Supporting Information

Sensitivity of a Strained C-C Single Bond to Charge Transfer: Redox Activity in Mononuclear and Dinuclear Ruthenium Complexes of Bis(arylimino)acenaphthene (BIAN) Ligands

Prasenjit Mondal,[#] Hemlata Agarwala,[#] Rahul Dev Jana,[#] Sebastian Plebst,[§] Anita Grupp,[§] Fabian Ehret,[§] Shaikh M. Mobin,[$] Wolfgang Kaim[*,§] and Goutam Kumar Lahiri[*,#]

[#]Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

[§]Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

[$]Discipline of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, Indore 452017, India

Table S1. Selected Crystallographic Data for BIAN (R= Me) Ligand

empirical formula	$C_{13}H_{10}N$
fw	180.22
crystal system	monoclinic
space group	$C2$
a (Å)	20.0456(15)
b (Å)	8.7754(6)
c (Å)	5.5713(4)
α (deg)	90
β (deg)	103.404(7)
γ (deg)	90
V (Å^3)	953.34(12)
Z	4
μ (mm^{-1})	0.566
T (K)	150(2)
D_{calcd} (g cm^{-3})	1.256
F(000)	380
θ range(deg)	4.54 to 71.86
data/restraints/ parameters	1217 / 1 / 129
R1, wR2 [I>2σ(I)]	0.0305, 0.0884
R1, wR2(all data)	0.0309, 0.0889
GOF	1.140
largest diff. peak/hole,(e Å^{-3})	0.143 /-0.125

Table S2. Experimental and DFT Calculated Selected Bond Lengths (Å) and Bond angles (º) for BIAN (R= Me) Ligand

bond length (Å)	X-ray	DFT			
		$(BIAN)^{+}$ (S=1/2)	(BIAN) (S=0)	$(BIAN)^{\bullet-}$ (S=1/2)	$(BIAN)^{2-}$ (S=0)
N(1)-C(1)	1.4193(17)	1.365	1.405	1.371	1.338
N(1)-C(8)	1.269(2)	1.288	1.276	1.323	1.371
C(8)-C(8)#1	1.534(2)	1.521	1.530	1.463	1.421
C(8)-C(9)	1.475(2)	1.474	1.487	1.487	1.483
C(9)-C(10)	1.380(2)	1.390	1.383	1.387	1.389
C(9)-C(14)	1.4127(19)	1.416	1.419	1.423	1.425
C(10)-C(11)	1.411(3)	1.414	1.419	1.423	1.428
C(11)-C(12)	1.370(3)	1.389	1.384	1.383	1.383
C(12)-C(13)	1.414(2)	1.421	1.421	1.427	1.434
C(13)-C(14)	1.401(3)	1.410	1.412	1.403	1.395
bond angle (º)					
C(8)-N(1)-C(1)	122.30(14)	129.92	123.49	125.10	123.29
N(1)-C(8)-C(9)	133.04(12)	132.53	132.98	130.44	126.62
C(14)-C(9)-C(8)	106.67(12)	106.72	106.79	107.15	107.71
N(1)-C(8)-C(8)#1	120.69(9)	120.75	120.52	122.02	124.99
C(10)-C(9)-C(8)	134.77(15)	134.47	134.40	135.39	135.55
C(10)-C(9)-C(14)	118.54(17)	118.76	118.77	117.38	116.68
C(13)-C(14)-C(9)	123.13(10)	123.39	123.25	124.44	125.43
C(9)#1-C(14)-C(9)	113.7(2)	113.21	113.48	111.12	109.14

Table S3. Experimental and DFT Calculated Selected Bond Lengths (Å) for 1a^{n} (molecule B)

bond length (Å)	X-ray	DFT		
		1a^{+} (S=1/2)	**1a** (S=0)	**1a**$^{-}$ (S=1/2)
Ru(2)-N(3)	1.995(4)	2.095	2.058	2.092
Ru(2)-N(4)	2.009(5)	2.097	2.060	2.093
Ru(2)-O(5)	2.026(3)	2.032	2.079	2.090
Ru(2)-O(6)	2.048(4)	2.043	2.086	2.111
Ru(2)-O(7)	2.053(4)	2.043	2.087	2.112
Ru(2)-O(8)	2.027(3)	2.032	2.080	2.092
N(3)-C(58)	1.316(7)	1.301	1.313	1.346
N(4)-C(47)	1.303(7)	1.301	1.313	1.346
N(3)-C(35)	1.427(7)	1.430	1.425	1.402
N(4)-C(41)	1.441(7)	1.430	1.424	1.402
C(47)-C(58)	1.447(8)	1.492	1.466	1.430
C(47)-C(48)	1.478(8)	1.466	1.472	1.473
C(48)-C(49)	1.393(8)	1.385	1.384	1.387
C(49)-C(50)	1.405(9)	1.417	1.420	1.424
C(50)-C(51)	1.378(9)	1.386	1.384	1.381
C(51)-C(52)	1.404(9)	1.422	1.423	1.428
C(52)-C(53)	1.405(9)	1.422	1.423	1.428
C(53)-C(54)	1.362(9)	1.386	1.384	1.382
C(54)-C(55)	1.430(9)	1.417	1.420	1.424
C(55)-C(56)	1.367(8)	1.385	1.384	1.387
C(56)-C(57)	1.418(8)	1.424	1.425	1.428
C(57)-C(48)	1.421(8)	1.424	1.425	1.428
C(56)-C(58)	1.479(8)	1.466	1.471	1.473
C(52)-C(57)	1.398(8)	1.409	1.407	1.400

Table S4. Experimental and DFT Calculated Selected Bond Lengths (Å) for $5a^n$ (molecule B)

bond length (Å)	X-ray	DFT			
		5a$^+$ (S=1/2)	**5a** (S=0)	**5a**$^-$ (S=1/2)	**5a**$^{2-}$ (S=0)
Ru(2)-N(5)	1.991(6)	2.101	2.062	2.093	2.142
Ru(2)-N(6)	1.999(5)	2.102	2.063	2.096	2.143
Ru(2)-O(9)	2.054(5)	2.038	2.080	2.100	2.115
Ru(2)-O(10)	2.040(5)	2.032	2.077	2.084	2.092
Ru(2)-O(11)	2.026(5)	2.037	2.080	2.100	2.116
Ru(2)-O(12)	1.996(6)	2.032	2.078	2.083	2.091
N(5)-C(58)	1.313(9)	1.301	1.314	1.346	1.366
N(6)-C(47)	1.321(8)	1.301	1.314	1.346	1.366
C(47)-C(58)	1.422(9)	1.493	1.464	1.429	1.415
N(5)-C(35)	1.412(10)	1.427	1.419	1.389	1.365
N(6)-C(41)	1.422(8)	1.427	1.418	1.389	1.365
C(47)-C(48)	1.460(9)	1.4634	1.470	1.476	1.478
C(48)-C(49)	1.373(10)	1.386	1.384	1.385	1.388
C(49)-C(50)	1.411(11)	1.417	1.420	1.423	1.425
C(50)-C(51)	1.363(12)	1.386	1.384	1.382	1.381
C(51)-C(52)	1.416(12)	1.422	1.423	1.426	1.429
C(52)-C(53)	1.419(11)	1.422	1.423	1.426	1.429
C(53)-C(54)	1.344(12)	1.386	1.383	1.382	1.381
C(54)-C(55)	1.415(11)	1.416	1.420	1.423	1.425
C(55)-C(56)	1.357(10)	1.386	1.384	1.385	1.388
C(56)-C(57)	1.410(10)	1.424	1.425	1.426	1.427
C(57)-C(48)	1.422(9)	1.424	1.425	1.426	1.426
C(56)-C(58)	1.484(9)	1.463	1.470	1.475	1.479
C(52)-C(57)	1.406(10)	1.408	1.407	1.402	1.399

Table S5. Selected Experimental Bond Angles (º) for 1a, 2a, 4a and 5a (molecule A)

bond angle (º)	**1a**	**2a**	**4a**	**5a**
N(1)-Ru(1)-N(2)	80.70(19)	80.58(14)	80.20(12)	80.2(2)
N(1)-Ru(1)-O(1)	90.07(17)	89.80(13)	94.55(11)	94.1(2)
N(2)-Ru(1)-O(1)	87.15(18)	91.60(13)	174.67(11)	174.3(2)
N(1)-Ru(1)-O(4)	89.49(17)	94.13(13)	90.69(11)	90.1(2)
N(2)-Ru(1)-O(4)	94.21(17)	174.71(13)	92.09(11)	91.3(2)
O(1)-Ru(1)-O(4)	178.48(16)	88.24(12)	87.02(10)	88.37(19)
N(1)-Ru(1)-O(2)	96.60(17)	176.83(13)	93.06(11)	92.8(2)
N(2)-Ru(1)-O(2)	176.96(18)	96.44(13)	88.93(11)	88.8(2)
O(1)-Ru(1)-O(2)	91.47(16)	91.39(12)	92.30(10)	91.84(19)
O(4)-Ru(1)-O(2)	87.14(15)	88.85(12)	176.23(10)	177.11(19)
N(1)-Ru(1)-O(3)	175.52(16)	93.63(13)	175.58(11)	176.27(19)
N(2)-Ru(1)-O(3)	94.88(18)	88.85(13)	95.97(11)	96.4(2)
O(1)-Ru(1)-O(3)	88.93(16)	176.57(12)	89.31(10)	89.27(19)
O(4)-Ru(1)-O(3)	91.62(16)	91.63(12)	91.67(10)	91.51(19)
O(2)-Ru(1)-O(3)	87.79(15)	85.18(12)	84.61(10)	85.62(19)
C(15)-C(14)-C(13)	135.9(7)	135.7(5)	136.1(4)	135.9(7)
C(23)-C(14)-C(13)	104.4(6)	105.2(4)	105.0(3)	105.2(6)
C(21)-C(22)-C(24)	136.1(6)	135.7(4)	136.2(4)	135.8(6)
C(23)-C(22)-C(24)	104.7(6)	105.5(4)	104.7(3)	105.0(6)

Table S6. Selected Experimental Bond Angles (º) for 1a, 2a, 4a and 5a (molecule B)

bond angle (º)	**1a**	**2a**	**4a**	bond angle (º)	**5a**
N(3)-Ru(2)-N(4)	80.56(18)	80.70(15)	80.55(12)	N(5)-Ru(2)-N(6)	79.8(2)
N(3)-Ru(2)-O(5)	93.41(16)	87.82(17)	94.47(12)	N(5)-Ru(2)-O(9)	94.9(2)
N(4)-Ru(2)-O(5)	89.13(16)	88.31(15)	174.59(11)	N(6)-Ru(2)-O(9)	173.4(2)
N(3)-Ru(2)-O(8)	90.64(15)	95.02(16)	86.23(12)	N(5)-Ru(2)-O(12)	85.1(3)
N(4)-Ru(2)-O(8)	91.07(16)	174.76(15)	89.52(11)	N(6)-Ru(2)-O(12)	89.2(2)
O(5)-Ru(2)-O(8)	175.92(15)	88.51(16)	88.03(11)	O(9)-Ru(2)-O(12)	86.4(3)
N(3)-Ru(2)-O(6)	93.26(16)	177.15(15)	95.56(12)	N(5)-Ru(2)-O(10)	95.9(2)
N(4)-Ru(2)-O(6)	173.72(16)	96.63(14)	90.76(11)	N(6)-Ru(2)-O(10)	92.7(2)
O(5)-Ru(2)-O(6)	92.36(14)	91.13(16)	91.84(11)	O(9)-Ru(2)-O(10)	91.7(2)
O(8)-Ru(2)-O(6)	87.88(14)	87.60(14)	178.21(11)	O(12)-Ru(2)-O(10)	178.0(2)
N(3)-Ru(2)-O(7)	176.40(16)	95.00(15)	176.38(12)	N(5)-Ru(2)-O(11)	177.0(2)
N(4)-Ru(2)-O(7)	96.73(17)	91.65(14)	96.36(11)	N(6)-Ru(2)-O(11)	97.6(2)
O(5)-Ru(2)-O(7)	84.15(15)	177.13(15)	88.55(11)	O(9)-Ru(2)-O(11)	87.6(2)
O(8)-Ru(2)-O(7)	91.78(14)	91.74(15)	91.89(11)	O(12)-Ru(2)-O(11)	93.3(3)
O(6)-Ru(2)-O(7)	89.49(15)	86.02(14)	86.33(10)	O(10)-Ru(2)-O(11)	85.8(2)
C(47)-C(48)-C(49)	135.6(6)	135.8(5)	136.7(4)	C(47)-C(48)-C(49)	137.0(7)
C(47)-C(48)-C(57)	105.4(5)	105.1(4)	104.9(3)	C(47)-C(48)-C(57)	105.0(6)
C(55)-C(56)-C(58)	135.5(6)	135.7(5)	136.4(4)	C(55)-C(56)-C(58)	137.0(7)
C(58)-C(56)-C(57)	105.4(5)	105.2(4)	104.7(3)	C(58)-C(56)-C(57)	102.8(6)

Table S7. Experimental and DFT Calculated Selected Bond Angles (º) for 1a^{n} (molecule B)

bond angle (º)	X-ray	DFT		
		1a^{+} (*S*=1/2)	**1a** (*S*=0)	**1a**$^{-}$ (*S*=1/2)
N(3)-Ru(2)-N(4)	80.56(18)	78.84	79.03	79.64
N(3)-Ru(2)-O(5)	93.41(16)	91.59	93.06	92.37
N(4)-Ru(2)-O(5)	89.13(16)	89.15	89.32	89.23
N(3)-Ru(2)-O(8)	90.64(15)	89.17	89.78	89.48
N(4)-Ru(2)-O(8)	91.07(16)	91.60	93.36	92.58
O(5)-Ru(2)-O(8)	175.92(15)	179.02	176.41	177.62
N(3)-Ru(2)-O(6)	93.26(16)	96.55	96.94	97.08
N(4)-Ru(2)-O(6)	173.72(16)	175.31	175.96	176.71
O(5)-Ru(2)-O(6)	92.36(14)	90.13	91.06	91.16
O(8)-Ru(2)-O(6)	87.88(14)	89.17	86.43	87.13
N(3)-Ru(2)-O(7)	176.40(16)	175.29	176.12	176.86
N(4)-Ru(2)-O(7)	96.73(17)	96.51	97.13	97.26
O(5)-Ru(2)-O(7)	84.15(15)	89.10	86.27	87.07
O(8)-Ru(2)-O(7)	91.78(14)	90.19	91.03	91.16
O(6)-Ru(2)-O(7)	89.49(15)	88.11	86.90	86.03
C(47)-C(48)-C(49)	135.6(6)	135.69	136.13	136.73
C(47)-C(48)-C(57)	105.4(5)	105.32	105.35	105.86
C(55)-C(56)-C(58)	135.5(6)	135.69	136.13	136.73
C(58)-C(56)-C(57)	105.4(5)	105.31	105.34	105.85

Table S8. Experimental and DFT Calculated Selected Bond Angles (º) for 5a^{n} (molecule B)

bond angle (º)	X-ray	DFT			
		5a^{+} (*S*=1/2)	**5a** (*S*=0)	**5a**$^{-}$ (*S*=1/2)	**5a**$^{2-}$ (*S*=0)
N(5)-Ru(2)-N(6)	79.8(2)	78.44	78.65	79.36	80.02
N(5)-Ru(2)-O(9)	94.9(2)	96.56	97.20	98.06	98.59
N(6)-Ru(2)-O(9)	173.4(2)	174.80	175.84	177.35	177.50
N(5)-Ru(2)-O(12)	85.1(3)	88.34	88.83	89.43	90.79
N(6)-Ru(2)-O(12)	89.2(2)	92.16	93.81	92.46	90.59
O(9)-Ru(2)-O(12)	86.4(3)	89.08	86.31	86.88	87.35
N(5)-Ru(2)-O(10)	95.9(2)	92.53	94.03	92.55	90.22
N(6)-Ru(2)-O(10)	92.7(2)	88.76	89.03	89.58	90.51
O(9)-Ru(2)-O(10)	91.7(2)	90.07	91.03	91.14	91.57
O(12)-Ru(2)-O(10)	178.0(2)	178.85	176.32	177.39	178.62
N(5)-Ru(2)-O(11)	177.0(2)	174.61	175.75	177.16	177.35
N(6)-Ru(2)-O(11)	97.6(2)	96.46	97.12	97.84	98.705
O(9)-Ru(2)-O(11)	87.6(2)	88.58	87.03	84.75	82.76
O(12)-Ru(2)-O(11)	93.3(3)	90.11	91.05	91.17	91.56
O(10)-Ru(2)-O(11)	85.8(2)	89.09	86.26	86.95	87.46
C(47)-C(48)-C(49)	137.0(7)	135.73	136.19	136.75	136.82
C(47)-C(48)-C(57)	105.0(6)	105.28	105.27	105.66	106.09
C(55)-C(56)-C(58)	137.0(7)	135.71	136.17	136.71	136.89
C(58)-C(56)-C(57)	102.8(6)	105.28	105.27	105.65	106.08

Table S9. Calculated MO Composition for 1a (molecule B) in *S* = 0 State

MO	energy (eV)	% composition		
		Ru	acac	BIAN
LUMO+5	0.043	2	7	91
LUMO+4	-0.260	3	91	6
LUMO+3	-0.318	6	78	16
LUMO+2	-0.385	1	7	92
LUMO+1	-1.553	3	1	97
LUMO	-2.014	23	6	72
HOMO	-4.405	66	21	13
HOMO-1	-4.632	48	28	24
HOMO-2	-4.758	64	22	14
HOMO-3	-5.750	14	77	10
HOMO-4	-5.906	24	50	26
HOMO-5	-6.104	10	25	65

