Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for

Pyrimidine-containing β-iminoenolate difluoroboron complexes acting as non-traditional π-gelators and mechanofluorochromic dyes

Wenhua Mi, Zhiyu Qu, Jingbo Sun, Fushuang Zhang, Lu Zhai, Jinyu Zhao, Kaiqi Ye*

Sate Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, P. R. China.

Corresponding Author: yekq@jlu.edu.cn

Table S1 Photophysical data of **CPPA**, **TCPPA**, **CPPAB**, **TCPPAB** in different solvents.

Compound	Solvents	λ_{abs}^{max}/nm	λ_{em}/nm	Stokes shift[a]/cm^{-1}	Φ_F[b]
CPPA	Cyclohexane	289, 376	459, 485	4809	< 0.01
	Toluene	291, 376	462	4951	< 0.01
	THF	290, 370	462	5382	< 0.01
	Chloroform	290, 370	474	5930	< 0.01
	CH_2Cl_2	290, 370	478	6107	< 0.01
	DMSO	292, 376	501	6636	< 0.01
TCPPA	Cyclohexane	296, 387	472, 453	4653	< 0.01
	Toluene	294, 380	455	4338	< 0.01
	THF	294, 388	483	5069	< 0.01
	Chloroform	295, 382	499	6138	< 0.01
	CH_2Cl_2	295, 382	508	6454	< 0.01
	DMSO	295, 386	529	7003	< 0.01
CPPAB	Cyclohexane	289, 322, 339, 410, 430	446, 486	1969	0.97
	Toluene	291, 325, 339, 411	482	3584	0.95
	THF	290, 323, 338, 402	522	5719	0.44
	Chloroform	290, 325, 340, 413	535	5521	0.51
	CH_2Cl_2	291, 325, 340, 409	551	6301	0.42
	DMSO	289, 326, 340, 404	583	7600	0.03
TCPPAB	Cyclohexane	295, 371, 429, 445	465, 491	1805	0.74
	Toluene	297, 375, 430	504	3415	0.53
	THF	293, 373, 435	565	5289	0.34
	Chloroform	294, 374, 429	571	5797	0.46
	CH_2Cl_2	297, 374, 429	595	6861	0.06

[a] Calculated from the difference of λ_{em} and λ_{abs}^{max};

[b] Fluorescence quantum yields were determined by a standard method with diphenylanthracene in benzene (Φ_F = 0.85, λ_{ex} = 390 nm) as reference.

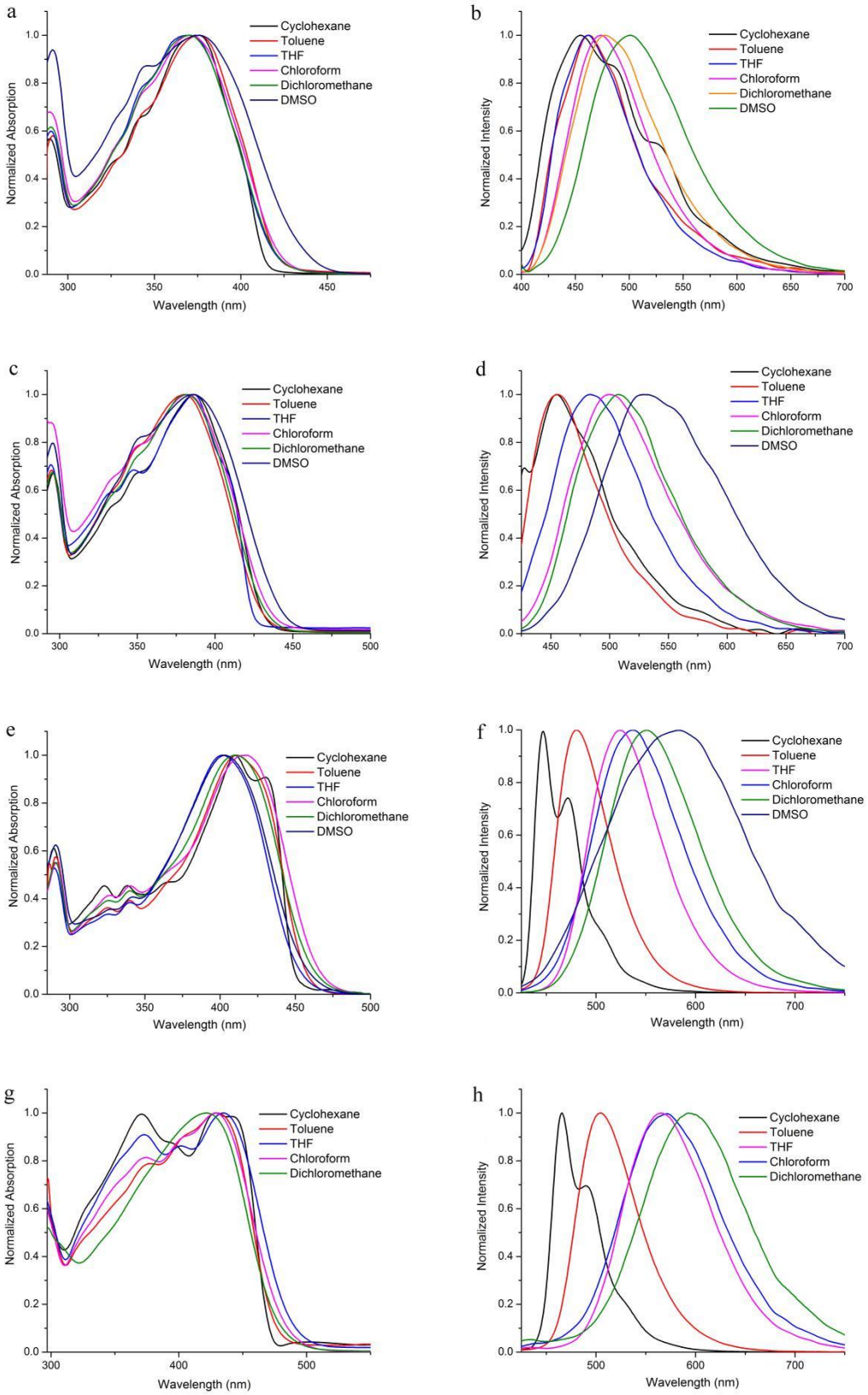

Figure S1. Normalized UV-vis absorption spectra of **CPPA** (a), **TCPPA** (c), **CPPAB** (e) and **TCPPAB** (g) and fluorescence emission spectra of **CPPA** (b), **TCPPA** (d), **CPPA** (f) and **TCPPAB** (h) in different solvents (5.0×10^{-5} M, λ_{ex} = 390 nm).

