

Supplementary information

An isotropic three-dimensional organic semiconductor 2-(thiopyran-4-ylidene)-1,3-benzodithiole (TP-BT): asymmetric molecular design to suppress access resistance

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Instrumental procedures

Melting points were measured using a Büchi Melting Point M-565. NMR spectra were recorded on a JEOL JNM-ECZ-600R. The chemical shifts (δ) were referenced to chloroform (CHCl_3 ; $\delta = 7.24$). High-resolution mass spectra were measured using a JMS-T100 GCV.

Synthetic experimental procedures

All reactions were carried out under nitrogen atmosphere. 1,2-Benzenedithiol, 1,1'-thiocarbonyldiimidazole, *n*-butyllithium/hexane solution (*n*-BuLi/hexane), tetrahydro-4*H*-pyran-4-one, tetrahydro-4*H*-thiopyran-4-one and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were purchased and used without purification. Tetrahydrofuran (THF) was distilled over calcium hydride (CaH_2) under argon (Ar) atmosphere and further distilled over sodium benzophenone, again under Ar. Xylene and triethyl phosphite ($\text{P}(\text{OEt})_3$) were distilled over CaH_2 .

Detailed synthetic procedures

1,3-Benzodithiole-2-thione (**1**)

1,2-Benzenedithiol (500 mg, 3.52 mmol) was dissolved in 10 mL of THF. *n*-BuLi/hexane (1.59 M, 5.75 mL, 9.14 mmol) was added to the solution at -76°C . After the mixture was stirred for 15 min at -76°C , 1,1'-thiocarbonyldiimidazole (815 mg, 4.57 mmol) in THF (20 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight. After cooling in an ice bath, ammonium chloride (NH_4Cl) aq. (25 mL) was added. The mixture was filtered with celite and extracted with CH_2Cl_2 , and the extract was washed with brine. After the extracts were dried with anhydrous magnesium sulphate (MgSO_4), the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (with CH_2Cl_2 as the eluent) to afford **1** (588 mg, 3.19 mmol) as orange crystals at a 91% yield.

m. p. 166.7–168.1°C

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.57 (dd, *J* = 6.0, 3.0 Hz, 2H, ArH), 7.00 (dd, *J* = 6.0, 3.0 Hz, 2H, ArH)

¹³C NMR (600 MHz, CDCl₃): δ (ppm) = 212.0, 141.0, 127.3, 121.7

Diethyl 1,3-benzodithiol-2-yl phosphonate (2)

1 (369 mg, 2 mmol) was dissolved in 300 mL of xylene. The solution was heated at 90°C, and 50 mL of P(OEt)₃ was added. After the mixture had been stirred at 90°C for 1 h, it was refluxed overnight. The reaction mixture was then allowed to cool to 80°C, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (with ethyl acetate/hexane (3:1) as the eluent) to afford the crude product. The crude product was washed with hexane to afford **2** as colourless crystals (230 mg, 0.79 mmol) at a 40% yield.

m. p. 113.6–114.7°C

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.16 (dd, *J* = 5.4, 3.6 Hz, 2H, ArH), 7.00 (dd, *J* = 5.4, 3.6 Hz, 2H, ArH), 4.83 (d, *J*_{PCH} = 5.4 Hz, 1H, PCH), 4.14 (m, 4H, POCH₂), 1.19 (t, *J*_{HCCH} = 7.2 Hz, 6H, OCCH₃)

¹³C NMR (600 MHz, CDCl₃): δ (ppm) = 136.7, 125.9, 122.1, 64.3 (d), 44.2 (d), 16.3 (d)

2-(Tetrahydropyran-4-ylidene)-1,3-benzodithiole (3a)

2 (486 mg, 1.5 mmol) was dissolved in 40 mL of THF. *n*-BuLi/hexane (1.59 M, 1.04 mL, 1.65 mmol) was added to the solution at –76°C. After the mixture had been stirred for 15 min at –76°C, tetrahydro-4*H*-pyran-4-one (0.152 mL, 1.65 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. After cooling in an ice bath, NH₄Cl aq. (30 mL) was added. The mixture was extracted using CH₂Cl₂ and washed with brine. After the extracts were dried with anhydrous MgSO₄, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (with CH₂Cl₂ as the eluent) to afford **3a** as colourless crystals (342 mg, 1.45 mmol) at a 97% yield.

m. p. 148.0–150.3°C

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.15 (dd, *J* = 6.0, 3.0 Hz, 2H, ArH), 7.02 (dd, *J* = 6.0, 3.0 Hz, 2H, ArH), 3.67 (t, *J*_{HCCH} = 5.4 Hz, 4H, CCH₂O), 2.68 (t, *J*_{HCCH} = 5.4 Hz, 4H, CH₂CO)

¹³C NMR (600 MHz, CDCl₃): δ (ppm) = 135.9, 125.4, 122.5, 121.5, 120.2, 67.4, 33.5

