Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Syn-BN-Heteroacence Cored Conjugated Oligomers with Finely Tuned Blue-Violet Luminescent Properties

Wanzheng Zhang,[a] Yubin Fu,[b] Peirong Qiang,[a] Jens Hunger,[b] Shuai Bi,[a] Wenbei Zhang,[a] Fan Zhang*[a]

[a]School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

[b]Center for Advancing Electronics Dresden (cfaed) and Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

E-mail: *fan-zhang@sjtu.edu.cn*

Table of Contents

1 Experimental Details

Materials and Equipment.

All reagents were purchased from Sigma-Aldrich and Admas-beta. Thiophene-2-boronic acid pinacol ester[1] were prepared using literature methods. All reactions were carried out under a nitrogen atmosphere and performed using Schlenk techniques. *Syn*-BN-heteroacenes **1** and **4** were prepared according to our previous report.[2]

^{1}H and ^{13}C NMR spectra were referenced to residual signals of the deuterated solvent. High-resolution electrospray ionization mass spectrometry was performed on a QTof spectrometer. High-resolution MALDI-MS measurements were performed on Bruker solariX 7T FTICR. Ultraviolet-visible (UV-Vis) spectra were recorded on a HITACHI U-4100 Spectrophotometer. The fluorescence spectroscopy (PL) emission spectra were obtained with a FluoroMax-4 spectrophotometer. Thermogravimetric analysis (TGA) was measured with a heating rate of 20 °C min^{-1} under flowing N_2. CV was performed in anhydrous dichloromethane containing recrystallized tetra-n-butyl-ammoniumhexafluorophosphate ($TBAPF_6$, 0.1M) as supporting electrolyte at 298 K. A conventional three electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgCl reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of nitrogen. Geometry optimizations and the analysis of HOMOs and LUMOs were performed at the DFT level (RB3LYP/6-311G(d)). The initial structures were determined by X-ray diffraction analyses. All calculations were performed using Gaussian 09.

Compound **2**

N-bromosuccinimide (NBS, 190 mg, 1.06 mmol) was added to a solution of compound **1** (320 mg, 0.53 mmol) in 15 mL $CHCl_3$ at 0 °C, and the mixed solution was stirred at this temperature for 2 hours. After removal of the solvent under reduced pressure, the residue was washed with petroleumether to give compound **2** as a yellow solid (280 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.29 (s, 1H), 7.73 (s, 1H), 7.57-7.55 (m, 4H), 7.50-7.44 (m, 6H), 7.11 (s, 2H), 4.17 (t, 4H, *J* = 8.0 Hz), 1.86-1.80 (m, 4H), 1.28-1.16 (m, 12H), 0.81 (t, 6H, *J* = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 151.3, 140.5, 139.7, 138.9, 135.2, 131.9, 127.9, 127.8, 121.2, 117.9, 111.2, 103.4; *m/z*[M+H]$^+$ calcd for $C_{38}H_{41}B_2Br_2N_2S_2$ 769.1261; HR-ESI observed 769.1235.

Compound **3a**

In a Schlenk flask, **2** (160 mg, 0.21 mmol), thiophene-2-boronic acid pinacol ester (190 mg, 0.89 mmol) and Na_2CO_3 (99 mg, 0.93 mmol) were charged under the protection of nitrogen. After adding 20 mL toluene, 7 mL ethanol and 7 mL water, the mixture was degassed for 30 min. $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) was added, then the mixture was heated to 90 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 4:1) to give product **3a** as yellow solid (100 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.54 (s, 1H), 7.74 (s, 1H), 7.63-7.61 (m, 4H), 7.53-7.46 (m, 6H), 7.28-7.27 (m, 2H), 7.24-7.22 (m, 3H), 7.05-7.03 (m, 2H), 4.18 (t, 4H, J = 8 Hz), 1.91-1.83 (m, 4H), 1.25-1.18 (m, 12H), 0.82 (t, 6H, J =8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.2, 139.2, 137.5, 135.5, 131.9, 128.8, 127.9, 127.8, 124.6, 124.3, 121.6, 118.4, 103.4, 48.6, 31.5, 30.1, 26.9, 22.6, 14.0; $m/z[M+H]^+$ calcd for $C_{46}H_{47}B_2N_2S_4$ 777.2818; HR-ESI observed 777.2797.

Compound **3b**

In a Schlenk flask, **2** (77 mg, 0.1 mmol), trimethylsilylacetylene (37 mg, 0.38 mmol), CuI (4.5 mg, 0.024 mmol), triethylamine (0.5 ml, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and 20 ml THF were charged under the protection of nitrogen. The mixture was heated to 70 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 5:1) to give product **3b** as yellow solid (62 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.46 (s, 1H), 7.71 (s, 1H), 7.57-7.55 (m, 4H), 7.49-7.43(m, 6H), 7.31 (s, 2H), 4.17 (t, 4H, J = 8 Hz), 1.88-1.82 (m, 4H), 1.28-1.20 (m, 12H), 0.81 (t, 6H, J =8.0 Hz), 0.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 151.0, 140.6, 139.8, 138.9, 138.7, 131.9, 127.8, 121.9, 121.0, 118.1, 103.4, 99.9, 98.0, 48.6, 31.5, 30.0, 26.9, 22.6, 14.0, 0.1; $m/z[M+H]^+$ calcd for $C_{48}H_{59}B_2N_2S_2Si_2$ 805.3855; HR-ESI observed 805.3796.

Compound **3c**

In a Schlenk flask, **2** (120 mg, 0.16 mmol), tolylboronic (70 mg, 0.51 mmol) and Cs_2CO_3 (170 mg, 0.5 mmol) were charged under the protection of nitrogen. After adding 23 mL toluene, 8 mL ethanol and 8 mL water, the mixture was degassed for 30 min. $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added, then the mixture was heated to 90 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 3:1) to give product **3c** as yellow solid (100 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.64 (s, 1H), 7.74 (s, 1H), 7.65-7.59 (m, 8H), 7.52-7.46 (m, 6H), 7.34 (s, 2H), 7.20 (d, 2H, J = 8 Hz), 4.19 (t, 4H, J = 8 Hz), 2.38 (s, 6H), 1.88-1.82 (m, 4H), 1.28-1.20 (m, 12H), 0.81 (t, 6H, J =8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.3, 142.5, 139.0, 137.4, 132.0, 131.6, 129.5, 127.8, 127.7, 126.1, 121.7, 118.6, 103.3, 48.6, 31.5, 30.1, 26.9, 22.6, 21.2, 14.0; $m/z[M]^+$ calcd for $C_{52}H_{54}B_2N_2S_2$ 792.3909; HR-MALDI-MS observed 792.3907.

Compound **5**

N-bromosuccinimide (NBS, 370 mg, 2.05 mmol) was added to a solution of compound

4 (730 mg, 1 mmol) in 30 mL $CHCl_3$ at 0 °C, and the mixed solution was stirred at this temperature for 2 hours. After removal of the solvent under reduced pressure, the residue was washed with petroleumether to give compound **5** as a yellow solid (620 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.52 (s, 1H), 7.74 (s, 1H), 7.56-7.54 (m, 10H), 7.29 (s, 2H), 4.16 (t, 4H, J = 8 Hz), 1.89-1.82 (m, 4H), 1.31-1.20 (m, 12H), 0.82 (t, 6H, J = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 151.4, 144.4, 140.0, 139.1, 135.3, 131.2, 130.8, 128.5, 121.7, 121.0, 119.0, 114.0, 103.3, 48.8, 31.4, 30.1, 26.9, 22.6, 14.0; m/z[M]$^+$ calcd for $C_{42}H_{40}B_2Br_2N_2S_4$ 880.0622; HR-MALDI-MS observed 880.0621.

Compound **6a**

In a Schlenk flask, **5** (130 mg, 0.15 mmol), thiophene-2-boronic acid pinacol ester (170 mg, 0.8 mmol) and Na_2CO_3 (85 mg, 0.8 mmol) were charged under the protection of nitrogen. After adding 20 mL toluene, 7 mL ethanol and 7 mL water, the mixture was degassed for 30 min. $Pd(PPh_3)_4$ (34 mg, 0.03 mmol) was added, then the mixture was heated to 90 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 4:1) to give product **6a** as yellow solid (100 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.54 (s, 1H), 7.74 (s, 1H), 7.62-7.54 (m, 10H), 7.38 (s, 2H), 7.19, (d, 2H, J = 4.8 Hz), 7.08 (d, 2H, J = 3.6 Hz), 6.98-6.96 (m, 2H), 4.16 (t, 4H, J = 6.4 Hz), 1.90-1.84 (m, 4H), 1.29-1.21 (m, 12H), 0.82 (m, 6H, J =6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 152.3, 143.4, 140.3, 139.8, 139.3, 138.11, 137.4, 131.5, 131.1, 128.6, 128.4, 127.9, 124.6, 124.0, 121.1, 119.4, 115.8, 103.5, 49.0, 31.7, 30.4, 27.1, 22.8, 14.2; m/z[M]$^+$ calcd for $C_{50}H_{46}B_2N_2S_6$ 888.2166; HR-MALDI-MS observed 888.2172.

Compound **6b**

In a Schlenk flask, **5** (180 mg, 0.2 mmol), trimethylsilylacetylene (82 mg, 0.84 mmol), CuI (13 mg, 0.07 mmol), triethylamine (0.2 ml, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) and 15 ml THF were charged under the protection of nitrogen. The mixture was heated to 70 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 5:1) to give product **6b** as yellow solid (150 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.54 (s, 1H), 7.75 (s, 1H), 7.57-7.55 (m, 4H), 7.59-7.55(m, 6H), 7.44 (s, 2H), 4.16 (t, 4H, J = 8 Hz), 1.90-1.82 (m, 4H), 1.29-1.20 (m, 12H), 0.82 (t, 6H, J =8.0 Hz), 0.23 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 154.1, 145.4, 140.2, 139.6, 135.9, 131.4, 130.8, 128.6, 128.5, 125.2, 124.7, 121.5, 119.2, 103.4, 100.0, 98.7, 49.0, 31.6, 29.9, 27.1, 22.8, 24.2, 0.1; m/z[M]$^+$ calcd for $C_{52}H_{58}B_2N_2S_4Si_2$ 916.3202; HR-MALDI-MS observed 916.3220

Compound **6c**

In a Schlenk flask, **5** (180 mg, 0.2 mmol), tolylboronic (100 mg, 0.76 mmol) and Cs_2CO_3 (290 mg, 0.9 mmol) were charged under the protection of nitrogen. After adding 20 mL toluene, 7 mL ethanol and 7 mL water, the mixture was degassed for 30 min. Pd(PPh_3)$_4$ (23 mg, 0.02 mmol) was added, then the mixture was heated to 90 °C and stirred overnight. The reactant was poured into brine and extracted with ethyl acetate for several times. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product was purified by chromatography on silica gel (PE/CH_2Cl_2 = 3:1) to give product **6c** as yellow solid (110 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.51 (s, 1H), 7.68 (s, 1H), 7.61-7.54 (m, 10H), 7.43 (s, 2H), 7.39 (d, 2H, *J* = 8 Hz), 7.12 (d, 2H, *J* = 8 Hz), 4.12 (t, 4H, *J* = 8 Hz), 2.34, (s, 6H), 1.88-1.81 (m, 4H), 1.27-1.17 (m, 12H), 0.83 (t, 6H, *J* =8.0 Hz), 0.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 152.0, 147.1, 143.4, 140.5, 139.2, 137.7, 137.6, 132.4, 131.6, 131.1, 129.7, 128.5, 128.3, 125.8, 121.1, 119.5, 114.6, 103.3, 49.0, 31.7, 30.4, 27.1, 22.8, 21.4, 14.2; *m/z*[M]$^+$ calcd for $C_{56}H_{54}B_2N_2S_4$ 904.3350; HR-MALDI-MS observed 904.3355.

