Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2021

I. Materials and instrumentations

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under nitrogen atmosphere in oven-dried glassware. Glassware was dried in an oven at 120 °C and cooled under a stream of inert gas before use. Both toluene and triethylamine were distilled over calcium hydride. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker DRX400 and AVANCE III HD-500 spectrometers at 298 K and referenced to the residual signals of the solvent. HR-MS were recorded on a Thermo Scientific™ Orbitrap ID-X™ Tribrid™ mass spectrometer. All the solvents employed for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

II Supplementary data

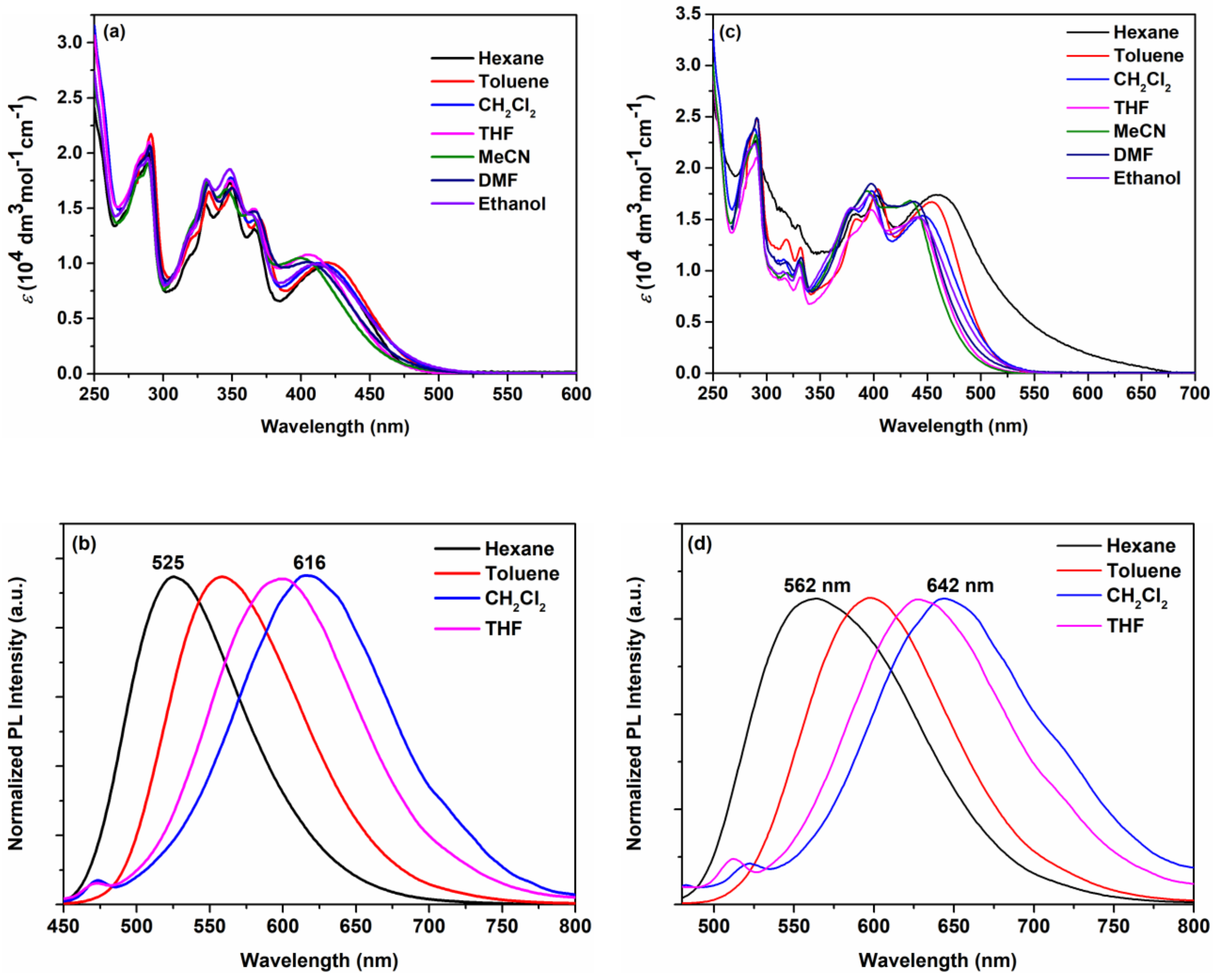


Fig. S1 Absorption spectra of **3a** (a) and **3b** (c), and PL spectra of **3a** (b) and **3b** (d) in several solvents of different polarities. (λ_{ex} = 414 and 445 nm for **3a** and **3b**, respectively)

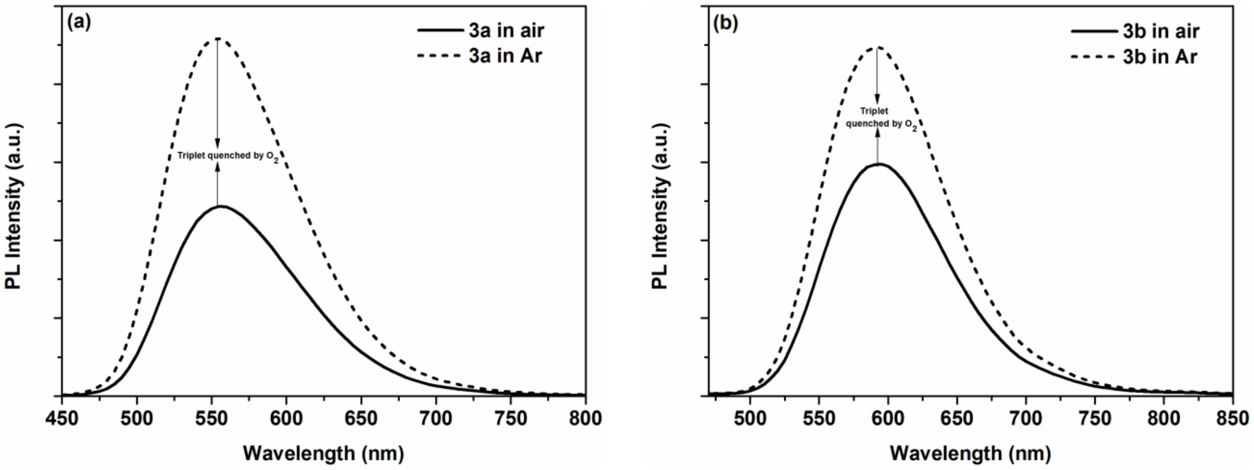


Fig. S2 Photoluminescence spectra of **3a** (a) and **3b** (b) under aerated toluene solution (solid lines) and degassed condition (short dashed lines). (λ_{ex} = 414 and 445 nm for **3a** and **3b**, respectively)

