Visualisation of Helical Structures of Poly(diphenylacetylene)s Bearing Chiral Amide Pendants by Atomic Force Microscopy

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Experimental Details

Instruments

Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Cypher AFM system (Asylum Research, Oxford Instruments) at room temperature with standard silicon cantilevers (including AC160-NG, AC55 purchased from OPUS; Multi75Al-G from Budget sensors) in the tapping mode. The absorption and circular dichroism (CD) spectra were recorded in a 1-mm quartz cell at 25 °C using a JASCO V-650 spectrophotometer and JASCO J-725 CD spectropolarimeter, respectively. The temperature was controlled with a JASCO PTC-348WI apparatus. The size exclusion chromatography (SEC) measurements were performed with a JASCO PU-2080 liquid chromatograph equipped with a UV-vis (JASCO UV-970) detector at 40 °C using a Shodex KF-805L GPC column. The temperature was controlled with a JASCO CO-1560 column oven. THF was used as the eluent at a flow rate of 1.0 mL/min. The molar mass calibration curves were obtained with polystyrene standards (Tosoh, Japan).

Materials

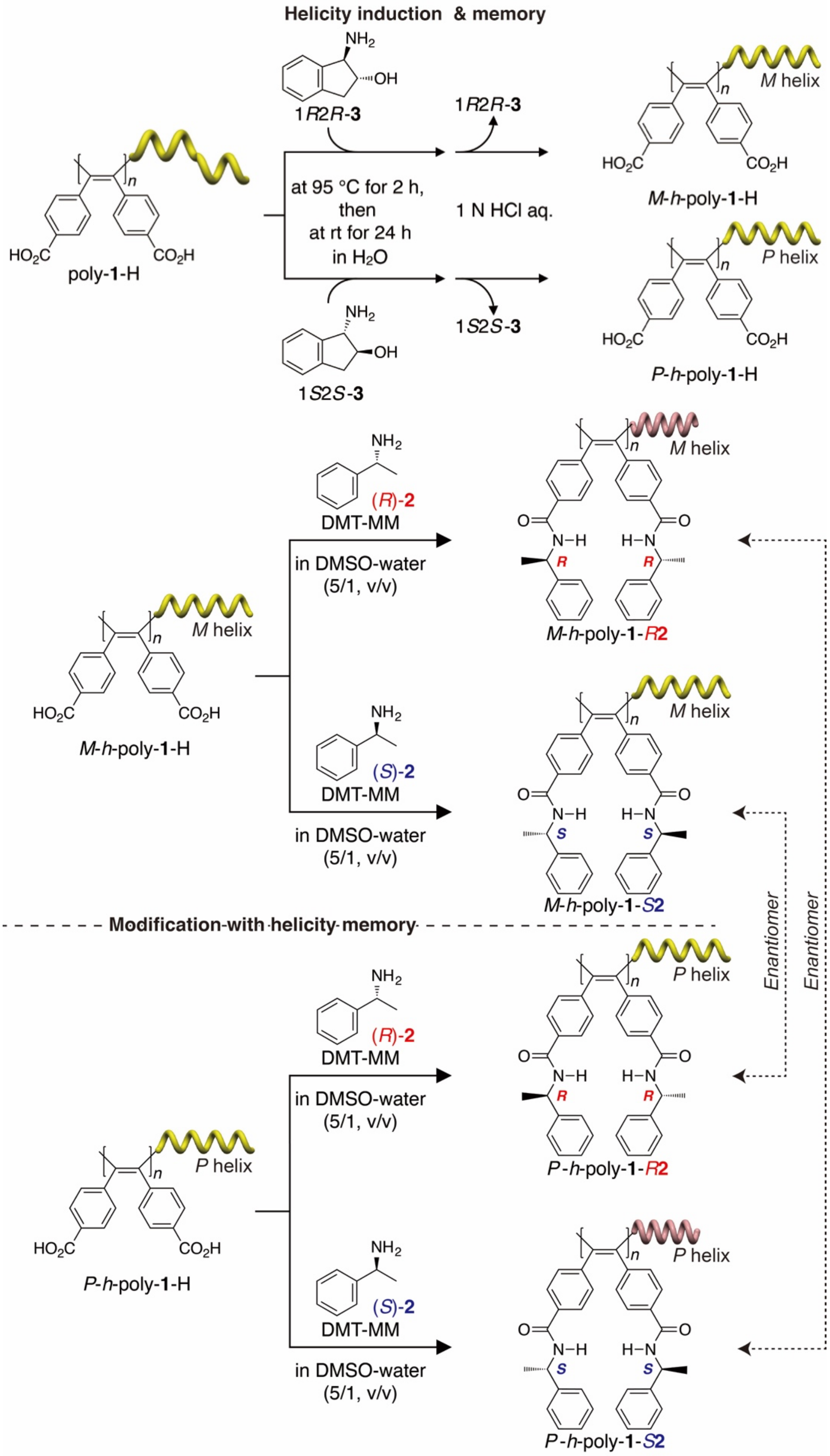
4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) was prepared according to the reported method.[S1] Poly-**1**-H was prepared according to the reported method.[S2] The number-average molar mass (M_n) and molar-mass dispersity (M_w/M_n) were 6.1 × 10^4 and 1.6, respectively, as determined by SEC as its heptyl ester. *P*-*h*-poly-**1**-H and *M*-*h*-poly-**1**-H were obtained using (1*R*,2*R*)-1-amino-2-indanol ((1*R*2*R*)-**3**) and (1*S*,2*S*)-1-amino-2-indanol ((1*S*2*S*)-**3**), respectively, as a helix-inducer as shown in Scheme S1 (top) according to the reported method.[S3] *P*-*h*-poly-**1**-*S***2** and *P*-*h*-poly-**1**-*R***2** were prepared by the reactions of *P*-*h*-poly-**1**-H with (*S*)- and (*R*)-1-phenylethylamine ((*S*)- and (*R*)-**2**), respectively, using DMT-MM as shown in Scheme S1 (middle), while *M*-*h*-poly-**1**-*R***2** and *M*-*h*-poly-**1**-*S***2** were prepared by the reactions of *M*-*h*-poly-**1**-H with (*R*)-**2** and (*S*)-**2**, respectively, using DMT-MM as shown in Scheme S1 (bottom) according to the previously reported procedure.[S4]

