

Supporting Information For: The deep insights into polymorphism initiated by exploring multicolor conversion materials

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Experimental

Measurement and characterization

The UV-vis spectra were determined on a Mapada UV-3200pcs spectrophotometer. Fluorescence measurements were taken on Agilent Cary Eclipse fluorescence spectrophotometer. Fluorescent quantum yields of solids were obtained by FLs980 full-featured Steady/Transient Fluorescence Spectrometer (Edinburgh). ¹H NMR spectra and ¹³C NMR spectra were obtained with a Varian inova instrument at 400 MHz and 100 MHz using tetramethylsilane (TMS) as the internal standard, and CDCl₃ as the solvent in all cases. Glass transition temperature and melting point were 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 K α radiation in the range of $10^\circ < 2\theta < 90^\circ$.

Materials and Synthesis

THF and CH₂Cl₂ were dried according to standardized procedures previously described. 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 silicagel (200-300 mesh), and crystallization from analytical grade solvents. Reactions were monitored by using thin layer chromatography (TLC).

According to the reported method, benzophenone was used as a reagent to synthesize TPE; then TPE and acetyl chloride were acylated by Friedel-Crafts to obtain compound Ac-TPE; condensation with methyl fumarate and NaH (60%) by Claisen. The boron complexes were synthesized to produce a β-diketones intermediate which were then boronated with BF₃·OEt₂ in CH₂Cl₂. The target molecules were characterized by ¹H NMR, ¹³C NMR.

2,2-difluoro-4-(furan-2-yl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinane (TPEB2F)

Adding methyl 2-furoate (0.98g, 7.8mmol) to THF solution in which acetyl-TPE (1g, 2.6mmol) is dissolved, then NaH (60% 0.16 g, 3.9 mmol) was quickly added, and the mixture was heated to 75 °C in an oil bath under argon and refluxed for 12 hours. TLC detection reaction progress (petroleum ether/ ethyl acetate=15/1). After completion of the reaction, the reaction solution was cooled to room temperature, and added diluted hydrochloric acid, poured into ice water, extracted with dichloromethane, and organic layer was collected. The organic layer was dried over anhydrous Na₂SO₄, the solvent was removed under reduced pressure, brown oily

β -diketone precursor was obtained. The diketone precursor was dried under vacuum and then dissolved in 20 ml of dichloromethane, added boron trifluoride diethyl ether complex to the above solution, stirred at room temperature in argon atmosphere for 24 hours. The mixture was quenched by the addition of water, and the organic layer was collected and dried over anhydrous Na_2SO_4 . The crude product was purified by column chromatography (silica gel, 5:1 v/v, petroleum ether/ ethyl acetate) to afford product **TPEB2F** as orange solid, yield 63%, m.p. 190.0–192.0°C. ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.82 (m, 2H), 7.75 (dd, $J=1.7, 0.8$ Hz, 1H), 7.57 (dd, $J=3.7, 0.8$ Hz, 1H), 7.24-7.10 (m, 11H), 7.08-6.97 (m, 7H), 6.71 (dd, $J=3.7, 1.7$ Hz, 1H) (**Fig. S5**). ^{13}C NMR (101 MHz, CDCl_3) δ 182.06, 170.89, 151.79, 149.28, 148.46, 143.79, 142.91, 142.86, 142.68, 139.50, 132.10, 131.33, 131.31, 131.24, 129.56, 128.43, 128.06, 128.02, 127.76, 127.31, 127.05, 127.02, 121.33, 114.22, 92.43, 0.01(**Fig. S6**). HRMS (MALDI-TOF): m/z 539.1598, $[\text{M}+\text{Na}]^+$, calculated 539.1606(**Fig. S11**).

2,2-difluoro-4-(furan-3-yl)-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,13,214-dioxaborinine (TPEB3F)

Compound **TPEB3F** was prepared by following the synthetic procedure for compound **TPEB2F**.

