Supplementary Information

for

Boosting anion sensing of O/S-bridged biscarbazole-triarylboron sensors via charge-transfer inhibition and heavy-atom effect

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Detailed Information for Experimental Section

Reagents and Materials

1,4-Diiodobenzene, n-Butyllithium (2.5 M solution in n-hexane), Dimesitylfl uoroborane, 4,6-Dibromodibenzofuran, 4,6-DibroMo-Dibenzothiophene, 2-Nitrophe nylboronic acid, Tri-tert-butylphosphine tetrafluoroborate ($t(Bu)_3PH{\cdot}BF_4$), triphen ylphosphine (PPh_3) anhydrous sodium sulfate, palladium acetate ($Pd(OAC)_2$), X-Phos, Sodium carbonate (Na_2CO_3), Potassium tert-butoxide (t-BuOK), tetrahydro furan (THF), petroleum ether (PE), dichloromethane (DCM), ethyl acetate (EA), 1,2-Dichlorobenzene (O-DCB) and secondary deionized water. Tetrabutylammoni um salts (F^-, ACO^-, $H_2PO_4^-$, HCO_3^-, HSO_4^-, ClO_4^-, PF_6^-, BF_4^-, NO_3^-, Cl^-, Br^- and I^-) are purchased from commercial suppliers (the Energy Chemical in shan ghai of China) and used without further purification.

Physical Characterization

The ^1H NMR, ^{13}C NMR, and ^{19}F NMR of compounds in $CDCl_3$ or DMSO-d_6 relative to tetramethylsilane (TMS) are measured at room temperature using a JNMECZ400s MHz spectrometer. High-resolution time-of-flight mass spectrometry data are recorded on an Agilent 6545 Q-TOF LC/MS instrument. UV-visible and fluorescent spectra are obtained using a UV-2700 double-beam ultraviolet-visible spectrometer and a Varian Cary Eclipse fluorescence spectrometer or a CCD spectrophotometer (Simtrum, M/200-1000C). The excitation wavelength for solution photoluminescence measurement was set at 365 nm.

Solvatochromic experiment

O-2B and **S-2B** were separately dissolved in THF to prepare sensors solutions with a concentration of 1×10^{-4} M. Subsequently, these solutions were diluted with other solvents (Hexane=Hex, Toluene=Tol, THF, DCM, Acetone=Ace, DMF, MeCN) in a volume ratio of 9 : 1 to obtain final solutions with a concentration of 1.0×10^{-5} M. Their UV-vis absorption spectra and PL spectra were measured at room temperature,

and the relevant results are shown in **Fig. S14**.

Anion sensing studies

O-2B and **S-2B** were dissolved in THF to produce a 1.5×10^{-4} M solution, and are diluted 60 times to obtain the final test concentration of 0.9×10^{-5} M. The tetrabutylammonium salt solution of each anion was prepared in THF to 0.9×10^{-3} M. The anion solution was added into the probe solution, and the spectral data was recorded by UV-vis and emission spectra to investigate the selectivity of sensors to anions (F^-, ACO^-, $H_2PO_4^-$, HCO_3^-, HSO_4^-, ClO_4^-, PF_6^-, BF_4^-, NO^-, Cl^-, $Br^-$and I^-).

Response time experiment

Added 2.4 equivalents of F^- to sensors **O-2B** and **S-2B** with a concentration of 0.9×10^{-5} M respectively, and measured the PL spectra every one min.

Limit of detection (LOD)

The LOD of the F^- were calculated according to the following formula:

$$LOD = 3\partial C/k$$

∂: Standard deviation, which was obtained by measuring the fluorescence intensity of blank solution **O-2B** and **S-2B** over 20 times and calculating according to the standard deviation formula, the related spectra and data are shown in **Fig. S16**. *k*: Added different times of F^- solution into the same probe solution in sequence, and recorded the related fluorescence intensity of the sensor-F^- solutions, thereby the fluorescence intensities corresponding to different multiples of F^- were plotted, and then the slope is obtained by linear fitting; C: Molar concentration of sensors solution.

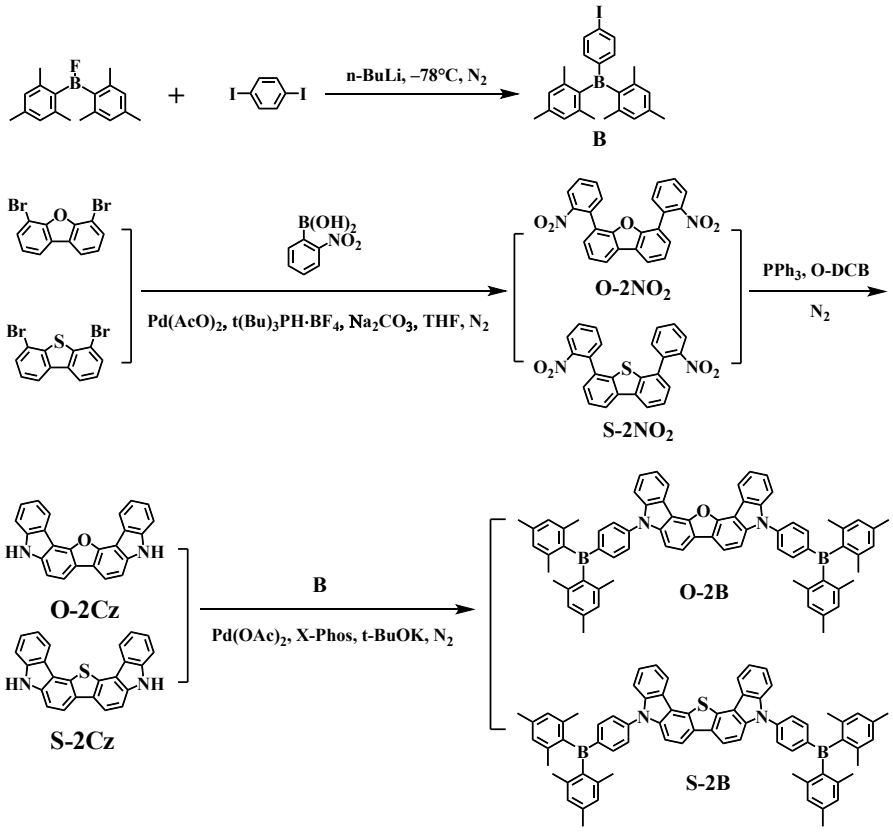
^{19}F NMR titration experiment

5.0 mg sensors **O-2B** and **S-2B** were dissolved in 500 μL $CDCl_3$ to obtained a blank sensors solution with a concentration of 1.0×10^{-2} M. The F^- solution with a concentration of 1.0×10^{-2} was also prepared in $CDCl_3$. Then the ^{19}F NMR spectra of those ion-sensor mixtures with varying the equivalent of F^- were acquired.

