

The Impact of Structural Modification on Electrochromic and Electroluminescent Properties of D-A-D Benzothiadiazole Derivatives with a Fluorene Linker and (Bi)Thiophene Units

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Supporting Information

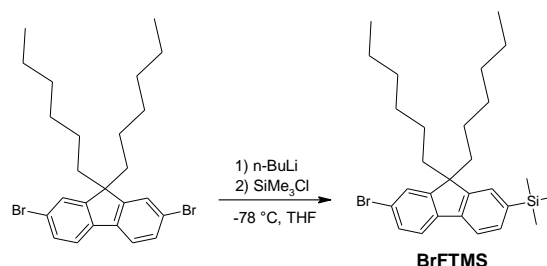
Experimental details

Synthesis

9,9-dihexyl-2,7-dibromofluorene, tetrakis(triphenylphosphine)palladium(0), *n*-butyllithium solution (2.38 M in hexane), bromine, sodium acetate, chlorotrimethylsilane, sodium carbonate and magnesium sulphate were purchased from Merck. Dry solvents for all syntheses were purchased from Merck, whereas solvents for extraction and column chromatography were delivered by CHEMPUR. Column chromatography was performed using Merck silica gel 60 (0.040 – 0.063 mm). All reactions were carried out under dry argon.

¹H and ¹³C NMR spectra were recorded on a Varian Mercury (500 and 125 MHz) spectrometer. Mass spectra were measured by TOF method on an Maldi SYNAPT G2-S HDMS (Waters) mass spectrometer. All final products were subject to C, H and N elemental analysis.

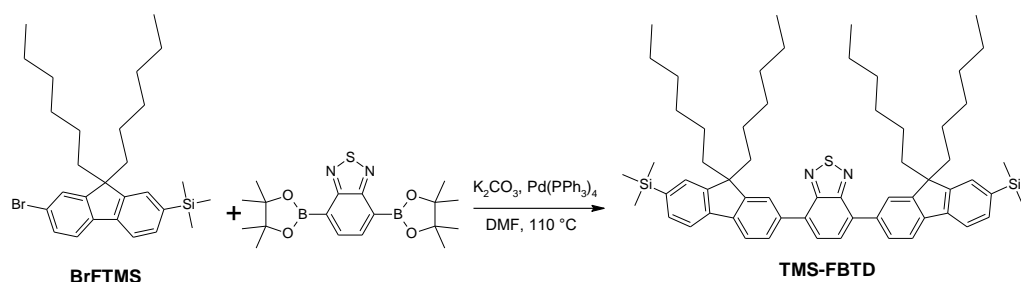
Synthesis of (7-bromo-9,9-dihexyl-9H-fluorene-2-yl)trimethylsilane (BrFTMS)



In a 100 ml four-necked flask under an argon flow 5.00 g (10.16 mmol) of a 9,9-dihexyl-2,7-dibromofluorene was dissolved in 40 ml of anhydrous THF. The solution was cooled to -78°C and then 4.48 ml (10.66 mmol) *n*-BuLi (2.38 M in hexane) was slowly added. After 1 h at this temperature, the reaction mixture was allowed to warm gently to room temperature. In the next step, chlorotrimethylsilane (1.24 g, 11.41 mmol) was added dropwise and stirred overnight at room temperature. The resultant solution was extracted with dichloromethane (100 ml) and washed with water. Finally, the organic phase was separated, and dried with anhydrous magnesium sulphate, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, eluent: hexane), yielding 4.10 g of BrFTMS in the form of colorless oil (83%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64 (dd, $J = 7.5, 0.7$ Hz, 1H), 7.56 (dd, $J = 8.0, 0.4$ Hz, 1H), 7.49 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.47 – 7.42 (m, 3H), 2.00 – 1.87 (m, 4H), 1.16 – 1.01 (m, 12H), 0.77 (t, $J = 7.1$ Hz, 6H), 0.69 – 0.55 (m, 4H), 0.31 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 153.31, 149.62, 140.76, 140.25, 139.80, 132.08, 130.00, 127.69, 126.35, 121.25, 121.18, 119.13, 55.46, 40.18, 31.48, 29.66, 23.73, 22.63, 14.13, -0.76.

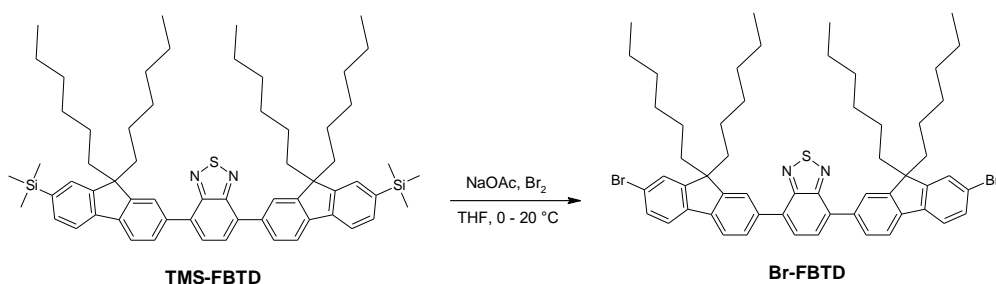
Synthesis of 4,7-bis(9,9-dihexyl-7-(trimethylsilyl)-9H-fluoren-2-yl)benzo[*c*][1,2,5]thiadiazole (TMS-FBTD)



$\text{Pd(PPh}_3)_4$ (0.43 g, 0.37 mmol) was added to a suspension of 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (1.45 g, 3.74 mmol) in dry DMF (100 ml) and then purged with argon for 15 min. The mixture was stirred to afford a clear yellow solution. Then, BrFTMS (3.99 g, 8.22 mmol) and potassium carbonate (2.27 g, 16.44 mmol) were added, and the mixture was stirred for 20 h at 110°C . After cooling down, the obtained reaction mixture was treated with brine (50 ml) and extracted with methylene chloride (100 ml). Finally, the organic phase was dried over anhydrous magnesium sulphate. The solvent was removed in a rotary evaporator and the crude product was purified by column chromatography (silica gel, eluent: hexane/methylene chloride, 9/1 v/v), to obtain 2.20 g of a yellow powder (62%).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (dd, $J = 7.8, 1.6$ Hz, 2H), 7.97 (d, $J = 1.1$ Hz, 2H), 7.90 – 7.87 (m, 4H), 7.76 (dd, $J = 7.4, 0.7$ Hz, 2H), 7.55 – 7.52 (m, 4H), 2.11 – 1.98 (m, 8H), 1.19 – 1.06 (m, 24H), 0.88 – 0.75 (m, 20H), 0.34 (s, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.51, 151.47, 150.64, 141.45, 141.41, 139.49, 136.45, 133.76, 132.03, 128.25, 128.06, 127.81, 124.15, 119.98, 119.37, 55.29, 40.22, 31.54, 29.79, 23.96, 22.67, 14.17, -0.70.

