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Electronic Supplementary Information

Electrocatalytic hydrogen evolution using hybrid electrodes based on single-walled carbon nanohorns and cobalt(II) polypyridine complexes

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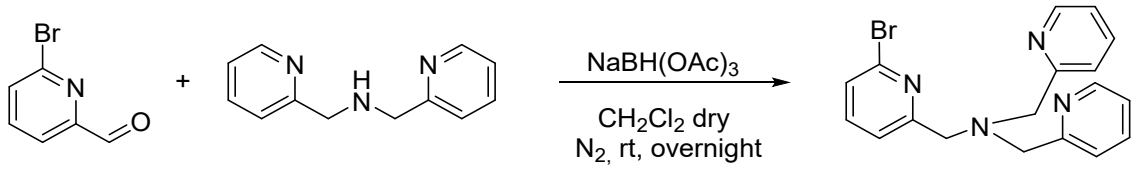
1. Synthesis and Characterization

1.1 Synthesis of 1-(6-bromopyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine 6a



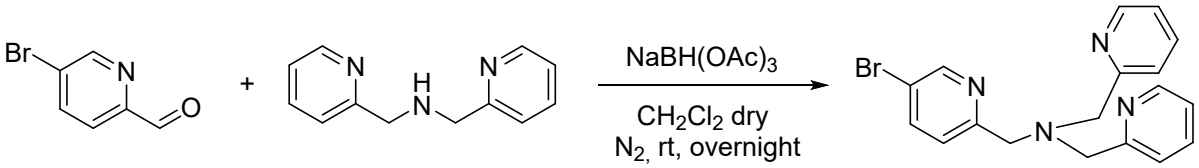
4a **5** **6a**

Compound **6a** has been synthesized according to literature.[1] In a Schlenk apparatus, 6-bromopicolinaldehyde **4a** (1.6 g, 8.33 mmol) and bis(pyridin-2-ylmethyl)amine **5** (1.5 mL, 8.6 mmol) were dissolved in 15 mL of dry CH_2Cl_2 under N_2, and left under stirring for 1 hour. Three aliquots of $NaBH(OAc)_3$ (0.59 g, 2.78 mmol) were added waiting 20 minutes between each addition. After the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The resulting dark orange oil was dissolved in EtOAc and the solution washed with 0.1 M solution of KOH (3x100 mL). The organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The resulting orange oil was precipitated by crystallization from CH_3CN/Et_2O to yield the products **6a** as a pale-yellow solid. (2.22 g, 6.02 mmol, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 5.0 Hz, 2H), 7.65 (td, *J* = 7.6 Hz, 1.8 Hz, 2H), 7.59 – 7.44 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.11 (m, 2H), 3.88 (s, 4H), 3.87 (s, 2H).

ESI-MS (m/z): $[M+H]^+$ calcd. for $[C_{18}H_{17}BrN_4+H]^+$ 369.0715; found 369.0717.

1.2 Synthesis of 1-(5-bromopyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine 6b



4b **5** **6b**

In a Schlenk apparatus, 5-bromopicolinaldehyde **4b** (1.6 g, 8.33 mmol) and bis(pyridin-2-ylmethyl)amine **5** (1.5 mL, 8.6 mmol) were dissolved in 15 mL of dry CH_2Cl_2 under N_2, and left under stirring for 1 hour. Three aliquots of $NaBH(OAc)_3$ (0.59 g, 2.78 mmol) were added waiting 20 minutes between each addition. After the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The resulting brown oil was dissolved in EtOAc and the solution washed with 0.1 M solution of KOH (3x100 mL). The organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The resulting brown oil was

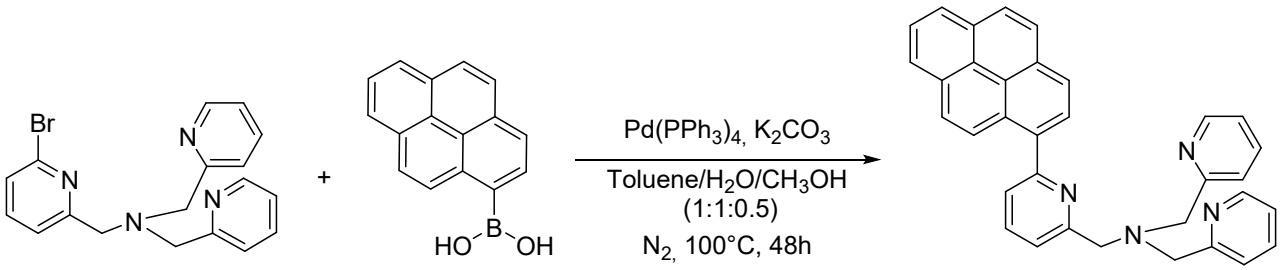
precipitated by crystallization from THF/Hexane to yield the products **6b** as a pale-yellow solid. (1.97 g, 5.34 mmol, 64%).

^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 8.66 – 8.30 (m, 3H), 7.75 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.56 – 7.44 (m, 3H), 7.20 – 7.06 (m, 2H), 3.87 (s, 4H), 3.84 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.16, 158.17, 150.16, 149.27, 139.10, 136.55, 124.49, 123.14, 122.18, 60.26, 59.52.

ESI-MS (m/z): $[M+H]^+$ calcd. for $[C_{18}H_{17}BrN_4+H]^+$ 369.0715; found 369.0715.

1.3 Synthesis of 1-(6-(pyren-1-yl)pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine 8a



6a **7** **8a**

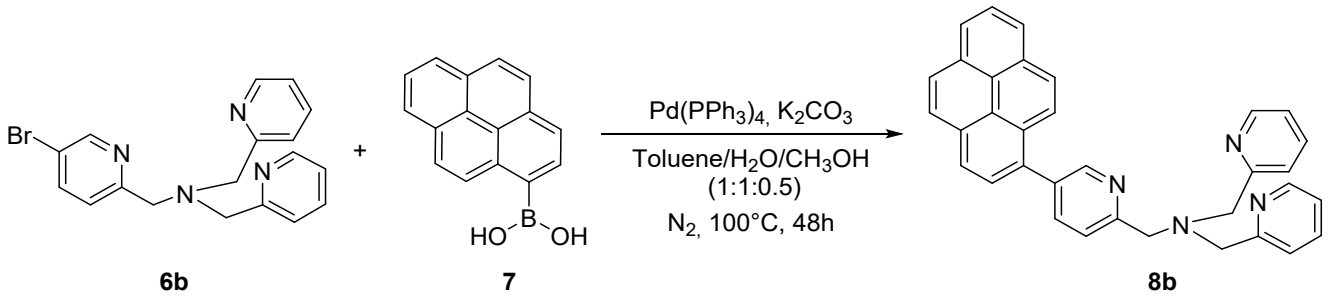
In a Schlenk apparatus, a mixture of **6a** (0.50 g, 1.35 mmol), pyren-1-ylboronic acid **7** (0.43 g, 2.04 mmol), $Pd(PPh_3)_4$ (15.7 mg, 0.013 mmol, 1 mol%) and K_2CO_3 (0.42 g, 3.06 mmol) was dissolved in 12.5 mL of degassed H_2O/toluene/CH_3OH (1:1:0.5) mixture. The mixture was stirred under N_2 for 48 hours at 100 °C. The solvent was removed under reduced pressure. The resulting green oil was dissolved in $CHCl_3$ and the solution washed with H_2O. The organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Product **8a** was obtained as a yellow oil (0.57 g, 1.17 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ (ppm): 8.56 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 9.3 Hz, 1H), 8.27 – 8.07 (m, 7H), 8.05 – 7.99 (m, 2H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.71 – 7.65 (m, 4H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.18 – 7.15 (m, 2H), 4.07 – 4.01 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.24, 159.19, 158.49, 148.85, 136.58, 136.29, 135.54, 131.91, 131.81, 131.12, 131.11, 130.85, 130.64, 128.39, 128.27, 127.63, 127.59, 127.50, 127.17, 127.12, 125.77, 125.61, 125.09, 124.86, 124.83, 124.79, 124.70, 124.59, 123.81, 122.87, 121.85, 120.91, 60.29, 60.18.

ESI-MS (m/z): $[M+H]^+$ calcd. for $[C_{34}H_{26}N_4+H]^+$, 491.2236; found 491.2231.

1.4 Synthesis of 1-(5-(pyren-1-yl)pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine 8b



6b **7** **8b**

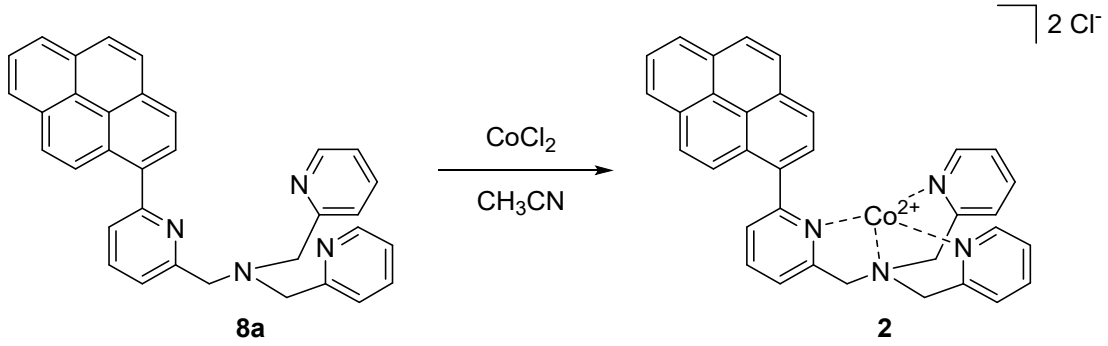
In a Schlenk apparatus, a mixture of **6b** (0.50 g, 1.35 mmol), pyren-1-ylboronic acid **7** (0.43 g, 2.04 mmol), $Pd(PPh_3)_4$ (15.7 mg, 0.013 mmol, 1 mol%) and K_2CO_3 (0.42 g, 3.06 mmol) was dissolved in 12.5 mL of degassed H_2O/toluene/CH_3OH (1:1:0.5) mixture. The mixture was stirred under N_2 for 48 hours at 100 °C. The solvent was removed under reduced pressure. The resulting green oil was dissolved in $CHCl_3$ and the solution washed with H_2O. The organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Product **8b** was obtained as a yellow oil (0.53 g, 1.08 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ (ppm): 8.80 (d, *J* = 2.2 Hz, 1H), 8.57 (d, *J* = 4.8 Hz, 2H), 8.16 – 8.09 (m, 3H), 8.05 – 7.93 (m, 5H), 7.89 – 7.86 (m, 2H), 7.77 – 7.75 (m, 1H), 7.66 – 7.65 (m, 4H), 7.15 – 7.11 (m, 2H), 4.06 – 4.02 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33, 158.13, 150.18, 149.11, 149.09, 138.47, 138.22, 136.47, 136.39, 135.08, 133.50, 131.33, 130.98, 130.81, 130.78, 128.62, 127.99, 127.92, 127.75, 127.51, 127.25, 126.12, 125.36, 125.03, 124.87, 124.72, 124.68, 124.42, 123.06, 123.00, 122.56, 122.05, 60.40, 60.08.

ESI-MS (m/z): $[M+H]^+$ calcd. for $[C_{34}H_{26}N_4+H]^+$, 491.2236; found 491.2276.

1.5 Synthesis of Complex 2



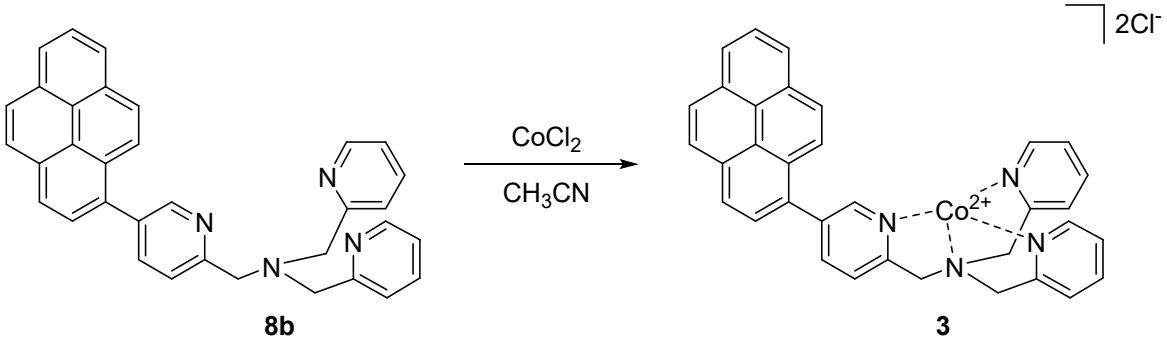
8a **2**

To a suspension of ligand **8a** (50 mg, 0.10 mmol) in CH_3CN (10 mL), $CoCl_2$ was added (13 mg, 0.10 mmol). The solution was stirred at room temperature for 1 hour and the reaction was followed by ESI-MS. The product **2** was obtained as a green solid in quantitative yield (63 mg, 0.10 mmol) after slow evaporation of the solvent.

ESI-MS (m/z): $[M+Cl]^+$ calcd. for $[C_{34}H_{26}CoN_4Cl]^+$, 584.1178; found 584.1208

Elemental analysis: Calc. $C_{34}H_{26}CoN_4$. 2 Cl 4 H_2O: C = 58.97%, H = 4.95%, N = 8.09%, Found: C = 58.32%, H = 4.72%, N = 7.85%

1.6 Synthesis of Complex 3



8b **3**

To a suspension of ligand **8b** (50 mg, 0.10 mmol) in CH_3CN (10 mL), $CoCl_2$ was added (13 mg, 0.10 mmol). The solution was stirred at room temperature for 1 hour and the reaction was followed by ESI-MS. The product **3** was obtained as a green solid in quantitative yield (63 mg, 0.10 mmol) after slow evaporation of the solvent.

