Supporting Information for

Synthesis and Properties of the anti and syn Isomers of Dibenzothieno[b,d]pyrrole

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1. Synthesis

General: Chemicals were purchased from Aldrich, Alfa Aesar and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Diethyl ether and o-DCB were dried and distillated immediately prior to use. 2,2’-Bibenzo[h]thiophene S1 (2), 3-bromobenzo[h]thiophene S2 (4) and 3,3’-bibeno[h]thiophene S3 (5) was synthesized according to the literatures. Melting points were measured with a WRR melting point apparatus. 1H-NMR (400
MHz) and $^{13}$C-NMR (75 and 100 MHz) spectra were obtained on a Bruker DMX-400 and DMX-300 NMR Spectrometer using tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) and EI MS were both recorded on Micromass GCT-MS spectrometer. FT-IR spectra were determined using a Perkin-Elmer Tensor 27 spectrometer. Elemental analyses were performed on a Carlo Erba model 1160 elemental analyzer.

2,2'-Bibeno[b]thiophene$^{31}$ (2)

To a stirred solution of benzo[b]thiophene (4.15 g, 31 mmol) in 170 ml of anhydrous diethyl ether at room temperature was added dropwise a solution of n-BuLi (15.4 ml, 38.5 mmol) under argon atmosphere during 20 minutes. The reaction mixture was heated at reflux with stirring under an inert gas atmosphere for 6 h and then allowed to cool to room temperature. Anhydrous copper (II) chloride (4.16 g, 31 mmol) was then added in four portions and the mixture was again heated under reflux for 4 h. After being allowed to cool to room temperature, the mixture was left to stand for 1h. The dirty brown-green precipitate was filtered off, and the organic layer was washed with dilute HCl solution and water. The precipitate was washed several times with THF and the filtrate combined with the ether phase. The combined organic phases were dried with anhydrous MgSO$_4$, concentrated, and the residue was purified by recrystallization from toluene to get a light yellow solid 3.01 g (73%) of 2: $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.82 (dd, $J = 17.20$ Hz, $J = 7.20$ Hz, 4H), 7.51 (s, 2H), 7.38 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 140.4, 139.6, 137.4, 125.1, 124.9, 123.9, 122.3, 121.6; EI-MS m/z (%) 266 (M+, 100%).

3-Nitro-2-(benzothiophen-2-yl)benzothiophene (3).

To a solution of compound 2 (1.26 g, 4.7 mmol) in glacial AcOH (150 mL) at 60 °C was added slowly a mixture of fuming HNO$_3$ (100%, 0.4 mL) and glacial AcOH (20 mL). On heating the reaction mixture for 30 min at 60 °C, the initially formed precipitate redissolved. The solution was cooled down and poured into H$_2$O, and then the yellow precipitate was formed rapidly and collected by filtration. The obtained
solid was washed with water and dried in vacuo to get a yellow solid (1.42 g, 97%): mp 133–135 °C; $^1$HNMR (400 MHz, Acetone-d$_6$) δ 8.27 (d, $J = 8.36$ Hz, 1H), 8.15 (d, $J = 7.96$ Hz, 1H), 8.07 (m, 3H), 7.72 (m, 2H), 7.52 (m, 2H); $^{13}$CNMR (75 MHz, CDCl$_3$) δ 128.3, 127.3, 127.1, 126.5, 125.4, 125.1, 124.1, 122.5, 122.3; EI-MS m/z (%) 311 (M$^+$, 100%); HRMS m/z Calcd for C$_{16}$H$_9$NS$_2$: 311.0075, Found: 311.0073; Anal. Calcd for C$_{16}$H$_9$NO$_2$S$_2$: C, 61.72; H, 2.91; N, 4.50. Found: C, 61.60; H, 3.03; N, 4.42.

