Supporting Information For: The inherent mechanism of mechanochromism under different stress: electron cloud density distribution, J-type stacking, pore structure and collapse of J-type stacking

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Experimental

Measurement and characterization

^{1}H NMR spectra were obtained through a Varian inova-400-MHz NMR, the tetramethylsilane (TMS) was employed as the internal standard for calibration. ^{19}F NMR spectra were obtained through a Varian inova-376-MHz NMR in $CDCl_3$ solvent. ^{13}C NMR spectra were recorded on a Varian inova-100-MHz spectrometer and $CDCl_3$ was used as the solvent in all cases. The UV-vis absorption spectra were obtained from a spectrophotometer MaPada UV-3200PCS. Fluorescent emission spectra were obtained on a Hitachi F-2500 fluorescence spectrophotometer. Fluorescent quantum yields were acquired through a FLs980 full-featured Steady/Transient Fluorescence Spectrometer (Edinburgh). Glass transition temperature and melting point was measured by carried out DSC measurements using DSC Q2000 (TA, America). MALDI/HRMS were record on an UltrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker, Germany). Powder XRD measurements were performed on the D8 Advance (Bruker) with Cu Kα radiation in the range of $10^o < 2\theta < 90^o$. Digital photographs were taken by Canon 550D (Canon, Japan) digital cameras. Fluorescence lifetimes were measured by using an Edinburgh Instrument FLSP920 fluorescence spectrophotometer, and all the samples were excited at 360 nm. Fluorescence microscopy photos were obtained on OLYMPUS BX53.The theoretical calculation were calculated by density functional theory (DFT) in Gaussian 09 at the B3LYP/6-31G (d,p) level.

Materials and Synthesis.

THF and CH_2Cl_2 were dried following the standardized procedures described previously. All the other chemicals and reagents used in this study were of analytical grade without further purification. In general, all the intermediates and final compounds were purified by column chromatography on silica gel (200-300 mesh), and crystallization from analytical grade solvents. Reactions were monitored by using thin layer chromatography (TLC). The synthetic routes for **TPEDKBF$_2$OMe, TPEDKBF$_2$OEt, TPEDKBF$_2$OBu, TPEDKBF$_2$OHe** and **TPEDKBF$_2$ONo** are shown in Scheme 1. Firstly, TPE was synthesized by using benzophenone as the reagent strictly follow the reported procedures; then Friedel-Crafts acylation reaction occurred between TPE and acetyl chloride, then the compound Ac-TPE are generated; Next, five β-diketonate intermediates and the corresponding complexes were prepared by condensation and boron-complexation reaction, respectively. The target molecules were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MALDI-TOF mass spectrometry thereafter.

2,2-difluoro-4-(4-methoxyphenyl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide(TPEDKBF$_2$OMe)

NaH (60%, 0.20 g, 4.80 mmol) was added quickly to a dry flask which contains the solution of Methyl p-methoxybenzoate (0.48g, 2.88 mmol) in THF (20 mL) at room temperature. Then, acetyl-TPE (0.90 g, 2.40 mmol) was added later. After the mixture was refluxed under 90 ℃ for 24 h in argon atmosphere, it was cooled to room temperature. Then, the mixture was acidified with dilute HCl. The mixture was poured into water and extracted with dichloromethane for three times. Then the organic phase was combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and a yellow residue solid was collected. Then, the solid was dried under vacuum followed by dissolving in CH_2Cl_2 (50 mL). The boron trifluoride diethyl ether (0.6 mL, 4.80 mmol) was added to the above solution, which was stirred in argon environment with the pressure of 1 atm at room temperature for 24 h. In order to quench the reaction, water was added. The organic layer was separated and dried over Na_2SO_4. After removal of the solvent, the raw product was further purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, v/v = 2/1) to obtain the **TPEDKBF$_2$OMe** (0.53 g) as a yellow solid. Yield 40% m.p. 265.0–266.0 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.14 (d,J=12.0, 2H), 7.89 (d,J=8.0, 2H), 7.22-7.14 (m, 11Hh), 7.07-7.03 (m, 9H), 3.95 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 181.64, 180.89, 165.21, 161.77, 151.24, 143.58, 142.96, 142.92, 142.73, 139.54, 132.03, 131.49, 131.33, 131.31, 131.25, 129.93, 128.14, 128.04, 127.99, 127.76, 127.25, 126.98, 124.31, 114.64, 92.37, 55.79. ^{19}F NMR (376 MHz, Chloroform-*d*) δ/ppm= -140.81 (d, J = 23.1 Hz). HRMS (MALDI-TOF): m/z 537.2046 [[M-F]$^+$, calculated 537.2021]

4-(4-ethoxyphenyl)-2,2-difluoro-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide(TPEDKBF$_2$OEt)

Compound **TPEDKBF$_2$OEt** was prepared by following the synthetic procedure for compound **TPEDKBF$_2$OMe**. The raw product was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, v/v = 7/4), to afford **TPEDKBF$_2$OEt** (0.52 g) as a yellow solid. Yield: 38%. m.p. 286.0–287.0 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.13 (d,J=12.0, 2H), 7.88 (d,J=8.0, 2H), 7.22-7.214 (m, 11H), 7.07-7.00 (m, 9H), 4.18 (q,J=8.0, 2H), 1.49 (t,J=7.2, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 181.65, 180.75, 165.10, 151.17, 143.55, 142.97, 142.92, 142.74, 139.55, 132.01, 131.52, 131.33, 131.31, 131.25, 129.97, 128.11, 128.03, 127.99, 127.75, 127.24, 126.99, 126.97, 124.06, 115.03, 92.32 64.23, 14.59. ^{19}F NMR (376 MHz, Chloroform-*d*) δ/ppm = -140.80 (d, *J* = 23.1 Hz). HRMS (MALDI-TOF): m/z 551.2197 [[M-F]$^+$, calculated 551.2178]

4-(4-butoxyphenyl)-2,2-difluoro-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide(TPEDKBF$_2$OBu)

Compound **TPEDKBF$_2$OBu** was synthesised by following the synthetic procedure for compound **TPEDKBF$_2$OMe**. The crude product was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, v/v = 7/4), to afford **TPEDKBF$_2$OBu** (0.50 g) as a yellow solid. Yield: 35%. m.p. 287.0–289.0 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.12 (d,J=8.0, 2H), 7.88 (d,J=8.0, 2H), 7.22-7.14 (m, 11H), 7.07-7.01 (m, 9H), 4.10 (t,J=6.4, 2H), 1.87-1.80 (m, 2H), 1.59-1.49 (m, 2H), 1.02 (t,J=7.6, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 181.65, 180.73, 165.32, 159.49, 151.15, 143.54, 142.97, 142.92, 142.74, 139.56, 132.01, 131.52, 131.33, 131.31, 131.25, 129.98, 128.11, 128.03, 127.99, 127.75, 127.24, 126.97, 124.00, 115.05, 92.31, 68.38, 31.03, 19.16, 13.80. ^{19}F NMR (376 MHz, Chloroform-*d*) δ/ppm = -140.82 (d, *J* = 23.1 Hz). HRMS (MALDI-TOF): m/z 579.2515 [[M-F]$^+$, calculated 579.2491]

2,2-difluoro-4-(4-(hexyloxy)phenyl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide(TPEDKBF$_2$OHe)

Compound **TPEDKBF$_2$OHe** was synthesised by following the synthetic procedure for compound **TPEDKBF$_2$OMe**. The crude product was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, v/v = 7/4), to generated highly purified**TPEDKBF$_2$OHe** (0.53 g) as a yellow solid. Yield: 35%. m.p. 287.0–289.0 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.12 (d,J=8.0, 2H), 7.88 (d,J=8.0, 2H), 7.22-7.14 (m, 11H), 7.07-7.00 (m, 9H), 1.88-1.81 (m, 2H), 1.49 (q,J=8.0, 2H), 1.39-1.37 (m, 4H), 0.96-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 181.65, 180.68, 165.33, 143.55, 142.93, 132.01, 131.53, 131.32, 131.25, 129.97, 128.12, 128.04, 127.99, 127.76, 127.24, 127.00, 126.98, 92.33, 68.71, 31.52, 28.98, 25.62, 22.58, 14.03. ^{19}F NMR (376 MHz, Chloroform-*d*) δ/ppm = -140.81 (d, *J* = 23.1 Hz). HRMS (MALDI-TOF): m/z 607.2931 [[M-F]$^+$, calculated 607.2804]

2,2-difluoro-4-(4-(nonyloxy)phenyl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide(TPEDKBF$_2$ONo)

Compound **TPEDKBF$_2$ONo** was synthesised by following the synthetic procedure for compound **TPEDKBF$_2$OMe**. The crude product was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether, v/v = 7/4), to produce highly purified **TPEDKBF$_2$ONo** (0.57 g) as a yellow solid. Yield: 36%. m.p. 287.0–289.0 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ/ppm = 8.12 (d,J=8.0, 2H), 7.88 (d,J=8.0, 2H), 7.22-7.14 (m, 11H), 7.07-7.00 (m, 9H), 4.09 (t,J=8.0, 2H), 1.88-1.81 (m, 2H), 1.51-1.32 (m, 12H), 0.91 (t,J=8.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 181.63， 180.65， 165.33， 164.95， 151.14， 143.54, 142.98， 142.93， 142.75， 139.57， 132.01， 131.53， 131.34, 131.32， 131.25, 131.23， 129.96， 128.12， 128.04， 127.99， 127.76， 126.98， 124.21， 123.96， 115.06， 114.96， 92.34, 68.71， 31.88， 29.51， 29.35， 29.26， 29.02， 25.95， 22.69， 14.14. ^{19}F NMR (376 MHz, Chloroform-*d*) δ/ppm = -140.82 (d, *J* = 23.1 Hz). HRMS (MALDI-TOF): m/z 649.3406 [[M-F]$^+$, calculated 649.3273].

