Supporting Information

Effect of positional isomerism on the spectroelectrochemical response of 3,6-bis(2-pyridyl)-diketopyrrolopyrrolate bridged bis(carbonylhydridoruthenium) compounds

Arijit Singha Hazari,[a] Prabir Ghosh,[a] Katharina Beyer,[b] Brigitte Schwederski,[b] 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*

Table S1 Selected crystallographic data for **1** and **2**

	1	**2**
empirical formula	$C_{90}H_{70}N_4O_4P_4Ru_2$	$C_{90}H_{70}N_4O_4P_4Ru_2$
formula weight	1597.52	1597.52
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.5994(3)	11.1737(3)
b (Å)	12.0532(4)	12.5673(3)
c (Å)	16.8855(4)	16.7521(4)
α (deg)	101.756(2)	89.742(2)
β (deg)	104.220(2)	71.246(2)
γ (deg)	101.333(3)	72.049(2)
V (Å^3)	1976.97(10)	2107.34(10)
Z	1	1
μ (mm^{-1})	0.516	0.484
T (K)	150(2)	150(2)
ρ_{calcd} (g cm^{-3})	1.342	1.259
F (000)	818	818
θ range (deg)	2.346 to 25.000	2.035 to 24.997
data / restraints / parameters	6960 / 2 / 482	7396 / 2 / 483
R_1, wR_2 [$I > 2\sigma(I)$]	0.0618, 0.1254	0.0380, 0.0954
R_1, wR_2(all data)	0.0821, 0.1369	0.0420, 0.0978
GOF on F^2	1.090	1.061
largest difference in peak and hole (e Å^{-3})	2.234 and –0.641	0.723 and –0.567

Table S2 Selected experimental and DFT ((U)B3LYP) calculated bond lengths (Å) for $\mathbf{1}^{n}$

Bond lengths (Å)	X-ray	DFT		
	1	$\mathbf{1}^{+}$ (S=1/2)	**1** (S=0)	$\mathbf{1}^{-}$ (S=1/2)
Ru1-N1	2.134(4)	2.195	2.166	2.164
Ru1-N2	2.183(5)	2.253	2.281	2.250
Ru1-H1	1.51(2)	1.613	1.607	1.623
Ru1-C45	1.844(12)	1.863	1.870	1.867
Ru1-P1	2.3638(14)	2.445	2.441	2.446
Ru1-P2	2.3554(14)	2.439	2.438	2.405
C1-C2	1.452(7)	1.469	1.463	1.461
C1-N1	1.422(6)	1.437	1.414	1.394
C1-O1	1.248(6)	1.225	1.244	1.258
C3-N1	1.370(7)	1.341	1.372	1.400
C3-C4	1.456(7)	1.452	1.450	1.419
C4-N2	1.364(6)	1.359	1.361	1.376
C45-O2	1.166(13)	1.161	1.162	1.167

Table S3 Experimental and DFT calculated selected bond angles (deg) for $\mathbf{1}^{n}$

Bond angles (deg)	X-ray	DFT		
	1	$\mathbf{1}^{+}$ (S=1/2)	**1** (S=0)	$\mathbf{1}^{-}$ (S=1/2)
N1-Ru1-N2	76.46(16)	74.50	74.76	76.10
N1-Ru1-P1	88.56(11)	88.97	89.35	91.60
N1-Ru1-P2	89.12(11)	94.29	89.94	91.27
N1-Ru1-C45	176.5(4)	170.71	179.50	173.64
N2-Ru1-P1	90.09(11)	94.43	93.65	94.50
N2-Ru1-P2	91.09(11)	95.30	93.69	94.54
N2-Ru1-C45	106.7(5)	96.25	104.94	97.80
C45-Ru1-P1	89.9(4)	87.25	90.27	87.03
C45-Ru1-P2	92.3(4)	90.99	90.46	91.01
P1-Ru1-P2	177.08(5)	170.23	172.15	170.92

Table S4 Selected experimental and DFT ((U)B3LYP) calculated bond lengths (Å) for $\mathbf{2}^{n}$

Bond lengths (Å)	X-ray	DFT		
	2	$\mathbf{2}^{+}$ (S=1/2)	**2** (S=0)	$\mathbf{2}^{-}$ (S=1/2)
Ru1-N1	2.144(2)	2.213	2.214	2.192
Ru1-N2	2.174(2)	2.195	2.200	2.190
Ru1-H1	1.45(6)	1.618	1.629	1.644
Ru1-C45	1.905(4)	1.872	1.867	1.868
Ru1-P1	2.3534(7)	2.444	2.428	2.417
Ru1-P2	2.3664(7)	2.442	2.430	2.418
C1-C2	1.460(4)	1.468	1.463	1.463
C1-N1	1.410(4)	1.436	1.409	1.388
C1-O1	1.235(3)	1.227	1.245	1.261
C3-N1	1.378(3)	1.336	1.368	1.391
C3-C4	1.441(4)	1.452	1.447	1.416
C4-N2	1.359(4)	1.363	1.363	1.383
C45-O2	1.161(2)	1.158	1.161	1.164

Table S5 Experimental and DFT calculated selected bond angles (deg) for $\mathbf{2}^{n}$

Bond angles (deg)	X-ray	DFT		
	2	$\mathbf{2}^{+}$ (S=1/2)	**2** (S=0)	$\mathbf{2}^{-}$ (S=1/2)
N1-Ru1-N2	76.45(9)	74.82	75.56	76.43
N1-Ru1-P1	87.84(6)	96.22	95.37	94.69
N1-Ru1-P2	88.00(6)	97.27	95.25	94.66
N1-Ru1-C45	105.88(18)	102.88	103.23	102.20
N2-Ru1-P1	90.24(6)	91.38	91.09	90.91
N2-Ru1-P2	89.73(6)	91.66	91.46	91.22
N2-Ru1-C45	176.58(17)	177.69	178.78	178.61
C45-Ru1-P1	87.35(17)	89.00	89.18	89.41
C45-Ru1-P2	92.85(17)	88.47	88.47	88.66
P1-Ru1-P2	175.73(2)	166.49	169.37	170.64

Table S6 Energies of DFT ((U)B3LYP/LanL2DZ/6-31G*) optimised structures of $\mathbf{1}^n$ and $\mathbf{2}^n$

Complex	*E* (Hartrees)		$\Delta E_{(1–2)}$	$\Delta E_{(1^{+}–2^{+})}$	$\Delta E_{(1^{-}–2^{-})}$
	S = 0	*S* = 1/2	0.0055099 Hartrees 1209.283264 cm^{-1} 14.46624355 kJ/mol	0.0071802 Hartrees 1575.87173833 cm^{-1} 18.851616536 kJ/mol	0.0046221 Hartrees 1014.433687 cm^{-1} 12.13532447 kJ/mol
1	−5544.9759883	–			
$\mathbf{1}^{+}$	–	−5544.7979163			
$\mathbf{1}^{-}$	–	−5545.0211764			
2	–5544.9814982	–			
$\mathbf{2}^{+}$	–	–5544.8050965			
$\mathbf{2}^{-}$	–	–5545.0257985			

Table S7 DFT calculated selected MO compositions of $\mathbf{1}^n$ and $\mathbf{2}^n$

Complex	MO	Fragments	%contribution
1 (*S*=0)	HOMO	DPPP/PPh_3/Ru	84/10/05
	LUMO	DPPP/PPh_3/Ru	87/11/02
$\mathbf{1}^+$ (*S*=1/2)	SOMO	DPPP/PPh_3/Ru	80/11/07
$\mathbf{1}^-$ (*S*=1/2)	SOMO	DPPP/PPh_3/Ru	90/08/01
2 (*S*=0)	HOMO	DPPP/PPh_3/Ru	90/06/04
	LUMO	DPPP/PPh_3/Ru	81/11/08
$\mathbf{2}^+$ (*S*=1/2)	SOMO	DPPP/Ru/PPh_3	64/23/13
$\mathbf{2}^-$ (*S*=1/2)	SOMO	DPPP/PPh_3/Ru	89/08/02

