Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Tailor-made isostructural copper(II) and nickel(II) complexes with a newly designed (N,N)-donor scaffold for functional mimics of alkaline phosphatase

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Supporting Information

Contents

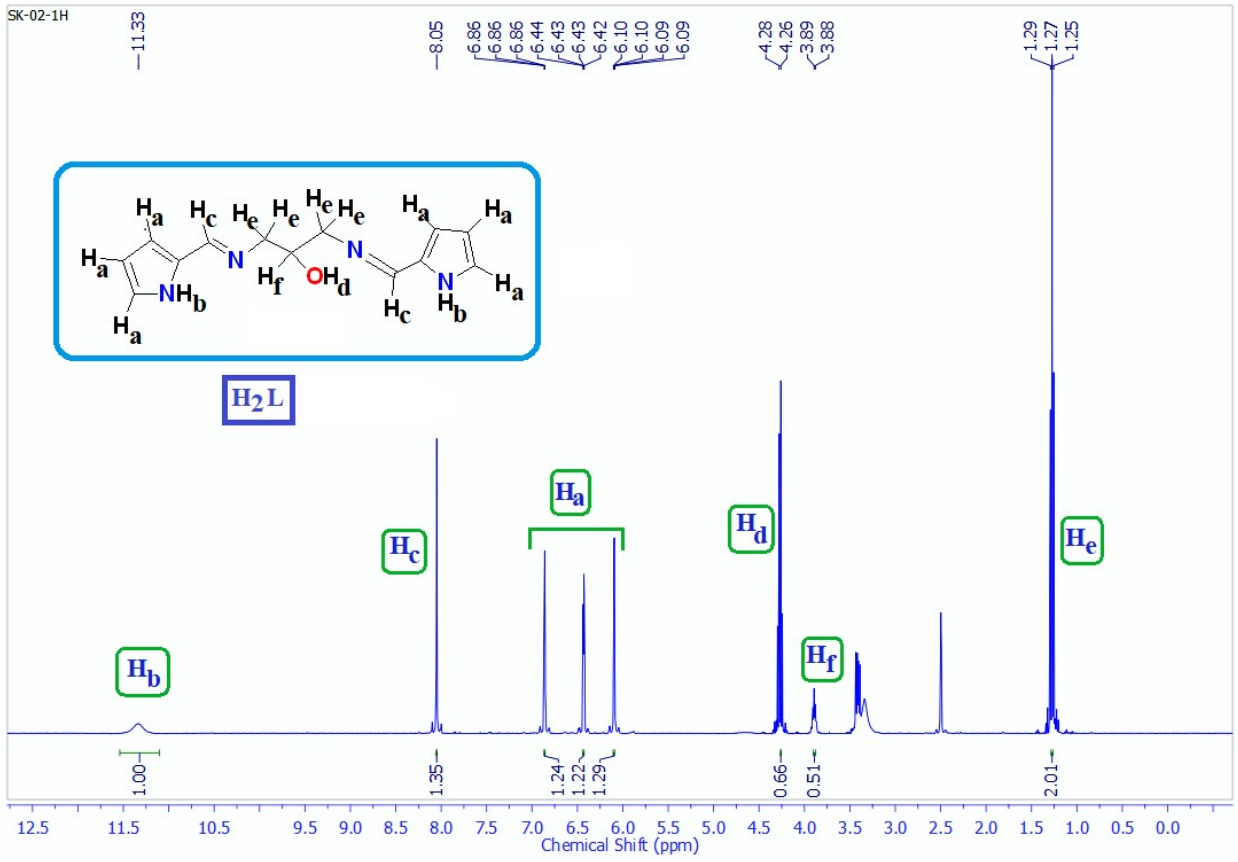


Fig. S1. ^{1}H NMR spectrum of H_2**L**in DMSO-d6.

