Biliazine: A ring open phthalocyanine analog with a meso hydrogen bond.

Briana R. Schrage,[a] Victor N. Nemykin,[b] and Christopher J. Ziegler[a]

a Department of Chemistry, University of Akron, Akron, Ohio 44312-3601, United States
b Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Supplementary Information

Table of Contents

General Information

Experimental

All reagents and starting materials were purchased from commercial vendors and used without further purification. 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 Cary 100 Bio UV-visible spectrometer.

X-ray intensity data were measured on a Bruker CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, λ = 1.54178 Å, Mo Kα radiation, λ =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 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

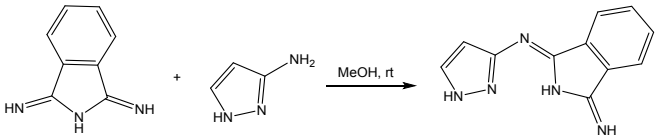
The starting geometries of compounds **1** and **3** were optimized using a B3LYP exchange–correlation functional.[3] Energy minima in optimized geometry were confirmed by the frequency calculations (absence of the imaginary frequencies). The solvent effect was modeled using the polarized continuum model (PCM).[4] In all calculations, $CHCl_3$ was used as the solvent. In PCM-TDDFT calculation, the first 50 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 QMForge program was used for molecular orbital analysis in all cases.[7]

Full citation for Gaussian

Gaussian 09, Revision D.01,. Frisch, M. J; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;. Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.;. Cioslowski, J.; Stefanov, B. B.; Liu, G.;. Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2009.

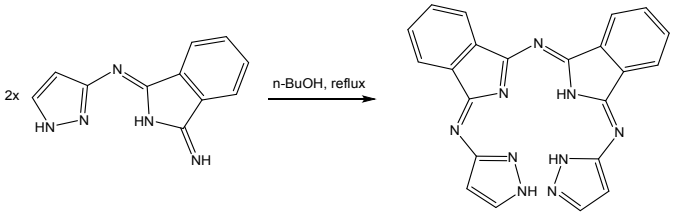
Syntheses.

Synthesis of 1. 1,3-Diiminoisoindoline (1.00 g, 6.89 mmol) and 3-amino pyrazole (0.57 g, 6.89 mmol) were dissolved in methanol (20 mL) and stirred at room temperature for 1 hour. The resultant solid was filtered, washed with cold methanol, and air dried to give a yellow solid. Crystals suitable for X-ray diffraction were grown by slow evaporation from DMF.



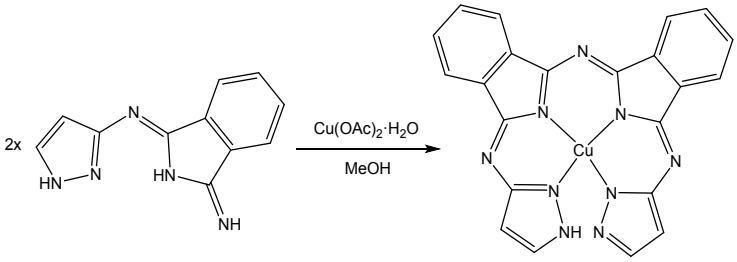
1: Yield: 1.16 g (79.6%). ^{1}H NMR (300 MHz, d_6 - DMSO): δ = 12.66 (s, 1H), 8.70 (s, 2H), 7.90 (d, J = 7.0 Hz, 1H), 7.76 (d, J = 6.7 Hz, 1H), 7.57 (m, 2H), 7.47 (s, 1H), 6.64 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, d_6 - DMSO): δ = 170.2, 163.8, 140.7, 134.4, 131.1, 129.9, 121.2, 100.5. HRMS (ESI-TOF, positive mode) m/z: calcd for $C_{11}H_{10}N_5$ 212.0931, found 212.0935 $[M+H]^+$.

Synthesis of H_2BlzH (2). Compound **1** (0.10 g, 2.37 mmol) was dissolved in n-butanol (7 mL) and heated to a reflux for 1 hour. The resultant solid was filtered, washed with cold n-butanol, and air dried to give a red solid. Crystals suitable for X-ray diffraction were grown by slow evaporation from DMF.

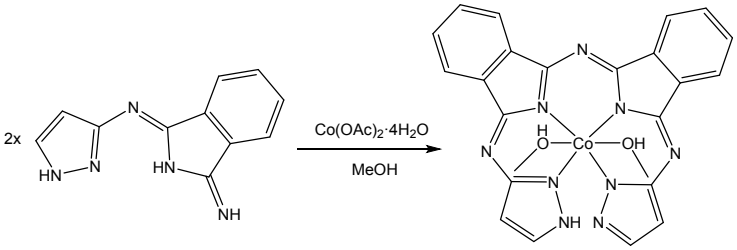


H_2BlzH (2): Yield: 0.088 g (91.5%). HRMS (ESI-TOF, positive mode) m/z: calcd for $C_{22}H_{15}N_9Na$ 428.1343, found 428.1346 $[M+Na]^+$.

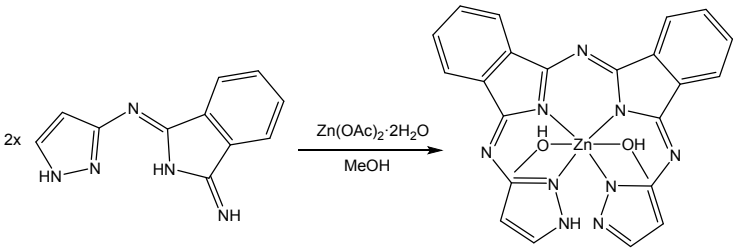
Synthesis of MBlzH complexes. A solution of $M(OAc)_2$ hydrate (M = Co, Cu, Zn) (0.12 mmol), and two equivalents of **1** (0.05 g, 0.24 mmol) in MeOH (4.00 mL) were heated until all of the solids dissolved. The mixture was then stirred at room temperature for 1 hour. The resultant precipitate was filtered and washed with cold MeOH. The compounds were isolated as brown (**Co(BlzH)(MeOH)$_2$**) (**4**), and red (**Cu(BlzH) (3)** and **Zn(BlzH)(MeOH)$_2$**) (**5**) solids. Crystals suitable for X-ray diffraction were grown by slow evaporation of MeOH (**Co(BlzH)(MeOH)$_2$,** and **Zn(BlzH)(MeOH)$_2$**), and slow evaporation of THF (**Cu(BlzH)**).



Cu(BlzH) (3): Yield: 0.050 g (91.0%). HRMS (ESI-TOF, positive mode) m/z: calcd for $C_{22}H_{14}CuN_9$ 467.0663, found 467.0646 $[M+H]^+$.



Co(BlzH)(MeOH)$_2$ (4): Yield: 0.049 g (78.3%). HRMS (ESI-TOF, positive mode) m/z: calcd for $C_{22}H_{14}CoN_9$ 463.0699, found 463.0681 $[M+H]^+$.



Zn(BlzH)(MeOH)$_2$ (5): Yield: 0.052 g (82.2%). ^{1}H NMR (500 MHz, d_6 - DMSO): δ = 16.73 (s, NH), 8.17 (m, 2H), 7.99 (m, 1H), 7.77 (m, 2H), 7.72 (m, 4H), 7.53 (d, J = 1.3 Hz, 2H), 6.63 (d, J = 1.3 Hz, 2H), 4.06 (q, J = 5.3 Hz, $CH_3O\mathit{H}$), 3.17 (d, J = 5.0 Hz, $C\mathit{H}_3OH$). $^{13}C\{^1H\}$ NMR (125 MHz, d_6 - DMSO): δ = 172.8, 157.8, 156.0, 140.4, 138.7, 131.7, 130.6, 122.4, 121.6, 107.1. HRMS (ESI-TOF, positive mode) m/z: calcd for $C_{22}H_{14}N_9Zn$ 468.0658, found 468.0665 $[M+H]^+$.

