Electronic Supplementary Information

(36 pages)

Molecular and Electronic Structure of Nonradical Homoleptic Pyridyl-azo-oxime Complexes of Cobalt(III) and the Azo-oxime Anion Radical Congener: An Experimental and Theoretical Investigation

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Table S1 Selected optimized geometrical parameters of **2a**, **3a**$^{+}$ and **3a** in the ground and lower lying triplet excited states at B3LYP level

Bond Lengths (Å)								
2a			**3a**$^{+}$			**3a**		
	S_0	T_1		S_0	T_1		S_0	T_1
Co1–N6	1.966	1.962	Co53–N43	1.970	1.950	Co53–N43	1.960	1.957
Co1–N8	1.941	1.924	Co53–N45	1.877	1.871	Co53–N45	1.872	1.872
N6–N7	1.298	1.370	Co53–O51	1.909	1.908	Co53–O51	1.914	1.900
N8–O2	1.275	1.311	N45–N46	1.296	1.359	N45–N46	1.329	1.359
Co1–N10	1.960	1.961	N44–O51	1.336	1.355	N44–O51	1.355	1.372
Co1–N12	1.950	1.956	Co53–N47	1.970	1.975	Co53–N47	1.959	1.957
N10–N11	1.294	1.295	Co53–N49	1.877	1.881	Co53–N49	1.873	1.872
N12–O3	1.279	1.280	Co53–O52	1.909	1.912	Co53–O52	1.915	1.900
Co1–N14	1.942	1.938	N49–N50	1.296	1.298	N49–N50	1.327	1.359
Co1–N16	1.944	1.939	N48–O52	1.336	1.336	N48–O52	1.352	1.372
N14–N15	1.298	1.299						
N16–O4	1.274	1.273						
Bond Angles (°)								
2a			**3a**$^{+}$			**3a**		
	S_0	T_1		S_0	T_1		S_0	T_1
N6–Co1–N8	80.675	79.988	N43–Co53–N45	81.723	82.004	N43–Co53–N45	81.740	81.755
N6–Co1–N10	99.472	98.735	N43–Co53–N47	94.370	94.153	N43–Co53–N47	93.740	91.850
N6–Co1–N12	85.824	85.106	N43–Co53–N49	102.501	101.682	N43–Co53–N49	100.475	101.675
N6–Co1–N14	168.301	168.580	N43–Co53–O51	164.566	164.392	N43–Co53–O51	164.831	164.904
N6–Co1–N16	91.600	92.531	N43–Co53–O52	89.340	89.628	N43–Co53–O52	88.936	90.226
N8–Co1–N10	171.037	170.347	N45–Co53–N47	102.501	102.277	N45–Co53–N47	100.464	101.675
N8–Co1–N12	91.060	90.413	N45–Co53–N49	173.884	174.594	N45–Co53–N49	176.809	175.142
N8–Co1–N14	90.103	90.489	N45–Co53–O51	82.847	82.408	N45–Co53–O51	83.091	83.181
N8–Co1–N16	86.896	87.501	N45–Co53–O52	92.852	93.273	N45–Co53–O52	94.759	93.421
N10–Co1–N1	80.028	79.939	N47–Co53–N49	81.724	81.514	N47–Co53–N49	81.742	81.755
N10–Co1–N1	90.762	91.700	N47–Co53–O51	89.343	89.904	N47–Co53–O51	88.903	90.227
N10–Co1–N1	102.046	102.131	N47–Co53–O52	164.566	164.358	N47–Co53–O52	164.768	164.904
N12–Co1–N1	101.634	101.375	N49–Co53–O51	92.853	93.817	N49–Co53–O51	94.685	93.420
N12–Co1–N1	176.945	177.091	N49–Co53–O52	82.847	82.858	N49–Co53–O52	83.026	83.181
N14–Co1–N1	80.654	80.681	O51–Co53–O52	91.033	90.492	O51–Co53–O52	92.425	91.652

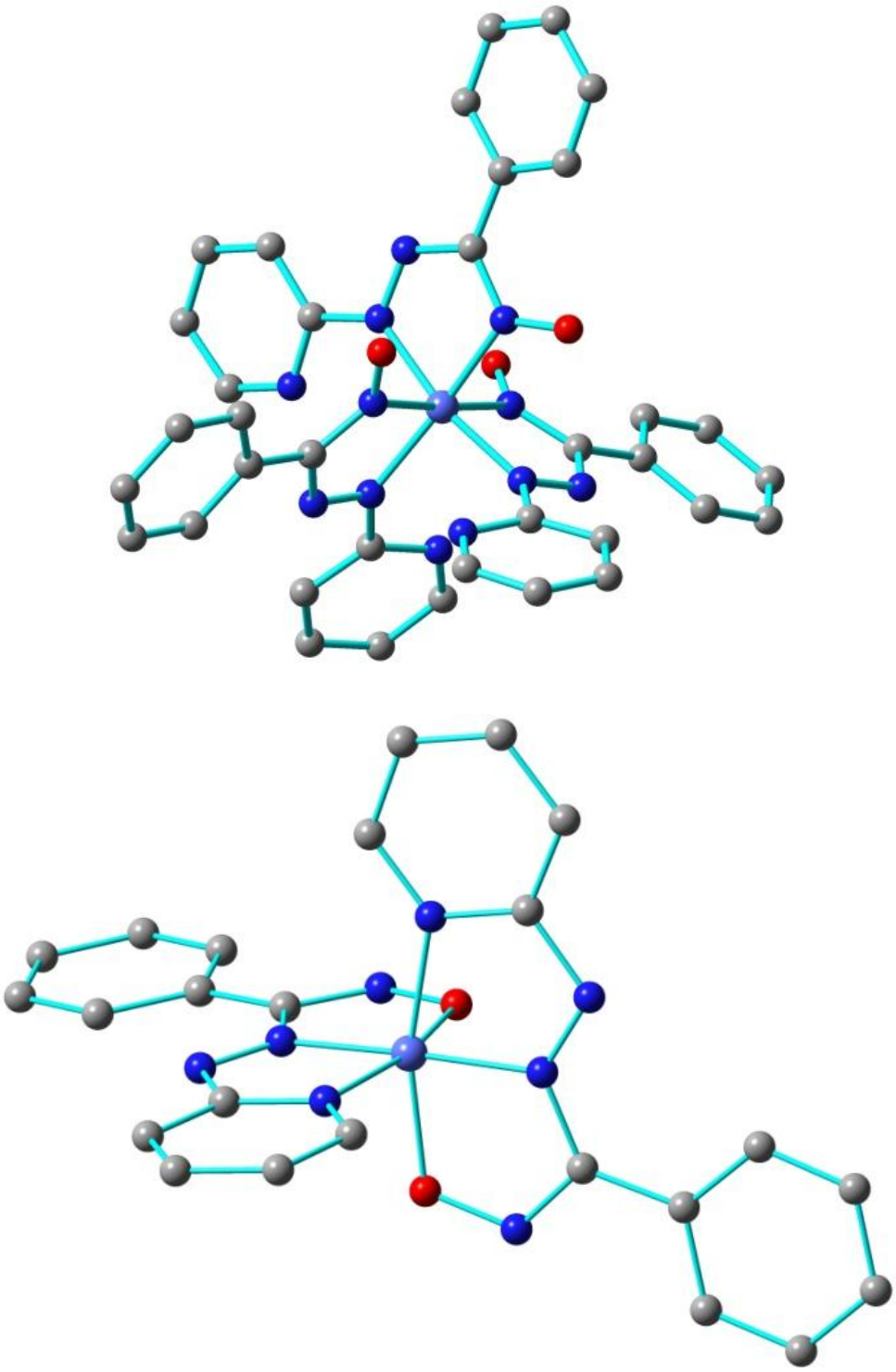

Fig. S1 Optimized molecular structures of **2a** (top) and **3a**$^{+}$ (bottom) (Co: cyan, N: blue, O: red, C: grey. Hydrogen atoms of are omitted for clarity).

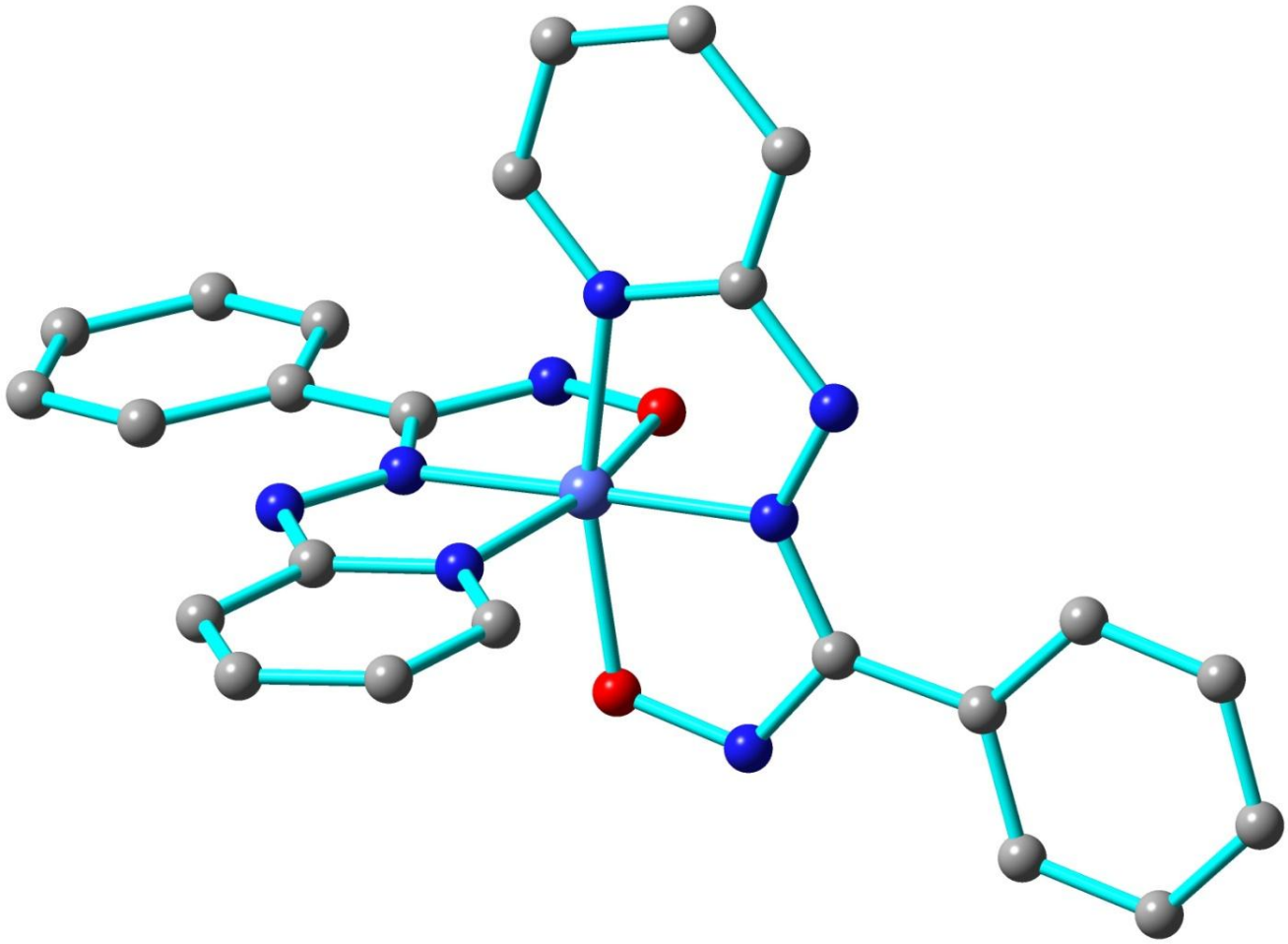

Fig. S2 Optimized molecular structures of **3a** (Co: cyan, N: blue, O: red, C: grey. Hydrogen atoms are omitted for clarity).

