Electronic Supplementary Information for Dalton Transactions

A Divergent Strategy for Covalently-Tethered $(tpy)_2Ru(II)$ Systems Based on Rh_2(*N,N'*-diphenylbenzamidinates)$_4$

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A. Synthesis

Rh_2(*N,N'*-diphenyl-4-{(4'-amidotpy)(4'-tolyltpy)Ru]$(PF_6)_2$}-benzamidinate)$_4$ (5) In a typical preparation, **4** (0.29 g, 0.30 mmol) is heated to reflux in thionyl chloride for 3 h. Excess thionyl chloride is removed by vacuum distillation and the residue is dried under vacuum. To this residue is charged acetonitrile (40 mL) and triethylamine (0.30 g, 3.0 mmol). **3** (0.050 g, 0.004 mmol) is then added portion wise as an acetonitrile solution (5 mL) and the reaction mix is heated to reflux under an inert atmosphere for 30 min. The intensely dark red solution is then concentrated for purification by column chromatography using silica and 7:2 CH_3CN / $KNO_{3\ (aq,\ sat)}$. The desired fractions are concentrated and precipitated from $KPF_{6\ (aq,\ sat)}$ solution. The resulting precipitate was taken up in CH_3CN and precipitated from H_2O, filtered and dried to give 0.149 g of product in 77 % yield. R_f = 0.48 (SiO_2 substrate, 7:2 CH_3CN / $KNO_{3\ (aq,\ sat)}$ as eluent). ^1H NMR (400 MHz, CD_3CN) δ ppm 9.47 (br, 4H), 9.20 (m, 8H), 9.05 (s, 8H), 8.67 (m, 16H), 8.15 (d, J = 8.0 Hz, 8H), 8.00 (m, 16H), 7.62 (d, J = 8.0 Hz, 8H), 7.51 (d, J = 4.7 Hz, 8H), 7.36 (d, J = 4.7 Hz, 8H), 7.26 (m, 8H), 7.19 (m, 8H), 6.16 (br, 8H), 5.58 (br, 8H). ESI-MS: $[M]^{8+}$ cald for $C_{228}H_{168}N_{36}O_4Rh_2Ru_4$, 510.85416; found, 510.85434.

$[M(PF_6)]^{7+}$ 604.402, $[M(PF_6)_2]^{6+}$ 729.461, $[M(PF_6)_3]^{5+}$ 904.348, $[M(PF_6)_4]^{4+}$ 1166.674, $[M(PF_6)_5]^{3+}$ 1603.900.

