

Supporting Information

Syntheses and Properties of 11-Ring-Fused Linear Thienoacenes

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1. Experiment and device fabrication

The energy level calculation method was used to determine the HOMO.

$$E_{HOMO} = -(E_{ox}^{onset} - Fc/Fc^+ + 4.8)$$

$$E_{LOMO} = E_g + E_{HOMO}$$

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on Bruker 400 M nuclear resonance spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, and m = multiplet. Flash column chromatography was performed using 200-300 mesh silica gel. To gain more insight into the frontier energy levels, density functional theory (DFT) calculations were performed on all the products using Gaussian 09 program with the 6-31G(d) basis set. The geometries of molecules at ground state were optimized with DFT at the m062x/6-31g(d) level using Gaussian program. In order to investigate the photophysical properties, the excited electronic structures of molecules were calculated at the PBE0/TZVP level with the time-dependent density functional theory (TD-DFT) method, and the excited energy and oscillator strength can also be obtained from the calculation result at the same time. The UV absorption spectroscopy were obtained by broaden the oscillator strength at corresponding excited energy using Multiwfn program.

OFET devices were fabricated in a BGBC configuration on Si/SiO₂ substrates with 50 nm thick gold electrodes. The SiO₂ dielectric layer was 300 nm thick. The source-drain electrodes were interdigitated with channel length varying from 2.5 to 40 μm and channel width varying from 0.1

to 1 mm. Substrates were cleaned softly with IPA and acetone, making sure that the prefabricated electrodes are not damaged. Then, OTMS treatment was performed on the substrates that were placed in an oven with OTMS at a temperature of 120 °C for 5 h. The glass crucibles were cleaned thoroughly in piranha solution (3:1 solution of sulfuric acid and hydrogen peroxide) to remove all organic residues and then washed with isopropyl alcohol and acetone. A chloroform solution of BBDTB-H (5 mg mL⁻¹) was then deposited by spin-coating at 3000 rpm for 60s on the OTMS-treated substrate to form organic semiconducting layers.

2. Synthesis, ¹H-NMR, ¹³C-NMR and MS spectra

The synthetic route of **DT-H** was reported in the literature.¹

Synthesis of compound 1. Under N₂ condition, **DT-H** (1.4 g, 2.19 mmol), dissolved in 120 mL dry THF and cooled to 0°C, dropped *n*-BuLi (1.6 mL, 1.6M) in the system slowly. The mixture was brought to room temperature and stirred for 2 h. Then cooled to -78°C and dropped TIPSCl (0.95mL). After stirring at room temperature overnight, the reaction was extracted with DCM (50 mL) three times and the organic layer was washed with brine several times, and dried over anhydrous MgSO₄. After the removal of solvent, the residue was purified by petroleum ether to get a yellow oil **1** (yield: 78%). ¹H NMR (400 MHz, CDCl₃, δ, ppm), δ 7.56 (d, J=5.2Hz, 1H), 7.49 (s, 1H), 7.38 (d, J=5.3Hz, 1H), 3.25-3.18 (m, 4H), 1.21-1.19 (d, J=7.4Hz, 18H) ppm. MALDI-TOF MS: calculated for C₄₇H₇₄S₄Si 794.4443, found 794.4402.

Synthesis of compound 2. Compound **1** (3.225 g, 0.004 mol) dissolved in 110 mL dry THF and kept the system under N₂ protection. Added NBS (1.084 g, 0.006 mol) at 0 °C, wrapped the flask with aluminum foil to avoid light, restored to room temperature slowly, and quenched by water after 12 h reaction. Extracted with DCM, washed with saturated sodium chloride solution, and

dried with anhydrous sodium sulfate. Used petroleum ether over the column. The product of this step is a yellow solid (yield: 90%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm), δ 7.48 (s, 1H), 7.38 (s, 1H), 3.23-3.19 (t, $J=7.4\text{Hz}$, 2H), 3.12-3.08 (t, $J=8.6\text{Hz}$, 2H), 1.21-1.18 (d, $J=7.4\text{Hz}$, 18H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 140.39, 139.15, 137.70, 135.02, 134.65, 133.52, 131.96, 130.84, 130.56, 127.39, 122.71, 113.88, 53.40, 31.95, 31.18, 31.00, 30.36, 30.18, 29.77, 29.74, 29.72, 29.70, 29.61, 29.49, 29.39, 22.71, 18.64, 14.12, 11.87. MALDI-TOF MS: calculated for $\text{C}_{47}\text{H}_{73}\text{BrS}_4\text{Si}$ 872.3548, found 872.3537.

Synthesis of compound 3. 2 (200 mg, 0.23 mmol) was dissolved in 30 mL anhydrous diethyl ether under N_2 protection. The system was stirred at $-78\text{ }^\circ\text{C}$ for 30 min and added LDA (0.13ml, 2M), stirred at $-78\text{ }^\circ\text{C}$ for 30 min, then increased the temperature to $0\text{ }^\circ\text{C}$, stirred at $0\text{ }^\circ\text{C}$ for 30 min, then cooled down to $-78\text{ }^\circ\text{C}$, added CuCl_2 (123 mg, 0.91 mmol). After adding, moved to room temperature and stirred overnight. The mixture was extracted with DCM (50 mL) three times. After the combination, the organic layer was washed with brine several times and dried over anhydrous MgSO_4 . After the removal of the solvent, the residue was purified by petroleum ether to get a yellow solid 3 (yield: 52%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm), δ 7.46 (s, 2H), 3.24-3.20 (t, $J=7.4\text{Hz}$, 4H), 3.18-3.14 (t, $J=7.4\text{Hz}$, 4H), 1.77-1.71 (m, 4H), 1.67-1.62 (m, 4H), 1.46-1.41 (m, 6H), 1.20-1.18 (d, $J=7.4\text{Hz}$, 36H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 140.36, 139.68, 138.41, 138.14, 135.26, 134.44, 133.88, 132.26, 131.85, 131.26, 130.97, 130.54, 127.42, 105.29, 77.32, 77.00, 76.69, 31.96, 31.94, 30.30, 29.78, 29.75, 29.73, 29.71, 29.69, 29.62, 29.55, 29.39, 22.71, 18.65, 14.12, 11.88, MALDI-TOF MS: calculated for $\text{C}_{94}\text{H}_{144}\text{BrS}_4\text{Si}_2$ 1742.6939, found 1742.6873.

Synthesis of BBDTB-TIPS. Under N_2 condition, **3** (500 mg, 0.286 mmol) didodecylboronic acid diester (1.06 g, 1.72 mmol), degassed K_2CO_3 solution (2 M, 4 mL), degassed dry THF (100

mL) and Pd(PPh₃)₄ (150mg, 0.13mmol) were filled in a two-neck flask and the mixture was stirred at 90 °C for 12 h. The mixture was cooled to room temperature and then concentrated under reduced pressure. Finally, the crude products were purified by column chromatography using petroleum ether to afford the principal product as a yellow solid **BBDTB-TIPS** (yield: 59%).¹H NMR (400 MHz, CDCl₃, δ, ppm), δ 7.52 (s, 2H), 3.27-3.19 (m, 12H), 1.22-1.20 (d, J=7.4Hz, 36H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 139.52, 137.63, 136.70, 133.85, 133.50, 132.97, 130.80, 130.61, 130.38, 130.30, 130.23, 129.56, 129.41, 129.30, 76.15, 75.94, 75.73, 31.00, 30.97, 30.96, 30.92, 29.44, 29.29, 29.13, 28.80, 28.78, 28.74, 28.47, 21.72, 17.67, 13.12, 10.92. MALDI-TOF MS: calculated for C₁₂₀H₁₉₄S₈Si₂ 1947.2485, found 1947.2403. CCDC:2204238

By-product was obtained by column chromatography as a yellow solid **DT-DT** (yield: trace amount). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 2H), 7.48 (s, 2H), 3.17 (m, 8H), 1.73(m, 8H), 1.67(m, 8H), 1.18(d, J=8.4Hz, 18H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 140.44, 139.63, 139.03, 137.70, 136.52, 135.16, 134.32, 133.75, 131.92, 131.06, 130.58, 127.41, 116.44, 31.95, 31.19, 30.38, 30.22, 29.79, 29.74, 29.71, 29.67, 29.62, 29.54, 29.42, 29.40, 22.71, 18.64, 14.14, 11.85. MALDI-TOF MS: calculated for C₉₄H₁₄₆S₈Si₂ 1586.87 found 1586.9.

Synthesis of BBDTB-H. Under N₂ condition, **BBDTB-TIPS** (0.3 g, 6.32 mmol) was dissolved in 100 mL dry THF and put the system in the ice-water mixture for 30 min. At 0 °C, TBAF (0.3 mL, 1 mol/L) was slowly added dropwise to the system. After reacting at 0 °C for 30 min, removed the ice-water bath and stirred at room temperature for 24 h. Then added 10 mL of water to quench the reaction. and then concentrated under reduced pressure. Finally, the crude products were purified by column chromatography using petroleum ether to get a yellow solid **BBDTB-H** (yield: 82%).¹H NMR (400 MHz), δ 7.45 (d, J=4.8Hz, 2H), 7.26 (d, J=5.1Hz, 2H), 3.25-3.21 (m, 8H), 3.11-3.08 (m, 4H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 136.02, 134.82, 134.37, 134.11, 133.99,

131.63, 131.36, 131.33, 131.31, 131.23, 130.67, 130.40, 127.85, 119.72, 77.22, 77.01, 76.79, 32.00, 31.98, 31.96, 29.88, 29.85, 29.82, 29.80, 29.75, 29.47, 29.43, 22.73, 22.70. MALDI-TOF MS: calculated for $C_{102}H_{154}S_8$ 1634.9816, found 1634.9841.

Synthesis of BBDTB-Br. Compound **BBDTB-H** (24 mg, 0.04 mmol) dissolved in 6 mL dry THF, keep the system under N_2 protection, Added NBS (22 mg, 1.2 tendency for) at 0 °C, wrapped the flask with aluminum foil to avoid light, restored to room temperature slowly, quenched by water after 12 h reaction. Extracted with DCM, washed with saturated sodium chloride solution, and dried with anhydrous sodium sulfate. Used petroleum ether over the column. The product of this step is a yellow solid (yield: 50%). 1H NMR (400 MHz), δ 7.20 (s, 2H), 3.22-3.16 (m, 8H), 3.01-2.97 (m, 4H)ppm. MALDI-TOF MS: calculated for $C_{102}H_{152}Br_2S_8$ 1790.8026, found 1790.7958.

