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Single crystal field-effect transistor of tetrabenzoporphyrin with one-dimensionally extended columnar packing motif exhibiting efficient charge transport property

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Supporting Information

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1. Materials and Methods

Reagents for synthesis were purchased from Wako, Nacalai Tesque, and Sigma Aldrich, and were reagent-grade quality, obtained commercially, and used without further purification. Unless stated otherwise, column chromatography was carried out on silica gel 60N (Kanto Chemical, 40-50 μm). Analytical thin layer chromatography (TLC) was performed on Art. 5554 (Merck, KGaA). The ^{1}H NMR (600 MHz) was recorded on a JEOL JNM-ECX 600 spectrometer and reported as chemical shifts (δ) in ppm relative to TMS ($\delta = 0$). High-resolution MS was carried out on a MALDI-TOF (Bruker Autoflex II). X-ray crystallographic data were recorded at 103 K on a Rigaku R-AXIS RAPID/S using Mo-Kα radiation ($\lambda = 0.71073$ Å). Polarized optical images of the thin films were obtained using ZEISS Axio Scope.A1 microscope. Out-of-plane thin-film XRD measurements were carried out on a Rigaku SmartLAb X-ray reflectometer with θ–2θ scan mode by using Cu-Kα radiation ($\lambda = 1.5418$ Å). TEM observation was carried out with a JEOL JEM-3100FEF operated at 300 kV. DigitalMicrograph 3.4.3 was used for indexing of SAED patterns. The assessment of theoretically predicted growth morphology was carried out using modelling routines available in Materials studio. Crystal morphology predictions were performed allowing a minimum dhkl of 1.300 Å and a miximum values for the three Miller indexes were set to 3, 3, 3, respectively. The overall number of growing faces was limited to 200.

2. Sample preparation for TEM measurements

TIPS-BP derivatives (1 mg) was dissolved in dehydrated toluene (1 ml), and then the compound was completely dissolved by using sonication. The resulting toluene solution was filtered. A TEM grid on an octadecyltrichlorosilane (OTS) modified Si/SiO_2 surface was placed at the center of a watch-glass. Then, the toluene solution of TIPS-BP derivative was dropped on the TEM grid by using micropipette, and the TEM grid was covered by another watch-glass. After slow evaporation of the toluene solution, single crystals were grown on the TEM grid. Finally, the TEM grid was dried at 60 ºC for 4 h before TEM measurements.

3. POM image

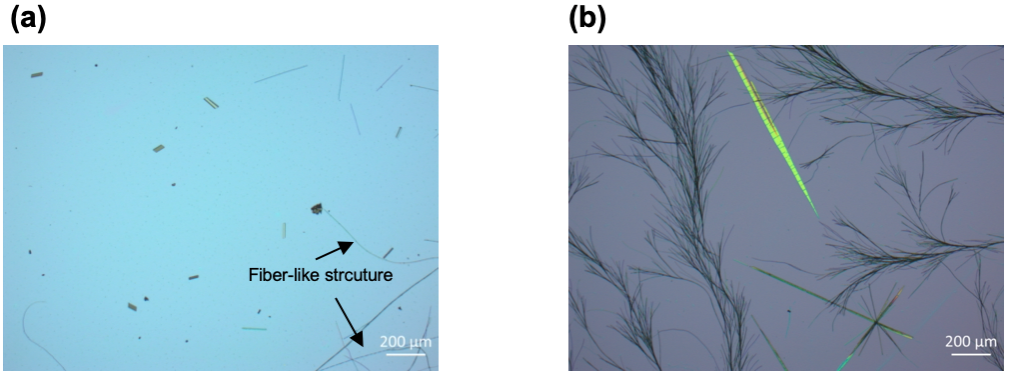


Fig. S1. POM image of wire-shaped crystal and fiber-like structure of **TIPS-CuBP**. (b) Crystal formation of **TIPS-CuBP** on Si/SiO_2/OTS substrate with high humidity mainly gives fiber-like structure.

4. XRD measurements

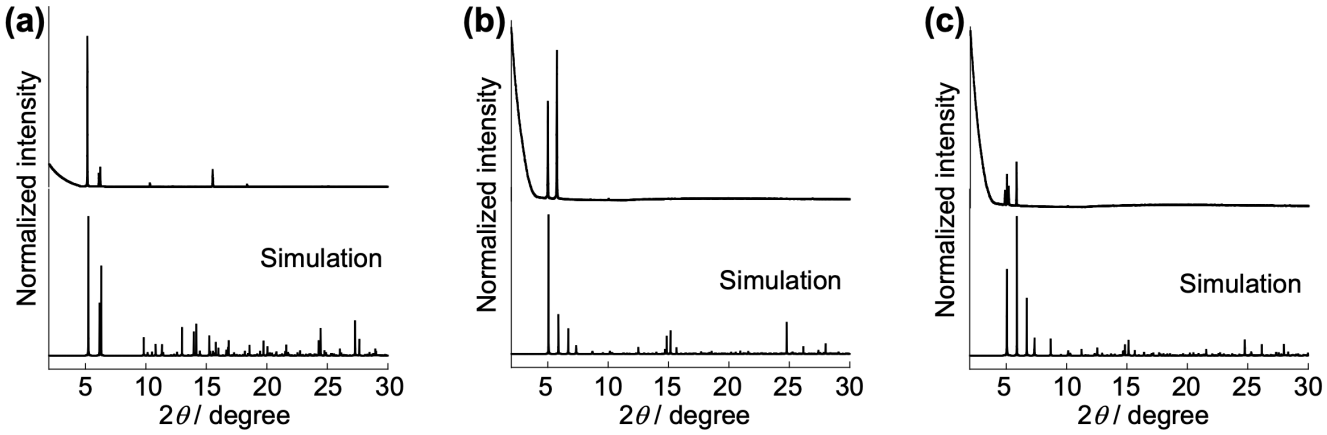


Fig. S2. Experimental out-of-plane XRD and simulated powder XRD patterns of (a) **TIPS-H_2BP**, (b) **TIPS-ZnBP**, and (c) **TIPS-CuBP**.