Table S2 Frontier Molecular Orbital Composition (%) in the Ground State for **3a**

Orbital	α - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
132	L+5	-0.96	0	25	3	16	56	π*(L)
131	L+4	-1.41	1	91	2	4	2	π*(L)
130	L+3	-1.47	54	15	20	7	4	d_z^2(Co) + π*(L)
129	L+2	-1.55	7	77	4	5	7	π*(L)
128	L+1	-1.91	61	17	1	20	1	$d_{x^2-y^2}$(Co) + π*(L)
127	L	-3.69	4	25	36	35	1	π*(L)
126	H	-4.54	3	27	39	31	0	π*(L)
125	H–1	-5.88	1	12	11	28	48	π(L)
124	H–2	-5.92	5	13	13	24	46	π(L)
123	H–3	-6.68	0	0	0	0	100	π(L)
122	H–4	-6.71	0	0	0	2	98	π(L)
121	H–5	-6.72	6	8	4	66	16	π(L)
		HOMO–LUMO gap = 0.85 eV						
Orbital	β - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
131	L+5	-1.32	1	94	2	94	0	π*(L)
130	L+4	-1.44	3	85	3	85	4	π*(L)
129	L+3	-1.48	57	10	22	10	3	d_z^2(Co) + π*(L)
128	L+2	-1.92	60	16	1	22	1	$d_{x^2-y^2}$(Co) + π*(L)
127	L+1	-3.03	3	30	35	31	1	π*(L)
126	L	-3.11	3	30	35	31	1	π*(L)
125	H	-5.64	1	14	14	23	48	π(L)
124	H–1	-5.72	4	12	13	22	49	π(L)
123	H–2	-6.59	7	7	4	73	10	π(L)
122	H–3	-6.69	0	0	0	0	99	π(L)
121	H–4	-6.72	0	0	0	0	100	π(L)
120	H–5	-6.75	12	11	3	61	12	π(L)
		HOMO–LUMO gap = 2.53 eV						

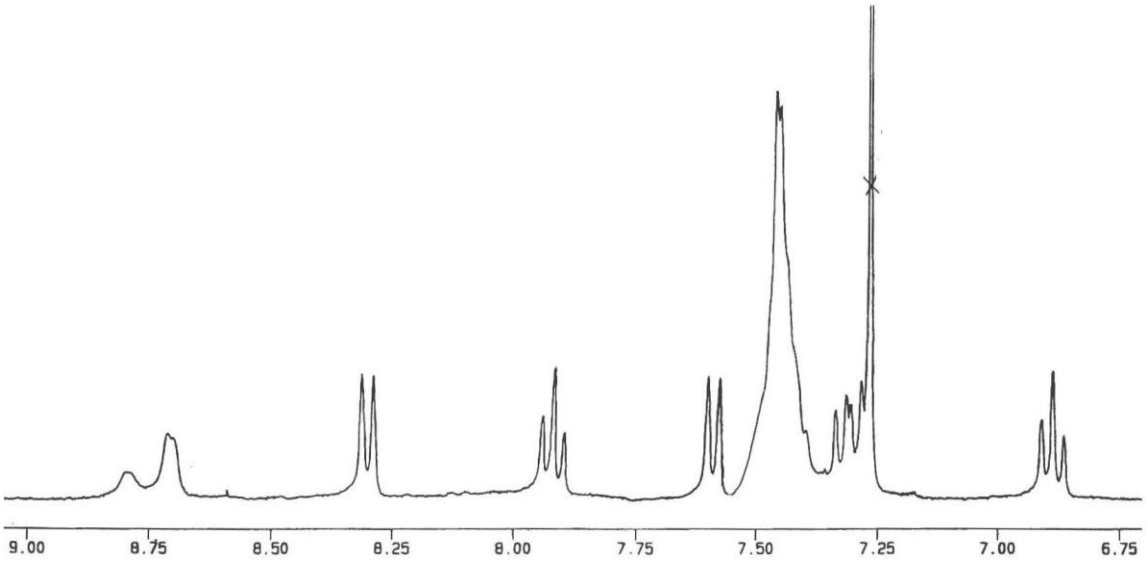

Fig. S3 ^{1}H NMR spectrum of **1a**.

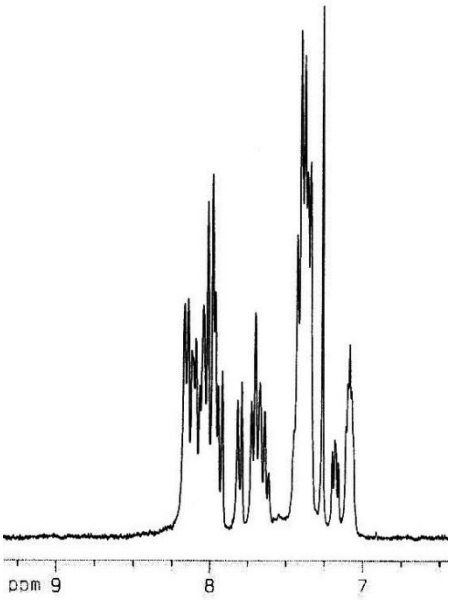

Fig. S4 ^{1}H NMR spectrum of **2a**.

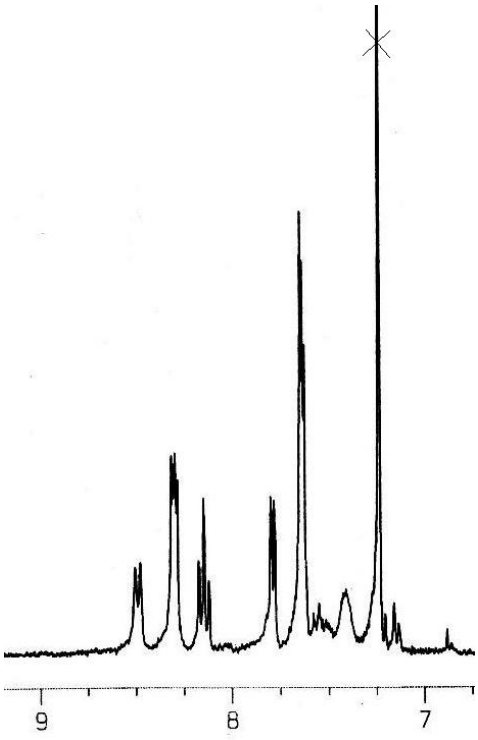

Fig. S5 ^{1}H NMR spectrum of **3a**$^{+}$.

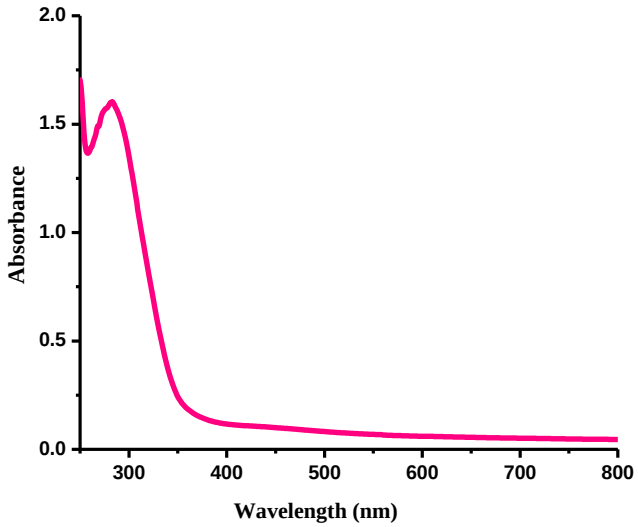

Fig. S6 Experimental absorption spectra of **1b** in acetonitrile.