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,[1] and the SMD solvation model (solvent = tetrahydrofuran) is used.

Synthesis details for B, O-2NO_2, S-2NO_2, O-2Cz, S-2Cz, O-2B and S-2B



Scheme S1. Synthetic routes of sensors **O-2B** and **S-2B**.

B:

Under a N_2 protection, 4.43 g of 1,4-diiodobenzene was dissolved in 45 mL of ultra-dry THF, and the solution was cooled to −78 °C. Then, 6.7 mL of n-butyllithium solution was slowly added dropwise. After reacting for 1 hour, 3.0 g of dimesitylfluoroborane was added to the reaction mixture. After 10 minutes, the reaction mixture was warmed to room temperature and stirred for another hour before the reaction was quenched by adding water. The mixture was extracted three times with DCM and water. The organic phase was dried over anhydrous sodium sulfate, mixed with silica gel powder, and then concentrated under reduced pressure. Finally, the crude product was purified by column chromatography using PE as the eluent.

B: white solid, yield: 59.01%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 7.6 Hz, 2H), 6.82 (s, 4H), 2.31 (s, 6H), 2.00 (s, 12H).

O-2NO$_2$ and S-2NO$_2$:

Under an N_2 atmosphere, add the following reagents sequentially into a 100 mL pressure tube: 4,6-dibromodibenzofuran (1.0 equiv.), 2-nitrophenylboronic acid (3.0 equiv.), $t(Bu)_3PH{\cdot}BF_4$ (0.6 equiv.), $Pd(OAC)_2$ (0.2 equiv.), sodium carbonate aqueous solution (9.4 mol/L) and THF 40 mL. The mixture was heated to 110 ºC. After reacted 20 hours, water was added and extracted with DCM, dry the combined organic layers over anhydrous sodium sulfate. Concentrate the solution to dryness by rotary evaporation. The target compound is insoluble in EA. Add EA and perform centrifugation. Finally, vacuum dry to obtain the compound **O-2NO$_2$**.The synthetic method of **S-2NO$_2$** is similar to **O-2NO$_2$**.

O-2NO$_2$: beige solid, yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 6.9 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.73 (t, J = 7.5 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.49–7.40 (m, 4H).

S-2NO$_2$: yellow solid, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.9 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.61–7.50 (m, 6H), 7.30 (d, J =

7.3 Hz, 2H).

O-2Cz and S-2Cz:

Added **O-2NO₂** (1.0 equiv.), PPh_3 (5.0 equiv.), and 40 mL o-dichlorobenzene into a 100 mL pressure-resistant tube. The mixture was heated to 180 ºC. After the mixture was stirred at this temperature for 20 hours, it was filtered under reduced pressure and the crude product was subjected to column chromatography (PE : EA= 5 : 1) to obtain **O-2Cz**. The synthetic method of **S-2Cz** is similar to that of **O-2Cz**.

O-2Cz: white solid, yield: 54%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 2H), 8.58 (d, J = 7.7 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 9.6 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 6.6 Hz, 2H), 7.39 (t, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.18, 139.94, 139.86, 122.4, 120.28, 119.89, 117.82, 116.26, 111.72, 108.25, 107.62. TOF-MS (ESI): m/z calculated for $C_{24}H_{13}N_2O$ $[M]^+$: 346.1106, observed $[M-H]^+$: 345.1050.

S-2Cz: gray solid, yield: 56%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.75 (s, 2H), 8.42 (d, J = 8.2 Hz, 2H), 8.32 (d, J = 7.3 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.0 Hz, 2H), 7.39 (t, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.09, 138.65, 130.26, 128.76, 126.00, 121.74, 121.34, 119.82, 119.45, 116.63 , 111.93, 109.91. TOF-MS (ESI): m/z calculated for $C_{24}H_{15}N_2S$ $[M]^+$: 362.0950, observed: 363.0933 $[M+H]^+$.

O-2B and S-2B:

Under a N_2 atmosphere, successively added **O-2Cz** or **S-2Cz** (1.0 equiv.), **B** (2.1 equiv.), $Pd(OAC)_2$ (0.4 equiv.), X-phos (0.6 equiv.), t-BuOK (3.0 equiv.) and 20 ml toluene solution in a 100 mL pressure-resistant tube. Control the reaction temperature at 85 °C, after 7 hours of reaction, water was added and extracted with DCM, and the crude product was purified by silica gel column chromatography (PE : DCM= 3 : 1)). Subsequently, an appropriate amount of methanol was added to the oily substance obtained by column chromatography to induce the precipitation of solids. Finally, the

precipitated solid is collected by centrifugation and dried to obtain the target compound.

O-2B： white solid, yield: 52.26%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 6.2, 2.5 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 4H), 7.68 (d, *J* = 8.1 Hz, 4H), 7.63 – 7.57 (m, 2H), 7.56 – 7.51 (m, 6H), 6.89 (s, 8H), 2.35 (s, 12H), 2.13 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.14, 141.10, 140.96, 140.29, 140.08, 139.04, 138.11, 128.44, 126.26, 125.96, 123.05, 121.52, 120.96, 117.74, 117.38, 110.11, 109.50, 105.80, 23.67, 21.37. TOF-MS(ESI): m/z calculated for $C_{72}H_{64}B_2N_2O$: 994.5205 $[M]^+$, observed: 995.5295 $[M+H]^+$.

S-2B: yellow solid, yield: 55.57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.46 (m, 2H), 8.25 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 8.3 Hz, 6H), 7.62 (d, *J* = 4.9 Hz, 2H), 7.56 – 7.50 (m, 4H), 6.90 (s, 8H), 2.35 (s, 12H), 2.14 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.67, 140.95, 140.41, 139.06, 138.96, 138.13, 131.92, 129.82, 128.44, 126.26, 125.90, 122.89, 121.98, 120.91, 118.91, 117.88, 110.24, 108.02, 23.67, 21.37. TOF-MS(ESI): m/z calculated for $C_{72}H_{64}B_2N_2S$: 1010.4976 $[M]^+$, observed: 1011.5044 $[M+H]^+$.

