Electronic supplementary information for

Substituent effect on the ligand-centred electrocatalytic hydrogen evolution of antimony(III) corroles

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1. General information

All reagents were purchased commercially and were used without further purification unless otherwise pointed out. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. The NMR spectra were referenced to the $CDCl_3$ residual solvent signal (7.26 ppm). UV-vis spectra in CH_2Cl_2 were recorded using a Hitachi U-3010 spectrophotometer at room temperature. High-resolution mass spectra (HRMS) were obtained using the Bruker microQ-TOF-QII high resolution spectrometer in the electrospray ionization (ESI) mode using Bruker Daltonics coupled to a Water Acquinty system. X-ray photoelectron spectroscopy (XPS) was measured using an Axis Ultra DLD spectrophotometer, correcting the binding energies by comparing to C 1s peak (284.8 eV) by the adventitious hydrocarbon. Electrochemical measurements were performed with a CHI-660E electrochemical workstation at room temperature under saturated N_2. The three-electrode cell had glass carbon (GC) as the working electrode, graphite rod as the counter electrode, saturated $Ag/AgNO_3$ as the reference electrode in DMF, and Ag/AgCl as the reference electrode in aqueous solutions. Ferrocene was added as an internal standard in DMF. The $E_{1/2}$ value of reference Fc/Fc+ coupe is -0.005 V in DMF. Controlled potential electrolysis (CPE) test was performed in a single electrolytic cell filled with 20 mL of buffer solution (DMF: H_2O 1:2) with 0.1 M KCl and 0.25 M KH_2PO_4.

2. Synthesis methods

5,10,15-tris (pentafluorophenyl) corrole (**$F_{15}C$**), 5,15-bis (pentafluorophenyl)-10-(phen-yl) corrole (**$F_{10}C$**), 5,15-bis (phenyl)-10-(pentafluoropheny) corrole (**F_5C**), 5,10,15-tris (phe-nyl) corrole (**F_0C**), 5,10,15-tris (pentafluorophenyl) Sb(III) corrole (**$F_{15}C$-Sb**) and 5,10,15-tris (phenyl) corrole Sb(III) (**F_0C-Sb**) were prepared by previously published procedures.[1-3]

5,10,15-tris (pentafluorophenyl) corrole ($F_{15}C$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (d, J = 4.3 Hz, 2H), 8.77 (d, J = 4.7 Hz, 2H), 8.58 (t, J = 5.3 Hz, 4H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.18 (s,2F), -137.72 (s,4F), -152.10 (s,2F), -152.69 (s,1F), -161.34 (s,4F), -161.82 (s,2F). HRMS-ESI: *m/z* calcd. for $[C_{37}H_{11}F_{15}N_4+H^+]$: 797.0817 $[M+H]^+$; found: 797.0815.

5,15-bis (pentafluorophenyl)-10-(phenyl) corrole ($F_{10}C$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.10 (s, 2H), 8.72 (s, 4H), 8.55 (s, 2H), 8.18 (s, 2H), 7.82 – 7.73 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.86 (s, 4F), -152.86 (s, 2F), -161.78 (s, 4F). HRMS-ESI: *m/z* calcd. for $[C_{37}H_{16}F_{10}N_4+H^+]$: 707.1288 $[M+H]^+$; found: 707.1284.

5,15-bis (phenyl)-10-(pentafluoropheny) corrole (F_5C)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 (s, 4H), 8.55 (s, 2H), 8.43 (s, 2H), 8.34 (d, J = 7.4 Hz, 4H), 7.81 (d, J = 7.9 Hz, 4H), 7.74 (d, J = 7.6 Hz, 2H).^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.43 (d, *J* = 24.8 Hz, 2F), -153.90 (t, *J* = 20.9 Hz, 1F), -162.44 (t, *J* = 20.8 Hz, 2F). HRMS-ESI: *m/z* calcd. for [$C_{37}H_{21}F_5N_4$+H$^+$]: 617.1759 [M+H] $^+$; found: 617.1752.

5,10,15-tris (phenyl) corrole (F_0C)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 – 8.66 (m, 4H), 8.42 (d, *J* = 62.1 Hz, 8H), 8.14 (s, 2H), 7.76 (d, *J* = 7.1 Hz, 9H). HRMS-ESI: *m/z* calcd. for [$C_{37}H_{26}N_4$+H$^+$]: 527.2230 [M+H] $^+$; found: 527.2232.

5,10,15-tris (pentafluorophenyl) Sb(III) corrole ($F_{15}C$-Sb)

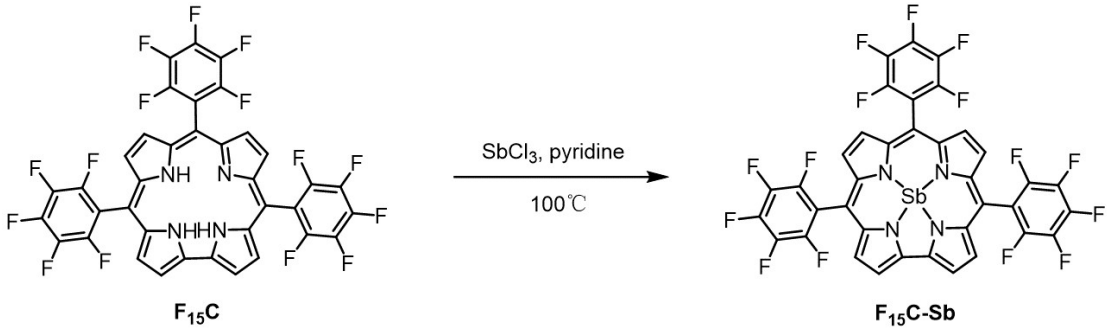

Fig. S1 Synthetic routes of Sb(III) corrole

The specific synthesis steps of Sb(III) corrole are exemplified by **$F_{15}C$-Sb**. Dissolve 100 mg **$F_{15}C$** (0.13 mmol) and 480 mg $SbCl_3$ (2.02 mmol) in a round-bottomed flask with 10 ml pyridine. Then the temperature was raised to 100°C and reacted for 2 hours, and the solution turned into dark green. Remove excess solvent with a rotary evaporator, and fill the column with 100 ~ 200 mesh silica gel. Use dichloromethane and hexane (DCM/Hex) (V/V) = 3/1 as an eluent to purify the product. After recrystallization obtain green solid (96.26 mg, yield 83.50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.25 (d, J = 4.2 Hz, 2H), 8.90 (dd, J = 4.7, 1.4 Hz, 2H), 8.72 (d, J = 4.2 Hz, 2H), 8.65 (d, J = 4.6 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.75 (dd, *J* = 24.9, 7.1 Hz, 2F), -136.99 (ddd, *J* = 74.3, 24.9, 8.6 Hz, 2F), -137.32 (dd, *J* = 24.3, 8.3 Hz, 2F), -152.31 (t, *J* = 21.0 Hz, 2F), -152.64 (t, *J* = 20.9 Hz, 1F), -161.31 to -162.07 (m, 6F). HRMS-ESI: m/z calcd. for [$C_{37}H_{11}F_{15}$N4+H$^+$]: 914.9620 [M+H] $^+$; found: 914.9623.

5,15-bis (pentafluorophenyl)-10-(phenyl) Sb(III) corrole ($F_{10}C$-Sb)

The synthetic route was similar to **$F_{15}C$-Sb**, after recrystallization obtain pure antimony corrole (green solid, yield 86.52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (d, *J* = 4.2 Hz,

2H), 8.91 (dd, *J* = 4.7, 1.5 Hz, 2H), 8.87 (d, *J* = 4.6 Hz, 2H), 8.78 (dd, *J* = 4.2, 1.3 Hz, 2H), 8.35 (s, 1H), 7.97 (s, 1H), 7.83 – 7.70 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.87 (ddd, *J* = 24.6, 8.2, 3.0 Hz, 2F), -137.46 (ddd, *J* = 23.9, 8.5, 3.0 Hz, 2F), -152.93 (t, *J* = 21.0 Hz, 2F), -161.87 (dddd, *J* = 57.6, 24.5, 20.8, 8.5 Hz, 4F). HRMS-ESI: *m/z* calcd. for [$C_{37}H_{16}F_{10}N_4$+H^+]: 824.0013 [M+H] $^+$; found: 824.0005.

5,15-bis (phenyl)-10-(pentafluoropheny) Sb(III) corrole (F_5C-Sb)

The synthetic route was similar to **F_{15}C-Sb**, after recrystallization obtain pure antimony corrole (green solid, yield 76.53%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (dd, *J* = 10.8, 4.3 Hz, 4H), 8.77 (d, *J* = 4.2 Hz, 2H), 8.56 (d, *J* = 4.6 Hz, 2H), 8.24 (s, 4H), 7.83 – 7.75 (m, 6H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -137.22 (ddd, *J* = 73.5, 24.8, 8.8 Hz, 2F), -153.84 (t, *J* = 21.1 Hz, 1F), -162.29 (dddd, *J* = 33.8, 21.3, 14.5, 8.4 Hz, 2F). HRMS-ESI: *m/z* calcd. for [$C_{37}H_{21}F_5N_4$+H^+]: 734.0484 [M+H] $^+$; found: 734.0486.

5,10,15-tris (phenyl) Sb(III) corrole (F_0C-Sb)

The synthetic route was similar to **F_{15}C-Sb**, after recrystallization obtain pure antimony corrole (green solid, yield 80.13%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (dd, *J* = 28.5, 4.4 Hz, 4H), 8.78 (dd, *J* = 16.1, 4.4 Hz, 4H), 8.40 – 8.21 (m, 6H), 7.85 – 7.72 (m, 9H). HRMS-ESI: m/z calcd. for [$C_{37}H_{26}N_4$+H+]: 644.0955 [M+H] +; found: 644.0957.

References:

1 S. Mondal, A. Garai, P. K. Naik, J. K. Adha and S. Kar, *Inorg. Chim. Acta.*, 2020, **501**, 119300.

2 L. Huang, A. Ali, H. Wang, F. Cheng and H. Liu, *J. Mol. Catal. A Chem.*, 2017, **426**, 213-222.

3 I. Luobeznova, M. Raizman, I. Goldberg and Z. Gross, *Inorg. Chem.*, 2006, **45**, 386-394.

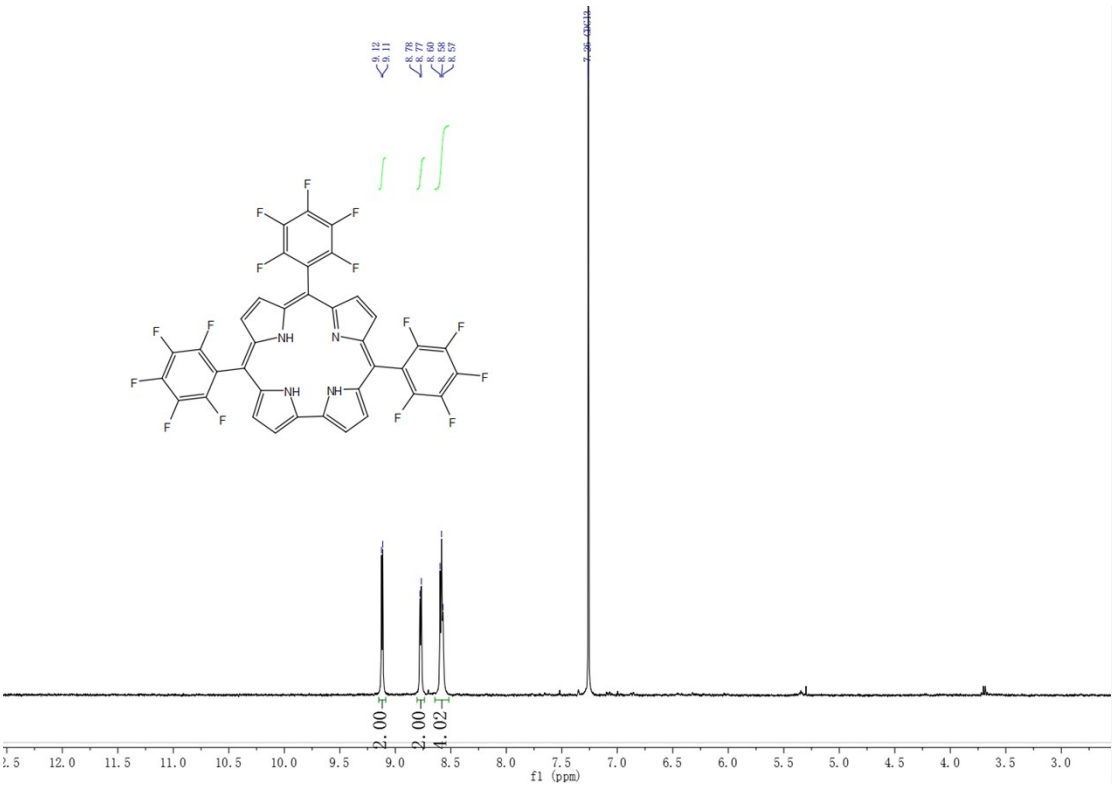

Fig. S2 ^{1}H NMR spectrum of **F_{15}C**

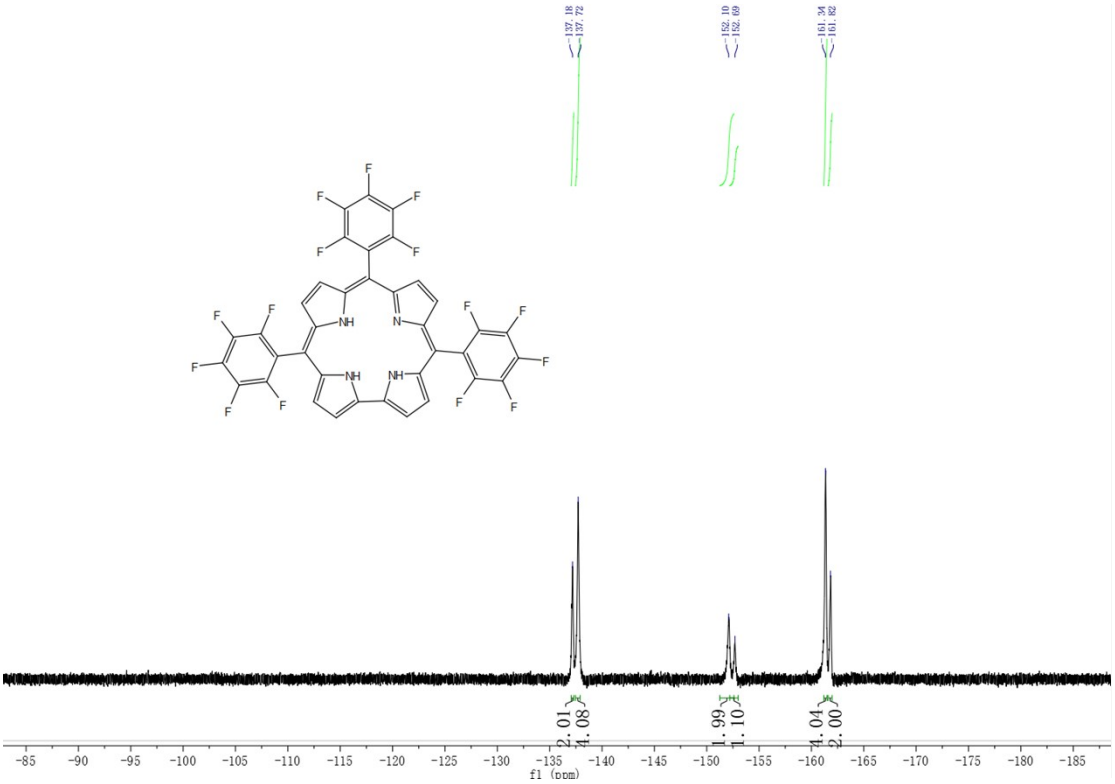

Fig. S3 ^{19}F NMR spectrum of **F_{15}C**

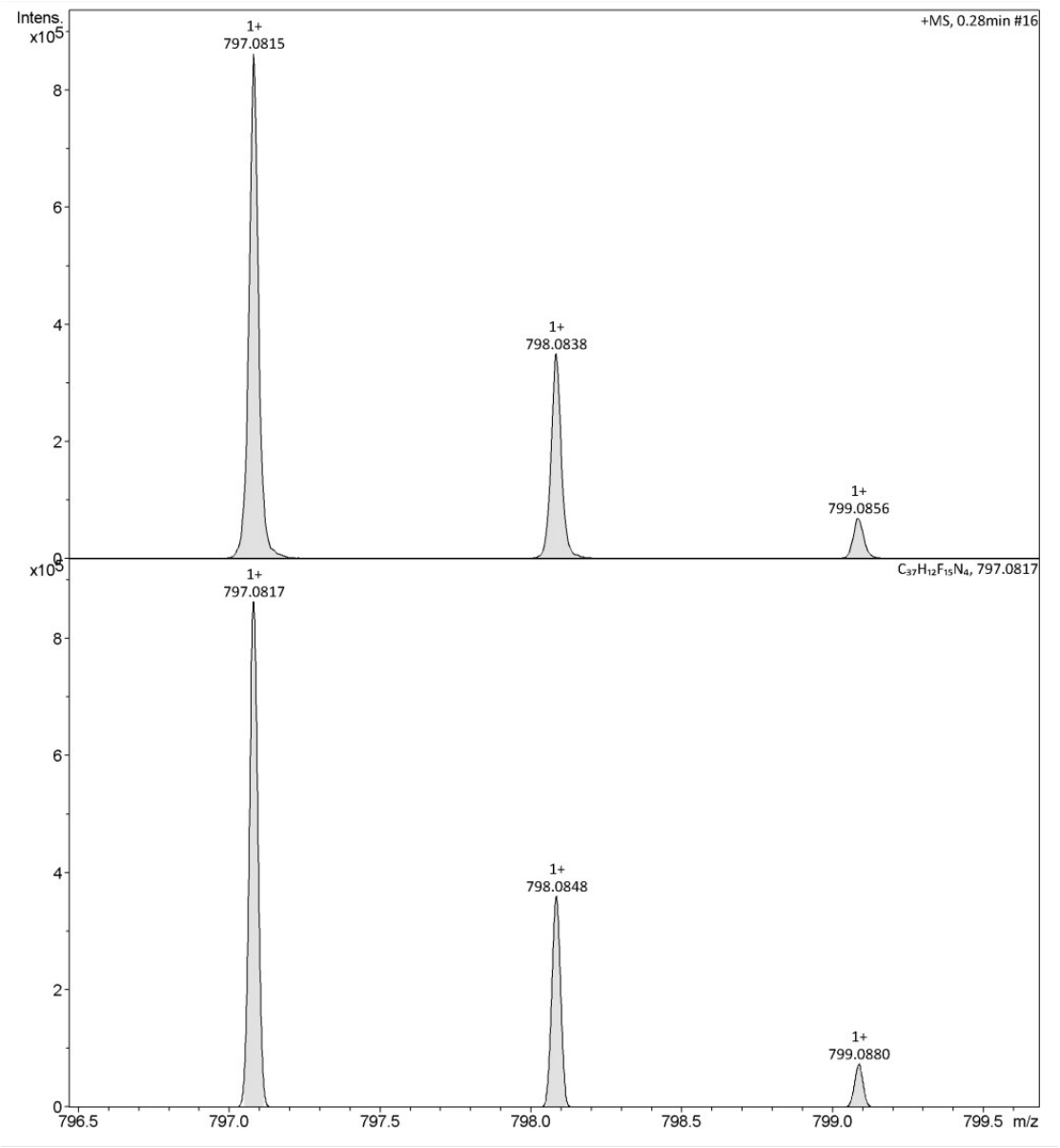

