Supporting Information

Effects of Stretching on Molecular Packing Structure of Conjugated Polymers with Hydrogen Bonding

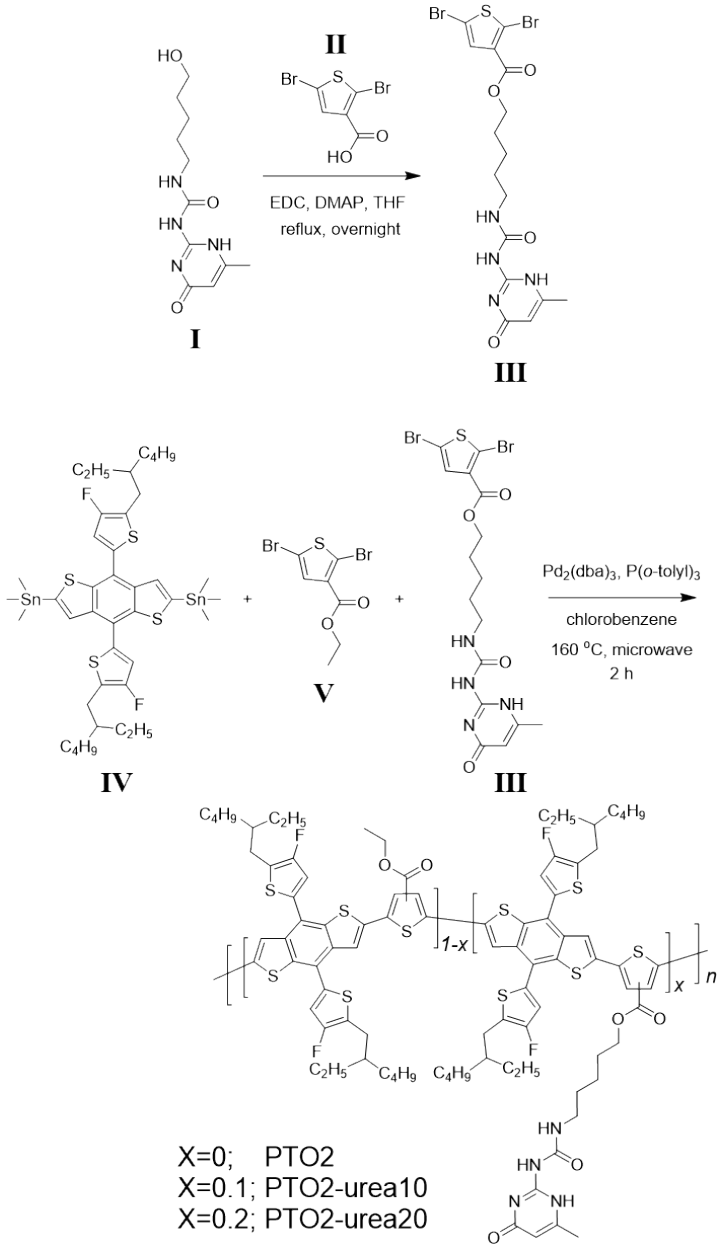
Eul-Yong Shin, [+,a] Sungmin Park, [+,a] Hyungju Ahn, [b] Hyunjung Jin, [a] In Soo Kim, [c] Jun Hong Noh [d] and Hae Jung Son *[a,e]

[a]. Advanced Photovoltaics Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea. E-mail: hjson@kist.re.kr
[b]. Pohang Accelerator Laboratory, Kyungbuk, Pohang, 37673, Republic of Korea.
[c]. Nanophotonics Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea.
[d]. School of Civil, Environmental and Architectural Engineering, Korea University, Seoul 02841, Republic of Korea.
[e]. Graduate School of Energy and Environment (KU-KIST GREEN SCHOOL), Korea University, Seoul 02841, Republic of Korea.

1. General

Unless stated otherwise, all of chemicals for synthesis, characterization, and device fabrication were purchased from Sigma-Aldrich and used without further purification step. 1-(5-hydroxypentyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (I), 2,5-dibromothiophene-3-carboxylic acid (II), and ethyl 2,5-dibromothiophene-3-carboxylate (V) were synthesized according to the procedures reported in the literature.[1, 2] (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (IV) was purchased from Sunatech and used without further purification. The synthesized monomer was characterized by measuring ^{1}H and ^{13}C NMR using a Bruker Ascend 400 spectrometer in $CDCl_3$ at 298 K. To prove a hydrogen bonding, ^{1}H NMR spectra of PTO2-urea20 and compound III were obtained using Agilent Technologies 600 MHz FT NMR using C2D2Cl4 solution in the range of 298 K to 343 K. The splitting patterns were shown as singlet (s), doublet (d), triplet (t), triplet of doublet (td), and multiplet (m) for ^{1}H NMR data. The ultraviolet-visible (UV–Vis) absorption spectra of the polymer solution and films were obtained by a PerkinElmer Lambada 35. The solution UV–Vis spectra were obtained in a 1 cm path quartz cuvette with a concentration of 5×10^{-5} M in chlorobenzene. And the film samples for UV–Vis were prepared

by spin-coating in nitrogen-filled gloves box with 10 mg/mL solution in chlorobenzene. Elemental analysis of compound III was performed using a Thermo Scientific FLASH 2000 CHNS elemental analyzer. The number average molecular weight (M_n) and the dispersity ($Đ$) of the synthesized polymers were estimated using a Waters gel-permeation chromatography (GPC) system at 80 ^oC with 1,2-dichlorobenzene as the eluent and polystyrene narrow standards were used for calibration.



Scheme S1. Synthetic scheme of the monomer and polymers.

2. Synthesis

2.1. Synthesis of monomer

5-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)pentyl 2,5-dibromothiophene-3-carboxylate (III) : 1-(5-hydroxypentyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (I) (422.5 mg, 1.66 mmol), 2,5-dibromothiophene-3-carboxylic acid (II) (712.6 mg, 2.49 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (386.9 mg, 2.49 mmol), and 4-dimethylaminopyridine (DMAP) (40.6 mg, 0.33 mmol) were placed in a reaction flask and dissolved in anhydrous tetrahydrofuran (THF, 16.6 mL) after purging with dry argon. The reaction mixture was refluxed overnight with a water condenser and then cooled down to room temperature. The reaction mixture was poured into 1M HCl aqueous solution and the organic layer was extracted with chloroform. Excess solvent was removed by rotary evaporator and the concentrated fraction was precipitated into an acetone-filled flask. The product (374 mg, 43.1%) was obtained through filtering and washing with excess acetone.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) : 13.12 (s, 1H), 11.88 (s, 1H), 10.25 (t, 1H), 7.35 (s, 1H), 5.83 (s, 1H), 4.31 (t, *J*=6.4 Hz, 2H), 3.32 (td, *J*=7.5 Hz, 2H), 2.26 (s, 3H), 1.88-1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) : 173.00, 160.83, 156.60, 154.65, 148.23, 131.99, 131.75, 118.97, 111.29, 106.71, 65.14, 39.70, 28.92, 28.17, 23.34, 18.97. Anal. calcd for $C_{16}H_{18}Br_2N_4O_4S$: C 36.80, H 3.47, N 10.73, S 6.14; found: C 37.42, H 3.62, N 10.86, S 6.19.