Table S1. HOMO/LUMO energy levels of **TPEDKBF$_2$OMe, TPEDKBF$_2$OEt, TPEDKBF$_2$OBu, TPEDKBF$_2$OHe** and **TPEDKBF$_2$ONo.**

	gap/(eV)	LUMO (eV)	HOMO(eV)[d]
TPEDKBF$_2$OMe	1.478	-3.635	-5.113
TPEDKBF$_2$OEt	1.488	-3.605	-5.094
TPEDKBF$_2$OBu	1.622	-3.404	-5.026
TPEDKBF$_2$OHe	1.627	-3.388	-5.015
TPEDKBF$_2$ONo	1.630	-3.388	-5.018

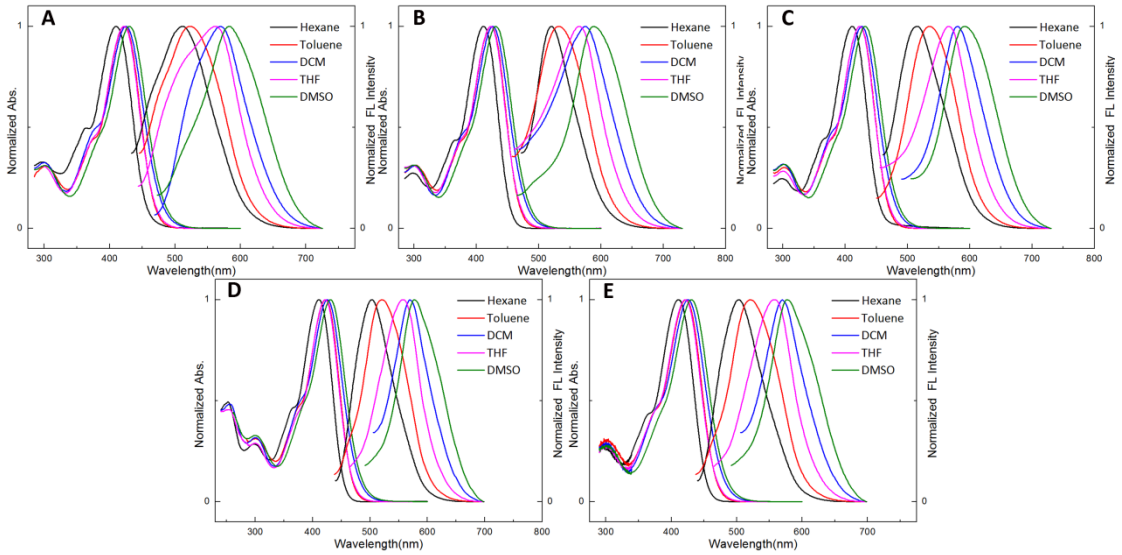

Figure S1. Normalized UV-vis absorption and fluorescence emission spectra of **TPEDKBF$_2$OMe (A), TPEDKBF$_2$OEt (B), TPEDKBF$_2$OBu (C), TPEDKBF$_2$OHe (D) and TPEDKBF$_2$ONo (E)** in different solvents (1.0×10^{-5} mol/L), fluorescence were excited at 420nm.

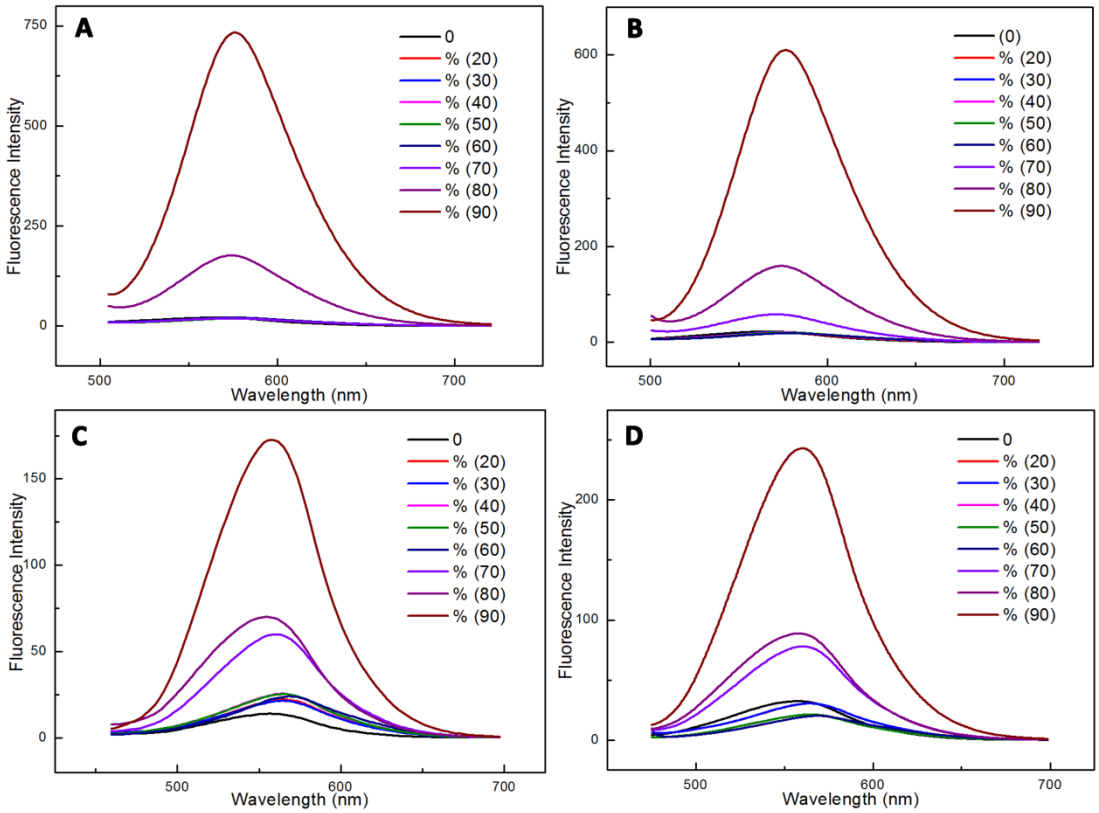

Figure S2. Fluorescence spectra of **TPEDKBF$_2$OEt (A), TPEDKBF$_2$OBu (B), TPEDKBF$_2$OHe (C) and TPEDKBF$_2$ONo (D)** in THF and THF/water mixtures. Luminogen concentration: 1×10^{-5} mol/L ; excitation wavelength: 420 nm.

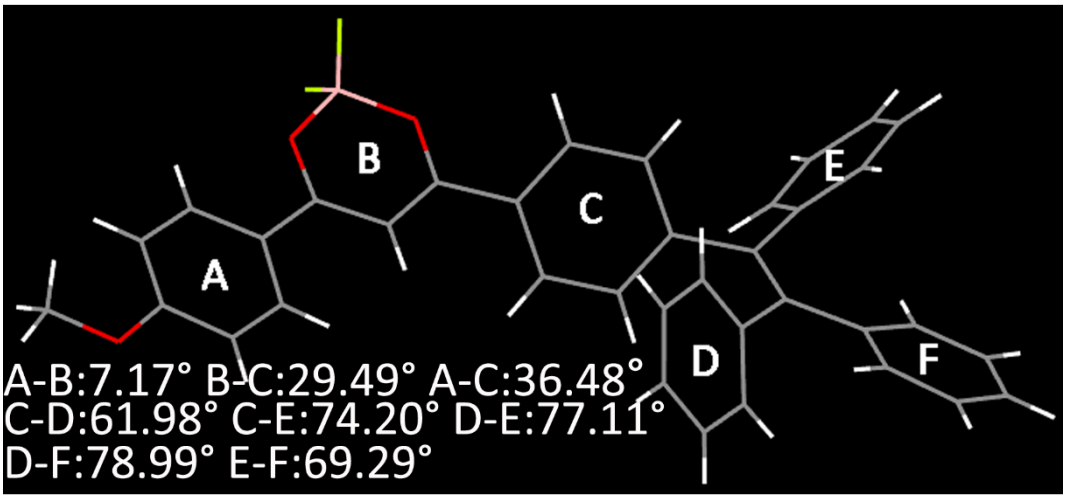

Figure S3. Molecular conformation of **TPEDKBF$_2$OMe** in the crystal.

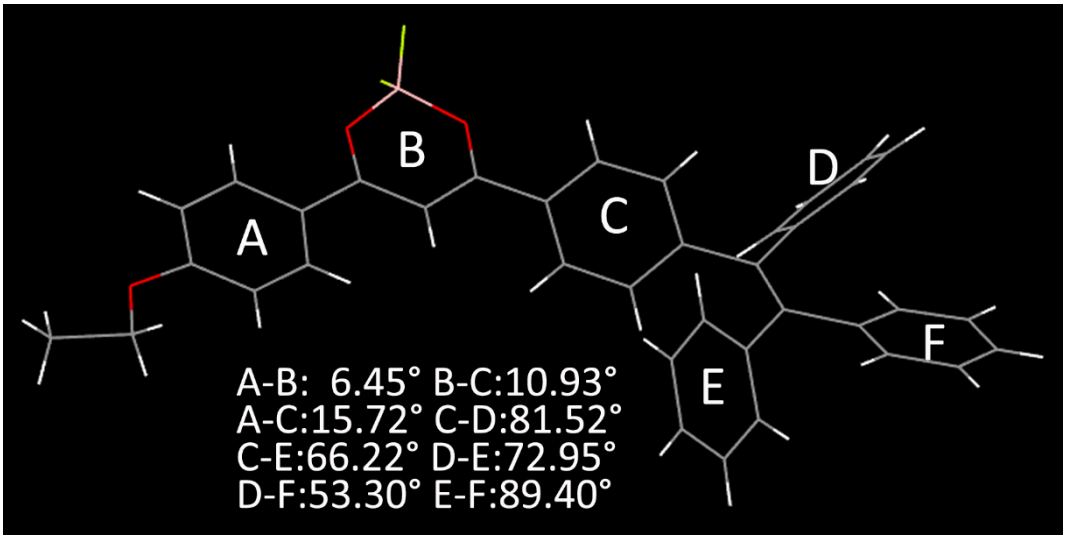

Figure S4. Molecular conformation of **TPEDKBF$_2$OEt** in the crystal.

