

Supplementary Information for:

Synthesis of a helical π -conjugated polymer with dynamic hydrogen-bonded network in the helical cavity and its circularly polarized luminescence property

Tomoyuki Ikai,^{*a} Seiya Awata^a and Ken-ichi Shinohara^b

^a Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^b School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahi-dai, Nomi 923-1292, Japan

^{*}To whom correspondence should be addressed. E-mail: ikai@se.kanazawa-u.ac.jp.

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1. Materials

Anhydrous solvents (chloroform, acetonitrile, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide and tetrahydrofuran (THF)) and common organic solvents were purchased from Kanto Kagaku (Tokyo, Japan). Ethylamine was from Tokyo Kasei Kogyo (TCI) (Tokyo, Japan). Copper (I) iodide (CuI) was from Sigma-Aldrich (St. Louis, MO, USA). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) and *N,N*-dimethyl-4-aminopyridine (DMAP) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) was purchased from Nacalai (Kyoto, Japan). Diisopropylamine (DIPA) was obtained from Kishida (Osaka, Japan). GLB-**1**^{S1} and the compound **2**^{S2} were prepared according to a literature procedure.

2. Instruments

NMR spectra were obtained on a JNM-ECA 500 (JEOL) (500 MHz for ¹H, 125 MHz for ¹³C) spectrometer in CDCl₃ and DMSO-*d*₆ using tetramethylsilane or a solvent residual peak as the internal standard. IR spectra were obtained using a JASCO (Hachioji, Japan) Fourier Transform IR-4700 spectrophotometer. The molecular weights and distributions of poly-**1** were estimated using size-exclusion chromatography equipped with a TSKgel MultiporeH_{XL}-M column (Tosoh, Tokyo, Japan), a JASCO PU-2080 Plus high-performance liquid chromatography (HPLC) pump and a JASCO UV-970 UV/VIS detector at 450 nm, where chloroform was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). Absorption and circular dichroism (CD) spectra were measured using a JASCO V-570 (a scanning rate of 200 nm min⁻¹ and a bandwidth of 0.5 nm) and a JASCO J-720L (a scanning rate of 100 nm min⁻¹ and a bandwidth of 0.5 nm) spectrometers, respectively, with a 0.10, 1.0 or 10 mm in path length quartz cell (UV-grade) (GL Sciences, Tokyo, Japan). The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy). Fluorescence quantum yields were measured on a JASCO FP-8500 using quinine sulfate in 0.5 M sulfuric acid aqueous solution as a standard material. CPL spectra in solution states were recorded at room temperature on a JASCO CPL-300 with 10 mm in path length quartz cell (GL Sciences, UV-grade). A spin-coated film prepared on a quartz substrate (Daico MFG, USQ-grade) from a chloroform solution of poly-**1** (10 mg mL⁻¹) was used for solid-state spectral measurements. A scanning rate of 100 (solution state) or 50 (film

state) nm min^{-1} , an excitation bandwidth of 3000 μm , a monitoring bandwidth of 3000 μm , a response time of 2 (solution state) or 8 (film state) seconds and 2 times (solution state) or single (film state) accumulation were employed. Dynamic light scattering (DLS) measurements were performed on a Nano partica SZ-100 (Horiba, Kyoto, Japan) equipped with a 10 mW diode pumped solid state laser (532 nm) at 25 °C. Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

3. Synthesis

Thieno[3,4-*b*]thiophene-based monomer (**3**) was synthesized according to Scheme 1. Ethylamine (2 M in tetrahydrofuran, 0.82 mL, 1.64 mmol), **2** (472 mg, 1.08 mmol) and DMAP (198 mg, 1.62 mmol) were dissolved in anhydrous DMF (10.8 mL) and the solution was cooled to 0 °C. To this solution was added EDC-HCl (312 mg, 1.63 mmol) and the mixture was stirred at room temperature for 18 h. The mixture was diluted with ethyl acetate, washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane/ethyl acetate (3/1, v/v) as the eluent to give the desired product as a pale yellow solid (181 mg, 42% yield). ^1H NMR (500 MHz, CDCl_3 , rt): δ 7.28 (s, 1H, ArH), 6.06 (br, 1H, NH), 3.49 (m, 2H, CH_2), 1.27 (t, $J = 7.4$ Hz, 3H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , rt): δ 161.77, 151.18, 145.84, 145.76, 119.64, 66.15, 61.38, 35.22, 14.80. IR (KBr, cm^{-1}): 1624 (C=O). Calcd for $\text{C}_9\text{H}_7\text{I}_2\text{NOS}_2$: C, 23.34; H, 1.52; N, 3.02. Found: C, 23.33; H, 1.68; N, 3.05.

4. Polymerization

Copolymerization of GLB-**1** with **3** by Sonogashira–Hagihara cross-coupling was carried out using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst in a dry Schlenk flask under nitrogen atmosphere in a similar way as reported previously (Scheme 1).^{S2}

Spectroscopic data for poly-**1**. ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 55 °C): δ 8.65 (br, 1H, NH), 8.10–7.00 (m, 7H, ArH), 5.60–4.90 (m, 4H, CH), 4.50–3.90 (m, 7H, CH_2 , CH), 3.70–3.20 (m, 27H, CH_2 , OCH_3), 1.09 (br, 3H, CH_3). IR (KBr, cm^{-1}): 2192 ($\text{C}\equiv\text{C}$), 1754 (C=O), 1648 (C=O). Calcd for

C₄₈H₄₉NO₁₇S₂·0.7H₂O: C, 58.32; H, 5.14; N, 1.42. Found: C, 58.11; H, 5.25; N, 1.42.