MS (EI): *m/z* 236 [M]⁺

HRMS (EI): *m/z* calcd for C₈H₁₂OS₂: 236.0330 [M]⁺; found: 236.0335

2-(Tetrahydrothiopyran-4-ylidene)-1,3-benzodithiole (3b)

2 (581 mg, 2 mmol) was dissolved in 40 mL of THF. *n*-BuLi/hexane (1.59 M, 1.38 mL, 2.2 mmol) was added to the solution at –76°C. After the mixture had been stirred for 15 min at –76°C, tetrahydro-4*H*-thiopyran-4-one (256 mg, 2.2 mmol) in THF (15 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight. After cooling in an ice bath, NH₄Cl aq. (30 mL) was added. The mixture was extracted by CH₂Cl₂ and washed with brine. After the extracts were dried with anhydrous MgSO₄, the

solvent was removed in vacuo. The residue was purified by silica gel column chromatography (with CH₂Cl₂ as the eluent) to afford **3b** as colorless crystals (494 mg, 1.96 mmol) at a 98% yield.

m. p. 166.7–168.1°C

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.14 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.00 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 2.65 (t, *J*_{HCC} = 5.4 Hz, 4H, CCH₂S), 2.51 (t, *J*_{HCC} = 5.4 Hz, 4H, CH₂CS)

¹³C NMR (600 MHz, CDCl₃): δ (ppm) = 135.8, 125.4, 123.6, 122.3, 121.5, 35.3, 29.1

MS (EI): *m/z* 252 [M]⁺

HRMS (EI): *m/z* calcd for C₈H₁₂S₃: 252.0101 [M]⁺; found: 252.0101

2-(Pyran-4-ylidene)-1,3-benzodithiole (P-BT)

A solution of DDQ (284 mg, 1.25 mmol) in xylene (28 mL) was added dropwise for 30 min to a gently refluxing solution of **3a** (118 mg, 0.5 mmol) in xylene (40 mL) at 130°C. The reaction mixture was stirred for 30 min using reflux (150°C). After the reaction mixture was cooled, the precipitate was filtered, washed with CS₂ and removed. The solvent of the filtrate was removed in vacuo. The residue was purified by silica gel column chromatography (with CS₂ as the eluent) to afford P-BT as pale orange crystals (60 mg, 0.26 mmol) at a 52% yield. The P-BT was purified by recrystallisation from the CS₂/EtOH solution and vacuum sublimation.

m. p. 164.9°C (decomp.)

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.16 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.02 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 6.45 (broad, 2H, CCHO), 5.53 (d, *J*_{HCC} = 6.6 Hz, 2H, CHCO)

¹³C NMR (600 MHz, CDCl₃): δ (ppm) = 140.8, 136.3, 125.5, 121.6, 113.8, 108.8, 108.1

MS (EI) *m/z* 232 [M]⁺

HRMS (EI) *m/z* calcd for C₈H₈OS₂: 232.0017 [M]⁺; found: 232.0015

Anal. Calcd for C₈H₈OS₂: C, 62.04; H, 3.47; S, 27.60. Found: C, 61.82; H, 3.49; S, 27.49.

2-(Thiopyran-4-ylidene)-1,3-benzodithiole (TP-BT)

The TP-BT (151 mg) was obtained (0.61 mmol, 61%) as orange crystals by a similar method as for the synthesis of P-BT. It was purified by recrystallisation from the CS₂/EtOH solution and vacuum sublimation.

m. p. 200.7°C (decomp.)

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.19 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.00 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 6.15 (d, *J*_{HCC} = 10.8 Hz, 2H, CHCS), 6.02 (broad, 2H, CCHS)

¹³C NMR (600 MHz, CDCl₃, 40°C): δ (ppm) = 136.2, 125.6, 123.8, 121.6, 118.3, 116.9, 114.6

MS (EI): *m/z* 248 [M]⁺

HRMS (EI): *m/z* calcd for C₈H₈S₃: 247.9788 [M]⁺; found: 247.9783

Anal. Calcd for C₈H₈S₃: C, 58.03; H, 3.25; S, 38.72. Found: C, 57.89; H, 3.24; S, 38.72.

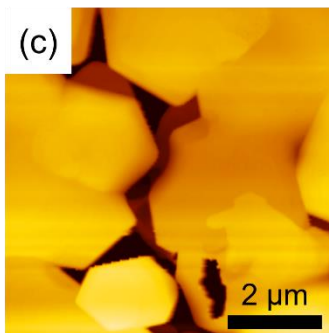
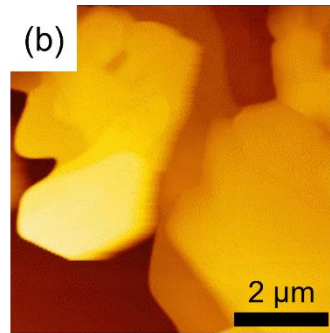
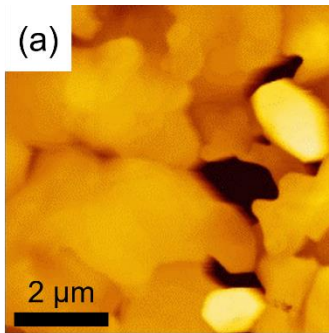


Fig. S1 AFM images of P-BT films with different thicknesses on substrates: (a) 140, (b) 290 and (c) 400 nm.