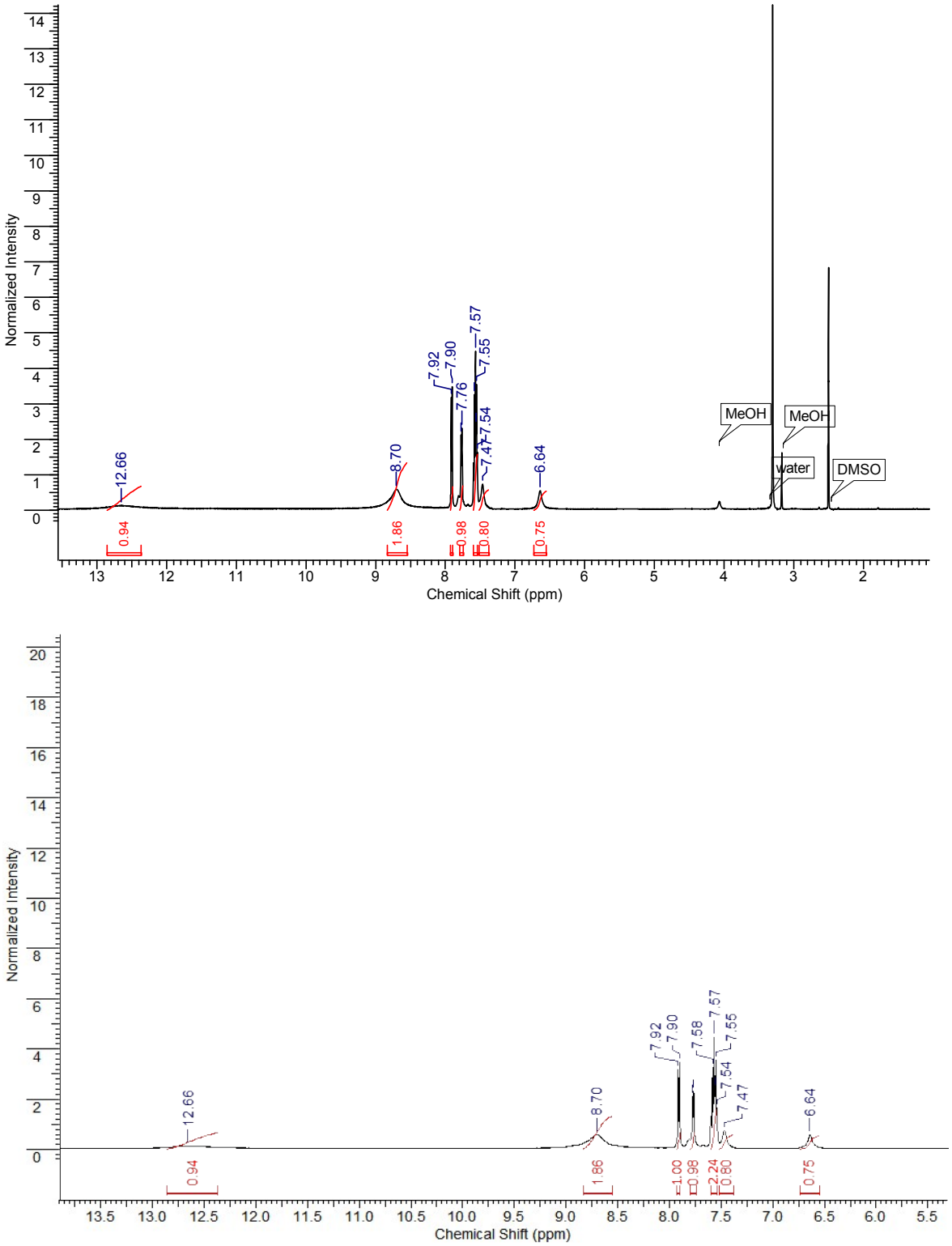


Figure S1: ^{1}H NMR (500 MHz) of **1** in d6-DMSO.

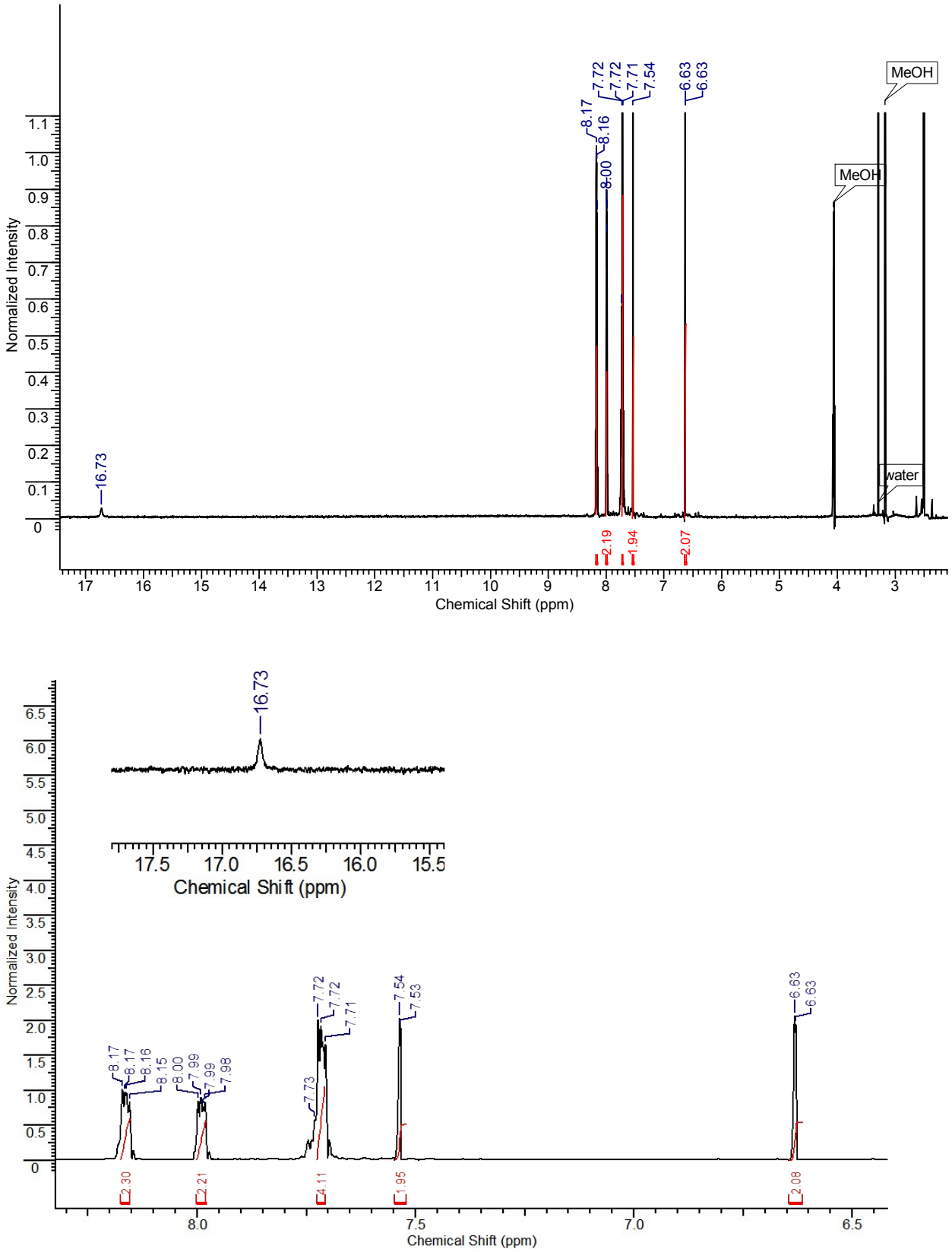


Figure S2: ^{1}H NMR (500 MHz) of **5** in d6-DMSO.

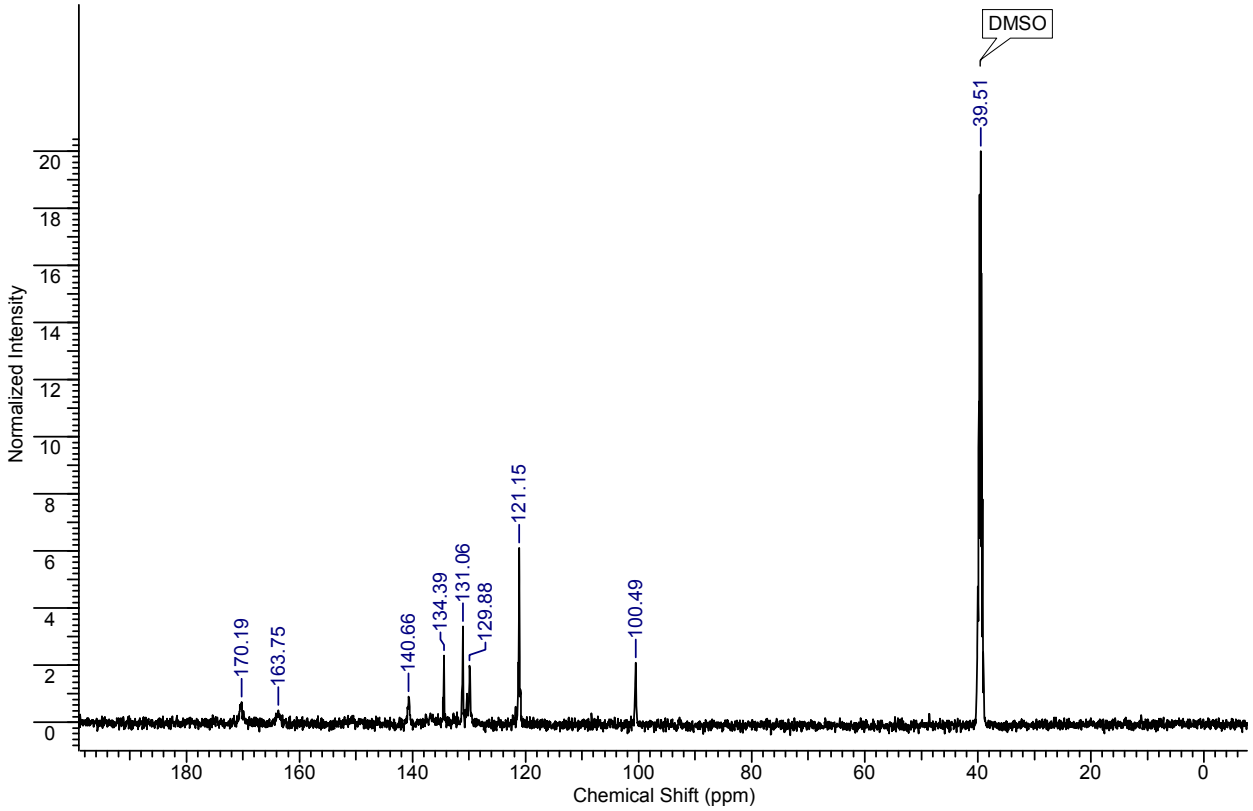


Figure S3: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **1** in d6-DMSO.

