Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting material

for

Radical pathway and O_2 participation in benzyl alcohol oxidation, catechol and aminophenol oxidase activity studies with novel zinc complexes: functional modeling of galactose oxidase enzyme, Experimental and theoretical investigation

*Ashish Kumar Dhara, Udai Pratap Singh, Kaushik Ghosh**

Department of Chemistry, Indian Institute of Technology, Roorkee, Roorkee-247667, Uttarakhand, INDIA

Corresponding author: Kaushik Ghosh. Email: ghoshfcy@iitr.ernet.in

Fax: +91-1332-273560

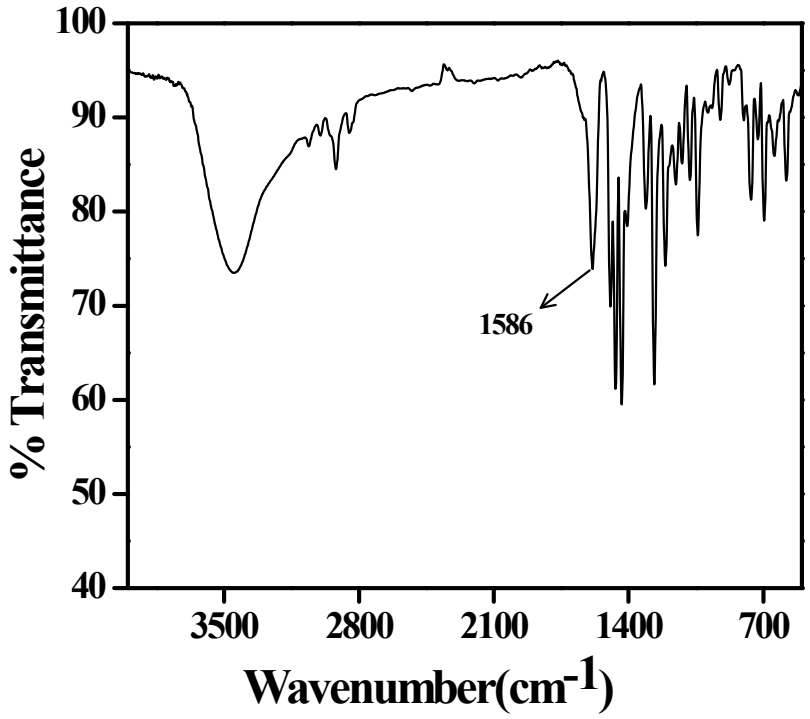


Figure S1. Infrared spectrum of ligand OMe-PhimpH . IR (KBr disk, cm^{-1}): 1586 (νC=N) cm^{-1}.

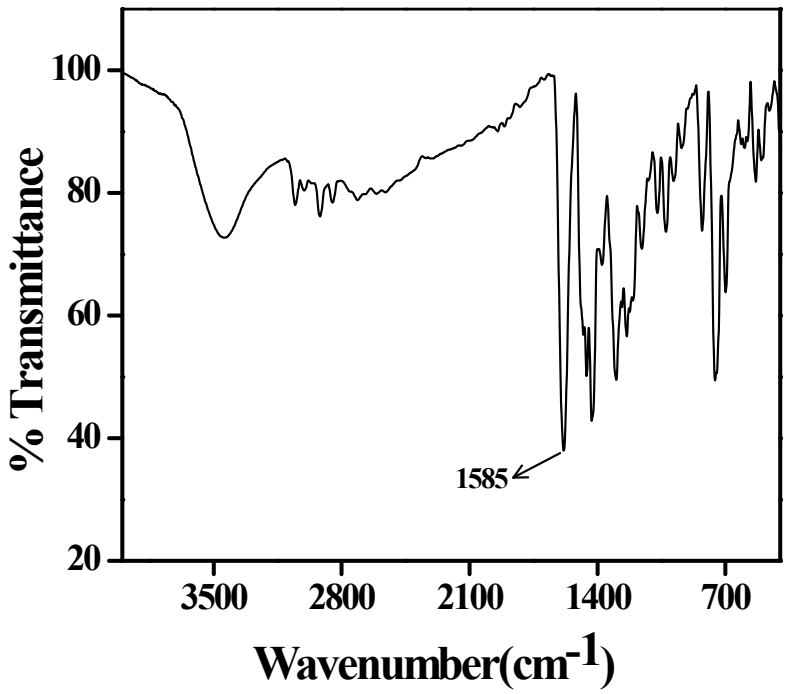


Figure S2. Infrared spectrum of ligand Me-PhimpH . IR (KBr disk, cm^{-1}): 1585 (νC=N) cm^{-1}.

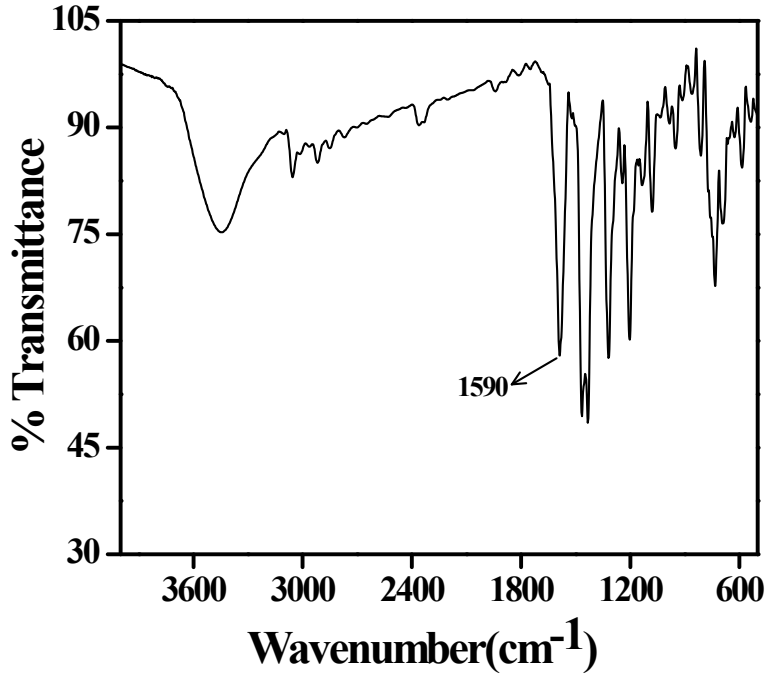


Figure S3. Infrared spectrum of ligand N-PhimpH. IR (KBr disk, cm^{-1}): 1590 (νC=N) cm^{-1}.

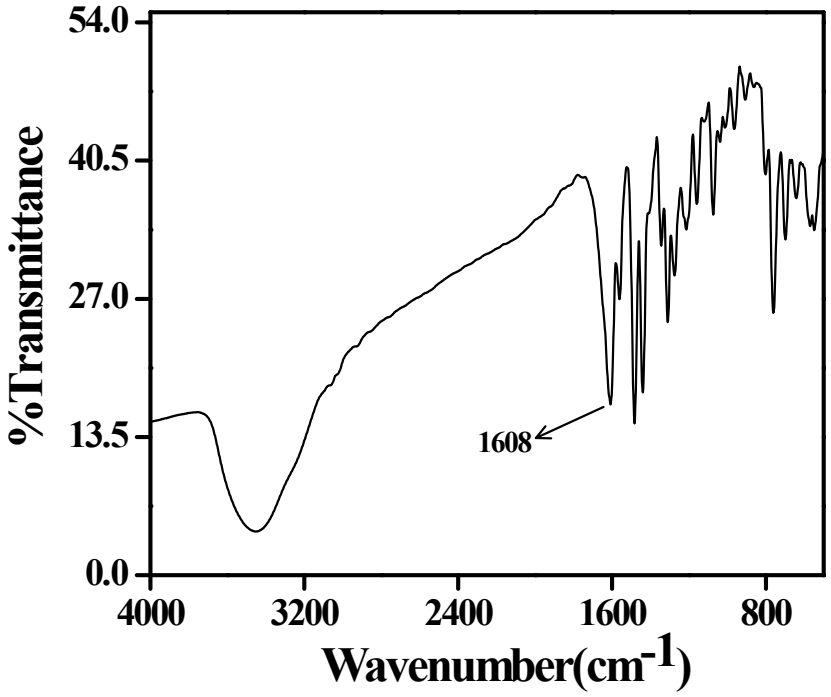


Figure S4. Infrared spectrum of ligand PhimpH. IR (KBr disk, cm^{-1}): 1608 (νC=N) cm^{-1}.

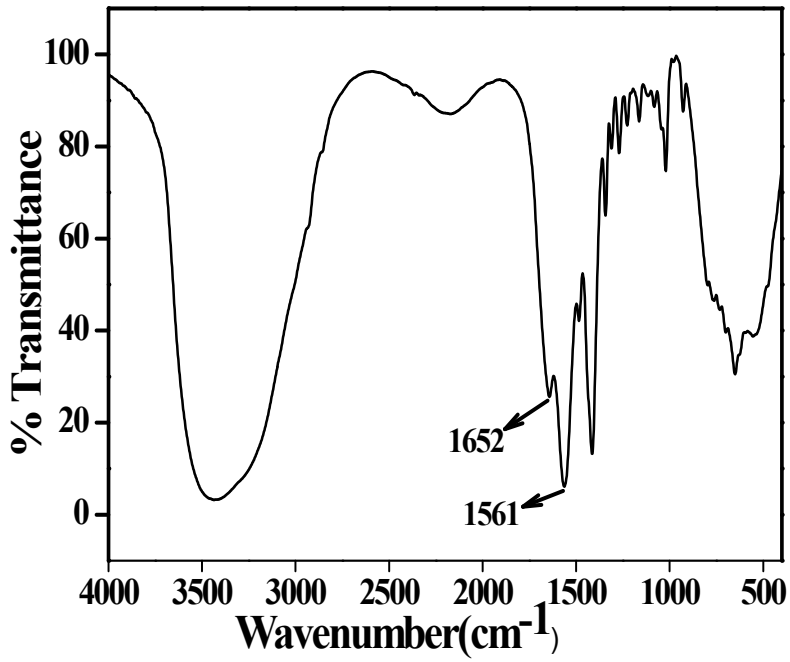


Figure S5. Infrared spectrum of complex **1**. IR (KBr disk, cm^{-1}): 1652 (νC=N) cm^{-1}.

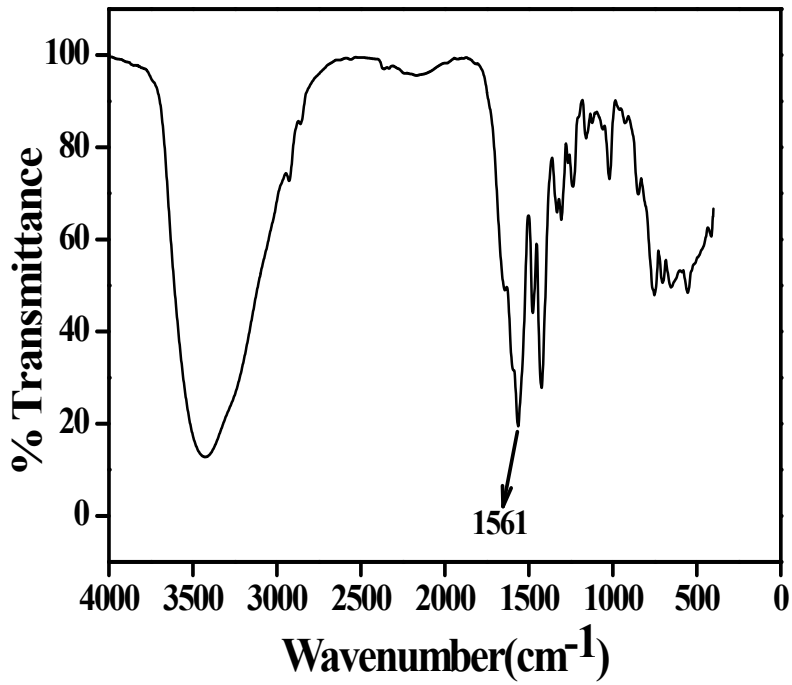


Figure S6. Infrared spectrum of complex **2**. IR (KBr disk, cm^{-1}): 1561 (νC=N) cm^{-1}.

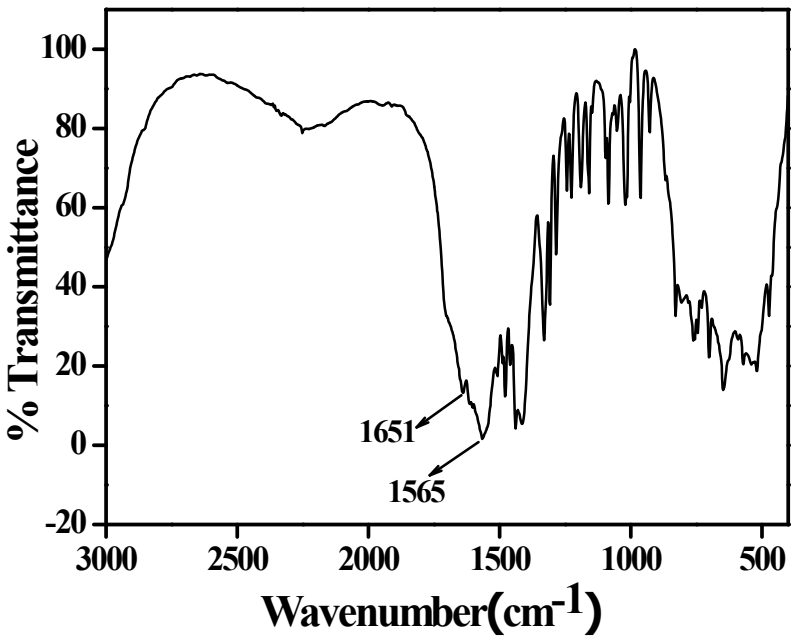


Figure S7. Infrared spectrum of complex **3**. IR (KBr disk, cm^{-1}): 1651 (νC=N) cm^{-1}.

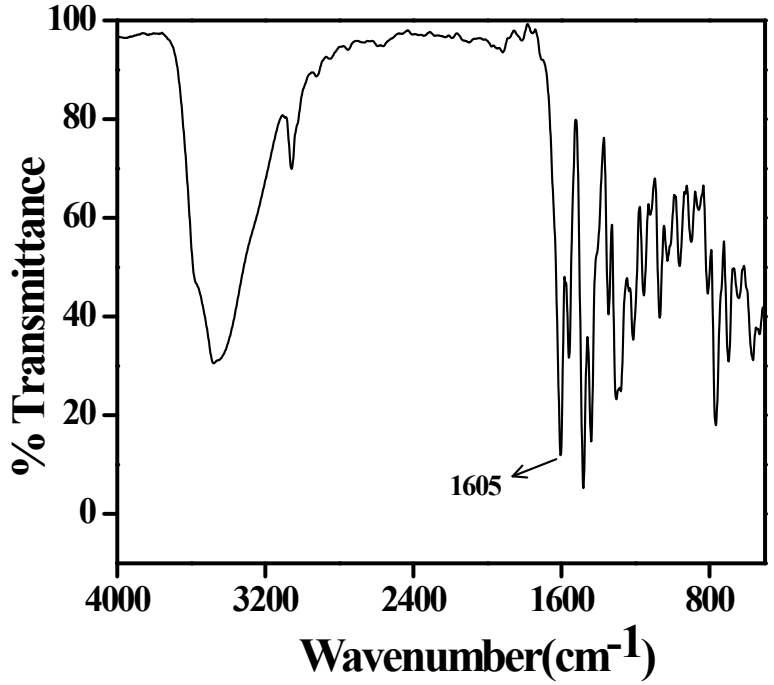


Figure S8. Infrared spectrum of complex **4**. IR (KBr disk, cm^{-1}): 1605 (νC=N) cm^{-1}.

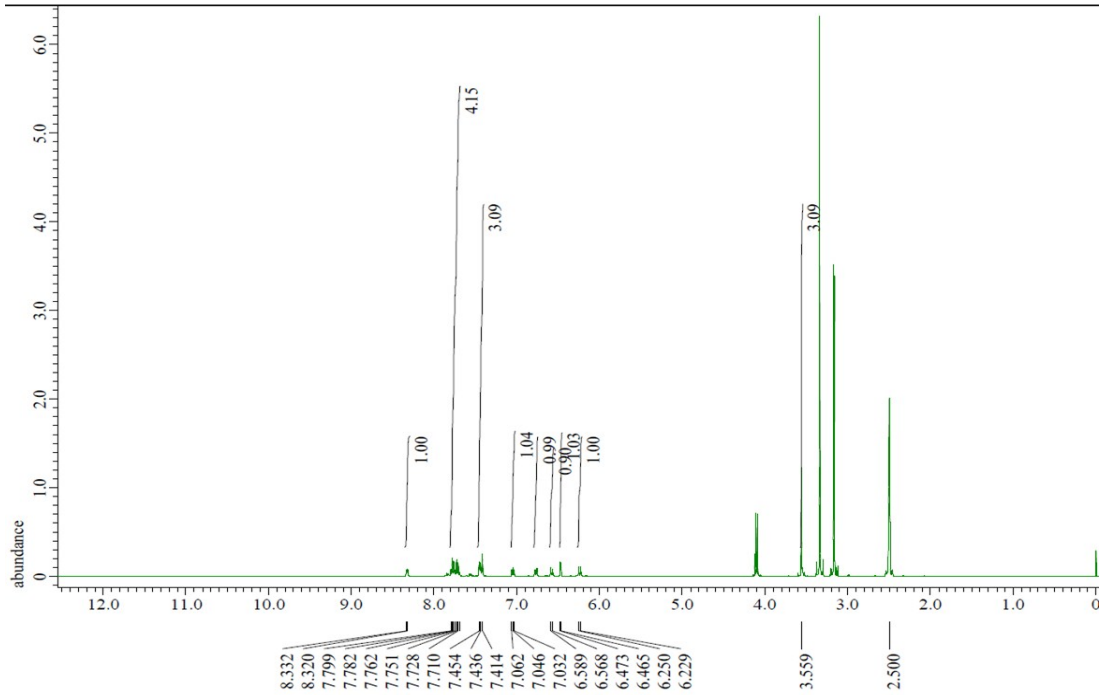


Figure S9. ^{1}H NMR spectrum of complex **1** in DMSO at room temperature.

