SUPPORTING INFORMATION

Alkyne substituted Thummel type photocatalysts

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S1. Crystal structure selected bond lengths and angles

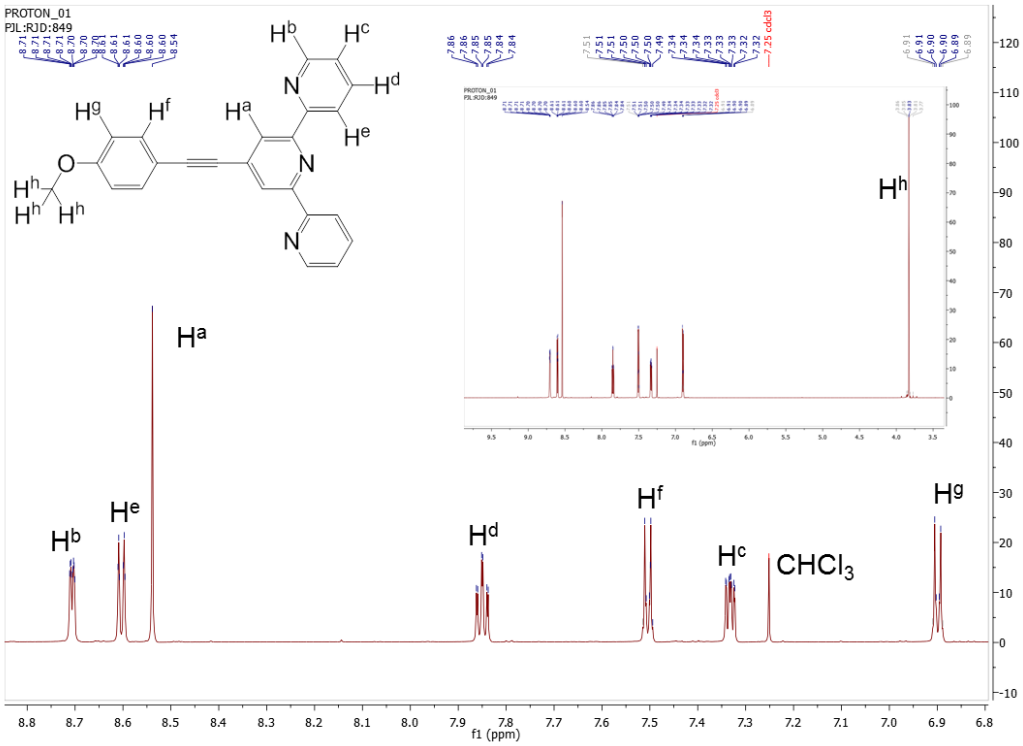

Figure S1.1 ^{1}H NMR spectra of **L²** recorded in $CDCl_3$.

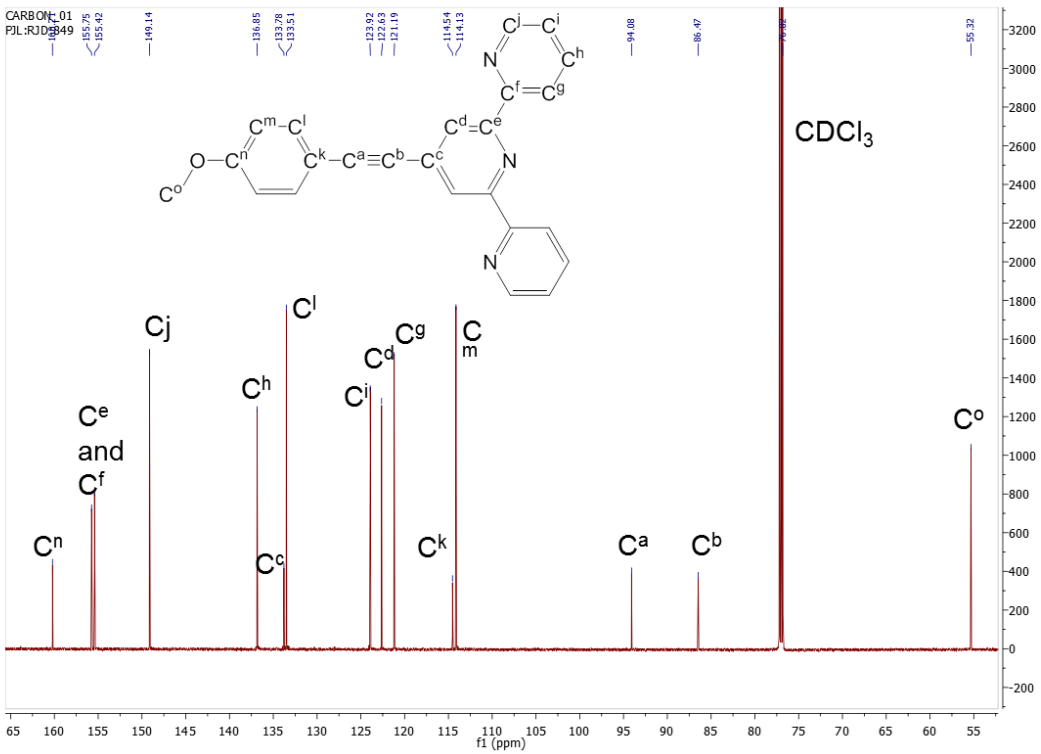

Figure S1.2 ^{13}C NMR spectra of **L²** recorded in $CDCl_3$.

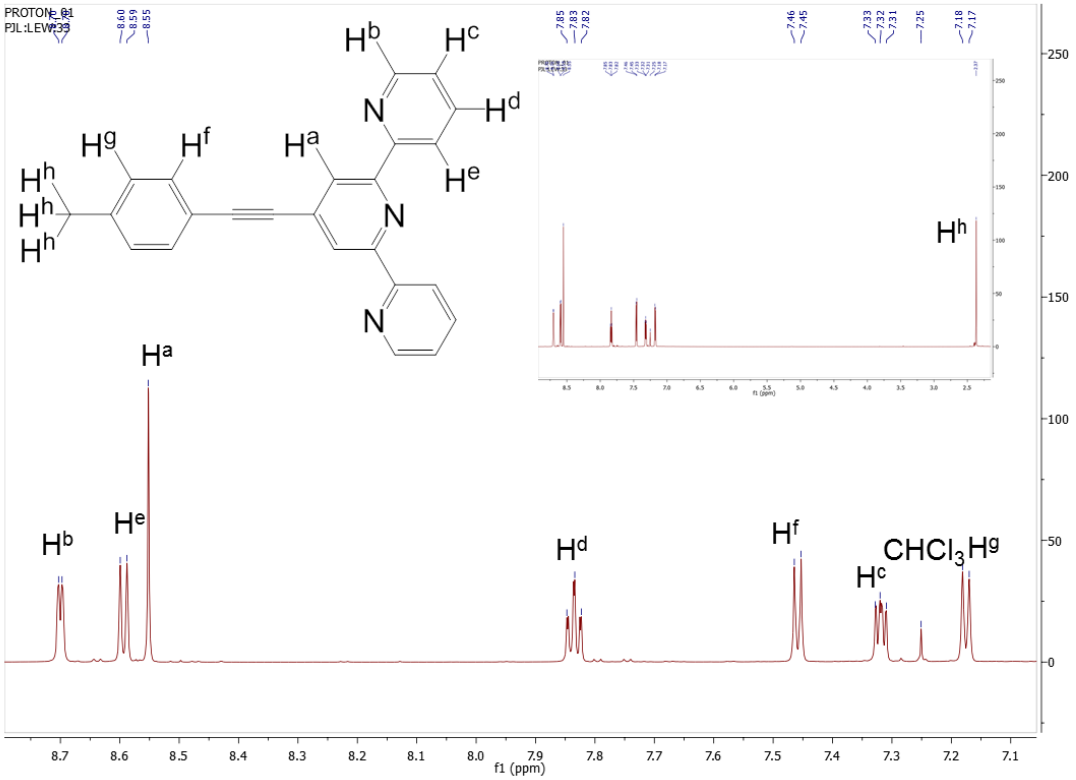

Figure S1.3 ^{1}H NMR spectra of **L^{3}** recorded in $CDCl_3$.

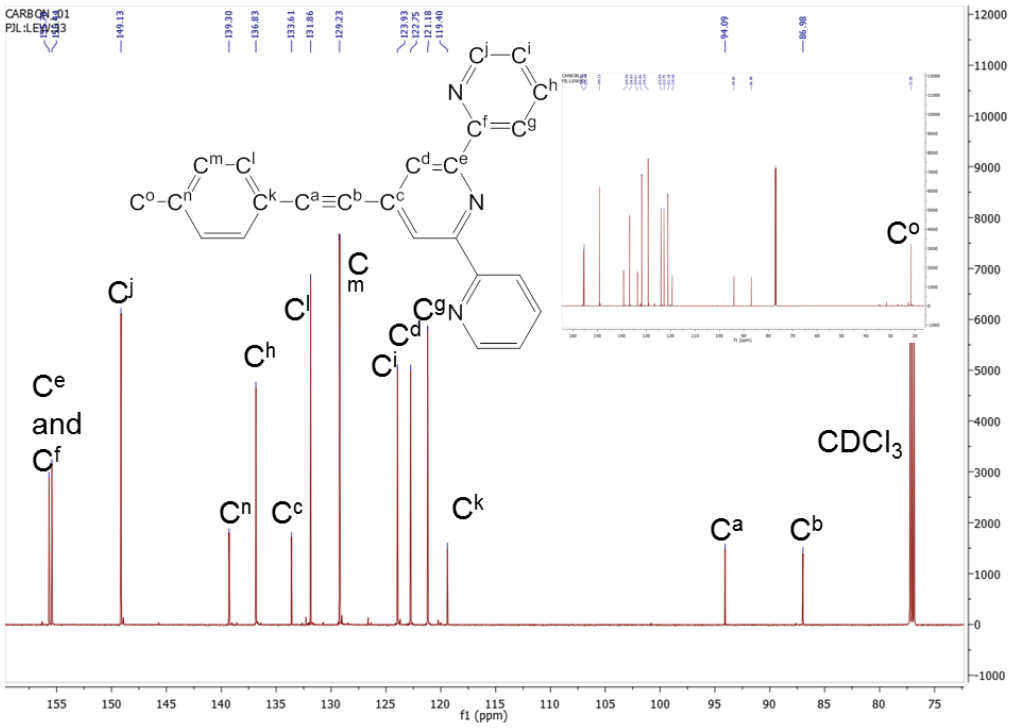

Figure S1.4 ^{13}C NMR spectra of **L^{3}** recorded in $CDCl_3$.

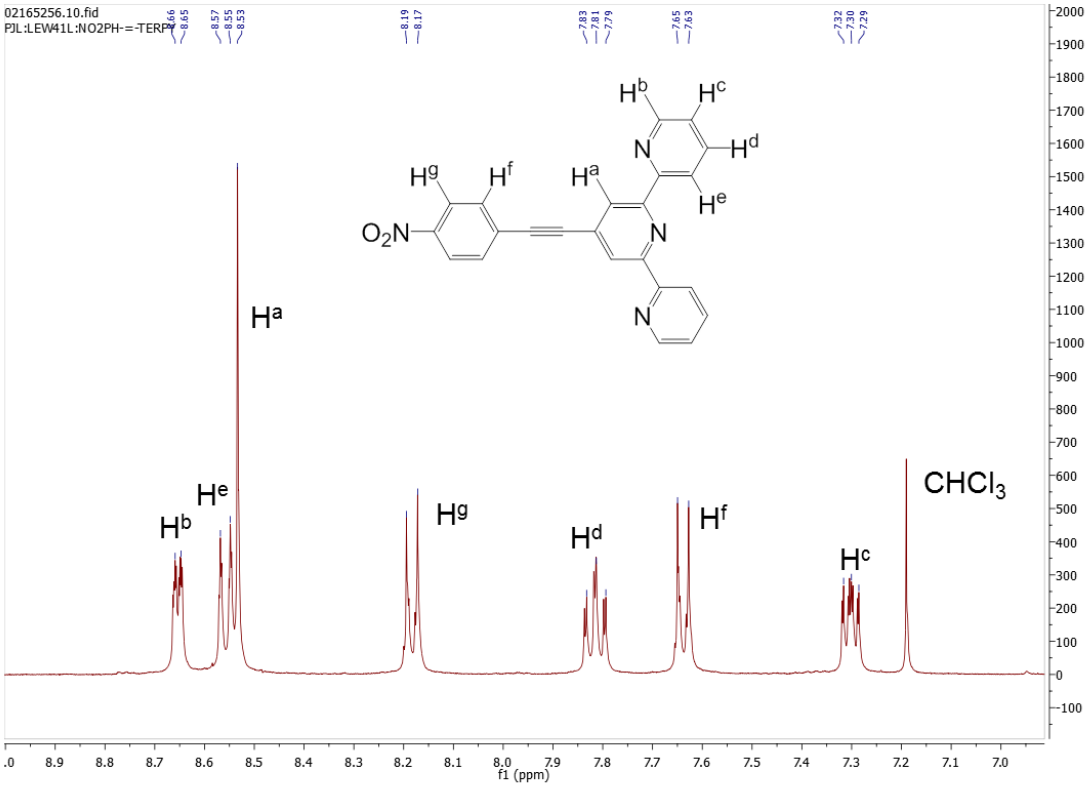

Figure S1.5 ^{1}H NMR spectra of **L^{4}** recorded in $CDCl_3$.

