Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Ruthenium nitrosyl complexes with molecular framework $[Ru^{II}(dmdptz)(bpy)(NO)]^{n+}$ (dmdptz: *N*,*N*-dimethyl-4,6-di(pyridin-2-yl)-1,3,5-triazin-2-amine and bpy: 2,2'-bipyridine). Electronic structure, reactivity aspects, photorelease, and scavenging of NO

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Table S1

IR Vibrational Frequencies (cm^{-1}) of Complexes[a]

complex	$\nu_{ClO_4^-}$	ν_{NO}	ν_{NO_2}
[**1**](ClO_4)	1079/616	–	–
[**2**](ClO_4)$_2$	1081/619	–	–
[**3**](ClO_4)	1077/616	–	1332/1286
[**4**](ClO_4)$_3$	1066/616	1914	–
[**4**](ClO_4)$_2$	1065/616	1550[a]	–

[a]Broad band involving ν_{NO} (±5 cm^{-1}).

Table S2

Selected crystallographic data for [**4**]$(ClO_4)_3$.

Complex	[**4**]$(ClO_4)_3$
Empirical formula	$C_{25}H_{22}N_9O_{13}Cl_3Ru$
Formula weight	863.93
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	22.621(3)
b (Å)	10.9659(14)
c (Å)	14.998(2)
α (deg)	90
β (deg)	102.130(16)
γ (deg)	90
V (Å^3)	3637.4(10)
Z	4
T (K)	290
μ (mm^{-1})	0.723
ρ_{calcd} (g cm^{-3})	1.578
F (000)	1736.0
2θ range (deg)	4.638 to 58.894
data/restraints/parameters	8379/0/462
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.1722, wR_2 = 0.4224
R_1, wR_2 (all data)	R_1 = 0.2722, wR_2 = 0.4846
Goodness-of-fit on F^2	1.168
Largest difference between peak and hole (e Å^{-3})	2.58/-1.41

Table S3
Selected bond distances (Å) and bond angles (°) for [**4**]$(ClO_4)_3$.

Bond distance / Bond angle	[**4**]$(ClO_4)_3$ (X = N6)
Ru1–N1	2.12(1)
Ru1–N2	1.96(1)
Ru1–N3	2.14(1)
Ru1–N4	2.10(1)
Ru1–N5	2.13(1)
Ru1–X	1.72(1)
O1–X	1.17(2)
Ru1–X–O1	171(1)
N1–Ru1–N2	80.5(5)
N2–Ru1–N3	79.0(5)
N1–Ru1–N3	158.9(5)
N4–Ru1–N5	78.0(5)
N1–Ru1–X	92.7(6)
N2–Ru1–X	96.7(6)
N3–Ru1–X	94.3(6)
N4–Ru1–X	95.1(6)
N5–Ru1–X	172.2(5)
N5–Ru1–N1	85.0(5)
N5–Ru1–N2	90.4(5)
N5–Ru1–N3	90.4(5)
N2–Ru1–N4	168.1(6)
N3–Ru1–N4	98.7(5)
N1–Ru1–N4	100.4(5)

For [4]$(ClO_4)_3$ CCDC-2006984 contains the supplementary crystallographic data.

Table S4. DFT Calculated Selected MO Compositions for 4^{3+} in *S* = 0 State

MO	energy (eV)	% composition			
		Ru	dmdptz	bpy	NO
LUMO+5	-3.034	44	42	05	09
LUMO+4	-3.214	04	01	92	03
LUMO+3	-3.362	16	74	08	03
LUMO+2	-3.634	02	96	00	02
LUMO+1	-4.579	23	07	03	66
LUMO	-4.592	24	05	06	65
HOMO	-7.679	03	92	02	03
HOMO-1	-7.953	01	00	99	00
HOMO-2	-8.384	38	50	11	00
HOMO-3	-8.543	00	99	00	00
HOMO-4	-8.723	03	94	01	02
HOMO-5	-8.898	18	67	15	00

