Electronic Supplementary Information for:

Electrodeposition behavior of homoleptic transition metal acetonitrile complexes interrogated with piezoelectric gravimetry

David J. Sconyers and James D. Blakemore*

Department of Chemistry, University of Kansas 1567 Irving Hill Road, Lawrence, KS 66045

*To whom correspondence should be addressed: blakemore@ku.edu

Contents

IR Spectra	
Figure S1. IR spectrum of [Mn(NCMe) ₄][BF ₄] ₂ .	S 3
Figure S2. IR spectrum of [Fe(NCMe) ₆ [BF ₄] ₂ .	S 4
Figure S3. IR spectrum of [Ni(NCMe) ₆][BF ₄] ₂ .	S5
Figure S4. IR spectrum of $[Cu(NCMe)_4][PF_6]$.	S 6
Figure S5. IR spectrum of [Zn(NCMe) ₆][BF ₄] _{2.}	S 7
Figure S6. IR spectra of the homoleptic acetonitrile complexes.	S 8
Electrochemistry & EQCM	
Figure S7. Cyclic voltammetry of [Mn(NCMe) ₄][BF ₄] ₂ treated with DMFH ⁺ .	S 9
Figure S8. Cyclic voltammetry of [Fe(NCMe) ₆][BF ₄] ₂ treated with DMFH ⁺ .	S10
Figure S9. Cyclic voltammetry of [Ni(NCMe) ₆][BF ₄] ₂ treated with DMFH ⁺ .	S11
Figure S10. Cyclic voltammetry of [Cu(NCMe) ₄][PF ₆] treated with DMFH ⁺ .	S12
Figure S11. Cyclic voltammetry of $[Zn(NCMe)_6][BF_4]_2$ treated with DMFH ⁺ .	S13
Figure S12. EQCM data of $[Mn(NCMe)_4][BF_4]_2$ treated with DMFH ⁺ .	S 14
Figure S13. EQCM data of $[Fe(NCMe)_6][BF_4]_2$ treated with DMFH ⁺ .	S15
Figure S14. EQCM data of [Ni(NCMe) ₆][BF ₄] ₂ treated with DMFH ⁺ .	S16
Figure S15. EQCM data of $[Cu(NCMe)_4][PF_6]$ treated with DMFH ⁺ .	S17
Figure S16. EQCM data of $[Zn(NCMe)_6][BF_4]_2$ treated with DMFH ⁺ .	S18
Figure S17. Mass profile of [Mn(NCMe) ₄][BF ₄] ₂ during cyclic voltammetry.	S19
Figure S18. Derivative of mass change with respect to time for Mn(II).	S20
Figure S19. Mass profile of [Fe(NCMe) ₆][BF ₄] ₂ during cyclic voltammetry.	S21
Figure S20. Derivative of mass change with respect to time for Fe(II).	S22
Figure S21. Mass profile of [Ni(NCMe) ₆][BF ₄] ₂ during cyclic voltammetry.	S23
Figure S22. Derivative of mass change with respect to time for Ni(II).	S24
Figure S23. Mass profile of [Cu(NCMe) ₄][PF ₆] during cyclic voltammetry.	S25
Figure S24. Derivative of mass change with respect to time for Cu(I).	S26
Figure S25. Mass profile of [Zn(NCMe) ₆][BF ₄] ₂ during cyclic voltammetry.	S27
Figure S26. Derivative of mass change with respect to time for Zn(II).	S28

Figure S27. Corrosion of [Fe(NCMe) ₆][BF ₄] ₂ treated with DMFH ⁺ .	S29
Figure S28. Corrosion of [Ni(NCMe) ₆][BF ₄] ₂ treated with DMFH ⁺ .	S 30
Figure S29. Corrosion of $[Cu(NCMe)_4][PF_6]$ treated with DMFH ⁺ .	S 31
XPS	
Figure S30. Survey XPS spectrum of bare HOPG electrode.	S32
Figure S31. Survey XPS spectrum of HOPG electrode following electrodeposition of Mn.	S33
Figure S32. High resolution spectrum of Mn 2p region following electrodeposition of Mn.	S34
Figure S33. High resolution spectrum of N 1s region following electrodeposition of Mn.	S35
Figure S34. Survey spectrum of HOPG electrode following electrodeposition of Fe.	S36
Figure S35. High resolution spectrum of Fe 2p region following electrodeposition of Fe.	S37
Figure S36. High resolution spectrum of N 1s region following electrodeposition of Fe.	S38
Figure S37. Survey spectrum of HOPG electrode following electrodeposition of Ni.	S39
Figure S38. High resolution spectrum of Ni 2p region following electrodeposition of Ni.	S40
Figure S39. High resolution spectrum of N 1s region following electrodeposition of Ni.	S41
Figure S40. Survey XPS spectrum of HOPG electrode following electrodeposition of Cu.	S42
Figure S41. High resolution spectrum of Cu 2p region following electrodeposition of Cu.	S43
Figure S42. High resolution spectrum of N 1s region following electrodeposition of Cu.	S44
Figure S43. Survey XPS spectrum of HOPG electrode following electrodeposition of Zn.	S45
Figure S44. High resolution spectrum of Mn 2p region following electrodeposition of Zn.	S46
Figure S45. High resolution spectrum of N 1s region following electrodeposition of Zn.	S47