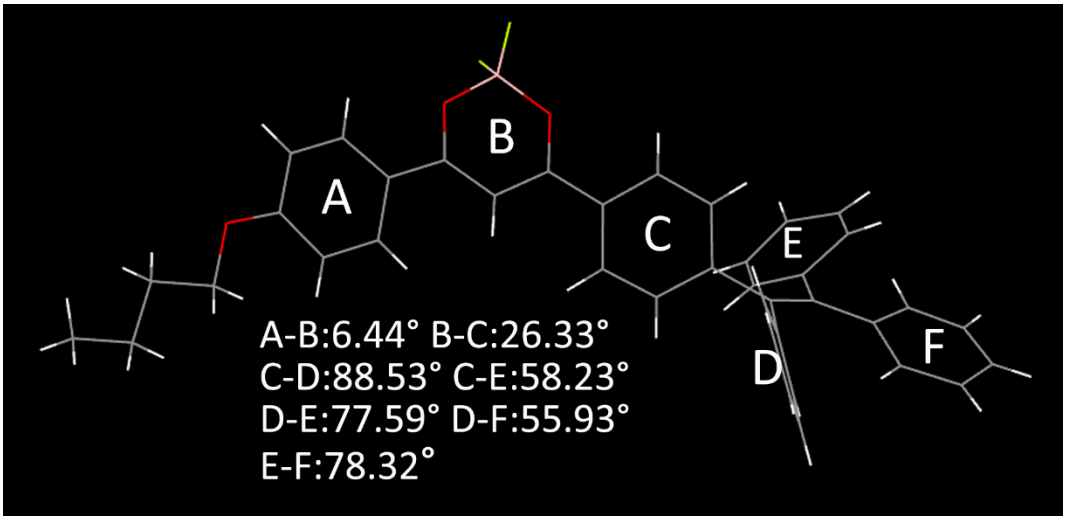

Figure S5. Molecular conformation of **TPEDKBF$_2$OBu** in the crystal.

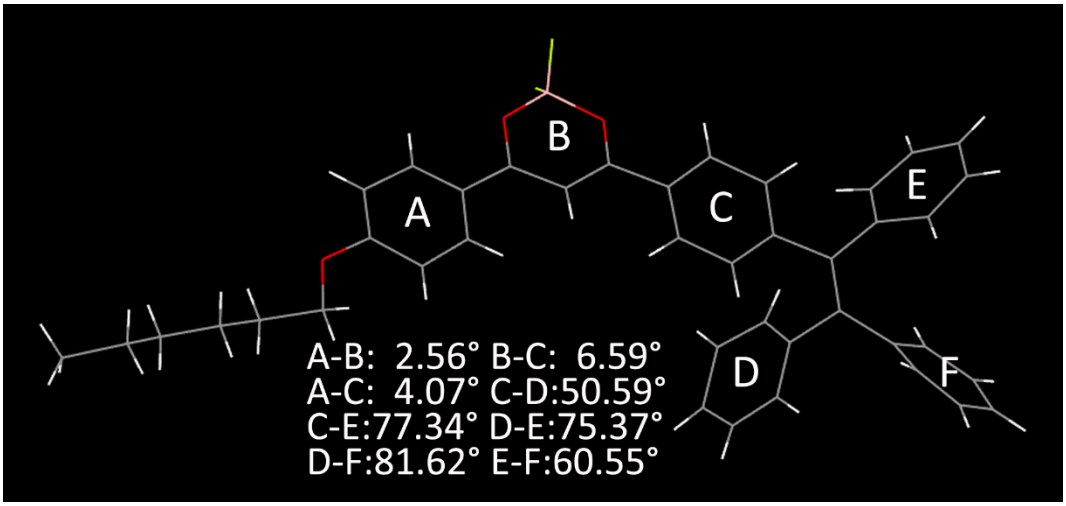

Figure S6. Molecular conformation of **TPEDKBF$_2$OHe** in the crystal.

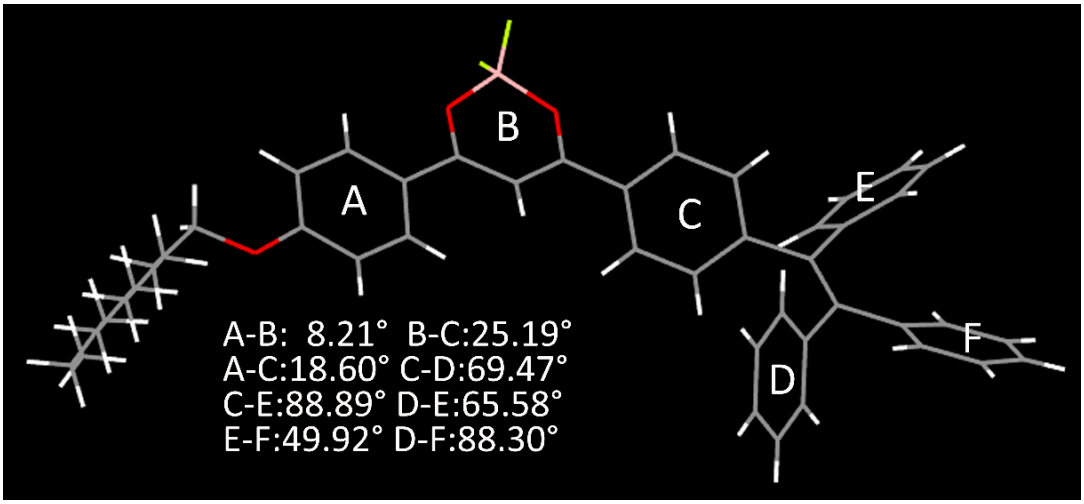

Figure S7. Molecular conformation of **TPEDKBF$_2$ONo** in the crystal.

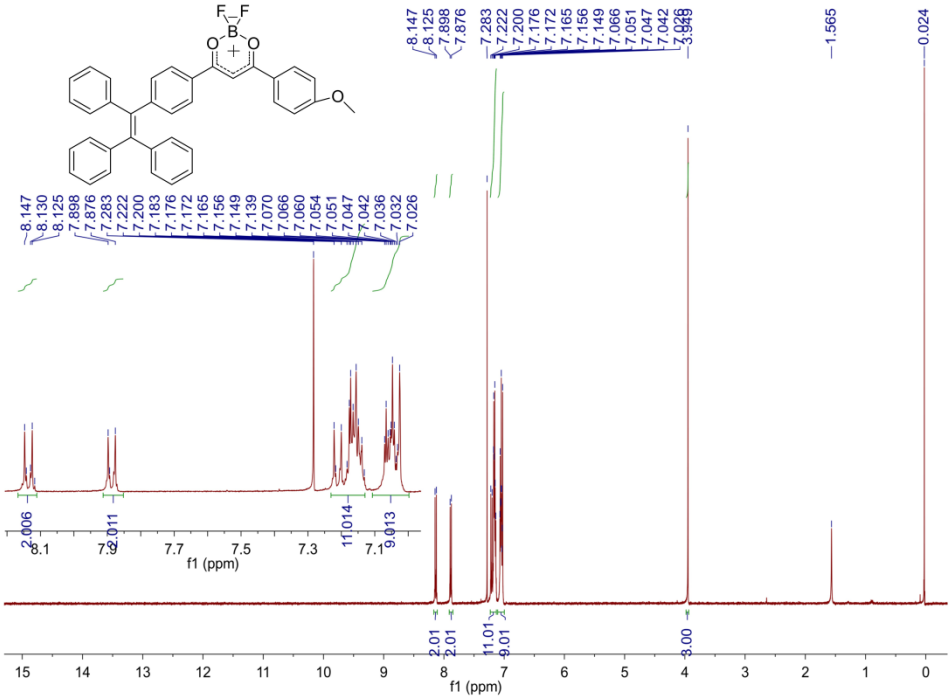

Figure S8 ^{1}H NMR (400 MHz) spectrum of compound **TPEDKBF$_2$OMe** in $CDCl_3$.

