Supplementary Information

Stabilizing a Ni^{II}-aqua complex via intramolecular hydrogen bonds: synthesis, structure, and redox properties

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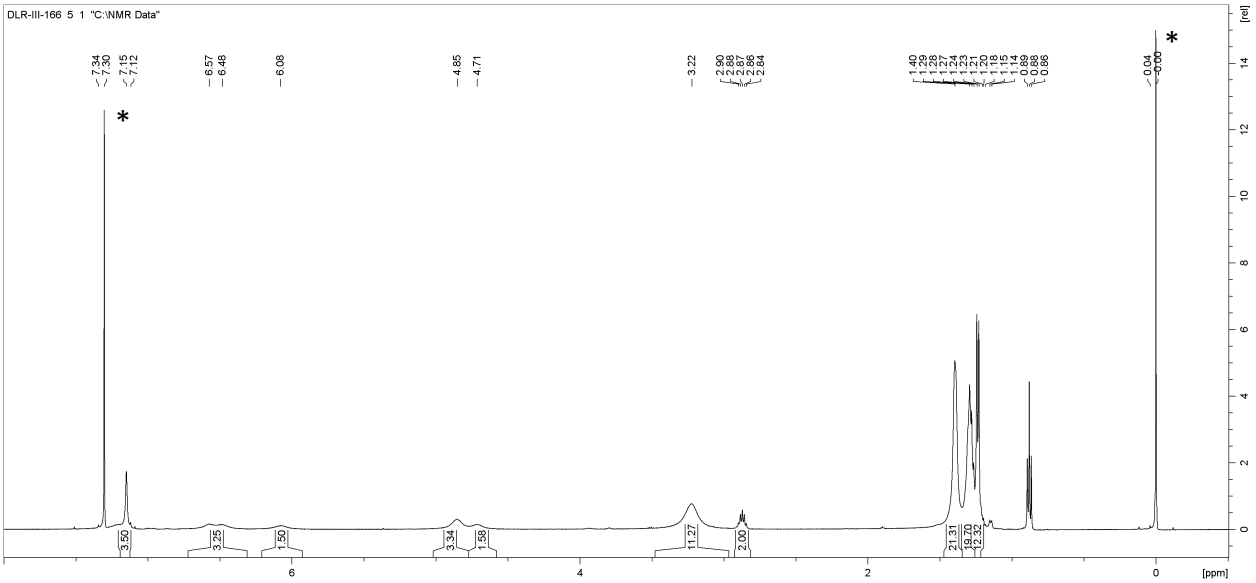
A