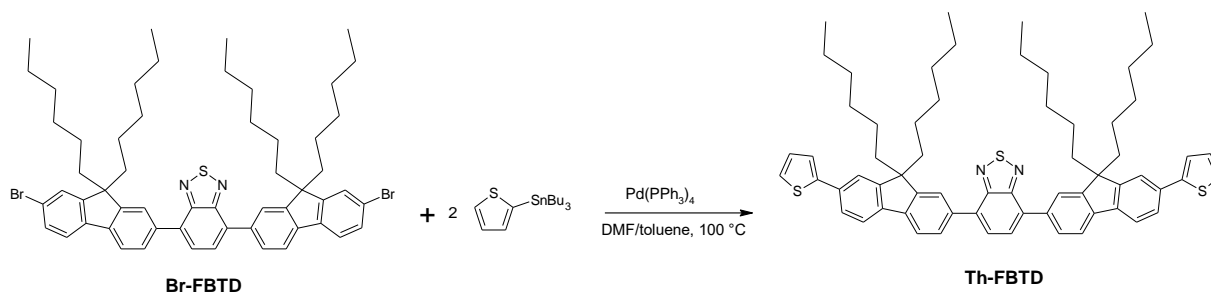
Synthesis of 4,7-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (Br-FBTD)



To a solution of TMS-FBTD (2.00 g, 2.12 mmol) in a dry THF (80 ml) sodium acetate (0.35 g, 4.26 mmol) was added. Next, the solution was cooled down to 0 °C and bromine (1.58 g, 9.88 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature conditions. After this time, methylene chloride was added, the mixture was washed with water (50ml) and aqueous solution of disodium thiosulfate (30ml). Finally, the organic phase was dried over anhydrous magnesium sulphate. The solvent was removed in a rotary evaporator and the crude product was purified by crystallization from chloroform/methanol mixture, to obtain 1.91 g of yellow-green solid (94%).

¹H NMR (500 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.95 (d, *J* = 1.2 Hz, 2H), 7.88 (s, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.48 (m, 4H), 2.12 – 1.92 (m, 8H), 1.19 – 1.04 (m, 24H), 0.82 – 0.71 (m, 20H). ¹³C NMR (126 MHz, CDCl₃) δ 154.44, 153.70, 150.90, 140.39, 139.81, 136.75, 133.67, 130.23, 128.48, 128.07, 126.42, 124.11, 121.47, 121.45, 119.98, 55.72, 40.36, 31.62, 29.82, 23.97, 22.74, 14.17.

Synthesis of 4,7-bis(9,9-dihexyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (Th-FBTD)

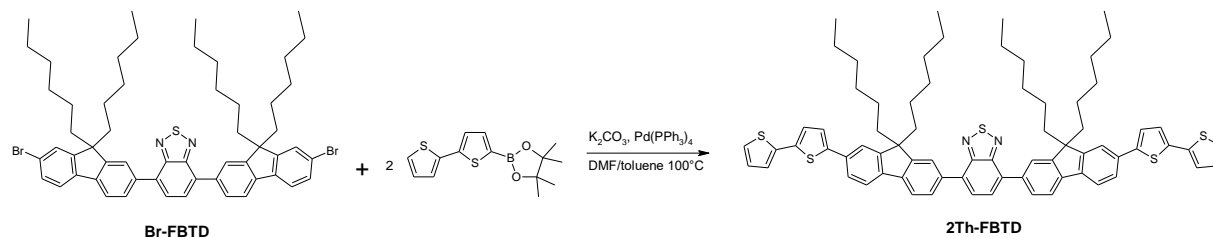


Pd(PPh₃)₄ (0.036 g, 0.031 mmol) was added to a suspension of Br-FBTD (0.30 g, 0.31 mmol) in a mixture of dry toluene (20 ml) and DMF (40 ml). Then, a 2-(tributylstannyl)thiophene (0.29 g, 0.78 mmol) was added dropwise and the resulting mixture was heated to 100 °C and stirred for 20 h. After cooling to ambient temperature dichloromethane was added (100ml) and the obtained mixture was washed with brine (50 ml), water (50 ml). Finally, the organic phase was dried over anhydrous magnesium sulphate. The crude product was purified by chromatographic columns (silica gel, eluent: hexane/ methylene chloride, 5/1 v/v) followed by crystallization from chloroform/methanol mixture yielding 0.13 g of yellow crystals (41%).

¹H NMR (500 MHz, CDCl₃) δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.98 (d, *J* = 1.4 Hz, 2H), 7.90 (s, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.65 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.62 (d, *J* = 1.3 Hz, 2H), 7.41 (dd, *J* = 3.5, 1.1 Hz, 2H), 7.31 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 2H), 2.16 – 2.01 (m, 8H), 1.18 – 1.05 (m, 24H), 0.87 – 0.79 (m, 8H), 0.78 (t, *J* = 7.0 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 154.51, 152.30, 151.45, 145.33, 141.00, 140.37, 136.42, 133.71, 133.60, 128.41, 128.23, 128.04, 125.19, 124.74, 124.09, 123.10, 120.50, 120.43, 119.91, 55.50, 40.49, 31.63, 29.88, 24.02, 22.74, 14.18. Elemental analysis: Calcd for

C₆₄H₇₂N₂S₃: C, 79.62, H, 7.75, N, 2.90. Found: C, 79.31, H, 7.40, N, 2.94. TOF MS AP+ (m/z): M⁺ calcd for C₆₄H₇₃N₂S₃ 965.4936, found 965.4941. Mp: 104-105 °C.

Synthesis of 4,7-bis(7-([2,2'-bithiophen]-5-yl)-9,9-dihexyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (2Th-FBTD)



2,2'-Bithiophene-5-boronic acid pinacol ester (0.22 g, 0.75 mmol) and K₂CO₃ (0.19 g, 1.38 mmol) were added to a stirred suspension of Br-FBTD (0.30 g, 0.31 mmol) in a mixture of toluene (20 ml) and DMF (40 ml). After 15 min Pd(PPh₃)₄ (0.036 g, 0.031 mmol) was added to the flask and stirred at 100 °C for 20 h under argon. The obtained reaction mixture was first cooled to room temperature and then treated with water (30 ml) and brine (30 ml). In the next step, the product was extracted with methylene chloride (100 ml). Then the organic phase was dried over anhydrous magnesium sulphate. The solvent was removed in a rotary evaporator and the crude product was purified by column chromatography (silica gel, eluent: hexane/methylene chloride, 5/1 v/v). The final product was crystallized from a chloroform/hexane mixture yielding 0.21 g of orange crystals (61%).

¹H NMR (500 MHz, CDCl₃) δ 8.05 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.99 (d, *J* = 1.2 Hz, 2H), 7.91 (s, 2H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.64 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.61 (d, *J* = 1.2 Hz, 2H), 7.33 (d, *J* = 3.7 Hz, 2H), 7.24 (d, *J* = 4.4 Hz, 4H), 7.20 (d, *J* = 3.7 Hz, 2H), 7.07–7.04 (m, 2H), 2.17–2.01 (m, 8H), 1.20–1.05 (m, 24H), 0.88–0.80 (m, 8H), 0.78 (t, *J* = 7.0 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 154.50, 152.37, 151.46, 144.04, 140.94, 140.52, 137.69, 136.62, 136.48, 133.70, 133.24, 128.44, 128.05, 124.84, 124.81, 124.49, 124.10, 123.74, 123.72, 120.56, 120.06, 119.94, 55.52, 40.49, 31.64, 29.88, 24.03, 22.74, 14.19. Elemental analysis: Calcd for C₇₂H₇₆N₂S₅: C, 76.55, H, 6.78, N, 2.48. Found: C, 76.24, H, 6.63, N, 2.47. TOF MS AP+ (m/z): M⁺ calcd for C₇₂H₇₇N₂S₅ 1129.4690, found 1129.4694. Mp: 212-213 °C.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The TGA and DSC data were acquired using a Mettler Toledo TGA/DSC 3+ apparatus in the temperature ranging from 30 °C to 800 °C under argon flow at 10 °C min⁻¹ heating rate.

