Supporting Information

Tuning-up and Driving a Redox-active Rotor

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Synthesis and Characterization

Materials

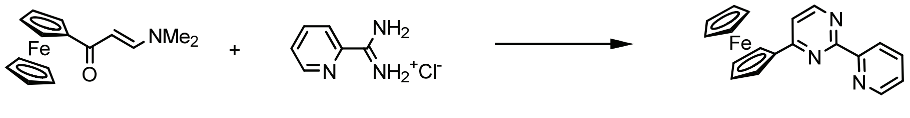
2,9-Bis(9-anthracenyl)-1,10-phenanthroline (L$_{Anth2}$)[1] and tetrakis(acetonitrile)copper(I) tetrafluoroborate[2] were prepared according to literature methods.

3-(Dimethylamino)-1-ferrocenylprop-2-en-1-one (1)

Acetylferrocene(1.14g, 5mmol) was refluxed in 5 ml of dimethylformamide dimethyl acetal for 2 days. The solvent was evaporated, and the residue was purified by silica-gel column chromatography eluted with chloroform/methanol. The crude product washed with diethylether gave dark red microcrystals. Yield: 0.48 g (34 %).

^{1}H-NMR (500MHz, CDCl$_3$) δ7.71(d, J = 13 Hz, 1H), 5.36(d, J = 13 Hz, 1H), 4.78(s, 2H), 4.38(s, 2H), 4.16(s, 5H), 3.0(br, 6H).

2-(2-pyridyl)-4-ferrocenylpyrimidine (H-Fcpmpy)

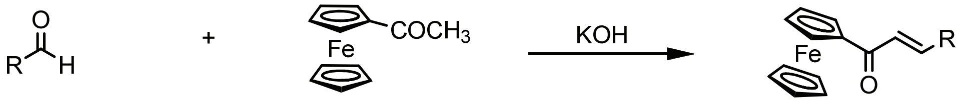


Under a nitrogen atmosphere, sodium hydride (2.3mmol, 55% dispersion in oil) was carefully added to an anhydrous ethanol (5 mL). **1** (283 mg, 1mmol) and 2-pyridylamidinium chloride (236 mg, 1.5 mmol) was added and refluxed for 15h. Resulting light-brown suspension was filtered, and the solvent was evaporated. The residue was purified with alumina column chromatography eluted with chroloform to gave a brown solid Yield: 266 mg (78 %).

^{1}H-NMR (500MHz, CDCl$_3$) δ8.85(d, J = 4.0Hz, 1H), 8.76(d, J = 5.3Hz, 1H), 8.61(d, J = 7.8Hz, 1H), 7.89(td, J = 7.8Hz, 1.4Hz 1H), 7.42(ddd, J = 7.8Hz, 4.4Hz, 1.4Hz 1H), 7.31(d, J = 5.3Hz, 1H), 5.11(t, *J* = 1.9 Hz, 2H) , 4.55(t, *J* = 1.9 Hz, 2H) , 4.08(s, 5H).

Elemental Analysis Calcd. for $C_{19}H_{15}FeN_3{\cdot}0.2H_2O$, C: 66.19, H: 4.50, N: 12.19. Found, C: 66.24. H: 4.43, N: 11.94.

Typical Procedure for the synthesis of 3-aryl-1-ferrocenylprop-2-en-1-one (aryl = 4-tolyl, 1-naphtyl, 9-anthryl)



To a suspension of Acetylferrocene(2.28g 10mmol) in 10% KOHaq (7ml) and ethanol (7ml), arylaldehyde (10 mmol) was added. Ethanol was added until the reaction mixture became a homogeneous solution. The product was precipitated in the course of the reaction, filtered and washed with small amount of ethanol and water.

In the case of 9-anthryl compound, the solvent was evaporated from the reaction mixture and purified with silica-gel chromatography eluted with chloroform.

Yield: 30-50%

3-(4-tolyl)-1-ferrocenylprop-2-en-1-one

^{1}H-NMR (500MHz, $CDCl_3$) δ 7.78(d, *J* = 16 Hz, 1H), 7.56(d, *J* = 8 Hz, 2H), 7.24(d, *J* = 8 Hz, 2H) , 7.10(d, *J* = 16 Hz, 1H) , 4.92(t, *J* = 1.9 Hz, 2H) , 4.56(t, *J* = 1.9 Hz, 2H) , 4.21(s, 5H), 2.40(s, 3H).

