Chemistry–A European Journal

Supporting Information

Theoretical and Experimental Investigation of Functionalized Cyanopyridines Yield an Anolyte with an Extremely Low Reduction Potential for Nonaqueous Redox Flow Batteries

Thomas P. Vaid, Monique E. Cook, Jessica D. Scott, Marino Borjesson Carazo, Jonathan Ruchti, Shelley D. Minteer, Matthew S. Sigman, Anne J. McNeil, and Melanie S. Sanford*
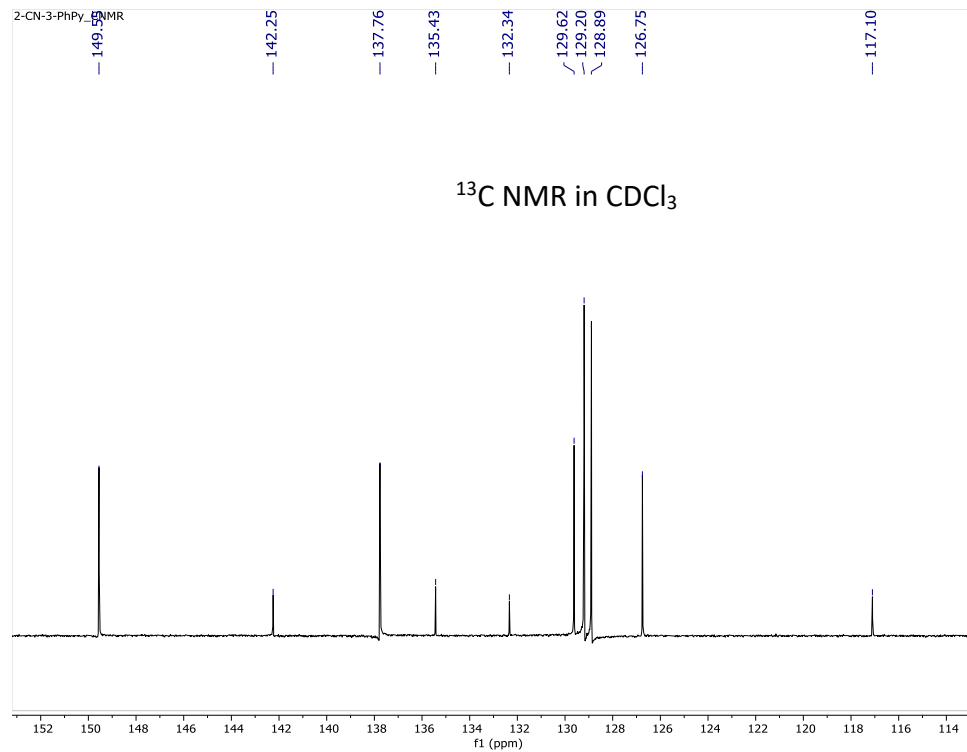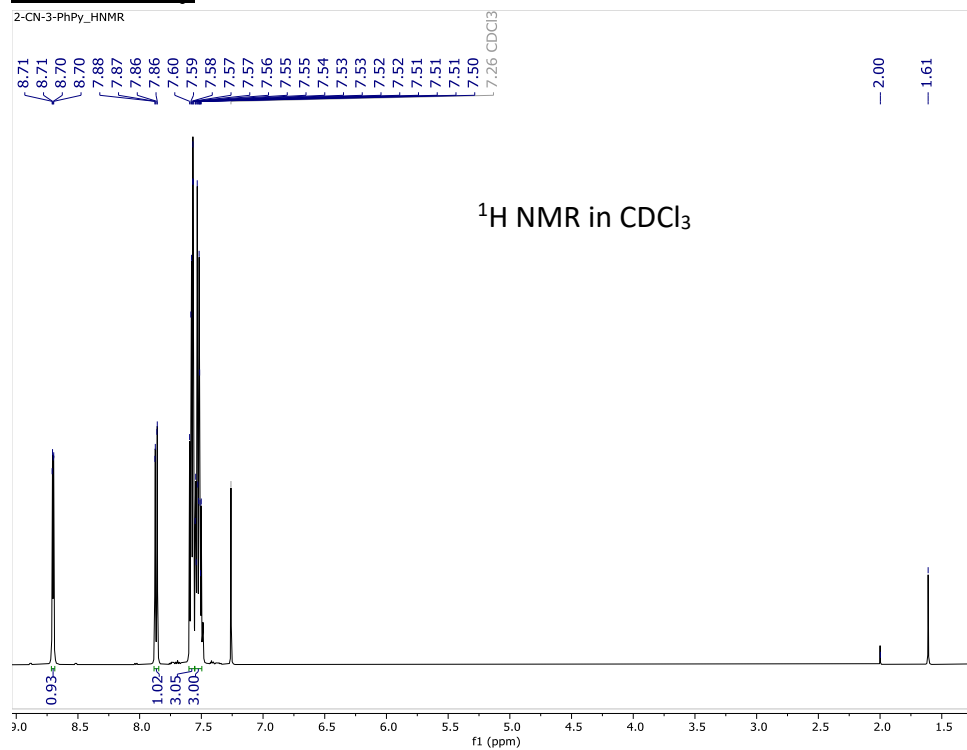
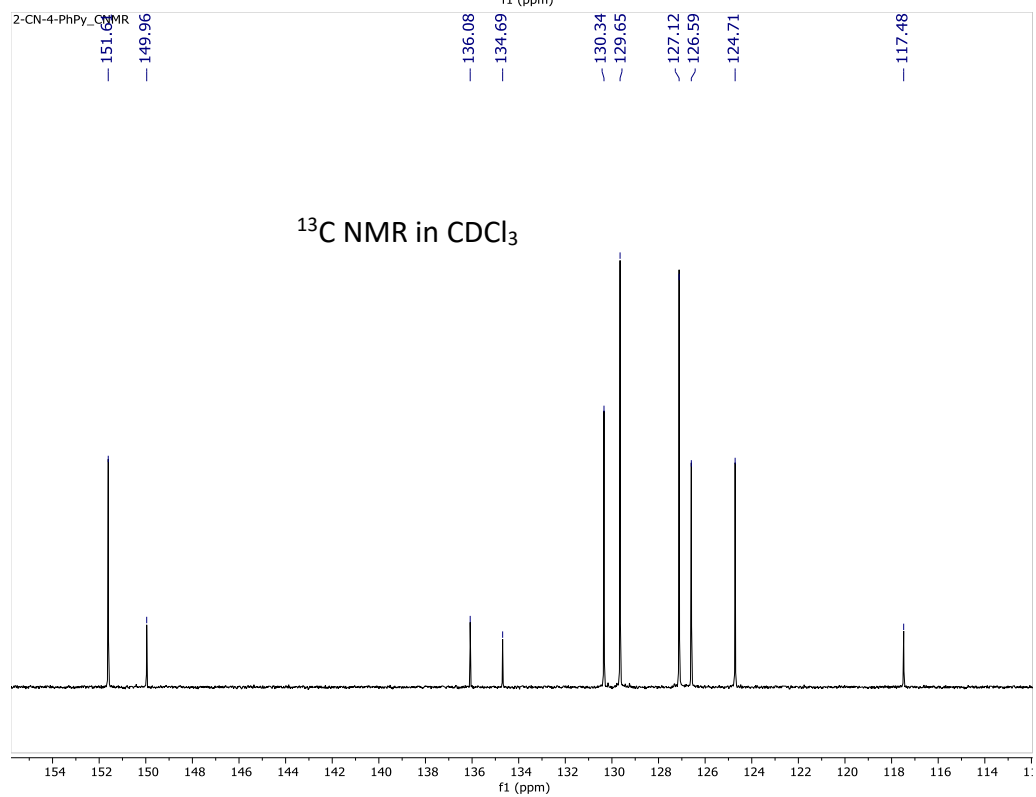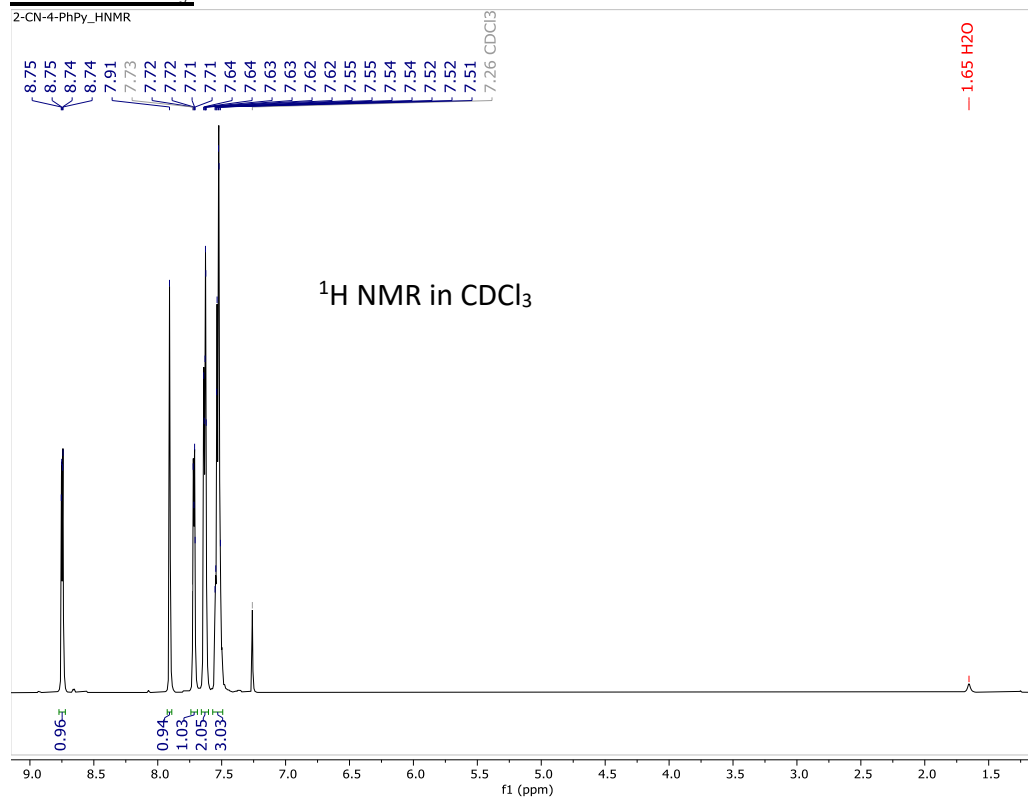# Supporting Information