Methyl 3-Furancarboxylate was condensed with acetyl-TPE to give β -diketone. The brown crude β -diketone precursor coordinated with $\text{BF}_3\cdot\text{OEt}_2$ in CH_2Cl_2 , the crude product was purified by column chromatography (silica gel, 5:1 v/v, petroleum ether/ ethyl acetate) to afford **TPEB3F** as a light green solid, yield 58%, m.p. 208.2–210.8°C ^1H NMR (400 MHz, CDCl_3) δ 8.31 (t, $J=1.1$ Hz, 1H), 7.84 (d, $J=8.6$ Hz, 2H), 7.55 (t,

J=1.7 Hz, 1H), 7.23-7.11 (m, 11H), 7.05-6.99 (m, 6H), 6.84 (dd, J=2.1, 0.8 Hz, 1H), 6.72 (s, 1H) (**Fig. S7**). ^{13}C NMR (101 MHz, CDCl_3) δ 182.02, 177.69, 154.28, 151.82, 149.26, 145.26, 143.80, 142.88, 142.86, 142.66, 139.45, 132.11, 131.32, 131.24, 129.33, 128.36, 128.06, 128.03, 127.78, 127.31, 127.07, 127.03, 122.62, 108.33, 93.92(**Fig. S8**). HRMS (MALDI-TOF): m/z 539.1605, $[\text{M}+\text{Na}]^+$, calculated 539.1606(**Fig. S12**).

Table S1. Peak absorption/emission wavelengths (λ , in nm) of **TPEB2F** and **TPEB3F** in hexane, DCM, THF and DMSO.

	TPEB2F		TPEB3F	
	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$
Hexane	363,418	509	348,403	495
DCM	375,429	623	359,414	612
THF	373,425	590	358,407	550
DMSO	381,433	649	368,414	633

Table S2. Peak emission wavelengths (λ , in nm) and quantum yields (Φ) of five crystals in different solid states.

	2R	3Y	3R	3N	3F
λ_{solid}	560	553	553	553	553
$\lambda_{\text{crystals}}$	586	547	580	617	602
λ_{sg}	589	536	566	569	574
λ_{ground}	608	587	567	609	611
λ_{fumed}	584	566	572	592	575
λ_{heated}	584	565	566	574	575
$\Delta\lambda_1$	3	-11	-14	-48	-28
$\Delta\lambda_2$	22	40	-13	-8	9
Φ_{crystals}	0.093	0.192	0.016	--	--
Φ_{ground}	0.366	0.160	0.092	--	--

$\lambda_{\text{sg}} = \lambda_{\text{slightly ground}}$, $\Delta\lambda_1 = \lambda_{\text{sg}} - \lambda_{\text{crystals}}$, $\Delta\lambda_2 = \lambda_{\text{ground}} - \lambda_{\text{crystals}}$, "--", represent blue shift. 0.092 is the quantum yields of 3R after slightly grinding.

Table S3. Energy level, minimum energy and dipole moment of each crystal, **2Ya-d** were constructed based on crystals **3Y**.

	Dipole(dye)		Etotal(a.u.)
	Single molecule	Molecular pair	
2R	7.4611	0.0001	-3443.57201214
2Y _a		1.3942	-3443.56998296

2Y _b		5.6834	-3443.57089941
2Y _c		5.3682	-3443.57149546
2Y _d		3.5036	-3443.57270219
3F		0.0002	-3443.57059234
3N		0.0002	-3443.57059235
3R	7.2363	0.0000	-3443.57046053
3Y	8.1469	0.2270	-3443.57144147