B

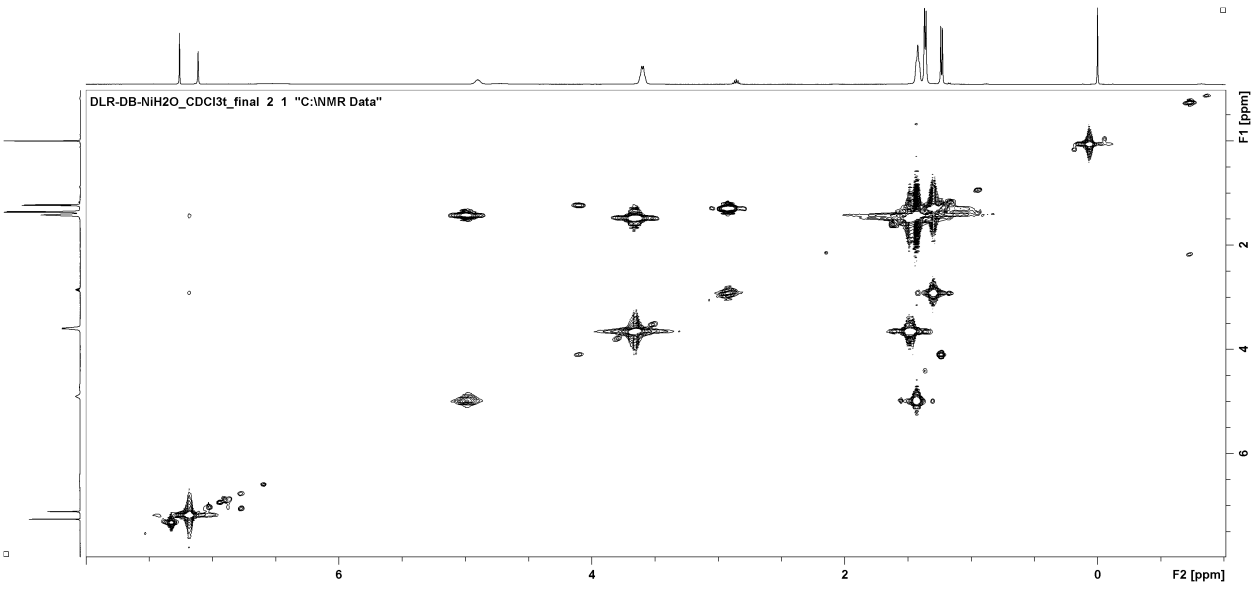


Figure S1. ^{1}H NMR spectrum of [Ni(ibaps)(H_2O)]$^-$ measured at 218 K (**A**) and its COSY spectrum collected at room temperature (**B**). The spectra were recorded in $CDCl_3$.

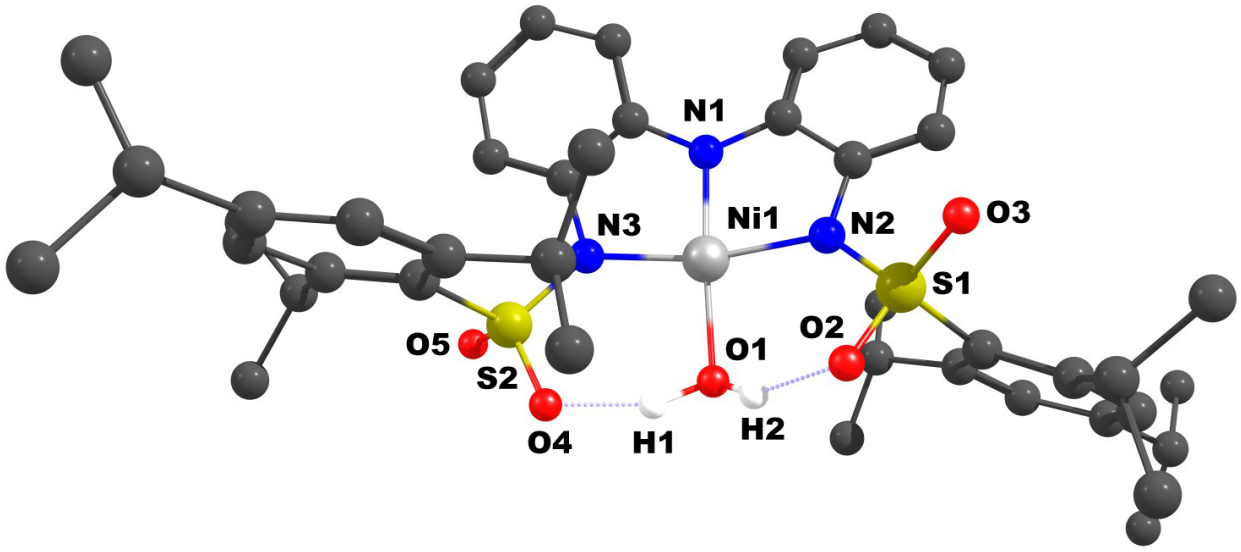


Figure S2. DFT computed structure for $[Ni(ibaps)(H_2O)]^-$.

