Bis(pyridineylidene)isoindoline, an isoindoline chelate with a delocalized electronic structure

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Supplementary Information

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for compounds **1, Zn(1), Cu(1),** and **Ni(1).**

General Information

Experimental

All reagents and starting materials were purchased from commercial vendors and used without further purification. 1,3-diiminoisoindoline (DII) was synthesized according to previously published procedures.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received.

NMR spectra were recorded on 300 MHz and 500 MHz spectrometers and chemical shifts were given in ppm relative to residual solvent resonances (^{1}H NMR and ^{13}C NMR spectra). High-resolution mass spectrometry experiments were performed on a Bruker MicroTOF-III and MicroTOF-qIII instruments. Infrared spectra were collected on Thermo Scientific Nicolet iS5 that was equipped with an iD5 ATR. UV-visible spectra were recorded on a Shimadzu UV-2600 UV-Visible spectrophotometer.

X-ray intensity data were measured on a Bruker CCD-based and PHOTON II CPAD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, $\lambda = 1.54178$ Å, Mo Kα radiation, $\lambda = 0.71073$ Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K (Oxford Cryosystems). The detector was placed at a distance of 5.00 cm from the crystal. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1),[2] and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged.

Electrochemistry measurements were conducted using a CHI 820D potentiostat in a standard three-electrode configuration. Platinum wire was used as the counter electrode. The working electrode used was a 2 mm diameter platinum disk. A nonaqueous Ag/Ag$^+$ reference

electrode was used by immersing silver wire in a degassed dimethylformamide (DMF) solution of 0.01 M $AgNO_3$ /0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). All potentials were referenced to the ferrocene/ferrocenium couple. The concentration of analyte was 1.0 mM, and the supporting electrolyte was 0.1 M $TBAPF_6$ dissolved in DMF.