Calculations

To assist the interpretation of the experimental results, we have performed density functional theory (DFT) and time-dependent density functional theory (TD-DFT) simulations with Tamm-Dancoff approximation (TDA) using the ORCA 4.2.1 quantum chemistry software.²⁻⁴ All molecular orbital (MO) iso surfaces were visualised using Gabedit 2.5.0⁵ or Avogadro 1.2.0.^{6,7}

Geometry optimisations in the ground state (S₀) and single point energy (SPE) calculations were performed at the CAM-B3LYP⁸/def2-SVP⁹ level of theory, using CPCM for CH₂Cl₂ in all cases. All calculations were performed using a dense grid (Grid6), and *very tight* geometry and SCF convergence. Frequency calculations found all respective optimised geometries to be local energetic minima.

UV-Vis absorption and Fluorescence spectroscopy

Optical spectroscopy studies were performed using UV-Vis Hewlett Packard spectrophotometer 8453 and Camlin Modular Fluorescence Spectrometer fluoroSENS Pro-11. Fluorescence quantum yield in solution as well as solid-state was determined using a direct method by a Camlin Modular Fluorescence Spectrometer fluoroSENS Pro-11 with an integrating sphere. UV-Vis and Fluorescence spectra were collected in dichloromethane (DCM; HPLC grade, Sigma Aldrich) and toluene (anhydrous

99,8%, Sigma Aldrich) at $C = 10^{-6}$ or 10^{-7} M. Fluorescence quantum yields were determined for 10^{-7} M solutions using an excitation wavelength of 420 nm. Time-resolved decays in solution were recorded with a Horiba DeltaFlex TCSPC system using a 405 nm DeltaDiode light source.

To analyse the fluorescence properties of investigated compounds in a non-polar matrix (Zeonex 480 Cyclo Olefin Polymer, Zeon) two solutions in toluene have been prepared for each of the monomers. The films were obtained by mixing a 2 mg mL^{-1} solution of the emitter with a 200 mg mL^{-1} solution of Zeonex in toluene to give a weight ratio of 1:99 (analyte:host). The mixture was then drop-cast onto a sapphire substrate and dried on a hotplate at 80°C for 15 minutes.

OLED devices

OLEDs were fabricated by spin-coating/evaporation hybrid method. Patterned pre-cleaned indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of $20\ \Omega/\text{sq}$ and ITO thickness of 100 nm were used. The substrates were first washed with acetone and then sonicated in acetone and isopropanol for 15 min each time. Substrates were then dried using an air gun and transferred into an oxygen plasma generator for 6 min at full power.

The hole injection layer (PEDOT Al4083), hole transport/electron blocking layer (PVKH), and emitting layer (PVK:PBD + emitter) were spin-coated, whereas the electron transport layer (TPBi) and cathode (LiF/Al) were evaporated. 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene, (TPBi, LUMTEC); poly(*N*-vinylcarbazole), $M = 1.1 \times 10^6$ Da (PVKH, Sigma Aldrich); poly(*N*-vinylcarbazole), $M = 90000$ Da (PVK, Acros Organics); 5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, (PBD, Sigma Aldrich); LiF (99.995%, Sigma Aldrich); and Aluminium pellets (99.9995%, Lesker).

The hole injection layer (PEDOT Al4083, Ossila) was spin-coated and annealed on a hotplate at 120°C for 15 min to give a 30 nm film. PVKH layer was deposited from chloroform:chlorobenzene (95:5 v/v) solution (3 mg mL^{-1}) to give a 10 nm layer. The emitting layer was deposited from a toluene solution (the total concentration of PVK+PBD was 10 mg mL^{-1}). The luminescent dopants were dissolved in a solution of blend host to obtain a final 5% (w/w) concentration in the emitting layer. All solutions were filtrated directly before use with a PVDF (organic solvents) or PES (PEDOT Al4083) syringe filter with a $0.45\ \mu\text{m}$ pore size. The electron transport (TPBi) and electron injection (LiF) layers as well as the cathode (Al) were thermally evaporated. Thermally deposited layers were produced using Kurt J. Lesker Spectros II deposition system at 10^{-6} mbar base pressure. All organic materials and aluminium were deposited at a rate of $1\ \text{Å s}^{-1}$. The LiF layer was deposited at a rate of $0.1\text{--}0.2\ \text{Å s}^{-1}$. Characterisation of OLED devices was conducted in a 10 inch integrating sphere (Labsphere) connected to a Source Measure Unit (SMU, Keithley) and coupled with a spectrometer USB4000 (Ocean Optics). Further details are available in reference.¹ Devices of $4 \times 2\text{ mm}$ pixel size were used for the study.

Atomic Force Microscopy (AFM)

The Nanosurf CoreAFM microscope working in a tapping mode with the AFM HQ:NSC18/Al BS (MikroMasch) probe (resonance frequency 75 kHz, force constant $2.8\ \text{Nm}^{-1}$) was used.

Electrochemistry and spectroelectrochemistry

Electrochemical analyses were performed using an Eco Chemie AUTOLAB model M101 potentiostat. The typical three-electrode cell was used. A platinum disk electrode (diameter: 1 mm) was used as a working electrode, platinum coil was employed as an auxiliary electrode, and silver wire was used as a pseudo reference electrode of which potential was calibrated versus ferrocene/ferrocinium redox couple. In the case of reduction processes, electrochemical analyses were conducted with solutions purged with argon for *ca.* 15 min before each measurement, while the measurement itself was conducted under inert argon gas flow. UV-Vis spectroelectrochemical measurements were carried out using UV-Vis Hewlett Packard spectrophotometer 8453 coupled with OMNI potentiostat in 2 mm quartz cell equipped with the ITO as working electrode which was previously covered with the film obtained using CV technique in standard three-electrode set up described above (but instead of platinum, ITO working electrode was used), platinum spiral as an auxiliary electrode and silver wire as a pseudo reference electrode. In all electrochemical and spectroelectrochemical measurements, 0.1M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 ; TCl>98%) in dichloromethane (DCM; HPLC grade, Sigma Aldrich) was used as supporting electrolyte. In the case of electrochemical investigations of studied compounds (including electrochemical polymerization), the analyses were performed for 0.5 mM or 1.0 mM solutions prepared in supporting electrolytes. All investigated polymeric films were obtained electrochemically using CV techniques and three-electrode cell. Electrochemical and spectroelectrochemical characterization of obtained polymeric films were registered in the monomer-free electrolyte.