2 ^{1}H and ^{13}C NMR Spectra for New Compounds

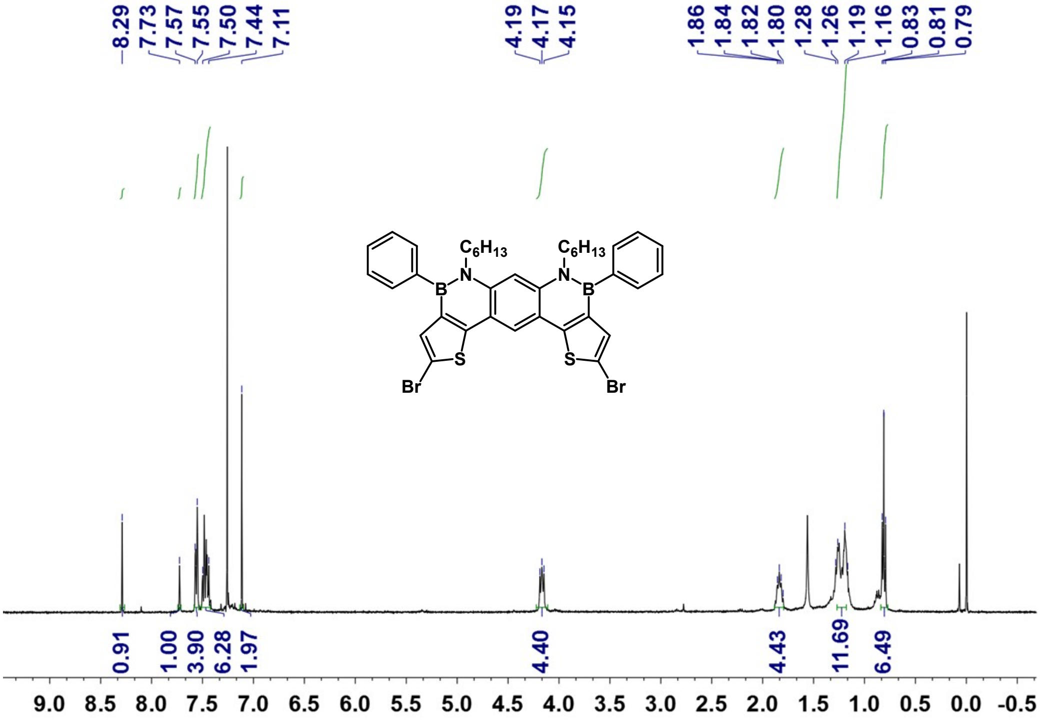


Figure S1 ^{1}H NMR spectrum of **2** ($CDCl_3$)

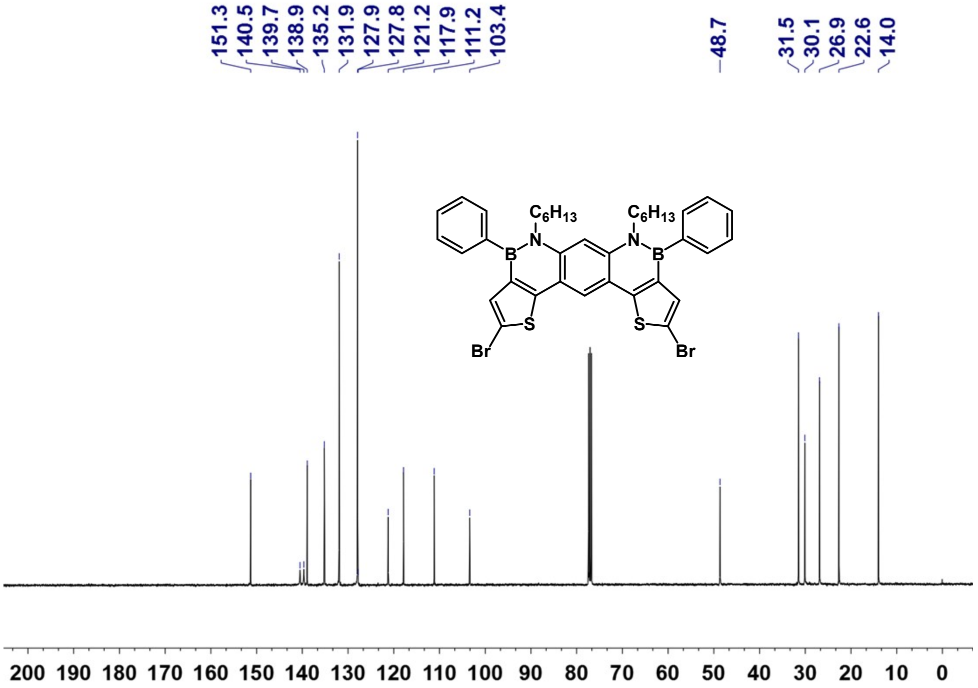


Figure S2 ^{13}C NMR spectrum of **2** ($CDCl_3$)

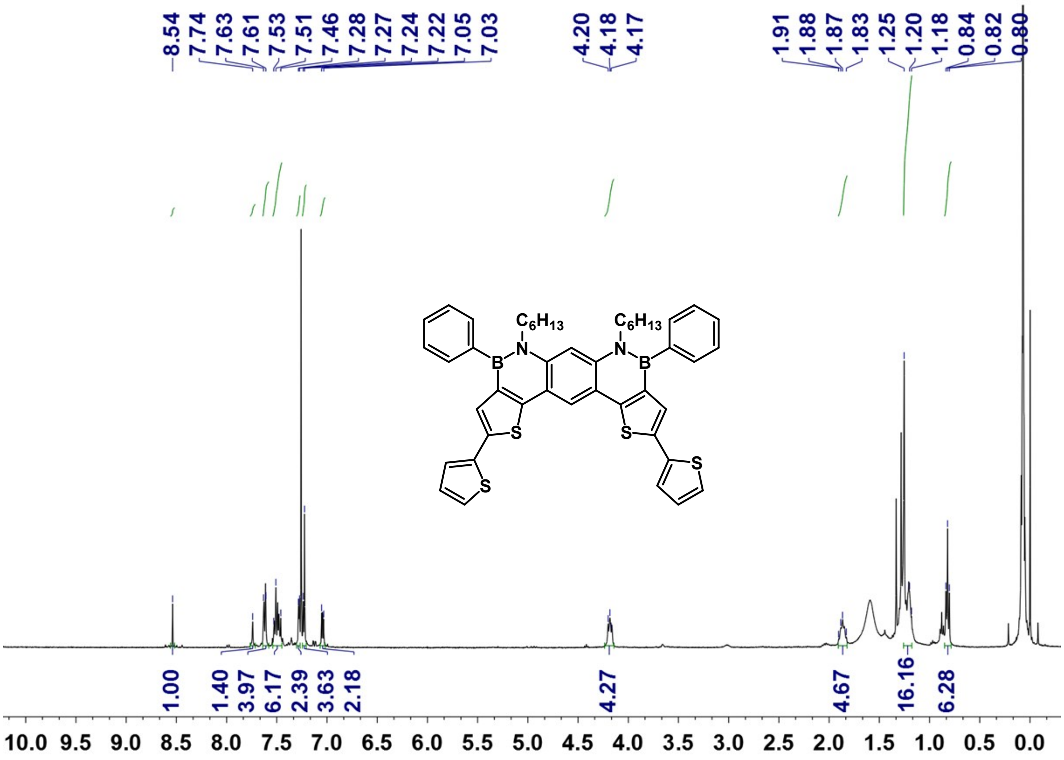


Figure S3 ^{1}H NMR spectrum of **3a** ($CDCl_3$)

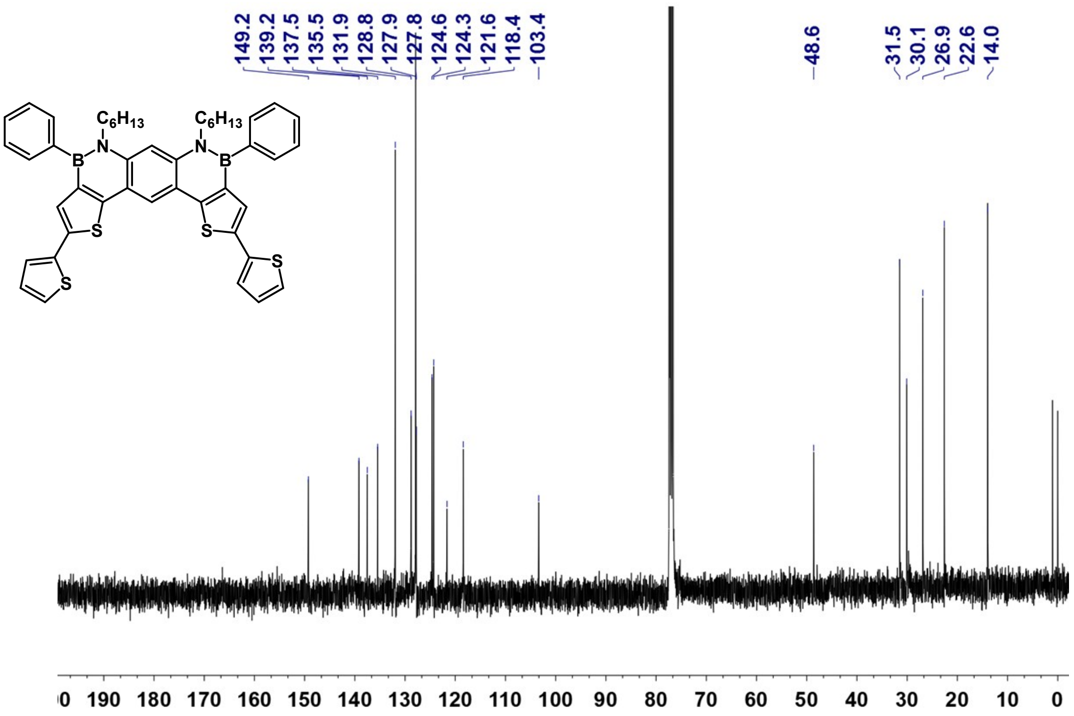


Figure S4 ^{13}C NMR spectrum of **3a** ($CDCl_3$)

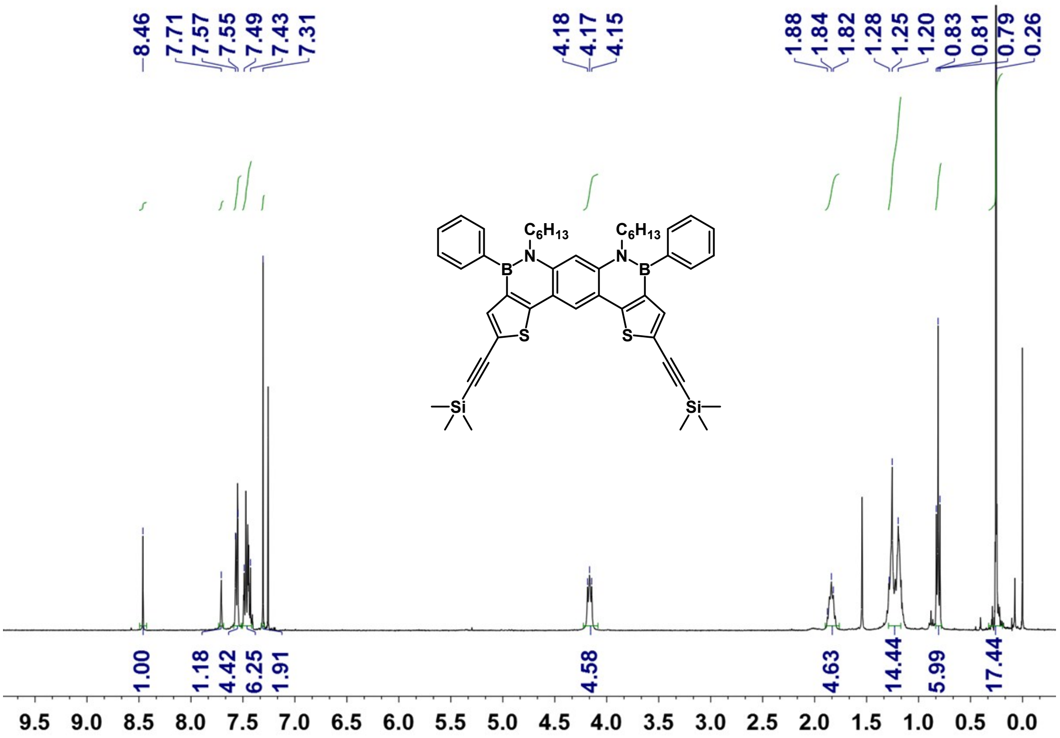


Figure S5 ^{1}H NMR spectrum of **3b** ($CDCl_3$)