Fig. S4 ESI-HRMS spectrum of **$F_{15}C$**

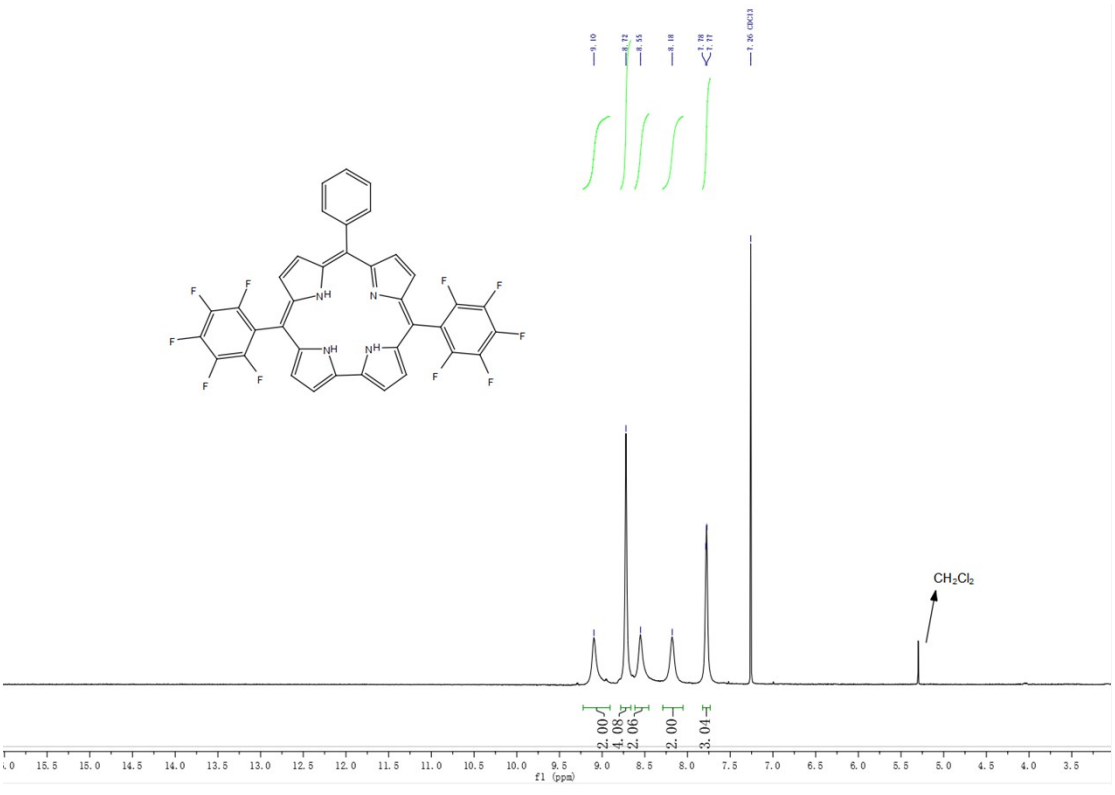

Fig. S5 ^{1}H NMR spectrum of **$F_{10}C$**

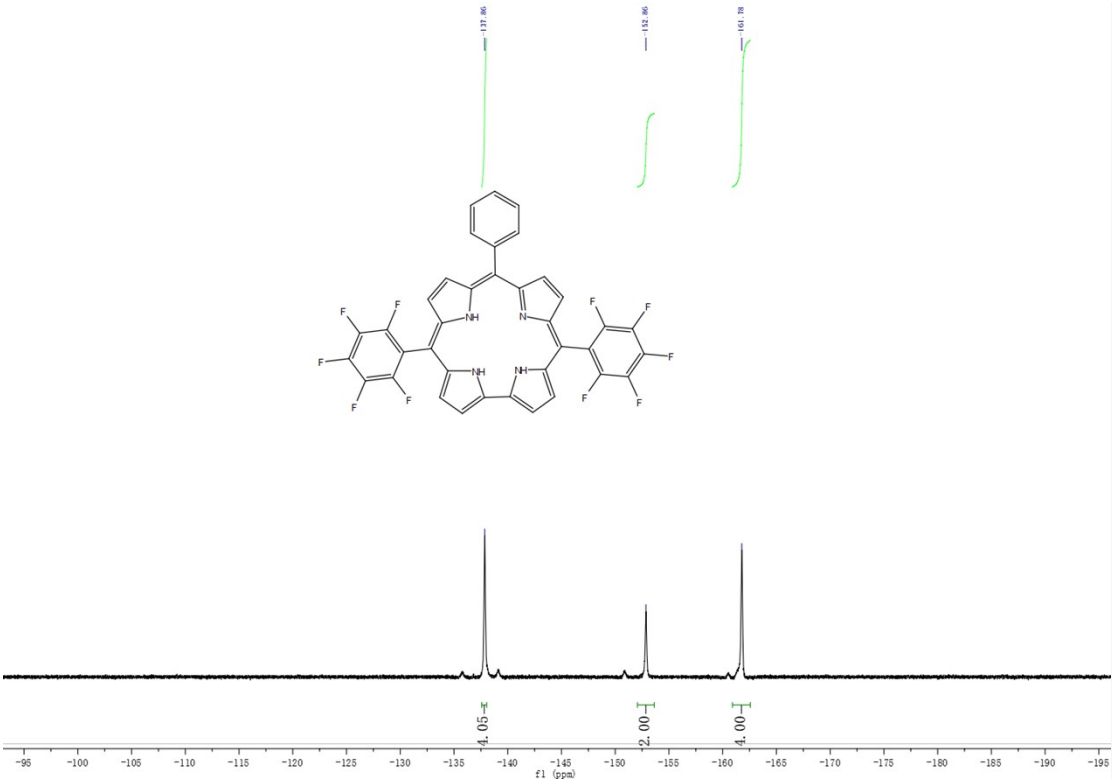

Fig. S6 ^{19}F NMR spectrum of **$F_{10}C$**

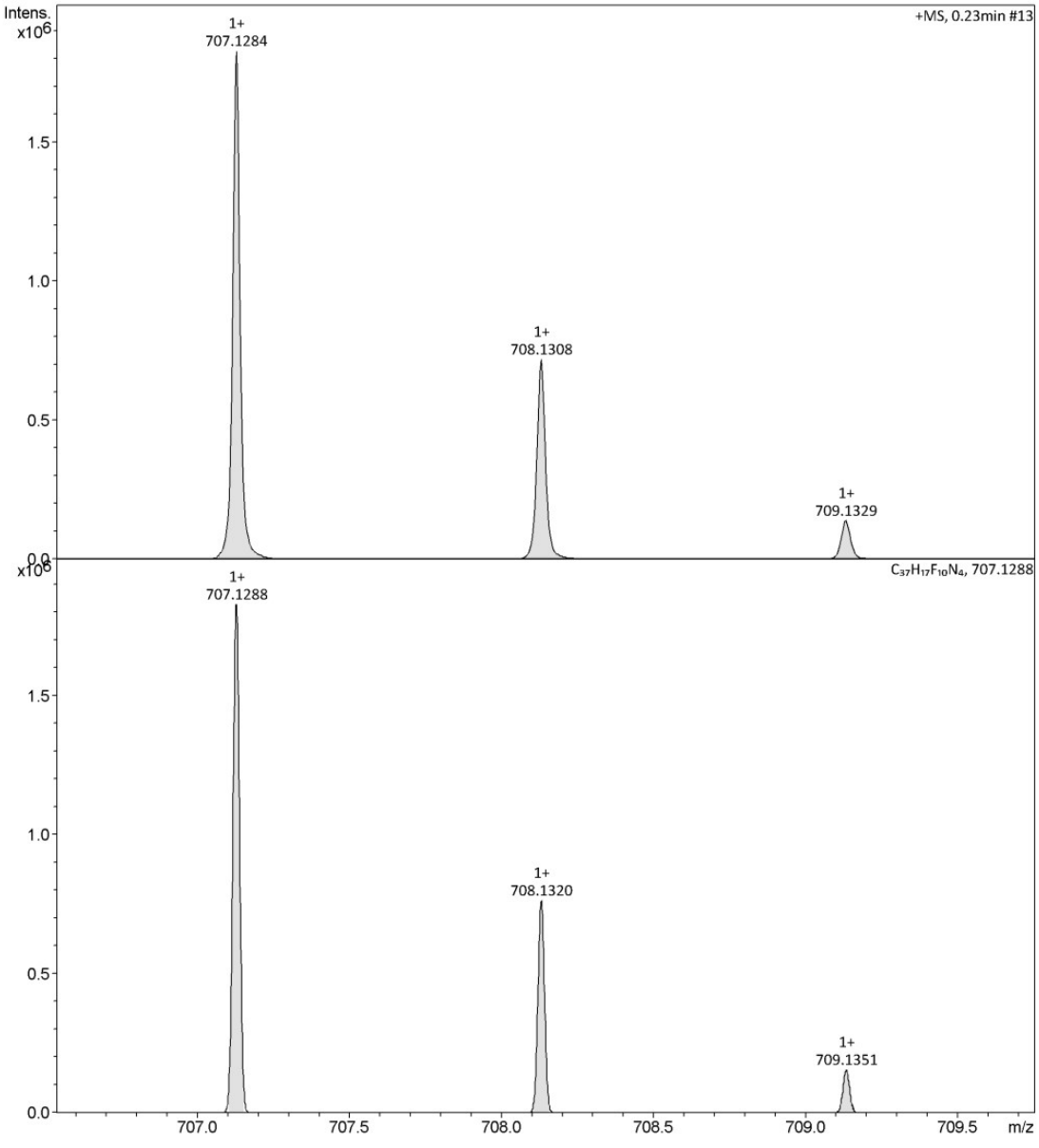

Fig. S7 ESI-HRMS spectrum of **F_{10}C**

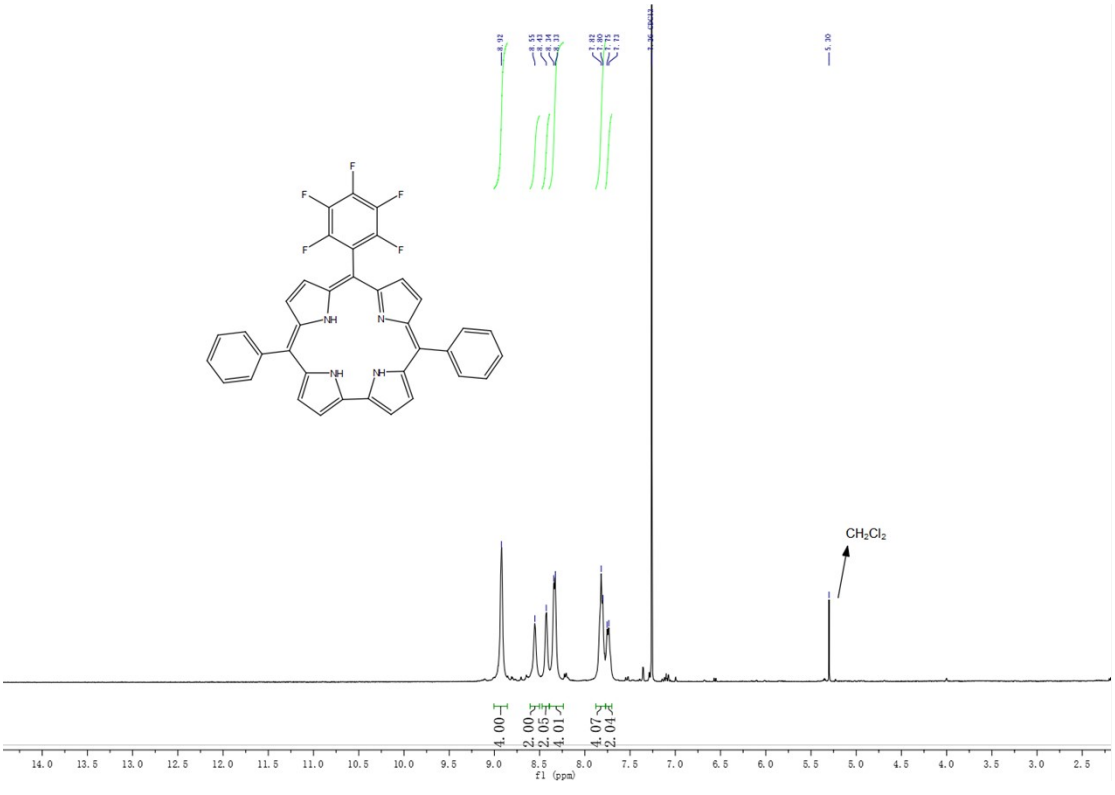

Fig. S8 ^{1}H NMR spectrum of **F_5C**

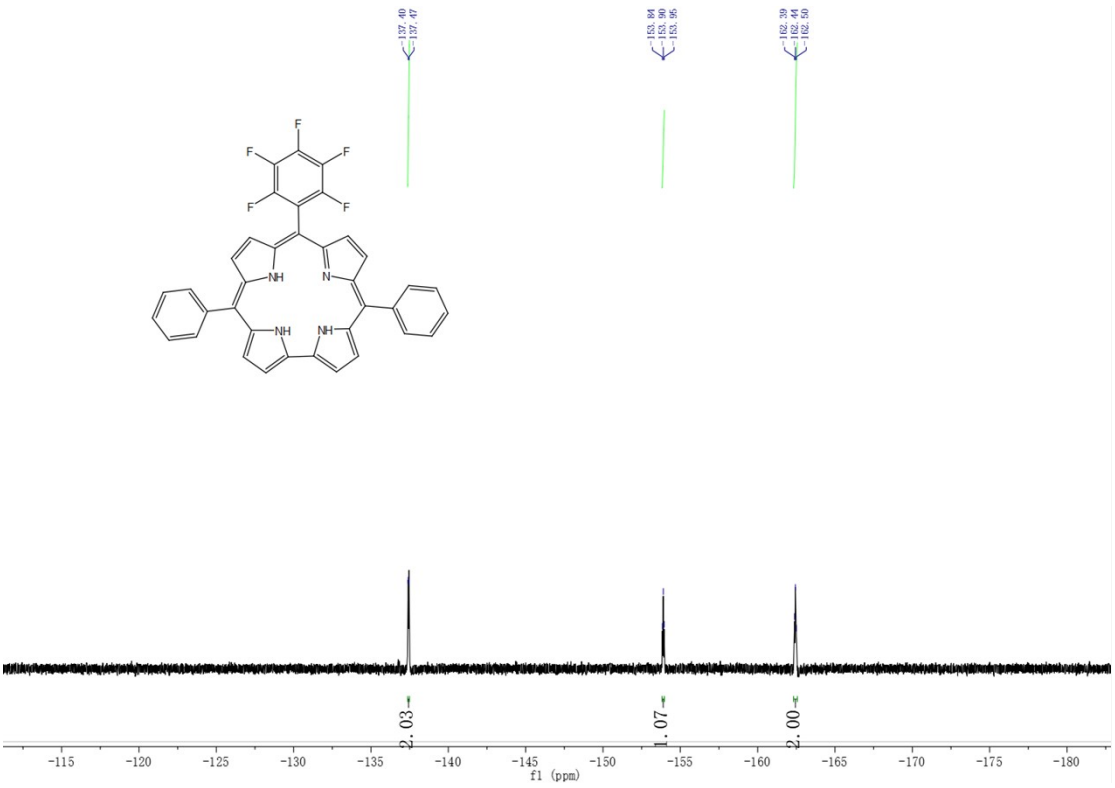

Fig. S9 ^{19}F NMR spectrum of **F_5C**

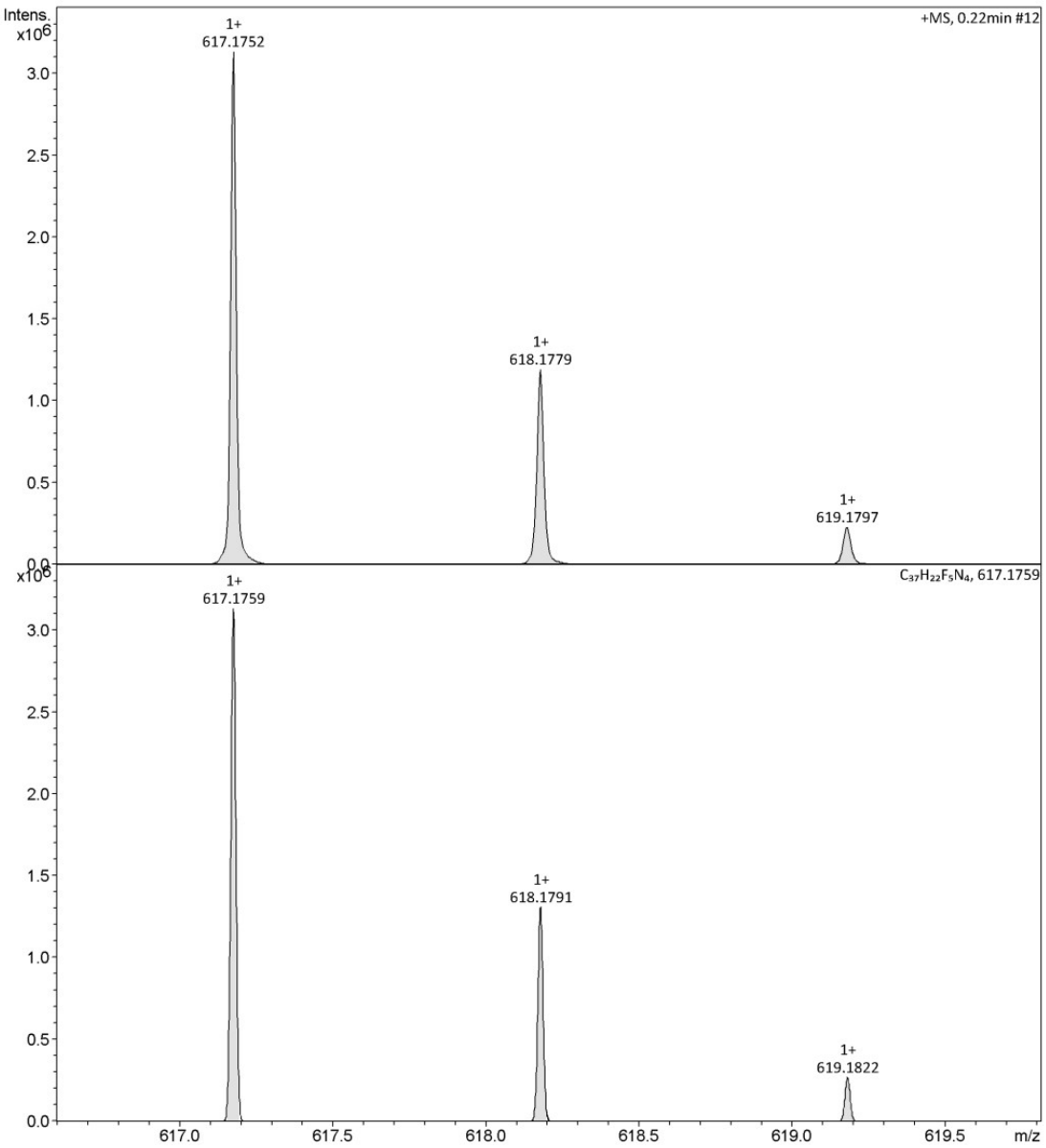

Fig. S10 ESI-HRMS spectrum of **F_5C**

