Supporting Information for

Probing a silent metal: A Combined X-ray Absorption and Emission Spectroscopic Study of Biologically Relevant Zinc Complexes

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Sample calculation input files for bis(benzoato-O)bis(thiourea-S)zinc(II) for XES (left) and XAS data (right).

```
!RKS B3LYP TightOpt TightSCF ZORA-def2-TZVP
!SARC/J D3BJ RIJCOSX ZORA
!FREQ PAL8 Largeprint Printbasis

%xes
CoreOrb 0
OrbOp 0
end

*xyz 0 1
O   -4.73509633471595 -0.33989320618859 8.45692252911864
C   -5.91283128245614  0.06217706725197 8.78501193027164
C   -6.98169908438880 -0.99404197769231 8.79615025738138
…
```

```
!RKS B3LYP TightSCF ZORA-def2-TZVP
!SARC/J D3BJ RIJCOSX ZORA
!PAL8 Normalprint MOREAD

%moinp "benzurea_a.gbw"

%tddft
orbwin[0]= 0,0,-1,-1
doquad true
nroots 300
maxdim 50
end

* xyzfile 0 1 benzurea_a.xyz
```

The generated output files were used together with the command orca_mapspc, as shown below:
XES: orca_mapspc name.mpi8.out xesq -eV -x09000 -x110000 -n10001 -w2.25
XAS: orca_mapspc name.mpi8.out absq -eV -x09000 -x110000 -n10001 -kw0.03

Optimized geometry coordinates of relevant complexes.

c. $Zn(BzO)_2(SC(NH_2)_2)_2$

8	-4.757184000	-0.262468000	8.331585000
6	-5.912918000	0.072291000	8.760510000
6	-6.929359000	-1.029247000	8.804646000
6	-6.557240000	-2.348966000	8.549221000
1	-5.523137000	-2.564022000	8.318869000
6	-7.506440000	-3.361266000	8.588477000
1	-7.210853000	-4.384696000	8.393836000
6	-8.834099000	-3.059538000	8.871187000
1	-9.575283000	-3.848820000	8.895114000
6	-9.210246000	-1.744058000	9.123292000
1	-10.243809000	-1.508139000	9.344199000
6	-8.259218000	-0.733255000	9.098712000
1	-8.528952000	0.294193000	9.301168000
8	-6.241032000	1.217130000	9.123730000
8	-1.879671000	-0.259091000	7.566520000
6	-0.672330000	0.106315000	7.359392000
6	0.347985000	-0.993986000	7.334931000
6	-0.034643000	-2.322228000	7.524467000
1	-1.080736000	-2.546570000	7.679725000
6	0.919132000	-3.331306000	7.517423000
1	0.616130000	-4.360314000	7.666097000
6	2.260824000	-3.020418000	7.325138000
1	3.004440000	-3.807938000	7.323426000
6	2.647568000	-1.697335000	7.136670000
1	3.692377000	-1.454103000	6.987185000

6	1.694358000	-0.688108000	7.139096000
1	1.975637000	0.345998000	6.994866000
30	-3.300237000	0.987901000	8.040394000
8	-0.301568000	1.283951000	7.193385000
16	-2.436428000	2.210764000	9.908130000
6	-3.585938000	3.433659000	10.240529000
7	-4.868762000	3.346587000	9.955611000
7	-3.137636000	4.571701000	10.826865000
1	-5.474258000	4.135629000	10.118788000
1	-5.306779000	2.478103000	9.570407000
1	-2.173317000	4.593900000	11.110414000
1	-3.776499000	5.171863000	11.322751000
16	-4.111149000	2.574847000	6.456524000
6	-2.869491000	3.735028000	6.269327000
7	-3.228778000	4.972279000	5.843138000
1	-2.542453000	5.577075000	5.421388000
1	-4.184321000	5.098921000	5.557508000
7	-1.596572000	3.510469000	6.516321000
1	-1.215890000	2.582681000	6.817189000
1	-0.932056000	4.265355000	6.443760000

d. $Zn(BzO)_2(pyNH_2)_2$

8	-4.634485000	-0.205016000	7.286244000
6	-5.541515000	0.008825000	8.136391000
6	-6.819117000	-0.764049000	8.091543000
6	-6.981767000	-1.785948000	7.145064000
1	-6.157682000	-1.997941000	6.463473000
6	-8.174292000	-2.507108000	7.090226000
1	-8.296151000	-3.303368000	6.354053000
6	-9.214516000	-2.209651000	7.976991000
1	-10.148626000	-2.772033000	7.931076000
6	-9.057332000	-1.191046000	8.922102000
1	-9.869123000	-0.957079000	9.612979000
6	-7.862986000	-0.472325000	8.981049000
1	-7.720304000	0.327127000	9.707950000
8	-5.394401000	0.909777000	9.051788000
1	-4.790360000	1.391930000	10.683184000
7	-3.979402000	2.777697000	6.850496000
6	-3.573046000	2.735608000	5.554596000
6	-4.237113000	3.511488000	4.570320000
1	-3.903478000	3.459541000	3.533390000
6	-5.290123000	4.323225000	4.943356000
1	-5.806328000	4.920846000	4.190633000
6	-5.690857000	4.374981000	6.289323000

1	-6.518179000	5.000702000	6.618613000
6	-5.007250000	3.582825000	7.194346000
1	-5.285111000	3.552281000	8.248904000
7	-4.332947000	1.955617000	11.410482000
1	-4.574775000	1.806975000	12.379873000
8	-2.209825000	-0.204999000	9.372111000
6	-1.302798000	0.008846000	8.521964000
6	-0.025191000	-0.764020000	8.566815000
6	0.137462000	-1.785917000	9.513296000
1	-0.686624000	-1.997912000	10.194885000
6	1.329990000	-2.507072000	9.568137000
1	1.451851000	-3.303330000	10.304312000
6	2.370214000	-2.209612000	8.681375000
1	3.304327000	-2.771989000	8.727293000
6	2.213029000	-1.191008000	7.736262000
1	3.024819000	-0.957039000	7.045387000
6	1.018679000	-0.472292000	7.677311000
1	0.875995000	0.327158000	6.950409000
30	-3.422165000	1.372909000	8.329175000
7	-2.864921000	2.777690000	9.807861000
6	-3.271328000	2.735639000	11.103744000
6	-1.153404000	4.374889000	10.369074000
1	-0.326037000	5.000563000	10.039809000
6	-1.837020000	3.582759000	9.464035000
1	-1.559125000	3.552190000	8.409486000
8	-1.449920000	0.909791000	7.606560000
7	-2.511480000	1.955528000	5.247827000
1	-2.054044000	1.391851000	5.975120000
1	-2.269693000	1.806869000	4.278429000
6	-2.607260000	3.511498000	12.088035000
1	-2.940937000	3.459585000	13.124954000
6	-1.554193000	4.323174000	11.715026000
1	-1.037984000	4.920779000	12.467759000

