Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Reversible Pyrrole-Based Proton Storage/Release in Ruthenium(II) Complexes

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Experimental section

Materials, Synthesis and Characterization. Unless stated otherwise, all manipulations were performed under an inert atmosphere using a standard Schlenk line. The NMR spectra were recorded on a Bruker AVANCE(III) spectrometer. Infrared spectrum (KBr) was recorded on a Nicolet 6700 spectrometer FT-IR spectrophotometer. UV-Vis spectra were recorded on Agilent Technologies Cary 8454 UV-Vis at ambient temperature with a 1 cm quarts cell. The ligand 2-(2'-pyridyl)pyrrole (py-pyr), 2-(2'-6'-bromo-pyridyl)pyrrole (Br-py-pyr)[1] and ruthenium precursor $[Ru(bpy)_2Cl_2 \cdot 2H_2O]$[2] were prepared according to literature methods.

ESI-MS measurements: ESI-MS was performed in a Bruker Daltonik GmbH, Bremen mass spectrometer equipped with an electrospray ionization (ESI) source, and the experimental parameters were as following: capillary temperature, 200 ^oC; capillary voltage, 3500 V; flow rate, 4 L/min; hexapole, 400 Vpp.

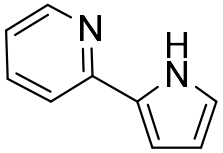
X-ray Diffraction studies: Diffraction data was record on a Bruker CCD diffractometer with monochromatized Mo-Kα radiation (λ= 0.71073 Å). The collected frames are processed using the software SAINT. The absorption correction is processed with SADABS. The structure was solved by a direct method and refined by full matrix least squares method on F^2 using the SHELXTL software package. Refined atomic positions of non-hydrogen atoms with anisotropic parameters. All hydrogen atoms are introduced at their geometrical positions and refined into riding atoms.

Electrochemical measurements: Cyclic voltammetry was performed on a CHI Instruments CHI610A electrochemical analyzer. This workstation contains a digital simulation package as part of the software package to operate the workstation (CHI version 2.06). The working electrode was a glassy carbon electrode, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl electrode in saturated KCl. Electrochemical measurements were performed in acetonitrile solution containing 0.1 M Bu_4NPF_6 electrolyte in a one compartment cell. Scan rate = 100 mV s^{-1}.

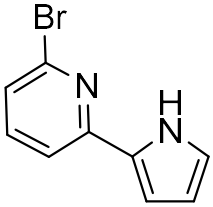
Determination of Dissociation Constants of $[\mathbf{1'}]^{2+}$ and $[\mathbf{2'}]^{2+}$ by UV-Vis Spectrophotometry:[3-5] The absorbance of complex $[\mathbf{1'}]^{2+}$ or $[\mathbf{2'}]^{2+}$ (20 μM) in CH_3CN/H_2O solutions (v/v=1:49, 3 mL) at different pH value was determined by Agilent Technologies Cary 8454 UV-Vis at ambient temperature with a 1 cm quarts cell. Part of pH 0.03 to 0.91 was prepared with 1M aqueous hydrochloric acid, and part of pH greater than 0.91 was prepared with Britton-Robinson buffer solutions. For $[\mathbf{1'}]^{2+}$ and $[\mathbf{2'}]^{2+}$, 465 nm and 360 nm were selected as the measurement wavelength respectively. According to the formula $pKa = pH + lg(A-A_B)/(A_{HB}-A)$, in which A_{HB} is the absorbance in the completely undissociated proton state, A_B is the absorbance in the completely dissociation state of proton and A is the absorbance of a state between the two states, plotted the curve of absorbance-pH values and the slope was the dissociation constant.

DFT calculations：The geometric optimization and vibrational frequency were performed using the density functional theory (DFT) with the B3LYP-D3 functional, which is the B3LYP hybrid functional[6] combined with an empirical dispersion correction developed by Grimme.[7] The 6-31G*

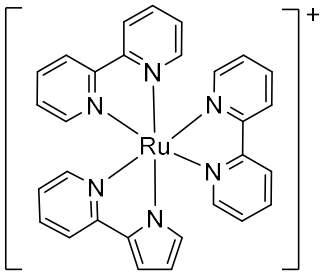
basis set[8] was used for C H N O S Br and F atom along with the Stuttgart/Dresden (SDD)[9] energy-consistent pseudopotentials for Ru atom. All optimized geometries were in C_1 symmetry and determined to be the minima on the potential energy surface without imaginary frequencies. The electrostatic potential (ESP), HOMO-LUMO orbitals and NBO charges were calculated at the same level of theory based on the optimized structures. And the solvent affect was also taken into account using the self-consistent reaction field (SCRF) and polarizable continuum model (PCM)[10] with the acetonitrile solvent. An appropriate connection between a reactant and a product for each reaction step was confirmed by IRC[11] calculations, and the geometry of a transition state was at first shifted by perturbing the geometries very slightly along the reaction coordinate and released for equilibrium optimization. To discuss the energetics of the protonation processes, single-point energy calculations at the optimized geometries were performed at the B3LYP-D3/def2-TZVP[12] level of theory. All calculations of this work were carried out through the Gaussian 09 program package[13].



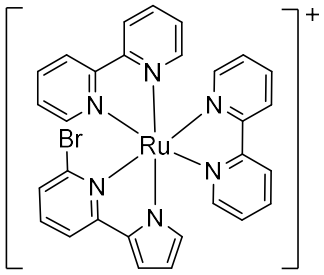
2-(2'-pyridyl)pyrrole(py-pyr)



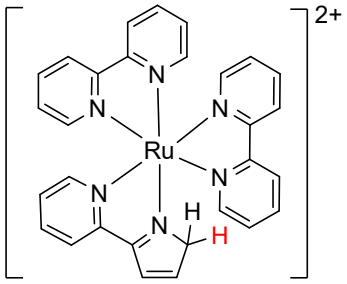
2-(2'-6'-bromo-pyridyl)pyrrole(Br-py-pyr)



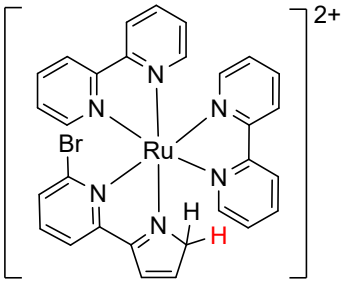
$[Ru(bpy)_2(py\text{-}pyr)]^+$ ($[\mathbf{1}]^+$)



$[Ru(bpy)_2(Br\text{-}py\text{-}pyr)]^+$ ($[\mathbf{2}]^+$)



$[Ru(bpy)_2(py\text{-}pyr\text{-}H\alpha)]^{2+}$ ($[\mathbf{1'}]^{2+}$)



$[Ru(bpy)_2(Br\text{-}py\text{-}pyr\text{-}H\alpha)]^{2+}$ ($[\mathbf{2'}]^{2+}$)

Synthesis of [1]·PF_6 : $Ru(bpy)_2Cl_2·2H_2O$ (130 mg, 0.25 mmol, 1 equiv), py-pyr (36 mg, 0.25 mmol, 1 equiv) and t-BuOK (28 mg, 0.25 mmol, 1 equiv) were placed in a 50 ml two-neck round bottom flask with 5 mL of methanol. The reaction mixture was refluxed overnight under nitrogen atmosphere and filtered. The color of mixture was changed from violet to dark-red. The aqueous solution of NH_4PF_6 (10 equiv, 407.5 mg in 1.0 mL H_2O) was added into the filtrate to give black precipitate. The residual solid was redissolved in dichloromethane (10 mL) and washed with deionized water (3 × 5 mL) to remove excess of NH_4PF_6. Subsequently the organic solution was dried by anhydrous Na_2SO_4 and concentrated in vacuum. The ether (3 mL) was added to give [**1**]·PF_6 as dark red powder. Yield: 147 mg (84%). The concentrated dichloromethane solution of [**1**]·PF_6 was layered by ether to give black needle crystals which were suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (δ, 400 MHz, CD_3CN, 20 °C): 8.39 (dd, J=14.4,6.8 Hz, 4H), 8.12 (d, J=5.2 Hz, 1H), 8.0-7.83 (m, 5H), 7.78 (d, J=5.2Hz, 1H), 7.61-7.47 (m, 3H), 7.41-7.29 (m, 3H), 7.29-7.22 (m, 1H), 7.20 (d, J=5.6 Hz, 1H), 6.84 (d, J=2Hz, 1H), 6.71-6.58 (m, 1H), 6.11 (q, J=1.6 Hz, 1H), 5.89(s, 1H). ESI-MS (m/z): calcd for $Ru_1N_6C_{29}H_{23}$ [**1**]$^+$, 577.1030; found 577.0733.

Synthesis of [2]·PF_6 : The mixture of $Ru(bpy)_2Cl_2·2H_2O$ (130 mg, 0.25 mmol, 1 equiv), Br-py-pyr (55.75 mg, 0.25 mmol, 1 equiv) and t-BuOK (28 mg, 0.25 mmol, 1 equiv) in methanol (5 mL) was refluxed overnight and then filtered. The color of mixture was changed from violet to dark-brown. The aqueous solution of NH_4PF_6 (10 equiv, 407.5 mg in 1.0 mL H_2O) was added into the filtrate to give black precipitate. The residual solid was redissolved in dichloromethane (10 mL) and washed with deionized water (3 × 5 mL) to remove excess of NH_4PF_6. The organic solution was dried by anhydrous Na_2SO_4 and concentrated in vacuum. The ether (3 mL) was added to give [**2**]·PF_6 as dark brown powder. Yield: 160 mg (82%). The concentrated dichloromethane solution of [**2**]·PF_6 was layered by ether to give black needle crystals which were suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (δ, 400 MHz, CD_3CN, 20°C): 8.55 (d, J=5.6 Hz, 1H), 8.42 (d, J=7.6 Hz, 2H), 8.35 (d, J=8.8 Hz, 2H), 7.97-7.91 (m, 2H), 7.91-7.85 (m, 1H), 7.84 (d, J=6.8Hz, 2H), 7.58 (d, J=8.0 Hz, 1H), 7.54 (t, J=5.6 Hz, 1H), 7.45-7.40 (m, 1H), 7.39-7.32 (m, 2H), 7.25 (d, J=5.6 Hz, 1H), 7.18 (t, J=6.4Hz, 2H), 6.95-6.89 (m, 2H), 6.13 (q, J=1.6 Hz, 1H), 5.73(s, 1H). ESI-MS (m/z): calcd for $Ru_1N_6C_{29}H_{22}Br_1$ [**2**]$^+$, 635.0130; found 635.0324.

Synthesis of [1']·$(OTf)_2$: A solution of [**1**]·PF_6 (196.28 mg, 0.28 mmol, 1 equiv) in dichloromethane (5 mL) was added 1 equiv of HOTf (0.28 mmol, 25.5 μL). The color of reaction mixture was turned from dark-red to orange-red immediately. The mixture was stirred for a more 5 minutes. A ether solution (5 mL) of HOTf (10 μL) was added to give brick-red precipitation of [**1'**]·$(OTf)_2$. The precipitation was washed with ether (3 × 5 mL) and dried under vacuum. Yield: 185.8 mg (78%). ^{1}H NMR (δ, 400 MHz, CD_3CN, 20°C): 8.48 (q, J=8.0 Hz, 4H), 8.38 (d, J=8.0 Hz, 1H), 8.14-7.99 (m, 5H), 7.82 (dd, J=12.4, 5.6 Hz, 2H), 7.72 (dd, J=14.4, 5.6 Hz, 2H), 7.62 (dd, J=10.4, 5.6 Hz, 2H), 7.52-7.39 (m, 5H), 7.39-7.31 (m, 1H), 4.66, 4.02 (ABq, J=26.8 Hz, 2H). ESI-MS (m/z) : calcd for $Ru_1N_6C_{30}O_3F_3S_1H_{23}$ [**1'** + OTf - H]$^+$, 706.0550; found 706.0640.

Synthesis of [2']·(OTf)$_2$: A solution of [**2**]·PF_6 (218.4 mg, 0.28 mmol, 1 equiv) in dichloromethane (5 mL) was added 1 equiv of HOTf (0.28 mmol, 25.5 μL). The color of reaction mixture was turned from dark-brown solution to reddish-brown immediately. The mixture was stirred for a more 5 minutes. A ether solution (5 mL) of HOTf (10 μL) was added to give brick-red precipitation of [**2'**]·$(OTf)_2$. The precipitation was washed with ether (3 × 5 mL) and dried under vacuum. Yield: 190 mg (73%). The [**2'**]·$(OTf)_2$ solution in CH_2Cl_2 was layered by 0.1 mM HOTf solution of Et_2O to give darkish-red single crystals which were suitable for X-ray diffraction analysis. ^{1}H NMR (δ, 400 MHz, CD_3CN, 20 °C): 8.52 (d, J=7.6 Hz, 2H), 8.45 (t, J=6.8 Hz, 2H), 8.37 (d, J = 7.6 Hz, 1H), 8.17-8.07 (m, 3H), 8.05-7.93 (m, 2H), 7.79 (d, J=8.0 Hz, 1H), 7.75 (d, J=5.2 Hz, 1H), 7.67 (d, J = 5.6 Hz, 1H), 7.62 (d, J=5.6 Hz, 2H), 7.57-7.43 (m, 4H), 7.30 (q, J=6.0 Hz, 2H), 4.52, 3.97 (ABq, J=26.4 Hz, 2H). ESI-MS (m/z) : calcd for $Ru_1N_6C_{30}O_3F_3S_1H_{22}Br_1$ [**2'** + OTf - H]$^+$, 783.9650; found 783.9926.

Triggering Cationic Polymerization of 2,2-dimethyloxirane: The sample tube was charged with 2,2-dimethyloxirane monomer and acetonitrile solution of [**1'**]$^{2+}$ (0.4 mol%) or [**2'**]$^{2+}$ (0.4 mol%). After stirred for five minutes the color of the mixture turned to red from orange. Then the mixture was diluted with acetonitrile and characterized with ESI-MS. A set of mass peaks with the interval in m/z of 72 clearly demonstrated the successful progress of polymerization of 2,2-dimethyloxirane by pyrrolium [**1'**]$^{2+}$ or [**2'**]$^{2+}$.

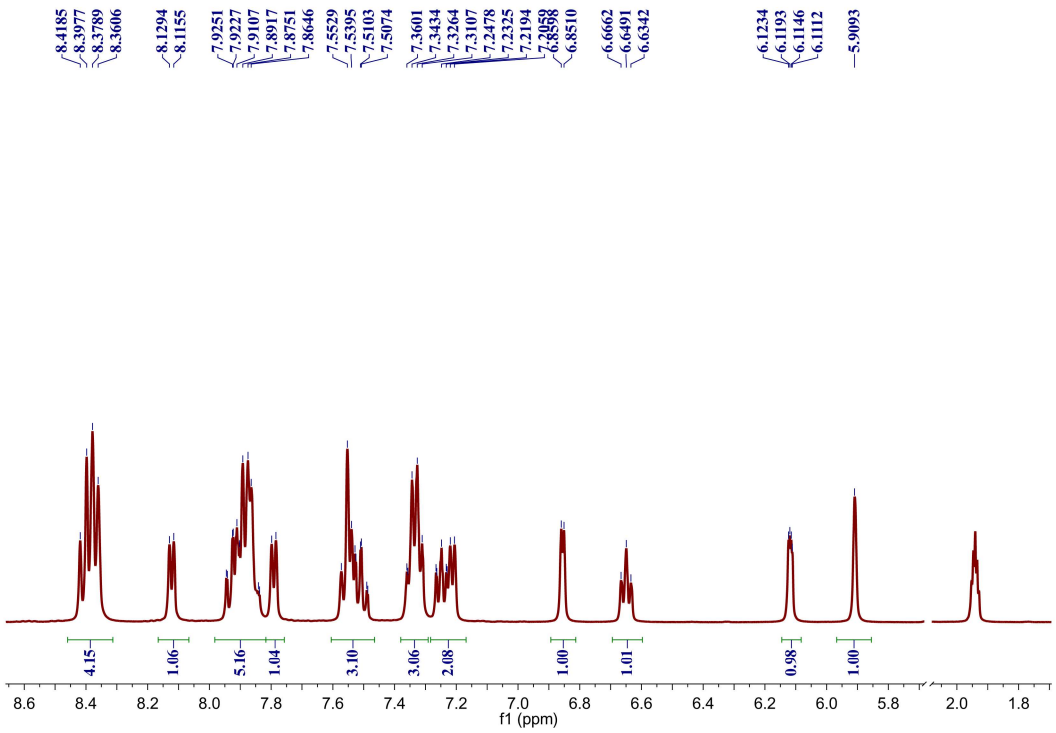


Figure S1. ^{1}H NMR (CD_3CN, 400 MHz, 20 °C) spectrum of [**1**]$^{+}$.

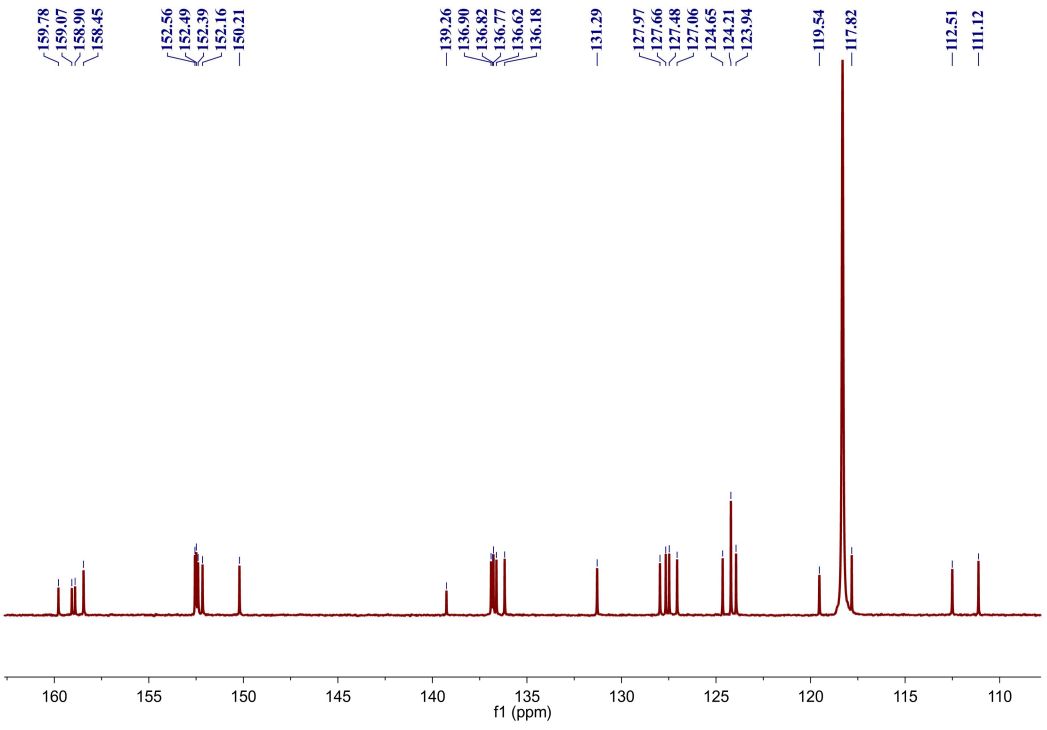


Figure S2. ^{13}C NMR (CD_3CN, 101 MHz, 20 °C) spectrum of [**1**]$^{+}$.