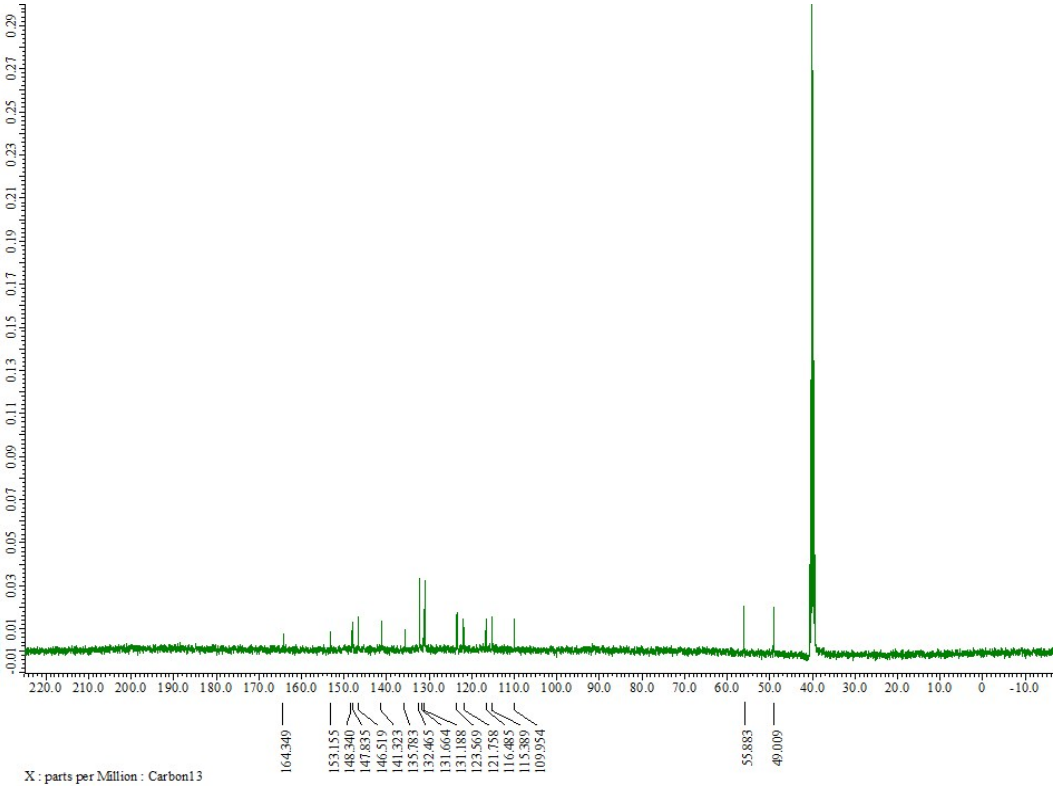


Figure S10. ^{13}C NMR spectrum of complex **1** in DMSO at room temperature.

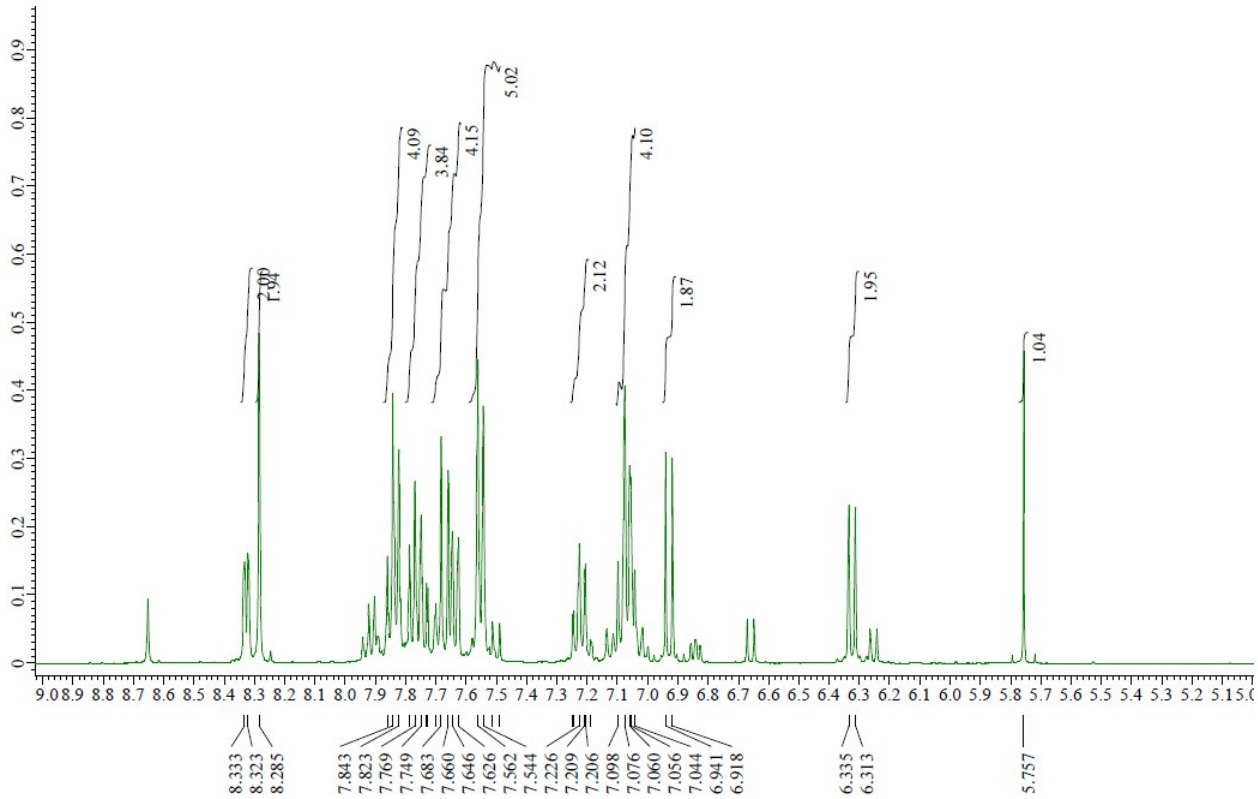


Figure S11. ^{1}H NMR spectrum of complex **3** in DMSO at room temperature.

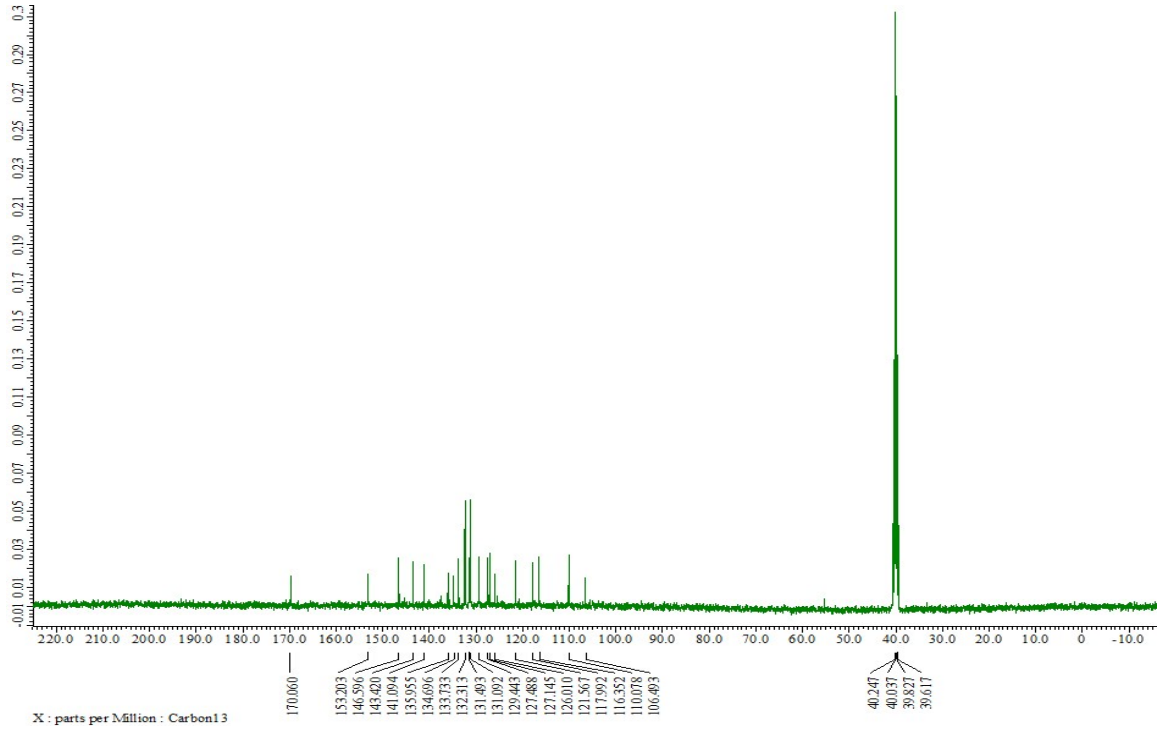


Figure S12. ^{13}C NMR spectrum of complex **3** in DMSO at room temperature.

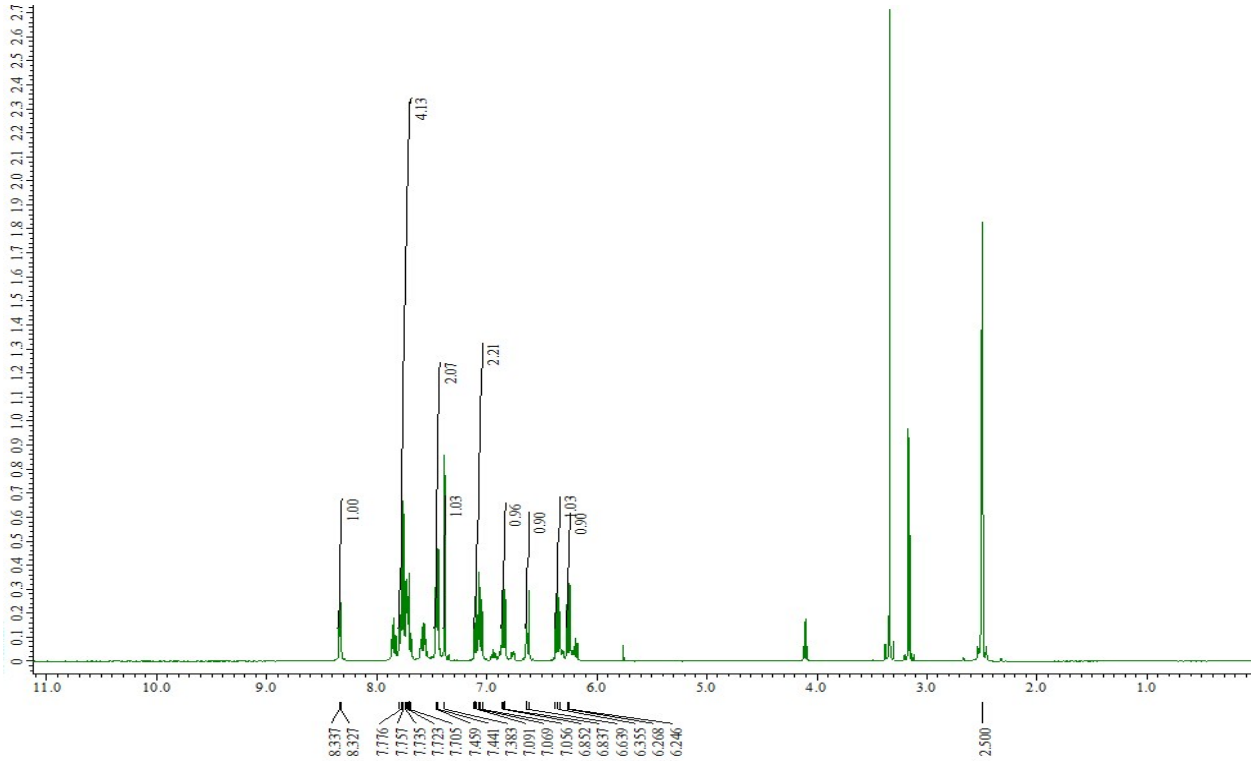


Figure S13. ^{1}H NMR spectrum of complex **4** in DMSO at room temperature.

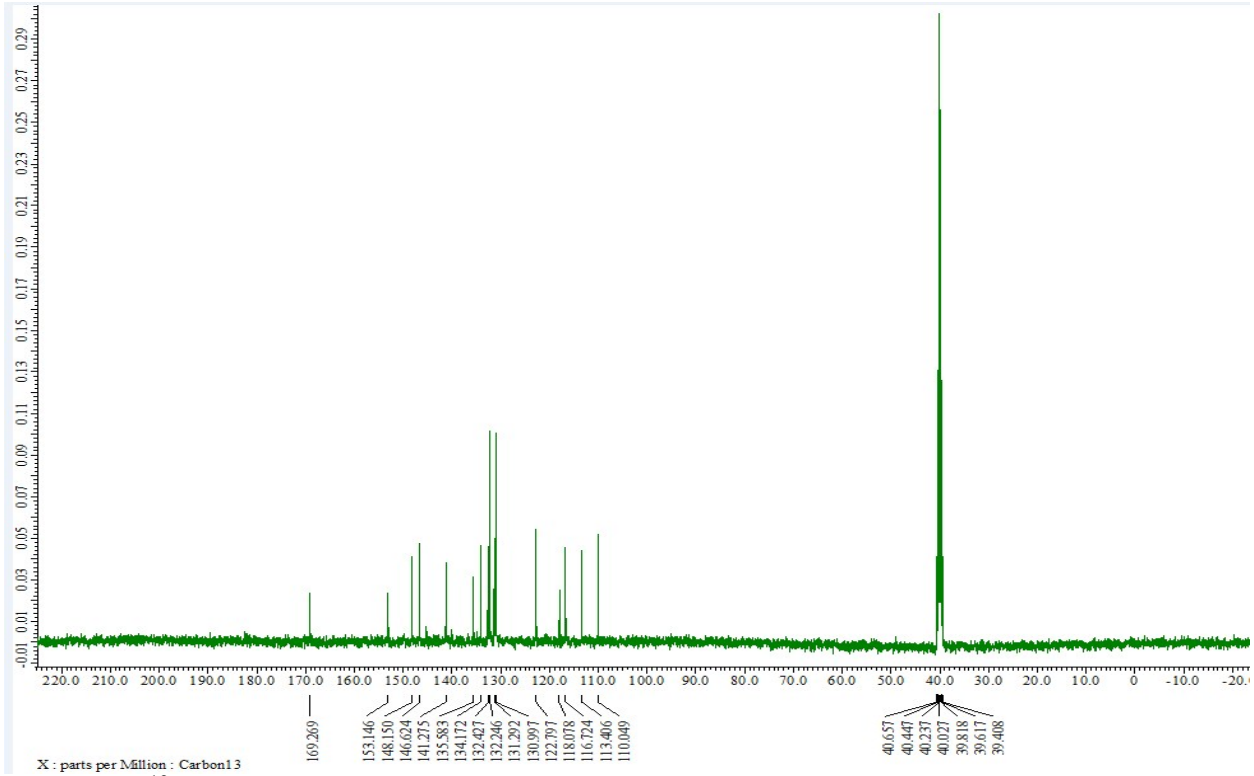


Figure S14. ^{13}C NMR spectrum of complex **4** in DMSO at room temperature.

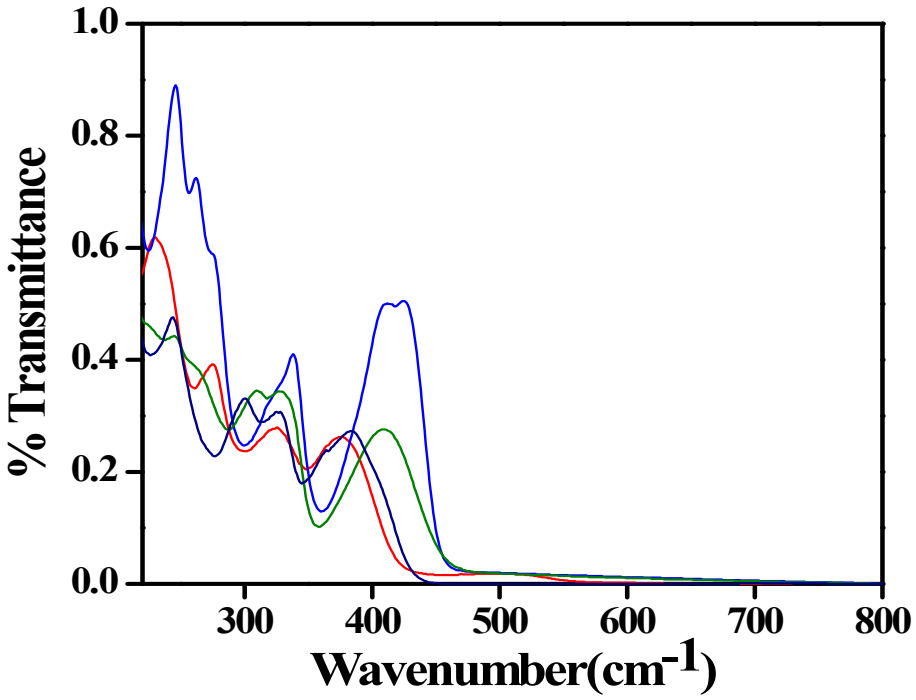


Figure S15. Electronic absorption spectra of **1** (—), **2** (—), **3**.CH_3CN (—), and **4** (—) in acetonitrile solvent.

Table S1 Non-covalent interactions observed in the packing diagrams of complex **1** and complex **3**.CH_3CN.

	Distance (Å)	Comments
		1
1.	(H21…Cl2) 2.763	Intermolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring
2.	(H18…Cl1) 2.799	Intramolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring
3.	(H1… Cl2) 2.791	Intramolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring
		3.CH_3CN
1.	(H24…Cl5) 2.845	Intermolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring
2.	(H6…Cl5) 2.769	Intramolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring
3.	(H17…Cl3) 2.840	Intramolecular hydrogen bonding between chloride ion and aryl hydrogen of phenyl ring

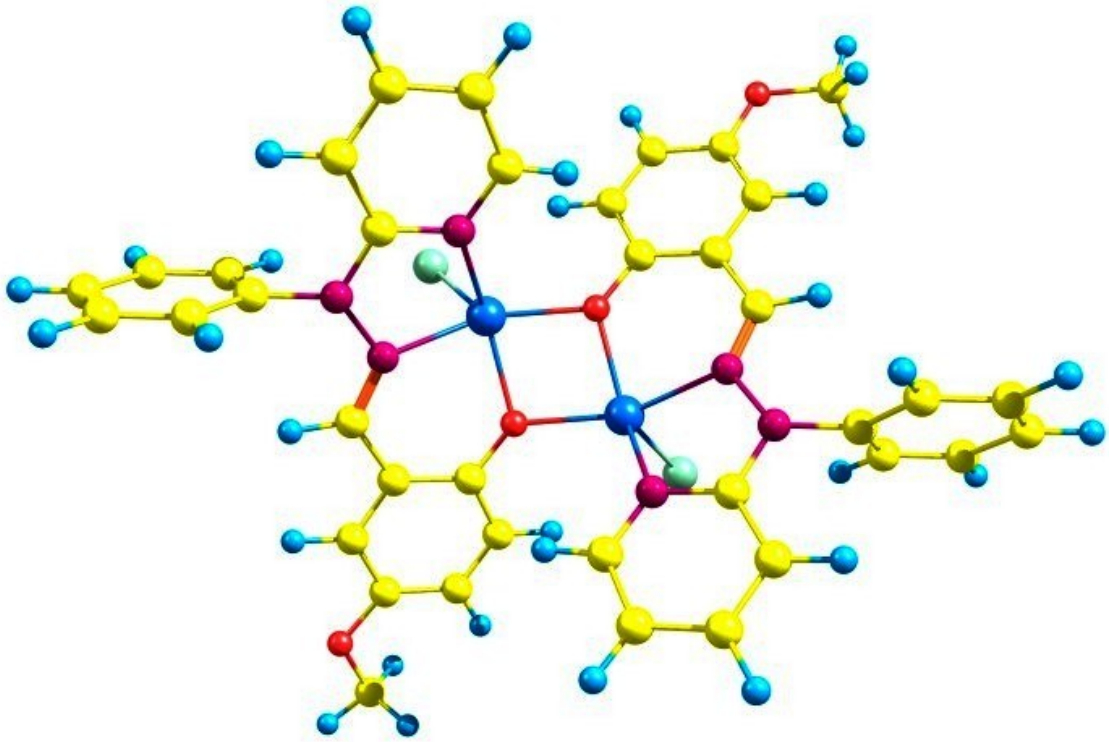


Figure S16. Optimized structure of complex **1**.

