Appendix E: Chapter 6 Supplementary

E.1 Instrumentation

E.1.1 UV/Visible spectroscopy

UV-Visible absorbance spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. Small molecule complexes were recorded in acetonitrile at 10^{-5} M and the polymeric analogues were recorded in chloroform at 10^{-5} M.

E.1.2 Vibrational spectroscopy

All ground state vibrational measurements were taken using KBr disks on a Nicolet 5700 FT-IR spectrometer. Continuous wave excitation was used for all Raman measurements. A Modu-laser Stellar-Pro argon laser provided 6–8 mW of 488 and 514 nm excitation at the sample. Raman and Rayleigh scattering light was collected from the cell using a 180° backscattering geometry. Rayleigh scattering was rejected using Raman edge filters from Iridian Technologies. The scattered photons were focused onto the entrance slit (110 µm) of an Acton Spectra Pro® 2550i, 0.500 m imaging single stage monochromator/spectrograph and detected with a Roper Scientific Spec-10:100B CCD detector, controlled by WinSpec software. The detector was liquid nitrogen cooled to –110°C. Raman scattering was dispersed with a 1200 g/mm holographic diffraction grating.

E.1.3 Electrochemistry

Cyclic voltammetry was obtained using a glassy carbon working electrode, Pt counter electrode and Ag/AgCl reference electrode, $\nu = 0.1$ V s^{-1} on a BAS 100B Electrochemical Workstation (Bioanalytical System Inc). Complexes were recorded in acetonitrile, 0.1 M $TBAPF_6$ at 10^{-3} M.

E.2 Computational

E.2.1 Accuracy of DFT models

Table E.2.1.1 Mean difference in bond length between crystallographic data and DFT models.

Complex	Mean difference in bond length (Å)
$[Ru(L^1)_2](PF_6)_2$	0.073
$[Ru(L^1)(Terpy)](PF_6)_2$	0.016
$[Ru(L^1)(PhTerpy)](PF_6)_2$	0.026
$[Ru(L^2)_2](PF_6)_2$	0.027
$[Ru(L^3)(Terpy)](PF_6)_2$	0.027
$[Ru(L^3)(PhTerpy)](PF_6)_2$	0.039
$[Ru(L^1)(bbp)](PF_6)_2$	0.027
$[Ru(L^1)(bpp)](PF_6)_2$	0.040

Table E.2.1.2 MAD values for each DFT model.

Complex	**MAD values (cm^{-1})**
$[Ru(L^1)_2](PF_6)_2$	6.17
$[Ru(L^1)(Terpy)](PF_6)_2$	4.84
$[Ru(L^1)(PhTerpy)](PF_6)_2$	5.81
$[Ru(L^2)_2](PF_6)_2$	3.96
$[Ru(L^2)(Terpy)](PF_6)_2$	4.19
$[Ru(L^2)(PhTerpy)](PF_6)_2$	3.63
$[Ru(L^3)(Terpy)](PF_6)_2$	5.62
$[Ru(L^3)(PhTerpy)](PF_6)_2$	3.57
$[Ru(L^1)(bbp)](PF_6)_2$	3.08
$[Ru(L^2)(bbp)](PF_6)_2$	3.43
$[Ru(L^4)(Terpy)](PF_6)_2$	6.96
$[Ru(L^4)(PhTerpy)](PF_6)_2$	3.60
$[Ru(L^1)(bpp)](PF_6)_2$	6.21
$[Ru(L^2)(bpp)](PF_6)_2$	4.12

E.3 Assignment of the Electronic Spectra

Table E.3.1 First 10 excitations of $[Ru(L^1)_2]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
539	2.3675	0.0089	HOMO → LUMO	0.69	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO	0.13	Ru → OTerpy(L^1)	
523	2.3675	0.0025	HOMO-2 → LUMO+1	0.15	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO	0.66	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.17	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+3	-0.10	Ru → OTerpy(L^1)	
505	2.4526	0.0155	HOMO → LUMO+1	0.60	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	-0.26	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO	0.50	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.19	Ru → OTerpy(L^1)	
480	2.5809	0.0575	HOMO → LUMO+1	0.10	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	0.35	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.20	Ru → OTerpy(L^1)	