Table S8 Composition and energies of selected molecular orbitals of **1** (*S*=0)

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
HOMO–5	-5.646	0.24	0.64	0.10	0.02	0.00
HOMO–4	-5.572	0.58	0.18	0.21	0.03	0.00
HOMO–3	-5.486	0.60	0.14	0.23	0.03	0.01
HOMO–2	-5.267	0.75	0.09	0.04	0.10	0.01
HOMO–1	-4.874	0.42	0.46	0.10	0.01	0.00
HOMO	-3.912	0.05	0.84	0.10	0.00	0.00
LUMO	-1.9	0.02	0.87	0.11	0.00	0.00
LUMO+1	-0.737	0.04	0.80	0.14	0.02	0.00
LUMO+2	-0.625	0.17	0.04	0.77	0.02	0.01
LUMO+3	-0.587	0.07	0.59	0.33	0.01	0.00
LUMO+4	-0.533	0.15	0.09	0.72	0.03	0.00
LUMO+5	-0.451	0.07	0.02	0.91	0.00	0.00

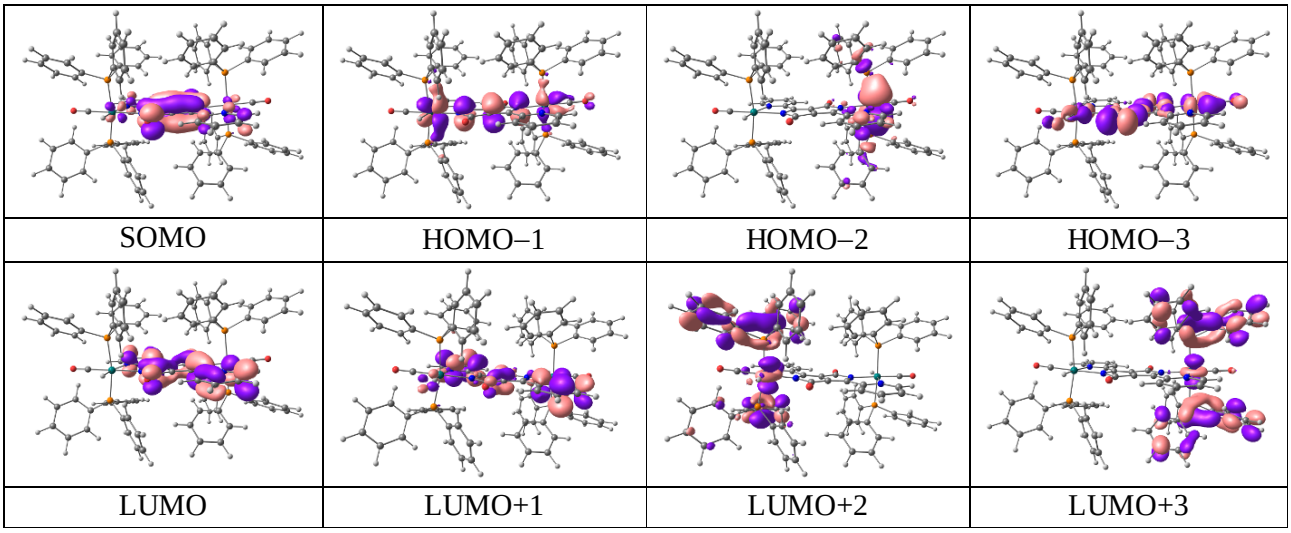


Table S9 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (S=1/2)

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
			α-spin			
HOMO–5	-8.252	0.10	0.01	0.88	0.01	0.00
HOMO–4	-8.221	0.54	0.06	0.40	0.00	0.00
HOMO–3	-8.198	0.63	0.05	0.31	0.01	0.00
HOMO–2	-7.964	0.14	0.07	0.78	0.00	0.00
HOMO–1	-7.823	0.20	0.10	0.68	0.01	0.00
SOMO	-7.424	0.07	0.80	0.11	0.01	0.00
LUMO	-5.128	0.01	0.93	0.05	0.00	0.00
LUMO+1	-3.638	0.04	0.85	0.08	0.03	0.00
LUMO+2	-3.248	0.04	0.91	0.05	0.00	0.00
LUMO+3	-3.126	0.02	0.89	0.07	0.02	0.00
LUMO+4	-2.995	0.29	0.04	0.61	0.05	0.00
LUMO+5	-2.992	0.29	0.05	0.61	0.05	0.00
			β-spin			
HOMO–5	-8.252	0.12	0.01	0.87	0.04	0.00
HOMO–4	-8.249	0.04	0.01	0.94	0.01	0.00
HOMO–3	-8.197	0.69	0.06	0.26	0.00	0.00
HOMO–2	-8.176	0.62	0.06	0.31	0.01	0.00
HOMO–1	-7.932	0.15	0.03	0.81	0.00	0.00
HOMO	-7.757	0.22	0.16	0.60	0.02	0.00
LUMO	-5.931	0.03	0.88	0.08	0.01	0.00
LUMO+1	-4.738	0.02	0.91	0.06	0.01	0.00
LUMO+2	-3.467	0.04	0.86	0.07	0.03	0.00
LUMO+3	-3.208	0.03	0.92	0.05	0.00	0.00
LUMO+4	-3.059	0.02	0.84	0.10	0.04	0.00
LUMO+5	-2.991	0.29	0.04	0.61	0.05	0.00

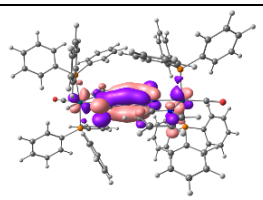
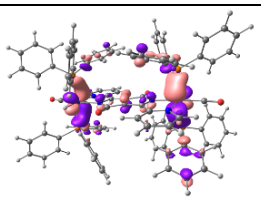
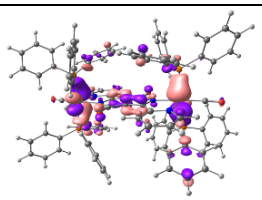
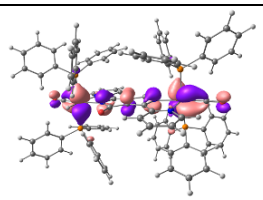
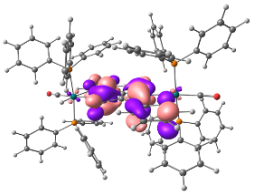
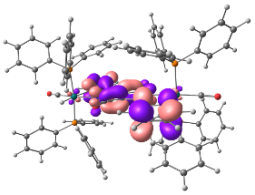
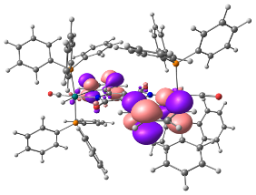
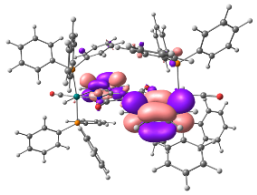
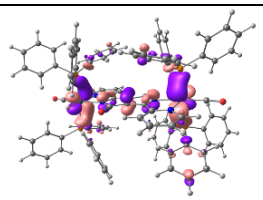
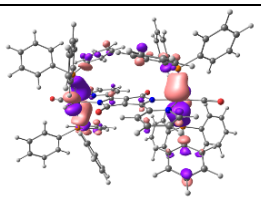
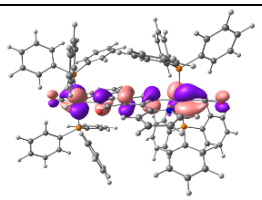
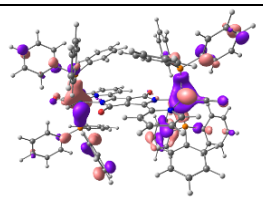
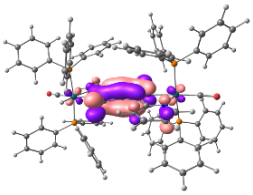
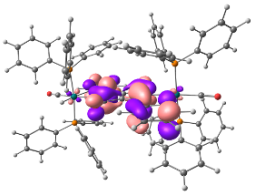
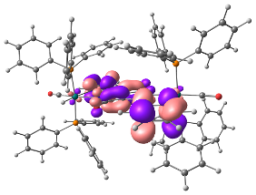
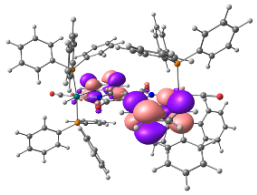
α-spin			
			
SOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO−1	HOMO−2	HOMO−3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
			α-spin			
HOMO–5	-3.596	0.56	0.29	0.14	0.02	0.00
HOMO–4	-3.401	0.03	0.89	0.07	0.01	0.00
HOMO–3	-2.996	0.01	0.91	0.08	0.00	0.00
HOMO–2	-2.506	0.12	0.70	0.15	0.04	0.00
HOMO–1	-1.703	0.02	0.86	0.11	0.01	0.00
SOMO	-0.548	0.01	0.90	0.08	0.00	0.00
LUMO	1.196	0.24	0.03	0.70	0.04	0.00
LUMO+1	1.205	0.23	0.03	0.70	0.04	0.00
LUMO+2	1.406	0.06	0.04	0.79	0.11	0.00
LUMO+3	1.432	0.02	0.02	0.93	0.03	0.00
LUMO+4	1.447	0.04	0.02	0.91	0.03	0.00
LUMO+5	1.462	0.04	0.02	0.89	0.05	0.00
			β-spin			
HOMO–5	-3.623	0.76	0.15	0.09	0.00	0.00
HOMO–4	-3.478	0.35	0.47	0.15	0.03	0.00
HOMO–3	-3.362	0.03	0.89	0.07	0.01	0.00
HOMO–2	-2.956	0.01	0.91	0.08	0.00	0.00
HOMO–1	-2.48	0.11	0.69	0.15	0.04	0.00
HOMO	-1.332	0.02	0.86	0.12	0.01	0.00
LUMO	0.655	0.02	0.87	0.11	0.01	0.00
LUMO+1	1.199	0.24	0.03	0.70	0.04	0.00
LUMO+2	1.207	0.23	0.03	0.70	0.04	0.00
LUMO+3	1.415	0.05	0.01	0.85	0.09	0.00
LUMO+4	1.433	0.02	0.02	0.93	0.03	0.00
LUMO+5	1.449	0.04	0.01	0.91	0.03	0.00

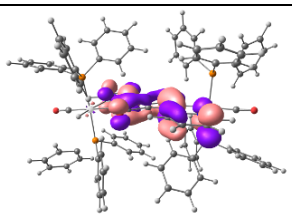
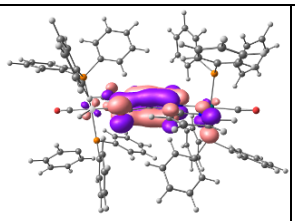
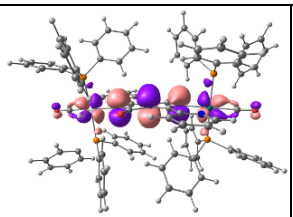
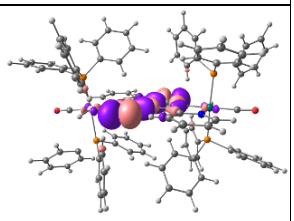
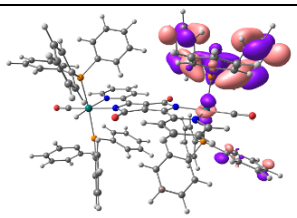
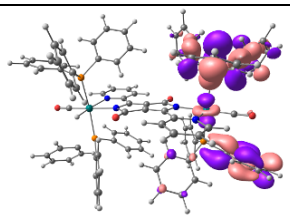
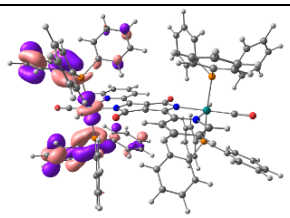
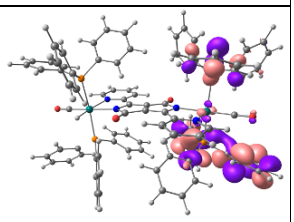
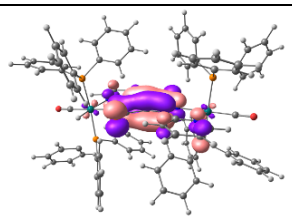
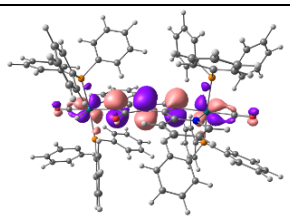
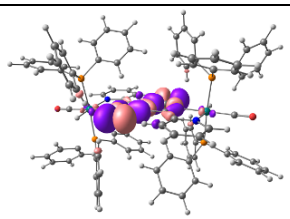
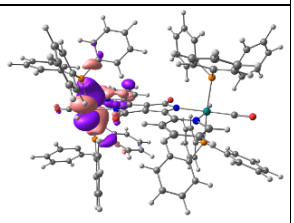
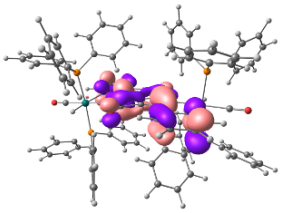
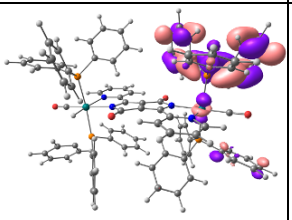
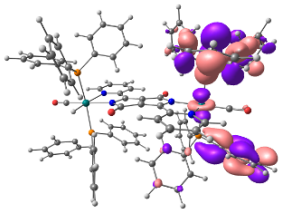
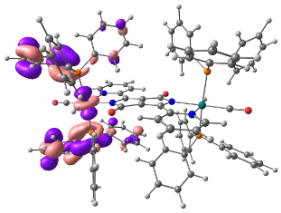
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S11 Composition and energies of selected molecular orbitals of **2** (*S*=0)

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
HOMO–5	-5.834	0.15	0.41	0.41	0.00	0.02
HOMO–4	-5.769	0.40	0.43	0.09	0.03	0.06
HOMO–3	-5.655	0.65	0.10	0.23	0.01	0.01
HOMO–2	-5.289	0.61	0.18	0.07	0.01	0.12
HOMO–1	-4.979	0.48	0.44	0.07	0.00	0.00
HOMO	-4.209	0.04	0.90	0.06	0.00	0.00
LUMO	-2.229	0.08	0.81	0.11	0.00	0.00
LUMO+1	-1.039	0.03	0.83	0.12	0.03	0.00
LUMO+2	-0.866	0.04	0.73	0.21	0.02	0.00
LUMO+3	-0.717	0.25	0.04	0.70	0.01	0.01
LUMO+4	-0.682	0.24	0.03	0.70	0.02	0.01
LUMO+5	-0.577	0.01	0.74	0.25	0.00	0.00

