Electronic Supplementary Material (ESI) for Chemical Science.

Scrutinizing Metal-Ligand Covalency and Redox Non-Innocence Via Nitrogen K-edge X-ray Absorption Spectroscopy

Supporting Information

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EXAMPLE ORCA INPUT FILES

Single Point and TD-DFT XAS Calculation:

```
!B3LYP RIJCOSX ZORA-def2-TZVP(-f) def2/J ZORA CPCM UKS PAL4
!NormalPrint TightSCF Grid4 NoFinalGrid UNO UCO

%basis newgto 3d Metal Atom "CP(PPP)"
      end

%tddft   NRoots 100
       MaxDim 1000
       OrbWin[0] = LowestEnergyDonorOrbital, HighestEnergyDonorOrbital, -1, -1
       OrbWin[1] = LowestEnergyDonorOrbital, HighestEnergyDonorOrbital, -1, -1
       DoQuad true
       end

%method SpecialGridAtoms Metal Atomic Number
      SpecialGridIntAcc 7
      end

%MaxCore 4000

%SCF
    MaxIter 500
    end

* xyz Charge SpinMultiplicity
Coordinates
*
```

DFT-ROCIS XAS Calculation:

```
!B3LYP RIJCOSX ZORA-def2-TZVP(-f) def2/J ZORA CPCM ROKS PAL4
!NormalPrint TightSCF Grid4 NoFinalGrid UNO UCO MOREAD NOITER

%moinp "TD-DFT FILENAME.qro"

%basis newgto 3d Metal Atom "CP(PPP)" end
      end

%rocis  NRoots 100
```

MaxDim 500
SOC false
DoRI true
DoQuad true
DoHigherMult false
DoLowerMult false
PrintLevel 3
Orbwin ***LowestEnergyDonorOrbital***, ***HighestEnergyDonorOrbital***,0,500
DoDFTCIS true
DFTCIS_c = 0.21, 0.49, 0.29
end

%method SpecialGridAtoms ***Metal Atomic Number***
SpecialGridIntAcc 7
end

%MaxCore 4000

* xyz ***Charge SpinMultiplicity***
Coordinates
*

INPUT COORDINATES FOR ORCA CALCULATIONS

$[Co(NH_3)_5Cl]Cl_2$
Charge = +2, Spin Multiplicity = 1

Co	0.00000	0.00000	0.00000
Cl	0.01293	0.02389	2.26445
N	0.04647	1.96725	0.04135
H	-0.75554	2.27849	0.27200
H	0.26367	2.27480	-0.76513
H	0.65193	2.23650	0.63494
N	-0.02360	-1.95468	0.03116
H	-0.86328	-2.24115	0.09842
H	0.44500	-2.24535	0.73012
H	0.33839	-2.26844	-0.71978
N	-1.96335	0.06528	-0.03923
H	-2.23043	0.53587	-0.74568
H	-2.26210	0.45343	0.70469
H	-2.28615	-0.76293	-0.09342
N	0.01235	-0.06825	-1.94963
H	0.17443	0.74521	-2.27481
H	-0.77917	-0.35018	-2.24078
H	0.64673	-0.62899	-2.22306
N	1.94876	0.00000	-0.00000
H	2.24492	-0.32186	-0.77597
H	2.24572	-0.51129	0.66610
H	2.24546	0.83279	0.11027

$[Co(NH_3)_6]Cl_3$
Charge = +3, Spin Multiplicity = 1

Co	0.00000	0.00000	0.00000
N	-1.96658	0.02337	0.05966
H	-2.27933	-0.78391	-0.14612
H	-2.27323	0.61951	-0.52528
H	-2.23514	0.24687	0.87811
N	-0.03694	0.03692	-1.97032
H	0.35210	-0.69822	-2.28770
H	0.40158	0.75452	-2.26214
H	-0.88111	0.07050	-2.25125
N	-0.01505	-1.96419	-0.05857
H	0.06285	-2.28587	0.76615
H	0.66578	-2.25134	-0.55587
H	-0.78063	-2.24377	-0.41539
N	1.96808	-0.00053	-0.00047
H	2.26480	-0.77069	0.33215
H	2.26466	0.67316	0.50041
H	2.26450	0.09712	-0.83374
N	0.00000	1.96588	0.00000
H	0.05544	2.26235	0.83841
H	-0.75294	2.26253	-0.37095
H	0.69758	2.26238	-0.46457
N	0.05125	-0.06894	1.96290
H	0.05470	0.75982	2.28757
H	0.78841	-0.49329	2.22471
H	-0.66537	-0.50311	2.26300

$[Ni(NH_3)_6]Cl_2$
Charge = +2, Spin Multiplicity = 3

Ni	0.00000	0.00000	0.00000
N	0.03303	-1.52991	1.46279
H	-0.41323	-2.25753	1.14888
H	-0.36932	-1.23075	2.22265
H	0.89481	-1.75610	1.64471
N	0.01019	1.40675	1.59724
H	-0.60504	1.16038	2.22133
H	-0.19574	2.23242	1.27606
H	0.83710	1.42624	1.97822
N	-2.11808	0.01420	0.03802
H	-2.42145	0.81476	-0.27166
H	-2.40723	-0.10899	0.89109
H	-2.43548	-0.65539	-0.48978
N	0.02809	1.55606	-1.44671
H	0.22756	1.20683	-2.26270
H	0.65829	2.17151	-1.21735
H	-0.78931	1.95459	-1.47817
N	-0.02098	-1.43000	-1.53527
H	0.17308	-2.24878	-1.18966
H	0.60098	-1.21004	-2.16236
H	-0.84447	-1.45055	-1.91905
N	2.15315	0.00000	0.00000
H	2.45655	-0.78593	0.34527
H	2.45690	0.69179	0.50714
H	2.45693	0.09247	-0.85295

$[Cu(NH_3)_4](SO_4)$
Charge = +2, Spin Multiplicity = 2

Cu	0.00000	0.00000	-0.00000
N	0.00000	2.01192	-0.00000
H	0.51025	2.41405	0.69170
H	0.32965	2.30266	-0.80432
H	-0.83502	2.40556	0.03744
N	1.99663	0.07670	-0.23536
H	2.29217	0.51749	-1.02204
H	2.35820	0.50902	0.48748
H	2.42594	-0.74134	-0.22497
N	-0.00000	-2.01192	0.00000
H	-0.51025	-2.41405	-0.69170
H	-0.32965	-2.30266	0.80432
H	0.83502	-2.40556	-0.03744
N	-1.99663	-0.07670	0.23536
H	-2.29217	-0.51749	1.02204
H	-2.35820	-0.50902	-0.48748
H	-2.42594	0.74134	0.22497

$[Ni(en)_3]Cl_2$
Charge = +2, Spin Multiplicity = 3

Ni	0.00000	0.00000	0.00000
C	-1.58679	-2.39170	-0.51854
C	-2.45153	-1.51868	0.32880
C	0.23550	1.74277	-2.34472
C	-0.49038	2.54097	-1.32109
C	2.41201	-0.59013	1.57841
C	1.50858	0.17720	2.51374
H	0.07675	-2.48011	0.60102
H	0.60191	-0.20302	-2.46965
H	-0.00644	1.97277	-3.16179
H	1.10114	1.91393	-2.34273
H	-0.38429	3.32222	-1.45330
H	-1.45520	2.48714	-1.32990
H	-0.45733	2.39436	0.61302
H	0.79602	2.38254	0.14490
H	2.44660	-0.72382	-0.35407
H	2.56018	0.74675	0.11350
H	3.25676	-0.36208	1.81345
H	0.36038	-2.37779	-0.88831
H	2.31026	-1.53538	1.75081
H	1.68443	1.09433	2.34656
H	1.68046	-0.08892	3.39723
H	-0.43427	0.50546	2.46295
H	-0.08592	-0.93290	2.42074
H	-1.77836	-2.19100	-1.32060
H	-1.74230	-3.20405	-0.30622
H	-2.29190	-1.64080	1.33194
H	-3.22409	-1.65411	0.21109
H	-2.45098	0.37115	0.63306
H	-2.47204	0.05898	-0.70138
H	-0.75953	0.08145	-2.40404
N	-0.16622	-2.08639	-0.21724
N	-2.11580	-0.11524	0.05188
N	0.00649	0.31484	-2.10103
N	-0.00000	2.13035	-0.00000
N	2.12600	-0.14510	0.19043
N	0.11870	-0.06718	2.13408

$[Cu(en)_2](OTf)_2$
Charge = +2, Spin Multiplicity = 2

Cu	0.00000	0.00000	0.00000
N	1.57595	-0.18665	-1.24894
H	1.36924	-0.01874	-2.02618
H	2.27393	0.38050	-1.10018
C	2.02243	-1.60347	-1.22697
H	2.59601	-1.75981	-0.46036
H	2.52533	-1.80548	-2.03121
C	0.80415	-2.48341	-1.14617
H	0.28971	-2.42104	-1.96604
H	1.06563	-3.40822	-1.01619
N	-0.00000	-2.01163	0.00000
H	0.35854	-2.36447	0.73466
H	-0.80992	-2.52484	0.05017
N	-1.57595	0.18665	1.24894
H	-1.36924	0.01874	2.02618
H	-2.27393	-0.38050	1.10018
C	-2.02243	1.60347	1.22697
H	-2.59601	1.75981	0.46036
H	-2.52533	1.80548	2.03121
C	-0.80415	2.48341	1.14617
H	-0.28971	2.42104	1.96604
H	-1.06563	3.40822	1.01619
N	0.00000	2.01163	-0.00000
H	-0.35854	2.36447	-0.73466
H	0.80992	2.52484	-0.05017

$[Zn(en)_3]Cl_2$
Charge = +2, Spin Multiplicity = 1

Zn	0.00000	-0.00000	0.00000
N	-2.13195	0.34112	0.46594

N	0.46623	-0.23188	2.16535
N	2.20379	-0.09917	-0.10370
C	-2.25253	1.74875	0.88942
C	1.89441	-0.61351	2.30115
C	2.71408	0.15898	1.24082
H	-2.54659	-0.16693	1.19817
H	-2.72458	-0.05045	-0.35422
H	-3.29768	1.94333	0.99571
H	-2.45552	1.99263	1.96467
H	-0.44454	-0.76356	2.21501
H	0.24063	0.47993	2.66808
H	2.42197	-1.37127	2.86836
H	2.62918	0.54894	-0.75878
H	2.42015	-0.86242	-0.42750
H	2.67707	1.21451	1.04725
H	3.66031	-0.05689	1.03979
N	0.00000	2.20877	-0.00000
N	-0.24807	-0.02905	-2.21303
N	-0.31128	-2.16433	-0.30991
C	-1.41010	2.63188	-0.08896
H	0.44124	2.68499	-0.73804
H	0.63697	2.54731	0.81047
C	-0.17928	-1.43785	-2.67600
H	0.43213	0.77841	-2.21230
H	-0.98025	0.40468	-2.50644
C	-0.89607	-2.33338	-1.63814
H	-0.90340	-2.61303	0.38162
H	0.44078	-2.55935	-0.19776
H	-1.41497	3.69315	0.03424
H	-1.79597	3.09230	-1.03551
H	0.35028	-1.94443	-3.47423
H	-1.87360	-2.17549	-1.22285
H	-0.83485	-3.32245	-1.65729

[Mn(bpy)$_3$](PF$_6$)$_2$
Charge = +2, Spin Multiplicity = 6

Mn	0.00000	0.00000	0.00000
N	-0.19303	-0.14858	-2.23478
N	-2.20554	-0.17800	-0.43481
N	0.24867	-2.20777	0.32362
N	-0.28652	-0.36881	2.18964
N	2.15314	0.64177	0.09143
N	-0.00000	2.23023	0.00000
C	-1.45165	-0.29401	-2.73064
C	-1.65299	-0.40436	-4.09634
H	-2.52840	-0.54962	-4.43623
C	-0.60348	-0.30459	-4.94548
H	-0.74927	-0.35119	-5.88329
C	0.68914	-0.12912	-4.45285
H	1.43452	-0.05500	-5.03728
C	0.84599	-0.06834	-3.07883
H	1.71951	0.03257	-2.72186
C	-2.55474	-0.28421	-1.74473
C	-3.89482	-0.33122	-2.12285
H	-4.12881	-0.40168	-3.04138
C	-4.89024	-0.27675	-1.15084
H	-5.80684	-0.28055	-1.39723
C	-4.52145	-0.21369	0.16814
H	-5.17860	-0.20730	0.85391
C	-3.17233	-0.15961	0.48570
H	-2.92472	-0.10728	1.40014
C	-0.00942	-2.67582	1.56191
C	-0.05546	-4.03017	1.82423
H	-0.23204	-4.34686	2.70317
C	0.15799	-4.92336	0.78848
H	0.12240	-5.85913	0.95060
C	0.42015	-4.45228	-0.47449
H	0.57069	-5.05097	-1.19570
C	0.46062	-3.08891	-0.67125
H	0.64390	-2.75616	-1.54194
C	-0.24554	-1.64457	2.61026
C	-0.43186	-1.96932	3.95502
H	-0.38458	-2.87449	4.24176
C	-0.68890	-0.95458	4.87020
H	-0.83140	-1.16273	5.78469
C	-0.73572	0.35415	4.44046
H	-0.90233	1.06311	5.05009
C	-0.53165	0.60182	3.09656
H	-0.56544	1.49986	2.79498
C	2.37701	1.97770	0.19818
C	3.65218	2.48145	0.42650
H	3.79959	3.41962	0.48544
C	4.69036	1.60568	0.56426
H	5.56219	1.93898	0.73989
C	4.49664	0.25596	0.45501
H	5.21976	-0.35403	0.53904
C	3.19122	-0.19152	0.21562
H	3.03796	-1.12455	0.13884
C	1.20272	2.85699	0.06304
C	1.27602	4.25393	-0.01340
H	2.11877	4.69311	0.02841
C	0.11809	4.99039	-0.15179
H	0.15757	5.93869	-0.18357
C	-1.08030	4.35330	-0.24224
H	-1.88295	4.84540	-0.36419
C	-1.10192	2.97901	-0.15422
H	-1.94185	2.53925	-0.20545

[Fe(bpy)$_3$](PF$_6$)$_2$
Charge = +2, Spin Multiplicity = 1

Fe	0.00000	0.00000	0.00000
C	-0.21077	-0.01898	-3.13055
C	0.24295	-0.01512	-4.44618
C	1.60656	-0.20043	-4.67815
C	2.46214	-0.37854	-3.59321
C	1.93856	-0.37321	-2.29461
N	0.60864	-0.19651	-2.07633
C	2.77931	-0.52730	-1.08621
C	4.13153	-0.88641	-1.14427
C	2.88077	-0.38795	1.23576
C	4.23297	-0.71831	1.24980
C	4.86701	-0.98104	0.03478
H	-1.26800	0.11823	-2.90168
H	-0.46161	0.12925	-5.26398
H	2.00347	-0.20114	-5.69339
H	2.34602	-0.18971	2.16491
H	4.76772	-0.77457	2.19704
H	5.92044	-1.25919	0.00338
N	2.16004	-0.29199	0.10171
C	1.10796	2.93769	0.06381

C	1.08045	4.32111	-0.08557
C	-0.14953	4.93931	-0.31444
C	-1.29981	4.15682	-0.38829
C	-1.20079	2.76949	-0.22689
N	-0.00000	2.17450	0.00000
C	-2.36727	1.86255	-0.31692
C	-3.68659	2.32757	-0.37620
C	-3.10266	-0.34277	-0.45050
C	-4.43523	0.05066	-0.53560
C	-4.73146	1.41348	-0.48942
H	2.04520	2.41154	0.24746
H	2.00495	4.89321	-0.02202
H	-0.21437	6.02017	-0.44010
H	-2.83113	-1.39857	-0.46687
H	-5.21782	-0.70133	-0.62732
H	-5.76295	1.76251	-0.53718
N	-2.08406	0.53245	-0.34443
H	-3.90078	3.39351	-0.32785
H	-2.26304	4.62442	-0.58302
H	4.60808	-1.09838	-2.09942
H	3.52990	-0.50668	-3.75969
C	-0.74913	-3.87606	1.86911
C	-0.72345	-4.82391	0.85061
C	-0.86744	-1.69296	3.93081
C	-0.86866	-0.63238	4.83167
H	-0.90385	-4.19083	2.89917
H	-0.86094	-5.88050	1.08013
H	-1.08669	-2.70015	4.27965
H	-1.08444	-0.80735	5.88560
C	-0.57024	-2.52069	1.55985
C	-0.51734	-4.39802	-0.46360
C	-0.58914	-1.45399	2.57818
C	-0.59258	0.65368	4.36191
C	-0.33939	-3.03972	-0.70164
N	-0.36273	-2.11146	0.27762
C	-0.32976	0.82355	3.00716
N	-0.32370	-0.19753	2.12476
H	-0.49082	-5.10158	-1.29466
H	-0.58190	1.51552	5.02783
H	-0.17219	-2.66912	-1.71307
H	-0.11328	1.81185	2.60152

$[Co(bpy)_3](PF_6)_2$
Charge = +2, Spin Multiplicity = 2

Co	0.00000	0.00000	0.00000
N	0.00000	2.14380	-0.00000
C	1.17837	2.72780	0.22230
C	1.29929	4.11018	0.31164
C	0.17444	4.90378	0.13412
C	-0.99905	4.32045	-0.11045
C	-1.06895	2.94694	-0.16117
N	2.04594	0.50310	0.28223
C	2.36024	1.81061	0.37283
C	3.63279	2.23974	0.56915
C	4.66481	1.32168	0.69417
C	4.34981	0.02005	0.59658
C	3.06433	-0.38842	0.40782
N	-2.06809	-0.09055	-0.52645
C	-2.33574	-0.15938	-1.83600
C	-3.65063	-0.23590	-2.31784
C	-4.69698	-0.18040	-1.42761
C	-4.43290	-0.05286	-0.06432
C	-3.08009	-0.03229	0.31022
N	0.01228	-0.19639	-2.10974
C	-1.16087	-0.21899	-2.73245
C	-1.28044	-0.30113	-4.10824
C	-0.15458	-0.37541	-4.87280
C	1.07347	-0.36914	-4.23677
C	1.12098	-0.29457	-2.88764
N	0.23772	-2.09107	0.30501
C	-0.06422	-2.52952	1.55320
C	0.02691	-3.86771	1.91299
C	0.43503	-4.77724	0.95594
C	0.78263	-4.31436	-0.30879
C	0.64743	-2.98636	-0.58075
N	-0.41327	-0.22531	2.07722
C	-0.48858	-1.48307	2.51242
C	-0.95248	-1.77457	3.80735
C	-1.34652	-0.75708	4.62426
C	-1.23245	0.53526	4.19336
C	-0.76020	0.76320	2.93328
H	2.14480	4.50848	0.48970
H	0.23929	5.85107	0.18908
H	-1.77951	4.84671	-0.24942
H	-1.91661	2.54362	-0.31747
H	3.81915	3.17190	0.62184
H	5.56093	1.60102	0.84506
H	5.04053	-0.63136	0.65929
H	2.87340	-1.31879	0.36383
H	-3.81754	-0.32531	-3.24988
H	-5.59319	-0.22778	-1.73992
H	-5.13164	0.01685	0.57712
H	-2.88173	0.02721	1.23793
H	-2.13849	-0.30403	-4.51690
H	-0.21234	-0.43093	-5.82015
H	1.87691	-0.41774	-4.74406
H	1.97147	-0.31142	-2.46273
H	-0.18523	-4.15099	2.79565
H	0.48113	-5.70503	1.15905
H	1.13453	-4.89211	-0.94714
H	0.86028	-2.68574	-1.45707
H	-0.98409	-2.67082	4.11531
H	-1.70078	-0.94550	5.48642
H	-1.47368	1.25978	4.76092
H	-0.67235	1.66415	2.64229

$[Co(bpy)_3](BF_4)_2(PF_6)$
Charge = +3, Spin Multiplicity = 1

Co	0.00000	0.00000	0.00000
N	0.00000	1.93022	0.00000
N	-1.85131	0.21298	0.54477
N	-0.40628	0.09691	-1.88978
N	1.82887	-0.10894	-0.60260
N	-0.08676	-1.93104	0.13157
N	0.46057	-0.12889	1.85325
C	1.00867	2.73494	-0.32927
H	1.82166	2.35948	-0.58470
C	0.88429	4.12924	-0.30398
H	1.61328	4.67448	-0.49901
C	-0.30524	4.66547	0.00400

