Substitution Pattern Controlled Charge Transport in BN-Embedded Aromatics-Based Single-Molecule Junctions

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1. Fluoride anion titrations experiments

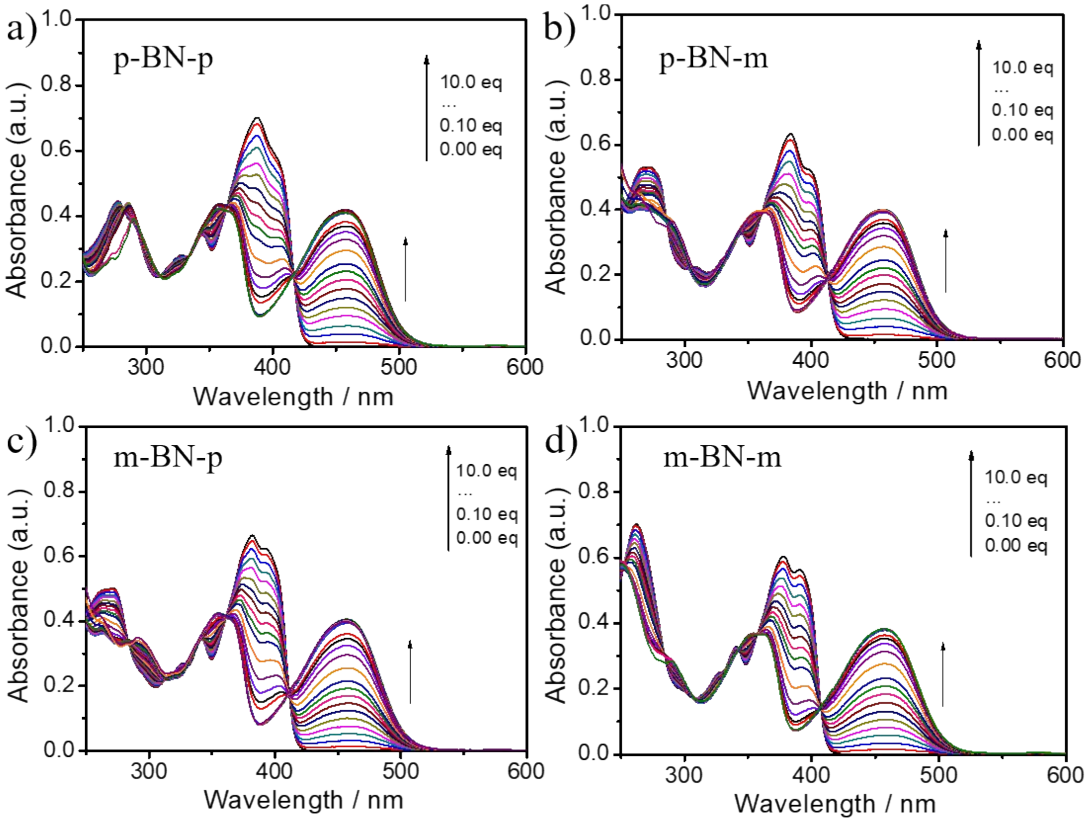


Figure S1. Fluoride anion titrations monitored by UV−vis absorption for compound a) p-BN-p, b) p-BN-m, c) m-BN-p, and d) m-BN-m respectively, in THF (10 μM).

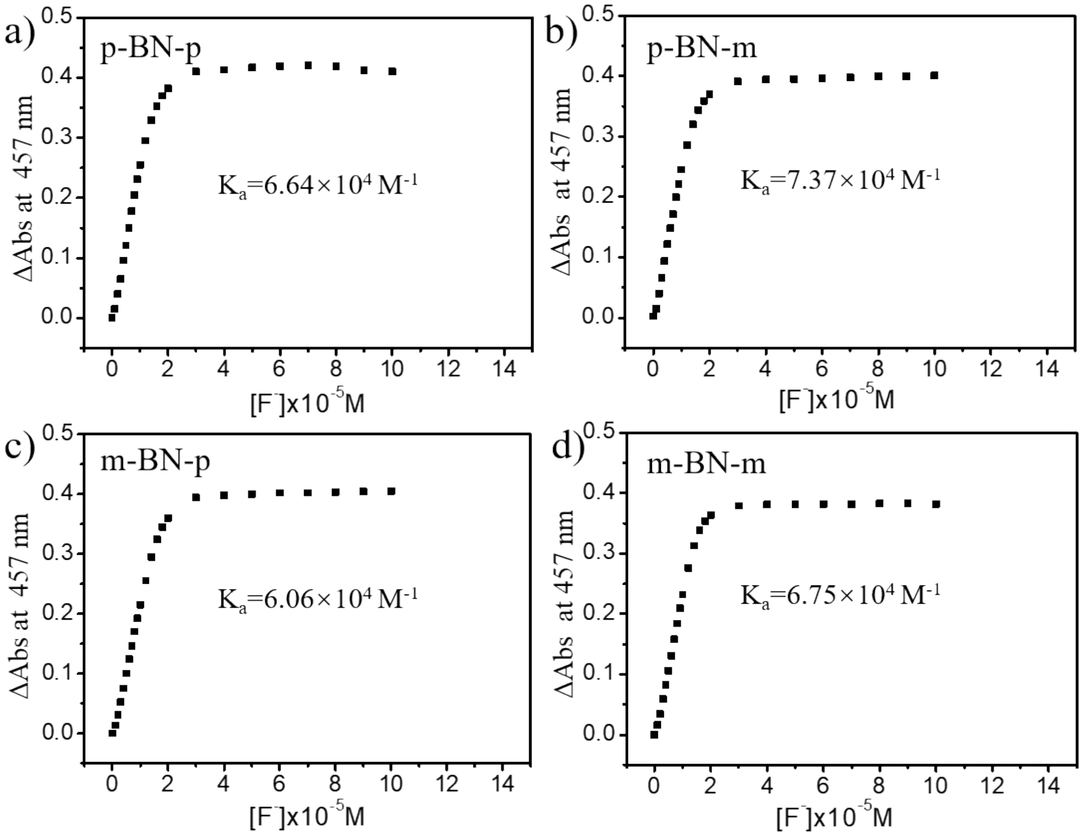


Figure S2. The changes of absorbance intensity at 457 nm for compound a) p-BN-p, b) p-BN-m, c) m-BN-p, and d) m-BN-m, respectively, during the titration of 0-10 eq. Fluoride anion.

2. Cyclic voltammograms experiments

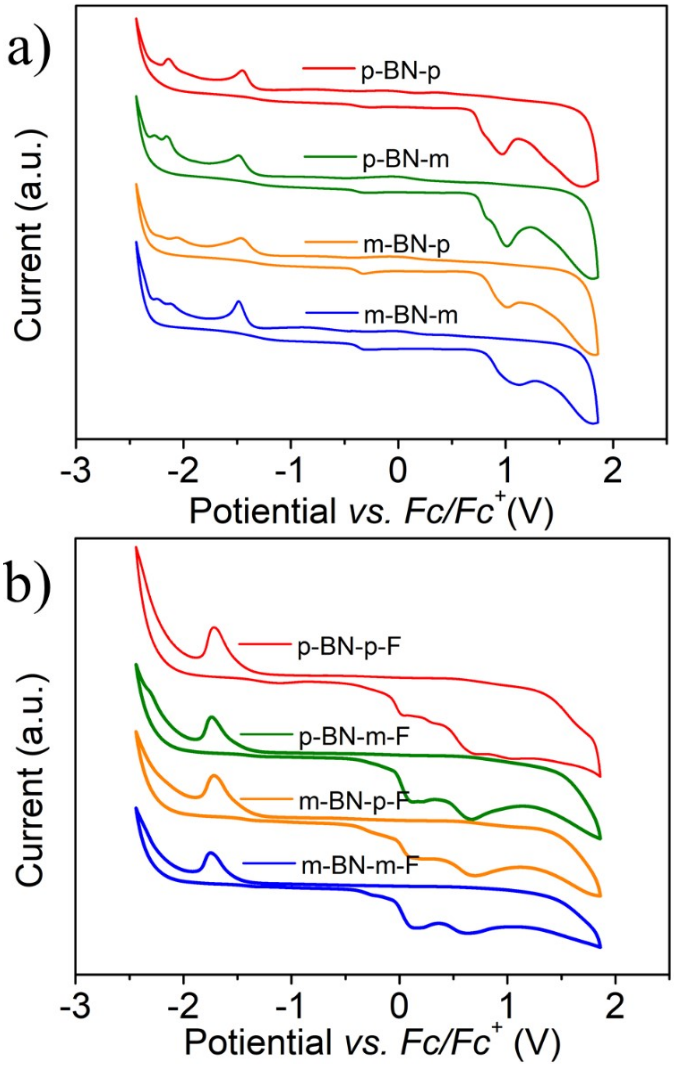


Figure S3. Cyclic voltammograms of p-BN-p, p-BN-m, m-BN-p and m-BN-M, respectively, and the profile after the addition of TBAF.

3. Summarized photophysical and electrochemical parameters

Table S1. Photophysical and electrochemical parameters of the BN-incorporated derivatives and their fluoride-coordinated analogues.

Sample	HOMO^{exp} (eV)[a]	LUMO^{exp} (eV) [a]	E_g^{exp} (eV)[b]	E_g^{opt} (eV)[c]
p-BN-p	-5.50	-3.46	2.04	2.94
p-BN-p-F	-4.36	-3.33	1.03	2.46
p-BN-m	-5.53	-3.45	2.08	2.96
p-BN-m-F	-4.42	-3.30	1.12	2.46
m-BN-p	-5.58	-3.51	2.07	2.99
m-BN-p-F	-4.38	-3.33	1.05	2.46
m-BN-m	-5.61	-3.43	2.18	3.02
m-BN-m-F	-4.39	-3.28	1.11	2.46

[a] E_{HOMO} and E_{LUMO} are obtained from the onset of the first oxidation and reduction curve, respectively. [b] E_g is calculated by $E_g=E_{LUMO}-E_{HOMO.}$ [c] The optical energy band gap E_g is calculated by the onset of absorption spectra. Notes: Cyclic voltammetry (CV) measurements were performed in DCM solution using $TBAPF_6$ as the electrolyte and calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple, with a scanning rate of 100 mV s^{-1}.