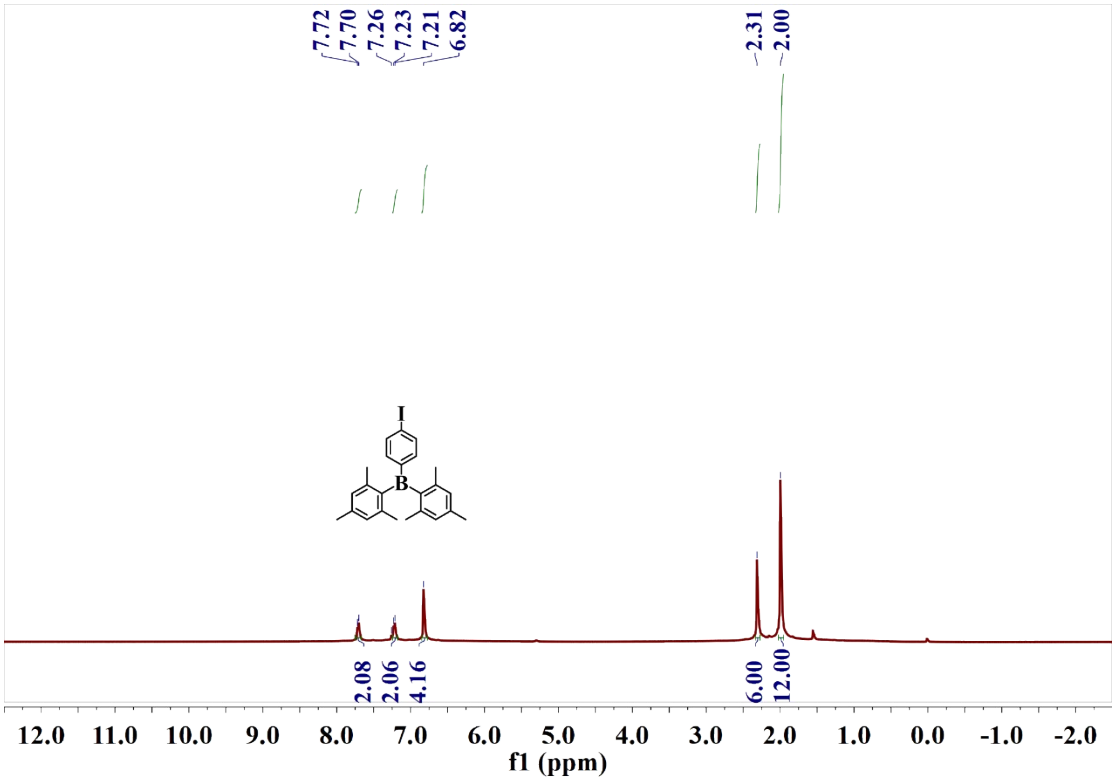


Fig. S1. [1]H NMR spectra of **B**.

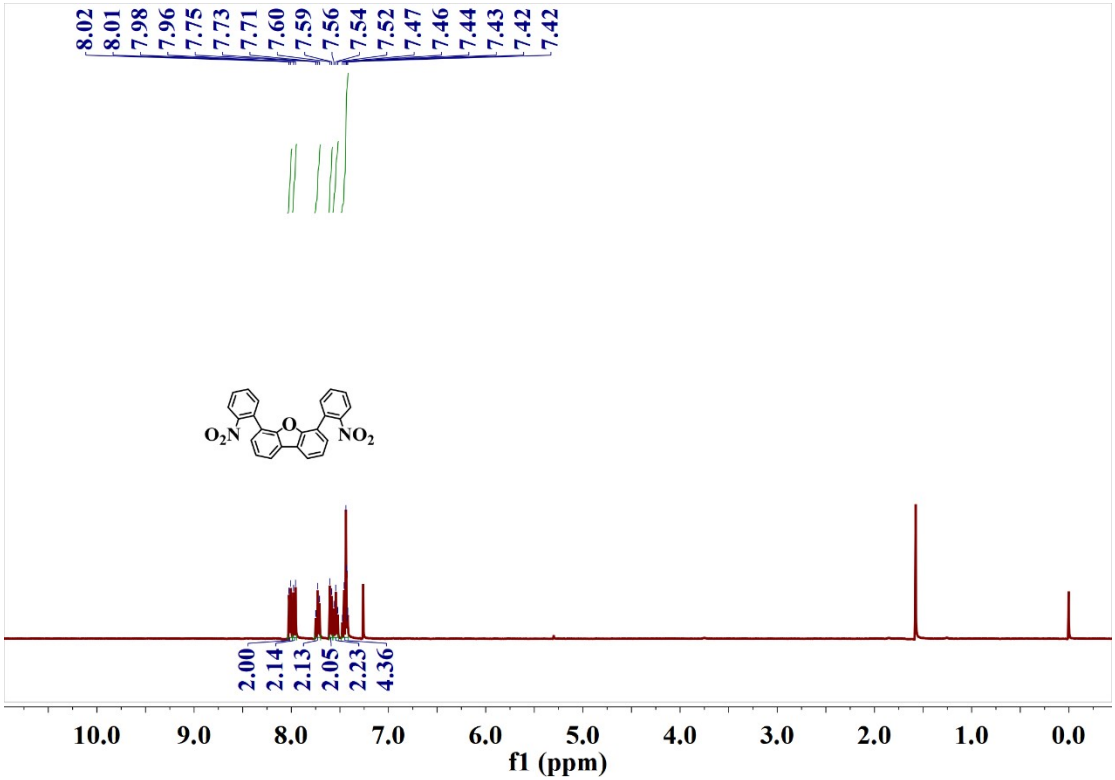


Fig. S2. [1]H NMR spectra of **O-2NO$_2$**.

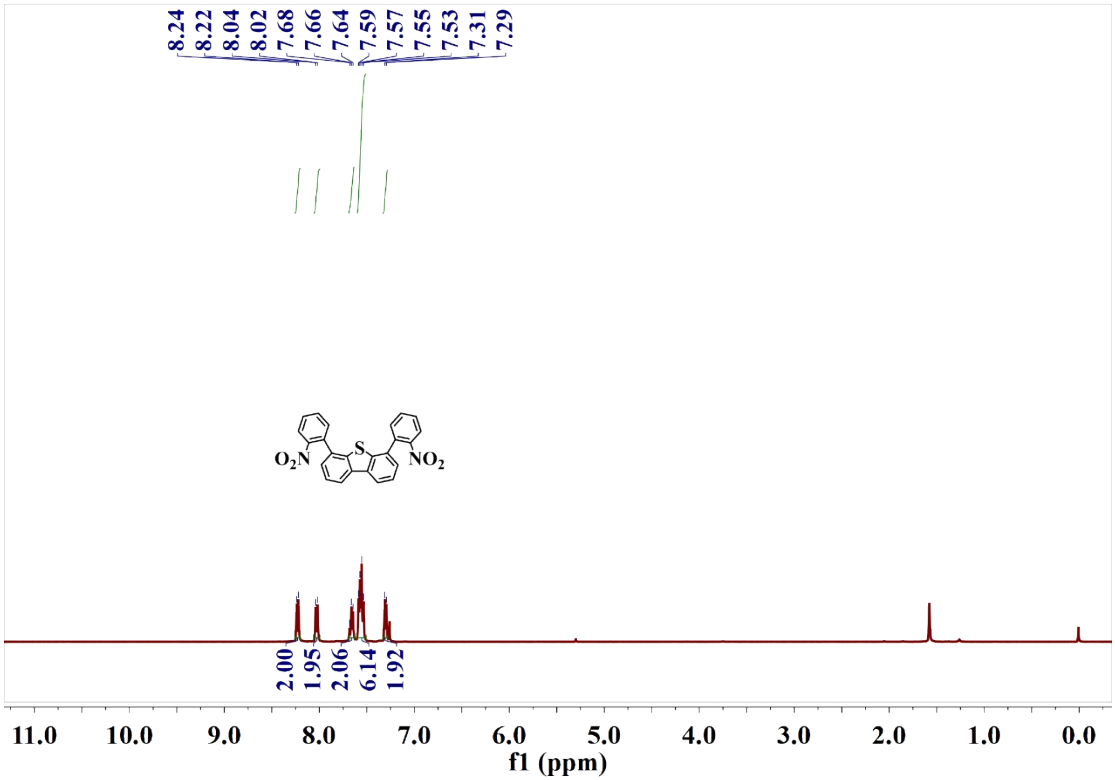


Fig. S3. ^{1}H NMR spectra of **S-2NO$_2$**.