H	-0.41087	5.58904	-0.00002
C	-1.36552	3.85651	0.32317
H	-2.19235	4.23099	0.52608
C	-1.20272	2.49732	0.34083
C	-2.23380	1.51021	0.70733
C	-3.48672	1.79828	1.14183
H	-3.74958	2.68606	1.23032
C	-4.36594	0.80132	1.45282
H	-5.20573	1.00751	1.79466
C	-4.01781	-0.45413	1.26425
H	-4.63310	-1.13688	1.40754
C	-2.69844	-0.75727	0.84022
H	-2.42838	-1.64386	0.76871
C	-1.59496	0.21043	-2.44802
H	-2.33944	0.17979	-1.89082
C	-1.81362	0.37199	-3.81757
H	-2.67252	0.41652	-4.17215
C	-0.67334	0.46380	-4.63308
H	-0.75130	0.63083	-5.54351
C	0.56002	0.29993	-4.04851
H	1.31783	0.28304	-4.58747
C	0.70645	0.15950	-2.68197
C	1.96441	0.03114	-1.95922
C	3.22085	0.09371	-2.54320
H	3.30063	0.19547	-3.46550
C	4.33249	0.00542	-1.77274
H	5.17884	0.07333	-2.15083
C	4.18288	-0.18536	-0.42793
H	4.93049	-0.28093	0.11756
C	2.92278	-0.23468	0.11223
H	2.83977	-0.36372	1.02861
C	-0.36384	-2.77862	-0.85302
H	-0.42813	-2.44519	-1.71899
C	-0.55921	-4.12202	-0.65131
H	-0.78528	-4.69268	-1.35139
C	-0.40525	-4.58335	0.63655
H	-0.51706	-5.48994	0.81091
C	-0.09431	-3.74581	1.65879
H	-0.01357	-4.06205	2.53125
C	0.09666	-2.42010	1.36974
C	0.45757	-1.36112	2.36764
C	0.78276	-1.62480	3.68364
H	0.78260	-2.49707	4.00584
C	1.10675	-0.56918	4.50837
H	1.31914	-0.72663	5.40001
C	1.11638	0.74477	4.00654
H	1.33908	1.47393	4.53790
C	0.77847	0.88489	2.69028
H	0.76652	1.74732	2.34224

$[Ni(bpy)_3](PF_6)_2$
Charge = +2, Spin Multiplicity = 3

Ni	0.00000	0.00000	0.00000
C	0.26771	-2.82564	-1.04666
C	0.31341	-4.15243	-0.87127
C	0.08686	-4.74305	0.49111
C	-0.11558	-3.78028	1.62998
C	-0.14011	-2.45278	1.39186
N	0.00415	-1.94290	0.05844
C	-0.27678	-1.39008	2.44291
C	-0.52697	-1.63317	3.74378
C	-0.26949	1.08142	2.83875
C	-0.52449	0.89797	4.14525
C	-0.66596	-0.48996	4.70628
H	0.43677	-2.42323	-2.03490
H	0.51887	-4.80168	-1.71596
H	0.15919	-5.83592	0.66034
H	-0.18586	2.08919	2.45585
H	-0.64064	1.75401	4.80139
H	-0.90572	-0.66586	5.77452
N	-0.12780	-0.04271	1.95003
C	2.80218	-0.01149	1.15809
C	4.13103	0.12379	1.03360
C	4.75468	0.27737	-0.32657
C	3.83002	0.25778	-1.51197
C	2.50256	0.12594	-1.32374
N	1.95039	-0.00000	0.00000
C	1.47921	0.10595	-2.41700
C	1.75544	0.10416	-3.73669
C	-0.97468	-0.07056	-2.86903
C	-0.76247	-0.08702	-4.19241
C	0.63406	0.02441	-4.73673
H	2.37023	-0.10484	2.14496
H	4.75885	0.13311	1.91811
H	5.84775	0.41278	-0.45004
H	-1.98634	-0.15803	-2.49784
H	-1.60161	-0.18730	-4.87306
H	0.83187	-0.02390	-5.82619
N	0.12382	0.04185	-1.94649
H	2.77282	0.13335	-4.10066
H	4.25161	0.36577	-2.50179
H	-0.65027	-2.64118	4.11537
H	-0.21258	-4.17771	2.63004
C	-3.75261	1.74758	0.03886
C	-4.75058	0.63672	0.15796
C	-1.56535	3.79313	-0.25479
C	-0.39492	4.70173	-0.36796
H	-4.11236	2.76929	0.04486
H	-5.83279	0.84691	0.27087
H	-2.55328	4.22849	-0.31270
H	-0.55270	5.76628	-0.49289
C	-2.43763	1.46046	-0.04149
C	-4.20672	-0.76342	0.20614
C	-1.36009	2.47822	-0.11590
C	0.97525	4.12441	-0.29769
C	-2.88544	-0.98597	0.11783
N	-1.96055	0.10454	-0.02550
C	1.12252	2.81062	-0.14939
N	-0.03069	1.94349	-0.05540
H	-4.88804	-1.59782	0.31970
H	1.84170	4.77633	-0.36974
H	-2.51879	-1.99965	0.15743
H	2.12481	2.41972	-0.10119

$[Zn(bpy)_3](PF_6)_2$
Charge = +2, Spin Multiplicity = 1

Zn	0.00000	0.00000	0.00000
C	-0.97885	4.27424	-0.39378
H	-1.74116	4.78947	-0.52591
C	1.37874	4.06670	-0.12589

H	2.22086	4.45418	-0.06907
C	-1.06684	2.91563	-0.20759
H	-1.90814	2.52176	-0.22638
C	0.27375	4.84731	-0.37589
H	0.37239	5.75871	-0.53241
N	-0.00000	2.12810	0.00000
N	2.09729	0.48430	0.11620
C	-4.77204	-0.50429	0.97461
H	-5.67343	-0.57875	1.19149
C	2.35573	1.79621	0.29012
C	-2.47623	-0.40934	1.62920
C	-3.81778	-0.52271	1.97267
H	-4.07115	-0.60897	2.86334
C	-4.38856	-0.37768	-0.33529
H	-5.01621	-0.37076	-1.02078
C	-3.03216	-0.25982	-0.60607
H	-2.76422	-0.18064	-1.49304
N	-2.10191	-0.25453	0.32884
N	-0.13415	-0.19656	2.15178
C	-1.59590	-0.76353	3.94449
H	-2.45682	-0.94652	4.24753
C	-1.38157	-0.44426	2.61469
N	-0.05209	-0.11538	-2.17785
C	4.38042	-0.01007	0.65452
H	5.05591	-0.64093	0.75779
N	0.28061	-2.07497	-0.39101
C	3.61570	2.24748	0.66239
H	3.77431	3.15637	0.77526
C	1.22931	2.70899	0.03786
C	0.52140	-0.44509	-4.85862
H	0.73360	-0.55790	-5.75789
C	-0.09314	0.91457	-3.03671
H	-0.31653	1.75614	-2.71134
C	3.09570	-0.40149	0.28379
H	2.92318	-1.30428	0.14797
C	0.21888	-2.43604	-1.67459
C	0.88220	-0.23533	3.02313
H	1.73836	-0.05275	2.70648
C	0.18394	0.77590	-4.39693
H	0.13836	1.50692	-4.97034
C	0.24783	-1.33053	-2.66404
C	0.19597	-4.36686	0.25623
H	0.20208	-5.00943	0.92913
C	0.11436	-4.73587	-1.07463
H	0.04249	-5.63304	-1.30518
C	0.26466	-3.03431	0.55805
H	0.30333	-2.78043	1.45222
C	0.55392	-1.52172	-4.00571
H	0.77706	-2.36801	-4.32164
C	4.63111	1.33183	0.86630
H	5.47286	1.61564	1.14234
C	-0.53366	-0.80830	4.81750
H	-0.66959	-1.02631	5.71169
C	0.14288	-3.76492	-2.06393
H	0.10990	-3.99934	-2.96281
C	0.73362	-0.52656	4.35212
H	1.46638	-0.53499	4.92505

[Ru(bpy)$_3$](BPh$_4$)$_2$
Charge = +2, Spin Multiplicity = 1

Ru	0.00000	0.00000	-0.00000
H	-2.86219	-0.69273	5.18066
C	-2.30969	-0.56344	4.25050
C	-2.98749	-0.41159	3.04481
H	-4.07577	-0.42284	3.02536
C	-0.91345	-0.54767	4.24153
H	-4.95472	-0.14210	1.17148
C	-4.27247	-0.04480	0.32907
H	-0.33549	-0.66311	5.15741
C	-2.26739	-0.24675	1.85671
C	-4.77310	0.11346	-0.95950
H	-5.84838	0.14066	-1.13328
C	-2.88983	-0.07841	0.54003
C	-0.24819	-0.38179	3.03264
N	-0.89641	-0.23119	1.85442
C	-3.87185	0.23607	-2.01906
N	-2.01001	0.04262	-0.50439
H	0.83904	-0.36202	2.99060
C	-2.50836	0.19769	-1.75292
H	-4.21205	0.36211	-3.04598
H	-1.77798	0.28754	-2.55450
H	2.11025	1.49930	-5.36689
C	1.72327	1.19276	-4.39557
C	1.35022	2.14700	-3.45400
H	1.44469	3.20670	-3.68398
C	1.59248	-0.15857	-4.06931
H	0.81370	4.51674	-2.20838
C	0.46466	4.06207	-1.28305
H	1.87094	-0.94453	-4.76996
C	0.85515	1.74152	-2.20992
C	0.04765	4.86397	-0.22510
H	0.06745	5.94958	-0.31578
C	0.43456	2.66915	-1.15520
C	1.09553	-0.50583	-2.81881
N	0.72731	0.41306	-1.89604
C	-0.39462	4.24993	0.94837
N	0.00000	2.07214	0.00000
H	0.97760	-1.54925	-2.53333
C	-0.40460	2.86218	1.02150
H	-0.73180	4.83222	1.80478
H	-0.73860	2.35129	1.92251
H	0.93006	-5.88444	-0.13941
C	0.72994	-4.81345	-0.12844
C	1.71569	-3.91773	0.27417
H	2.69380	-4.28409	0.58067
C	-0.51441	-4.31205	-0.51564
H	4.07502	-2.84039	1.12587
C	3.72513	-1.80998	1.10100
H	-1.31966	-4.97063	-0.83821
C	1.44724	-2.54466	0.28411
C	4.57618	-0.77447	1.47439
H	5.59576	-0.98746	1.79417
C	2.41806	-1.52444	0.69178
C	-0.72717	-2.93899	-0.48772
N	0.22427	-2.05810	-0.10035
C	4.09725	0.53638	1.42993
N	1.95297	-0.23530	0.65200
H	-1.68293	-2.51486	-0.78904
C	2.79037	0.76373	1.01551
H	4.72289	1.38238	1.71107
H	2.38461	1.77256	0.97255

[Rh(bpy)$_3$](PF$_6$)$_3$
Charge = +3, Spin Multiplicity = 1

Rh	0.00000	0.00000	0.00000
N	-2.05143	-0.08257	-0.12565
C	-2.52424	-0.18279	-1.44126
C	-3.90226	-0.44256	-1.63458
C	-4.76014	-0.50483	-0.45292
C	-4.25420	-0.29767	0.73160
C	-2.89432	-0.07119	0.94378
H	-4.25890	-0.54860	-2.51984
H	-5.68969	-0.72189	-0.55410
H	-4.84742	-0.28563	1.48550
H	-2.55501	0.08595	1.82860
N	0.22259	-2.03398	0.21050
N	0.01492	0.36605	2.02404
N	-0.23606	-0.15321	-2.03759
N	0.00000	2.05693	0.00000
N	2.04997	-0.15321	-0.07131
C	-1.57674	-0.23992	-2.43696
C	1.56016	-2.45213	0.18815
C	-0.80374	-2.91195	0.38394
C	0.02744	1.73102	2.34206
C	-0.01221	-0.59743	2.98594
C	0.78491	-0.14624	-2.93861
C	-0.00069	2.61287	1.28661
C	0.02597	2.83179	-1.11946
C	2.51407	-1.46905	0.06139
C	2.89940	0.89502	-0.25558
C	-1.86556	-0.15195	-3.81994
C	1.84123	-3.79943	0.51914
C	-0.50857	-4.24301	0.67846
H	-1.71455	-2.61617	0.30859
C	-0.15855	2.10002	3.69596
C	-0.16447	-0.21432	4.31846
H	0.06788	-1.52458	2.74778
C	0.48188	-0.09116	-4.29902
H	1.69736	-0.17435	-2.63966
C	0.19616	4.00943	1.40759
C	0.18908	4.21008	-0.98059
H	-0.06228	2.43302	-1.98891
C	3.88897	-1.71551	-0.16817
C	4.25629	0.63608	-0.44891
H	2.56660	1.79612	-0.25640
C	-0.74187	-0.06228	-4.75023
H	-2.77378	-0.17628	-4.13084
C	0.71261	-4.69075	0.77978
H	2.74735	-4.11628	0.54503
H	-1.23259	-4.86125	0.79667
C	-0.26628	1.03256	4.68848
H	-0.18693	3.02577	3.94950
H	-0.17964	-0.89394	4.99543
H	1.20210	-0.09011	-4.93281
C	0.30216	4.79534	0.17987
H	0.23280	4.42346	2.27324
H	0.20341	4.75517	-1.76994
C	4.75352	-0.57005	-0.44498
H	4.23946	-2.60807	-0.11709
H	4.85413	1.37576	-0.57485
H	-0.91221	0.04141	-5.68919
H	0.87800	-5.59747	1.04792
H	-0.43546	1.25564	5.60664
H	0.47852	5.73729	0.23492
H	5.68084	-0.71498	-0.64619

[Os(bpy)$_3$](PF$_6$)$_2$
Charge = +2, Spin Multiplicity = 1

Os	0.00000	0.00000	0.00000
C	-1.19186	0.79615	2.67470
C	-1.66701	0.55995	3.92115
C	-1.91395	-0.72295	4.35184
C	-1.68672	-1.77292	3.49532
C	-1.17976	-1.48929	2.24413
N	-0.88705	-0.22507	1.84126
H	-1.05206	1.81429	2.34197
H	-1.85525	1.39064	4.58497
H	-2.28217	-0.90212	5.35172
H	-1.89699	-2.78899	3.79452
N	1.93633	-0.22507	0.65400
N	0.00000	2.05615	-0.00000
N	-0.27498	-2.03512	0.10210
N	-1.82952	0.43283	-0.83263
N	1.05522	-0.00371	-1.76472
C	-0.88608	-2.52883	1.21072
C	2.29605	-0.35881	1.95136
C	2.91703	-0.23419	-0.28641
C	1.02542	2.82220	0.43831
C	-1.11131	2.68158	-0.46912
C	0.10573	-2.90871	-0.85829
C	-2.73543	-0.49580	-1.21655
C	-2.14117	1.74327	-1.01112
C	0.50010	0.14497	-2.98953
C	2.40128	-0.17254	-1.68820
C	-1.21054	-3.86234	1.34998
C	3.60125	-0.38395	2.31332
H	1.53128	-0.44444	2.70942
C	4.25727	-0.28260	0.03663
C	0.90469	4.16922	0.51672
H	1.95276	2.35248	0.73202
C	-1.26630	4.05177	-0.43036
C	-0.21572	-4.22191	-0.77253
H	0.67215	-2.55323	-1.70661
C	-3.86887	-0.13658	-1.86576
H	-2.55089	-1.53875	-1.00424
C	-3.29517	2.15392	-1.64562
C	1.24567	0.01327	-4.11291
H	-0.55323	0.36964	-3.07255
C	3.20146	-0.28782	-2.80594
C	-0.88237	-4.71597	0.32464
H	-1.70923	-4.22521	2.23642
C	4.59808	-0.33908	1.36642
H	3.86212	-0.44102	3.35966
H	5.01653	-0.27422	-0.73123
C	-0.24072	4.80187	0.09235
H	1.71954	4.75395	0.91704
H	-2.16669	4.52163	-0.79735
H	0.05625	-4.88975	-1.57637
C	-4.16182	1.18760	-2.09600
H	-4.55190	-0.90064	-2.20608

H	-3.51097	3.20258	-1.78663
C	2.60079	-0.21147	-4.03926
H	0.76925	0.08682	-5.07922
H	4.26735	-0.43578	-2.71574
H	-1.14446	-5.76278	0.37888
H	5.63633	-0.34820	1.66542
H	-0.33217	5.87571	0.16937
H	-5.06274	1.46384	-2.62466
H	3.18522	-0.32645	-4.94073

(^{n}Bu$_4$N)[RuNCl$_4$]
Charge = -1, Spin Multiplicity = 1

Ru	0.00000	0.00000	0.00000
Cl	-1.11862	-1.93530	-0.58141
N	0.00000	-0.00000	1.56981
Cl	-1.93530	1.11862	-0.58141
Cl	1.11862	1.93530	-0.58141
Cl	1.93530	-1.11862	-0.58141

(^{n}Bu$_4$N)[ReNCl$_4$]
Charge = -1, Spin Multiplicity = 2

Re	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.65852
Cl	2.28675	0.00000	-0.57018
Cl	-2.28674	0.00002	-0.57018
Cl	0.00001	-2.28664	-0.57020
Cl	-0.00001	2.28665	-0.570

(^{n}Bu$_4$N)[OsNCl$_4$]
Charge = -1, Spin Multiplicity = 1

Os	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.60459
Cl	-1.93222	1.12521	-0.57954
Cl	1.12521	1.93222	-0.57954
Cl	1.93222	-1.12521	-0.57954
Cl	-1.12521	-1.93222	-0.57954

(PNP)NiCl
Charge = 0, Spin Multiplicity = 1

Ni	0.00000	0.00000	0.00000
P	0.00000	2.20128	0.00000
C	-1.63017	2.49705	-0.71664
C	-2.09501	3.66222	-1.31291
C	-3.34920	3.73790	-1.90060
C	-3.86325	4.99460	-2.55571
C	-4.13022	2.58232	-1.87016
C	-3.69896	1.41288	-1.28297
C	-2.43349	1.32674	-0.67595
N	-1.88602	0.17607	-0.11984
C	-2.70051	-0.88938	0.29289
C	-4.00262	-0.75456	0.79846
C	-4.70730	-1.86797	1.22655
C	-4.16063	-3.15172	1.19358
C	-4.93836	-4.33082	1.72761
C	-2.87052	-3.28004	0.72254
C	-2.13749	-2.17622	0.28795
P	-0.38919	-2.16114	-0.17012
C	1.18616	3.14935	-1.03558
C	1.31220	2.45749	-2.38900
C	2.55013	3.31278	-0.35965
C	0.01608	2.98267	1.67022
C	-0.99037	2.26379	2.56238
C	-0.23159	4.47972	1.64604
C	-0.24388	-2.81629	-1.88578
C	-0.82451	-4.21462	-2.04882
C	-0.86661	-1.82624	-2.86231
C	0.40561	-3.40359	0.93247
C	0.32345	-2.91664	2.37155
C	1.84004	-3.72707	0.52603
Cl	2.13718	-0.17984	0.22765
H	-1.53095	4.43157	-1.33338
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H	-3.72756	4.97205	-3.40248
H	-4.92803	2.61401	-2.28626
H	-4.20196	0.63543	-1.34122
H	-4.36863	0.07380	0.87890
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H	-4.88815	-4.38098	2.64283
H	-4.68451	-5.13425	1.40435
H	-2.47637	-4.09675	0.72975
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H	1.85792	2.97517	-2.95218
H	0.49203	2.38172	-2.78732
H	3.15364	3.77715	-0.94929
H	2.50686	3.81961	0.47585
H	2.93006	2.43460	-0.09206
H	0.86250	2.81687	1.99912
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H	-1.07643	4.70246	1.30771
H	0.44513	4.95191	1.12715
H	0.66170	-2.79179	-2.02691
H	-0.68300	-4.51210	-2.93677
H	-1.71832	-4.19773	-1.89891
H	-0.43927	-4.83849	-1.45069
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H	-0.10346	-4.15361	0.86988
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H	-0.55868	-2.76294	2.61692
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H	2.22307	-4.41643	1.11594
H	2.41170	-2.91206	0.49501
H	1.88244	-4.08848	-0.32989

[PNPNiCl](OTf)
Charge = +1, Spin Multiplicity = 2

Ni	0.00000	0.00000	0.00000
Cl	2.12203	-0.20287	0.26963
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C	-3.62658	1.29596	-1.47504	H	-2.46693	-3.97750	1.03223
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C	-2.65195	-0.81803	0.39672	H	0.79023	2.29848	-2.70194
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C	0.46660	-3.46180	0.79052	H	2.17323	-4.60173	0.69817
C	1.78549	-3.88042	0.14812	H	1.65827	-4.25013	-0.72901
C	0.67231	-2.97662	2.22569	H	1.14226	-3.67647	2.71646
C	-0.46001	-2.76480	-1.93165	H	1.31824	-2.16727	2.22040
C	-1.18075	-1.74055	-2.80935	H	-0.12351	-2.75114	2.60850
C	-1.07363	-4.15550	-2.04804	H	0.45068	-2.79899	-2.12778
H	-1.43777	4.26203	-1.73192	H	-0.75620	-0.89725	-2.76143
H	-3.09088	5.53016	-2.94203	H	-2.15094	-1.61576	-2.53590
H	-3.40492	4.57516	-3.98902	H	-1.18009	-2.00376	-3.73921
H	-4.47534	4.92153	-2.99433	H	-1.98727	-4.18079	-1.74442
H	-4.79844	2.41665	-2.62981	H	-0.62172	-4.82802	-1.50026
H	-4.14503	0.54933	-1.51542	H	-1.05672	-4.44045	-2.95360
H	-4.21430	0.28908	0.99075				

Table S1. Elemental analysis results.

