

Supporting information

Photoinduced Cationic Polycondensation in Solid State Towards Ultralow Band Gap Conjugated Polymers

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Materials

Unless otherwise stated, all chemicals and solvents were purchased from commercial sources and were used without further purification. THF and toluene were refluxed over sodium and benzophenone and distilled prior to use.

General Procedure for the Synthesis of monomers and polymers

The synthesis of the polymers **PTT-Ni** and **PTT-L** is described in **Scheme S1**. The synthesis of the monomer **M** and compound **3** were developed by our group before.¹ The compounds **4** and **5** were mono-brominated from compound **3**. The monomer **M1** was synthesized *via* two steps dealkylation/alkylation from compound **4**. We are the first group that applied KCPT² to the dibromo-thienothiophene monomer **M** and obtained polymer **PTT-Ni**. In this reaction, one equivalent of *i*-PrMgCl was reacted with the monomer **M** and formed a Grignard reagent. In this step, two isomers are expected due to the low selectivity of the C-Br bonds. The isomers further reacted

by adding the catalyst Ni(dppp)Cl₂ to form the polymer **PTT-Ni**. The polymer **PTT-L** was synthesized through a photochemical polymerization reaction. The monomer **M1** was sealed in a vial, protected with N₂, then the vial was exposed to visible light and then the polymer **PPT-L** was formed at solid state. The compound **9** was dimerized from compound **M1**, followed by a bromination to get the monomer **M2** and **M3**. The detailed synthetic process of the monomers and polymers are as follows. The two polymers are expected to have different regioregularity, we will discuss this below in the characterizations.

Methyl 6-bromothieno[3,4-b]thiophene-2-carboxylate (4); Methyl 4-bromothieno[3,4-b]thiophene-2-carboxylate (5) Compound **3** (3.96 g, 20.0 mmol) was dissolved in 100 mL of anhydrous DMF. The *N*-bromosuccinimide (NBS) (3.56 g, 20 mmol) dissolved in 80 mL DMF was added to the solution dropwise at 0 °C over 3h. The reaction mixture was stirred at 0 °C for 2 h in the dark. Then the mixture was poured into water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO₄, and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography using a hexanes/dichloromethane (DCM) mixture (1/1 by volume) as eluent to afford a pink solid (4.32 g, 78%). The solid contains two mono-brominated isomers, according to the ¹H NMR, the ratio of the two monomers is close to 2:3, which was not able to be further isolated with silica gel chromatography. ¹H NMR (500 MHz, CDCl₃, δ/ppm): 7.67 (s, 2H), 7.58 (d, *J* = 0.85, 3H), 7.53 (s, 2H), 7.25 (d, *J* = 0.85, 3H), 3.92 (s, 15H). GC-MS (C₈H₅BrO₂S₂) *m/z*: calcd for 277.2; found 277.8.

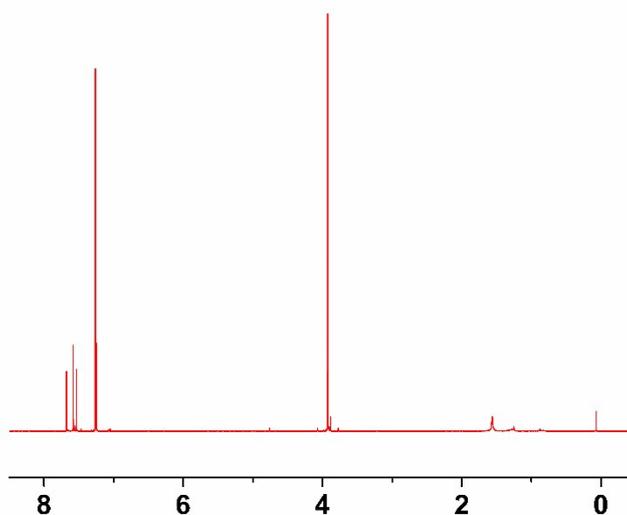


Fig. S1 ^1H NMR spectrum for compounds **4** and **5**

6-Bromothieno[3,4-b]thiophene-2-carboxylic acid (6); 4-Bromothieno[3,4-b]thiophene-2-carboxylic acid (7) To a solution of the isomers mixture (**4** and **5**) (4.00 g, 14.4 mmol) in THF/H₂O (360 mL, 2/1) was added LiOH•H₂O (2.92 g, 69.5 mmol) at room temperature. The reaction mixture was refluxed for 6 h. After cooling to room temperature, the THF was removed in vacuo. The residue was acidified with 1M HCl and filtered to afford pale yellow solid (3.65 g, 96%). The isomers mixture was directly used for the next step without further purification. ^1H NMR (500 MHz, DMSO, δ /ppm): 8.03 (s, 1H), 7.81 (s, 2H), 7.76 (s, 1H), 7.46 (s, 2H). GC-MS (C₇H₃BrO₂S₂) m/z: calcd for 263.1; found:263.8.

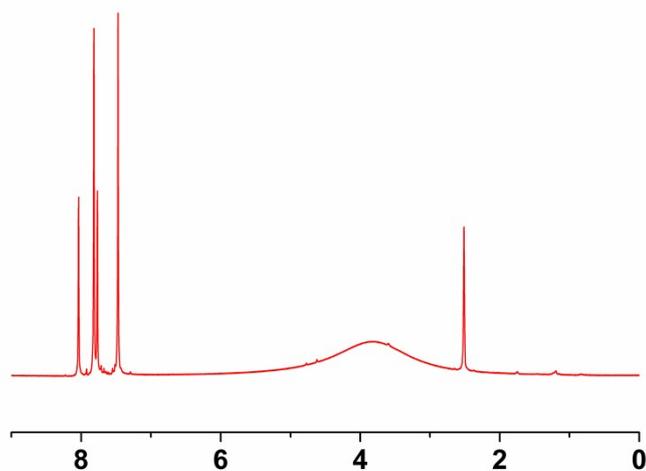


Fig. S2 ¹H NMR spectrum for compounds **6** and **7**

2-Ethylhexyl 6-bromothieno[3,4-b]thiophene-2-carboxylate (M1); 2-Ethylhexyl 4-bromothieno[3,4-b]thiophene-2-carboxylate (8) To a solution of the mixed isomers (**6** and **7**) (263.1 mg, 1.0 mmol), DCC (247.4 mg, 1.2 mmol) and DMAP (146.6mg, 1.2 mmol) in DCM (5 mL) was added 2-ethylhexan-1-ol (0.79 mL, 5 mmol) at room temperature. The reaction mixture was stirred for 24 h under N₂ protection. The reaction was diluted with DCM (30 mL), washed with water (10 mL) and brine (10 mL), dried over anhydrous Na₂SO₄. The organic phase was concentrated in vacuo and the residue was purified by column chromatography (silica gel, DCM/hexane = 2:3) to afford **M1** (178 mg) and **8** (77 mg), total yield was 68%. They are both colorless oils.