e. $Zn(SPh)_4$

30	-0.929808000	0.789444000	-0.669967000
16	-0.623285000	1.795111000	1.490317000
16	-0.097782000	-1.397379000	-0.120825000
16	-3.133011000	0.378770000	-1.488607000
16	0.108001000	1.991089000	-2.450389000
6	1.712729000	2.423517000	-1.880778000
6	2.408188000	3.477003000	-2.502377000
6	2.350678000	1.770859000	-0.811510000
6	3.669799000	3.864187000	-2.073797000
1	1.926463000	4.001316000	-3.318859000

6	3.608498000	2.168034000	-0.382287000
1	1.843674000	0.958094000	-0.311011000
6	4.284961000	3.214232000	-1.006251000
1	4.173775000	4.686671000	-2.572265000
1	4.062765000	1.651461000	0.456471000
1	5.258366000	3.533776000	-0.651213000
6	-3.771317000	1.941052000	-1.969570000
6	-4.785294000	2.019537000	-2.943277000
6	-3.324735000	3.153568000	-1.414787000
6	-5.307686000	3.239565000	-3.350903000
1	-5.144066000	1.099518000	-3.389362000
6	-3.842479000	4.370215000	-1.828532000
1	-2.558466000	3.133649000	-0.654074000
6	-4.838769000	4.430942000	-2.802020000
1	-6.081800000	3.261355000	-4.112607000
1	-3.453325000	5.278678000	-1.381308000
1	-5.236701000	5.384128000	-3.133165000
6	-0.097583000	-2.330393000	-1.607834000
6	-0.040195000	-1.742694000	-2.883593000
6	-0.133012000	-3.736826000	-1.549614000
6	-0.030219000	-2.521920000	-4.030249000
1	-0.000866000	-0.664171000	-2.965670000
6	-0.117596000	-4.511874000	-2.702066000
1	-0.187368000	-4.210155000	-0.575860000
6	-0.067400000	-3.913746000	-3.958779000
1	0.005455000	-2.028139000	-4.995964000
1	-0.154242000	-5.594424000	-2.616160000
1	-0.064557000	-4.516512000	-4.859998000
6	-0.548416000	3.548884000	1.473878000
6	-0.644701000	4.242880000	2.697817000
6	-0.386033000	4.327567000	0.313966000
6	-0.597507000	5.628329000	2.755280000
1	-0.767796000	3.665965000	3.606944000
6	-0.345396000	5.713677000	0.377760000
1	-0.292430000	3.834523000	-0.642922000
6	-0.452792000	6.385157000	1.593568000
1	-0.678744000	6.124925000	3.718051000
1	-0.219850000	6.274377000	-0.542498000
1	-0.419629000	7.468579000	1.636898000

f. $Zn(^{Me}Im)_2(SPh)_2$

30	-0.428805000	3.632691000	2.293323000
16	-1.475704000	2.605861000	0.507416000
7	-1.872363000	4.838838000	3.181948000
7	-3.947208000	5.387754000	3.635480000

6	-3.019159000	2.201394000	1.279384000
6	-4.214078000	2.350713000	0.562919000
6	-5.445397000	2.135214000	1.170489000
6	-5.516814000	1.765756000	2.509990000
6	-4.335256000	1.587933000	3.223427000
6	-3.103028000	1.784933000	2.615609000
6	-1.958177000	5.131240000	4.524624000
6	-3.244815000	5.470649000	4.821876000
6	-3.081909000	5.003467000	2.677812000
6	-5.382101000	5.533510000	3.476071000
1	-4.166385000	2.664186000	-0.472214000
1	-6.354098000	2.262588000	0.593854000
1	-6.475451000	1.600833000	2.985537000
1	-4.369323000	1.281748000	4.261996000
1	-2.193334000	1.632570000	3.181962000
1	-1.099505000	5.055771000	5.168631000
1	-3.718213000	5.759513000	5.743254000
1	-3.365752000	4.809570000	1.658491000
1	-5.618608000	5.557086000	2.415336000
1	-5.717784000	6.459223000	3.942429000
1	-5.896856000	4.686035000	3.927552000
16	0.618374000	2.602254000	4.077099000
7	1.017113000	4.838193000	1.407554000
6	2.159007000	2.194814000	3.300877000
6	1.105041000	5.132825000	0.065526000
6	2.226097000	5.000802000	1.913653000
6	3.356040000	2.340542000	4.014548000
6	2.238595000	1.780037000	1.963856000
6	2.392431000	5.471468000	-0.229381000
1	0.247159000	5.059358000	-0.579773000
7	3.093125000	5.385783000	0.957823000
1	2.508233000	4.804776000	2.933034000
6	4.585380000	2.123761000	3.403428000
1	3.311583000	2.652347000	5.050330000
6	3.468877000	1.581826000	1.352493000
1	1.327218000	1.630137000	1.399546000
1	2.867386000	5.761445000	-1.149605000
6	4.527954000	5.529630000	1.119537000
6	4.652618000	1.756560000	2.063074000
1	5.495802000	2.248371000	3.977956000
1	3.499688000	1.277237000	0.313353000
1	4.763023000	5.550404000	2.180653000
1	4.865263000	6.456102000	0.655849000
1	5.042391000	4.682670000	0.666745000
1	5.609718000	1.590823000	1.584730000