5. Molecular modeling

An all-atom molecular dynamics (MD) simulation was carried out using the Forcite module of the BIOVIA Materials Studio 2017 (Dassault Systèmes BIOVIA, San Diego, CA, USA) on the supercomputer system (PRIMERGY CX250, Fujitsu, Tokyo, Japan). A 20-mer model of poly-**1** was built at the torsion angle between units was set to -134° , based on a previous report.^{S2} The MD cell was built by means of usual procedure of the Amorphous Cell module. The MD cell length and angle were ($a = 100 \text{ \AA}$, $b = 100 \text{ \AA}$, $c = 100 \text{ \AA}$) and ($\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$), respectively. Here, a single polymer chain was put in the center of the cell, and the solvent molecules of chloroform were packed in the cell at density of 1.492 g cm^{-3} . Sequentially, the geometry of the MD cell was optimized. Simulation in the NVT ensemble (constant number of atoms, volume and temperature) was conducted at 298 K for 20 ps (time step of 0.2-fs, 100,000 steps) and the NPT ensemble (constant number of atoms, pressure and temperature) was conducted at pressure of $1.013 \times 10^{-4} \text{ GPa}$ and at 298 K for 3,000 ps (time step of 1.0-fs, 3,000,000 steps) to equilibrate the MD cell. The Nose thermostat was used to control the temperature. The Berendsen barostat was used to control the pressure. After the equilibration at 298 K, simulation in the NVE ensemble (constant number of atoms, volume and energy) was conducted for 1,000 ps (time step of 1.0-fs, 1,000,000 steps) as the production run. The COMPASS II (ver. 1.2) forcefield was used, and the charges were assigned by the forcefield.

Supporting data

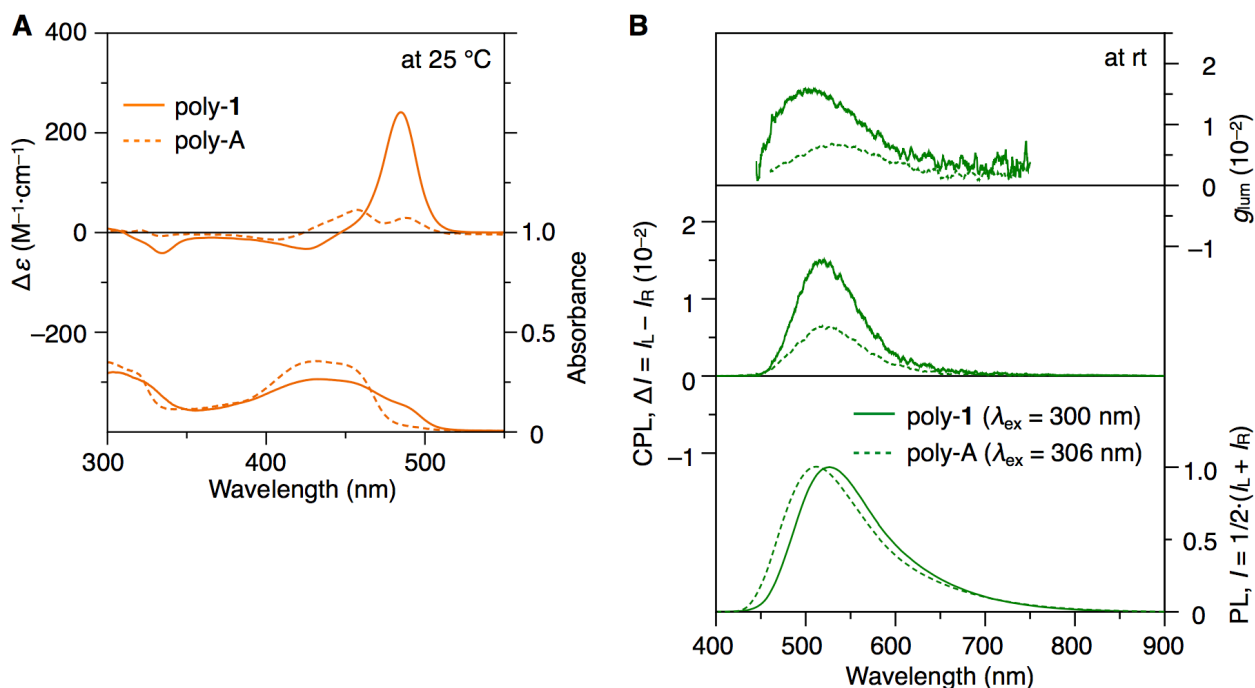


Fig. S1 Absorption/CD (A) and PL/CPL/ g_{lum} (B) spectra of poly-1 and poly-A in chloroform. The spectra in (A) and (B) were obtained from polymer solutions of 1.0×10^{-4} M (cell length: 1.0 mm) and 1.0×10^{-5} M (cell length: 10 mm), respectively.

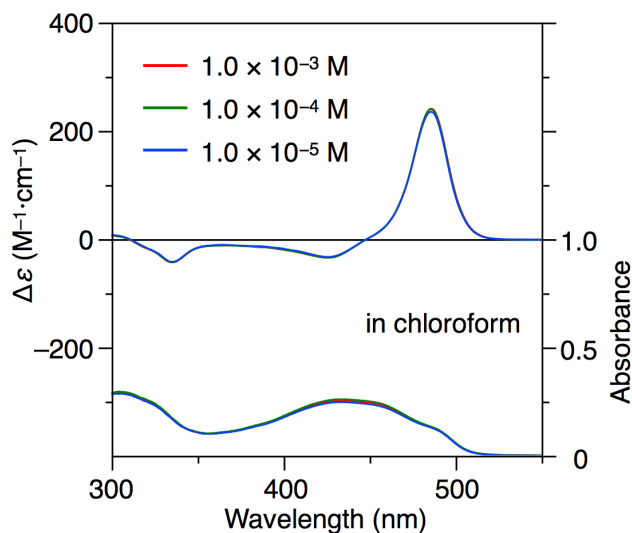


Fig. S2 CD and absorption spectra of poly-1 in chloroform at 25 °C. The spectra indicated by red, green and blue lines were obtained from polymer solutions of 1.0×10^{-3} M (cell length: 0.10 mm), 1.0×10^{-4} M (cell length: 1.0 mm) and 1.0×10^{-5} M (cell length: 10 mm), respectively.