Electrochromism

p(Th-FBTD) and **p(2Th-FBTD)** thin layers for measurement of electrochromic properties were electrodeposited on ITO electrode by electrochemical oxidation using cyclic voltammetry. Monomer solutions at a concentration 0.5 mM in 0.1 M

Bu₄NPF₆/DCM as supporting electrolyte was used. The polymer layers were washed and stored for at least 12 hours in CH₂Cl₂ to remove residual monomers. Electrochromic measurement was made in monomer-free 0.1 M Bu₄NPF₆/ CH₂Cl₂. Photos were recorded with Digital Camera Canon DS126271. Modular spectrometer StellarNet equipped with a reflectance probe, Ocean Optics QE65000, NIRQuest512 diode array spectrometer, and Autolab PGSTAT100N potentiostat were used to collect chronocoulograms and the associated changes in absorbance electrodeposited layers recorded during electrochromic switching.

Results

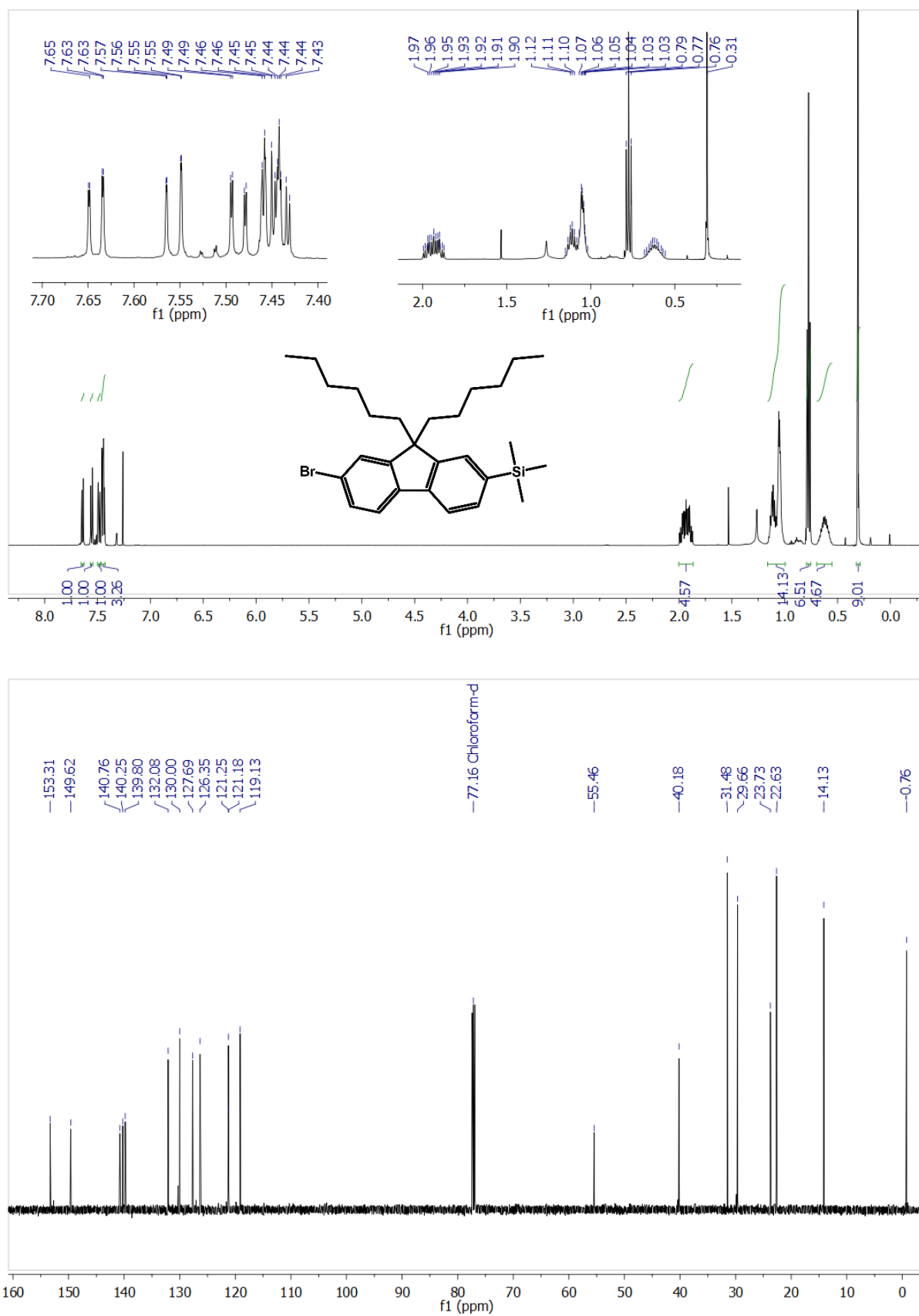


Figure S1. ^1H NMR and ^{13}C NMR spectra (CDCl_3) of BrFTMS.