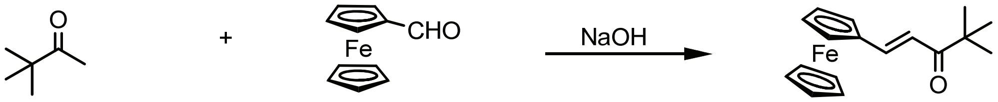
3-(1-naphthyl)-1-ferrocenylprop-2-en-1-one

^{1}H-NMR (500MHz, $CDCl_3$) δ 8.64(d, *J* = 15Hz, 1H), 8.32(d, *J* = 8.5 Hz, 1H), 7.94-7.88(m, 3H), 7.61(t, *J* = 6.8 Hz, 1H) , 7.57-7.53(m, 2H), 7.22(d, *J* = 15 Hz, 1H), 4.96(t, *J* = 1.9 Hz, 2H), 4.62(t, *J* = 1.9 Hz, 2H) 4.25(s, 5H).

3-(9-anthryl)-1-ferrocenylprop-2-en-1-one

^{1}H-NMR (500MHz, $CDCl_3$) δ 8.73(d, *J* = 16 Hz, 1H), 8.49(s, 1H), 8.35(d, *J* = 8 Hz, 2H), 8.07-8.04(m, 2H), 7.56-7.51(m, 4H), 7.13(d, *J* = 16 Hz, 2H) , 4.92(t, *J* = 1.9 Hz, 2H) , 4.62(t, *J* = 1.9 Hz, 2H) , 4.30(s, 5H), 2.40(s, 3H).

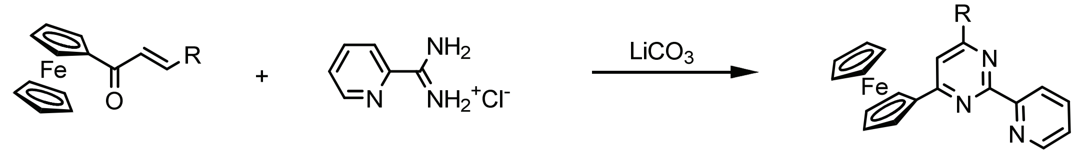
3-ferrocenyl -1-*tert*-butyl-prop-2-en-1-one



NaOH (0.2 g, 5 mmol), pinacolon (0.5 g, 5mmol) and ferrocenylcalbaldehyde(1.07g. 5mmol) were ground until liquid reactant turned to solid. The resulted mixture is extracted with dichloromethane, washed with sat. NH_4Claq and water. The crude product was purified with silica-gel column chromatography eluted with chloroform. Yield: 399 mg (27 %).

^{1}H-NMR (500MHz, $CDCl_3$) δ7.58(d, J = 15 Hz, 1H), 6.72(d, J = 15 Hz, 1H) , 4.52(t, J = 1.8 Hz, 2H) , 4.42(t, J = 1.8 Hz, 2H) , 4.15(s, 5H), 1.20(s, 9H).

Typical Procedure for the synthesis of RFcpmpy (R = 4-tolyl, 1-Naph, 9-Anth)



Under a nitrogen atmosphere, 3-aryl-1-ferrocenylprop-2-en-1-one (1mmol), 2-pyridylamidinium chloride (3mmol) and $LiCO_3$(10 mmol) was stirred at 100°C in dimethylacetamide (5 mL) for 24 h. The resulted solution was extracted with dichloromethane or ethyl acetate, and purification with alumina column chromatography eluted with ethyl acetate/hexane or dichloromethane gave the compound in 10-30% yield.

4-tolylFcpmpy

^{1}H-NMR (500MHz, $CDCl_3$) δ8.89(d, J = 4.8 Hz, 1H), 8.66(d, J = 8.0 Hz, 1H), 8.17(d, J = 8.2 Hz, 2H), 7.90(td, J = 7.5 Hz, 1.5 Hz, 1H), 7.71(s, 1H), 7.42(ddd, J = 7.5Hz, 4.5Hz, 1.0Hz, 1H), 7.36(d, J = 8.2 Hz, 2H), 5.18(t, J = 2.0 Hz, 2H), 4.55(t, J = 2.0 Hz, 2H), 4.10 (s, 5H), 2.46(s, 3H).

Elemental Analysis Calcd. for $C_{26}H_{21}FeN_3{\cdot}0.2H_2O$, C: 71.80, H: 4.96, N: 9.66. Found, C: 71.98, H: 5.01, N: 9.32.

1-NaphFcpmpy

^{1}H-NMR (500MHz, $CDCl_3$) δ8.87(d, J = 4.7 Hz, 1H), 8.66(d, J = 8.2 Hz, 1H), 8.22-8.20(m, 1H), 7.99(d, J = 8.2 Hz, 1H), 7.97-7.94(m, 1H), 7.90(td, J = 7.7 Hz, 1.7 Hz, 1H), 7.82(d, J = 6.7 Hz, 1H), 7.64-7.60(m, 2H), 7.57-7.52(m, 2H), 7.41(dd, J = 7.2Hz, 4.9Hz, 1H), 5.17(t, J = 1.7 Hz, 2H), 4.56(t, J = 1.7 Hz, 2H), 4.14(s, 5H).