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I. NMR spectra

2-CN-3-PhPy

8.71, 8.71, 8.70, 8.70, 7.88, 7.87, 7.86, 7.86, 7.60, 7.59, 7.58, 7.57, 7.57, 7.56, 7.55, 7.55, 7.54, 7.53, 7.53, 7.52, 7.52, 7.51, 7.51, 7.51, 7.51, 7.50

7.26 CDCl3

2.00, 1.61

^{1}H NMR in CDCl$_3$

0.93, 1.02, 3.05, 3.00

f1 (ppm)

149.5, 142.25, 137.76, 135.43, 132.34, 129.62, 129.20, 128.89, 126.75, 117.10

^{13}C NMR in CDCl$_3$

f1 (ppm)

2-CN-4-PhPy

2-CN-4-PhPy_HNMR

8.75
8.75
8.74
8.74
7.91
7.73
7.72
7.72
7.71
7.71
7.64
7.64
7.63
7.63
7.62
7.62
7.55
7.55
7.54
7.54
7.52
7.52
7.51
7.26 CDCl3

— 1.65 H2O

^{1}H NMR in CDCl$_3$

0.96

0.94
1.03
2.05
3.03

f1 (ppm)

2-CN-4-PhPy_CNMR

151.62
149.96
136.08
134.69
130.34
129.65
127.12
126.59
124.71
117.48

^{13}C NMR in CDCl$_3$

f1 (ppm)

2-CN-5-PhPy

2-CN-5-PhPy_HNMR

8.95
8.95
8.02
8.01
8.00
8.00
7.78
7.78
7.77
7.77
7.76
7.62
7.61
7.61
7.60
7.60
7.60
7.59
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.50
7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.26 CDCl3
1.55

^{1}H NMR in CDCl$_3$

0.91
1.01
0.98
2.05
3.05

f1 (ppm)

2-CN-5-PhPy_CNMR

149.70
140.01
136.03
135.02
132.41
129.61
129.59
128.58
127.47
117.48

^{13}C NMR in CDCl$_3$

f1 (ppm)

S4

2-CN-6-PhPy

2-CN-6-PhPy_HNMR

8.18
8.17
8.16
8.16
8.02
8.02
8.01
8.00
7.95
7.93
7.92
7.90
7.90
7.88
7.88
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.26 CDCl3
5.95

2.17
2.04 H2O
1.76

1.27
1.26
1.24

^{1}H NMR in CDCl$_3$

1.00
3.01
2.21
3.13

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

2-CN-6-PhPy_CNMR

167.08
156.32
149.49
138.46
138.32
129.63
128.99
127.08
123.40
120.94

^{13}C NMR in CDCl$_3$

165 160 155 150 145 140 135 130 125 120 11
f1 (ppm)

S5

3-CN-2-PhPy

3-CN-2-PhPy

8.89
8.89
8.88
8.88
8.10
8.09
8.08
8.07
7.94
7.94
7.93
7.92
7.92
7.91
7.54
7.54
7.53
7.53
7.52
7.51
7.40
7.39
7.38
7.37
7.26 CDCl3
2.05
1.57
1.25

^{1}H NMR in CDCl$_3$

0.95
1.01
1.95
3.03
1.07

f1 (ppm)

3CN2PhPy-Synth-F-2-4B_CNMR

161.1
152.74
141.91
137.25
130.33
128.97
128.79
121.64
117.74
107.58

^{13}C NMR in CDCl$_3$

f1 (ppm)

3-CN-4-PhPy

3-CN-4-PhPy_HNMR

8.96
8.83
8.81
7.65
7.64
7.63
7.63
7.62
7.62
7.61
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.48
7.47
7.26 cdcl3
7.26 CDCl3
1.67 H2O
1.22

^{1}H NMR in CDCl$_3$

0.91
1.00
2.03
3.06
1.00

f1 (ppm)

3-CN-4-PhPy_CNMR

154.17
152.96
152.46
135.54
130.39
129.33
128.52
123.89
116.83
108.72

^{13}C NMR in CDCl$_3$

f1 (ppm)

3-CN-5-PhPy

3-CN-5-PhPy_HNMR

9.03, 9.03, 8.86, 8.85, 8.13, 8.13, 8.12, 7.58, 7.58, 7.58, 7.57, 7.57, 7.56, 7.56, 7.55, 7.54, 7.54, 7.53, 7.52, 7.52, 7.51, 7.50, 7.50, 7.49, 7.49, 7.48, 7.48, 7.47

7.26 CDCl3

^{1}H NMR in CDCl$_3$

1.00, 0.93, 1.00, 2.18, 2.18, 1.05

f1 (ppm)

3-CN-5-PhPy_CNMR

151.66, 150.82, 137.35, 137.13, 135.58, 129.62, 129.40, 127.31, 116.71, 110.24

^{13}C NMR in CDCl$_3$

f1 (ppm)

S8

3-CN-6-PhPy

3-CN-6-PhPy_HNMR

8.95
8.95
8.06
8.05
8.05
8.04
8.04
8.02
8.01
8.00
8.00
7.86
7.85
7.52
7.52
7.52
7.51
7.26 CDCl3

^{1}H NMR in CDCl$_3$

0.87
2.07
1.00
1.08
3.06

f1 (ppm)

3-CN-6-PhPy_CNMR

160.6
152.61
140.01
137.51
130.77
129.23
127.52
120.14
117.14
108.02

^{13}C NMR in CDCl$_3$

f1 (ppm)

4-CN-2-PhPy

8.86
8.86
8.85
8.85
8.01
8.00
7.99
7.99
7.94
7.94
7.94
7.54
7.53
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.45
7.45
7.44
7.44
7.26 CDCl3

^{1}H NMR in CDCl$_3$

1.00

2.09
1.03

3.17
1.00

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

158.88
158.80
150.76
137.44
130.35
129.22
127.10
123.29
122.17
121.33
116.87

^{13}C NMR in CDCl$_3$

164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)

4-CN-3-PhPy

4-CN-3-PhPy_HNMR

8.87
8.76
8.75
7.63
7.62
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.53
7.53
7.51
7.26 CDCl3

^{1}H NMR in CDCl$_3$

1.00
1.01
1.07
2.11
3.22

f1 (ppm)

4-CN-3-PhPy_CNMR

151.13
148.86
138.83
134.55
129.69
129.28
128.93
126.17
118.95
116.46

^{13}C NMR in CDCl$_3$

f1 (ppm)

Me₃-3-CN-6-PhPy

¹H NMR in CDCl₃

¹³C NMR in CDCl₃

II. DFT Calculation Methods and Data

Reduction potentials.