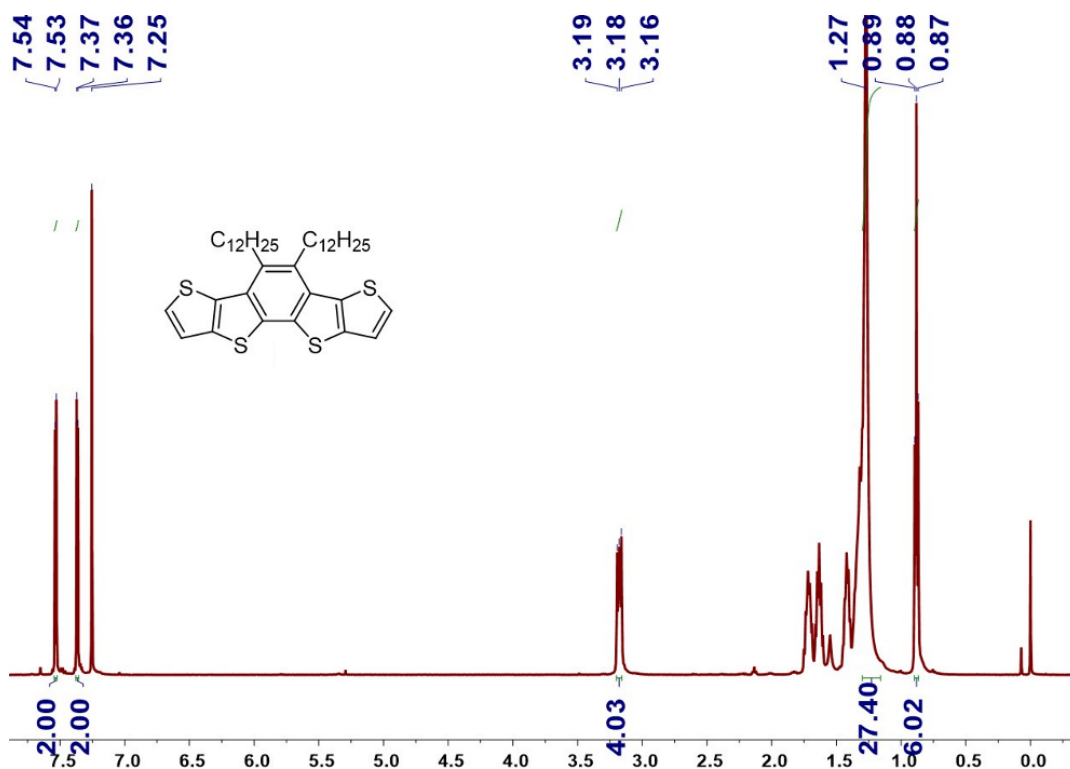


Figure S1. ¹H-NMR spectra of compound **DT-H**. (400 MHz, CDCl₃, 298K)

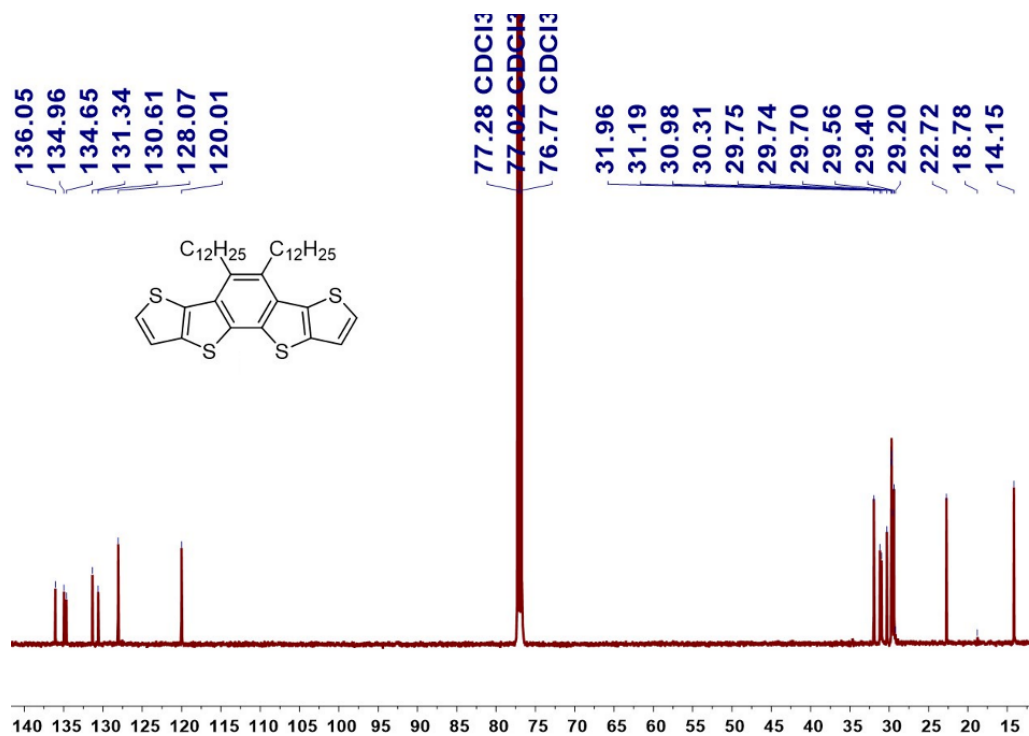


Figure S2. ¹³C-NMR spectra of compound **DT-H**. (101 MHz, CDCl₃, 298K)

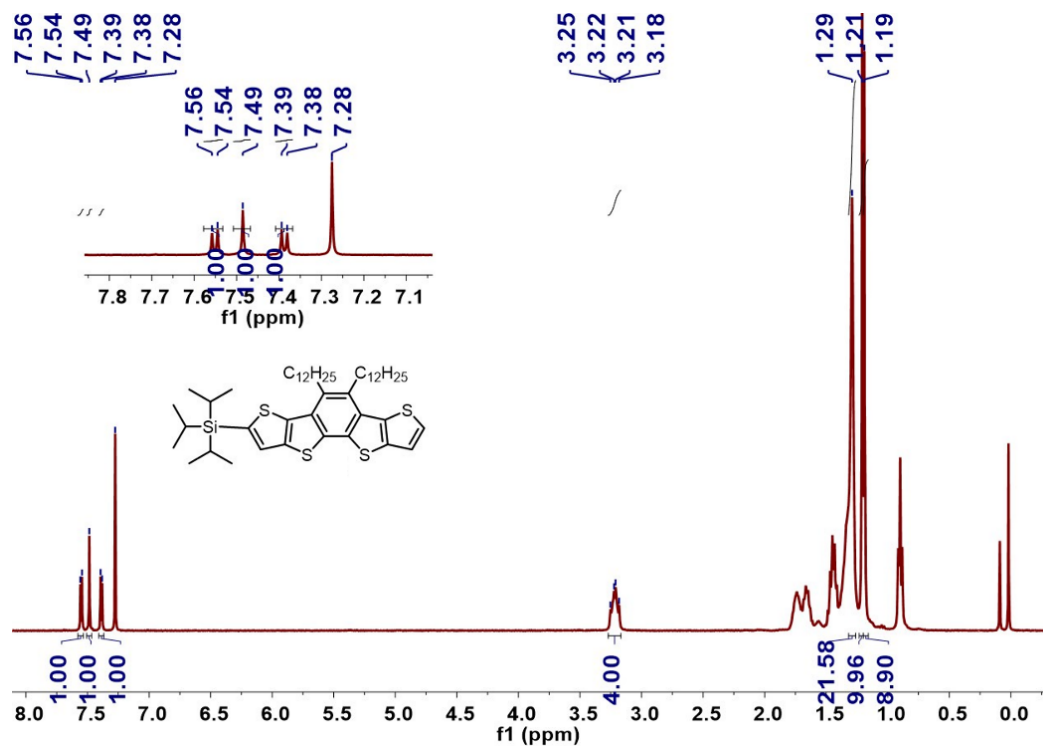


Figure S3. $^1\text{H-NMR}$ spectra of compound **1**. (400 MHz, CDCl_3 , 298K)

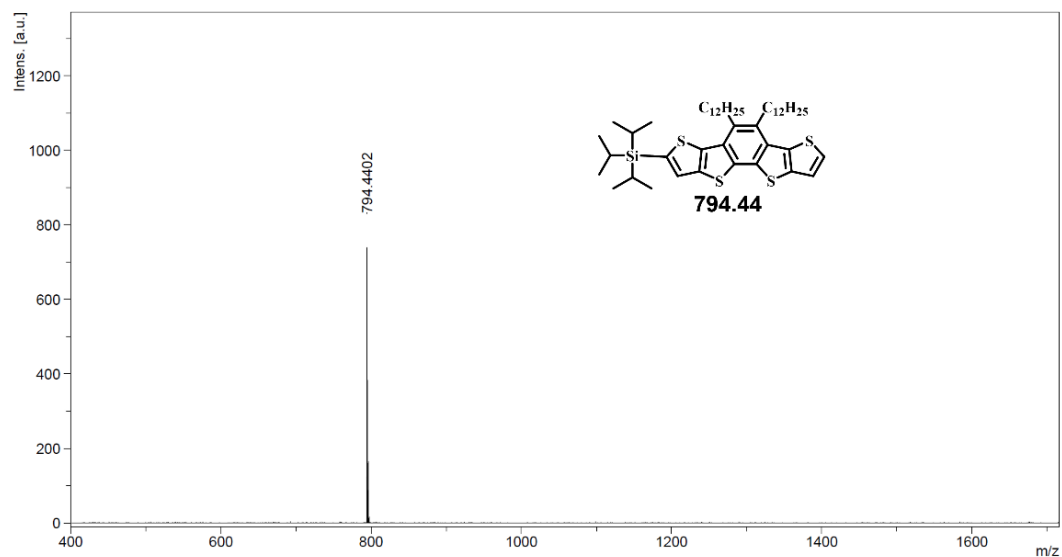


Figure S4. MALDI-TOF MS spectra of compound **1**.