B. ^{1}**H** **NMR**

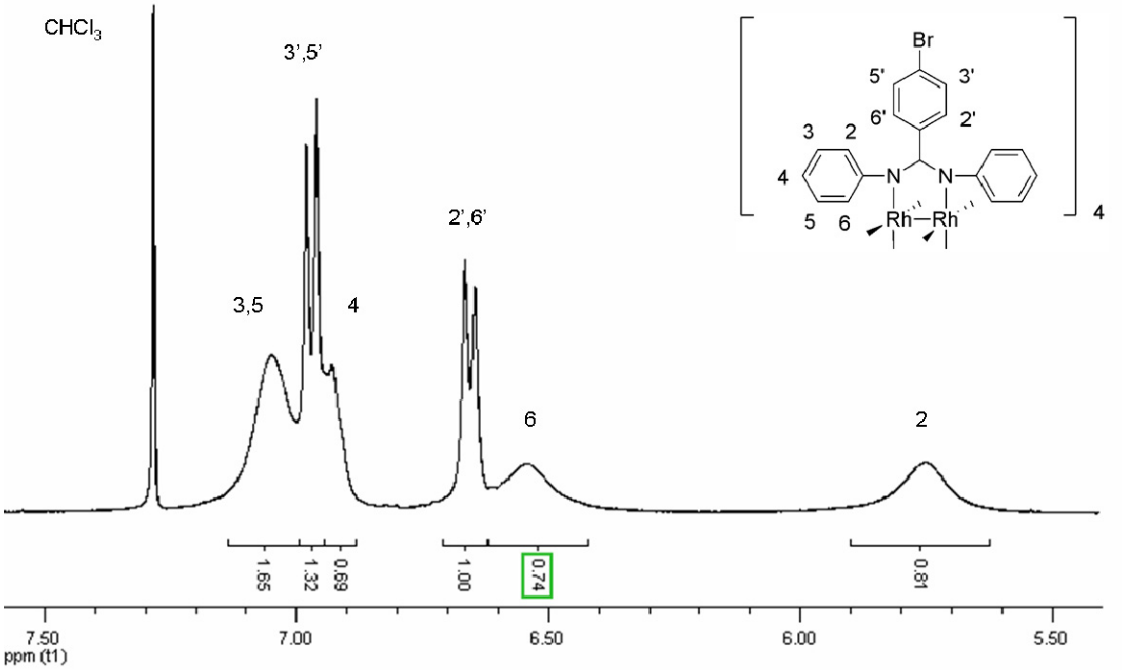

Figure B.1. Complex **1** in $CDCl_3$.

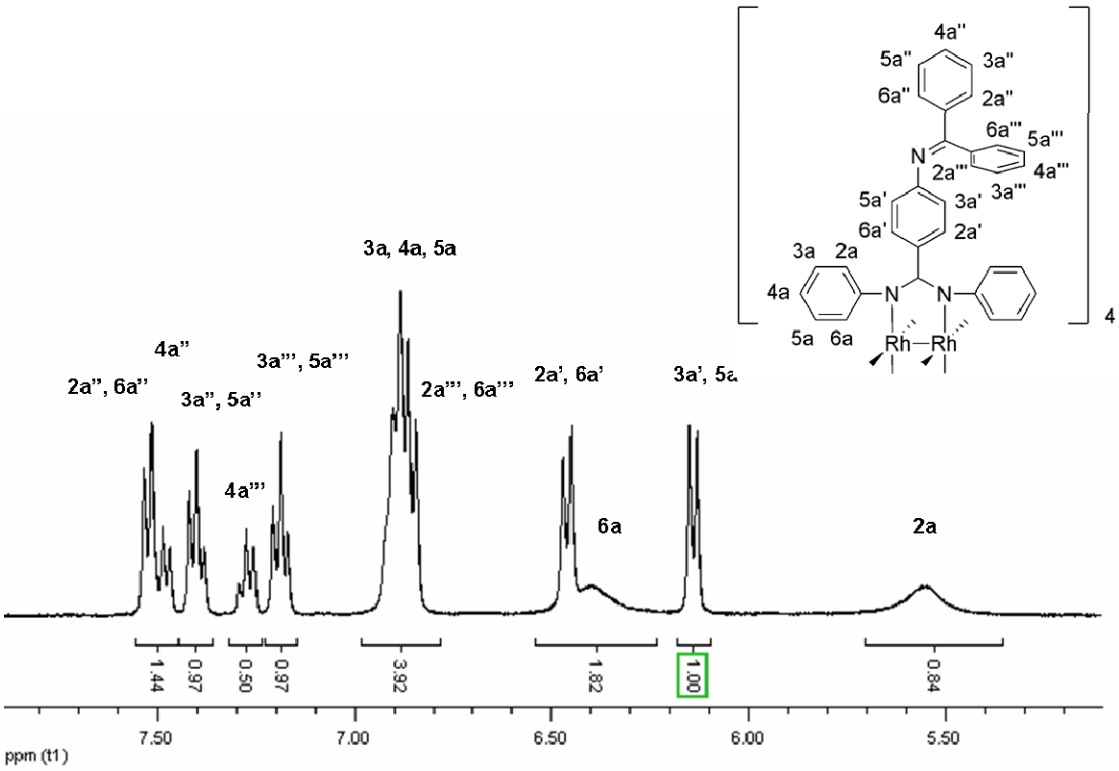

Figure B.2. Complex **2** in d_6-DMSO.