Elemental Analysis Calcd. for $C_{29}H_{21}FeN_3{\cdot}0.6(C_4H_{10}O)$, C: 73.69, H: 5.32, N: 8.21. Found, C: 73.41. H: 4.97, N: 8.40.

9-Ant-Fcpmpy

^{1}H-NMR (500MHz, $CDCl_3$) δ8.85(d, J = 3.1 Hz, 1H), 8.69(d, J = 7.8 Hz, 1H), 8.60(s, 1H), 8.09(d, J = 8.5 Hz, 2H), 7.88(t, J = 6.7 Hz, 1H), 7.77(d, J = 8.5 Hz, 2H), 7.58(s, 1H), 7.51-7.47(m, 2H), .7.44-7.38(m, 3H), 5.30(s, 2H), 5.18(s, 2H), 4.15(s, 5H).

Elemental Analysis Calcd. for $C_{29}H_{21}FeN_3{\cdot}0.26(CH_2Cl_2)$, C: 74.05, H: 4.39, N: 7.79. Found, C: 74.37. H: 4.73, N: 7.36.

^{t}BuFcpmpy

Under a nitrogen atmosphere, 3-ferrocenyl-1-*tert*-butyl-prop-2-en-1-one (296 mg, 1mmol), 2-pyridylamidinium chloride (473 mg, 3mmol) and $LiCO_3$(740 mg, 10 mmol) was stirred at 100°C in dimethylacetamide (5 mL) for 21 h. The resulted solution was extracted with ethyl acetate, purified with alumina column chromatography eluted with ethyl acetate/hexane. Yield: 101mg (25%)

^{1}H-NMR (500MHz, $CDCl_3$) δ 8.86(d, J = 4.3 Hz, 1H), 8.58(d, J = 7.8 Hz, 1H), 7.86(td, J = 7.8 Hz, 1.6 Hz, 1H), 7.39-7.36(m, 2H),5.12(t, J = 1.7 Hz, 2H) , 4.50(t, J = 1.7 Hz, 2H) , 4.06(s, 5H), 1.48(s, 9H).

Elemental Analysis Calcd. for $C_{23}H_{23}FeN_3{\cdot}$, C: 69.53, H: 5.84, N: 10.58. Found, C: 69.36. H: 5.88, N:10.60.

Typical Procedure for the synthesis of [Cu(RFcpmpy)(L_{Anth})]BF_4

Under a nitrogen atmosphere, 2,9-bis(9-anthracenyl)-1,10-phenanthroline and 1equiv. of $[Cu(CH_3CN)_4]BF_4$ was stirred for 30min in dichloromethane. To the resulted orange clear solution, 1equiv. of RFcpmpy was added and the solution immediately changed to deep red. To the filtered solution, diethyl ether was added to precipitate the product as a deep red solid to gave the complex in 60-90% yield.

^{1}H-NMR spectra of Cu complexes are shown in Figure S1,S2.

[Cu(HFcpmpy)(L_{Anth2})]BF_4

ESI-TOF-MS *m*/*z* 936.04 (calcd for $[M-BF_4]^+$, 936.18)

Elemental Analysis Calcd. for $C_{59}H_{39}CuBF_4FeN_5{\cdot}0.2CH_2Cl_2$, C: 68.29, H: 3.81, N: 6.73. Found, C: 68.19. H: 4.12, N: 6.49.

[Cu(4-tolylFcpmpy)(L_{Anth2})]BF_4

ESI-TOF-MS *m*/*z* 1026.15 (calcd for $[M-BF_4]^+$, 1026.23)

Elemental Analysis Calcd. for $C_{66}H_{45}CuBF_4FeN_5{\cdot}0.2CH_2Cl_2$, C: 70.28, H: 4.05, N: 6.19. Found, C: 70.44. H: 4.35, N: 5.82.

[Cu(1-NaphFcpmpy)(L_{Anth2})]BF_4

ESI-TOF-MS(HR) *m*/*z* 1062.2264 (calcd for $[M-BF_4]^+$, 1062.2323)

Elemental Analysis Calcd. for $C_{60}H_{41}CuBF_4FeN_5 \cdot 0.2CH_2Cl_2 \cdot 0.8C_4H_{10}O$, C: 72.39, H: 4.21, N: 5.64. Found, C: 72.20. H: 4.28, N: 5.40.

[Cu(9-AnthFcpmpy)(L_{Anth2})]BF_4

ESI-TOF-MS *m*/*z* 1112.2463 (calcd for $[M-BF_4]^+$, 1112.2480)

Elemental Analysis Calcd. for $C_{73}H_{47}CuBF_4FeN_5 \cdot 0.2CH_2Cl_2 \cdot 1.8C_4H_{10}O$, C: 71.49, H: 4.88, N: 5.18. Found, C: 71.33, H: 4.48, N: 4.78.