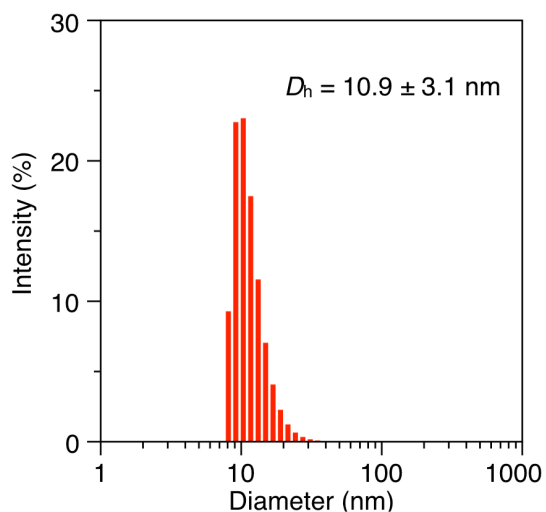


Fig. S3 Histogram analysis of the DLS measurement of poly-**1** in chloroform at 25 °C. [Glucose unit] = 1.0×10^{-5} M.

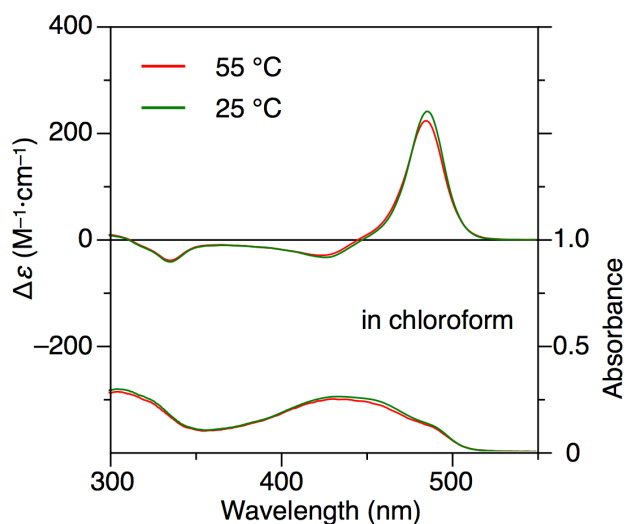


Fig. S4 CD and absorption spectra of poly-**1** in chloroform at 25 and 55 °C. [Glucose unit] = 1.0×10^{-4} M.

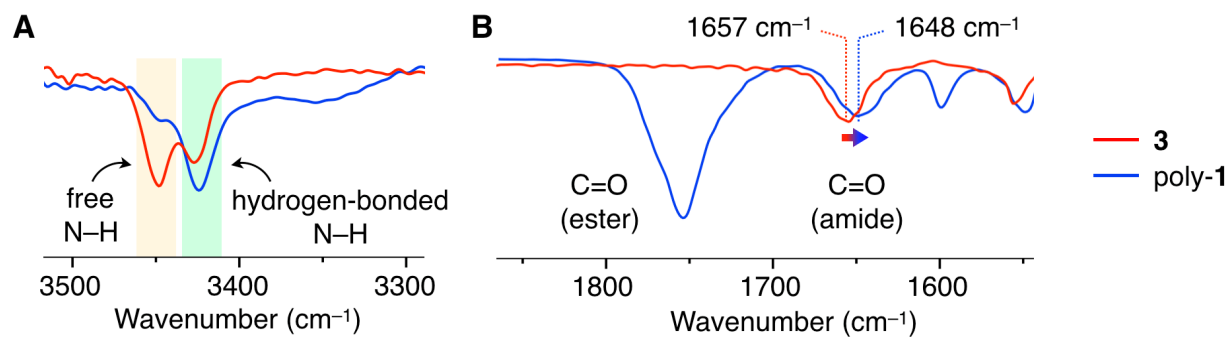


Fig. S5 IR spectra of poly-**1** and **3** in chloroform at room temperature. [Glucose unit] = 1.0×10^{-3} M.