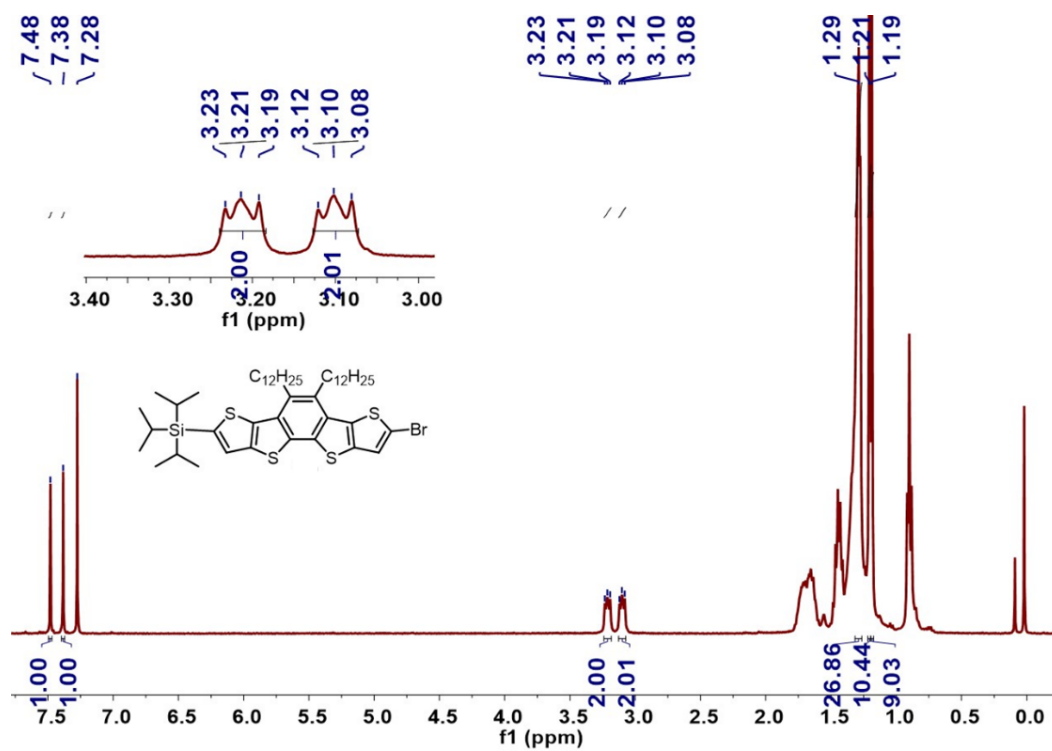


Figure S5 $^1\text{H-NMR}$ spectra of compound **2**. (400 MHz, CDCl_3 , 298K)

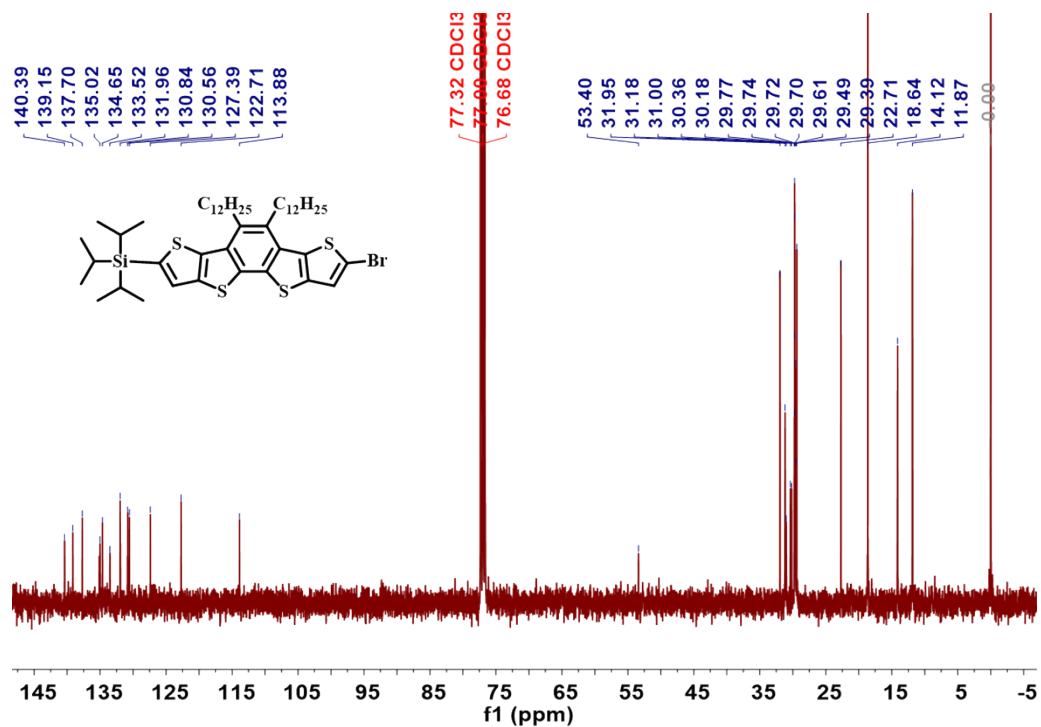


Figure S6. ¹³C-NMR spectra of compound 2. (101 MHz, CDCl₃, 298K)

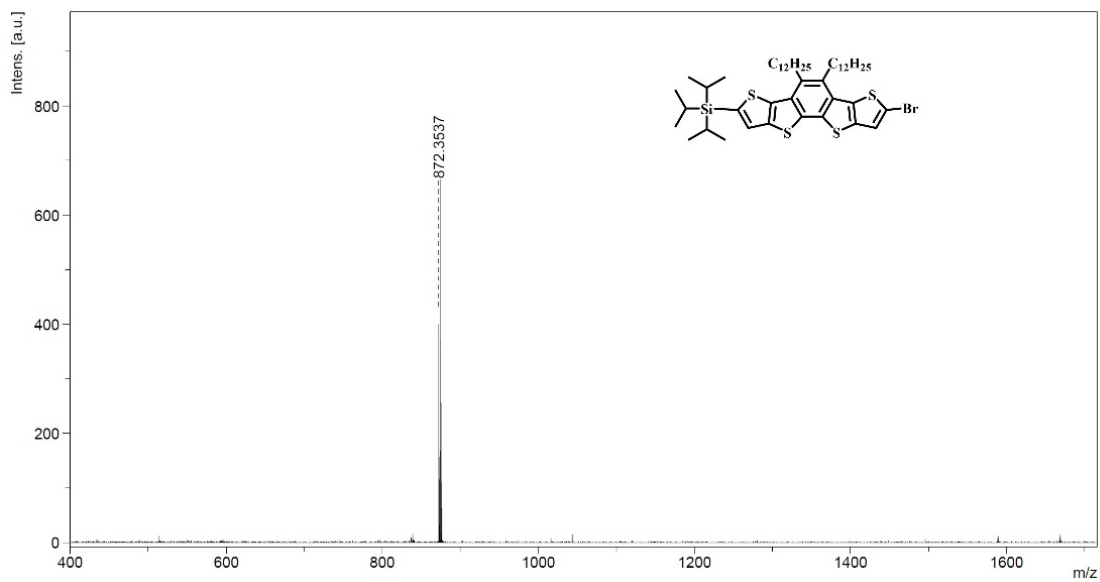


Figure S7. MALDI-TOF MS spectra of compound 2.

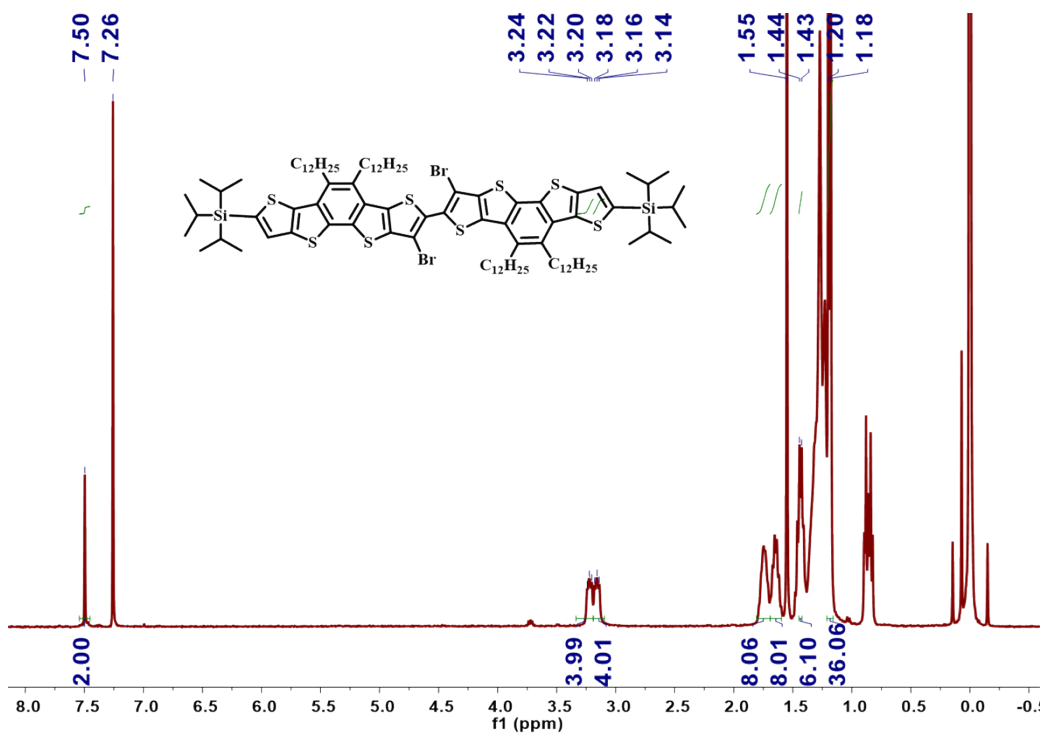


Figure S8. ^1H -NMR spectra of compound 3. (400 MHz, CDCl_3 , 298K)