ESI-MS (m/z): $[M+Cl]^+$ calcd. for $[C_{34}H_{26}CoN_4Cl]^+$, 584.1178; found 584.1208

Elemental analysis: Calc. $C_{34}H_{26}CoN_4$. 2 Cl 4 H_2O: C = 58.97%, H = 4.95%, N = 8.09%, Found: C = 58.41%, H = 4.63%, N = 7.80%

2. Crystallographic data for complex 3

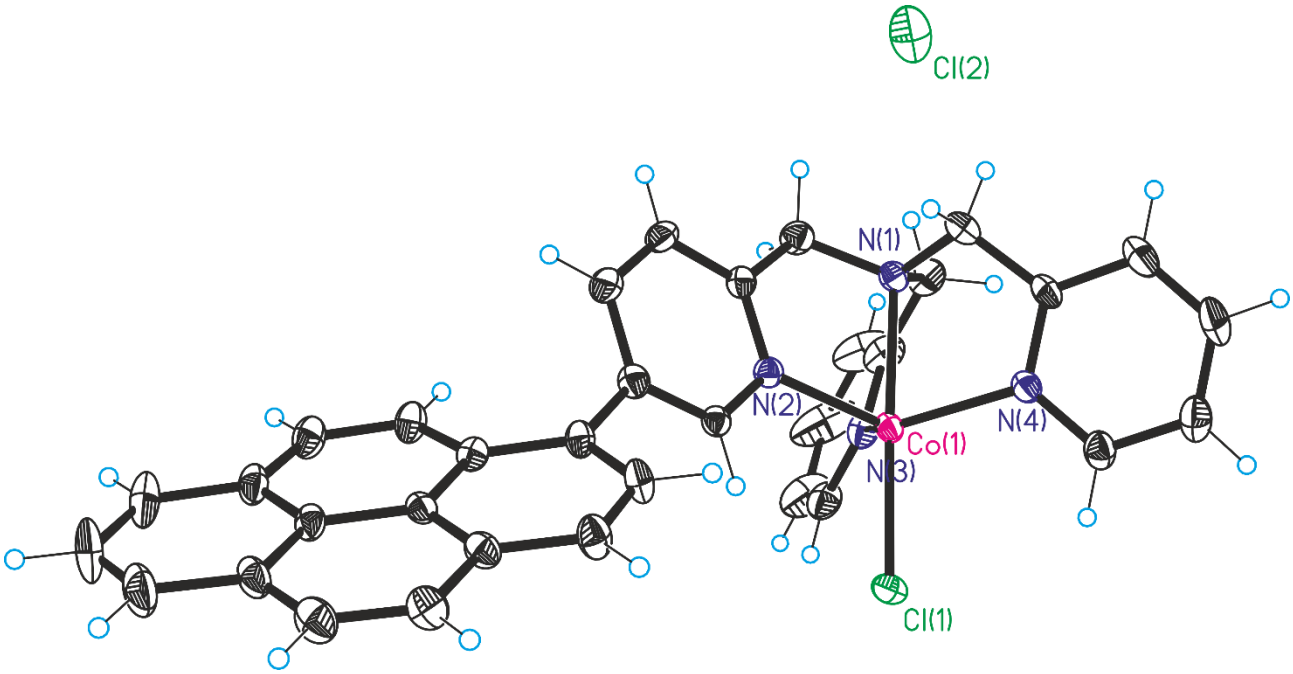


Figure S1. Crystal structure of complex **3**.

Table S1. Crystal data and structure refinement for **3**

Empirical formula	C34 H26 Cl2 Co N4 x 3.5 H2O	
Formula weight	683.47	
Temperature	263(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca (no. 61)	
Unit cell dimensions	a = 14.348(3) Å	α = 90°.
	b = 9.1460(16) Å	β = 90°.
	c = 49.790(9) Å	γ = 90°.
Volume	6534(2) $Å^3$	
Z	8	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.731 mm^{-1}	
F(000)	2832	
Crystal size	0.180 x 0.100 x 0.060 mm^3	
Theta range for data collection	2.454 to 23.000°.	
Index ranges	-15<=h<=15, -10<=k<=10, -54<=l<=54	
Reflections collected	48316	
Independent reflections	4515 [R(int) = 0.0700]	

Completeness to theta = 23.000°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.958 and 0.813
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4515 / 0 / 415
Goodness-of-fit on F^2	1.199
Final R indices [I>2sigma(I)]	R1 = 0.0816, wR2 = 0.1911
R indices (all data)	R1 = 0.0919, wR2 = 0.1958
Extinction coefficient	n/a
Largest diff. peak and hole	0.809 and -0.679 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	3661(1)	5634(1)	6063(1)	39(1)
Cl(1)	2357(1)	6557(2)	6257(1)	58(1)
N(1)	4917(4)	4841(6)	5860(1)	44(1)
N(2)	4306(3)	4446(5)	6363(1)	41(1)
N(3)	4396(4)	7519(6)	5996(1)	54(2)
N(4)	3132(4)	4580(6)	5734(1)	44(1)
C(1)	5630(5)	4546(8)	6065(1)	54(2)
C(2)	5182(4)	4004(7)	6320(1)	42(2)
C(3)	5649(5)	3158(8)	6504(1)	52(2)
C(4)	5210(5)	2760(8)	6740(1)	56(2)
C(5)	4302(5)	3199(7)	6787(1)	47(2)
C(6)	3886(4)	4045(6)	6594(1)	39(1)
C(7)	3760(4)	2695(7)	7026(1)	44(2)
C(8)	2901(5)	2052(8)	6984(1)	56(2)
C(9)	2368(5)	1498(8)	7190(1)	57(2)
C(10)	2691(5)	1564(7)	7452(1)	48(2)
C(11)	2173(5)	968(8)	7670(1)	60(2)
C(12)	2487(6)	1013(9)	7922(1)	66(2)
C(13)	3350(6)	1711(8)	7984(1)	58(2)
C(14)	3692(7)	1806(11)	8246(2)	84(3)
C(15)	4506(8)	2476(13)	8298(2)	103(3)

C(16)	5032(7)	3113(10)	8096(2)	87(3)
C(17)	4739(5)	3057(8)	7829(1)	56(2)
C(18)	5236(5)	3698(8)	7614(2)	60(2)
C(19)	4938(5)	3591(8)	7357(1)	53(2)
C(20)	4094(4)	2843(6)	7290(1)	41(2)
C(21)	3560(4)	2252(6)	7505(1)	41(2)
C(22)	3884(5)	2345(7)	7772(1)	47(2)
C(23)	5206(5)	6011(9)	5680(2)	65(2)
C(24)	5090(5)	7445(9)	5815(2)	68(2)
C(25)	5648(7)	8650(11)	5774(3)	117(4)
C(26)	5477(8)	9906(12)	5918(4)	147(6)
C(27)	4784(8)	9963(10)	6091(3)	106(4)
C(28)	4243(6)	8766(8)	6130(2)	67(2)
C(29)	4638(5)	3539(9)	5710(1)	62(2)
C(30)	3700(5)	3705(7)	5595(1)	48(2)
C(31)	3399(7)	2984(9)	5365(2)	71(2)
C(32)	2509(7)	3141(10)	5282(2)	78(2)
C(33)	1924(6)	3999(10)	5420(2)	72(2)
C(34)	2251(5)	4731(8)	5647(1)	57(2)
O(1)	7538(6)	9621(14)	5301(2)	171(4)
O(2)	7869(5)	7120(15)	5560(2)	210(6)
O(3)	7435(6)	7010(16)	6106(2)	183(5)
O(4)	7879(18)	4960(60)	6329(8)	390(30)
Cl(2)	9333(6)	8934(10)	5002(1)	151(3)
Cl(3)	9522(6)	5979(13)	5151(2)	194(4)

Table S3. Bond lengths [Å] and angles [°] for **3**.

Co(1)-N(4)	2.048(5)
Co(1)-N(3)	2.049(6)
Co(1)-N(2)	2.065(5)
Co(1)-N(1)	2.192(5)
Co(1)-Cl(1)	2.2675(19)
N(1)-C(23)	1.455(9)
N(1)-C(29)	1.460(9)
N(1)-C(1)	1.473(8)
N(2)-C(2)	1.339(8)

N(2)-C(6)	1.348(7)
N(3)-C(28)	1.341(9)
N(3)-C(24)	1.342(10)
N(4)-C(30)	1.335(8)
N(4)-C(34)	1.344(9)
C(1)-C(2)	1.504(9)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.375(9)
C(3)-C(4)	1.384(9)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(9)
C(4)-H(4)	0.9300
C(5)-C(6)	1.373(9)
C(5)-C(7)	1.494(9)
C(6)-H(6)	0.9300
C(7)-C(8)	1.382(9)
C(7)-C(20)	1.403(8)
C(8)-C(9)	1.377(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.386(9)
C(9)-H(9)	0.9300
C(10)-C(21)	1.422(9)
C(10)-C(11)	1.423(9)
C(11)-C(12)	1.336(10)
C(11)-H(11)	0.9300
C(12)-C(13)	1.427(11)
C(12)-H(12)	0.9300
C(13)-C(14)	1.396(11)
C(13)-C(22)	1.430(10)
C(14)-C(15)	1.344(13)
C(14)-H(14)	0.9300
C(15)-C(16)	1.384(13)
C(15)-H(15)	0.9300
C(16)-C(17)	1.400(10)
C(16)-H(16)	0.9300
C(17)-C(18)	1.411(10)
C(17)-C(22)	1.418(10)
C(18)-C(19)	1.353(9)

C(18)-H(18)	0.9300
C(19)-C(20)	1.430(9)
C(19)-H(19)	0.9300
C(20)-C(21)	1.424(9)
C(21)-C(22)	1.408(9)
C(23)-C(24)	1.483(11)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.378(12)
C(25)-C(26)	1.376(17)
C(25)-H(25)	0.9300
C(26)-C(27)	1.318(17)
C(26)-H(26)	0.9300
C(27)-C(28)	1.356(12)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300
C(29)-C(30)	1.469(10)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.391(10)
C(31)-C(32)	1.350(12)
C(31)-H(31)	0.9300
C(32)-C(33)	1.338(12)
C(32)-H(32)	0.9300
C(33)-C(34)	1.392(10)
C(33)-H(33)	0.9300
C(34)-H(34)	0.9300

N(4)-Co(1)-N(3)	117.1(2)
N(4)-Co(1)-N(2)	119.8(2)
N(3)-Co(1)-N(2)	109.3(2)
N(4)-Co(1)-N(1)	77.2(2)
N(3)-Co(1)-N(1)	77.2(2)
N(2)-Co(1)-N(1)	77.99(19)
N(4)-Co(1)-Cl(1)	102.10(16)
N(3)-Co(1)-Cl(1)	100.48(19)
N(2)-Co(1)-Cl(1)	104.98(15)
N(1)-Co(1)-Cl(1)	176.79(15)
C(23)-N(1)-C(29)	111.4(6)

C(23)-N(1)-C(1)	111.4(5)
C(29)-N(1)-C(1)	113.4(6)
C(23)-N(1)-Co(1)	105.9(4)
C(29)-N(1)-Co(1)	106.3(4)
C(1)-N(1)-Co(1)	108.0(4)
C(2)-N(2)-C(6)	118.4(5)
C(2)-N(2)-Co(1)	117.6(4)
C(6)-N(2)-Co(1)	124.0(4)
C(28)-N(3)-C(24)	119.9(7)
C(28)-N(3)-Co(1)	123.3(6)
C(24)-N(3)-Co(1)	116.7(5)
C(30)-N(4)-C(34)	117.9(6)
C(30)-N(4)-Co(1)	118.1(4)
C(34)-N(4)-Co(1)	124.0(5)
N(1)-C(1)-C(2)	110.4(5)
N(1)-C(1)-H(1A)	109.6
C(2)-C(1)-H(1A)	109.6
N(1)-C(1)-H(1B)	109.6
C(2)-C(1)-H(1B)	109.6
H(1A)-C(1)-H(1B)	108.1
N(2)-C(2)-C(3)	121.3(6)
N(2)-C(2)-C(1)	116.0(5)
C(3)-C(2)-C(1)	122.7(6)
C(2)-C(3)-C(4)	119.6(6)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	119.8(6)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(6)-C(5)-C(4)	117.0(6)
C(6)-C(5)-C(7)	120.4(6)
C(4)-C(5)-C(7)	122.4(6)
N(2)-C(6)-C(5)	123.8(6)
N(2)-C(6)-H(6)	118.1
C(5)-C(6)-H(6)	118.1
C(8)-C(7)-C(20)	119.2(6)
C(8)-C(7)-C(5)	118.3(6)
C(20)-C(7)-C(5)	122.5(6)
C(9)-C(8)-C(7)	122.5(6)

C(9)-C(8)-H(8)	118.7
C(7)-C(8)-H(8)	118.7
C(8)-C(9)-C(10)	120.1(6)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(9)-C(10)-C(21)	119.1(6)
C(9)-C(10)-C(11)	121.8(6)
C(21)-C(10)-C(11)	119.1(6)
C(12)-C(11)-C(10)	121.9(7)
C(12)-C(11)-H(11)	119.0
C(10)-C(11)-H(11)	119.0
C(11)-C(12)-C(13)	120.7(7)
C(11)-C(12)-H(12)	119.7
C(13)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	122.3(8)
C(14)-C(13)-C(22)	118.6(8)
C(12)-C(13)-C(22)	119.1(6)
C(15)-C(14)-C(13)	120.8(9)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(14)-C(15)-C(16)	121.9(8)
C(14)-C(15)-H(15)	119.0
C(16)-C(15)-H(15)	119.0
C(15)-C(16)-C(17)	120.7(9)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	123.6(8)
C(16)-C(17)-C(22)	117.9(8)
C(18)-C(17)-C(22)	118.6(6)
C(19)-C(18)-C(17)	121.7(7)
C(19)-C(18)-H(18)	119.2
C(17)-C(18)-H(18)	119.2
C(18)-C(19)-C(20)	121.6(7)
C(18)-C(19)-H(19)	119.2
C(20)-C(19)-H(19)	119.2
C(7)-C(20)-C(21)	118.9(6)
C(7)-C(20)-C(19)	123.7(6)
C(21)-C(20)-C(19)	117.4(6)
C(22)-C(21)-C(10)	119.3(6)

C(22)-C(21)-C(20)	120.7(6)
C(10)-C(21)-C(20)	120.0(5)
C(21)-C(22)-C(17)	120.0(6)
C(21)-C(22)-C(13)	119.8(6)
C(17)-C(22)-C(13)	120.1(6)
N(1)-C(23)-C(24)	109.8(6)
N(1)-C(23)-H(23A)	109.7
C(24)-C(23)-H(23A)	109.7
N(1)-C(23)-H(23B)	109.7
C(24)-C(23)-H(23B)	109.7
H(23A)-C(23)-H(23B)	108.2
N(3)-C(24)-C(25)	119.4(9)
N(3)-C(24)-C(23)	115.5(6)
C(25)-C(24)-C(23)	125.0(9)
C(26)-C(25)-C(24)	119.0(11)
C(26)-C(25)-H(25)	120.5
C(24)-C(25)-H(25)	120.5
C(27)-C(26)-C(25)	120.6(10)
C(27)-C(26)-H(26)	119.7
C(25)-C(26)-H(26)	119.7
C(26)-C(27)-C(28)	119.6(11)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
N(3)-C(28)-C(27)	121.4(9)
N(3)-C(28)-H(28)	119.3
C(27)-C(28)-H(28)	119.3
N(1)-C(29)-C(30)	111.4(6)
N(1)-C(29)-H(29A)	109.3
C(30)-C(29)-H(29A)	109.3
N(1)-C(29)-H(29B)	109.3
C(30)-C(29)-H(29B)	109.3
H(29A)-C(29)-H(29B)	108.0
N(4)-C(30)-C(31)	121.4(7)
N(4)-C(30)-C(29)	114.8(6)
C(31)-C(30)-C(29)	123.8(7)
C(32)-C(31)-C(30)	119.7(8)
C(32)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(33)-C(32)-C(31)	119.9(7)

C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(32)-C(33)-C(34)	119.1(8)
C(32)-C(33)-H(33)	120.5
C(34)-C(33)-H(33)	120.5
N(4)-C(34)-C(33)	122.0(7)
N(4)-C(34)-H(34)	119.0
C(33)-C(34)-H(34)	119.0

