

Supporting Information

First application of antimony(III) corrole for electrocatalytic hydrogen evolution

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Experimental Instrumentation

UV-Vis spectra in CH₃CN solution were recorded on a Hitachi U-3010 spectrophotometer at room temperature. HRMS was performed using a Bruker Maxis impact mass spectrometer with an electrospray ionization (ESI) source. ¹H and ¹⁹F spectra were recorded at room temperature using a Bruker Avance III 400 MHz in CDCl₃ solution. XPS was acquired using Thermo Scientific K-Alpha + electron spectrometer from Thermo Fisher using 225 WAlK α radiation, correcting the binding energies by comparing to C1s peak (284.8 eV) by the adventitious hydrocarbon. The single crystal structure of the complex was obtained from Rigaku Oxford Diffraction. SEM observations were performed on a Nova NanoSEM 430 scanning electron microscope.

Synthetic of 10-(4-nitrophenyl)-5,15-bis-pentafluorophenyl corrole (4-NBPC)

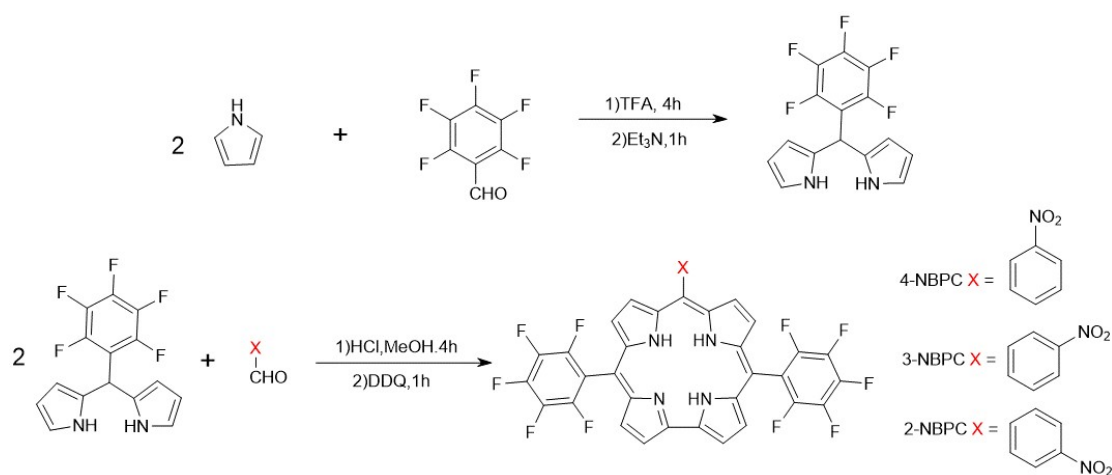


Fig S1. Schematic of the synthesis of 2-NBPC, 3-NBPC and 4-NBPC

The specific synthesis steps are exemplified by 4-NBPC. Add 320 mL of vacuum-distilled pyrrole and 5.60 g of pentafluorobenzaldehyde (28.56 mmol) into a 500 mL round-bottomed flask, then add 240 μL of trifluoroacetic acid, stir at room temperature for 4 hours, next add 220 μL of triethylamine to neutralize the reaction. for 1 hour. Remove excess pyrrole by distillation under reduced pressure, fill the column with 100 ~ 200 mesh silica gel, and purify the product with the eluent of dichloromethane (DCM)/hexane (Hex) (V/V) = 1/1 to obtain beige powder 5-(pentafluorophenyl)-dipyrromethane as solid

Dissolve 0.151g 4-nitrobenzaldehyde (1.0 mmol) and 0.629g 5-(pentafluorophenyl)-dipyrromethane (2.0 mmol) in 125 mL of methanol in a 500 mL dry round-bottomed flask, stir thoroughly to dissolve. Then, a solution of HCl aq (36%, 15 mL) dissolved in 125 mL H₂O was added, and the reaction was stirred at room temperature for 4 hours. After extraction three times with DCM and H₂O, it was dried over anhydrous sodium sulfate. Then 1.2 g of p-chlorobenzoquinone was added and the reaction was stirred for 2 hours. Use 300 ~ 400 mesh silica gel as column chromatography and DCM/Hex = 3/1 as the eluent to obtain pure corrole solid. After recrystallization from DCM/Hex to obtain pure purple 10-(2-nitrophenyl)-5,15-bis-pentafluorophenyl corrole (4-NBPC) (210 mg, yield 28.65%). MS: (ESI-HRMS) m/z 752.1165 [M+H]⁺, calculated: m/z 752.1139 [M+H]⁺. ¹H NMR (500 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 4.2 Hz, 2H), 8.76 (d, *J* = 4.7 Hz, 2H), 8.70 – 8.53 (m, 6H), 8.37 (d, *J* = 8.0 Hz, 2H). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -137.88 (d, *J* = 20.6 Hz 4F), -152.28(2F), -161.50(4F).

Synthetic of 10-(4-nitrophenyl)-5,15-bis-pentafluorophenyl Antimony corrole (4-NBPC-Sb)

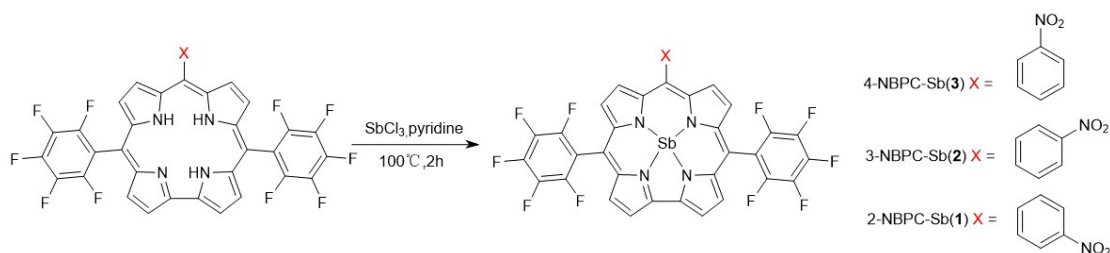


Fig S2. Schematic of the synthesis of 1-3

The specific synthesis steps are exemplified by 4-NBPC-Sb. Dissolve 200 mg 4-NBPC (0.27 mmol) and 1 g SbCl_3 in a round-bottomed flask with 20 ml pyridine. Then the temperature was raised to 100°C and reacted for 1 hour, 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 (DCM)/hexane (Hex) (V/V) = 1/1 as an eluent to purify the product. After recrystallization obtain green solid (205 mg, yield 86.50%) MS: (ESI-HRMS) m/z 868.9868 [M], calculated: m/z 868.9869 [M]. ^1H NMR (500 MHz, Chloroform-*d*) δ 9.34 (dd, $J = 5.9, 4.1$ Hz, 2H), 9.00 – 8.91 (m, 2H), 8.81 (dd, $J = 7.5, 4.4$ Hz, 4H), 8.65 (s, 3H), 8.19 (s, 1H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -136.62-137.05 (m, 2F), -137.19-137.86 (m, 2F), -152.12-152.91 (m, 2F), -159.98-162.76 (m, 4F).

Synthetic of 10-(3-nitrophenyl)-5,15-bis-pentafluorophenyl corrole (3-NBPC)

The synthetic route was similar to 4-NBPC, after recrystallization from DCM/Hex to obtain pure corrole (260 mg, yield 35.47%): MS: (ESI-HRMS) m/z 752.1167 [M+H]⁺, calculated: m/z 752.1165 [M+H]⁺. ^1H NMR (500 MHz, Chloroform-*d*) δ 9.14 (d, $J = 4.2$ Hz, 2H), 9.04 (s, 1H), 8.77 (d, $J = 4.7$ Hz, 2H), 8.69 – 8.54 (m, 5H), 8.51 (d, $J = 7.5$ Hz, 1H), 7.96 (t, $J = 7.9$ Hz, 1H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -137.68 (d, $J = 24.3$ Hz, 2F), -138.00 (d, $J = 24.2$ Hz, 2F), -152.39 (d, $J = 26.9$ Hz, 2F), -161.57 (dd, $J = 86.2, 22.5$ Hz, 4F).

Synthetic of 10-(3-nitrophenyl)-5,15-bis-pentafluorophenyl Antimony corrole (3-NBPC-Sb)

The synthetic route was similar to 4-NBPC-Sb, after recrystallization obtain pure antimony corrole (215 mg, yield 90.72%): MS: (ESI-HRMS) m/z 868.9869 [M], calculated: m/z 868.9869 [M]. ^1H NMR (500 MHz, Chloroform-*d*) δ 9.34 (t, $J = 3.7$ Hz, 2H), 9.24 (s, 1H), 8.97 (dt, $J = 4.2, 2.0$ Hz, 2H), 8.89 – 8.67 (m, 5H), 8.67 – 8.61 (m, 1H), 7.94 (s, 1H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -135.81-137.73 (m, 4F), -152.58 (t, $J = 20.8$ Hz, 2F), -161.65 (d, $J = 103.5$ Hz, 4F).

Synthetic of 10-(2-nitrophenyl)-5,15-bis-pentafluorophenyl corrole (2-NBPC)

The synthetic route was similar to 4-NBPC, after recrystallization from DCM/Hex to obtain pure corrole (241 mg, yield 32.88%): MS: (ESI-HRMS) m/z 752.1162 [M+H]⁺, calculated: m/z 752.1165 [M+H]⁺. ^1H NMR (500 MHz, Chloroform-*d*) δ 9.10 (d, $J = 4.4$ Hz,

2H), 8.69 (d, $J = 4.6$ Hz, 2H), 8.60 – 8.43 (m, 4H), 8.42 – 8.36 (m, 1H), 8.23 (s, 1H), 8.01 – 7.92 (m, 2H).¹⁹F NMR (471 MHz, Chloroform-*d*) δ -137.25 (d, $J = 32.3$ Hz, 2F), -137.56-138.60 (m, 2F), -152.61 (2F), -161.67 (d, $J = 156.8$ Hz, 4F).

Synthetic of 10-(2-nitrophenyl)-5,15-bis-pentafluorophenyl Antimony corrole (2-NBPC-Sb)

The synthetic route was similar to 4-NBPC-Sb, after recrystallization obtain pure antimony corrole (209 mg, yield 88.19%): MS: (ESI-HRMS) m/z 868.9874 [M], calculated: m/z 868.9869 [M].¹H NMR (500 MHz, Chloroform-*d*) δ 9.31 (d, $J = 4.2$ Hz, 2H), 8.91 (dd, $J = 4.7, 1.6$ Hz, 2H), 8.82 – 8.74 (m, 2H), 8.67 (d, $J = 4.7$ Hz, 2H), 8.49 – 8.43 (m, 1H), 8.08 – 8.03 (m, 1H), 7.95 (tt, $J = 7.5, 5.7$ Hz, 2H).¹⁹F NMR (471 MHz, Chloroform-*d*) δ -136.35 (dd, $J = 24.1, 7.0$ Hz, 2F), -137.72 (dd, $J = 24.3, 8.4$ Hz, 2F), -152.72 (2F), -160.96-163.37 (m, 2F).