Computational Details

The starting geometries of compounds **BPI**, **1**, **Zn(1), Cu(1),** and **Ni(1)** were optimized using a B3LYP exchange–correlation functional.[3] Energy minima in optimized geometry were confirmed by the frequency calculations (absence of the imaginary frequencies). The solvent effect was modeled using the polarized continuum model (PCM).[4] In all calculations, DMF was used as the solvent ($CHCl_3$ for BPI). In PCM-TDDFT calculation, the first 30 states were calculated. All atoms were modeled using the 6-311G(d)[5] basis set. Gaussian 09 software was used in all calculations. [6] The QM Forge program was used for molecular orbital analysis in all cases.[7]
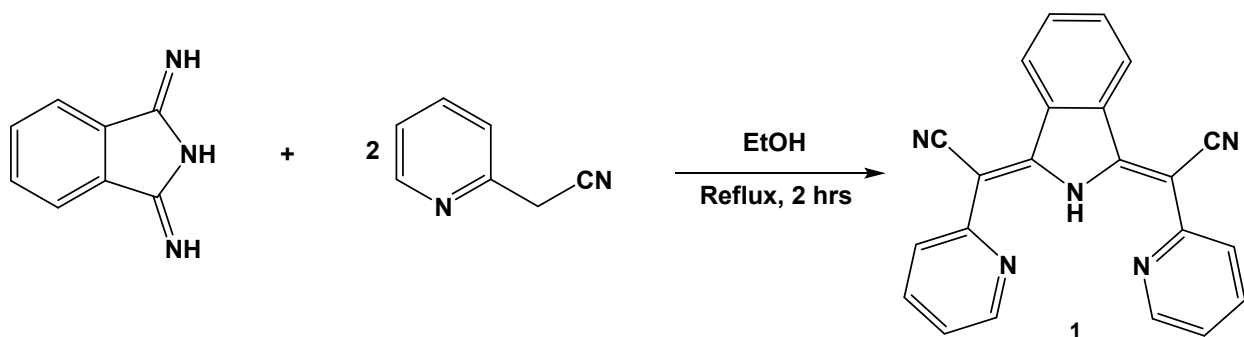
Synthesis of **1**: 1.00 g of DII (7 mmol), and 1.6 mL of 2-pyridylacetonitrile (14 mmol) were mixed in 30 mL of EtOH and refluxed for 2 hours. After cooling to room temperature, the precipitate was filtered, washed with cold EtOH, and dried in a vacuum oven, yielding an orange solid. Yield: 1.75 g (72%). MP: (decomp) 280°C. ESI MS (positive mode) $[C_{22}H_{13}N_5Na]^+$ calculated $[M+Na]^+$ 370.1063 m/z, found 370.1021 m/z. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.25 (m, 2H), 7.67 (m, 2H,), 7.82 (dd, 4H), 8.73 (m, 2H) and 8.81 (dd, 2H). ^{13}C NMR{^{1}H}: due to limited solubility we were unable to get ^{13}C NMR. Crystals suitable for X-ray diffraction were grown in DMF.
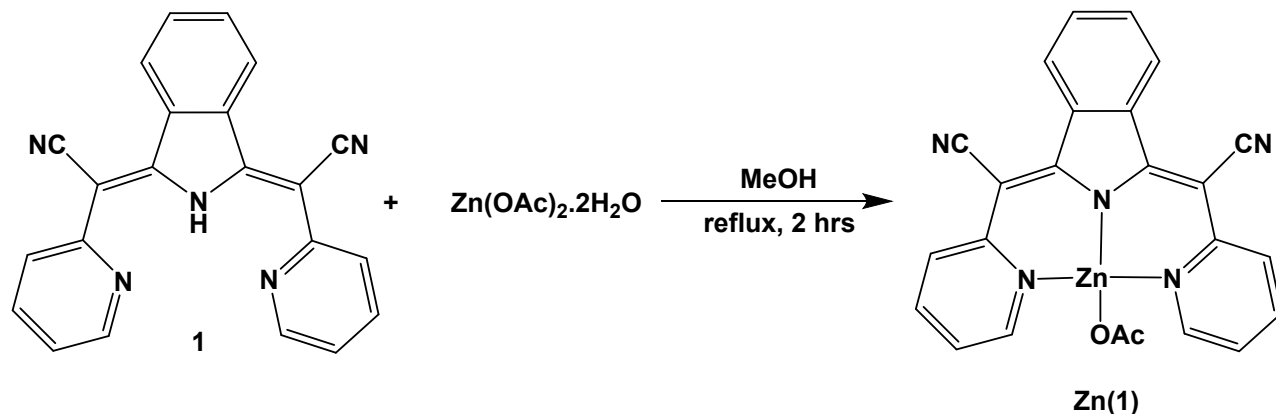
Synthesis of **Zn(1)**: 50.80 mg of **1** (146.24 mmol), and 32.80 mg (146.24 mmol) of Zn(OAc)$_2$.2H$_2$O were dissolved in MeOH (20 mL) and refluxed for 2 hours. The resulting solution was cooled down to room temperature, filtered, washed with cold MeOH and dried in vacuum oven to get reddish brown powder of pure compound **2**. Yield: 68 mg (87%). ESI MS (positive mode) $[C_{24}H_{15}N_5O_2ZnNa]^+$ calculated $[M+Na]^+$ 492.0420 m/z, found 492.0421 m/z. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.99 (s, 3H), 7.35 (m, 2H), 7.65 (m, 2H), 7.91 (m, 2H), 8.13 (m, 2H), 8.75 (m, 2H), 8.91 (m, 2H).). ^{13}C NMR{^{1}H}: due to limited solubility we were unable to get ^{13}C NMR. Crystals suitable for X-ray diffraction were grown in chloroform.
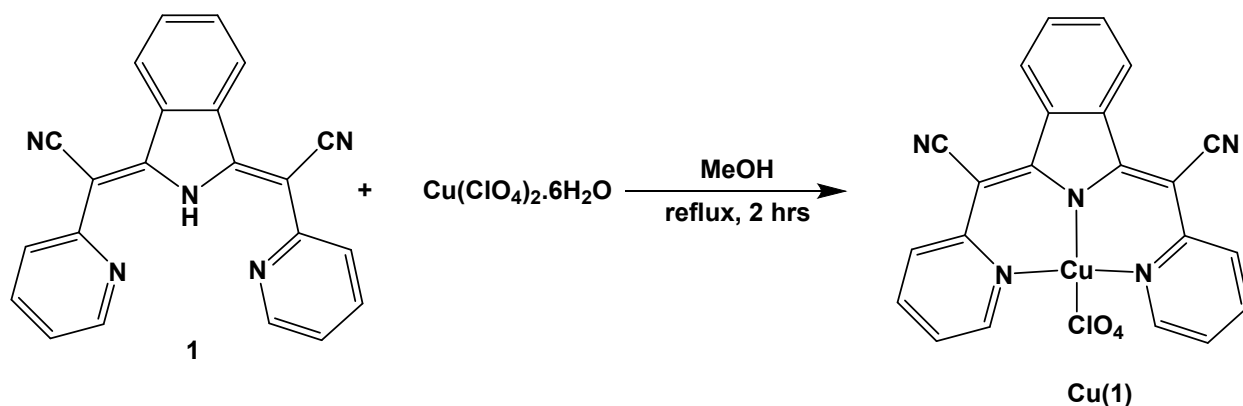
Synthesis of **Cu(1):** 50 mg of **1** (143.93 mmol) and 53.33 mg (143.93 mmol) of Cu(ClO$_4$)$_2$.6H$_2$O were dissolved in MeOH (20 mL) and refluxed for 2 hours. The resulting solution was cooled down to room temperature, filtered, washed with cold MeOH and dried in a vacuum oven to get brown powder of pure compound **Cu(1)**. Yield: 41 mg (56%). ESI MS (negative mode) [C$_{22}$H$_{12}$Cl$_2$CuN$_5$O$_8$]$^-$ calculated [M]$^-$ 606.936 m/z, found 606.935 m/z. ^{1}H NMR: due to paramagnetic nature we were unable to get ^{1}H NMR. Crystals suitable for X-ray diffraction were grown in DMF.
