Supplementary Information

for

Tuning solvatochromism and F⁻ sensing via acceptor stoichiometry-mediated charge-transfer modulation in triarylboron-indolocarbazole systems

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General information

Under the condition of nitrogen, the Suzuki coupling reactions are carried out with Schlenk technique. All reagents used shall be used as received. Thin layer chromatography silica gel plate was used to monitor the reaction. Fast column chromatography using 200-300 mesh silica gel purchased by Qingdaohaiyang Chemical Company, Shandong, China.

Reagents

Tetrakis(triphenylphosphine)palladium were prepared from literatures[1], acetic acid, 1,2-cyclohexanedione, bromobutane, 4-Bromophenylhydrazine hydrochloride, *N*-bromosuccinimide (NBS), 2-aminophenol, bis(pinacolato)diboron, Pd(dppf)Cl_2, sodium carbonate, *p*-iodobenzene, bis(trimethylphenyl) boron fluoride, tetrahydrofuran (THF)， *N*, *N*-dimethylformamide (DMF), tetrabutylammonium salt (F^-, Cl^-, Br^-, I^-, AcO^-, BF_4^-, PF_6^-, HSO_4^-, NO_3^-, ClO_4^- and $H_2PO_4^-$) were purchased from commercial suppliers (the Energy Chemical in shanghai of China) , which used without further purification. The organic solvents used in the experiments were all analytically, and the water was secondary deionized water.

Apparatus

NMR spectra were acquired on JNM-ECZ400s MHz nuclear magnetic resonance (NMR) spectrometer at room temperature using $CDCl_3$ and DMSO-d_6 as solvent. High resolution TOF-MS data were recorded at the Agilent 6545 Q-TOF LC/MS. The UV-Vis absorption spectra and the photoluminescence (PL) spectra were obtained by UV-2700 double beam UV-visible spectrophotometer, and a Varian Cary Eclipse fluorescence spectrometer or a CCD spectrophotometer (Simtrum, M/200-1000C), respectively.

Relative Quantum Yield Calculation

Calculate the relative quantum yield using the following equation with quinine sulfate as the reference standard (in 0.1 M H_2SO_4):

$$Q_S = Q_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^2}{\eta_R^2}$$

where “Q” represents the quantum yield, “I” represents the integral area of the sensor emission spectrum, “A” represents the absorbance measured at the excitation wavelength, “η” represents the refractive index of the solvent used, and the subscripts “S” and “R” represent the reference object and the test object, respectively.

Limit of Detection (LOD)

The limit of detection for F^- is determined according to the following relationship:

$$LOD = \frac{3\sigma c}{k} \qquad \text{Eq 1}$$

σ:

First, the fluorescence intensities of the blank sensor solutions ICZ-1B and ICZ-2B were tested by PL spectra for 20 times (**Fig. S6**). Then, the average values (μ) of these fluorescence intensities are calculated. After that, the standard deviations were calculated according to the related formula from a textbook.[2] Here, the calculations of standard deviations are conducted on the Origin software.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \mu)}{n}} \qquad \text{Eq 2}$$

k:

Fluorescence intensities of the samples of sensor solutions adding with different multiplicities of F^- solutions were obtained. Then, calibration curves between fluorescence intensities and F^- contents are constructed (**Fig. 2k** and **2l** in the main-text). Finally, the values of *k* are obtained from the linear fitting results of the calibration curves, which are the slopes of the fitting curves. The fitting operations are conducted on the Origin software

c: Molar concentration of sensors solutions.

Photophysical properties

Dissolve **ICZ-1B** and **ICZ-2B** in various solvents to obtain a reserve solution with a concentration of 2.0×10^{-5} M, including, DMF, acetone (Ace), dichloromethane (DCM), THF, ethyl acetate (EA), chloroform (CHL), 1,4-dioxane (Diox), diethyl ether (Et_2O), toluene (Tol), petroleum ether (PE), tested using UV-Vis absorption and PL spectra.

Anion sensing studies

The stock THF solutions of probes **ICZ-1B** and **ICZ-2B** solution at 2.0×10^{-3} M were diluted 100 times to obtain a final concentration for 2.0×10^{-5} M, and the tetrabutylammonium salts solutions of each anion were prepared as 2.0×10^{-3} M in THF. The anion solutions were added to the probe solution, the spectral data were recorded by UV-Vis and PL spectra, the changes in the spectra data were analyzed to explore the probe's selectivity to anions.

^{19}F NMR titration experiment

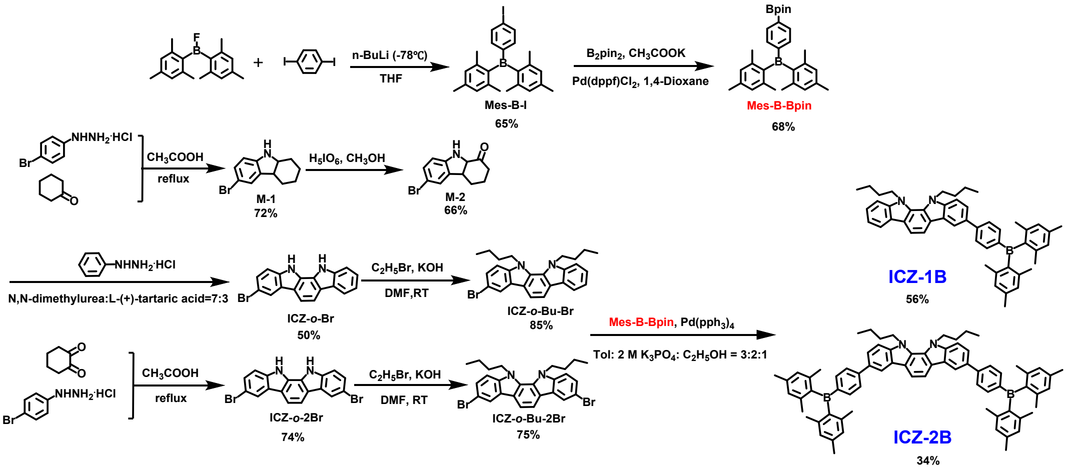
3.5 mg (**ICZ-1B**) and 5.1 mg (**ICZ-2B**) of the sensors were dissolved in 500 μL of $CDCl_3$ to prepare blank sensor solutions with a concentration of 1.0×10^{-2} M. Meanwhile, an F^- solution with a concentration of 2.0×10^{-1} M was prepared in $CDCl_3$. Subsequently, ^{19}F NMR spectra of the ion-sensor mixtures were acquired by varying the equivalent amounts of ions.

Theoretical Calculations

The ground state geometry (S_0) is optimized and obtained from density functional theory (DFT) calculations under the PBE1PBE/6-31G level. The time-dependent density functional theory (TD-DFT) calculations under the PBE1PBE/6-311G* level. All the calculations are done using Gaussian 16 software,[3] and the SMD solvation model (solvent = tetrahydrofuran) is used. For calculation convenient, the n-Bu groups have been replaced with methyl groups.

Synthesis details for the ICZ-1B and ICZ-2B, and other compounds.

The final compounds are named **ICZ-1B** and **ICZ-2B**.



Scheme S1. Synthesis route for **ICZ-1B** and **ICZ-2B**.