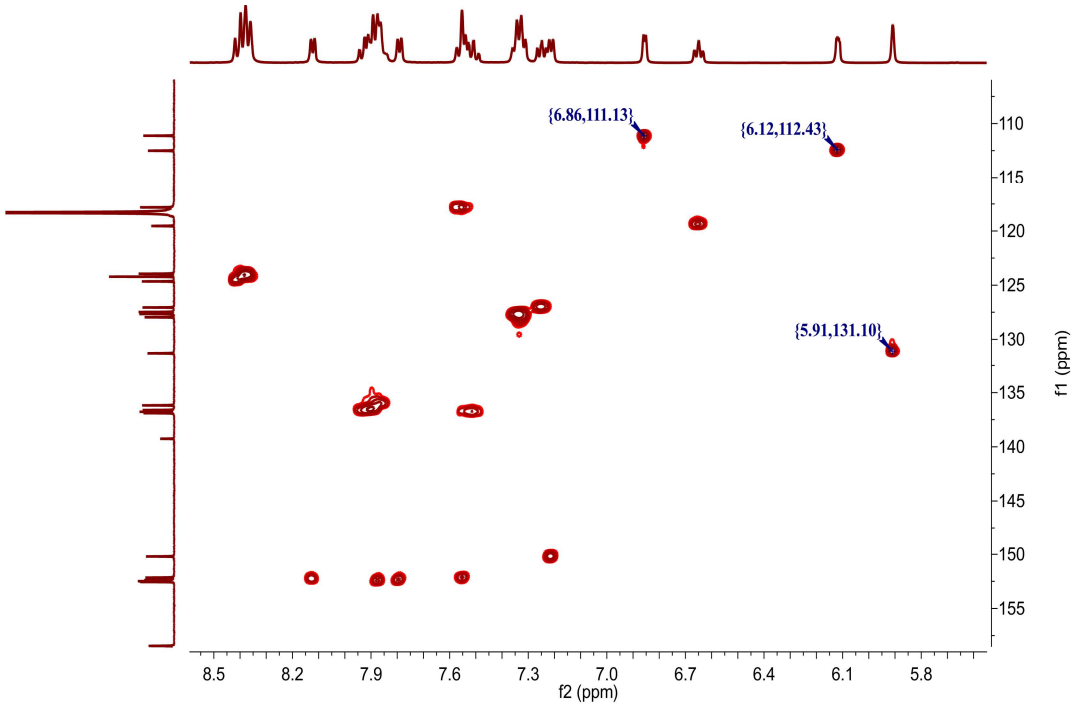


Figure S3. ^{1}H-^{13}C gHSQC spectrum of [**1**]$^{+}$.

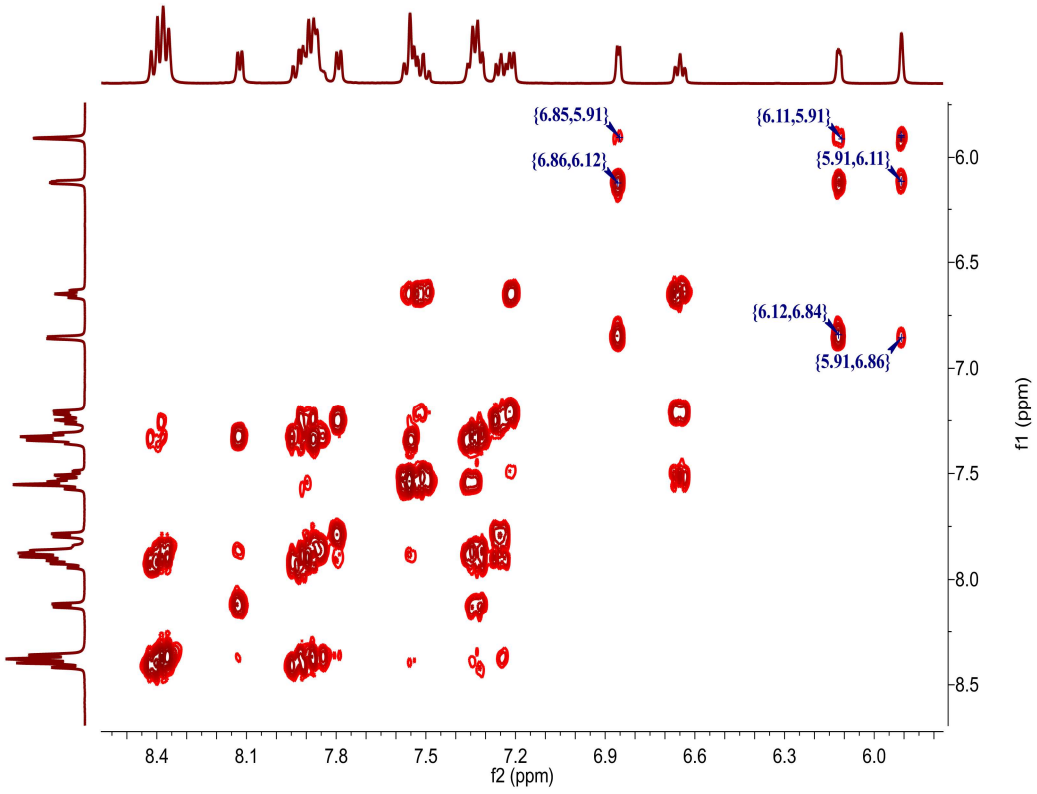


Figure S4. ^{1}H-^{1}H COSY NMR spectrum of [**1**]$^{+}$.

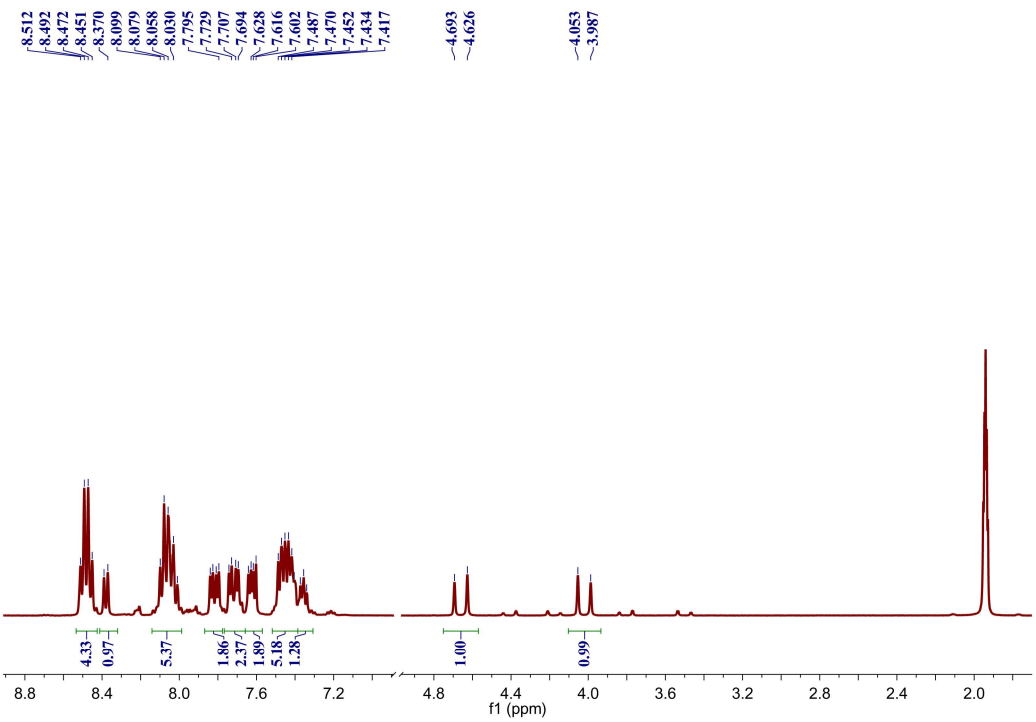


Figure S5. ^{1}H NMR (CD_3CN, 400 MHz, 20 °C) spectrum of [**1'**]$^{2+}$.

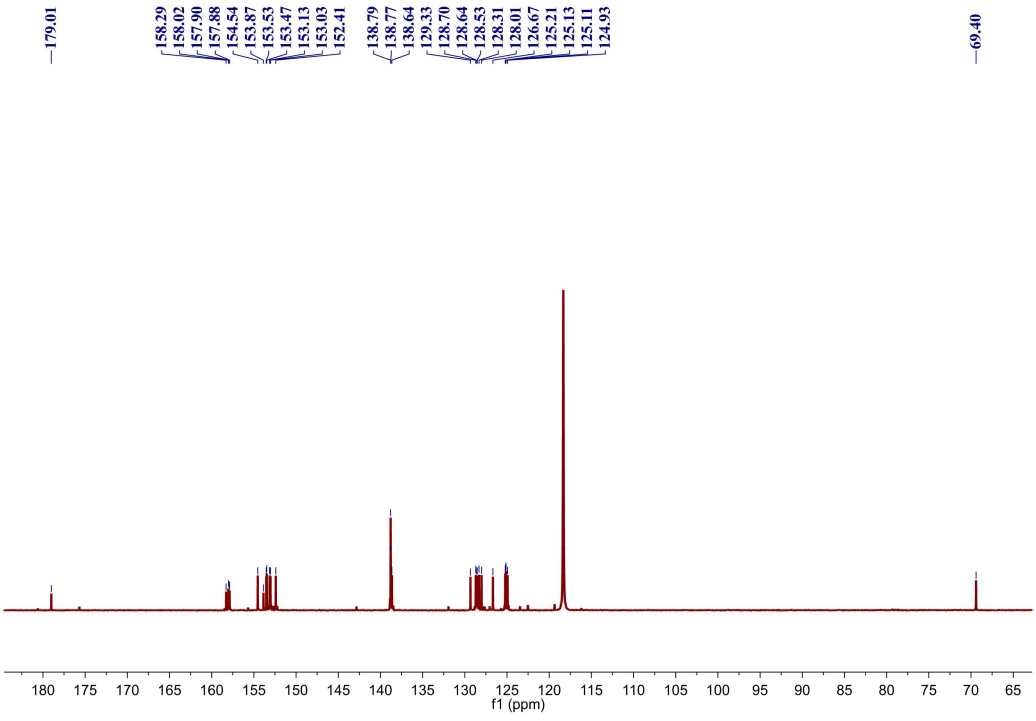


Figure S6. ^{13}C NMR (CD_3CN, 101 MHz, 20 °C) spectrum of [**1'**]$^{2+}$.

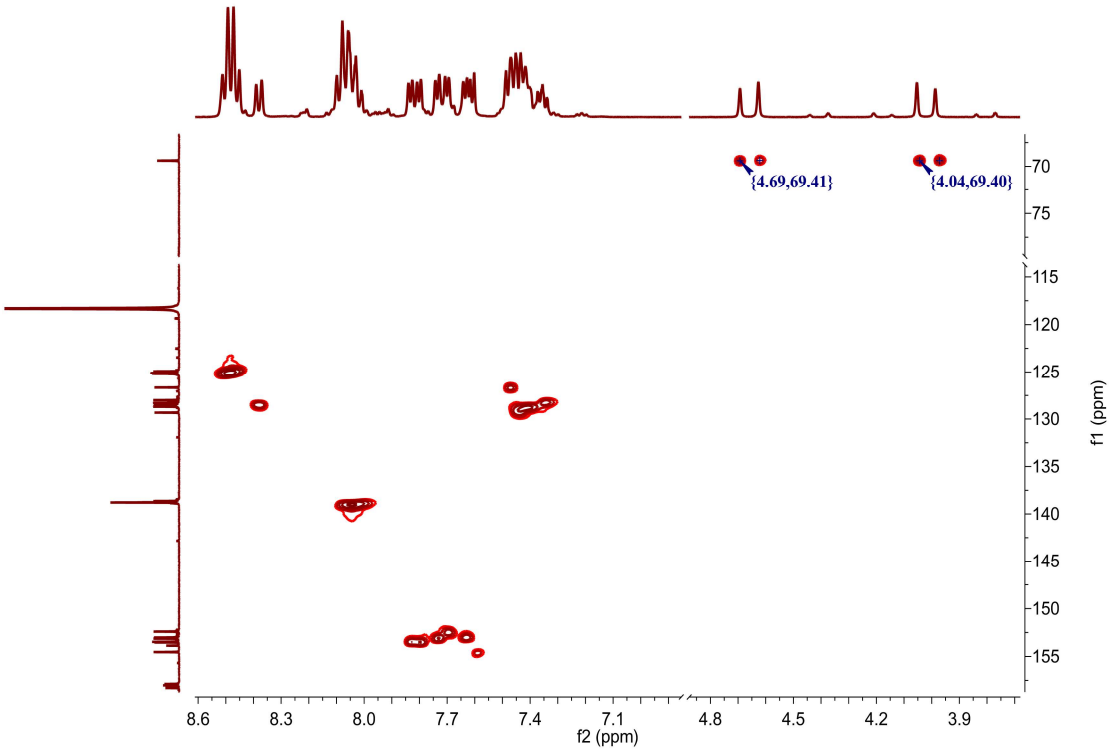


Figure S7. ^{1}H-^{13}C gHSQC spectrum of [**1'**]$^{2+}$.

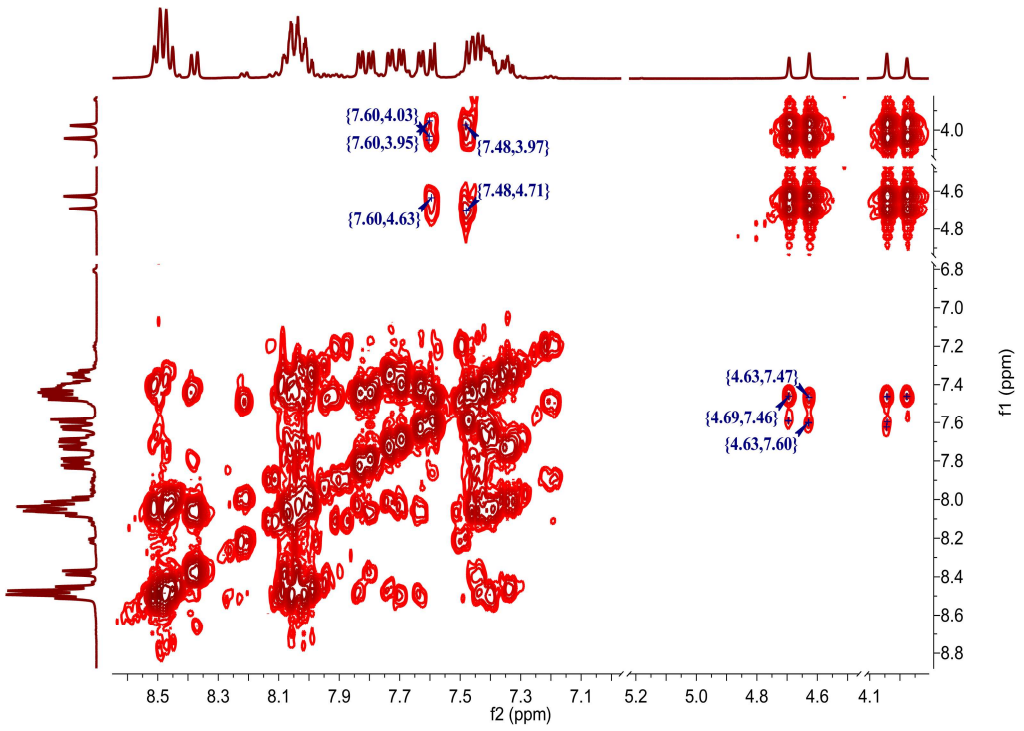


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of [**1'**]$^{2+}$.

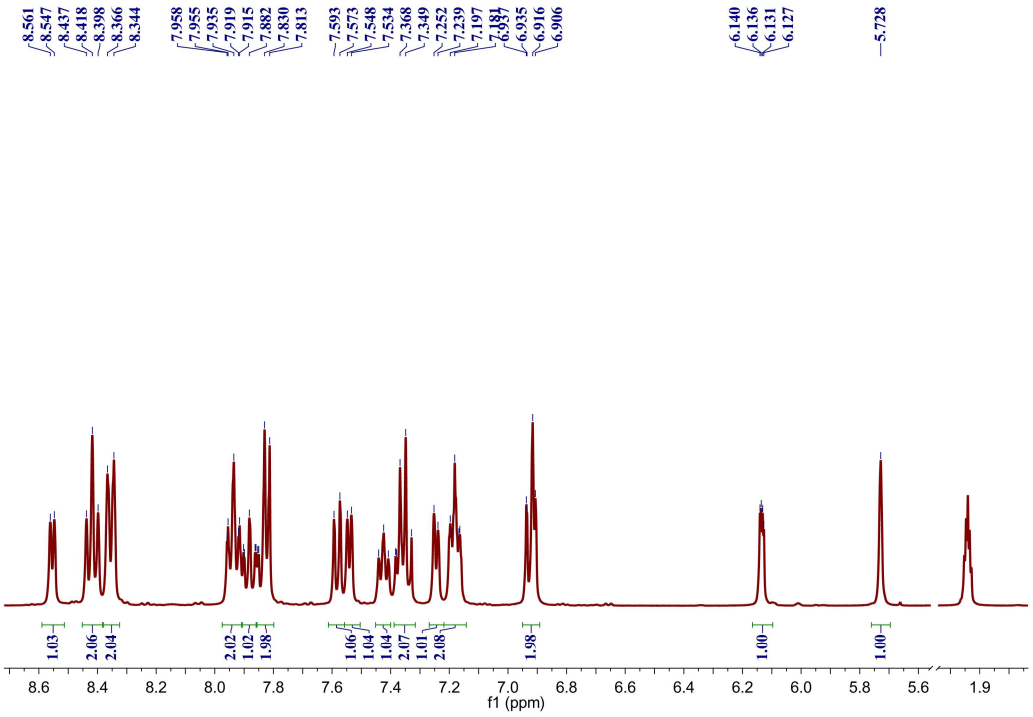


Figure S9. ^{1}H NMR (CD_3CN, 400 MHz, 20 °C) spectrum of [**2**]$^{+}$.