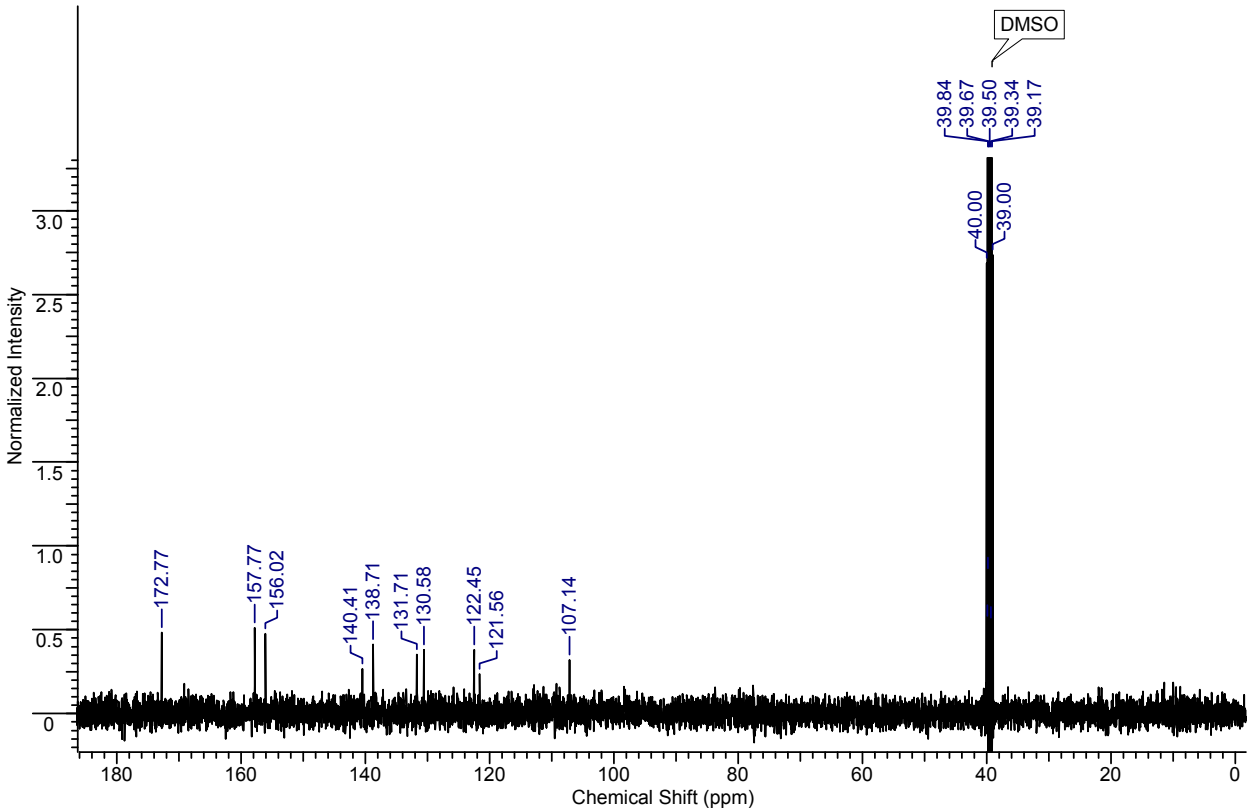


Figure S4: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **5** in d6-DMSO.

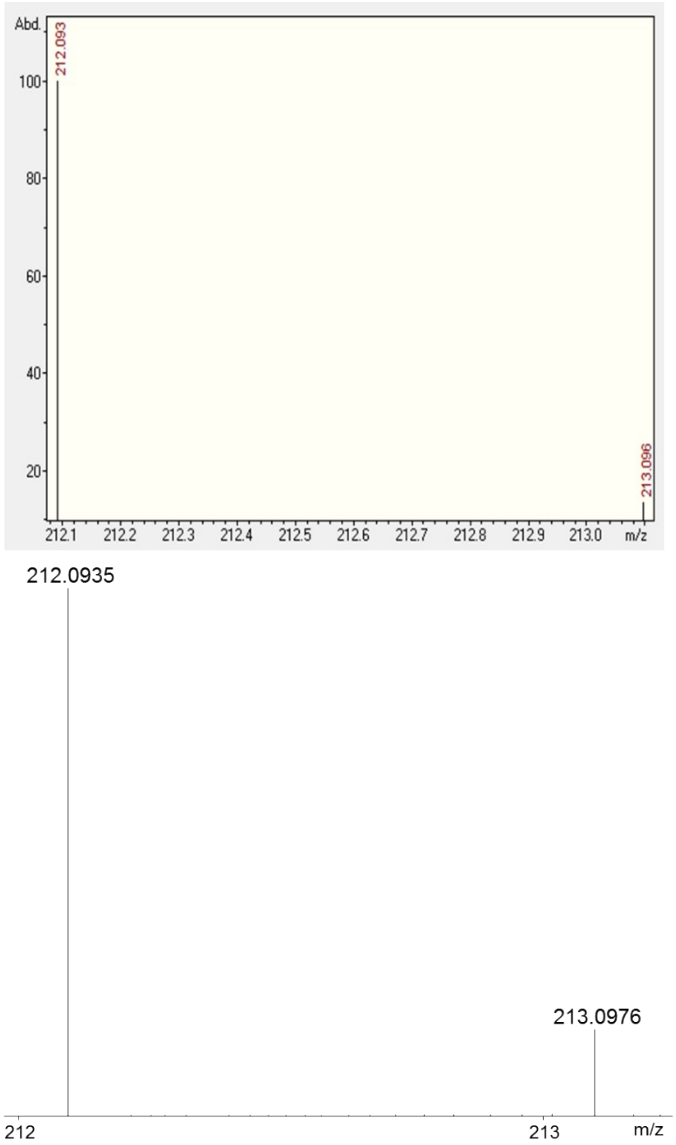


Figure S5: High-resolution ESI mass spectra of **1**. Top: calculated spectrum. Bottom: experimental spectrum.

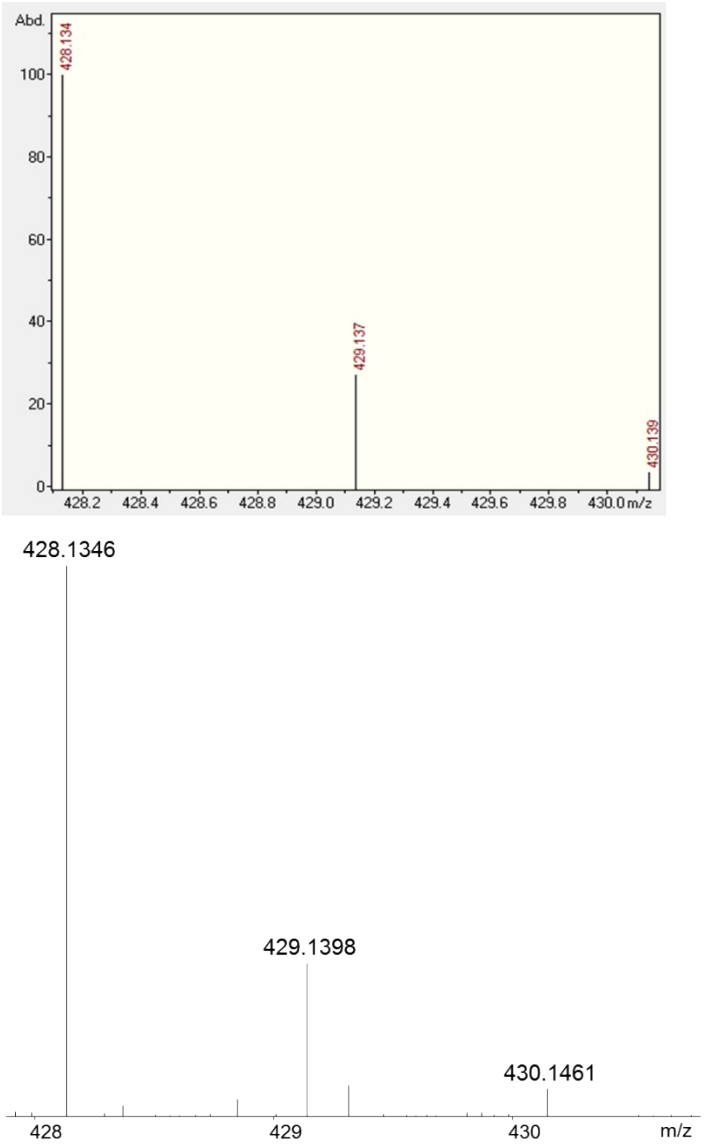


Figure S6: High-resolution ESI mass spectra of **2**. Top: calculated spectrum. Bottom: experimental spectrum.

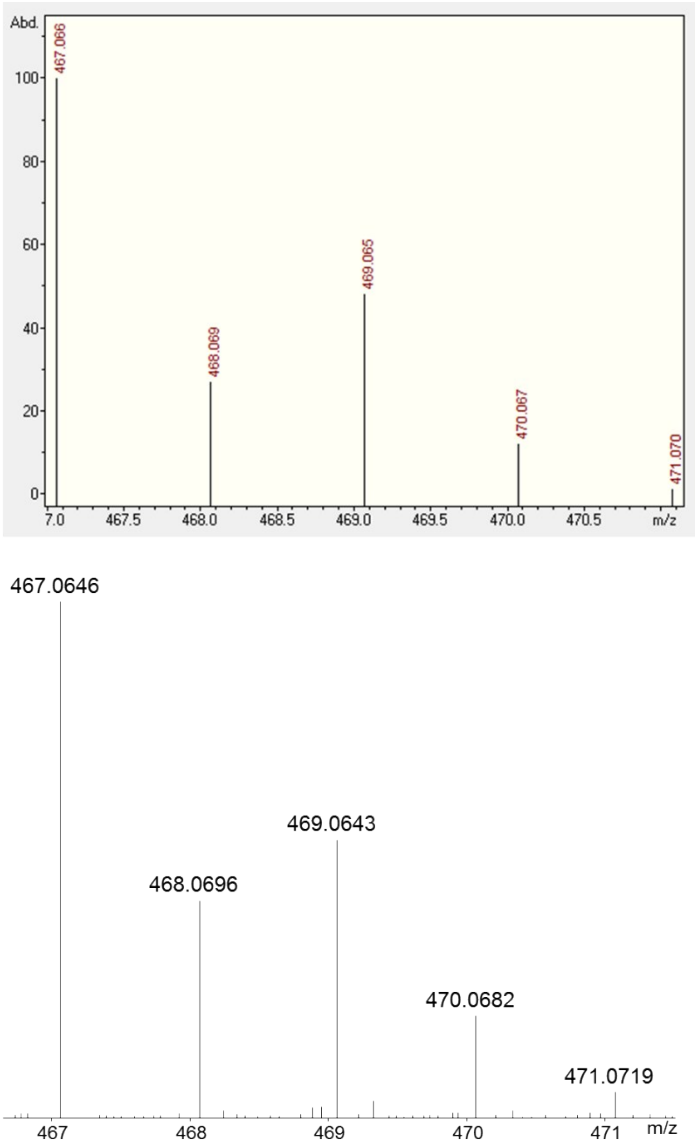


Figure S8: High-resolution ESI mass spectra of **3.** Top: calculated spectrum. Bottom: experimental spectrum.