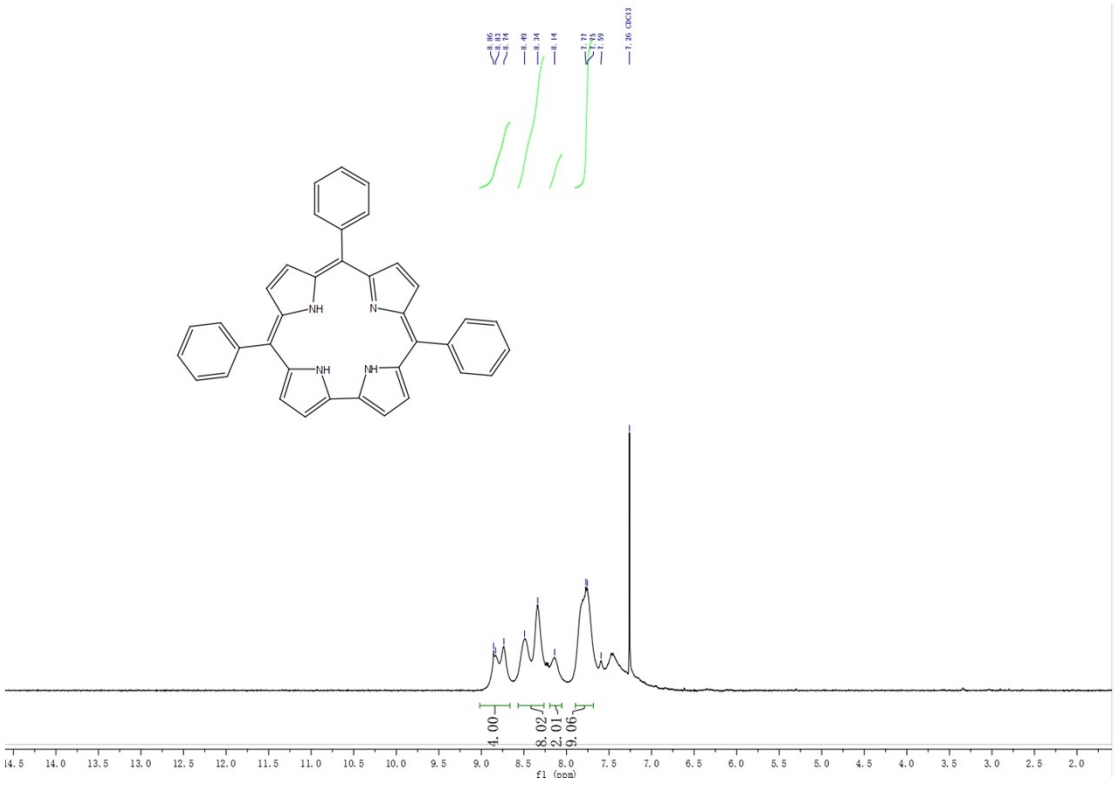

Fig. S11 ^{1}H NMR spectrum of **F_0C**

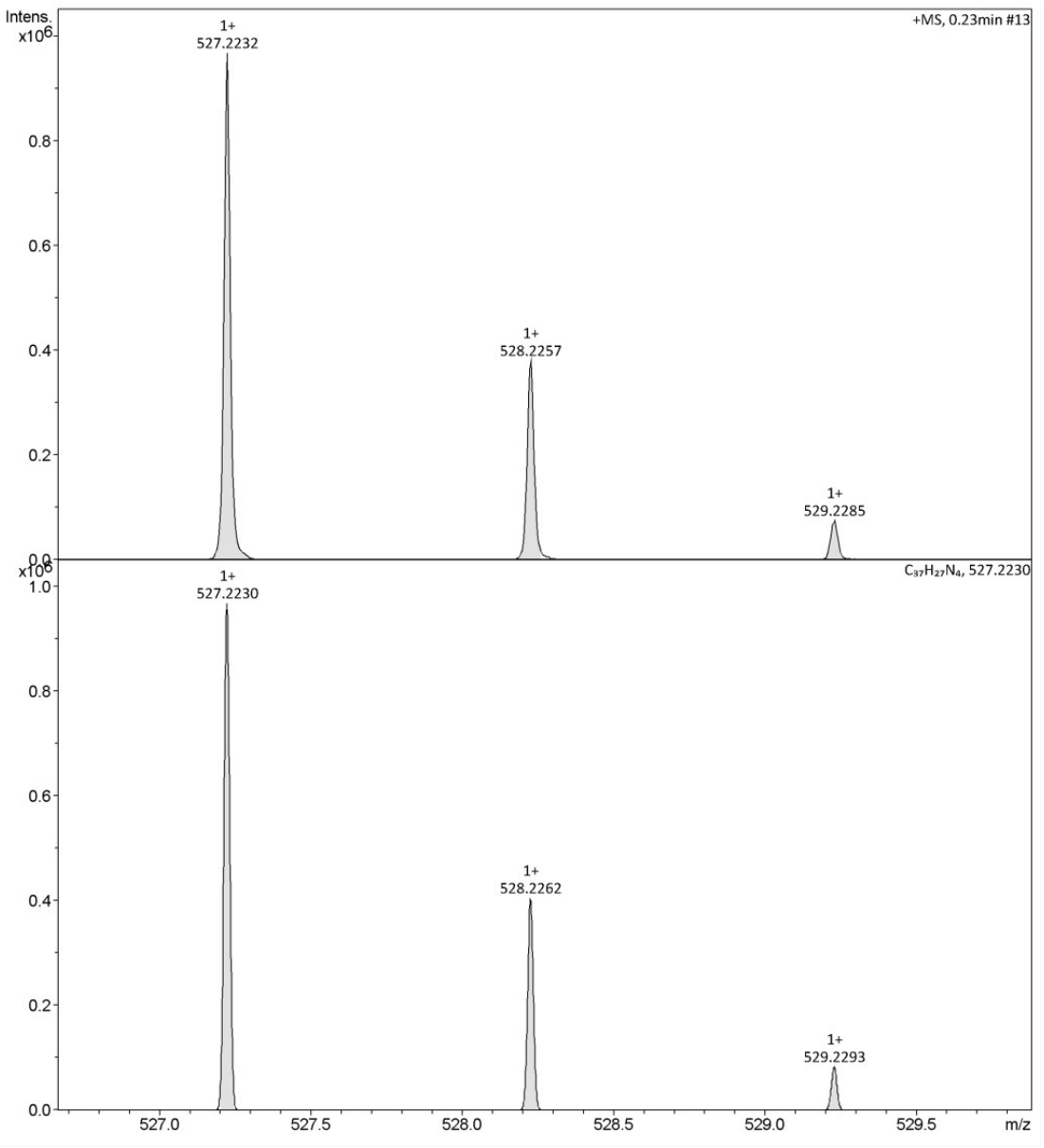

Fig. S12 ESI-HRMS spectrum of **F_0C**

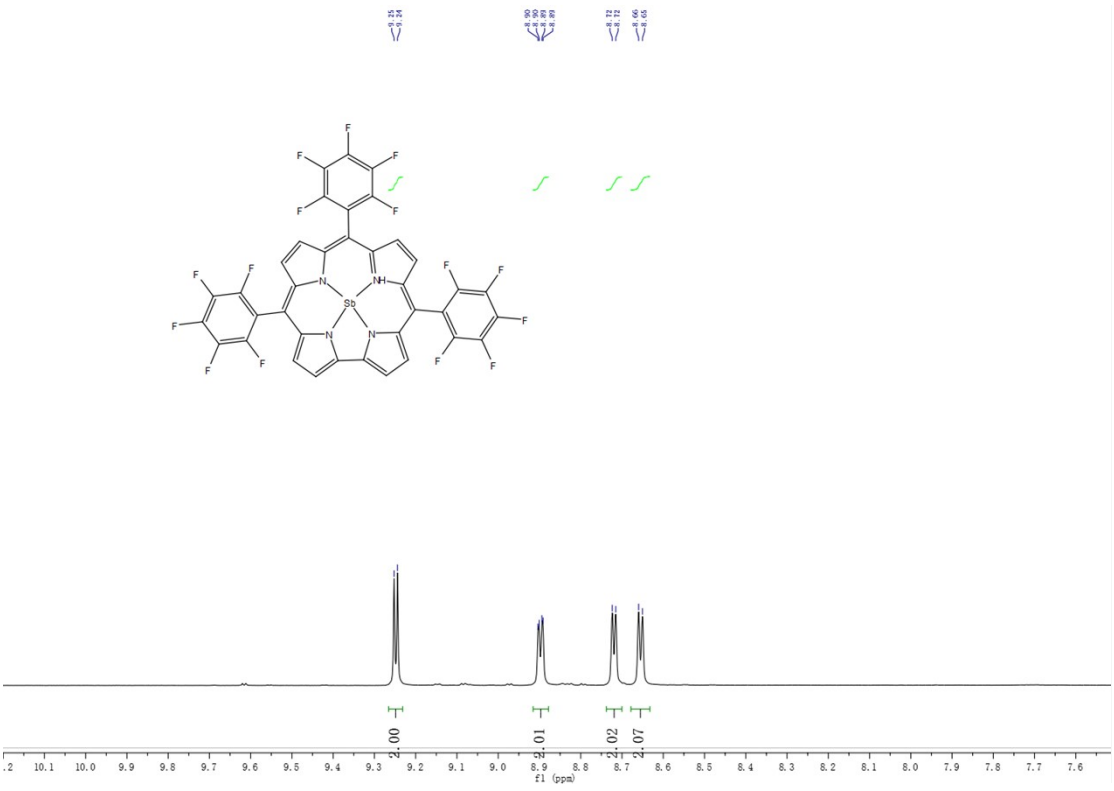

Fig. S13 ^{1}H NMR spectrum of **F_{15}C-Sb**

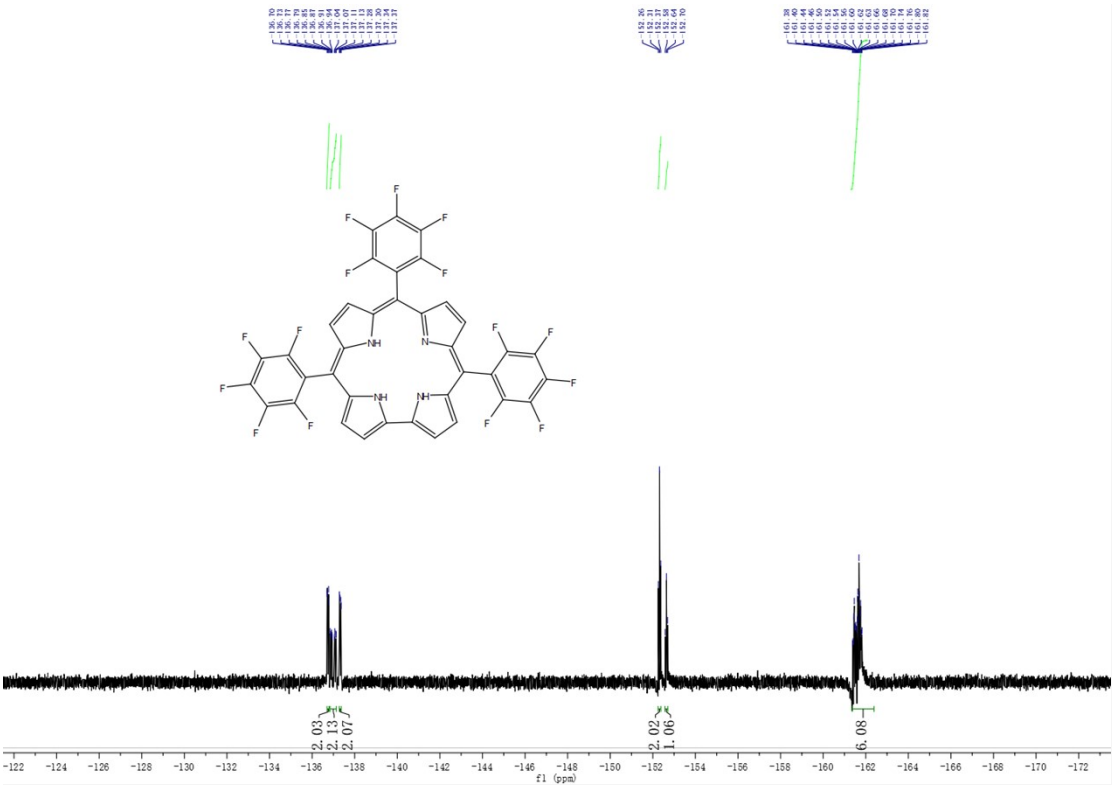

Fig. S14 ^{19}F NMR spectrum of **F_{15}C-Sb**

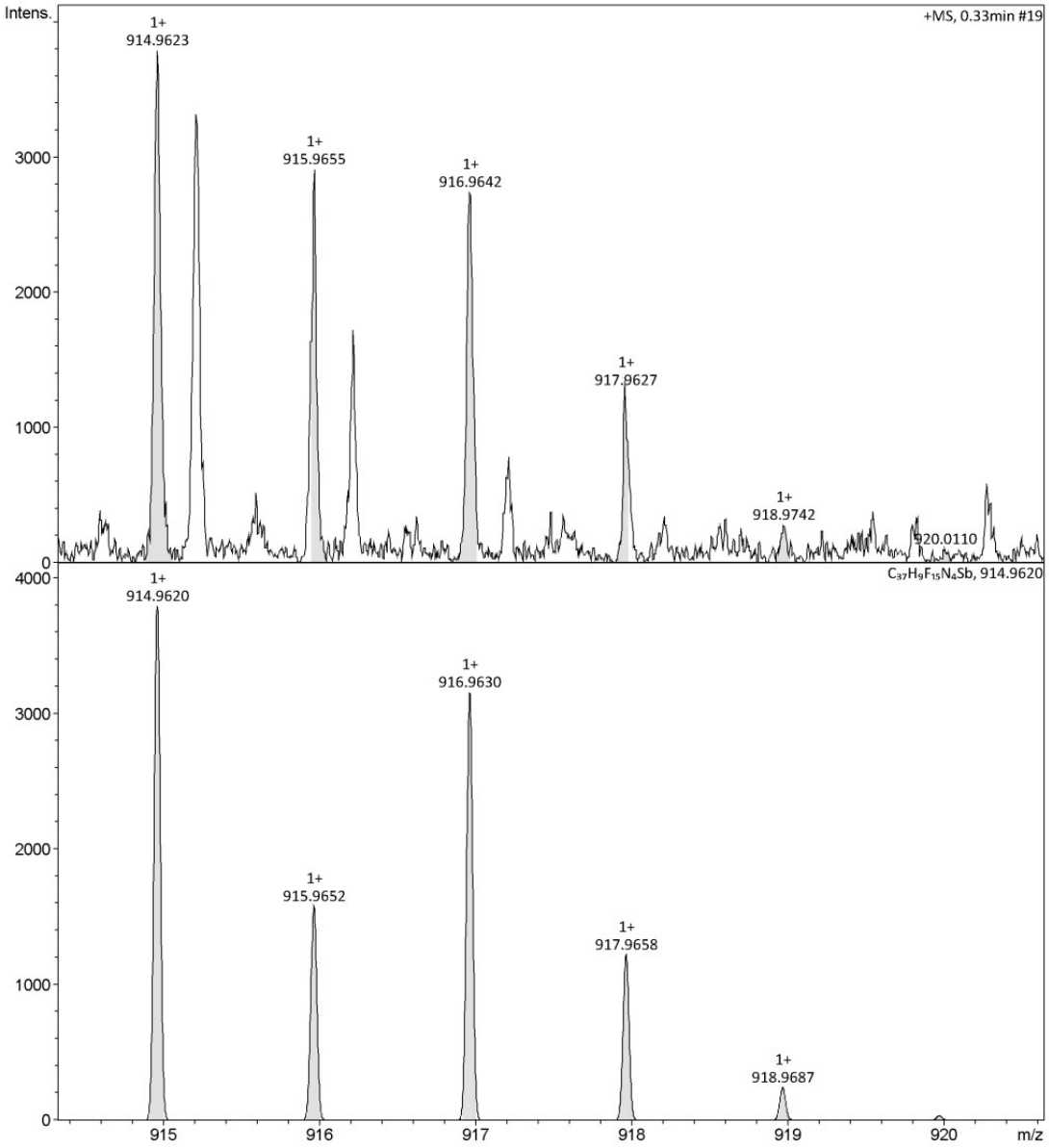

Fig. S15 ESI-HRMS spectrum of **F_{15}C-Sb**

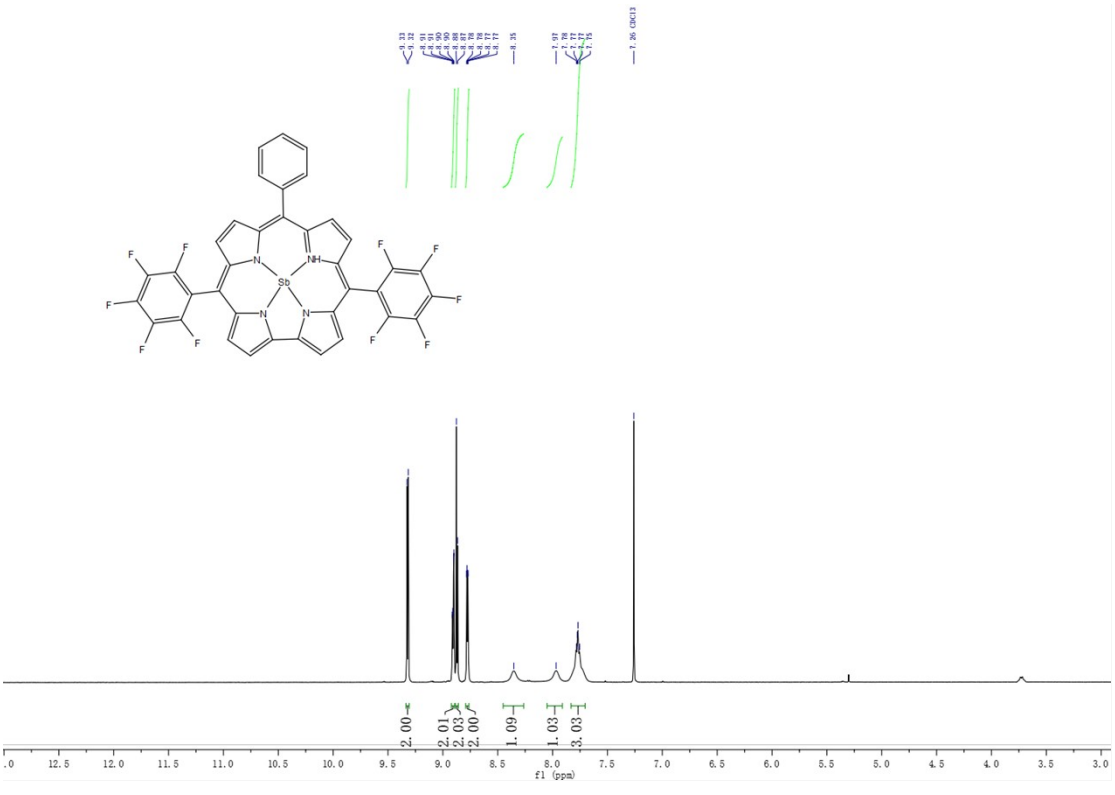

Fig. S16 ^{1}H NMR spectrum of **F_{10}C-Sb**