		Predicted			Experimental		
Compound	**Formula**	**% C**	**% H**	**% N**	**% C**	**% H**	**% N**
$[Co(NH3)_6]Cl_3$	$CoN_6H_{18}Cl_3$	0.00	6.78	31.42	0.12	6.73	31.59
$[Co(NH_3)_5Cl]Cl_2$	$CoN_5H_{15}Cl_3$	0.00	6.04	27.96	0.15	5.95	27.73
$[Ni(NH_3)_6]Cl_2$	$NiN_6H_{18}Cl_2$	0.00	7.83	36.26	0.21	7.66	35.23
$[Cu(NH_3)_4](SO_4)\cdot H_2O$	$CuN_4H_{16}SO_5$	0.00	6.51	22.61	0.12	5.59	22.31
$[Cu(en)_2](OTf)_2\cdot H_2O$	$CuC_6N_4H_{18}F_6O_7S_2$	14.42	3.63	11.21	15.02	3.29	11.66
$[Ni(en)_3]Cl_2\cdot 2H_2O$	$NiC_6N_6H_{28}Cl_2O_2$	20.83	8.16	24.29	21.10	8.16	24.31
$[Zn(en)_3]Cl_2\cdot H_2O$	$ZnC_6N_6H_{26}C_{l2}O$	21.54	7.83	25.12	21.26	6.93	24.42
$[Mn(bpy)_3](PF_6)_2$	$MnC_{30}H_{24}N_6P_2F_{12}$	44.29	2.97	10.33	44.22	2.83	10.32
$[Fe(bpy)_3](PF_6)_2$	$FeC_{30}H_{24}N_6P_2F_{12}$	44.25	2.97	10.32	44.14	2.95	10.35
$[Co(bpy)_3](PF_6)_2$	$CoC_{30}H_{24}N_6P_2F_{12}$	44.08	2.96	10.28	44.01	2.79	10.20
$[Co(bpy)_3](BF_4)_2(PF_6)$	$CoC_{30}H_{24}N_6B_2PF_{14}$	42.59	2.86	9.93	42.05	3.33	9.85
$[Ni(bpy)_3](PF_6)_2$	$NiC_{30}H_{24}N_6P_2F_{12}$	44.09	2.96	10.28	44.13	2.83	10.27
$[Zn(bpy)_3](PF_6)_2$	$ZnC_{30}H_{24}N_6P_2F_{12}$	43.74	2.94	10.20	43.72	2.84	10.09
$[Ru(bpy)_3](BPh_4)_2$	$RuC_{78}H_{64}N_6B_2$	77.55	5.34	6.96	77.21	5.25	6.98
$[Rh(bpy)_3](PF_6)_3$	$RhC_{30}H_{24}N_6P_3F_{18}$	35.80	2.40	8.35	35.80	2.51	8.39
$[Os(bpy)_3](PF_6)_2$	$OsC_{30}H_{24}N_6P_2F_{12}$	37.98	2.55	8.86	36.62	2.35	8.31
$(^nBu_4N)[RuNCl_4]$	$RuN_2Cl_4C_{16}H_{36}$	38.48	7.27	5.61	38.86	7.20	5.31
$(^nBu_4N)[ReNCl_4]$	$ReN_2Cl_4C_{16}H_{36}$	32.88	6.21	4.79	32.62	6.17	4.57
$(^nBu_4N)[OsNCl_4]$	$OsN_2Cl_4C_{16}H_{36}$	32.65	6.17	4.76	32.25	6.02	4.52

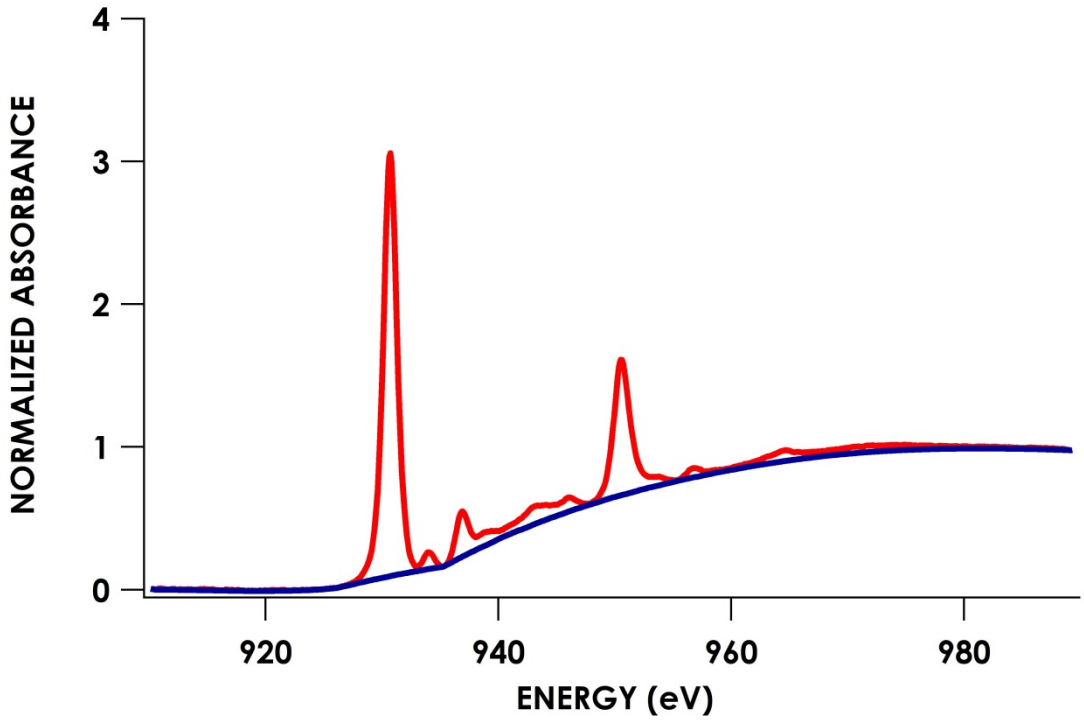

Fig. S1. Cu $L_{2,3}$-edge XAS normalized spectra of $(nmph)_2[CuCl_4]$ in red with SNIP background in blue.

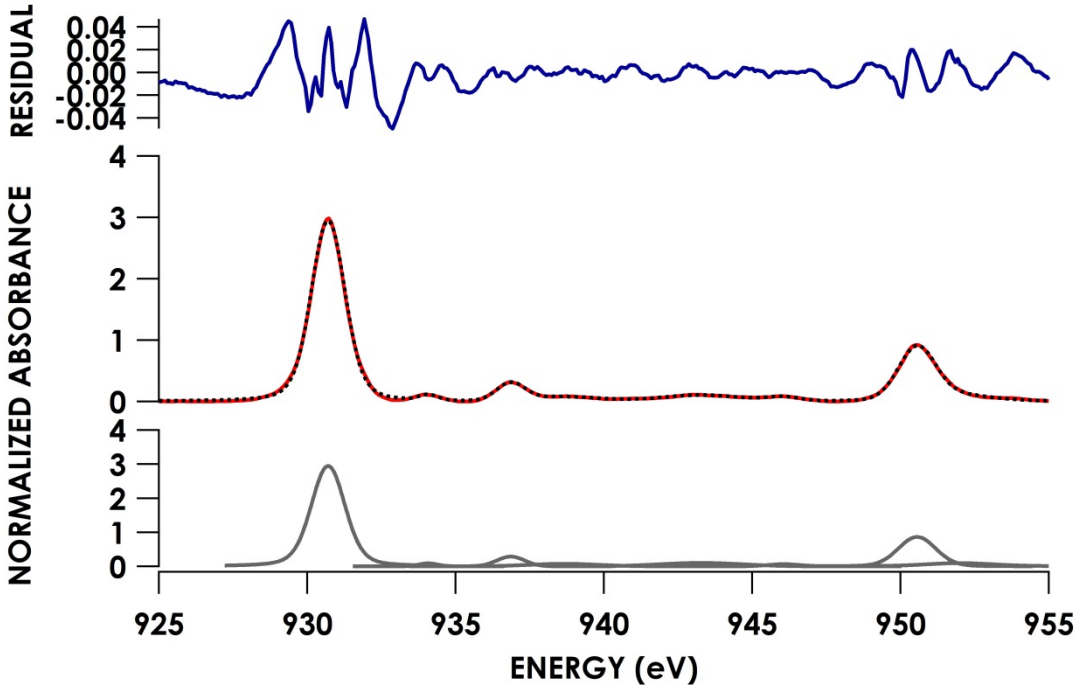

Fig. S2. Fit Cu $L_{2,3}$-edge XAS spectra of $(nmph)_2[CuCl_4]$ showing experimental spectra in red, individual pseudo-Voigt peaks below in grey, composite fit spectra in a dotted black line overlaid on the experimental, and residual intensity above in blue.

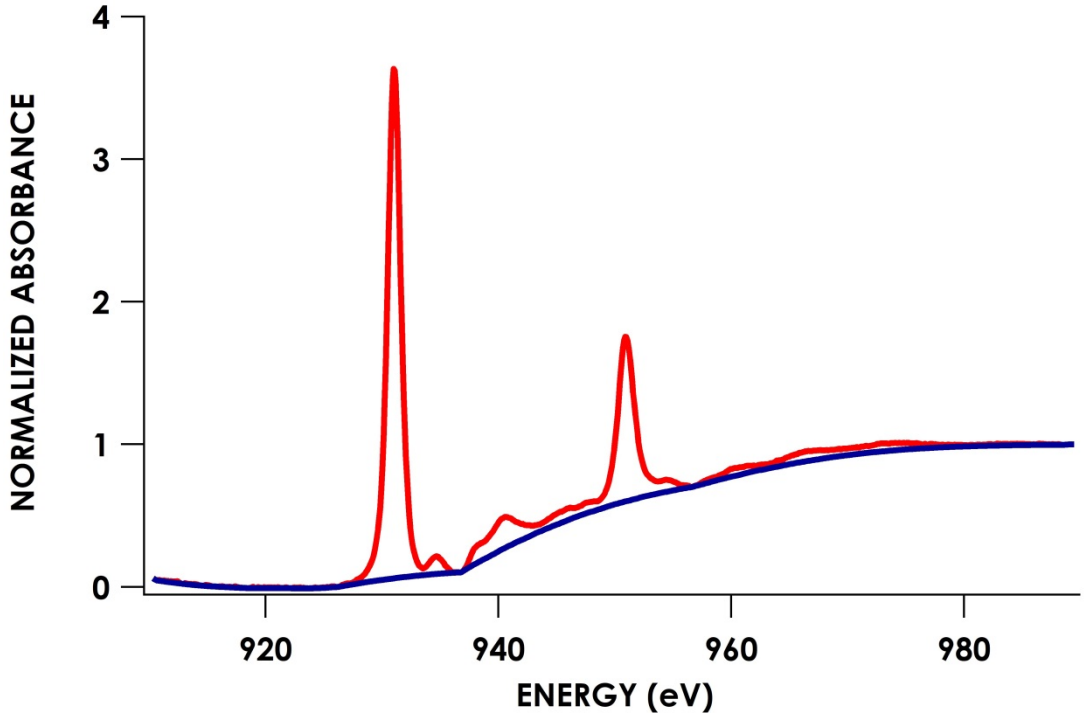

Fig. S3. Cu $L_{2,3}$-edge XAS normalized spectra of $[Cu(en)_2](OTf)_2$ in red with SNIP background in blue.

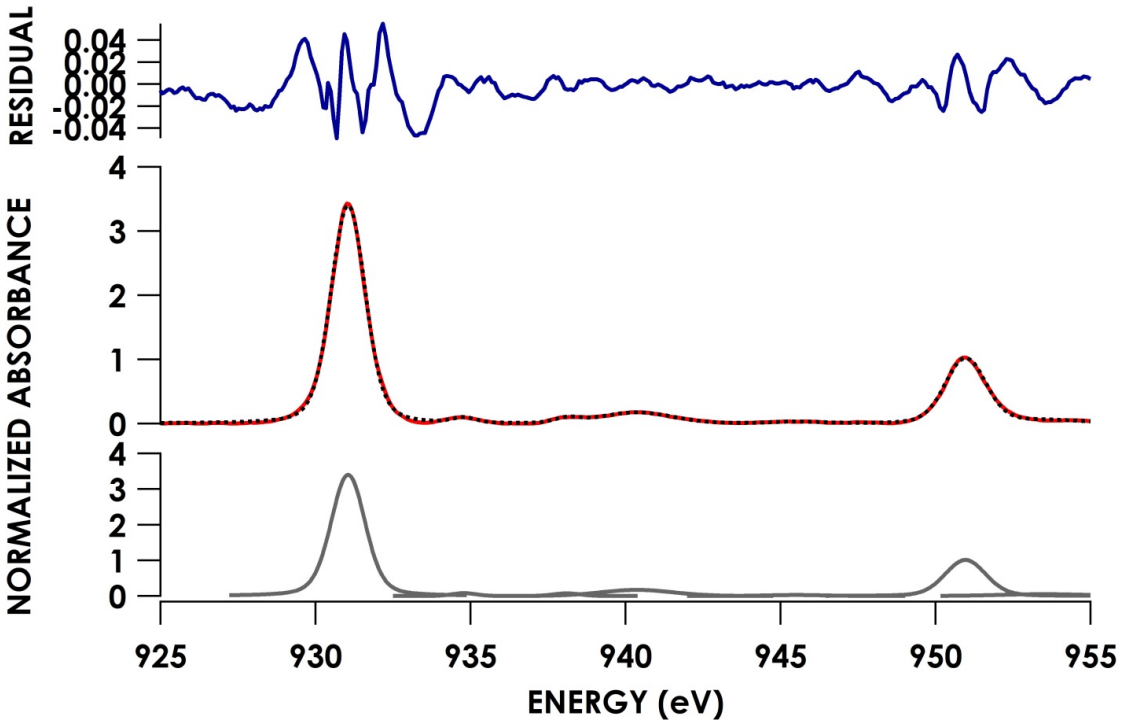

Fig. S4. Fit Cu $L_{2,3}$-edge XAS spectra of $[Cu(en)_2](OTf)_2$ showing experimental spectra in red, individual pseudo-Voigt peaks below in grey, composite fit spectra in a dotted black line overlaid on the experimental, and residual intensity above in blue.

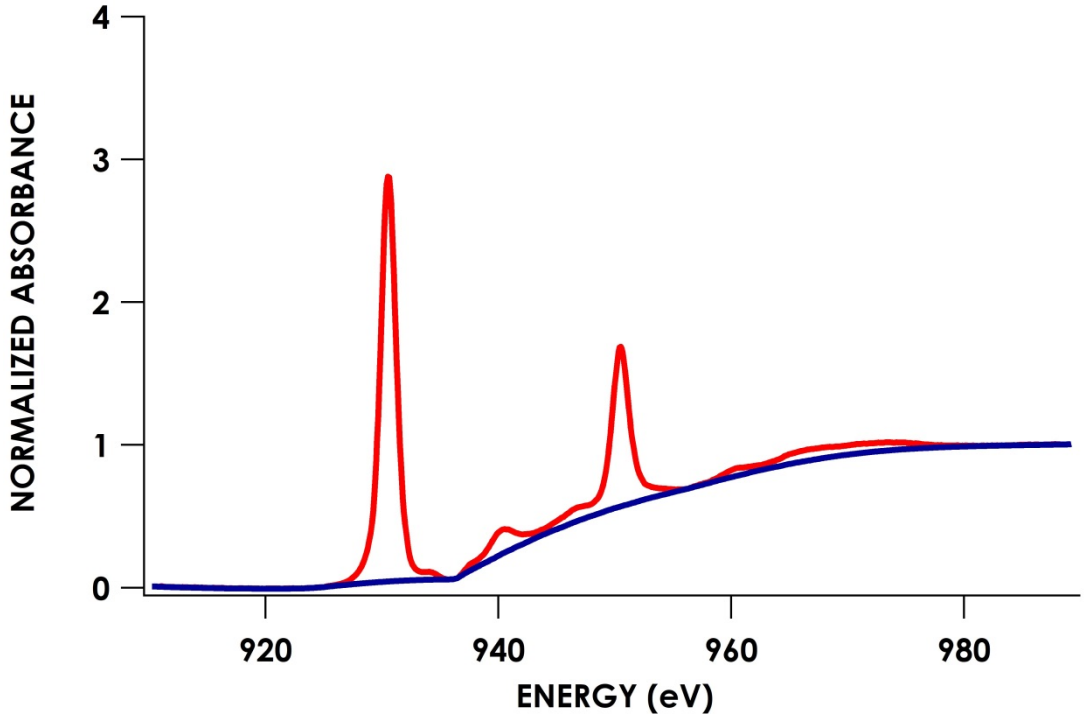

Fig S5. Cu $L_{2,3}$-edge XAS normalized spectra of $[Cu(NH_3)_4](SO_4)$ in red with SNIP background in blue.

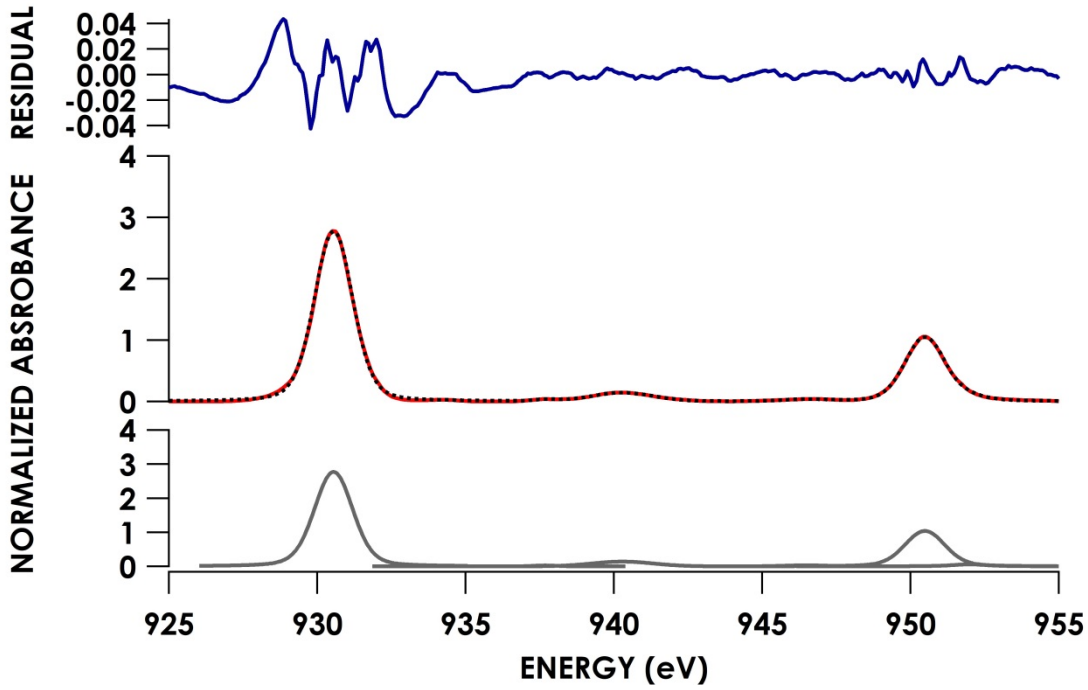

Fig. S6. Fit Cu $L_{2,3}$-edge XAS spectra of $[Cu(NH_3)_4](SO_4)$ showing experimental spectra in red, individual pseudo-Voigt peaks below in grey, composite fit spectra in a dotted black line overlaid on the experimental, and residual intensity above in blue.