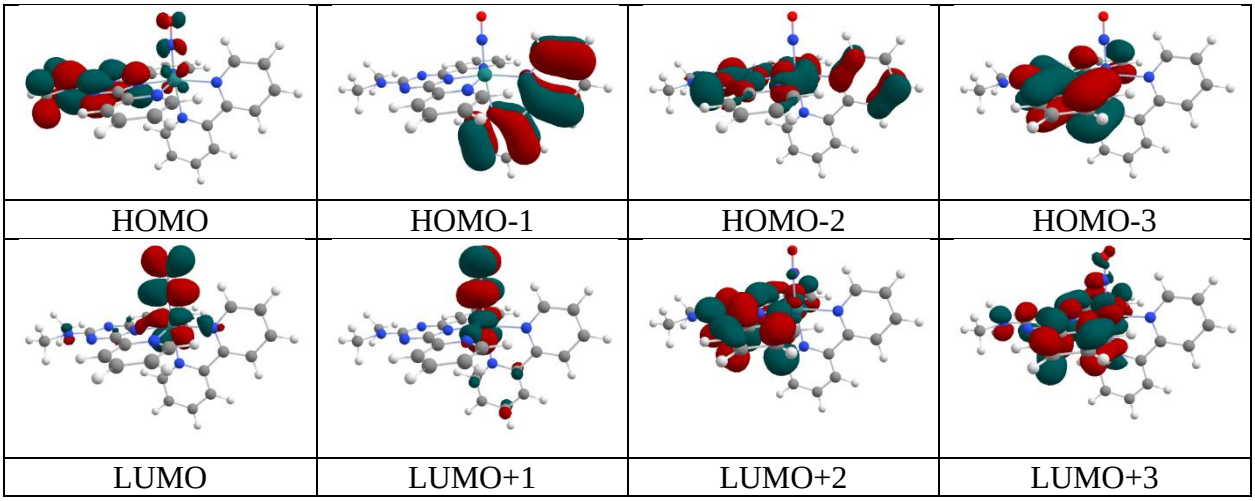
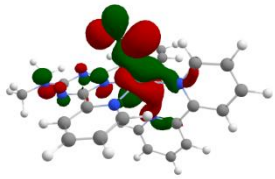
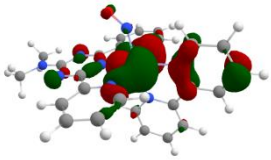
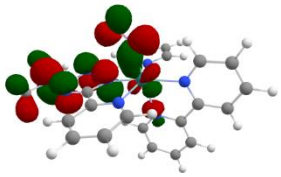
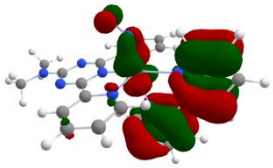
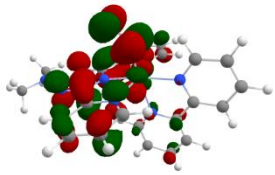
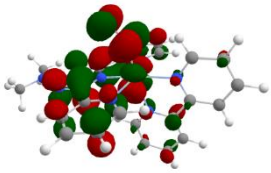
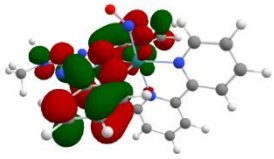
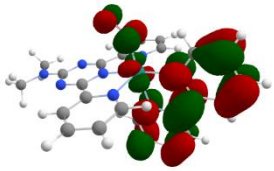
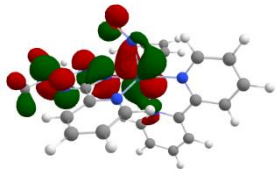
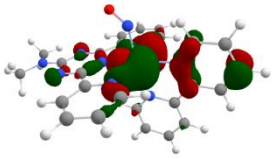
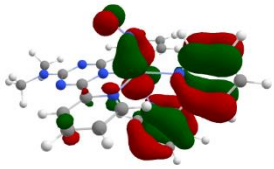
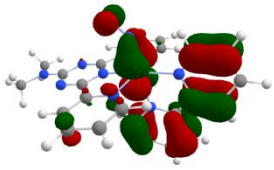
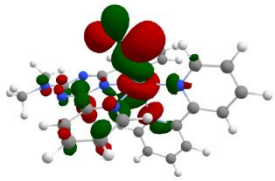
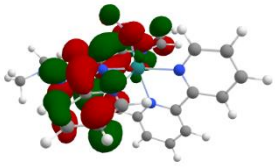
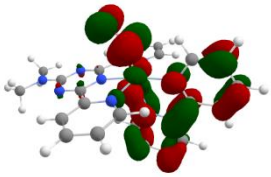
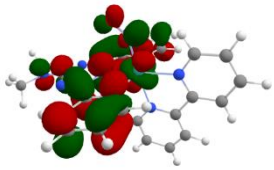