Measurements

Sample preparation and AFM imaging

Stock solutions of *P*-*h*-poly-**1**-*S***2** and *M*-*h*-poly-**1**-*R***2** in dry THF (0.05 mg/mL) were prepared. In case of *P*-*h*-poly-**1**-*R***2** and *M*-*h*-poly-**1**-*S***2**, THF–acetone (9/1, v/v) mixed solvent was used for better solubility to prepare their stock solutions (0.05 mg/mL). Samples for the

AFM measurements of *P*-*h*-poly-**1**-*S***2**, *P*-*h*-poly-**1**-*R***2**, *M*-*h*-poly-**1**-*S***2**, and *M*-*h*-poly-**1**-*R***2** were prepared by spin casting 20-μL aliquots of the stock solutions on freshly cleaved highly oriented pyrolytic graphite (HOPG) at room temperature, and the solvents were then evaporated at room temperature under toluene environment (detailed procedure presented in **Fig. S1**). Acetone was used as an annealing solvent instead of toluene for yellow-colored *P*-*h*-poly-**1**-*R***2** and *M*-*h*-poly-**1**-*S***2**. The AFM measurements were performed by operating the AFM in the amplitude modulation mode using a Cypher AFM system with different types of cantilevers (including AC160-NG, AC55 purchased from OPUS; Multi75Al-G from Budget sensors). To obtain high-resolution images, the cantilevers were driven either at first or second eigenmode. **Fig. 3** is obtained by using a Multi75Al-G cantilever (Budget sensors) with a nominal spring constant of 3 N/m and tip radius of < 10 nm and resonance frequency of 75 kHz. The cantilevers were driven at their second eigenmode. The acquisition parameters for the second eigenmode are: $f_{second} = 349.37$ kHz; $k_{second} = 37.72$ nN/nm. **Fig.4a** was obtained by using a Multi75Al-G cantilever (Budget sensors). The cantilevers were driven at their second eigenmode. The acquisition parameters for the second eigenmode are: $f_{second} = 373.290$ kHz kHz; $k_{second} = 45.54$ nN/nm. **Fig. 4b** and **S6** are acquired by using a Multi75Al-G cantilever. The cantilevers were driven at their second eigenmode. The acquisition parameters for the second eigenmode are: $f_{second} = 374$ kHz; $k = 47.16$ nN/nm. **Fig. S4** is obtained by using an SSS-NCHR cantilever (Nanosensors) with a nominal spring constant of 42 N/m and tip radius of 2 nm and resonance frequency of 330 kHz. The typical settings of the AFM for the high-magnification observations were as follows: the scan rates range from 2–10 Hz. The obtained AFM images were rendered using WSXM or Gwyddion software. We first performed simple image flattening and tilt corrections for the AFM images. To obtain chain-to-chain distances and helical pitch distances, we analysed line profiles along the polymer chain perpendicular to and parallel to the chain direction, respectively, over the domain with well-aligned polymer chains (**Fig. S2**). To measure the chain-to-chain distances, we used both height and phase images, while for helical pitch distances only phase images were used. For the statistics, similar line profile analysis was performed for some images.



Scheme S1. Synthesis of diastereomeric *P*-*h*-poly-**1**-*S***2** and *P*-*h*-poly-**1**-*R***2** and the corresponding enantiomeric counterparts (*M*-*h*-poly-**1**-*R***2** and *M*-*h*-poly-**1**-*S***2**) through the reaction of *P*-*h*-poly-**1**-H with (*S*)- and (*R*)-**2** and *M*-*h*-poly-**1**-H with (*R*)- and (*S*)-**2**, respectively, using DMT-MM.

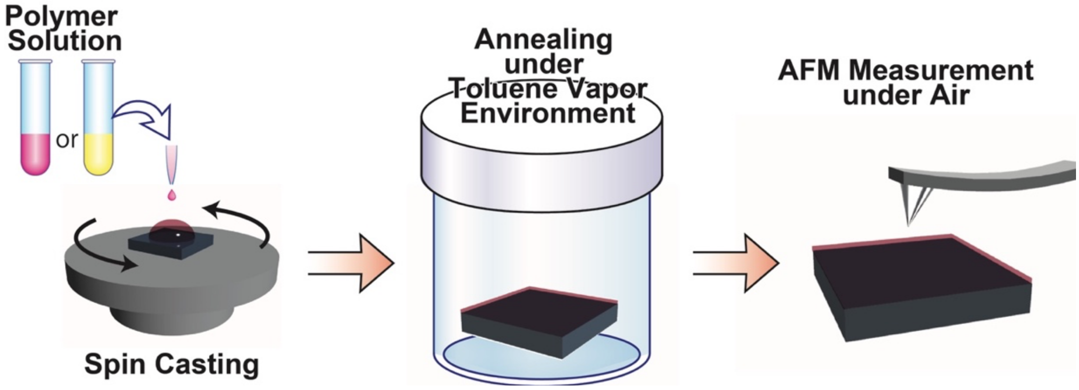


Fig. S1. Schematic representation of the AFM sample preparation.

