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Supporting Information

Synthesis, Characterization, and Electrocatalytic Activity of Bis(pyridylimino)Isoindoline Cu(II) and Ni(II) Complexes

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Figure S1. ¹H-NMR of BPI_{Me}H in CD₃OD.



Figure S2. 13 C-NMR of BPI_{Me}H in CD₃OD

Crystallographic Data

Table S1. Sample and crys	stal data for BPI _{Me} H	
Identification code	Farnum190122	
Chemical formula	$C_{20}H_{17}N_5$	
Formula weight	327.39 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.020 x 0.147 x 0.16	ol mm
Crystal habit	clear dark yellow fragment	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 17.0417(5) Å	$\alpha = 90^{\circ}$
	b = 18.0681(5) Å	$\beta = 95.5780(10)^{\circ}$
	c = 10.6393(3) Å	$\gamma = 90^{\circ}$
Volume	3260.45(16) Å ³	
Ζ	8	
Density (calculated)	1.334 g/cm ³	
Absorption coefficient	0.656 mm^{-1}	
F(000)	1376	

Table S2. Data collection and structure refinement for $\mbox{BPI}_{\mbox{Me}}\mbox{H}$

Diffractometer	Bruker D8 VENTURE κ-geometry diffractometer	
Radiation source	Incoatec IµS DIAMOND microfocus sealed tube (Cu K α , $\lambda = 1.54178$ Å)	
Theta range for data collection	2.60 to 66.58°	
Index ranges	-19<=h<=20, -21<=k<=21, -12<=l<=12	
Reflections collected	52352	
Independent reflections	5762 [R(int) = 0.0510]	
Coverage of independent reflections	100.0%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9870 and 0.9020	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5762 / 0 / 463	
Goodness-of-fit on F ²	1.036	
Final R indices	4929 data; R1 = 0.0378, wR2 = 0.0977	

	$l \ge 2\sigma(l)$
	all data R1 = 0.0451, wR2 = 0.1038
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0512P) ² +1.1219P] where P=(F_o^2 +2 F_c^2)/3
Largest diff. peak and hole	0.189 and -0.187 eÅ ⁻³
R.M.S. deviation from mean	0.039 eÅ ⁻³
R.M.S. deviation from mean	$0.039 \text{ e}\text{\AA}^{-3}$

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Figure S3. ORTEP diagram of $BPI_{Me}H$ with thermal ellipsoids shown at 50% probability. H atoms are omitted for clarity.

Table S3. Sample and crystal data for [Cu(BPI_{Me})(H₂O)₂]ClO₄

Identification codeFarnum190927SSBChemical formulaC20H20ClCuN5O6

525.40 g/mol	
100(2) K	
1.54178 Å	
0.063 x 0.067 x 0.078 mm	
metallic light yellow-green Fragment	
orthorhombic	
P b c n	
a = 17.2059(4) Å	$\alpha = 90^{\circ}$
b = 14.7317(4) Å	$\beta = 90^{\circ}$
c = 16.7143(4) Å	$\gamma = 90^{\circ}$
4236.61(18) Å ³	
8	
1.647 g/cm ³	
3.061 mm ⁻¹	
2152	
	525.40 g/mol 100(2) K 1.54178 Å 0.063 x 0.067 x 0.078 mm metallic light yellow-gree orthorhombic P b c n a = 17.2059(4) Å b = 14.7317(4) Å c = 16.7143(4) Å 4236.61(18) Å ³ 8 1.647 g/cm ³ 3.061 mm ⁻¹ 2152

Table S4. Data collection and structure refinement for	[Cu(BPI _{Me})(H ₂ O) ₂]ClO ₄
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Diffractometer	Bruker D8 VENTURE κ-geometry diffractometer	
Radiation source	Incoatec IµS DIAMOND microfocus sealed tube (Cu K α , λ = 1.54178 Å)	
Theta range for data collection	3.95 to 74.58°	
Index ranges	-21<=h<=21, -18<=k<=18, -20<=l<=20	
Reflections collected	164983	
Independent reflections	4342 [R(int) = 0.0719]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8310 and 0.7960	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4342 / 6 / 316	
Goodness-of-fit on F ²	1.052	
Δ/σ_{max}	0.001	
Final R indices	3767 data; R1 = 0.0415, wR2 = 0.1158 $I > 2\sigma(I)$	
Weighting scheme	all data $R1 = 0.0477$, $wR2 = 0.1224$ $w=1/[\sigma^2(F_o^2)+(0.0733P)^2+4.3829P]$ where $P=(F_o^2+2F_c^2)/3$	