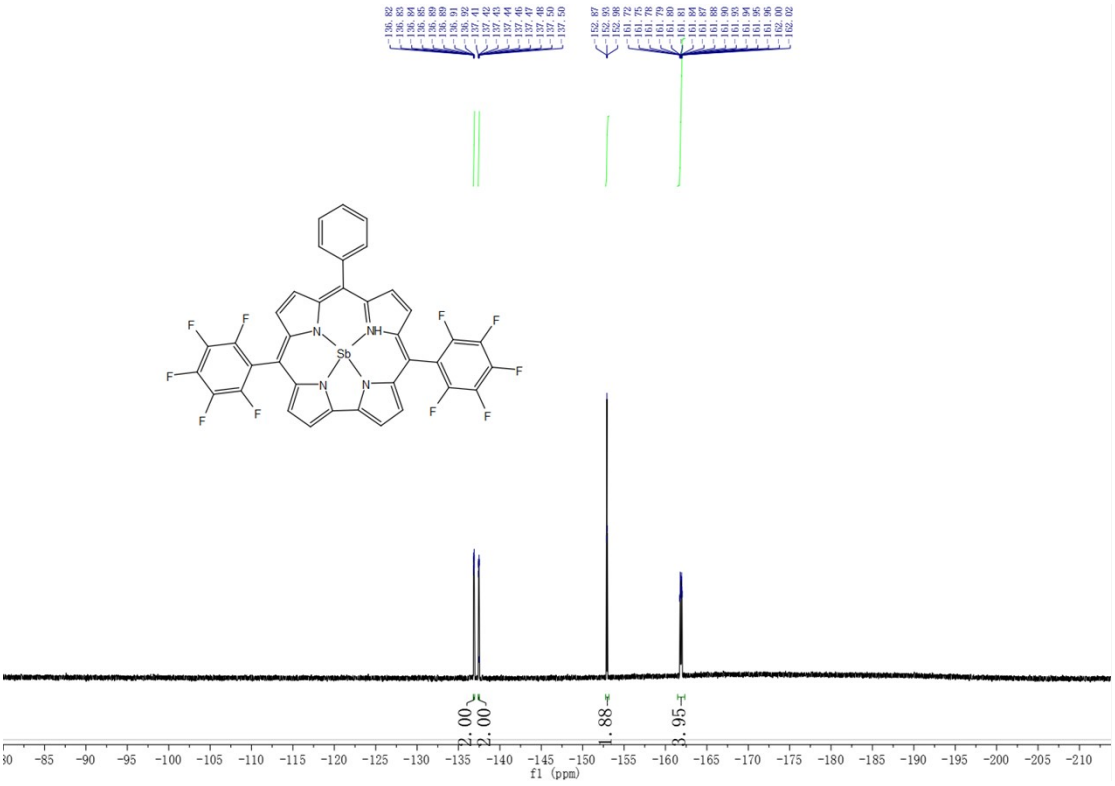

Fig. S17 ^{19}F NMR spectrum of **F_{10}C-Sb**

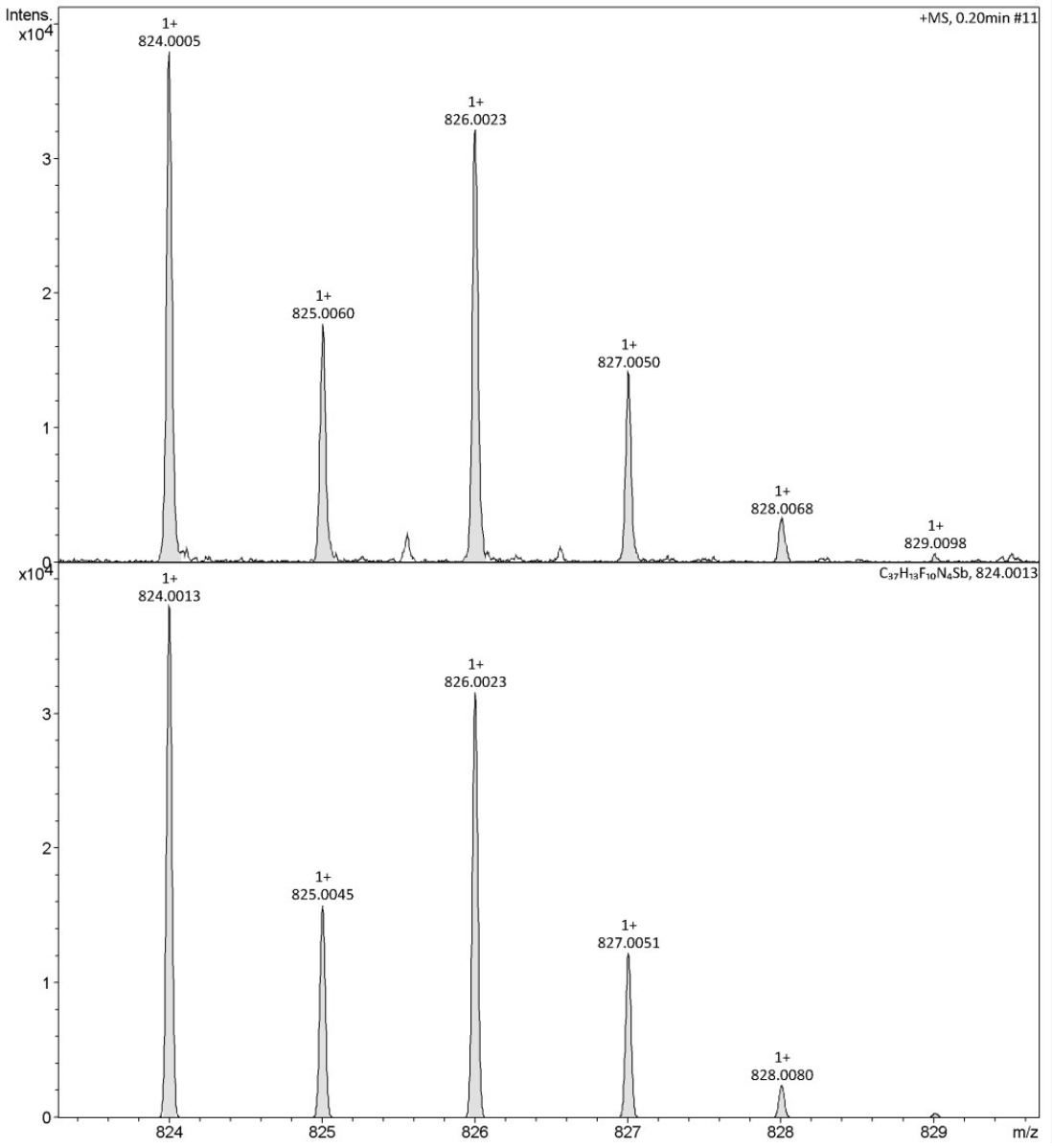

Fig. S18 ESI-HRMS spectrum of **F_{10}C-Sb**

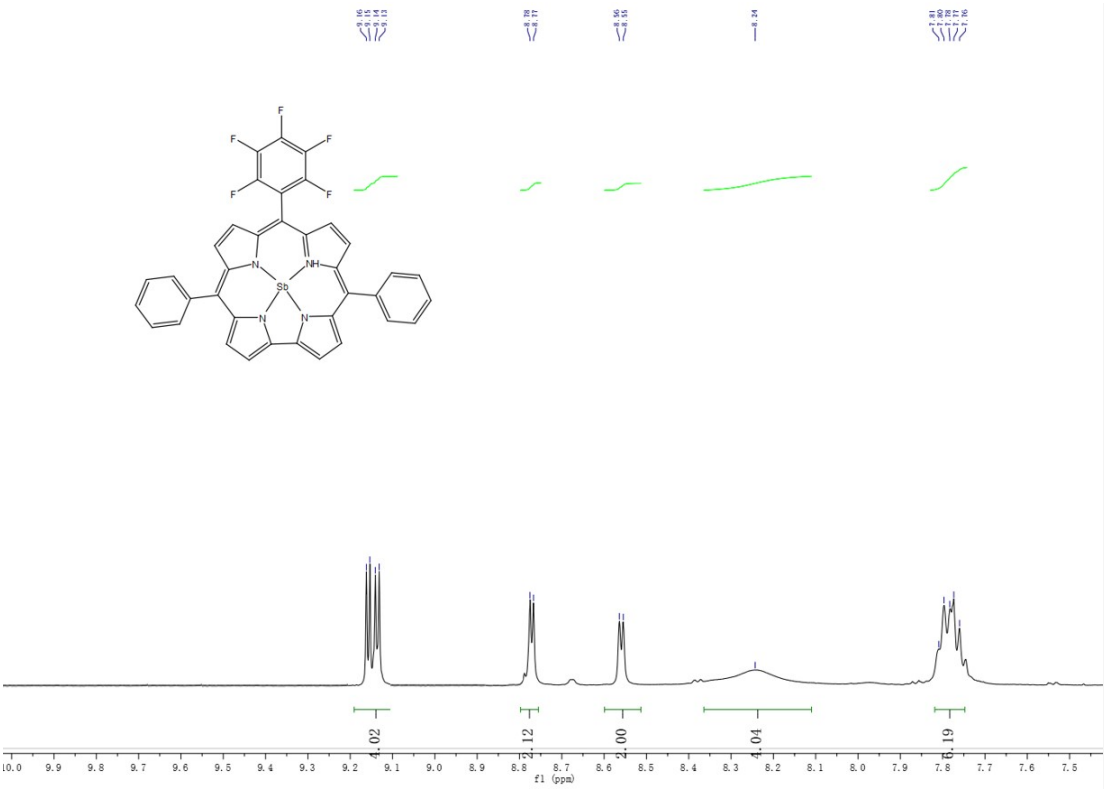

Fig. S19 ^{1}H NMR spectrum of **F_5C-Sb**

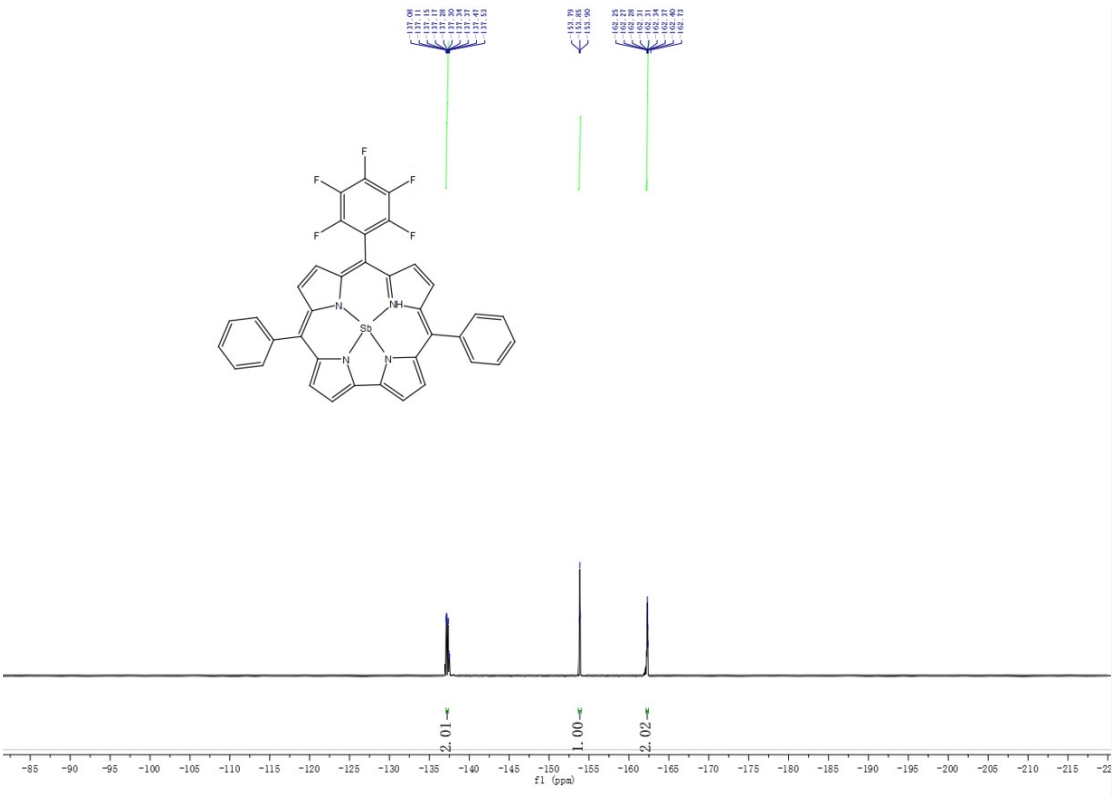

Fig. S20 ^{19}F NMR spectrum of **F_5C-Sb**

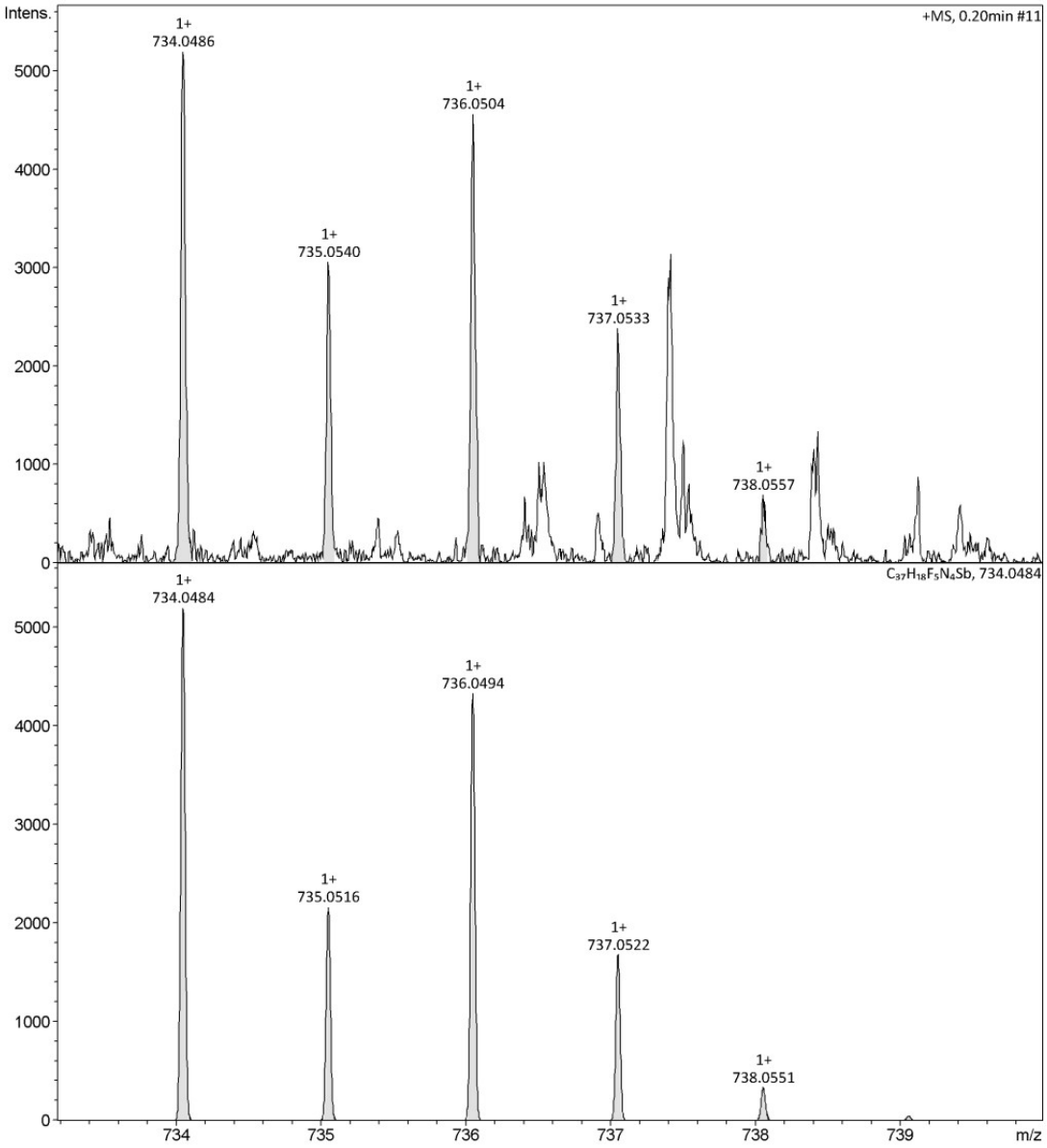

Fig. S21 ESI-HRMS spectrum of **F_5C-Sb**

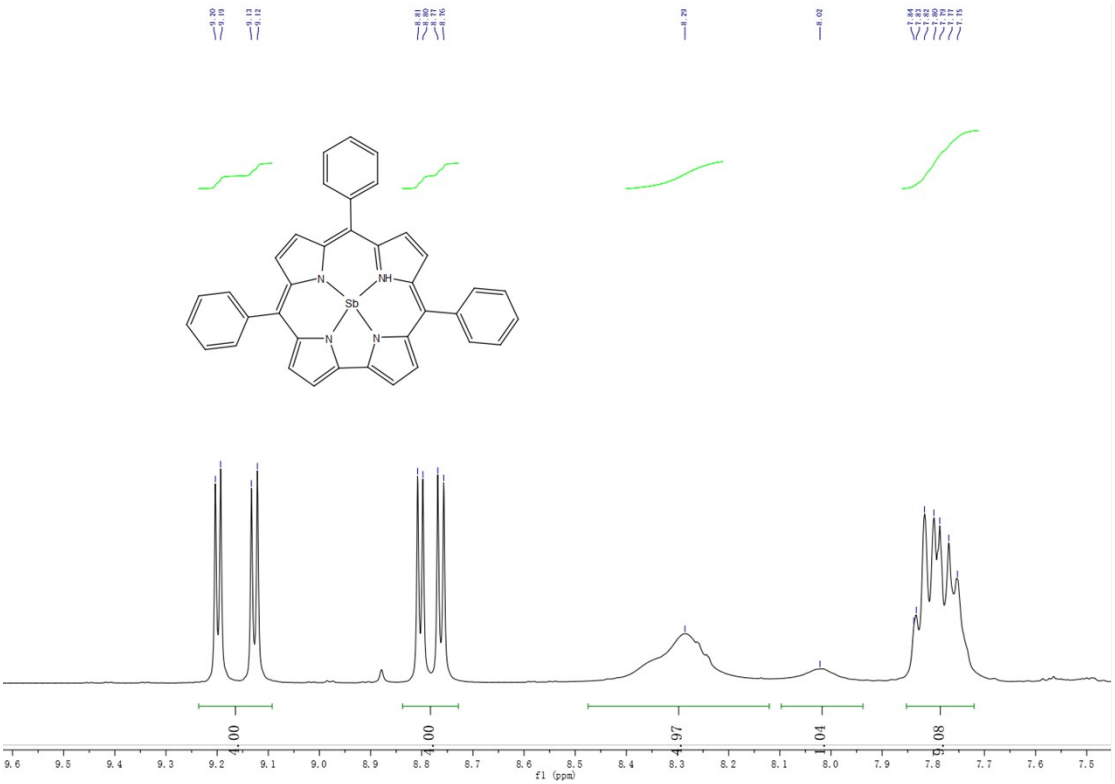

Fig. S22 ^{1}H NMR spectrum of **F_0C-Sb**

