Supporting Information

Inner-sphere electron transfer at the ruthenium-azo interface

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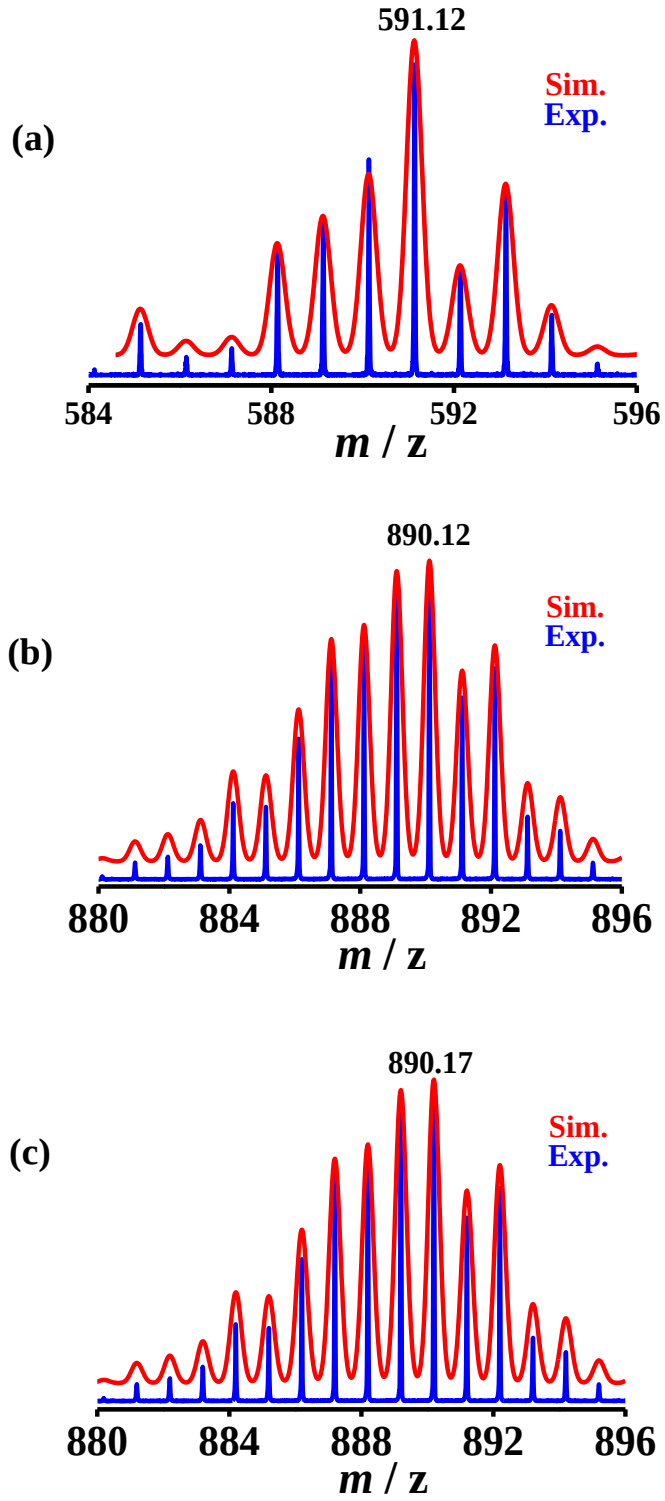
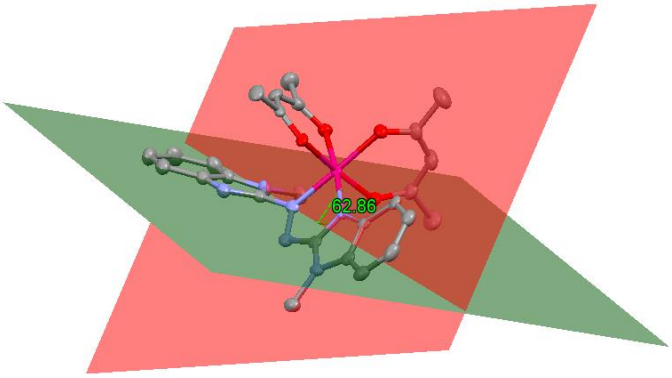


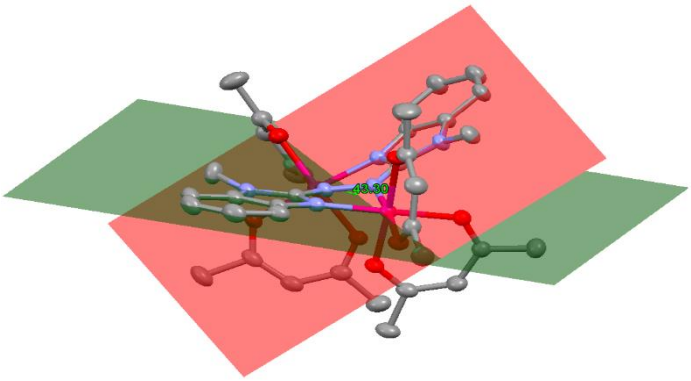
Fig. S1 Experimental and simulated ESI(+) mass spectra of (a) {**1**+H}$^+$, (b) {**2**}$^+$, (c) {([**2**]ClO_4)-ClO_4}$^+$ in CH_3CN (red line, simulated and blue line, experimental).

1



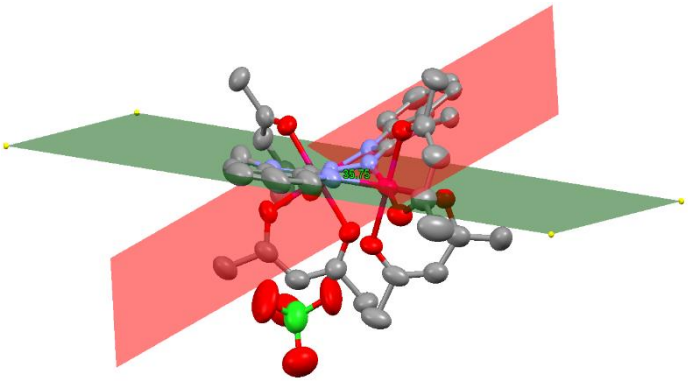
62.86°

2



43.30°

[**2**]ClO_4



35.75°

Fig. S2 Non-planarity of the coordinated **abim**.

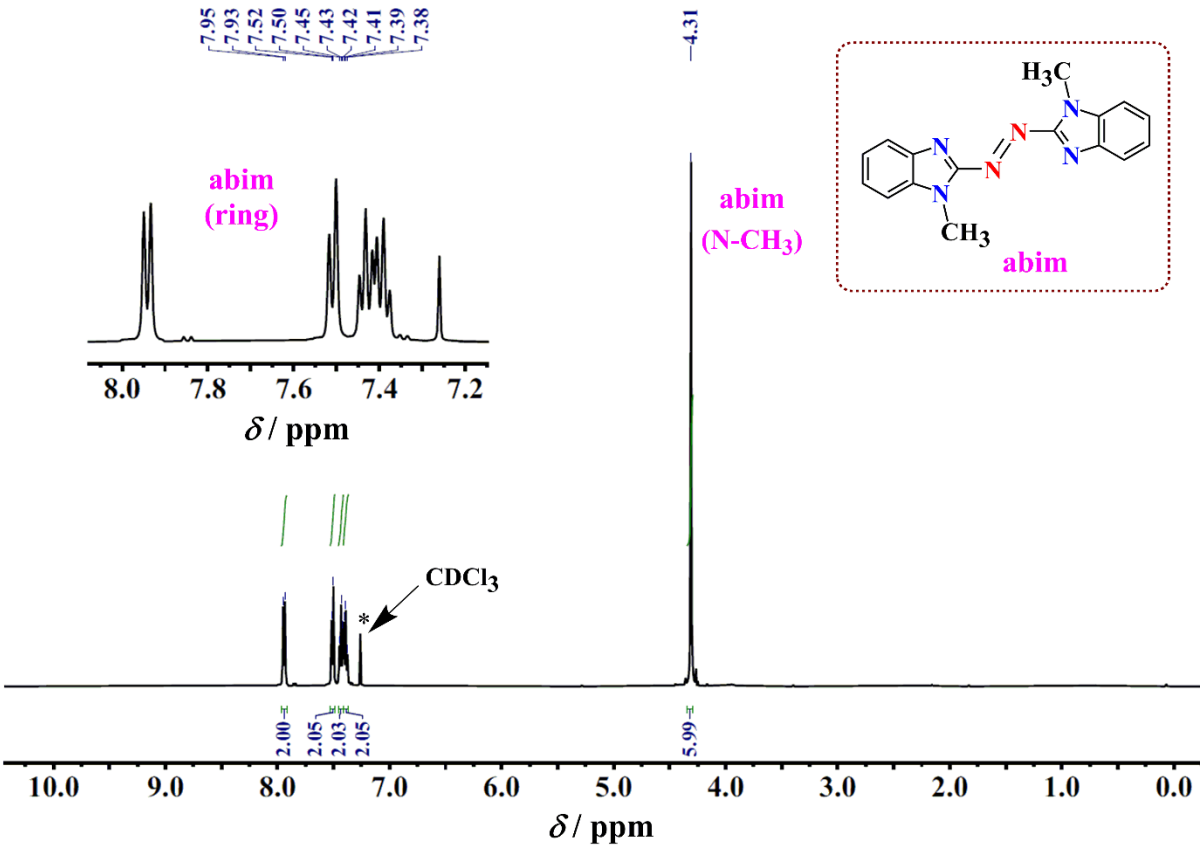


Fig. S3a ^{1}H NMR of **abim** in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

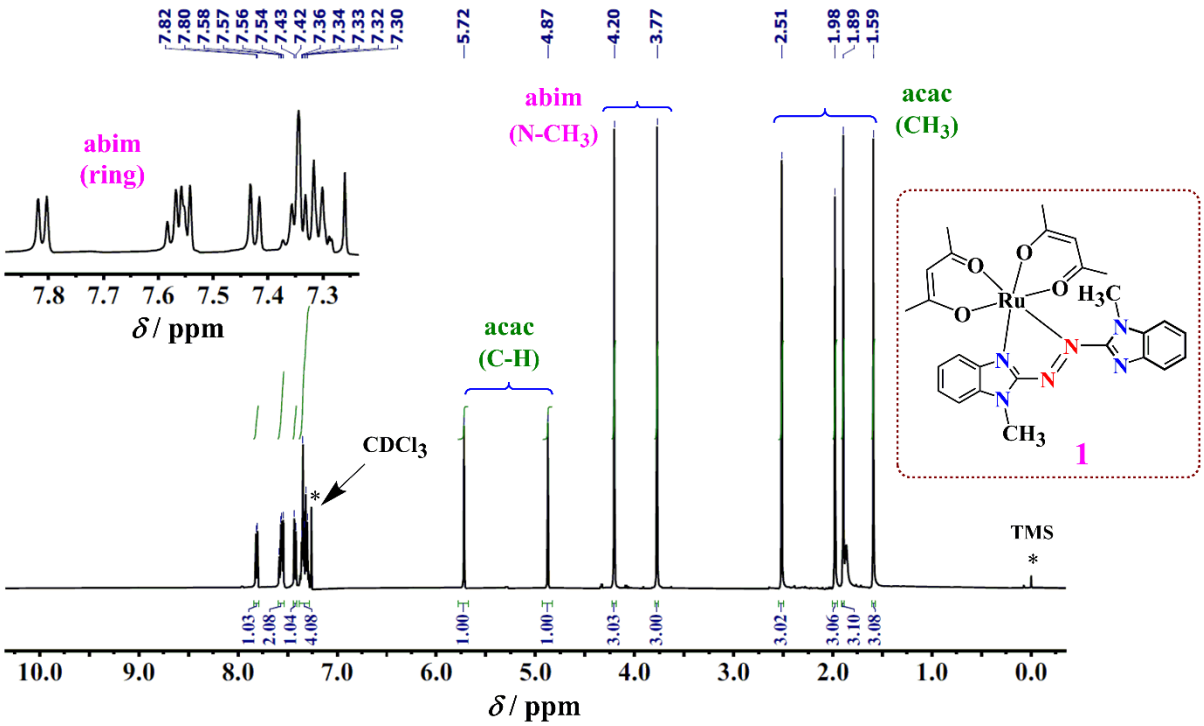


Fig. S3b ^{1}H NMR of **1** in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

