Electronic Supplementary Information *for*

Fluoride-Regulated Colorimetric and Fluorometric Switch Based on AIEgens through B-F Dynamic Covalent Reaction

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1. Experimental Section

Synthesis of ((Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene) (DTDB). A mixture of tetrakis(triphenylphosphine)platinum ($Pt(PPh_3)_4$) (0.35 g, 1 mol%), bis(pinacolato)diboron (14.25 g, 56.0 mmol) and diphenylacetylene (5.00 g, 28.0 mmol) were added in DMF (150 mL) under the protection of N_2, and the mixture was heated at 90 °C for 24 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and then the organic layer was dried by $MgSO_4$. The crude product of DTDB was obtained after removal of the solvent under reduced pressure. DTDB (4.5 g) was obtained by washing several times with ethanol as a white solid in a 38% yield. Molecular formula: $C_{26}H_{34}B_2O_4$. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.09-7.00 (m, 6H), 6.96-6.93 (m, 4H), 1.32 (s, 24H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 141.25, 129.31, 127.42, 125.79, 84.07, 24.89. HRMS (ESI) m/z: $[M+H]^+$ 433.2607 (calcd.for $C_{26}H_{34}B_2O_4$, $[M+H]^+$ 433.2643).

Synthesis of (4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane) (TTDB). A mixture of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (DTDB) (2.00 g, 4.63 mmol), bromobenzene (1.09 g, 6.95 mmol), potassium carbonate (1.28 g, 9.25 mmol) and $Pd(PPh_3)_4$ (53.47 mg, 0.046 mmol) were added in a mixed solvent containing THF (80 mL) and toluene (50 mL) under the protection of N_2, and then the mixture was heated at 80 °C for 24 h. After the reaction was completed, the mixture was poured into water and extracted three times with ethyl acetate, and then the organic layer was dried by $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:15) as eluent. The final product TTDB was obtained by recrystallization with ethanol as a white solid (1.33 g) in 75% yield. Molecular formula: $C_{26}H_{27}BO_2$. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.34 (d, 2H), 7.32–7.28 (m, 3H), 7.13 (d, 2H), 7.10–7.03 (m, 6H), 6.97 (d, 2H), 1.13 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ(ppm) 151.40, 144.66, 141.69, 130.93, 129.42, 127.52, 126.77, 125.85, 83.69, 24.55. HRMS (ESI) m/z: $[M+H]^+$ 383.2182 (calcd. for $C_{26}H_{27}BO_2$, $[M+H]^+$ 383.2104).

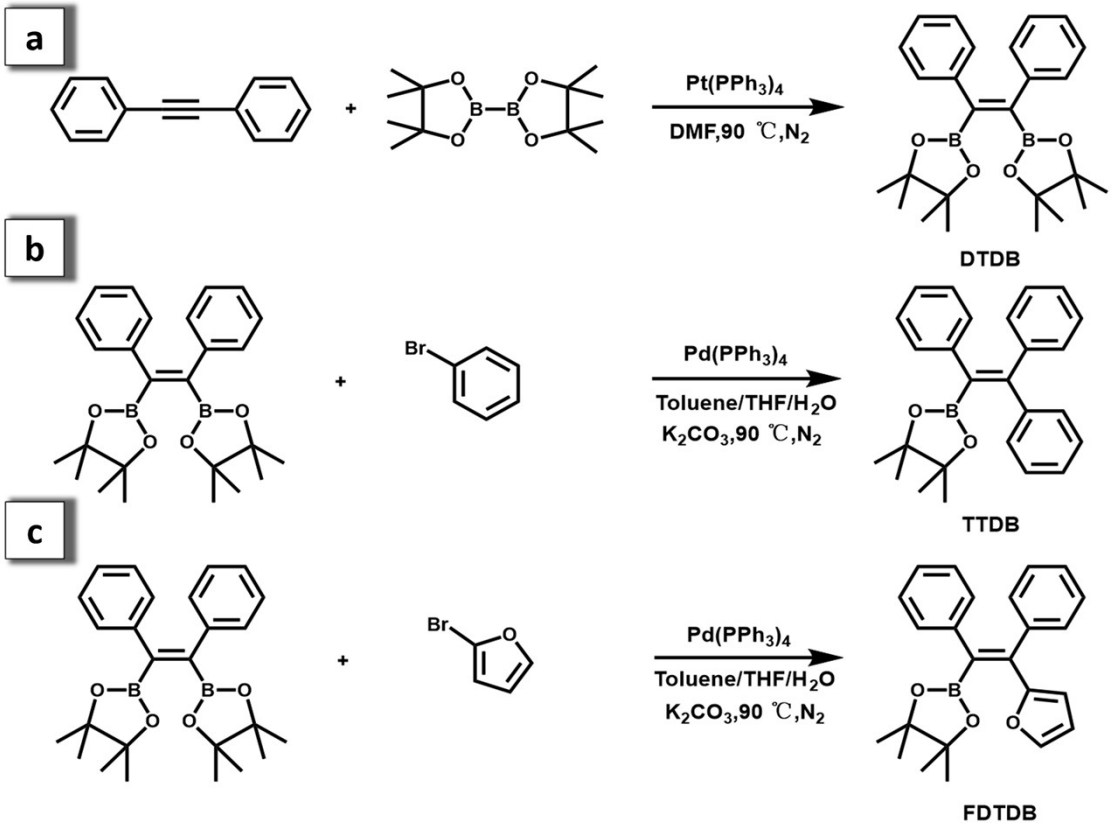
Synthesis of ((E)-2-(2-(furan-2-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2 -dioxaborolane) (FDTDB). A mixture of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)ethene (DTDB) (2.00 g, 4.63 mmol), 2-bromofuran (1.03 g, 6.95 mmol), potassium carbonate (1.28 g, 9.25 mmol) and $Pd(PPh_3)_4$ (53.47 mg, 0.046 mmol) were added in a mixed solvent containing THF (80 mL) and toluene (50 mL) under the protection of N_2, and then the mixture was heated at 80 °C for 24 h. After the reaction was completed, the mixture was poured into water and extracted three times with ethyl acetate, and then the organic layer was dried by $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:10) as eluent. The final product FDTDB was obtained by recrystallization with ethanol as a pale yellow solid (1.38 g) in 80% yield. Molecular formula: $C_{24}H_{25}BO_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (s, 1H), 7.19–6.98 (m, 10H), 6.38 (s, 1H), 5.98 (s, 1H), 1.36 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ(ppm) 156.13, 141.69, 140.46, 138.65, 137.73, 130.81, 129.33, 127.71, 127.11, 125.82, 111.78, 110.90, 84.08, 24.87. HRMS (ESI) m/z: $[M+H]^+$ 373.1987 (calcd. for $C_{24}H_{25}BO_3$, $[M+H]^+$ 373.1897).