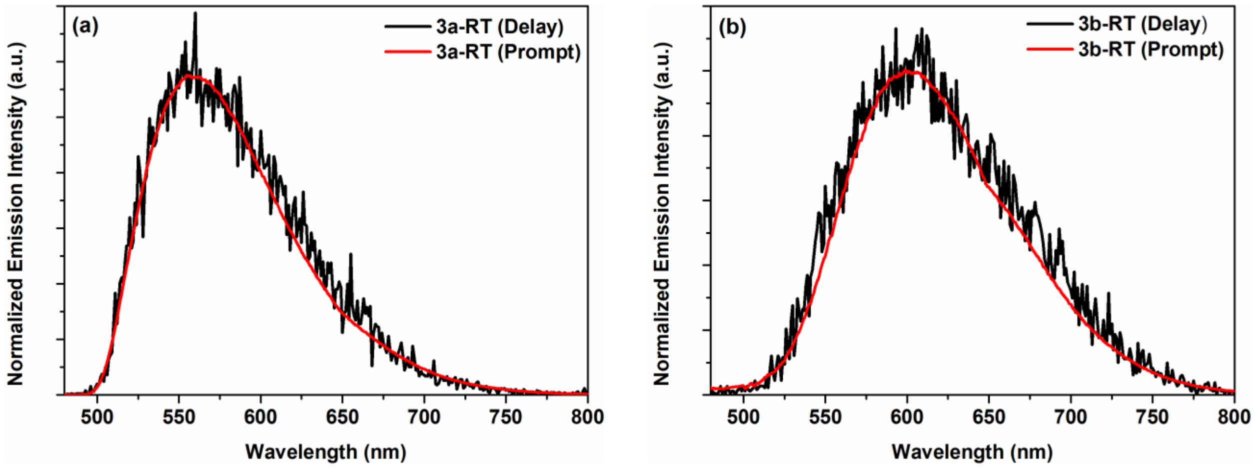
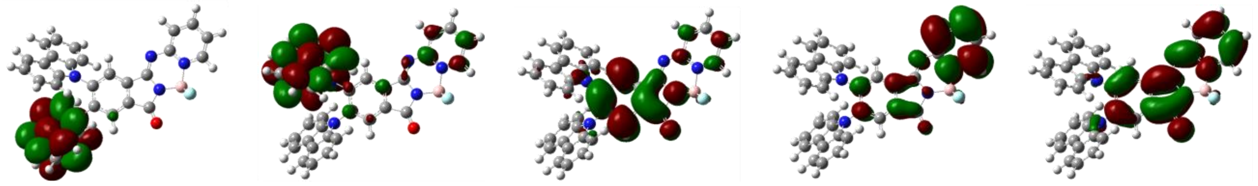
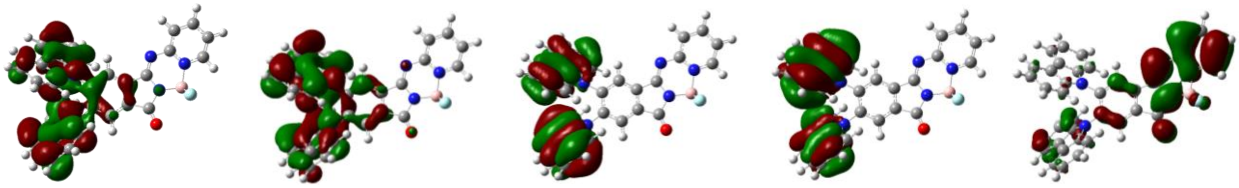


Fig. S3 Prompt fluorescence (red) and emission spectra (black) of **3a** (a) and **3b** (b) with delays of 50 μs based on time-resolved technology at room temperature (RT).

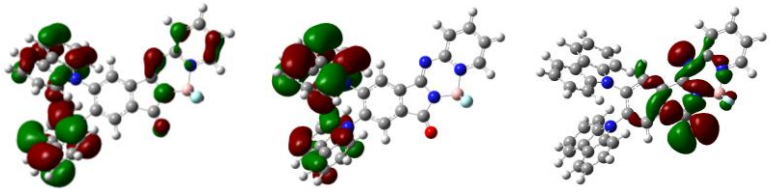
3a



LUMO+4 LUMO+3 LUMO+2 LUMO+1 LUMO

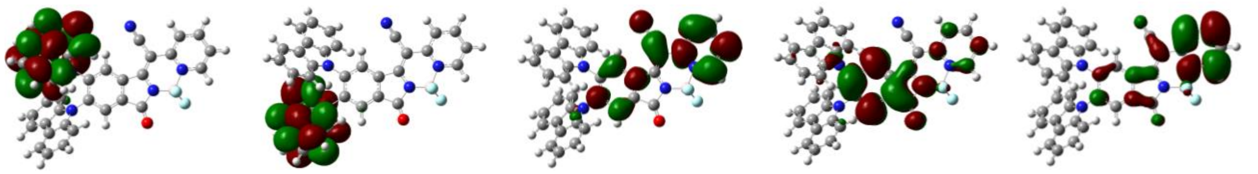


HOMO HOMO-1 HOMO-2 HOMO-3 HOMO-4

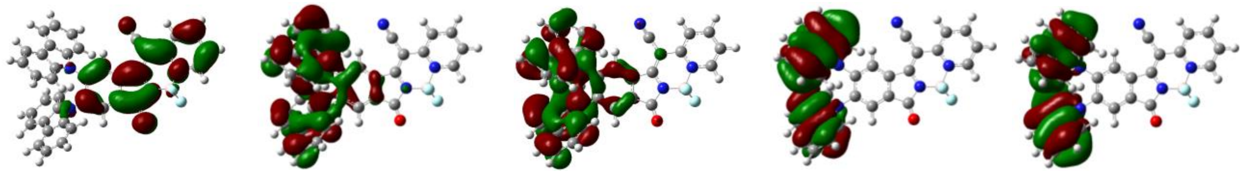


HOMO-5 HOMO-6 HOMO-7

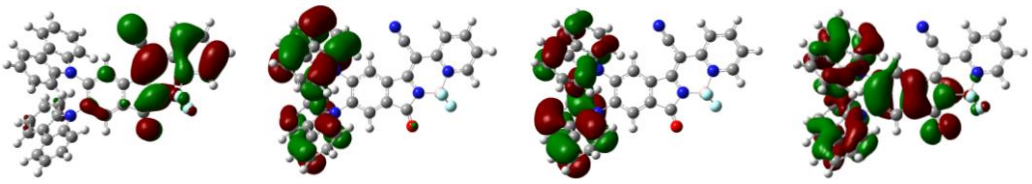
3b



LUMO+5 LUMO+4 LUMO+3 LUMO+2 LUMO+1



LUMO HOMO HOMO-1 HOMO-2 HOMO-3



HOMO-4 HOMO-5 HOMO-6 HOMO-7

Fig. S4 π-MOs angular nodal patterns of **3a** and **3b**.

Table S1. (1) Calculated electronic excitation energies, oscillator strengths, and eigenvectors for the TD-DFT spectra of **3a** and **3b** carried out using the CAM-B3LYP functional with 6-31G(d) basis sets.