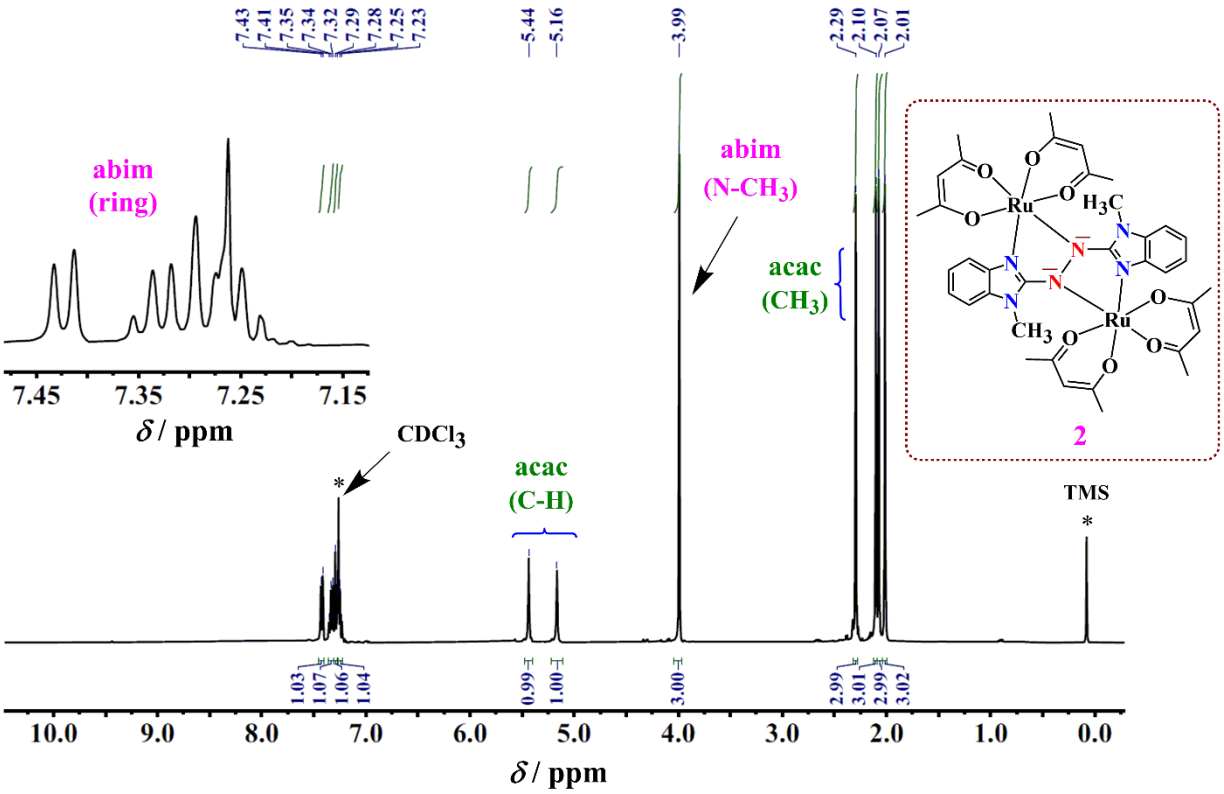


Fig. S3c ^{1}H NMR of **2** in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

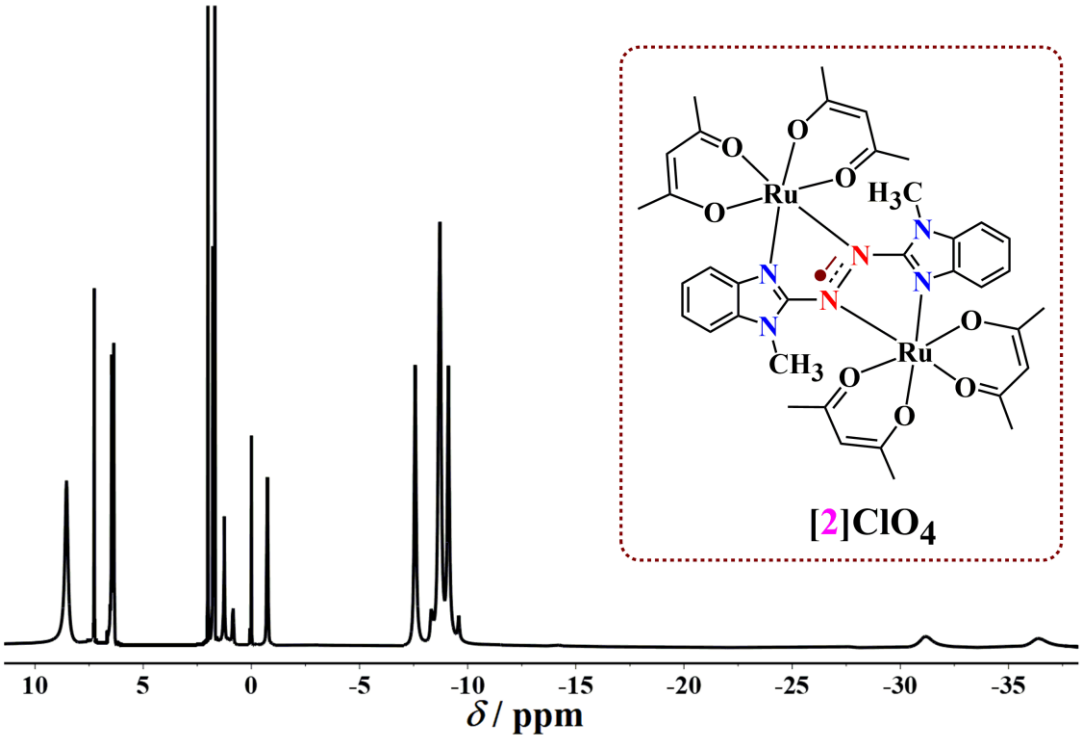


Fig. S3d ^{1}H NMR of [**2**]ClO_4 in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

Determination of Solution Magnetic Moment (Evans method) of [2]ClO_4

Solution magnetic moment of ruthenium (III) complex [**2**]ClO_4 was determined by Evans method. The crystalline complex (3.7 mg) was dissolved in $CDCl_3$ (~0.56 mL) taken in a NMR tube (5 mm). In another coaxial NMR tube only reference $CDCl_3$ solvent was taken. Proton NMR of sample together with the Evans tube was recorded, which showed two peaks corresponding to the solvent residual peak of $CDCl_3$ in the sample and reference. The shift in the position due to the paramagnetic Ru(III) was noted to be 0.037 ppm. Experiments were carried out in 500 MHz NMR spectrometer at 298 K.

$$\chi_g = \frac{-3\Delta f}{4\pi \nu_0 m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad \text{..... eq. 1}$$

The mass susceptibility (χ_g) was calculated using eq. 1, where Δf is the shift in frequency (in Hz), ν_0 is the operating frequency of NMR spectrometer (in Hz), m is the concentration of the substance (g/mL), d_0 and d_s are the densities of pure solvent and solution, respectively, and χ_0 is the mass susceptibility of the solvent. The molar susceptibility (χ_m) is obtained by multiplying the mass susceptibility (χ_g) by the molar mass. This result was used to calculate the effective magnetic moment μ_{eff} (eq. 2).

$$\chi_M = 132.7 \times 10^{-5} \ \text{cm}^3/\text{mol}$$

$$\mu_{eff} = 2.83 \times (\chi_M T)^{1/2} \ \text{BM} \qquad \text{..... eq. 2}$$

$$= 2.83 \times (132.7 \times 10^{-5} \times 298.15)^{1/2} \ \text{BM}$$

$$= 1.78 \ \text{BM}$$

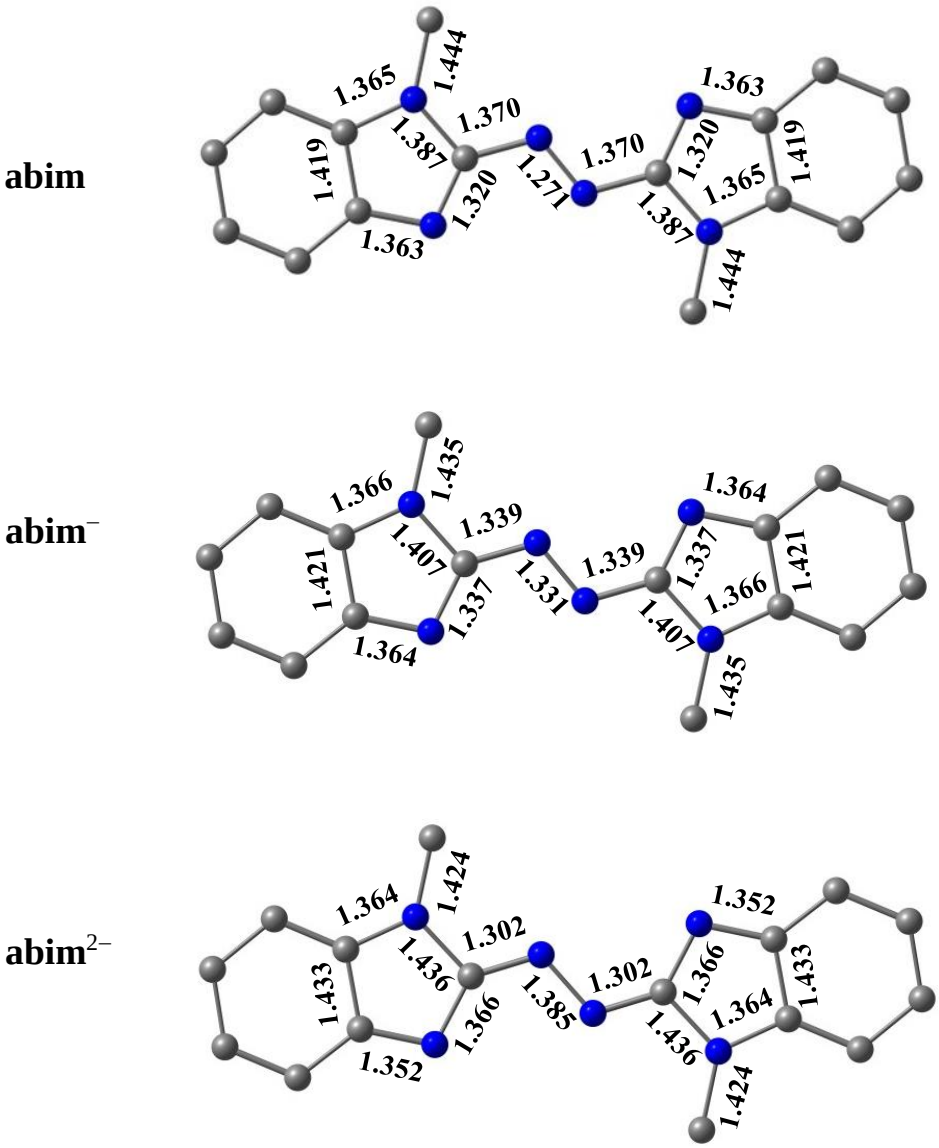
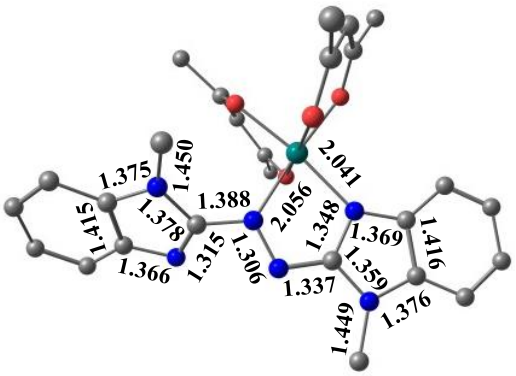
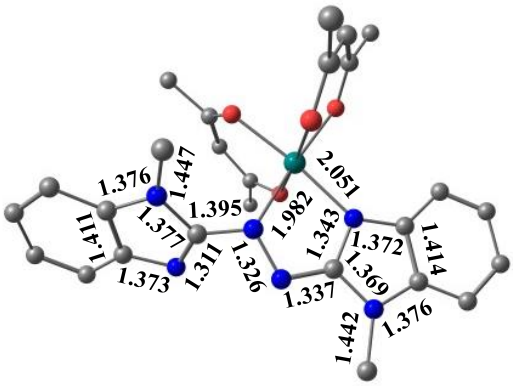


Fig. S4a DFT optimized (M06L/TZVP/SDD) structures of **abim**^{n} (n = 0, –1, –2).

1^{+} (***S***=1/2)



1 (***S***=0)



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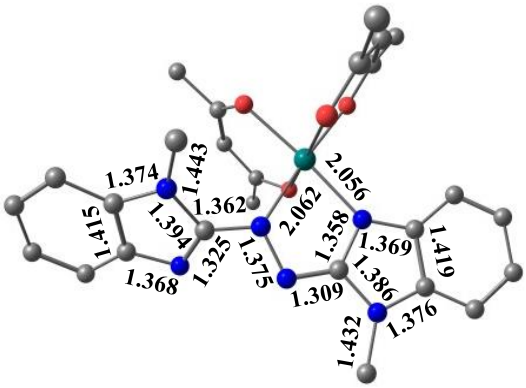


1^{2-} (***S***=0)

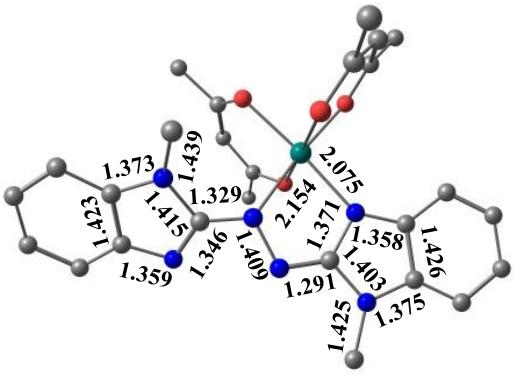


Fig. S4b DFT optimized (M06L/TZVP/SDD) structures of **1**^{n} (n = 0, ±1, –2).