Characterization of UV-Visible and Fluorescence Properties of All Samples.

UV−vis absorption spectra were recorded using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder. Time-resolved fluorescence measurements were conducted with EPL-series lasers. The absolute PL quantum yields of all samples were determined using an integrating sphere equipped in FLS980 spectrophotometer for at least three times.

2. Supplementary Schemes and Figures



Scheme S1. Synthesis routes of DTDB (a), TTDB (b), and FDTDB (c).

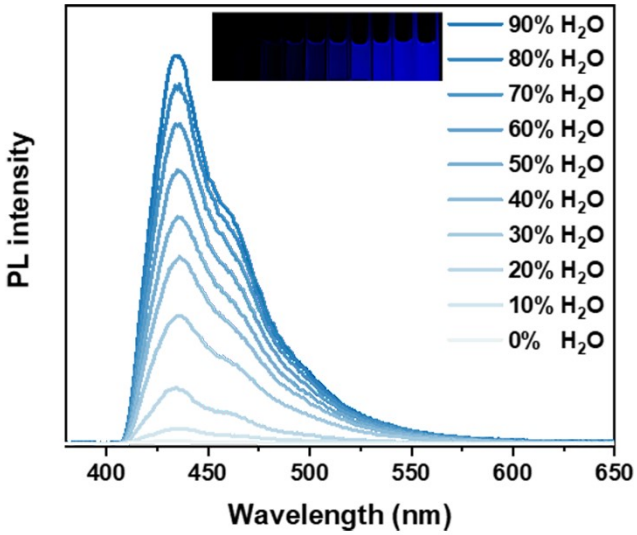


Figure S1. PL intensity spectra and images of FDTDB in THF (50.0 mM) with increasing amounts of water from 0% to 90%.

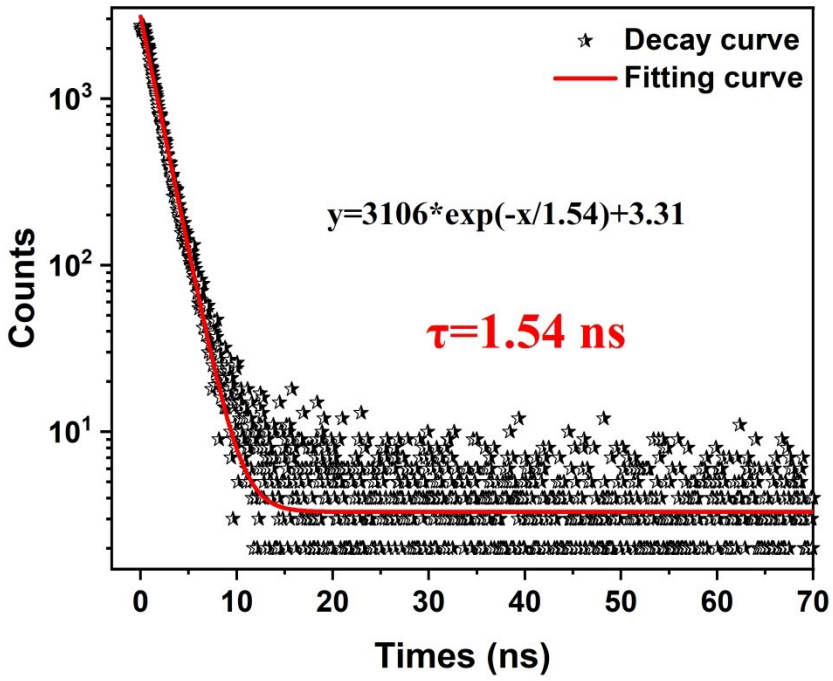


Figure S2. Time-resolved PL decay curve of FDTDB in solid state.

