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Understanding and Manipulating Helical Nanofilaments in Binary Systems with Achiral Dopants

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ABSTRACT: Herein we report the relationship between helical pitch of the helical nanofilament (HNF) phase formed by bent-core molecule NOBOW and the concentration of achiral dopants 5CB and octane, using linearly polarized resonant soft X-ray scattering (RSoXS). Utilizing theory-based simulation, which fits well with the

experiments, the molecular helices in the filament were probed and the superstructure of helical 5CB directed by groove of HNFs was observed. Quantitative pitch determination with RSoXS reveals that helical pitch variation is related to 5CB concentration with no temperature dependence. Doping rod-like immiscible 5CB let to a pitch shortening of up to 30%, which was attributed to a change in interfacial tension. Shedding light not only on phase behavior of binary systems, but also enabling control over pitch length, our work may benefit various applications of HNF-containing binary systems, including optical rotation devices, circularly polarized light emitters and chirality transfer agents.

KEYWORDS: liquid crystal, helical pitch, resonant soft X-ray scattering, helical nanofilament, B4 phase, bent-core molecules

Chirality has been an attractive scientific topic since its discovery in 1848 by Louis Pasteur[1]. In many kinds of materials, including catalysts[2], blue phases materials[3-4] and MOF[5], chirality is an important property. Precisely understanding the process of self-assembly from a molecular perspective is a critical challenge, for which studying chirality has much to reveal. Recently, it has been found that bent-core achiral molecules are able to form chiral structures by spontaneous symmetry breaking[6-9]. Due to the asymmetry of their instantaneous molecular conformations, bent-core molecules self-assemble into robust helical nanofilaments (HNFs) forming large homochiral domains[9-10]. HNFs are particularly interesting in different ways. Scientifically, their seemingly simple structure poses some fundamental questions of mechanistic understanding on chirality generation from achiral molecules. Regarding application, the extraordinary stability of the HNF phase offers numerous opportunities in functional binary systems. Though some theoretical work has analyzed the potential impact of system chirality on HNF generation[11-13], experimental studies on factors leading to HNF structure are still rare.

Introducing extra dopants into a liquid crystal (LC) chiral system may lead to the occurrence of extra helical twisting power, which can modify the equilibrium state by changing the pitch, opening possibilities such as creating photomodulated chiro-optic devices[14]. On the other hand, introducing dopants could greatly enhance the system tunability. Studying the effect of dopants has resulted in the construction of binary phase diagrams[15] and dopant-induced phases such as antiferroelectric[16] and novel smectics[17]. Also, considerable research is dedicated to properties, for example, dopant dependence of helical twisting power in cholesteric liquid crystals[18] and highly ordered alignment of HNFs in a nematic field[19]. Recently, increasing attention has been given to achiral rod-like dopants, like 5CB (4-Cyano-4'-pentylbiphenyl) and 5PCB (4'-Cyano-[1,1'-biphenyl]-4-yl 4-pentylbenzoate) in HNFs. As the HNFs are formed, such dopants are expelled and nanoconfined within the nanofilament networks, creating a binary system with total phase separation[8,20]. The nanofilament networks not only form 3D chemical and physical organogels with large surface/volume ratio (~100 m^2/cm^3) entrapping the expelled organic dopants[8,21], but also exhibit strong ability to transfer chirality to coated rod-like dopants[17,22-23]. Intense investigations have been conducted on chirality induction in binary systems. Several applications were reported recently, including enhanced, electric-field controlled optical activity[17,24], morphological chirality transferred by nanopatterning[25] and circularly polarized luminescence[26]. On the other hand, rational molecular design has created filaments of different sizes[27] and aligned homochiral domains on millimeter scale[19,28-29]. In spite of all these investigations, two questions remain unsolved for years. First, due to unavailability of a suitable experimental method, there has been a lack of quantitative research on pitch variation in binary chiral system, even though such knowledge is important for their chiro-optical properties. Second, it is always challenging to determine the chiral superstructure of dopants in binary systems, especially when the dopants are in isotropic state and pre-aligned by HNFs. In order to make real-world applications like displays[30] and ferroelectric devices[31], these two long-standing questions need to be addressed.