Table E.3.1 Continued First 10 excitations of $[Ru(L^1)_2]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	0.11	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.48	Ru → OTerpy(L^1)	
467	2.6547	0.0221	HOMO → LUMO+1	-0.13	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	0.12	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.44	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO	-0.18	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	-0.25	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	-0.37	Ru → OTerpy(L^1)	
458	2.7075	0.0610	HOMO-1 → LUMO+3	-0.13	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+1	0.18	Ru → OTerpy(L^1)	
			HOMO → LUMO+2	0.42	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.13	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO+1	0.27	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO+2	0.58	Ru → OTerpy(L^1)	
451	2.7447	0.0415	HOMO-2 → LUMO+3	0.16	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+2	-0.16	Ru → OTerpy(L^1)	

Table E.3.1 Continued First 10 excitations of $[Ru(L^1)_2]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
449	2.7608	0.1617	HOMO-2 → LUMO	-0.17	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+2	0.17	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO+3	0.10	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.37	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+3	0.38	Ru → OTerpy(L^1)	
			HOMO → LUMO+1	0.22	Ru → OTerpy(L^1)	
			HOMO → LUMO+2	0.26	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.10	Ru → OTerpy(L^1)	
445	2.7817	0.0819	HOMO-2 → LUMO	0.12	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+3	-0.13	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	-0.36	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+3	0.53	Ru → OTerpy(L^1)	
			HOMO → LUMO+2	-0.13	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.12	Ru → OTerpy(L^1)	
444	2.7916	0.0182	HOMO-2 → LUMO+2	-0.21	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+3	0.64	Ru → OTerpy(L^1)	

Table E.3.2 First 10 excitations of $[Ru(L^1)(Terpy)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
539	2.29	0.01070	HOMO → LUMO	0.68	Ru → OTerpy(L^1)	MLCT
511	2.42	0.01032	HOMO → LUMO+1	0.63	Ru → Terpy	MLCT
			HOMO → LUMO+2	-0.24	Ru → OTerpy(L^1) and Terpy	
477	2.59	0.03000	HOMO-2 → LUMO	0.24	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+1	0.10	Ru → Terpy	
			HOMO-1 → LUMO	0.43	Ru → OTerpy(L^1)	
			HOMO → LUMO+1	-0.14	Ru → Terpy	
			HOMO → LUMO+2	-0.43	Ru → OTerpy(L^1) + Terpy	
			HOMO → LUMO+3	-0.11	Ru → Terpy	
458	2.70	0.0632	HOMO-2 → LUMO+1	0.49	Ru → Terpy	MLCT
			HOMO-1 → LUMO+1	-0.26	Ru → Terpy	
			HOMO → LUMO+1	0.13	Ru → Terpy	
			HOMO → LUMO+2	0.11	Ru → OTerpy(L^1) + Terpy	
			HOMO → LUMO+3	0.35	Ru → Terpy	

Table E.3.2 Continued First 10 excitations of $[Ru(L^1)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-1 → LUMO+1	0.21	Ru → Terpy	
			HOMO-1 → LUMO+2	0.61	Ru → OTerpy(L^1) + Terpy	MLCT
447	2.77	0.0261	HOMO-1 → LUMO+3	0.14	Ru → Terpy	
			HOMO → LUMO+3	0.13	Ru → Terpy	
			HOMO-2 → LUMO+1	0.16	Ru → Terpy	
			HOMO-2 → LUMO+2	0.58	Ru → OTerpy(L^1) + Terpy	
			HOMO-2 → LUMO+3	0.13	Ru → Terpy	
446	2.77	0.0182	HOMO-1 → LUMO+2	0.11	Ru → OTerpy(L^1) + Terpy	MLCT
			HOMO → LUMO+2	0.15	Ru → OTerpy(L^1) + Terpy	
			HOMO → LUMO+3	-0.15	Ru → Terpy	
			HOMO-2 → LUMO	0.14	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO+2	-0.26	Ru → OTerpy(L^1) + Terpy	
			HOMO-1 → LUMO	0.25	Ru → OTerpy(L^1)	MLCT
442	2.80	0.1679	HOMO → LUMO+1	0.19	Ru → Terpy	
			HOMO → LUMO+2	0.40	Ru → OTerpy(L^1) + Terpy	
			HOMO → LUMO+3	-0.30	Ru → Terpy	

