

Impact of Tailoring BTBT-based Hole-Transporting Materials on Perovskite Photovoltaics under Indoor Illumination

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References

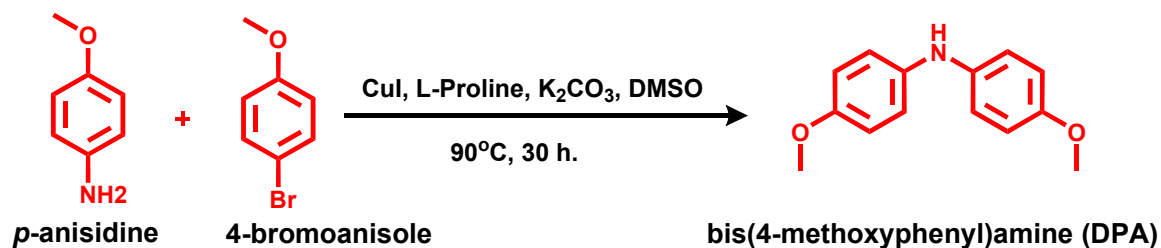
SI 1. General information

All the chemicals used in the present study were purchased from chemical vendors (TCI, Alfa Aesar, Sigma Aldrich, etc.) and were used without subsequent purification. Before use, all solvents were distilled by standard methods using suitable drying agents such as Calcium hydride. Thin layer chromatography was analyzed on Merck silica gel 60 F₂₅₄, and UV light (254 nm, 366 nm) was used to detect the results. Column chromatography and flash column chromatography were carried out on Merck silica gel with a mesh size of 100–200. The ¹H NMR spectrum was analyzed at 400 MHz on a Bruker Avance III spectrometer, and the ¹³C NMR spectrum was recorded at 500 MHz on the same instrument. The chemical shift was expressed in parts per million (ppm) and was relative to tetramethylsilane (TMS). All NMR experiments were carried out at 25 °C, and deuterated solvents purchased from Sigma Aldrich were used as received. High-resolution mass spectrometry was carried out using an ESI-ToF mass spectrometer Bruker maXis 4G UHR MS/MS or a Bruker ultrafleXtreme (nitrogen UV-laser, 337 nm) instrument. UV-Vis. absorption spectra and photoluminescence (PL) spectra were performed using a Shimadzu UV-1800 spectrophotometer and a Fluorolog-3 spectrophotometer, respectively. The samples were measured in a 10mm×10mm quartz cuvette. Cyclic voltammetry (CV) was recorded on a BAS100 electrochemical analyzer by using a conventional three-electrode system. A 0.1 M solution of Bu₄NPF₆ in dry distilled dichloromethane was used as the supporting electrolyte, with ferrocenium-ferrocene (Fc/Fc⁺) identified as the internal standard, and the scan rate was 100 mV s⁻¹. The highest occupied molecular orbital (HOMO) energy levels (eV) were calculated by using the following formula: $-[4.8 + (E_{\text{oxi}} - E_{1/2(\text{Fc}/\text{Fc}^+)})]$ eV and the lowest unoccupied molecular orbital (LUMO) energy levels (eV) were inferred from HOMO and the energy gap (E_g). We used a three-electrode system involving a Pt-gauze as a working electrode, a Pt-wire as a counter electrode, and a silver/silver chloride wire as the pseudo reference electrode.

SI 2. Experimental procedures

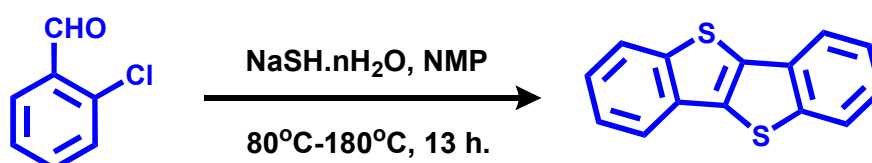
The general scheme for the synthesis of all intermediates and the final product was adapted from the previous reports. Buchwald-Hartwig's amination reaction carried out the final step of the scheme.

Bis(4-methoxyphenyl)amine (DPA):



In a 100 ml round-bottom flask, a mixture of 4-bromoanisole (1.0 g, 5.3 mmol) and p-anisidine (0.98 g, 8.0 mmol) in 50 ml of dimethylsulfoxide was stirred under a nitrogen atmosphere. K₂CO₃ (1.47 g, 10.7 mmol), *L*-proline (0.12 g, 1.0 mmol), and CuI (0.10 g, 0.5 mmol) were introduced into the reaction and refluxed at 90°C for 30 hours. After the completion of the reaction, the crude was poured into 200 ml of ice water and extracted with ethyl acetate. The combined organic layer was dried over sodium sulphate, and the solvent was concentrated on a rota-evaporator. The crude was purified on silica gel column chromatography using ethylacetate: hexane (1:20) as an eluent to obtain DPA as a white crystalline solid with a 66% yield (0.800 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 6.93 (d, *J* = 8.7 Hz, 4H), 6.82 (d, *J* = 8.9 Hz, 4H), 5.28 (s, 1H), 3.78 (s, 6H); ¹³C NMR (500 MHz, CDCl₃): δ [ppm] = 154.26, 137.98, 119.57, 114.75, 55.68.

Benzo[b]benzo[4,5]thieno[2,3-d]thiophene (BTBT) :

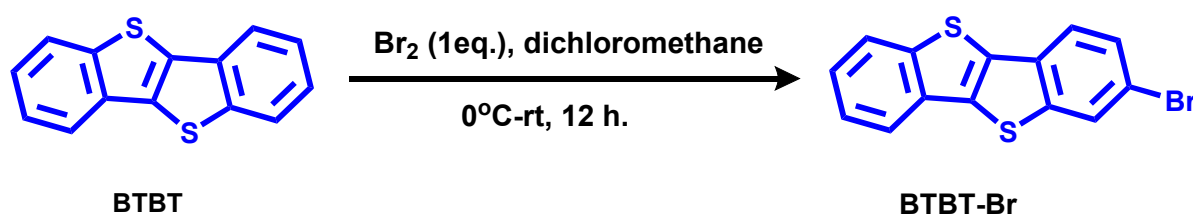


2-chlorobenzaldehyde

**benzo[b]benzo[4,5]thieno[2,3-d]thiophene
(BTBT)**

In a 100 ml two-neck round bottom flask, a solution of sodium hydrosulphide hydrate (10 g, 71.5 mmol) in NMP (50 ml) was purged under the protection of nitrogen for 15 minutes until the colour of the solution turned green. 2-chlorobenzaldehyde (12 g, 215 mmol) was added, which turned the colour of the solution yellow. The solution was heated at 80°C for 1 hour. When the solution turned from yellow to black, the mixture was refluxed at 180°C for another 10 hours. The resulting reaction mixture was poured into a 50 ml saturated aqueous ammonium chloride solution and filtered. The residue was washed with water and acetone, respectively, and dried under vacuum to obtain BTBT as a yellow solid with a 32% yield (6.56 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.99 – 7.83 (m, 4H), 7.42 (dtd, J = 16.4, 7.3, 1.2 Hz, 4H); ¹³C NMR (500 MHz, CDCl₃): δ [ppm] = 142.28, 133.46, 133.13, 125.04, 124.91, 124.07, 121.64.

2-bromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene (BTBT-Br) :



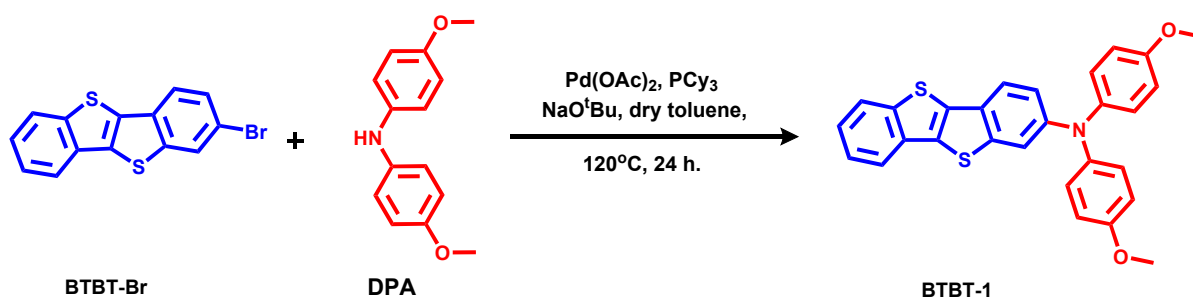
BTBT

BTBT-Br

In a 100 ml two-neck round bottom flask fitted with a condenser, a magnetic bead, and a dropping funnel, a solution of BTBT (400 mg, 1.66 mmol) in dichloromethane (40 ml) was stirred at 0°C. Bromine (0.12 ml, 2.50 mmol) and dichloromethane (20 ml) were prepared in a dropping funnel and added dropwise to the solution at this temperature. The mixture was stirred for 12 hours at room temperature. The resulting reaction mixture was quiche with saturated

aqueous sodium bisulphate solution and extracted with dichloromethane. The crude was purified by column chromatography using hexane as the eluent to get BTBT-Br as a white solid with a 47% yield (0.250 g). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ [ppm] = 8.03 (d, J = 1.7 Hz, 1H), 7.91 – 7.89 (m, 1H), 7.86 – 7.84 (m, 1H), 7.71 – 7.69 (m, 1H), 7.55 – 7.52 (m, 1H), 7.47 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H); $^{13}\text{C NMR}$ (500 MHz, CDCl_3): δ [ppm] = 143.68, 142.34, 133.80, 132.96, 132.85, 131.91, 128.30, 126.53, 125.35, 125.07, 124.09, 122.56, 121.65, 118.59.