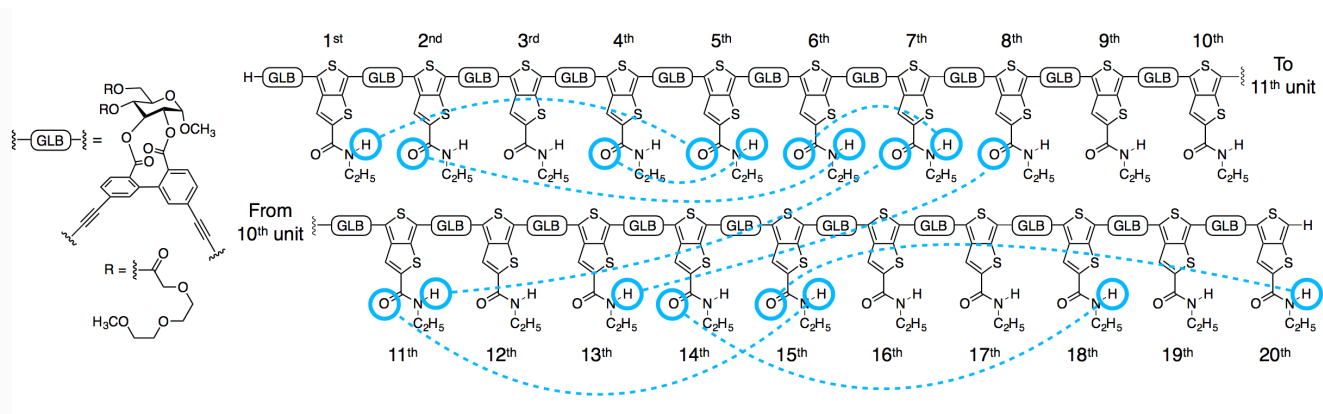


Fig. S6 Combinations of the NH hydrogen and carbonyl oxygen forming a hydrogen bond at 1000 ps in the all-atom MD simulation.

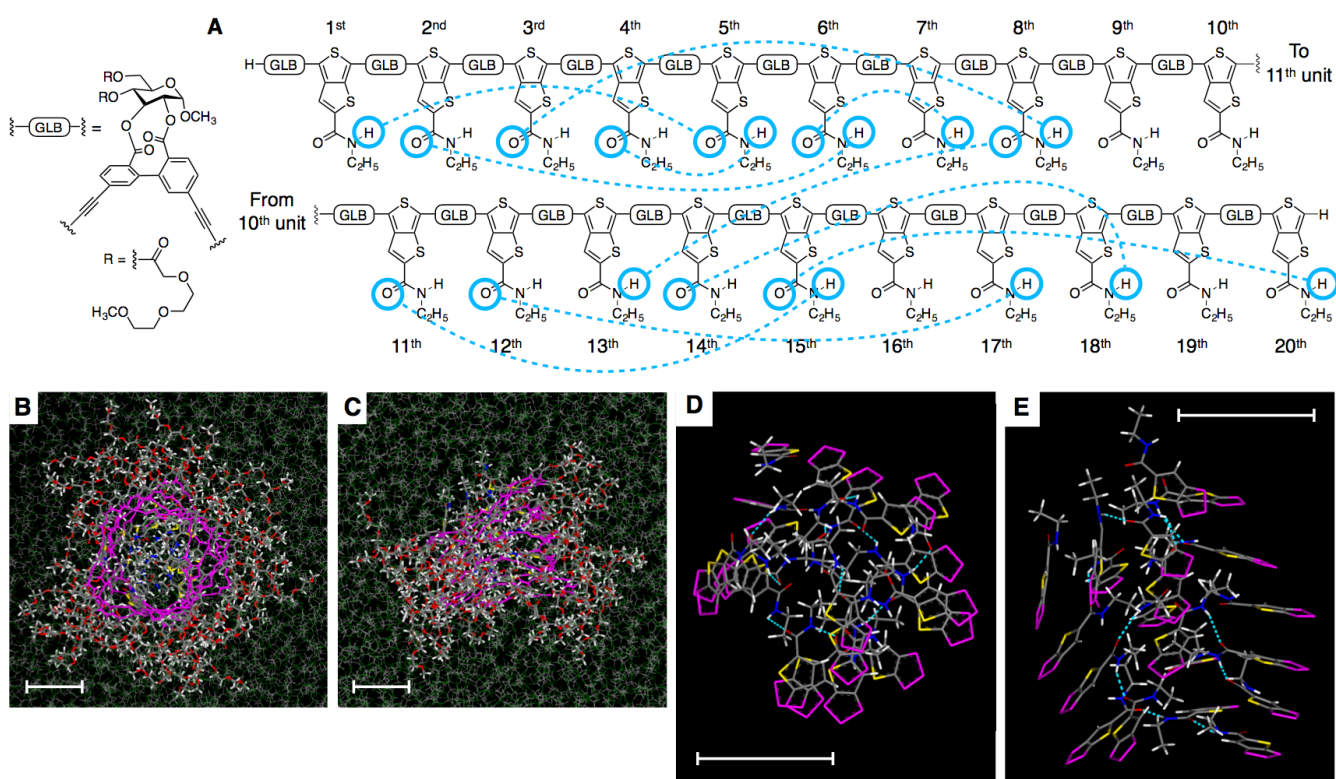


Fig. S7 (A) Combinations of the NH hydrogen and carbonyl oxygen forming a hydrogen bond at 0 ps in the all-atom MD simulation. (B) Top view and (C) side view of the corresponding molecular model of the helically folded poly-1 in chloroform, represented by stick models. The poly-1 backbone is highlighted in purple. (D, E) Simplified molecular models displaying only the TT units in (B) and (C), respectively. The chloroform solvent molecules are represented by line models in (B) and (C). The hydrogen bonds are indicated by blue dashed lines in (D) and (E). All the scale bars represent 1.0 nm.