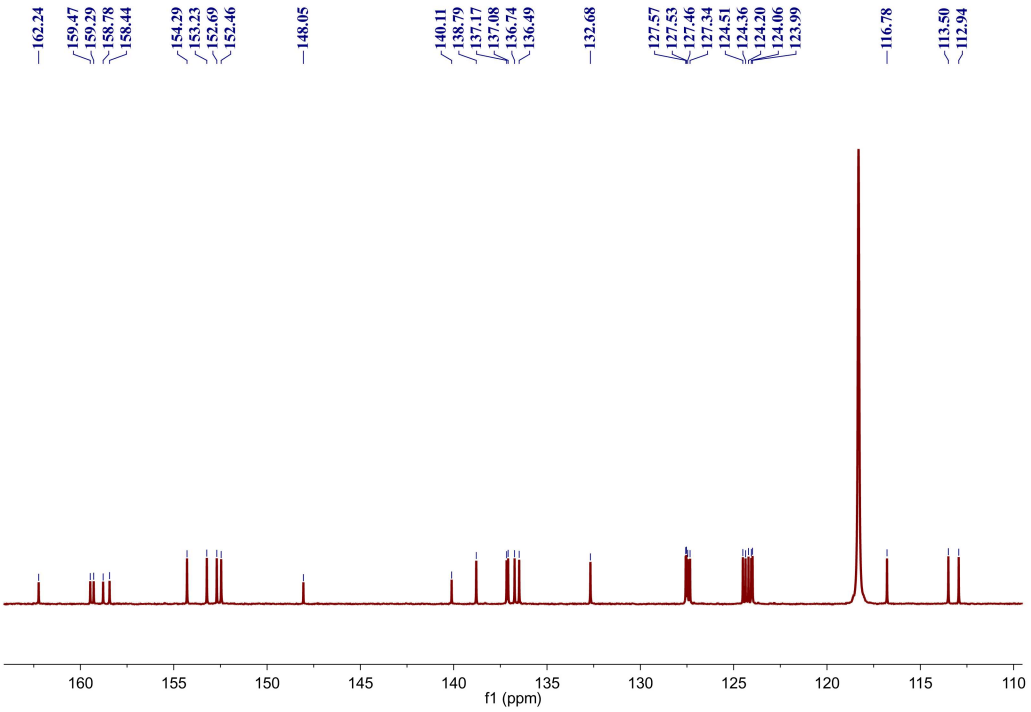


Figure S10. ^{13}C NMR (CD_3CN, 101 MHz, 20 °C) spectrum of [**2**]$^{+}$.

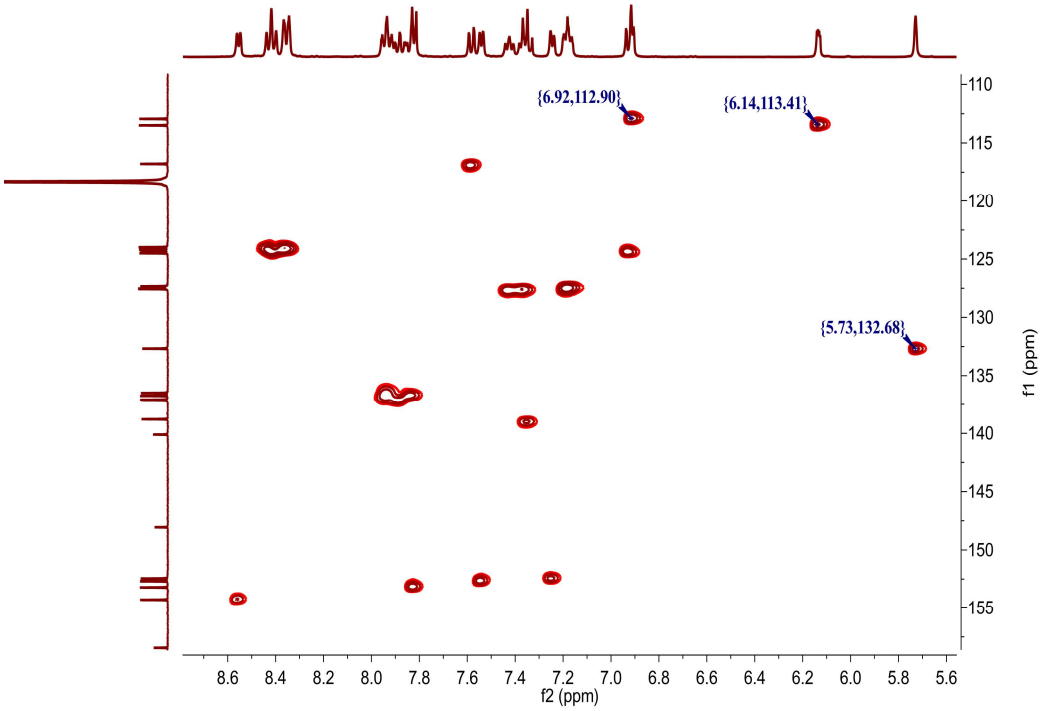


Figure S11. ^{1}H-^{13}C gHSQC spectrum of [**2**]$^{+}$.

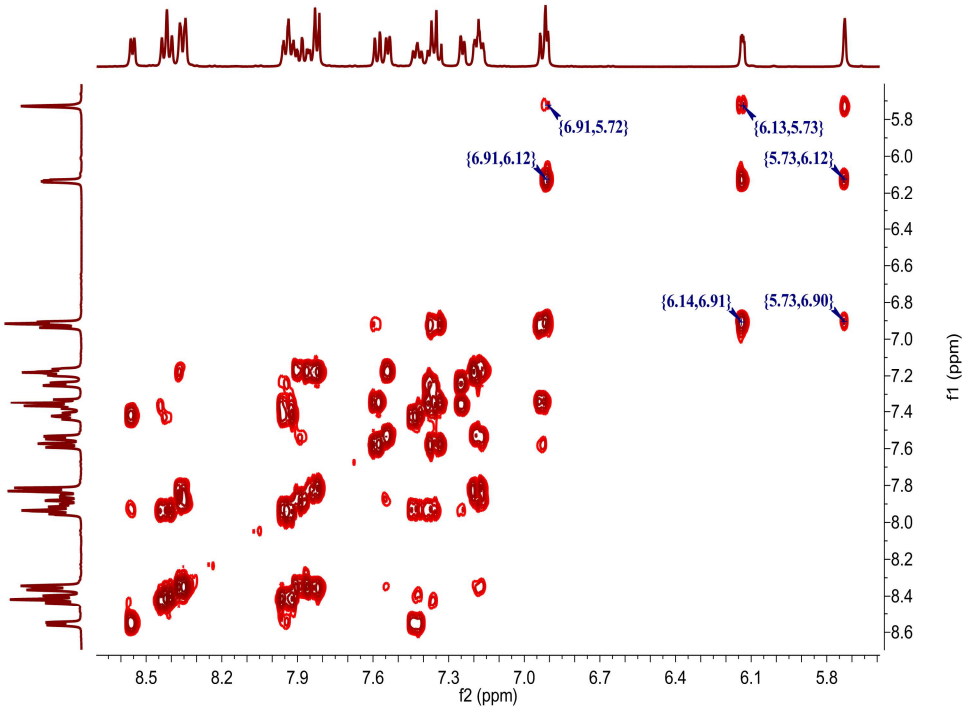


Figure S12. ^{1}H-^{1}H COSY NMR spectrum of [**2**]$^{+}$.

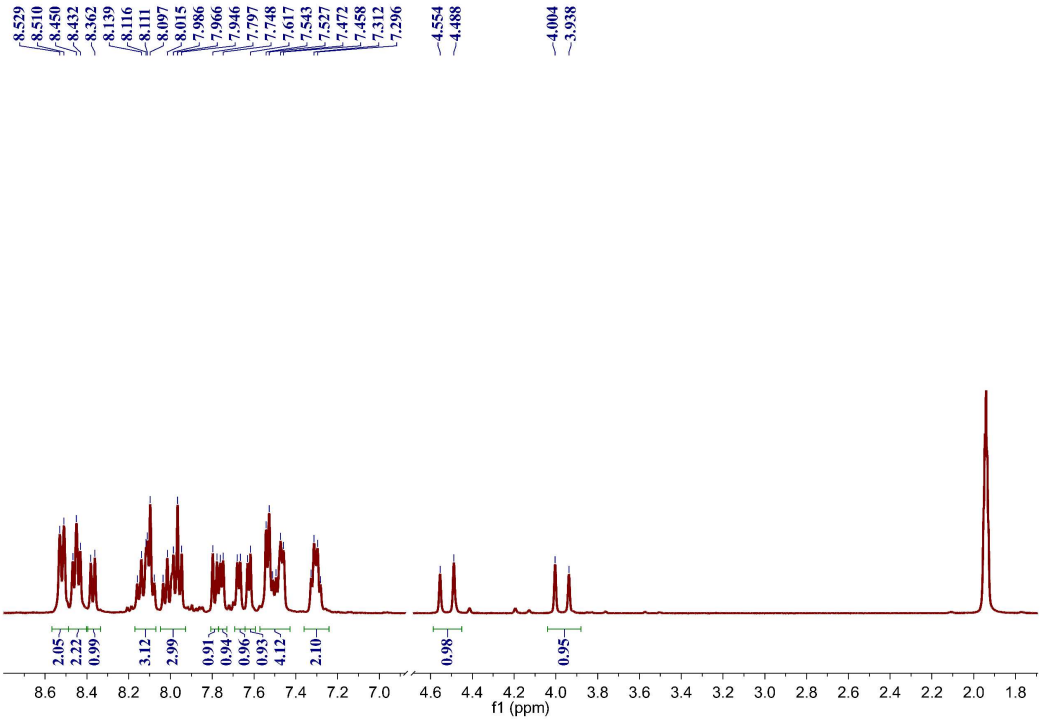


Figure S13. ^{1}H NMR (CD_3CN, 400 MHz, 20 °C) spectrum of [**2'**]$^{2+}$.

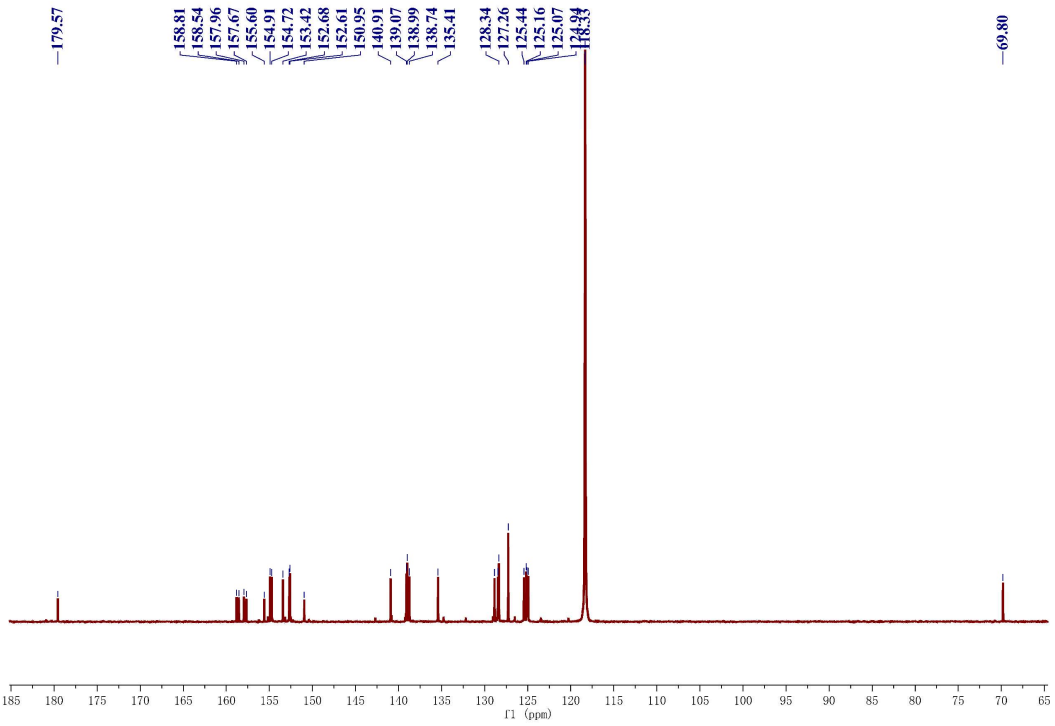


Figure S14. ^{13}C NMR (CD_3CN, 101 MHz, 20 °C) spectrum of [**2'**]$^{2+}$.

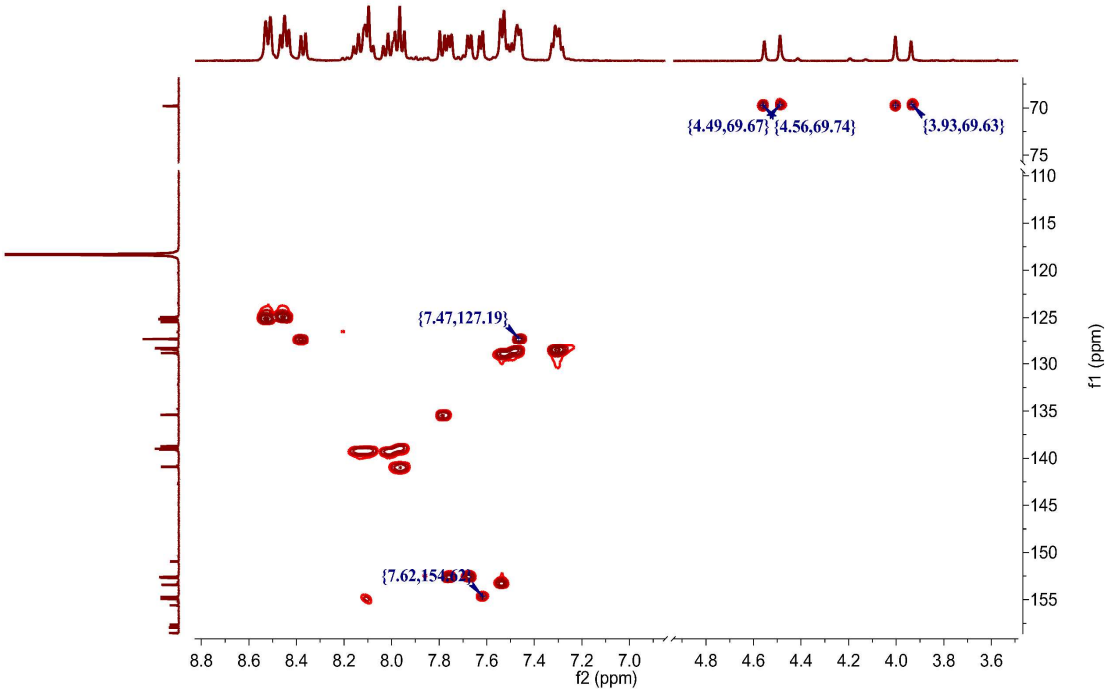


Figure S15. ^{1}H-^{13}C gHSQC spectrum of [**2'**]$^{2+}$.

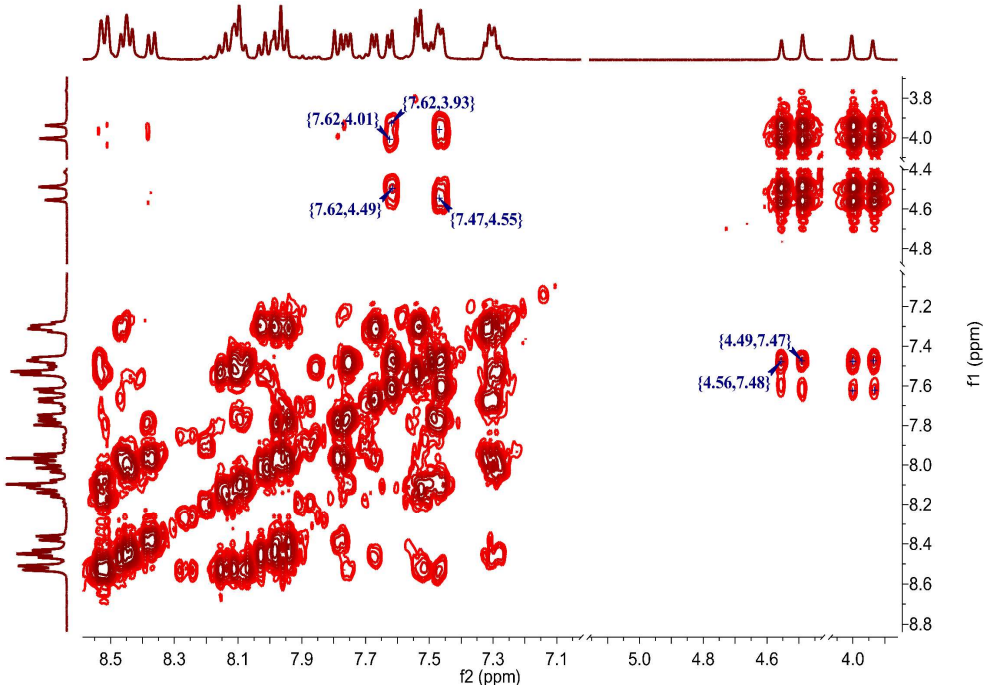


Figure S16. ^{1}H-^{1}H COSY NMR spectrum of [**2'**]$^{2+}$.

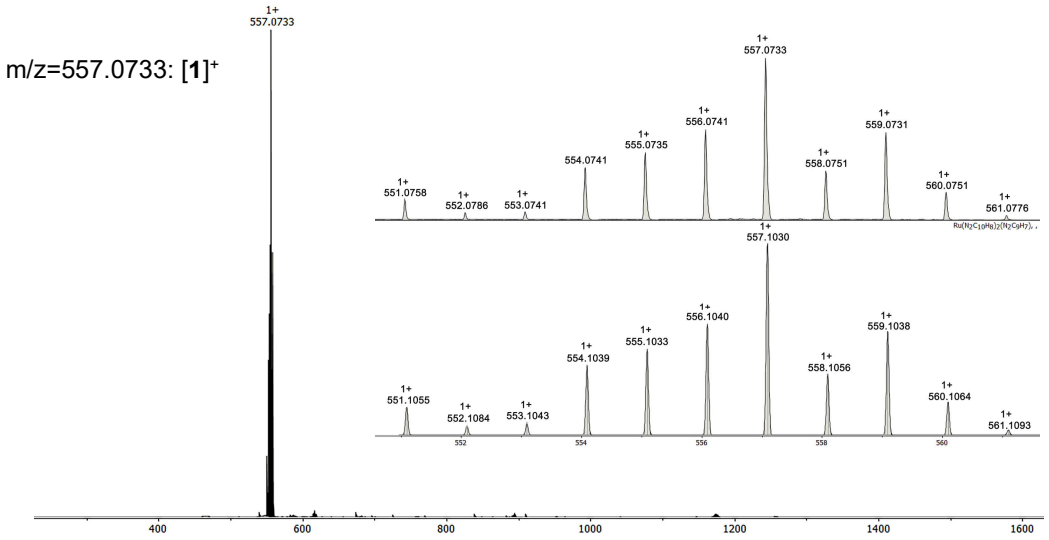


Figure S17. ESI-MS spectrum of [**1**]$^{+}$ in acetonitrile. Inset: Above is the observed isotope pattern and below is the predicted isotope distribution.