IR Spectra



Figure S1. IR spectrum of [Mn(NCMe)4][BF4]2. Solid state IR spectrum of the homoleptic manganese complex.



Figure S2. IR spectrum of [Fe(NCMe)₆[BF4]₂. Solid state IR spectrum of the homoleptic iron complex.



Figure S3. IR spectrum of [Ni(NCMe)₆][BF₄]₂. Solid state IR spectrum of the homoleptic nickel complex.



Figure S4. IR spectrum of [Cu(NCMe)₄]**[PF**₆**].** Solid state IR spectrum of the homoleptic copper complex.



Figure S5. IR spectrum of [Zn(NCMe)₆][BF₄]₂. Solid state IR spectrum of the homoleptic zinc complex.



Figure S6. IR spectra of the homoleptic acetonitrile complexes. Solid state IR spectra detailing the N-C stretch associated with acetonitrile ligands of the solvento complexes (\sim 2200 cm⁻¹). Minor impurity of water due to the acutely hygroscopic nature of the complexes can be observed in some cases near 3300 cm⁻¹.

Electrochemistry & EQCM



Figure S7. Cyclic voltammetry of $[Mn(NCMe)_4][BF_4]_2$ treated with DMFH⁺. Cyclic voltammetry on a 2 mM solution homoleptic manganese complex treated with three equivalents of [DMFH][OTf]. HOPG working electrode, Pt counter electrode, CE, Ag^{+/0} Ref. Scan rate: 100 mV/s.



Figure S8. Cyclic voltammetry of $[Fe(NCMe)_6][BF_4]_2$ treated with DMFH⁺. Cyclic voltammetry on a 2 mM solution homoleptic iron complex treated with three equivalents of [DMFH][OTf]. HOPG working electrode, Pt counter electrode, CE, Ag^{+/0} Ref. Scan rate: 100 mV/s.



Figure S9. Cyclic voltammetry of [Ni(NCMe)₆][**BF**₄]₂ **treated with DMFH**⁺. Cyclic voltammetry on a 2 mM solution homoleptic nickel complex treated with three equivalents of [DMFH][OTf]. HOPG working electrode, Pt counter electrode, CE, Ag^{+/0} Ref. Scan rate: 100 mV/s.



Figure S10. Cyclic voltammetry of [Cu(NCMe)4][PF6] treated with DMFH⁺. Cyclic voltammetry on a 2 mM solution homoleptic copper complex treated with three equivalents of [DMFH][OTf]. HOPG working electrode, Pt counter electrode, CE, $Ag^{+/0}$ Ref. Scan rate: 100 mV/s.



Figure S11. Cyclic voltammetry of $[Zn(NCMe)_6][BF_4]_2$ treated with DMFH⁺. Cyclic voltammetry on a 2 mM solution homoleptic zinc complex treated with three equivalents of [DMFH][OTf]. HOPG working electrode, Pt counter electrode, CE, Ag^{+/0} Ref. Scan rate: 100 mV/s.



Fig S12. EQCM data of [Mn(NCMe)4][BF4]2 treated with DMFH⁺. EQCM experiments with voltammetry (black) and mass data (gray) for a solution containing [Mn(NCMe)4][BF4]2 treated with three equivalents of dimethylformamidinium triflate. Conditions: 2 mM [Mn], 6 mM DMFH⁺, 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag+/0 reference electrode. Scan rate: 100 mV/s.