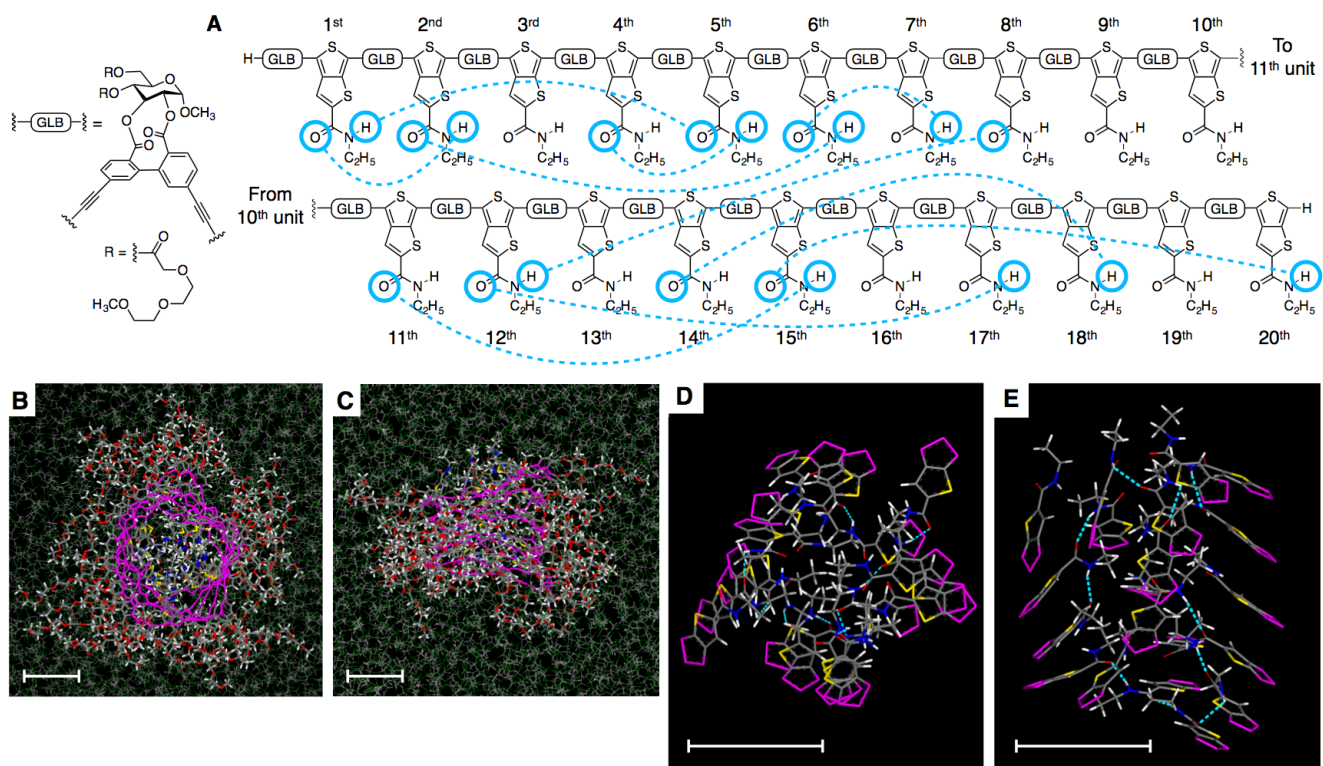


Fig. S8 (A) Combinations of the NH hydrogen and carbonyl oxygen forming a hydrogen bond at 500 ps in the all-atom MD simulation. (B) Top view and (C) side view of the corresponding molecular model of the helically folded poly-**1** in chloroform, represented by stick models. The poly-**1** backbone is highlighted in purple. (D, E) Simplified molecular models displaying only the TT units in (B) and (C), respectively. The chloroform solvent molecules are represented by line models in (B) and (C). The hydrogen bonds are indicated by blue dashed lines in (D) and (E). All the scale bars represent 1.0 nm.