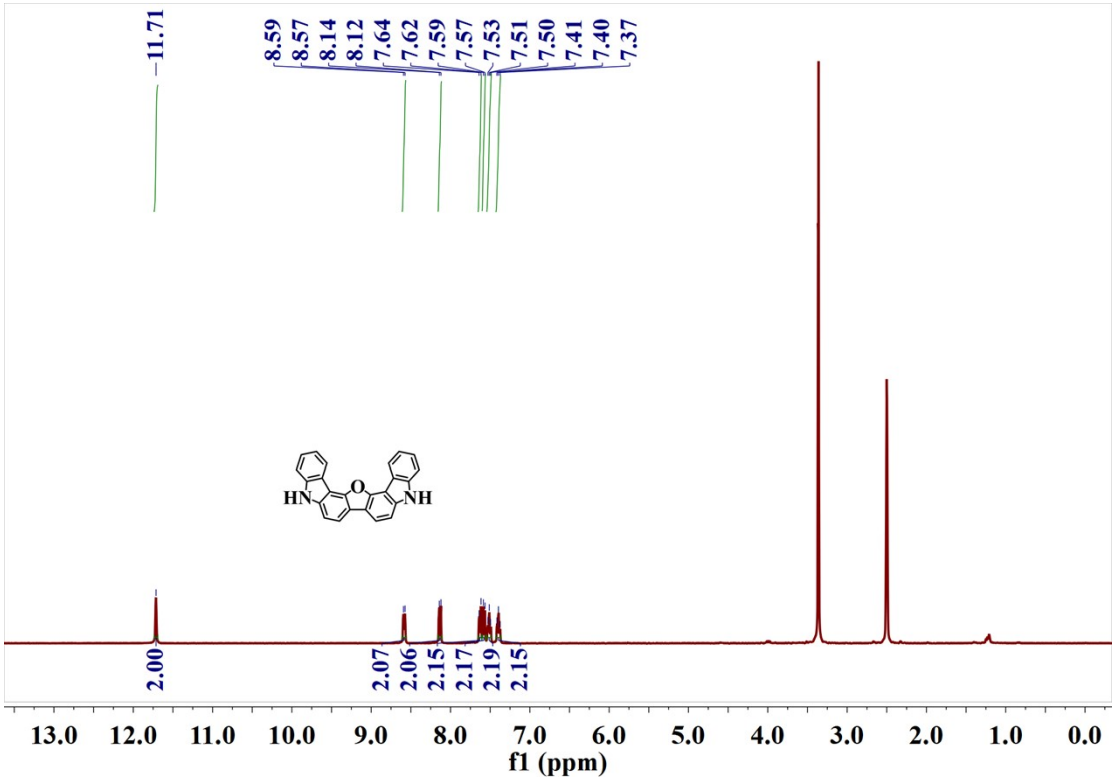


Fig. S4. ^{1}H NMR spectra of **O-2Cz**.

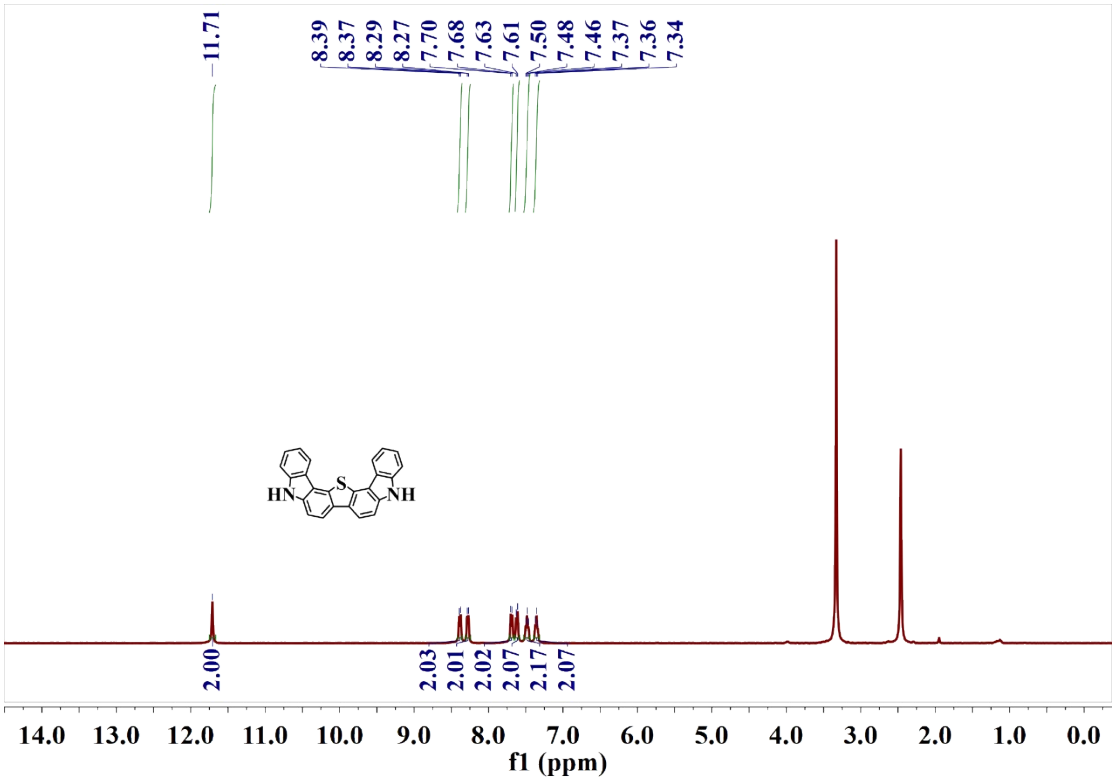


Fig. S5. ^{1}H NMR spectra of **S-2Cz**.