3. NMR and ESI-MS Characterizations

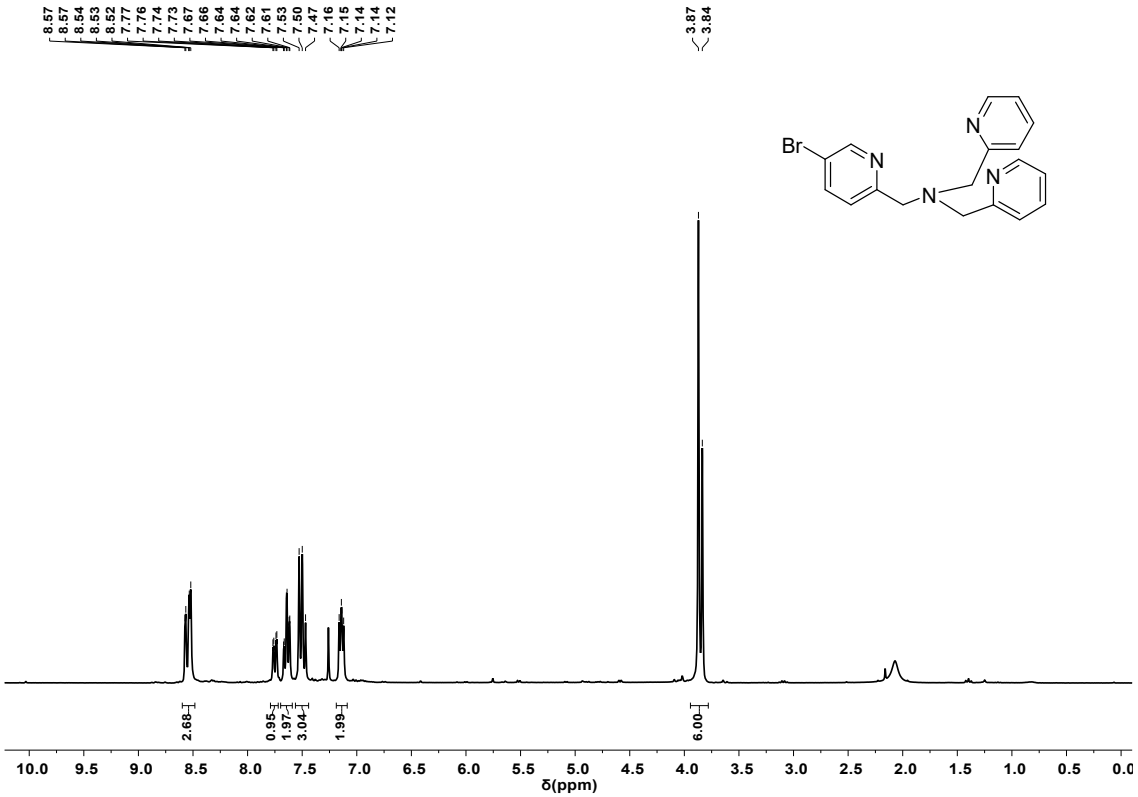


Figure S2 ^{1}H-NMR spectrum (300 MHz, 301 K, $CDCl_3$) of **6b**.

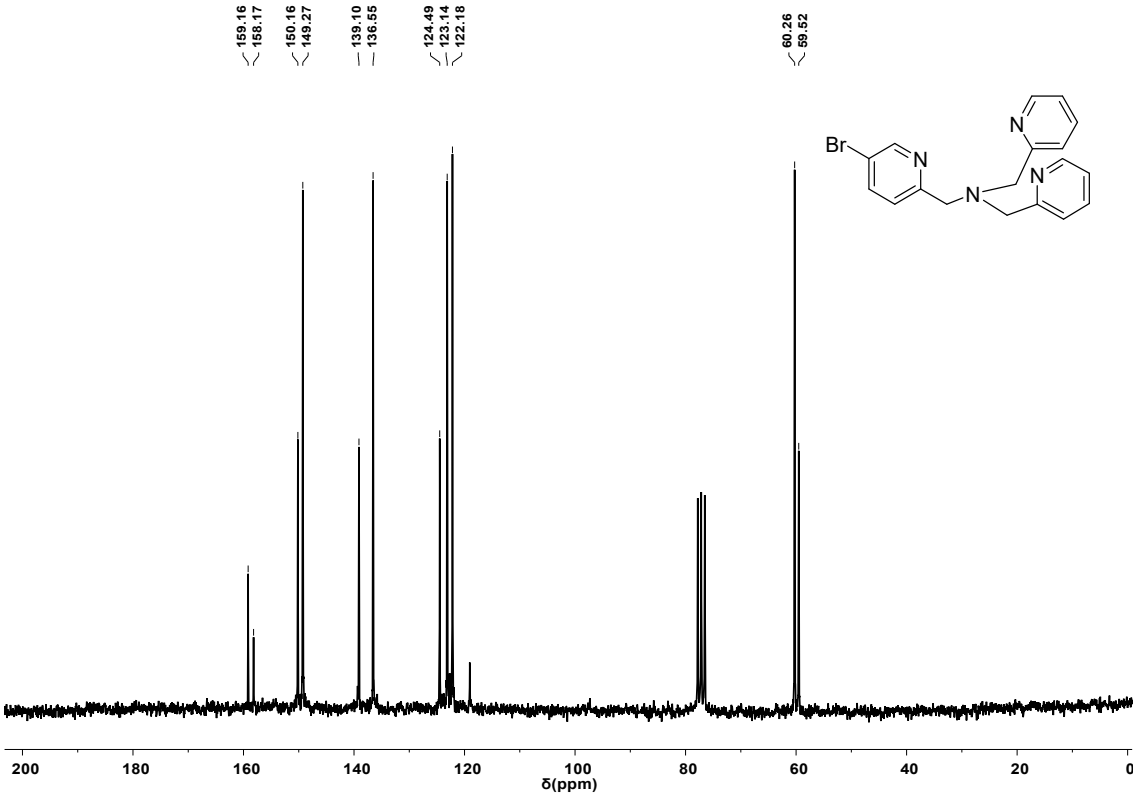


Figure S3 ^{13}C-NMR spectrum (300 MHz, 301 K, $CDCl_3$) of **6b**.

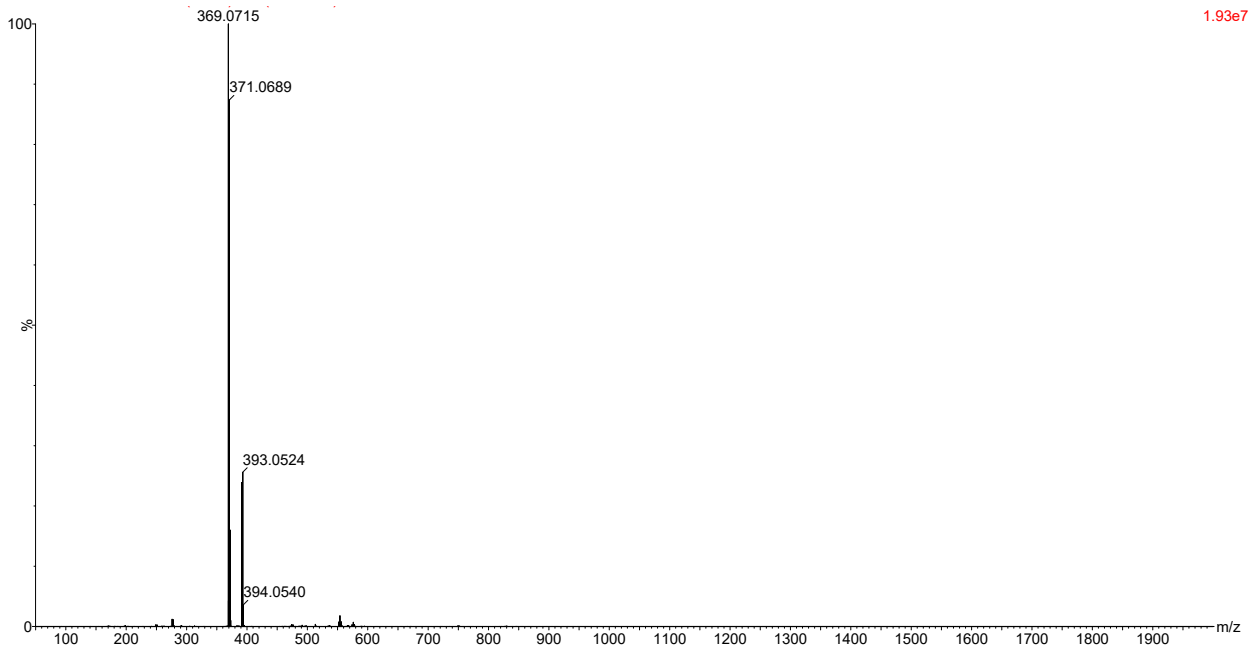


Figure S4 HRMS (ESI-TOF) spectrum of **6b**.

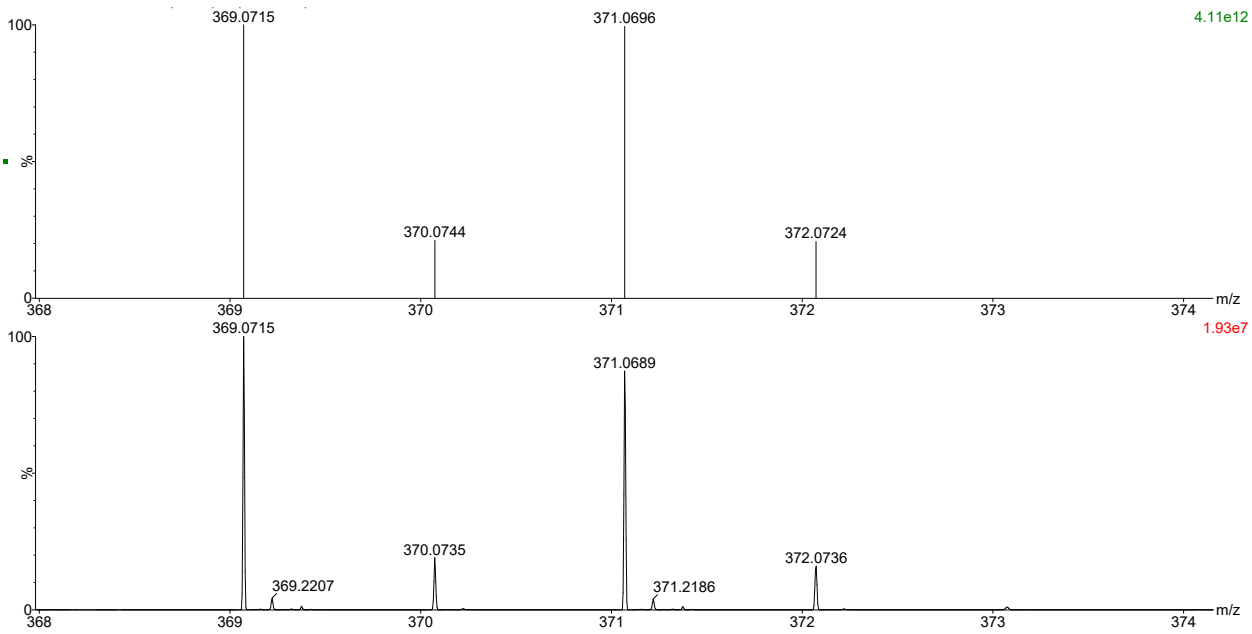


Figure S5 Experimental (bottom) and calculated (top) isotopic distribution in the HRMS (ESI-TOF) spectrum of **6b** corresponding to $[C_{18}H_{17}BrN_4+H]^+$.

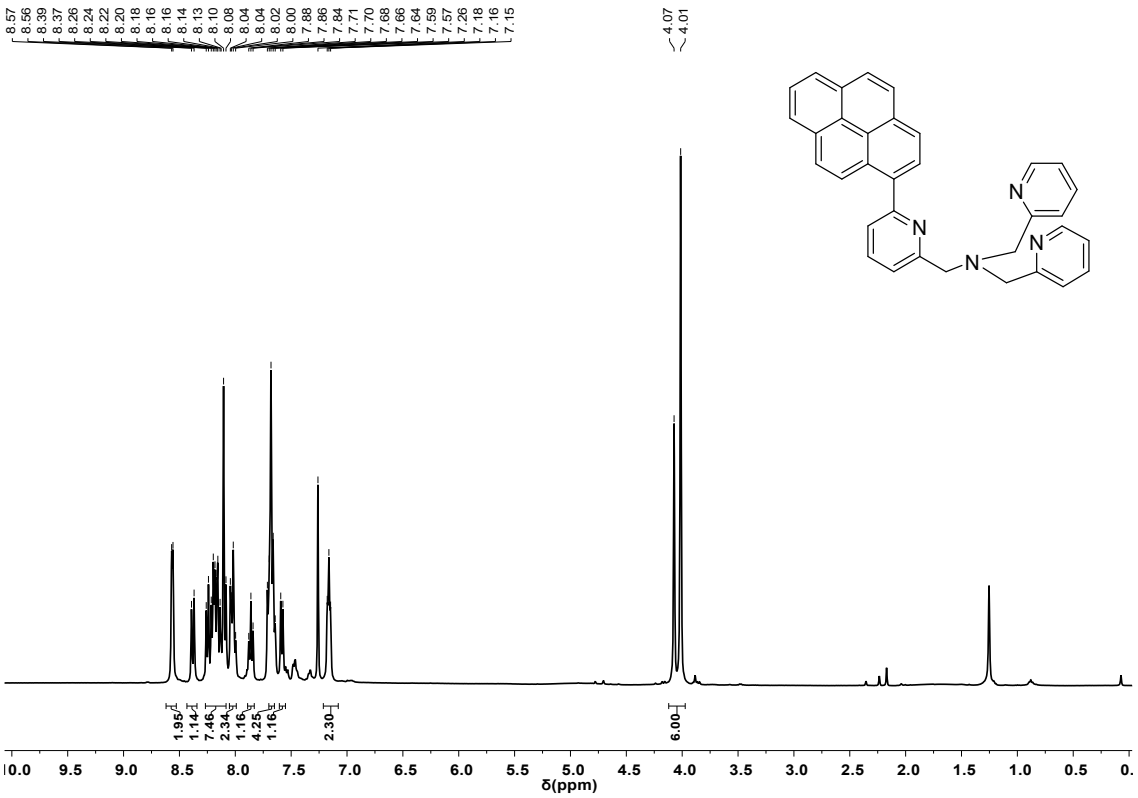


Figure S6. ^{1}H-NMR spectrum (400 MHz, 301 K, $CDCl_3$) of **8a**.