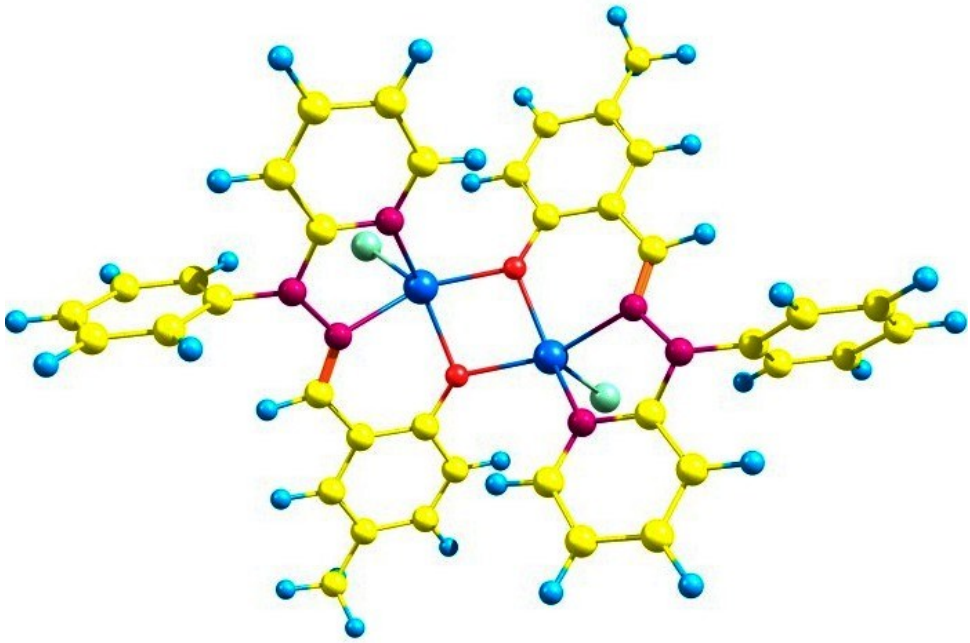


Figure S17. Optimized structure of complex **2.**

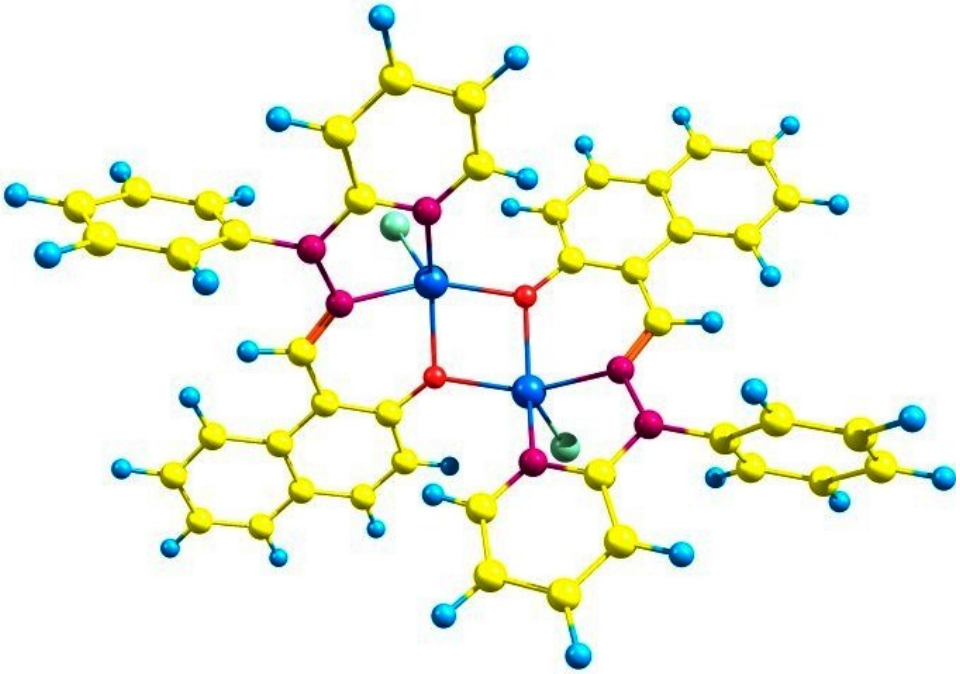


Figure S18. Optimized structure of complex **3**.CH_3CN.

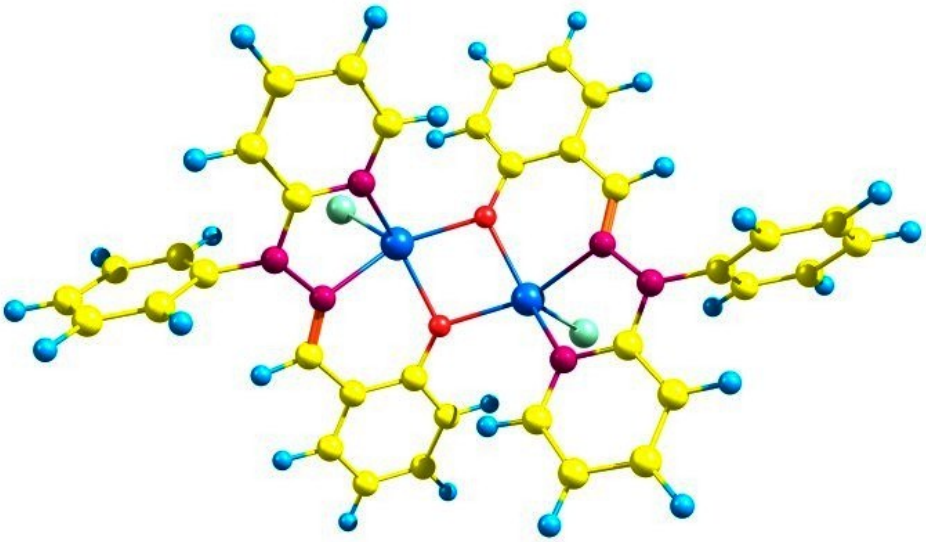
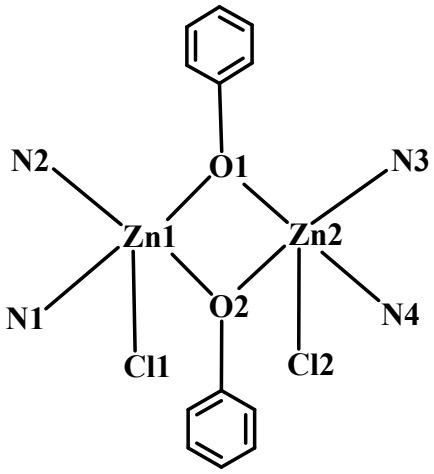
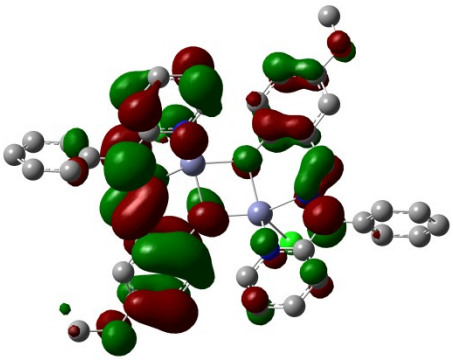
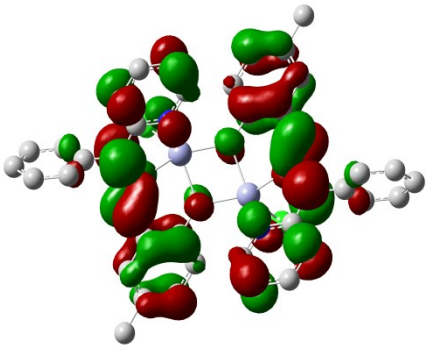
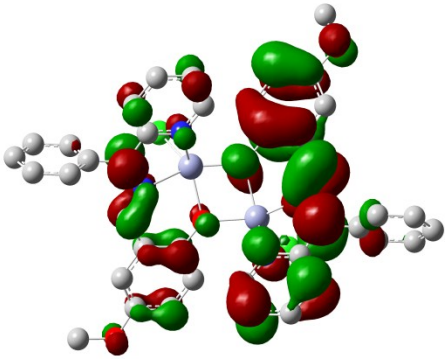
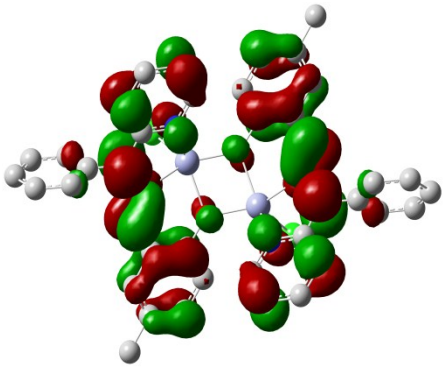
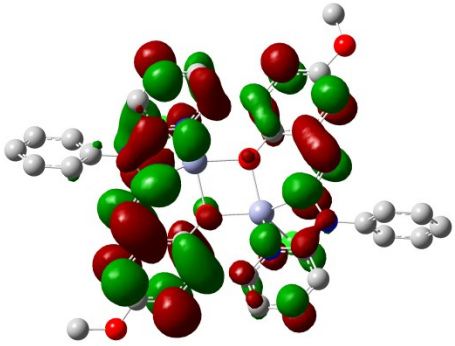
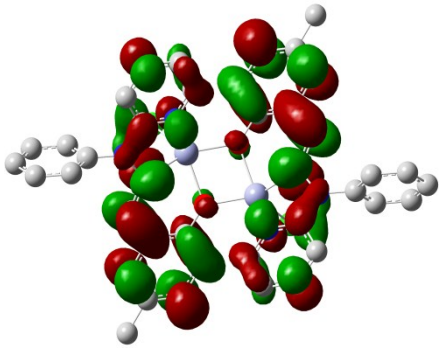


Figure S19. Optimized structure of complex **4**

Table S2. Experimental and theoretical bond length data of complexes **1** and **3**.CH_3CN



Bond length	Complex **1**		Complex **3**.CH_3CN	
	X-Ray	DFT	X-Ray	DFT
Zn1-O1	2.044	2.055	2.045	2.067
Zn1-O2	2.039	2.056	2.028	2.069
Zn2-O1	2.064	2.062	2.022	2.069
Zn2-O2	2.039	2.049	2.079	2.067
Zn1-N1	2.156	2.181	2.134	2.162
Zn1-N2	2.120	2.167	2.084	2.163
Zn2-N3	2.149	2.062	2.147	2.162
Zn2-N4	2.110	2.049	2.073	2.163
Zn1-Cl1	2.237	2.370	2.229	2.357
Zn2-Cl2	2.231	2.373	2.226	2.358

	Complex **1**	Complex **2**
HOMO		
HOMO-1		
LUMO		

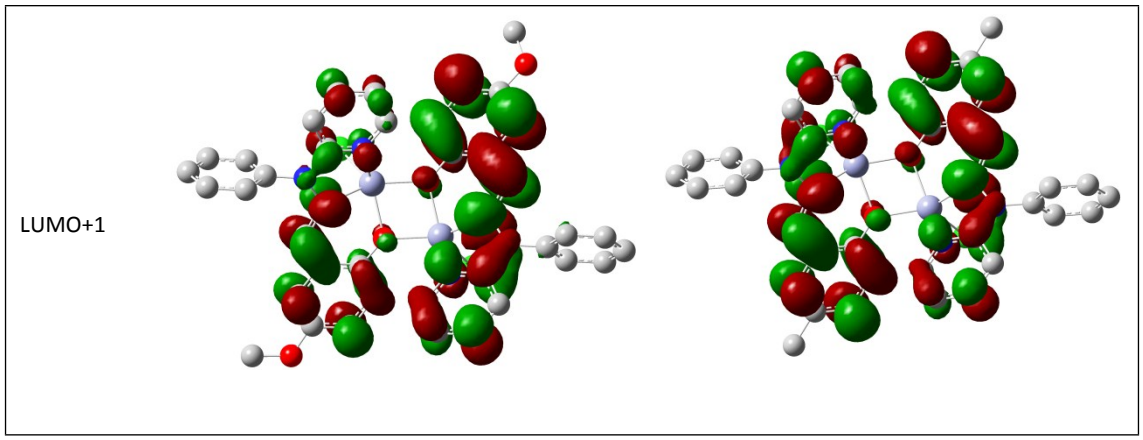
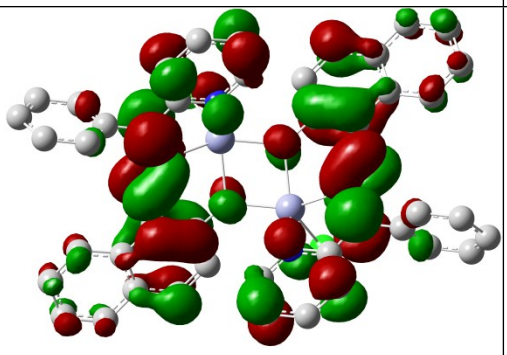
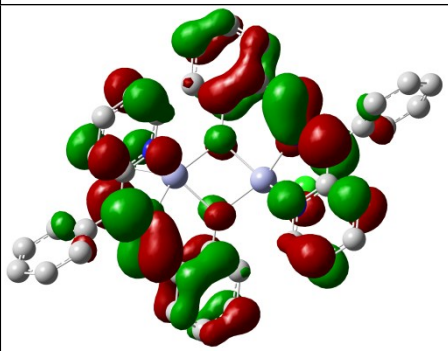


Figure S20. HOMO LUMO diagram of complexes **1** and **2**.

	Complex **3**	Complex **4**
HOMO		

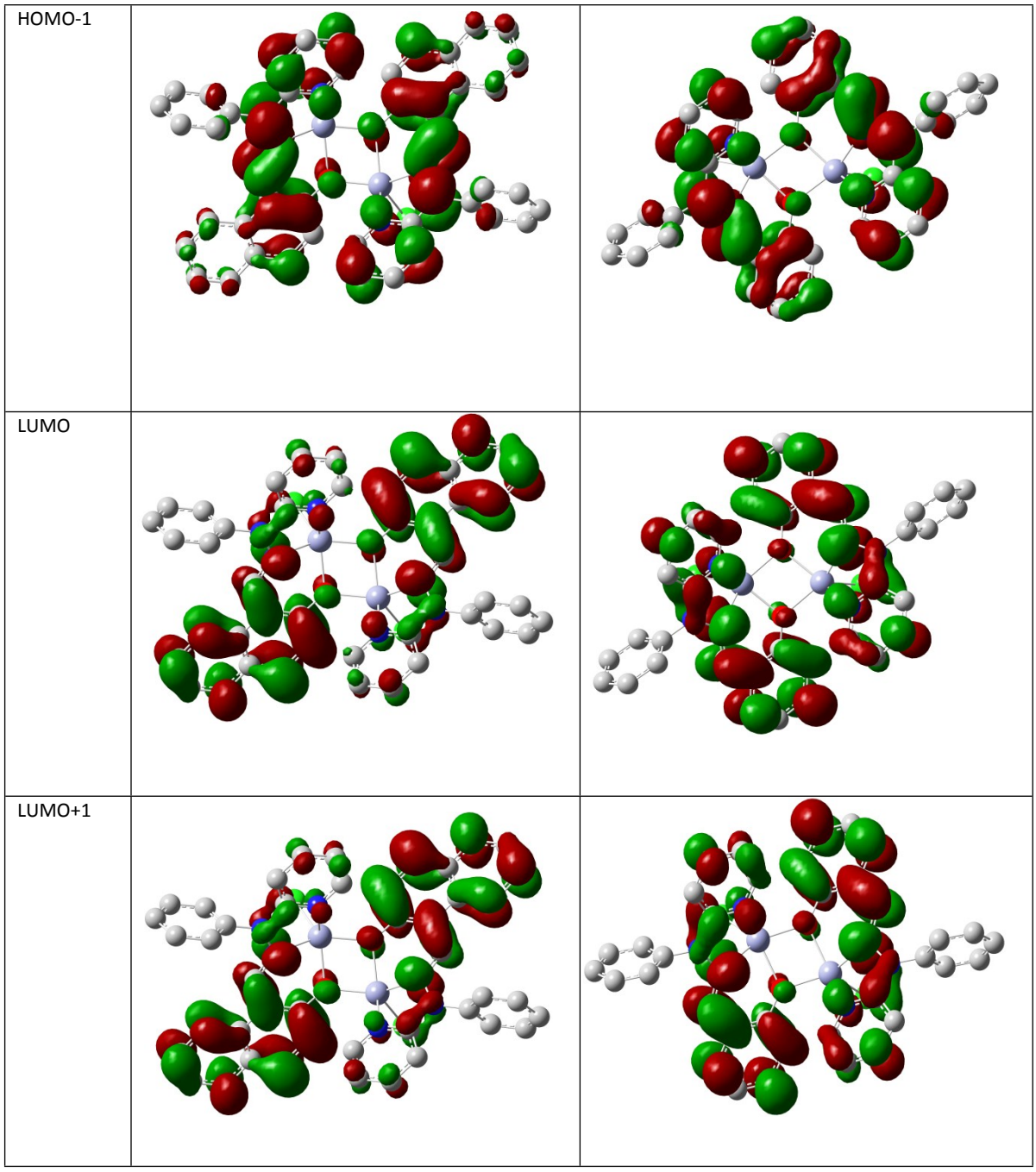


Figure S21. HOMO LUMO diagram of complexes **3** and **4.**

Table S3 Data for yield, elemental analysis and IR spectral studies.