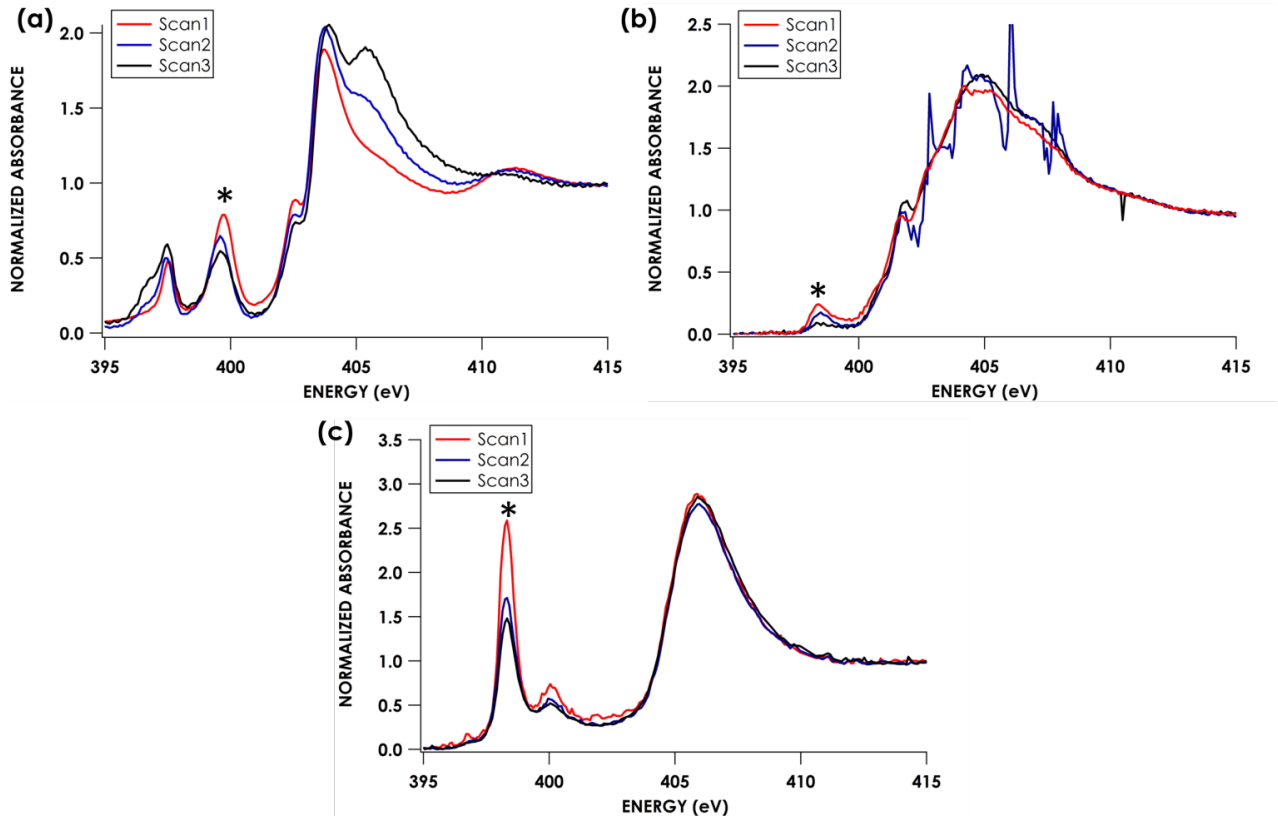

Fig. S7. N K-edge XAS photodamage scans at a single sample position for (a) $[Co(NH_3)_6]Cl_3$ (b) $[Ni(en)_3]Cl_2$ and (c) $(^nBu_4N)[RuNCl_4]$.