g. $Zn(^{Me}Im)_4$

30	18.615736000	0.000019000	-3.723859000
7	17.288612000	-1.069184000	-2.657174000
7	16.095597000	-2.800368000	-2.027176000
6	16.289721000	-0.626645000	-1.809895000
1	16.187011000	0.407893000	-1.531737000
6	17.138148000	-2.384863000	-2.759487000
1	17.756998000	-3.046356000	-3.340945000
6	15.544604000	-1.696603000	-1.412975000
1	14.693806000	-1.767627000	-0.758227000
6	15.653914000	-4.186829000	-1.895083000
1	16.246351000	-4.807272000	-2.561632000
1	14.604149000	-4.267246000	-2.172756000
1	15.796282000	-4.524377000	-0.869746000
7	19.943525000	1.069019000	-2.657759000
7	21.137531000	2.799896000	-2.028781000
6	20.943171000	0.626203000	-1.811515000
1	21.045946000	-0.408381000	-1.533553000
6	20.094167000	2.384674000	-2.760095000
1	19.474875000	3.046360000	-3.340857000
6	21.688903000	1.695965000	-1.415221000
1	22.540349000	1.766761000	-0.761293000
6	21.579471000	4.186288000	-1.896839000
1	20.986981000	4.806810000	-2.563268000
1	22.629179000	4.266519000	-2.174779000
1	21.437419000	4.523893000	-0.871476000
7	17.546415000	1.327533000	-4.789991000
7	15.815119000	2.520723000	-5.419349000
6	17.988837000	2.326842000	-5.636834000
1	19.023351000	2.429751000	-5.915007000
6	16.230730000	1.477842000	-4.687563000
1	15.569303000	0.858677000	-4.106369000
6	16.918818000	3.072102000	-6.033318000
1	16.847706000	3.923221000	-6.687638000
6	14.428615000	2.962330000	-5.551213000
1	13.808267000	2.369654000	-4.884786000
1	14.348134000	4.012009000	-5.273232000
1	14.091003000	2.820230000	-6.576565000
7	19.684685000	-1.327260000	-4.790694000
7	21.415861000	-2.520240000	-5.420807000
6	19.242079000	-2.326370000	-5.637678000
1	18.207493000	-2.429248000	-5.915597000
6	21.000403000	-1.477583000	-4.688619000
1	21.661965000	-0.858574000	-4.107415000
6	20.312026000	-3.071469000	-6.034664000

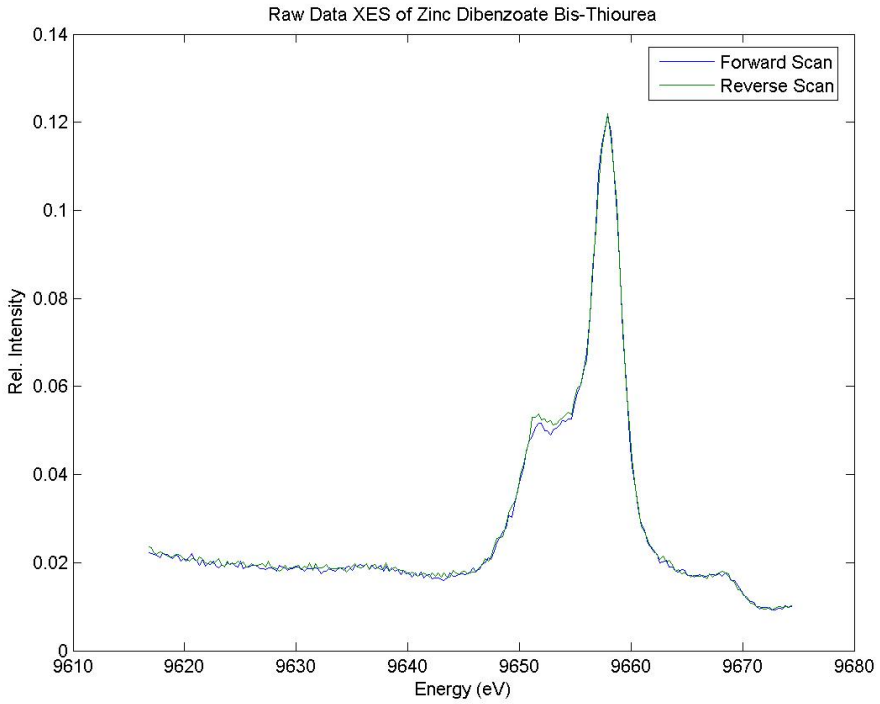
1	20.382993000	-3.922407000	-6.689237000
6	22.802332000	-2.961850000	-5.553024000
1	23.422829000	-2.369259000	-4.886662000
1	22.882858000	-4.011562000	-5.275178000
1	23.139734000	-2.819641000	-6.578431000