5. Channel length and width

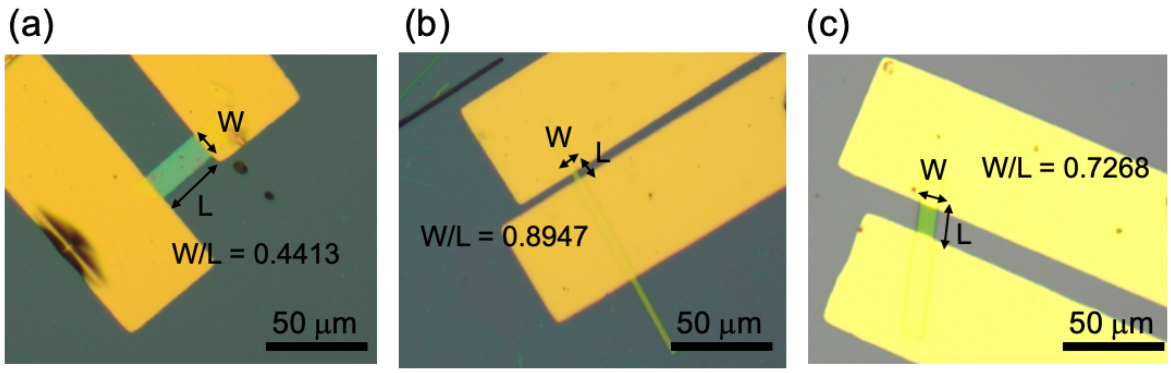


Fig. S3. Representative microscope image of channel length and width of single-crystal-based OFET of (a) **TIPS-H_2BP**, (b) **TIPS-ZnBP**, and (c) **TIPS-CuBP**.

6. Single-crystal-based OFETs

The highly *n*-doped silicon wafers with a 300 nm-thick thermally grown SiO_2 layer were cleaned with deionized (DI) water, piranha solution (H_2SO_4:H_2O_2 = 2:1), deionized (DI) water, pure isopropanol for 10 min, respectively, under an ultrasonic bath. Then substrates were dried with a flow of nitrogen gas. Treatment of the Si/SiO_2 wafers with OTS was carried out by the vapor-deposition method. The clean wafers were dried under vacuum at 90 ºC for 1 h in order to eliminate the influence of moisture. After cooling to RT, one drop of OTS was placed on the center of system. Subsequently, this system was heated to 120 ºC and maintained for 2 h under vacuum followed with an ultra-sonication in hexane, chloroform and isopropanol for 10 min, respectively. Then, a toluene solution of **TIPS-H_2BP** (1.0 mg/ml for **TIPS-H_2BP** and **TIPS-CuBP**, 0.5 mg/ml for **TIPS-ZnBP**) was drop-casted on the OTS-modified substrate, giving single crystals on surface. Source and drain electrodes were deposited on the crystal by using gold layer glue technique.

All electrical characteristics of the devices were measured at room temperature using a semiconductor parameter analyser (Keithley 4200 SCS) and Micromanipulator 6150 probe station. The filed-effect hole mobilities were determined in the saturation regime by using the equation of $I_{DS} = (\mu WCi/2L)(V_G–V_{th})^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, Ci (10 nF cm^{-2} for OTS-modified Si/SiO_2 substrate) is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_{th} is the threshold voltage, respectively. The effective channel length and width were measured by microscope image of the substrate.

