

Supplementary Information

for

Thioether S-Ligation in a Side-on μ - η^2 : η^2 -Peroxo Dicopper(II) Complex

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Figure S-5. Cyclic voltammograms of ferrocene (Black), **1A** (red), and **2A** (blue) (DMF, 100 mM TBAPF₆, 1 mM Cu complex).

Table S-1. Selected bond distances and angles of $[(ANS)Cu^I(CH_3CN)]BARf$.

Table S-2. Selected bond distances and angles of $[(ANS)Cu^I(Cl)_2]$.

I. General Considerations and Instrumentation

All reagents and solvents were purchased from commercial sources and were of reagent quality. Dichloromethane (CH_2Cl_2), diethylether (Et_2O), and methanol (CH_3OH) were purified and dried by passing through a double alumina column solvent purification system by Innovative Technologies, Inc. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. Deoxygenation of these solvents was achieved by bubbling Ar for 30 min and/or carrying out three freeze/pump/thaw cycles. Air-sensitive compounds were handled under an Ar atmosphere using standard Schlenk techniques or within a MBraun Labmaster 130 inert-atmosphere (N_2 atmosphere; < 1 ppm O_2 , < 1 ppm H_2O) glove-box. Molecular oxygen (Airgas Inc., Radnor, PA) was dried by passing it through a laboratory gas drying unit (W. A. Hammond Drierite Co., Xenia, Ohio) and introduced to reaction solutions by bubbling through an 18-gauge, 24-inch-long stainless steel syringe needle. $[\text{Cu}^{\text{I}}(\text{MeCN})_4]\text{B}(\text{C}_6\text{F}_5)_4$ was prepared by literature procedures.^{1,2} $\text{KB}(\text{C}_6\text{F}_5)_4$ was purchased from BOULDER SCIENTIFIC Company.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a Bruker 400 MHz spectrometer and chemical shifts are reported in ppm (δ) downfield from an internal TMS (Me_4Si) reference and the residual solvent proton peak. **Infrared Spectra** were recorded on a Mattson Instruments 4030 Galaxy Series FT-IR spectrometer. Measuring the solution IR spectra of carbonyl adducts (as a solution in THF) were recorded using standard solution IR cells. Air sensitive cuprous THF solutions were prepared in a glove box (N_2 filled, MBraun) and then removed using 20 ml vials sealed with a 14/20 rubber septum. Carbon monoxide gas (Airgas Inc., Radnor, PA) was introduced to the corresponding solution via bubbling for 20-30 s through an 18-gauge, 24-inch-long stainless steel syringe needle. The resulting solution was transferred to a solution IR cell by the gas-tight syringe under the CO atmosphere. **Elemental Analyses** were performed by Desert Analytics, Tucson, AZ for air-sensitive samples. **Mass Spectrometry** was conducted at the mass spectrometry facility at the Johns Hopkins University. ESI mass spectra (Johns Hopkins University facility) were acquired using a Finnigan LCQDeca ion-trap mass spectrometer equipped with an electrospray ionization source (Thermo Finnigan, San Jose, CA). Samples were dissolved in CH_3OH and introduced into the instrument at a rate of 10ml/min using a syringe pump via a silica capillary line. The heated capillary temperature was 250 $^\circ\text{C}$ and the spray voltage was 5kV. **Cyclic voltammetry** measurements were undertaken in DMF using a BAS 100B electrochemical analyzer with a glassy carbon working electrode and a platinum wire auxiliary electrode. Potentials were recorded versus a Ag/AgNO_3 electrode. The voltammograms are plotted versus the $\text{Fe}(\text{cp})_2^{+/0}$ potential which was measured as an external standard. Scans were run at 50-200 mV/s under an argon atmosphere using ca. 0.1M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. **X-ray Crystallography** was performed at the X-ray diffraction facility at Johns Hopkins University. Suitable single crystals of $[(\text{ANS})\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$ (**1A**) and $[(\text{ANS})\text{Cu}^{\text{II}}(\text{Cl})_2]$ (**1B**) were mounted in Paratone-N oil on the end of a glass fiber and transferred to the N_2 cold stream (110K) of an Oxford Diffraction Xcalibur3 system equipped with