[Cu(^{t}BuFcpmpy)(L_{Anth2})]BF_4

ESI-TOF-MS *m*/*z* 993.43 (calcd for $[M-BF_4]^+$, 992.24)

Elemental Analysis Calcd. for $C_{63}H_{47}CuBF_4FeN_5 \cdot 0.3CH_2Cl_2$, C: 68.76. H: 4.34, N: 6.33. Found, C: 68.96. H: 4.51, N: 5.94.

Physical Measurements

X-ray structural analysis

Single crystals of [Cu(FcMpmpy)(L_{Anth})]BF_4 were obtained by diffusing benzene into a acetone solution, and *p*-xylene into a dichloromethane solution of the complex. Diffraction data for single crystal X-ray analysis were collected with AFC10 diffractometer coupled with Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated MoKα radiation (λ = 0.7107 Å). Lorentz-polarization and numerical absorption corrections were performed with the program Crystal Clear 1.3.6. The structures were solved by the direct method using SIR 92 program[3] and refined against F^2 using SHELXL-97.[4] WinGX software was used to prepare the material for publication.[5] There are disorders in the position of BF_4^- anion and solvent molecules in the crystals, which were treated by PART option of SHELEX-97. The crystallographic data are listed in Table S1.

Electrochemical measurements

Cyclic voltammograms were recorded with ALS 650B electrochemical analyzers (BAS. Co., Ltd.). The working electrode was a 3mmϕ glassy carbon, a platinum wire served as the auxiliary electrode, and the reference electrode was an Ag^+/Ag electrode (a silver wire immersed in 0.1 M Bu_4NClO_4/0.01 M $AgClO_4/CH_3CN$). Sample concentration was 5×10^{-4} M. The solutions were deoxygenated with pure argon before measurement.

A simulated cyclic voltammogram were obtained with the BAS Digisim 3.03a software, based on square scheme shown in Figure 3d.

Thermodynamic Analysis

The molar ratios of the isomers were determined with the signal integration in ^{1}H-NMR spectra, recorded with a Bruker DRX500 spectrometer. The sample in acetone-d_6 was rapidly (~10min) cooled to 213K , then spectra at variable temperatures were recorded in the heating process, taking ca. 20 min to record each 10 K interval data. The van't Hoff plot was plotted according to reference 6, setting the equilibrium constant as [*o*-Fc]/[*i*-Fc]. The data points obeyed linearity in the temperature region where the inversion motion is sufficiently fast to reach the equilibrium state.

The relative isomer stability in monooxidized state was determined from the relative stability in reduced state and redox potential of each isomer[7].

$$RTlnK = nFE^0$$

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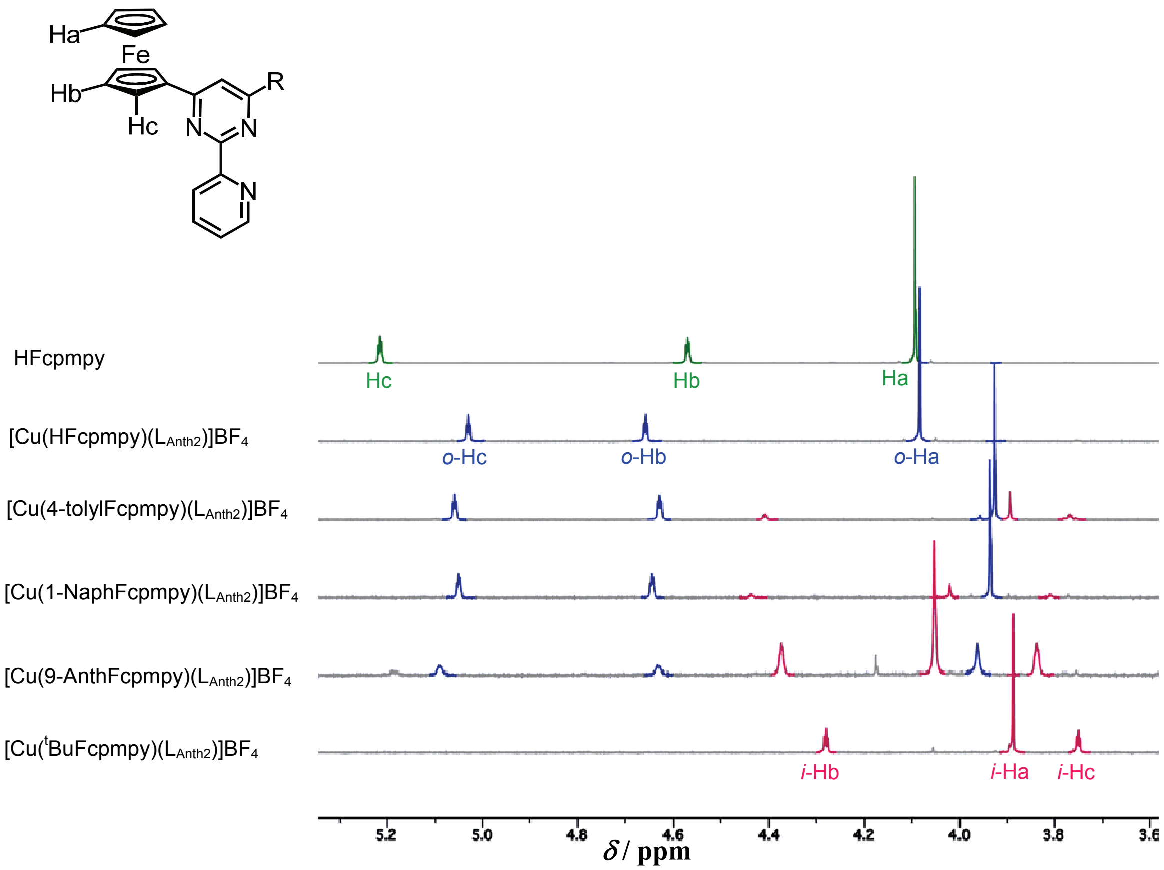