M-1： In a 100 mL Schlenk tube, 4-Bromophenylhydrazine hydrochloride (2.74 g, 1.2 mmol) was added in batches within 30 min to a solution of cyclohexanone (1.00 g, 1.0 mmol) in CH_3COOH (15 mL). Heated under reflux at 120°C for 8 h, the reaction was complete. The reaction mixture was cooled to room temperature, filtered with ice water to obtain a yellow crude product, eluted with PE: EA (V: V = 4:1) as the eluent, and purified by column chromatography to obtain a white solid. Yield: 72%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 7.48 (d, J = 1.9 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.08 (dd, J = 8.5, 2.0 Hz, 1H), 2.69 (t, J = 5.8 Hz, 2H), 2.58 (s, 2H), 1.96 – 1.61 (m, 4H).

M-2: Periodic acid (0.90 g, 1.0 mmol) and 10 mL of methanol were added to a 100 mL round-bottom flask and stirred at room temperature for 30 min. The reaction solution was cooled to -10°C, and then **M-1** (1.00g, 1.0 mmol) methanol (15 mL) solution was slowly added dropwise to the reaction mixture. After the dropwise addition was completed, the reaction solution was naturally raised to room temperature and the reaction took 2 h. Finally, pure water was added and filtered to obtain a pale-yellow crude product, with PE: EA (V: V = 5:1) as the eluent, and purified by column chromatography to obtain a white solid. Yield: 66%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.90 (s, 1H), 7.40 (d, J = 10.6 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 2.93 (t, J = 5.9 Hz, 2H), 2.61 – 2.52 (m, 2H), 2.18 – 2.09 (m, 2H).

ICZ-*o*-Br: Under the protection of nitrogen atmosphere, 1,3-dimethyl urea: L-tartaric acid (m: m =7:3) was first added to 100 mL of Schlenk tube, and heated to 80°C to melt, then 1,2-cyclohexanedione (0.81 g, 1.5 mmol) and **M-2** (1.00 g, 1.0 mmol) were added after 1 h, and the reaction was carried out for 4 h to obtain a brick-red solution. Cooled to room temperature, pure water was added to filter to obtain a light red crude product, and PE: EA (V: V = 5:1) was used as the eluent, and the white solid was purified by column chromatography. Yield: 50%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 11.12 (s, 1H), 8.39 (s, 1H), 8.16 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 3.0 Hz, 2H), 7.68 (t, J = 8.3 Hz, 2H), 7.50 (d, J = 8.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H).

ICZ-*o*-Bu-Br: To a 100 mL round-bottom flask were added **ICZ-*o*-Br** (1.00 g, 1.0 mmol), C_2H_5Br (1.20 g, 3.0 mmol), KOH (0.50 g, 3.0 mmol), and 15 mL DMF to give a pale-yellow solution. The reaction was completed at room temperature for 7 h. Finally, white solid was obtained by column chromatography with PE: DCM (V: V = 3:1) as eluent. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 1.6 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 8.9 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 4.56 (dq, J = 7.9, 4.2 Hz, 4H), 1.65 (dt, J = 15.9, 7.8 Hz, 4H), 1.17 – 1.00 (m, 4H), 0.83 – 0.72 (m, 6H).

ICZ-*o*-2Br: Under the protection of nitrogen atmosphere, to a 100 mL Schlenk tube were added 1，2-cyclohexanedione (1.00 g, 1.0 mmol) and *p*-bromophenylhydrazine hydrochloride (5.21 g, 2.5 mmol), and 20 mL CH_3COOH was added, followed by heating at reflux for 12 h at 120°C. After cooling to room temperature, pure water was added and filtered to obtain yellow crude product, which was purified by column chromatography with PE: EA (V: V = 2:1) as eluent to obtain white solid. Yield: 74%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (s, 2H), 8.40 (s, 2H), 7.97 (s, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 9.8 Hz, 2H).

ICZ-*o*-Bu-2Br: To a 100 mL round-bottom flask were added, **ICZ-*o*-2Br** (1.00 g, 1.0 mmol)，C_2H_5Br (0.99 g, 3.0 mmol)，KOH (0.41 g, 3.0 mmol), and 15 mL DMF to give a pale yellow solution. The reaction was completed at room temperature for 7 h. Finally, white solid was obtained by column chromatography with PE: DCM (V: V = 6:1) as eluent. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 2.0 Hz, 2H), 7.87 (s, 2H), 7.54 (dd, J = 8.6, 1.9 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 4.59 – 4.46 (m, 4H), 1.62 (t, J = 7.6 Hz, 4H), 1.05 (h, J = 7.4 Hz, 4H), 0.76 (t, J = 7.3 Hz, 6H).

Mes-B-I: Under the protection of nitrogen atmosphere, *p*-iodobenzene (5.90 g, 1.2 mmol) and 40 mL of THF were added to a 100 mL three-necked flask, stirred at room temperature for 10 min. Then, the three-necked flask was placed in an insulating bottle containing liquid nitrogen, maintaining a temperature of -78°C, and *n*-BuLi (14 mL, 1.2 mmol) was slowly added while maintaining a certain temperature. After the addition was complete, the reaction was continued for 1 h. After transferring to room temperature, bis(trimethylphenyl) boron fluoride (4.00 g, 1.0 mmol) was added to the three-necked flask, and the reaction was continued until complete. Finally, the organic phase was obtained by filtering with ice water, eluted with PE: DCM (V: V = 10:1) as the eluent, and purified by column chromatography to obtain a white solid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.81 (s, 4H), 2.30 (s, 6H), 1.98 (s, 12H).

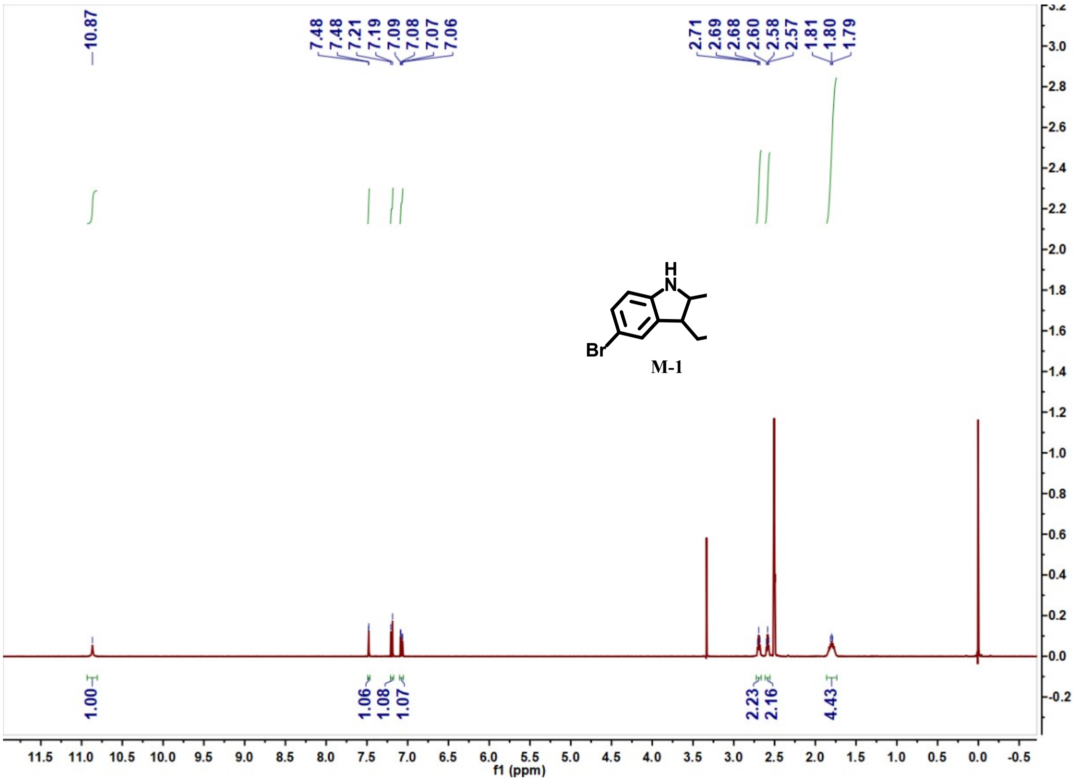
Mes-B-Bpin: Under the protection of nitrogen atmosphere, **Mes-B-I** (2.00 g, 1.0 mmol), B_2pin_2 (3.37 g, 3.0 mmol), CH_3COOK (1.30 g, 3.0 mmol), Pd(dppf) Cl_2 (0.32 g, 0.1 mmol) were added to a 100 mL Schlenk tube, and 20 mL of 1,4-dioxane was added, and the reaction was continued at 80°C for 12 h until the reaction was complete. Finally, it was cooled to room temperature, and PE: DCM (V: V = 6:1) was used as the eluent, and the white solid was purified by column chromatography. Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 6.83 (s, 4H), 2.32 (s, 6H), 1.99 (s, 12H), 1.36 (s, 12H).