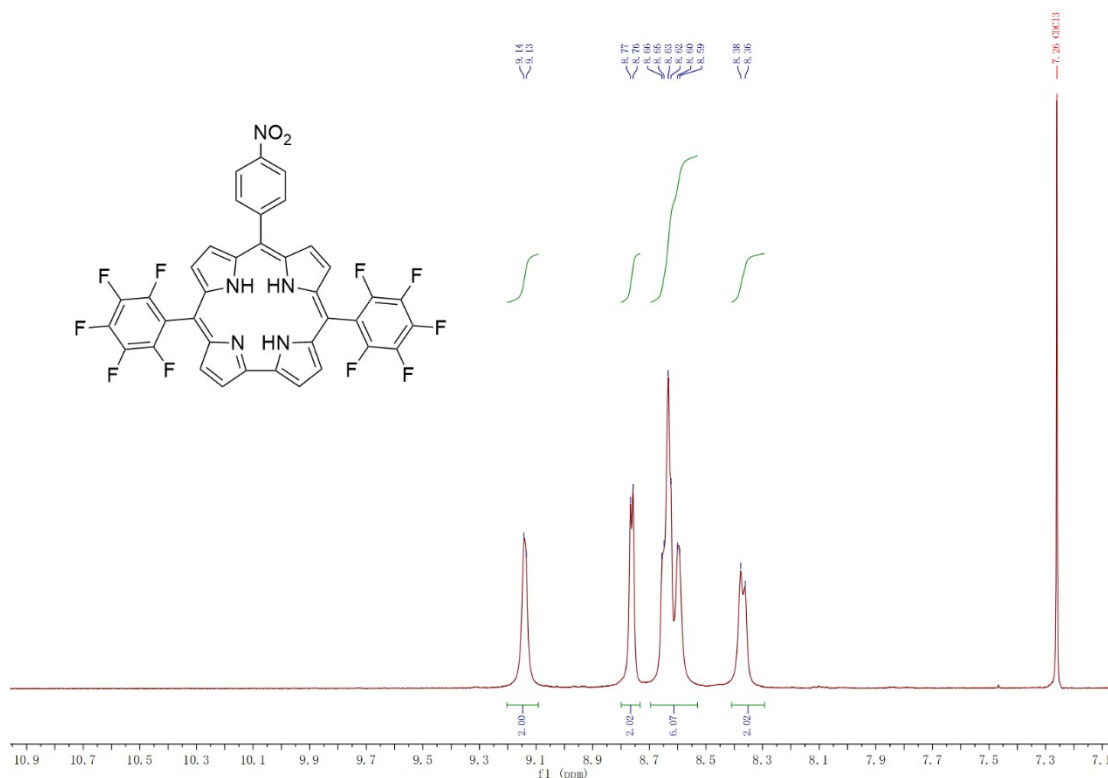


Fig S3. ¹H NMR spectrum of 4-NBPC

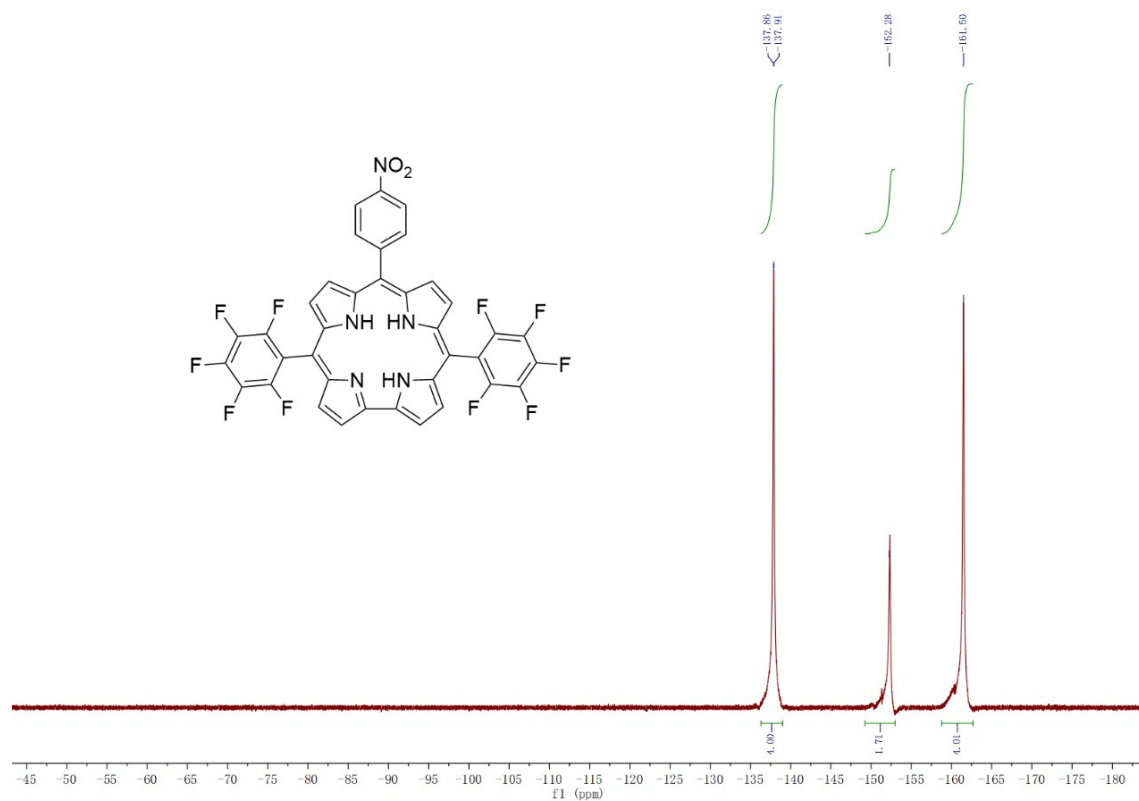


Fig S4. ^{19}F NMR spectrum of 4-NBPC

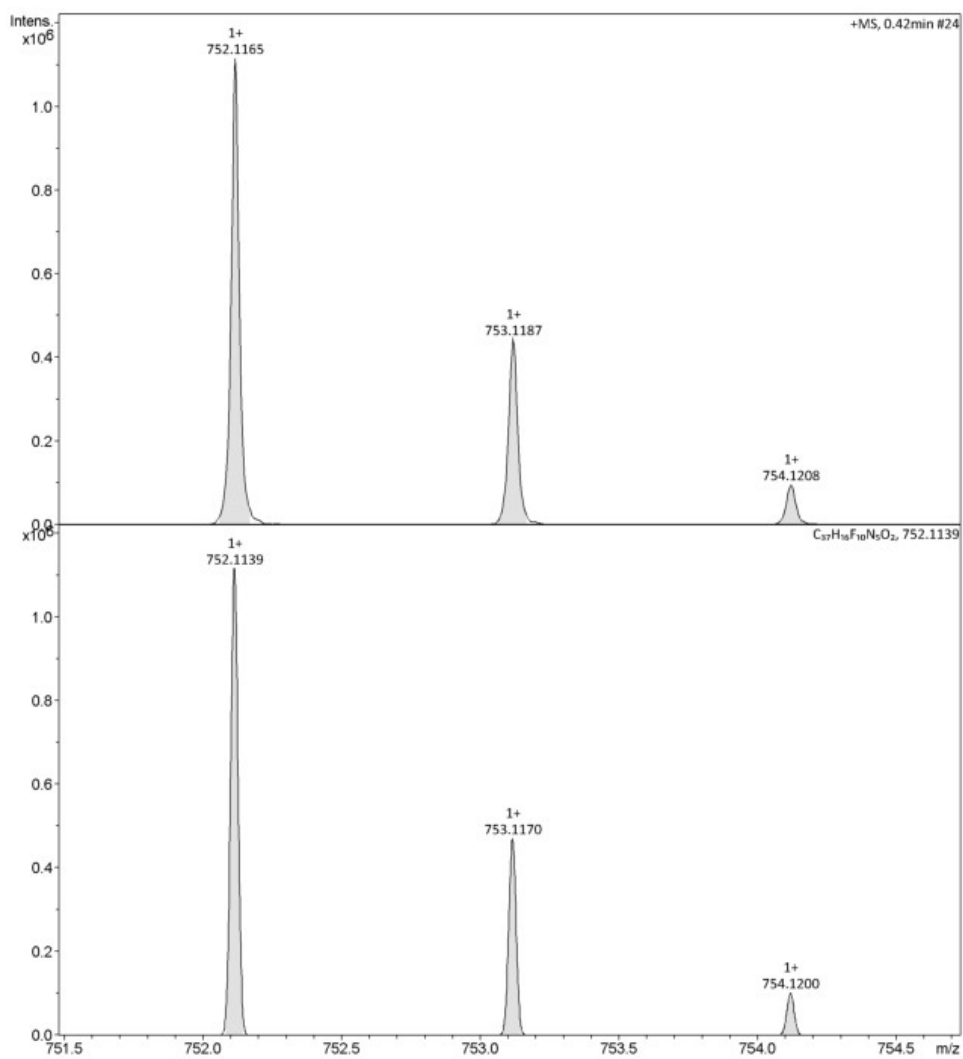


Fig S5. ESI-HRMS spectrum of 4-NBPC

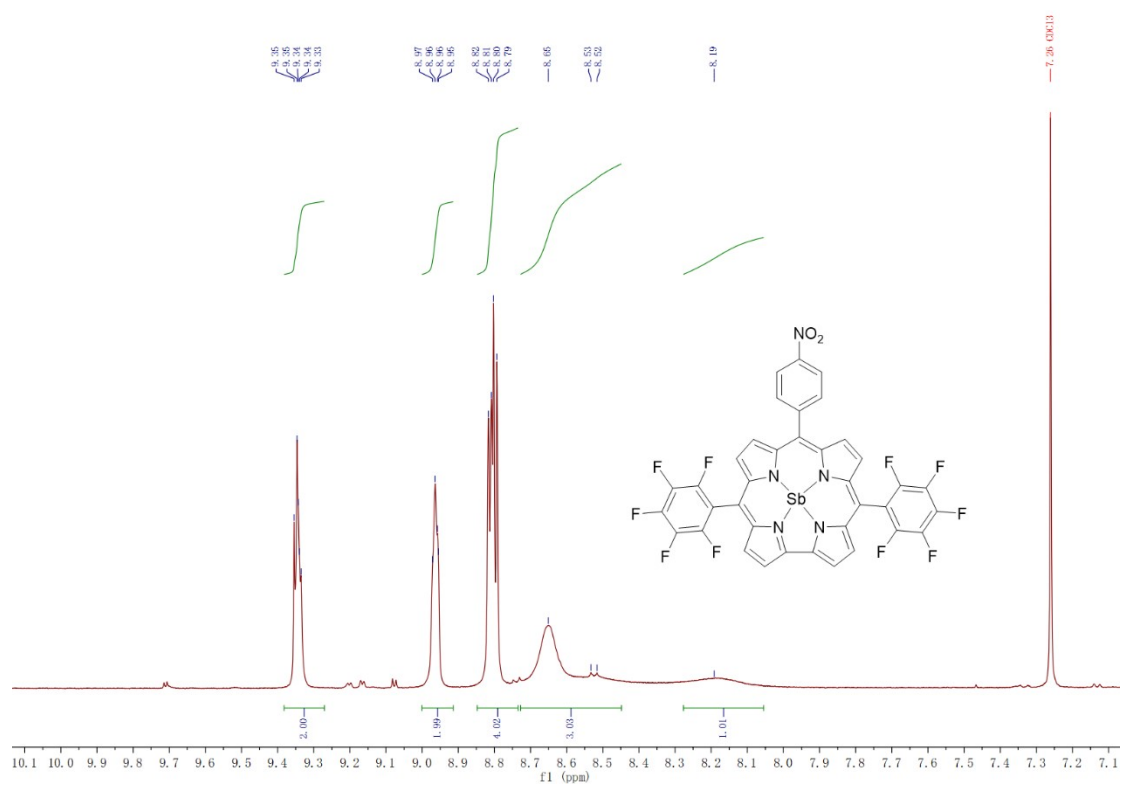


Fig S6. ^1H NMR spectrum of Complex 3

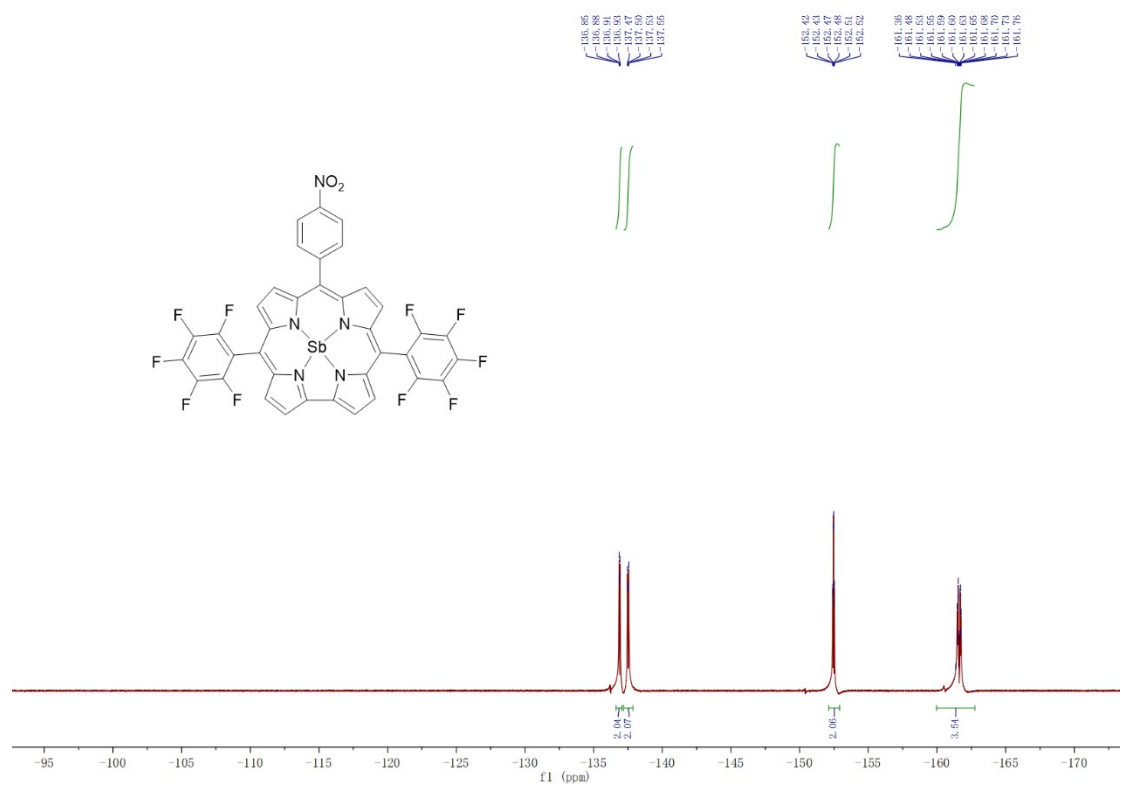


Fig S7. ^{19}F NMR spectrum of Complex 3

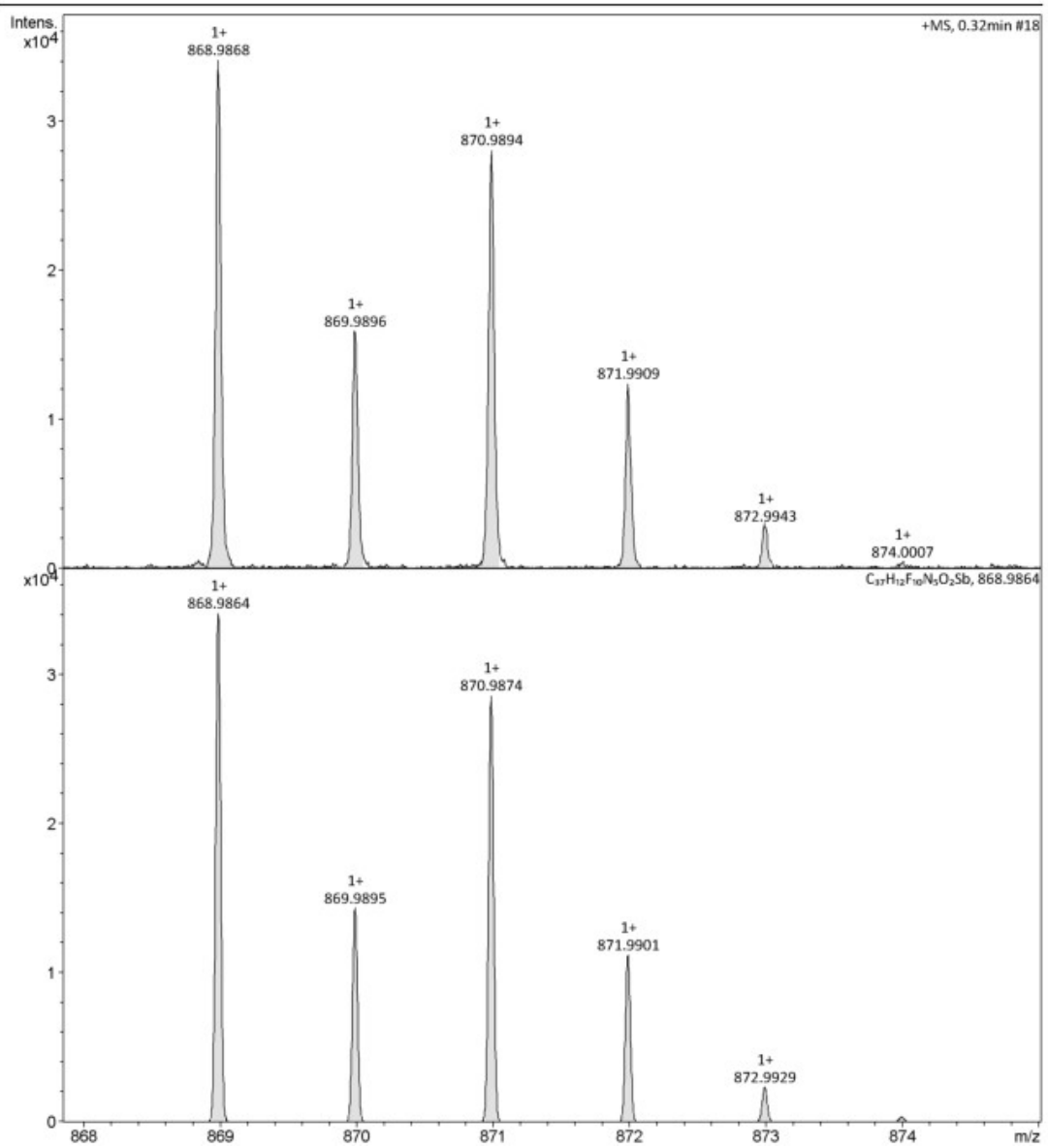


