

Supporting Information

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**Self-Assembly of Semiconducting Photoluminescent Peptide
Nanowires in the Vapor Phase****

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Experimental Section

Synthesis of cyclo-FF Nanowires (NWs): Linear diphenylalanine (FF) peptide in a lyophilized form was obtained from Bachem AG (Bubendorf, Switzerland). Single crystalline cyclo-FF NWs were synthesized in a horizontal furnace; linear-FF powder in an alumina boat was placed at the center of an alumina tube. The carrier argon gas was supplied through a mass-flow controller at the rate of 20-100 sccm. Si-substrates were placed at the downstream end of the tube. The upstream and downstream zone of the tube was maintained at 250 °C and 180 °C, respectively, and no catalyst was used for cyclo-FF NW synthesis.

Characterization of Single Crystalline cyclo-FF NWs: After coating the cyclo-FF NWs with platinum using SCD005 Pt-coater (Bal-Tec AG, Liechtenstein), we observed them using an S-4800 field emission scanning electron microscope (Hitachi High-Technologies CO., Japan). Thermogravimetric analyses (TGA) of FF powder and NWs were carried out using a thermogravimetric analyzer Q50 (TA Instrument, DE). After equilibration at 40 °C for 30 min, samples were heated up to 400 °C at a constant rate of 10 K min⁻¹ in a nitrogen environment. Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were taken using a Tecnai F20 TEM (Philips, Japan) that were operated at 200 kV, and a JEM 3010 TEM (JEOL, Japan) that were operated at 300 kV. Single NW Raman spectrums were obtained using a home-built micro-Raman system that was equipped with a thermoelectrically cooled CCD detector.^[1] The NW was illuminated by the 632.8 nm light of a He-Ne

laser whose light was linearly polarized and its polarization direction was controlled by rotating a half-wave plate. The incident laser beam (~500 nm diameter) was focused on a point of a single NW, which was then placed on a thin Ag film of 300 nm thickness. A diffuse reflectance spectrum (DRS) was recorded using a UV-Vis spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra of each sample in a fine-powder form were obtained using a DARSA PRO 5100 PL system (Professional Scientific Instrument Co., Korea) under continuous Xe-lamp excitation (500 W) at room temperature. Each NW and NT was illuminated by a halogen lamp and their scattering spectra were recorded by a spectrometer coupled to a dark-field microscope system. *I-V* curves of single NW devices were measured using a semiconductor characterization system (4200-SCS/F, Keithley Instruments Inc., Cleveland, Ohio) in an air atmosphere via a manual probe station (Summit 11862b, Cascade Microtech Inc., Beaverton, OR). The surface of a single NW was scanned using a Nanoscope III Multimode AFM (Digital Instruments Inc., Santa Barbara, CA) under ambient conditions.

Collection and Refinement of PXRD patterns: High resolution PXRD data of NT and NW samples were collected at the 8C2 high-resolution powder diffraction beamline of the Pohang Accelerator Laboratory in Pohang, Korea. The incident X-ray was vertically collimated by a mirror and monochromatized to the wavelength of 1.5494(1) Å by using a double-crystal Si (111) monochromator. The detector arm of the vertical scan diffractometer is composed of seven sets of soller slits, flat Ge (111) crystal analyzers, anti-scatter baffles, and scintillation detectors with each set separated by 20 degrees. The specimen of ca. 0.2 g powder was prepared by flat plate side loading method to avoid preferred orientation, and the sample was then rotated about a vector normal to the surface during the measurement to increase sampling statistics and to reduce preferred orientation effects. Step scan was performed at room temperature from 6° in 2θ with 0.01° increment and 1° overlaps to the next detector bank up to 131° in 2θ. The obtained experimental powder diffraction patterns are in good agreement with a simulated powder diffraction pattern of the previously reported single crystal structural data.^[2] With this unit cell structure, we performed Pawley^[3] refinement to optimize the lattice parameters iteratively until no change