	State [a]	Energy [eV]	λ [nm]	f [b]	Orbitals (coefficient) [c]
3a	S_1	3.37	368	0.1153	HOMO->LUMO (87%)
	S_2	3.50	354	0.2741	H-1->LUMO (83%)
	S_3	3.93	315	0.0487	H-8->LUMO (78%)
	S_4	4.00	310	0.2401	H-4->LUMO (40%), H-2->LUMO (37%)
	S_5	4.02	309	0.2242	H-4->LUMO (32%), H-2->LUMO (55%)
3b	S_1	3.15	394	0.0885	HOMO->LUMO (89%)
	S_2	3.25	382	0.3996	H-4->LUMO (10%), H-1->LUMO (81%)
	S_3	3.63	341	0.3681	H-4->LUMO (79%)
aza-BF core[d]	S_2	3.69	336	0.382	HOMO->LUMO (83%), H−2-> LUMO (13%)
CN-BF core[d]	S_1	3.32	374	0.426	HOMO->LUMO (93%)

[a] Excited state: S = Singlet, T = Triplet. [b] Oscillator strength (<0.002 are not included). [c] MOs involved in the transitions with H and L denoting the HOMO and LUMO, respectively. [d] reference data.

(2) Energy levels of the singlet and triplet states of **3a** and **3b** on the basis of TD-DFT results with B3LYP/6-31G(d). The energies are the adiabatic values computed with the optimization geometries of T_1 and S_1 excited states.

	State [a]	Energy [eV]	λ [nm]	f [b]	Orbitals (coefficient) [c]
3a	S_1	2.71	458	0.0071	HOMO->LUMO (94%)
	S_2	3.07	403	0.0201	H-1->LUMO (88%)
	T_1	1.97	628	0	H-7->LUMO (12%), H-4->LUMO (30%), HOMO->LUMO (41%)
	T_2	2.53	490	0	H-7->LUMO (19%), H-4->LUMO (51%), HOMO->LUMO (12%)
	T_3	2.93	423	0	H-1->LUMO (73%)
	T_4	3.06	405	0	H-3->L+3 (12%), H-3->L+4 (18%), H-2->L+4 (26%)
	T_5	3.07	403	0	H-3->L+3 (14%), H-3->L+4 (12%), H-2->L+3 (33%)
3b	S_1	2.47	502	0.0022	HOMO->LUMO (95%)
	S_2	2.85	435	0.0095	H-1->LUMO (87%)
	T_1	1.46	847	0	H-4->LUMO (84%)
	T_2	2.39	519	0	H-7->LUMO (20%), HOMO->LUMO (53%)
	T_3	2.71	457	0	H-1->LUMO (78%)
	T_4	3.05	407	0	H-3->L+4 (27%), H-2->L+4 (16%)
	T_5	3.06	405	0	H-3->L+5 (12%), H-2->L+5 (33%)

[a] Excited state: S = Singlet, T = Triplet. [b] Oscillator strength. [c] MOs involved in the transitions with H and L denoting the HOMO and LUMO, respectively.

Table S2. Crystal data and experimental details of **3a** and **3b**.

Compound	**3a**	**3b**
CCDC number	2046309	2046310
Empirical formula	$C_{37}H_{22}BF_2N_5O$	$C_{39}H_{22}BF_2N_5O$
Formula weight (g mol^{-1})	601.40	625.42
Temperature	193 K	296 K
Radiation	GaK$_\alpha$ (λ = 1.34139)	MoK$_\alpha$ (λ = 0.71073)
Crystal System	Monoclinic	Triclinic
Space Group	*C2/c*	*P-1*
Unit cell dimensions	a = 27.1150(7) Å, b = 11.5861(3) Å, c = 18.6719(5) Å, α = 90°, β = 105.101(1)°, γ = 90°	a = 8.939(8) Å, b = 9.493(8) Å, c = 17.408(16) Å, α = 88.857(13)°, β = 84.196(14)°, γ = 88.477(12)°
Volume (Å^3)	5663.3(3)	1469(2)
Z	8	2
$\rho_{calc.}$ (g cm^{-3})	1.411	1.414
μ (mm^{-1})	0.503	0.096
F (000)	2480	644
Crystal size (mm^3)	0.14 × 0.12 × 0.11	0.18 × 0.16 × 0.15
$2\theta_{max}$ (°)	53.883	26.859
Index ranges	-32=<h<=32, -13=<k<=13, -16=<l<=22	-11=<h<=11, -12=<k<=11, -21=<l<=17
Reflections collected	20966	12548
Independent reflections	5159	6178
Reflections with $I>2\sigma(I)$	3969	3099
R_{int}	0.0371	0.0602
Data completeness (to 2θ)	99.4% (53.594°)	98.8% (25.242°)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5159/0/415	6178/0/433
Goodness-of-fit on F^2	1.035	0.957
R_1 , wR_2 (all data)	0.0579, 0.1016	0.1448, 0.2032
R_1 , wR_2 , $I>2\sigma(I)$	0.0399, 0.0920	0.0621, 0.1534
$\Delta\rho$/eÅ^{-3} max, min	0.229, -0.166	0.240, -0.233

Table S3. Selected bond lengths of complexes **3a** and **3b** determined by X-ray diffraction

3a		**3b**	
Bond	Bond length (Å)	Bond	Bond length (Å)
N3-C31	1.3735(22)	N3-C32	1.3573(37)
N3-C37	1.3976(22)	N3-C31	1.4038(37)
C37-O1	1.2126(22)	C31-O1	1.2088(38)
N4-C31	1.2879(23)	N4-C34	1.3456(40)
N4-C32	1.3941(20)	N5-C39	1.1316(45)
N2-C25	1.4180(22)	N2-C25	1.4101(39)
N1-C26	1.4126(21)	N1-C29	1.4140(42)
N5-C32	1.3628(23)	B1-F1	1.3520(42)
B1-F1	1.3624(21)	B1-F2	1.3688(44)
B1-F2	1.3781(25)	B1-N4	1.6007(49)
B1-N5	1.5976(26)	B1-N3	1.5362(43)
B1-N3	1.5232(23)	C33-C39	1.4222(43)

Table S4. Hydrogen bond details of **3a** and **3b**.

3a			**3b**		
Bond	Length (Å)	Angle (°)	Bond	Length (Å)	Angle (°)
N4···H30-C30	2.9195(2)	150.578(1)	F2···H18-C18	2.7173(3)	137.830(2)
O1···H22-C22	2.7610(1)	144.763(1)	F2···H36-C36	2.5109(3)	119.237(2)
O1···H35-C35	2.6689(1)	124.281(1)	F1···H6-C6	2.7735(3)	112.385(2)
O1···H36-C36	2.6793(1)	124.892(1)	-	-	-
F1···H16-C16	2.7533(1)	165.280(1)	-	-	-
F2···H17-C17	2.6891(1)	118.863(1)	-	-	-
F2···H16-C16	2.5186(1)	126.872(1)	-	-	-
F2···H10-C10	2.5109(1)	161.487(1)	-	-	-