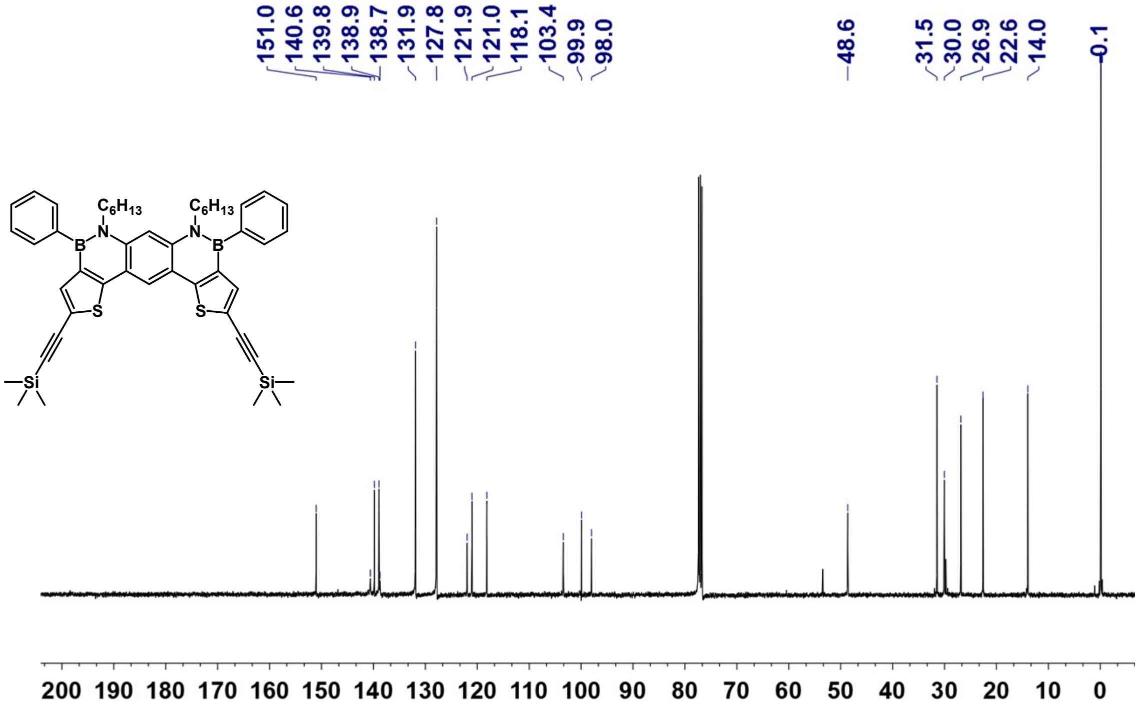


Figure S6 ^{13}C NMR spectrum of **3b** $(CDCl_3)$

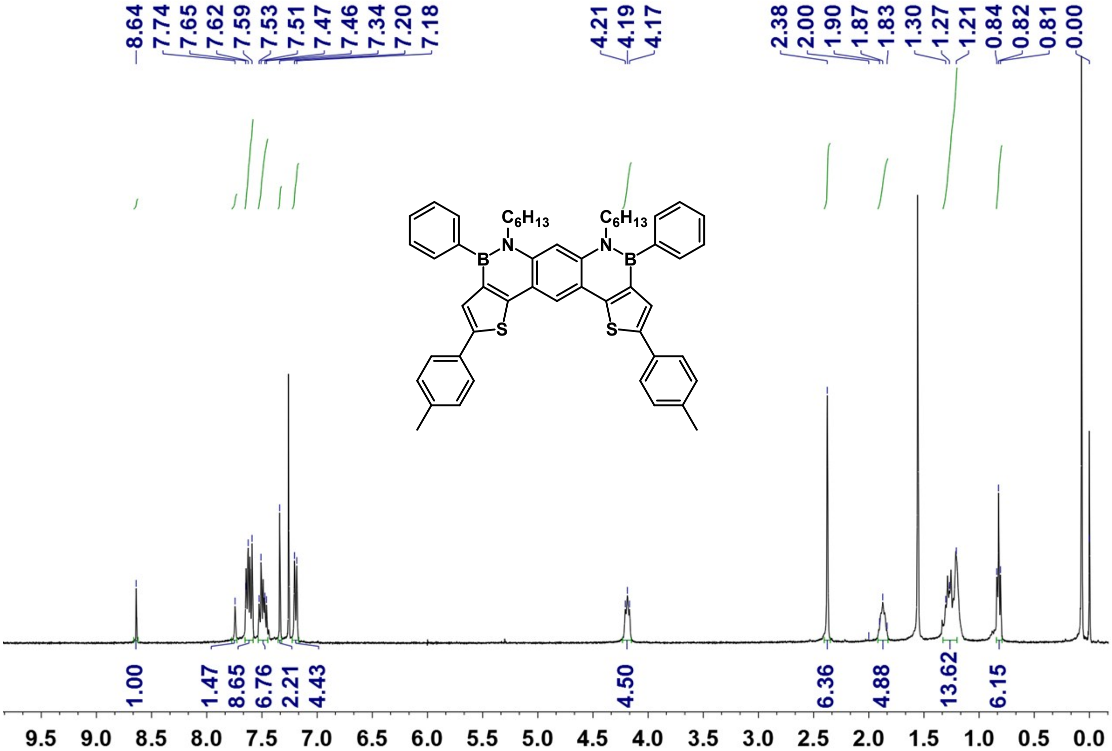


Figure S7 ^{1}H NMR spectrum of **3c** $(CDCl_3)$

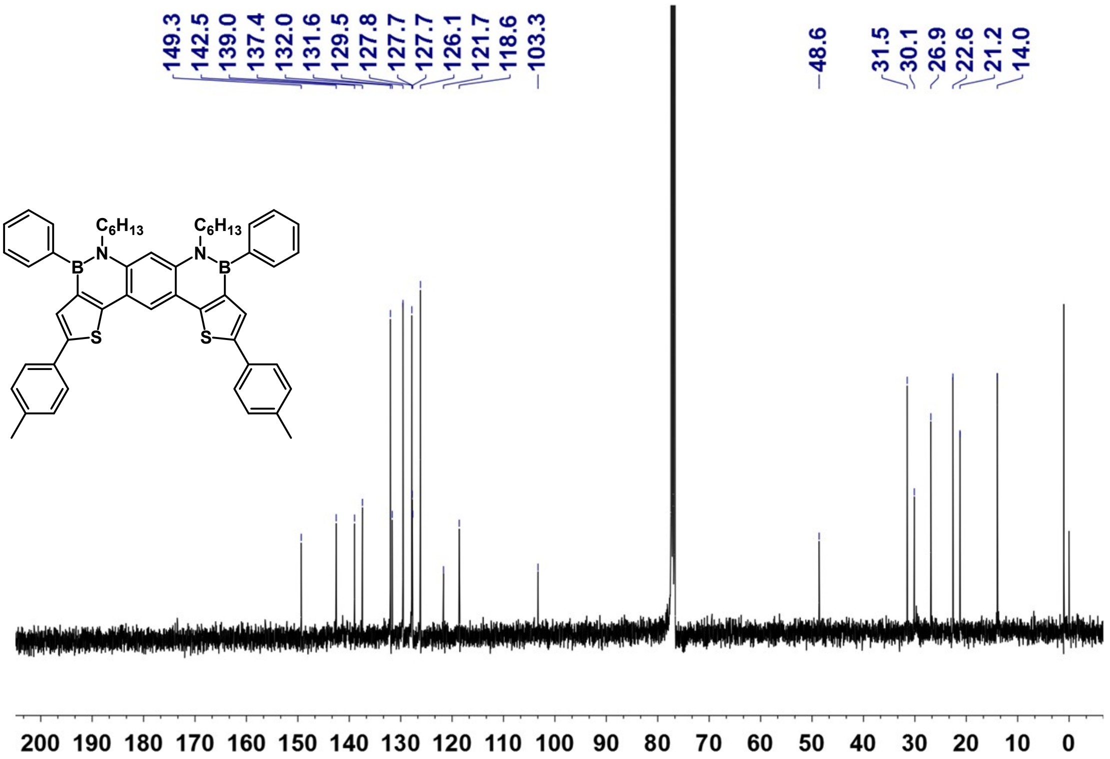


Figure S8 ^{13}C NMR spectrum of **3c** ($CDCl_3$)

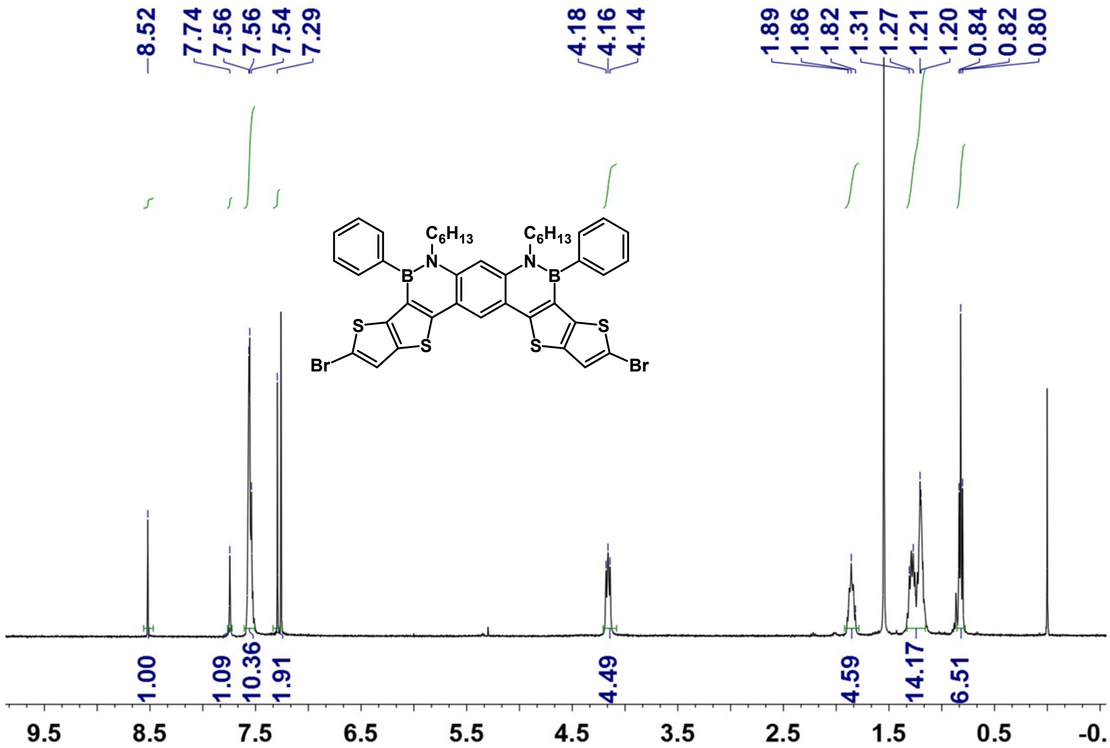


Figure S9 ^{1}H NMR spectrum of **5** ($CDCl_3$)

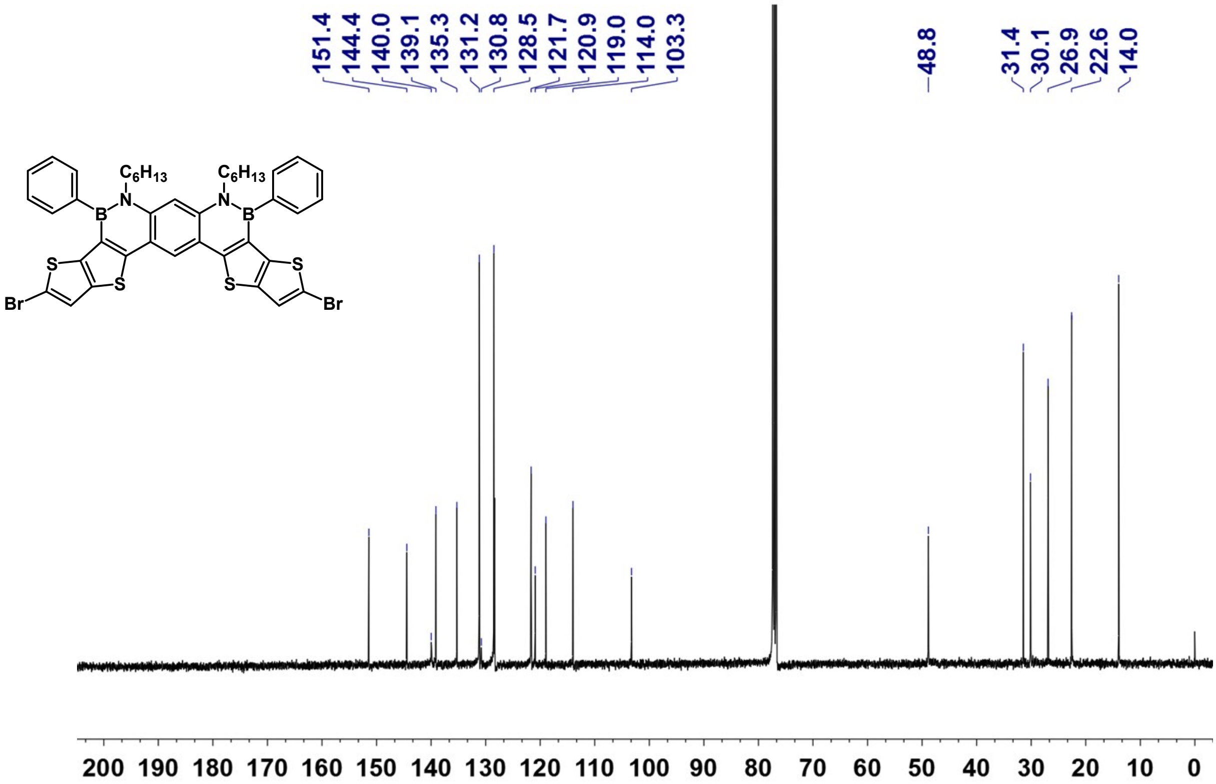


Figure S10 ^{13}C NMR spectrum of **5** ($CDCl_3$)

