

Supporting Online Material for

Physico-chemical confinement of helical nanofilaments

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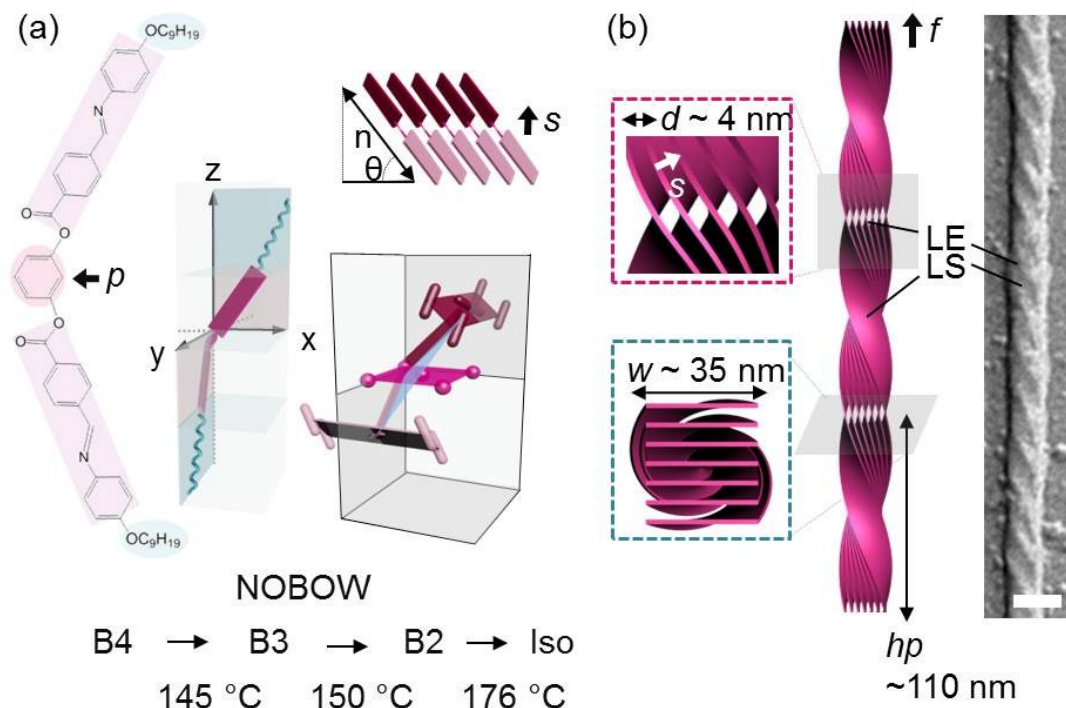
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This Supplementary contains:

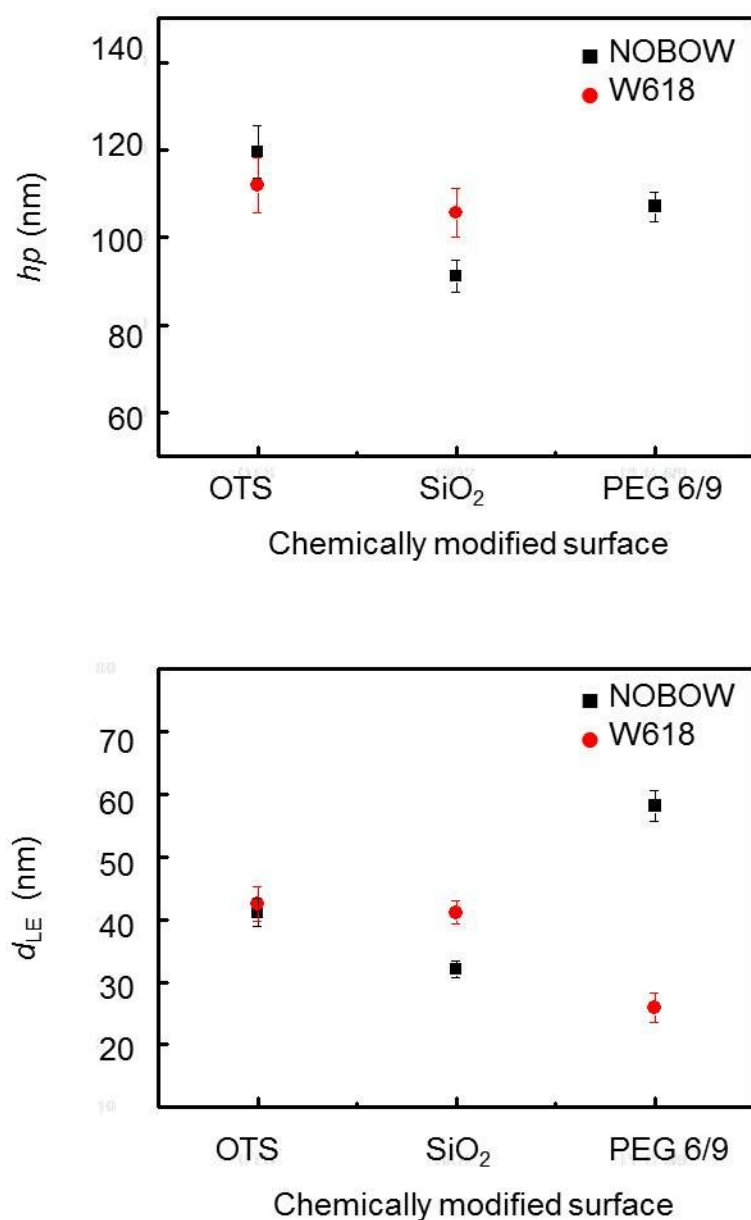
Figures S1-S6

Figure S1



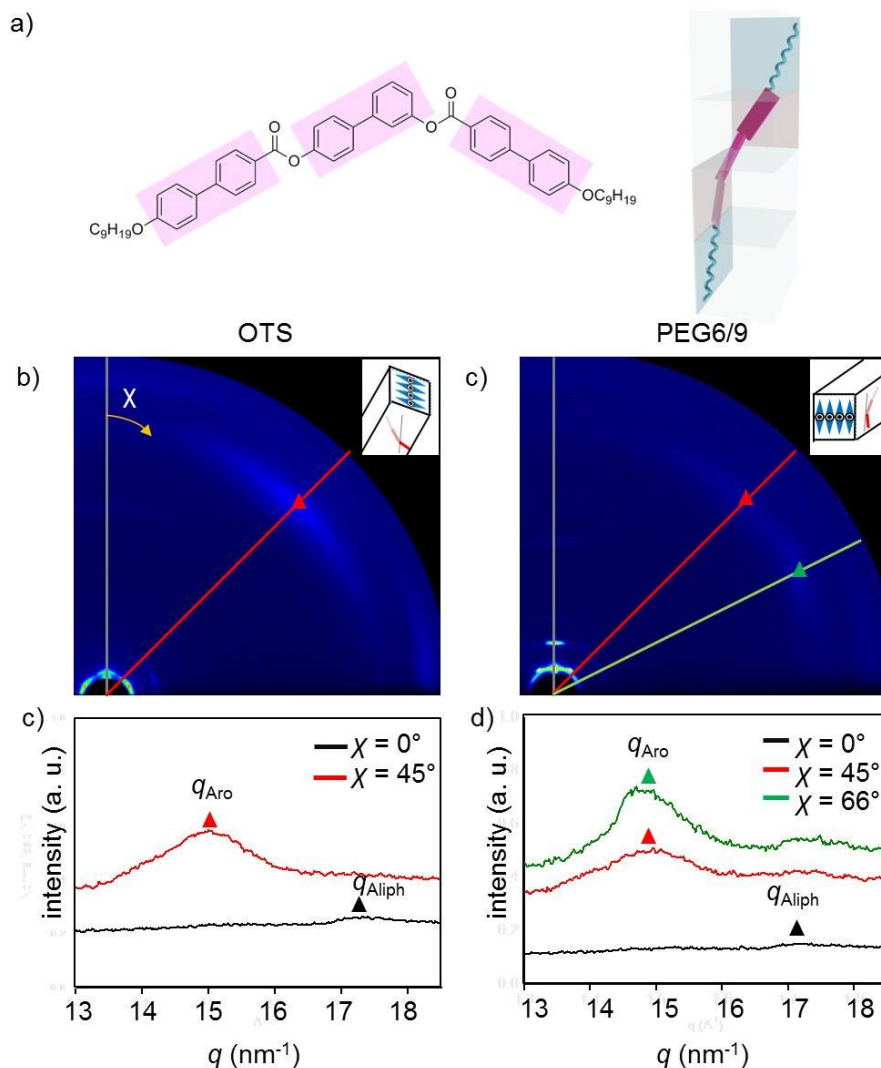
S1. Classic HNF structure is made of NOBOW, bent-core molecule which has two-fold symmetry with arms of aromatic plane¹⁶. This molecules are conformed in a molecular layer with tilt angle at B2 phase. Owing to their in-layer mismatch of aromatic plane, the molecular layer is deformed as saddle-splayed form. Spontaneous saddle-splay deformation leads to form helical nanofilament structure at B4 phase³. Reprinted with permission from ref. 16. Copyright 2014, National Academy of Sciences.