Table S5. DFT Calculated Selected MO Compositions for 4^{2+} in *S* = 1/2 State

MO	energy (eV)	% composition			
		Ru	dmdptz	bpy	NO
		α-MO			
LUMO+5	-1.719	14	83	02	01
LUMO+4	-1.821	02	54	44	00
LUMO+3	-2.154	15	09	24	52
LUMO+2	-2.739	08	85	03	04
LUMO+1	-2.805	06	08	74	11
LUMO	-3.172	01	94	02	03
SOMO	-4.583	26	08	06	61
HOMO-1	-7.059	72	18	10	01
HOMO-2	-7.144	07	83	02	08
HOMO-3	-7.492	07	02	89	02
HOMO-4	-7.713	55	18	11	15
HOMO-5	-8.109	01	97	01	00
		β-MO			
LUMO+5	-1.704	10	88	02	01
LUMO+4	-1.815	02	56	42	00
LUMO+3	-1.902	09	15	33	43
LUMO+2	-2.765	05	06	85	05
LUMO+1	-2.789	04	91	03	02
LUMO	-3.136	01	96	02	01
HOMO	-6.903	29	63	03	06
HOMO-1	-7.027	72	17	10	01
HOMO-2	-7.487	10	03	85	02
HOMO-3	-7.679	56	17	14	13
HOMO-4	-7.866	37	53	03	07
HOMO-5	-8.105	01	98	01	00

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

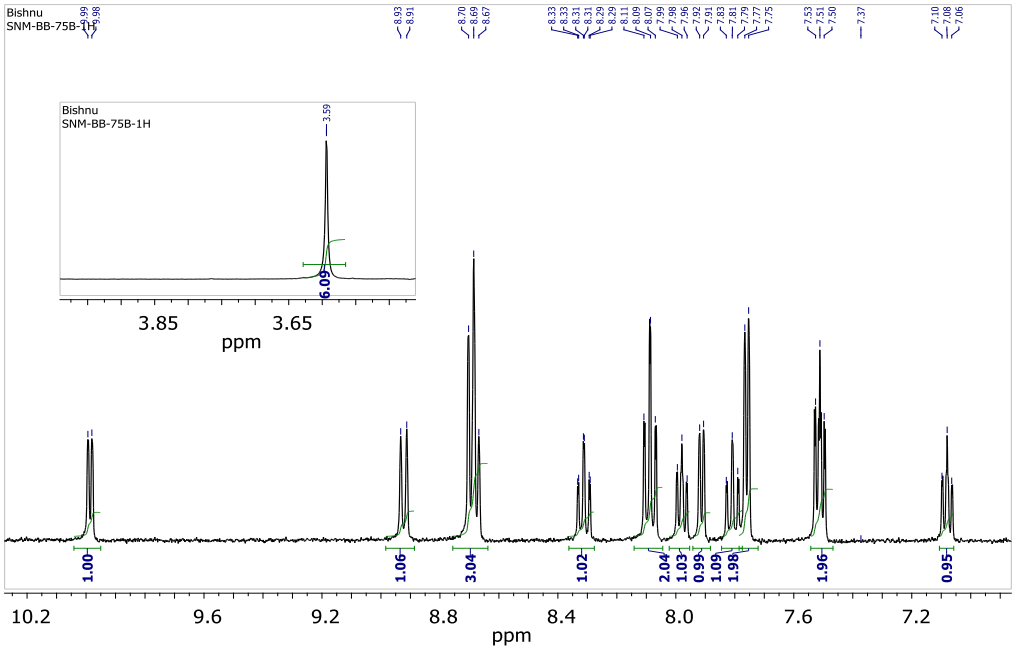


Fig. S1. ^{1}H NMR spectra of [**1**](ClO_4) in $(CD_3)_2SO$ at room temperature.

