main peaks start to disappear at T = 43 °C and are completely gone 46.5 °C. The peak T_m is 40.3 °C from DSC. The peaks do not reappear in the 1D SAXS profile cooled back down to 30.0 °C.

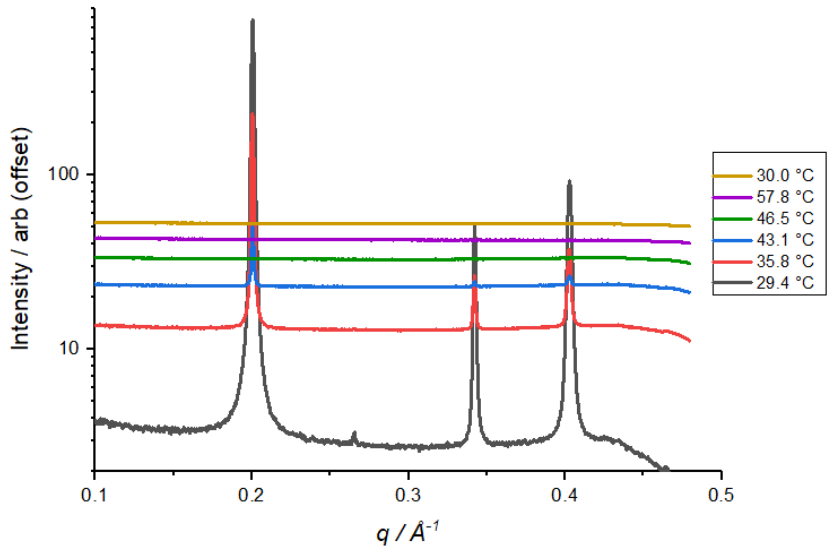

Figure S6: 1D SAXS profiles during heating of $TBAFC_6$.

Figure S7 shows the 1D WAXS profiles of the heating and cooling of $TBAFC_6$. The crystalline peaks disappear completely at 42.9 °C and as seen in the SAXS, the WAXS crystalline peaks do not reappear on cooling.

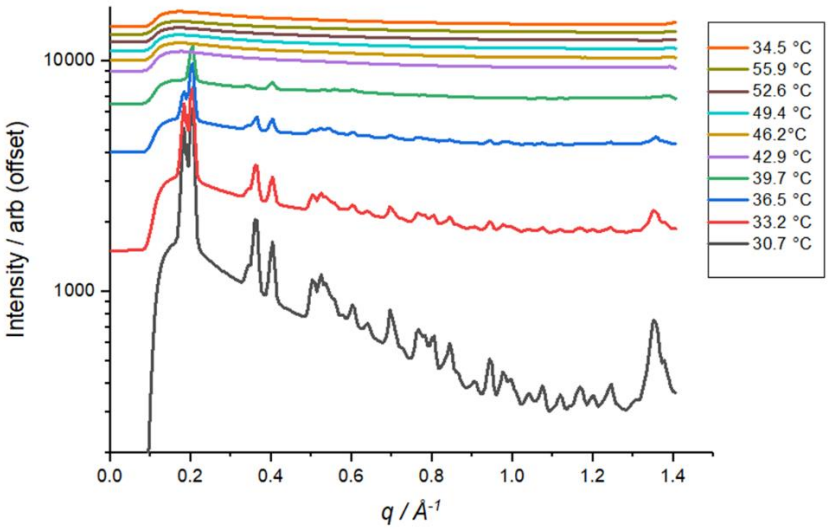

Figure S7: 1D WAXS profiles during heating and cooling of $TBAFC_6$.

CrownC$_6$

Figure S8 shows the 1D SAXS/WAXS during the heat-cool of crownC$_6$. Both profiles show the disappearance of the scattering peaks by 90 ^{o}C (T_m 82 ^{o}C and 85 ^{o}C), However, on cooling the peaks do not return.