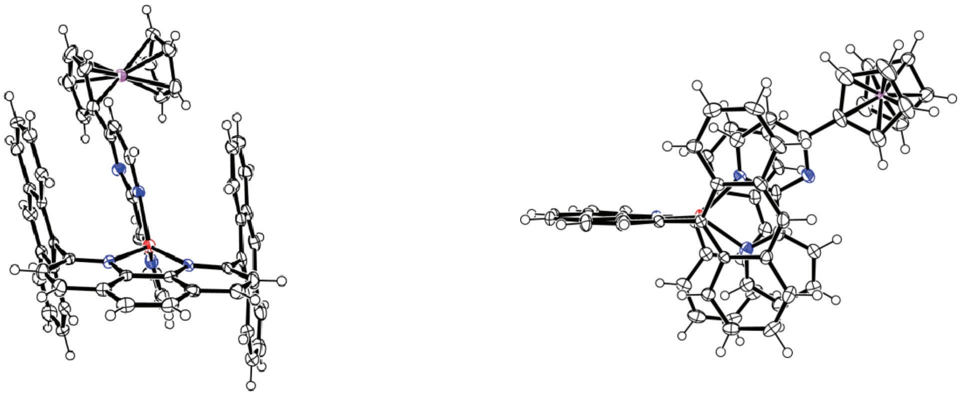
Figure S1 ^{1}HNMR spectra of [Cu(RFcpmpy)(L$_{Anth2}$)]BF$_4$ in acetone-d_6 recorded at 293 K. Signals assigned to isomers are shown in red for *i*-Fc and ble for *o*-Fc.

Table S-1 Crystallographic Data and Refinement Parameters

Compound	$[Cu(HFcpmpy)(L_{Anth2})]BF_4 \cdot (benzene)_3$	$[Cu(1\text{-}NaphFcpmpy)(L_{Anth2})]BF_4 \cdot (CH_2Cl_2)_2$	$[Cu(9\text{-}AnthFcpmpy)(L_{Anth2})]BF_4 \cdot (CH_2Cl_2)\ (p\text{-}xylene)_2$
Formula	$C_{77}H_{57}BCuF_4FeN_5$	$C_{71}H_{49}BCl_4CuF_4FeN_5$	$C_{90}H_{69}BCl_2CuF_4FeN_5$
FW	1258.48	1320.15	1462.15
Crystal system	triclinic	monoclinic	triclinic
a / Å	10.747(5)	11.964(5)	11.548(5)
b / Å	11.762(5)	22.314(5)	15.399(5)
c / Å	12.896(5)	24.781(5)	22.187(5)
α	75.128(5)	90	71.587(5)
β	70.329(5)	117.169(12)	85.665(5)
γ	86.267(5)	90	68.815(5)
V / Å^3	1483.2	5886	3487
Spacegroup	$P1$	$P2_1/c$	P-1
Z	1	4	2
$R_1{}^a$	0.052	0.0562	0.0696
$wR_2{}^b$	0.1426	0.1515	0.197
GOF^c	1.037	1.028	1.063