$[Co(NH_3)_6]^{3+}$

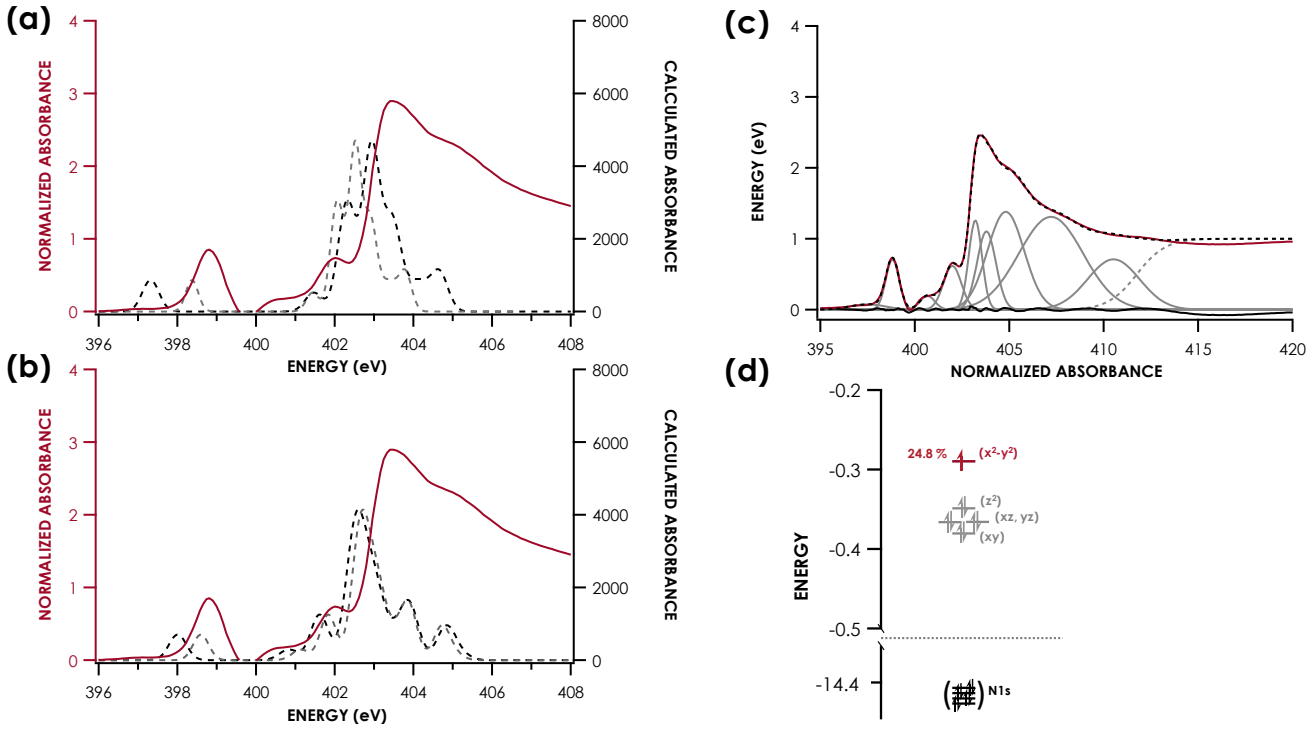

Fig. S8. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Co(NH_3)_5Cl]^{2+}$

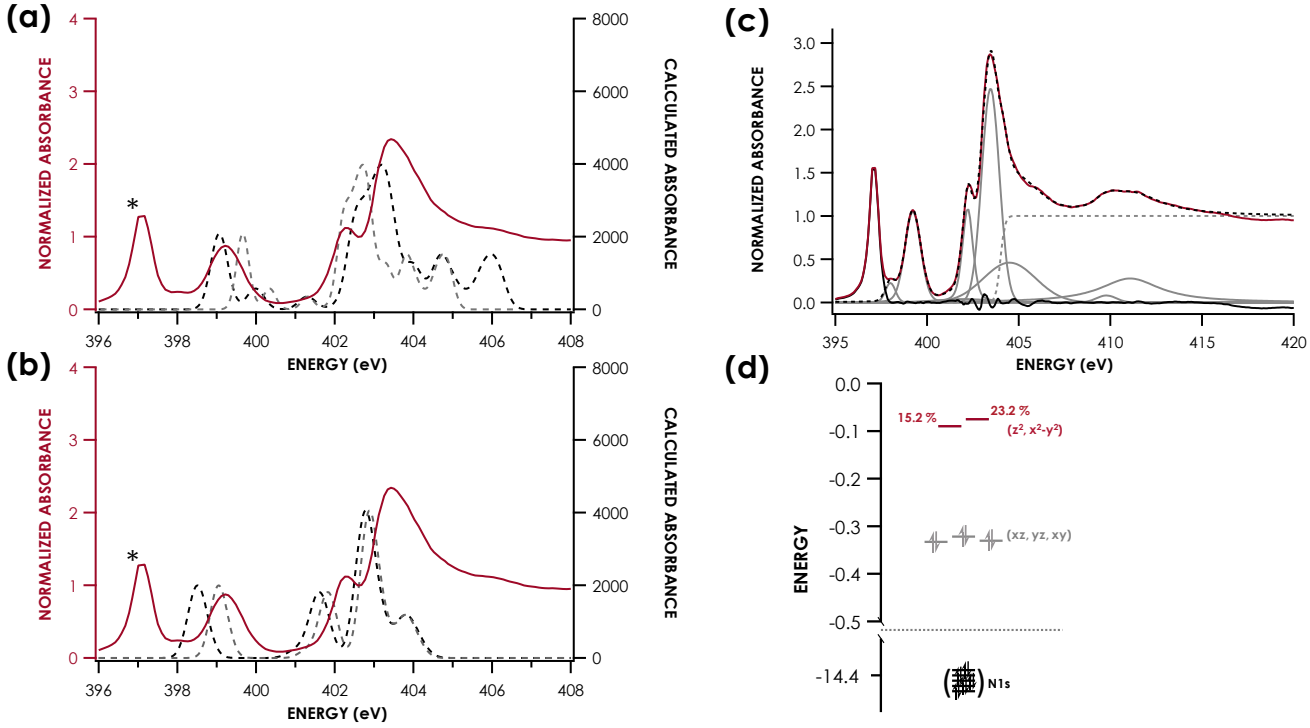

Fig. S9. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Ni(NH_3)_6]^{2+}$

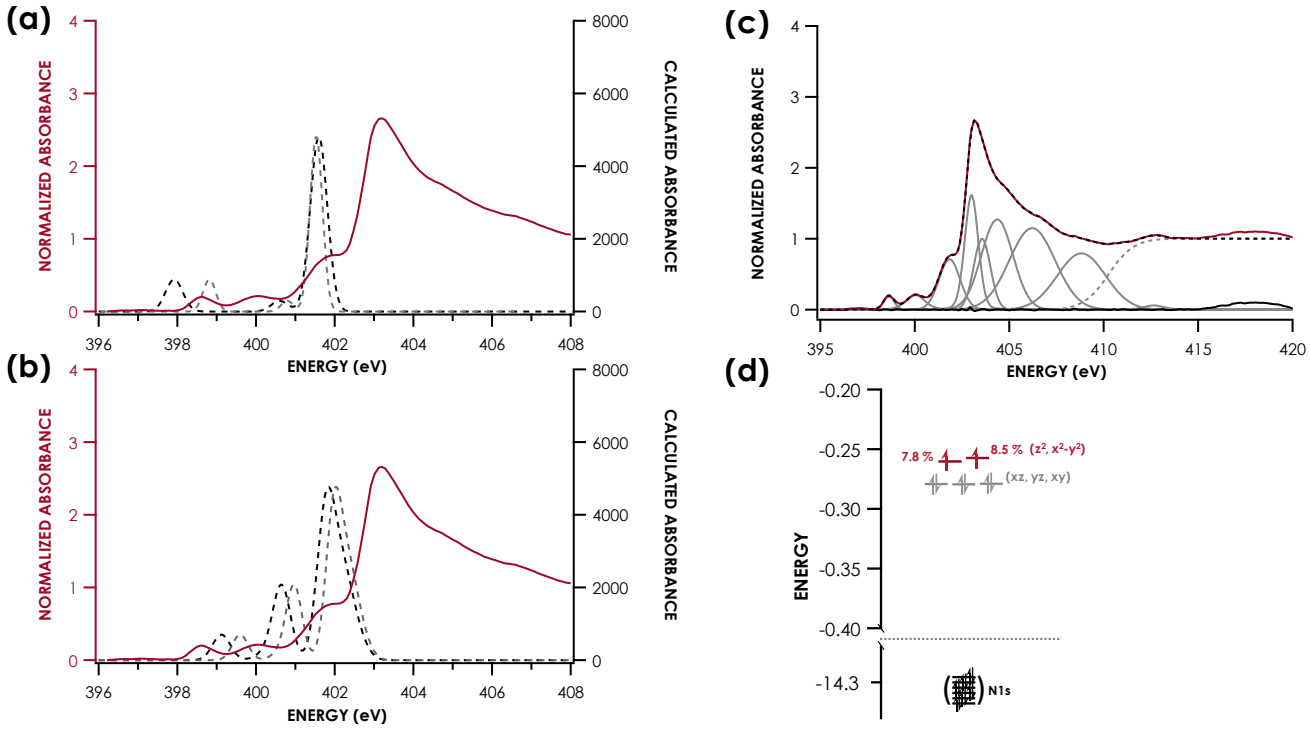

Fig. S10. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Cu(NH_3)_4]^{2+}$

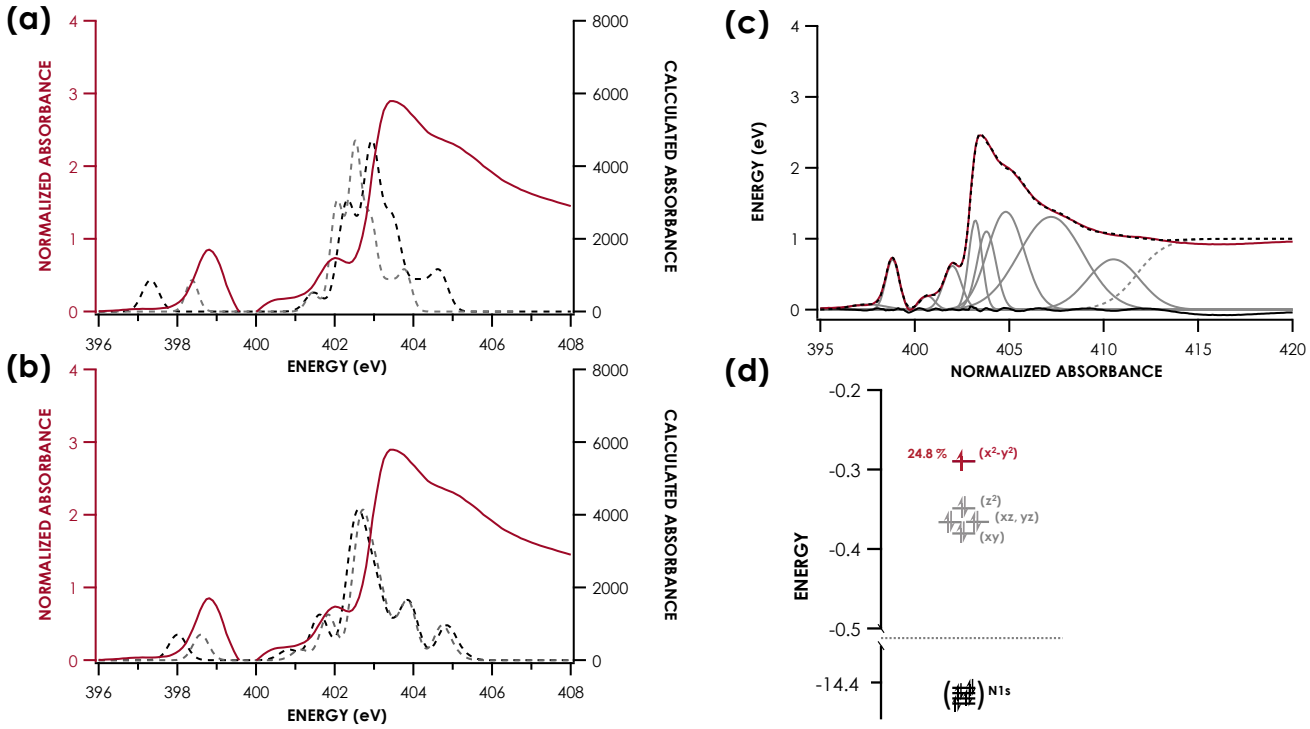

Fig. S11. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Ni(en)_3]^{2+}$

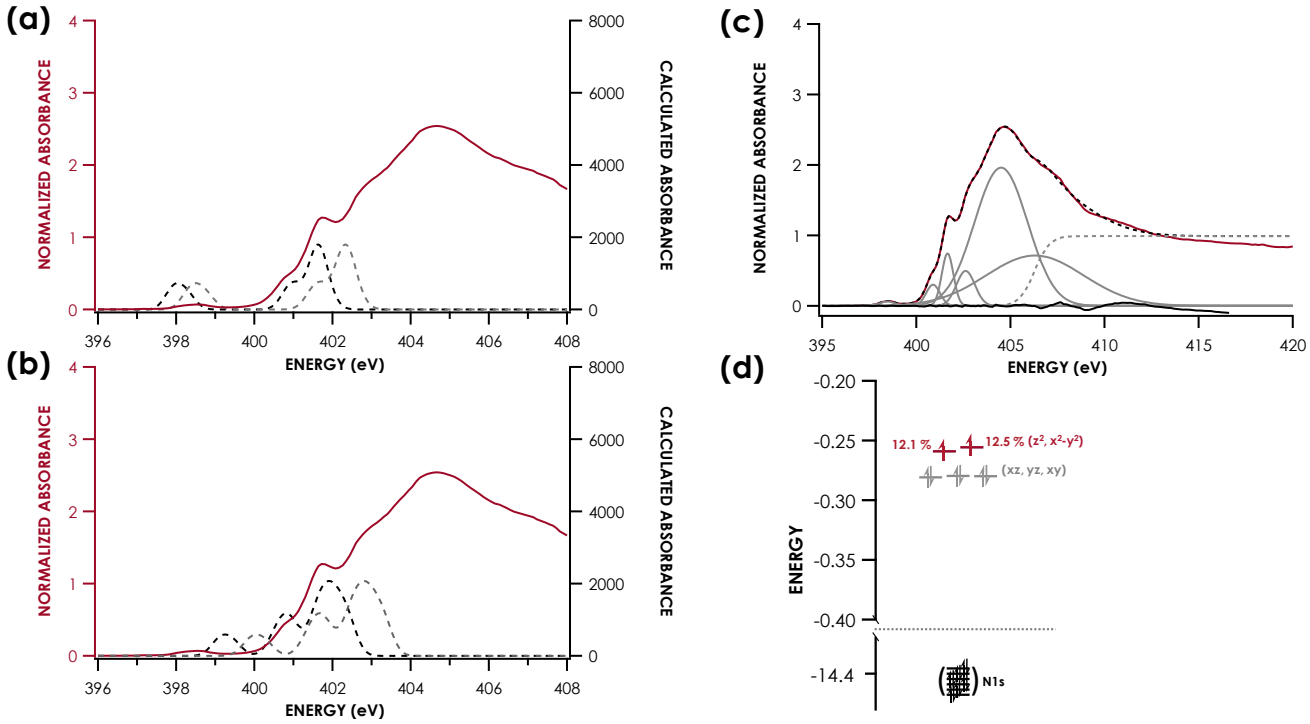

Fig. S12. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Cu(en)_2]^{2+}$

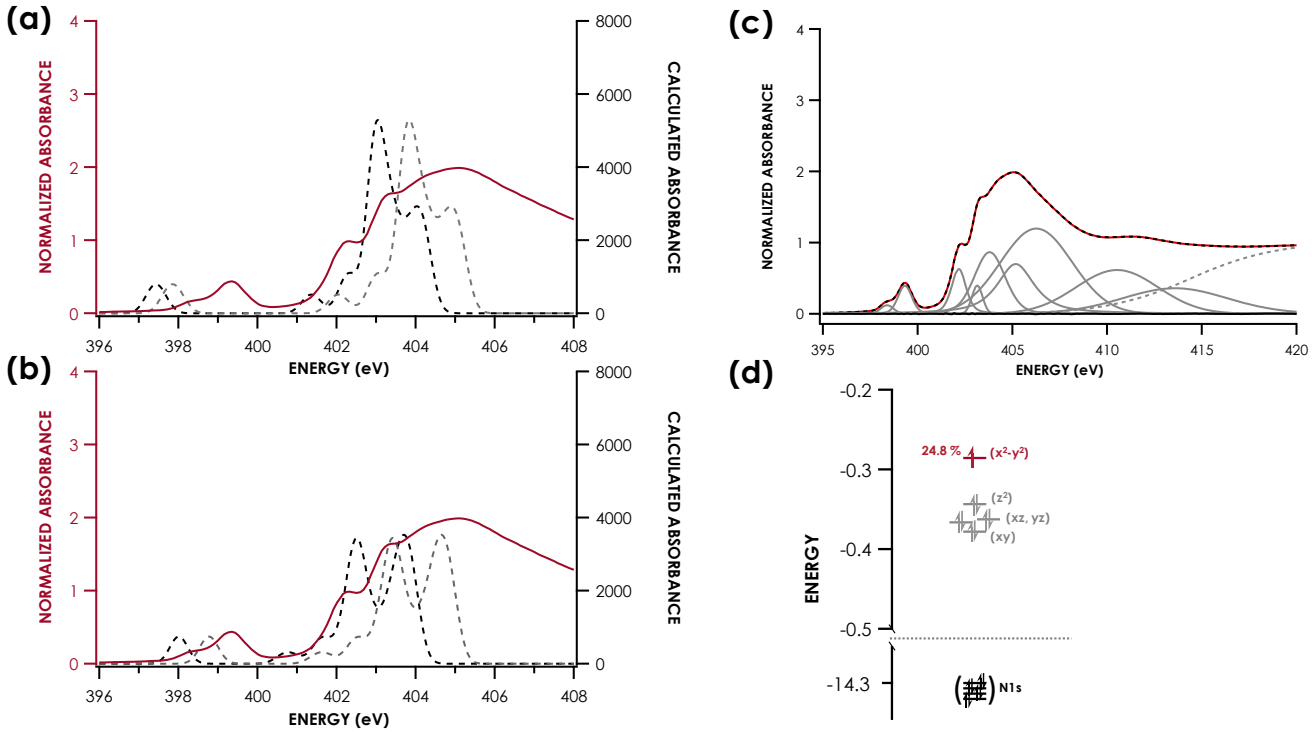

Fig. S13. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Zn(en)_3]^{2+}$

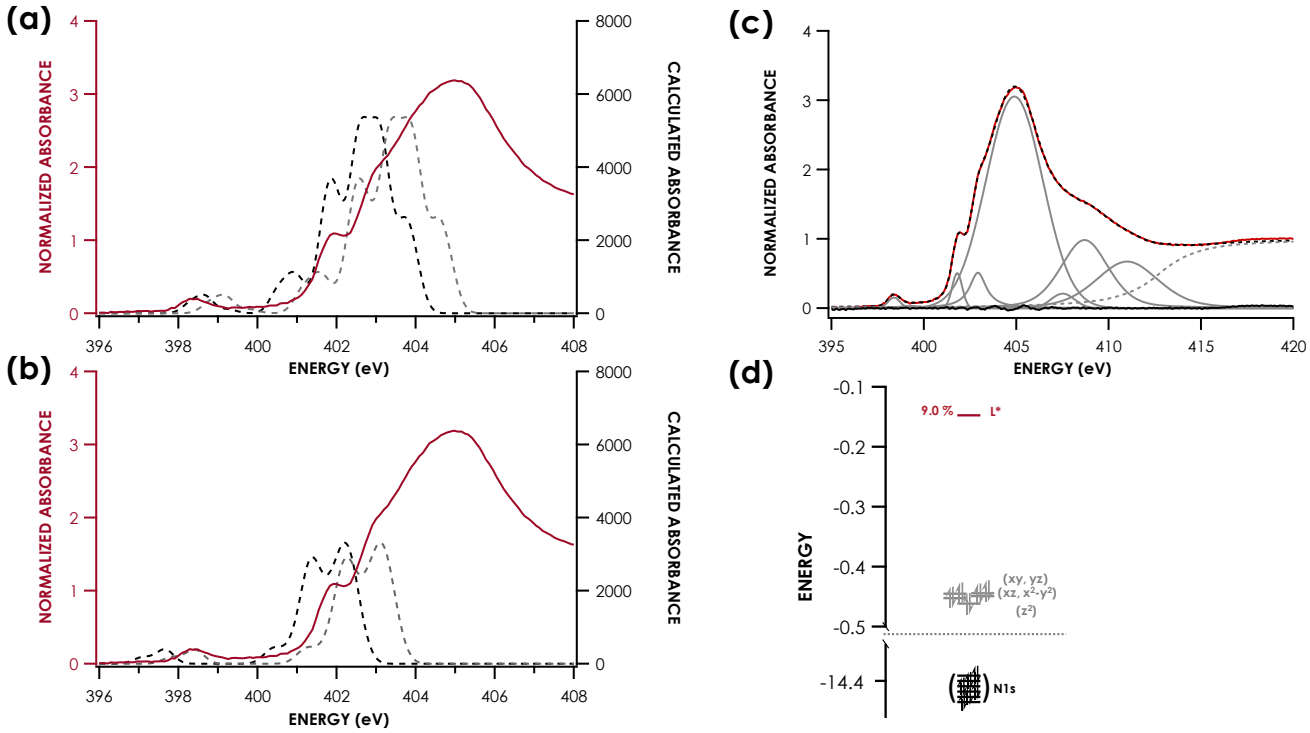

Fig. S14. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Mn(bpy)_3]^{2+}$

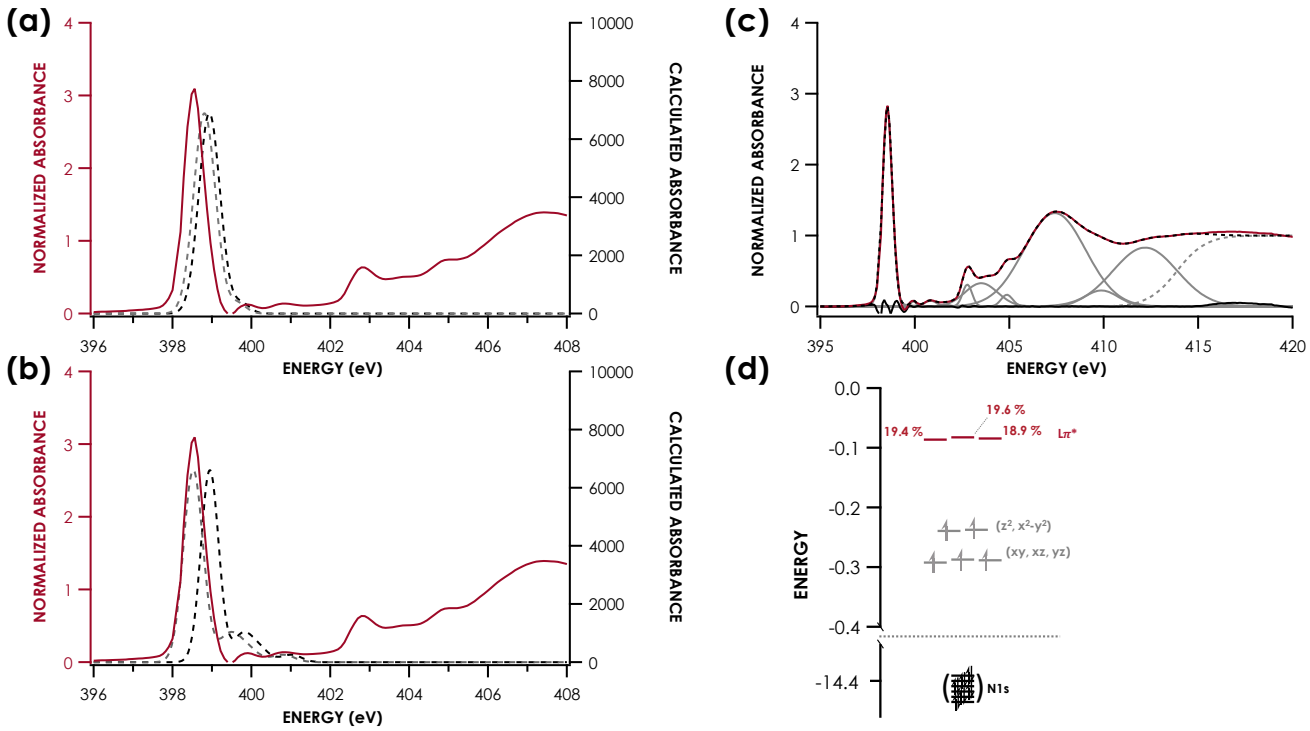

Fig. S15. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[Fe(bpy)$_3$]$^{2+}$

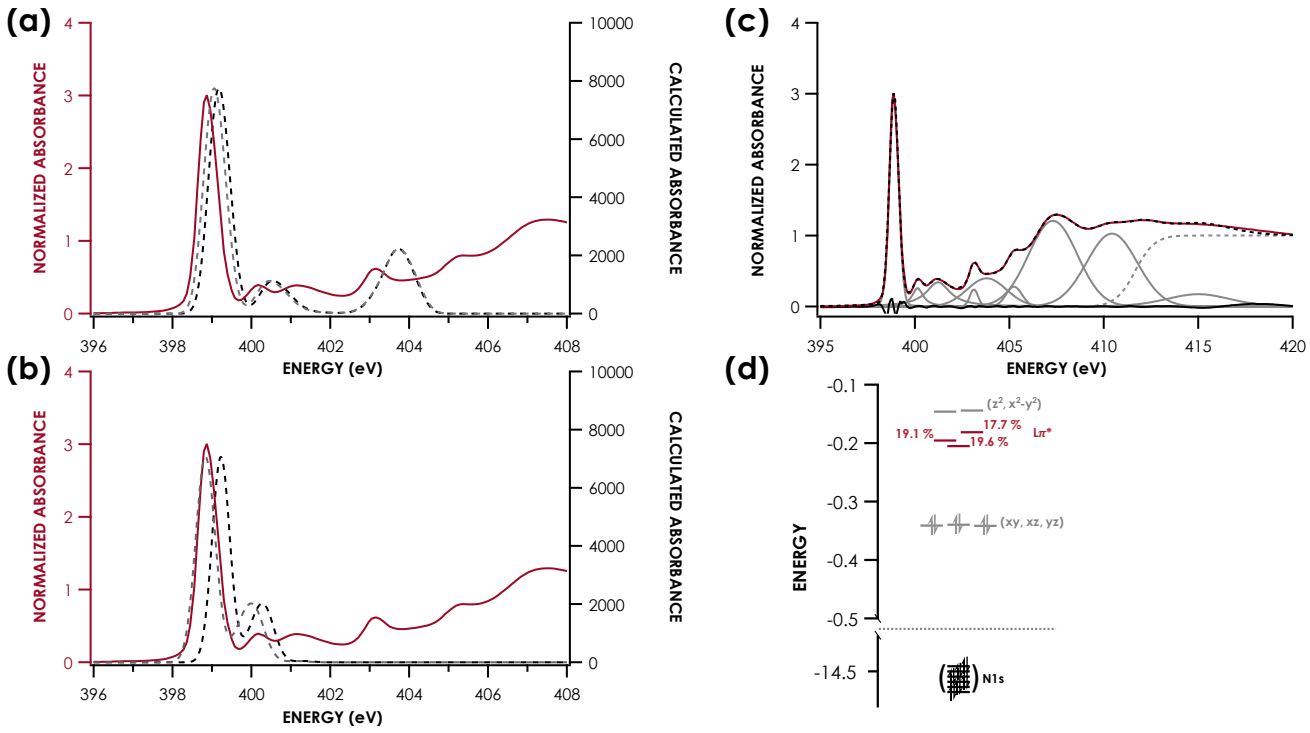

Fig. S16. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[Co(bpy)$_3$]$^{2+}$

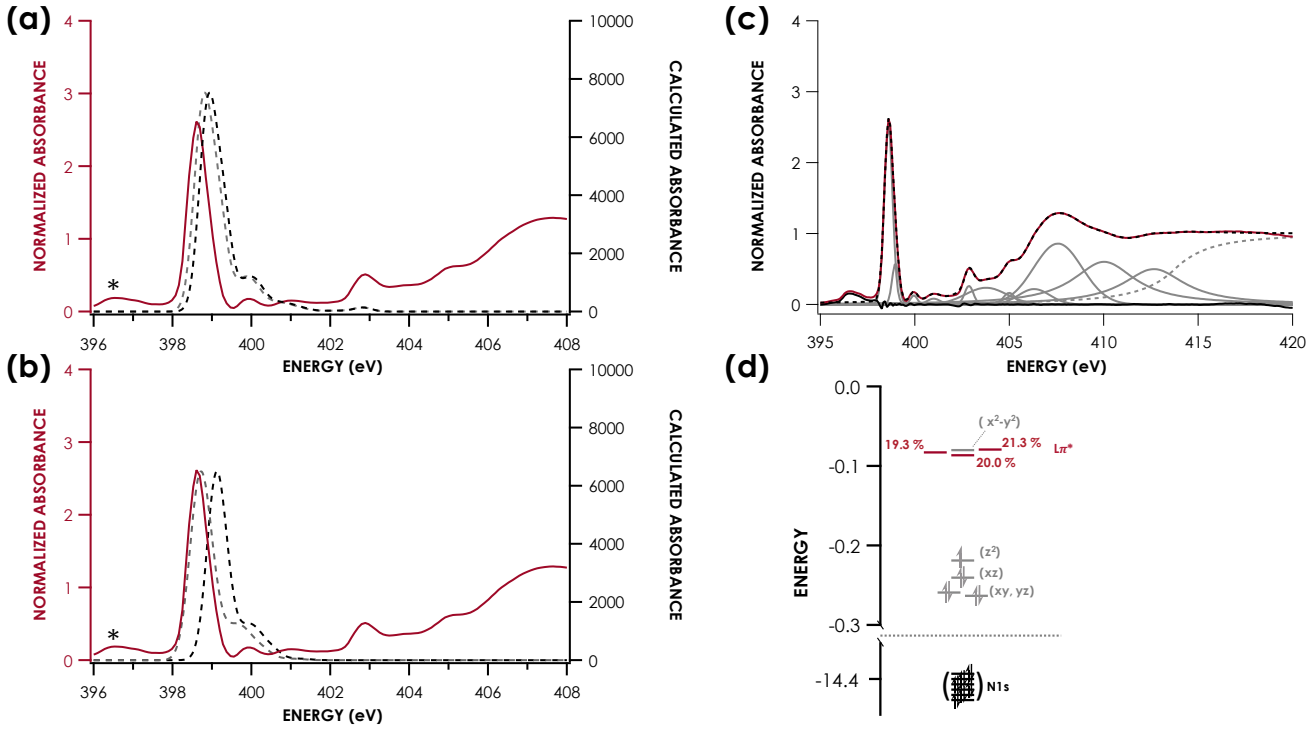

Fig. S17. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).* *denotes Co second order L_2 transition.*

[Co(bpy)$_3$]$^{3+}$

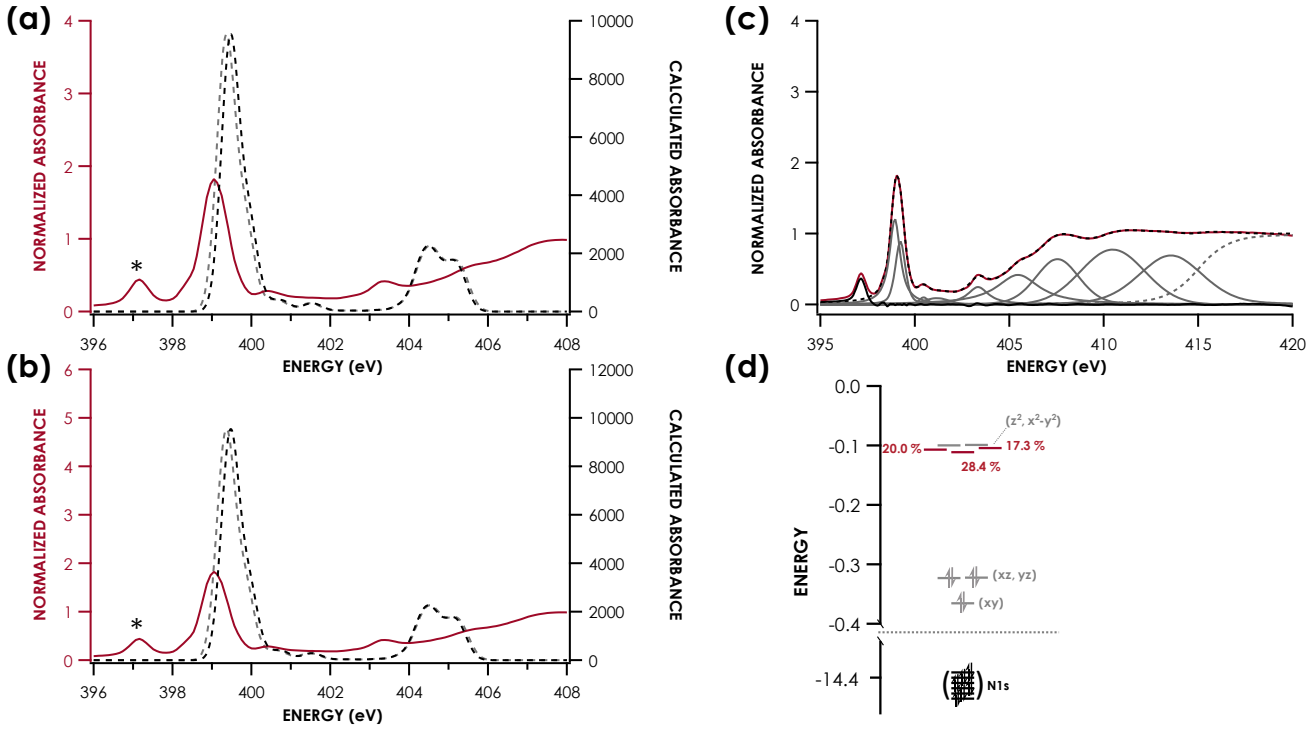

Fig. S18. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).* *denotes Co second order L_2 transition.*

$[Ni(bpy)_3]^{2+}$

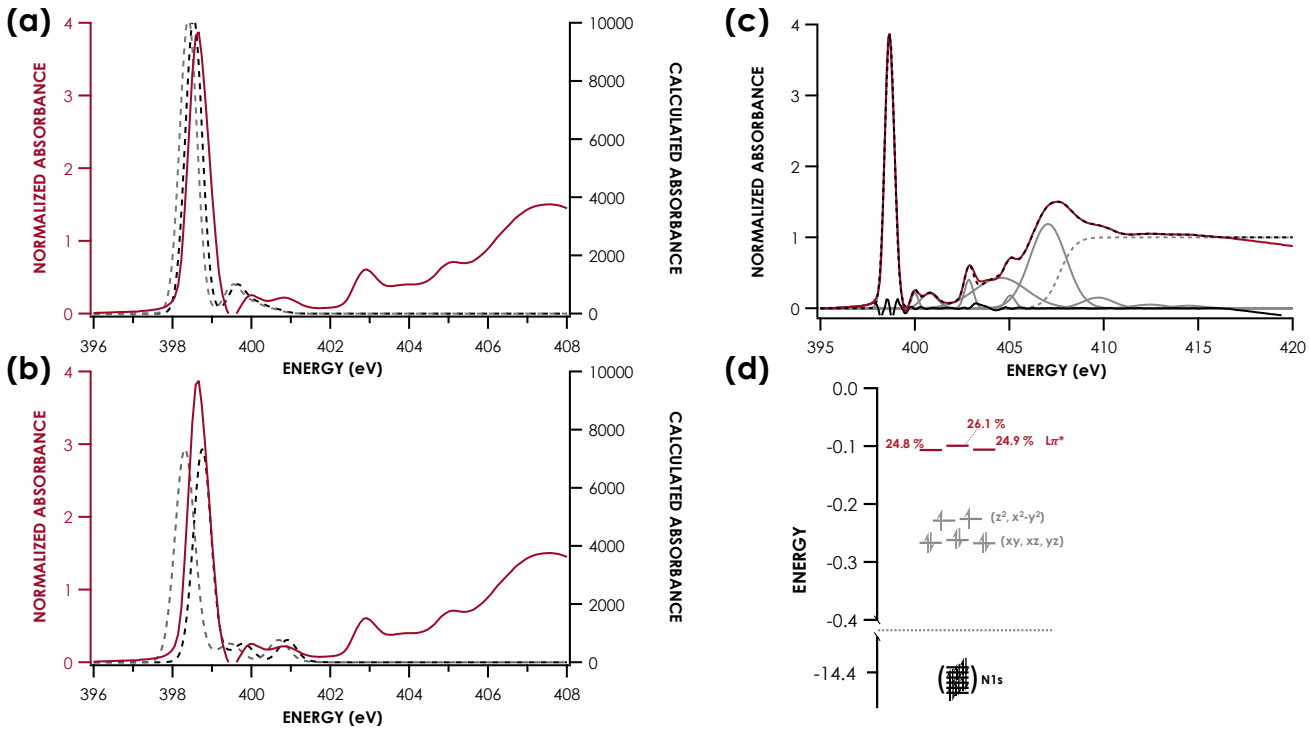

Fig. S19. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Zn(bpy)_3]^{2+}$

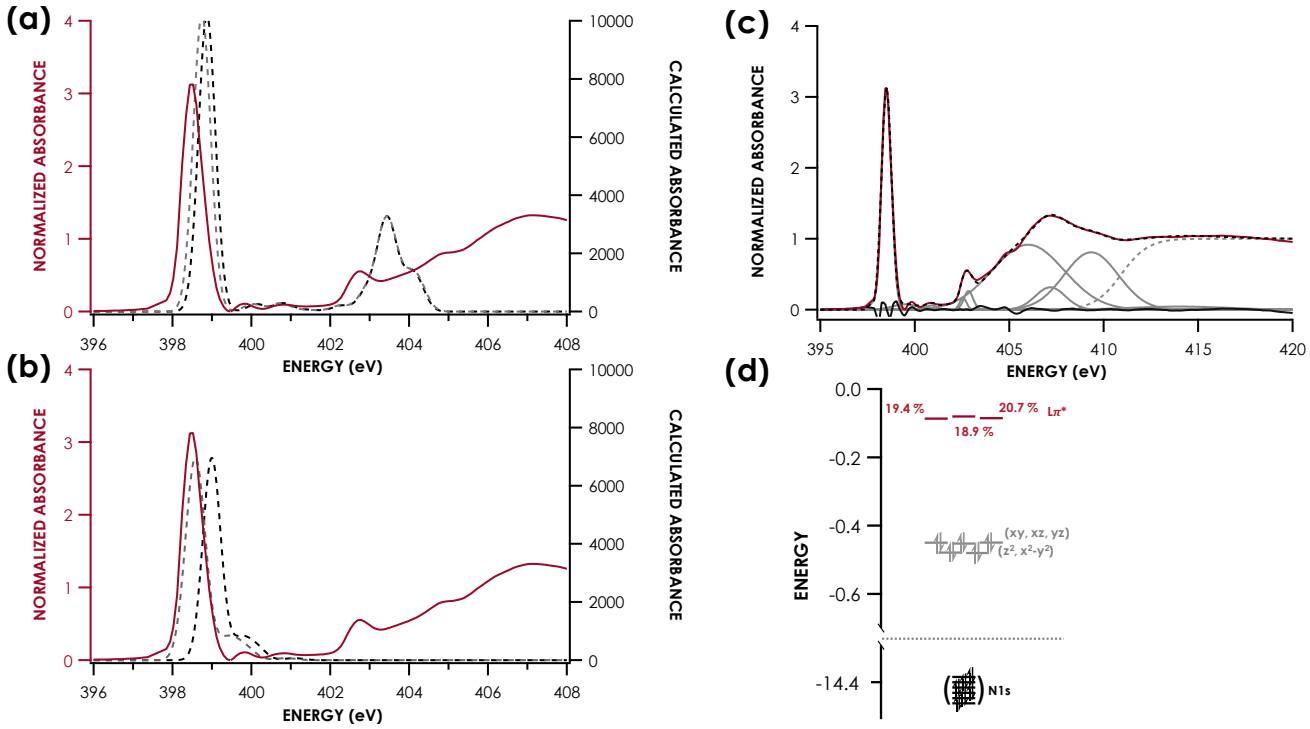

Fig. S20. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[Rh(bpy)$_3$]$^{3+}$