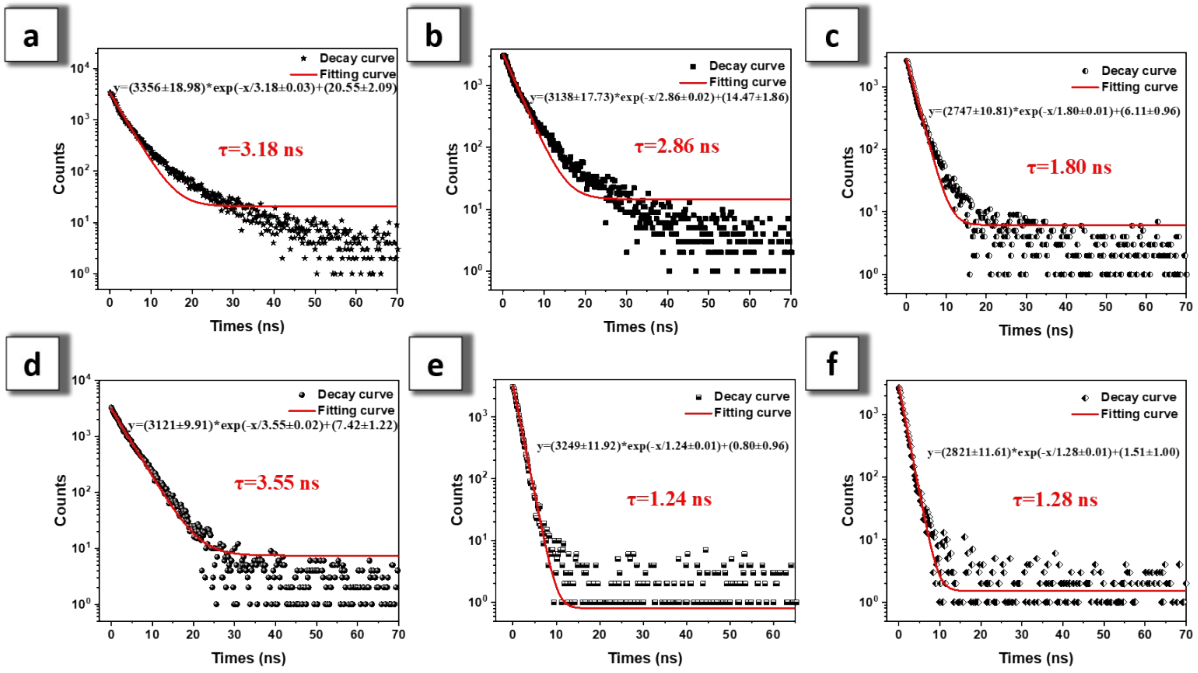


Figure S3. Time-resolved PL decay curves of (a) DTDB-2F, (b) TTDB-F, and (c) FDTDB-F in dispersed state, and (d) DTDB-2F, (e) TTDB-F, and (f) FDTDB-F in THF solution (500 μM).

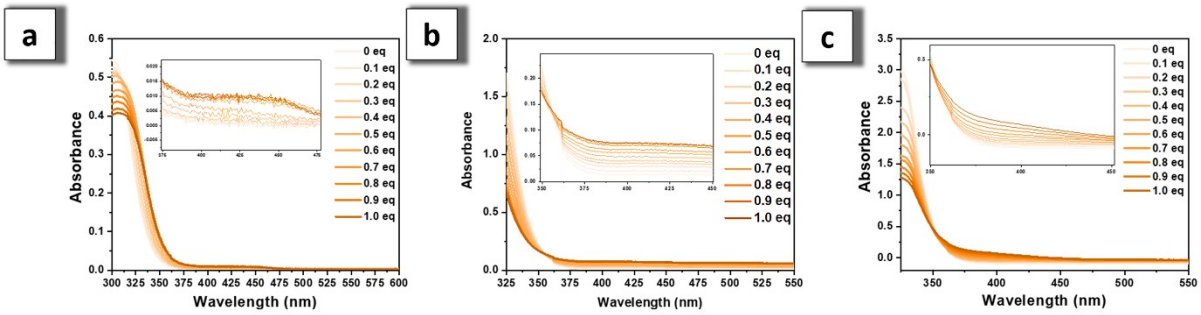


Figure S4. Changes in UV-Vis absorption spectra of (a) DTDB (500 μM), (b) TTDB (500 μM) and (c) FDTDB (500 μM) in THF solution upon addition 0-1 eq. of TBAF.