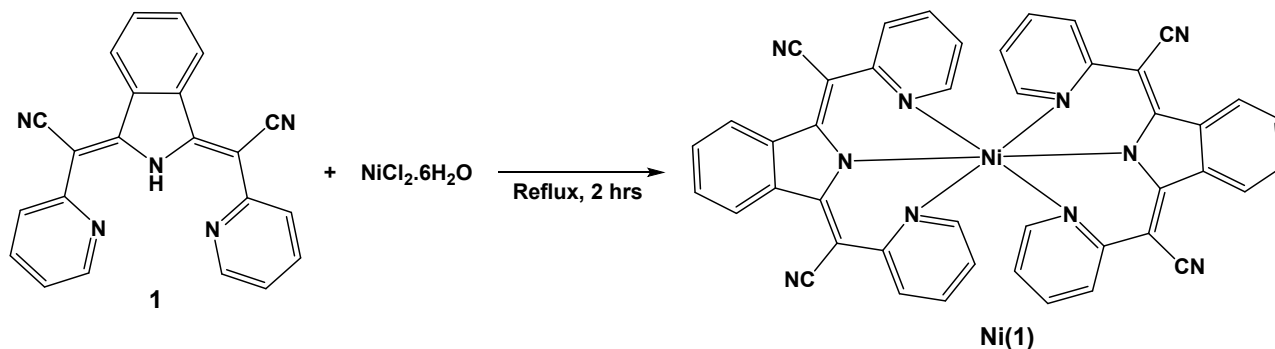
Synthesis of **Ni(1):** Two equivalents of **1** (75 mg, 215.90 mmol) and one equivalent of NiCl$_2$.6H$_2$O (107.95 mmol, 25.66 mg) were dissolved in DMF (20 mL) and refluxed for 2 hours. The resulting solution was cooled down to room temperature left to evaporate to form dark red crystals of compound **Ni(1)**. Yield: 64 mg (79%). ESI MS (negative mode) [C$_{44}$H$_{23}$N$_{10}$ NiNa]$^-$ calculated [M+Na-H]$^-$ 772.1364 m/z, found 772.1430 m/z. ^{1}H NMR: due to paramagnetic nature we were unable to get ^{1}H NMR. Crystals suitable for X-ray diffraction were grown in DMF.
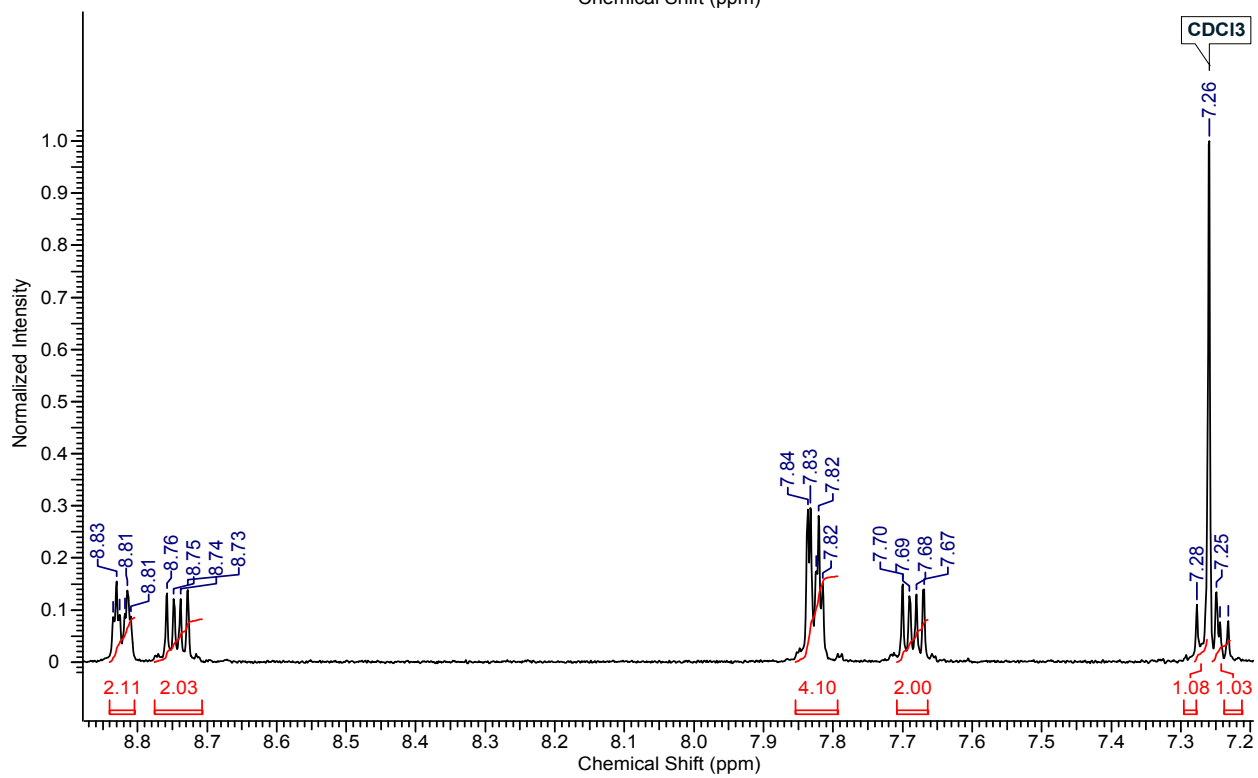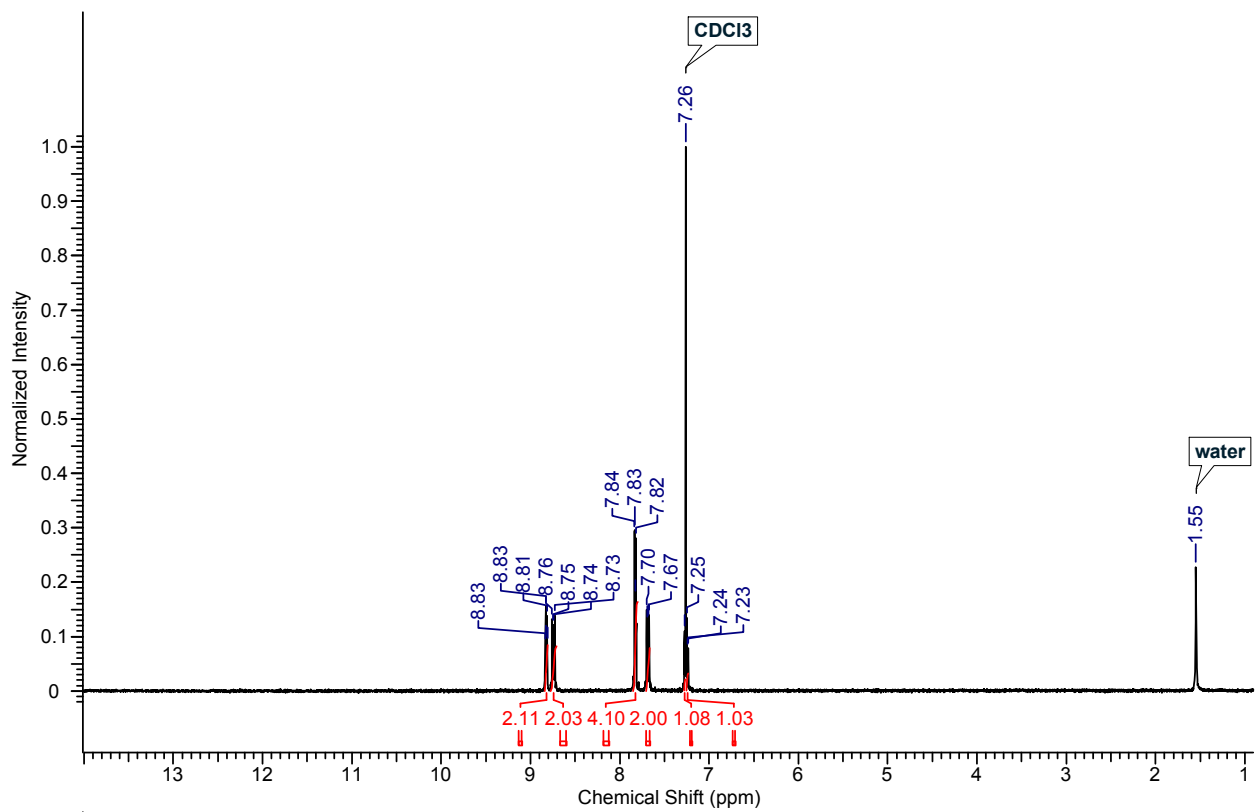
Figure S1: ^{1}H NMR (300 MHz) of **1** in CDCl$_3$
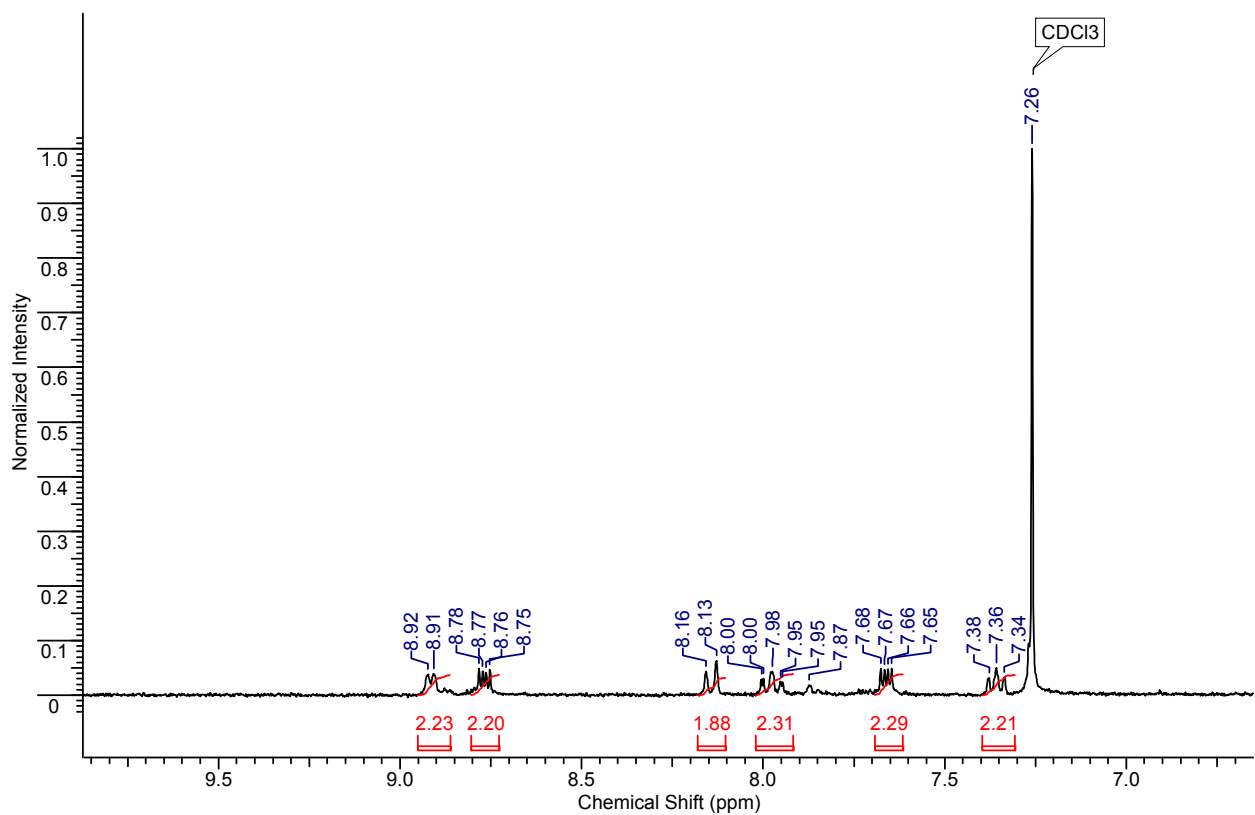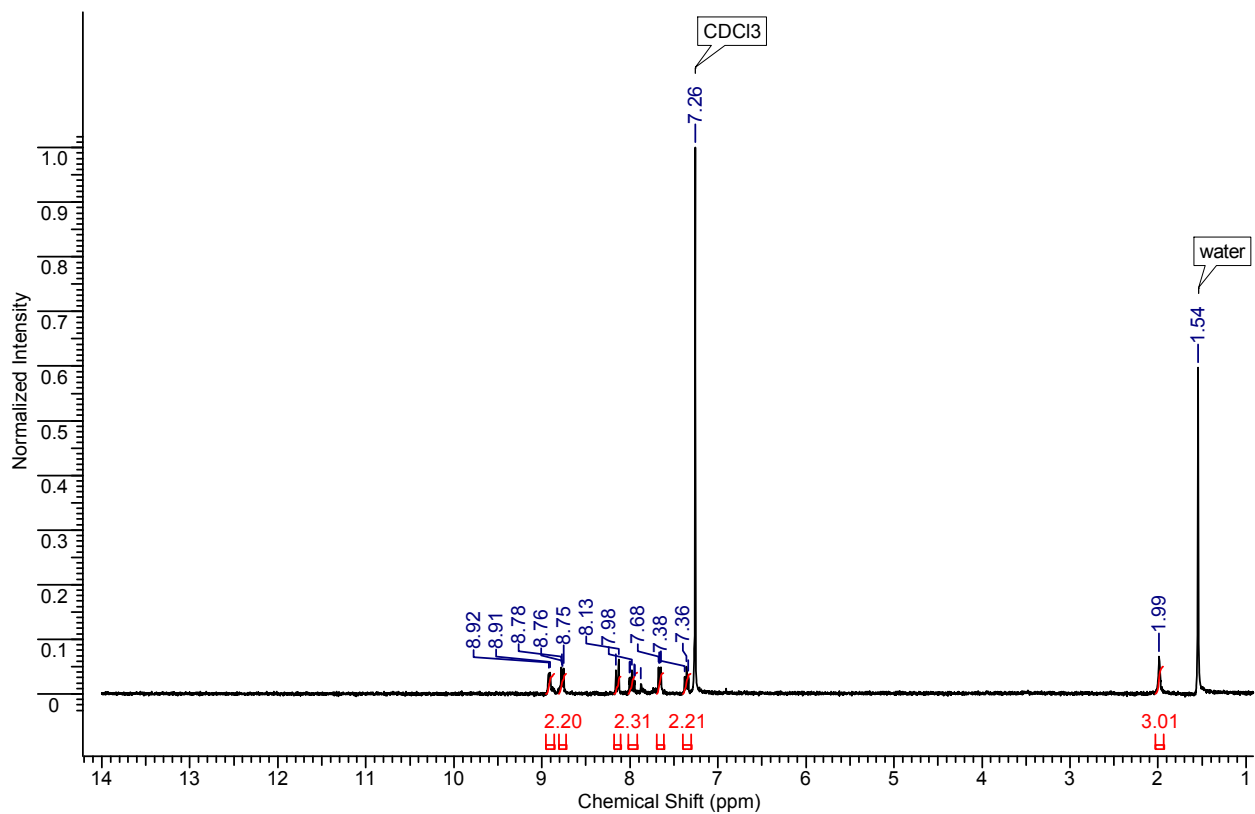
Figure S2: ^{1}H NMR (300 MHz) of **Zn(1)** in CDCl$_3$
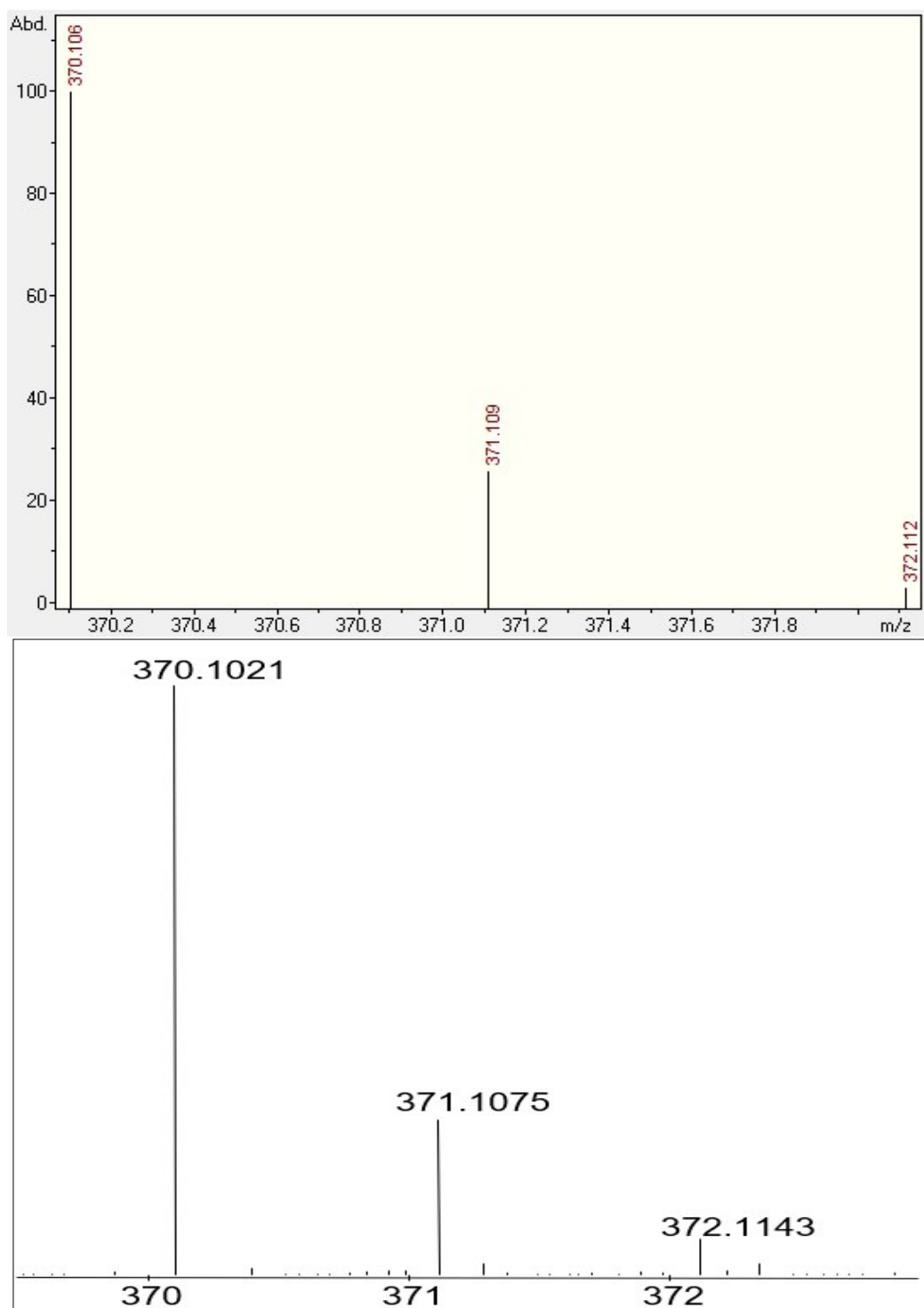
Figure S3: ESI mass spectra of **1.** Top: calculated spectrum. Bottom: experimental spectrum.
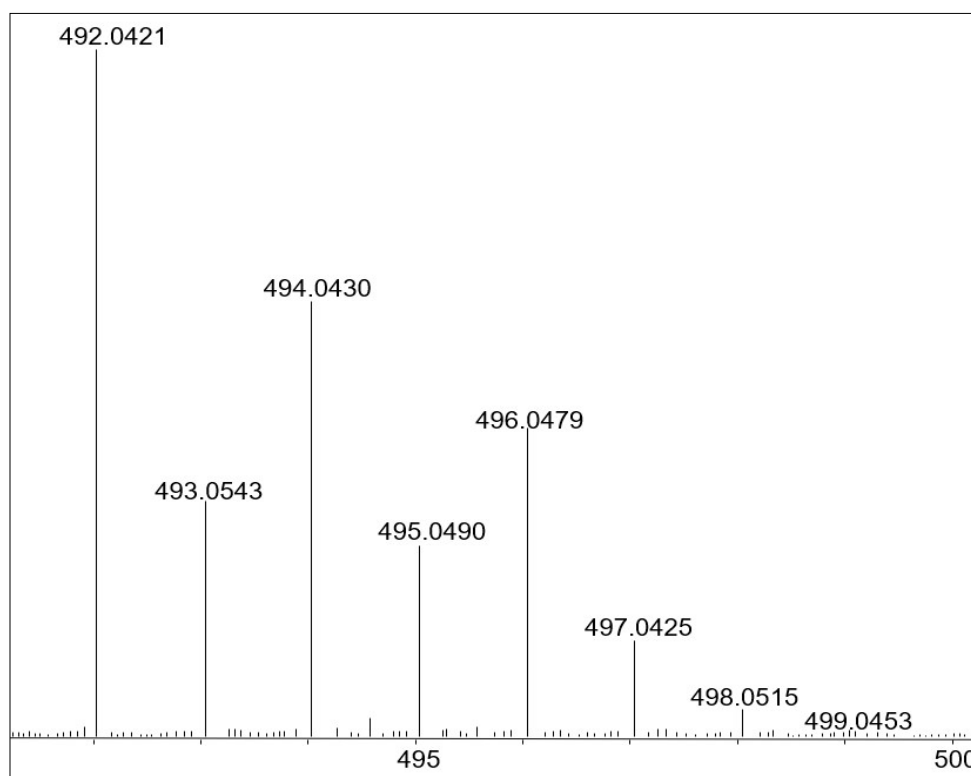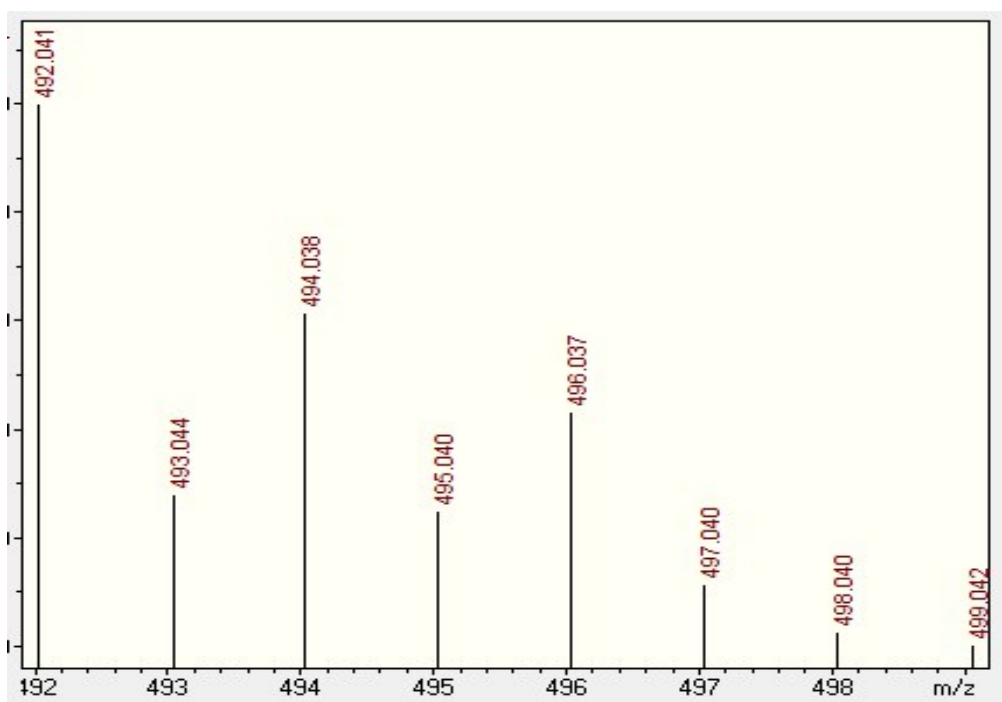
Figure S4: ESI mass spectra of **Zn(1).** Top: calculated spectrum. Bottom: experimental spectrum.
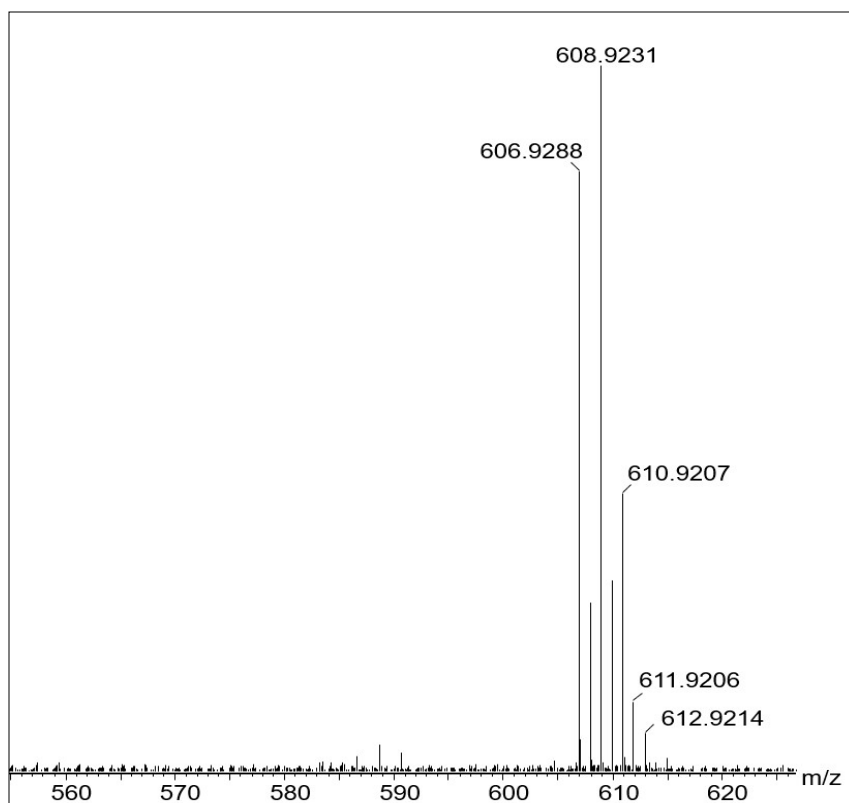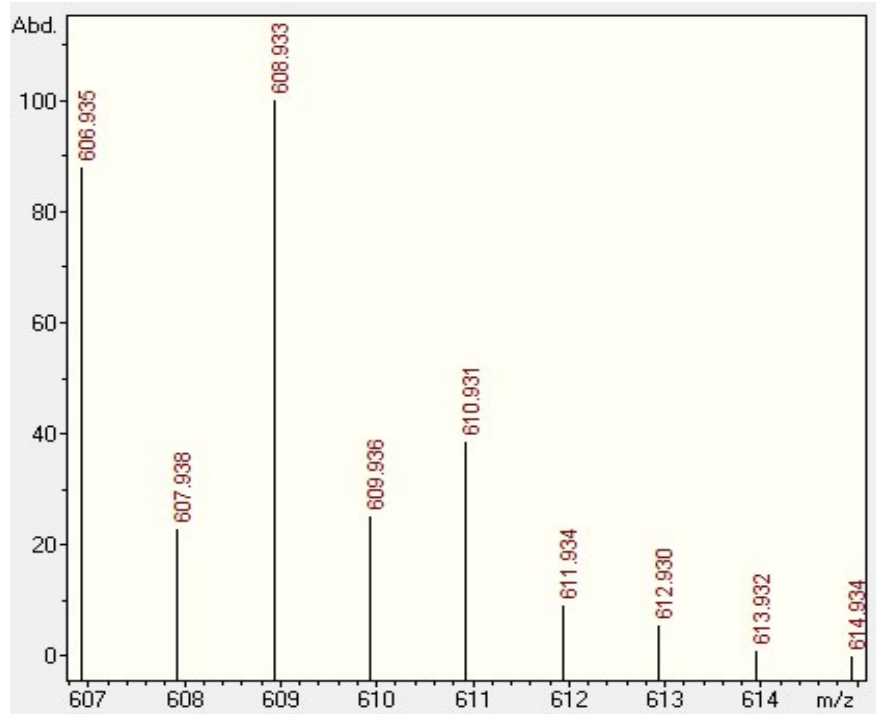
Figure S5: ESI mass spectra of **Cu(1).** Top: calculated spectrum. Bottom: experimental spectrum.
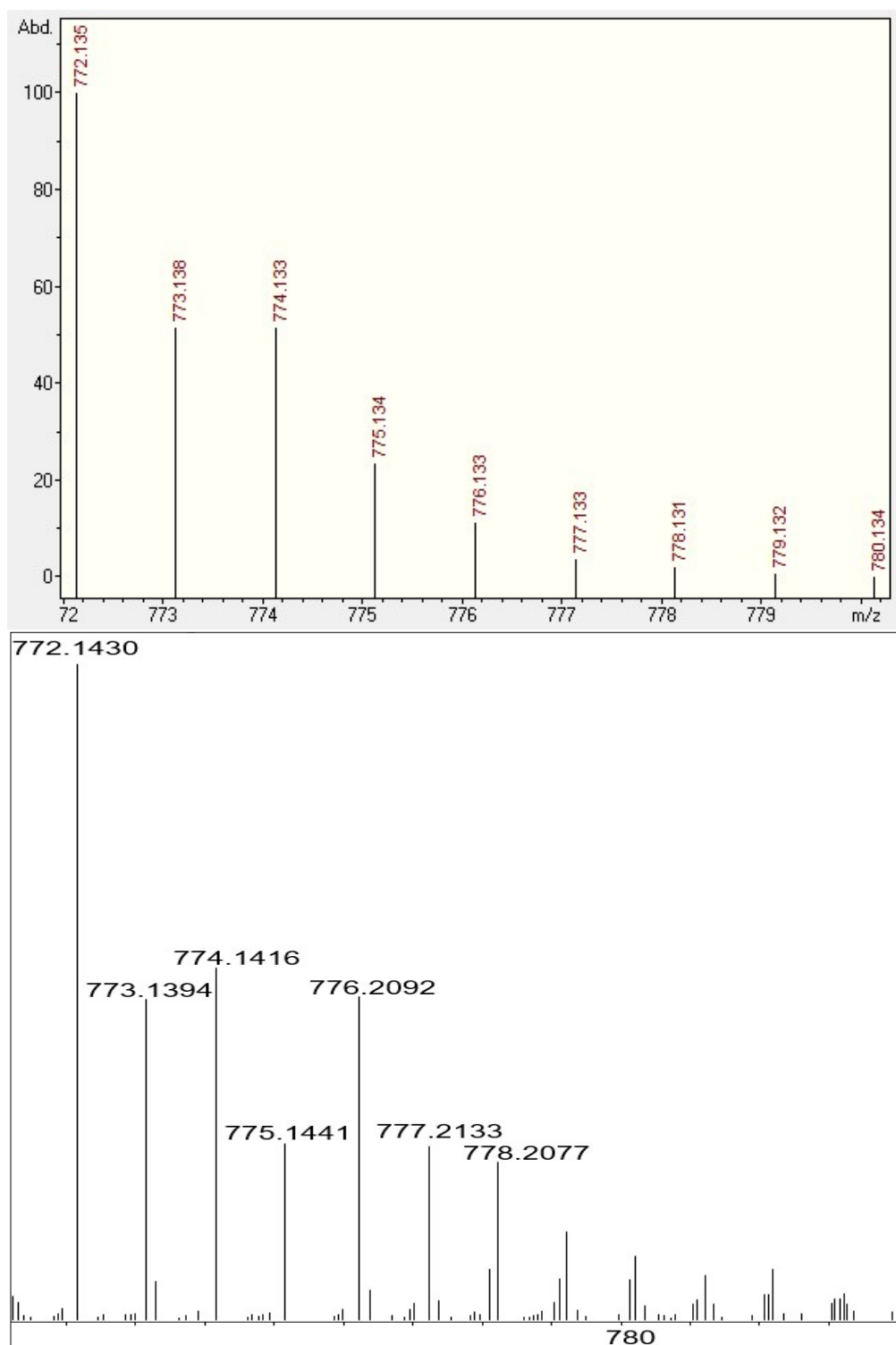
Figure S6: ESI mass spectra of **Ni(1).** Top: calculated spectrum. Bottom: experimental spectrum.
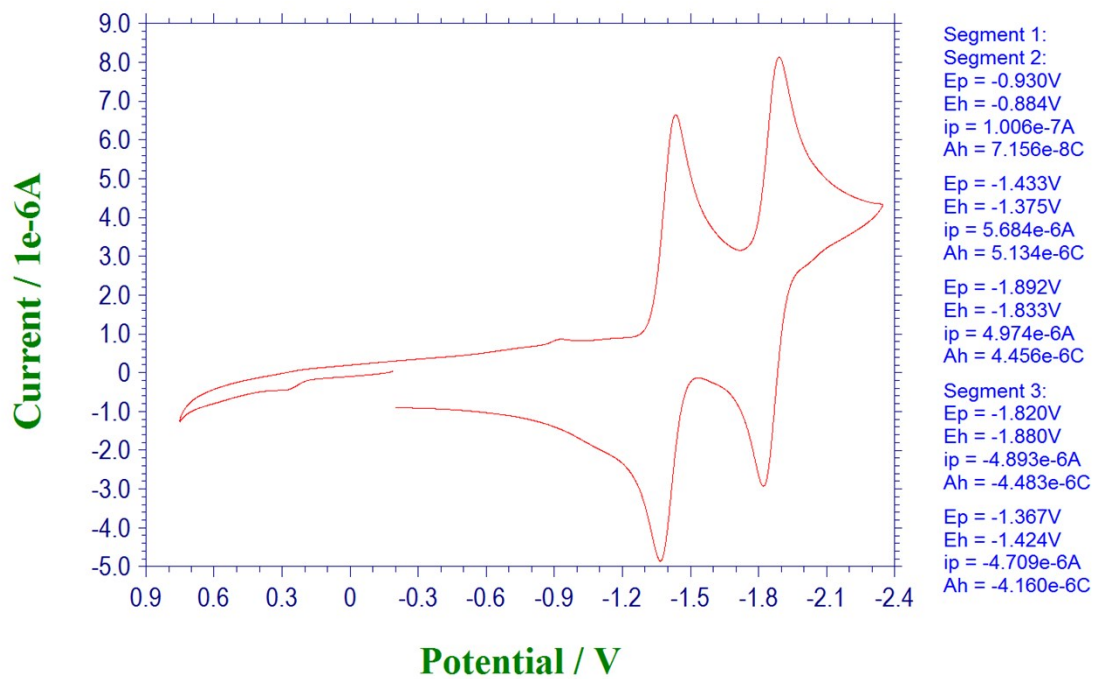
Figure S7: Cyclic voltammogram of compound **1** in DMF/0.1 TBAPF$_6$ (scan toward positive potentials).
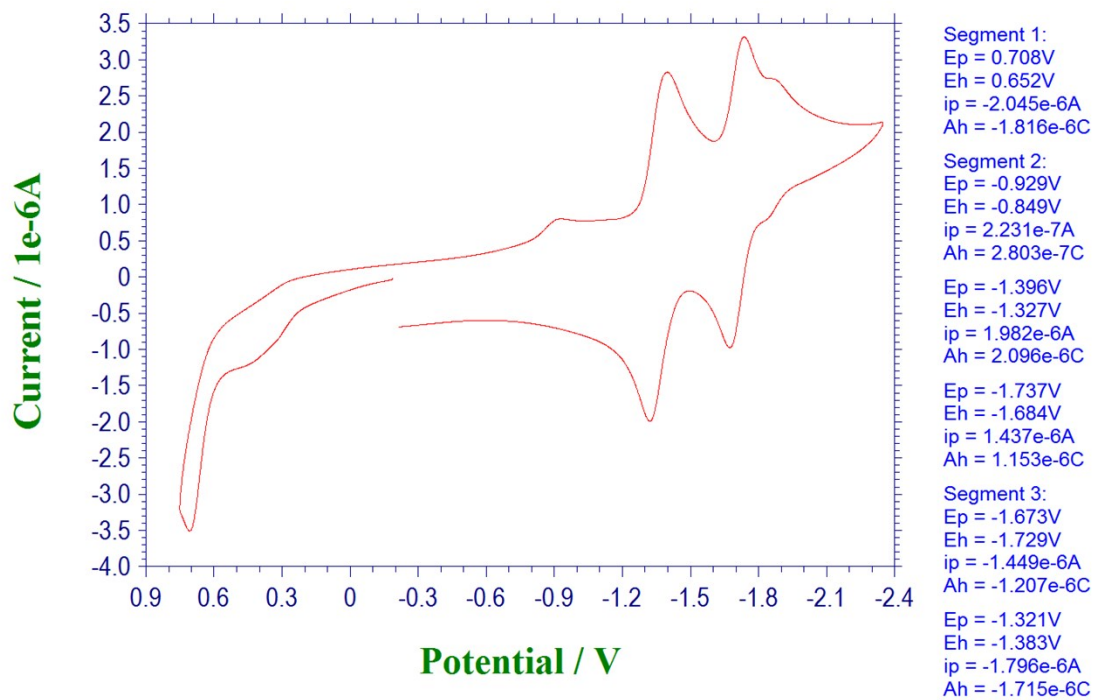
Figure S8: Cyclic voltammogram of compound **Zn(1)** in DMF/0.1 TBAPF$_6$ (scan toward positive potentials).
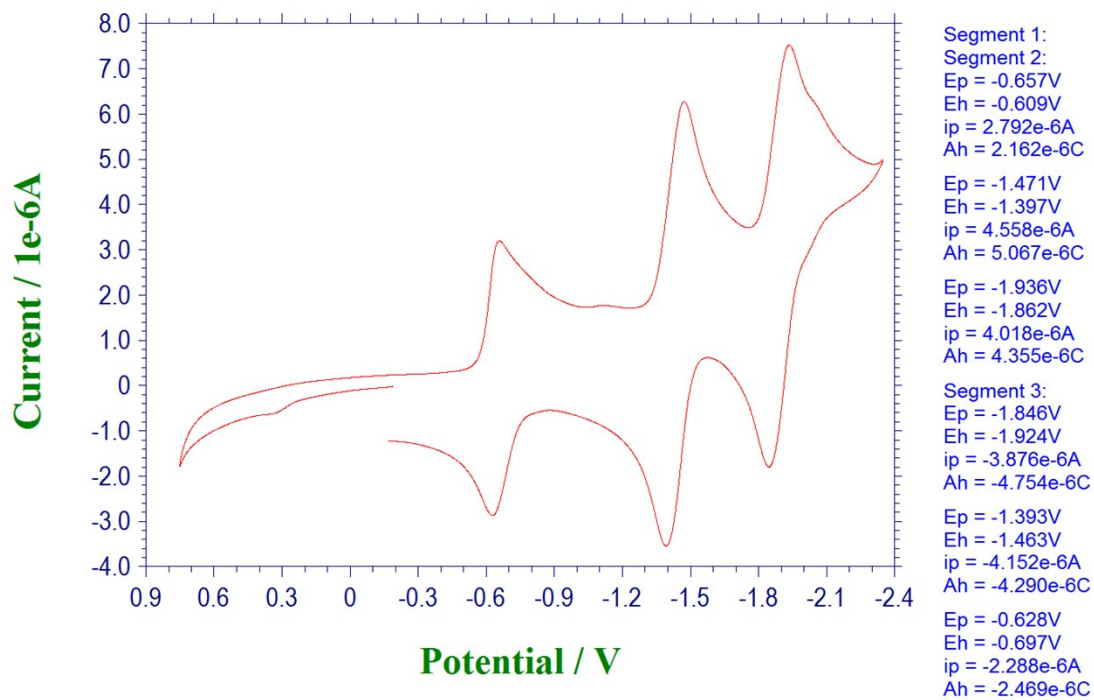
Figure S9: Cyclic voltammogram of compound **Cu(1)** in DMF/0.1 TBAPF$_6$ (scan toward positive potentials).
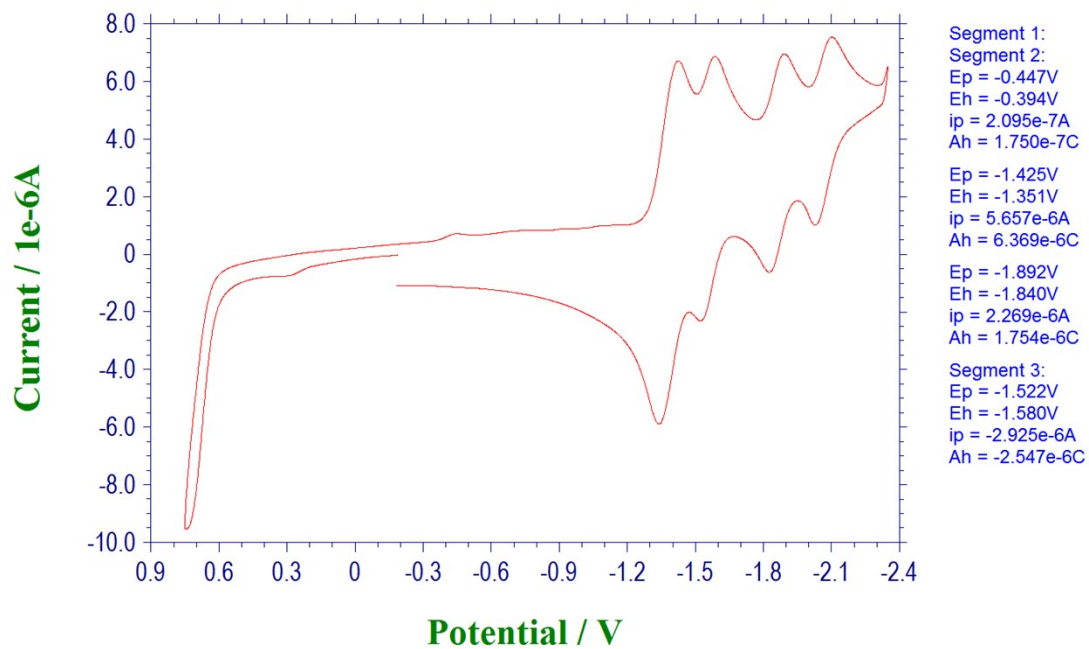
Figure S10: Cyclic voltammogram of compound **Ni(1)** in DMF/0.1 TBAPF$_6$ (scan toward positive potentials).
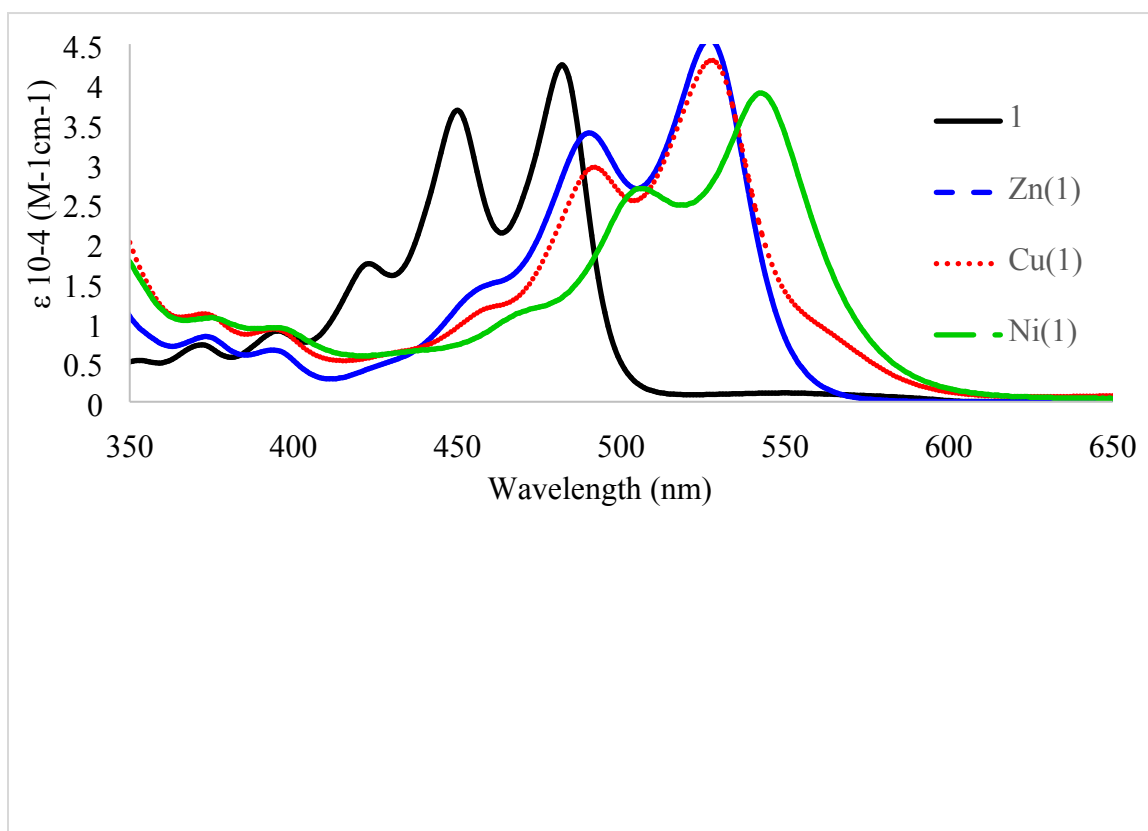
Figure S11: The UV-visible spectra of BPYI and its metal complexes in DMF solution.
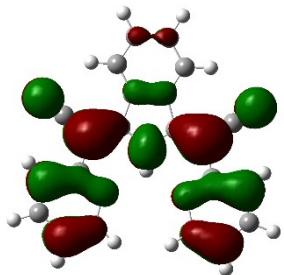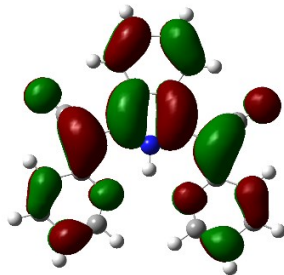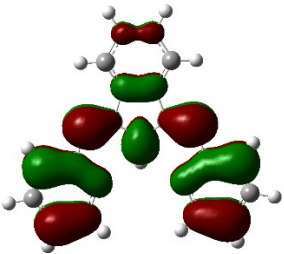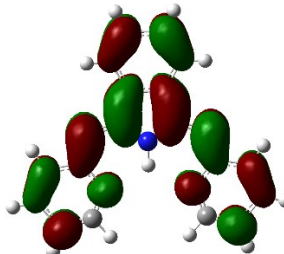
Compound	HOMO	LUMO
BPYI (1)		
BPI		

