Supporting Information

Varying electronic structural forms of ruthenium complexes of non-innocent 9,10-phenanthrenequinonoid ligands

Abhishek Mandal,[a] Tanaya Kundu,[a] Fabian Ehret,[b] Martina Bubrin,[b] Shaikh M. Mobin,[c] Wolfgang Kaim*[b] and Goutam Kumar Lahiri*[a]

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India. E-mail: lahiri@chem.iitb.ac.in*

[b]*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany. E-mail: kaim@iac.uni-stuttgart.de*

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

Table S1 Experimental (X-ray) bond distances (Å) of **2** (molecule **B**, molecule **C** and molecule **D**)

Bond distances (Å)					
Molecule **B**		Molecule **C**		Molecule **D**	
Ru(2)-N(3)	1.962(2)	Ru(3)-N(5)	1.972(2)	Ru(4)-N(7)#1	1.960(2)
Ru(2)-N(4)	1.964(2)	Ru(3)-N(6)	1.952(2)	Ru(4)-N(7)	1.960(2)
Ru(2)-O(5)	2.0541(18)	Ru(3)-O(9)	2.053(2)	Ru(4)-O(13)	2.031(2)
Ru(2)-O(6)	2.075(19)	Ru(3)-O(10)	2.079(18)	Ru(4)-O(13)#1	2.031(2)
Ru(2)-O(7)	2.0612(18)	Ru(3)-O(11)	2.062(2)	Ru(4)-O(14)	2.087(19)
Ru(2)-O(8)	1.997(19)	Ru(3)-O(12)	2.017(2)	Ru(4)-O(14)#1	2.087(19)
C(25)-N(3)	1.325(4)	C(49)-N(5)	1.319(4)	C(73)-N(7)	1.310(4)
C(38)-N(4)	1.312(4)	C(62)-N(6)	1.320(4)	C(73)-C(73)#1	1.451(5)
C(25)-C(26)	1.451(4)	C(49)-C(50)	1.454(4)	C(73)-C(74)	1.453(4)
C(25)-C(38)	1.437(4)	C(49)-C(62)	1.437(4)	C(74)-C(75)	1.408(4)
C(26)-C(27)	1.407(4)	C(50)-C(51)	1.402(4)	C(74)-C(79)	1.415(4)
C(26)-C(31)	1.415(4)	C(50)-C(55)	1.422(4)	C(75)-C(76)	1.374(4)
C(27)-C(28)	1.365(4)	C(51)-C(52)	1.374(4)	C(76)-C(77)	1.383(5)
C(28)-C(29)	1.386(5)	C(52)-C(53)	1.387(5)	C(77)-C(78)	1.377(4)
C(29)-C(30)	1.371(5)	C(53)-C(54)	1.370(4)	C(78)-C(79)	1.400(4)
C(30)-C(31)	1.398(4)	C(54)-C(55)	1.397(4)	C(79)-C(79)#1	1.477(5)
C(31)-C(32)	1.472(4)	C(55)-C(56)	1.476(4)		
C(32)-C(33)	1.410(4)	C(56)-C(57)	1.415(4)		
C(32)-C(37)	1.403(4)	C(56)-C(61)	1.408(4)		
C(33)-C(34)	1.367(5)	C(57)-C(58)	1.371(5)		
C(34)-C(35)	1.383(5)	C(58)-C(59)	1.384(5)		
C(35)-C(36)	1.376(4)	C(59)-C(60)	1.375(4)		
C(36)-C(37)	1.397(4)	C(60)-C(61)	1.398(4)		
C(37)-C(38)	1.463(4)	C(61)-C(62)	1.456(4)		

Table S2 Experimental bond distances (Å) of **3** (molecule **E)**

	Bond distances (Å)
Ru(1)-N(1)	1.9341(18)
Ru(1)-O(1)	2.0412(15)
Ru(1)-O(2)	2.0195(15)
Ru(1)-O(3)	2.0111(16)
Ru(1)-O(4)	2.0704(15)
Ru(1)-O(5)	2.0502(15)
C(1)-N(1)	1.332(3)
C(14)-O(1)	1.287(3)
C(1)-C(2)	1.451(3)
C(1)-C(14)	1.433(3)
C(2)-C(3)	1.401(3)
C(2)-C(7)	1.416(3)
C(3)-C(4)	1.378(3)
C(4)-C(5)	1.387(4)
C(5)-C(6)	1.373(4)
C(6)-C(7)	1.408(3)
C(7)-C(8)	1.471(3)
C(8)-C(9)	1.406(3)
C(8)-C(13)	1.413(3)
C(9)-C(10)	1.373(4)
C(10)-C(11)	1.387(4)
C(11)-C(12)	1.379(3)
C(12)-C(13)	1.404(3)
C(13)-C(14)	1.445(3)

Table S3 Experimental (X-ray) and DFT calculated selected bond angles (º) of $\mathbf{1}^n$

	X-ray	DFT			
		$\mathbf{1}^+$ (S=1/2)	**1** (S=0)	$\mathbf{1}^-$ (S=1/2)	$\mathbf{1}^{2-}$ (S=0)
O(1)-Ru(1)-O(2)	80.88(11)	76.18	78.29	80.37	80.45
O(1)-Ru(1)-O(3)	92.00(12)	88.78	90.86	90.57	89.89
O(1)-Ru(1)-O(4)	174.05(10)	173.50	174.75	175.89	176.27
O(1)-Ru(1)-O(5)	96.41(12)	97.47	97.11	95.96	96.22
O(1)-Ru(1)-O(6)	87.51(12)	90.76	90.40	90.12	89.61
O(2)-Ru(1)-O(3)	91.83(12)	90.73	91.96	90.52	89.71
O(2)-Ru(1)-O(4)	94.60(12)	97.35	96.64	95.77	96.04
O(2)-Ru(1)-O(5)	177.27(10)	173.62	175.39	176.18	176.49
O(2)-Ru(1)-O(6)	86.33(12)	88.72	89.50	90.12	89.69
O(3)-Ru(1)-O(4)	91.99(12)	90.68	90.67	90.86	91.35
O(3)-Ru(1)-O(5)	88.56(12)	89.76	87.82	88.45	89.18
O(3)-Ru(1)-O(6)	178.14(10)	179.36	178.24	179.13	179.27
O(4)-Ru(1)-O(5)	88.09(12)	89.01	87.98	87.92	87.31
O(4)-Ru(1)-O(6)	88.36(12)	89.72	88.19	88.48	89.12
O(5)-Ru(1)-O(6)	93.27(12)	90.76	90.80	90.96	91.40

Table S4 Experimental and DFT calculated selected bond angles (°) of $\mathbf{2}^n$ (molecule **A**)

	X-ray	DFT			
		$\mathbf{2}^+$ (S=1/2)	**2** (S=0)	$\mathbf{2}^-$ (S=1/2)	$\mathbf{2}^{2-}$ (S=0)
N(1)-Ru(1)-N(2)	78.07(9)	75.89	76.79	77.11	76.35
N(1)-Ru(1)-O(1)	89.55(9)	88.16	90.56	90.55	90.05
N(1)-Ru(1)-O(2)	173.10(8)	172.82	174.11	173.40	174.32
N(1)-Ru(1)-O(3)	99.49(9)	97.47	97.33	97.43	98.11
N(1)-Ru(1)-O(4)	93.00(9)	93.84	94.01	92.28	91.51
N(2)-Ru(1)-O(1)	91.23(9)	93.86	94.00	92.36	91.53
N(2)-Ru(1)-O(2)	95.11(9)	97.52	97.33	97.32	98.00
N(2)-Ru(1)-O(3)	176.87(8)	172.74	174.11	174.53	174.45
N(2)-Ru(1)-O(4)	91.77(8)	88.14	90.49	90.40	89.93
O(1)-Ru(1)-O(2)	91.67(8)	89.46	90.03	90.23	90.63
O(1)-Ru(1)-O(3)	86.76(8)	88.79	85.98	87.31	88.04
O(1)-Ru(1)-O(4)	176.41(8)	177.47	174.22	176.42	178.08
O(2)-Ru(1)-O(3)	87.35(8)	89.26	88.55	88.15	87.54
O(2)-Ru(1)-O(4)	86.09(8)	88.74	85.79	87.17	87.93
O(3)-Ru(1)-O(4)	90.33(8)	89.41	89.92	90.15	90.62

Table S5 Experimental (X-ray) and DFT calculated selected bond angles (°) of $\mathbf{3}^n$ (molecule **F**)