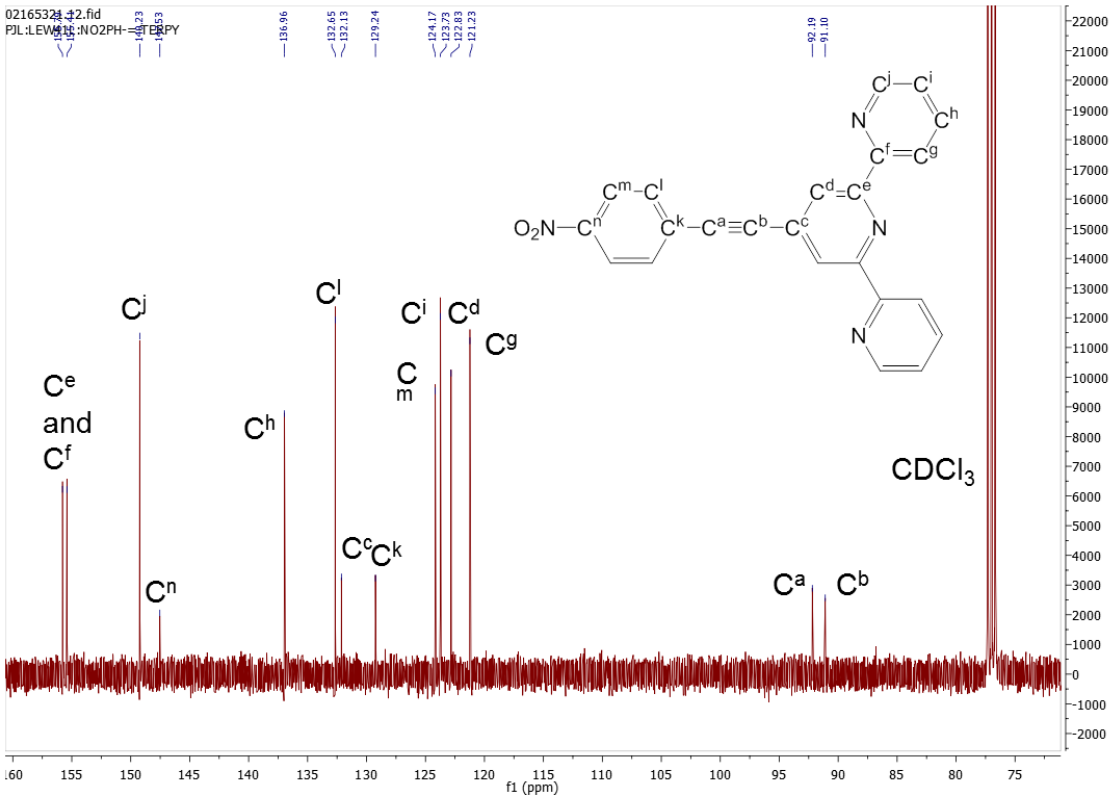

Figure S1.6 ^{13}C NMR spectra of **L^{3}** recorded in $CDCl_3$.

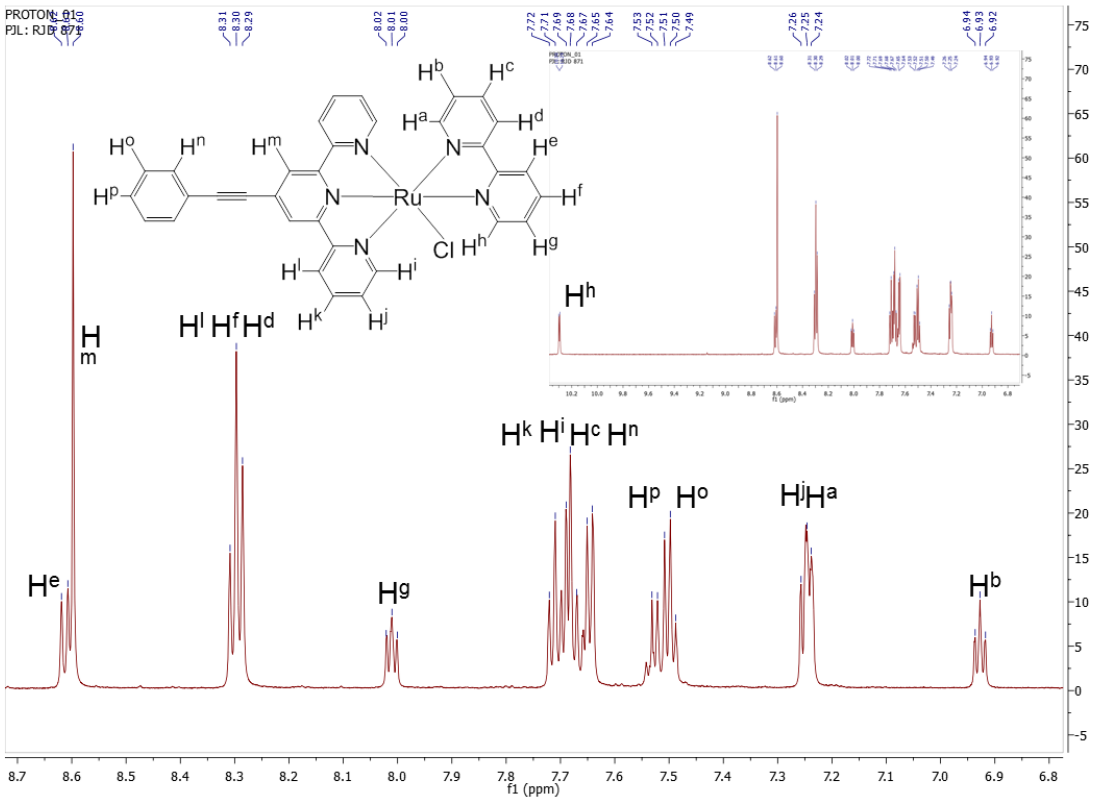

Figure S1.7 ^{1}H NMR spectra of [**1**Cl]PF_6 recorded in CD_3CN.

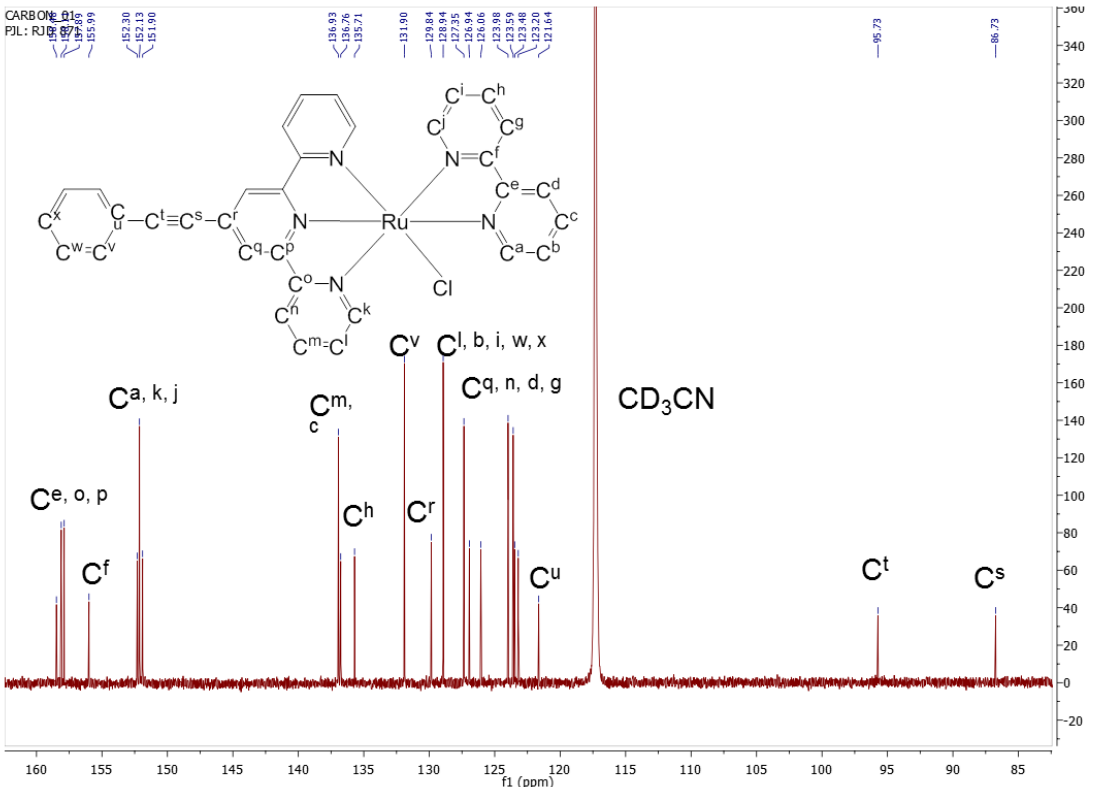

Figure S1.8 ^{13}C NMR spectra of [**1**Cl]PF_6 recorded in CD_3CN.

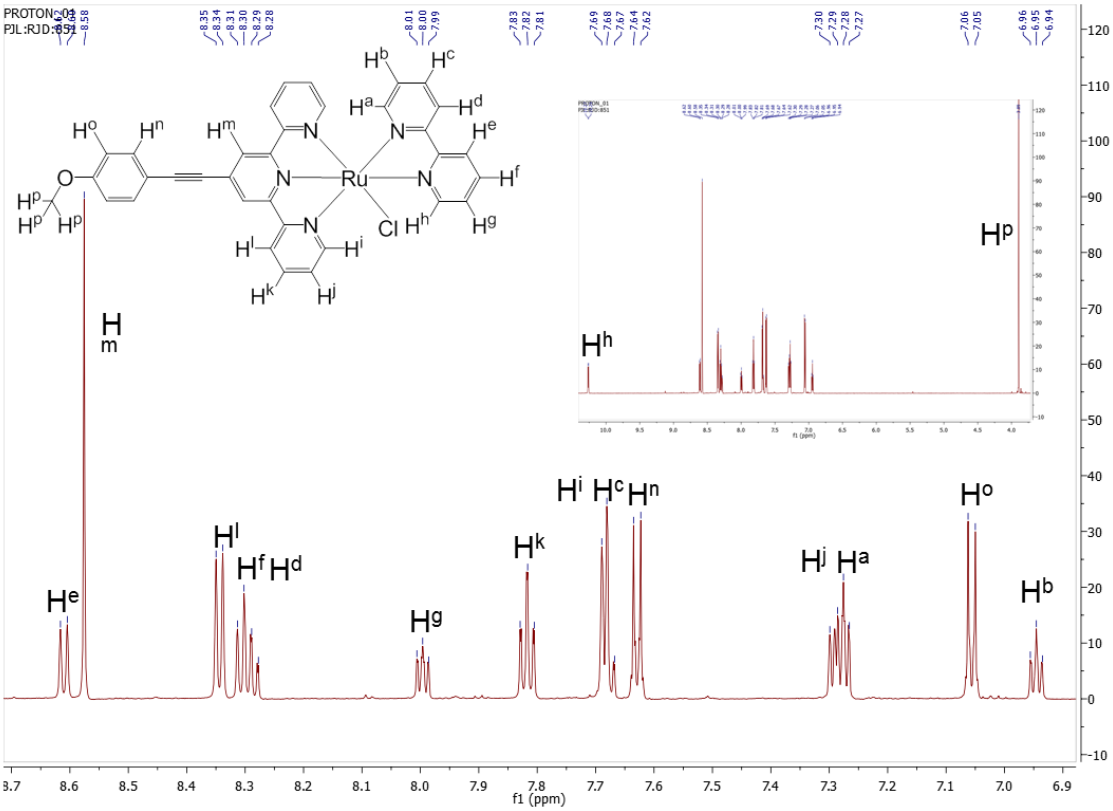

Figure S1.9 ^{1}H NMR spectra of [**2**Cl]PF_6 recorded in CD_3CN.