All calculations were done in Spartan (Wavefunction, Inc.). Reduction potentials were calculated using a straightforward method in which the energy of each neutral molecule and its radical anion is calculated (B3LYP/6-311+G**//B3LYP/6-31G*). All were done in "polar solvent," which uses a conductor-like polarizable continuum model for the solvent with a dielectric constant of 37.22, very close to that of acetonitrile. The energy of the radical anion was subtracted from the energy of the neutral molecule to obtain the electron affinity (using, in all cases, just the "electronic energy" from the calculation). A constant offset of 4.87 V was then subtracted to convert those electron affinities (expressed in eV) to solution-phase reduction potentials (in V) versus a $Fc^{+/0}$ reference.[1,2]

The calculated energies of the neutral molecules and radical anions (in hartrees) are given in the following tables.   The difference between the two gives the electron affinity, which was then converted to an electron affinity in eV.   Subtraction of 4.87 V gives a solution-phase oxidation potential vs $Fc^{+/0}$. Table S1 gives the results for the cyanopyridines, and Table S2 for the cyanophenylpyridines.

Table S1. Calculated Reduction Potentials of Cyanopyridines

molecule	neutral energy (hartrees)	radical anion energy (hartrees)	EA (hartrees)	EA (eV)	$E_{1/2}$ (V)
2-cyanopyridine	340.626906	340.718267	0.091361	2.486060715	-2.383939
3-cyanopyridine	340.628169	340.716285	0.088116	2.397759722	-2.47224
4-cyanopyridine	340.62619	340.724179	0.097989	2.666417875	-2.203582

Table S2. Calculated Reduction Potentials of Cyanophenylpyridines

molecule	neutral energy (hartrees)	radical anion energy (hartrees)	EA (hartrees)	EA (eV)	$E_{1/2}$ (V)
2-CN-3-PhPy	571.738383	571.831454	0.093071	2.532592209	-2.33740779
2-CN-4-PhPy	571.741965	571.837367	0.095402	2.596021983	-2.27397802
2-CN-5-PhPy	571.741673	571.839761	0.098088	2.669111803	-2.2008882
2-CN-6-PhPy	571.742554	571.833782	0.091228	2.482441599	-2.3875584
3-CN-2-PhPy	571.740948	571.831358	0.09041	2.460182674	-2.40981733
3-CN-4-PhPy	571.740486	571.835978	0.095492	2.598471009	-2.27152899
3-CN-5-PhPy	571.741991	571.831257	0.089266	2.429052832	-2.44094717
3-CN-6-PhPy	571.745349	571.843785	0.098436	2.67858137	-2.19141863
4-CN-2-PhPy	571.74171	571.840989	0.099279	2.701520581	-2.16847942
4-CN-3-PhPy	571.737819	571.837781	0.099962	2.720105967	-2.14989403

Dimerization free energies.

The free energy of dimerization (ΔG_{dim}) for the radical anions of both the cyanopyridines and cyanophenylpyridines were calculated as follows. The geometry of each radical anion and each dimeric dianion was optimized in the gas phase (B3LYP-D3/6-311++G**) and a vibrational and thermodynamic calculation was performed at the same level and basis set. Then, for each radical anion or dimer, a single-point energy calculation was performed (B3LYP-D3/6-311++G**) with the C-PCM "polar solvent" model in Spartan (dielectric constant of 37.22, close the reported value of 35.9 for CH$_3$CN at 25 °C), and the solvation energies were used as a correction to the gas-phase calculated free energies. All of the calculated free energies and solvation energies are given in Table S3 for both cyanopyridines and cyanophenylpyridines.

Table S3. Calculated Free Energies of Dimerization for Cyanopyridines and Cyanophenylpyridines

radical anion and dimerization position	gas phase radical anion energy (hartrees)	gas phase dimer energy (hartrees)	ΔG_{dim}, gas phase (hartrees)	ΔG_{dim} gas (kcal/mol)	radical anion solvation energy (kcal/mol)	dimer solvation energy (kcal/mol)	ΔG_{dim}, solution (kcal/mol)
2-CNPy•⁻, C2	340.586811	681.037543	0.136079	85.39	57.62699367	172.1428786	28.50
2-CNPy•⁻, C5	340.586811	681.089677	0.083945	52.68	57.62699367	152.0383283	15.89
2-CNPy•⁻, C6	340.586811	681.055332	0.11829	74.23	57.62699367	162.0231863	27.46
3-CNPy•⁻, C4	340.588368	681.093876	0.08286	52.00	54.1468881	162.2851578	-2.00
3-CNPy•⁻, C6	340.588368	681.10691	0.069826	43.82	54.1468881	151.1855316	0.92
3-CNPy•⁻, C6, iso	340.588368	681.098917	0.077819	48.83	54.1468881	156.9271418	0.20
3-CNPy•⁻, C4-C6	340.588368	681.104481	0.072255	45.34	54.1468881	154.6522852	-1.02
4-CNPy•⁻, C2	340.594369	681.06055	0.128188	80.44	54.36341485	159.571027	29.60
4-CNPy•⁻, C3	340.594369	681.076566	0.112172	70.39	54.36341485	160.7083582	18.41
4-CNPy•⁻, C4	340.594369	681.054053	0.134685	84.52	54.36341485	165.4699415	27.77
3-CN-2-PhPy•⁻, C6	571.647818	1143.21847	0.077168	48.42	51.30668739	152.2377889	-1.20
3-CN-4-PhPy•⁻, C6	571.651949	1143.21823	0.085671	53.76	50.66545976	151.9509774	3.14
3-CN-5-PhPy•⁻, C4	571.646873	1143.221	0.072747	45.65	50.532634	158.3110715	-11.60
3-CN-5-PhPy•⁻, C6	571.646873	1143.2228	0.070951	44.52	50.532634	151.5433909	-5.96
3-CN-6-PhPy•⁻, C4	571.660962	1143.22642	0.095507	59.93	49.63877696	152.5236865	6.69
3-CN-6-PhPy•⁻, C6	571.660962	1143.20677	0.115153	72.26	49.63877696	148.2705035	23.27
with K+ present							
3-CN-6-PhPy•⁻, C4	1171.57911	2343.16633	-0.008102	-5.08	21.34729547	31.44315577	6.17
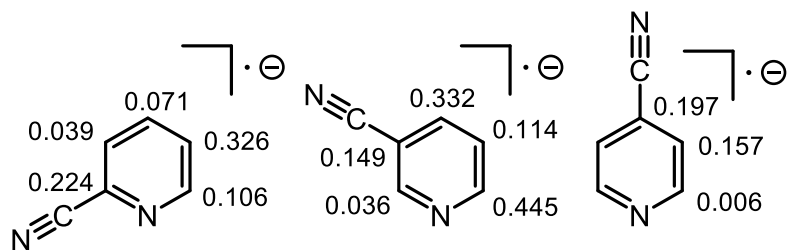
Figure S1. Mulliken spin densities calculated for the ring carbons of the 2-CNPy$^{\bullet-}$, 3-CNPy$^{\bullet-}$, and 4-CNPy$^{\bullet-}$ radical anions.
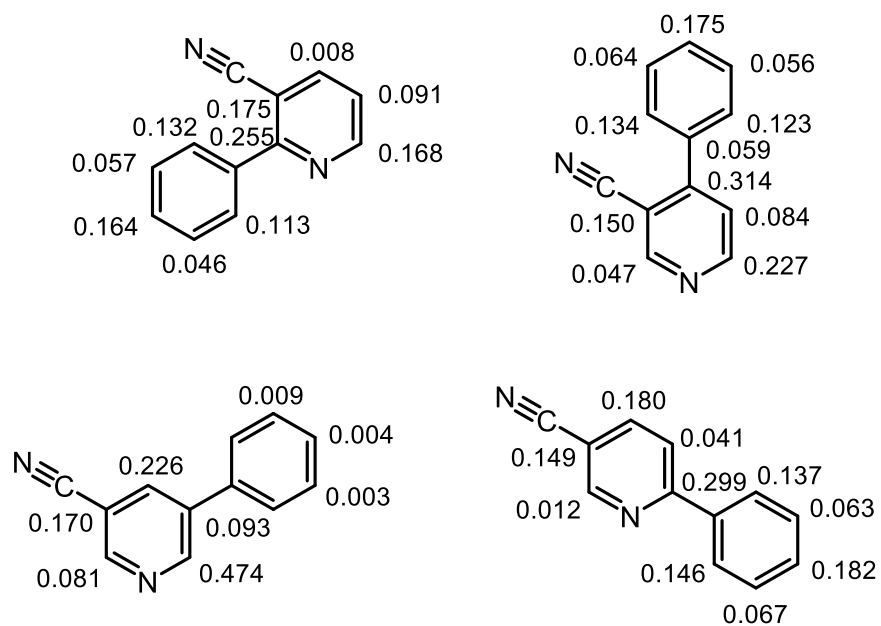
Figure S2. Mulliken spin densities calculated for the ring carbons of 3-CN-2-PhPy$^{\bullet-}$, 3-CN-4-PhPy$^{\bullet-}$, 3-CN-5-PhPy$^{\bullet-}$ and 3-CN-6-PhPy$^{\bullet-}$ radical anions.

