

Electronic Supplementary Information

Electrically-controlled near-infrared chiroptical switching of enantiomeric dinuclear ruthenium complexes

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1. Experimental Section

Materials

n-Propylisocyanate, hydrazine monohydrate, 2,2'-bipyridine, O,O'-dibenzoyl-L-tartartic acid, O,O'-dibenzoyl-D-tartartic acid, tetrabutylammonium hexafluorophosphate and tetrabutylammonium chloride were purchased from Aldrich Chemicals Canada. RuCl₃·3H₂O was purchased from Pressure Chemicals Co. and ammonium hexafluorophosphate was from SynQuest labs Inc. 1,2-Di(N-propylcarbonyl)hydrazide, cis-Ru(bpy)₂Cl₂·2H₂O and (±)-[Ru(bpy)₂(py)₂]Cl₂ were prepared according to published procedures.¹⁻³ All solvents were of ACS reagent grade or higher. Both chemicals and solvents were used as received.

Measurements

The ¹H-NMR and ¹³C-NMR spectra were measured using Bruker-300 FR-NMR spectrometers. The UV-vis-NIR absorption spectra were recorded on a Lambda 900 Perkin-Elmer spectrophotometer. Circular Dichroism (CD) spectra were recorded on an Olis DSM 17 spectropolarimeter with either PMT (250-900 nm) or InGaAs (600-1400 nm) detector. High Resolution ESI spectra were recorded on the 7.0T Actively Shielded Fourier Transform Ion Cyclotron Resonance Mass Spectrometers. Cyclic voltammograms (CV) and other electrochemical experiments were performed on a BAS 100 electrochemical workstation. Glass carbon working electrode, platinum counter electrode and silver pseudoreference electrode were used together, all the potentials were corrected using ferrocenium/ferrocene (Fc⁺/Fc⁰) and reported relative to NHE.

Synthesis

Resolution of (\pm) -[Ru(bpy)₂(py)₂]Cl₂

The Hua's procedure⁴ for resolution of (\pm) -[Ru(bpy)₂(py)₂]Cl₂ was modified as follows: A 0.5 M aqueous solution of disodium O,O'-dibenzoyl-L-tartrate was prepared by neutralizing O,O'-dibenzoyl-L-tartartic acid with sodium hydroxide. (\pm) -[Ru(bpy)₂(py)₂]Cl₂ (2.53 g, 3.94 mmol) was directly added in the aqueous solution of disodium O,O'-dibenzoyl-L-tartrate (25.2 mL, 0.5 M). After (\pm) -[Ru(bpy)₂(py)₂]Cl₂ was dissolved under sonication, the mixture was stirred for several hours until fine red crystals of Λ -[Ru(bpy)₂(py)₂][O,O'-dibenzoyl-L-tartrate]•12H₂O came out. The mixture was allowed to stand in a covered container at room temperature for one or two days. The red crystals (1.15 g, 50.8% yield) were then collected by filtration, washed with cold water and air dried. Λ -[Ru(bpy)₂(py)₂][O,O'-dibenzoyl-L-tartrate]•12H₂O can be converted into Λ -[Ru(bpy)₂(py)₂](PF₆)₂ by the addition of NH₄PF₆ in water solution. PF₆ salt could precipitate from the water and was collected and air dried. Then the chloride salt, Λ -[Ru(bpy)₂(py)₂]Cl₂, was isolated by addition of tetrabutylammonium chloride to a solution of the PF₆ salt in acetone and dried in the air. Finally, enantiomerically pure Λ -[Ru(bpy)₂(py)₂]Cl₂ was obtained as red solid (CD in acetonitrile: $\Delta\epsilon_{299} = +112 \text{ M}^{-1}\text{cm}^{-1}$, $\Delta\epsilon_{284} = -14.6 \text{ M}^{-1}\text{cm}^{-1}$).