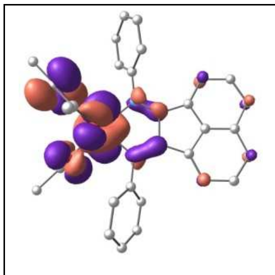
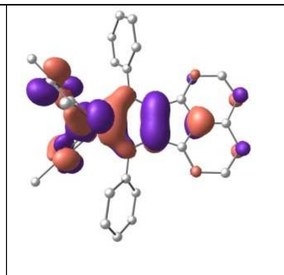
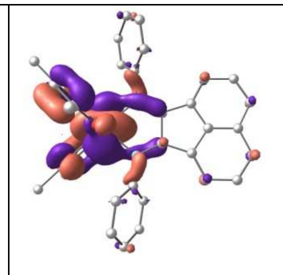
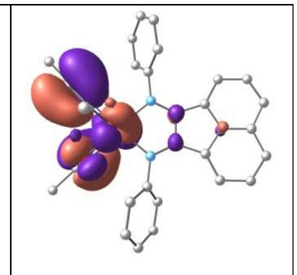
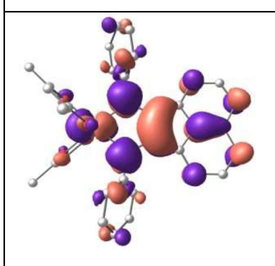
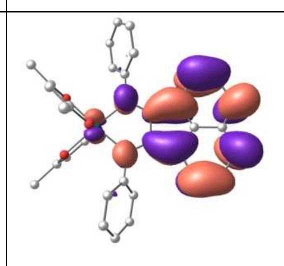
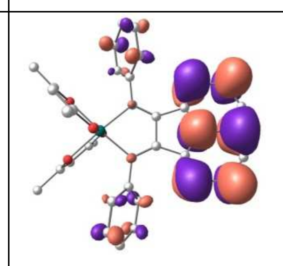
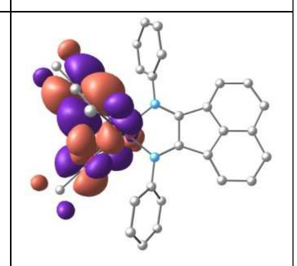
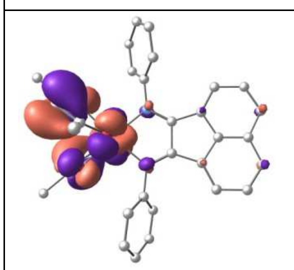
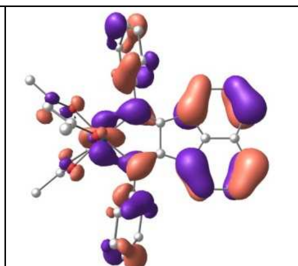
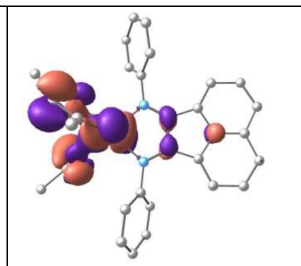
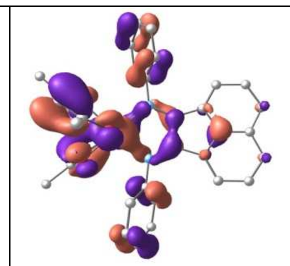
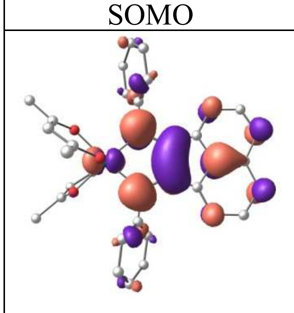
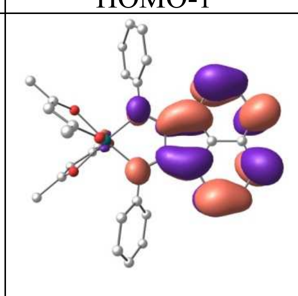
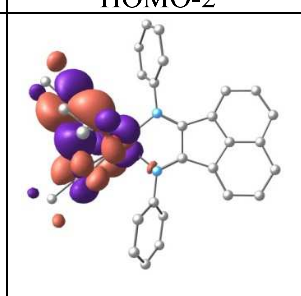
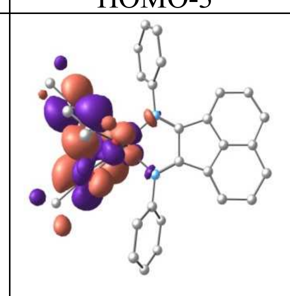
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10. Calculated MO Composition for 1a^{+} (molecule B) in S = 1/2 State

MO	energy (eV)	% composition		
		Ru	acac	BIAN
		α-MO		
LUMO+5	-3.676	6	89	6
LUMO+4	-3.698	4	89	6
LUMO+3	-3.777	40	21	39
LUMO+2	-3.877	53	35	12
LUMO+1	-4.851	1	1	99
LUMO	-5.743	8	2	90
SOMO	-8.686	18	78	5
HOMO-1	-8.756	21	72	7
HOMO-2	-8.804	14	2	84
HOMO-3	-9.323	10	16	74
HOMO-4	-9.354	6	5	89
HOMO-5	-9.414	41	29	30
		β-MO		
LUMO+5	-3.571	48	36	16
LUMO+4	-3.668	3	93	4
LUMO+3	-3.676	9	85	6
LUMO+2	-4.791	4	1	95
LUMO+1	-5.708	11	3	86
LUMO	-6.364	69	20	10
HOMO	-8.549	30	61	9
HOMO-1	-8.634	29	35	37
HOMO-2	-9.076	13	34	53
HOMO-3	-9.115	44	41	15
HOMO-4	-9.299	28	10	61
HOMO-5	-9.338	3	12	85

α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

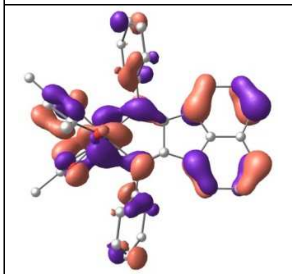
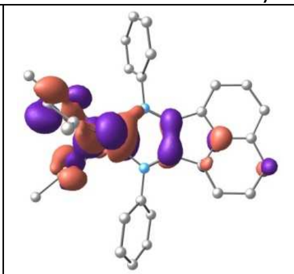
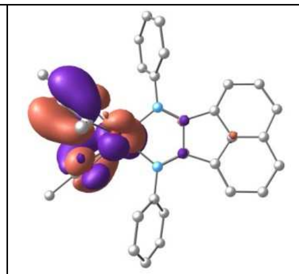
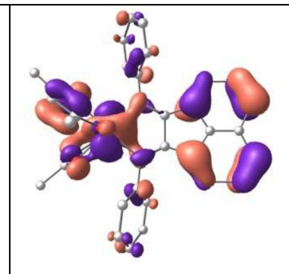
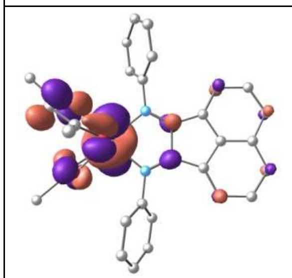
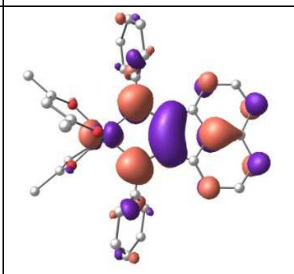
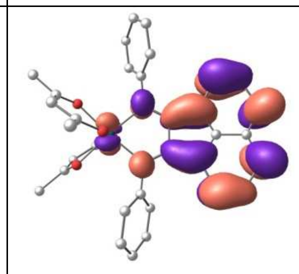
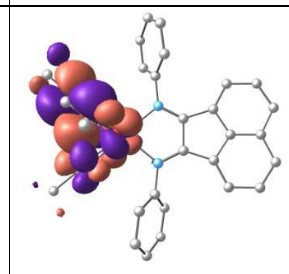
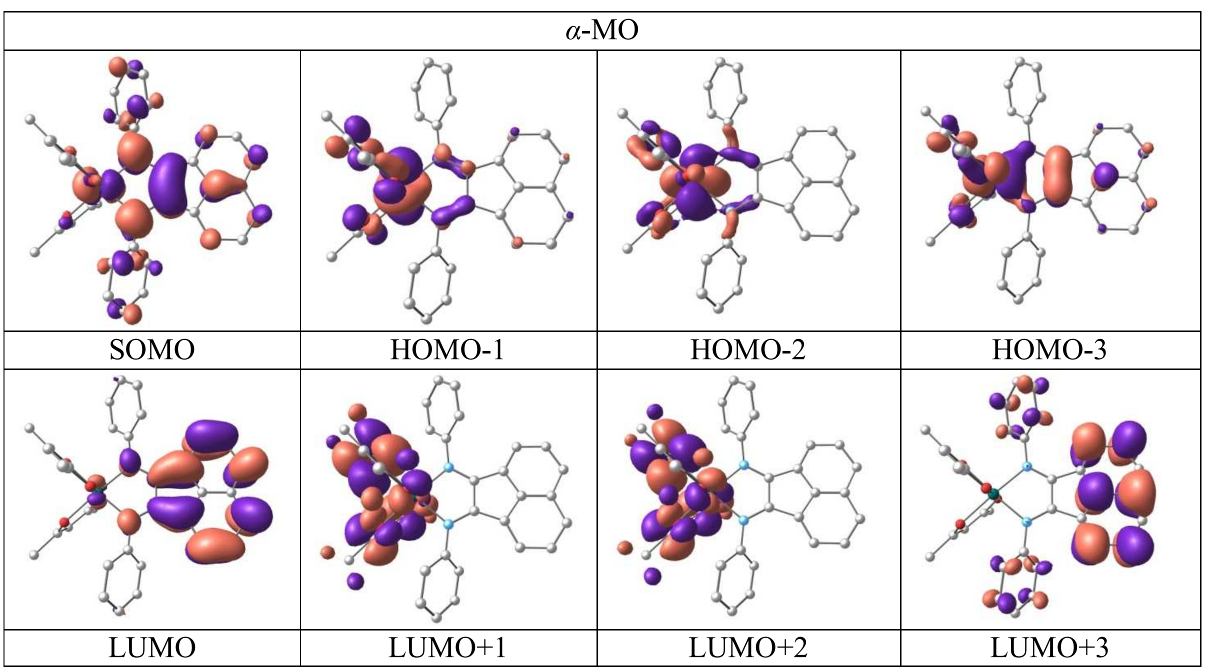
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11. Calculated MO Composition for 1a^{-} (molecule B) in S = 1/2 State

MO	energy (eV)	% composition		
		Ru	acac	BIAN
		α-MO		
LUMO+5	2.940	10	4	85
LUMO+4	2.885	3	3	94
LUMO+3	2.616	3	1	96
LUMO+2	2.508	6	85	9
LUMO+1	2.452	2	94	4
LUMO	1.290	3	1	97
SOMO	0.050	17	4	79
HOMO-1	-1.046	72	18	10
HOMO-2	-1.454	74	16	10
HOMO-3	-1.634	62	19	19
HOMO-4	-2.750	7	87	6
HOMO-5	-2.847	9	35	56
		β-MO		
LUMO+5	2.906	3	3	94
LUMO+4	2.682	3	1	96
LUMO+3	2.519	6	85	9
LUMO+2	2.480	4	91	5
LUMO+1	1.627	13	7	80
LUMO	1.471	3	1	96
HOMO	-0.946	70	16	13
HOMO-1	-1.110	66	15	19
HOMO-2	-1.362	73	16	11
HOMO-3	-2.652	8	16	76
HOMO-4	-2.717	4	90	6
HOMO-5	-2.975	16	70	14



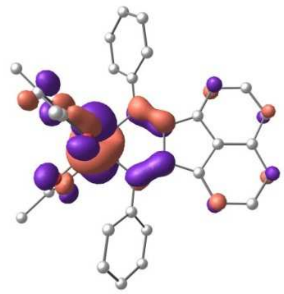
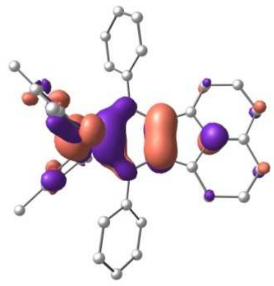
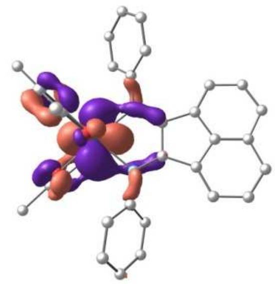
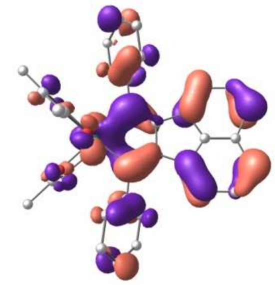
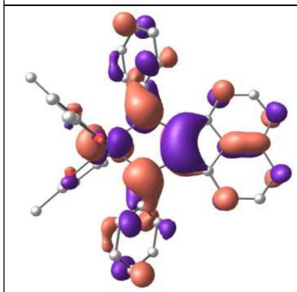
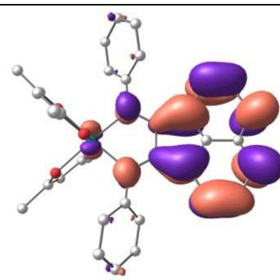
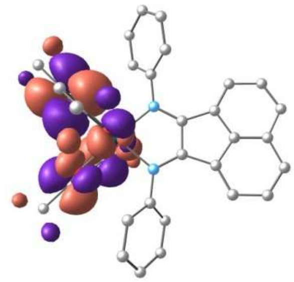
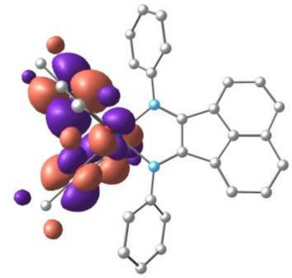
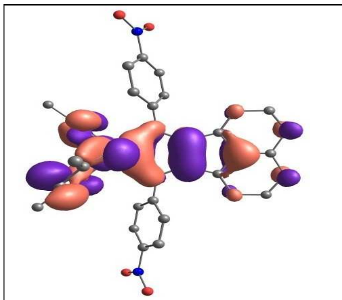
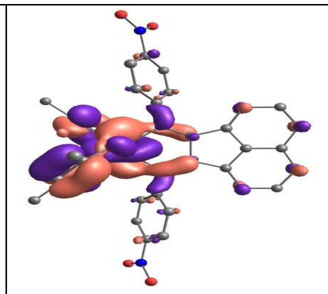
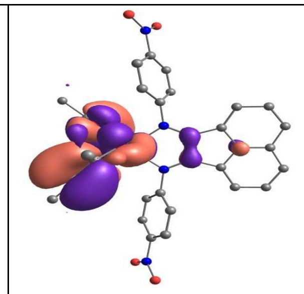
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

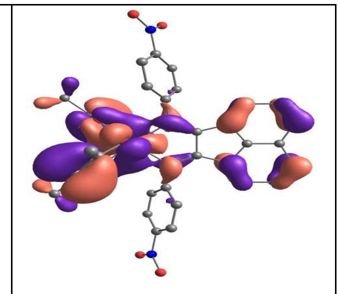
Table S12. Calculated MO Composition for 5a (molecule B) in S = 0 State

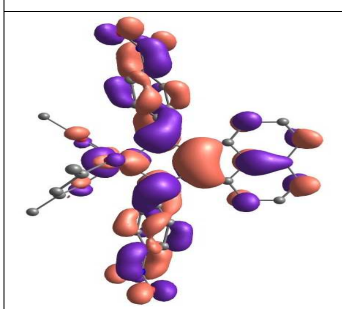
MO	energy (eV)	% composition		
		Ru	acac	BIAN
LUMO+5	-0.670	4	21	75
LUMO+4	-0.851	1	2	97
LUMO+3	-1.972	3	1	96
LUMO+2	-2.144	4	1	95
LUMO+1	-2.670	1	1	98
LUMO	-2.799	20	5	75
HOMO	-5.009	61	27	11
HOMO-1	-5.280	45	30	25
HOMO-2	-5.377	63	23	14
HOMO-3	-6.123	17	74	9
HOMO-4	-6.379	34	50	16
HOMO-5	-6.662	11	15	75

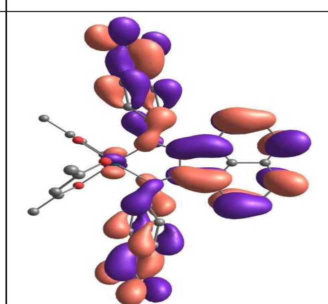

HOMO

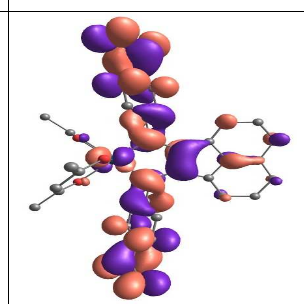

HOMO-1


HOMO-2


HOMO-3


LUMO


LUMO+1


LUMO+2

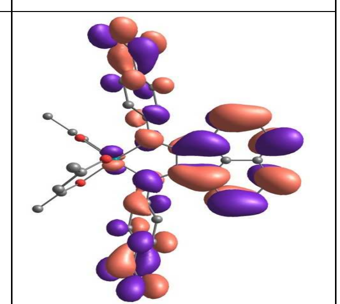
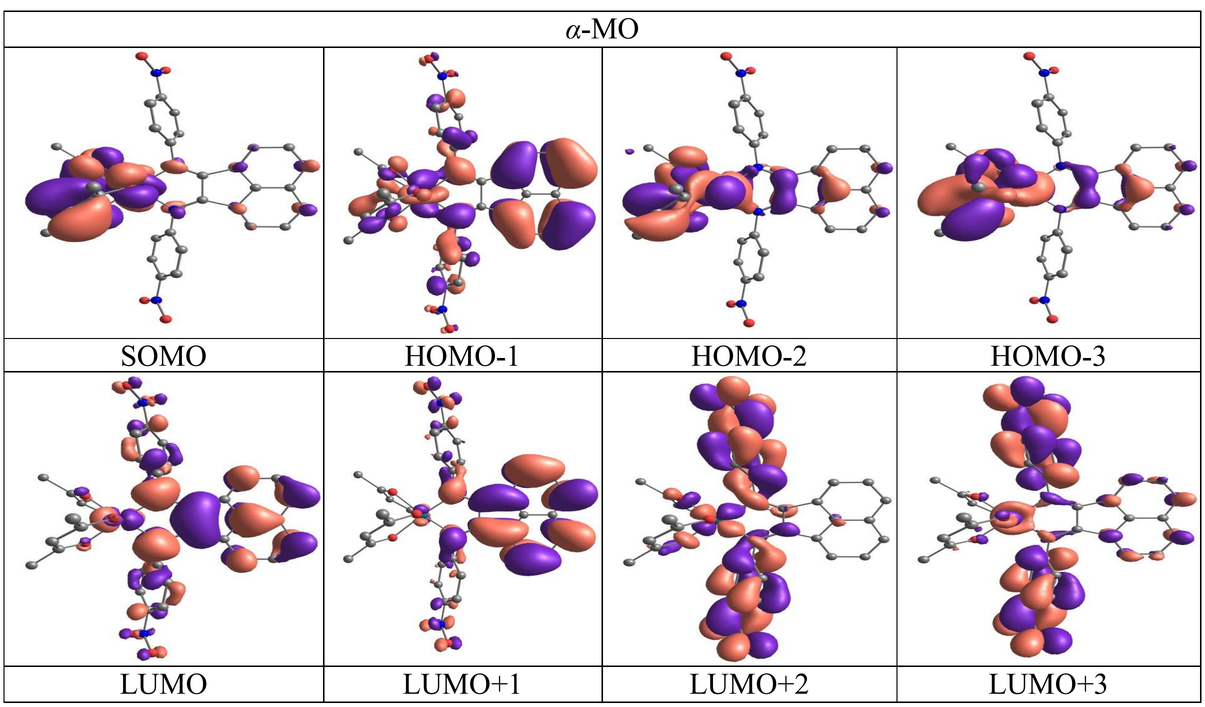

LUMO+3

Table S13. Calculated MO Composition for 5a$^+$ (molecule B) in S = 1/2 State

MO	energy (eV)	% composition		
		Ru	acac	BIAN
		α-MO		
LUMO+5	-4.132	5	87	8
LUMO+4	-4.241	46	38	16
LUMO+3	-4.818	8	5	87
LUMO+2	-4.875	12	5	83
LUMO+1	-5.341	1	1	98
LUMO	-6.327	8	2	88
SOMO	-9.131	18	78	4
HOMO-1	-9.202	21	73	6
HOMO-2	-9.335	14	3	83
HOMO-3	-9.842	46	35	19
HOMO-4	-9.987	42	10	47
HOMO-5	-10.104	6	20	74
		β-MO		
LUMO+5	-4.109	8	85	7
LUMO+4	-4.796	4	2	94
LUMO+3	-4.823	7	3	90
LUMO+2	-5.284	4	1	95
LUMO+1	-6.296	11	3	86
LUMO	-6.846	68	21	10
HOMO	-8.986	28	64	8
HOMO-1	-9.136	30	40	30
HOMO-2	-9.559	45	41	14
HOMO-3	-9.579	12	25	63
HOMO-4	-9.840	52	23	25
HOMO-5	-10.083	2	23	75