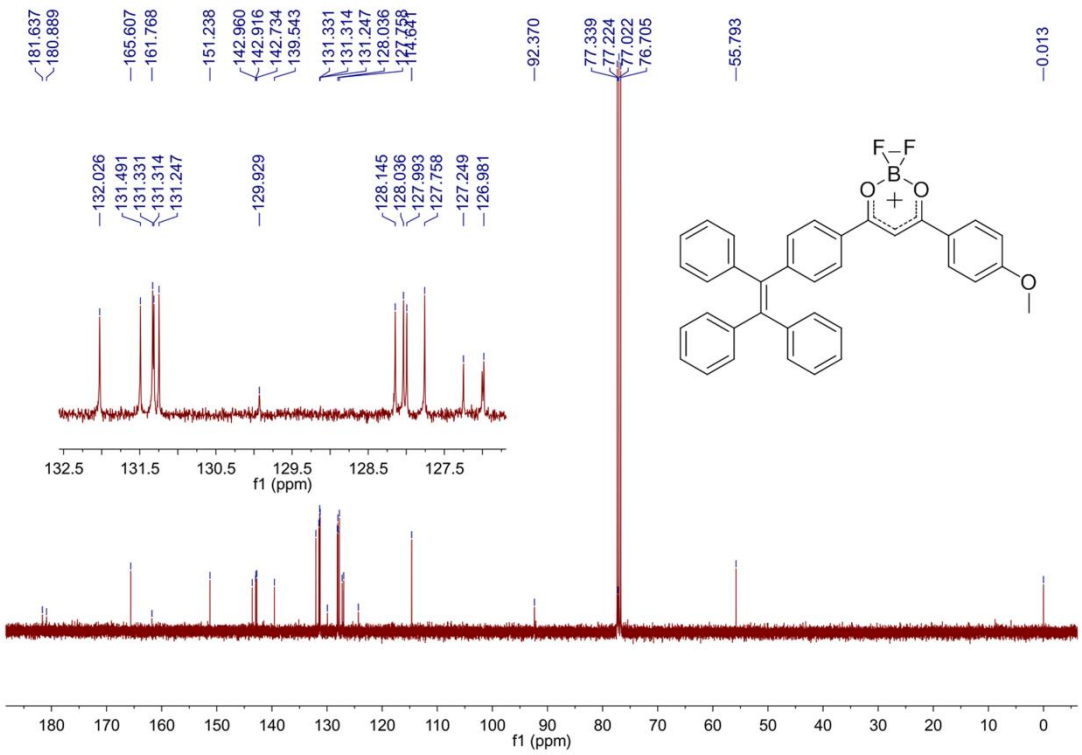

Figure S9 ^{13}C NMR (100 MHz) spectrum of compound **TPEDKBF$_2$OMe** in $CDCl_3$.

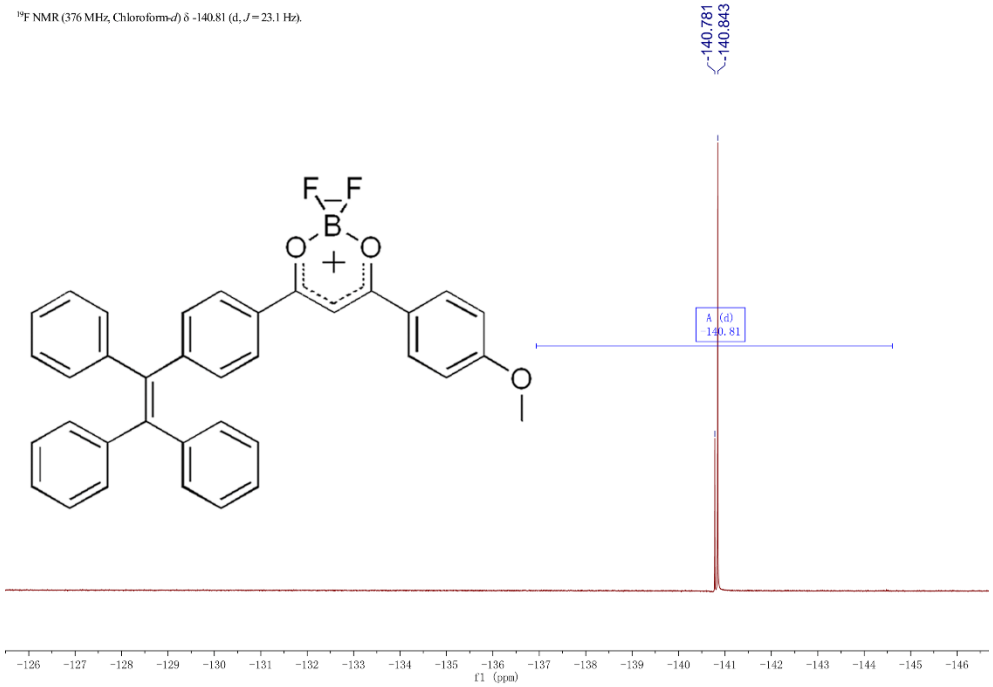

Figure S10 ^{19}F NMR (376 MHz) spectrum of compound **TPEDKBF$_2$OMe** in $CDCl_3$.

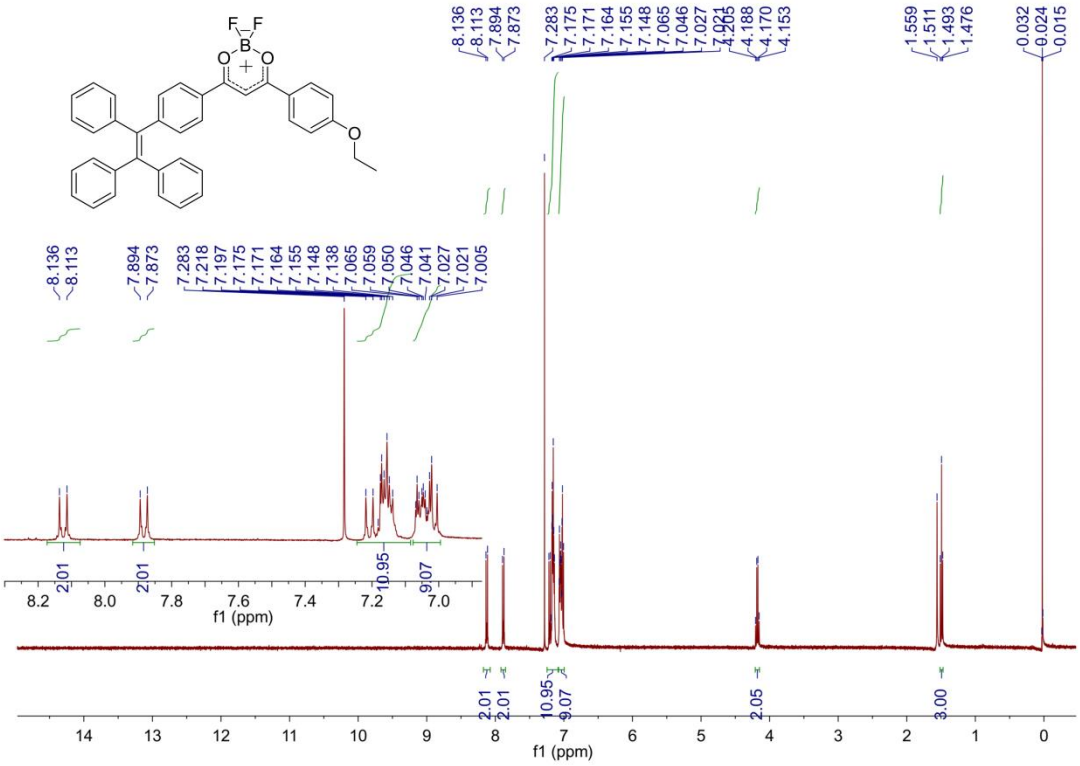

Figure S11 ^{1}H NMR (400 MHz) spectrum of compound **TPEDKBF$_2$OEt** in $CDCl_3$.

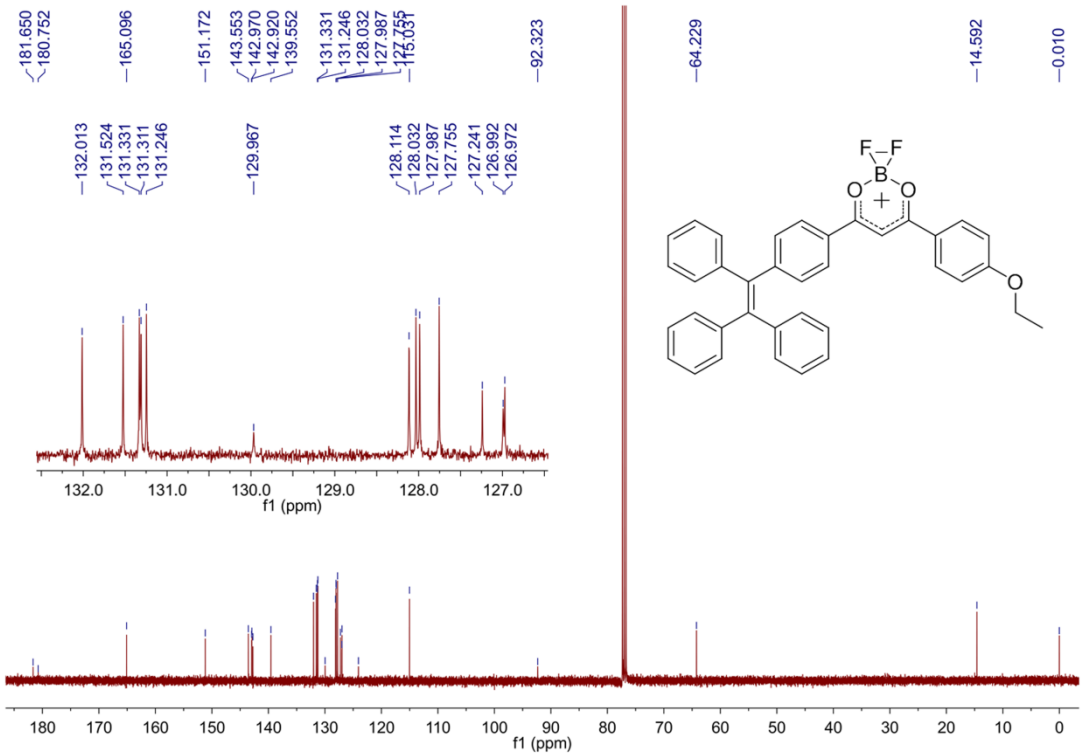

Figure S12 ^{13}C NMR (100 MHz) spectrum of compound **TPEDKBF$_2$OEt** in $CDCl_3$.