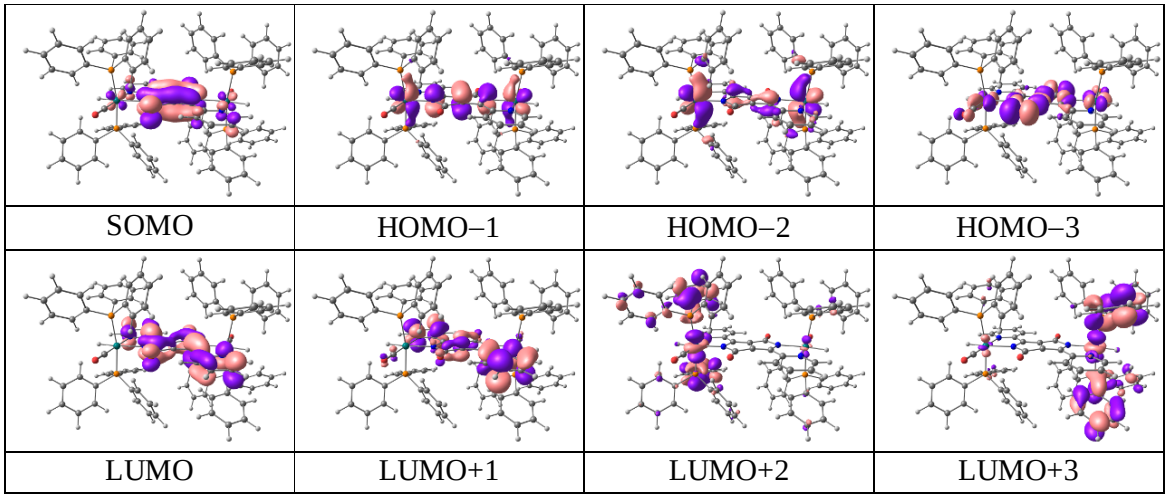


Table S12 Composition and energies of selected molecular orbitals of $\mathbf{2}^{+}$ (S=1/2)

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
			α-spin			
HOMO–5	-8.28	0.69	0.07	0.07	0.11	0.00
HOMO–4	-8.208	0.61	0.07	0.07	0.02	0.00
HOMO–3	-8.147	0.29	0.03	0.67	0.01	0.00
HOMO–2	-8.032	0.20	0.23	0.57	0.00	0.00
HOMO–1	-7.562	0.23	0.53	0.24	0.00	0.00
SOMO	-7.488	0.23	0.64	0.13	0.00	0.00
LUMO	-5.129	0.01	0.93	0.05	0.00	0.00
LUMO+1	-3.551	0.04	0.89	0.06	0.01	0.00
LUMO+2	-3.182	0.03	0.89	0.06	0.01	0.00
LUMO+3	-3.024	0.01	0.90	0.08	0.01	0.00
LUMO+4	-2.822	0.27	0.04	0.67	0.02	0.00
LUMO+5	-2.808	0.02	0.04	0.67	0.02	0.00
			β-spin			
HOMO–5	-8.276	0.73	0.06	0.09	0.12	0.01
HOMO–4	-8.259	0.69	0.07	0.11	0.12	0.01
HOMO–3	-8.156	0.43	0.03	0.53	0.01	0.00
HOMO–2	-8.126	0.25	0.03	0.72	0.01	0.00
HOMO–1	-7.884	0.13	0.49	0.38	0.00	0.00
HOMO	-7.329	0.28	0.52	0.19	0.00	0.00
LUMO	-6.052	0.10	0.81	0.09	0.00	0.00
LUMO+1	-4.772	0.02	0.91	0.06	0.00	0.00
LUMO+2	-3.414	0.04	0.89	0.06	0.01	0.00
LUMO+3	-3.149	0.03	0.89	0.06	0.01	0.00
LUMO+4	-2.96	0.01	0.90	0.09	0.00	0.00
LUMO+5	-2.814	0.27	0.04	0.67	0.02	0.00

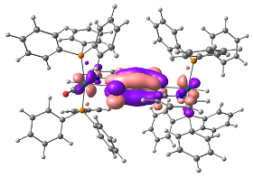
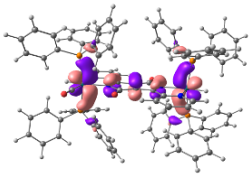
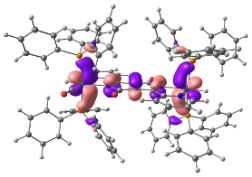
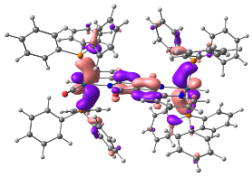
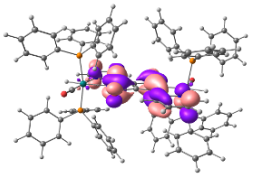
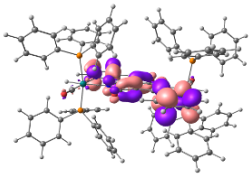
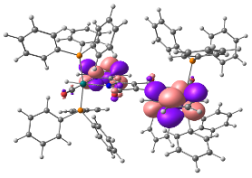
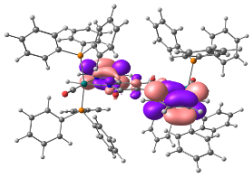
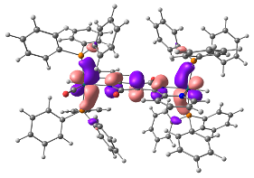
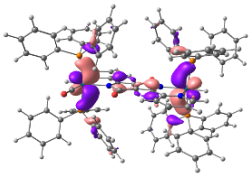
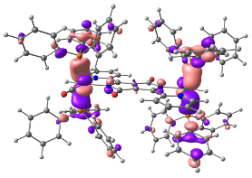
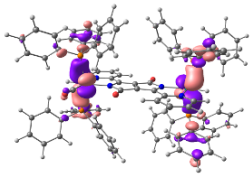
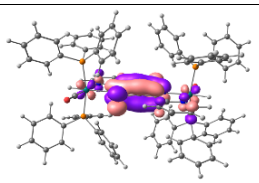
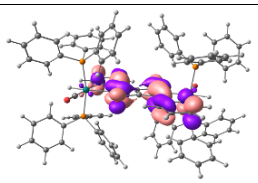
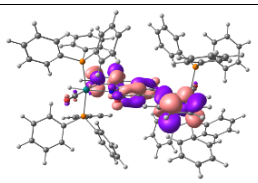
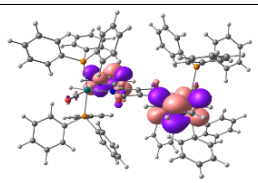
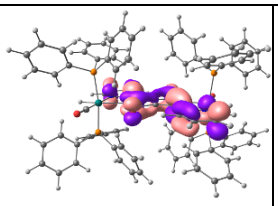
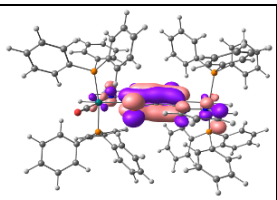
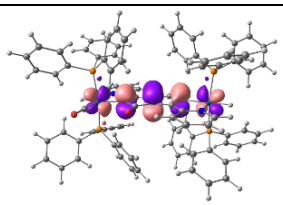
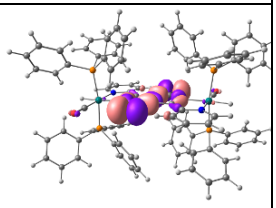
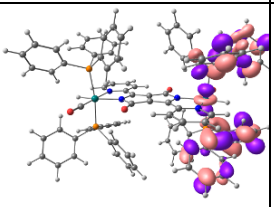
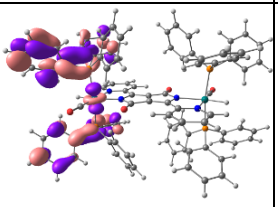
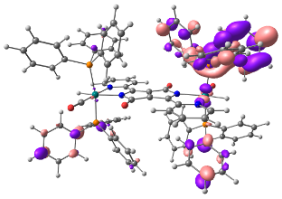
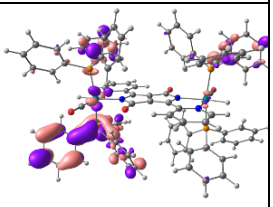
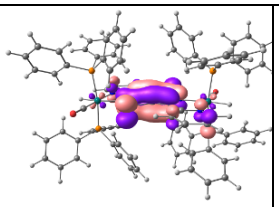
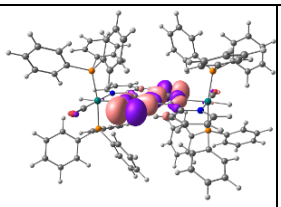
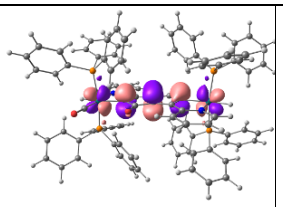
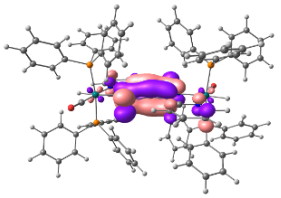
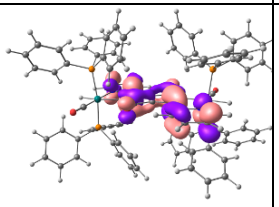
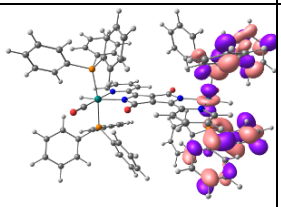
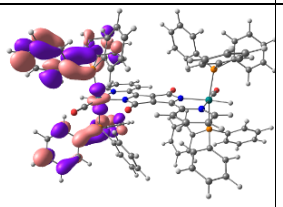
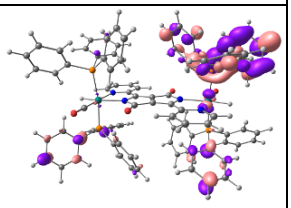
α-spin			
			
SOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO–1	HOMO–2	HOMO–3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

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

MO	Energy (eV)	Composition				
		Ru	DPPP	PPh_3	CO	H
			α-spin			
HOMO–5	-3.107	0.59	0.22	0.19	0.00	0.00
HOMO–4	-3.022	0.07	0.81	0.06	0.03	0.02
HOMO–3	-2.703	0.02	0.91	0.07	0.01	0.00
HOMO–2	-1.924	0.26	0.62	0.12	0.00	0.00
HOMO–1	-1.229	0.04	0.86	0.10	0.00	0.00
SOMO	-0.008	0.01	0.90	0.08	0.01	0.00
LUMO	1.235	0.14	0.01	0.82	0.01	0.01
LUMO+1	1.238	0.15	0.02	0.82	0.01	0
LUMO+2	1.347	0.07	0.02	0.91	0	0
LUMO+3	1.355	0.07	0.02	0.91	0	0
LUMO+4	1.383	0.07	0.01	0.92	0	0
LUMO+5	1.403	0.09	0.02	0.89	0	0
			β-spin			
HOMO–5	-3.561	0.75	0.08	0.03	0.13	0.00
HOMO–4	-3.014	0.54	0.29	0.17	0.00	0.00
HOMO–3	-2.993	0.07	0.82	0.06	0.02	0.02
HOMO–2	-2.666	0.02	0.91	0.07	0.01	0.00
HOMO–1	-1.894	0.26	0.62	0.12	0.00	0.00
HOMO	-0.894	0.03	0.86	0.11	0.00	0.00
LUMO	1.164	0.02	0.84	0.13	0.01	0.00
LUMO+1	1.235	0.14	0.01	0.82	0.01	0.01
LUMO+2	1.238	0.14	0.02	0.82	0.01	0.00
LUMO+3	1.348	0.07	0.02	0.91	0.00	0.00
LUMO+4	1.358	0.07	0.02	0.91	0.00	0.00
LUMO+5	1.384	0.07	0.01	0.91	0.00	0.00

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

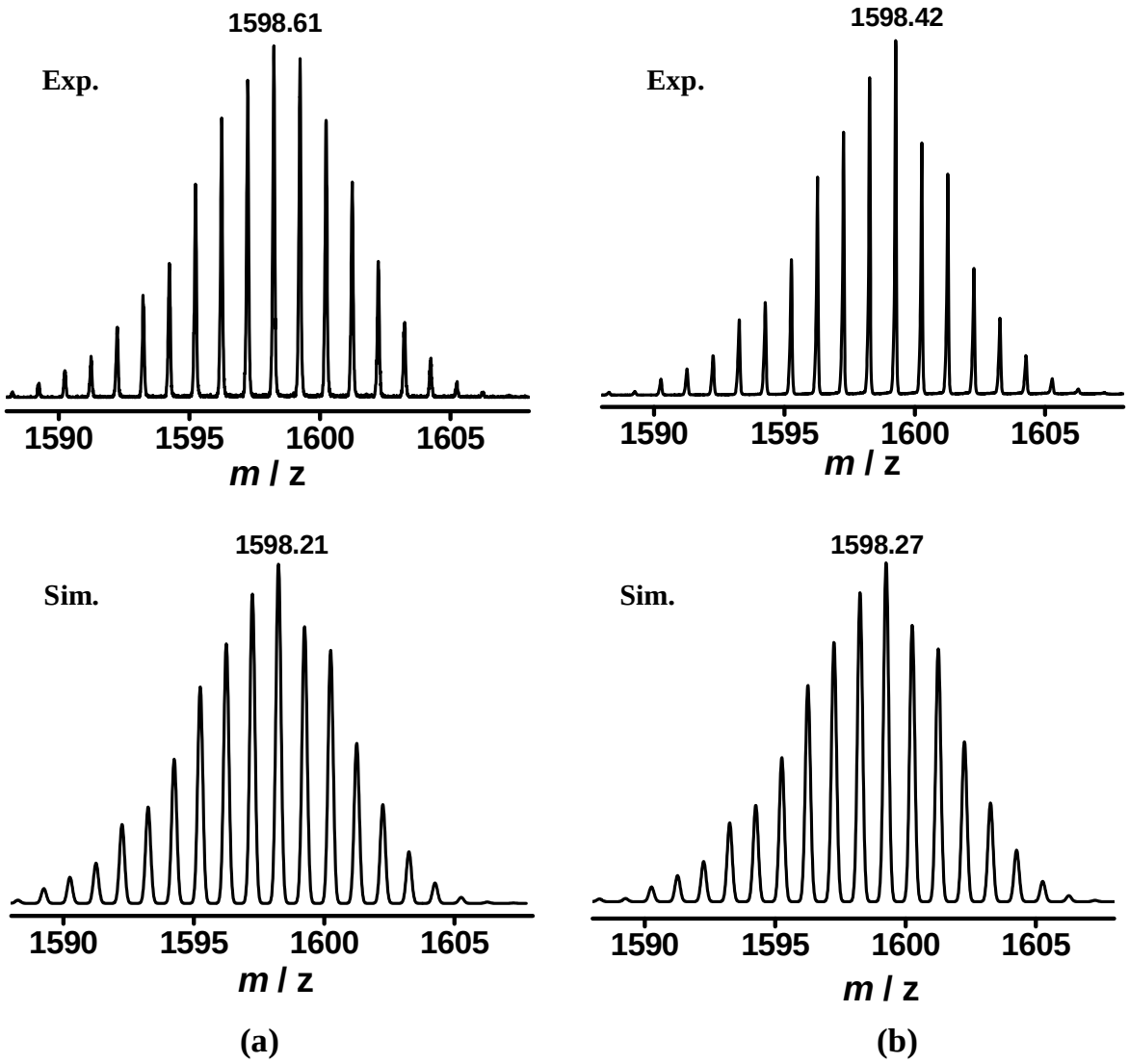


Fig. S1 ESI-MS (+) spectra of (a) [**1**+H^+**]** and (b) [**2**+H^+**]** in CH_2Cl_2 respectively.