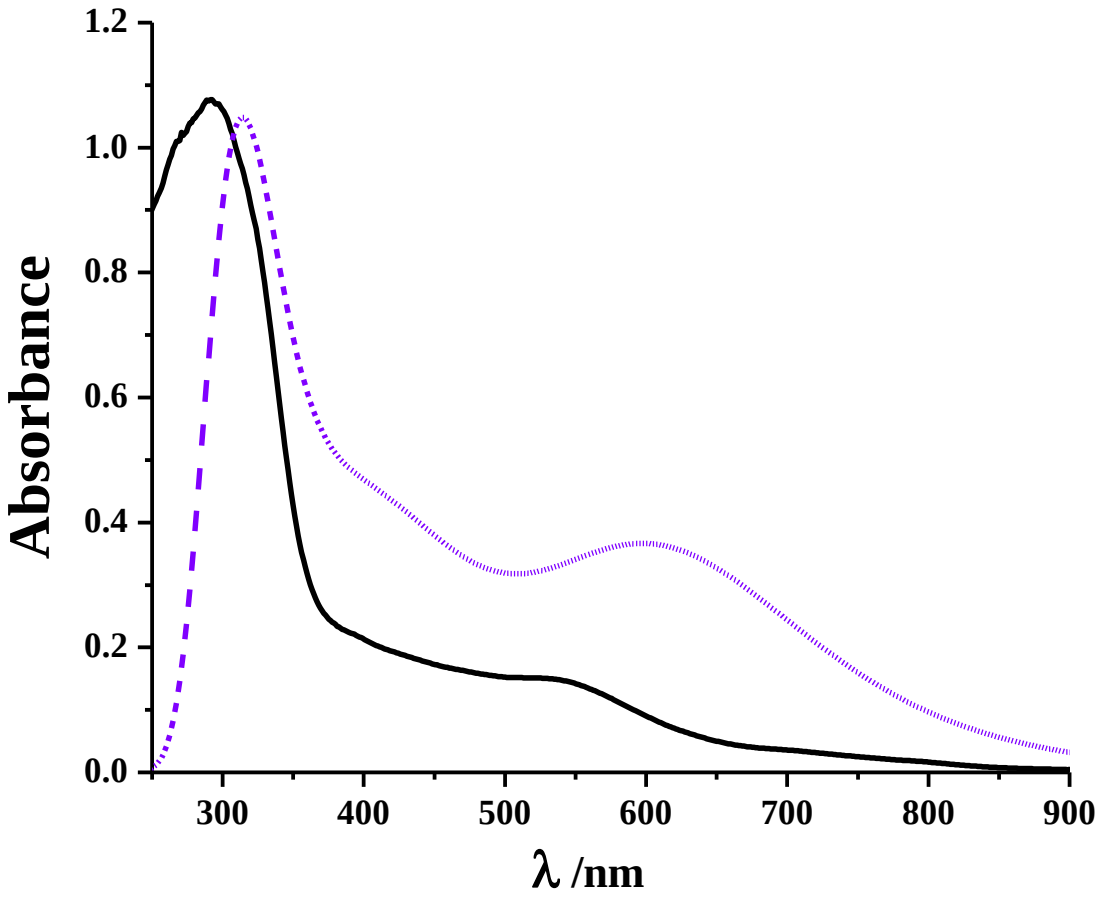

Fig. S7 Experimental (Black bold line) and theoretical (Blue dotted line) absorption spectra of **3a** in acetonitrile

Table S3 Main optical transition at the TD-DFT/B3LYP/6-31G Level for the complex **2a** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in acetonitrile

	Composition	E (eV)	Oscillator strength	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1.	H – 3 → L + 2 (36%) H – 2 → L (14%) H → L + 2 (11%)	2.2988	0.0268	539.34	ILCT/LLCT	544
2.	H – 1 → L + 2 (27%) H → L + 2 (21%) H – 1 → L + 1 (18%)	2.4376	0.1194	508.64	ILCT/LLCT	
3.	H – 4 → L (20%) H – 1 → L + 2 (17%) H – 3 → L (12%)	2.4485	0.0371	506.36	ILCT/LLCT	
4.	H – 10 → L (57%)	3.2786	0.0278	378.16	ILCT/LLCT	
5.	H – 8 → L + 2 (27%)	3.3310	0.0662	372.21	ILCT/LLCT	
6.	H – 9 → L + 1 (25%) H – 8 → L + 1 (21%)	3.3664	0.0357	368.30	ILCT/LLCT	
7.	H – 3 → L + 4 (31%)	3.8140	0.1607	325.07	LMCT/ILCT	319
8.	H → L + 6 (31%)	4.2075	0.4497	294.67	ILCT/LLCT	
9.	H → L + 6 (37%)	4.2262	0.3248	293.37	ILCT/LLCT	
10.	H – 2 → L + 5 (21%) H → L + 7 (14%)	4.2686	0.2640	290.46	ILCT/LLCT	

Table S4 Main optical transition at the TD-DFT/B3LYP/6-31G Level for the complex **3a** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in acetonitrile

	Composition	E (eV)	Oscillator Strength	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1.	H − 1 → L (α) (30%) H → L + 1 (β) (54%)	1.9669	0.0629	630.36	ILCT/LLCT	~600
2.	H − 2 → L (α) (36%) H – 1 → L (β) (49%)	2.0038	0.0711	618.75	ILCT/LLCT	
3.	H → L + 3 (α) (50%) H – 2 → L (β) (14%) H – 6 → L (α) (10%)	2.4040	0.0219	515.73	ILCT/LLCT/ MLCT	~535
4.	H → L + 3 (α) (27%) H − 5 → L (β) (24%) H − 2 → L (β) (10%)	2.4219	0.0102	511.93	LMCT/ILCT/LLCT	
5.	H − 1 → L + 3 (α) (51%)	4.0398	0.0943	306.91	LMCT	
6.	H − 2 → L + 3 (α) (38%) H − 1 → L + 4 (β) (22%)	4.0818	0.1003	303.75	LMCT/ILCT/LLCT	
7.	H → L + 9 (α) (18%) H − 1 → L + 4 (α) (10%)	4.1503	0.0379	298.73	ILCT/LLCT	
8.	H − 1 → L + 4 (α) (15%) H → L + 9 (α) (11%)	4.1694	0.0255	297.37	ILCT/LLCT	292

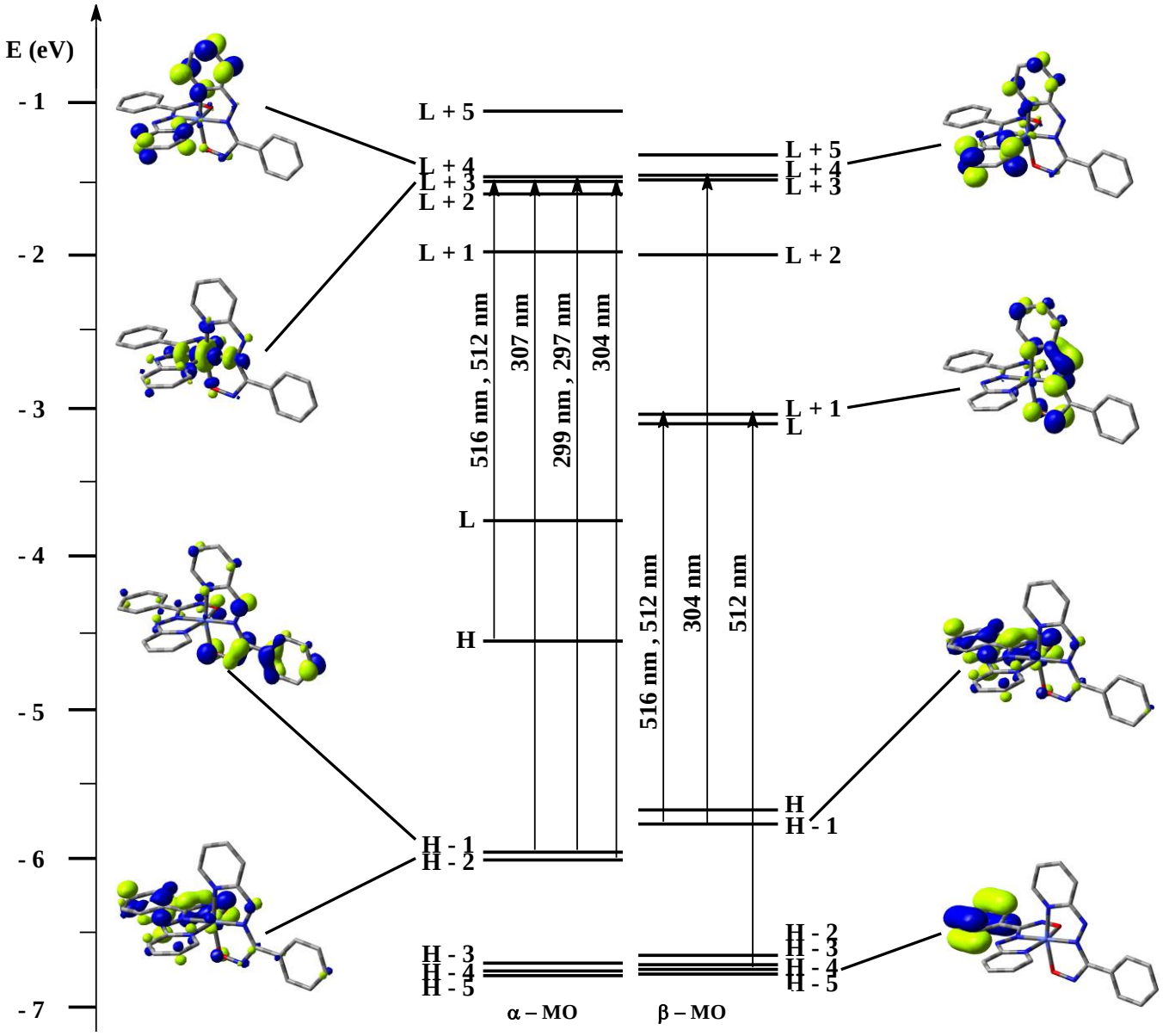

Fig. S8 Partial molecular orbital diagram related to the absorption of complex **3a** with some selected isodensity frontier molecular orbital mainly involved in the electronic transitions.

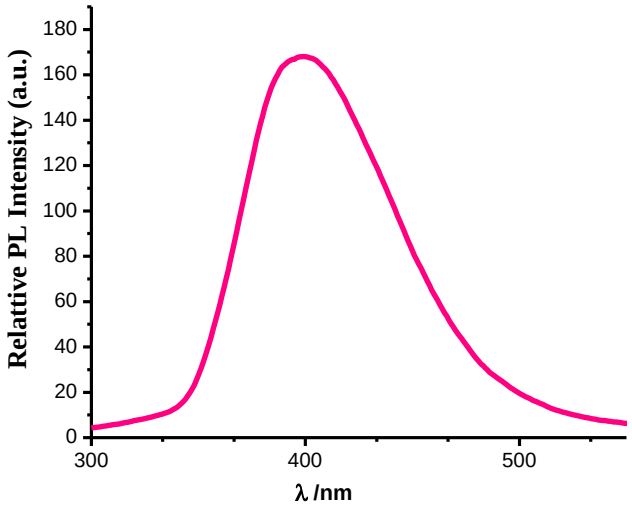

Fig. S9 Luminescence spectra of ligand **1b** in acetonitrile at room temperature.