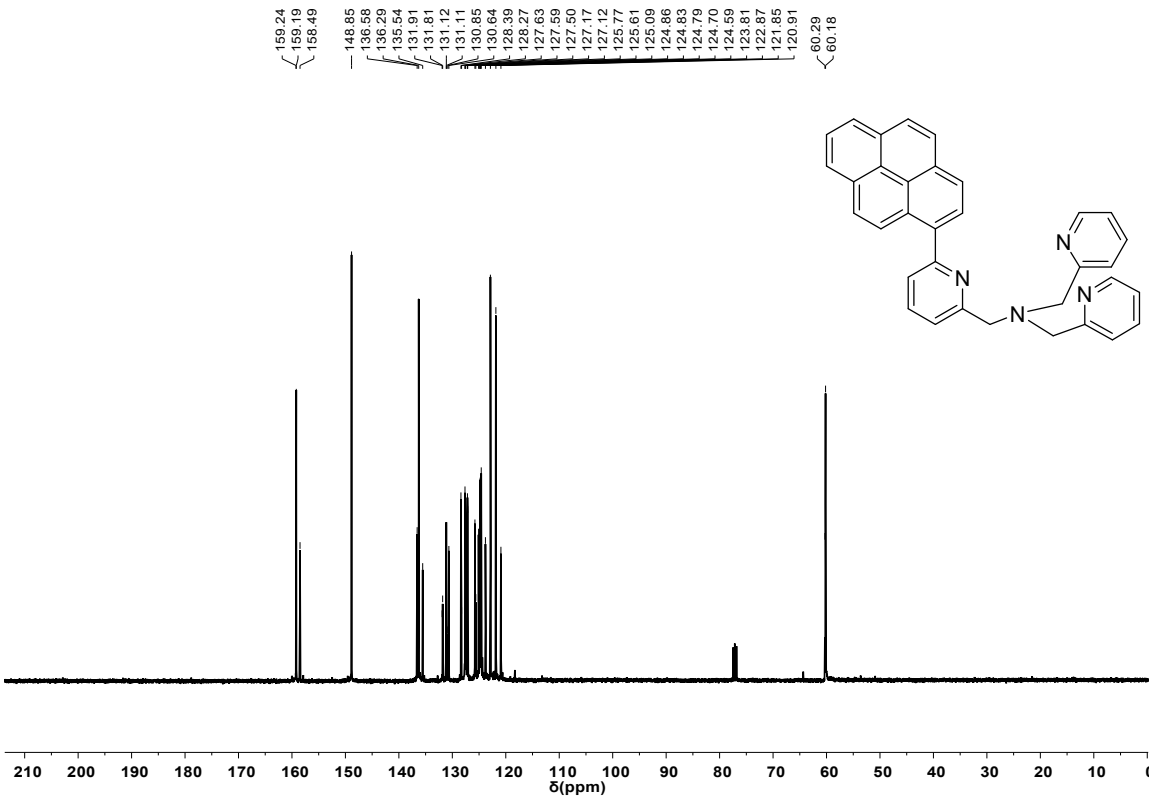


Figure S7. ^{13}C-NMR spectrum (400 MHz, 301 K, $CDCl_3$) of **8a**.

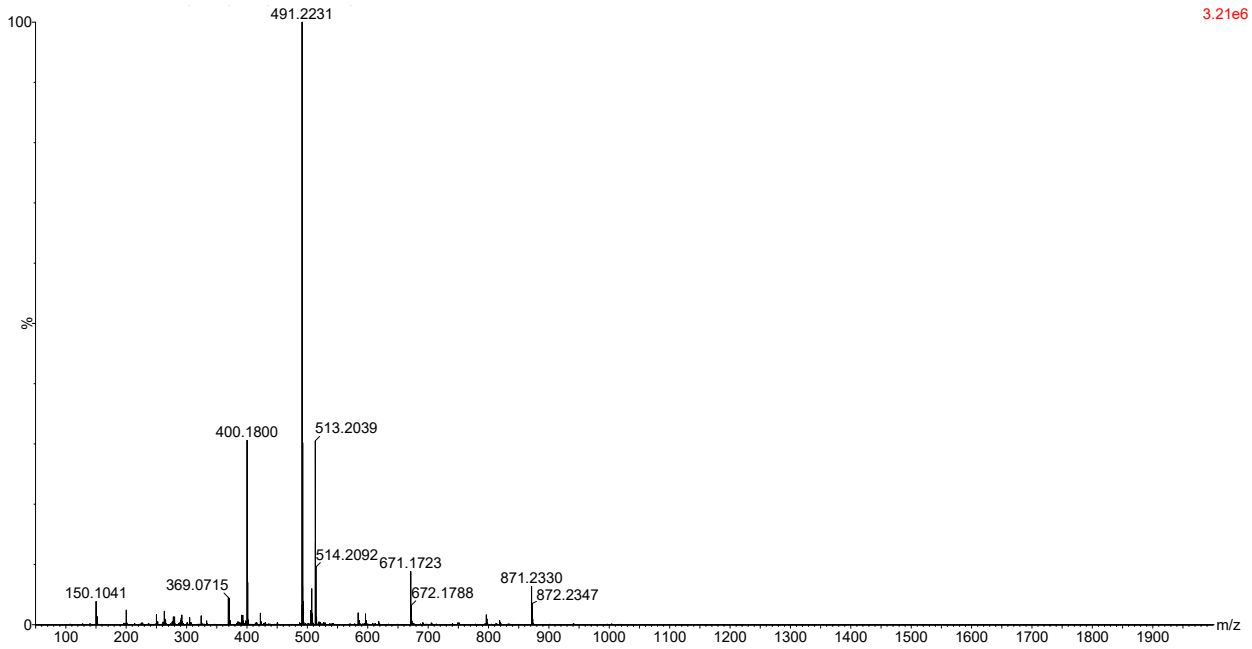


Figure S8. HRMS (ESI-TOF) spectrum of **8a**.

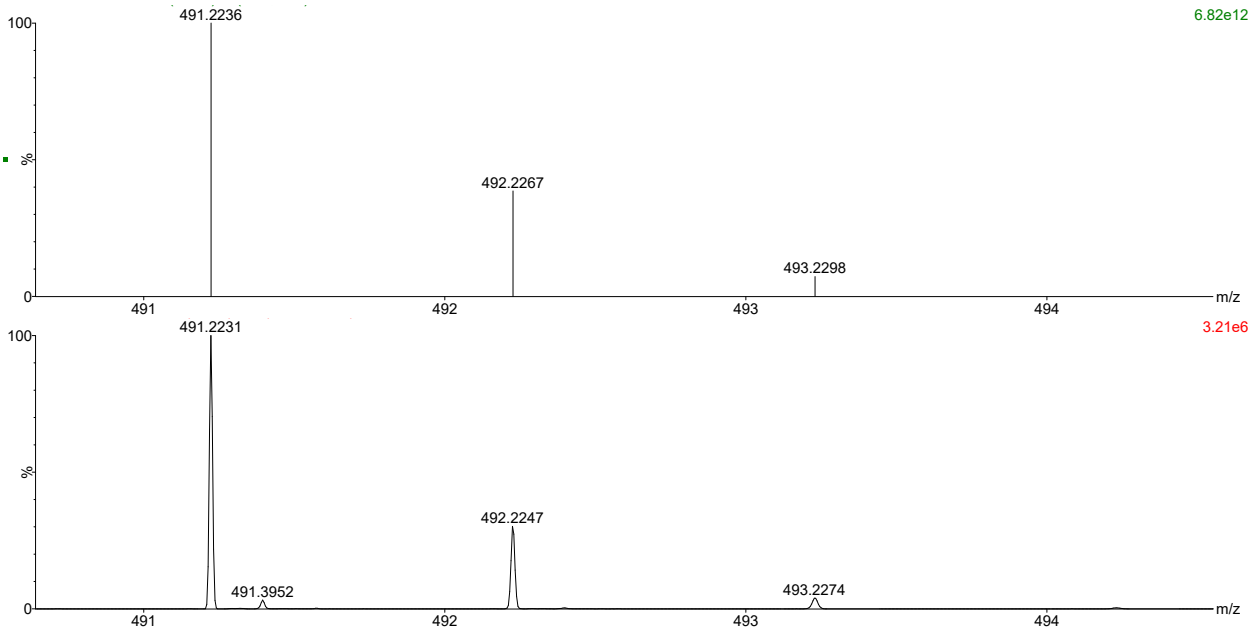


Figure S9. Experimental (bottom) and calculated (top) isotopic distribution in the HRMS (ESI-TOF) spectrum of **8a** corresponding to $[C_{34}H_{26}N_4+H]^+$.

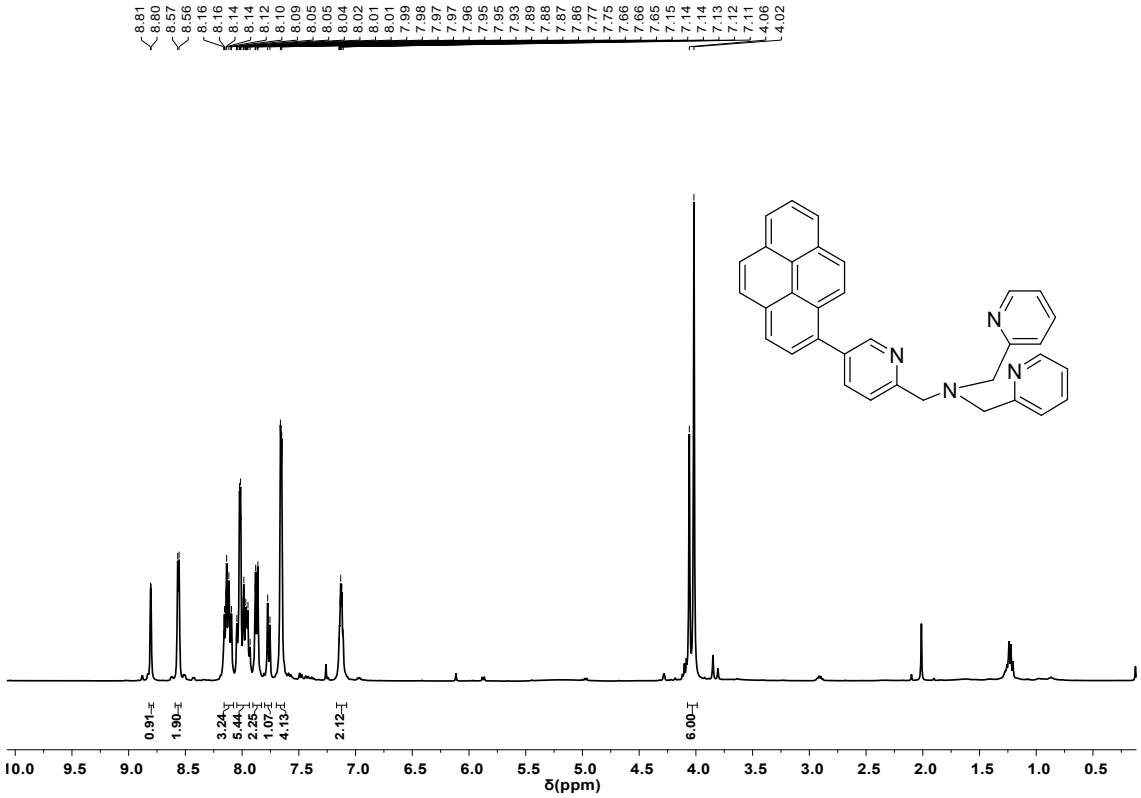


Figure S10. ^{1}H-NMR spectrum (400 MHz, 301 K, $CDCl_3$) of **8b**.

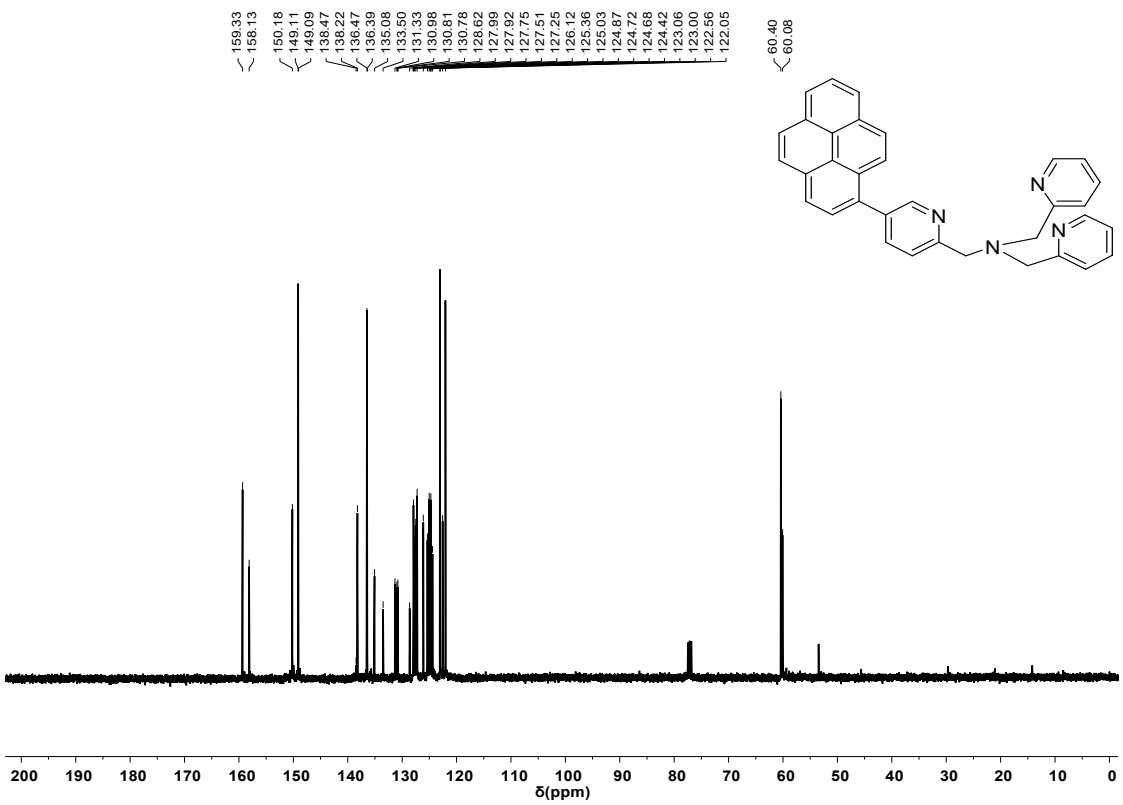


Figure S11. ^{13}C-NMR spectrum (400 MHz, 301 K, $CDCl_3$) of **8b**.

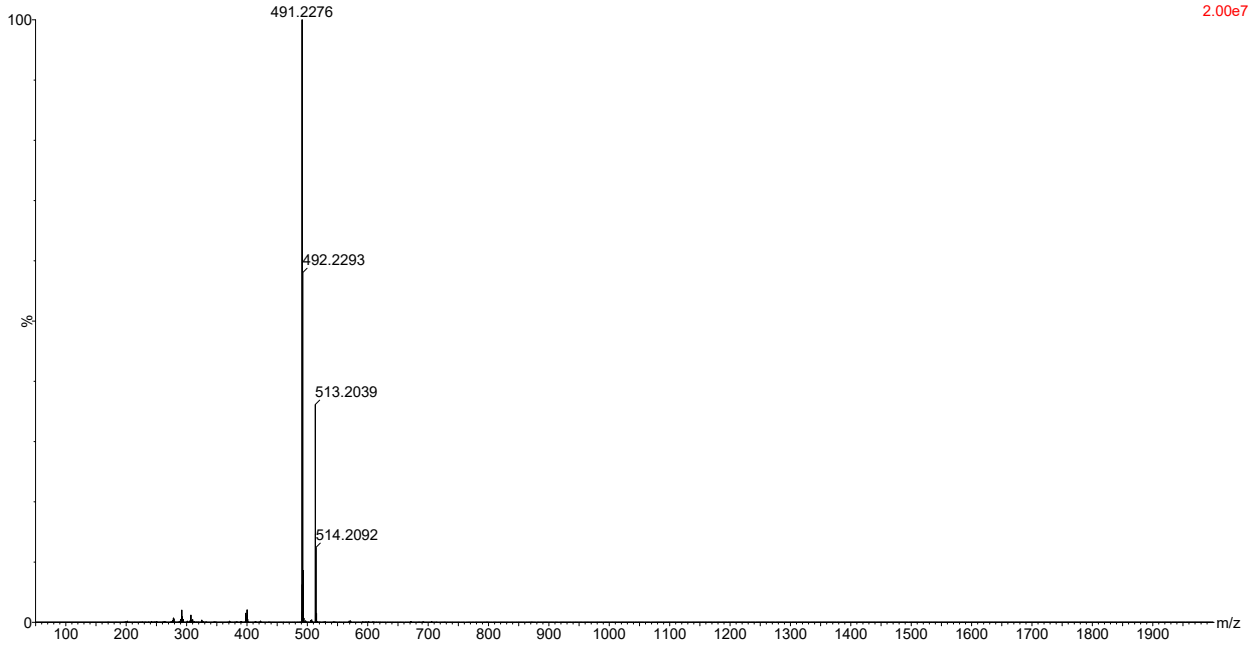


Figure S12. HRMS (ESI-TOF) spectrum of **8b**.