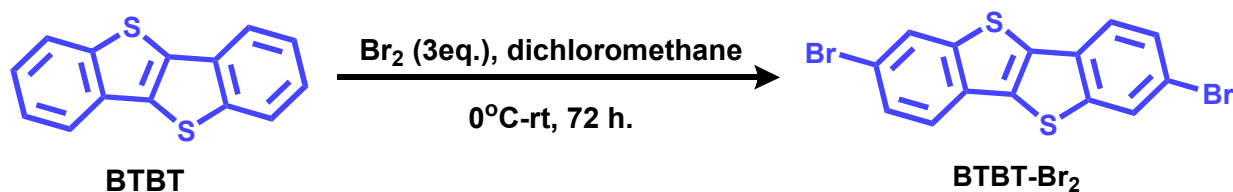
***N,N*-bis(4-methoxyphenyl)benzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophen-2-amine (BTBT-1) :**



Under the flow of nitrogen, BTBT-Br (200 mg, 0.62 mmol) and DPA (215 mg, 0.94 mmol) were added to a 50 ml round bottom flask containing 15 ml of dry toluene. After stirring at room temperature for 20 minutes, sodium tert-butoxide (180 mg, 1.88 mmol), tricyclohexylphosphine (20 mg, 0.05 mmol), and palladium acetate (6 mg, 0.02 mmol) were added to the flask sequentially and kept at 120°C for 24 hours. After the completion of the reaction, crude was poured into water and extracted with ethyl acetate. The organic layer was dried over sodium sulphate and concentrated using a rota evaporator. The crude was purified by column chromatography using 5% ethyl acetate in hexane as eluent to get the desired product as a colourless solid with a 53% yield (150 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ [ppm] = 7.80 (d, J = 8.0 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.57 (dd, J = 8.5, 4.0 Hz, 1H), 7.36 (dd, J = 7.2, 1.0 Hz, 1H), 7.32 (dd, J = 4.6, 1.6 Hz, 2H), 7.27 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.04 – 7.01 (m, 4H), 6.80 – 6.77 (m, 4H), 3.74 (s, 6H); $^{13}\text{C NMR}$ (500 MHz, CDCl_3): δ [ppm] = 56.03, 141.83, 140.98, 133.44, 126.58, 124.82, 124.33, 123.96, 121.74, 121.11, 119.66, 115.16,

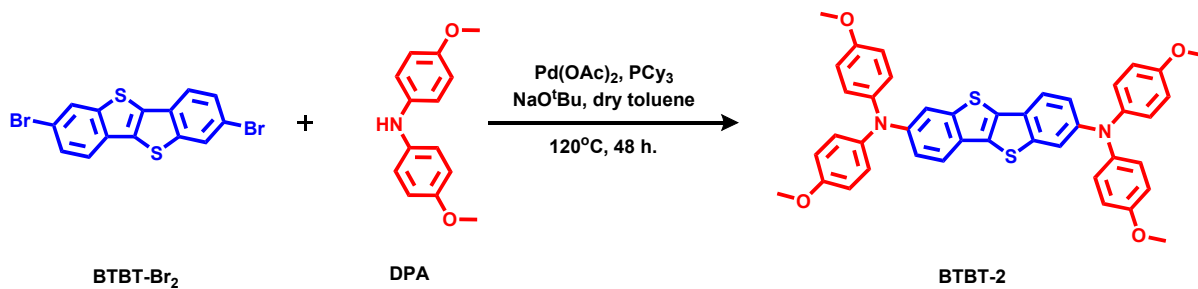
114.85, 55.55; **HRMS (DCM:MeOH):** m/z [calculated neutral mass for $C_{26}H_{21}NO_2S$] = 447.101 $[M]^+$ and m/z (observed) = 448.109 $[M+H]^+$

2,7-dibromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene (BTBT-Br₂):



In a 50 ml two-neck round bottom flask fitted with a condenser, a magnetic bead, and a dropping funnel, a solution of BTBT (1.0 g, 4.1 mmol) in 40 ml dichloromethane stirred at 0°C. Parallely, 0.64 ml of bromine (12.5 mmol) in 20 ml of dichloromethane was prepared in a dropping funnel and added dropwise to the round bottom flask at this temperature. The mixture was stirred for 72 hours at room temperature, and the resulting reaction mixture was quenched with a saturated aqueous sodium bisulphate solution and extracted with dichloromethane. The resulting crude was purified by column chromatography using hexane as eluent, with a yield of 42% (0.700 g). The compound is almost insoluble in most organic solvents and is unable to be characterized.[1]

N²,N²,N⁷,N⁷-tetrakis(4-methoxyphenyl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2,7-diamine (BTBT-2) :



In a 50 ml single neck round bottom flask, BTBT-Br₂ (200 mg, 0.62 mmol) and DPA (426 mg, 1.86 mmol) were mixed in 25 ml of dry toluene. After 20 minutes of stirring under the

protection of nitrogen at room temperature, sodium tert-butoxide (360 mg, 3.76 mmol), tricyclohexylphosphine (20 mg, 0.05 mmol), and palladium acetate (6 mg, 0.02 mmol) were added to the flask sequentially and refluxed at 120°C for 48 hours. After the completion of the reaction, the crude was poured into water and extracted with ethyl acetate. The organic layer was dried over sodium sulphate and concentrated using a rota evaporator. The crude was purified by column chromatography using 5% ethyl acetate in hexane as eluent to obtain the desired product as a colourless white, fluorescent solid with a 52% yield (130 mg). **¹H NMR (400 MHz, CDCl₃):** δ [ppm] = 7.55 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 2.0 Hz, 2H), 7.07 (d, J = 8.9 Hz, 8H), 7.05 (d, J = 2.1 Hz, 2H), 6.84 (d, J = 9.0 Hz, 8H), 3.80 (s, 12H); **¹³C NMR (500 MHz, CDCl₃):** δ [ppm] = 155.93, 154.91, 143.35, 141.93, 126.43, 123.67, 123.49, 121.23, 119.84, 114.79, 114.43, 55.54; **HRMS (DCM:MeOH):** m/z [calculated neutral mass for C₂₆H₂₁NO₂S] = 694.195 [M]⁺ and m/z (observed) = 694.194 [M]⁺

SI 3. A simple analysis of the relative costs of BTBT-1 and BTBT-2

Recently, Petrus et al. applied the model to evaluate the cost of hole transport materials.[2]

The required amount of reactants, reagents, catalysts, and solvents to synthesize 1 gram of BTBT-1 and BTBT-2 was determined for each synthesis step and published.

Table S1. Materials quantities and cost for the synthesis of DPA.

Chemicals/company	Price (\$) (kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g/ml)	Solvent (in ml)	Workup (in g or ml)	
p-Anisidine/Alfa Aeser	165 \$/kg	0.98			0.161
4-bromoanisole/ TCI	146 \$/kg	1.00			0.146
Copper iodide/TCI	369 \$/kg	0.10			0.036
L-Proline/Spectrochem	97 \$/kg	0.12			0.011
Pottasiumcarbonate/Finar	20 \$/kg	1.47			0.029
DMSO/Finar	70 \$/L		50.00		3.500
Silica gel (100-200 mesh)/Merck	17 \$/kg			50.00 g	0.850
Hexane/Finar	18 \$/L			250.00 ml	4.500
Ethylacetate/Finar	9 \$/L			65.00 ml	0.585
Total					9.818

DPA: Yield, 66%, 0.800 g, 9.818 \$

The cost of 1 g is 12.272 \$

Table S2. Materials quantities and cost for the synthesis of BTBT.

Chemicals/company	Price (\$) (kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	

o-chlorobenzaldehyde/ Spectrochem	31 \$/kg	12.00			0.372
Sodiumhydrosulfidehydrate/ Sigma Aldrich	97 \$/kg	10.00			1.158
NMP/Sigma Aldrich	108 \$/L		50.00		5.400
Total					6.930

BTBT: Yield, 32%, 6.56 g, 6.93 \$

The cost of 1 g is 1.056 \$

Table S3. Materials quantities and cost for the synthesis of BTBT-Br.

Chemicals/company	Price (\$ (kg or L))	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
BTBT	1056 \$/kg	0.40			0.422
Bromine/Finar	282 \$/L		0.12		0.033
Dichloromethane AR/Finar	17 \$/L		60.00		1.020
Silicagel(100-200 mesh)/Merck	17 \$/kg			30.00 g	0.510
Sodium-bisulphate/Finar	15 \$/kg			4.00 g	0.059
Hexane/Finar	18 \$/L			100.00 ml	1.800
Total					3.844

BTBT-Br: Yield, 47%, 0.250 g, 3.844 \$

The cost of 1 g is 15.370 \$

Table S4. Materials quantities and cost for the synthesis of BTBT-1.

Chemicals/company	Price (\$) (kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
BTBT-Br	15370 \$/kg	0.200			3.074
DPA	12272 \$/kg	0.215			2.630
Sodium <i>tert</i> -butoxide/TCI	259 \$/kg	0.180			0.046
Palladiumacetate/TCI	298 \$/g	0.006			0.298
Tricyclohexylphosphine/TCI	34 \$/g	0.020			0.680
Toluene/Finar	11 \$/L		15.00		0.165
Silicagel(100-200 mesh)/Merck	17 \$/kg			50.00 g	0.850
Hexane/Finar	18 \$/L			200.00	3.600
Ethylacetate/Finar	9 \$/L			60.00	0.540
Total					11.883

BTBT-1: Yield, 53%, 0.150 g, 11.883 \$

The cost of 1 g is 79.22s \$

This is about (1/7)th of the costs of purified Spiro-OMeTAD (565 \$/g, high purity, SIGMA/Merck)

Table S5. Materials quantities and cost for the synthesis of BTBT-Br₂.

Chemicals/company	Price (\$) (kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
BTBT	1056 \$/kg	1.00			1.056

Bromine/ Finar	282 \$/L		0.64		0.180
Dichloromethane AR/Finar	17 \$/L		60.00		1.020
Silicagel(100-200 mesh)/Merck	17 \$/kg			50.00 g	0.850
Sodium-bisulphate/Finar	15 \$/kg			4.00 g	0.059
Hexane/Finar	18 \$/L			200.00 ml	3.600
Total					6.765

BTBT-Br₂: Yield, 42%, 0.700 g, 6.765 \$

The cost of 1 g is 9.66 \$

Table S6. Materials quantities and cost for the synthesis of BTBT-2.

