Supporting Information

Symmetry-Dictated Mesophase Formation and Phase Diagram of Perfluorinated Polyhedral Oligomeric Silsesquioxanes

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**Experimental Section**

**Chemicals and Solvents.** The following chemicals were used as received: octavinylPOSS (V₈T₈, Hybrid Plastics, OL1160), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Tokyo Chemical Industry Co. Ltd., >99%), tetrahydrofuran (THF, Thermo Fisher Scientific Inc., HPLC), 1H,1H,2H,2H-perfluorodecanethiol (Aladdin Reagent Inc., 97%), trifluorotoluene (TFT, J&K Chemicals, 99%), NaHCO₃ (Beijing Tongguang Industry of Fine Chemicals Company, 99%), Na₂SO₄ (Beijing Tongguang Industry of Fine Chemicals Company, 99%), acetone (Concord Chemical Industry Co. Ltd., HPLC grade), silver trifluoromethanesulfonate (J&K Chemicals, 98%), trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Tokyo Chemical Industry Co. Ltd., >99%), petroleum ether (PE, b.p. 60-90 °C, Beijing Tongguang Industry of Fine Chemicals Company, 95%), methanol (MeOH, Beijing Tongguang Industry of Fine Chemicals Company, 99.7%), CDCl₃ (99.8%D, Cambridge Isotope Laboratories, Inc., 99.9%), tetramethylsilane (Cambridge Isotope Laboratories, Inc., 99.9%). Synthesis of T₈F₇(OH) and diadducts para-T₈F₆(OH)₂, meta-T₈F₆(OH)₂ and ortho-T₈F₆(OH)₂ were performed according to the literature.¹,²

**Instrumentation and Characterizations.** All ¹H and ¹³C NMR spectra were acquired in CDCl₃ (99%D, J&K Chemicals) using a Bruker 400 MHz NMR spectrometer. The ¹H NMR spectra were referenced to the residual proton impurities in the CDCl₃ at δ 7.27 ppm. The ¹³C NMR spectra were referenced to ¹³CDCl₃ at δ 77.00 ppm. The ²⁹Si NMR spectra were acquired in CDCl₃ using a Bruker 500 MHz NMR spectrometer and referenced to tetramethylsilane (TMS) at δ 0.00 ppm. Ultraviolet (UV) light irradiation of the samples was carried out with a 2 × 15 W Vilber Lourmat UV bench lamp VL-215L,
emitting around 365 nm wavelength. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a MALDI TOF/TOF 5800 mass spectrometer (AB Sciex, USA). All spectra were measured in positive reflection mode with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix and was prepared in CHCl$_3$ at a concentration of 20 mg mL$^{-1}$. The samples were dissolved in CHCl$_3$ at a concentration of 5 mg mL$^{-1}$. Silver trifluoromethane sulfonate (AgTFA) served as cationizing agent and was prepared in MeOH-CHCl$_3$ (1/3, v/v) at a concentration of 10 mg mL$^{-1}$. The sample was prepared by depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample. FT-IR spectra were recorded on a Nicolet IS50 Fourier transform infrared spectrometer. Samples were ground with KBr pellet under IR lamp and pressed into a wafer. A Linkam hot stage was used for the assistant of heating and cooling experiments. Polarized optical microscopy (POM) observation was performed on a Nikon DS-Ri1 microscope. An Instec HCS302 hot stage was used for controlling the temperature. Thermogravimetric analyses (TGA) experiments were performed on a TA Q600 analyzer with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) experiments were performed on a TA Q100 analyzer with a heating rate of 10 °C/min and the first cooling curves and second heating curves were used in the article. The X-ray diffraction data were recorded at beamline BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.24 Å and Beamline 1W2A of the Beijing Synchrotron Radiation Facility (BSRF) a wavelength of 1.54 Å. Some of the X-ray diffraction data were also recorded on the Xeuss 2.0 instrument with the wavelength of 1.54 Å. Silver behenate (with the $d$-spacing of 58.38
Å) was used for the calibration of sample to detector distance. Samples are put steady in the glass capillaries with the diameter of 1 mm. Due to the heating hysteresis of glass, all phase transition temperatures were referenced from DSC curves. Before the experiment, samples were first heated up to isotropic state (transparent colorless liquid) which is about 120 °C to eliminate the thermal history. After cooling down to room temperature the capillary was installed on the hot stage and in situ X-ray studies were done. Shear experiment were performed at about 55–65 °C, below the melting temperature. ¹H MAS NMR experiments were performed on a Bruker AVANCE III 400MHz WB Solid-State NMR Spectrometer using a double-resonance MAS probe supporting rotors of outer diameter 2.5 mm with a spinning frequency of 35 kHz. For all samples, the 90° pulse length was 2.0 μs, and a recycle delay of 10 s was used. For one-dimensional MAS experiments, 8-16 transients were averaged. The probe temperature is about 27 °C during the experiments. Temperature dependent ¹H solid-state MAS NMR experiments were carried out using a commercial JOEL 3.2 mm MAS probe with the spinning frequency of 15 kHz. ¹H MAS NMR spectra were recorded with a single pulse excitation, a 90° pulse length of 1.0 μs and a recycle delay of 5.0 s.