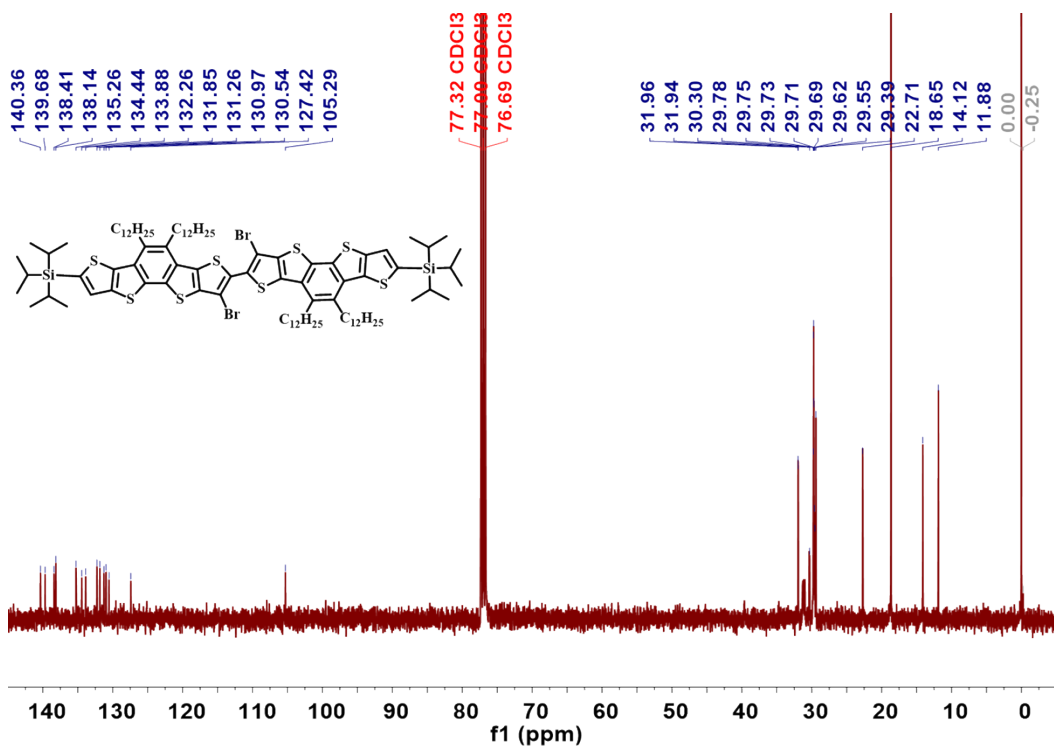


Figure S9. ^{13}C -NMR spectra of compound 3. (101 MHz, CDCl_3 , 298K)

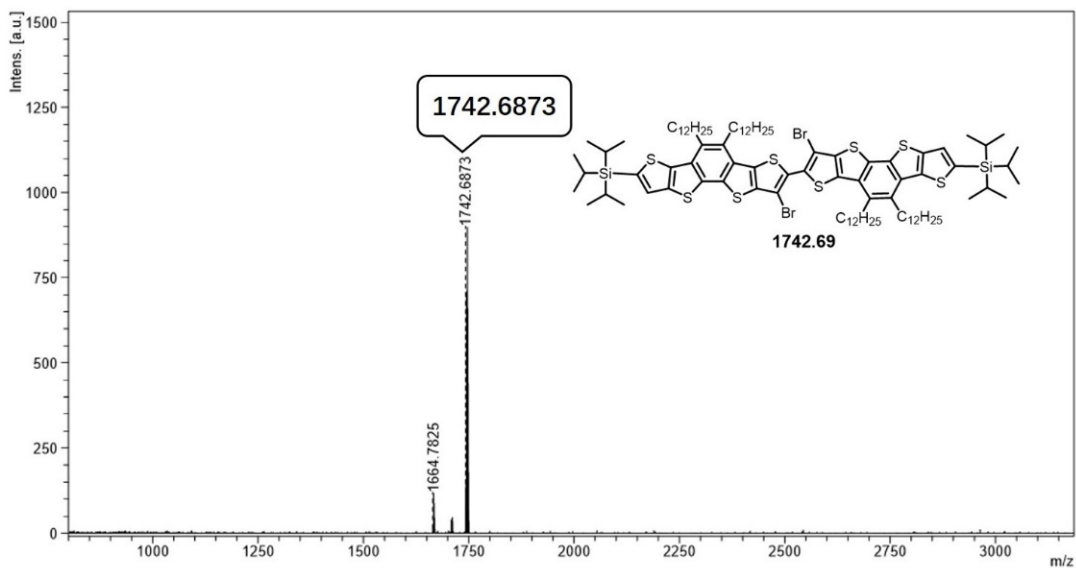


Figure S10. MALDI-TOF MS spectra of compound 3.

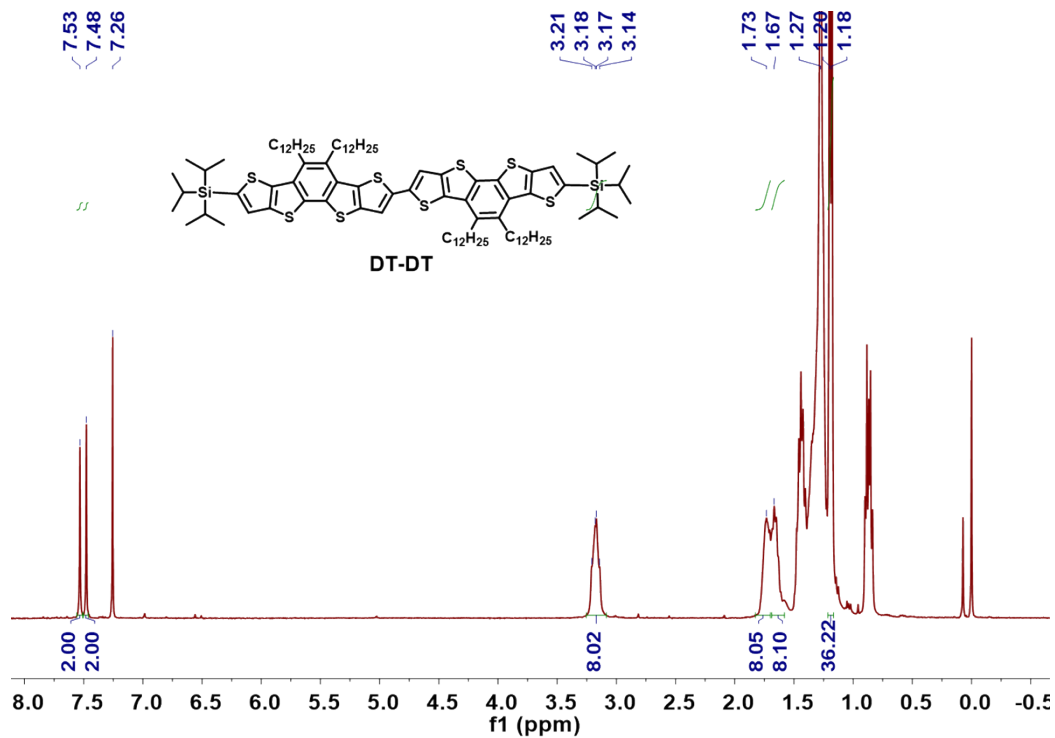


Figure S11. ¹H-NMR spectra of DT-DT. (400 MHz, CDCl₃, 298K)

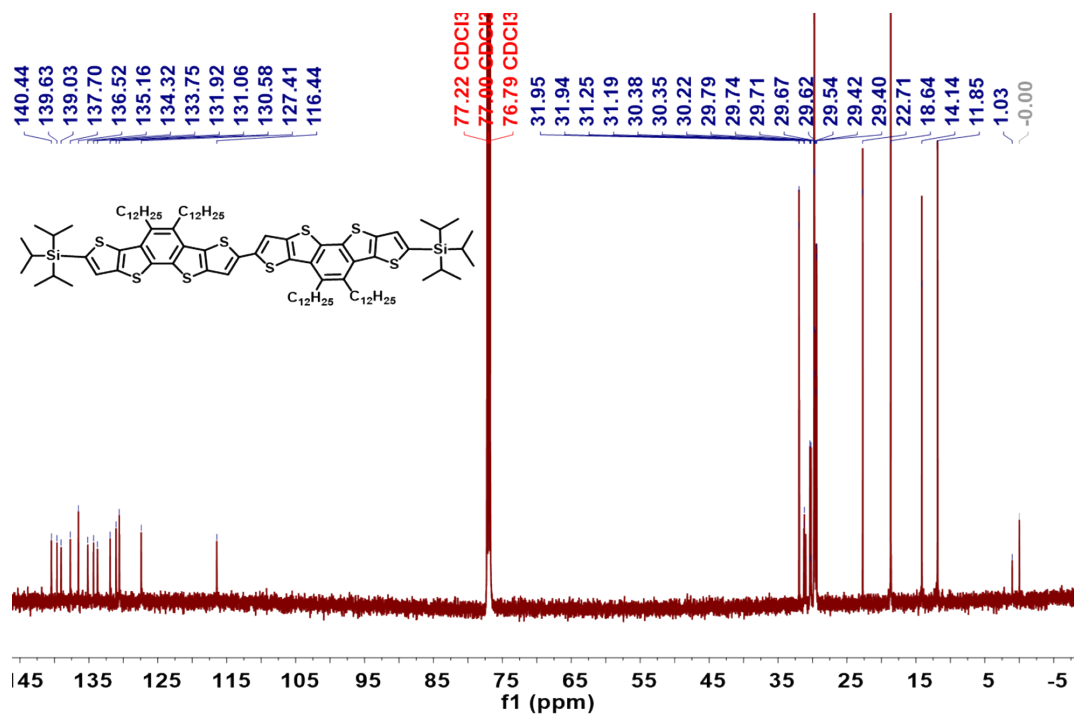


Figure S12. ¹³C-NMR spectra of **DT-DT**. (101 MHz, CDCl₃, 298K)

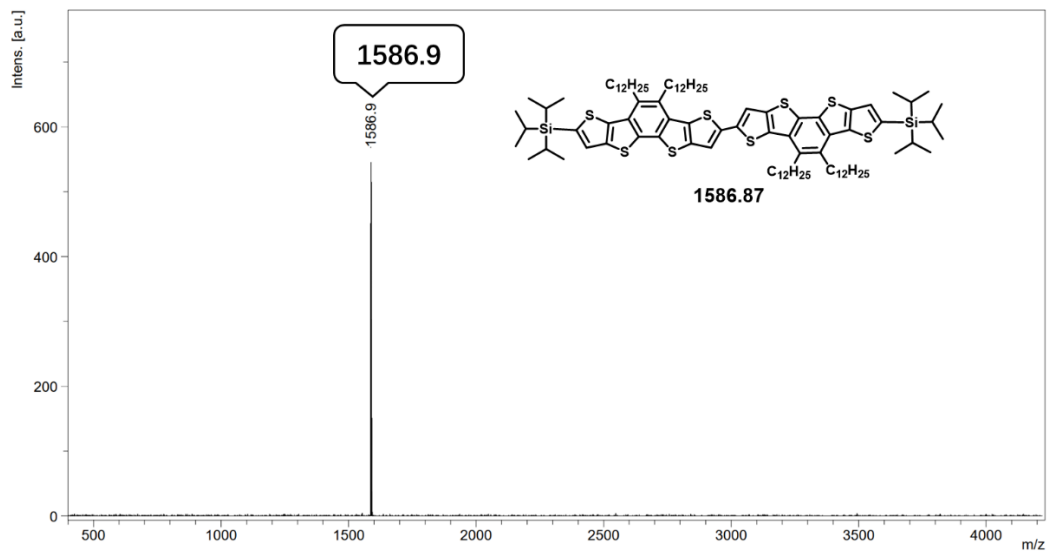


Figure S13. MS spectra of **DT-DT**.