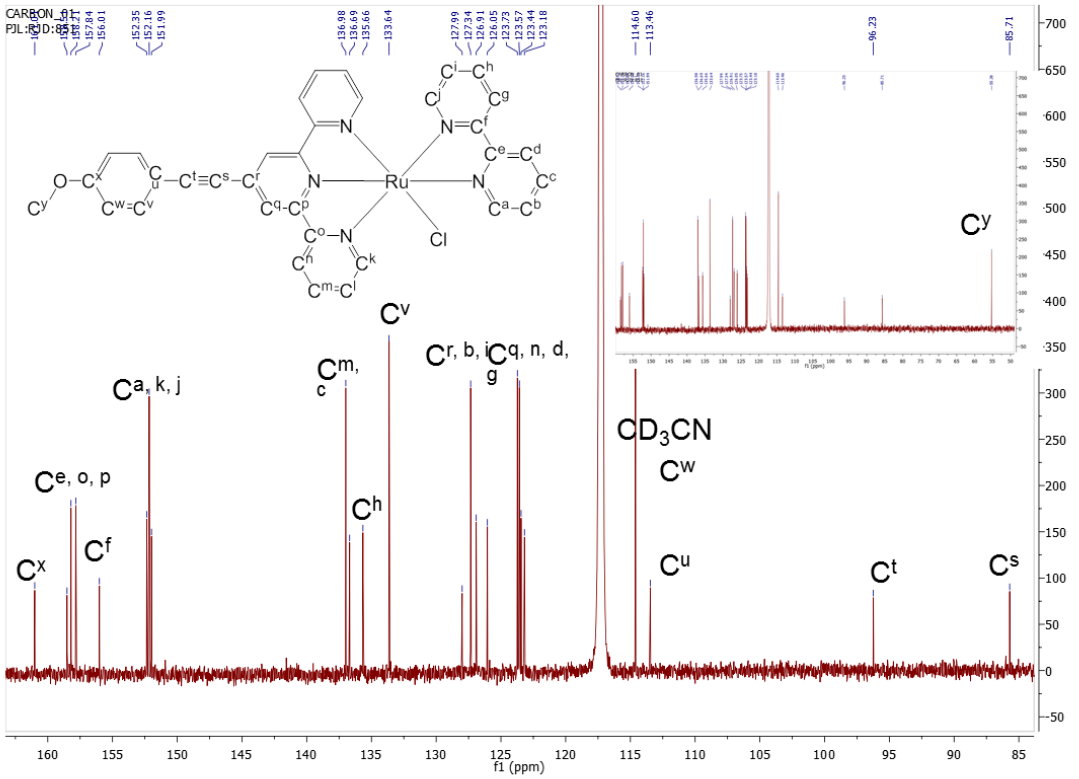

Figure S1.10 ^{13}C NMR spectra of [**2**Cl]PF_6 recorded in CD_3CN.

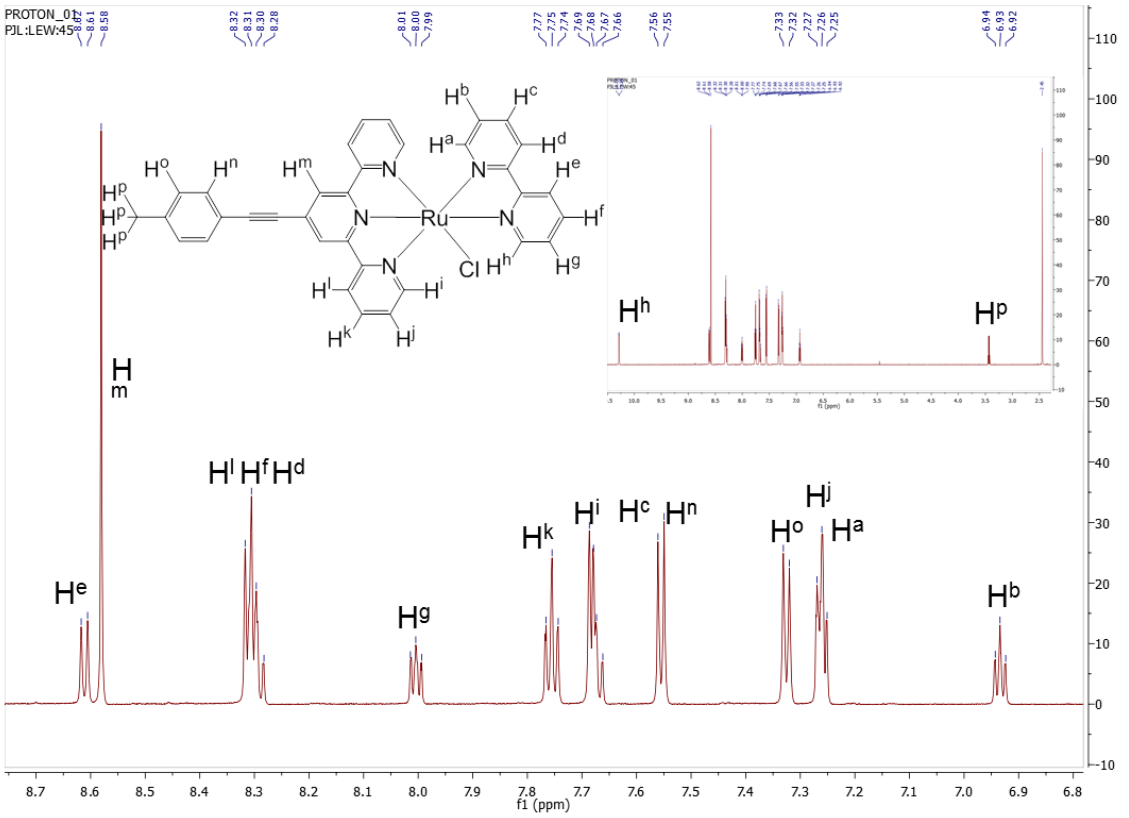

Figure S1.11 ^{1}H NMR spectra of [**3**Cl]PF_6 recorded in CD_3CN.

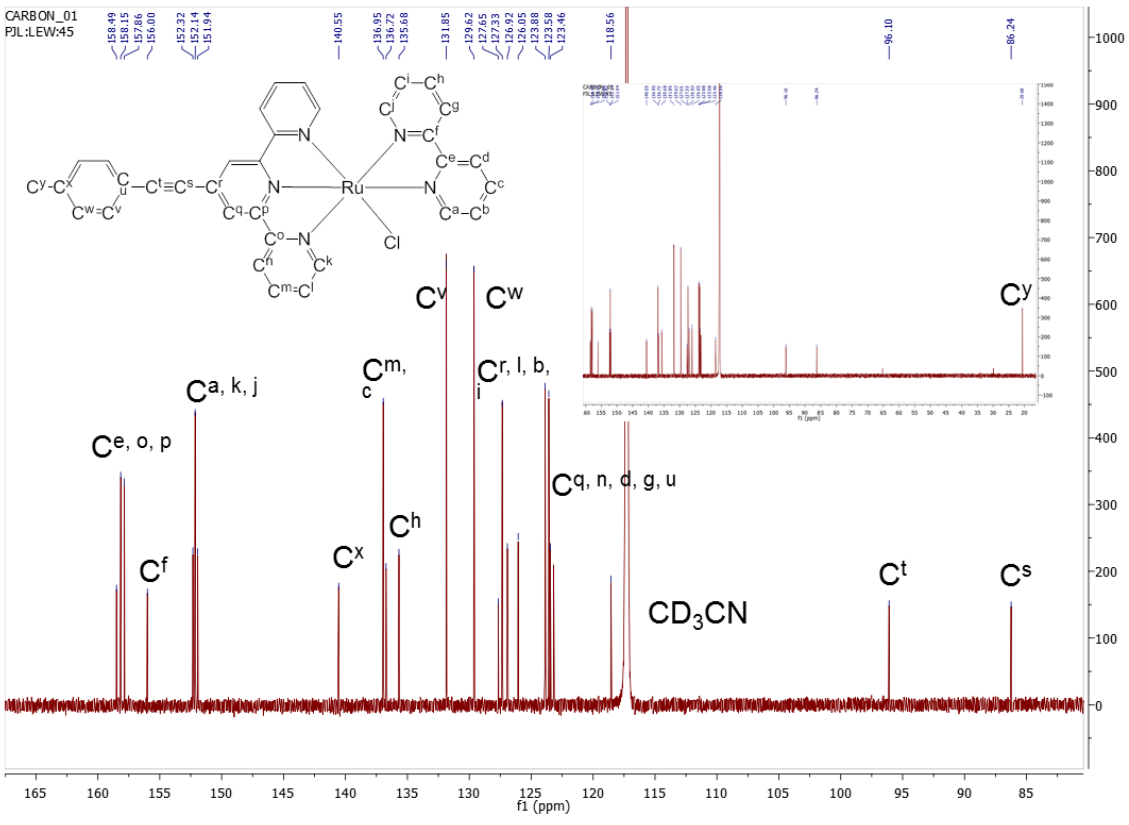

Figure S1.12 ^{13}C NMR spectra of [**3**Cl]PF_6 recorded in CD_3CN.

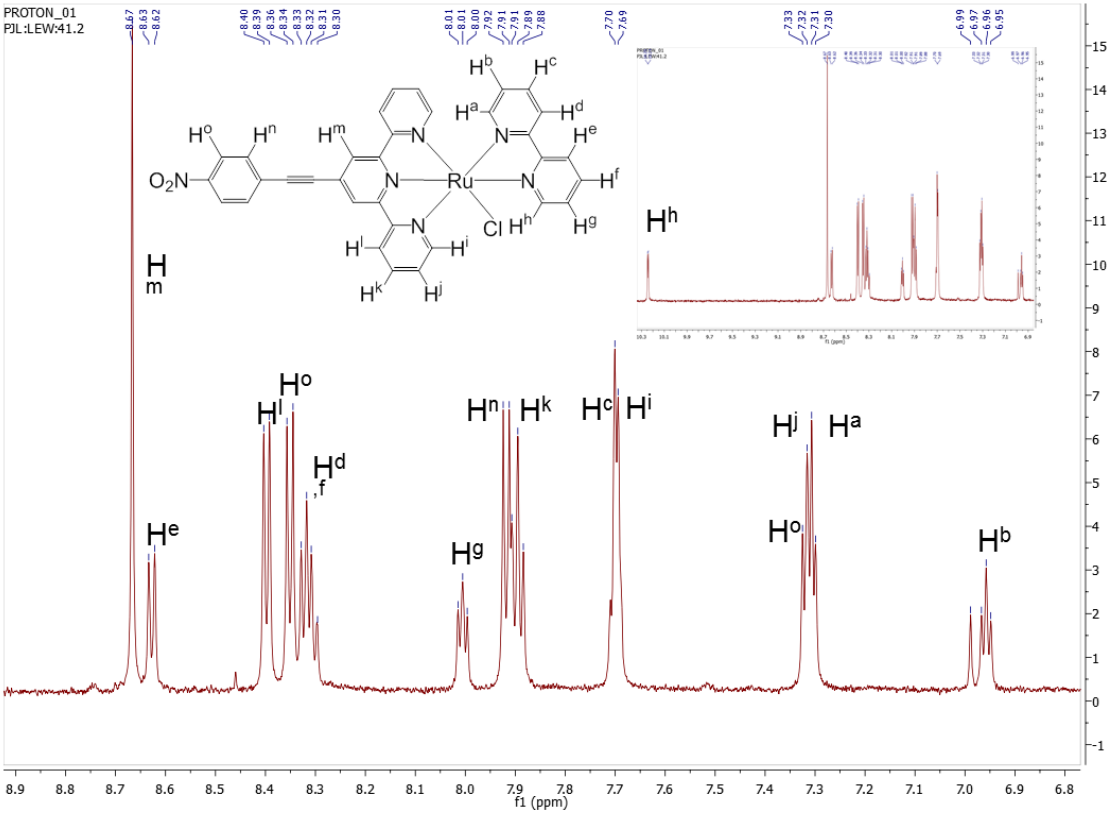

Figure S1.13 ^{1}H NMR spectra of [**4**Cl]PF_6 recorded in CD_3CN.