Figure S2



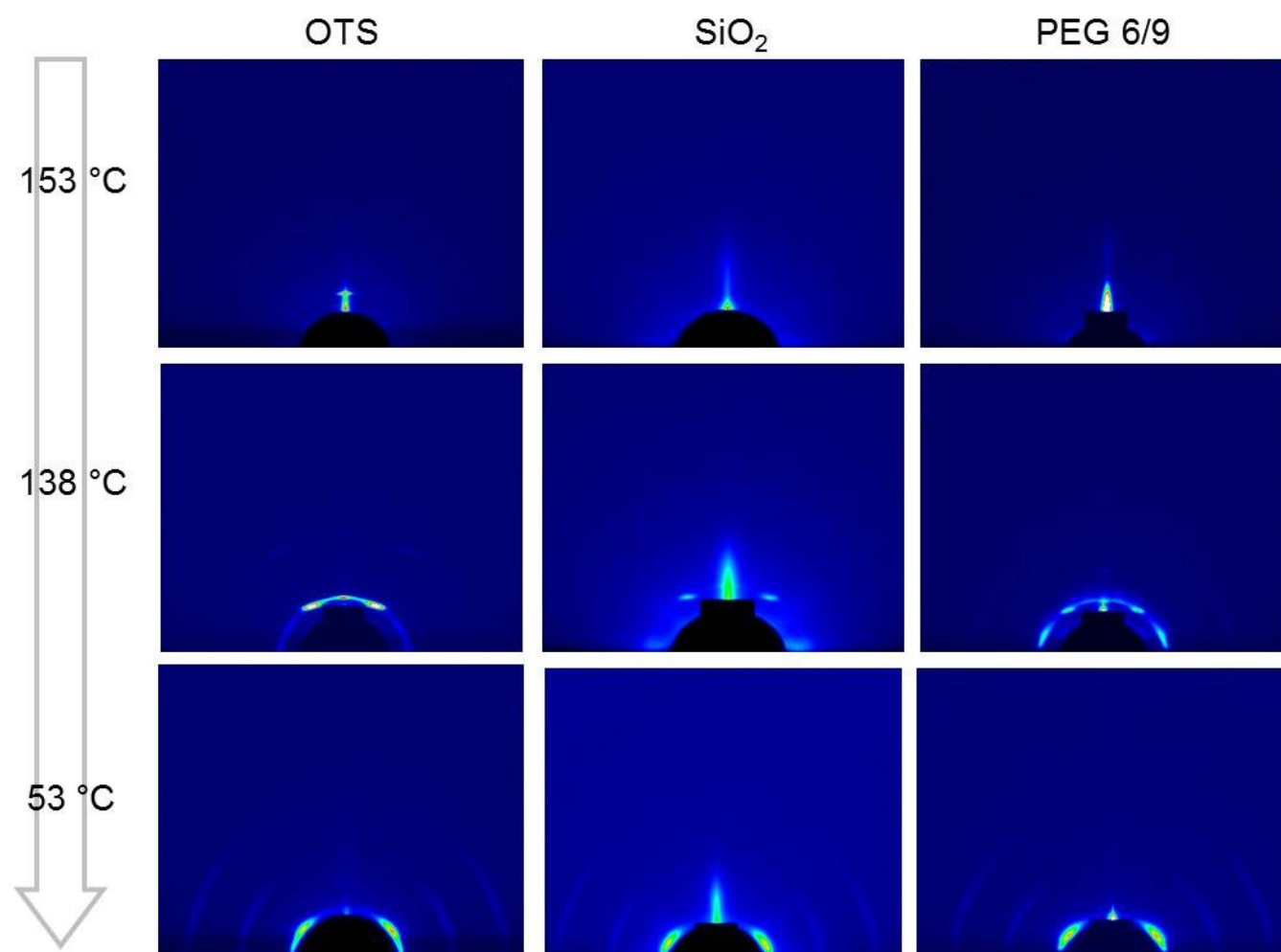
S2. Half-pitch (hp) and layer edge thickness (d_{LE}) distribution of nanoconfined HNFs and HNF_(mod)s in nanochannels depending on the various surface modification. Helical pitches of both NOBOW and W618 were the largest in OTS-coated nanochannel which has the LC molecular-phobic property among the all of SAM chemicals. In contrast, d_{LE} at the PEG 6/9-modified surface of HNF is the thickest because molecular layers preferred to adhere to the nanochannel wall.