Here we report *in situ* pitch measurement and phase characterization of the binary systems with different achiral dopants. Resonant soft X-ray scattering (RSoXS), as a combination of scattering and absorption[32], is performed in the vicinity of elemental absorption edges. At the absorption edge, the non-spherical outer orbitals of atoms are involved in the scattering process due to absorption of the incoming beam. This makes the scattering dependent not only on electron density fluctuations, but also on orientation of orbitals. Resonant diffraction on short-pitch helices then becomes similar to light diffraction from a LC thermometer giving the color equivalent to the helical pitch in the appropriately chosen cholesteric LC. The specific advantage of RSoXS is that such low energy X-rays are used that absorption edge of elements even as light as carbon can be reached, benefiting from its abundance in organic materials. The use of a polarized incident beam additionally enables quantitative comparison between experimental intensities, revealing orientational order[33-42], see details in supplementary information (SI), Section 1. Besides, the width of HNFs (w) was determined by small angle X-ray scattering (SAXS) to evaluate the size of nanofilaments. By further applying resonant scattering theory, the molecular packing in HNFs is simulated and the physical merit behind the scattering signal is deciphered. Doping rod-like 5CB into bent-core NOBOW leads to decrement of helical pitch, in contrast, octane exhibits no significant influence as a dopant. Based on resonant harmonics (2^{nd}, 3^{rd}, 4^{th}…) and a halo exclusively shown in NOBOW/5CB binary system as well as RSoXS probed at K-edge of oxygen, we revealed the effects of interfacial tension on pitch decrement and characterized the chiral superstructure of 5CB.

The material used in this study is NOBOW (P-8-OPIMB, Fig. 1a), whose phase sequence is shown in the left y-axis of Fig.1b. One dopant is 5CB, a typical rod-like achiral molecule whose isotropic temperature is above 35 ^{o}C. Another dopant is octane, which is isotropic above -57 ^{o}C and evaporates ~125 ^{o}C. To understand the phase behavior of the binary systems, we prepared a series of NOBOW/dopant mixtures, with dopant weight percentage varying from 0 to 90, see details in Table S1. Mixtures of NOBOW/5CB were firstly heated to melting point, then drop-casted onto a 100 nm

thick silicon nitride membrane and covered by another membrane to prepare a sandwiched cell. NOBOW/octane mixtures were prepared in a slightly different way while the pure NOBOW was firstly melt and then cooled down to ~120 ºC before octane was subsequently added. All samples were held in room temperature for one day before experiments, see details in SI, Section 1. Several cycles of heating and cooling were conducted to mix NOBOW and dopants well. RSoXS depending on dopant concentration, temperature, beam energy and time have been performed to investigate the helical pitch and self-assembly behavior of the binary systems.

According to phase diagram shown in Fig. 1b[17], B2 and B3 phases are suppressed due to doping and the robust B4 phase as a soft crystal[43] dominates. The resonant scattering data were collected at 70 ºC for NOBOW/5CB system to learn the phase behavior of the binary system when dopants are in isotropic state. CCD images and schematic representations of NOBOW/5CB mixture were shown in Fig. 1c-e. The half-pitch $p/2$ of HNFs decreased dramatically from ~130 nm to ~93 nm as 5CB concentration increased. In contrast, NOBOW/octane system didn't change much in Fig. 1f-h. The relationship between helical pitch variation and dopant concentration is plotted in Fig. S8. Unlike reported cases[44], such pitch decrement is induced by achiral rod-like dopant 5CB without any axial chirality.