M1 ¹H NMR (500 MHz, CDCl₃ δ/ppm): 7.53 (d, *J* = 0.85, 1H), 7.21 (d, *J* = 0.85, 1H), 4.24 (m, 2H), 1.71 (m, 1H), 1.47-1.30 (m, 8H), 0.96-0.88 (m, 6H). ¹³C NMR (CDCl₃ δ/ppm): 163.0, 146.1, 141.0, 139.1, 122.5, 112.8, 103.0, 68.4, 39.0, 30.7, 29.2, 24.1, 23.2, 14.3, 11.3. GC-MS (C₁₅H₁₉BrO₂S₂) *m/z*: calcd for 375.3; found: 375.9.

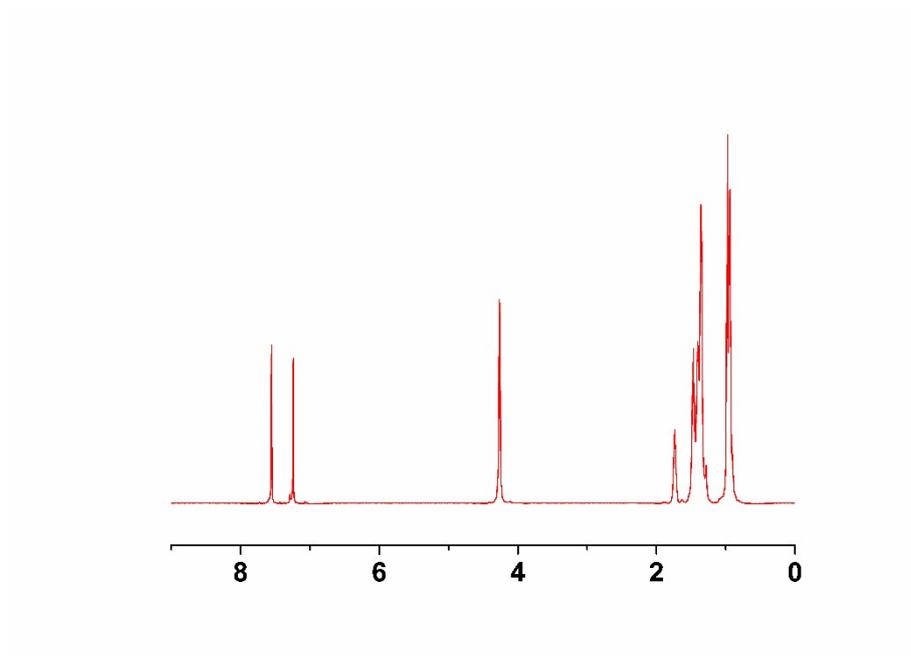


Fig. S3 ^1H NMR spectrum for compounds **M1**

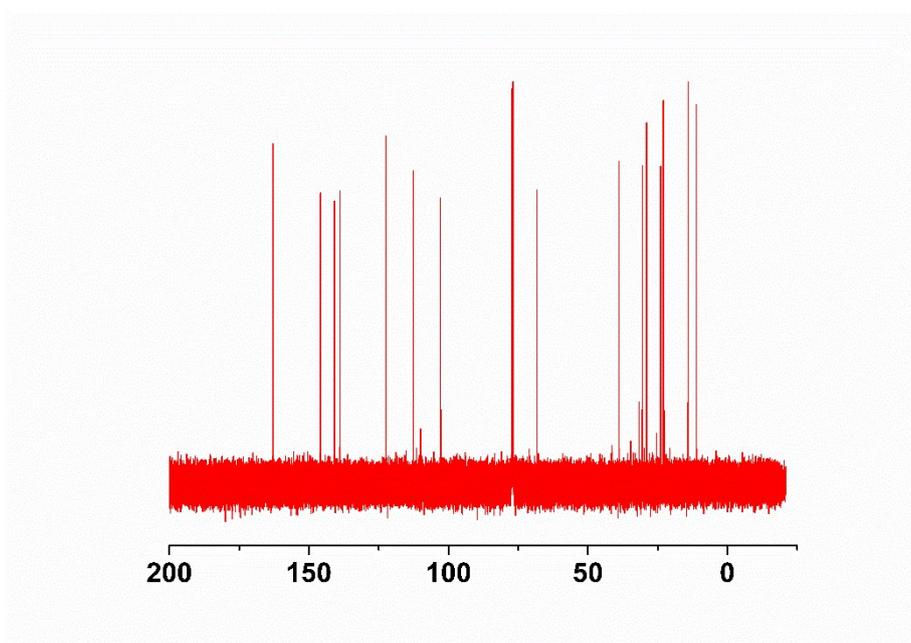


Fig. S4 ^{13}C NMR spectrum for compounds **M1**

8 ^1H NMR (500 MHz, CDCl_3 δ/ppm): 7.64 (s, 1H), 7.50 (s, 1H), 4.24 (m, 2H), 1.69 (m, 1H), 1.46-1.33 (m, 8H), 0.96-0.89 (m, 6H). ^{13}C NMR (CDCl_3 δ/ppm): 162.8, 145.2, 141.2, 140.4, 124.1, 118.1, 97.9, 68.1, 38.9, 30.5, 29.0, 23.9, 23.0, 14.1, 11.1. GC-MS

(C₁₅H₁₉BrO₂S₂) m/z: calcd for 375.3; found: 375.9.