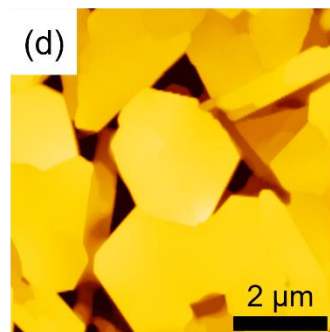
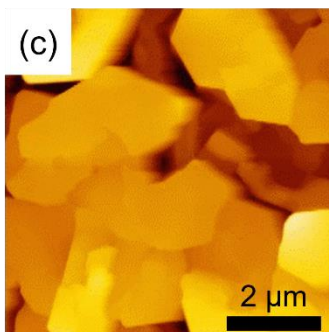
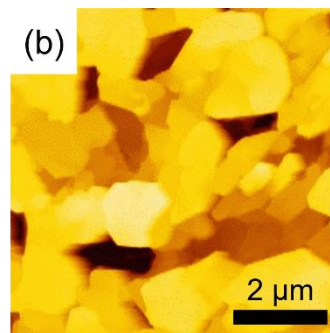
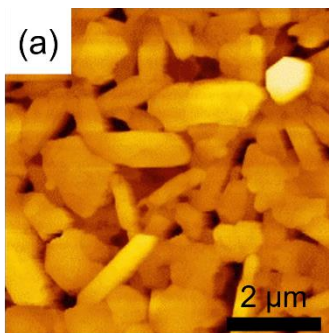


Fig. S2 AFM images of TP-BT films with different thicknesses on substrates: (a) 145, (b) 245, (c) 330 and (d) 370 nm.

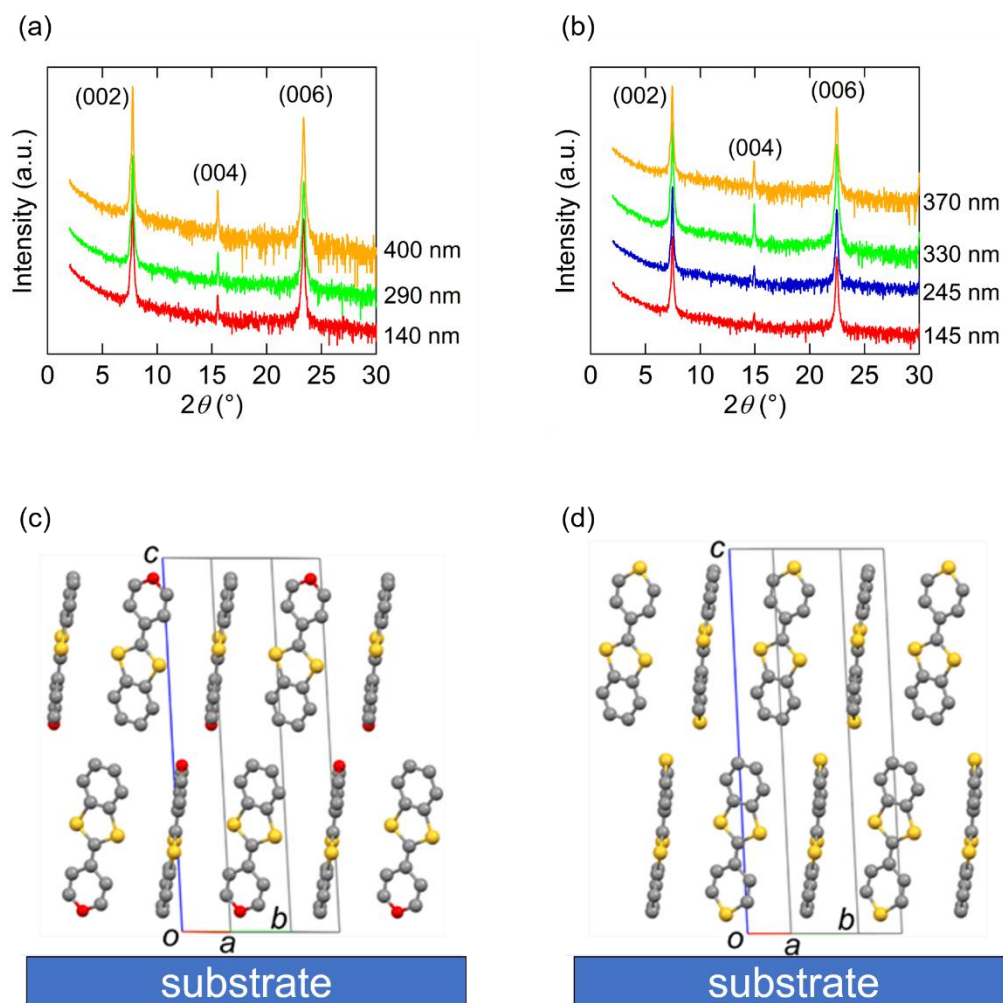


Fig. S3 XRD patterns of (a) P-BT and (b) TP-BT for each film thickness and molecular arrangement on substrates of (c) P-BT and (d) TP-BT.

