

Electronic supplementary information

Preferential orientation of anisotropic polymer rods toward macroscopic chain ordering

Takashi Kitao,^{ab} Alexandre Legrand,^c Taizo Mori,^{de} Katsuhiko Ariga^{df} and Takashi Uemura^{*a}

^a*Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan. E-mail: uemurat@g.ecc.u-tokyo.ac.jp*

^b*PRESTO, Japan Science and Technology Agency (JST) 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.*

^c*Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.*

^d*International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.*

^e*Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.*

^f*Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-0827, Japan.*

To whom correspondence should be addressed.

Email: uemurat@g.ecc.u-tokyo.ac.jp

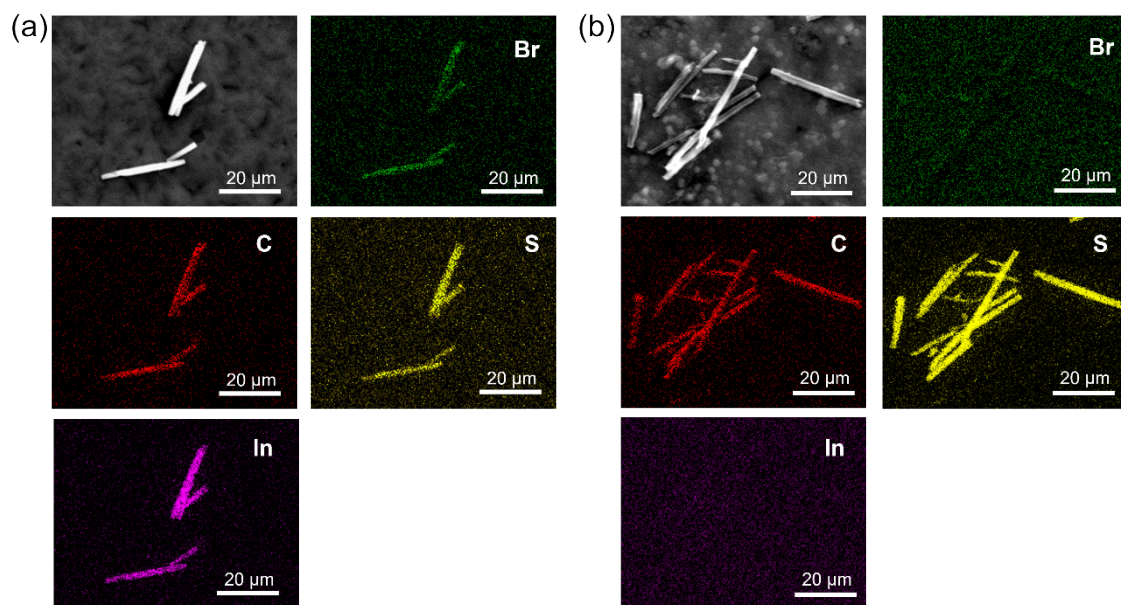


Fig. S1. SEM-EDX elemental mapping of (a) 1-PTh and (b) isolated PTh from **1**, demonstrating the removal of **1** during polymer recovery.