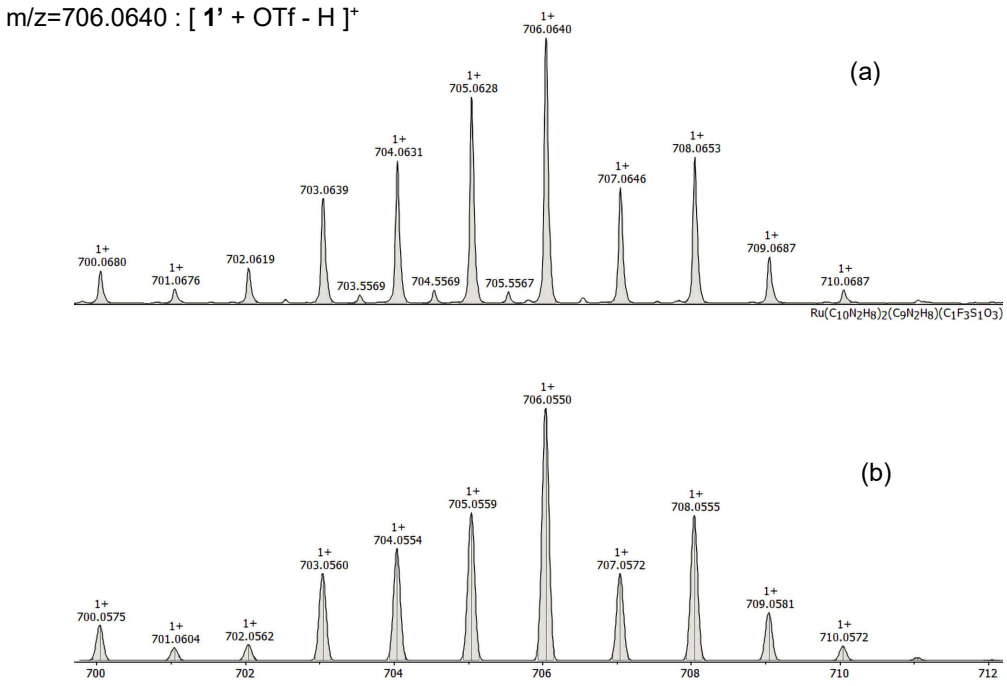


Figure S18. ESI-MS spectrum of [**1'**]$^{2+}$ in acetonitrile: (a) Observed isotope pattern of [**1'**]$^{2+}$ and (b) predicted isotope distribution of [**1'**]$^{2+}$.

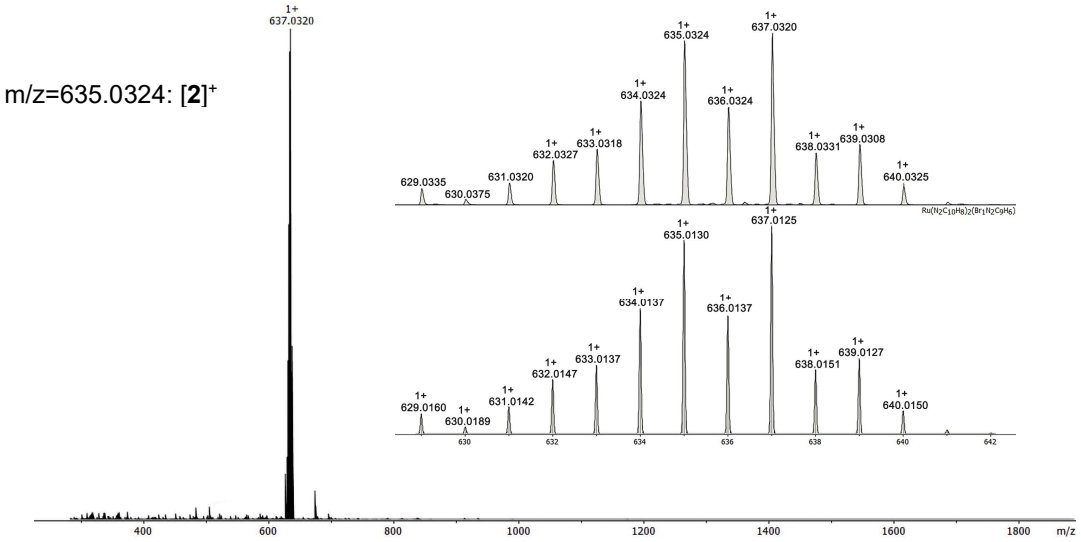


Figure S19. ESI-MS spectrum of [**2**]$^{+}$ in acetonitrile. Inset: Above is the observed isotope pattern and below is the predicted isotope distribution.

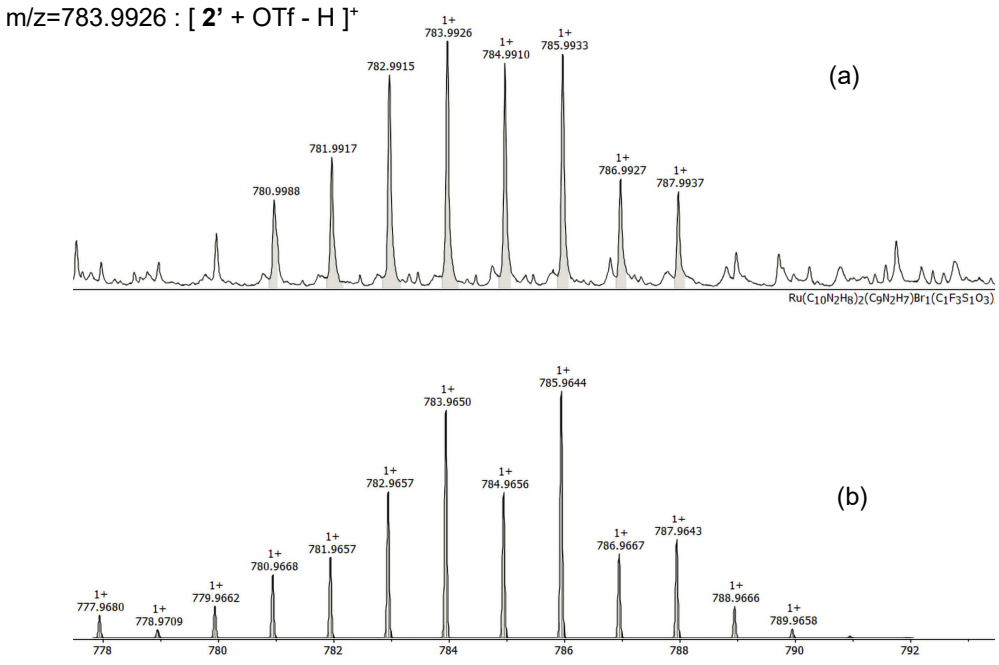


Figure S20. ESI-MS spectrum of [**2'**]$^{2+}$ in acetonitrile: (a) Observed isotope pattern of [**2'**]$^{2+}$ and (b) predicted isotope distribution of [**2'**]$^{2+}$.

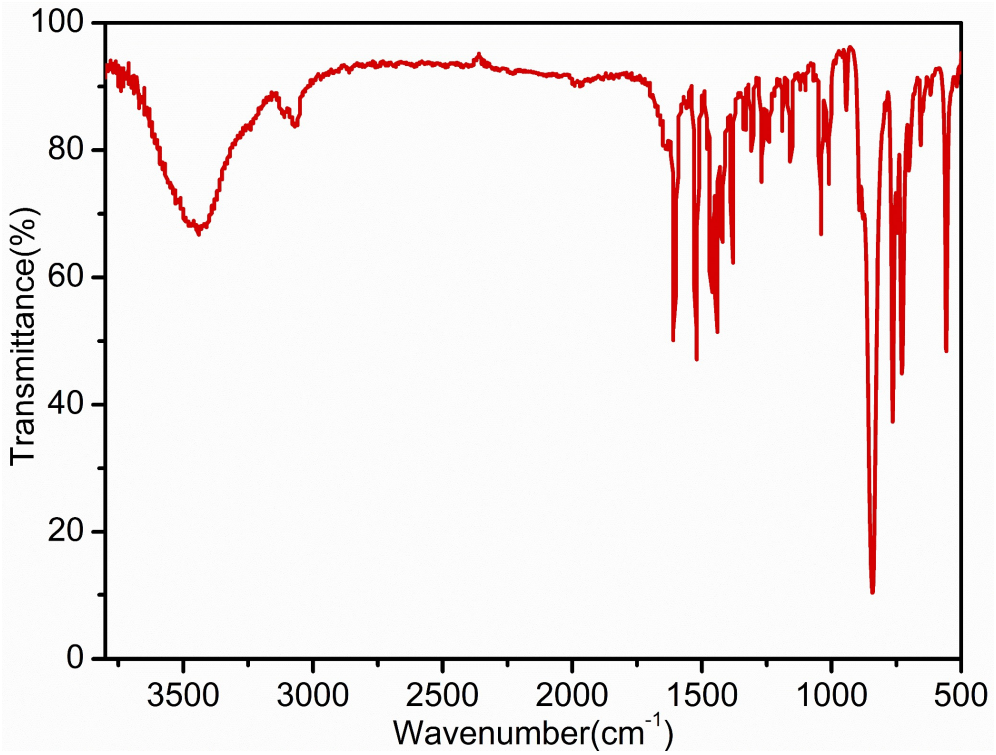


Figure S21. IR spectrum of [**1**]$^{+}$.

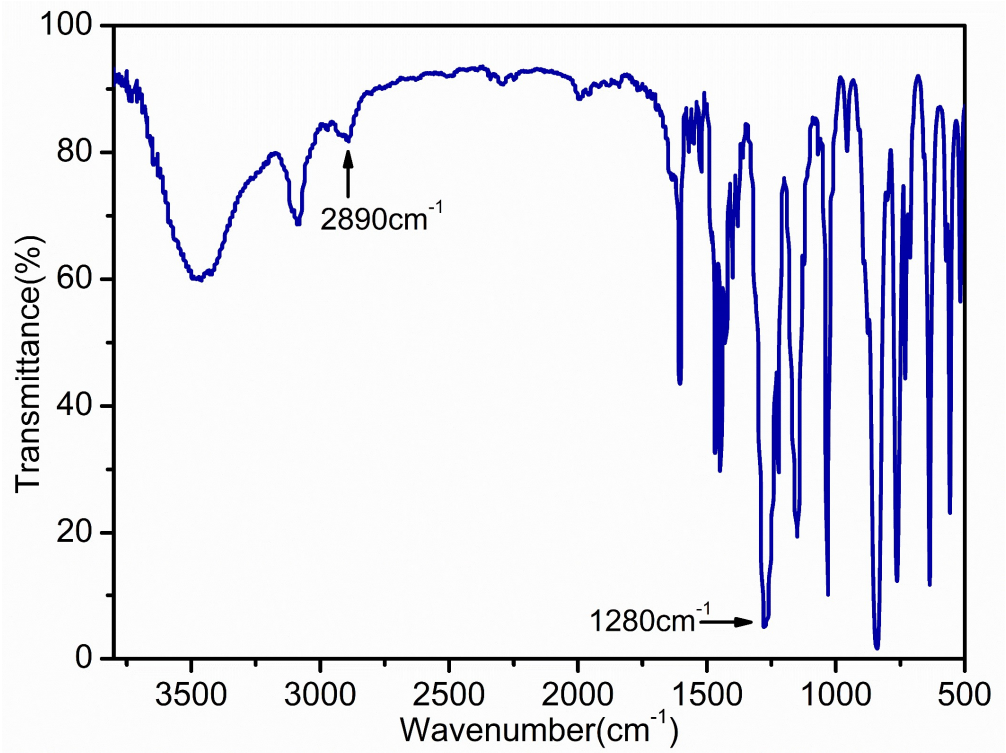


Figure S22. IR spectrum of [**1'**]$^{2+}$.

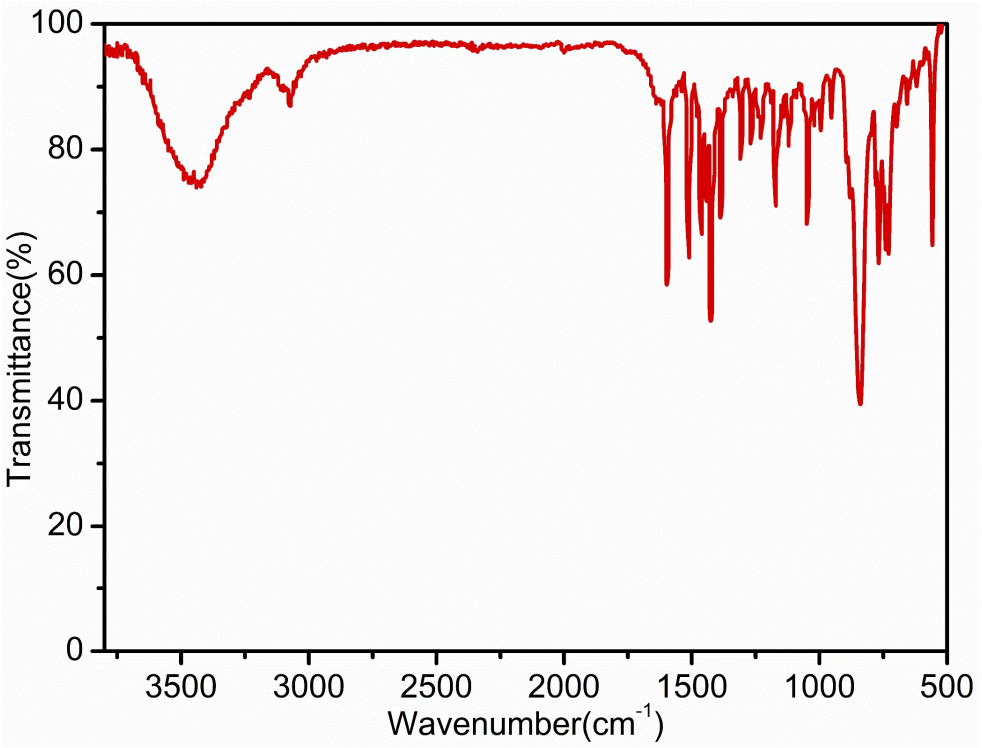


Figure S23. IR spectrum of [**2**]$^{+}$.

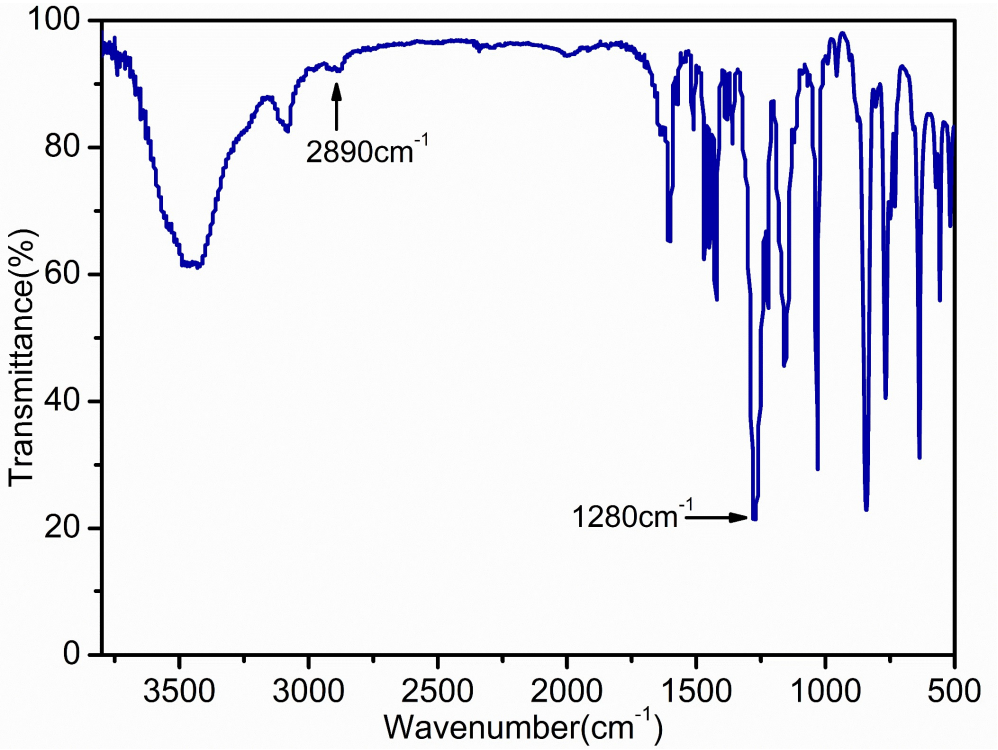


Figure S24. IR spectrum of [**2'**]^{2}.

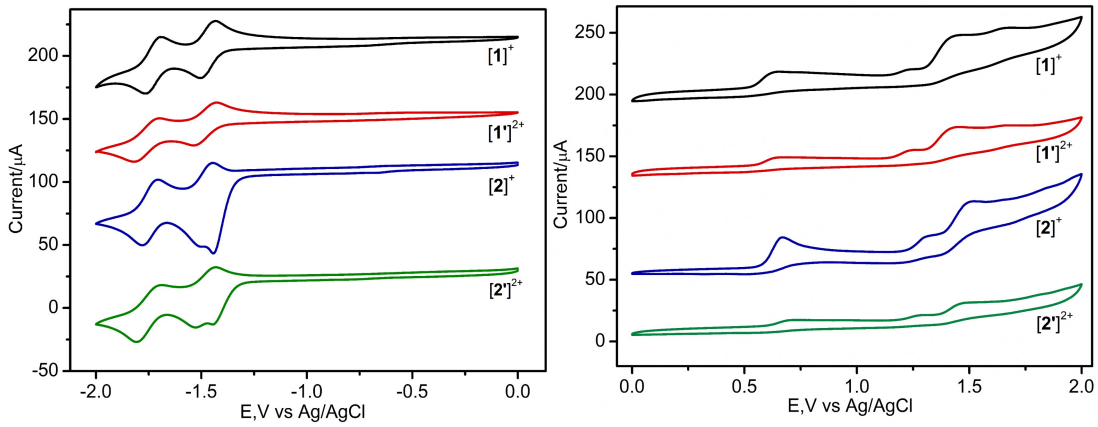


Figure S25. Cyclic voltammograms of separate 1 mM MeCN solutions of [**1**]$^{+}$ (black) , [**1'**]$^{2+}$ (red) , [**2**]$^{+}$ (blue) and [**2'**]$^{2+}$ (green) at room temperature with Bu_4NPF_6 as supporting electrolyte (0.1 M). Ag/AgCl is used as reference electrode, Pt wire as the counter electrode and glassy carbon as the working electrode. Scan rate = 100 mV s^{-1}.