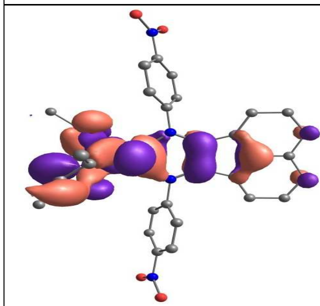
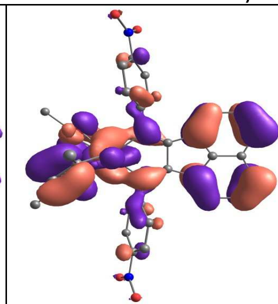
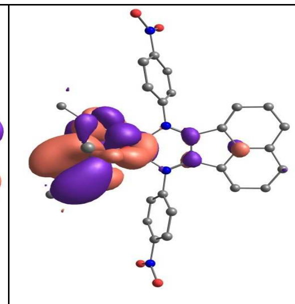
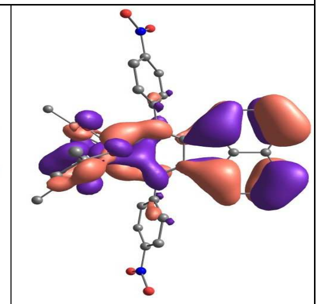
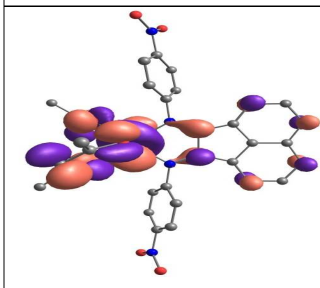
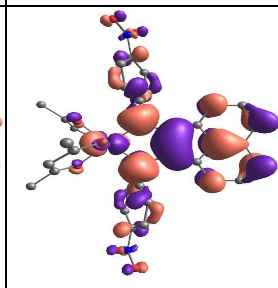
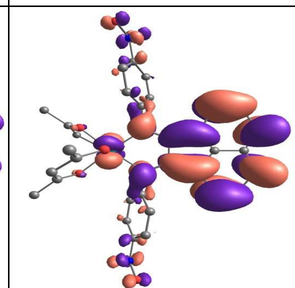
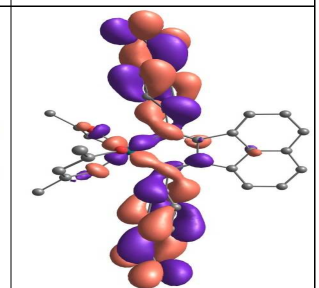
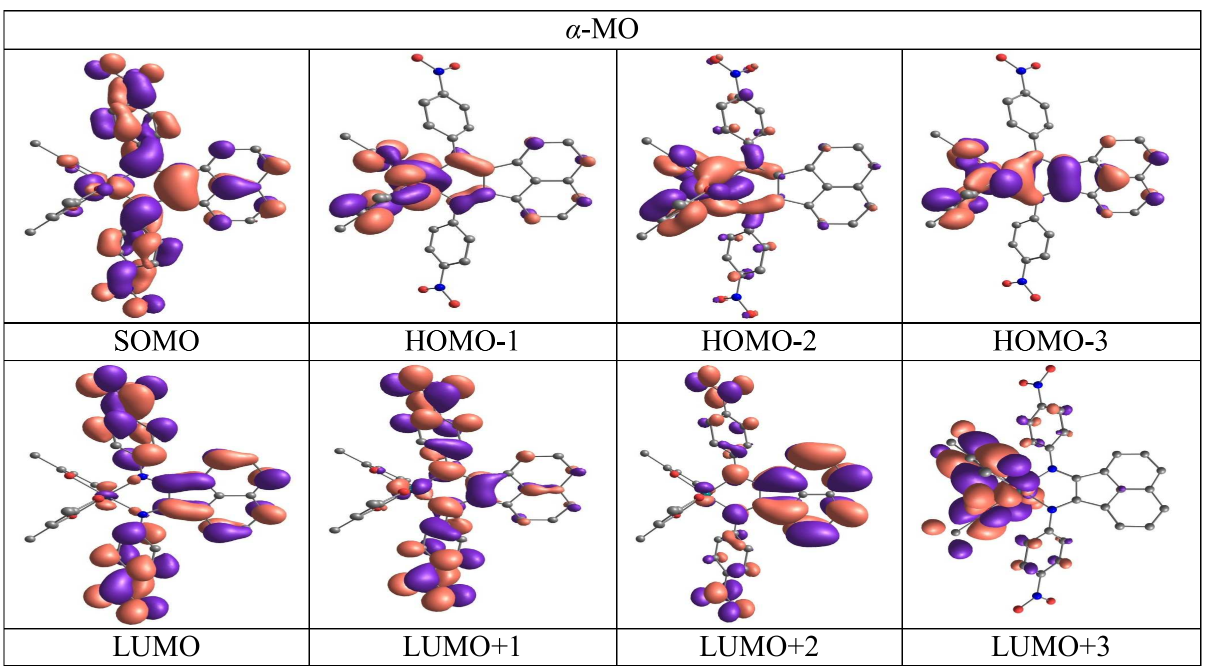
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14. Calculated MO Composition for 5a^{-} (molecule B) in S = 1/2 State

MO	energy (eV)	% composition		
		Ru	acac	BIAN
		α-MO		
LUMO+5	1.868	2	8	90
LUMO+4	1.842	6	82	12
LUMO+3	1.791	3	87	10
LUMO+2	0.604	2	1	97
LUMO+1	0.401	4	1	95
LUMO	0.125	1	1	98
SOMO	-0.836	14	3	82
HOMO-1	-1.889	69	21	10
HOMO-2	-2.342	73	16	11
HOMO-3	-2.462	59	22	19
HOMO-4	-3.426	10	84	6
HOMO-5	-3.591	14	53	33
		β-MO		
LUMO+5	1.853	6	83	11
LUMO+4	1.821	4	89	7
LUMO+3	0.905	11	5	84
LUMO+2	0.738	2	1	97
LUMO+1	0.374	1	1	98
LUMO	0.225	7	3	90
HOMO	-1.806	69	19	12
HOMO-1	-1.986	62	16	22
HOMO-2	-2.254	73	16	12
HOMO-3	-3.386	5	90	5
HOMO-4	-3.501	9	33	58
HOMO-5	-3.712	16	50	34



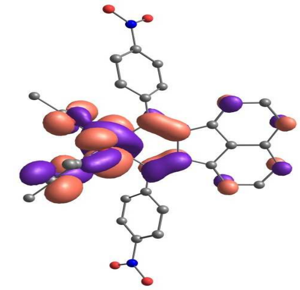
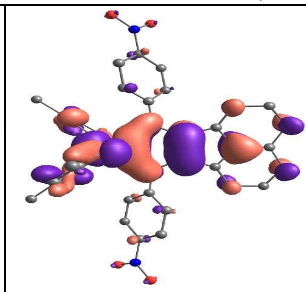
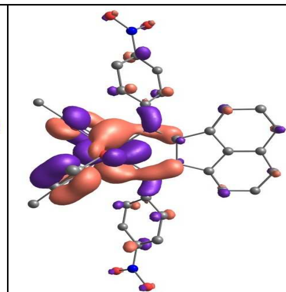
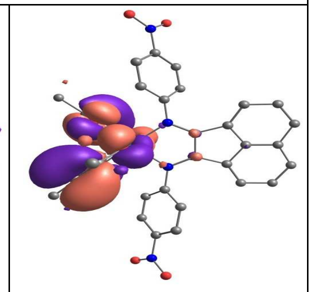
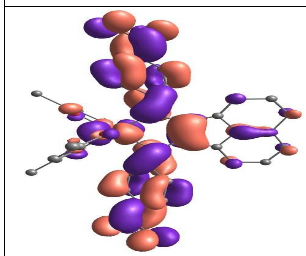
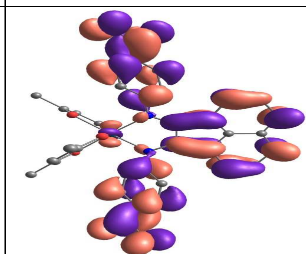
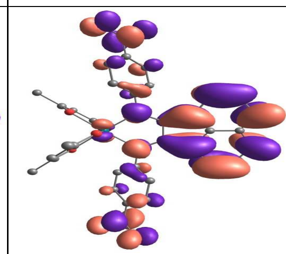
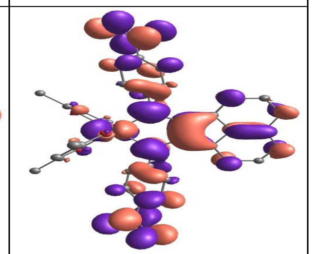
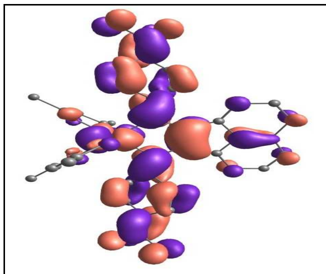
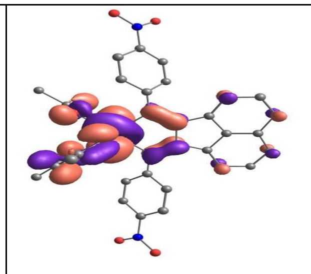
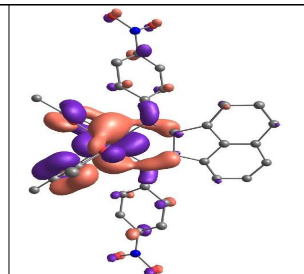
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

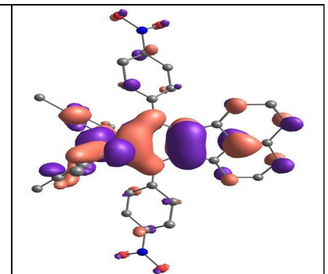
Table S15. Calculated MO Composition for 5a^{2-} (molecule B) in S = 0 State

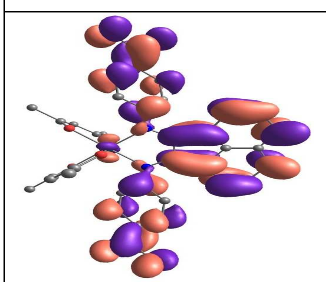
MO	energy (eV)	% composition		
		Ru	acac	BIAN
LUMO+5	4.516	2	1	97
LUMO+4	4.426	6	87	6
LUMO+3	4.353	3	94	3
LUMO+2	3.486	5	2	93
LUMO+1	3.403	2	1	97
LUMO	2.902	1	1	98
HOMO	1.937	16	4	80
HOMO-1	1.009	73	17	11
HOMO-2	0.577	74	14	12
HOMO-3	0.540	62	15	23
HOMO-4	-0.682	8	9	83
HOMO-5	-0.817	4	89	7

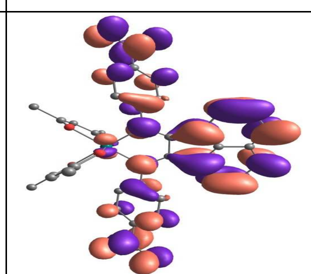

HOMO

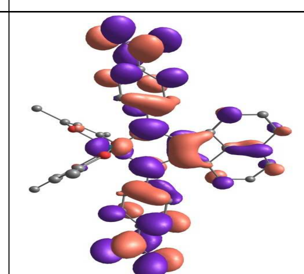

HOMO-1


HOMO-2


HOMO-3


LUMO


LUMO+1


LUMO+2

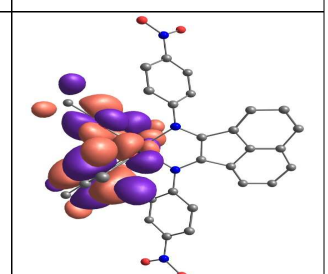

LUMO+3

Table S16. Energies of DFT Optimized 2b^{n} (n = 4+, 3+, 2+, 1+, 0, 1–, 2–)

Comppex	E (Hartrees)			$\Delta E_{\text{(HE-LE)}}$[a]
	$S = 0$	$S = 1/2$	$S = 1$	
2b^{2+}	-4585.3390668	-	-	-
2b^{3+}	-	-4584.9736581	-	-
2b^{4+}	-4584.5156890	-	-4584.5349132	0.0192242 Hartrees 0.5231173767 eV 50.47314094 kJ/mol 12.06337021 kcal/mol 4219.224182 cm^{-1}
2b^{+}	-	-4585.5739339	-	-
2b	-4585.7122708		-4585.7121299	0.0001409 Hartrees 0.0038340861 eV 0.3699329782 kJ/mol 0.0884161037 kcal/mol 30.92397537 cm^{-1}
2b^{-}	-	-4585.7851089	-	-
2b^{2-}	-4585.7487191	-	-	-

[a]HE = Spin state in higher in energy and LE = Spin state in lower in energy.

Table S17. Experimental and DFT Calculated Selected Bond Lengths (Å) for 2b^{n}

bond length (Å)	X-ray	DFT						
		2b^{4+} (S=1)	**2b**$^{3+}$ (S=1/2)	**2b**$^{2+}$ (S=0)	**2b**$^{+}$ (S=1/2)	**2b** (S=0)	**2b**$^{-}$ (S=1/2)	**2b**$^{2-}$ (S=0)
Ru(1)-N(1)	2.032(9)	2.082	2.100	2.104	2.088	2.077	2.116	2.102
Ru(1)-N(2)	2.056(9)	2.154	2.151	2.169	2.162	2.158	2.195	2.221
Ru(1)-N(6)	2.053(10)	2.113	2.111	2.101	2.112	2.106	2.098	2.080
Ru(1)-N(7)	1.947(9)	2.020	2.025	1.985	1.990	1.993	1.978	1.977
Ru(1)-N(9)	2.053(11)	2.122	2.122	2.102	2.112	2.112	2.109	2.110
Ru(2)-N(3)	2.027(9)	2.082	2.109	2.103	2.085	2.078	2.118	2.103
Ru(2)-N(4)	2.101(9)	2.155	2.171	2.168	2.162	2.156	2.195	2.217
Ru(2)-N(5)	2.062(10)	2.114	2.094	2.102	2.114	2.106	2.098	2.080
Ru(2)-N(8)	1.949(8)	2.020	1.976	1.986	1.990	1.993	1.977	1.977
Ru(2)-N(10)	2.058(11)	2.123	2.096	2.102	2.111	2.111	2.109	2.110
Ru(1)-Cl(1)	2.370(3)	2.384	2.365	2.443	2.452	2.472	2.494	2.527
Ru(2)-Cl(2)	2.387(3)	2.385	2.439	2.443	2.455	2.471	2.495	2.527
N(1)-C(7)	1.271(15)	1.315	1.309	1.302	1.307	1.321	1.342	1.357
N(2)-C(18)	1.291(14)	1.315	1.310	1.307	1.309	1.319	1.346	1.365
C(7)-C(18)	1.478(16)	1.493	1.496	1.488	1.477	1.458	1.430	1.414
N(3)-C(31)	1.319(15)	1.315	1.303	1.302	1.306	1.321	1.342	1.357
N(4)-C(42)	1.298(15)	1.315	1.307	1.307	1.309	1.319	1.347	1.365
C(31)-C(42)	1.453(18)	1.492	1.494	1.488	1.478	1.458	1.431	1.414

Table S18. Selected Experimental Bond Angles (º) for [2b](ClO_4)$_2$ and [3b](ClO_4)$_2$

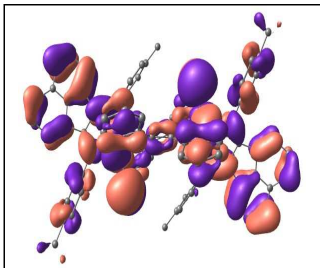
bond angles (º)	[**2b**](ClO_4)$_2$	bond angles (º)	[**3b**](ClO_4)$_2$
N(7)-Ru(1)-N(1)	95.3(4)	N(4)-Ru(1)-N(2)	92.73(12)
N(7)-Ru(1)-N(9)	79.0(4)	N(4)-Ru(1)-N(5)	79.42(12)
N(1)-Ru(1)-N(9)	94.7(4)	N(2)-Ru(1)-N(5)	87.61(12)
N(7)-Ru(1)-N(6)	80.8(4)	N(4)-Ru(1)-N(3)	80.65(12)
N(1)-Ru(1)-N(6)	89.7(4)	N(2)-Ru(1)-N(3)	95.74(12)
N(9)-Ru(1)-N(6)	159.6(4)	N(5)-Ru(1)-N(3)	159.92(12)
N(7)-Ru(1)-N(2)	172.8(4)	N(4)-Ru(1)-N(1)	170.90(12)
N(1)-Ru(1)-N(2)	77.7(4)	N(2)-Ru(1)-N(1)	78.63(12)
N(9)-Ru(1)-N(2)	102.7(4)	N(5)-Ru(1)-N(1)	97.19(12)
N(6)-Ru(1)-N(2)	97.6(4)	N(3)-Ru(1)-N(1)	102.88(12)
N(7)-Ru(1)-Cl(1)	90.1(3)	N(4)-Ru(1)-Cl(1)	91.23(9)
N(1)-Ru(1)-Cl(1)	174.2(3)	N(2)-Ru(1)-Cl(1)	174.79(9)
N(9)-Ru(1)-Cl(1)	88.4(3)	N(5)-Ru(1)-Cl(1)	89.80(9)
N(6)-Ru(1)-Cl(1)	89.0(3)	N(3)-Ru(1)-Cl(1)	88.23(9)
N(2)-Ru(1)-Cl(1)	96.9(3)	N(1)-Ru(1)-Cl(1)	97.23(8)
N(8)-Ru(2)-N(3)	92.9(4)		
N(8)-Ru(2)-N(5)	79.8(4)		
N(8)-Ru(2)-N(10)	80.4(4)		
N(8)-Ru(2)-N(4)	171.2(4)		
N(3)-Ru(2)-N(5)	90.9(4)		
N(3)-Ru(2)-N(10)	94.8(4)		
N(3)-Ru(2)-N(4)	79.0(4)		
N(5)-Ru(2)-N(10)	159.6(4)		
N(5)-Ru(2)-N(4)	96.9(4)		
N(10)-Ru(2)-N(4)	103.4(4)		
N(3)-Ru(2)-Cl(2)	178.5(3)		
N(4)-Ru(2)-Cl(2)	99.6(3)		
N(5)-Ru(2)-Cl(2)	89.6(3)		
N(8)-Ru(2)-Cl(2)	88.6(3)		
N(10)-Ru(2)-Cl(2)	85.2(3)		