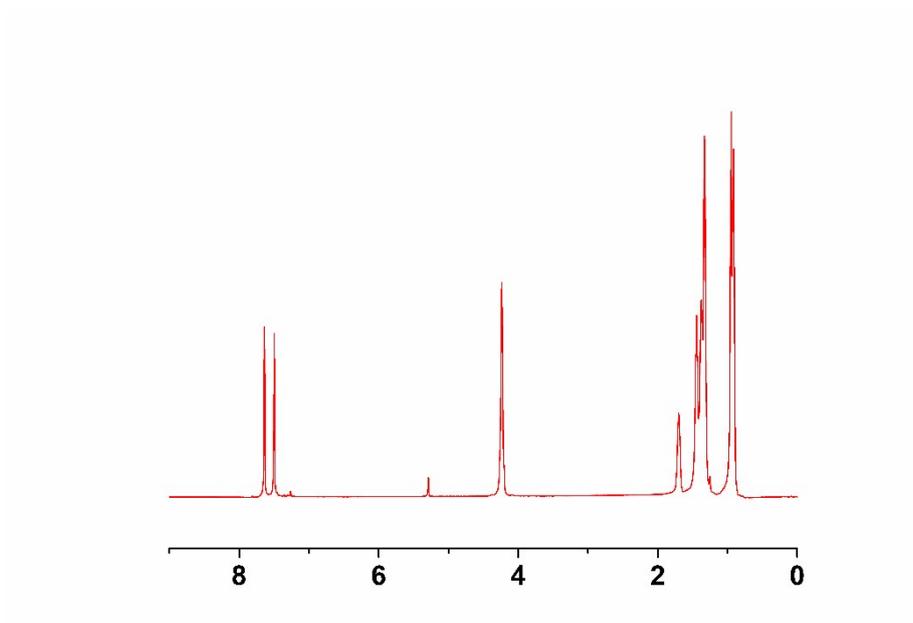


Fig. S5 ¹H NMR spectrum for compounds **8**

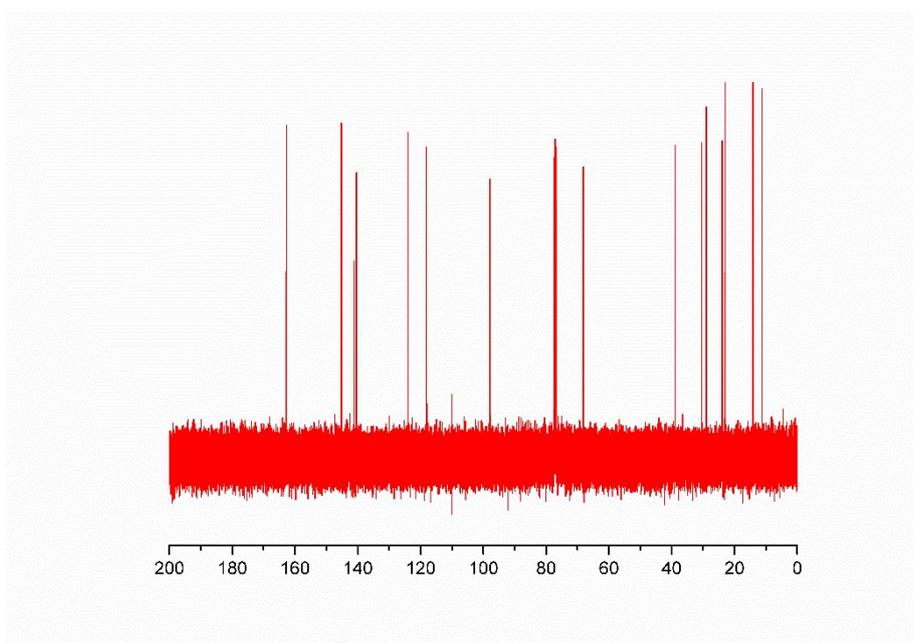


Fig. S6 ¹³C NMR spectrum for compounds **8**

Bis(2-ethylhexyl) [6,6'-bithieno[3,4-b]thiophene]-2,2'-dicarboxylate (9) Under an inert atmosphere, a mixture of compound **M1** (1.2 g, 3.2 mmol), Bis(tributyltin) (2.5 g, 4.3 mmol), Pd(PPh₃)₄ (180 mg, 0.16 mmol) in 10 mL of anhydrous toluene and 10 mL

of DMF was stirred at 100 °C for 24 h. The reaction was quenched with 10 mL H₂O. The mixture extracted with DCM 3 times. The combined organic fractions were washed with water (2 x 20 mL) and dried over MgSO₄. The solvent was evaporated and under vacuum and the residue was purified by silica gel (DCM/Hexane 3/2) affording the title compound as a red solid (0.84 g, 89%). ¹H NMR (500 MHz, CDCl₃ δ/ppm): 8.00 (d, *J* = 0.70, 2H), 7.30 (d, *J* = 0.70, 2H), 4.26 (m, 4H), 1.73 (m, 2H), 1.47-1.31 (m, 16H), 0.97-0.90 (m, 12H); ¹³C NMR (CDCl₃ δ/ppm): 162.8, 142.0, 140.8, 140.7, 127.2, 123.5, 110.9, 68.2, 38.8, 30.5, 29.0, 24.0, 23.0, 14.1, 11.1; MS (Maldi-tof): *m/z* calcd for C₃₀H₃₈O₄S₄: 590.9; found: 590.2.