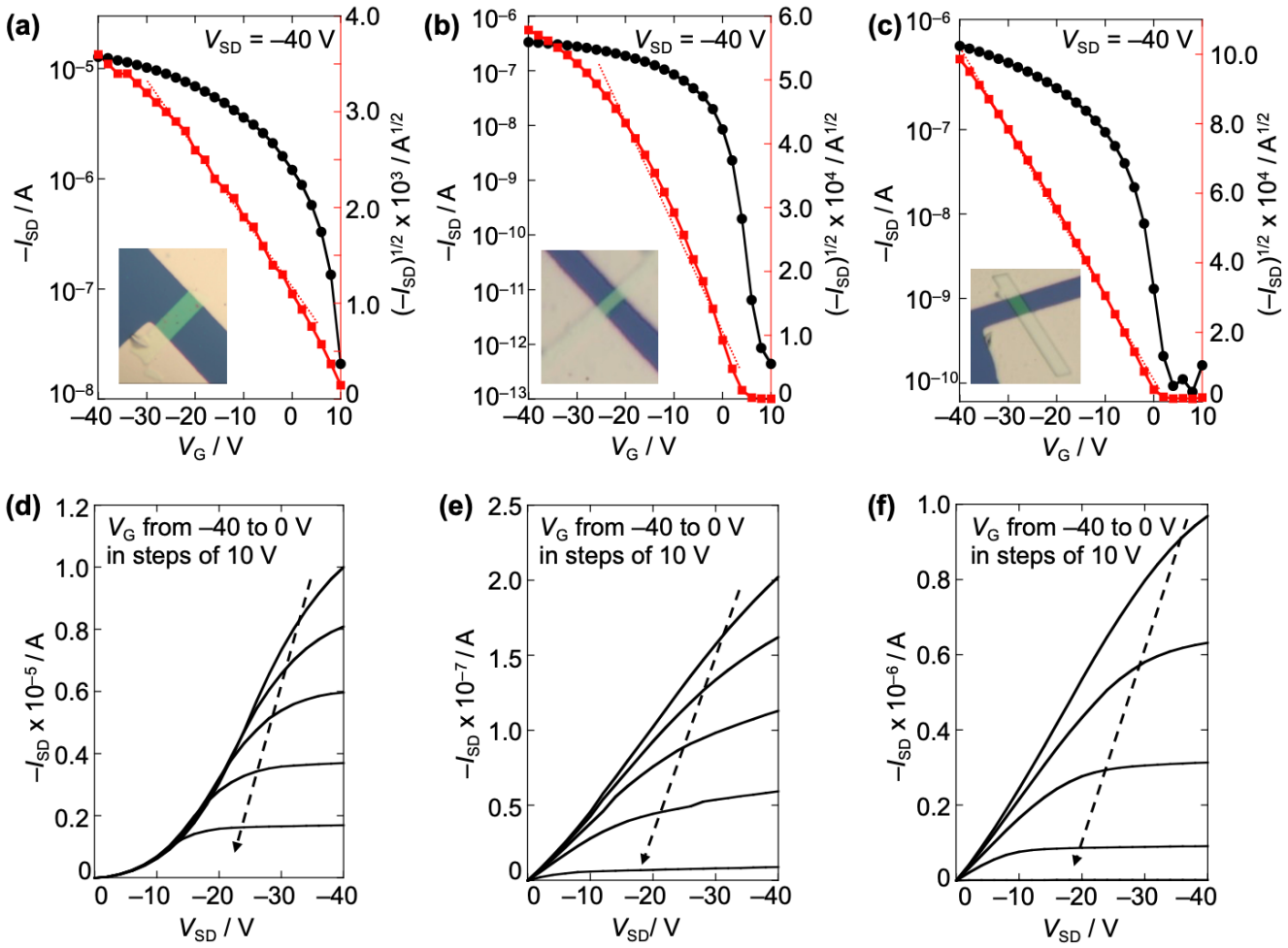


Fig. S4. Transfer (a–c) and output (d–f) characteristics of the device of (a, d) **TIPS-H_2BP**, (b, e) **TIPS-ZnBP**, and (c, f) **TIPS-CuBP** crystals which showed the best hole mobility.

7. Bias stress stability

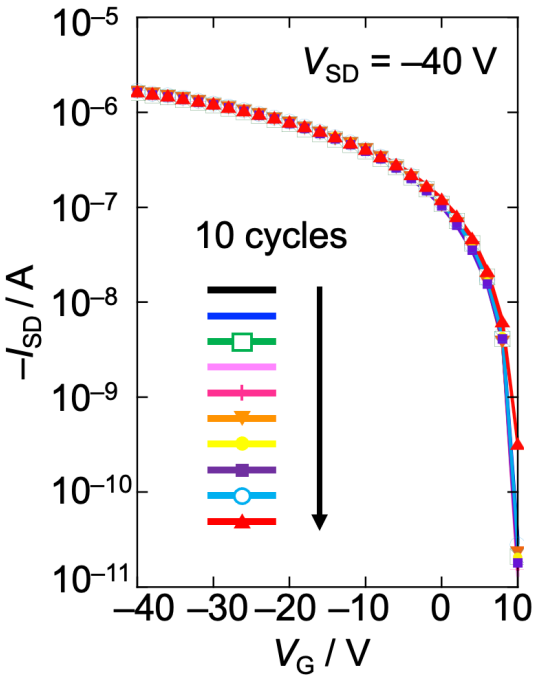


Fig. S5. Bias stress stability curves of OFETs based on ribbon-shaped crystals of **TIPS-H$_2$BP**.