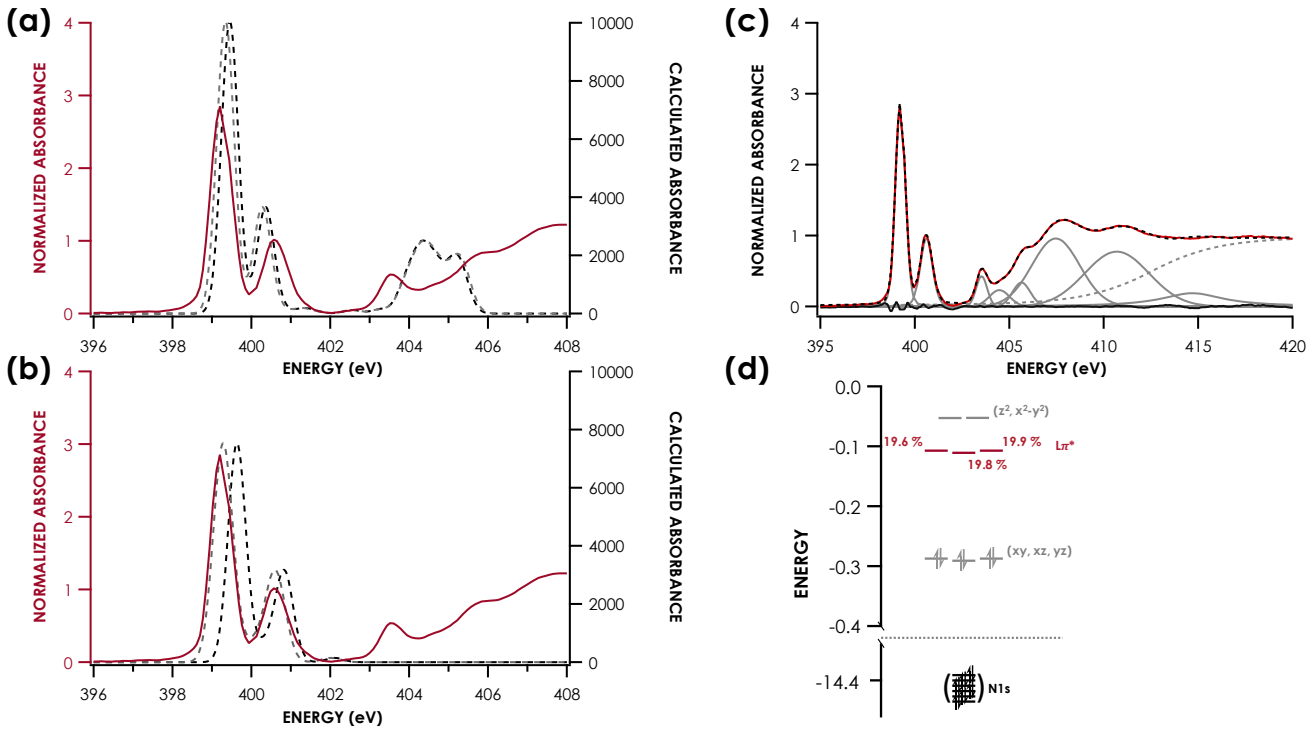

Fig. S21. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

$[Os(bpy)_3]^{2+}$

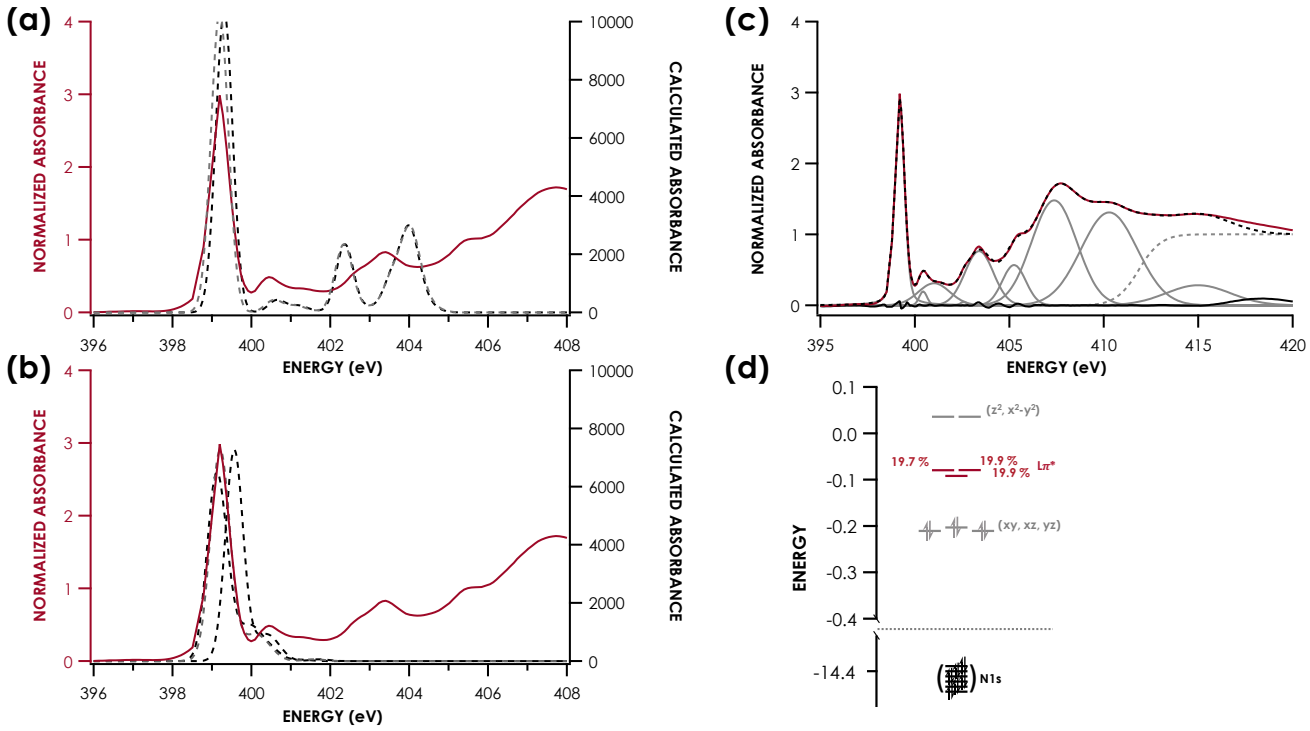

Fig. S22. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[RuNCl$_4$]$^-$

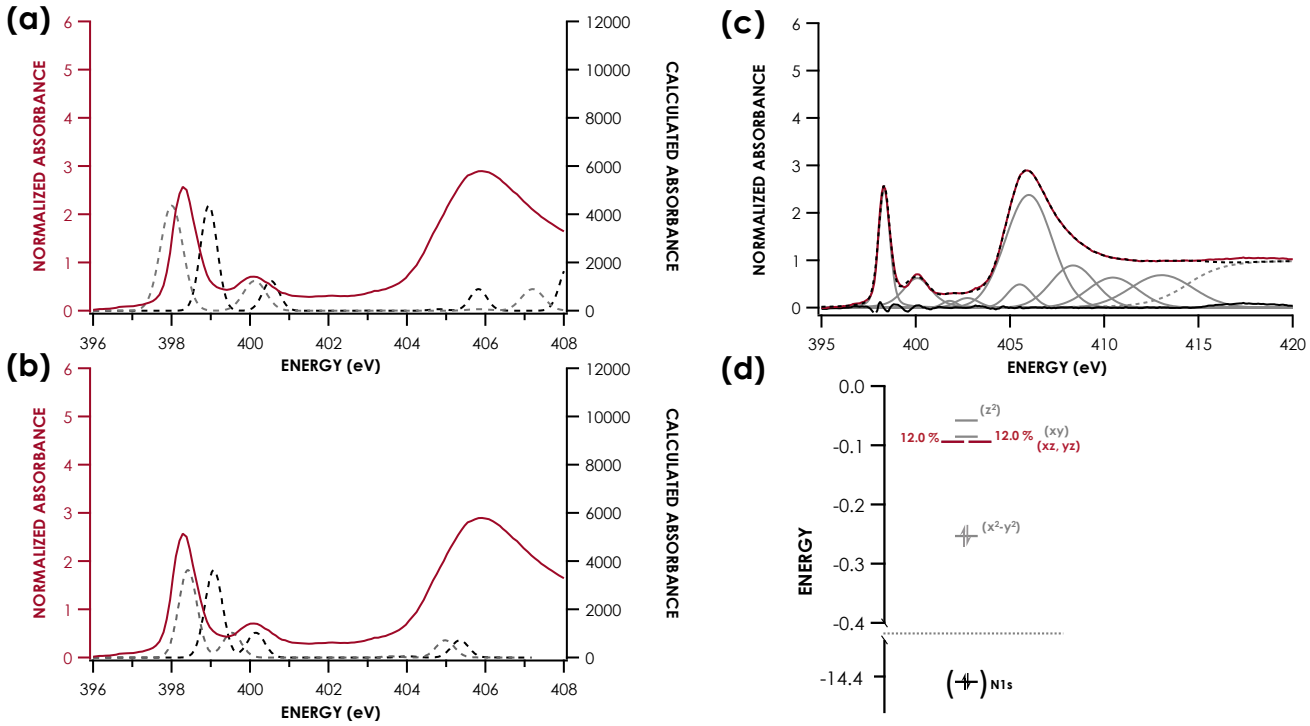

Fig. S23. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[ReNCl$_4$]$^-$

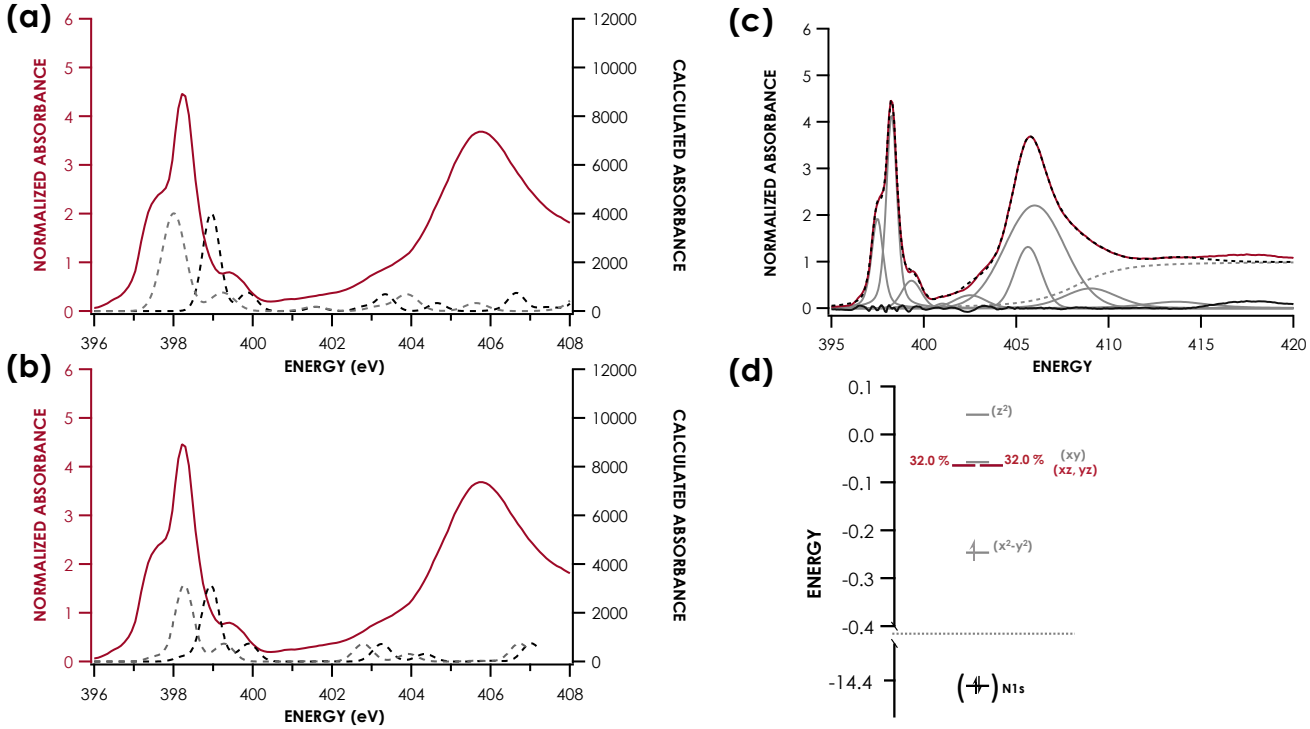

Fig. S24. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

[OsNCl$_4$]$^-$

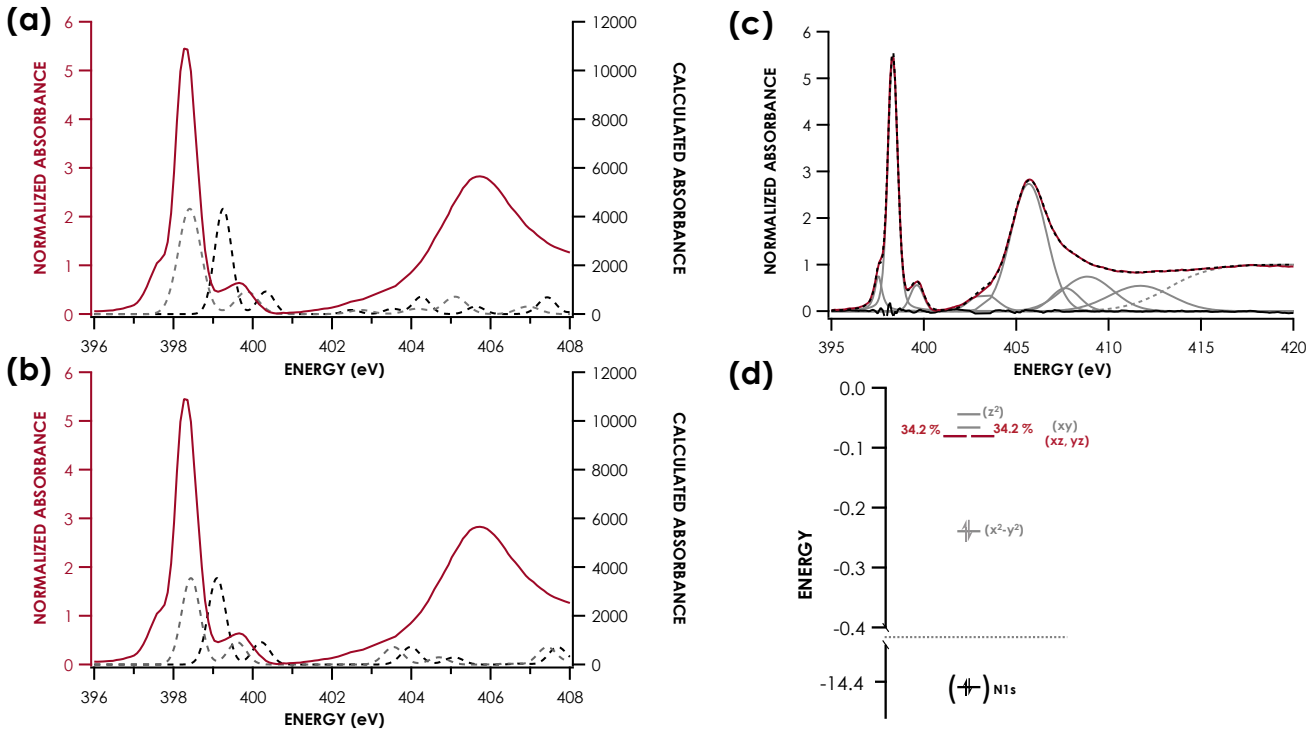

Fig. S25. Experimental overlay with DFT/ROCIS (a) and TDDFT (b) calculated spectra shifted according to global fit (black) and ligand class (grey). Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black) (c). Molecular orbital diagram showing N-donor orbitals in black, acceptor orbitals in red denoting nitrogen p character, and unparticipating d orbitals in grey (d).

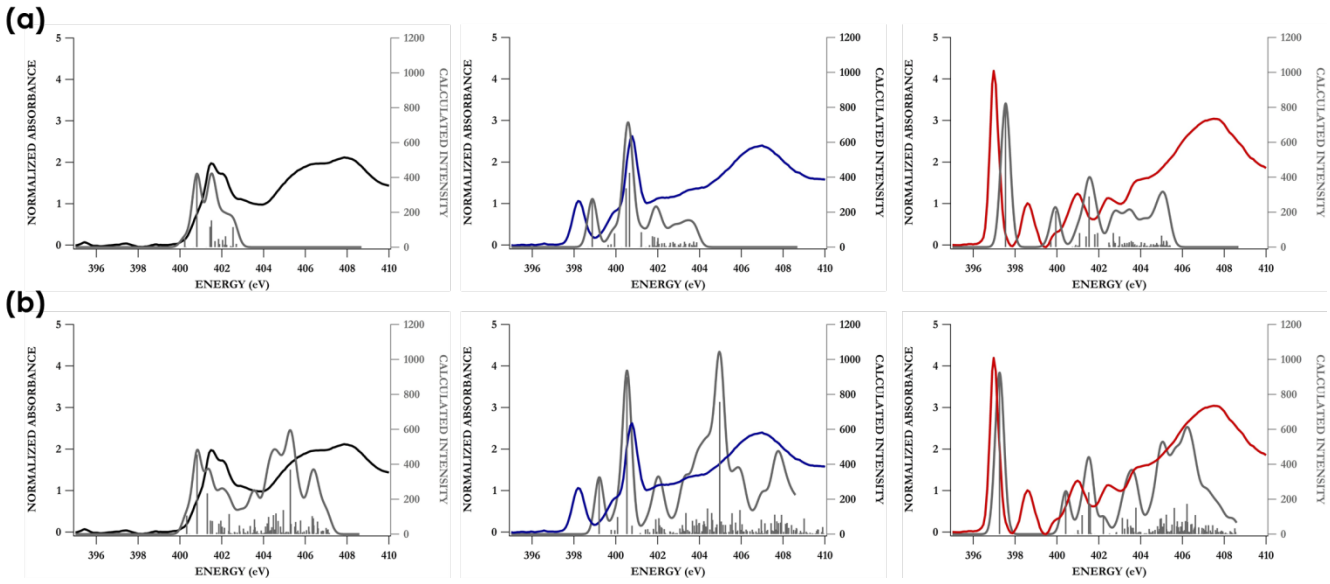

Fig. S26. Overlay of experimental and TDDFT (a) and DFT/ROCIS (b) calculated N K-edge XAS spectra for PNPH (black), (PNP)NiCl (blue), and [(PNP)NiCl](OTf) (red) with energies shifted according to global correlation plot seen in Fig 3a and 3c.