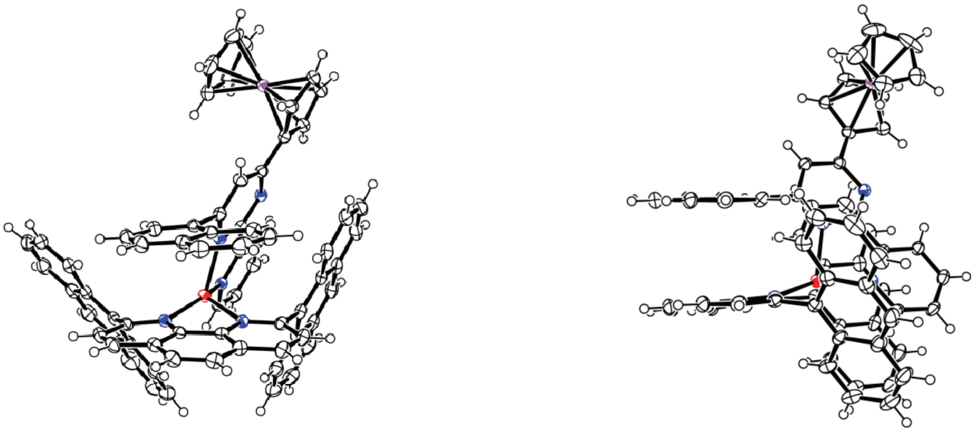
$^a R1 = \Sigma||F^o|-|F^c||/\Sigma|F^o|$ ($I>2\sigma(I)$). $^b wR2 = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma w(F^{o2})^2]^{1/2}$ ($I>2\sigma(I)$). ^{c}GoF = $[\Sigma(w(F^{o2}-F^{c2})^2/\Sigma(N^r-N^p)^2]$

$[Cu(4\text{-}tolFcpmpy)(L_{Anth2})]BF_4{\cdot}(benzene)_3$



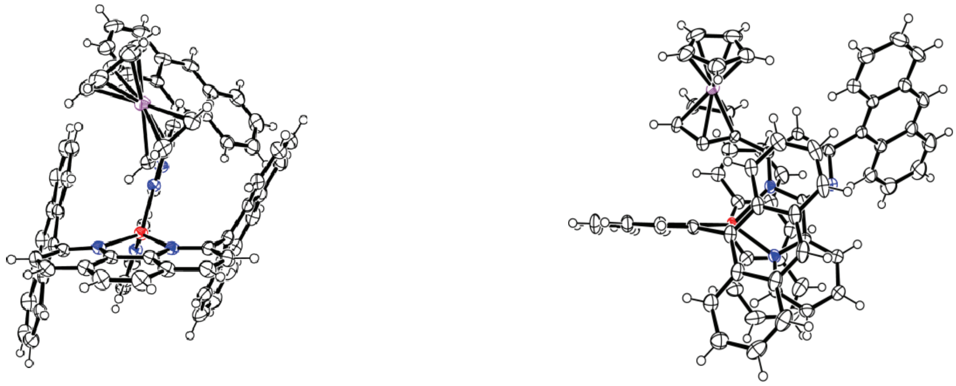
Front view **Side View**

$[Cu(1\text{-}NaphFcpmpy)(L_{Anth2})]BF_4{\cdot}(CH_2Cl_2)_2$



Front view **Side View**

$[Cu(9\text{-}AnthFcpmpy)(L_{Anth2})]BF_4{\cdot}(CH_2Cl_2)\ (p\text{-}xylene)_2$



Front view **Side View**

Figure S3 ORTEP drawings of $[Cu(RFcpmpy)(L_{Anth2})]^+$. Anions and Sovent molecules are omitted for clarity. Ellipsoids are drawn in 50% probability.