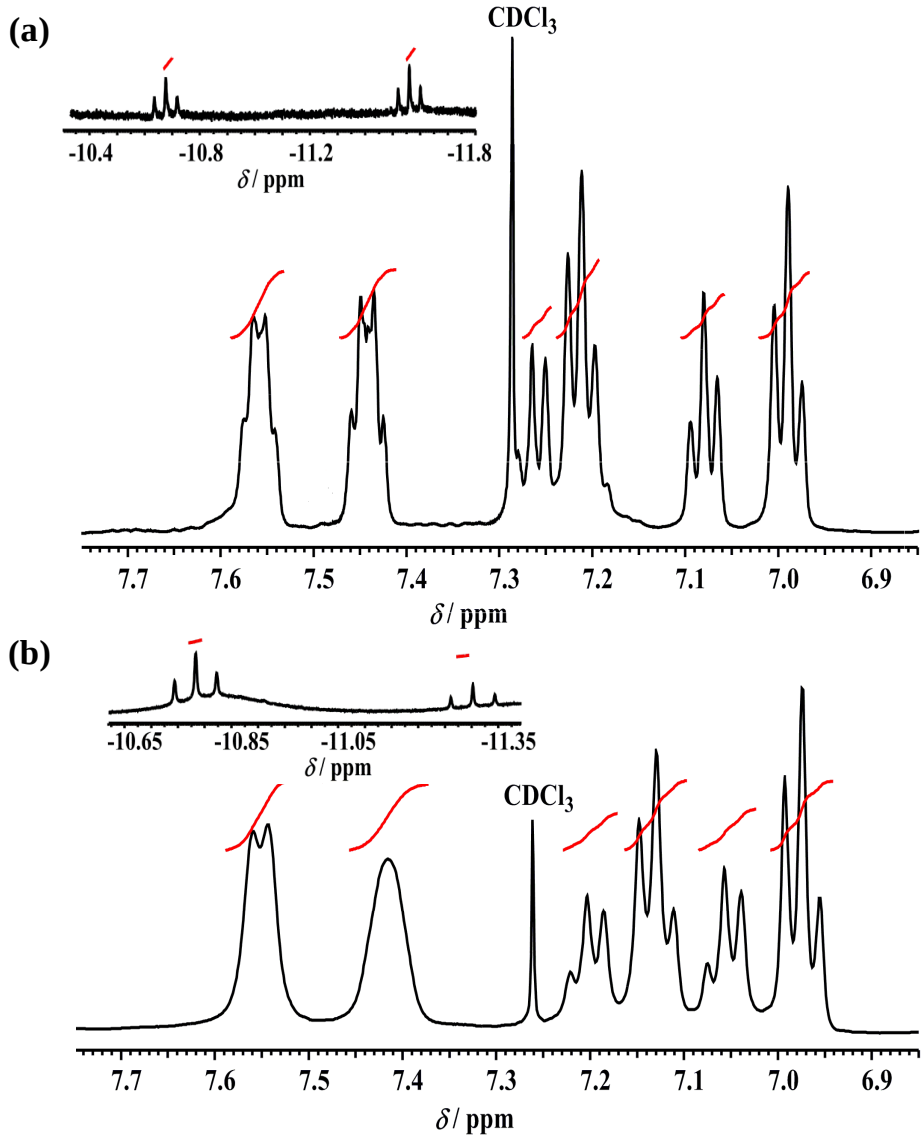


Fig. S2 ^{1}H NMR spectra of (a) **1** and (b) **2** in $CDCl_3$.

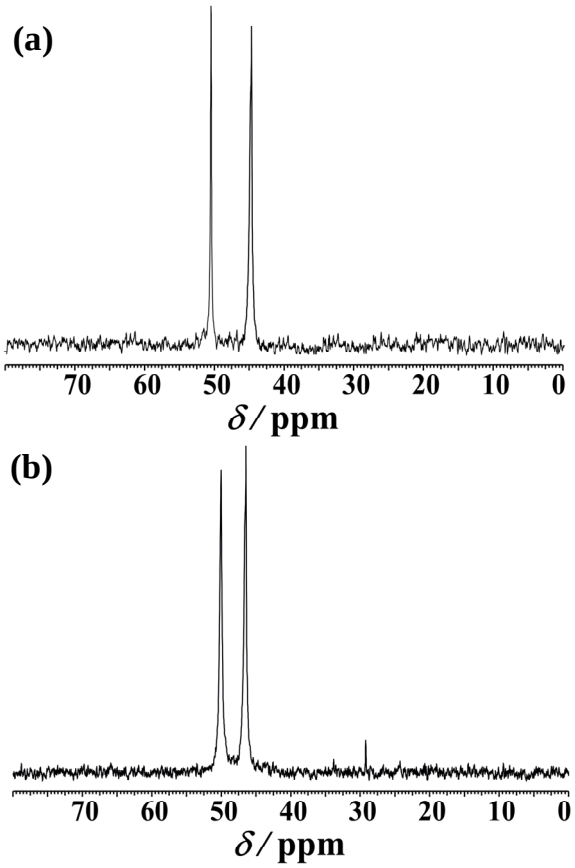


Fig. S3 ^{31}P NMR spectra of (a) **1** and (b) **2** in $CDCl_3$.

