

Supporting Information

[1]Benzothieno[3,2-*b*][1]benzothiophene-Based Dyes: Effect of Ancillary Moiety on Mechanochromism and Aggregation-Induced Emission

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1. Experimental

1.1 Materials

The starting materials sodium hydrosulfide hydrate, o-chlorobenzaldehyde, bromine, palladium(II) acetate, methyltriphenylphosphonium bromide purchased from Sigma-Aldrich, 4-dimethylaminobenzaldehyde, bromotriphenylethylene and 4-vinylphenylboronic acid were purchased from TCI, n-butyllithium solution from Hychem Laboratories Pvt. Ltd. and Silica gel was purchased from Fluka. The solvents were purified by standard procedures and purged with nitrogen before use. All other chemicals used in this work were analytical grade and were used without further purification. All reactions were performed under inert atmosphere.

1.2 Methods/Characterization

^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker 400-MHz or 500-MHz spectrometer using TMS as standard and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet and tt triplet of triplet. Purifications were carried out through silica gel using 100-200 mesh and 230-400 mesh. High resolution mass spectra were measured on a Shimadzu LCMS 2010 EV model with ESI probe. MALDI is recorded on Bruker ultraflex TOF. Absorption spectra in solution and solid were recorded on Scimadzu UV-1800 and UV-2600 model spectrophotometer respectively. The Photoluminescence (PL) spectra were recorded using Fluorolog3 spectrofluorometer (Spex model, JobinYvon) at their respective excitation (λ_{ex}) wavelength. The following equation was followed to calculate the QY values.

$$\Phi_{\text{sample}} = \Phi_{\text{ref}} \frac{A_{\text{ref}}}{A_{\text{sample}}} + \frac{F_{\text{sample}}}{F_{\text{ref}}} + \frac{n_{\text{sample}}}{n_{\text{ref}}}$$

Here, the sample is denoted as an unknown compound and reference (ref) is a known compound. Φ = quantum yield, A = absorbance at the excitation wavelength, F = integrated emission area, n = Refractive index of the solvent containing compound. Temperature dependent emission study also used the same instrument. Fluorescence Life time decay

measurements was carried out by using time-correlated single photon counting (TCSPC) setup (Fluorolog-3 Triple Illuminator, IBH Horiba JobinYvon) using a laser of 375 nm for excitation.

The compounds are well fitted with the bi-exponential equation and decay of the excited state of a molecule to ground state calculations are done with the following equation.^{34,35}

$$\alpha(t) = \alpha_1 \exp\left(\frac{-t}{\tau_1}\right) + \alpha_2 \exp\left(\frac{-t}{\tau_2}\right)$$

Where α is the amplitude of the compounds (%), τ represents decay lifetimes related to intrinsic exciton relaxation (excitons and photons; excitons and defects interaction), t is time. The average lifetime of the compounds in different solvents is calculated from the below equation.

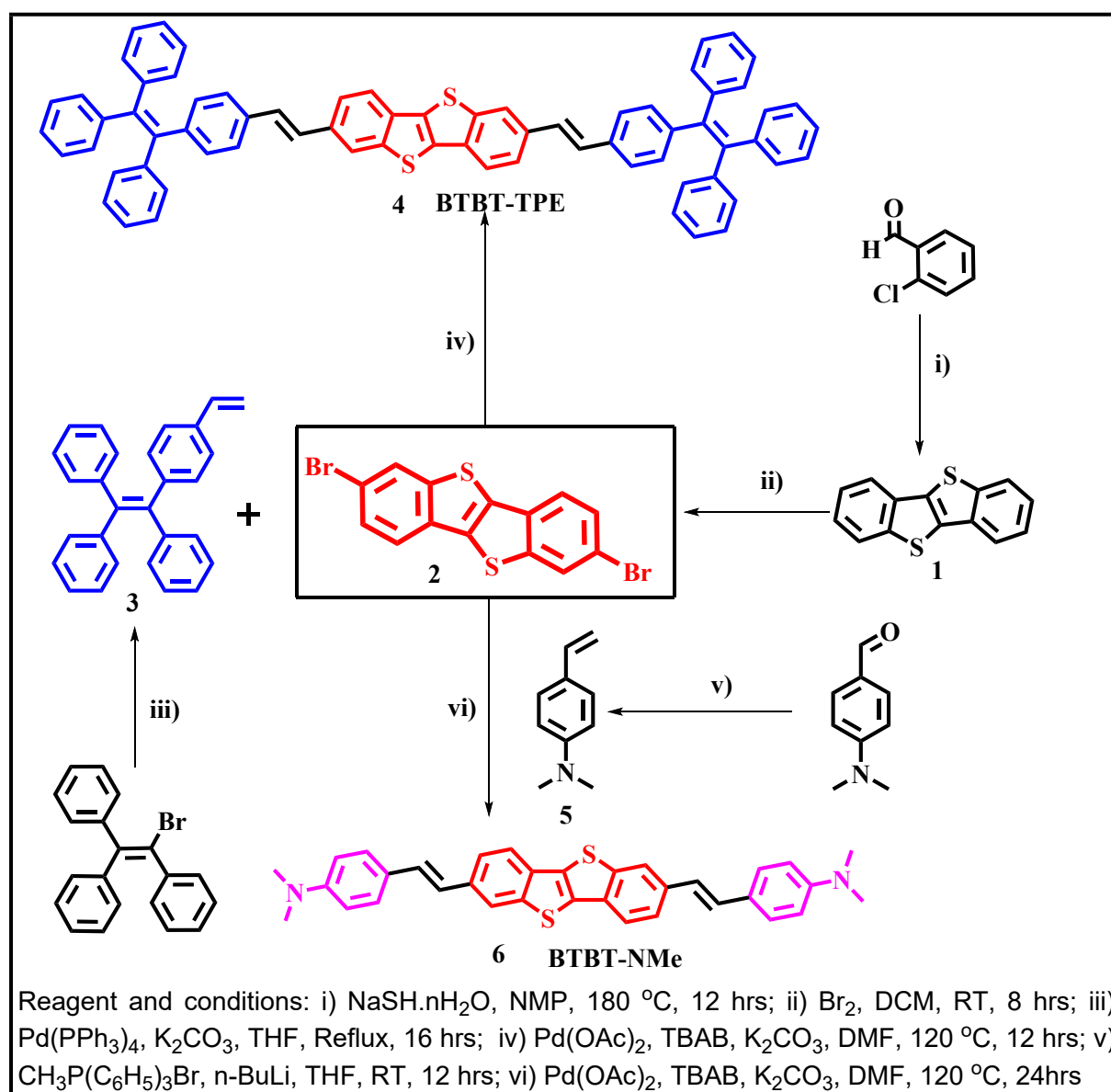
$$\tau_{(ave)} = \left(\frac{\alpha_1 \tau_1^2}{\alpha_1 \tau_1}\right) + \left(\frac{\alpha_2 \tau_2^2}{\alpha_2 \tau_2}\right)$$

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was performed with a CH Instruments 620C electrochemical analyzer with dichloromethane using 0.1 M TBAPF6 as the supporting electrolyte, a Ag/AgCl electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt wire as the counter electrode and ferrocene/ferrocenium (Fc/Fc⁺) as an external reference. Morphology was confirmed by Zeiss Ultra™ 55 model FE-SEM at 5 kV accelerating voltage. Powder X-ray diffraction analysis was measured from the range of 0-80° θ by using Bruker D-8 Advance Powder X-Ray Diffractometer. Theoretical calculations were measured with DFT and TD-DFT by using Gaussian g16 programme suite. BTBT-TPE and BTBT-NMe were fully optimized in neutral with gas phase. B3LYP correlation functional with 6-311g (d,p) basis set was used for all atoms.¹⁻³ TD-DFT calculations were performed at B3LYP/6-311g (d,p) level of theory in DCM solution.^{4,5} Optimized geometry's are calculated by Gaussian 09.50 and absorption spectrum as well as interpret the nature of transition used GaussSum software. Surfaces of the molecular orbitals picturized by using the Gaussview⁶ and major as well minor contributions are calculated by GaussSum software.

2. Synthesis

Simple one-step synthesis of [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) was carried out from o-chlorobenzaldehyde. Further BTBT bromination was carried out as per reports,⁷ Suzuki-Miyaura Coupling was carried out to get the compound **3** in good yield,⁸ Wittig olefination was carried out with methyltriphenylphosphonium bromide and 4-

dimethylaminobenzaldehyde to get **5** with 78% yield,⁹ finally Heck reaction to produce trans-symmetrical **BTBT-TPE** and **BTBT-NMe**.¹⁰



Scheme S1 Synthetic routes of **BTBT-TPE** and **BTBT-NMe** molecules

2.1 Synthetic process of the Molecules

(1) [1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT)

Sodium hydrosulfide hydrate (17.94 g, 0.320 mol) was added to a solution of o-chlorobenzaldehyde (15 g, 0.106 mol) in NMP (30 mL) at 80 °C and stirred for 1 h. Then, mixture was heated to 180 °C and stirred for 10 h at the same temperature. The resulting mixture was poured into a saturated aqueous ammonium chloride solution (saturated, 200 ml) and cooled with an ice-bath. The resulting precipitate was collected by filtration and washed with

water and acetone. The precipitate dissolved in chloroform, and the solution was passed through a short silica gel column. Evaporation of the solvent gave crude BTBT, which was further purified by recrystallization from toluene to pure BTBT as a white solid (7.42 g, 29%). ¹H NMR (CDCl₃, 400 MHz): δ 7.93 (d, J=7.90 Hz, 2H), 7.89 (d, J=8.1 Hz, 2H), 7.47 (dd, J=7.6, 7.3 Hz, 2H), 7.41 (dd, J=8.0, 7.3 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 142.27, 133.46, 133.13, 124.98, 124.07, 121.64.

(2) 2,7-dibromo[1]benzothieno[3,2-*b*]benzothiophene

In a 500 mL round bottom flask, BTBT (5 g, 20.83 mmol) is dissolved in DCM (250 mL). A solution of Br₂ (3.66 g, 22.91 mmol) in DCM (75 mL) is added dropwise, and the reaction is left stirring at room temperature overnight. The second Br₂ equivalent (3.66 g in 75 mL of DCM) is therefore added dropwise. Reaction is left stirring at room temperature for two more days. During this time, a white precipitate appears in the flask, which is collected on a Buchner funnel. The white solid is washed with DCM and aqueous NaHSO₃ (10% w/w). This crude is purified by extraction in a Soxhlet apparatus using DCM as solvent. The product crystallizes in the cold solvent, and it is collected by filtration. Silvery flakes (2.73 g, 33.0% yield).

¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 1.7 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.58 (dd, J = 8.5, 1.7 Hz, 2H).

(3) (2-(4-vinylphenyl) ethene-1,1,2-triyl) tribenzene

Bromotriphenylethylene (2.5 g, 7.45 mmol) and 4-vinylphenylboronic acid (1.65 g, 11.18 mmol) were dissolved in a mixture of toluene (45 mL), TBAB (0.19 g, 0.74 mmol) and 1.2 M potassium carbonate aqueous solution (10 mL). The mixture was stirred at room temperature for 0.5 h under N₂ gas followed by adding Pd(PPh₃)₄ (86 mg, 0.07 mmol) and then heated to 90 °C for 24 h. After that the mixture was poured into water and extracted three times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After moving the solvent under reduced pressure, the residue was chromatographed on a silica gel column with CH₂Cl₂/n-hexane as an eluent to give a faint white powder with 90% yield (2.4 g.)

¹H NMR (400 MHz, CDCl₃): δ 7.16–6.97 (m, 19H), 6.61 (dd, J = 17.6, 10.9 Hz, 1H), 5.66 (d, J = 17.6 Hz, 1H), 5.17 (d, J = 10.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 143.70, 143.39, 141.08, 140.61, 136.62, 135.54, 131.36, 127.69, 126.44, 125.56, 113.48.

(4) BTBT-TPE

A mixture of 2,7-dibromo[1]benzothieno[3,2-*b*]benzothiophene (0.650 g, 1.63 mmol), (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (2.33 g, 6.52 mmol), Pd(OAc)₂ (7.5 mg, 0.03 mmol), K₂CO₃ (0.67 g, 4.89 mmol), and tetrabutylammonium bromide (1.31 g, 4.07 mmol) in anhydrous DMF (20 mL) was reacted under nitrogen atmosphere at 120 °C for 24 h. After complete reaction, the mixture was extracted with dichloromethane and H₂O and then washed with water three times. The combined organic phases were dried over anhydrous Na₂SO₄. After concentrating the crude product, the residue was purified by column chromatography on silica gel with petroleum ether/ dichloromethane to obtain a yellow powder **BTBT-TPE** (820 mg, 36%).

¹H NMR (500 MHz, CDCl₃): δ (ppm): δ 7.97 (2H), 7.81 (2H), 7.59 (2H), 7.28 (d, 4H), 7.09 (m, 38H). ¹³C NMR (126 MHz, CDCl₃) δ = 143.75, 136.61, 131.83, 131.35, 128.89, 127.67, 126.48, 125.90, 125.55, 123.54, 121.6, 113.47. MALDI- TOF m/z calcd. for C₇₀H₄₈S₂ m/z [M+H]⁺ 952.3197, found 952.3910. HRMS (ESI): m/z calcd for C₇₀H₄₉S₂ (M+H)⁺ 953.3276, found 953.32289.