Chemicals/company	Price (\$) (Kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
BTBT-Br ₂	9660 \$/kg	0.200			1.932
DPA	12272 \$/kg	0.426			5.227
Sodium <i>tert</i> -butoxide/TCI	259 \$/kg	0.360			0.093
Palladiumacetate/TCI	298 \$/g	0.006			0.298
Tricyclohexylphosphine/TCI	34 \$/g	0.020			0.680
Toluene/Finar	11 \$/L		15.00		0.165
Silicagel(100-200 mesh)/Merck	17 \$/kg			50.00 g	0.850
Hexane/Finar	18 \$/L			300.00 ml	5.400
Ethylacetate/Finar	9 \$/L			65.00 ml	0.585
Total					15.230

BTBT-2: Yield, 52%, 0.130 g, 15.230 \$

The cost of 1 g is 117.153 \$

This is about (1/5)th of the cost of purified Spiro-OMeTAD (565 \$/g, high purity, SIGMA/Merck)

SI 4. DFT calculations

The Gaussian 09 package with B3LYP/6-31G⁺(d,p) was used to perform density functional theory (DFT) calculations, from which the optimized structure, highest occupied molecular orbital (HOMO) energy levels, and lowest unoccupied molecular orbital (LUMO) energy levels were calculated for both the HTMs, BTBT-1 and BTBT-2.

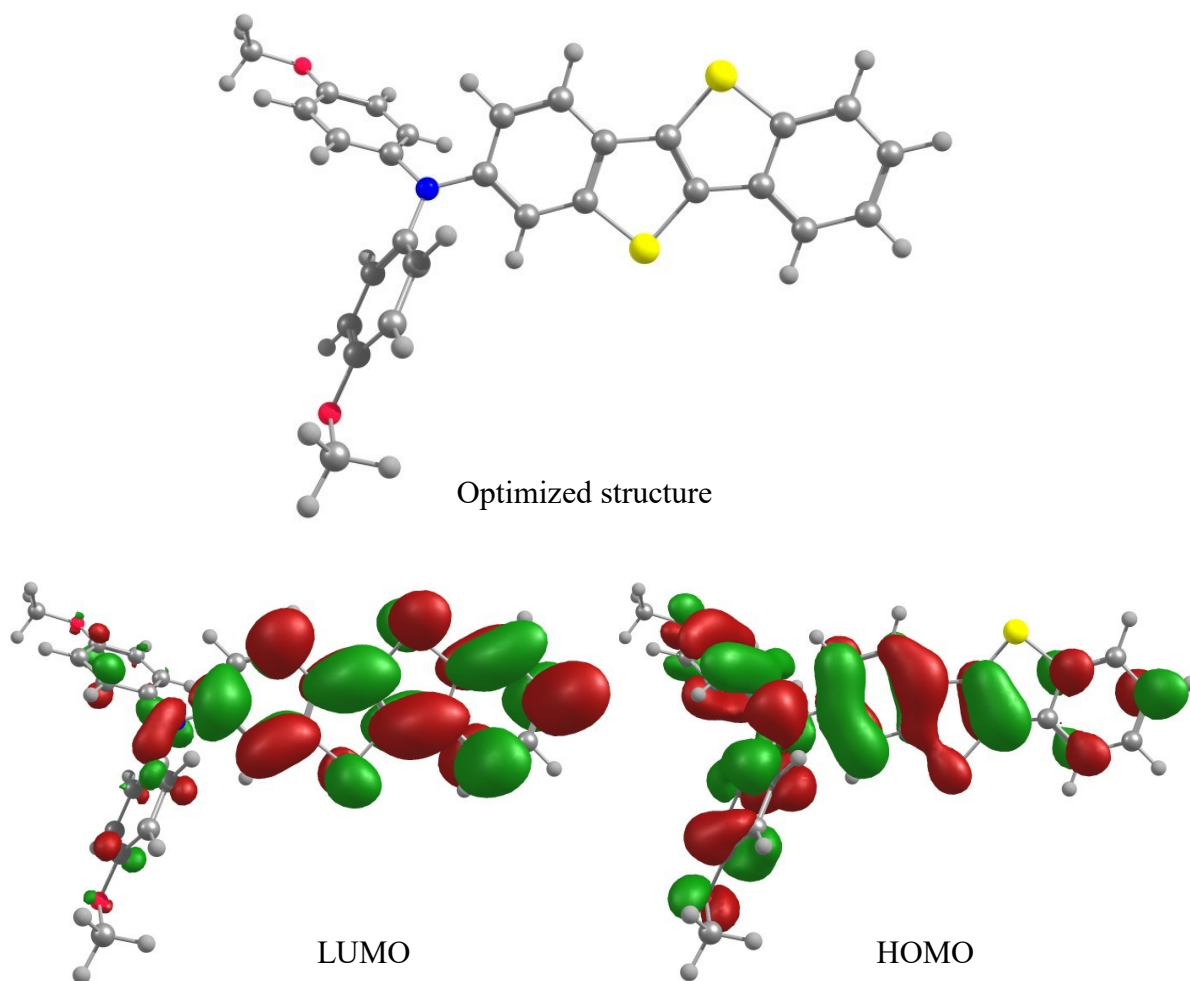


Figure S1. Optimized structure and FMOs of BTBT-1. Left: Lowest Unoccupied Molecular Orbital [LUMO (-1.10 eV)]; right: Highest Occupied Molecular Orbital [HOMO (-4.64 eV)]; band gap: 3.54 eV; Dipole moment: 3.03.

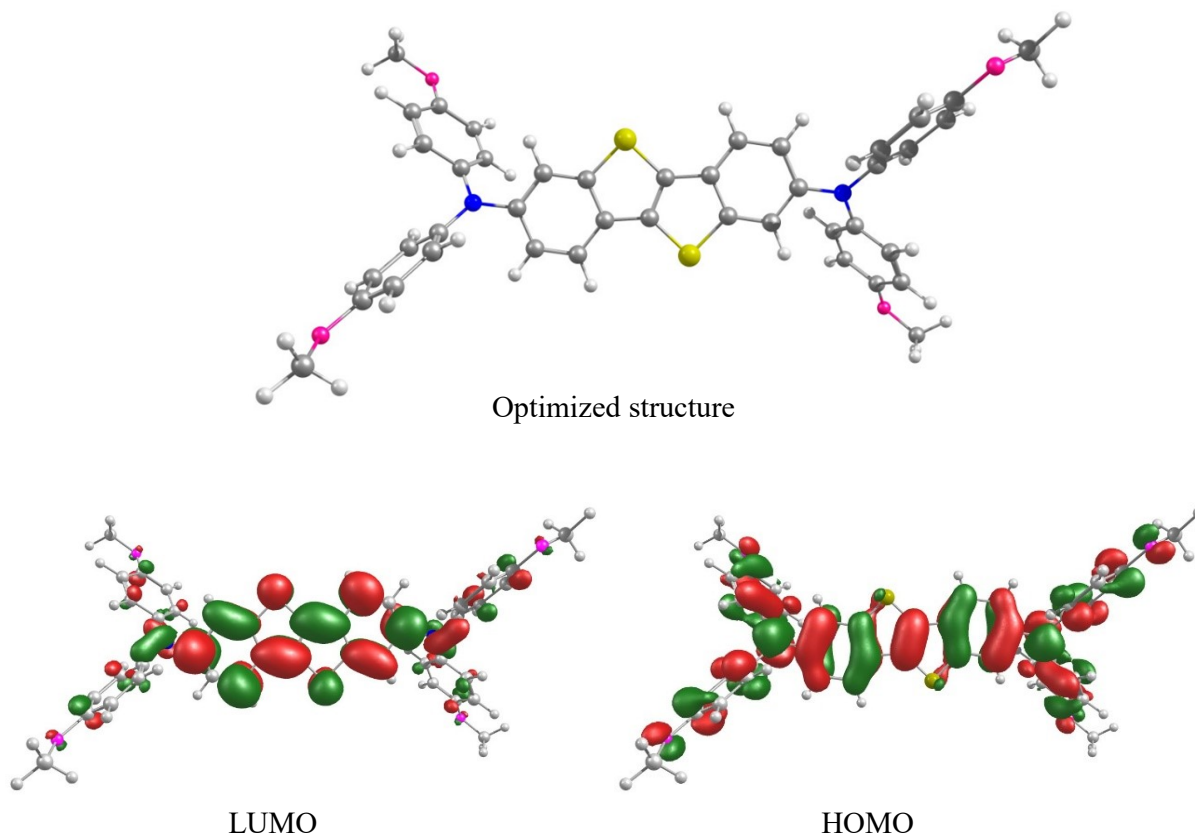


Figure S2. Optimized structure and FMOs of BTBT-2. Left: Lowest Unoccupied Molecular Orbital [LUMO (-0.97 eV)]; right: Highest Occupied Molecular Orbital [HOMO (-4.36 eV)]; band gap: 3.39 eV; Dipole moment: 3.03.

SI 5. Photophysical and electrochemical study

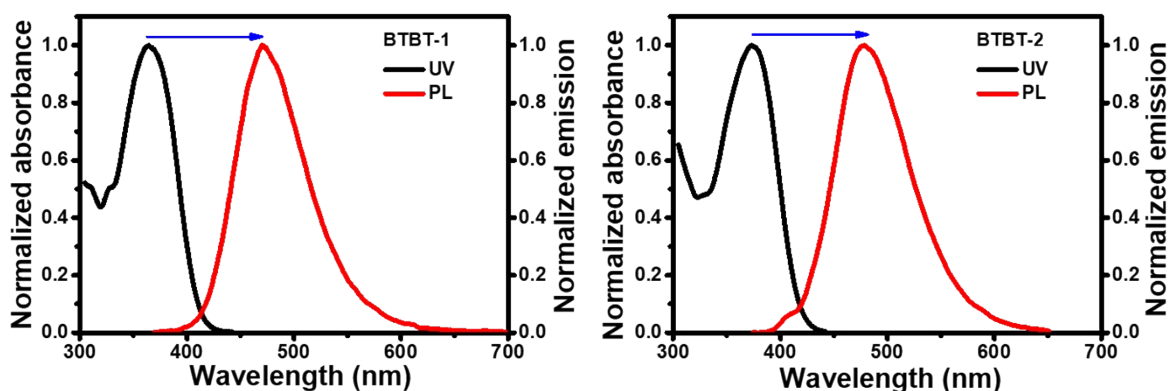


Figure S3. Normalized UV-Vis. absorption and Normalized photoluminescence emission curve (DCM 10^{-5} M) of BTBT-1 and BTBT-2.