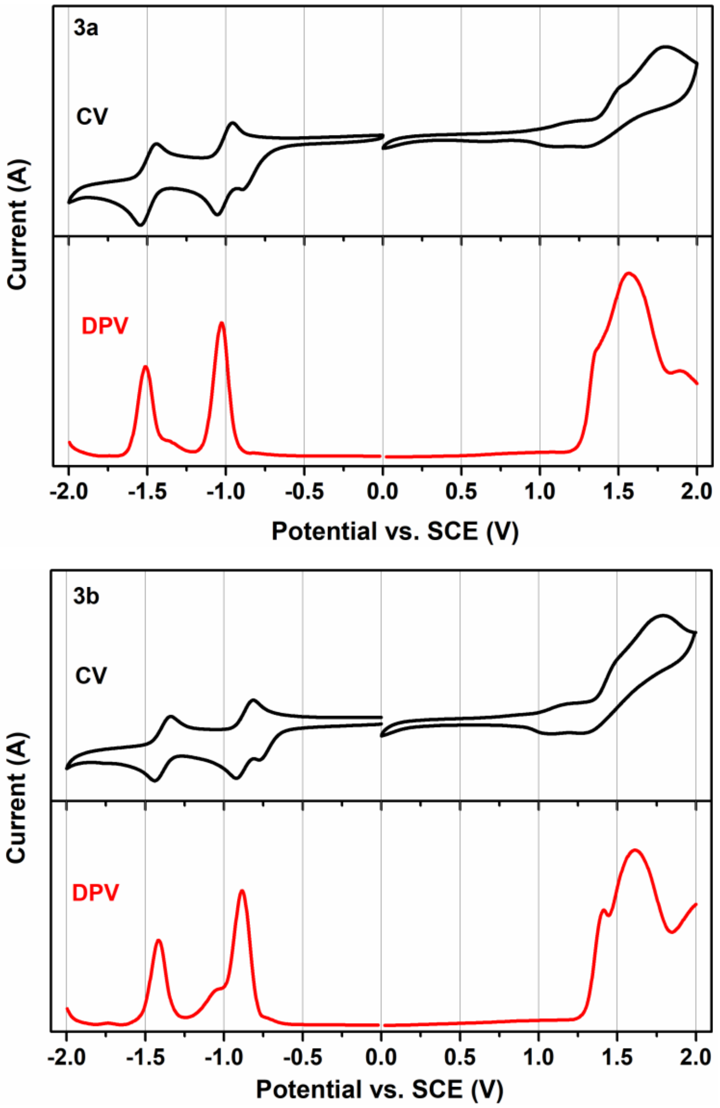
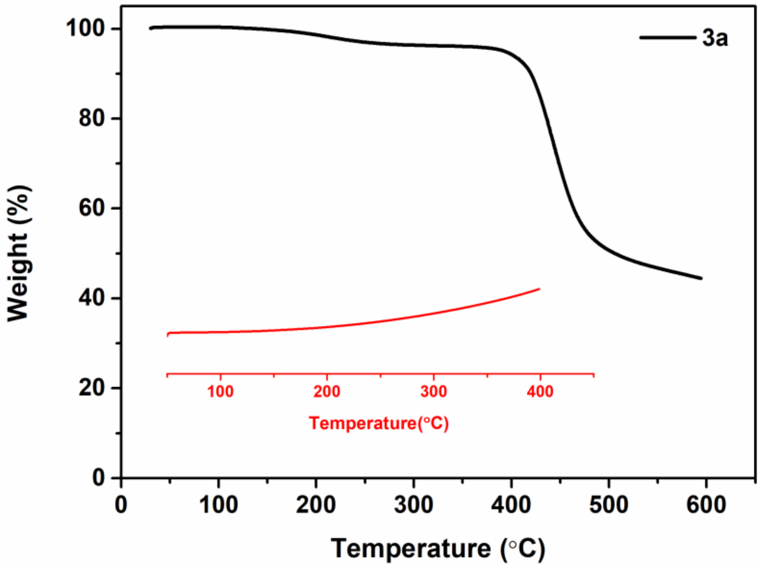


Fig. S5 Cyclic voltammograms (CV, black lines) and differential pulse voltametric curves (DPV, red lines) of **3a** and **3b** (1.0 mM) measured in degassed dichloromethane with 0.1M TBAPF$_6$ at room temperature, using saturated calomel as reference electrode, glassy carbon as working electrode, and platinum wire as auxiliary electrode. Scan rate: 100 mV/s.

Table S5. Electrochemical data acquired and HOMO-LUMO energy band gaps of **3a** and **3b**.[a]

	E_{red}^1 (V)	E_{red}^2 (V)	E_{ox} (V)	E_{red}^{onset} (V)	E_{ox}^{onset} (V)	LUMO (eV)	HOMO (eV)	E_g (eV)
3a	-1.01	-1.50	1.49, 1.79	-1.03	1.36	-3.37	-5.76	2.39
3b	-0.87	-1.39	1.47, 1.78	-0.88	1.41	-3.52	-5.81	2.29

[a] E_{red}^1 = the first reduction potential; E_{red}^2 = the second reduction potential (All reversible reduction potentials reported as $E_{1/2} = ((E_{ap}+E_{cp})/2)$ in V where E_{ap} and E_{cp} are the anodic and cathodic peak potentials, respectively); E_{ox} = the irreversible oxidation peak potentials; E_{red}^{onset} = the onset reduction potential; $E_{LUMO} = -e(E_{red}^{onset} + 4.4)$; E_{ox}^{onset} = the onset oxidation potential; $E_{HOMO} = -e(E_{ox}^{onset} + 4.4)$; $E_g = E_{LUMO} - E_{HOMO}$. The onset potentials are obtained according to DPV traces.