Figure S12. DFT-predicted frontier orbitals for BPYI (**1**) and BPI**.**

Compound	
Compound	
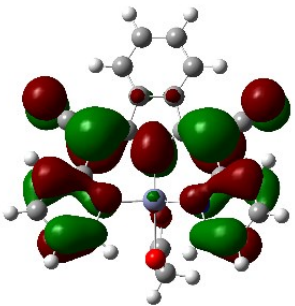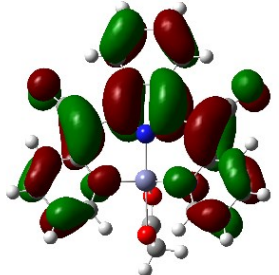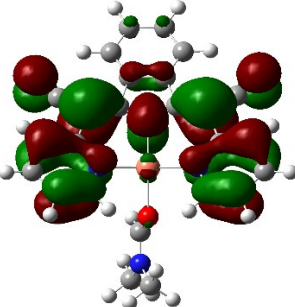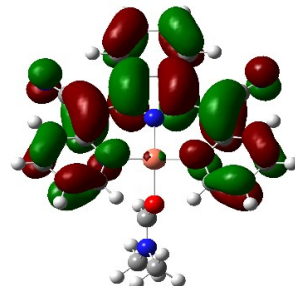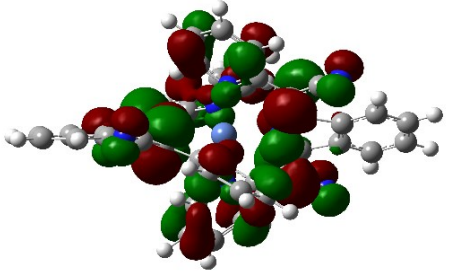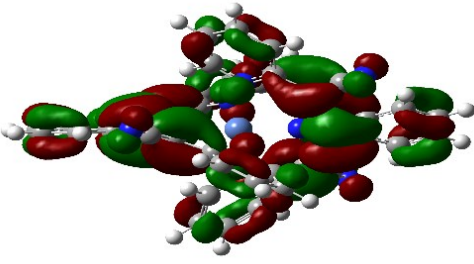
	HOMO	LUMO
Zn(1)		
Cu(1)		
Ni(1)		