Using disodium O,O'-dibenzoyl-D-tartrate and following the above procedure, enantiomerically pure Δ -[Ru(bpy)₂(py)₂][O,O'-dibenzoyl-D-tartrate]•12H₂O (1.11g, 49.2% yield) was obtained from (\pm) -[Ru(bpy)₂(py)₂]Cl₂ (2.53 g, 3.94 mmol). Enantiomerically pure Δ -[Ru(bpy)₂(py)₂]Cl₂ was then obtained after anion exchange as above (CD in acetonitrile: $\Delta\epsilon_{299} = -106 \text{ M}^{-1}\text{cm}^{-1}$, $\Delta\epsilon_{284} = -15.1 \text{ M}^{-1}\text{cm}^{-1}$).

Synthesis of Λ,Λ -**1** and Δ,Δ -**1**

The mixture of Λ -[Ru(bpy)₂(py)₂][O,O'-dibenzoyl-L-tartrate]•12H₂O (1.15g, 1.0 mmol), 1,2-di(N-propylcarbonyl)hydrazide ligand (125 mg, 0.6 mmol) and NaOH (130 mg) in 50 mL of 4:1 DMF/H₂O solution was heated at 110 °C for approximately 17 h under argon atmosphere. The dark reaction solution was then cooled to room temperature. After addition of 50 mL of deoxygenated water, the product was precipitated by the addition of an excess of NH₄PF₆ salt. The isolated product was purified by chromatography using neutral alumina gels and acetone as eluent. The purple band was collected, concentrated under the reduced pressure, re-dissolved in a small amount of acetone and precipitated out in diethyl ether. After drying in vacuum at room temperature overnight, Λ,Λ -**1** was obtained as purple solid (95 mg, 14.4%). Similarly, Δ,Δ -**1** (134 mg, 20.3% yield) was prepared from Δ -[Ru(bpy)₂(py)₂][O,O'-dibenzoyl-D-tartrate]•12H₂O.

Reference

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2. B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.* 1978, **17**, 3334-3341.

3. O. Morgan, S. Wang, S. Bae and R. Engel, *J. Chem. Soc., Dalton Trans.*, 1997, 3773-3776.

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2. CD spectra

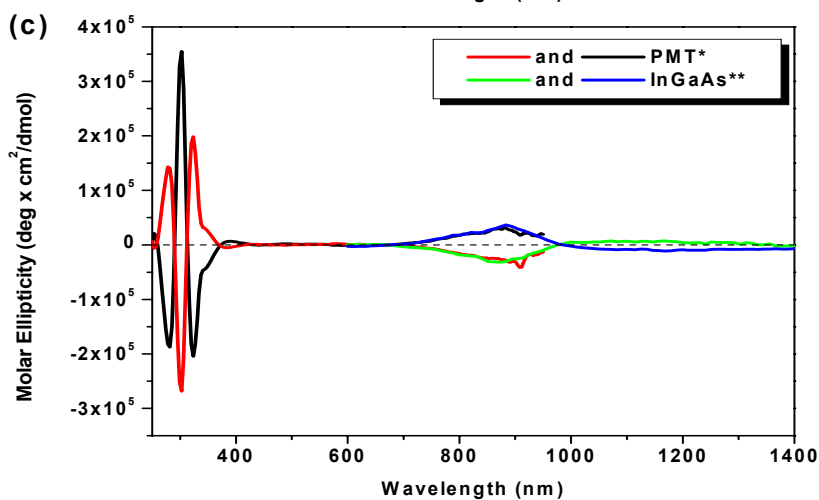
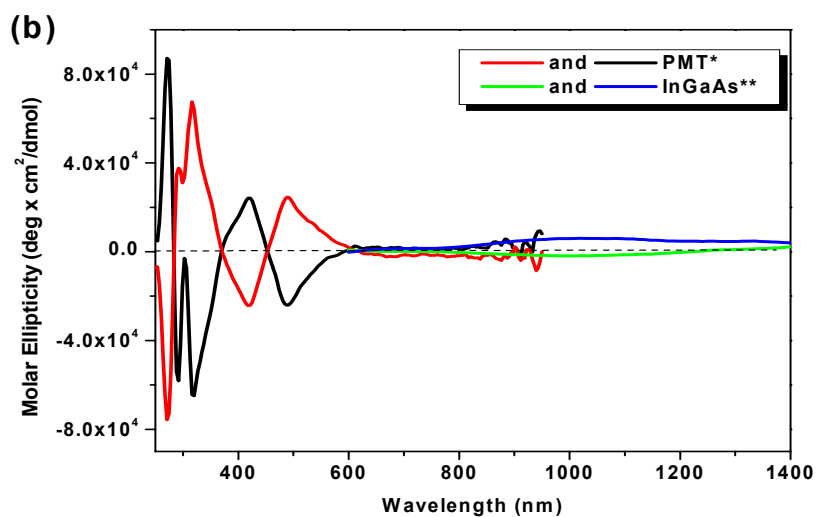
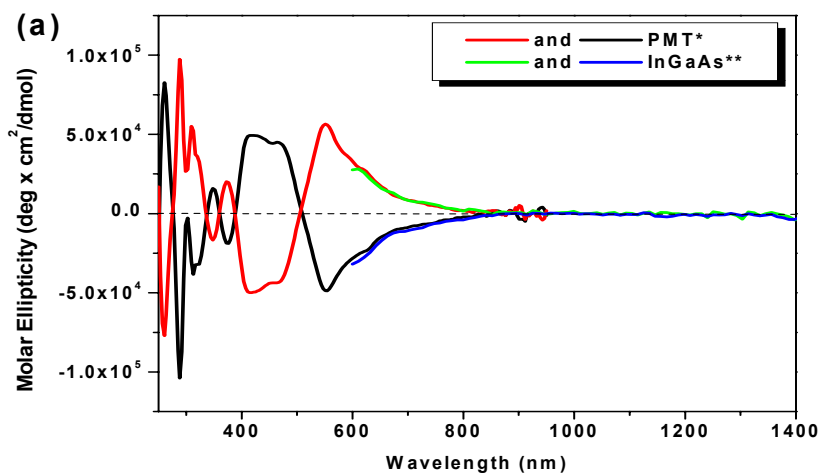