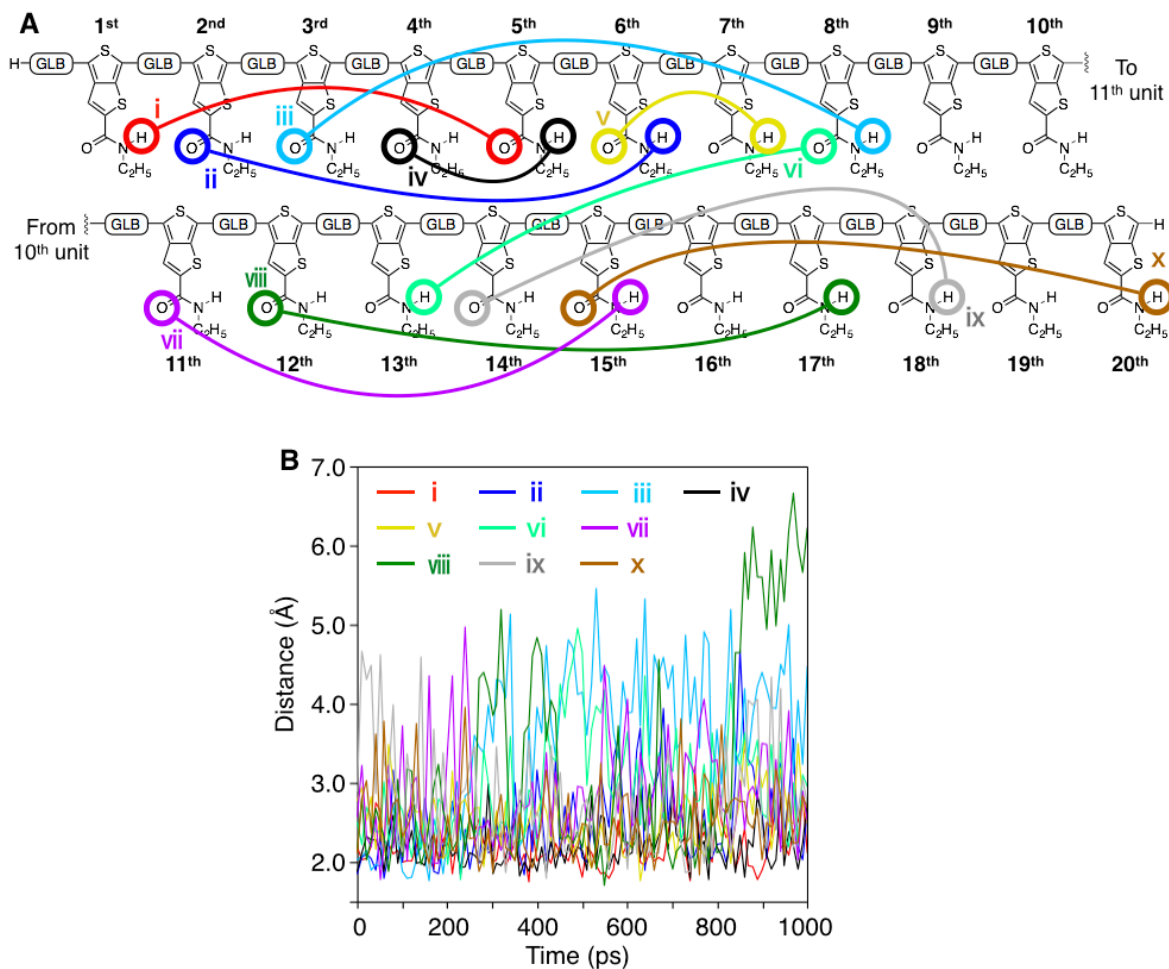


Fig. S9 (A) Same data as Fig. S7A except for coloring and numbering. (B) Plots of the interatomic distances between the NH hydrogen and carbonyl oxygen indicated by the arrows (i–viii) in (A) as a function of the calculation time.

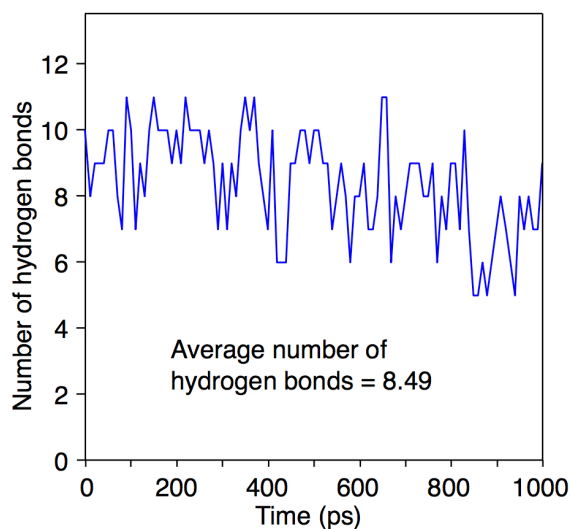


Fig. S10 Number of hydrogen bonds formed in the poly-1 model in the all-atom MD simulation as a function of the calculation time.

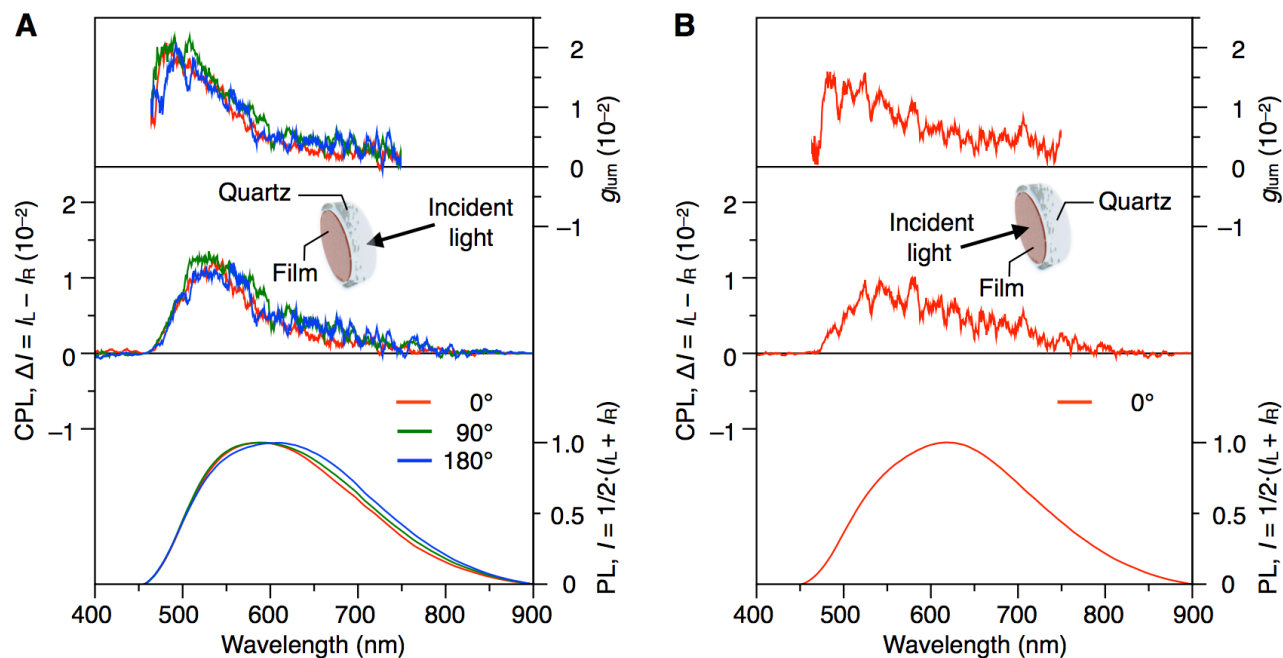


Fig. S11 PL (bottom), CPL (middle) and g_{lum} (top) spectra of the chloroform-cast film of poly-1 at room temperature. The spectra were measured at different rotation angles (A) and by reversing a quartz plate to be an incident light/quartz/film arrangement (B). $\lambda_{ex} = 300$ nm.