Complex	Yield (%)	Elemental analysis			IR data (cm^{-1}, KBr pellets)
		C	H	N	$\nu_{C=N}$
1	71	54.10	3.03	9.55	1652
2	74	56.60	4.00	10.42	1561
3	74	60.33	3.34	9.21	1651
4	81	55.60	3.78	10.11	1605

Table S4 Frontier molecular orbital composition in the ground state for complex **2**

Orbital	Energy	Contribution					Main bond type
		Zn	O	N	Cl	Phenolato ring	
L+5	–1.2460	0	0	5	0	0	π*(L)
L+4	–1.2465	0	0	5	0	0	π*(L)
L+3	–1.3796	0	1	15	0	14	π*(L)+ π*(Phenolato ring)
L+2	–1.4261	0	0	14	0	13	π*(L)+ π*(Phenolato ring)
L+1	–1.8805	1	4	20	0	39	π*(L)+ π*(Phenolato ring)
L	–1.8969	1	3	21	0	38	π*(L)+ π*(Phenolato ring)
H	–5.3712	0	11	22	2	67	π (L)+ π (Phenolato ring)
H-1	–5.4314	1	9	22	3	66	π (L)+ π (Phenolato ring)
H-2	–6.1302	2	6	2	51	39	π(L)+ π(Phenolato ring)+n(Cl)
H-3	–6.1800	5	1	1	92	2	π(L)+ π(Phenolato ring)+n(Cl)
H-4	–6.2020	3	1	1	90	4	π(L))+n(Cl)+π(Phenolato ring)
H-5	–6.2085	2	5	1	51	43	π(L))+n(Cl)+π(Phenolato ring)

Table S5 Frontier molecular orbital composition in the ground state for complex **3**

Orbital	Energy	Contribution					Main bond type
		Zn	O	N	Cl	Phenolato ring	
L+5	–1.1197	0	0	4	0	0	π*(L)
L+4	–1.1200	0	0	4	0	0	π*(L)
L+3	–1.2432	0	1	15	0	9	π*(L)+ π*(Phenolato ring)
L+2	–1.2884	0	1	15	0	11	π*(L)+ π*(Phenolato ring)
L+1	–1.7292	1	2	23	1	21	π*(L)+ π*(Phenolato ring)
L	–1.7478	2	2	23	0	21	π*(L)+ π*(Phenolato ring)
H	–5.3938	0	19	17	2	65	π (L)+ π (Phenolato ring)
H-1	–5.4736	1	15	18	4	60	π (L)+ π (Phenolato ring)
H-2	–6.0396	1	4	14	32	37	π(L)+ π(Phenolato ring)+n(Cl)
H-3	–6.0948	1	5	14	31	39	π(L)+ π(Phenolato ring)+n(Cl)
H-4	–6.1158	5	1	1	88	5	π(L))+ n(Cl)
H-5	–6.1245	4	1	2	87	6	π(L))+ n(Cl)

Table S6 Frontier molecular orbital composition in the ground state for complex **4**

Orbital	Energy	Contribution					Main bond type
		Zn	O	N	Cl	Phenolato ring	
L+5	–1.1407	0	0	4	0	0	π*(L)
L+4	–1.1409	0	0	4	0	0	π*(L)
L+3	–1.2852	0	1	16	0	11	π*(L)+π*(Phenolato ring)
L+2	–1.3309	0	0	15	0	11	π*(L)+π*(Phenolato ring)
L+1	–1.7837	1	2	23	1	24	π*(L)+π*(Phenolato ring)
L	–1.8969	1	2	23	1	24	π*(L)+π*(Phenolato ring)
H	–5.5566	0	19	21	3	67	π (L)+π (Phenolato ring)
H-1	–5.6303	1	14	21	3	60	π (L)+π (Phenolato ring)
H-2	–6.1190	2	5	9	45	34	π(L)+π(Phenolato ring)+n(Cl)
H-3	–6.1702	4	1	2	87	4	π(L)+π(Phenolato ring)+n(Cl)
H-4	–6.1900	4	1	2	83	9	π(L))+n(Cl)+π(Phenolato ring)
H-5	–6.1909	2	5	6	53	33	π(L))+n(Cl)+π(Phenolato ring)

Table S7 Selected parameters for the vertical excitation (UV-vis absorptions) of the complexes **1** and **2**. Excitation energy (eV) and oscillator strengths (f), assignment of the transition calculated by TDDFT//B3LYP/LANL2DZ on the optimized ground state geometries

Electronic transitions	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	λ_{exp} (nm)	CI	Assign
	Complex 1						
$S_0 \rightarrow S_3$	H–1 → L (62.89%) H–1 → L+1 (20.2%) H → L+1 (16.87%)	3.00	0.0246	412	410	0.644 0.207 –0.173	ILCT ILCT ILCT
$S_0 \rightarrow S_4$	H–1 → L (23.58%) H–1 → L+1 (76.4%)	3.05	0.1239	405	410	–0.205 0.665	ILCT ILCT
$S_0 \rightarrow S_7$	H–1 → L+2 (100%)	3.48	0.0470	355	328	0.685	ILCT
$S_0 \rightarrow S_{20}$	H–7 → L (19.6%) H–7 → L+1 (10.6%) H–6 → L+1 (7.56%) H–4 → L (6.25%) H–3 → L (28.28%) H–2 → L+1 (11.6%) H–3 → L+5 (4%) H → L+6 (9.75%)	3.86	0.2844	320	308	–0.320 0.173 –0.123 0.102 0.461 –0.189 0.159 0.102	ILCT ILCT ILCT ILCT ILCT ILCT ILCT ILCT
$S_0 \rightarrow S_{38}$	H–8 → L+1 (7.81%) H–7 → L+2 (10.4%) H–6 → L+2 (16.5%) H–6 → L+3 (21.6%) H–3 → L+2 (6.91%) H–2 → L+2 (9.87%) H–1 → L+8 (9.48%) H–1 → L+9 (6.51%) H → L+9 (11.11%)	4.28	0.0210	289	258	0.147 0.196 –0.310 0.407 –0.130 –0.186 –0.178 0.122 –0.209	ILCT ILCT ILCT ILCT ILCT ILCT ILCT ILCT ILCT
	Complex 2						
$S_0 \rightarrow S_4$	H–1→ L+1 (100%)	3.28	0.1620	377	375	0.693	ILCT
$S_0 \rightarrow S_6$	H–2→ L (11.56%)					–0.117	ILCT

	H–1 → L+2 (29.8%) H → L+3 (58.54%)	3.64	0.0859	340	324	0.304 0.596	ILCT ILCT
$S_0 \rightarrow S_{18}$	H–7 → L+1 (20.5%) H–6 → L (22%) H–3 → L+1 (47.5%) H → L+7 (10%)	3.92	0.3165	315	324	0.238 0.255 0.551 0.116	ILCT ILCT ILCT ILCT
$S_0 \rightarrow S_{36}$	H–12 → L+1 (9.9%) H–8 → L+1 (41.1%) H–6 → L+3 (10.7%) H–2 → L+3 (17.2%) H → L+8 (20.96%)	4.34	0.1209	285	273	–0.126 0.524 –0.136 –0.219 –0.267	ILCT ILCT ILCT ILCT ILCT

Table S8 Selected parameters for the vertical excitation (UV-vis absorptions) of the complexes **3** and **4**. Excitation energy (eV) and oscillator strengths (f), assignment of the transition calculated by TDDFT//B3LYP/LANL2DZ on the optimized ground state geometries

Electronic transitions	**Composition**	**E (eV)**	**Oscillator strength (*f*)**	**λ_{theo} (nm)**	**λ_{exp} (nm)**	**CI**	**Assign**
	Complex 3						
$S_0 \rightarrow S_4$	H–1 → L+1 (74.5%) H→ L (25.5%)	3.16	0.3822	391	414	0.655 0.224	ILCT ILCT
$S_0 \rightarrow S_{15}$	H–7 → L+1 (15.3%) H–6 → L (19.2%) H–5 → L+1 (14%) H–3 → L+1 (19.8%) H–2 → L (25%) H → L+4 (6.6%)	3.77	0.1934	329	334	–0.241 –0.303 0.222 0.312 0.392 –0.104	ILCT ILCT ILCT ILCT ILCT ILCT
$S_0 \rightarrow S_{60}$	H–8 → L+2 (9%) H–1 → L+9 (16.7%) H–1 → L+10 (35%)	4.53	0.0575	273	275	0.104 –0.193 –0.406 0.454	ILCT ILCT ILCT ILCT

	H→ L+11 (39%)						
	Complex 4						
$S_0 \rightarrow S_2$	H→ L (100%)	3.27	0.1164	378	368	0.697	ILCT
$S_0 \rightarrow S_8$	H–6 → L (6.86%) H–5 → L+1(17.53%) H–4 → L (14.76%) H–2 → L (16.36%) H–1 → L+2(19.96%) H→ L+3(24.50%)	3.74	0.0795	331	329	0.110 0.281 0.237 0.262 0.320 0.393	ILCT ILCT ILCT ILCT ILCT ILCT
$S_0 \rightarrow S_{20}$	H–7 → L+1 (17.1%) H–6 → L (24.01%) H–5 → L+1 (27.6%) H–3 → L+1 (13.5%) H–1 → L+2 (10.1%) H→ L+2 (7.60%)	3.96	0.3405	312	300	–0.259 –0.363 0.418 –0.204 –0.153 –0.115	ILCT ILCT ILCT ILCT ILCT ILCT
$S_0 \rightarrow S_{36}$	H–9 → L (5.90%) H–8 → L+1 (13.3%) H–7 → L+2 (13%) H–6 → L+3 (17.7%) H–4 → L+3 (6.61%) H–2 → L+3 (23.8%) H–1 → L+6 (12.7%) H→ L+8 (7%)	4.40	0.1441	282	245	0.101 0.228 0.222 –0.301 0.113 0.406 0.216 –0.119	ILCT ILCT ILCT ILCT ILCT ILCT ILCT ILCT

Table S9 Analysis for complex **1**: Natural Bond Orbitals and Occupancy

Valence bond orbitals	Occupancy	Antibonding orbitals	Occupancy	bond type
BD(1) C13 – N82	1.9827	BD*(1) C13 – N82	0.01430	Single

BD(2) C13 – N82	1.9405	BD*(2) C13 – N82	0.26051	Double
BD(1) C15 – N83	1.9790	BD*(1) C15 – N83	0.05244	Single
BD(1) C26 – N83	1.97744	BD*(1) C26 – N83	0.04513	Single
BD(1) C26 – N84	1.98025	BD*(1) C26 – N84	0.03011	Single
BD(1) C33 – N 4	1.98226	BD*(1) C33 – N84	0.01776	Single
BD(2) C33 – N84	1.77159	BD*(2) C33 – N84	0.46302	Double
BD(1) C39 – O78	1.98765	BD*(1) C39 – O78	0.03685	Single
BD(1) C43 – N79	1.98269	BD*(1) C43 – N79	0.01439	Single
BD(2) C43 – N79	1.94068	BD*(2) C43 – N79	0.27178	Double
BD(1) C45 – N80	1.97898	BD*(1) C45 – N80	0.05236	Single
BD(1) C56 – N80	1.97740	BD*(1) C56 – N80	0.04506	Single
BD(1) C56 – N81	1.98021	BD*(1) C56 – N81	0.03008	Single
BD(1) C63 – N81	1.98225	BD*(1) C63 – N81	0.01773	Single
BD(2) C63 – N81	1.77133	BD*(2) C63 – N81	0.46231	Double
BD(1) C65 – O76	1.99056	BD*(1) C65 – O76	0.02611	Single
BD(1) C66 – O75	1.99061	BD*(1) C66 – O75	0.02588	Single
BD(1) C67 – O78	1.99110	BD*(1) C67 – O78	0.01120	Single
BD(1) C71 – O77	1.99101	BD*(1) C71 – O 77	0.01063	Single
BD(1) N79 – N80	1.97893	BD*(1) N79 – N 80	0.05049	Single
BD(1) N82 – N83	1.97905	BD*(1) N82 – N 83	0.05068	Single
LP(1)Zn 1	1.99905	LP*(1)Zn 1	0.31725	Lone pair
LP(2)Zn 1	1.99854	LP*(7)Zn 1	0.14103	
LP(1)Zn 2	1.99905	LP*(6)Zn 2	0.31796	
LP(2)Zn 2	1.99853	LP*(7)Zn 2	0.14133	
LP(1) O 75	1.91396			
LP(2) O 75	1.85470			
LP(1) O 76	1.91386			
LP(2) O 76	1.85383			
LP(1) N 79	1.86308			
LP(1) N 80	1.69100			
LP(1) N 81	1.85254			

LP(1) N 82	1.86361
LP(1) N 83	1.68965
LP(1) N 84	1.85225

Table S10 Analysis for complex **1**: Natural Bond Orbitals and coefficient/hybrids

Valence bond	coefficient/hybrids	Antibond	coefficient/hybrids
BD(1) C13 – N82	0.6199($sp^{2.16}$) 0.7846($sp^{1.35}$)	BD*(1) C13 – N82	0.7846($sp^{2.16}$) -0.6199($sp^{1.35}$)
BD(2) C13 – N82	0.6120(sp^{1}) 0.7909(sp^{1})	BD*(2) C13 – N82	0.7909(sp^{1}) -0.6120(sp^{1})
BD(1) C15 – N83	0.6079($sp^{2.77}$) 0.7940($sp^{1.78}$)	BD*(1) C15 – N83	0.7940($sp^{2.77}$) -0.6079($sp^{1.78}$)
BD(1) C26 – N83	0.6106($sp^{2.39}$)0.7919($sp^{1.82}$)	BD*(1) C26 – N83	0.7919($sp^{2.39}$) -0.6106($sp^{1.82}$)
BD(1) C26 – N84	0.6283($sp^{2.18}$)0.7780($sp^{1.77}$)	BD*(1) C26 – N84	0.7780($sp^{2.18}$) -0.6283($sp^{1.77}$)
BD(1) C33 – N84	0.6165($sp^{2.31}$) 0.7874 ($sp^{1.70}$)	BD*(1) C33 – N84	0.7874($sp^{2.31}$) -0.6165($sp^{1.70}$)
BD(2) C33 – N84	0.5796 (sp^{1}) 0.8149(sp^{1})	BD*(2) C33 – N84	0.8149(sp^{1}) -0.5796(sp^{1})
BD(1) C39 – O78	0.5643 ($sp^{3.01}$)0.8256($sp^{2.23}$)	BD*(1) C39 – O78	0.8256($sp^{3.01}$) -0.5643($sp^{2.23}$)
BD(1) C43 – N79	0.6203 ($sp^{2.16}$)0.7843 ($sp^{1.35}$)	BD*(1) C43 – N79	0.7843($sp^{2.16}$) -0.6203($sp^{1.35}$)
BD(2) C43 – N79	0.6106 (sp^{1})0.7919 (sp^{1})	BD*(2) C43 – N79	0.7919(sp^{1}) -0.6106(sp^{1})
BD(1) C45 – N80	0.6083 ($sp^{2.76}$) 0.7937($sp^{1.78}$)	BD*(1) C45 – N80	0.7937($sp^{2.76}$) -0.6083($sp^{1.78}$)
BD(1) C56 – N80	0.6106 ($sp^{2.39}$) 0.7920($sp^{1.82}$)	BD*(1) C56 – N80	0.7920($sp^{2.39}$) -0.6106($sp^{1.82}$)
BD(1) C56 – N81	0.6284 ($sp^{2.18}$) 0.7779($sp^{1.77}$)	BD*(1) C56 – N81	0.7779($sp^{2.18}$) -0.6284($sp^{1.77}$)
BD(1) C63 – N81	0.6165 ($sp^{2.31}$) 0.7874($sp^{1.70}$)	BD*(1) C63 – N81	0.7874($sp^{2.31}$) -0.6165($sp^{1.70}$)
BD(2) C63 – N81	0.5795 (sp^{1}) 0.8150(sp^{1})	BD*(2) C63 – N81	0.8150(sp^{1}) -0.5795(sp^{1})
BD(1) C65 – O76	0.5708 ($sp^{2.78}$) 0.8211($sp^{1.88}$)	BD*(1) C65 – O76	0.8211($sp^{2.78}$) -0.5708($sp^{1.88}$)
BD(1) C66 – O75	0.5709 ($sp^{2.77}$) 0.8210($sp^{1.87}$)	BD*(1) C66 – O75	0.8210($sp^{2.77}$) -0.5709($sp^{1.87}$)
BD(1) C67 – O78	0.5637 ($sp^{3.80}$) 0.8260($sp^{2.87}$)	BD*(1) C67 – O78	0.8260($sp^{3.80}$) -0.5637($sp^{2.87}$)
BD(1) C71 – O77	0.5627 ($sp^{3.82}$) 0.8266($sp^{2.86}$)	BD*(1) C71 – O 77	0.8266($sp^{3.82}$) -0.5627($sp^{2.86}$)
BD(1) N79 – N80	0.6886 ($sp^{3.24}$) 0.7251($sp^{2.67}$)	BD*(1) N79 – N 80	0.7251($sp^{3.24}$) -0.6886($sp^{2.67}$)
BD(1) N82 – N83	0.6890 ($sp^{3.22}$) 0.7248($sp^{2.66}$)	BD*(1) N82 – N 83	0.7248($sp^{3.22}$) -0.6890($sp^{2.66}$)

Table S11 Second-Order Perturbation Stabilization Energies ΔE(2) for complex **1**

Donor	**Acceptor**	**E(2) kcal/mol**

LP (2) O 75	LP*(7)Zn 2	17.23
LP (2) O 75	LP*(8)Zn 2	10.27
LP (3) O 75	BD*(2) C 42 - C 66	35.02
LP (2) O 75	LP*(8)Zn 1	26.23
LP (2) O 76	LP*(7)Zn 1	17.78
LP (2) O 76	LP*(8)Zn 1	10.67
LP (3) O 76	BD*(2) C 12 - C 65	33.46
LP (2) O 77	BD*(2) C 9 - C 10	22.84
LP (2) O 78	BD*(2) C 39 - C 40	26.20
LP (1) N 79	LP*(6)Zn 1	17.60
LP (1) N 79	LP*(7)Zn 1	24.53
LP (1) N 80	BD*(2) C 43 - N 79	24.04
LP (1) N 80	BD*(2) C 56 - C 57	39.68
LP (1) N 81	LP*(9)Zn 1	20.31
LP (1) N 81	LP*(6)Zn 1	18.36
LP (1) N 82	LP*(6)Zn 2	17.30
LP (1) N 83	BD*(2) C 13 - N 82	24.21
LP (1) N 83	BD*(2) C 26 - C 27	39.65
LP (1) N 84	LP*(6)Zn 2	18.46
LP (4)Cl 3	LP*(6)Zn 1	70.23

Table S12 Analysis for complex **2**: Natural Bond Orbitals and Occupancy

Valence bond	**Occupancy**	**Antibond**	**Occupancy**	**bond type**
BD(1) O5 – C13	1.99068	BD*(1) O5 – C13	0.02629	Single
BD(1) O6 – C44	1.99068	BD*(1) O6 – C44	0.02629	Single
BD(1) N7 – N8	1.97886	BD*(1) N7 – N8	0.05097	Single
BD(1) N7 – C22	1.98269	BD*(1) N7 – C22	0.01440	Single
BD(2) N7 – C22	1.94131	BD*(2) N7 – C22	0.26850	Double
BD(1) N8 – C24	1.97744	BD*(1) N8 – C24	0.04488	Single
BD(1) N8 – C33	1.97897	BD*(1) N8 – C33	0.05233	Single