8. Gate-dependence saturation mobility

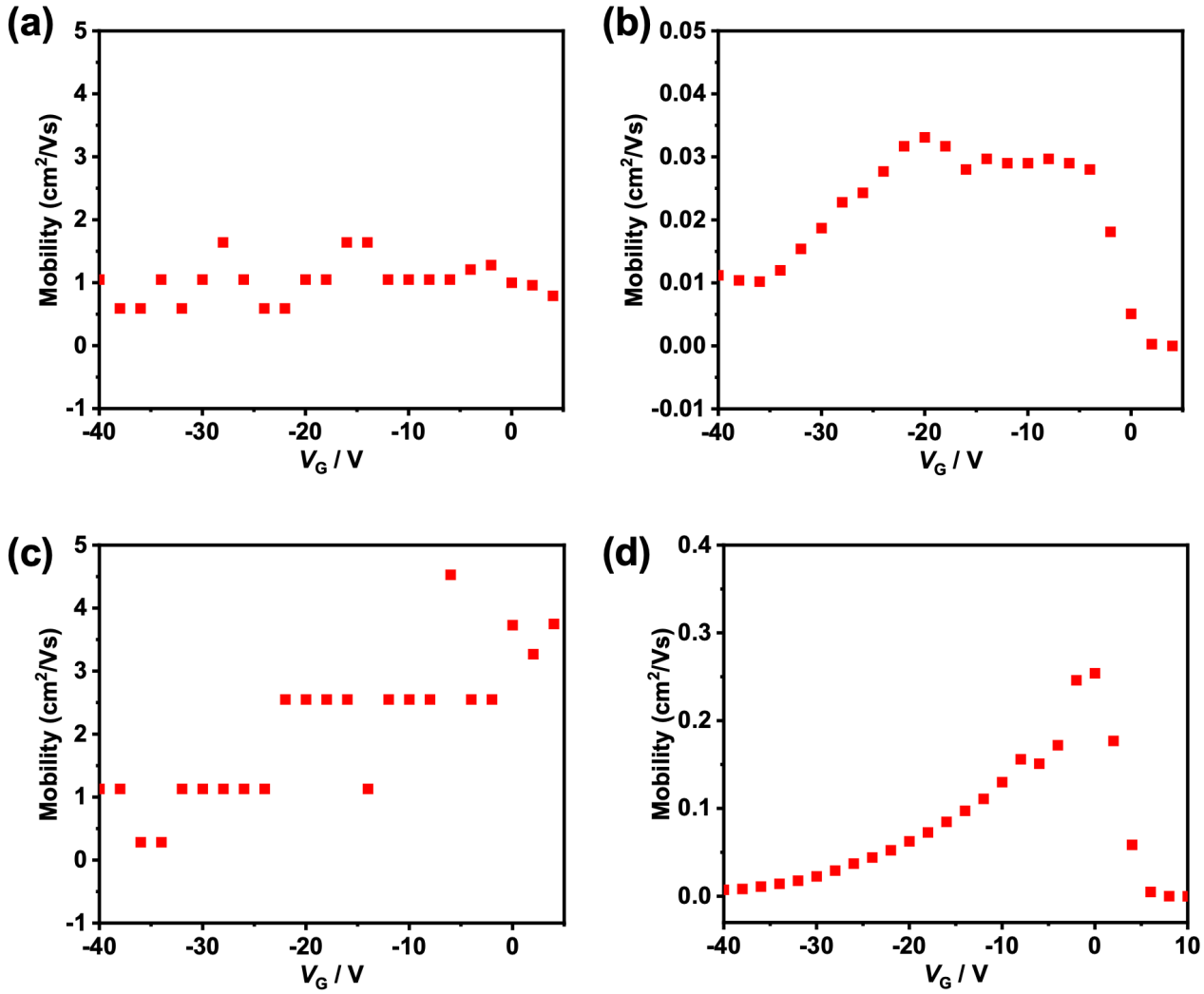


Fig. S6. The gate-dependence saturation mobility. (a,b) Extracted from *I-V* curves in Figure 6a-6b, respectively, and (c,d) extracted from *I-V* curves in Figure S4a-4b, respectively.

9. Single crystal X-ray analysis

TIPS-H_2BP (CCDC: 2099221)

Empirical formula	$C_{58}H_{62}N_4Si_2$	
Formula weight	871.29	
Temperature	103 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 8.9318(8) Å	α = 63.316(5)º
	b = 15.8384(14) Å	β = 78.745(6)º
	c = 18.7438(17) Å	γ = 81.031(6)º
Volume	2354.7(4) Å^3	
Z	2	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	932	
Crystal size	0.150 × 0.010 × 0.010 mm^3	
Theta range for data collection	2.202 to 25.351°	
Index ranges	$-10 \le h \le 10$, $-19 \le k \le 19$, $-22 \le l \le 22$	
Reflections collected	32403	
Independent reflections	8610 [R(int) = 0.2244]	
Completeness to theta = 23.500°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.2847	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8610 / 0 / 589	
Goodness-of-fit on F^2	0.998	
Final R indices [I > 2sigma(I)]	R_1 = 0.0986, wR_2 = 0.1973	
R indices (all data)	R_1 = 0.2048, wR_2 = 0.2446	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.464 and –0.375 e.Å^{-3}	

TIPS-ZnBP (CCDC: 2099222)

Empirical formula	$C_{58}H_{60}N_4Si_2Zn$	
Formula weight	934.65	
Temperature	103 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 12.9207(2) Å	α = 101.5873(7)º
	b = 15.7074(3) Å	β = 108.2265(7)º
	c = 19.0205(4) Å	γ = 97.6339(7)º
Volume	3511.50(11) Å^3	
Z	3	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.620 mm^{-1}	
F(000)	1482	
Crystal size	0.280 × 0.070 × 0.050 mm^3	
Theta range for data collection	1.936 to 27.484°	
Index ranges	$-15 \le h \le 16$, $-20 \le k \le 20$, $-24 \le l \le 24$	
Reflections collected	61191	
Independent reflections	16079 [R(int) = 0.0284]	
Completeness to theta = 27.484°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8395	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16079 / 0 / 1074	
Goodness-of-fit on F^2	1.072	
Final R indices [I > 2sigma(I)]	R_1 = 0.0403, wR_2 = 0.1089	
R indices (all data)	R_1 = 0.0448, wR_2 = 0.1127	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.437 and –0.702 e.Å^{-3}	

TIPS-CuBP (CCDC: 2099223)

Empirical formula	$C_{58}H_{60}N_4Si_2Cu$	
Formula weight	932.82	
Temperature	103 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 12.9584(3) Å	α = 101.5277(7)°
	b = 15.6807(3) Å	β = 108.3473(7)°
	c = 19.0596(4) Å	γ = 97.3928(7)°
Volume	3524.59(12) Å^3	
Z	3	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.560 mm^{-1}	
F(000)	1479	
Crystal size	0.250 × 0.200 × 0.180 mm^3	
Theta range for data collection	1.937 to 27.486°	
Index ranges	$-16 \le h \le 15$, $-20 \le k \le 20$, $-24 \le l \le 24$	
Reflections collected	60254	
Independent reflections	16130 [R(int) = 0.0406]	
Completeness to theta = 27.486°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8332	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16130 / 0 / 995	
Goodness-of-fit on F^2	1.156	
Final R indices [I > 2sigma(I)]	R_1 = 0.0621, wR_2 = 0.1790	
R indices (all data)	R_1 = 0.0781, wR_2 = 0.1956	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.314 and –1.315 e.Å^{-3}	