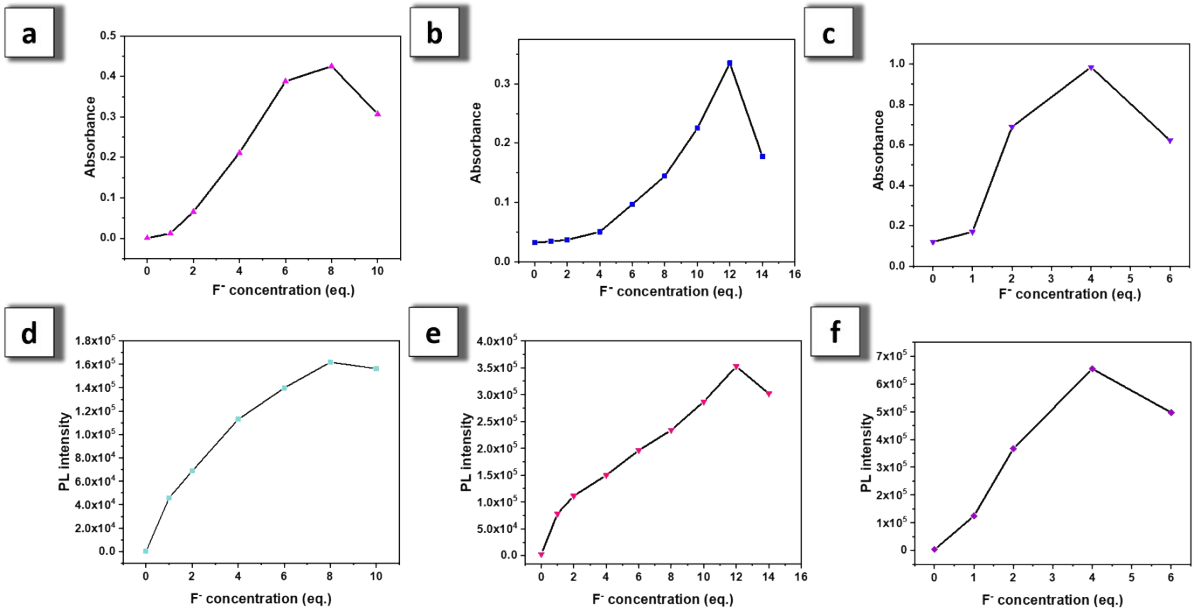


Figure S5. A line graph of PL intensity and F^- concentration of DTDB (a), TTDB(b) and FDTDB(c) in THF (500 μM). A line graph of Absorbance and F^- concentration of DTDB (d), TTDB(e) and FDTDB(f) in THF (500 μM).

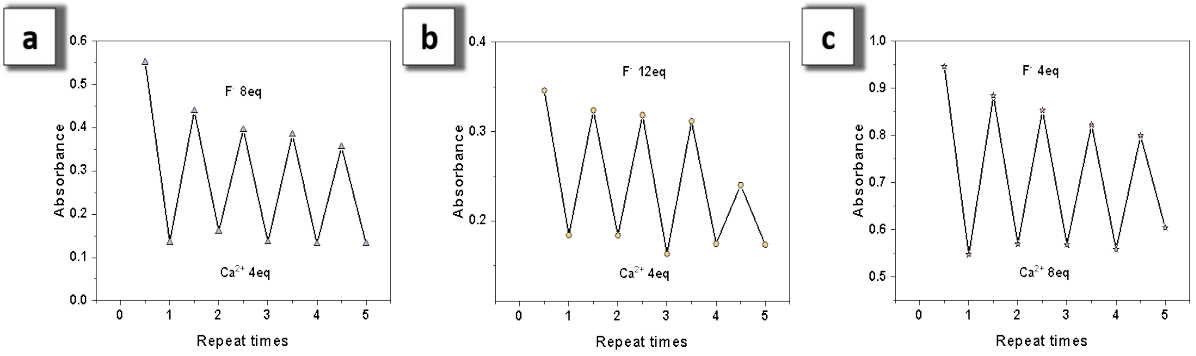


Figure S6. Recycling of DTDB (a), TTDB (b), and FDTDB (c) in THF solution (500 μM) as a function of addition F^- (TBAF) and Ca^{2+} ($CaCl_2$) respectively.

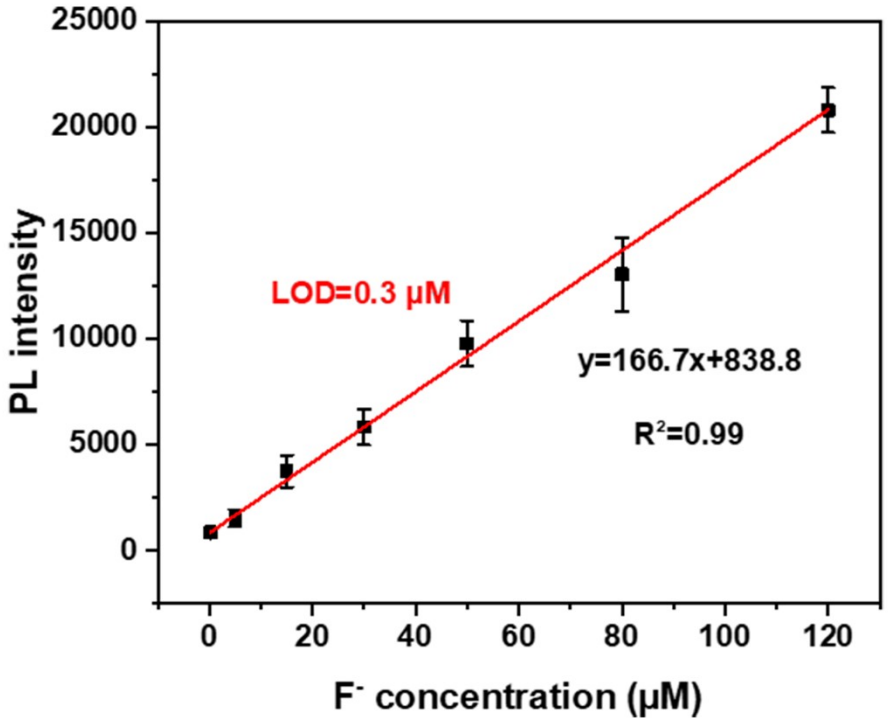


Figure S7. Calibration curve between PL intensity and F^- concentration in the scope of 1.1−120.0 μM.

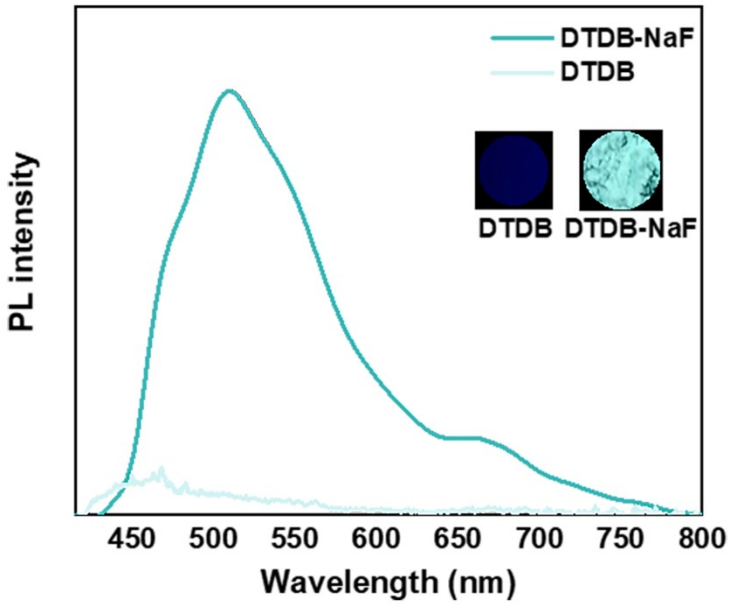


Figure S8. Change in PL spectra of DTDB in solid state upon addition of NaF. Insets: Fluorescent photographs of these solids were taken under UV light.