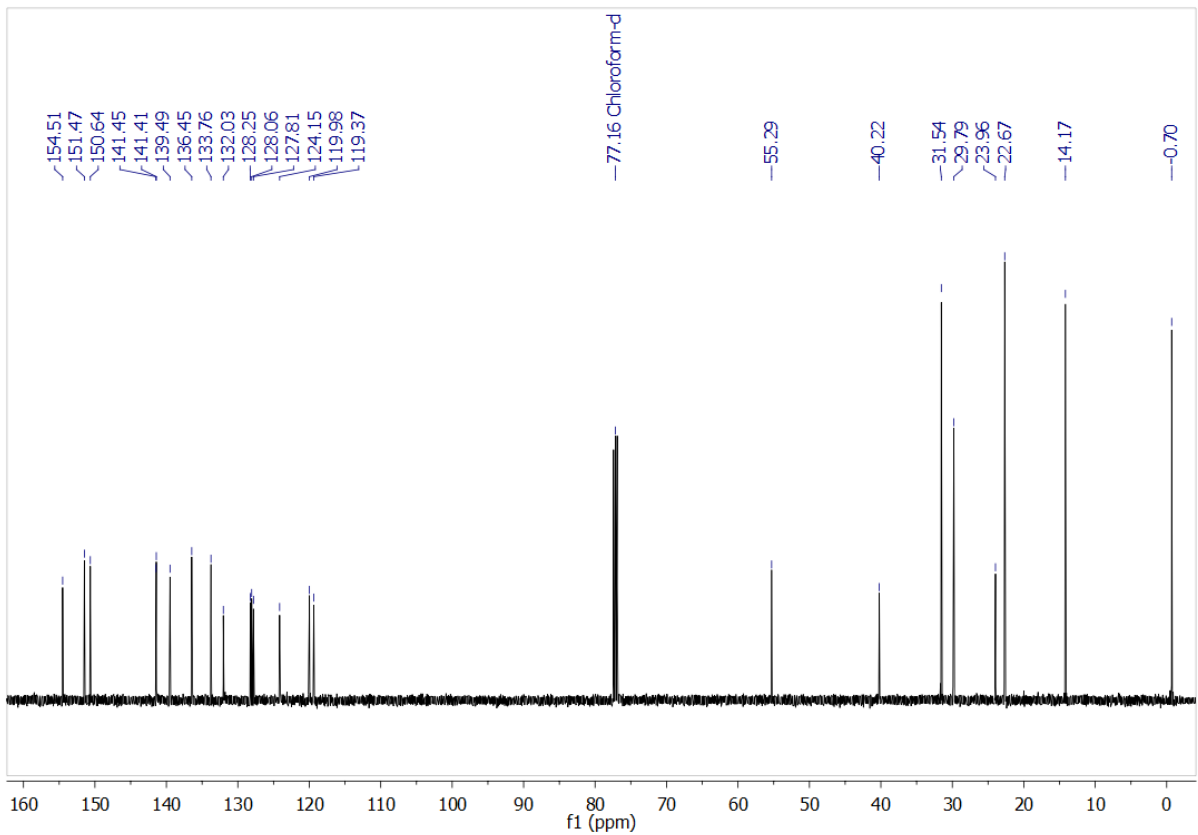
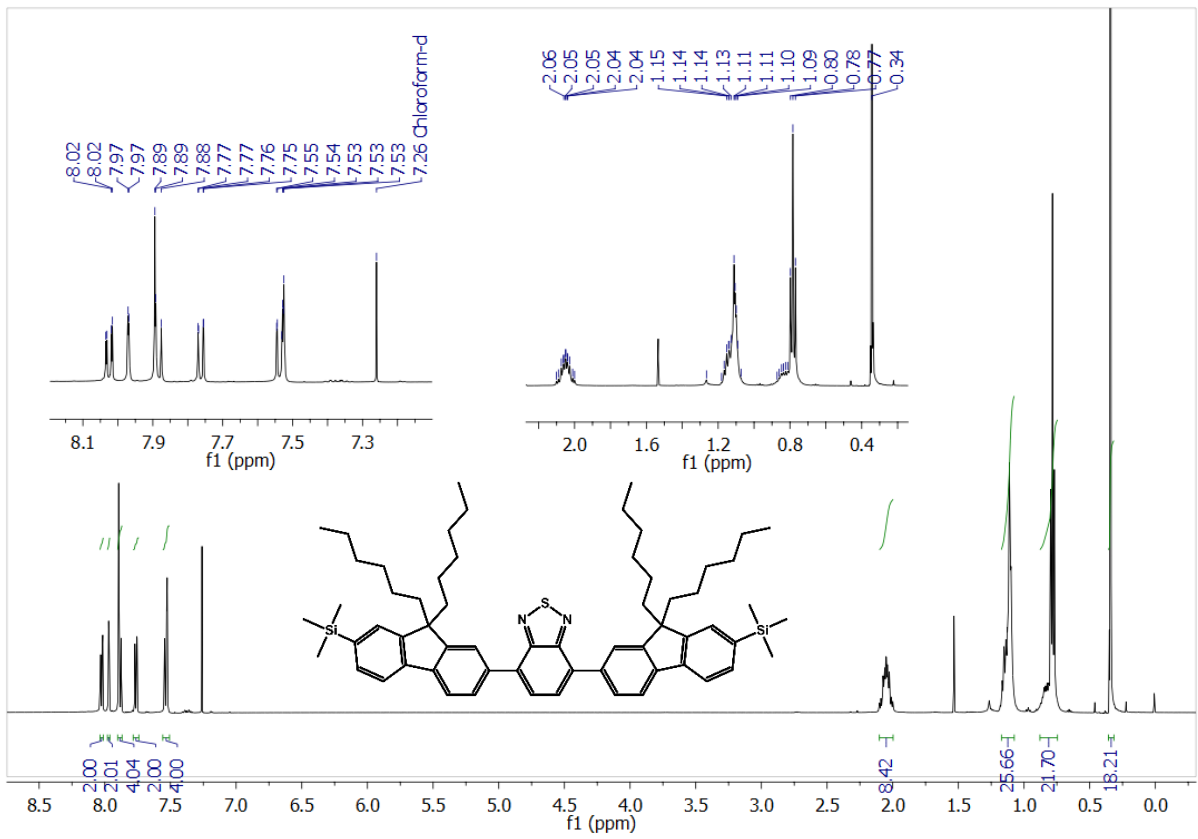


Figure S2. ¹H NMR and ¹³C NMR spectra (CDCl₃) of TMS-FBTD.

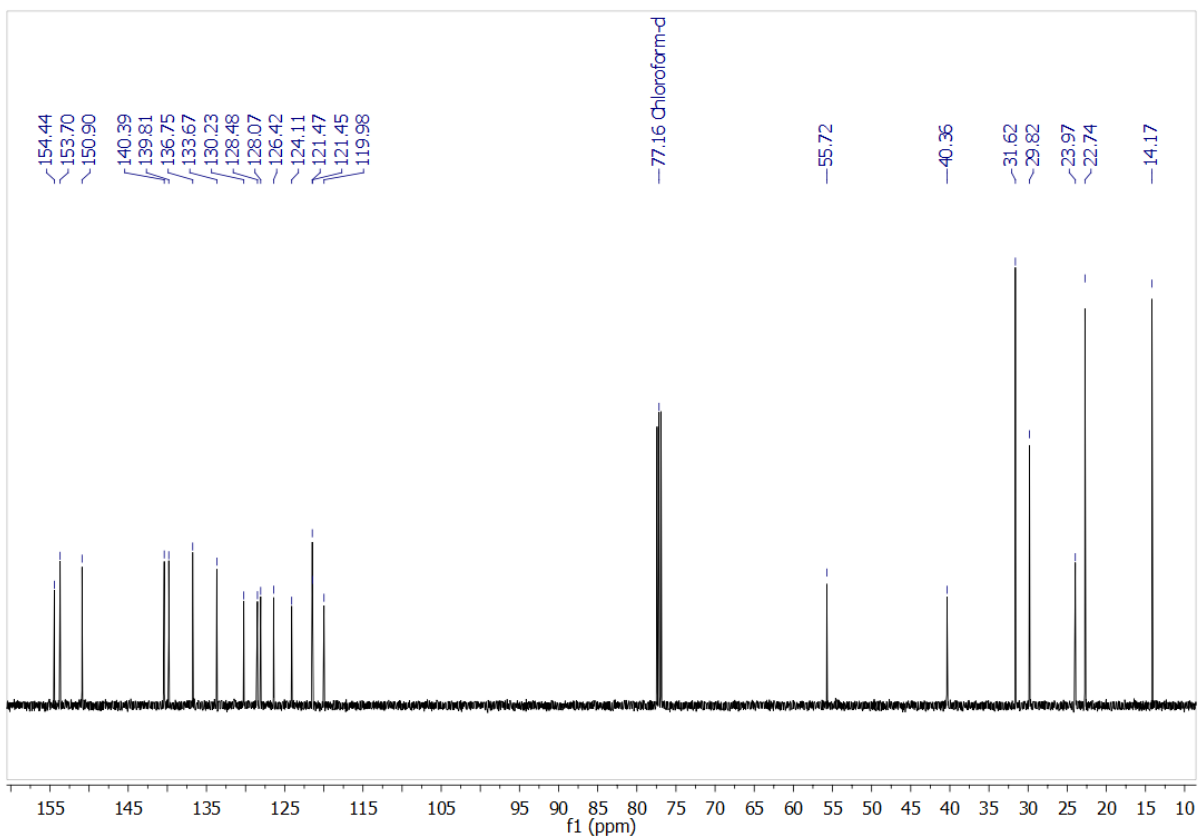
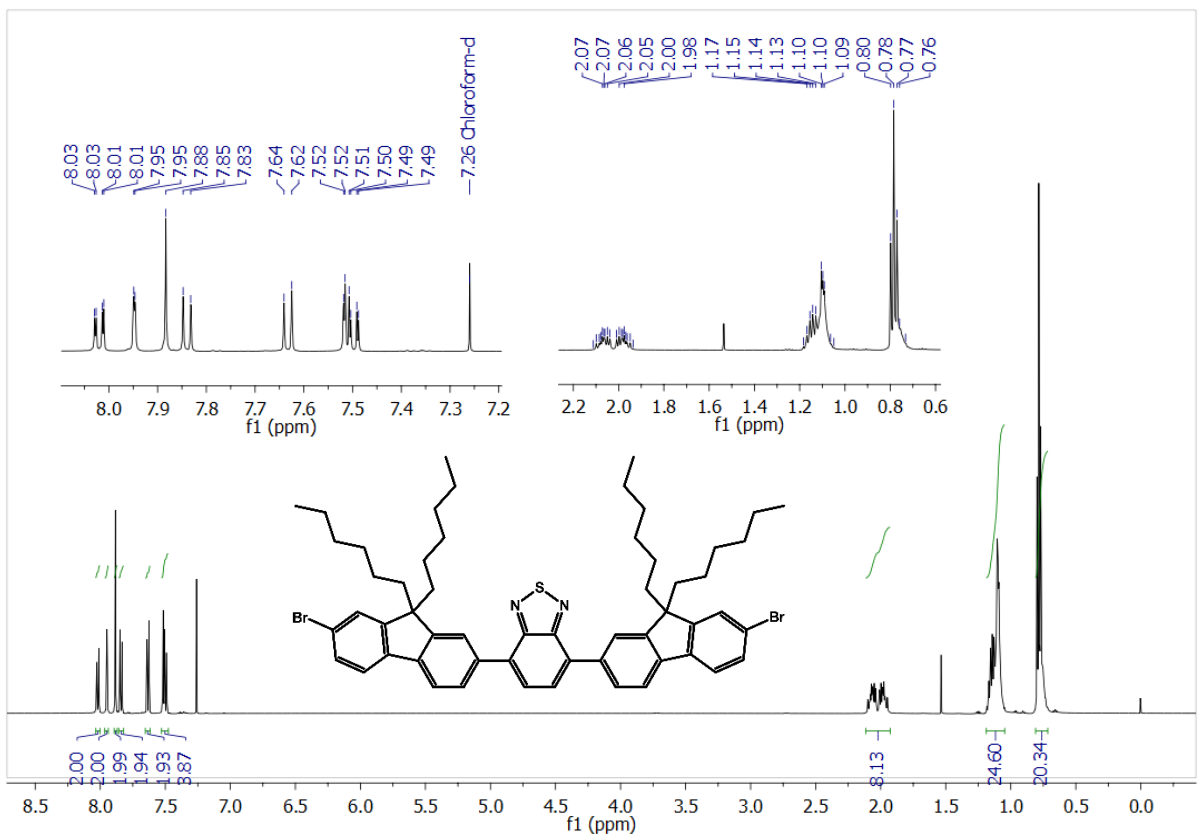