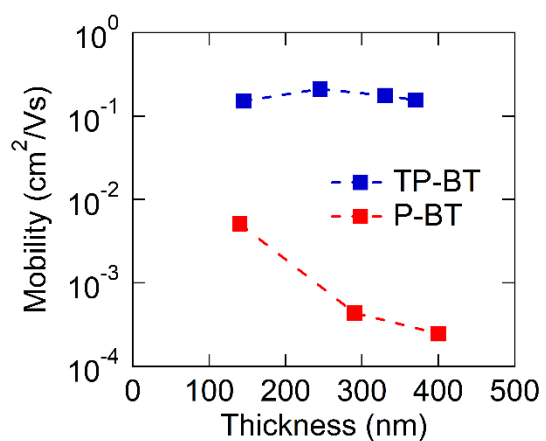


Fig. S4 Film thickness dependence of OTFT mobility.

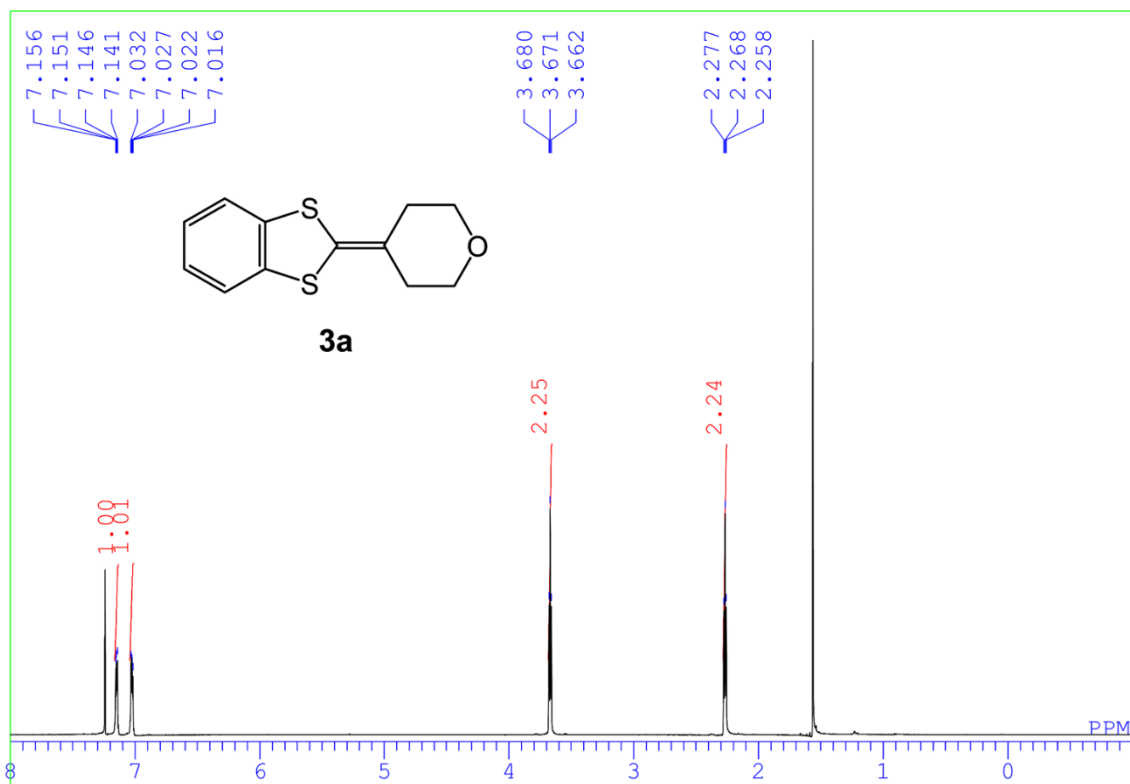


Fig. S5 ¹H NMR spectrum of **3a**.

