

Electronic Supplementary Information for “Macroscopically Oriented Lyotropic Chromonic Liquid Crystalline Nanofiber Embedding Self-Assembled Sunset-Yellow FCF Nanocolumns”

Young-Jin Kim,^{†a} Dea-Yoon Kim,^{†a} Jong-Hoon Lee,^a Changwoon Nah,^a Joong Hee Lee,^a Myong-Hoon Lee,^a Hak Young Kim,^b Shiao-Wei Kuo,^c Seunghan Shin^{*d} and Kwang-Un Jeong^{*a}

^a*Department of Polymer-Nano Science and Technology and Department of Flexible and Printable Electronics and Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea*

^b*Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea.*

^c*Department of Materials Science and Optoelectronic Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan.*

^d*Chonan R&D centre, Korea Institute of Industrial Technology, Chonan, 330-825, Korea. E-mail:*

* To whom the correspondence should be addressed. E-mail: kujeong@jbnu.ac.kr and shshin@kitech.re.kr

[†]These authors contributed equally to this work.

Materials and sample preparation: Sunset-Yellow FCF (SSY) was purchased from Sigma Aldrich and purified several times by washing with ethanol. Utilizing the HPLC test combined with pH (JEIO Tech. Nr.04310034) and Fourier transform infrared (FT IR) measurements, the purity of SSY was estimated to be over 99.0%. To avoid possible problems because of Na⁺ ions in SSY, Na⁺ ions in SSY were exchanged with H⁺ ions by the proton exchange reaction. Dowex G-26 (Dow Chemicals), a polystyrene-based strongly acidic cation exchanger, was used for the proton exchange process. Before the proton exchange reaction, Dowex G-26 was first washed with HCl to get rid of organic and inorganic impurities and then with water and ethanol mixture. The proton exchange reaction of H-SSY was schematically illustrated in Fig. S1. The proton exchanged Sunset-Yellow FCF was shortened as H-SSY in this research. As a stabilizing polymeric material, poly(vinylpyrrolidone) (PVP, Sigma-Aldrich, M_w=1,300,000 g/mol) was purchased from Sigma-Aldrich and used without further fractionation.

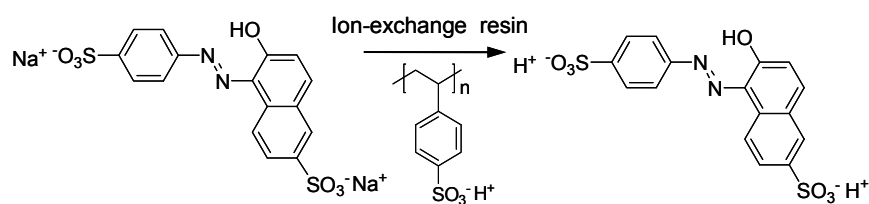


Fig. S1 Schematic diagram of the ion exchange reaction of SSY.

The ion-exchanged H-SSY was vacuum-dried at 25 °C for 24 h. Based on the morphological observations, the optimized contents of PVP and H-SSY in PVP/H-SSY/H₂O solution were determined as 5 and 28 wt%, respectively. The electrospinning conditions of PVP/H-SSY/H₂O solution were also optimized based on the SEM images of nanofibers and the H-SSY molecular orientations in the PVP/H-SSY nanofibers. The PVP/H-SSY nanofibers were prepared by electrospinning at following conditions: concentration = 33 wt%, electric voltage = 15 kV, distance between tip and corrector (TCD) = 15 cm, rotation speed of collector = 1000 rpm, and flow rate of solutions = 5 ml/h. Especially, by increasing the rotational speed of collector above the electrospinning speed, the uniaxially aligned PVP/H-SSY nanofiber mats were prepared. The electrospun PVP/H-SSY nanofibers were kept in a vacuum before further characterizations. To test the stability of PVP/H-SSY nanofiber, the PVP/H-SSY nanofibers were annealed for 12 h at 220 °C which is the temperature above the glass transition temperature of PVP ($T_g = 180$ °C).

For differential scanning calorimetry (DSC) experiments, the sample weight was about 5 mg and the pan weights were kept constant with a precision of ± 0.001 mg. Phase structures and molecular orientations in PVP/H-SSY nanofibers were investigated via cross-polarized optical microscopy (POM) and two-dimensional (2D) wide angle x-ray diffraction (WAXD) experiments. Additionally polarized FT IR was applied to study molecular packing, interactions and conformations in the molecular levels. Samples for the polarized FT IR

experiments were prepared by placing aligned nanofibers on a silicon wafer.

Equipment and Experiments: POM (Nikon Dxm 1200) was used to construct a phase diagram of the PVP/H-SSY/H₂O solution. Additionally, to investigate molecular orientations in the uniaxially oriented PVP/H-SSY nanofibers on the micrometer length scale, the long axis of nanofiber was rotated with respect to polarizer and analyzer. Morphological investigations on the sub-micrometer length scale were conducted by SEM (JSM 5900 and JSM 6400).