Figure S3. ¹H NMR and ¹³C NMR spectra (CDCl₃) of Br-FBTD.

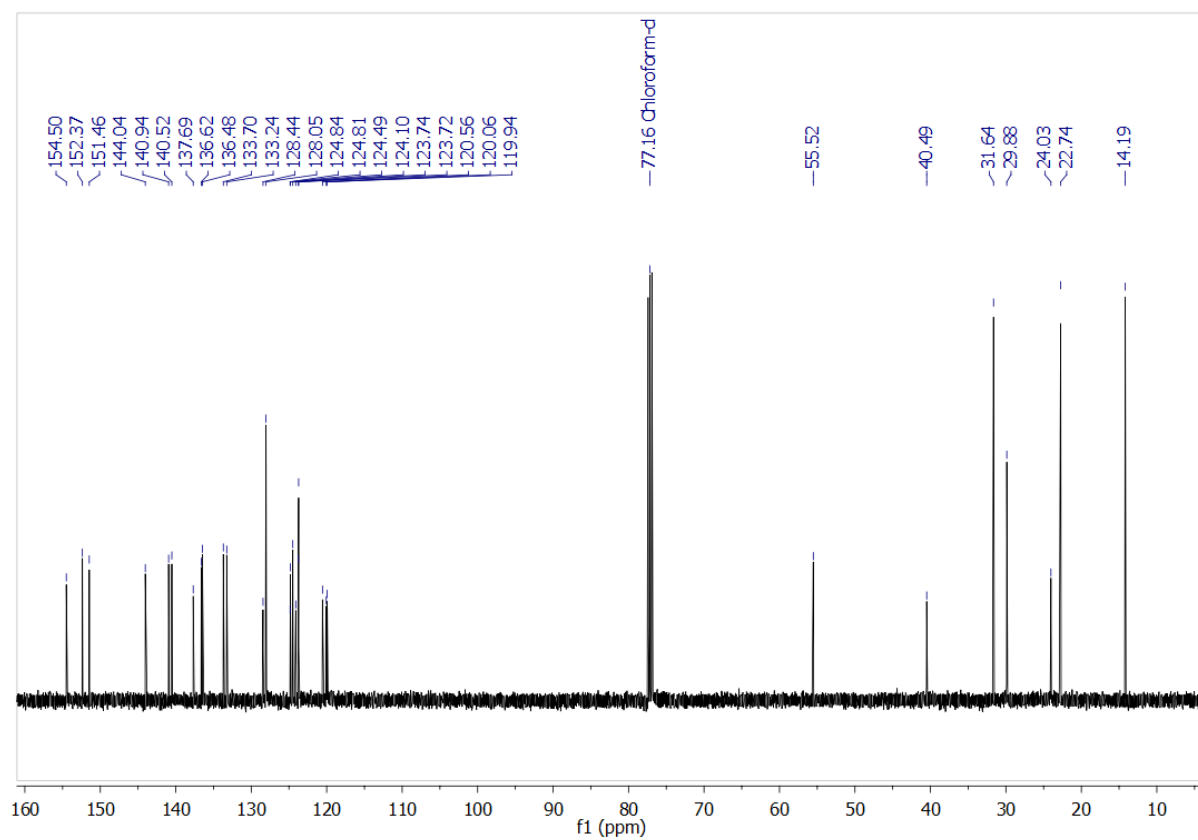
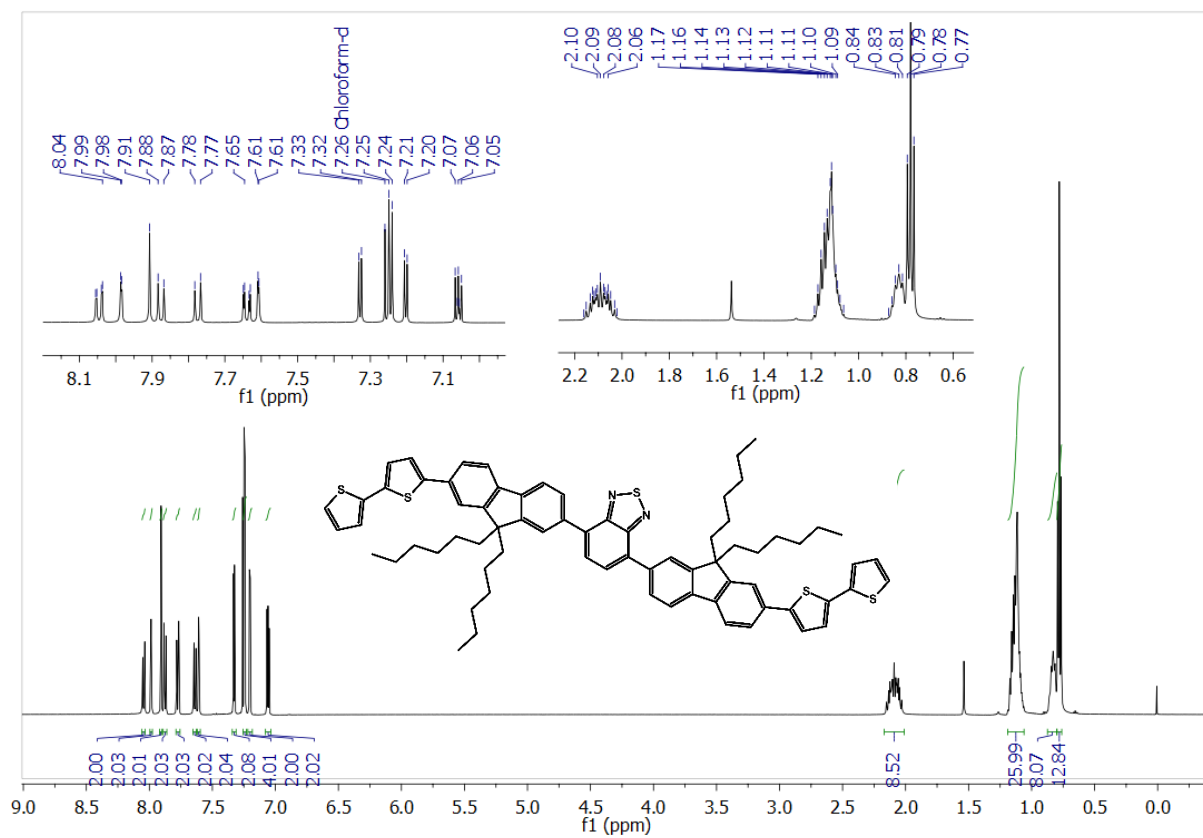