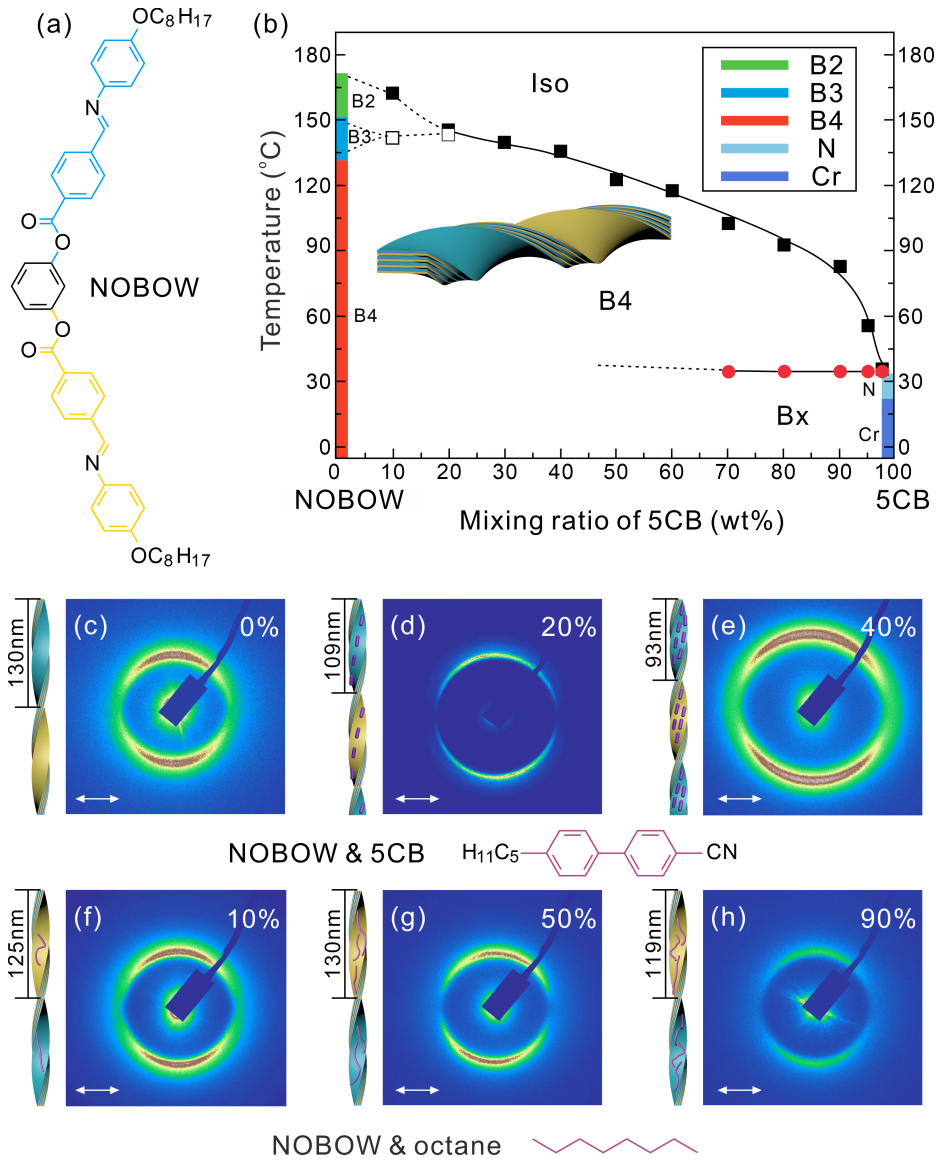

Figure 1. (a) Molecular structure of NOBOW, blue and yellow parts stand for two halves creating front and back half-layers in HNFs; (b) Phase diagram of NOBOW/5CB binary system with schematic representation of HNFs[17]; (c-e) RSoXS CCD images of pure NOBOW, 20% and 40% NOBOW/5CB mixtures at 70 °C, 284 eV with schematic representations; (f-h) RSoXS CCD images and schematic representations of NOBOW/octane mixtures at the same X-ray energy and temperature as NOBOW/5CB mixtures. White arrows indicate the direction of linear polarized beam.

To decipher the signal-structure relationship based on resonant scattering, a quantitative simulation of resonant signal from HNFs was done. Following Dmitrienko's idea[45] and

convolution property of Fourier transform, bent-core molecule can be decomposed into two halves with opposite conical angles, see Fig. 2a, b. Structure factor is computed by applying proper rotation matrix to tensorial form factor. Resonant scattering signals were simulated by the Fourier transform of the structure factor[35,40,46]. The theoretical computation suggests only one fundamental peak $2q_{HNFs}$, corresponding to half pitch, is supposed to be observed, see details in SI, Section 2. Taking laboratory coordinate into consideration, the angular intensity distribution of half pitch signal on 2D detector can be obtained as a function of azimuth angle α and conical angle θ. As shown in Fig. 2c, the computed resonant signal position and polarization both fit well with experimental results shown in Fig. 2d, probing the molecular helices in HNFs.