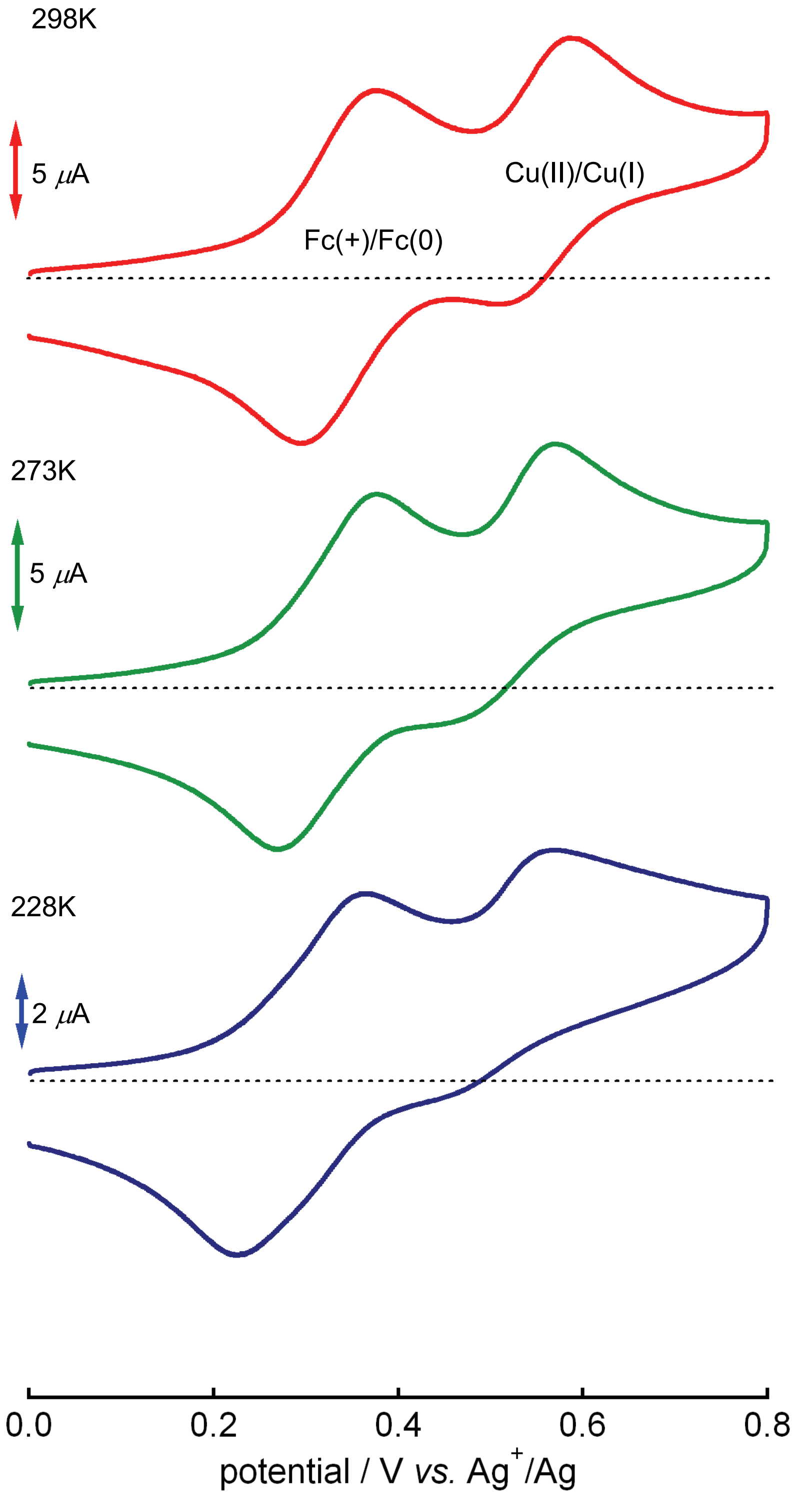


Figure S4 Cyclic voltammograms of [Cu(9-AnthFcpmpy)(L_{Anth2})]$^+$ in 0.1M $^n Bu_4NBF_4$.-acetone recorded in 298 K(red), 273 K(green) and 228 K(blue) with scan rate at 0.1 Vs^{-1}.