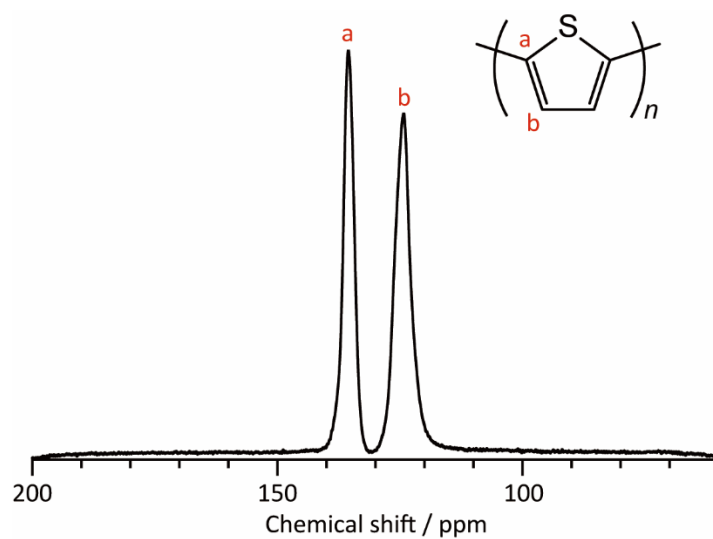


Fig. S2. Solid-state ^{13}C -NMR spectrum of PTh liberated from **1**. The two peaks at 125 and 136 ppm were attributed to the carbons at the 2,5- and 3,4-positions of the thiophene ring, respectively. PTh did not show any additional peaks, thus indicating that a linear PTh devoid of branching was obtained.^{1,2}

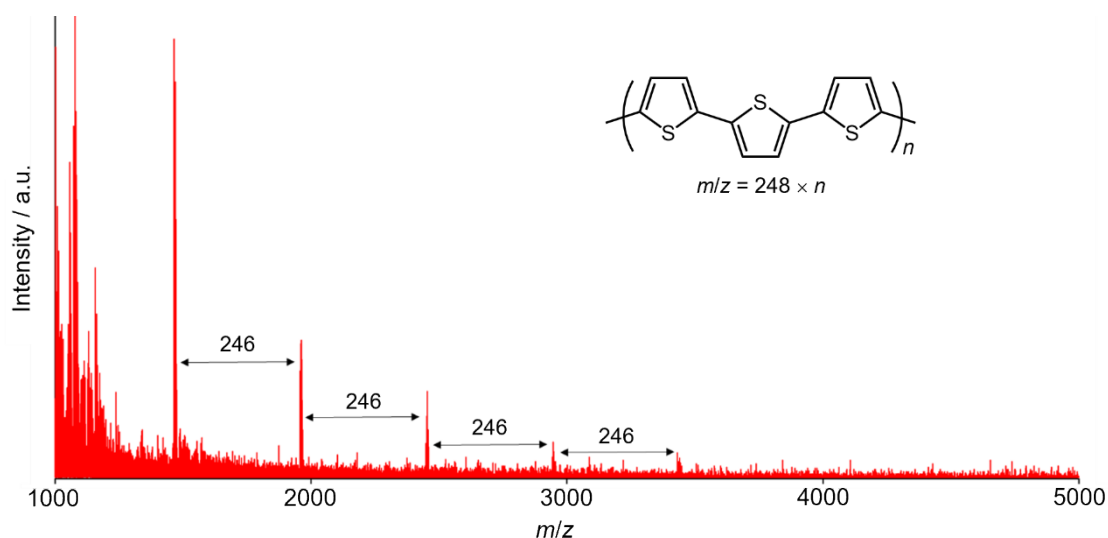


Fig. S3. MALDI-TOF-MS spectrum of the isolated PTh.