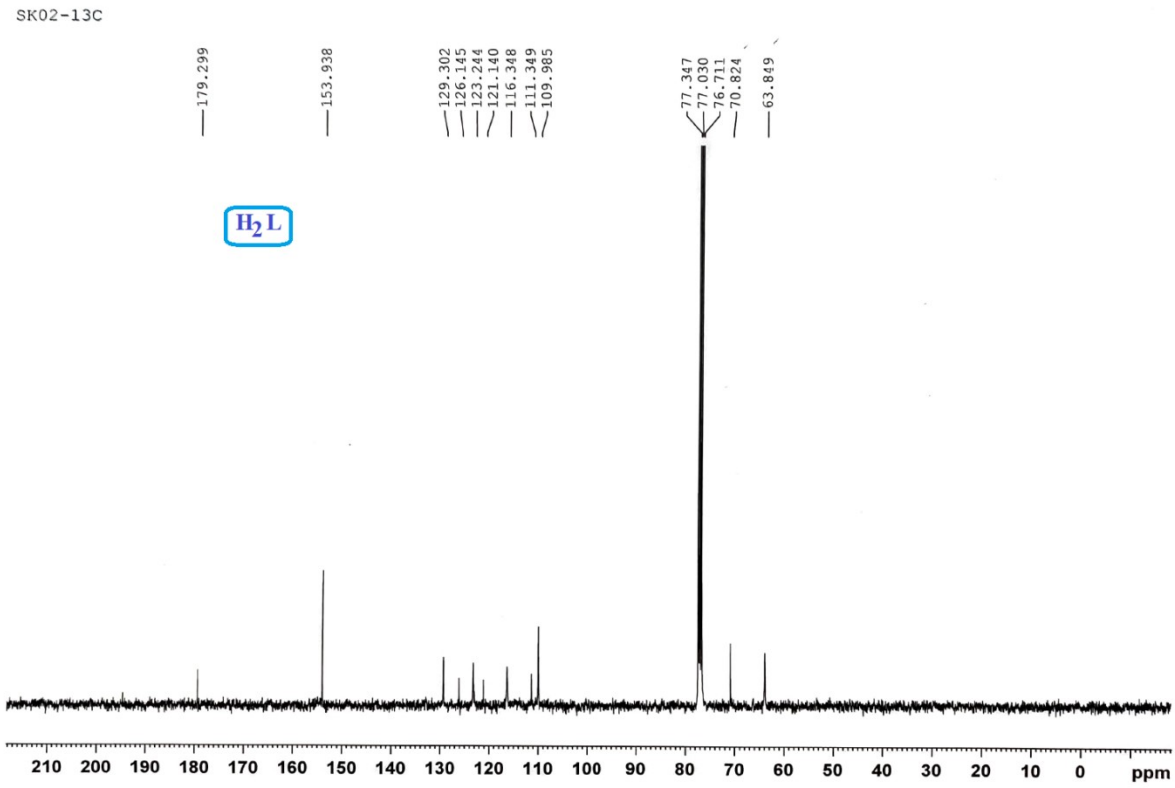


Fig. S2. ^{13}C NMR spectrum of H_2**L**in $CDCl_3$

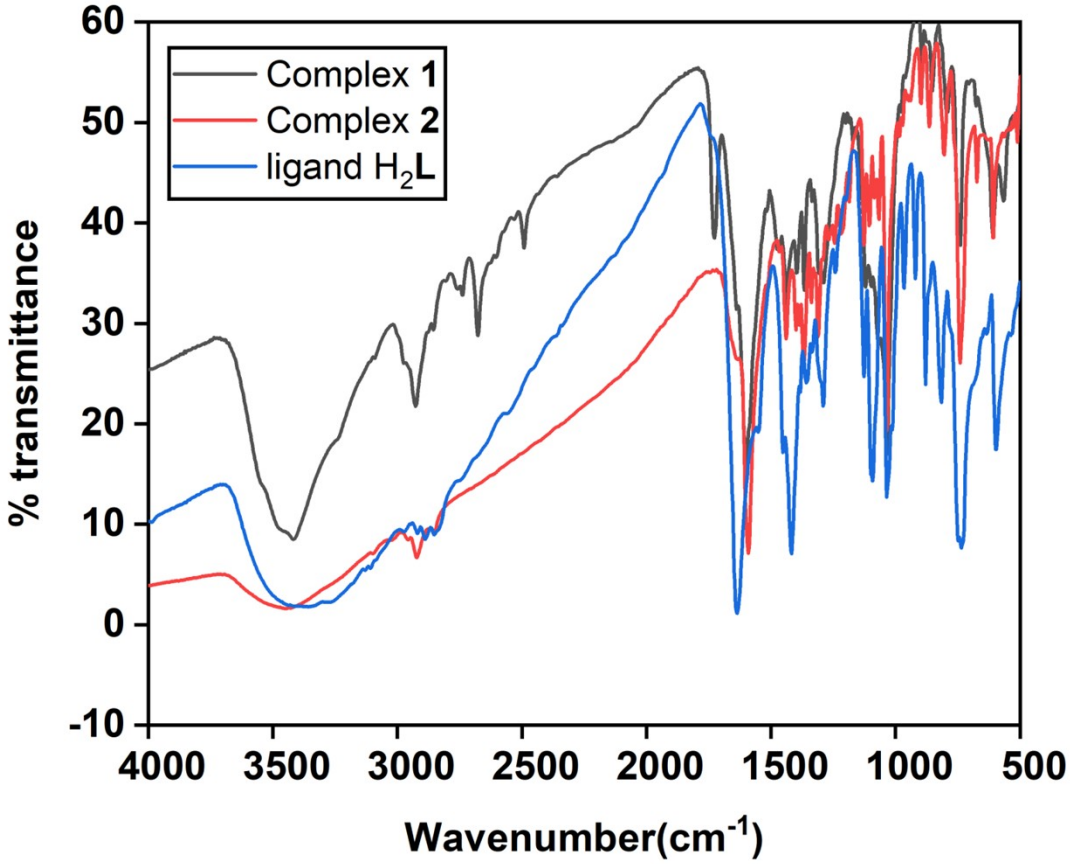


Fig. S3. FT-IR spectra of H_2**L, 1** and **2**

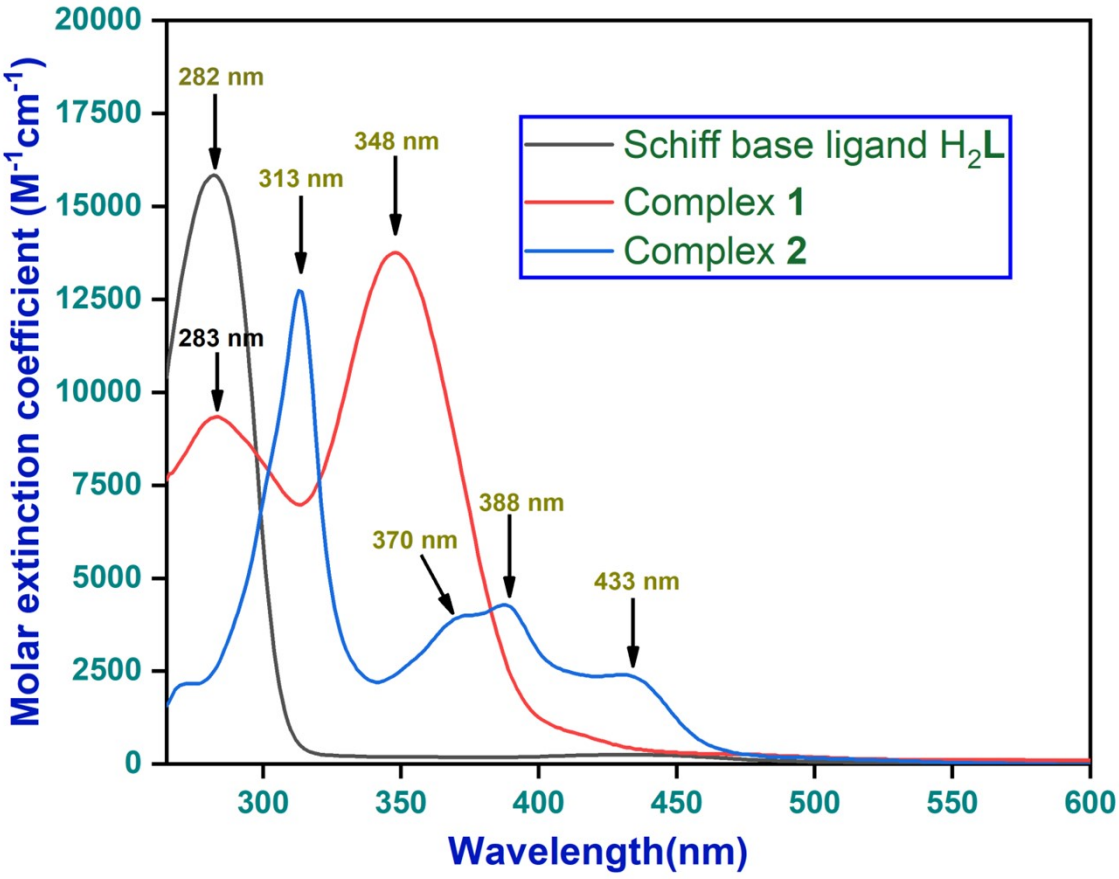
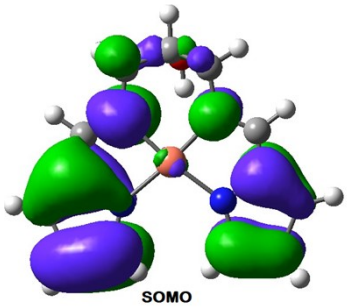
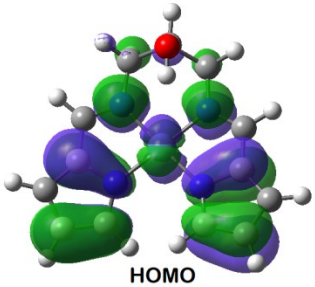


Fig.S4. UV-Vis spectra of H_2**L** and metal complexes in aq. DMF medium

	Complex 1	**Complex 2**
HOMO/SOMO	 E_{SOMO}=-130.77kcal/moL	 E_{HOMO}=-127.45kcal/moL

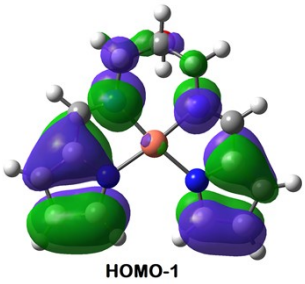
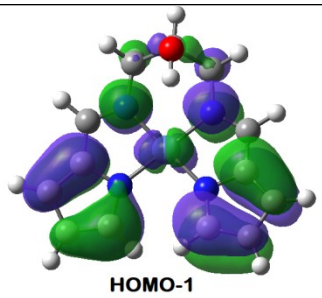
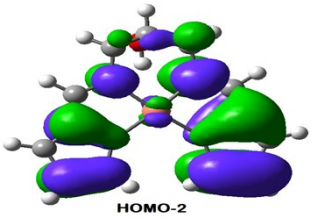
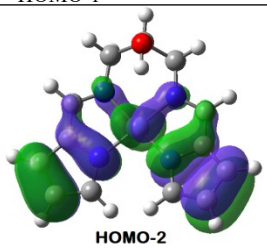
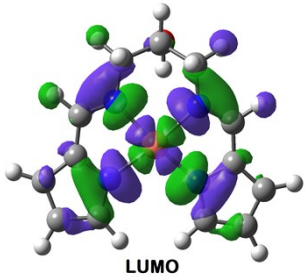
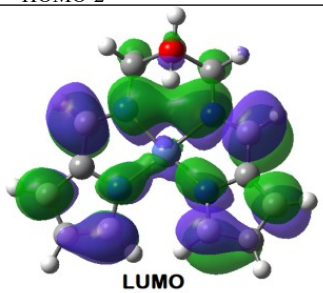
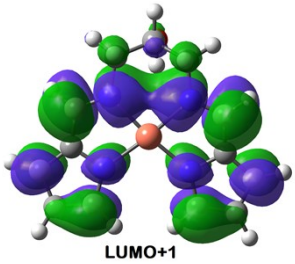
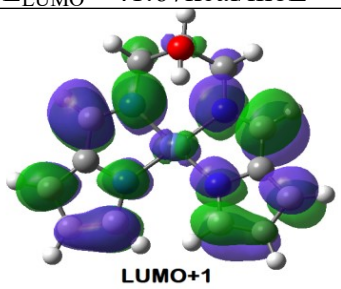
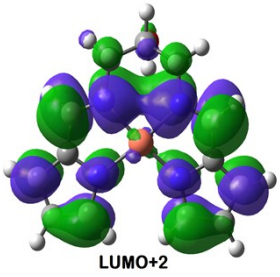
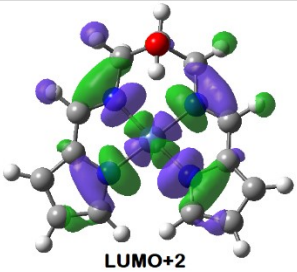
HOMO -1	 E_{HOMO-1}=-131.38kcal/moL	 E_{HOMO-1}=-130.29kcal/moL
HOMO-2	 E_{HOMO-2}=-131.66kcal/moL	 E_{HOMO-2}=-139.24kcal/moL
LUMO	 E_{LUMO}=-48.37 kcal/moL	 E_{LUMO}=-41.67kcal/moL
LUMO+1	 E_{LUMO+1}=-39.55kcal/moL	 E_{LUMO+1}=-30.62kcal/moL
LUMO+2	 E_{LUMO+2}=-38.96kcal/moL	 E_{LUMO+2}=-27.35kcal/moL