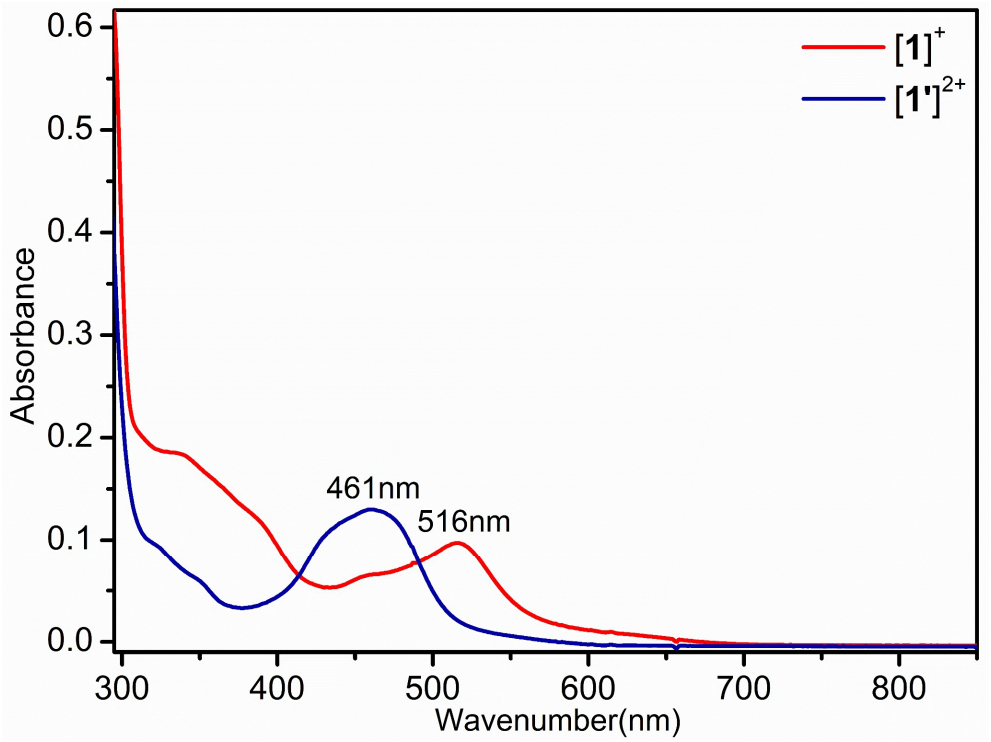


Figure S26. UV–Vis absorption spectra of complexes [**1**]$^{+}$ and [**1'**]$^{2+}$.

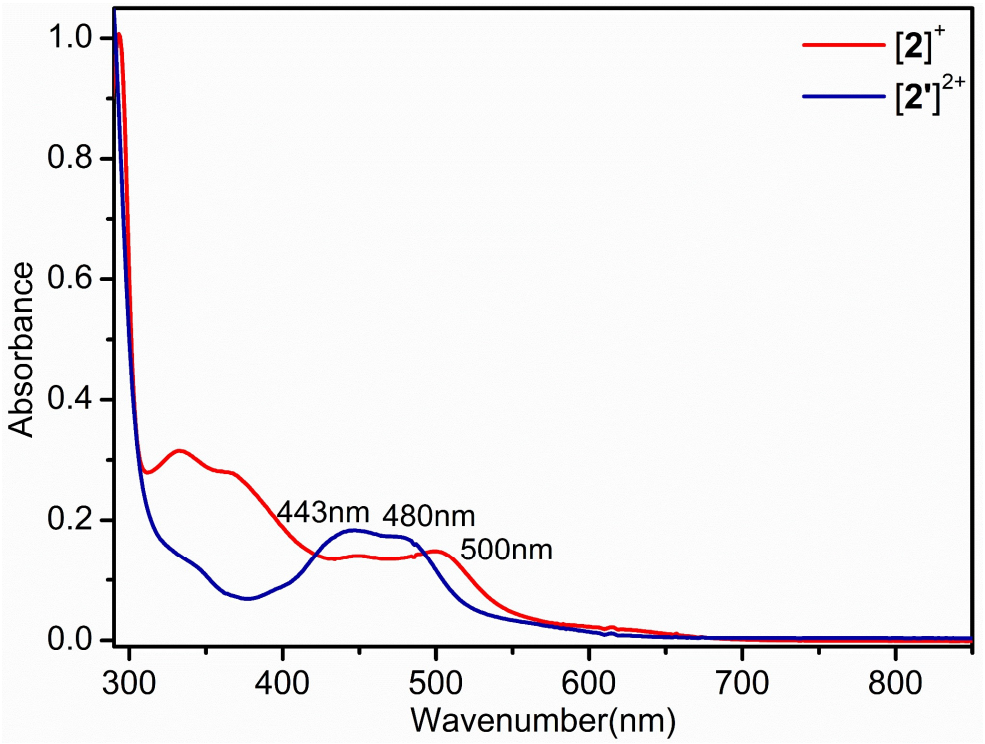


Figure S27. UV–Vis absorption spectra of complexes [**2**]$^{+}$ and [**2'**]$^{2+}$.

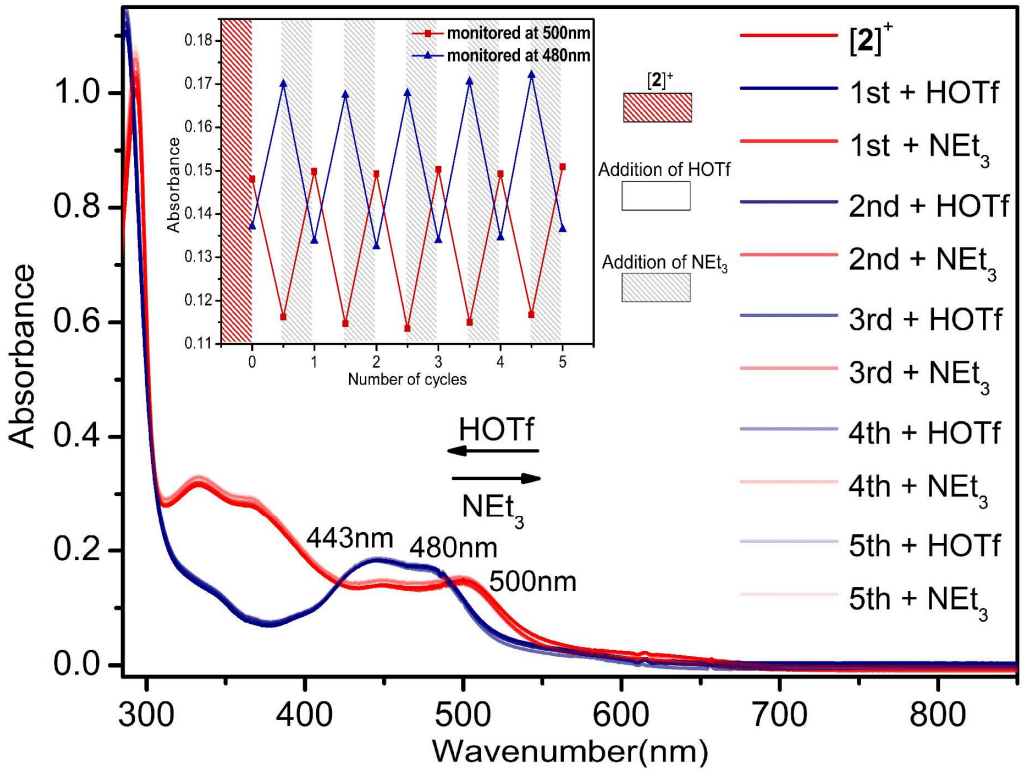


Figure S28. UV-Vis spectra of reversible switching of [**2**]$^{+}$ and [**2'**]$^{2+}$ in acetonitrile (concentration=1 × 10^{-5} M) by alternate addition of HOTf and NEt_3 for five repeating cycles. Inset: Changes of absorbance monitored at the wavelength of 500 nm and 480 nm.

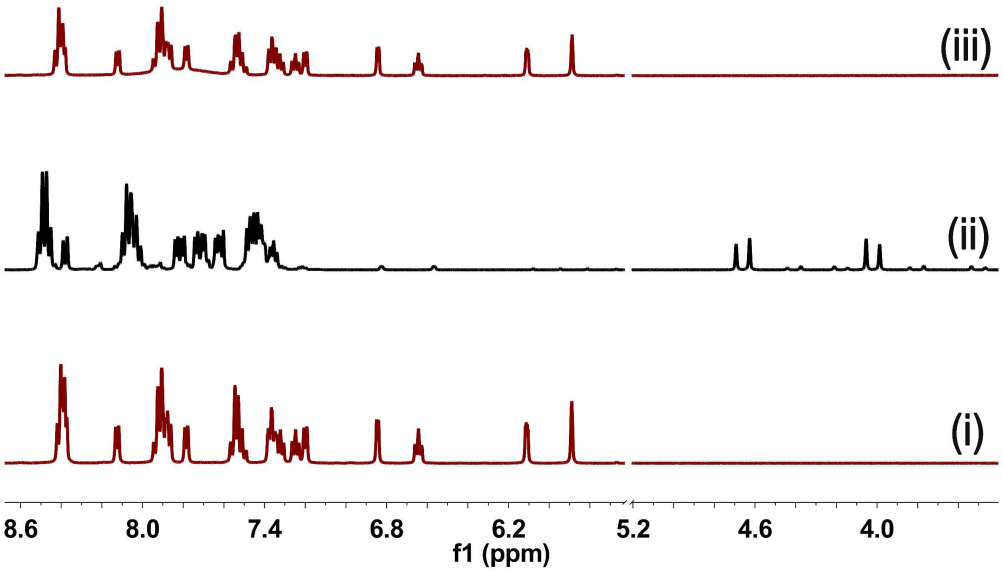


Figure S29. ^{1}H NMR spectra (CD_3CN) showing reversible switching between [**1**]$^{+}$ and [**1'**]$^{2+}$:(i) spectrum of [**1**]$^{+}$; (ii) addition 1 equiv HOTf to [**1**]$^{+}$; (iii) subsequent addition of 1 equiv. NEt_3.

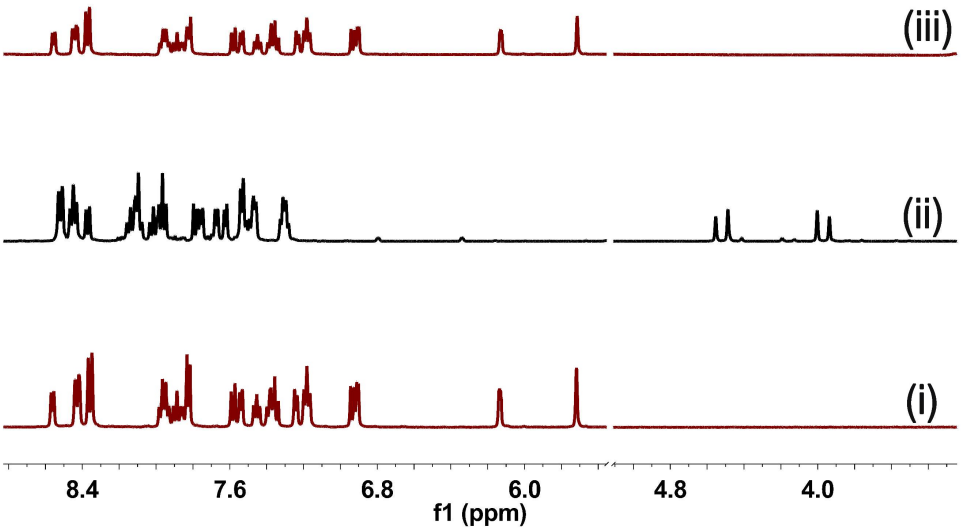


Figure S30. ^{1}H NMR spectra (CD_3CN) showing reversible switching between [**2**]$^{+}$ and [**2'**]$^{2+}$:(i) spectrum of [**2**]$^{+}$; (ii) addition 1 equiv HOTf to [**2**]$^{+}$; (iii) subsequent addition of 1 equiv. NEt_3.

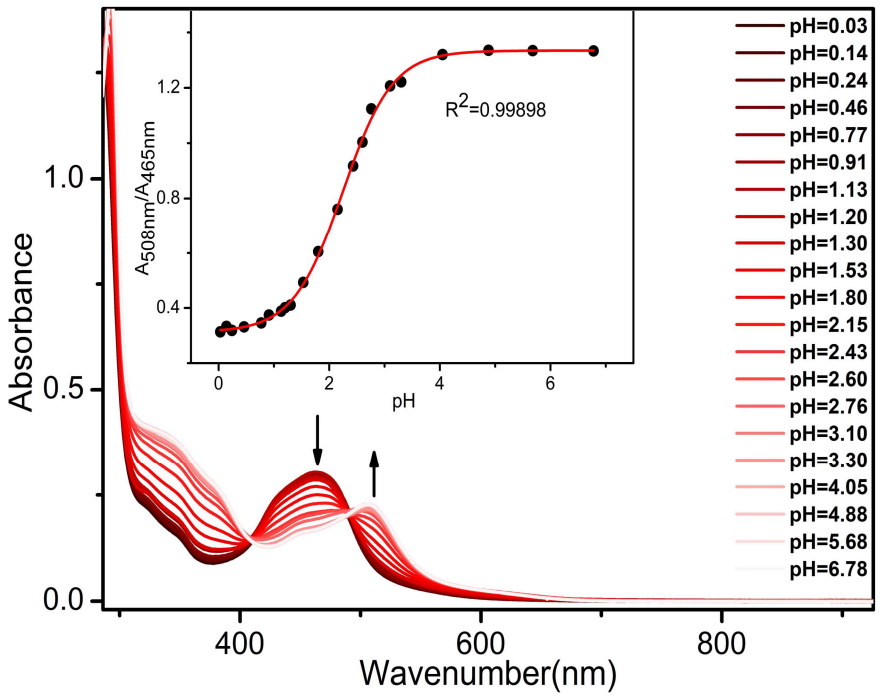


Figure S31. Absorption spectra of [**1**]$^+$ (20μM) in CH_3CN/H_2O solutions (v/v=1:49) at different pH. Inset: Change in A_{508nm}/A_{465nm} at different pH.

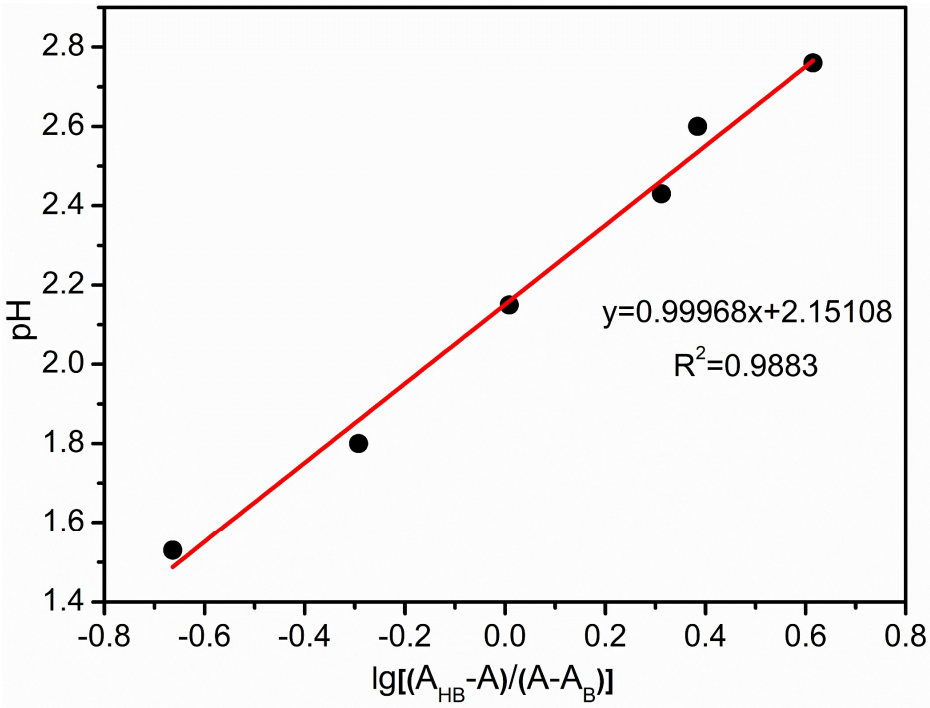


Figure S32. The curve of absorbance-pH values of [**1**]$^+$ in CH_3CN/H_2O solutions.

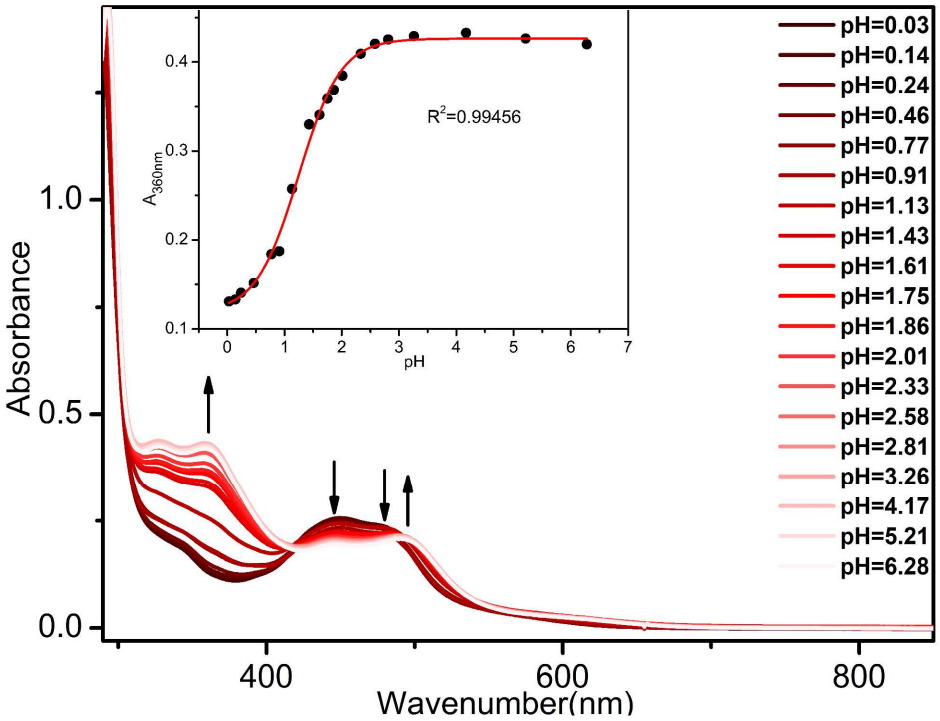


Figure S33. Absorption spectra of [**2**]$^{+}$ (20μM) in CH_3CN/H_2O solutions (v/v=1:49) at different pH. Inset: Change in A_{360nm} at different pH.