h. $Zn(^{Me}Im)_6$

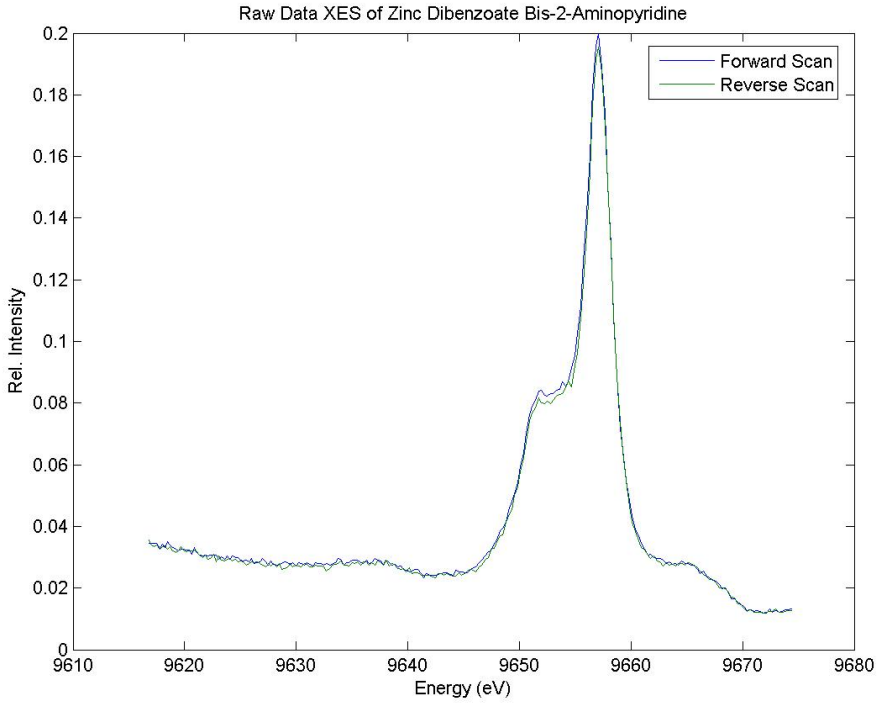
30	15.526614000	0.646268000	-3.079572000
7	15.397531000	-0.523604000	-1.213433000
7	16.137095000	-1.875288000	0.361300000
6	14.953519000	-0.064381000	0.006821000
1	14.366748000	0.830977000	0.098756000
6	16.103682000	-1.613788000	-0.962963000
1	16.606058000	-2.218706000	-1.697301000
6	15.406247000	-0.893496000	0.993315000
1	15.278565000	-0.873646000	2.061809000
6	16.860509000	-2.961827000	1.010685000
1	17.337108000	-3.574110000	0.248242000
1	16.174603000	-3.579884000	1.588328000
1	17.625382000	-2.555814000	1.671676000
7	17.396419000	1.529720000	-2.324015000
7	19.345765000	2.555936000	-2.309954000
6	18.015869000	1.284212000	-1.117812000
1	17.552098000	0.693045000	-0.350067000
6	18.220582000	2.301665000	-3.014120000
1	18.041816000	2.678848000	-4.006181000
6	19.226433000	1.914230000	-1.097689000
1	19.997422000	1.967806000	-0.348705000
6	20.493652000	3.343988000	-2.742395000
1	20.306160000	3.725958000	-3.743094000
1	21.387047000	2.720767000	-2.755761000
1	20.648978000	4.182151000	-2.065713000
7	13.656724000	-0.236849000	-3.837047000
7	11.708394000	-1.265037000	-3.852877000
6	13.036824000	0.010419000	-5.042671000
1	13.499893000	0.603454000	-5.809391000
6	12.833437000	-1.011006000	-3.148373000
1	13.012746000	-1.390220000	-2.157184000
6	11.826838000	-0.620674000	-5.063810000
1	11.055796000	-0.673567000	-5.812795000
6	10.561351000	-2.055112000	-3.421922000
1	10.749347000	-2.439018000	-2.422062000
1	9.667359000	-1.432782000	-3.407104000
1	10.406762000	-2.891995000	-4.100359000
7	16.666564000	-0.959219000	-4.031694000

7	18.390384000	-2.084475000	-4.813287000
6	16.198668000	-1.992052000	-4.814660000
1	15.147399000	-2.151312000	-4.976168000
6	17.985879000	-1.045980000	-4.053689000
1	18.668110000	-0.392139000	-3.540016000
6	17.259930000	-2.696903000	-5.309307000
1	17.309821000	-3.558315000	-5.952151000
6	19.774471000	-2.450834000	-5.087301000
1	20.426368000	-1.839006000	-4.469168000
1	19.938937000	-3.499510000	-4.844906000
1	20.010992000	-2.274443000	-6.136334000
1	15.907718000	3.454472000	-1.200757000
6	14.856164000	3.293717000	-1.358869000
6	13.795789000	4.004057000	-0.870218000
1	13.746975000	4.872182000	-0.236427000
1	11.118375000	4.804181000	-1.326026000
7	14.386822000	2.252685000	-2.130046000
7	12.664495000	3.386840000	-1.358106000
6	13.067591000	2.339960000	-2.106971000
6	11.280818000	3.755048000	-1.084391000
1	12.384286000	1.680734000	-2.612160000
1	10.628201000	3.144998000	-1.703522000
1	11.043329000	3.578246000	-0.035618000
1	13.421573000	3.843462000	-7.832840000
1	14.442236000	3.510429000	-4.463992000
1	13.707080000	4.862828000	-6.409602000
6	14.946092000	2.906384000	-5.198032000
6	14.185346000	4.251714000	-7.171945000
7	14.911743000	3.167318000	-6.522399000
7	15.655328000	1.818308000	-4.947166000
6	15.645293000	2.187364000	-7.154150000
6	16.100447000	1.359931000	-6.167347000
1	15.772905000	2.167468000	-8.222654000
1	14.869525000	4.871606000	-7.749677000
1	16.689911000	0.466345000	-6.259244000