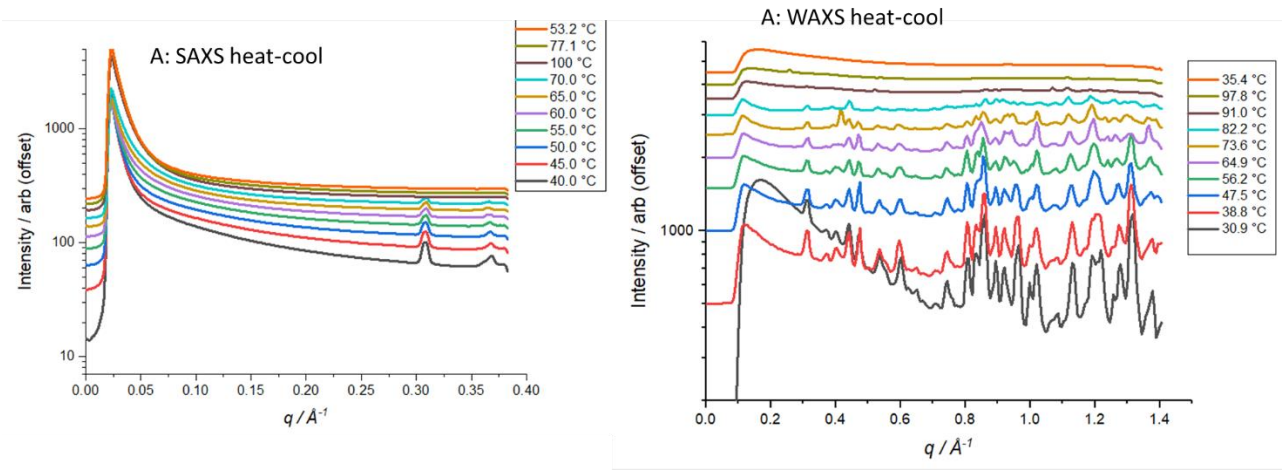

Figure S8: 1D SAXS/WAXS profiles during heating- and cooling of crownC$_6$.

CrownC$_8$

Figure S9 shows the 1D WAXS profiles of the heating and cooling of crownC$_8$. The crystalline peaks disappear completely at 84.2 ^{o}C (T_m = 81.2 ^{o}C). The WAXS crystalline peaks do not reappear on cooling.

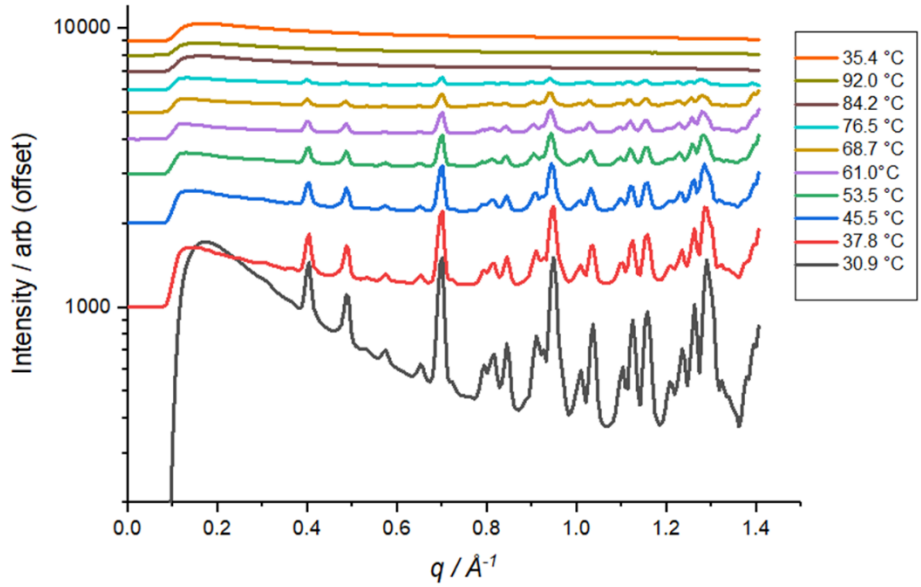

Figure S9: 1D WAXS profiles during heating and cooling of crownC$_8$.

POSS C_6 without F^- ion encapsulation

Figure S10A shows the 1D WAXS profiles of the heating and S10B cooling of POSS C_6 compound (without F^- ion encapsulation). On heating the WAXS peaks all disappear by ~132 ^oC (T_m for C_6 is 125 ^oC). On cooling the WAXS peaks return.