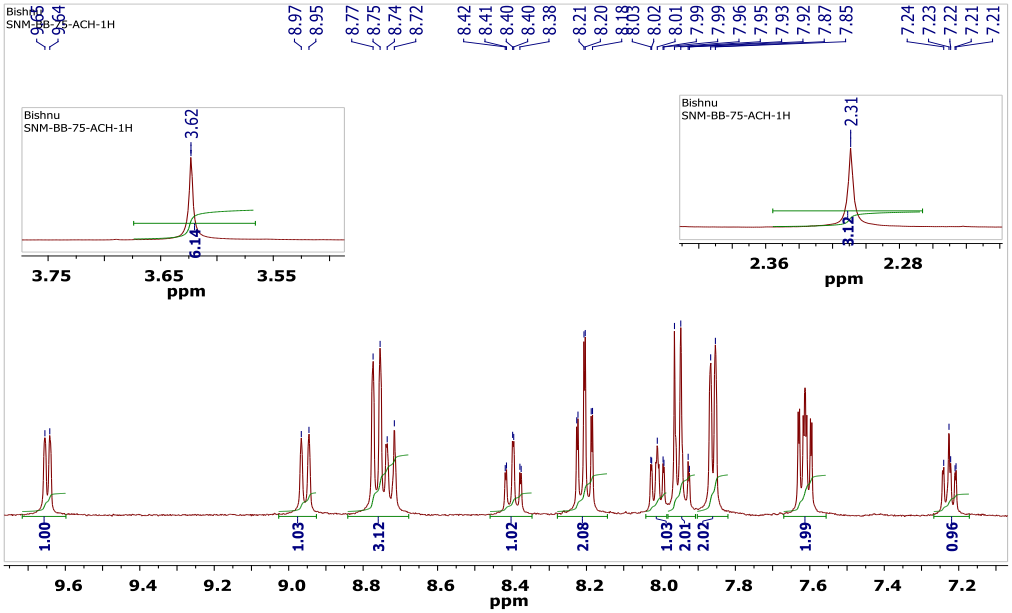


Fig. S2. ^{1}H NMR spectra of [**2**]$(ClO_4)_2$ in $(CD_3)_2SO$ at room temperature.

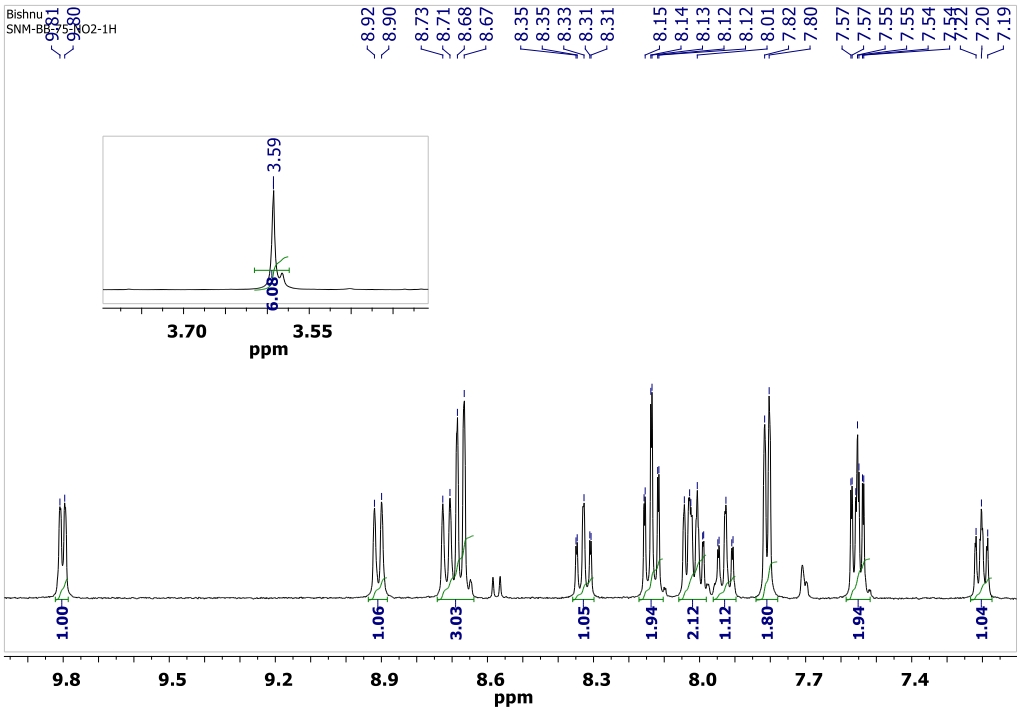


Fig. S3. ^{1}H NMR spectra of [**3**](ClO_4) in $(CD_3)_2SO$ at room temperature.