Figure S5. ¹H NMR and ¹³C NMR spectra (CDCl₃) of 2Th-FBTD.

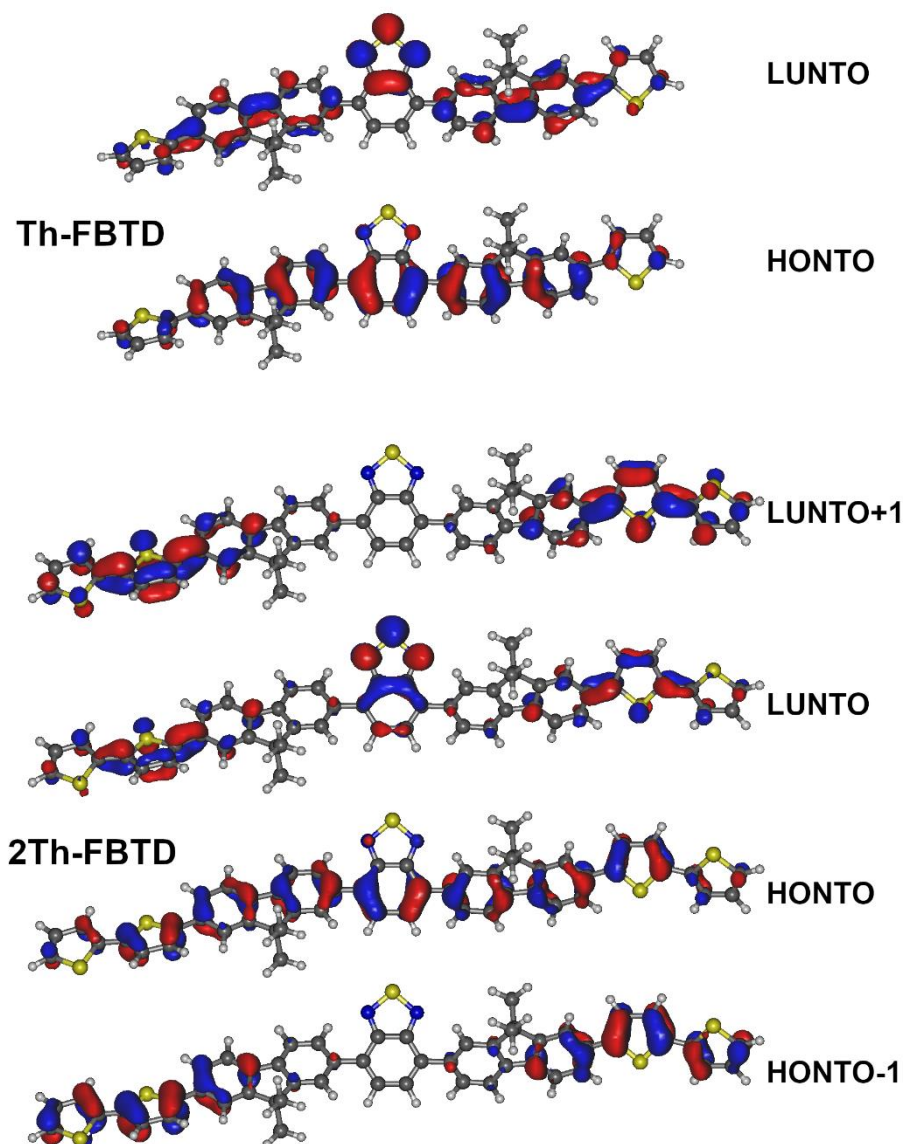


Figure S6. The highest occupied and lowest unoccupied natural transition orbitals (NTOs): HONTO and LUNTO, respectively, for the S_3 state, calculated at the ground state (S_0) geometry of **Th-FBTD** and **2Th-FBTD**, using the CAM-B3LYP/def2-SVP/CPCM(CH_2Cl_2) level of theory. HONTO-1 \rightarrow LUNTO+1 transition significantly (32%) contributes to the S_3 in **2Th-FBTD**, thus the respective NTOs are also displayed.

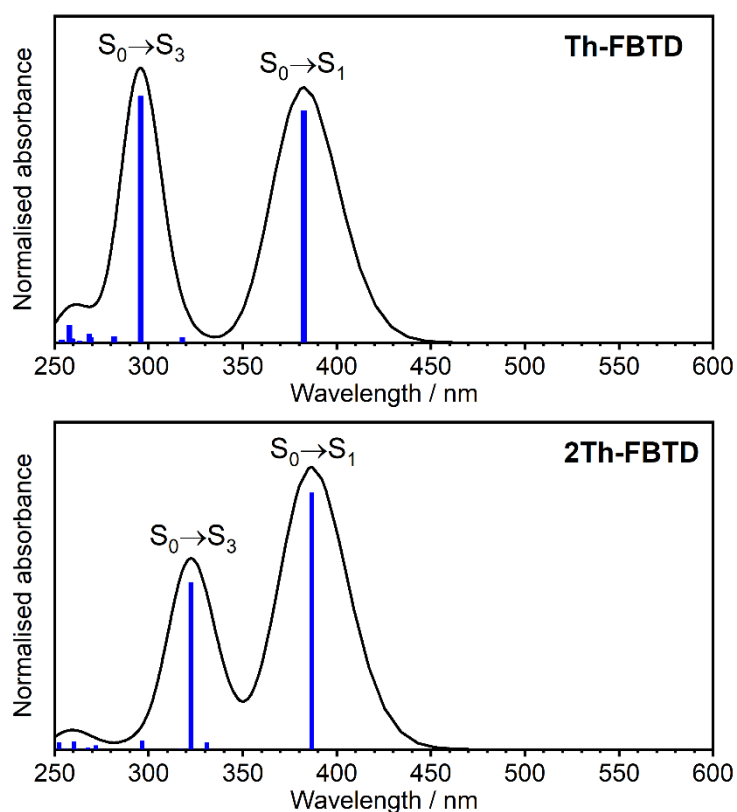


Figure S7. Absorption spectra of **Th-FBTD** and **2Th-FBTD** calculated using the CAM-B3LYP/def2-SVP/CPCM(CH₂Cl₂) level of theory. The spectra are modelled with Gaussian curves (FWHM = 0.35 eV).