	X-ray	DFT			
		$\mathbf{3}^+$ (S=1/2)	**3** (S=0)	$\mathbf{3}^-$ (S=1/2)	$\mathbf{3}^{2-}$ (S=0)
N(2)-Ru(2)-O(6)	79.36(7)	76.16	77.45	78.69	78.57
N(2)-Ru(2)-O(7)	174.91(7)	172.90	175.23	174.98	174.76
N(2)-Ru(2)-O(8)	91.42(6)	88.20	90.59	90.45	89.71
N(2)-Ru(2)-O(9)	96.11(7)	97.79	96.50	97.08	97.84
N(2)-Ru(2)-O(10)	91.79(7)	93.50	95.50	92.49	91.03
O(6)-Ru(2)-O(7)	96.26(6)	97.07	97.79	96.30	96.22
O(6)-Ru(2)-O(8)	90.47(6)	91.46	91.26	90.79	90.33
O(6)-Ru(2)-O(9)	174.25(6)	173.60	173.83	175.66	176.28
O(6)-Ru(2)-O(10)	90.61(6)	88.24	89.97	89.79	89.64
O(7)-Ru(2)-O(8)	91.21(6)	89.86	89.15	89.89	90.81
O(7)-Ru(2)-O(9)	88.41(6)	89.05	88.26	87.94	87.38
O(7)-Ru(2)-O(10)	85.63(6)	88.37	85.80	87.19	88.44
O(8)-Ru(2)-O(9)	86.08(6)	90.42	87.57	88.26	88.68
O(8)-Ru(2)-O(10)	176.76(6)	178.15	174.92	177.07	179.25
O(9)-Ru(2)-O(10)	93.08(6)	90.07	91.73	91.38	91.40

Table S6 ^{1}H NMR spectral data of **1**, **2** and **3** in $CDCl_3$

		δ (*J*/Hz)		
Complex	N-H	Q ligand	acac ligand	
			C-H	CH_3
1	-	8.63(8.2)[a], 8.54(7.96)[a], 7.86(7.6)[b], 6.99(6.79)[b]	5.22[c]	2.67[c], 2.09[c]
2	11.55[c]	8.53(9.04)[a], 8.40(9.28)[a], 7.59[d]	5.47[c]	2.39[c], 1.77[c]
3	14.04[c]	9.05(8.02)[a], 8.68(7.88)[a], 8.38(8.24)[b], 7.85(7.66)[b], 7.58[d]	5.65[c], 5.46[c]	2.59[c], 2.34[c], 2.01[c], 1.97[c]

[a]Doublet.

[b] Doublet of doublet.

[c]Singlet.

[d]Owing to overlapping it does not seem possible to determine *J* values for doublets or triplets unequivocally.

Table S7 Selected molecular orbitals along with their energies and compositions of **1** in *S* = 0 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_1
LUMO+10	1.335	76	17	7
LUMO+9	1.208	69	23	8
LUMO+8	0.724	3	1	96
LUMO+7	0.230	49	40	11
LUMO+6	0.184	49	26	25
LUMO+5	0.169	1	1	98
LUMO+4	-0.645	5	94	1
LUMO+3	-0.707	5	92	3
LUMO+2	-0.952	1	2	97
LUMO+1	-1.135	1	0	99
LUMO	-3.222	35	9	56
HOMO	-4.942	61	31	8
HOMO-1	-5.159	49	24	27
HOMO-2	-5.257	65	17	18
HOMO-3	-6.090	19	74	7
HOMO-4	-6.256	15	53	32
HOMO-5	-6.397	10	24	66
HOMO-6	-6.915	5	90	5
HOMO-7	-7.167	2	5	93
HOMO-8	-7.351	6	33	61
HOMO-9	-7.448	8	59	33
HOMO-10	-7.882	11	72	17

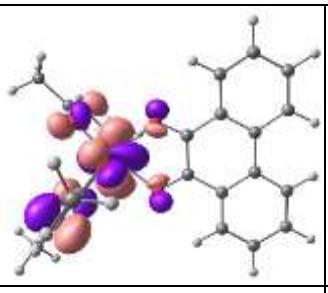
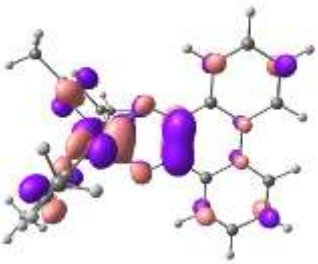
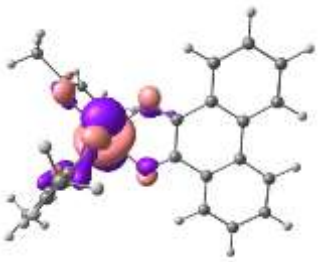
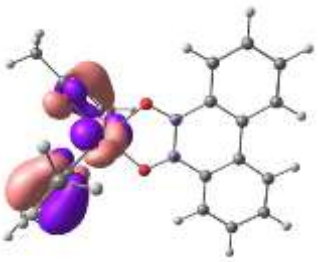
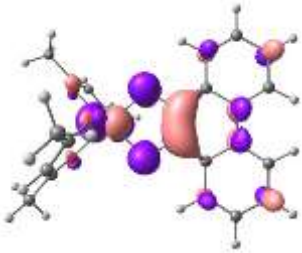
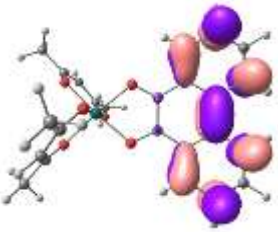
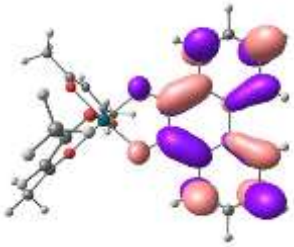
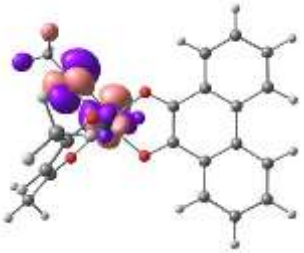
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{+}$ in $S = 1/2$ state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_1
		α-spin		
LUMO+10	-1.512	76	16	8
LUMO+9	-1.538	68	20	12
LUMO+8	-2.331	0	0	100
LUMO+7	-2.912	0	0	100
LUMO+6	-3.527	16	80	4
LUMO+5	-3.992	2	96	2
LUMO+4	-4.143	3	2	93
LUMO+3	-4.183	9	7	84
LUMO+2	-4.215	40	42	18
LUMO+1	-4.231	56	21	23
LUMO	-6.746	9	3	88
SOMO	-8.829	22	72	6
HOMO-1	-9.313	17	79	4
HOMO-2	-9.371	8	2	90
HOMO-3	-9.505	63	20	17
HOMO-4	-9.561	37	43	20
HOMO-5	-10.192	17	8	75
HOMO-6	-10.444	6	83	11
HOMO-7	-10.446	31	45	24
HOMO-8	-10.618	16	23	61
HOMO-9	-11.101	4	12	84
HOMO-10	-11.102	32	61	7
		β-spin		
LUMO+10	-1.535	68	20	12
LUMO+9	-2.341	0	0	100

LUMO+8	-2.929	0	0	100
LUMO+7	-3.244	53	39	8
LUMO+6	-3.734	4	93	3
LUMO+5	-4.109	11	86	3
LUMO+4	-4.127	52	24	24
LUMO+3	-4.157	0	0	99
LUMO+2	-4.221	5	1	94
LUMO+1	-6.279	70	24	6
LUMO	-6.732	24	7	69
HOMO	-8.969	28	52	20
HOMO-1	-9.048	51	37	12
HOMO-2	-9.225	8	18	74
HOMO-3	-9.477	32	45	23
HOMO-4	-9.615	44	45	11
HOMO-5	-10.278	4	66	29
HOMO-6	-10.377	3	41	56
HOMO-7	-10.596	8	12	80
HOMO-8	-10.891	9	82	9
HOMO-9	-11.112	1	4	95
HOMO-10	-11.518	17	71	12