Table S19. Experimental and DFT Calculated Selected Bond Angles (º) for 2b*n*

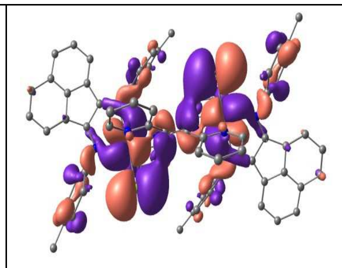
bond angle (º)	X-ray	DFT						
		2b^{4+} (*S*=1)	**2b**$^{3+}$ (*S*=1/2)	**2b**$^{2+}$ (*S*=0)	**2b**$^{+}$ (*S*=1/2)	**2b** (*S*=0)	**2b**$^{–}$ (*S*=1/2)	**2b**$^{2–}$ (*S*=0)
N(7)-Ru(1)-N(1)	95.3(4)	100.57	98.70	98.54	97.37	96.63	97.15	96.15
N(7)-Ru(1)-N(9)	79.0(4)	78.45	78.30	79.13	79.09	79.16	79.21	79.68
N(1)-Ru(1)-N(9)	94.7(4)	89.44	88.95	92.97	93.54	93.76	92.19	93.78
N(7)-Ru(1)-N(6)	80.8(4)	79.31	78.85	79.38	79.03	78.84	79.34	79.30
N(1)-Ru(1)-N(6)	89.7(4)	92.17	90.34	91.84	91.86	92.62	91.610	90.89
N(9)-Ru(1)-N(6)	159.6(4)	157.62	156.76	158.45	157.96	157.66	158.51	158.83
N(7)-Ru(1)-N(2)	172.8(4)	179.19	177.20	175.82	174.79	174.56	175.36	175.10
N(1)-Ru(1)-N(2)	77.7(4)	78.75	78.50	77.29	77.46	78.03	78.34	79.12
N(9)-Ru(1)-N(2)	102.7(4)	101.07	101.47	101.26	101.76	102.07	101.95	101.78
N(6)-Ru(1)-N(2)	97.6(4)	101.14	101.15	100.29	100.27	100.19	99.53	99.37
N(7)-Ru(1)-Cl(1)	90.1(3)	84.53	86.16	86.18	87.47	87.90	87.19	85.80
N(1)-Ru(1)-Cl(1)	174.2(3)	173.79	174.57	175.25	175.12	175.42	175.57	178.05
N(9)-Ru(1)-Cl(1)	88.4(3)	88.14	89.68	87.38	86.79	86.47	87.76	86.65
N(6)-Ru(1)-Cl(1)	89.0(3)	92.24	92.99	89.55	89.63	88.85	90.04	89.38
N(2)-Ru(1)-Cl(1)	96.9(3)	96.11	96.63	97.98	97.69	97.44	97.33	98.93
N(8)-Ru(2)-N(3)	92.9(4)	100.72	101.02	98.62	97.30	96.56	97.00	96.01
N(8)-Ru(2)-N(5)	79.8(4)	79.29	79.99	79.36	79.04	78.87	79.32	79.32
N(8)-Ru(2)-N(10)	80.4(4)	78.42	79.10	79.11	79.09	79.19	79.23	79.70
N(8)-Ru(2)-N(4)	171.2(4)	179.24	178.37	175.90	174.77	174.56	175.25	175.08
N(3)-Ru(2)-N(5)	90.9(4)	92.04	92.15	91.67	91.67	92.72	91.26	90.77
N(3)-Ru(2)-N(10)	94.8(4)	89.54	92.05	93.01	93.56	93.58	92.50	93.89
N(3)-Ru(2)-N(4)	79.0(4)	78.74	77.35	77.28	77.47	78.07	78.33	79.18
N(5)-Ru(2)-N(10)	159.6(4)	157.56	159.08	158.41	157.99	157.73	158.52	158.87
N(5)-Ru(2)-N(4)	96.9(4)	101.23	99.98	100.61	100.79	100.35	99.77	99.57
N(10)-Ru(2)-N(4)	103.4(4)	101.02	100.94	100.97	101.21	101.84	101.71	101.55
N(3)-Ru(2)-Cl(2)	178.5(3)	173.84	174.74	175.24	175.18	175.54	175.87	178.03
N(4)-Ru(2)-Cl(2)	99.6(3)	96.14	97.43	97.98	97.73	97.53	97.57	98.88
N(5)-Ru(2)-Cl(2)	89.6(3)	92.32	89.35	89.60	89.67	88.77	89.93	89.22
N(8)-Ru(2)-Cl(2)	88.6(3)	84.37	84.20	86.13	87.50	87.85	87.11	85.92
N(10)-Ru(2)-Cl(2)	85.2(3)	88.09	88.31	87.46	86.89	86.58	87.82	86.81

Table S20. Calculated MO Composition for $2b^{2+}$ in S = 0 State

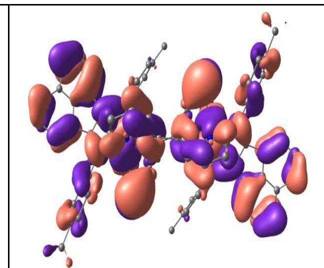
MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
LUMO+5	-5.732	1	2	97	0
LUMO+4	-6.221	6	88	4	2
LUMO+3	-6.483	12	7	80	1
LUMO+2	-6.596	13	9	77	1
LUMO+1	-6.914	17	75	6	2
LUMO	-7.350	5	89	6	0
HOMO	-9.366	45	7	28	19
HOMO-1	-9.412	54	8	10	28
HOMO-2	-9.476	46	9	22	24
HOMO-3	-9.742	28	13	12	48
HOMO-4	-9.814	28	8	55	10
HOMO-5	-9.865	25	5	59	11



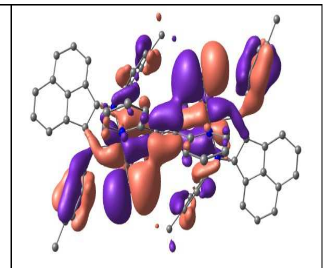
HOMO



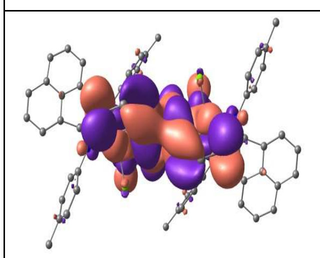
HOMO-1



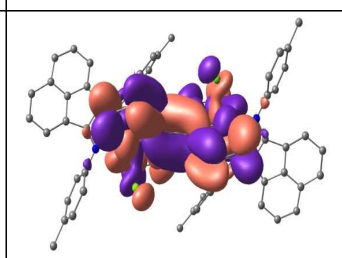
HOMO-2



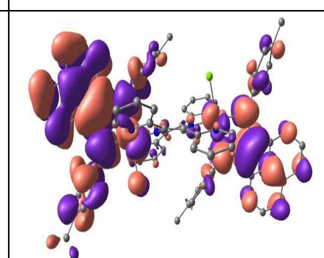
HOMO-3



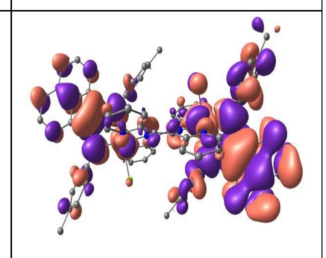
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S21. Calculated MO Composition for 2b^{3+} in *S* = 1/2 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
		α-MO			
LUMO+5	-7.877	1	2	97	0
LUMO+4	-8.408	5	92	3	1
LUMO+3	-8.831	7	4	89	0
LUMO+2	-8.860	7	4	89	0
LUMO+1	-9.288	13	84	2	2
LUMO	-9.565	5	93	2	0
SOMO	-11.699	6	2	90	2
HOMO-1	-11.714	6	2	91	2
HOMO-2	-12.073	41	5	28	26
HOMO-3	-12.105	11	1	74	14
HOMO-4	-12.120	8	1	85	6
HOMO-5	-12.175	18	5	44	33
		β-MO			
LUMO+5	-8.783	5	91	3	1
LUMO+4	-7.852	9	5	86	1
LUMO+3	-8.806	9	4	86	1
LUMO+2	-9.276	14	82	2	2
LUMO+1	-9.533	9	87	4	1
LUMO	-10.803	56	9	20	16
HOMO	-11.279	45	13	28	14
HOMO-1	-11.767	11	3	78	7
HOMO-2	-11.793	17	4	70	8
HOMO-3	-11.964	49	5	15	30
HOMO-4	-12.113	6	2	87	5
HOMO-5	-12.122	15	5	52	29

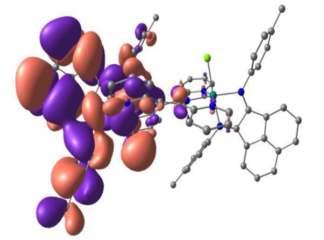
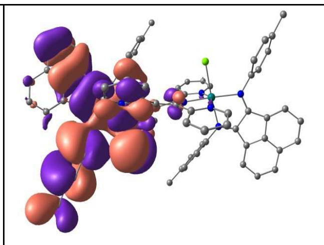
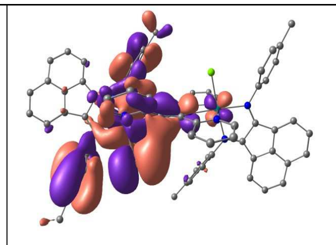
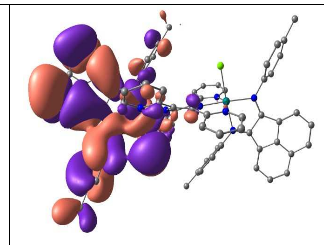
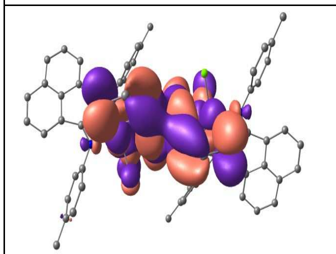
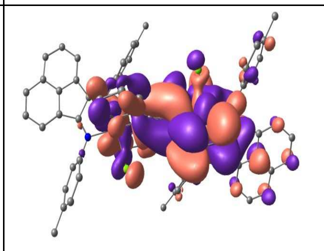
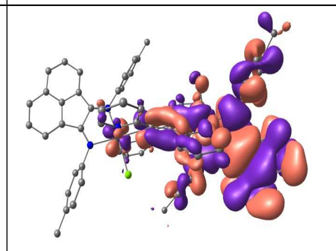
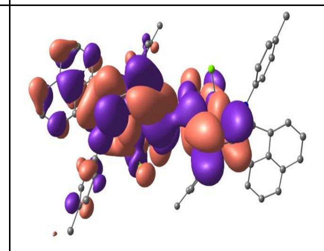
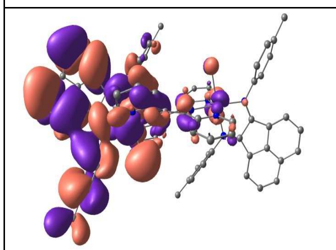
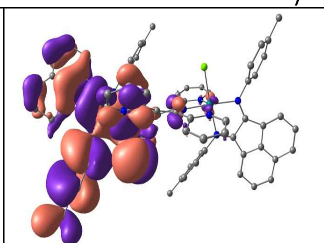
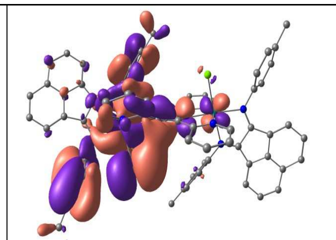
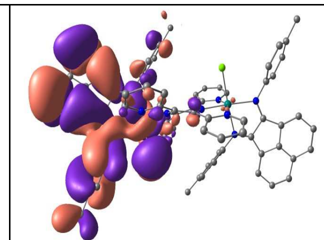
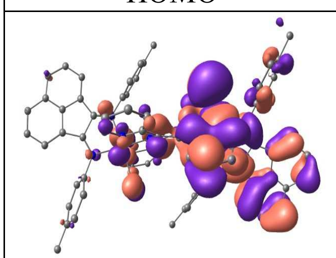
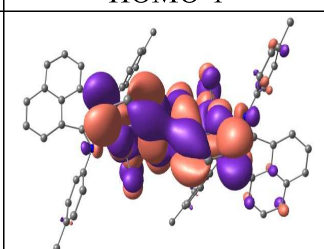
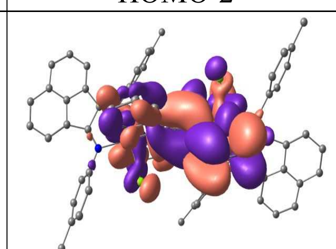
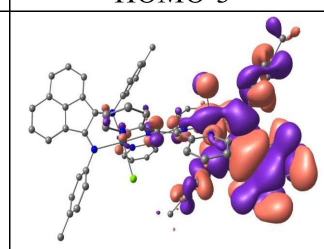
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S22. Calculated MO Composition for 2b^{4+} in S = 1 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
		α-MO			
LUMO+5	-10.065	19	68	9	4
LUMO+4	-10.665	3	3	94	1
LUMO+3	-10.988	4	92	3	1
LUMO+2	-11.117	6	3	91	0
LUMO+1	-11.643	11	86	2	2
LUMO	-11.868	5	93	2	0
SOMO1	-13.660	3	1	94	1
SOMO2	-13.893	3	2	94	1
HOMO-2	-14.067	3	1	95	1
HOMO-3	-14.201	5	2	83	10
HOMO-4	-14.273	4	1	95	1
HOMO-5	-14.348	8	2	78	12
		β-MO			
LUMO+5	-10.906	8	3	88	1
LUMO+4	-11.018	8	4	88	1
LUMO+3	-11.614	13	83	2	2
LUMO+2	-11.766	12	82	4	1
LUMO+1	-12.525	52	14	21	14
LUMO	-12.836	45	13	31	10
HOMO	-13.655	12	4	79	6
HOMO-1	-13.848	19	5	69	7
HOMO-2	-14.007	4	2	91	4
HOMO-3	-14.155	7	2	87	4
HOMO-4	-14.165	9	2	74	15
HOMO-5	-14.305	16	3	66	15

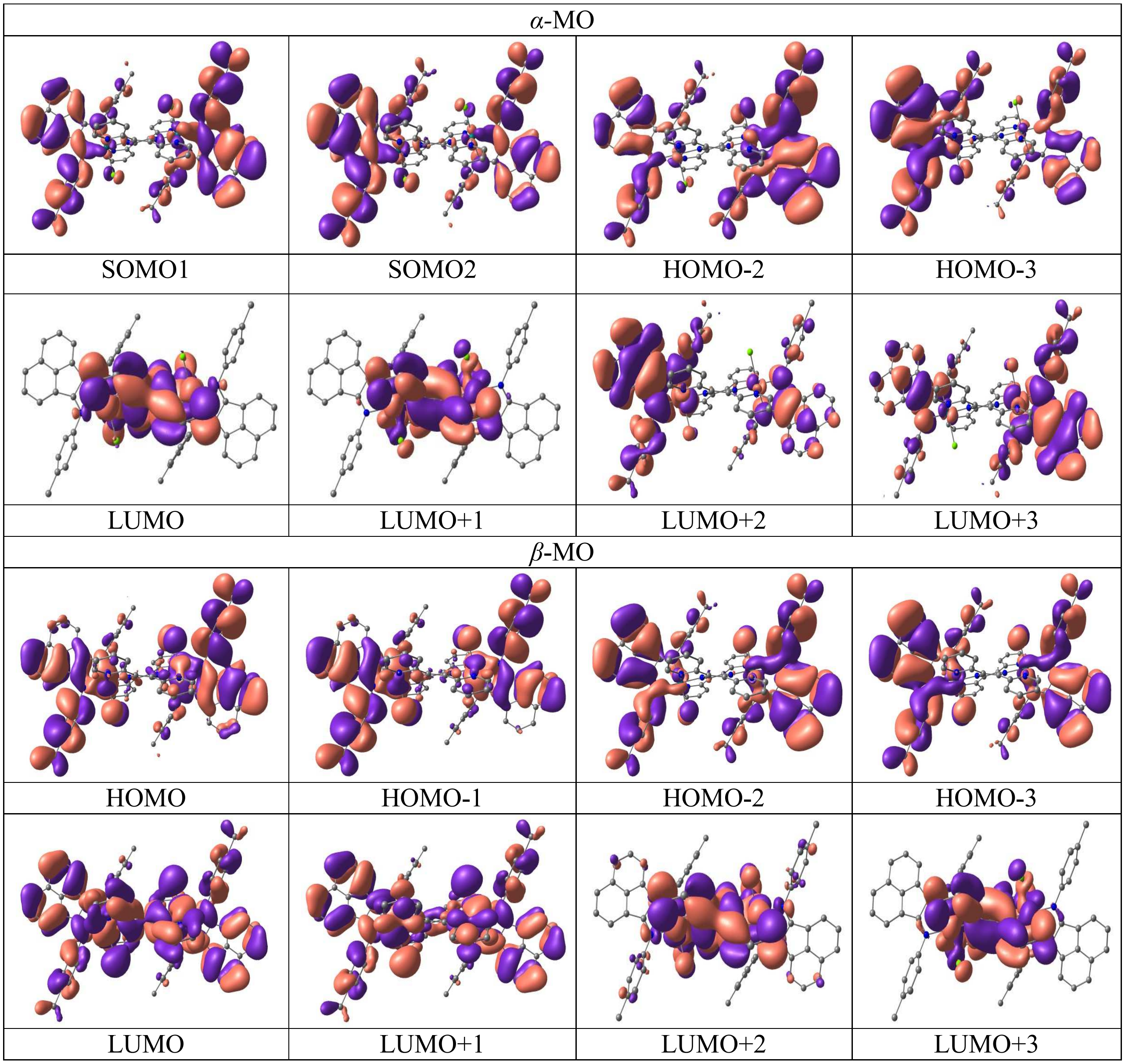

α-MO
SOMO1
SOMO2
HOMO-2
HOMO-3
LUMO
LUMO+1
LUMO+2
LUMO+3
β-MO
HOMO
HOMO-1
HOMO-2
HOMO-3
LUMO
LUMO+1
LUMO+2
LUMO+3

Table 23. Calculated MO Composition for 2b$^+$ in *S* = 1/2 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
		α-MO			
LUMO+5	-3.579	5	91	2	1
LUMO+4	-3.867	1	1	97	1
LUMO+3	-3.875	1	1	97	1
LUMO+2	-4.123	13	82	3	2
LUMO+1	-4.409	13	6	80	1
LUMO	-4.427	13	4	82	1
SOMO	-5.390	5	90	5	0
HOMO-1	-6.911	58	8	10	24
HOMO-2	-6.914	60	7	8	25
HOMO-3	-6.985	54	9	11	25
HOMO-4	-7.194	39	10	7	45
HOMO-5	-7.455	68	12	19	1
		β-MO			
LUMO+5	-3.860	2	1	97	0
LUMO+4	-3.869	2	1	97	0
LUMO+3	-4.019	12	84	3	2
LUMO+2	-4.183	8	80	11	1
LUMO+1	-4.401	12	4	83	1
LUMO	-4.432	9	13	77	0
HOMO	-6.873	57	11	10	22
HOMO-1	-6.918	62	6	7	25
HOMO-2	-6.961	56	9	11	25
HOMO-3	-7.189	40	9	7	44
HOMO-4	-7.455	68	13	19	1
HOMO-5	-7.496	68	10	20	2