(5) N, N-Dimethylamino-4-vinylbenzene

n-BuLi (2.5 M in hexane, 12.54 mL, 31.36 mmol), was added dropwise to a solution of methyltriphenylphosphonium bromide (11.20 g, 31.36 mmol) in THF (80 mL) at room temperature under the atmosphere of nitrogen. After stirring for 15 min, a solution of 4-dimethylaminobenzaldehyde (4 g, 26.81 mmol) in THF (40 mL) was added dropwise and the resulting mixture was stirred at room temperature for 16h. After that, water (30 mL) and diethyl ether (30 mL) were added and two layers were separated. The aqueous solution was extracted with ethyl ether for three times and the combined organic extracts were dried over Na₂SO₄ filtered, and concentrated in vacuo. The crude reaction product was purified by flash column chromatography (petroleum ether/diethyl ether) to provide N, N-dimethylamino-4-vinylbenzene as a pale-yellow oil (3.1g, 78%).

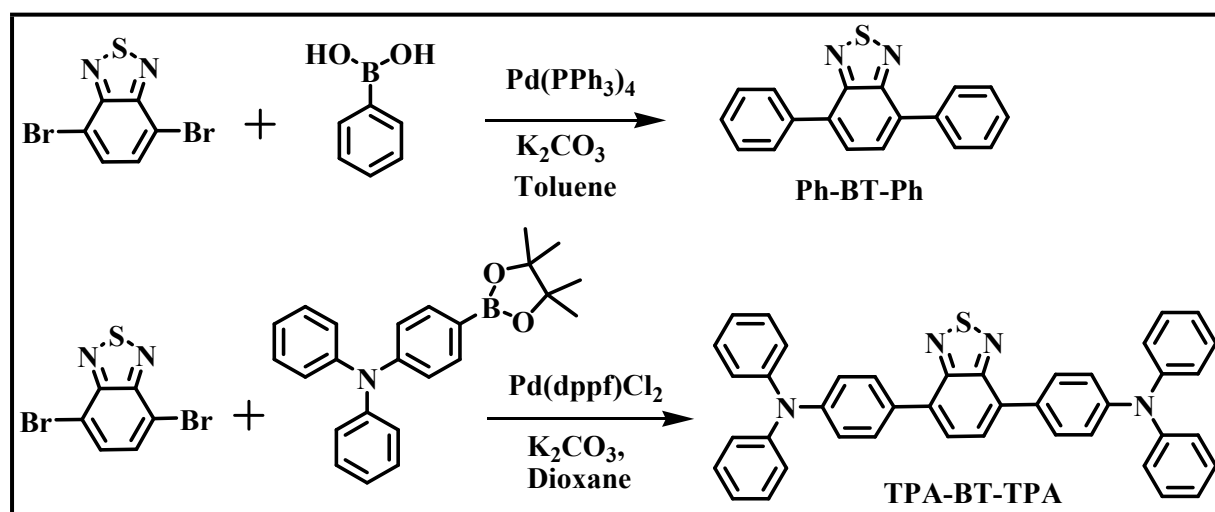
¹H NMR (500 MHz, CDCl₃): δ 7.30 (d, J = 8.5 Hz, 2H), 6.68(d, J = 8.4 Hz, 2H), 6.62 (dd, J = 17.5, 10.9 Hz, 1H), 5.53 (d, J = 17.5 Hz, 1H), 5.01 (d, J = 10.8 Hz, 1H), 2.94 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 150.31, 136.65, 127.19, 126.26, 112.38, 109.39, 40.57.

(6) BTBT-NMe

A mixture of 2,7-dibromo[1]benzothieno[3,2-b]benzothiophene (1.98 g, 4.97 mmol), N,N-dimethyl-4-vinylaniline (2.96 g, 19.89 mmol), Pd(OAc)₂ (22 mg, 0.09 mmol), K₂CO₃ (2.06 g, 14.92 mmol), and tetrabutylammonium (4.01 g, 12.43 mmol) in anhydrous DMF (30 mL) was reacted under nitrogen atmosphere at 120 °C for 24 h. After complete reaction, the mixture was extracted with dichloromethane and water and then washed with water three times. The combined organic phases were dried over anhydrous Na₂SO₄. After concentrating the crude product, the residue was purified by column chromatography on silica gel with petroleum ether/ dichloromethane to obtain a yellow powder **BTBT-NMe** (950 mg, 36%)

¹H NMR (400 MHz, CDCl₃): δ 8.01-7.71 (m, 2H), 7.70-7.57 (m, 2H), 7.49-7.34 (m, 2H), 7.22-6.99 (m, 2H), 6.82 (d, 2H), 6.74 (d, 2H), 3.01 (s, 12H). HRMS (ESI) m/z calcd. for C₃₄H₃₁N₂S₂: m/z [M+H]⁺ 531.19232, found 531.19441.

2.2 Scheme of the dye synthesis



2.3 Synthetic process of dyes

(1) Ph-BT-Ph (4,7-diphenylbenzo[c][1,2,5]thiadiazole)

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (1.35 g, 4.59 mmol), phenylboronic acid (1.34 g, 11.0 mmol), Pd(PPh₃)₄ (32 mg, 0.027 mmol) and potassium carbonate (3.17 g, 23.0 mmol) in a solvent mixture of toluene (20 mL) and water (7.3 mL) was heated at 85 °C and stirred for 24hrs under nitrogen. After cooling, chloroform (50 mL) was added. Then, the solution was washed with water (30 mL × 2) and sat. brine (30 mL). The obtained organic solution was dried over Na₂SO₄. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform/hexane (1:2, v/v) as eluent to afford Ph-BT-Ph as a greenish white powder (1.26 g, 4.38 mmol, 95%).

^1H NMR (400 MHz, CDCl_3); δ 7.46 (tt, $J = 1.5$ and 7.6 Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 4H), 7.79 (s, 2H), 7.79–7.97 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3); δ 154.14, 137.47, 133.41, 129.29, 128.68, 128.43, 128.19.

(2) TPA-BT-TPA (4,4'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(*N,N*-diphenylaniline))

A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (400 mg, 1.36 mmol), 4-(diphenylamino) phenylboronic ester (983 mg, 3.40 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (55 mg, 0.07 mmol), K_2CO_3 (1.89 g, 13.6 mmol), toluene (24 mL) and DMF (8 mL) was refluxed under a N_2 atmosphere for 20 hours. The mixture was poured into water and extracted with DCM. After the organic phase was washed with water thoroughly and it was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum, and then the crude product was purified by silica-gel column chromatography using DCM/PE (1:4) as the eluent and the compound TPA-BT-TPA as a red solid was obtained (yield: 95%).

^1H NMR (400 MHz, CDCl_3); δ 7.88 (d, $J = 8.7$ Hz, 4H), 7.74 (s, 2H), 7.30 (t, $J = 7.8$ Hz, 8H), 7.21 (t, $J = 8.6$ Hz, 12H), 7.07 (t, $J = 7.3$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3); δ 153.12, 146.94, 146.45, 131.13, 129.97, 128.87, 128.33, 126.42, 123.86, 122.27, 121.91.

3. Figures and Tables:

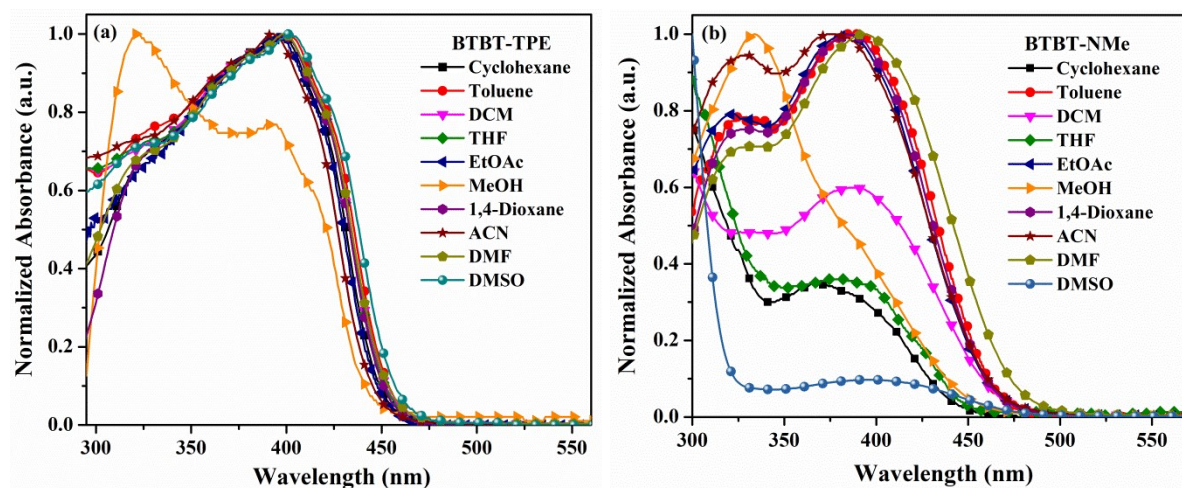


Fig. S1 UV-absorption spectra of a) BTBT-TPE and b) BTBT-NMe in different solvents (1×10^{-5} M) in the range of 250–800 nm.

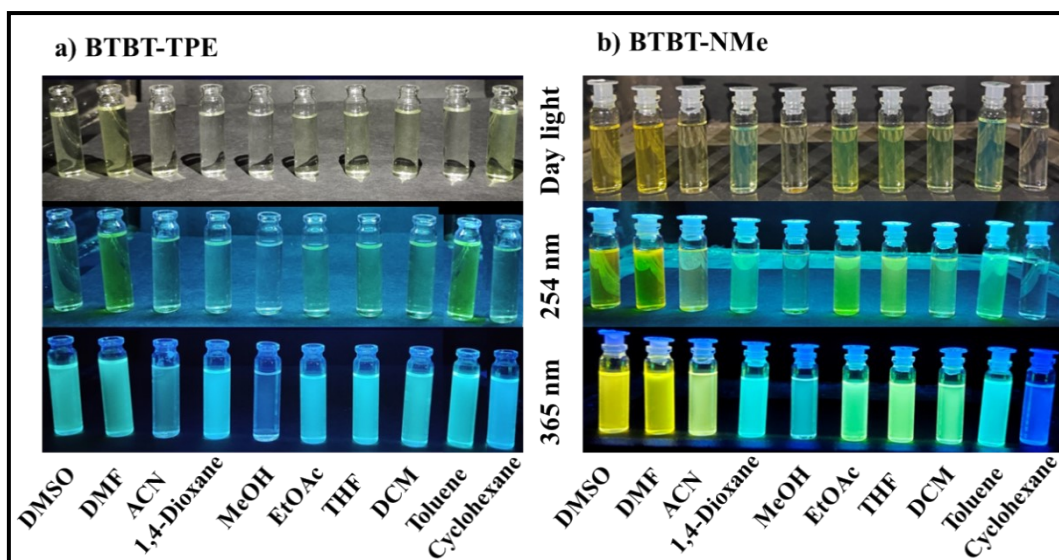


Fig. S2 Optical images of Solvatochromism under normal light, short and long wavelength for a) BTBT-TPE and b) BTBT-NMe.

Table S1. Photophysical values and quantum yield of the BTBT-TPE.

BTBT-TPE					
S. No.	Solvent	λ_{Abs} (nm)	λ_{Em} (nm)	ϵ (L mol ⁻¹ cm ⁻¹) ^a	PLQY (%) ^b
1.	Cyclohexane	397	457	21866	0.031
2.	Toluene	401	463	19466	0.017
3.	DCM	399	469	17600	0.035
4.	THF	380	438	21333	0.035
5.	EtOAc	385	464	22400	0.016
6.	MeOH	322, 394	462	21866	0.026
7.	1,4 Dioxane	397	435	16533	0.008
8.	ACN	394	471	21066	0.013
9.	DMF	399	450	23733	0.065
10.	DMSO	402	476	18933	0.033
11.	Solid	414	527	-	-

^a ϵ values are calculated from the absorption spectral data.

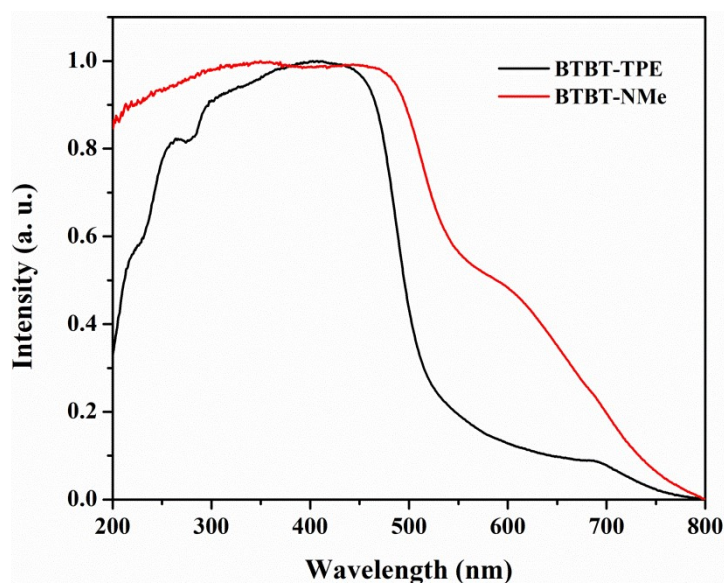
^bMeasured by using the reference in the solution phase.