4. Single-crystal X-ray structure and crystal data of p-BN-p

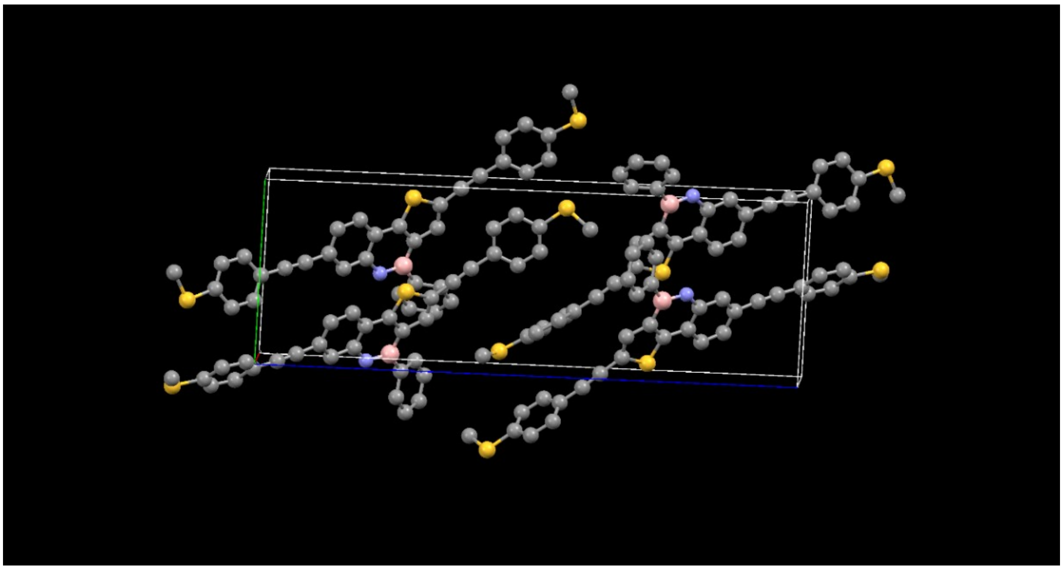


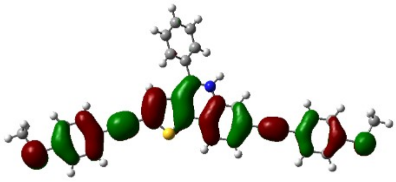
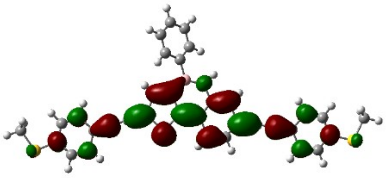
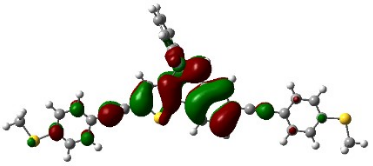
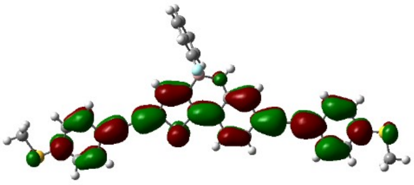
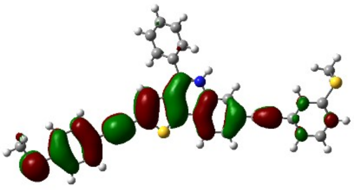
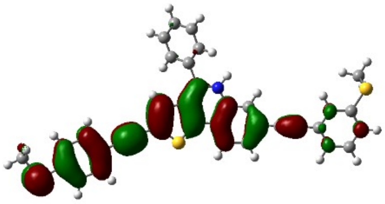
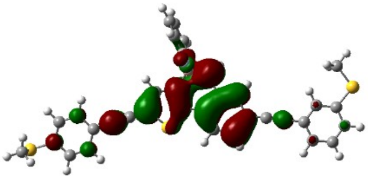
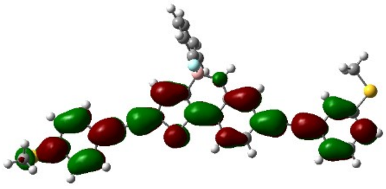
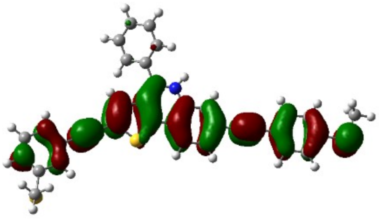
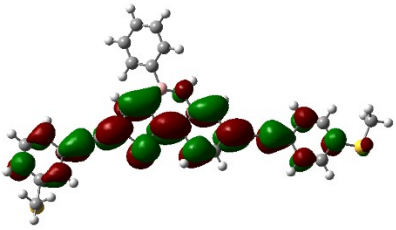
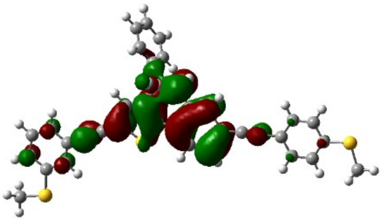
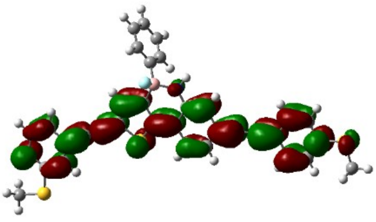
Figure S4. Single-crystal X-ray structure of p-BN-p.

Table S2. Crystal data and structure refinement for p-BN-p.

Empirical formula	$C_{34} H_{24} B N S_3$	
Formula weight	553.53	
Temperature	192.99 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.1902(3) Å	α= 88.437(2)°.
	b = 10.2138(3) Å	β= 86.185(2)°.
	c = 28.5888(8) Å	γ = 69.035(2)°.
Volume	2772.38(14) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	1.709 mm^{-1}	
F(000)	1152	
Crystal size	0.1 x 0.06 x 0.05 mm^3	
Theta range for data collection	2.695 to 54.946°.	
Index ranges	-12<=h<=12, -11<=k<=12, -34<=l<=34	
Reflections collected	36406	
Independent reflections	15955 [R(int) = 0.0602]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7508 and 0.5038
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15955 / 3 / 1413
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0571, wR2 = 0.1376
R indices (all data)	R1 = 0.0724, wR2 = 0.1525
Absolute structure parameter	0.479(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.364 and -0.490 e.Å^{-3}

5. The frontier molecular orbitals and energy levels calculated from DFT

Sample	HOMO	LUMO
p-BN-p		
p-BN-p-F		
p-BN-m		
p-BN-m-F		
m-BN-p		
m-BN-p-F		

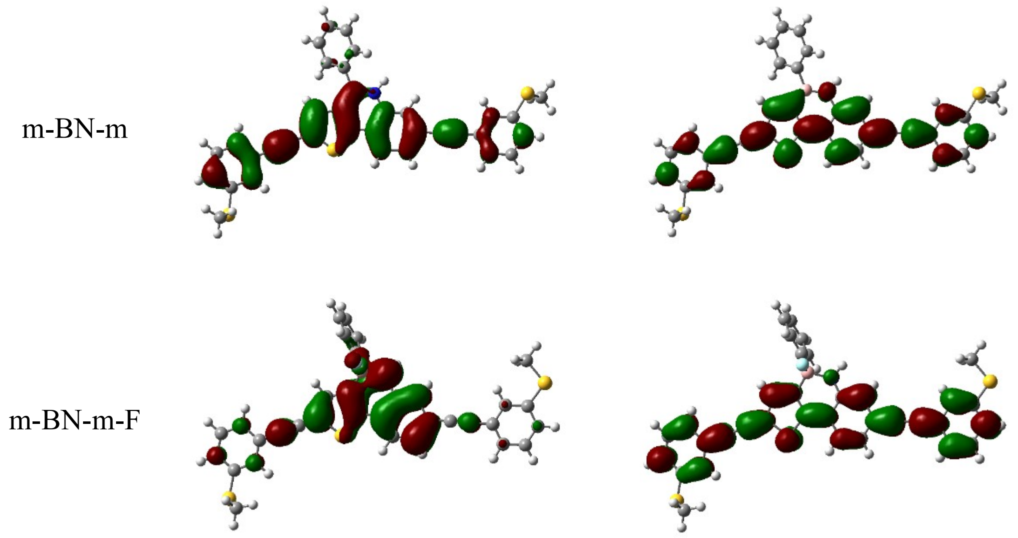


Figure S5. DFT-calculated frontier molecular orbitals of the BN-incorporated derivatives and their fluoride-coordinated analogues.

Table S3. The energies of frontier molecular orbitals calculated from DFT.

Sample	HOMO^{cal} (eV)	LUMO^{cal} (eV)	E_g^{cal} (eV)
p-BN-p	-5.04	-1.88	3.16
p-BN-p-F	-1.86	0.67	2.53
p-BN-m	-5.13	-1.96	3.17
p-BN-m-F	-2.00	0.47	2.47
m-BN-p	-5.18	-1.95	3.23
m-BN-p-F	-1.88	0.65	2.53
m-BN-m	-5.31	-2.02	3.29
m-BN-m-F	-1.96	0.56	2.52

6. Synthetic routes

Compound p-SMe, m-SMe and Br-Th were synthesized according to the reported literatures.[1-3]

Synthesis of compound BN-Br

Compound Br-Th (1.80 g, 7.08 mmol) was dissolved in 90 ml o-DCB under argon atmosphere. After Et_3N(2.93 g, 21.25 mmol) was added into the solution, $PhBCl_2$ (1.69 g, 10.62 mmol) was injected slowly and heated to 180 °C for 12 h. After cooling to the room temperature, the solvent was removed by reduced-pressure distillation and the residue was extracted with DCM and washed for several times. The combined organic phase was dried over Na_2SO_4 and filtered. Then, the solvent was evaporated in vacuum and the product was purified by chromatography (DCM: PE = 1:5) to give product BN-Br as white solid in 90% yield (2.17 g, 6.37 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 3H), 7.77 (d, *J* = 4.8 Hz, 2H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.54-7.50 (m, 3H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.36, 138.83, 133.11, 131.71, 129.55, 128.37, 126.31, 124.92, 124.63, 121.50, 120.99, 120.65.