Fig.S5. HOMO LUMO of the complex **1** and complex **2**

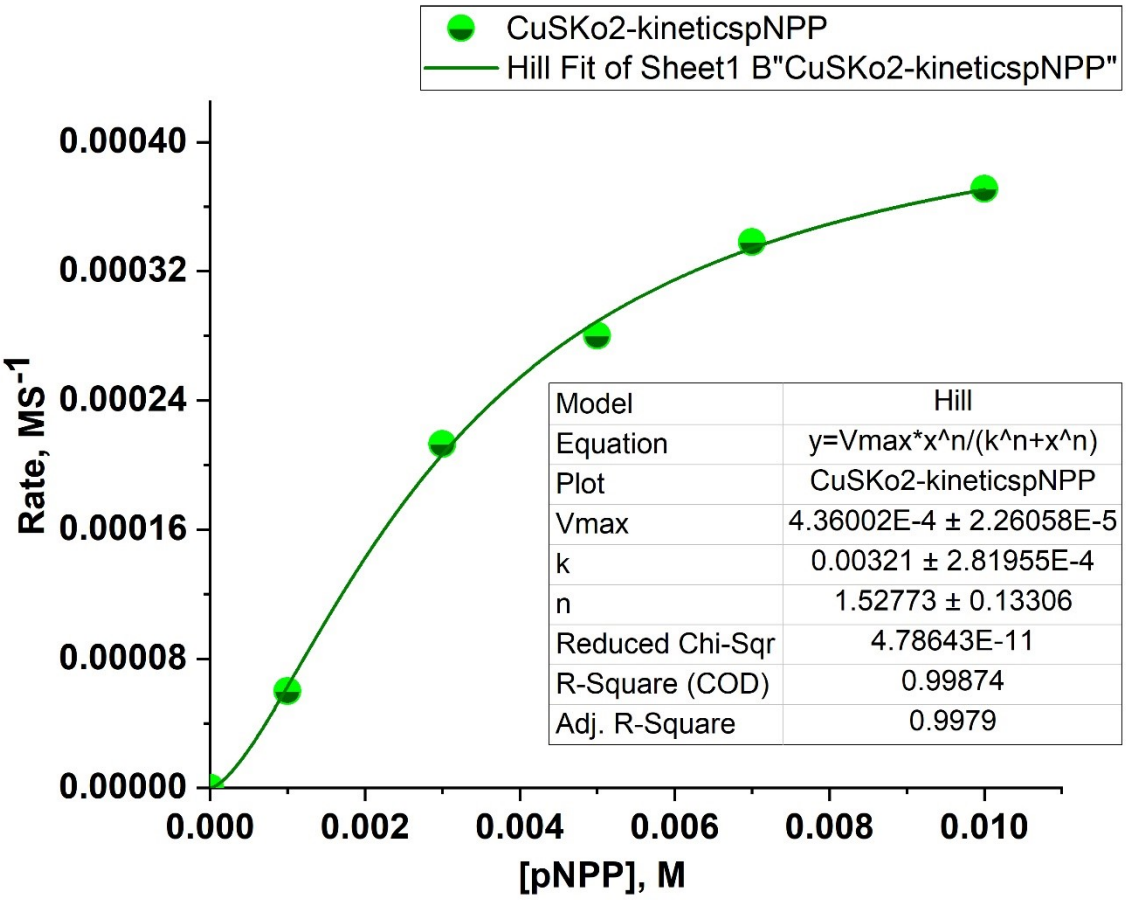


Fig. S6. Plot of rate vs [pNPP] for the Cu(II) complex-mediated catalytic hydrolysis of pNPP.

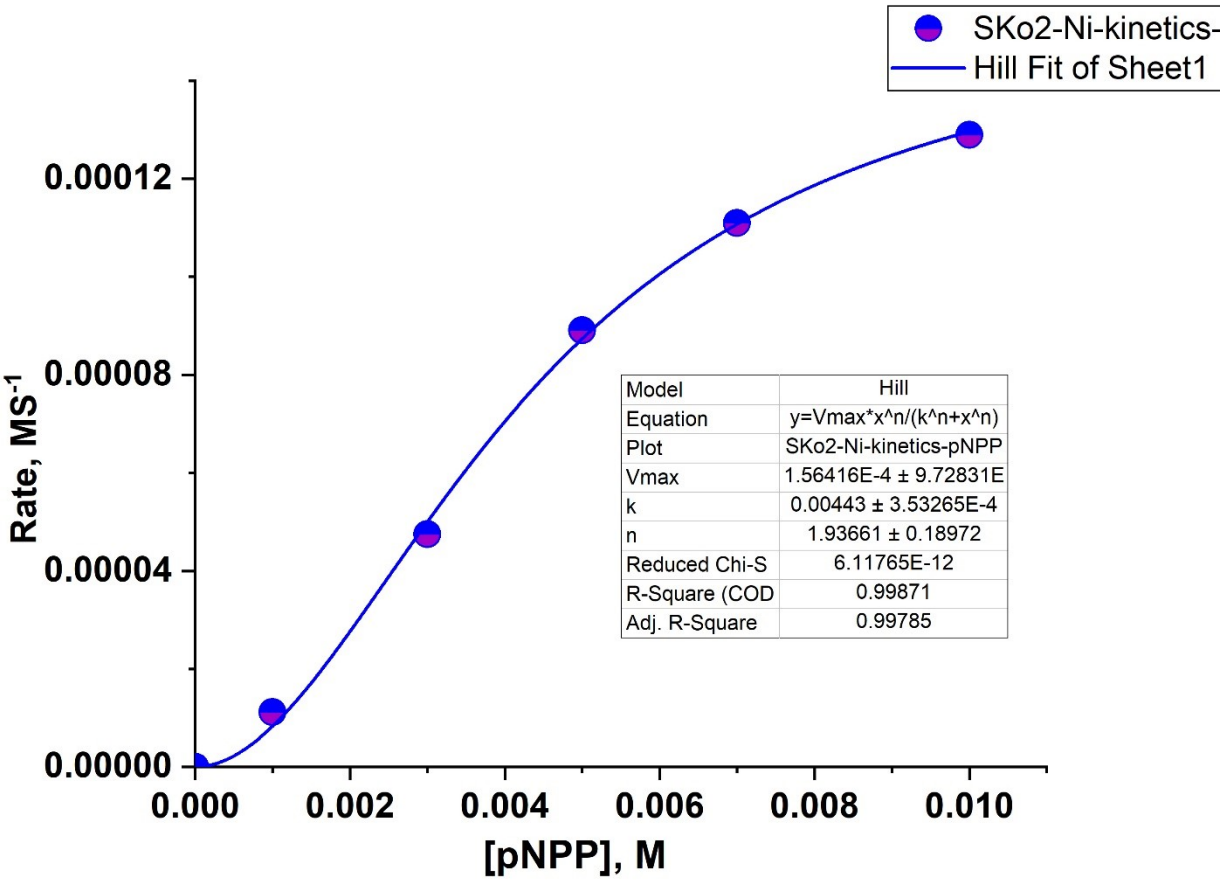


Fig. S7. Plot of rate vs [pNPP] for the Ni(II) complex-mediated catalytic hydrolysisofpNPP.