Table S2. Photophysical values and quantum yield of the **BTBT-NMe**.

BTBT-NMe					
S. No.	Solvent	λ_{Abs} (nm)	λ_{Em} (nm)	() ^a	PLQY (%)^b
1.	Cyclohexane	275, 368	443	22666	0.183
2.	Toluene	387	468	25600	0.244
3.	DCM	290, 374	497	25600	0.033
4.	THF	378	499	21066	0.145
5.	EtOAc	383	497	20533	0.183
6.	MeOH	335	424	20000	0.111
7.	1,4 Dioxane	331, 389	472	23733	0.089
8.	ACN	328, 378	517	18933	0.067
9.	DMF	328, 393	535	19466	0.037
10.	DMSO	399	533	18933	0.099
11.	Solid	353, 468	547	-	-

^a ϵ values are calculated from the absorption spectral data.

^bMeasured by using the reference in the solution phase.

**Fig. S3** Solid state UV absorption (Diffuse reflectance spectra) of **BTBT-TPE** and **BTBT-NMe**.

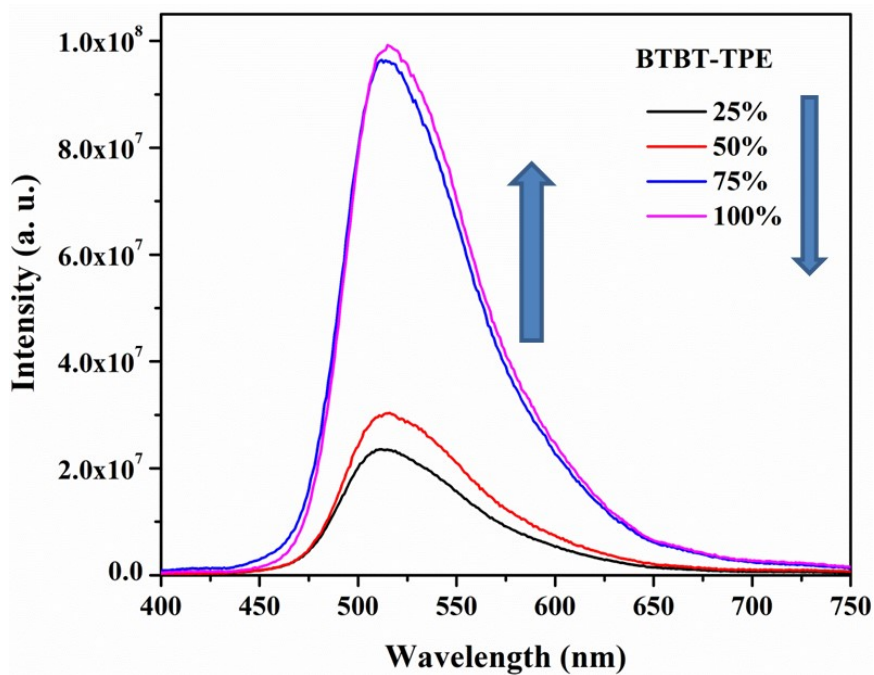


Fig. S4 Solid PL emission of the **BTBT-TPE** molecule with different ratio level from 25-100%.

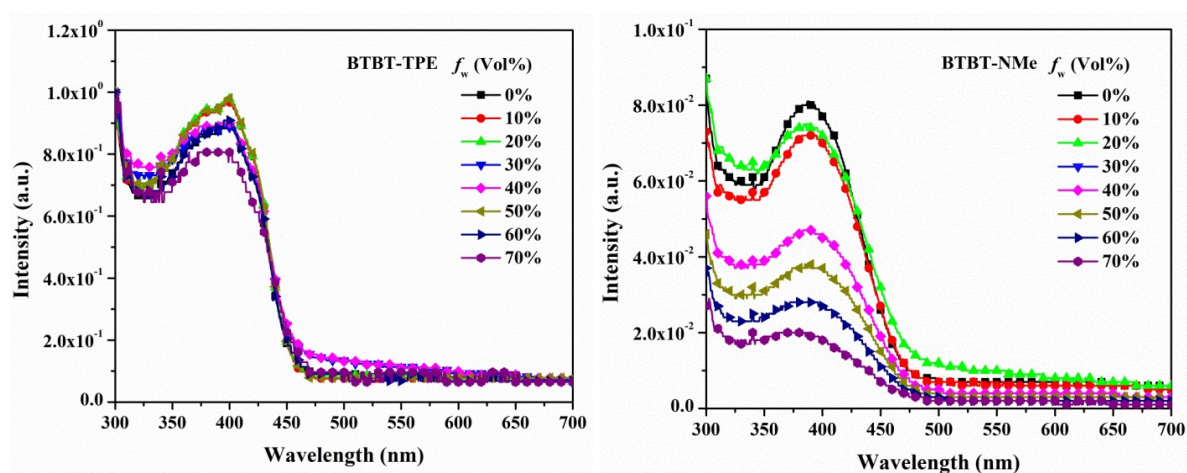


Fig. S5 UV absorption spectra of the **BTBT-TPE** (left) and **BTBT-NMe** (right) in THF+Water solvent

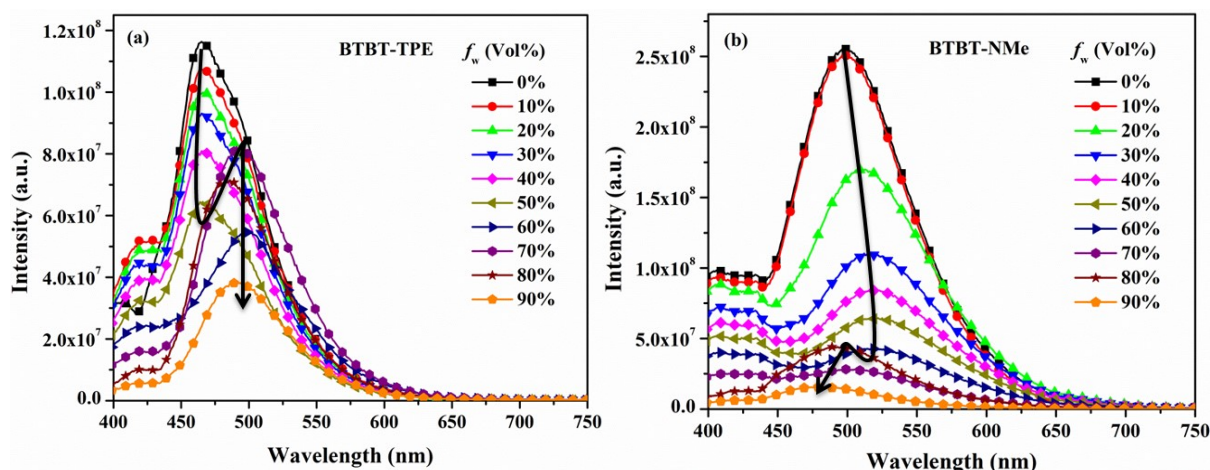


Fig. S6 Aggregation emission study of a) **BTBT-TPE** and b) **BTBT-NMe** in THF+Water solvent f_w (Vol%).

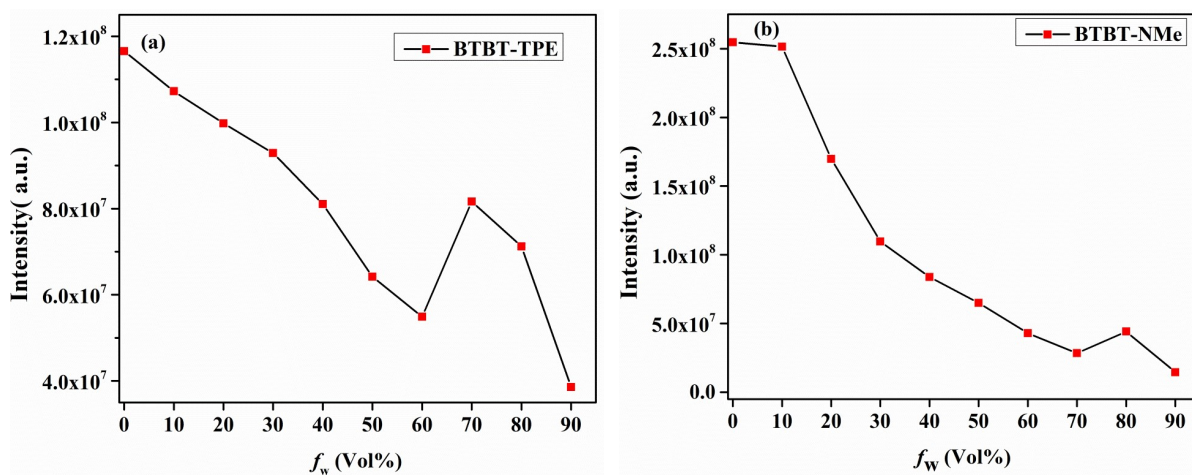


Fig. S7 Aggregation PL study of a) **BTBT-TPE** and b) **BTBT-NMe** in THF+Water solvent f_w (Vol%) their intensity ratio against f_w .

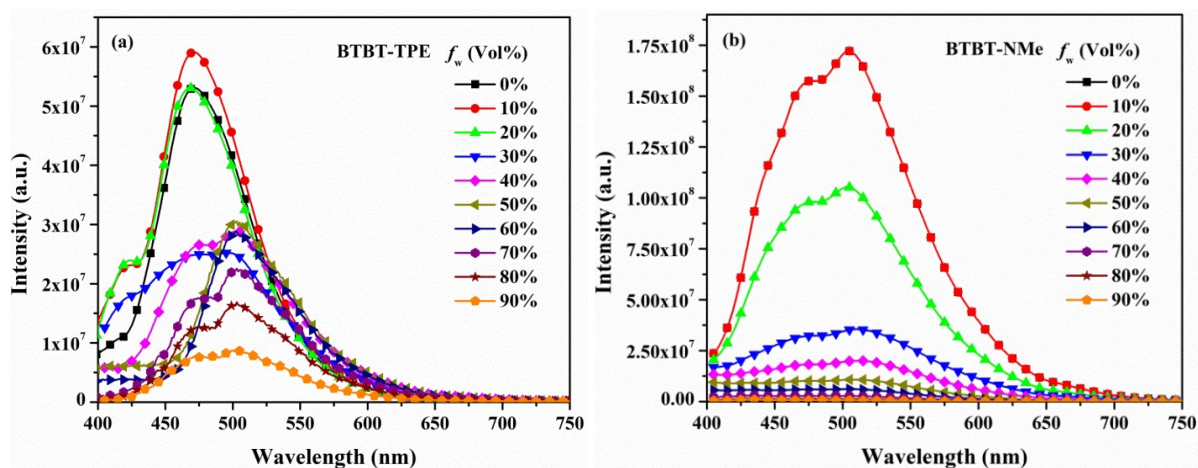


Fig. S8 Aggregation emission study of a) **BTBT-TPE** and b) **BTBT-NMe** in DMF+Water from 0-90%.

Table S3. QY of the **BTBT-TPE** and **BTBT-NMe** in DMF+Water (f_w (Vol%)).

S.No.	f_w (Vol%)	BTBT-TPE (QY)	BTBT-NMe (QY)
1	0	0.0654	0.0368
2	10	0.0714	0.3230
3	20	0.0739	0.2076
4	30	0.0527	0.0911
5	40	0.0748	0.0423
6	50	0.0933	0.0092
7	60	0.1261	0.0167
8	70	0.1748	0.0029
9	80	0.1988	0.0014
10	90	0.1703	0.0092

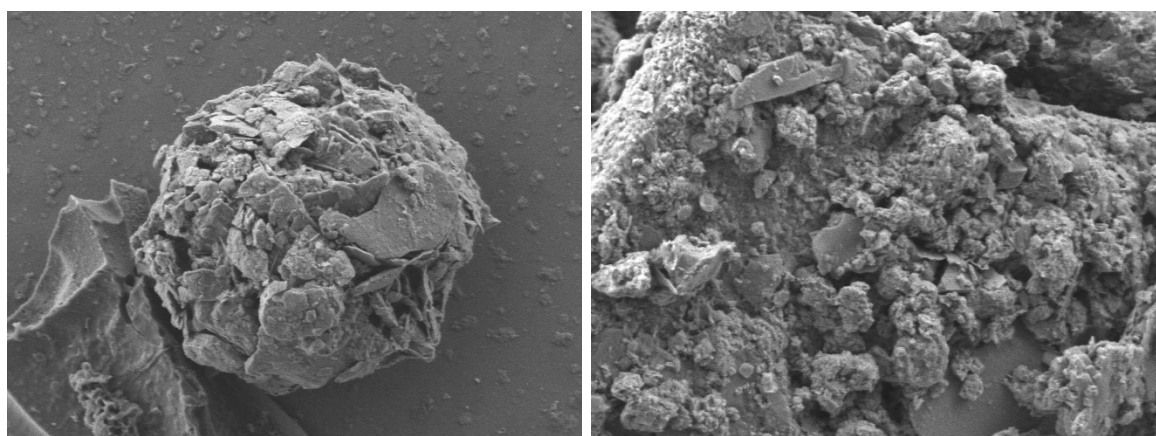


Fig. S9 FESEM images (1 μm) at 70% and 80% (f_w (Vol%)) in THF+Water of **BTBT-TPE** (right) and **BTBT-NMe** (left).