3-bromobenzob[b]thiophene$^{S2}$ (4)

NBS (4.48 g, 25 mmol) was added in small portions under darkness to a solution of benzo[b]thiophene (3.38 g, 25 mmol) in 100 mL of CHCl$_3$/glacial AcOH (1:1) at room temperature. The reaction mixture was stirred at room temperature for another 10 hours before being poured into water. After extraction with methylene chloride, the organic phase was separated, dried over anhydrous MgSO$_4$, and concentrated. The residue was purified by column chromatography (silica gel, eluent: petroleum) to get a colorless liquid 4.35 g (82%) of 4: $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 8.04 (d, $J = 8.09$ Hz, 1H), 7.84 (m, 2H), 7.57 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 139.0, 137.9, 125.7, 125.4, 123.9, 123.5, 123.1, 108.1; EI-MS m/z (%) 212 (M$^+$, 100%).

3,3'-bibenzob[b]thiophene$^{S3}$ (5)

2.5 M n-BuLi (8.8 ml, 22.0 mmol) was added dropwise to a solution of 4 (3.78 g, 17.7 mmol) in anhydrous diethyl ether (150 ml) at −78 °C under nitrogen with stirring. After stirring for 1 h at −78 °C, anhydrous copper (II) chloride (2.38 g, 17.7 mmol) was added in three portions. The reaction mixture was then warmed to room temperature and stirred overnight. The dirty deep gray precipitate was filtered off and washed with diethyl ether three times. The obtained solution was washed with dilute HCl solution and water, and then dried with anhydrous MgSO$_4$, concentrated. The residue was purified by column chromatography (silica gel, eluent: petroleum) to get a light yellow solid 1.60 g (68%) of 5: $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.96 (d, $J = 8.24$ Hz, 2H), 7.75 (d, $J = 7.16$ Hz, 2H), 7.55 (s, 2H), 7.41 (m, 4H); $^{13}$C NMR (75
MHz, CDCl₃, ppm) δ140.4, 138.8, 131.6, 124.9, 124.8, 124.5, 123.4, 123.0; EI-MS m/z (%) 266 (M⁺, 100%).

2-Nitro-3-(benzothiophen-3-yl)benzothiophene (6).
This compound was prepared from 5 according to the procedure for 3. The reaction solution was poured into H₂O and extracted with CH₂Cl₂. The combined organic layers were washed with water, dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, eluent: petroleum) to get a yellow solid in 95% yield: mp 146–148 °C; ¹H NMR (400 MHz, Acetone-d₆) δ 8.20 (d, J = 8.17 Hz, 1H), 8.13 (d, J = 7.38 Hz, 1H), 7.98 (s, 1H), 7.75 (t, J = 7.64 Hz, 1H), 7.62 (d, J = 8.08 Hz, 1H), 7.54 (t, J = 7.22 Hz, 1H), 7.47 (t, J = 8.52 Hz, 2H), 7.38 (t, J = 7.04 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 130.0, 127.5, 127.2, 126.4, 125.3, 125.1, 123.3, 123.1, 122.9; EI-MS m/z (%) 311 (M⁺, 100%); HRMS m/z Calcd for C₁₆H₉NS₂: 311.0075, Found: 311.0072; Anal. Calcd for C₁₆H₉NO₂S₂: C, 61.72; H, 2.91; N, 4.50. Found: C, 61.74; H, 3.05; N, 4.51.

Dibenzothieno[3,2-b:2'3'-d]pyrrole (anti-1).
A mixture of compound 3 (280 mg, 0.90 mmol), PPh₃ (590 mg, 2.25 mmol) and o-DCB (7 mL) was heated under reflux in an inert atmosphere. After 20 h, the reaction was cooled to R. T. The solvent was distilled off and the crude product was purified by column chromatography (silica gel, eluent: petroleum/CH₂Cl₂ = 1:1) to provide 196 mg of the title compound as a light yellow solid (78%): mp 264–268 °C; IR (KBr) 3413, 3049, 1592, 1503, 1463, 1435, 1396, 1292, 1098, 1054, 1018, 851, 746, 720, 441 cm⁻¹; ¹H NMR (400 MHz, Acetone-d₆) δ 11.94 (s, 1H), 7.98 (dd, J = 19.04 Hz, J = 7.88 Hz, 4H), 7.43 (t, J = 7.54 Hz, 2H), 7.32 (t, J = 7.60 Hz, 2H); ¹³C NMR (75 MHz, Acetone-d₆) δ 143.3, 139.5, 129.6, 126.5, 126.1, 125.6, 120.9, 116.7; EI-MS m/z (%) 279 (M⁺, 100%); HRMS m/z Calcd for C₁₆H₉NS₂: 279.0176, Found: 279.0179. Anal. Calcd for C₁₆H₉NS₂: C, 68.79; H, 3.25; N, 5.01. Found: C, 68.78; H, 3.29; N, 4.96.