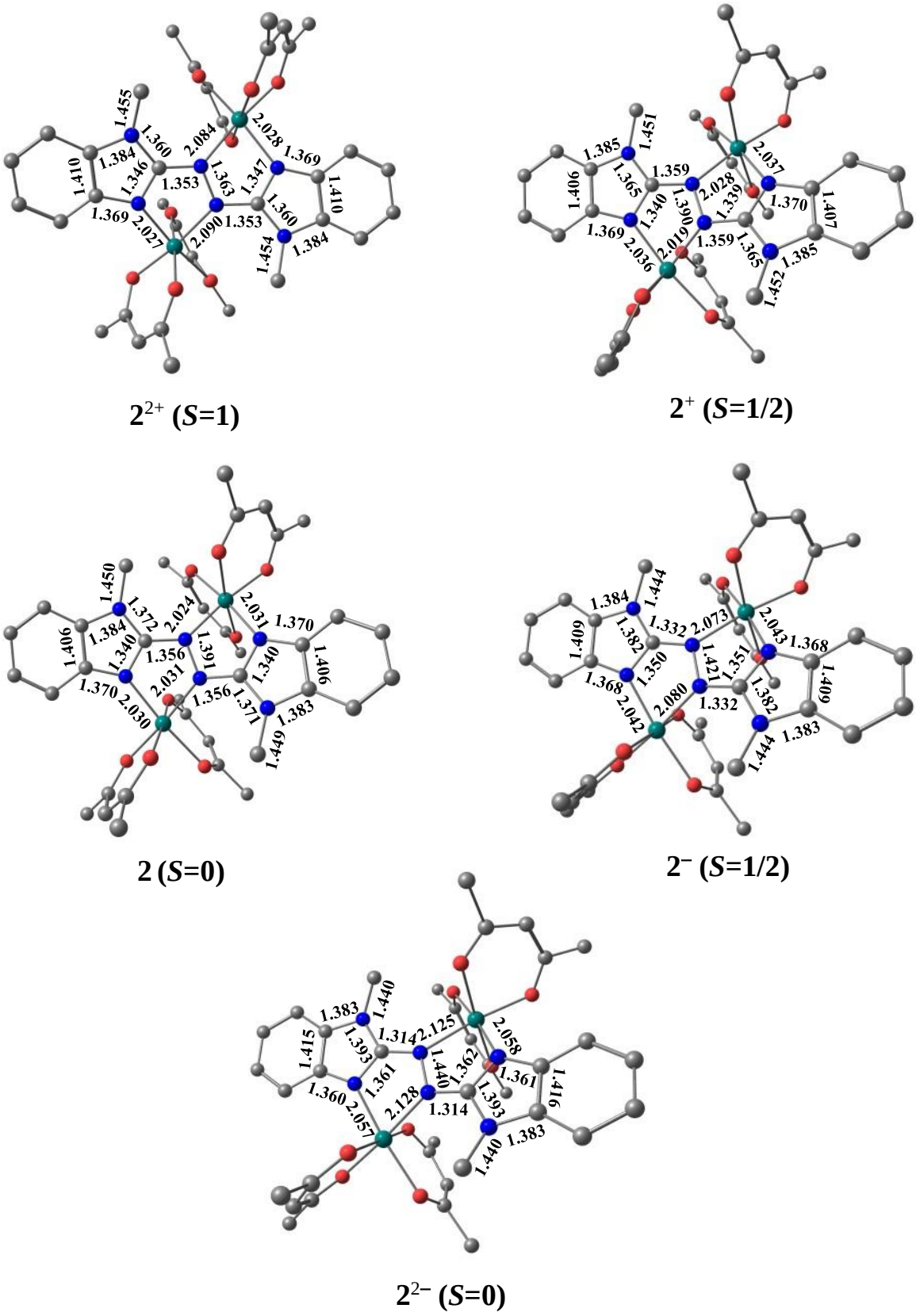


Fig. S4c DFT optimized (M06L/TZVP/SDD) structures of $\mathbf{2}^{n}$ (n = 0, ±1, ±2).

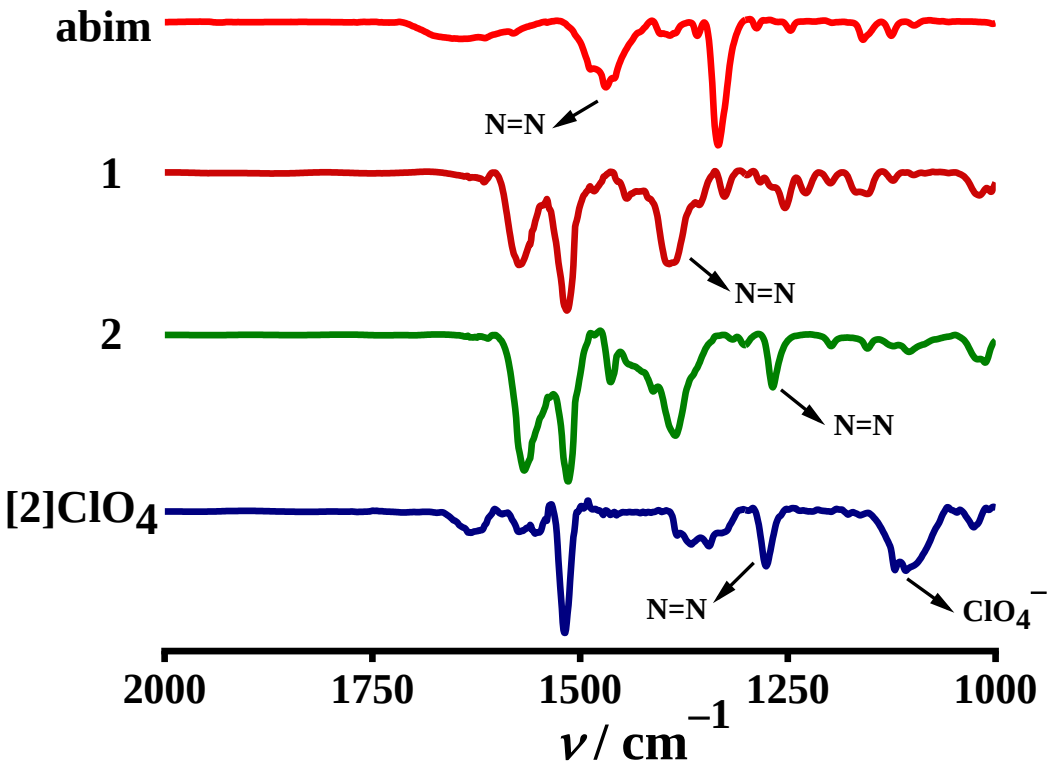


Fig. S5 FT-IR spectra of **abim**, **1**, **2** and [**2**]ClO_4 as KBr pellets.

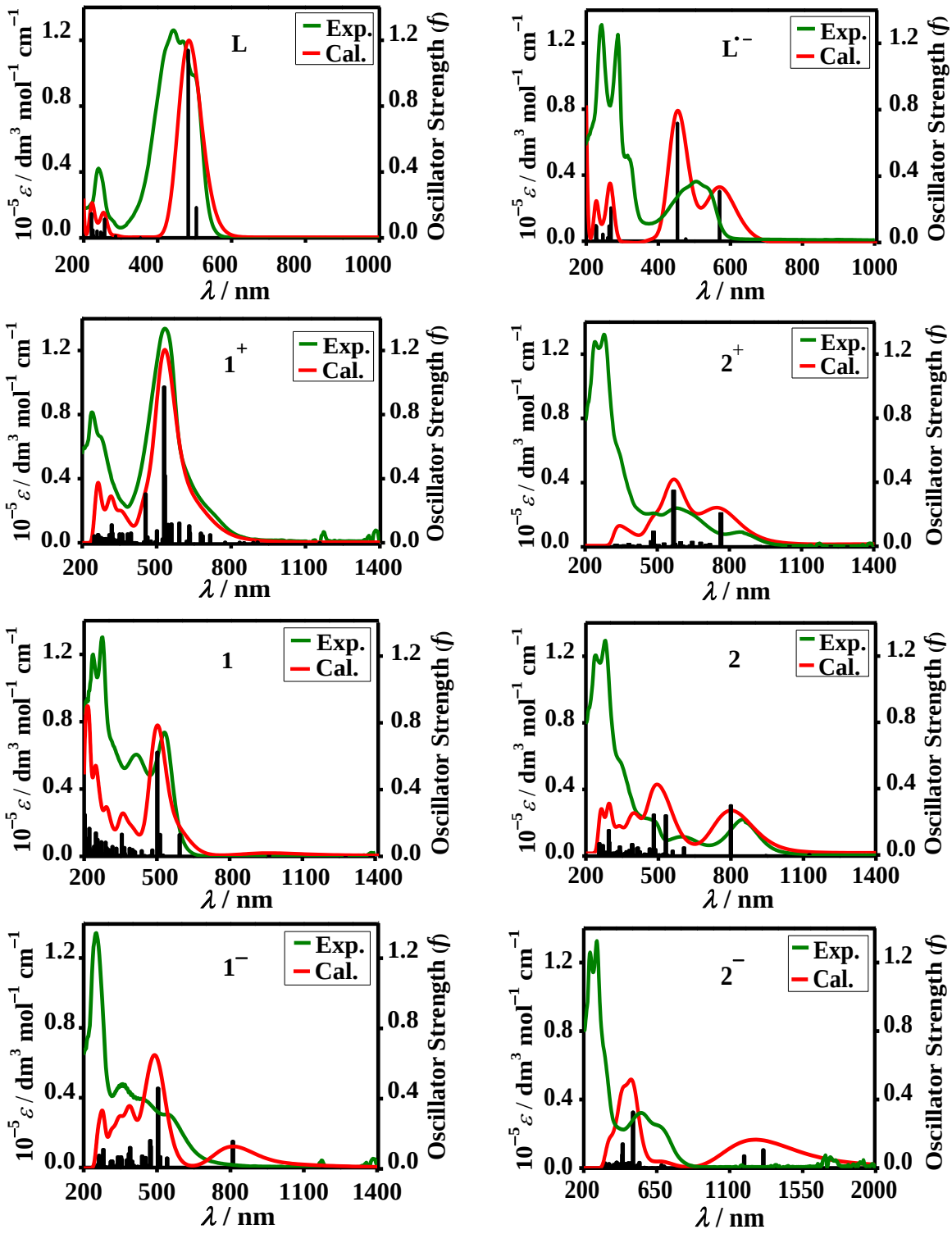


Fig. S6 Experimental and TD-DFT (M06L(CPCM)/TZVP/SDD) calculated electronic spectra in CH_2Cl_2. Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full-width at half-maximum of 2000 cm^{-1}.