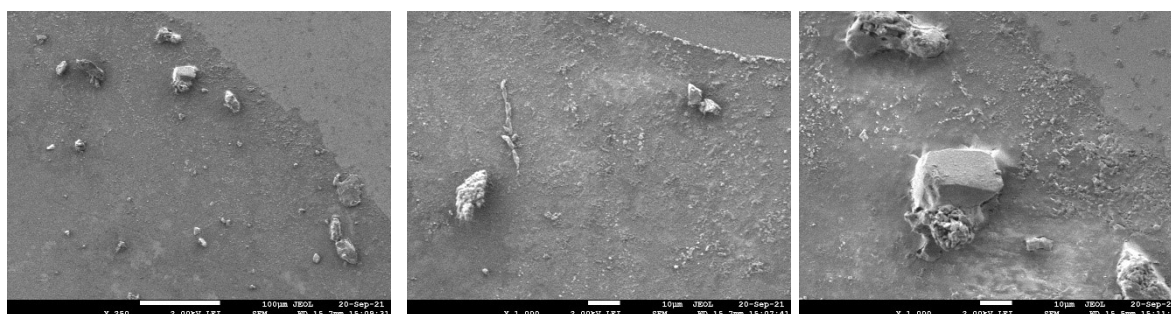


Fig. S10 FESEM images of AIE at 70% (f_w (Vol%)) THF+Water of **BTBT-TPE** (100, 10, 10 μm).

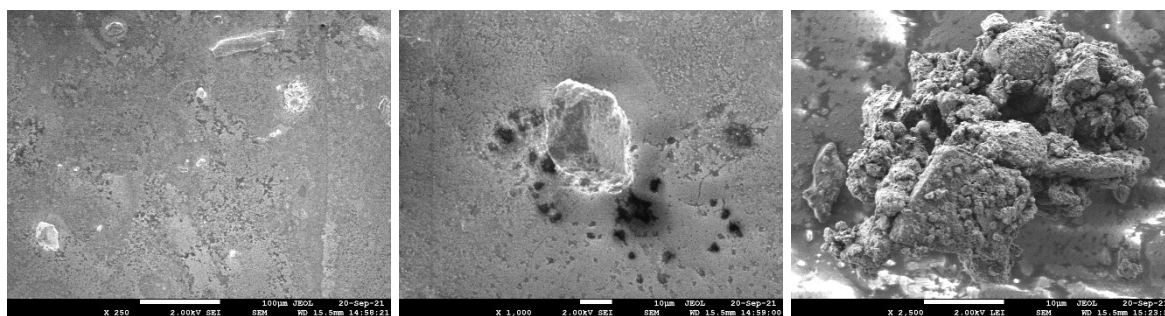


Fig. S11 FESEM images of AIE at 80% (f_w (Vol%)) THF+Water of **BTBT-NMe** (100, 10, 10 μm).

Lifetime

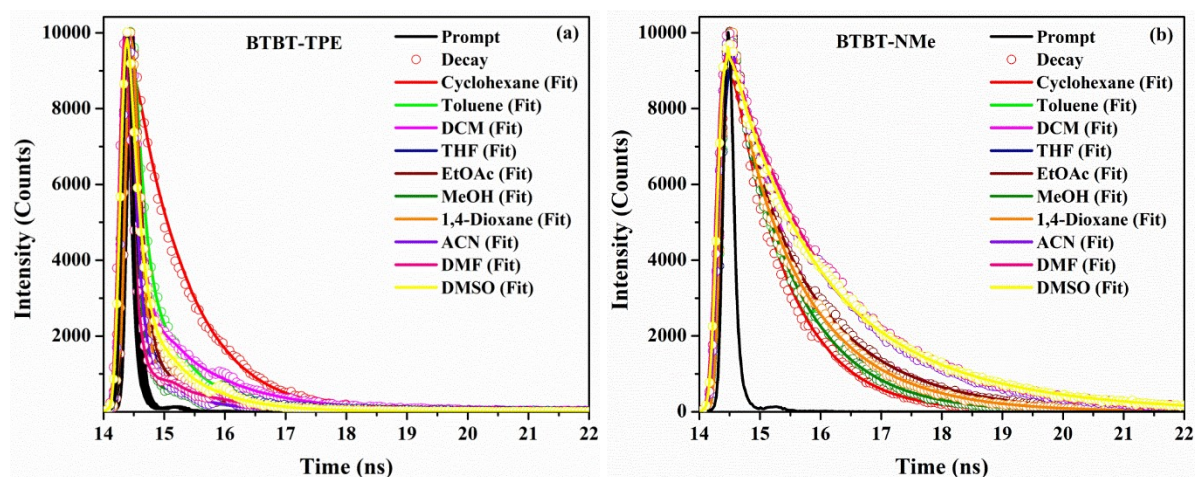


Fig. S12 Lifetime of the a) **BTBT-TPE** and b) **BTBT-NMe** in different solvents with linear fitting.

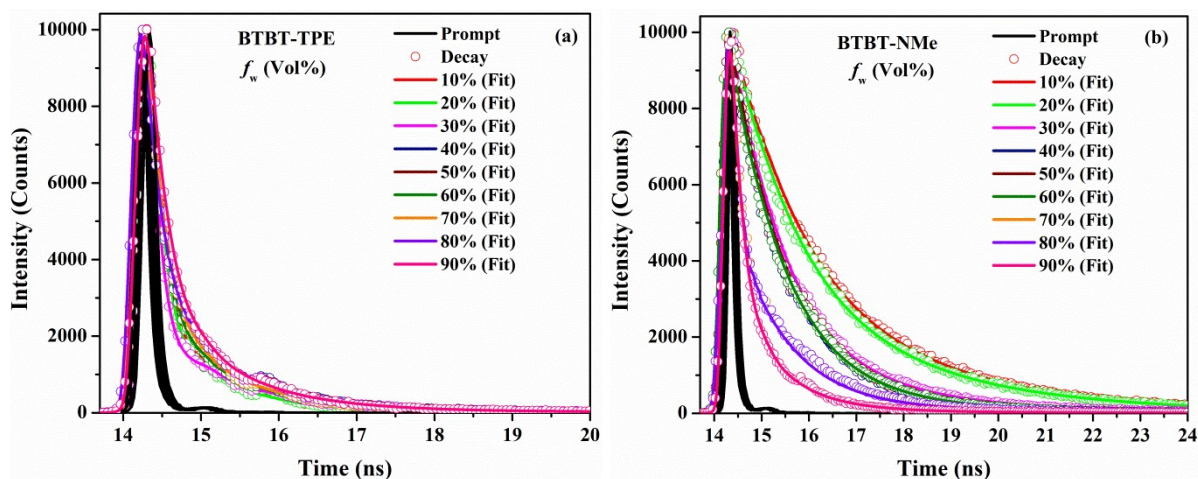


Fig. S13 Lifetime of a) **BTBT-TPE** and b) **BTBT-NMe** in THF+Water solvent (f_w (Vol%)) with linear fitting.

Table S4. Lifetime analysis of **BTBT-TPE** with their τ values and respective χ^2 in THF+Water (f_w (Vol%)).

BTBT-TPE								
%Water	τ_1	τ_2	τ_3	α_1 (%)	α_2 (%)	α_3 (%)	χ^2	Average Lifetime (τ, ns)
10	0.132	0.842	-	53.74	46.26	-	1.166	0.733
20	0.130	0.849	-	58.11	41.89	-	1.031	0.723
30	0.092	1.074	-	54.79	45.21	-	1.008	0.982
40	0.154	1.114	-	46.96	53.04	-	1.089	1.009
50	0.173	1.123	-	50.26	49.74	-	1.188	0.995
60	0.186	1.108	-	55.03	44.97	-	1.195	0.951
70	0.214	1.090	-	55.18	44.82	-	1.114	0.920
80	0.179	0.882	4.478	41.05	52.81	5.53	0.935	2.185
90	0.224	0.959	4.768	48.5	45.98	6.14	1.059	2.201

Table S5. Lifetime analysis **BTBT-NMe** with their τ values and respective χ^2 in THF+Water (f_w (Vol%)).

BTBT-NMe								
%Water	τ_1	τ_2	τ_3	α_1 (%)	α_2 (%)	α_3 (%)	χ^2	Average Lifetime (τ, ns)
10	1.273	3.101	-	43.65	56.35	-	1.085	2.660
20	1.260	3.300	-	63.1	36.9	-	1.110	2.494
30	1.012	2.663	-	64.13	35.87	-	1.208	1.995
40	0.932	2.118	-	61.4	38.6	-	1.115	1.630
50	0.963	1.973	-	84.95	15.05	-	1.205	1.232
60	1.058	2.497	-	86.49	13.51	-	1.142	1.445
70	1.090	4.060	-	86.84	13.16	-	1.200	2.161
80	1.099	1.235	3.452	52.05	43.55	4.40	1.101	1.440

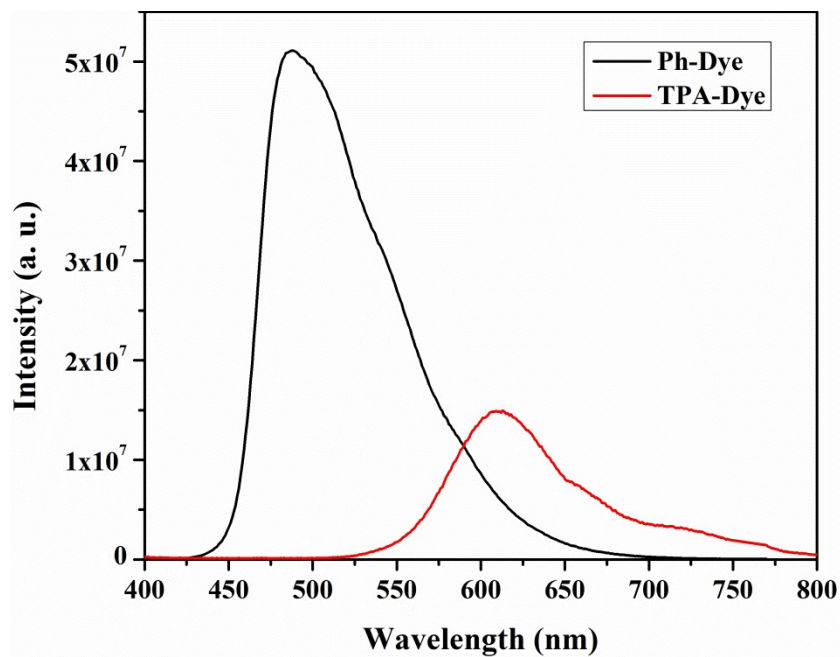


Fig. S14 PL Emission spectra of the yellow (Ph, 487 nm) and orange dye (TPA, 609 nm).

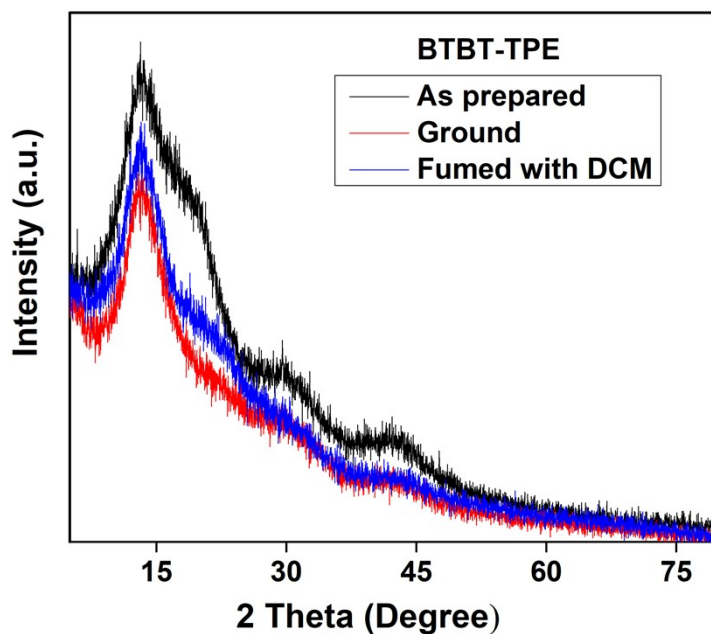


Fig. S15 MFC analysis of BTBT-TPE with PXRD.