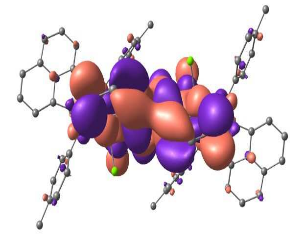
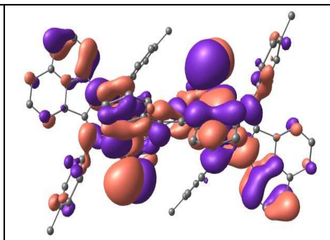
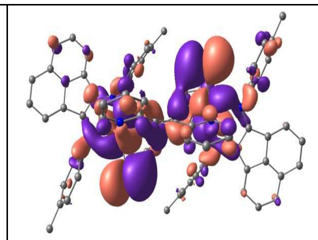
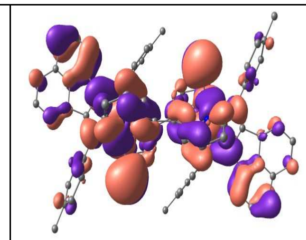
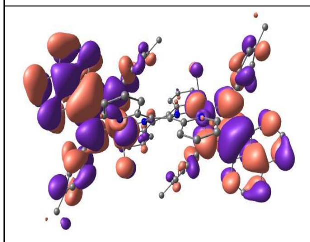
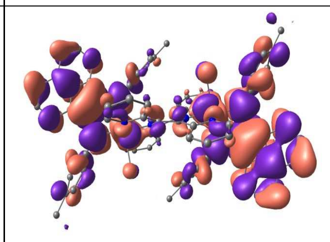
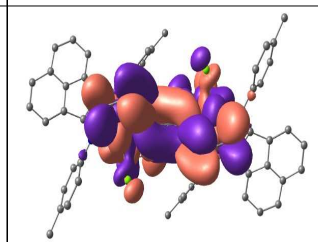
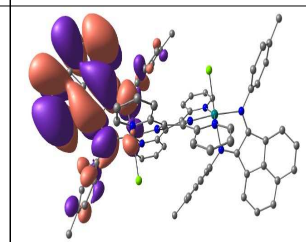
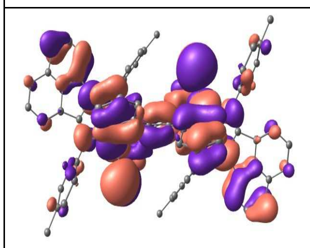
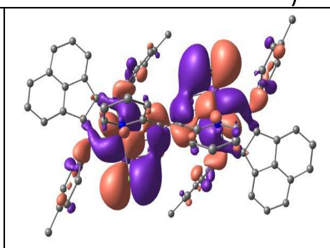
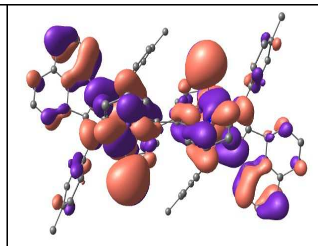
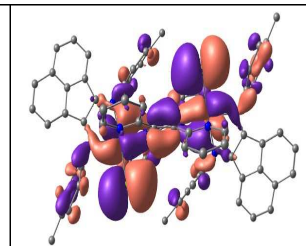
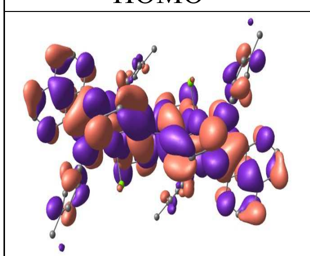
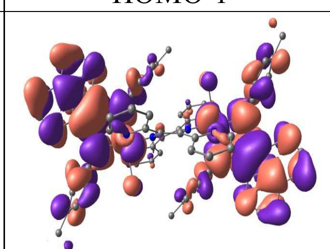
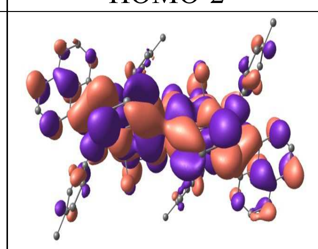
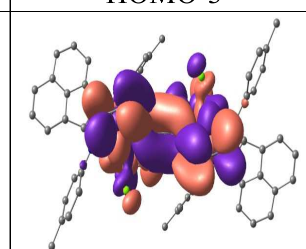
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S24. Calculated MO Composition for 2b in *S* = 0 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
LUMO+5	-1.214	5	91	2	1
LUMO+4	-1.699	11	84	3	2
LUMO+3	-1.799	2	1	96	1
LUMO+2	-1.813	2	1	97	0
LUMO+1	-2.149	15	21	63	1
LUMO	-2.253	14	5	80	1
HOMO	-2.901	4	72	24	0
HOMO-1	-4.640	58	11	12	19
HOMO-2	-4.664	63	7	7	23
HOMO-3	-4.731	58	9	11	22
HOMO-4	-4.939	45	9	6	40
HOMO-5	-5.146	68	16	16	0

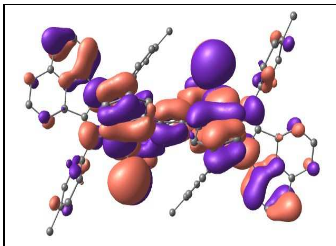
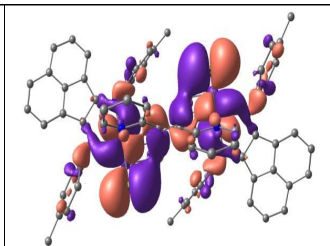
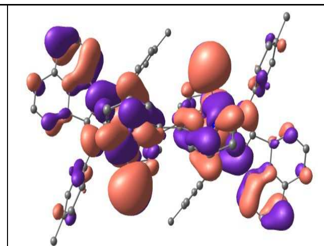
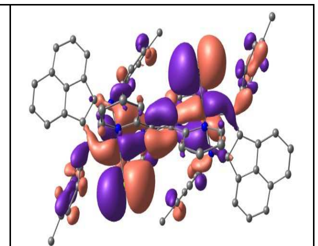
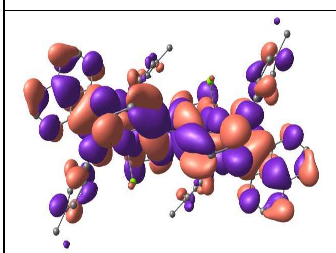
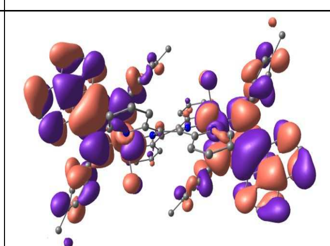
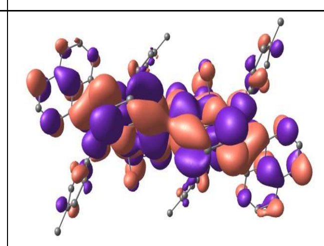
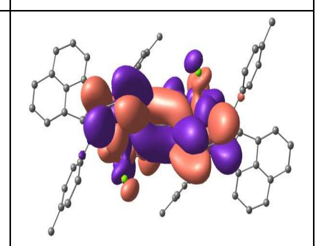
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S25. Calculated MO Composition for 2b^{-} in S = 1/2 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
		α-MO			
LUMO+5	1.409	4	91	5	0
LUMO+4	0.723	5	91	3	1
LUMO+3	0.419	2	1	97	0
LUMO+2	0.418	2	3	95	0
LUMO+1	0.272	12	82	4	2
LUMO	-0.144	11	75	13	1
SOMO	-0.987	15	5	79	1
HOMO-1	-1.083	10	16	74	0
HOMO-2	-2.409	61	11	13	15
HOMO-3	-2.434	67	8	6	19
HOMO-4	-2.503	60	10	13	17
HOMO-5	-2.768	48	12	6	35
		β-MO			
LUMO+5	0.613	9	40	50	1
LUMO+4	0.603	2	6	91	1
LUMO+3	0.599	2	2	96	0
LUMO+2	0.557	10	5	84	1
LUMO+1	0.522	7	52	40	1
LUMO	0.195	14	81	3	2
HOMO	-1.279	7	88	4	1
HOMO-1	-2.360	60	9	17	14
HOMO-2	-2.384	65	9	7	18
HOMO-3	-2.446	57	10	17	15
HOMO-4	-2.685	69	13	17	2
HOMO-5	-2.736	69	13	17	1

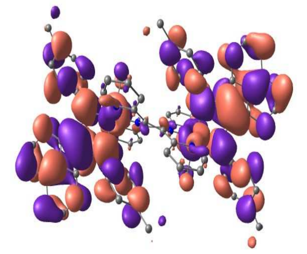
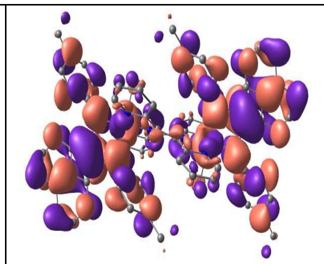
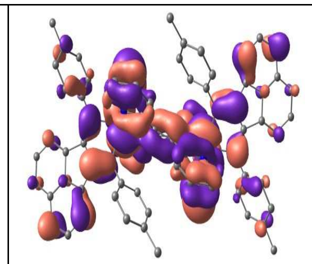
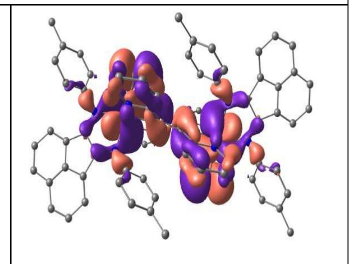
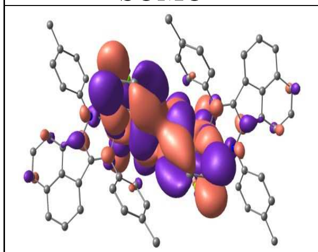
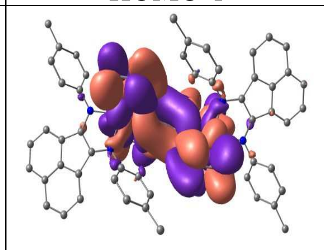
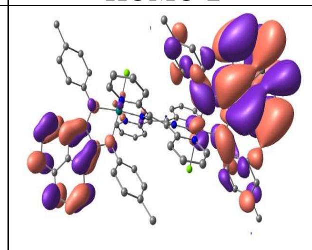
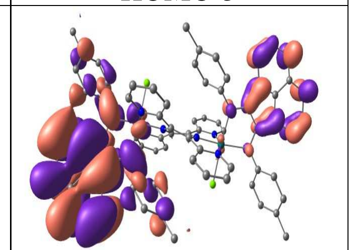
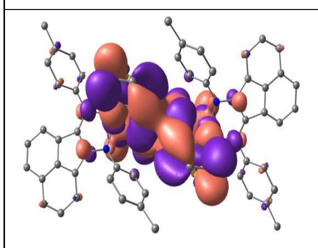
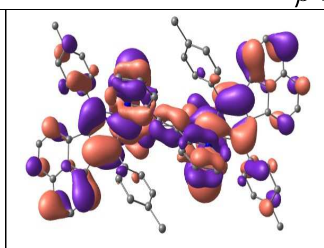
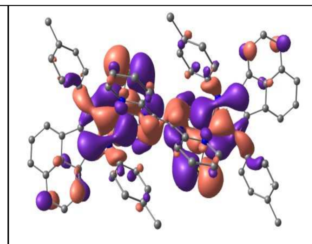
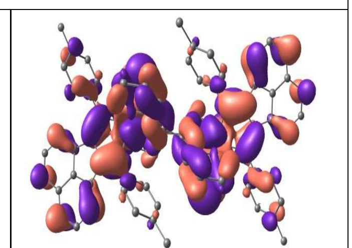
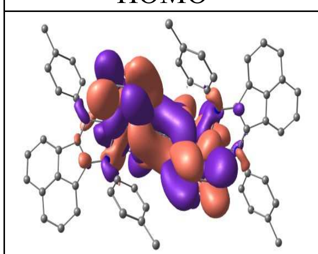
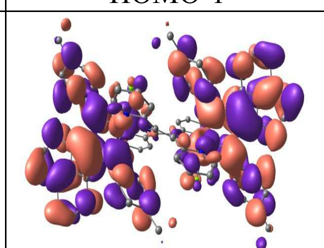
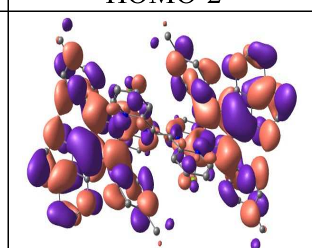
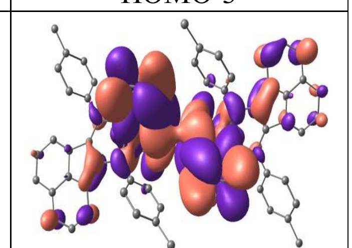
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26. Calculated MO Composition for 2b^{2-} in S = 0 State

MO	energy (eV)	% composition			
		Ru	tppz	BIAN	Cl
LUMO+5	3.551	3	94	3	0
LUMO+4	2.847	6	90	3	1
LUMO+3	2.527	2	5	92	1
LUMO+2	2.524	2	4	94	0
LUMO+1	2.457	12	77	9	2
LUMO	1.961	15	27	57	1
HOMO	1.528	13	5	82	1
HOMO-1	1.199	5	64	32	0
HOMO-2	-0.190	62	11	14	12
HOMO-3	-0.228	68	10	7	15
HOMO-4	-0.287	61	11	15	13
HOMO-5	-0.635	50	13	6	31

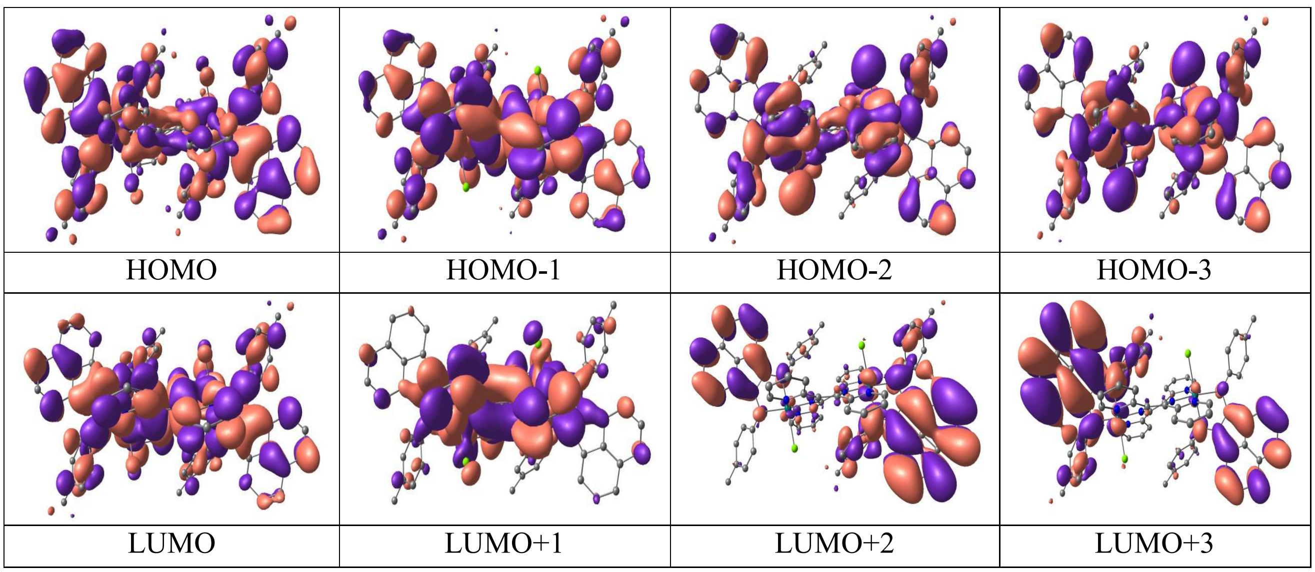


Table S27. UV-vis-NIR Spectroelectrochemical Data for 1b^{n}, 3b^{n} and 4b^{n} in CH_3CN/0.1 M Bu_4NPF_6

complex	λ [nm] (ε [$M^{-1}cm^{-1}$])
1b^{4+}	915(2340), 536(sh), 404(32570), 380(sh), 316(27220)
1b^{3+}	1854(1110), 602(14140), 399(27750), 378(sh), 325(sh), 315(26630)
1b^{2+}	613(31150), 428(16280), 384(2450), 362(24830), 329(23580), 306(26730)
1b^{+}	1041(7750), 916(3000), 613(33440), 443(22280), 402(22200), 316(28190)
1b	1132(sh), 984(3910), 637(18400), 484(sh), 438(21840), 394(22020), 360(sh), 307(28450)
1b^{-}	1170(sh), 1029(3830), 677(16000), 438(22660), 398(sh), 360(25700), 307(30050)
1b^{2-}	1034(9680), 912(5670), 666(16630), 423(24470), 350(27190), 335(sh), 311(27400)
3b^{4+}	827(2980), 545(sh), 404(35740), 312(29900)
3b^{3+}	1882(1750), 615(16130), 394(31280), 305(sh)
3b^{2+}	621(29700), 423(22880), 380(28350), 302(27110)
3b^{+}	1046(8590), 919(3600), 618(36170), 436(30140), 403(31290), 311(28950)
3b	1118(sh), 987(4970), 856(5040), 632(21500), 434(27390), 394(28950), 377(sh) 301(30700)
3b^{-}	1170(sh), 1010(450), 669(18350), 438(25980), 365(31070), 304(34280)
4b^{4+}	929(3680), 480(sh), 407(45480), 385(sh), 312(35830)
4b^{3+}	1826(1320), 912(sh) 606(19560), 396(37950), 380(sh), 325(34710), 315(35070)
4b^{2+}	613(41990), 422(23340), 385(44340), 360(35040), 331 (30870), 307(35830)
4b^{+}	1031(15440), 905(6170), 618(60580), 438(38010), 403(41240), 317(48730)
4b	1116(sh), 1035(7850), 656(33020), 482(sh), 428(38860), 397(sh), 368(42960), 302(50690)
4b^{-}	1681(460), 1202(sh), 1096(8030), 710(30280), 433(43100), 370(49860), 304(55450)
4b^{2-}	1017(14843), 895(10010), 681(28350), 428(48040), 360(51430), 301(sh)