2.2. Synthesis of polymers

PTO2 : (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (IV) (188.1 mg, 0.2 mmol), ethyl 2,5-dibromothiophene-3-carboxylate (V) (62.8 mg, 0.2 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (3.7

mg, 4.0 μmol), and tri(o-tolyl)-phosphine (P(*o*-tolyl)$_3$) (9.7 mg, 32.0 μmol) were placed in a microwave reaction flask and dissolved in anhydrous chlorobenzene (0.6 mL). The reaction mixture was purged with dry argon for 20 min and a microwave-assisted reaction was performed at 160 °C for 2 h. The crude polymer was precipitated into acetone and the precipitates were filtered with a thimble filter. The polymer was purified by sequential Soxhlet extraction with methanol, hexane, ethyl acetate, dichloromethane, and chloroform. The polymer in chloroform fraction was condensed by rotary evaporator and precipitated in methanol and then filtered to obtain. (86.3 mg, 56.3%) GPC: M_n = 52.6 kg/mol, $Đ$ = 2.21

PTO2-urea10 : 5-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)pentyl 2,5-dibromothiophene-3-carboxylate (III) (10.4 mg, 0.02 mmol), (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (IV) (188.1 mg, 0.2 mmol), ethyl 2,5-dibromothiophene-3-carboxylate (V) (56.5 mg, 0.18 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (3.7 mg, 4.0 μmol), and tri(o-tolyl)-phosphine (P(*o*-tolyl)$_3$) (9.7 mg, 32.0 μmol) were placed in a microwave reaction flask and dissolved in anhydrous chlorobenzene (0.6 mL). The reaction mixture was purged with dry argon for 20 min and a microwave-assisted reaction was performed at 160 °C for 2 h. The crude polymer was precipitated into acetone and the precipitates were filtered with a thimble filter. The polymer was purified by sequential Soxhlet extraction with methanol, hexane, ethyl acetate, cyclohexane, and chloroform. The polymer in chloroform fraction was condensed by rotary evaporator and precipitated in methanol and then filtered to obtain. (141 mg, 89.5%) GPC: M_n = 10.4 kg/mol, $Đ$ = 1.78

PTO2-urea20 : PTO2-urea20 was synthesized according to the similar procedure to that for PTO2-urea10, with 5-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)pentyl 2,5-dibromothiophene-3-carboxylate (III) (10.4 mg, 0.02 mmol), (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (IV) (94.0 mg, 0.1 mmol), ethyl 2,5-dibromothiophene-3-carboxylate (V) (25.1 mg, 0.08 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (1.9 mg, 2.0 μmol), and tri(o-tolyl)-phosphine (P(*o*-tolyl)$_3$) (4.9 mg, 16.0 μmol). (73 mg, 90.3%) GPC: M_n = 10.8 kg/mol, $Đ$ = 2.00

3. Electrochemical Properties

The electrochemical properties of synthesized polymers were obtained by cyclic voltammetry (CV) using a CH instruments electrochemical analyzer. Three electrodes system was used consisted of a glassy carbon working electrode, platinum (Pt) wire counter electrode, and Ag/AgCl reference electrode. The measurement was performed under argon purging and 0.1 M deoxygenated tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) solution in acetonitrile was used as an electrolyte. The potential sweep rate was 50 mV/s and the polymer sample was placed on the working electrode by drop-casting. The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was used as a standard to calibrate the potential. The energy levels of highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated according to the following equations, where E_{ox} is the onset oxidation potential vs. Fc/Fc^+ and E_{red} is the onset reduction potential vs. Fc/Fc^+.

$$E_{HOMO} = -4.8 - E_{ox} \text{ (eV)}$$

$$E_{LUMO} = -4.8 + E_{red} \text{ (eV)}$$

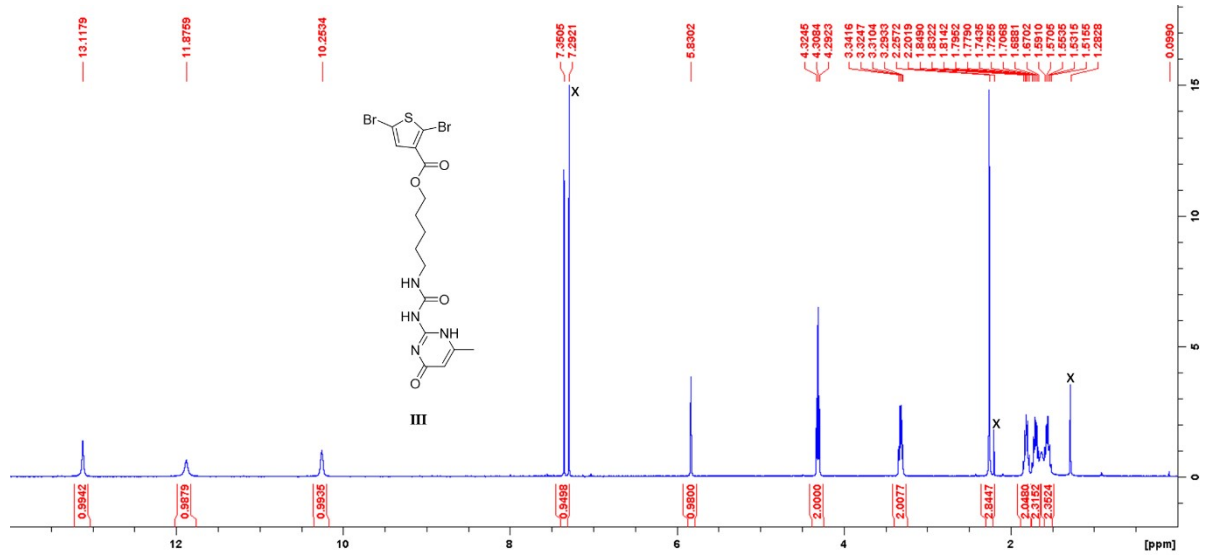


Fig. S1. ^{1}H NMR spectrum of compound Ⅲ, x marks are residual solvents.

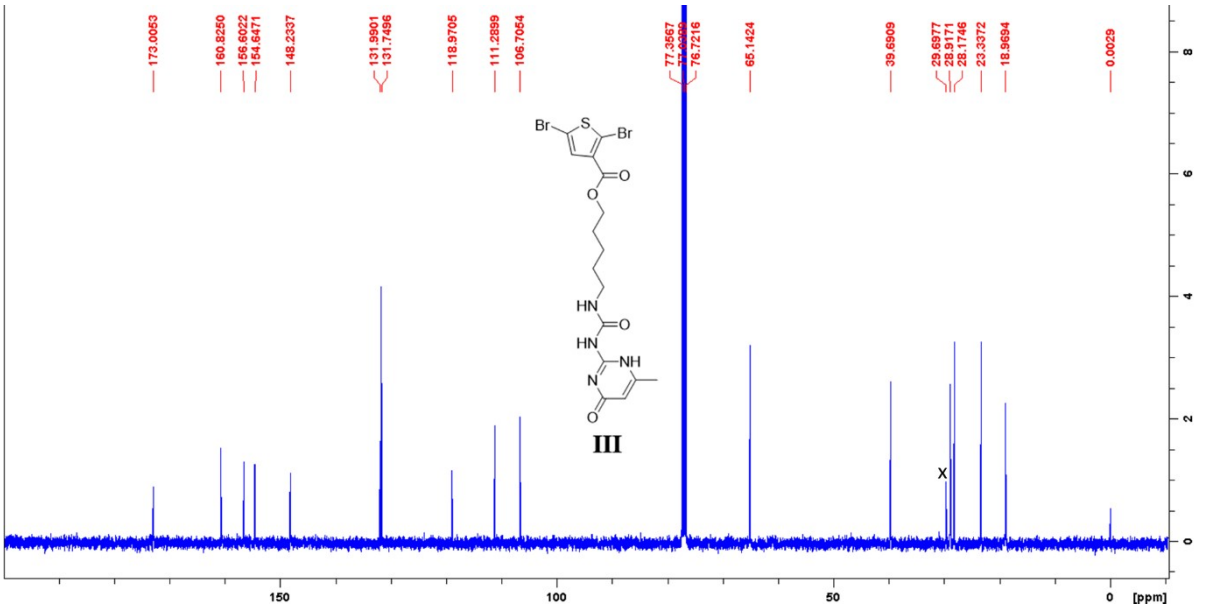


Fig. S2. ^{13}C NMR spectrum of compound III. X mark is a residual solvent.