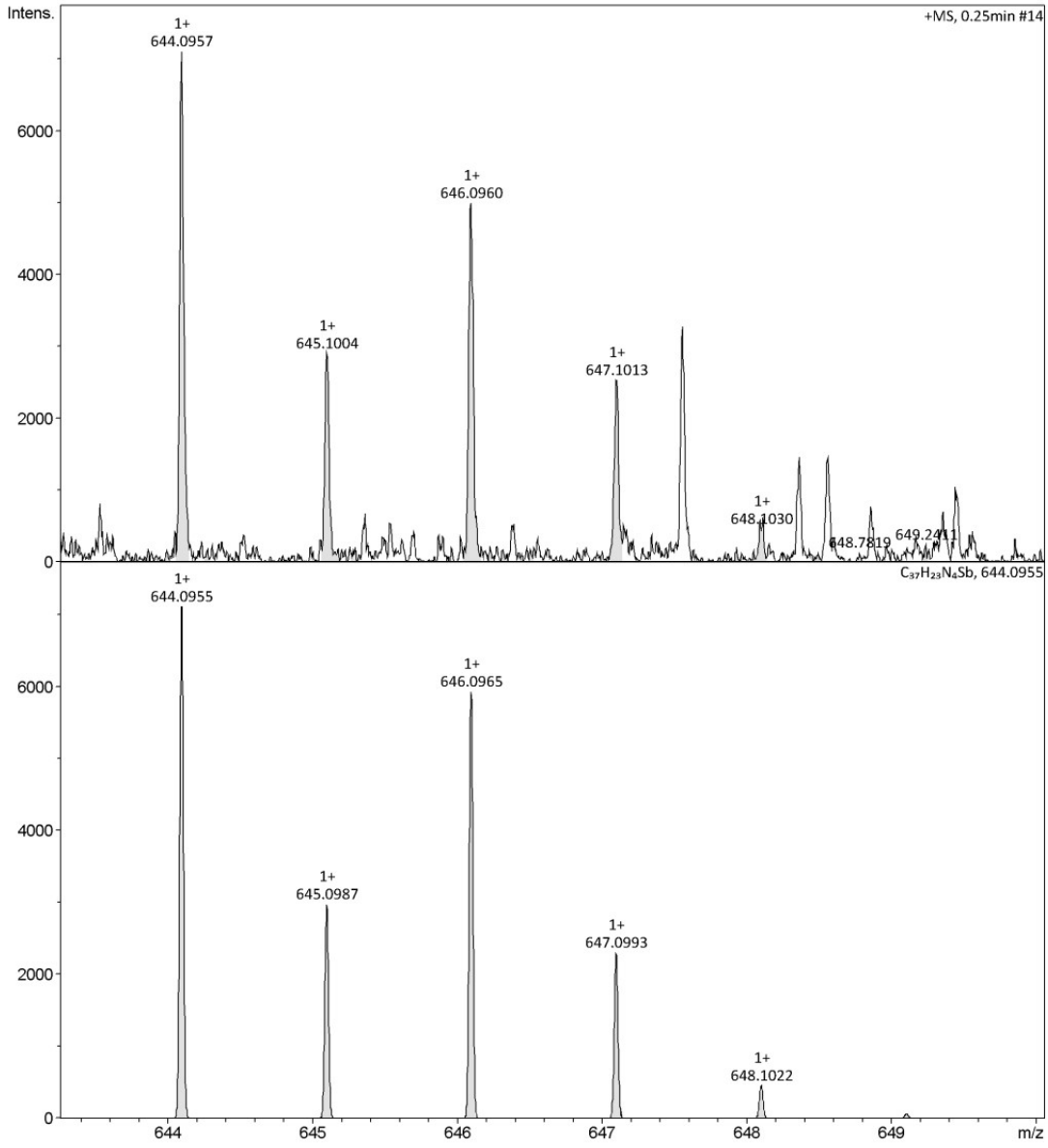

Fig. S23 ESI-HRMS spectrum of **F_0C-Sb**

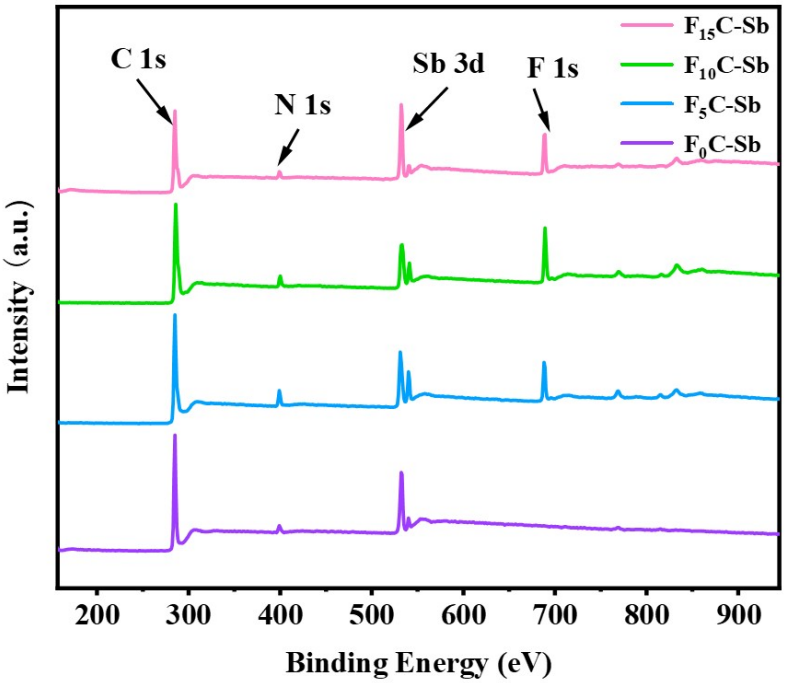

Fig. S24 XPS survey scan spectrum (**F_{15}C-Sb** to **F_0C-Sb**).

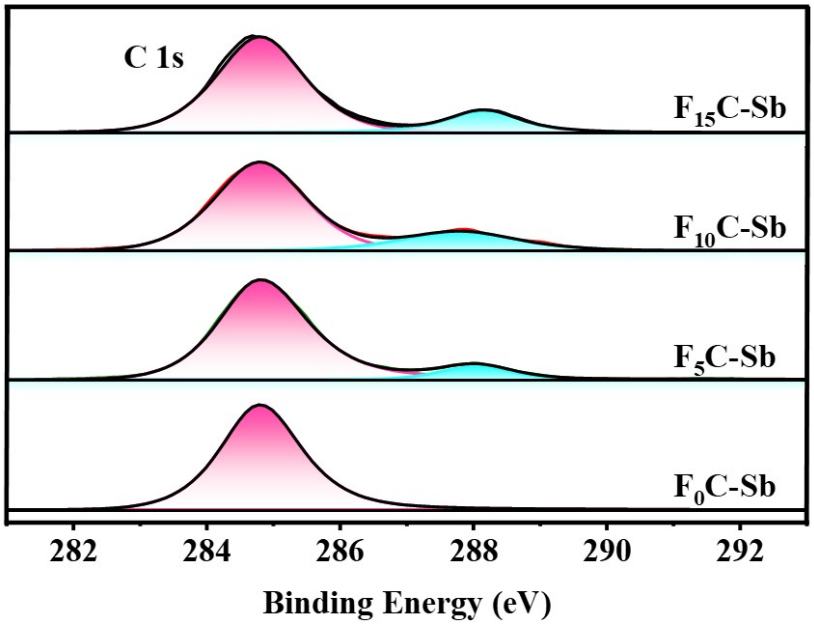

Fig. S25 XPS spectra for C 1s (**F_{15}C-Sb** to **F_0C-Sb**).

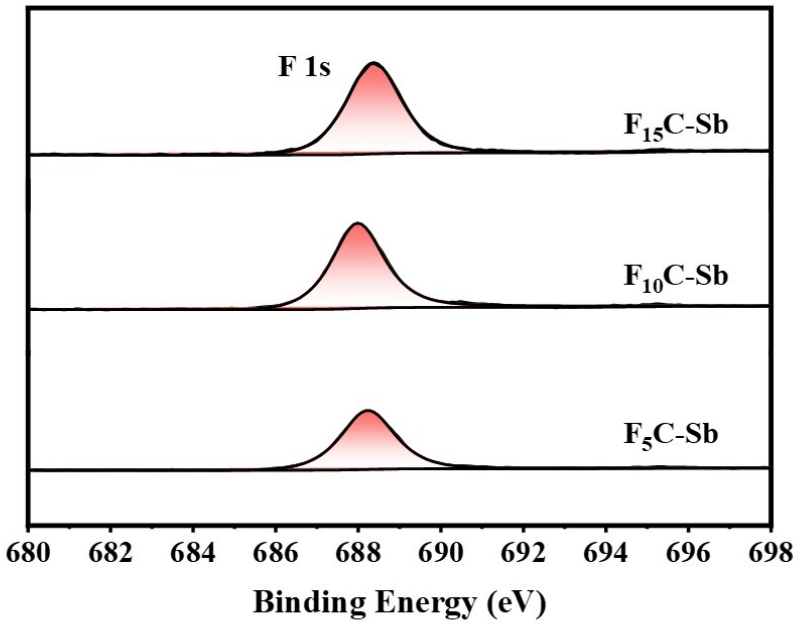

Fig. S26 XPS spectra for F 1s (**F_{15}C-Sb** to **F_0C-Sb**).

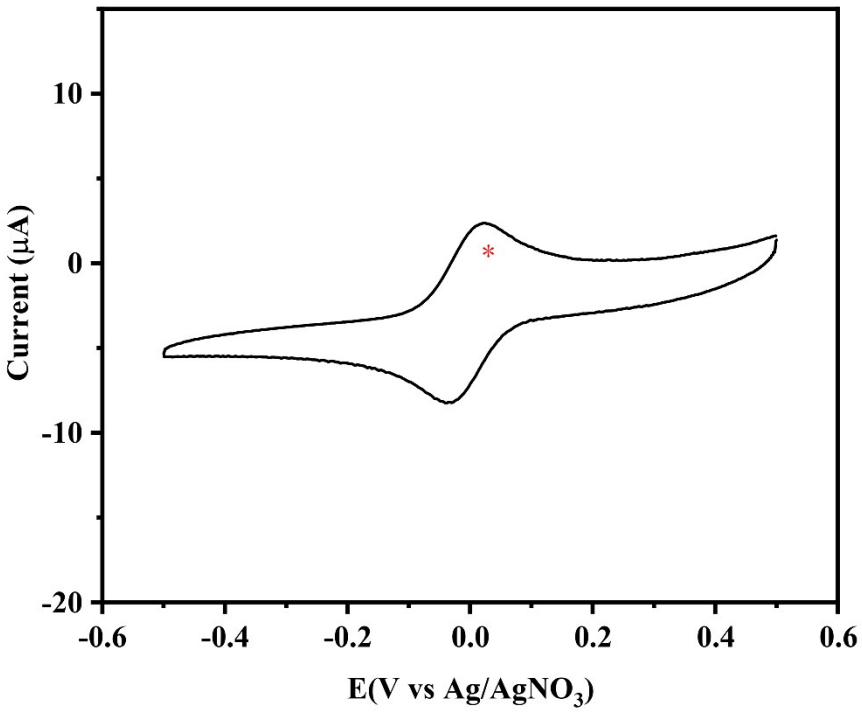

Fig. S27 The redox couple of Fc+/Fc in DMF containing 0.1M TBAP with blank glassy carbon