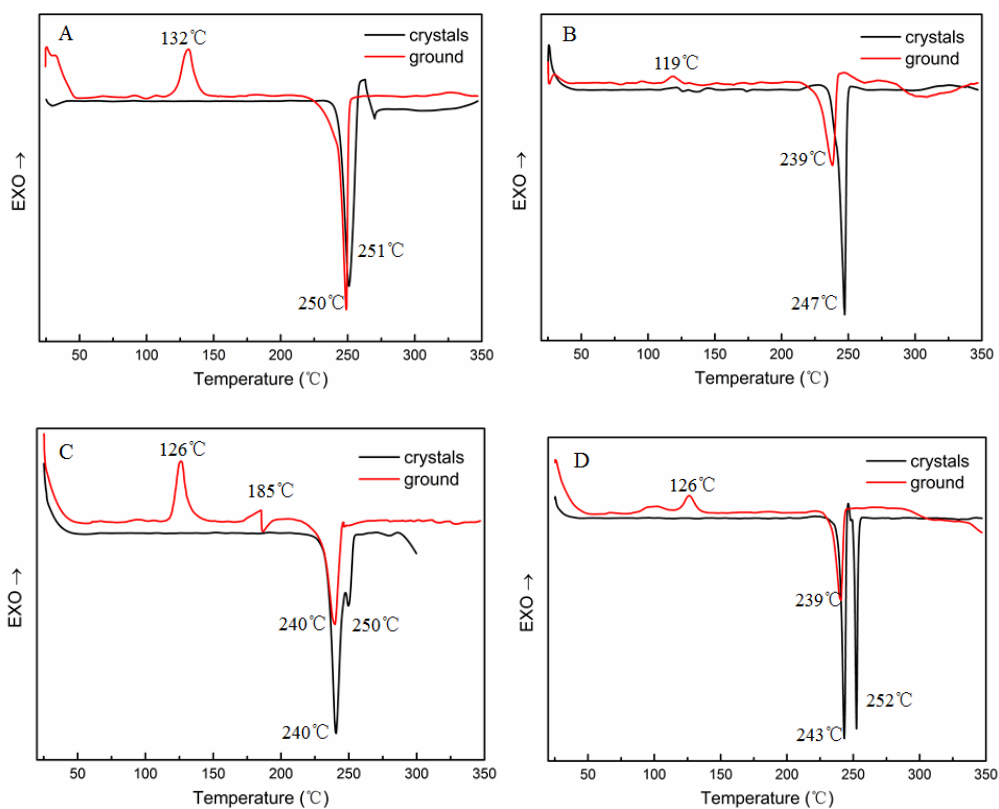


Fig S1. DSC thermograms of (A) 2R, (B) 3Y, (C) 3R, (D) 3N in different state.

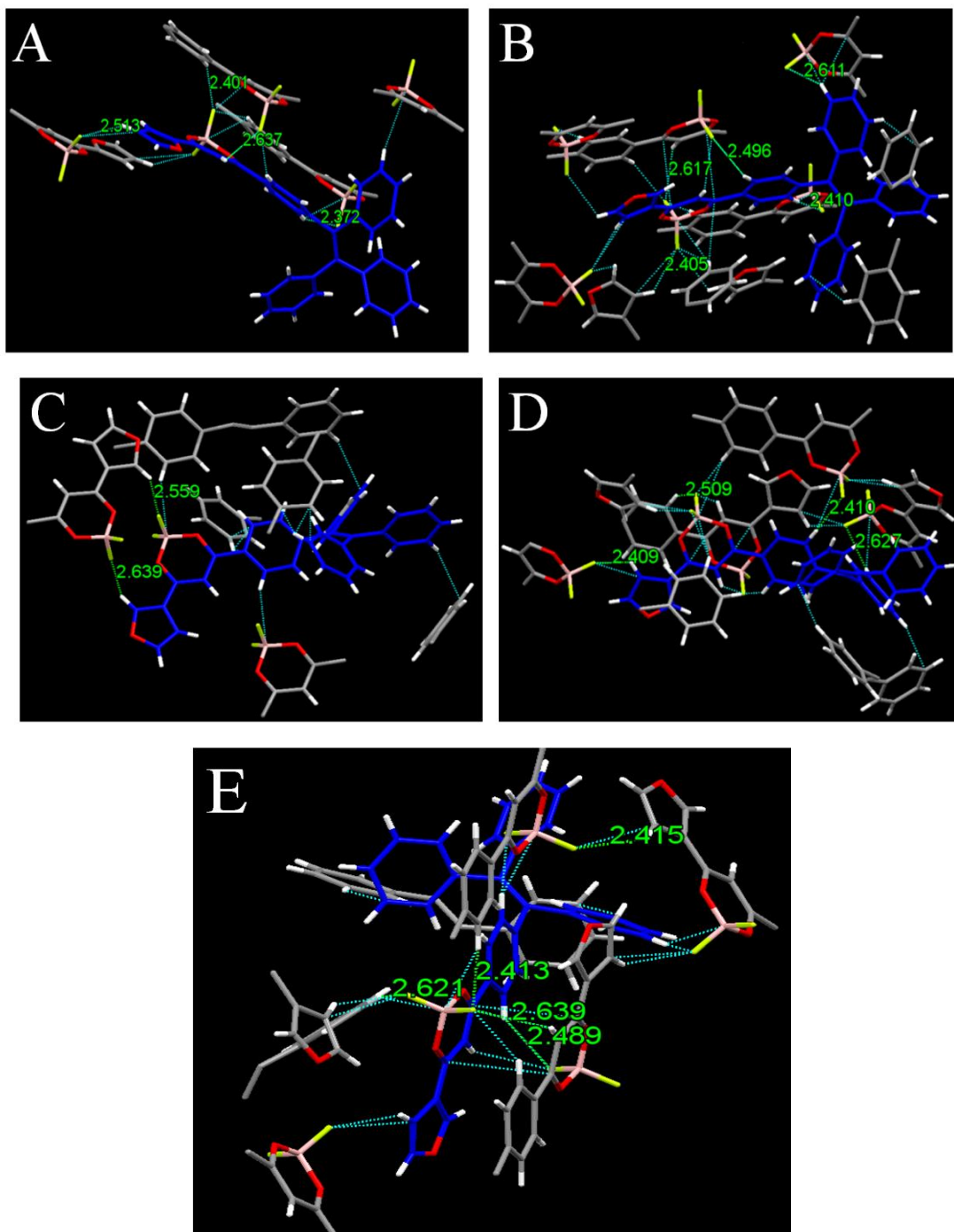


Fig S2. Various intermolecular hydrogen bonds and weak interactions of (A) **2R**, (B) **3R** and (C) **3Y**, (D) **3N**, (E) **3F** (Only shows the key length of C-H...F).