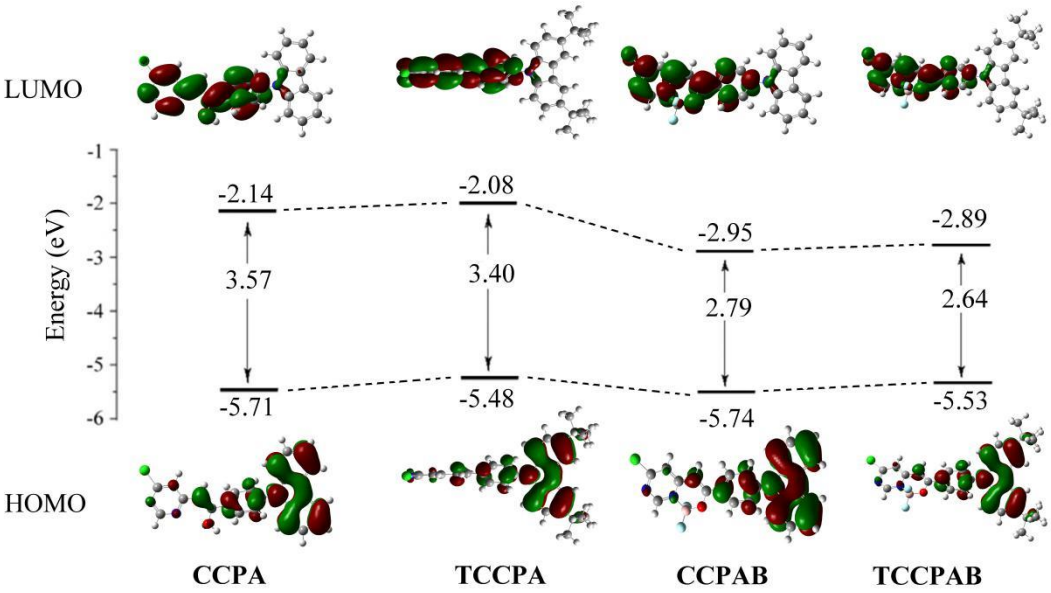

Figure S2. Energy levels and molecular orbital surfaces of **CCPA**, **TCCPA**, **CCPAB** and **TCCPAB** in the optimized ground-state structures.

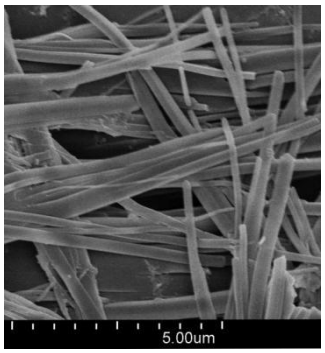

Figure S3. SEM image of the xerogel **TCPPAB** obtained from methylcyclohexane/1,4-dioxane (v/v = 10/1).

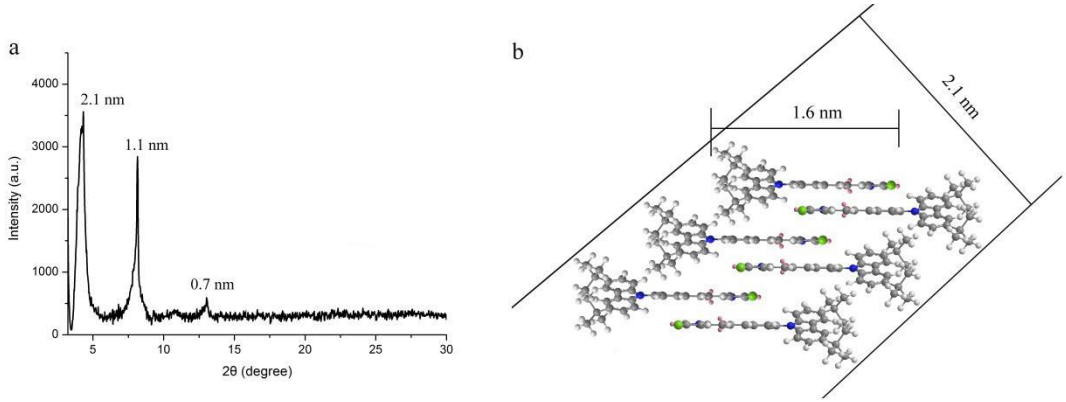

Figure S4. (a) XRD pattern of xerogel **TCPPA** and (b) the proposed molecular packing in xerogel **TCPPA** obtained from cyclohexane.

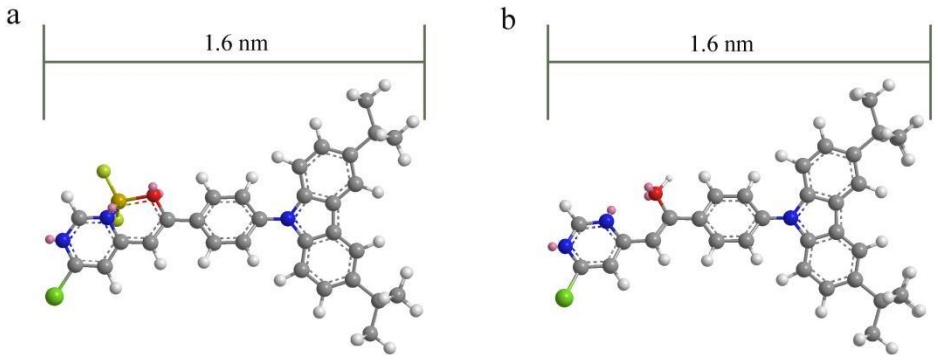

Figure S5. The molecular configurations of **TCPPAB** (a) and **TCPPA** (b) in optimized geometry based on DFT calculations.