Dibenzothieno[2,3-b:3',2'-d]pyrrole (syn-1).
This compound was prepared from 6 according to the procedure for \textit{anti-1}. The crude product was purified by column chromatography (silica gel, eluent: petroleum/CH₂Cl₂ = 1:1) to get the title compound as a light yellow solid (51%): mp 179–181 °C; IR (KBr) 3061, 2920, 2235, 1577, 1533, 1473, 1433, 1366, 1311, 1260, 1183, 1135, 1097, 1068, 1032, 995, 930, 842, 753, 728, 679, 605, 460, 419 cm⁻¹; \textit{¹}HNMR (400 MHz, CDCl₃) δ 7.81 (d, $J = 8.04$ Hz, 2H), 7.57 (m, 1H), 7.50 (m, 2H), 7.40 (m, 3H), 5.63 (m, 1H); \textit{¹³}CNMR (75 MHz, Acetone-d₆) δ 143.3, 139.5, 129.6, 126.5, 126.1, 125.5, 120.9, 116.7, 31.2; EI-MS $m/z$ (%) 278 ((M⁺−1), 100%), 279 (M⁺, 75%); HRMS $m/z$ Calcd for C₁₆H₉NS₂: 279.0176, Found: 279.0172. Anal. Calcd for C₁₆H₉NS₂: C, 68.79; H, 3.25; N, 5.01. Found: C, 68.56; H, 3.21; N, 5.12.

\textit{N}-Hexyldibenzothieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (7).

To a solution of compound \textit{anti-1} (157 mg, 0.56 mmol) in 50 mL of DMF was added KOH (158 mg, 2.82 mmol). After the solution was stirred at 50 °C for 2 h under nitrogen, 1-bromohexane (0.1 ml, 0.71 mmol) was added. The mixture was stirred at 50 °C for 24 h and then quenched with water. The aqueous layer was extracted three times with diethyl ether. The organic fractions were dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: petroleum) to get a light yellow solid 128 mg (63%) of 7: mp 134–136 °C; \textit{¹}HNMR (400 MHz, Acetone-d₆) δ 8.15 (d, $J = 8.04$ Hz, 2H), 7.97 (d, $J = 8.04$ Hz, 2H), 7.48 (t, $J = 7.60$ Hz, 2H), 7.35 (t, $J = 7.62$ Hz, 2H), 4.98 (t, $J = 7.42$ Hz, 2H), 2.13 (m, 2H), 1.61 (m, 2H), 1.40 (m, 4H), 0.83 (t, $J = 7.23$ Hz, 3H); \textit{¹³}CNMR (100 MHz, CDCl₃) δ 142.0, 137.6, 127.6, 124.6, 124.5, 123.3, 118.9, 114.7, 47.6, 31.7, 31.3, 26.7, 22.7, 14.1; EI-MS $m/z$ (%) 363 (M⁺, 100%); Anal. Calcd for C₁₆H₆NS₂: C, 72.68; H, 5.82; N, 3.85. Found: C, 72.53; H, 5.90; N, 4.02.
Figure S1. High-resolution mass spectra of anti-1 (top) and syn-1 (bottom).

Seen from the conjugated degree of the whole molecule, the conjugated degree of anti-1 is larger than that of syn-1. anti-1 molecule has stable electronic structure, but syn-1 molecule is not the most stable structure. To extend the conjugated degree of syn-1, it forms the syn-1’ structure. Seen from Figure S1, we found the difference of their mass spectra. anti-1 forms the strongest molecular ion peak, while syn-1 forms the strongest fractional ion peak when a hydrogen atom leaves. This indicates the syn-1’ structure, because only the hydrogen at the carbon near to the nitrogen is easier to leave in mass spectrum. syn-1’ without one H atom forms a stable electronic structure, while the syn-1 structure could not obtain the more stable structure by this way. For anti-1, the structure with the H at N atom is most stable and has the largest conjugation, so other forms are all not reasonable.