Synthesis of ICZ-1B and ICZ-2B

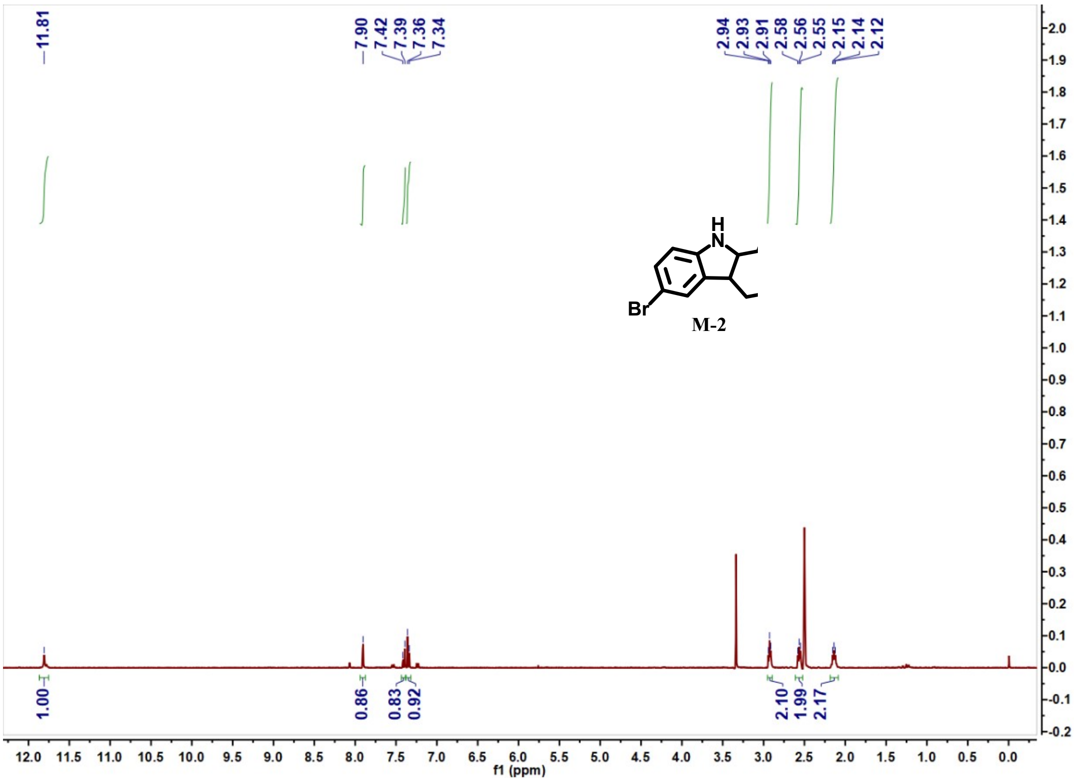
Under the protection of nitrogen atmosphere, 50 mL of Schlenk tube was added with **ICZ-*o*-Bu-Br** (2.00 g, 1.0 mmol)/ **ICZ-*o*-Bu-2Br** (2.00 g, 1.0 mmol), **Mes-B-Bpin** (2.30 g, 1.2 mmol/3.58 g, 2.2 mmol), $Pd(pph_3)_4$ (0.52 g, 0.1 mmol/0.44 g, 0.1 mmol) and Tol: 2 M K_3PO_4: ethanol (V: V: V = 3:2:1) mixed solution, heated and refluxed for 5 h, eluted with PE: DCM (V: V = 6:1) as eluent, and the product was obtained after column chromatography purification.

ICZ-1B is a pale-yellow solid. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.12 (d, J = 7.6 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.75 (dd, J = 15.1, 8.3 Hz, 3H), 7.64 – 7.61 (m, 3H), 7.59 – 7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 6.85 (s, 4H), 4.59 (q, J = 8.8 Hz, 4H), 2.32 (s, 6H), 2.07 (s, 12H), 1.69 – 1.65 (m, 4H), 1.11 (dt, J = 14.6, 7.2 Hz, 4H), 0.78 (td, J = 7.4, 4.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.48, 143.30, 143.09, 141.98, 140.96, 138.60, 137.50, 137.36, 132.99, 130.40, 130.02, 128.47, 128.36, 128.17, 128.06, 126.76, 126.07, 124.68, 124.46, 120.11, 118.51, 113.30, 111.63, 48.33, 31.24, 23.66, 21.43, 20.15, 13.83. TOF-MS (ESI): m/z calculated for $C_{50}H_{53}BN_2$: 692.4364[M]$^+$, observed : 693.4364[M+H]$^+$.

ICZ-2B is a pale-yellow solid. Yield: 34%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H), 8.03 (s, 2H), 7.77 (dd, J = 17.6, 8.2 Hz, 6H), 7.63 (dd, J = 12.4, 8.2 Hz, 6H), 6.87 (s, 8H), 4.62 (t, J = 7.4 Hz, 4H), 2.34 (s, 12H), 2.09 (s, 1.76, 24H), 1.73 – 1.70 (m, 4H), 1.1 5 – 1.10 (m, 4H), 0.80 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.41, 143.09, 141.95, 140.95, 138.59, 137.40, 133.05, 130.40, 128.25, 126.73, 124.82, 118.67, 113.29, 111.69, 48.38, 31.26, 23.64, 21.35, 20.13, 13.81. TOF-MS (ESI): m/z calculated for: 1016.6393[M]$^+$， observed: 1017.6393[M+H]$^+$.