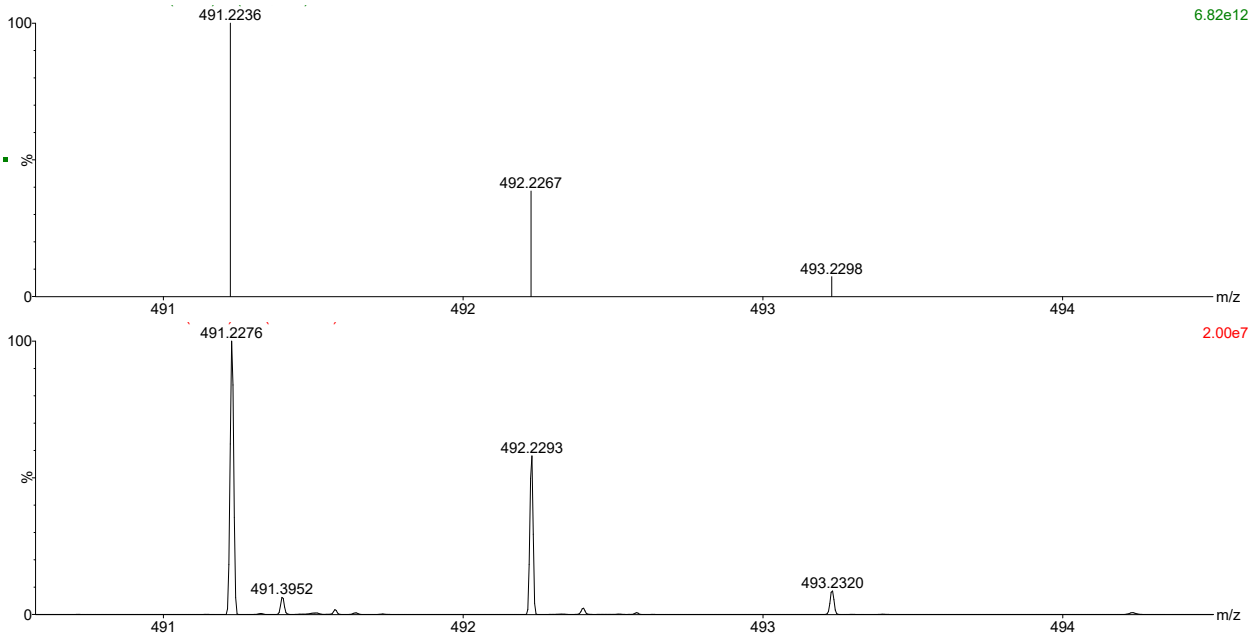


Figure S13. Experimental (bottom) and calculated (top) isotopic distribution in the HRMS (ESI-TOF) spectrum of **8b** corresponding to $[C_{34}H_{26}N_4+H]^+$.

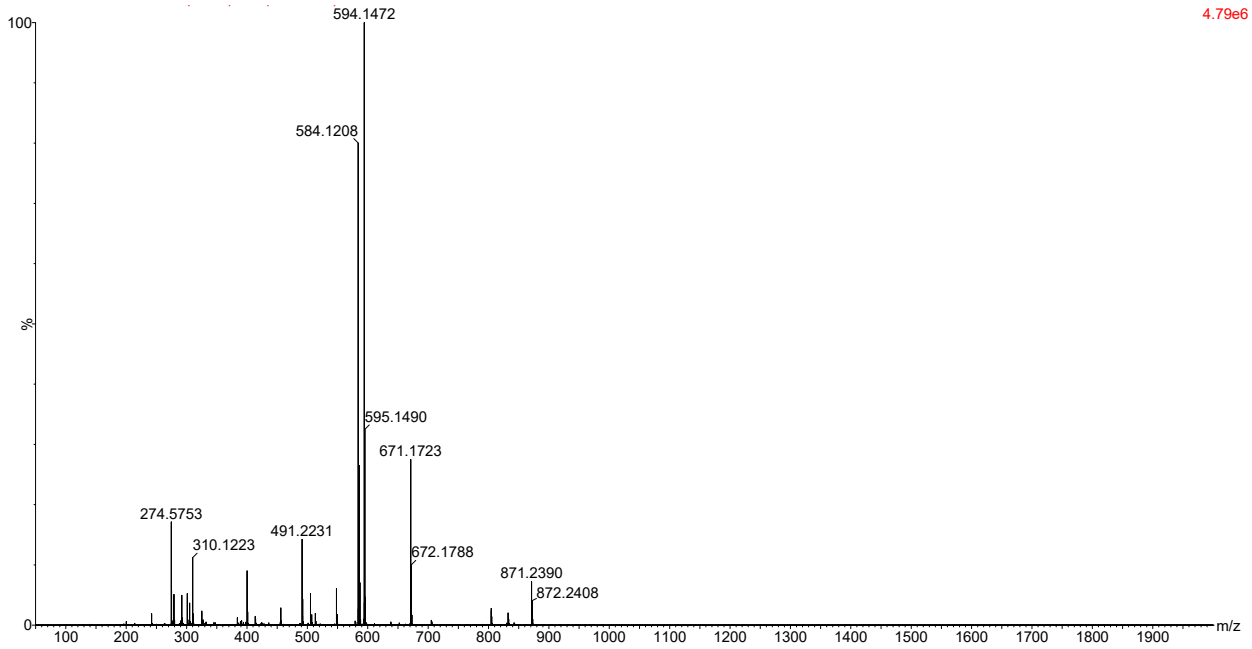


Figure S14. HRMS (ESI-TOF) spectrum of **2**.

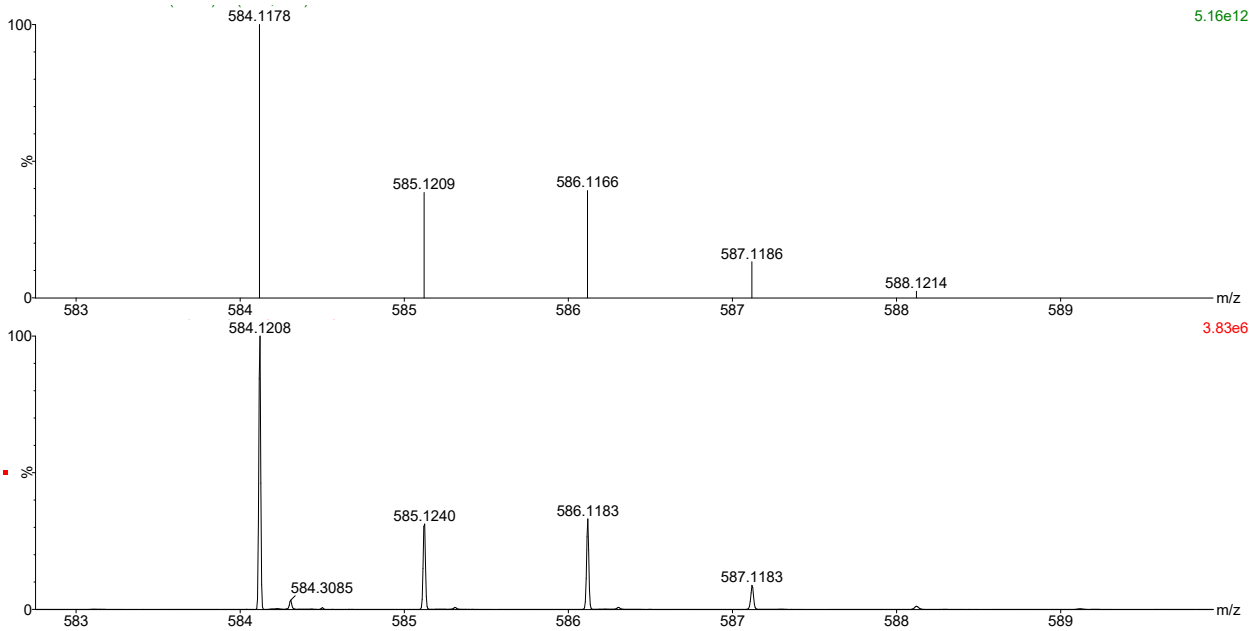


Figure S15. Experimental (bottom) and calculated (top) isotopic distribution in the HRMS (ESI-TOF) spectrum of **2** corresponding to $[C_{34}H_{26}CoN_4Cl]^+$.

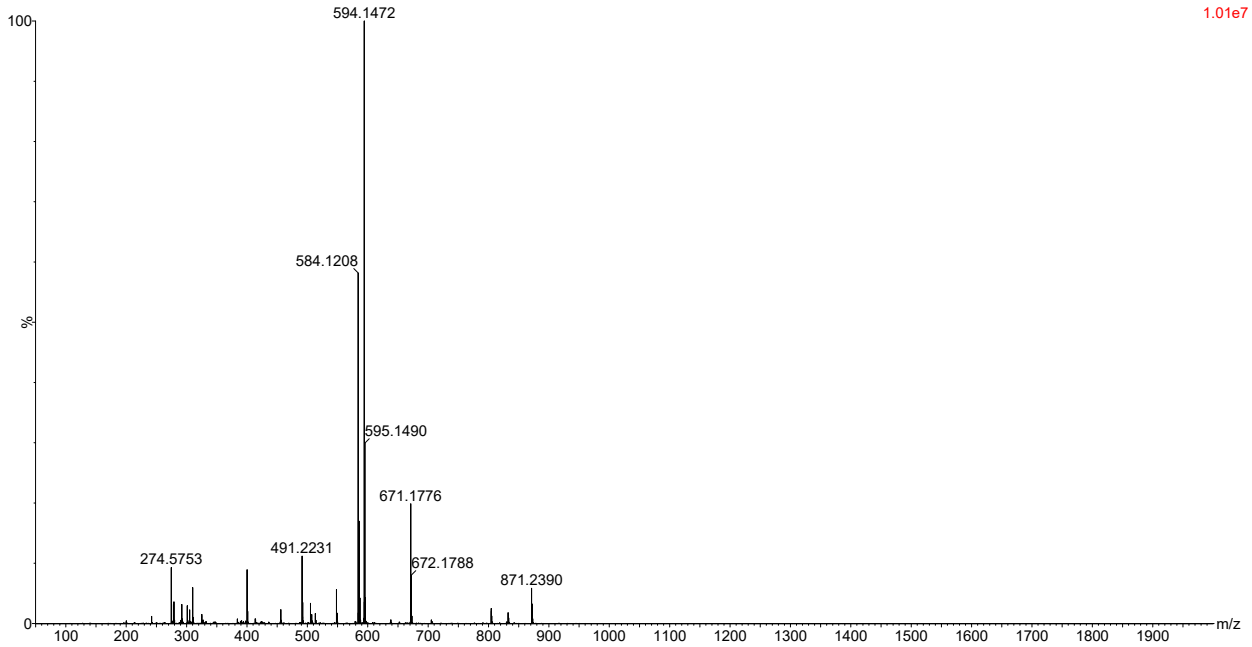


Figure S16. HRMS (ESI-TOF) spectrum of **3**.

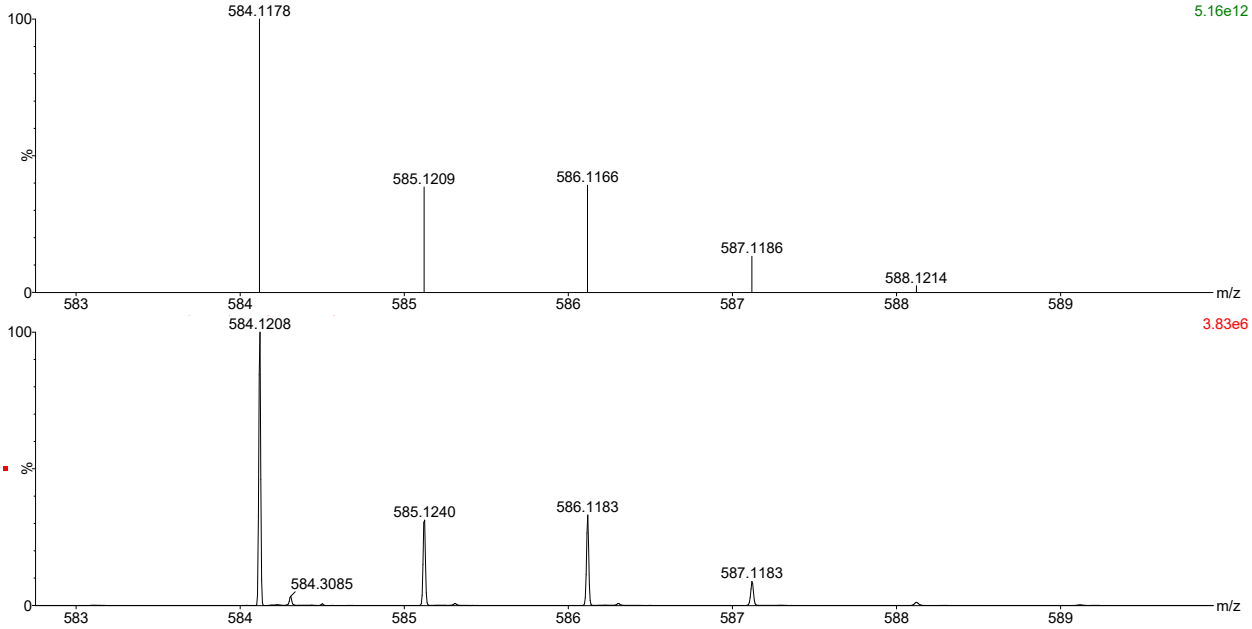


Figure S17. Experimental (bottom) and calculated (top) isotopic distribution in the HRMS (ESI-TOF) spectrum of **3** corresponding to $[C_{34}H_{26}CoN_4Cl]^+$.