NMR spectral data

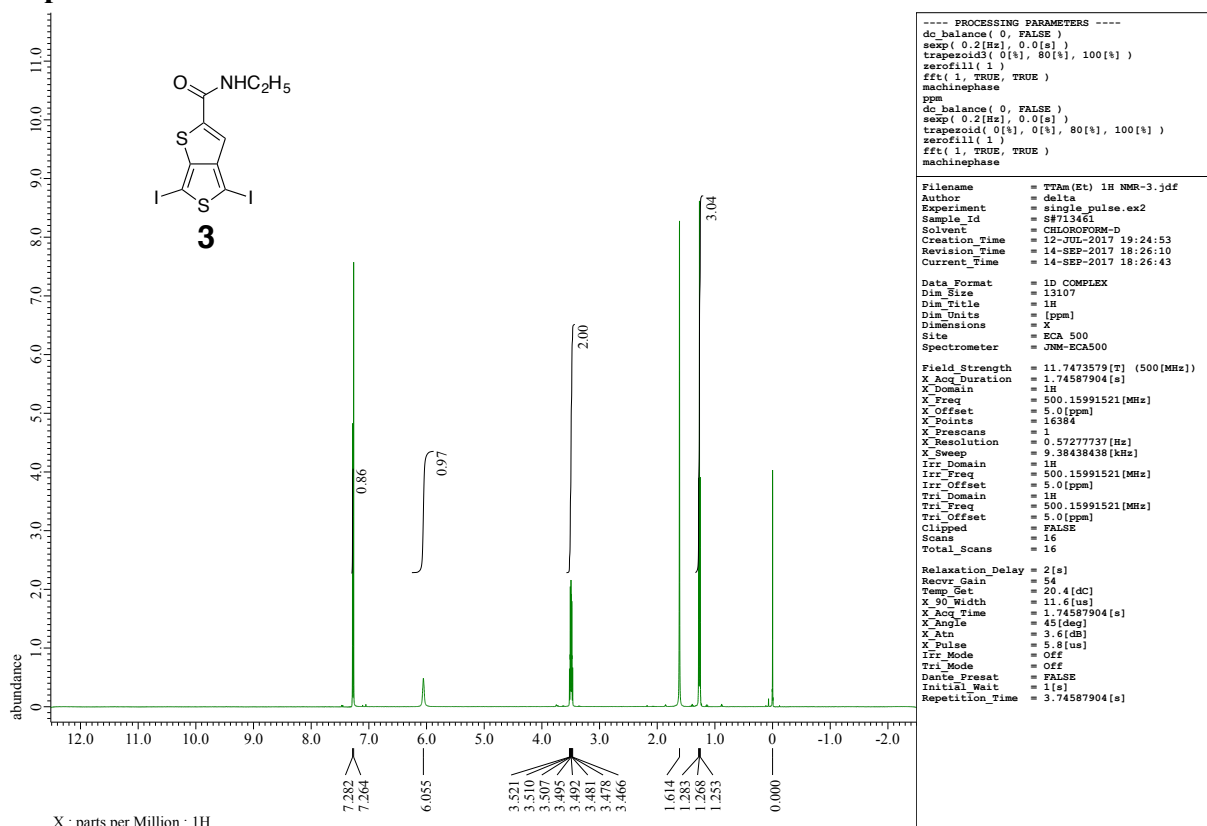


Fig. S12 ¹H NMR (500 MHz, CDCl₃, rt) spectrum of **3**.