Fig. S1. CD spectra of Λ,Λ -1 (red and green) and Δ,Δ -1 (black and blue) in (a) $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}$, (b) $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and (c) $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ state. *PMT detector with a working range from 250 to 950 nm. **InGaAs detector with a working range from 600 to 1400 nm.

3. NMR Spectra

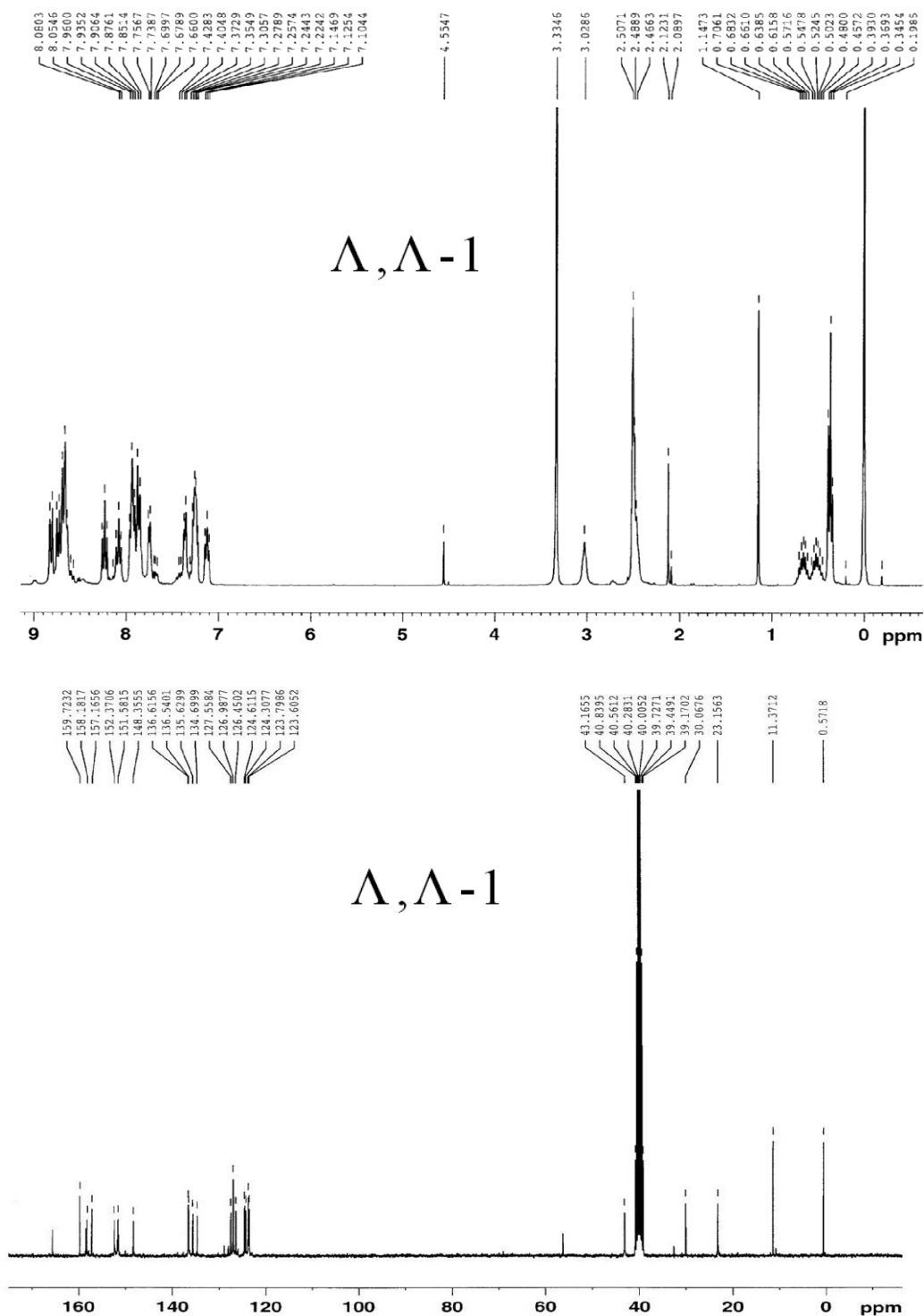


Fig. S2. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of Δ,Δ -1 in d_6 -DMSO.