M-1

10.87
7.48
7.48
7.21
7.19
7.09
7.08
7.07
7.06
2.71
2.69
2.68
2.60
2.58
2.57
1.81
1.80
1.79
1.00
1.06
1.08
1.07
2.23
2.16
4.43
H
N
Br
11.5 11.0 10.5 10.0 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 -0.5
f1 (ppm)
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2


M-2

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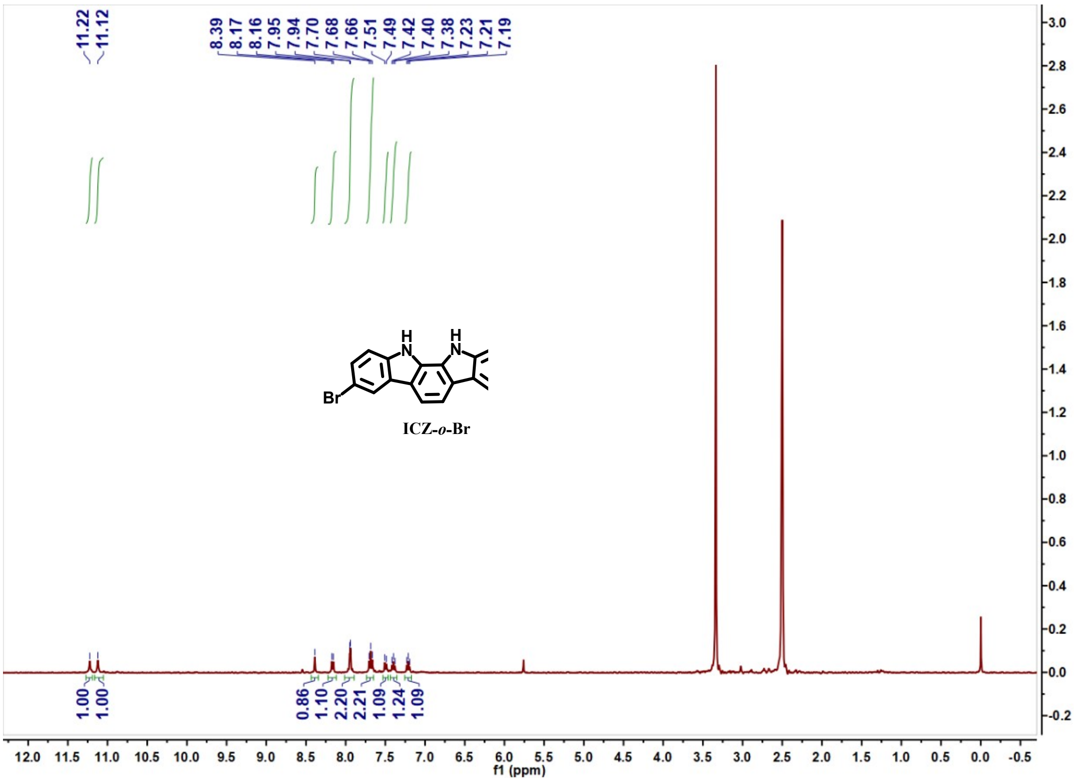
7.90
7.42
7.39
7.36
7.34
2.94
2.93
2.91
2.58
2.56
2.55
2.15
2.14
2.12
1.00
0.86
0.83
0.92
2.10
1.99
2.17
H
N
Br
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2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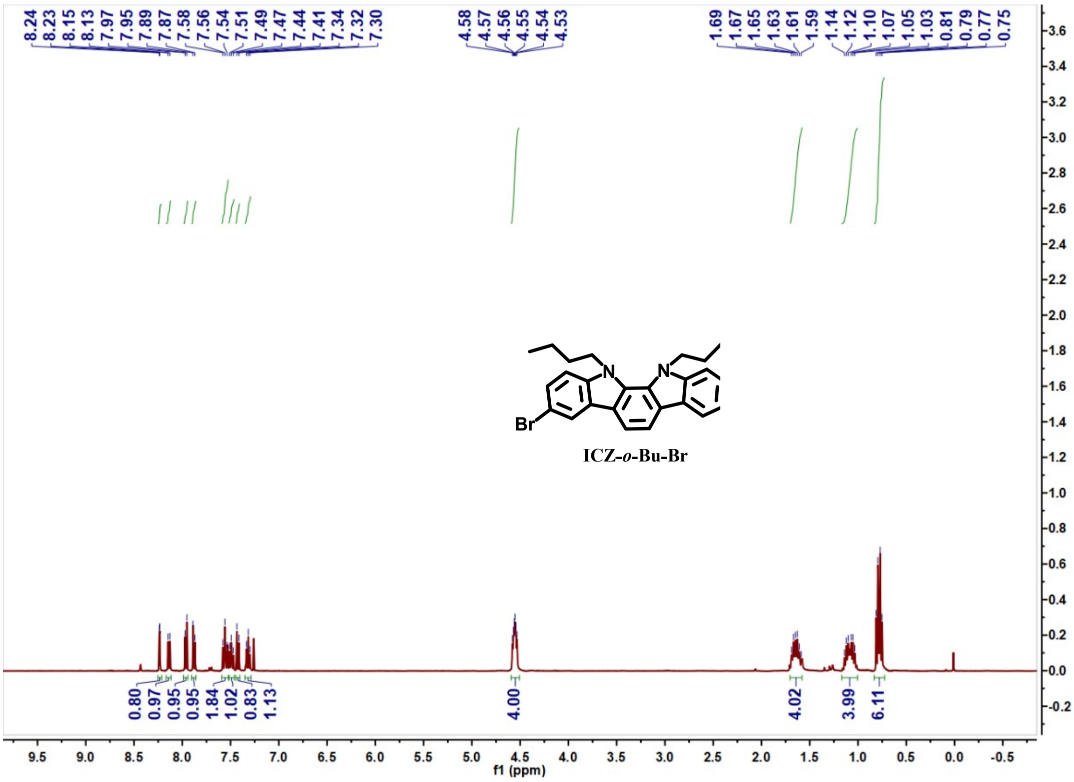
7.42
7.40
7.38
7.23
7.21
7.19
Br
H
N
ICZ-*o*-Br
1.00
1.00
0.86
1.10
2.20
2.21
1.09
1.24
1.09
f1 (ppm)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7.47
7.44
7.41
7.34
7.32
7.30
4.58
4.57
4.56
4.55
4.54
4.53
1.69
1.67
1.65
1.63
1.61
1.59
1.14
1.12
1.10
1.07
1.05
1.03
0.81
0.79
0.77
0.75
Br
N
ICZ-*o*-Bu-Br
0.80
0.97
0.95
0.95
1.84
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1.13
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4.02
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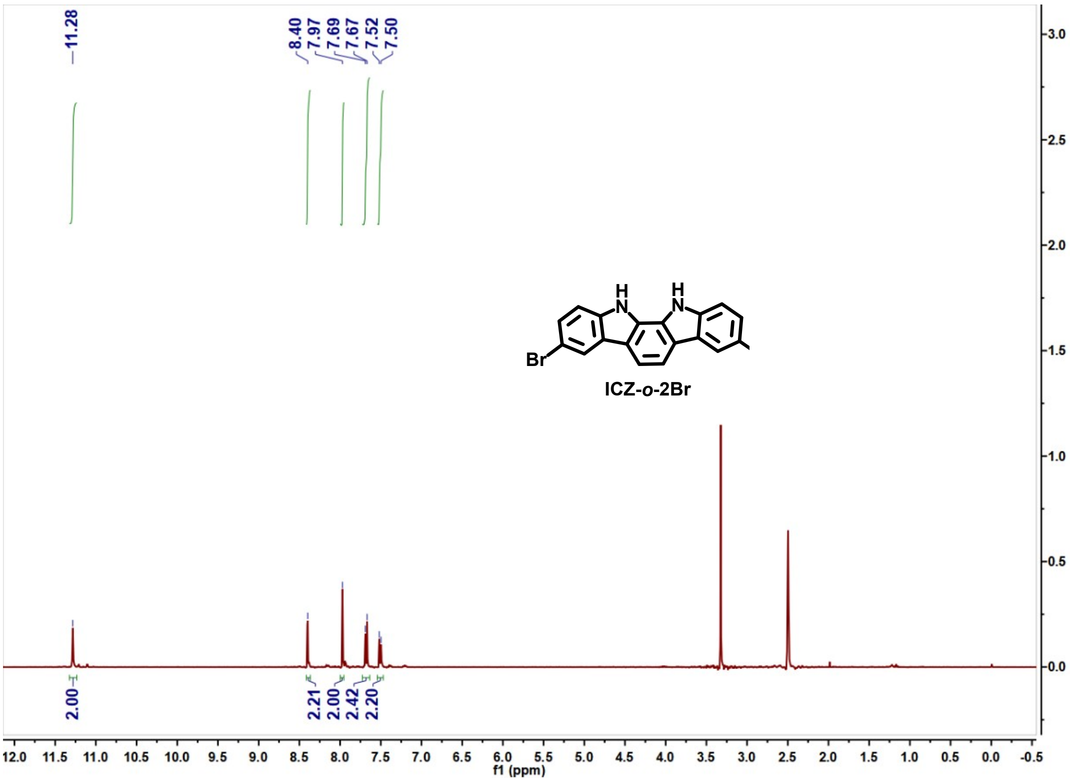
6.11
f1 (ppm)