4. Electrochemistry in acetonitrile

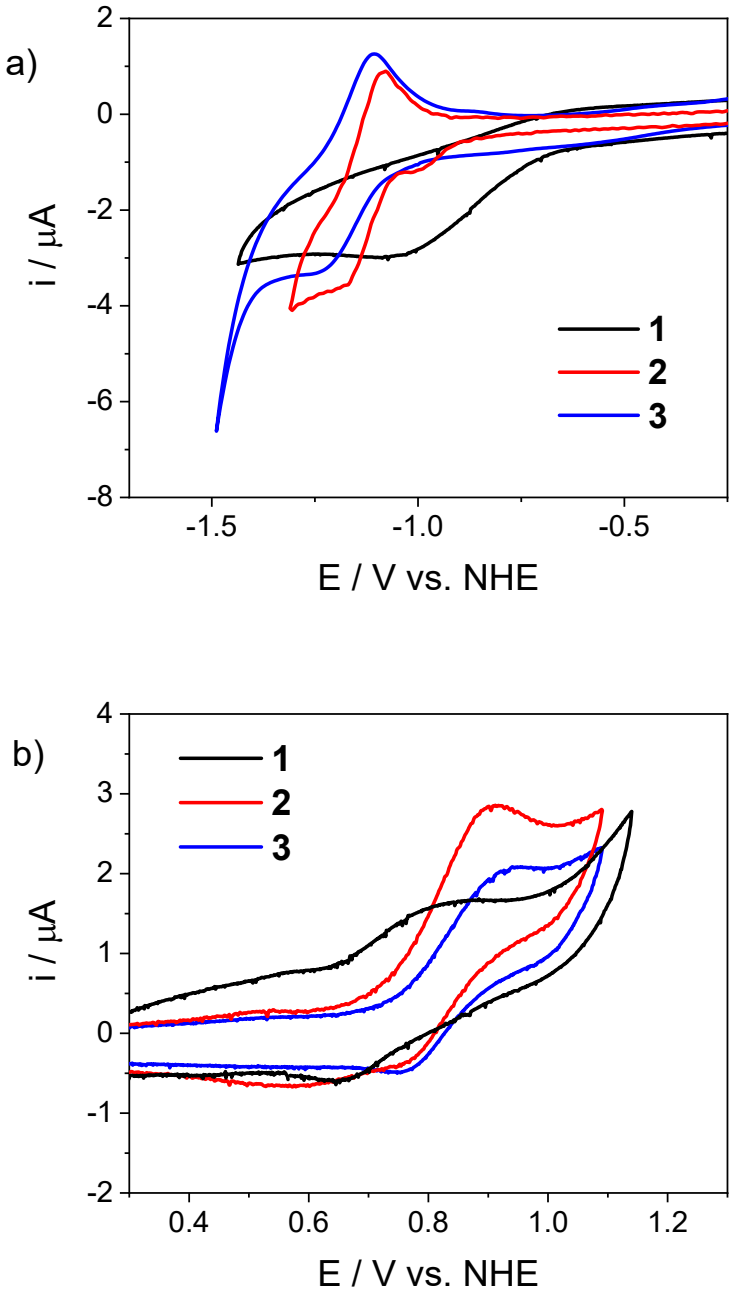


Figure S18. CVs (scan rate 0.1 V/s) of complexes **1-3** in nitrogen-purged acetonitrile (0.1 M $LiClO_4$).

5. Electrode characterization

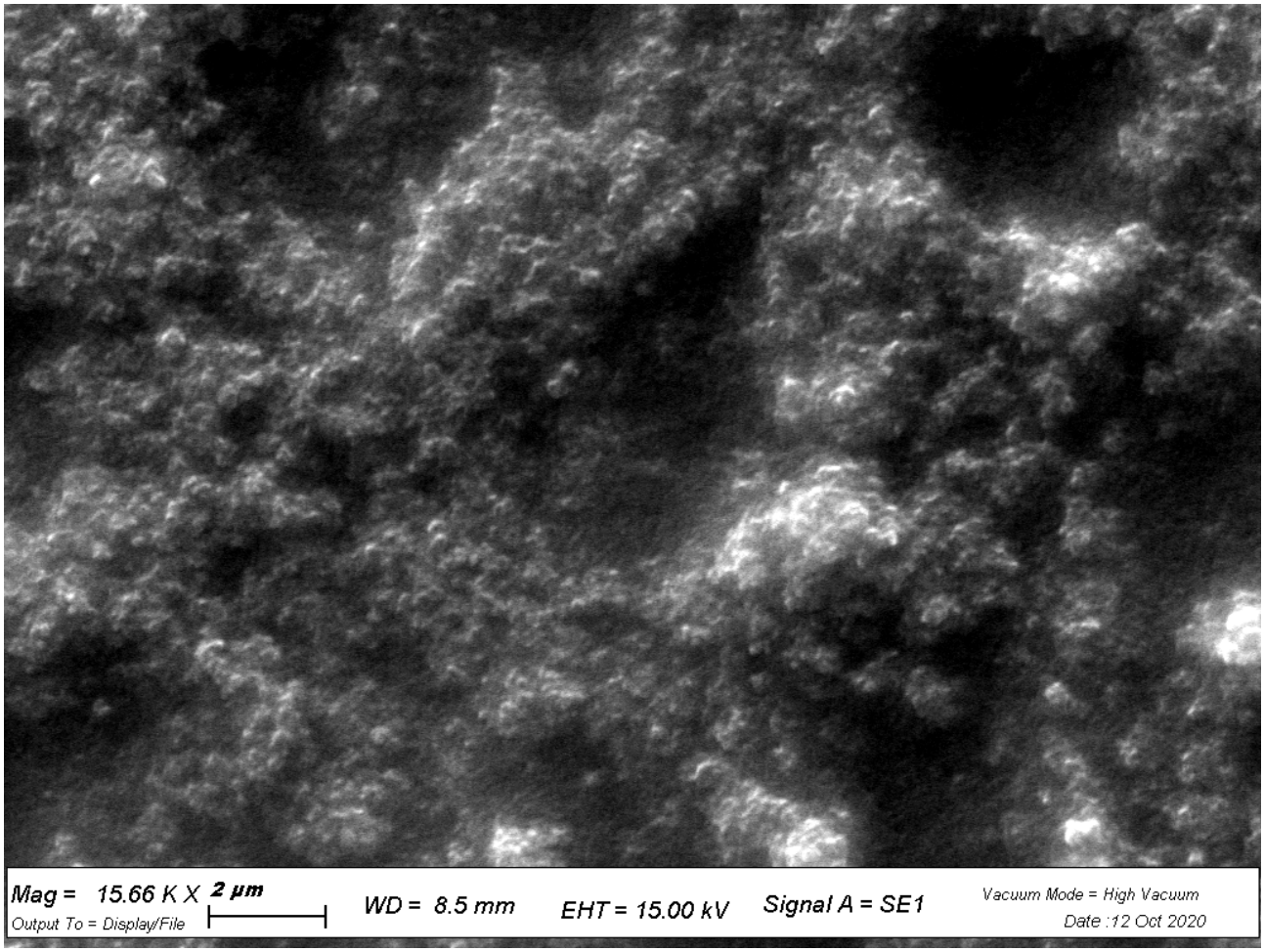
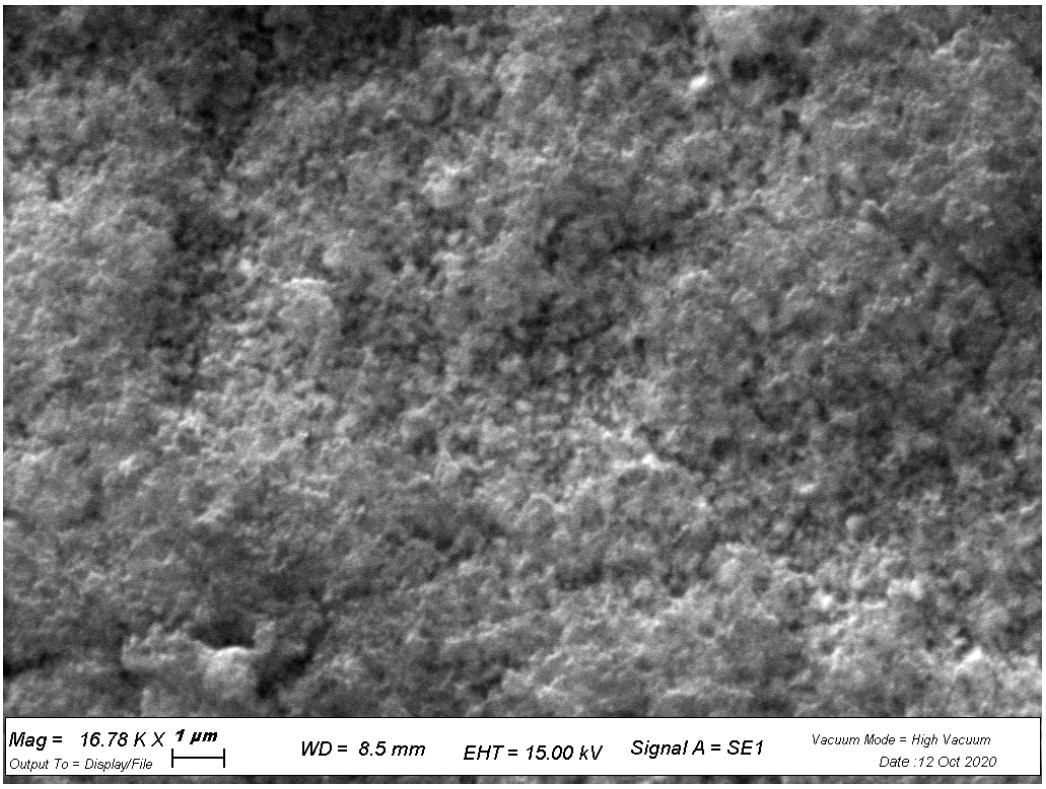


Figure S19. SEM micrograph of SWCNHs film onto FTO.

a)



b)

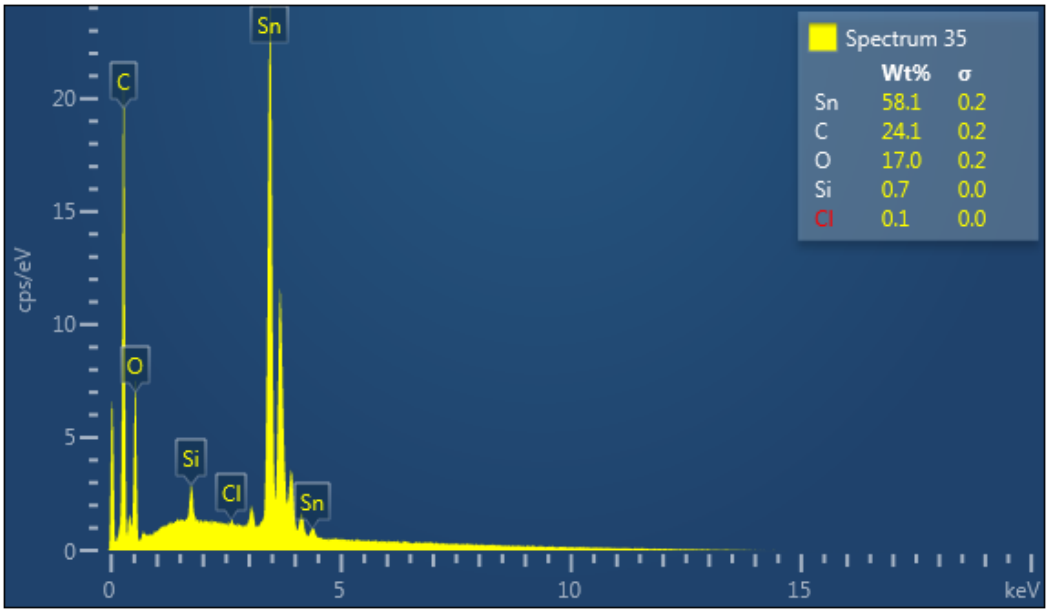


Figure S20. a) SEM micrograph and b) EDS analysis of SWCNHs-**1** onto FTO.

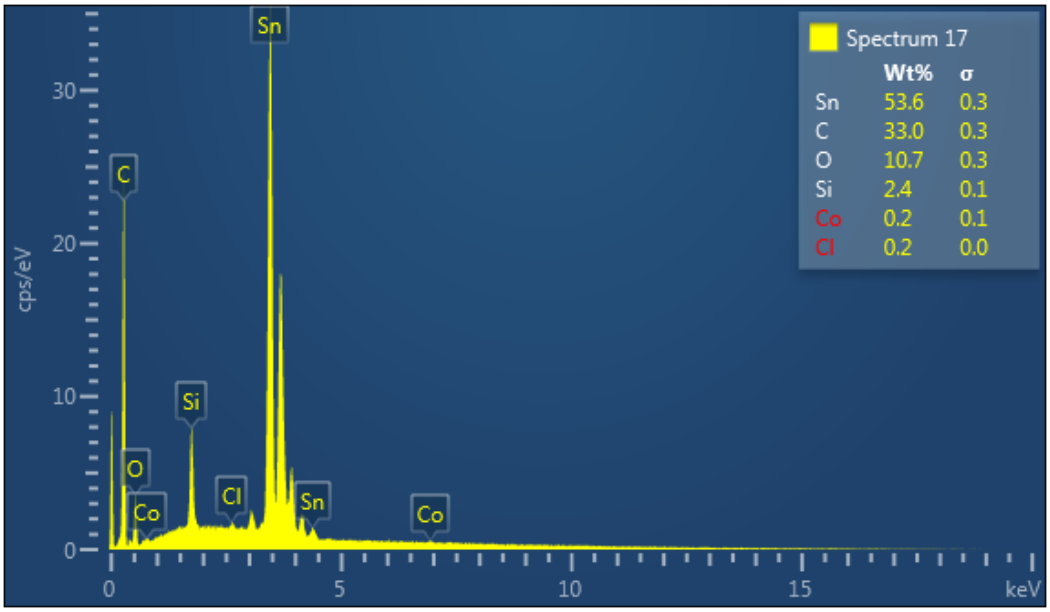
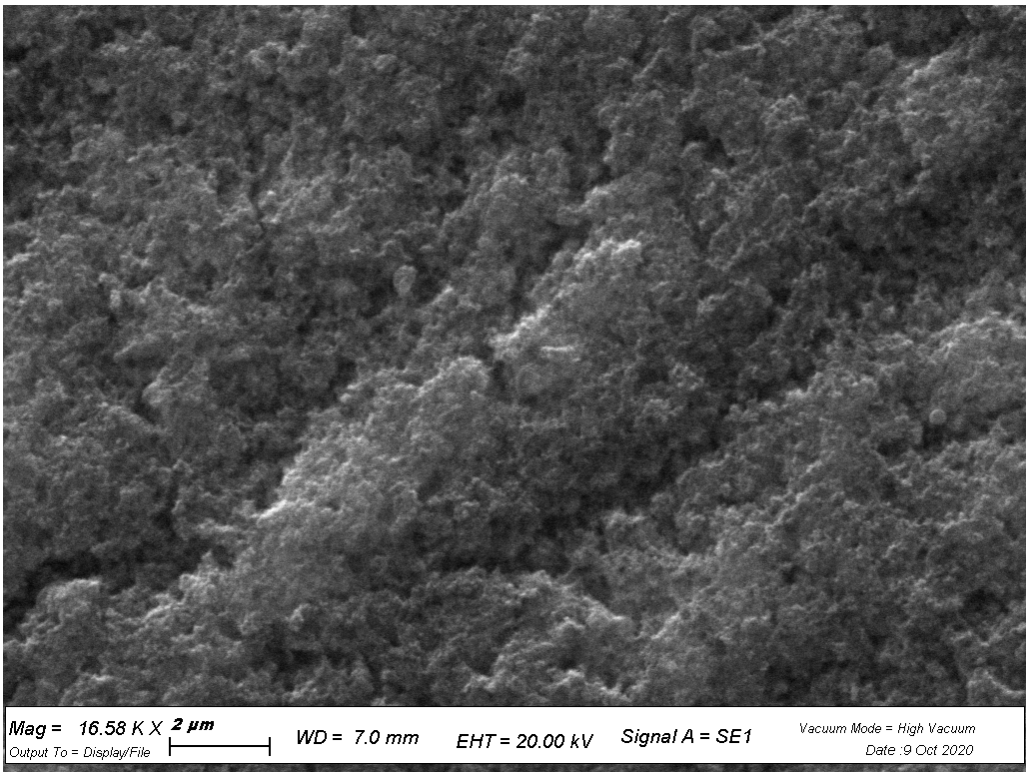