was obtained in the R_{WP} value. The orthogonal polynomials with 20 coefficients were used as the basis set for fitting the experimental background. In Rietveld^[4] refinements, the positions and torsional angles of cyclo-FF molecules were explicitly considered as structural degrees of freedom. The March-Dollase function was selected for the preferred orientation correction and an anisotropic temperature factor was applied for all heavy atoms. During the refinement process, a pseudo-Voigt profile function and Berar-Baldinozzi asymmetry correction^[5] were chosen to fit the entire pattern. Rietveld refinement gave good convergence even when all parameters were refined simultaneously. Most of the molecular modeling, including Pawley and Rietveld refinements, were carried out using *Reflex*, a software package for crystal structure determination from powder diffraction patterns, and were implemented in MS modeling version 4.2 (Accelrys Inc.).^[6]

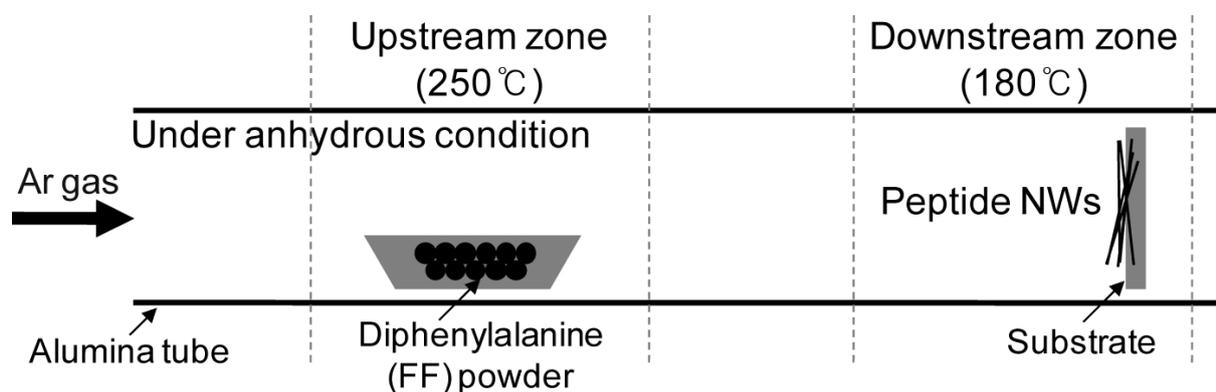


Figure S1. Schematic illustration for the synthesis of cyclo-FF NWs through vapor-transport process. Linear-FF powder was heated at 250 °C under anhydrous condition and NWs were formed on a Si substrate at 180 °C. The average diameter of the cyclo-FF NWs measured by SEM was approximately 90 nm and their length exceeded 10 μm .