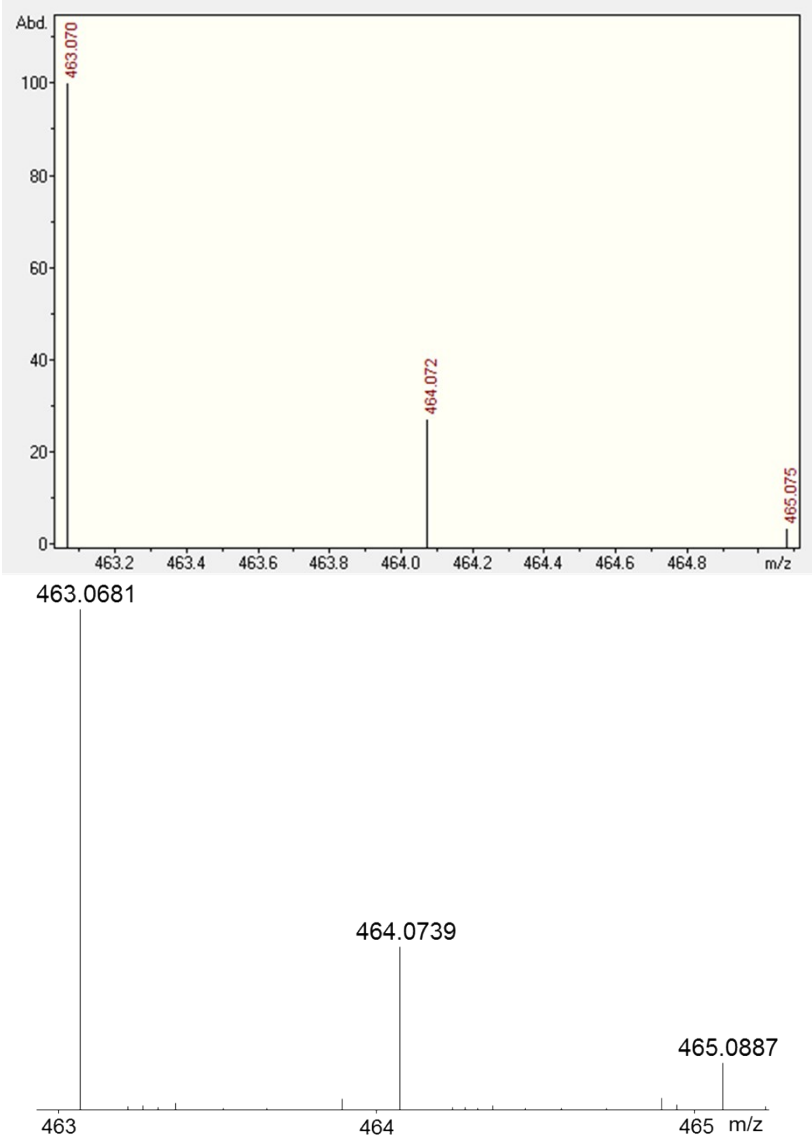


Figure S7: High-resolution ESI mass spectra of **4**. Top: calculated spectrum. Bottom: experimental spectrum.

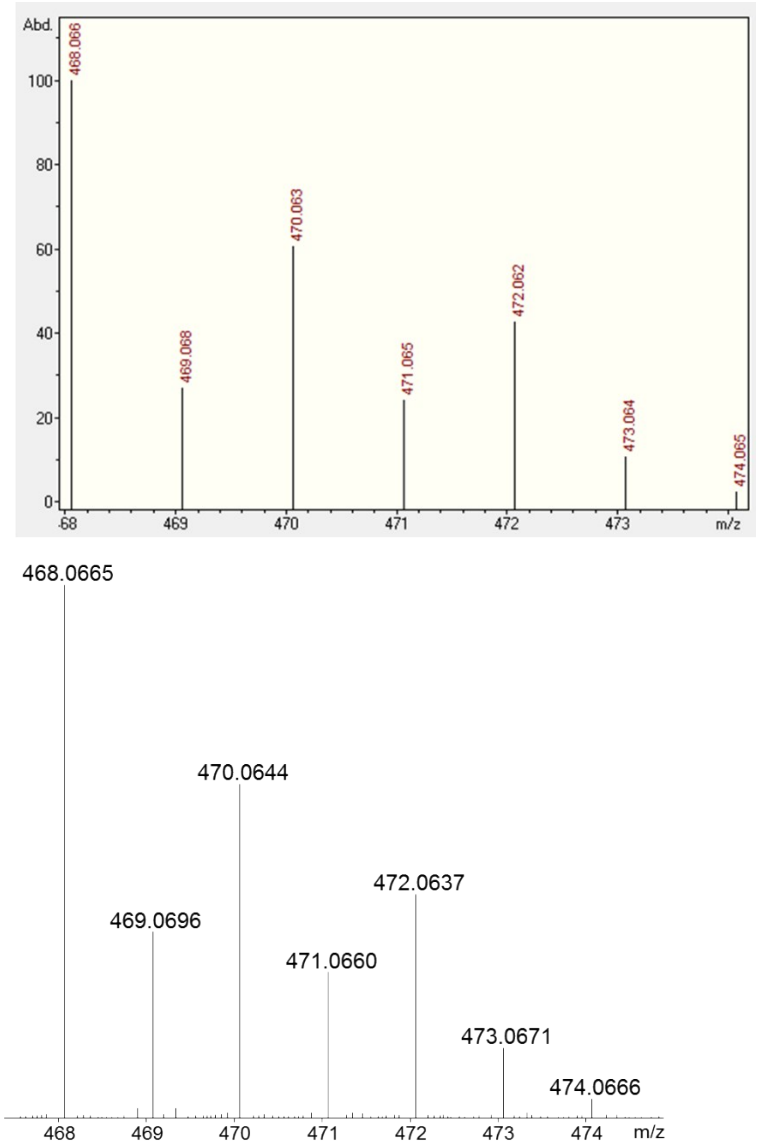


Figure S9: High-resolution ESI mass spectra of **5**. Top: calculated spectrum. Bottom: experimental spectrum.

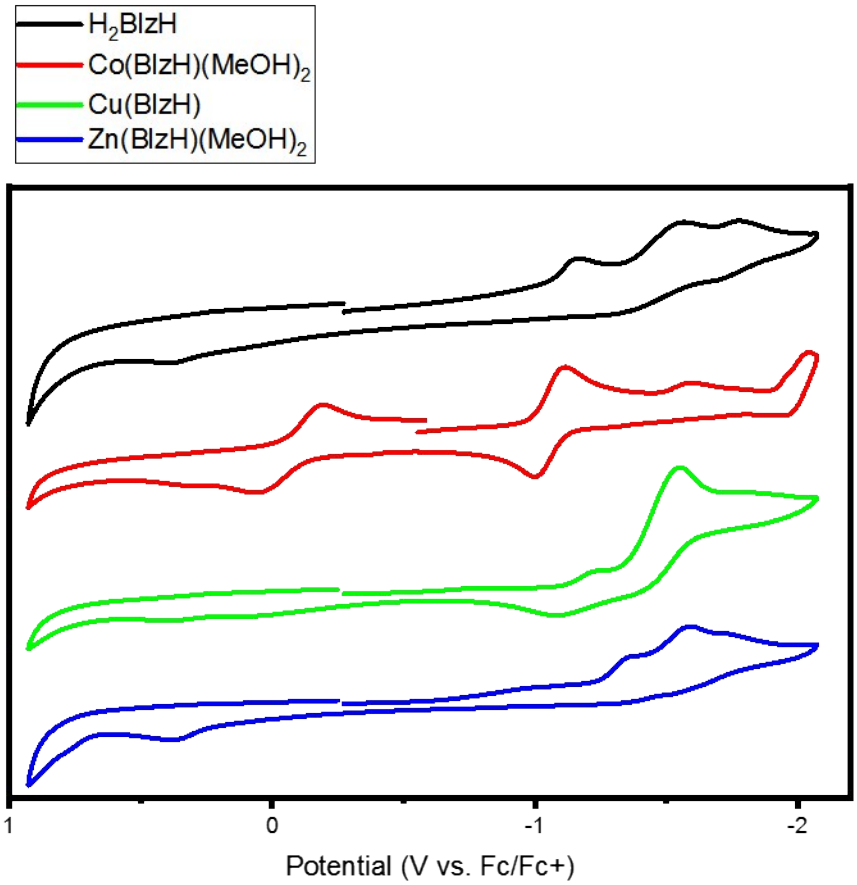


Figure S10: Cyclic voltammograms in DMF/0.1 $TBAPF_6$.