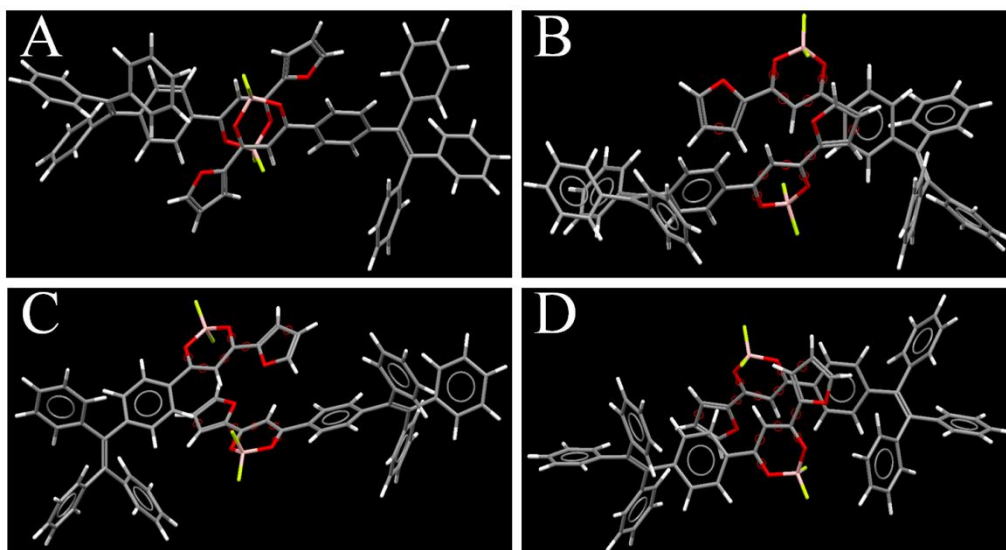


Fig S4. Hypothetical crystals of (A) **2Y_a**, (B) **2Y_b**, (C) **2Y_c**, (D) **2Y_a** based on crystals **3Y** and isomerism.