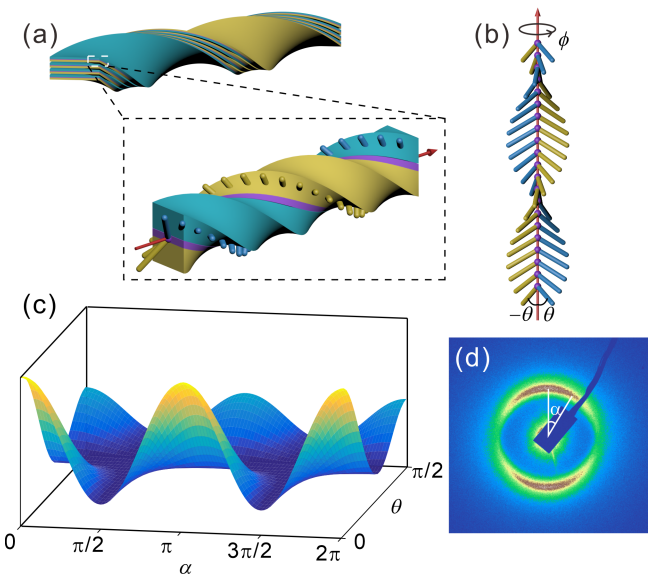

Figure 2. (a) Schematic model of NOBOW in HNFs; (b) Simplified model of NOBOW in HNFs. Blue and yellow halves are computed individually and red arrow indicates the z direction used in computation; (c) Resonant scattering intensity associated with azimuth angle α and conical angle θ. For all θ between 0 and π/2, the scattering intensity distribution is in line with (d) experimental result, suggesting the existence of molecular helices in HNFs. White arrow indicates the direction of linear polarized beam.

To understand the distinct effects of doping 5CB and octane, UV/Vis absorption spectra of all pure materials and mixtures were recorded to investigate the interactions between

NOBOW/5CB and NOBOW/octane mixtures (Figs. 3a and S3). By comparing the recorded absorption spectra with sum of pure compounds with wt% (Fig. S4), certain difference can be recognized only when 5CB concentration is low (Figs. 3b and S5). Such results qualitatively proved that 5CB interacts differently with NOBOW compared with octane, see details in SI, Section 3. To further illustrate how distinct interactions affect the helical pitch, we put our focus on the high order harmonics and the halo near fundamental peak in RSoXS, which is exclusively observed in NOBOW/5CB systems while pitch decreased as in Fig. 3c. To understand the physical merit behind these resonant signals, energy and temperature-dependent RSoXS scans were conducted.

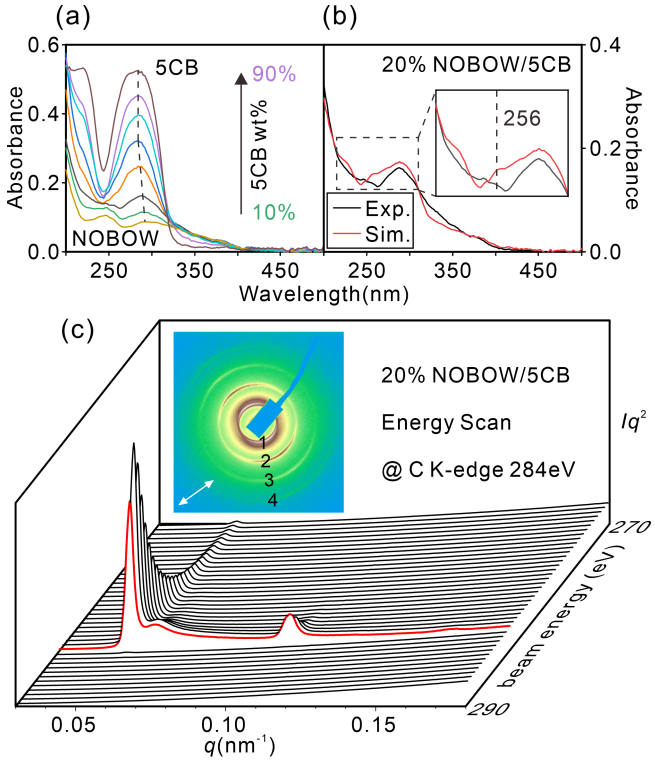

Figure 3. (a) UV/Vis absorption spectra of two pure materials NOBOW and 5CB as well as all NOBOW/5CB mixtures at 70 ºC. Dashed line indicates the peak shift of NOBOW/5CB mixtures which stops at 50% concentration due to the fully coating of 5CB; (b) Differences can be observed between experimental (Exp.) and simulated (Sim.) absorption spectra of 20% NOBOW/5CB mixture; (c) Energy scan of 20% NOBOW/5CB mixture from 270 eV to 290 eV in step of 0.5 eV. The sample was kept

in room temperature for two months. High order harmonics and a halo appeared around 284 eV. CCD image at 284 eV is shown at back left. Red thick line indicates the scattering at 284 eV. White arrow indicates the direction of linear polarized beam.