V. CVs of Cyanophenylpyridines
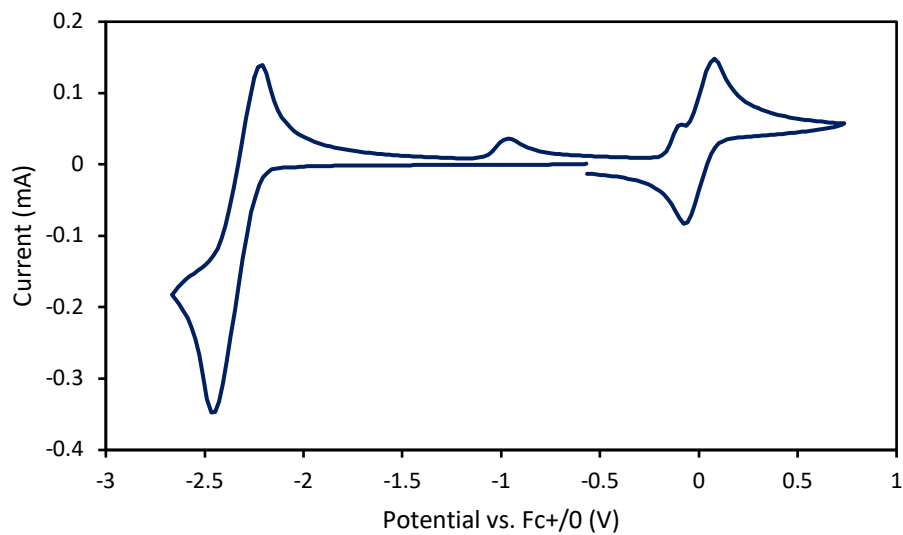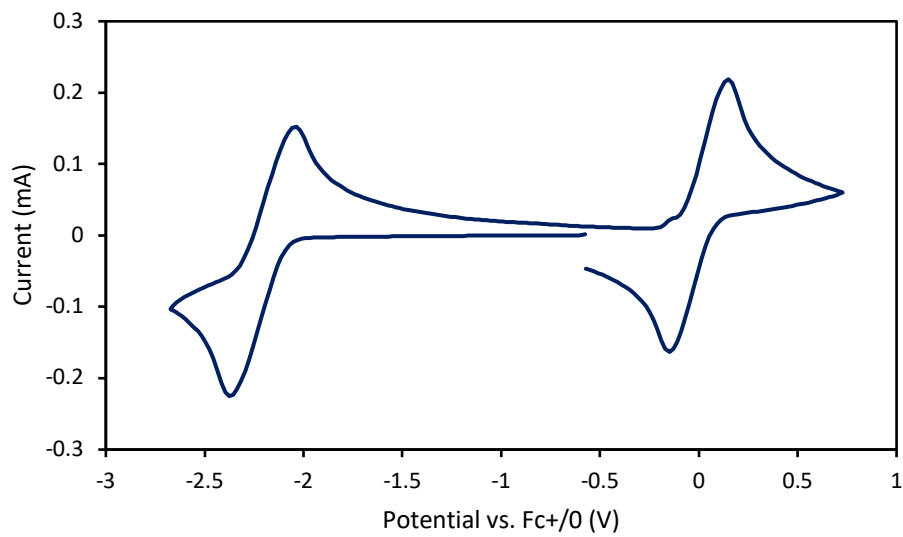
2-CN-3-PhPy