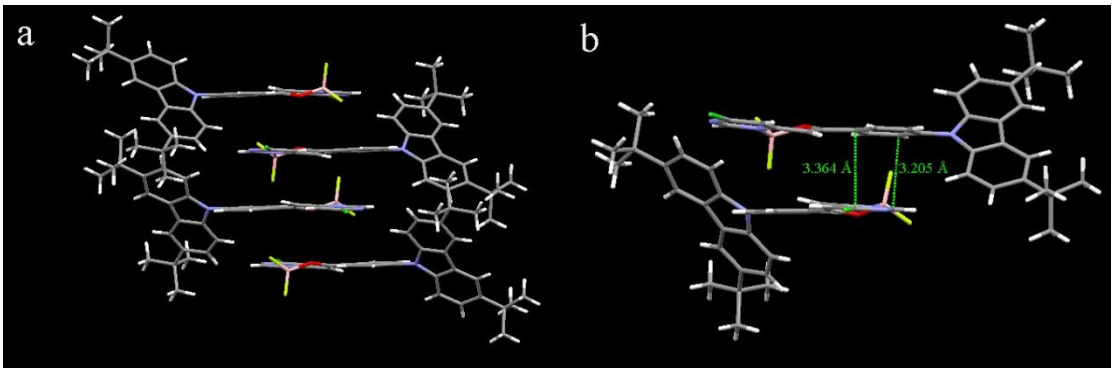

Figure S6. (a) Single-crystal structure of **TCPPAB** from side view and (b) π-π interactions in single crystal.

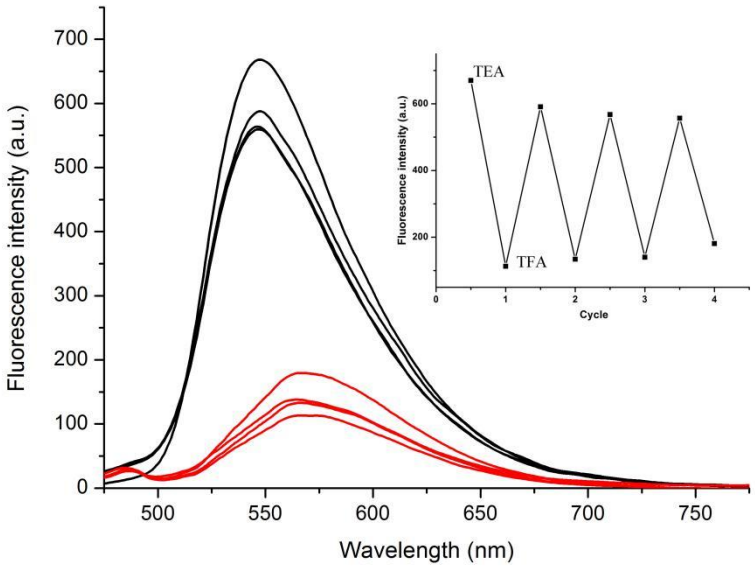

Figure S7. The fluorescence emission spectra of **TCPPAB** in xerogel-based film upon exposed to TFA (red) and TEA vapors (black) repeatedly (λ_{ex} = 420 nm). Inset: the emission intensity at 547 nm of **TCPPAB** in xerogel-based film upon exposed to TFA and TEA vapors repeatedly.

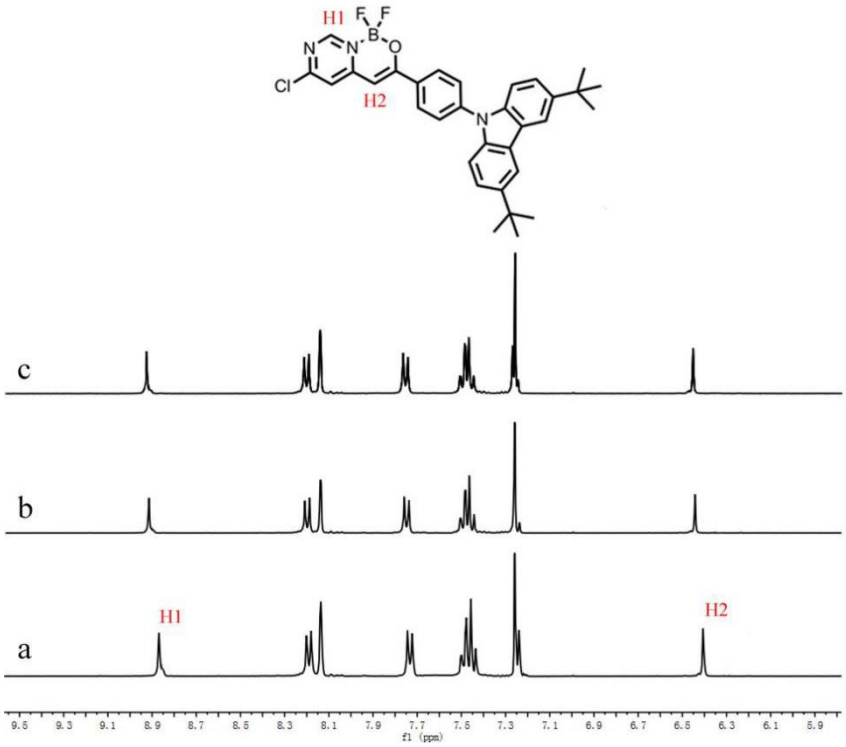

Figure S8. ^{1}H NMR spectra of **TCPPAB** before (a) and after adding 6.0 equiv. (b) as well as 20.0 equiv. (c) of TFA in $CDCl_3$.