11.28
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7.52
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2.00
2.21
2.00
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2.20
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Br
H
N
12.0 11.5 11.0 10.5 10.0 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 -0.5
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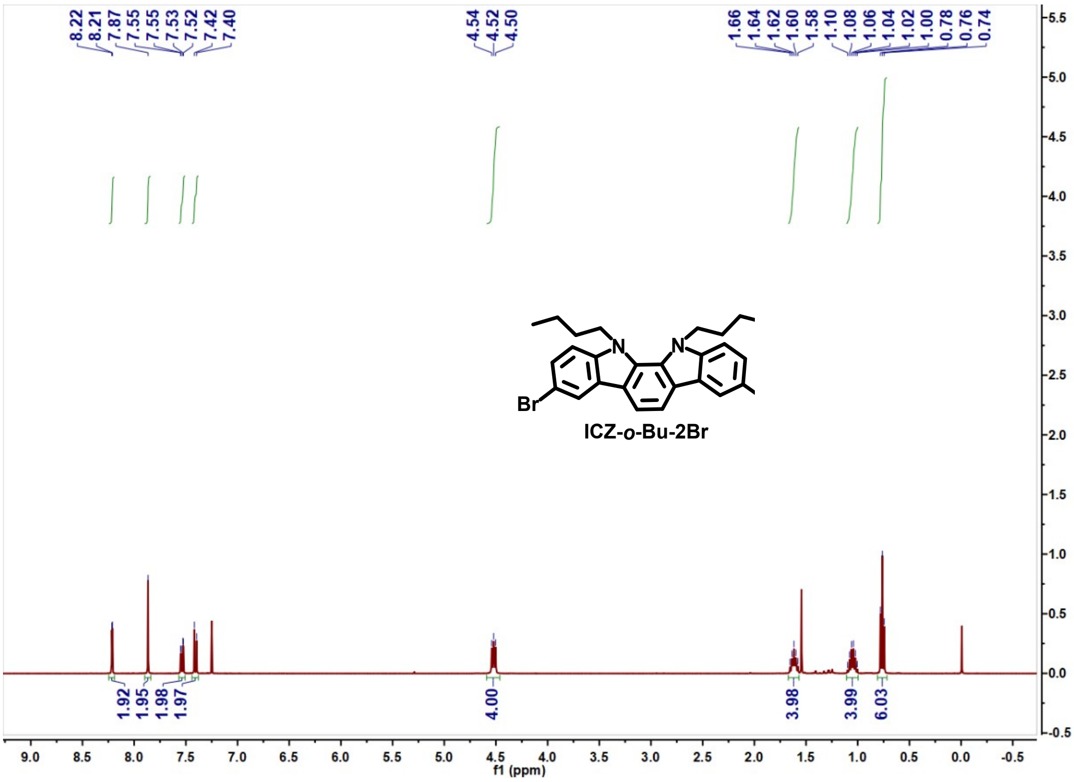

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7.55
7.55
7.53
7.52
7.42
7.40
4.54
4.52
4.50
1.66
1.64
1.62
1.60
1.58
1.10
1.08
1.06
1.04
1.02
1.00
0.78
0.76
0.74
1.92
1.95
1.98
1.97
4.00
3.98
3.99
6.03
ICZ-*o*-Bu-2Br
Br
N
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
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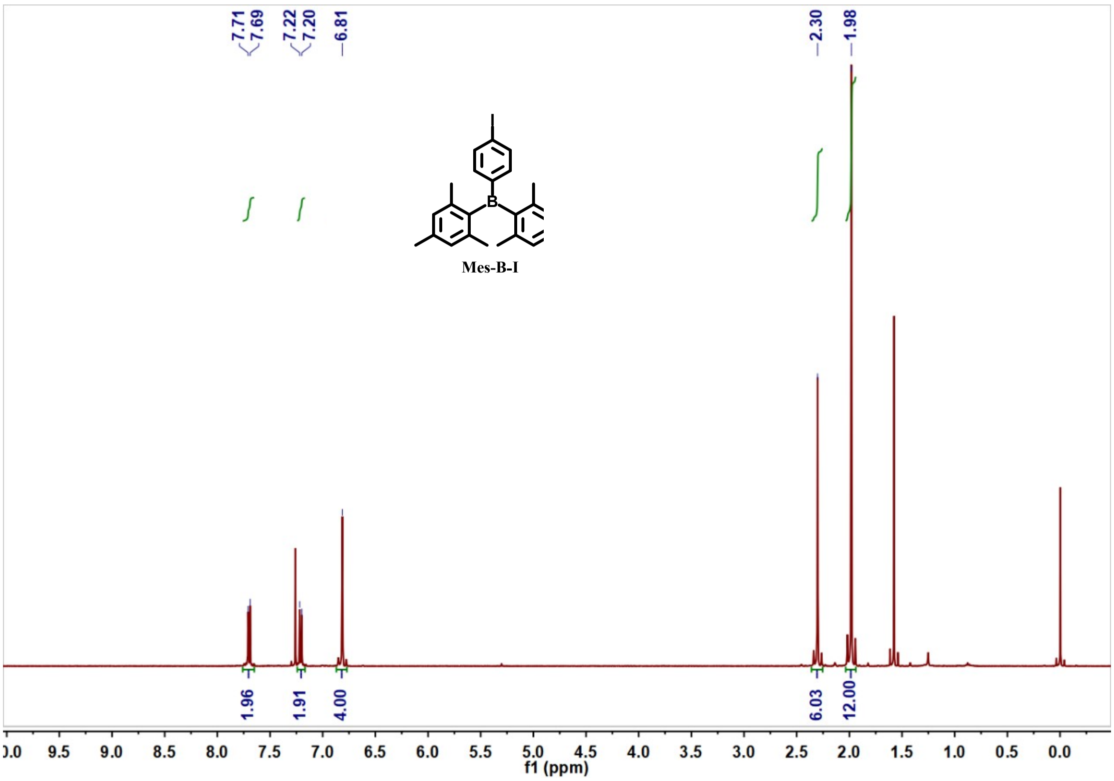
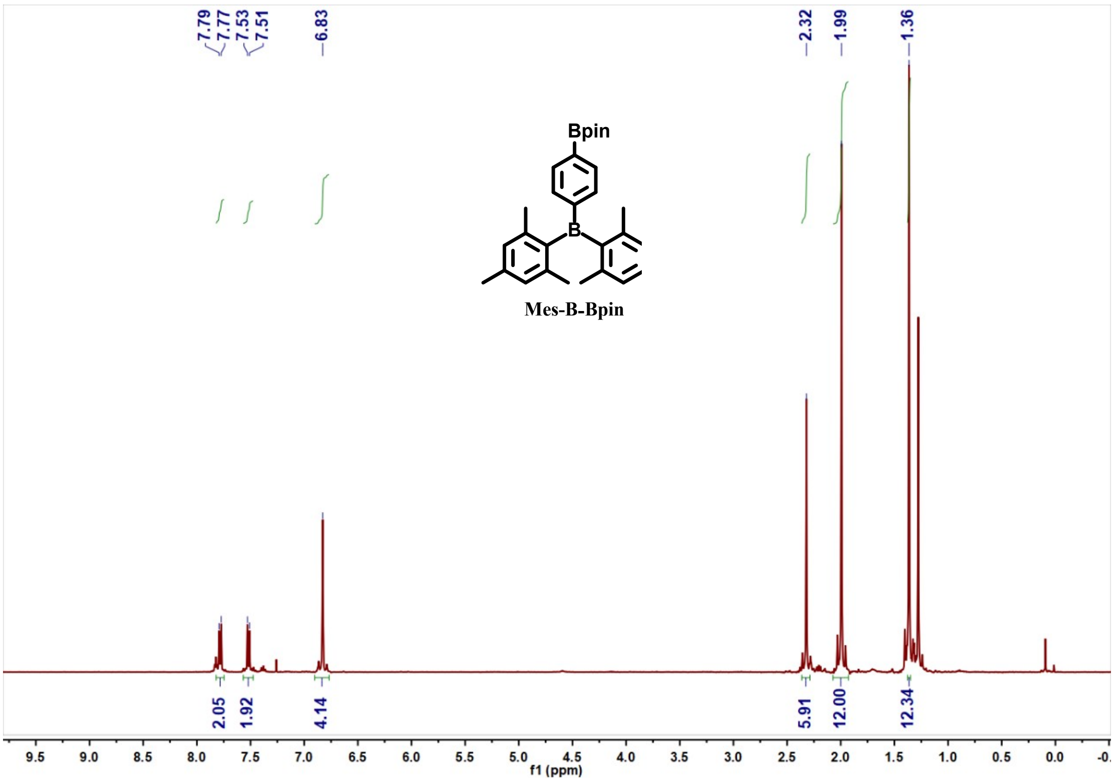