Figure S13. EQCM data of [Fe(NCMe)6][BF4]2 treated with DMFH⁺. EQCM experiments with voltammetry (black) and mass data (gray) for a solution containing [Fe(NCMe)6][BF4]2 treated with three equivalents of dimethylformamidinium triflate. Conditions: 2 mM [Fe], 6 mM DMFH⁺, 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag+/0 reference electrode. Scan rate: 100 mV/s.



Figure S14. EQCM data of [Ni(NCMe)₆][**BF**₄]₂ **treated with DMFH**⁺**.** EQCM experiments with voltammetry (black) and mass data (gray) for a solution containing [Ni(NCMe)₆][**B**F₄]₂ treated with three equivalents of dimethylformamidinium triflate. Conditions: 2 mM [Ni], 6 mM DMFH⁺, 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag+/0 reference electrode. Scan rate: 100 mV/s.



Figure S15. EQCM data of $[Cu(NCMe)_4][PF_6]$ treated with DMFH⁺. EQCM experiments with voltammetry (black) and mass data (gray) for a solution containing $[Cu(NCMe)_4][BF_4]_2$ treated with three equivalents of dimethylformamidinium triflate. Conditions: 2 mM [Cu], 6 mM DMFH⁺, 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag+/0 reference electrode. Scan rate: 100 mV/s.



Figure S16. EQCM data of $[Zn(NCMe)_6][BF_4]_2$ treated with DMFH⁺. EQCM experiments with voltammetry (black) and mass data (gray) for a solution containing $[Zn(NCMe)_6][BF_4]_2$ treated with three equivalents of dimethylformamidinium triflate. Conditions: 2 mM [Zn], 6 mM DMFH⁺, 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag+/0 reference electrode. Scan rate: 100 mV/s.



Figure S17. Mass profile of [Mn(NCMe)4][BF4]2 during cyclic voltammetry. Mass profile of the manganese solvento complex during potential excursion from -0.2 V to -2.45 V (vs. Fc^{+/0}) and back again during a cyclicvoltammogram. The black line is the raw mass data from the EQCM, whereas the red line is the data smoothed by adjacent averaging, for further analysis of the derivative with respect to time. Conditions: 2 mM [Mn], 0.1 M TBAPF₆, Au EQCM disk working electrode, Pt counter electrode, Ag^{+/0} reference electrode. Scan rate: 100 mV/s.



Figure S18. Derivative of mass change with respect to time for Mn(II). Calculation of the derivative of mass change at the electrode surface during cyclic voltammetry with the homoleptic acetonitrile manganese complex, with respect to time. Data from Figure S17, collected on a Au EQCM electrode, was differentiated to generate the above plot. A single, smooth acceleration during mass deposition is observed with subsequent deceleration.



Figure S19. Mass profile of [Fe(NCMe)₆][**BF**₄]₂ **during cyclic voltammetry.** Mass profile of the iron solvento complex during potential excursion from 0 V to -2.05 V (vs. Fc^{+/0}) and back again during cyclic voltammetry. The black line is the raw mass data from the EQCM, whereas the red line is the data smoothed by adjacent averaging, for further analysis of the derivative with respect to time. Conditions: 2 mM [Fe], 0.1 M TBAPF₆, Au EQCM disk working electrode, Pt counter electrode, Ag^{+/0} reference electrode. Scan rate: 100 mV/s.



Figure S20. Derivative of mass change with respect to time for Fe(II). Calculation of the derivative of mass change at the electrode surface during cyclic voltammetry with the homoleptic acetonitrile iron complex, with respect to time. Data from Figure S19, collected on a Au EQCM electrode, was differentiated to generate the above plot. A single, smooth acceleration during mass deposition is observed with subsequent deceleration.



Figure S21. Mass profile of [Ni(NCMe)₆][**BF**₄]₂ **during cyclic voltammetry.** Mass profile of the nickel solvento complex during potential excursion from 0.6 V to -1.85 V (vs. Fc^{+/0}) and back again during cyclic voltammetry. The black line is the raw mass data from the EQCM, whereas the red line is the data smoothed by adjacent averaging, for further analysis of the derivative with respect to time. Conditions: 2 mM [Ni], 0.1 M TBAPF₆, Au EQCM disk working electrode, Pt counter electrode, Ag^{+/0} reference electrode. Scan rate: 100 mV/s.