Table E.3.2 Continued First 10 excitations of $[Ru(L^1)(Terpy)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+3	-0.26	Ru → Terpy	
426	2.91	0.0375	HOMO-1 → LUMO+2	-0.13	Ru → OTerpy(L^1) + Terpy	MLCT
			HOMO-1 → LUMO+3	0.61	Ru → Terpy	
			HOMO-2 → LUMO+2	0.14	Ru → OTerpy(L^1) + Terpy	
425	2.91	0.0213	HOMO-2 → LUMO+3	0.60	Ru → Terpy	MLCT
			HOMO-1 → LUMO+3	0.29	Ru → Terpy	
			HOMO-2 → LUMO	0.12	Ru → OTerpy(L^1)	
			HOMO-2 → LUMO+1	-0.24	Ru → Terpy	
			HOMO-2 → LUMO+2	0.12	Ru → OTerpy(L^1) + Terpy	
			HOMO-1 → LUMO	0.21	Ru → OTerpy(L^1)	
388	3.19	0.0024	HOMO-1 → LUMO+1	0.13	Ru → Terpy	MLCT
			HOMO → LUMO+2	0.13	Ru → OTerpy(L^1) + Terpy	
			HOMO → LUMO+3	0.41	Ru → Terpy	
			HOMO → LUMO+8	-0.24	Ru → OTerpy(L^1) + Phosphazene	

Table E.3.3 First 10 excitations of $[Ru(L^1)(PhTerpy)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
539	2.29	0.0085	HOMO → LUMO	0.68	Ru → OTerpy(L^1)	MLCT
525	2.35	0.0030	HOMO-2 → LUMO+1	-0.16	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO	0.66	Ru → OTerpy(L^1)	
515	2.40	0.0146	HOMO-1 → LUMO+1	-0.37	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+2	-0.10	Ru → OTerpy(L^1)	
			HOMO → LUMO+1	0.55	Ru → PhTerpy	
479	2.58	0.1076	HOMO-2 → LUMO	0.49	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+1	-0.25	Ru → PhTerpy	
			HOMO-1 → LUMO+2	0.12	Ru → OTerpy(L^1)	
			HOMO → LUMO+2	-0.38	Ru → OTerpy(L^1)	
468	2.64	0.1131	HOMO-1 → LUMO+1	0.42	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+3	-0.14	Ru → PhTerpy	
			HOMO → LUMO+1	0.32	Ru → PhTerpy	
			HOMO → LUMO+2	-0.29	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.28	Ru → PhTerpy	

Table E.3.3 Continued First 10 excitations of $[Ru(L^1)(PhTerpy)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-1 → LUMO+2	0.56	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+3	-0.20	Ru → PhTerpy	
456	2.71	0.0060	HOMO → LUMO+2	0.30	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+3	0.12	Ru → PhTerpy	
			HOMO-2 → LUMO+1	-0.13	Ru → PhTerpy	
448	2.76	0.0430	HOMO-2 → LUMO+2	0.65	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+3	-0.14	Ru → PhTerpy	
			HOMO-2 → LUMO	0.23	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	-0.27	Ru → OTerpy(L^1)	
444	2.78	0.1615	HOMO → LUMO+1	-0.11	Ru → PhTerpy	MLCT
			HOMO → LUMO+2	-0.32	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.45	Ru → PhTerpy	

Table E.3.3 Continued First 10 excitations of $[Ru(L^1)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	-0.15	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.24	Ru → OTerpy(L^1)	
436	2.83	0.0936	HOMO-1 → LUMO+3	0.56	Ru → PhTerpy	MLCT
			HOMO → LUMO+2	-0.10	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.22	Ru → PhTerpy	
			HOMO-2 → LUMO	-0.27	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	-0.23	Ru → PhTerpy	
			HOMO-1 → LUMO+3	-0.28	Ru → PhTerpy	
			HOMO-1 →LUMO+8	0.14	Ru → OTerpy(L^1) + PhTerpy	MLCT
391	3.16	0.0088	HOMO → LUMO+1	-0.12	Ru → PhTerpy	
			HOMO → LUMO+2	-0.16	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.32	Ru → PhTerpy	
			HOMO → LUMO+8	-0.19	Ru → OTerpy(L^1) + PhTerpy	

Table E.3.4 First 10 excitations of $[Ru(L^2)_2]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
528	2.34	0.0122	HOMO-2 → LUMO	0.68	Ru → OPhTerpy(L^2)	MLCT
518	2.39	0.0131	HOMO-2 → LUMO+1	0.68	Ru → OPhTerpy(L^2)	MLCT
490	2.53	0.5243	HOMO-2 → LUMO+2	-0.19	Ru → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO	0.48	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+1	0.43	Ru → OPhTerpy(L^2)	
468	2.70	0.0200	HOMO-2 → LUMO+2	0.19	Ru → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	0.43	Ru → OPhTerpy(L^2)	
			HOMO-2 → LUMO+9	-0.11	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO	-0.29	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+1	0.39	Ru → OPhTerpy(L^2)	
457	2.70	0.0028	HOMO-3 → LUMO+2	-0.10	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+2	0.67	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+3	0.14	Ru → OPhTerpy(L^2)	