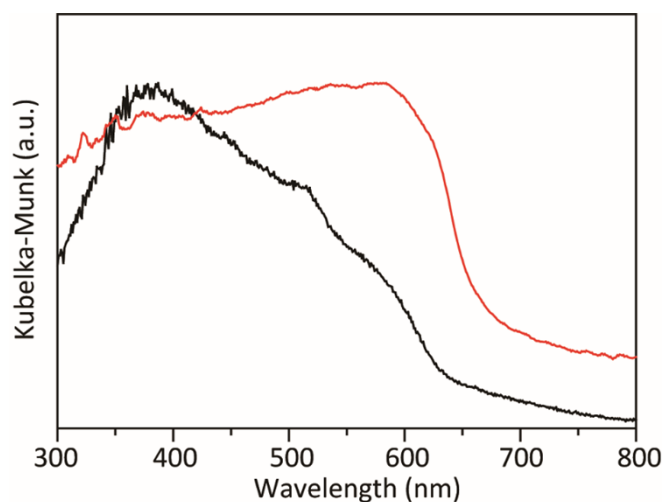


Fig. S4. UV/vis spectra of PTh prepared by solution polymerization (black) and isolated from **1** (red). PTh liberated from **1** exhibited a red-shifted absorption in the π - π^* transition region (400–600 nm) with respect to bulk PTh prepared by solution polymerization.³ In addition, note that the spectrum of the isolated PTh showed a shoulder above 600 nm, corresponding to exciton coupling among neighboring PTh chains.³ These results indicated the high degree of intra and interchain order of the PTh chains.³ The bulk PTh contain large quantities of intra- and inter-chain conjugation defects because of their irregular molecular configuration and random arrangement. Since the confined PTh chains were aligned perfectly by the geometrical constraint of the host MOF, the polymer chains could be easily packed with each other during the isolation process, leading to the highly ordered chain structures.

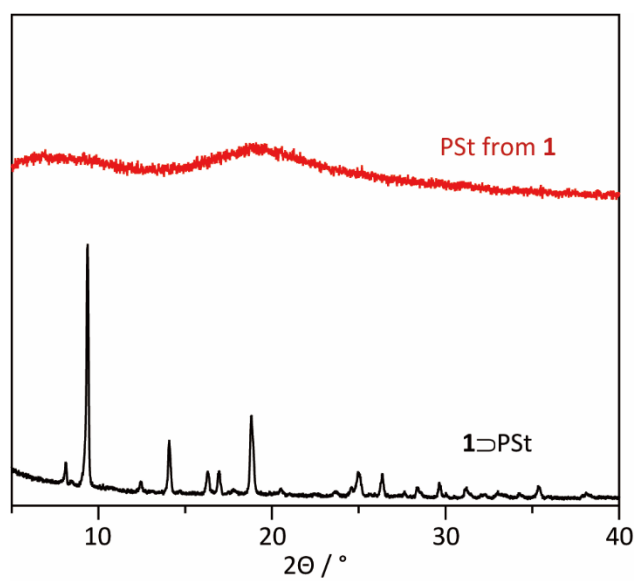


Fig. S5. XRPD patterns of 1-PSt and PSt liberated from 1.

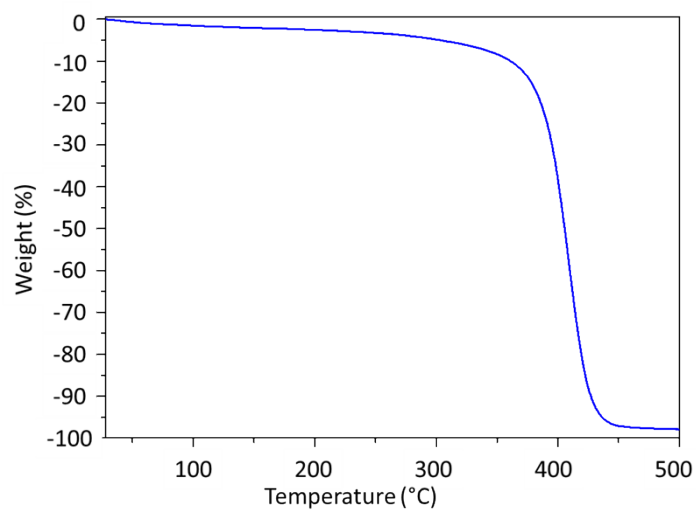


Fig. S6. TG profile of PSt isolated from 1. Complete degradation up to 500 $^\circ\text{C}$ indicated that the isolated PSt was not contaminated with inorganic impurities.