Largest diff. peak and hole	1.141 and -0.623 eÅ ⁻³
R.M.S. deviation from mean	0.074 eÅ ⁻³

Table S5. Sample and crystal data for [Ni(BPI_{Me})(H₂O)₂]ClO₄

Identification code	Farnum190314SS	
Chemical formula	C22H30ClN5NiO9	
Formula weight	602.67 g/mol	
Temperature	103(2) K	
Wavelength	1.54178 Å	
Crystal size	0.097 x 0.142 x 0.482 r	nm
Crystal habit	clear dark green-yellow	v Rod
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.6873(11) Å	$\alpha=84.050(4)^\circ$
	b = 10.7272(14) Å	$\beta=78.261(5)^\circ$
	c = 11.5524(14) Å	$\gamma = 82.171(5)^\circ$
Volume	1280.7(3) Å ³	
Ζ	2	
Density (calculated)	1.563 g/cm ³	
Absorption coefficient	2.592 mm^{-1}	
F(000)	628	

Table S6. Data collection and structure refinement for [Ni(BPI_{Me})(H₂O)₂]ClO₄

Diffractometer	Bruker D8 VENTURE κ-geometry diffractometer
Radiation source	Incoatec IµS DIAMOND microfocus sealed tube (Cu K α , λ = 1.54178 Å)
Theta range for data collection	4.25 to 66.65°
Index ranges	-11<=h<=12, -12<=k<=12, -13<=l<=13
Reflections collected	24584
Independent reflections	4448 [R(int) = 0.0644]
Coverage of independent reflections	98.1%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7870 and 0.3680
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma \mathrm{w}(\mathrm{F_o}^2 - \mathrm{F_c}^2)^2$
Data / restraints / parameters	4448 / 11 / 379
Goodness-of-fit on F ²	1.077
Δ/σ_{max}	0.001
Final R indices	4283 data; R1 = 0.0578, wR2 = 0.1652 $I > 2\sigma(I)$

	all data $R1 = 0.0588$, $wR2 = 0.1661$
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0829P) ² +3.7690P] where P=(F_o^2 +2 F_c^2)/3
Largest diff. peak and hole	0.666 and -0.498 eÅ ⁻³
R.M.S. deviation from mean	0.098 eÅ ⁻³

L = \	
Farnum190405SS	
$C_{40}H_{37}ClCu_2N_{10}O_7$	
932.32 g/mol	
110(2) K	
1.54178 Å	
0.042 x 0.093 x 0.1	34 mm
pale yellow-red blo	ck
triclinic	
P -1	
a = 12.7098(8) Å	$\alpha = 98.945(2)^{\circ}$
b = 13.5419(8) Å	$\beta = 101.969(2)^{\circ}$
c = 14.1463(9) Å	$\gamma = 116.890(2)^{\circ}$
2035.8(2) Å ³	
2	
1.521 g/cm ³	
2.423 mm ⁻¹	
956	
	Farnum190405SS $C_{40}H_{37}ClCu_2N_{10}O_7$ 932.32 g/mol 110(2) K 1.54178 Å 0.042 x 0.093 x 0.1 pale yellow-red bloc triclinic P -1 a = 12.7098(8) Å b = 13.5419(8) Å c = 14.1463(9) Å 2035.8(2) Å^3 2 1.521 g/cm^3 2.423 mm^{-1} 956

Table S7. Sample and crystal data for [Cu₂(BPI_{Me})₂(OH)]ClO₄

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Table S8. Data collection and structure refinement for $[Cu_2(BPI_{Me})_2(OH)]ClO_4$

Diffractometer	Bruker D8 VENTURE κ-geometry diffractometer
Radiation source	Incoatec IµS DIAMOND microfocus sealed tube (Cu K α , $\lambda = 1.54178$ Å)
Theta range for data collection	3.33 to 68.43°
Index ranges	-15<=h<=15, -16<=k<=16, -17<=l<=17
Reflections collected	51818
Independent reflections	7465 [R(int) = 0.0411]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9050 and 0.7370
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7465 / 0 / 560
Goodness-of-fit on F ²	1.075
Δ/σ_{max}	0.001
Final R indices	7319 data; $R1 = 0.0323$, $wR2 = 0.0831$
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$$\label{eq:Weighting scheme} \begin{array}{l} I > 2\sigma(I) \\ all \ data \qquad R1 = 0.0327, \ wR2 = 0.0833 \\ w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 2.6476P] \\ where \ P = (F_o^2 + 2F_c^2)/3 \\ \ Largest \ diff. \ peak \ and \ hole \\ R.M.S. \ deviation \ from \ mean \\ 0.060 \ e \ A^{-3} \end{array}$$



Figure S4. ORTEP diagram of $[Cu_2(BPI_{Me})_2(OH)]ClO_4$ with thermal ellipsoids shown at 50% probability. Solvent molecules outside the coordination sphere are omitted for clarity.