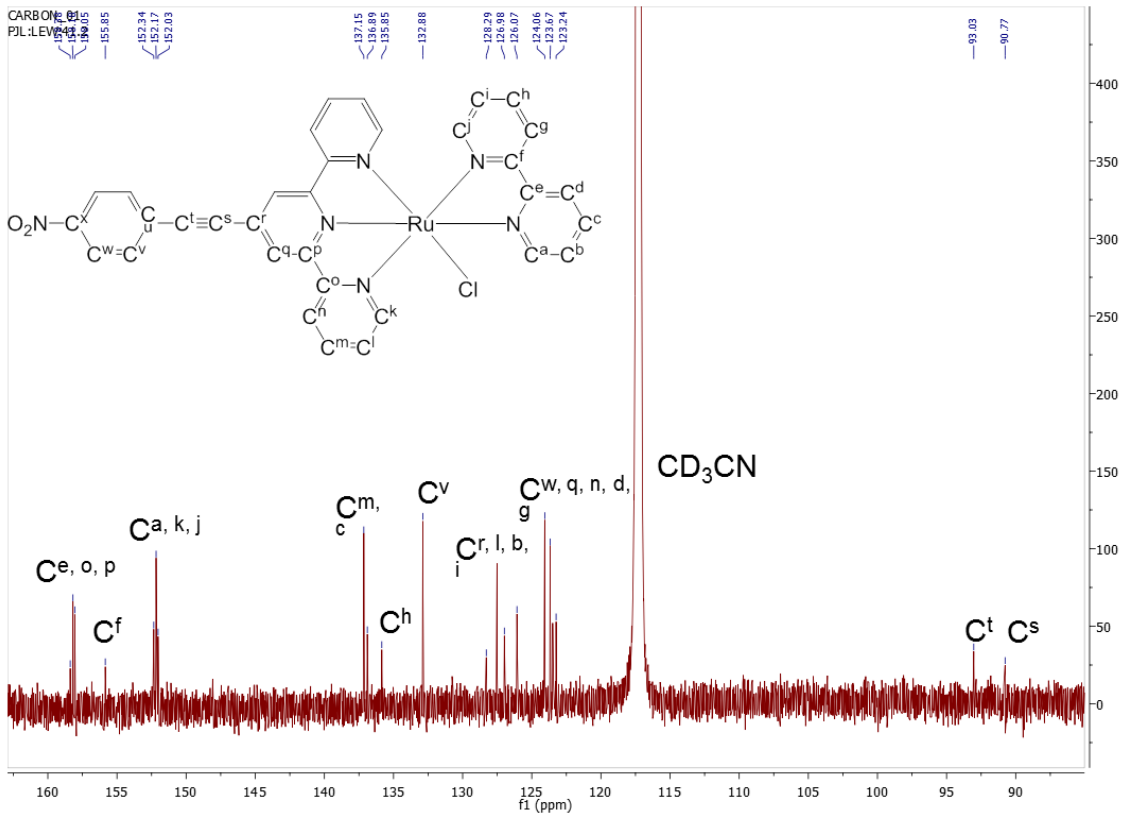

Figure S1.14 ^{13}C NMR spectra of [**4**Cl]PF_6 recorded in CD_3CN.

S2. Crystal structure refinement, selected bond lengths and angles

Table S2.1. Crystal and Refinement Data for $\mathbf{L^3}$, [**3**Cl]$PF_6 \cdot CH_3CN \cdot C_4H_{10}O$ and [**4**Cl]$PF_6 \cdot 2CH_3CN$

Compound	$\mathbf{L^3}$	[**3**Cl]$PF_6 \cdot CH_3CN \cdot C_4H_{10}O$	[**4**Cl]$PF_6 \cdot 2CH_3CN$
molecular formula	$C_{24}H_{17}N_3$	$C_{40}H_{38}ClF_6N_6OPRu$	$C_{37}H_{28}ClF_6N_8O_2PRu$
M (g mol^{-1})	347.41	900.25	898.16
T (K)	120	120	120
crystal system	Monoclinic	Triclinic	Triclinic
space group	$P2_1/c$	P-1	P-1
a (Å)	4.7572(4)	12.0142(14)	10.5971(4)
b (Å)	19.9132(17)	13.6517(16)	12.7714(5)
c (Å)	18.6841(16)	24.769(3)	15.9819(6)
α (deg.)	90	74.903(3)	69.0510(10)
β (deg.)	91.698(3)	81.701(3)	74.7880(10)
γ (deg.)	90	82.307(3)	68.1910(10)
V (Å^3)	1769.2(3)	3861.4(8)	1854.38(12)
Z	4	4	2
μ (Mo Kα) mm^{-1}	0.078	0.587	0.615
ρ_{calc} (g cm^{-3})	1.304	1.549	1.609
2Θ range for data collection (°)	2.98-52	3.1-59	2.76-57
number of unique reflections	16451	66133	22279
data/restrains/ parameters	3470/0/312	21526/150/1002	9367/3/626
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0712$	$R_1 = 0.0590$	$R_1 = 0.0442$
	$wR_2 = 0.1651$	$wR_2 = 0.1529$	$wR_2 = 0.0878$
R indices (all data)	$R_1 = 0.1277$	$R_1 = 0.0910$	$R_1 = 0.0783$
	$wR_2 = 0.1865$	$wR_2 = 0.1767$	$wR_2 = 0.1012$
goodness-of-fit on F^2	1.016	1.024	0.999

Table S2.2 Bond Lengths for **L^3**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
N1	C1	1.347(4)		C9	C10	1.387(4)
N1	C5	1.342(4)		C10	C11	1.489(4)
N2	C6	1.344(4)		C11	C12	1.380(4)
N2	C10	1.347(4)		C12	C15	1.376(5)
N3	C11	1.346(4)		C13	C14	1.376(5)
N3	C13	1.334(4)		C14	C15	1.381(5)
C1	C2	1.375(5)		C16	C17	1.202(4)
C2	C3	1.385(5)		C17	C18	1.434(4)
C3	C4	1.371(5)		C18	C19	1.399(4)
C4	C5	1.392(4)		C18	C23	1.390(4)
C5	C6	1.484(4)		C19	C20	1.375(5)
C6	C7	1.391(4)		C20	C21	1.397(4)
C7	C8	1.396(4)		C21	C22	1.388(4)
C8	C9	1.391(4)		C21	C24	1.497(5)
C8	C16	1.433(4)		C22	C23	1.390(5)

Table S2.3 Bond Angles for **L^3**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C5	N1	C1	117.2(3)		C9	C10	C11	121.8(3)
C6	N2	C10	118.1(3)		N3	C11	C10	116.1(3)
C13	N3	C11	117.2(3)		N3	C11	C12	122.2(3)
N1	C1	C2	124.0(3)		C12	C11	C10	121.8(3)
C1	C2	C3	117.7(3)		C15	C12	C11	119.7(3)
C4	C3	C2	119.6(3)		N3	C13	C14	124.1(4)
C3	C4	C5	119.0(3)		C13	C14	C15	118.2(3)
N1	C5	C4	122.3(3)		C12	C15	C14	118.6(3)
N1	C5	C6	116.3(3)		C17	C16	C8	176.6(3)
C4	C5	C6	121.3(3)		C16	C17	C18	177.0(3)
N2	C6	C5	115.4(3)		C19	C18	C17	120.5(3)
N2	C6	C7	123.0(3)		C23	C18	C17	121.3(3)
C7	C6	C5	121.6(3)		C23	C18	C19	118.2(3)
C6	C7	C8	118.7(3)		C20	C19	C18	120.6(3)
C7	C8	C16	121.5(3)		C19	C20	C21	121.6(3)
C9	C8	C7	118.3(3)		C20	C21	C24	120.0(3)
C9	C8	C16	120.2(3)		C22	C21	C20	117.8(3)
C10	C9	C8	119.4(3)		C22	C21	C24	122.3(3)
N2	C10	C9	122.5(3)		C21	C22	C23	121.0(3)
N2	C10	C11	115.7(3)		C18	C23	C22	120.8(3)

Table S2.4 Bond Lengths for **3Cl**·CH_3CN·$C_5H_{10}O$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru1	Cl1	2.4093(10)		C4A	C5A	1.386(6)
Ru1	N1	2.073(3)		C5A	C6A	1.471(6)
Ru1	N2	1.963(3)		C6A	C7A	1.387(5)
Ru1	N3	2.066(3)		C7A	C8A	1.402(6)
Ru1	N4	2.035(3)		C8A	C9A	1.406(6)
Ru1	N5	2.082(3)		C8A	C16A	1.432(6)
N1	C1	1.336(5)		C9A	C10A	1.379(5)
N1	C5	1.368(5)		C10A	C11A	1.480(5)
N2	C6	1.354(5)		C11A	C12A	1.380(6)
N2	C10	1.354(5)		C12A	C13A	1.385(6)
N3	C11	1.372(5)		C13A	C14A	1.375(7)
N3	C15	1.338(5)		C14A	C15A	1.375(6)
N4	C25	1.346(5)		C16A	C17A	1.197(6)
N4	C29	1.366(5)		C17A	C18A	1.436(6)
N5	C30	1.354(5)		C18A	C19A	1.395(7)
N5	C34	1.345(5)		C18A	C23A	1.401(6)
C1	C2	1.384(6)		C19A	C20A	1.391(6)
C2	C3	1.379(6)		C20A	C21A	1.386(8)
C3	C4	1.381(6)		C21A	C22A	1.394(7)
C4	C5	1.390(6)		C21A	C24A	1.516(6)
C5	C6	1.474(6)		C22A	C23A	1.385(6)
C6	C7	1.388(5)		C25A	C26A	1.379(6)
C7	C8	1.406(6)		C26A	C27A	1.385(7)
C8	C9	1.401(6)		C27A	C28A	1.377(7)
C8	C16	1.435(6)		C28A	C29A	1.396(6)
C9	C10	1.385(5)		C29A	C30A	1.467(6)
C10	C11	1.480(6)		C30A	C31A	1.393(6)
C11	C12	1.387(6)		C31A	C32A	1.383(7)
C12	C13	1.380(6)		C32A	C33A	1.381(7)
C13	C14	1.376(7)		C33A	C34A	1.381(6)
C14	C15	1.391(6)		P1A	F1	1.703(5)
C16	C17	1.197(6)		P1A	F2B	1.834(6)
C17	C18	1.432(6)		P1A	F3A	1.553(6)
C18	C19	1.406(6)		P1A	F4A	1.389(6)
C18	C23	1.388(6)		P1A	F5B	1.649(6)
C19	C20	1.389(6)		P1A	F6B	1.535(8)
C20	C21	1.395(7)		P1B	F1	1.527(4)
C21	C22	1.384(7)		P1B	F2A	1.570(4)
C21	C24	1.511(6)		P1B	F3B	1.630(4)
C22	C23	1.391(6)		P1B	F4B	1.632(4)
C25	C26	1.372(6)		P1B	F5A	1.580(4)
C26	C27	1.388(6)		P1B	F6A	1.633(7)
C27	C28	1.384(7)		P2	F7	1.605(3)
C28	C29	1.387(6)		P2	F8A	1.613(4)
C29	C30	1.460(6)		P2	F8B	1.598(4)