Figure S3



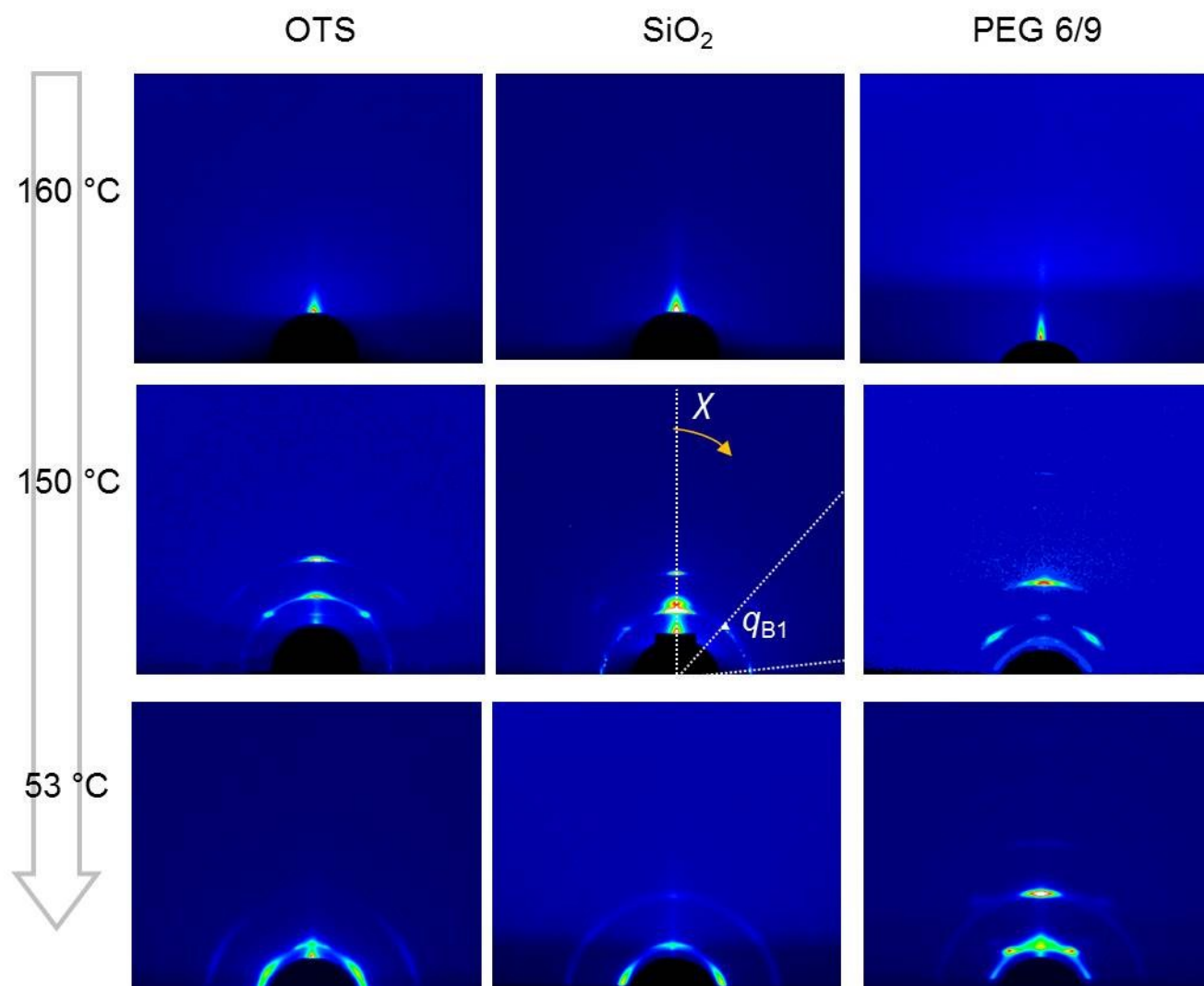
S3. GIXD analysis of $\text{HNF}_{(\text{mod})}$ structure in a range of wide angle at room temperature. Referred from B4 phase of NOBOW molecule³, when the aromatic rings placed in plane such as (0 1 1), (1 1 1), (1 0 -1), these three parts can be shown as a bent-joined magenta line in (a). At the OTS-treated surface (b), aromatic peak of $\text{HNF}_{(\text{mod})}$ ($q_{\text{Aro}} = 15.0 \text{ nm}^{-1}$) strongly appeared at $\chi = 45^\circ$ because layers were placed at diagonal direction and then aromatic planes tilted with 45° against z axis. Besides, aromatic peaks of bamboo-like structure (c) were diffused at around $\chi = 45^\circ$ and $\chi = 66^\circ$ ($q_{\text{Aro}} = 15 \text{ nm}^{-1}$, $q_{\text{Aliph}} = 17.2 \text{ nm}^{-1}$). These orientational differences of molecules were based on the molecular model. (Fig. 4.)