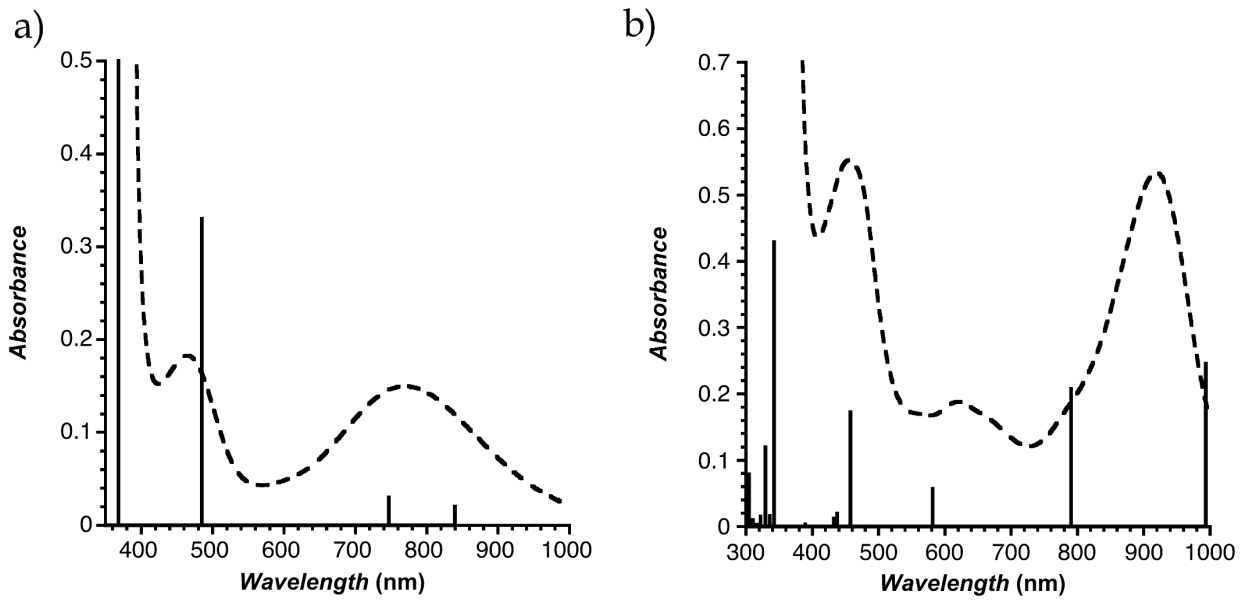


Figure S3. TD-DFT computed vertical excitations for (**A**) [Ni(ibaps)(H_2O)]- and (**B**) [Ni(ibaps)(H_2O)] compared to the experimentally determined electronic absorption spectra (dashed lines).