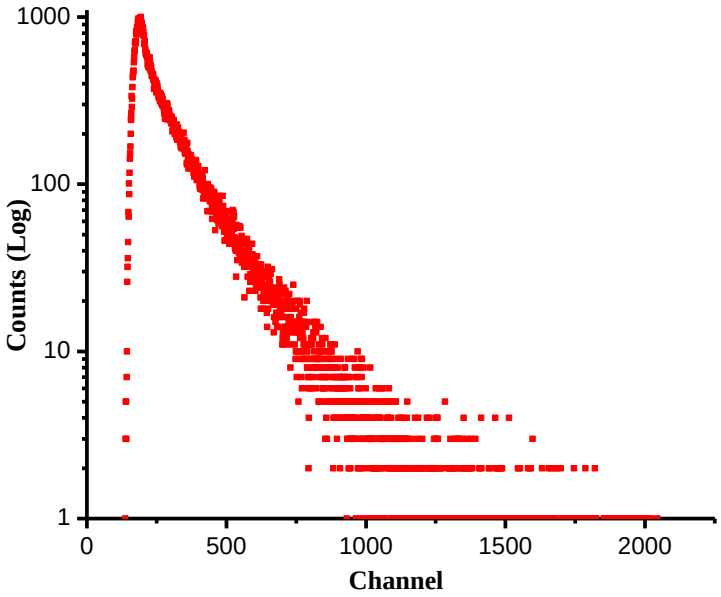

Fig. S10 Changes in the time-resolved photoluminescence decay of ligand **1b** in acetonitrile at room temperature obtained with 330 nm excitation. The emission at 398 nm was monitored for ligand **1b**.

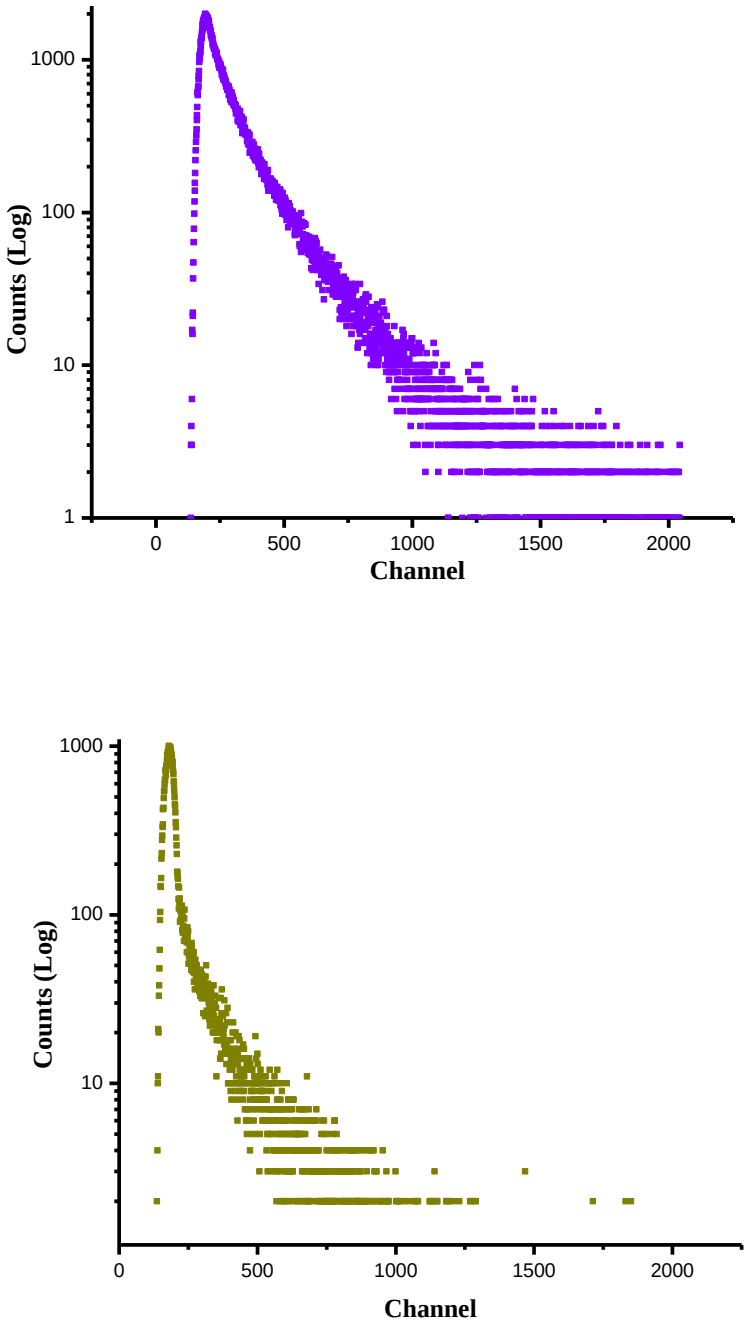

Fig. S11 Changes in the time-resolved photoluminescence decay of complexes **2a** (top) and **3a**$^{+}$ (bottom) in acetonitrile at room temperature obtained with 330 nm excitation. The emission at 396 and 393 nm was monitored for complexes **2a** and **3a**$^{+}$ respectively.

Table S5 Comparison of selected optimized geometrical parameters of **2a** and **3a**$^{+}$ in the ground and lower lying triplet excited states at B3LYP levels with experimental crystallographic data

Bond Lengths (Å)[a]							
2a				**3a**$^{+}$			
	Expt.	S_0	T_1		Expt.	S_0	T_1
$Co-N_{oxime}$	1.918(2)	1.945	1.940	$Co-O_{oxime}$	1.891(4)	1.909	1.910
$Co-N_{azo}$	1.922(2)	1.956	1.954	$Co-N_{azo}$	1.838(5)	1.877	1.876
$N_{azo}-N_{azo}$	1.285(3)	1.297	1.321	$Co-N_{py}$	1.943(5)	1.970	1.963
$N_{oxime}-O_{oxime}$	1.253(3)	1.276	1.288	$N_{azo}-N_{azo}$	1.272(6)	1.296	1.329
$C_{oxime}-N_{oxime}$	1.351(3)	1.366	1.376	$N_{oxime}-O_{oxime}$	1.342(6)	1.336	1.346
				$C_{oxime}-N_{oxime}$	1.308(8)	1.344	1.368
Bond Angles (°)[a]							
2a				**3a**$^{+}$			
	Expt.	S_0	T_1		Expt.	S_0	T_1
$N_{oxime}-Co-N_{azo}$	80.08(9)	80.45	80.203	$N_{azo}-Co-N_{py}$	79.7(2)	81.724	81.759
				$N_{azo}-Co-O_{oxime}$	83.0(2)	82.847	82.633
				$N_{py}-Co-O_{oxime}$	162.6(2)	164.566	164.375

[a] average value

Table S6 Frontier Molecular Orbital Composition (%) in the Ground State for **2a** and **3a**$^{+}$ in acetonitrile solvent by means of CPCM model

	Orbital	MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
2a	190	L+5	-0.95	1	77	2	4	16	π*(L)
	189	L+4	-1.55	55	2	7	31	5	d_{x2-y2} + π*(L)
	188	L+3	-1.69	57	8	24	9	2	d_{z2}(Co) + π*(L)
	187	L+2	-2.67	1	15	42	41	1	π*(L)
	186	L+1	-2.89	3	15	40	42	1	π*(L)
	185	L	-3.02	3	13	41	41	1	π*(L)
	184	H	-5.52	1	11	14	27	47	π(L)
	183	H–1	-5.57	2	13	14	24	47	π(L)
	182	H–2	-5.73	2	10	12	28	49	π(L)
	181	H–3	-6.05	1	1	8	77	12	π(L)
	180	H–4	-6.54	4	4	10	69	14	π(L)
	179	H–5	-6.61	0	0	0	1	98	π(L)
	HOMO–LUMO gap = 2.50 eV								

	Orbital	MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
3a^{+}	131	L+5	-4.86	0	95	2	2	0	π*(L)
	130	L+4	-4.92	2	90	3	3	2	π*(L)
	129	L+3	-5.22	58	7	22	9	3	d_{z2}(Co) + π*(L)
	128	L+2	-5.60	60	15	1	24	1	d_{x2-y2} + π*(L)
	127	L+1	-6.82	3	28	41	27	1	π*(L)
	126	L	-6.86	3	28	41	28	1	π*(L)
	125	H	-8.89	0	5	7	19	68	π(L)
	124	H–1	-8.92	2	5	7	17	69	π(L)
	123	H–2	-9.24	0	0	0	0	99	π(L)
	122	H–3	-9.24	0	0	0	0	99	π(L)
	121	H–4	-10.12	7	11	6	59	17	π(L)
	120	H–5	-10.20	6	18	9	37	31	π(L)
	HOMO–LUMO gap = 2.03 eV								

Table S7 Frontier Molecular Orbital Composition (%) in the Excited State for **2a**

Orbital	α - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Phenyl	Main Bond Type
191	L + 5	–0.82	1	88	1	2	8	π*(L)
190	L + 4	–1.16	24	9	14	12	41	$d_{x^2-y^2}$(Co) + π*(L)
189	L + 3	–1.32	50	3	8	28	11	d_{z^2}(Co) + π*(L)
188	L + 2	–1.51	41	8	20	9	23	d_{z^2}/ $d_{x^2-y^2}$(Co) + π*(L)
187	L + 1	–2.58	2	14	41	43	1	π*(L)
186	L	–2.73	3	15	39	43	0	π*(L)
185	H	–4.92	4	12	38	43	3	π(L)
184	H – 1	–5.42	1	13	15	24	47	π(L)
183	H – 2	–5.50	2	13	14	26	44	π(L)
182	H – 3	–5.97	2	2	6	79	11	π(L)
181	H – 4	–6.22	4	18	16	30	33	π(L)
180	H – 5	–6.54	0	0	0	2	97	π(L)
Orbital	β - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Phenyl	Main Bond Type
189	L + 5	–1.25	53	2	8	31	6	$d_{x^2-y^2}$(Co) + π*(L)
188	L + 4	–1.42	53	7	22	13	3	d_{z^2}(Co) + π*(L)
187	L + 3	–1.90	3	18	31	42	6	π*(L)
186	L + 2	–2.59	3	14	40	42	1	π*(L)
185	L + 1	–2.73	3	16	39	41	1	π*(L)
184	L	–3.95	2	21	27	15	34	π*(L)
183	H	–5.41	1	14	15	23	47	π(L)
182	H – 1	–5.49	2	14	13	26	45	π(L)
181	H – 2	–5.90	2	1	10	76	11	π(L)
180	H – 3	–6.28	5	3	7	74	11	π(L)
179	H – 4	–6.54	0	0	0	0	100	π(L)
178	H – 5	–6.63	0	0	0	1	99	π(L)