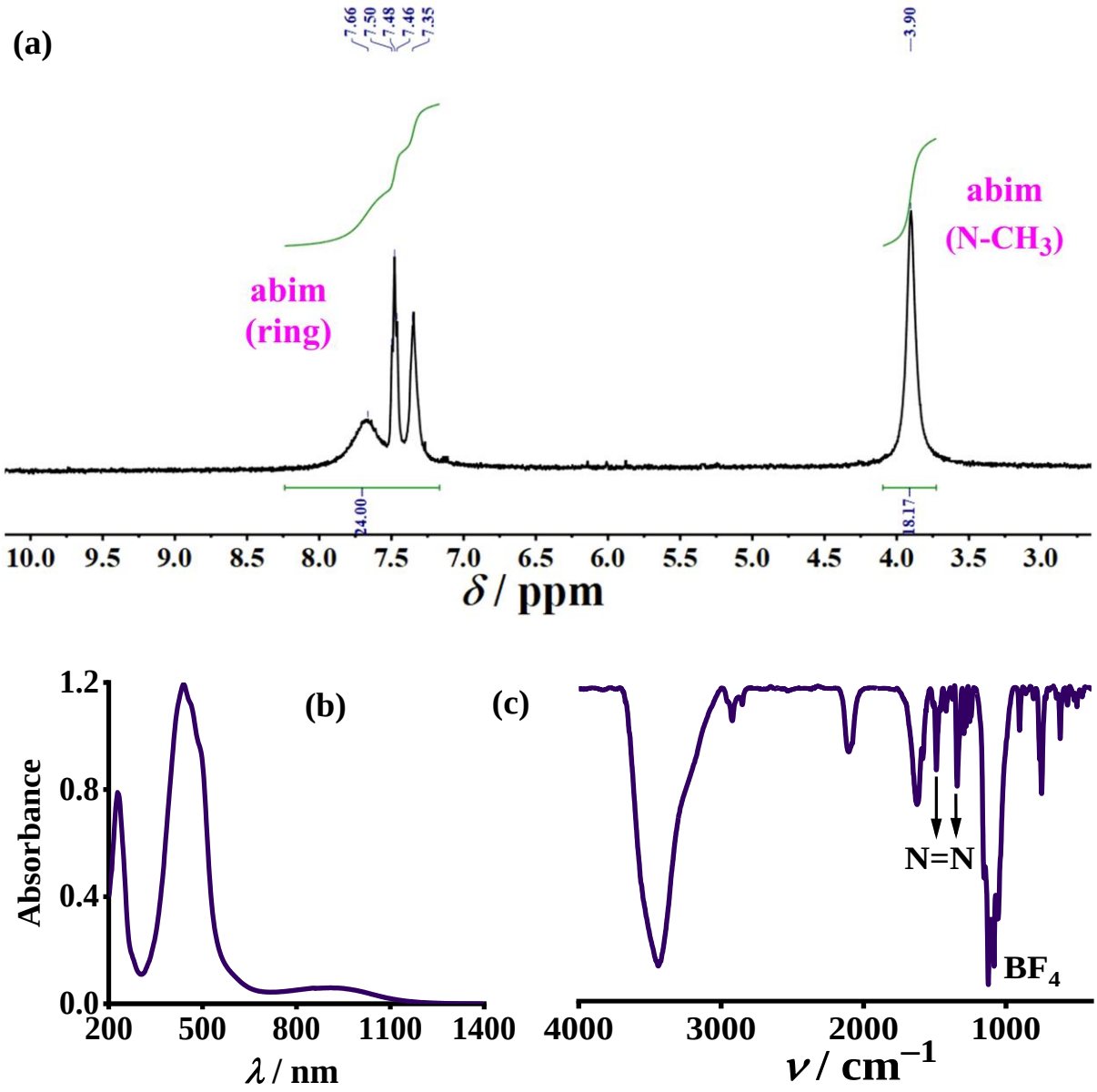


Fig. S7 Spectroscopic features of [**3**](BF$_4$)$_2$. (a) ^{1}H NMR (δ = 0-10 ppm) in CD$_3$CN using TMS as an internal standard, (b) qualitative electronic spectrum in CH$_3$CN, (c) FT-IR spectra.

Table S1 Selected crystallographic parameters for **abim**, **1**, **2**, [**2**]ClO_4 and [**3**]$(BF_4)_2$

Complex	**abim**	**1.**C_6H_6	**2**	[**2**]ClO_4	[**3**]$(BF_4)_2$
empirical formula	$C_{16}H_{14}N_6$	$C_{32}H_{34}N_6O_4Ru$	$C_{36}H_{42}N_6O_8Ru_2$	$C_{36}H_{42}ClN_6O_{12}Ru_2$	$C_{48}H_{42}B_2F_8N_{18}Cu_2$
formula weight	290.33	667.72	888.89	988.34	1171.69
crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
space group	*C12/c1*	*P*ī	*P*ī	*C12/c1*	*P*ī
a (Å)	29.8216(12)	10.0985(3)	11.6157(2)	27.4670(4)	12.0872(6)
b (Å)	5.7535(3)	12.2520(3)	11.8944(3)	18.9358(3)	12.9737(4)
c (Å)	8.0262(4)	12.9961(3)	15.6228(3)	15.8522(3)	18.0164(7)
α (deg)	90	104.342(2)	68.586(2)	90	107.070(3)
β (deg)	92.646(4)	98.741(2)	89.761(2)	91.1157(15)	101.629(4)
γ (deg)	90	94.354(2)	76.019(2)	90	90.142(3)
V (Å^3)	1375.66(11)	1528.89(7)	1941.48(8)	8243.3(2)	2639.61(19)
Z	4	2	2	8	2
μ (mm^{-1})	0.090	4.533	0.834	7.103	0.888
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
D_{calcd} (g cm^{-3})	1.402	1.450	1.521	1.593	1.474
F(000)	608	688	904	4008	1192
θ range(deg)	2.735 to 24.991	3.567 to 64.995	1.895 to 32.308	2.835 to 64.981	1.646 to 25.000
data/restraints/ parameters	1209/0/101	5113/0/394	12094/0/479	6940/0/524	9294/0/773
R1, wR2 [I>2σ(I)]	0.0453, 0.1154	0.0514, 0.1302	0.0444, 0.1066	0.0649, 0.1706	0.0622, 0.1485
R1, wR2 (all data)	0.0549, 0.1231	0.0544, 0.1339	0.0629, 0.1167	0.0788, 0.1867	0.1064, 0.1723
GOF	1.068	1.079	1.049	1.044	1.040
largest diff. peak/hole [e Å^{-3}]	0.400/-0.240	1.759/-0.878	1.602/-0.981	1.338/-0.826	0.838/-0.580

Table S2 Selected experimental and DFT calculated (M06L/SDD/TZVP) bond lengths (Å)

bond lengths	abim		bond lengths	**1**.C_6H_6		**2**		[**2**]ClO_4	
	X-ray	DFT		X-ray	DFT	X-ray	DFT	X-ray	DFT
N1-N1′	1.271(3)	1.271	Ru1-N1	1.937(3)	1.981	1.988(2)	2.031	2.019(5)	2.019
C1-N2	1.320(2)	1.320	Ru1-N2	2.022(3)	2.050	1.999(2)	2.030	2.008(6)	2.036
C7-N3	1.368(2)	1.365	Ru2-N3	-	-	1.984(2)	2.024	2.009(5)	2.027
C1-N3	1.373(2)	1.387	Ru2-N4	-	-	2.009(3)	2.031	2.014(5)	2.036
C2-C7	1.411(3)	1.418	Ru1-O1	2.057(3)	2.085	2.037(2)	2.073	2.019(4)	2.044
C1-N1	1.397(2)	1.370	Ru1-O2	2.026(2)	2.062	2.028(2)	2.076	2.015(4)	2.051
C2-N2	1.379(2)	1.363	Ru1-O3	2.055(2)	2.079	2.056(2)	2.085	2.050(5)	2.066
			Ru1-O4	2.025(2)	2.057	2.011(2)	2.050	1.999(4)	2.035
			Ru2-O5	-	-	2.047(2)	2.074	2.019(4)	2.044
			Ru2-O6	-	-	2.049(2)	2.081	2.012(4)	2.049
			Ru2-O7	-	-	2.055(2)	2.087	2.011(4)	2.066
			Ru2-O8	-	-	2.011(2)	2.046	1.988(5)	2.034
			N1-N3	1.341(4)	1.327	1.430(3)	1.391	1.392(7)	1.389
			C1-N3	1.360(4)	1.336	1.360(4)	1.355	1.377(8)	1.358
			C9-N1	1.426(4)	1.395	1.358(4)	1.356	1.378(8)	1.358
			C1-N2	1.330(5)	1.342	1.339(4)	1.339	1.327(8)	1.339
			C9-N4	1.303(4)	1.311	1.345(4)	1.339	1.317(8)	1.338
			C9-N6	1.359(5)	1.376	1.378(4)	1.371	1.365(8)	1.365
			C1-N5	1.360(5)	1.368	1.383(4)	1.371	1.357(8)	1.365
			C2-C7	1.418(5)	1.414	1.404(4)	1.406	1.378(11)	1.406
			C10-C15	1.406(5)	1.411	1.408(4)	1.405	1.398(9)	1.406
			Ru1···Ru2	-	-	4.685	4.700	4.665	4.659

Table S3 Selected experimental bond lengths (Å)

Bond	**abim**	Bond	**1.**C_6H_6	**2**	[**2**]ClO_4	Bond	[**3**]$(BF_4)_2$
N1-C1	1.397(2)	Ru1-N1	1.937(3)	1.988(2)	2.019(5)	Cu1-N1	2.032(4)
N2-C1	1.320(2)	Ru1-N2	2.022(3)	1.999(2)	2.008(6)	Cu1-N2	2.083(4)
N3-C1	1.373(2)	Ru1-O1	2.057(3)	2.037(2)	2.019(4)	Cu1-N10	1.983(4)
N1-N1	1.271(3)	Ru1-O2	2.026(2)	2.028(2)	2.015(4)	Cu1-N13	1.980(4)
N2-C2	1.379(2)	Ru1-O3	2.055(2)	2.056(2)	2.050(5)	Cu2-N4	2.000(4)
N3-C7	1.368(2)	Ru1-O4	2.025(2)	2.011(2)	1.999(4)	Cu2-N8	2.195(4)
C2-C7	1.411(3)	N1-N3	1.341(4)	1.430(3)	1.392(7)	Cu2-N7	1.984(4)
		N1-C9	1.426(4)	1.358(4)	1.378(8)	Cu2-N16	2.015(4)
-	-	N2-C1	1.330(5)	1.339(4)	1.327(8)	N1-N3	1.304(5)
-	-	N2-C2	1.381(4)	1.379(4)	1.390(9)	N7-N9	1.293(5)
-	-	N3-C1	1.360(4)	1.360(4)	1.377(8)	N14-N15	1.265(6)
-	-	N4-C9	1.303(4)	1.345(4)	1.317(8)	N1-C9	1.381(6)
-	-	N5-C1	1.360(5)	1.383(4)	1.357(8)	N2-C1	1.343(6)
		N6-C9	1.359(5)	1.378(4)	1.365(8)	N3-C1	1.360(6)
-	-	Ru2-N3	-	1.984(2)	2.009(5)	N2-C2	1.372(6)
-	-	Ru2-N4	-	2.009(3)	2.014(5)	N4-C9	1.334(6)
-	-	Ru2-O5	-	2.047(2)	2.019(4)	N7-C24	1.399(6)
-	-	Ru2-O6	-	2.049(2)	2.012(4)	N8-C16	1.336(6)
-	-	Ru2-O7	-	2.055(2)	2.011(4)	N8-C17	1.381(6)
-	-	Ru2-O8	-	2.011(2)	1.988(5)	N10-C24	1.322(6)
-	-	N4-C10	-	1.375(4)	1.389(8)	N16-C40	1.335(7)
-	-	N6-C15	-	1.391(4)	1.380(8)	N16-C41	1.404(7)
						N14-C32	1.379(6)
						N15-C40	1.389(7)

Table S4 Selected experimental bond angles (deg)

Bond angles	**1.**C_6H_6	**2**	[**2**]ClO_4	Bond angles	[**3**]$(BF_4)_2$
N1-Ru1-N2	76.88(12)	76.81(10)	76.1(2)	N1-Cu1-N2	78.85(15)
N1-Ru1-O1	176.16(9)	172.40(10)	173.20(19)	N1-Cu1-N10	136.02(15)
N1-Ru1-O2	92.96(11)	95.23(10)	95.21(19)	N1-Cu1-N13	106.59(16)
N1-Ru1-O3	97.18(11)	100.08(9)	100.85(18)	N2-Cu1-N10	110.31(15)
N1-Ru1-O4	90.93(11)	89.76(10)	88.79(18)	N2-Cu1-N13	118.07(16)
N2-Ru1-O1	101.35(11)	98.52(10)	98.8(2)	N10-Cu1-N13	105.87(16)
N2-Ru1-O2	91.07(11)	91.08(10)	93.7(2)	N4-Cu2-N7	131.67(16)
N2-Ru1-O3	174.00(9)	176.90(9)	175.83(18)	N4-Cu2-N8	104.11(14)
N2-Ru1-O4	88.31(11)	86.69(9)	84.5(2)	N4-Cu2-N16	106.71(16)
O1-Ru1-O2	90.47(10)	90.82(9)	89.60(19)	N7-Cu2-N8	76.74(15)
O1-Ru1-O3	84.63(10)	84.55(9)	83.97(18)	N7-Cu2-N16	118.56(16)
O1-Ru1-O4	85.60(10)	83.93(9)	86.18(18)	N8-Cu2-N16	109.73(16)
O2-Ru1-O3	88.34(10)	89.33(9)	89.34(19)	-	-
O2-Ru1-O4	175.81(8)	173.93(9)	175.11(19)	-	-
O3-Ru1-O4	92.71(10)	93.21(9)	92.7(2)	-	-
N3-Ru2-N4	-	77.79(10)	77.5(2)	-	-
N3-Ru2-O5	-	174.31(9)	173.44(19)	-	-
N3-Ru2-O6	-	94.05(9)	94.57(19)	-	-
N3-Ru2-O7	-	98.55(9)	99.74(19)	-	-
N3-Ru2-O8	-	89.55(9)	90.5(2)	-	-
N4-Ru2-O5	-	99.14(10)	97.54(19)	-	-
N4-Ru2-O6	-	90.19(10)	93.86(19)	-	-
N4-Ru2-O7	-	176.12(9)	176.5(2)	-	-
N4-Ru2-O8	-	85.98(9)	85.0(2)	-	-
O5-Ru2-O6	-	90.73(9)	90.02(18)	-	-
O5-Ru2-O7	-	84.40(9)	85.04(18)	-	-
O5-Ru2-O8	-	85.44(9)	84.77(19)	-	-
O6-Ru2-O7	-	91.36(9)	88.55(18)	-	-
O6-Ru2-O8	-	174.08(9)	174.47(19)	-	-
O7-Ru2-O8	-	92.75(9)	92.84(19)	-	-