Fig S8. ESI-HRMS spectrum of Complex 3

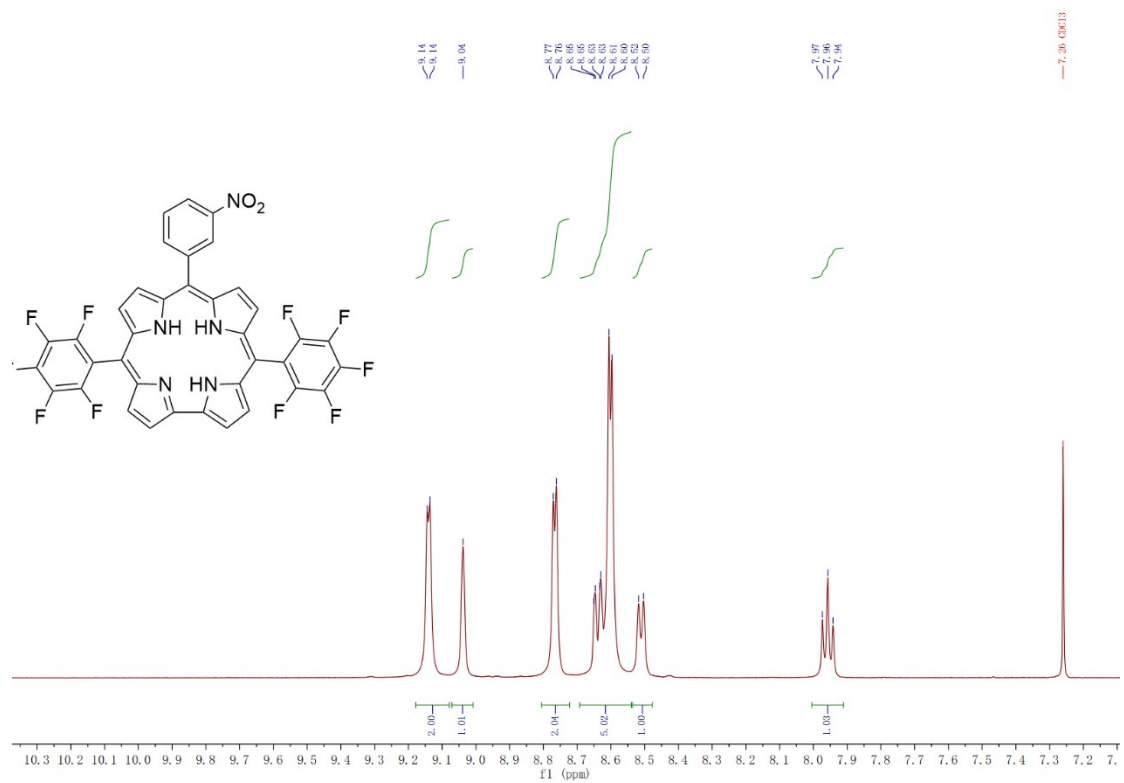


Fig S9. ¹⁹F NMR spectrum of 3-NBPC

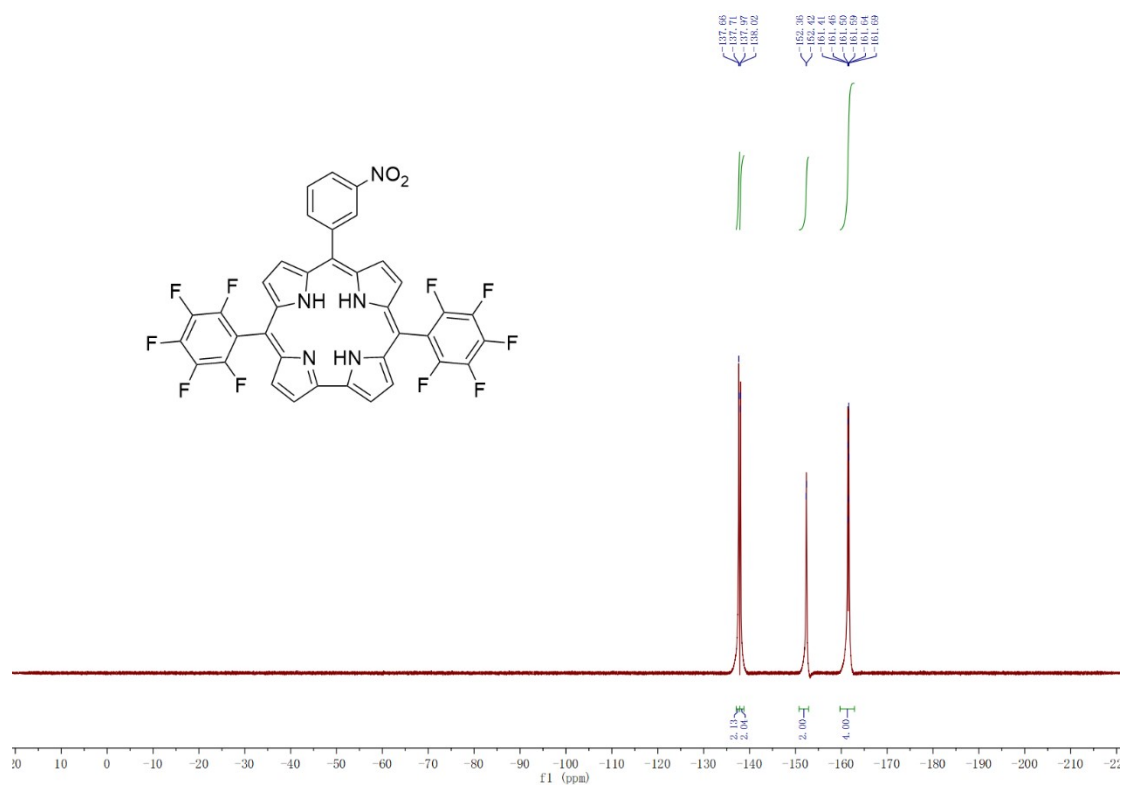


Fig S10. ¹⁹F NMR spectrum of 3-NBPC

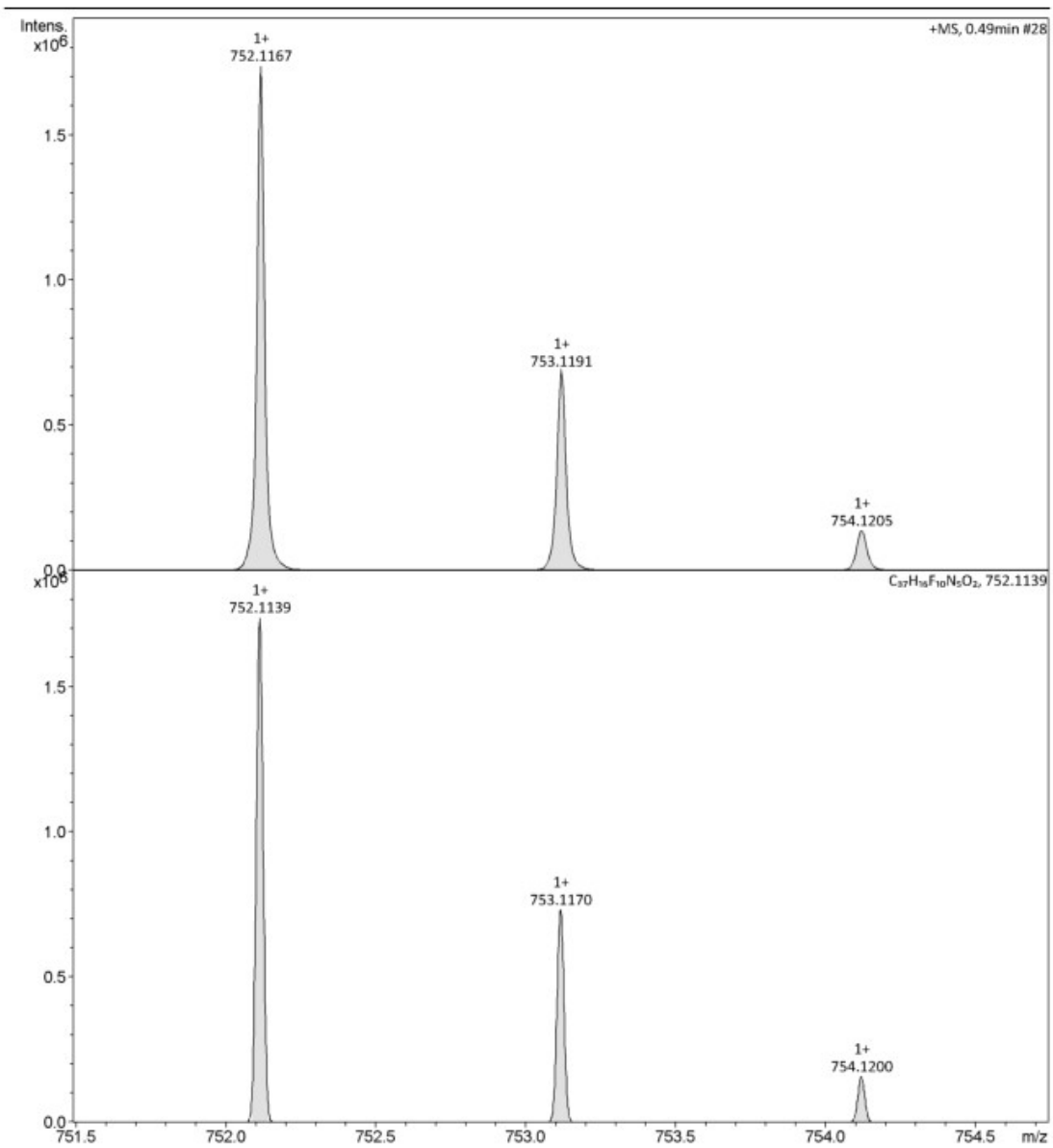


Fig S11. ESI-HRMS spectrum of 3-NBPC

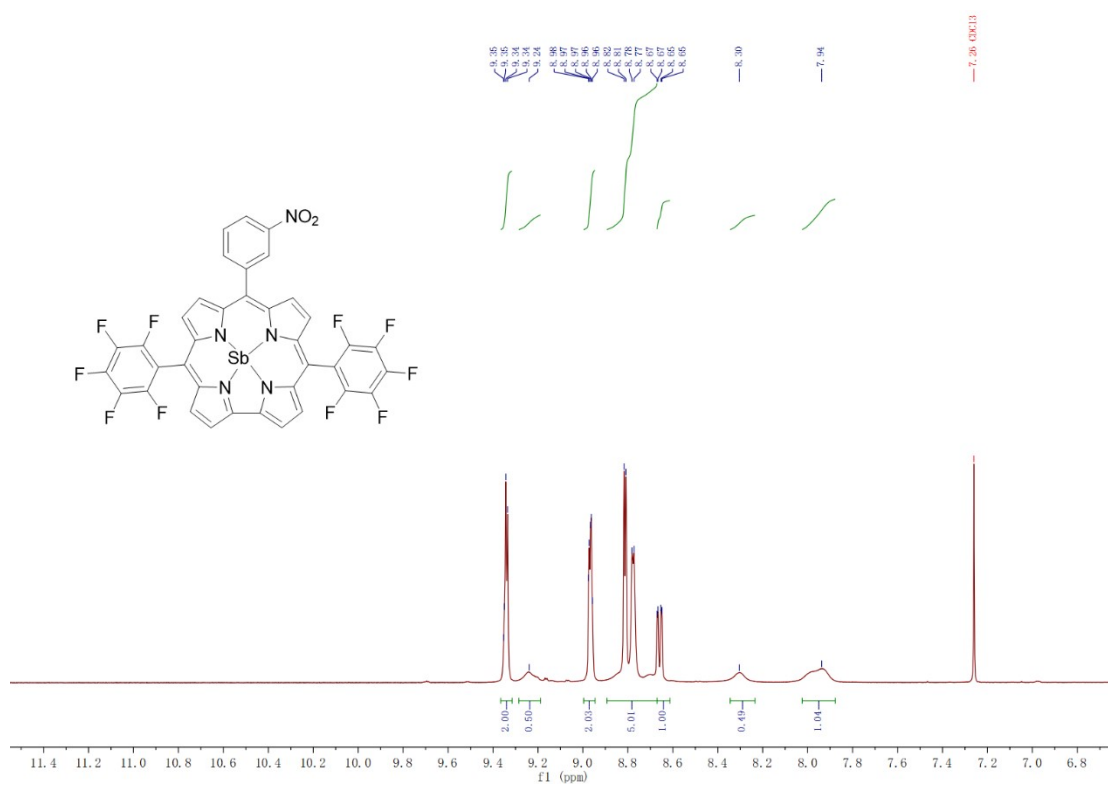


Fig S12. ¹H NMR spectrum of Complex 2

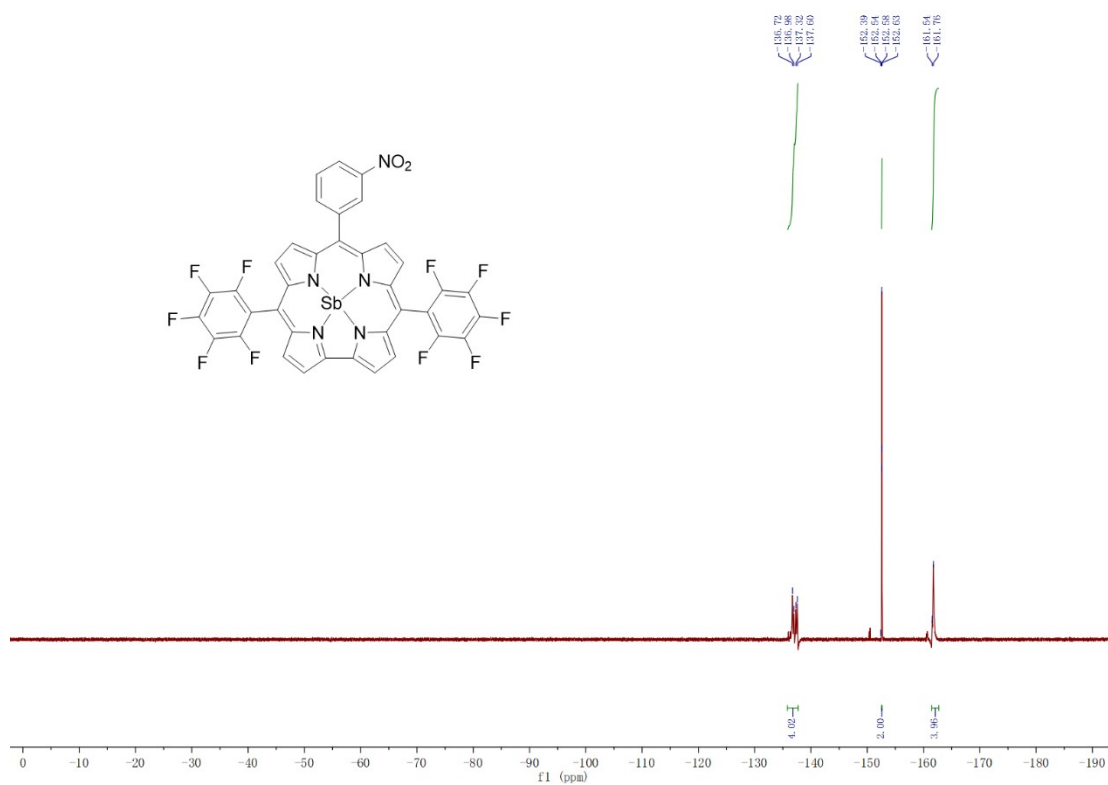


Fig S13. ¹⁹F NMR spectrum of Complex 2

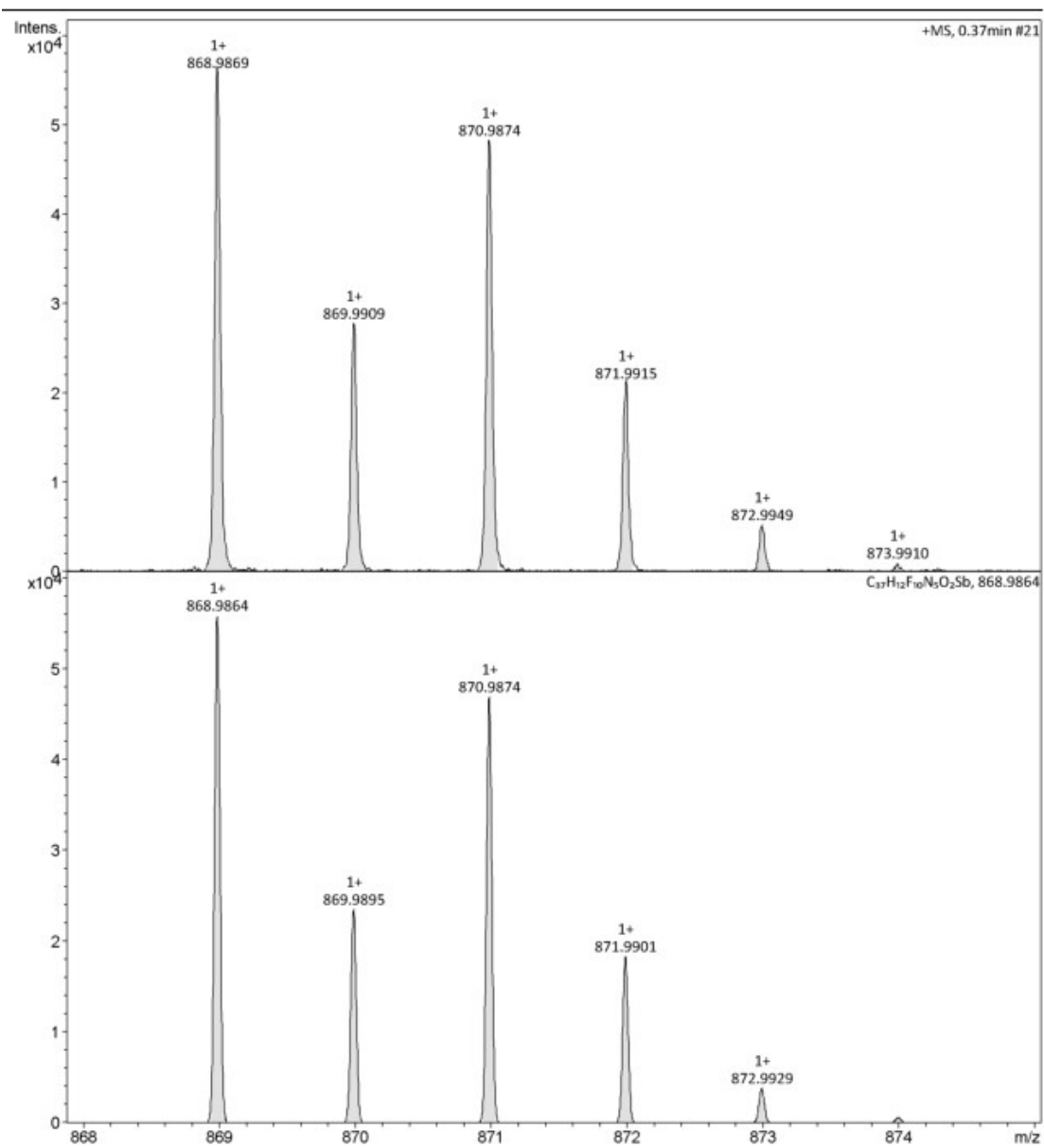