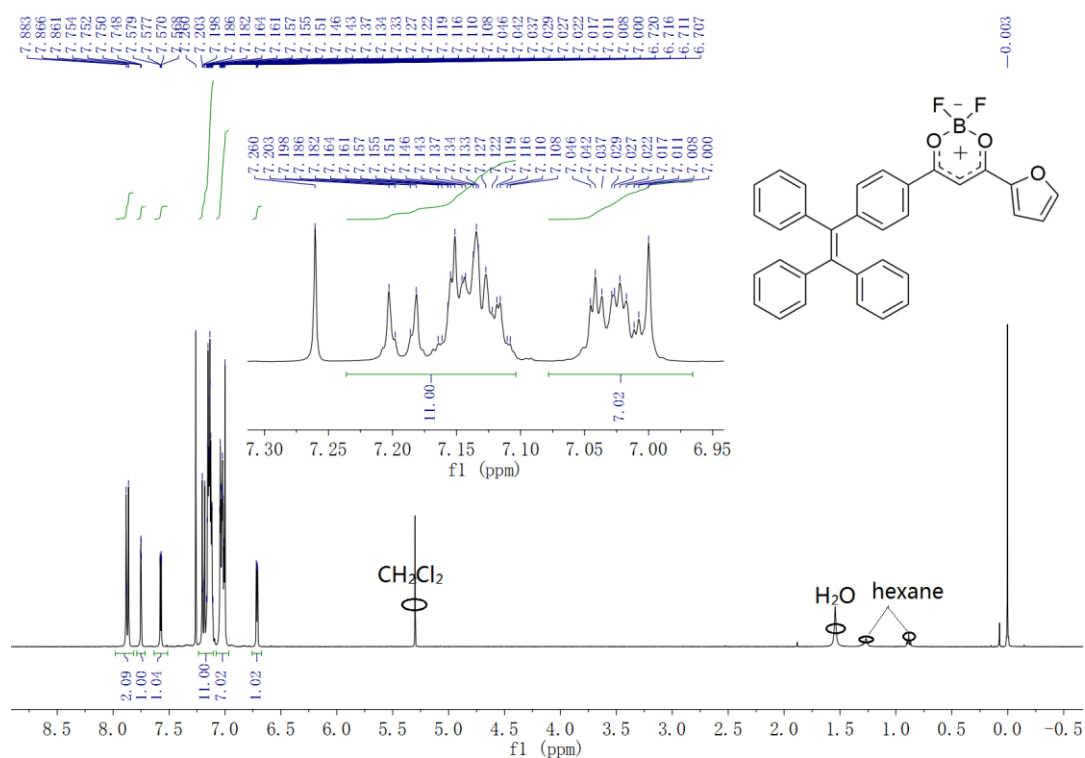


Fig S5. ¹H NMR (400 MHz) spectrum of **TPEB2F** in CDCl₃.

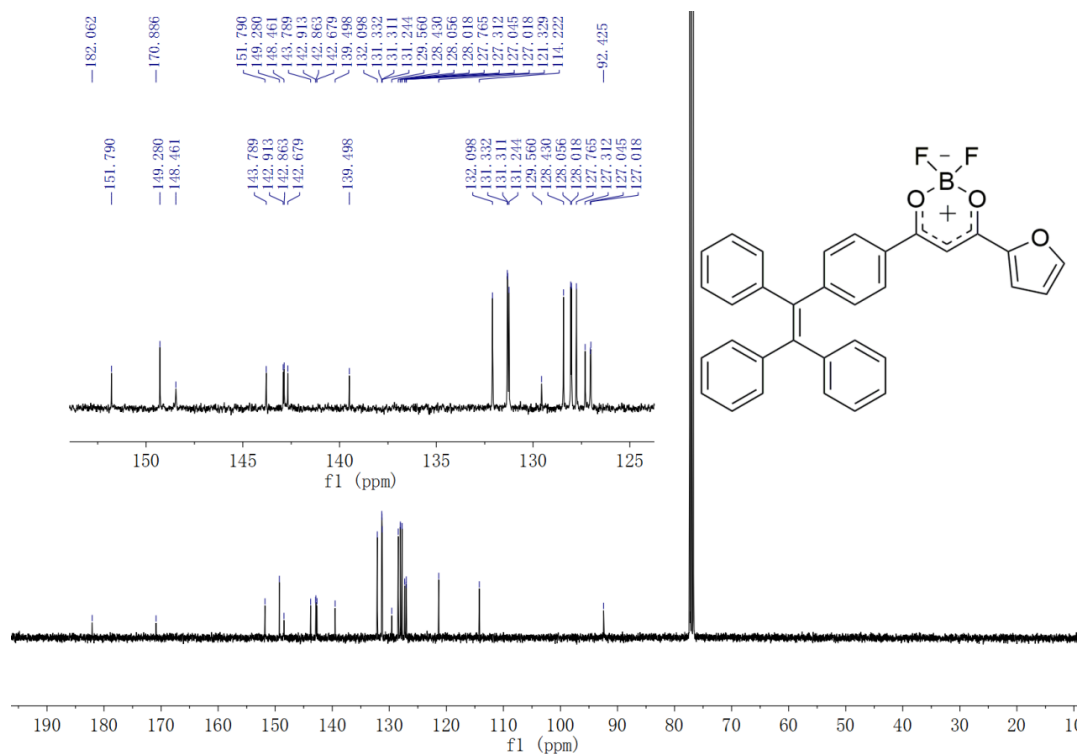


Fig S6. ^{13}C NMR (100 MHz) spectrum of **TPEB2F** in CDCl_3 .