Figure S22. Derivative of mass change with respect to time for Ni(II). Calculation of the derivative of mass change at the electrode surface during cyclic voltammetry with the homoleptic acetonitrile nickel complex, with respect to time. Data from Figure S21, collected on a Au EQCM electrode, was differentiated to generate the above plot. A single, smooth acceleration during mass deposition is observed with subsequent deceleration.



Figure S23. Mass profile of [Cu(NCMe)4][PF6] during cyclic voltammetry. Mass profile of the copper solvento complex during potential excursion from -0.2 V to -1.46 V (vs. Fc^{+/0}) during cyclic voltammetry. The black line is the raw mass data from the EQCM, whereas the red line is the data smoothed by adjacent averaging, for further analysis of the derivative with respect to time. Conditions: 2 mM [Cu], 0.1 M TBAPF6, Au EQCM disk working electrode, Pt counter electrode, Ag^{+/0} reference electrode. Scan rate: 100 mV/s.



Figure S24. Derivative of mass change with respect to time for Cu(I). Calculation of the derivative of mass change at the electrode surface during cyclic voltammetry with the homoleptic acetonitrile iron complex, with respect to time. Data from Figure S23, collected on a Au EQCM electrode, was differentiated to generate the above plot. A single, smooth acceleration during mass deposition is observed with subsequent slow deceleration. Distinct changes in the derivative at longer timescales arise from noise in the mass data near the termination of the anodic sweep.



Figure S25. Mass profile of $[Zn(NCMe)_6][BF_4]_2$ during cyclic voltammetry. Mass profile of the manganese solvento complex during potential excursion from 0.1 V to -1.89 V (vs. Fc^{+/0}) and back again during cyclic voltammetry. The black line is the raw mass data from the EQCM, whereas the red line is the data smoothed by adjacent averaging, for further analysis of the derivative with respect to time. Conditions: 2 mM [Zn], 0.1 M TBAPF₆, Au EQCM disk working electrode, Pt counter electrode, Ag^{+/0} reference electrode. Scan rate: 100 mV/s.



Figure S26. Derivative of mass change with respect to time for Zn(II). Calculation of the derivative of mass change at the electrode surface during cyclic voltammetry with the homoleptic acetonitrile iron complex, with respect to time. Data from Figure S25, collected on a Au EQCM electrode, was differentiated to generate the above plot. Shown is a complex



Figure S27. Corrosion of [Fe(NCMe)₆][BF₄]₂ treated with DMFH⁺. Shown is the EQCMmonitored corrosion of heterogeneous material, electrodeposited from a 2 mM solution of the homoleptic iron complex (black) and a preparation including 6 mM DMFH⁺ (gray). Briefly, linear sweep voltammetry was performed, sweeping the voltage from 0 V to -2.05 V vs Fc^{+/0}. Upon completion of the cathodic excursion, the electrode was returned to open circuit and the stability of the formed material was observed by piezoelectric gravimetry. The electrodeposited iron is fairly stable but quickly undergoes chemical corrosion in the presence of acid.



Figure S28. Corrosion of [Ni(NCMe)₆][**B**F4]₂ **treated with DMFH**⁺. Shown is the EQCMmonitored corrosion of heterogeneous material, electrodeposited from a 2 mM solution of the homoleptic nickel complex (black) and a preparation including 6 mM DMFH⁺ (gray). Briefly, linear sweep voltammetry was performed, sweeping the voltage from 0 V to –2.05 V vs Fc^{+/0}. Upon completion of the cathodic excursion, the electrode was returned to open circuit and the stability of the formed material was observed by piezoelectric gravimetry. The electrodeposited nickel is modestly stable but quickly undergoes chemical corrosion in the presence of acid. Two distinct regimes are apparent in the acid-treated data (gray), suggesting that structuring or speciation may generate materials of mixed stability.



Figure S29. Corrosion of [Cu(NCMe)4][PF6] treated with DMFH⁺. Shown is the EQCMmonitored corrosion of heterogeneous material, electrodeposited from a 2 mM solution of the homoleptic copper complex (black) and a preparation including 6 mM DMFH⁺ (gray). Briefly, linear sweep voltammetry was performed, sweeping the voltage from 0 V to -2.05 V vs Fc^{+/0}. Upon completion of the cathodic excursion, the electrode was returned to open circuit and the stability of the formed material was observed by piezoelectric gravimetry. The electrodeposited copper is only moderately stable even in the absence of a proton source, but rapidly undergoes chemical corrosion in the presence of acid.