2-CN-4-PhPy

2-CN-5-PhPy
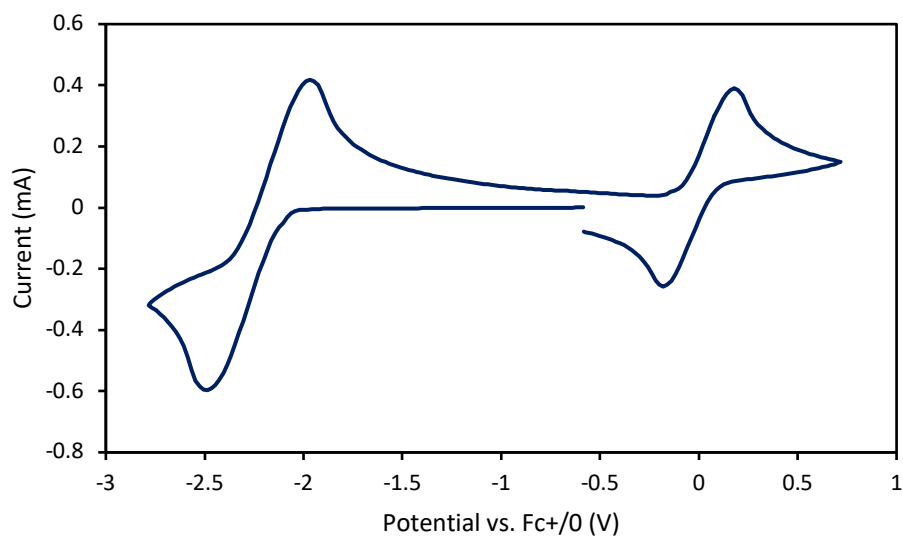
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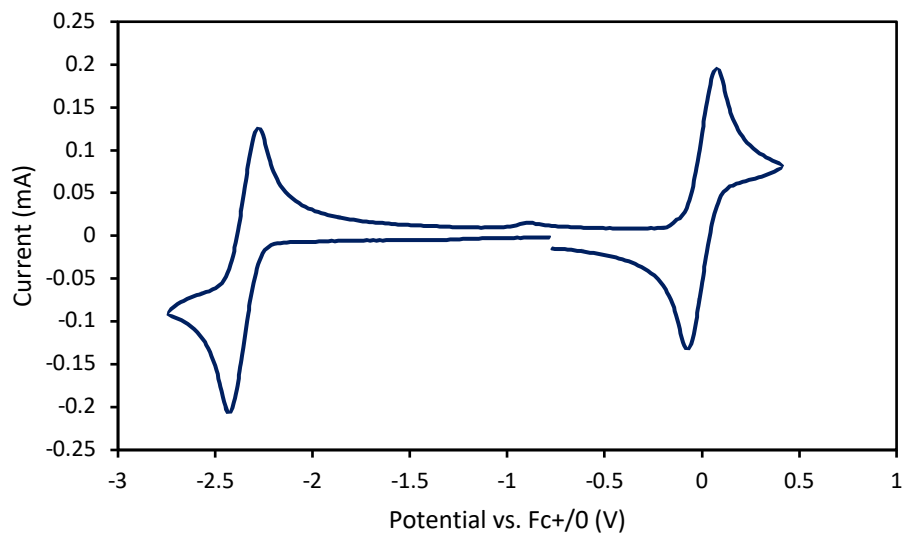
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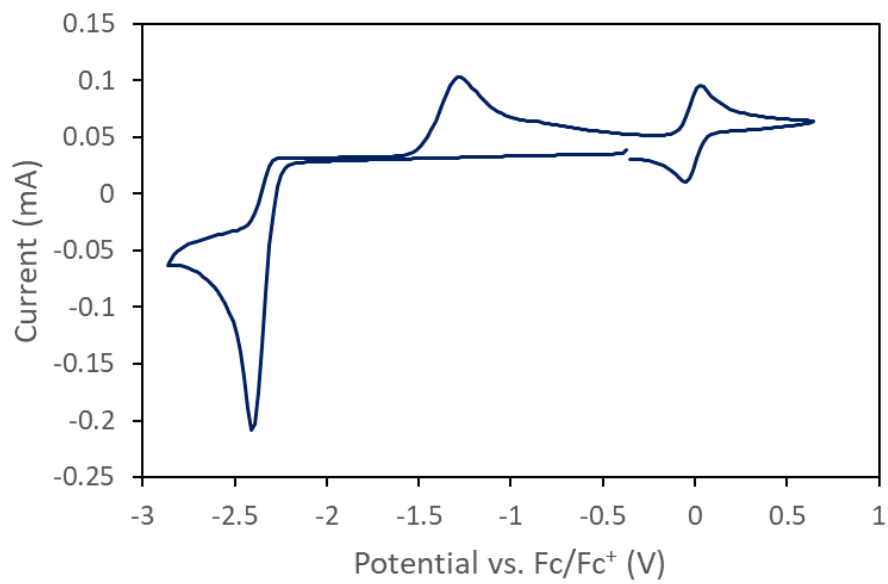
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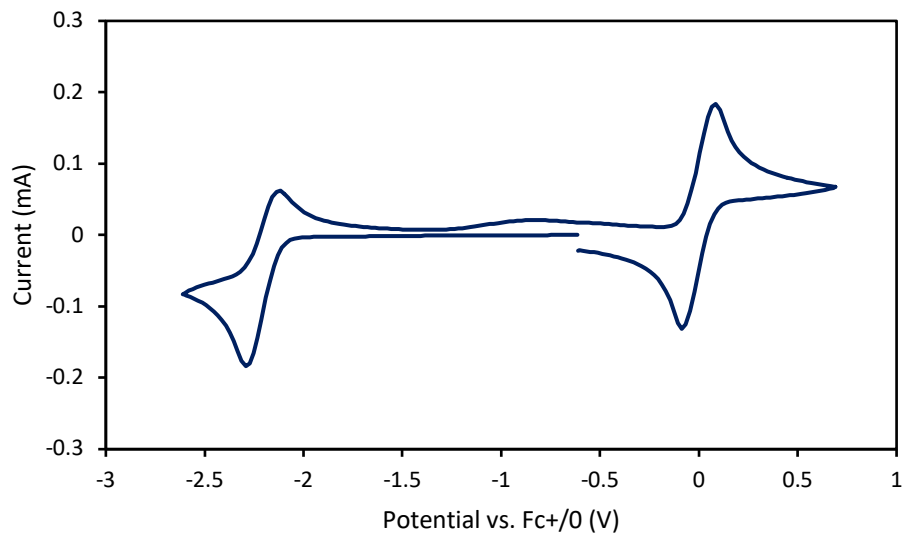
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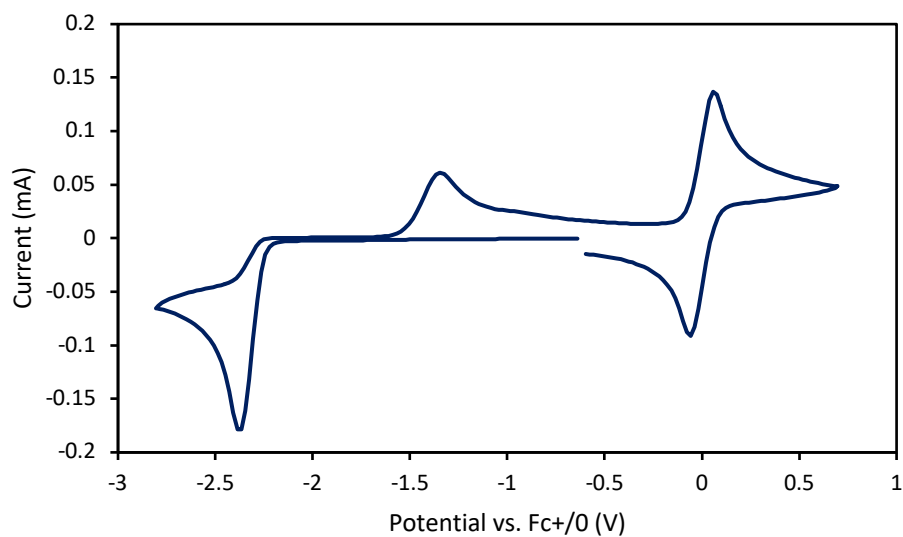
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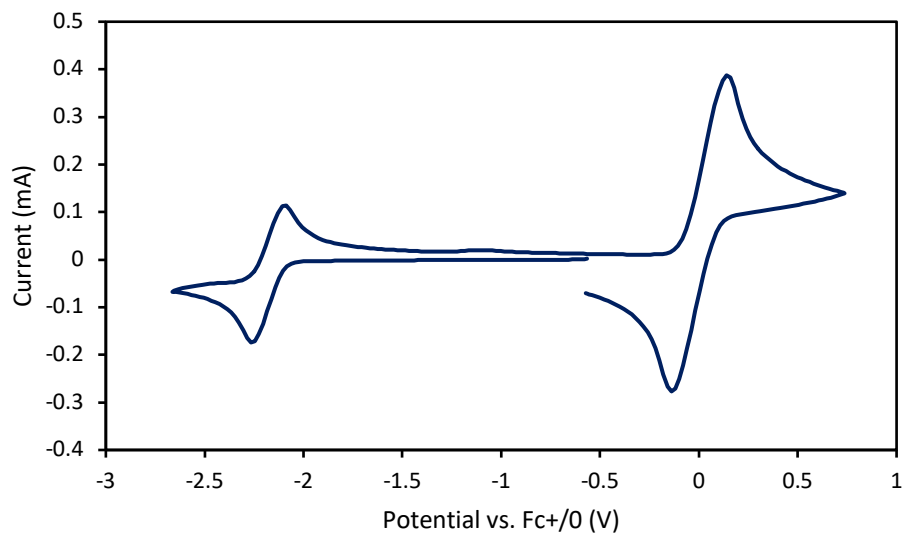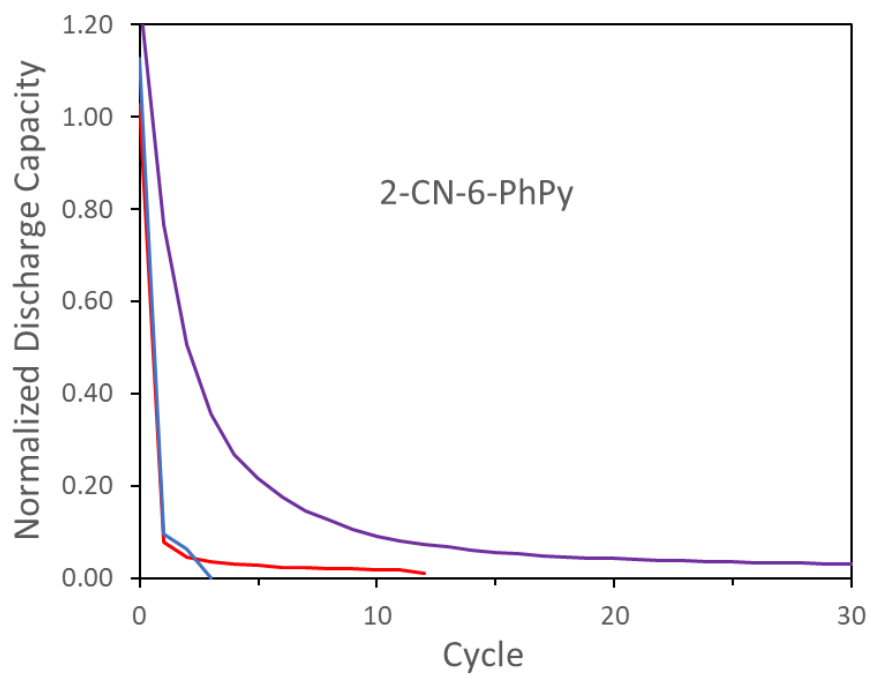