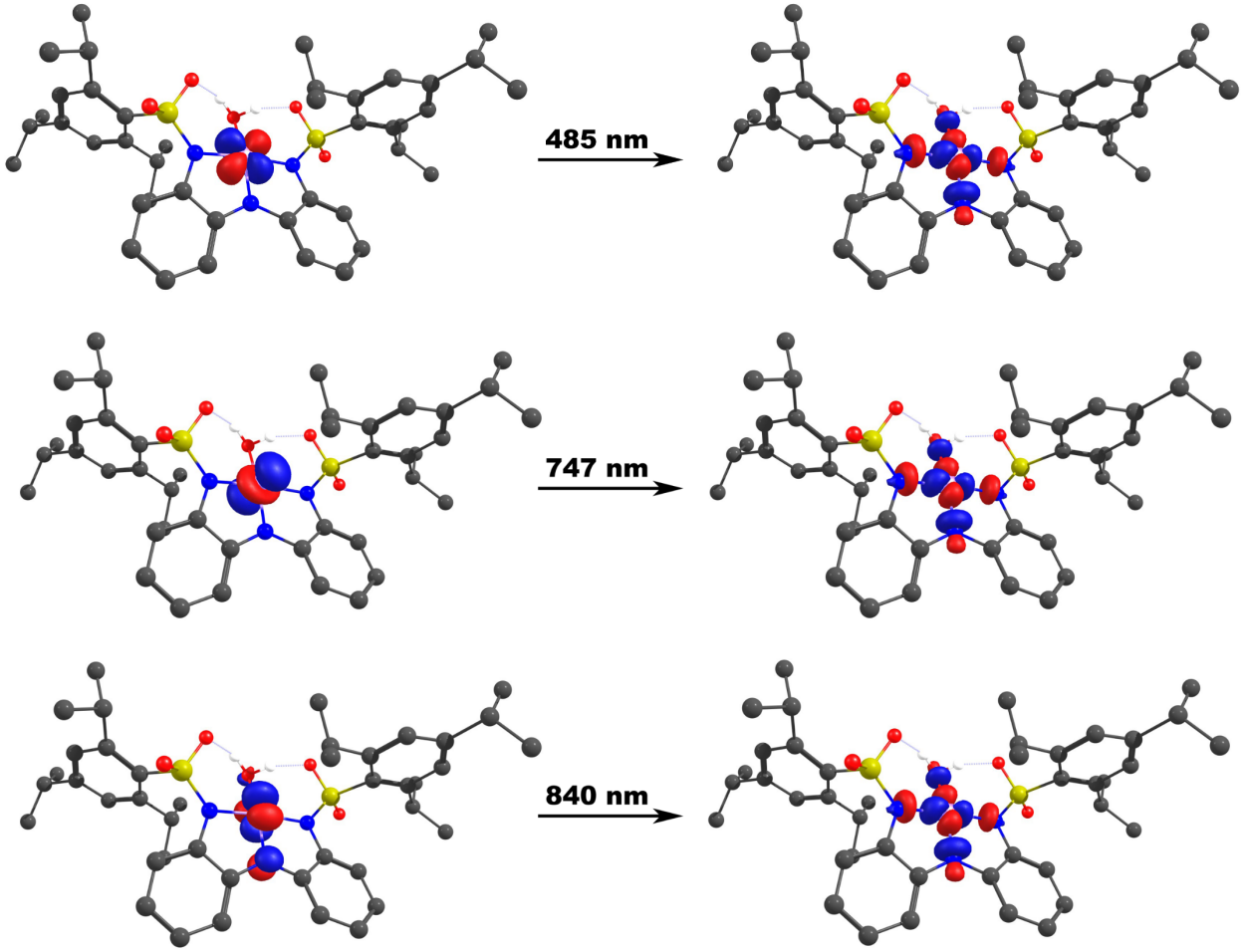


Figure S4. Highest occupied to lowest unoccupied natural transition orbitals for select vertical excitations of [Ni(ibaps)(H_2O)]$^-$.