Enhance optics [Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$)] and a CCD detector. The frames were integrated and a face indexed absorption correction and an inter-frame scaling correction were also applied with the Oxford Diffraction *CrysAlisRED* software package (CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta). The structures were solved using direct methods and refined using the Bruker *SHELXTL* (v6.1) software package (Sheldrick, G.M. 2000). **Resonance Raman** was carried out in collaboration with Prof. Edward I. Solomon at Stanford University. Resonance Raman spectra were recorded on a Princeton Instruments ST-135 back-illuminated CCD detector and on a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/mm holographic spectrograph gratings. Excitation was provided by a Coherent I90C-K Kr⁺ ion laser ($\lambda_{\text{ex}} = 413.1\text{nm}, 568.2\text{nm}$) or an Innova Sabre 25/7 Ar⁺ CW ion laser ($\lambda_{\text{ex}}=379.5\text{nm}$). The spectral resolution was $< 2 \text{ cm}^{-1}$. Spectra were recorded at powers ranging from 5mW to 20mW at the sample and the samples were cooled to 77K in a quartz liquid nitrogen finger Dewar (Wilmad). Baseline spectra were collected using ground, activated charcoal. **Low Temperature UV-vis Spectra** were obtained with a Cary 50 Bio spectrophotometer equipped with a fiber optic coupler (Varian) and a fiber optic dip probe (Hellma: 661.302-QX-UV-2mm-for-low-temperature). For the low temperature measurements with a Cary 50 Bio spectrophotometer, a hexane/N₂(l) bath ($-94 \text{ }^\circ\text{C}$) was used and the steady temperature was monitored with the type T thermocouple thermometer (Model 650, Omega engineering, CT). Air sensitive solutions were prepared in a glove box (N₂ filled, MBraun) and carried out in custom made Schlenk tubes designed for the dip probe (Chemglass: JHU-0407-271MS) or Schlenk cuvettes. The cuvette assembly consisted of a two-window quartz cuvette (2 mm path) connected, via a 12 cm glass tube, to a 14/20 female ground glass joint.

II. Synthesis of Ligands

ANSH: N,N,N'-Trimethyl-1,3-propanediamine (1.16 g, 10 mmol) and propylene sulfide (0.89 g, 12 mmol) were dissolved in THF (20 ml). The reaction mixture was refluxed for 12 hrs under Ar. After cooling to room temperature and THF removed by rotary evaporation, the yellow oil obtained (1.65 g, 8.7 mmol, 87%) was purified by column chromatography (Al₂O₃, hexane:ethylacetate (1:1), R_f = 0.4). ¹H NMR (CDCl₃): δ 3.08 (m, 1H), 2.36 (m, 6H), 2.26 (s, 6H), 2.25 (s, 3H), 1.64 (q, J = 7.5 Hz, 2H), 1.26 (d, J = 3 Hz, 3H). ¹³C NMR (CDCl₃): δ 67.16 (CH₂), 57.89 (CH₂), 56.03 (CH₂), 45.68 (CH₃), 42.39 (CH₃), 33.55 (CH), 25.73 (CH₂), 21.73 (CH₃). ESI mass spectrum: m/z 191.35 (M + 1)⁺.

ANS: ANSH (2.5 g, 13.0 mmol) was dissolved in THF (20 ml). Sodium hydride (1.6 g, 65.0 mmol) was slowly introduced with vigorous stirring in the pre-cooled (ice bath) solution. The reaction mixture was stirred for 30 min under Ar. (2-Bromoethyl)benzene (2.92 g, 16 mmol) was introduced to the solution, and the mixture was refluxed for 16 hrs under Ar. After cooling to room temperature, ethanol (20 ml) was added to deactivate any unreacted sodium hydride. The resulting solution was

filtered and the solvent was removed by rotary evaporation. The crude yellow oil obtained was dissolved in CH_2Cl_2 and washed three times with brine. The organic layer was separated, dried over anhydrous MgSO_4 , then filtered and concentrated under vacuum. The yellow oil obtained (2.84 g, 9.6 mmol, 74%) was purified by column chromatography (Silica gel, CH_2Cl_2 :methanol (4:1) $R_f = 0.3$). ^1H NMR (CDCl_3): δ 7.28 (m, 5H), 2.87 (m, 5H), 2.40 (m, 6H), 2.30 (s, 6H), 2.22 (s, 3H), 1.71 (q, $J = 7.8$ Hz, 2H), 1.27 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 139.50 (Ar), 128.61 (Ar), 126.48 (Ar), 64.46 (CH_2), 57.77 (CH_2), 56.18 (CH_2), 50.98 (CH_3), 45.23 (CH_3), 42.83 (CH_2), 38.31 (CH), 36.68 (CH_2), 32.02 (CH_2), 19.90 (CH_3). ESI mass spectrum: m/z 295.64 ($M + 1$)⁺.

