Supporting Information

Unusual Interfacial Freezing Phenomena in

Hexacontane/Silica Composites

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Experimental section

1. Surface modification of Stöber silica particles

Prior to the surface functionalization of SiO_2, the dry SiO_2 nanoparticles were treated with piranha solution for 4 h at room temperature in order to activate the –OH groups on the nanoparticle surface. After removal from the solution, the powders were rinsed copiously with deionized water, and then dried at 110 °C overnight to remove physical adsorbed water on silica surface.

1 g of activated silica was added into 100 ml of anhydrous toluene and the mixture was stirred at 120 °C for 2 h. Then, 0.5 g of 3-Aminopropyltriethoxysilane (APTES, Sigma-Aldrich) was introduced into the mixture and reacted for 24 h at 120 °C under a dry nitrogen atmosphere. The mixture was centrifuged to obtain silica nanoparticles. To remove the unreacted organosilane, the silica powders were washed with toluene, ethanol and methanol successively. Modified silica samples were then dried at 110 °C in a vacuum oven for 12 h before further used.

2. Preparation of $C_{60}H_{122}$/modified silica composites

To ensure the homogeneities of samples, solution mixing method was applied to prepare the $C_{60}H_{122}$/modified SiO_2 composites. Firstly, $C_{60}H_{122}$ was dissolved in toluene at 70 °C, and SiO_2 particles were well-dispersed in toluene with sonication. Then the two solutions were mixed with desired volume to achieve the composites with different silica weight loadings and stirred for 24 h at 70 °C. Eventually, the composite specimens were obtained through solvent evaporation and subsequently dried under vacuum at 50 °C for 12 h.

3. Characterization.

Temperature-dependent X-ray diffraction (XRD) experiments were performed on an X′Pert Pro MPD X-ray diffractometer with the temperature region similar to that for DSC measurements, using Cu Kα radiation (1.54 Å), power of 40 mA/40 kV, and rotating angle $2\theta = 5-40°$. The heating and cooling rates were all 2 °C/min, and at each temperature point, the samples were equilibrated for about 5 min before data collection.

Differential scanning calorimetry (DSC) measurements were performed with a Q2000 (TA Instruments) in the temperature range of 80~110 °C under nitrogen atmosphere. In order to ensure the reproducibility, two or three measurements were recorded for each sample.

The grazing incidence X-ray diffraction (GIXD) measurements of the *n*-alkane film structure were carried out on a Xeuss SAXS/WAXS system (Xenocs SA, France).To do the temperature-dependent GIXD measurement, a Linkam thermal stage was used for temperature control. A multilayer focused Cu Kα X-ray source (GeniX3D Cu ULD), generated at 50 kV and 0.6 mA, was utilized. The wavelength of the X-ray radiation was 0.15418 nm. A semiconductor detector (Pilatus 300 K, DECTRIS, Swiss) with a resolution of 487×195 pixels (pixel size = 172×172 m^2) was applied to collect the scattering signals. Each GIXD pattern was collected with an exposure time of 600 seconds. The incident beam made an angle of ~ 0.1^o with the SiO_2 surface.

The proton NMR magnetization relaxation study was carried out on a 400 MHZ

Bruker spectrometer by standard Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence at 378 K. A $\pi/2$ pulse width of 5 µs was used for ^{1}H NMR experiments. The recycle delay time was 5 s. The adamantine ($C_{10}H_{16}$) at 1.91 ppm was taken as reference.

Results

The phase transition of $C_{60}H_{122}/SiO_2$ composites was characterized by variable-temperature XRD as shown in Figure S1. When the temperature decreases to the crystallization temperature (99 °C), two diffraction peaks at $2\theta = 21.3°$ and $23°$ corresponding to the (110) and (200) planes of the orthorhombic crystal appear.