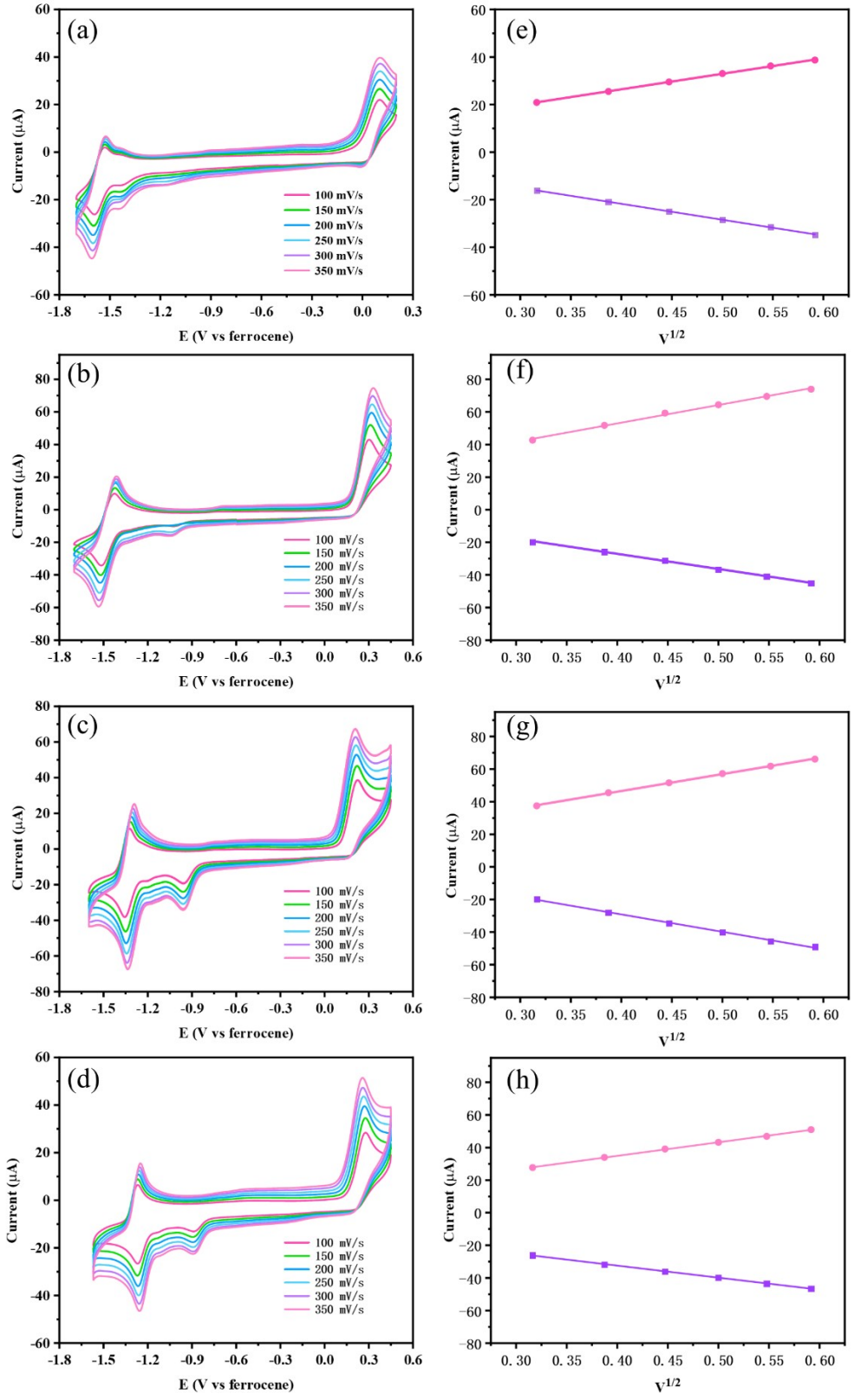

Fig. S28 CVs with a varying scan rate (v) from 100 mV/s to 350 mV/s and the maximum current (i_p) plots of [Sb-corrole]/[Sb-corrole]$^-$ reduction and first oxidation waves vs. the scan rate ($v^{1/2}$). (**F_{15}C-Sb** (a, e), **F_{10}C-Sb** (b, f), **F_5C-Sb** (c, g) and **F_0C-Sb** (d, h))

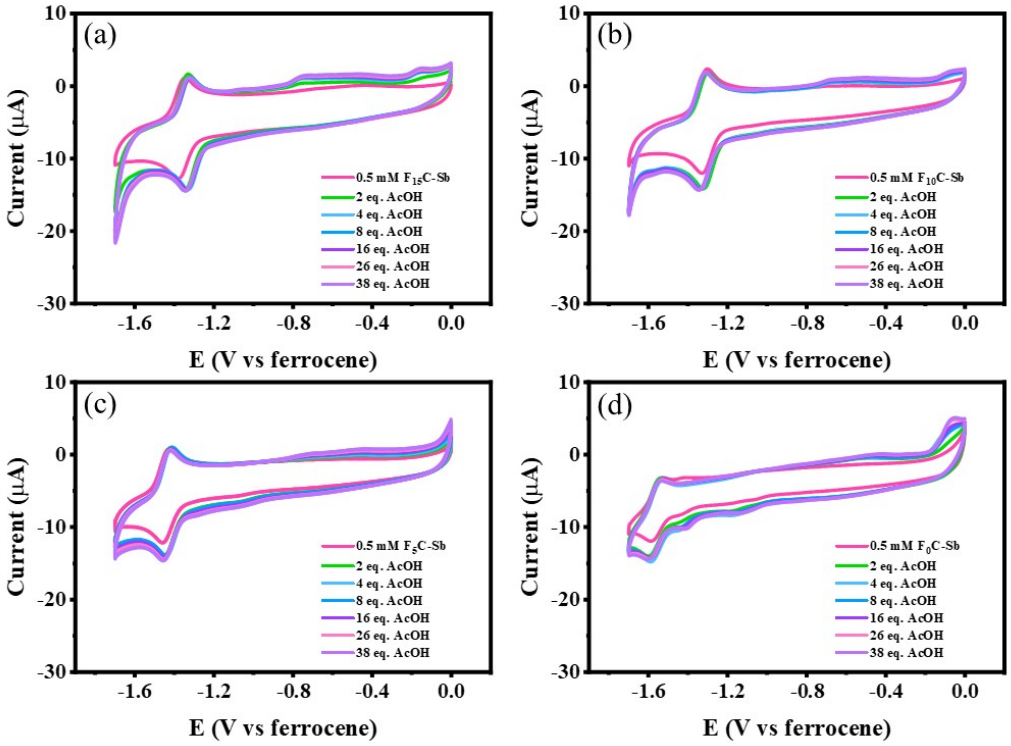

Fig. S29 CVs of 0.5 mM antimony complexes (**F_{15}C-Sb** to **F_0C-Sb**) (a-d) with increasing amounts of AcOH from 0 to 38 equivalents in N_2-saturated DMF

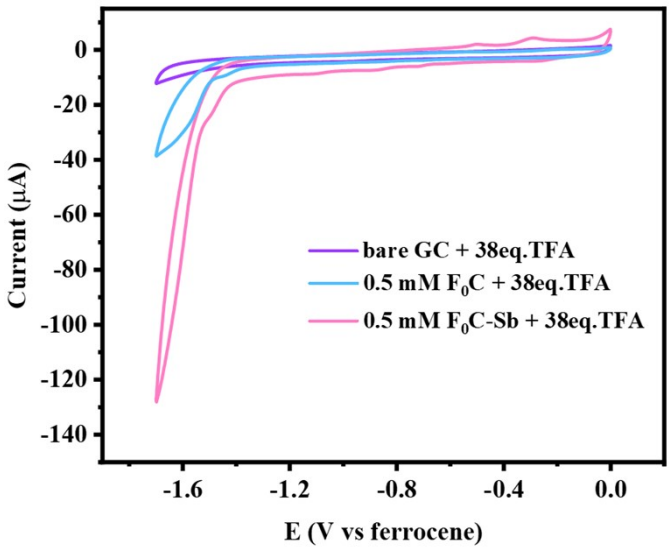

Fig. S30 CVs of bare glassy carbon electrode, 0.5 mM **F_0C** and 0.5 mM **F_0C-Sb** in DMF with 38 equivalents TFA

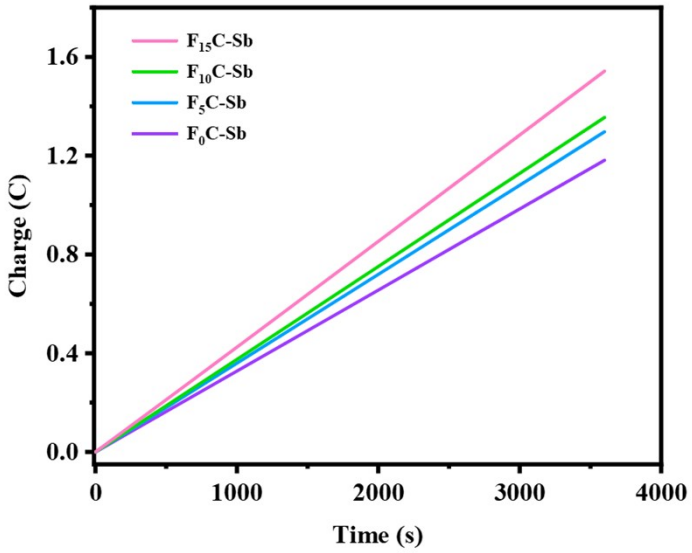

Fig. S31 Charge of 0.5 mM **F_{15}C-Sb**, **F_{10}C-Sb**, **F_5C-Sb** and **F_0C-Sb** after 1 h of electrolysis in DMF with 38 equivalents TFA

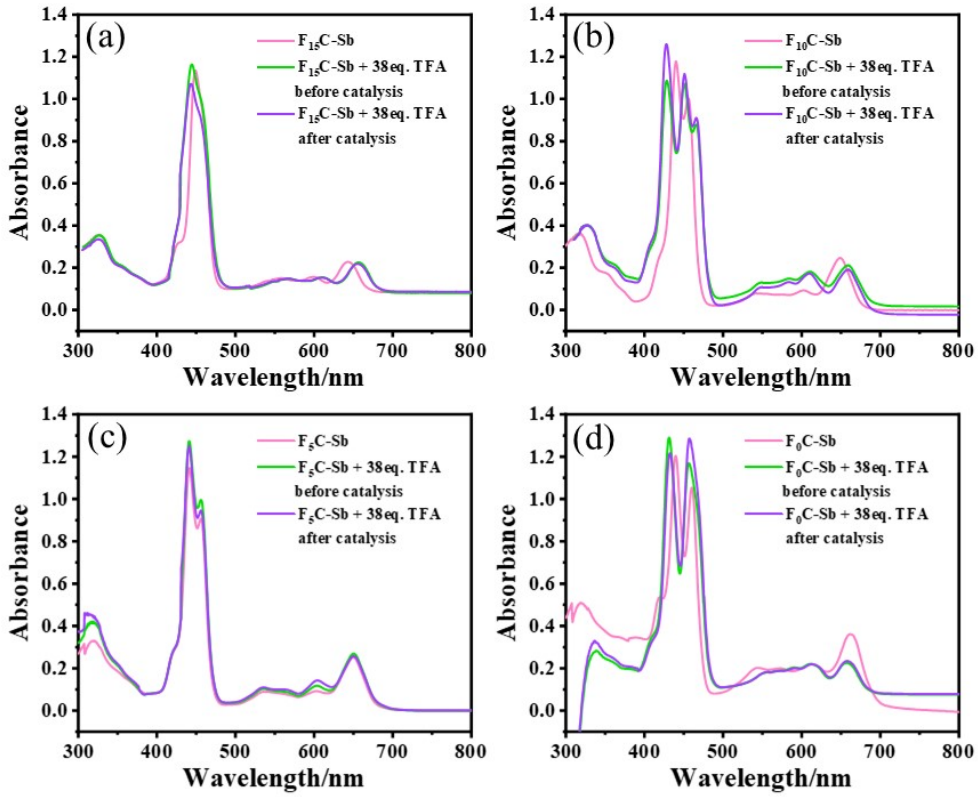

Fig. S32 UV-vis spectra of 0.5 mM **F_{15}C-Sb** to **F_0C-Sb** in DMF with 38 equivalents TFA and after 1 h electrolysis

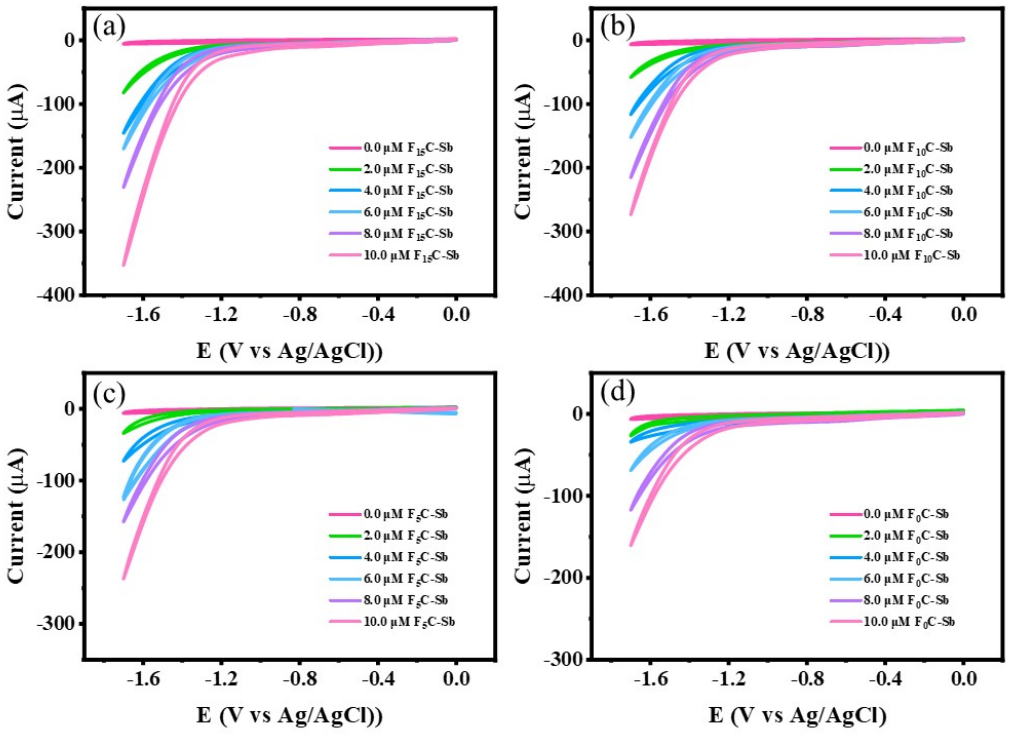

Fig. S33 CVs of various concentrations of **F_{15}C-Sb**, **F_{10}C-Sb**, **F_5C-Sb** and **F_0C-Sb** (0.0 μM–10.0 μM) in buffer solutions at pH=7.0 (V_{DMF}/V_{H2O} = 1/2).

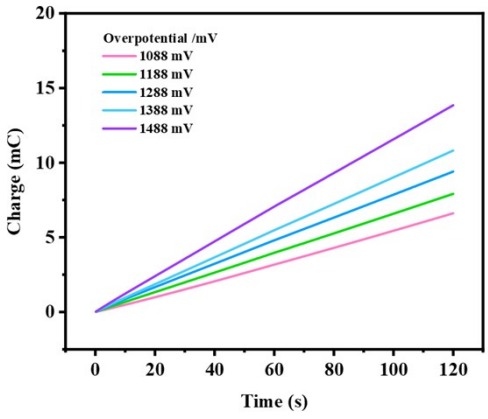

Fig. S34 Charge accumulation of electrolyzing 0.20 M buffer at pH=7.0 without catalyst under different applied potentials (-1.7 V to -2.1 V vs Ag/AgCl) for 2 minutes.