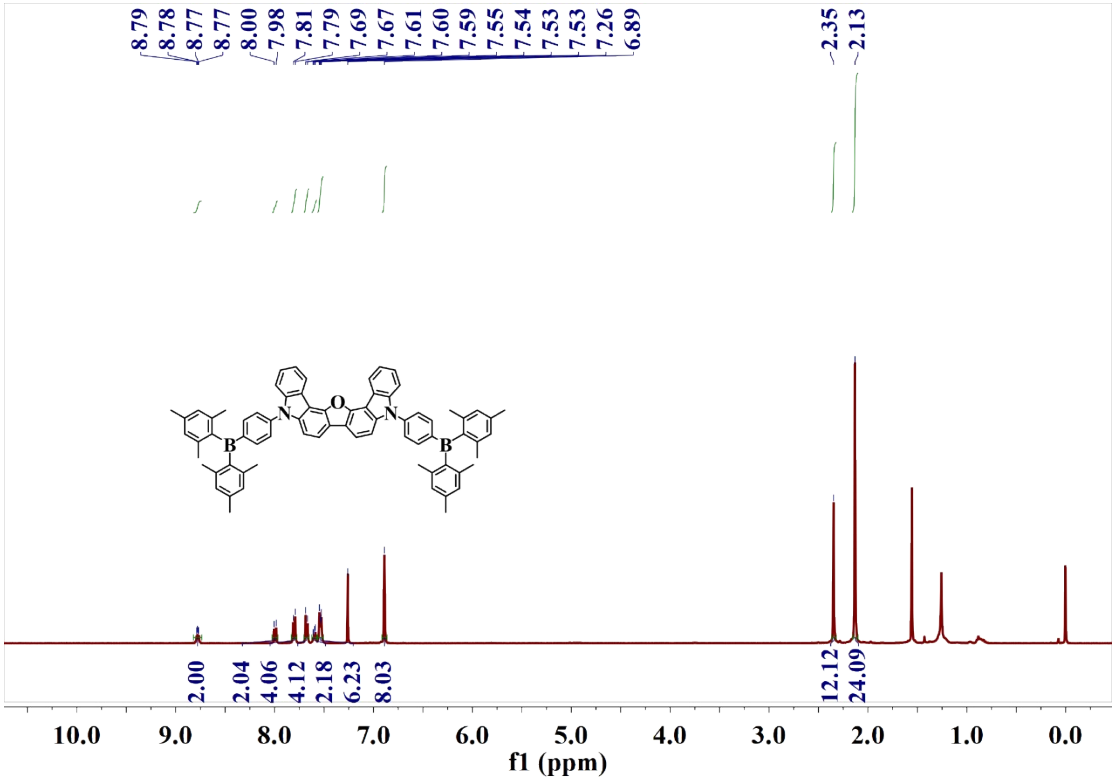


Fig. S6. ^{1}H NMR spectra of **O-2B**.

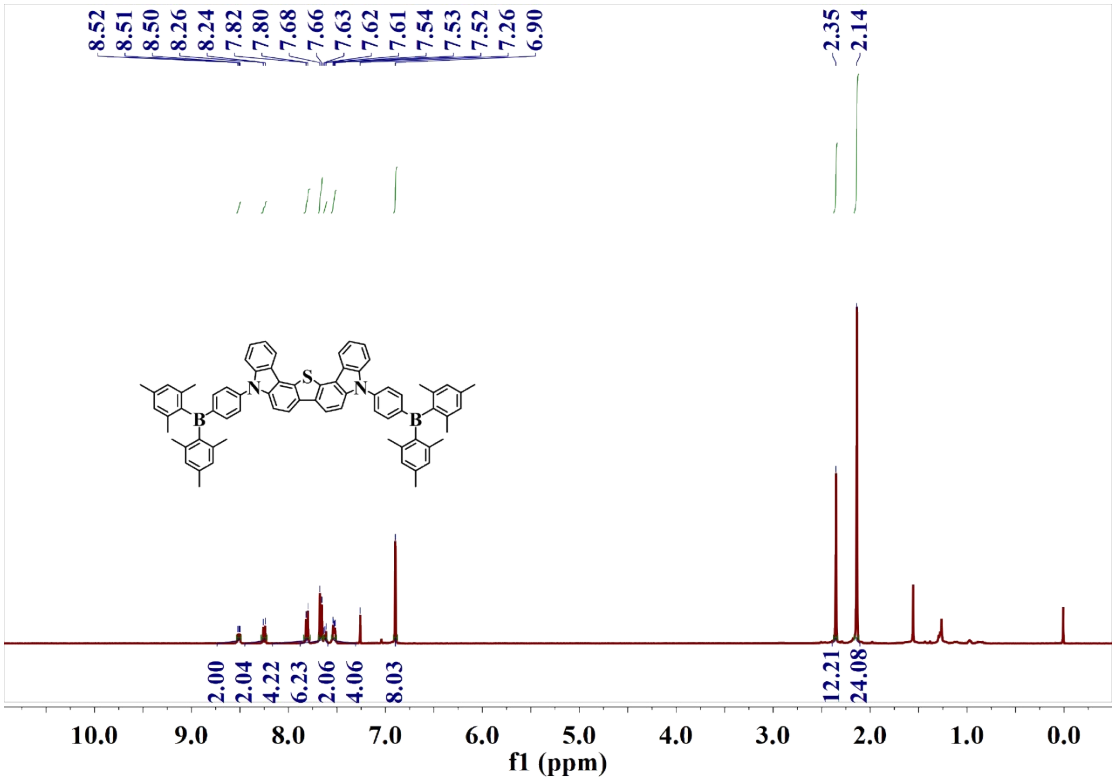


Fig. S7. ^{1}H NMR spectra of **S-2B**.