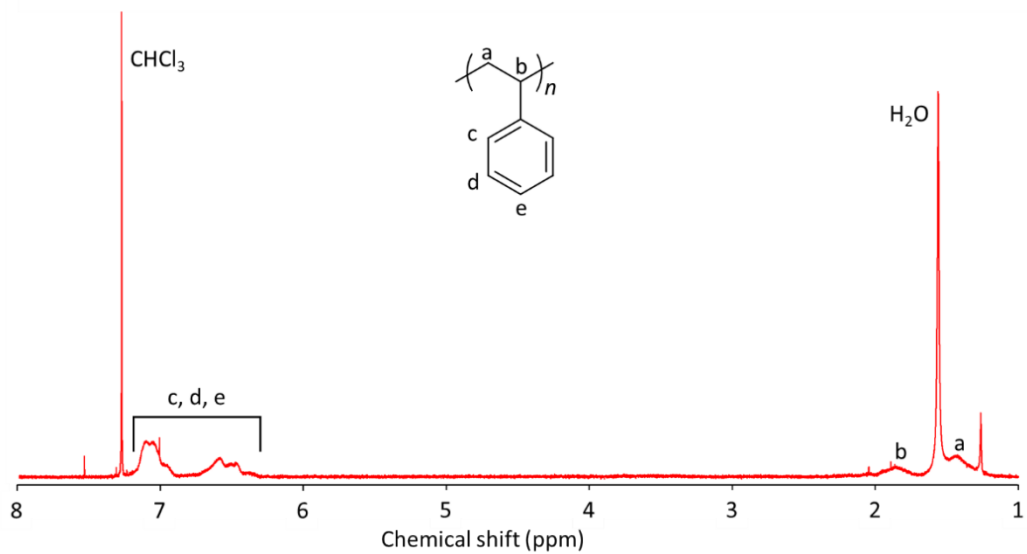


Fig. S7. $^1\text{H-NMR}$ spectrum of PSt isolated from **1** in CDCl_3 .

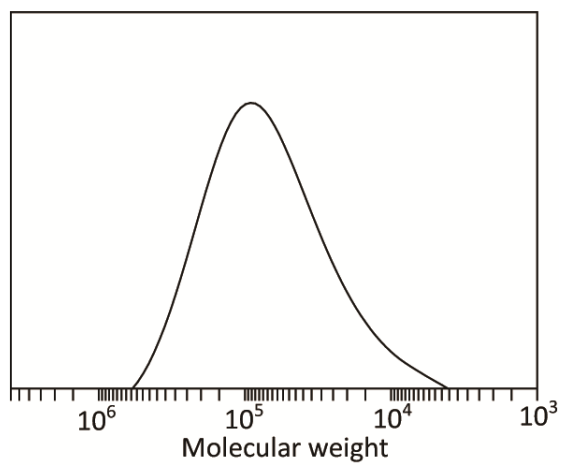


Fig. S8. GPC profile of PSt liberated from **1** ($M_n = 39,000$, $M_w/M_n = 2.73$).

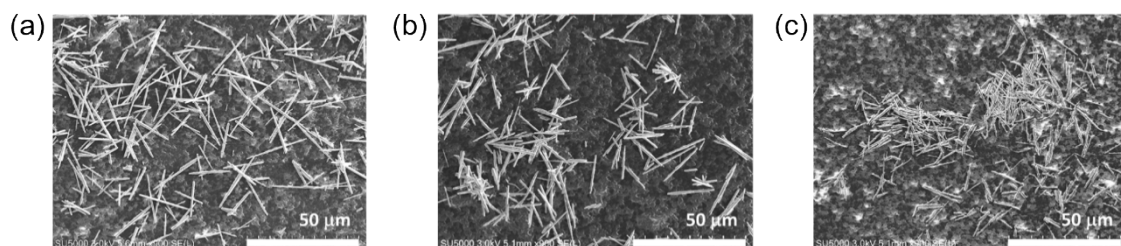


Fig. S9. SEM images of (a) **1**, (b) **1**-PSt, and (c) PSt isolated from **1**. The morphology of the PSt particles recovered from **1** retained the microrod shape of the original host.