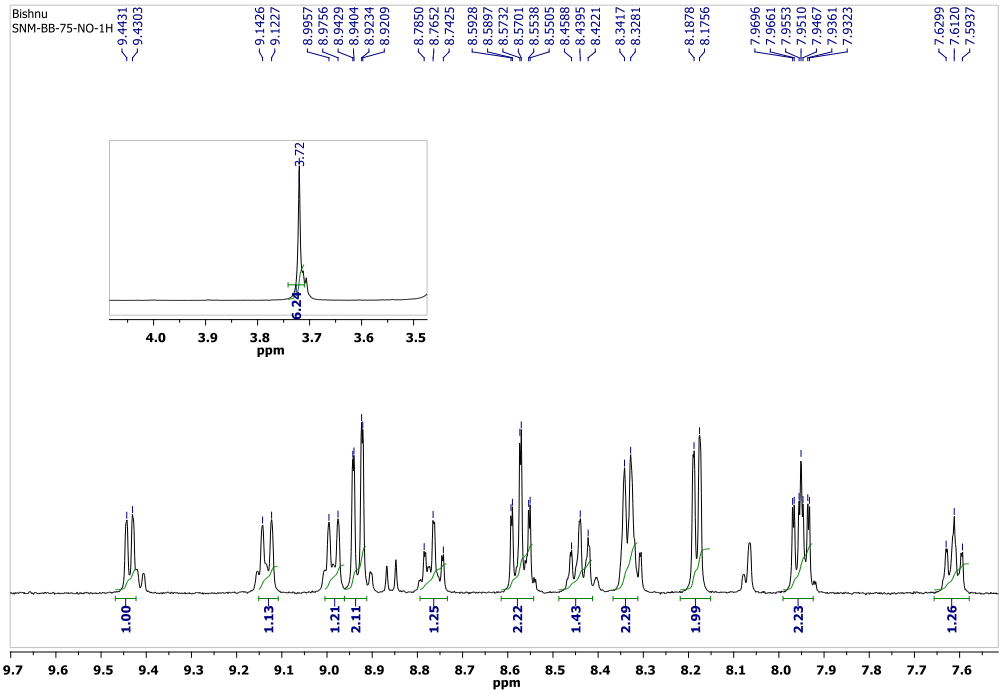


Fig. S4. ^{1}H NMR spectra of [**4**]$(ClO_4)_3$ in $(CD_3)_2SO$ at room temperature.