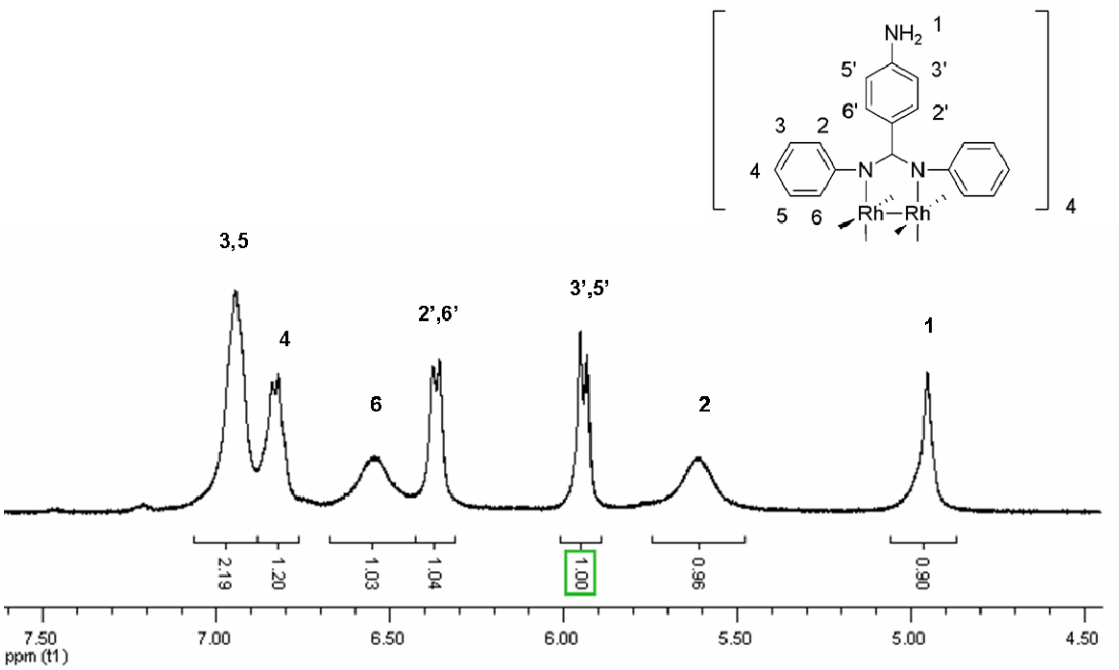

Figure B.3. Complex **3** in d_6-DMSO.