Figure S21. EDS analysis of SWCNHs-**2** onto FTO.

a)



b)

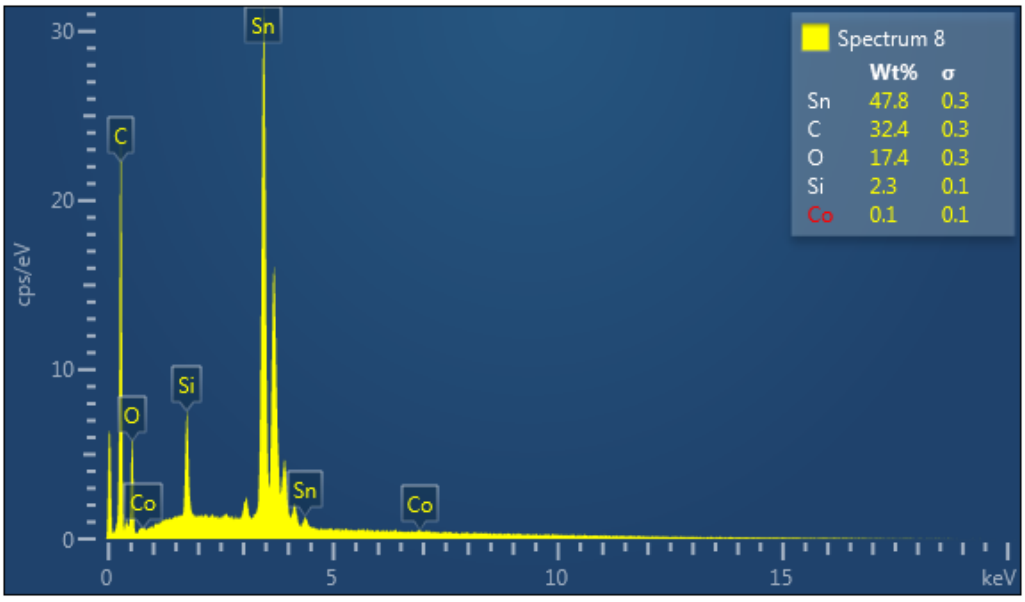


Figure S22. a) SEM micrograph and b) EDS analysis of SWCNHs-**3** onto FTO.

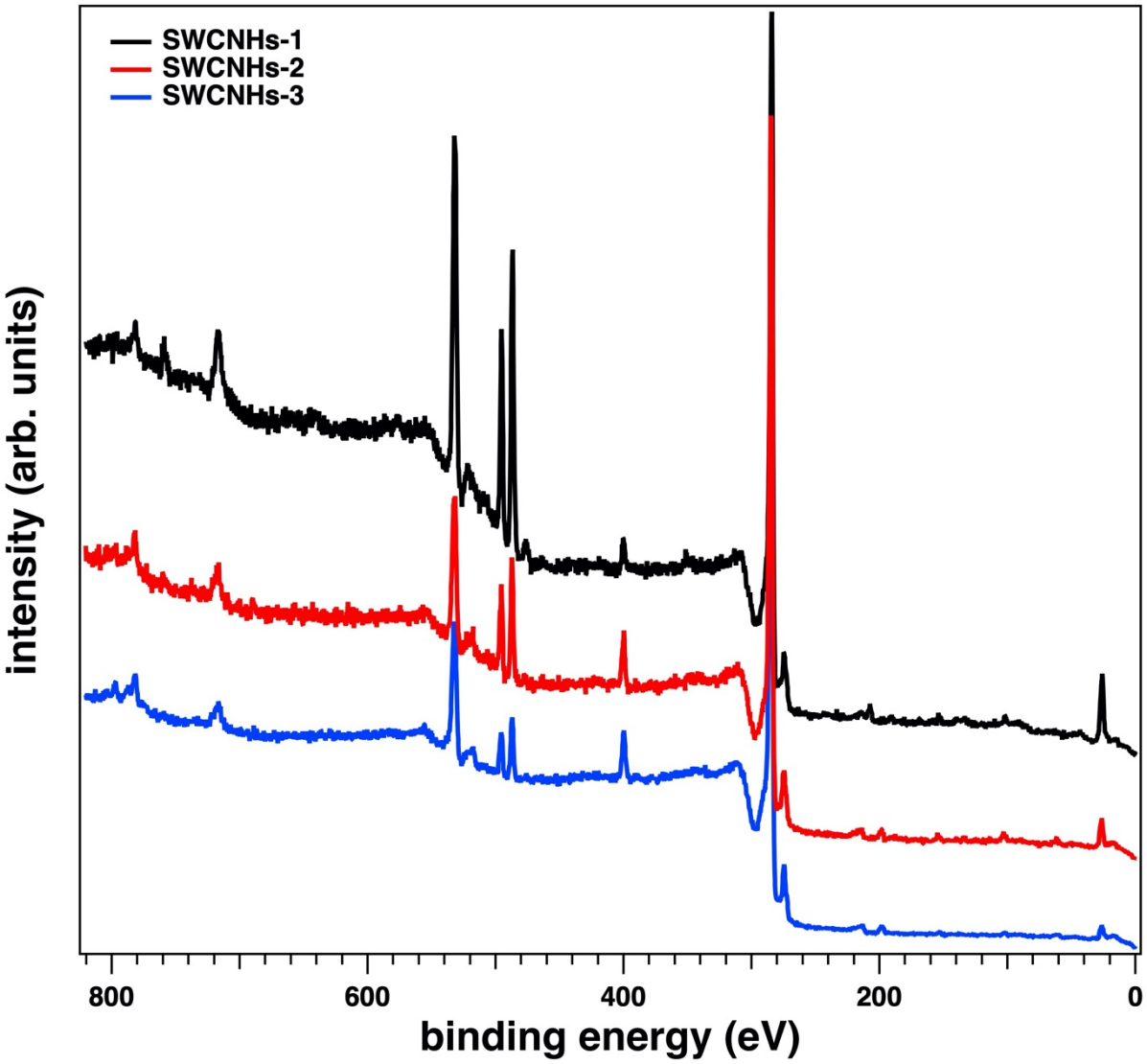


Figure S23. XPS survey spectra of the three different electrodes. (Al Kα, normal emission).

Table S4. Atomic fraction (at %) of C, Co, N in the samples. The data were obtained as the average of three measurements (systematic and statistical error ±0.5%), the Co/N ratio minimizes the systematic error, so the overall uncertainty is ±0.2%.

Atomic %	**1**	**2**	**3**
C	97.4	95.0	94.3
N	2.7	4.0	4.5
Co	0.6	1.0	1.2
Co/N	0.22	0.20	0.26

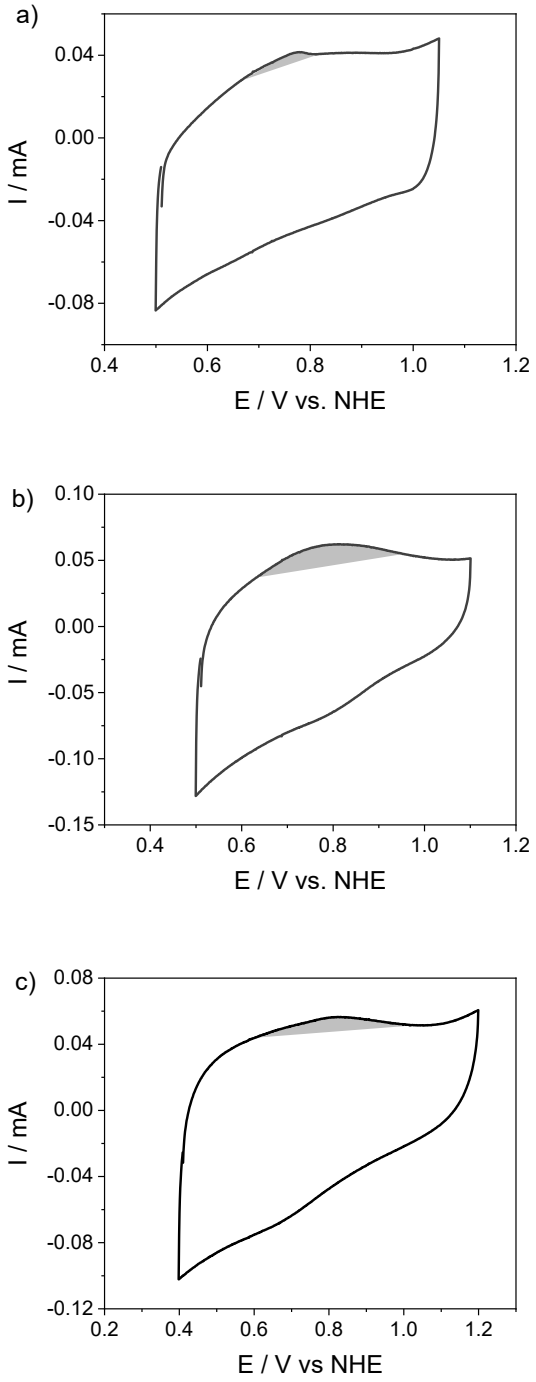


Figure S24. Representative CVs under anodic scan (scan rate of 0.01 V/s) of a) SWCNHs-**1,** b) SWCNHs-**2**, and c) SWCNHs-**3** in 1 M phosphate buffer (pH 7.4). The surface concentration (Γ) of the cobalt complex was estimated according to eq S1, where I = integrated anodic peak (grey area in the figures), F = faraday's constant, S = electrode surface area (1 cm^2), and v = scan rate. The results reported in the main article have been obtained as averages over four different samples.

$$\Gamma\left[mol \cdot cm^{-2}\right] = \frac{I\left[V \cdot Q \cdot s^{-1}\right]}{F\left[Q \cdot mol^{-1}\right] \cdot S\left[cm^2\right] \cdot v\left[V \cdot s^{-1}\right]} \quad \text{(S1)}$$

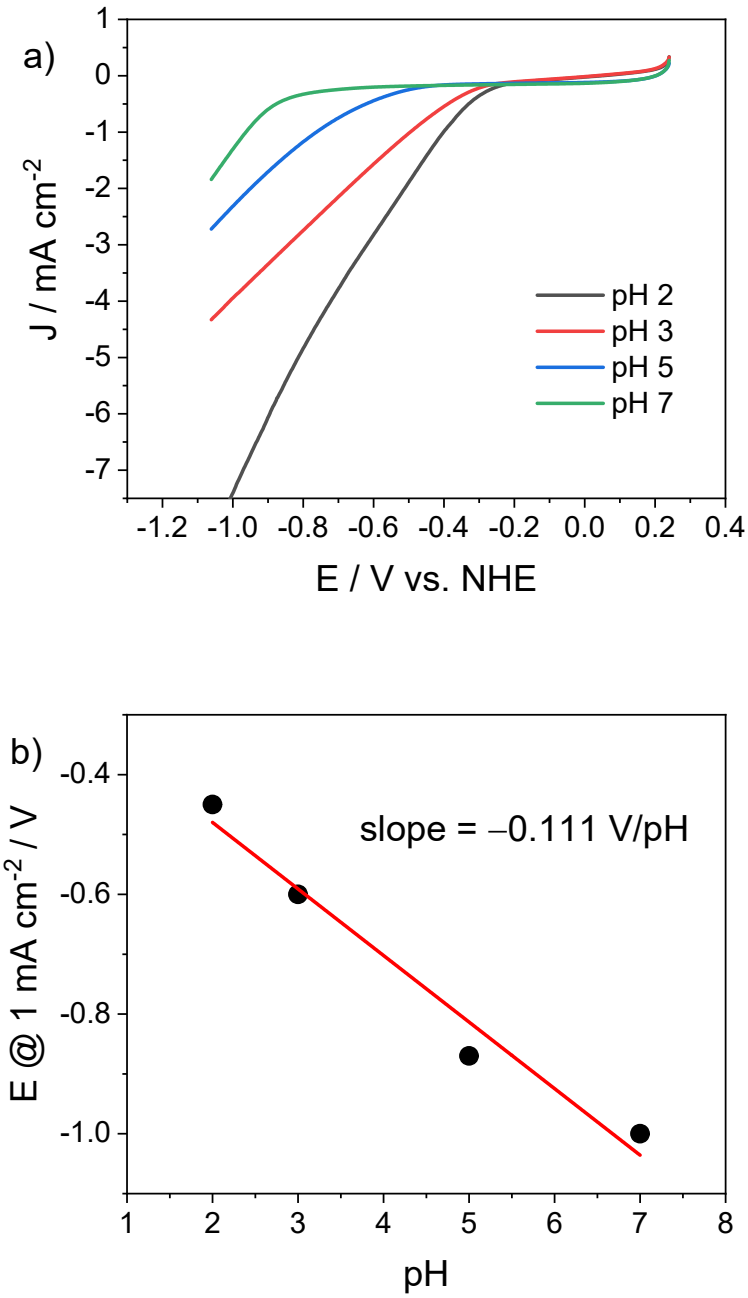


Figure S25. a) Linear sweep voltammetry (scan rate of 10 mV/s) of SWCNHs-**2** in 1 M Britton-Robinson buffer at different pH and b) plot of the potential at 1 mA·cm^{-2} vs. pH.

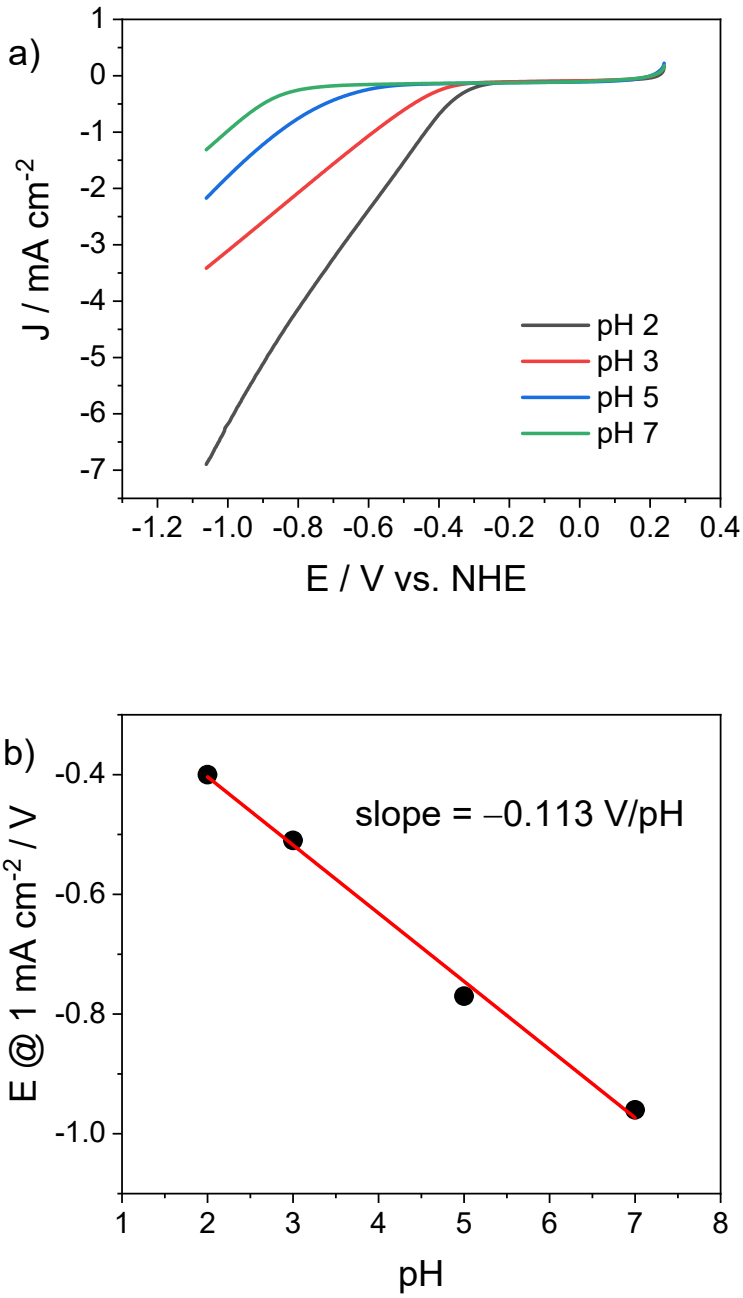


Figure S26. a) Linear sweep voltammetry (scan rate of 10 mV/s) of SWCNHs-**3** in 1 M Britton-Robinson buffer at different pH and b) plot of the potential at 1 mA·cm^{-2} vs. pH.