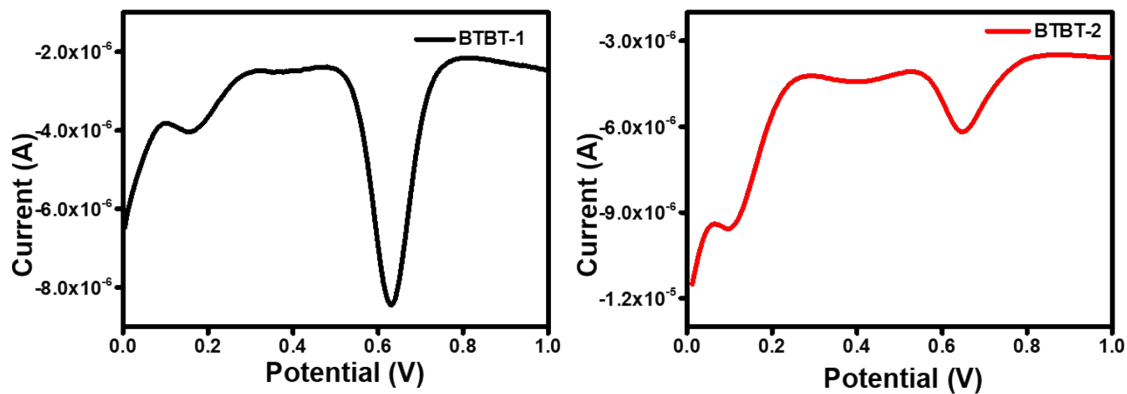


Figure S4. Differential pulse voltammogram of BTBT-1 and BTBT-2.

Experimental Section for Device Fabrication:

(a) *Materials Used:* Lead iodide (PbI_2), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), isopropyl alcohol (IPA), chlorobenzene, toluene, acetonitrile, bis (trifluoromethane)sulfonimide lithium salt (Li-TFSI) and 4-tert-butyl pyridine were acquired from Sigma-Aldrich. Tin oxide (SnO_2 particles dispersed solution of H_2O in 3:1) nano-particle was purchased from Alfa-Aesar. Methyl ammonium iodide (MAI), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III)-tris(bis(tri-fluoromethylsulfonyl) imide) (FK209) from Tokyo Chemical Industry (TCI) and 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) were ordered from 1-Materials. Materials and chemicals were used as received. We have synthesised small HTMs BTBT-1 and BTBT-2 in our lab.

(b) *PPV Device Fabrication and Characterizations:* Perovskite solar cells with glass/indium-doped tin oxide (ITO)/ tin (IV) oxide (SnO_2)/ FAMAPbI₃/BTBT-1 or BTBT-2 or spiro-OMeTAD/gold (Au) architectures were fabricated within a glove box. To begin with, etched ITO substrates were cleaned using detergent, deionized water, acetone, and isopropyl alcohol. The substrates were then placed in an oven for 2h at 70°C before ozone plasma treatment for 20min. After that, 15% tin (IV) oxide colloidal dispersion in H_2O was deposited on the ITO glass by spin coating (2000rpm for 20s) and then heated for half an hour at 150°C. For

FAMAPbI₃ film deposition, MAI:FAI:PbI₂ (1.35 M:0.15 M:1.5 M) were mixed in 1mL solvent (4:1 anhydrous DMF:DMSO). Then, the precursor was spin-coated onto the SnO₂ layer with an antisolvent method at spin rate of 4000rpm for 20s. After 10s of spinning, 200 μ L of toluene was immediately dripped on the film, followed by thermal annealing at 120 °C for 5min. To deposit HTL on perovskite layer via spin coating (spin rate of 3000 rpm, time 20 s), we used BTBT-1 and BTBT-2 solution containing 10mg per ml in chlorobenzene and spiro OMeTAD solution containing 73 mg spiro-OMeTAD per 1mL chlorobenzene with Li-TFSI (28 μ L; mother solution: acetonitrile, 530 mg mL⁻¹), TBP (28 μ L), and FK209 (18 μ L; mother solution: acetonitrile, 300mgmL⁻¹). Finally, 80 nm thick Au was thermally evaporated as a top electrode under vacuum of ($<4\times 10^{-6}$ Torr) using a mask. The electrical characterizations were made with FYTRONIX-9712 source meter under a simulated indoor LED light source (300-2000 lx) and one-sun conditions (100 mWcm⁻²) using a TriSOL standard solar simulator. The indoor LED light simulator consists of commercial purchase Osram E27 LED lamps, which are calibrated for 1000 lx (321.6 μ W cm⁻¹) with standard luxmeter and optical power meter (PM160) from Thorlabs. The intensity of the solar simulator was calibrated by using a standard mono-Si solar cell (SN-1000-TC-K-QZ, VLSI standards S/N 105100602) before every set of measurements which is certified by the VLSI Standards incorporated.

(c) Thin Film Characterizations: The perovskite thin films were characterized for absorption capability by UV–visible absorption spectroscopy (UV2080N, Analytical Technologies Ltd.). Field emission-scanning electron microscopy (FE-SEM) was performed using an FE-SEM Carl Zeiss, Ultra Plus and contact angles were measured using the instrument Surface Electro-Optics (SEO), Phoenix.

SI 6. Photovoltaic measurements

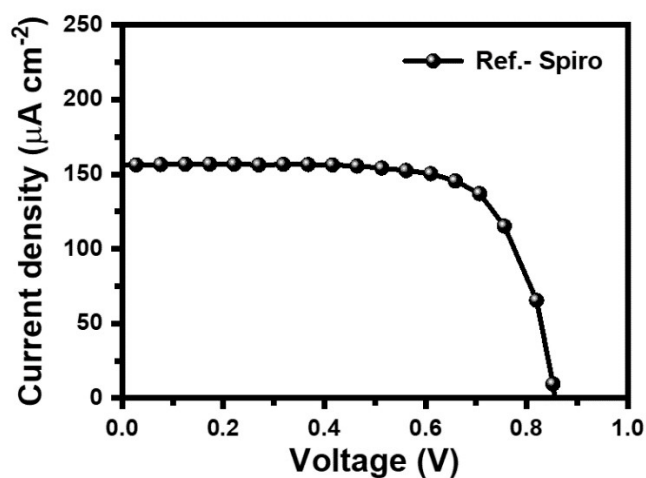


Figure S5. J - V curve of the cell with doped Spiro-OMeTAD under 1000 lux.

Table S7. PV parameters of PVs with Spiro-OMeTAD HTM under 1000 lux

Devices	V_{oc} (V)	J_{sc} ($\mu A cm^{-2}$)	FF (%)	PCE (%)
Spiro Reference	0.86	158.7	67.2	28.13

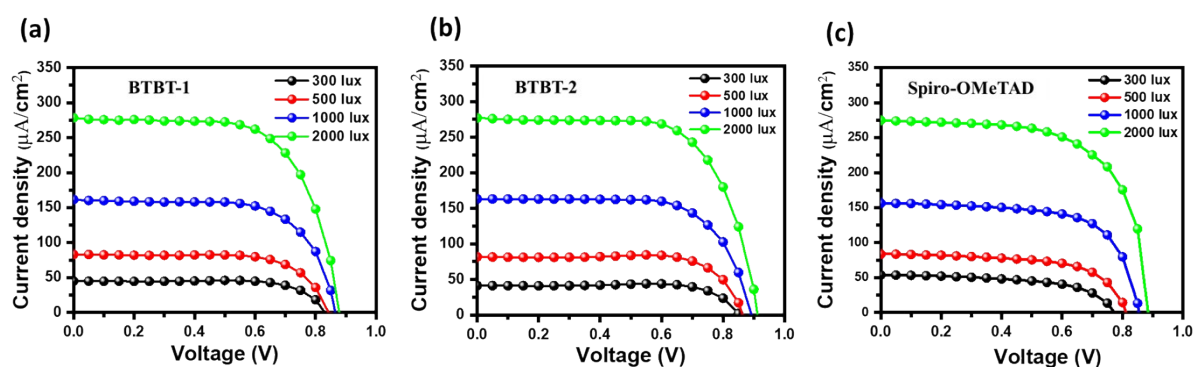


Figure S6. J - V responses of the fabricated (a) BTBT-1, (b) BTBT-2, and (c) Spiro-OMeTAD HTMs-modified PSCs under light intensities from 300 lux to 2000 lux.

Table S8. Champion PV performance of PVs fabricated employing BTBT-1 HTM under different indoor light intensities (from 300 lux to 2000 lux).

Illuminance (lux)	V_{OC} (V)	J_{SC} ($\mu A/cm^2$)	FF (%)	PCE
300	0.83	47.5	67.3	27.58

BTBT- 1	500	0.84	81.2	67.4	28.69
	1000	0.87	159.9	67.5	29.19
	2000	0.88	279.7	66.9	25.65

Table S9. Champion PV performance of PVs fabricated employing BTBT-2 HTM under different indoor light intensities (from 300 lux to 2000 lux).