X-ray Photoelectron (XP) Spectra



Figure S30. Survey XP spectrum of bare HOPG electrode. Survey X-ray photoelectron spectrum for a blank electrode, showing signals only for carbon (C 1s) and adventitious oxygen (O 1s, O KLL) present as a result of either trace water during handling in ambient conditions or partial oxidation of the electrode material.



Figure S31. Survey XP spectrum of HOPG electrode following electrodeposition from a solution containing Mn(II). Survey X-ray photoelectron spectrum detailing the numerous species present on an HOPG electrode following electrodeposition from the manganese homoleptic acetonitrile complex. An HOPG electrode (surface area = 1 cm^2) was polarized at – 2.07 V vs Fc^{+/0} for 5 min, then rinsed with dry MeCN and transferred to the XPS instrument. Exposure to air upon transfer results in the conversion of manganese (0) metal to manganese (III) oxide (as evidenced by Mn LMM, Mn 2p, Mn 3p signals). Adventitious oxygen is observed in the data (O 1s, O KLL), as seen in spectra collected on bare HOPG surfaces. Additionally, signals assigned to phosphorous (P 2p), nitrogen (N 1s) and fluorine (F 1s, F KLL) suggest that TBA PF6 is either trapped in the heterogeneous material formed upon reduction or incompletely rinsed from the surface.



Figure S32. High resolution spectrum of Mn 2p region following electrodeposition from a solution containing Mn(II). Manganese 2p region of carbon electrode prepared as described in Figure S31. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Green lines are the Mn 2p3/2 and Mn 2p1/2 peaks. Predicted area ratio of 2:1 agrees with measured data. Blue lines are possible paramagnetic satellites which may arise from small amounts of Mn²⁺ on the electrode surface.



Figure S33. High resolution spectrum of N 1s region following electrodeposition from a solution containing Mn(II). Nitrogen 1s region of carbon electrode following electrodeposition of manganese from the homoleptic acetonitrile precursor. The electrode was prepared as described in Figure S31. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. The blue line is the fit of the N 1s peak, indicating the presence of only one nitrogen-containing species on the surface.



Figure S34. Survey spectrum of HOPG electrode following electrodeposition from a solution containing Fe(II). Survey X-ray photoelectron spectrum detailing the numerous species present on an HOPG electrode following electrodeposition from the iron homoleptic acetonitrile complex. An HOPG electrode (surface area = 1 cm^2) was polarized at -1.69 V vs Fc^{+/0} for 5 min, then rinsed with dry MeCN and transferred to the XPS instrument. Exposure to air upon transfer results in the conversion of iron (0) metal to iron (III) oxide (as evidenced by Fe LMM, Fe 2p signals). Adventitious oxygen is observed in the data (O 1s, O KLL), as seen in spectra collected on bare HOPG surfaces. Additionally, signals assigned to phosphorous (P 2p, P 2s), nitrogen (N 1s) and fluorine (F 1s, F KLL) suggest that TBA PF6 is either trapped in the heterogeneous material formed upon reduction or incompletely rinsed from the surface.



Figure S35. High resolution spectrum of Fe 2p region following electrodeposition from a solution containing Fe(II). Iron 2p region of carbon electrode prepared as described in Figure S34. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Blue lines are the Fe 2p3/2 and Fe 2p1/2 peaks. Predicted area ratio of 2:1 agrees with measured data.



Figure S36. High resolution spectrum of N 1s region following electrodeposition from a solution containing Fe(II). Nitrogen 1s region of carbon electrode following electrodeposition of iron from the homoleptic acetonitrile precursor. The electrode was prepared as described in Figure S34. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. The blue line is the fit of the N 1s peak, indicating the presence of only one nitrogen-containing species on the surface.



Figure S37. Survey spectrum of HOPG electrode following electrodeposition from a solution containing Ni(II). Survey X-ray photoelectron spectrum detailing the numerous species present on an HOPG electrode following electrodeposition from the nickel homoleptic acetonitrile complex. An HOPG electrode (surface area = 1 cm^2) was polarized at -1.55 V vs Fc^{+/0} for 5 min, then rinsed with dry MeCN and transferred to the XPS instrument. Exposure to air upon transfer results in the conversion of nickel (0) metal to nickel oxide (as evidenced by Ni 2p, Ni LMM, Ni 3p, Ni 3s signals). Adventitious oxygen is observed in the data (O 1s, O KLL), as seen in spectra collected on bare HOPG surfaces. Additionally, signals assigned to phosphorous (P 2p, P 2s), nitrogen (N 1s) and fluorine (F 1s) suggest that TBA PF6 is either trapped in the heterogeneous material formed upon reduction or incompletely rinsed from the surface.