Table S2.4 continued Bond Lengths for **3Cl**·CH_3CN·$C_5H_{10}O$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
C30	C31	1.392(6)		P2	F9A	1.609(4)
C31	C32	1.383(7)		P2	F9B	1.592(4)
C32	C33	1.374(7)		P2	F10A	1.583(4)
C33	C34	1.376(6)		P2	F10B	1.614(4)
Ru1A	Cl1A	2.4089(11)		P2	F11A	1.617(4)
Ru1A	N1A	2.065(3)		P2	F11B	1.588(4)
Ru1A	N2A	1.949(3)		P2	F12	1.576(3)
Ru1A	N3A	2.067(3)		O1	C5S	1.358(10)
Ru1A	N4A	2.039(3)		O1	C7S	1.437(13)
Ru1A	N5A	2.075(3)		O2	C11S	1.398(10)
N1A	C1A	1.339(5)		O2	C9S	1.366(8)
N1A	C5A	1.374(5)		C6S	C5S	1.480(13)
N2A	C6A	1.352(5)		C7S	C8S	1.599(16)
N2A	C10A	1.351(5)		C10S	C9S	1.459(10)
N3A	C11A	1.372(5)		C11S	C12S	1.619(14)
N3A	C15A	1.337(5)		N1SB	C1SB	1.15(2)
N4A	C25A	1.356(5)		C1SB	C2SB	1.35(3)
N4A	C29A	1.362(5)		N2S	C3S	1.124(15)
N5A	C30A	1.364(6)		C4S	C3S	1.468(17)
N5A	C34A	1.351(6)		N3S	C3SA	1.125(14)
C1A	C2A	1.379(6)		C4SA	C3SA	1.378(14)
C2A	C3A	1.384(7)		C2SA	C1SA	1.462(16)
C3A	C4A	1.388(6)		N1SA	C1SA	1.162(18)

Table S2.5 Bond Angles for **3Cl**·CH_3CN·$C_5H_{10}O$.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ru1	Cl1	90.00(9)		C9A	C8A	C16A	121.5(4)
N1	Ru1	N5	101.75(13)		C10A	C9A	C8A	118.8(4)
N2	Ru1	Cl1	87.52(10)		N2A	C10A	C9A	121.1(4)
N2	Ru1	N1	79.68(13)		N2A	C10A	C11A	112.3(3)
N2	Ru1	N3	79.92(13)		C9A	C10A	C11A	126.6(4)
N2	Ru1	N4	99.65(13)		N3A	C11A	C10A	115.1(4)
N2	Ru1	N5	177.75(13)		N3A	C11A	C12A	121.3(4)
N3	Ru1	Cl1	90.41(9)		C12A	C11A	C10A	123.6(4)
N3	Ru1	N1	159.55(13)		C11A	C12A	C13A	119.0(4)
N3	Ru1	N5	98.61(13)		C14A	C13A	C12A	119.6(4)
N4	Ru1	Cl1	172.69(10)		C13A	C14A	C15A	119.1(4)
N4	Ru1	N1	89.89(13)		N3A	C15A	C14A	122.6(4)
N4	Ru1	N3	92.24(13)		C17A	C16A	C8A	174.8(5)
N4	Ru1	N5	78.67(13)		C16A	C17A	C18A	175.6(5)
N5	Ru1	Cl1	94.20(10)		C19A	C18A	C17A	120.8(4)
C1	N1	Ru1	127.9(3)		C19A	C18A	C23A	118.7(4)
C1	N1	C5	118.9(4)		C23A	C18A	C17A	120.4(4)
C5	N1	Ru1	113.3(3)		C20A	C19A	C18A	120.8(5)
C6	N2	Ru1	118.7(3)		C21A	C20A	C19A	120.4(5)
C10	N2	Ru1	118.5(3)		C20A	C21A	C22A	118.8(4)
C10	N2	C6	122.4(3)		C20A	C21A	C24A	120.9(5)
C11	N3	Ru1	113.4(3)		C22A	C21A	C24A	120.3(5)
C15	N3	Ru1	128.1(3)		C23A	C22A	C21A	121.4(5)
C15	N3	C11	118.6(4)		C22A	C23A	C18A	119.9(4)
C25	N4	Ru1	124.8(3)		N4A	C25A	C26A	122.4(4)
C25	N4	C29	118.9(4)		C25A	C26A	C27A	119.0(4)
C29	N4	Ru1	116.2(3)		C28A	C27A	C26A	119.3(4)
C30	N5	Ru1	115.1(3)		C27A	C28A	C29A	119.7(4)
C34	N5	Ru1	126.1(3)		N4A	C29A	C28A	120.9(4)
C34	N5	C30	118.8(4)		N4A	C29A	C30A	114.8(4)
N1	C1	C2	122.6(4)		C28A	C29A	C30A	124.3(4)
C3	C2	C1	118.8(4)		N5A	C30A	C29A	114.5(3)
C2	C3	C4	119.4(4)		N5A	C30A	C31A	121.4(4)
C3	C4	C5	119.5(4)		C31A	C30A	C29A	124.1(4)
N1	C5	C4	120.8(4)		C32A	C31A	C30A	119.3(5)
N1	C5	C6	115.1(3)		C33A	C32A	C31A	119.7(4)
C4	C5	C6	124.1(4)		C32A	C33A	C34A	118.4(5)
N2	C6	C5	113.0(3)		N5A	C34A	C33A	123.3(4)
N2	C6	C7	120.0(4)		F1	P1A	F2B	74.9(3)
C7	C6	C5	126.9(4)		F3A	P1A	F1	85.8(4)
C6	C7	C8	118.9(4)		F3A	P1A	F2B	84.6(5)
C7	C8	C16	119.7(4)		F3A	P1A	F5B	167.5(5)
C9	C8	C7	119.4(4)		F4A	P1A	F1	97.5(4)
C9	C8	C16	120.8(4)		F4A	P1A	F2B	171.4(6)
C10	C9	C8	119.5(4)		F4A	P1A	F3A	99.3(6)

Table S2.5 continued Bond Angles for **3Cl**·CH_3CN·$C_5H_{10}O$.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N2	C10	C9	119.7(4)		F4A	P1A	F5B	92.1(5)
N2	C10	C11	113.1(3)		F4A	P1A	F6B	80.6(5)
C9	C10	C11	127.2(4)		F5B	P1A	F1	87.5(3)
N3	C11	C10	114.8(3)		F5B	P1A	F2B	83.4(4)
N3	C11	C12	120.9(4)		F6B	P1A	F1	178.1(4)
C12	C11	C10	124.2(4)		F6B	P1A	F2B	106.9(5)
C13	C12	C11	119.8(4)		F6B	P1A	F3A	94.7(5)
C14	C13	C12	119.2(4)		F6B	P1A	F5B	92.2(4)
C13	C14	C15	119.0(4)		F1	P1B	F2A	101.6(3)
N3	C15	C14	122.5(4)		F1	P1B	F3B	88.0(3)
C17	C16	C8	175.0(5)		F1	P1B	F4B	83.9(3)
C16	C17	C18	179.2(5)		F1	P1B	F5A	94.8(3)
C19	C18	C17	120.6(4)		F1	P1B	F6A	175.6(3)
C23	C18	C17	120.7(4)		F2A	P1B	F3B	88.5(4)
C23	C18	C19	118.7(4)		F2A	P1B	F4B	169.9(5)
C20	C19	C18	119.9(4)		F2A	P1B	F5A	98.5(4)
C19	C20	C21	121.2(4)		F2A	P1B	F6A	75.0(4)
C20	C21	C24	120.5(5)		F3B	P1B	F4B	83.3(4)
C22	C21	C20	118.4(4)		F3B	P1B	F6A	94.7(4)
C22	C21	C24	121.1(5)		F4B	P1B	F6A	99.9(4)
C21	C22	C23	121.1(4)		F5A	P1B	F3B	171.8(5)
C18	C23	C22	120.6(4)		F5A	P1B	F4B	89.4(4)
N4	C25	C26	122.5(4)		F5A	P1B	F6A	83.0(4)
C25	C26	C27	119.3(4)		P1B	F1	P1A	7.99(18)
C28	C27	C26	118.5(4)		F7	P2	F8A	85.9(3)
C27	C28	C29	120.2(4)		F7	P2	F9A	86.8(4)
N4	C29	C28	120.5(4)		F7	P2	F10B	86.4(3)
N4	C29	C30	114.9(4)		F7	P2	F11A	89.3(3)
C28	C29	C30	124.6(4)		F8A	P2	F10B	156.2(5)
N5	C30	C29	115.0(3)		F8A	P2	F11A	83.9(4)
N5	C30	C31	120.8(4)		F8B	P2	F7	92.0(5)
C31	C30	C29	124.1(4)		F8B	P2	F8A	14.3(5)
C32	C31	C30	119.7(4)		F8B	P2	F9A	89.0(5)
C33	C32	C31	118.9(4)		F8B	P2	F10B	170.3(5)
C32	C33	C34	119.3(4)		F8B	P2	F11A	71.0(5)
N5	C34	C33	122.5(4)		F9A	P2	F8A	75.7(5)
N1A	Ru1A	Cl1A	91.60(9)		F9A	P2	F10B	81.4(5)
N1A	Ru1A	N3A	159.75(13)		F9A	P2	F11A	159.5(5)
N1A	Ru1A	N5A	101.36(13)		F9B	P2	F7	92.3(4)
N2A	Ru1A	Cl1A	90.02(10)		F9B	P2	F8A	90.0(5)
N2A	Ru1A	N1A	79.98(13)		F9B	P2	F8B	102.7(6)
N2A	Ru1A	N3A	79.78(13)		F9B	P2	F9A	14.9(5)
N2A	Ru1A	N4A	96.68(14)		F9B	P2	F10B	67.9(5)
N2A	Ru1A	N5A	174.99(14)		F9B	P2	F11A	173.6(5)
N3A	Ru1A	Cl1A	87.74(10)		F10A	P2	F7	92.3(3)

Table S2.5 continued Bond Angles for **3Cl**·CH_3CN·$C_5H_{10}O$.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N3A	Ru1A	N5A	98.87(13)		F10A	P2	F8A	173.7(4)
N4A	Ru1A	Cl1A	173.27(10)		F10A	P2	F8B	160.6(5)
N4A	Ru1A	N1A	90.21(13)		F10A	P2	F9A	110.2(5)
N4A	Ru1A	N3A	92.80(13)		F10A	P2	F9B	96.1(5)
N4A	Ru1A	N5A	78.52(14)		F10A	P2	F10B	29.1(3)
N5A	Ru1A	Cl1A	94.76(10)		F10A	P2	F11A	90.1(4)
C1A	N1A	Ru1A	128.5(3)		F10A	P2	F11B	65.6(5)
C1A	N1A	C5A	118.5(3)		F10B	P2	F11A	118.5(4)
C5A	N1A	Ru1A	113.0(3)		F11B	P2	F7	87.4(4)
C6A	N2A	Ru1A	119.0(3)		F11B	P2	F8A	108.3(5)
C10A	N2A	Ru1A	119.6(3)		F11B	P2	F8B	95.7(6)
C10A	N2A	C6A	121.5(3)		F11B	P2	F9A	172.7(5)
C11A	N3A	Ru1A	113.1(3)		F11B	P2	F9B	161.6(6)
C15A	N3A	Ru1A	128.3(3)		F11B	P2	F10B	93.8(5)
C15A	N3A	C11A	118.5(4)		F11B	P2	F11A	24.7(4)
C25A	N4A	Ru1A	124.9(3)		F12	P2	F7	177.4(2)
C25A	N4A	C29A	118.6(4)		F12	P2	F8A	91.9(3)
C29A	N4A	Ru1A	116.5(3)		F12	P2	F8B	86.1(5)
C30A	N5A	Ru1A	115.3(3)		F12	P2	F9A	91.4(4)
C34A	N5A	Ru1A	126.8(3)		F12	P2	F9B	86.5(4)
C34A	N5A	C30A	117.9(4)		F12	P2	F10A	90.1(3)
N1A	C1A	C2A	122.5(4)		F12	P2	F10B	95.2(3)
C1A	C2A	C3A	119.6(4)		F12	P2	F11A	91.7(3)
C2A	C3A	C4A	118.5(4)		F12	P2	F11B	94.5(4)
C5A	C4A	C3A	119.8(4)		C5S	O1	C7S	115.2(9)
N1A	C5A	C4A	121.0(4)		C9S	O2	C11S	118.5(7)
N1A	C5A	C6A	115.1(3)		O1	C5S	C6S	114.4(9)
C4A	C5A	C6A	123.9(4)		O1	C7S	C8S	100.6(10)
N2A	C6A	C5A	113.0(3)		O2	C11S	C12S	110.8(7)
N2A	C6A	C7A	120.1(4)		O2	C9S	C10S	111.6(6)
C7A	C6A	C5A	126.9(3)		N1SB	C1SB	C2SB	171(2)
C6A	C7A	C8A	119.5(4)		N2S	C3S	C4S	176.4(15)
C7A	C8A	C9A	119.2(4)		N3S	C3SA	C4SA	175.3(14)
C7A	C8A	C16A	119.4(4)		N1SA	C1SA	C2SA	174.7(12)