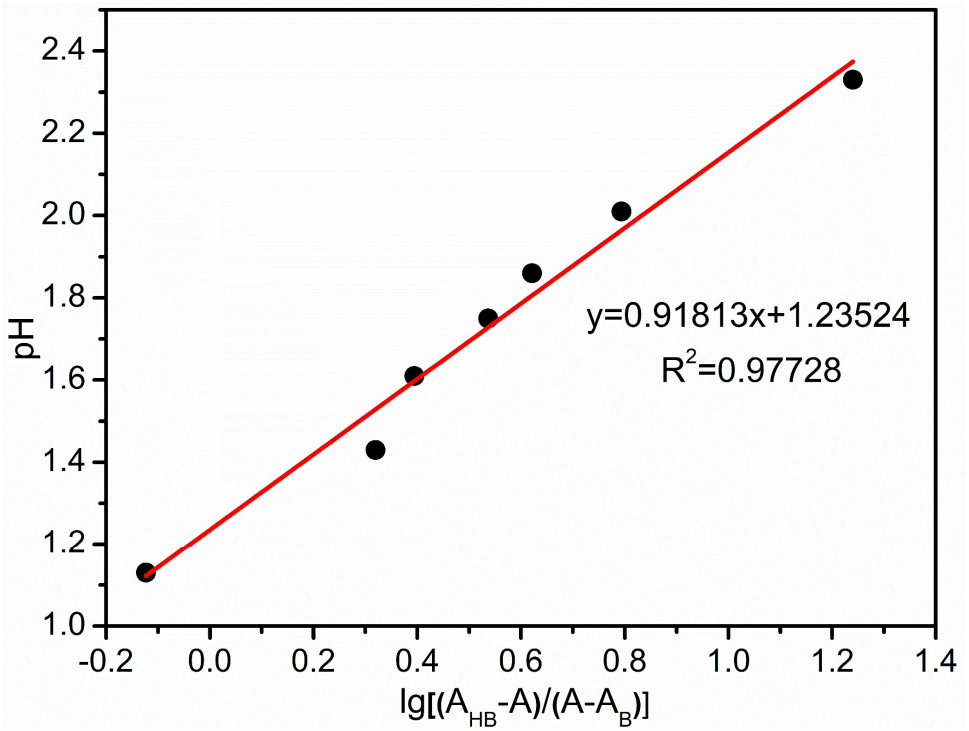


Figure S34. The curve of absorbance-pH values of [**2**]$^{+}$ in CH_3CN/H_2O solutions.

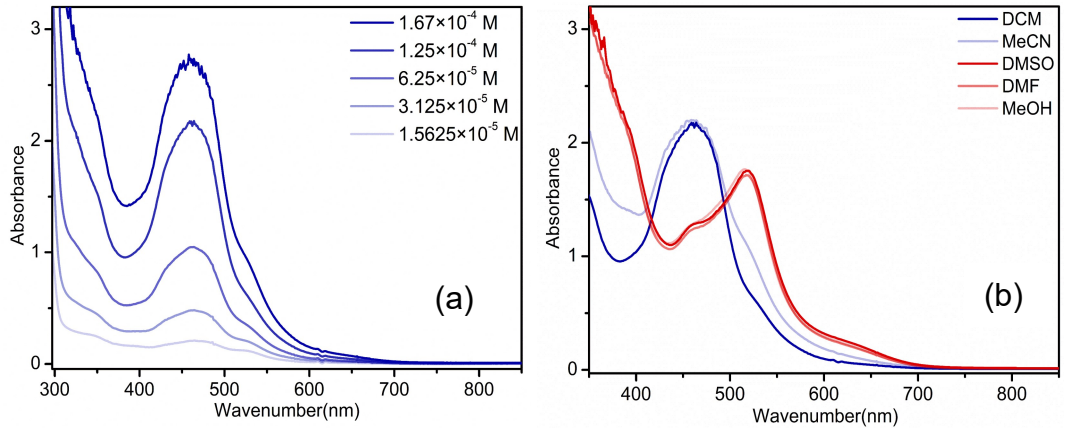


Figure S35. (a) UV-Vis absorption spectra of different concentration dichloromethane solutions of [**1'**]$^{2+}$;(b) UV-Vis absorption spectra of [**1'**]$^{2+}$ (1.25 × 10^{-4} M) in different solvents.

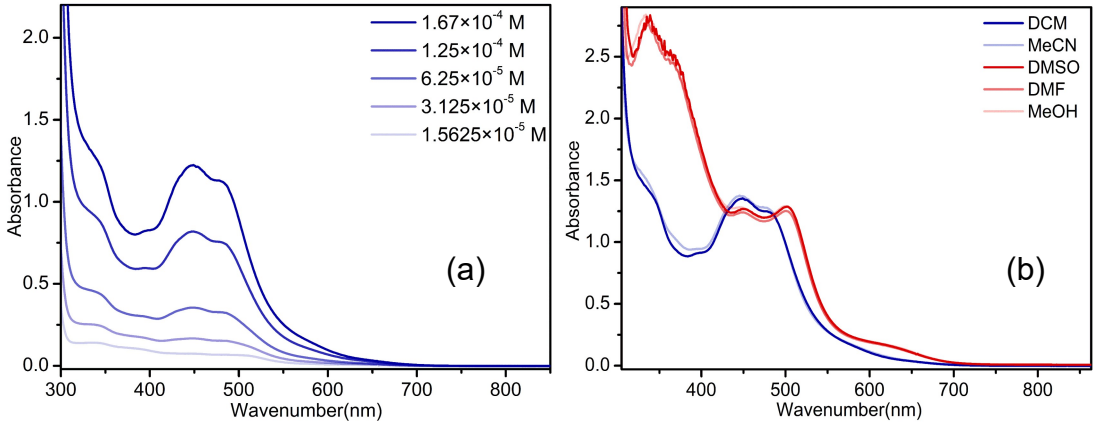


Figure S36. (a) UV-Vis absorption spectra of different concentration dichloromethane solutions of [**2'**]$^{2+}$;(b) UV-Vis absorption spectra of [**2'**]$^{2+}$ (1.25 × 10^{-4} M) in different solvents.

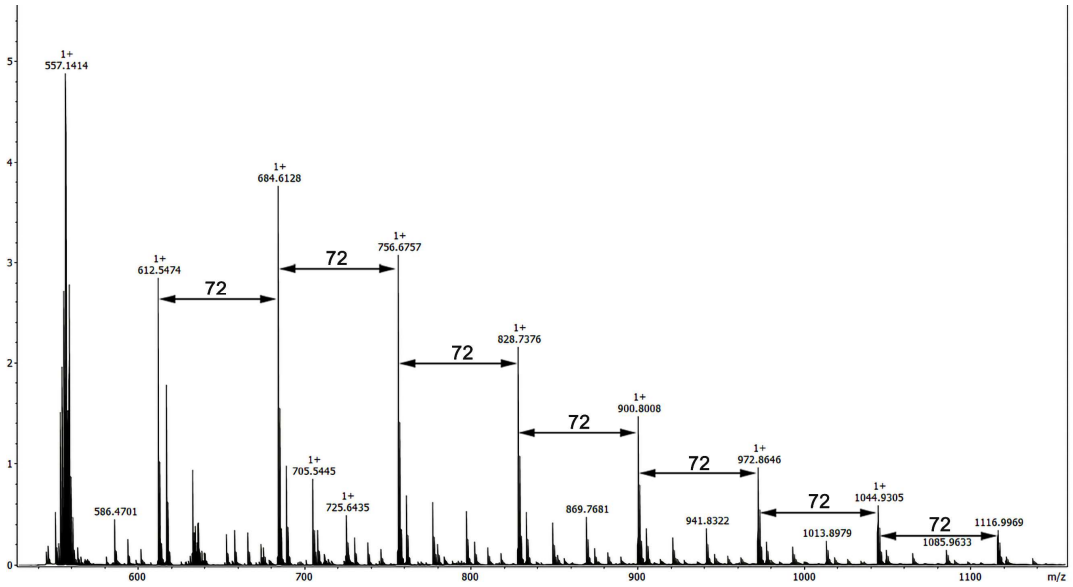


Figure S37. ESI-MS spectrum of the mixture of the methyl propylene oxide and [**1'**]$^{2+}$ (0.4 mol%).

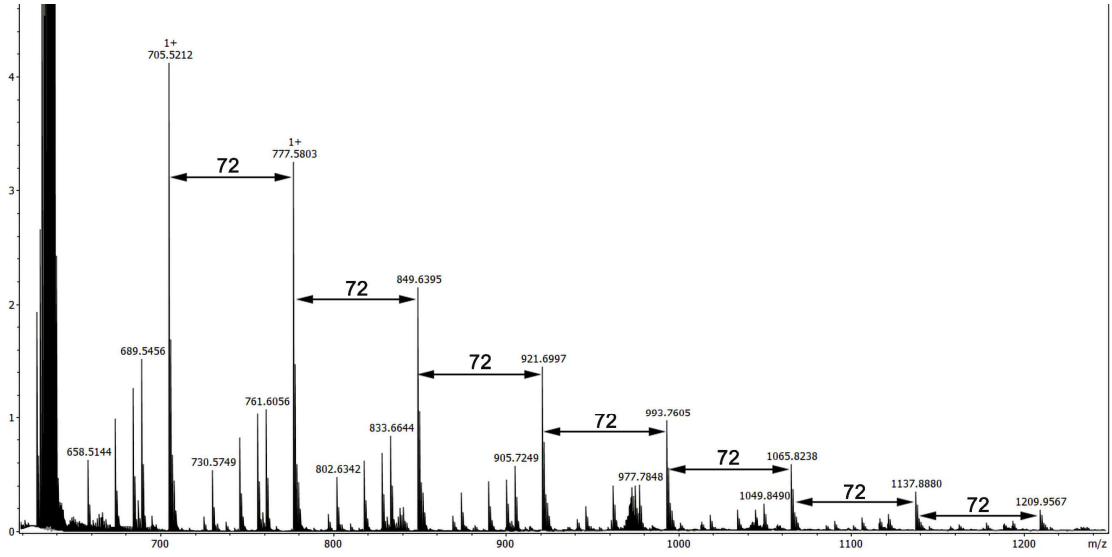


Figure S38. ESI-MS spectrum of the mixture of the methyl propylene oxide and [**2'**]$^{2+}$ (0.4 mol%).

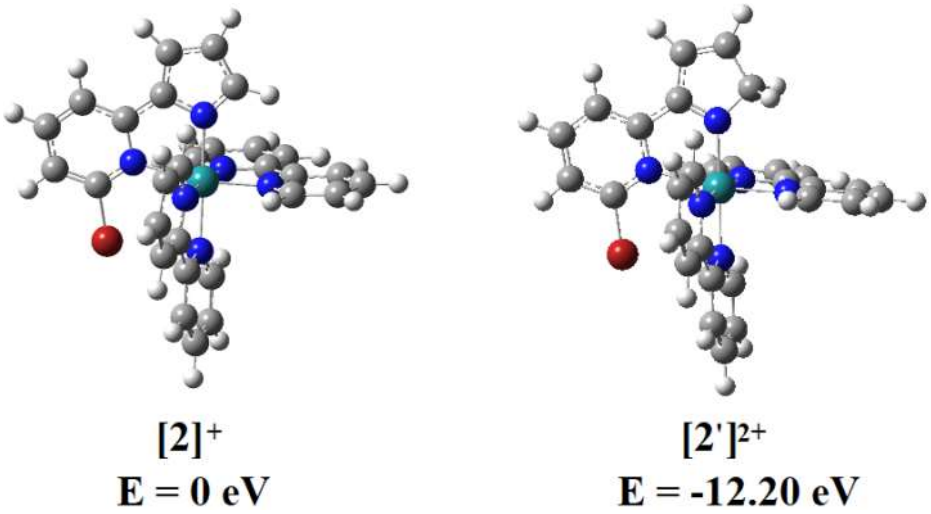


Figure S39. Optimized geometries for [**2**]$^{+}$ and [**2'**]$^{2+}$.

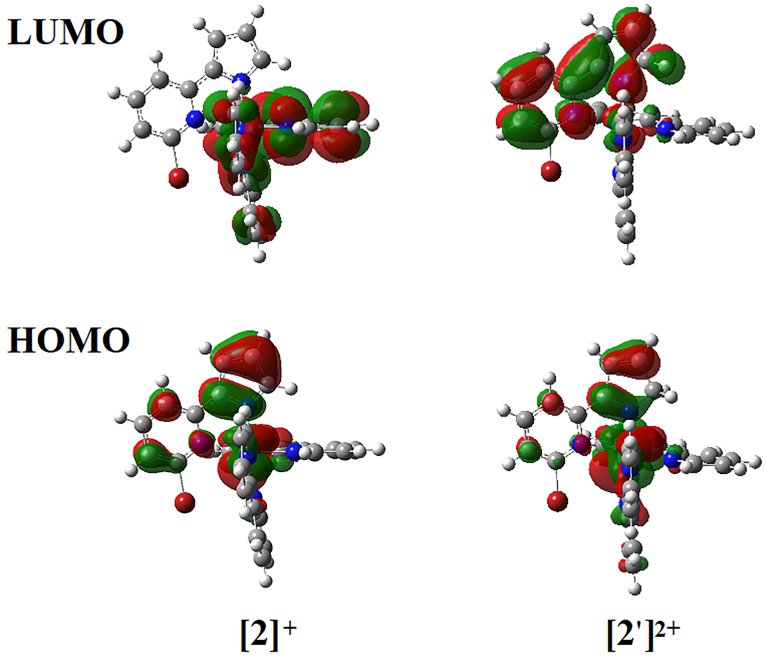


Figure S40. HOMO and LUMO orbitals for [**2**]$^{+}$ and [**2'**]$^{2+}$.

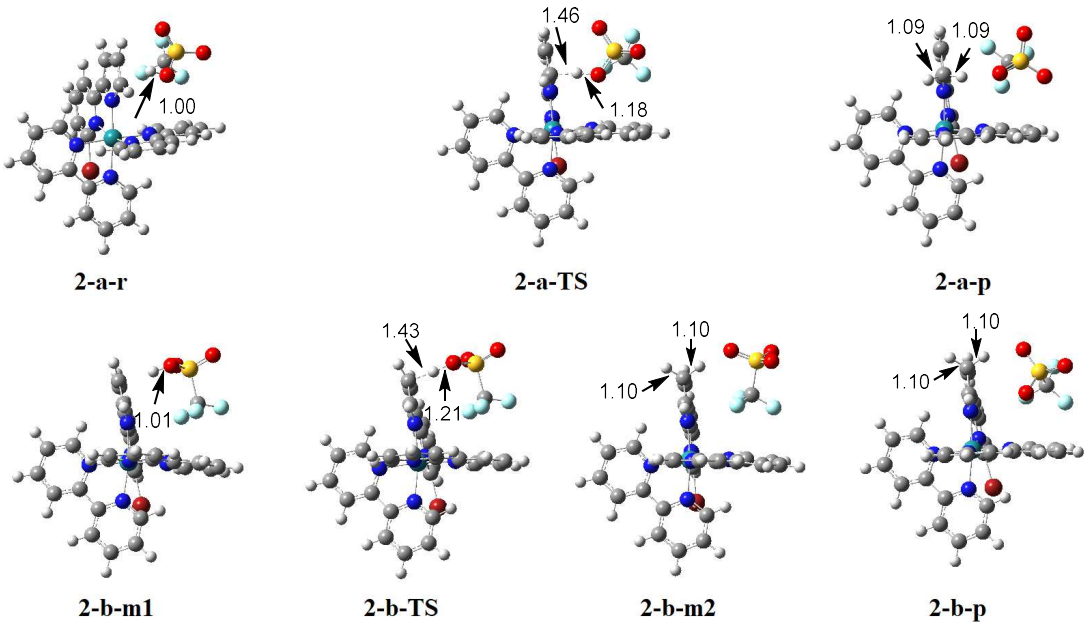


Figure S41. Optimized structures of intermediates and transition states for protonation of [**2**]$^{+}$. Selected interatomic distances are presented in Å.

Table S1. Crystal data and structure refinement for [**2**]·PF_6.

Identification code	[**2**]·PF_6
Empirical formula	C29.50 H24 Br Cl F6 N6 P Ru
Formula weight	823.95
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 11.9319(3) Å alpha = 109.5330(10)°
	b = 12.0830(3) Å beta = 101.7030(10)°
	c = 13.2689(3) Å gamma = 102.4560(10)°
Volume	1680.07(7) $Å^3$
Z, Calculated density	2, 1.629 Mg/m^3
Absorption coefficient	1.846 mm^{-1}
F(000)	816
Crystal size	0.321 x 0.197 x 0.114 mm^3
Theta range for data collection	1.706 to 27.626°
Limiting indices	-15<=h<=15, -15<=k<=15, -16<=l<=17
Reflections collected / unique	22086 / 7707 [R(int) = 0.0162]
Completeness to theta = 25.242	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6536 / 0 / 424
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1798
R indices (all data)	R1 = 0.0702, wR2 = 0.1919
Extinction coefficient	n/a
Largest diff. peak and hole	2.318 and -0.738 e. $Å^{-3}$

Table S2. Selected bond lengths [Å] and angles [°] of [**2**]·PF_6.

Ru(1)-N(1)	2.072(3)	N(2)-Ru(1)-N(1)	78.21(14)
Ru(1)-N(2)	2.065(4)	N(4)-Ru(1)-N(3)	78.05(15)
Ru(1)-N(3)	2.158(4)	N(6)-Ru(1)-N(5)	79.15(15)
Ru(1)-N(4)	2.038(4)	N(4)-C(1)-C(2)	109.4(5)
Ru(1)-N(5)	2.044(3)	C(3)-C(2)-C(1)	107.9(5)
Ru(1)-N(6)	2.045(4)	C(2)-C(3)-C(4)	105.7(5)
C(1)-C(2)	1.397(8)	N(4)-C(4)-C(3)	109.1(5)
C(1)-N(4)	1.349(6)	N(5)-Ru(1)-N(1)	174.60(13)
C(2)-C(3)	1.388(9)	N(4)-Ru(1)-N(2)	171.58(14)
C(3)-C(4)	1.417(7)	N(6)-Ru(1)-N(3)	169.21(14)
C(4)-N(4)	1.373(6)		
C(9)-Br(2)	1.885(5)		
C(1)-H(1)	0.930		
C(2)-H(2)	0.930		
C(3)-H(3)	0.929		

Table S3. Crystal data and structure refinement for [**2'**]·$(OTf)_2$.

Identification code	[**2'**]·$(OTf)_2$
Empirical formula	C31 H23 Br F6 N6 O6 Ru S1.76
Formula weight	926.88
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 19.5132(6) Å alpha = 90°
	b = 10.8824(3) Å beta = 116.331(2)°
	c = 18.0933(5) Å gamma = 90°
Volume	3443.49(18) $Å^3$
Z, Calculated density	4, 1.788 Mg/m^3
Absorption coefficient	1.808 mm^{-1}
F(000)	1840
Crystal size	0.211 x 0.167 x 0.112 mm^3
Theta range for data collection	2.204 to 26.435°
Limiting indices	-24<=h<=24, -13<=k<=13, -21<=l<=22
Reflections collected / unique	52177 / 7067 [R(int) = 0.0420]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6282
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7067 / 35 / 534
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1663
R indices (all data)	R1 = 0.1042, wR2 = 0.1914
Extinction coefficient	n/a
Largest diff. peak and hole	1.131 and -1.625 e. $Å^{-3}$

Table S4. Selected bond lengths [Å] and angles [°] of [**2'**]·$(OTf)_2$.