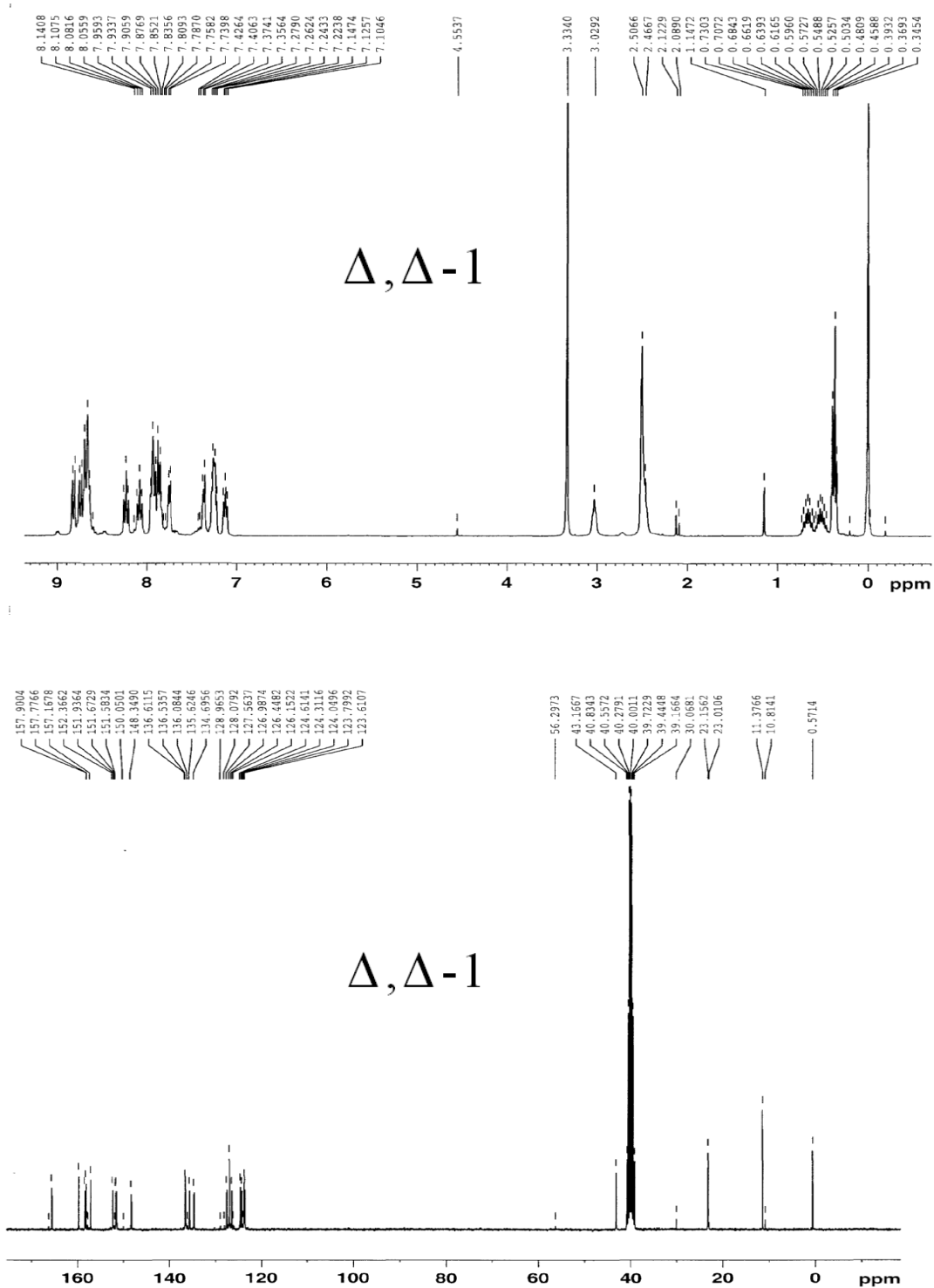


Fig. S3. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of Δ,Δ -1 in d_6 -DMSO.