10. NMR

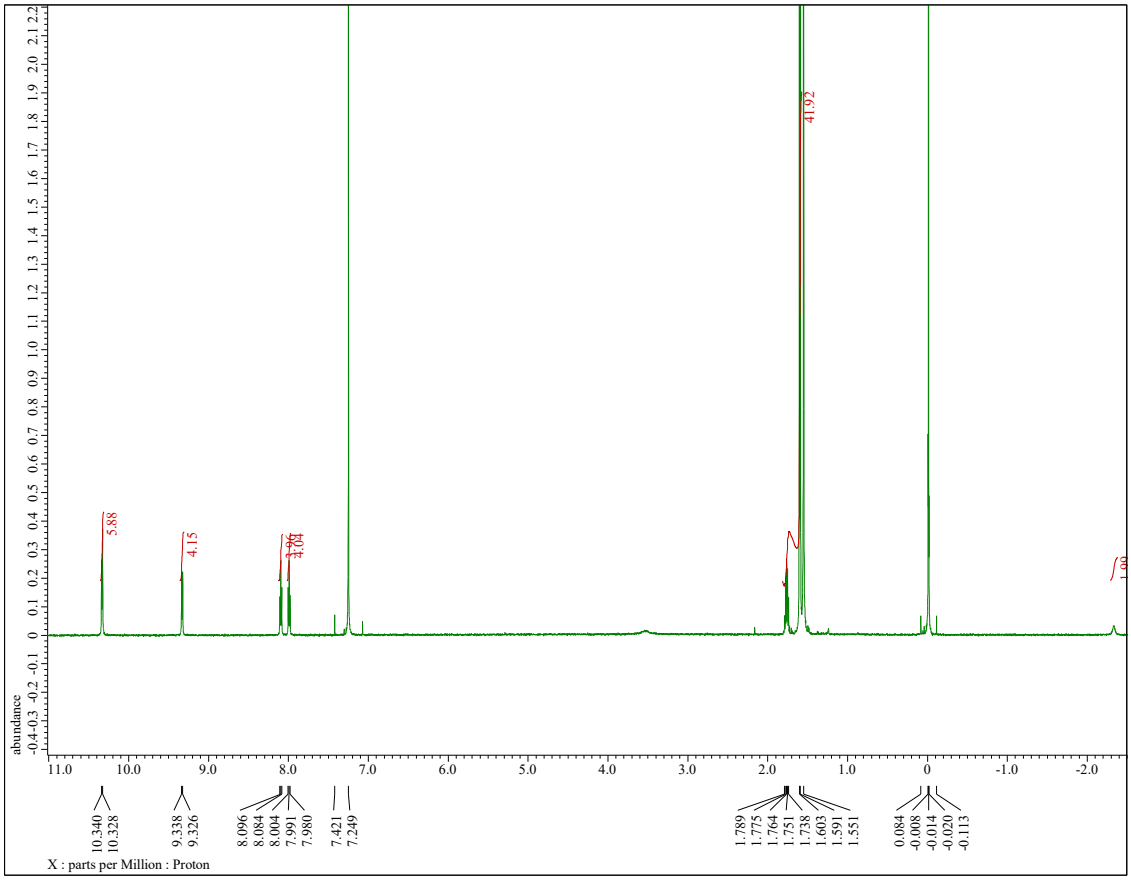


Fig. S7. ^{1}H NMR spectrum of **TIPS-H_2BP** in $CDCl_3$ at room temperature.