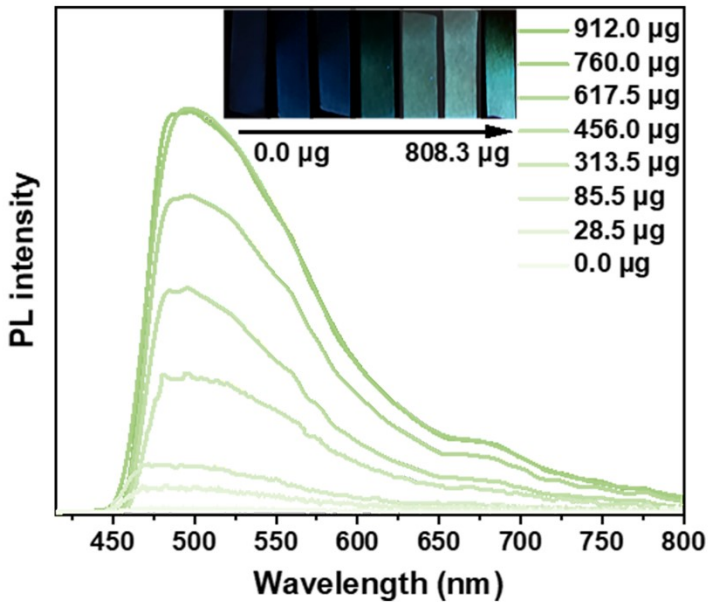


Figure S9. Change in PL spectra of DTDB in filter papers increasing the content of fluoride ion (NaF). Insets: Photographs showing fluorescence change after adding different amounts of fluoride ion from 0 µg to 912.0 µg.

3. NMR and HRMS Spectra of Compounds

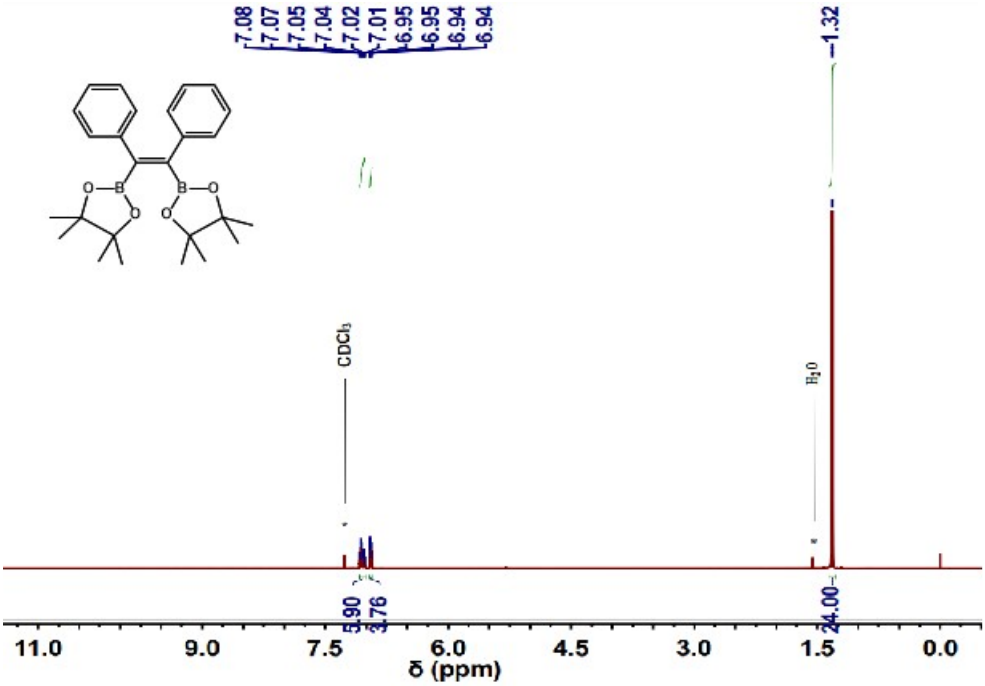


Figure S10. ^{1}H NMR spectrum of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene) (DTDB) in $CDCl_3$