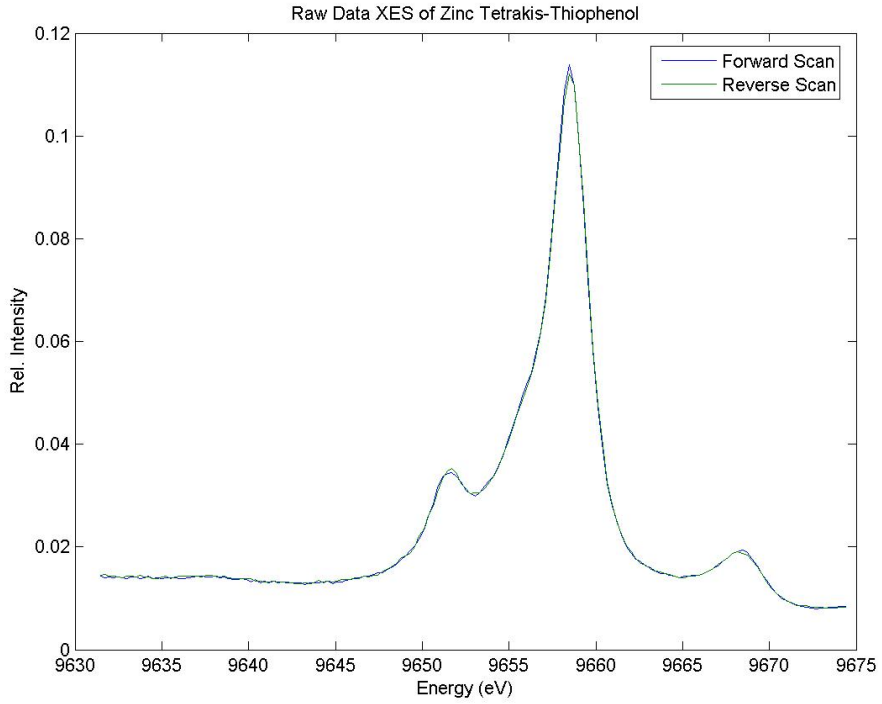
a. $Zn(BzO)_2(SC(NH_2)_2)_2$



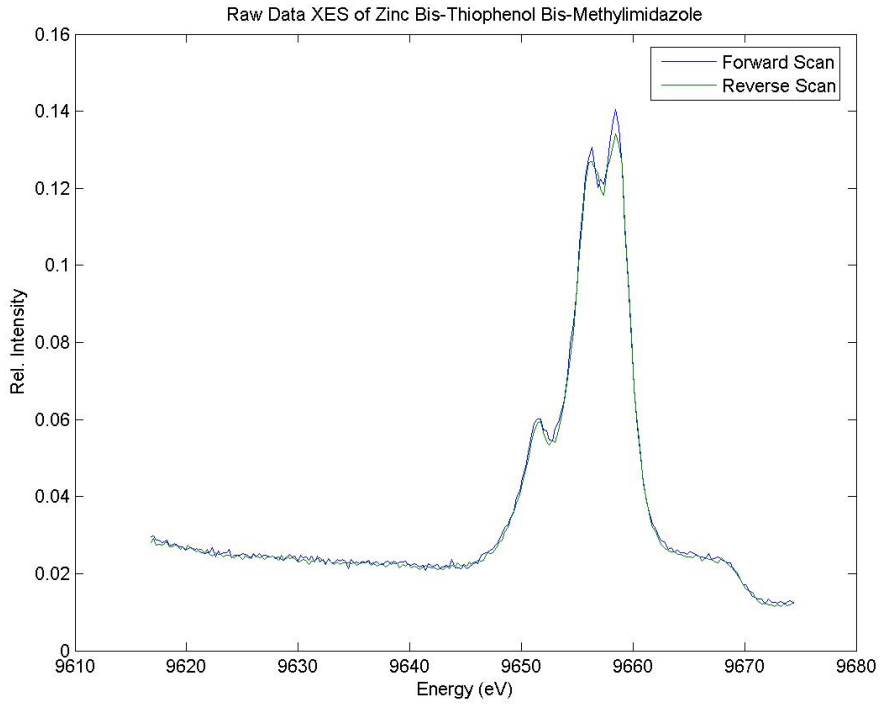
b. $Zn(BzO)_2(pyNH_2)_2$



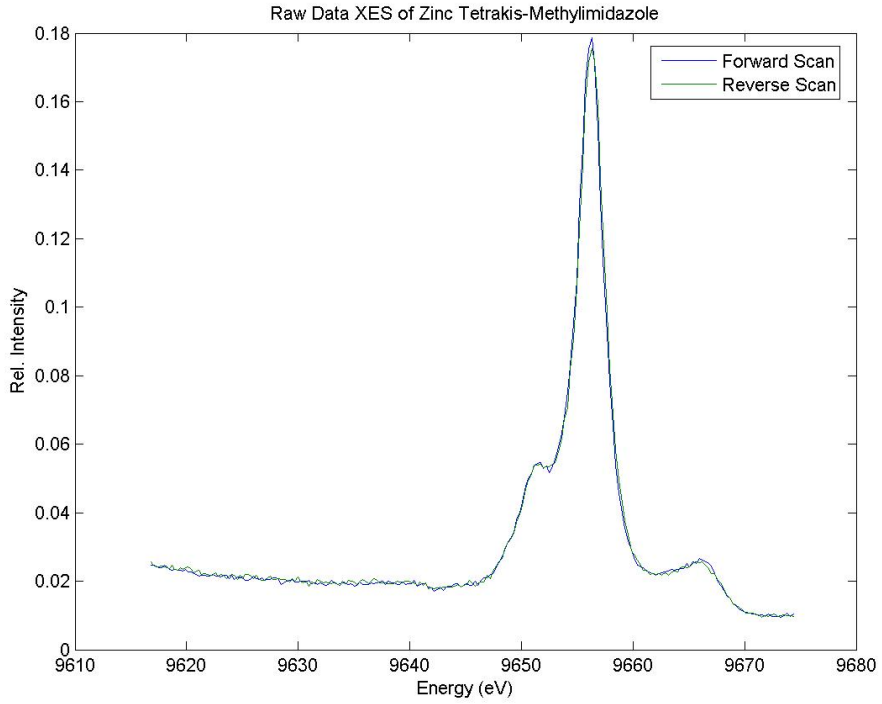
c. $Zn(SPh)_4$



d. $Zn(^{Me}Im)_2(SPh)_2$



e. $Zn(^{Me}Im)_4$



f. $Zn(^{Me}Im)_6$