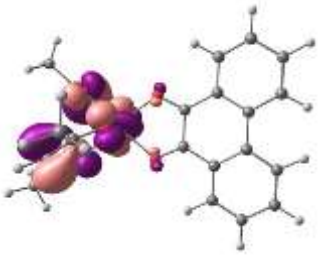
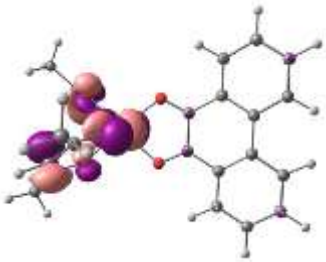
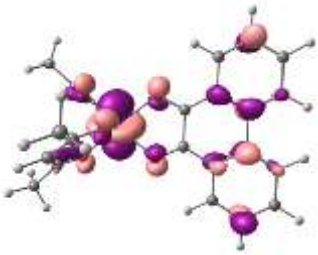
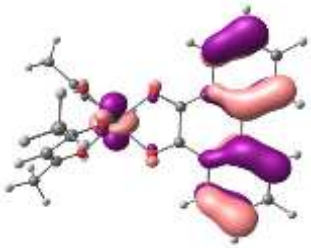
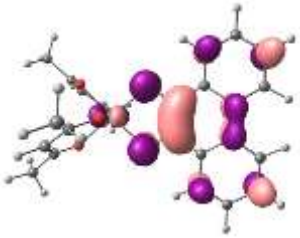
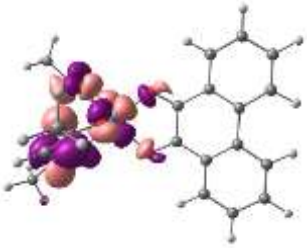
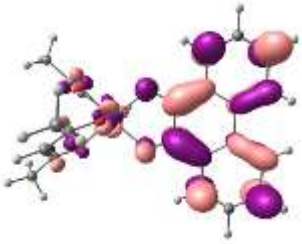
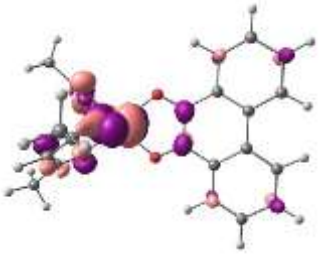
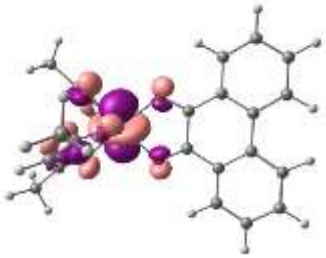
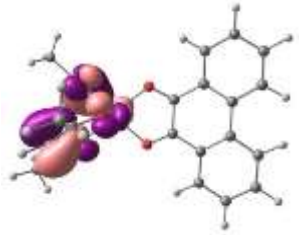
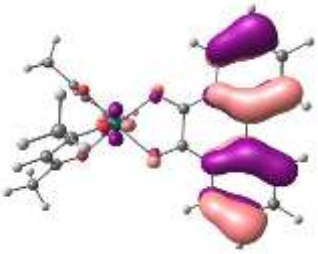
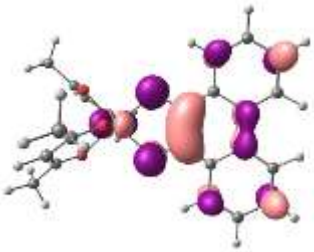
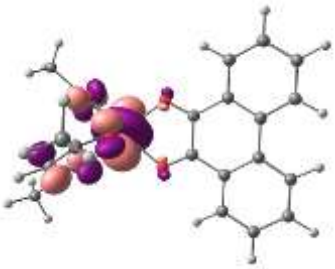
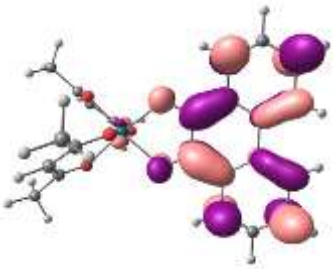
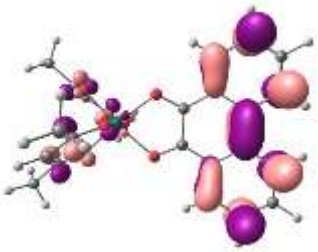
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{-}$ in $S = 1/2$ state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_1
		α-spin		
LUMO+10	4.082	58	34	8
LUMO+9	4.075	60	29	11
LUMO+8	4.027	15	12	73
LUMO+7	3.951	40	32	28
LUMO+6	3.788	54	38	8
LUMO+5	3.681	59	34	7
LUMO+4	3.493	0	0	99
LUMO+3	2.457	5	40	55
LUMO+2	2.400	3	61	36
LUMO+1	2.356	2	96	2
LUMO	2.169	1	0	99
SOMO	-0.906	19	5	76
HOMO-1	-1.407	69	20	11
HOMO-2	-1.648	76	16	8
HOMO-3	-2.147	53	29	17
HOMO-4	-2.969	15	79	6
HOMO-5	-2.973	6	43	51
HOMO-6	-3.093	9	45	46
HOMO-7	-3.729	3	10	86
HOMO-8	-3.789	2	6	93
HOMO-9	-3.899	11	31	57
HOMO-10	-4.065	4	8	88
		β-spin		
LUMO+10	4.093	51	40	9
LUMO+9	4.037	5	3	93

LUMO+8	4.008	54	32	14
LUMO+7	3.945	58	34	7
LUMO+6	3.832	58	35	6
LUMO+5	3.669	5	4	91
LUMO+4	2.631	2	3	96
LUMO+3	2.426	7	90	3
LUMO+2	2.399	5	92	3
LUMO+1	2.207	1	2	97
LUMO	0.918	32	10	57
HOMO	-1.217	62	17	21
HOMO-1	-1.235	58	17	25
HOMO-2	-1.422	75	16	9
HOMO-3	-2.856	5	92	3
HOMO-4	-2.896	3	29	68
HOMO-5	-3.054	9	60	31
HOMO-6	-3.640	2	5	94
HOMO-7	-3.692	3	86	11
HOMO-8	-3.820	11	28	60
HOMO-9	-3.850	4	6	90
HOMO-10	-4.393	6	55	38

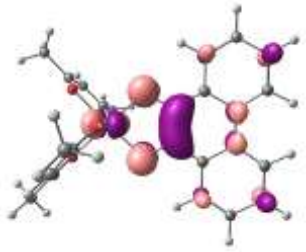
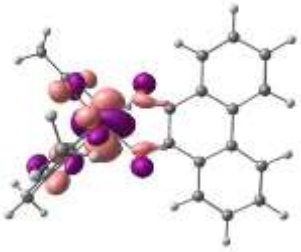
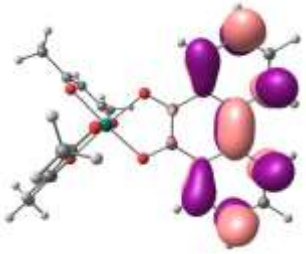
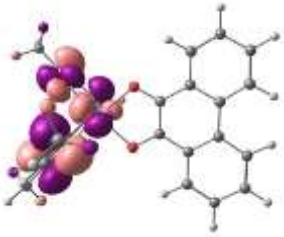
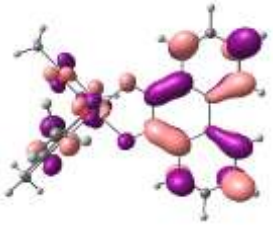
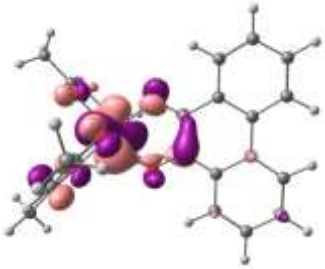
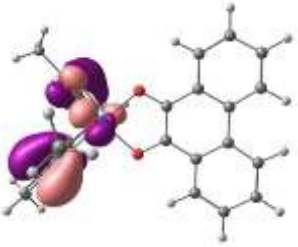
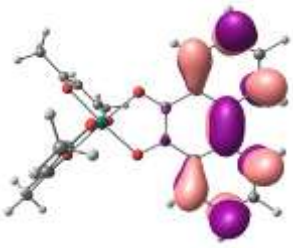
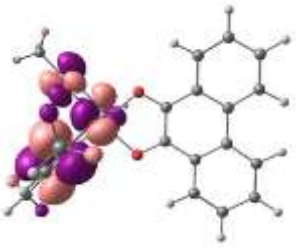
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{2-}$ in $S = 0$ state

MO	Energy (eV)	% Composition		
		Ru	acac	Q_1
LUMO+10	7.524	24	53	23
LUMO+9	7.494	17	70	14
LUMO+8	7.320	0	0	100
LUMO+7	6.877	6	5	88
LUMO+6	6.739	48	35	17
LUMO+5	6.666	51	42	7
LUMO+4	6.625	50	46	4
LUMO+3	5.765	3	12	85
LUMO+2	5.590	8	82	10
LUMO+1	5.470	4	94	2
LUMO	5.373	2	1	97
HOMO	3.114	32	8	59
HOMO-1	2.503	76	14	10
HOMO-2	2.323	72	18	10
HOMO-3	1.948	53	14	33
HOMO-4	0.432	2	25	74
HOMO-5	0.296	4	92	4
HOMO-6	0.159	6	64	31
HOMO-7	-0.003	12	17	71
HOMO-8	-0.337	3	60	37
HOMO-9	-0.403	2	4	94
HOMO-10	-0.561	3	7	89