ANSPH: N,N,N' -Trimethyl-1,3-propanediamine (1.16 g, 10 mmol) and 2-chloroethyl phenyl sulfide (2 g, 11.6 mmol) were dissolved in acetonitrile (20 ml). Potassium carbonate (0.5 g, 36.2 mmol) was slowly introduced with vigorous stirring in solution. The reaction mixture was stirred for 30 min under Ar and then brought to a reflux for 16 hrs. After cooling to room temperature, the resulting solution was filtered and the solvent was removed by rotary evaporation. The crude yellow oil was dissolved in CH_2Cl_2 and washed three times with brine. The organic layer was separated, dried over anhydrous MgSO_4 , then filtered and concentrated under vacuum. The yellow oil obtained (0.60 g, 2.4 mmol, 24%) was purified by column chromatography (Silica gel, CH_2Cl_2 :methanol (4:1) $R_f = 0.4$). ^1H NMR (CDCl_3): δ 7.25 (m, 5H), 3.04 (t, $J = 8.25$ Hz, 2H), 2.64 (t, $J = 6.6$ Hz, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 2.27 (m, 5H), 2.21 (s, 6H), 1.65 (q, $J = 1.5$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 136.83 (Ar), 129.07 (Ar), 129.03 (Ar), 125.98 (Ar), 57.93 (CH_2), 56.82 (CH_2), 55.80 (CH_2), 45.67 (CH_3), 42.33 (CH_3), 31.35 (CH_2), 25.71 (CH_2). ESI mass spectrum: m/z 253.54 ($M + 1$)⁺.

III. Synthesis of Cu(I) Complexes and Their Copper-Dioxygen Adducts.

$[(\text{ANS})\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$: ANS (0.5 g, 1.70 mmol) and $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{B}(\text{C}_6\text{F}_5)_4$ (1.23 g, 1.36 mmol) were dissolved and stirred for 30 mins in degassed THF (15 ml) under Ar at room temperature. The complex precipitated as a greenish white powder upon addition of deoxygenated heptane (60 ml). The supernatant was decanted, and the resulting greenish white powder (1.23 g, 1.18 mmol, 87%) was washed two times with deoxygenated heptane and dried under vacuum. The product was recrystallized from ether/heptane. X-ray quality crystals were obtained via this route (Figure 1, main text). ^1H NMR (CD_2Cl_2): δ 7.29 (m, 5H), 3.14 (s, 2H), 3.00 (s, 3H), \sim 2.60(m, 6H), 2.36 (s, 9H), 2.18 (s, CH_3CN), \sim 1.70 (m, 2H), 1.41 (s, 3H). Anal. Calcd. for $\text{C}_{43}\text{H}_{33}\text{BCuF}_{20}\text{N}_3\text{S}$: C, 47.90; H, 3.09; N, 3.90. Found: C, 47.90; H, 3.29; N, 3.64. ESI-MS $[(\text{ANS})\text{Cu}^{\text{I}}]^+$ $\text{C}_{17}\text{H}_{30}\text{CuN}_2\text{S}$ exp m/z : 357.13 (100.0%), 358.13 (20.8%), 359.13 (47.0%), 360.12 (8.9%), 361.12 (2.1%) calc m/z : 357.14 (100.0%), 358.15 (20.2%), 359.14 (51.0%), 360.14 (9.8%), 361.14 (2.2%).

Table S-1. Selected bond distances and angles for [(ANS)Cu^I(CH₃CN)]BArF (**1A**).

Cu-N	Bond distance (Å)	X-Cu-X	Bond angle (°)
Cu(1)-S(1)	2.292(4)	N(1)-Cu(1)-N(2)	106.8(3)
Cu(1)-N(1)	2.056(7)	N(1)-Cu(1)-S(1)	112.6(3)
Cu(1)-N(2)	2.122(7)	N(2)-Cu(1)-S(1)	88.7(3)
Cu(1)-N(3)	1.935(8)	N(3)-Cu(1)-N(1)	114.8(5)
		N(3)-Cu(1)-N(2)	113.4(6)
		N(3)-Cu(1)-S(1)	117.2(5)