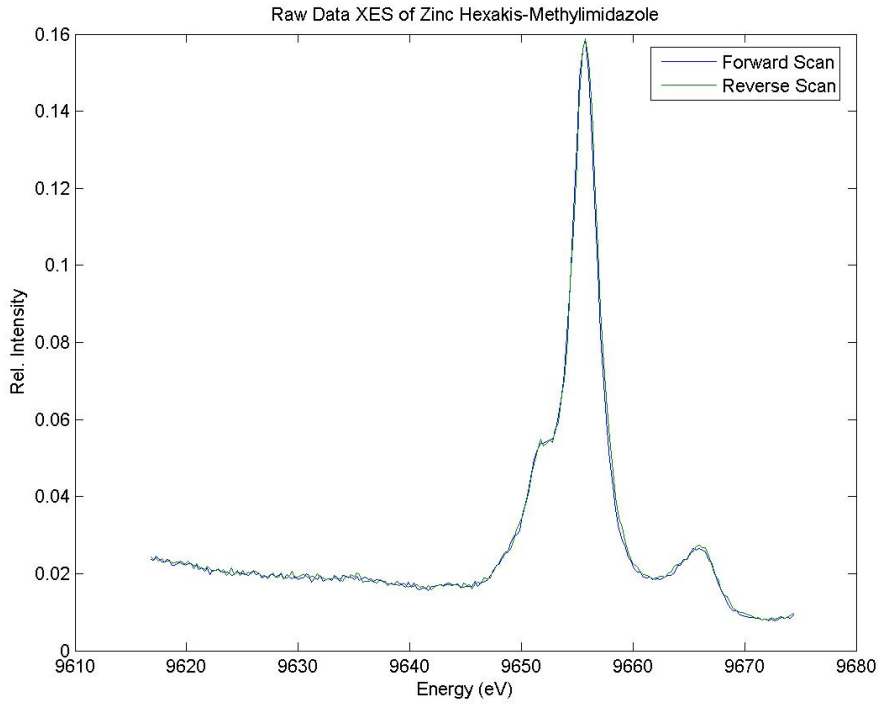
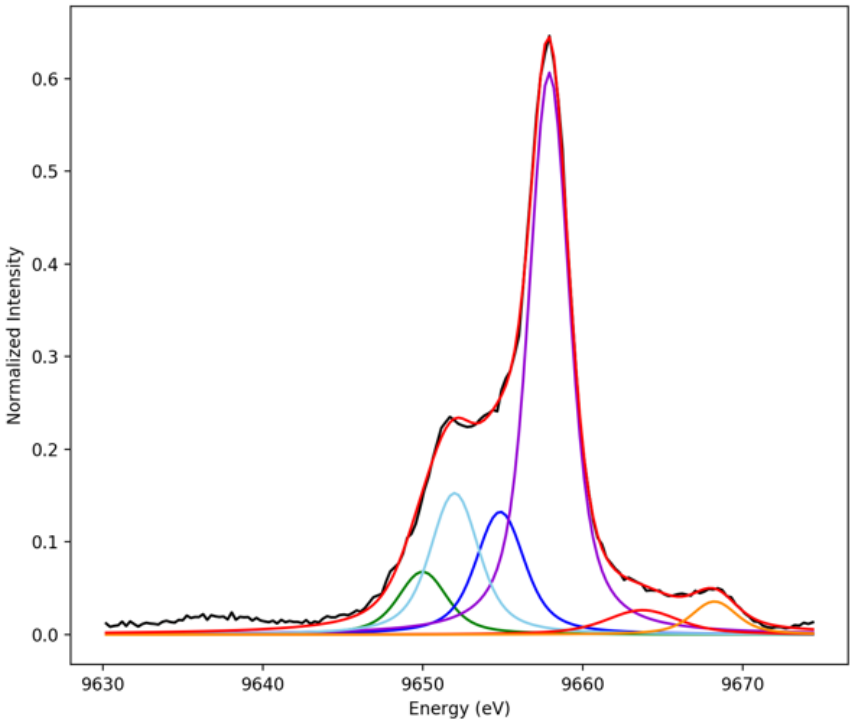
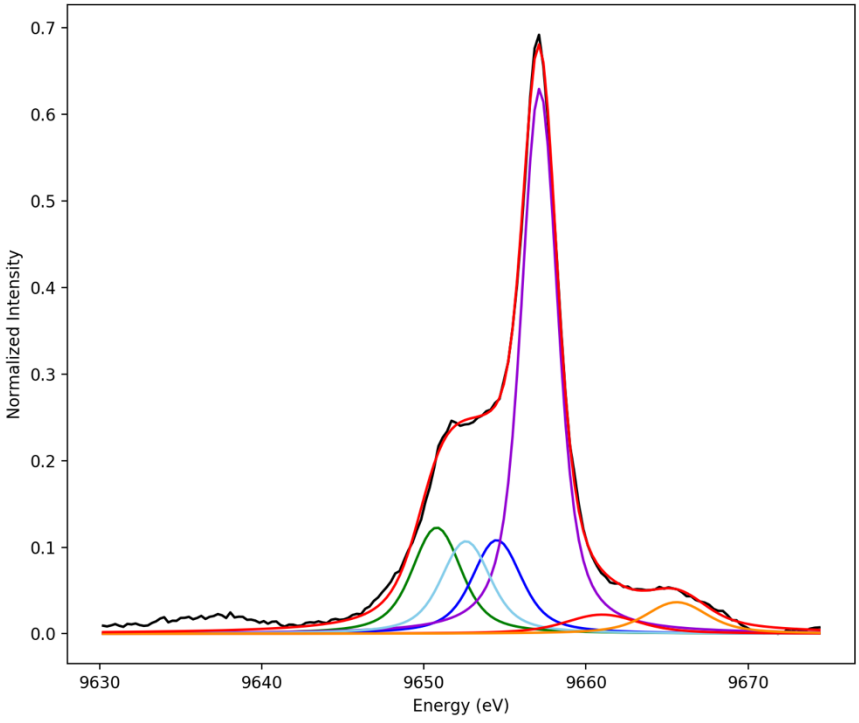


Figure S1. Zn VtC XES cans were collected from both lowest to highest energy and highest to lowest energy. The forward and reverse scans are shown for each complex.