Synthesis of compound Br-BN-Br

Compound BN-Br (1.00 g, 2.94 mmol) was dissolved in DCM. After cooling to 0 °C, NBS (523 mg, 2.94 mmol) in 10 ml DCM was added slowly into the flask in the dark and stirred overnight. After the reaction was completed, the solvent was evaporated and the residue was purified by chromatography (DCM:PE=1:5) to give a white solid (1.01 g, 2.41 mmol), yielding 82%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.77 (s, 1H), 7.71-7.68 (m, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.53-7.51 (m, 3H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 1H).

Synthesis of compound p-BN-p

Compound Br-BN-Br (197 mg, 0.47 mmol), CuI (8.96 mg, 0.047 mmol), $PdCl_2(PPh_3)_2$ (33 mg, 0.047 mmol) were added into 50 ml Schenk tube under argon atmosphere. Then, 10 ml degassed NEt_3 was injected into the system, followed by the addition of compound p-SMe (153 mg, 1.03 mmol) with syringe. The solution was heated at 60 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO4, after the solvent was removed, a crude which was purified by recrystallization with DCM/PE to afford a yellow powder p-BN-p (182 mg, 0.33 mmol) in 70% yield. ^1H NMR (600 MHz, $C_2Cl_4D_2$) δ 7.94 (s, 1H), 7.92-7.91 (m, 2H), 7.90-7.88 (d, *J* = 8.4 Hz, 1H) 7.87 (s, 1H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.58-7.54 (m, 3H), 7.53(d, *J* = 8.4 Hz, 2H) 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.26 (d, *J* = 8.4, 2H), 7.25 (d, *J* = 8.4, 2H), 2.53 (s, 1H), 2.53 (s, 1H).^{13}C NMR (150 MHz, $C_2Cl_4D_2$) δ 151.82, 139.54, 139.38, 137.63, 136.62, 132.82, 131.74, 131.51, 129.46, 128.19, 125.43, 125.40, 124.93, 124.70, 122.63, 122.39, 121.60, 120.54, 118.76, 118.47, 94.34, 90.61, 89.13, 82.91, 15.03, 15.00. TOF-MS-EI $C_{34}H_{24}BNS_3$ m/z [M^+] calcd for 553.1164 found: 553.1169.

Synthesis of compound p-BN-Br

Compound Br-BN-Br (400 mg, 0.96 mmol), CuI (9.14 mg, 0.048 mmol), $PdCl_2(PPh_3)_2$ (33.5 mg, 0.048 mmol) were added into 100 ml Schenk tube under argon atmosphere. Then, 20 ml degassed THF and NEt_3 (1:1, volume) were injected into the tube, followed by the addition of compound p-SMe (142 mg, 0.96 mmol) with syringe. The solution was heated at 60 ^oC for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO_4, after the solvent was removed, a crude which was purified by chromatography with DCM/PE=1/5 to afford a white powder p-BN-Br (278 mg, 0.57 mmol) in 60% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 8.04 - 8.01 (m, 2H), 7.99 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.62-7.56 (m, 5H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 151.84, 140.83, 140.75, 137.22, 134.30, 132.09, 130.04, 128.58, 126.78, 126.05, 125.03, 122.37, 121.79, 121.71, 119.61, 117.99, 94.98, 83.21, 14.63.

Synthesis of compound p-BN-m

Compound p-BN-Br (194 mg, 0.40 mmol), CuI (3.8 mg, 0.02 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) were added into 50 ml Schenk tube under argon atmosphere. After that, 10 ml degassed THF and NEt_3 (1:1, volume) were injected into the system, followed by the addition of compound m-SMe (65 mg, 0.44 mmol) with syringe. The solution was heated at 60 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO_4, after the solvent was removed, a crude which was purified by recrystallization with DCM/PE to afford a yellow powder p-BN-m (150 mg, 0.27 mmol) in 68% yield. ^{1}H NMR (400 MHz, $C_2Cl_4D_2$) δ 7.93-7.88 (m, 5H), 7.60 (s, 1H), 7.58-7.55 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J*=8, *J*=1.2Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 9.2 Hz, 1H), 7.27-7.22(m, 3H), 2.53 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) δ 151.93, 139.73, 138.79, 137.78, 136.77, 133.01, 131.69, 129.65, 128.72, 128.37, 128.17, 126.35, 125.53, 125.15, 124.89, 124.87, 123.45, 122.63, 122.48, 121.95, 120.88, 118.61, 94.56, 90.38, 89.58, 83.08, 15.49, 15.15. TOF-MS-EI $C_{34}H_{24}BNS_3$ m/z [M^+] calcd for 553.1164 found: 553.1166. TOF-MS-EI $C_{34}H_{24}BNS_3$ m/z [M^+] calcd for 553.1164 found: 553.1169.

Synthesis of compound m-BN-Br

Compound Br-BN-Br (200 mg, 0.48 mmol), CuI (9.14 mg, 0.024 mmol), $PdCl_2(PPh_3)_2$ (33.5 mg, 0.024 mmol) were added into 50 ml Schenk tube under argon atmosphere. Then, 10 ml degassed THF and NEt_3 (1:1, volume) were injected into the tube, followed by the addition of compound m-SMe (71 mg, 0.48 mmol) with syringe. The solution was heated at 60 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO_4, after the solvent was removed, a crude which was purified by chromatography with DCM/PE=1/5 to afford a white powder m-BN-Br (127 mg, 0.26 mmol) in 55% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.99-7.97 (m, 3H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.57-7.53 (m, 3H), 7.46 (s, 1H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38-7.31 (m, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 152.07, 140.78, 139.76, 137.69, 134.29, 130.03, 129.69, 128.57, 128.09, 128.03, 127.05, 126.78, 125.02, 122.99, 122.38, 121.79, 121.43, 119.58, 94.59, 83.62, 14.88.

Synthesis of compound m-BN-p

Compound m-BN-Br (100 mg, 0.21 mmol), CuI (2 mg, 0.01 mmol), $PdCl_2(PPh_3)_2$ (7.2mg, 0.01 mmol) were added into 50 ml Schenk tube under argon atmosphere. After that, 10 ml degassed NEt_3 was injected into the system, followed by the addition of compound p-SMe (34 mg, 0.21 mmol) with syringe. The solution was heated at 60 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO4, after the solvent was removed, a crude which was purified by recrystallization with DCM/PE to afford a yellow powder m-BN-p (68 mg, 0.13 mmol) in 60% yield. ^1H NMR (600 MHz, C_2Cl_4 D_2) δ 7.96 (s, 1H), 7.92-7.89 (m, 3H), 7.87 (s, 1H), 7.60 (d, J = 1.2 Hz, 1H), 7.57-7.54 (m, 3H), 7.53 (d, J = 8.4 Hz, 2H), 7.44 (s, 1H), 7.43 (dd, J = 8.4, 1.2 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.27-7.24 (m, 3H), 2.53 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, C_2Cl_4 D_2) δ 151.82, 139.18, 138.46, 137.45, 136.79, 132.60, 131.52, 129.25, 128.33, 128.11, 127.98, 127.55, 126.09, 125.22, 124.74, 124.50, 122.81, 122.50, 121.83, 121.40, 120.29, 118.53, 93.76, 90.43, 88.89, 83.00, 15.11, 14.81. TOF-MS-EI $C_{34}H_{24}BNS_3$ m/z [M^+] calcd for 553.1164 found: 553.1167.

Synthesis of compound m-BN-m

Compound Br-BN-Br (250 mg, 0.60 mmol), CuI (11.35 mg, 0.06 mmol), $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol) were added into 50 ml Schenk tube under argon atmosphere. After that, 10 ml degassed NEt_3 was injected into the system, followed by the addition of compound m-SMe (195 mg, 1.31 mmol) with syringe. The solution was heated at 60 °C for overnight. After cooling to room temperature, the reaction mixture was concentrated and extracted 3 times with EA. The combined organic layers were dried with Na_2SO_4, after the solvent was removed, a crude which was purified by recrystallization with DCM/PE to afford a yellow powder m-BN-m (215 mg, 0.39 mmol) in 65% yield. ^1H NMR (400 MHz, C_2Cl_4 D_2) δ 7.96 (s, 1H), 7.93-7.88 (m, 4H), 7.60-7.56 (m, 4H), 7.46-7.42 (m, 3H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (td, J = 7.6, 3.2 Hz, 2H), 7.27-7.25 (m, 2H), 2.54 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, C_2Cl_4 D_2) δ

151.72, 138.43, 138.37, 137.38, 136.75, 132.58, 129.23, 128.35, 128.30, 128.06, 127.95, 127.75, 127.52, 126.04, 125.95, 124.76, 124.48, 123.02, 122.77, 122.15, 121.88, 121.53, 120.42, 93.76, 90.00, 89.14, 82.98, 15.08, 15.07. TOF-MS-EI $C_{34}H_{24}BNS_3$ m/z [M^+] calcd for 553.1164 found: 553.1166.

7. ^{1}H NMR, ^{13} C NMR and HRMS spectra.