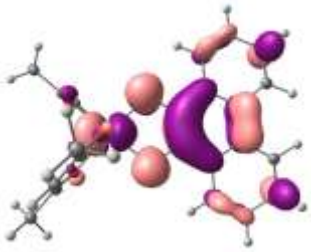
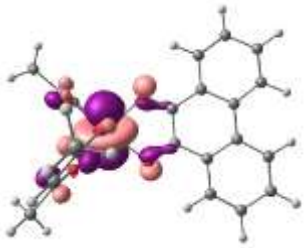
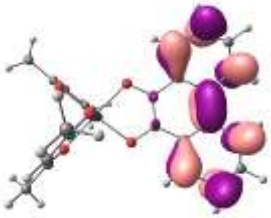
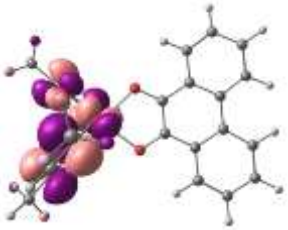
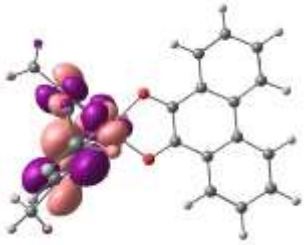
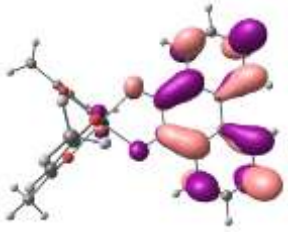
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Selected molecular orbitals along with their energies and compositions of **2** in *S* = 0 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_2
LUMO+10	1.306	50	20	30
LUMO+9	0.981	66	18	16
LUMO+8	0.750	73	20	7
LUMO+7	0.707	2	1	97
LUMO+6	0.460	70	10	20
LUMO+5	0.311	2	1	97
LUMO+4	-0.445	3	94	2
LUMO+3	-0.454	5	89	6
LUMO+2	-0.785	1	5	94
LUMO+1	-1.109	1	0	99
LUMO	-2.445	31	7	62
HOMO	-4.628	65	25	10
HOMO-1	-5.010	49	27	25
HOMO-2	-5.066	60	24	16
HOMO-3	-5.789	15	76	9
HOMO-4	-6.059	25	58	17
HOMO-5	-6.321	10	13	78
HOMO-6	-6.612	4	89	8
HOMO-7	-6.955	3	32	65
HOMO-8	-7.029	8	69	23
HOMO-9	-7.230	4	23	73
HOMO-10	-7.609	14	71	15

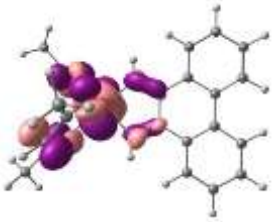
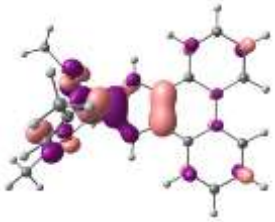
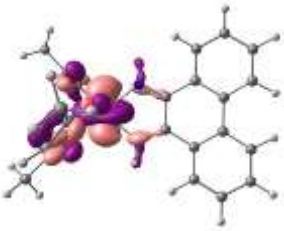
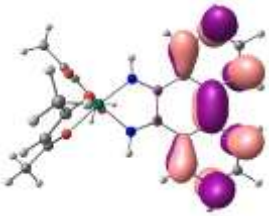
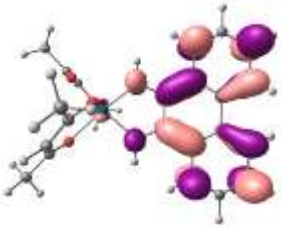
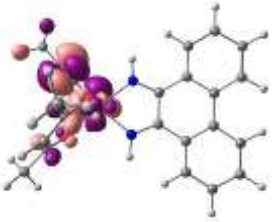
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Selected molecular orbitals along with their energies and compositions of $\mathbf{2}^{+}$ in S =1/2 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_2
		α-spin		
LUMO+10	-1.606	51	7	43
LUMO+9	-2.098	52	6	42
LUMO+8	-2.153	0	0	100
LUMO+7	-2.698	1	0	99
LUMO+6	-3.337	43	17	40
LUMO+5	-3.427	2	96	2
LUMO+4	-3.876	3	94	3
LUMO+3	-3.978	1	1	99
LUMO+2	-4.034	1	0	99
LUMO+1	-4.097	55	36	9
LUMO	-6.063	14	3	83
SOMO	-8.702	17	80	3
HOMO-1	-9.109	19	74	8
HOMO-2	-9.184	9	2	89
HOMO-3	-9.396	35	37	27
HOMO-4	-9.515	48	13	38
HOMO-5	-9.906	45	16	39
HOMO-6	-10.210	4	85	11
HOMO-7	-10.370	22	62	16
HOMO-8	-10.377	16	29	55
HOMO-9	-10.859	41	51	8
HOMO-10	-10.904	0	5	95
		β-spin		
LUMO+10	-2.094	53	6	41
LUMO+9	-2.153	0	0	100

LUMO+8	-2.706	1	0	99
LUMO+7	-3.026	42	16	42
LUMO+6	-3.164	40	53	7
LUMO+5	-3.854	5	93	2
LUMO+4	-3.970	21	71	8
LUMO+3	-4.005	2	4	94
LUMO+2	-4.018	1	0	99
LUMO+1	-6.019	20	4	75
LUMO	-6.199	70	21	9
HOMO	-8.824	24	63	13
HOMO-1	-9.010	32	57	12
HOMO-2	-9.131	34	44	22
HOMO-3	-9.267	4	5	92
HOMO-4	-9.585	64	29	6
HOMO-5	-10.005	4	88	8
HOMO-6	-10.157	3	6	91
HOMO-7	-10.309	11	20	69
HOMO-8	-10.634	10	84	6
HOMO-9	-10.907	0	6	94
HOMO-10	-11.325	20	68	12

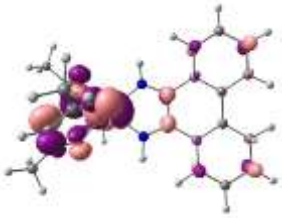
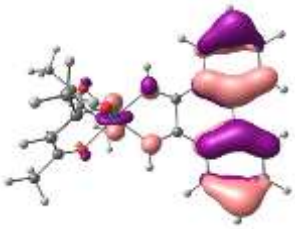
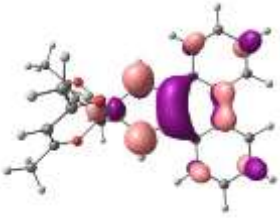
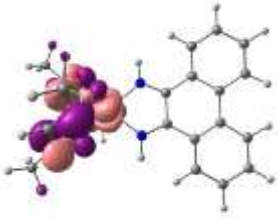
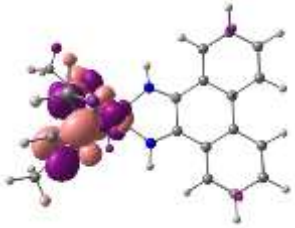
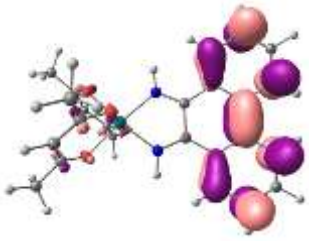
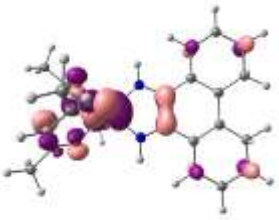
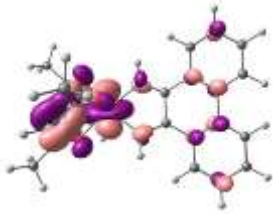
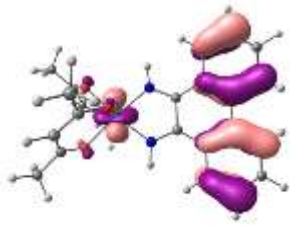
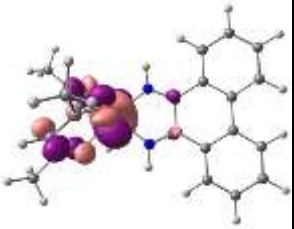
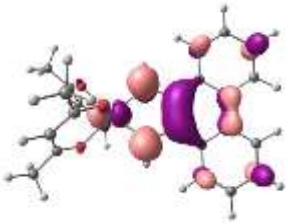
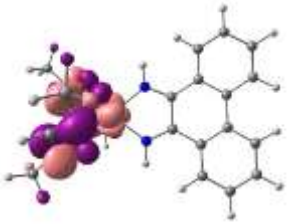
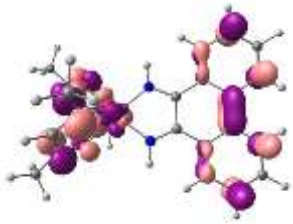
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Selected molecular orbitals along with their energies and compositions of $\mathbf{2}^{-}$ in S =1/2 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_2
		α-spin		
LUMO+10	4.430	26	33	41
LUMO+9	4.071	44	42	15
LUMO+8	4.054	1	1	98
LUMO+7	4.024	60	37	3
LUMO+6	3.950	62	31	6
LUMO+5	3.616	10	4	85
LUMO+4	3.567	68	15	17
LUMO+3	2.587	5	46	48
LUMO+2	2.526	2	54	43
LUMO+1	2.477	2	96	2
LUMO	2.173	1	0	98
SOMO	-0.127	22	5	73
HOMO-1	-1.048	73	17	10
HOMO-2	-1.447	74	17	9
HOMO-3	-1.846	54	24	22
HOMO-4	-2.722	9	85	6
HOMO-5	-2.797	9	49	42
HOMO-6	-2.987	11	36	53
HOMO-7	-3.508	3	88	9
HOMO-8	-3.595	4	8	88
HOMO-9	-3.844	6	82	12
HOMO-10	-3.875	5	12	83
		β-spin		
LUMO+10	4.150	41	44	15
LUMO+9	4.132	46	31	23