Fig S14. ESI-HRMS spectrum of Complex 2

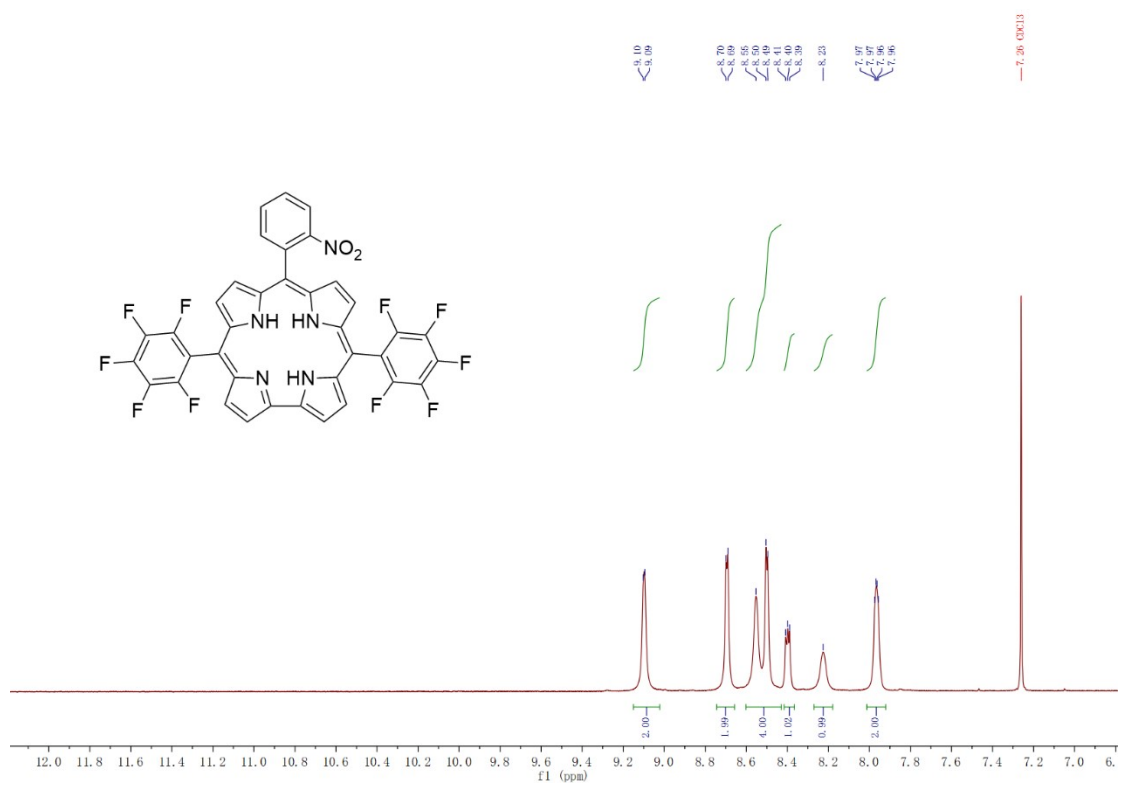


Fig S15. ¹H NMR spectrum of 2-NBPC

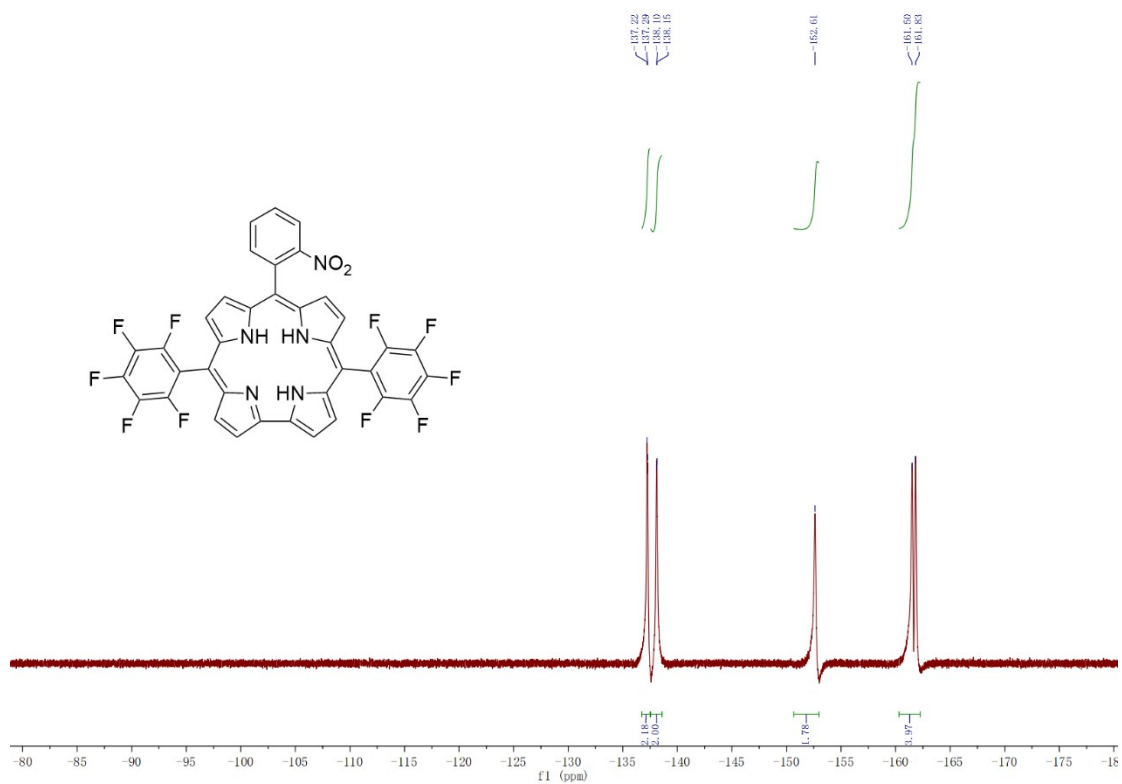


Fig S16. ¹⁹F NMR spectrum of 2-NBPC

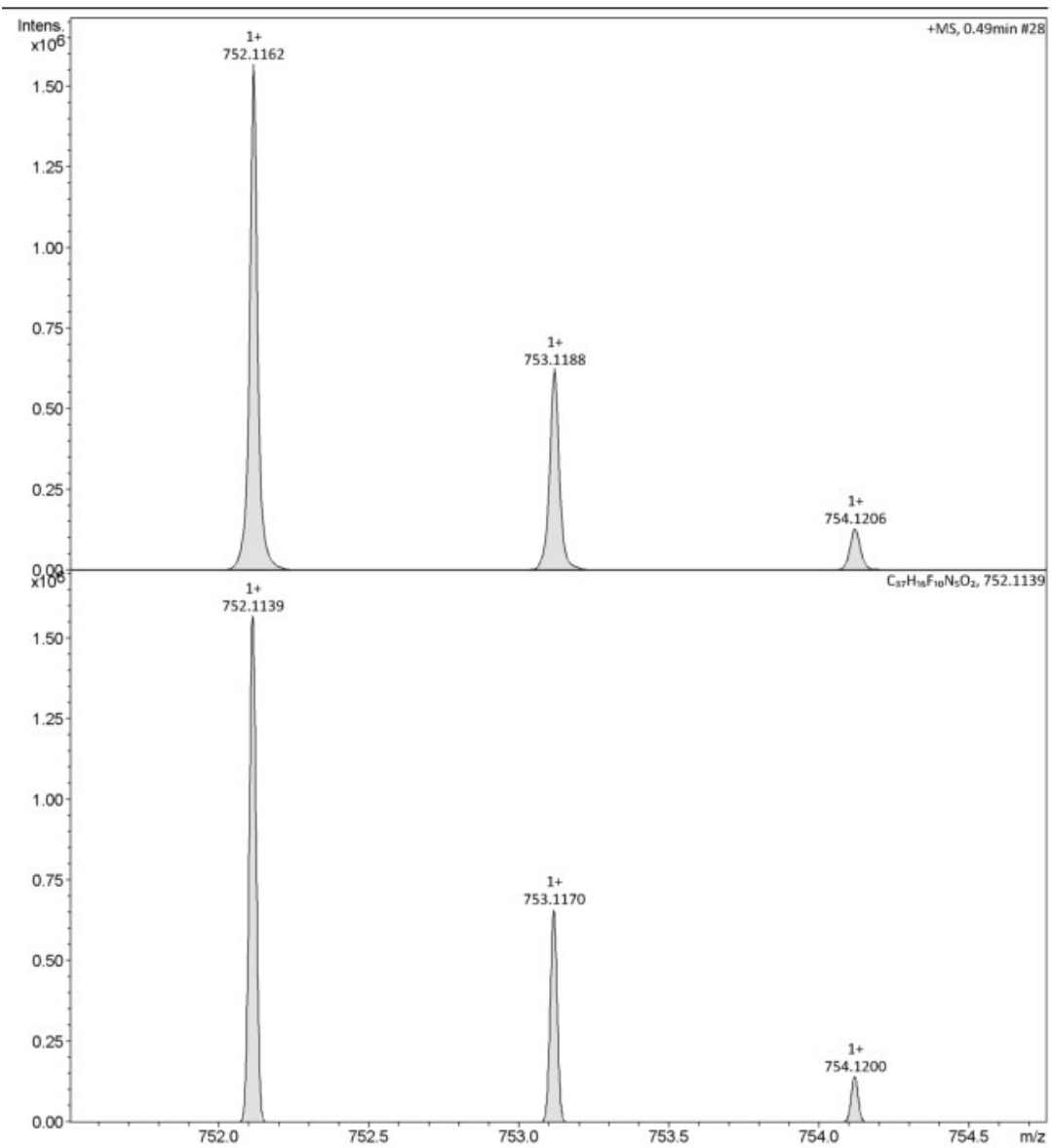


Fig S17. ESI-HRMS spectrum of 2-NBPC

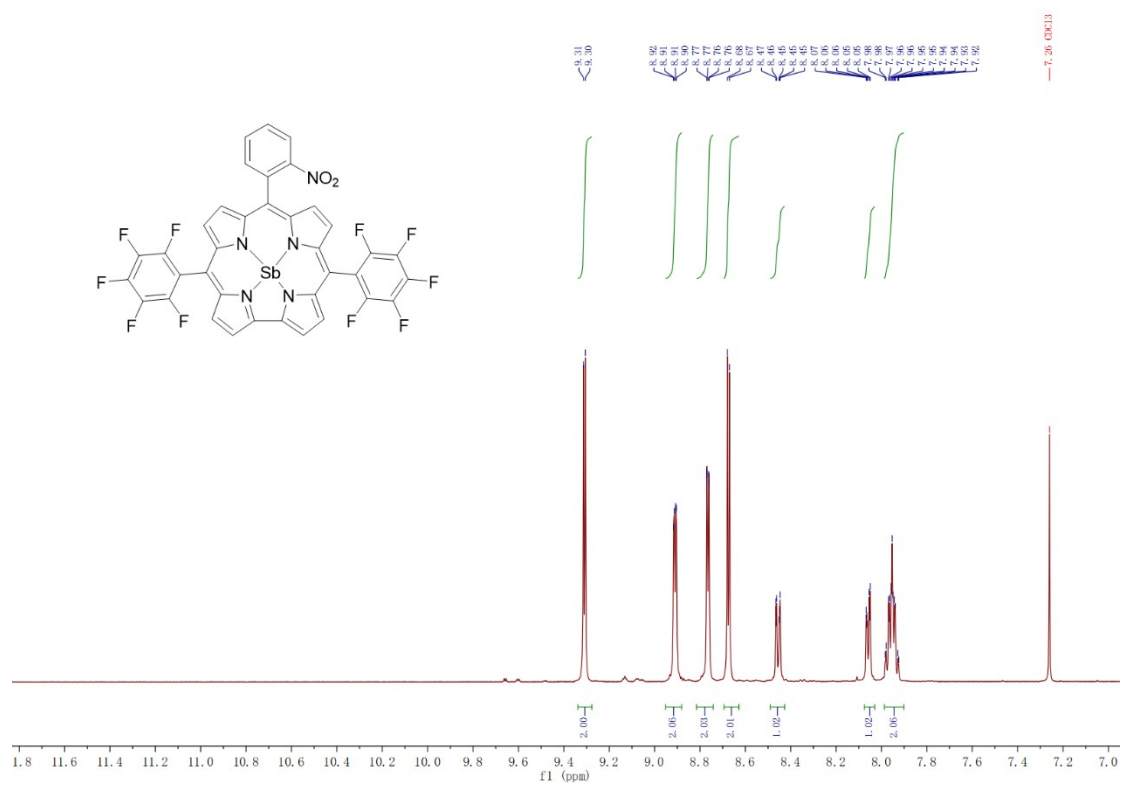


Fig S18. ¹H NMR spectrum of Complex 1

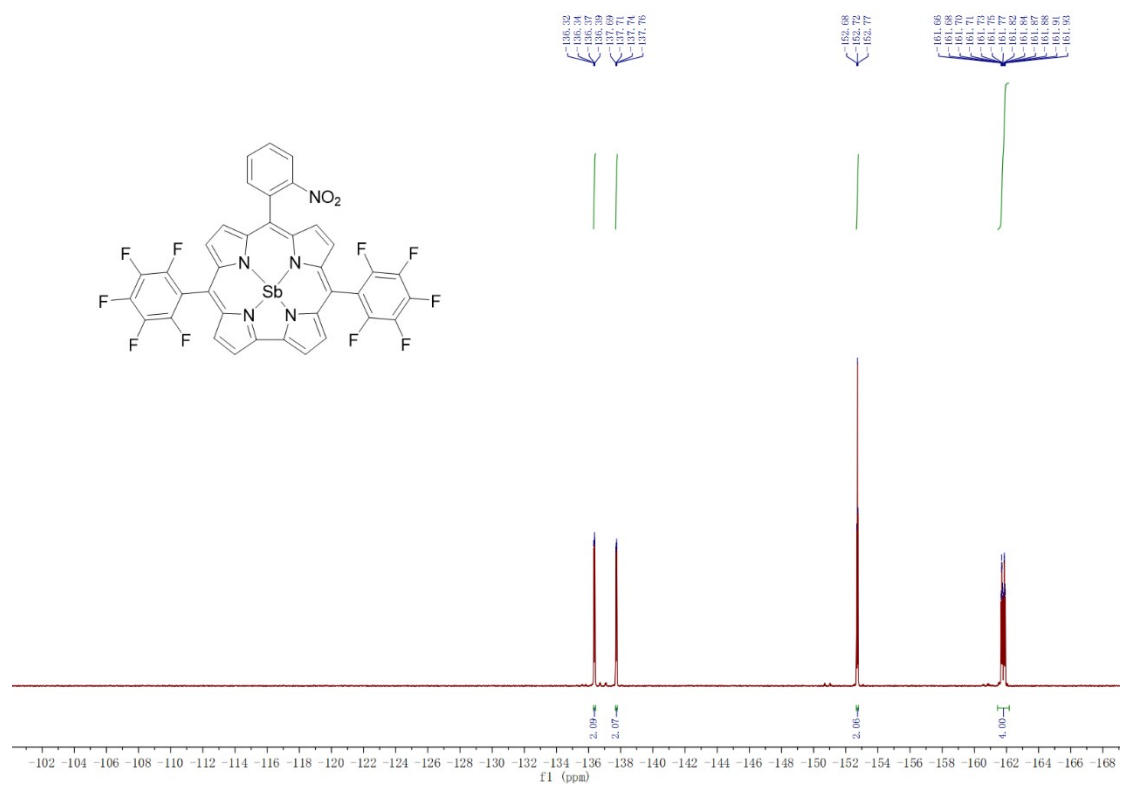


Fig S19. ¹⁹F NMR spectrum of Complex 1