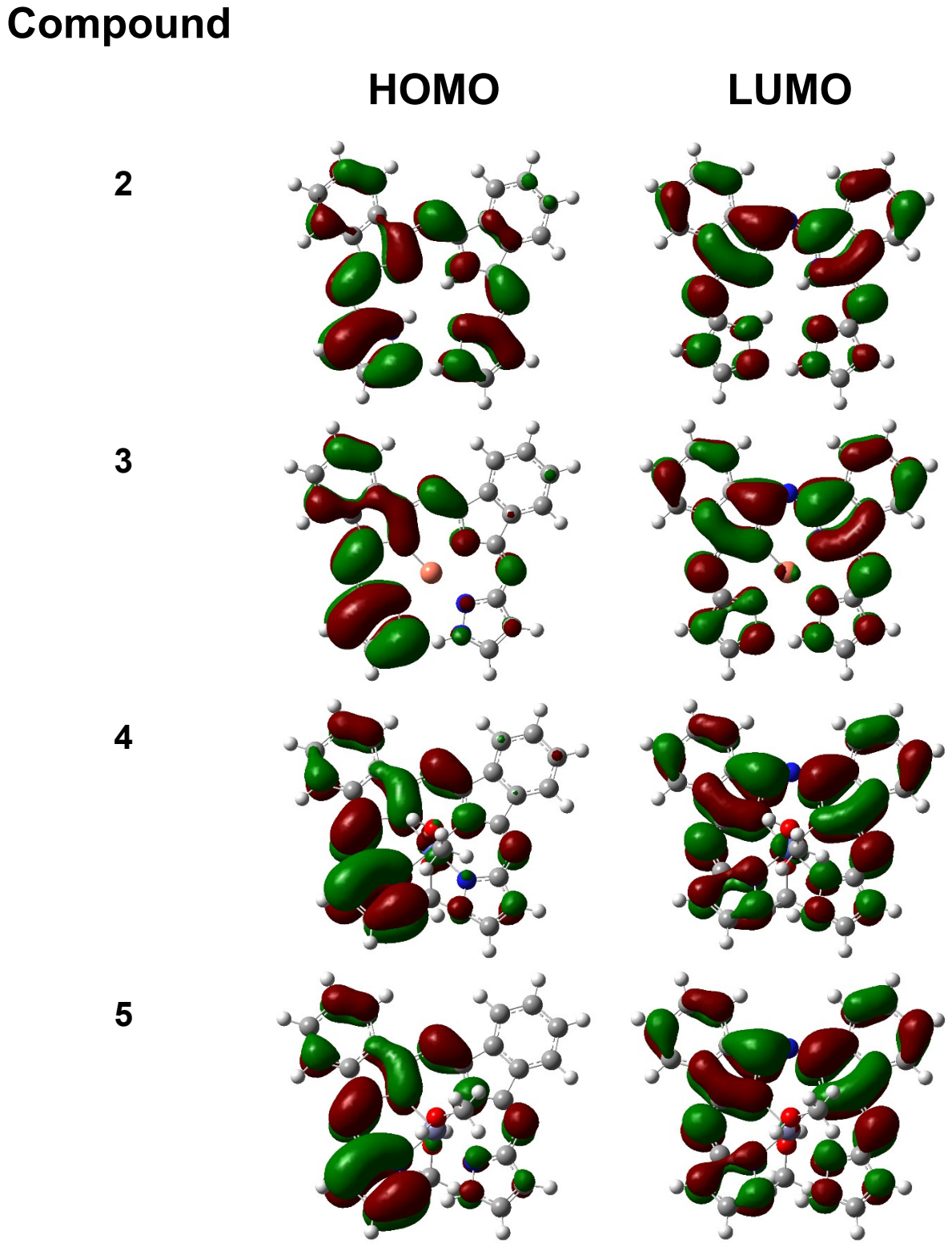


Figure S11. B3LYP DFT-predicted frontier orbitals for compounds **2-5**.

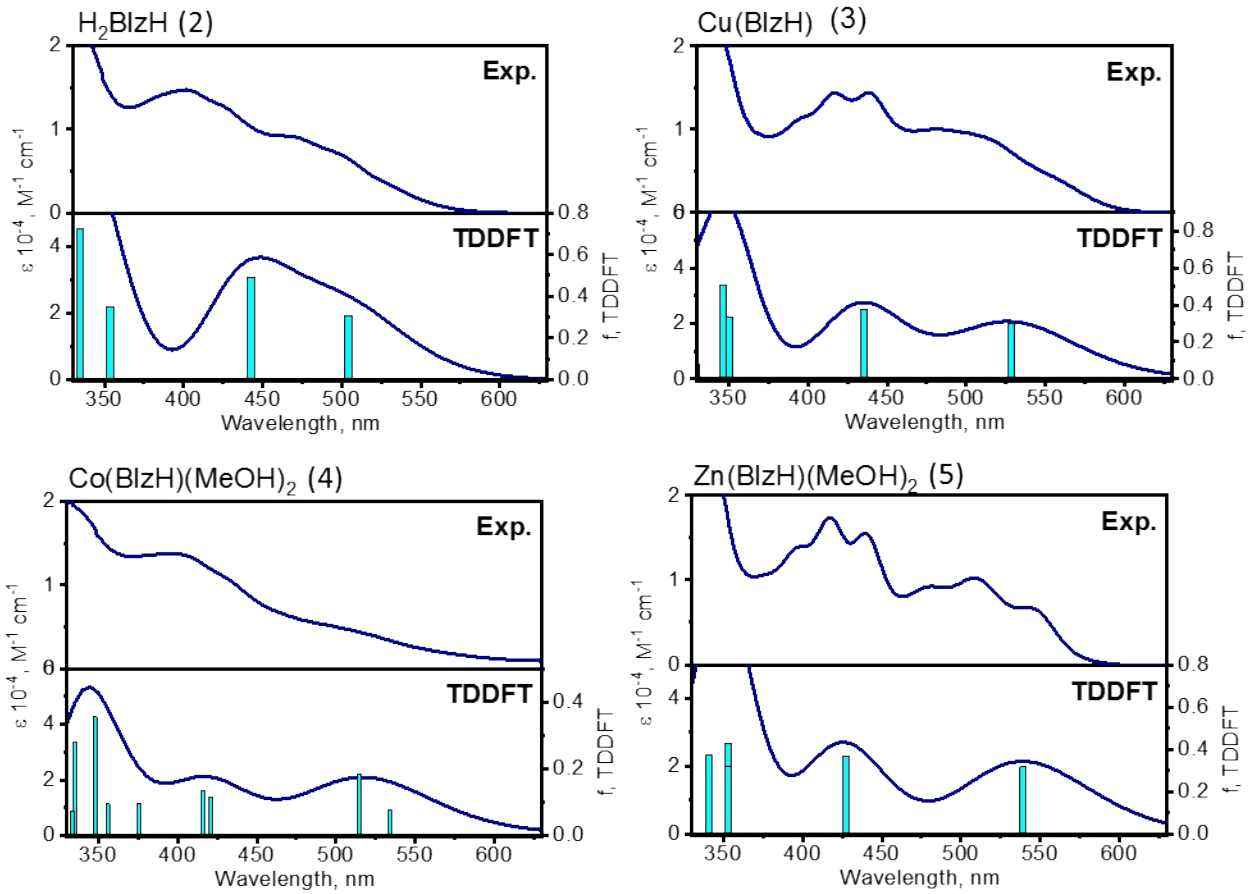


Figure S12: Experimental and B3LYP TDDFT-predicted spectra for compounds **2-5.**

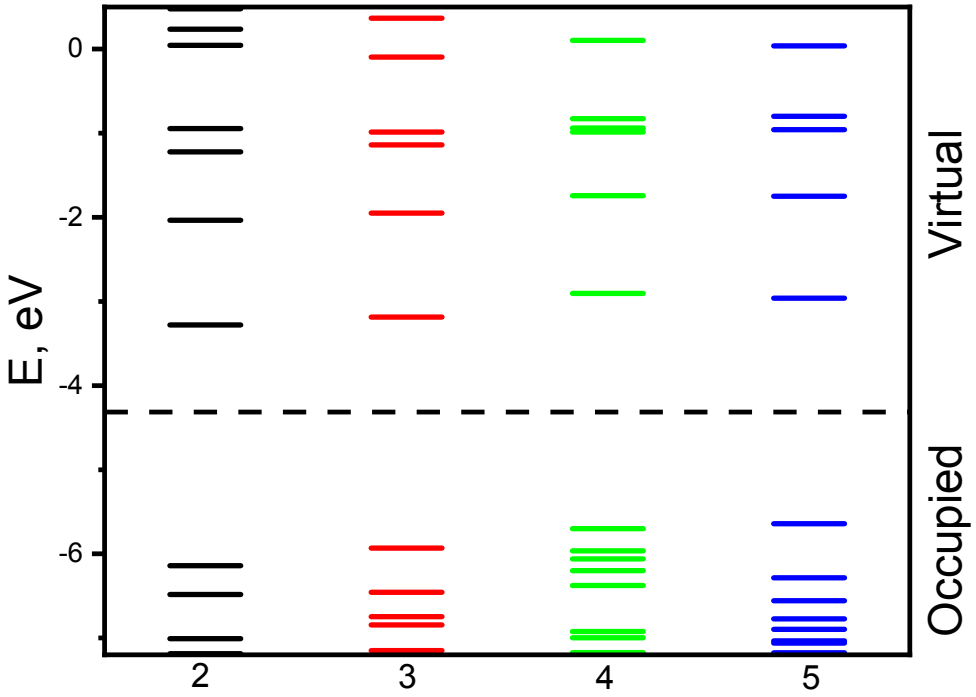


Figure S13: B3LYP α-spin relative energies of the frontier orbitals for compounds **2-5.**