Ru(1)-N(1)	2.068(5)	N(2)-Ru(1)-N(1)	78.50(19)
Ru(1)-N(2)	2.061(5)	N(4)-Ru(1)-N(3)	76.7(2)
Ru(1)-N(3)	2.187(5)	N(6)-Ru(1)-N(5)	79.4(2)
Ru(1)-N(4)	2.044(5)	N(4)-C(1)-C(2)	100.9(6)
Ru(1)-N(5)	2.052(5)	C(3)-C(2)-C(1)	111.1(7)
Ru(1)-N(6)	2.037(5)	C(2)-C(3)-C(4)	106.5(7)
C(1)-C(2)	1.500(10)	N(4)-C(4)-C(3)	111.7(7)
C(1)-N(4)	1.497(8)	N(5)-Ru(1)-N(1)	172.35(19)
C(2)-C(3)	1.341(11)	N(4)-Ru(1)-N(2)	176.5(2)
C(3)-C(4)	1.449(9)	N(6)-Ru(1)-N(3)	165.5(2)
C(4)-N(4)	1.303(8)		
C(9)-Br(2)	1.873(7)		
C(1)-H(1A)	0.971		
C(1)-H(1B)	0.969		
C(2)-H(2)	0.930		
C(3)-H(3)	0.93		

Table S5. Natural Bond Orbital (NBO) charges for [**2**]$^+$ and [**2'**]$^{2+}$.

Atom [**2**]$^+$	Charge (a.u.)	Atom [**2'**]$^{2+}$	Charge (a.u.)
Ru1	0.18	Ru1	0.19
Br	0.09	Br	0.13
N1	-0.37	N1	-0.38
N2	-0.37	N2	-0.38
N3	-0.44	N3	-0.40
N4	-0.43	N4	-0.35
N5	-0.36	N5	-0.37
N6	-0.35	N6	-0.35
C1	-0.05	C1	-0.30
C2	-0.34	C2	-0.15
C3	-0.29	C3	-0.27
C4	0.05	C4	0.24

Table S6. Selected bond lengths and angles for [**2**]$^{+}$ and [**2'**]$^{2+}$.

Bond length(Å)/angle(°)	[**2**]$^{+}$	Exp.	Bond length(Å)/angle(°)	[**2'**]$^{2+}$	Exp.
Ru(1)-N(1)	2.090	2.072(3)	Ru(1)-N(1)	2.092	2.068(5)
Ru(1)-N(2)	2.099	2.065(4)	Ru(1)-N(2)	2.099	2.061(5)
Ru(1)-N(3)	2.203	2.158(4)	Ru(1)-N(3)	2.209	2.187(5)
Ru(1)-N(4)	2.055	2.038(4)	Ru(1)-N(4)	2.034	2.044(5)
Ru(1)-N(5)	2.061	2.044(3)	Ru(1)-N(5)	2.076	2.052(5)
Ru(1)-N(6)	2.055	2.045(4)	Ru(1)-N(6)	2.059	2.037(5)
C(1)-C(2)	1.408	1.397(8)	C(1)-C(2)	1.497	1.500(10)
C(1)-N(4)	1.351	1.349(6)	C(1)-N(4)	1.461	1.497(8)
C(2)-C(3)	1.403	1.388(9)	C(2)-C(3)	1.349	1.341(11)
C(3)-C(4)	1.409	1.417(7)	C(3)-C(4)	1.458	1.449(9)
C(4)-N(4)	1.377	1.373(6)	C(4)-N(4)	1.309	1.303(8)
C(9)-Br(2)	1.911	1.885(5)	C(9)-Br(2)	1.897	1.873(7)
C(1)-H(1)	1.082	0.930	C(1)-H(1A)	1.098	0.971
C(2)-H(2)	1.082	0.930	C(1)-H(1B)	1.097	0.969
C(3)-H(3)	1.082	0.929	C(2)-H(2)	1.082	0.930
N(2)-Ru(1)-N(1)	78.0	78.21(14)	C(3)-H(3)	1.081	0.93
N(4)-Ru(1)-N(3)	77.9	78.05(15)	N(2)-Ru(1)-N(1)	78.0	78.50(19)
N(6)-Ru(1)-N(5)	79.0	79.15(15)	N(4)-Ru(1)-N(3)	76.6	76.7(2)
N(4)-C(1)-C(2)	109.8	109.4(5)	N(6)-Ru(1)-N(5)	79.0	79.4(2)
C(3)-C(2)-C(1)	106.8	107.9(5)	N(4)-C(1)-C(2)	104.3	100.9(6)
C(2)-C(3)-C(4)	106.1	105.7(5)	C(3)-C(2)-C(1)	108.7	111.1(7)
N(4)-C(4)-C(3)	109.4	109.1(5)	C(2)-C(3)-C(4)	106.7	106.5(7)
N(5)-Ru(1)-N(1)	174.8	174.60(13)	N(4)-C(4)-C(3)	111.9	111.7(7)
N(4)-Ru(1)-N(2)	171.2	171.58(14)	N(5)-Ru(1)-N(1)	173.0	172.35(19)
N(6)-Ru(1)-N(3)	169.1	169.21(14)	N(4)-Ru(1)-N(2)	174.2	176.5(2)
			N(6)-Ru(1)-N(3)	168.7	165.5(2)

Table S7. Cartesian coordinates of optimized geometry of [**2**]$^{+}$.

SCF energy = -4113.2584533 hartree

ZPE = 0.455436 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	-0.28705200	-0.17723700	0.21979400
Br	2.29471700	0.82425600	-2.28533900
N	0.72549400	0.79563200	1.76834300
N	-0.15901300	1.78737200	-0.51081100
N	-1.35789000	-0.97164000	-1.35268100
N	-0.35669800	-1.97382600	1.21636300
N	1.64847500	-1.08092600	-0.32006300
N	-2.20913600	0.29815000	0.77357400
C	0.80665000	-2.71128000	1.21598200
C	0.47287500	2.67672200	0.30344300
C	-3.19157700	-0.12906500	-0.07237400
C	-1.60494500	-2.11960800	-3.44581800
H	-1.12628700	-2.61693500	-4.28205200
C	-2.54909700	0.96087700	1.89611400
H	-1.72765000	1.27314200	2.52904600
C	1.88588000	-2.23838100	0.40324700
C	-2.71407600	-0.83800200	-1.27109100
C	1.02552300	2.10799300	1.54629800
C	2.62831700	-0.67159800	-1.14325300
C	-1.22606300	-2.57641300	2.05806600
H	-2.21362100	-2.16499500	2.22467100
C	1.90273100	0.88605800	3.85870700
H	2.22154200	0.36750000	4.75603800
C	-2.99245300	-1.98451700	-3.37401400
H	-3.63088800	-2.37542000	-4.15911700

C	0.66501400	-3.81156200	2.08542000
H	1.40639200	-4.57288400	2.29276600
C	-0.04583200	4.48614900	-1.20494800
H	0.00518000	5.53616200	-1.47316200
C	-0.82545600	-1.60308500	-2.41780300
H	0.25421300	-1.68068100	-2.42825700
C	-3.54912900	-1.33712400	-2.27472100
H	-4.62350200	-1.22154200	-2.20093700
C	-4.53843700	0.10694900	0.21776600
H	-5.31146900	-0.23999900	-0.45685300
C	1.15236300	0.20872800	2.90448600
H	0.87497300	-0.83026400	3.03087000
C	-0.63110200	-3.72422100	2.61769100
H	-1.09677100	-4.40855300	3.31602000
C	0.54748700	4.03292500	-0.03081100
H	1.05192700	4.73232300	0.62436500
C	-0.71397000	3.57032700	-2.01935300
H	-1.19981700	3.87732500	-2.93886900
C	3.12534600	-2.90280800	0.32734500
H	3.27742600	-3.79587800	0.92254100
C	-0.74625000	2.23538400	-1.63609300
H	-1.23578600	1.48588500	-2.24608300
C	-3.87059000	1.22478700	2.23523200
H	-4.09163700	1.76027800	3.15168000
C	3.87009800	-1.27816600	-1.27262300
H	4.60506300	-0.87968300	-1.95942300
C	2.23203400	2.22281500	3.63225500
H	2.82372500	2.78004600	4.35093500
C	-4.88427400	0.78868700	1.38083100

H	-5.92708800	0.97506100	1.61464300
C	4.12045000	-2.41764500	-0.49929600
H	5.08114200	-2.91885500	-0.56521700
C	1.78623100	2.83685400	2.46551400
H	2.03302000	3.87343800	2.27206600

Table S8. Cartesian coordinates of optimized geometry of [**2'**]$^{2+}$.

SCF energy = -4113.7067086 hartree

ZPE = 0.468644 hartree

Charge = 2 Multiplicity = 1

Atom	X	Y	Z
Ru	0.28150200	0.14211600	0.21826500
C	1.60024500	2.42116900	2.04901200
H	2.49629000	2.51068200	1.42053600
H	1.84935100	1.72523700	2.86001100
C	1.09143200	3.74323400	2.53438200
H	1.66051000	4.41480100	3.16399500
C	-0.15544400	3.92921200	2.05358900
H	-0.80452400	4.77983400	2.21139800
C	-0.47771900	2.74995900	1.25730500
C	-1.67097400	2.41542500	0.49100600
C	-2.78761700	3.24433400	0.45906100
H	-2.79085500	4.16561200	1.02870800
C	-3.88839300	2.87205000	-0.30900100
H	-4.77522800	3.49479700	-0.35008700
C	-3.82399900	1.68914300	-1.03269400
H	-4.64549300	1.36126300	-1.65666700

C	-2.66335300	0.91239700	-0.95200700
C	-1.15918700	-0.37445100	2.88127800
H	-0.88008600	0.65545500	3.06424600
C	-1.88885700	-1.10113600	3.81448700
H	-2.18847200	-0.63106500	4.74419600
C	-2.21809900	-2.42490800	3.52421600
H	-2.78887500	-3.02290200	4.22654600
C	-1.80348100	-2.97294100	2.31373700
H	-2.05547800	-3.99751900	2.07078600
C	-1.06917900	-2.19356500	1.41569100
C	-0.58021400	-2.68173400	0.11341100
C	-0.72105500	-4.00120700	-0.32556800
H	-1.20901200	-4.73858200	0.29927900
C	-0.22195600	-4.36812200	-1.57203800
H	-0.32647600	-5.38938500	-1.92247400
C	0.41625200	-3.40528500	-2.35366900
H	0.82402300	-3.64406800	-3.32932500
C	0.52417400	-2.11002700	-1.86155800
H	0.99901600	-1.32770100	-2.44000700
C	0.90145500	1.68561600	-2.34785300
H	-0.16777800	1.85544100	-2.33206400
C	1.70620900	2.19452100	-3.36103200
H	1.25963000	2.77836800	-4.15770600
C	3.07676100	1.93814700	-3.32287000
H	3.73450500	2.31995800	-4.09625600
C	3.59507000	1.18148400	-2.27489800
H	4.65672300	0.97305500	-2.23093600
C	2.73618100	0.69434800	-1.28694400
C	3.17095100	-0.12122800	-0.13838200

C	4.49670000	-0.48807200	0.10411500
H	5.28245400	-0.17816800	-0.57340500
C	4.80555200	-1.25525300	1.22424900
H	5.83240500	-1.54407800	1.42089200
C	3.77737700	-1.64333200	2.08273600
H	3.96967300	-2.24107700	2.96634700
C	2.47631600	-1.25084900	1.79028000
H	1.64586200	-1.52739600	2.42751700
N	-0.75480400	-0.89912600	1.70859100
N	0.03395600	-1.74786000	-0.66275400
N	-1.59683900	1.22719400	-0.20328800
N	0.50099000	1.88020700	1.25215200
N	1.39774000	0.95074300	-1.33499900
N	2.17377000	-0.50583200	0.71028000
Br	-2.62053900	-0.65875800	-2.01512300

Table S9. Cartesian coordinates of optimized geometry of **2-a-r**.

SCF energy = -5075.2925244 hartree

ZPE = 0.495022 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.93225900	0.31291100	0.23718200
Br	2.25957700	-2.53888100	-1.78554500
N	2.48267800	-0.16314800	1.54161400
N	2.60812900	0.49361000	-1.00840200
N	-0.48113600	0.89620400	-1.15669300
N	-0.56153200	0.21897700	1.64767900
N	0.39091200	-1.82802500	0.19881300
N	1.01675000	2.35912100	0.42357100

C	-1.14661900	-1.00714500	1.84469700
C	3.81103100	0.30842900	-0.39656500
C	0.10911600	3.05618700	-0.32047700
C	-2.11378800	0.52905300	-2.87448300
H	-2.63923900	-0.17874200	-3.50381400
C	1.83615700	3.02652700	1.25865300
H	2.53530600	2.42092800	1.82143600
C	-0.62796400	-2.11508800	1.08779600
C	-0.72012900	2.23713200	-1.22112000
C	3.73821300	-0.13032700	1.00898300
C	0.86817200	-2.85975700	-0.51968200
C	-1.22942500	1.12501600	2.40052700
H	-0.94093100	2.16767100	2.41239100
C	3.38828900	-0.92258600	3.62942600
H	3.20561200	-1.22746300	4.65381000
C	-2.37412500	1.89793100	-2.94054200
H	-3.11238800	2.29064100	-3.63150200
C	-2.21886900	-0.88403000	2.74319000
H	-2.88590400	-1.66810300	3.07499800
C	4.97565500	0.94139700	-2.41107300
H	5.89936800	1.11412300	-2.95326300
C	-1.16836600	0.06886800	-1.96599700
H	-0.93916700	-0.98469000	-1.86851900
C	-1.66750100	2.75831500	-2.10581000
H	-1.85042500	3.82493700	-2.14758100
C	0.00991400	4.44574900	-0.20839100
H	-0.72094100	4.99028300	-0.79331000
C	2.31992700	-0.55126500	2.82151700
H	1.29873800	-0.55464400	3.18345300

C	-2.27803600	0.48122900	3.09423300
H	-2.97480400	0.94857700	3.77791400
C	5.00941000	0.52720600	-1.08278200
H	5.96057900	0.38427900	-0.58474200
C	3.73788400	1.13514800	-3.02595000
H	3.66138700	1.45963900	-4.05774800
C	-1.13778700	-3.41543600	1.22856700
H	-1.94050700	-3.59028000	1.93518000
C	2.58225700	0.90222400	-2.28998200
H	1.59915100	1.02824000	-2.72756200
C	1.78632100	4.40742200	1.40697600
H	2.46540700	4.89689100	2.09590900
C	0.41388400	-4.17036900	-0.43228000
H	0.85352400	-4.94128100	-1.05134200
C	4.67708200	-0.89640300	3.09455800
H	5.53405800	-1.18462600	3.69417900
C	0.85236600	5.12984400	0.66326700
H	0.78018100	6.20805600	0.75812800
C	-0.61716400	-4.44713900	0.46821300
H	-1.00090000	-5.45783100	0.56420700
C	4.85037300	-0.49697500	1.77240600
H	5.84209500	-0.47995400	1.33756300
C	-4.54400200	-1.11279400	-0.55098100
F	-3.37031100	-1.60944300	-0.15832600
F	-5.51718600	-1.96392000	-0.23372600
F	-4.52832300	-0.92033500	-1.86857100
O	-5.34721400	0.17935600	1.66334400
O	-3.42701300	1.16000500	0.36068800
O	-5.69339900	1.31023300	-0.59322500

S	-4.88727100	0.51458400	0.32078500
H	-2.97933100	0.99191500	1.24744100

Table S10. Cartesian coordinates of optimized geometry of **2-a-TS**.

SCF energy = -5075.2865548 hartree

ZPE = 0.490876 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.78164300	0.25019000	0.23741900
Br	2.85397500	-1.94903300	-1.95800200
N	2.29577000	0.13481500	1.67185700
N	2.43990300	0.98361600	-0.82720400
N	-0.56467500	0.53288600	-1.31090600
N	-0.68014500	-0.37673300	1.52266600
N	0.87668200	-1.94521000	0.04140500
N	0.26328800	2.22169000	0.51810500
C	-0.84446800	-1.69953100	1.68865200
C	3.59607900	1.07202900	-0.11353900
C	-0.65808700	2.72062900	-0.35607100
C	-1.73570100	-0.10976000	-3.30222700
H	-1.96678000	-0.88758300	-4.02101000
C	0.72259000	3.00554200	1.51253200
H	1.45175000	2.55405400	2.17362300
C	-0.02087400	-2.57428300	0.87959200
C	-1.09190600	1.78563700	-1.40773700
C	3.53130300	0.54164600	1.26047200
C	1.63873900	-2.74248500	-0.72527600

C	3.20782100	-0.45964900	3.81168400
H	3.03405100	-0.85761100	4.80513500
C	-2.28155100	1.16976900	-3.41005600
H	-2.95197600	1.42078400	-4.22499900
C	-1.83750100	-1.96199500	2.67326700
H	-2.18700900	-2.93467800	2.99250200
C	4.71147400	2.12343900	-1.97602600
H	5.59888300	2.56253100	-2.41947300
C	-0.88988100	-0.38974000	-2.23684400
H	-0.44571900	-1.36808200	-2.10706500
C	-1.95586100	2.12429200	-2.45182000
H	-2.36833800	3.12319300	-2.51951800
C	-1.13556700	4.02672400	-0.22193200
H	-1.87566800	4.41107300	-0.91273700
C	2.14734000	-0.35192700	2.92000400
H	1.14466700	-0.65700400	3.19201300
C	-2.27953100	-0.72587900	3.11179100
H	-3.05592600	-0.53183300	3.83932900
C	4.74675100	1.63638000	-0.67293500
H	5.66074800	1.70361200	-0.09613300
C	3.51757600	2.04206900	-2.69311000
H	3.43888800	2.41110100	-3.70958200
C	-0.12284700	-3.96692400	0.94865500
H	-0.84367700	-4.41187600	1.62445000
C	2.40954600	1.46770600	-2.08231000
H	1.46889800	1.36831600	-2.60888600
C	0.28539200	4.31228100	1.69302800
H	0.68306600	4.90204500	2.51114500
C	1.59471800	-4.13459600	-0.71060200

H	2.24583600	-4.70346900	-1.36140100
C	4.47687400	-0.05265600	3.39927900
H	5.32941100	-0.12685300	4.06606500
C	-0.66295900	4.83137200	0.81067500
H	-1.03066900	5.84563200	0.92370700
C	0.69436600	-4.75609300	0.15179300
H	0.63191800	-5.83862300	0.19034200
C	4.63647800	0.45180400	2.11212500
H	5.61564200	0.76655300	1.77337200
C	-4.36475800	-1.07877300	-0.61451200
F	-3.17951900	-1.60711300	-0.27951500
F	-5.31375400	-2.00551400	-0.46428000
F	-4.32608400	-0.69239000	-1.89149500
O	-5.13942500	-0.19129700	1.77550200
O	-3.36054700	1.08233500	0.55157500
O	-5.69352500	1.21051700	-0.25876000
S	-4.74621500	0.38105400	0.48589800
C	-1.60184800	0.27549400	2.33863400
H	-1.38158400	1.29111200	2.65800400
H	-2.63419900	0.64862700	1.37688200

Table S11. Cartesian coordinates of optimized geometry of **2-a-p**.