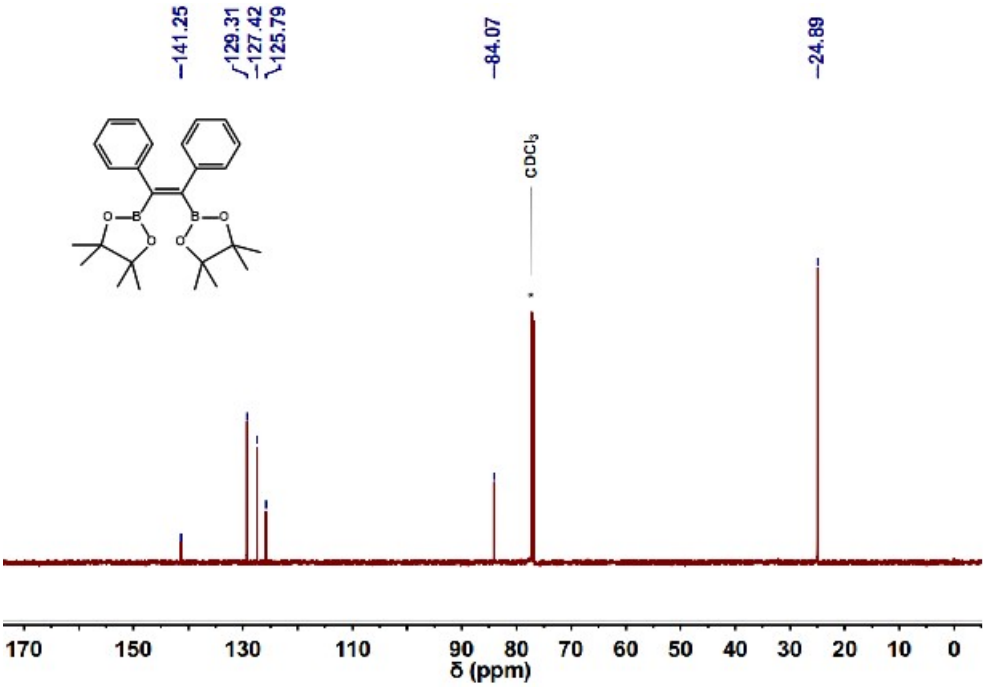


Figure S11. ^{13}C NMR spectrum of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene) (DTDB) in $CDCl_3$

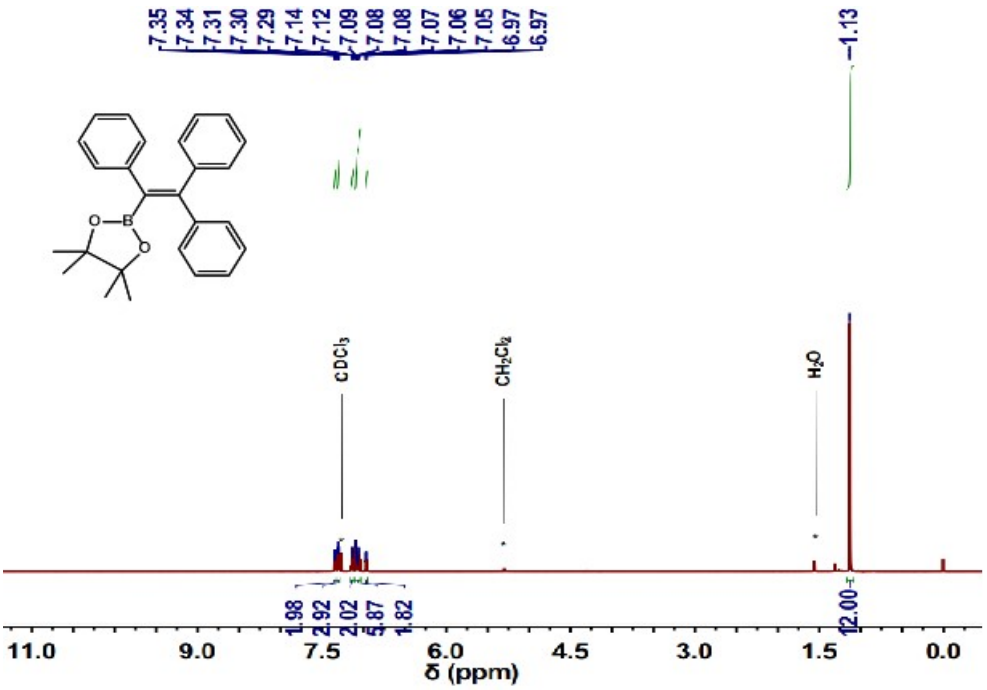


Figure S12. ^{1}H NMR spectrum of (4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane) (TTDB) in $CDCl_3$

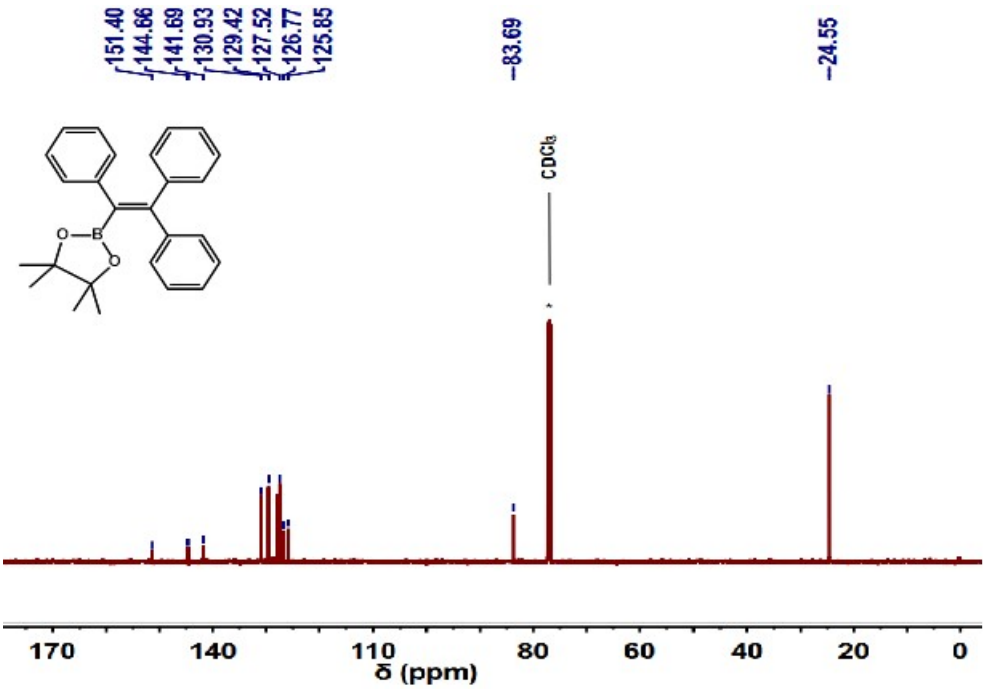


Figure S13. ^{13}C NMR spectrum of (4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane) (TTDB) in $CDCl_3$