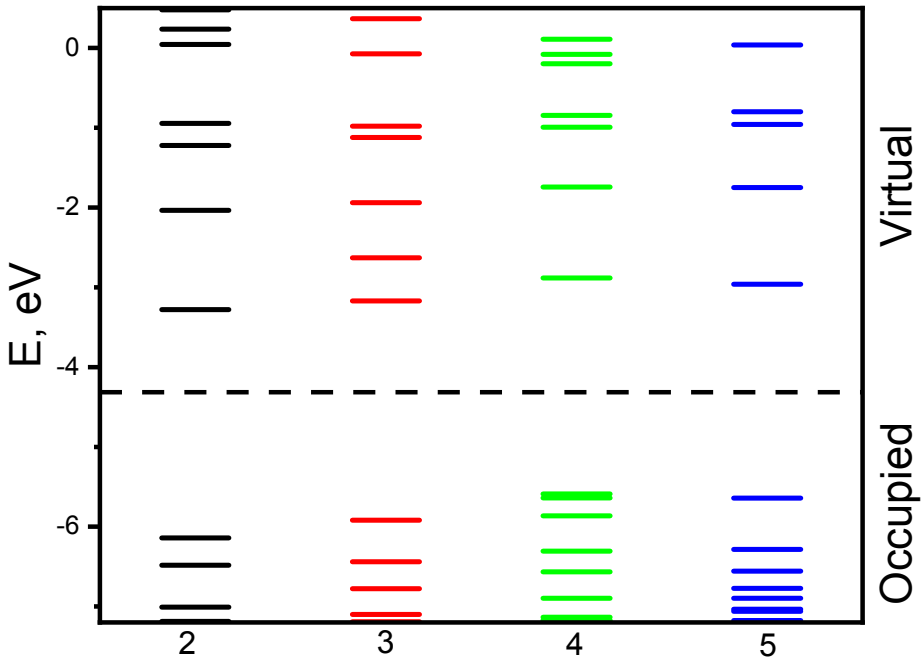


Figure S14: B3LYP β-spin relative energies of the frontier orbitals for compounds **2-5.**

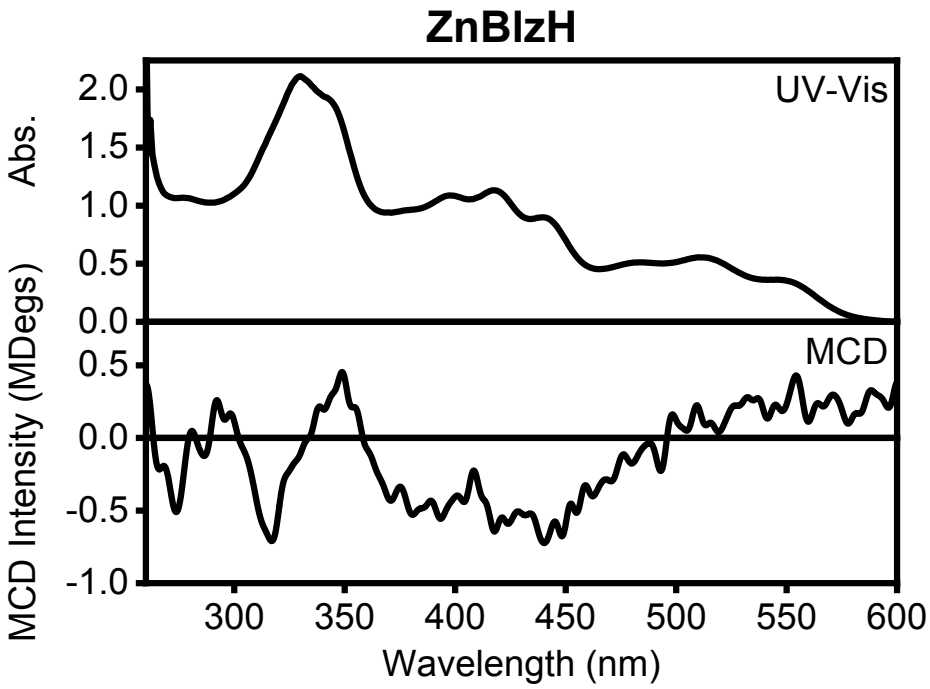


Figure S15: UV−Vis and MCD spectra of **5**.

Table S1: X-ray crystal data and structure parameters for compounds **1** and **2.**

Compound	**1**	**2**
Empirical formula	$C_{11}H_9N_5$	$C_{22}H_{15}N_9$
Formula weight	211.23	405.43
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
a/ Å	11.6141(5)	4.579(6)
b/ Å	12.7038(5)	17.112(13)
c/ Å	13.4922(6)	23.460(16)
α(°)	90	92
β(°)	99.080(3)	93.02(8)
γ(°)	90	90
Volume (Å^3)	1965.74(15)	1836(3)
Z	8	4
Dc (Mg/m^3)	1.427	1.467
μ (mm^{-1})	0.757	0.772
F(000)	880	840
reflns collected	6403	11216
indep. reflns	1687	3125
GOF on F^2	1.046	1.015
R1 (on F_o^2, I > 2σ(I))	0.0461	0.0674
wR2 (on F_o^2, I > 2σ(I))	0.1266	0.1725
R1 (all data)	0.0530	0.1127
wR2 (all data)	0.1336	0.1976

Table S2: X-ray crystal data and structure parameters for compounds **3-5.**

Compound	**3**	**4**	**5**
Empirical formula	$C_{22}H_{13}CuN_9$	$C_{24}H_{21}CoN_9O_2$	$C_{24}H_{21}N_9O_2Zn$
Formula weight	466.95	526.43	532.87
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/ Å	4.6467(4)	6.8635(3)	6.8862(4)
b/ Å	16.7271(17)	23.0498(13)	23.1744(14)
c/ Å	23.289(2)	14.1576(8)	14.2313(8)
α(°)	90	90	90
β(°)	92.885(7)	102.251(3)	102.434(4)
γ(°)	90	90	90
Volume (Å^3)	1807.9(3)	2188.8(2)	2217.8(2)
Z	4	4	4
Dc (Mg/m^3)	1.716	1.598	1.596
μ (mm^{-1})	1.994	6.531	1.153
F(000)	948	1084	1096
reflns collected	8721	11209	21335
indep. reflns	2876	3325	5523
GOF on F^2	1.008	1.050	1.048
R1 (on F_o^2, I > 2σ(I))	0.0490	0.0468	0.0511
wR2 (on F_o^2, I > 2σ(I))	0.1239	0.1159	0.1083
R1 (all data)	0.0851	0.0590	0.0910
wR2 (all data)	0.1454	0.1228	0.1229

Table S3: B3LYP TDDFT-predicted energies and expansion coefficients for compound **2** (only excited states with f > 0.05 and λ > 270 nm are listed).

```
Excited State   1:      Singlet-A      2.4592 eV  504.17 nm  f=0.3090  <S**2>=0.000
    105 ->106         0.70100
 Excited State   2:      Singlet-A      2.8023 eV  442.43 nm  f=0.4910  <S**2>=0.000
    104 ->106         0.69021
    105 ->107         0.10982
 Excited State   6:      Singlet-A      3.5049 eV  353.75 nm  f=0.3514  <S**2>=0.000
    101 ->106         0.69603
 Excited State  10:      Singlet-A      3.7046 eV  334.67 nm  f=0.7245  <S**2>=0.000
     96 ->106        -0.22629
    105 ->107         0.65249
Excited State  11:      Singlet-A      3.9610 eV  313.01 nm  f=0.1170  <S**2>=0.000
     96 ->106        -0.47194
    104 ->107         0.48817
    105 ->107        -0.10861
Excited State  12:      Singlet-A      3.9786 eV  311.63 nm  f=0.2803  <S**2>=0.000
     96 ->106         0.44692
    104 ->107         0.49200
    105 ->107         0.20010
 Excited State  15:      Singlet-A      4.3505 eV  284.99 nm  f=0.0579  <S**2>=0.000
     94 ->106        -0.13756
    103 ->107         0.66263
    105 ->108         0.12371
 Excited State  17:      Singlet-A      4.4945 eV  275.86 nm  f=0.2811  <S**2>=0.000
     94 ->106         0.59067
    101 ->107         0.12483
    103 ->107         0.15040
    105 ->108        -0.17464
    105 ->109        -0.19579
```