Table S8 Frontier Molecular Orbital Composition (%) in the Excited State for **3a**$^{+}$

Orbital	α - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
132	L+5	–4.44	1	68	5	3	22	π*(L)
131	L+4	–4.57	1	89	2	4	4	π*(L)
130	L+3	–4.8	10	39	6	11	33	π*(L)
129	L+2	–4.91	50	9	19	9	13	d_z^2(Co)+ π*(L)
128	L+1	–5.31	62	16	1	20	1	$d_{x^2-y^2}$(Co)+ π*(L)
127	L	–6.6	3	27	39	30	1	π*(L)
126	H	–8.42	3	21	39	36	0	π(L)
125	H–1	–8.66	1	6	9	18	66	π(L)
124	H–2	–9.1	0	0	0	0	100	π(L)
123	H–3	–9.57	2	12	8	23	55	π(L)
122	H–4	–10.01	6	10	5	64	14	π(L)
121	H–5	–10.05	0	0	0	0	99	π(L)
Orbital	β - MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
130	L+5	–4.6	1	90	2	4	3	π*(L)
129	L+4	–4.89	58	7	23	8	4	d_z^2(Co)+ π*(L)
128	L+3	–5.35	60	16	1	23	1	$d_{x^2-y^2}$(Co)+ π*(L)
127	L+2	–5.85	3	34	28	30	5	π*(L)
126	L+1	–6.59	3	25	38	33	1	π*(L)
125	L	–7.53	2	18	18	18	44	π*(L)
124	H	–8.64	1	7	10	16	65	π(L)
123	H–1	–9.1	0	0	0	0	100	π(L)
122	H–2	–9.81	6	9	5	63	16	π(L)
121	H–3	–9.96	9	17	8	40	26	π(L)
120	H–4	–9.97	0	0	0	0	99	π(L)
119	H–5	–10.16	6	16	13	25	41	π(L)

Table S9 Crystal data and structure refinement parameters for complexes **2a** and **3a**$^{+}$**ClO**$_4^{-}$

Compound	**2a**	**3a**$^{+}$**ClO**$_4^{-}$
Formula	$C_{36}H_{27}N_{12}CoO_3$	$C_{24}H_{18}N_8CoClO_6$
Molecular weight	734.63	608.84
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*C*2/c
Crystal size mm^3	0.32x0.21x0.16	0.33x0.19x0.13
A [Å]	11.2383(7)	35.6180(12)
B [Å]	11.5516(7)	8.8888(3)
c [Å]	13.2395(8)	17.5969(6)
α [°]	82.504(3)	90.00
β [°]	85.045(3)	111.657(4)
γ [°]	83.943(3)	90.00
V [Å]	1689.95(18)	5177.9(3)
Z	2	8
ρ_{calc} [g/cm^3]	1.444	1.562
T (K)	296(2)	293(2)
μ [mm^{-1}]	0.565	0.823
F(0 0 0)	756	2480
θ Range (°)	1.56 – 27.54	2.34 – 25.00
Reflections collected	26943	38325
Independent reflections	7680	4569
R_1[a], wR_2[b] (all data)	0.0805, 0.1908	0.1164, 0.2186
R_1, wR_2 [$I > 2\sigma(I)$]	0.0605, 0.1719	0.0701, 0.1903
GOF	1.005	1.050
CCDC	964213	964214

[a] $R1 = \sum |Fo| - |Fc| / \sum |Fo|$. [b] $wR2 = [\sum w(Fo2 - Fc2)2 / \sum w(Fo2)2]1/2$.

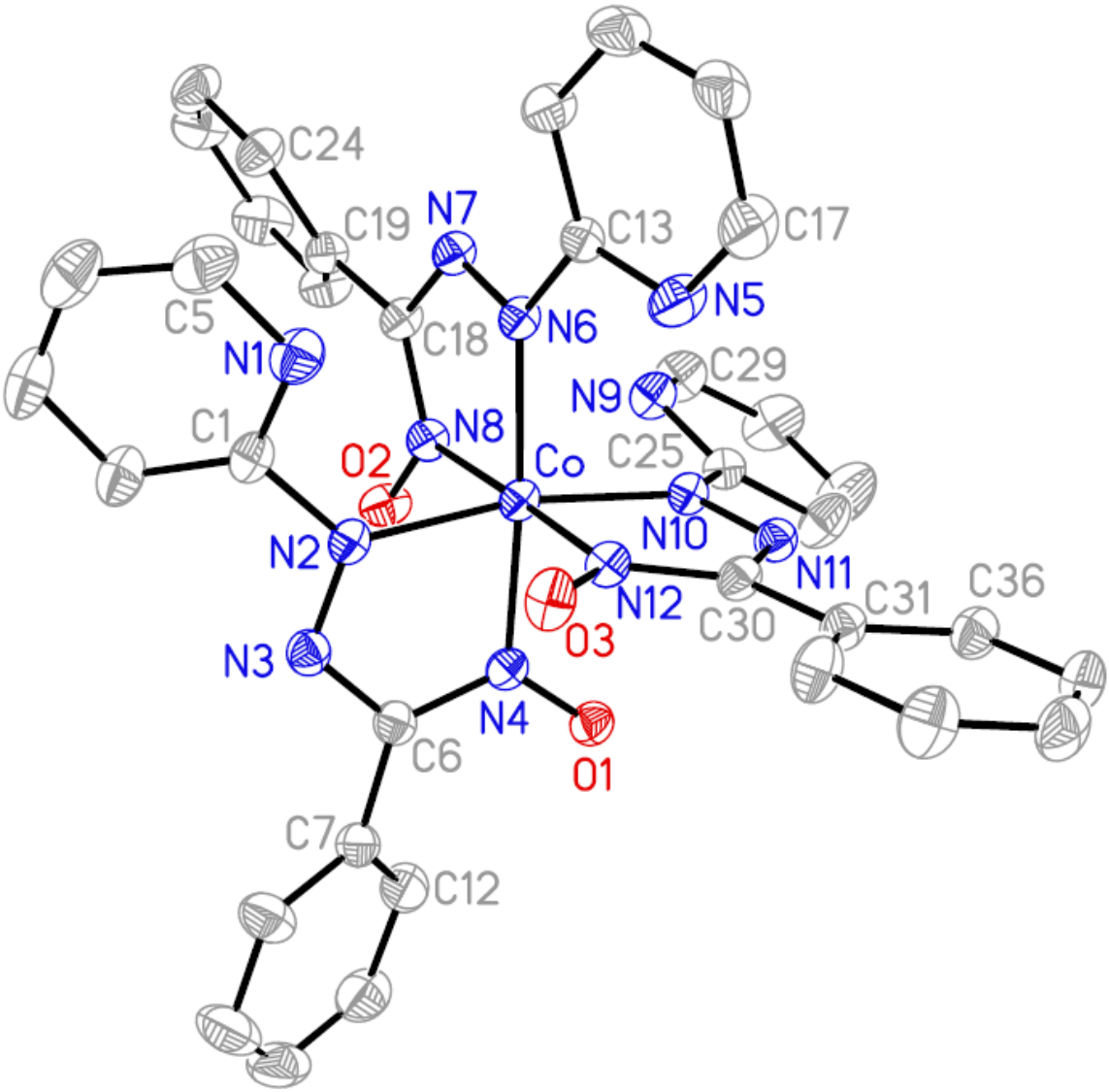

Fig. S12 OPTEP plot of **2a** (Hydrogen atoms are omitted for clarity).

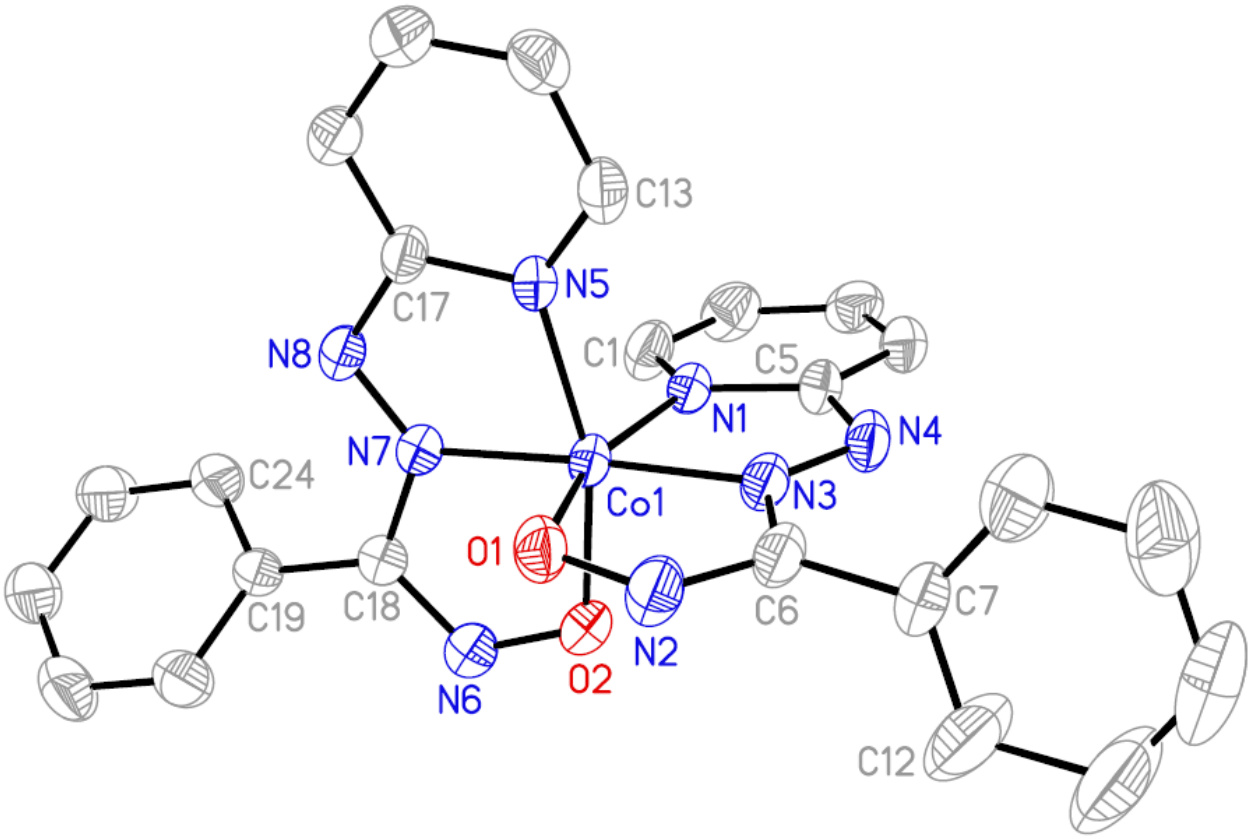

Fig. S13 OPTEP plot of **3a**$^{+}$ cation (Hydrogen atoms and counter anion have omitted for clarity).