Table S2.6 Selected Bond Lengths for **4Cl**·2CH_3CN**.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ru1	Cl1	2.3927(8)		C8	C16	1.424(4)
Ru1	N1	2.071(3)		C9	C10	1.381(4)
Ru1	N2	1.950(3)		C10	C11	1.468(4)
Ru1	N3	2.060(3)		C11	C12	1.386(5)
Ru1	N4	2.088(3)		C12	C13	1.368(5)
Ru1	N5	2.027(3)		C13	C14	1.378(5)
O1	N6	1.225(4)		C14	C15	1.379(5)
O2	N6	1.220(4)		C16	C17	1.201(5)
N1	C1	1.344(4)		C17	C18	1.432(4)
N1	C5	1.368(4)		C18	C19	1.399(5)
N2	C6	1.350(4)		C18	C23	1.392(5)
N2	C10	1.355(4)		C19	C20	1.383(5)
N3	C11	1.374(4)		C20	C21	1.384(5)
N3	C15	1.338(4)		C21	C22	1.367(5)
N4	C24	1.349(4)		C22	C23	1.386(5)
N4	C28	1.367(4)		C24	C25	1.381(5)
N5	C29	1.360(4)		C25	C26	1.376(5)
N5	C33	1.354(4)		C26	C27	1.385(5)
N6	C21	1.467(4)		C27	C28	1.377(5)
C1	C2	1.375(5)		C28	C29	1.478(4)
C2	C3	1.372(5)		C29	C30	1.381(4)
C3	C4	1.386(5)		C30	C31	1.382(5)
C4	C5	1.382(4)		C31	C32	1.383(5)
C5	C6	1.474(4)		C32	C33	1.372(5)
C6	C7	1.383(4)		N8	C3S	1.132(5)
C7	C8	1.407(5)		C3S	C4S	1.456(6)
C8	C9	1.393(5)				

Table S2.7 Selected Bond Angles for **4Cl**·2CH_3CN.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ru1	Cl1	89.27(7)		C6	C7	C8	118.7(3)
N1	Ru1	N4	100.87(10)		C7	C8	C16	120.3(3)
N2	Ru1	Cl1	88.06(7)		C9	C8	C7	119.7(3)
N2	Ru1	N1	79.41(10)		C9	C8	C16	119.9(3)
N2	Ru1	N3	80.28(11)		C10	C9	C8	119.2(3)
N2	Ru1	N4	176.02(11)		N2	C10	C9	120.0(3)
N2	Ru1	N5	97.58(10)		N2	C10	C11	113.3(3)
N3	Ru1	Cl1	89.37(7)		C9	C10	C11	126.7(3)
N3	Ru1	N1	159.68(10)		N3	C11	C10	115.1(3)
N3	Ru1	N4	99.44(10)		N3	C11	C12	121.2(3)
N4	Ru1	Cl1	95.91(7)		C12	C11	C10	123.8(3)
N5	Ru1	Cl1	174.36(8)		C13	C12	C11	119.6(3)
N5	Ru1	N1	92.02(10)		C12	C13	C14	119.5(3)
N5	Ru1	N3	91.31(10)		C13	C14	C15	118.8(3)
N5	Ru1	N4	78.45(10)		N3	C15	C14	123.0(3)
C1	N1	Ru1	128.5(2)		C17	C16	C8	177.8(4)
C1	N1	C5	117.9(3)		C16	C17	C18	178.5(4)
C5	N1	Ru1	113.6(2)		C19	C18	C17	119.6(3)
C6	N2	Ru1	119.4(2)		C23	C18	C17	120.1(3)
C6	N2	C10	122.1(3)		C23	C18	C19	120.4(3)
C10	N2	Ru1	118.4(2)		C20	C19	C18	119.9(3)
C11	N3	Ru1	112.9(2)		C19	C20	C21	118.2(3)
C15	N3	Ru1	129.2(2)		C20	C21	N6	117.8(3)
C15	N3	C11	117.8(3)		C22	C21	N6	119.3(3)
C24	N4	Ru1	126.6(2)		C22	C21	C20	122.9(3)
C24	N4	C28	118.0(3)		C21	C22	C23	119.0(3)
C28	N4	Ru1	115.4(2)		C22	C23	C18	119.5(3)
C29	N5	Ru1	117.3(2)		N4	C24	C25	121.9(3)
C33	N5	Ru1	124.7(2)		C26	C25	C24	120.0(3)
C33	N5	C29	118.0(3)		C25	C26	C27	118.5(3)
O1	N6	C21	117.9(3)		C28	C27	C26	119.6(3)
O2	N6	O1	123.2(3)		N4	C28	C27	121.8(3)
O2	N6	C21	118.9(3)		N4	C28	C29	114.0(3)
N1	C1	C2	122.5(3)		C27	C28	C29	124.2(3)
C3	C2	C1	120.0(3)		N5	C29	C28	114.7(3)
C2	C3	C4	118.5(3)		N5	C29	C30	121.7(3)
C5	C4	C3	119.7(3)		C30	C29	C28	123.6(3)
N1	C5	C4	121.5(3)		C29	C30	C31	119.6(3)
N1	C5	C6	114.6(3)		C30	C31	C32	118.8(3)
C4	C5	C6	123.9(3)		C33	C32	C31	119.3(3)
N2	C6	C5	113.0(3)		N5	C33	C32	122.6(3)
N2	C6	C7	120.2(3)		N7	C1S	C2S	178.9(6)
C7	C6	C5	126.8(3)		N8	C3S	C4S	179.5(5)

S3. DFT model validation

As a means of validating the computational models both the structural and vibrational accuracy were compared to with the experimental data by measuring the mean average deviation (MAD) values of both the Raman data and X-ray crystallography data shown in Tables S3.1-2. Only the chloro-complexes (**1-4Cl**) were considered as the aqua-complexes (**1-4H_2O**) could not be obtained as a pure species.

Table S3.1 Bond length comparison

Bonds	Bond lengths (Å)					
	[**1Cl**]$^+$	[**2Cl**]$^+$	[**3Cl**]$^+$		[**4Cl**]$^+$	
	DFT	DFT	X-ray	DFT	X-ray	DFT
Ru(1)-N(1)	1.975	1.976	1.963(3)	1.975	1.950 (3)	1.971
Ru(1)-N(2)	2.085	2.086	2.073(3)	2.086	2.071 (3)	2.086
Ru(1)-N(3)	2.085	2.086	2.066(3)	2.086	2.060 (3)	2.086
Ru(1)-N(4)	2.063	2.062	2.035(3)	2.062	2.027 (3)	2.065
Ru(1)-N(5)	2.095	2.094	2.082 (3)	2.094	2.088 (3)	2.097
Ru(1)-Cl(1)	2.462	2.462	2.4093(10)	2.462	2.3927 (8)	2.459
C(16)-C(17)	1.229	1.230	1.197 (6)	1.229	1.201 (5)	1.227

Table S3.2 X-ray MAD values

Complex	X-ray MAD values (Å)
[**3Cl**]$^+$	0.024
[**4Cl**]$^+$	0.028

Table S3.3 Vibrational MAD values

Complex	Vibrational MAD values (cm^{-1})
[**1Cl**]$^+$	10.2
[**2Cl**]$^+$	11.0
[**3Cl**]$^+$	10.3
[**4Cl**]$^+$	10.0

S4 Orbital Contributions

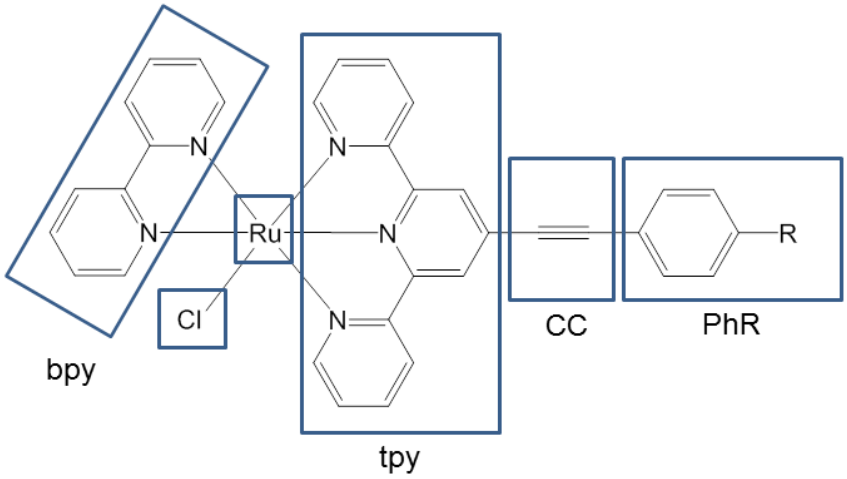

Figure S4.1 Molecular components of [**1**Cl]$^+$-[**4**Cl]$^+$, where R = H, OMe, Me, NO_2.

Table S4.1 Molecular compounds contributing to the molecular orbitals for [**1**Cl]$^+$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	Cl	bpy	tpy	CC	PhR
151	L+6	-1.43	1	0	0	85	3	10
150	L+5	-1.49	2	0	97	1	0	0
149	L+4	-1.73	1	0	72	27	0	0
148	L+3	-1.83	0	0	0	67	11	21
147	L+2	-2.46	5	0	29	65	0	0
146	L+1	-2.58	3	0	64	33	0	0
145	LUMO	-2.83	9	1	1	75	7	7
144	HOMO	-5.68	70	10	7	13	0	0
143	H-1	-5.75	61	10	3	16	5	5
142	H-2	-5.93	76	0	15	9	0	0
141	H-3	-6.77	5	9	0	14	25	47
140	H-4	-7.27	1	13	2	84	0	0

Table S4.2 Molecular compounds contributing to the molecular orbitals for [**2**Cl]$^{+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	Cl	bpy	tpy	CC	PhR
159	L+6	-1.40	6	0	26	68	0	0
158	L+5	-1.48	2	0	97	1	0	0
157	L+4	-1.73	1	0	72	27	0	0
156	L+3	-1.77	0	0	0	73	10	16
155	L+2	-2.45	5	0	25	70	0	0
154	L+1	-2.57	3	0	68	29	0	0
153	LUMO	-2.79	9	1	1	77	6	6
152	HOMO	-5.66	70	10	7	13	0	0
151	H-1	-5.68	54	8	2	14	8	13
150	H-2	-5.91	76	0	15	9	0	0
149	H-3	-6.34	12	6	1	11	13	58
148	H-4	-7.25	1	12	2	85	0	0

Table S4.3 Molecular compounds contributing to the molecular orbitals for [**3**Cl]$^{+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	Cl	bpy	tpy	CC	PhR
155	L+6	-1.41	1	0	0	84	4	11
154	L+5	-1.48	2	0	97	1	0	0
153	L+4	-1.73	1	0	72	27	0	0
152	L+3	-1.80	0	0	0	71	11	18
151	L+2	-2.45	5	0	27	68	0	0
150	L+1	-2.57	3	0	66	31	0	0
149	LUMO	-2.81	9	1	1	76	7	7
148	HOMO	-5.67	70	10	7	13	0	0
147	H-1	-5.72	59	10	3	15	6	7
146	H-2	-5.92	76	0	15	9	0	0
145	H-3	-6.60	7	7	0	13	21	52
144	H-4	-7.26	1	12	2	85	0	0

Table S4.4 Molecular compounds contributing to the molecular orbitals for [**4**Cl]$^{+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	Cl	bpy	tpy	CC	PhR
162	L+6	-1.51	2	0	97	1	0	0
161	L+5	-1.75	1	0	72	27	0	0
160	L+4	-1.82	0	0	0	68	10	21
159	L+3	-2.51	6	0	40	54	0	0
158	L+2	-2.61	2	0	54	44	0	0
157	L+1	-2.80	8	1	1	72	5	14
156	LUMO	-3.63	2	0	0	8	5	85
155	HOMO	-5.73	70	10	7	13	0	0
154	H-1	-5.85	62	11	3	17	4	3
153	H-2	-6.00	76	0	15	9	0	0
152	H-3	-7.17	2	19	1	17	28	33
151	H-4	-7.31	1	13	3	83	0	0

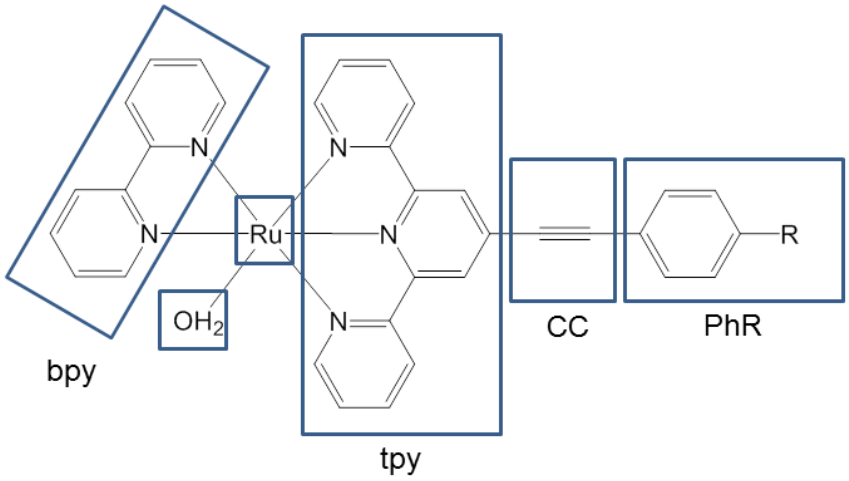

Figure S4.2 Molecular components of $[\mathbf{1}H_2O]^{2+}$-$[\mathbf{4}H_2O]^{2+}$, where R = H, OMe, Me, NO_2.