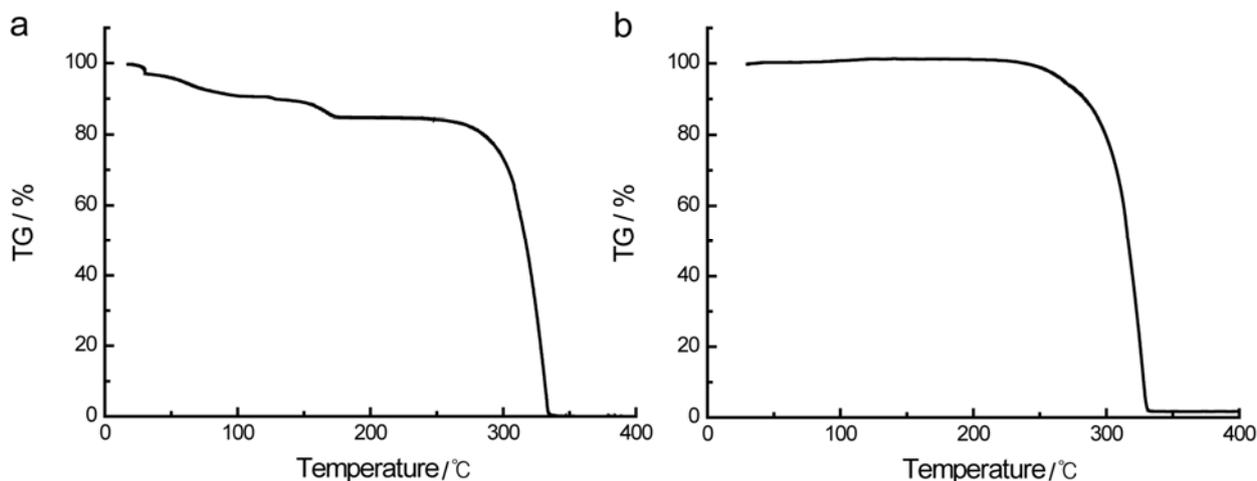


Figure S2. TGA of (a) Linear-FF powders; (b) Cyclo-FF NWs formed from FF at $5\text{ }^{\circ}\text{C min}^{-1}$ heating rate in N_2 . FF powder lost water at approximately $100\text{ }^{\circ}\text{C}$, and thermal vaporization of FF powder began at $250\text{ }^{\circ}\text{C}$. No mass loss at temperatures up to $250\text{ }^{\circ}\text{C}$ indicates the high thermal stability of as-synthesized NWs.

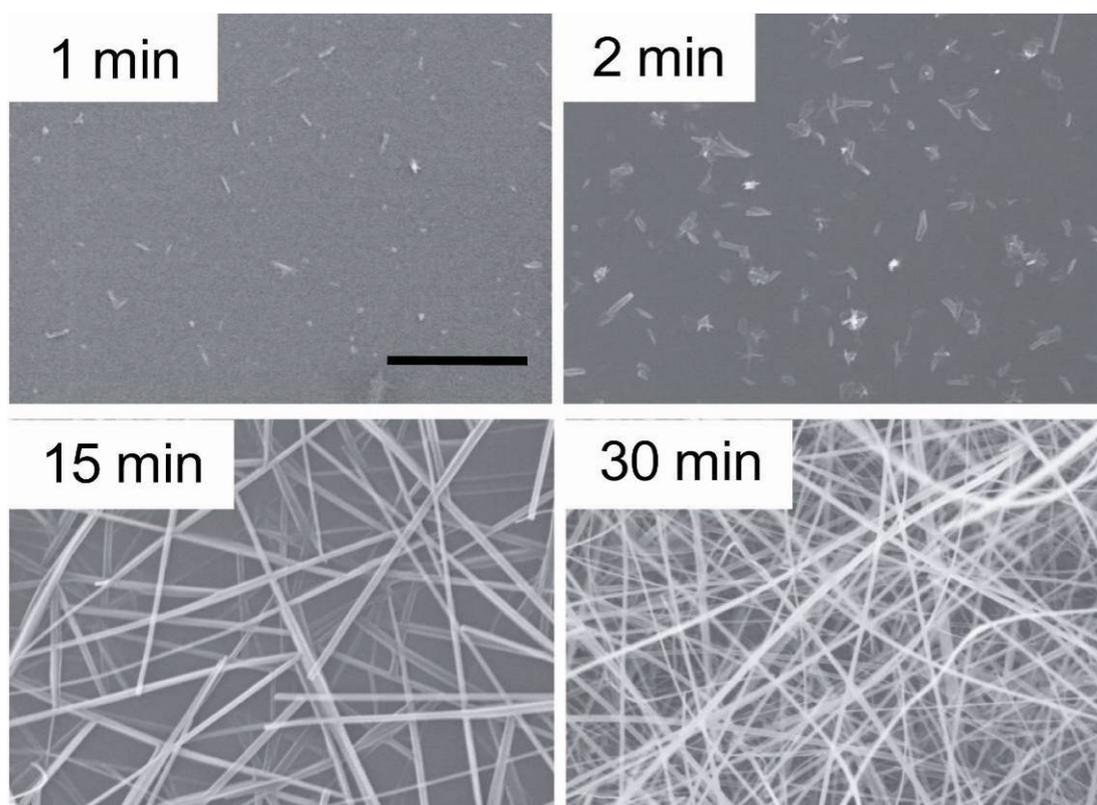


Figure S3. Time evolution of cyclo-FF NW growth during the vapor-transport process. After the formation of nuclei on substrate, short peptide fibrils grew into NWs with both a very high aspect ratio (> 100) and a long persistence length (over $10\text{ }\mu\text{m}$). Scale bar: $5\text{ }\mu\text{m}$.