Table E.3.4 Continued First 10 excitations of $[Ru(L^2)_2]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
454	2.73	0.0354	HOMO-1 → LUMO+2	0.66	Ru → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO+3	0.18	Ru → OPhTerpy(L^2)	
448	2.76	0.0349	HOMO → LUMO+2	-0.14	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+3	0.66	Ru → OPhTerpy(L^2)	
443	2.79	0.2585	HOMO-2 → LUMO+2	0.55	Ru → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	-0.15	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO	0.14	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+2	0.10	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+3	-0.32	Ru → OPhTerpy(L^2)	
442	2.80	0.0686	HOMO-2 → LUMO+2	0.30	Ru → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	-0.15	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+2	-0.16	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+3	0.57	Ru → OPhTerpy(L^2)	

Table E.3.4 Continued First 10 excitations of $[Ru(L^2)_2]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	0.47	Ru → OPhTerpy(L^2)	
			HOMO-2 → LUMO+9	0.21	Ru → OPhTerpy(L^2)	
394	3.14	0.0035	HOMO-1 → LUMO	0.24	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	-0.25	Ru → OPhTerpy(L^2)	

Table E.3.5 First 10 excitations of $[Ru(L^2)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
522	2.37	0.0139	HOMO-1 → LUMO	0.68	Ru → OPhTerpy(L^2)	MLCT
518	2.39	0.0150	HOMO-1 → LUMO+1	0.68	Ru → Terpy	MLCT
480	2.58	0.2572	HOMO-2 → LUMO+1	0.30	Ru → Terpy	MLCT
			HOMO-1 →LUMO +2	0.22	Ru → Terpy + OPhTerpy(L^2)	
			HOMO-1 → LUMO+3	0.12	Ru → Terpy + OPhTerpy(L^2)	
			HOMO → LUMO	0.55	Ru → OPhTerpy(L^2)	
450	2.75	0.0268	HOMO → LUMO+2	0.67	Ru → Terpy + OPhTerpy(L^2)	MLCT
			HOMO → LUMO+3	0.12	Ru → Terpy + OPhTerpy(L^2)	
444	2.79	0.0116	HOMO-3 → LUMO +3	-0.10	OPhTerpy(L^2) → Terpy + OPhTerpy(L^2)	MLCT
			HOMO → LUMO+2	-0.12	Ru → Terpy + OPhTerpy(L^2)	
			HOMO → LUMO+3	0.67	Ru → Terpy + OPhTerpy(L^2)	
439	2.81	0.2599	HOMO-2 → LUMO+1	-0.16	Ru → Terpy	MLCT
			HOMO-1 → LUMO+2	0.64	Ru → Terpy + OPhTerpy(L^2)	
			HOMO → LUMO	-0.14	Ru → OPhTerpy(L^2)	
438	2.82	0.0150	HOMO-2 → LUMO+2	0.69	Ru → Terpy + OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	0.10	Ru → Terpy + OPhTerpy(L^2)	

Table E.3.5 Continued First 10 excitations of $[Ru(L^2)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
347	3.56	0.0053	HOMO-1 → LUMO+21	0.67	Ru → Terpy	MLCT
			HOMO-1 → LUMO+32	-0.10	Ru → OPh	
434	2.85	0.0366	HOMO-2 → LUMO+3	0.68	Ru → Terpy + OPhTerpy(L^2)	MLCT
391	3.16	0.0080	HOMO-2 → LUMO+1	0.29	Ru → Terpy	MLCT
			HOMO-1 → LUMO+3	0.46	Ru → Terpy + OPhTerpy(L^2)	
			HOMO-1 → LUMO+8	0.24	Ru → Terpy + OPhTerpy(L^2)	
			HOMO → LUMO	0.23	Ru → OPhTerpy(L^2)	
347	3.56	0.0053	HOMO-1 → LUMO+21	0.67	Ru → Terpy	MLCT
			HOMO-1 → LUMO+32	-0.10	Ru → OPh	