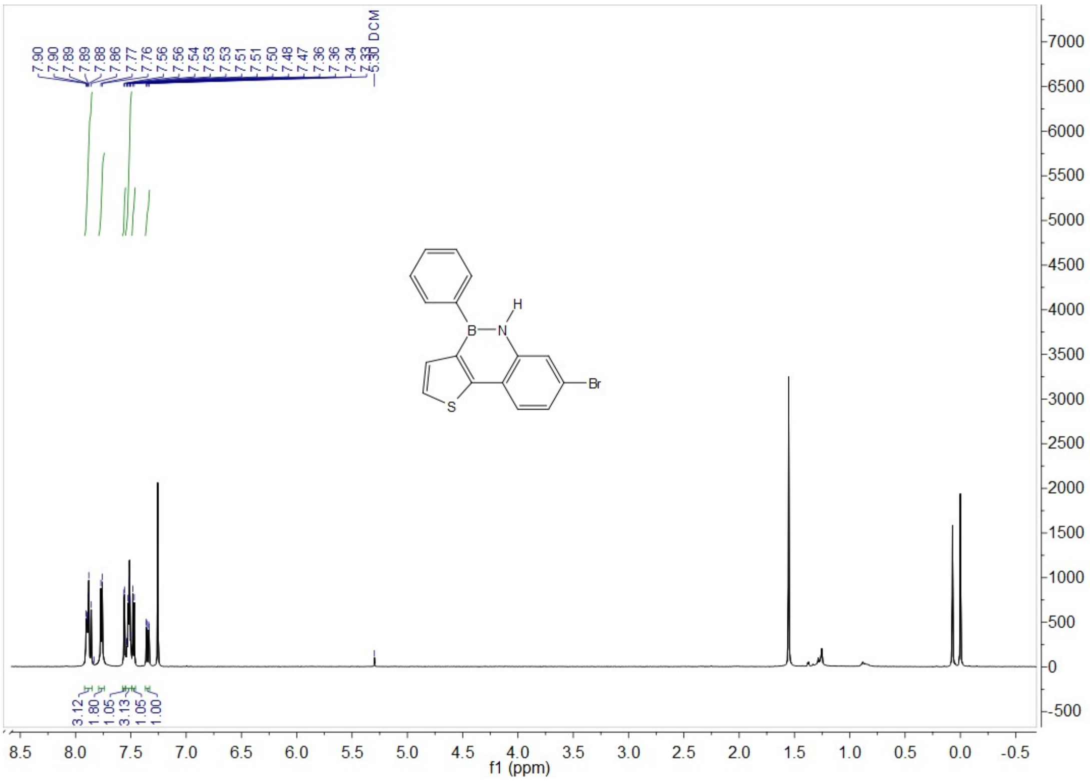


Figure S6. ^{1}H NMR spectrum of BN-Br in CDCl$_3$.

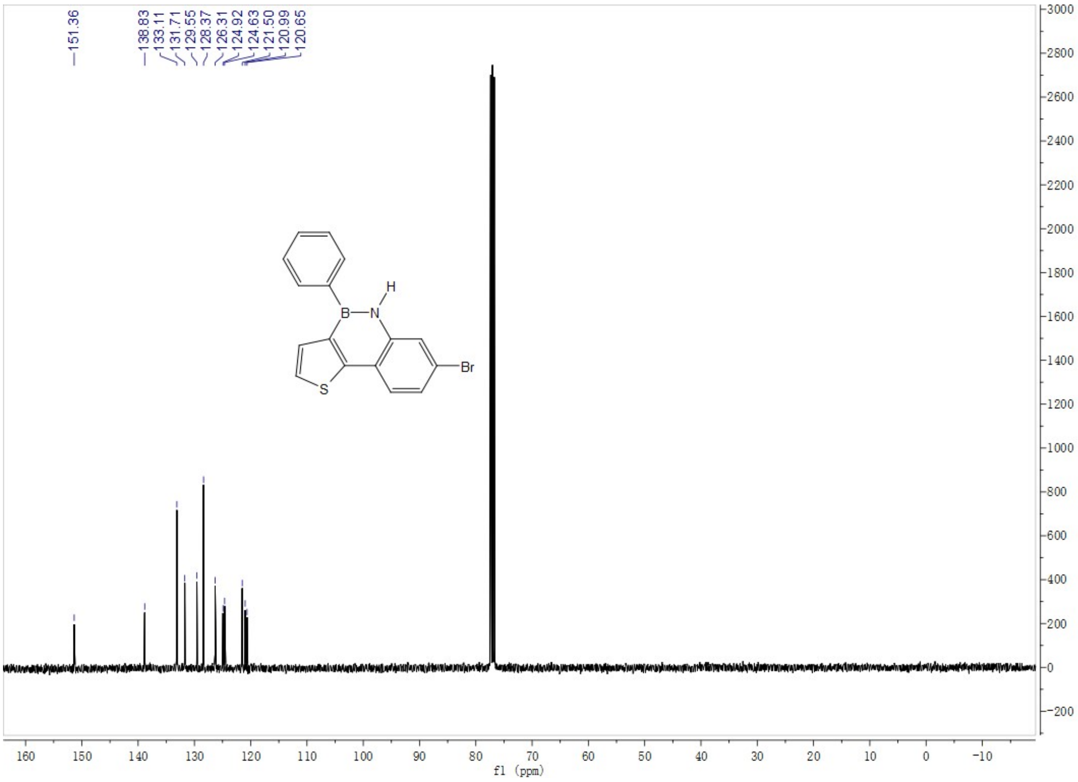


Figure S7. ^{13}C NMR spectrum of BN-Br in CDCl$_3$.

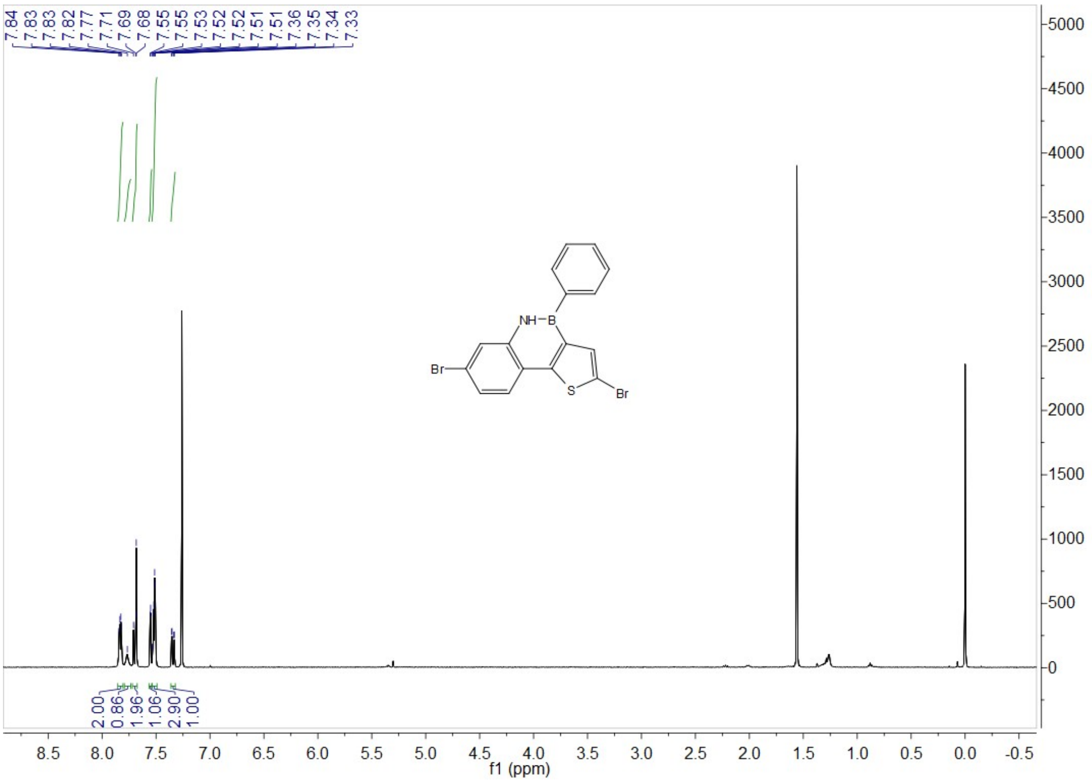


Figure S8. ^{1}H NMR spectrum of Br-BN-Br in CDCl$_3$.

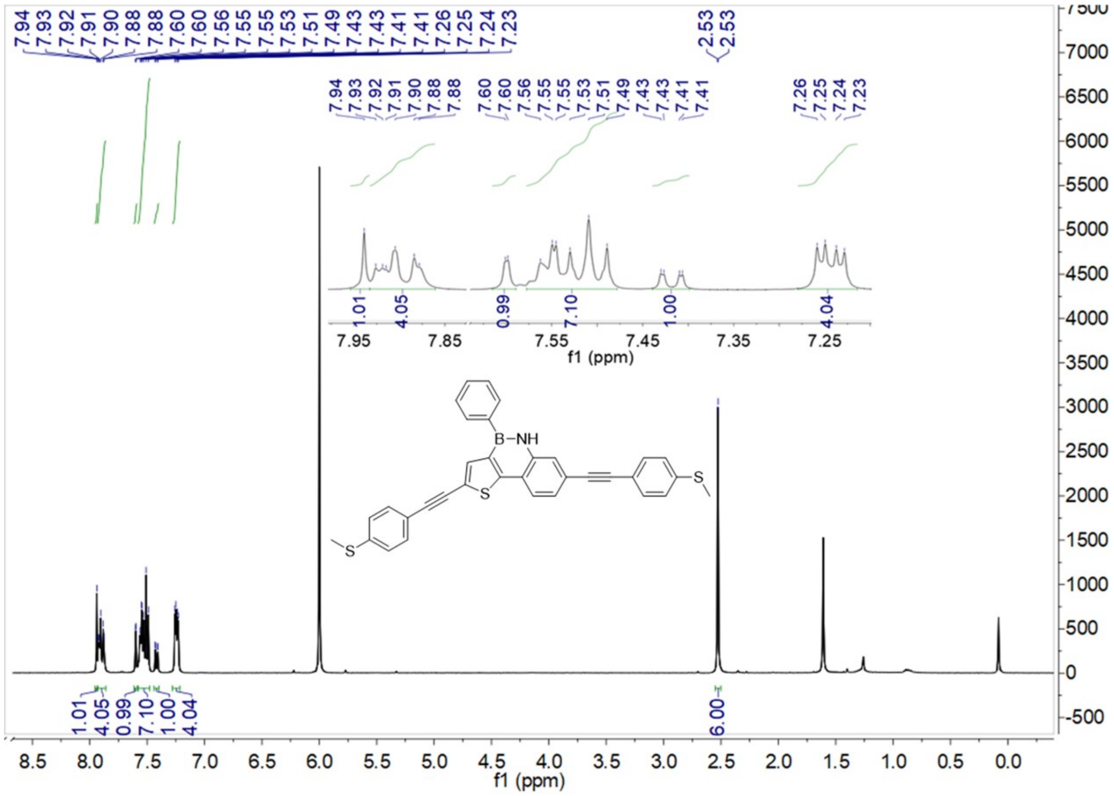


Figure S9. ^{1}H NMR spectrum of p-BN-p in C$_2$Cl$_4$D$_2$.