Figure S13. DFT-predicted frontier orbitals for the metal complexes of (**1**).
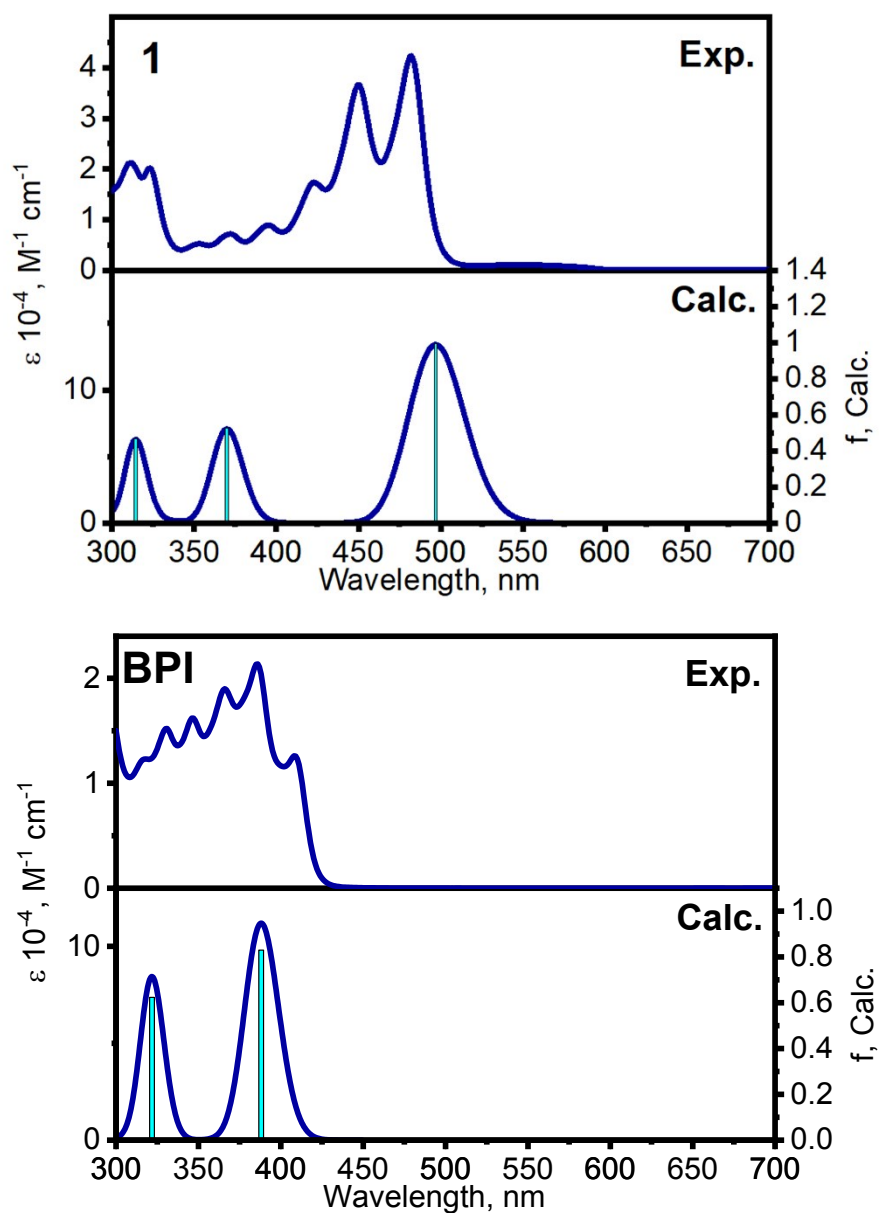
Figure S14: Experimental and TDDFT-predicted spectra for compounds BPYI (**1**) and BPI.
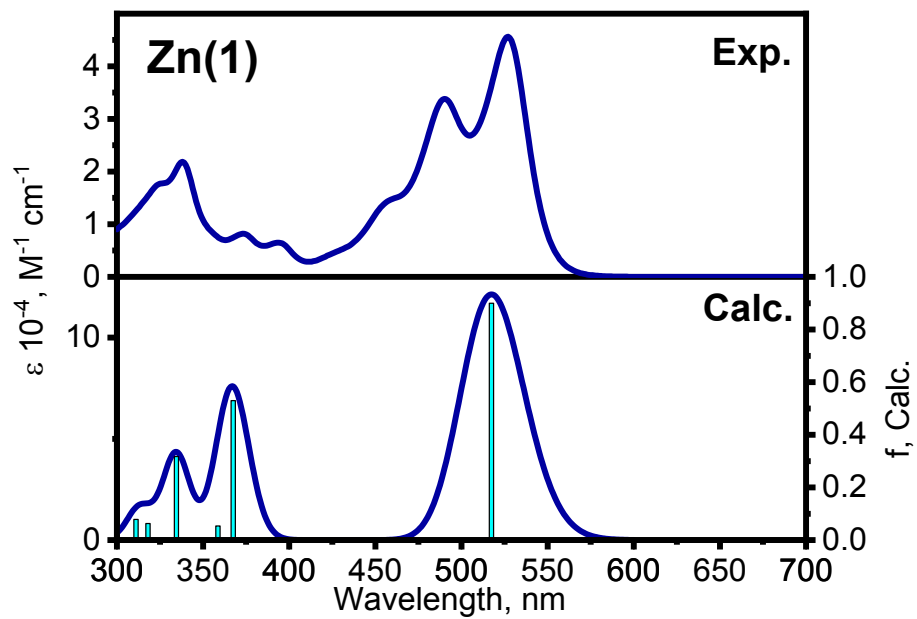
Figure S15: Experimental and TDDFT-predicted spectra for **Zn(1).**
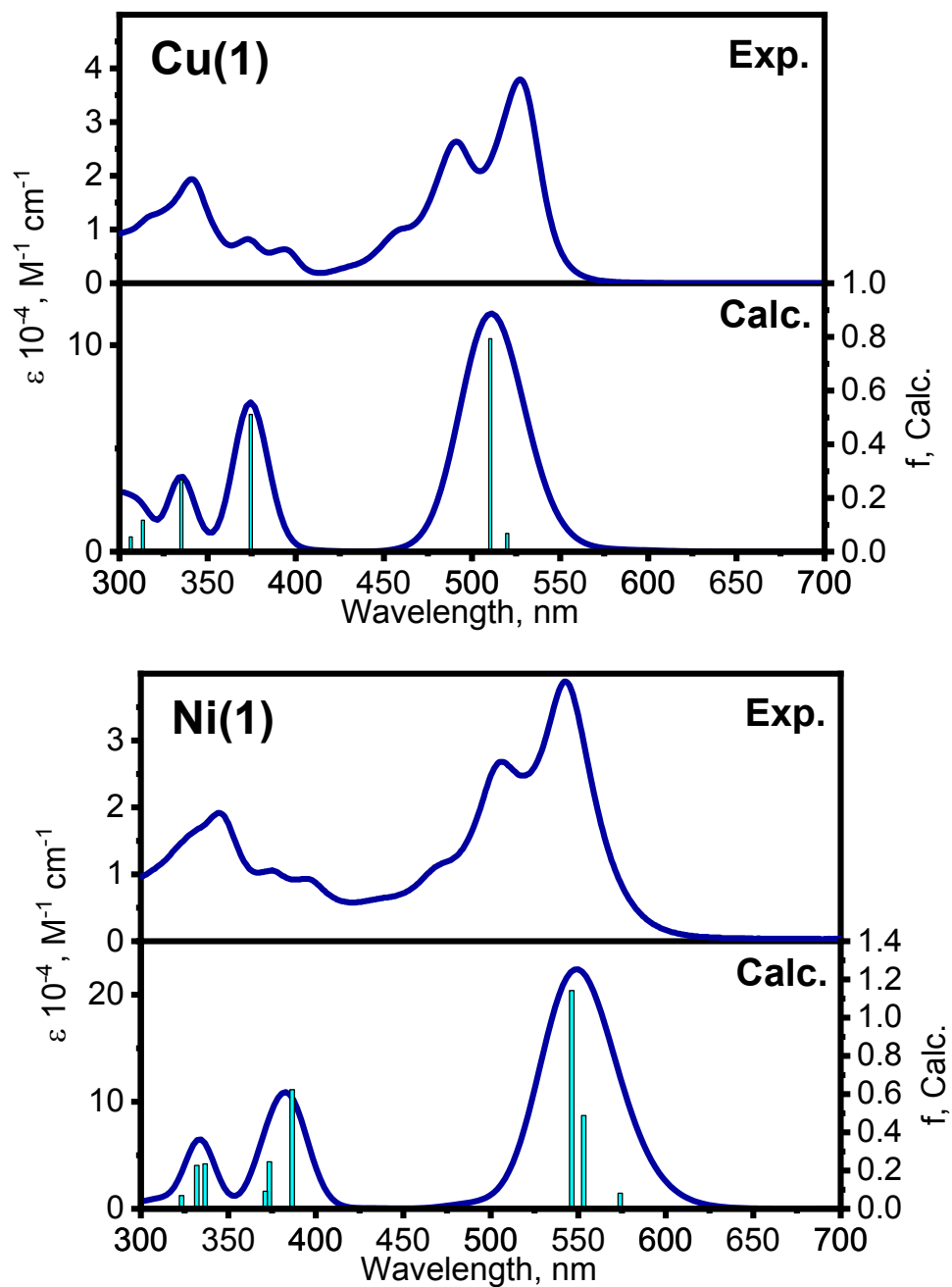
Figure S15: Experimental and TDDFT-predicted spectra for compounds **Cu(1)** and **Ni(1).**
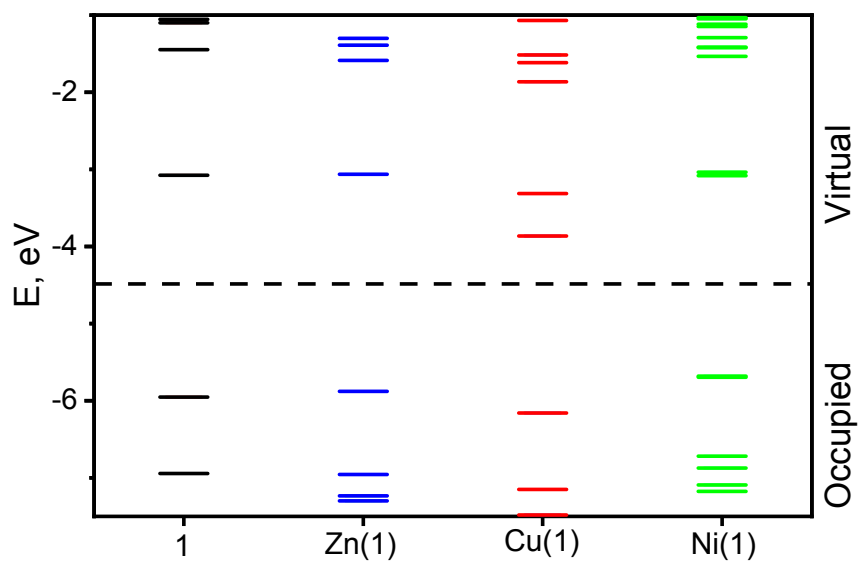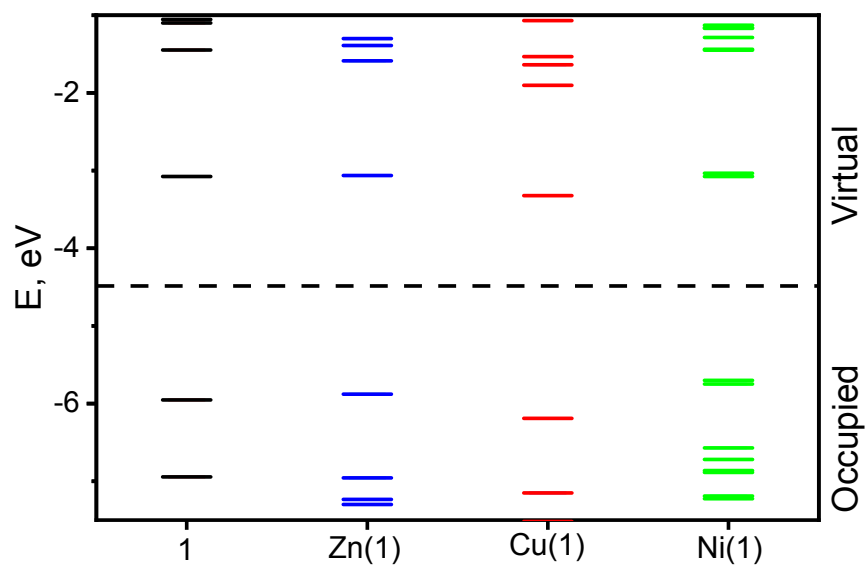
Figure S16: B3LYP α-spin relative energies of the frontier orbitals for compounds**.**