Table S5 Composition and energies of selected molecular orbitals of **abim** (*S*=0)

MO	Energy (eV)	Composition	
		azo	ring
HOMO-5	-6.710	0.02	0.98
HOMO-4	-6.335	0.13	0.87
HOMO-3	-5.810	0.00	1.00
HOMO-2	-5.797	0.00	1.00
HOMO-1	-5.605	0.63	0.37
HOMO	-5.407	0.09	0.91
LUMO	-3.393	0.47	0.53
LUMO+1	-1.055	0.02	0.98
LUMO+2	-0.715	0.08	0.92
LUMO+3	-0.393	0.01	0.99
LUMO+4	-0.387	0.00	1.00
LUMO+5	0.924	0.04	0.96

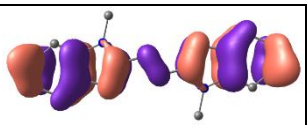
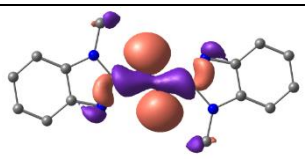
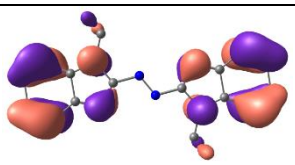
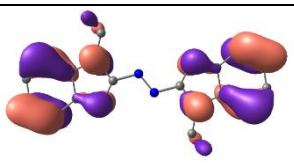
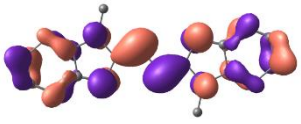
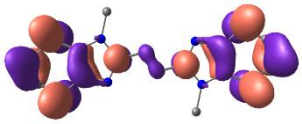
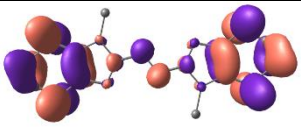
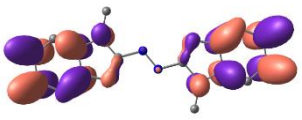
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S6 Composition and energies of selected molecular orbitals of **abim**$^-$ (S=1/2)

MO	Energy (eV)	Composition	
		azo	ring
	α-spin		
HOMO-5	-2.980	0.02	0.98
HOMO-4	-2.438	0.00	1.00
HOMO-3	-2.421	0.00	1.00
HOMO-2	-1.830	0.12	0.88
HOMO-1	-1.618	0.56	0.44
SOMO	-0.084	0.42	0.58
LUMO	2.251	0.02	0.98
LUMO+1	2.560	0.07	0.93
LUMO+2	2.856	0.01	0.99
LUMO+3	2.857	0.00	1.00
LUMO+4	4.107	0.00	1.00
LUMO+5	4.127	0.00	1.00
	β-spin		
HOMO-5	-2.895	0.02	0.98
HOMO-4	-2.805	0.08	0.92
HOMO-3	-2.296	0.01	0.99
HOMO-2	-2.246	0.00	1.00
HOMO-1	-1.562	0.16	0.84
HOMO	-1.382	0.53	0.47
LUMO	0.568	0.34	0.66
LUMO+1	2.371	0.02	0.98
LUMO+2	2.762	0.07	0.93
LUMO+3	2.921	0.00	1.00
LUMO+4	2.938	0.03	0.97
LUMO+5	4.095	0.00	1.00

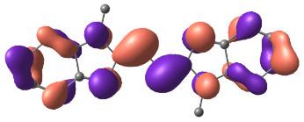
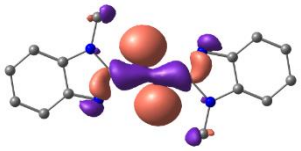
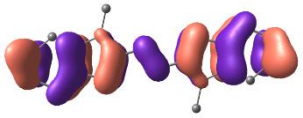
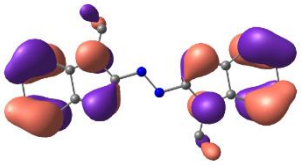
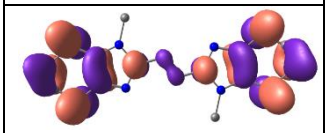
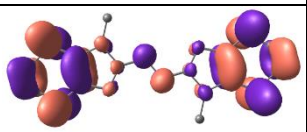
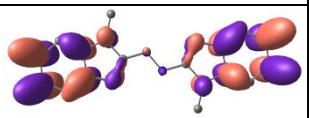
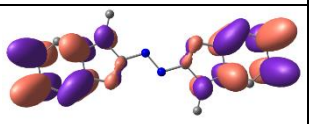
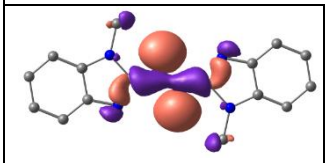
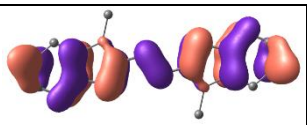
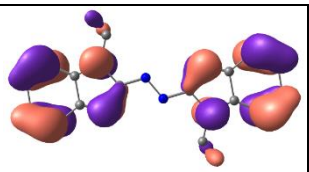
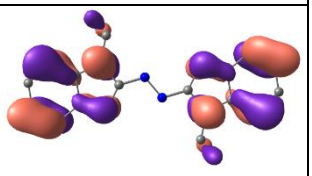
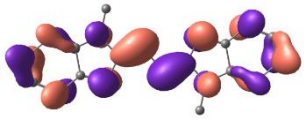
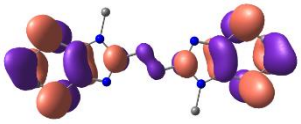
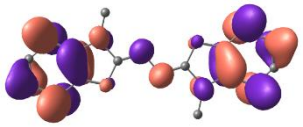
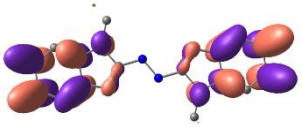
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 Composition and energies of selected molecular orbitals of **abim**$^{2-}$ (*S*=0)

MO	Energy (eV)	Composition	
		azo	ring
HOMO-5	0.722	0.01	0.99
HOMO-4	1.030	0.00	1.00
HOMO-3	1.098	0.01	0.99
HOMO-2	1.923	0.16	0.84
HOMO-1	2.598	0.41	0.59
HOMO	4.025	0.32	0.68
LUMO	5.723	0.02	0.98
LUMO+1	6.093	0.05	0.95
LUMO+2	6.224	0.00	1.00
LUMO+3	6.259	0.04	0.96
LUMO+4	6.829	0.00	1.00
LUMO+5	6.847	0.00	1.00

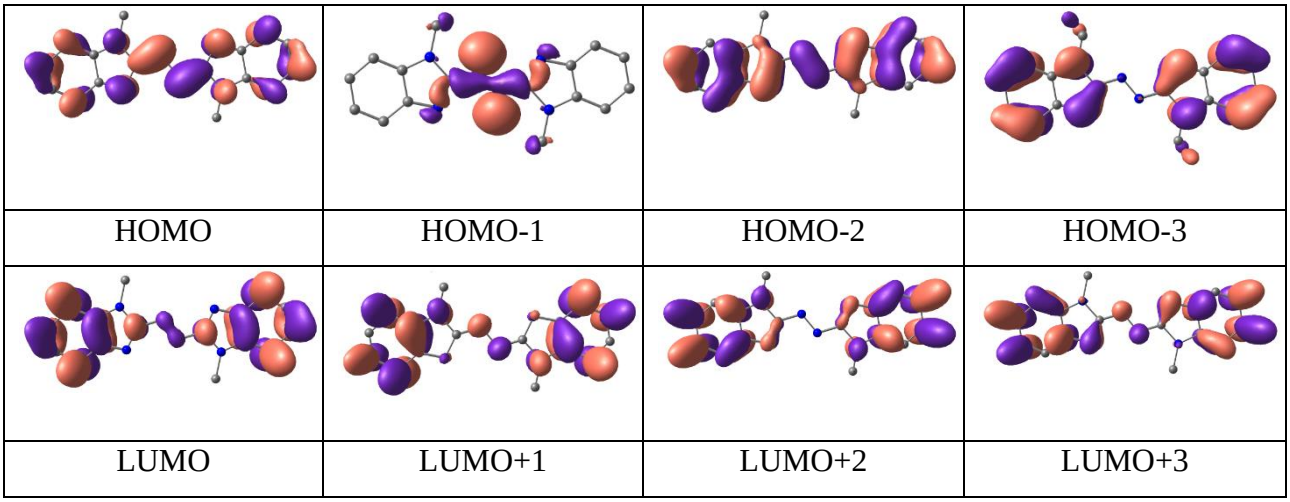


Table S8 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (S=1/2)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
		α-spin		
HOMO-5	-8.943	0.09	0.32/0.01	0.57
HOMO-4	-8.623	0.68	0.14/0.03	0.14
HOMO-3	-8.433	0.52	0.28/0.04	0.17
HOMO-2	-8.194	0.14	0.75/0.02	0.09
HOMO-1	-8.144	0.40	0.23/0.02	0.35
SOMO	-8.081	0.20	0.67/0.04	0.08
LUMO	-6.576	0.11	0.47/0.37	0.04
LUMO+1	-5.041	0.31	0.08/0.03	0.58
LUMO+2	-5.004	0.20	0.26/0.02	0.52
LUMO+3	-4.748	0.37	0.18/0.10	0.34
LUMO+4	-4.542	0.37	0.17/0.01	0.46
LUMO+5	-3.857	0.03	0.87/0.07	0.03
		β-spin		
HOMO-5	-8.951	0.15	0.64/0.02	0.19
HOMO-4	-8.807	0.04	0.14/0.01	0.81
HOMO-3	-8.345	0.46	0.37/0.06	0.11
HOMO-2	-8.224	0.55	0.24/0.07	0.14
HOMO-1	-8.168	0.10	0.85/0.02	0.03
HOMO	-7.989	0.46	0.39/0.02	0.13
LUMO	-7.020	0.62	0.13/0.02	0.23
LUMO+1	-6.550	0.17	0.44/0.34	0.05
LUMO+2	-4.931	0.07	0.18/0.01	0.73
LUMO+3	-4.897	0.13	0.15/0.01	0.71
LUMO+4	-4.287	0.47	0.20/0.12	0.21
LUMO+5	-4.093	0.45	0.23/0.00	0.31

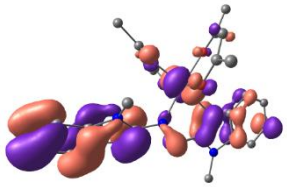
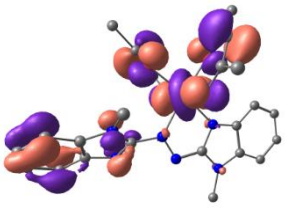
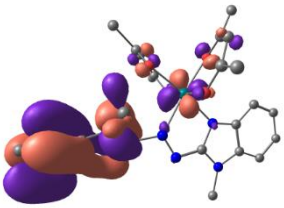
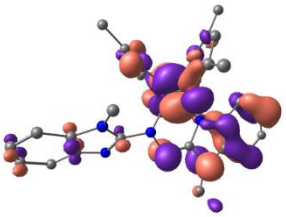
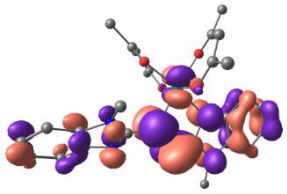
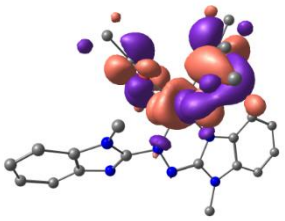
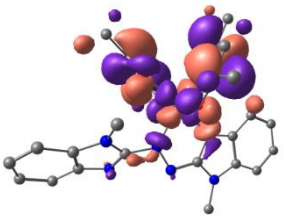
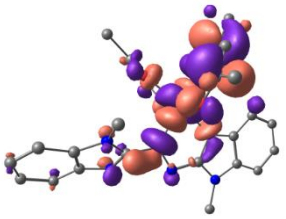
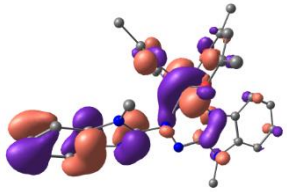
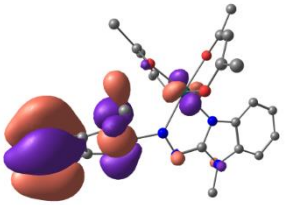
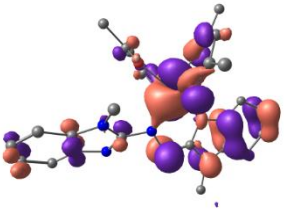
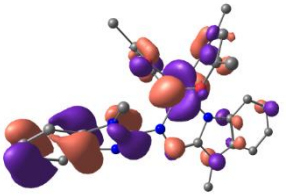
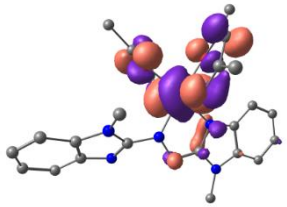
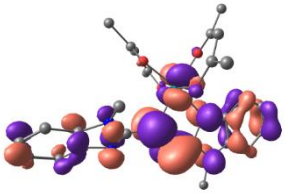
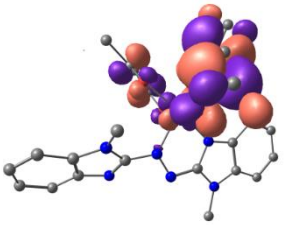
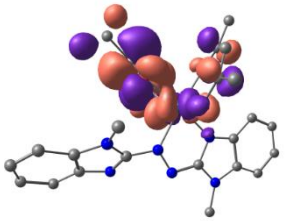
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S9 Composition and energies of selected molecular orbitals of **1** (*S*=0)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
HOMO-5	-5.550	0.07	0.66/0.05	0.23
HOMO-4	-5.505	0.08	0.30/0.01	0.62
HOMO-3	-5.438	0.04	0.89/0.05	0.02
HOMO-2	-4.776	0.52	0.17/0.11	0.20
HOMO-1	-4.463	0.67	0.15/0.04	0.14
HOMO	-4.035	0.71	0.09/0.02	0.18
LUMO	-3.212	0.26	0.40/0.27	0.07
LUMO+1	-1.534	0.06	0.25/0.01	0.69
LUMO+2	-1.430	0.11	0.15/0.03	0.70
LUMO+3	-1.125	0.22	0.61/0.06	0.11
LUMO+4	-0.930	0.24	0.52/0.07	0.17
LUMO+5	-0.828	0.32	0.43/0.04	0.21