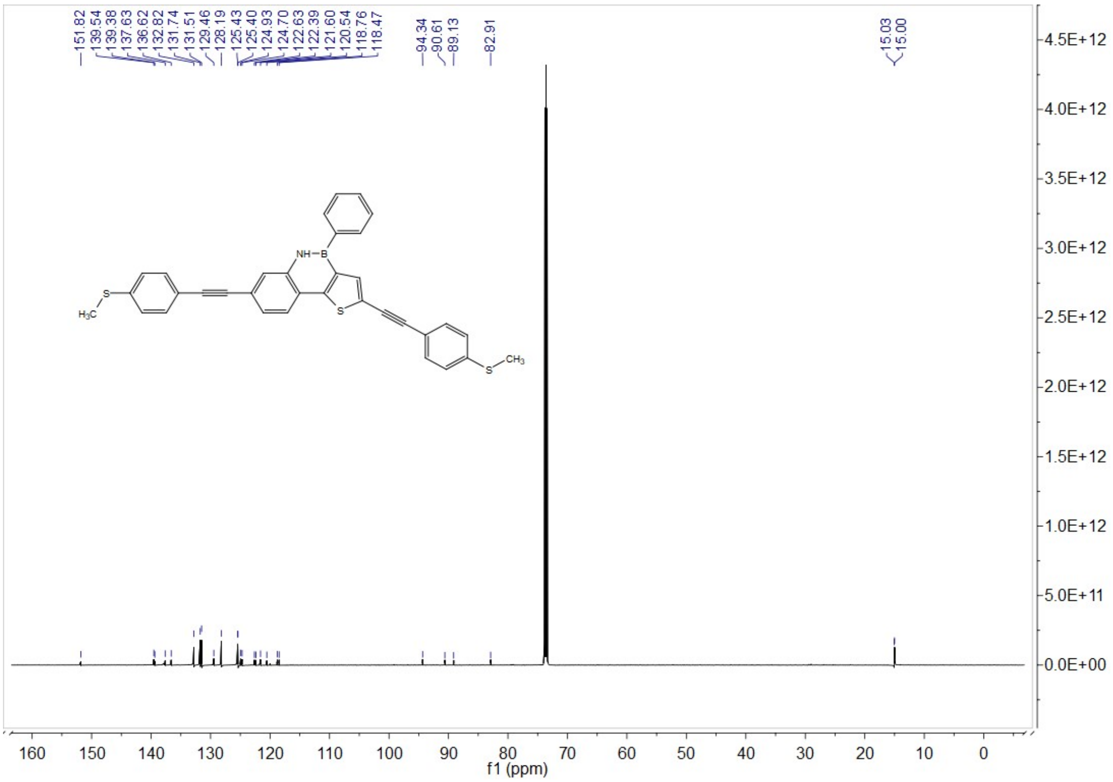


Figure S10. ^{13}C NMR spectrum of p-BN-p in $C_2Cl_4D_2$.

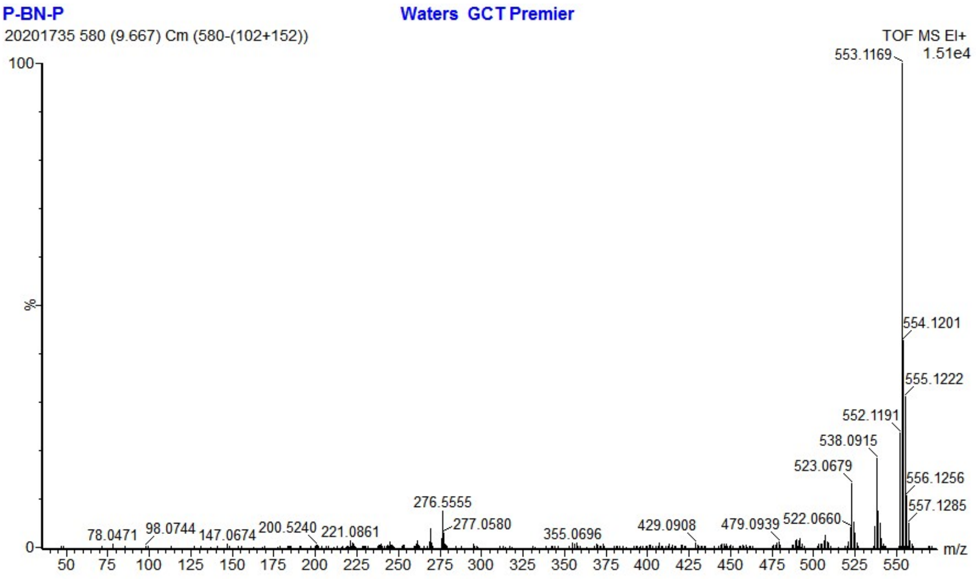


Figure S11. HRMS spectrum of p-BN-p.

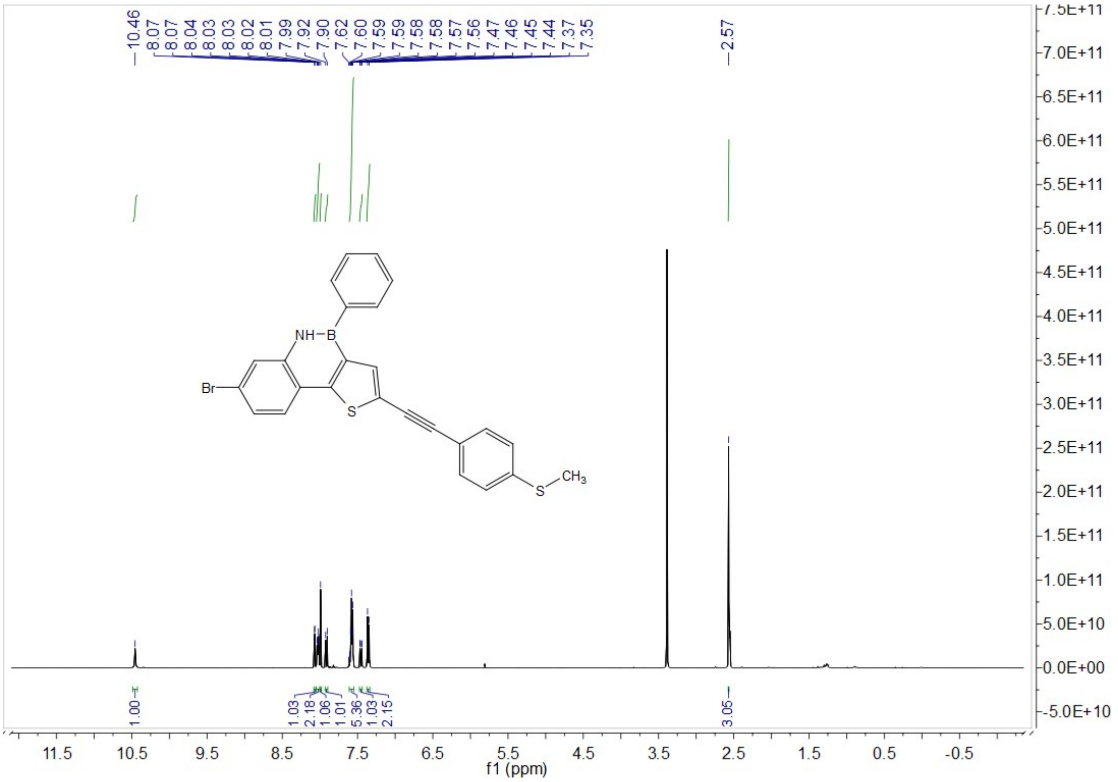


Figure S12. ^{1}H NMR spectrum of p-BN-Br in DMSO-d$_6$.

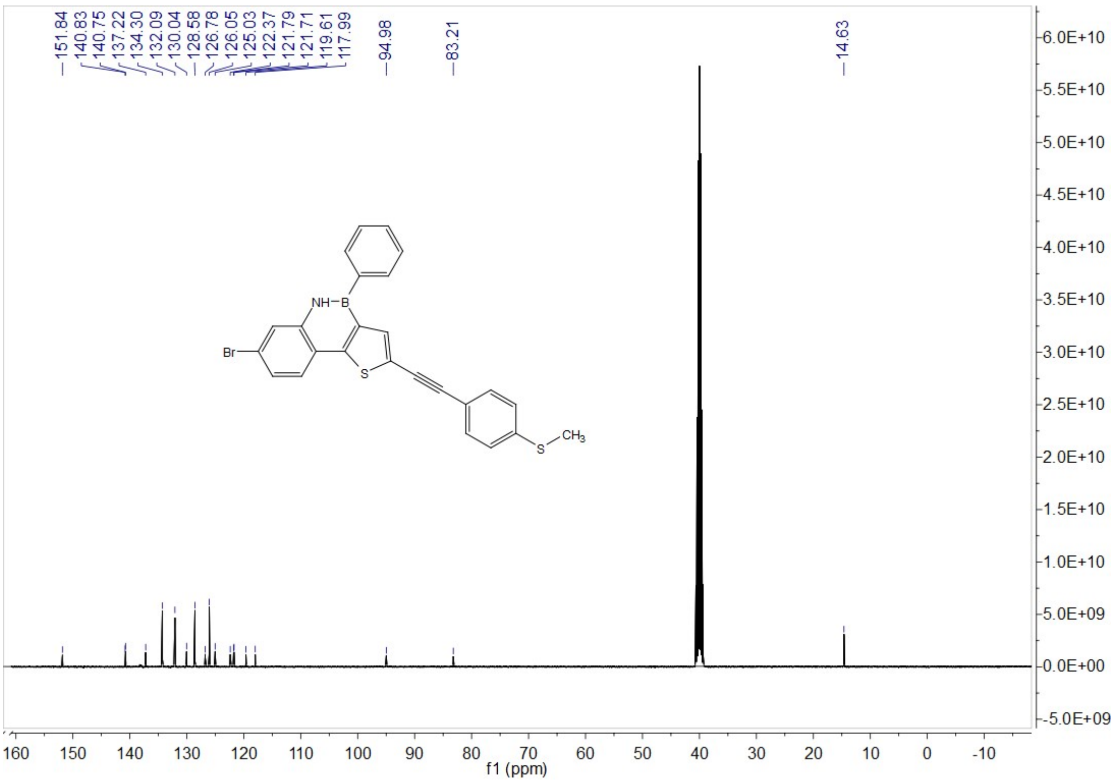


Figure S13. ^{13}C NMR spectrum of p-BN-Br in DMSO-d$_6$.