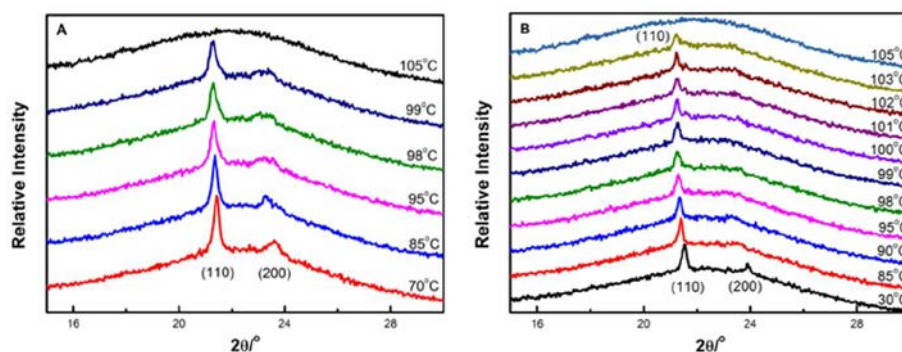Figure S1. Variable-temperature XRD patterns of $C_{60}H_{122}/SiO_2$ composites with $\varphi_{C60H122}=10\%$ both during cooling (A) and heating (B) process.
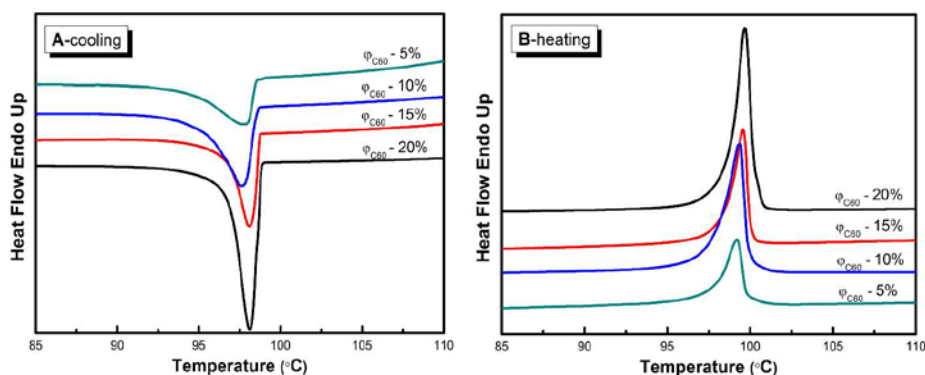

Figure S2. DSC curves of $C_{60}H_{122}/$modified SiO_2 composites during cooling (A) and heating (B) processes.
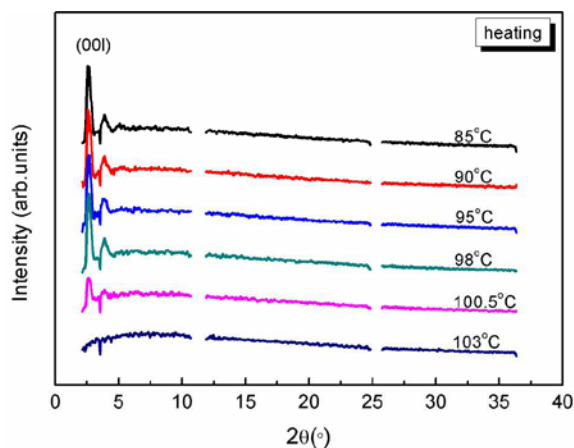
Figure S3. Variable-temperature grazing-incidence X-ray diffraction patterns of $C_{60}H_{122}$ thin film

adsorbed on the silicon wafer during heating process.

Proton NMR relaxation experiments were performed to investigate the molecular dynamics of $C_{60}H_{122}$. The ^1H NMR spectra of the pure $C_{60}H_{122}$ and $C_{60}H_{122}/SiO_2$ composites are displayed in Figure S4. There are two characteristic resonance peaks at ~0.99 ppm for terminal methyl group (CH_3), ~1.40 ppm for CH_2 group of $C_{60}H_{122}$.[1] The ^1H transverse relaxation times (T_2) of above two parts were measured and the relaxation data are shown in Table S1. T_2 values could be extracted by fitting magnetization relaxation model using the following function:[2]

$$I(t) = I(0)*\exp(-t/T_2)$$

where $I(t)$ is the signal intensity, $I(0)$ is the intensity at t = 0. For the CH_2 proton relaxation, the decay time, T_2, is 377.35 ms for pure $C_{60}H_{122}$, but the composites show the short decay time, T_2 = 38.33 and 30.08 ms for $C_{60}H_{122}/SiO_2$ composite with $\varphi_{C60H122}$ = 10 and 3 wt %, respectively. It has been reported that the larger the amplitude of chain motions is, the longer the T_2 will be.[3]
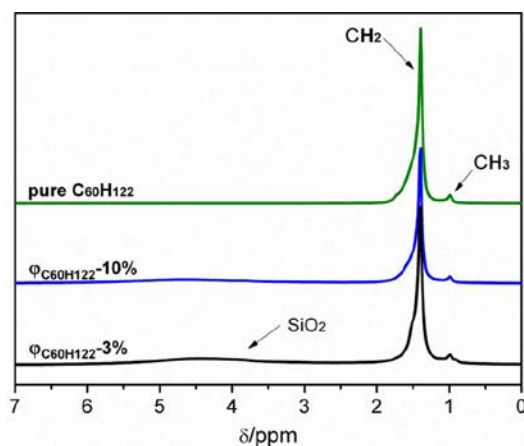
Figure S4. ^{1}H NMR spectra of $C_{60}H_{122}/SiO_2$ composites with various compositions at 378 K, the

percentage inset is for $\varphi_{C60H122}$.

Table S1 T_2 values of the proton of CH_2 and CH_3 of pure $C_{60}H_{122}$ and $C_{60}H_{122}/SiO_2$ composites

Sample	CH_2 T_2 (ms)	CH_3 T_2 (ms)
Pure $C_{60}H_{122}$	377.35	438.60
Composite-10wt%	38.33	44.31
Composite-3wt%	30.08	34.98

References

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