Table E.3.6 First 10 excitations of $[Ru(L^2)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.61	Ru → OPhTerpy(L^2)	
522	2.37	0.0139	HOMO-2 → LUMO+1	0.23	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO	-0.17	Ru → OPhTerpy(L^2)	
			HOMO-2 → LUMO	-0.23	Ru → OPhTerpy(L^2)	
521	2.38	0.0135	HOMO-2 → LUMO+1	0.60	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+1	-0.20	Ru → PhTerpy	
			HOMO-2 → LUMO+1	0.11	Ru → PhTerpy	
			HOMO-2 → LUMO+2	0.18	Ru → OPhTerpy(L^2) and PhTerpy	
			HOMO-1 → LUMO	0.14	Ru → OPhTerpy(L^2)	
486	2.54	0.4202	HOMO-1 → LUMO+1	0.38	Ru → PhTerpy	MLCT
			HOMO → LUMO	0.45	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+1	-0.20	Ru → PhTerpy	
452	2.73	0.0214	HOMO → LUMO+2	0.68	Ru → OPhTerpy(L^2) and PhTerpy	MLCT
			HOMO-2 → LUMO+2	0.18	Ru → OPhTerpy(L^2) and PhTerpy	
449	2.75	0.0250	HOMO-1 → LUMO+2	0.66	Ru → OPhTerpy(L^2) and PhTerpy	MLCT
447	2.77	0.0178	HOMO → LUMO+3	0.67	Ru → OPhTerpy(L^2) and PhTerpy	MLCT

Table E.3.6 Continued First 10 excitations of $[Ru(L^2)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
444	2.79	0.0192	HOMO-2 → LUMO+3	0.21	Ru → OPhTerpy(L^2) and PhTerpy	MLCT
			HOMO-1 → LUMO+3	0.64	Ru → OPhTerpy(L^2) and PhTerpy	
441	2.80	0.2944	HOMO-2 → LUMO+2	0.64	Ru → OPhTerpy(L^2) and PhTerpy	MLCT
			HOMO-1 → LUMO+1	-0.11	Ru → PhTerpy	
			HOMO-1 → LUMO+2	-0.17	Ru → OPhTerpy(L^2) and PhTerpy	
			HOMO → LUMO	-0.10	Ru → OPhTerpy(L^2)	
393	3.14	0.0027	HOMO-2 → LUMO+2	0.46	Ru → OPhTerpy(L^2) and PhTerpy	MLCT
			HOMO-2 → LUMO+8	-0.21	Ru → OPhTerpy(L^2) + Phosphazene	
			HOMO-1 → LUMO	0.10	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+1	0.22	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+3	-0.14	Ru → OPhTerpy(L^2) and PhTerpy	
			HOMO → LUMO+10	-0.22	Ru → PhTerpy	
			HOMO →LUMO+11	0.10	Ru → OPh + Phosphazene	
348	3.56	0.0017	HOMO-2 → LUMO+22	0.64	Ru → Ru-N*	MLCT
			HOMO-1 → LUMO+22	-0.20	Ru → Ru-N*	

Table E.3.7 First 10 excitations of $[Ru(L^3)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
557	2.22	0.0149	HOMO → LUMO+1	0.29	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+2	0.62	Ru → Terpy	
514	2.41	0.0047	HOMO-2 → LUMO	-0.33	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+1	0.54	Ru → Terpy	
			HOMO → LUMO+2	-0.26	Ru → Terpy	
463	2.67	0.0096	HOMO-1 → LUMO+1	0.64	Ru → Terpy	MLCT
			HOMO-1 → LUMO+2	-0.20	Ru → Terpy	
458	2.70	0.0575	HOMO-2 → LUMO	0.13	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+1	0.57	Ru → Terpy	
			HOMO-2 → LUMO+2	-0.31	Ru → Terpy	
456	2.71	0.2513	HOMO-2 → LUMO	-0.36	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+1	0.20	Ru → Terpy	
			HOMO-1 → LUMO	0.10	Ru → Obbp(L^3)	
			HOMO-1 → LUMO+2	0.41	Ru → Terpy	
			HOMO → LUMO+1	-0.20	Ru → Terpy	
			HOMO → LUMO+3	0.20	Ru → Terpy	