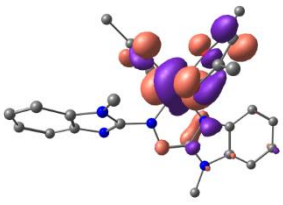
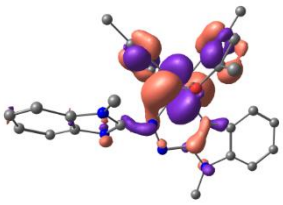
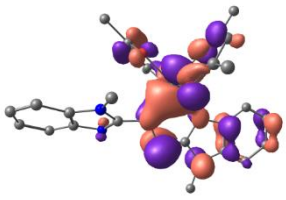
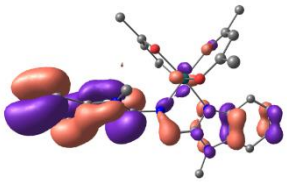
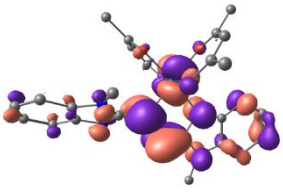
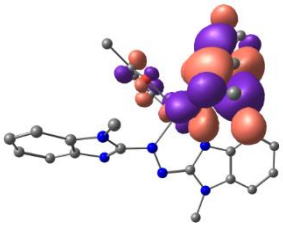
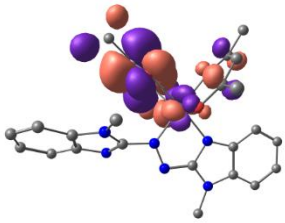
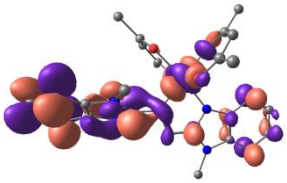
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Composition and energies of selected molecular orbitals of $\mathbf{1}^{-}$ (S=1/2)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
		α-spin		
HOMO-5	-2.592	0.06	0.13/0.01	0.80
HOMO-4	-2.328	0.07	0.78/0.10	0.05
HOMO-3	-1.512	0.56	0.17/0.10	0.17
HOMO-2	-1.153	0.72	0.14/0.02	0.12
HOMO-1	-0.723	0.75	0.09/0.01	0.15
SOMO	-0.256	0.26	0.42/0.25	0.07
LUMO	1.338	0.06	0.23/0.01	0.71
LUMO+1	1.490	0.10	0.19/0.03	0.68
LUMO+2	1.837	0.12	0.77/0.03	0.09
LUMO+3	2.158	0.10	0.70/0.07	0.13
LUMO+4	2.347	0.43	0.28/0.02	0.26
LUMO+5	2.477	0.55	0.20/0.01	0.24
		β-spin		
HOMO-5	-2.572	0.02	0.91/0.03	0.04
HOMO-4	-2.555	0.04	0.16/0.03	0.76
HOMO-3	-2.195	0.08	0.75/0.12	0.05
HOMO-2	-1.069	0.64	0.15/0.08	0.12
HOMO-1	-0.971	0.63	0.18/0.05	0.14
HOMO	-0.571	0.74	0.10/0.02	0.15
LUMO	0.300	0.27	0.43/0.21	0.09
LUMO+1	1.358	0.07	0.24/0.01	0.69
LUMO+2	1.508	0.10	0.19/0.03	0.67
LUMO+3	1.927	0.09	0.80/0.03	0.07
LUMO+4	2.299	0.16	0.65/0.07	0.12
LUMO+5	2.457	0.57	0.19/0.01	0.23

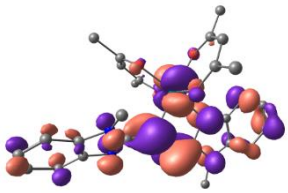
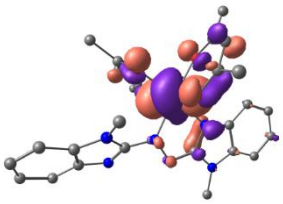
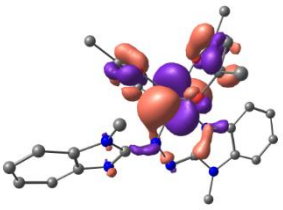
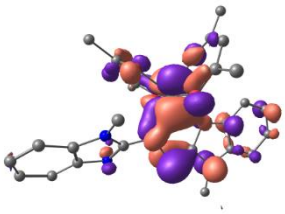
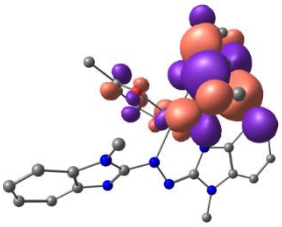
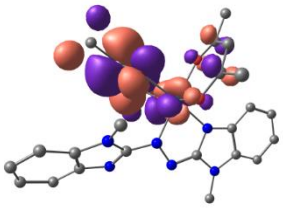
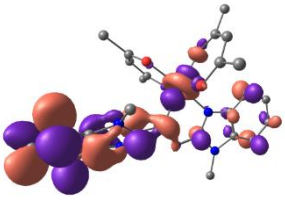
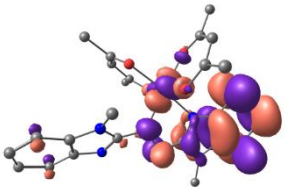
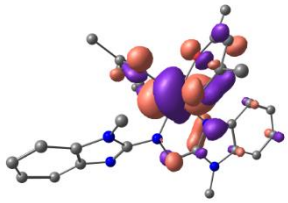
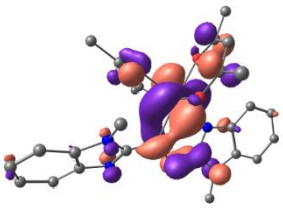
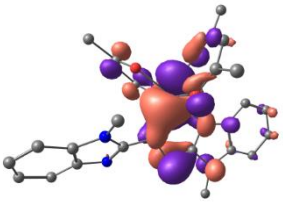
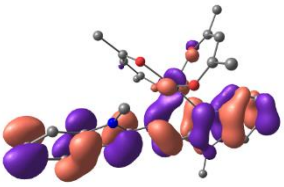
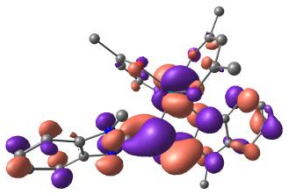
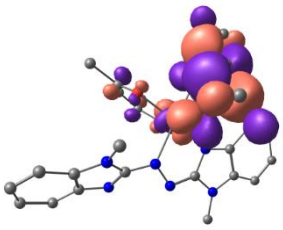
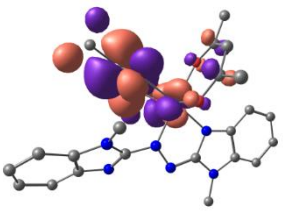
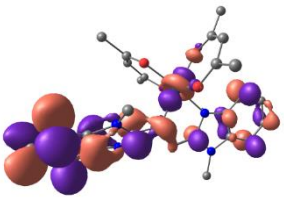
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Composition and energies of selected molecular orbitals of $\mathbf{1}^{2-}$ (*S*=0)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
HOMO-5	0.454	0.04	0.61/0.28	0.07
HOMO-4	1.010	0.08	0.76/0.13	0.04
HOMO-3	1.981	0.52	0.21/0.12	0.14
HOMO-2	2.112	0.70	0.16/0.01	0.13
HOMO-1	2.562	0.75	0.09/0.01	0.15
HOMO	2.955	0.33	0.37/0.18	0.11
LUMO	4.146	0.06	0.22/0.01	0.72
LUMO+1	4.317	0.08	0.29/0.02	0.60
LUMO+2	4.719	0.59	0.13/0.01	0.27
LUMO+3	4.900	0.12	0.70/0.02	0.16
LUMO+4	5.185	0.10	0.55/0.05	0.30
LUMO+5	5.418	0.17	0.44/0.04	0.35

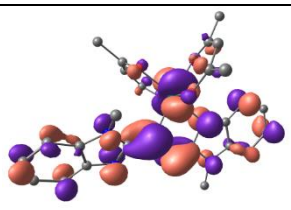
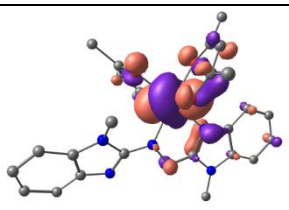
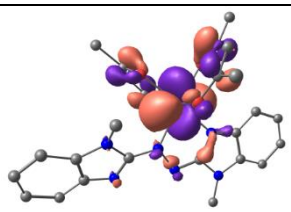
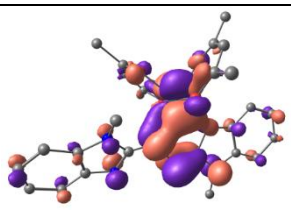
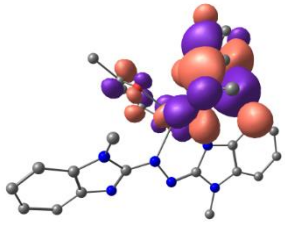
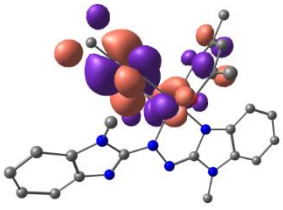
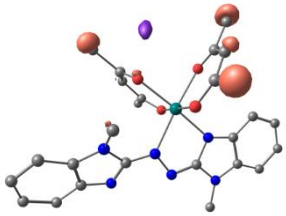
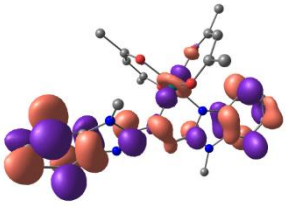
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S12 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2+}$ (S=1)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
		α-spin		
HOMO-5	-7.962	0.37	0.12/0.05	0.46
HOMO-4	-7.825	0.44	0.28/0.04	0.25
HOMO-3	-7.515	0.50	0.20/0.02	0.28
HOMO-2	-7.342	0.55	0.19/0.07	0.19
SOMO 2	-7.339	0.69	0.11/0.03	0.17
SOMO 1	-6.838	0.60	0.14/0.03	0.24
LUMO	-6.249	0.36	0.27/0.25	0.11
LUMO+1	-4.584	0.25	0.10/0.06	0.59
LUMO+2	-4.512	0.10	0.30/0.00	0.59
LUMO+3	-4.252	0.43	0.16/0.09	0.32
LUMO+4	-4.031	0.06	0.24/0.01	0.69
LUMO+5	-3.975	0.12	0.23/0.03	0.62
		β-spin		
HOMO-5	-8.011	0.16	0.21/0.03	0.60
HOMO-4	-7.775	0.47	0.15/0.08	0.30
HOMO-3	-7.656	0.58	0.23/0.03	0.16
HOMO-2	-7.291	0.68	0.12/0.03	0.16
HOMO-1	-7.227	0.68	0.10/0.02	0.19
HOMO	-6.688	0.56	0.19/0.04	0.21
LUMO	-6.421	0.59	0.18/0.04	0.19
LUMO+1	-6.170	0.43	0.22/0.22	0.13
LUMO+2	-4.500	0.09	0.20/0.03	0.68
LUMO+3	-4.447	0.09	0.20/0.01	0.70
LUMO+4	-4.038	0.08	0.25/0.02	0.65
LUMO+5	-3.981	0.13	0.20/0.05	0.63