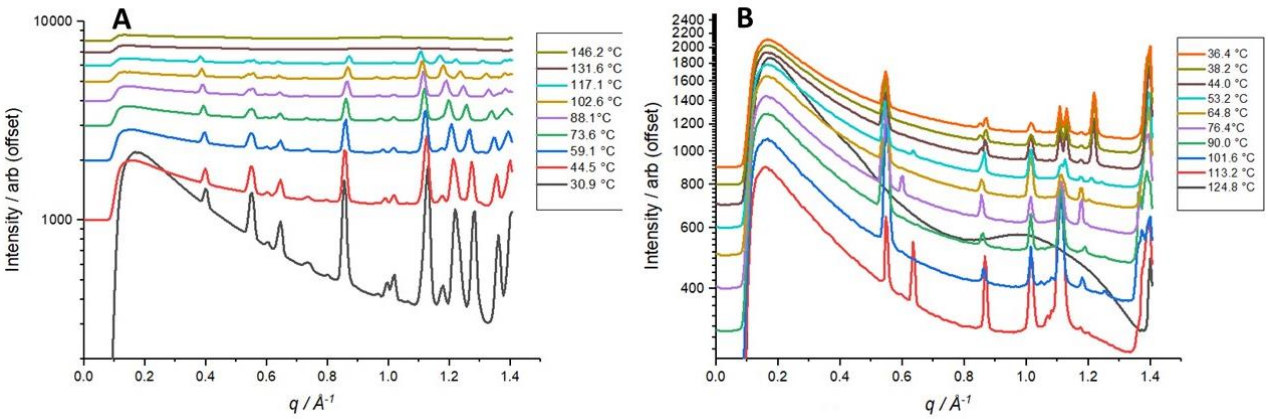

Figure S10: 1D WAXS profiles of (A) heating and (B) cooling of POSS C_6.

POSS C_8 without F^- ion encapsulation

Figure S11A shows the 1D WAXS profiles of the heating and S11B cooling of POSS C_8 compound (without F^- ion encapsulation). On heating the WAXS peaks all disappear by ~123 ^oC (T_m for C_6 is 128 ^oC). On cooling the WAXS peaks return.

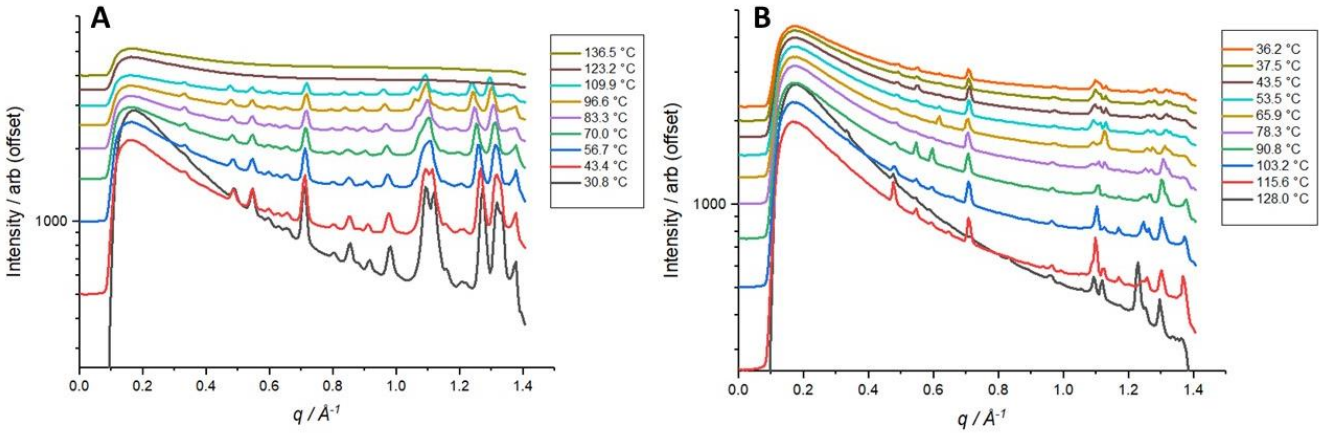

Figure S11: 1D WAXS profiles of (A) heating and (B) cooling of POSS C_8.

4. References

(S1) P. G Taylor, A. R. Bassindale, Y, El Aziz, M. Pourny, P. N. Horton and M. B. Hursthous, *Dalton. Trans.,* 2012, 41, 2048-2059.

(S2) Y. El Aziz, P. G. Taylor, R. A. Bassindale, S. J. Coles and M. B. *Organometallics*, 2016, 35, 4004-4013.