Table S4.5 Molecular compounds contributing to the molecular orbitals for $[\mathbf{1}H_2O]^{2+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	H_2O	bpy	tpy	CC	PhR
151	L+10	-0.53	1	0	0	44	5	50
150	L+9	-0.68	0	0	0	0	0	100
149	L+8	-0.88	67	19	8	6	0	0
148	L+7	-1.53	5	0	38	56	0	0
147	L+6	-1.54	1	0	0	86	4	10
146	L+5	-1.62	1	0	89	9	0	0
145	L+4	-1.82	1	0	67	31	0	0
144	L+3	-1.96	1	0	0	69	11	19
143	L+2	-2.59	5	0	35	60	0	0
142	L+1	-2.69	2	0	59	39	0	0
141	LUMO	-3.07	7	0	0	77	7	7
140	HOMO	-5.96	76	2	8	14	0	0
139	H-1	-6.15	76	0	15	9	0	0
138	H-2	-6.18	59	0	2	16	11	12
137	H-3	-6.95	20	0	1	14	20	45
136	H-4	-7.43	1	0	10	85	0	5
135	H-5	-7.44	0	0	1	4	0	95
134	H-6	-7.50	1	0	89	10	0	0
133	H-7	-8.14	0	0	0	5	86	9
132	H-8	-8.23	2	0	0	97	0	0
131	H-9	-8.59	2	0	0	31	24	42
130	H-10	-8.72	0	0	57	43	0	0

Table S4.6 Molecular compounds contributing to the molecular orbitals for $[\mathbf{2}H_2O]^{2+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	H_2O	bpy	tpy	CC	PhR
159	L+10	-0.50	68	3	3	15	1	9
158	L+9	-0.83	0	0	0	1	0	99
157	L+8	-1.05	68	18	8	6	0	0
156	L+7	-1.68	1	0	0	83	5	11
155	L+6	-1.71	5	0	46	49	0	0
154	L+5	-1.75	2	0	89	9	0	0
153	L+4	-1.99	1	0	60	39	0	0
152	L+3	-2.08	1	0	0	75	10	14
151	L+2	-2.75	5	0	35	60	0	0
150	L+1	-2.84	2	0	59	39	0	0
149	LUMO	-3.17	8	1	0	79	6	6
148	HOMO	-6.04	38	1	2	13	13	34
147	H-1	-6.24	79	0	8	12	0	0
146	H-2	-6.31	72	0	15	12	0	0
145	H-3	-6.62	38	2	1	12	6	40
144	H-4	-7.59	1	0	17	82	0	0
143	H-5	-7.65	1	0	81	16	0	1
142	H-6	-7.65	0	0	1	1	0	98
141	H-7	-8.11	3	1	0	22	33	42
140	H-8	-8.20	0	0	0	5	86	9
139	H-9	-8.40	2	0	0	97	0	0
138	H-10	-8.90	0	0	64	36	0	0

Table S4.7 Molecular compounds contributing to the molecular orbitals for [**3**H_2O]$^{2+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	H_2O	bpy	tpy	CC	PhR
155	L+10	-0.60	2	0	0	40	6	53
154	L+9	-0.75	0	0	0	0	0	100
153	L+8	-1.08	67	20	8	6	0	0
152	L+7	-1.69	1	0	0	84	5	10
151	L+6	-1.70	5	0	39	56	0	0
150	L+5	-1.80	1	0	89	10	0	0
149	L+4	-2.00	1	0	68	31	0	0
148	L+3	-2.09	1	0	0	73	10	16
147	L+2	-2.76	5	0	30	65	0	0
146	L+1	-2.86	2	0	64	34	0	0
145	LUMO	-3.23	7	0	0	78	7	7
144	HOMO	-6.13	76	2	8	14	0	0
143	H-1	-6.27	48	0	2	15	13	22
142	H-2	-6.32	76	0	15	9	0	0
141	H-3	-6.93	31	0	1	13	12	42
140	H-4	-7.50	0	0	0	0	0	100
139	H-5	-7.61	1	0	9	91	0	0
138	H-6	-7.67	1	0	91	8	0	0
137	H-7	-8.23	0	0	0	5	85	9
136	H-8	-8.40	1	0	0	93	2	4
135	H-9	-8.51	4	0	0	30	28	37
134	H-10	-8.90	0	0	57	43	0	0

Table S4.8 Molecular compounds contributing to the molecular orbitals for $[\mathbf{4}H_2O]^{2+}$.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)					
			Ru	H_2O	bpy	tpy	CC	PhR
162	L+10	-0.91	66	19	9	7	0	0
161	L+9	-1.18	0	0	0	0	0	100
160	L+8	-1.55	5	0	39	56	0	0
159	L+7	-1.55	1	0	0	82	4	13
158	L+6	-1.64	1	0	89	10	0	0
157	L+5	-1.84	1	0	67	32	0	0
156	L+4	-1.93	1	0	0	70	10	19
155	L+3	-2.64	6	0	52	43	0	0
154	L+2	-2.73	1	0	42	56	0	0
153	L+1	-3.01	6	0	0	69	4	20
152	LUMO	-3.68	2	0	0	13	6	79
151	HOMO	-6.01	76	2	8	14	0	0
150	H-1	-6.20	76	0	15	9	0	0
149	H-2	-6.31	69	0	3	16	6	5
148	H-3	-7.36	10	0	0	17	30	41
147	H-4	-7.47	0	0	21	79	0	0
146	H-5	-7.52	1	0	79	20	0	0
145	H-6	-7.98	0	0	0	0	0	100
144	H-7	-8.26	2	0	0	97	0	0
143	H-8	-8.37	0	0	0	5	80	15
142	H-9	-8.66	0	0	0	1	8	92
141	H-10	-8.74	0	0	57	42	0	0

S5. Electronic spectra assignment

On the basis that the computational models are valid the electronic spectra were assigned by calculating each of the electronic transitions associated with the MLCT band. Shown in the following tables are first ten non-zero oscillator strength.

Table S5.1. First 10 excitations of [**1**Cl]$^{+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
15469.01	646.45	0.0109	HOMO→LUMO	96	MLCT
17341.84	576.63	0.0019	H-2→LUMO	94	MLCT
18192.76	549.66	0.0063	HOMO→L+1	81	MLCT
18346.01	545.07	0.1241	H-1→LUMO HOMO→L+2	57 40	MLCT
19088.85	523.86	0.0007	H-1→L+1 H-1-→>L+2	77 18	MLCT
20246.26	493.91	0.0358	H-1→L+1 H-1→L+2	19 77	MLCT
20394.67	490.32	0.2771	H-2→L+2 H-1→LUMO HOMO→L+1 HOMO→L+2	25 19 17 32	MLCT
21137.51	473.092	0.0554	H-2→L+1 H-2→L+2	72 25	MLCT
22854.68	437.54	0.0159	H-2→L+1 H-2→L+2 HOMO→L+2	16 41 18	MLCT
26051.08	383.86	0.0707	HOMO→L+3	86	MLCT

Table S5.2. First 10 excitations of [**2**Cl]$^{+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
15652.10	638.89	0.0117	HOMO→LUMO	96	MLCT
17491.06	571.72	0.0022	H-2→LUMO	92	MLCT
18103.23	552.38	0.0050	HOMO→L+1	82	MLCT
18283.10	546.95	0.1736	H-1→LUMO HOMO→L+2	62 33	MLCT
18821.07	531.31	0.0005	H-1→L+1 H-1→L+2	77 14	MLCT
20054.30	498.64	0.0351	H-1→L+1 H-1→L+2	16 79	MLCT
20306.76	492.44	0.3216	H-2→L+2 H-1→LUMO HOMO→L+1 HOMO→L+2	22 17 16 37	MLCT
21116.54	473.56	0.0520	H-2→L+1 H-2→L+2	68 30	MLCT
22764.34	439.28	0.0194	H-2→L+1 H-2→L+2 HOMO→L+2	18 40 18	MLCT
25442.93	393.03	0.4514	H-3→LUMO	86	MLCT

Table S5.3. First 10 excitations of [**3**Cl]$^{+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
15568.22	642.33	0.0114	HOMO→LUMO	96	MLCT
17424.92	573.89	0.0020	H-2→LUMO	93	MLCT
18148.40	551.01	0.0047	HOMO→L+1	82	MLCT
18333.10	545.46	0.1413	H-1→LUMO HOMO→L+2	60 36	MLCT
18969.48	527.16	0.0006	H-1→L+1 H-1→L+2	78 16	MLCT
20176.09	495.63	0.0358	H-1→L+1 H-1→L+2	18 78	MLCT
20364.02	491.06	0.2944	H-2→L+2 H-1→LUMO HOMO→L+1 HOMO→L+2	24 18 16 34	MLCT
21128.64	473.29	0.0536	H-2→L+1 H-2→L+2	70 27	MLCT
22817.58	438.25	0.0164	H-2→L+1 H-2→L+2 HOMO→L+2	17 40 19	MLCT
26046.24	383.93	0.0434	HOMO→L+4	94	MLCT

Table S5.4. First 10 excitations of [**4**Cl]$^{+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
13345.34	749.32	0.0025	HOMO→LUMO HOMO→L+1	77 22	MLCT
15414.97	648.71	0.0001	H-2→LUMO H-2→L+1	74 25	MLCT
15802.12	632.82	0.3921	H-1→LUMO	94	MLCT
17454.76	572.90	0.0108	HOMO→LUMO HOMO→L+1	22 75	MLCT
18479.90	541.12	0.0101	HOMO→L+2 HOMO→L+3	72 22	MLCT
19087.24	523.91	0.0042	H-1→L+1 HOMO→L+2 HOMO→L+3	44 10 39	MLCT
19370.34	516.25	0.0014	H-2→LUMO H-2→L+1 H-1→L+2 H-1→L+3	20 49 18 12	MLCT
19680.06	508.12	0.0004	H-2→L+1 H-1→L+2 H-1→L+3	23 54 15	MLCT
20506.78	487.64	0.0382	H-1→L+2 H-1→L+3	26 69	MLCT
20711.65	482.81	0.1893	H-2→L+3 H-1→L+1 HOMO→L+2 HOMO→L+3	30 35 15 16	MLCT

Table S5.5. First 10 excitations of [**1**H_2O]$^{2+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
15988.43	625.45	0.0136	HOMO→LUMO	95	MLCT
17581.39	568.78	0.0028	H-1→LUMO	96	MLCT
19422.77	514.85	0.0026	HOMO→L+1 HOMO→L+2	69 24	MLCT
19827.66	504.34	0.1494	H-2→LUMO HOMO→L+2	56 31	MLCT
21466.59	465.84	0.3451	H-2→LUMO H-1→L+2 HOMO→L+1 HOMO→L+2	21 37 19 21	MLCT
21629.51	462.33	0.0001	H-2→L+1 H-2→L+2	65 27	MLCT
21993.27	454.68	0.1015	H-1→L+1 H-1→L+2	81 14	MLCT
22663.52	441.23	0.0234	H-2→L+1 H-2→L+2	29 65	MLCT
23841.91	419.42	0.0373	H-2→LUMO H-1→L+1 H-1→L+2 HOMO→L+2	13 12 39 20	MLCT
26107.54	383.03	0.0086	HOMO→L+3 HOMO→L+8 HOMO→L+11	11 48 28	MLCT