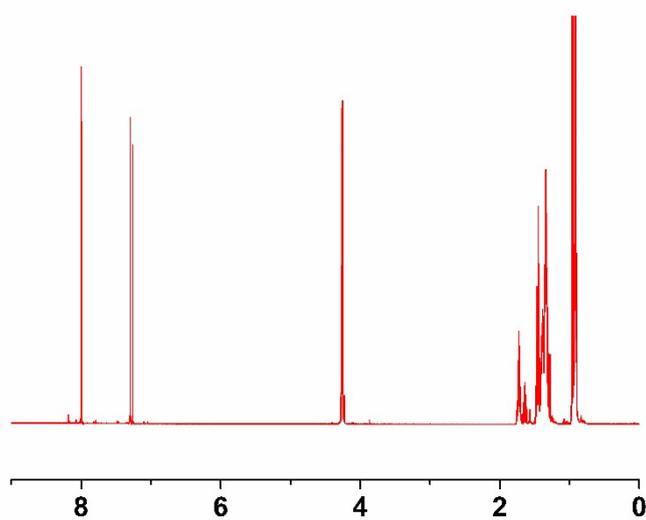


Fig. S7 ¹H NMR spectrum for compounds **9**

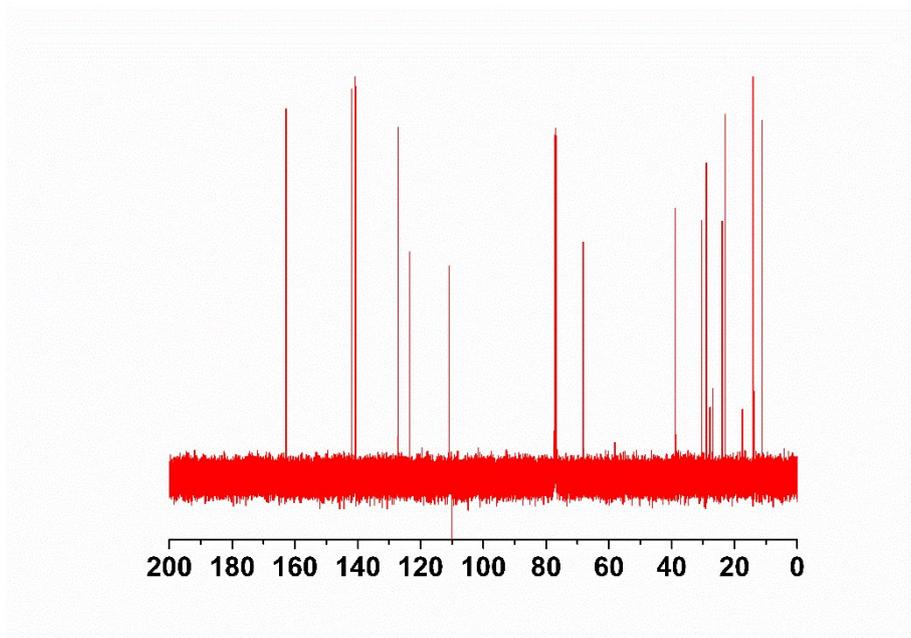


Fig. S8 ^{13}C NMR spectrum for compounds **9**

Bis(2-ethylhexyl)4-bromo-[6,6'-bithieno[3,4-b]thiophene]-2,2'-dicarboxylate(M2);

Bis(2-ethylhexyl)4,4'-dibromo-[6,6'-bithieno[3,4-b]thiophene]-2,2'-dicarboxylate

(M3) Compound **9** (472 mg, 0.8 mmol) was dissolved in 25 mL of DMF, NBS (142 mg, 0.8 mmol) dissolved in 15 mL DMF was added to the solution dropwise at 0 °C over 1h. The reaction mixture was stirred at 0 °C for 2 h in the dark. Then the mixture was poured into water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO_4 , and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography using a DCM/Hexanes mixture (3/2 by volume) as eluent to isolated two red solids,

M2 (365 mg, 68%). ^1H NMR (500 MHz, CDCl_3 δ /ppm): 7.77 (s, 1H), 7.71 (s, 1H), 7.14 (s, 1H), 4.22 (m, 4H), 1.71 (m, 2H), 1.45-1.33 (m, 16H), 0.97-0.92 (m, 12H); ^{13}C NMR (CDCl_3 δ /ppm): 162.7, 162.4, 142.3, 141.8, 141.2, 141.0, 140.9, 140.5, 128.7, 126.2,

124.2, 123.0, 111.2, 97.4, 68.4, 68.4, 38.9, 38.9, 30.7, 30.6, 29.1, 29.1, 24.1, 24.0, 23.1, 23.1, 14.3, 14.2, 11.2, 11.2; MS (Maldi-tof): m/z calcd for $C_{30}H_{37}BrO_4S_4$: 669.8; found: 669.7.