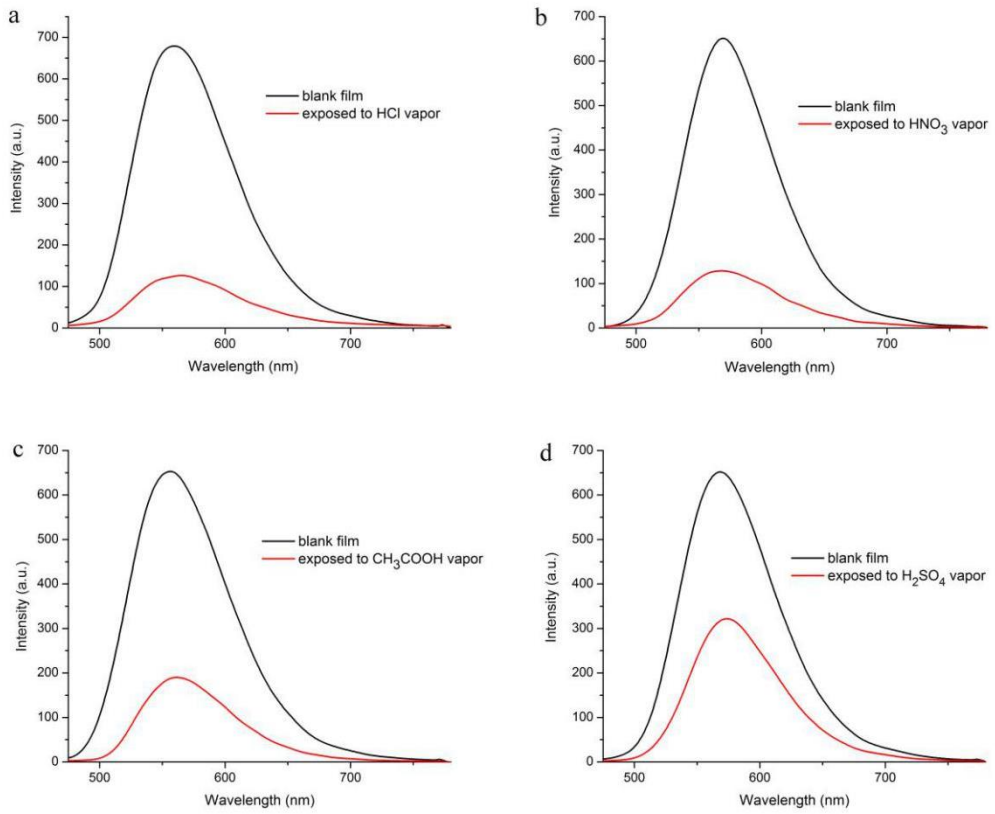

Figure S9. Fluorescence spectral changes of xerogel-film **TCPPAB** upon exposure to vapors of (a) HCl, (b) HNO_3, (c) CH_3COOH, (d) H_2SO_4.

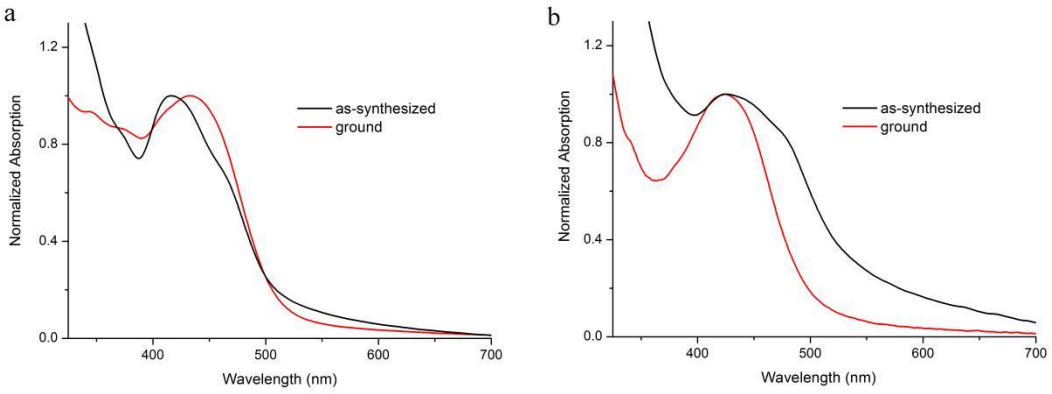

Figure S10. UV-vis spectra of **TCPPAB** (a) and **CPPAB** (b) in different solid-state measured in a reflection mode.

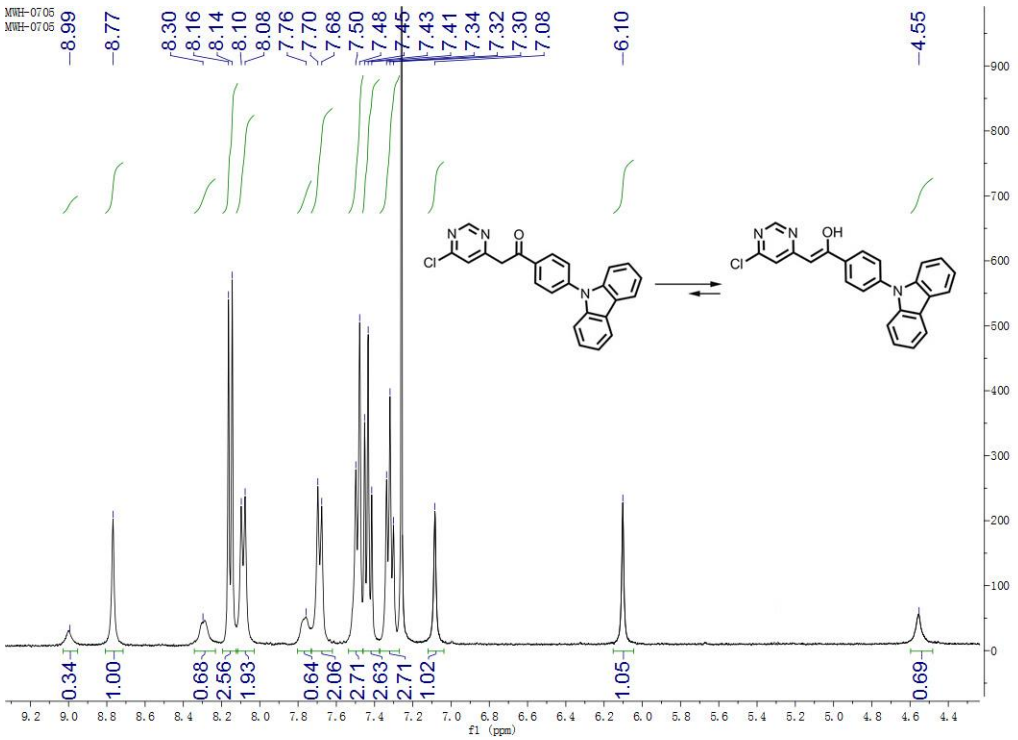

Figure S11. ^{1}H NMR (400 MHz) spectrum of **CPPA** in $CDCl_3$.