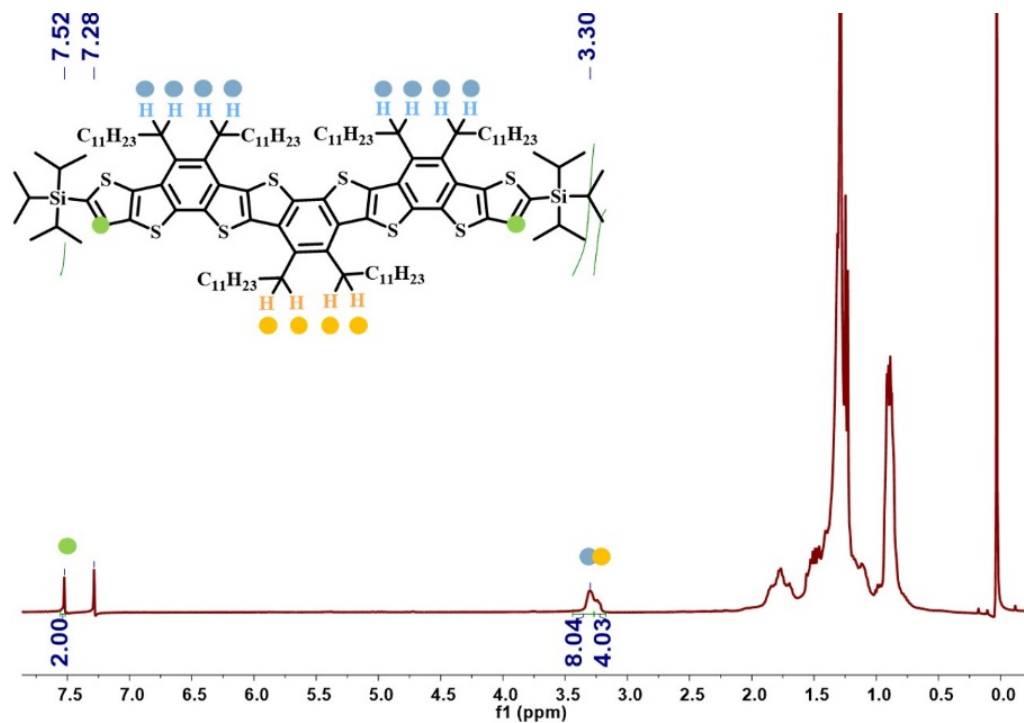


Figure S14. ¹H-NMR spectra of **BBDTB-TIPS**. (400 MHz, CDCl₃, 298K)

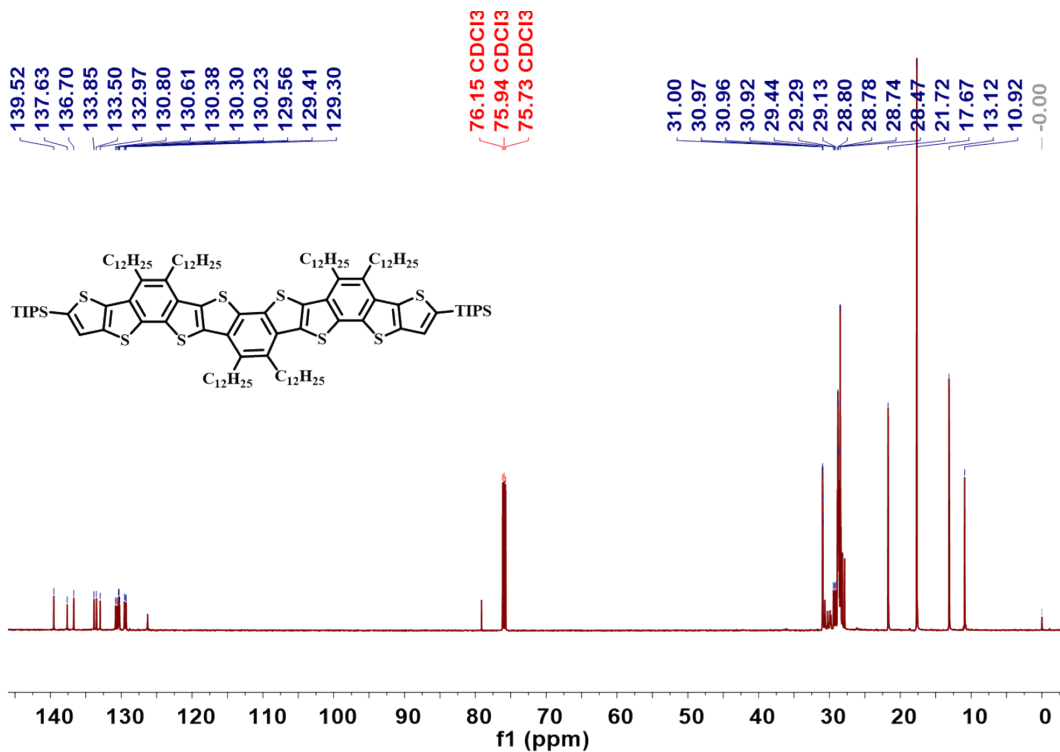


Figure S15. ¹³C-NMR spectra of **BBDTB-TIPS**. (151 MHz, CDCl₃, 298K)

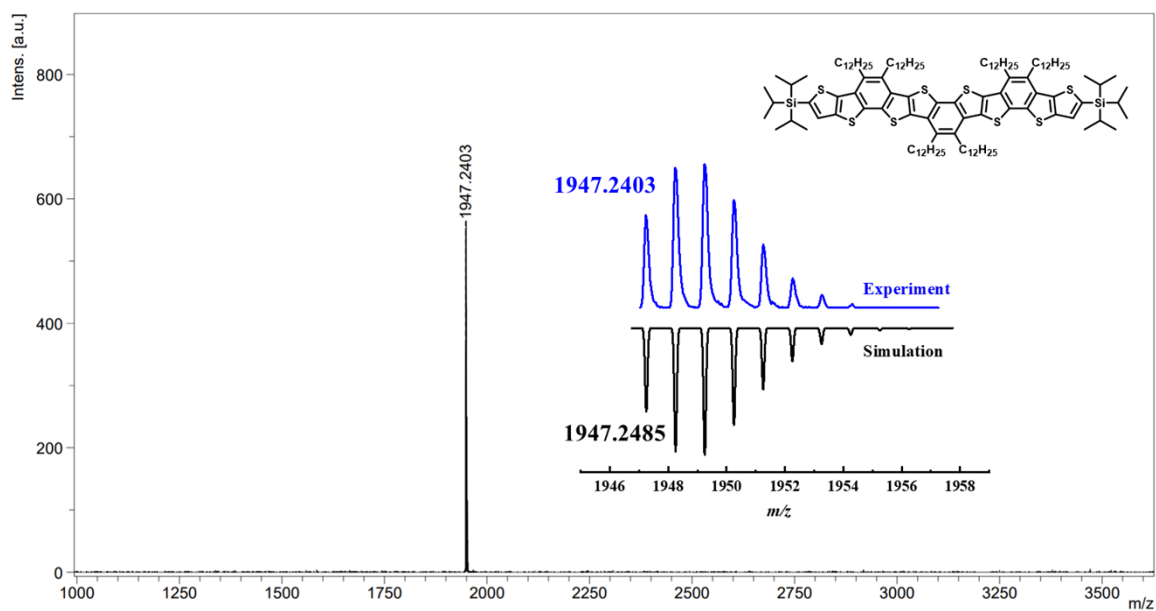


Figure S16. MS spectra of **BBDTB-TIPS**.

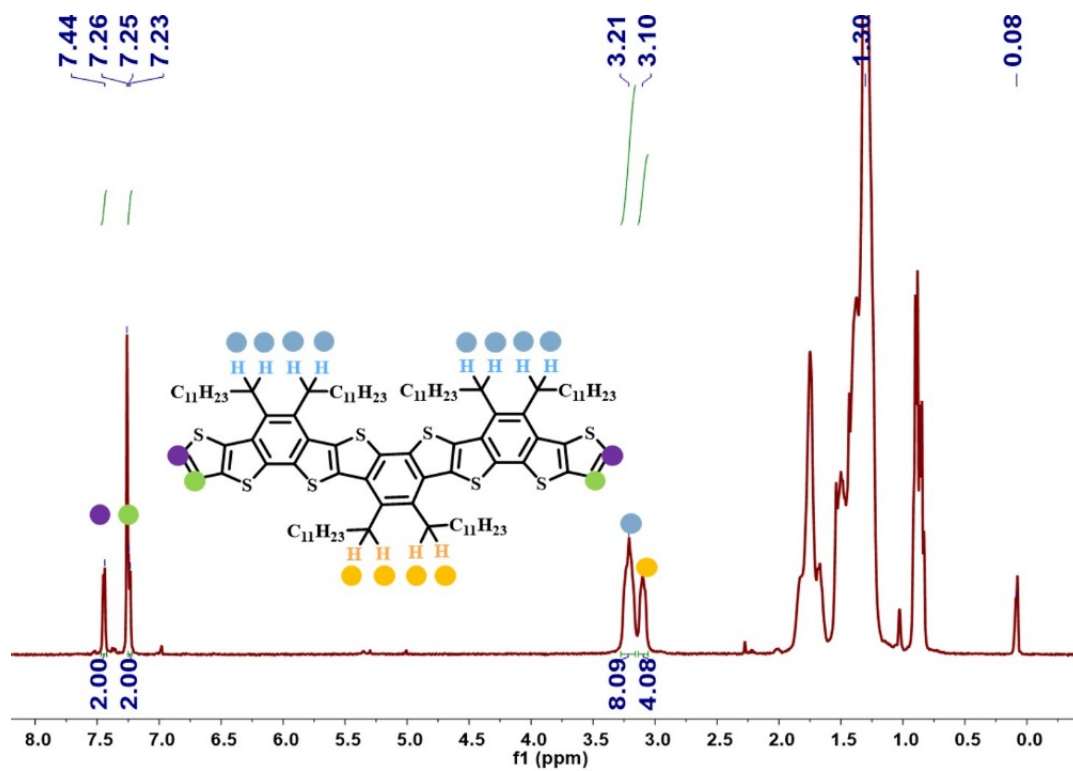


Figure S17. $^1\text{H-NMR}$ spectra of **BBDTB-H**. (400 MHz, CDCl_3 , 298K)