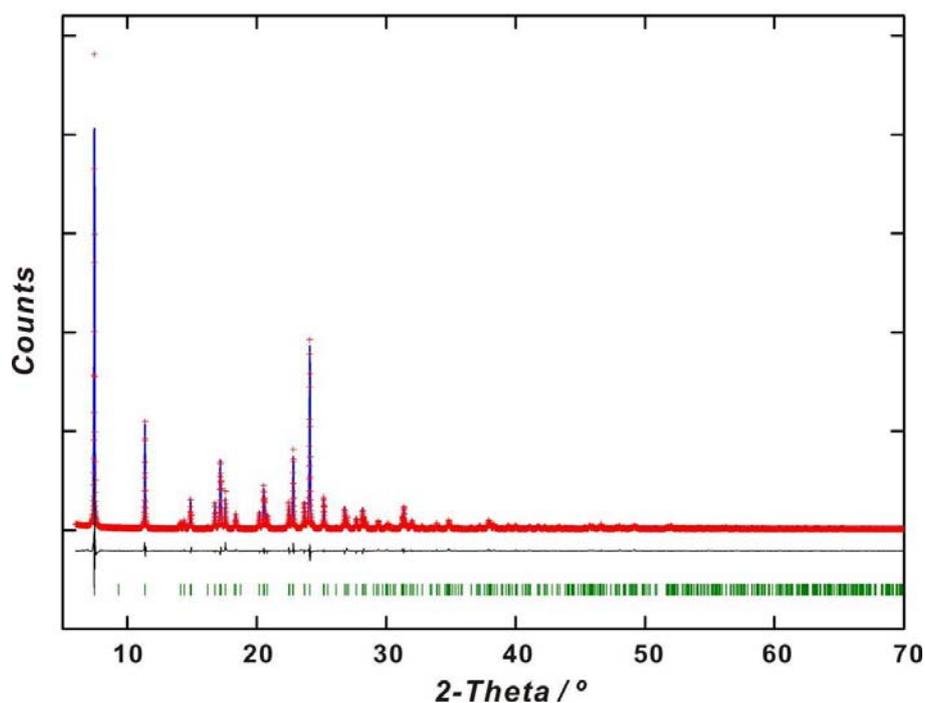


Figure S4. Rietveld refinement pattern of cyclo-FF NWs using PXRD data at 300 K. Plus (+) marks represent the observed intensities, and the solid line defines calculated ones. A difference (obs. – calc.) plot (black) is shown beneath. Green tick marks below the difference plot indicate the reflection position.