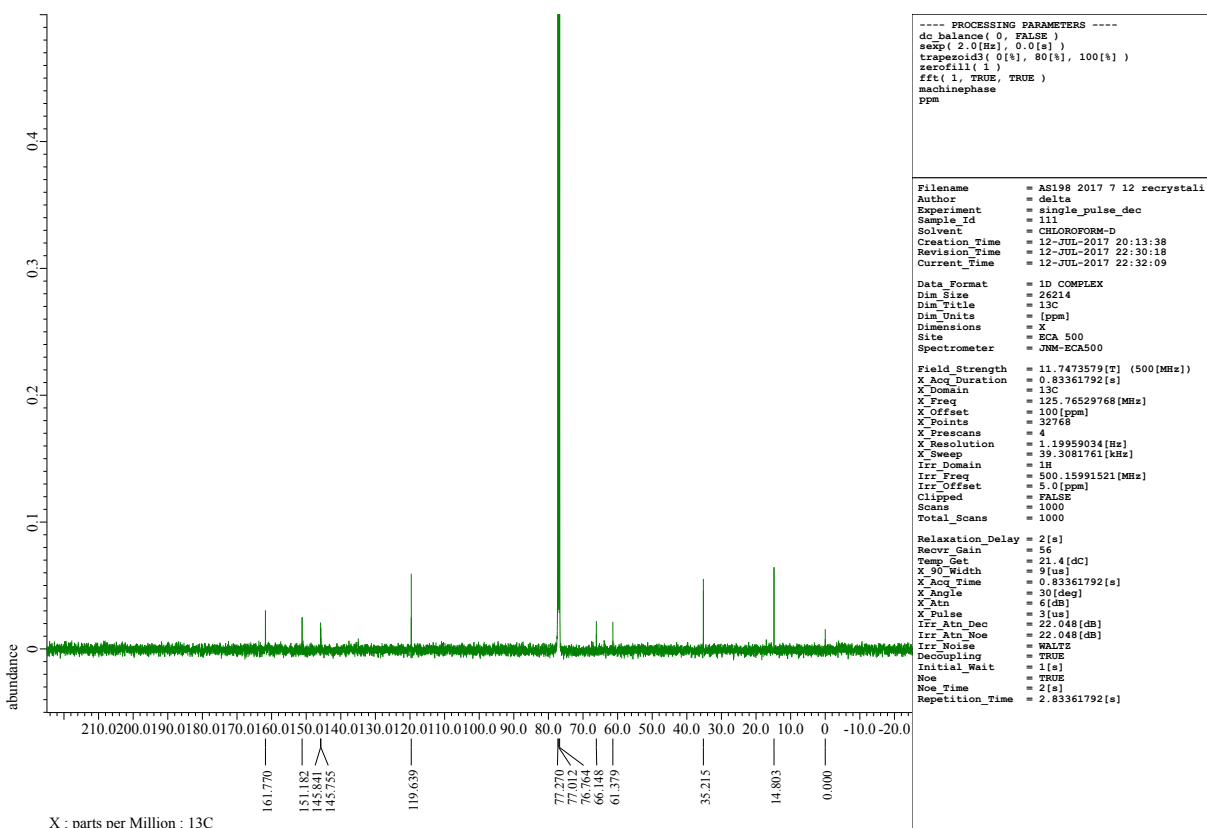


Fig. S13 ¹³C NMR (125 MHz, CDCl₃, rt) spectrum of **3**.

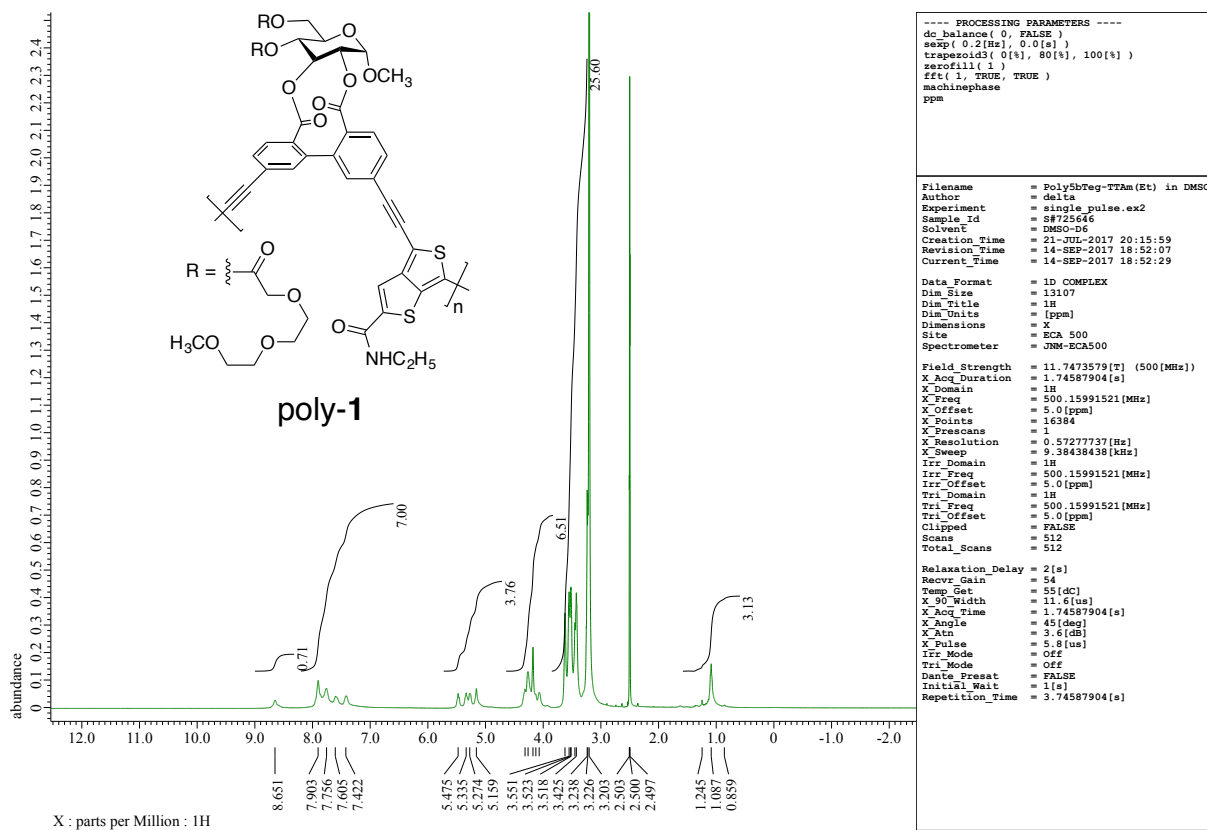


Fig. S14 ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 55 $^\circ\text{C}$) spectrum of poly-1.

Captions for supporting movies

Movie S1. Animation of all-atom MD simulation in the NVE ensemble of the 20-mer model of poly-**1** (CPK model) in chloroform (stick model) at 0–1000 ps as the production run. The poly-**1** backbone is highlighted in purple and the hydrogen atoms of chloroform are omitted to simplify the view.

Movie S2. Same simulation result as Movie S1 except that chloroform solvent molecules and the hydrogen atoms in poly-**1** are omitted to simplify the view. The poly-**1** model is represented by stick model and its backbone is highlighted in purple.

Movie S3. Same simulation result as Movie S1 except that only the TT units in poly-**1** (stick model) are displayed. The hydrogen bonds are indicated by blue dashed lines and the poly-**1** backbone is highlighted in purple.

References

- S1. T. Ikai, S. Shimizu, S. Awata, T. Kudo, T. Yamada, K. Maeda and S. Kanoh, *Polym. Chem.*, 2016, **7**, 7522–7529.
- S2. T. Ikai, S. Awata, T. Kudo, R. Ishidate, K. Maeda and S. Kanoh, *Polym. Chem.*, 2017, **8**, 4190–4198.