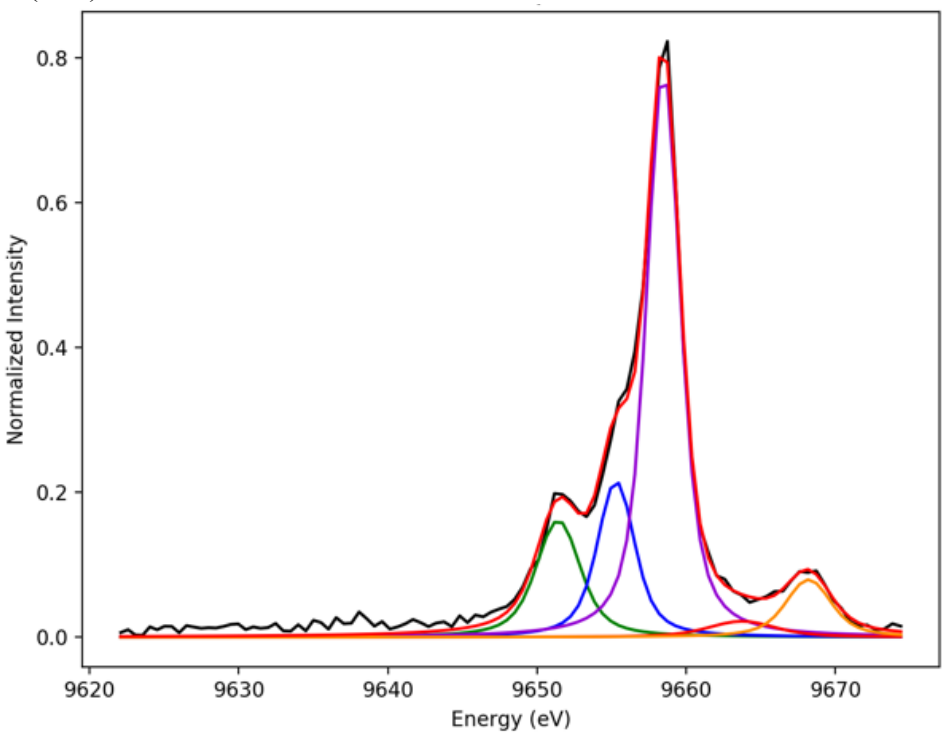
a. $Zn(BzO)_2(SC(NH_2)_2)_2$



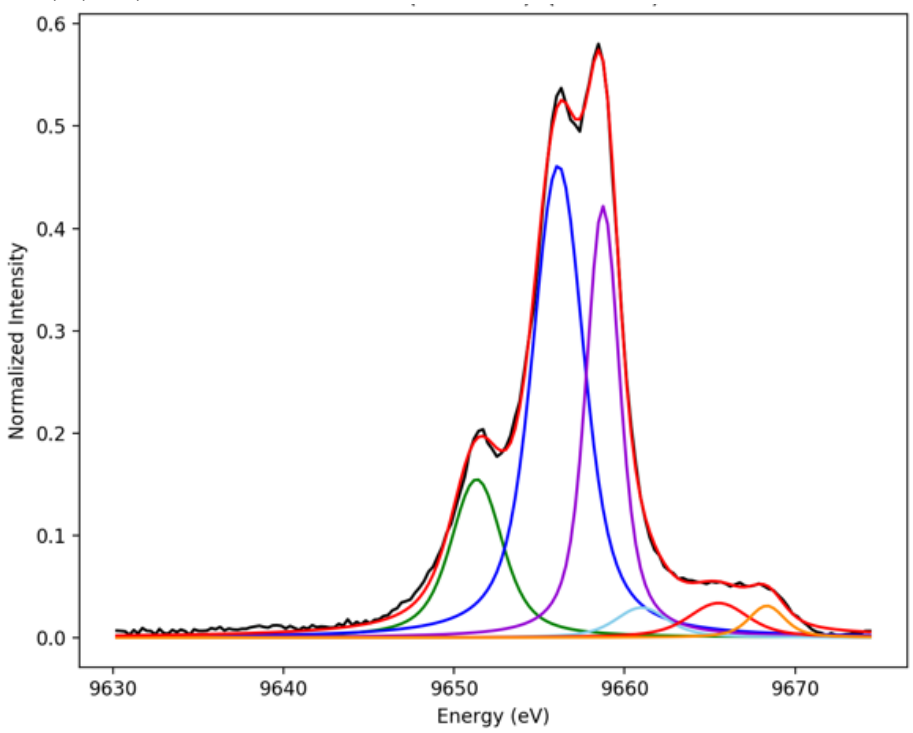
b. $Zn(BzO)_2(pyNH_2)_2$



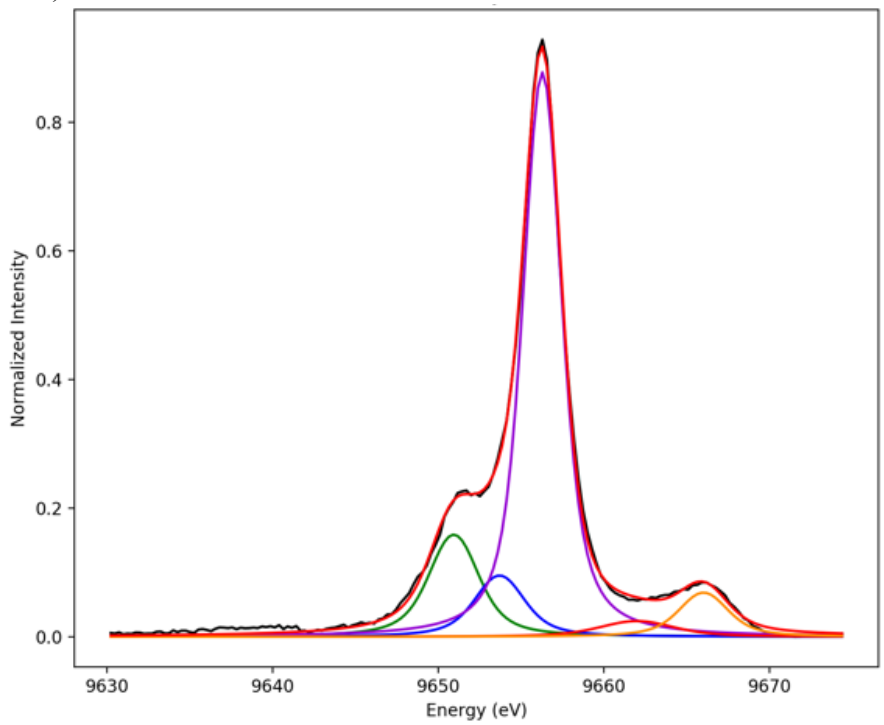
c. $Zn(SPh)_4$



d. $Zn(^{Me}Im)_2(SPh)_2$



e. $Zn(^{Me}Im)_4$



f. $Zn(^{Me}Im)_6$

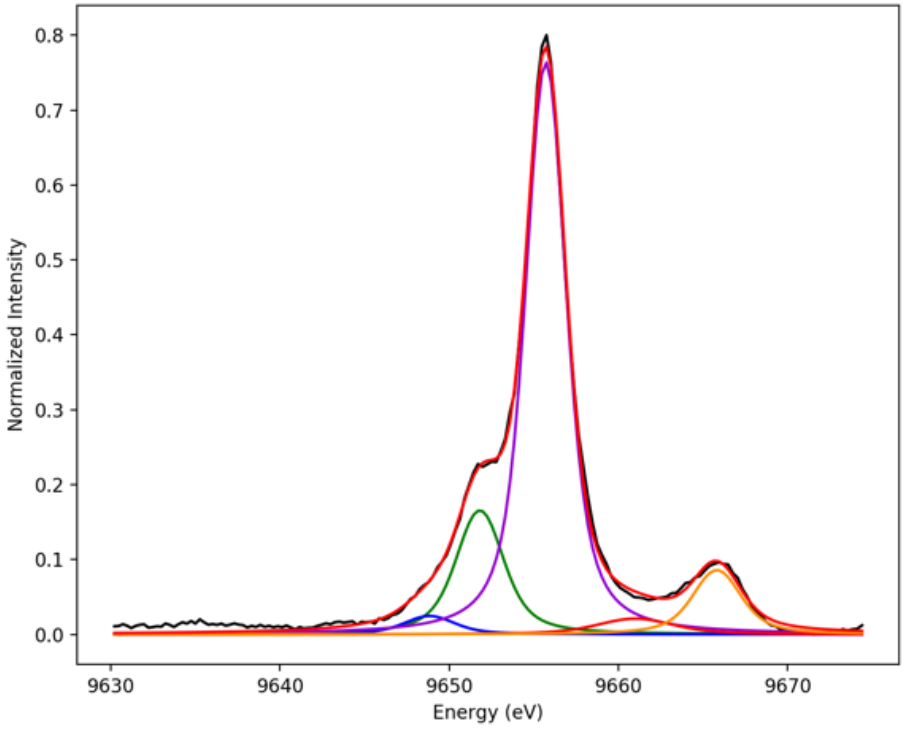


Figure S2. Fits to experimental VtC XES data

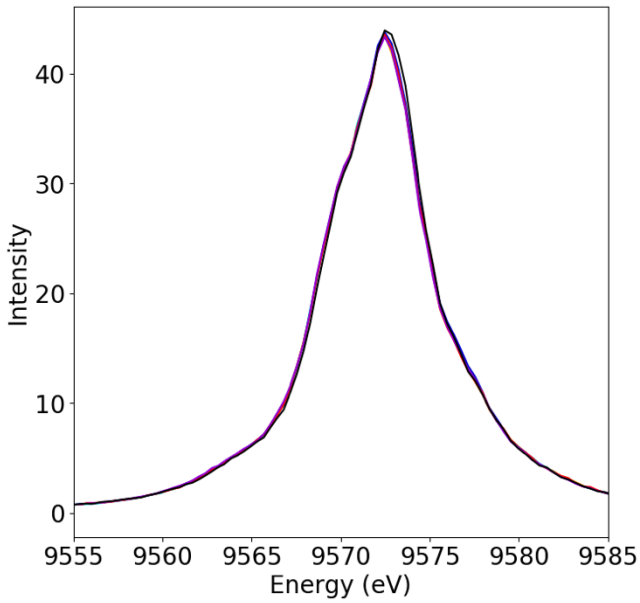
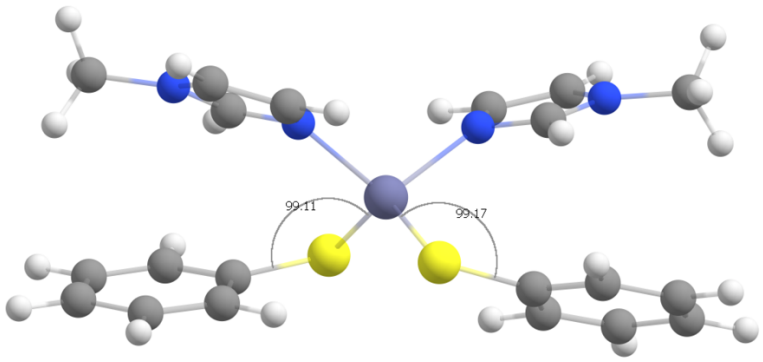