[(ANSPH)Cu^I(CH₃CN)]B(C₆F₅)₄: ANSPH (0.1 g, 0.40 mmol) and [Cu^I(CH₃CN)₄]B(C₆F₅)₄ (0.30 g, 0.33 mmol) were dissolved and stirred for 30 mins in deoxygenated THF (15 ml) under Ar at room temperature. The complex precipitated as a greenish white powder upon addition of degassed heptane (60 ml) into the reaction mixture. The supernatant was decanted, and the resulting greenish white powder (0.25 g, 0.24 mmol, 73%) was washed two times with degassed heptane and dried under vacuum. The product was recrystallized from ether/heptane. ¹H NMR (CD₂Cl₂): δ 7.45 (m, 5H), ~ 3.23 (m, 3H), ~ 2.64(m, 5H), 2.52 (s, 9H), 2.12 (s, CH₃CN), ~ 1.77 (m, 2H), 1.41 (s, 3H). Anal. Calcd. for C₄₀H₂₇BCuF₂₀N₃S: C, 46.37; H, 2.63; N, 4.06. Found: C, 46.12; H, 2.32; N, 3.91. ESI-MS [(ANSPH)Cu^I]⁺ C₁₄H₂₄CuN₂S exp m/z: 315.18 (100.0%), 316.18 (17.2%), 317.18 (51.2%), 318.18 (8.7%), 319.18 (2.2%) calc m/z: 315.10 (100.0%), 316.10 (16.2%), 317.09 (50.4%), 318.10 (8.3%), 319.09 (2.1%).

[(TMPD)Cu^I(CH₃CN)]B(C₆F₅)₄. Stack and co-workers³ previously synthesized TMPD-copper(I) complexes with triflate or perchlorate counteranions, but we wished to make the -B(C₆F₅)₄ salt for reasons of consistency (with our own complexes) and solubility. TMPD (0.1 g, 0.77 mmol) and [Cu^I(CH₃CN)₄]B(C₆F₅)₄ (0.71 g, 0.77 mmol) were dissolved and stirred for 30 mins in deoxygenated CH₂Cl₂ (15 ml) under Ar at room temperature. The complex precipitated as a white powder upon addition of degassed heptane (60 ml) to the reaction mixture. The supernatant was decanted, and the resulting white powder (0.65 g, 0.71 mmol, 92%) was washed two times with degassed heptane and dried under vacuum.

Generation of side-on peroxo dicopper(II) complex [{(ANS)Cu^{II}}]₂(μ-η²:η²-O₂²⁻)²⁺ (1P**) and bis-μ-oxo dicopper(III) [{(ANSPH)Cu^{III}}]₂(μ-O²⁻)₂²⁺ (**3O**) in Acetone.** [{(ANS)Cu^{II}}]₂(μ-η²:η²-O₂²⁻)²⁺ (**1P**) (UV-vis spectrum given in Figure 2. In main text) and bis-μ-oxo dicopper(III) [{(ANSPH)Cu^{III}}]₂(μ-O²⁻)₂²⁺ (**3O**) (Figure S-1, below) were generated in Acetone at -94 °C by bubbling O_{2(g)} (5-10 seconds) directly into the solution of either [(ANS)Cu^I(CH₃CN)]⁺ (**1A**) or [(ANSPH)Cu^I(CH₃CN)]⁺ (**3A**).

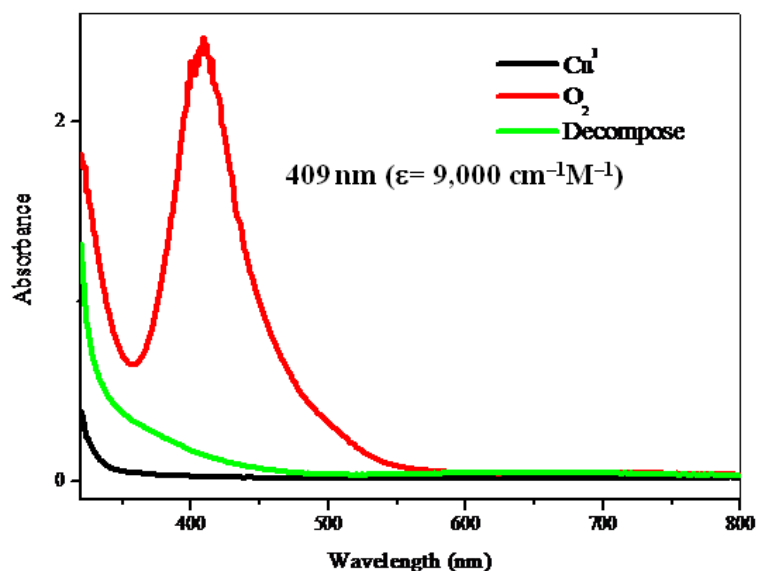


Figure S-1. UV-Vis changes upon reaction of O₂ with [(ANSPh)Cu(CH₃CN)]⁺ (**3A**) (**black**) in Acetone at -94 °C giving [{(ANSPh)Cu^{III}}₂(μ-O²⁻)₂]²⁺ (**3O**) (**red**); warming to RT leads to a decomposition product (**green**).