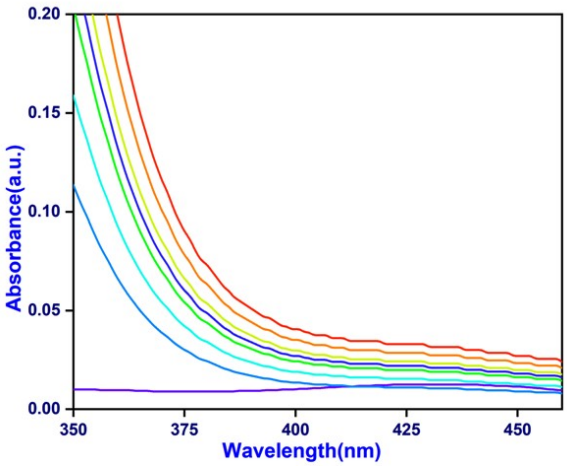


Fig S8. Spectrophotometric titration of H_2**L**withpNPP in 1:10 in aq. DMF

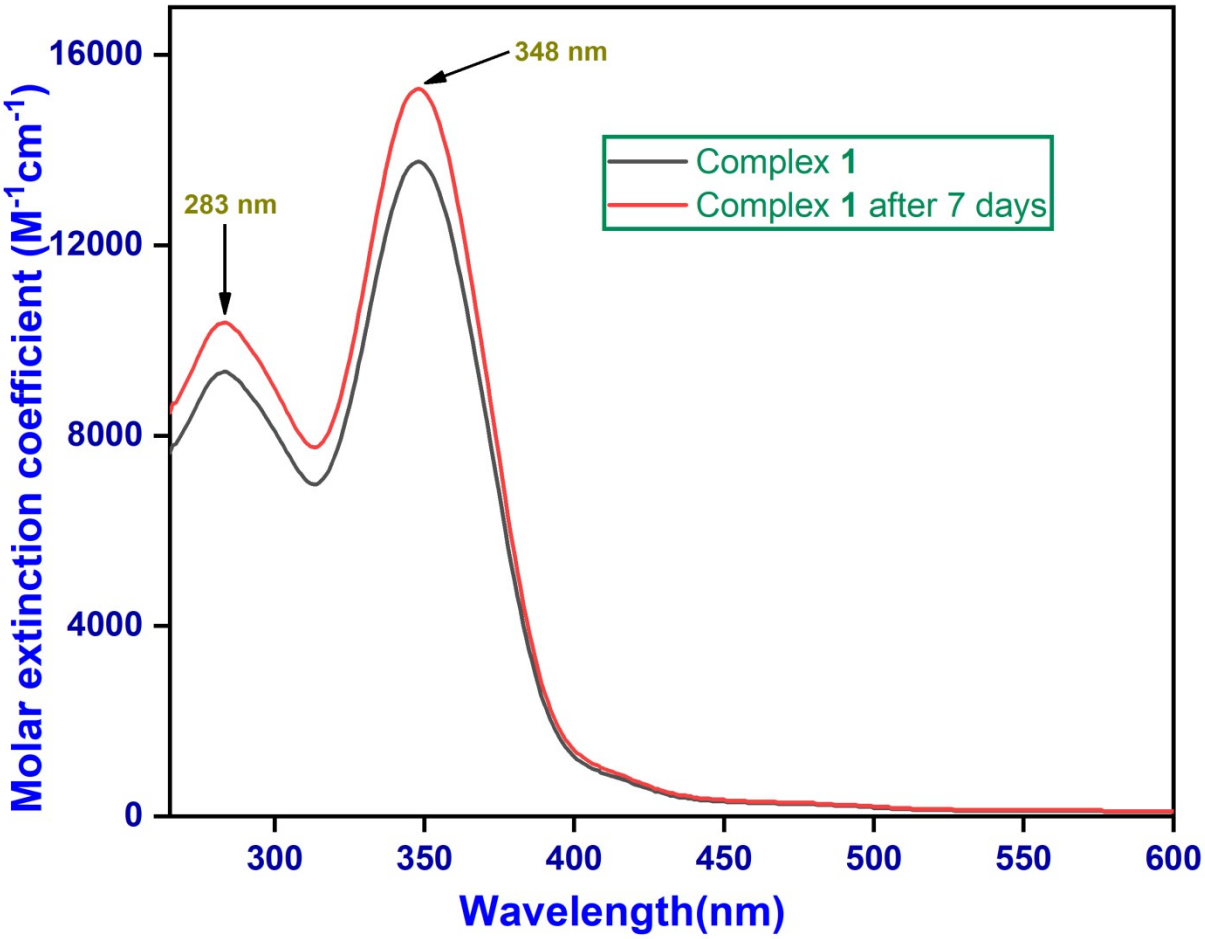


Fig. S9. UV-Vis spectra of the Cu(II) complex at 0 min and after 7 days in aq. DMF medium

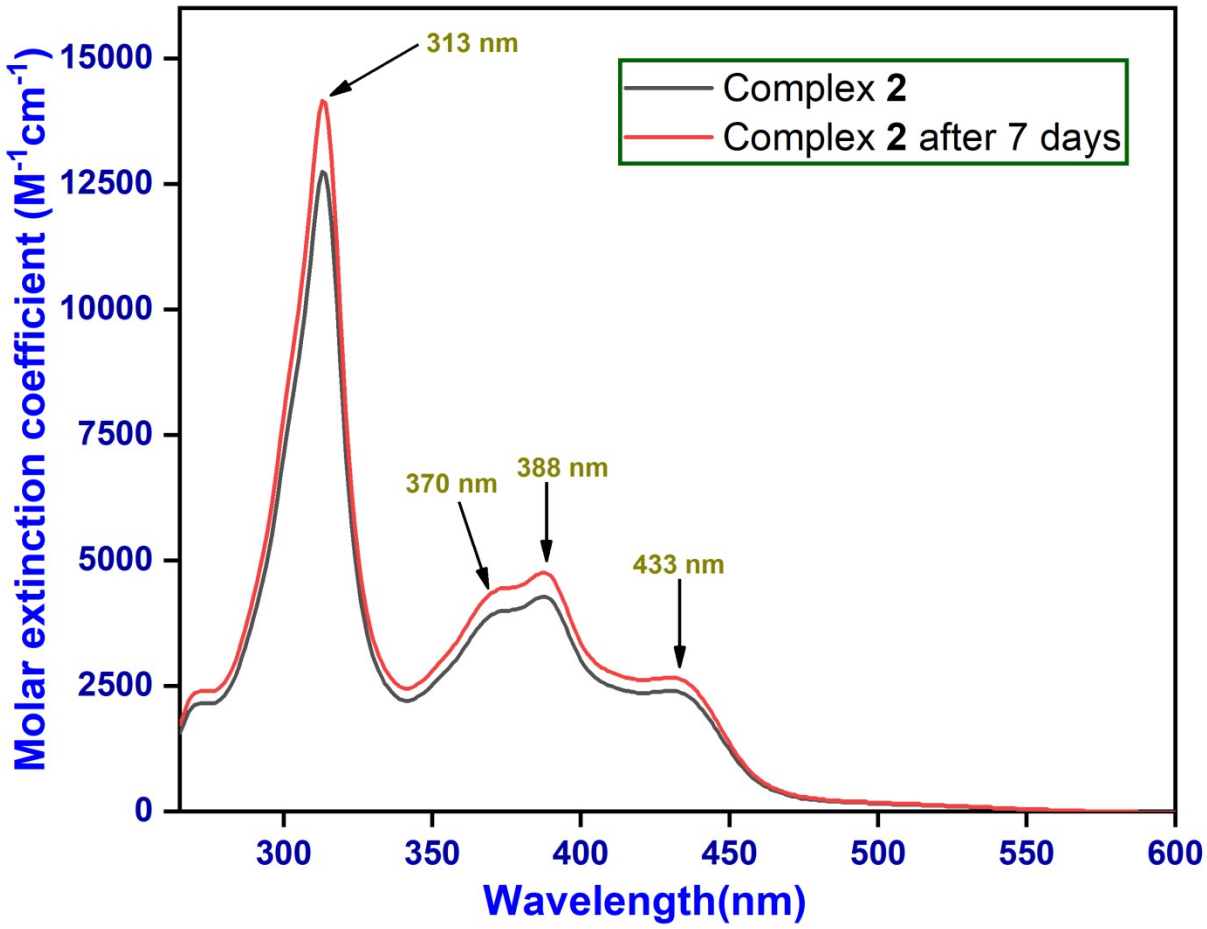


Fig. S10. UV-Vis spectra of the Ni(II) complex at 0 min and after 7 days in aq. DMF medium