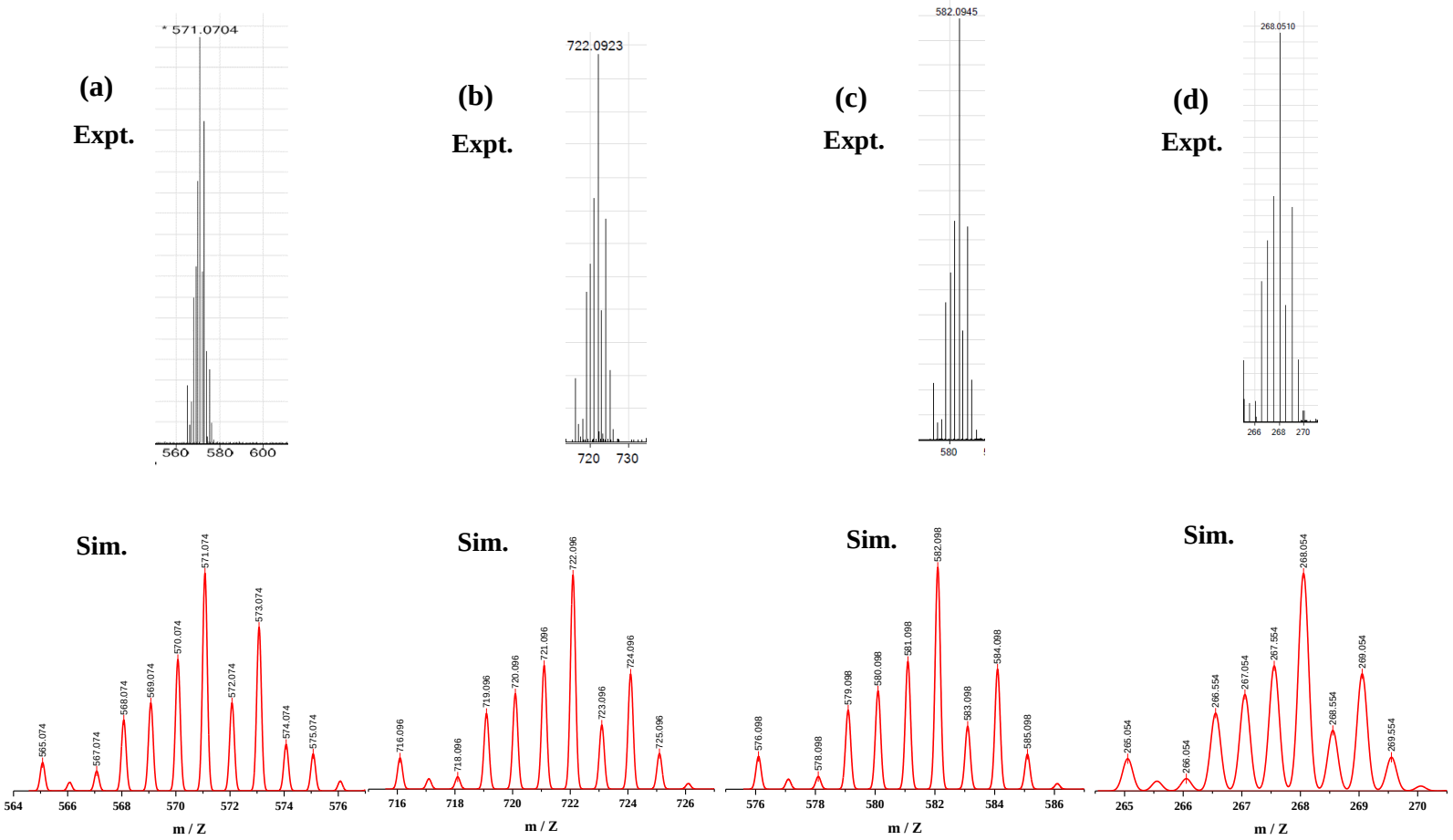


Fig. S5. ESI-MS(+) spectra of (a) [**1**](ClO_4) (b) [**2**](PF_6)$_2$ (c) [**3**](ClO_4) and (d) [**4**](ClO_4)$_3$ in acetonitrile.

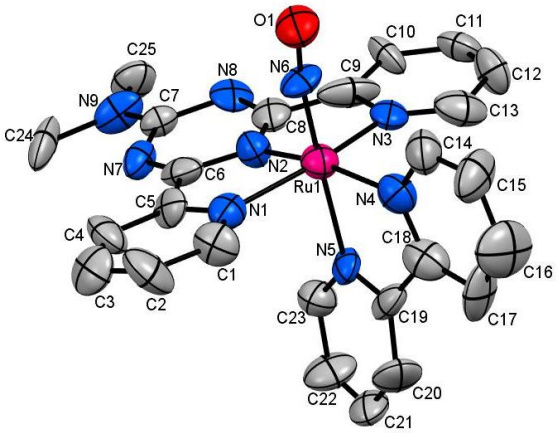


Fig. S6. Molecular structure of the cation $[Ru^{II}(dmdptz)(bpy)(NO^{+})]^{3+}$ $[\mathbf{4}]^{3+}$. Ellipsoids are drawn at 40% probability. Hydrogen atoms are omitted for clarity.