Table S5.6. First 10 excitations of [**2**H_2O]$^{2+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
17087.78	585.21	0.0074	H-1→LUMO	95	MLCT
18105.65	552.31	0.0103	H-2→LUMO	95	MLCT
19091.27	523.79	0.4255	HOMO→LUMO	79	MLCT
20179.32	495.55	0.0003	H-3→L+1 HOMO→L+1 HOMO→L+2	10 62 20	MLCT
20389.83	490.44	0.0007	H-1→L+1 H-1→L+2	57 41	MLCT
21080.25	474.37	0.0280	HOMO→L+1 HOMO→L+2	24 65	MLCT
21590.80	463.16	0.0754	H-2→L+2 H-1→L+1 H-1→L+2	21 30 42	MLCT
22213.46	450.17	0.2724	H-2→L+1	86	MLCT
23706.41	421.82	0.1316	H-3→LUMO H-2→L+2 HOMO→LUMO	31 40 12	MLCT
24746.06	404.10	0.1010	H-3→LUMO H-2→L+2	52 22	MLCT

Table S5.7. First 10 excitations of $[\mathbf{3}H_2O]^{2+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
16099.74	621.12	0.0142	HOMO→LUMO	96	MLCT
17693.50	565.17	0.0030	H-2→LUMO	96	MLCT
19366.31	516.36	0.0024	HOMO→L+1 HOMO→L+2	73 21	MLCT
19751.84	506.28	0.2133	H-1→LUMO HOMO→L+2	60 27	MLCT
21394.00	467.42	0.3890	H-2→L+2 H-1→LUMO HOMO→L+1 HOMO→L+2	31 19 19 27	MLCT
21403.68	467.20	0.0001	H-1→L+1 H-1→L+2	66 21	MLCT
22002.95	454.48	0.0843	H-2→L+1 H-2→L+2	76 20	MLCT
22453.017	445.37	0.0222	H-1→L+1 H-1→L+2	24 68	MLCT
23744.31	421.15	0.0514	H-2→L+1 H-2→L+2 H-1→LUMO HOMO→L+2	14 39 12 19	MLCT
26129.31	382.71	0.0073	HOMO→L+8 HOMO→L+11	48 29	MLCT

Table S5.8. First 10 excitations of $[\mathbf{4}H_2O]^{2+}$.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Contributions (%)		Assignment
14743.91	678.24	0.0069	HOMO→LUMO HOMO→L+1	67 30	MLCT
16344.93	611.81	0.0009	H-1→LUMO H-1→L+1	67 31	MLCT
18940.44	527.97	0.4351	H-2→LUMO	73	MLCT
19557.46	511.31	0.0112	HOMO→LUMO HOMO→L+1	31 67	MLCT
19703.45	507.52	0.0070	HOMO→L+2 HOMO→L+3	50 44	MLCT
20989.11	476.43	0.2746	H-2→LUMO H-1→L+3 HOMO→L+2 HOMO→L+3	16 14 34 28	MLCT
21072.18	474.55	0.0010	H-1→LUMO H-1→L+1	32 65	MLCT
21947.30	455.63	0.0497	H-1→L+2 H-1→L+3	78 15	MLCT
22266.70	449.10	0.0001	H-2→L+2 H-2→L+3	48 47	MLCT
22534.47	443.76	0.0528	H-2→L+1 H-1→L+2 H-1→L+3	53 13 19	MLCT

S6. Assignment of vibrational spectra

On the basis that the SDD provided a valid model of the cationic complex the assignments were made based on the calculated spectra.

Table S6.1. Assignment of RR for [**1**Cl]$^{+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
582	595	Asymm. in-plane ring bending of tpy-≡-Ph and bpy v. delocalised
663	674	symm. in-plane ring bending of tpy-≡-Ph
688	732	Symm. out-of-plane ring bending of tpy
754	751	Symm. out-of-plane ring bending of tpy and bpy
921	904	Asymm. out-of-plane ring bending of tpy
1024	1027	Symm. in-plane ring stretching of tpy
1049	1053	Symm. in-plane ring stretching of tpy
1074	1078	Symm. in-plane ring stretching of tpy
1141	1141	Asymm. in-plane ring stretching of tpy
1164	1167	Symm. in-plane ring stretching of bpy
1270	1270	Asymm. in-plane ring stretching of tpy-≡-Ph
1357	1394	Symm. in-plane ring stretching of tpy-≡-Ph
1459	1459	Asymm. bpy ring stretch and H-wag
1523	1523	Asymm. bpy ring stretch and H-wag
1562	1573	Asymm. bpy ring stretch and H-wag
1604	1590	Symm. in-plane ring stretching of tpy-≡-Ph, H-stretch

Table S6.2. Assignment of RR for [**2**Cl]$^{+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
565	595	Asymm. in-plane ring bending of tpy-≡-PhOMe and bpy v. delocalised
682	689	Symm. in-plane ring bending of tpy-≡-PhOMe
923	967	Asymm. out-of-plane ring bending of tpy
1024	1016	Symm. in-plane ring stretching of tpy
1049	1052	Symm. in-plane ring stretching of tpy
1076	1078	Symm. in-plane ring stretching of tpy
1141	1141	Asymm. in-plane ring stretching of tpy
1164	1166	Symm. in-plane ring stretching of bpy
1259	1261	Symm. in-plane ring stretching of bpy
1286	1286	Asymm. in-plane ring stretching of tpy, H-wag
1357	1395	Symm. in-plane ring stretching of tpy-≡-PhOMe,
1469	1458	Asymm. bpy ring stretch and H-wag
1523	1521	Asymm. bpy ring stretch and H-wag
1562	1573	Asymm. bpy ring stretch and H-wag
1602	1597	Symm. in-plane ring stretching of tpy-≡-PhOMe, H-stretch

Table S6.3. Assignment of RR for [**3**Cl]$^{+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
622	624	Asymm. out-of-plane ring bending of bpy and tpy-≡-PhMe, v. delocalised
661	666	Symm. in-plane ring bending of tpy-≡-PhMe
688	694	Symm. in-plane ring bending of tpy-≡-PhMe
763	785	Symm. in-plane ring bending of tpy-≡-PhMe
923	968	Symm. in-plane ring bending of tpy-≡-PhMe
1024	1016	Symm. in-plane ring stretching of tpy
1049	1052	Symm. in-plane ring stretching of tpy
1072	1078	Asymm. in-plane ring stretching of tpy
1114	1120	Symm. in-plane ring stretching of tpy-≡-PhMe
1141	1141	Asymm. in-plane ring stretching of tpy
1166	1167	Symm. in-plane ring stretching of bpy
1278	1271	Asymm. in-plane ring stretching of tpy, H-wag
1357	1395	Symm. in-plane ring stretching of tpy-≡-PhMe,
1459	1459	Asymm. bpy ring stretch and H-wag
1519	1522	Asymm. bpy ring stretch and H-wag
1558	1573	Asymm. bpy ring stretch and H-wag
1604	1596	Symm. in-plane ring stretching of tpy-≡-PhMe, H-stretch

Table S6.4. Assignment of RR for [**4**Cl]$^{+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
553	543	Symm. out-of-plane ring bending of tpy-≡-$PhNO_2$ and bpy v. delocalised
682	675	Symm. in-plane ring bending of tpy-≡-$PhNO_2$
923	968	Symm. out-of-plane ring bending of tpy
1024	1015	Symm. in-plane ring stretching of tpy
1049	1052	Symm. in-plane ring stretching of tpy
1076	1095	Asymm. in-plane ring stretching of tpy
1141	1141	Asymm. in-plane ring stretching of tpy
1166	1168	Symm. in-plane ring stretching of bpy
1257	1261	Symm. in-plane ring stretching of tpy-≡-$PhNO_2$
1274	1270	Asymm. in-plane ring stretching of tpy
1357	1339	Asymm. in-plane ring stretching of tpy
1469	1471	Symm. in-plane ring stretching of tpy-≡-$PhNO_2$
1523	1523	Asymm. bpy ring stretch and H-wag
1562	1574	Asymm. bpy ring stretch and H-wag
1604	1589	Symm. in-plane ring stretching of tpy-≡-$PhNO_2$, H-stretch

Table S6.5. Assignment of RR for [**1**H_2O]$^{2+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
538	550	Assym. Bpy and tpy-≡-Ph out-of-plane wag
584	585	Assym. H_2O wag
665	673	Symm. Ph-≡-tpy in-plane ring distortion
686	684	Symm. -Ph H-wag out-of-plane
750	747	Symm. H-wag out-of-plane bpy and tpy
902	902	Symm. H-wag out-of-plane tpy
1024	1024	Asymm. tpy and bpy in-plane ring distortion
1047	1047	Asymm. bpy in-plane ring distortion
1074	1078	Symm tpy in-plane H-wag
1139	1139	Asymm tpy in-plane H-wag
1170	1172	Symm bpy in-plane H-wag
1284	1285	Asymm tpy in-plane H-wag
1361	1344	Asymm tpy-≡-Ph in-plane H-wag
1471	1470	Symm tpy-≡-Ph in-plane H-wag
1521	1527	Symm bpy in-plane H-wag
1560	1567	Symm tpy-≡-Ph in-plane ring distortion
1602	1579	Symm. in-plane ring stretching of tpy-≡-Ph H-stretch

Table S6.6. Assignment of RR for $[\mathbf{2}H_2O]^{2+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	Assignment
667	662	Symm. in-plane ring distortion MeOPh-≡-tpy
1024	1025	Symm. in-plane H-wag MeOPh-≡-tpy
1170	1170	Symm. in-plane H-wag MeOPh-≡-tpy
1278	1278	Symm. in-plane ring distortion MeOPh-≡-tpy
1319	1311	Asymm. in-plane ring distortion MeOPh-≡-tpy
1361	1345	Asymm. in-plane ring distortion MeOPh-≡-tpy
1482	1480	Asymm. in-plane ring distortion MeOPh-≡-tpy
1552	1567	Symm. in-plane ring distortion MeOPh-≡-tpy
1600	1581	Symm. in-plane ring stretching of MeOPh-≡-tpy H-stretch

Table S6.7. Assignment of RR for $[\mathbf{3}H_2O]^{2+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	Assignment
553	550	Assym. out-of-plane ring distortion bpy and MePh-≡-tpy
682	692	Assym. in-plane ring distortion MePh-≡-tpy
794	794	Sym. out-of-plane H-wag tpy
923	908	Assym. out-of-plane H-wag tpy
1047	1047	Assym. in-plane ring distortion bpy
1141	1138	Assym. in-plane ring distortion MePh-≡-tpy
1276	1275	Sym. in-plane ring distortion MePh-≡-tpy
1359	1344	Sym. in-plane ring distortion MePh-≡-tpy
1471	1463	Sym. in-plane ring distortion of bpy
1525	1527	Sym. in-plane ring distortion of bpy
1563	1569	Sym. in-plane ring distortion MePh-≡-tpy
1604	1598	Symm. in-plane ring stretching of MePh-≡-tpy H-stretch

Table S6.8. Assignment of RR for [**4**H_2O]$^{2+}$.

ν_{RR} (cm^{-1})	ν_{calc} (cm^{-1})	**Assignment**
624	621	Symm. out-of-plane ring distortion tpy
667	674	Symm. in-plane ring distortion NO_2Ph-≡-tpy
690	674	Symm. in-plane ring distortion NO_2Ph-≡-tpy
790	790	Asymm. out-of-plan H-wag tpy
923	911	Asymm. out-of-plan H-wag tpy
1027	1024	Asymm. in-plane ring distortion NO_2Ph-≡-tpy and bpy
1049	1047	Asymm. in-plane ring distortion bpy
1143	1138	Asymm. in-plane ring distortion NO_2Ph-≡-tpy
1288	1285	Asymm. out-of-plan H-wag NO_2Ph-≡-tpy
1359	1342	Asymm. in-plane ring distortion NO_2Ph-≡-tpy
1471	1470	Symm. in-plane ring distortion NO_2Ph-≡-tpy
1525	1527	Asymm. in-plane ring distortion bpy
1594	1586	Symm. in-plane ring distortion NO_2Ph-≡-tpy
1608	1601	Symm. in-plane ring stretching of NO_2Ph-≡-tpy H-stretch