Temperature scans at the C K-edge were shown in Fig. S9-S10, suggesting temperature-independent helical pitches for all binary systems. The minor difference between heating and cooling is attributed to distinct thermal history. Judged from the 2D scattering patterns in Fig. S11, 40% is the highest concentration allowing halo. Combining with different scattering intensity trend in Fig. S12, we speculate that 40% of 5CB is almost enough to fully coat the HNFs, which is close to the concentration of macroscopic phase separation (50%) in NOBOW/8CB binary system[15]. Although helical pitch is temperature independent, CCD images in Fig. S11 suggest that nearly fully coated HNFs respond to temperature to a certain extent, as indicated by intensity variation, which is explained in SI, Section 5. Then, 20% NOBOW/5CB mixture was tested upon heating and cooling around melting point, shown in Fig. S13. Harmonics didn't change much until isotropic phase and formed simultaneously with fundamental peak upon cooling. This indicates that harmonics are generated upon HNFs formation, a signal from molecular packing in HNFs. On contrary, halo vanished upon cooling from isotropic state, suggesting a long-term procedure between HNFs and dopant.

Apart from temperature scans, energy scans were conducted in the vicinity of C K-edge as shown in Figs. S14-S15 and the correlations at C K-edge were shown in Table S2. all signals are sensitive to beam energy, originating from orientational order. It's long been an unsolved question that how rod-like dopants express chirality while being confined in the HNFs networks. Here, by extending our resonant experiments to oxygen absorption edges, we are able to decipher the chiral superstructure of 5CB in binary systems. RSoXS experiments at the C and O K-edge were conducted with 20% NOBOW/5CB mixture, see Fig. 4. The intensity of halo decreased significantly at O K-edge. Similar situation can be found in 10% NOBOW/5CB mixture in Fig. S16. Such decrease suggests that oxygen-free 5CB contributes to the resonant halo. Previous work

suggests that rod-like molecules are immiscible with NOBOW[47] and undergoes pre-alignment in isotropic state[22]. The resonant halo indicates that 5CB are directed by the groove of HNFs and showing a *pseudo* helical packing in isotropic state, as shown by schematic representations in Fig. 1c-e. Similar model has been raised before to explain the molecular packing of dopants in nematic phase[17,19,22]. However, no direct evidence was found to support the chirality generation of 5CB in isotropic state.

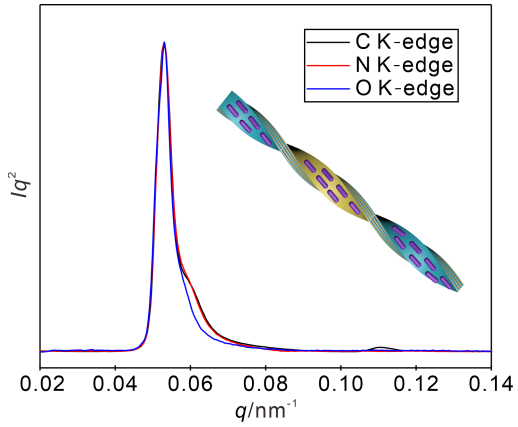

Figure 4. 1D plots of 20% NOBOW/5CB mixture at different absorption edges. Black line represents C K-edge at 284eV, red line is at O K-edge at 531.5eV. Two curves are normalized to exhibit the variation of halo. The halo intensity decreases at oxygen K-edge, suggesting oxygen-free 5CB molecules contribute to the resonant halo by twisting as shown in the inset scheme.