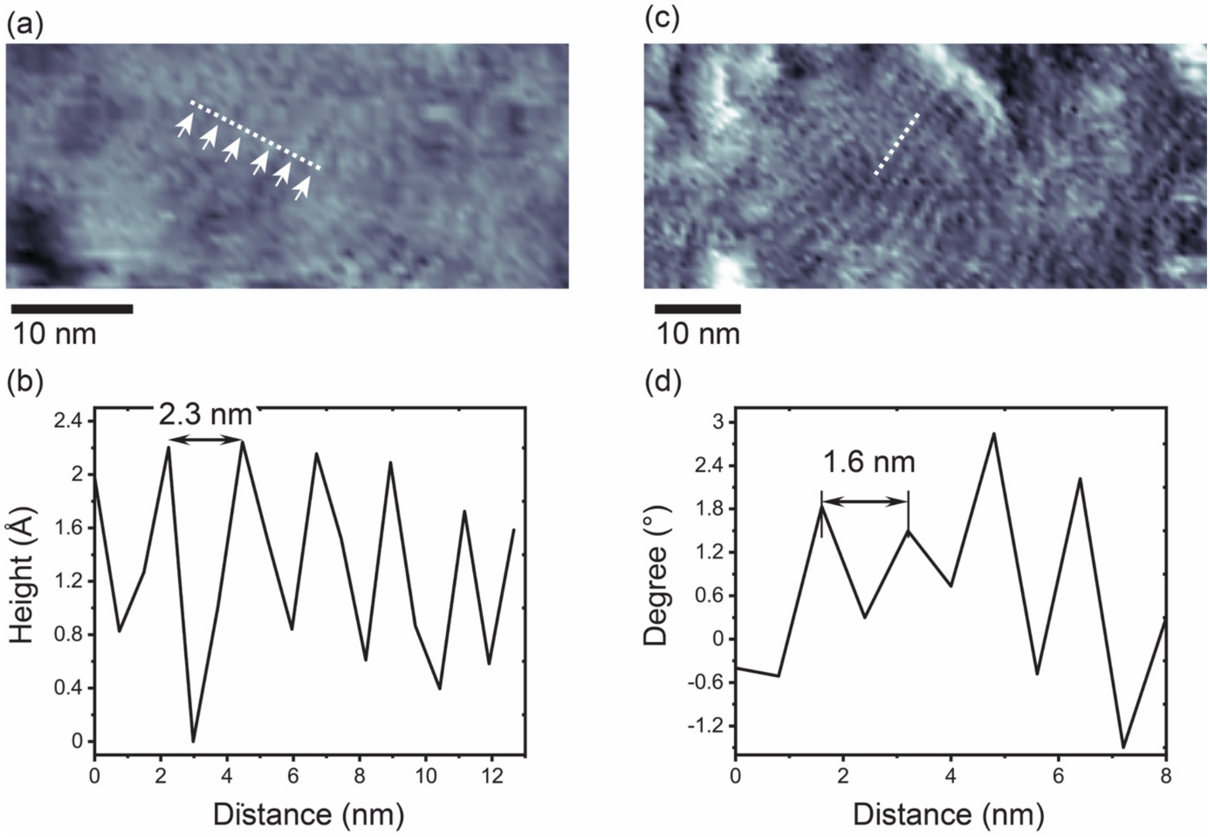


Fig. S2. (a) High-resolution height image of *P*-*h*-poly-**1**-*S***2** (red) with a left-handed helical arrangement of the pendant groups. (b) A representative cross-sectional profile along the white dashed line in the image (a) showing chain-to-chain distance of 2.3 nm. (c) High-resolution phase image of *P*-*h*-poly-**1**-*S***2** (red) with a left-handed helical arrangement of the pendant groups. (d) A representative cross-sectional profile along the white dashed line in the image (c) showing helical pitch distance of 1.6 nm.

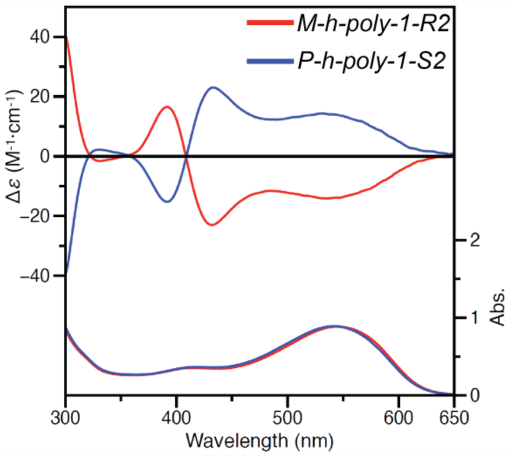


Fig. S3. CD and absorption spectra of *P*-*h*-poly-**1**-*S***2** and *M*-*h*-poly-**1**-*R***2** in THF (1 mM) at 25 °C.