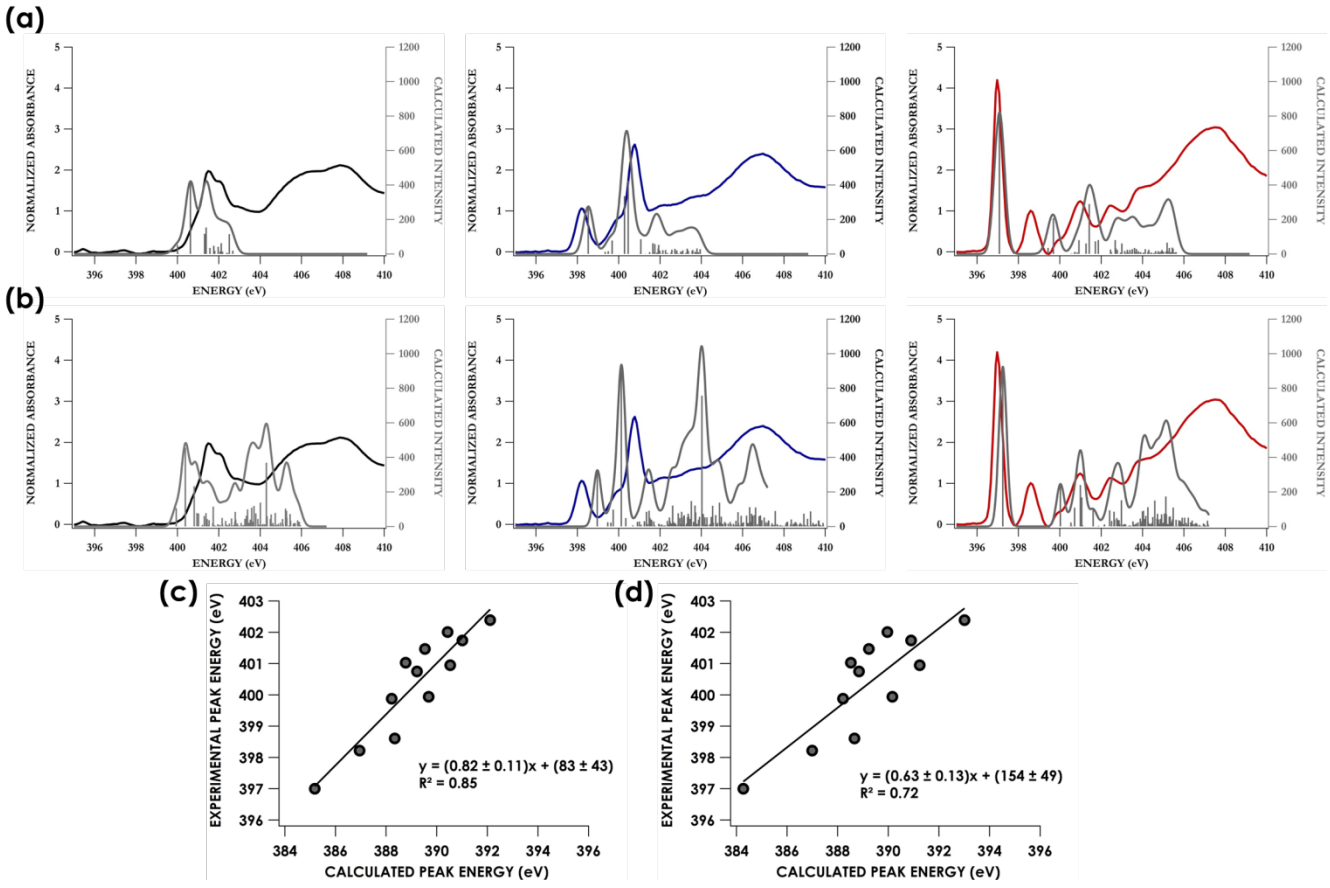

Fig. S27. Overlay of experimental and TDDFT (a) and DFT/ROCIS (b) calculated N K-edge XAS spectra for PNPH (black), (PNP)NiCl (blue), and [(PNP)NiCl](OTf) (red) with energies shifted according to PNP ligand-class correlation plot seen in (c) and (d).

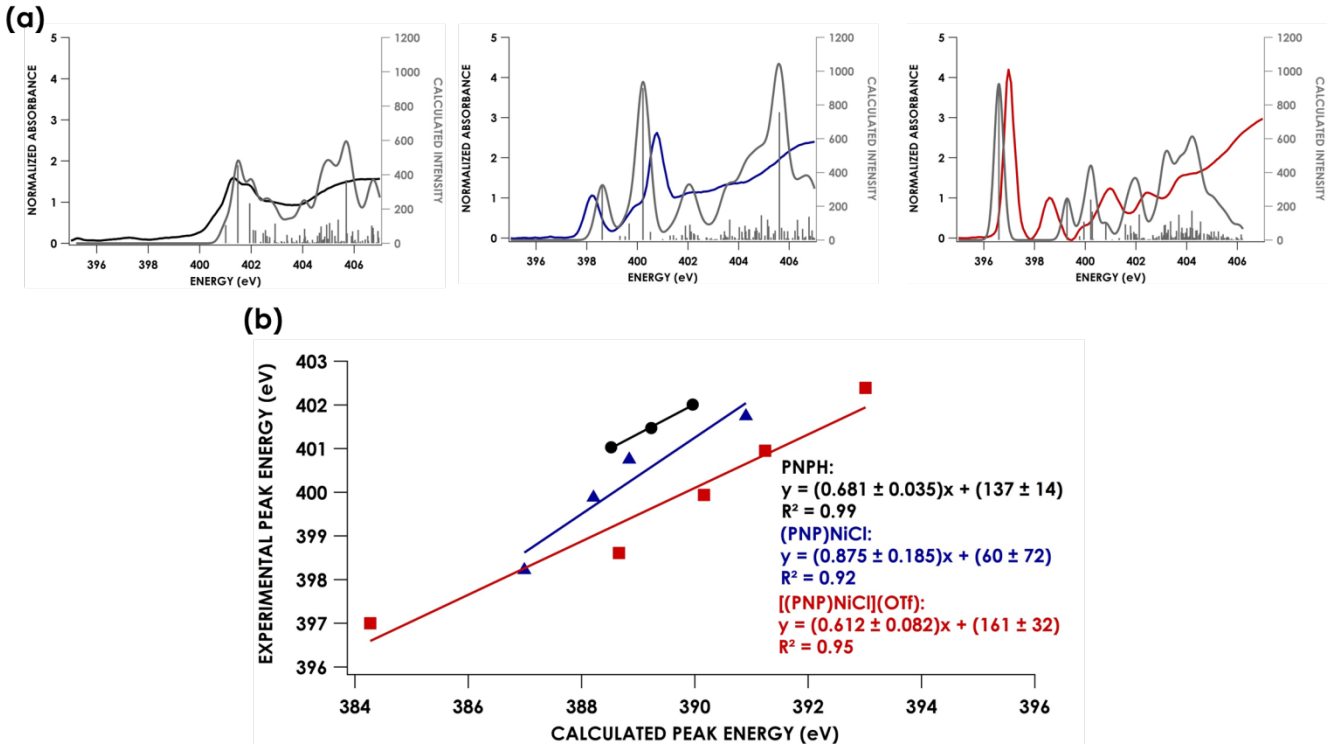

Fig. S28. Overlay of experimental and DFT/ROCIS (a) calculated N K-edge XAS spectra for PNPH (black), (PNP)NiCl (blue), and [(PNP)NiCl](OTf) (red) with energies shifted according to individual correlation plots seen in (b).

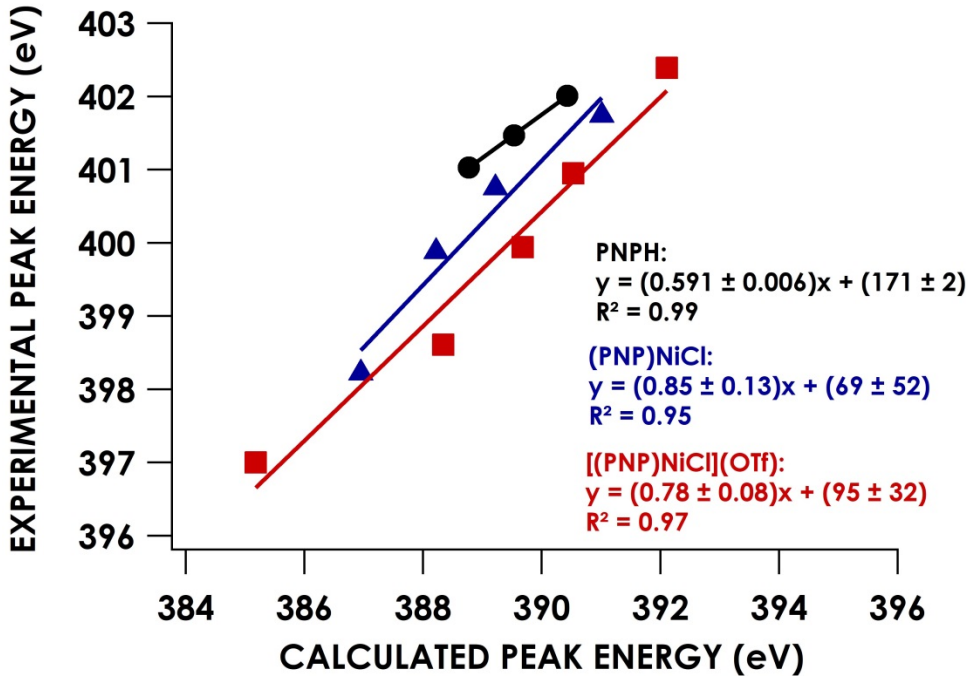

Fig. S29. Correlation of experimental N K-edge XAS pre-edge peak energies with TDDFT calculated energies for PNPH (red), (PNP)NiCl (green), and [(PNP)NiCl](OTf) (blue).

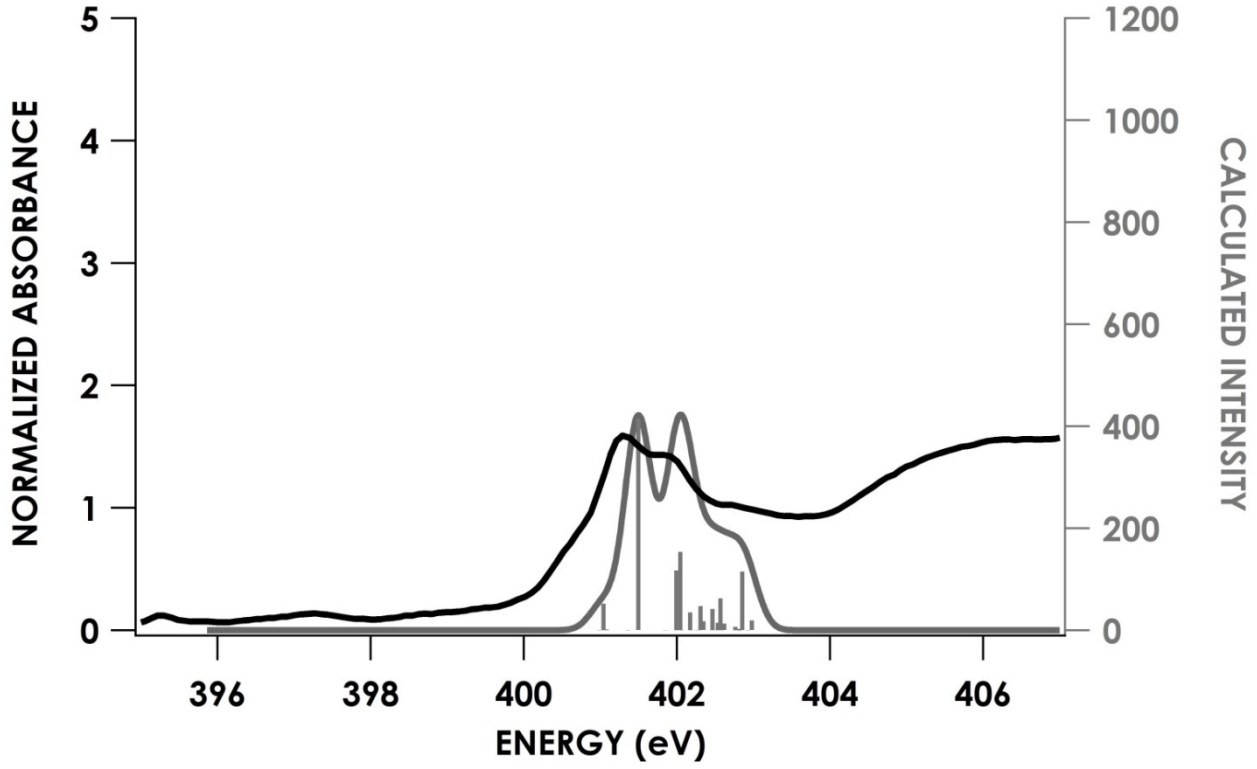

Fig. S30. Overlay of PNPH experimental and TD-DFT calculated (grey) N K-edge XAS spectra with energies shifted according to individualized correlation plot seen above in Fig S26.

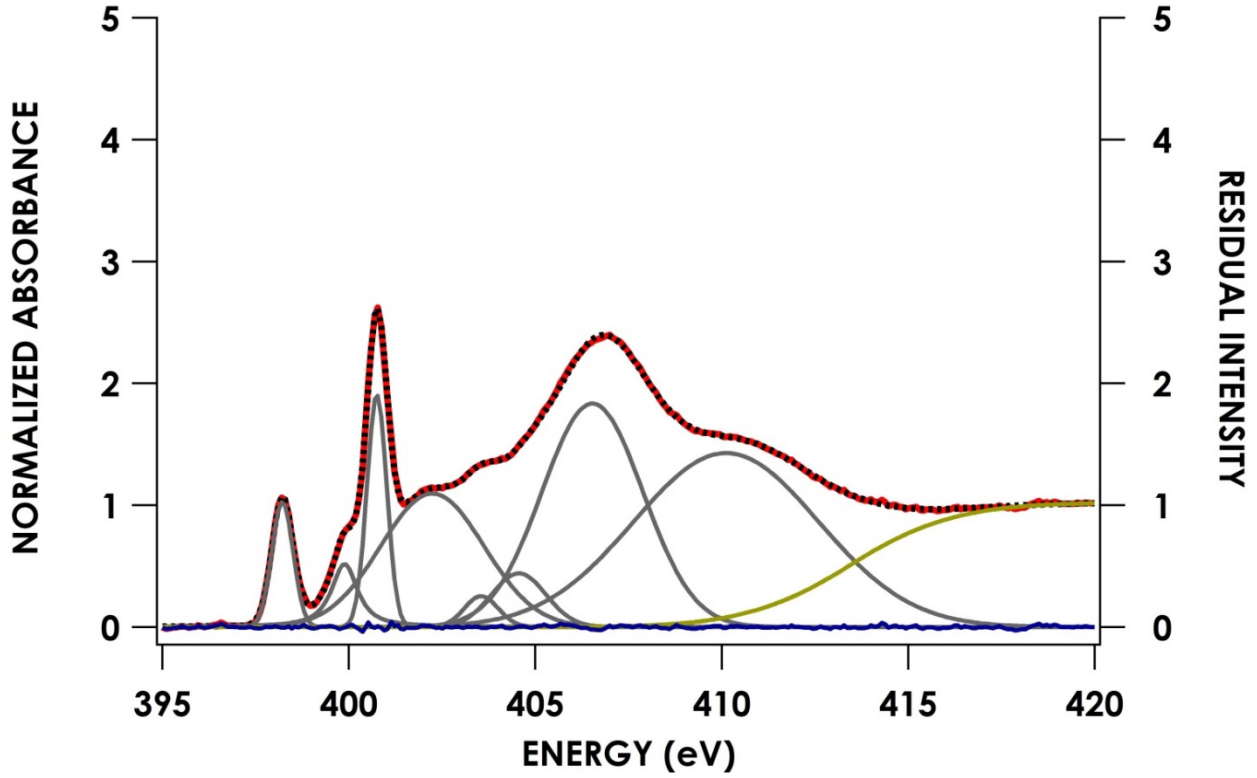

Fig. S31. Fit N K-edge XAS spectra of (PNP)NiCl showing experimental spectra in red, individual pseudo-Voigt peaks below in grey, the edge step-jump function in yellow, composite fit spectra in a dotted black line overlaid on the experimental, and residual intensity below in blue.

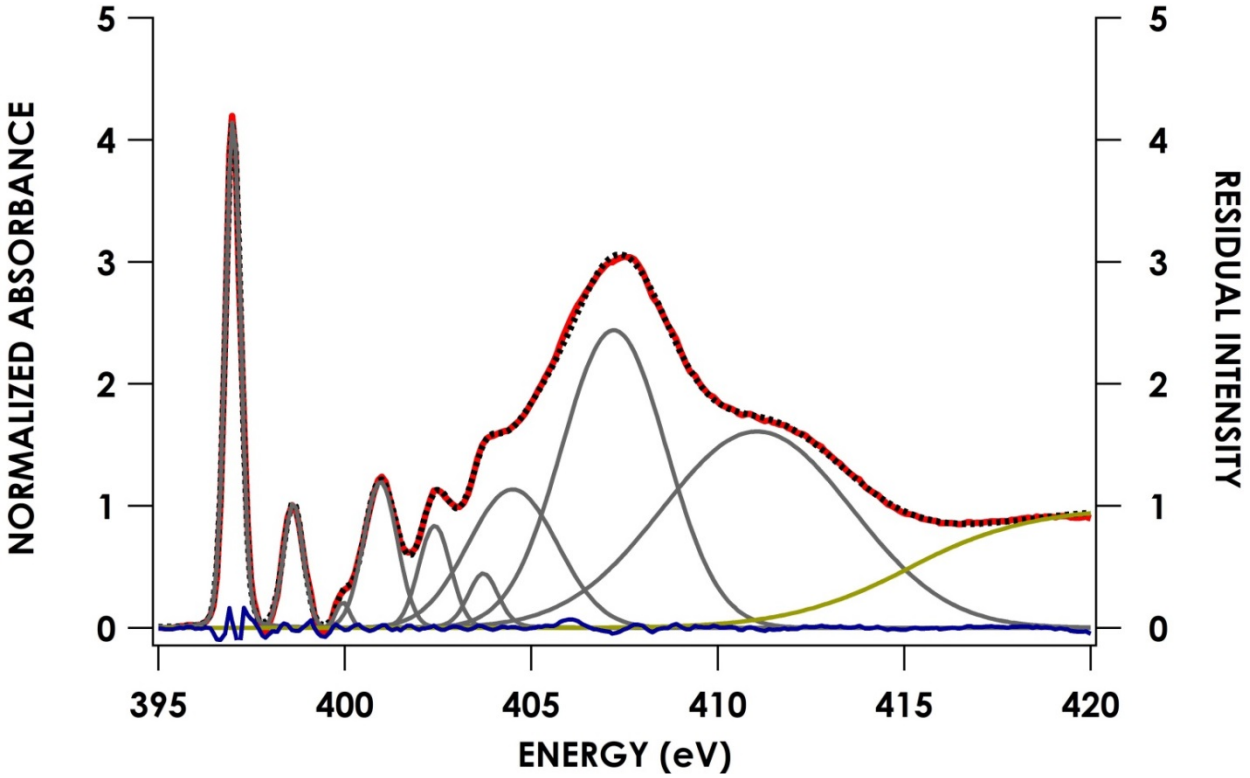

Fig. S32. Fit N K-edge XAS spectra of [(PNP)NiCl](OTf) showing experimental spectra in red, individual pseudo-Voigt peaks below in grey, the edge step-jump function in yellow, composite fit spectra in a dotted black line overlaid on the experimental, and residual intensity below in blue.