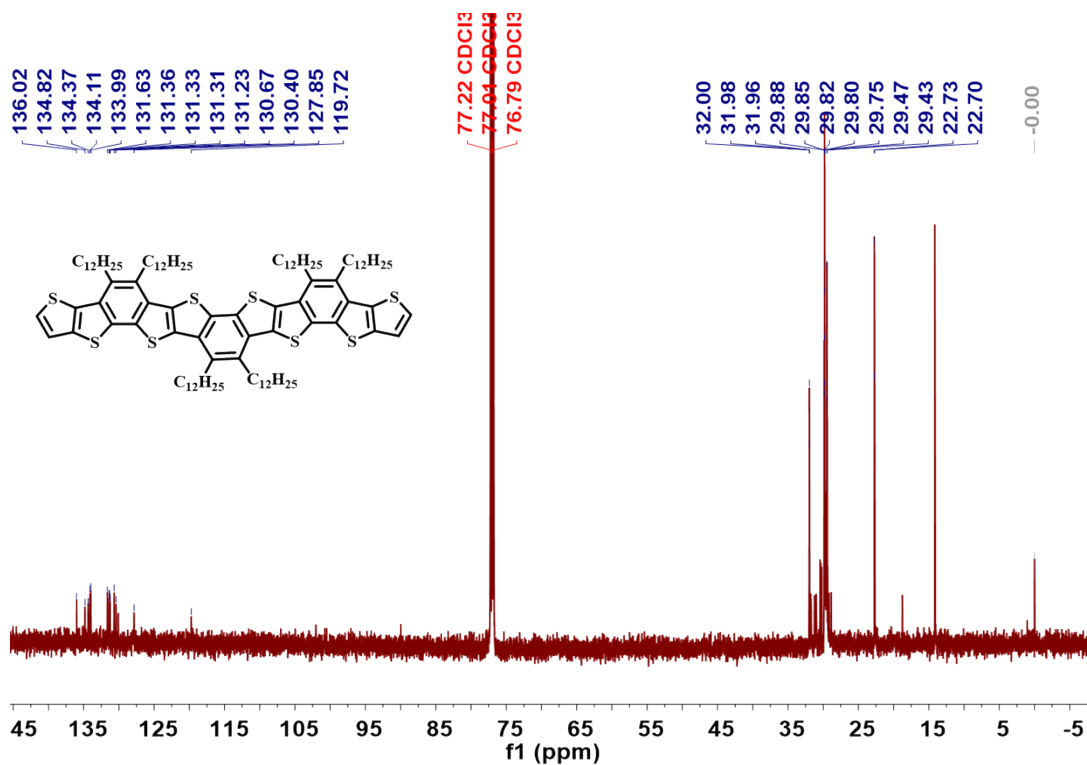


Figure S18. ^{13}C -NMR spectra of **BBDTB-H**. (151 MHz, $CDCl_3$, 298K)

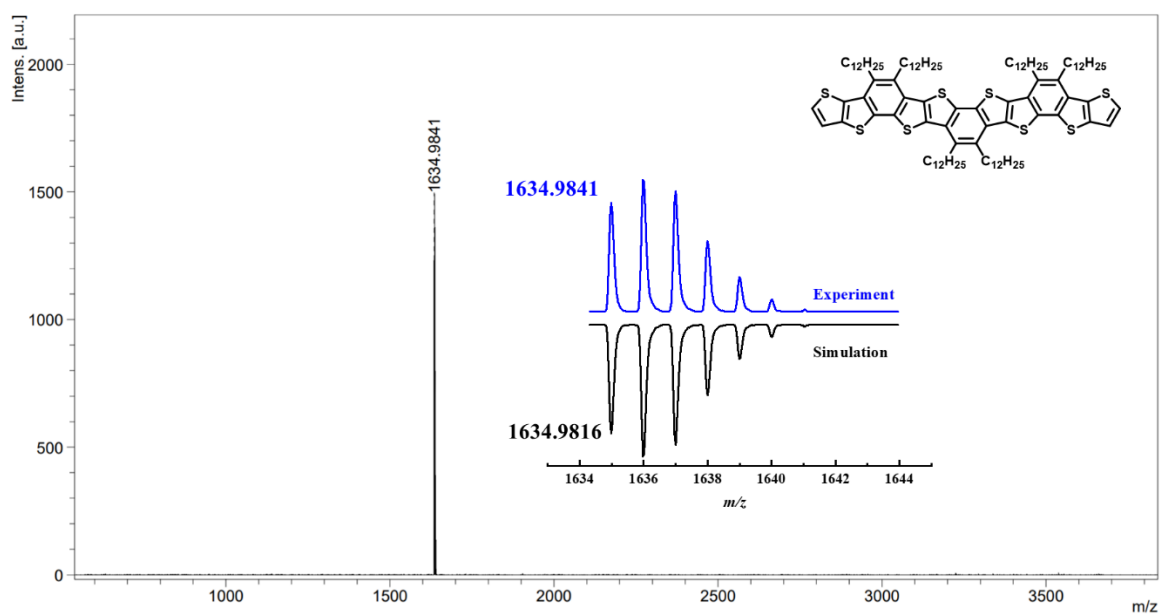


Figure S19. MS spectra of **BBDTB-H**.

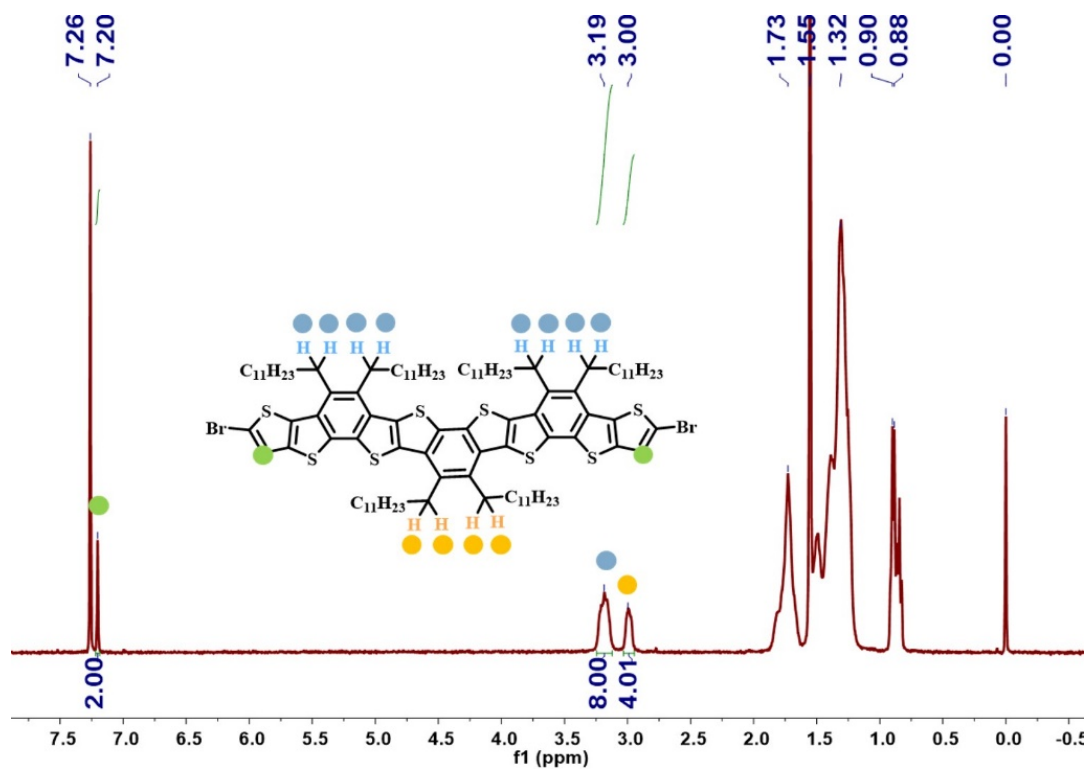


Figure S20. $^1\text{H-NMR}$ spectra of **BBDTB-Br**. (400 MHz, CDCl_3 , 298K)

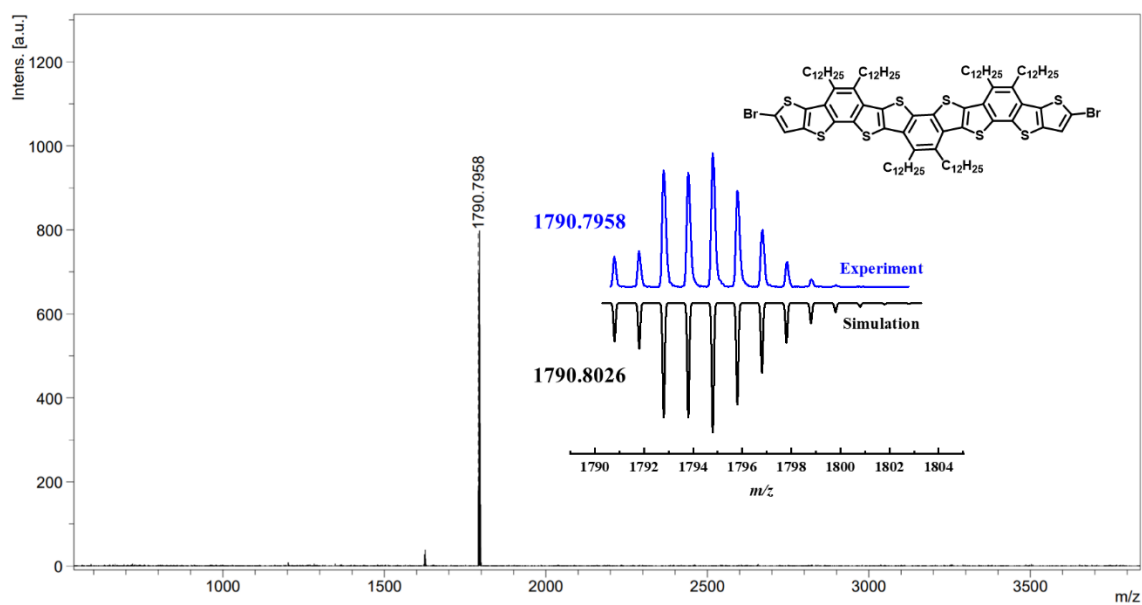


Figure S21. MS spectra of **BBDTB-Br**.