BD(1) N9 – C24	1.98020	BD*(1) N9 – C24	0.03012	Single
BD(1) N9 – C31	1.98226	BD*(1) N9 – C31	0.01775	Single
BD(2) N9 – C31	1.77157	BD*(2) N9 – C31	0.46294	Double
BD(1) N10 – N11	1.97886	BD*(1) N10 – N11	0.05097	Single
BD(1) N10 – C53	1.98269	BD*(1) N10 – C53	0.01440	Single
BD(2) N10 – C53	1.94130	BD*(2) N10 – C53	0.26853	Double
BD(1) N11 – C55	1.97744	BD*(1) N11 – C55	0.04488	Single
BD(1) N11 – C64	1.97897	BD*(1) N11 – C64	0.05233	Single
BD(1) N12 – C55	1.98020	BD*(1) N12 – C55	0.03012	Single
BD(1) N12 – C62	1.98226	BD*(1) N12 – C62	0.01775	Single
BD(2) N12 – C62	1.77160	BD*(2) N12 – C62	0.46295	Double
LP(1)Zn 1	1.99905	LP*(6)Zn 1	0.31783	Lone pair
LP(2)Zn 1	1.99853	LP*(7)Zn 1	0.14137	
LP(1)Zn 2	1.99905	LP*(6)Zn 2	0.31783	
LP(2)Zn 2	1.99853	LP*(7)Zn 2	0.14137	
LP (1) O5	1.91445			
LP (2) O5	1.85476			
LP (1) O6	1.91444			
LP (2) O6	1.85477			
LP(1) N7	1.86314			
LP(1) N8	1.69131			
LP(1) N9	1.85252			
LP (1) N10	1.86313			
LP (1) N11	1.69127			
LP (1) N12	1.85251			

Table S13. Analysis for complex **2**: Natural Bond Orbitals and coefficient/hybrids

Valence bond	**coefficient/hybrids**	**Antibond**	**coefficient/hybrids**
BD(1) O5 – C13	0.8214($sp^{1.86}$) 0.5703($sp^{2.79}$)	BD*(1) O5 – C13	0.5703($sp^{1.86}$) -0.8214($sp^{2.79}$)
BD(1) O6 – C44	0.8214 ($sp^{1.86}$) 0.5703($sp^{2.79}$)	BD*(1) O6 – C44	0.5703($sp^{1.86}$) -0.8214($sp^{2.79}$)
BD(1) N7 – N8	0.6884 ($sp^{3.25}$) 0.7253($sp^{2.67}$)	BD*(1) N7 – N8	0.7253($sp^{3.25}$) -0.6884($sp^{2.67}$)

BD(1) N7 – C22	0.7844 ($sp^{1.35}$) 0.6202($sp^{2.16}$)	BD*(1) N7 – C22	0.6202($sp^{1.35}$) -0.7844($sp^{2.16}$)
BD(2) N7 – C22	0.7929(sp^{1}) 0.6093(sp^{1})	BD*(2) N7 – C22	0.6093 (sp^{1}) -0.7929 (sp^{1})
BD(1) N8 – C24	0.7918($sp^{1.82}$) 0.6107($sp^{2.38}$)	BD*(1) N8 – C24	0.6107($sp^{1.82}$) -0.7918($sp^{2.38}$)
BD(1) N8 – C33	0.7937 ($sp^{1.78}$) 0.6083($sp^{2.76}$)	BD*(1) N8 – C33	0.6083($sp^{1.78}$) -0.7937($sp^{2.76}$)
BD(1) N9 – C24	0.7779 ($sp^{1.77}$) 0.6284($sp^{2.18}$)	BD*(1) N9 – C24	0.6284($sp^{1.77}$) -0.7779($sp^{2.18}$)
BD(1) N9 – C31	0.7873 ($sp^{1.71}$) 0.6165($sp^{2.31}$)	BD*(1) N9 – C31	0.6165($sp^{1.71}$) -0.7873($sp^{2.31}$)
BD(2) N9 – C31	0.8151 (sp^{1}) 0.5794 (sp^{1})	BD*(2) N9 – C31	0.5794 (sp^{1}) -0.8151 (sp^{1})
BD(1) N10 – N11	0.6884 ($sp^{3.25}$) 0.7253($sp^{2.67}$)	BD*(1) N10 – N11	0.7253($sp^{3.25}$) -0.6884($sp^{2.67}$)
BD(1) N10 – C53	0.7844 ($sp^{1.35}$) 0.6202($sp^{2.16}$)	BD*(1) N10 – C53	0.6202($sp^{1.35}$) -0.7844($sp^{2.16}$)
BD(2) N10 – C53	0.7929 (sp^{1}) 0.6093(sp^{1})	BD*(2) N10 – C53	00.6093(sp^{1}) -0.7929 (sp^{1})
BD(1) N11 – C55	0.7918 ($sp^{1.82}$) 0.6107($sp^{2.38}$)	BD*(1) N11 – C55	0.6107($sp^{1.82}$) -0.7918($sp^{2.38}$)
BD(1) N11 – C64	0.7937 ($sp^{1.78}$) 0.6083($sp^{2.76}$)	BD*(1) N11 – C64	0.6083($sp^{1.78}$) -0.7937($sp^{2.76}$)
BD(1) N12 – C55	0.7779 ($sp^{1.77}$) 0.6284($sp^{2.18}$)	BD*(1) N12 – C55	0.6284($sp^{1.77}$) -0.7779($sp^{2.18}$)
BD(1) N12 – C62	0.7873 ($sp^{1.71}$) 0.6165($sp^{2.31}$)	BD*(1) N12 – C62	0.6165($sp^{1.71}$) -0.7873($sp^{2.31}$)
BD(2) N12 – C62	0.8151 (sp^{1}) 0.5793(sp^{1})	BD*(2) N12 – C62	0.5793(sp^{1}) -0.8151(sp^{1})

Table S14 Second-Order Perturbation Stabilization Energies △E(2) for complex **2**

Donor	Acceptor	E(2) kcal/mol
LP (2) O 5	LP*(8)Zn 1	26.54
LP (1) N 7	154. LP*(6)Zn 1	17.51
LP (1) N 7	155. LP*(7)Zn 1	24.95
LP (1) N 9	LP*(6)Zn 1	18.44
LP (1) N 9	LP*(7)Zn 1	16.63
LP (1) N 9	LP*(9)Zn 1	20.51
LP (2) O 5	LP*(7)Zn 2	17.19
LP (2) O 5	LP*(8)Zn 2	10.84
BD (2) N 9 - C 31	BD*(2) C 24 - C 25	25.86
BD (2) N 9 - C 31	BD*(2) C 27 - C 29	10.06
LP (3) O 5	BD*(2) C 13 - C 14	34.09

LP (1) N 8	BD*(2) N 7 - C 22	23.75
LP (1) N 8	BD*(2) C 24 - C 25	39.80
LP (2) O 6	LP*(7)Zn 1	17.19
. LP (2) O 6	LP*(8)Zn 1	10.84
LP (2) O 6	LP*(8)Zn 2	26.53
LP (1) N 10	LP*(6)Zn 2	17.51
LP (1) N 10	LP*(7)Zn 2	24.94
LP (1) N 12	LP*(6)Zn 2	18.44
LP (1) N 12	LP*(7)Zn 2	6.65
LP (1) N 12	LP*(9)Zn 2	20.50

Table S15 Analysis for complex **3**: Natural Bond Orbitals and Occupancy

Valence bond	**Occupancy**	**Antibond**	**Occupancy**	**bond type**
BD (1) O3 – C5	1.9902	BD*(1) O3 – C5	0.02524	Single
BD (1) O4 – C17	1.9902	BD*(1) O4 – C17	0.02524	Single
BD (1) N28 – C41	1.9800	BD*(1) N28 – C41	0.02990	Single
BD (1) N28 – C77	1.9822	BD*(1) N28 – C77	0.01770	Single
BD (2) N28 – C77	1.77310	BD*(2) N28 – C77	0.46568	Double
BD (1) N29 – N30	1.97876	BD*(1) N29 – N30	0.05178	Single
BD (1) N29 – C31	1.98236	BD*(1) N29 – C31	0.01460	Single
BD (2) N29 – C31	1.94103	BD*(2) N29 – C31	0.28270	Double
BD (1) N30 – C35	1.97929	BD*(1) N30 – C35	0.05222	Single
BD (1) N30 – C41	1.97757	BD*(1) N30 – C41	0.04450	Single
BD (1) N48 – N49	1.97876	BD*(1) N48 – N49	0.05178	Single
BD (1) N48 – C67	1.98236	BD*(1) N48 – C67	0.01460	Single
BD (2) N48 – C67	1.94103	BD*(2) N48 – C67	0.28276	Double
BD (1) N49 – C56	1.97929	BD*(1) N49 – C56	0.05222	Single
BD (1) N49 – C86	1.97757	BD*(1) N49 – C86	0.04450	Single
BD (1) C52 – N85	1.98224	BD*(1) C52 – N85	0.01770	Single
BD (2) C52 – N85	1.77309	BD*(2) C52 – N85	0.46570	Double

BD (1) N85 – C86	1.98008	BD*(1) N85 – C86	0.02989	Single
LP (1)Zn 1	1.99905	LP*(6)Zn 1	0.31922	Lone pair
LP (2)Zn 1	1.99854	LP*(7)Zn 1	0.14343	
LP (1)Zn 2	1.99905	LP*(6)Zn 2	0.31919	
LP (2)Zn 2	1.99852	LP*(7)Zn 2	0.14341	
LP (1) O 3	1.91579			
LP (2) O 3	1.85584			
LP (1) O 4	1.91578			
LP (2) O 4	1.85584			
LP (1) N 28	1.85155			
LP (1) N 29	1.86288			
LP (1) N 30	1.68823			
LP (1) N 48	1.86287			
LP (1) N 49	1.68825			
LP (1) N 85	1.85154			

Table S16 Analysis for complex **3**: Natural Bond Orbitals and coefficient/hybrids

Valence bond	**coefficient/hybrids**	**Antibond**	**coefficient/hybrids**
BD (1) O3 – C5	0.8216($sp^{1.83}$) 0.5700($sp^{2.81}$)	BD*(1) O3 – C5	0.5700($sp^{1.83}$) -0.8216($sp^{2.81}$)
BD (1) O4 – C17	0.8216($sp^{1.83}$) 0.5700($sp^{2.81}$)	BD*(1) O4 – C17	0.5700($sp^{1.83}$) -0.8216($sp^{2.81}$)
BD (1) N28 – C41	0.7778($sp^{1.78}$) 0.6285($sp^{2.18}$)	BD*(1) N28 – C41	0.6285($sp^{1.78}$) -0.7778($sp^{2.18}$)
BD (1) N28 – C77	0.7874($sp^{1.70}$) 0.6165($sp^{2.31}$)	BD*(1) N28 – C77	0.6165($sp^{1.70}$) -0.7874($sp^{2.31}$)
BD (2) N28 – C77	0.8159(sp^{1}) 0.5781(sp^{1})	BD*(2) N28 – C77	0.5781(sp^{1}) -0.8159(sp^{1})
BD (1) N29 – N30	0.6872($sp^{3.30}$) 0.7265($sp^{2.65}$)	BD*(1) N29 – N30	0.7265($sp^{3.30}$) -0.6872($sp^{2.65}$)
BD (1) N29 – C31	0.7841($sp^{1.35}$) 0.6206($sp^{2.17}$)	BD*(1) N29 – C31	0.6206($sp^{1.35}$) -0.7841($sp^{2.17}$)
BD (2) N29 – C31	0.7946(sp^{1}) 0.6071(sp^{1})	BD*(2) N29 – C31	0.6071(sp^{1}) -0.7946(sp^{1})
BD (1) N30 – C35	0.7933($sp^{1.77}$) 0.6088($sp^{2.75}$)	BD*(1) N30 – C35	0.6088($sp^{1.77}$) -0.7933($sp^{2.75}$)
BD (1) N30 – C41	0.7920($sp^{1.81}$) 0.6106($sp^{2.38}$)	BD*(1) N30 – C41	0.6106($sp^{1.81}$) -0.7920($sp^{2.38}$)
BD (1) N48 – N49	0.6872($sp^{3.30}$) 0.7265($sp^{2.65}$)	BD*(1) N48 – N49	0.7265($sp^{3.30}$) -0.6872($sp^{2.65}$)
BD (1) N48 – C67	0.7841($sp^{1.35}$) 0.6206($sp^{2.17}$)	BD*(1) N48 – C67	0.6206($sp^{1.35}$) -0.7841($sp^{2.17}$)
BD (2) N48 – C67	0.7946(sp^{1}) 0.6071(sp^{1})	BD*(2) N48 – C67	0.6071(sp^{1}) -0.7946(sp^{1})

BD (1) N49 – C56	0.7933 (sp $^{1.77}$) 0.6088(sp $^{2.75}$)	BD*(1) N49 – C56	0.6088(sp $^{1.77}$) -0.7933(sp$^{2.75}$)
BD (1) N49 – C86	0.7920 (sp $^{1.81}$) 0.6106(sp $^{2.38}$)	BD*(1) N49 – C86	0.6106(sp $^{1.81}$) -0.7920(sp$^{2.38}$)
BD (1) C52 – N85	0.6165(sp $^{2.31}$) 0.7874(sp $^{1.70}$)	BD*(1) C52 – N85	0.7874(sp $^{2.31}$) -0.6165(sp$^{1.70}$)
BD (2) C52 – N85	0.5781(sp ^{1}) 0.8160 (sp ^{1})	BD*(2) C52 – N85	0.8160(sp ^{1}) -0.5781(sp ^{1})
BD (1) N85 – C86	0.7778(sp $^{1.78}$) 0.6285(sp $^{2.18}$)	BD*(1) N85 – C86	0.6285(sp $^{1.78}$) -0.7778(sp$^{2.18}$)

Table S17 Second-Order Perturbation Stabilization Energies △E(2) for complex **3**

Donor	Acceptor	E(2) kcal/mol
LP (2) O 3	LP*(8)Zn 1	27.38
LP (1) N 48	LP*(6)Zn 1	17.88
LP (1) N 48	LP*(7)Zn 1	27.21
LP (1) N 85	LP*(6)Zn 1	18.44
LP (1) N 85	LP*(9)Zn 1	20.30
LP (2) O 3	LP*(7)Zn 2	13.37
LP (2) O 3	LP*(8)Zn 2	12.77
BD (2) C 5 - C38	BD*(2) C 6 - C 7	20.40
BD (2) C 5 - C38	BD*(2) C 8 - C 10	12.96
BD (2) C 5 - C38	BD*(2) N48 - C67	30.58
BD (2) C 8 - C10	BD*(2) C 5 - C38	20.94
BD (2) C 8 - C10	BD*(2) C 6 - C 7	15.42
BD (2) C50 - C69	BD*(2) C52 - N85	39.45
LP (3) O 3	BD*(2) C 5 - C38	39.18
LP (1) N 49	BD*(2) N48 - C67	23.58
LP (1) N 49	BD*(2) C54 - C86	41.24
LP (2) O 4	LP*(7)Zn 1	13.33
LP (2) O 4	LP*(8)Zn 1	12.79
LP (2) O 4	LP*(8)Zn 2	27.40
LP (1) N 28	LP*(6)Zn 2	18.45
LP (1) N 29	LP*(6)Zn 2	17.88
LP (1) N 29	LP*(7)Zn 2	27.20

Table S18 Analysis for complex **4**: Natural Bond Orbitals and Occupancy

Valence bond	Occupancy	Antibond	Occupancy	bond type
BD (1) O5 – C13	1.99090	BD* (1) O5 – C13	0.02632	Single
BD (1) O6 – C44	1.99090	BD* (1) O6 – C44	0.02632	Single
BD (1) N7 – N8	1.97896	BD* (1) N7 – N8	0.05091	Single
BD (1) N7 – C22	1.98284	BD* (1) N7 – C22	0.01444	Single
BD (2) N7 – C22	1.94140	BD* (2) N7 – C22	0.26619	Double
BD (1) N8 – C24	1.97740	BD* (1) N8 – C24	0.04495	Single
BD (1) N8 – C33	1.97887	BD* (1) N8 – C33	0.05237	Single
BD (1) N9 – C24	1.98025	BD* (1) N9 – C24	0.03019	Single
BD (1) N9 – C31	1.98226	BD* (1) N9 – C31	0.01778	Single
BD (2) N9 – C31	1.77159	BD* (2) N9 – C31	0.46347	Double
BD (1) N10 – N11	1.97897	BD* (1) N10 – N11	0.05091	Single
BD (1) N10 – C53	1.98284	BD* (1) N10 – C53	0.01444	Single
BD (2) N10 – C53	1.94140	BD* (2) N10 – C53	0.26619	Double
BD (1) N11 – C55	1.97740	BD* (1) N11 – C55	0.04495	Single
BD (1) N11 – C64	1.97887	BD* (1) N11 – C64	0.05237	Single
BD (1) N12 – C55	1.98025	BD* (1) N12 – C55	0.03019	Single
BD (1) N12 – C62	1.98226	BD* (1) N12 – C62	0.01778	Single
BD (2) N12 – C62	1.77160	BD* (2) N12 – C62	0.46348	Double
LP (1)Zn 1 LP (2)Zn 1	1.99905 1.99852	LP*(6)Zn 1 LP*(7)Zn 1	0.31824 0.14120	Lone pair
LP (1)Zn 2	1.99905	LP*(6)Zn 2	0.31823	
LP (2)Zn 2	1.99852	LP*(7)Zn 2	0.14120	
LP (1) O 5	1.85487			
LP (2) O 5	1.79385			
LP (1) O 6	1.91457			
LP (2) O 6	1.85487			
LP(1) N 7	1.86317			

LP(1) N 8	1.69184
LP(1) N 9	1.85225
LP(1) N 10	1.86317
LP(1) N 11	1.69183
LP(1) N 12	1.85224

Table S19 Analysis for complex **4**: Natural Bond Orbitals and coefficient/hybrids