We simulated the ¹H-NMR spectrum of syn-1’ structure by ChemDraw (Figure S2), and obviously, we can classify four groups of aromatic H atoms (δ = 7.02(1H),
7.04(1H); [δ = 7.18 (2H)]; [δ = 7.26 (1H)]; [δ = 7.32(1H), 7.33(2H)], which is consistent with our reported result (four groups of aromatic H atoms). Therefore, it can further confirm that the speculated syn-1’ structure is reasonable.

**Figure S2.** The simulated ^1^H-NMR spectrum of syn-1’ structure by ChemDraw.

**Figure S3.** Infrared spectra of anti-1 and syn-1.

2. **Single-crystal X-ray analysis of anti-1 and 7**

The measurement was made on a Rigaku MM-007 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and
SHELXS-97, and refined by using SHELXL-97. Hydrogen atoms were located at the calculated positions. Absorption correction was applied using semi-empirical from equivalents.

**anti-1**, $\text{C}_{16}\text{H}_{9}\text{NS}_{2}$, $M = 279.36$, crystal dimension $0.39 \times 0.36 \times 0.15$ mm, monoclinic, space group $P2_1/n$, $a = 9.916(2)$, $b = 10.619(2)$, $c = 23.425(5)$ Å, $\alpha = 90.00$, $\beta = 96.04(3)$, $\gamma = 90.00^\circ$, $V = 2453.0(8)$ Å$^3$, $Z = 8$, $D_c = 1.513$ g·cm$^{-3}$, $T = 173(2)$ K, $\mu = 0.415$ mm$^{-1}$, $\theta$ range $2.11$–$25.00^\circ$, 7940 reflection collected, 4328 of which were independent ($R_{int} = 0.0199$), GOF = 1.168, 343 parameters, $R_1 = 0.0623$, $wR_2 = 0.0993$ for all reflections. CCDC 697266.

**7**, $\text{C}_{22}\text{H}_{21}\text{NS}_{2}$, $M = 363.52$, crystal dimension $0.14 \times 0.12 \times 0.04$ mm, monoclinic, space group $P2_1/c$, $a = 11.582(2)$, $b = 8.1596(16)$, $c = 19.770(4)$ Å, $\alpha = 90.00$, $\beta = 106.89(3)$, $\gamma = 90.00^\circ$, $V = 1787.7(6)$ Å$^3$, $Z = 4$, $D_c = 1.351$ g·cm$^{-3}$, $T = 113(2)$ K, $\mu = 0.302$ mm$^{-1}$, $\theta$ range $1.84$–$27.87^\circ$, 12637 reflection collected, 4248 of which were independent ($R_{int} = 0.0717$), GOF = 1.033, 227 parameters, $R_1 = 0.0567$, $wR_2 = 0.1106$ for all reflections. CCDC 697267.

**Figure S4.** The crystal structure of **anti-1**, (a,c) hydrogen atoms removed for clarity.
3. Physicochemical properties

Methods: TGA measurements were carried out on a TA SDT 2960 instruments under a dry nitrogen flow, heating from room temperature (R. T.) to 500 °C, with a heating rate of 10 °C/min. Electronic absorption spectra were measured on a Jasco V570 UV-vis spectrophotometer. Emission spectra were recorded on Hitachi F-4500 fluorescence spectrometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled CHI660C instruments at R. T. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple ($E^{1/2} = +0.46$ V measured under identical conditions).

Figure S5. The crystal packing structure of 7, hydrogen atoms removed for clarity.

Figure S6. TGA scan of anti-1, syn-1 and 7.
Figure S7. Absorption (a) and fluorescence (b) spectra of anti-1, syn-1 and 7 in CH₂Cl₂.

Figure S8. Absorption (a) and fluorescence (b) spectra of anti-1, syn-1 and 7 for vapor deposited films on the quartz substrate.

Figure S9. Absorption spectra of anti-1 for drop coating films on the quartz substrate.
Figure S10. The picture of **anti-1**, **syn-1** and 7 for drop coating films from toluene solution (1 mg/mL) on the quartz substrate.