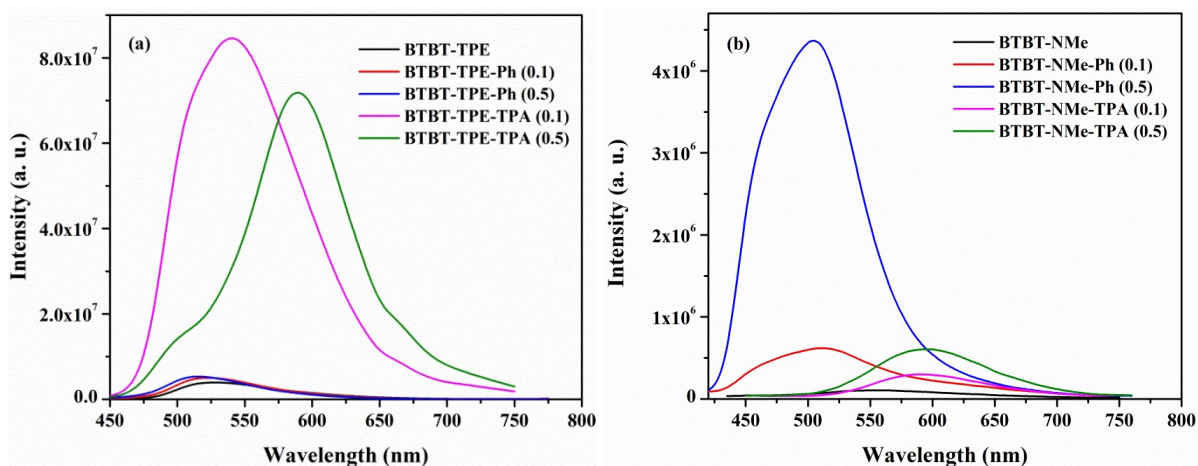


Fig S16 MFC solid emission of the a) **BTBT-TPE** and b) **BTBT-NMe** in different ratio of Ph and TPA ligand.

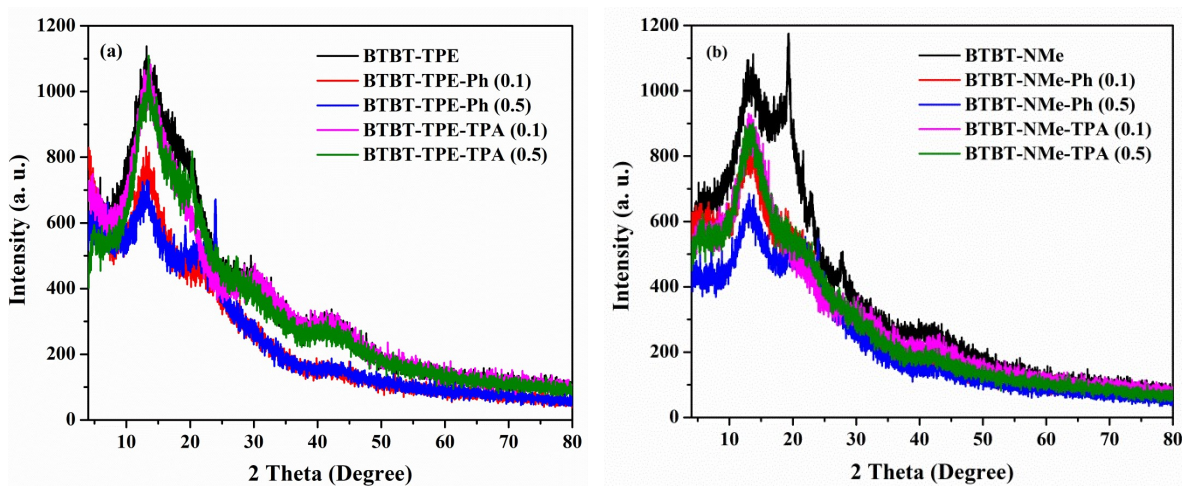


Fig. S17 Comparative intensity ratio of PXRD data of a) **BTBT-TPE** and b) **BTBT-NMe** in different dopant ratio.

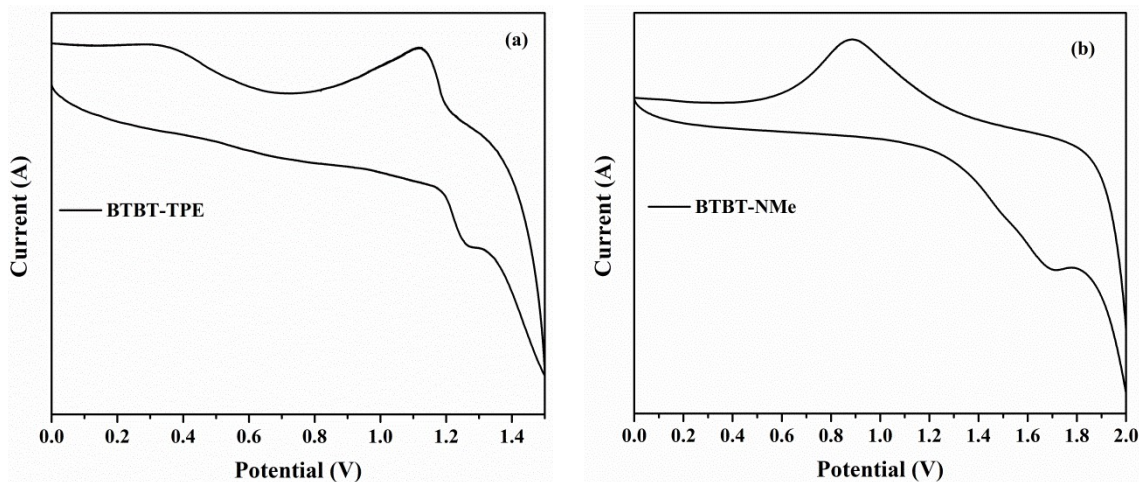


Fig. S18 Cyclicvoltammograms of a) **BTBT-TPE** and b) **BTBT-NMe** in DCM solution.

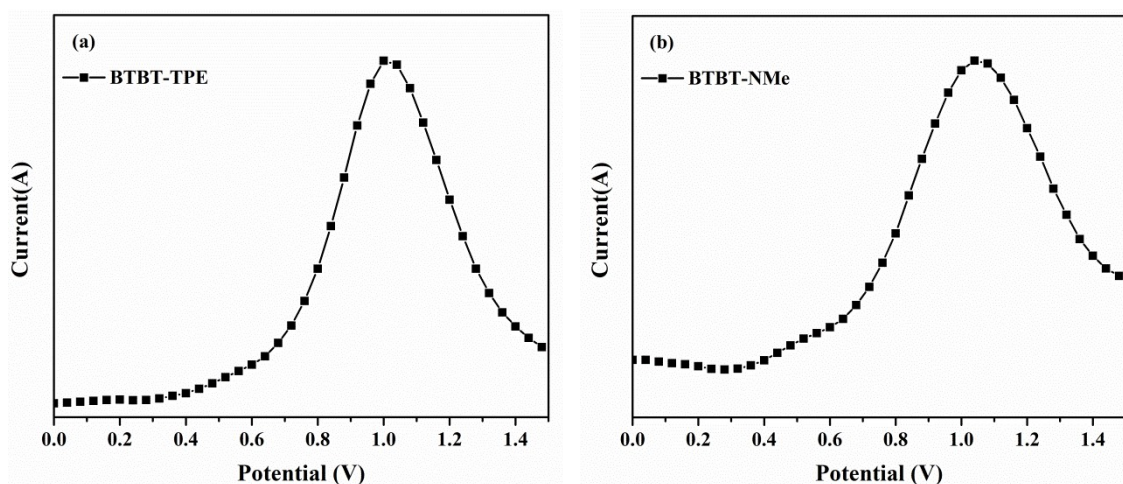


Fig. S19 Differential pulse voltammogram of a) **BTBT-TPE** and b) **BTBT-NMe**.

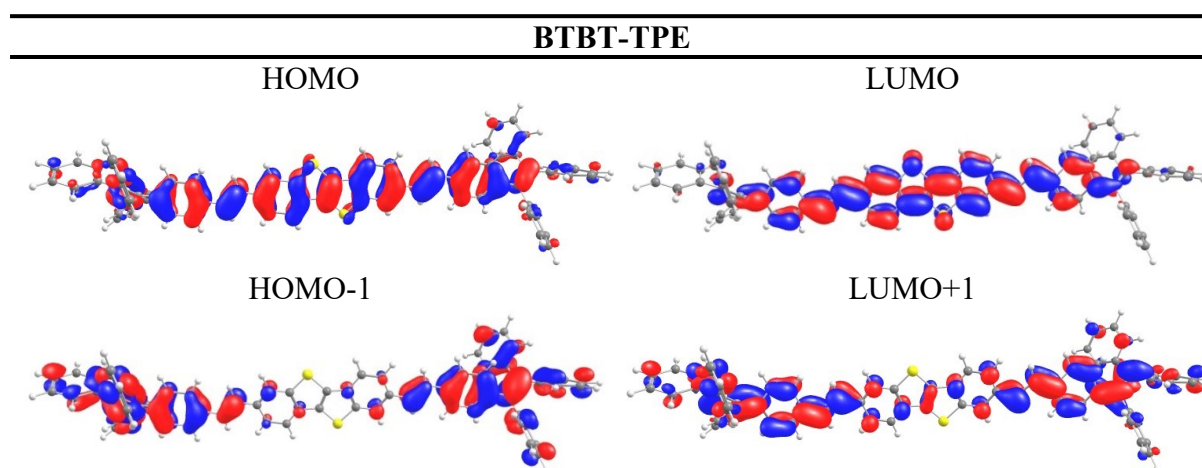
Table S6. HOMO-LUMO Energy levels of **BTBT-TPE** and **BTBT-NMe**.

Name	λ_{\max} (nm)	E_{oxd} (V)	HOMO [eV]	E_{0-0}	LUMO [eV]
BTBT-TPE	399	1.00	-5.80	2.82	-2.98
BTBT-NMe	386	1.04	-5.84	2.85	-2.98

Table S7. Theoretical calculation of the energy states and their comparison with observed one.

Name	λ_{\max} (nm)		HOMO [eV]		E_{0-0}	LUMO [eV]	
	Observed	Theoretical	Observed	Theoretical	Observed	Observed	Theoretical
BTBT-TPE	399	393	-5.80	-5.06	2.82	-2.98	-2.075
BTBT-NMe	386	395	-5.84	-4.83	2.85	-2.98	-1.46

Table S8. HOMO-LUMO frontier orbital of the **BTBT-TPE** and **BTBT-NMe**.



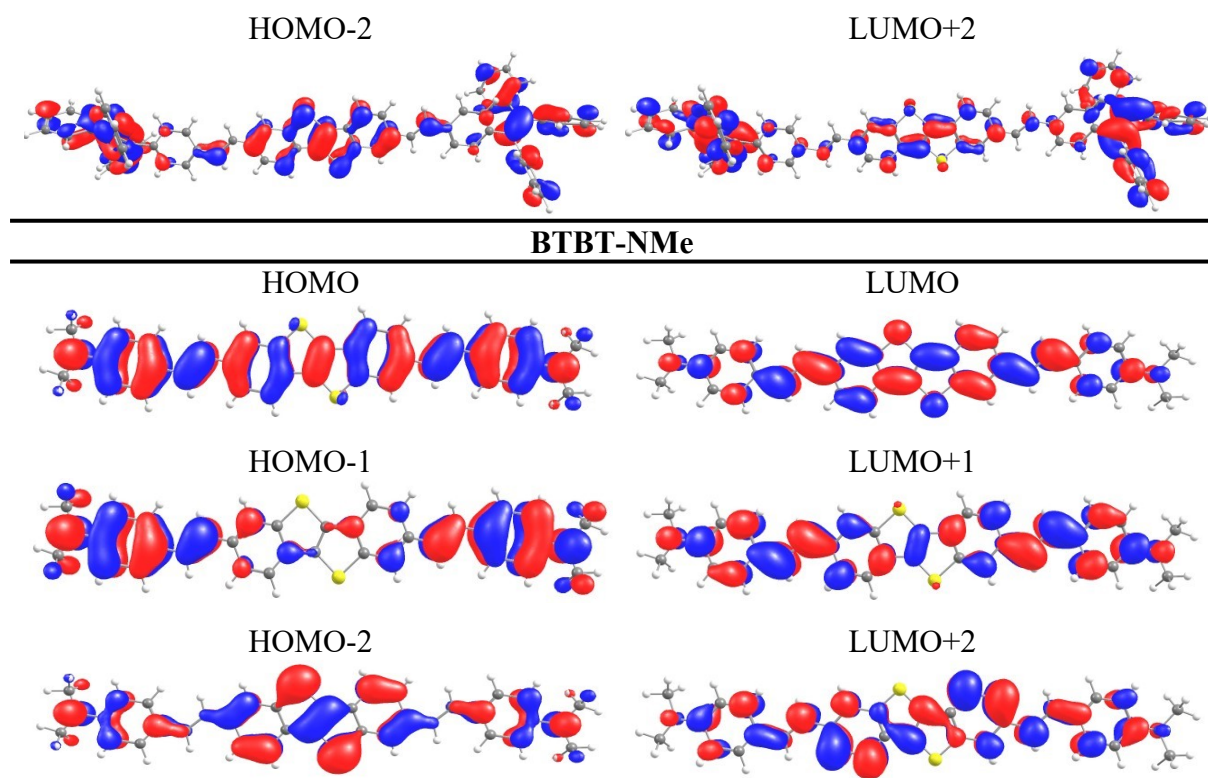


Table S9. Theoretical calculation of the energy states and their Oscillation strength with major contribution.