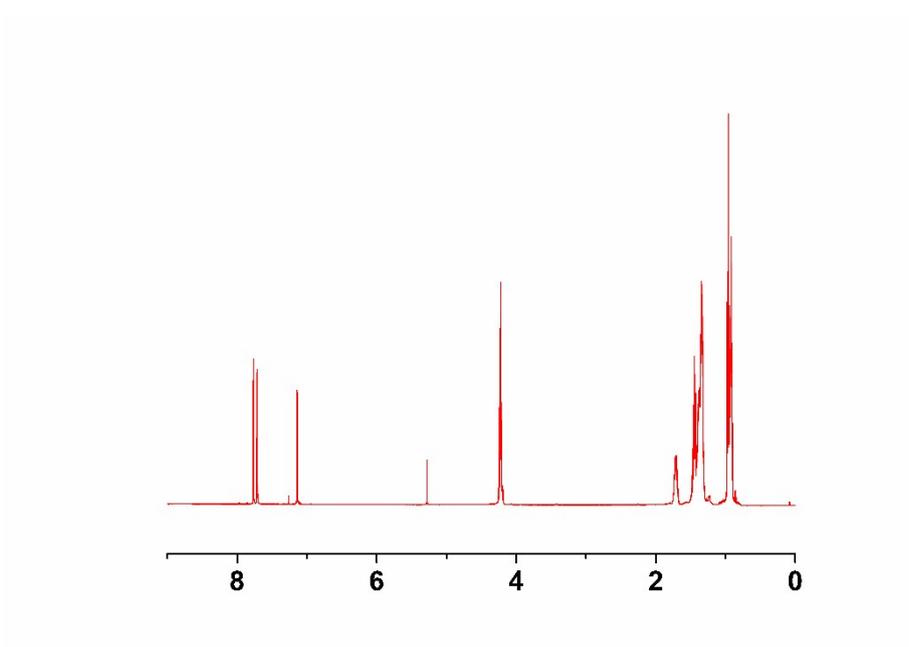


Fig. S9 ¹H NMR spectrum for compounds **M2**

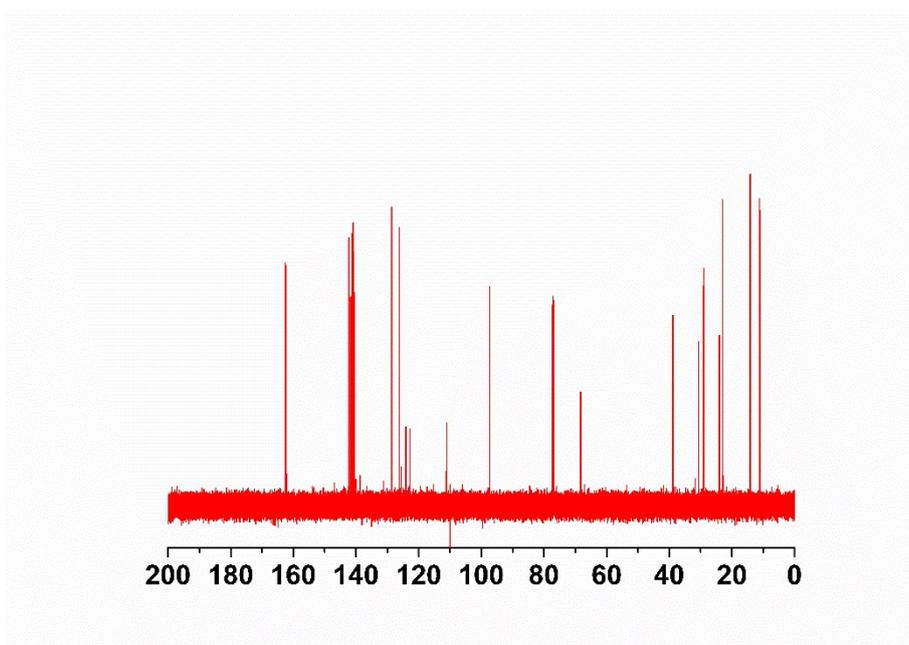


Fig. S10 ¹³C NMR spectrum for compounds **M2**

M3 (75 mg 13%). ^1H NMR (500 MHz, CDCl_3 δ /ppm): 7.52 (s, 2H), 4.22 (m, 4H), 1.72 (m, 2H), 1.47-1.36 (m, 16H), 0.98-0.93 (m, 12H); ^{13}C NMR (CDCl_3 δ /ppm): 162.2, 142.5, 141.6, 140.1, 127.5, 123.5, 97.9, 68.6, 38.9, 30.7, 29.1, 24.1, 23.2, 14.3, 11.3; MS (Maldi-tof): m/z calcd for $\text{C}_{30}\text{H}_{36}\text{Br}_2\text{O}_4\text{S}_4$: 748.6; found: 748.1.

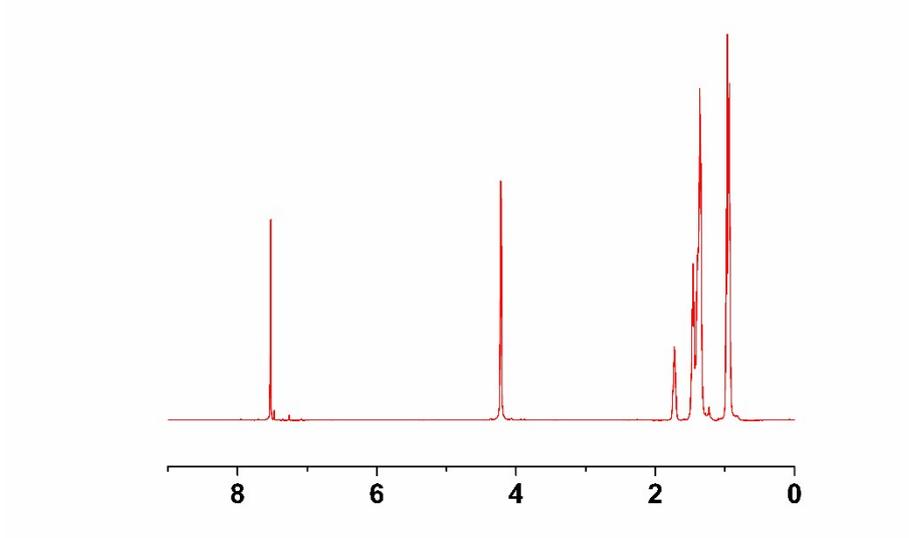


Fig. S11 ^1H NMR spectrum for compounds **M3**

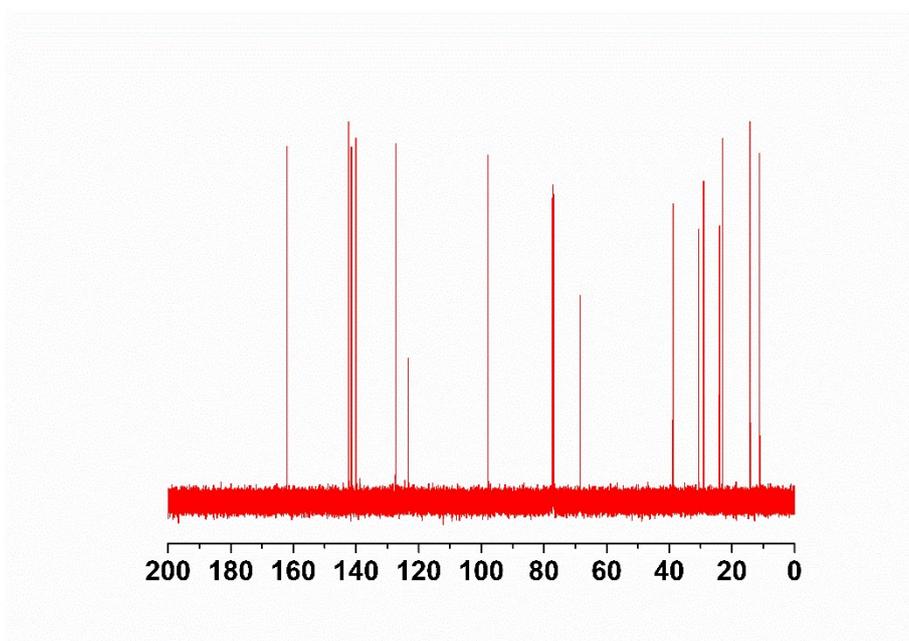


Fig. S12 ^{13}C NMR spectrum for compounds **M3**

PTT-Ni A two-neck round-bottomed flask was heated under reduced pressure and then cooled to room temperature under an N₂ atmosphere. **M** (136 mg, 0.3 mmol) was placed in the flask. Dry THF (1 mL) was added into the flask *via* a syringe, and the mixture was stirred at 0 °C. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.15 mL, 0.3 mmol) *via* a syringe, and the mixture was stirred at 0 °C for 1 h, then the flask was moved to an Argon glove box. Ni(dppp)Cl₂ (3.5 mg, 0.0064 mmol, 2.1 mol %) in THF (0.5 mL) was added to the mixture at room temperature, and then the mixture was stirred at room temperature for 12 h. 5M hydrochloric acid was added and the mixture was extracted with CHCl₃. The organic layer was concentrated under reduced pressure. To the residue was added MeOH. The precipitate was washed well with MeOH and collected as the target polymer **PTT-Ni** [Mn: 3687, polydispersity (PDI): 1.21] as a dark blue solid (73 mg, 83%). ¹H NMR (500 MHz, CDCl₃ δ/ppm) 8.17-7.41 (br, 1H), 4.29 (br, 2H), 1.67-0.90 (br, 15H). FT-IR: 1436 nm, 1462 nm (C-C Stretching vibration). Elem. Anal. Calcd. for (C₁₅H₁₈O₂S₂)_n (%): C, 60.78; H, 6.80; S, 21.63. Found (%): C, 58.22; H, 5.46; S, 21.49, Br, 0.0.