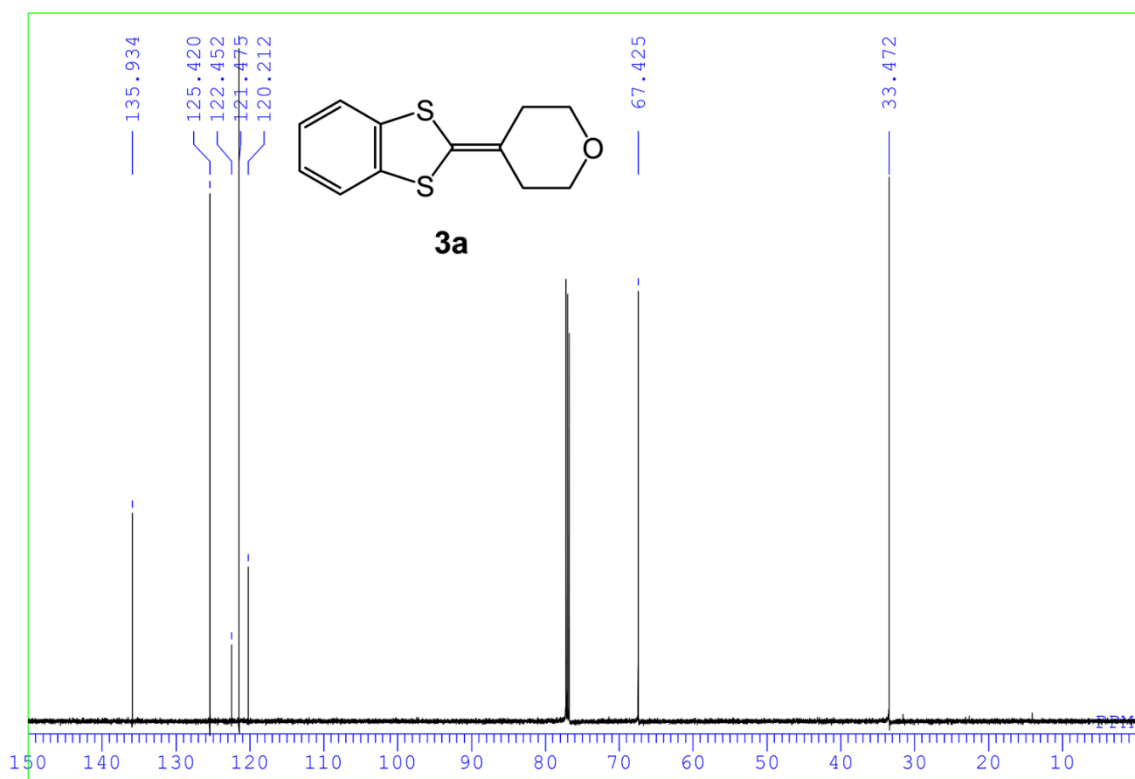


Fig. S6 ¹³C NMR spectrum of **3a**.

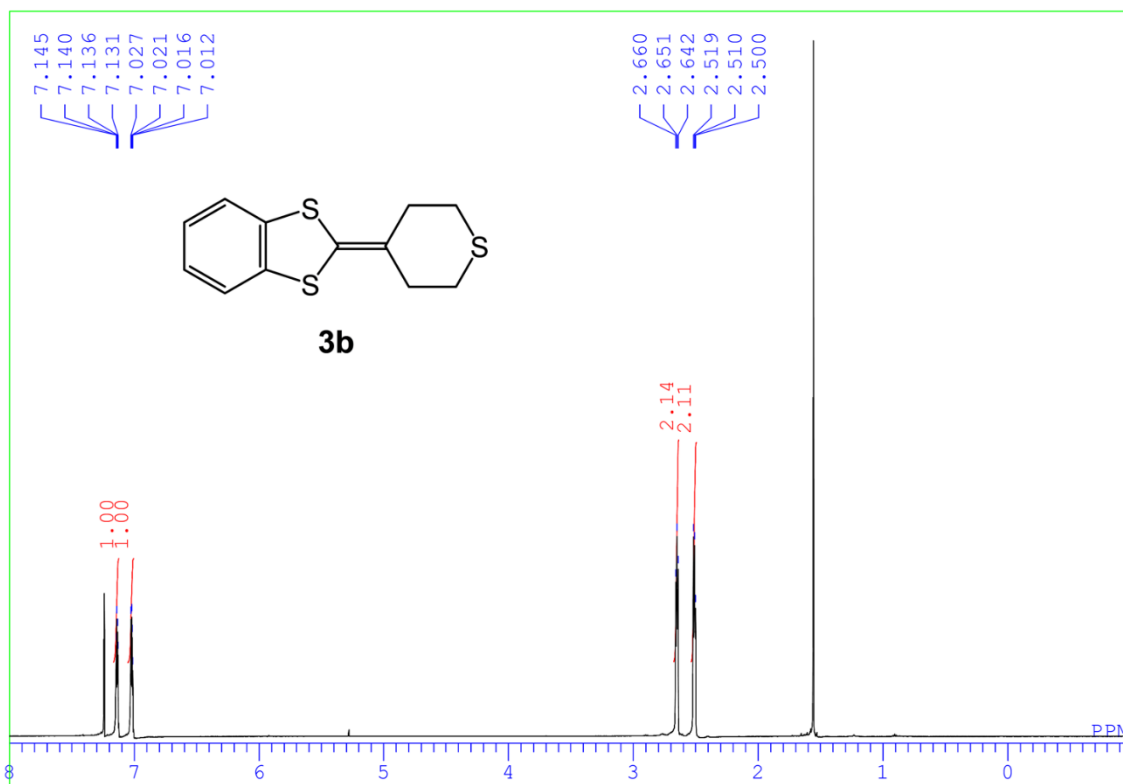


Fig. S7 ¹H NMR spectrum of **3b**.