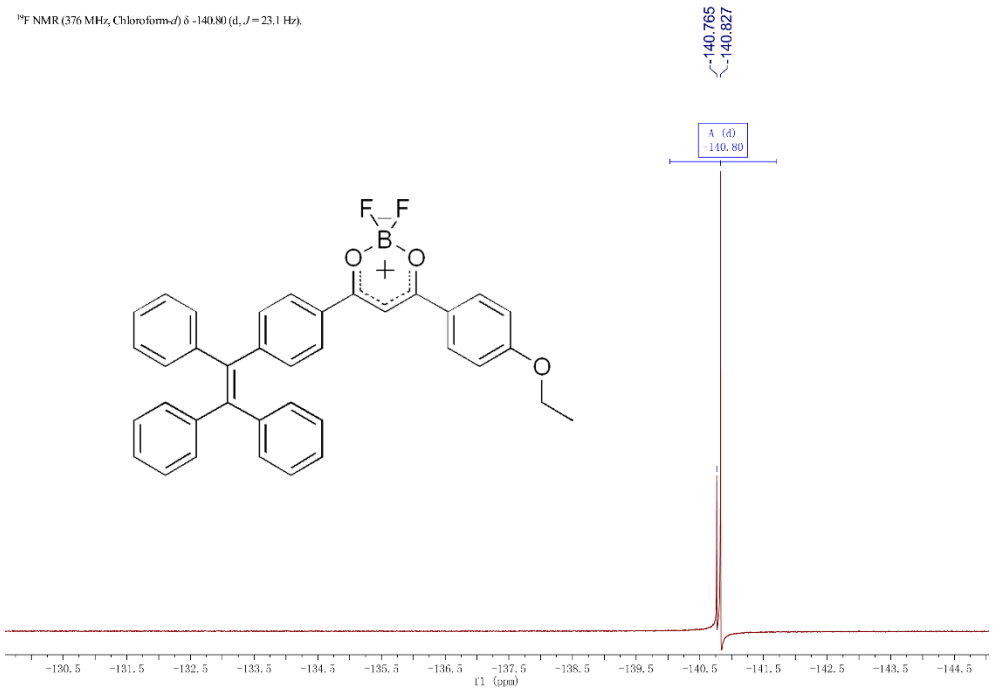

Figure S13 ^{19}F NMR (376 MHz) spectrum of compound **TPEDKBF$_2$OEt** in $CDCl_3$.

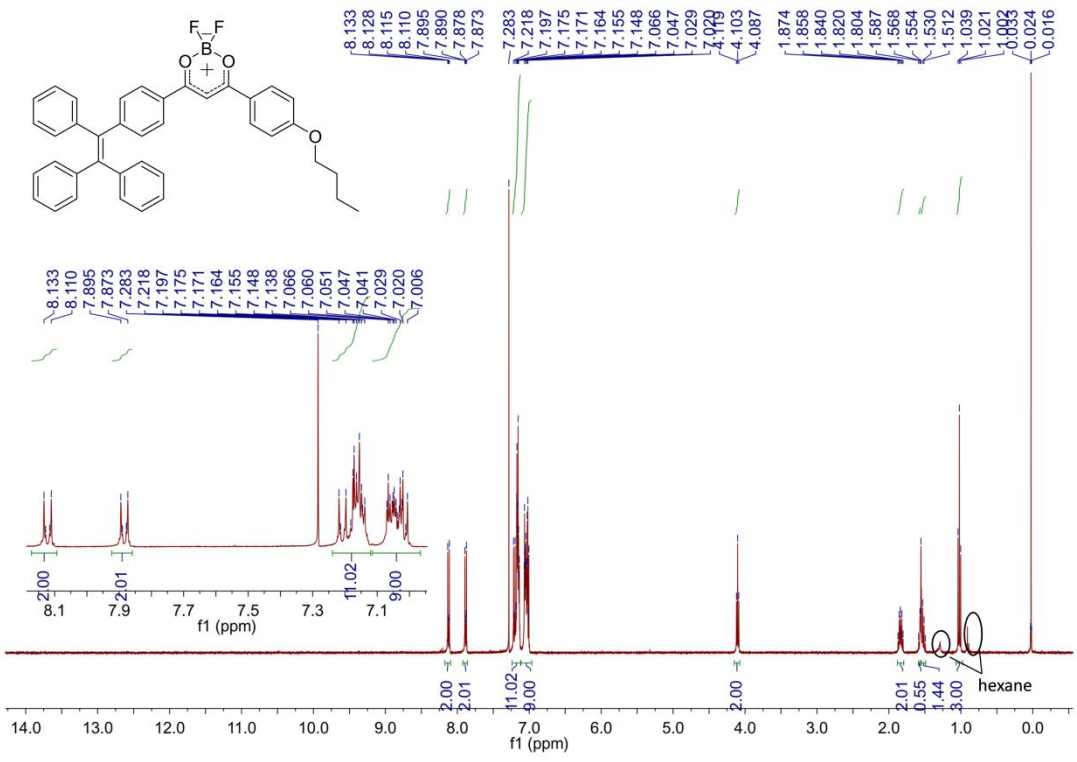

Figure S14 ^{1}H NMR (400 MHz) spectrum of compound **TPEDKBF$_2$OBu** in $CDCl_3$.

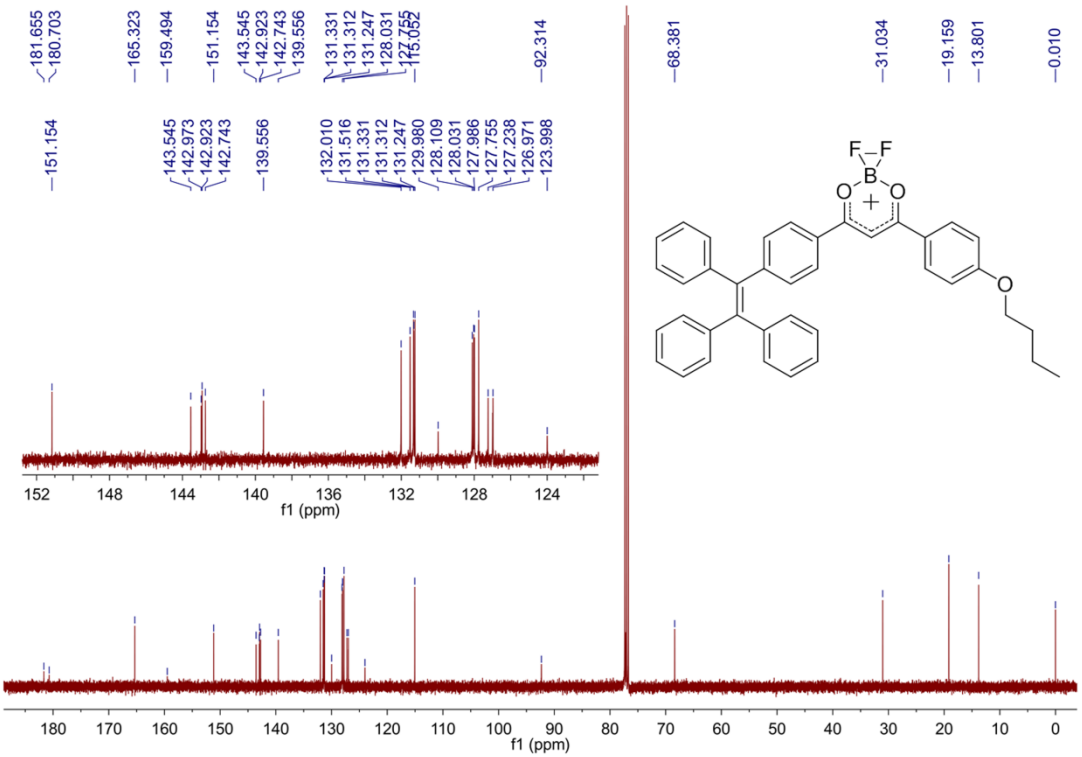

Figure S15 ^{13}C NMR (100 MHz) spectrum of compound **TPEDKBF$_2$OBu** in $CDCl_3$.

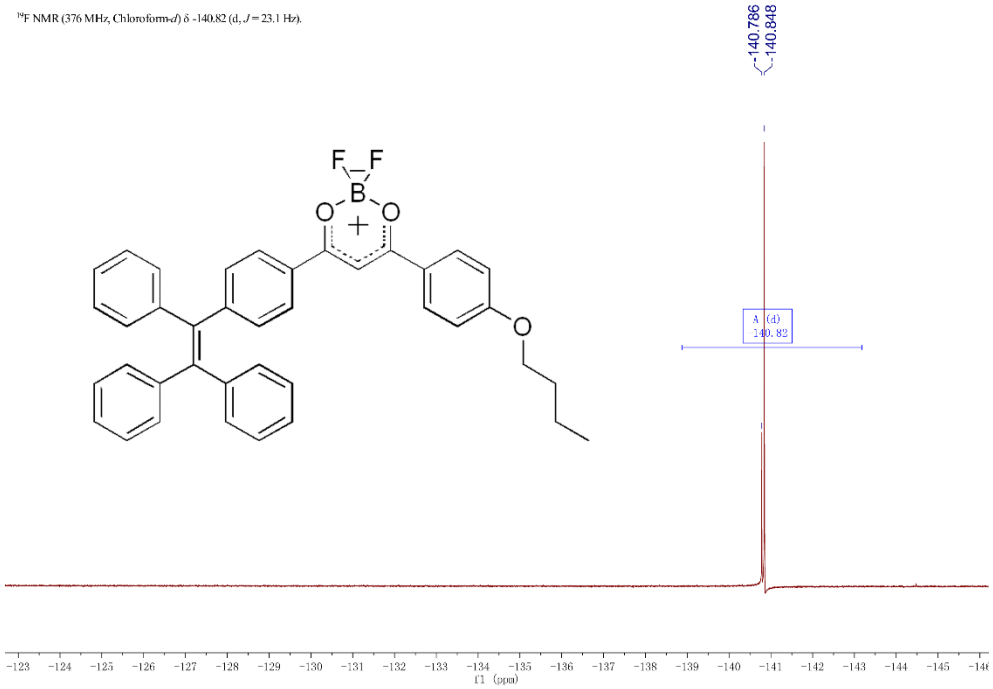

Figure S16 ^{19}F NMR (376 MHz) spectrum of compound **TPEDKBF$_2$OBu** in $CDCl_3$.