	Illuminance (lux)	V_{OC} (V)	J_{SC} (μA/cm²)	FF (%)	PCE (%)
BTBT- 2	300	0.86	48.82	71.3	31.12
	500	0.87	82.2	71.2	31.78
	1000	0.89	160.6	71.4	31.73
	2000	0.91	278.86	70.2	28.75

Table S10. Champion PV performance of PVs fabricated employing Spiro-OMeTAD HTM under different indoor light intensities (from 300 lux to 2000 lux).

	Illuminance (lux)	V_{OC} (V)	J_{SC} (μA/cm²)	FF (%)	PCE (%)
Reference Spiro	300	0.78	54.02	65.4	28.64
	500	0.82	83.49	67.4	28.80
	1000	0.86	159.7	67.6	28.87
	2000	0.89	274.21	66.8	25.39

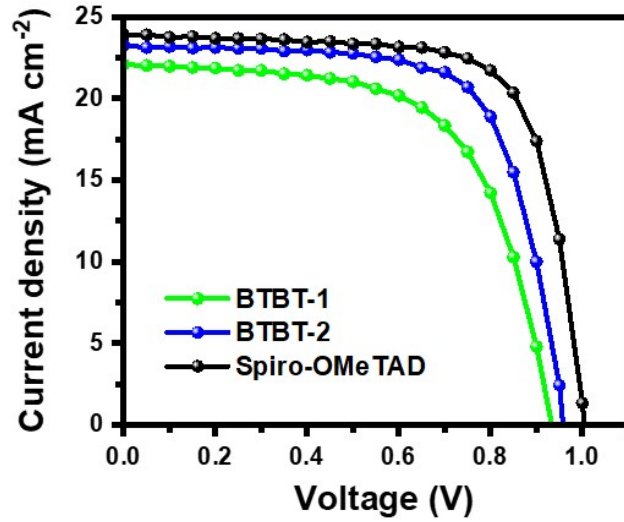


Figure S7. J - V curve of the cells with BTBT-1, BTBT-2 and Spiro-OMeTAD HTMs under one sun conditions.

Table S11. PV properties of PSCs with BTBT-1, BTBT-2, and Spiro-OMeTAD HTMs under one sun conditions.

Devices	V_{OC} (V)	J_{SC} ($\mu\text{A}/\text{cm}^2$)	FF (%)	PCE (%)
BTBT-1	0.94	22.22	61.54	13.26
BTBT-2	0.98	23.37	70.06	16.05
Spiro Reference	1.06	23.86	72.25	18.28

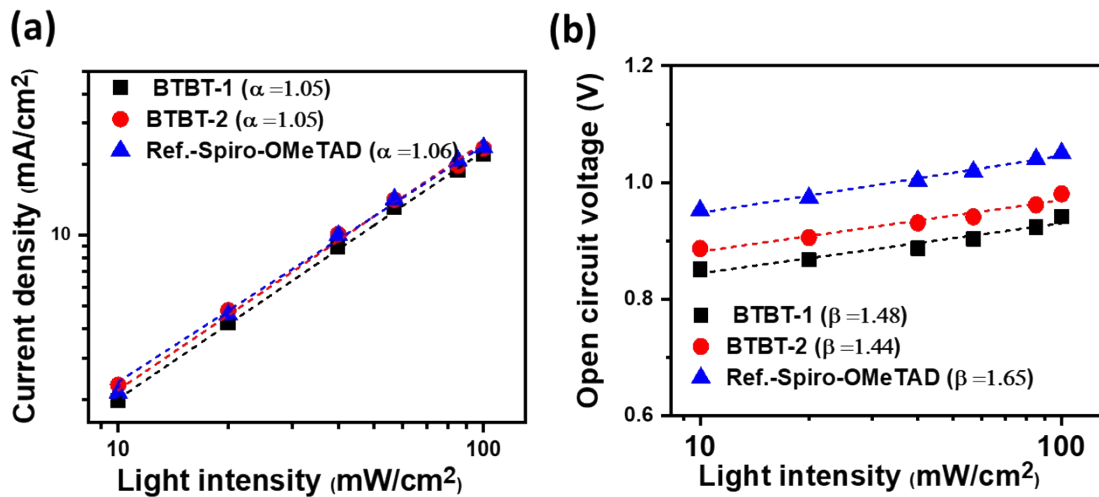


Figure S8. Plot of (a) J_{SC} and (b) V_{OC} versus light intensity curves of PPVs with BTBT-1, BTBT-2, and Spiro-OMeTAD HTMs under solar simulated light.

SI 7. ^1H NMR and ^{13}C NMR spectrum

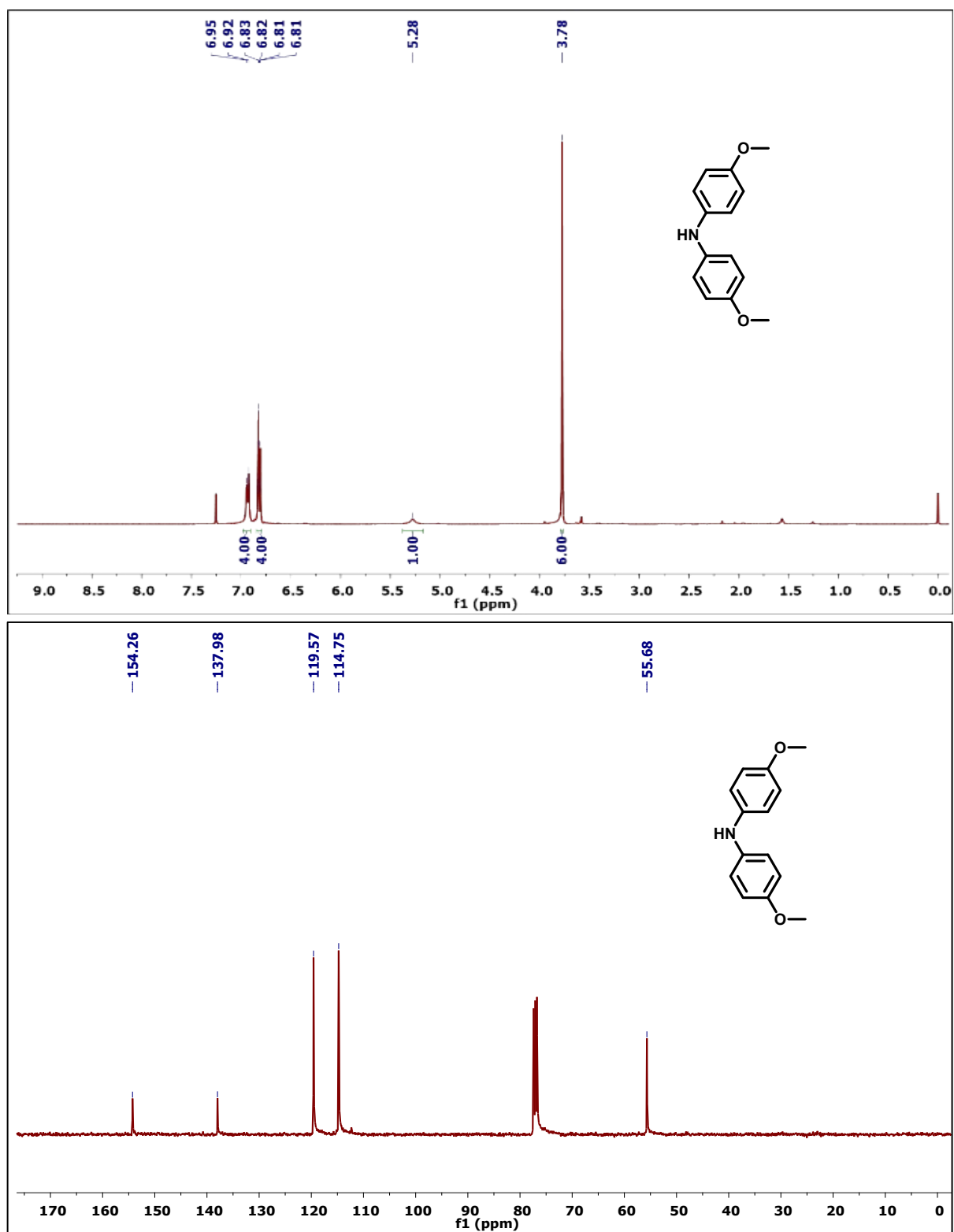


Figure S9. ^1H NMR (CDCl_3 , 400 MHz, rt.) and ^{13}C NMR (CDCl_3 , 500 MHz, rt.) spectra of

DPA.