LUMO+8	4.114	1	0	99
LUMO+7	3.985	63	31	6
LUMO+6	3.807	43	23	34
LUMO+5	3.576	68	15	17
LUMO+4	2.727	3	3	94
LUMO+3	2.581	6	89	5
LUMO+2	2.571	6	89	5
LUMO+1	2.222	2	2	95
LUMO	1.548	26	13	62
HOMO	-0.846	72	15	13
HOMO-1	-1.102	52	15	33
HOMO-2	-1.288	73	17	9
HOMO-3	-2.601	6	34	60
HOMO-4	-2.661	4	86	11
HOMO-5	-2.926	14	61	25
HOMO-6	-3.372	5	8	87
HOMO-7	-3.478	3	87	11
HOMO-8	-3.639	5	11	84
HOMO-9	-3.813	5	81	13
HOMO-10	-4.302	8	80	12

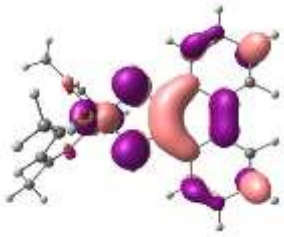
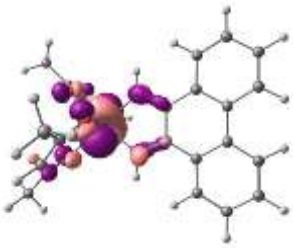
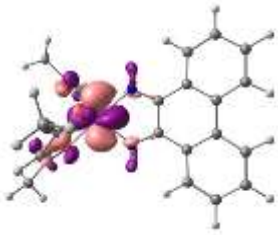
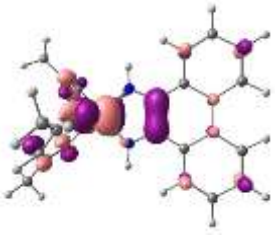
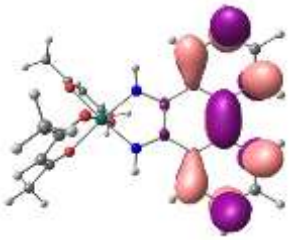
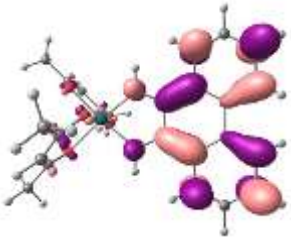
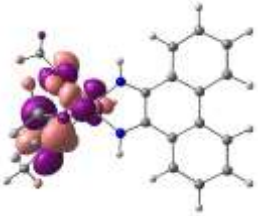
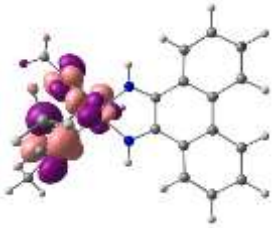
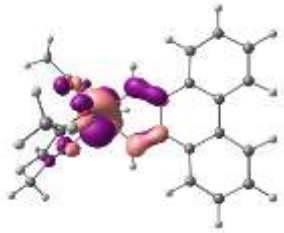
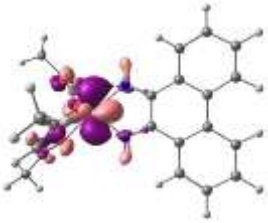
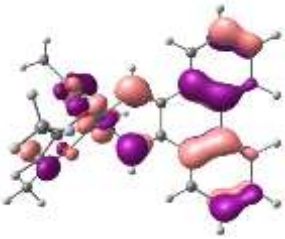
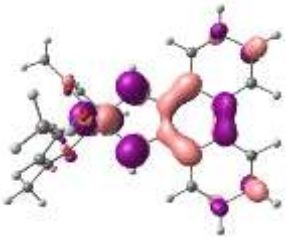
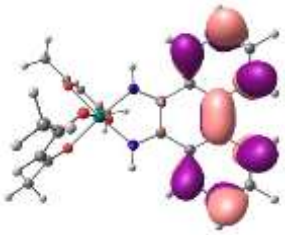
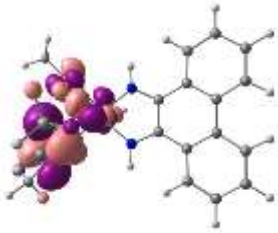
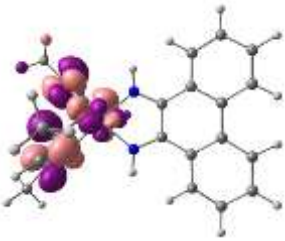
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S14 Selected molecular orbitals along with their energies and compositions of $\mathbf{2}^{2-}$ in *S*=0 state

MO	Energy (eV)	% Composition		
		Ru	acac	Q_2
LUMO+10	7.749	4	42	54
LUMO+9	7.558	18	70	12
LUMO+8	7.387	0	0	100
LUMO+7	7.131	9	12	80
LUMO+6	6.577	54	42	5
LUMO+5	6.565	54	42	5
LUMO+4	6.272	66	24	10
LUMO+3	5.867	3	3	94
LUMO+2	5.570	7	88	5
LUMO+1	5.503	5	89	6
LUMO	5.429	3	7	90
HOMO	3.706	25	9	66
HOMO-1	2.646	74	12	14
HOMO-2	2.207	76	17	8
HOMO-3	1.996	58	15	27
HOMO-4	0.790	7	13	80
HOMO-5	0.335	3	91	6
HOMO-6	0.173	9	75	16
HOMO-7	-0.119	5	11	83
HOMO-8	-0.311	3	53	44
HOMO-9	-0.440	5	54	41
HOMO-10	-0.679	5	73	22

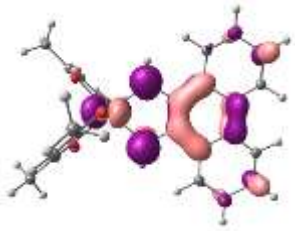
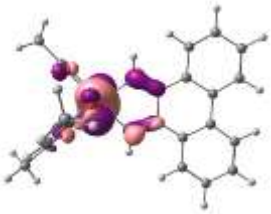
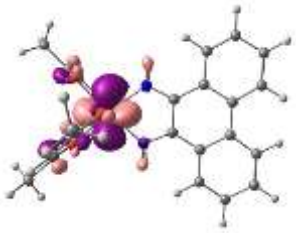
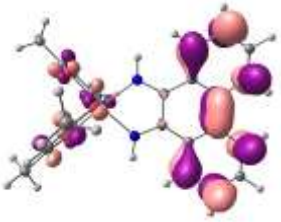
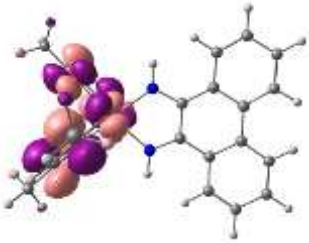
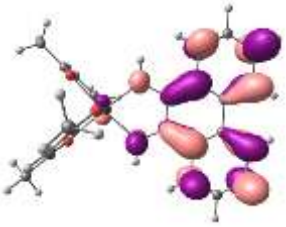
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S15 Selected molecular orbitals along with their energies and compositions of **3** in *S* = 0 state