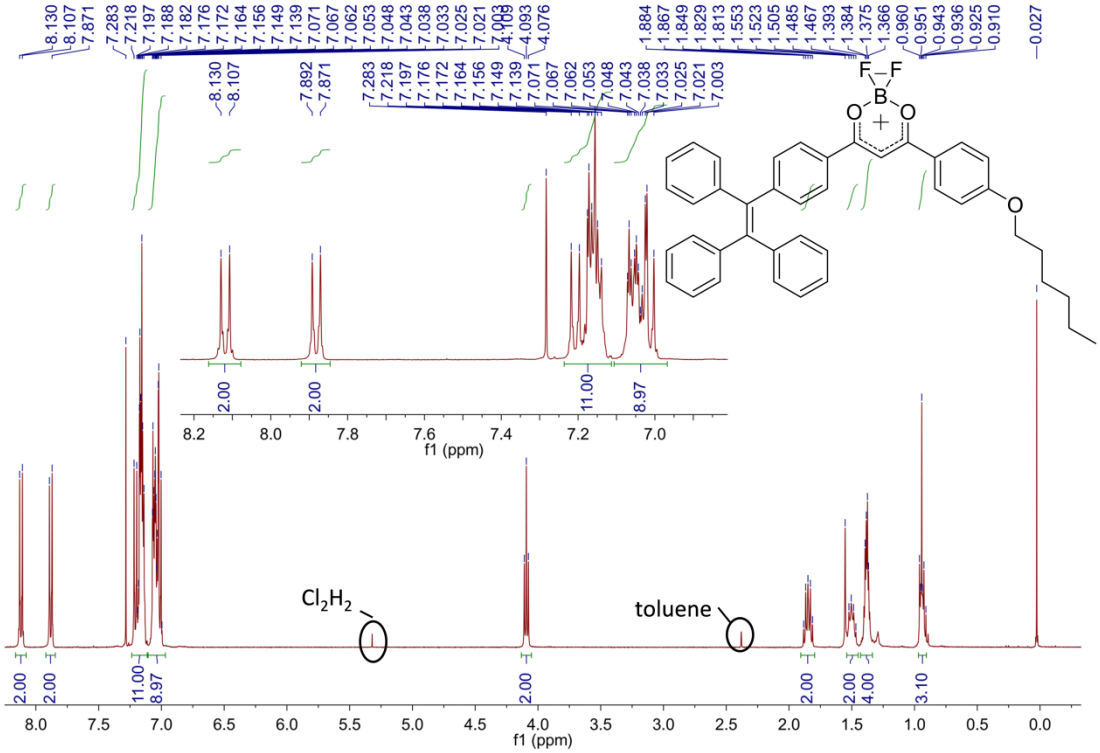

Figure S17 ^{1}H NMR (400 MHz) spectrum of compound **TPEDKBF$_2$OHe** in $CDCl_3$.

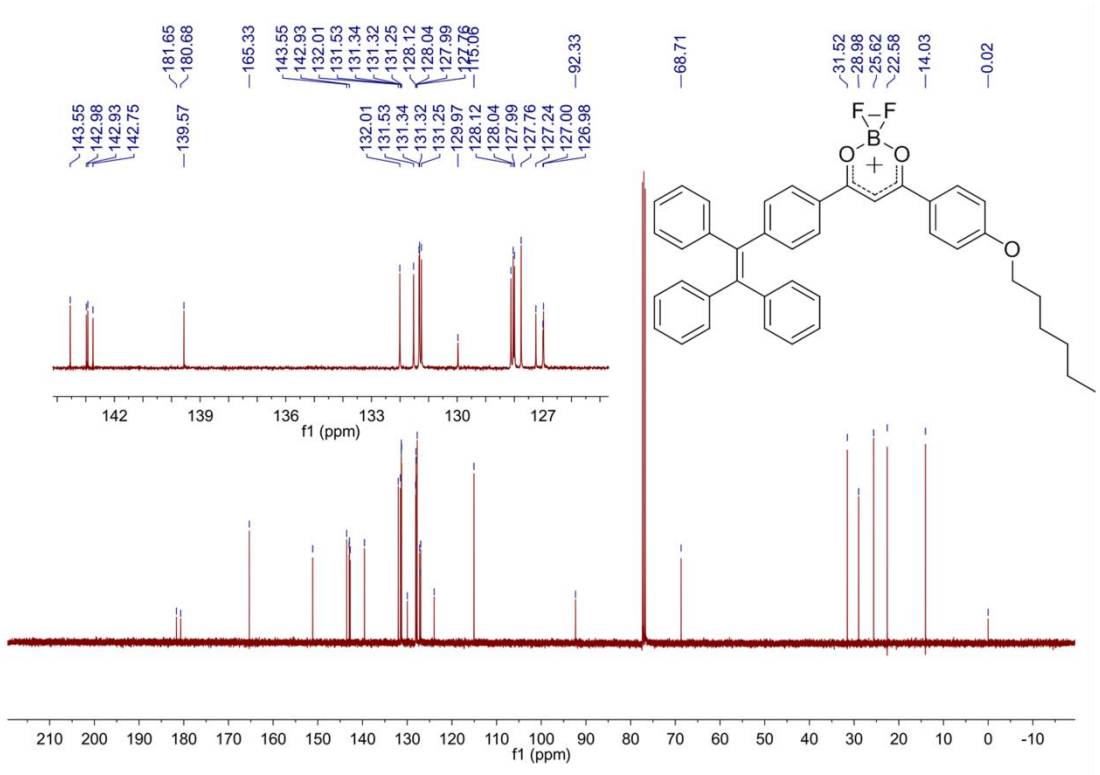

Figure S18 ^{13}C NMR (100 MHz) spectrum of compound **TPEDKBF$_2$OHe** in $CDCl_3$.

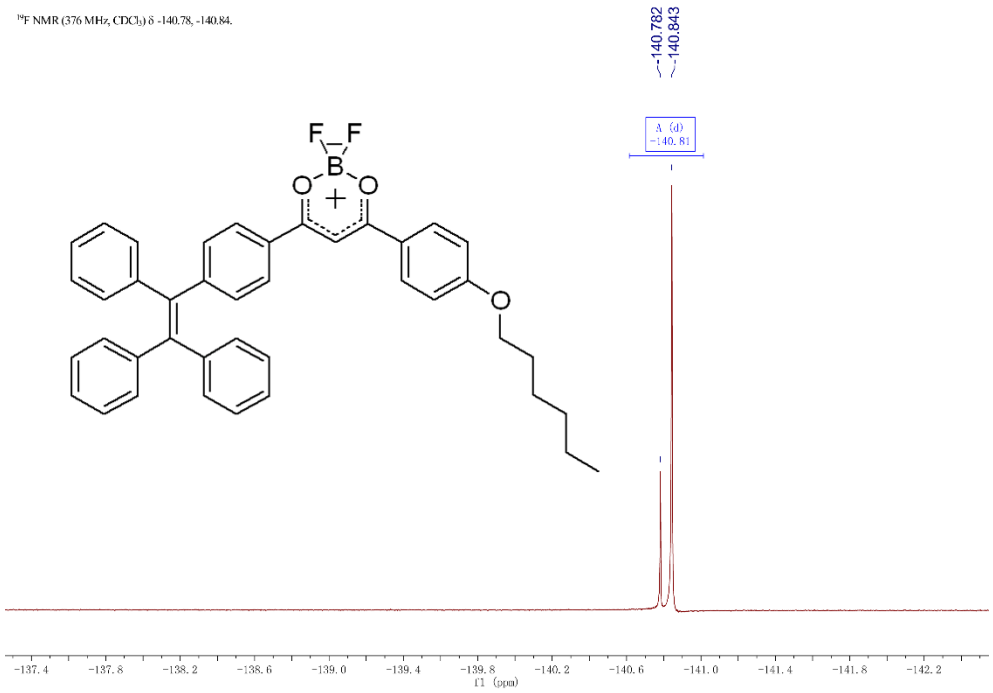

Figure S19 ^{19}F NMR (376 MHz) spectrum of compound **TPEDKBF$_2$OHe** in $CDCl_3$.