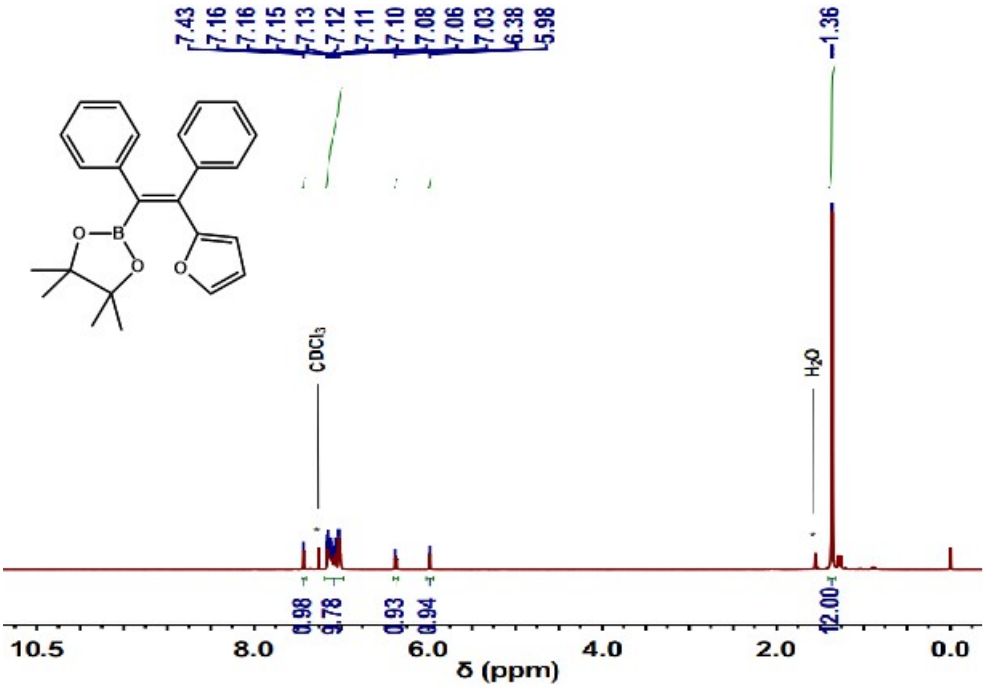


Figure S14. ^{1}H NMR spectrum of (E)-2-(2-(furan-2-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (FDTDB) in $CDCl_3$

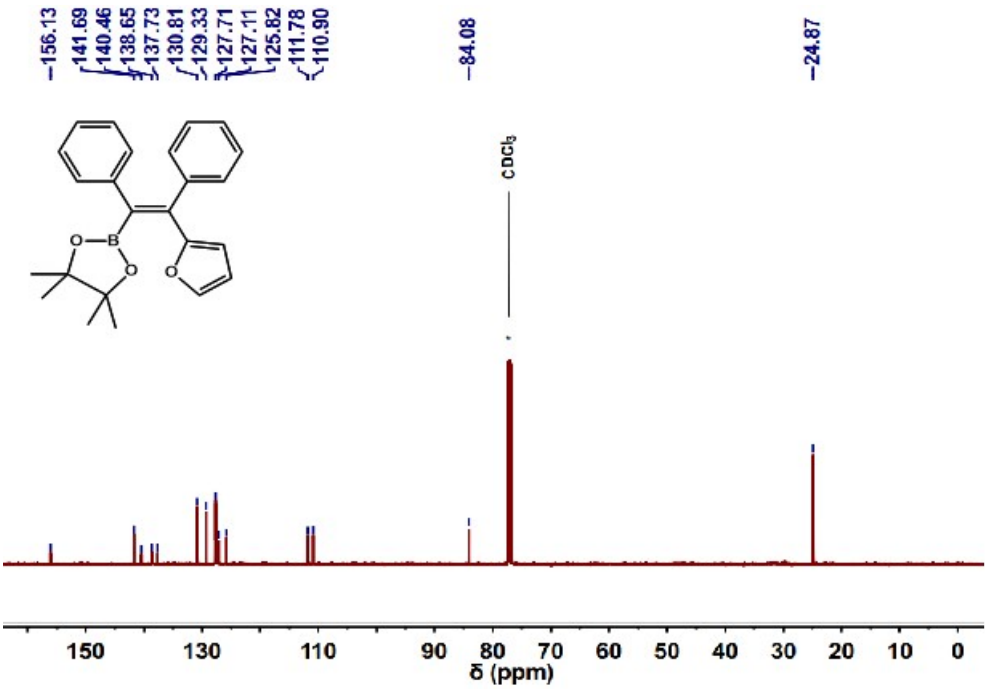


Figure S15. ^{13}C NMR spectrum of (E)-2-(2-(furan-2-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (FDTDB) in $CDCl_3$