Valence bond	coefficient/hybrids	Antibond	coefficient/hybrids
BD (1) O5 – C13	0.8215($sp^{1.85}$) 0.5702($sp^{2.80}$)	BD* (1) O5 – C13	0.5702 ($sp^{1.85}$) - 0.82 ($sp^{2.80}$)
BD (1) O6 – C44	0.8215($sp^{1.85}$) 0.5702($sp^{2.80}$)	BD* (1) O6 – C44	0.5702($sp^{1.85}$) -0.8215($sp^{2.80}$)
BD (1) N7 – N8	0.6889($sp^{3.23}$) 0.7249($sp^{2.67}$)	BD* (1) N7 – N8	0.7249($sp^{3.23}$) -0.6889($sp^{2.67}$)
BD (1) N7 – C22	0.7844($sp^{1.35}$) 0.6202($sp^{2.16}$)	BD* (1) N7 – C22	0.6202($sp^{1.35}$) -0.7844($sp^{2.16}$)
BD (2) N7 – C22	0.7924(sp^{1}) 0.6100(sp^{1})	BD* (2) N7 – C22	0.6100(sp^{1}) -0.7924(sp^{1})
BD (1) N8 – C24	0.7918($sp^{1.82}$) 0.6108($sp^{2.38}$)	BD* (1) N8 – C24	0.6108($sp^{1.82}$) -0.7918($sp^{2.38}$)
BD (1) N8 – C33	0.7939($sp^{1.78}$) 0.6081($sp^{2.77}$)	BD* (1) N8 – C33	0.6081($sp^{1.78}$) -0.7939($sp^{2.77}$)
BD (1) N9 – C24	0.7780($sp^{1.77}$) 0.6282($sp^{2.18}$)	BD* (1) N9 – C24	0.6282($sp^{1.77}$) -0.7780($sp^{2.18}$)
BD (1) N9 – C31	0.7874($sp^{1.70}$) 0.616 ($sp^{2.31}$)	BD* (1) N9 – C31	0.616($sp^{1.70}$) -0.7874($sp^{2.31}$)
BD (2) N9 – C31	0.8151 (sp^{1}) 0.5793(sp^{1})	BD* (2) N9 – C31	0.57931 (sp^{1}) -0.8151(sp^{1})
BD (1) N10 – N11	0.6889($sp^{3.23}$) 0.7249($sp^{2.67}$)	BD* (1) N10 – N11	0.7249($sp^{3.23}$) -0.6889($sp^{2.67}$)
BD (1) N10 – C53	0.7844 ($sp^{1.35}$) 0.6202($sp^{2.16}$)	BD* (1) N10 – C53	0.6202($sp^{1.35}$) -0.7844($sp^{2.16}$)
BD (2) N10 – C53	0.7924 (sp^{1}) 0.6100(sp^{1})	BD* (2) N10 – C53	0.6100(sp^{1}) -0.7924(sp^{1})
BD (1) N11 – C55	0.7918 ($sp^{1.82}$) 0.6108($sp^{2.38}$)	BD* (1) N11 – C55	0.6108($sp^{1.82}$) -0.7918($sp^{2.38}$)
BD (1) N11 – C64	0.7939 ($sp^{1.78}$) 0.6081($sp^{2.77}$)	BD* (1) N11 – C64	0.608($sp^{1.78}$) -0.7939($sp^{2.77}$)
BD (1) N12 – C55	0.7780 ($sp^{1.77}$) 0.6282($sp^{2.18}$)	BD* (1) N12 – C55	0.6282($sp^{1.77}$) -0.7780($sp^{2.18}$)
BD (1) N12 – C62	0.7874 ($sp^{1.70}$) 0.6164($sp^{2.31}$)	BD* (1) N12 – C62	0.6164($sp^{1.70}$) -0.7874($sp^{2.31}$)
BD (2) N12 – C62	0.8151 (sp^{1}) 0.5793(sp^{1})	BD* (2) N12 – C62	0.5793 (sp^{1}) -0.8151(sp^{1})

Table S20 Second-Order Perturbation Stabilization Energies △E(2) for complex **4**

Donor	Acceptor	E(2) kcal/mol
LP (2) O 5	LP*(8)Zn 1	26.64
LP (1) N 7	LP*(6)Zn 1	17.58

LP (1) N 7	LP*(7)Zn 1	24.86
LP (1) N 9	LP*(6)Zn 1	18.52
LP (1) N 9	LP*(9)Zn 1	20.52
LP (2) O 5	LP*(7)Zn 2	17.23
LP (2) O 5	LP*(8)Zn 2	10.55
LP (3) O 5	BD*(2) C3 – C14	34.75
LP (1) N 8	BD*(2) N7 – C22	23.87
LP (1) N 8	BD*(2) C24 – C25	39.38
LP (2) O 6	LP*(7)Zn 1	17.23
LP (2) O 6	LP*(8)Zn 1	10.56
. LP (1) N 10	LP*(6)Zn 2	17.59
LP (1) N 10	LP*(7)Zn 2	24.86
LP (2) O 6	LP*(8)Zn 2	26.64
LP (1) N 12	LP*(6)Zn 2	18.52
LP (1) N 12	LP*(9)Zn 2	20.52
LP (3) O 6	BD*(2) C44 – C45	34.75
LP (1) N 11	BD*(2) N10 – C53	23.87
LP (1) N 11	BD*(2) C55 – C56	39.38

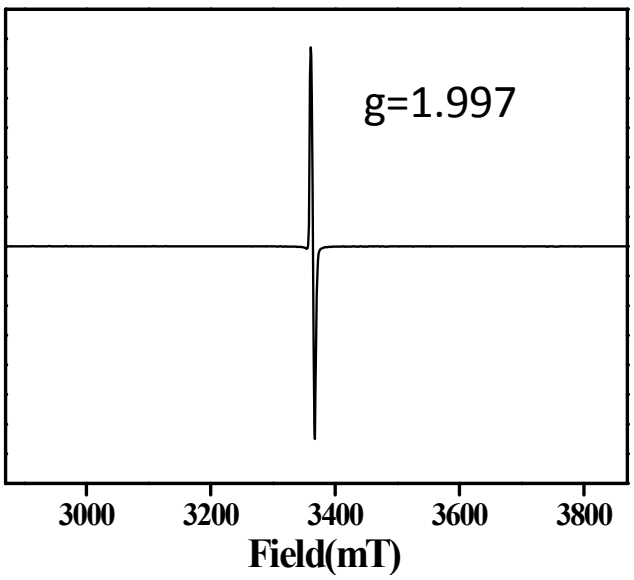


Figure S22. X–band EPR spectrum of phenoxyl radical complex derived from **1** in acetonitrile at 25°C

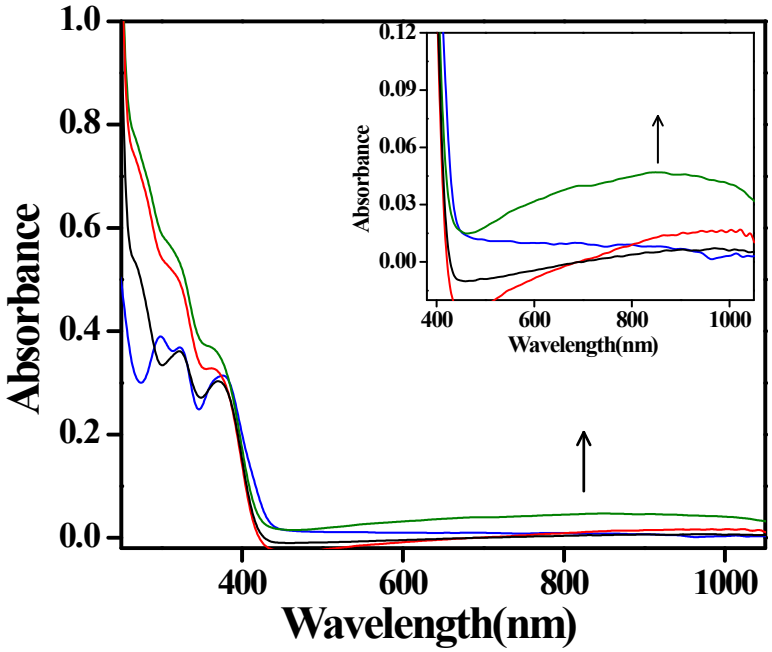


Figure S23 UV-vis spectral change observed after the oxidation of complex **2** (20 μM) in presence of CAN 1equi to 3 equivalent in acetonitrile solvent at 25°C.

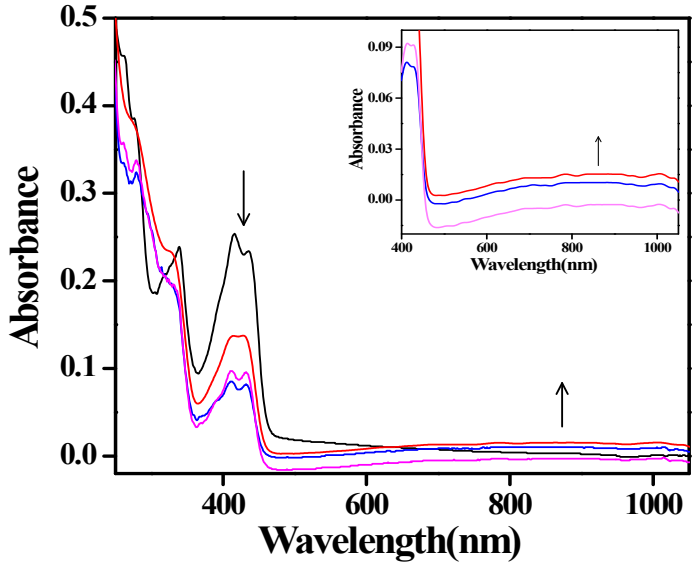


Figure S24 UV-vis spectral change observed after the oxidation of complex **3** (20 μM) in presence of CAN 1equi to 3 e equivalent in acetonitrile solvent at 25°C.

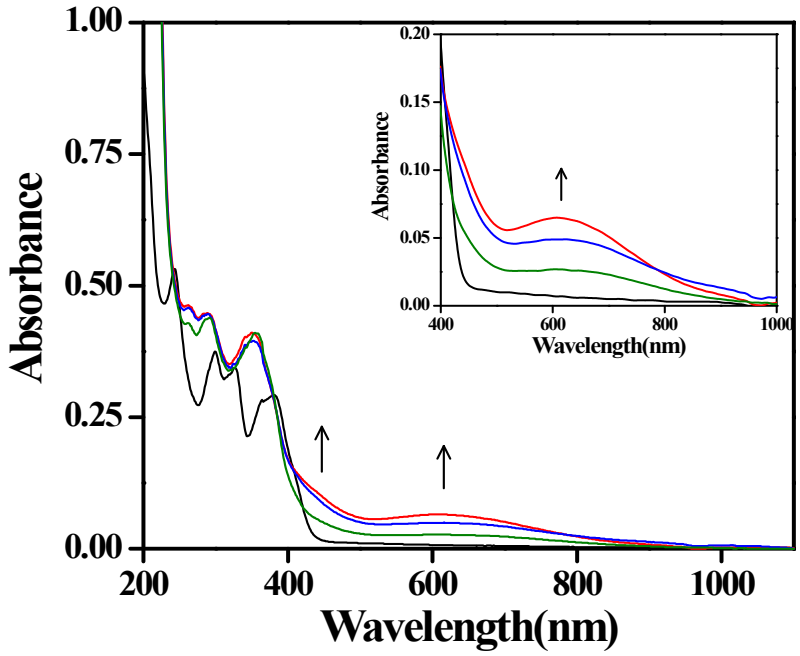


Figure S25 UV-vis spectral change observed after the oxidation of complex **4** (20 μM) in presence of CAN 1equi to 3 equivalent in acetonitrile solvent at 25°C.

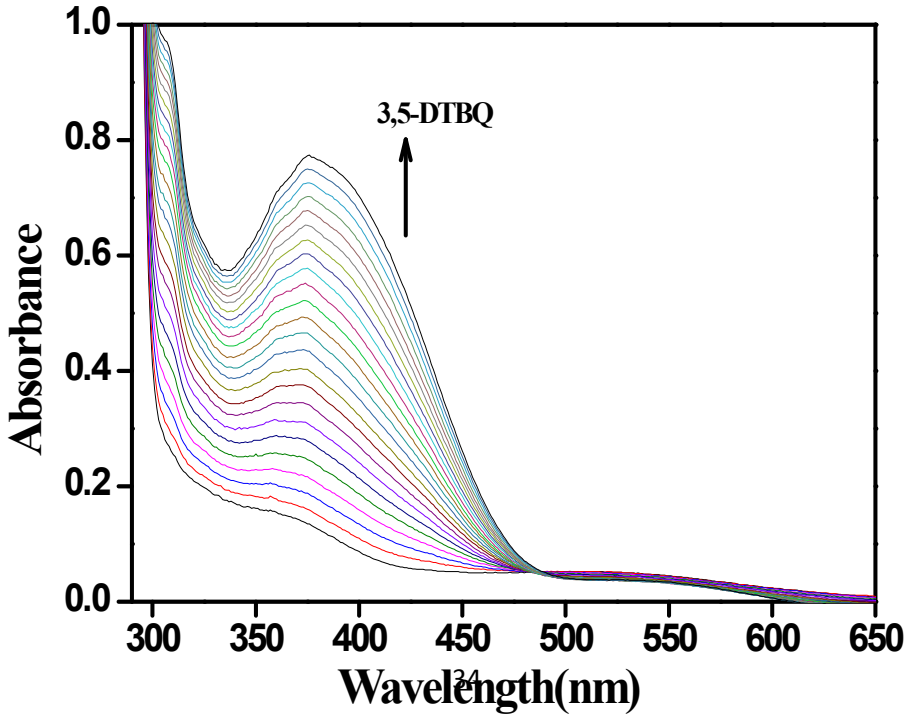


Figure S26. UV-vis spectra in range (300-500 nm): (i) **2** (1×10^{-4}M) in acetonitrile; (ii) 3,5-DTBC (1×10^{-2}M) in acetonitrile; (iii) changes in UV-vis spectra of complex **2** upon addition of 100-fold 3,5-DTBC for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

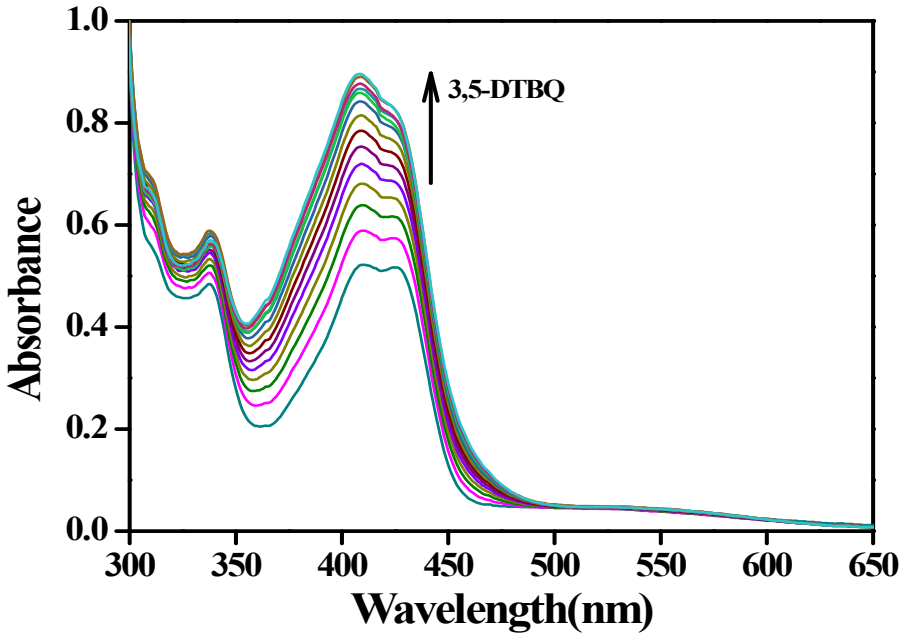


Figure S27. UV-vis spectra in range (300-500 nm): (i) **3** (1×10^{-4}M) in acetonitrile; (ii) 3,5-DTBC (1×10^{-2}M) in acetonitrile; (iii) changes in UV-vis spectra of complex **3** upon addition of 100-fold 3,5-DTBC for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

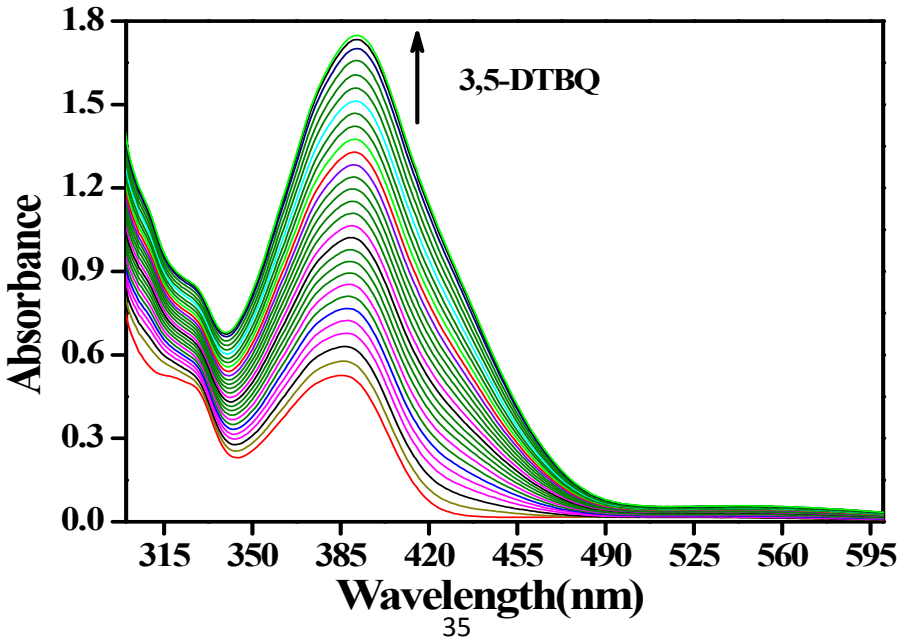


Figure S28. UV-vis spectra in range (300-500 nm): (i) **4** (1×10^{-4}M) in acetonitrile; (ii) 3,5-DTBC (1×10^{-2}M) in acetonitrile; (iii) changes in UV-vis spectra of complex **4** upon addition of 100-fold 3,5-DTBC for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

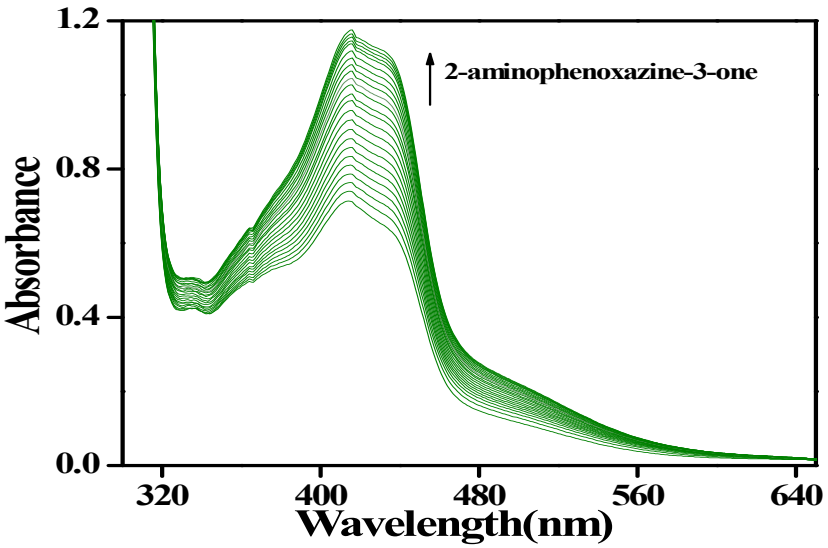


Figure S29. UV-vis spectral changes for the oxidation of 2-aminophenol (1×10^{-2} mol dm^{-3}) catalyzed by the complex **2** (1×10^{-4} mol dm^{-3}) for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