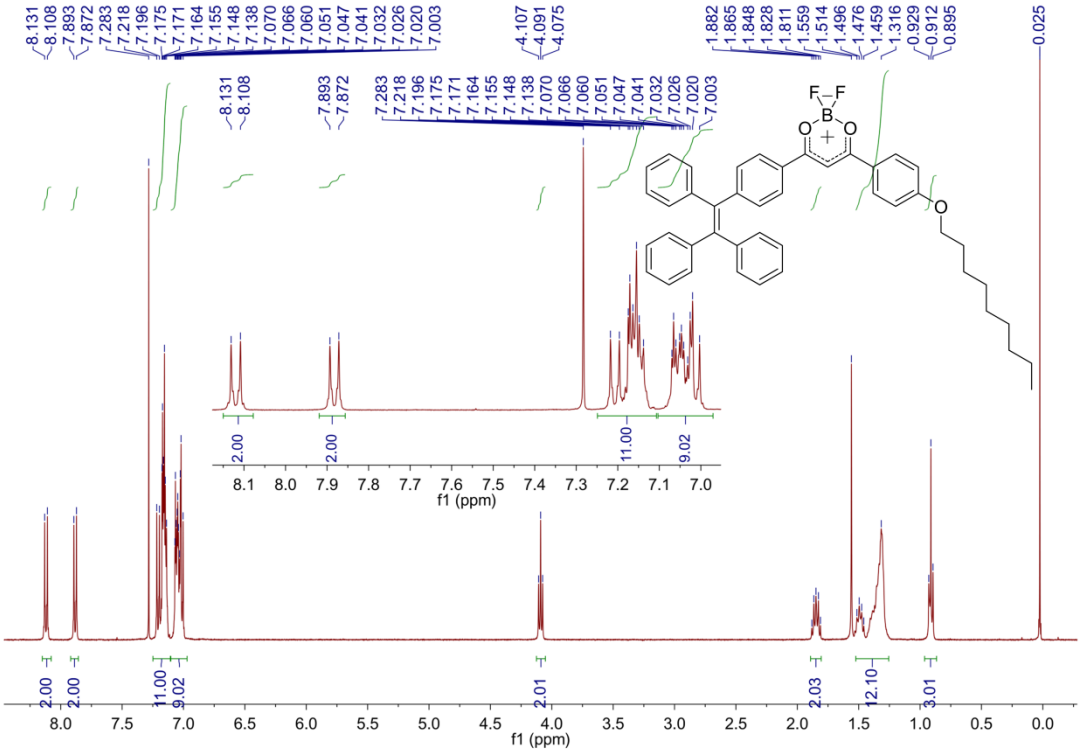

Figure S20 ^{1}H NMR (400 MHz) spectrum of compound **TPEDKBF$_2$ONo** in $CDCl_3$.

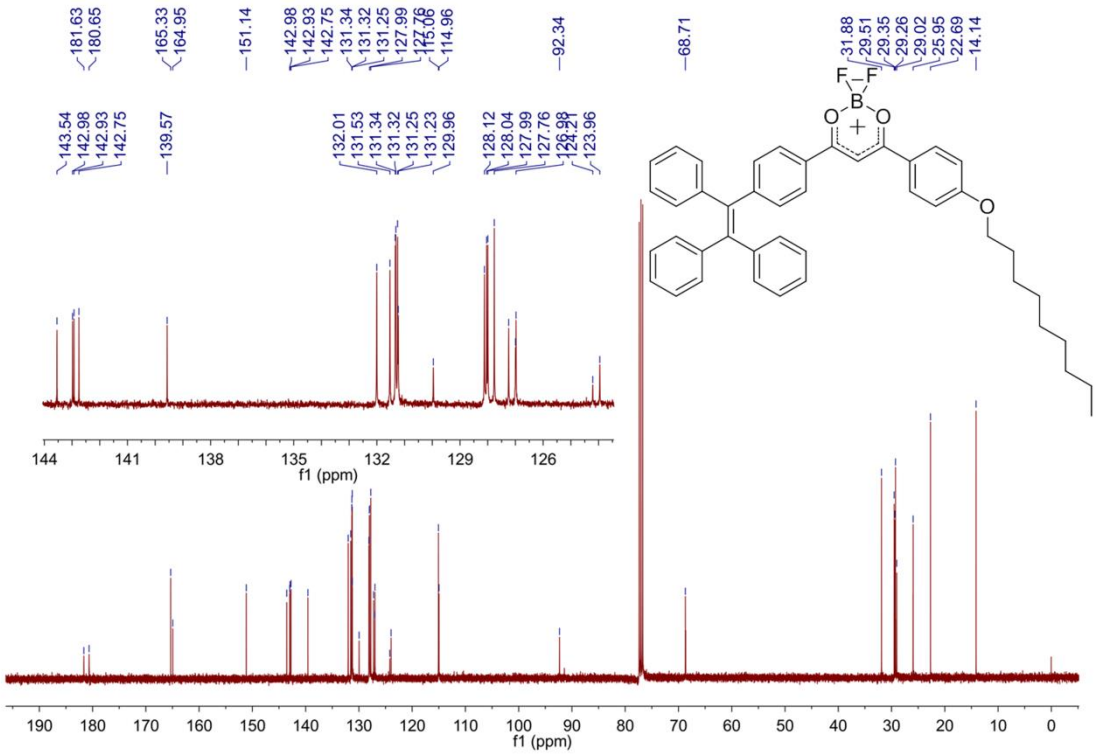

Figure S21 ^{13}C NMR (100 MHz) spectrum of compound **TPEDKBF$_2$ONo** in $CDCl_3$.

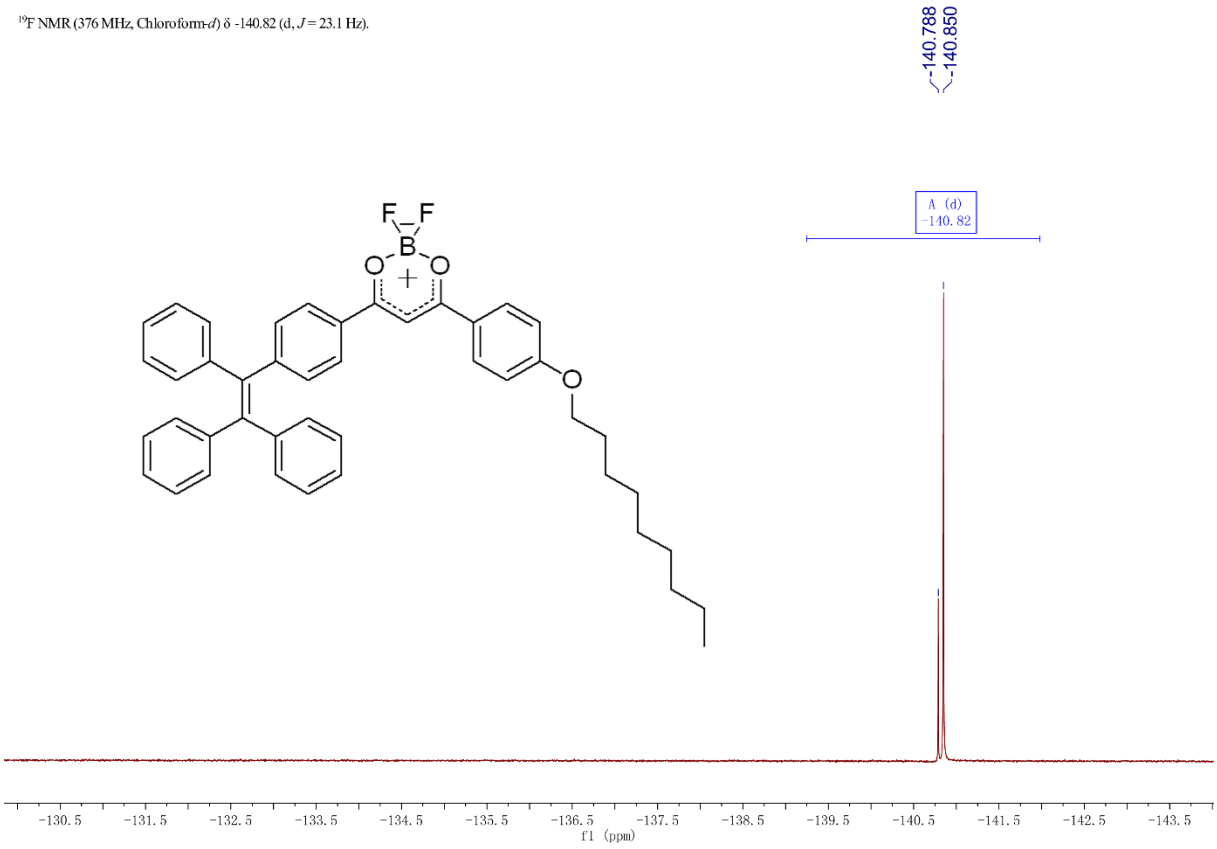

Figure S22 ^{19}F NMR (376 MHz) spectrum of compound **TPEDKBF$_2$ONo** in $CDCl_3$.

Figure S23 MALDI/TOF MS spectrum of compound **TPEDKBF$_2$OMe**.

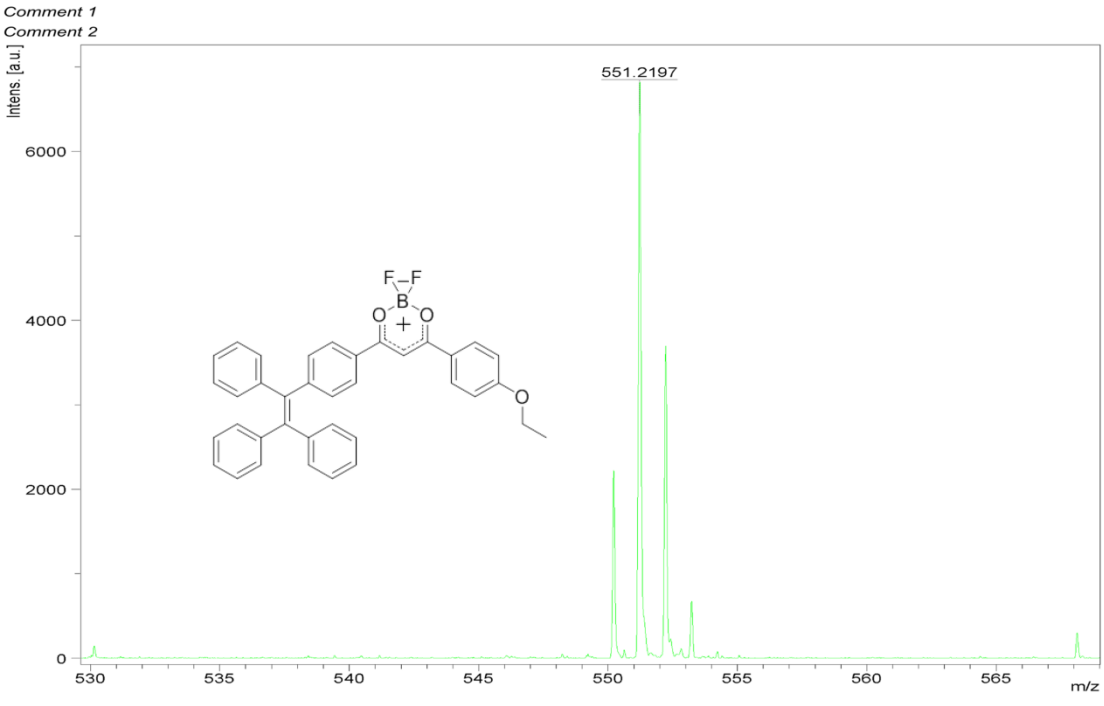

Figure S24 MALDI/TOF MS spectrum of compound **TPEDKBF$_2$OEt**.