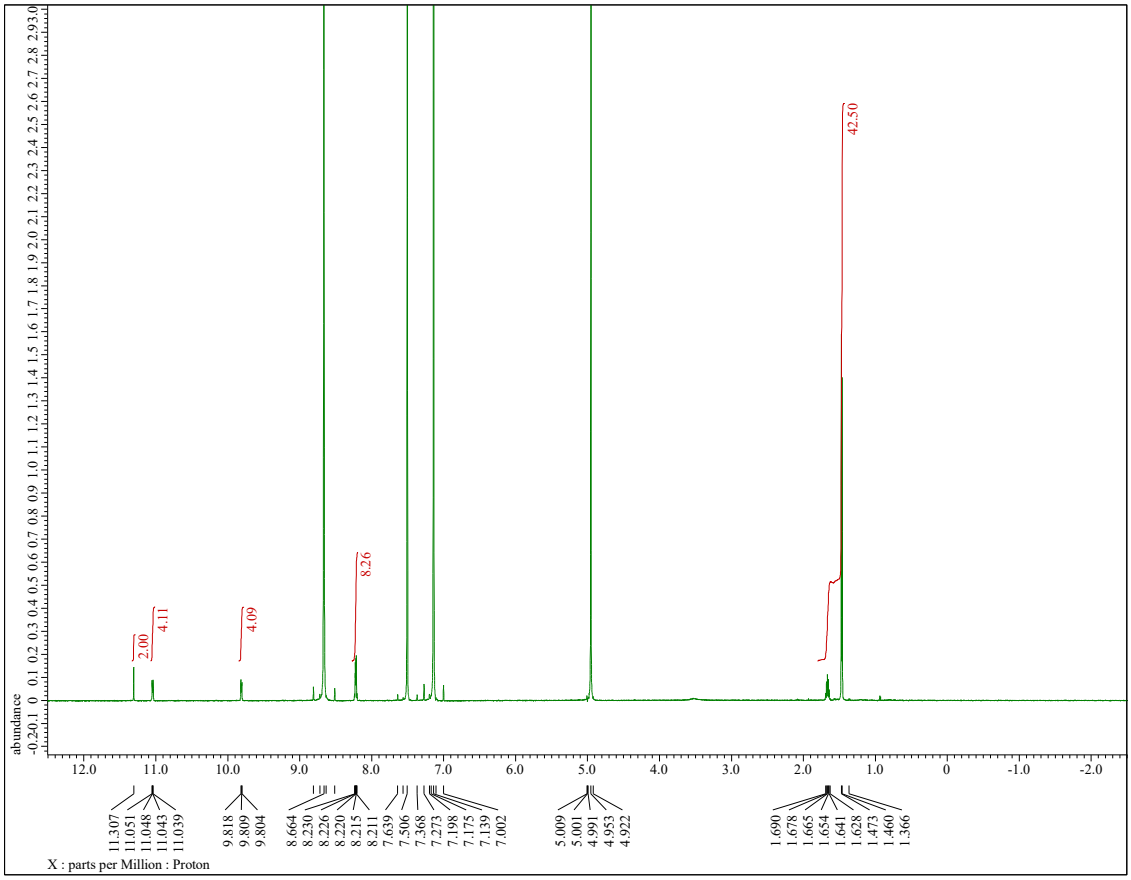
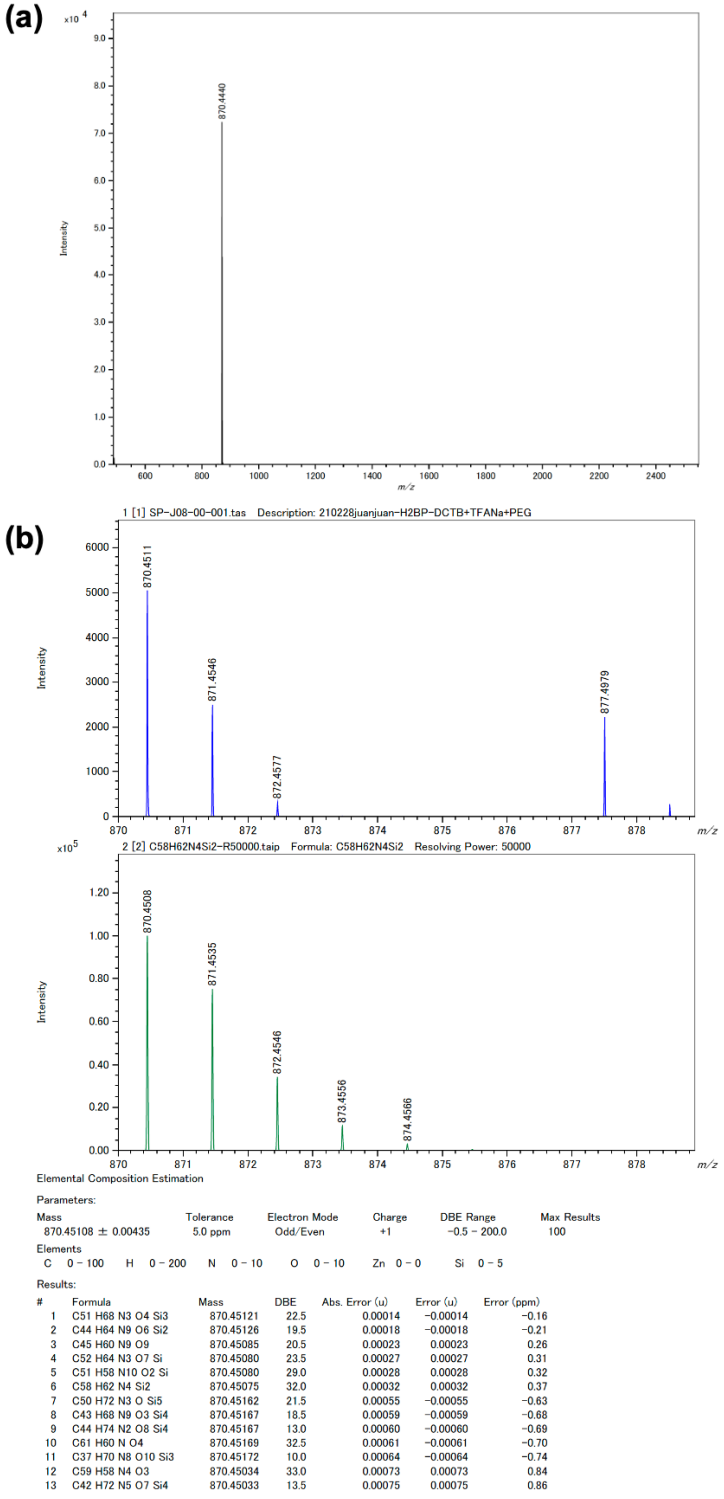


Fig. S8. ^{1}H NMR spectrum of **TIPS-ZnBP** in pyridine-d_5 at room temperature.