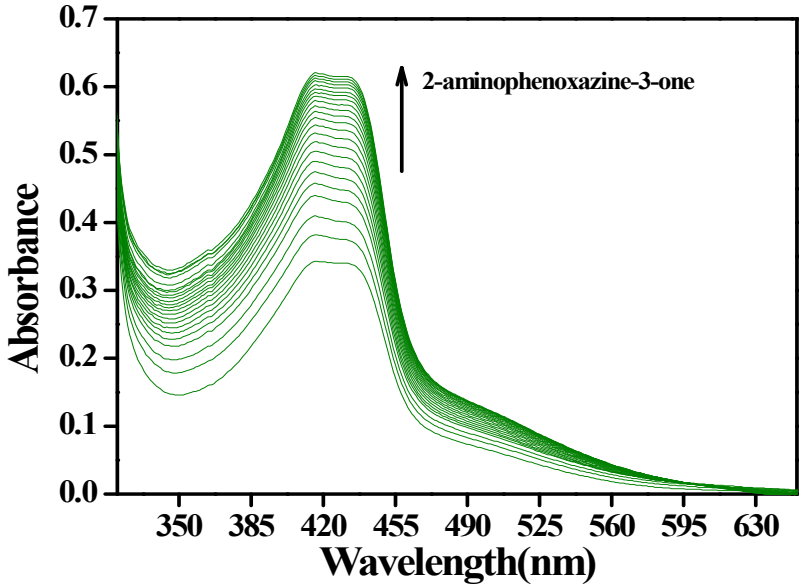


Figure S30. UV-vis spectral changes for the oxidation of 2-aminophenol (1×10^{-2} mol dm^{-3}) catalyzed by the complex **3** (1×10^{-4} mol dm^{-3}) for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

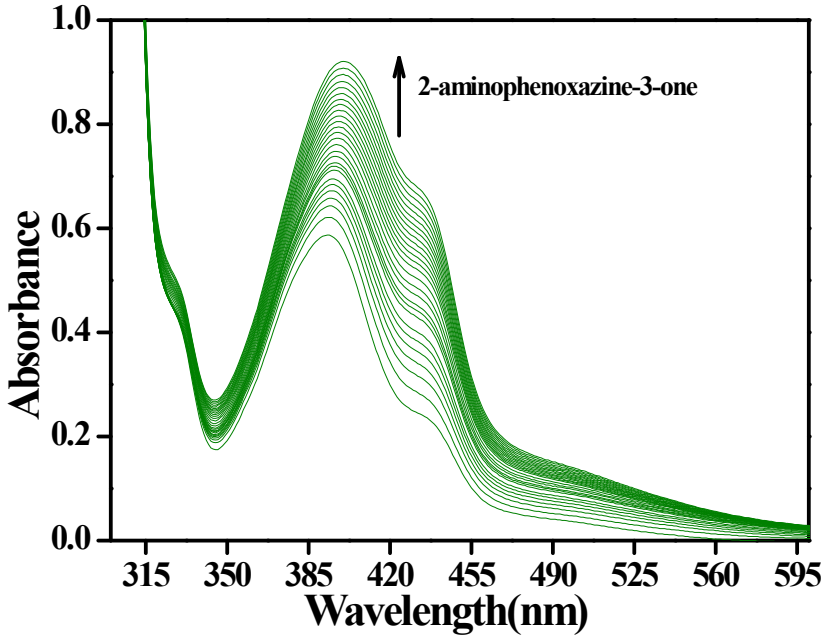


Figure S31. UV-vis spectral changes for the oxidation of 2-aminophenol (1×10^{-2} mol dm^{-3}) catalyzed by the complex **4** (1×10^{-4} mol dm^{-3}) for up to 2 hours of reaction in dioxygen-saturated acetonitrile at 25 °C.

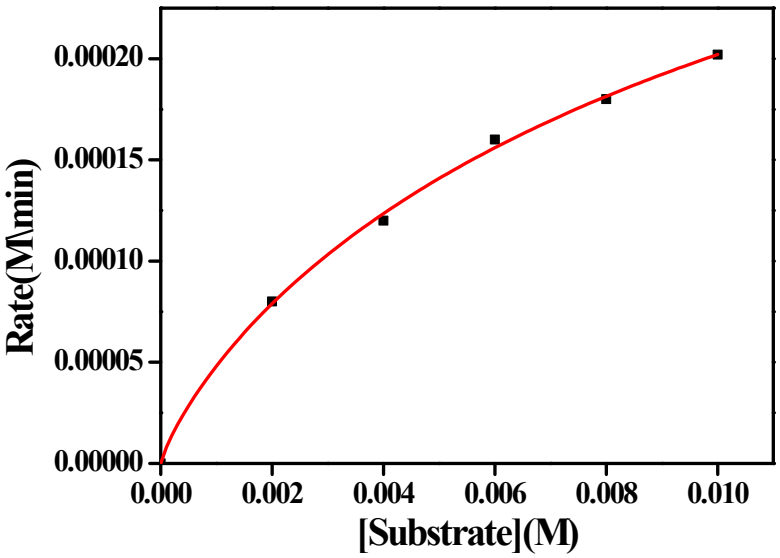


Figure S32. Plot of the initial rates versus substrate concentrations of 3,5-DTBC for the oxidation reaction catalyzed by complex **2**.

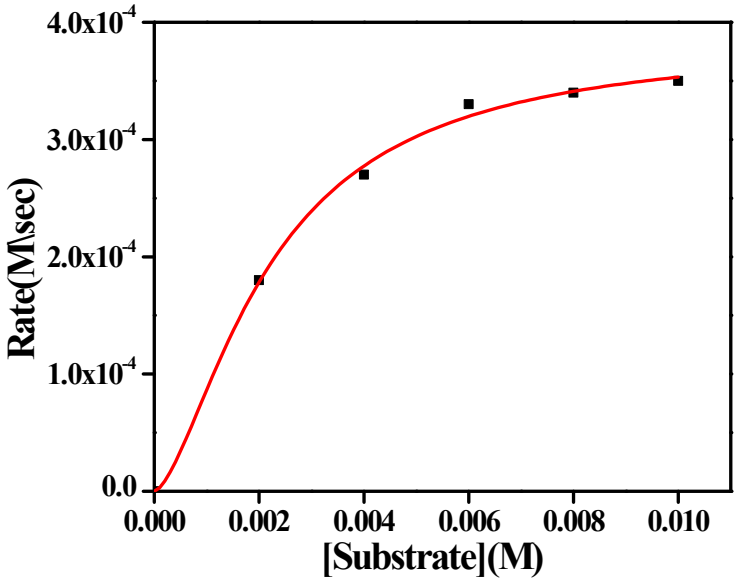


Figure S33. Plot of the initial rates versus substrate concentrations of 3,5-DTBC for the oxidation reaction catalyzed by complex **3**.

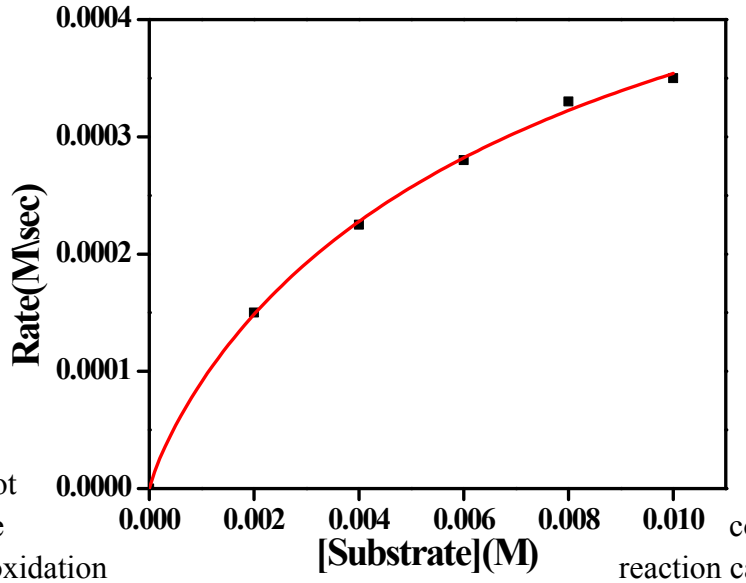


Figure S34. Plot of the initial rates versus substrate concentrations of 3,5-DTBC for the oxidation reaction catalyzed by complex **4**.

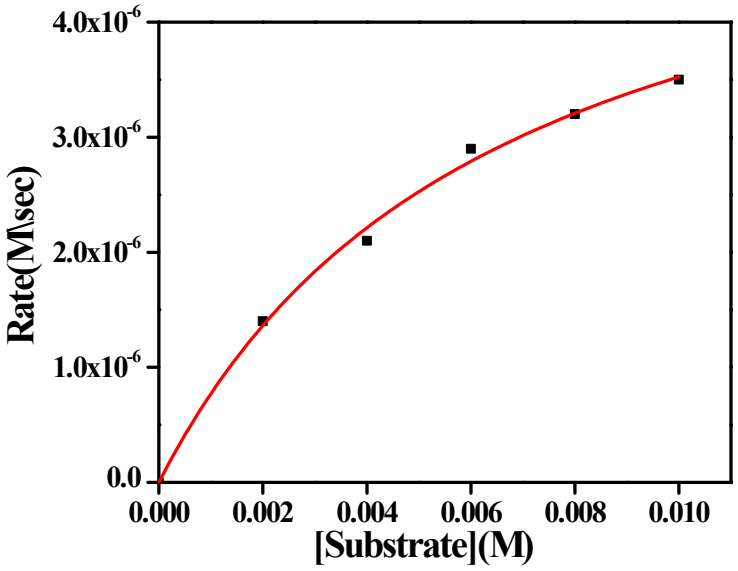


Figure S35. Plot of the initial rates versus substrate concentrations for the oxidation of 2-amino phenol by complex **2**.

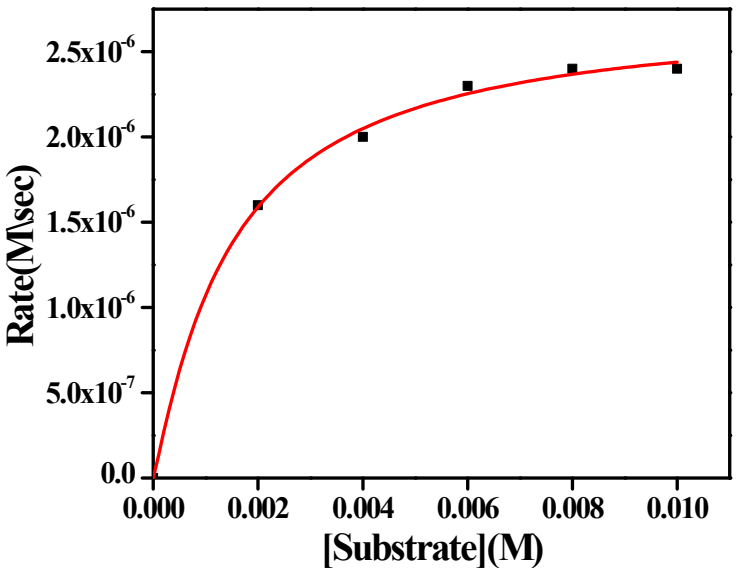


Figure S36. Plot of the initial rates versus substrate concentrations for the oxidation of 2-amino phenol by complex **3**.

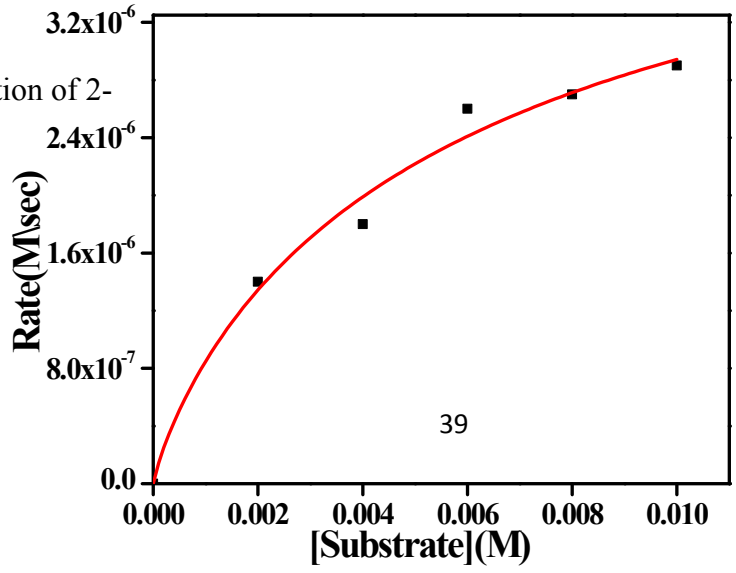


Figure S37. Plot of the initial rates versus substrate concentrations for the oxidation of 2-amino phenol by complex **4**.

Table S21. Crystal data and structural refinement parameters for complexes $[Zn_2(OMe\text{-}Phimp)_2(Cl)_2]$ (**1**) and $[Zn_2(N\text{-}Phimp)_2(Cl)_2]\cdot CH_3CN$ (**3**·CH_3CN).

	1	**3**·CH_3CN
Empirical formula	$C_{38}H_{32}Cl_2N_6O_4Zn_2$	$C_{44}H_{32}Cl_2N_6O_2Zn_2$
Formula weight	838.38	919.49
Temperature /K	293(2)	296(2)
Λ (Å) (Mo-Kα)	0.71073	0.71073
Crystal system	Triclinic	orthorhombic
Space group	P -1	P c a 21
A (Å)	11.506(7)	19.314(4)
B (Å)	11.966(7)	12.669(3)
C (Å)	15.127(9)	17.150(4)
α (˚)	84.49(3)	90.00
γ (˚)	63.54(3)	90.00
B (˚)	89.19(3)	90.00
V (Å^3)	1854.9(19)	4196.4(16)
Z	2	4
ρ_{calc} (gcm^{-3})	1.501	1.455
F(000)	856.0	1880.0
Theta range	1.45−26.94	1.61−26.420
Index ranges	$-11< h< 11$, $-12< k< 12$, $-15< l< 13$	$-23< h< 13$, $-14< k< 15$, $-21< l< 21$

Data/restraints/par.	4361/0/244	6602/157/497
GOF[a] on F^2	0.882	0.940
*R*1[b] [$I > 2\sigma(I)$]	0.0439	0.0553
*R*1[all data]	0.0754	0.1223
*wR*2[c] [$I > 2\sigma(I)$]	0.1111	0.1296
*wR*2 [all data]	0.1408	0.1699

GOF = $[\Sigma[w(F_o^2 - F_c^2)^2] / M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [(F_o^2)^2]]^{1/2}$.

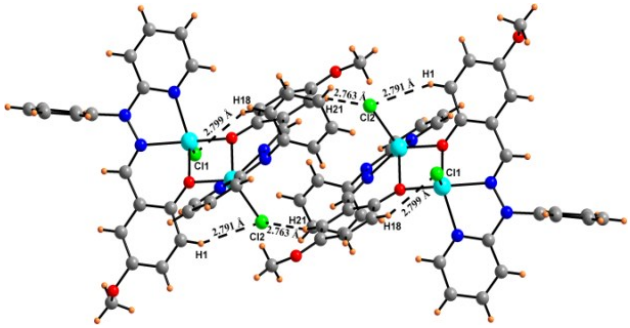


Figure S38. Intermolecular and intramolecular hydrogen bonding network between chloride ion and aryl hydrogen in complex **1**.

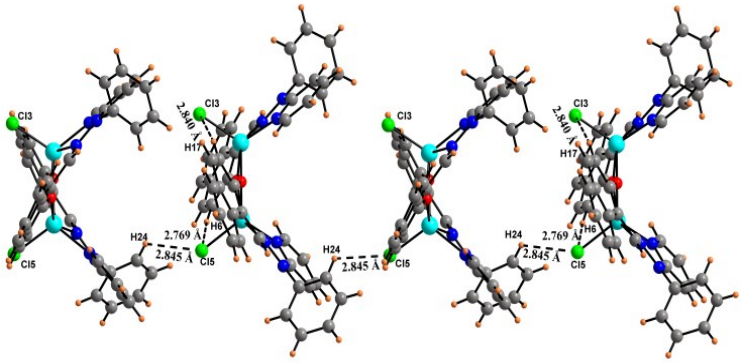


Figure S39. Intermolecular and intramolecular hydrogen bonding network between chloride ion and aryl hydrogen in complex **3**·CH_3CN.

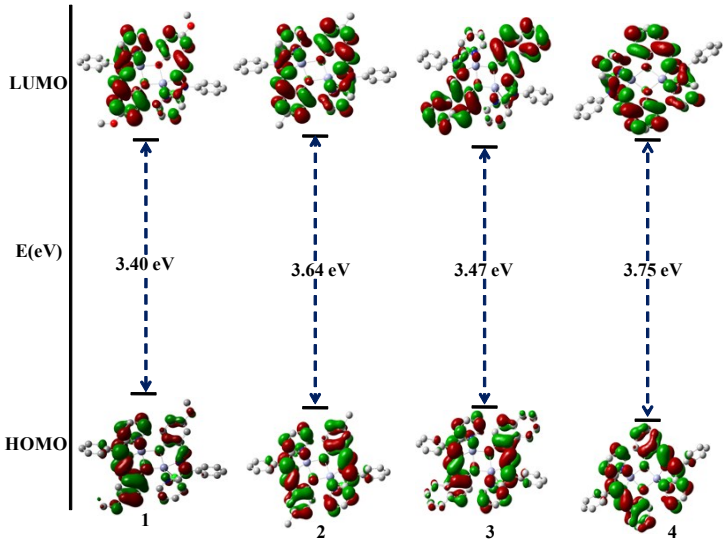
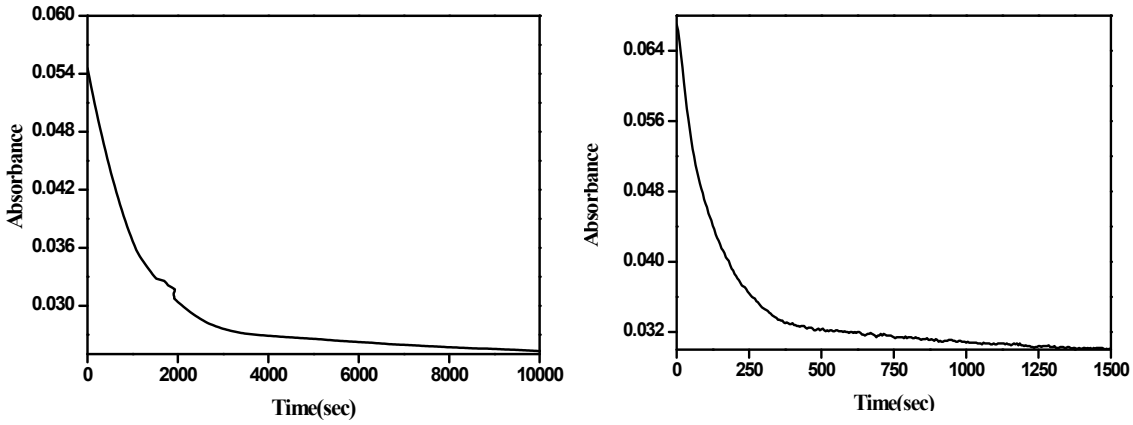
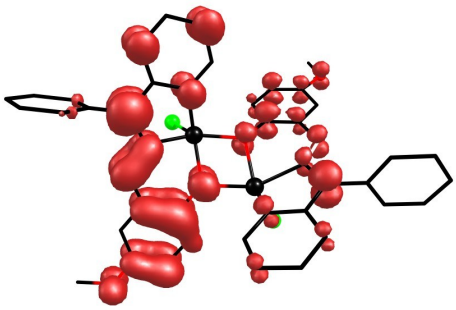


Figure S40. The HOMO–LUMO energy gaps for the complexes **1**, **2**, **3**·CH_3CN, and **4**. The green and reddish brown color part of the FMO plots give rise to the different phases of the molecular wave functions however the isovalue was 0.02 au.