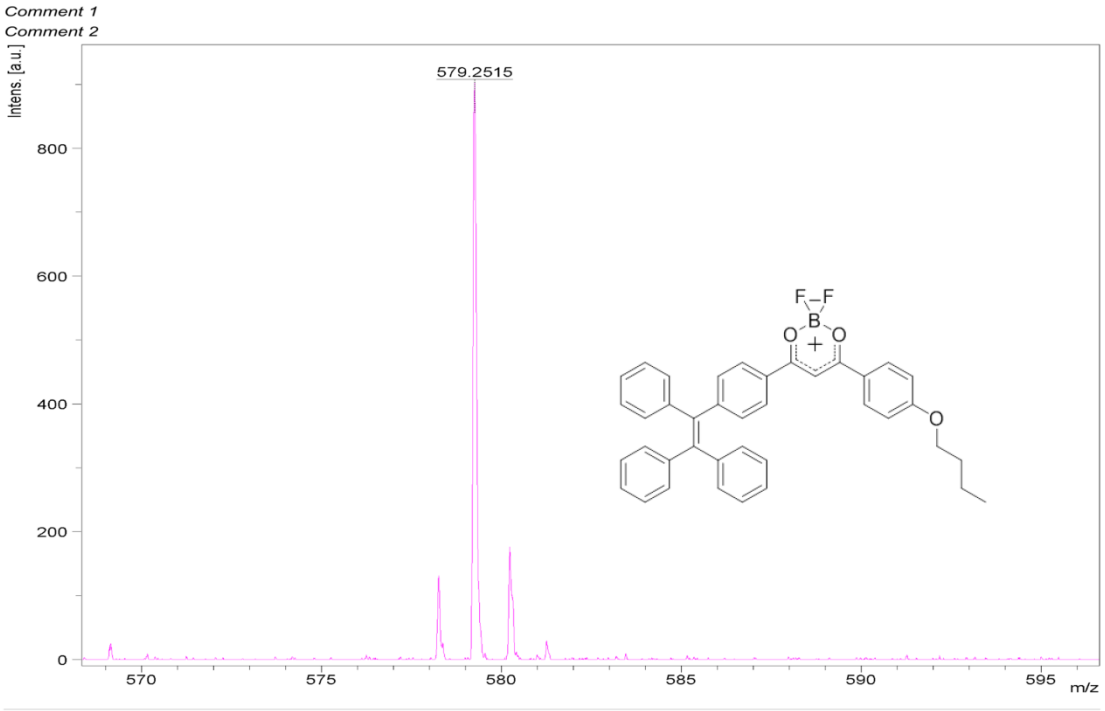

Figure S25 MALDI/TOF MS spectrum of compound **TPEDKBF$_2$OBu**.

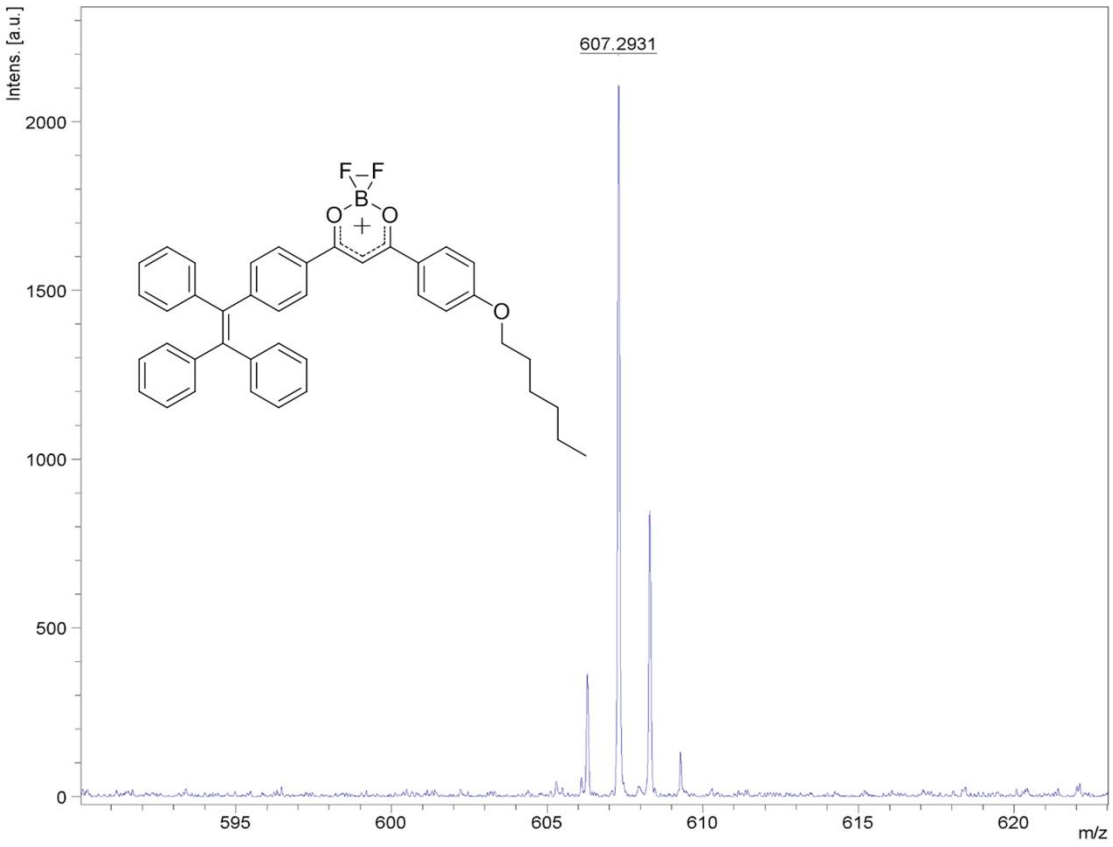

Figure S26 MALDI/TOF MS spectrum of compound **TPEDKBF$_2$OHe**.

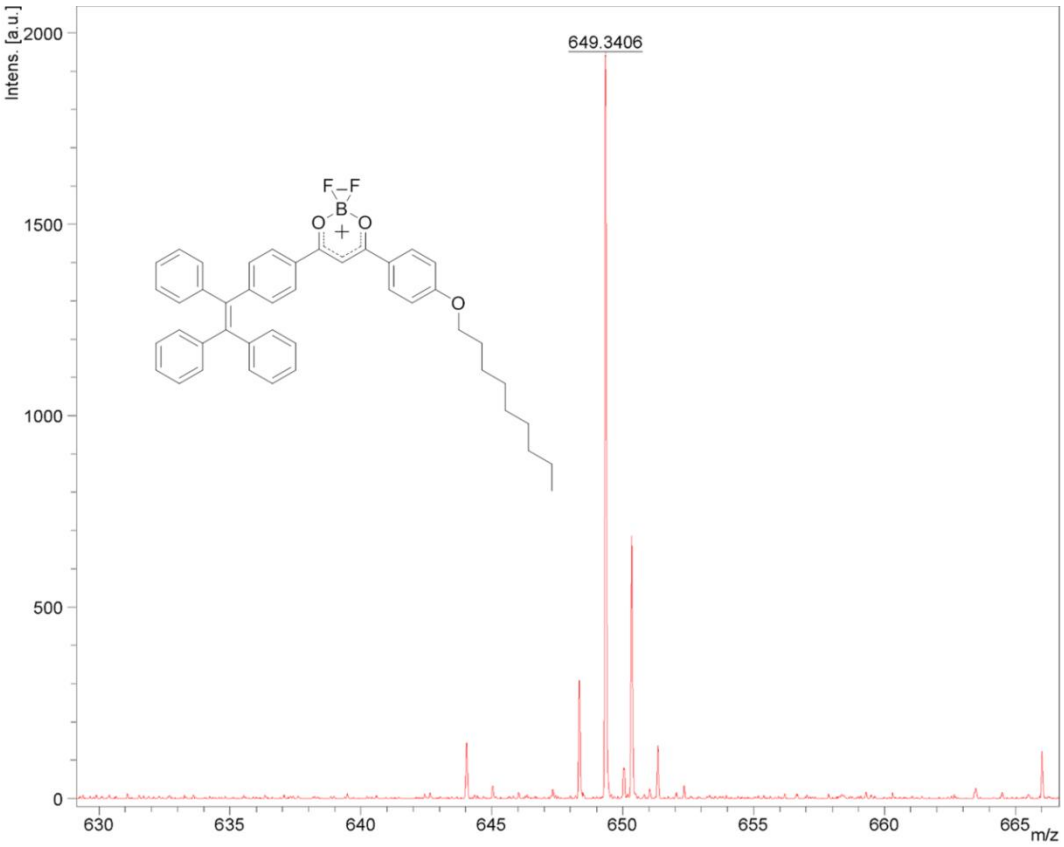

Figure S27 MALDI/TOF MS spectrum of compound **TPEDKBF$_2$ONo**.