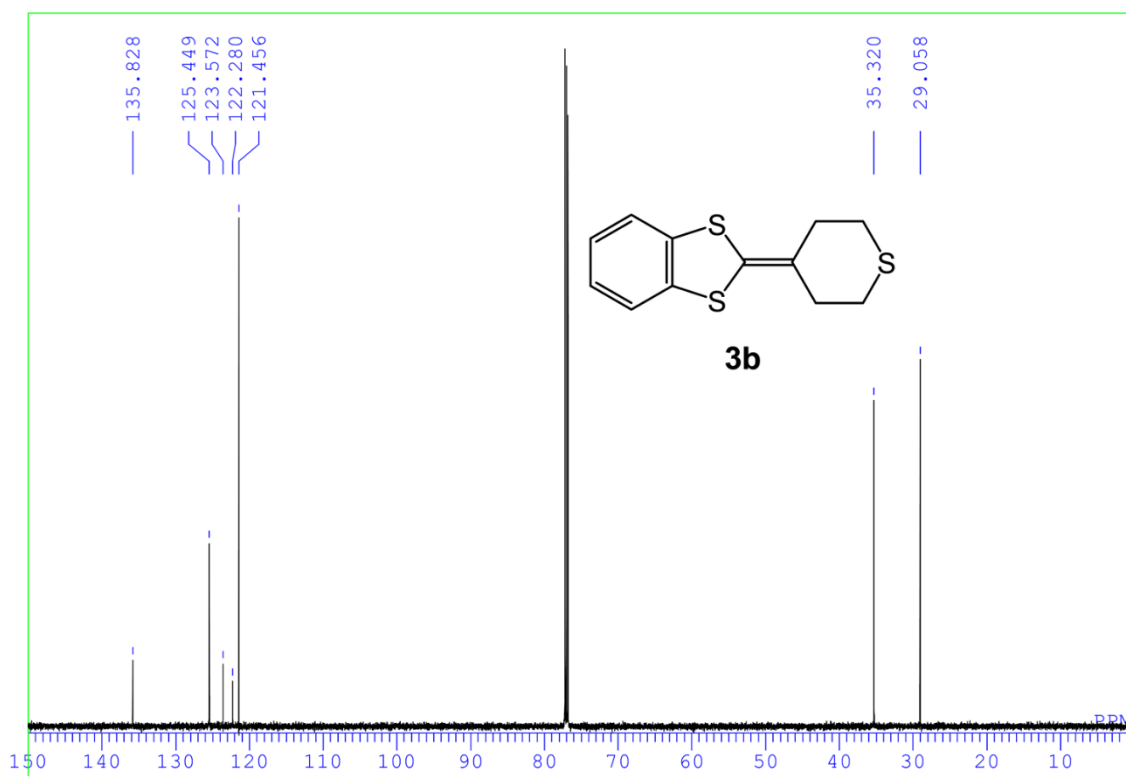


Fig. S8 ¹³C NMR spectrum of **3b**.