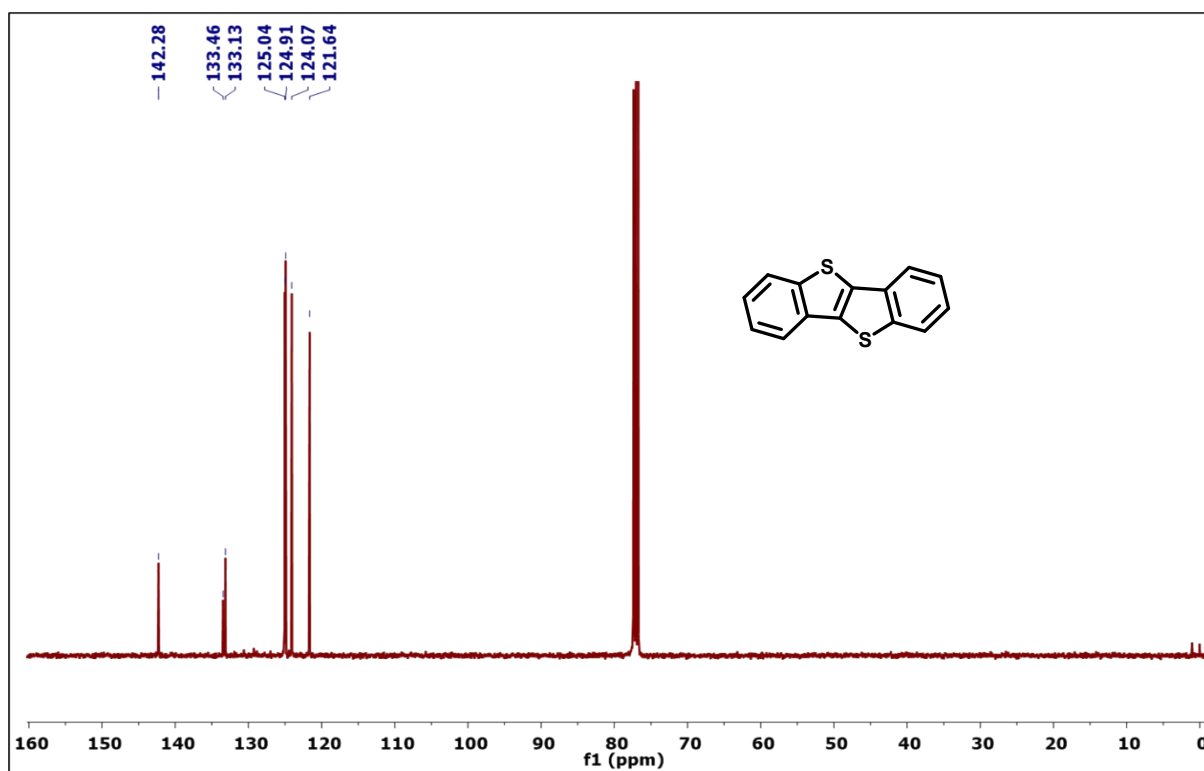
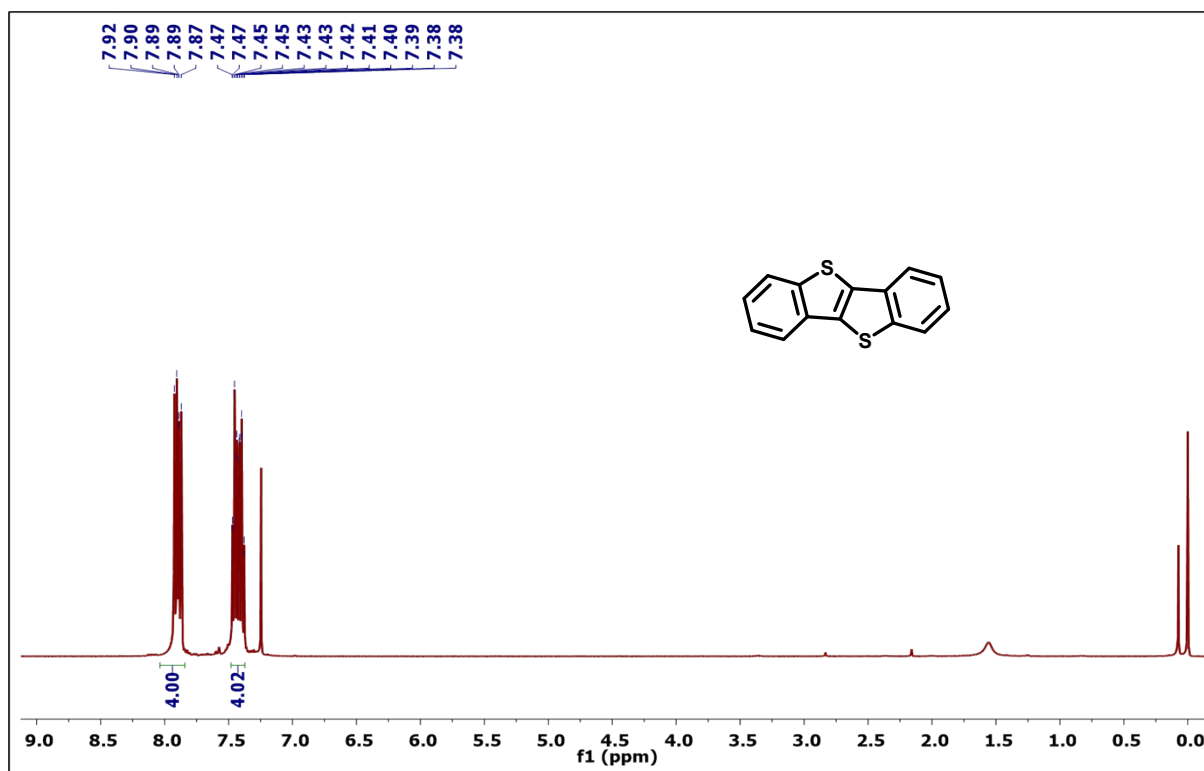


Figure S10. ¹H NMR (CDCl₃, 400 MHz, rt.) and ¹³C NMR (CDCl₃, 500 MHz, rt.) spectra of BTBT.

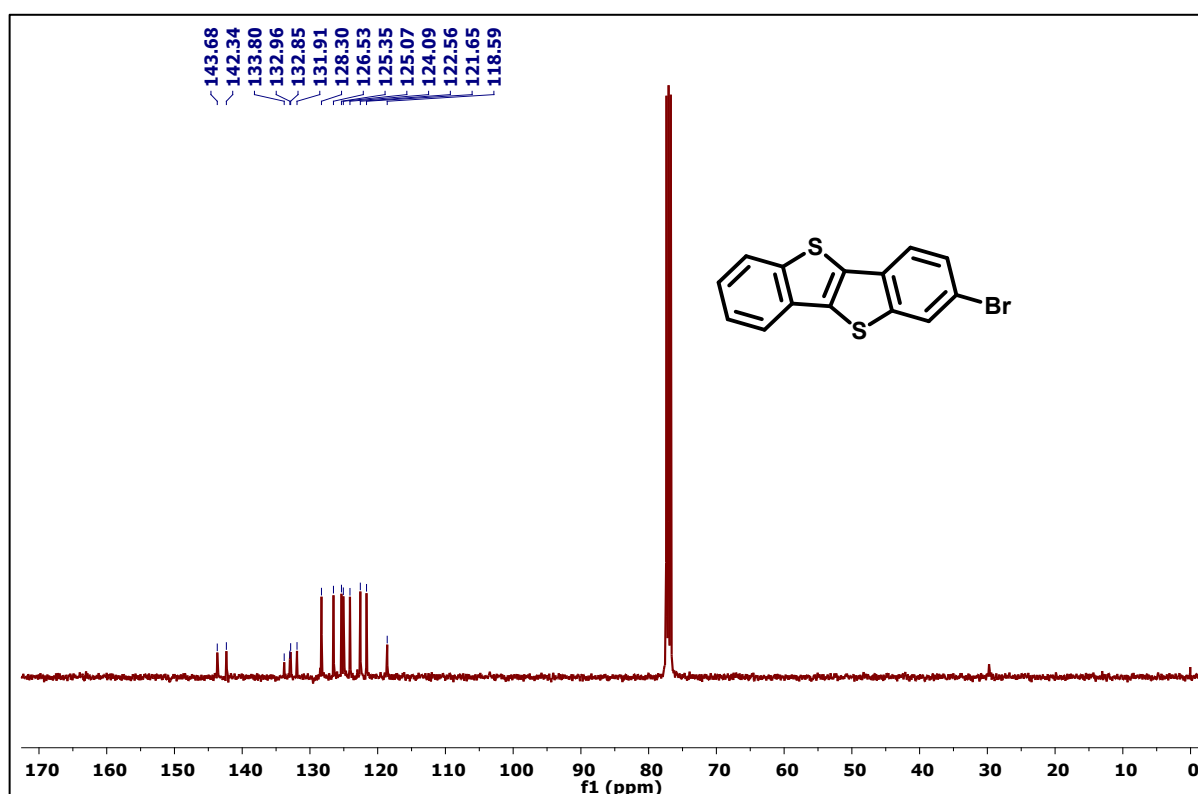
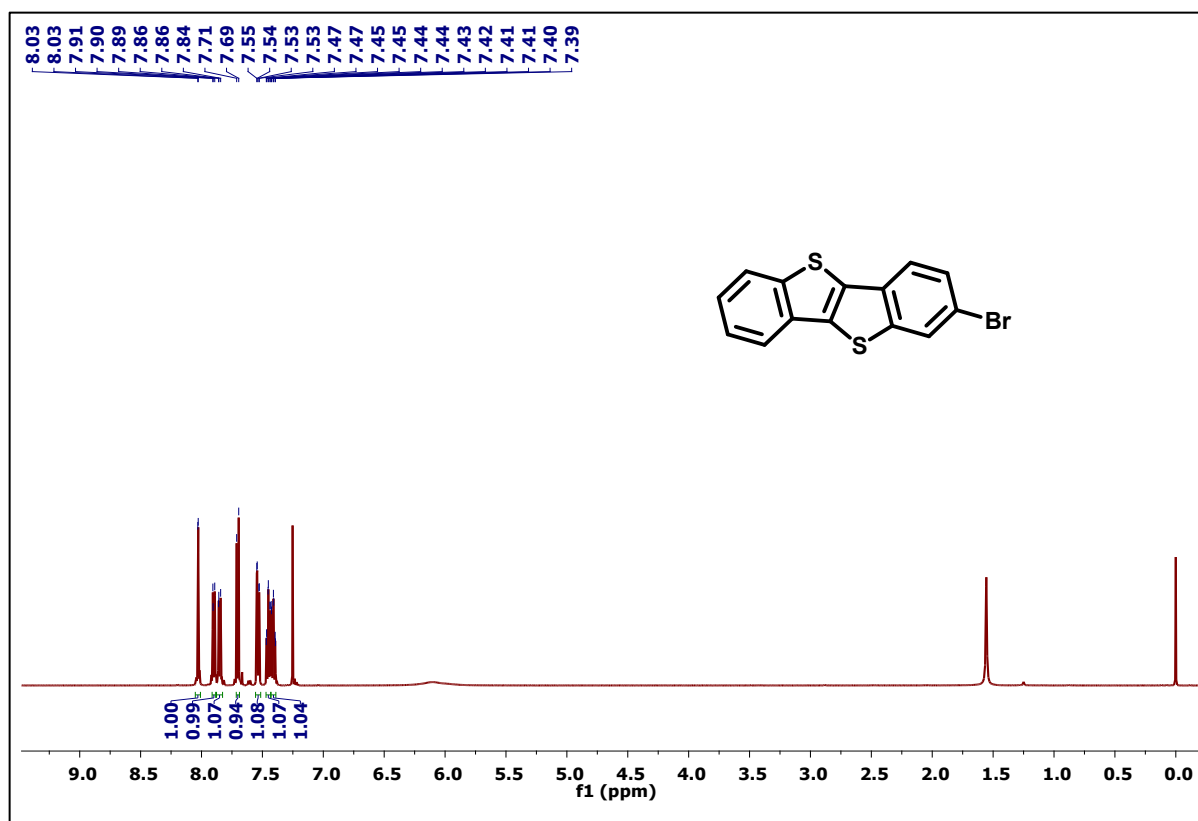


Figure S11. ^1H NMR (CDCl_3 , 400 MHz, rt.) and ^{13}C NMR (CDCl_3 , 500 MHz, rt.) spectra of BTBT-Br.