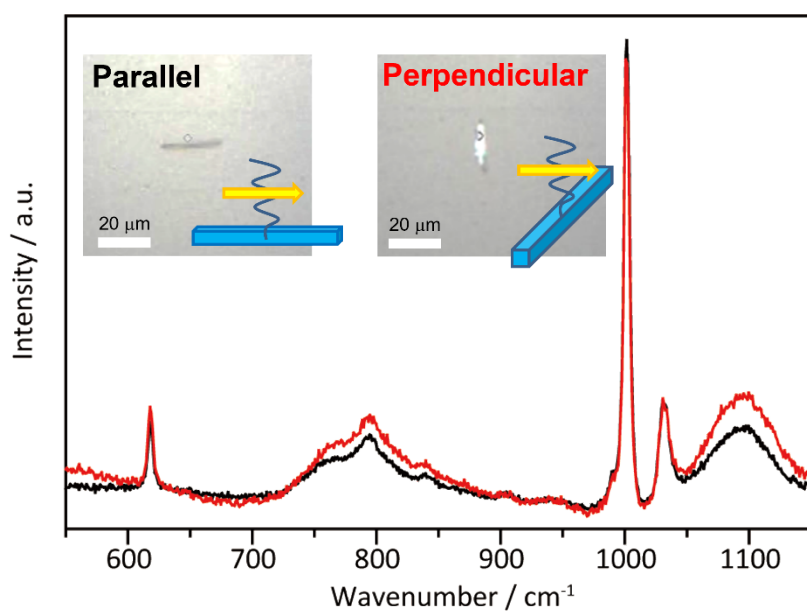


Fig. S10. Raman spectra of PSt using polarized Raman lasers parallel (black) and perpendicular (red) to the long axis of the particle. The insets show the optical micrographs of the PSt particles.

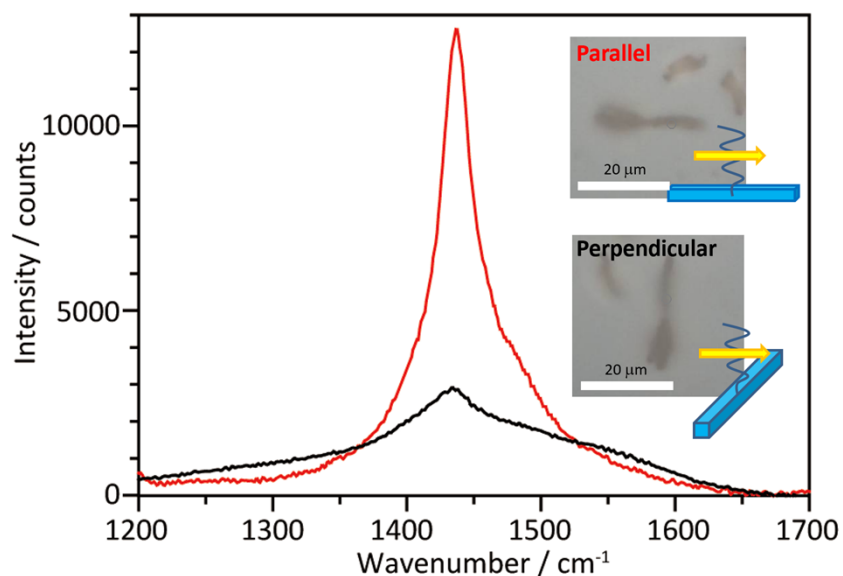


Fig. S11. Raman spectra of PTh using polarized Raman lasers parallel (red) and perpendicular (black) to the long axis of the particle. The insets show the optical micrographs of the PTh rods. When the excitation laser is polarized along the chain orientation direction, it can strongly interact with the C=C bonds of PTh.⁴ The higher Raman signal was obtained using the polarized laser parallel to the long axis of the rods, confirming the alignment of the PTh chains along this direction, in consistent with the electron diffraction analysis (Fig. 5).