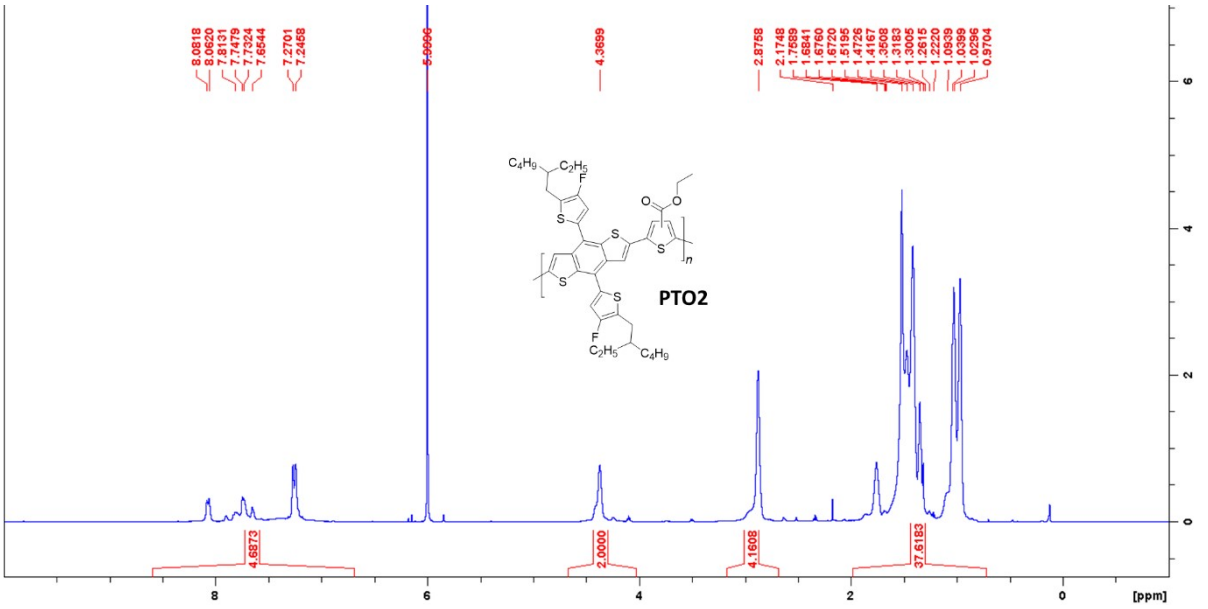


Fig. S3. ^{1}H NMR spectrum of PTO2 in $C_2D_2Cl_4$ at 343 K.

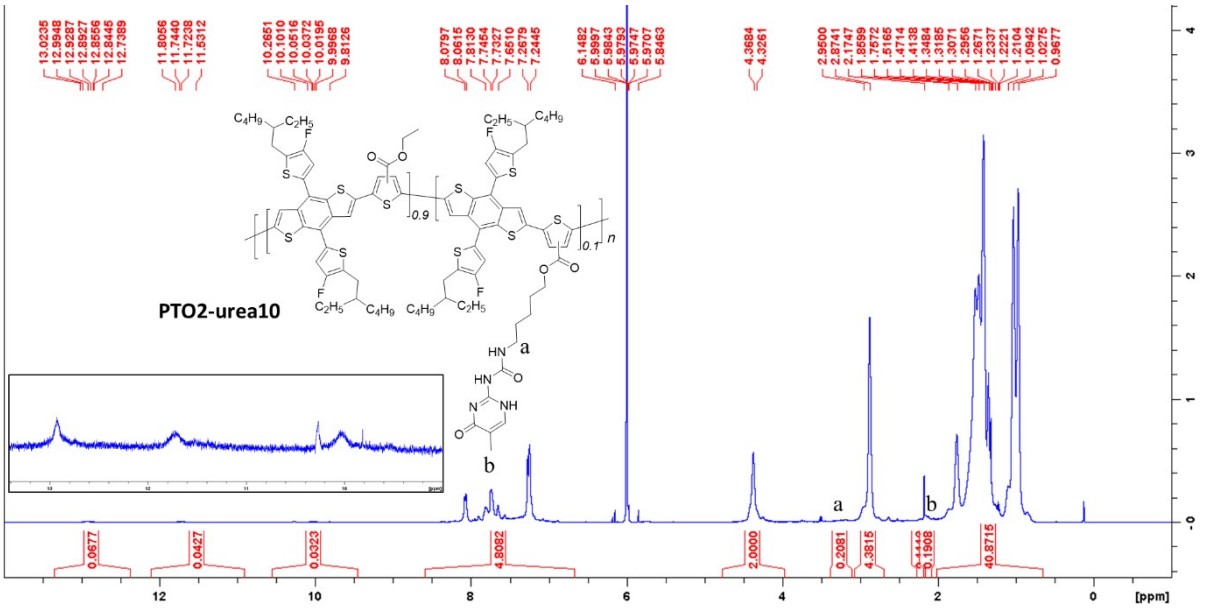


Fig. S4. ^{1}H NMR spectrum of PTO2-urea10 in $C_2D_2Cl_4$ at 343 K.

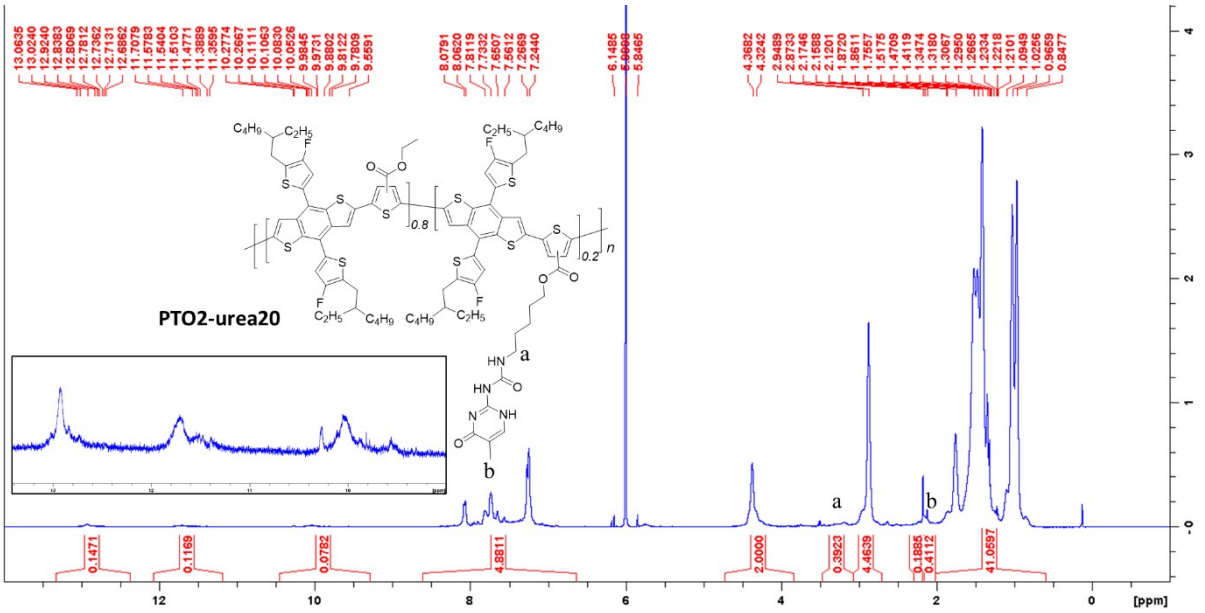
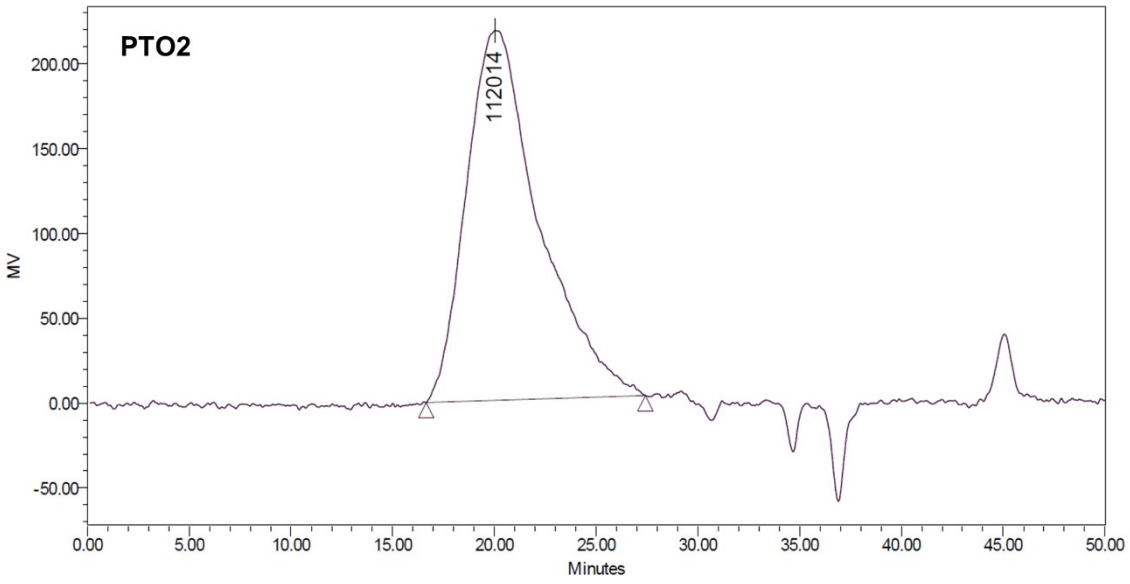