4-CN-2-PhPy
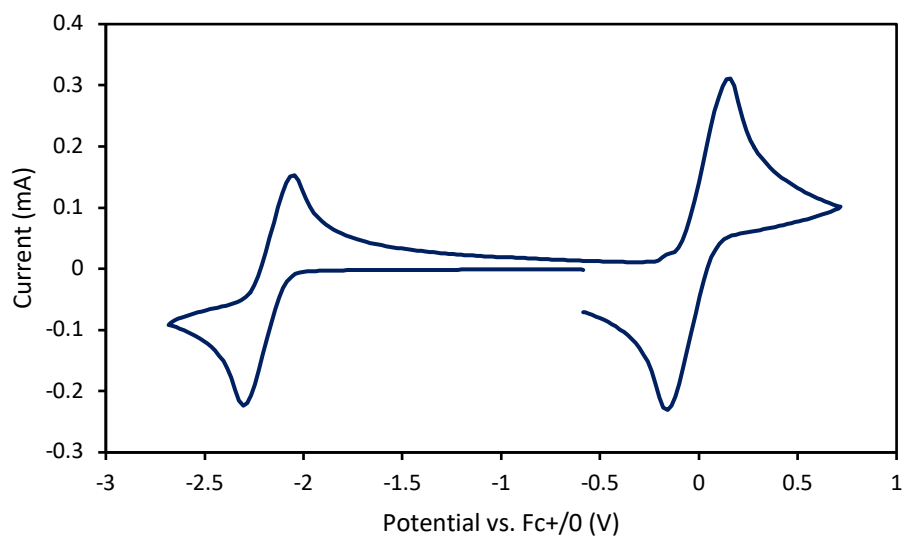
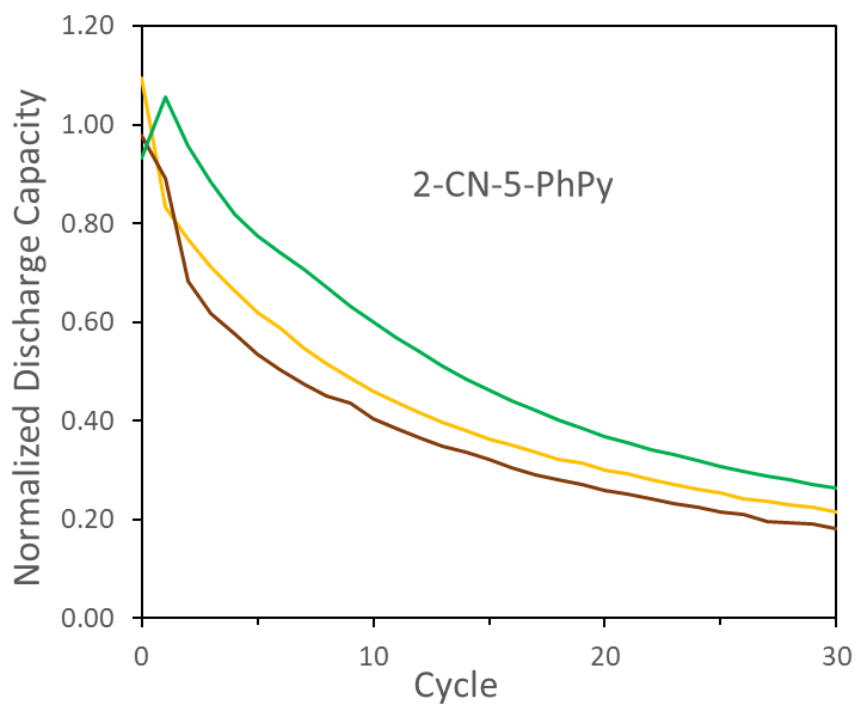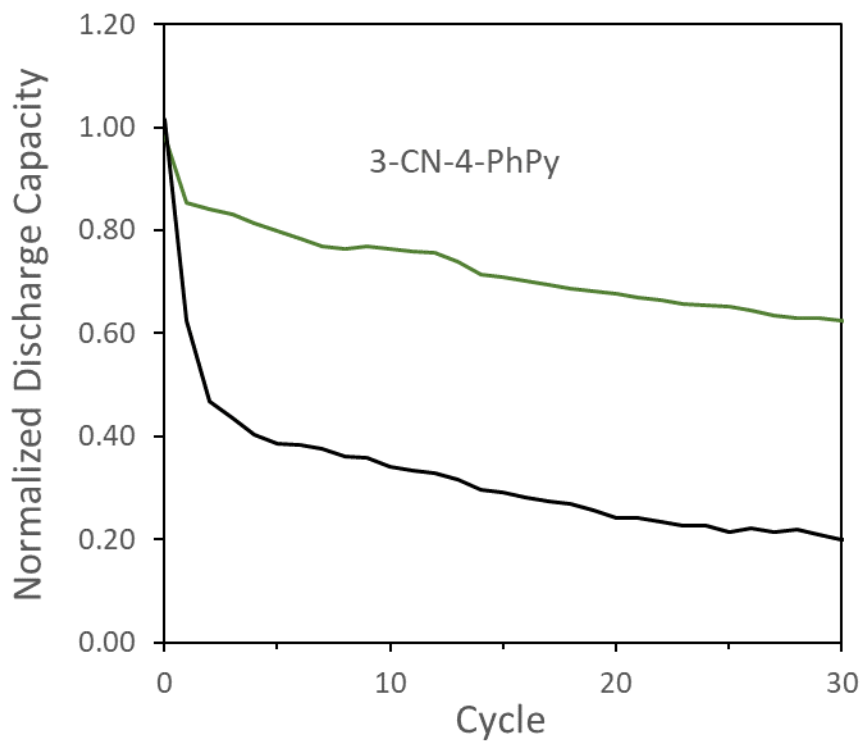**4-CN-3-PhPy**
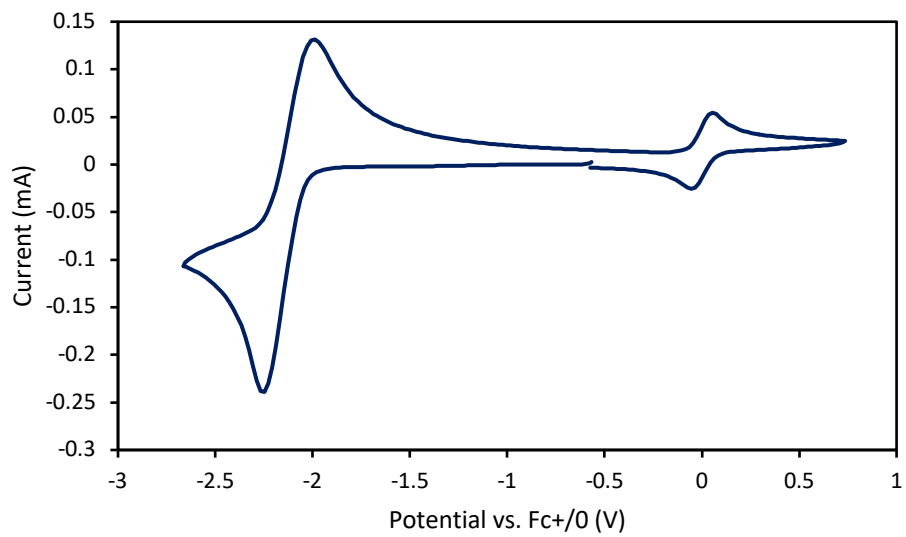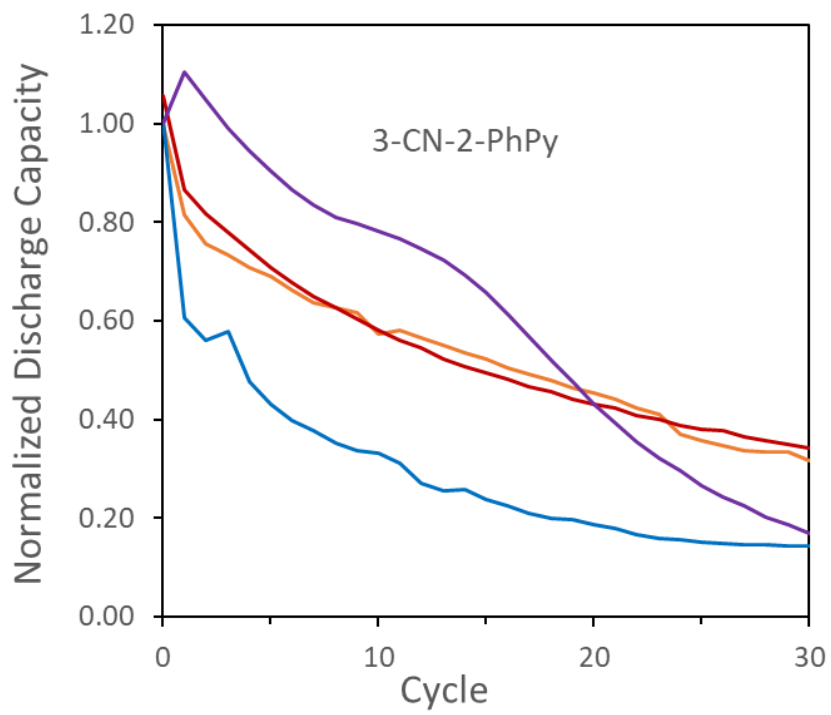
Me₃-3-CN-6-PhPy
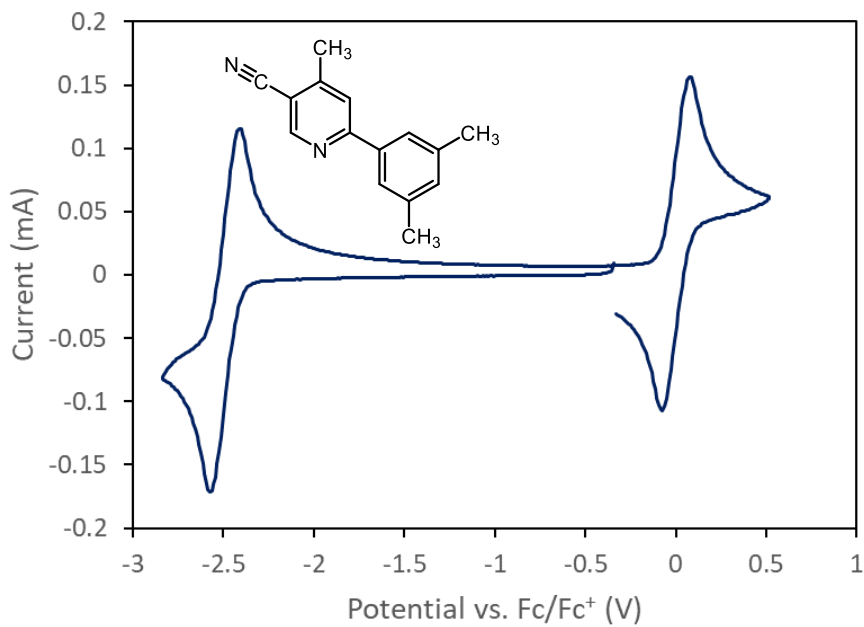
Figure S3. Cyclic voltammograms of the cyanophenylpyridines at a glassy carbon electrode in CH₃CN with 0.50 M [NBu₄][PF₆] at a scan rate of 100 mV/s, all with a ferrocene internal standard with potentials adjusted to $E_{1/2}$ (Fc$^{+/0}$) = 0 V.