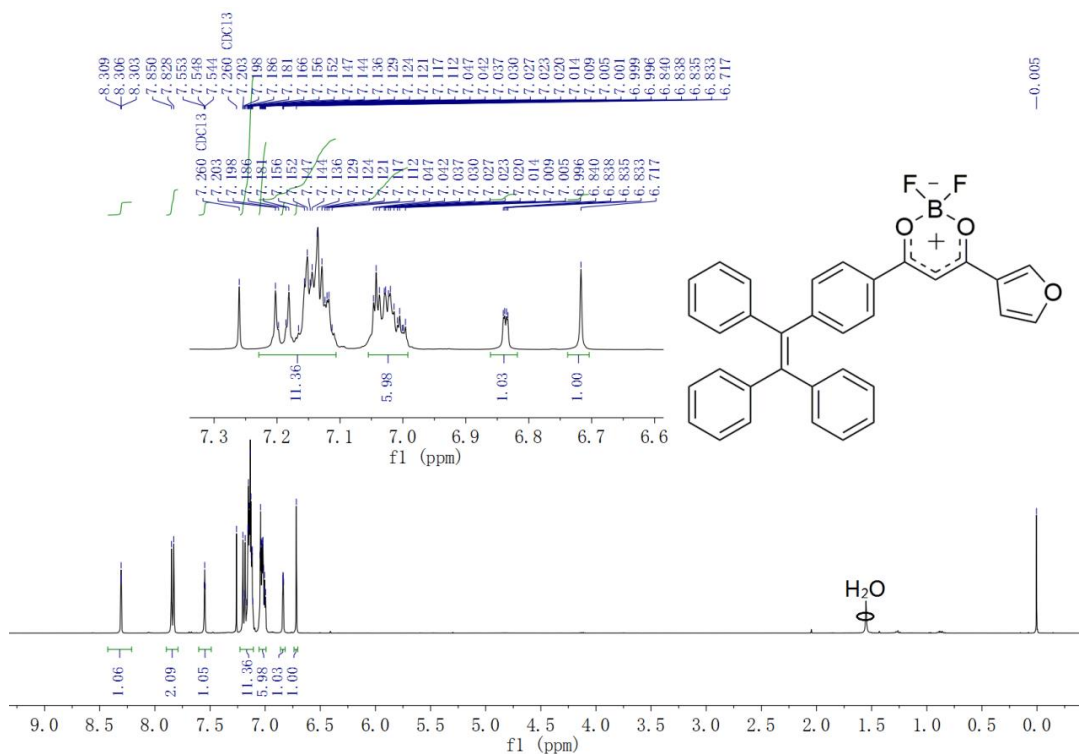


Fig S7. ^1H NMR (400 MHz) spectrum of **TPEB3F** in CDCl_3 .

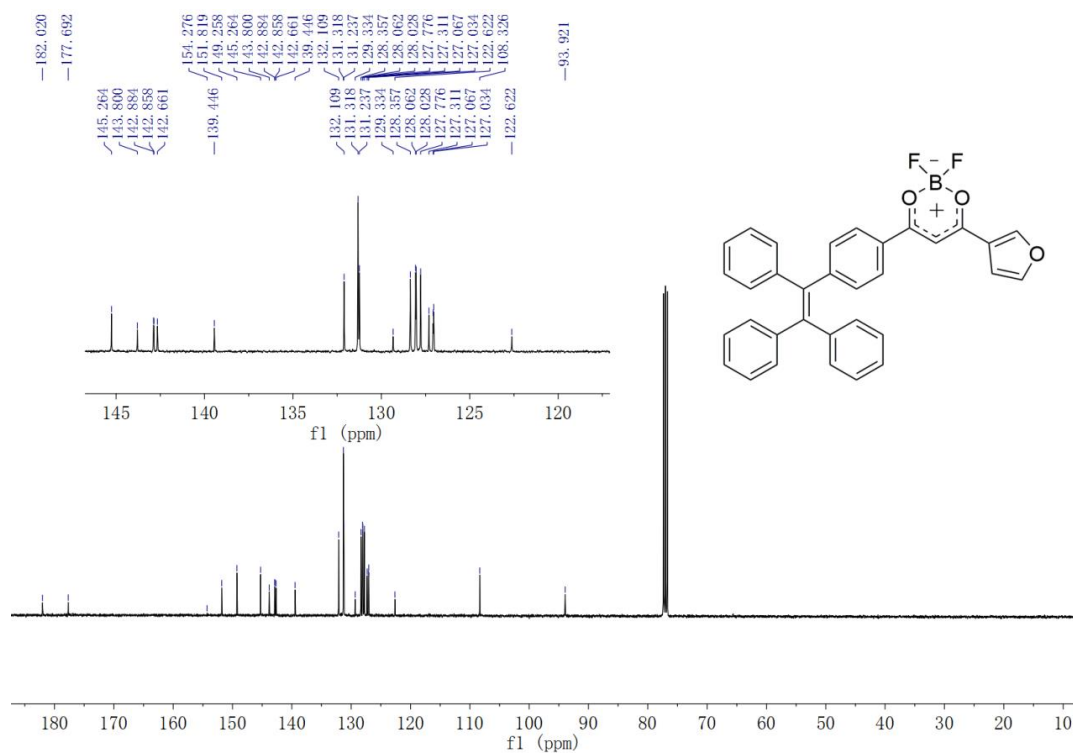


Fig S8. ^{13}C NMR (100 MHz) spectrum of **TPEB3F** in CDCl_3 .