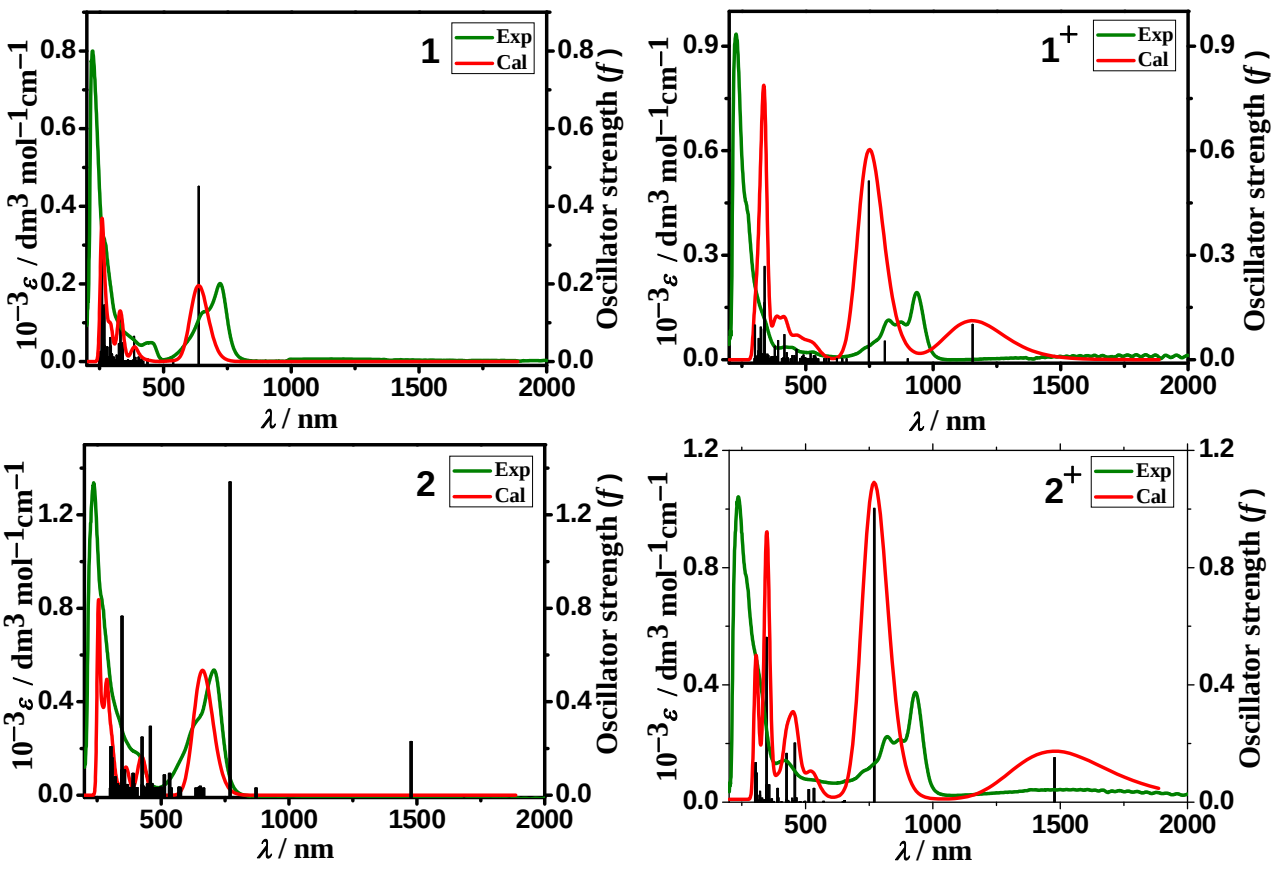


Fig. S4 Experimental (UV-VIS-NIR/CH_2Cl_2) and TD-DFT ((U)B3LYP/CPCM/CH_2Cl_2) calculated spectra of $\mathbf{1}^n$ and $\mathbf{2}^n$. Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 2000 cm^{-1}.

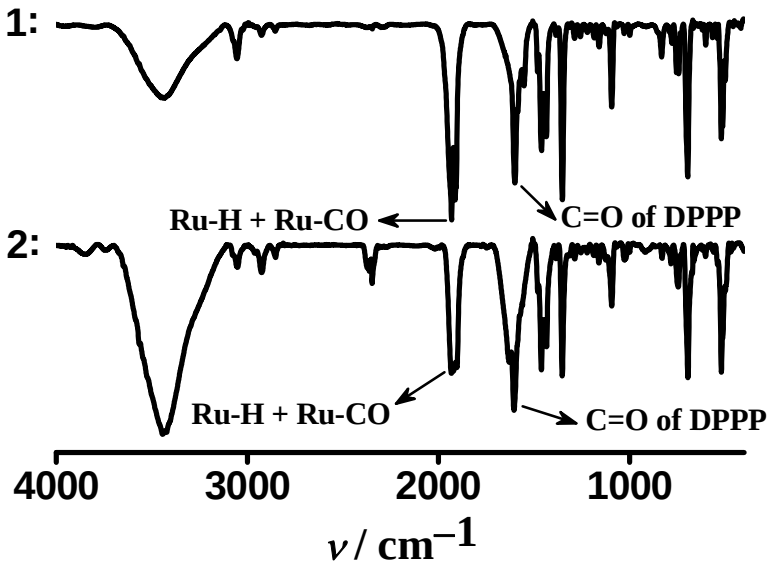


Fig. S5 IR spectra of **1** and **2** as KBr disk.

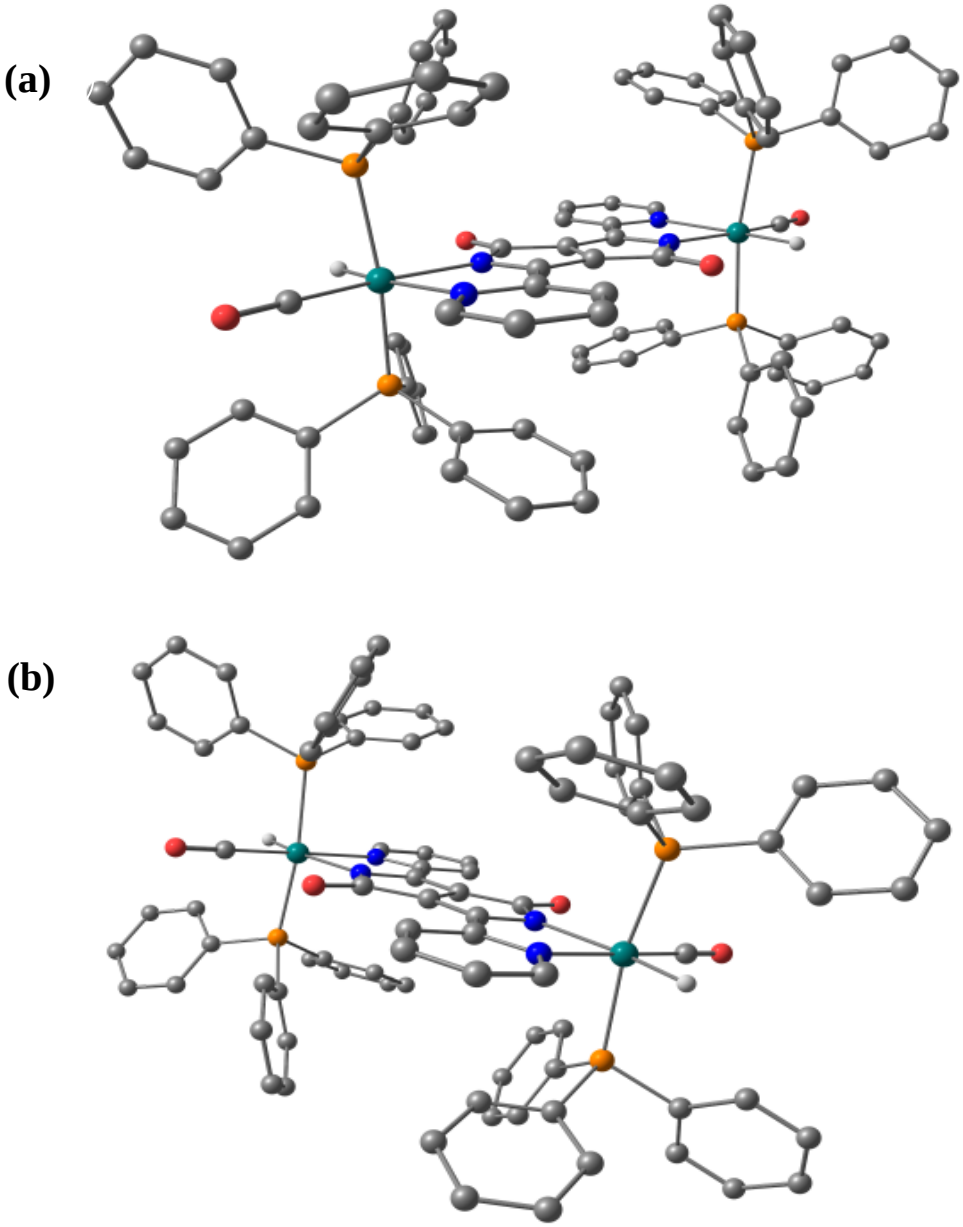
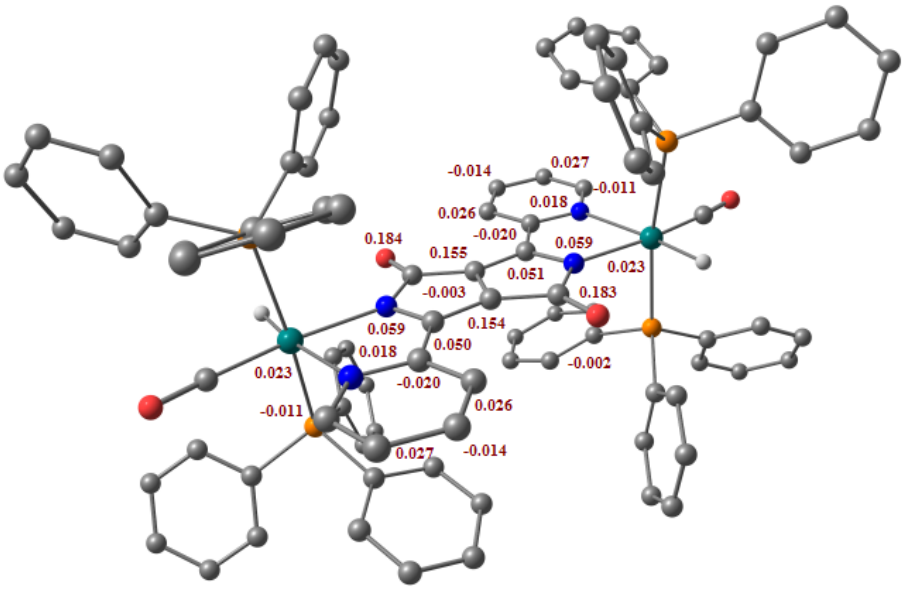
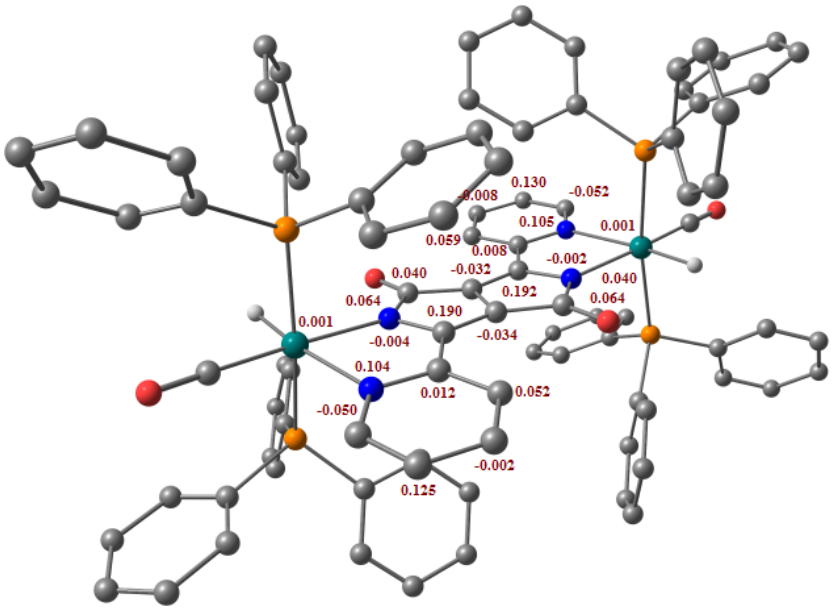