IV. Synthesis and Characterization of Copper(II) Complex (**1B**).

[(ANS)Cu^{II}(Cl)₂]: ANS (0.5 g, 1.70 mmol) and Cu^{II}Cl₂·H₂O (0.29 g, 1.7 mmol) were dissolved and stirred for 30 mins in degassed CH₂Cl₂ (15 ml) under Ar at room temperature. The resulting green solution was layered with diethylether and pentane. After 1-2 days a green crystalline material was isolated. After washing this two times with pentane and vacuum drying, the yield of green crystalline product was 0.38 g (0.89 mmol, 53%). UV-vis (CH₂Cl₂; λ_{max}, nm; ε, M⁻¹cm⁻¹, Figure S-2): 396, 3500; 293, 4000; 775, 200. Anal. Calcd. for C₁₇H₃₀Cl₂CuN₂S: C, 47.60; H, 7.05; N, 6.53. Found: C, 47.41; H, 7.17; N, 6.41. X-ray quality green crystals were obtained from the synthesis.

Table S-2. Selected bond distances and angles for [(ANS)Cu^{II}(Cl)₂].

Cu-N	Bond distance (Å)	X-Cu-X	Bond angle (°)
Cu(1)-S(1)	2.3870(6)	N(1)-Cu(1)-N(2)	96.10(7)
Cu(1)-N(1)	2.0714(18)	N(1)-Cu(1)-Cl(2)	91.49(5)
Cu(1)-N(2)	2.1362(19)	N(2)-Cu(1)-Cl(2)	141.80(5)
Cu(1)-Cl(1)	2.4394(6)	N(1)-Cu(1)-S(1)	178.39(6)
Cu(1)-Cl(2)	2.3061(6)	N(2)-Cu(1)-S(1)	84.46(5)
		Cl(2)-Cu(1)-S(1)	87.15(2)
		N(1)-Cu(1)-Cl(1)	93.24(5)
		N(2)-Cu(1)-Cl(1)	95.58(5)
		Cl(2)-Cu(1)-Cl(1)	121.36(2)
		S(1)-Cu(1)-Cl(1)	88.20(2)

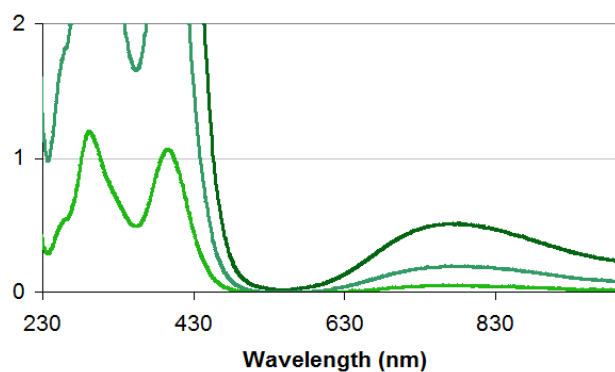


Figure S-2. Absorbance spectra of $[(\text{ANS})\text{Cu}^{\text{II}}(\text{Cl})_2]$ (**1B**) in CH_2Cl_2 .

V. rR spectrum for $[\{(\text{ANSPH})\text{Cu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2\}^{2+}$.

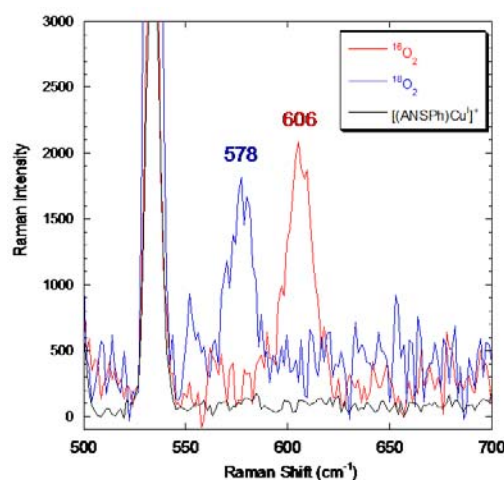


Figure S-3. rR spectra of $[\{(\text{ANSPH})\text{Cu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2\}^{2+}$ (**3O**) in acetone with $^{16}\text{O}_2$ (red) and $^{18}\text{O}_2$ isotopic substitution (blue) ($\lambda_{\text{ex}} = 406.7\text{nm}$, 77K, 5mW power).