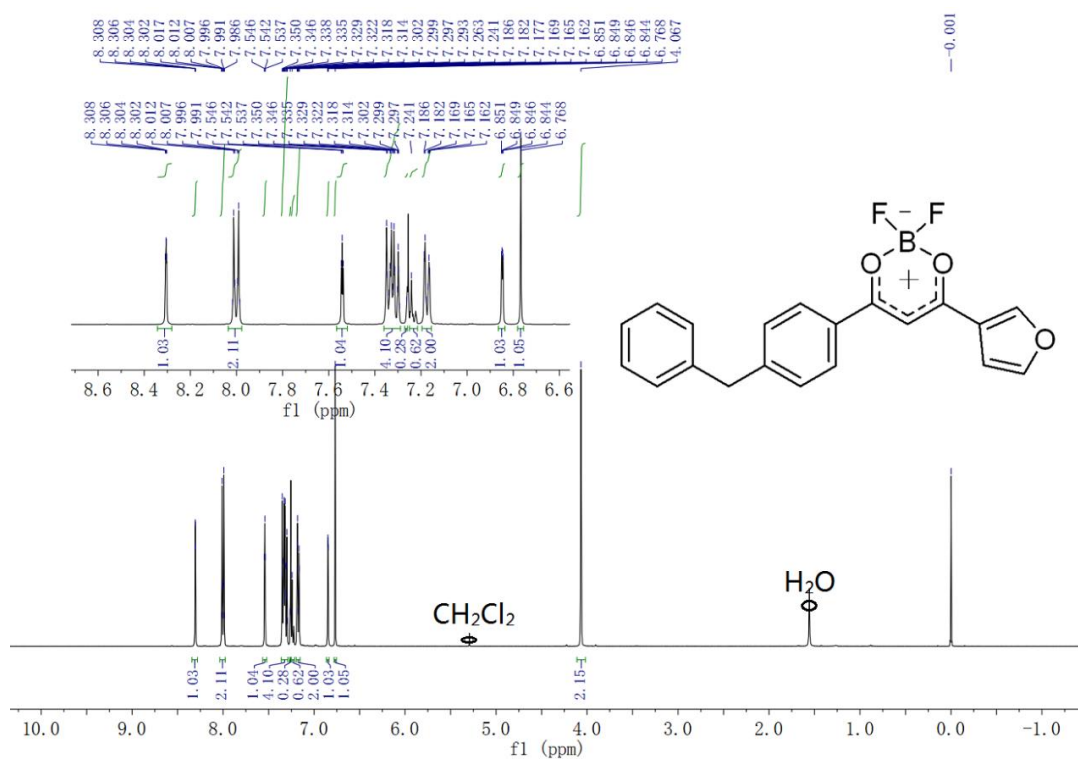


Fig S9. ^1H NMR (400 MHz) spectrum of By-product in CDCl_3 .