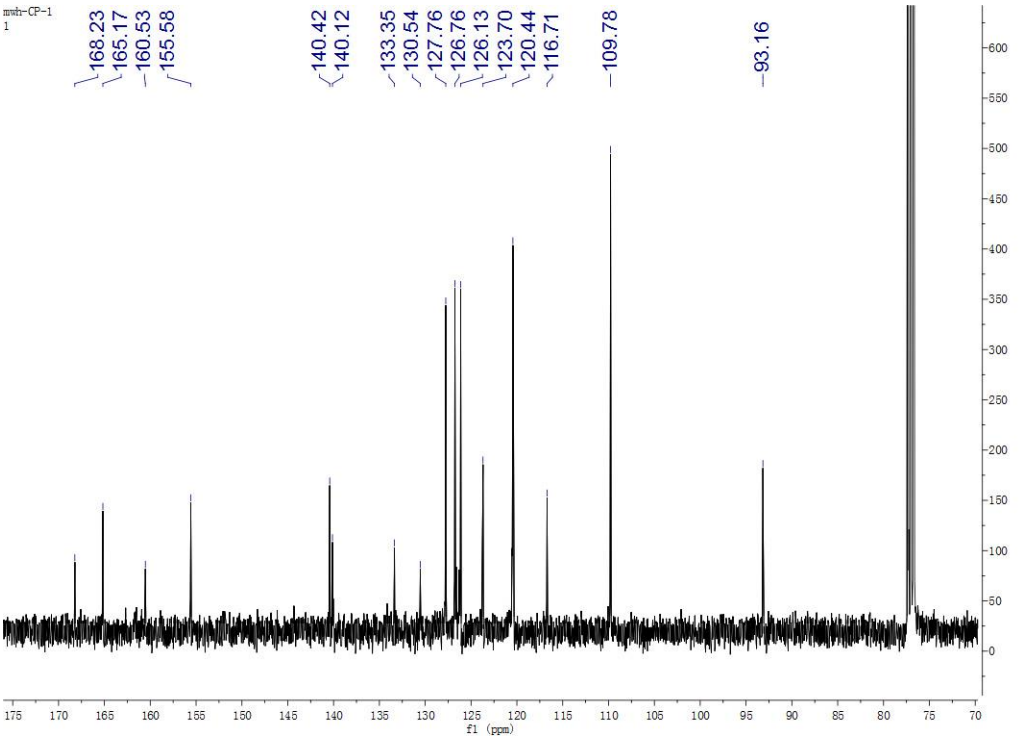

Figure S12. ^{13}C NMR (100 MHz) spectrum of **CPPA** in $CDCl_3$.

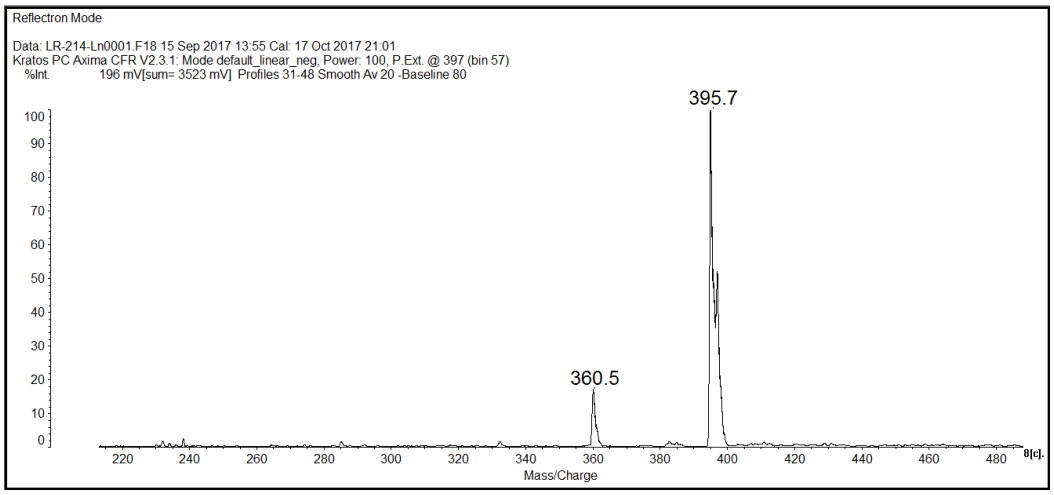

Figure S13. The MALDI-TOF mass spectrum of **CPPA**.

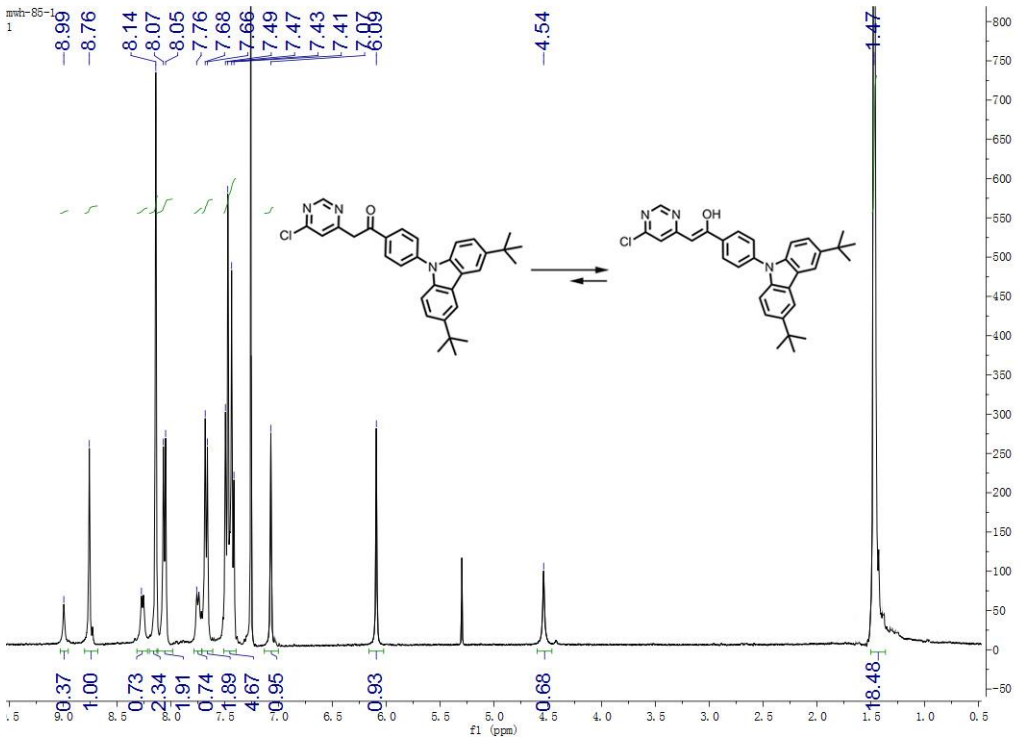

Figure S14. ^{1}H NMR (400 MHz) spectrum of **TCPPA** in $CDCl_3$.