S. No.	Compound Name	λ_{exp} (nm)	λ_{cal} (nm)	f	State	Major contribution (%)
1.	BTBT-TPE	399	394	3.9539	S1	H-1->L+1 (12%), HOMO->LUMO (76%)
		348		0.1039	S2	H-1->LUMO (38%), HOMO->L+1 (40%)
		317		0.3136	S3	H-2->LUMO (29%), H-1->L+1 (27%), HOMO->L+2 (20%)
		300		0.1122	S4	H-3->LUMO (66%)
		296		0.2467	S5	H-4->LUMO (16%), H-2->L+1 (21%), H-1->L+2 (23%), HOMO->L+3 (22%)
		279		0.0149	S6	H-1->LUMO (25%), HOMO->L+1 (18%)
		272		0.2595	S7	H-2->LUMO (15%), H-2->L+2 (11%), H-1->L+3 (26%), HOMO->L+4 (18%)
		269		0.0003	S8	H-9->LUMO (10%), H-1->LUMO (12%), HOMO->L+1 (12%), HOMO->L+7 (11%)

264	0.0105	S9	H-1->L+5 (11%), HOMO->L+6 (11%)
263	0.0041	S10	
262	0.1958	S11	H-4->L+1 (14%), HOMO->L+2 (12%)
255	0.0164	S12	H-4->LUMO (34%), H-1->L+4 (11%), HOMO->L+3 (14%)

Table S10. Theoretical calculation of the energy states and their Oscillation strength with major contribution.

S. No.	Compound Name	λ_{exp} (nm)	λ_{cal} (nm)	f	State	Major contribution (%)
2.	BTBT-NMe	374	396	3.5325	S1	H-1->L+1 (12%), HOMO->LUMO (80%)
			297	0.1306	S3	H-3->LUMO (38%), H-2->LUMO (38%)
			284	0.1912	S4	H-3->LUMO (12%), H-2->LUMO (20%), H-1->L+1 (27%), HOMO->L+2 (24%)
			269	0.0998	S7	H-1->L+5 (36%), HOMO->L+4 (14%), HOMO->L+6 (22%)
			251	0.1554	S9	H-3->LUMO (36%), HOMO->L+2 (25%)
			244	0.158	S11	H-2->LUMO (16%), H-1->L+1 (22%), HOMO->L+4 (18%), HOMO->L+6 (12%)

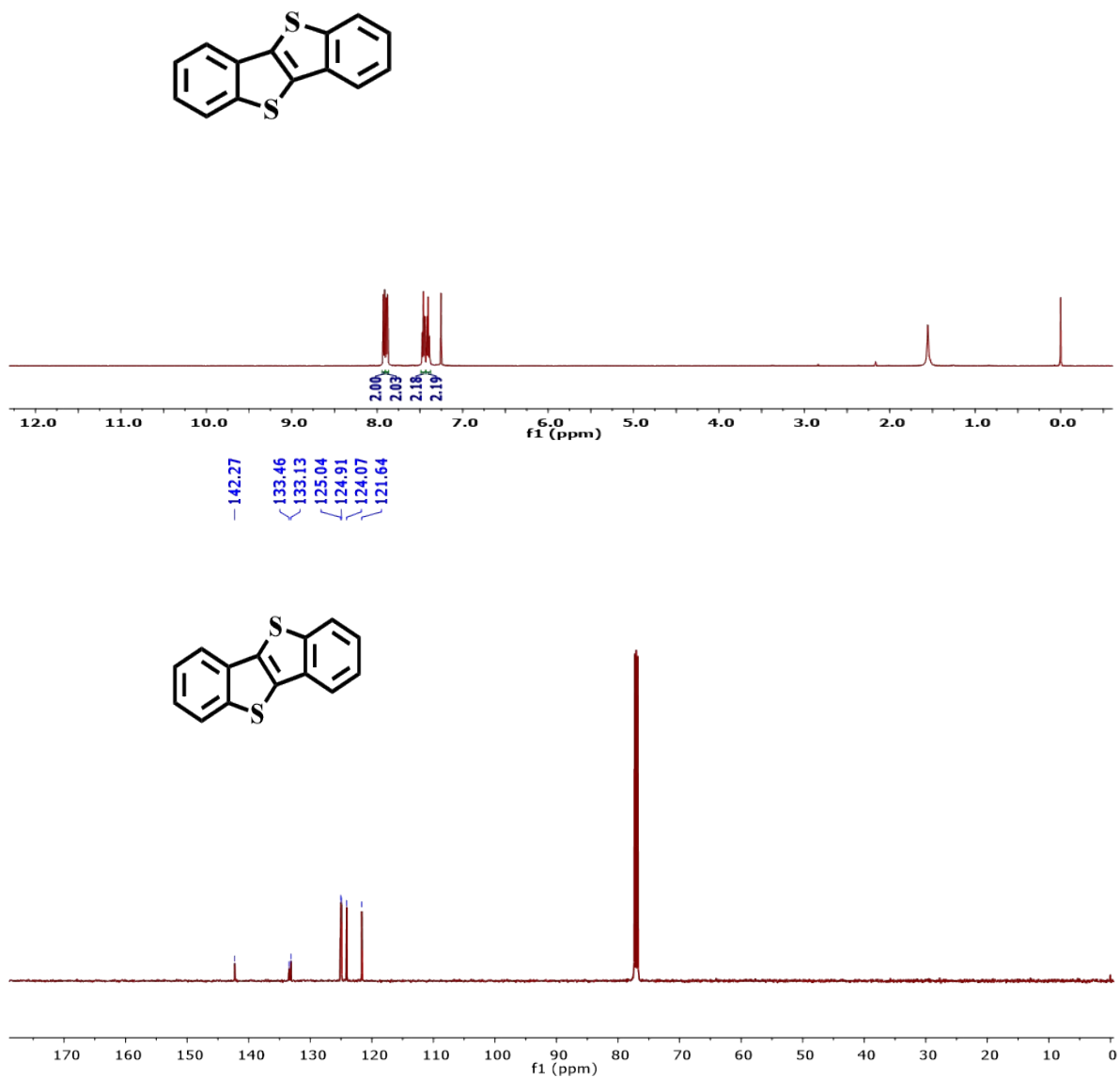


Fig. S20 ¹H and ¹³C NMR Spectra of BTBT recorded in CDCl₃.

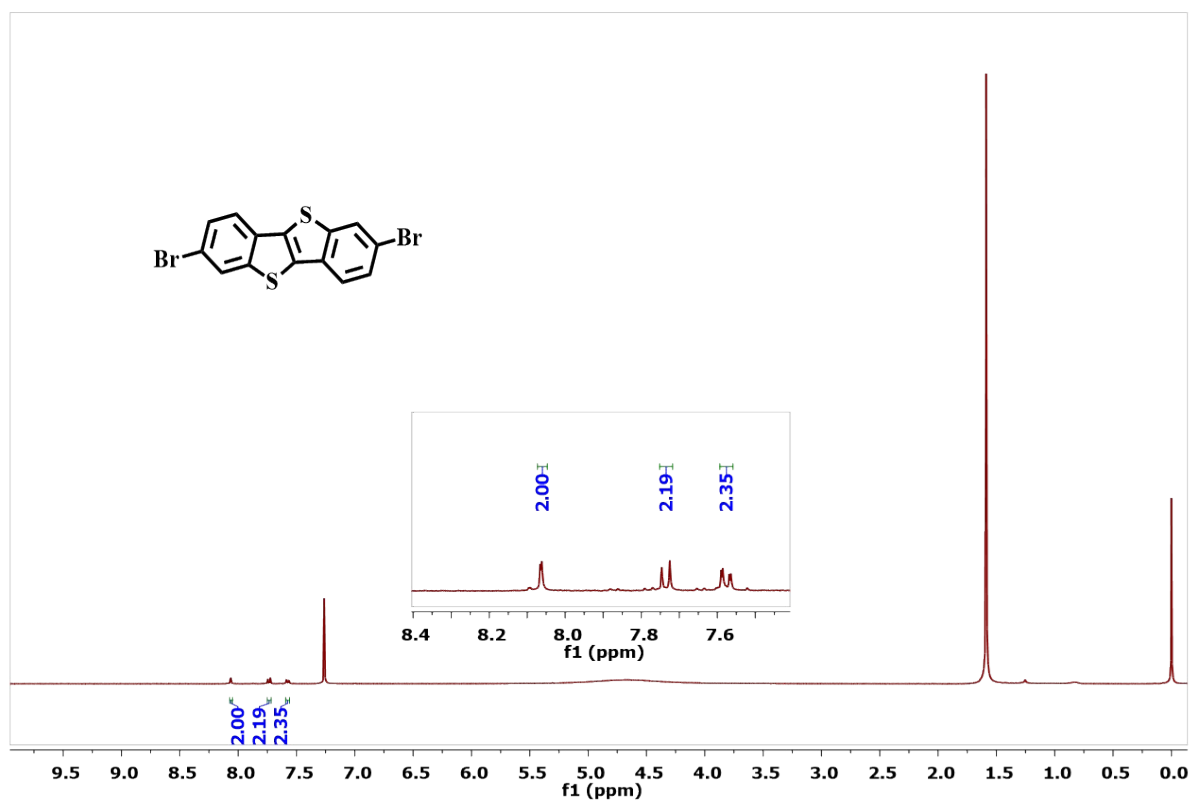


Fig. S21 ¹H NMR Spectra of 2,7-dibromo[1]benzothieno[3,2-*b*]benzothiophene recorded in CDCl₃.

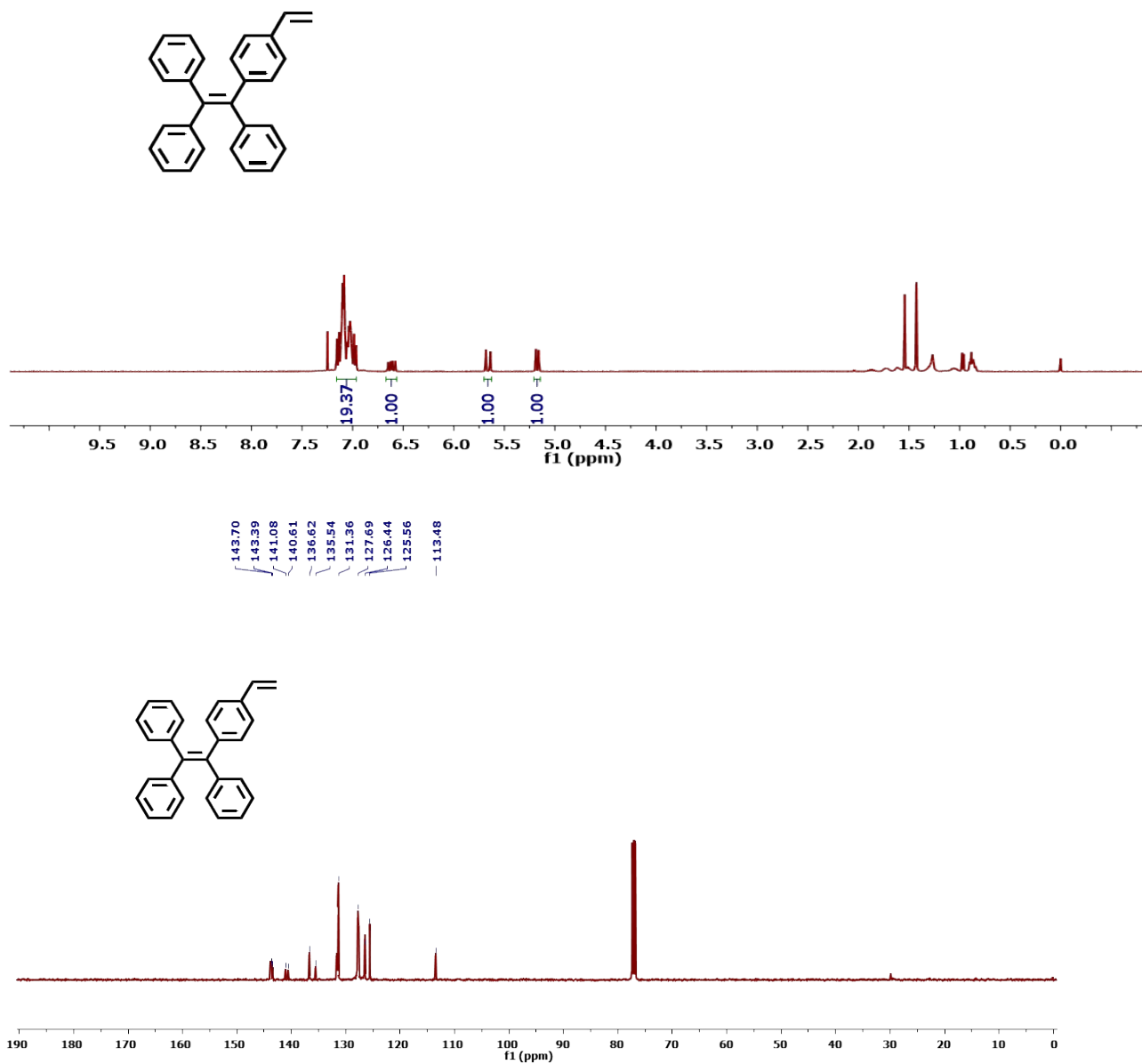


Fig. S22 ^1H and ^{13}C NMR Spectra of (2-(4-vinylphenyl) ethene-1,1,2-triyl) tribenzene recorded in CDCl_3 .