Thermal transitions of the PVP/H-SSY nanofibers were investigated using a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. The temperatures and heat flows were calibrated using standard materials (benzoic acid and indium) at 10 °C/min cooling and subsequent heating rate. The heating experiments always preceded the cooling experiments to eliminate the previous thermal histories, and the cooling and heating rates were kept identical. The transition temperatures were determined by measuring the onset and peak temperatures from both the cooling and heating scans.

2D WAXD experiments on the oriented nanofibers were conducted using an imaging system (Rigaku, R-AXIS-IV) with 18 kW rotating anode x-ray generators. The diffraction peak positions and widths were calibrated with silicon crystals of the known crystal size in the high 2 θ -angle region (> 15°) and silver behenate in the low 2 θ -angle region. The diameter of x-ray beam is ~ 0.3 mm. A 30 min exposure time was required for a high-quality pattern and the background scatterings were subtracted from the sample scans.

Molecular interactions on the molecular levels and molecular packings in the anisotropically oriented nanofiber mats were also evaluated by polarized FT IR spectroscopy (Jasco FT/IR-300E) by rotating azimuthal angles from 0° to 90° with respect to the long axis of nanofiber. The resolution of FT IR was 1 cm⁻¹ and 40 scans were averaged for each

spectrum. The Cerius² (Version 4.6) simulation software from Accelrys was also used to calculate the minimal energy geometry of the H-SSY in the isolated gas-phase utilizing the COMPASS force field.

Thermal transitions: DSC experiments were first conducted during cooling and subsequent heating at 10 °C/min scanning rate to detect thermal transitions of PVP/H-SSY nanofibers. Based on the DSC results, the PVP/H-SSY nanofibers showed an endothermic first-order thermal transition at 255 °C with $T_g = 180$ °C, but the annealed ones only exhibited T_g . (Fig. S2). This represented that the H-SSY molecules confined in PVP nanofibers were recrystallized around 255 °C so that the electrospun PVP/H-SSY nanofibers at room temperature were considered to be in a metastable state.

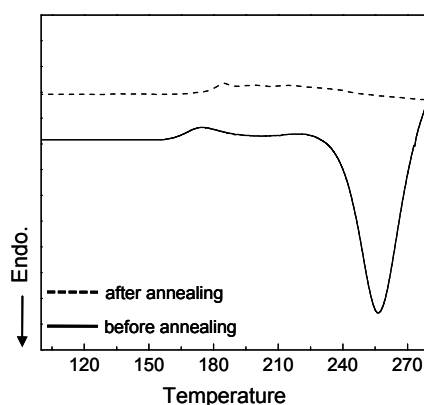


Fig. S2 DSC thermograms of the PVP/H-SSY nanofibers before and after the annealing process at 220 °C for 12 h.

Orientation of H-SSY nanocolumns in the PVP/H-SSY nanofibers: To obtain all diffractions available in the H-SSY crystal, the uniaxially oriented H-SSY mats were first grinded to powders and 2D WAXD pattern was taken at room temperature as shown in Fig. S3a. In the 1D WAXD powder pattern (Fig. S3c) obtained by scanning the 2D WAXD, diffraction information about H-SSY molecular arrangements appeared on two different length scales. One is on the nanometer scale in the low 2θ -angle region between 1.5° and 11° ,

where the lateral packing information of nanocolumns can be obtained. Diffractions on the sub-nanometer scale between 11° and 30° can provide information about the H-SSY molecular packing inside of nanocolumns as well as about the molecular correlation between nanocolumns. Four Bragg reflections at $2\theta = 5.0^\circ$, 5.2° , 7.5° , and 10.37° appeared in the low 2θ -angle region, which corresponded to d -spacings of 1.77, 1.70, 1.18, and 0.85 nm, respectively. On the basis of the triangulation method of building a $2D-a^*b^*$ lattice of the unit cell, these four Bragg reflections can be assigned to be the (100), (010), ($\bar{1}10$) and (020), respectively. Through the refinement of the reciprocal $2D-a^*b^*$ lattice, a 2D unit cell in real space was calculated with dimensions of $a = 1.70$ nm, $b = 1.78$ nm, and $\gamma = 84.5^\circ$. On the meridian of the 2D WAXD pattern of the annealed PVP/H-SSY nanofibers (Fig. S3b), a pair of diffractions appeared at $2\theta = 27.2^\circ$ (d -spacing = 0.327 nm) corresponding to the π - π stacking of H-SSY molecules. Therefore, c of the unit cell can be identified to be $c = 0.554$ nm. This identification can be further supported by the diffractions at (hk1) planes.