Figure S17: B3LYP β-spin relative energies of the frontier orbitals for compounds**.**
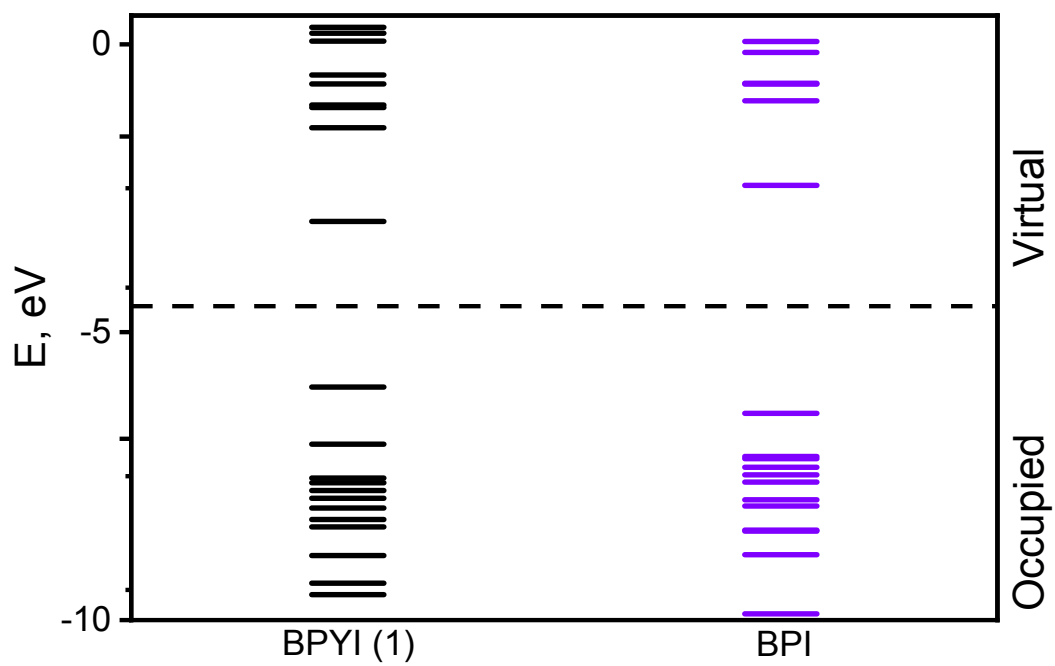
Figure S17: B3LYP relative energies of the frontier orbitals for BPYI (1) and BPI.
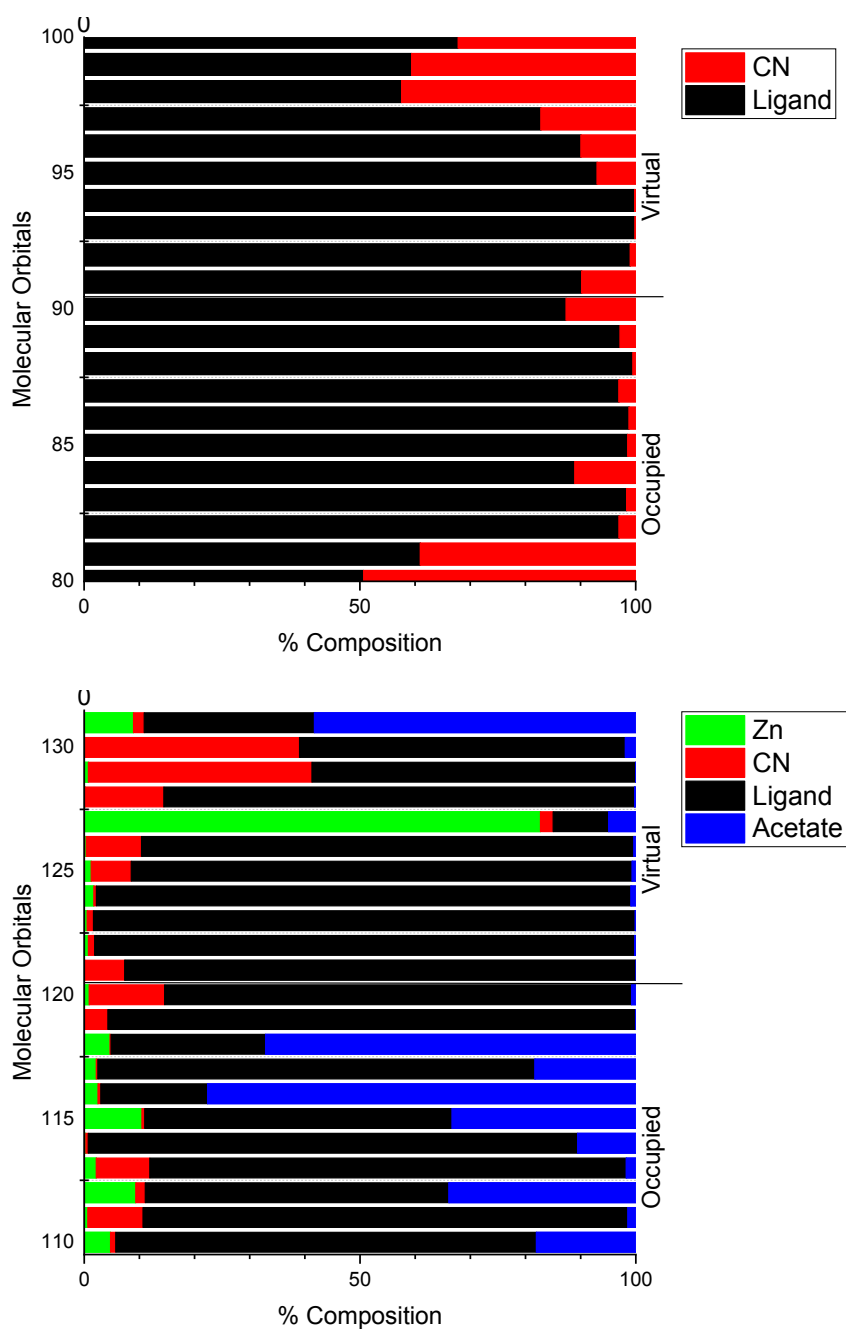
Figure S18: Orbital compositions for **1** and **Zn(1).**
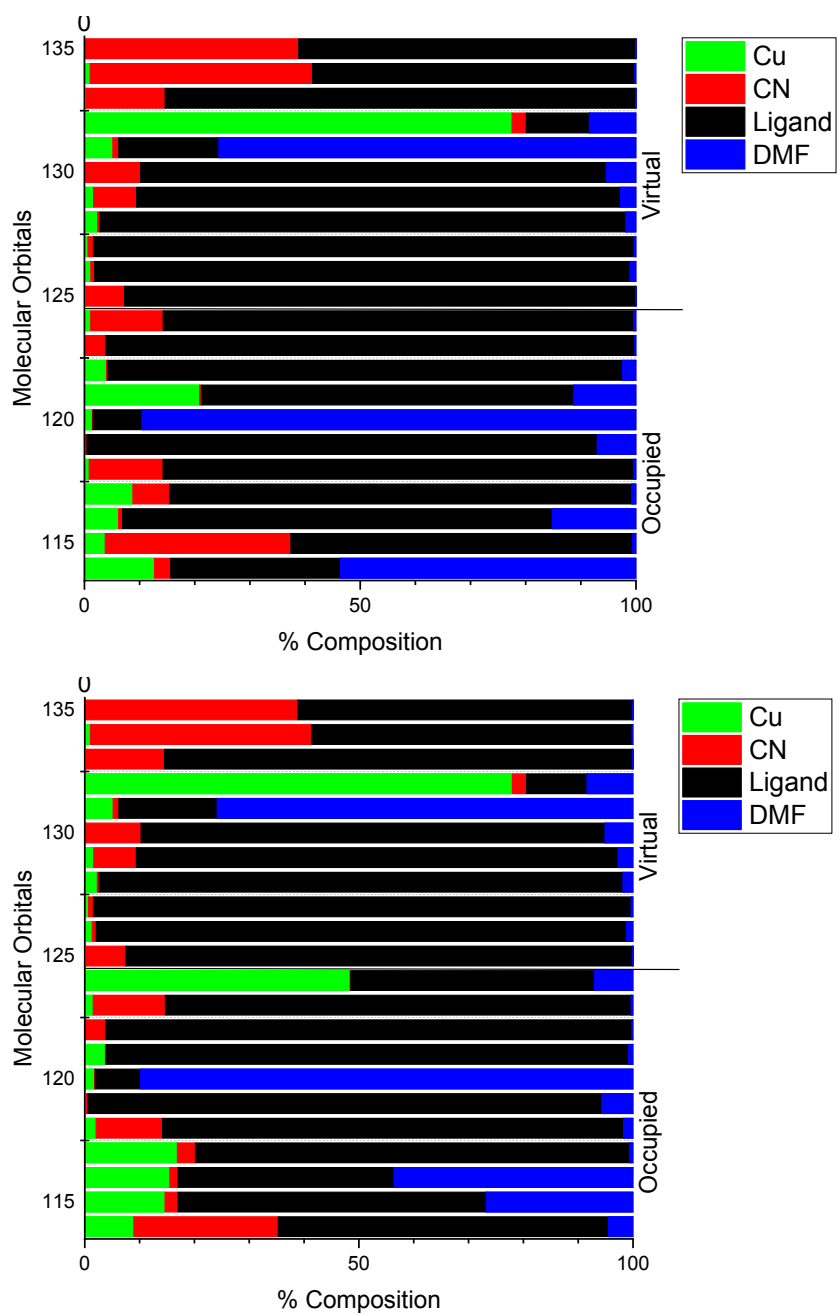
Figure S19: Orbital compositions for **Cu(1),** α-spin on top and β-spin on bottom.
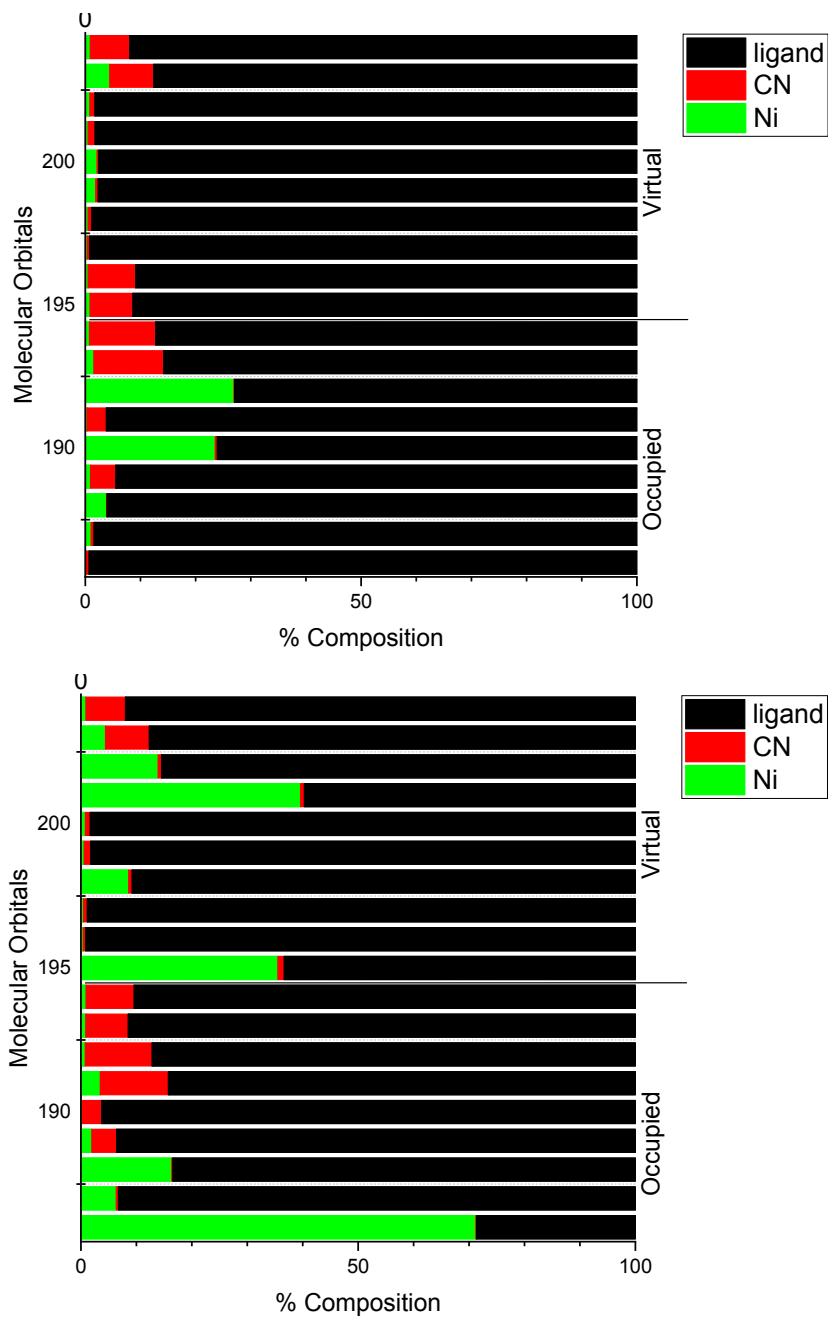
Figure S20: Orbital compositions for **Ni(1),** α-spin on top and β-spin on bottom.