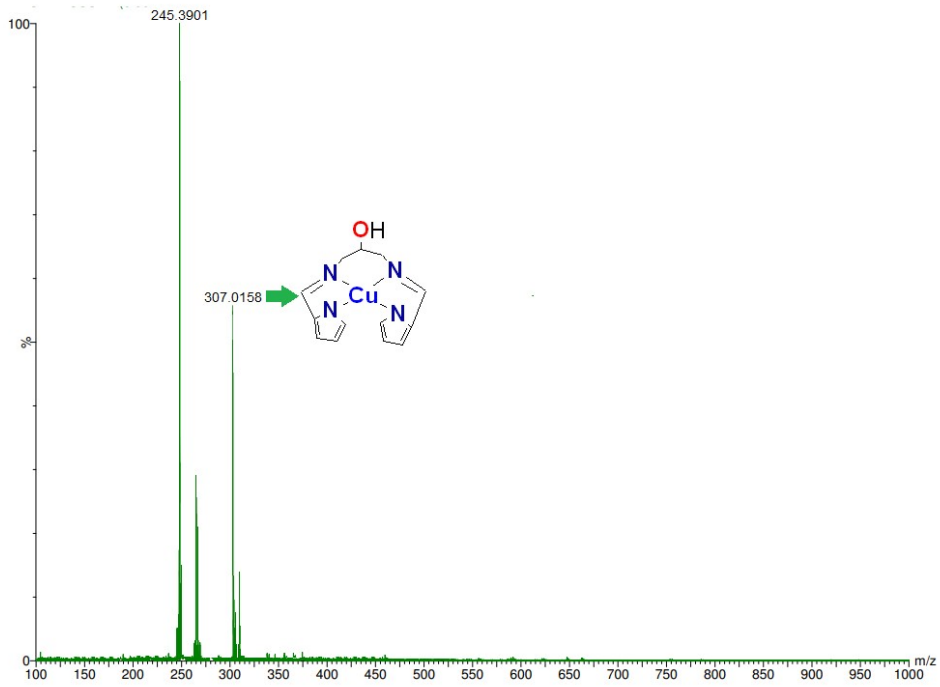


Fig. S11. ESI-Ms spectrum of the copper(II)-Schiff base complex in aq. methanol

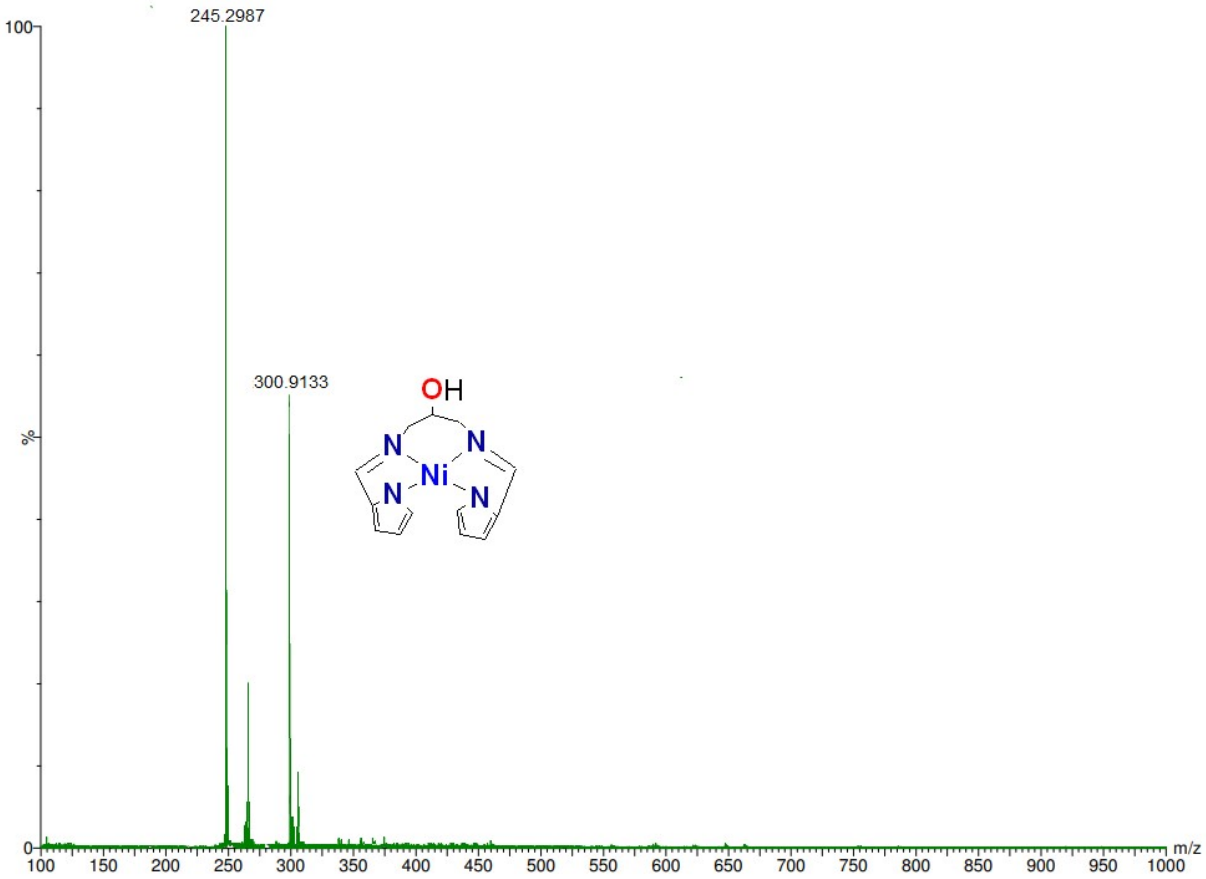


Fig. S12. ESI-Ms spectrum of the nickel(II)-Schiff base complex in aqueous methanol