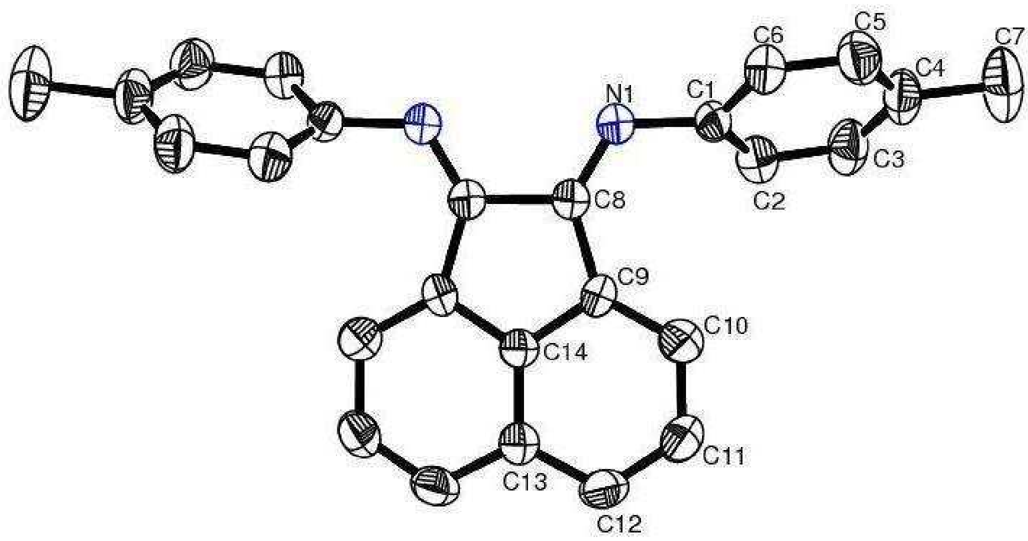
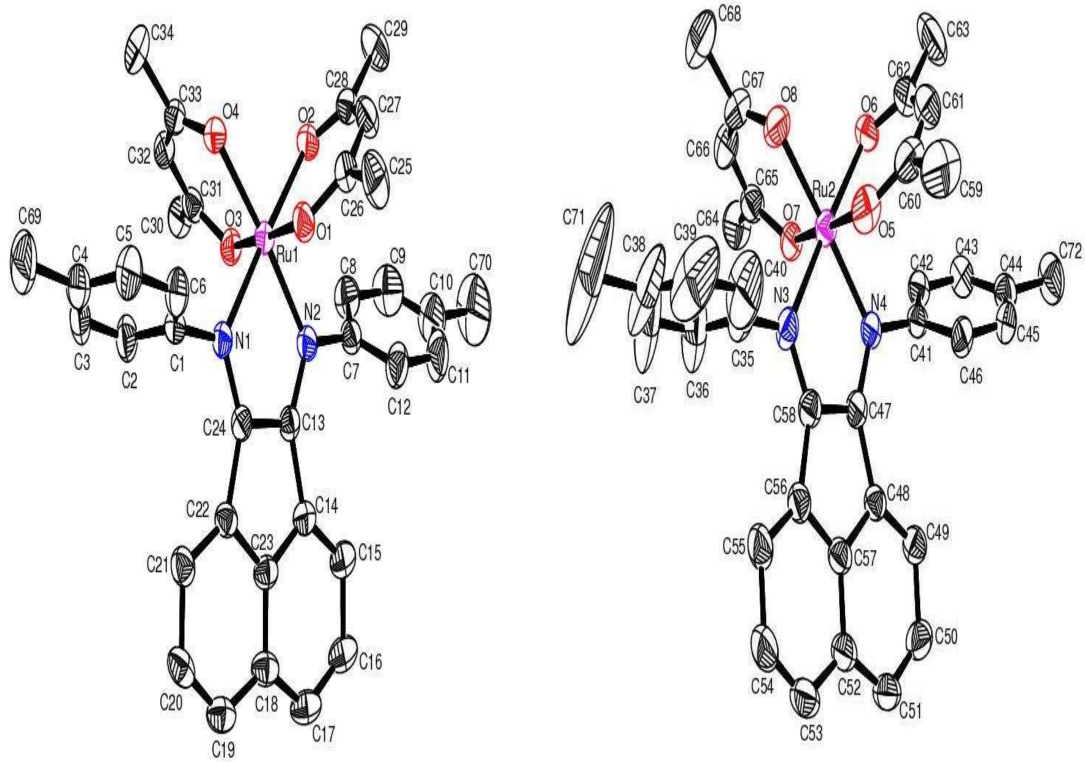
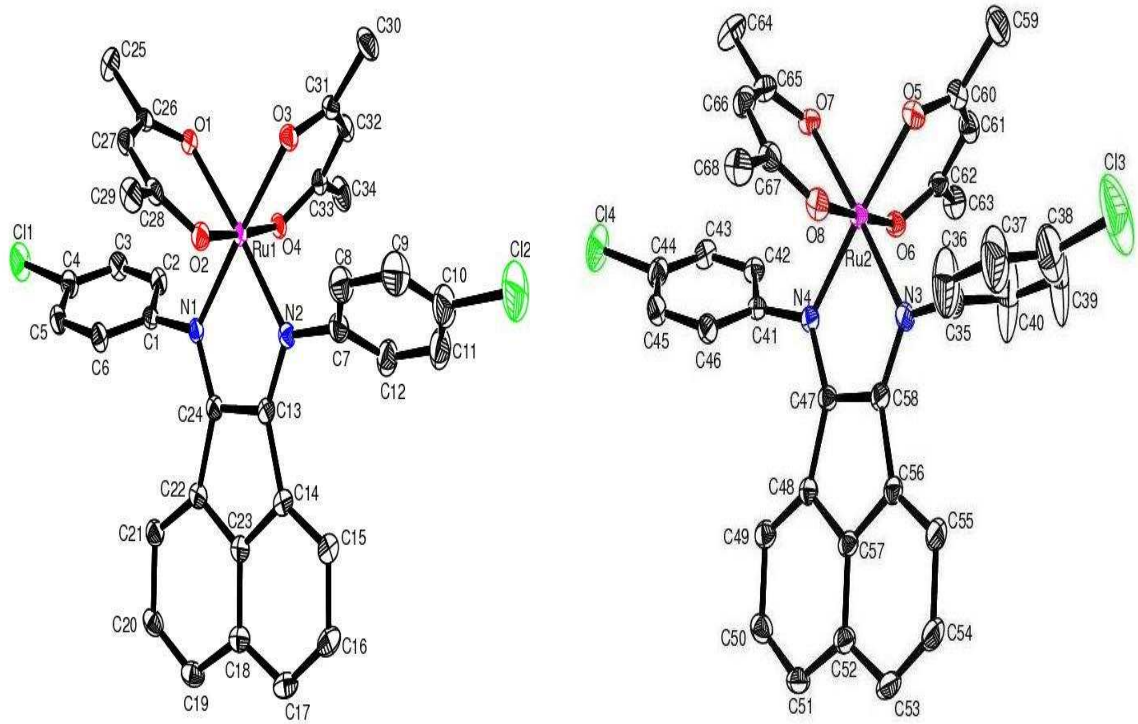


Figure S1. ORTEP diagram of BIAN ligand (R=Me). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



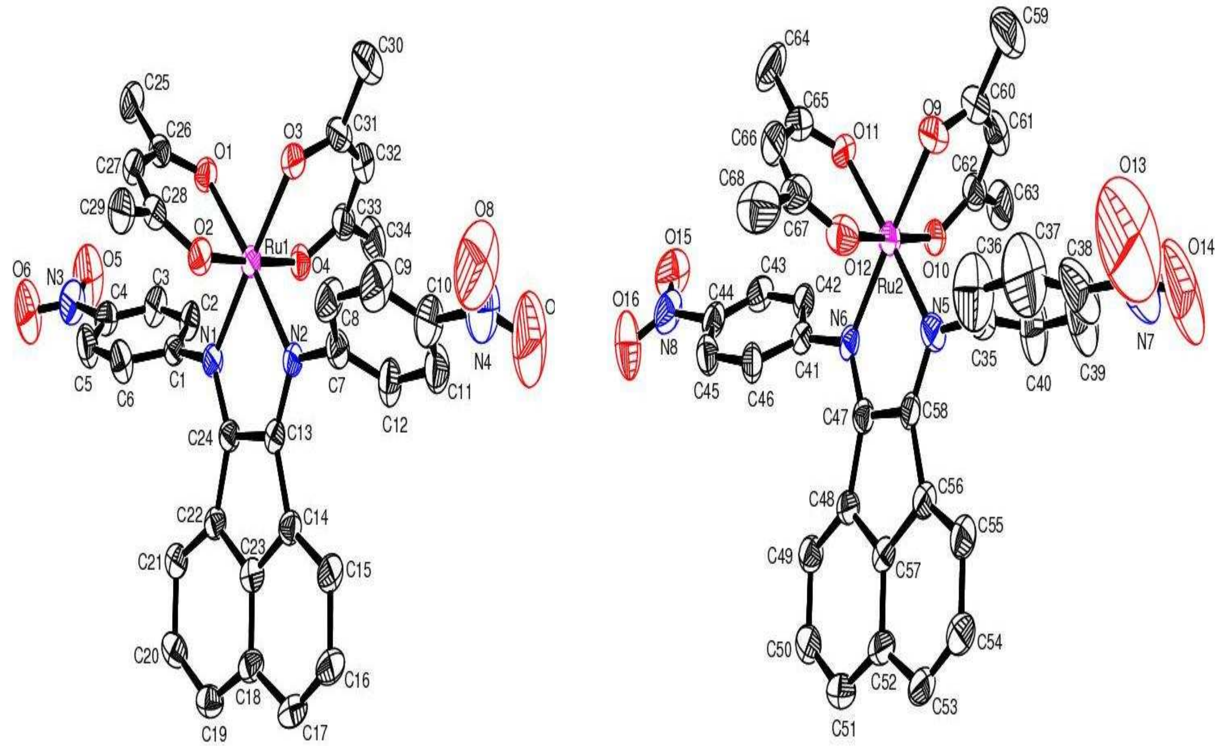
molecule A **molecule B**

Figure S2. ORTEP diagram of **2a.** Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



molecule A **molecule B**

Figure S3. ORTEP diagram of **4a.** Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



molecule A **molecule B**

Figure S4. ORTEP diagram of **5a.** Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

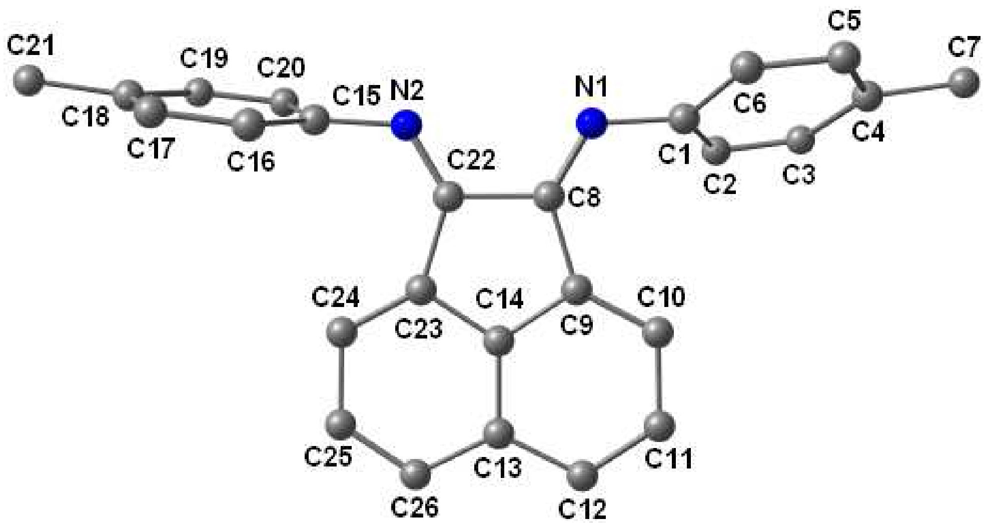


Figure S5. DFT optimized geometry of BIAN ligand (R= Me).

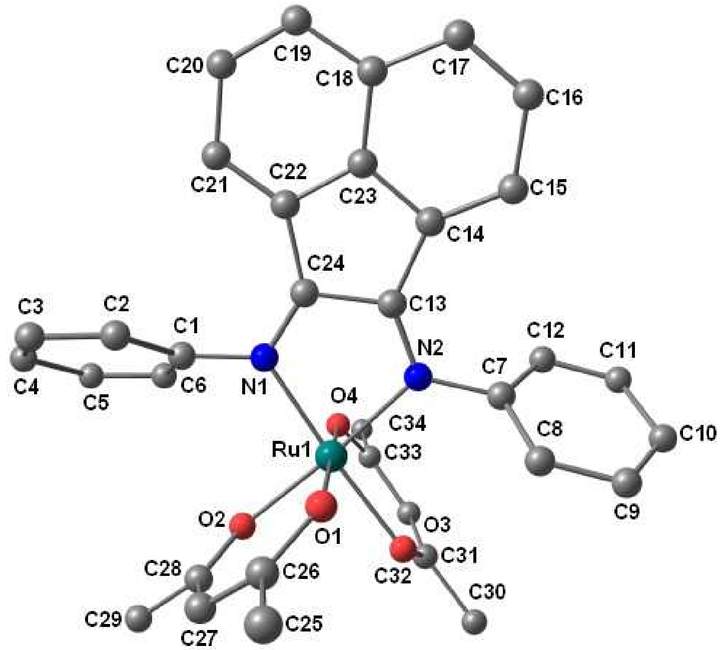


Figure S6. DFT optimized geometry of **1a** (**molecule B**).

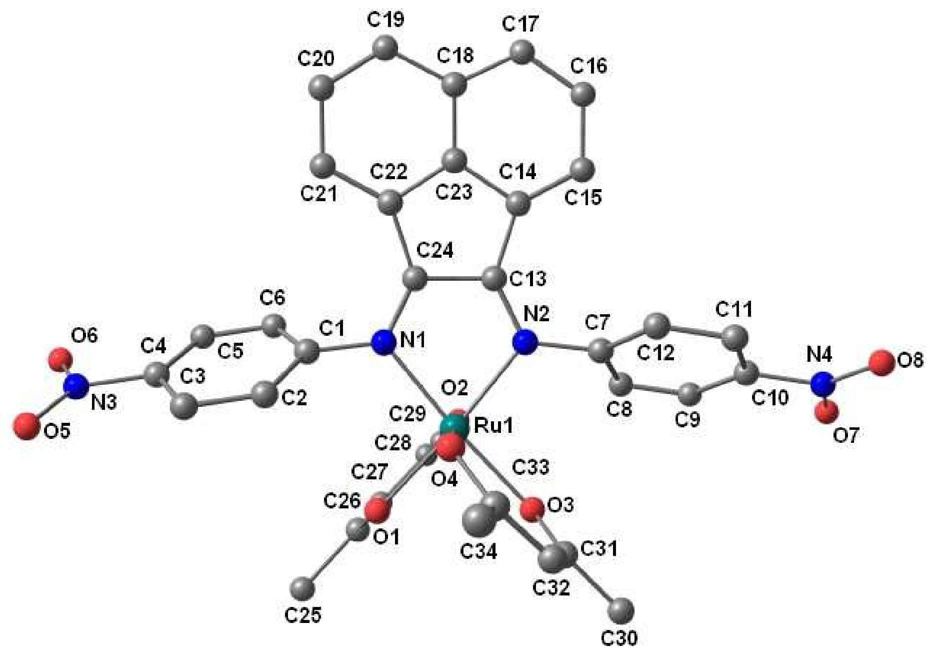


Figure S7. DFT optimized geometry of **5a** (**molecule B**).

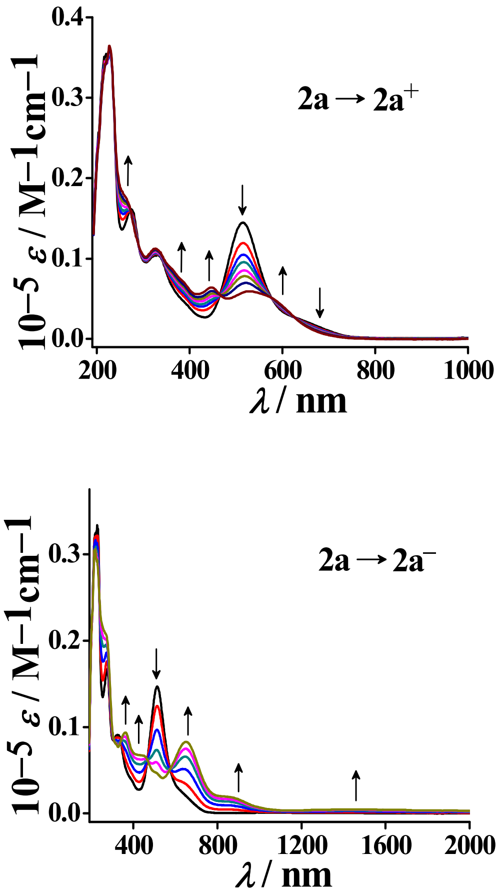


Figure S8. UV-vis-NIR spectroelectrochemistry of **2a**^{n} in CH_3CN/0.1M NBu_4PF_6.

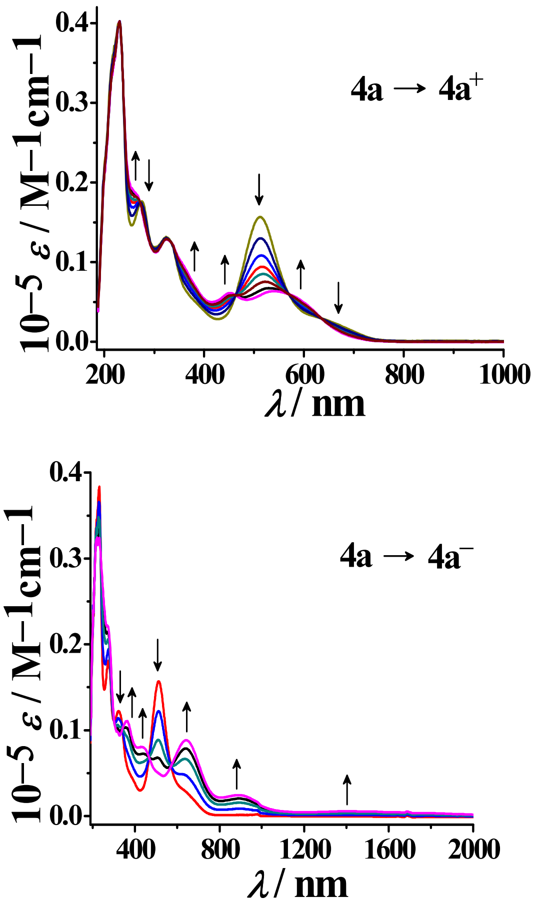


Figure S9. UV-vis-NIR spectroelectrochemistry of **4a**^{n} in CH_3CN/0.1M NBu_4PF_6.

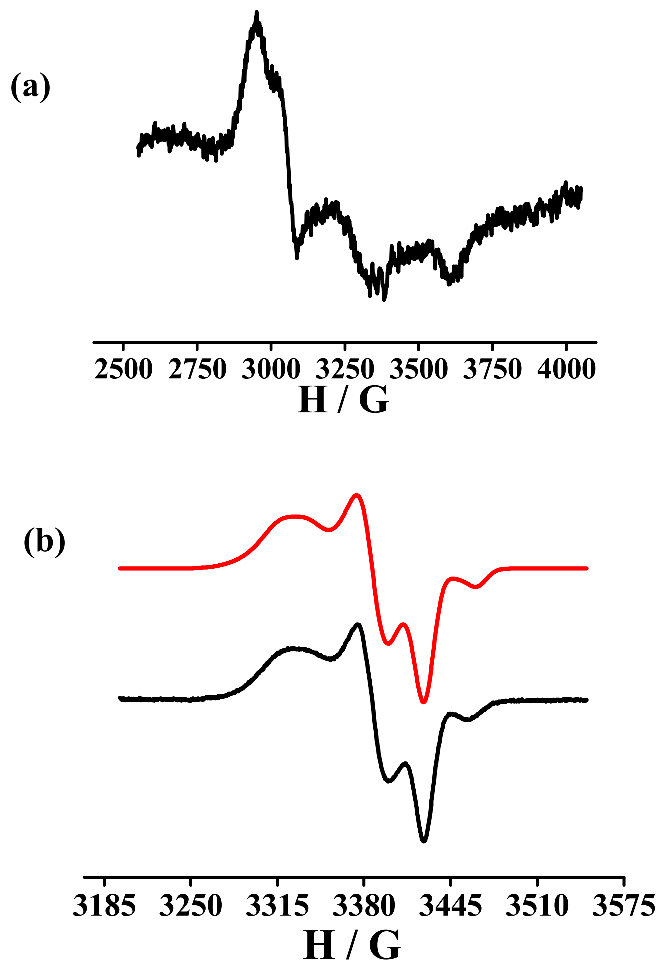


Figure S10. EPR spectra of electrogenerated (a) **2a**$^{+}$ and (b) **2a**$^{-}$ (black, experimental; red, simulated) in CH_3CN/0.1M NBu_4PF_6 at 110 K.

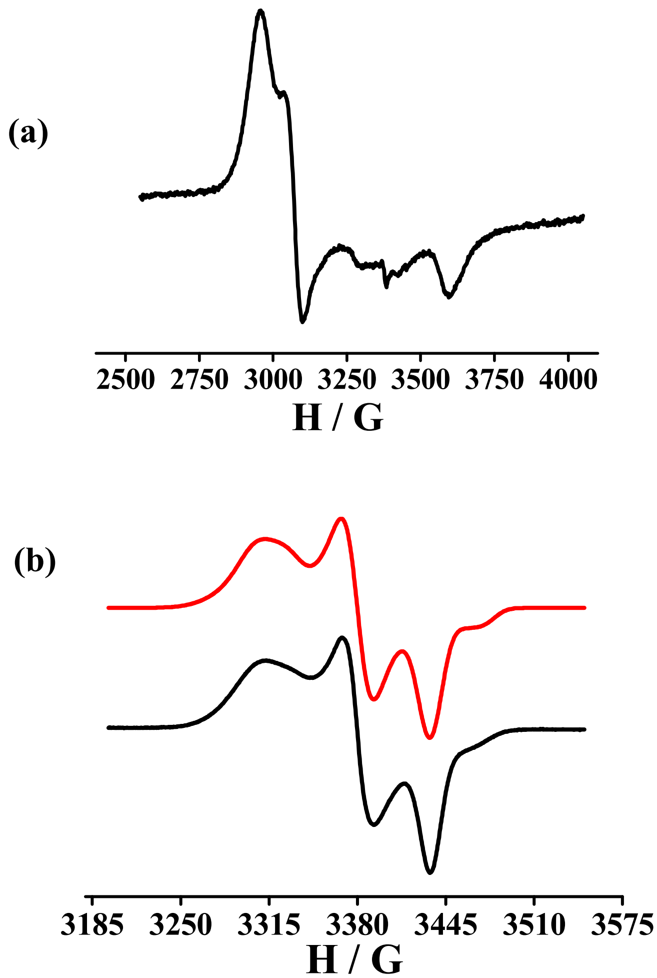


Figure S11. EPR spectra of electrogenerated (a) **4a**$^{+}$ and (b) **4a**$^{-}$ (black, experimental; red, simulated) in CH_3CN/0.1M NBu_4PF_6 at 110 K.