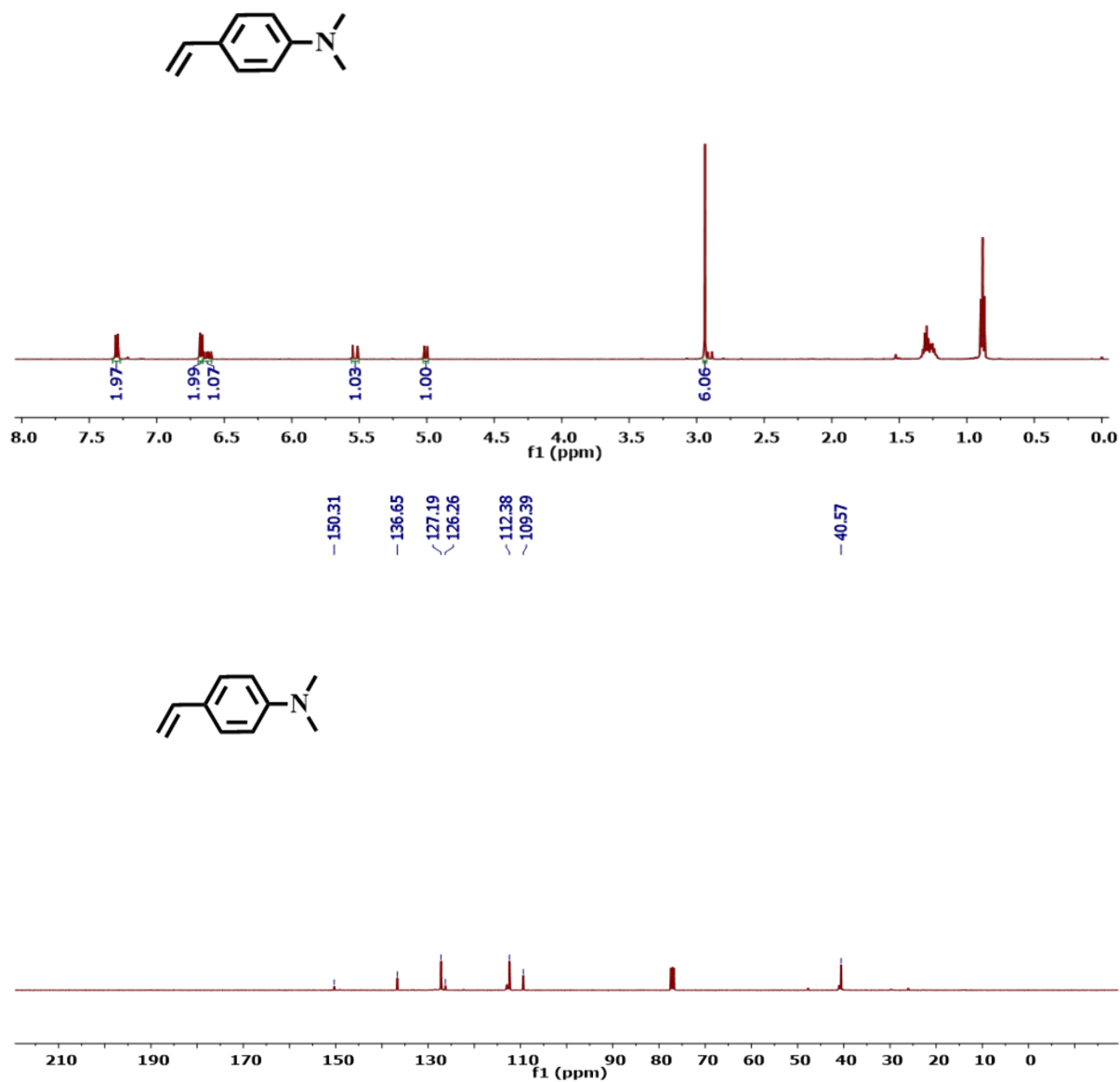


Fig. S23 ¹H and ¹³C NMR Spectra of N, N-Dimethylamino-4-vinylbenzene recorded in CDCl₃.

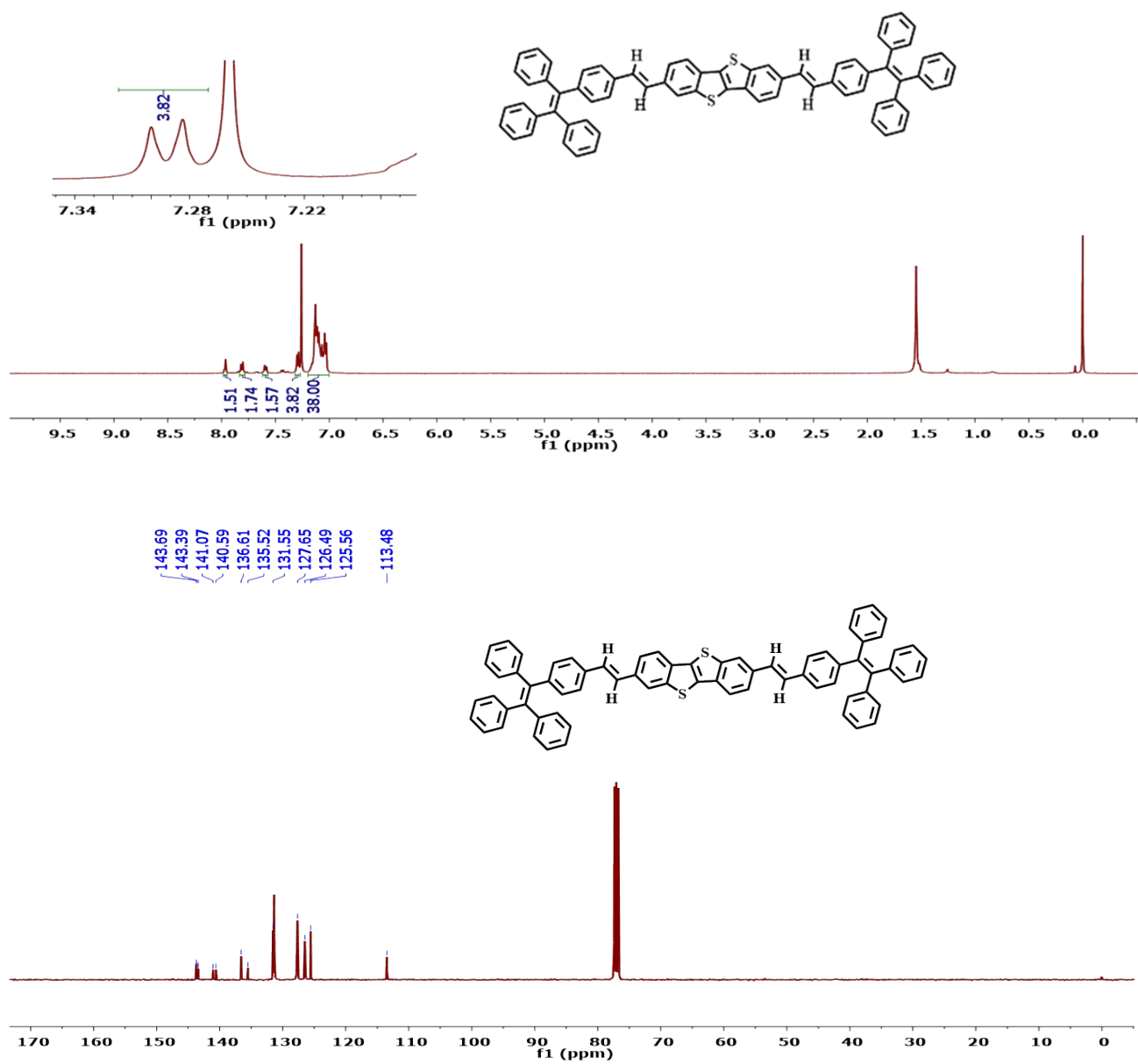


Fig. S24 ^1H and ^{13}C NMR Spectra of BTBT-TPE recorded in CDCl_3 .

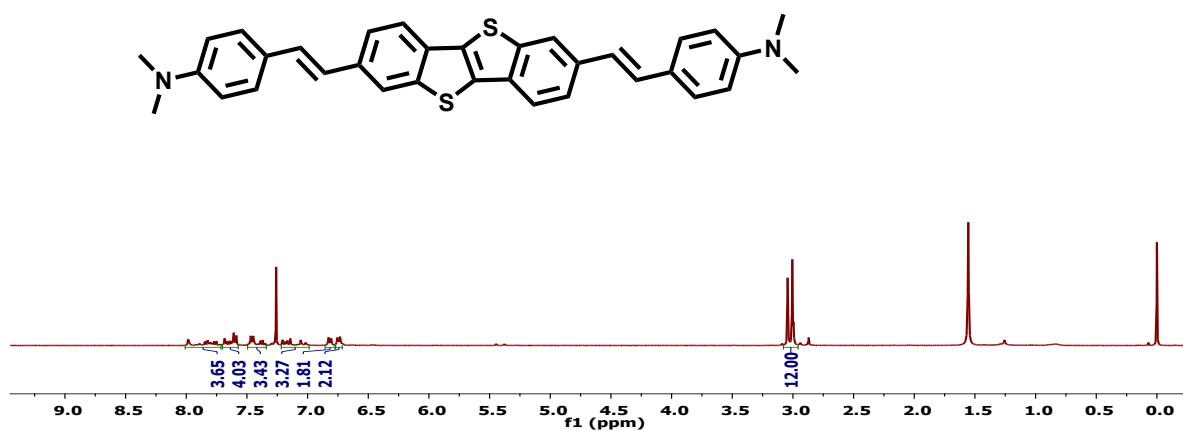


Fig. S25 ¹H NMR Spectra of BTBT-NMe recorded in CDCl₃.

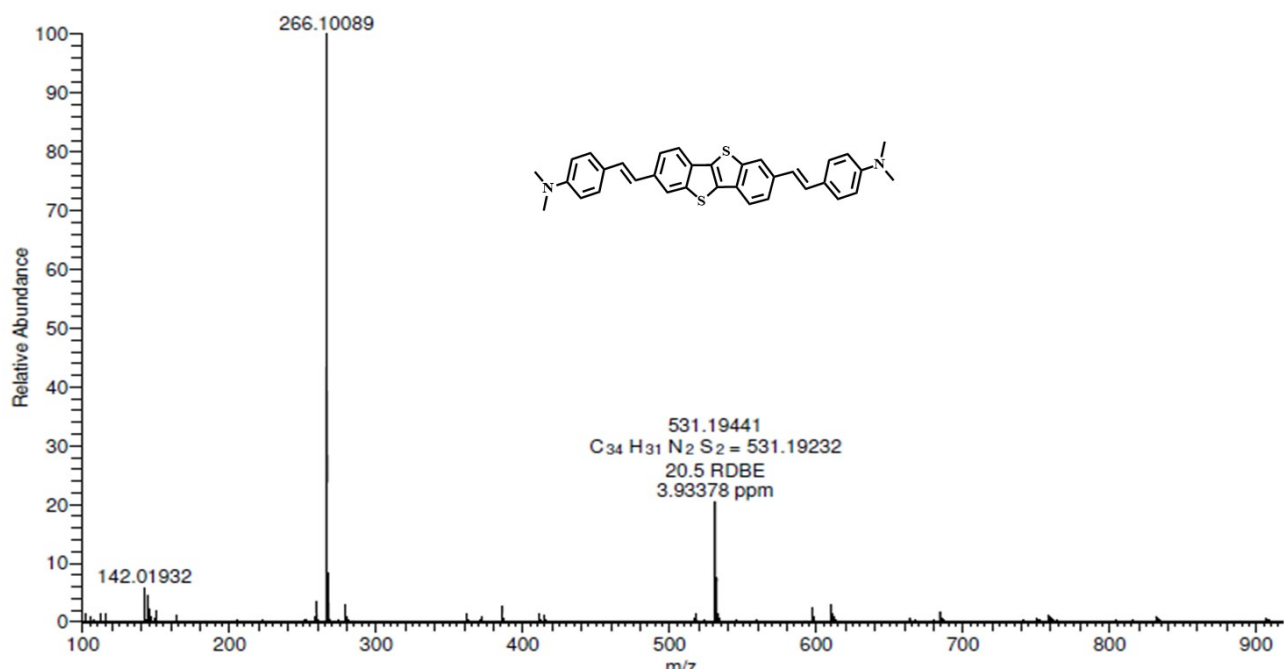


Fig. S26 HRMS Spectra of BTBT-NMe.