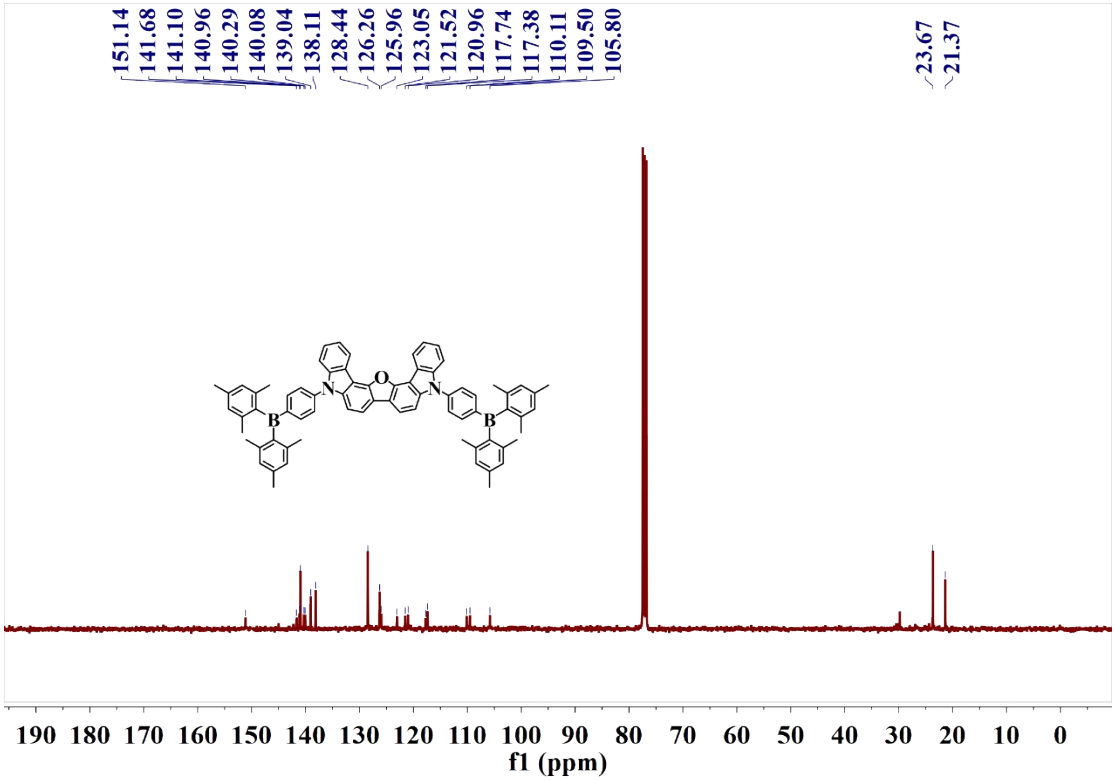


Fig. S8. ^{13}C NMR spectra of **O-2B**.

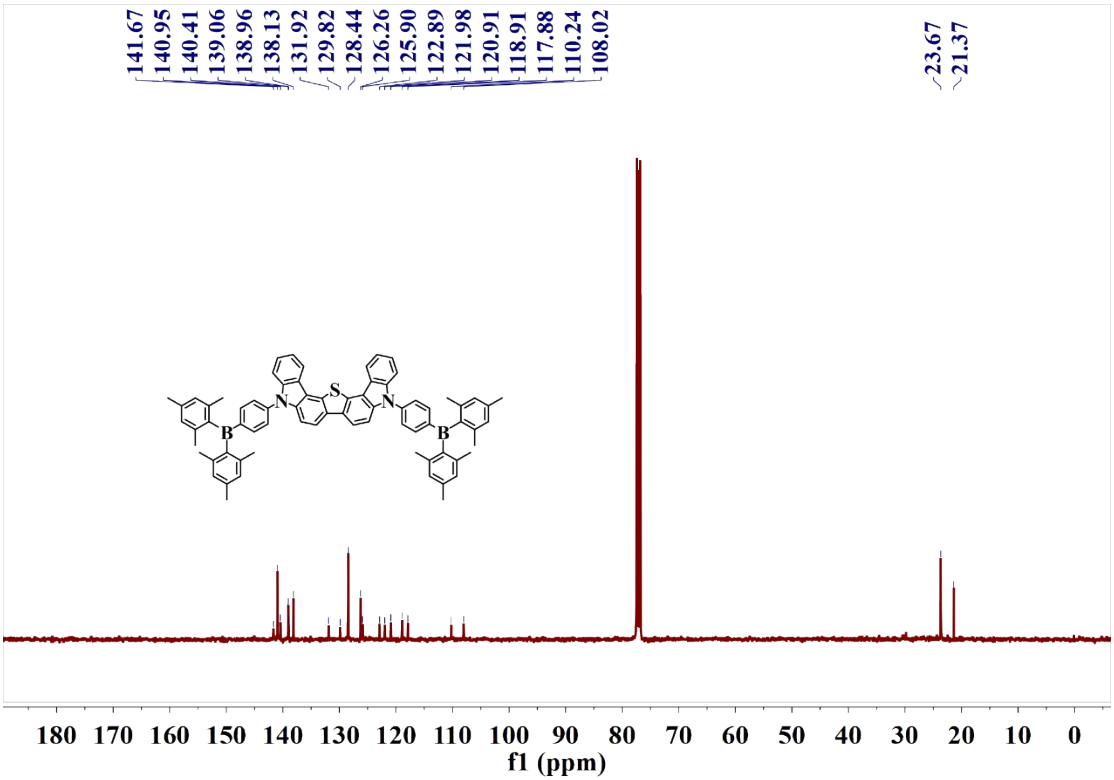


Fig. S9. ^{13}C NMR spectra of **S-2B**.

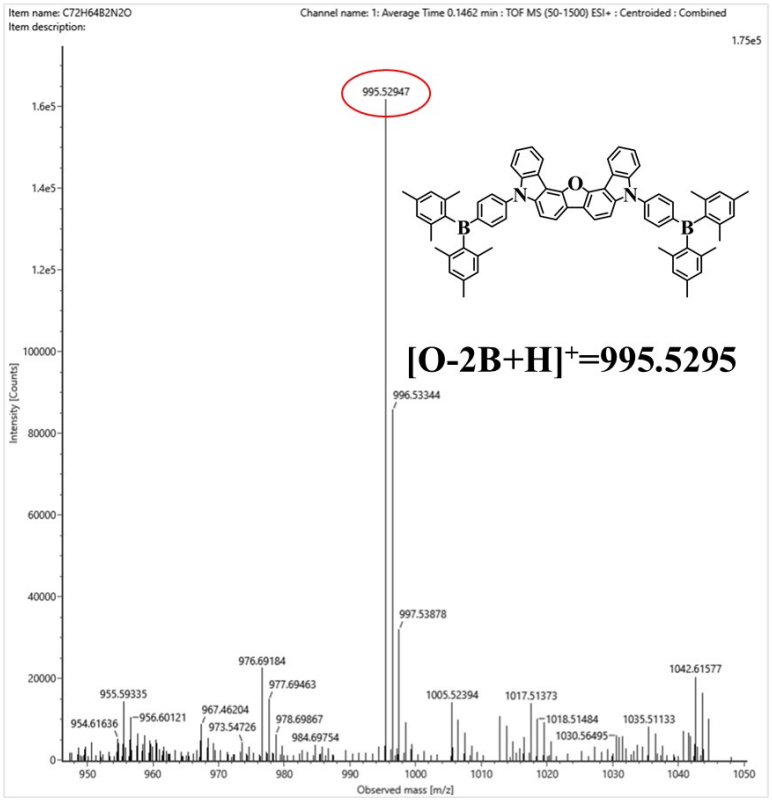


Fig. S10. High resolution mass spectra of **O-2B**.