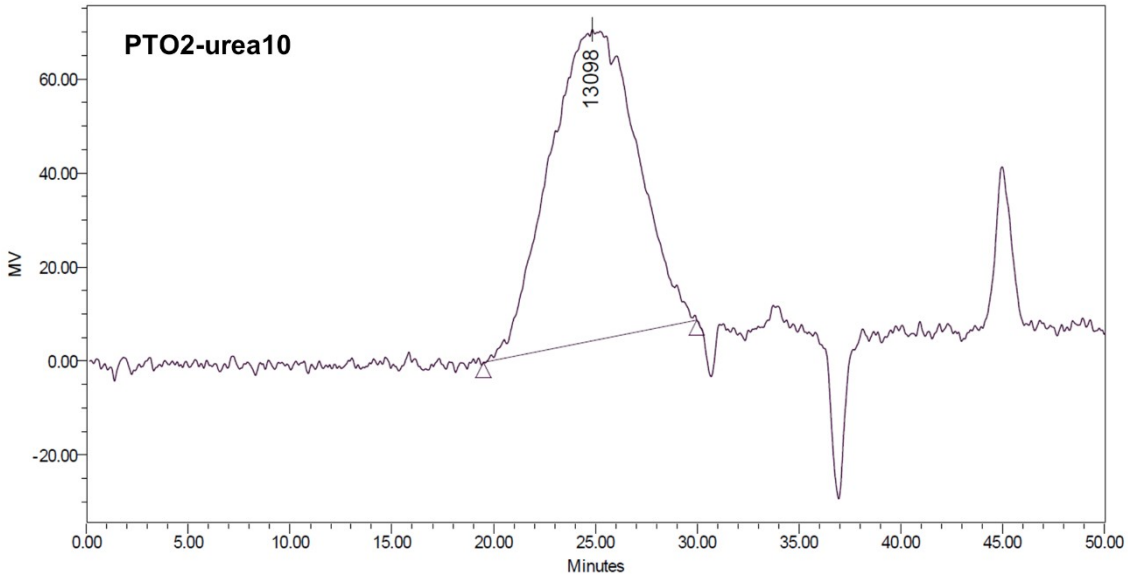
Fig. S5. ^{1}H NMR spectrum of PTO2-urea20 in $C_2D_2Cl_4$ at 343 K.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		52629	116519	112014	202120	300632	2.213983	1.734654	2.580117

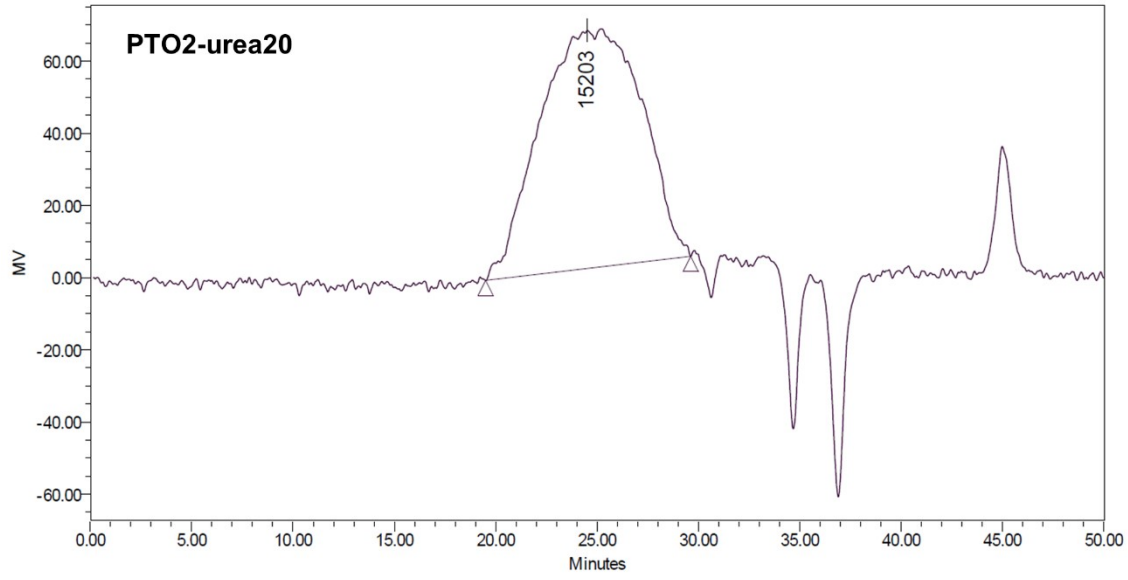
Fig. S6. GPC data of PTO2.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		10399	18482	13098	31225	46310	1.777342	1.689452	2.505616

Fig. S7. GPC trace of PTO2-urea10.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		10768	21565	15203	38955	57683	2.002661	1.806415	2.674866

Fig. S8. GPC trace of PTO2-urea20.