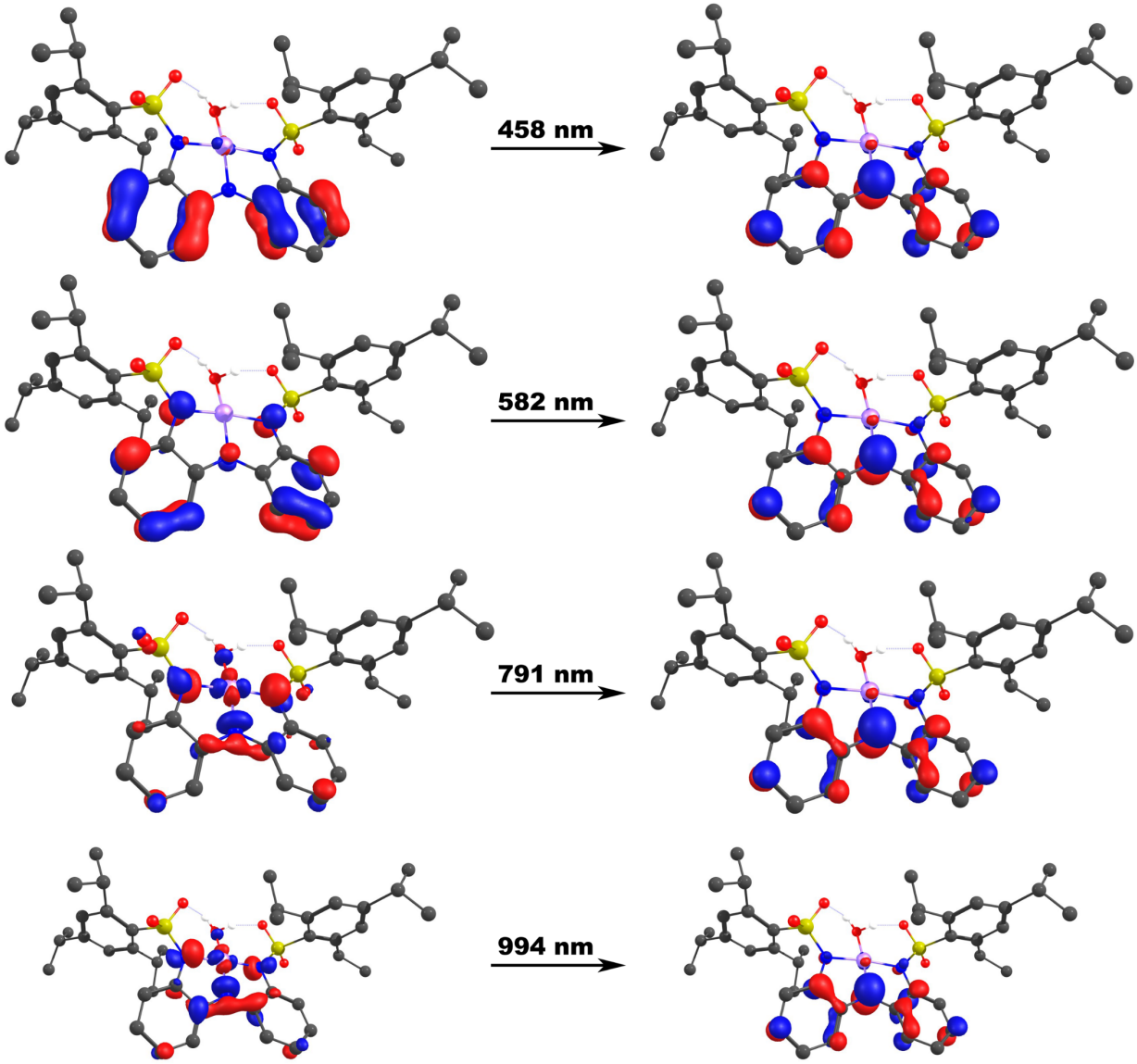


Figure S5. Highest occupied to lowest unoccupied natural transition orbitals for select vertical excitations of [Ni(ibaps)(H_2O)].

Table S1. DFT optimized coordinates for [Ni(ibaps)(H_2O)]$^-$.