Table S1: X-ray crystal data and structure parameters for compounds **1, Zn(1), Cu(1), and Ni(1).**

Compound	1 BPYI	Zn(1)	Cu(1)	Ni(1)
CCDC	2043926	2043927	2043928	2043929
Empirical formula	$C_{25}H_{20}N_6O$	$C_{24}H_{15}N_5O_2Zn$	$C_{25}H_{19}ClCuN_6O_5$	$C_{44}H_{24}N_{10}Ni$
Formula weight	420.47	470.78	582.45	751.44
Crystal system	Tetragonal	Triclinic	Monoclinic	Tetragonal
Space group	$P4_1$	P-1	$P2_1/n$	$I4_1/acd$
a/ Å	12.557(3)	7.9525(11)	8.025	17.9413(11)
b/ Å	12.557	10.8324(15)	28.235	17.9413(11)
c/ Å	25.933(6)	12.7721(19)	10.565	42.212(2)
α(°)	90	69.282(8)	90	90
β(°)	90	75.267(9)	101.66	90
γ(°)	90	83.931(9)	90	90
Volume (Å^3)	4089.2(19)	995.1(3)	2344.4	13587.6(18)
Z	8	2	4	16
Dc (Mg/m^3)	1.366	1.571	1.650	1.469
μ (mm^{-1})	0.088	1.268	1.098	0.623
F(000)	1760	480	1188	6176
reflns collected	5255	15222	51946	15457
indep. reflns	5255	3577	5789	3006
GOF on F^2	1.033	1.050	1.072	0.989
R1 (on F_o^2, I > 2σ(I))	0.1284	0.0922	0.0988	0.0531
wR2 (on F_o^2, I > 2σ(I))	0.2852	0.2340	0.2303	0.1009
R1 (all data)	0.2387	0.1511	0.1248	0.1089
wR2 (all data)	0.3539	0.2727	0.2402	0.1154

Equation 1: Evans NMR method calculation for effective magnetic moment

$$\mu_{eff} = \sqrt{\frac{3\,k_B}{N_A\beta^2}\left(\chi_M^P T\right)}$$

k_B = Boltzmann constant
N_A = Avogadro's number
β = Bohr magneton
$\boldsymbol{x}_P$ = molar susceptibility
T = absolute temperature (K)

Equation 2: Evans NMR method calculation for mass susceptibility

$$\chi = \frac{\delta v^p}{v_o S_f m^p} + \chi_o$$

δv^p = Shift in frequency for an internal inert reference; regular methanol (Hz)
v_o = frequency of the NMR spectrometer (Hz)
S_f = Shape factor of the NMR spectrometer; $4\pi/3$ sample axis parallel to magnetic field
m^p = concentration of solute (g/mL)
$\boldsymbol{x}_\circ$ = mass susceptibility of the deuterated solvent (mL/g)

Equation 3: Evans NMR method calculation for molar susceptibility

$$\chi_M^P = \frac{\delta v^p M^p}{v_o S_f m^p} - \chi_M^{dia}$$

δv^p = Shift in frequency for an internal inert reference; regular methanol (Hz)
M^P = Molecular weight of solute (g/mol)
v_o = frequency of the NMR spectrometer (Hz)
S_f = Shape factor of the NMR spectrometer; $4\pi/3$ sample axis parallel to magnetic field
m^p = concentration of solute (g/mL)
χ_M^{dia} = diamagnetic constant (mL/mol)

Table S2: Evans NMR method data and parameters.

Compound	Ni	Cu
Mass (mg)	1.5	1.6
Volume (mL)	1	1
Deuterated Solvent	Methanol	Methanol
Mass Susceptibility of solvent (mL/g)	5.3×10^{-7}	5.3×10^{-7}
Shift in frequency (Hz)	14.02	15.67
Temperature (K)	303.15	303.15
Molecular weight of solute (g/mol)	751.44	509.36
Frequency of NMR spectrometer (Hz)	4×10^{8}	4×10^{8}
Mass Susceptibility (mL/g)	6.1×10^{-6}	6.37×10^{-6}
Molar Susceptibility (mL/mol)	4.59×10^{-3}	3.24×10^{-3}
Diamagnetic constant (mL/mol)	-3.87×10^{-4}	-2.30×10^{-4}
μ_{eff} (μ_{β})	3.4	2.8

Table S3: TDDFT-predicted energies and expansion coefficients for compound **1** (only excited states with f > 0.05 and λ > 270 nm are listed).

Excited State   1:   Singlet-A   2.4950 eV 496.93 nm f=0.9941 <S**2>=0.000
        90 -> 91   0.70623

Excited State   2:   Singlet-A   3.3510 eV 369.99 nm f=0.5238 <S**2>=0.000
        89 -> 91   0.69523
        90 -> 92   -0.10532
Excited State   6:   Singlet-A   3.9424 eV 314.49 nm f=0.4650 <S**2>=0.000
        89 -> 91   0.10142
        90 -> 92   0.69331

Table S4: TDDFT-predicted energies and expansion coefficients for compound **BPI** (only excited states with f > 0.05 and λ > 270 nm are listed).

Excited State   1:   Singlet-B2   3.1945 eV 388.12 nm f=0.8299 <S**2>=0.000
        78 -> 79   0.70141
Excited State   5:   Singlet-A1   3.8525 eV 321.83 nm f=0.6237 <S**2>=0.000
        77 -> 79   0.69420
Excited State   8:   Singlet-A1   4.5389 eV 273.16 nm f=0.4748 <S**2>=0.000
        69 -> 79   0.11265
        71 -> 79   -0.12727
        78 -> 80   0.64409
        78 -> 81   0.15667

Table S5: TDDFT-predicted energies and expansion coefficients for compound **Zn(1)** (only excited states with f > 0.05 and λ > 270 nm are listed).

Excited State   1:   Singlet-A   2.3962 eV 517.42 nm f=0.8999 <S**2>=0.000
        120 ->121   0.70374
Excited State   2:   Singlet-A   3.3738 eV 367.49 nm f=0.5297 <S**2>=0.000
        119 ->121   0.69910
Excited State   3:   Singlet-A   3.4570 eV 358.65 nm f=0.0535 <S**2>=0.000
        117 ->121   0.60845
        118 ->121   -0.34795
Excited State   5:   Singlet-A   3.7062 eV 334.53 nm f=0.3172 <S**2>=0.000
        120 ->122   0.69836
Excited State   6:   Singlet-A   3.8983 eV 318.05 nm f=0.0631 <S**2>=0.000
        120 ->123   0.69942
Excited State   7:   Singlet-A   3.9854 eV 311.10 nm f=0.0785 <S**2>=0.000
        120 ->124   0.69731
Excited State 12:   Singlet-A   4.4742 eV 277.11 nm f=0.3183 <S**2>=0.000
        113 ->121   0.12669
        114 ->121   0.29144
        120 ->125   0.60068
        120 ->126   -0.12703

Table S6: TDDFT-predicted energies and expansion coefficients for compound **Cu(1)** (only excited states with f > 0.05 and λ > 270 nm are listed).

```
Excited State   6: 2.003-A     2.3843 eV  519.99 nm  f=0.0683  <S**2>=0.753
   124A ->125A      -0.21501
    97B ->124B       0.26046
   100B ->124B       0.54514
   101B ->124B       0.25681
   105B ->124B      -0.16894
   107B ->124B       0.37628
   113B ->124B      -0.18799
   114B ->124B       0.18689
   120B ->124B      -0.29054
   122B ->124B      -0.27741
   123B ->125B      -0.21708
Excited State   7: 2.004-A     2.4294 eV  510.35 nm  f=0.7930  <S**2>=0.754
   124A ->125A       0.66736
   100B ->124B       0.19036
   107B ->124B       0.19517
   120B ->124B      -0.10645
   123B ->125B       0.65482
Excited State  14: 2.010-A     3.3106 eV  374.51 nm  f=0.5113  <S**2>=0.760
   123A ->125A       0.69976
   122B ->125B       0.69403
Excited State  20: 2.006-A     3.6993 eV  335.15 nm  f=0.2676  <S**2>=0.756
   124A ->126A       0.69145
   123B ->126B       0.69855
Excited State  25: 2.037-A     3.9574 eV  313.30 nm  f=0.1175  <S**2>=0.787
   124A ->127A       0.68834
   123B ->127B       0.68525
Excited State  27: 2.005-A     4.0462 eV  306.42 nm  f=0.0552  <S**2>=0.755
   120A ->125A      -0.12475
   124A ->128A       0.66939
   109B ->124B      -0.12525
   116B ->124B       0.15483
   120B ->125B      -0.13076
   123B ->128B       0.66380
Excited State  30: 2.019-A     4.1321 eV  300.05 nm  f=0.0805  <S**2>=0.769
   124A ->128A       0.10073
   101B ->124B       0.14283
   105B ->124B      -0.13620
   109B ->124B       0.18458
   110B ->124B       0.11946
   113B ->124B       0.34615
   114B ->124B      -0.50127
   115B ->124B      -0.16911
   116B ->124B      -0.18618
   117B ->124B       0.61714
   120B ->124B       0.10620
Excited State  31: 2.061-A     4.1742 eV  297.02 nm  f=0.0704  <S**2>=0.812
   119A ->125A       0.17589
```

```
124A ->128A      -0.12568
 99B ->124B       0.10553
100B ->124B       0.13426
101B ->124B      -0.10506
109B ->124B      -0.27997
111B ->124B       0.24661
113B ->124B       0.10912
115B ->124B      -0.44315
116B ->124B       0.65767
117B ->124B       0.12566
119B ->125B       0.12378
123B ->128B      -0.11082
```
Excited State 35: 2.049-A   4.3439 eV 285.42 nm f=0.1382 <S**2>=0.800
```
119A ->125A      -0.18548
124A ->129A       0.10594
100B ->124B       0.21375
101B ->124B      -0.23817
109B ->124B      -0.40353
111B ->124B      -0.18453
114B ->124B      -0.31031
115B ->124B       0.59600
116B ->124B       0.15164
119B ->125B      -0.23175
```
Excited State 36: 2.165-A   4.4056 eV 281.42 nm f=0.1936 <S**2>=0.921
```
105B ->124B       0.20757
107B ->124B       0.31356
113B ->124B       0.76446
114B ->124B       0.19205
117B ->124B      -0.25556
118B ->125B      -0.23091
123B ->130B      -0.21268
```
Excited State 40: 2.240-A   4.5501 eV 272.49 nm f=0.2571 <S**2>=1.005
```
115A ->125A      -0.12448
119A ->125A      -0.20544
124A ->129A      -0.52422
114B ->125B       0.19495
119B ->125B      -0.17010
121B ->128B      -0.12306
123B ->129B       0.70334
```
Excited State 41: 2.072-A   4.5657 eV 271.56 nm f=0.1223 <S**2>=0.823
```
118A ->125A      -0.35625
124A ->130A      -0.22758
105B ->124B      -0.28012
107B ->124B      -0.34218
110B ->124B       0.11848
114B ->124B       0.46756
115B ->124B       0.15618
116B ->125B      -0.11215
117B ->124B       0.26516
118B ->125B      -0.32042
123B ->130B      -0.31323
```

Table S7: TDDFT-predicted energies and expansion coefficients for compound **Ni(1)** (only excited states with f > 0.05 and λ > 270 nm are listed).

Excited State 8: 3.699-A   2.1601 eV 573.96 nm f=0.0814 <S**2>=3.171
    193A -> 196A   -0.56232
    194A -> 195A   0.78738
    191B -> 194B   0.23828
Excited State 10: 3.019-A   2.2415 eV 553.12 nm f=0.4881 <S**2>=2.028
    193A -> 195A   0.48975
    194A -> 196A   0.50885
    191B -> 193B   0.37794
    192B -> 194B   0.58831
Excited State 11: 3.031-A   2.2695 eV 546.29 nm f=1.1416 <S**2>=2.046
    193A -> 196A   0.67808
    194A -> 195A   0.28707
    182B -> 195B   0.10028
    191B -> 194B   0.52656
    192B -> 193B   0.38981
Excited State 24: 3.005-A   3.2080 eV 386.49 nm f=0.6230 <S**2>=2.007
    189A -> 195A   0.15229
    191A -> 196A   0.68671
    189B -> 193B   0.16214
    190B -> 194B   0.67533
Excited State 29: 3.072-A   3.3198 eV 373.46 nm f=0.2461 <S**2>=2.109
    189A -> 195A   0.76278
    191A -> 196A   -0.24291
    189B -> 193B   0.56773
Excited State 32: 3.151-A   3.3410 eV 371.10 nm f=0.0913 <S**2>=2.232
    187A -> 195A   -0.46255
    188A -> 196A   -0.43393
    193A -> 199A   -0.12498
    194A -> 200A   -0.10206
    187B -> 193B   -0.35859
    188B -> 194B   -0.42407
    192B -> 195B   0.46508
Excited State 43: 3.094-A   3.6822 eV 336.71 nm f=0.2352 <S**2>=2.144
    194A -> 198A   0.69486
    183B -> 193B   -0.11959
    184B -> 194B   -0.12309
    186B -> 193B   0.12277
    191B -> 196B   -0.19786
    192B -> 197B   0.62753
Excited State 48: 3.071-A   3.7349 eV 331.96 nm f=0.2271 <S**2>=2.108
    185A -> 195A   -0.10336
    186A -> 196A   -0.10447
    193A -> 197A   0.69758
    194A -> 201A   -0.17693

```
    191B -> 196B      0.63797
    191B -> 200B     -0.12999
    192B -> 197B      0.11851
Excited State  54:  3.119-A      3.8356 eV  323.25 nm  f=0.0690  <S**2>=2.182
    193A -> 199A      0.53547
    194A -> 200A      0.23341
    185B -> 201B     -0.10268
    191B -> 198B      0.75996
Excited State  99:  3.500-A      4.4536 eV  278.39 nm  f=0.1505  <S**2>=2.813
    181A -> 196A      0.10872
    182A -> 195A     -0.17776
    185A -> 195A     -0.11147
    187A -> 201A      0.16936
    188A -> 197A     -0.16198
    188A -> 202A     -0.10812
    190A -> 199A      0.20182
    192A -> 200A     -0.21922
    193A -> 203A      0.18160
    194A -> 204A      0.17369
    172B -> 193B      0.10928
    175B -> 194B      0.16361
    179B -> 194B     -0.34614
    184B -> 194B      0.12231
    187B -> 199B     -0.11060
    188B -> 196B      0.14438
    191B -> 203B      0.64180
    192B -> 199B      0.10345
    192B -> 204B      0.16474
Excited State 104:  3.114-A      4.4757 eV  277.02 nm  f=0.5376  <S**2>=2.175
    185A -> 195A      0.19268
    186A -> 196A      0.10475
    193A -> 203A     -0.25341
    194A -> 204A     -0.48353
    183B -> 193B     -0.17939
    192B -> 204B      0.74358
```