Mes-B-I



Mes-B-Bpin

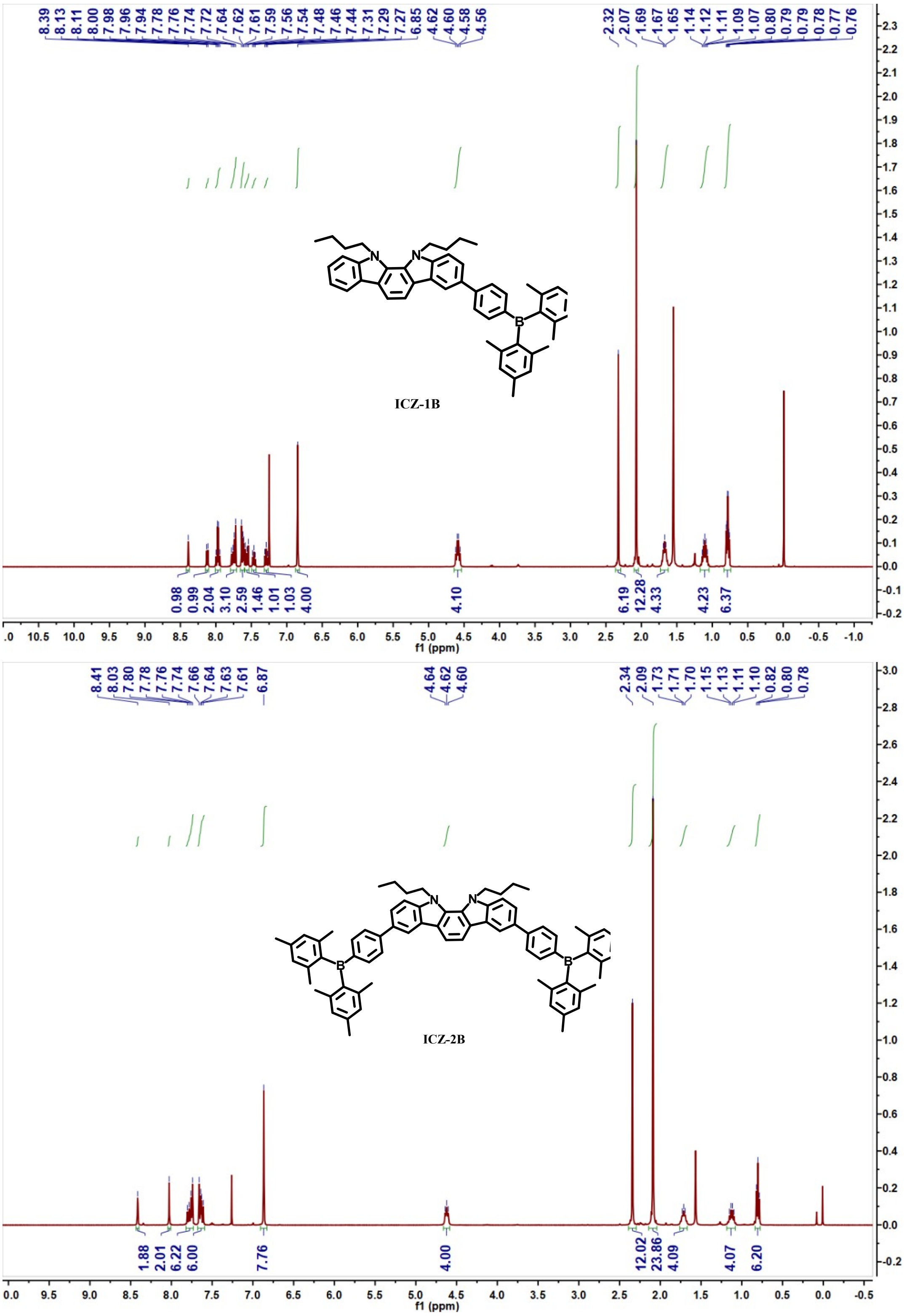


Fig. S1 ^{1}H NMR spectra of the concerned compounds, and the target compound **ICZ-1B** and **ICZ-2B**