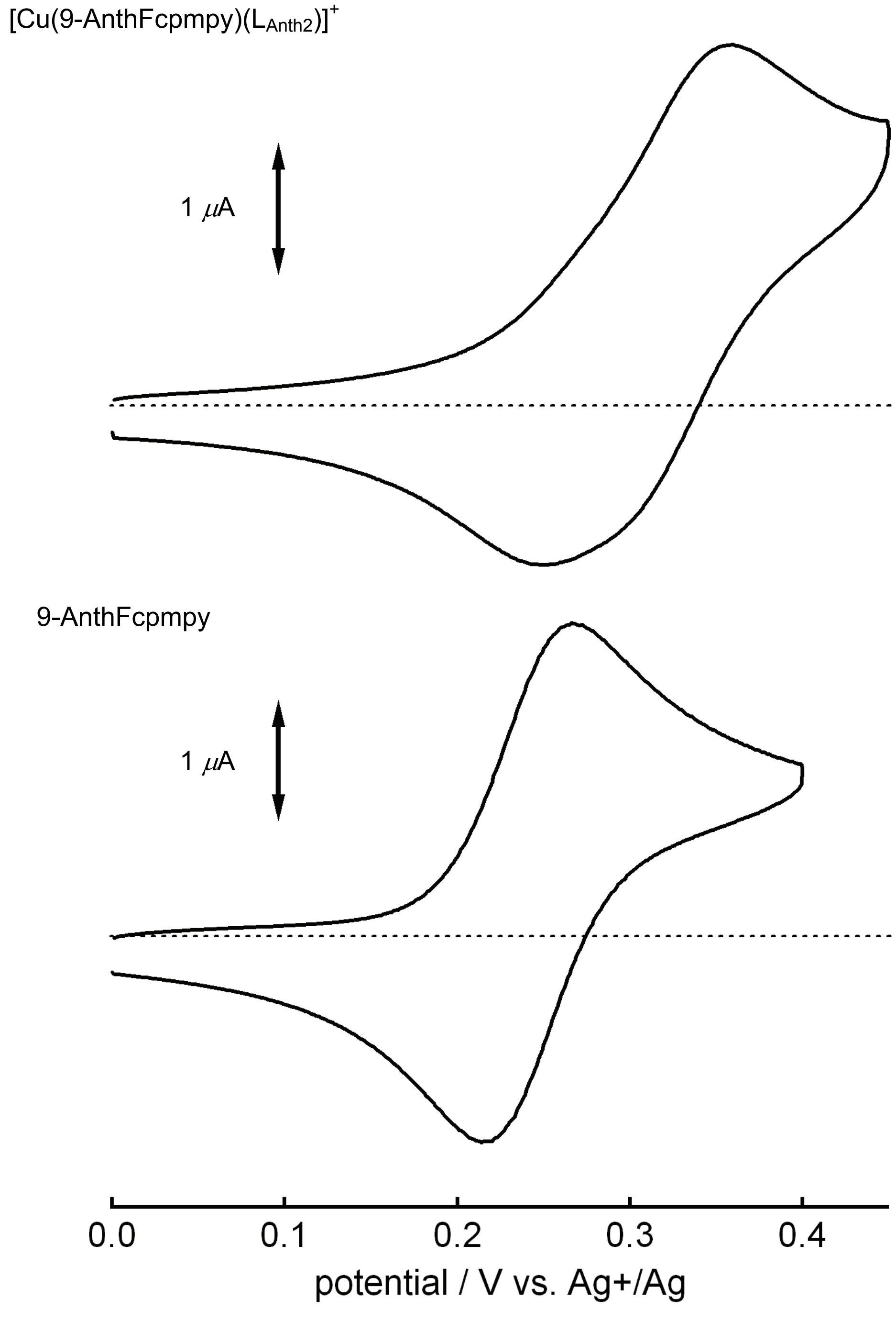


Figure S5 Cyclic voltammograms of [Cu(9-AnthFcpmpy)(L$_{Anth2}$)]$^+$ (above,at 228 K) and 9-AnthFcpmpy(below, at 213 K) in 0.1M ^{n}Bu$_4$NBF$_4$.-acetone recorded with scan rate at 0.025 Vs^{-1} .

Table S-2 Electrochemical Parameters from Simulation Analysis

E_i / V	0.325
E_o / V	0.265
K_{io}(Fc)	0.45
k_{io}(Fc) / s^{-1}	0
k_{io}(Fc^+) / s^{-1}	0.025/100
D / cm^2s^{-1}	3×10^{-6}
R /Ω	800
Cdl / F	1.5×10^{-6}

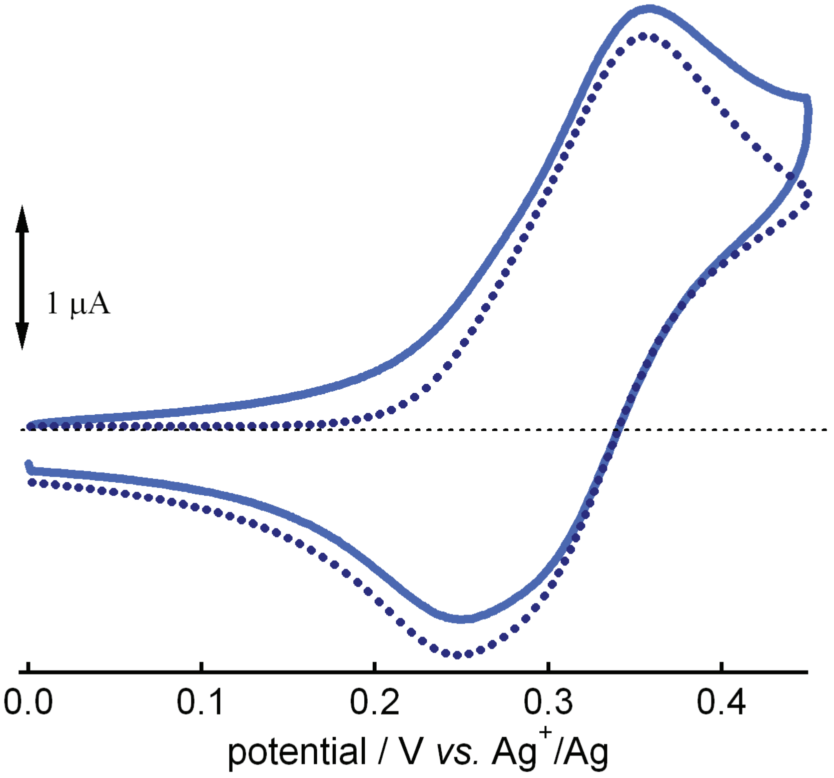


Figure S6 Cyclic voltammograms of [Cu(9-AnthFcpmpy)(L_{Anth2})]$^+$ in 0.1M $^nBu_4NBF_4$.-acetone recorded with scan rate at 0.025 Vs^{-1} at 228 K(straight line) and its simulated voltammogram (dotted line).

References

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