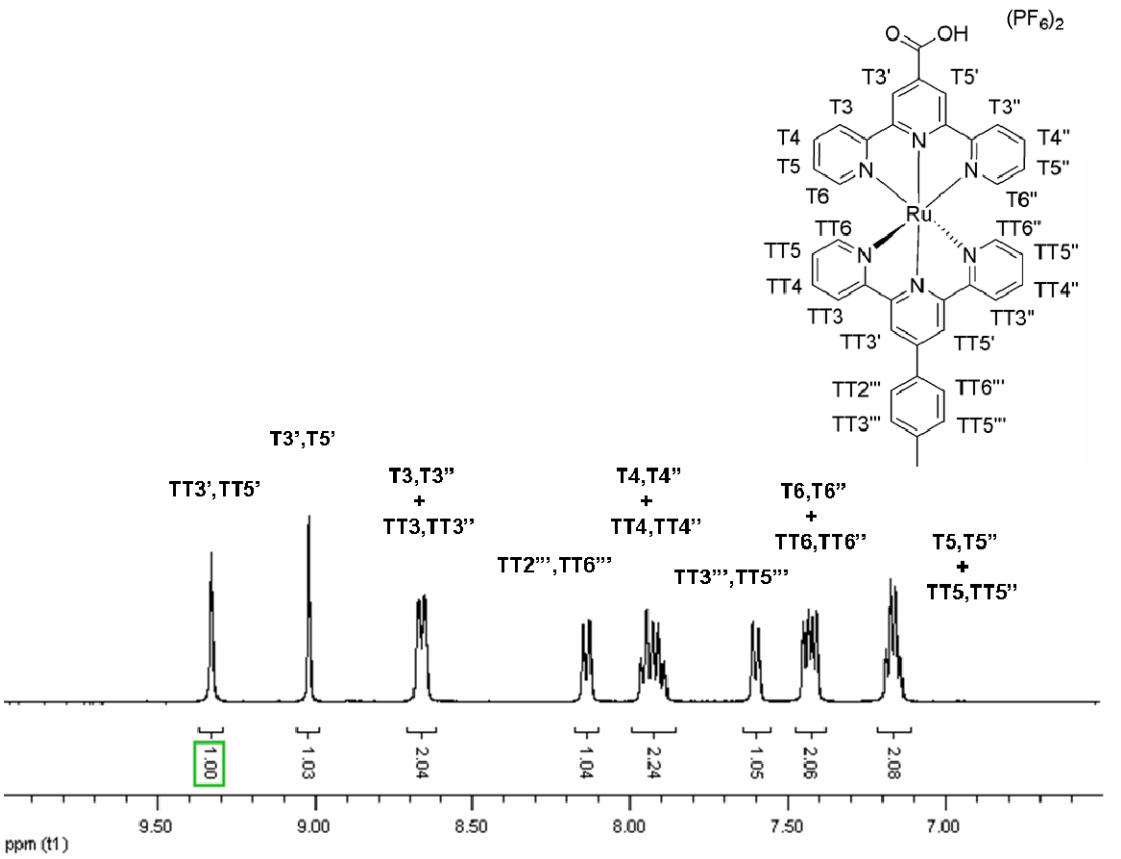

Figure B.4. Complex **4** in CD_3CN. Methyl resonance at 2.57 ppm (not shown).

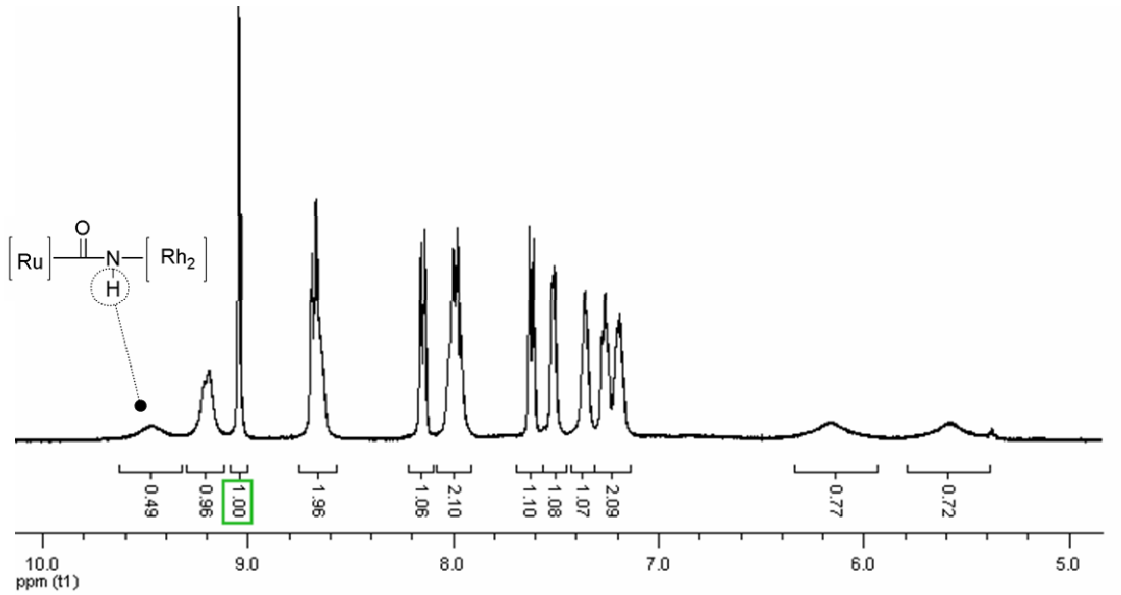

Figure B.5. Complex **5** in CD_3CN.