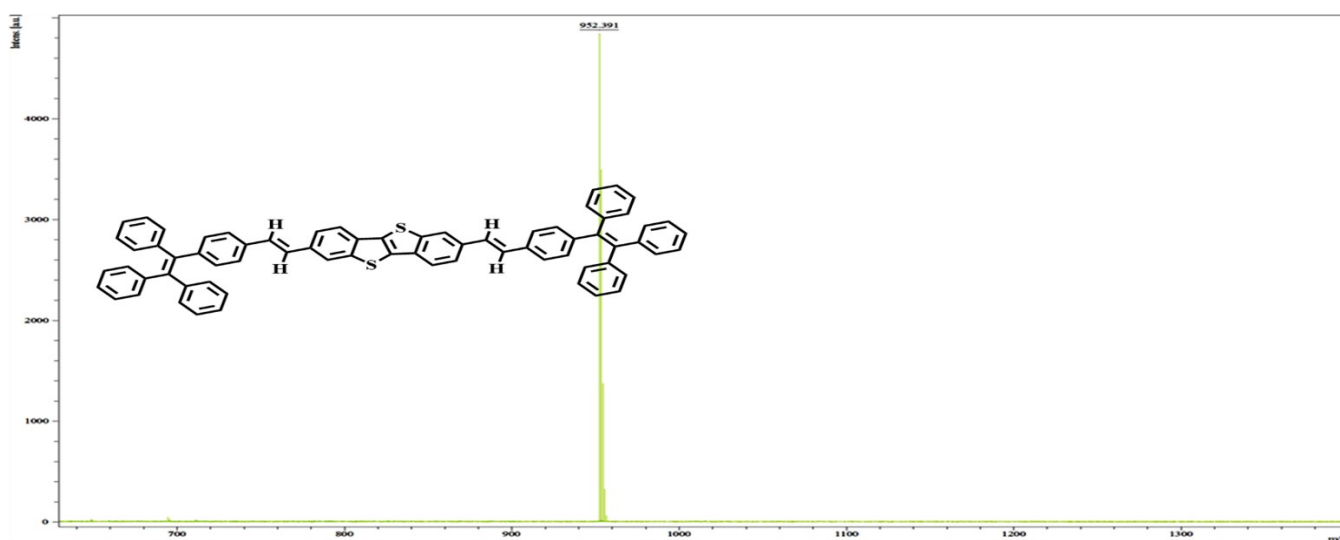
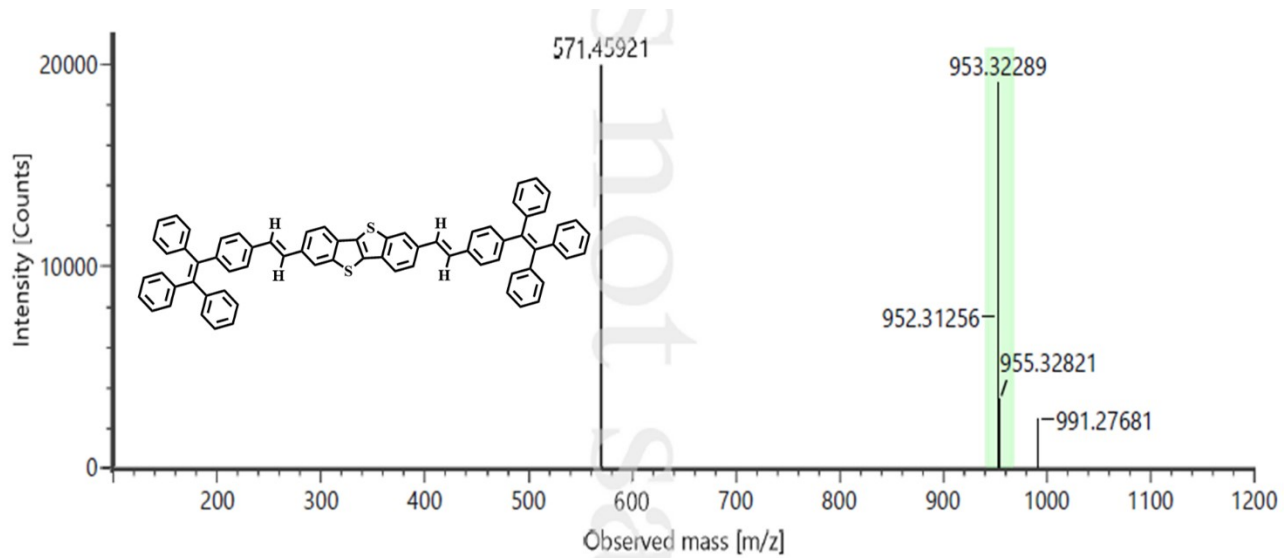


Fig. S27 HRMS and MALDI-TOF Spectra of BTBT-TPE.

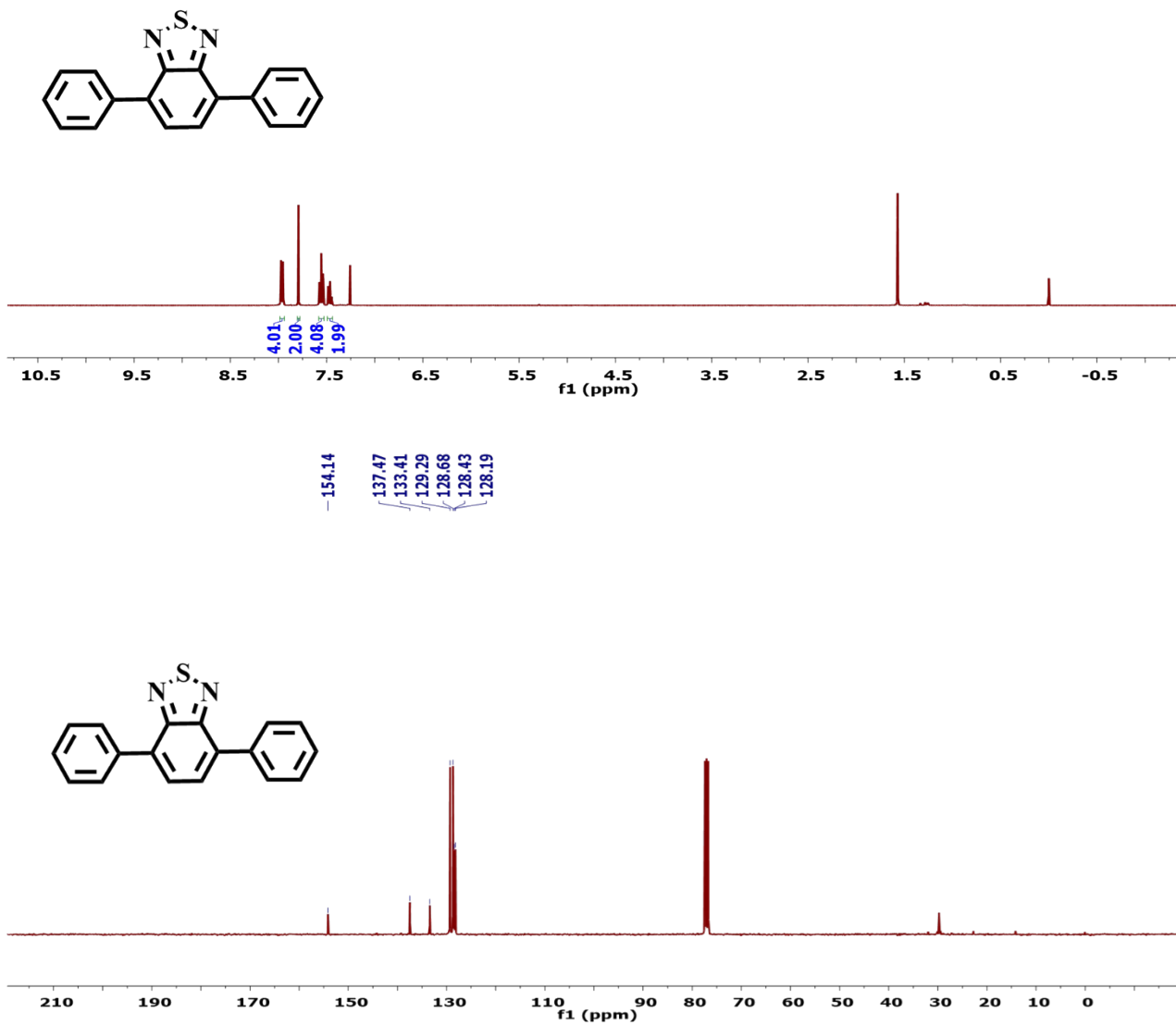


Fig. S28 ^1H and ^{13}C NMR Spectra of Ph-BT-Ph recorded in CDCl_3 .

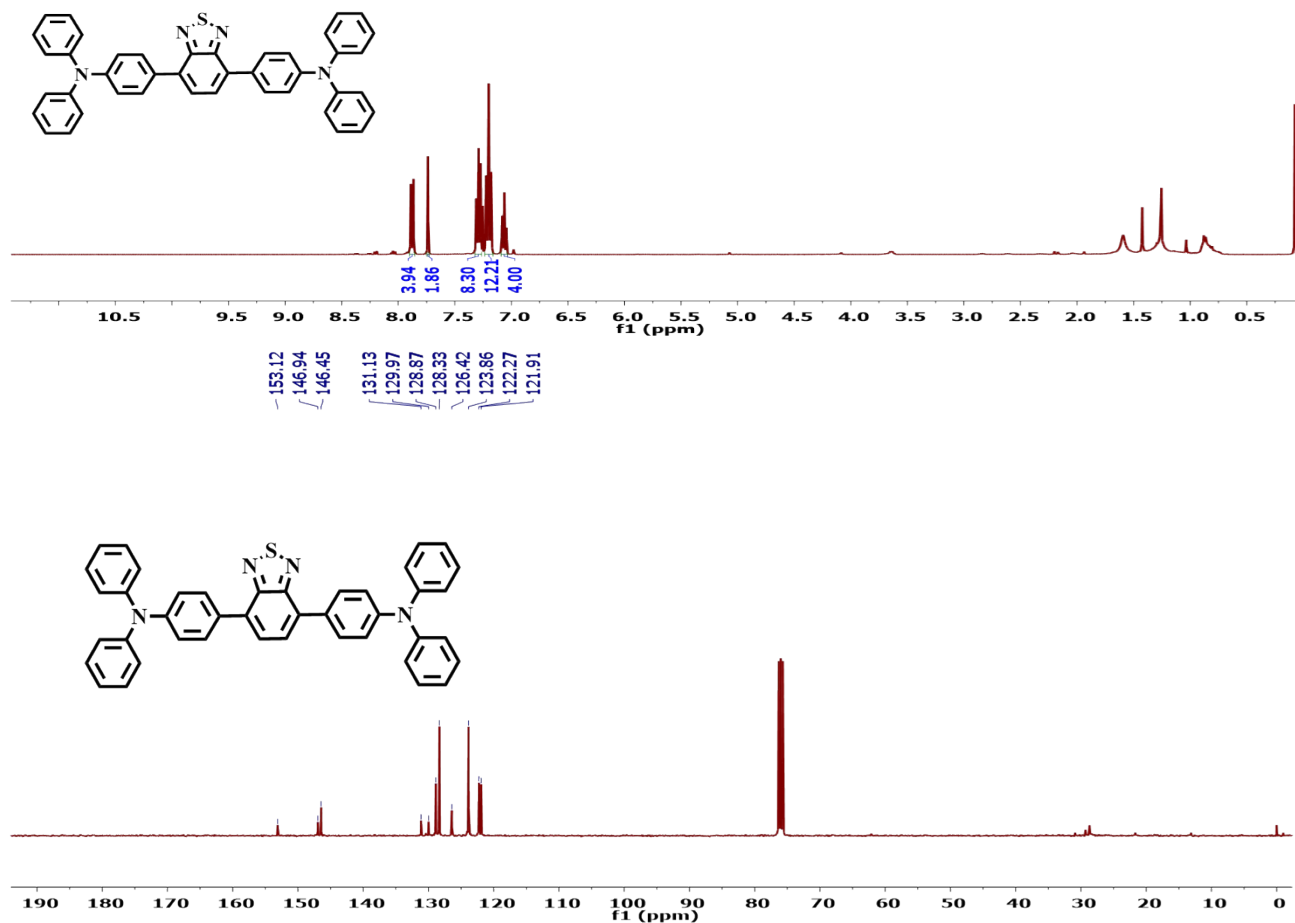


Fig. S29 ^1H and ^{13}C NMR Spectra of TPA-PH-TPA recorded in CDCl_3 .

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