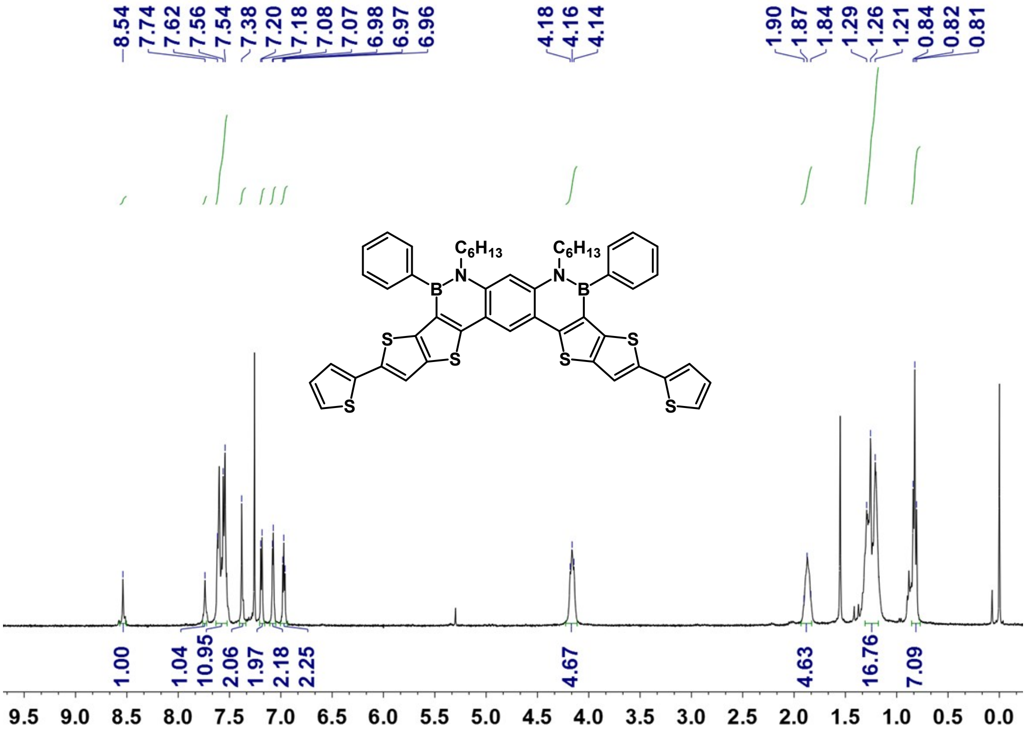


Figure S11 ^{1}H NMR spectrum of **6a** ($CDCl_3$)

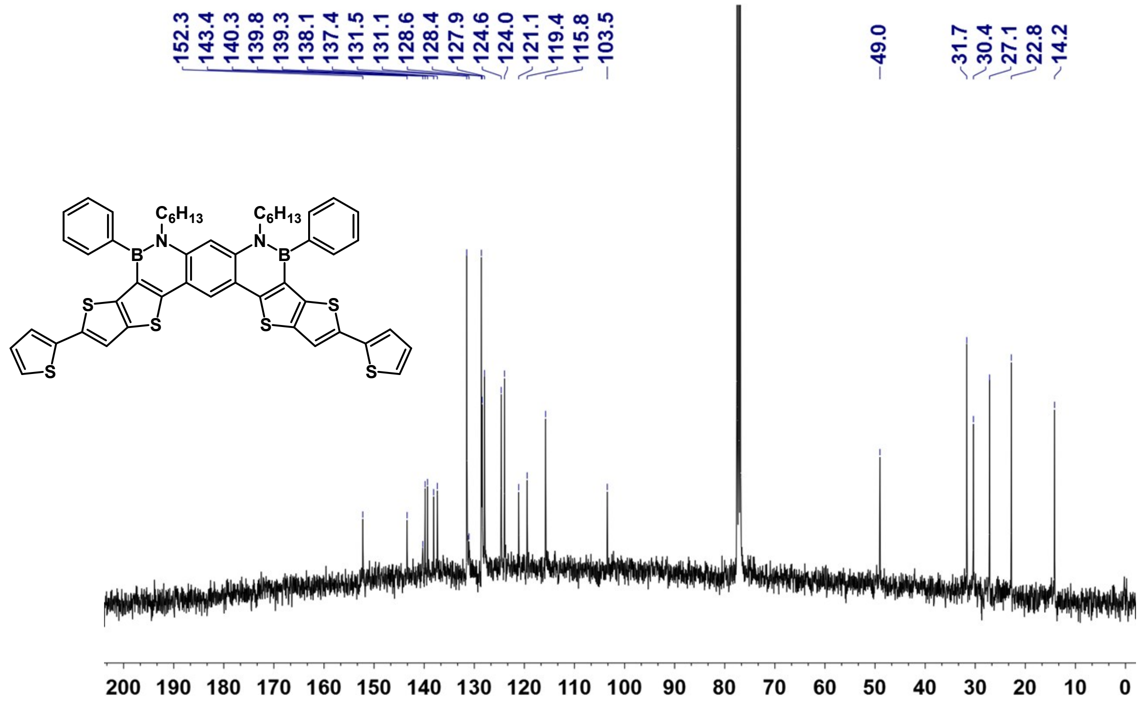


Figure S12 ^{13}C NMR spectrum of **6a** ($CDCl_3$)

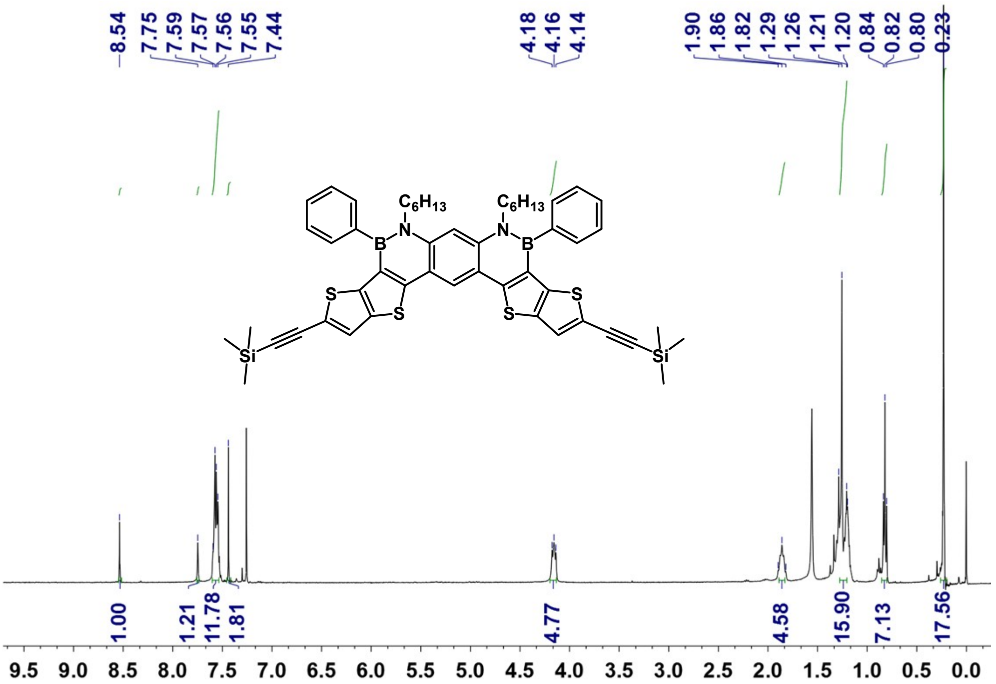


Figure S13 ^{1}H NMR spectrum of **6b** ($CDCl_3$)

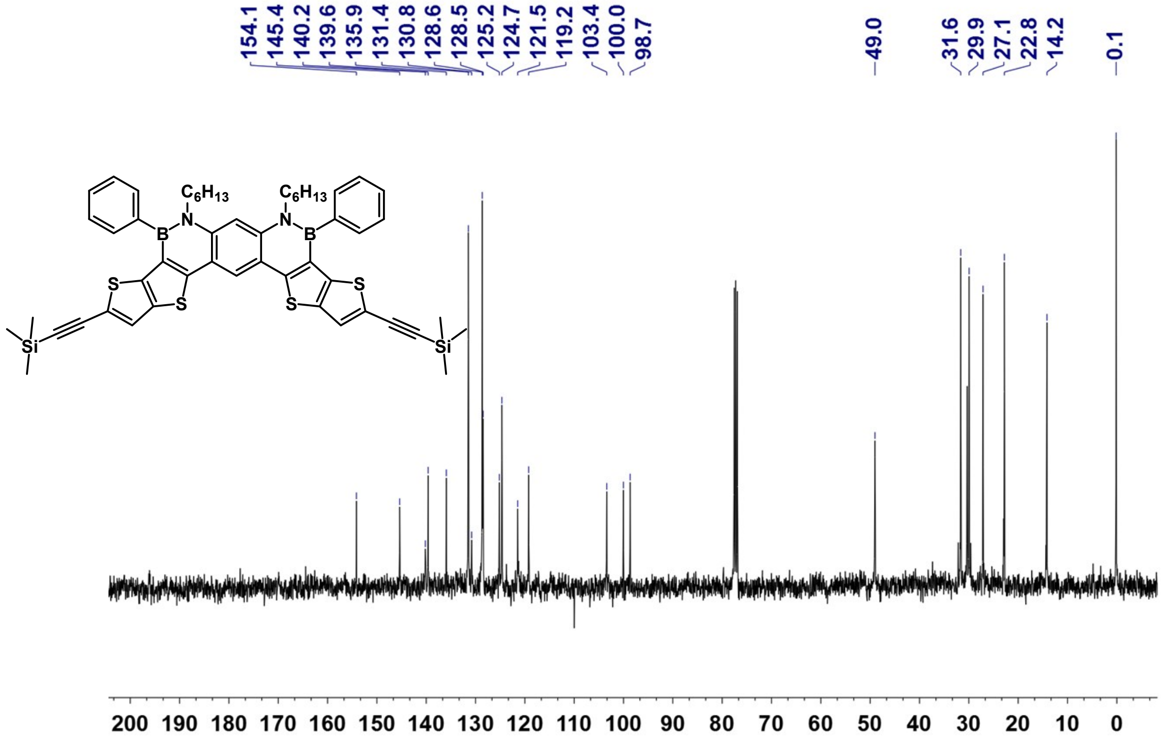


Figure S14 ^{13}C NMR spectrum of **6b** ($CDCl_3$)

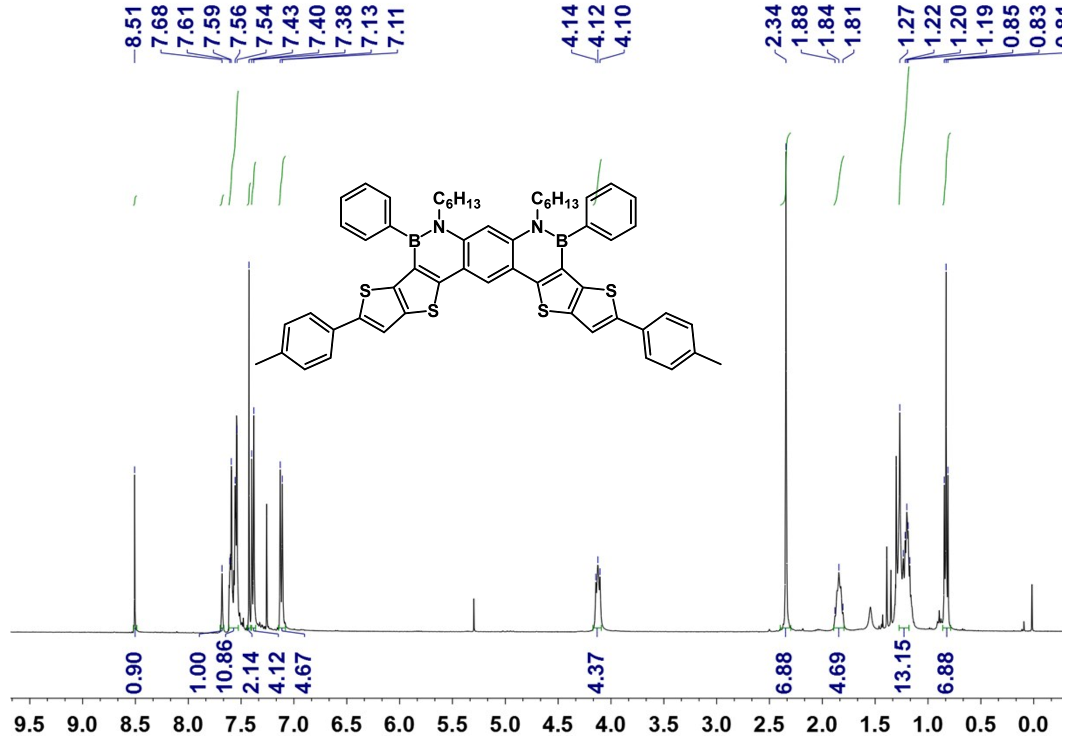


Figure S15 ^{1}H NMR spectrum of **6c** ($CDCl_3$)