Ni	5.622988287	4.873833225	7.150510382
S	6.860822563	6.129839654	9.861964069
S	3.462309716	5.485724683	4.885789414
O	5.749678983	6.745876533	6.811066937
H	5.931859840	7.209115862	7.671002086
H	4.875066150	7.039254146	6.453016720
O	6.350186944	7.382844118	9.222704988
O	8.293760415	6.196319768	10.217540541
O	3.386429048	6.740486492	5.700450841
O	2.180366151	4.773907754	4.702384914
N	5.734669664	3.048947284	7.285092698
N	6.565784815	4.879172566	8.841814687
N	4.540680068	4.503042564	5.607505937
C	6.259371396	2.549832748	8.464098709
C	6.275058697	1.215301755	8.912307023
H	5.767619097	0.447488901	8.344355740
C	6.905981861	0.866458651	10.111211104
H	6.906350222	-0.173721830	10.427711858
C	7.532937572	1.839965022	10.882237226
H	8.056532424	1.574937545	11.796823738
C	7.479145276	3.183182338	10.483124654
H	7.971395743	3.930278091	11.089929242
C	6.808017288	3.556194020	9.315970308
C	5.332192212	2.341728969	6.160664282
C	5.598392817	0.997947243	5.833847747
H	6.202213586	0.386867539	6.490358906
C	5.134664892	0.445790477	4.635081363
H	5.356424032	-0.594867995	4.411310465
C	4.405779346	1.219765545	3.736504855
H	4.034848606	0.793656762	2.808307449
C	4.166235839	2.571448707	4.021092595
H	3.617808408	3.172924898	3.306161389
C	4.629987455	3.138665492	5.209228015
C	5.831456183	5.956095999	11.377878449
C	6.391395352	5.937589401	12.685693876
C	5.502034085	5.956208767	13.769065651
H	5.920665307	5.957245954	14.769999285
C	4.115900192	5.980534357	13.624635400
C	3.607646824	5.976375871	12.327750658
H	2.529674375	5.991601517	12.192886026
C	4.422774879	5.965383377	11.190225899
C	7.882258216	5.935747070	13.056371214
H	8.467032785	5.711655322	12.170714082
C	8.230576705	4.862793037	14.107509057
H	7.801032525	5.073692815	15.093066864
H	9.318819557	4.817567153	14.231968054

H	7.885126039	3.870758625	13.795039788
C	8.319157219	7.336618263	13.530605207
H	8.145429387	8.088132085	12.752715709
H	9.389065403	7.338592412	13.771202734
H	7.771271226	7.645495584	14.428937827
C	3.185981283	6.008497670	14.829044459
H	2.158817281	6.029414671	14.441922197
C	3.329269586	4.739402455	15.691029270
H	3.153684950	3.835121692	15.097836550
H	2.604820074	4.753520999	16.513609533
H	4.331320308	4.665457454	16.129944280
C	3.387308165	7.279486700	15.676251731
H	4.393417014	7.314834840	16.110694981
H	2.666460794	7.306078809	16.501718867
H	3.248648115	8.183996036	15.073675640
C	3.691319753	5.976963892	9.843128005
H	4.412308562	5.885598688	9.036274626
C	2.938465965	7.303006194	9.624940129
H	2.132289387	7.440800934	10.355002957
H	2.492378095	7.314589673	8.623435566
H	3.620654471	8.155636104	9.703596612
C	2.746552665	4.766883217	9.704192254
H	3.294581356	3.824524155	9.815011548
H	2.280692283	4.773065748	8.711788005
H	1.941474771	4.779645348	10.446926549
C	4.011331619	6.000940120	3.206429613
C	2.997482865	6.481179533	2.334032556
C	3.344109944	6.718298619	0.998661039
H	2.571151685	7.057549762	0.314330359
C	4.638941494	6.551003095	0.509739135
C	5.627378924	6.192813334	1.425705264
H	6.656429914	6.123242772	1.086198604
C	5.362757596	5.932295300	2.777589927
C	1.556341453	6.826104990	2.735738960
H	1.447559930	6.718587709	3.812439424
C	1.228027293	8.297897364	2.409023175
H	1.947472682	8.978040892	2.878776247
H	0.230138751	8.544805277	2.790375092
H	1.227890802	8.498206140	1.331919445
C	0.539352306	5.871858337	2.083654373
H	0.573111116	5.932414100	0.989387547
H	-0.478500381	6.129385673	2.400376630
H	0.736515065	4.836751484	2.377703671
C	4.957924131	6.798856912	-0.957874068
H	4.008993635	7.031488682	-1.458748076
C	5.887566381	8.014016472	-1.141857472
H	5.456558550	8.914974712	-0.691366102
H	6.052489392	8.210769600	-2.207666014