Table S8: DFT optimized geometry of compound **1.**

```
----------------------------------------------------------------------
Center   Atomic    Atomic        Coordinates (Angstroms)
Number   Number    Type       X         Y         Z
----------------------------------------------------------------------
  1        6        0      -2.038857  -3.258985  -0.057884
  2        1        0      -1.187090  -3.931563  -0.089187
  3        6        0      -3.334263  -3.765451  -0.041210
  4        1        0      -3.507123  -4.834732  -0.057735
  5        6        0      -4.387492  -2.855015  -0.002507
  6        1        0      -5.416348  -3.197406   0.012907
  7        6        0      -4.107627  -1.496342   0.015558
  8        1        0      -4.915437  -0.776281   0.044625
  9        6        0      -2.766961  -1.070382  -0.004386
 10        6        0      -2.426885   0.368090   0.008097
 11        6        0      -3.528374   1.264493   0.021816
 12        6        0      -1.148478   0.895988   0.004641
 13        6        0      -0.707241   2.299105   0.004012
 14        6        0      -1.413382   3.502378   0.007831
 15        1        0      -2.493203   3.526537   0.014070
 16        6        0      -0.698407   4.698157   0.003754
 17        1        0      -1.236949   5.639202   0.006774
 18        6        0       0.697746   4.698244  -0.004113
 19        1        0       1.236168   5.639355  -0.007281
 20        6        0       1.412865   3.502533  -0.008025
 21        1        0       2.492683   3.526818  -0.014247
 22        6        0       0.706863   2.299207  -0.004037
 23        6        0       1.148302   0.896092  -0.004609
 24        6        0       2.426790   0.368404  -0.007963
 25        6        0       3.528161   1.264944  -0.021591
 26        6        0       2.767112  -1.070041   0.004505
 27        6        0       4.107835  -1.495743  -0.015095
 28        1        0       4.915534  -0.775537  -0.043682
 29        6        0       4.387935  -2.854378   0.002760
 30        1        0       5.416849  -3.196579  -0.012417
 31        6        0       3.334874  -3.765011   0.040984
 32        1        0       3.507925  -4.834268   0.057327
 33        6        0       2.039371  -3.258781   0.057441
 34        1        0       1.187728  -3.931525   0.088423
 35        7        0      -0.000043   0.141702   0.000041
 36        1        0      -0.000044  -0.880124  -0.000003
 37        7        0      -1.752593  -1.955606  -0.039136
 38        7        0      -4.456768   1.957363   0.033506
 39        7        0       1.752880  -1.955447   0.038838
 40        7        0       4.456524   1.957852  -0.033172
----------------------------------------------------------------------
```
E_h = **-1120.173695 Hartree**

Table S9: DFT optimized geometry of compound **BPI.**

```
-------------------------------------------------------------------
Center   Atomic    Atomic         Coordinates (Angstroms)
Number   Number    Type        X        Y         Z
-------------------------------------------------------------------
  1        7        0      0.000000   1.946679  -1.751293
  2        7        0      0.000000   0.000000   0.210966
  3        7        0      0.000000   2.409879   0.618461
  4        6        0      0.000000   0.704739   4.789695
  5        1        0      0.000000   1.236565   5.734627
  6        6        0      0.000000   4.231754  -0.943798
  7        1        0      0.000000   4.898771  -0.092163
  8        6        0      0.000000   1.161289   0.987110
  9        6        0      0.000000   2.423456  -3.014758
 10        1        0      0.000000   1.680330  -3.805118
 11        6        0      0.000000   1.427955   3.583609
 12        1        0      0.000000   2.511231   3.573232
 13        6        0      0.000000   0.703512   2.391736
 14        6        0      0.000000   2.837363  -0.717412
 15        6        0      0.000000   3.791188  -3.321390
 16        1        0      0.000000   4.120774  -4.352744
 17        6        0      0.000000   4.709200  -2.256902
 18        1        0      0.000000   5.775656  -2.449945
 19        7        0      0.000000  -1.946679  -1.751293
 20        7        0      0.000000  -2.409879   0.618461
 21        6        0      0.000000  -0.704739   4.789695
 22        1        0      0.000000  -1.236565   5.734627
 23        6        0      0.000000  -4.231754  -0.943798
 24        1        0      0.000000  -4.898771  -0.092163
 25        6        0      0.000000  -1.161289   0.987110
 26        6        0      0.000000  -2.423456  -3.014758
 27        1        0      0.000000  -1.680330  -3.805118
 28        6        0      0.000000  -1.427955   3.583609
 29        1        0      0.000000  -2.511231   3.573232
 30        6        0      0.000000  -0.703512   2.391736
 31        6        0      0.000000  -2.837363  -0.717412
 32        6        0      0.000000  -3.791188  -3.321390
 33        1        0      0.000000  -4.120774  -4.352744
 34        6        0      0.000000  -4.709200  -2.256902
 35        1        0      0.000000  -5.775656  -2.449945
 36        1        0      0.000000   0.000000  -0.807567
-------------------------------------------------------------------
```

E_h = -966.678725 Hartree

Table S10: DFT optimized geometry of compound **Zn(1).**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.683375	-2.232021	-0.894964
2	1	0	3.446142	-1.485468	-0.717084
3	6	0	2.992427	-3.460970	-1.449828
4	1	0	4.010392	-3.686023	-1.741546
5	6	0	1.959169	-4.381614	-1.608665
6	1	0	2.146102	-5.357817	-2.041646
7	6	0	0.680060	-4.037749	-1.207449
8	1	0	-0.128346	-4.745233	-1.332260
9	6	0	0.419957	-2.769152	-0.653189
10	6	0	-0.960981	-2.434195	-0.244807
11	6	0	-1.819947	-3.556546	-0.103803
12	6	0	-1.504519	-1.166324	-0.058718
13	6	0	-2.917508	-0.793959	0.173222
14	6	0	-4.084546	-1.536904	0.346096
15	1	0	-4.077763	-2.616838	0.338850
16	6	0	-5.288528	-0.859007	0.539468
17	1	0	-6.201097	-1.427008	0.682807
18	6	0	-5.330357	0.534982	0.550321
19	1	0	-6.275278	1.044853	0.702370
20	6	0	-4.169305	1.286688	0.367484
21	1	0	-4.227196	2.365074	0.377029
22	6	0	-2.959976	0.617765	0.183468
23	6	0	-1.572504	1.077502	-0.045872
24	6	0	-1.107613	2.378077	-0.221848
25	6	0	-2.029831	3.445317	-0.055259
26	6	0	0.244476	2.797804	-0.646985
27	6	0	0.424672	4.088691	-1.181217
28	1	0	-0.422219	4.754986	-1.272941
29	6	0	1.674306	4.506827	-1.604019
30	1	0	1.799911	5.500255	-2.019562
31	6	0	2.757668	3.638338	-1.489942
32	1	0	3.754778	3.922011	-1.801826
33	6	0	2.527254	2.385719	-0.950327
34	1	0	3.332129	1.677628	-0.804148
35	6	0	2.952418	0.083983	2.133468
36	6	0	3.812425	0.048525	3.375950
37	1	0	3.311797	0.537189	4.211915
38	1	0	4.780061	0.514242	3.191908
39	1	0	3.985750	-0.995290	3.655213
40	7	0	-0.767486	-0.020511	-0.132105
41	7	0	1.440648	-1.884622	-0.509218

42	7	0	1.314357	1.967686	-0.540818
43	7	0	-2.489478	-4.495390	0.013701
44	7	0	-2.752413	4.340787	0.084504
45	8	0	1.680309	0.038052	2.276589
46	8	0	3.474187	0.127764	0.992968
47	30	0	1.200464	0.044820	0.282884

E$_h$ = -3127.570282 Hartree

Table S11: DFT optimized geometry of compound **Cu(1).**

```
-------------------------------------------------------------------------
Center   Atomic   Atomic          Coordinates (Angstroms)
Number   Number    Type        X          Y          Z
-------------------------------------------------------------------------
  1        6        0       -1.995164   2.589000  -1.127781
  2        1        0       -2.830687   1.903864  -1.140055
  3        6        0       -2.144840   3.901833  -1.529140
  4        1        0       -3.106268   4.253779  -1.879965
  5        6        0       -1.031330   4.737346  -1.461548
  6        1        0       -1.096791   5.775793  -1.764866
  7        6        0        0.168185   4.226156  -1.002952
  8        1        0        1.039049   4.864457  -0.950897
  9        6        0        0.270118   2.875747  -0.614492
 10        6        0        1.555581   2.348781  -0.138837
 11        6        0        2.530720   3.345659   0.137200
 12        6        0        1.906443   1.016381   0.029025
 13        6        0        3.218680   0.474043   0.431838
 14        6        0        4.427149   1.075394   0.784473
 15        1        0        4.547087   2.147537   0.806508
 16        6        0        5.507605   0.261342   1.121243
 17        1        0        6.449812   0.719068   1.401024
 18        6        0        5.389154  -1.127963   1.101994
 19        1        0        6.239614  -1.746037   1.367009
 20        6        0        4.187262  -1.737577   0.745195
 21        1        0        4.123501  -2.814775   0.737555
 22        6        0        3.099086  -0.930541   0.412132
 23        6        0        1.717109  -1.231758  -0.008758
 24        6        0        1.151998  -2.480747  -0.229030
 25        6        0        1.934741  -3.636745   0.037959
 26        6        0       -0.184919  -2.764902  -0.764853
 27        6        0       -0.496205  -4.060651  -1.222278
 28        1        0        0.249915  -4.840938  -1.166132
 29        6        0       -1.740464  -4.337327  -1.756391
 30        1        0       -1.966961  -5.335686  -2.112351
 31        6        0       -2.689231  -3.318854  -1.834882
 32        1        0       -3.675735  -3.483679  -2.248182
 33        6        0       -2.340114  -2.070678  -1.359066
 34        1        0       -3.045411  -1.251306  -1.377777
 35        6        0       -3.048591  -0.072296   1.631785
 36        1        0       -2.300623  -0.453029   2.331269
 37        6        0       -4.572331  -0.359081   3.496880
 38        1        0       -3.668194  -0.706769   3.992745
 39        1        0       -5.314915  -1.158788   3.506872
 40        1        0       -4.968888   0.501222   4.038810
 41        6        0       -5.389846   0.513535   1.310455
```

42	1	0	-5.795902	1.419900	1.763741
43	1	0	-6.173605	-0.245079	1.272447
44	1	0	-5.044283	0.731713	0.304931
45	29	0	-0.860584	0.116339	-0.302090
46	7	0	1.059779	-0.040989	-0.191993
47	7	0	-0.825852	2.080863	-0.684205
48	7	0	-1.126987	-1.792882	-0.835182
49	7	0	3.288920	4.193253	0.355913
50	7	0	2.529136	-4.607579	0.251073
51	7	0	-4.273293	0.020684	2.116395
52	8	0	-2.731309	0.244365	0.456613

E$_h$ = -3008.566038 Hartree

Table S12: DFT optimized geometry of compound **Ni(1).**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.970011	-1.676388	2.316321
2	1	0	-1.696273	-0.878138	2.256601
3	6	0	-1.186933	-2.762418	3.147393
4	1	0	-2.082649	-2.813960	3.753560
5	6	0	-0.231151	-3.775430	3.152928
6	1	0	-0.361367	-4.662731	3.762434
7	6	0	0.907909	-3.624896	2.383029
8	1	0	1.675356	-4.386229	2.408649
9	6	0	1.089064	-2.468060	1.595557
10	6	0	2.387023	-2.240008	0.940737
11	6	0	3.287957	-3.335260	1.016880
12	6	0	2.857819	-1.049858	0.383700
13	6	0	4.277383	-0.674115	0.203923
14	6	0	5.481587	-1.349019	0.409764
15	1	0	5.510138	-2.383180	0.718028
16	6	0	6.679373	-0.666789	0.200888
17	1	0	7.619800	-1.184318	0.355634
18	6	0	6.679159	0.667881	-0.203995
19	1	0	7.619422	1.185467	-0.359527
20	6	0	5.481119	1.349983	-0.411886
21	1	0	5.509254	2.384137	-0.720239
22	6	0	4.277177	0.674937	-0.205016
23	6	0	2.857507	1.050589	-0.383877
24	6	0	2.386305	2.240849	-0.940338
25	6	0	3.286922	3.336358	-1.016221
26	6	0	1.088117	2.468725	-1.594780
27	6	0	0.906213	3.625985	-2.381445
28	1	0	1.673036	4.387978	-2.406309
29	6	0	-0.232803	3.776121	-3.151498
30	1	0	-0.363602	4.663723	-3.760440
31	6	0	-1.187780	2.762346	-3.146854
32	1	0	-2.083322	2.813510	-3.753314
33	6	0	-0.970301	1.676051	-2.316273
34	1	0	-1.696083	0.877331	-2.257029
35	7	0	2.069928	0.000309	0.000066
36	7	0	0.111824	-1.532620	1.532868
37	7	0	0.111474	1.532621	-1.532689
38	7	0	3.978618	-4.265278	1.065667
39	7	0	3.977328	4.266582	-1.064800
40	28	0	0.000004	0.000006	0.000247

41	6	0	0.969975	1.676428	2.316317
42	1	0	1.696245	0.878184	2.256608
43	6	0	1.186884	2.762470	3.147376
44	1	0	2.082598	2.814028	3.753545
45	6	0	0.231091	3.775472	3.152896
46	1	0	0.361298	4.662783	3.762389
47	6	0	-0.907965	3.624917	2.382997
48	1	0	-1.675417	4.386245	2.408605
49	6	0	-1.089108	2.468068	1.595539
50	6	0	-2.387061	2.239989	0.940715
51	6	0	-3.288043	3.335203	1.016870
52	6	0	-2.857825	1.049836	0.383667
53	6	0	-4.277380	0.674080	0.203878
54	6	0	-5.481588	1.348978	0.409709
55	1	0	-5.510145	2.383140	0.717974
56	6	0	-6.679367	0.666741	0.200821
57	1	0	-7.619799	1.184264	0.355559
58	6	0	-6.679139	-0.667928	-0.204064
59	1	0	-7.619398	-1.185521	-0.359604
60	6	0	-5.481093	-1.350021	-0.411950
61	1	0	-5.509219	-2.384174	-0.720308
62	6	0	-4.277155	-0.674969	-0.205069
63	6	0	-2.857478	-1.050604	-0.383927
64	6	0	-2.386255	-2.240853	-0.940399
65	6	0	-3.286843	-3.336386	-1.016283
66	6	0	-1.088060	-2.468701	-1.594834
67	6	0	-0.906135	-3.625942	-2.381524
68	1	0	-1.672950	-4.387941	-2.406413
69	6	0	0.232890	-3.776048	-3.151568
70	1	0	0.363705	-4.663634	-3.760529
71	6	0	1.187858	-2.762264	-3.146888
72	1	0	2.083409	-2.813407	-3.753337
73	6	0	0.970359	-1.675992	-2.316283
74	1	0	1.696135	-0.877269	-2.257008
75	7	0	-2.069917	-0.000314	0.000027
76	7	0	-0.111857	1.532638	1.532864
77	7	0	-0.111426	-1.532590	-1.532710
78	7	0	-3.978867	4.265096	1.065711
79	7	0	-3.977330	-4.266558	-1.064721

E$_h$ = -3747.535260 Hartree

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