MO	Energy (eV)	% Composition		
		Ru	acac	Q_3
LUMO+10	1.320	75	19	6
LUMO+9	0.891	40	24	36
LUMO+8	0.755	67	12	21
LUMO+7	0.553	2	1	97
LUMO+6	0.248	49	41	10
LUMO+5	0.219	1	1	98
LUMO+4	-0.488	3	95	2
LUMO+3	-0.651	6	90	4
LUMO+2	-0.853	1	3	96
LUMO+1	-1.110	1	0	99
LUMO	-2.795	33	8	59
HOMO	-4.827	63	29	8
HOMO-1	-5.129	51	26	23
HOMO-2	-5.231	58	21	21
HOMO-3	-5.928	18	74	8
HOMO-4	-6.197	20	54	26
HOMO-5	-6.355	10	18	72
HOMO-6	-6.738	4	90	6
HOMO-7	-7.072	3	7	90
HOMO-8	-7.219	5	63	32
HOMO-9	-7.331	8	42	51
HOMO-10	-7.725	12	66	22

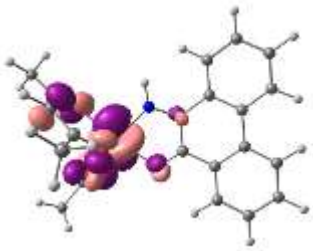
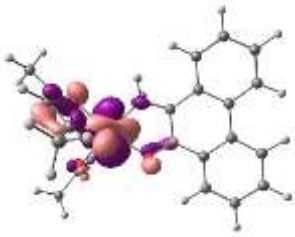
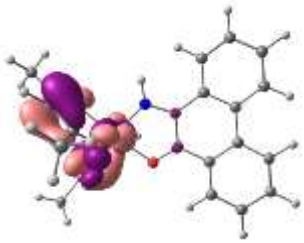
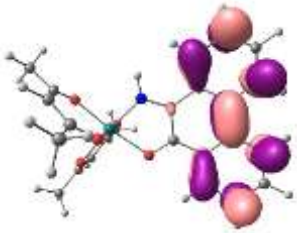
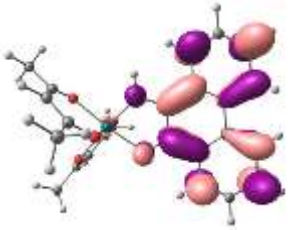
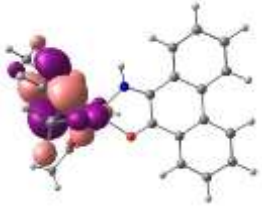
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{+}$ in S = 1/2 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_3
		α-spin		
LUMO+10	-1.515	72	20	9
LUMO+9	-1.969	43	6	50
LUMO+8	-2.215	0	0	100
LUMO+7	-2.783	0	0	99
LUMO+6	-3.449	40	39	21
LUMO+5	-3.764	16	74	10
LUMO+4	-4.013	3	30	67
LUMO+3	-4.031	2	63	35
LUMO+2	-4.057	1	5	95
LUMO+1	-4.253	56	29	15
LUMO	-6.390	13	3	84
SOMO	-8.789	17	80	3
HOMO-1	-9.196	24	65	11
HOMO-2	-9.307	6	6	88
HOMO-3	-9.498	37	32	30
HOMO-4	-9.508	56	24	20
HOMO-5	-10.047	25	10	65
HOMO-6	-10.327	5	86	9
HOMO-7	-10.431	28	51	20
HOMO-8	-10.467	22	27	51
HOMO-9	-10.971	13	26	60
HOMO-10	-11.008	28	47	25
		β-spin		
LUMO+10	-1.964	44	6	50
LUMO+9	-2.220	0	0	100

LUMO+8	-2.797	0	0	99
LUMO+7	-3.164	48	25	27
LUMO+6	-3.479	3	95	3
LUMO+5	-3.988	19	68	13
LUMO+4	-4.012	19	35	47
LUMO+3	-4.049	33	20	47
LUMO+2	-4.173	1	3	96
LUMO+1	-6.252	28	7	65
LUMO	-6.383	62	23	15
HOMO	-8.896	27	57	17
HOMO-1	-9.074	39	46	14
HOMO-2	-9.203	19	27	53
HOMO-3	-9.345	24	30	46
HOMO-4	-9.619	55	35	9
HOMO-5	-10.127	3	5	92
HOMO-6	-10.269	4	90	6
HOMO-7	-10.423	9	24	67
HOMO-8	-10.789	11	78	11
HOMO-9	-10.982	1	5	94
HOMO-10	-11.388	18	65	17

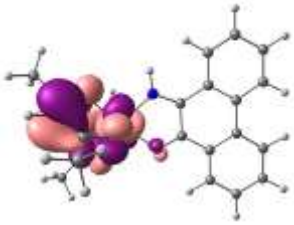
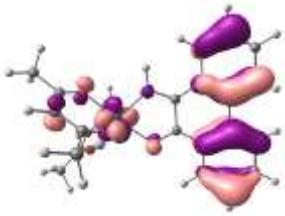
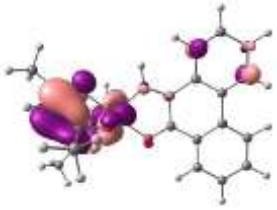
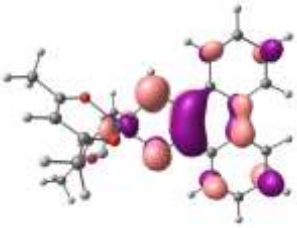
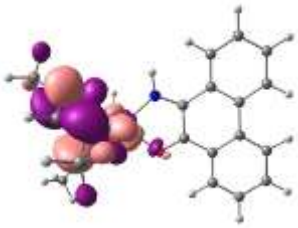
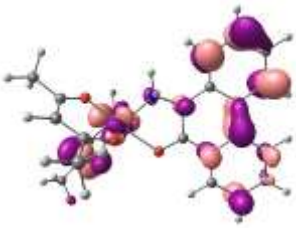
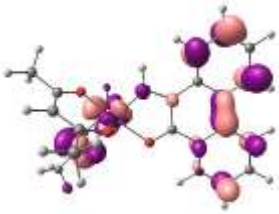
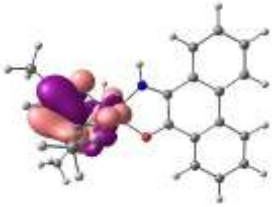
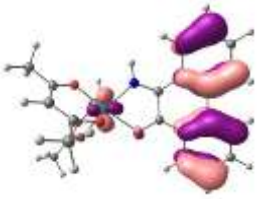
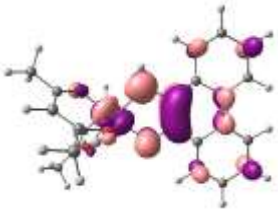
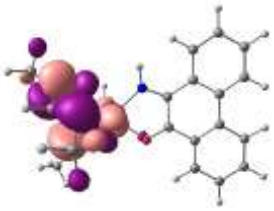
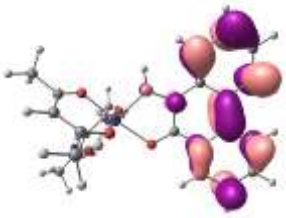
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 Selected molecular orbitals along with their energies and compositions of **3**$^{-}$ in *S* = 1/2 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_3
		α-spin		
LUMO+10	4.138	34	35	31
LUMO+9	4.071	60	34	7
LUMO+8	4.051	1	1	98
LUMO+7	4.004	60	37	3
LUMO+6	3.798	52	38	10
LUMO+5	3.749	62	18	20
LUMO+4	3.546	4	2	94
LUMO+3	2.556	5	71	24
LUMO+2	2.453	1	31	67
LUMO+1	2.403	3	93	4
LUMO	2.163	1	1	98
SOMO	-0.491	22	5	73
HOMO-1	-1.265	72	21	8
HOMO-2	-1.540	74	15	11
HOMO-3	-1.976	54	24	22
HOMO-4	-2.798	11	84	5
HOMO-5	-2.905	5	36	59
HOMO-6	-3.049	11	49	40
HOMO-7	-3.582	3	84	12
HOMO-8	-3.715	2	7	91
HOMO-9	-3.837	8	40	52
HOMO-10	-3.965	5	14	81
		β-spin		
LUMO+10	4.131	53	39	8
LUMO+9	4.078	7	5	88