4. High Resolution ESI Spectra

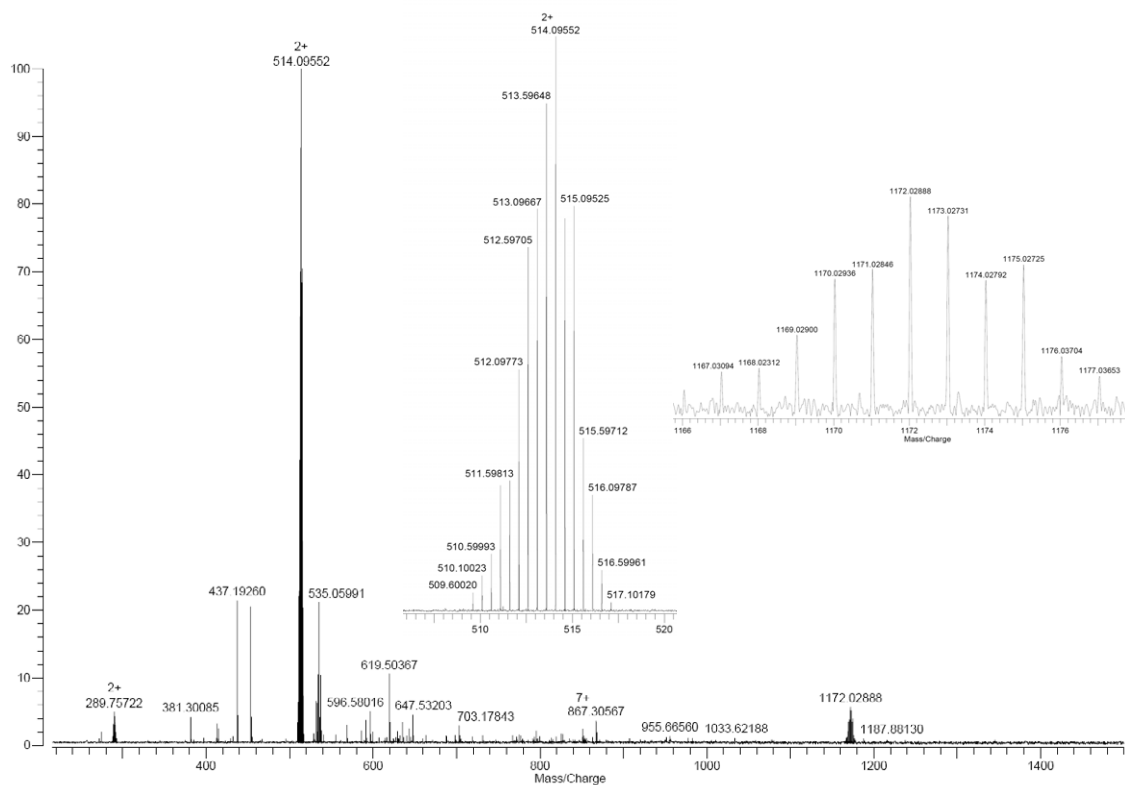


Fig. S4. High resolution ESI spectrum of Δ,Δ -1. A group of peaks at m/z 1172 (6%, M-PF₆) and 1187 (100%, M-2PF₆) is due to the ruthenium isotopes.