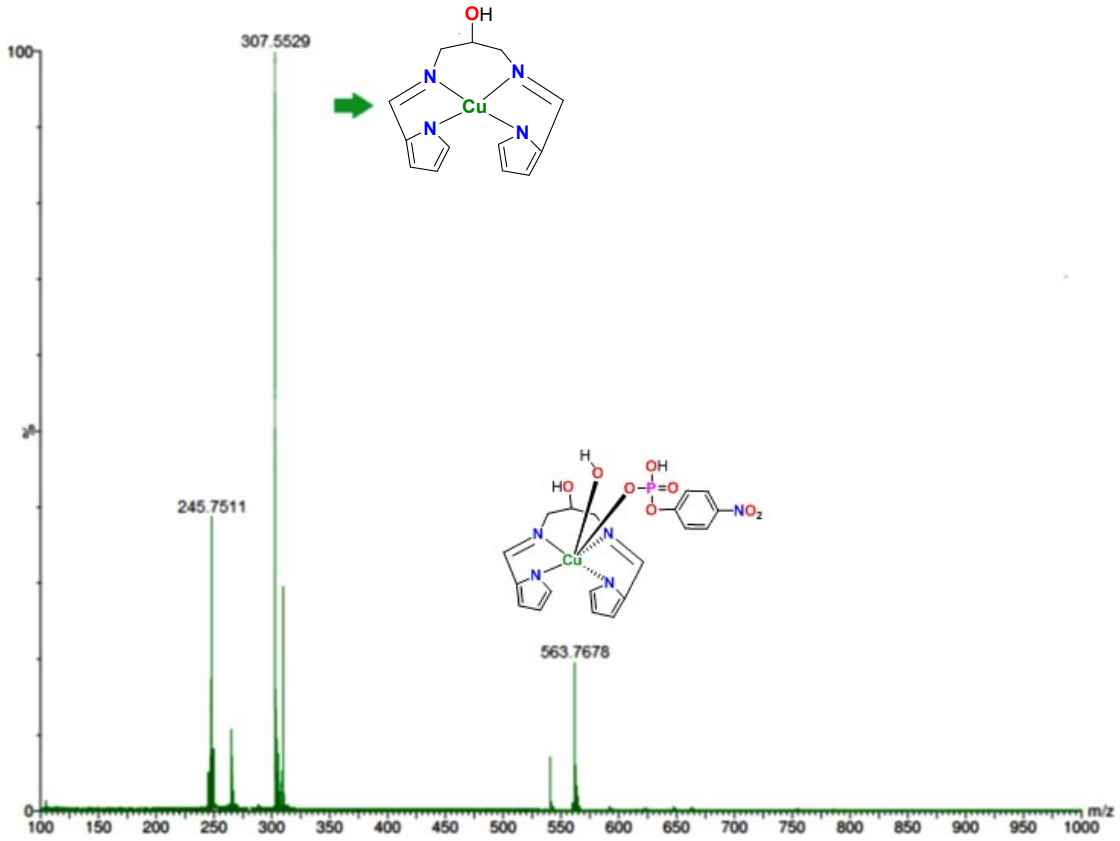


Fig. S13. ESI-Ms spectrum of the copper(II)-Schiff base complex in presence of pNPP in aq. methanol

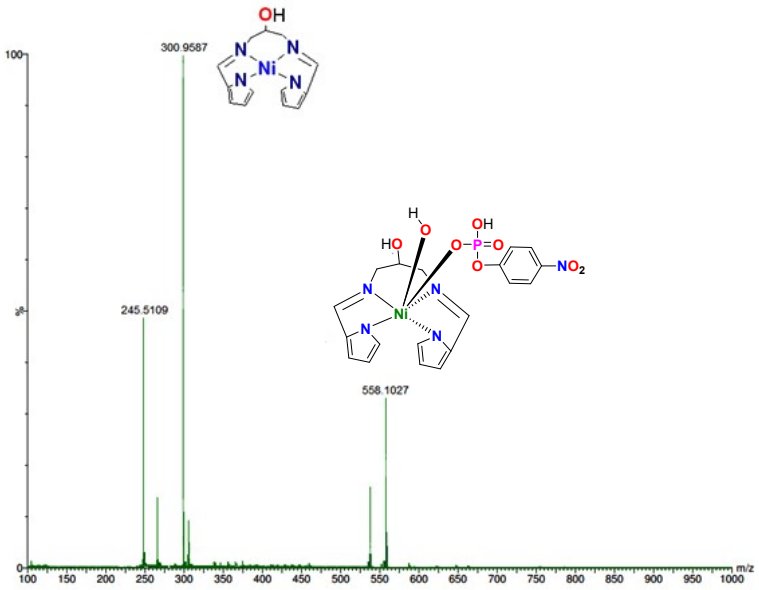


Fig. S14. ESI-Ms spectrum of the nickel(II)-Schiff base complex in presence of pNPP in aq. Methanol

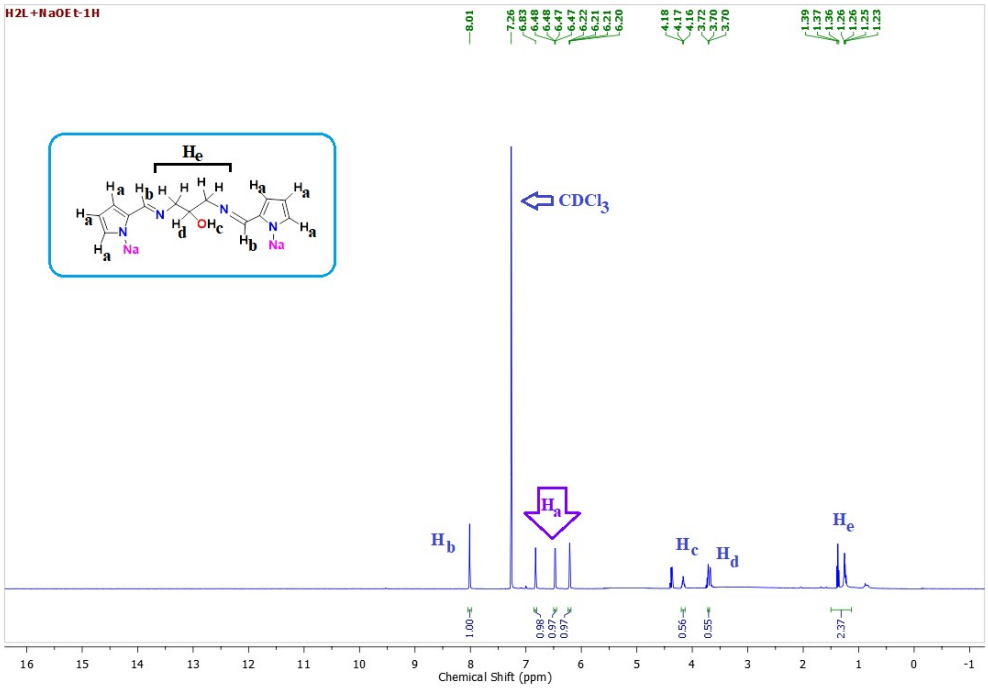


Fig. S15. ^{1}H NMR spectrum of the Na-salt of H_2**L** in $CdCl_3$.

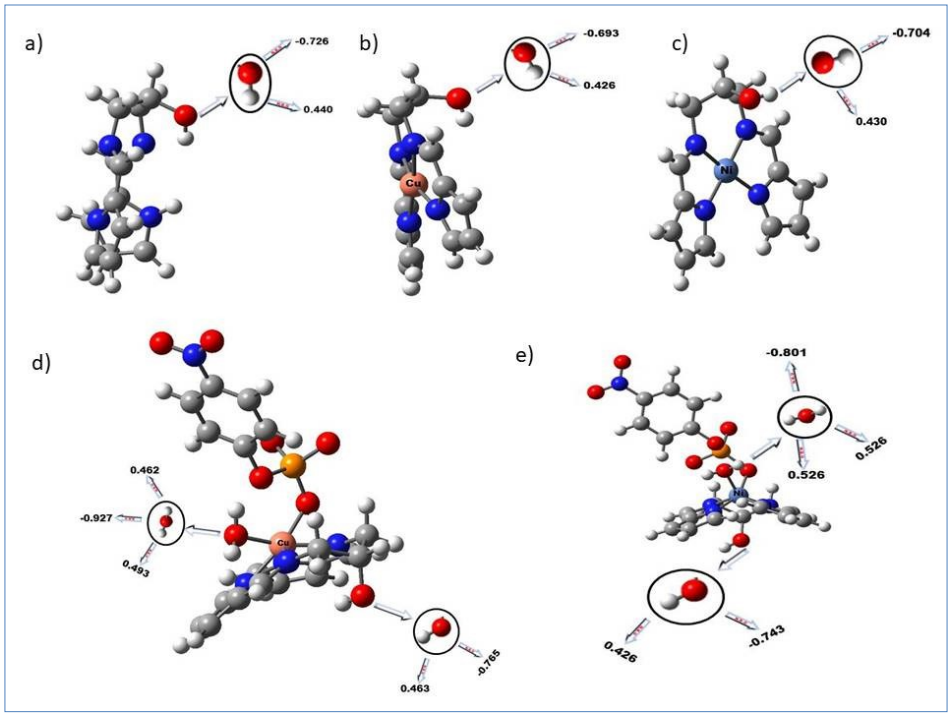


Fig. S16 Mulliken charge distribution on the oxygen and hydrogen atoms of the computationally optimized (a) ligand H_2L (b) complex1 (c) complex2 (d) complex 1+pNPP adduct (e) complex 2+pNPP adduct.