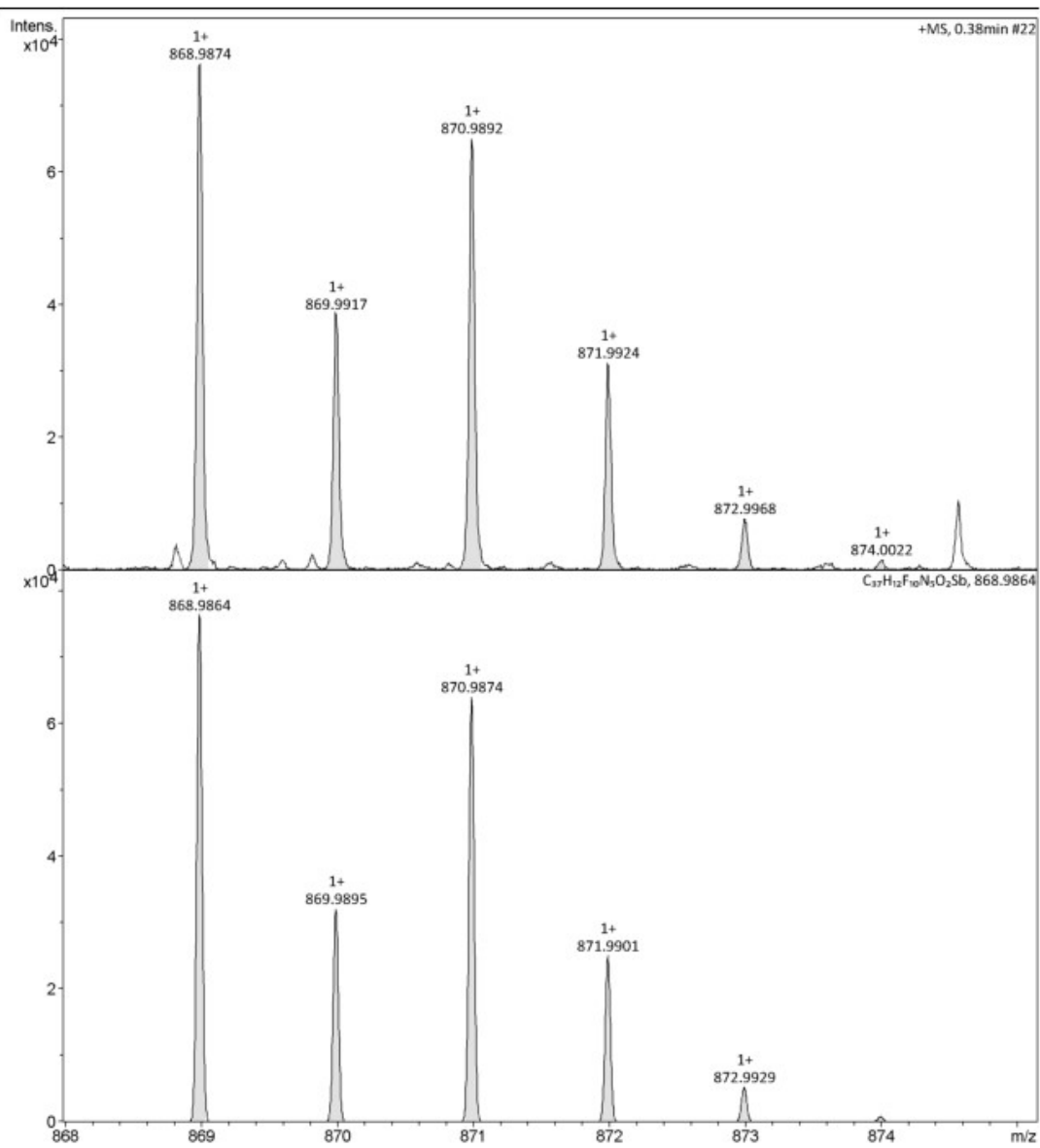


Fig S20. ESI-HRMS spectrum of Complex 1

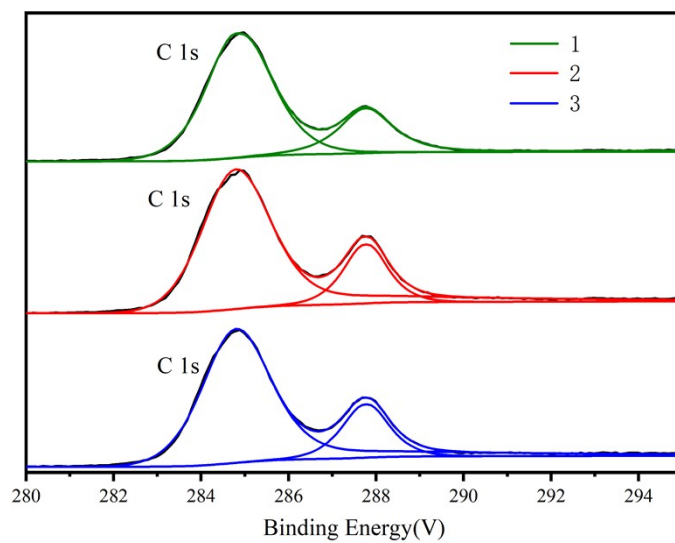


Fig S21. XPS spectra for C1s of complexes **1-3**.

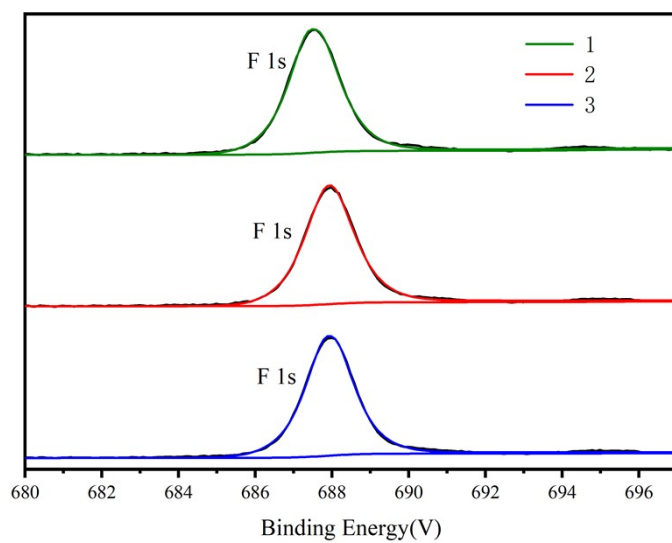


Fig S22. XPS spectra for F1s complexes **1-3**.

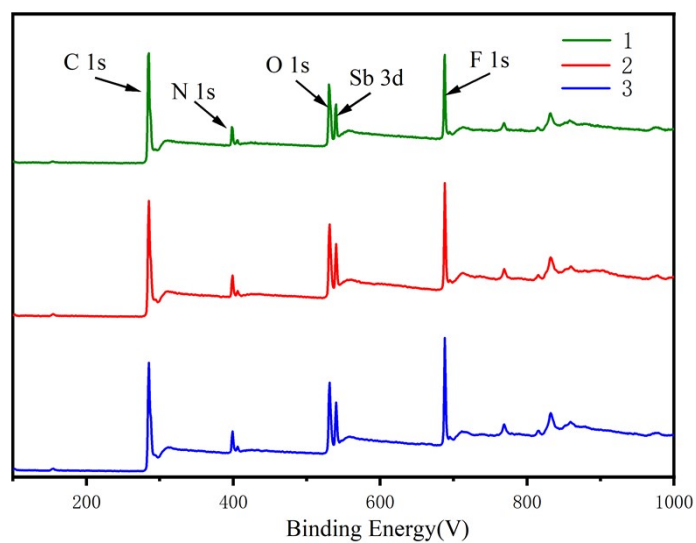


Fig S23. XPS survey scan spectrum of complexes **1-3**.

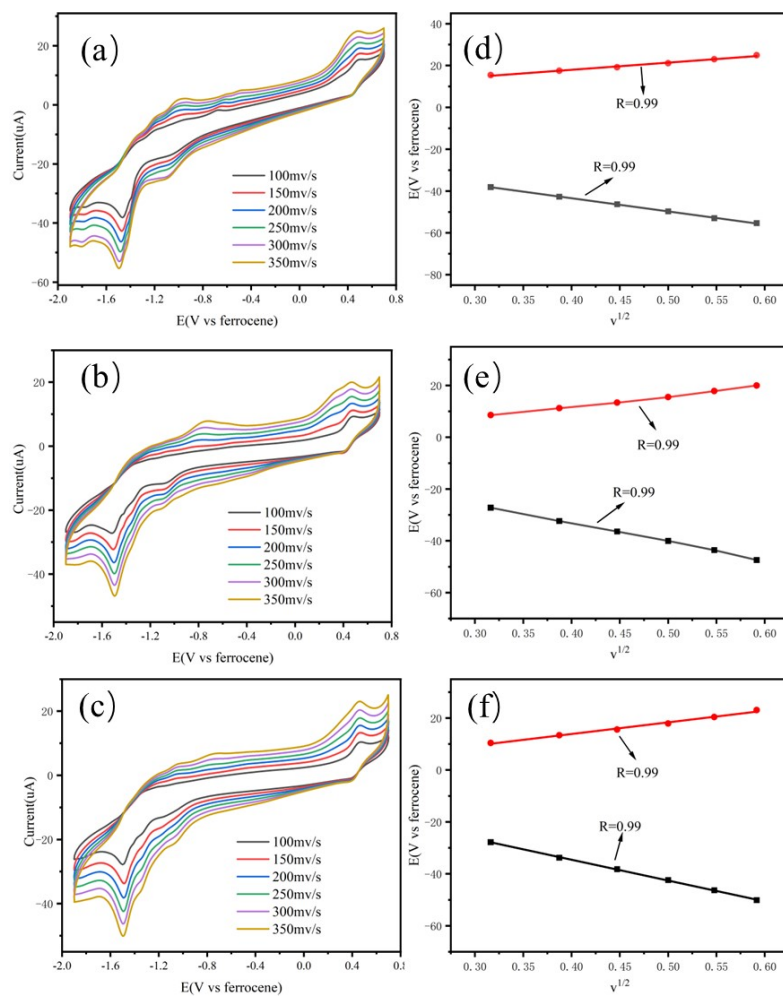