H	6.866159315	7.840460040	-0.678879810
C	5.545315174	5.546229116	-1.635115259
H	6.509681125	5.269329183	-1.193060038
H	5.708801681	5.731498834	-2.703092888
H	4.870917829	4.688282785	-1.537045158
C	6.591496320	5.686706573	3.662918112
H	6.273154770	5.493064795	4.682257308
C	7.470342941	6.954200757	3.710577365
H	7.876819597	7.211599397	2.725653921
H	8.316519800	6.792548008	4.389243118
H	6.902659634	7.815113244	4.079657377
C	7.414160722	4.467203267	3.204013749
H	6.798742663	3.562984121	3.172311153
H	8.240508568	4.293179857	3.903750615
H	7.853248032	4.616660660	2.210476421

Table S2. DFT optimized coordinates for [Ni(ibaps)(H_2O)].

Ni	5.617025042	4.908222100	7.171964233
S	6.884455989	6.083398318	9.943909600
S	3.471170429	5.595405558	4.869134158
O	5.806586016	6.776462184	6.864364505
H	6.008011515	7.235534402	7.721688694
H	4.958393723	7.116000775	6.484076990
O	6.428896874	7.346116783	9.295130355
O	8.320454973	6.041071970	10.267024064
O	3.471328298	6.843898734	5.686623862
O	2.178748890	4.896834243	4.750513468
N	5.714444086	3.060334649	7.256569885
N	6.502633331	4.838159075	8.907033402
N	4.553383338	4.575214985	5.585064800
C	6.178962596	2.529750286	8.433056431
C	6.144203588	1.171699232	8.831077839
H	5.637753126	0.440481735	8.216596900
C	6.705376376	0.782540934	10.035103245
H	6.666911222	-0.259067314	10.337495816
C	7.318550723	1.738364546	10.860593189
H	7.787708265	1.430548030	11.790418894
C	7.315038944	3.087957162	10.520904364
H	7.790483641	3.797081277	11.182389525
C	6.700062801	3.521302729	9.333291761
C	5.349144723	2.404315915	6.102164107
C	5.655026901	1.071136737	5.741606543
H	6.297133961	0.471586777	6.371760548
C	5.186482447	0.547244075	4.547842646
H	5.433565798	-0.473387640	4.273582222
C	4.410630854	1.342157400	3.689281574
H	4.033098188	0.926029626	2.759884566
C	4.147136546	2.675847023	3.990142098
H	3.574870701	3.274441219	3.293543470
C	4.637661657	3.240527477	5.178528802
C	5.853917270	5.926345972	11.447987714
C	6.423735438	5.893292714	12.753130213
C	5.536059547	5.890601901	13.836258673
H	5.953403916	5.875929033	14.836474531
C	4.148589191	5.913646723	13.693458235
C	3.635072826	5.938404228	12.399342996
H	2.556941757	5.959425053	12.268768033
C	4.446263448	5.949495518	11.259198756
C	7.919604477	5.920844327	13.101030070
H	8.486716750	5.544826056	12.254689907
C	8.287375204	5.035187126	14.307359460
H	7.924436977	5.436251055	15.259998685
H	9.378858526	4.972019799	14.382177821