C. Mass Spectrometry

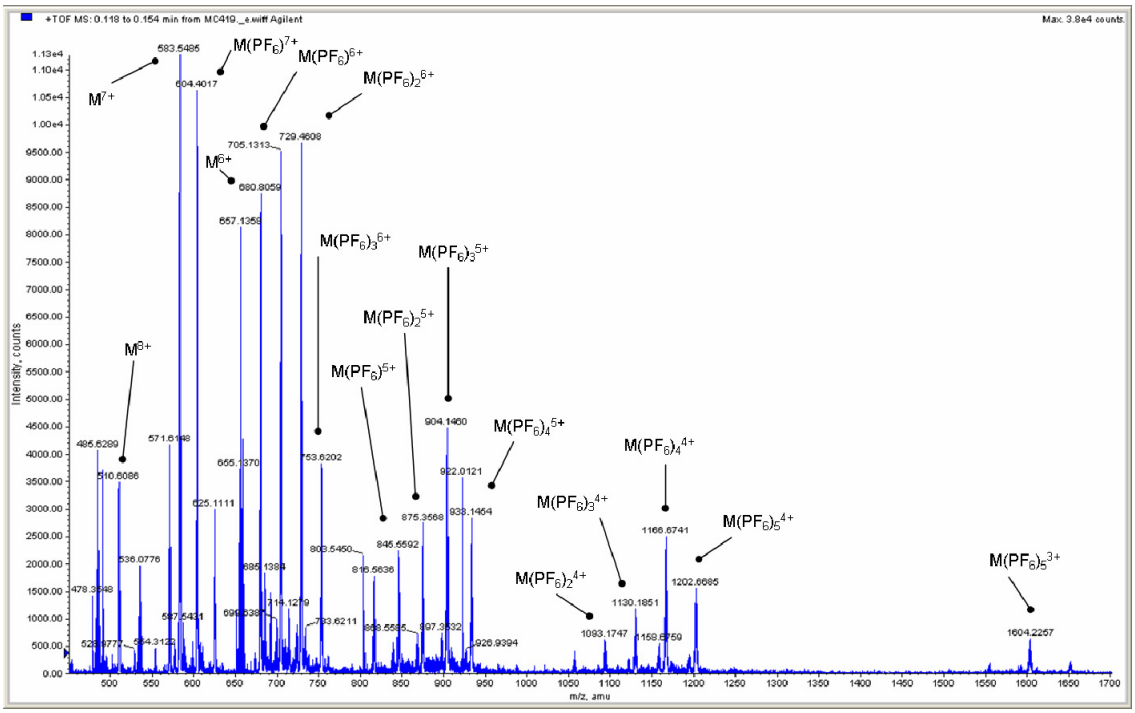

Figure C.1. ESI-MS of complex 5 (M = $C_{228}H_{168}N_{36}O_4Ru_4Rh_2$).