Figure S3. Overlay of Kβ mainline region for all measured samples.

a. Molecular model of geometry optimized Zn(^{Me}Im)$_2$(SPh)$_2$ with the angle of interest displayed



b. The effect of modulating the displayed angle on the VtC spectra, with the spectra of geometry optimized Zn(^{Me}Im)$_2$(SPh)$_2$ and the average of the geometry optimized Zn(^{Me}Im)$_4$ and Zn(SPh)$_4$ for reference.

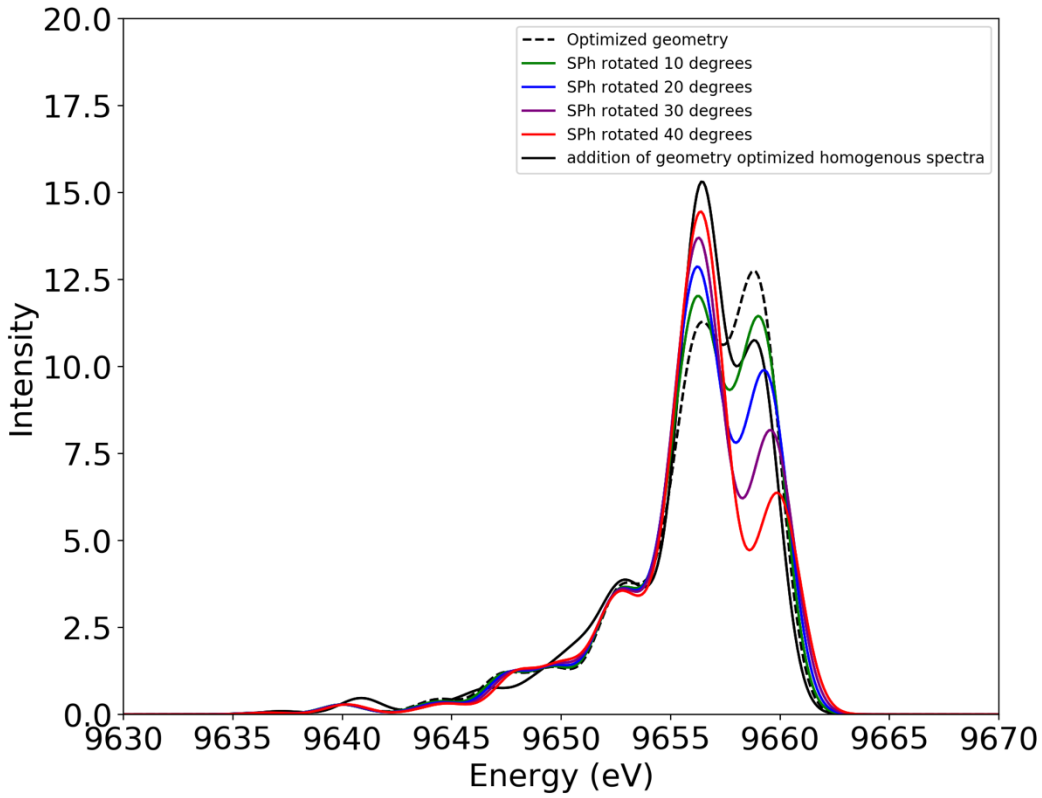


Figure S4. Zn(^{Me}Im)$_2$(SPh)$_2$ Ligand-Ligand Interaction Calculations