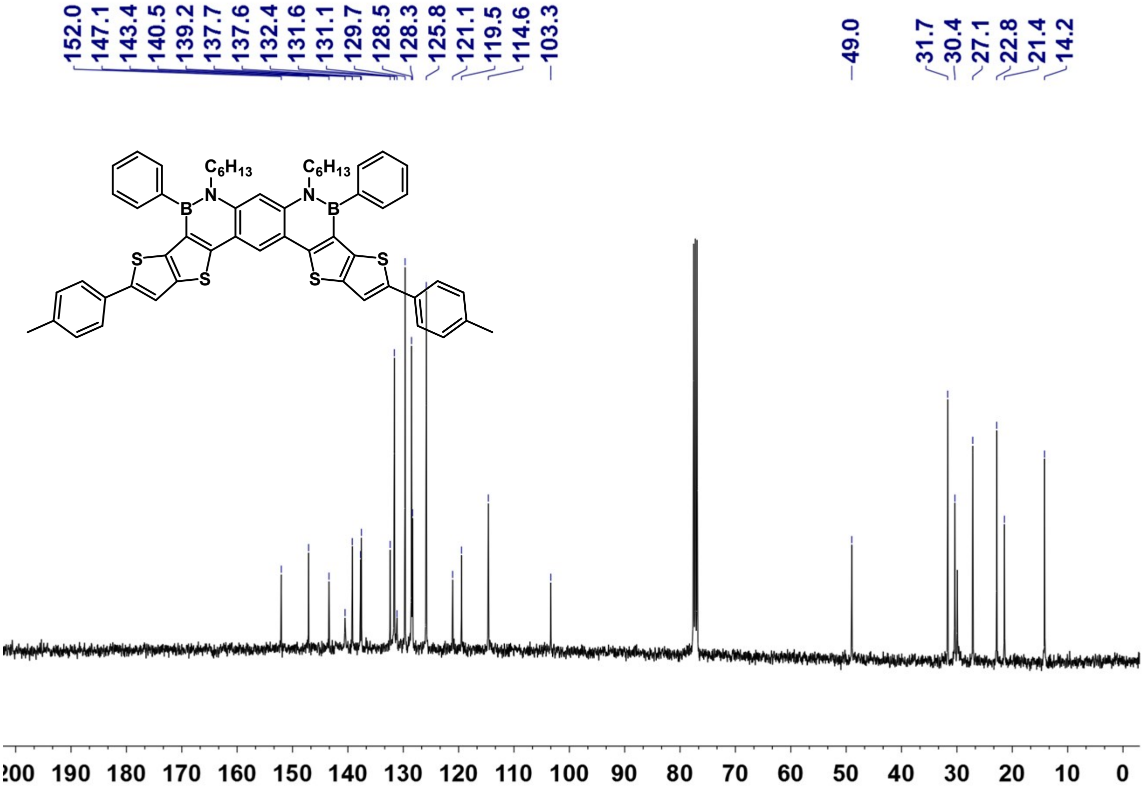


Figure S16 ^{13}C NMR spectrum of **6c** (CDCl$_3$)

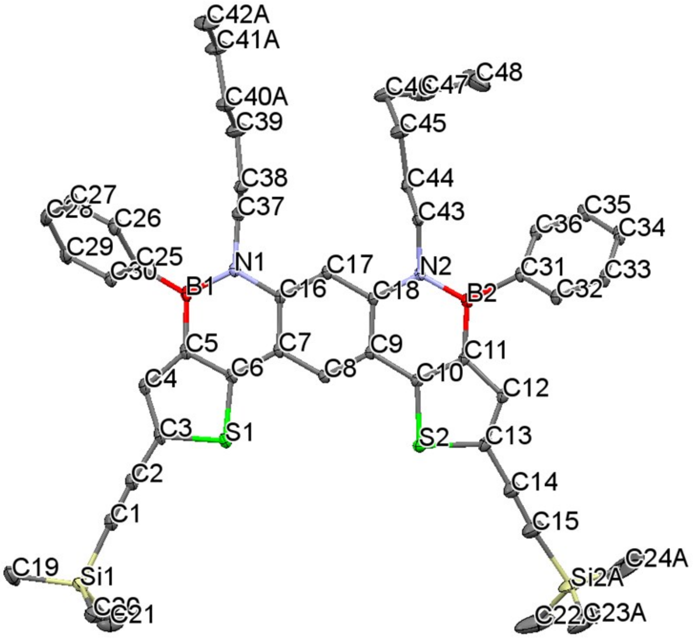
3 X-ray Crystallographic Analysis.

Table S1 Crystal data for compound **3b**.

Compound	**3b**
Formula	$C_{48}H_{58}B_2N_2S_2Si_2$
Formula Weight	804.88
T, *K*	100
Crystal system	triclinic
Space group	$P\bar{1}$
Shape	prism
Crystal dimension, mm^3	0.11×0.07×0.04
a, Å	8.3587(3)
b, Å	16.6395(5)
c, Å	17.2793(6)

α, °	97.127(2)
β, °	98.680(2)
γ, °	103.468(2)
V, Å3	2278.52(13)
Z	2
*ρ*calc, g/cm-3	1.173
F(000)	860
θ range, °	1.606 to 28.999
wR2 (all data)	0.1202
wR2	0.1107
R1 (all data)	0.0628
R1	0.0449
Independent reflections	12133
Reflections measured	46089
Goodness of fit indictor	1.032

Table S2 ORTEP drawing molecular structure, selected distances, and angles of **3b**



distances (Å)			
Si1-C1	1.8354(17)	C18-C17	1.3997(19)
Si2A-C15	1.850(2)	C8-C7	1.383(2)
N2-C18	1.4052(17)	C17-C16	1.3984(19)
N2-B2	1.434(2)	C7-C16	1.414(2)
N1-C16	1.4050(18)	C7-C6	1.4301(19)
N1-B1	1.432(2)	C5-C6	1.378(2)
C9-C18	1.4137(19)	C5-B1	1.526(2)
C9-C8	1.3841(19)	C31-B2	1.574(2)
C9-C10	1.429(2)	C25-B1	1.570(2)
C11-C10	1.375(2)	C2-C1	1.201(2)
C11-B2	1.532(2)	C14-C15	1.199(2)

angles (°)			
C18-N2-C43	116.35(11)	N1-B1-C5	117.00(13)
C18-N2-B2	122.75(12)	N1-B1-C25	122.90(14)
B2-N2-C43	120.47(12)	C5-B1-C25	119.90(13)
C16-N1-C37	117.58(12)	N2-B2-C11	116.35(13)
C16-N1-B1	122.70(13)	N2-B2-C31	124.41(13)
B1-N1-C37	119.60(12)	C11-B2-C31	119.20(13)
C2-C3-S1	117.77(12)	C14-C13-S2	118.92(13)

4 Optical Spectra

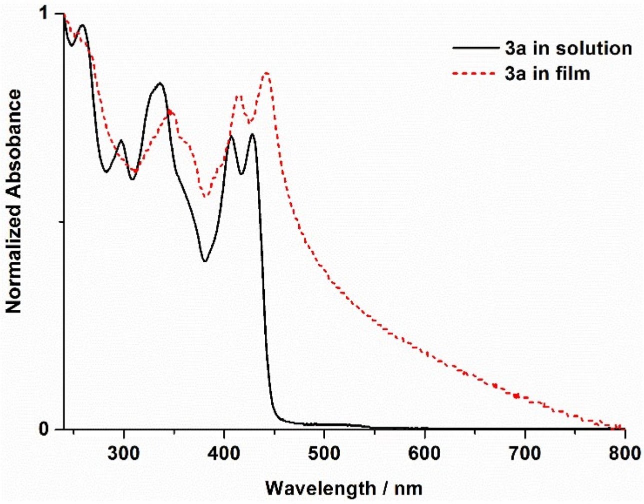


Figure S17 Normalized absorption spectra of compound **3a** in CH_2Cl_2 (solid line) and in film (dashed line).

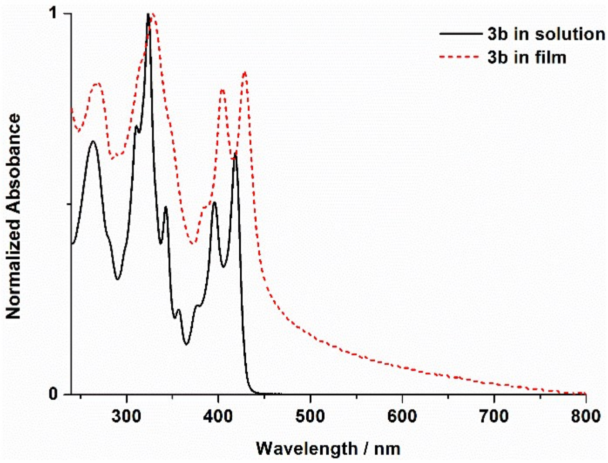


Figure S18 Normalized absorption spectra of compound **3b** in CH_2Cl_2 (solid line) and in film (dashed line).

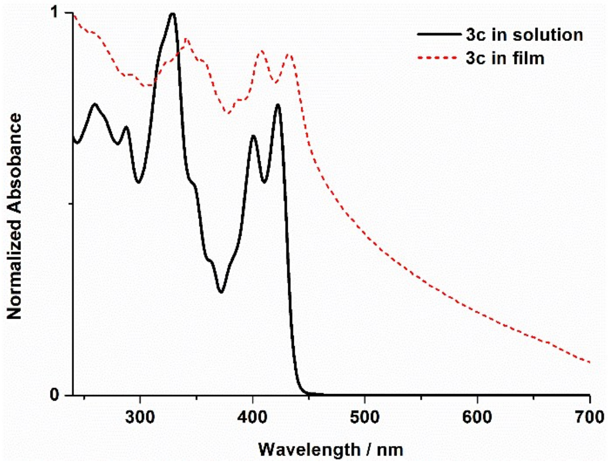


Figure S19 Normalized absorption spectra of compound **3c** in CH_2Cl_2 (solid line) and in film (dashed line).

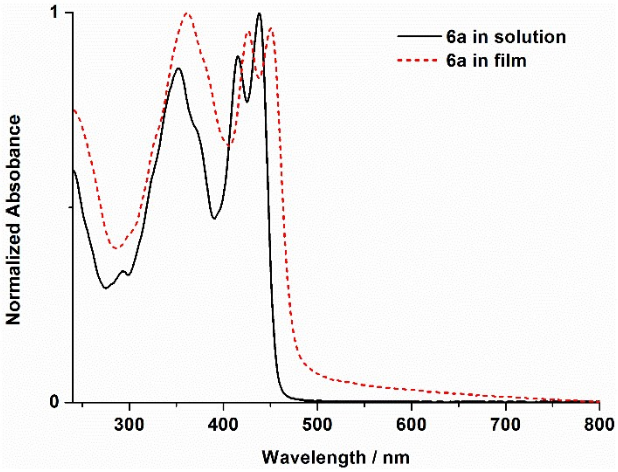


Figure S20 Normalized absorption spectra of compound **6a** in CH_2Cl_2 (solid line) and in film (dashed line).

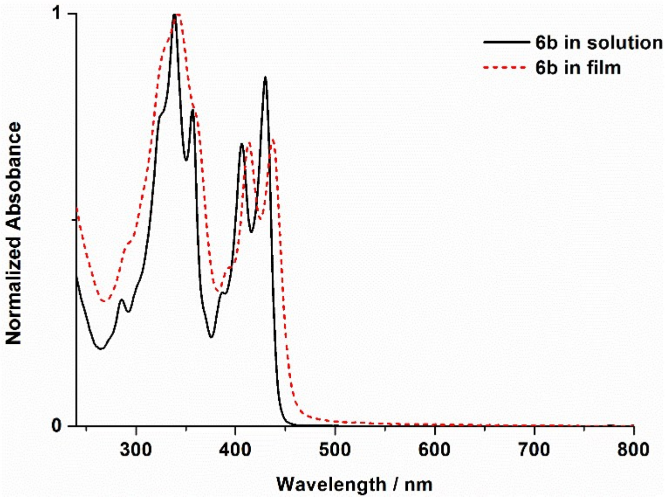


Figure S21 Normalized absorption spectra of compound **6b** in CH_2Cl_2 (solid line) and in film (dashed line).

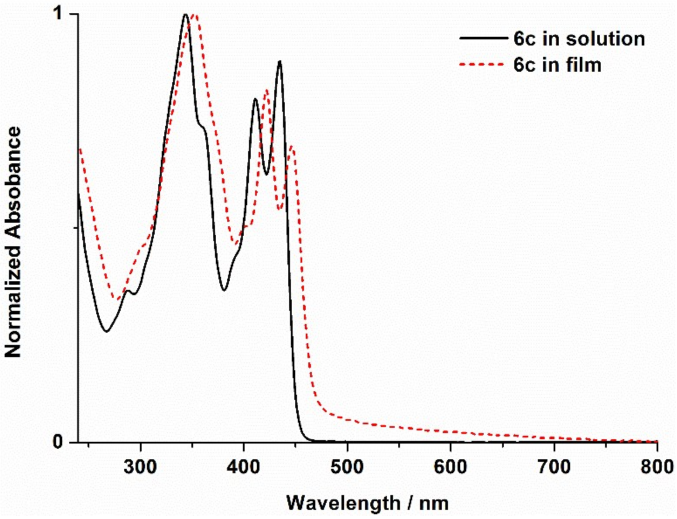


Figure S22 Normalized absorption spectra of compound **6c** in CH_2Cl_2 (solid line) and in film (dashed line).