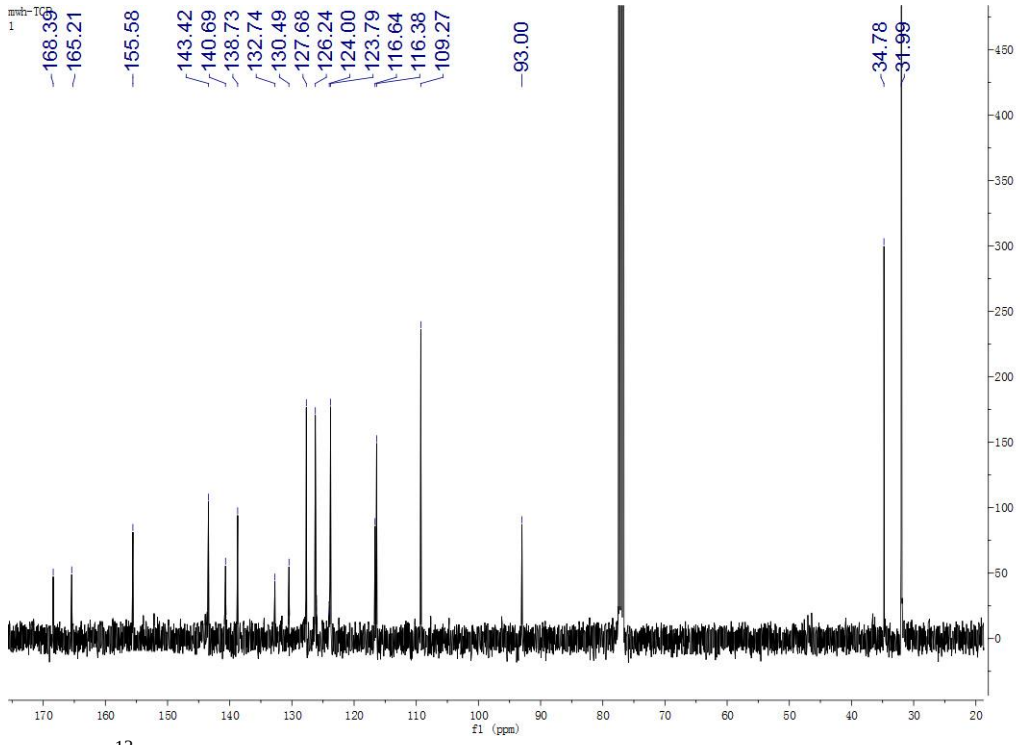

Figure S15. ^{13}C NMR (100 MHz) spectrum of **TCPPA** in $CDCl_3$.

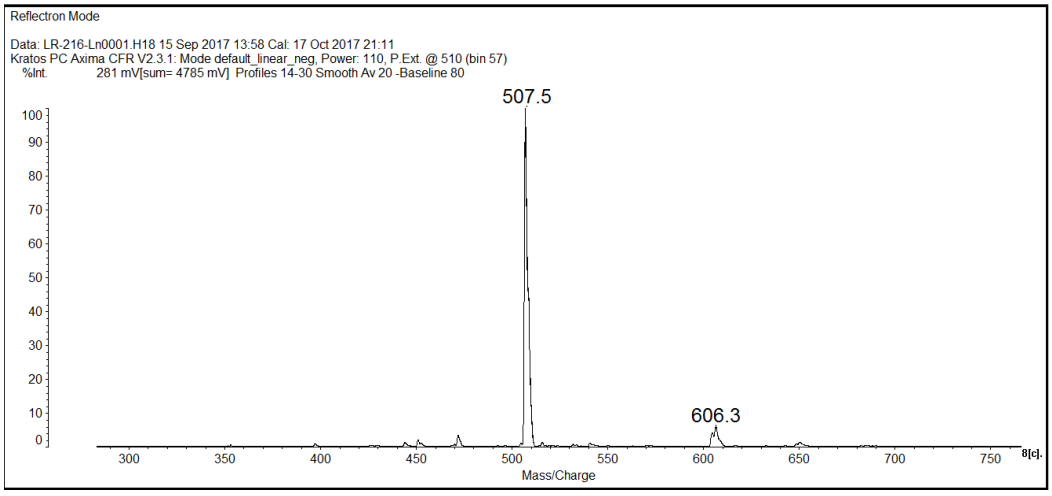

Figure S16. The MALDI-TOF mass spectrum of **TCPPA**.

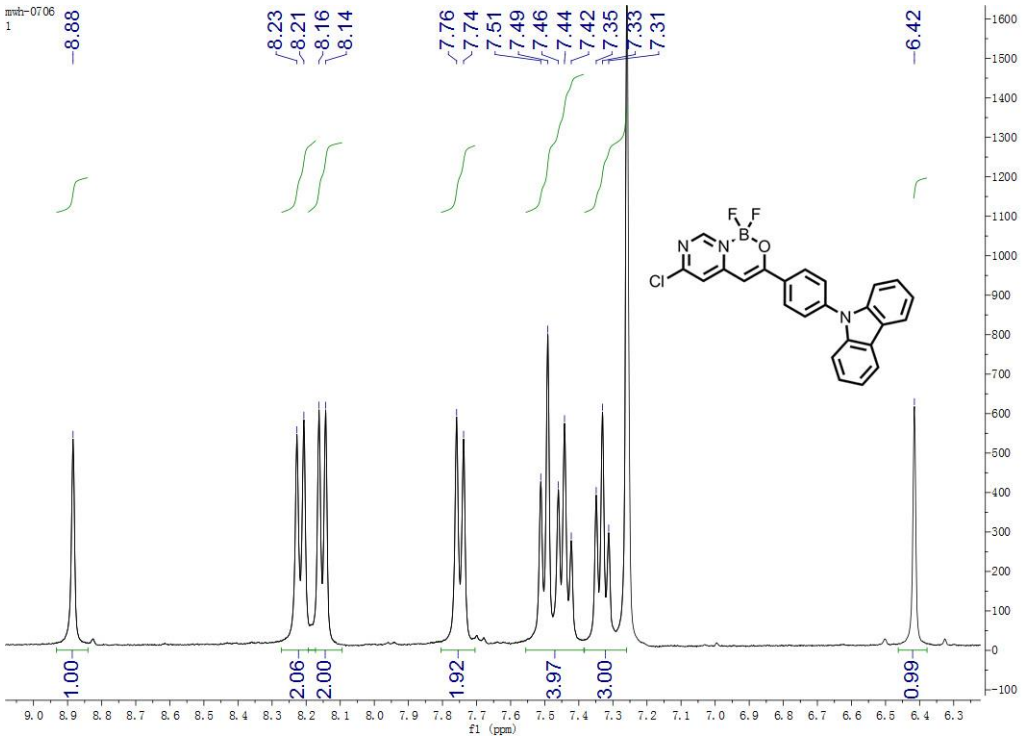

Figure S17. ^{1}H NMR (400 MHz) spectrum of **CPPAB** in $CDCl_3$.