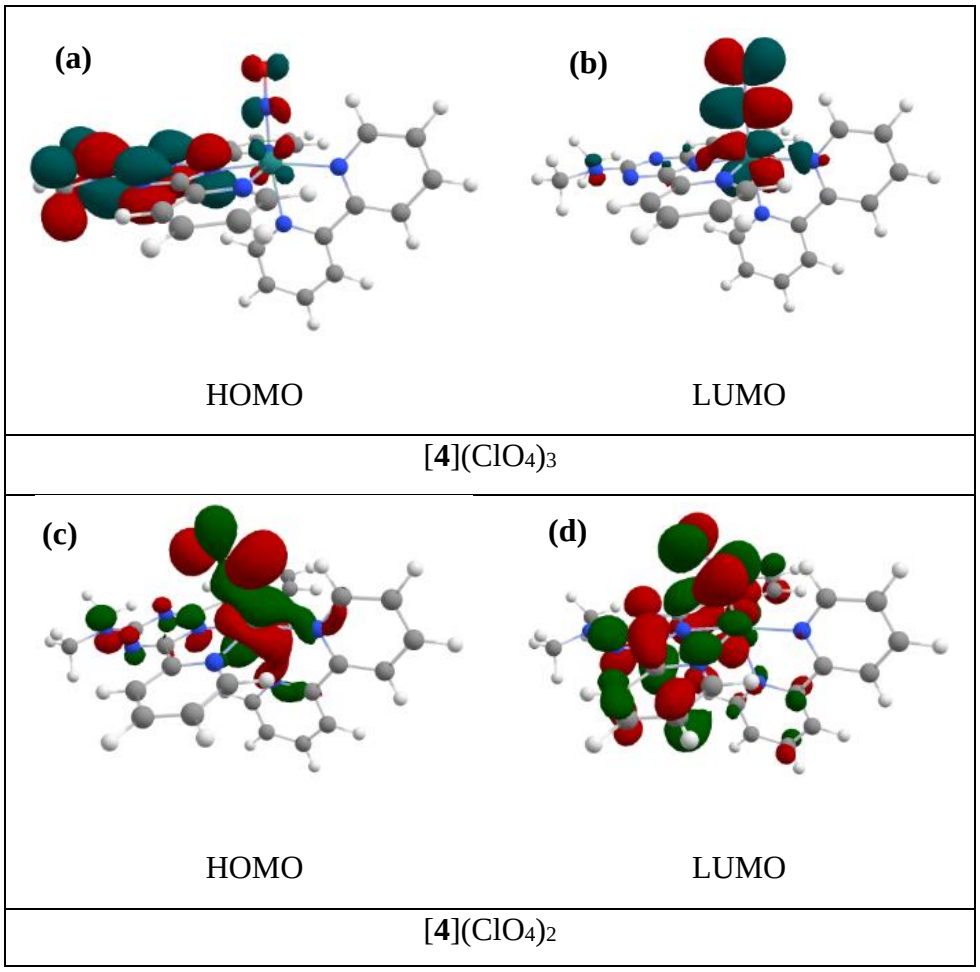


Fig. S7. Orbital representation of (a) HOMO of [**4**](ClO$_4$)$_3$ (b) LUMO of [**4**](ClO$_4$)$_3$, (c) HOMO of [**4**](ClO$_4$)$_2$ and (d) LUMO of [**4**](ClO$_4$)$_2$.

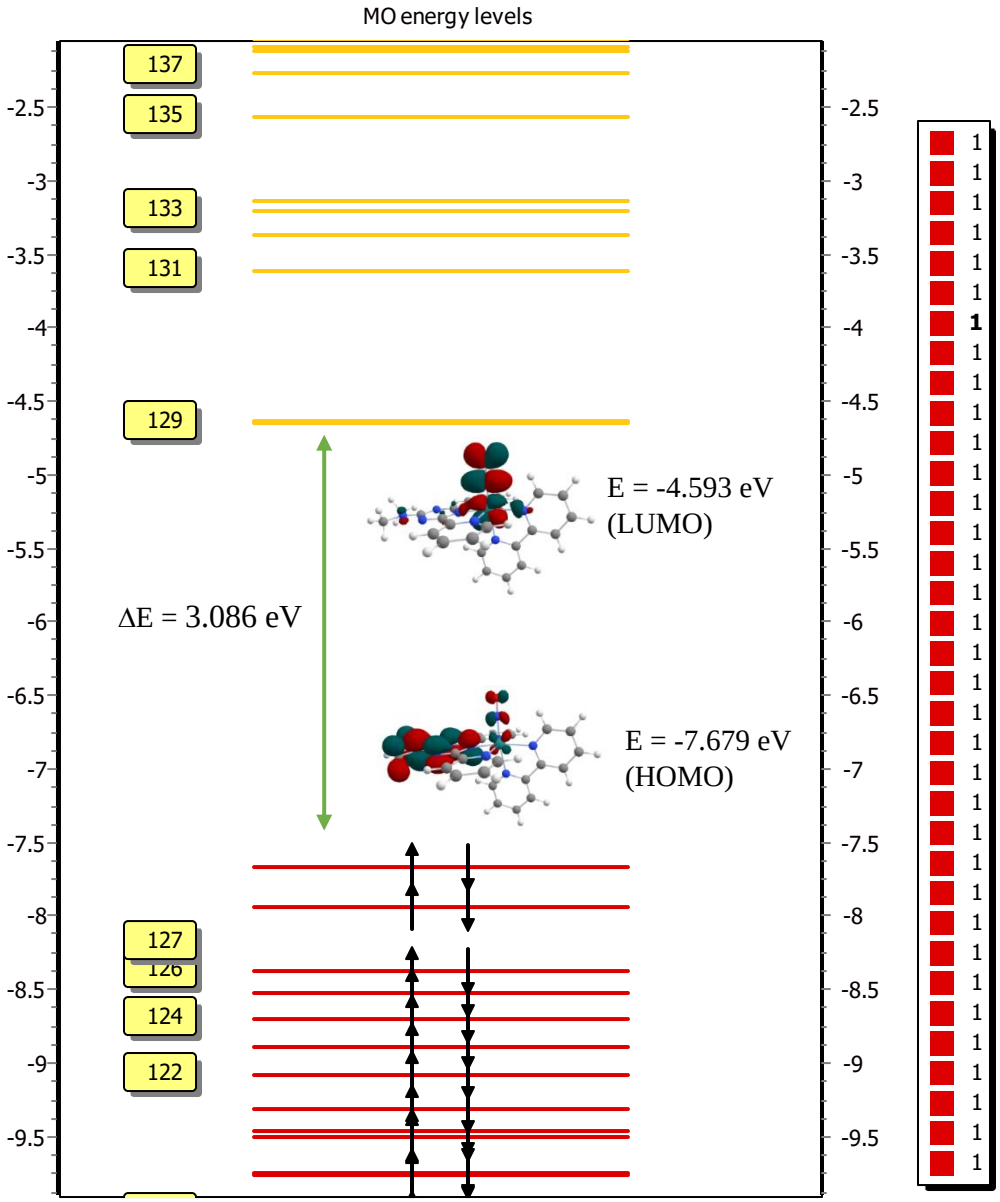


Fig. S8. Molecular Orbital energy diagram (zoomed) of [**4**]$(ClO_4)_3$.