Figure S4



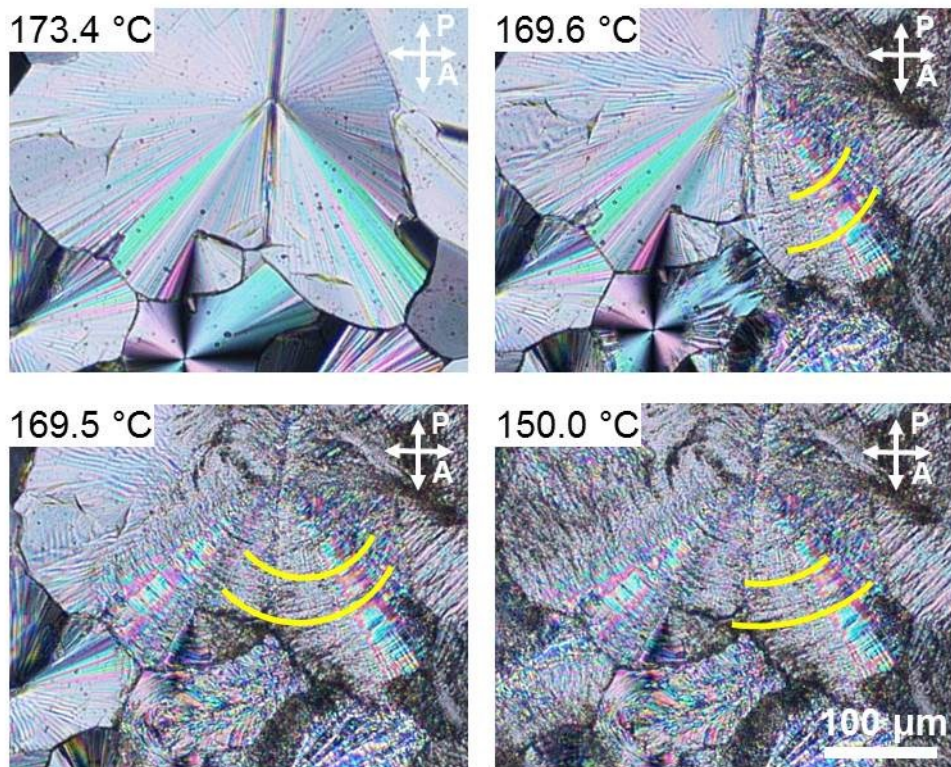
S4. Layer transformation of NOBOW in chemically modified AAO nanochannels during thermal phase transitions. In GIXD 2D pattern, from B2 to B4 phase transitions peaks of NOBOW confined in AAO nanochannels were clearly shown as first-order transition. The time that phase transition took place was different depending on the surface properties. However, the final HNF structures were same at all chemical-treated surfaces. Based on these results, B2-B4 phase transition can be regarded as a consistent phenomenon which has stable meso-structure that is superior to external circumstances.

Figure S5



S5. GIXD patterns of layer transformation of W618 in surface-modified AAO nanochannels. In contrast to NOBOW, layered structure transformation of W618 were distinctly different depending on the surface properties during B1-B4 phase transition. In the cases of OTS- and SiO_2 -coated surfaces, second-order peaks revealed that mesophase has discretized and modulated structure of B1 at 150 °C. And then $\text{HNF}_{(\text{mod})}$ s were finally formed near the room temperature similar to the HNFs. In the case of PEG 6/9-coated surface, however, strong peak which was placed at the second-order position at 150 °C still remained at 53 °C. Furthermore, the diagonal peaks of typical feature of HNF structure were weakened and new lattice peaks were strongly appeared at 53 °C. The lattice peaks in PEG 6/9 at B4 phase were correlated to B1 phase discrete peaks because the q value were same. It can be explained that higher phase structures were remained in lower phase owing to the external forces.

Figure S6



S6. Optical texture of bulk W618 on silicon wafer. During phase transition from B1 to B4, discreted domains of conventional B1 phase (173.4 °C) were spontaneously transformed as a continuous layer structure (yellow line) in a very narrow range of temperature. It showed that columnar structure can be spontaneously developed into layered structure upon cooling.