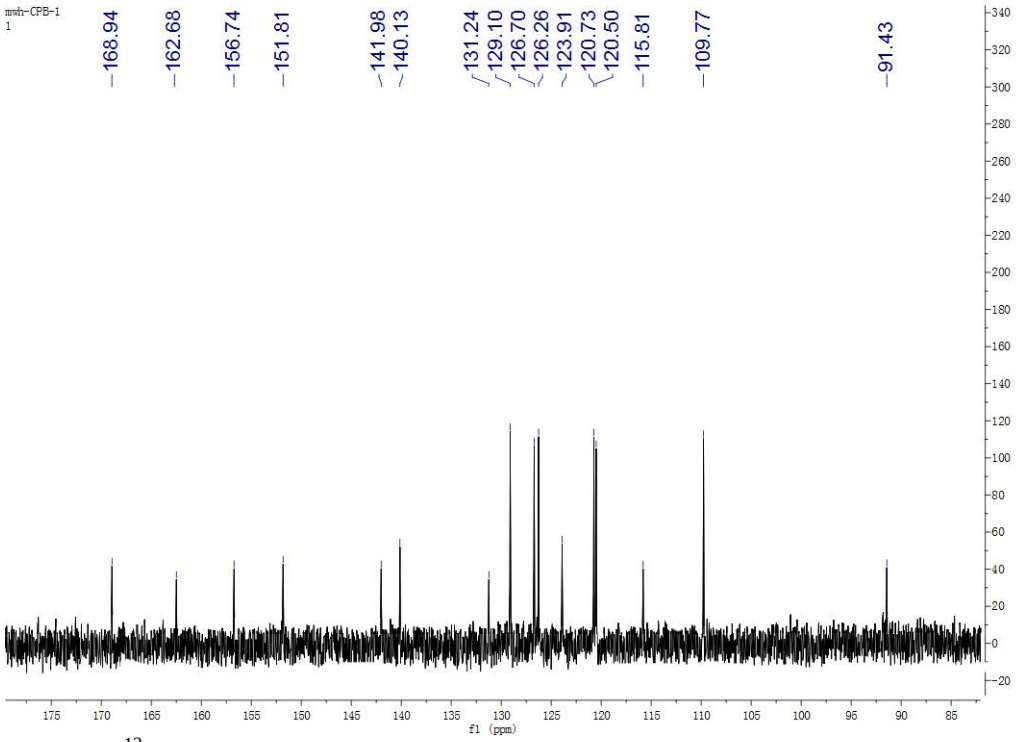

Figure S18. ^{13}C NMR (100 MHz) spectrum of **CPPAB** in $CDCl_3$.

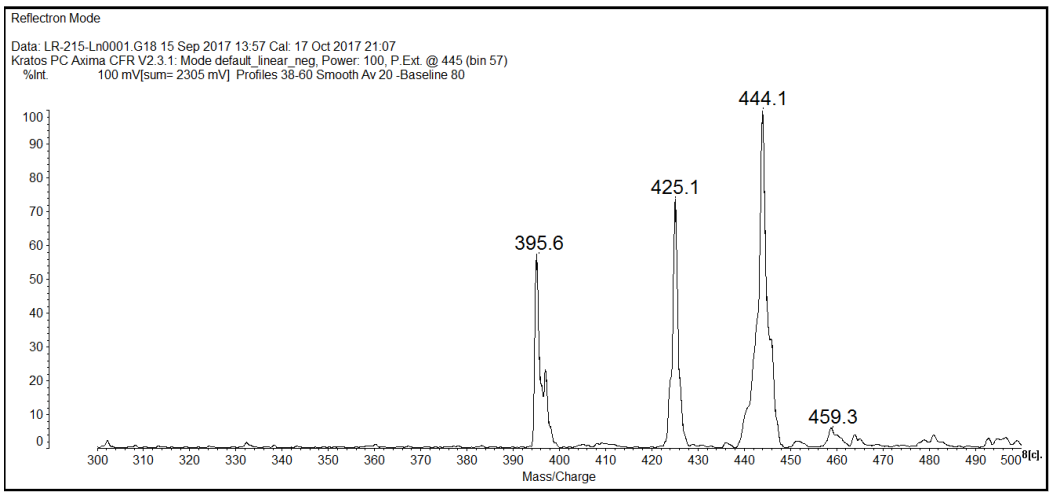

Figure S19. The MALDI-TOF mass spectrum of **CPPAB**.

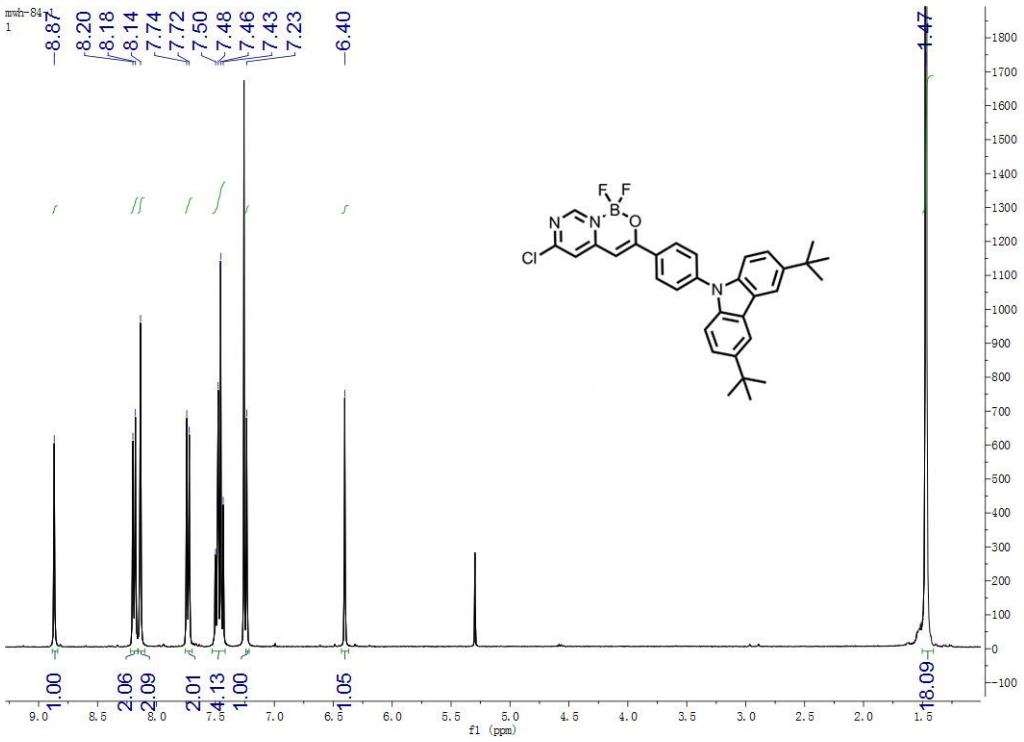

Figure S20. ^{1}H NMR (400 MHz) spectrum of **TCPPAB** in $CDCl_3$.