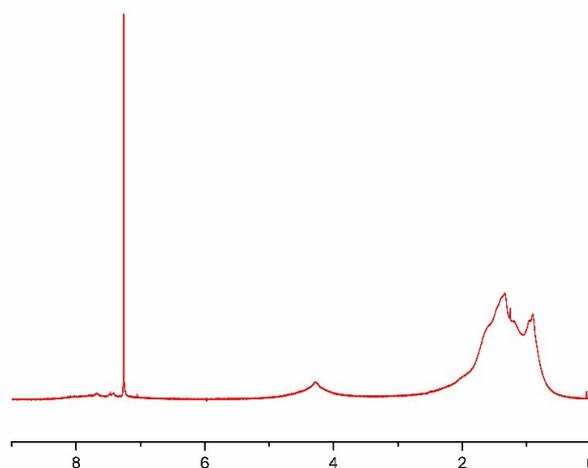


Fig. S13 ¹H NMR spectrum for compounds **PTT-Ni**

PTT-L This reaction was discovered by an accidental experiments, the monomer **M1** (1.2 g, 3.2 mmol) was sealed in a transparent glass vial under N₂ protected. The vial was shortly (around 10 min) exposed to the room light. The polymer **PTT-L** was then formed in the vial as dark blue solid. HBr was supposed to be a side product because when the vial was opened, a lot white gas escaped out. The blue solid was well washed with MeOH. The solid was then purified by washing with methanol, acetone, hexanes and chloroform in a Soxhlet extractor for 24 h in sequence. The dark blue polymer was dried from the chloroform fraction by rotary evaporation (Mn: 4475, PDI: 1.17). (0.91 g, 95%).

¹H NMR (500 MHz, CDCl₃ δ/ppm) 7.85 (br, 1H), 4.27 (br, 2H), 1.66-0.92 (br, 15H). FT-IR: 1456 nm (C-C Stretching vibration). Elem. Anal. Calcd. for (C₁₅H₁₈O₂S₂)_n (%): C, 60.78; H, 6.80; S, 21.63. Found (%): C, 61.27; H, 6.45; S, 19.89, Br, 0.0.

The reaction was able to be reproduced at smaller scale (100 mg, 0.27 mmol) under the same conditions as described above. The monomers which were protected from light were transferred into small vials under dark conditions, then the vials were closed with caps. The vials were then exposed to room light (normal lab conditions) for 10 min to one hour. Working up conditions were the same as above, molecular weight measurements from GPC showed almost no exposed-time dependence.

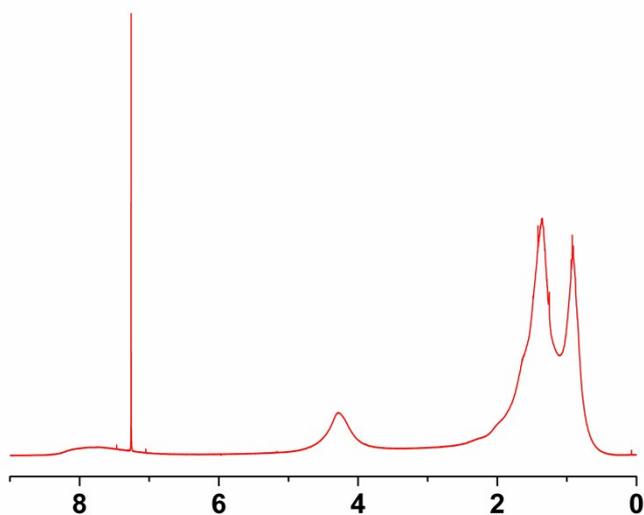
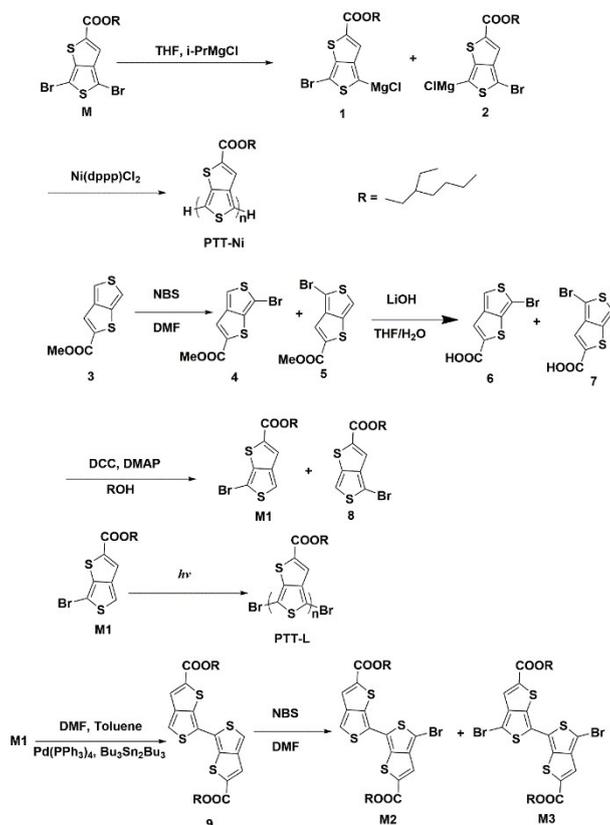


Fig. S14 ^1H NMR spectrum for compounds **PTT-L**



Scheme S1 Synthetic routes of monomers and polymers

Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker Ultraflex extreme MALDI-TOF mass spectrometer with dithranol as the ionization matrix. Fourier transform infrared (FT-IR) spectra were obtained on Thermo Nicolet iS50 Advanced FT-IR. GC-MS mass spectra were measured with Agilent SQ GC-MS (5977A single quad MS and 7890B GC. Ultraviolet-visible-Near IR (UV-vis-NIR) spectra of the polymers were measured on SHIMADZU UV-3600 spectrometer. The elemental analyses of the polymers were performed on an Elementar Vario EL III element analyzer for C, H, Br and S determination. Thermogravimetric analyses (TGA) were performed under nitrogen at a heating rate of 5 °C/min using a SHIMADZU TGA-50 analyzer. The average molecular weight and polydispersity index (PDI) of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with CHCl_3 as eluent and polystyrene as standard, there are two detectors for the instrument, refractive index detector and UV-Vis detector, in this study all the molecular weight are collected from the traces with the UV-vis detector. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode configuration and an electrochemistry workstation (AUTOLAB PGSTAT12). CV was conducted on an electrochemistry workstation with the polymer thin film on a Pt working electrode, Pt as the counter electrode as well, and Ag/AgCl as reference electrode in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate acetonitrile solution at a scan rate of 50 mV/s. Characterizations of polymers were performed by using NMR, GPC, TGA, UV-vis-

NIR and FTIR. The molecular weights (M_w) and polydispersity index (PDI) of the two homopolymers, were $M_w = 4.45$ kg/mol with PDI = 1.21 for **PTT-Ni** and $M_w = 5.23$ kg/mol with PDI = 1.17 for **PTT-L** determined by GPC (**Table 1**). The thermal properties of the polymers were determined by TGA under nitrogen atmosphere at a heating rate of 5 °C /min. The two copolymers (**PTT-Ni** and **PTT-L**) have good thermal stability with onset decomposition temperatures (Td) corresponding to 5% weight loss at **300 °C** and **303 °C**, respectively (**Fig. S15**).