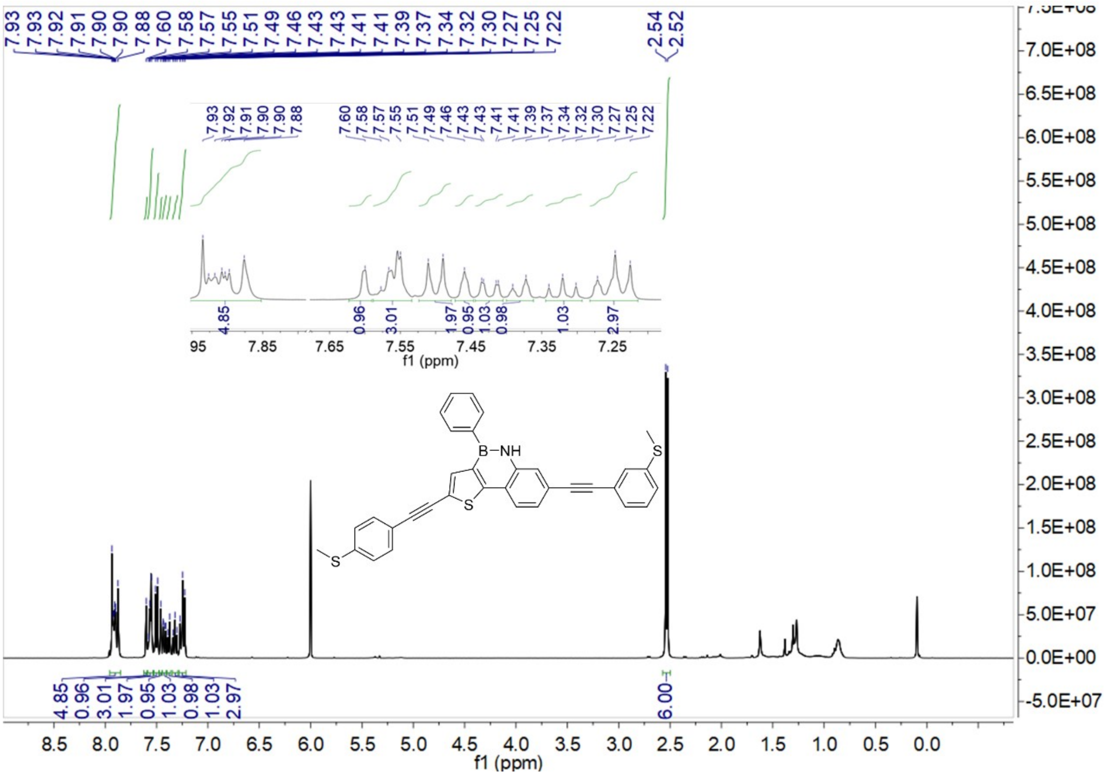


Figure S14. ^{1}H NMR spectrum of p-BN-m in $C_2Cl_4D_2$.

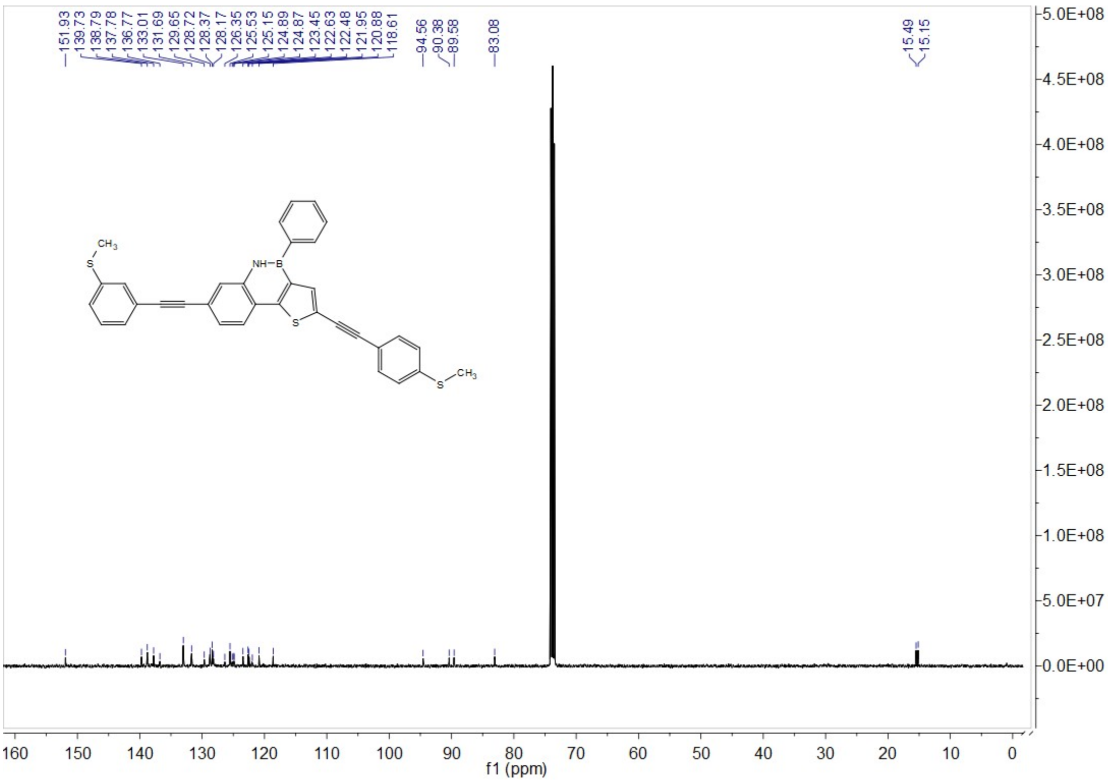


Figure S15. ^{13}C NMR spectrum of p-BN-m in $C_2Cl_4D_2$.

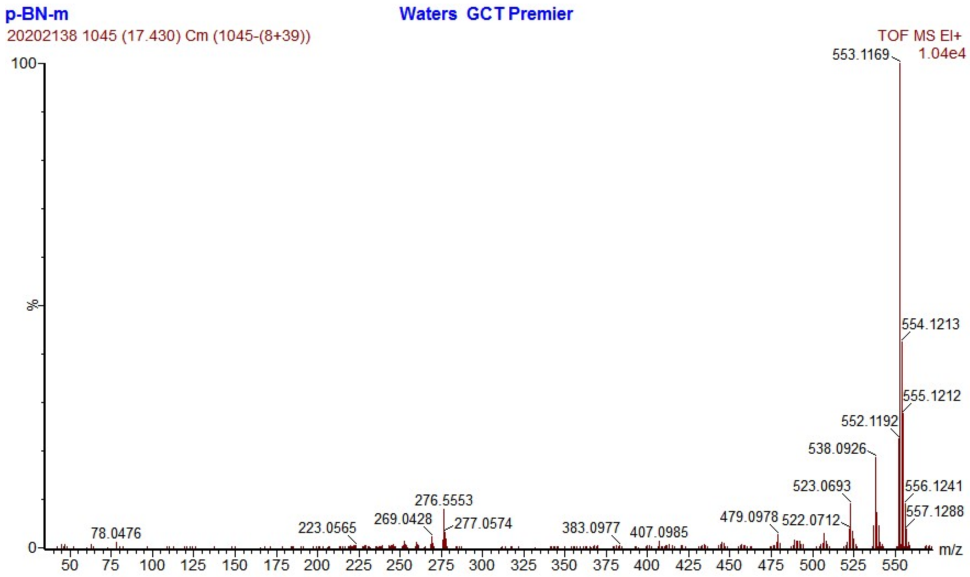


Figure S16. HRMS spectrum of p-BN-m.