Figure S38. High resolution spectrum of Ni 2p region following electrodeposition from a solution containing Ni(II). Nickel 2p region of carbon electrode prepared as described in Figure S37. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Green lines are the Ni 2p3/2 and Ni 2p1/2 peaks. Predicted area ratio of 2:1 agrees with measured data. Blue lines are paramagnetic satellites.



Figure S39. High resolution spectrum of N 1s region following electrodeposition from a solution containing Ni(II). Nitrogen 1s region of carbon electrode following electrodeposition of nickel from the homoleptic acetonitrile precursor. The electrode was prepared as described in Figure S37. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. The blue line is the fit of the N 1s peak, indicating the presence of only one nitrogen-containing species on the surface.



Figure S40. Survey spectrum of HOPG electrode following electrodeposition from a solution containing Cu(I). Survey X-ray photoelectron spectrum detailing the numerous species present on an HOPG electrode following electrodeposition from the copper homoleptic acetonitrile complex. An HOPG electrode (surface area = 1 cm^2) was polarized at -1.06 V vs Fc^{+/0} for 5 min, then rinsed with dry MeCN and transferred to the XPS instrument. Exposure to air upon transfer results in the conversion of copper (0) metal to copper (I) oxide (as evidenced by Cu 2p, Cu 3p, Cu 3d signals). Adventitious oxygen is observed in the data (O 1s), as seen in spectra collected on bare HOPG surfaces. Additionally, signals assigned to phosphorous (P 2p, P 2s), nitrogen (N 1s) and fluorine (F 1s, F KLL) suggest that TBA PF6 is either trapped in the heterogeneous material formed upon reduction or incompletely rinsed from the surface.



Figure S41. High resolution spectrum of Cu 2p region following electrodeposition from a solution containing Cu(I). Copper 2p region of carbon electrode prepared as described in Figure S40. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Green and blue lines are the Cu 2p3/2 and Cu 2p1/2 peak fits for copper metal and CuO, respectively. Predicted area ratio of 2:1 agrees with measured data.



Figure S42. High resolution spectrum of N 1s region following electrodeposition from a solution containing Cu(I). Nitrogen 1s region of carbon electrode following electrodeposition of copper from the homoleptic acetonitrile precursor. The electrode was prepared as described in Figure S40. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. The blue line is the fit of the N 1s peak, indicating the presence of only one nitrogen-containing species on the surface.



Figure S43. Survey spectrum of HOPG electrode following electrodeposition from a solution containing Zn(II). Survey X-ray photoelectron spectrum detailing the numerous species present on an HOPG electrode following electrodeposition from the zinc homoleptic acetonitrile complex. An HOPG electrode (surface area = 1 cm^2) was polarized at -1.06 V vs Fc^{+/0} for 5 min, then rinsed with dry MeCN and transferred to the XPS instrument. Exposure to air upon transfer results in the conversion of zinc (0) metal to zinc (II) oxide (as evidenced by Zn 2p, Zn 3s, Zn 3p signals). Adventitious oxygen is observed in the data (O 1s, O KLL), as seen in spectra collected on bare HOPG surfaces. Additionally, signals assigned to phosphorous (P 2s, P 2p), nitrogen (N 1s) and fluorine (F 1s, F KLL) suggest that TBA PF6 is either trapped in the heterogeneous material formed upon reduction or incompletely rinsed from the surface.



Figure S44. High resolution spectrum of Zn 2p region following electrodeposition from a solution containing Zn(II). Zinc 2p region of carbon electrode prepared as described in Figure S43. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Red and green lines are the Zn 2p3/2 and Zn 2p1/2 peaks respectively. Predicted area ratio of 2:1 agrees with measured data.



Figure S45. High resolution spectrum of N 1s region following electrodeposition of Zn(II). Nitrogen 1s region of carbon electrode following electrodeposition of zinc from the homoleptic acetonitrile precursor. The electrode was prepared as described in Figure S43. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. The blue line is the fit of the N 1s peak, indicating the presence of only one nitrogen-containing species on the surface.