Combining the pre-alignment of rod-like dopants[22] with the concentration limitation of harmonics, halo and pitch decrement, we speculate that limited immiscible dopant introduces anisotropic interfacial tension, which is a tension from the HNFs/dopant interface and potentially to be anisotropic along two half-layers of HNFs due to their mutually orthogonal lattice[9]. The interaction between HNFs and dopants can be estimated by Flory-Huggins interaction parameter χ, see details in SI, Section 5 and Fig. S17. Such anisotropic interfacial tension could disturb molecular packing in HNFs leading to pitch decrement, which will be discussed later. When 5CB concentration is higher than 40%, binary system forms macroscopic phase separation and the pre-

aligned 5CB fully covers the surface of HNFs, leaving only one stable resonant signal representing half pitch as observed from the experiments.

To further confirm our speculation that anisotropic interfacial tension has an effect on resonant signal, we chose the 40% and 50% NOBOW/5CB mixtures to learn how NOBOW/5CB binary system changed with time. Both samples were examined for three times, immediately after preparation (I), stored for one day (D) and sealed for two months (M). By comparing RSoXS results in Fig. S18, we found D and M samples reached thermal equilibrium state with identical fundamental peak intensity and correlation. Interestingly, harmonics appeared in both M sample. Though 5CB was well-mixed in D sample, the uniformity could lose after long enough time due to immiscible nature between NOBOW and 5CB. In contrast, doping miscible chloroform/octane leads to no harmonics regardless of concentration (Fig. S19). Thus, the anisotropic interfacial tension introduced by immiscible 5CB disturbs molecular packing in HNFs. The disturbance results in a molecular orientation field represented by rotation matrix containing Fourier series, which leads to harmonics after Fourier transform.

Apart from helical pitch, width of HNFs is also critical. We used SAXS to conduct *in situ* study of HNFs' width[48]. Fig. 5a is the SAXS temperature scan of 20% NOBOW/5CB mixture upon cooling from 160 ^{o}C to 30 ^{o}C. At 150 ^{o}C, B2 phase with two sharp peaks can be found as in Fig. 5b, consisting with phase diagram in Fig. 1b. Upon cooling, two broader peaks as in Fig. 5c appeared since 140 ^{o}C, indicating the formation of twisted HNF layers (B4 phase). Minor layer distance (d = ~4.8 nm) variation can be observed upon cooling compared with other systems, see Fig. S20, suggesting all 5CB are expelled by HNFs.

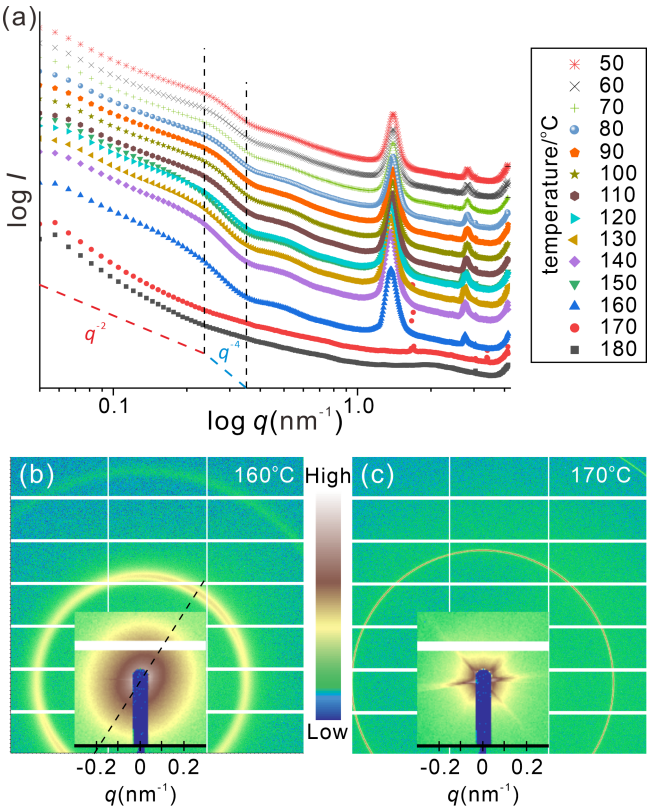

Figure 5. (a) SAXS temperature scan upon cooling for 20% NOBOW/5CB mixture and CCD images of (b) B2 and (c) B4 phase, respectively. In log-log plot, slope changed around 0.24 nm^{-1}, suggesting the nanofilament width of ~26 nm.