Table S10 Frontier Molecular Orbital Composition (%) in the Ground State for **2b** and **3b**$^{+}$

Complex	Orbital	MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
2b	202	L+5	-0.82	1	75	2	9	14	π*(L)
	201	L+4	-1.45	55	2	7	34	2	$d_{x^2-y^2}$(Co) + π*(L)
	200	L+3	-1.57	58	6	25	10	1	d_{z^2}(Co) + π*(L)
	199	L+2	-2.6	1	15	41	42	0	π*(L)
	198	L+1	-2.79	3	14	39	43	0	π*(L)
	197	L	-2.99	3	14	39	42	1	π*(L)
	196	H	-5.37	1	11	13	41	35	π(L)
	195	H–1	-5.41	2	13	14	35	36	π(L)
	194	H–2	-5.55	2	10	12	36	40	π(L)
	193	H–3	-5.97	1	1	8	83	6	π(L)
	192	H–4	-6.49	4	5	10	66	16	π(L)
	191	H–5	-6.56	0	0	0	1	99	π(L)
HOMO–LUMO gap = 2.38 eV									
Complex	Orbital	MO	Energy (EV)	Contribution (%) Co	Py	Azo	NO	Bz	Main Bond Type
3b^{+}	139	L+5	-4.7	0	95	2	3	0	π*(L)
	138	L+4	-4.79	2	89	3	5	1	π*(L)
	137	L+3	-5.16	59	7	22	10	2	d_{z^2}(Co) + π*(L)
	136	L+2	-5.54	60	16	1	23	0	$d_{x^2-y^2}$(Co) + π*(L)
	135	L+1	-6.75	3	26	38	32	1	π*(L)
	134	L	-6.76	3	27	39	31	1	π*(L)
	133	H	-8.56	0	5	8	18	68	π(L)
	132	H–1	-8.58	1	5	8	16	69	π(L)
	131	H–2	-9.15	0	0	0	0	100	π(L)
	130	H–3	-9.15	0	0	0	0	100	π(L)
	129	H–4	-10.01	7	14	8	58	14	π(L)
	128	H–5	-10.08	3	22	10	41	2	π(L)
HOMO–LUMO gap = 1.80 eV									

Table S11 Main optical transition at the TD-DFT/B3LYP/6-31G Level for the complex **2b** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in acetonitrile

	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1.	H – 2 → L (22%) H – 2 → L + 2 (16%) H – 1 → L + 2 (17%) H → L + 2 (28%)	2.3292	0.0237	532.29	ILCT/LLCT	541
2.	H – 1 → L + 1 (23%) H – 1 → L + 2 (46%) H → L + 2 (12%)	2.3590	0.1074	525.58	ILCT/LLCT	
3.	H – 6 → L (10%) H– 4 → L (14%) H – 2 → L + 2 (24%) H → L + 2 (11%)	2.4191	0.0498	512.51	ILCT/LLCT	
4.	H – 3 → L + 2 (16%) H – 2 → L + 2 (26%) H → L + 2 (13%)	2.4707	0.0363	501.81	ILCT/LLCT	
5.	H – 13 → L + 1 (10%) H – 11 → L (16%) H – 10 → L (15%) H – 8 → L + 1 (24%)	3.2333	0.0413	383.46	ILCT/LLCT	
6.	H – 10 → L + 1 (27%) H – 9 → L + 1 (28%)	3.3245	0.0719	372.94	ILCT/LLCT	
7.	H – 8 → L + 2 (64%)	3.4850	0.0429	355.77	ILCT/LLCT	
8.	H – 3 → L + 4 (32%)	3.8095	0.1934	325.46	LMCT	321
9.	H – 1 → L + 5 (18%)	4.1442	0.0746	299.18	ILCT/LLCT	
10.	H – 1 → L + 5 (46%)	4.1481	0.4411	298.89	ILCT/LLCT	
11.	H – 1 → L + 5 (26%)	4.1641	0.1658	297.75	ILCT/LLCT	
12.	H → L + 6 (20%)	4.1826	0.3426	296.43	ILCT/LLCT	

Table S12 Main optical transition at the TD-DFT/B3LYP/6-31G Level for the complex **3b**$^{+}$ with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in acetonitrile

	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1.	H – 1 → L+1 (51%) H → L (43%)	1.7509	0.0622	708.12	ILCT/LLCT	~650 (sh)
2.	H – 1 → L (52%) H → L+1 (42%)	1.7540	0.0532	706.88	ILCT/LLCT	
3.	H – 5 → L (49%) H – 4 → L+1 (37%)	2.7789	0.1105	446.17	ILCT/LLCT	~450 (sh)
4.	H – 6 → L (60%) H – 4 → L (16%)	2.9289	0.0119	423.31	ILCT/LLCT	
5.	H – 7 → L+3 (10%) H – 5 → L+3 (16%) H – 4 → L+2 (25%) H – 2 → L+2 (11%)	3.5609	0.0733	348.18	LMCT	
6.	H → L+4 (92%)	3.8367	0.1912	323.15	ILCT/LLCT	
7.	H – 13 → L (22%) H – 7 → L+3 (13%) H – 1 → L+6 (17%), H → L+7 (14%)	4.2751	0.7883	290.01	ILCT/LLCT	294

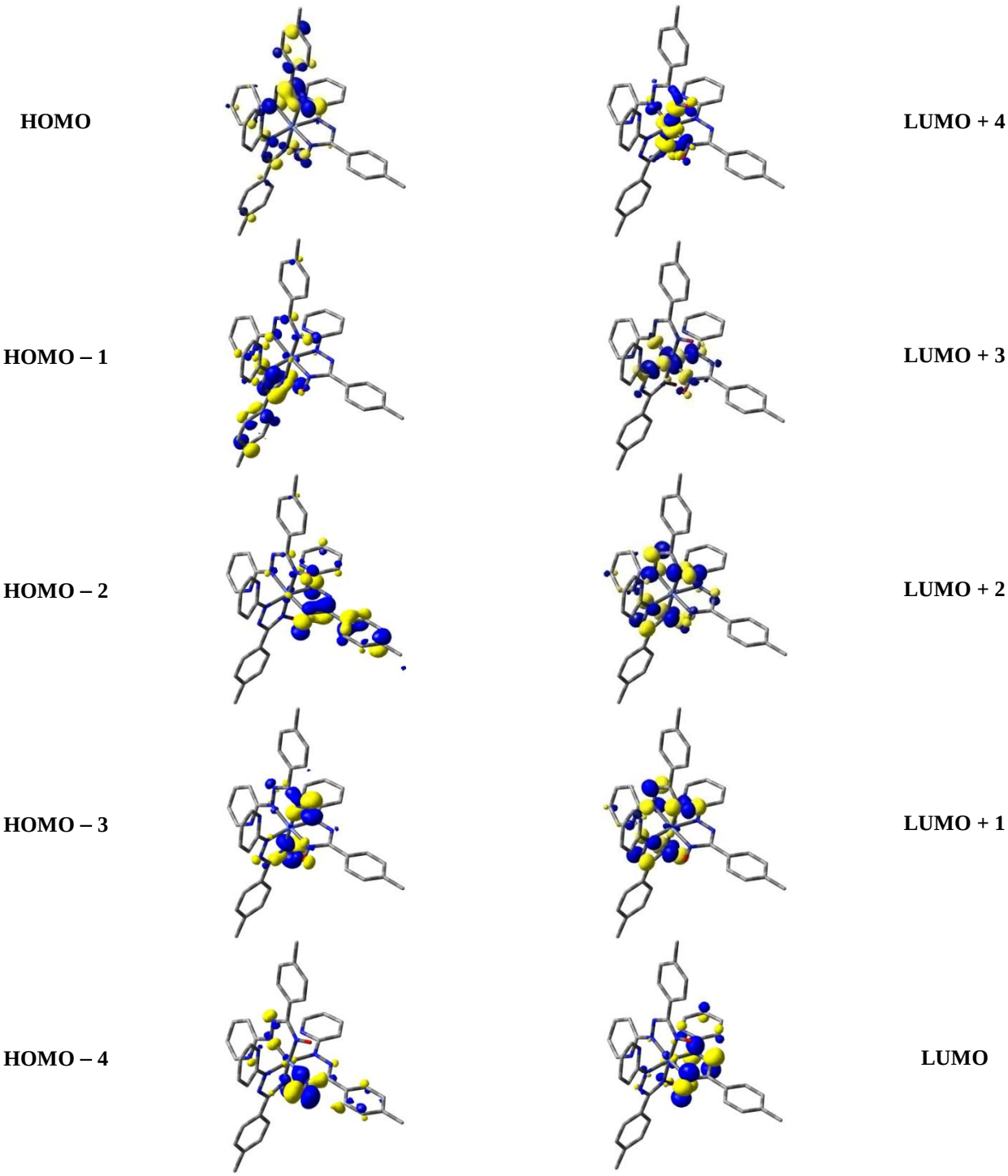

Fig. S14 Isodensity surface plots of some selected frontier molecular orbitals for the complexes **2b** at their optimized S_0 geometry in gas phase. Isodensity value 0.05 e Bohr^{-3}.