Fig S24. the maximum current (i_p) plots of $[\text{Sb-corrole}]/[\text{Sb-corrole}]^-$ reduction and first oxidation waves vs. the scan rate ($v^{1/2}$). complex **1**(a,d), **2**(b,e), and **3**(c,f)

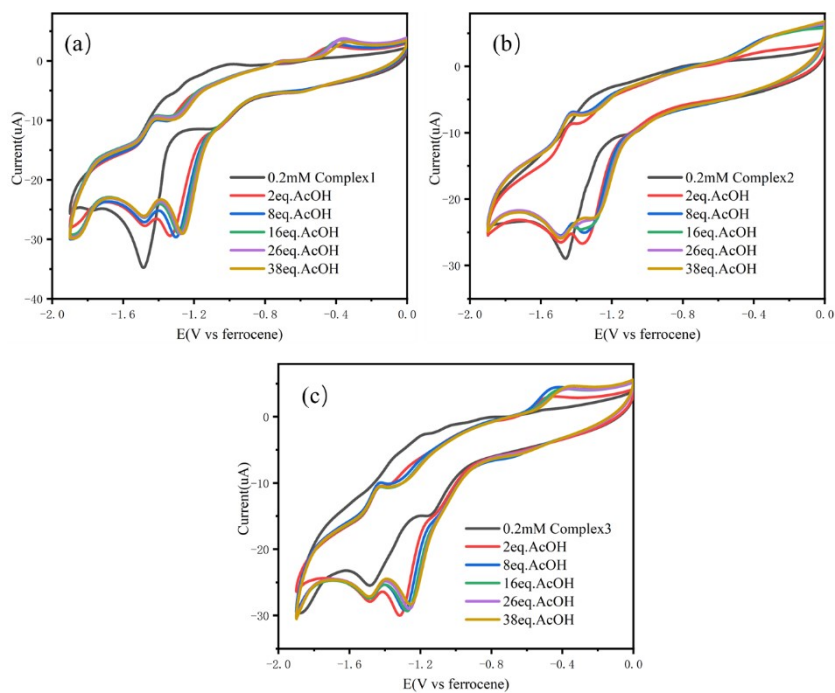


Fig 25. CVs of 0.2 mM antimony complexes **1-3** (a-c) with increasing amounts of TFA from 0 to 38 equivalents in N₂-saturated CH₃CN

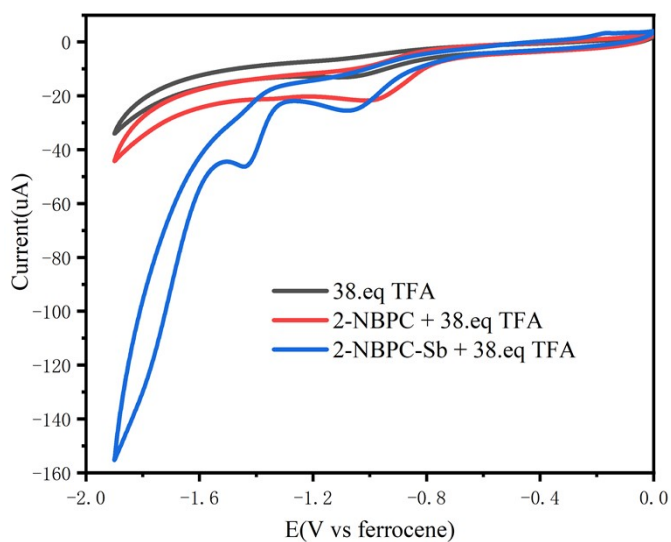


Fig S26. CVs of bare glassy carbon electrode(black), 2-NBPC(red), and 2-NBPC-Sb(blue) with 38.eq TFA in CH₃CN