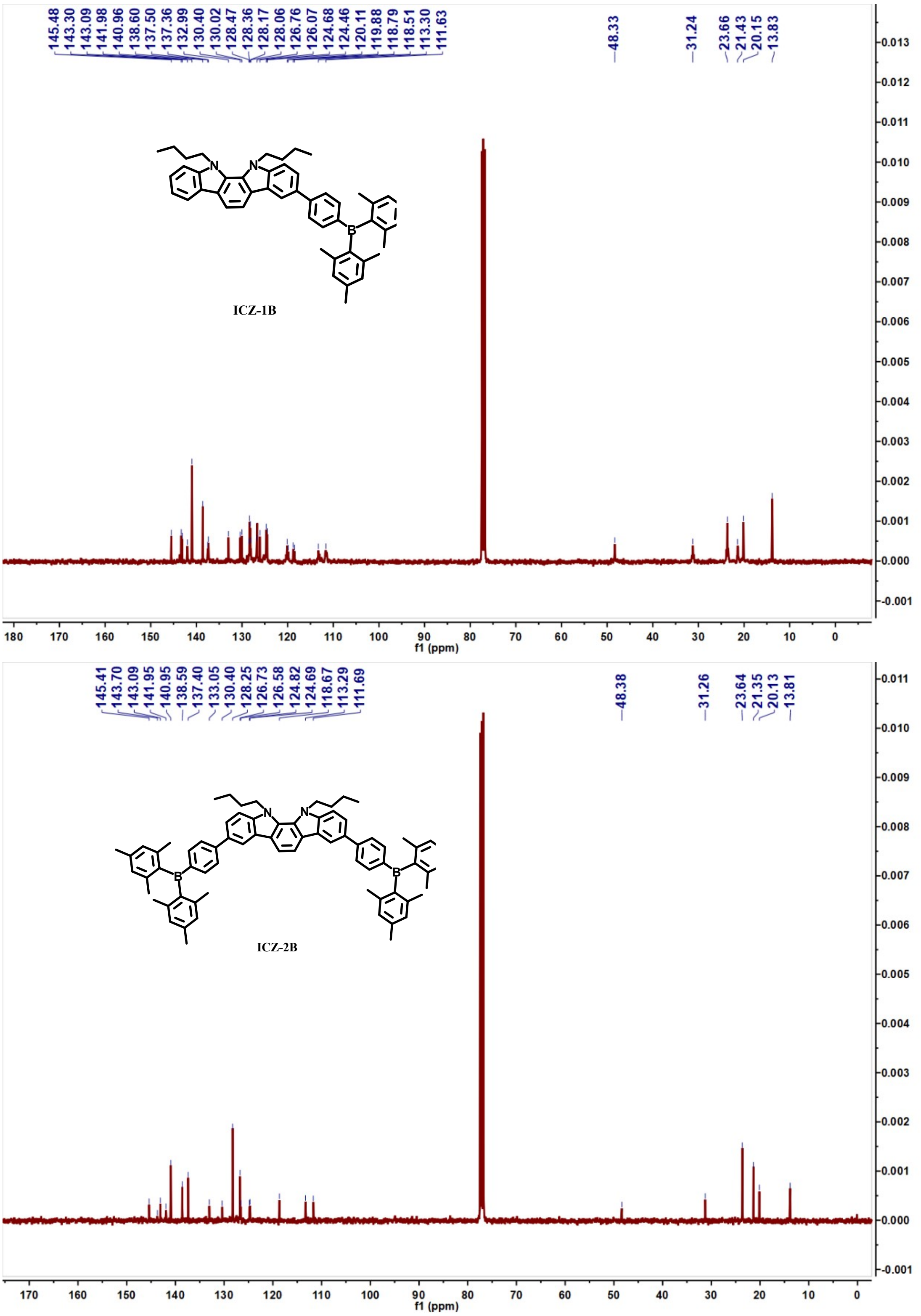


Fig. S2 ^{13}C NMR spectra of **ICZ-1B** and **ICZ-2B**

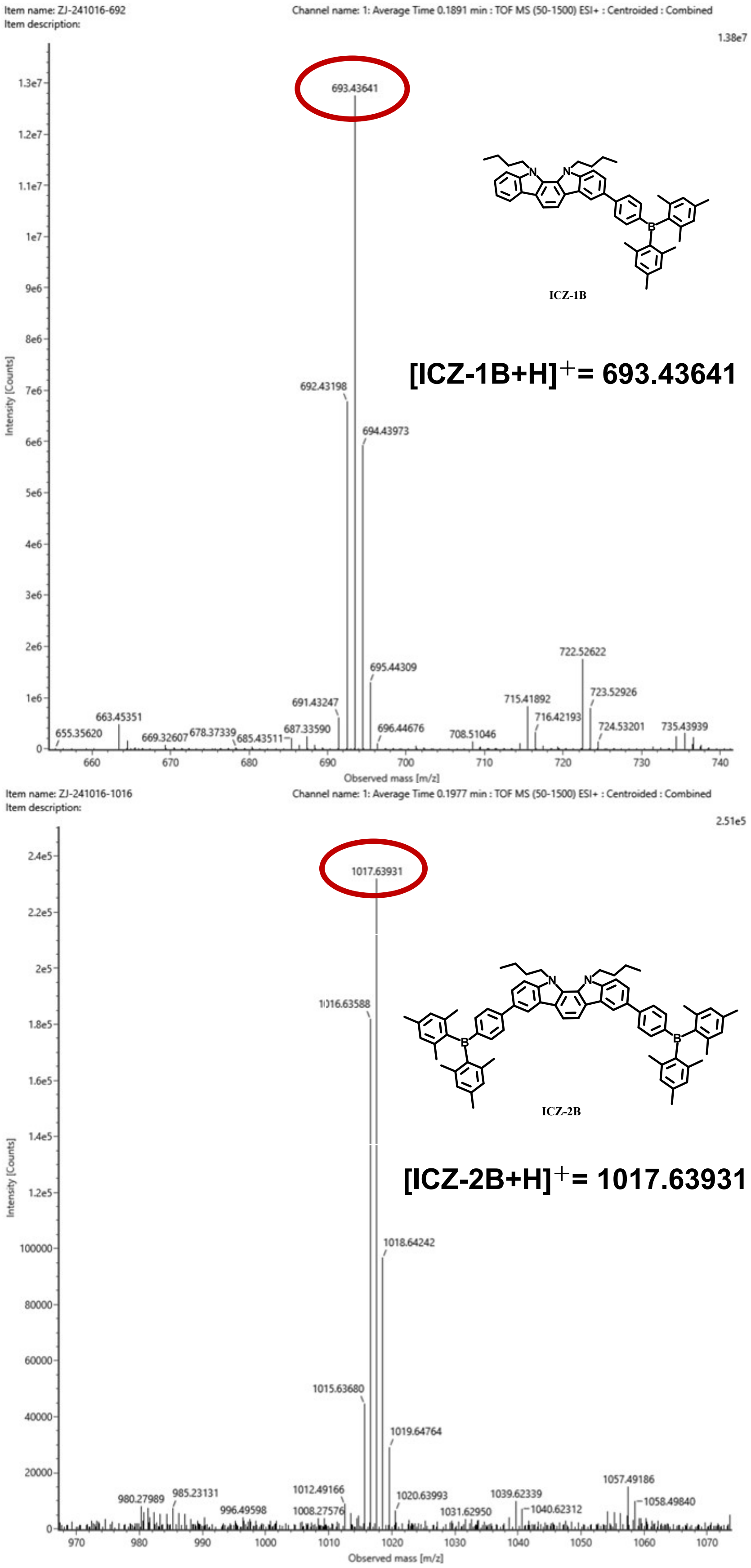


Fig. S3 High resolution mass spectra of **ICZ-1B** and **ICZ-2B**

Table S1. Photophysical properties of ICZ-1B and ICZ-2B in different solvents.

		ICZ-1B						**ICZ-2B**					
Solvent	**E_T(30) (kcal/mol)**	**Ɛ**	**λ_{abs} (nm)**	**λ_{em} (nm)**	**Stokes shift (nm)**	***I***	***Φ*(%)**	**Ɛ**	**λ_{abs} (nm)**	**λ_{em} (nm)**	**Stokes shift. (nm)**	***I***	***Φ*(%)**
DMF	43.2	38500	340	524	184	158	2.5	56800	357	535	178	128	2.3
Ace	42.2	33600	339	508	169	105	5.3	64150	356	510	154	141	3.2
DCM	40.7	37550	340	492	152	307	13.0	66000	356	491	135	438	9.9
CHL	39.1	40750	340	468	128	421	13.9	62050	356	466	110	578	11.6
EA	38.1	33350	338	480	142	368	14.4	71000	356	474	118	540	9.4
THF	37.4	35650	338	480	142	368	14.7	86000	358	477	119	539	11.3
Diox	36.0	34400	339	449	110	428	14.9	69400	356	451	95	678	10.8
Et_2O	34.5	20150	337	448	111	501	26.5	92600	354	445	91	815	9.0
Tol	32.5	40600	340	433	93	496	14.7	71750	358	432	74	706	11.3
PE	——	56550	338	410	72	773	12.1	67950	353	411	58	923	10.5

E_T(30): Dimroth and Reichardt solvent polarity parameter. *I*: fluorescence intensity. Ɛ: molar absorption coefficient. *Φ*: fluorescence quantum yield. Quantum yields are determined by using quinine sulfate. (*Φ*=0.54 in 0.1 M H_2SO_4) as a standard.