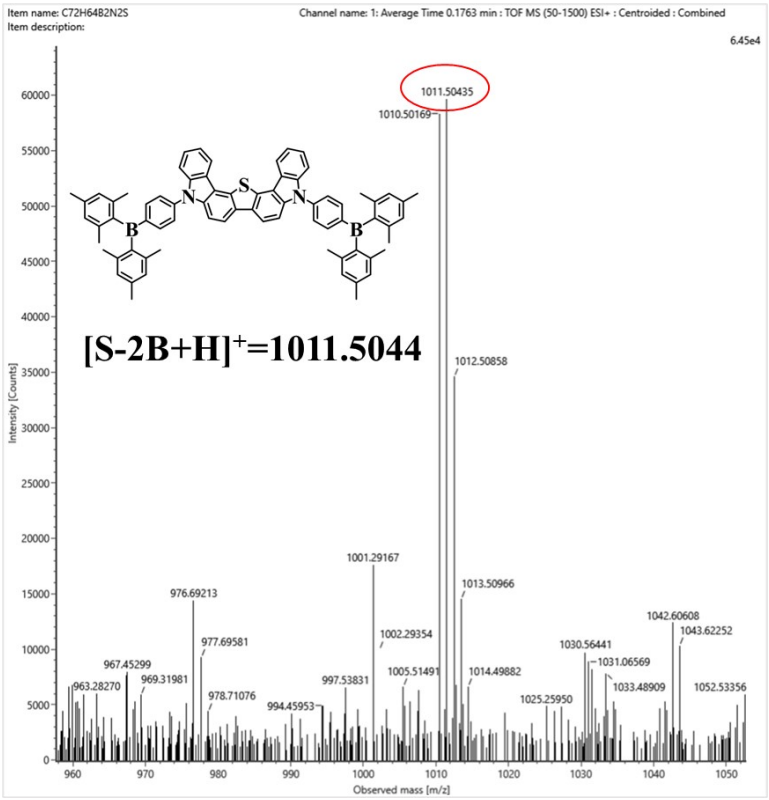


Fig. S11. High resolution mass spectra of **S-2B**.

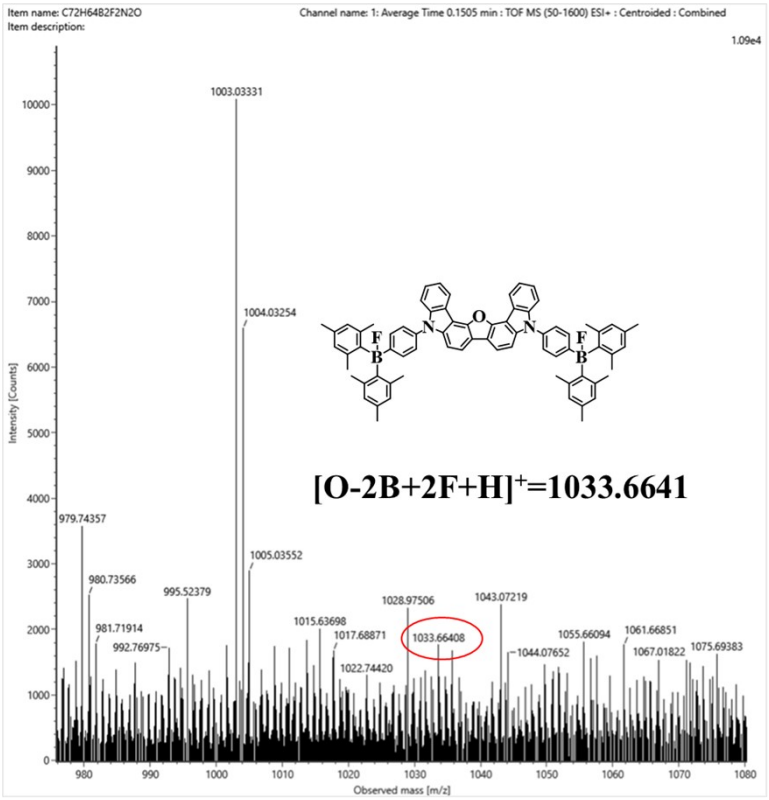


Fig. S12. High resolution mass spectra of **O-2B+2F**.

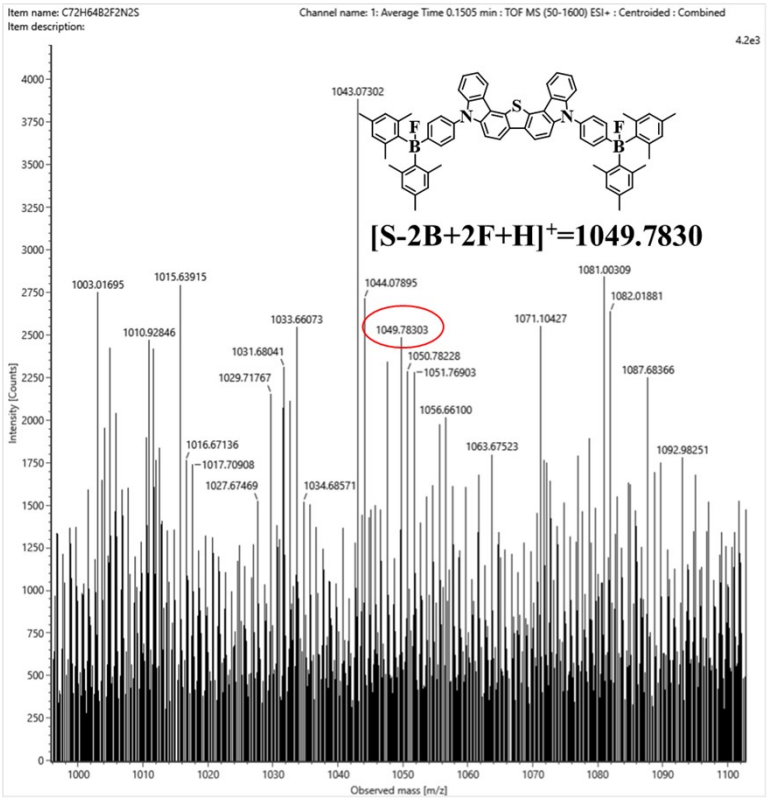


Fig. S13. High resolution mass spectra of **O-2B+2F**.