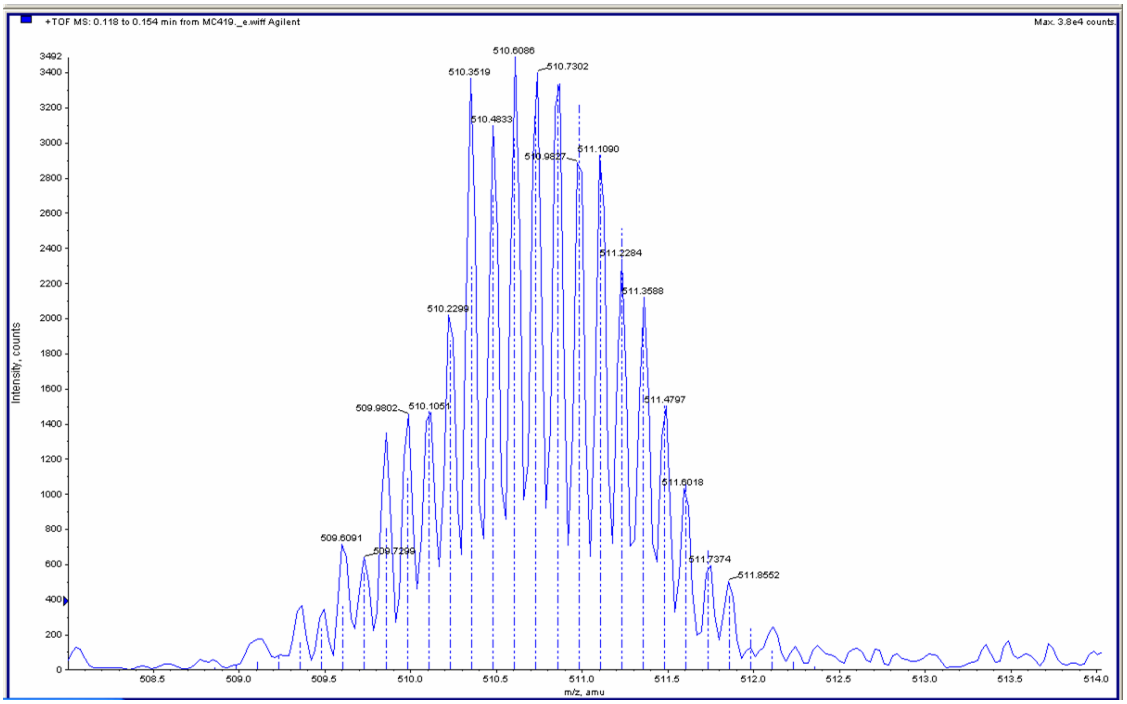

Figure C.2. Isotopic distribution for $[C_{228}H_{168}N_{36}O_4Ru_4Rh_2]^{8+}$.

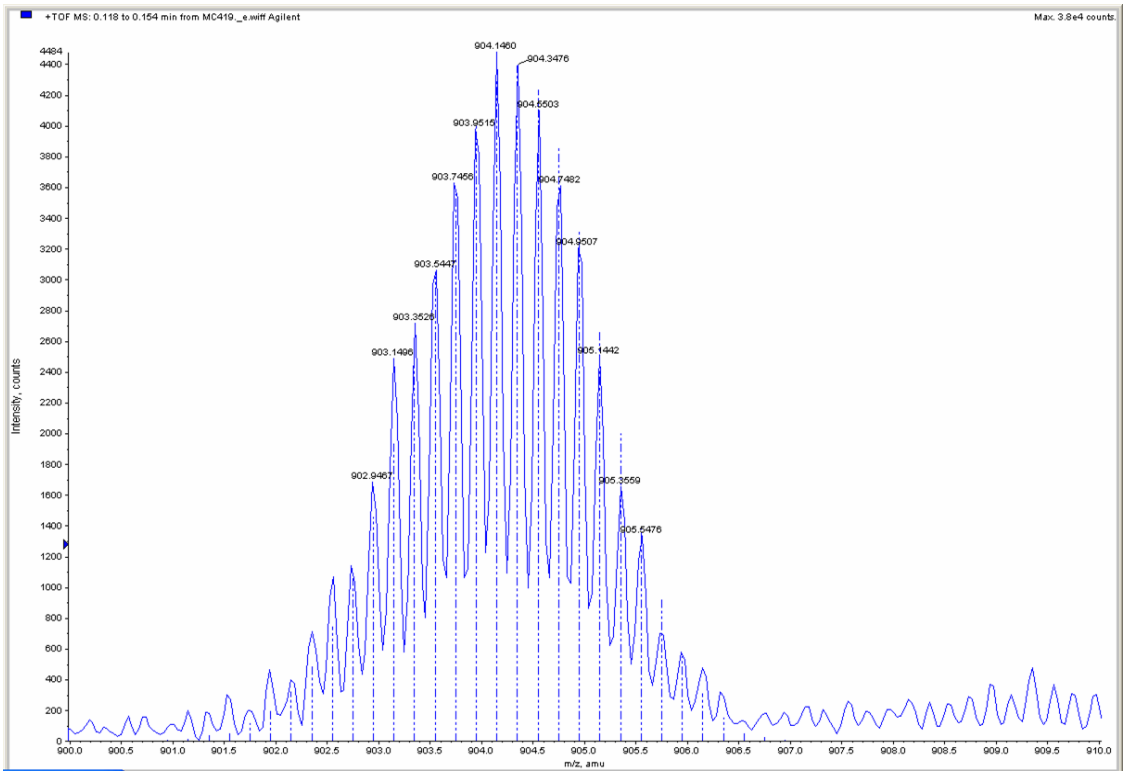

Figure C.3. Isotopic distribution for $[C_{228}H_{168}N_{36}O_4Ru_4Rh_2P_3F_{18}]^{5+}$.