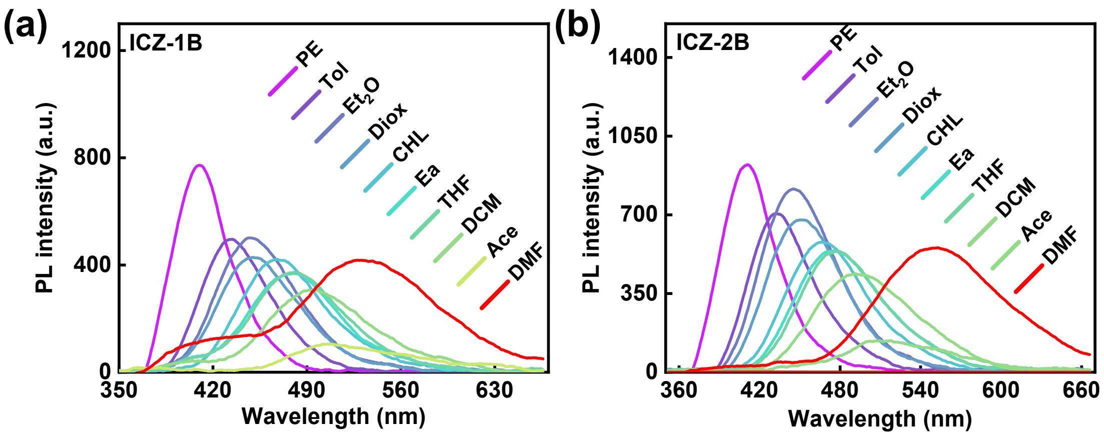


Fig. S4 Unnormalized fluorescence emission spectra of ICZ-1B (a) and ICZ-2B(b) in different solvents.

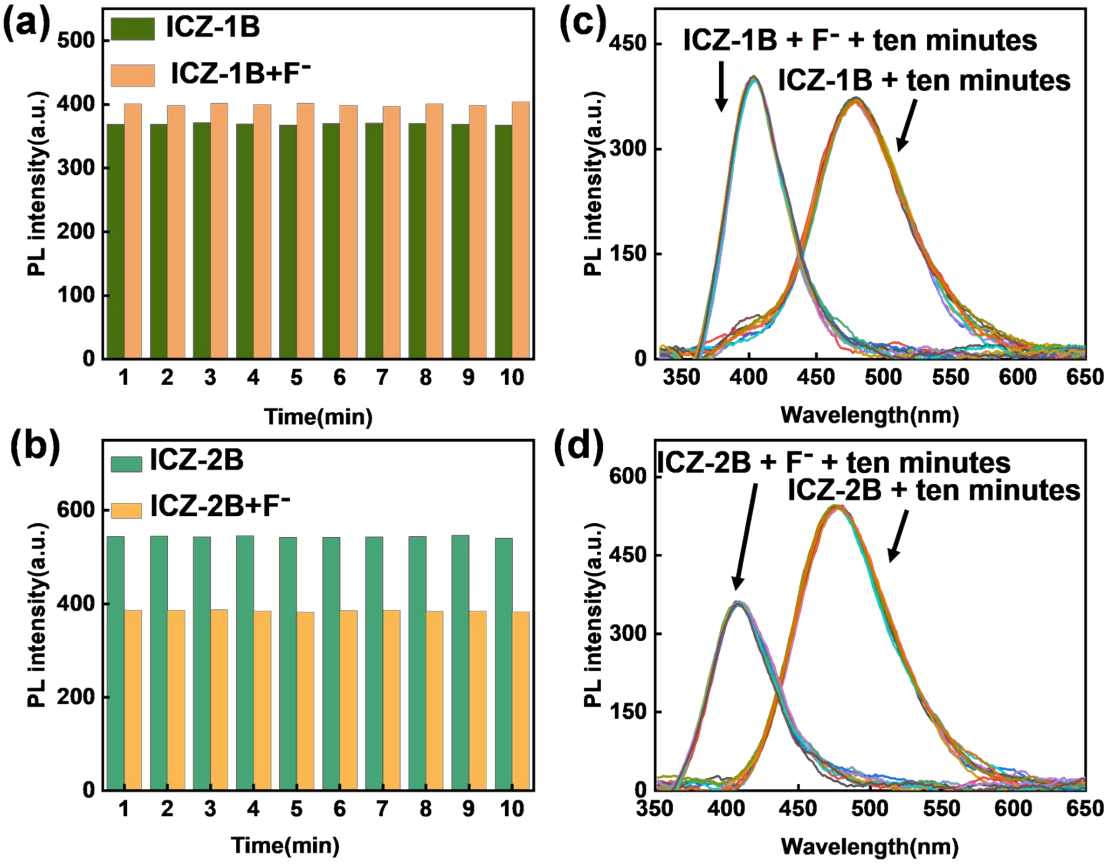


Fig. S5 **ICZ-1B** and **ICZ-2B** (a) and (b) response time results; (c) and (d) fluorescence spectra of fluorine-containing sensor solutions at different times.

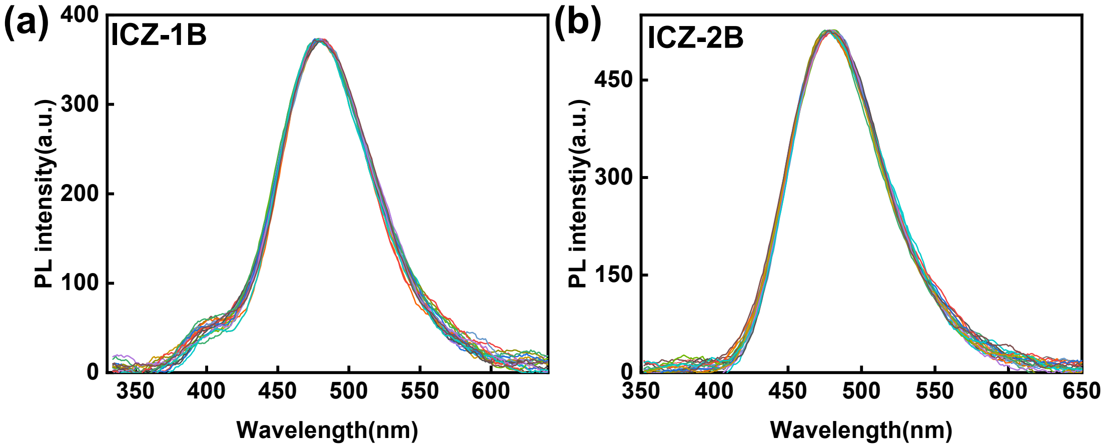


Fig. S6 Fluorescence spectra of the blank sensor solutions measured with 20 times, and the related standard deviation for **ICZ-1B** was 0.49, for **ICZ-2B** was 0.58.

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