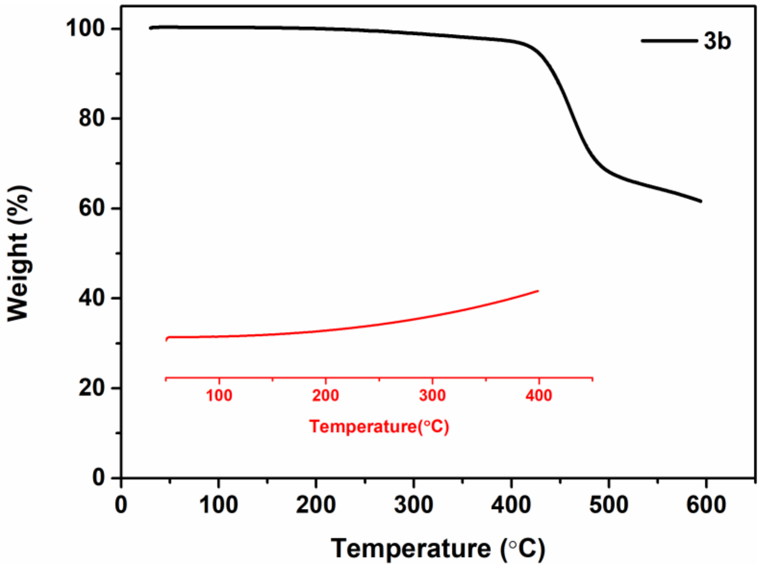
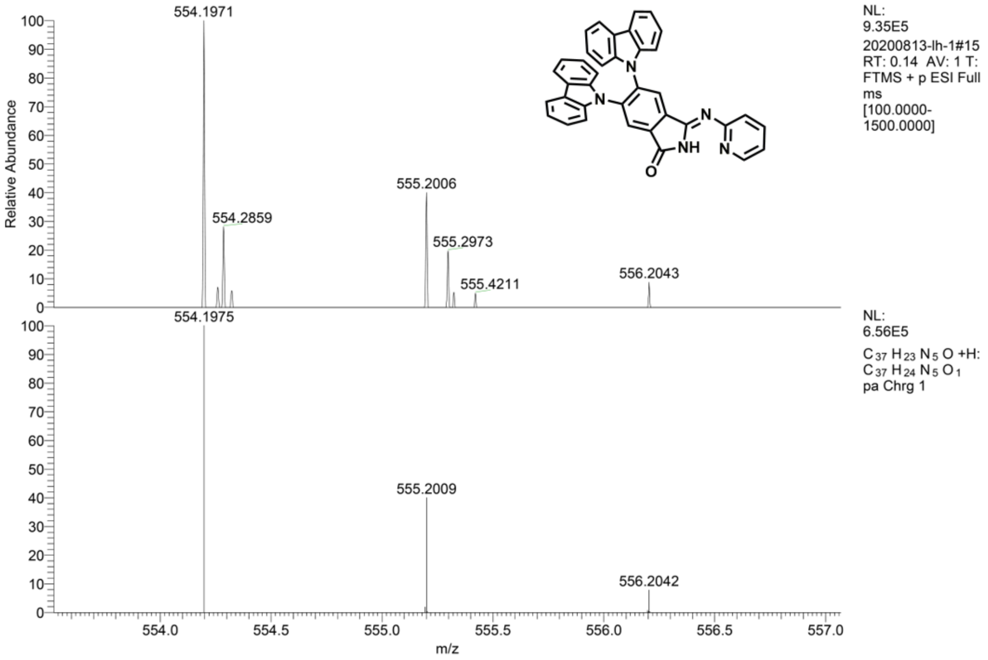
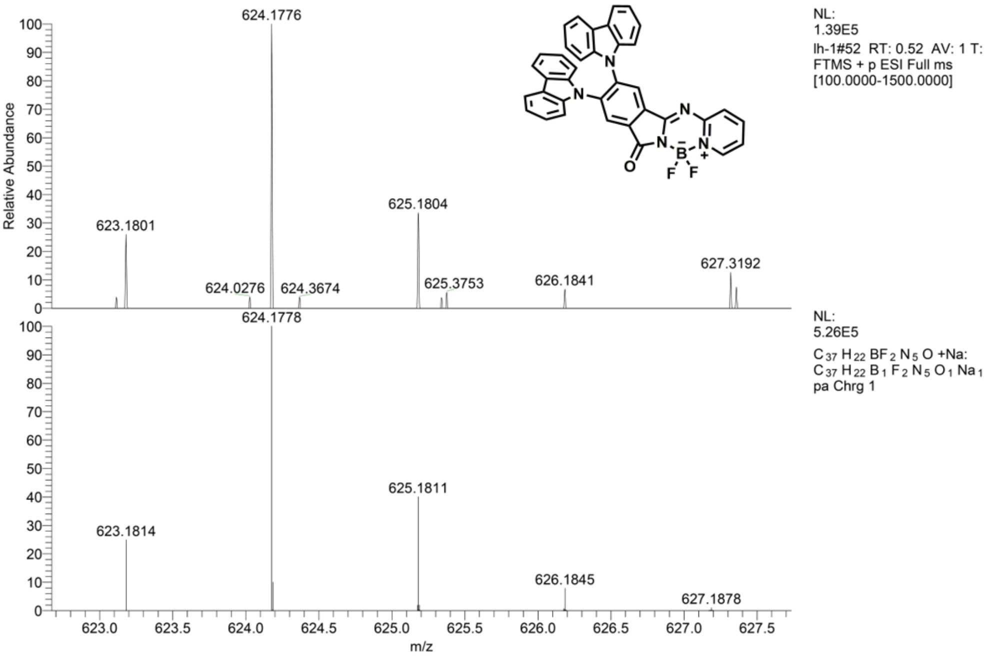
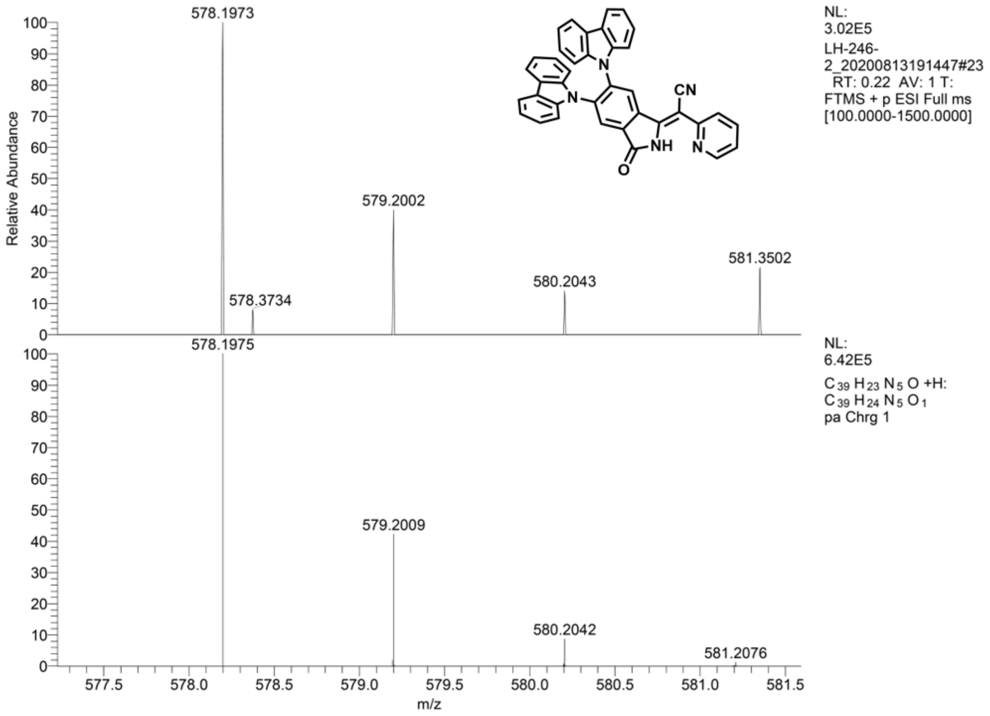


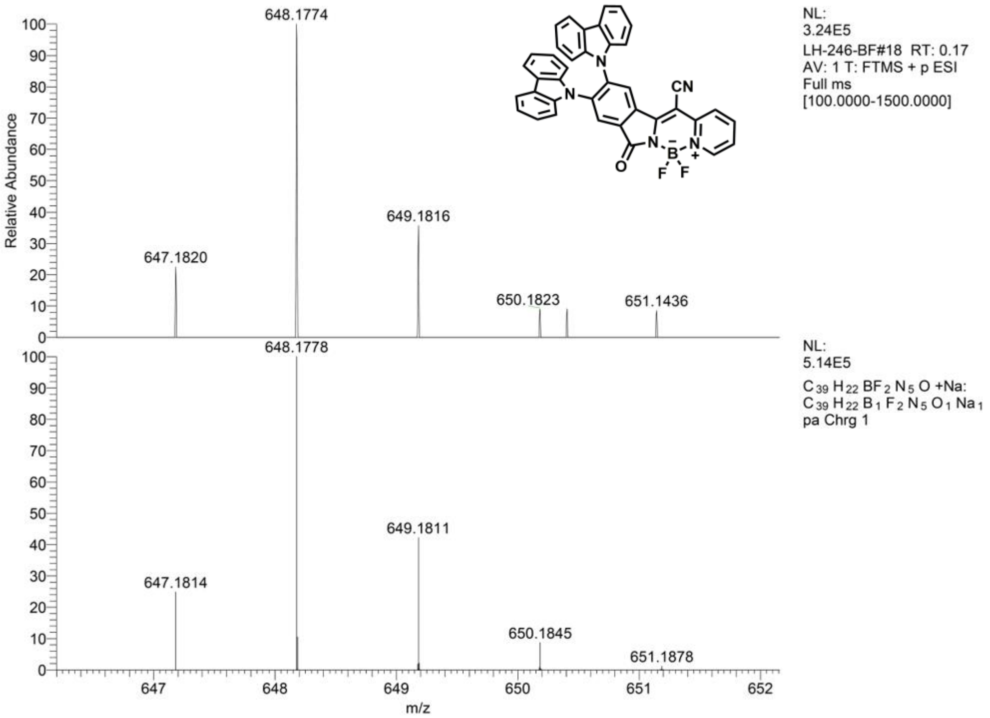
Fig. S6 TGA and DSC (inset) curves of **3a** (Top) and **3b** (Bottom).