Table S1. Excitation energies of **Th-FBTD** calculated at the CAM-B3LYP/def2-SVP/CPCM(CH₂Cl₂) level of theory.

State	Energy, eV	f_{osc}	Transition
S ₁	3.241	1.625	HOMO→LUMO (81%); HOMO-2→LUMO (11%)
S ₂	3.900	0.037	HOMO-1→LUMO (70%); HOMO→LUMO+2 (10%)
S ₃	4.193	1.725	HOMO→LUMO+1 (58%); HOMO-1→LUMO+2 (23%)
T ₁	2.225	-	HOMO→LUMO (52%); HOMO-2→LUMO (29%)
T ₂	2.870	-	HOMO→LUMO+2 (34%); HOMO-1→LUMO+1 (27%); HOMO-1→LUMO (13%)
T ₃	2.908	-	HOMO-1→LUMO+2 (35%); HOMO→LUMO+1 (27%)

Table S2. Excitation energies of **2Th-FBTD** calculated at the CAM-B3LYP/def2-SVP/CPCM(CH₂Cl₂) level of theory.

State	Energy, eV	f_{osc}	Transition
S ₁	3.207	2.632	HOMO→LUMO (63%); HOMO-2→LUMO (20%)
S ₂	3.747	0.070	HOMO→LUMO+1 (33%); HOMO-1→LUMO (30%); HOMO-1→LUMO+2 (30%)
S ₃	3.846	1.716	HOMO→LUMO+2 (44%); HOMO-1→LUMO+1 (31%); HOMO-2→LUMO (30%)
T ₁	2.223	-	HOMO→LUMO (36%); HOMO-2→LUMO (35%); HOMO-4→LUMO (11%)
T ₂	2.498	-	HOMO→LUMO+1 (33%); HOMO-1→LUMO+2 (31%)
T ₃	2.516	-	HOMO-1→LUMO+1 (36%); HOMO→LUMO+2 (29%)

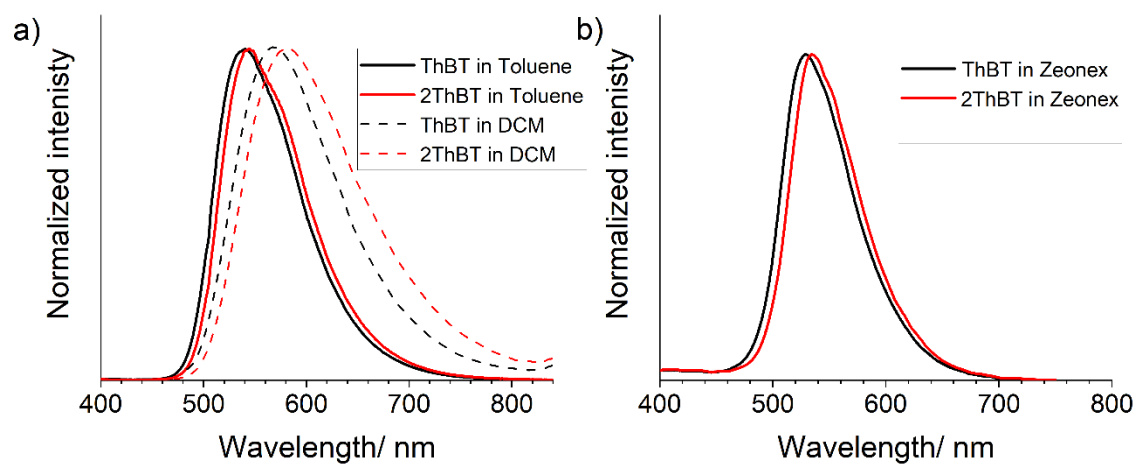


Figure S8. Photoluminescence spectra of **Th-FBTD** and **2Th-FBTD** in degassed toluene (continuous lines) and DCM (dashed lines) solution ($c = 10^{-6}$ M) (a) and in Zeonex matrix (b).

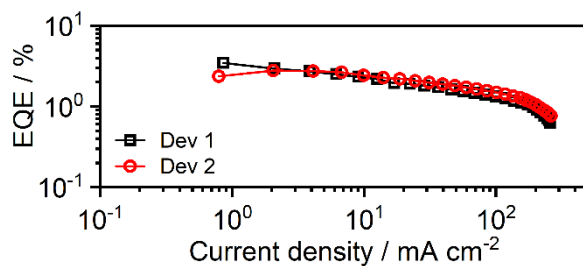


Figure S9. EQE-current density characteristics of OLED devices 1 and 2.

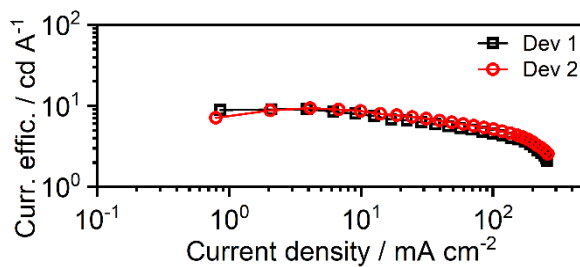


Figure S10. Current efficiency-current density characteristics of OLED devices 1 and 2.

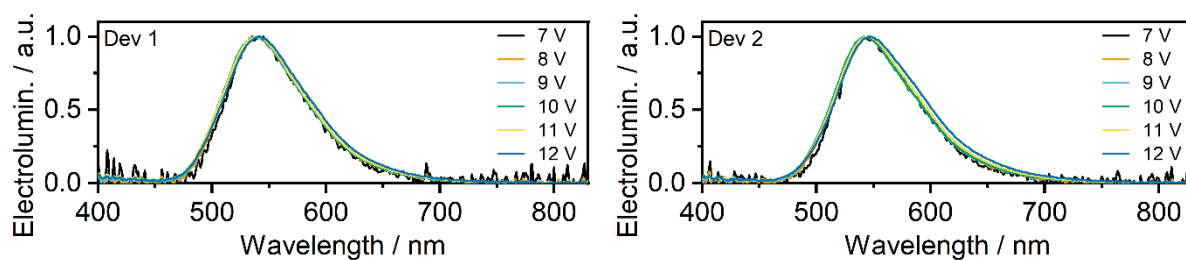


Figure S11. Electroluminescence spectra of devices 1 and 2 in function of applied voltage bias.

References:

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