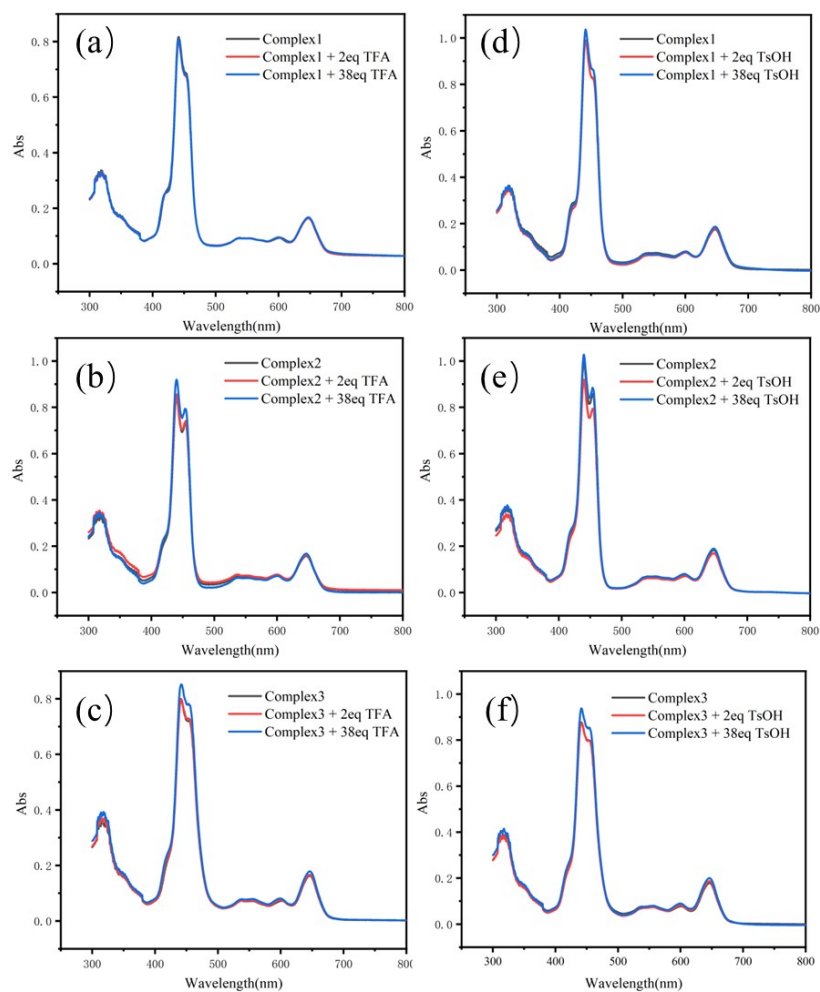


Fig S27. UV-Vis spectra of 0.2 mM complexes **1-3** in CH_3CN with 2 or 38 mM TFA(a-c) and 2 or 38 mM TsOH(d-f)

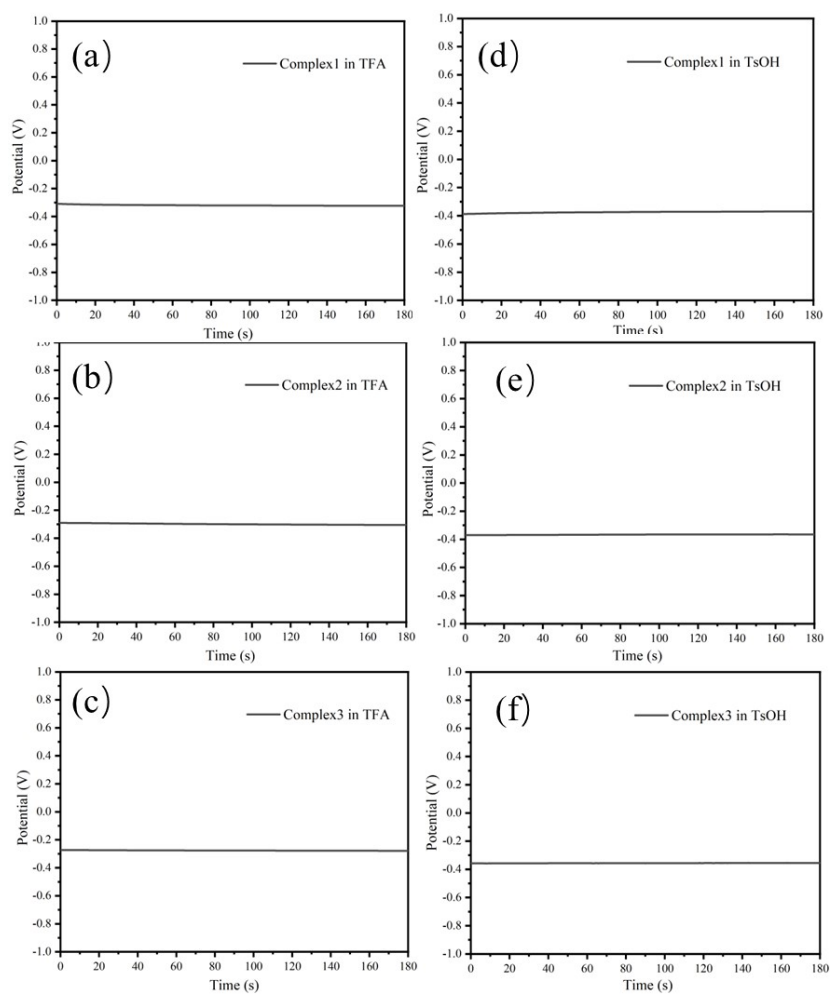


Fig S28. E_{ocp} of complex 1-3 by using TFA(a-c) and TsOH(d-f) as proton source

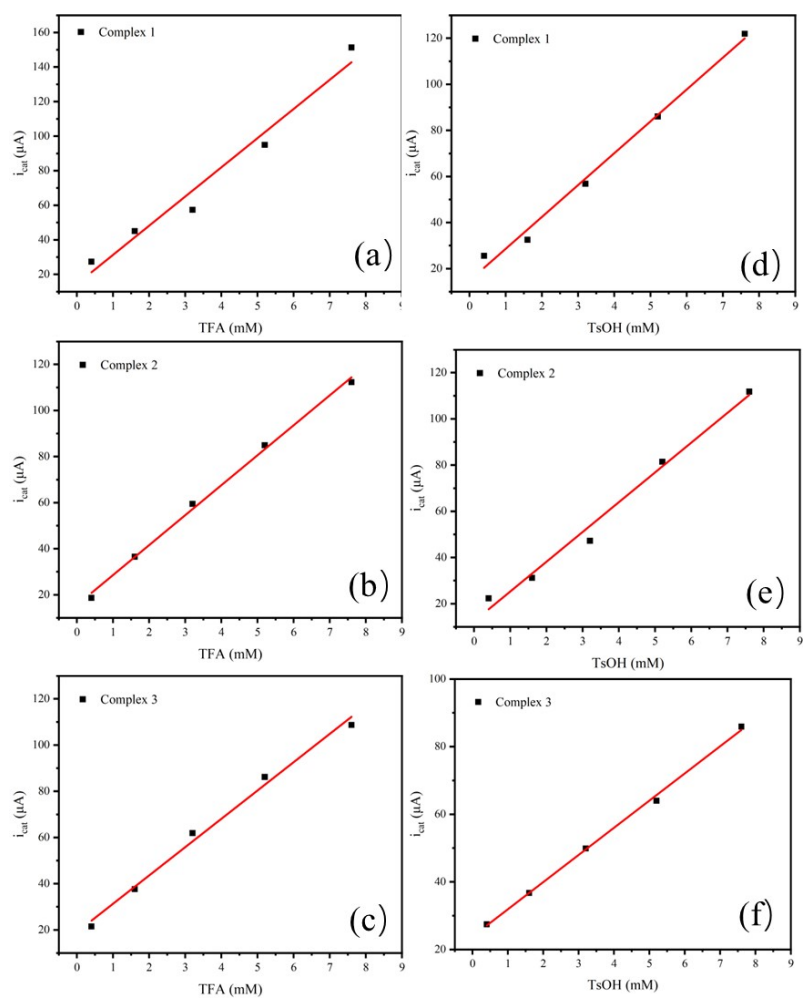


Fig S29. Plot of i_{cat} of complexes 1-3 versus TFA(a-c) and TsOH(d-f) concentrations

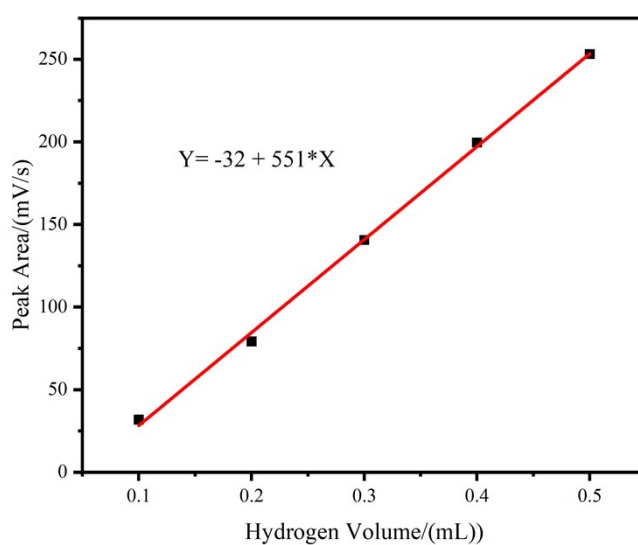


Fig S30. The hydrogen calibration plot from GC measurements.

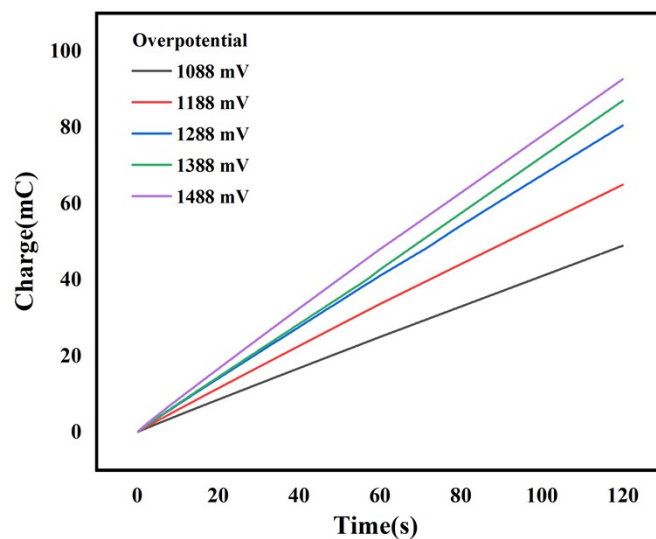


Fig S31. Charge buildup of bare glassy at a range of overpotentials in buffer solutions at pH=7.00

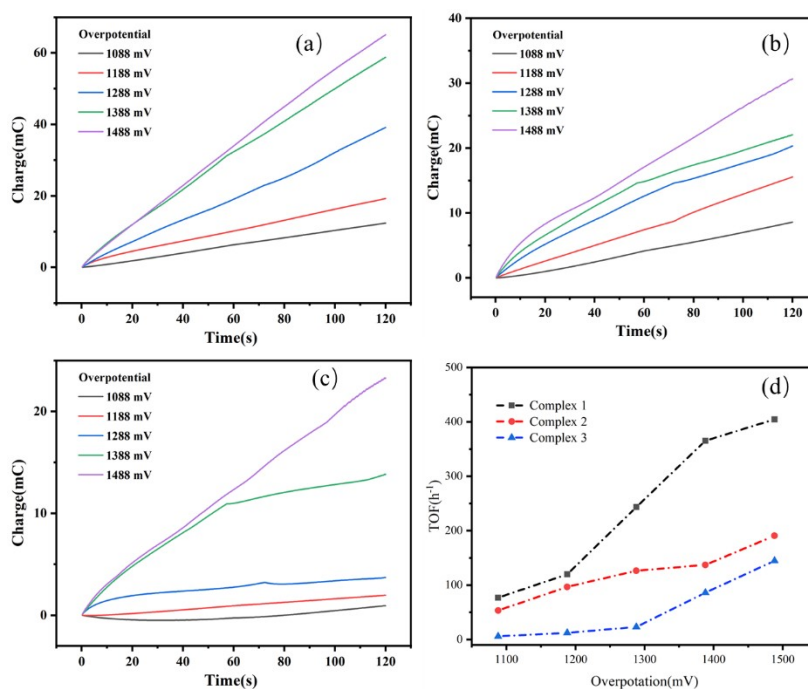


Fig S32. Charge buildup of 1.25 μM complexes **1-3** at a range of overpotentials in buffer solutions at pH=7.00(a-c). The TOF values of 1.25 μM complexes **1-3** at different overpotentials were calculated (d)

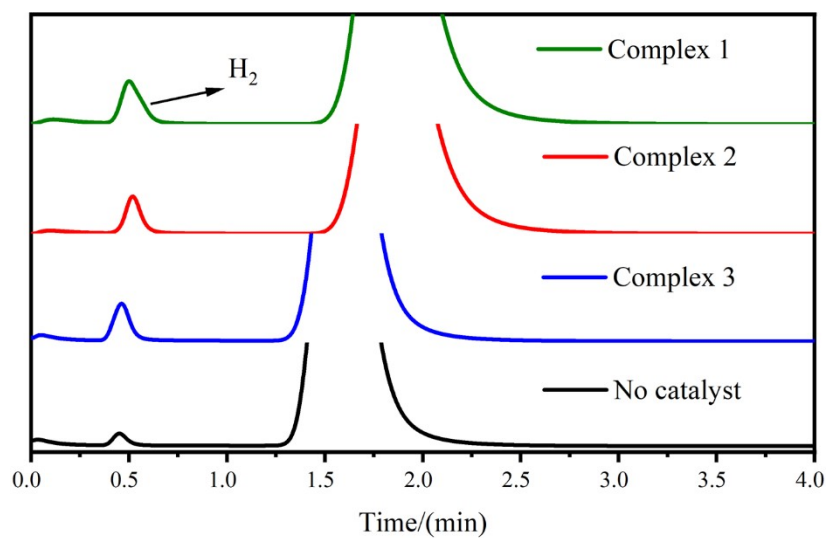


Fig S33. GC analysis for identification and quantification the hydrogen production after 1 h of electrolysis by complexes **1-3** (1.25 μM) in neutral aqueous medium ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 1/2$), the black line refers the control without catalyst.