LUMO+8	4.037	52	35	13
LUMO+7	3.933	56	35	8
LUMO+6	3.778	28	14	57
LUMO+5	3.729	62	19	19
LUMO+4	2.671	2	3	95
LUMO+3	2.561	5	92	3
LUMO+2	2.449	7	86	7
LUMO+1	2.206	2	3	95
LUMO	1.316	28	12	60
HOMO	-1.032	63	16	21
HOMO-1	-1.242	59	18	22
HOMO-2	-1.356	73	16	11
HOMO-3	-2.737	6	91	4
HOMO-4	-2.776	4	23	73
HOMO-5	-2.994	11	64	25
HOMO-6	-3.506	3	35	62
HOMO-7	-3.558	3	67	30
HOMO-8	-3.720	5	11	84
HOMO-9	-3.785	8	36	56
HOMO-10	-4.213	8	70	22

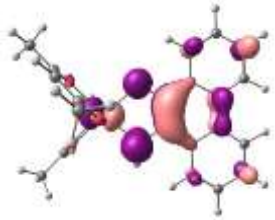
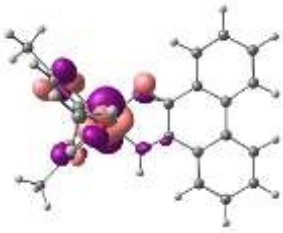
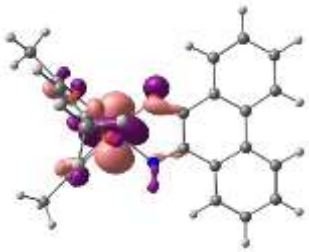
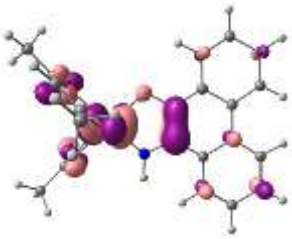
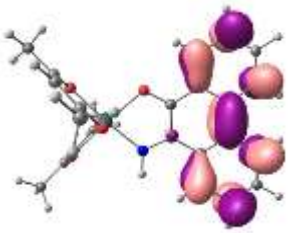
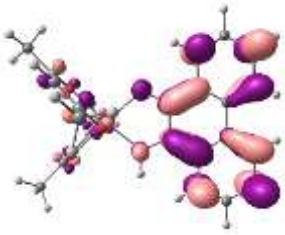
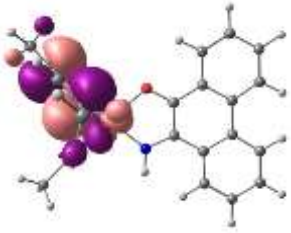
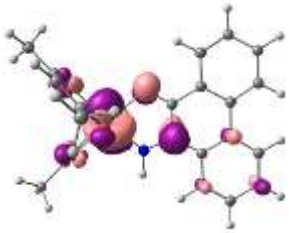
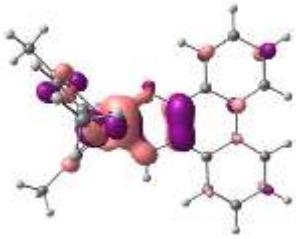
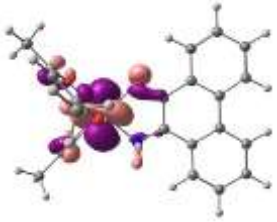
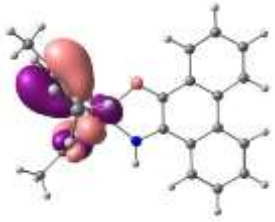
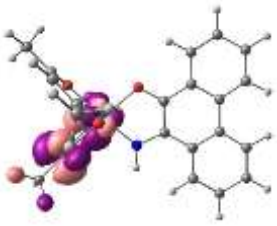
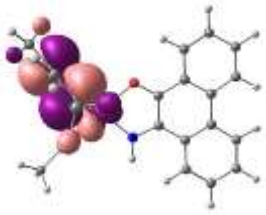
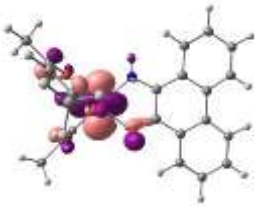
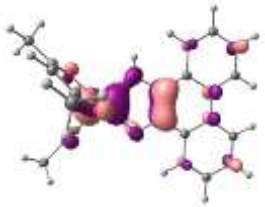
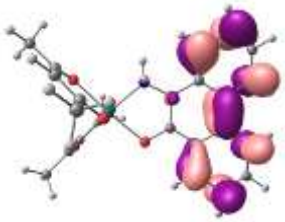
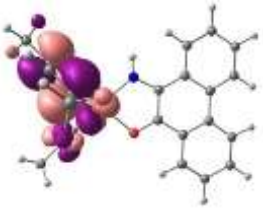
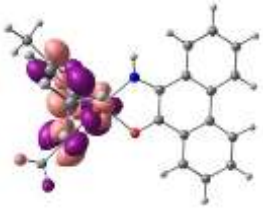
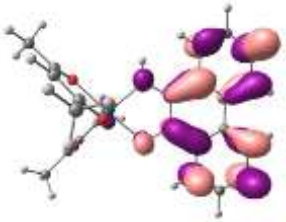
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S18 Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{2-}$ in *S*=0 state

MO	Energy	% Composition		
	(eV)	Ru	acac	Q_3
LUMO+10	7.681	6	32	62
LUMO+9	7.544	23	69	9
LUMO+8	7.338	0	0	100
LUMO+7	6.961	8	9	84
LUMO+6	6.646	50	42	8
LUMO+5	6.608	52	44	3
LUMO+4	6.499	59	29	13
LUMO+3	5.779	3	4	93
LUMO+2	5.608	7	88	5
LUMO+1	5.498	5	91	4
LUMO	5.377	2	4	94
HOMO	3.428	28	8	63
HOMO-1	2.582	76	14	10
HOMO-2	2.296	72	17	10
HOMO-3	1.994	56	14	30
HOMO-4	0.579	3	15	82
HOMO-5	0.340	4	92	4
HOMO-6	0.178	7	73	19
HOMO-7	-0.120	8	22	70
HOMO-8	-0.238	5	9	86
HOMO-9	-0.385	3	62	35
HOMO-10	-0.506	5	37	59

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

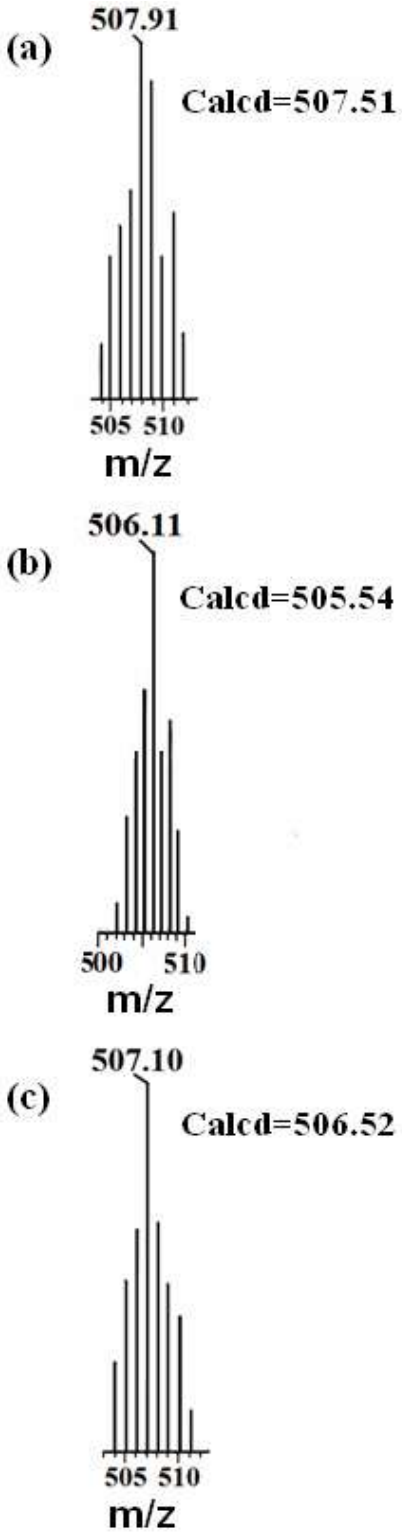


Fig. S1 ESI-MS of (a) **1**, (b) **2** and (c) **3** in acetonitrile.