**Synthesis of T₈F₇(OH)₂.** Synthesis of T₈F₇(OH)₂ followed the same protocol to that of T₈F₇(OH) and T₈F₆(OH)₂ diadducts except using thiolglycerol in the first step.¹² The sample was obtained as a white powder in ~80% yield. ¹H NMR (400 MHz, CDCl₃, ppm, δ): 3.77 (m, 2H, -CH₂O-), 3.58 (m, 1H, -CHO-), 2.80 – 2.66 (m, 32H, -CH₂SCH₂-), 2.37 (m, 14H, -SCH₂CH₂CF₂-), 1.08 (m, 16H, -SiCH₂CH₂-). ¹³C NMR (100 MHz, CDCl₃): δ 120-108 (m, -CH₂(CF₂)₂CF₃), 70.13 (-CHO-), 65.4 (-CH₂O-), 35.79 (-SCH₂CH₂OH), 32.15, 32.00, 31.86 (-CH₂CF₂-), 26.55 (SiCH₂CH₂SCH₂CH₂CF₂-), 26.35, 26.31 (-
SiCH$_2$CH$_2$SCH$_2$CH$_2$OH), 22.61 (-SiCH$_2$CH$_2$SCH$_2$CH$_2$CF$_2$-), 13.32, 13.26 (-SiCH$_2$CH$_2$SCH$_2$CH$_2$OH), 12.73, 12.69 (-SiCH$_2$CH$_2$SCH$_2$CH$_2$CF$_2$-). $^{29}$Si NMR (99 MHz, CDCl$_3$): $\delta$ -68.66, -68.72, -68.78, -68.83, -68.86. MS (MALDI-TOF, Da): Calcd. for [M·Ag$^+$] (AgC$_{72}$H$_{67}$F$_{85}$O$_{15}$S$_8$Si$_8$): 4206.8; Found: 4206.6.
Figure S1. $^1$H NMR spectrum of T$_8$F$_7$(OH)$_2$. Asterisks are resonances from residual CDCl$_3$ and TMS.
Figure S2. $^{13}$C NMR spectrum of T$_8$F$_7$(OH)$_2$. Asterisks are resonances from residual CDCl$_3$. 
Figure S3. $^{29}$Si NMR spectrum of to T$_8$F$_7$(OH)$_2$. 
Figure S4. MALDI-TOF MS spectrum of T₈F₇(OH)₂.
**Figure S5.** TGA curves of FPOSS derivatives.
Figure S6. POM images of T₈F₇(OH) at different temperature.
Figure S7. Temperature dependent WAXD profiles of T₈F₈ showing the phase transition.
Figure S8. Temperature dependent WAXD profiles of T₈F₇(OH) showing the phase transition.
Figure S9. WAXD studies of the sheared samples, from left to right are 2D patterns and the integration in the meridian region and equatorial region. From top to bottom are T₈F₇(OH), para-T₈F₆(OH)₂, meta-T₈F₆(OH)₂, and ortho-T₈F₆(OH)₂. The arrow shows the shear direction.
Figure S10. Temperature-dependent FT-IR spectra of $para$-$T_8F_6(OH)_2$ showed that there are no signal observed during heating and cooling at around 1630 cm$^{-1}$. 
Figure S11. $^1$H solid-state MAS NMR spectra of T$_8$F$_8$ (A), para-T$_8$F$_6$(OH)$_2$ (B), meta-T$_8$F$_6$(OH)$_2$ (C), ortho-T$_8$F$_6$(OH)$_2$ (D) and the corresponding assignments.
Figure S12. Temperature dependent $^1$H solid-state MAS NMR spectra of $meta$-T$_8$F$_6$(OH)$_2$ at 60$^\circ$C (A), 87$^\circ$C (B), and 120 $^\circ$C (C) and the corresponding assignments.
Figure S13. WAXD profiles of the crystal samples of \textit{para}-T₈F₆(OH)₂ (A), \textit{meta}-T₈F₆(OH)₂ (B), \textit{ortho}-T₈F₆(OH)₂ (C) obtained from solution crystallization.
References.