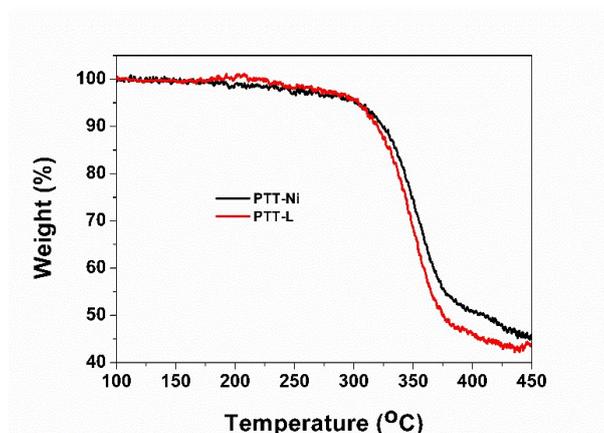


Fig. S15 TGA curves of polymers at scan rate of 5 °C/min

DFT calculations

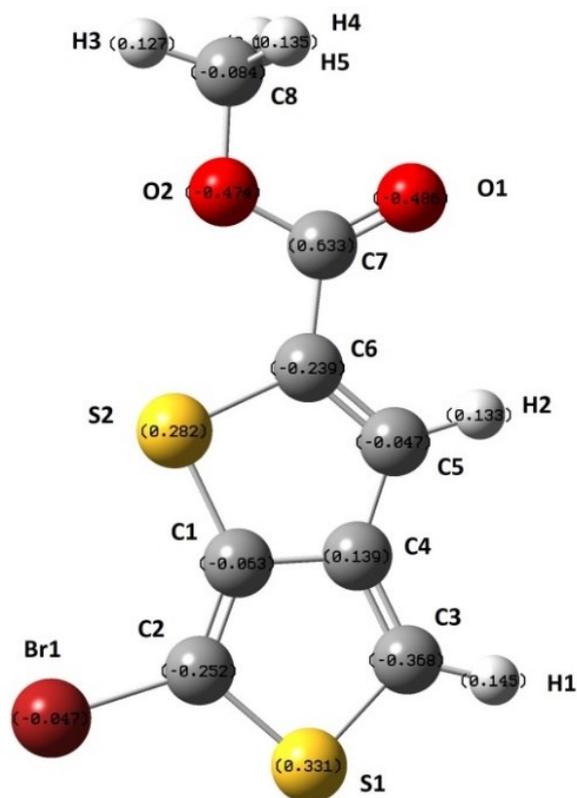


Fig. S16. Optimized geometry of monomer **M1** and calculated Mulliken charge distribution

Table S1. Calculated Mulliken charge on every atom of **M1**

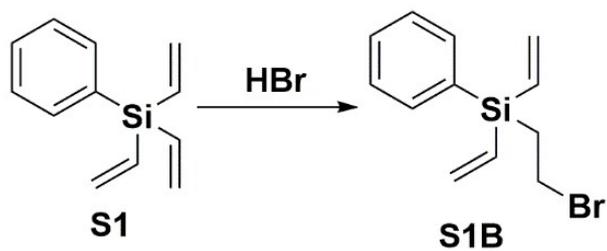
Atom	Calculated Mulliken charge (a.u.)
C1	-0.063
C2	-0.252
C3	-0.368
C4	-0.139
C5	-0.047
C6	-0.239
C7	-0.633
C8	-0.084

H1	0.145
H2	0.133
H3	0.127
H4	0.135
H5	0.135
O1	-0.486
O2	-0.474
Br1	-0.047
S1	0.331
S2	0.282

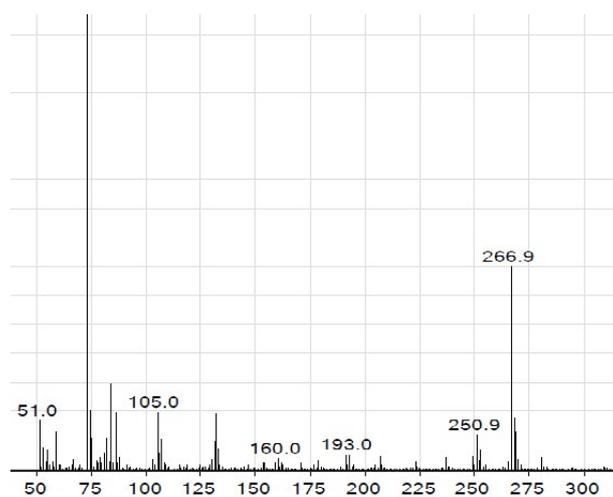
Side product investigation

As we have discussed in the main text, the polymerization will generate a side product HBr. It was initially proved just by observations, each time we opened the **PTT-L** reaction vial, we could feel a pressure and saw considerable amounts of white gas came out from the vial. To further prove the side product, the reaction below (scheme S2) was designed to investigate the exist of HBr. Compound **S1** is a known compound. S1 (10 mg) was dissolved in 1 mL dry hexane in a sealed vial under N₂ protected, 2 mL gas was from a **PTT-L** reaction vial transferred to this by using a syringe. The gas from the **PTT-L** reaction vial was supposed to be HBr contaminated, so an additional reaction was expected as below. After 7 days, GC-Mass was used to investigate the product. A product showed the spectrum as **Fig. S17**. The peak 266.9 can be assigned to the monobrominated product **S1B**. GC-MS (C₁₂H₁₅BrSi) m/z: calcd

for 267.2; found: 266.9.