11. HRMS



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
870.45108 ± 0.00435	5.0 ppm	Odd/Even	+1	−0.5 – 200.0	100

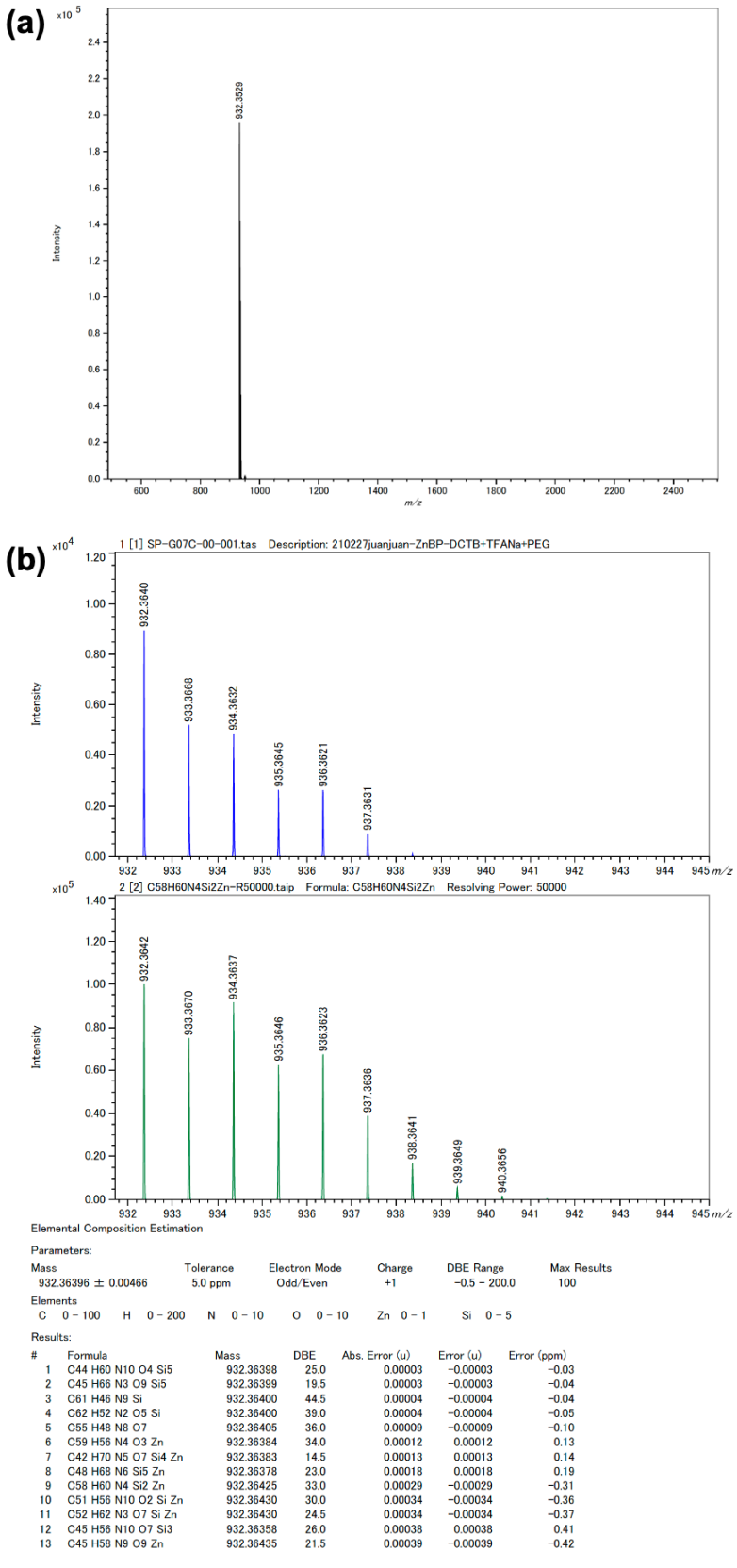
Elements

C 0 – 100 H 0 – 200 N 0 – 10 O 0 – 10 Zn 0 – 0 Si 0 – 5

Results:

#	Formula	Mass	DBE	Abs. Error (ω)	Error (ω)	Error (ppm)
1	C51 H68 N3 O4 Si3	870.45121	22.5	0.00014	−0.00014	−0.16
2	C44 H64 N9 O6 Si2	870.45126	19.5	0.00018	−0.00018	−0.21
3	C45 H60 N9 O9	870.45085	20.5	0.00023	0.00023	0.26
4	C52 H64 N3 O7 Si	870.45080	23.5	0.00027	0.00027	0.31
5	C51 H58 N10 O2 Si	870.45080	29.0	0.00028	0.00028	0.32
6	C58 H62 N4 Si2	870.45075	32.0	0.00032	0.00032	0.37
7	C50 H72 N3 O Si5	870.45162	21.5	0.00055	−0.00055	−0.63
8	C43 H68 N9 O3 Si4	870.45167	18.5	0.00059	−0.00059	−0.68
9	C44 H74 N2 O8 Si4	870.45167	13.0	0.00060	−0.00060	−0.69
10	C61 H60 N O4	870.45169	32.5	0.00061	−0.00061	−0.70
11	C37 H70 N8 O10 Si3	870.45172	10.0	0.00064	−0.00064	−0.74
12	C59 H58 N4 O3	870.45034	33.0	0.00073	0.00073	0.84
13	C42 H72 N5 O7 Si4	870.45033	13.5	0.00075	0.00075	0.86

Fig. S9. (a) MS spectrum and (b) HRMS spectra of **TIPS-H_2BP**.