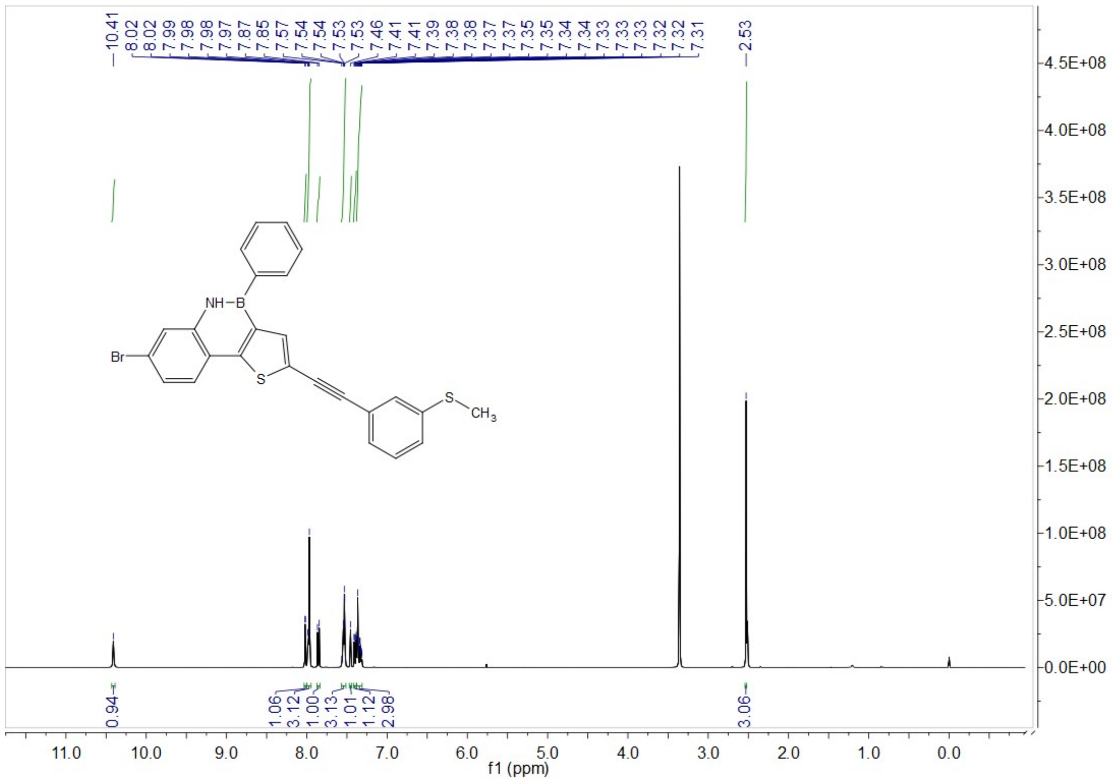


Figure S17. ^{1}H NMR spectrum of m-BN-Br in DMSO-d_6.

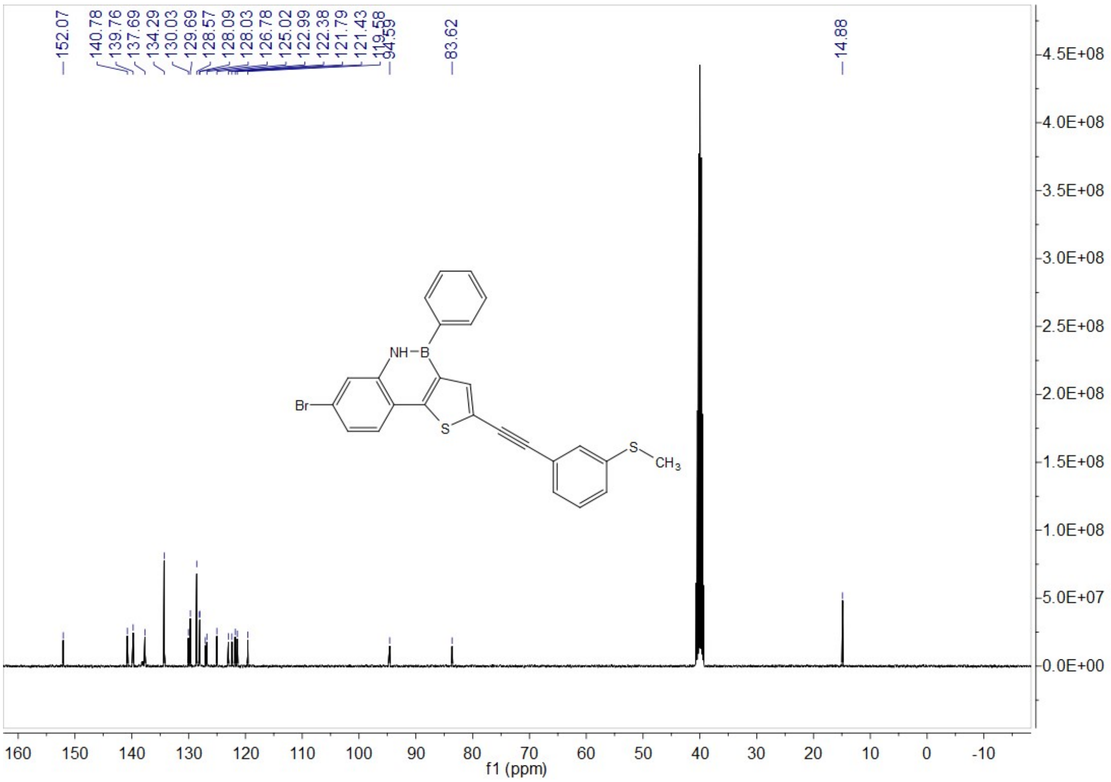


Figure S18. ^{13}C NMR spectrum of m-BN-Br in DMSO-d$_6$.

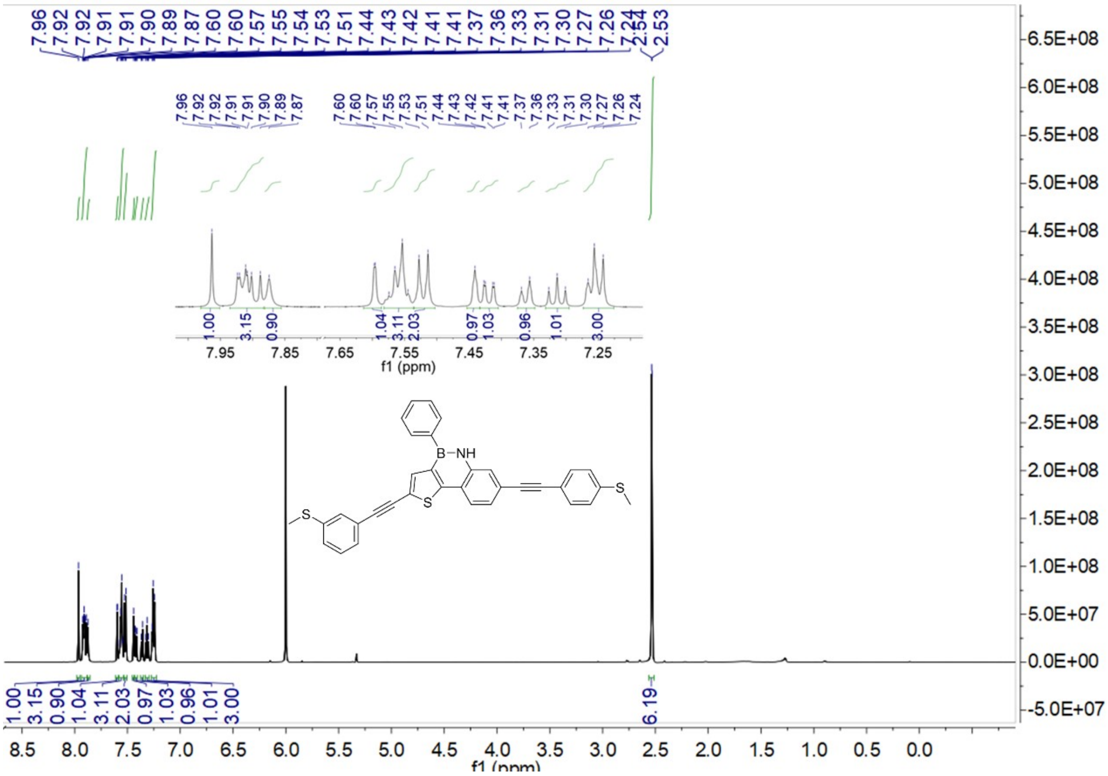


Figure S19. ^{1}H NMR spectrum of m-BN-p in $C_2Cl_4D_2$.

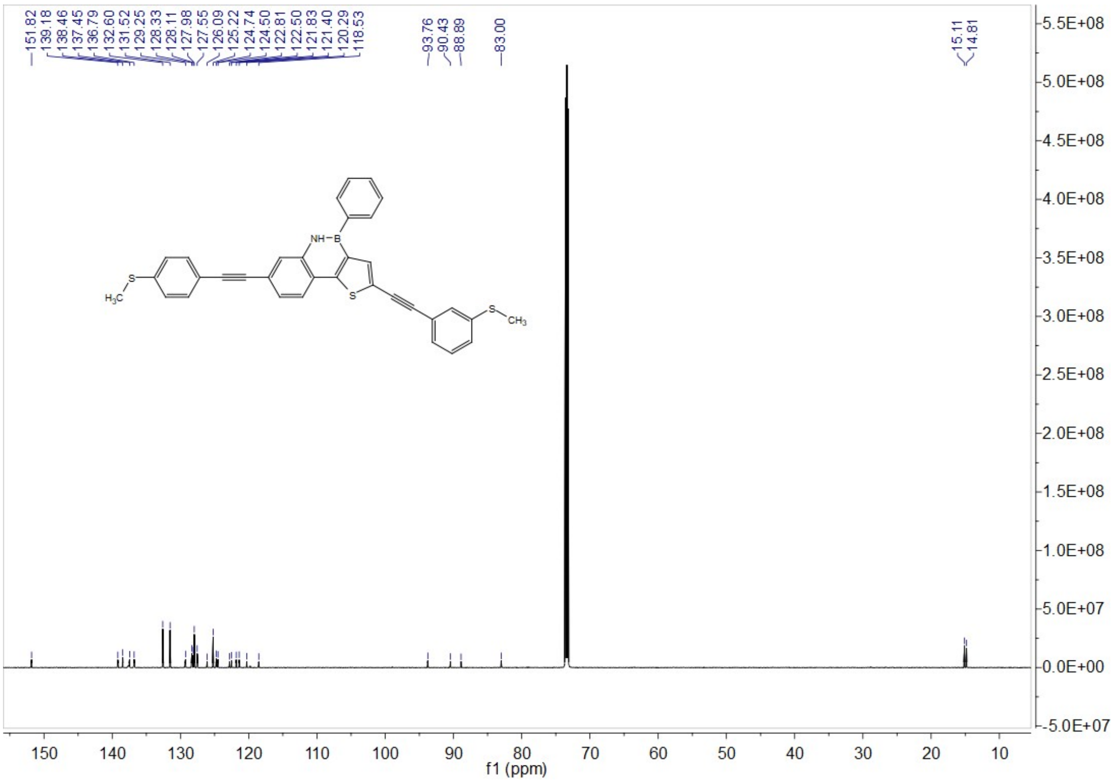


Figure S20. ^{13}C NMR spectrum of m-BN-p in $C_2Cl_4D_2$.