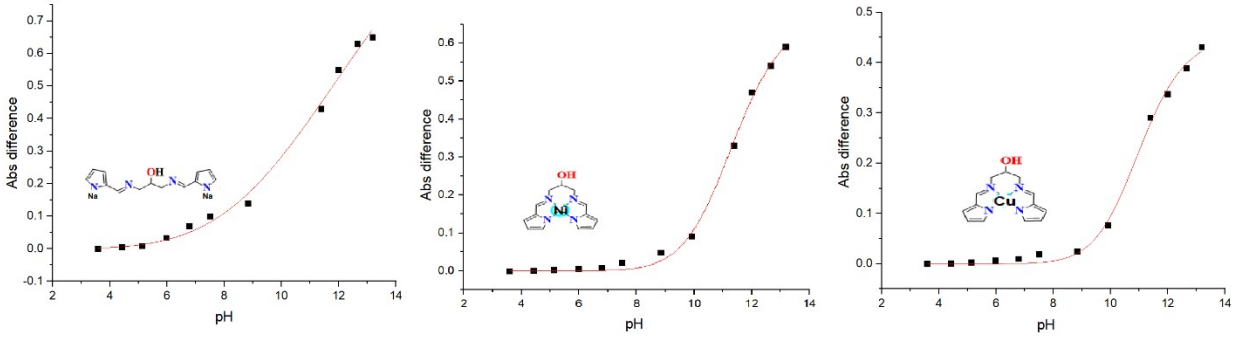


Fig.S17 Determination of the pka value of the ligand-OH in the Na salt of H_2L, complex1 and complex 2 using the difference of absorbance upon pH variation.

Table S1. Selected bond lengths (Å) and bond angles (°) for **1**

Bond length (Å)	XRD	DFT	Bond length (Å)	XRD	DFT
Cu1-N1	1.950(4)	1.972	Cu3 -N9	1.987(3)	1.987
Cu1-N2	1.973(4)	1.969	Cu3 -N10	2.000(3)	2.000
Cu1-N3	1.970(4)	2.022	Cu3 -N11	1.966(3)	1.966
Cu1-N4	1.999(4)	2.017	Cu3 -N12	1.958(3)	1.958
Cu2 -N1AA	1.993(4)	2.022	Cu4 -N14	1.999(3)	2.023
Cu2 -N0AA	1.978(4)	2.017	Cu4 -N16	1.984(3)	2.017
Cu2 -N7	1.958(3)	1.972	Cu4 -N13	1.962(3)	1.969
Cu2 -N8	1.948(3)	1.969	Cu4 -N15	1.958(3)	1.972

Bond angles (º)	XRD	DFT	Bond angles (º)	XRD	DFT
N1-Cu1 -N4	82.63(19)	82.780	N1A -Cu2-N0AA	91.44(14)	91.571
N1 -Cu1 -N2	103.5(2)	102.722	Cu2 -N1AA -C17	111.6(3)	111.439
N1 -Cu1 -N3	173.5(2)	171.786	N1AA-Cu2 -N7	173.14(14)	171.786
N3 -Cu1 -N4	91.34(15)	91.571	Cu2 -N1AA -C16	128.5(3)	128.124
N2 -Cu1 -N3	82.68(19)	82.897	N1AA -Cu2 -N8	82.92(14)	82.897
N2 -Cu1 -N4	173.34(17)	174.469	N0AA -Cu2 -N7	83.23(14)	82.780
Cu1 -N1 -C4	111.4(3)	111.488	Cu2 -N0AA -C14	126.6(3)	127.142
Cu1 -N1 -C1	141.2(5)	141.652	N0AA-Cu2-N8	174.28(15)	174.468
Cu1-N2-C10	110.7(3)	111.401	Cu2-N0AA-C26	112.2(3)	111.893
Cu1-N2-C13	142.5(5)	141.734	N7 -Cu2 -N8	102.47(15)	102.722
Cu1-N3-C8	126.9(3)	128.123	Cu2 -N7 -C25	110.6(3)	111.488
Cu1-N3-C9	112.4(3)	111.439	Cu2 -N7 -C22	142.4(3)	141.652
Cu1-N4-C0AA	127.9(3)	127.412	Cu2 -N8 -C21	143.1(3)	141.734
Cu1-N4-C1AA	111.4(3)	111.893	Cu2 -N8 -C18	111.6(3)	111.401
N10 -Cu3 -N11	170.61(13)	170.61	Cu3 -N12 -C34	141.8(3)	141.9
N9 -Cu3 -N10	91.71(13)	91.81	N14 -Cu4 -N15	166.81(13)	171.786
N10 -Cu3 -N12	82.96(13)	82.95	N13 -Cu4 -N16	173.52(13)	174.46
N11 -Cu3 -N12	103.22(14)	103.21	N14 -Cu4 -N16	91.55(13)	91.571

N9 -Cu3 -N12	173.47(13)	173.50	N15 -Cu4 -N16	83.00(13)	82.780
N9 -Cu3 -N11	82.55(14)	82.55	N13 -Cu4 -N14	83.03(13)	82.897
Cu3 -N9 -C27	127.4(2)	127.40	N13 -Cu4 -N15	103.05(13)	102.722
Cu3 -N9 -C39	112.3(3)	112.35	Cu4 -N13 -C45	143.3(3)	141.734
Cu3 -N10 -C30	111.6(2)	111.65	Cu4 -N13 -C48	110.0(2)	111.401
Cu3 -N10 -C29	128.1(2)	128.21	Cu4 -N14 -C49	111.1(3)	111.439
Cu3 -N11 -C35	142.8(3)	143.1	Cu4 -N14 -C50	128.7(3)	128.123
Cu3 -N11 -C38	111.1(3)	111.2	Cu4 -N15 -C44	142.2(3)	141.652
Cu3 -N12 -C31	111.1(2)	111.2	Cu4 -N15-C41	110.9(3)	111.488
Cu4 -N16 -C52	126.8(2)	127.142	Cu4 -N16-C40	111.9(3)	111.893

Table S2. Selected bond lengths (Å) and bond angles (°) for **2**

Bond length (Å)	XRD	DFT	Bond length (Å)	XRD	DFT
Ni2 - N3	1.891(2)	1.890	Ni1 -N27	1.913(2)	1.931
Ni2 - N9	1.9030(19)	1.902	Ni1 -N31	1.897(2)	1.922
Ni2 -N13	1.904(2)	1.904	Ni1 -N21	1.895(2)	1.897
Ni2 -N16	1.8944(19)	1.893	Ni1 -N34	1.888(2)	1.899

Bond angles (º)	XRD	DFT	Bond angles (º)	XRD	DFT
N3 -Ni2-N9	83.99(9)	84.004	N27-Ni1-N34	171.80(8)	172.11
N3 -Ni2-N13	175.35(9)	175.33	Ni1 -N34 -C35	112.79(17)	112.66
N3 -Ni2 -N16	98.25(9)	98.265	N31-Ni1-N34	83.79(9)	98.52
N9 -Ni2-N13	93.62(8)	93.596	Ni1-N34 -C38	140.60(18)	140.33
N9 -Ni2-N16	177.67(9)	177.636	N21-Ni1-N27	83.72(9)	83.92
Ni1-N21-C25	141.62(19)	140.67	N21-Ni1-N31	177.69(9)	175.77
Ni1-N21-C22	112.13(15)	112.45	Ni2 -N3-C7	141.35(19)	141.336
Ni1-N27-C26	113.44(17)	112.74	Ni2 -N3-C4	112.38(17)	112.36
Ni1 -N27-C28	128.26(17)	128.07	Ni2 -N9-C8	113.95(16)	113.93
Ni1-N31-C30	126.37(17)	126.29	Ni2 -N9-C10	127.76(17)	127.797
N13-Ni2-N16	84.10(8)	83.93	Ni2 -N13-C12	128.03(17)	128.033

N21-Ni1-N34	98.49(9)	98.52	Ni2 -N13-C14	113.33(17)	113.286
Ni1 -N31-C32	114.38(16)	113.51	Ni2 -N16-C20	141.64(19)	141.629
N27 -Ni1-N31	93.97(9)	94.24	Ni2 -N16-C17	111.76(15)	111.771