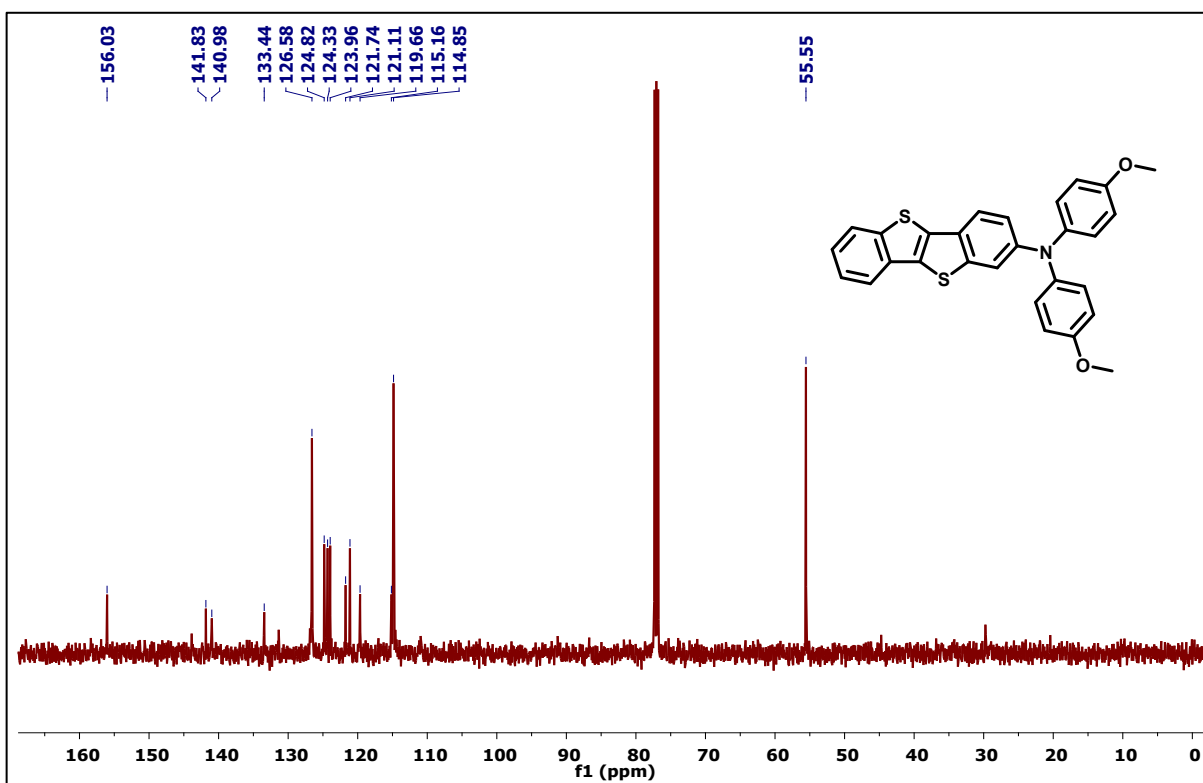
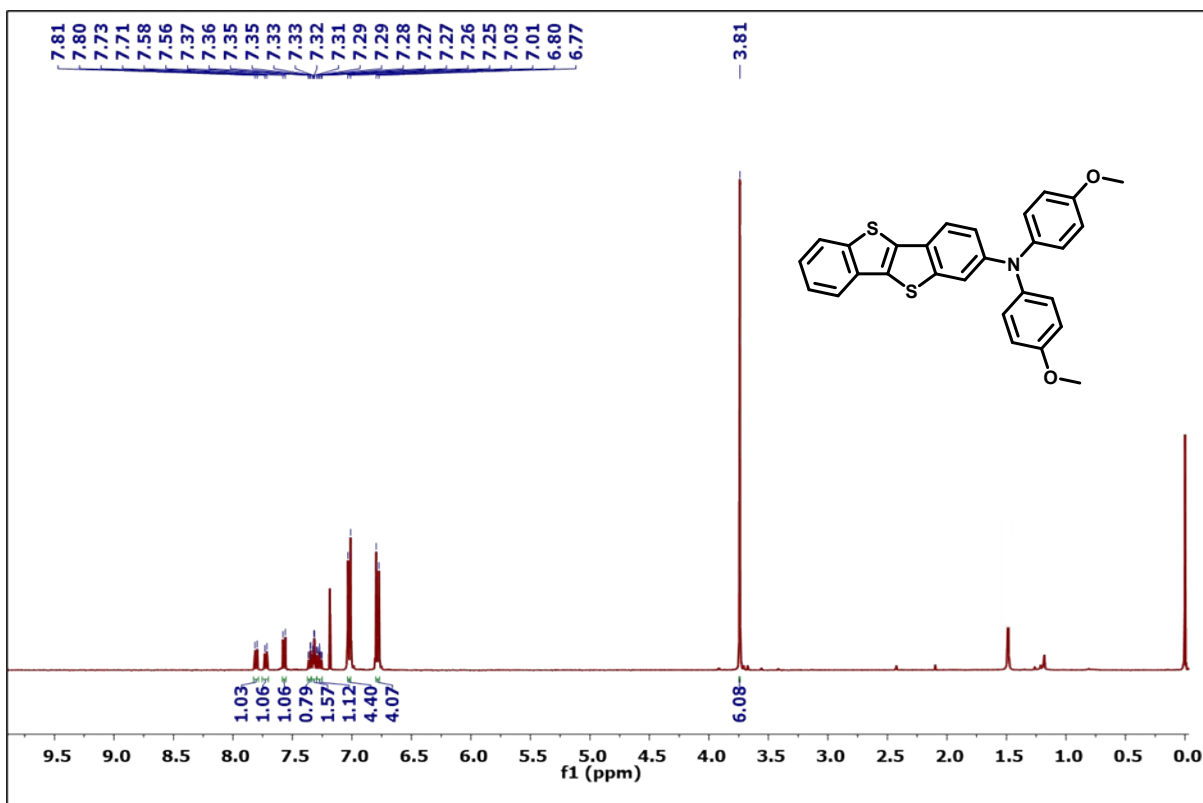


Figure S12. ¹H NMR (CDCl₃, 400 MHz, rt.) and ¹³C NMR (CDCl₃, 500 MHz, rt.) spectra of BTBT-1.