Figure S5. ESI mass spectrum of BPI_{Me}H in MeCN. a) Calculated ($[C_{20}H_{17}N_5 + H]^+$), 328.1562 b) Experimental, 328.1556.



Figure S6. ESI mass spectrum of $[Cu(BPI_{Me})(H_2O)_2]ClO_4$ in MeCN. Data are consistent with loss of H_2O ligands. a) Calculated $[C_{20}H_{16}N_5Cu]^+$, 389.0701 b) Experimental, 389.0733. c) Simulation of 80% $[Cu^{II}(BPI_{Me})]^+$ and 20% $[Cu^{I}(BPI_{Me}H)]^+$ to match observed peak pattern in experimental data. The presence of $[Cu^{I}(BPI_{Me}H)]^+$ is believed to result from reduction of Cu(II) to Cu(I) during the ESI-MS experiment. Similar results for copper complexes have been noted in the literature.^{1,2}



Figure S7. ESI mass spectrum of $[Cu_2(BPI_{Me})_2(OH)]ClO_4$ in MeCN. a) Calculated $[C_{40}H_{33}N_5OCu_2]^+$, 795.1523 b) Experimental, 390.0777. Experimental spectrum is consistent with a mixture of $[Cu^{II}(BPI_{Me})]^+$ and $[Cu^{II}(BPI_{Me}H)]^+$ resulting from reduction of copper during ESI-MS experiment.^{1,2} c) Simulation of calculated m/Z patterns for mixture of 34% $[Cu^{II}(BPI_{Me})]^+$ and $66\% [Cu^{I}(BPI_{Me}H)]^+$.



Figure S8. ESI mass spectrum of $[Ni(BPI_{Me})(H_2O)_2]ClO_4$ in MeCN. a) Calculated $[C_{20}H_{16}N_5Ni]^+$, 384.0759 b) Experimental, 384.0841.



Figure S9. ATR-IR spectra of $[BPI_{Me}H]$ (blue line), $[Cu-BPI_{Me}]^+$ ($[Cu(BPI_{Me})(H_2O)_2]ClO_4$, red line), and $[Ni-BPI_{Me}]^+$ ($[Ni(BPI_{Me})(H_2O)_2]ClO_4$, green line).

BPI _{Me} H			[Cu(BPI _{Me})(H ₂ O) ₂]ClO ₄			$[Ni(BPI_{Me})(H_2O)_2]ClO_4$		
λ	$\tilde{\mathbf{v}}$	$\Delta ilde{ ext{v}}$	λ	$\mathbf{\tilde{v}}$	$\Delta \tilde{\mathbf{v}}$	λ	$\mathbf{\tilde{v}}$	$\Delta ilde{ extbf{v}}$
(nm)	(cm^{-1})	(cm^{-1})	(nm)	(cm^{-1})	(cm^{-1})	(nm)	(cm^{-1})	(cm^{-1})
				π - π *(1)				
409	24,400		459	21,800		460	21,700	
387	25,800	1,390	431	23,200	1,420	431	23,200	1,460
367	27,300	1,410	407	24,600	1,370	406	24,600	1,430
π-π*(2)								
			356	28,100		354	28,300	
			338	29,600	1,500	337	29,700	1,430
			322	31,100	1,470	321	31,200	1,480

Table S9. Summary of UV-Visible Absorbance Peaks Showing Vibronic Progression

All data measured in MeCN solvet; π - π *(1) and π - π *(2) refer to separate electronic transitions; Difference in vibrational energy levels consistent with a C-H bending mode at 1440 cm⁻¹



Figure S10. Scan rate dependent CVs of (a) $[Cu-BPI_{Me}]^+$ and (b) $[Ni-BPI_{Me}]^+$ in CO₂-saturated MeCN with 0.1 M TBAPF₆. Y-axis shows the current normalized to (scan rate)^{1/2}.



Figure S11. CV data of 1 mM BPI_{Me}H in N_2 - and CO₂-saturated MeCN with 0.1 M TBAPF₆. Scan rate: 100 mV/s.



Figure S12. CVs obtained in fresh CO₂-saturated MeCN with 0.1 M TBAPF₆ for a GC rod electrode following CPE in the presence of $[Cu-BPI_{Me}]^+$ and subsequent rinsing with acetone. A clean GC rod electrode is shown for comparison (red). Scan rate: 100 mV/s.