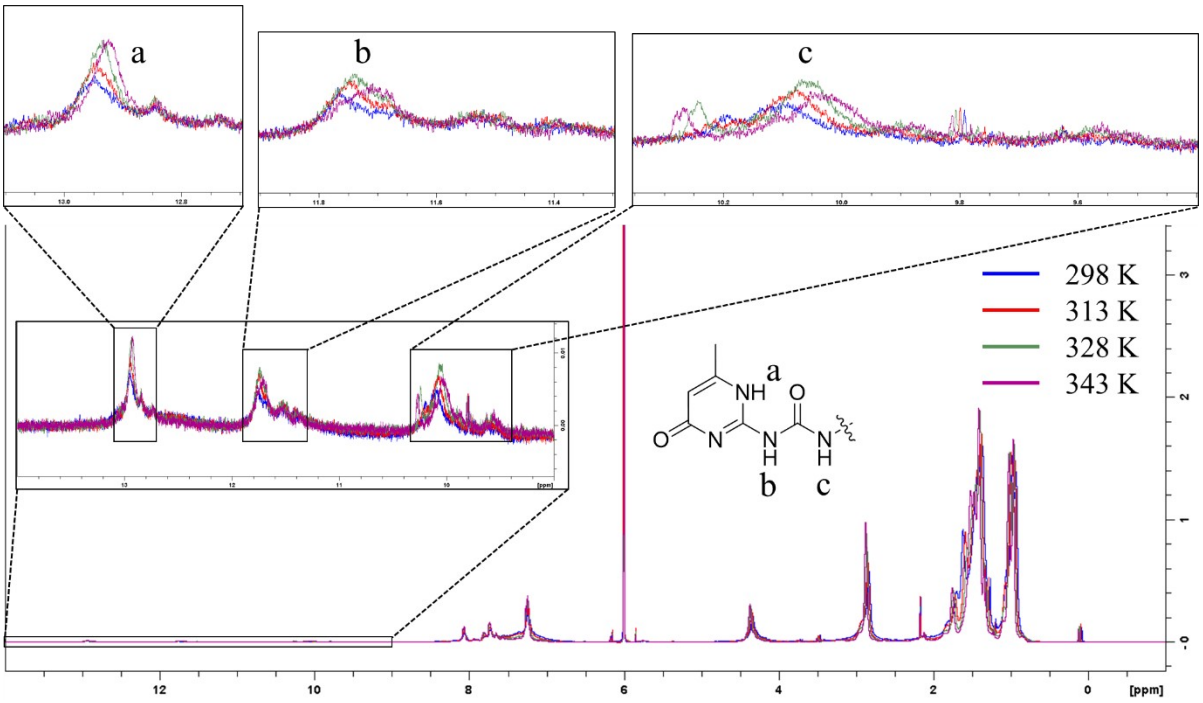


Fig. S9. ^{1}H NMR (600 MHz) spectra of PTO2-urea20 in a $C_2D_2Cl_4$ solution at various temperatures to prove the hydrogen bonding of the urea group.

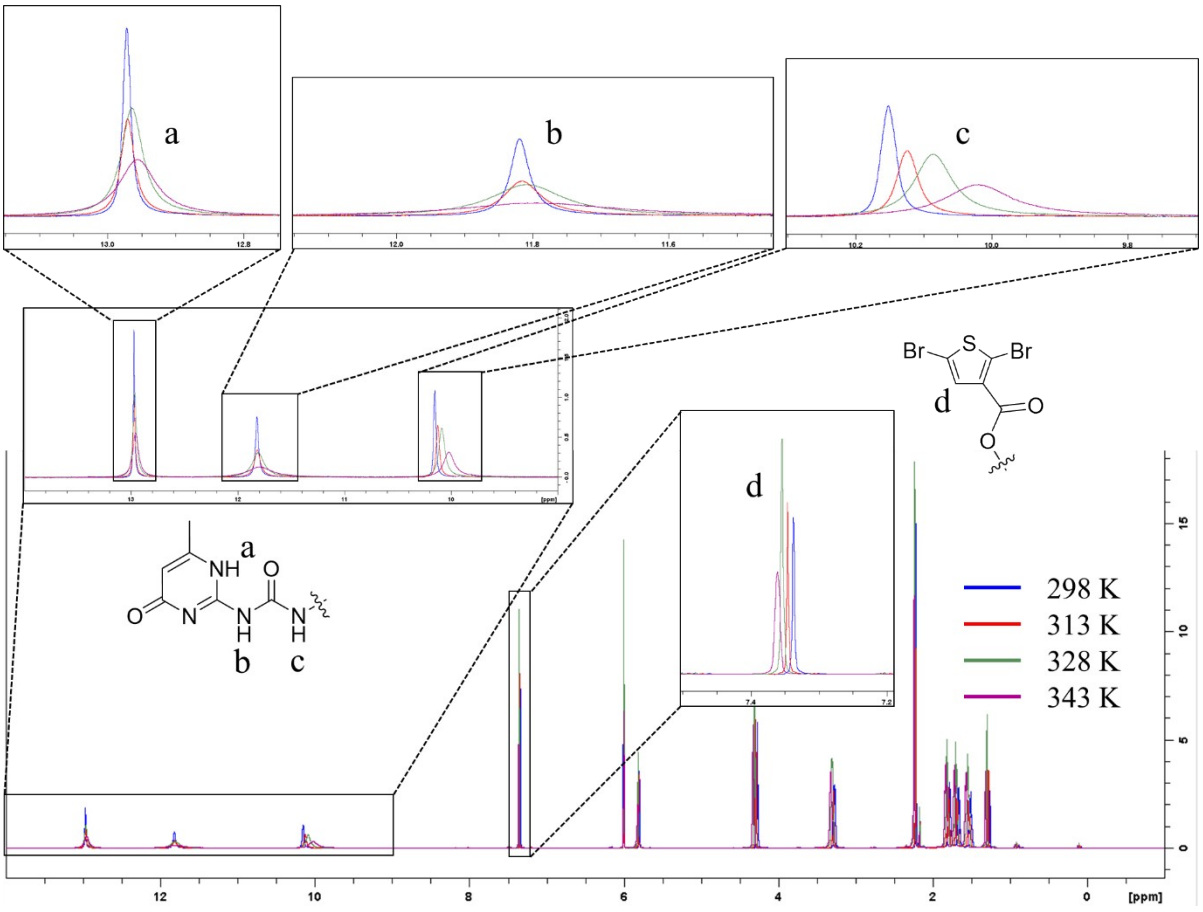


Fig. S10. ^{1}H NMR (600 MHz) spectra of compound III in a $C_2D_2Cl_4$ solution at various temperatures to prove the hydrogen bonding of the urea group.