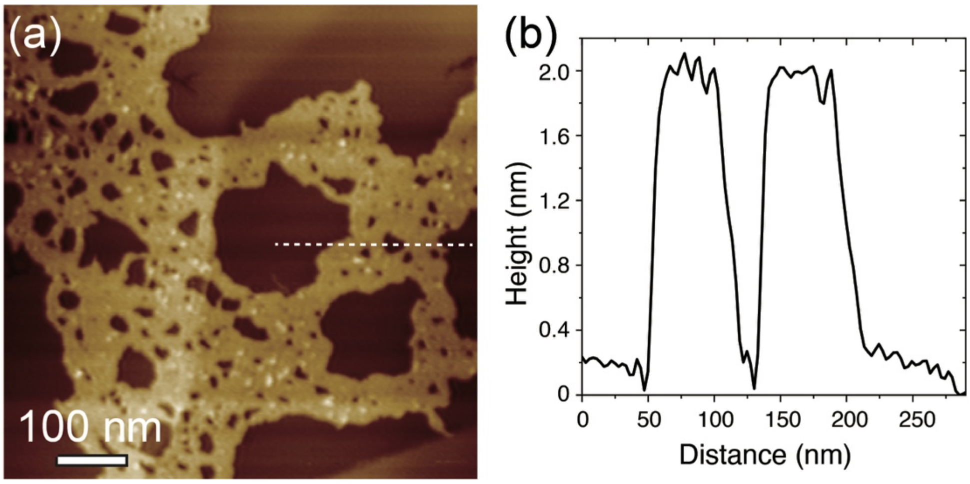


Fig. S4. AFM images of self-assembled *M*-*h*-poly-**1**-*R***2** (red) on HOPG. (a) AFM height image of the sample prepared by spin casting a dilute solution of *M*-*h*-poly-**1**-*R***2** (red) in THF (0.05 mg/mL) on HOPG, followed by exposure to toluene vapour for 12 h. (b) Cross-sectional profile along the white dashed line in panel (a), showing an island height of 1.7 nm.

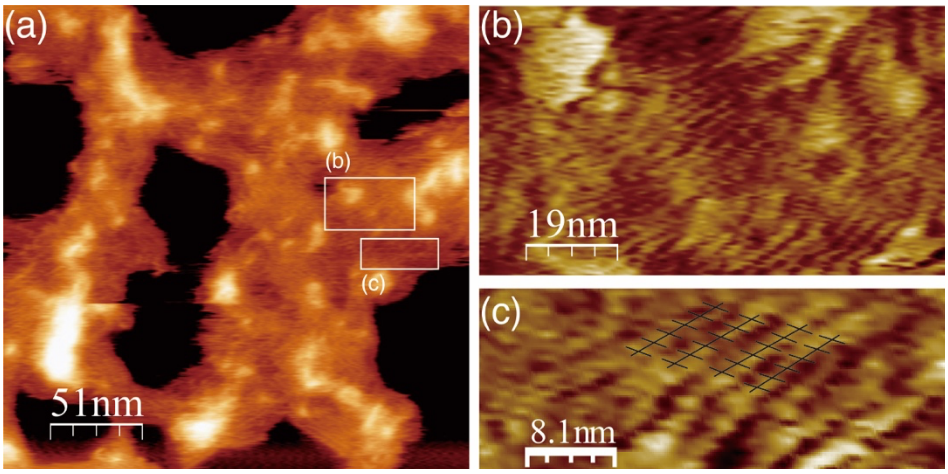


Fig. S5. (a) High-resolution height image of *M*-*h*-poly-**1**-*R***2**. (b, c) High-magnification AFM phase images of *M*-*h*-poly-**1**-*R***2** corresponding to the areas enclosed by rectangles in panel (a).