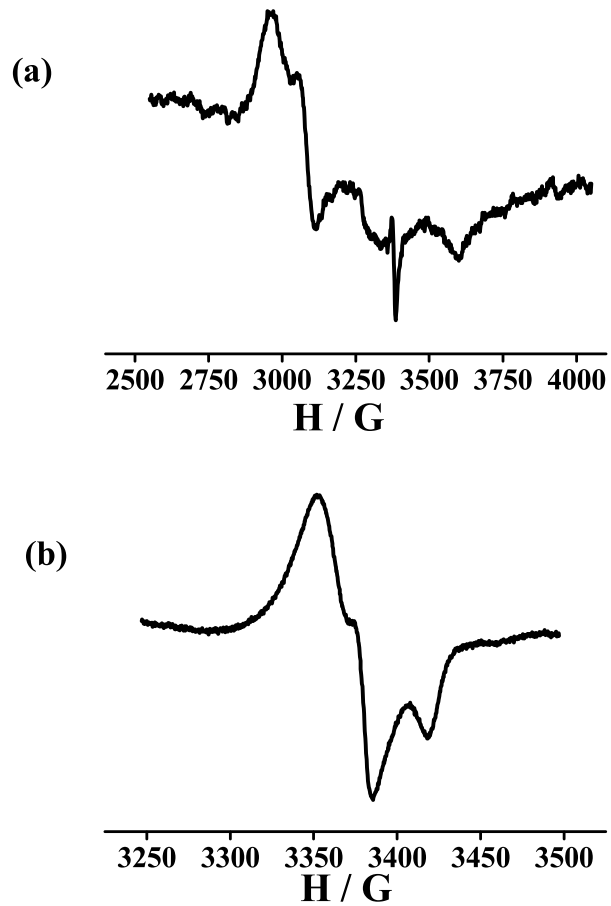


Figure S12. EPR spectra of electrogenerated (a) **5a**$^{+}$ and (b) **5a**$^{-}$ in CH_3CN/0.1M NBu_4PF_6 at 110 K.

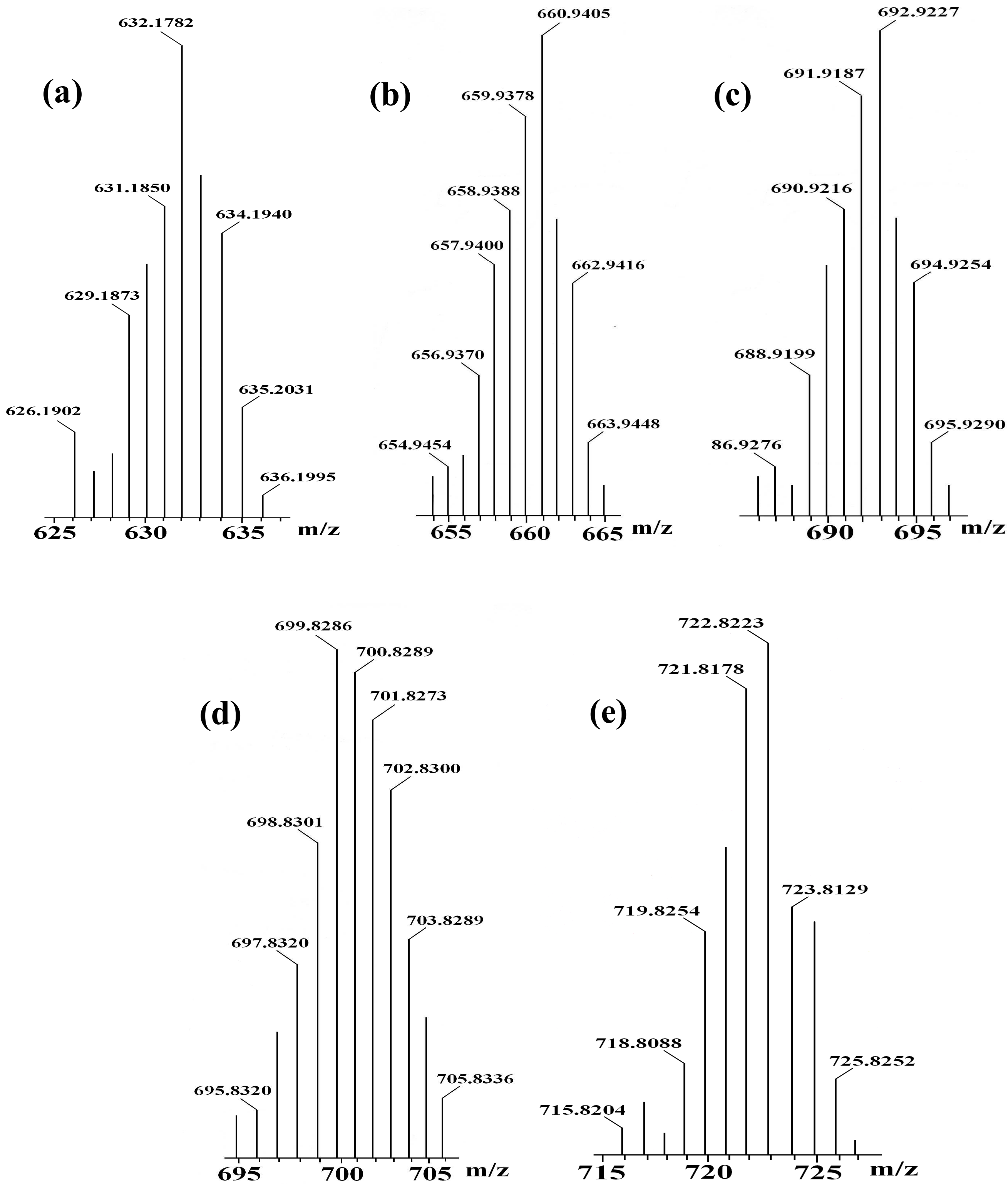


Figure S13. ESI-MS of (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a** and (e) **5a** in CH_3CN.

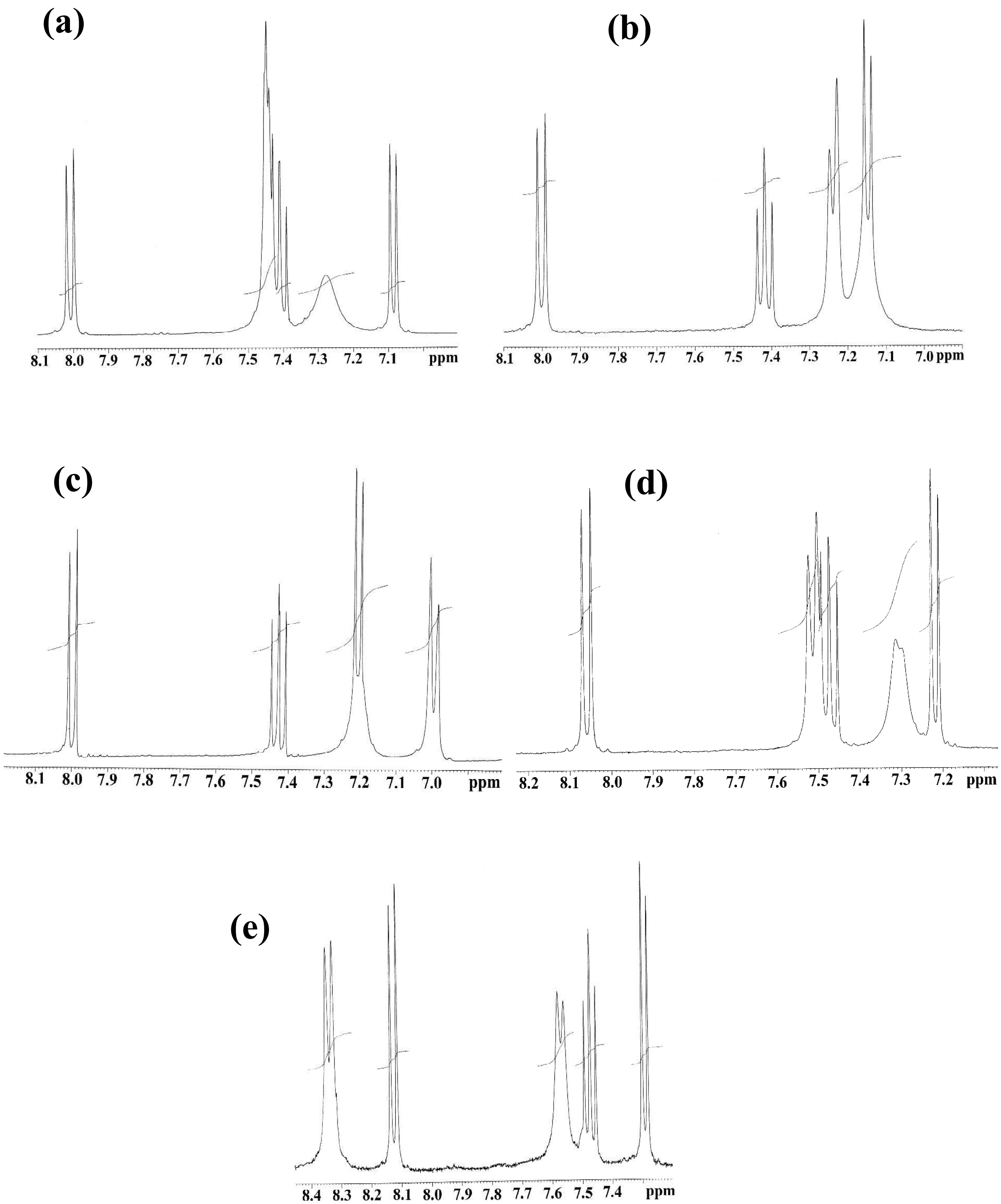


Figure S14. ^{1}H NMR spectra (aromatic region only) of (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a** and (e) **5a** in $(CD_3)_2SO$.

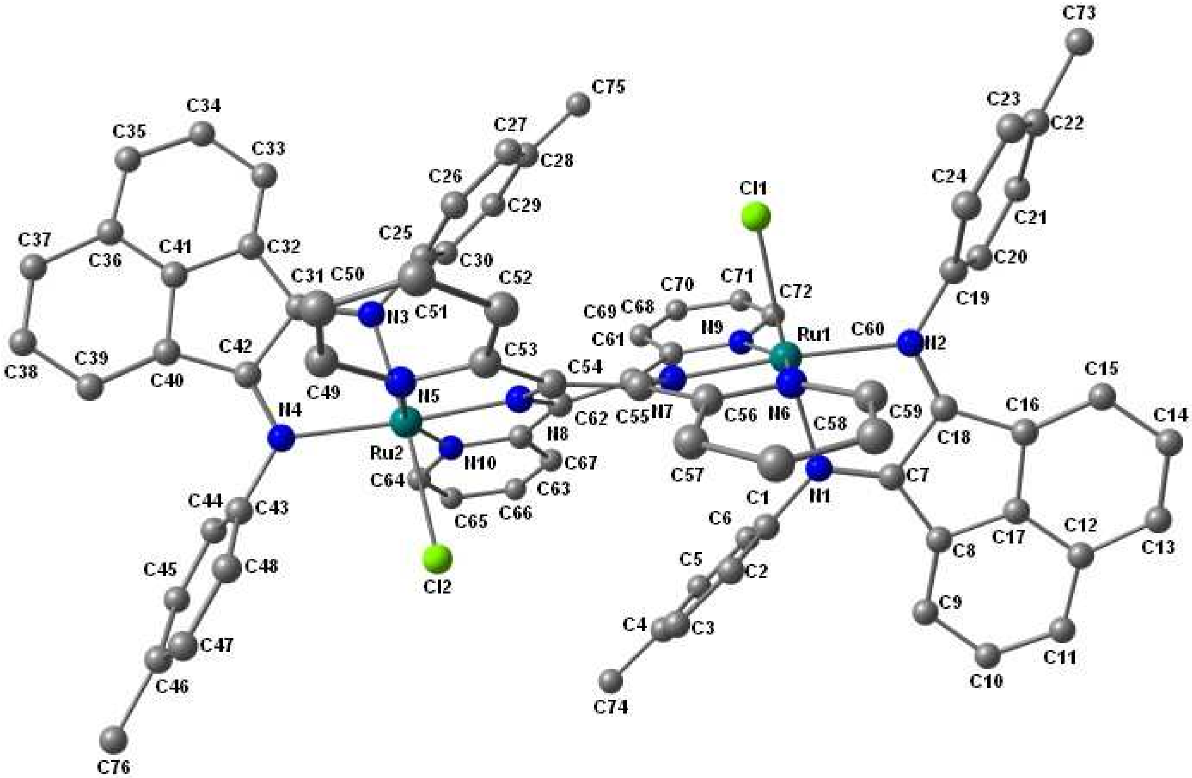


Figure S15. DFT optimized geometry of $\mathbf{2b}^{2+}$.

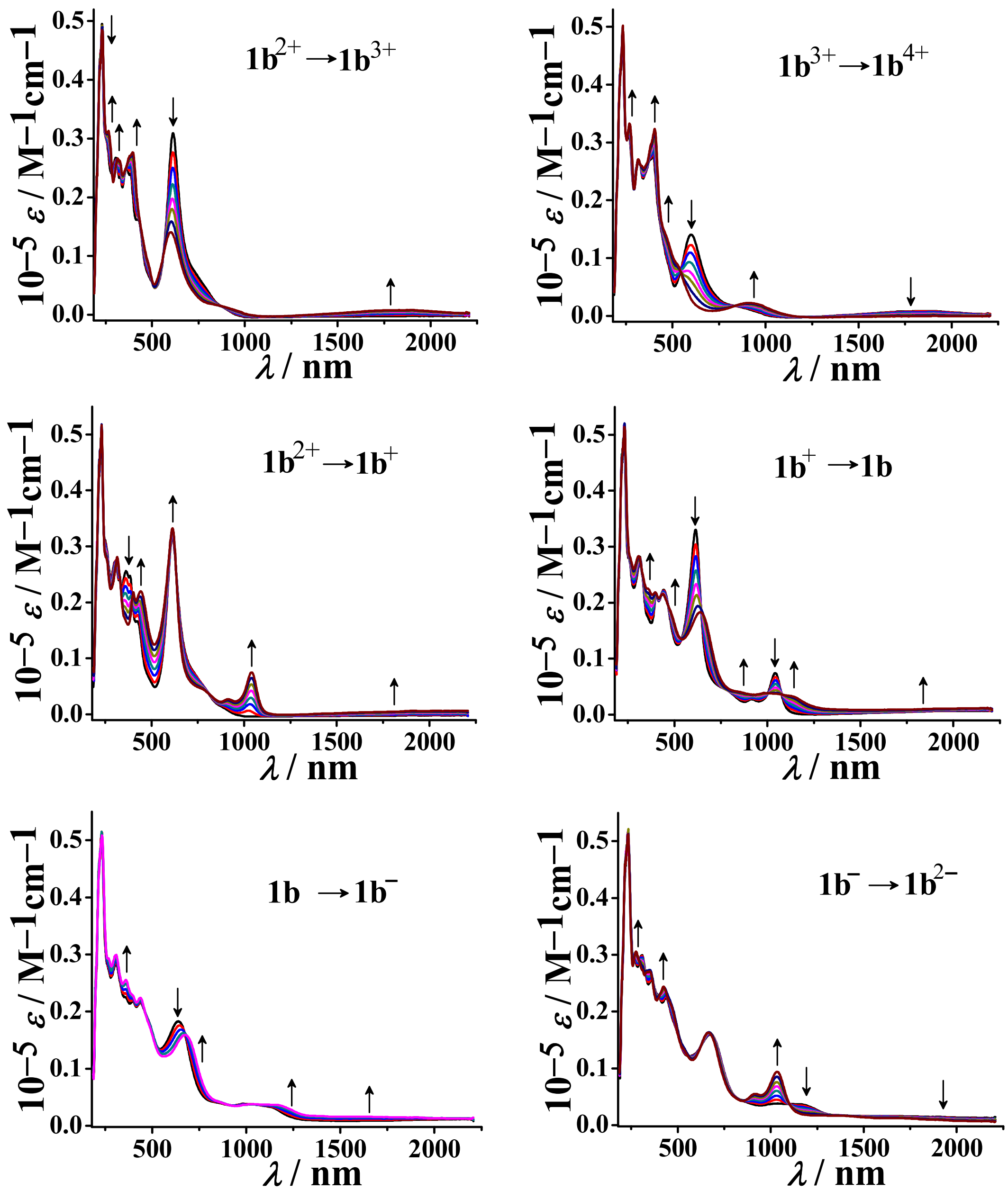


Figure S16. UV-vis-NIR spectroelectrochemistry of **1b**^{n} in CH_3CN/0.1M NBu_4PF_6.

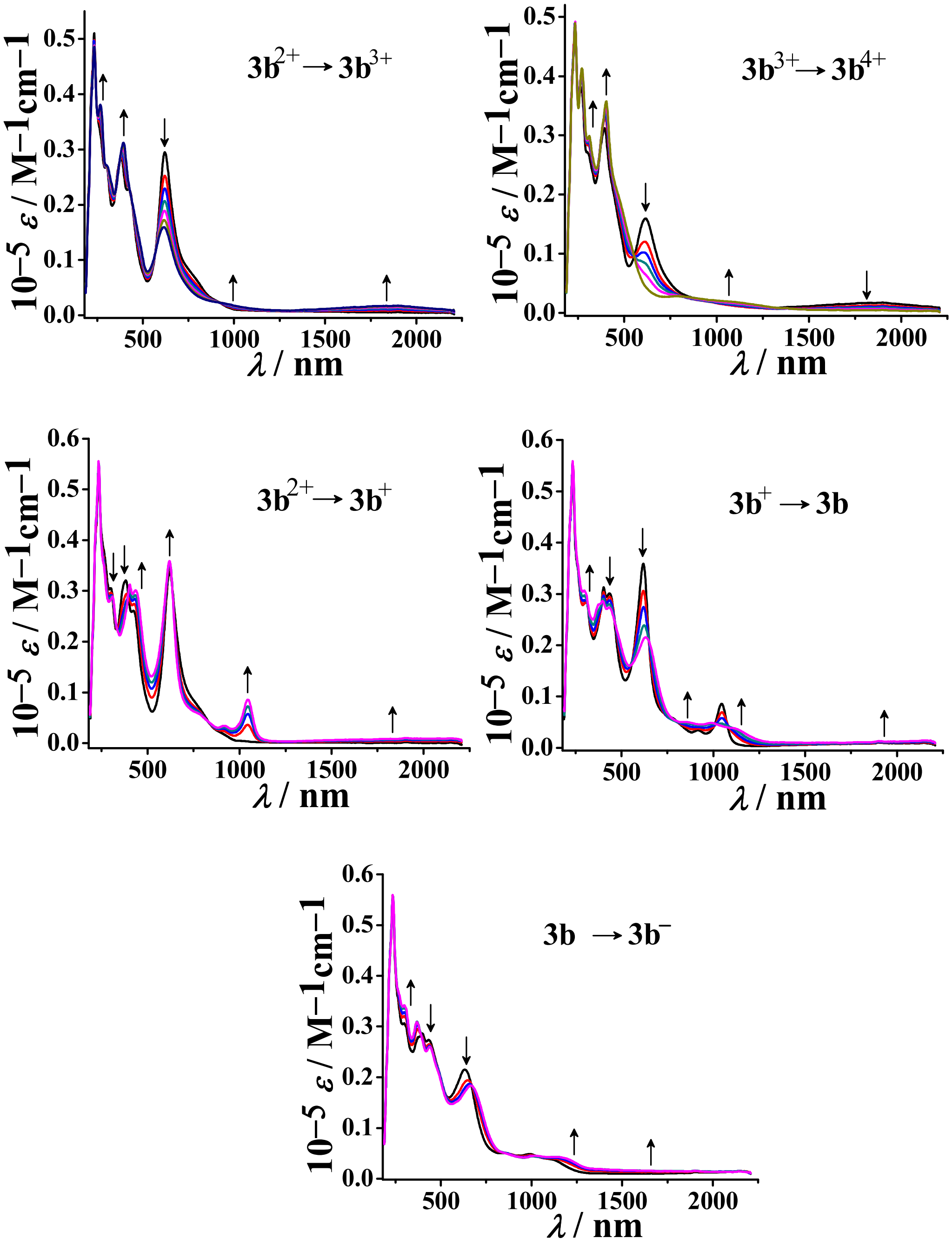


Figure S17. UV-vis-NIR spectroelectrochemistry of $\mathbf{3b}^{n}$ in CH_3CN/0.1M NBu_4PF_6.