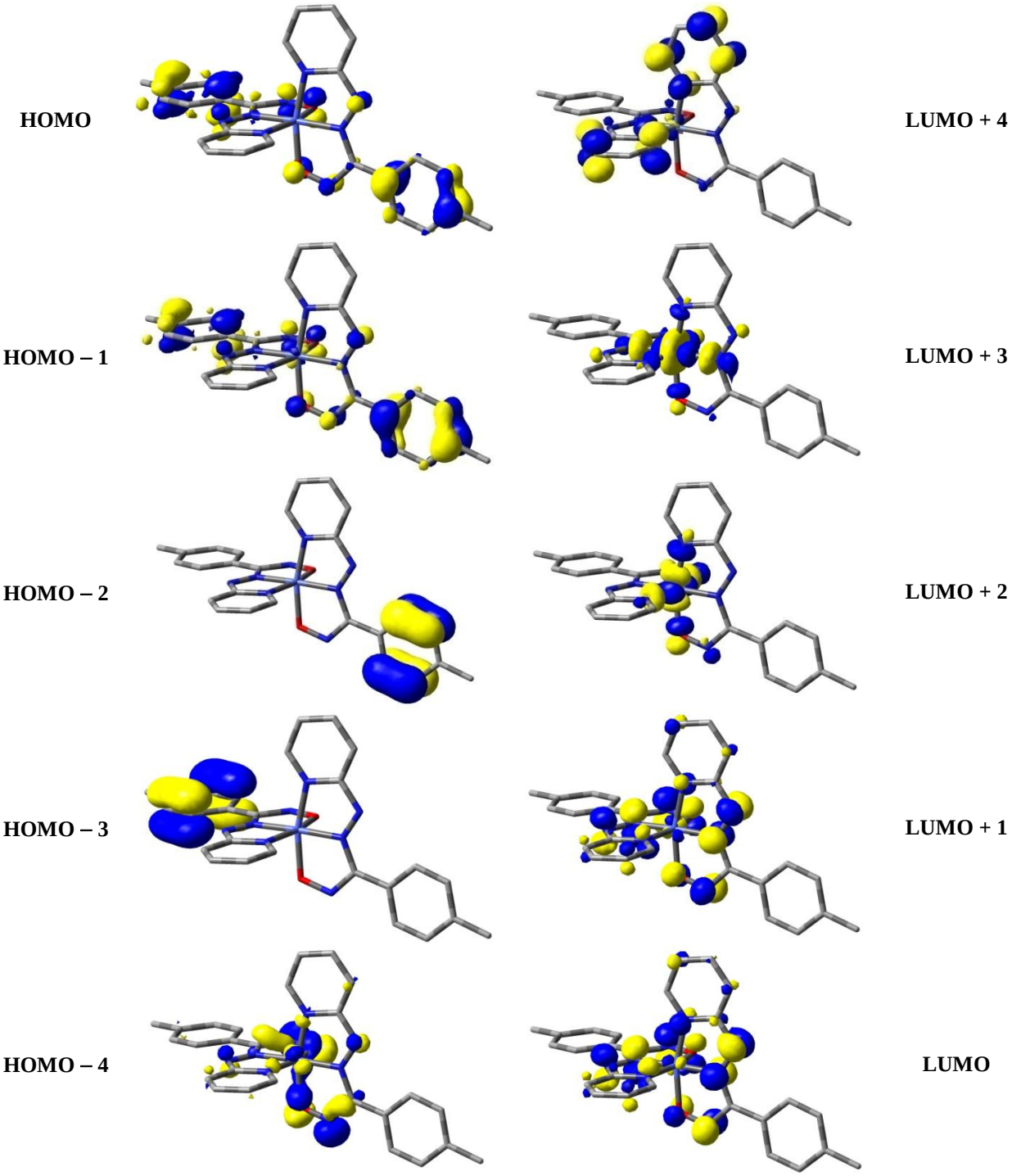

Fig. S15 Isodensity surface plots of some selected frontier molecular orbitals for the complexes **3b**$^{+}$ at their optimized S_0 geometry in gas phase. Isodensity value 0.05 e Bohr^{-3}.

Table S13 Coordinates of optimized geometry ^{1}**2a**

Tag	Symbol	X	Y	Z
1	Co	0.068585	0.059971	0.044721
2	O	1.255334	1.994877	1.769336
3	O	-2.06858	1.580118	1.172771
4	O	2.265959	0.042261	-1.77173
5	N	-0.95972	-0.58601	-3.04347
6	N	-0.37173	1.121523	-1.55035
7	N	-0.11315	2.386211	-1.41718
8	N	0.690962	1.798826	0.642466
9	N	1.044079	-2.92329	-0.93549
10	N	-0.82596	-1.61893	-0.42808
11	N	-2.10192	-1.62672	-0.21081
12	N	-1.7442	0.464191	0.639142
13	N	-1.09436	-1.12264	2.915213
14	N	0.827557	-0.76152	1.632852
15	N	2.103808	-0.98599	1.556163
16	N	1.878022	-0.25044	-0.59446
17	C	-0.88489	0.736341	-2.82159
18	C	-1.27719	1.68944	-3.78218
19	H	-1.20634	2.743377	-3.55529
20	C	-1.74945	1.230844	-5.00928
21	H	-2.06027	1.940227	-5.76874
22	C	-1.82045	-0.14854	-5.25197
23	H	-2.18134	-0.53645	-6.1974
24	C	-1.41586	-1.0172	-4.23655
25	H	-1.45088	-2.09341	-4.36575
26	C	0.44235	2.803268	-0.24912
27	C	0.722027	4.236045	-0.06896
28	C	0.522815	5.108484	-1.16359
29	H	0.180503	4.701087	-2.10618
30	C	0.764717	6.475162	-1.04
31	H	0.607239	7.125672	-1.89469
32	C	1.209037	7.008362	0.177052
33	H	1.397221	8.073157	0.272083
34	C	1.408597	6.155221	1.265839
35	H	1.751707	6.555517	2.214632
36	C	1.172463	4.781652	1.152281
37	H	1.333781	4.132915	1.99981
38	C	-0.29063	-2.80318	-1.00194
39	C	-1.11216	-3.78371	-1.59006
40	H	-2.18306	-3.64097	-1.61778
41	C	-0.50265	-4.91724	-2.1232
42	H	-1.10684	-5.69059	-2.58605
43	C	0.892766	-5.0478	-2.06089
44	H	1.396134	-5.91624	-2.46957
45	C	1.624541	-4.02367	-1.45652
46	H	2.704906	-4.06934	-1.37783
47	C	-2.64861	-0.51374	0.345999

48	C	-4.09064	-0.50152	0.63269
49	C	-4.75555	0.614445	1.186814
50	H	-4.19348	1.505914	1.421486
51	C	-6.13156	0.565506	1.433167
52	H	-6.62291	1.434985	1.858788
53	C	-6.87203	-0.58281	1.139197
54	H	-7.93959	-0.61314	1.333549
55	C	-6.22074	-1.69613	0.591454
56	H	-6.78214	-2.59633	0.360523
57	C	-4.85042	-1.65864	0.340944
58	H	-4.35029	-2.52266	-0.07749
59	C	0.239379	-0.96039	2.909924
60	C	1.01332	-0.97164	4.084991
61	H	2.080948	-0.81405	4.027581
62	C	0.358646	-1.17184	5.298581
63	H	0.924061	-1.17856	6.224348
64	C	-1.03242	-1.34712	5.31342
65	H	-1.57079	-1.49743	6.241933
66	C	-1.71709	-1.31092	4.096286
67	H	-2.79344	-1.43173	4.048564
68	C	2.715843	-0.73527	0.373037
69	C	4.145273	-1.04869	0.231994
70	C	4.876351	-0.79342	-0.94865
71	H	4.378861	-0.34981	-1.79798
72	C	6.236637	-1.11159	-1.01882
73	H	6.780781	-0.9048	-1.93519
74	C	6.895205	-1.68638	0.071626
75	H	7.951268	-1.92987	0.009774
76	C	6.177397	-1.94491	1.247034
77	H	6.675253	-2.39191	2.102038
78	C	4.821919	-1.63224	1.328546
79	H	4.269895	-1.83627	2.237124

Table S14 Coordinates of optimized geometry ^{1}**2b**

Tag	Symbol	X	Y	Z
1	Co	0.066358	0.057681	0.044656
2	O	1.253961	1.991309	1.771416
3	O	-2.07245	1.576408	1.174779
4	O	2.264118	0.04203	-1.773
5	N	-0.96594	-0.58376	-3.04363
6	N	-0.37426	1.121321	-1.54895
7	N	-0.11569	2.386351	-1.41388
8	N	0.688768	1.795248	0.644528
9	N	1.040694	-2.92493	-0.94166
10	N	-0.8284	-1.62099	-0.4294
11	N	-2.10473	-1.62909	-0.21119
12	N	-1.74609	0.460968	0.640522
13	N	-1.09418	-1.12598	2.916215
14	N	0.826339	-0.76602	1.631348
15	N	2.103102	-0.9905	1.55341
16	N	1.875084	-0.25209	-0.59601
17	C	-0.88569	0.738303	-2.8211
18	C	-1.27138	1.693022	-3.78305
19	H	-1.19599	2.74658	-3.55591
20	C	-1.74267	1.236628	-5.01123
21	H	-2.04817	1.947512	-5.7715
22	C	-1.81948	-0.14244	-5.25427
23	H	-2.1797	-0.52873	-6.20064
24	C	-1.42122	-1.01273	-4.23781
25	H	-1.46068	-2.08882	-4.3671
26	C	0.439858	2.80145	-0.24538
27	C	0.720242	4.23229	-0.06205
28	C	0.518148	5.112131	-1.15003
29	H	0.170118	4.712012	-2.09384
30	C	0.759119	6.476385	-1.02121
31	H	0.5939	7.12819	-1.87495
32	C	1.210964	7.026869	0.19245
33	C	1.406247	6.152439	1.271027
34	H	1.747955	6.548921	2.223043
35	C	1.172207	4.779623	1.156424
36	H	1.3344	4.133064	2.005589
37	C	-0.29422	-2.80415	-1.00552
38	C	-1.1168	-3.78396	-1.59383
39	H	-2.18771	-3.64091	-1.61926
40	C	-0.50849	-4.91671	-2.12978
41	H	-1.11371	-5.68924	-2.59277
42	C	0.887066	-5.04769	-2.07026
43	H	1.389556	-5.91559	-2.48124
44	C	1.619901	-4.02456	-1.46553
45	H	2.700429	-4.07037	-1.38876
46	C	-2.65079	-0.51703	0.347437
47	C	-4.09144	-0.50406	0.635076