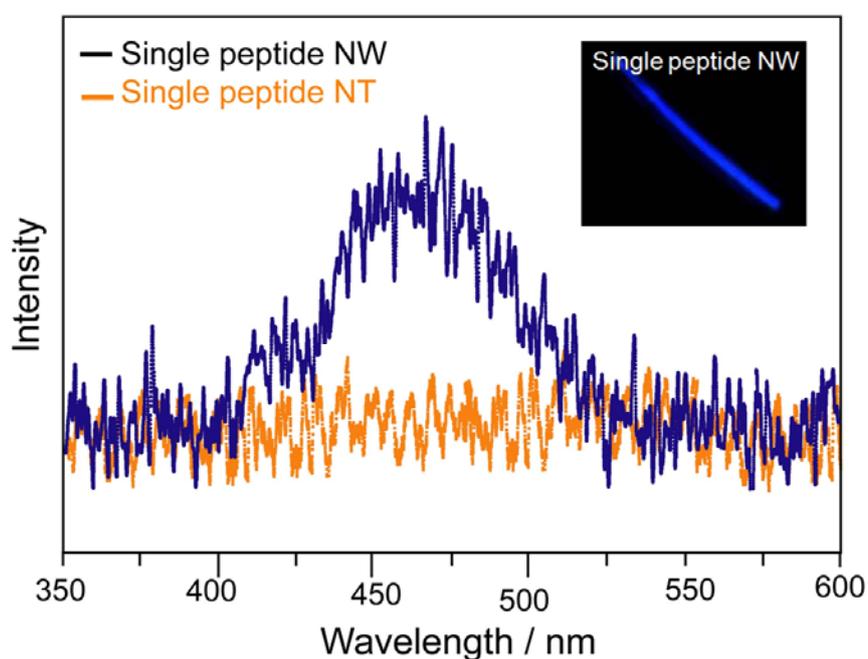


Figure S5. Spectra of single cyclo-FF NW (blue line) and linear-FF NT (orange line). Each nanowire and nanotube was illuminated by a halogen lamp, and their scattering spectra were recorded by a spectrometer that was coupled to a dark-field microscope system. The single NW exhibited strong blue emission centered at around 465 nm. Inset shows a dark-field microscope image of a single NW.

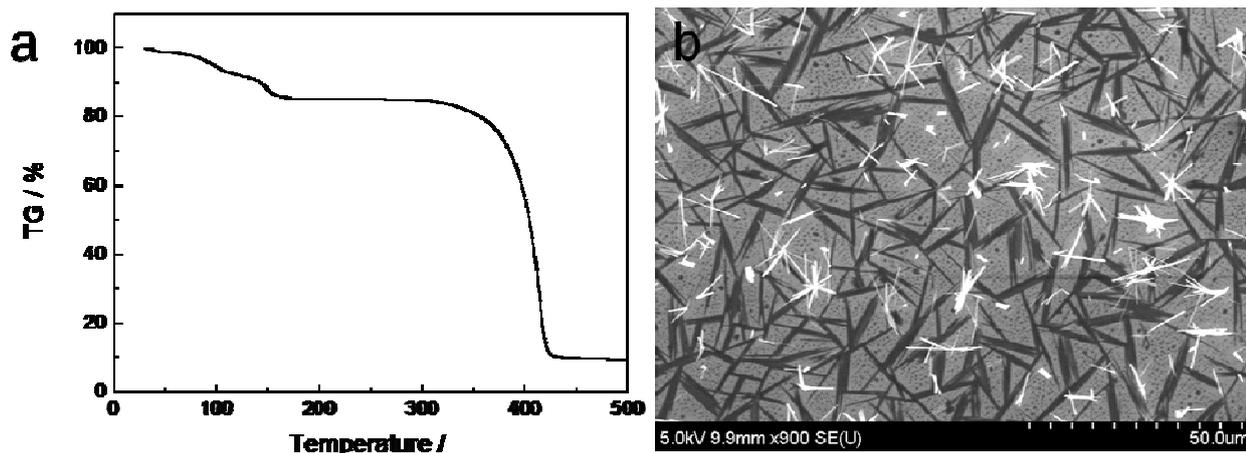


Figure S6. (a) TGA of Trp-Phe powder. TGA result indicates that Trp-Phe can vaporize under approx. 300 °C and is suitable for its application to vapor-transport process. (b) SEM image of Trp-Phe micro/nanostructures formed by vapor transport process. According to the SEM image, the synthesized Trp-Phe micro/nanostructures were quite different from the uniform NWs having a high aspect ratio that are self-assembled from Phe-Phe as a starting material, which indicates side chains of dipeptides can strongly influence the formation of NWs.

References

- [1] I. Yoon, T. Kang, W. Choi, J. Kim, Y. Yoo, S. Joo, Q. Park, H. Ihee, B. Kim, *J. Am. Chem. Soc.* **2009**, 131, 785-762.
- [2] M. Gdaniec, B. Liberek, *Acta Cryst.* **1986**, C42, 1343-1345.
- [3] G. S. Pawley, *J. Appl. Crystallogr.* **1981**, 14, 357-361.
- [4] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, 2, 65-71.
- [5] J. F. Berar, G. J. Baldinozzi, *J. Appl. Crystallogr.* **1993**, 26, 128-129.
- [6] Accelrys, *Material Studio Release Notes, Release 4.2, Accelrys Software, San Diego* **2006**.