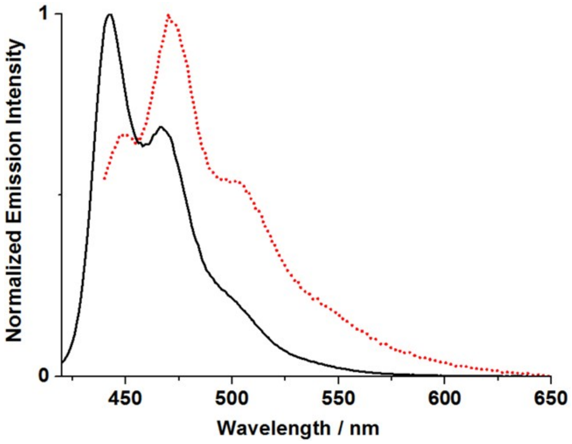


Figure S23 Normalized emission spectra of compound **3a** in CH_2Cl_2 (solid line, excitation at λ = 407 nm) and in film (dotted line, excitation at λ = 414 nm).

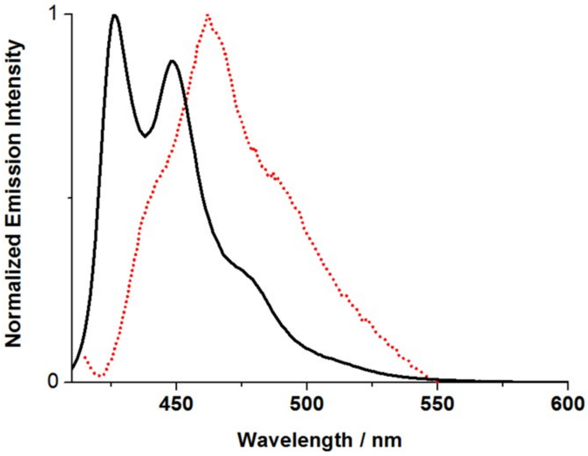


Figure S24 Normalized emission spectra of compound **3b** in CH_2Cl_2 (solid line, excitation at λ = 395 nm) and in film (dotted line, excitation at λ = 405 nm).

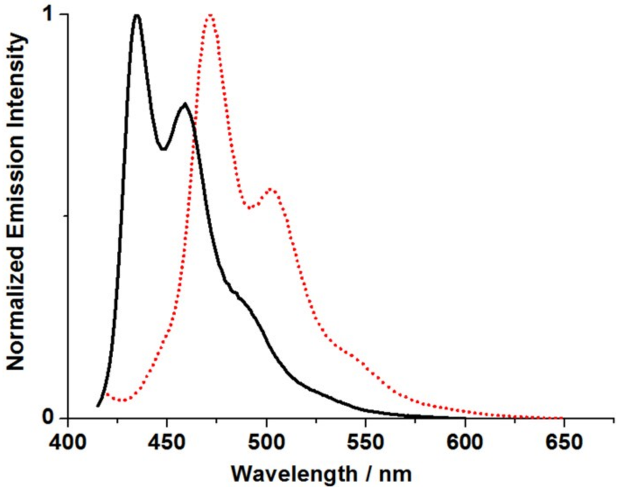


Figure S25 Normalized emission spectra of compound **3c** in CH_2Cl_2 (solid line, excitation at λ = 401 nm) and in film (dotted line, excitation at λ = 409 nm).

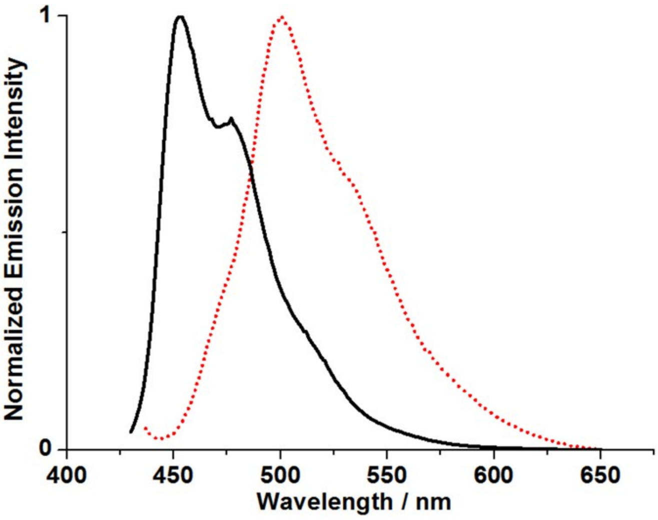


Figure S26 Normalized emission spectra of compound **6a** in CH_2Cl_2 (solid line, excitation at λ = 415 nm) and in film (dotted line, excitation at λ = 427 nm).

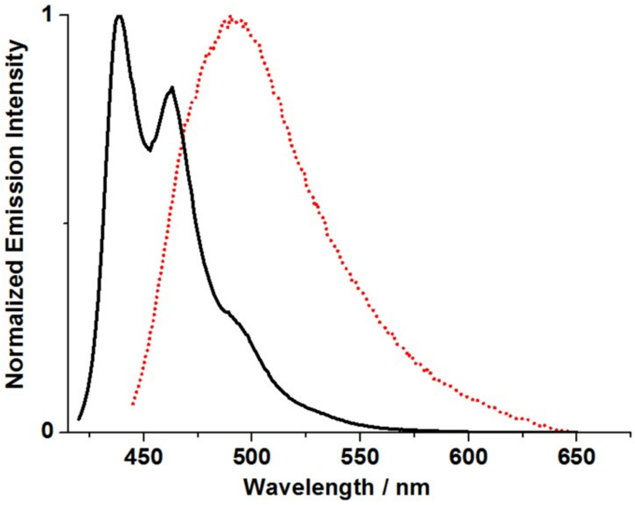


Figure S27 Normalized emission spectra of compound **6b** in CH_2Cl_2 (solid line, excitation at λ = 406 nm) and in film (dotted line, excitation at λ = 413 nm).

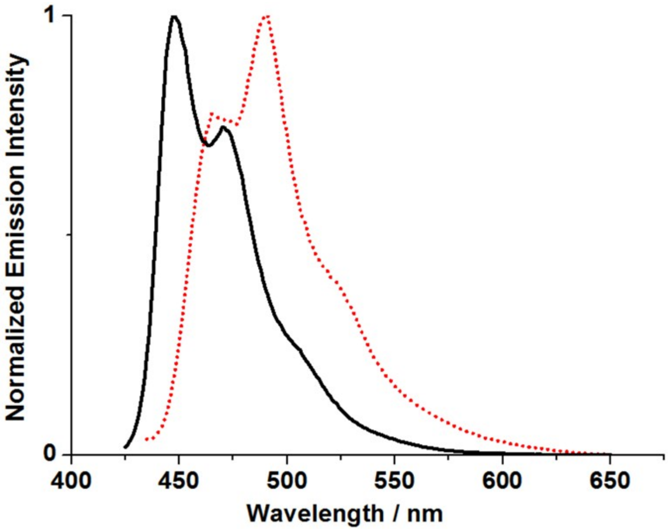
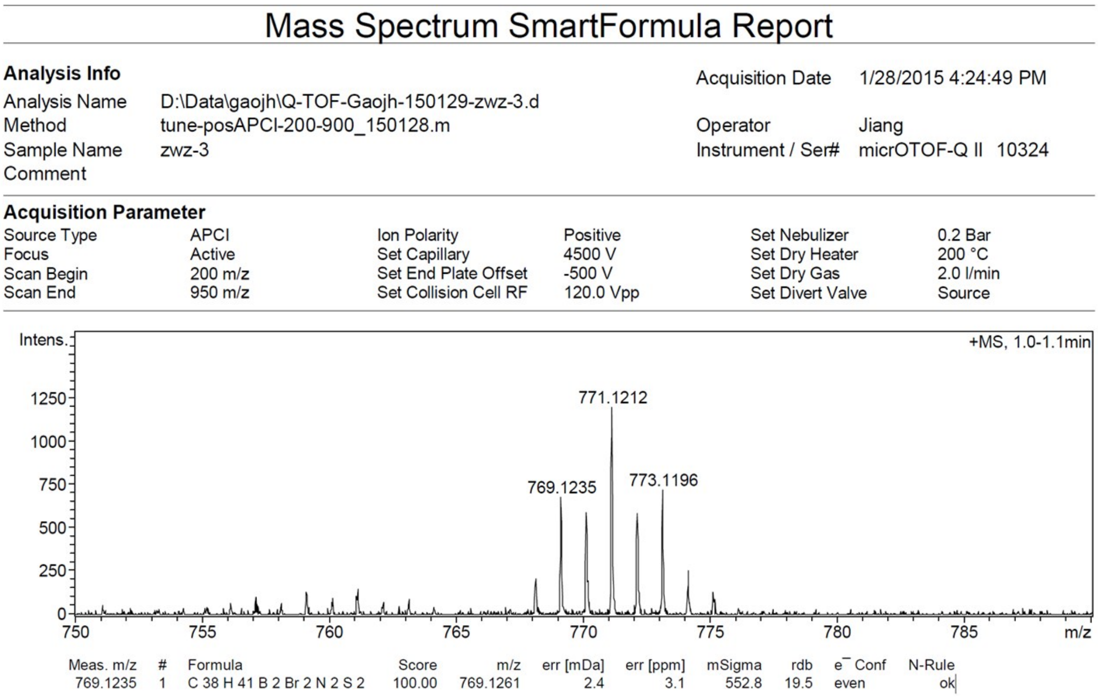


Figure S28 Normalized emission spectra of compound **6c** in CH_2Cl_2 (solid line, excitation at λ = 411 nm) and in film (dotted line, excitation at λ = 422 nm).

5 HRMS Spectra.



Mass Spectrum SmartFormula Report

Analysis Info

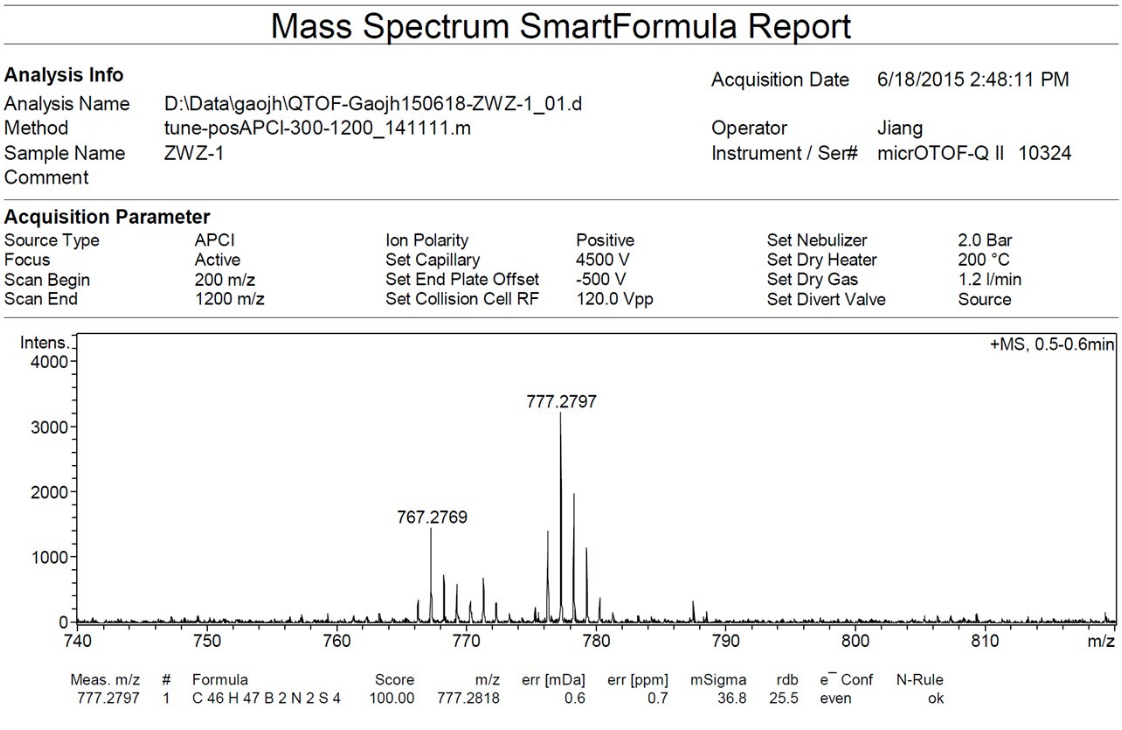
Analysis Name	D:\Data\gaojh\Q-TOF-Gaojh-150129-zwz-3.d	Acquisition Date	1/28/2015 4:24:49 PM
Method	tune-posAPCI-200-900_150128.m	Operator	Jiang
Sample Name	zwz-3	Instrument / Ser#	micrOTOF-Q II 10324
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	0.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	2.0 l/min
Scan End	950 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^{-} Conf	N-Rule
769.1235	1	C 38 H 41 B 2 Br 2 N 2 S 2	100.00	769.1261	2.4	3.1	552.8	19.5	even	ok

Figure S29 HR-ESI mass spectrum of compound **2**.