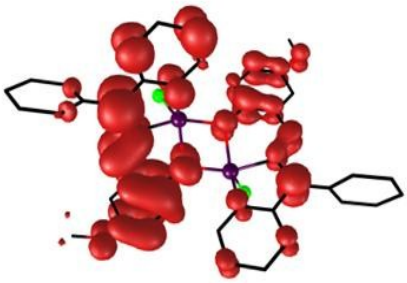


Complex **1** Complex **3**.CH_3CN

Figure S41. Plot between absorbance and time (sec) of phenoxyl radical decomposition rate of complexes **1** and **3**.CH_3CN



Oxidized species (1^{+})



Reduced species(1^{-})

Figure S42. Spin density plot of oxidised (**1**$^{+}$) and reduced (**1**$^{-}$) species

Table S22. Coordinates of the optimized structures of the complexes **1**, **2**, **3**.CH_3CN and **4**

Complex **1 (**B3LYP/LANL2DZ**)**

30	-1.225056000	0.936308000	-0.519451000
30	1.297242000	-0.943411000	-0.575741000
17	-2.410878000	2.169359000	-2.164577000
17	2.484496000	-2.058350000	-2.297291000
6	1.200518000	3.229696000	-1.592897000
1	0.165111000	3.241759000	-1.925019000
6	2.039987000	4.316657000	-1.875323000
1	1.633000000	5.166053000	-2.415215000
6	3.393843000	4.287018000	-1.470205000
6	3.883623000	3.164321000	-0.796155000
1	4.931153000	3.154102000	-0.504204000
6	3.050569000	2.052477000	-0.505134000
6	3.674868000	0.939306000	0.196498000
1	4.714947000	1.085557000	0.496727000

6	5.175810000	-1.274520000	1.208083000
6	5.867250000	-0.845174000	2.355793000
1	5.308724000	-0.474441000	3.211697000
6	7.274193000	-0.903479000	2.378592000
1	7.815377000	-0.576395000	3.262710000
6	7.977403000	-1.381038000	1.255041000
1	9.063653000	-1.423507000	1.273264000
6	7.275936000	-1.800017000	0.105634000
1	7.819045000	-2.164520000	-0.762227000
6	5.870963000	-1.747856000	0.075696000
1	5.308101000	-2.057947000	-0.802629000
6	2.932203000	-2.312417000	1.503732000
6	3.442637000	-3.376331000	2.290533000
1	4.478178000	-3.373319000	2.607702000
6	2.581825000	-4.418495000	2.644371000
1	2.955777000	-5.242333000	3.246604000
6	1.232851000	-4.397261000	2.222595000
1	0.541140000	-5.190223000	2.483985000
6	0.811205000	-3.325682000	1.430610000
1	-0.201496000	-3.264871000	1.048480000
6	-1.123464000	-3.180000000	-1.785707000
1	-0.083722000	-3.176595000	-2.104094000
6	-1.963273000	-4.235776000	-2.136292000
1	-1.592287000	-5.074837000	-2.717376000
6	-3.326591000	-4.226147000	-1.752928000
6	-3.827859000	-3.148082000	-1.022004000
1	-4.872879000	-3.112745000	-0.724870000
6	-2.984025000	-2.054906000	-0.654455000
6	-3.605716000	-0.987537000	0.112661000

1	-4.647921000	-1.147059000	0.399809000
6	-5.106042000	1.155168000	1.270190000
6	-5.796269000	1.700020000	0.167178000
1	-5.229394000	2.063598000	-0.687741000
6	-7.201244000	1.754326000	0.195448000
1	-7.740133000	2.175229000	-0.649271000
6	-7.908180000	1.266926000	1.314217000
1	-8.994318000	1.313146000	1.332162000
6	-7.210200000	0.718147000	2.408115000
1	-7.755265000	0.339731000	3.269108000
6	-5.803253000	0.656946000	2.386276000
1	-5.248715000	0.232580000	3.219559000
6	-2.861730000	2.164350000	1.645936000
6	-3.370982000	3.172787000	2.503600000
1	-4.407563000	3.152034000	2.816832000
6	-2.507031000	4.183737000	2.932434000
1	-2.879492000	4.964529000	3.590435000
6	-1.156607000	4.186781000	2.514353000
1	-0.462310000	4.955515000	2.834705000
6	-0.736542000	3.172188000	1.649631000
1	0.276958000	3.133656000	1.266426000
6	1.670976000	2.086491000	-0.905049000
6	-1.604658000	-2.069928000	-1.038134000
6	-5.495407000	-5.361911000	-1.859629000
1	-5.676260000	-5.355755000	-0.774386000
1	-5.870122000	-6.294531000	-2.286685000
1	-6.013765000	-4.509567000	-2.322453000
6	3.881691000	6.479186000	-2.457593000
1	3.554266000	6.193945000	-3.467393000

1	4.758347000	7.126961000	-2.525896000
1	3.068351000	7.013890000	-1.945933000
8	-0.750827000	-1.061676000	-0.701879000
8	0.817567000	1.055542000	-0.631408000
8	4.318072000	5.319948000	-1.694764000
8	-4.074006000	-5.341147000	-2.160187000
7	-2.994233000	0.120530000	0.450107000
7	-3.660012000	1.094194000	1.220812000
7	-1.570068000	2.189215000	1.215674000
7	3.065157000	-0.189242000	0.455378000
7	3.729573000	-1.213508000	1.156284000
7	1.641625000	-2.311029000	1.069505000

Complex **2** (B3LYP/LANL2DZ)

30	-1.370979000	0.778408000	-0.658088000
30	1.370971000	-0.777948000	-0.657965000
17	-2.710293000	1.802650000	-2.323824000
17	2.709982000	-1.801280000	-2.324470000
8	-0.644643000	-1.147167000	-0.793678000
8	0.644703000	1.147814000	-0.792337000
7	-3.006053000	-0.233166000	0.363830000
7	-3.779453000	0.664929000	1.127503000
7	-1.852186000	2.024273000	1.048188000
7	3.006196000	0.233072000	0.364065000
7	3.779439000	-0.665346000	1.127460000
7	1.851796000	-2.024185000	1.048068000
6	-1.364933000	-2.262318000	-1.099687000

6	-0.758560000	-3.316613000	-1.830936000
1	0.269482000	-3.189547000	-2.162184000
6	-1.471240000	-4.476936000	-2.146222000
1	-0.975676000	-5.259743000	-2.718326000
6	-2.823837000	-4.652952000	-1.750648000
6	-3.423130000	-3.614913000	-1.030719000
1	-4.462753000	-3.714668000	-0.718447000
6	-2.732168000	-2.413976000	-0.693585000
6	-3.474916000	-1.418256000	0.061893000
1	-4.483180000	-1.705060000	0.370297000
6	-3.120220000	1.840081000	1.509801000
6	-3.739965000	2.793814000	2.357773000
1	-4.757539000	2.643713000	2.696997000
6	-3.009133000	3.920495000	2.742792000
1	-3.467895000	4.661585000	3.392138000
6	-1.680259000	4.091392000	2.291796000
1	-1.087741000	4.953385000	2.577373000
6	-1.147631000	3.119565000	1.440300000
1	-0.145907000	3.206292000	1.034733000
6	-5.219860000	0.538957000	1.207000000
6	-5.824310000	-0.034624000	2.340840000
1	-5.202932000	-0.374667000	3.165596000
6	-7.226432000	-0.157533000	2.390811000
1	-7.700667000	-0.596128000	3.265061000
6	-8.011122000	0.285117000	1.307636000
1	-9.093393000	0.188871000	1.347050000
6	-7.395809000	0.850331000	0.171551000
1	-8.001291000	1.188822000	-0.665058000
6	-5.996625000	0.979235000	0.115110000

1	-5.498513000	1.405003000	-0.753609000
6	1.365168000	2.262745000	-1.098718000
6	0.758824000	3.317243000	-1.829707000
1	-0.269372000	3.190513000	-2.160623000
6	1.471729000	4.477356000	-2.145227000
1	0.976194000	5.260333000	-2.717127000
6	2.824532000	4.652977000	-1.750148000
6	3.423795000	3.614753000	-1.030481000
1	4.463560000	3.714187000	-0.718583000
6	2.732605000	2.414001000	-0.693133000
6	3.475333000	1.418036000	0.062033000
1	4.483800000	1.704507000	0.370091000
6	3.119906000	-1.840353000	1.509677000
6	3.739407000	-2.794327000	2.357549000
1	4.757046000	-2.644568000	2.696723000
6	3.008265000	-3.920820000	2.742534000
1	3.466849000	-4.662076000	3.391814000
6	1.679327000	-4.091319000	2.291583000
1	1.086565000	-4.953146000	2.577151000
6	1.146955000	-3.119310000	1.440132000
1	0.145215000	-3.205777000	1.034538000
6	5.219863000	-0.539659000	1.207083000
6	5.996622000	-0.979646000	0.115073000
1	5.498504000	-1.404995000	-0.753845000
6	7.395827000	-0.851000000	0.171659000
1	8.001300000	-1.189262000	-0.665050000
6	8.011162000	-0.286342000	1.308005000
1	9.093446000	-0.190302000	1.347539000
6	7.226473000	0.156030000	2.391298000

1	7.700731000	0.594207000	3.265745000
6	5.824337000	0.033393000	2.341181000
1	5.202950000	0.373271000	3.165998000
6	-3.582741000	-5.916172000	-2.116054000
1	-4.595979000	-5.910374000	-1.697323000
1	-3.674501000	-6.024530000	-3.205733000
1	-3.071638000	-6.814719000	-1.743627000
6	3.583637000	5.915989000	-2.115859000
1	3.675424000	6.024063000	-3.205565000
1	3.072668000	6.814699000	-1.743653000
1	4.596874000	5.910140000	-1.697123000

Complex **3** (B3LYP/LANL2DZ)

30	1.044483000	-1.189118000	-0.685265000
30	-1.044237000	1.188561000	-0.684926000
8	0.990309000	0.872098000	-0.861060000
8	-0.990246000	-0.872373000	-0.860328000
6	2.031668000	1.680999000	-1.176163000
6	4.121012000	3.495849000	-1.904843000
6	4.435735000	2.324488000	-1.129135000
6	1.754649000	2.854261000	-1.956397000
1	0.730006000	3.017764000	-2.280779000
6	2.763036000	3.728225000	-2.300272000
1	2.534490000	4.608280000	-2.897838000
6	5.151144000	4.405251000	-2.286993000
1	4.879629000	5.279467000	-2.875303000
6	-3.363083000	-1.411944000	-0.742652000
6	-4.435782000	-2.324499000	-1.129048000
6	-4.121022000	-3.495850000	-1.904767000
6	-2.031682000	-1.681166000	-1.175694000

6	-2.763022000	-3.728270000	-2.300039000
1	-2.534441000	-4.608272000	-2.897668000
6	-1.754636000	-2.854372000	-1.955972000
1	-0.729986000	-3.017906000	-2.280300000
6	-5.812544000	-2.116970000	-0.793910000
1	-6.122514000	-1.231252000	-0.248852000
6	-5.151151000	-4.405197000	-2.287085000
1	-4.879586000	-5.279409000	-2.875382000
6	-6.474794000	-4.182521000	-1.927978000
1	-7.255734000	-4.877603000	-2.224710000
7	-1.021577000	2.465177000	1.060580000
7	-2.848511000	0.691258000	0.397000000
7	-3.247241000	1.716920000	1.282997000
6	-3.680933000	-0.284490000	0.113806000
1	-4.677372000	-0.262329000	0.549612000
6	-6.800943000	-3.020298000	-1.176736000
1	-7.836869000	-2.827615000	-0.907155000
6	-4.643087000	1.967815000	1.570539000
6	-5.219481000	1.497234000	2.765260000
1	-4.605982000	0.951248000	3.477558000
6	3.363030000	1.411864000	-0.742931000
6	-5.416905000	2.668267000	0.622048000
1	-4.949819000	3.009841000	-0.298926000
6	-2.246441000	2.628760000	1.634416000
6	5.812437000	2.117017000	-0.793785000
1	6.122358000	1.231306000	-0.248683000
6	6.474756000	4.182625000	-1.927707000
1	7.255694000	4.877770000	-2.224302000
6	6.800853000	3.020409000	-1.176446000

1	7.836745000	2.827759000	-0.906714000
7	2.848418000	-0.691328000	0.396800000
7	3.247244000	-1.716859000	1.282979000
6	0.156199000	-4.334171000	2.329640000
1	-0.681607000	-4.976358000	2.577005000
6	0.000965000	-3.294230000	1.409763000
1	-0.946616000	-3.110848000	0.916142000
6	2.489498000	-3.676189000	2.561510000
1	3.474404000	-3.807520000	2.992213000
6	4.643084000	-1.967700000	1.570559000
6	5.219402000	-1.497231000	2.765374000
1	4.605866000	-0.951244000	3.477637000
6	6.778265000	-2.905860000	0.883123000
1	7.379187000	-3.446629000	0.156856000
6	6.582347000	-1.741708000	3.021770000
1	7.032052000	-1.383975000	3.944390000
6	5.416981000	-2.668080000	0.622079000
1	4.949992000	-3.009584000	-0.298968000
6	7.360924000	-2.445513000	2.081902000
1	8.413300000	-2.632629000	2.280504000
6	3.680817000	0.284466000	0.113562000
1	4.677237000	0.262356000	0.549419000
6	1.434793000	-4.526012000	2.902005000
1	1.603594000	-5.333667000	3.609460000
6	-7.360966000	2.445525000	2.081696000
1	-8.413381000	2.632548000	2.280172000
6	-6.582462000	1.741666000	3.021570000
1	-7.032205000	1.383885000	3.944154000
6	-6.778208000	2.906004000	0.883003000

1	-7.379093000	3.446821000	0.156742000
6	-0.000954000	3.294311000	1.409403000
1	0.946623000	3.110902000	0.915776000
6	-0.156172000	4.334430000	2.329086000
1	0.681661000	4.976624000	2.576333000
6	-2.489449000	3.676487000	2.561104000
1	-3.474341000	3.807859000	2.991828000
6	-1.434743000	4.526385000	2.901436000
1	-1.603554000	5.334210000	3.608692000
7	1.021597000	-2.465160000	1.060793000
6	2.246471000	-2.628636000	1.634618000
17	1.977270000	-2.602490000	-2.325153000
17	-1.977550000	2.602987000	-2.323928000

Complex **4** (B3LYP/LANL2DZ)

30	-1.446720000	0.627124000	-0.732511000
30	1.446699000	-0.626882000	-0.732519000
17	-2.888813000	1.496177000	-2.399678000
17	2.888806000	-1.495564000	-2.399883000
8	-0.519553000	-1.210920000	-0.869248000
8	0.519558000	1.211246000	-0.868638000
7	-2.966268000	-0.550331000	0.287649000
7	-3.832628000	0.263437000	1.044705000
7	-2.055912000	1.815970000	0.972383000
7	2.966332000	0.550272000	0.287834000
7	3.832620000	-0.263689000	1.044753000
7	2.055769000	-1.816059000	0.972163000

6	-1.114271000	-2.396041000	-1.177625000
6	-0.391976000	-3.376672000	-1.906472000
1	0.616821000	-3.136585000	-2.233929000
6	-0.973954000	-4.609410000	-2.225164000
1	-0.398863000	-5.336231000	-2.794283000
6	-2.297872000	-4.910099000	-1.826069000
6	-3.022114000	-3.953370000	-1.111680000
1	-4.045476000	-4.167215000	-0.805237000
6	-2.462475000	-2.688341000	-0.773745000
6	-3.308905000	-1.775539000	-0.021072000
1	-4.284625000	-2.165657000	0.278661000
6	-3.299393000	1.500848000	1.429623000
6	-4.017915000	2.384612000	2.274929000
1	-5.015380000	2.129157000	2.610730000
6	-3.409791000	3.581479000	2.661915000
1	-3.945513000	4.270780000	3.309318000
6	-2.104441000	3.889904000	2.215345000
1	-1.606216000	4.809232000	2.502029000
6	-1.470521000	2.978696000	1.366230000
1	-0.482218000	3.169256000	0.963423000
6	-5.255257000	-0.002652000	1.102920000
6	-5.818196000	-0.632522000	2.228077000
1	-5.179574000	-0.911310000	3.062576000
6	-7.202584000	-0.890001000	2.256734000
1	-7.645708000	-1.372956000	3.123891000
6	-8.009631000	-0.524457000	1.161291000
1	-9.077953000	-0.725115000	1.184246000
6	-7.434658000	0.098198000	0.034085000
1	-8.057191000	0.376974000	-0.811964000

6	-6.053790000	0.361710000	-0.001277000
1	-5.585147000	0.834030000	-0.862598000
6	1.114370000	2.396328000	-1.176996000
6	0.392108000	3.377097000	-1.905689000
1	-0.616738000	3.137143000	-2.233098000
6	0.974176000	4.609809000	-2.224320000
1	0.399106000	5.336734000	-2.793327000
6	2.298153000	4.910338000	-1.825306000
6	3.022365000	3.953474000	-1.111065000
1	4.045772000	4.167195000	-0.804685000
6	2.462639000	2.688465000	-0.773208000
6	3.309042000	1.775507000	-0.020693000
1	4.284793000	2.165520000	0.279076000
6	3.299279000	-1.501115000	1.429460000
6	4.017725000	-2.385086000	2.274617000
1	5.015211000	-2.129769000	2.610462000
6	3.409503000	-3.581967000	2.661399000
1	3.945169000	-4.271423000	3.308685000
6	2.104129000	-3.890212000	2.214773000
1	1.605829000	-4.809549000	2.501297000
6	1.470288000	-2.978810000	1.365811000
1	0.481972000	-3.169231000	0.962966000
6	5.255258000	0.002319000	1.103091000
6	6.053824000	-0.361853000	-0.001144000
1	5.585200000	-0.833976000	-0.862582000
6	7.434703000	-0.098408000	0.034335000
1	8.057262000	-0.377039000	-0.811743000
6	8.009651000	0.523992000	1.161694000
1	9.077980000	0.724599000	1.184739000

6	7.202569000	0.889350000	2.257174000
1	7.645674000	1.372111000	3.124448000
6	5.818172000	0.631939000	2.228400000
1	5.179523000	0.910590000	3.062925000
1	2.746928000	5.866651000	-2.078685000
1	-2.746578000	-5.866429000	-2.079503000