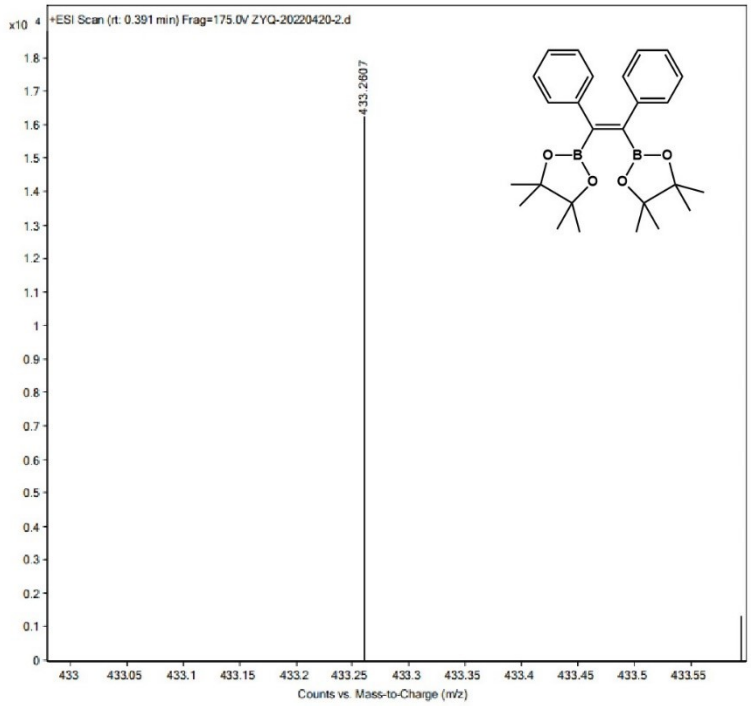


Figure S16. High-resolution mass spectrum of (Z)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene) (DTDB)

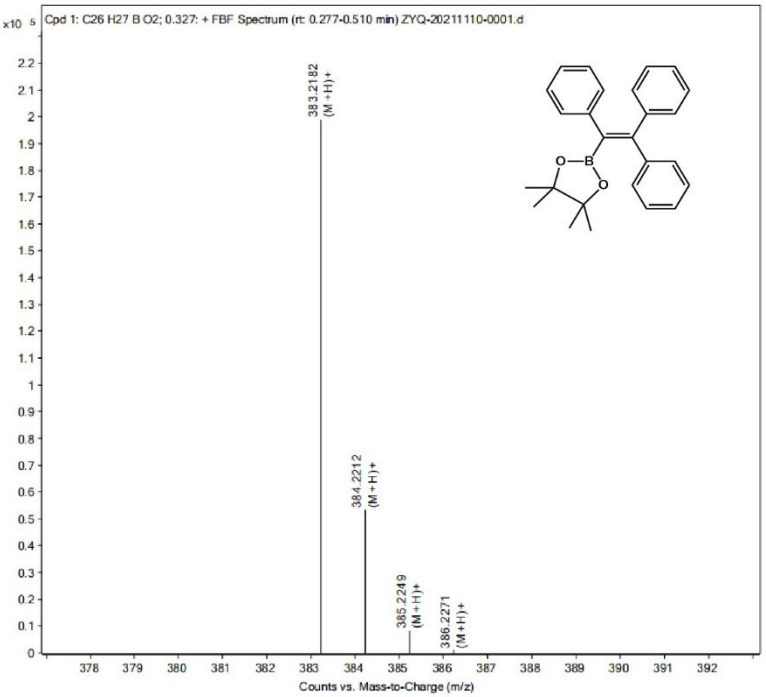


Figure S17. High-resolution mass spectrum of (4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane) (TTDB)

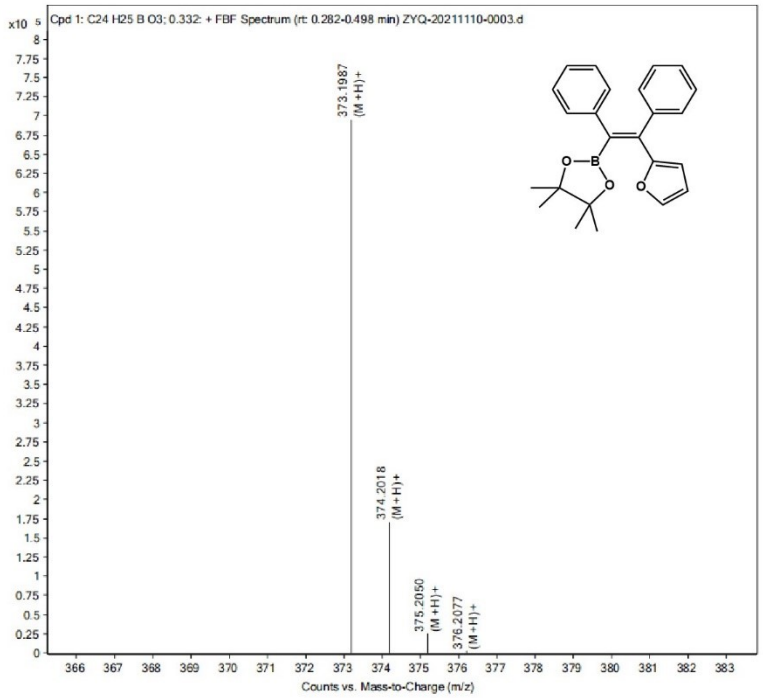


Figure S18. High-resolution mass spectrum of (E)-2-(2-(furan-2-yl)-1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (FDTDB)