48	C	-4.75789	0.602849	1.201351
49	H	-4.19819	1.49279	1.447627
50	C	-6.13292	0.550698	1.449151
51	H	-6.62025	1.417283	1.887528
52	C	-6.89494	-0.58706	1.149119
53	C	-6.22532	-1.69139	0.589049
54	H	-6.78564	-2.59205	0.351654
55	C	-4.85781	-1.65501	0.335801
56	H	-4.36306	-2.51885	-0.08975
57	C	0.239896	-0.96553	2.908656
58	C	1.015494	-0.97927	4.082825
59	H	2.083277	-0.82341	4.023706
60	C	0.362478	-1.17958	5.297189
61	H	0.929414	-1.18812	6.222059
62	C	-1.02891	-1.35255	5.314212
63	H	-1.56607	-1.5028	6.24347
64	C	-1.71524	-1.31417	4.098117
65	H	-2.79189	-1.43313	4.05181
66	C	2.713856	-0.7385	0.370115
67	C	4.142184	-1.05018	0.226488
68	C	4.874897	-0.79777	-0.95168
69	H	4.37995	-0.35676	-1.80398
70	C	6.234749	-1.11567	-1.02129
71	H	6.775413	-0.9096	-1.94095
72	C	6.915198	-1.68965	0.061357
73	C	6.178837	-1.94439	1.233926
74	H	6.675425	-2.39363	2.09008
75	C	4.825558	-1.6338	1.319124
76	H	4.27816	-1.84175	2.229816
77	C	8.389949	-2.01446	-0.01557
78	C	1.495141	8.50643	0.317362
79	C	-8.38509	-0.62827	1.401849
80	H	-8.70439	0.201127	2.040966
81	H	-8.95195	-0.55849	0.46335
82	H	-8.68443	-1.56425	1.888752
83	H	2.469454	8.763645	-0.12075
84	H	0.739262	9.105689	-0.20327
85	H	1.514136	8.822223	1.365458
86	H	8.980923	-1.34234	0.621186
87	H	8.594372	-3.03805	0.321816
88	H	8.766942	-1.91557	-1.03843

Table S15 Coordinates of optimized geometry ^{1}**3a**$^{+}$

Tag	Symbol	X	Y	Z
1	C	0.955297	2.120553	1.986437
2	H	1.940684	2.014533	1.551898
3	C	0.717756	2.977487	3.066494
4	H	1.535143	3.552953	3.481974
5	C	-0.57558	3.068985	3.595611
6	H	-0.77871	3.723329	4.434955
7	C	-1.60493	2.305564	3.037292
8	H	-2.61847	2.336354	3.414995
9	C	-1.30756	1.466454	1.961144
10	C	-2.53257	-0.98762	-0.336
11	C	-3.95925	-1.32818	-0.2483
12	C	-4.82563	-0.76988	0.71478
13	H	-4.4529	-0.05959	1.437609
14	C	-6.17282	-1.14124	0.74287
15	H	-6.82774	-0.70758	1.490867
16	C	-6.67637	-2.06477	-0.17796
17	H	-7.72271	-2.34908	-0.14931
18	C	-5.82075	-2.62449	-1.13667
19	H	-6.20158	-3.3444	-1.85272
20	C	-4.47636	-2.26418	-1.17533
21	H	-3.81643	-2.70283	-1.91325
22	C	-0.95517	2.12141	-1.98572
23	H	-1.94054	2.01536	-1.55116
24	C	-0.71758	2.978691	-3.06549
25	H	-1.53491	3.554423	-3.4807
26	C	0.575737	3.070192	-3.59466
27	H	0.778893	3.724789	-4.4338
28	C	1.605027	2.30645	-3.03666
29	H	2.618549	2.337242	-3.41441
30	C	1.307612	1.467018	-1.96078
31	C	2.532509	-0.98778	0.335657
32	C	3.9592	-1.32829	0.247942
33	C	4.476346	-2.26429	1.174955
34	H	3.816434	-2.70295	1.91289
35	C	5.820734	-2.62459	1.136248
36	H	6.201604	-3.34449	1.852288
37	C	6.676314	-2.06486	0.177508
38	H	7.722648	-2.34919	0.148807
39	C	6.172732	-1.14132	-0.74329
40	H	6.827629	-0.70764	-1.49131
41	C	4.825538	-0.76997	-0.71515
42	H	4.452788	-0.05966	-1.43795
43	N	-0.03397	1.384378	1.444641
44	N	-1.7595	-1.61551	-1.23857
45	N	-1.82714	-0.05414	0.418159
46	N	-2.30435	0.668112	1.38334
47	N	0.034032	1.384908	-1.44424

48	N	1.759399	-1.6159	1.238039
49	N	1.827097	-0.05411	-0.41829
50	N	2.304357	0.668424	-1.38324
51	O	-0.46403	-1.29132	-1.2807
52	O	0.463911	-1.29178	1.28015
53	Co	-0.000013	0.046001	-0.000061

Table S16 Coordinates of optimized geometry ^{1}**3b**$^{+}$

Tag	Symbol	X	Y	Z
1	C	0.957325	2.125439	1.975666
2	H	1.94256	2.014887	1.541888
3	C	0.721377	2.987353	3.051722
4	H	1.5398	3.562635	3.46537
5	C	-0.57242	3.084055	3.579522
6	H	-0.77447	3.74242	4.416003
7	C	-1.6031	2.32111	3.023937
8	H	-2.61677	2.355949	3.400887
9	C	-1.3077	1.476309	1.951137
10	C	-2.53546	-0.98363	-0.33606
11	C	-3.95969	-1.3218	-0.24543
12	C	-4.83546	-0.74208	0.694847
13	H	-4.47157	-0.01129	1.401821
14	C	-6.18123	-1.11322	0.723185
15	H	-6.83871	-0.65546	1.455721
16	C	-6.70173	-2.06402	-0.16855
17	C	-5.82052	-2.63716	-1.10691
18	H	-6.19525	-3.37391	-1.81073
19	C	-4.47841	-2.28035	-1.14916
20	H	-3.8188	-2.73826	-1.8758
21	C	-0.95517	2.11522	-1.9944
22	H	-1.94074	2.00832	-1.56046
23	C	-0.71763	2.971078	-3.07494
24	H	-1.53513	3.545225	-3.49199
25	C	0.576506	3.063307	-3.60267
26	H	0.779785	3.717016	-4.44249
27	C	1.605939	2.301919	-3.04262
28	H	2.61983	2.333473	-3.41927
29	C	1.308956	1.46324	-1.96548
30	C	2.532936	-0.98474	0.336542
31	C	3.957172	-1.32368	0.249387
32	C	4.47886	-2.26348	1.171439
33	H	3.821115	-2.70716	1.908541
34	C	5.820202	-2.62209	1.131597
35	H	6.196313	-3.34618	1.847809
36	C	6.698848	-2.0681	0.178765
37	C	6.174843	-1.13895	-0.73283
38	H	6.828898	-0.70044	-1.47995
39	C	4.829169	-0.76589	-0.707
40	H	4.462637	-0.05218	-1.42989
41	N	-0.03348	1.389378	1.436282
42	N	-1.76265	-1.61701	-1.23695
43	N	-1.82785	-0.04895	0.413403
44	N	-2.30553	0.678882	1.375961
45	N	0.034441	1.380795	-1.45063
46	N	1.759253	-1.61158	1.24118
47	N	1.82654	-0.05406	-0.41907

48	N	2.305498	0.667546	-1.3856
49	O	-0.46667	-1.29535	-1.27924
50	O	0.463659	-1.28791	1.281384
51	Co	-0.00059	0.046421	-0.0032
52	C	-8.15199	-2.47887	-0.11602
53	C	8.153726	-2.46879	0.146759
54	H	-8.26043	-3.46697	0.350606
55	H	-8.75175	-1.7726	0.465293
56	H	-8.5849	-2.54869	-1.12004
57	H	8.655091	-2.21844	1.090001
58	H	8.26343	-3.55067	0.003265
59	H	8.69132	-1.96667	-0.66238

Table S17 Coordinates of optimized geometry ^{2}**3a**

Tag	Symbol	X	Y	Z
1	C	-1.0335	2.002268	-1.9708
2	H	-2.00924	1.835795	-1.53284
3	C	-0.8452	2.880342	-3.03416
4	H	-1.68888	3.422385	-3.44202
5	C	0.451946	3.043674	-3.55889
6	H	0.620972	3.717048	-4.39184
7	C	1.513389	2.33626	-3.01123
8	H	2.523438	2.421539	-3.39023
9	C	1.273456	1.462492	-1.93193
10	C	2.546681	-0.98597	0.31557
11	C	3.987544	-1.28377	0.210438
12	C	4.826246	-0.6844	-0.75114
13	H	4.412421	0.029404	-1.44852
14	C	6.185222	-1.0129	-0.80257
15	H	6.816176	-0.54403	-1.55139
16	C	6.731438	-1.9343	0.095095
17	H	7.786725	-2.18474	0.049826
18	C	5.903534	-2.53455	1.053622
19	H	6.314805	-3.2539	1.75478
20	C	4.548331	-2.2164	1.113104
21	H	3.906125	-2.68249	1.849837
22	C	1.034927	1.989935	1.980635
23	H	2.010112	1.825511	1.540865
24	C	0.84675	2.861639	3.050067
25	H	1.690776	3.40088	3.46092
26	C	-0.44931	3.022017	3.576324
27	H	-0.61796	3.690216	4.41346
28	C	-1.51158	2.317765	3.024267
29	H	-2.52154	2.400839	3.403958
30	C	-1.27099	1.451837	1.940235
31	C	-2.54802	-0.98315	-0.31985
32	C	-3.98866	-1.28147	-0.21728
33	C	-4.54929	-2.20796	-1.12637
34	H	-3.90722	-2.66926	-1.86622
35	C	-5.90454	-2.52629	-1.06932
36	H	-6.31572	-3.2408	-1.77543
37	C	-6.73259	-1.93239	-0.107
38	H	-7.7879	-2.18296	-0.06371
39	C	-6.18654	-1.01709	0.796987
40	H	-6.81763	-0.55316	1.548732
41	C	-4.82755	-0.68843	0.748111
42	H	-4.41429	0.020657	1.450576
43	N	-0.00642	1.315105	-1.4268
44	N	1.825575	-1.63379	1.250857
45	N	1.822164	-0.08015	-0.42604
46	N	2.294552	0.726057	-1.37149
47	N	0.007433	1.306925	1.433669

48	N	-1.82558	-1.62575	-1.25868
49	N	-1.82272	-0.0817	0.426326
50	N	-2.29379	0.71715	1.374939
51	O	0.4996	-1.3564	1.284568
52	O	-0.50247	-1.35077	-1.29156
53	Co	0.000113	-0.02879	0.0000831