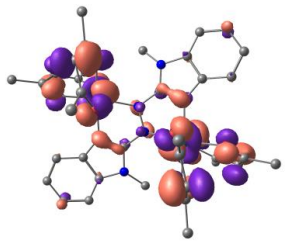
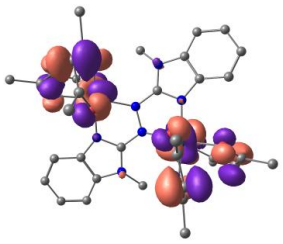
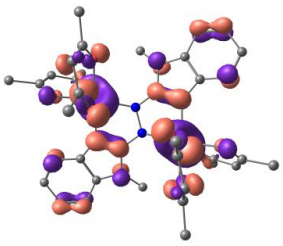
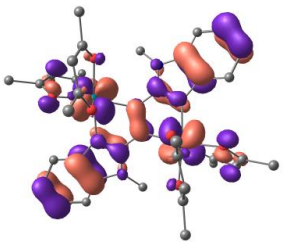
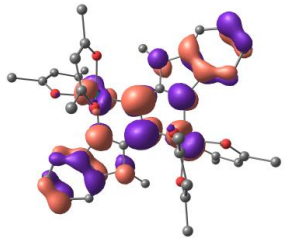
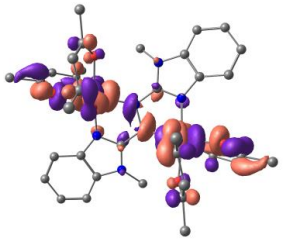
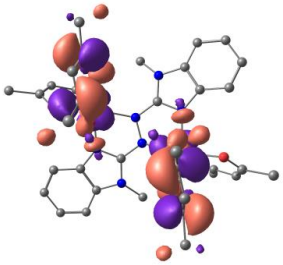
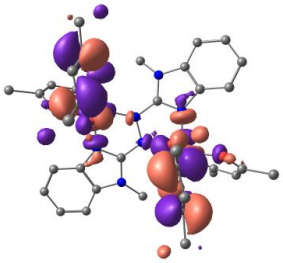
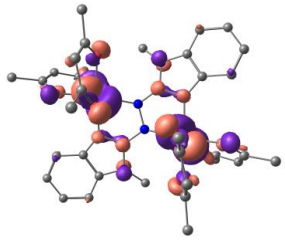
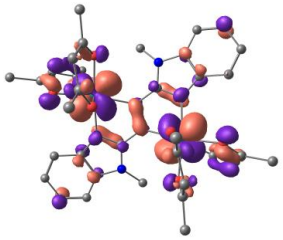
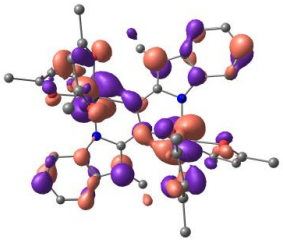
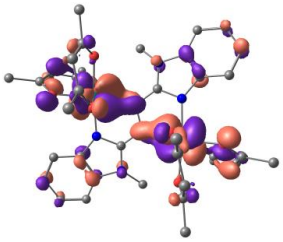
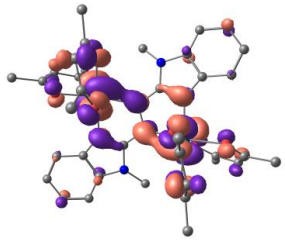
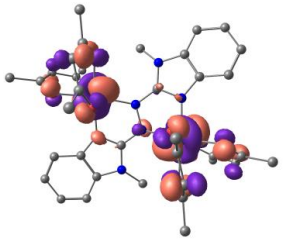
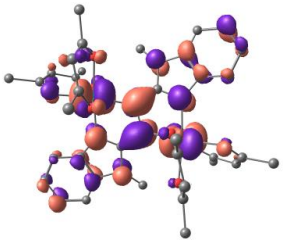
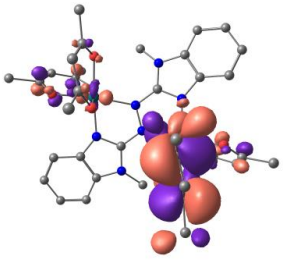
α-spin			
			
SOMO 1	SOMO 2	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energies of selected molecular orbitals of $\mathbf{2}^{+}$ (S=1/2)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
		α-spin		
HOMO-5	-10.834	0.46	0.40/0.02	0.12
HOMO-4	-10.578	0.43	0.33/0.02	0.21
HOMO-3	-10.556	0.46	0.33/0.04	0.17
HOMO-2	-10.415	0.60	0.18/0.02	0.20
HOMO-1	-10.220	0.41	0.21/0.01	0.37
SOMO	-10.168	0.42	0.21/0.05	0.33
LUMO	-9.218	0.22	0.37/0.30	0.10
LUMO+1	-7.310	0.49	0.06/0.11	0.34
LUMO+2	-7.200	0.24	0.27/0.00	0.48
LUMO+3	-7.151	0.30	0.24/0.02	0.44
LUMO+4	-7.098	0.30	0.15/0.05	0.50
LUMO+5	-6.912	0.13	0.18/0.01	0.68
		β-spin		
HOMO-5	-10.878	0.05	0.09/0.01	0.86
HOMO-4	-10.735	0.19	0.69/0.06	0.06
HOMO-3	-10.576	0.56	0.13/0.07	0.23
HOMO-2	-10.381	0.51	0.24/0.04	0.21
HOMO-1	-10.330	0.66	0.13/0.03	0.18
HOMO	-10.080	0.69	0.11/0.02	0.18
LUMO	-9.213	0.47	0.28/0.06	0.19
LUMO+1	-9.121	0.57	0.16/0.04	0.23
LUMO+2	-9.095	0.42	0.21/0.21	0.16
LUMO+3	-7.048	0.15	0.22/0.02	0.61
LUMO+4	-7.045	0.16	0.19/0.02	0.63
LUMO+5	-6.988	0.10	0.24/0.04	0.62

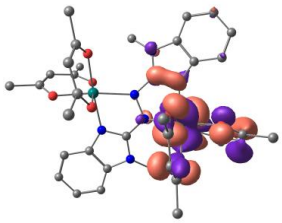
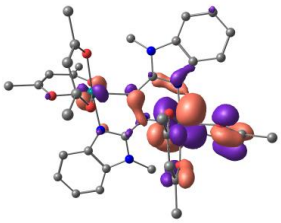
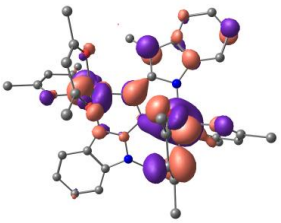
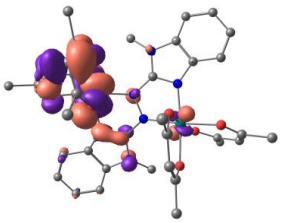
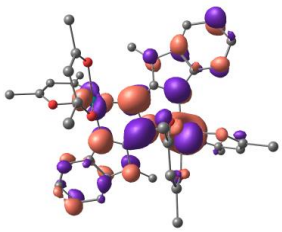
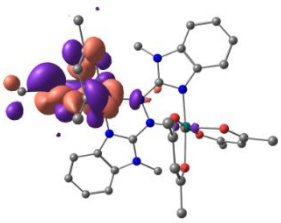
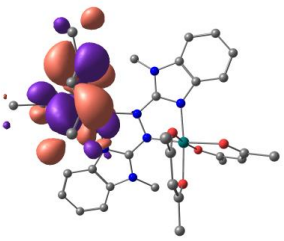
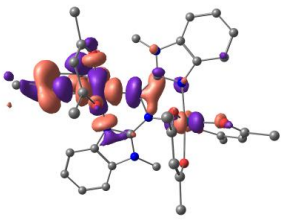
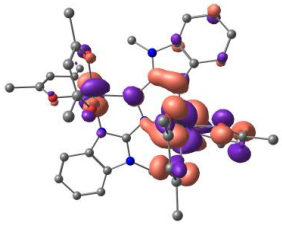
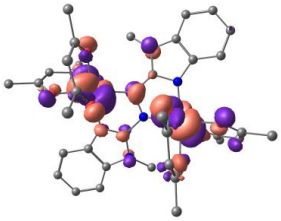
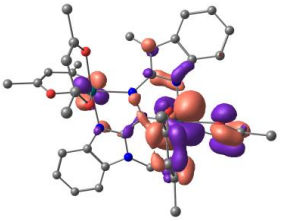
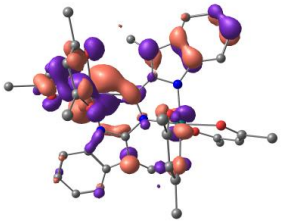
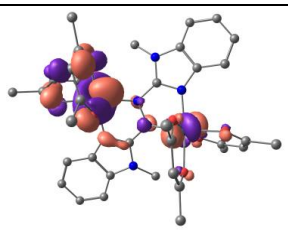
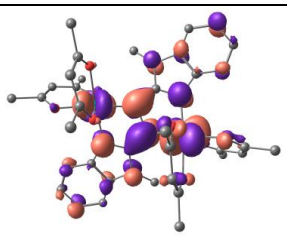
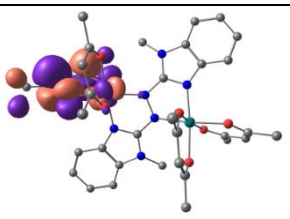
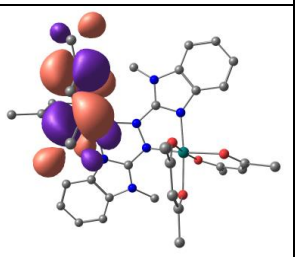
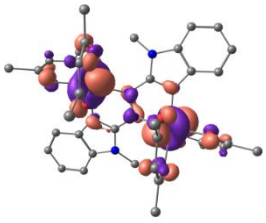
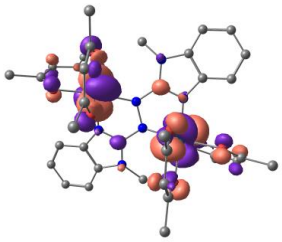
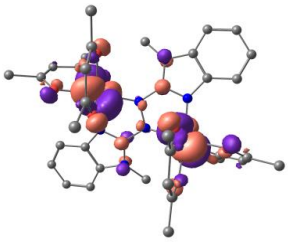
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

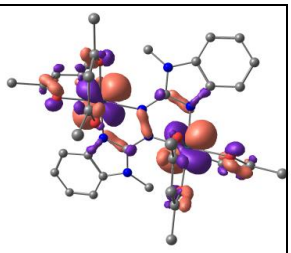
Table S14 Composition and energies of selected molecular orbitals of **2** (*S*=0)

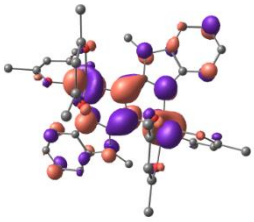
MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
HOMO-5	-4.918	0.25	0.33/0.15	0.26
HOMO-4	-4.459	0.70	0.13/0.03	0.14
HOMO-3	-4.291	0.74	0.10/0.02	0.13
HOMO-2	-4.120	0.74	0.07/0.01	0.18
HOMO-1	-3.872	0.67	0.14/0.01	0.18
HOMO	-3.745	0.62	0.16/0.06	0.17
LUMO	-3.282	0.45	0.23/0.22	0.11
LUMO+1	-1.476	0.05	0.33/0.01	0.61
LUMO+2	-1.475	0.05	0.21/0.02	0.72
LUMO+3	-1.374	0.12	0.13/0.05	0.71
LUMO+4	-1.306	0.08	0.24/0.01	0.68
LUMO+5	-1.030	0.03	0.78/0.03	0.16