Mass Spectrum SmartFormula Report

Analysis Info

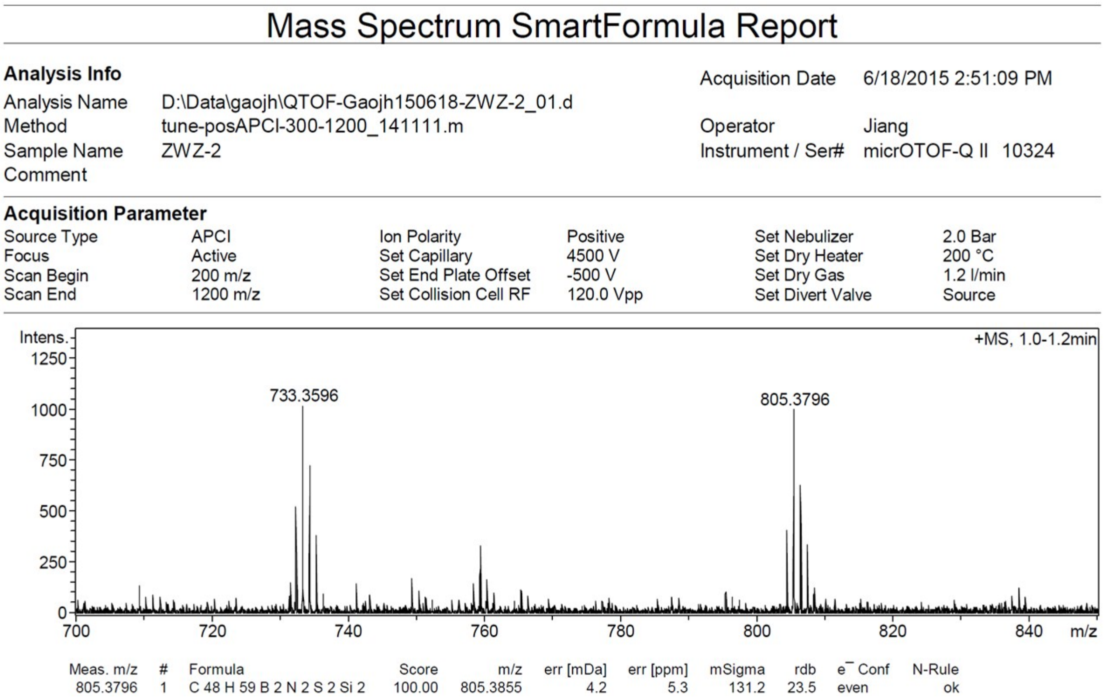
Analysis Name	D:\Data\gaojh\QTOF-Gaojh150618-ZWZ-1_01.d	Acquisition Date	6/18/2015 2:48:11 PM
Method	tune-posAPCI-300-1200_141111.m	Operator	Jiang
Sample Name	ZWZ-1	Instrument / Ser#	micrOTOF-Q II 10324
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.2 l/min
Scan End	1200 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^{-} Conf	N-Rule
777.2797	1	C 46 H 47 B 2 N 2 S 4	100.00	777.2818	0.6	0.7	36.8	25.5	even	ok

Figure S30 HR-ESI mass spectrum of compound **3a**.



Mass Spectrum SmartFormula Report

Analysis Info

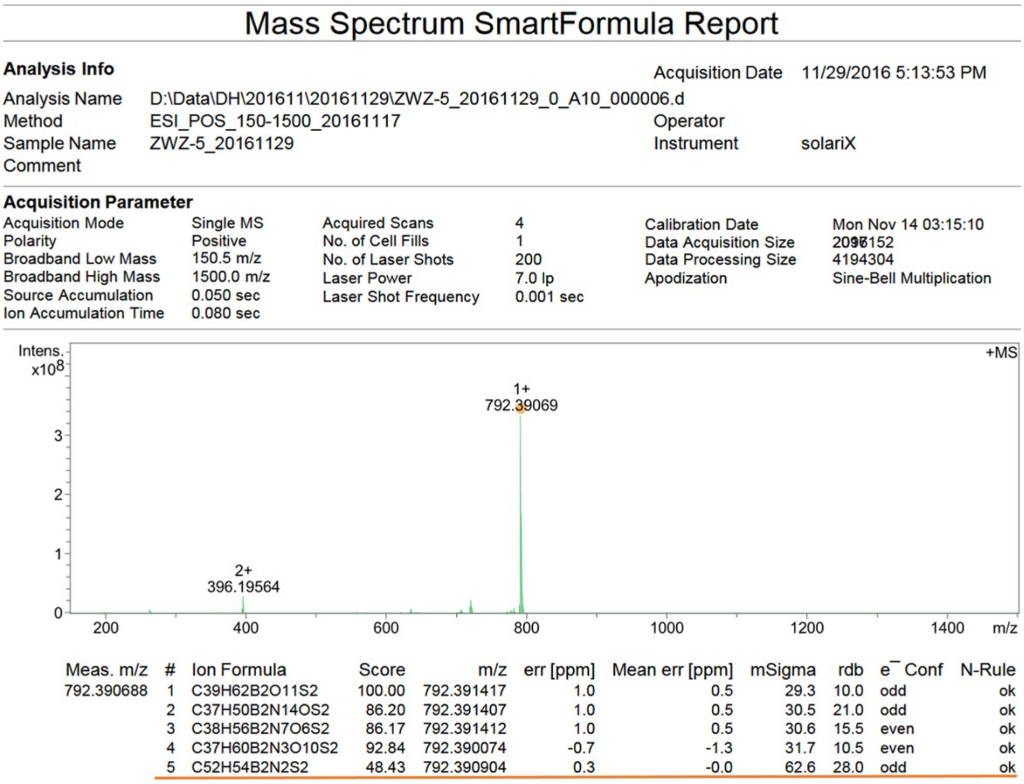
Analysis Name	D:\Data\gaojh\QTOF-Gaojh150618-ZWZ-2_01.d	Acquisition Date	6/18/2015 2:51:09 PM
Method	tune-posAPCI-300-1200_141111.m	Operator	Jiang
Sample Name	ZWZ-2	Instrument / Ser#	micrOTOF-Q II 10324
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.2 l/min
Scan End	1200 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
805.3796	1	C 48 H 59 B 2 N 2 S 2 Si 2	100.00	805.3855	4.2	5.3	131.2	23.5	even	ok

Figure S31 HR-ESI mass spectrum of compound **3b**.



Mass Spectrum SmartFormula Report

Analysis Info

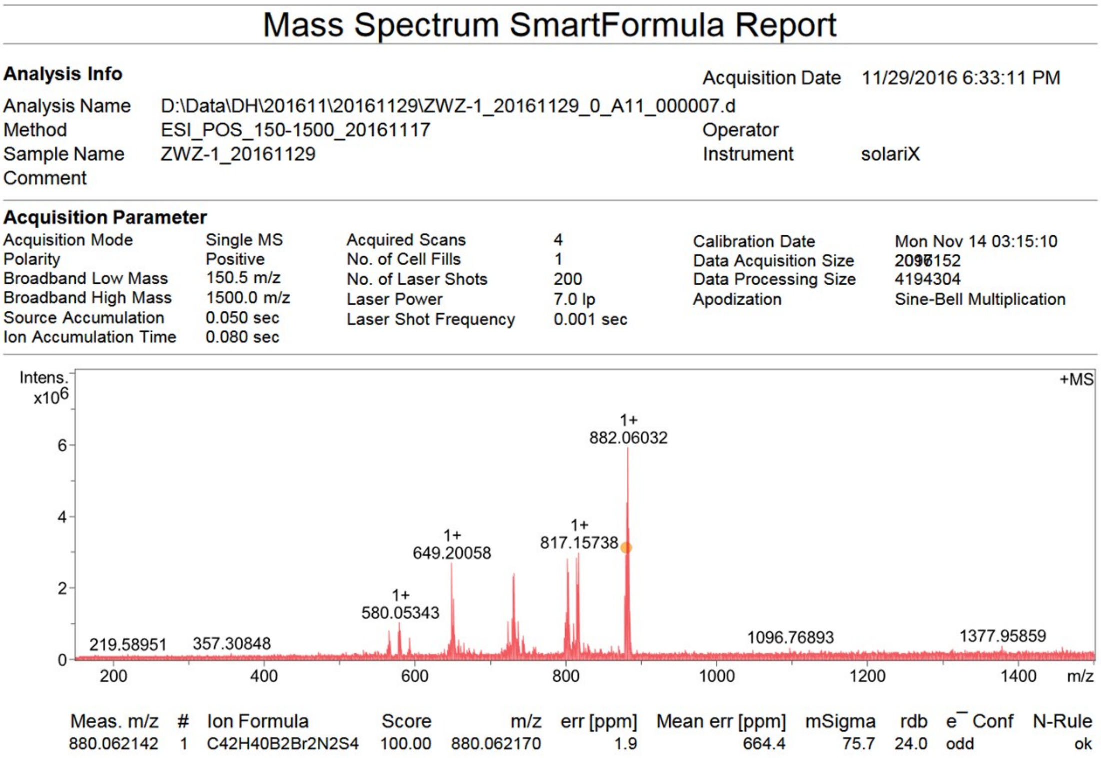
Analysis Name	D:\Data\DH\201611\20161129\ZWZ-5_20161129_0_A10_000006.d	Acquisition Date	11/29/2016 5:13:53 PM
Method	ESI_POS_150-1500_20161117	Operator	
Sample Name	ZWZ-5_20161129	Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	4	Calibration Date	Mon Nov 14 03:15:10
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	150.5 m/z	No. of Laser Shots	200	Data Processing Size	4194304
Broadband High Mass	1500.0 m/z	Laser Power	7.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.050 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.080 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
792.390688	1	C39H62B2O11S2	100.00	792.391417	1.0	0.5	29.3	10.0	odd	ok
	2	C37H50B2N14OS2	86.20	792.391407	1.0	0.5	30.5	21.0	odd	ok
	3	C38H56B2N7O6S2	86.17	792.391412	1.0	0.5	30.6	15.5	even	ok
	4	C37H60B2N3O10S2	92.84	792.390074	-0.7	-1.3	31.7	10.5	even	ok
	5	C52H54B2N2S2	48.43	792.390904	0.3	-0.0	62.6	28.0	odd	ok

Figure S32 HR-MALDI-MS spectrum of compound **3c**.



Mass Spectrum SmartFormula Report

Analysis Info

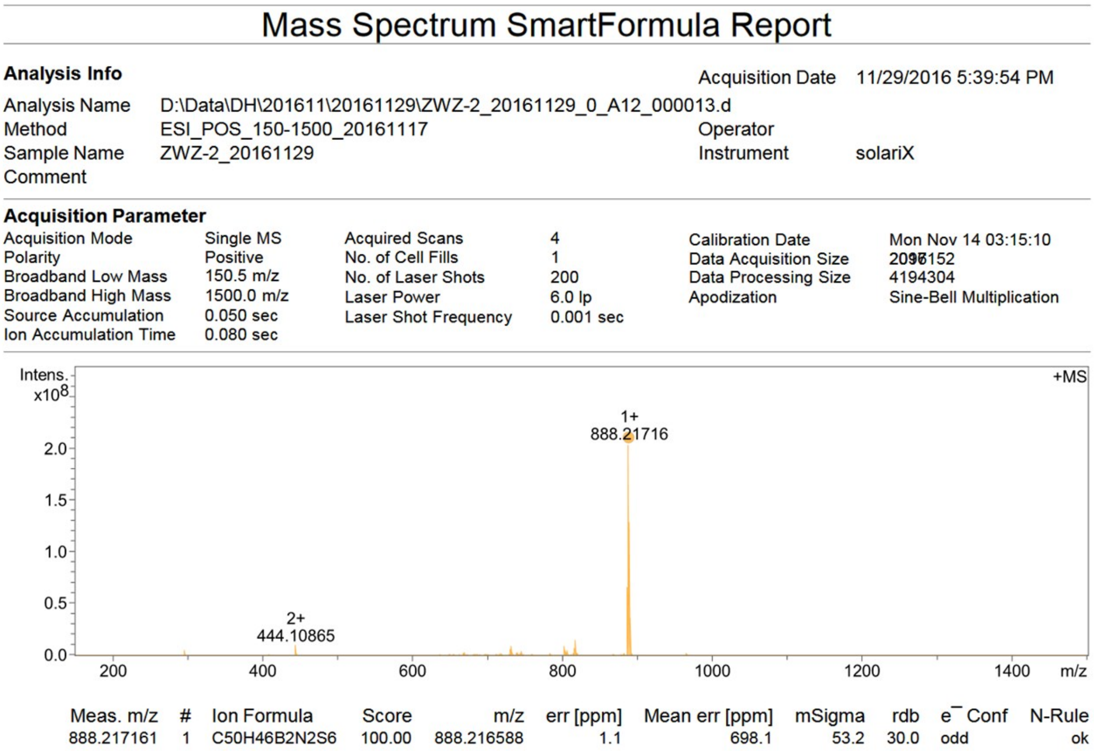
		Acquisition Date	11/29/2016 6:33:11 PM
Analysis Name	D:\Data\DH\201611\20161129\ZWZ-1_20161129_0_A11_000007.d		
Method	ESI_POS_150-1500_20161117	Operator	
Sample Name	ZWZ-1_20161129	Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	4	Calibration Date	Mon Nov 14 03:15:10
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	150.5 m/z	No. of Laser Shots	200	Data Processing Size	4194304
Broadband High Mass	1500.0 m/z	Laser Power	7.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.050 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.080 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e^- Conf	N-Rule
880.062142	1	C42H40B2Br2N2S4	100.00	880.062170	1.9	664.4	75.7	24.0	odd	ok

Figure S33 HR-MALDI-MS spectrum of compound **5**.