Scheme S2 A reaction of the HBr investigation



Count vs. mass-to-charge(m/z)

Fig. S17 GC-Mass spectrum of **S1B**

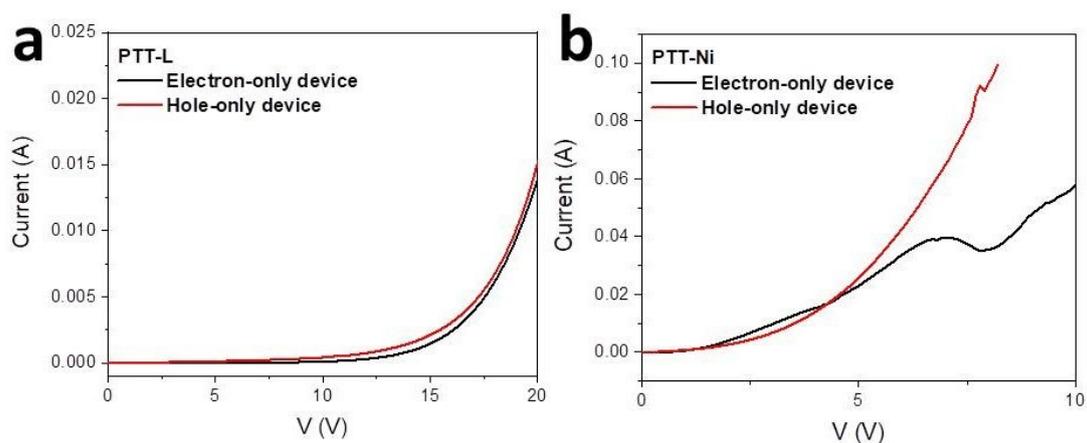


Fig. S18. I-V curves of hole-only and electron-only devices for a) **PTT-L** and b) **PTT-Ni** polymers.

Morphology investigation

Polymer samples for GIWAXS measurements were spin-coated from chlorobenzene solutions onto a polished silicon wafer coated with PEDOT:PSS. The films were annealed at 120 °C in glovebox for 30 min. The GIWAXS measurements were performed at 8ID-E beamline of Advanced Photon Source, Argonne National Laboratory with a radiation wavelength 1.1354 Å and beam incident angle 0.13°.

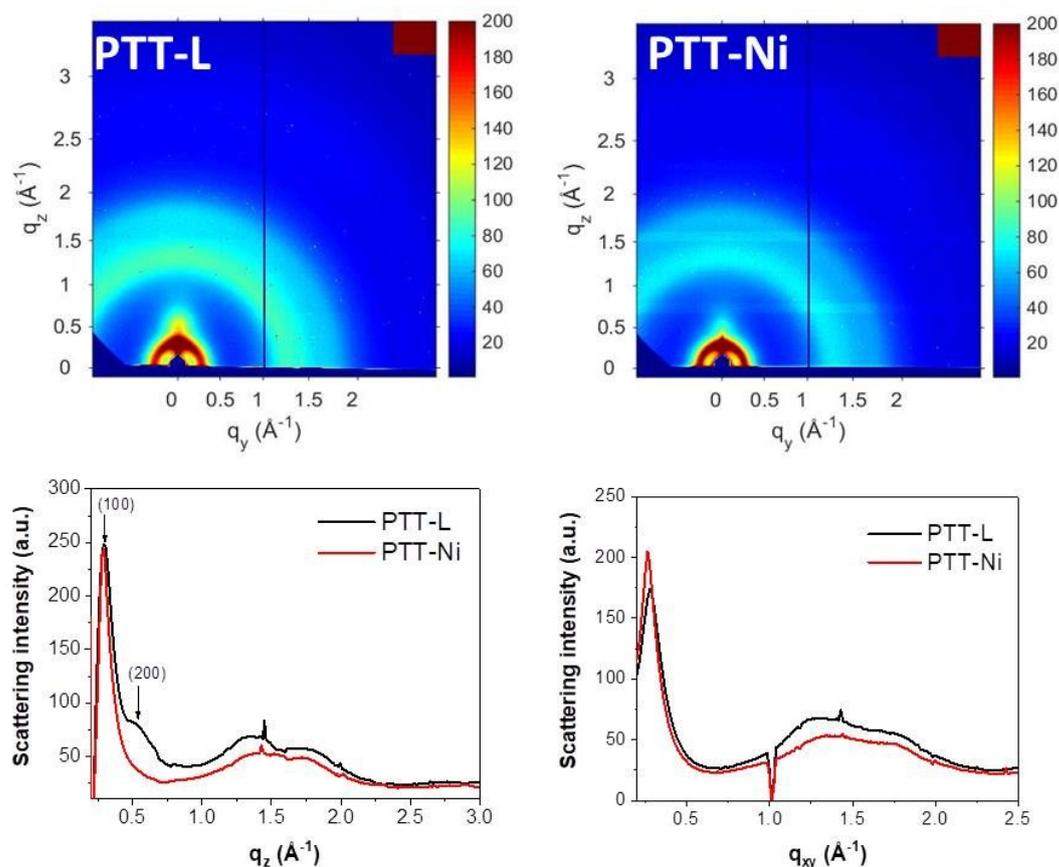


Fig. S19 2D GIWAXS scattering patterns of PTT-L and PTT-Ni films (top row) and 1D-linecuts in out-of-plane (q_z) direction and in-plane (q_{xy}) direction (bottom row)

Monomer absorption.

The monomers absorption spectrum is shown in **Fig. S20**. It was collected dilute solution (10^{-5} mol/L) in chloroform. It showed absorption in both UV and visible regions. The absorption spectrum is consistent with the experiment phenomenon that the monomer is not stable under visible light and even more unstable under UV-light. during the patterning experiment, we observed that the reaction speed increased significantly when we shined UV light on the monomer.

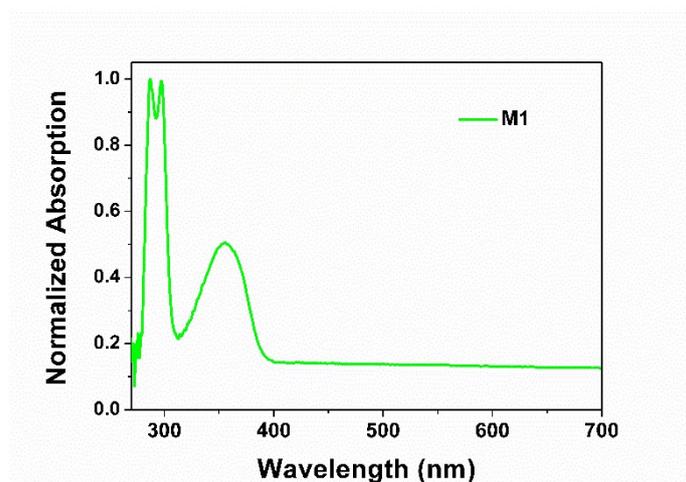


Fig. S20 Absorption spectrum of the monomer M1 in chloroform solution

References:

1. Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem.Soc.*, 2009, **131**, 7792.
2. A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169.