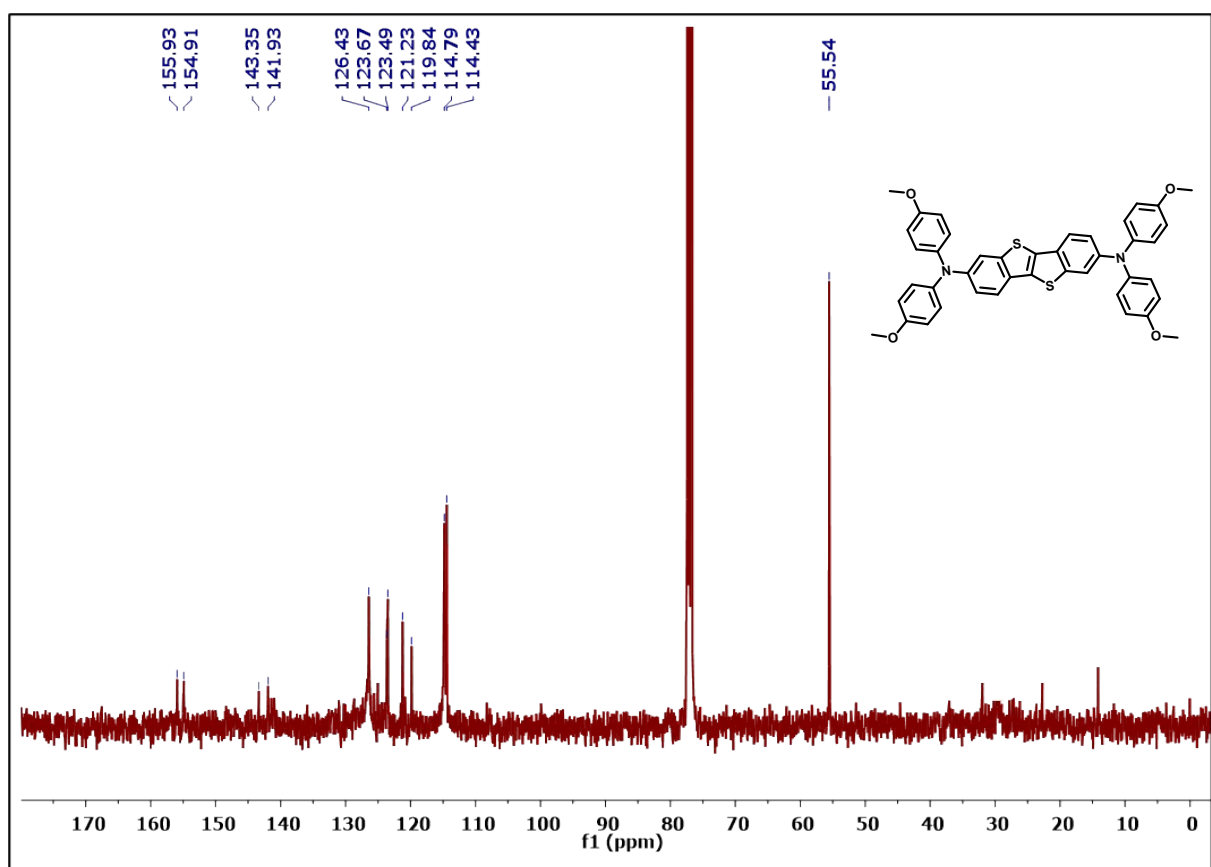
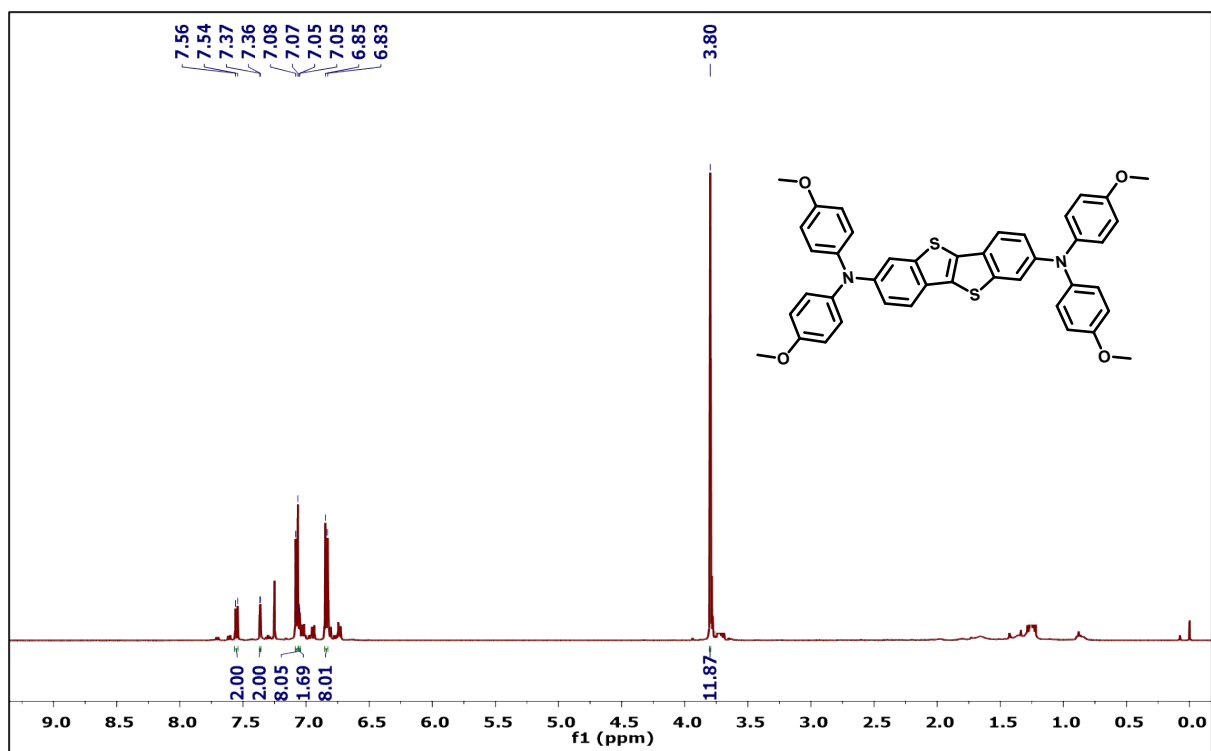


Figure S13. ¹H NMR (CDCl₃, 400 MHz, rt.) and ¹³C NMR (CDCl₃, 500 MHz, rt.) spectra of BTBT-2.

SI 8. Mass (HRMS) spectrum

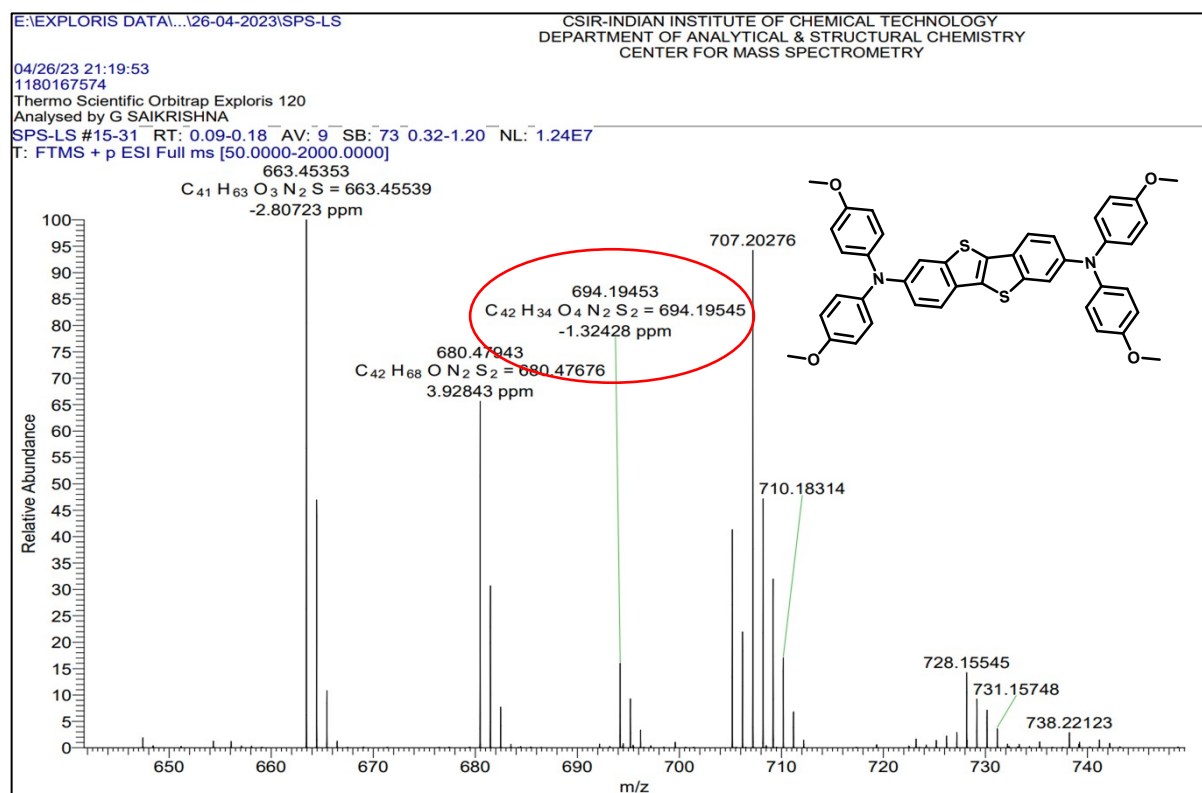
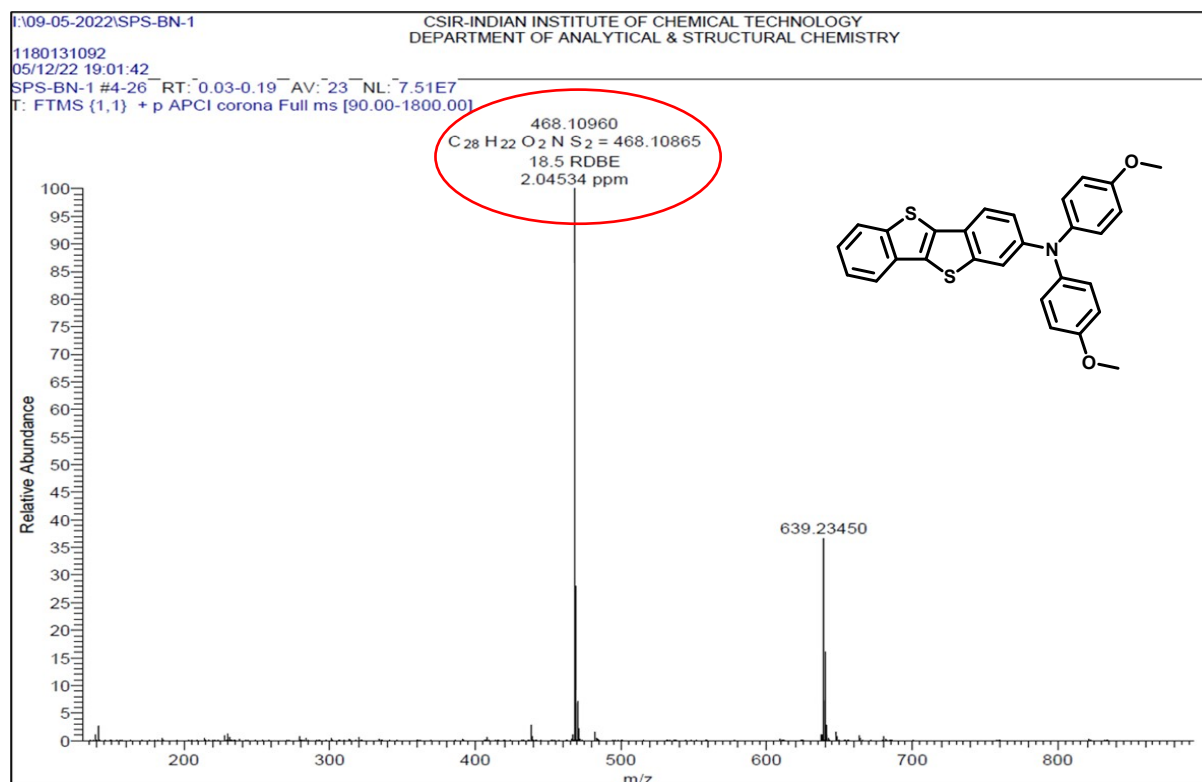


Figure S14. HRMS spectra of BTBT-1 and BTBT-2.

References

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- 2 M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159–12162.