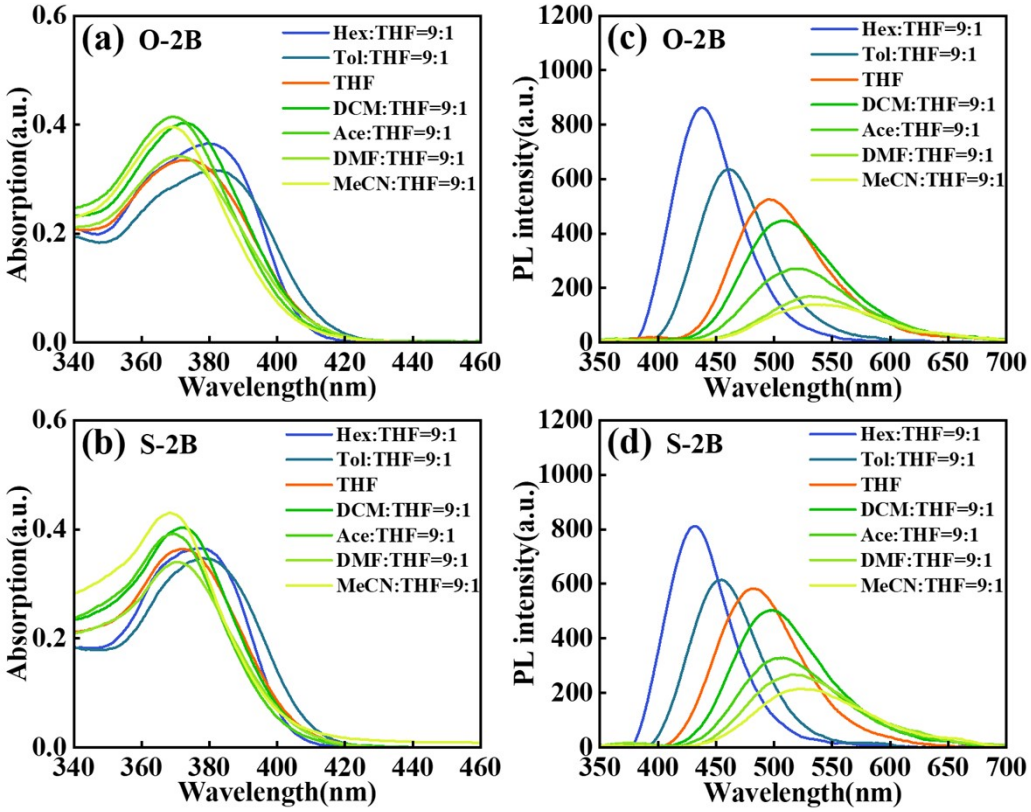


Fig. S14. (a) and (b) Absorption spectra and (c) and (d) PL spectra of sensors **O-2B** and **S-2B** in Vother solvents : V_{THF} = 9 : 1 (1.0×10^{-5} M).

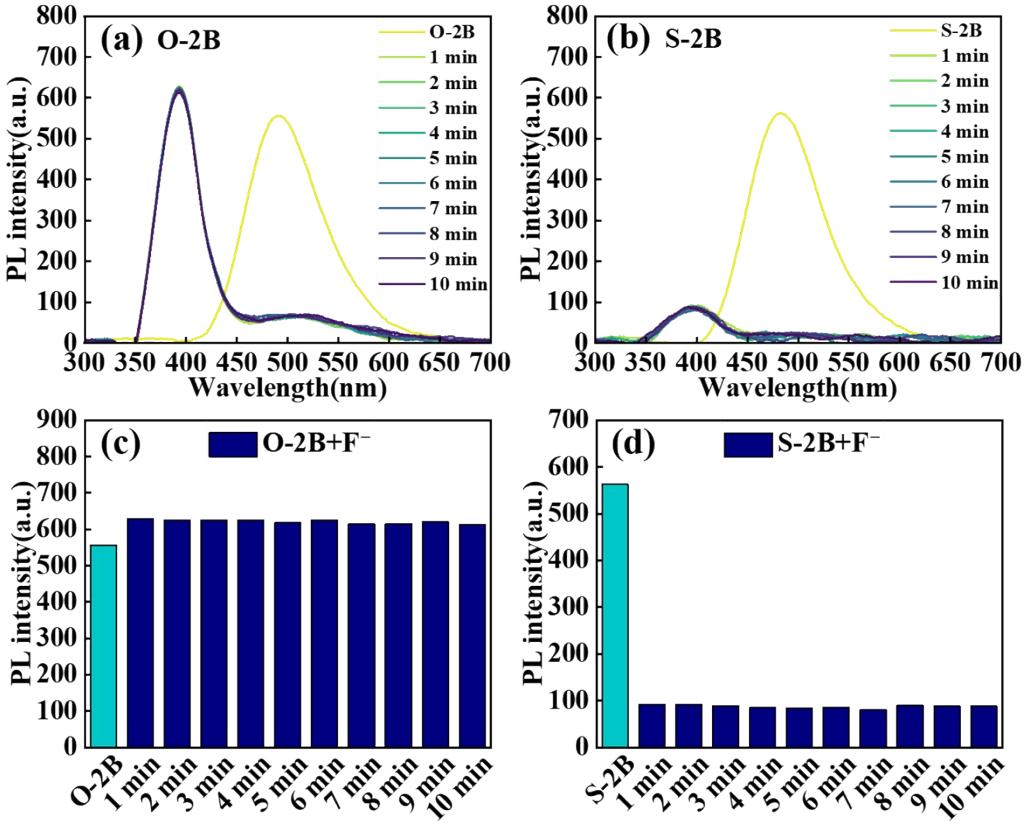


Fig. S15. When sensors **O-2B** and **S-2B** are added with 2.4 equivalent of F^-: (a) and (b) the change of PL spectra with the increase of time; (c) and (d) the change of fluorescence intensity with the increase of time.

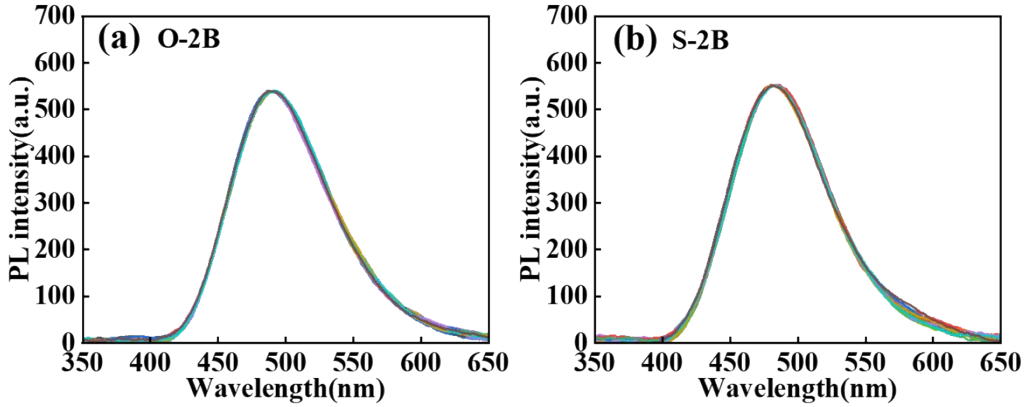


Fig. S16. PL spectra of the blank sensors solutions measured with 20 times: (a) **O-2B** is 0.62, (b) **S-2B** is 0.58.

Reference:

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.;

Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian16; Gaussian, Inc.: Wallingford, CT, 2016