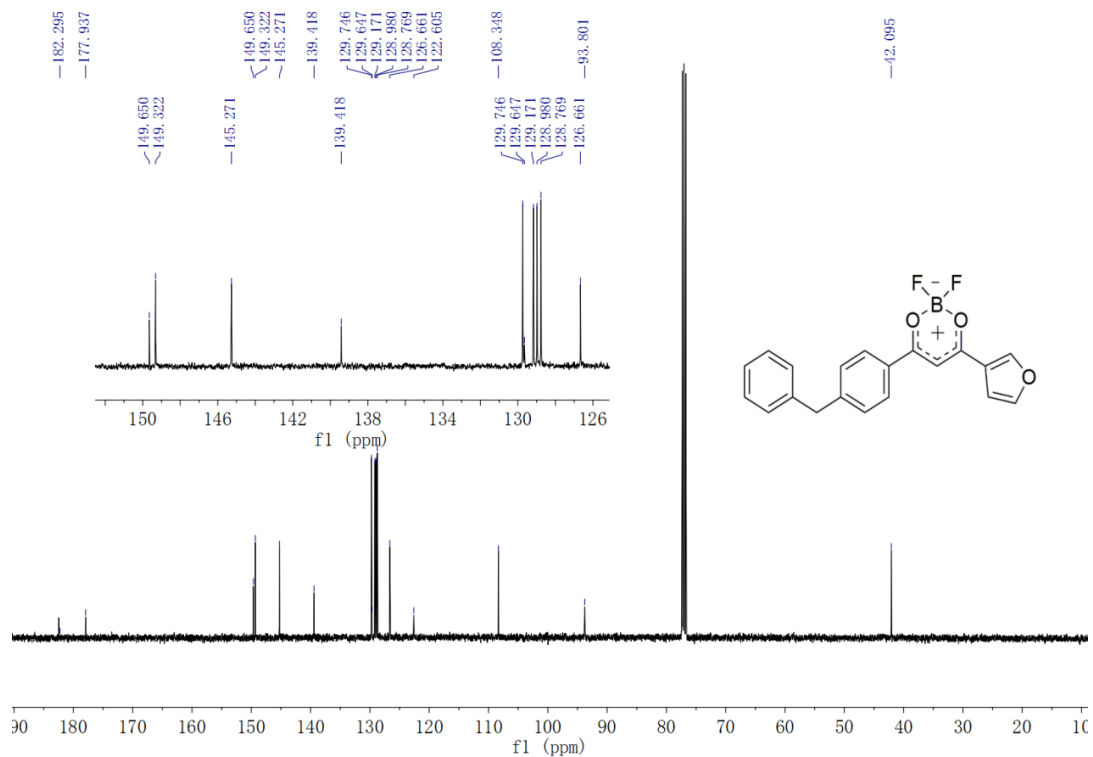


Fig S10. ¹³C NMR (100 MHz) spectrum of By-product in CDCl₃.

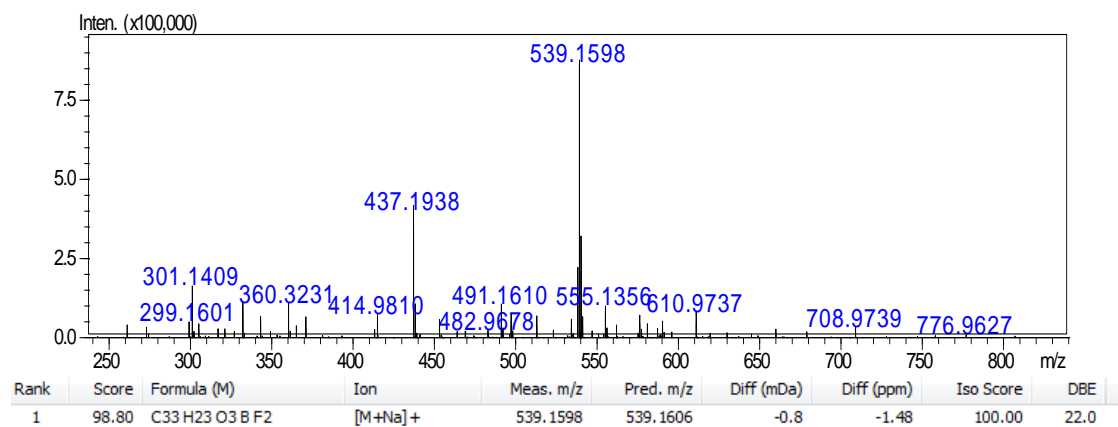
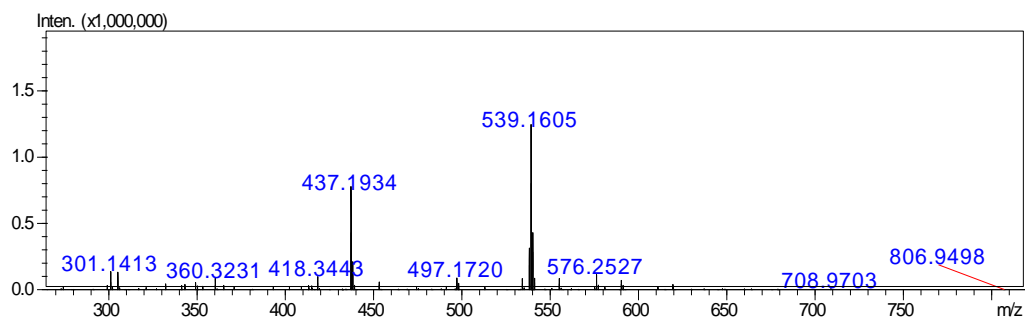


Figure S11. MALDI/TOF MS spectrum of TPEB2F.



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Diff (mDa)	Diff (ppm)	Iso Score	DBE
1	100.00	C33 H23 O3 B F2	[M+Na] ⁺	539.1603	539.1606	-0.3	-0.56	100.00	22.0

Figure S12. MALDI/TOF MS spectrum of **TPEB3F**.