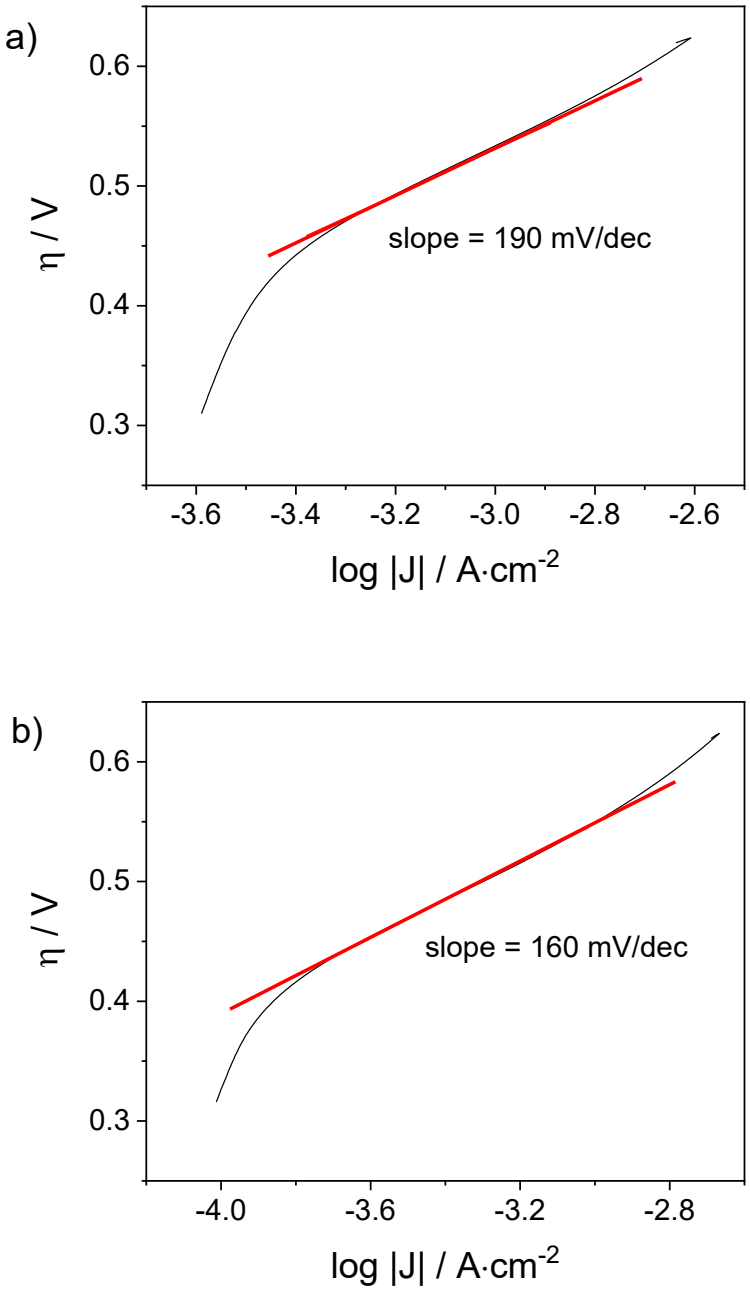


Figure S27. Tafel slope analyses of electrocatalytic HER in 1 M phosphate buffer at pH 7.4 by a) SWCNHs-**2** and SWCNHs-**3**.

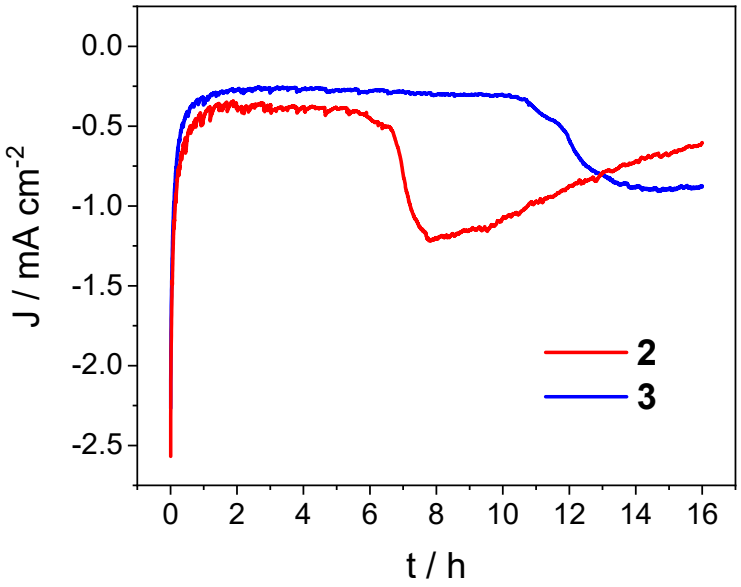


Figure S28. Chronoamperometry at −0.96 V vs. NHE of SWCNHs-**2** and SWCNHs-**3** electrodes (3.1 cm^2 surface area) in 1 M phosphate buffer at pH 7.4.

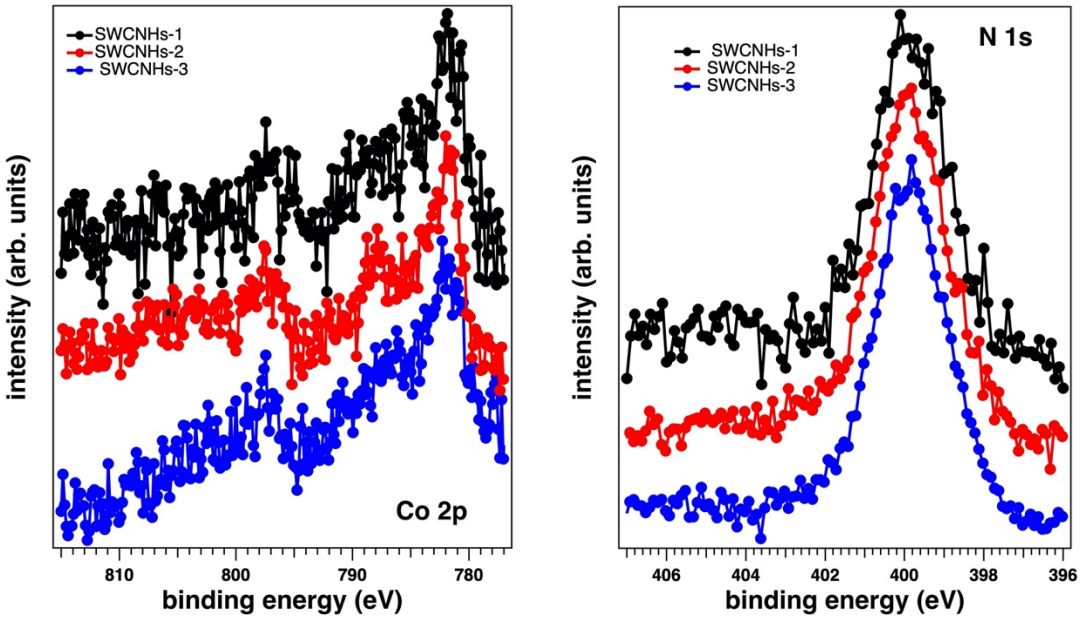


Figure S29. XPS Co 2p (left) e N 1s (right) after 1 h electrocatalysis.

Table S5. Atomic fraction (at %) of C, Co, N in the samples after 1 h electrolysis. The data were obtained as the average of three measurements (systematic and statistical error ±0.5%), the Co/N ratio minimizes the systematic error, so the overall uncertainty is ±0.2%.

Atomic %	**1**	**2**	**3**
C	92.6	92.9	93.6
N	6.3	6.4	5.2
Co	1.1	0.7	1.2
Co/N	0.17	0.11	0.23

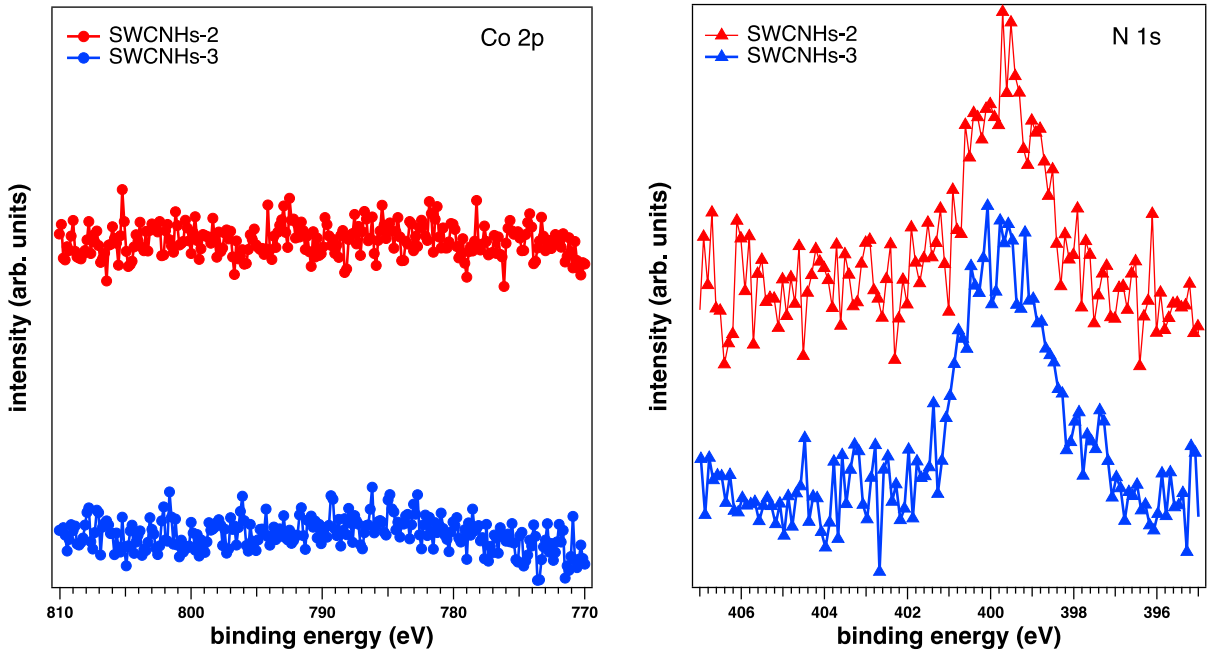


Figure S30. XPS Co 2p (left) e N 1s (right) after 6 h electrocatalysis.

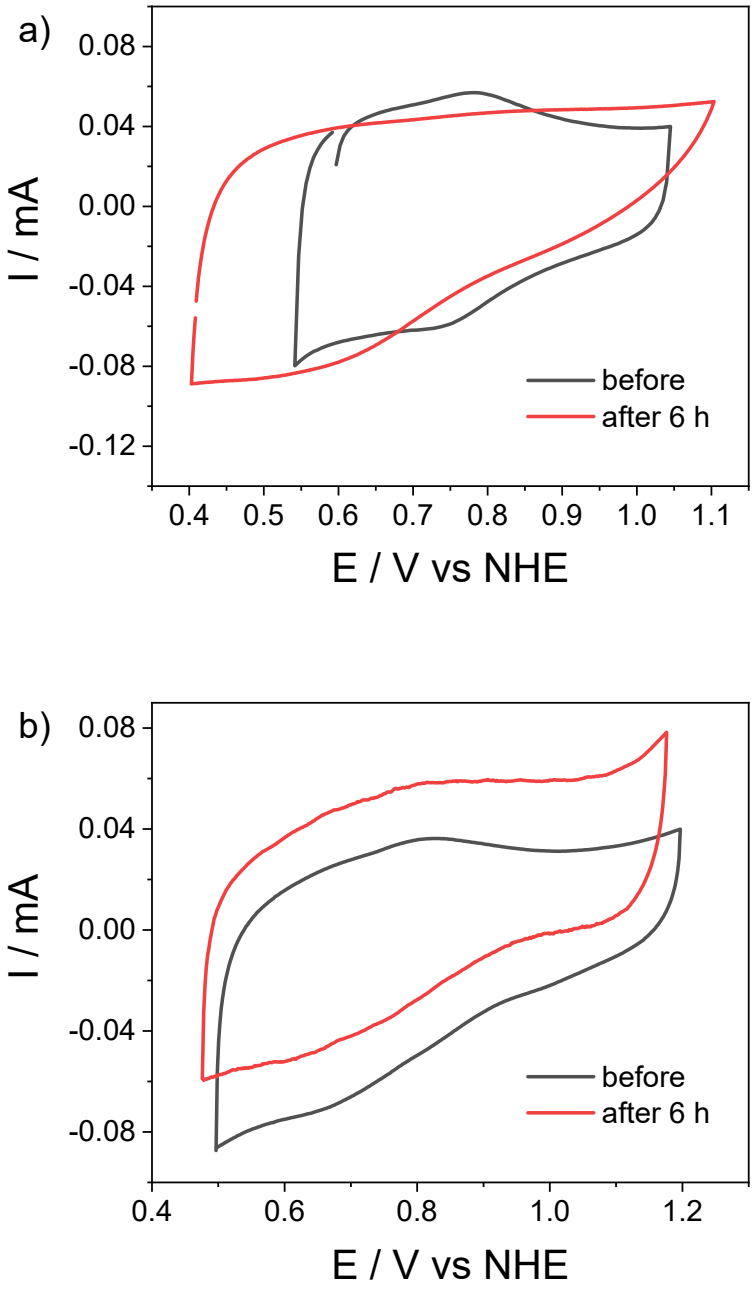


Figure S31. CVs under anodic scan (scan rate of 0.01 V/s) of a) SWCNHs-**2** and b) SWCNHs-**3** after 6 h electrolysis in 1 M phosphate buffer (pH 7.4). Complete disappearance of the cobalt oxidation process is observed for SWCNHs-**2**, whereas a weak signal (ca 5% of the initial value, from integration) persists in the case of SWCNHs-**2**.

6. References

1 F. A. Scaramuzzo, G. Licini and C. Zonta, *Chem. Eur. J.*, 2013, **19**, 16809.