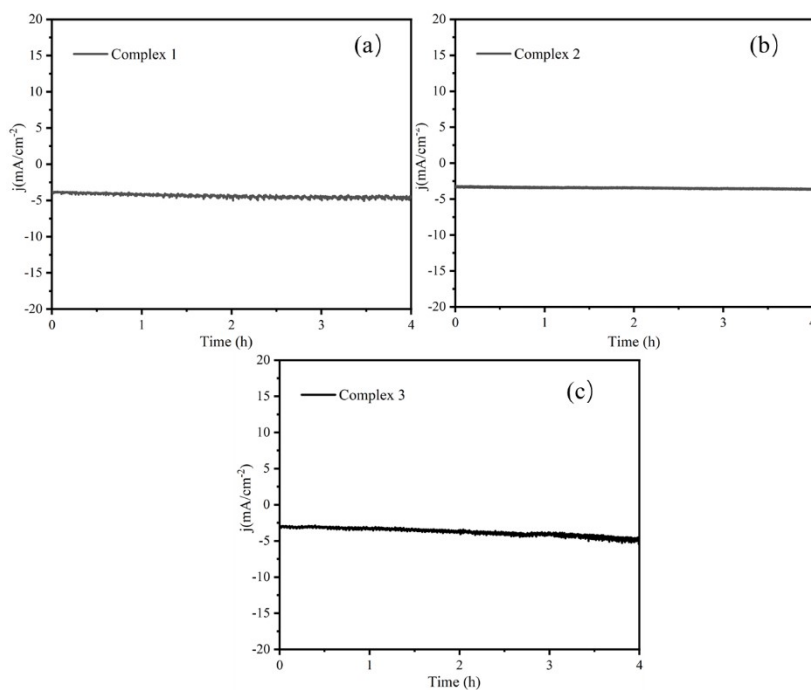


Fig S34. Current versus time for 4 h of 1.25 μM complexes **1-3** in buffer solution at pH = 7.0 at -1.9 V

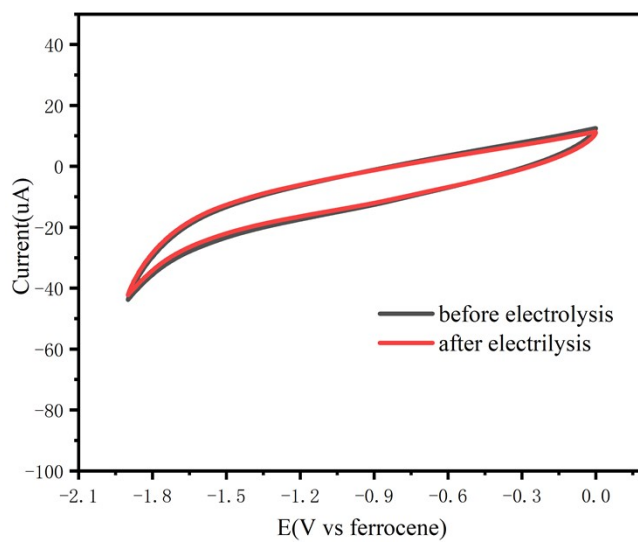


Fig S35. CVs of the GC working electrode before and after electrolysis in buffer

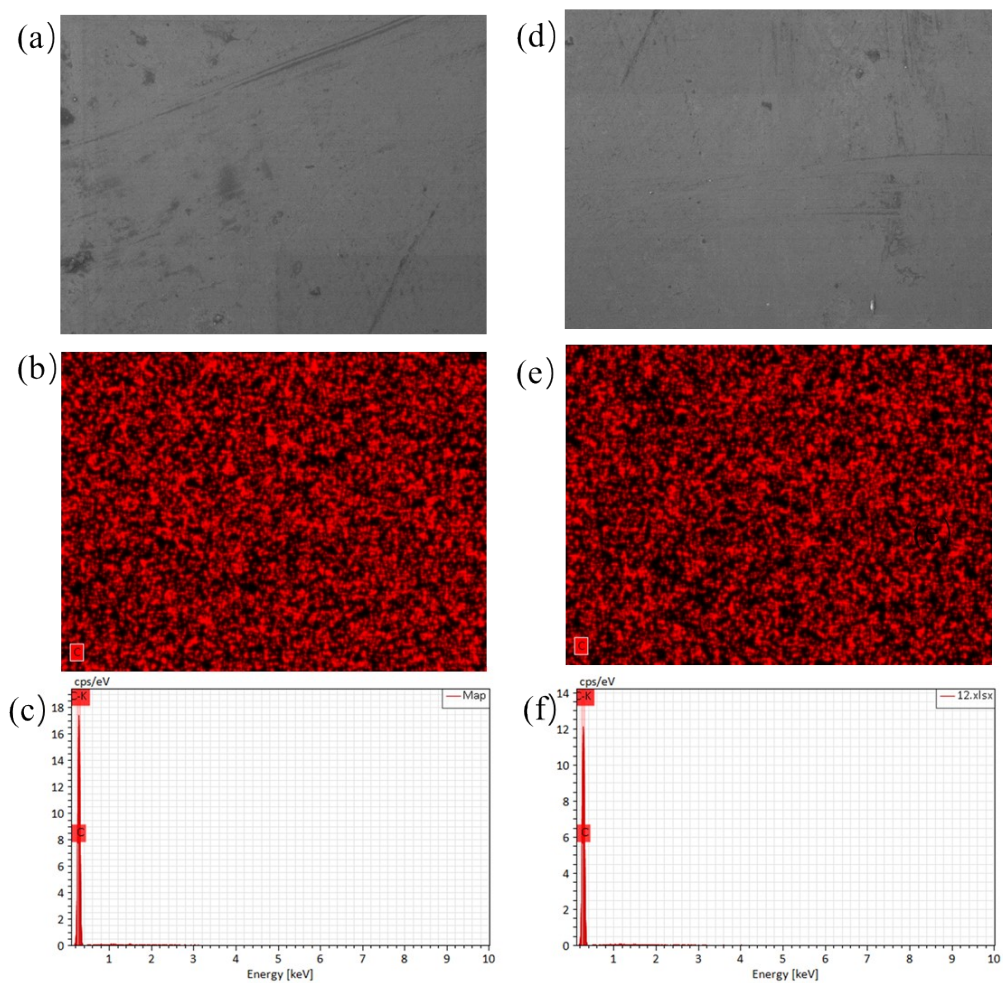


Fig S36. SEM images and EDX data of GC electrodes before (a-c) and after (d-f) electrolysis

Complex	Proton source	Overpotential (mV)	TOF (s ⁻¹)	Refs.
1	TFA	642	17.65	This work
1	TSOH	413	13.61	This work
2p	TFA	900	23.5	¹
3P	TFA	900	19.4	¹
4P	TFA	900	9.5	¹
(tpfc)MoV(O)	DMF-H ⁺	/	23	²
3 (tpfc)MoV(O)Br ₈	DMF-H ⁺	/	2.48	²
cobalt meso-5,15-bis(pentafluorophenyl)-10-(3-formylphenyl)corrole	TFA	600	134.5 6	³
cobalt meso-5,15-bis(pentafluorophenyl)-10-(3-formylphenyl)corrole	TSOH	600	62.17	³
1-PPh ₃	TFA	1010	11	⁴
2-PPh ₃	TFA	1010	17	⁴
2-Py	TFA	1010	15	⁴
2-Py	TFA	1010	19	⁴
[Ni-2] ⁻	TFA	360	3700	⁵
[Ni-3] ⁻	TFA	560	1500	⁵
(tpfc)Cu	TFA	/	49	⁶
((CF ₃) ₃ -tpfc)Cu	TFA	/	356	⁶
((CF ₃) ₄ -tpfc)Cu	TFA	/	227	⁶

Table S1. TOF and overpotential of corrole complexes as electrocatalysts for HER

Complex	Charge/C	Hydrogen gas/ μ mol	FE/%
1	2.38	9.84	80
2	2.10	7.53	69
3	2.01	7.38	71

Table S2. The amount of charge in one hour of electrolysis, the number of moles of hydrogen, and the FE in neutral buffer solution.(Blanks deducted)

Identification code	Complex 1
Empirical formula	C ₃₇ H ₁₂ F ₁₀ N ₅ O ₂ Sb
Formula weight	870.27
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.3971(4)
b/Å	14.1237(6)
c/Å	37.4265(14)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	6024.5(4)
Z	8
ρ_{calc} /g/cm ³	1.919
μ /mm ⁻¹	1.027
F(000)	3408.0
Crystal size/mm ³	0.12 × 0.08 × 0.05
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.184 to 52.768
Index ranges	-13 ≤ h ≤ 14, -17 ≤ k ≤ 16, -46 ≤ l ≤ 46
Reflections collected	26904
Independent reflections	6145 [R _{int} = 0.1037, R _{sigma} = 0.0775]
Data/restraints/parameters	6145/0/496
Goodness-of-fit on F ²	1.039
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0512, wR ₂ = 0.1049
Final R indexes [all data]	R ₁ = 0.0853, wR ₂ = 0.1194
Largest diff. peak/hole / e Å ⁻³	0.70/-0.88

Table S3. Crystal data and structure refinement for complex 1

Identification code	Complex 2
Empirical formula	C ₃₇ H ₁₂ F ₁₀ N ₅ O ₂ Sb
Formula weight	870.27
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	14.0880(4)
b/Å	7.8247(2)
c/Å	30.2785(9)
α/°	90
β/°	102.7170(10)
γ/°	90
Volume/Å ³	3255.85(16)
Z	4
ρ _{calc} /cm ³	1.775
μ/mm ⁻¹	0.950
F(000)	1704.0
Crystal size/mm ³	0.09 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.528 to 52.79
Index ranges	-17 ≤ h ≤ 12, -8 ≤ k ≤ 9, -37 ≤ l ≤ 37
Reflections collected	24091
Independent reflections	6552 [R _{int} = 0.0561, R _{sigma} = 0.0462]
Data/restraints/parameters	6552/0/496
Goodness-of-fit on F ²	0.999
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0875, wR ₂ = 0.2398
Final R indexes [all data]	R ₁ = 0.1050, wR ₂ = 0.2634
Largest diff. peak/hole / e Å ⁻³	5.23/-0.87

Table S4. Crystal data and structure refinement for complex **2**

Atom		Bond length, Å	Atom			Angle/°
Sb	N1	2.120(4)	N1	Sb1	N3	124.81(16)
Sb	N4	2.113(4)	N1	Sb1	N2	78.71(16)
Sb	N3	2.142(4)	N4	Sb1	N1	71.75(15)
Sb	N2	2.127(4)	N4	Sb1	N3	79.17(15)
O1	N5	1.241(6)	N4	Sb1	N2	126.29(16)
O2	N5	1.219(6)	N2	Sb1	N3	82.58(15)
N5	C14	1.465(7)	O1	N5	C14	117.9(5)
			O2	N5	O1	123.8(5)
			O2	N5	C14	118.3(4)

Table S5. Crystal data and structure refinement for complex **1**

Atom		Bond length, Å	Atom			Angle/°
Sb1	N4	2.131(6)	N4	Sb1	N1	125.3(2)
Sb1	N2	2.119(7)	N2	Sb1	N4	78.6(3)
Sb1	N3	2.125(7)	N2	Sb1	N3	124.6(3)
Sb1	N1	2.132(7)	N2	Sb1	N1	71.8(3)
O1	N5	1.220(10)	N3	Sb1	N4	82.4(2)
O2	N5	1.223(9)	N3	Sb1	N1	78.4(3)
N5	C15	1.474(12)	O1	N5	O2	123.4(8)
			O1	N5	C15	119.2(7)
			O2	N5	C15	117.4(8)

Table S6. Crystal data and structure refinement for complex **2**.

Complex	oxidation		Redution
	Sb ^{III} /Sb ^{IV}	-NO ₂ Ph	[Sb-corrole] / [Sb-corrole] ⁻
1	0.48	-1.05	-1.48
2	0.47	-1.08	-1.50
3	0.45	-1.12	-1.50

Table S7. Peak potentials of complexes **1-3** in CH₃CN containing 0.1 M TBAPF₆.

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