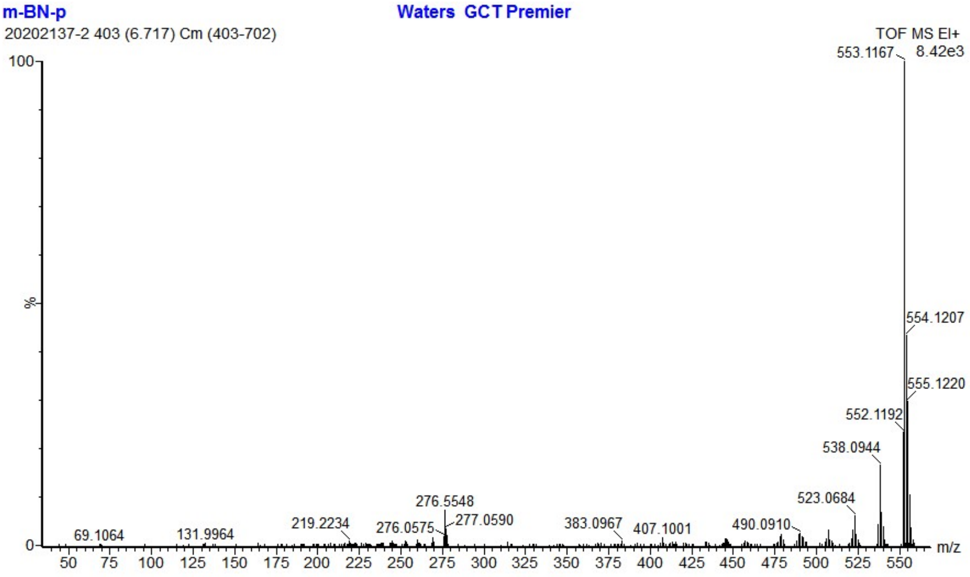


Figure S21. HRMS spectrum of m-BN-p.

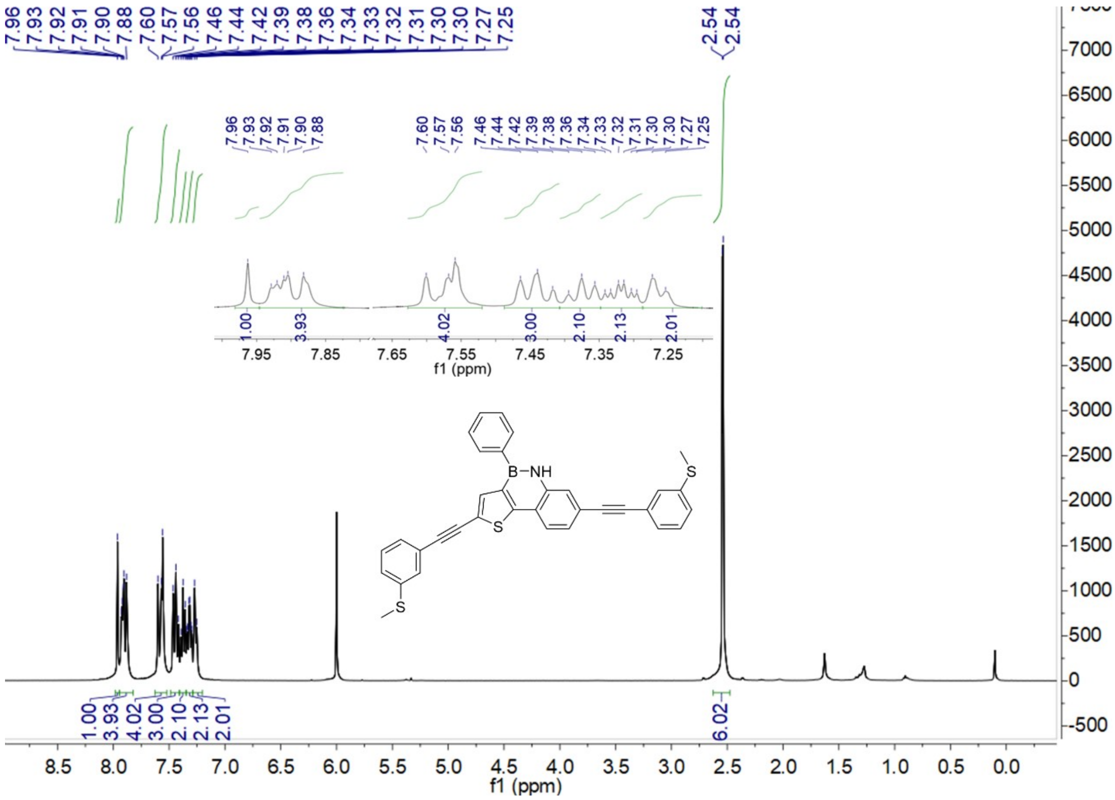


Figure S22. ^{1}H NMR spectrum of m-BN-m in $C_2Cl_4D_2$.

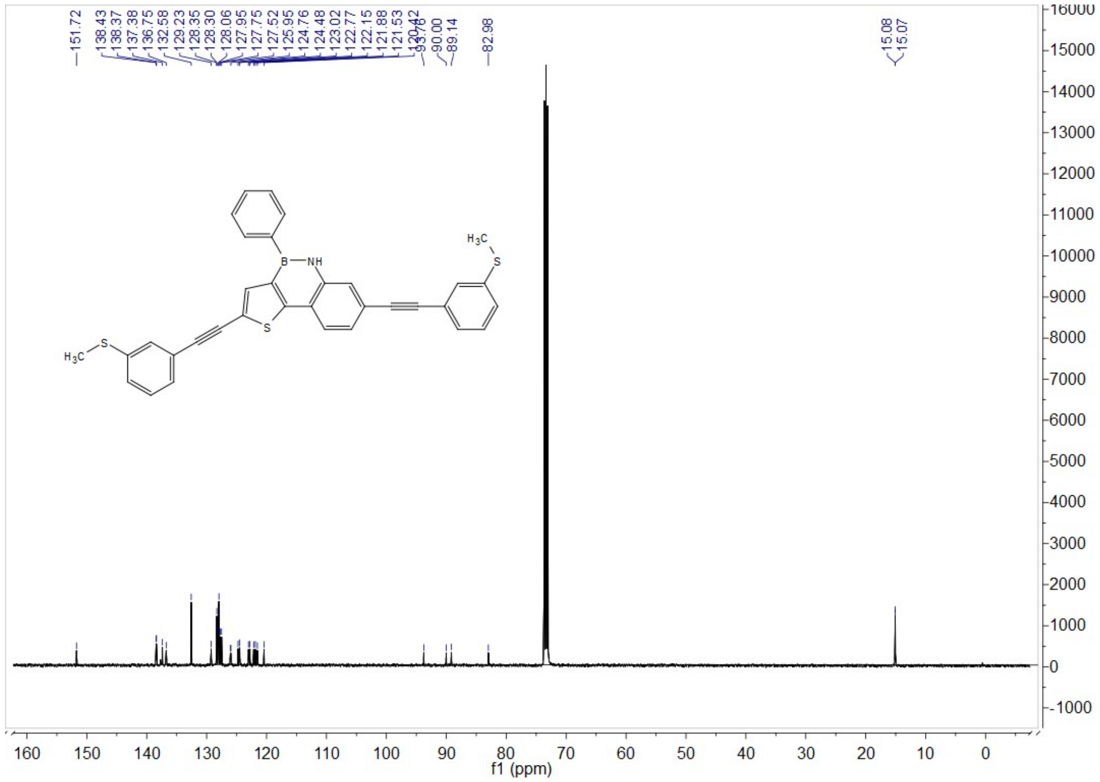


Figure S23. ^{13}C NMR spectrum of m-BN-m in $C_2Cl_4D_2$.

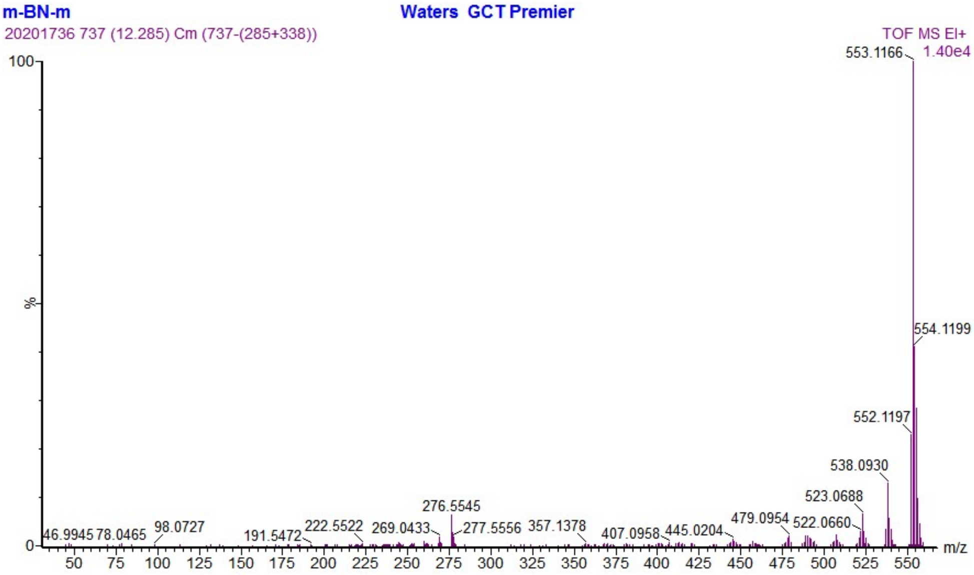


Figure S24. HRMS spectrum of m-BN-m.

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