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
932.36396 ± 0.00466	5.0 ppm	Odd/Even	+1	−0.5 – 200.0	100

Elements

C 0 – 100 H 0 – 200 N 0 – 10 O 0 – 10 Zn 0 – 1 Si 0 – 5

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C44 H60 N10 O4 Si5	932.36398	25.0	0.00003	−0.00003	−0.03
2	C45 H66 N3 O9 Si5	932.36399	19.5	0.00003	−0.00003	−0.04
3	C61 H46 N9 Si	932.36400	44.5	0.00004	−0.00004	−0.04
4	C62 H52 N2 O5 Si	932.36400	39.0	0.00004	−0.00004	−0.05
5	C55 H48 N8 O7	932.36405	36.0	0.00009	−0.00009	−0.10
6	C59 H56 N4 O3 Zn	932.36384	34.0	0.00012	0.00012	0.13
7	C42 H70 N5 O7 Si4 Zn	932.36383	14.5	0.00013	0.00013	0.14
8	C48 H68 N6 Si5 Zn	932.36378	23.0	0.00018	0.00018	0.19
9	C58 H60 N4 Si2 Zn	932.36425	33.0	0.00029	−0.00029	−0.31
10	C51 H56 N10 O2 Si Zn	932.36430	30.0	0.00034	−0.00034	−0.36
11	C52 H62 N3 O7 Si Zn	932.36430	24.5	0.00034	−0.00034	−0.37
12	C45 H56 N10 O7 Si3	932.36358	26.0	0.00038	0.00038	0.41
13	C45 H58 N9 O9 Zn	932.36435	21.5	0.00039	−0.00039	−0.42

Fig. S10. (a) MS spectrum and (b) HRMS spectra of **TIPS-ZnBP**.

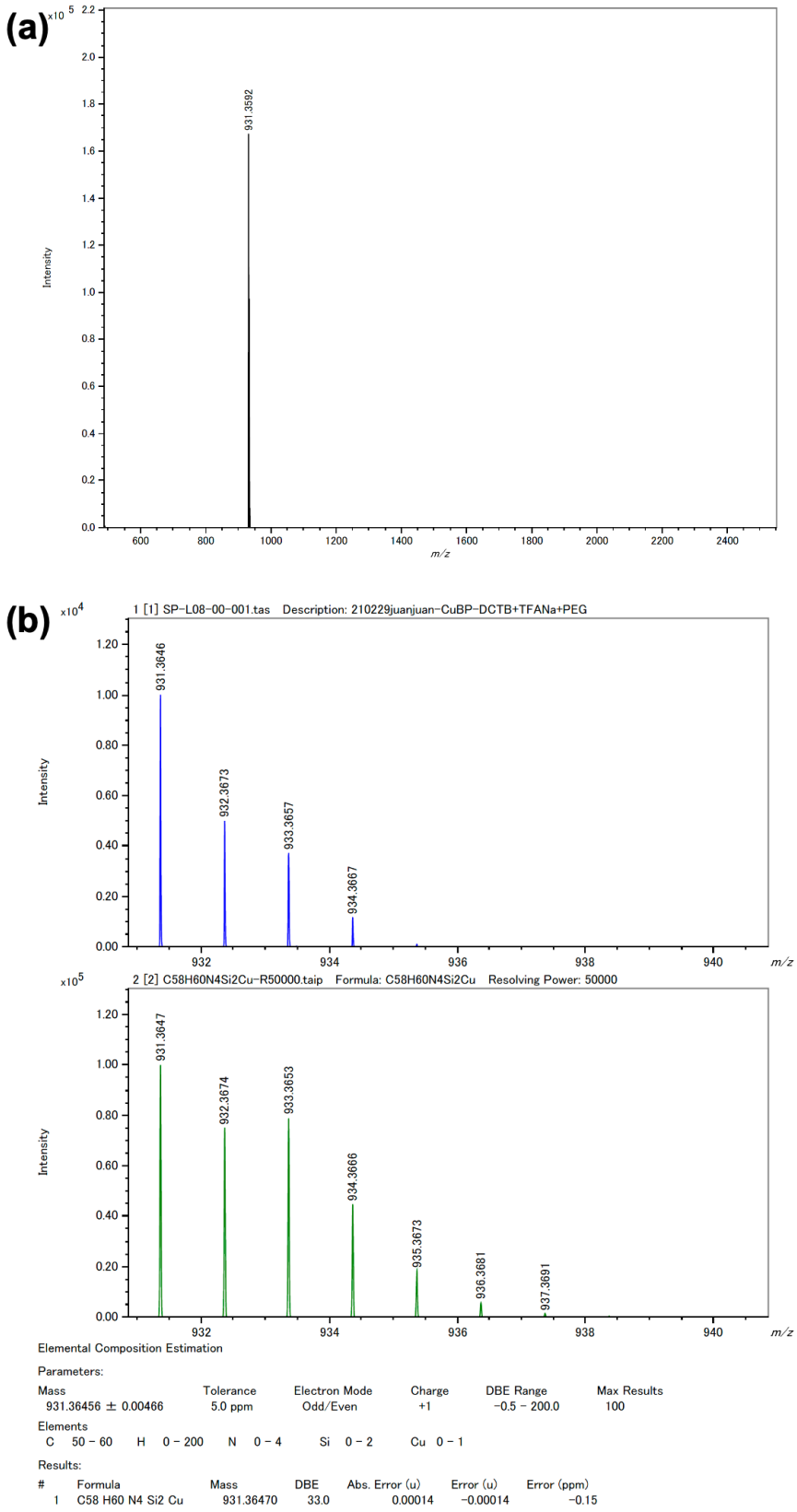


Fig. S11. (a) MS spectrum and (b) HRMS spectra of **TIPS-CuBP**.