Fig. S6 DFT (B3LYP/LANL2DZ/6-31G*) optimised structures of (a) **1** and (b) **2**.

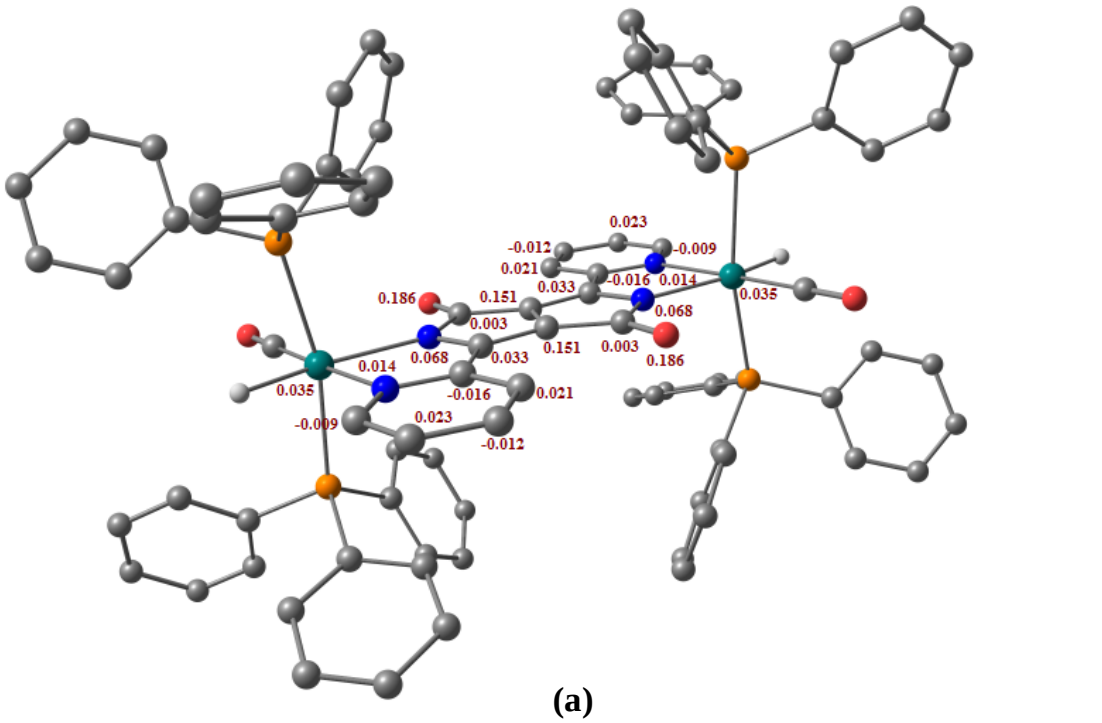


(a)

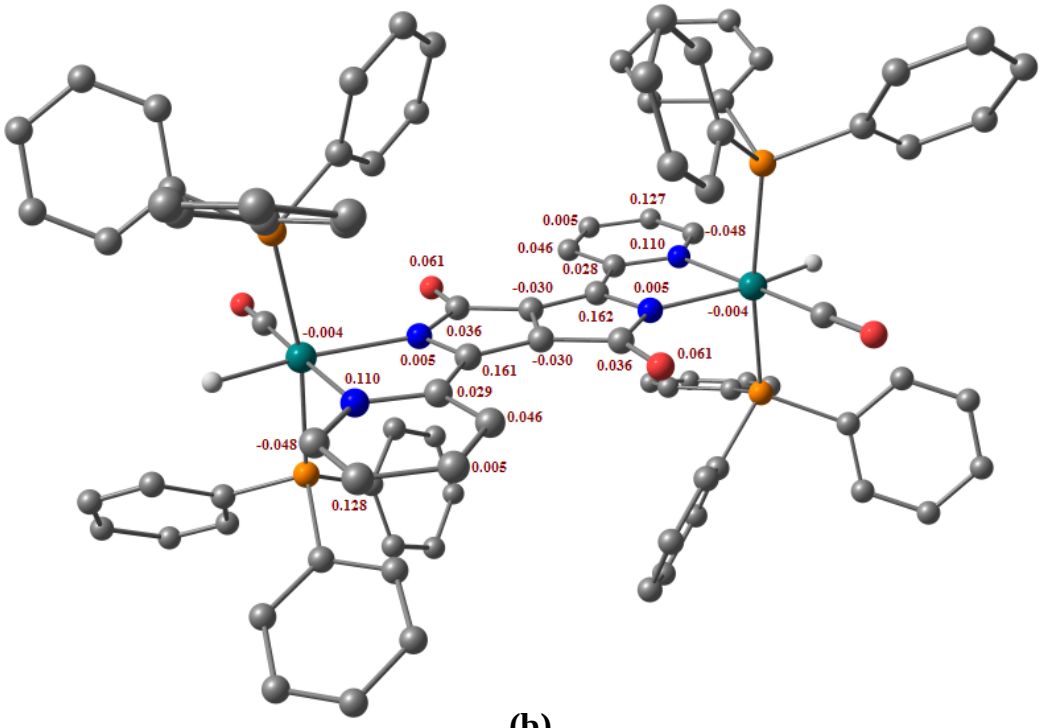


(b)

Fig. S7 DFT calculated Mulliken spin density values on specific atoms of (a) $\mathbf{1}^{+}$ (S=1/2) and (b) $\mathbf{1}^{-}$ (S=1/2).



(a)



(b)

Fig. S8 DFT calculated Mulliken spin density values on specific atoms of (a) $\mathbf{2}^{+}$ (*S*=1/2) and (b) $\mathbf{2}^{-}$ (*S*=1/2).