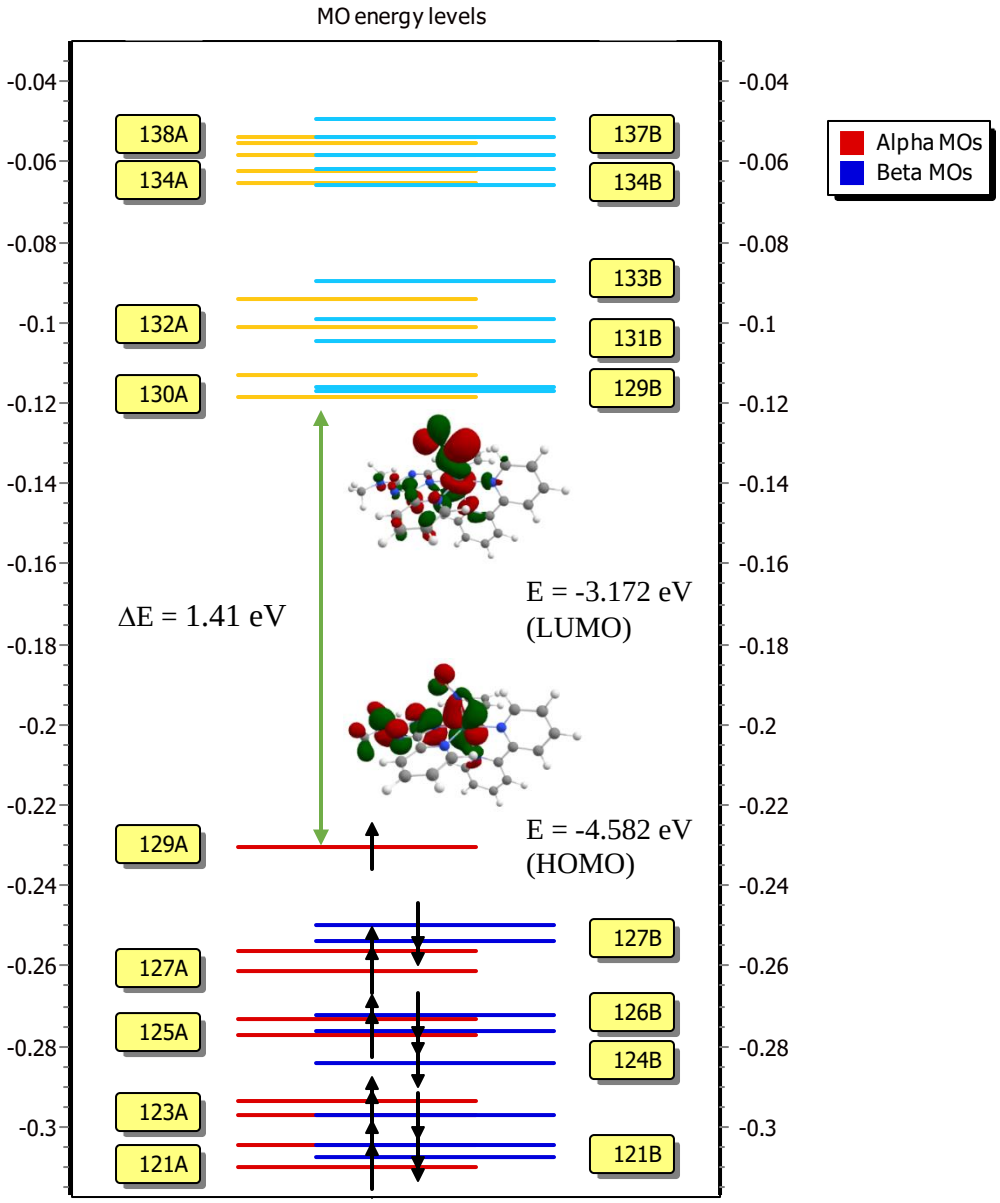


Fig. S9. Molecular Orbital energy diagram (zoomed) of [**4**]$(ClO_4)_2$.