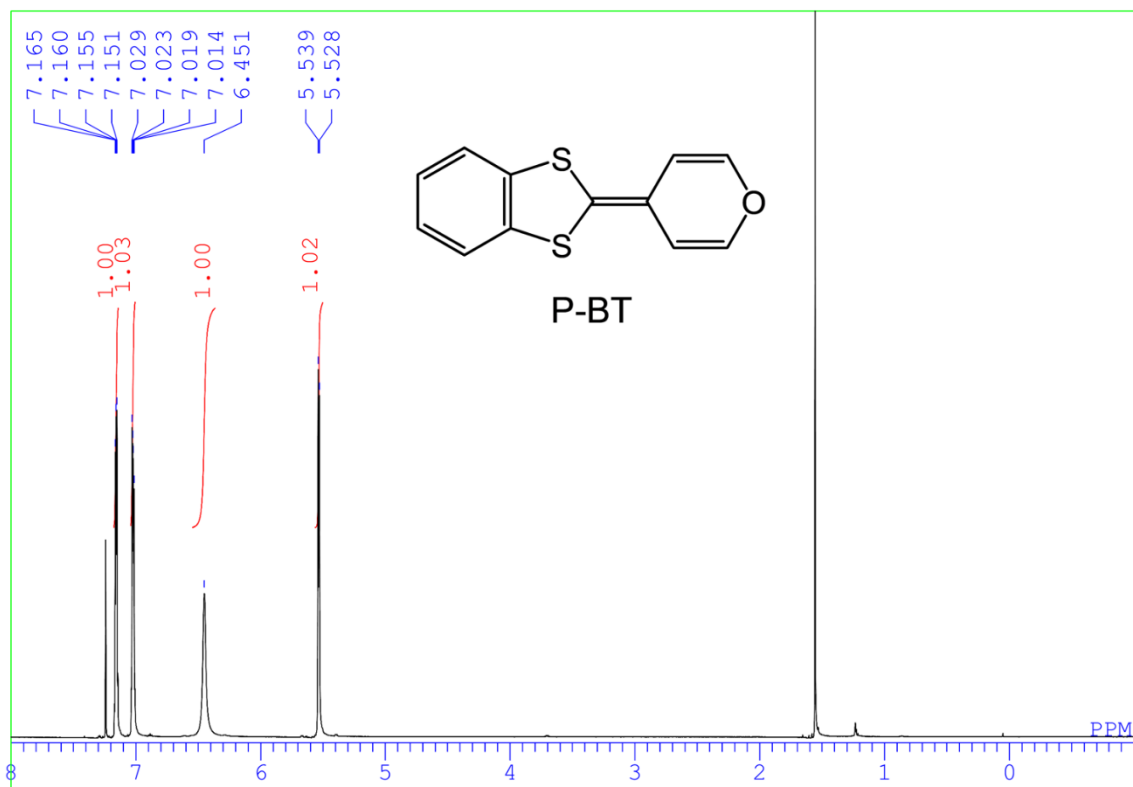


Fig. S9 ¹H NMR spectrum of P-BT.

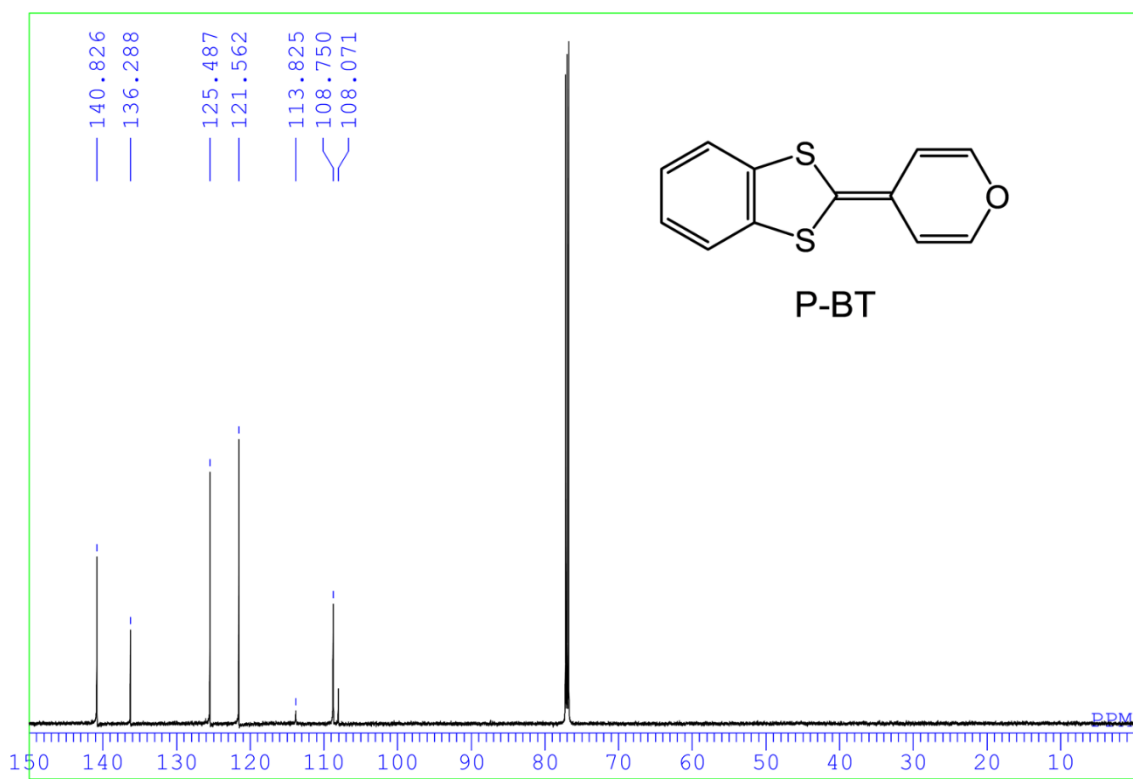


Fig. S10 ¹³C NMR spectrum of P-BT.