	[Cu-BPI _{Me}] ^{+ b}		[Ni-BPI _{Me}] ^{+ c}		
Time (min)	FE for	FE for	FE for	FE for	
Time (mm)	CO (%)	$H_{2}(\%)$	CO (%)	H_2 (%)	
5	75	0	83	0	
15	81	0	86	0	
25	79	0	80	0	
35	66	0	64	0	
45			55	0	
60			48	0	

Table S10. Summary of Faradaic Efficiencies (FE) for Rinsed Electrodes in CO₂-saturated MeCN^a

^aRinsed electrodes consisted of GC rod electrodes that had been previously exposed to CPE experiments with 0.5 M $[Cu-BPI_{Me}]^+$ or $[Ni-BPI_{Me}]^+$ in the same electrolyte conditions, 0.1 M TBAPF₆; ^b-2.45 V; ^c-2.5V

Table S11. Summary of Faradaic Efficiencies (FE) for Electrocatalysis in CO_2 -saturated MeCN + 5% H_2O^a

	[Cu-BPI _{Me}] ^{+ b}		Rinsed Electrode ^c		
Time (min)	FE for	FE for	FE for	FE for	
	CO (%)	$H_{2}(\%)$	CO (%)	$H_{2}(\%)$	
5	17	13			
10	21	16	88	0	
15	19	16			
20			91	0	
25	20	16			
30			84	0	
35	21	13			
45	29	16	83	0	

^aGC rod electrode, 0.1 M TBAPF₆; ^b-2.3 V; ^c-2.3 V



Figure S13. ¹H NMR spectrum showing formate at 8.63 ppm following CPE at -2.3 V of [Cu-BPI_{Me}]⁺ in CO₂-saturated MeCN with 5% H₂O and 0.1 M TBAPF₆.

Analysis of electrodeposited materials on glassy carbon electrodes

Figure S15 shows photograph images of GC rod electrodes post CPE. **Figure S16** shows SEM images for GC electrodes exposed to various deposition conditions. EDS data was measured using INCA software where the pink box in each image shows the area which was probed for elemental analysis. Note that the at% of elements depend on a number of factors including the size of the area being investigated and the background elements. Carbon is present in all measurements because of the nature of the electrode. Resulting analysis is presented in **Table S12**.



Figure S14. Images of GC rod electrodes after CPE experiments: a) $[Cu-BPI_{Me}]^+$ in MeCN, b) $[Cu-BPI_{Me}]^+$ in MeCN + 5% H₂O, c) $[Ni-BPI_{Me}]^+$ in MeCN.

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Element	GC ^a	$GC/[Cu-BPI_{Me}]^{+b}$	GC/[Ni-BPI _{Me}] ^{+c}	
С	96.08	33.38	86.54	
0	3.92	20.40	12.80	
Cu	0.00	46.22	0.00	
Ni	0.00	0.00	0.66	

Table S12. Summary of EDS data collected for glassy carbon (GC) electrodes

^aGC electrode blank, not exposed to CPE conditions; ^bCPE at -2.67 V for 1 hr, 1 mM [Cu-BPI_{Me}]⁺ in CO₂-saturated MeCN with 0.1 M TBAPF₆; ^cCPE at -2.5 V for 1 hr, 1 mM [Ni-BPI_{Me}]⁺ in CO₂-saturated MeCN with 0.1 M TBAPF₆



Figure S15. a) SEM image of a 5 mm GC disk electrode following CPE (-2.67 V) of 1 mM [Cu-**BPI_{Me}**]⁺ in CO₂-saturated MeCN with 0.1 M TBAPF₆. Concentric rings are scratches in the electrode present prior to the CPE experiment and not due to the electrolysis experiment. b) Zoomed in SEM image to focus on deposited material. c) SEM image of blank GC electrode. D) SEM image of GC disk electrode following CPE (-2.5 V) of 1 mM [**Ni-BPI_{Me}**]⁺ in CO₂-saturated MeCN with 0.1 M TBAPF₆. Pink boxes in images (b-d) indicate the area which was probed for elemental analysis.

References

1 L. Gianelli, V. Amendola, L. Fabbrizzi, P. Pallavicini and G. G. Mellerio, *Rapid Communications in Mass Spectrometry*, 2001, **15**, 2347–2353.

2 H. Lavanant, H. Virelizier and Y. Hoppilliard, J Am Soc Mass Spectrom, 1998, 9, 1217-1221.