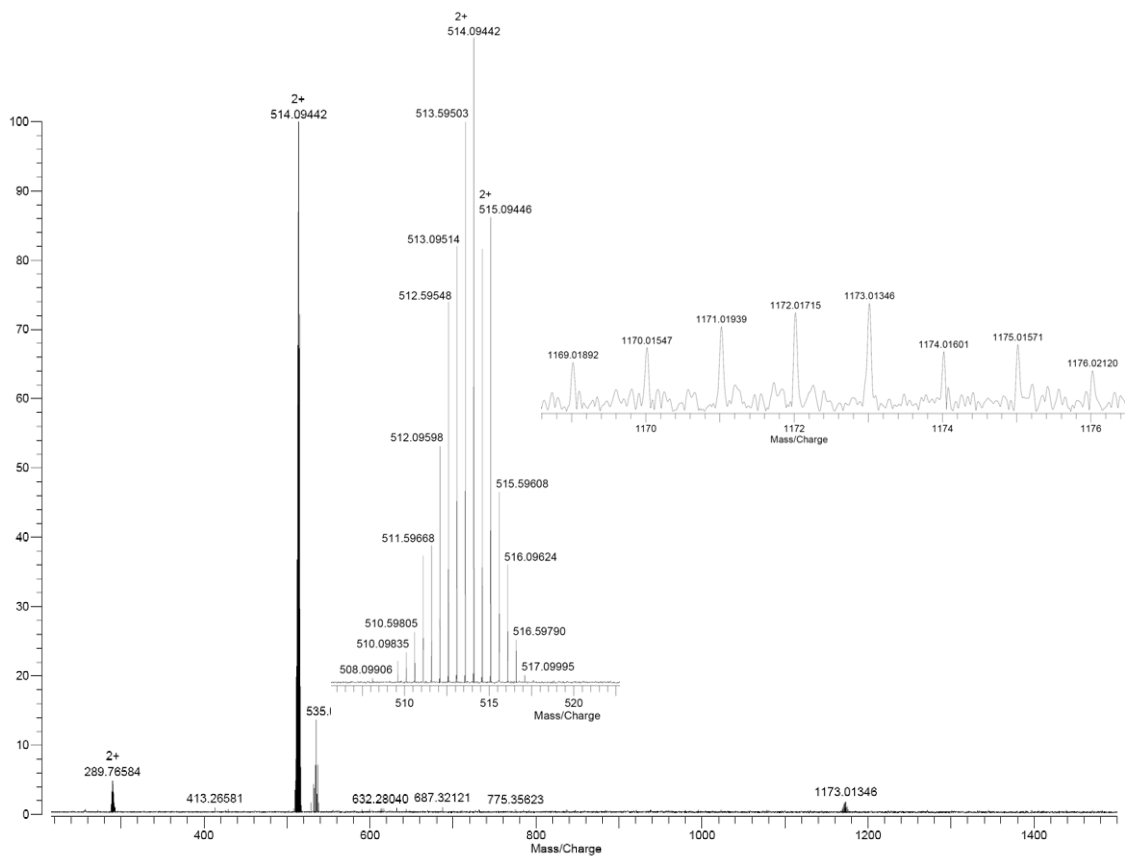


Fig. S5. High resolution ESI spectrum of Δ,Δ -1. A group of peaks at m/z 1173 (2%, M-PF₆) and 514 (100%, M-2PF₆) is due to the ruthenium isotopes.