Table S3. NBO charge distribution of the key intermediates of complex 1 and complex 2

Complex 1	NBO(q)	Complex 2	NBO(q)
Cu1	1.598	Ni1	1.393
P 34	2.161	P37	2.213
O52	-0.927	O34	-0.801
H53	0.462	H35	0.476
H54	0.438	H36	0.433
O36	-1.070	O39	-1.024
O37	-0.887	O40	-1.010
O35	-1.001	O38	-1.007
O51	-0.805	O54	-0.692

Coordinates of all the optimized geometries

Complex 1

Cu	5.711	13.043	6.366
N	4.315	12.152	7.416
N	6.231	11.165	5.917
N	5.614	14.898	6.984
N	7.105	13.774	5.157
O	9.103	11.903	6.015
H	8.576	11.98	6.638
C	4.553	10.796	7.462
C	5.587	10.322	6.643
H	5.804	9.418	6.625
C	5.035	15.682	7.919
H	4.357	15.404	8.493

C	2.834	11.179	8.8
H	2.122	11.072	9.389
C	3.262	12.379	8.236
H	2.882	13.212	8.401
C	7.346	15.003	5.399
H	8.019	15.453	4.942
C	3.647	10.193	8.332
H	3.607	9.29	8.553
C	7.931	13.018	4.209
H	8.706	13.549	3.961
H	7.419	12.84	3.405
C	6.568	15.666	6.372
C	5.584	16.951	7.911
H	5.345	17.664	8.459
C	8.387	11.712	4.817
H	9.018	11.317	4.18
C	7.252	10.699	4.982
H	6.842	10.537	4.116
H	7.618	9.859	5.3
C	6.559	16.946	6.925
H	7.103	17.658	6.68

Complex 2

Ni	0.238	8.774	6.831
O	2.176	7.192	4.391
H	1.618	6.707	3.991

N	-0.3	8.688	5.008
N	2.051	9.169	6.402
N	0.848	8.859	8.622
N	-1.546	8.252	7.176
C	2.218	8.963	8.69
C	-2.292	8.137	6.021
C	-1.55	8.383	4.842
H	-1.943	8.326	3.979
C	2.84	9.15	7.436
H	3.78	9.257	7.352
C	2.631	9.415	5.084
H	3.601	9.215	5.109
H	2.521	10.37	4.849
C	1.968	8.557	4.026
H	2.448	8.715	3.163
C	0.517	8.932	3.82
H	0.462	9.891	3.58
H	0.152	8.408	3.063
C	0.409	8.75	9.903
H	-0.502	8.673	10.161
C	1.487	8.765	10.783
H	1.443	8.698	11.73
C	-3.574	7.682	6.312
H	-4.278	7.519	5.694
C	-2.36	7.855	8.193

H	-2.111	7.817	9.11
C	2.639	8.897	10.02
H	3.533	8.934	10.338
C	-3.612	7.514	7.688
H	-4.359	7.219	8.196

Coordinates of all the optimized geometries of the metal complexes with pNPP (1+pNPP)

Cu adduct-

Cu	-1.22527	-0.17584	-2.28604
N	0.01298	-1.43282	-1.66998
N	0.12767	0.95871	-1.55411
N	-2.36347	-1.38729	-1.43131
N	-2.65373	0.95924	-1.71738
O	-1.4435	2.43294	0.38457
H	-1.44123	1.47284	0.38376
C	1.11255	-0.98728	-1.17245
C	1.2097	0.37454	-1.10718
H	2.06351	0.89929	-0.73057
C	-2.22377	-2.68223	-1.0989
H	-1.3459	-3.27825	-1.23345
C	1.2432	-3.17197	-1.08084
H	1.56946	-4.17786	-0.91679
C	0.00276	-2.77087	-1.62755
H	-0.79032	-3.41307	-1.94832

C	-3.74211	0.37289	-1.29883
H	-4.67015	0.8734	-1.11718
C	1.94449	-2.03963	-0.80194
H	2.92692	-1.97219	-0.38238
C	-2.58256	2.42224	-1.72576
H	-3.43252	2.81219	-1.20642
H	-2.58642	2.77185	-2.73705
C	-3.52769	-0.95961	-1.0889
C	-3.41376	-3.10161	-0.56324
H	-3.63888	-4.08707	-0.21223
C	-1.33336	2.91208	-0.95866
H	-1.33295	3.98224	-0.97342
C	0.02269	2.42942	-1.51318
H	0.17646	2.80913	-2.5017
H	0.77761	2.80751	-0.85582
C	-4.28167	-1.99759	-0.56186
H	-5.29634	-1.9638	-0.22355
P	-1.62176	0.67792	-5.01718
O	-0.98208	1.57181	-6.32761
O	-0.56293	0.77578	-3.70363
O	-1.8124	-0.95677	-5.48341
C	-5.75286	0.14879	-6.97018
C	-4.86703	0.17609	-5.88356
C	-4.03805	1.2894	-5.68423
C	-4.0895	2.36938	-6.57652

C	-4.97429	2.3399	-7.66263
C	-5.80636	1.23062	-7.85873
H	-6.38839	-0.69828	-7.1212
H	-4.82543	-0.65179	-5.20671
H	-3.45341	3.2165	-6.42837
H	-5.01499	3.16529	-8.34193
N	-6.73491	1.20305	-8.99766
O	-7.47141	0.22363	-9.17245
O	-6.78072	2.15909	-9.78199
O	-3.13981	1.32783	-4.57055
O	-1.91608	-1.00379	-3.76432
H	-2.1707	-1.46005	-4.74851
H	-2.87141	-1.05336	-3.68526

Ni adduct-

(2+pNPP)

Ni	-0.158	11.95749	6.51182
O	1.93938	9.89896	4.23006
H	1.5963	9.31546	3.54907
N	-0.53228	11.14855	4.83874
N	1.71784	11.97068	6.2494
N	0.44059	11.63972	8.23433
N	-1.27044	10.55471	6.99239
C	1.71411	11.64655	8.43259

C	-1.87065	9.91258	6.04986
C	-1.50608	10.2831	4.7942
H	-1.93824	9.89618	3.89508
C	2.46617	11.84515	7.31328
H	3.53511	11.88698	7.30639
C	2.35384	12.15569	4.93151
H	3.3855	11.88083	5.00756
H	2.27089	13.18648	4.656
C	1.7313	11.25963	3.84118
H	2.23483	11.46413	2.91956
C	0.21407	11.44587	3.61217
H	-0.01668	12.43882	3.28674
H	-0.07071	10.74411	2.85594
C	-0.21226	11.38831	9.38116
H	-1.27163	11.30572	9.5046
C	0.76374	11.25796	10.39345
H	0.58719	11.06364	11.43051
C	-2.74578	8.9654	6.56993
H	-3.40212	8.31615	6.02942
C	-1.61319	10.05346	8.19095
H	-1.2365	10.36645	9.14218
C	2.00899	11.43228	9.7744
H	2.97487	11.40355	10.23259
C	-2.57169	9.04201	7.9589
H	-3.06788	8.44954	8.69901

O	-1.59975	12.96454	6.94003
H	-1.45289	13.38778	7.78914
H	-2.13261	11.96665	4.60709
P	-1.1732	14.22856	5.24316
O	-0.84503	15.76258	4.5623
O	0.19693	13.57333	5.77749
O	-1.86445	13.21318	4.05359
C	-5.71818	14.73196	5.15578
C	-4.52296	14.16168	5.61611
C	-3.48422	14.98484	6.07256
C	-3.63929	16.37745	6.06572
C	-4.83385	16.94739	5.60591
C	-5.874	16.1252	5.15254
H	-6.51117	14.10338	4.80719
H	-4.4034	13.09817	5.61919
H	-2.8455	17.00591	6.4118
H	-4.95245	18.01067	5.60091
N	-7.12759	16.72609	4.67402
O	-8.04849	16.00289	4.27322
O	-7.26199	17.95672	4.67266
O	-2.26629	14.40471	6.54594