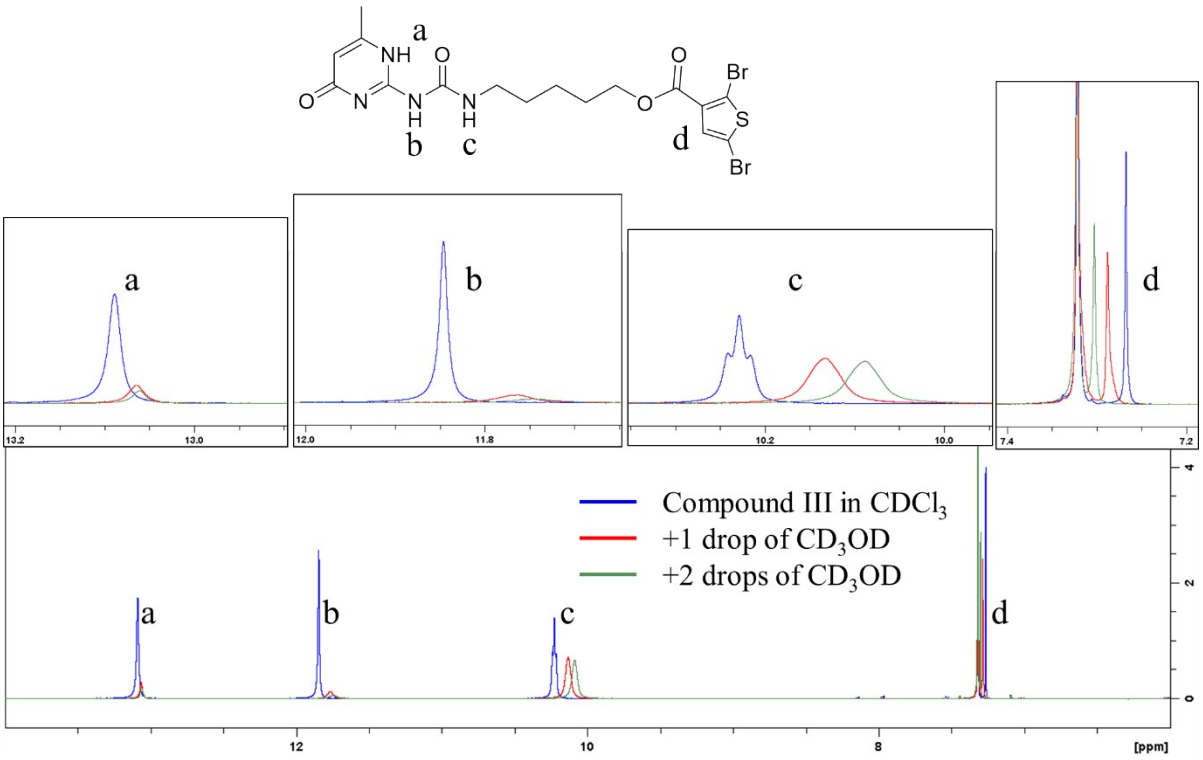


Fig. S11. ^{1}H NMR (400 MHz) spectra of compound III in $CDCl_3$ and a mixture with CD_3OD to prove the hydrogen bonding of the urea group.

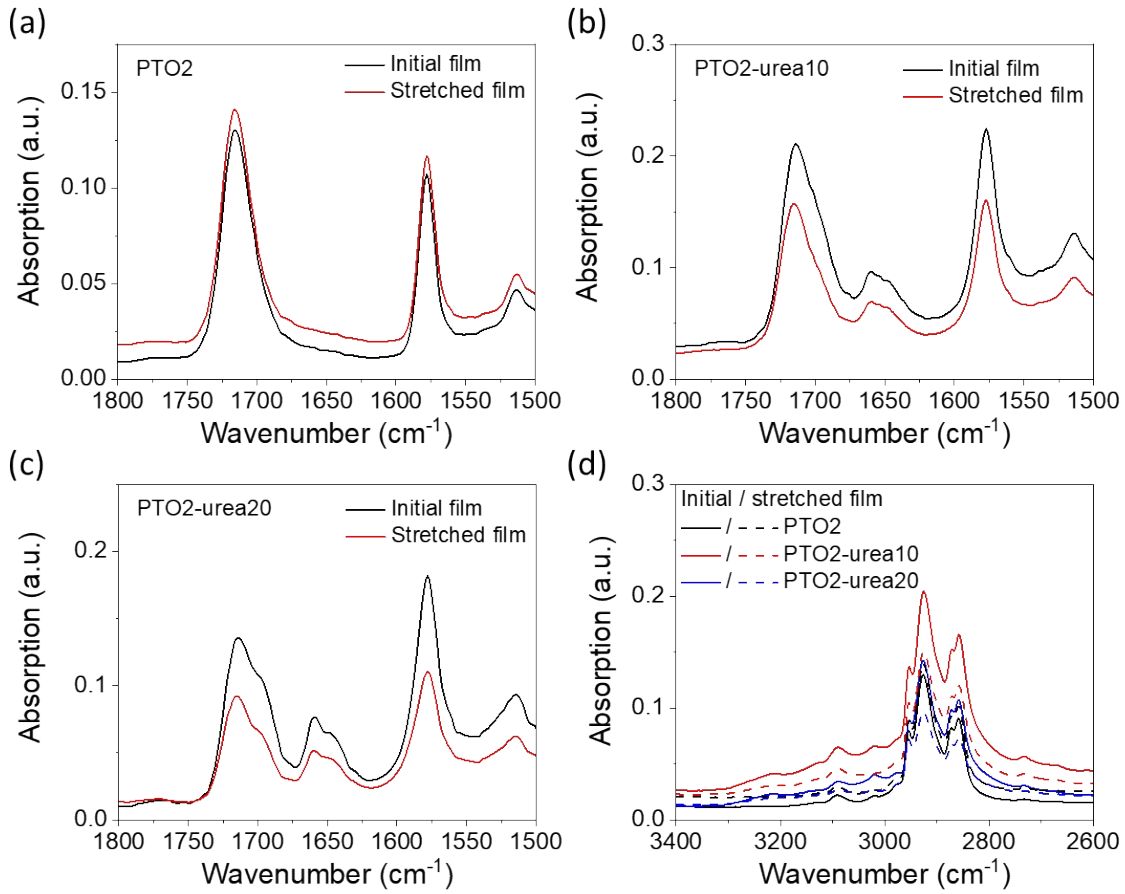


Fig. S12. Original FT-IR absorption spectra of (a) PTO2, (b) PTO2-urea10, and (c) PTO2-urea20 in the range of 1800-1500 cm^{-1} and (d) 3400-2500 cm^{-1} on a PDMS substrate before and after stretching.

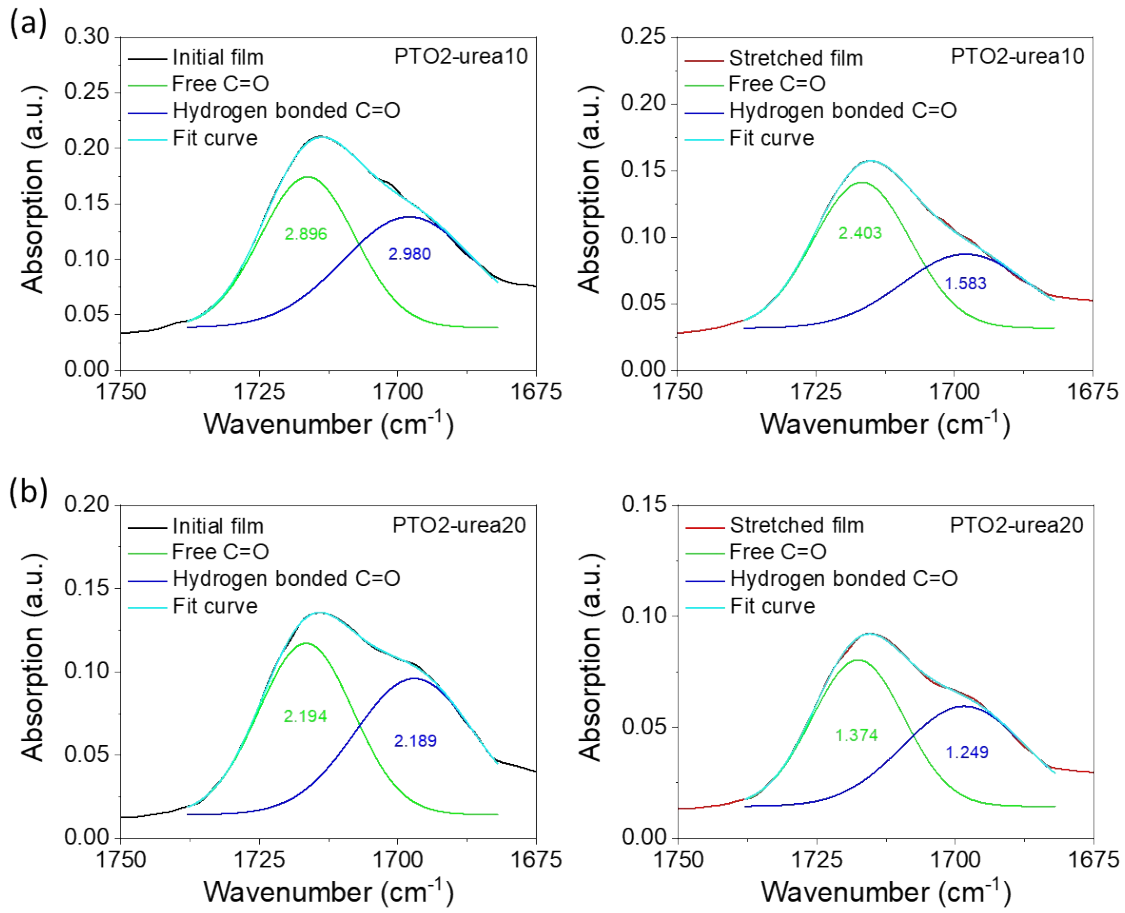


Fig. S13. Peak fitting analyses of the carbonyl (C=O) group vibration of (a) PTO2-urea10 and (b) PTO2-urea20 before and after stretching. The values inside of the spectra are the area of each fitted peak.