In 1D log-log plot, a slope transition in rather small angle region can be found around 0.24 nm^{-1}. The intensity is proportional to q^{-2} when q is lower than 0.24 nm^{-1} and varies like q^{-4} when being higher, see dashed line in Fig. 5a. The exponential fitting results are listed in Table S3. In the rather small angle region, the scattering signal is from the surfaces/interfaces of electron density continuums, which offers correlation between them, see details in SI, Section 6. According to the Porod's Law, an exponent -4 implies surface fractal morphologies with smooth surface[49-50]. Exponent of -2 represents the Gaussian coil like aggregation shape[51]. In our case, the aggregation is from the filaments. And the fractal domain vanishes as a result of filaments interwoven with each other, forming networks. As long as dimension is beyond the filament's width, filaments start to aggregate and the curve flattens. The turning point, 0.24 nm^{-1}, representing ~26 nm, is supposed to be the width of HNFs (w), which is in line with

FFTEM experiments[8-9]. 50% NOBOW/5CB mixture exhibited similar result with slope transition around ~29 nm (Fig. S21). The minor increment could be a result of 5CB fully coating along groove of HNFs. The thickness of 5CB is ~6 nm compared with pure NOBOW in Fig. S22a, b. Such value is qualitatively similar to 3.1 nm in NOBOW/8CB system determined by latent heat, which is supposed to be underestimated[22]. In contrast, octane has an even minor effect on width of HNFs in binary system. The thickness of octane is only ~2 nm with 50% concentration (see Fig. S22c, d), probably due to the chemical structure similarity between octane and aliphatic tails of NOBOW. SAXS study suggests that each filament contains only ~5 layers of NOBOW (w/d), which is thin enough for interfacial tension modifying the curvature of HNFs.

Utilizing both resonant and conventional X-ray scattering, we showed that anisotropic interfacial tension plays a critical role on helical pitch during HNFs formation. Such phenomenon can be explained by the continuum surface elasticity (CSE) model developed by Wang et.al[52]. Their model suggests that microbeam with anisotropic surface elasticity on two sides would twist under axial loading and the twist angle can be expressed as a function of axial loading and surface elasticity directions, see Fig. S23a. HNFs are similar to such model. The HNF layer contains NOBOW molecules tilting by β from layer normal. The projections of two halves are perpendicular with each other, see Fig. S23b. According to the CSE model, a mutually perpendicular surface elasticity leads to small twisting angle, i.e. large helical pitch. With only ~5 layers per filament, the anisotropic interfacial tension could tune the tilt angle β among several energetically accepted form[9], leading to the change of surface elasticity direction and curvature of nanofilaments.

To conclude, with in-depth decoding of resonant and conventional X-ray scattering signals, two binary systems including NOBOW and 5CB/octane were systemically studied. The molecular helices in HNFs and the chiral superstructure of 5CB in isotropic state directed by HNFs were probed by the model-dependent simulation and

resonant scattering at K-edge of different elements. Furthermore, an up to 30% pitch decrement induced by immiscible achiral dopant 5CB was revealed. Supported by a continuum surface elasticity model and DFT computation, anisotropic interfacial tension is accounted for this special phenomenon. The elucidation shades new light on the self-assembly behavior of HNF/dopant binary system and provides a new method manipulating the helical pitch of the robust HNFs. The NOBOW/5CB binary system is an analogue to many recent developed binary systems with applications in various filed including optical rotation devices[17,24], circularly polarized light emmiters[26] and chirality transfer agents[25]. And our work would offer new understandings and opportunities in the structural variation perspective for these applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org.

RSoXS calibration, SAXS profile and the RSoXS energy, temperature, time scan profiles of NOBOW/5CB, NOBOW/octane and NOBOW/chloroform, schematic representations of continuum elastic theory, molecular packing in HNFs, UV/Vis absorption spectra of all mixtures and theoretical computation of resonant signal.

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Author Contributions

F. L. and C. Z. initialized the project and C. Z. designed the experiments, Y.C. and T. T. performed the experiments. All authors analyzed the data. Y.C., T. T., L.Z. and F.L. wrote the manuscript with contributions from all authors. All authors have given approval to the final version of the manuscript.

‖ Y. C. and T. T. contribute equally to the manuscript.

Notes

The authors declare no competing financial interest.

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