III. HRMS

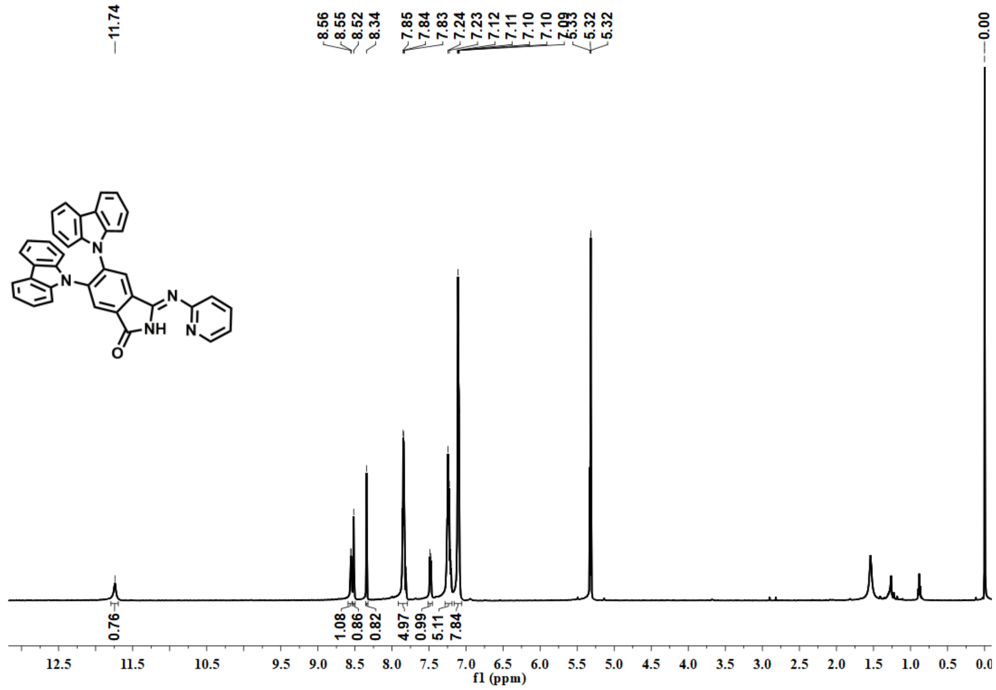

554.1971
554.2859
555.2006
555.2973
555.4211
556.2043
NL:
9.35E5
20200813-lh-1#15
RT: 0.14 AV: 1 T:
FTMS + p ESI Full ms
[100.0000-1500.0000]
554.1975
555.2009
556.2042
NL:
6.56E5
C 37 H 23 N 5 O +H:
C 37 H 24 N 5 O 1
pa Chrg 1
Relative Abundance
m/z
N
N
N
NH
N
O

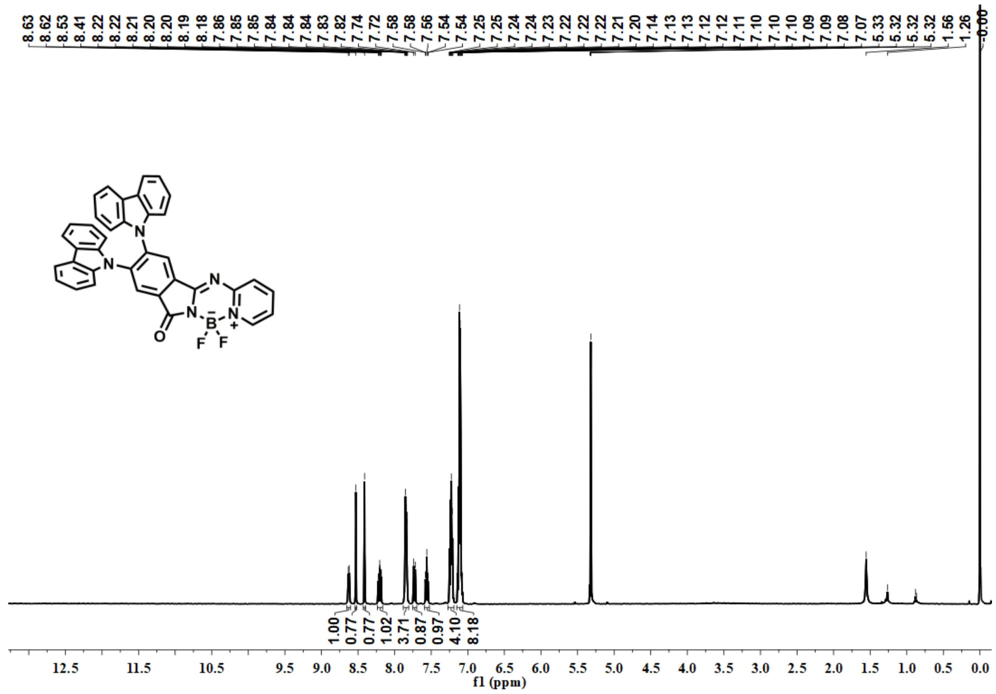

623.1801
624.0276
624.1776
624.3674
625.1804
625.3753
626.1841
627.3192
NL:
1.39E5
lh-1#52 RT: 0.52 AV: 1 T:
FTMS + p ESI Full ms
[100.0000-1500.0000]
623.1814
624.1778
625.1811
626.1845
627.1878
NL:
5.26E5
C 37 H 22 BF 2 N 5 O +Na:
C 37 H 22 B 1 F 2 N 5 O 1 Na 1
pa Chrg 1
Relative Abundance
m/z
N
N
N
N
B
N
F
F
O