IV. Bulk charge-discharge cycling of cyanophenylpyridines

2-CN-3-PhPy

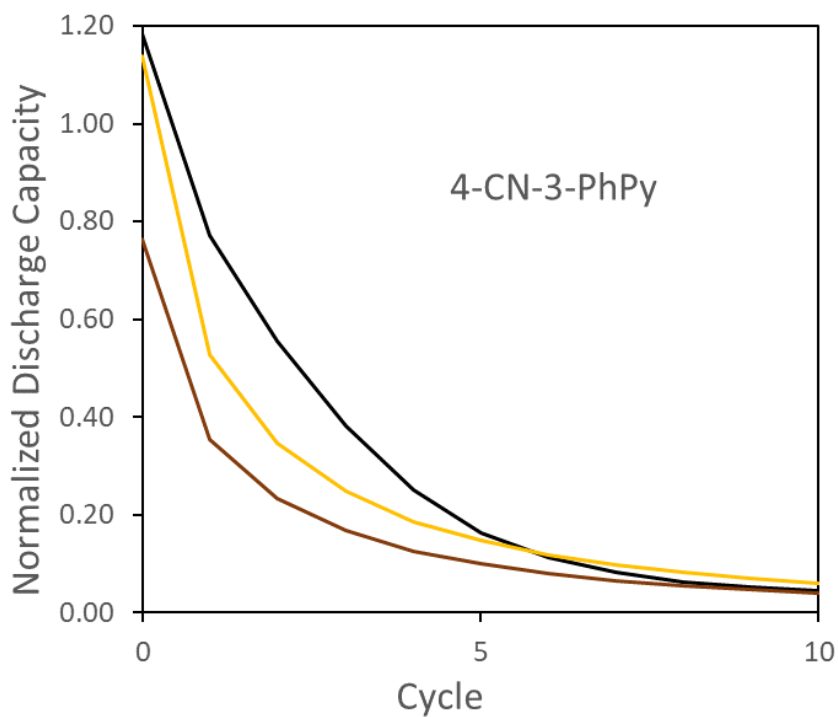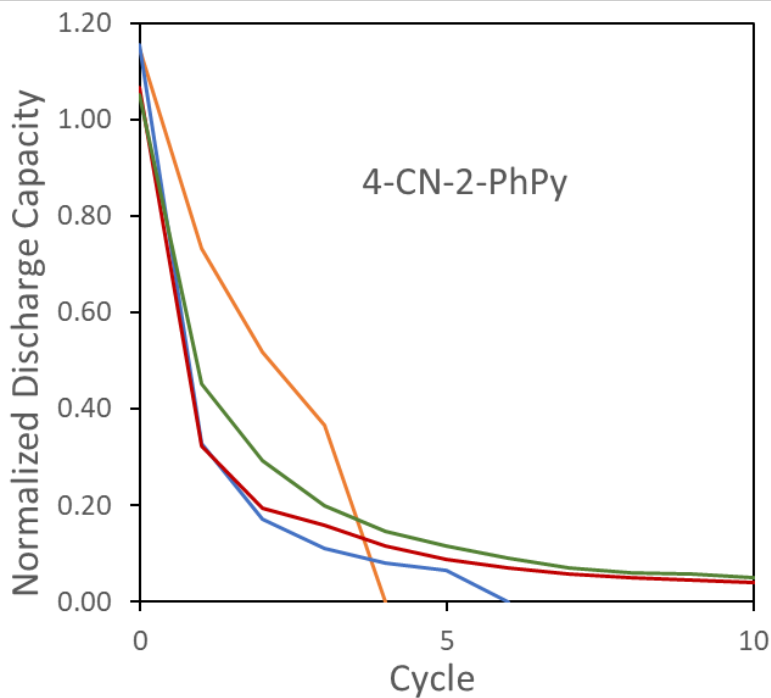2-CN-4-PhPy