Table S4: B3LYP TDDFT-predicted energies and expansion coefficients for compound **4** (only excited states with f > 0.05 and λ > 270 nm are listed).

```
Excited State  12:  2.785-A      2.3209 eV  534.20 nm  f=0.0765  <S**2>=1.688
   132A ->137A        0.26486
   133A ->137A        0.60604
   134A ->140A       -0.12426
   135A ->137A        0.26959
   136A ->137A        0.38617
   132B ->136B        0.34280
   133B ->136B       -0.13364
   134B ->136B        0.28425
   135B ->136B       -0.16384
Excited State  13:  2.374-A      2.4084 eV  514.80 nm  f=0.1838  <S**2>=1.159
   132A ->137A       -0.32869
   133A ->137A       -0.18363
   135A ->137A       -0.29027
   136A ->137A        0.51979
   136A ->138A       -0.10332
   131B ->136B        0.22793
   132B ->136B       -0.22049
   133B ->136B       -0.36501
   134B ->136B        0.25270
   135B ->136B       -0.35812
Excited State  21:  2.611-A      2.9470 eV  420.72 nm  f=0.1167  <S**2>=1.454
   131A ->137A       -0.13217
   132A ->137A       -0.47178
   133A ->137A       -0.11416
   136A ->138A       -0.11620
   129B ->136B       -0.10328
   130B ->136B        0.15923
   131B ->140B        0.21303
   132B ->136B        0.50229
   133B ->137B        0.11626
   134B ->137B        0.35201
   135B ->137B       -0.42651
Excited State  22:  2.933-A      2.9792 eV  416.16 nm  f=0.1352  <S**2>=1.901
   129A ->137A       -0.15933
   131A ->137A        0.18525
   132A ->137A       -0.43366
   133A ->138A        0.15732
   135A ->137A        0.12112
   136A ->138A        0.36069
   128B ->136B       -0.11927
   129B ->136B        0.15826
   130B ->136B       -0.14897
```

```
   132B ->136B       0.40231
   133B ->137B      -0.11569
   135B ->137B       0.50777
Excited State  27:  2.990-A     3.3015 eV  375.54 nm  f=0.0950  <S**2>=1.986
   129A ->137A      -0.37287
   131A ->137A       0.26155
   132A ->137A       0.10719
   135A ->138A      -0.26136
   136A ->138A       0.28184
   127B ->136B       0.24347
   128B ->136B      -0.18783
   129B ->136B       0.16008
   132B ->136B      -0.12724
   133B ->137B       0.42969
   134B ->137B       0.25685
   135B ->137B      -0.32391
Excited State  32:  2.978-A     3.4816 eV  356.12 nm  f=0.0946  <S**2>=1.968
   125A ->137A       0.11821
   126A ->137A       0.19008
   128A ->137A       0.28974
   129A ->137A      -0.26413
   133A ->138A      -0.21570
   135A ->138A       0.45049
   136A ->138A      -0.31823
   126B ->136B      -0.28663
   127B ->136B       0.21566
   128B ->136B      -0.18491
   129B ->136B       0.22202
   130B ->136B      -0.11108
   133B ->137B       0.24949
   135B ->137B       0.14540
Excited State  34:  2.331-A     3.5643 eV  347.85 nm  f=0.3552  <S**2>=1.109
   126A ->137A       0.10762
   131A ->137A      -0.24184
   133A ->138A       0.15825
   134A ->138A       0.14319
   135A ->138A       0.36431
   136A ->138A       0.52475
   126B ->136B      -0.12094
   127B ->136B       0.11745
   130B ->136B      -0.12333
   132B ->136B      -0.13071
   132B ->137B      -0.12723
   133B ->137B      -0.33816
   134B ->137B       0.41460
   135B ->137B      -0.11129
```

```
  135B ->138B       -0.11156
Excited State  39:  2.138-A      3.7010 eV  335.00 nm  f=0.2791  <S**2>=0.893
  125A ->137A        0.14247
  128A ->137A        0.40104
  129A ->137A       -0.45890
  127B ->136B       -0.49361
  128B ->136B        0.51759
Excited State  40:  3.153-A      3.7163 eV  333.62 nm  f=0.0729  <S**2>=2.235
  125A ->137A        0.13577
  126A ->137A       -0.15285
  128A ->137A        0.10627
  128A ->138A       -0.10190
  129A ->137A        0.31526
  132A ->138A       -0.18054
  133A ->138A        0.31989
  135A ->138A       -0.11143
  135A ->139A        0.11924
  136A ->139A       -0.22569
  136A ->140A        0.14853
  136A ->141A        0.21535
  124B ->136B       -0.18240
  126B ->136B       -0.12674
  127B ->139B        0.11218
  129B ->136B       -0.11938
  133B ->137B        0.30546
  133B ->138B       -0.17212
  133B ->139B        0.17244
  135B ->138B       -0.20176
  135B ->139B        0.20156
```

Table S5: B3LYP TDDFT-predicted energies and expansion coefficients for compound **3** (only excited states with f > 0.05 and λ > 270 nm are listed).

```
Excited State   5:  2.004-A      2.3456 eV  528.59 nm  f=0.3010  <S**2>=0.754
    119A ->120A        0.69956
    118B ->119B        0.70259
 Excited State  12:  2.067-A      2.8461 eV  435.63 nm  f=0.3752  <S**2>=0.818
    116A ->120A        0.18388
    118A ->120A        0.68381
    119A ->121A        0.13893
    117B ->119B        0.65881
Excited State  26:  2.143-A      3.5332 eV  350.91 nm  f=0.3358  <S**2>=0.898
    113A ->120A        0.30938
    119A ->121A        0.52709
    109B ->119B        0.17923
    112B ->119B        0.37356
    113B ->120B        0.23212
    117B ->119B       -0.12884
    117B ->121B       -0.16996
    118B ->121B        0.55269
 Excited State  29:  2.011-A      3.5752 eV  346.79 nm  f=0.5110  <S**2>=0.761
    113A ->120A        0.57761
    119A ->121A       -0.33367
    112B ->119B        0.61157
    113B ->120B       -0.16013
    118B ->121B       -0.32950
 Excited State  31:  2.057-A      3.7582 eV  329.90 nm  f=0.0810  <S**2>=0.808
    111A ->120A       -0.34604
    118A ->121A        0.10345
    119A ->121A       -0.14095
     97B ->120B       -0.12607
    109B ->119B       -0.11586
    110B ->120B        0.16399
    111B ->119B       -0.33941
    113B ->120B        0.75648
    117B ->121B        0.11008
    118B ->121B       -0.17835
 Excited State  32:  2.016-A      3.7908 eV  327.06 nm  f=0.0623  <S**2>=0.766
    109A ->120A       -0.20685
    111A ->120A        0.61494
    119A ->121A       -0.10229
    109B ->119B       -0.10131
    110B ->120B        0.11666
    111B ->119B        0.56910
    113B ->120B        0.42505
```

Excited State 36: 2.172-A 3.9645 eV 312.74 nm f=0.0823 <S**2>=0.929

109A ->120A	0.50418
111A ->120A	0.12638
118A ->121A	0.29162
108B ->119B	-0.16458
109B ->119B	0.57469
116B ->121B	0.11064
117B ->121B	0.42903

Excited State 40: 2.029-A 4.0378 eV 307.06 nm f=0.3370 <S**2>=0.779

108A ->120A	-0.13113
109A ->120A	-0.31193
118A ->121A	0.59298
119A ->121A	0.11805
109B ->119B	-0.32898
110B ->120B	0.10846
113B ->120B	-0.20414
117B ->121B	0.53710
118B ->121B	0.12619

Table S6: B3LYP TDDFT-predicted energies and expansion coefficients for compound **5** (only excited states with f > 0.05 and λ > 270 nm are listed).

```
Excited State   1:      Singlet-A      2.2998 eV  539.10 nm  f=0.3175  <S**2>=0.000
    137 ->138        0.70435
Excited State   2:      Singlet-A      2.8993 eV  427.63 nm  f=0.3693  <S**2>=0.000
    136 ->138        0.67795
    137 ->139        0.15393
 Excited State   8:      Singlet-A      3.5090 eV  353.33 nm  f=0.4289  <S**2>=0.000
    128 ->138       -0.43740
    136 ->138       -0.11440
    137 ->139        0.51376
Excited State   9:      Singlet-A      3.5213 eV  352.10 nm  f=0.3174  <S**2>=0.000
    128 ->138        0.52839
    136 ->138       -0.10473
    137 ->139        0.41969
Excited State  10:      Singlet-A      3.6391 eV  340.70 nm  f=0.3738  <S**2>=0.000
    130 ->138        0.68749
Excited State  12:      Singlet-A      4.0062 eV  309.48 nm  f=0.0669  <S**2>=0.000
    127 ->138        0.63824
    136 ->139        0.23401
 Excited State  13:      Singlet-A      4.0562 eV  305.67 nm  f=0.2337  <S**2>=0.000
    127 ->138       -0.23395
    136 ->139        0.64242
Excited State  15:      Singlet-A      4.2103 eV  294.47 nm  f=0.0684  <S**2>=0.000
    137 ->140        0.62622
    137 ->141       -0.28431
    135 ->139       -0.16253
 Excited State  21:      Singlet-A      4.4883 eV  276.24 nm  f=0.0888  <S**2>=0.000
    124 ->138       -0.14312
    125 ->138        0.48380
    133 ->139        0.42682
 Excited State  23:      Singlet-A      4.5644 eV  271.63 nm  f=0.1585  <S**2>=0.000
    123 ->138        0.13534
    124 ->138        0.13912
    125 ->138       -0.38292
    133 ->139        0.50938
    137 ->141        0.10430
```

Table S7: B3LYP DFT optimized geometry of compound **2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.782980	4.459405	-0.000074
2	1	0	2.925576	5.530171	-0.000240
3	6	0	3.737891	3.439037	-0.000402
4	1	0	4.813435	3.519249	-0.000885
5	6	0	3.003344	2.246232	0.000021
6	6	0	2.791933	-0.100460	-0.000039
7	6	0	3.417048	-1.436440	-0.000153
8	6	0	4.739860	-1.861764	-0.000125
9	1	0	5.558811	-1.150650	-0.000160
10	6	0	4.974011	-3.241619	-0.000042
11	1	0	5.994504	-3.611123	-0.000018
12	6	0	3.913438	-4.158666	0.000026
13	1	0	4.130419	-5.221975	0.000113
14	6	0	2.584134	-3.723214	0.000002
15	1	0	1.758772	-4.426597	0.000056
16	6	0	2.361111	-2.350445	-0.000101
17	6	0	1.131977	-1.537903	0.000008
18	6	0	-1.213996	-1.535576	0.000004
19	6	0	-2.513076	-2.213207	0.000034
20	6	0	-2.828548	-3.569211	0.000144
21	1	0	-2.048523	-4.321942	0.000247
22	6	0	-4.179946	-3.917321	0.000135
23	1	0	-4.464469	-4.964133	0.000216
24	6	0	-5.180124	-2.932699	0.000027
25	1	0	-6.221992	-3.235456	0.000017
26	6	0	-4.859513	-1.573320	-0.000076
27	1	0	-5.629863	-0.810544	-0.000137
28	6	0	-3.511884	-1.229072	-0.000079
29	6	0	-2.852141	0.081043	-0.000150
30	6	0	-2.800435	2.427653	-0.000117
31	6	0	-3.459386	3.682185	-0.000323
32	1	0	-4.523839	3.854657	-0.000612
33	6	0	-2.442373	4.613336	-0.000087
34	1	0	-2.448715	5.692142	-0.000088
35	7	0	1.536815	3.962112	0.000495
36	7	0	1.690270	2.626229	0.000522
37	1	0	0.881184	2.016625	0.000872
38	7	0	3.510769	0.978653	-0.000064
39	7	0	1.391214	-0.226251	0.000087
40	7	0	-0.067867	-2.168297	0.000091
41	7	0	-1.473821	-0.191790	-0.000130
42	1	0	-0.754961	0.523785	-0.000199
43	7	0	-3.457806	1.214767	-0.000180
44	7	0	-1.457363	2.590151	0.000187
45	7	0	-1.278166	3.919615	0.000235
46	1	0	-0.306488	4.261623	0.000333