![Figure S10](image)

Figure S11. The photostability of **anti-1** thin film deposited on quartz.

![Figure S11](image)

Figure S12. Cyclic voltammograms of **anti-1**, **syn-1** and 7 (c = 10^{-3} M) in CH_{2}Cl_{2} containing Bu_{4}NPF_{6} (0.01 M) as supporting electrolyte under nitrogen at room temperature, with a scan rate of 100 mV/s.

4. X-ray Diffraction Studies

X-ray diffraction (XRD) measurements were carried out with a 2-kW Rigaku x-ray diffraction system. XRD patterns were obtained using bragg-Brentano Geometry.
(0–20) with Cu Kα radiation as an X-ray source in the reflection mode at 45 kV and 300 mA.

Figure S13. X-ray diffraction of thin films deposited on OTS-treated Si/SiO₂ substrate (film thickness: 50 nm).

5. AFM Studies

AFM measurements were made in air using a Digital Instruments Nanoscope III in contacting mode.

Figure S14. AFM images of thin films deposited on OTS-treated Si/SiO₂ substrate (film thickness: 50 nm): (a) anti-1, (b) syn-1 and (c) 7.

6. Device fabrications and evaluations

FET devices were fabricated with a top-contact configuration. A thin film of about 50 nm was vacuum deposited on octadecyltrichlorosilane (OTS) treated Si/SiO₂ substrate at room temperature. An n-type Si wafer with a SiO₂ layer of 500 nm and a capacitance of 7.5 nF cm⁻² was used as the gate, and gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask. The channel length (L) and width (W) were 50 μm and 3 mm, respectively. The FET measurements
were carried out at room temperature in air using a HP 4140B semiconductor parameter analyzer. The mobility of devices based on anti-1 was calculated in the saturation regime. The equation was listed as follow:

\[ I_{DS} = \frac{W}{2L}C_i\mu(V_{GS} - V_{th})^2 \]

Where \( \mu \) is the field-effect mobility, \( L \) and \( W \) are the channel length and width, respectively, \( C_i \) is the insulator capacitance per unit area, and \( V_{GS} \) and \( V_{th} \) is the gate voltage and threshold voltage, respectively.

**Figure S15.** FET characteristics of device based on anti-1 thin film deposited on OTS/SiO\(_2\)/Si substrate under ambient conditions. (a) Output curves at different gate voltages. (b) Transfer curve in the saturated regime at a constant source–drain voltage of \(-100 \, \text{V}\) (black squares) and the square root of the absolute value of the current as a function of the gate voltage (white squares).

**Figure S16.** Mobilities and on/off ratios for a FET device based on anti-1 tested (a) over a period of one month in air; (b) for 100 times.
7. References


8. $^1$H and $^{13}$C NMR spectra

$^1$H NMR spectrum of 3
$^{13}$C NMR spectrum of 3
$^1$H NMR spectrum of 6

![NMR Spectrum Diagram]

- DMSO: 2.0267, 8.1824, 8.1343, 8.11459, 7.98358, 7.74704, 7.72547, 7.6296, 7.60277, 7.55824, 7.5433, 7.47302, 7.45195, 7.39730, 7.38016
- CH$_2$Cl$_2$: 5.62933
- H$_2$O: 2.82817, 2.79408
- Acetone-d$_6$: 2.08556, 2.05593, 2.05016
$^{13}$C NMR spectrum of 6
$^1$H NMR spectrum of anti-1
$^{13}$C NMR spectrum of anti-1
$^{1}H$ NMR spectrum of \textit{syn-1}
$^{13}$C NMR spectrum of syn-1
\(^1\)H NMR spectrum of 7

[Diagram showing NMR spectrum with peaks labeled]
$^{13}$C NMR spectrum of 7

ppm

- 142.053
- 137.610
- 127.673
- 124.647
- 124.525
- 123.261
- 118.931
- 114.697

CDCl$_3$

- 77.487
- 77.372
- 77.160
- 76.852

- 47.643
- 31.706
- 31.281
- 26.681
- 22.661
- 14.111