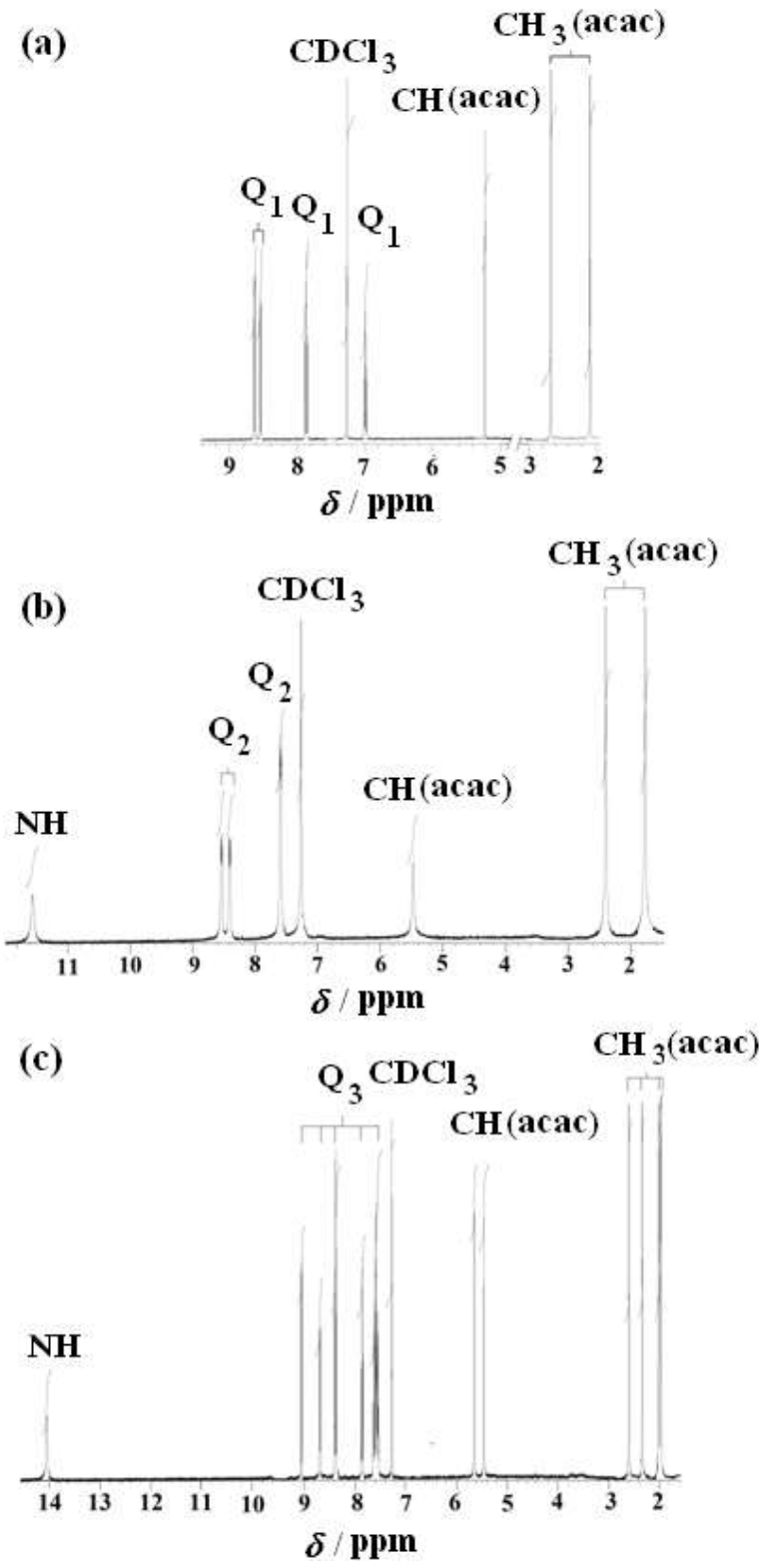


Fig. S2 ^{1}H NMR spectra of (a) **1**, (b) **2** and (c) **3** in $CDCl_3$.

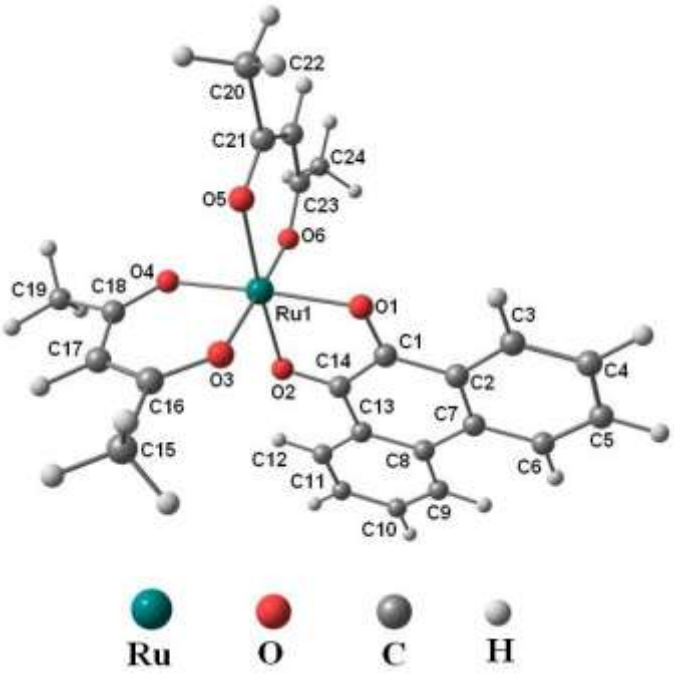


Fig. S3 DFT optimised structure of **1**.

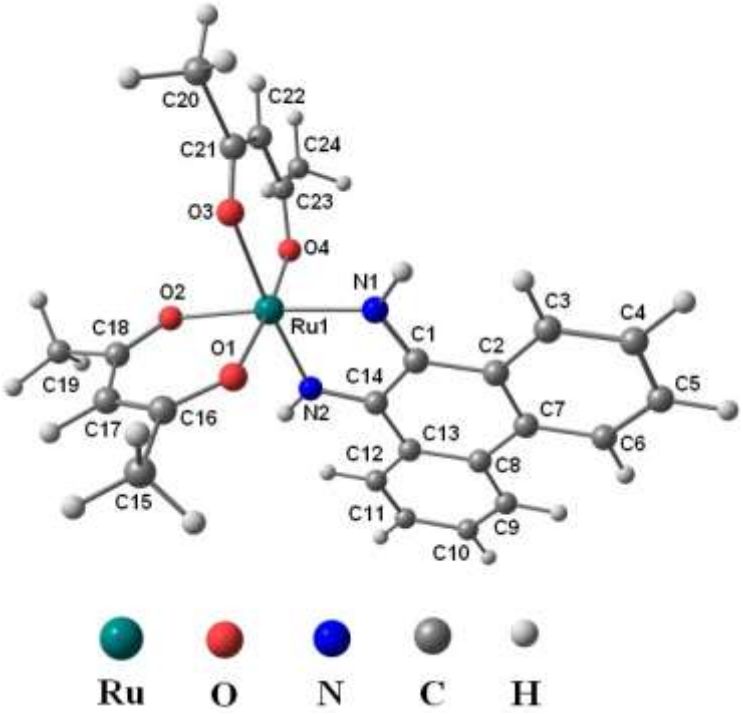


Fig. S4 DFT optimised structure of **2** (molecule **A**).

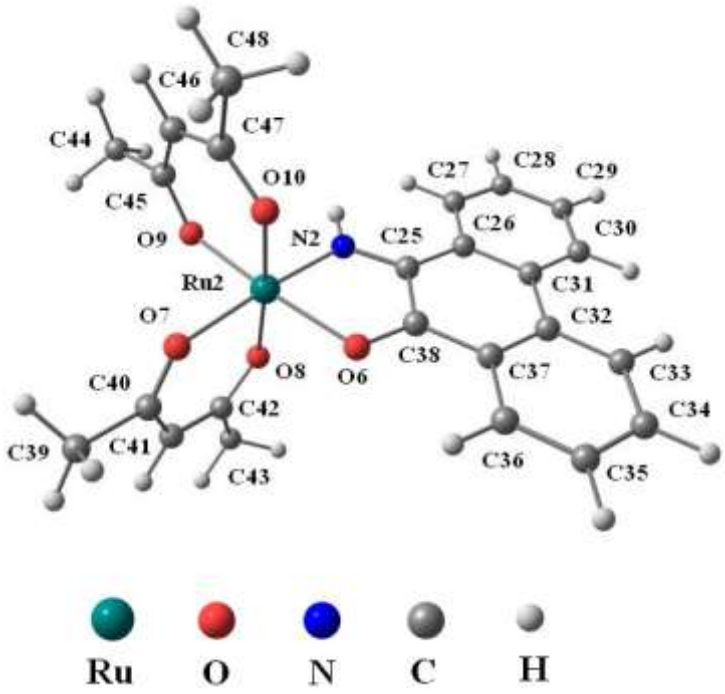


Fig. S5 DFT optimised structure of **3** (molecule **F**).