E_h = -1340.432492 Hartree

Table S8: B3LYP DFT optimized geometry of compound **4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.346697	-4.215028	0.269936
2	1	0	-2.361510	-5.292449	0.360639
3	6	0	-3.388028	-3.309595	0.176410
4	1	0	-4.453486	-3.481584	0.178723
5	6	0	-2.748848	-2.058851	0.081843
6	6	0	-2.786352	0.258199	-0.016240
7	6	0	-3.489566	1.540966	-0.068160
8	6	0	-4.841328	1.867341	-0.138580
9	1	0	-5.602461	1.095596	-0.177164
10	6	0	-5.176956	3.222868	-0.159579
11	1	0	-6.220723	3.515393	-0.215894
12	6	0	-4.187303	4.218716	-0.109202
13	1	0	-4.483484	5.262731	-0.126615
14	6	0	-2.833590	3.885359	-0.037887
15	1	0	-2.063582	4.647954	0.001322
16	6	0	-2.506285	2.531117	-0.018218
17	6	0	-1.221247	1.834369	0.045210
18	6	0	1.087125	1.905251	0.044322
19	6	0	2.335264	2.673239	0.062699
20	6	0	2.589186	4.039940	0.141982
21	1	0	1.779041	4.757229	0.213417
22	6	0	3.925494	4.446896	0.128632
23	1	0	4.165297	5.503562	0.190746
24	6	0	4.967784	3.510862	0.036386
25	1	0	5.995316	3.860263	0.028503
26	6	0	4.703987	2.140884	-0.044206
27	1	0	5.505148	1.413244	-0.114747
28	6	0	3.370848	1.743447	-0.029175
29	6	0	2.736143	0.422223	-0.088695
30	6	0	2.836911	-1.889110	-0.172779
31	6	0	3.539199	-3.111841	-0.269120
32	1	0	4.606655	-3.225930	-0.368359
33	6	0	2.569110	-4.088299	-0.197947
34	1	0	2.626177	-5.165525	-0.222646
35	6	0	0.437209	-1.872383	3.111066
36	1	0	-0.178529	-2.750452	2.898316
37	1	0	0.386490	-1.626338	4.175164
38	1	0	1.469969	-2.079344	2.838635
39	6	0	0.001975	-2.013752	-3.060863
40	1	0	1.008624	-2.441731	-3.042460
41	1	0	-0.293604	-1.803988	-4.092581

42	1	0	-0.699098	-2.717823	-2.618436
43	27	0	0.007137	-0.852720	0.022118
44	7	0	-1.163608	-3.566586	0.232306
45	7	0	-1.389195	-2.237822	0.114636
46	7	0	-3.410466	-0.872508	-0.007272
47	7	0	-1.398950	0.489406	0.051256
48	7	0	-0.082379	2.522028	0.079195
49	7	0	1.342547	0.569428	-0.043308
50	7	0	3.433868	-0.664445	-0.168386
51	7	0	1.500779	-2.127888	-0.052952
52	7	0	1.377917	-3.469856	-0.071929
53	1	0	0.382337	-3.821702	0.055815
54	8	0	0.029925	-0.747022	2.316336
55	8	0	-0.075113	-0.821809	-2.264741
56	1	0	0.546853	-0.170320	-2.613333
57	1	0	-0.864434	-0.493907	2.579161

E_h = -2953.612817 Hartree

Table S9: B3LYP DFT optimized geometry of compound **3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.558415	4.350422	0.001502
2	1	0	-2.611733	5.427912	0.002072
3	6	0	-3.540974	3.379134	0.000905
4	1	0	-4.611388	3.506584	0.000860
5	6	0	-2.845944	2.151299	0.000390
6	6	0	-2.772017	-0.174885	-0.000135
7	6	0	-3.420713	-1.493477	-0.000541
8	6	0	-4.757796	-1.874524	-0.001094
9	1	0	-5.551815	-1.136088	-0.001378
10	6	0	-5.035378	-3.244628	-0.001267
11	1	0	-6.066954	-3.581432	-0.001694
12	6	0	-4.003972	-4.196181	-0.000893
13	1	0	-4.255550	-5.251665	-0.001035
14	6	0	-2.662621	-3.805492	-0.000342
15	1	0	-1.859486	-4.533791	-0.000059
16	6	0	-2.395437	-2.439748	-0.000168
17	6	0	-1.134708	-1.688046	0.000354
18	6	0	1.185265	-1.658799	0.000565
19	6	0	2.459058	-2.380935	0.000676
20	6	0	2.756119	-3.741974	0.001010
21	1	0	1.968227	-4.486828	0.001410
22	6	0	4.103937	-4.104443	0.000836
23	1	0	4.378333	-5.154262	0.001114
24	6	0	5.115294	-3.129729	0.000291
25	1	0	6.153817	-3.444872	0.000136
26	6	0	4.810129	-1.766693	-0.000081
27	1	0	5.589611	-1.012852	-0.000506
28	6	0	3.464756	-1.410299	0.000119
29	6	0	2.788768	-0.110018	-0.000242
30	6	0	2.792131	2.222563	-0.001044
31	6	0	3.455596	3.461945	-0.001732
32	1	0	4.523983	3.614141	-0.002403
33	6	0	2.431844	4.397596	-0.001396
34	1	0	2.475015	5.477843	-0.001658
35	29	0	0.003042	1.074077	0.000194
36	7	0	-1.367778	3.723382	0.001428
37	1	0	-0.365273	4.064840	0.000861
38	7	0	-1.506492	2.384603	0.000674
39	7	0	-3.450908	0.924295	-0.000180
40	7	0	-1.379663	-0.349477	0.000392
41	7	0	0.027582	-2.321771	0.000722
42	7	0	1.396630	-0.323140	0.000112
43	7	0	3.425288	1.012768	-0.000850
44	7	0	1.439187	2.443266	-0.000298
45	7	0	1.235509	3.778035	-0.000513

E_h = -2979.786503 Hartree

Table S10: B3LYP DFT optimized geometry of compound **5**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.818163	-4.071130	0.029343
2	1	0	2.944761	-5.142343	0.048662
3	6	0	3.733809	-3.036943	-0.031094
4	1	0	4.809294	-3.105112	-0.070387
5	6	0	2.960299	-1.849502	-0.027661
6	6	0	2.750884	0.501655	-0.071081
7	6	0	3.339774	1.854782	-0.095886
8	6	0	4.656114	2.300654	-0.128022
9	1	0	5.483436	1.599427	-0.142668
10	6	0	4.872466	3.682392	-0.140876
11	1	0	5.887625	4.065567	-0.165993
12	6	0	3.798961	4.584557	-0.121326
13	1	0	4.000520	5.650905	-0.131313
14	6	0	2.477125	4.130433	-0.088839
15	1	0	1.641782	4.821858	-0.073047
16	6	0	2.268972	2.755062	-0.076358
17	6	0	1.037927	1.943164	-0.046075
18	6	0	-1.311598	1.823970	-0.010026
19	6	0	-2.615749	2.504878	-0.008535
20	6	0	-2.967225	3.851879	-0.019412
21	1	0	-2.208299	4.626702	-0.029171
22	6	0	-4.328336	4.166691	-0.016297
23	1	0	-4.640327	5.206195	-0.023889
24	6	0	-5.302235	3.156434	-0.003103
25	1	0	-6.352199	3.431962	-0.001241
26	6	0	-4.944434	1.805235	0.007697
27	1	0	-5.696557	1.023645	0.017978
28	6	0	-3.588327	1.494166	0.004520
29	6	0	-2.860042	0.214830	0.015970
30	6	0	-2.795233	-2.154653	0.059825
31	6	0	-3.441167	-3.407466	0.059214
32	1	0	-4.506375	-3.582956	0.036807
33	6	0	-2.402438	-4.330322	0.093783
34	1	0	-2.440854	-5.411568	0.105099
35	6	0	0.019924	-2.117926	-3.085223
36	1	0	1.034058	-2.500687	-3.232398
37	1	0	-0.433493	-1.884236	-4.052206
38	1	0	-0.580197	-2.866027	-2.572124
39	6	0	0.995342	-0.907037	3.244700
40	1	0	1.626665	-1.800324	3.249910
41	1	0	0.591669	-0.730996	4.245293

42	1	0	1.588535	-0.047147	2.940290
43	1	0	-0.635216	-1.767488	2.520169
44	1	0	0.571544	-0.271436	-2.627618
45	7	0	1.586863	-3.514022	0.067221
46	1	0	0.628311	-3.919297	0.105212
47	7	0	1.648759	-2.173037	0.032621
48	7	0	3.478977	-0.573382	-0.068954
49	7	0	1.359891	0.622505	-0.045947
50	7	0	-0.159521	2.518503	-0.030263
51	7	0	-1.487085	0.494209	0.004886
52	7	0	-3.444277	-0.942220	0.035714
53	7	0	-1.443232	-2.366610	0.096903
54	7	0	-1.206024	-3.698992	0.117294
55	8	0	0.019363	-0.959866	-2.236551
56	8	0	-0.066701	-1.022053	2.287481
57	30	0	-0.010477	-0.916159	0.023581

E_h = -3350.167009 Hartree

References

1 I.-S. Tamgho, J. T. Engle and C. J. Ziegler, *Tetrahedron Lett.*, 2013, **54**, 6114–6117.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–122.

3 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

4 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.

5 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, Ma. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *Inc. Wallingford, CT*.

7 Tenderholt, Adam L. *QMForge*, Version 2.4, https://qmforge.net