Mass Spectrum SmartFormula Report

Analysis Info

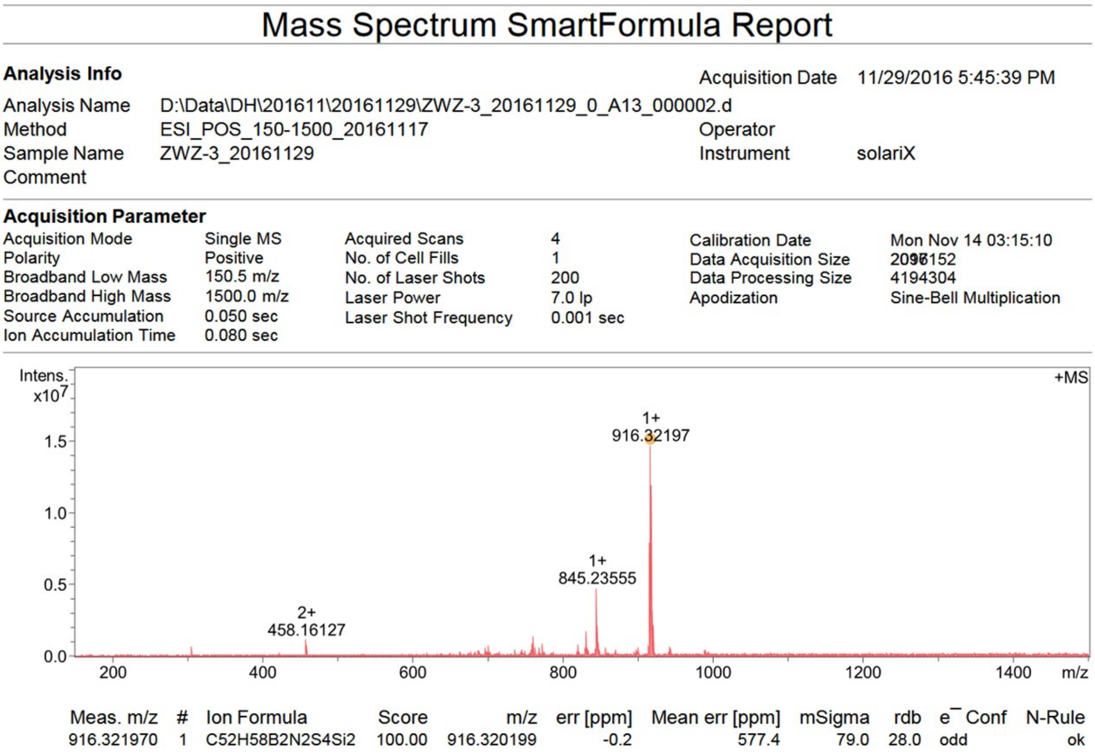
		Acquisition Date	11/29/2016 5:39:54 PM
Analysis Name	D:\Data\DH\201611\20161129\ZWZ-2_20161129_0_A12_000013.d		
Method	ESI_POS_150-1500_20161117	Operator	
Sample Name	ZWZ-2_20161129	Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	4	Calibration Date	Mon Nov 14 03:15:10
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	150.5 m/z	No. of Laser Shots	200	Data Processing Size	4194304
Broadband High Mass	1500.0 m/z	Laser Power	6.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.050 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.080 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e^- Conf	N-Rule
888.217161	1	C50H46B2N2S6	100.00	888.216588	1.1	698.1	53.2	30.0	odd	ok

Figure S34 HR-MALDI-MS spectrum of compound **6a**.



Mass Spectrum SmartFormula Report

Analysis Info

Acquisition Date 11/29/2016 5:45:39 PM

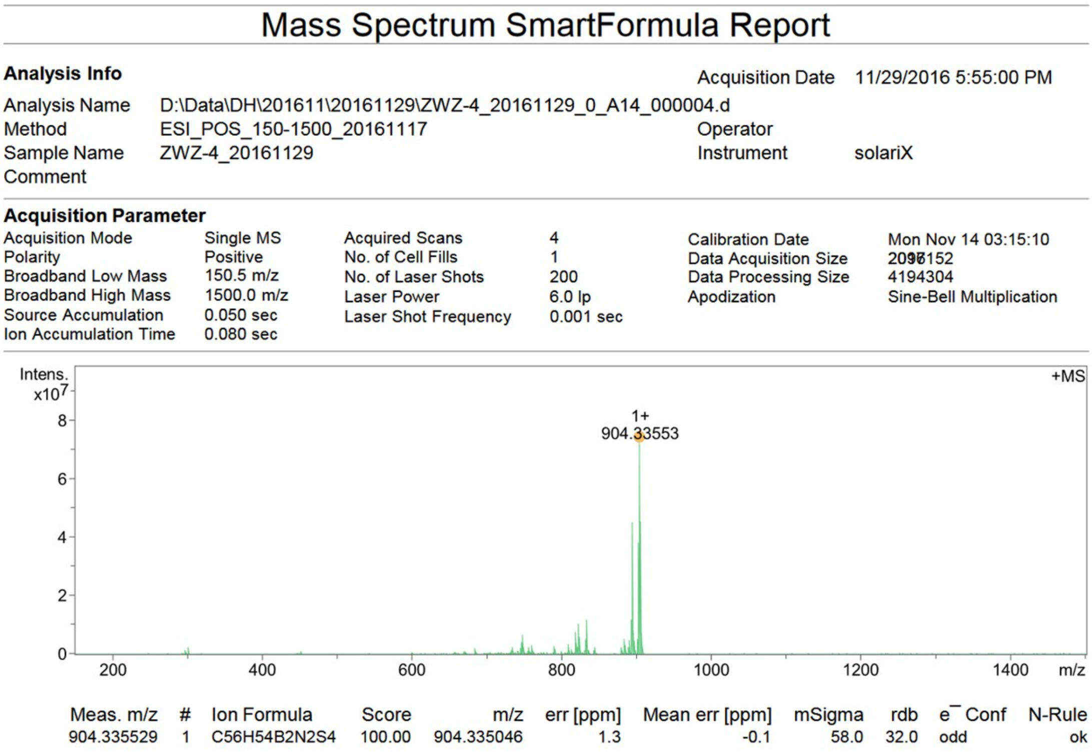
Analysis Name D:\Data\DH\201611\20161129\ZWZ-3_20161129_0_A13_000002.d
Method ESI_POS_150-1500_20161117
Operator
Sample Name ZWZ-3_20161129
Instrument solariX
Comment

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	4	Calibration Date	Mon Nov 14 03:15:10
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	150.5 m/z	No. of Laser Shots	200	Data Processing Size	4194304
Broadband High Mass	1500.0 m/z	Laser Power	7.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.050 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.080 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
916.321970	1	C52H58B2N2S4Si2	100.00	916.320199	-0.2	577.4	79.0	28.0	odd	ok

Figure S35 HR-MALDI-MS spectrum of compound **6b**.



Mass Spectrum SmartFormula Report

Analysis Info

Acquisition Date 11/29/2016 5:55:00 PM

Analysis Name D:\Data\DH\201611\20161129\ZWZ-4_20161129_0_A14_000004.d
Method ESI_POS_150-1500_20161117
Operator
Sample Name ZWZ-4_20161129
Instrument solariX
Comment

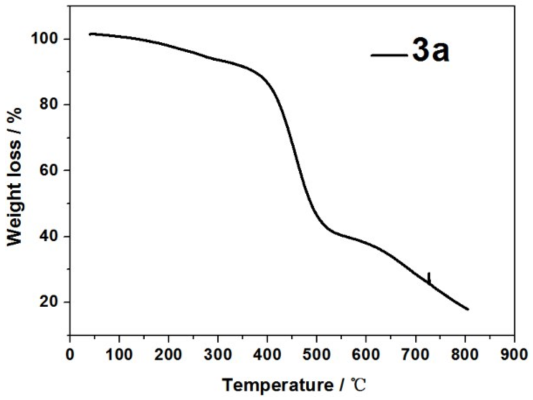
Acquisition Parameter

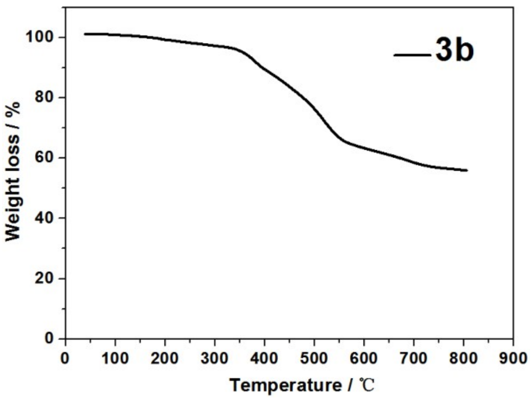
Acquisition Mode	Single MS	Acquired Scans	4	Calibration Date	Mon Nov 14 03:15:10
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	150.5 m/z	No. of Laser Shots	200	Data Processing Size	4194304
Broadband High Mass	1500.0 m/z	Laser Power	6.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.050 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.080 sec				

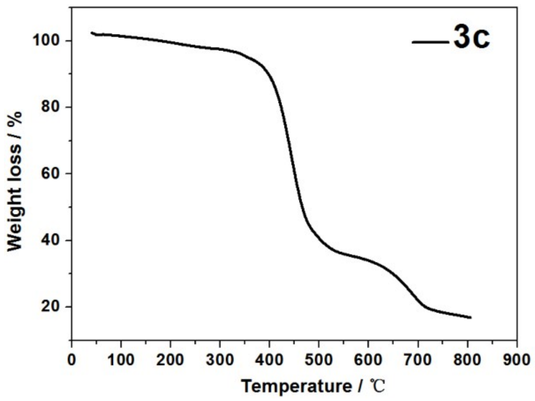
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
904.335529	1	C56H54B2N2S4	100.00	904.335046	1.3	-0.1	58.0	32.0	odd	ok

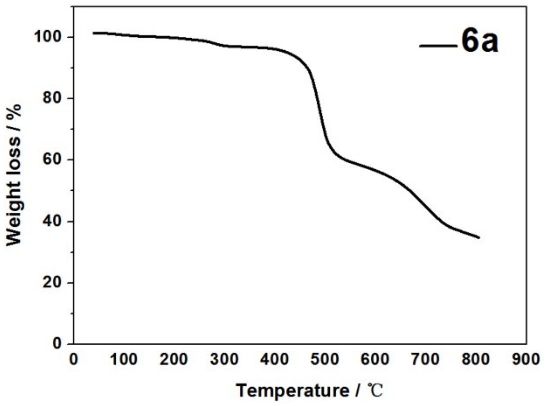
Figure S36 HR-MALDI-MS spectrum of compound **6c**.

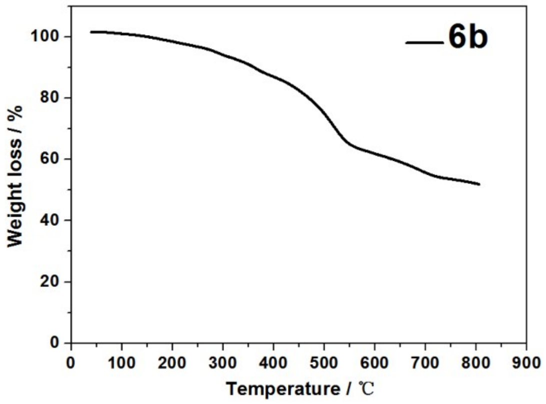
6 Thermal Stabilities of 3a-6c.

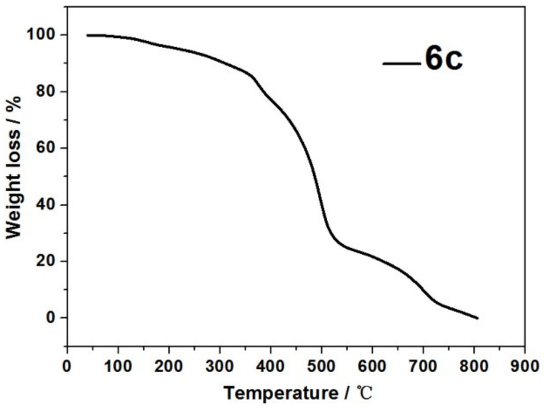












7 References.

(1) Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi, T. Baumgartner, *Chem. Eur. J.*, 2007, **13**, 7487.

(2) W. Z. Zhang, F. Zhang, R. Z. Tang, Y. B. Fu, X. Y. Wang, X. D. Zhuang, G. F. He and X. L. Feng, *Org. Lett.*, 2016, **18**, 3618.