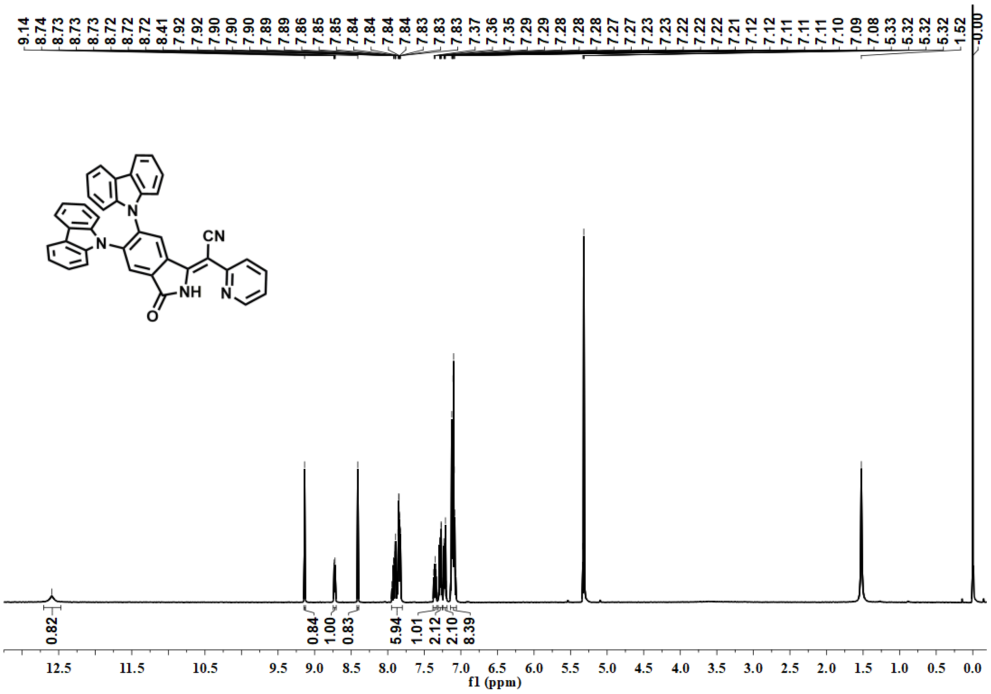

578.1973
NL:
3.02E5
LH-246-
2_20200813191447#23
RT: 0.22 AV: 1 T:
FTMS + p ESI Full ms
[100.0000-1500.0000]
Relative Abundance
579.2002
578.3734
580.2043
581.3502
CN
N
N
NH
N
O
NL:
6.42E5
578.1975
$C_{39}H_{23}N_5O$ +H:
$C_{39}H_{24}N_5O_1$
pa Chrg 1
579.2009
580.2042
581.2076
577.5
578.0
578.5
579.0
579.5
580.0
580.5
581.0
581.5
m/z

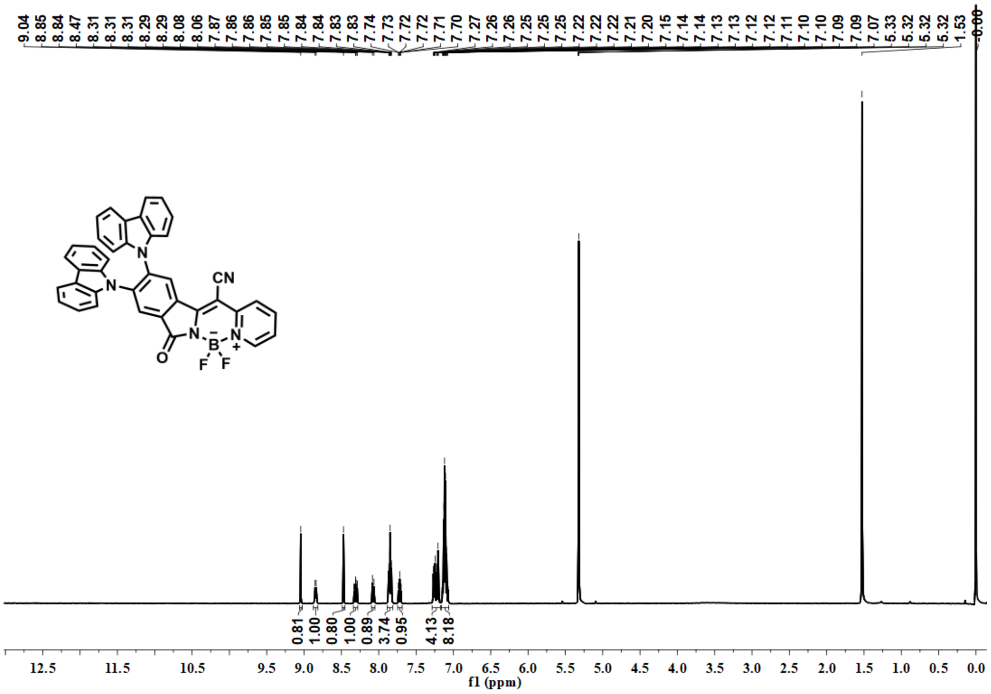

648.1774
NL:
3.24E5
LH-246-BF#18 RT: 0.17
AV: 1 T: FTMS + p ESI
Full ms
[100.0000-1500.0000]
Relative Abundance
647.1820
649.1816
650.1823
651.1436
CN
N
N
N
B
F
F
N
O
NL:
5.14E5
648.1778
$C_{39}H_{22}BF_2N_5O$ +Na:
$C_{39}H_{22}B_1F_2N_5O_1Na_1$
pa Chrg 1
647.1814
649.1811
650.1845
651.1878
647
648
649
650
651
652
m/z