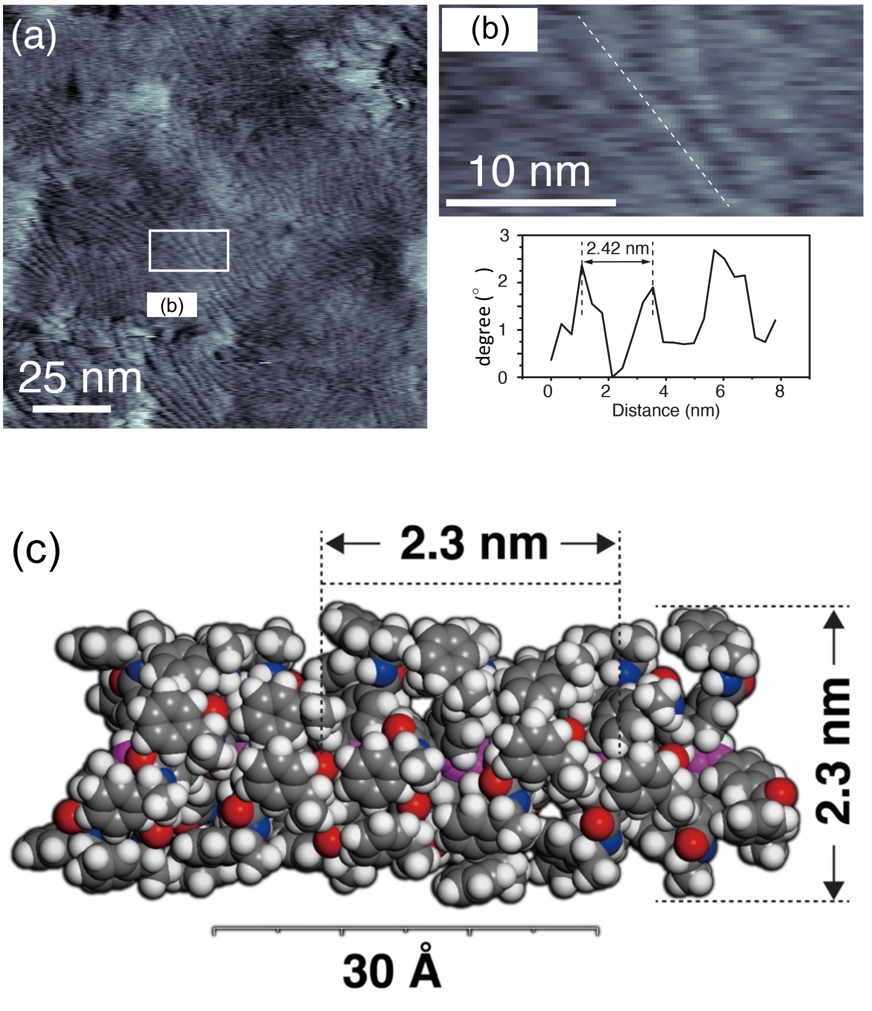


Fig. S6. (a) High-resolution AFM phase image of *M*-*h*-poly-**1**-*S***2** (yellow) prepared by spin casting of a dilute solution in THF–acetone (9/1, v/v) (0.05 mg/mL) on HOPG, followed by exposure to acetone vapour for 12 h. (b) High-magnification AFM phase image of *M*-*h*-poly-**1**-*S***2** corresponding to the area enclosed by a rectangle in panel (a) (top) and a representative cross-sectional profile along the white dashed line in the image showing a helical pith distance of 2.4 nm (bottom). (c) Calculated molecular model of the helical structure of *M*-*h*-poly-**1**-*S***2** with *cis*-*transoidal* stereoregular structure.[S4]

References

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