3. Optical spectra

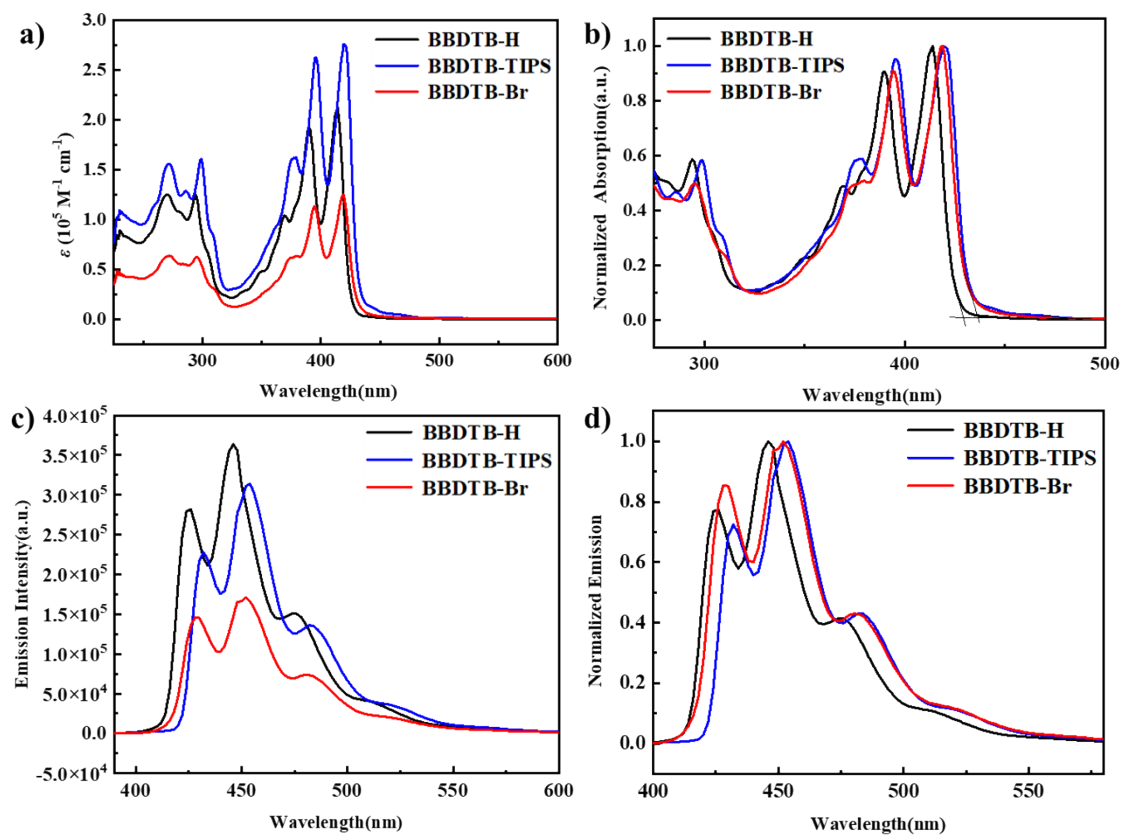


Figure S22. Absorption and emission spectra of **BBDTB-H**, **BBDTB-TIPS** and **BBDTB-Br**.

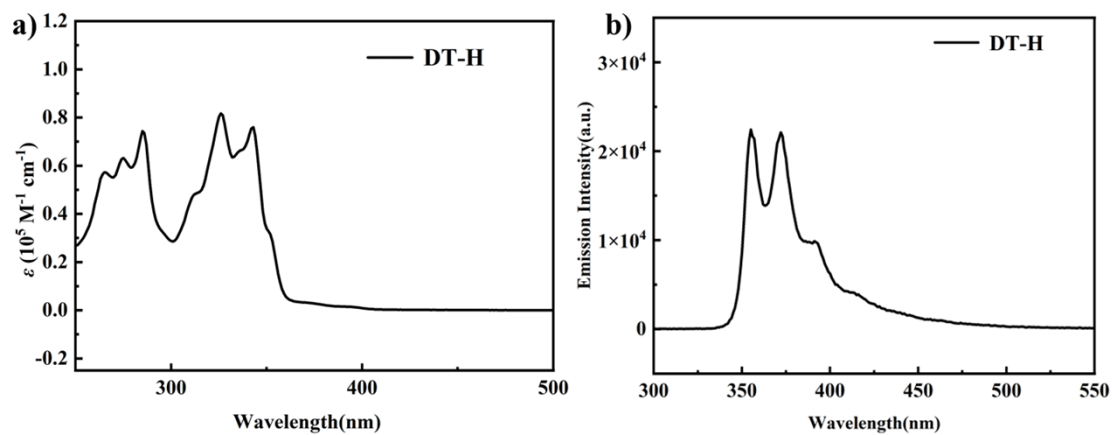


Figure S23. Absorption and emission spectra of **DT-H**.

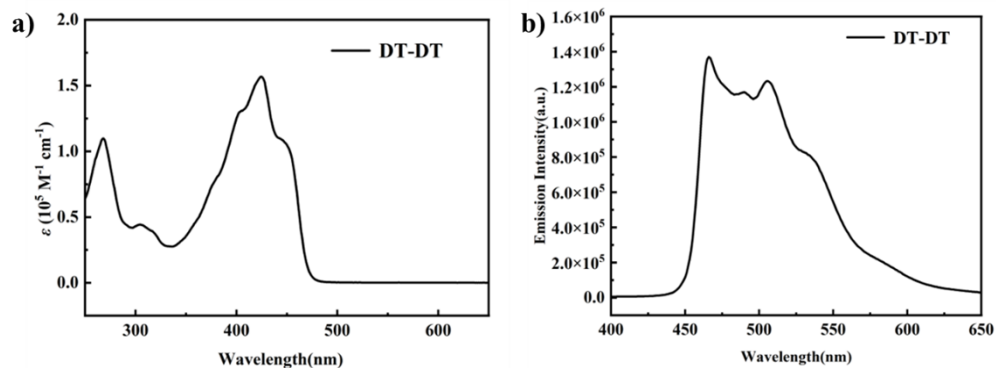


Figure S24. Absorption and emission spectra of DT-DT.

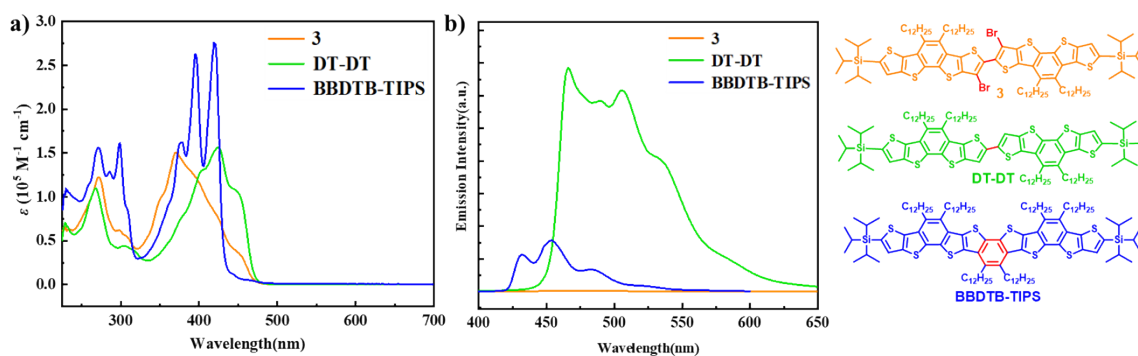


Figure S25 UV-vis absorption spectra and emission spectra of 3, DT-DT and BBDTB-TIPS

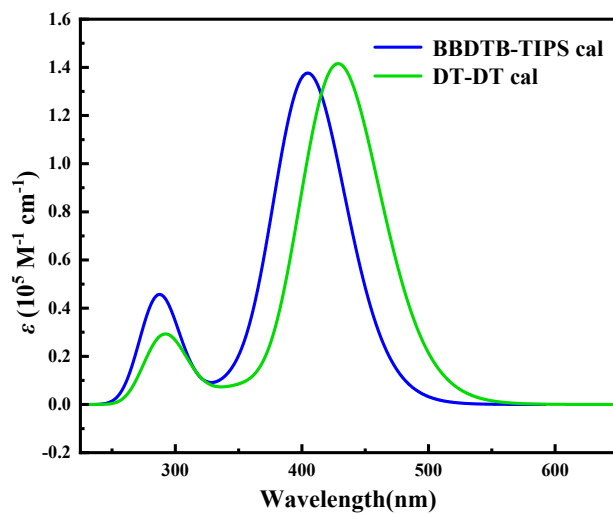


Figure S26. Calculated UV-vis absorption spectra of DT-DT and BBDTB-TIPS.

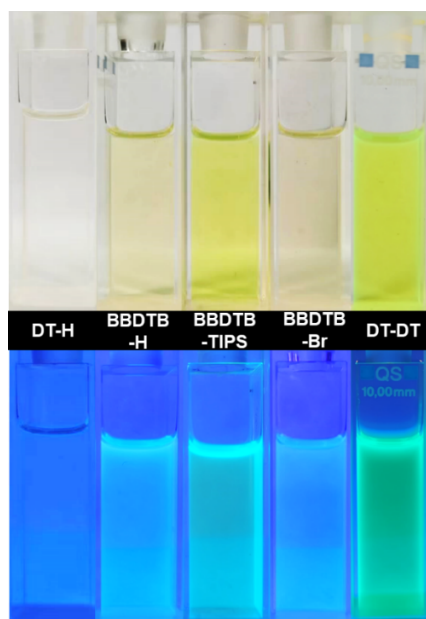


Figure S27. Photographs of **DT-H**, **BBDTB-H**, **BBDTB-TIPS**, **BBDTB-Br** and **DT-DT** in the daylight (top), and under 365 nm UV (bottom) in CH_2Cl_2 .