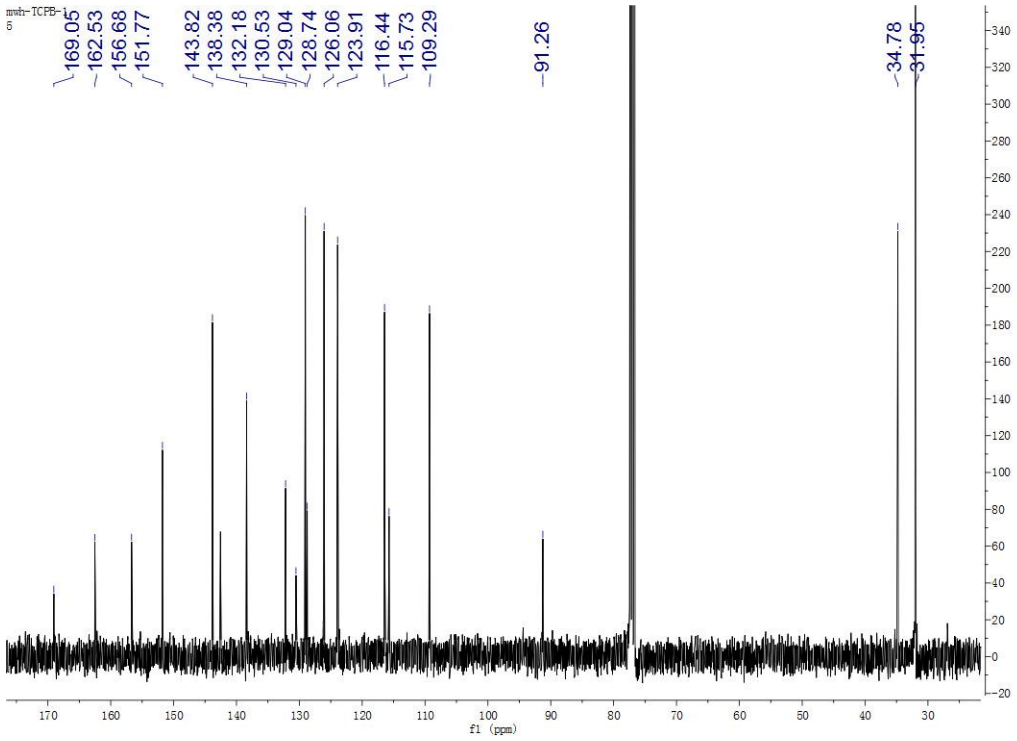

Figure S21. ^{13}C NMR (100 MHz) spectrum of **TCPPAB** in $CDCl_3$.

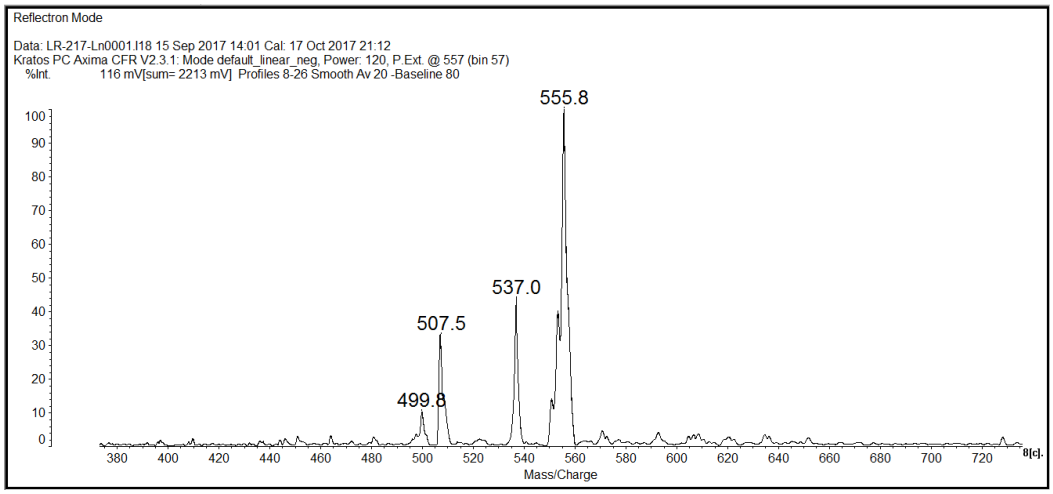

Figure S22. The MALDI-TOF mass spectrum of **TCPPAB**.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

Bond precision: C-C = 0.0018 A Wavelength=0.71073

Cell: a=24.409(2) b=9.5355(8) c=13.1083(10)
alpha=90 beta=103.983(3) gamma=90
Temperature: 160 K

	Calculated	Reported
Volume	2960.6(4)	2960.6(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C32 H31 B Cl F2 N3 O	C32 H31 B Cl F2 N3 O
Sum formula	C32 H31 B Cl F2 N3 O	C32 H31 B Cl F2 N3 O
Mr	557.86	557.86
Dx,g cm-3	1.252	1.252
Z	4	4
Mu (mm-1)	0.171	0.171
F000	1168.0	1168.0
F000’	1169.09	
h,k,lmax	31,12,17	31,12,17
Nref	6810	6784
Tmin,Tmax	0.978,0.981	
Tmin’	0.978	

Correction method= Not given

Data completeness= 0.996 Theta(max)= 27.513

R(reflections)= 0.0344(5592) wR2(reflections)= 0.0908(6784)

S = 1.020 Npar= 367

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 33 Ang**3

Alert level G

PLAT395_ALERT_2_G Deviating X-O-Y Angle From 120 for O1 121.1 Degree
PLAT434_ALERT_2_G Short Inter HL..HL Contact Cl1 ..F1 3.02 Ang.

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock 1 - ellipsoid plot