H	7.897231551	4.017274523	14.196378079
C	8.382472377	7.374374425	13.334778720
H	8.211009953	7.995482833	12.449700138
H	9.454824884	7.397078880	13.562053575
H	7.847510745	7.826753185	14.178542742
C	3.222790128	5.913261905	14.900951180
H	2.194543873	5.944348000	14.517880722
C	3.369420201	4.622738986	15.730061914
H	3.190951035	3.733601026	15.115328610
H	2.648040616	4.617068481	16.555284252
H	4.373035763	4.537827236	16.163242229
C	3.428259229	7.163098768	15.778261494
H	4.434853513	7.186362352	16.212232718
H	2.708514843	7.169615744	16.604881231
H	3.289590045	8.082296900	15.198464843
C	3.710305850	6.003938015	9.914862320
H	4.427238468	5.942857149	9.101929224
C	2.962178879	7.340192802	9.745652921
H	2.166803158	7.459492638	10.490081588
H	2.502152290	7.384097686	8.751641084
H	3.649558995	8.186983718	9.841346265
C	2.763291314	4.800872727	9.736795340
H	3.308087616	3.853556147	9.815807377
H	2.296347749	4.842059296	8.745915281
H	1.959918328	4.791635504	10.481107959
C	4.006390813	6.047298745	3.175251442
C	2.983847295	6.465323266	2.281502089
C	3.334929206	6.647452528	0.938688530
H	2.559053026	6.938807996	0.236364284
C	4.636136193	6.488326125	0.464572708
C	5.629184424	6.199433712	1.400724325
H	6.661891500	6.143696637	1.070500608
C	5.363039119	5.994919088	2.760597008
C	1.535656395	6.805008545	2.660941512
H	1.423319977	6.752280160	3.741715986
C	1.185226791	8.252922167	2.258343271
H	1.892483403	8.967966310	2.693159390
H	0.182839128	8.501543767	2.625955758
H	1.183387646	8.396974586	1.172491342
C	0.537181319	5.802327515	2.054126462
H	0.572141187	5.812759398	0.958346195
H	-0.485077728	6.057488318	2.357497339
H	0.750412503	4.784932802	2.395271355
C	4.957030594	6.673904882	-1.011434722
H	4.005996698	6.864044459	-1.525699010
C	5.863417007	7.897481958	-1.247872112
H	5.410790856	8.810233865	-0.844994671
H	6.031568528	8.044656787	-2.321003747

H	6.842102812	7.767218204	-0.771195575
C	5.571647775	5.402086526	-1.625799253
H	6.539610332	5.165779229	-1.168454942
H	5.735329336	5.540159189	-2.700724116
H	4.913766957	4.536682806	-1.489249297
C	6.588170335	5.829466529	3.667849737
H	6.264527752	5.660471605	4.689533373
C	7.413763310	7.133258780	3.680921812
H	7.822400120	7.369197272	2.691850729
H	8.255311825	7.031480638	4.376129407
H	6.805300228	7.983160623	4.008348668
C	7.464271585	4.627025475	3.267602614
H	6.889201174	3.695717809	3.265761765
H	8.289951927	4.516326585	3.980368697
H	7.905467666	4.753239747	2.272341554

Table S3. Assignments of the TD-DFT computed vertical excitations for [Ni(ibaps)(H_2O)]$^-$ and [Ni(ibaps)(H_2O)].

Complex	λ_{calc} (nm)	assignment	λ_{exp} (nm)
[Ni(ibaps)(H_2O)]$^-$	485 nm	d - d	465 nm
	747 nm	d - d	775 nm
	840 nm	d - d	
[Ni(ibaps)(H_2O)]^0	458 nm	Intraligand π* - π*	458 nm
	582 nm	Intraligand π* – π*	620 nm
	791 nm	MLCT d – π*	823 nm (sh)
	994 nm	MLCT d – π*	924 nm

Table S4. Crystallographic Data for $(Et_4N)[Ni^{II}(ibaps)(OH_2)]$.

Empirical Formula	$[C_{50}H_{76}NiN_5O_5S_2]$
Fw	935.97
T (K)	133(2)
Space group	$P\bar{1}$
a (Å)	9.116(2)
b (Å)	9.433(2)
c (Å)	28.383(7)
α(°)	93.064(3)
β(°)	90.198(3)
γ(°)	95.622(3)
Z	2
V (Å)	4244.3(5)
δ_{calcd} (Mg/m^3)	1.282
R1	0.0414
wR1	0.0925
GOF	1.041
CCDC #	1899747