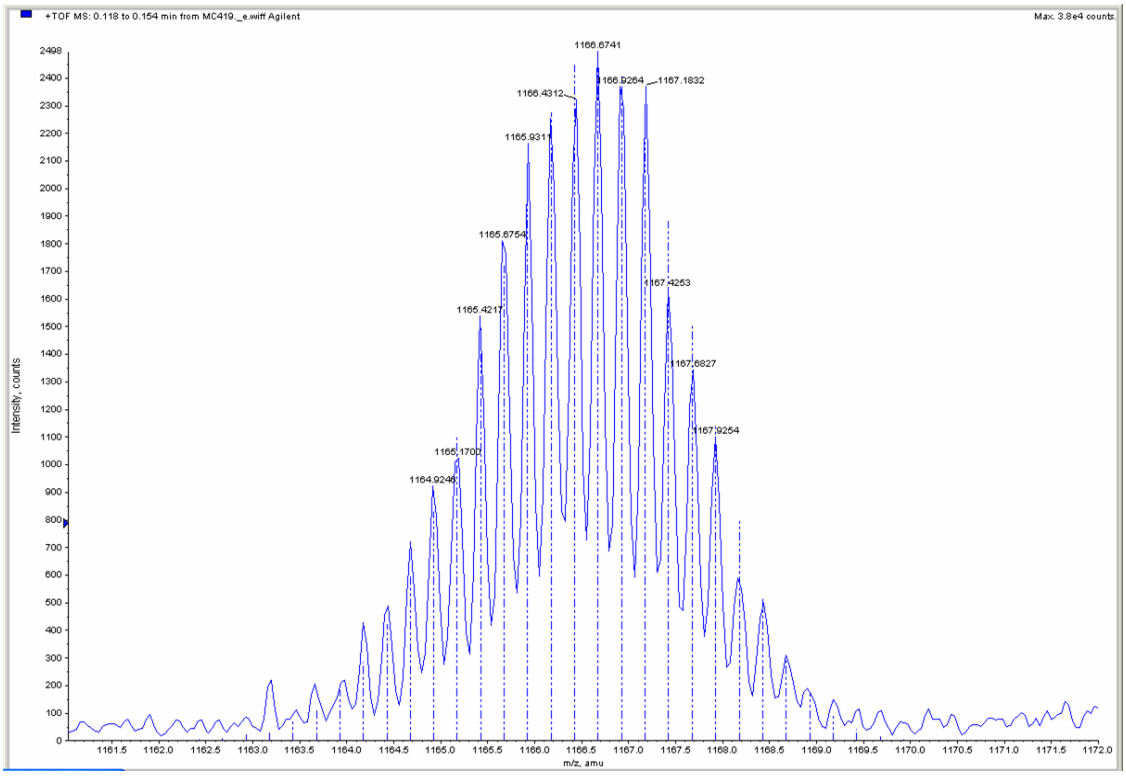

Figure C.4. Isotopic distribution for $[C_{228}H_{168}N_{36}O_4Ru_4Rh_2P_4F_{24}]^{4+}$.

D. Cyclic Voltammetry

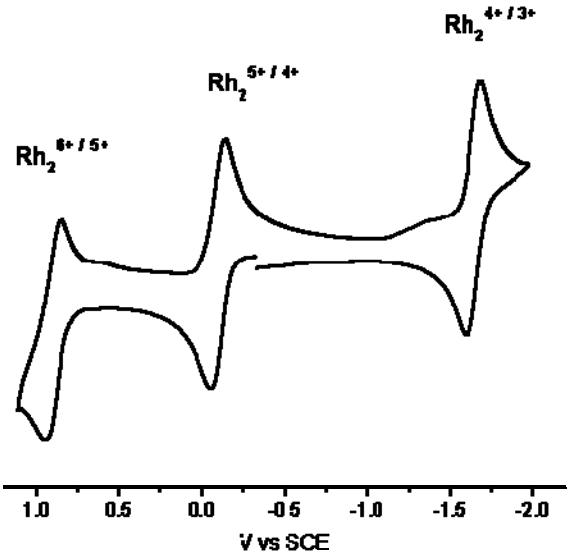

Figure D.1 Cyclic voltammogram of complex **3** (100 mVs^{-1} in 0.1 M $TBAPF_6/CH_3CN$).