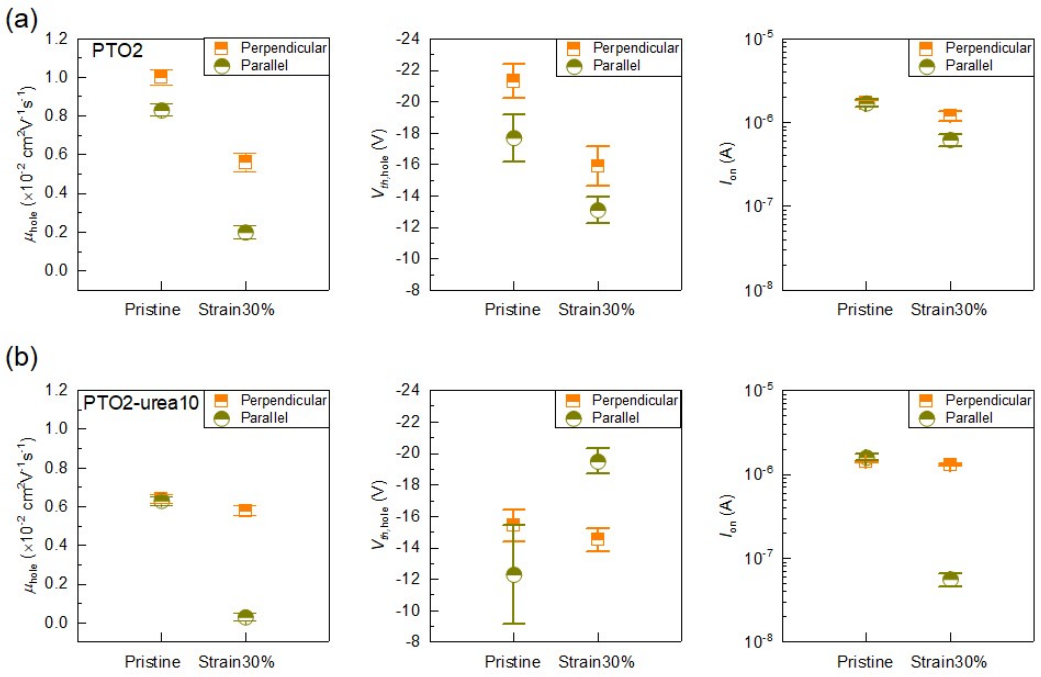


Fig. S14. Comparison of the hole mobility, threshold voltage, and on-current of the OTFTs based on a) PTO2 and b) PTO2-Urea10 where the polymer film was prepared after applying 0% or 30% strain along perpendicular or parallel to the channel direction of the OTFTs.

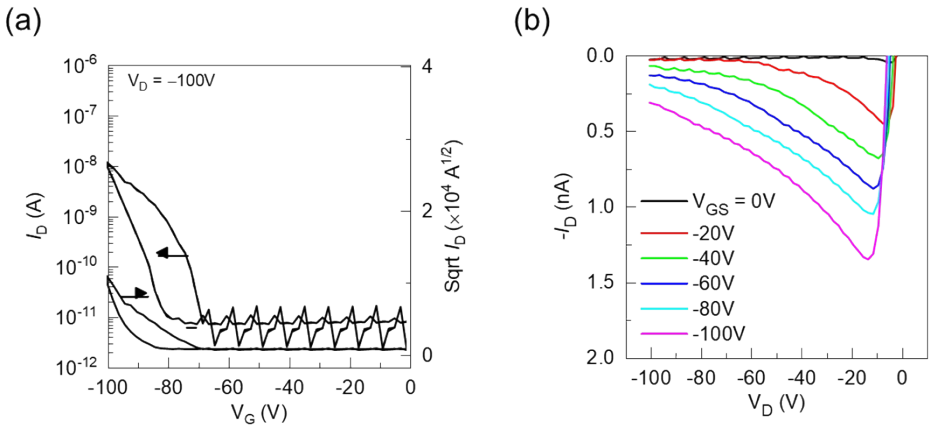


Fig. S15. (a) The transfer characteristics and (b) output characteristics of PTO2-urea20.

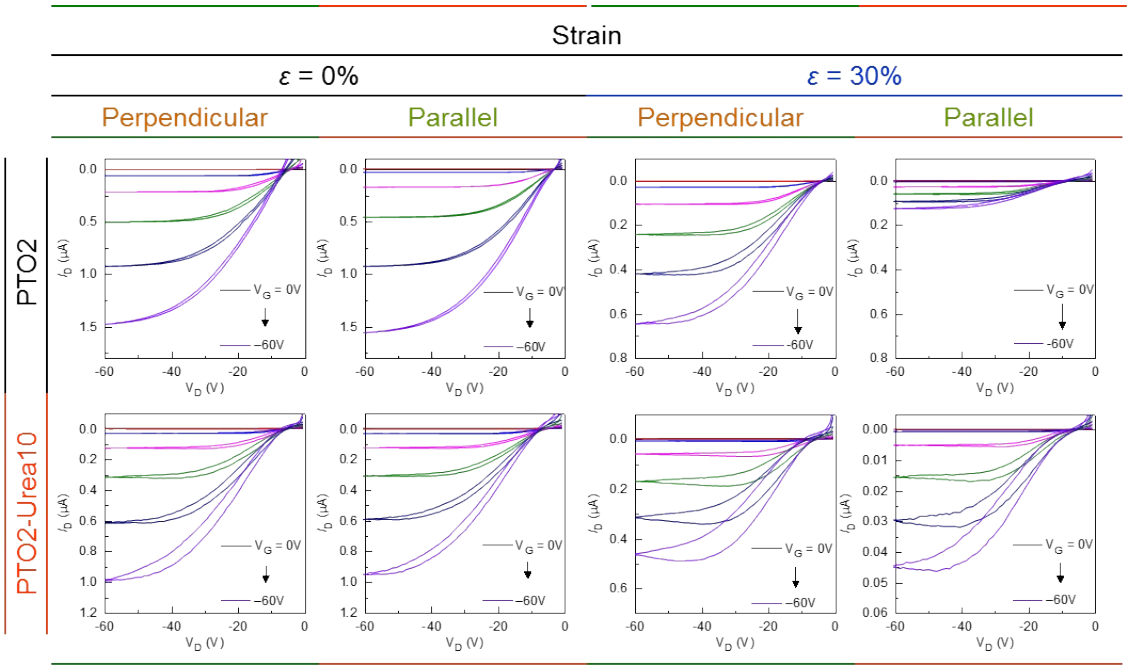


Fig. S16. Output characteristics of PTO2 and PTO2-urea10 under 0% and 30% strain. The direction of the strain was varied as perpendicular and parallel to the channel direction of OTFTs.