SCF energy = -5075.313697 hartree

ZPE = 0.496931 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.88167400	0.30425200	0.27269200
Br	1.27691800	-2.43125300	-2.24486000

N	2.36853800	-0.56268200	1.47581100
N	2.52685500	0.24945600	-1.03496300
N	-0.36618400	1.26634800	-1.07374000
N	-0.54207700	0.32605100	1.71846400
N	-0.00963300	-1.70460600	0.13876400
N	1.35897200	2.27532600	0.62563800
C	-1.16637600	-0.78599000	2.01132900
C	3.67208800	-0.27331500	-0.51879800
C	0.63642200	3.19342500	-0.07904300
C	-1.97298200	1.35490800	-2.84689000
H	-2.62666400	0.81370400	-3.51886900
C	2.26251700	2.69667700	1.53114400
H	2.80618800	1.92180900	2.05714500
C	-0.87785600	-1.94635100	1.18012200
C	-0.31223000	2.62698500	-1.05294000
C	3.56893200	-0.77530300	0.86346100
C	0.19416500	-2.72014100	-0.71128200
C	3.20849400	-1.60168600	3.47192800
H	3.02277300	-1.90407800	4.49626600
C	-1.92827600	2.74726600	-2.83463200
H	-2.54037400	3.32820400	-3.51616200
C	-2.08514000	-0.61631000	3.13056100
H	-2.71459900	-1.38861200	3.54975500
C	4.85989100	0.21599200	-2.55968000
H	5.76942700	0.19634100	-3.15053900
C	-1.17861700	0.65255900	-1.94965500
H	-1.18544100	-0.42688700	-1.91388900
C	-1.08947800	3.38905900	-1.92775400
H	-1.03760000	4.47069200	-1.90791300

C	0.81580700	4.56170900	0.14041900
H	0.23192600	5.28452600	-0.41562900
C	2.20488600	-0.96580100	2.75063500
H	1.23836400	-0.76419700	3.19379700
C	-2.00886200	0.67821900	3.50021000
H	-2.56585300	1.17077200	4.28670400
C	4.85144300	-0.30442500	-1.26911500
H	5.75801100	-0.72211400	-0.84957900
C	3.68511400	0.76683900	-3.07173800
H	3.64322900	1.19001900	-4.06897700
C	-1.47337900	-3.18529600	1.39519200
H	-2.14712500	-3.31954200	2.23201600
C	2.54493500	0.76492000	-2.27766500
H	1.60809800	1.16627800	-2.64206000
C	2.48528800	4.04403900	1.78813200
H	3.22188300	4.33333300	2.52894200
C	-0.36756200	-3.99144900	-0.56699200
H	-0.14846300	-4.76140800	-1.29560800
C	4.43459200	-1.83594300	2.85038200
H	5.24029600	-2.33480900	3.37831300
C	1.74576000	4.99326400	1.08198500
H	1.88913700	6.05367100	1.25998400
C	-1.20508300	-4.23010200	0.51557300
H	-1.65300700	-5.20745700	0.65825400
C	4.61342400	-1.41635900	1.53553600
H	5.55876200	-1.59122800	1.03755600
C	-4.21170200	-1.06659400	-0.13151600
F	-4.05998900	-1.54364800	1.11987400
F	-5.25915700	-1.69332800	-0.68845000

F	-3.10826600	-1.40563700	-0.83342600
O	-5.62348200	0.93680700	0.79631100
O	-3.18193100	1.29757300	0.40516500
O	-4.73982600	1.08079200	-1.54132800
S	-4.46835300	0.77698600	-0.11715300
C	-1.03554400	1.37697900	2.60368900
H	-0.20120800	1.85462400	3.13061000
H	-1.53055500	2.13758500	1.98741600

Table S12. Cartesian coordinates of optimized geometry of **2-b-m1**.

SCF energy = -5075.2922741 hartree

ZPE = 0.494772 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.84210800	0.29749600	0.26233400
Br	2.02406600	-2.17481400	-2.28002100
N	2.17970500	-0.42519900	1.70468400
N	2.68387300	0.51393500	-0.71480700
N	-0.27064600	1.13004300	-1.26758300
N	-0.77671800	0.05848900	1.52072900
N	0.26509900	-1.80119800	-0.11486200
N	0.94652100	2.29318100	0.73891500
C	-1.24488700	-1.22937700	1.65389100
C	3.77311200	0.09567000	-0.01270500
C	0.19786200	3.12633100	-0.04119500
C	-1.45803900	1.09290500	-3.35314900
H	-1.83429900	0.50683300	-4.18409500
C	1.61052100	2.79926400	1.79621200
H	2.18917000	2.09024800	2.37505500

C	-0.72574500	-2.22125100	0.75159000
C	-0.44752100	2.48108500	-1.19672100
C	3.48625800	-0.47861200	1.31411100
C	0.72233400	-2.71264000	-0.99076200
C	-1.36535700	0.81553200	2.47006900
H	-1.14389900	1.87011000	2.56460500
C	2.77436100	-1.43339700	3.80207300
H	2.44943800	-1.79159400	4.77255700
C	-1.66278100	2.47138400	-3.27904400
H	-2.20682700	2.99573600	-4.05734500
C	-2.15664400	-1.29496900	2.71792500
H	-2.69561300	-2.16706700	3.06203900
C	5.24382300	0.83250100	-1.77779800
H	6.24087000	0.94700500	-2.18978400
C	-0.76136000	0.46229900	-2.32980100
H	-0.58059900	-0.60371700	-2.34082900
C	-1.14725500	3.17011000	-2.19133200
H	-1.27850600	4.24311000	-2.12487300
C	0.09152300	4.48649000	0.26227900
H	-0.51913200	5.13690100	-0.35176600
C	1.84357700	-0.88809200	2.92556100
H	0.79706600	-0.81125800	3.19032000
C	-2.24203400	0.01824000	3.24056400
H	-2.80296700	0.33986200	4.11003900
C	5.06369000	0.23791500	-0.53294200
H	5.92300000	-0.10253300	0.03123500
C	4.12325100	1.28512500	-2.47553200
H	4.21207600	1.76372400	-3.44443300
C	-1.20554500	-3.54033900	0.73703700

H	-1.98836400	-3.82201300	1.43156600
C	2.86726300	1.10631800	-1.90984100
H	1.97004400	1.42175200	-2.42691500
C	1.54956900	4.14437500	2.13980800
H	2.09954400	4.50191900	3.00298400
C	0.29819000	-4.03394200	-1.06186300
H	0.72109100	-4.70327400	-1.79943900
C	4.10939100	-1.50909700	3.40514500
H	4.86228600	-1.93510400	4.05990000
C	0.76977900	5.00243300	1.36290600
H	0.69074300	6.05624900	1.60783700
C	-0.68792100	-4.45260400	-0.16532500
H	-1.04782800	-5.47621900	-0.18982700
C	4.46525000	-1.02372700	2.15054000
H	5.49718400	-1.07173600	1.82618400
C	-3.86961700	-0.01832200	-0.92658400
F	-2.87024100	-0.89817100	-0.84963600
F	-4.49099200	-0.15329600	-2.09488000
F	-3.38729600	1.22007300	-0.81607200
O	-4.93723200	-1.75571900	0.83381200
O	-4.53910100	0.61813800	1.59747500
O	-6.37126100	0.18912800	0.03005900
S	-5.09240300	-0.35389300	0.46362400
H	-3.73866100	0.23780700	2.08933100

Table S13. Cartesian coordinates of optimized geometry of **2-b-TS**.

SCF energy = -5075.2864879 hartree

ZPE = 0.490715 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.83038100	0.26792700	0.27665000
Br	2.27701400	-2.00966600	-2.29928200
N	2.20567900	-0.39978400	1.70898500
N	2.66013000	0.67605400	-0.66413500
N	-0.32905800	1.06819400	-1.24084100
N	-0.79344200	-0.13096000	1.48267200
N	0.43190300	-1.85490400	-0.18005200
N	0.78975200	2.25122300	0.81595800
C	-1.18811200	-1.46578700	1.54580900
C	3.77135000	0.34342100	0.04866300
C	0.02001300	3.06119200	0.03226400
C	-1.50702400	1.00632300	-3.32984600
H	-1.85482600	0.41596600	-4.16996800
C	1.40111800	2.76763300	1.89946200
H	2.00141600	2.07721300	2.47888400
C	-0.54292400	-2.38704900	0.63685600
C	-0.57287400	2.40685200	-1.14691600
C	3.51765100	-0.31498600	1.34289100
C	0.99794700	-2.69562900	-1.06365100
C	-1.51813900	0.55772000	2.35834500
H	-1.38889600	1.62469900	2.48362700
C	2.85684900	-1.45489800	3.76665500
H	2.55017200	-1.88960900	4.71139000
C	-1.76998900	2.37344500	-3.23851700
H	-2.33151000	2.88443400	-4.01327200
C	-2.18890700	-1.61959400	2.48553200
H	-2.70832000	-2.53063000	2.74765700
C	5.19441200	1.29659600	-1.65010200

H	6.18251300	1.53180000	-2.03121100
C	-0.78659800	0.39283200	-2.31212600
H	-0.55698500	-0.66401100	-2.33767700
C	-1.29483600	3.07884200	-2.13673800
H	-1.47744800	4.14313000	-2.05419400
C	-0.15787400	4.40895200	0.35580400
H	-0.78210600	5.04127500	-0.26335000
C	1.89485200	-0.95229400	2.89844400
H	0.84190800	-0.98441400	3.14655000
C	-2.48535200	-0.30039800	2.98421800
H	-2.93948800	-0.09357700	3.95028300
C	5.05088800	0.64080300	-0.43141400
H	5.92861600	0.37419900	0.14389600
C	4.04848600	1.65184200	-2.36235200
H	4.10798300	2.17022800	-3.31278200
C	-0.90025800	-3.73954800	0.57938100
H	-1.67217900	-4.11150600	1.24271100
C	2.80589600	1.32422100	-1.83477400
H	1.89238100	1.56385400	-2.36357000
C	1.26566800	4.10141400	2.26567900
H	1.77552100	4.46843500	3.14921900
C	0.69672300	-4.04895300	-1.17737000
H	1.20146100	-4.65772800	-1.91613000
C	4.19896800	-1.38989800	3.39317500
H	4.97731500	-1.77953600	4.04067400
C	0.46696000	4.93582500	1.48276000
H	0.33225700	5.98028000	1.74292100
C	-0.27129900	-4.57957700	-0.32551600
H	-0.53326700	-5.63097100	-0.38317100

C	4.52861100	-0.81209700	2.17081800
H	5.56536600	-0.75447900	1.86387300
C	-3.93188900	-0.03020100	-0.88040900
F	-2.88720900	-0.85662700	-0.73353800
F	-4.47876300	-0.23561100	-2.08006000
F	-3.49881700	1.23401800	-0.80649500
O	-5.11437000	-1.80356800	0.71953600
O	-4.61275100	0.47957900	1.63242200
O	-6.43878600	0.22578800	-0.00967500
S	-5.18536700	-0.36103800	0.46847200
H	-3.62453200	0.04590300	2.19268100

Table S14. Cartesian coordinates of optimized geometry of **2-b-m2**.

SCF energy = -5075.3091715 hartree

ZPE = 0.496276 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.80158600	0.15054200	0.25988000
Br	3.25202400	-1.49221300	-2.02473600
N	2.23860100	-0.10319700	1.75385100
N	2.45263900	1.16146000	-0.56195200
N	-0.45956400	0.62641500	-1.32581300
N	-0.70190200	-0.74109700	1.32611200
N	1.08046400	-1.96820000	-0.29462200
N	0.15954100	2.02967700	0.81299200
C	-0.79058200	-2.16240100	1.20312800
C	3.53587700	1.25232500	0.25787900
C	-0.68215900	2.64735300	-0.06469000
C	-1.41877100	0.29317100	-3.49791200

H	-1.57509700	-0.37043700	-4.34066200
C	0.48471000	2.64690600	1.96461100
H	1.15761900	2.10728900	2.61930600
C	0.17315900	-2.80053200	0.31734300
C	-0.97757000	1.88690800	-1.29214600
C	3.44535200	0.48545400	1.51349200
C	1.97397900	-2.55821000	-1.10912600
C	-1.61119000	-0.33929400	2.15973800
H	-1.73599900	0.70596800	2.40916100
C	3.09333400	-1.00672500	3.80833500
H	2.90906400	-1.60242400	4.69514900
C	-1.92896200	1.59094800	-3.48544600
H	-2.49560300	1.97320000	-4.32760800
C	-1.78534300	-2.64340300	1.98015300
H	-2.09440900	-3.67270200	2.09686500
C	4.64954300	2.70843900	-1.30930700
H	5.50594800	3.31025400	-1.59419900
C	-0.69235000	-0.15132700	-2.39948700
H	-0.26973700	-1.14750400	-2.36499200
C	-1.71006600	2.39196500	-2.36838500
H	-2.10259900	3.40066000	-2.33961200
C	-1.22063800	3.90267000	0.22682400
H	-1.90316500	4.37888900	-0.46581800
C	2.07723200	-0.82979800	2.87702700
H	1.10051300	-1.27278000	3.02314900
C	-2.42797400	-1.47961200	2.66415100
H	-2.41853000	-1.55328700	3.76095800
C	4.64638900	2.02326400	-0.09807900
H	5.49873500	2.09636200	0.56568000

C	3.53527300	2.60832000	-2.14198400
H	3.49037400	3.12127400	-3.09603500
C	0.16378600	-4.18120000	0.11504100
H	-0.57612800	-4.79082500	0.61955300
C	2.46153300	1.82789300	-1.73052600
H	1.58559700	1.71128700	-2.35515400
C	-0.01635800	3.89796900	2.30530800
H	0.27202000	4.35207500	3.24640700
C	2.02933800	-3.92889500	-1.35771500
H	2.78046300	-4.32442300	-2.02904800
C	4.33162600	-0.41047100	3.57113000
H	5.15035900	-0.52951100	4.27271800
C	-0.88707200	4.53551400	1.42140100
H	-1.30363200	5.50888200	1.65714800
C	1.10331200	-4.75531200	-0.73066500
H	1.11653000	-5.82603200	-0.90346600
C	4.50594800	0.34037700	2.41233200
H	5.46399400	0.80089400	2.20657900
C	-4.01665900	0.00870100	-0.45064700
F	-3.17699300	-1.04622500	-0.39360400
F	-4.12997000	0.37732800	-1.73480700
F	-3.44326500	1.02530900	0.22871900
O	-6.09312400	-1.59502500	-0.51692500
O	-5.35185700	-0.69751200	1.69786400
O	-6.46111900	0.81721100	0.05138100
S	-5.67604400	-0.41672000	0.27476200
H	-3.48601400	-1.35249200	2.37278500

Table S15. Cartesian coordinates of optimized geometry of **2-b-p**.

SCF energy = -5075.3097396 hartree

ZPE = 0.496328 hartree

Charge = 1 Multiplicity = 1

Atom	X	Y	Z
Ru	0.84786600	0.31199200	0.27594200
Br	1.68811700	-2.28283700	-2.26561300
N	2.37757700	-0.34001400	1.55353100
N	2.53699100	0.47713100	-0.95584100
N	-0.48884100	1.07160200	-1.11733800
N	-0.62663500	0.18873400	1.68849400
N	0.26673500	-1.80577200	0.11262000
N	1.05056800	2.33569000	0.59901500
C	-1.09719800	-1.13181600	1.97006700
C	3.71742000	0.11166300	-0.38534900
C	0.23614700	3.13489300	-0.14936400
C	-2.03124000	0.92414600	-2.94405200
H	-2.57864500	0.29200000	-3.63201700
C	1.87355200	2.89309700	1.50791700
H	2.49636100	2.20728200	2.06858900
C	-0.56937500	-2.19769800	1.13023000
C	-0.60475500	2.42869100	-1.13153900
C	3.61933000	-0.40593600	0.99161100
C	0.66258500	-2.76686000	-0.73907600
C	-1.24998600	1.02413500	2.45784000
H	-1.06268800	2.08895300	2.41591400
C	3.25626400	-1.27137100	3.58642600
H	3.06691000	-1.59522700	4.60356300
C	-2.15683000	2.31137900	-2.96891100
H	-2.80390300	2.79813600	-3.69087500

C	-2.01554300	-1.10709000	2.95841400
H	-2.56319800	-1.94163800	3.37284900
C	4.92576000	0.79050000	-2.35896700
H	5.85724600	0.90509200	-2.90304100
C	-1.19514900	0.34339900	-1.99756400
H	-1.07488500	-0.72941100	-1.92947700
C	-1.43842300	3.07000100	-2.04923900
H	-1.52065000	4.14981900	-2.05584700
C	0.23534500	4.52034500	0.03343100
H	-0.42176800	5.14822800	-0.55509800
C	2.21354400	-0.75918100	2.82341100
H	1.21361600	-0.67498200	3.22922600
C	4.92544900	0.25364500	-1.07529900
H	5.85942500	-0.04008600	-0.61294500
C	3.71315900	1.18618300	-2.92382900
H	3.66312100	1.61801300	-3.91703900
C	-0.93805600	-3.52863100	1.32617000
H	-1.59185400	-3.78553900	2.15099800
C	2.54607300	1.01335100	-2.19022100
H	1.58233500	1.28931600	-2.59886100
C	1.91899500	4.26453900	1.72788400
H	2.59637400	4.66552800	2.47318000
C	0.33566600	-4.11565500	-0.61183100
H	0.70068200	-4.83070100	-1.33769300
C	4.52550600	-1.35789300	3.01522600
H	5.36278100	-1.75873800	3.57649400
C	1.08104100	5.09207600	0.97984300
H	1.08475700	6.16656400	1.12881400
C	-0.46951300	-4.50304500	0.45485400

H	-0.73924300	-5.54522400	0.58827600
C	4.70539500	-0.91817900	1.70708500
H	5.68362400	-0.97978300	1.24717200
C	-4.25272900	-1.01263300	-0.60588900
F	-3.06481900	-1.55709800	-0.26712300
F	-5.20669200	-1.92676100	-0.36878200
F	-4.22816500	-0.77171100	-1.92903700
O	-4.90092200	0.03781000	1.71366800
O	-3.30812600	1.30197600	0.25981900
O	-5.72495400	1.14932000	-0.36931100
S	-4.58205000	0.55033200	0.35705100
C	-2.21508400	0.32287700	3.35380100
H	-2.03054800	0.52618900	4.41773200
H	-3.24700400	0.63464800	3.13149300

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