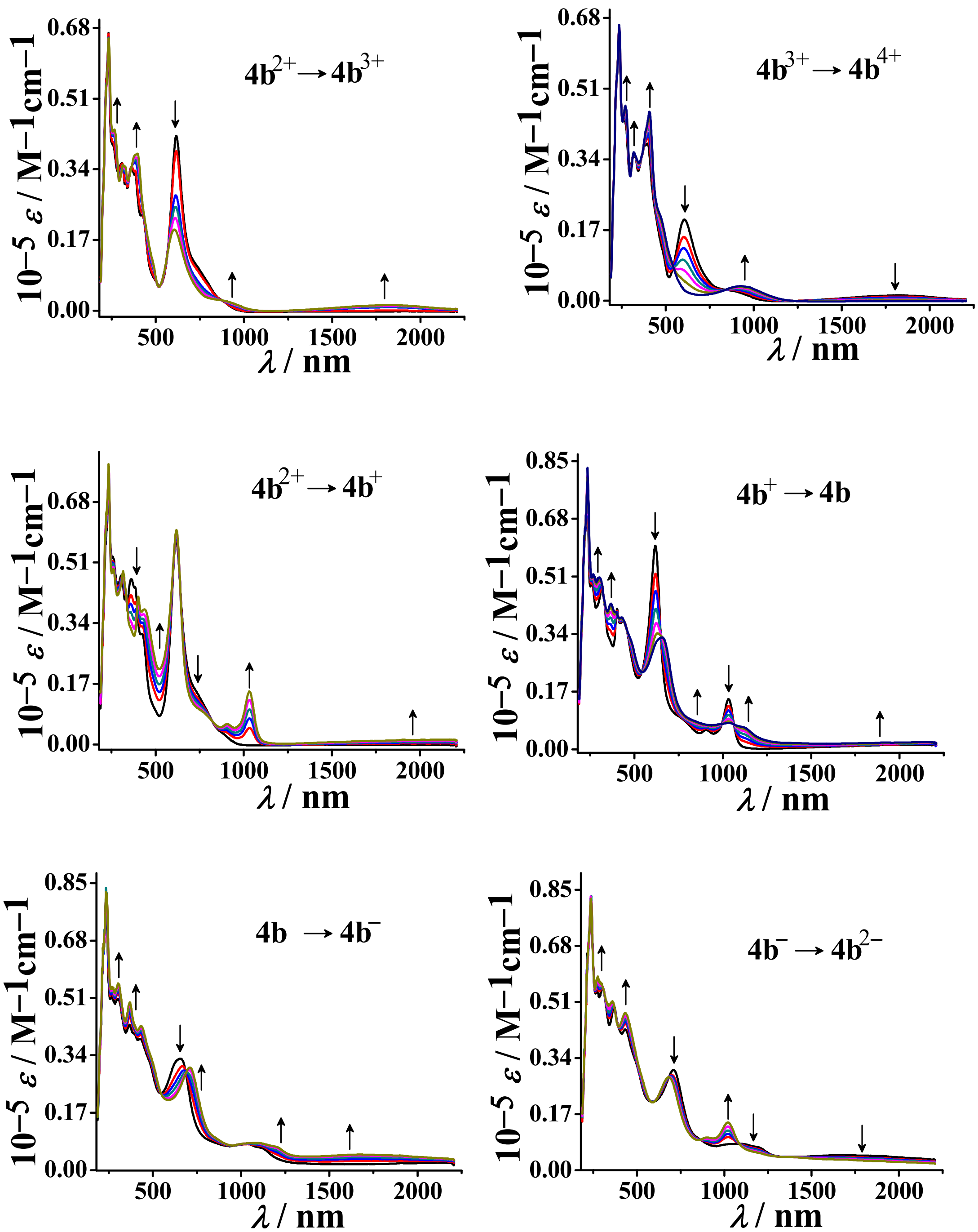


Figure S18. UV-vis-NIR spectroelectrochemistry of $\mathbf{4b}^{n}$ in CH_3CN/0.1M NBu_4PF_6.

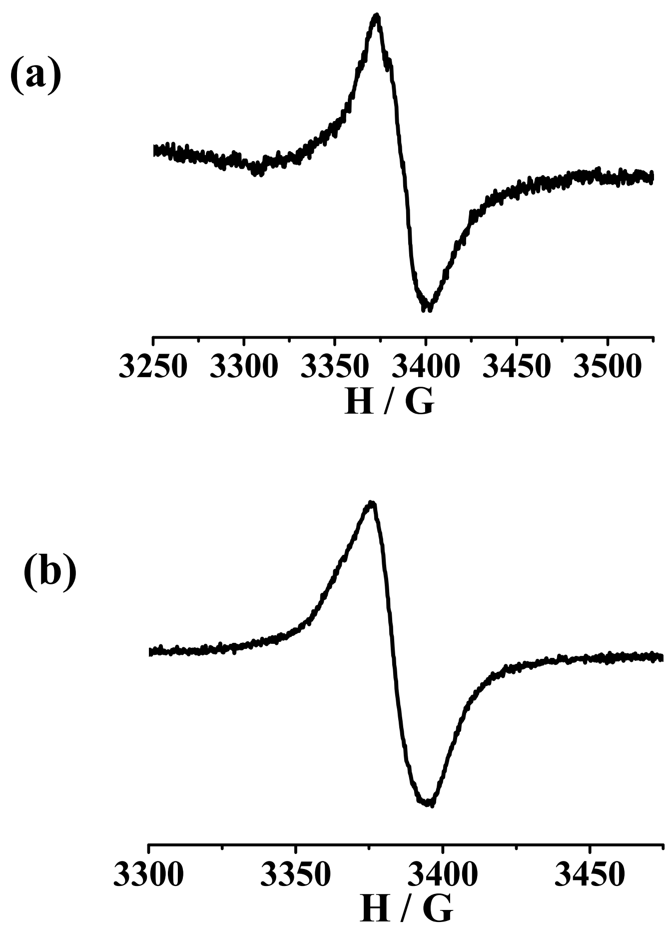


Figure S19. EPR spectra of electrogenerated (a) $\mathbf{1b}^{+}$ and (b) $\mathbf{2b}^{+}$ in CH_2Cl_2 at 110 K.

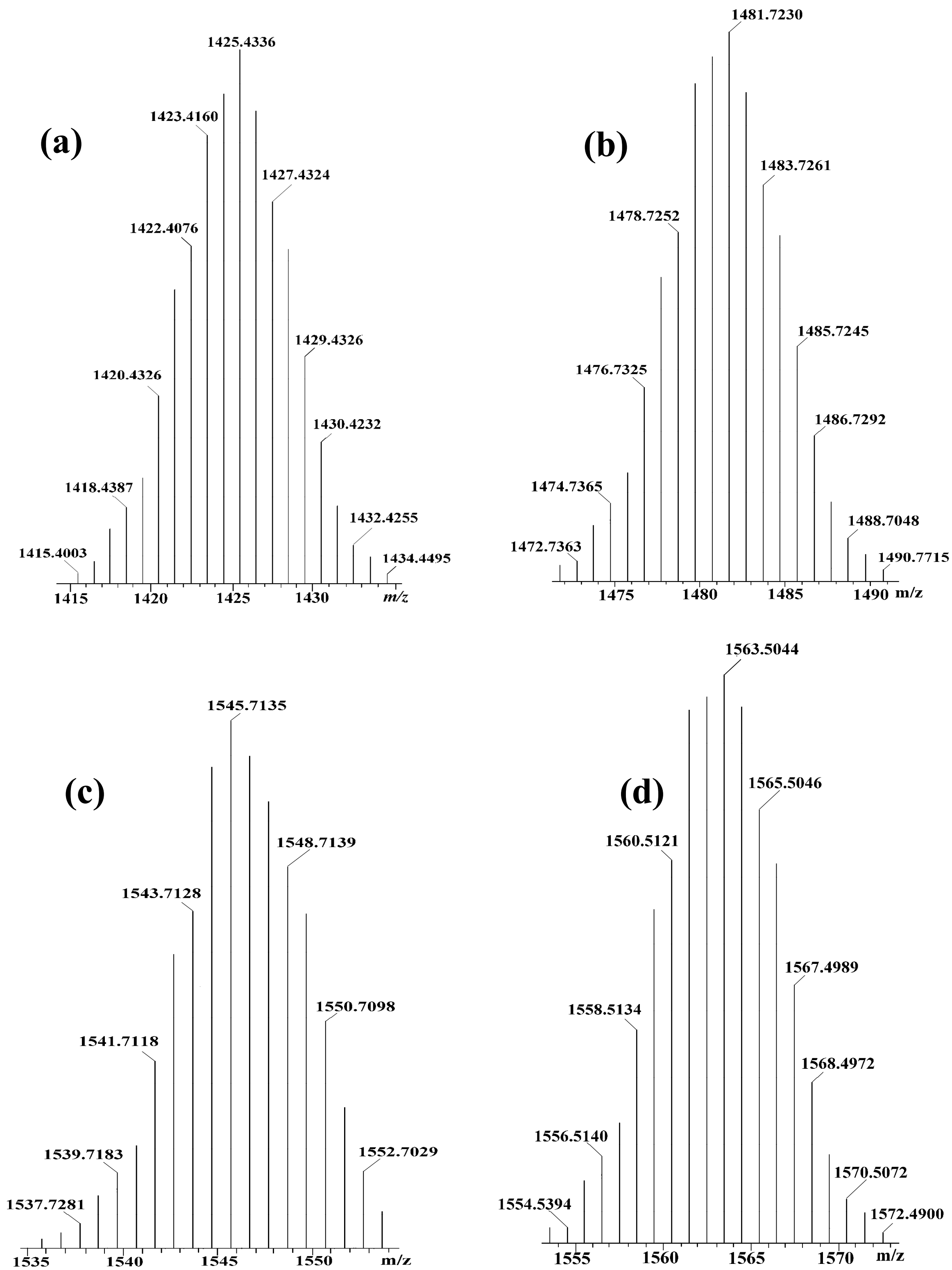


Figure S20. ESI-MS of (a) [**1b**]$(ClO_4)_2$, (b) [**2b**]$(ClO_4)_2$, (c) [**3b**]$(ClO_4)_2$ and (d) [4**b**]$(ClO_4)_2$ in CH_3CN.

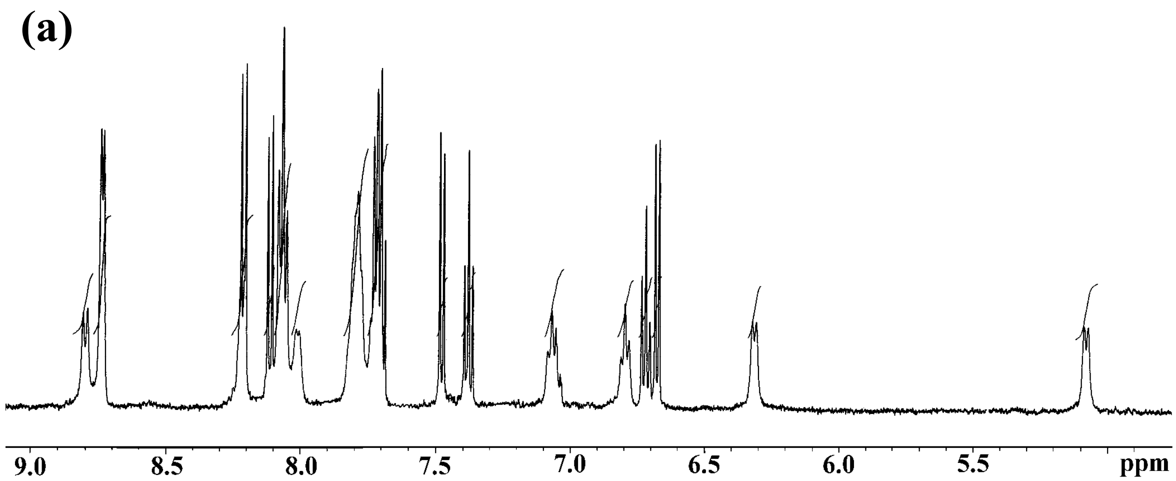


Figure S21a. ^{1}H NMR spectrum of [**1b**]$(ClO_4)_2$ in CD_3CN.

(b)

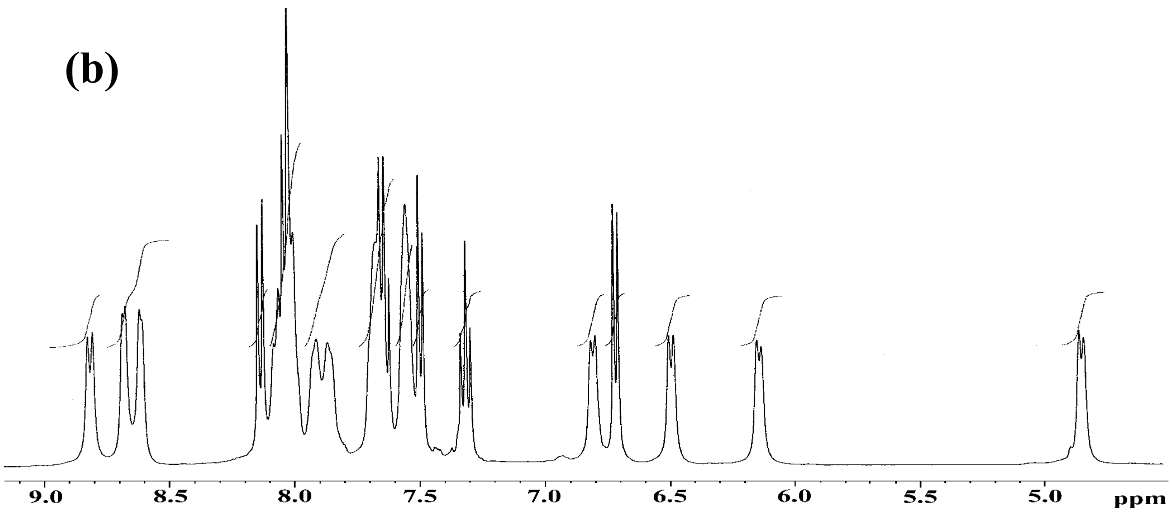


Figure S21b. ^{1}H NMR spectrum (aromatic region only) of [**2b**](ClO_4)$_2$ in CD_3CN.

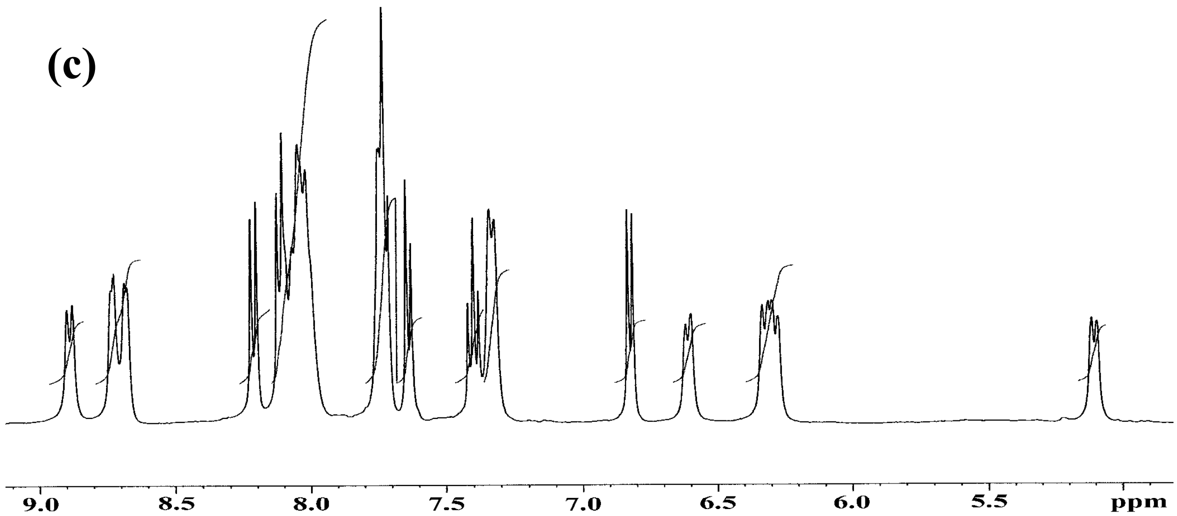


Figure S21c. ^{1}H NMR spectrum (aromatic region only) of [**3b**](ClO_4)$_2$ in CD_3CN.

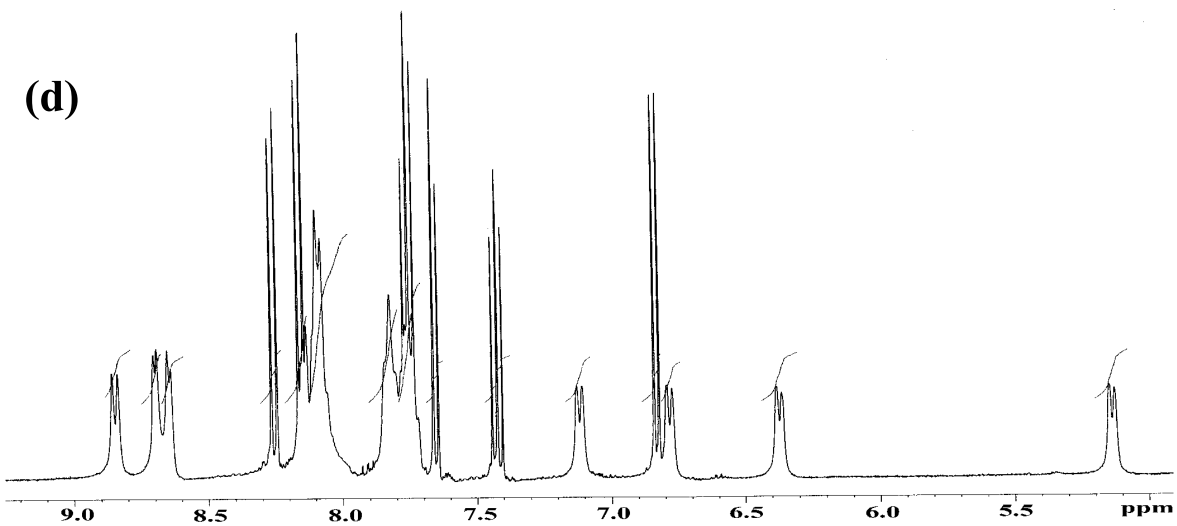


Figure S21d. ^{1}H NMR spectrum of [**4b**](ClO_4)$_2$ in CD_3CN.