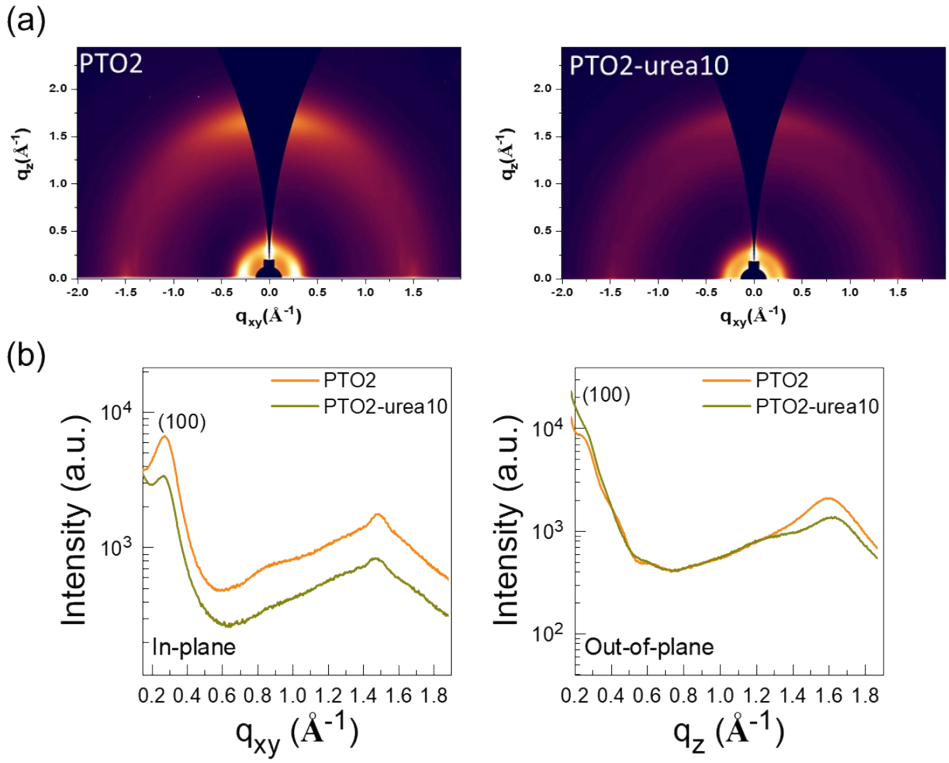


Fig. S17. (a) 2D grazing-incidence wide-angle X-ray diffraction patterns and (b) in-plane and out-of-plane line profile of the PTO2 and PTO2-urea10 on OTS/Si substrate.

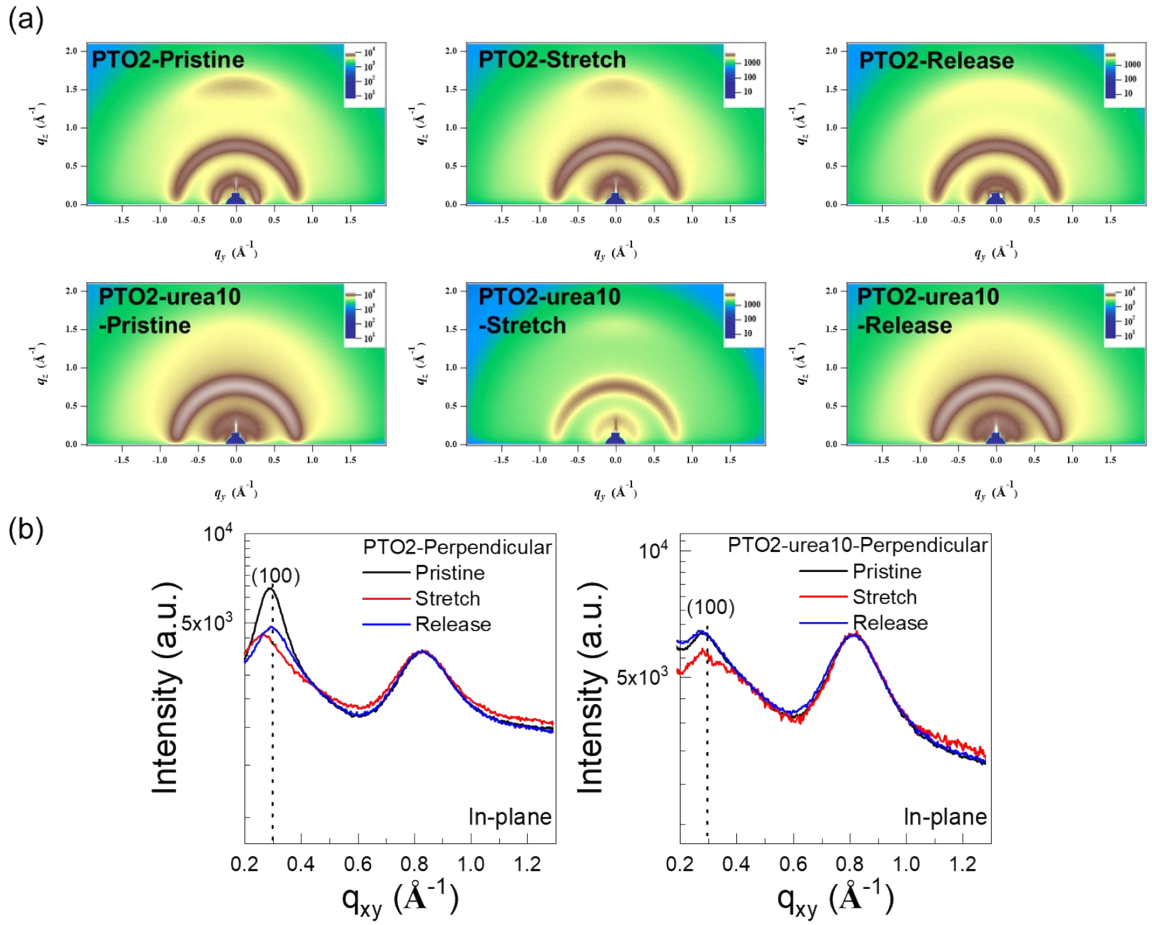


Fig. S18. (a) 2D grazing-incidence wide-angle X-ray diffraction patterns and (b) in-plane line profiles of the perpendicular direction for PTO2 and PTO2-urea10 on PDMS substrate.

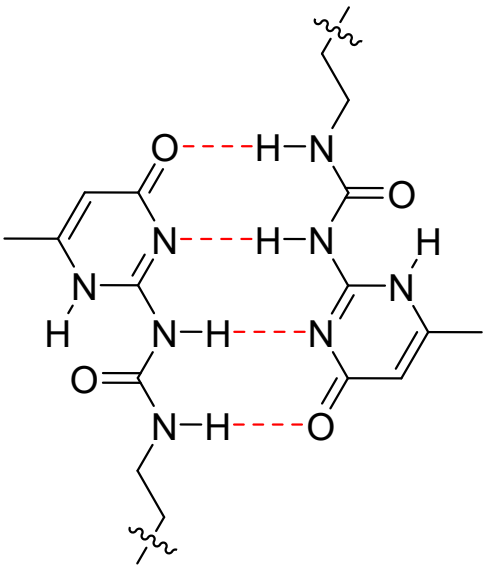


Fig. S19. The chemical structure of hydrogen bonding of urea functional group.

Table S1. Summary of electrical characteristics of PTO2-urea20 OTFTs.

Polymer	μ_{hole} [$cm^2 V^{-1} s^{-1}$]	V_{th} [V]	I_{on} [A] (at V_G = −100 V)
PTO2-urea20	6.77×10^{-4}	−83.8	1.9×10^{-8}

Reference

1. M. Brzeziński and T. Biela, *Macromolecules*, 2015, **48**, 2994-3004.
2. H. Yao, Y. Cui, D. Qian, C. S. Ponseca, Jr., A. Honarfar, Y. Xu, J. Xin, Z. Chen, L. Hong, B. Gao, R. Yu, Y. Zu, W. Ma, P. Chabera, T. Pullerits, A. Yartsev, F. Gao and J. Hou, *J. Am. Chem. Soc.*, 2019, **141**, 7743-7750.