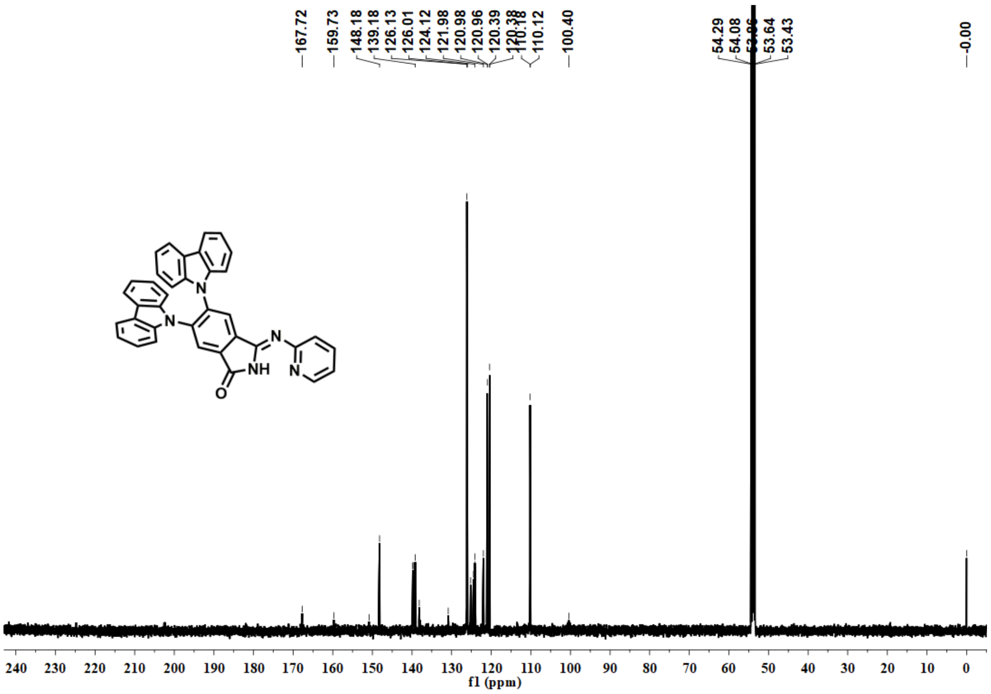
IV. ^{1}H, ^{13}C NMR

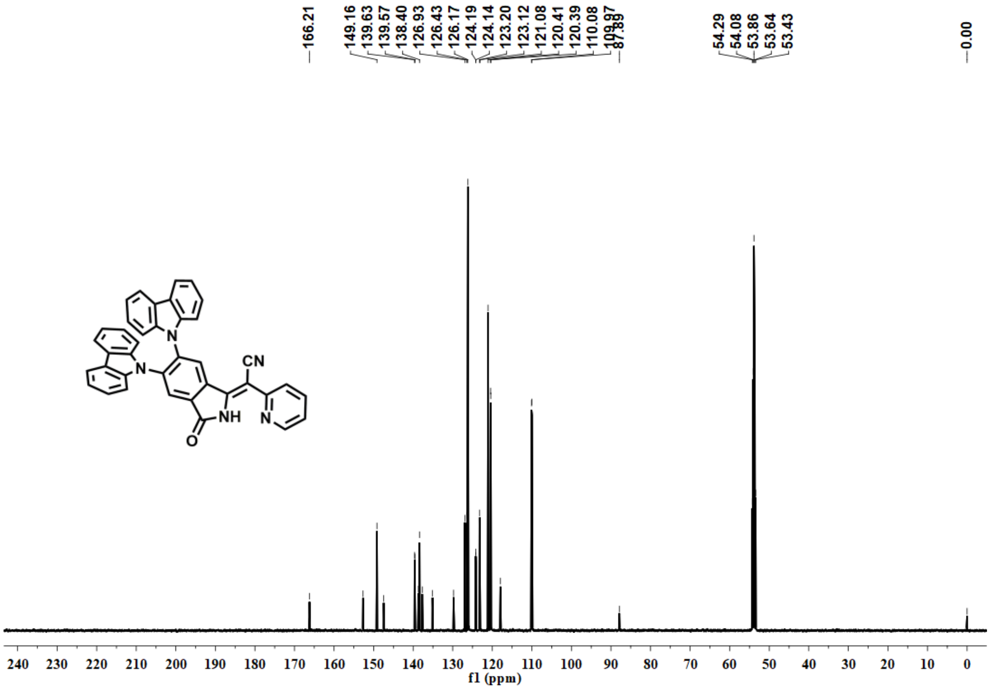

11.74
8.56
8.55
8.52
8.34
7.85
7.84
7.83
7.24
7.23
7.12
7.11
7.10
7.09
5.33
5.32
5.32
0.00
N
N
N
NH
N
O
0.76
1.08
0.86
0.82
4.97
0.99
5.11
7.84
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

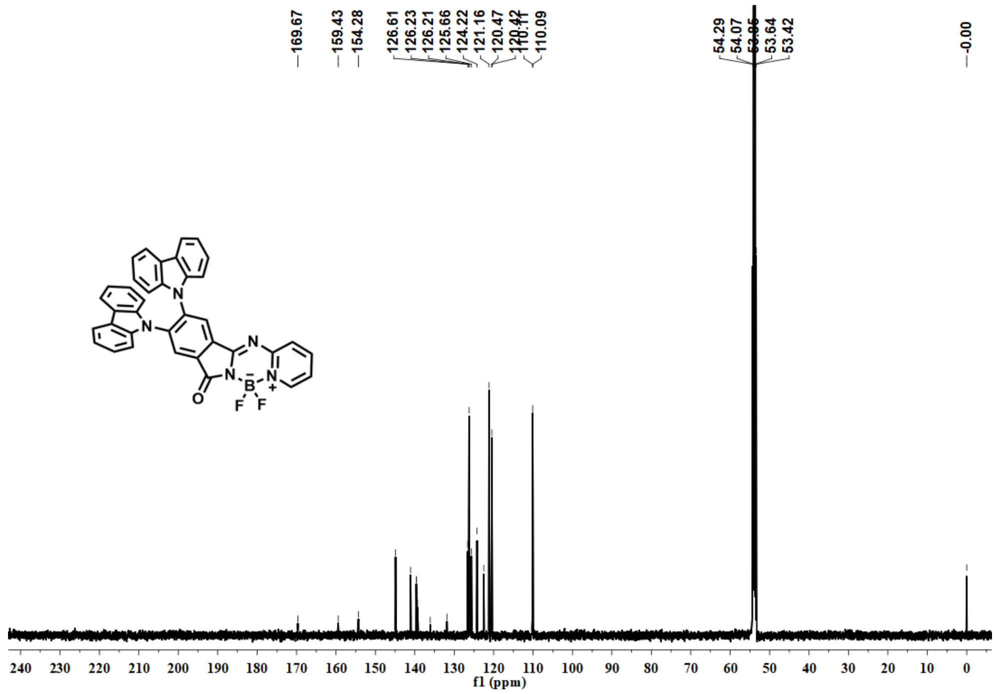

8.63
8.62
8.53
8.41
8.22
8.22
8.21
8.20
8.20
8.19
8.18
7.86
7.85
7.85
7.84
7.84
7.83
7.82
7.74
7.72
7.58
7.58
7.56
7.54
7.54
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.14
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.08
7.07
5.33
5.32
5.32
5.32
1.56
1.26
0.00
N
N
N
N
B
F
F
O
+
−
1.00
0.77
0.77
1.02
3.71
0.87
0.97
4.10
8.18
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.14
8.74
8.73
8.73
8.73
8.72
8.72
8.41
7.92
7.92
7.90
7.90
7.89
7.89
7.86
7.85
7.85
7.84
7.84
7.84
7.84
7.83
7.83
7.83
7.37
7.36
7.35
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.23
7.23
7.22
7.22
7.22
7.21
7.12
7.12
7.11
7.11
7.11
7.10
7.09
7.08
5.33
5.32
5.32
5.32
1.52
0.00
N
N
CN
NH
N
O
0.82
0.84
1.00
0.83
5.94
1.01
2.12
2.10
8.39
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


9.04
8.85
8.84
8.47
8.31
8.31
8.29
8.29
8.08
8.06
7.87
7.86
7.86
7.85
7.85
7.84
7.84
7.83
7.83
7.74
7.73
7.72
7.72
7.71
7.70
7.27
7.26
7.26
7.25
7.25
7.25
7.22
7.22
7.22
7.21
7.20
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.07
5.33
5.32
5.32
5.32
1.53
0.00
N
N
CN
N
B
N
O
F
F
0.81
1.00
0.80
1.00
0.89
3.74
0.95
4.13
8.18
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.72
159.73
148.18
139.18
126.13
126.01
124.12
121.98
120.98
120.96
120.39
120.38
110.18
110.12
100.40
54.29
54.08
53.86
53.64
53.43
-0.00
N
N
N
NH
N
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


166.21
149.16
139.63
139.57
138.40
126.93
126.43
126.17
124.19
124.14
123.20
123.12
121.08
120.41
120.39
110.08
109.97
87.89
54.29
54.08
53.86
53.64
53.43
-0.00
N
N
CN
NH
N
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


169.67
159.43
154.28
126.61
126.23
126.21
125.66
124.22
121.16
120.47
120.42
110.11
110.09
54.29
54.07
53.85
53.64
53.42
-0.00
N
N
N
O
N
B
N
F
F
+
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)