4. DFT Calculation

Table S1 Calculated UV absorption spectroscopy data about DT-DT

	E_g [eV]	λ_{abs} [nm]	f	transition	coefficient
S_1	2.8923	428.67	2.6235	HOMO > LUMO	0.975
S_2	3.5037	353.87	0.0053	HOMO-1 > LUMO	0.774
				HOMO-3 > LUMO	0.151
S_3	3.5227	351.96	0.1213	HOMO-2 > LUMO	0.921
S_4	3.6175	342.73	0.0006	HOMO-3 > LUMO	0.781
				HOMO-1 > LUMO	0.157
S_5	3.7015	334.96	0.0002	HOMO > LUMO+1	0.927
S_6	4.1084	301.78	0.227	HOMO > LUMO+2	0.744
				HOMO-3 > LUMO+1	0.147

S ₇	4.1771	296.82	0.0012	HOMO-2 > LUMO+1	0.528
				HOMO-5 > LUMO	0.253
				HOMO-1 > LUMO+2	0.057
S ₈	4.2001	295.19	0.062	HOMO-1 > LUMO+1	0.665
				HOMO-2 > LUMO+2	0.09
				HOMO-6 > LUMO	0.074
				HOMO > LUMO+2	0.069
S ₉	4.2598	291.06	0.0026	HOMO-5 > LUMO	0.651
				HOMO-2 > LUMO+1	0.162
				HOMO > LUMO+3	0.06
S ₁₀	4.2731	290.15	0.1237	HOMO-4 > LUMO	0.651
				HOMO-6 > LUMO	0.133
				HOMO-3 > LUMO+1	0.073

Table S2 Calculated UV absorption spectroscopy data about BBDTB-TIPS

	E_g [eV]	λ_{abs} [nm]	f	transition	coefficient
S ₁	3.0599	405.19	2.5245	HOMO > LUMO	0.967
S ₂	3.4524	359.12	0.1436	HOMO-1 > LUMO	0.925
S ₃	3.6472	339.94	0.0459	HOMO-2 > LUMO	0.855
				HOMO-1 > LUMO+1	0.063
S ₄	3.6903	335.97	0.0049	HOMO > LUMO+1	0.57
				HOMO-3 > LUMO	0.382
S ₅	3.7754	328.4	0.0129	HOMO-3 > LUMO	0.509
				HOMO > LUMO+1	0.332
				HOMO-4 > LUMO	0.07
S ₆	3.9556	313.44	0.009	HOMO-4 > LUMO	0.738

				HOMO-2 > LUMO+1	0.065
				HOMO > LUMO+1	0.061
				HOMO-3 > LUMO	0.051
				HOMO-1 > LUMO+1	0.801
S ₇	4.0947	302.79	0.0205	HOMO-2 > LUMO	0.091
				HOMO > LUMO+2	0.057
				HOMO > LUMO+2	0.528
S ₈	4.2529	291.53	0.5132	HOMO-3 > LUMO+1	0.3
				HOMO-2 > LUMO+1	0.622
				HOMO > LUMO+3	0.104
S ₉	4.2807	289.64	0.006	HOMO-4 > LUMO	0.094
				HOMO-1 > LUMO+2	0.056
S ₁₀	4.2895	289.04	0.0002	HOMO > LUMO+4	0.885

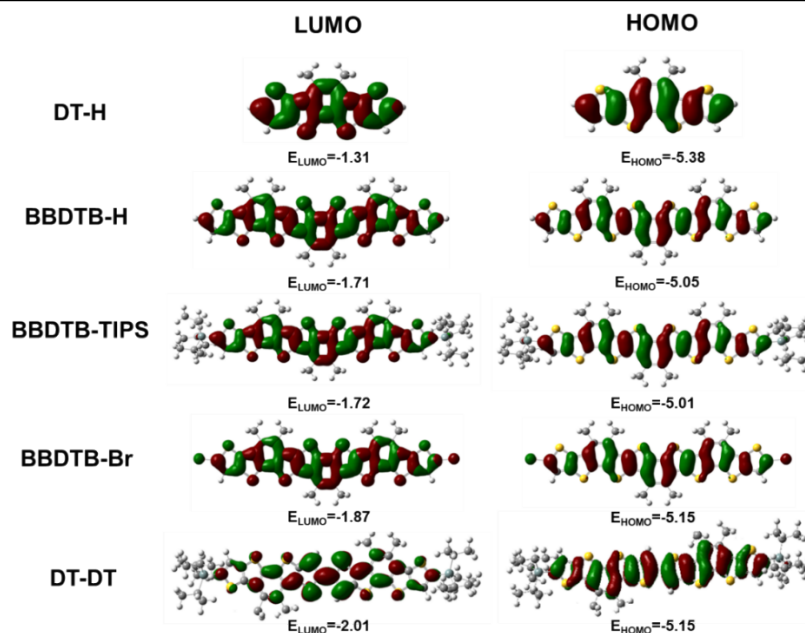


Figure S28. Optimized geometries of **DT-H**, **BBDTB-H**, **BBDTB-TIPS**, **BBDTB-Br**, and **DT-DT** and spatial electron distributions of frontier molecular orbitals (FMOs) and their energy

levels. B3LYP/6-31G(d) (dodecyl side chains are replaced by methyl groups for simplifying DFT calculation)

5. CV Curves

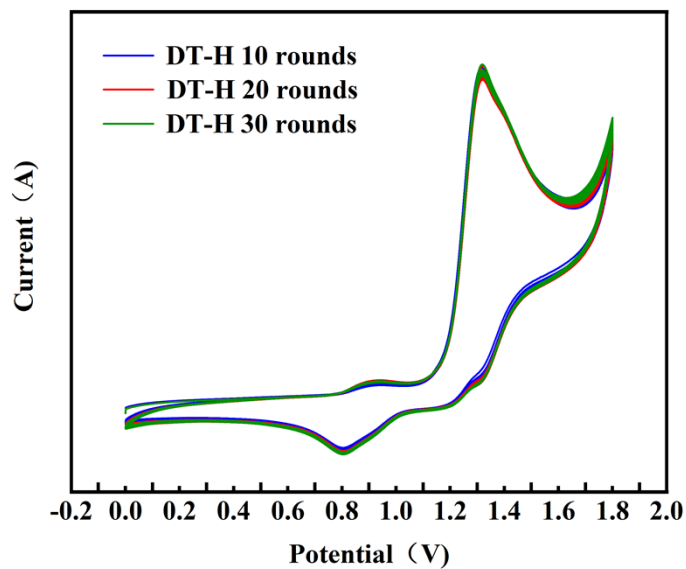


Figure S29. The CV curves of **DT-H** in CH_2Cl_2 .

6. Thermology Curves

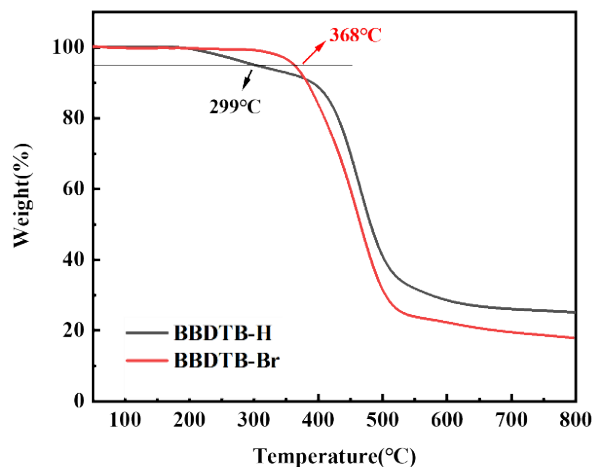


Figure S30. TGA curves of **BBDTB-H** and **BBDTB-Br** measured under N_2 at $10\text{ }^\circ\text{C min}^{-1}$.

7. Single crystal structures

Table S3. Single crystal data of **BBDTB-TIPS**

Compound	BBDTB-TIPS CCDC:2204238
Empirical formula	C ₁₂₀ H ₁₉₄ S ₈ Si ₂
Formula weight	1949.4
Crystal system	monoclinic
Space group	P21/c
a/Å	9.0909(12)
b/Å	46.860(6)
c/Å	27.679(4)
α /	90
β /	94.973(4)
γ /	90
Volume/Å ³	11747(3)
Z	4
μ /mm ⁻¹	1.267
F(000)	4280.0
Radiation	GaK α (λ = 1.34139)
2 Θ range for data collection/	3.28 to 99.308
Index ranges	-4 \leq h \leq 10, -53 \leq k \leq 53, -31 \leq l \leq 29
Reflections collected	73012
Independent reflections	17805
Data/restraints/parameters	17805/639/1250
Goodness-of-fit on F ²	1.132
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0860, wR ₂ = 0.2588

Final R indexes [all data]

$R_1 = 0.1069$, $wR_2 = 0.2849$

Largest diff. peak/hole / $e \text{ \AA}^{-3}$

0.84/-0.59



Figure S31. The side view single crystal structure of the **BBDTB** skeleton.

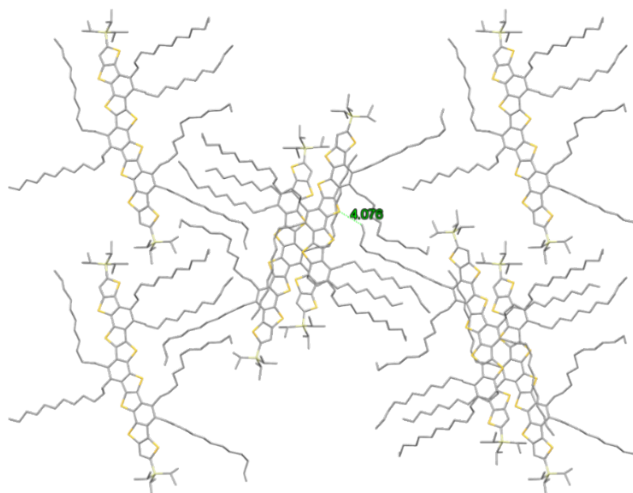


Figure S32. The packing arrangement of **BBDTB-TIPS** along the a-axis. S-C distance is 4.076Å.

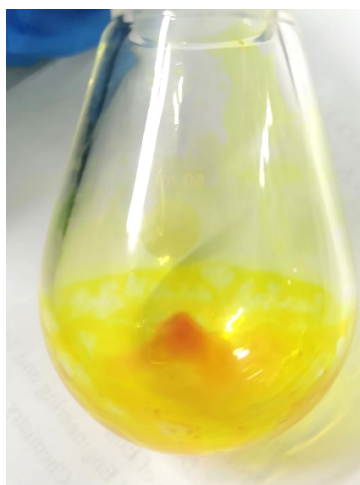


Figure S33. BBDTB-TIPS at the ambient state in rt.

8. OFET Characteristics

Table S4. OFET Characteristics of the **BBDTB-H**

Compound	Substrate	T _a /°C	$\mu_{h,ave}^a /$ cm ² V ⁻¹ S ⁻¹	$\mu_{h,max}^a /$ cm ² V ⁻¹ S ⁻¹	V _{th} /V	I _{on} /I _{off}
BBDTB-H	OTMS	25	0.0113	0.0175	-25±1	10 ⁶ ~10 ⁷
		100	0.0221	0.0285	-32±1	10 ⁷

^a Determined from the following equation in the saturation region; $I_{DS} = (W/2L) C_i \mu (V_{GS} - V_{th})^2$.

1 S. Liu, W. Cao, D. Xia, J. Zhang, J. Fan, C. An, R. Fan, S. Hao, K. Lin and Y. Yang, *Dyes and Pigments*, 2021, **193**, 109506.