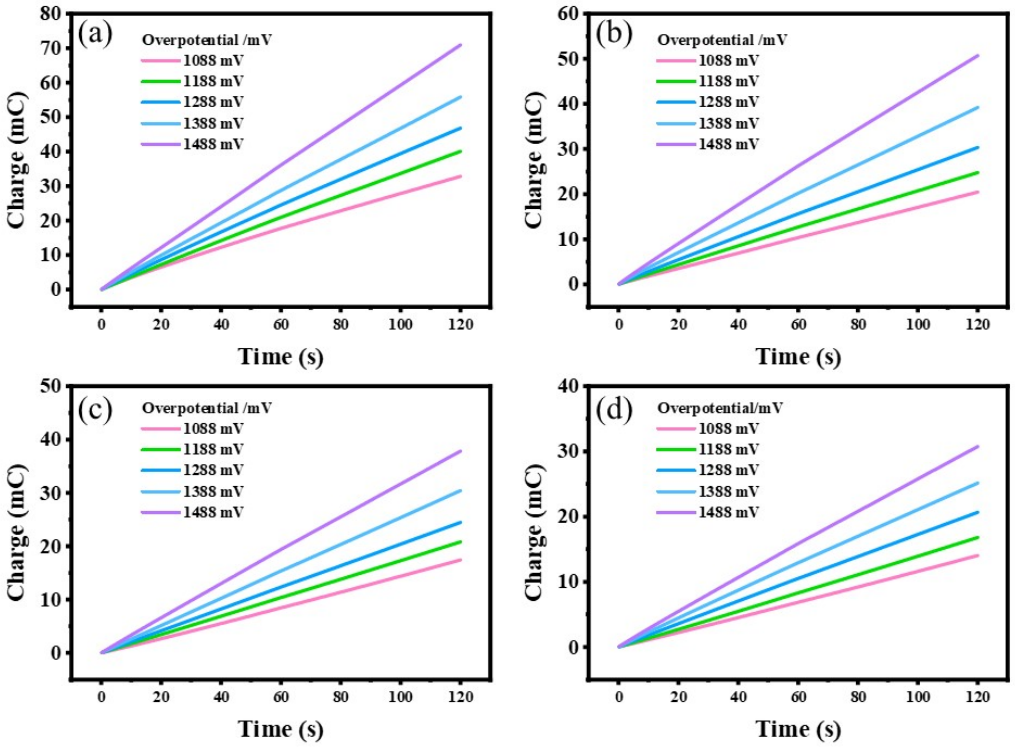

Fig. S35 Charge accumulation of electrolyzing 10 μM **F_{15}C-Sb**, **F_{10}C-Sb**, **F_5C-Sb** and **F_0C-Sb** at a range of overpotentials in buffer solutions at pH=7.0 for 2 minutes (a-d).

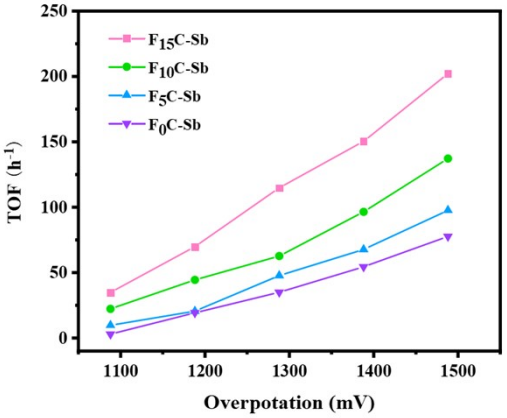

Fig. S36 TOF values of 10 μM **F_{15}C-Sb**, **F_{10}C-Sb**, **F_5C-Sb** and **F_0C-Sb** at different overpotentials in buffer solutions at pH=7.0.

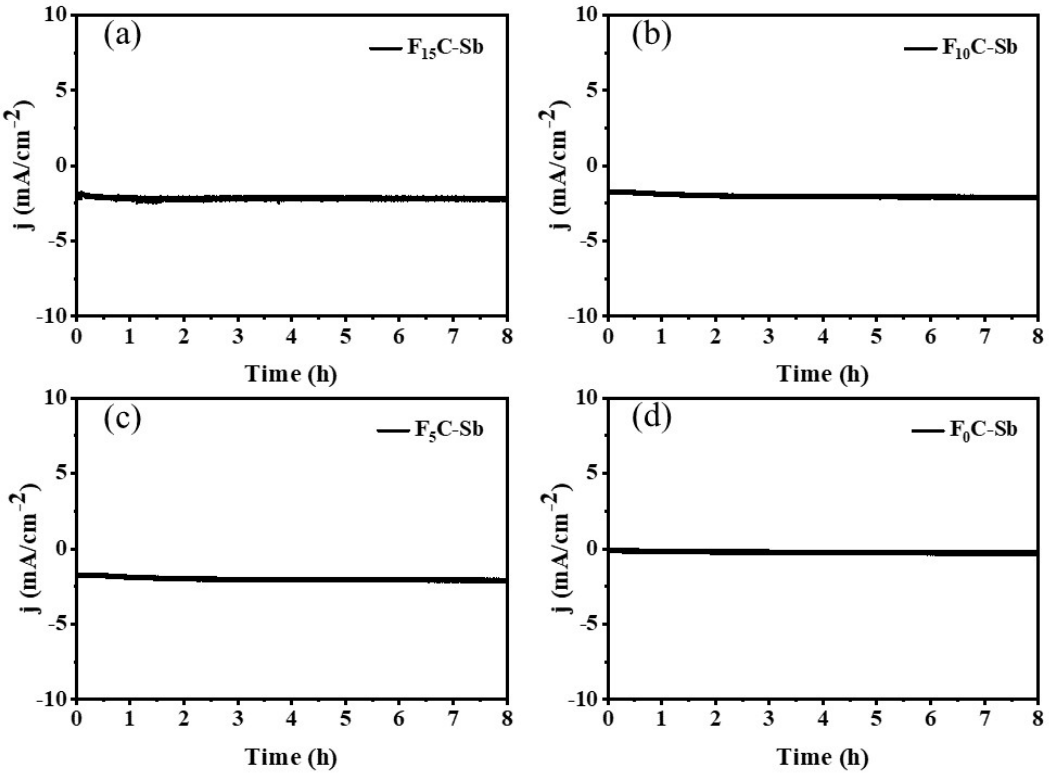

Fig. S37 Current versus 10 µM **F_{15}C-Sb**, **F_{10}C-Sb**, **F_5C-Sb** and **F_0C-Sb** in buffer solution at pH = 7.0 at -1.7 V for 8 h electrolysis.

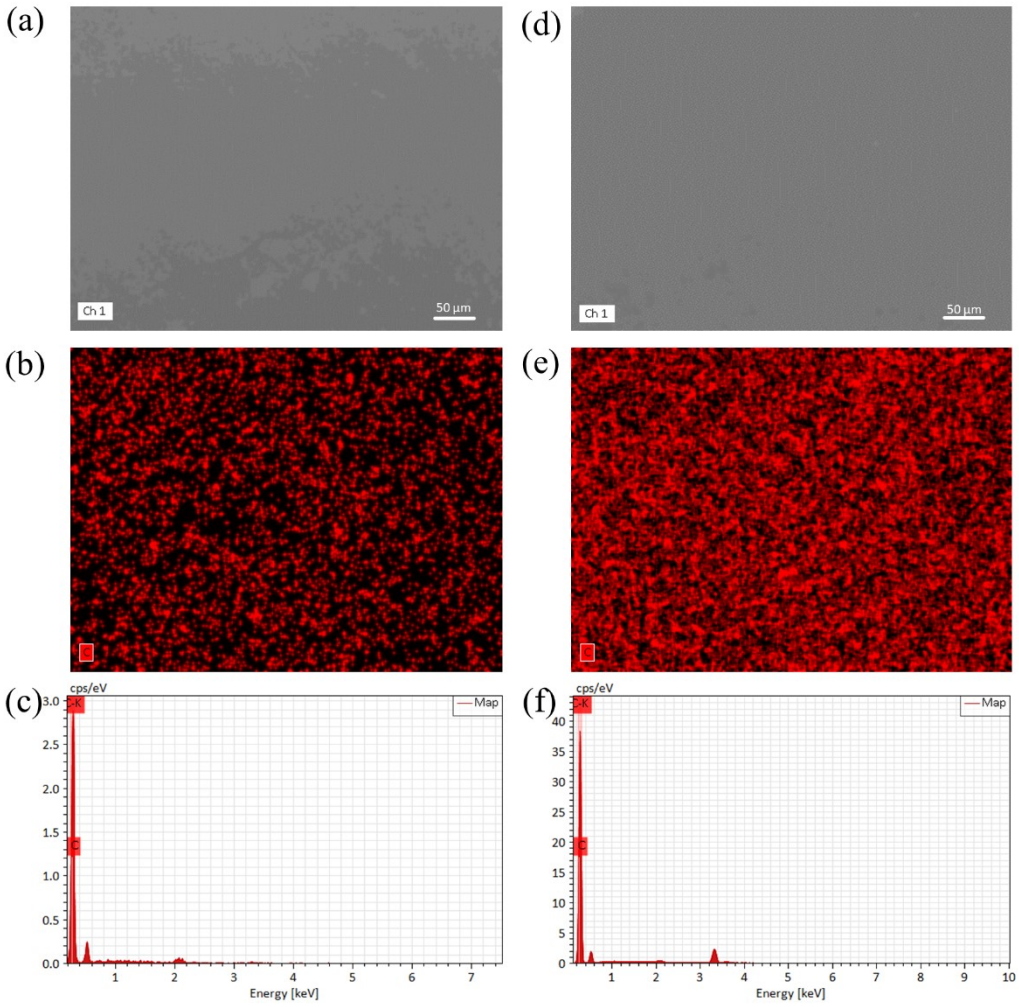

Fig. S38 SEM images and EDX data of GC electrodes before (a-c) and after (d-f) electrolysis.

Complex	Oxidation/V	Reduction/V
	[Sb-corrole] /[Sb-corrole] $^{+}$	[Sb-corrole] /[Sb-corrole] $^{-}$
F_{15}C-Sb	0.15	-1.41
F_{10}C-Sb	0.16	-1.46
F_{5}C-Sb	0.22	-1.50
F_{0}C-Sb	0.29	-1.55

Table S1 Redox potentials (V *vs* ferrocene) of antimony(III) corroles in DMF.

Complex	38 eq. TFA		38 eq. TsOH	
	i_c/i_p	TOF (s^{-1})	i_c/i_p	TOF (s^{-1})
F_{15}C-Sb	12.61	30.85	14.21	39.17
F_{10}C-Sb	11.55	25.88	12.41	29.87
F_5C-Sb	9.38	17.06	10.84	22.79
F_0C-Sb	6.90	9.24	9.80	18.63

Table S2 Catalytic activity parameter of four antimony(III) corroles in 38 eq. TFA and TsOH.

Complex	Protonsource	Overpotential (mV)	TOF	Refs.
F_{15}C-Sb(III)	19 mM TsOH	770	39.17 s^{-1}	This work
F_{15}C-Sb(III)	8 mM TFA	770	5.8 s^{-1}	This work
F_{10}C-Sb(III)	19 mM TFA	770	25.88 s^{-1}	This work
F_5C-Sb(III)	19 mM TFA	790	17.06 s^{-1}	This work
F_0C-Sb(III)	19 mM TFA	820	9.24 s^{-1}	This work
F_{15}C-P(V)	16 mM TFA	900	9.5 s^{-1}	[1]
F_{10}C-P(V)	16 mM TFA	900	19.4 s^{-1}	[1]
F_5C-P(V)	16 mM TFA	900	23.5 s^{-1}	[1]
F_0C-P(V)	16 mM TFA	900	721.8 s^{-1}	[1]
2-NBPC-Sb(III)	19 mM TFA	642	17.65 s^{-1}	[2]
3-NBPC-Sb(III)	19 mM TFA	660	12.48 s^{-1}	[2]
4-NBPC-Sb(III)	19 mM TFA	677	11.66 s^{-1}	[2]

F_{15}C-Sb(III)	10 mM TFA	720	1.86 s^{-1}	[3]
TTC-Sb(III)	20 mM TFA	460	6.72 s^{-1}	[3]
TDOC-Sb(III)	20 mM TFA	1010	2.63 s^{-1}	[3]
(corrolato)(oxo)-Sb(V)	50 mM TFA	420	0.44 h^{-1}	[4]
TPFC (oxo)-Mo(V)	29 mM DMF-H^+	/	23 s^{-1}	[5]
3 -TPFC (oxo)-Mo(V)	29 mM DMF-H^+	/	2.48 s^{-1}	[5]
3-BPFC-Co(III)	18.26 mM TFA	600	134.56 s^{-1}	[6]
3-BPFC-Co(III)	18.26 mM TsOH	600	62.17 s^{-1}	[6]
F_{15}C-Co(III)	5 mM TFA	1010	11 s^{-1}	[7]
TTC-Co(III)	5 mM TFA	1010	17 s^{-1}	[7]
F_{15}C-Mn	20 mM TFA	1343	69.34 h^{-1}	[8]
F_{10}C-Mn	20 mM TFA	1343	61.74 h^{-1}	[8]
F_{10}C-Si	16 mM TFA	1086	15.37 s^{-1}	[9]

Table S3 TOF and overpotential of corrole complexes as electrocatalysts for HER.

References:

1 G. Yang, Z. Ullah, W. Yang, K. H. Wook, Z. X. Liang, X. Zhan, G. Q. Yuan and H. Y. Liu, *Chemsuschem*, 2023, **16**, e202300211.

2 Q.-W. Yan, L.-W. Wu, Z.-W. Liu, F. Chen, C. Ling, H.-Y. Liu, X.-Y. Xiao and L.-P. Si, *Green chemistry*, 2024, **26**, 4574-4581.

3 S. Kumar, S. Fite, E. Remigi, A. Mizrahi, N. Fridman, A. Mahammed, T. P. Bender and Z. Gross, *Chem. Eur. J.*, 2024, **30**, e202402145.

4 R. Chakraborty, B. Ojha, T. Pain, T. W. Tsega, A. Tarai, N. C. Jana, C.-H. Hung and S. Kar, *Inorg. Chem.*, 2024, **63**, 21462-21473.

5 P. Yadav, I. Nigel-Etinger, A. Kumar, A. Mizrahi, A. Mahammed, N. Fridman, S. Lipstman, I. Goldberg and Z. Gross, *iScience*, 2021, **24**, 102924.

6 F. Jun-Jia, J. Lan, G. Yang, Y. Gao-Qing, L. Hai-Yang and S. Li-Ping, *New J. Chem.*, 2021, **45**, 5127-5136.

7 A. Kumar, S. Fite, A. Raslin, S. Kumar, A. Mizrahi, A. Mahammed and Z. Gross, *Acs Catal*, 2023, **13**, 13344-13353.

8 B. Wan, F. Cheng, J. Lan, Y. Zhao, G. Yang, Y.-M. Sun, L.-P. Si and H.-Y. Liu, *Int. J. Hydrogen Energy,* 2023, **48**, 5506-5517.

9 Z. W. Liu, G. Yang, S. Y. Xu, W. Y. Xie, Y. F. Yao, X. Y. Xiao, L. P. Si and H. Y. Liu, *Eur. J. Inorg. Chem.*, 2024, **27**, e202300790.