VI. IR Spectra for CO-adducts of the Copper(I) Complexes.

IR samples were prepared as millimolar solutions in $\sim 2\text{ mL}$ of degassed THF (for **1A** and **2A**) in 20 mL vials sealed with rubber septa. These solutions were bubbled for $\sim 10\text{ s}$ with CO, then a small portion of the solution was transferred to an IR cell via syringe. Spectra recorded were based on the average of 16 scans, 2 cm^{-1} resolution.

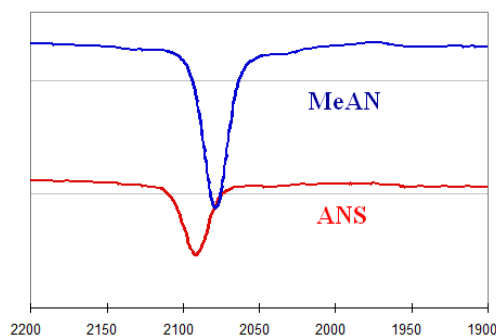


Figure S-4. IR spectra of $[(\text{ANS})\text{Cu}^{\text{I}}]^+$ (**1A**) in THF, $\nu_{\text{CO}} = 2092\text{ cm}^{-1}$ (red); and of $[(\text{MeAN})\text{Cu}^{\text{I}}]^+$ (**2A**) in same solvent, $\nu_{\text{CO}} = 2079\text{ cm}^{-1}$ (blue).

VII. Electrochemistry.

Cyclic voltammetry was carried out using a Bioanalytical Systems BAS-100B Electrochemistry Analyzer. The cell consisted of a three-necked round-bottom flask. The electrodes were inserted into the cell through hole-punched rubber septa, allowing for the entire system to be kept under an inert (Ar-N₂) atmosphere. A glassy carbon electrode, polished with diamond solution prior to each measurement, was used as the working electrode. The reference electrode was Ag/AgNO₃ (0.03M) in a 0.1M TBAPF₆ acetonitrile solution. A platinum wire was used as the counter electrode. The measurements were performed at room temperature under an Ar atmosphere in DMF solution containing 0.1 M TBAPF₆ and 10⁻³ M copper complex.

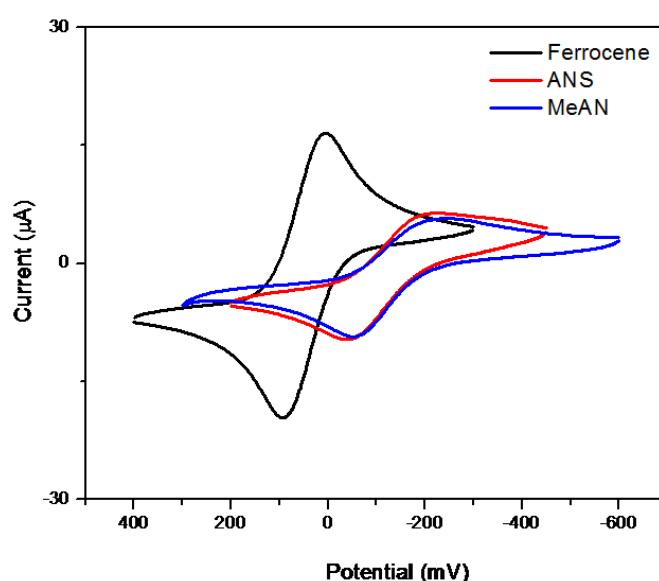


Figure S-5. Cyclic voltammograms of ferrocene (Black), **1A** (red), and **2A** (blue) (DMF, 100 mM TBAPF₆, 1 mM Cu complex). The E_{1/2} values obtained are given in Table 1 of the text.

VIII. References

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2. H. C. Liang, K. D. Karlin, R. Dyson, S. Kaderli, B. Jung and A. D. Zuberbuhler, *Inorg. Chem.* 2000, **39**, 5884.
3. V. Mahadevan, J. L. DuBois, B. Hedman, K. O. Hodgson and T. D. P. Stack, *J. Am. Chem. Soc.* 1999, **121**, 5583.