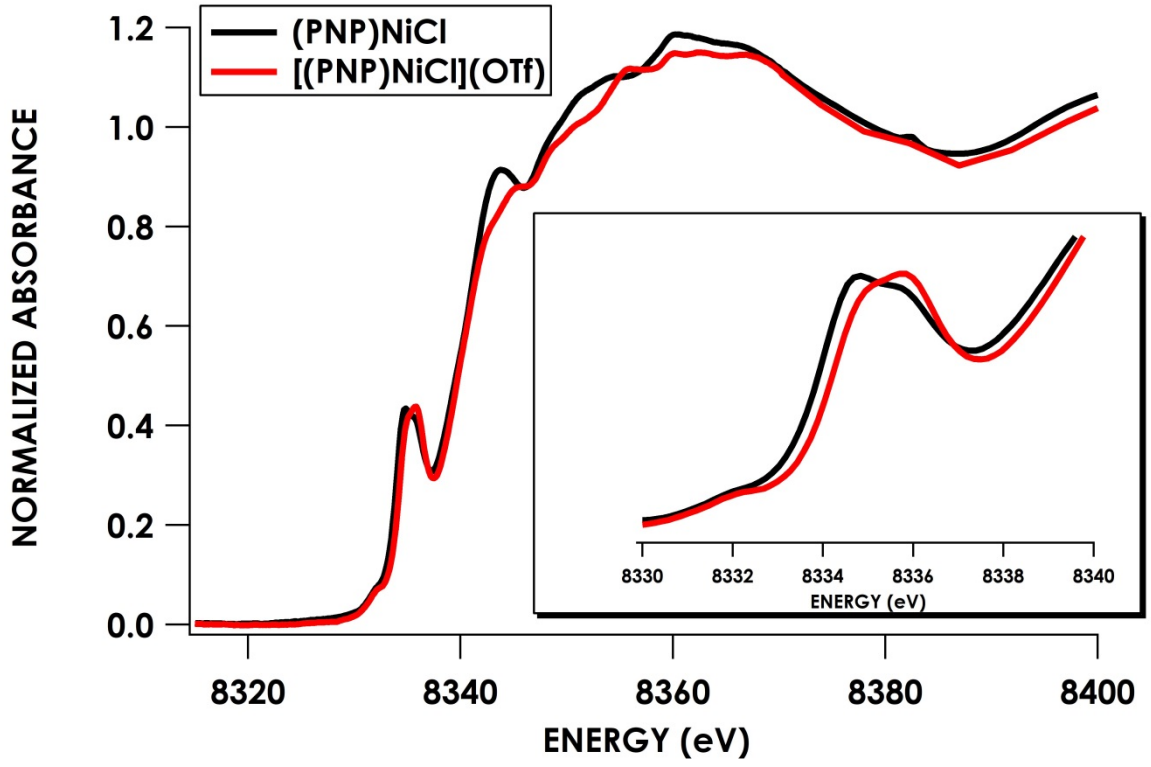

Fig. S33. Ni K-edge XAS spectra of (PNP)NiCl and [(PNP)NiCl](OTf) with the inset pre-edge region showing transitions into the Ni 3*d* LUMO and Ni 4*p*.

Radial Overlap Analysis

Radial wavefunctions for 1*s*, 2*p*, and 3*p* H-like orbitals ($R_{1,0}(r)$, $R_{2,1}(r)$, and $R_{3,1}(r)$):

$$\boldsymbol{R_{1,0}(r) = R_{1s} = 2 * \left(\frac{Z_1}{a_0}\right)^{\frac{3}{2}} * e^{-Z_1 * \frac{r}{a_0}}}$$

$$\boldsymbol{R_{2,1}(r) = R_{2p} = \frac{1}{\sqrt{24}} * \left(\frac{Z_2}{a_0}\right)^{\frac{3}{2}} * \left(Z_2 * \frac{r}{a_0}\right) * e^{-.5 * Z_2 * \frac{r}{a_0}}}$$

$$\boldsymbol{R_{3,1}(r) = R_{3p} = \left(\frac{1}{81}\right) * \sqrt{\frac{8}{3}} * \left(\frac{Z_3}{a_0}\right)^{\frac{3}{2}} * \left(\left(6 * Z_3 * \frac{r}{a_0}\right) - \left(Z_3 * \frac{r}{a_0}\right)^2\right) * e^{-\frac{1}{3} * Z_3 * r / a_0}}$$

With Z_1, Z_2, and Z_3 being the effective nuclear charge felt by the N1*s*/S1*s*, N2*p*, and S3*p* electrons, respectively. Evaluating the dipole matrix element for the N1*s*/2*p* and S1*s*/3*p* radial overlap,

$$\boldsymbol{< R_{2p}|r|R_{1s} > = \int_0^\infty r^2 * (R_{2,1}) * r * (R_{1,0})\, dr = 9.79796 * a_0 * Z_2 * \frac{(Z_1 * Z_2)^{\frac{3}{2}}}{(Z_1 + 0.5 * Z_2)^5}}$$

$$\boldsymbol{< R_{3p}|r|R_{1s} > = \int_0^\infty r^2 * (R_{3,1}) * r * (R_{1,0})\, dr = 864 * \sqrt{6} * Z_3 * (2 * Z_1 - Z_3) * \frac{(Z_1 * Z_3)^{\frac{3}{2}}}{(3 * Z_1 + Z_3)^6}}$$

Plotting as functions of Z_2 and Z_3 from 0 to 200, with a_0 = 0.532 Å and Z_1 = 6.7 for N1*s* and 15.7 for S1s as the Z_{eff} determined by Slater's rules:

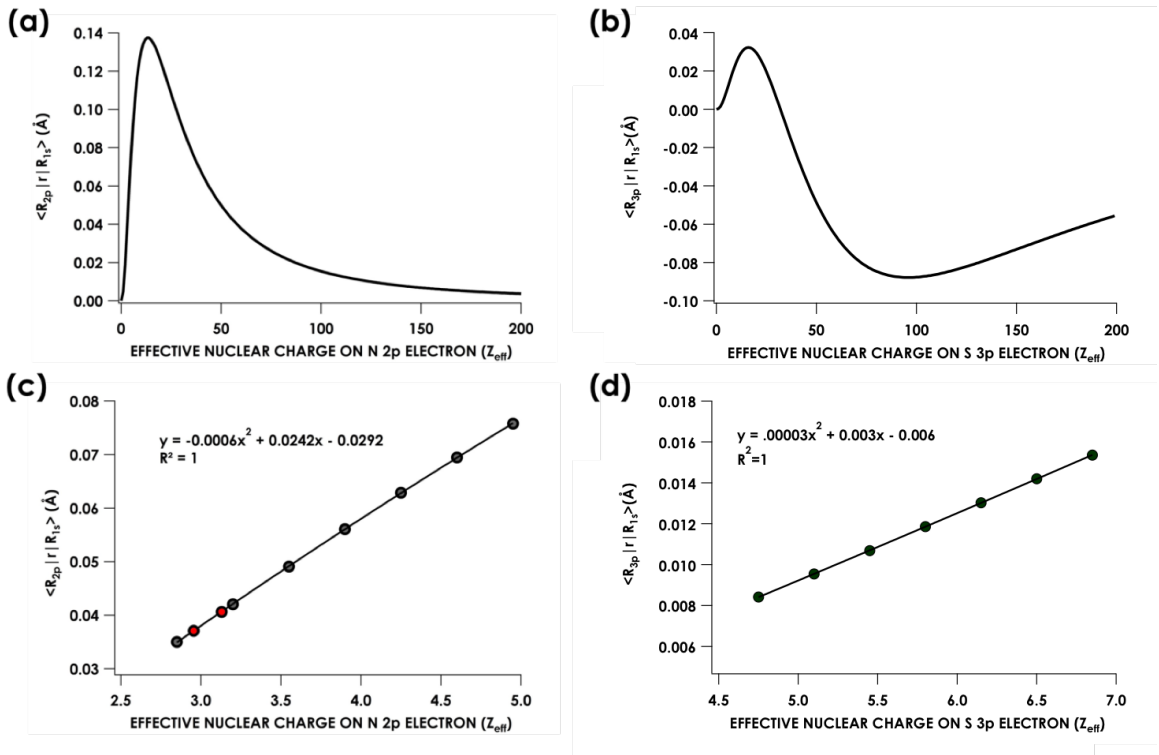

Fig. S34. Radial overlap integrals for N1*s*/2*p* (a) compared to S1*s*/3*p* (b) plotted as a function of Z_{eff}. Zoomed in overlap plots (c/d) with Z_{eff} values for effective valence shell populations from n = 0 to 6 (grey) and N 2*p* effective populations of 5.2 and 5.7 (red).

Python Fitting Description (Penelope)

Fitting Functions

XAS spectra result from multiple transitions which will undergo both instrument broadening as well as intrinsic broadening. Thus, each transition is best modelled as a pseudo-Voigt peak with both Gaussian and Lorentzian components. This fitting is carried out using Python.[1–7] This is given mathematically by

$$f_p(\omega,\mu,a,\sigma,\alpha) = a\big(\alpha * g(\omega,\mu,\sigma') + (1-\alpha) * l(\omega,\mu,\sigma)\big), \qquad \sigma' = \frac{\sigma}{\sqrt{2\ln 2}}$$

where *g* and *l* are normalized Gaussian and Lorentzian distributions, respectively:

$$g(\omega,\mu,\sigma') = \frac{1}{\sigma'\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\omega-\mu}{\sigma'}\right)^2}$$

$$l(\omega,\mu,\sigma) = \left(\frac{1}{\pi}\right)\frac{\sigma}{(\omega-\mu)^2+\sigma^2}$$

Here, ω is the energy, *a* is the area of the peak, σ is the full width at half max, μ is the position of the peak max, and α the degree of Gaussian vs Lorentzian character. For a full XAS spectrum, there will be several transitions that can be observed, often overlapping with each other. Thus, the full spectrum of peaks will be modeled by

$$F(\omega) = \sum_i^N f_p\big(\omega,\mu_i,a_i,\sigma_i,\alpha_i\big)$$

where *N* is the number of peaks. In general, adding more peaks will improve fit statistics, but users must exert caution in over fitting a spectrum. With excessive numbers of peaks there will not be a unique solution, and selecting an appropriate number of peaks to accurately model the raw data is a central challenge to the fitting procedure.

Additionally the rising edge of XAS spectra can best be modeled as a broadened step function given by

$$f_e(\omega,e0,a_e,w,\alpha_e) = \begin{cases} \omega < e0: & f_p(\omega,(e0+w),a',w,\alpha_e) \\ \omega \geq e0: & f_p\big((e0+w),(e0+w),a',w,\alpha_e\big) - f_p(\omega,(e0-w),a',w,\alpha_e), \end{cases}$$

$$a' = \frac{a_e}{(1-\alpha_e)/2w\sqrt{\pi\ln 2} + \alpha_e/w\pi}$$

where *e0* gives the inflection point, *w* the degree of broadening, and a_e the amplitude. The full pre-edge and near edge region is thus modeled by:

$$F(\omega) = f_e(\omega,e0,a_e,w,\alpha_e) + \sum_i^N f_p\big(\omega,\mu_i,a_i,\sigma_i,\alpha_i\big)$$

For XAS spectra, peaks in the EXAFS region can no longer be accurately modeled as pseudo-Voigt line shapes. As EXAFS oscillations take the shape of a damped step response function, there is a sharp overshoot close to the

excitation threshold. This is modeled in Penelope as large pseudo-Voigt peaks but it should be noted that these are not physical peaks and only necessary for correct fitting statistics at lower energy. Therefore, only analysis of peaks in the pre-edge or near-edge region that can be accurately reproduced were used for area and energy correlations.

General Spectra Fitting Procedure

The first step in fitting a data set is to manually inspect the data and determine whether a set of weights is needed for fitting data, as in the case of weak pre-edge peaks which will appear in the noise of larger rising edge features. The next step is to make an educated guess as to the number of peaks, and allow a totally random set of peaks to be fit to the data. Inspection of the resultant fits (**Figure S35**) will guide further refinement. In this case, the highest scoring fits have largely converged.

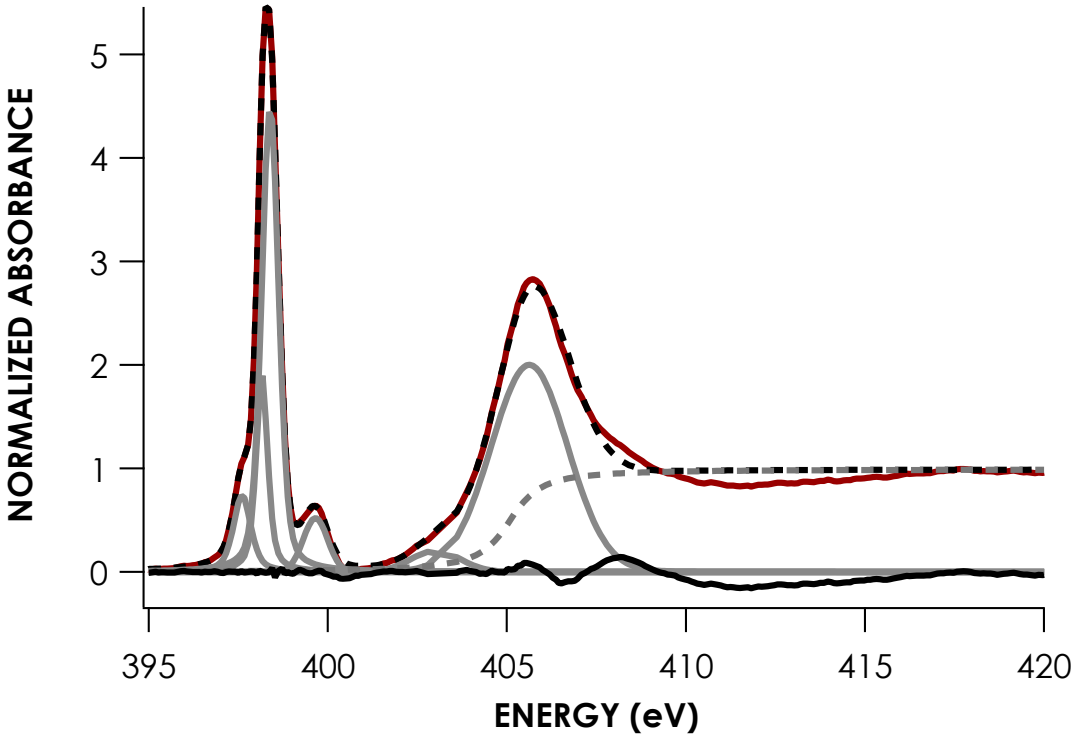

Figure S35. Representative fit as produced by the plotbestxanes function in MCFitting. Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black). In order to interpret the fit a histogram can be used (**Figure S36**).

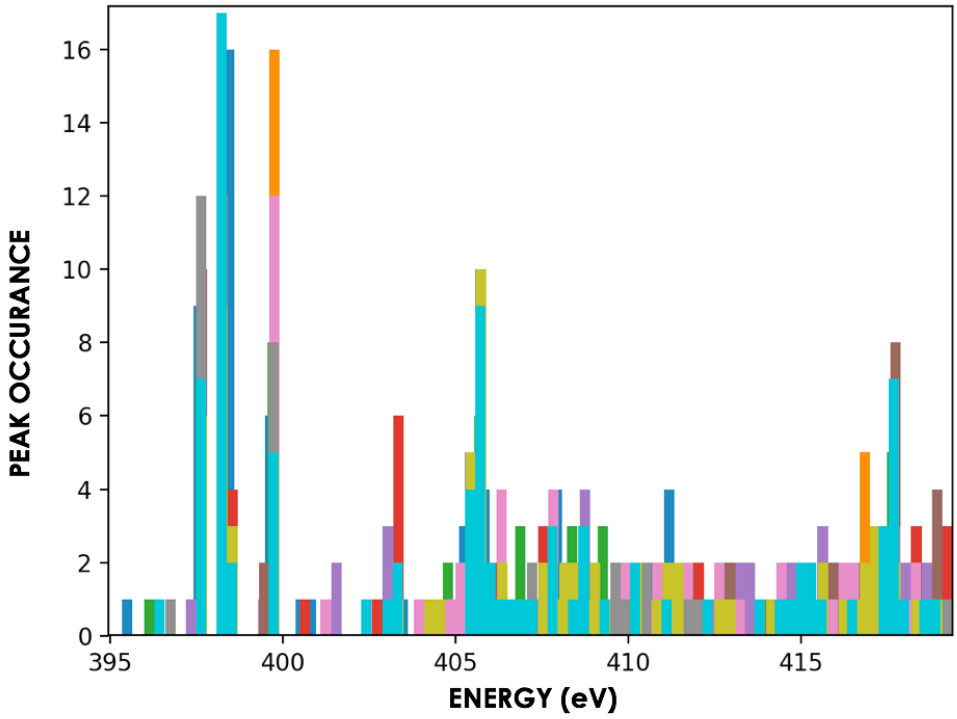

Figure S36. Histogram of peak locations from all fits performed.

By inspection, three peak energy values can be identified with a high degree of certainty at 397.5, 398, and 399.5 eV. After 405 eV there is more variation. At this point a more constrained fit is performed with sets of bounds for each peak based on the histogram. For this data set, 8 peaks were chosen for the constrained fit even though 10 were used in the initial random fit. The results of the constrained 8 peak fit are shown in Figure S37. It should be noted that though a fit may have a high degree of certainty, it is not necessarily unique or the best fit. By introducing bounds the user introduces bias to the fit to find a desired solution. To ensure variables were allowed a reasonable parameter space it is best to inspect histograms of their values and see if most values fall well within the bounds. Once a set of fits is finalized, they can be exported to CSV files for use with other programs.

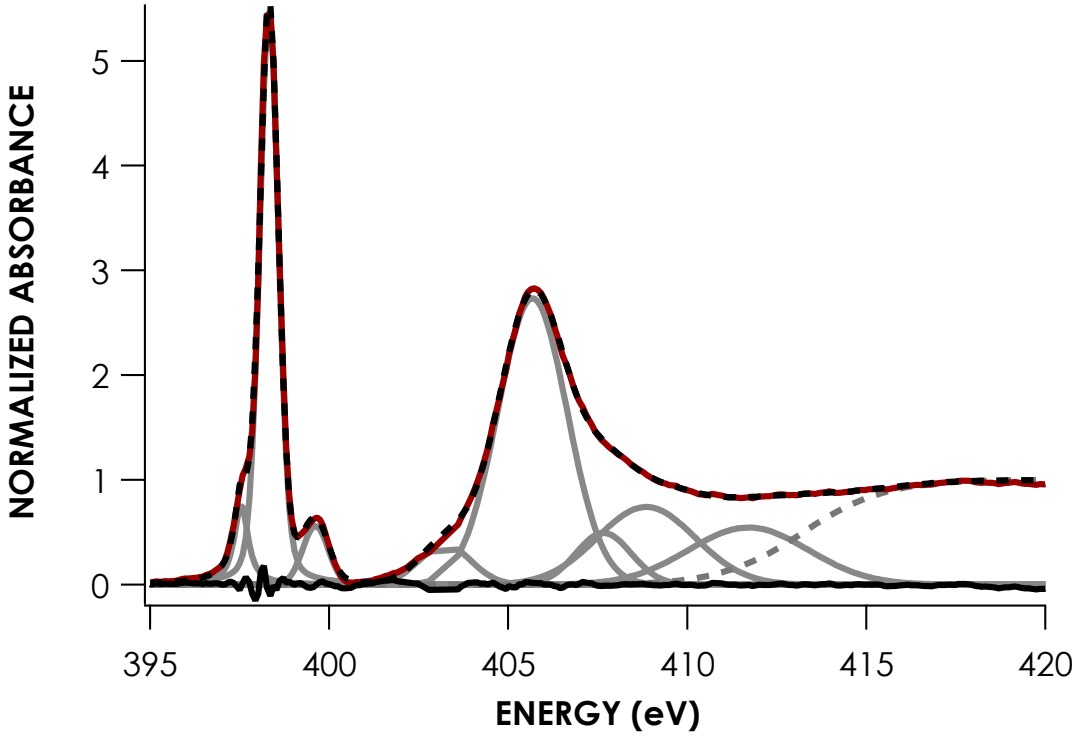

Figure S37. Final fit as produced by the plotbestxanes function in MCFitting. Fit N K-edge XAS experimental spectra (solid red), individual pseudo-Voigt peak (solid grey) the edge step-jump function (dashed grey), composite fit spectra (dashed black), and residual intensity (solid black). In order to interpret the fit a histogram can be used (**Figure S36**).

References

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