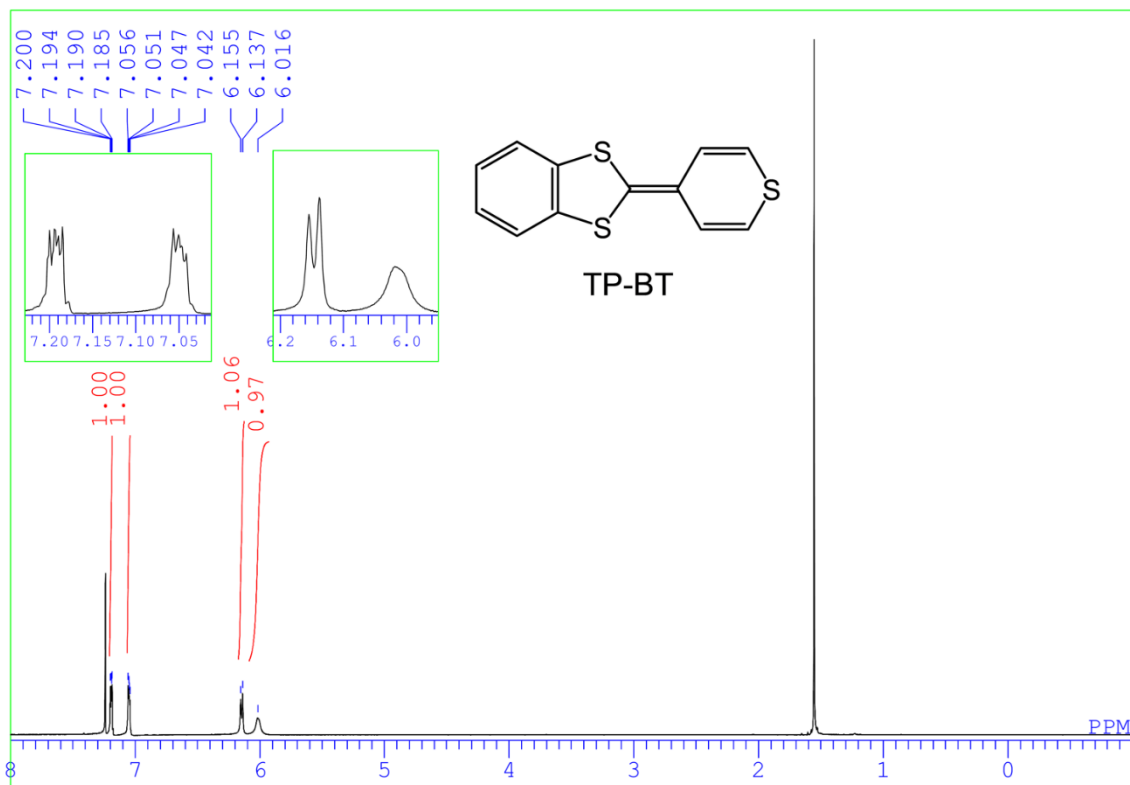


Fig. S11 ^1H NMR spectrum of TP-BT.

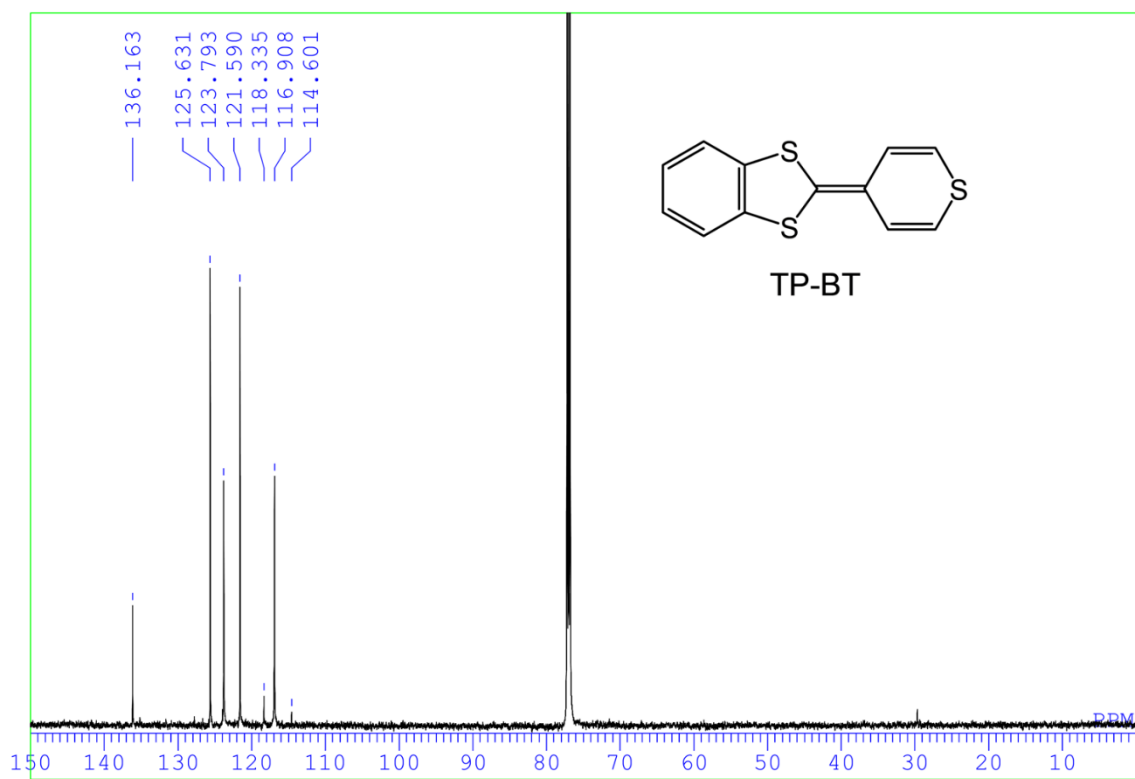


Fig. S12 ^{13}C NMR spectrum of TP-BT.