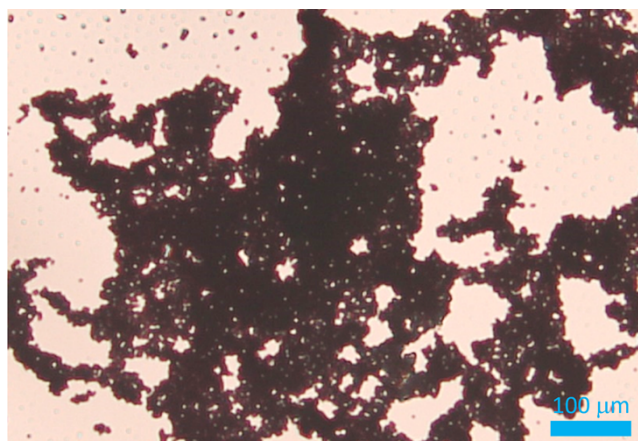
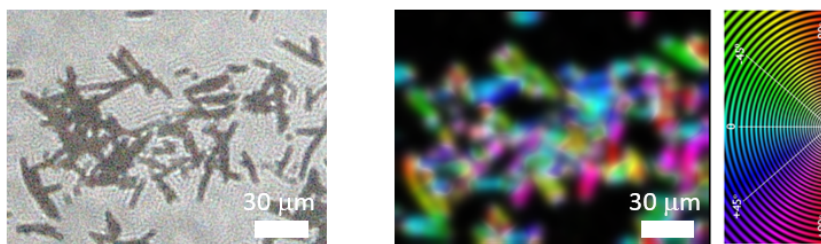


Fig. S12. Optical micrograph of the PTh particles with longer lengths (Fig. 4f) obtained by the vortex-LB technique.

(a)



(b)

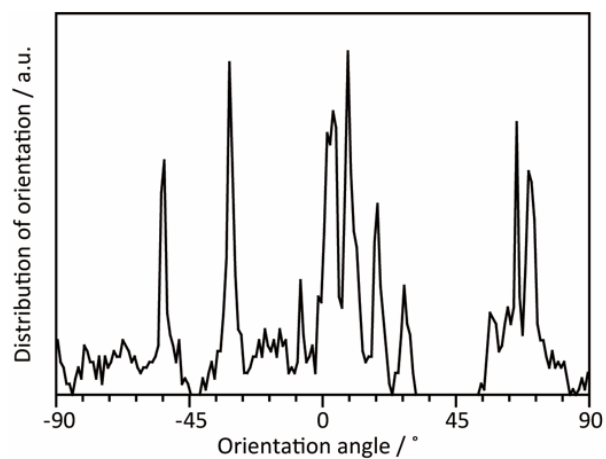


Fig. S13. (a) Microscope images and orientation analysis of long PTh rods before the mechanical rubbing treatment. Orientation analysis was color-coded according to the orientation color map from -90° to $+90^\circ$. (b) Angle orientation of the long PTh rods. The multiple peaks indicated the nearly isotropic orientational distribution of the PTh rods.

REFERENCES

- [1] J. Chen, J. Shu, S. Schobloch, A. Kroeger, R. Graf, R. Muñoz-Espí, K. Landfester and U. Ziener, *Macromolecules*, **2012**, *45*, 5108-5113.
- [2] M. Leclerc, F. M. Diaz and G. Wegner, *Makromol. Chem.*, **1989**, *190*, 3105-3116.
- [3] P. J. Brown, D. S. Thomas, A. Köhler, J. S. Wilson, J. S. Kim, C. M. Ramsdale, H. Sirringhaus and R. H. Friend, *Phys. Rev. B*, **2003**, *67*, 642031-6420316.
- [4] N. Kumari, M. Pandey, S. Nagamatsu, M. Nakamura and S. S. Pandey, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 11876-11883.