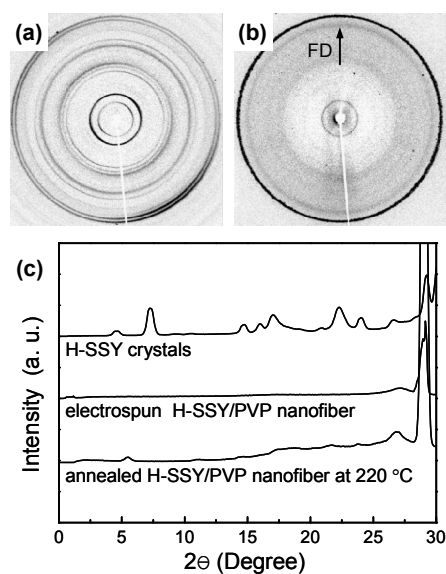


Fig. S3 2D WAXD patterns of (a) H-SSY powders at room temperature and (b) annealed PVP/H-SSY nanofibers. (c) 1D WAXD patterns obtained from the 2D WAXD patterns of H-SSY powders (Fig. S3a), PVP/H-SSY nanofiber (Fig. 4a) and annealed PVP/H-SSY nanofiber (Fig. S3b).

Degree of nanocolumn orientation in the PVP/H-SSY nanofibers were estimated to be 81% by the azimuthal scanning of the 2θ -angle between $2\theta = 26^\circ$ and 28° in the 2D WAXD of PVP/H-SSY nanofiber mats in Fig. S4. After the annealing process, the degree of nanocolumn orientation (π) decreased down to 69%. Here, π was defined by $(180^\circ - H^\circ) \times 100 / 180^\circ$ and H° was the half width of the intensity distribution on the Debye diffracted arc. Utilizing Scherrer equation, the correlation length along the H-SSY nanocolumn before and after the annealing process was also calculated to be 40 and 31 nm, respectively.

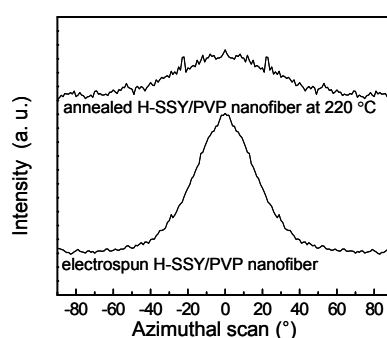


Fig. S4 Azimuthal scans of the 2θ -angle between 26° and 28° in the 2D WAXD of PVP/H-SSY nanofiber (Fig. 4a) and annealed PVP/H-SSY nanofiber (Fig. S2b).

For the investigation of molecular interactions in the uniaxially aligned PVP/H-SSY nanofibers, polarized FT IR spectra of PVP/H-SSY anisotropic nanofiber mats were also obtained by rotating the azimuthal axis with respect to the FD from 0° to 90° (Fig. S5). From these FT IR spectra, it was recognized that there was the absorption bands with the maximum intensity at 1558 , 1542 , 1163 and 1116 cm^{-1} . The absorption bands at 1726 and 1542 cm^{-1} can be identified as the aromatic C-H stretching vibrations in H-SSY, while the absorption bands for the sulfonate salts appeared at 1163 and 1116 cm^{-1} . The absorption intensity change of aromatic C-H and sulfonic acid group increased with the azimuthal angles. This result indicated that the in-plane of H-SSY was perpendicular to the long axis of the PVP/H-SSY nanofiber, which well matched with the result of WAXD.

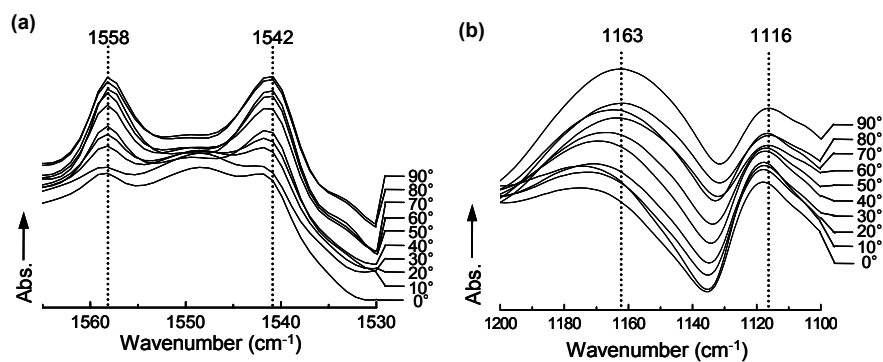


Fig. S5 Polarized FT IR spectra for uniaxially oriented PVP/H-SSY nanofibers: (a) between 1580 and 1530 cm^{-1} and (b) between 1200 and 1100 cm^{-1} . Here, the azimuthal axis is rotated from 0 to 90° with respect to the long axis of nanofiber.