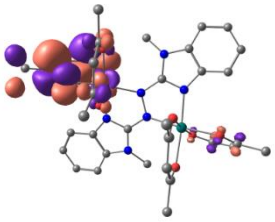

HOMO

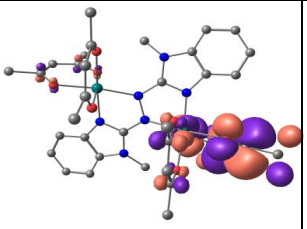

HOMO-1


HOMO-2


HOMO-3


LUMO


LUMO+1


LUMO+2

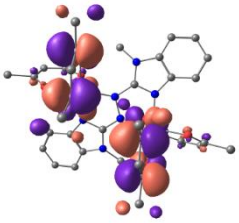

LUMO+3

Table S15 Composition and energies of selected molecular orbitals of $\mathbf{2}^{-}$ (S=1/2)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
		α-spin		
HOMO-5	-1.502	0.73	0.12/0.02	0.13
HOMO-4	-1.388	0.73	0.11/0.02	0.14
HOMO-3	-1.282	0.77	0.06/0.01	0.15
HOMO-2	-0.968	0.72	0.11/0.00	0.16
HOMO-1	-0.845	0.67	0.13/0.05	0.15
SOMO	-0.579	0.43	0.25/0.20	0.11
LUMO	1.095	0.05	0.18/0.01	0.76
LUMO+1	1.098	0.05	0.31/0.01	0.63
LUMO+2	1.257	0.13	0.14/0.04	0.68
LUMO+3	1.329	0.07	0.29/0.01	0.63
LUMO+4	1.698	0.03	0.79/0.02	0.16
LUMO+5	1.795	0.17	0.56/0.03	0.23
		β-spin		
HOMO-5	-1.779	0.31	0.35/0.19	0.16
HOMO-4	-1.401	0.71	0.13/0.02	0.13
HOMO-3	-1.232	0.75	0.10/0.01	0.13
HOMO-2	-0.918	0.73	0.08/0.00	0.18
HOMO-1	-0.859	0.72	0.11/0.00	0.16
HOMO	-0.667	0.66	0.15/0.06	0.13
LUMO	-0.167	0.45	0.25/0.17	0.13
LUMO+1	1.119	0.05	0.22/0.01	0.71
LUMO+2	1.127	0.07	0.28/0.01	0.64
LUMO+3	1.266	0.13	0.15/0.04	0.67
LUMO+4	1.338	0.07	0.29/0.01	0.63
LUMO+5	1.760	0.03	0.77/0.02	0.17

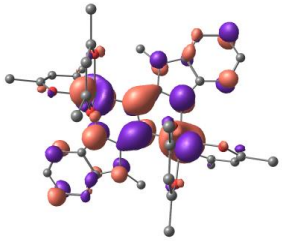
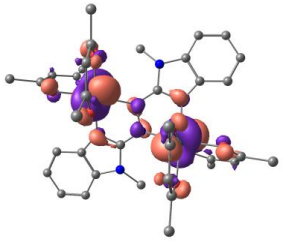
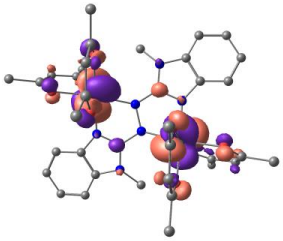
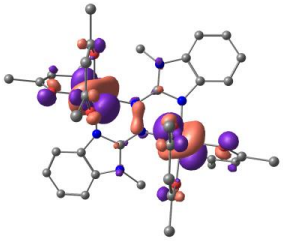
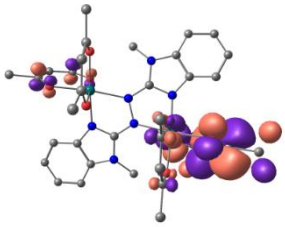
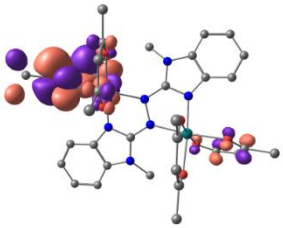
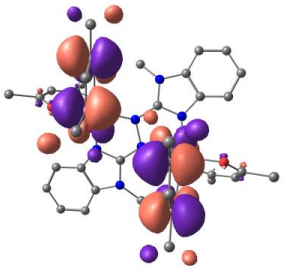
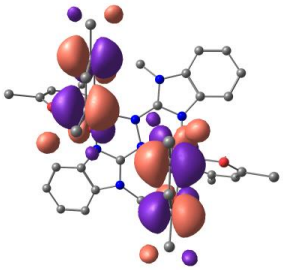
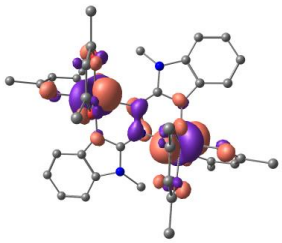
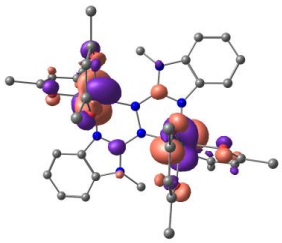
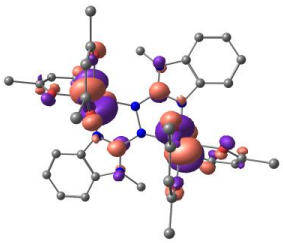
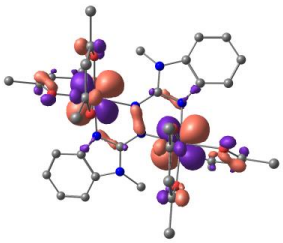
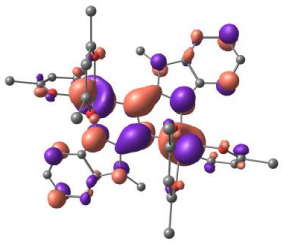
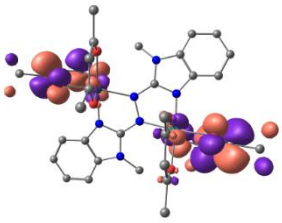
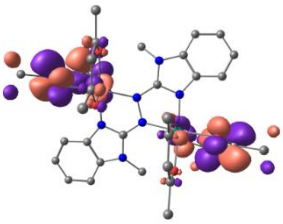
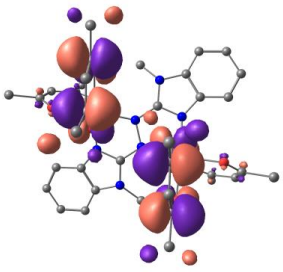
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2-}$ (*S*=0)

MO	Energy (eV)	Composition		
		Ru	**abim**(ring/azo)	acac
HOMO-5	1.457	0.71	0.13/0.02	0.14
HOMO-4	1.598	0.71	0.14/0.01	0.14
HOMO-3	1.811	0.74	0.08/0.02	0.17
HOMO-2	1.970	0.75	0.09/0.00	0.15
HOMO-1	2.120	0.68	0.13/0.05	0.14
HOMO	2.395	0.44	0.27/0.14	0.15
LUMO	4.661	0.05	0.20/0.01	0.74
LUMO+1	3.669	0.06	0.26/0.01	0.67
LUMO+2	3.828	0.19	0.16/0.03	0.61
LUMO+3	3.887	0.07	0.33/0.01	0.59
LUMO+4	4.344	0.55	0.20/0.01	0.24
LUMO+5	4.398	0.72	0.10/0.00	0.18

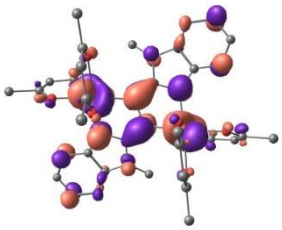
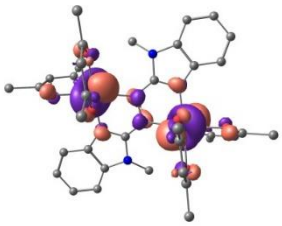
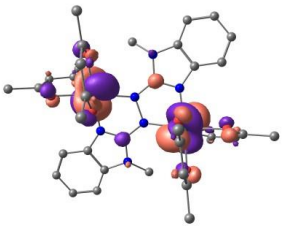
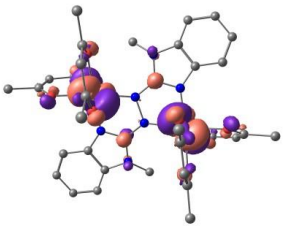
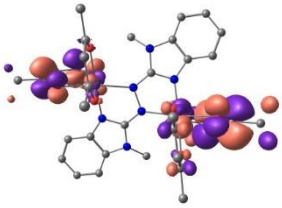
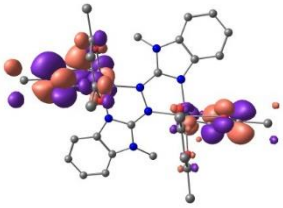
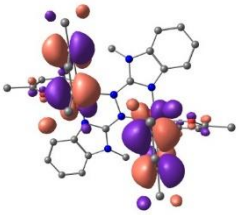
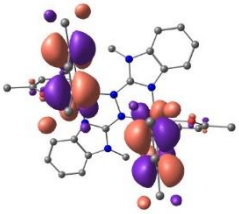
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 Experimental and TD-DFT (M06L(CPCM)/TZVP/SDD) calculated electronic transitions in CH_2Cl_2

λ [nm] expt (DFT)	ε /dm^3 mol^{-1} cm^{-1} (f)	Transitions	Character
abim(S=0)			
501(505)	19600(0.204)	HOMO-2→LUMO(0.60)	ring(π)→ring(π*)/azo(π*)
444(482)	25200(1.254)	HOMO→LUMO(0.61)	ring(π)→ring(π*)/azo(π*)
243(256)	8200(0.126)	HOMO→LUMO+2(0.52)	ring(π)→ring(π*)
abim$^-$(S=1/2)			
537(567)	6400(0.370)	HOMO(β)→LUMO(β)(0.95)	azo(π)/ring(π)→ring(π*)/azo(π*)
507(474)	7200(0.027)	HOMO-3(β)→LUMO(β)(0.96)	ring(π)→ring(π*)/azo(π*)
468(451)	6200(0.860)	HOMO(α)→LUMO(α)(0.94)	ring(π)/azo(π)→ring(π*)
315(383)	6930(0.024)	HOMO(α)→LUMO+3(α)(0.96)	ring(π)/azo(π)→ring(π*)
288(268)	10400(0.250)	HOMO(β)→LUMO+2(β)(0.49) HOMO(α)→LUMO+4(α)(0.49)	ring(π)/azo(π)→ring(π*) ring(π)/azo(π)→ring(π*)
1$^+$(S=1/2)			
744(666)	3000(0.040)	HOMO-5(β)→LUMO(β)(0.62)	abim(π)→Ru(dπ)/acac(π*)
531(560)	25600(0.156)	HOMO-4(β)→LUMO+1(β)(0.45) HOMO-6(α)→LUMO(α)(0.43)	acac(π)→abim(π*) abim(π)/acac(π)→abim(π*)
1(S=0)			
946(953)	340(0.011)	HOMO-1→LUMO(0.69)	Ru(dπ)/abim(π)→abim(π*)/Ru(dπ)
534(498)	14800(0.434)	HOMO-3→LUMO(0.55) HOMO-4→LUMO(0.39)	abim(π)→abim(π*)/Ru(dπ) acac(π)/abim(π)→abim(π*)/Ru(dπ)
414(397)	12200(0.029)	HOMO→LUMO+3(0.56)	Ru(dπ)→abim(π*)/Ru(dπ)
330(331)	12600(0.035)	HOMO-2→LUMO+3(0.66)	Ru(dπ)/abim(π)/acac(π)→abim(π*)/Ru(dπ)
1$^-$ (S=1/2)			
786(810)	580(0.078)	HOMO-2(β)→LUMO(β)(0.91)	Ru(dπ)/abim(π)→abim(π*)/Ru(dπ)
546(503)	5400(0.230)	HOMO-3(β)→LUMO(β)(0.84)	abim(π)→abim(π*)/Ru(dπ)
450(439)	7000(0.037)	HOMO-1(α)→LUMO+2(α)(0.59)	Ru(dπ)→abim(π*)
360(389)	8600(0.061)	HOMO(α)→LUMO+7(α)(0.64)	abim(π)/Ru(dπ)→abim(π*)/Ru(dπ)
2$^+$(S=1/2)			
848(763)	2200(0.209)	HOMO-2(α)→LUMO(α)(0.61)	Ru(dπ)/abim(π)→abim(π*)/Ru(dπ)
581(596)	5600(0.029)	HOMO-6(β)→LUMO+1(β)(0.50) HOMO-10(β)→LUMO(β)(0.39)	abim(dπ)/acac(π)→abim(π*)/Ru(dπ) abim(π)→Ru(dπ)/abim(π*)
485(483)	4800(0.094)	HOMO-12(α)→LUMO(α)(0.71)	acac(π)→abim(π*)/Ru(dπ)
2(S=0)			
854(801)	5200(0.249)	HOMO-2→LUMO(0.64)	Ru(dπ)→abim(π*)/Ru(dπ)

596(607) (531)	2800(0.037) (0.199)	HOMO-5→LUMO(0.66) HOMO-6→LUMO(0.52)	abim(π)/acac(π)/Ru(dπ)→abim(π*)/Ru(dπ) acac(π)→abim(π*)/Ru(dπ)
485(481)	5000(0.203)	HOMO-9→LUMO(0.57)	acac(π)/Ru(dπ)→abim(π*)/Ru(dπ)
347(340)	13200(0.043)	HOMO-4→LUMO+5(0.63)	Ru(dπ)→abim(π*)
2^{-}(*S*=1/2)			
674(680)	5600(0.013)	HOMO-5(β)→LUMO(β)(0.88)	abim(π)/Ru(dπ)→Ru(dπ)/abim(π*)
557(544)	7400(0.024)	HOMO-2(α)→LUMO+1(α)(0.69)	Ru(dπ)→acac(π*)/abim(π*)
332(332)	15000(0.024)	HOMO-5(β)→LUMO+5(β)(0.79)	abim(π)/Ru(dπ)→abim(π*)