3-CN-2-PhPy

3-CN-4-PhPy
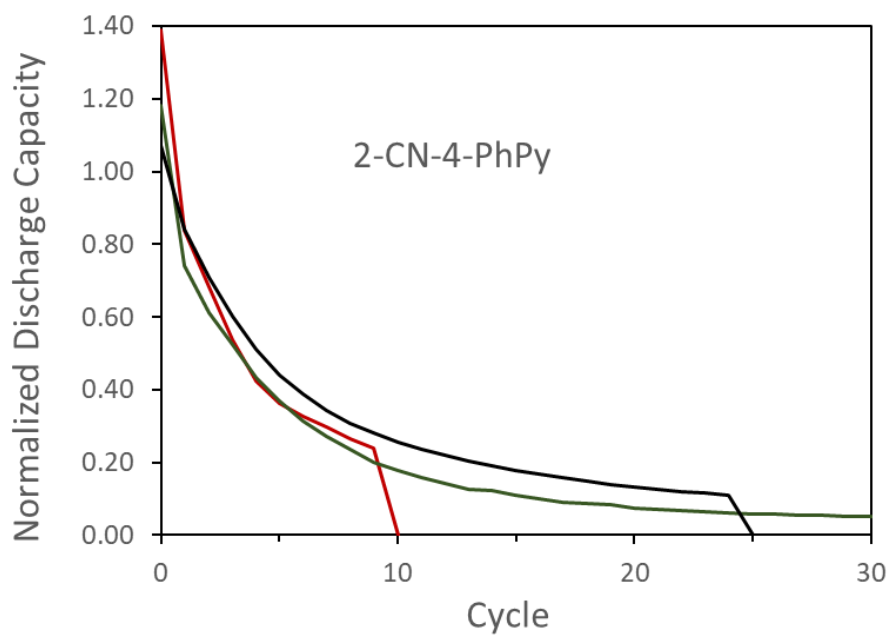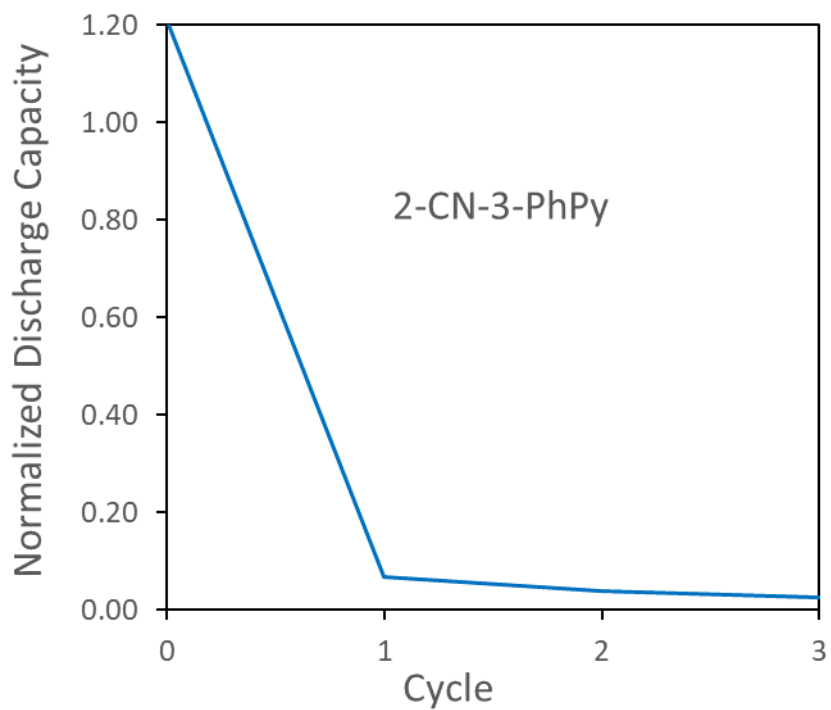
Figure S4. Normalized discharge capacity versus cycle number during bulk charge-discharge cycling for the cyanophenylpyridines. All runs used 5.0 mL of a 5.0 mM solution of active material in 0.50 M [NBu₄][PF₆] in CH₃CN, with a current of 5.00 mA. Different colors represent separate runs of the experiment. Capacity is normalized to a theoretical capacity of 0.67 mAh.

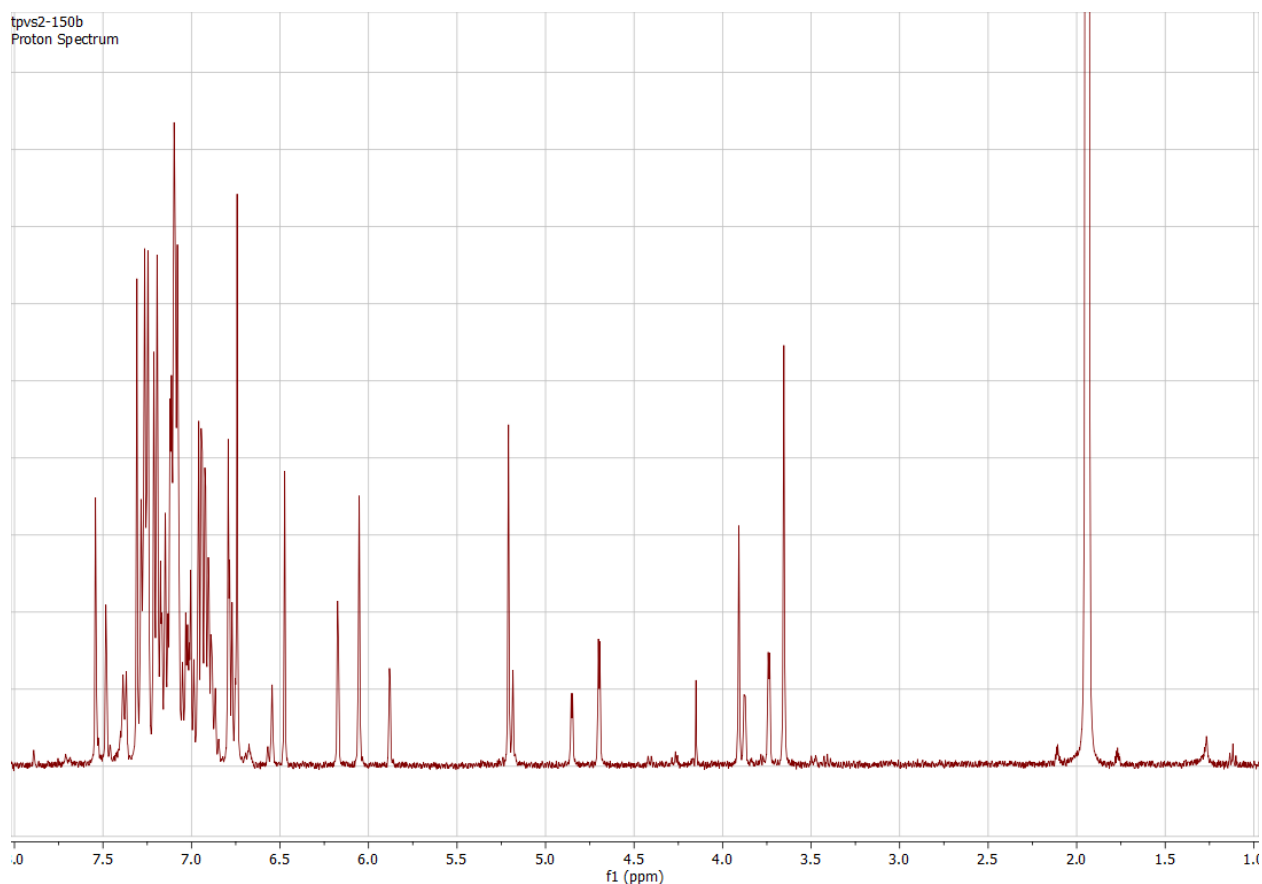# V. NMR of Reduced 3-CN-5-PhPy; Other Reported Low-Potential Anolytes

tpvs2-150b
Proton Spectrum

f1 (ppm)

Figure S5. ^{1}H NMR spectrum of a solution produced by the bulk-electrolysis reduction of 3-CN-5-PhPy in CD$_3$CN with 0.4 M KPF$_6$ supporting electrolyte.

Table S4. Battery Voltage and Capacity Fade Rate of Low-Potential Anolyte RFBs

anolyte	catholyte	nominal battery voltage (V)	capacity fade rate	reference
2-methyl-benzophenone	DBMMB	2.97	~ 0.5 %/cycle	3
N-methylphthalimide	ferrocene	1.97	0.16 %/day	4
9-fluorenone	DBMMB	2.37	~ 0.1-1 %/cycle	5
2,1,3-benzothiadiazole	DBMMB	2.36	0.1 %/cycle	6

DBMMB =
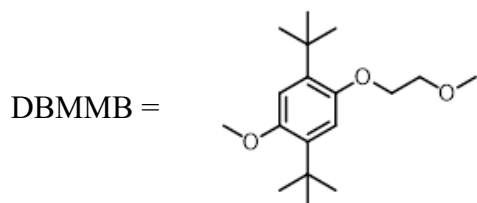
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