Table E.3.7 Continued First 10 excitations of $[Ru(L^3)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
428	2.89	0.0453	HOMO-1 → LUMO+3	0.67	Ru → Terpy	MLCT
424	2.92	0.0010	HOMO-2 → LUMO+3	0.68	Ru → Terpy	MLCT
			HOMO-2 → LUMO	0.33	Ru → Obbp(L^3)	
			HOMO-1 → LUMO+1	0.12	Ru → Terpy	
			HOMO-1 → LUMO+2	0.29	Ru → Terpy	
397	3.11	0.0229	HOMO → LUMO+1	0.15	Ru → Terpy	MLCT
			HOMO → LUMO+3	0.25	Ru → Terpy	
			HOMO → LUMO+5	0.12	Ru → Terpy	
			HOMO → LUMO+6	-0.26	Ru → Terpy	
377	3.28	0.0030	HOMO → LUMO+4	0.69	Ru → Phosphazene	MLCT
			HOMO →LUMO+18	0.10	Ru → OPh	
			HOMO → LUMO+20	0.51	Ru → Obbp(L^3) + Phosphazene	
359	3.44	0.0024	HOMO → LUMO+21	-0.32	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO → LUMO+22	0.12	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+26	-0.14	Ru → Ru	

Table E.3.8 First 10 excitations of $[Ru(L^3)(Terpy)]^+$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
638	1.94	0.0139	HOMO → LUMO	0.35	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+1	0.58	Ru → Terpy	
540	2.29	0.0046	HOMO-2 → LUMO	0.11	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+1	0.20	Ru → Terpy	
			HOMO → LUMO+2	0.64	Ru → Terpy	
			HOMO → LUMO+3	-0.13	Ru → Obbp(L^3) + Phosphazene	
519	2.38	0.0089	HOMO-2 → LUMO	-0.13	Ru → Obbp(L^3)	MLCT
			HOMO-1 → LUMO	-0.28	Ru → Obbp(L^3)	
			HOMO-1 → LUMO+1	0.11	Ru → Terpy	
			HOMO → LUMO	0.11	Ru → Obbp(L^3)	
			HOMO → LUMO+2	0.11	Ru → Terpy	
			HOMO →LUMO+3	0.55	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+4	-0.17	Ru → Obbp(L^3) + Phosphazene	

Table E.3.8 Continued First 10 excitations of $[Ru(L^3)(Terpy)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.13	Ru → Obbp(L^3)	
			HOMO-2 → LUMO+1	0.41	Ru → Terpy	
			HOMO-1 → LUMO	-0.39	Ru → Obbp(L^3)	
479	2.58	0.2035	HOMO-1 → LUMO+1	0.16	Ru → Terpy	MLCT
			HOMO-1 → LUMO+2	0.11	Ru → Terpy	
			HOMO → LUMO+2	-0.15	Ru → Terpy	
			HOMO → LUMO+3	-0.14	Ru → Obbp(L^3) + Phosphazene	
			HOMO-2 → LUMO+2	0.39	Ru → Terpy	
			HOMO-2 → LUMO+3	-0.12	Ru → Obbp(L^3) + Phosphazene	
460	2.69	0.0221	HOMO-1 → LUMO	0.16	Ru → Obbp(L^3)	MLCT
			HOMO-1 → LUMO+2	0.49	Ru → Terpy	
			HOMO-2 → LUMO+2	0.50	Ru → Terpy	
			HOMO-2 → LUMO+3	-0.12	Ru → Obbp(L^3) + Phosphazene	
459	2.69	0.0333	HOMO-1 → LUMO	0.16	Ru → Obbp(L^3)	MLCT
			HOMO-1 → LUMO+2	0.49	Ru → Terpy	

Table E.3.8 Continued First 10 excitations of $[Ru(L^3)(Terpy)]^+$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-3 → LUMO+3	0.12	Ru → Obbp(L^3) + Phosphazene	
			HOMO-2 → LUMO+1	0.28	Ru → Terpy	
			HOMO-1 → LUMO	0.22	Ru → Obbp(L^3)	
448	2.76	0.0373	HOMO-1 → LUMO+3	0.46	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO-1 → LUMO+4	-0.14	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+2	-0.10	Ru → Terpy	
			HOMO → LUMO+3	0.11	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+6	-0.13	Ru → Terpy	
			HOMO-1 → LUMO+3	-0.15	Ru → Obbp(L^3) + Phosphazene	
429	2.88	0.0015	HOMO → LUMO+3	0.26	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO → LUMO+4	0.60	Ru → Obbp(L^3) + Phosphazene	

Table E.3.8 Continued First 10 excitations of $[Ru(L^3)(Terpy)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	-0.17	Ru → Terpy	
			HOMO-1 → LUMO	-0.18	Ru → Obbp(L^3)	
			HOMO-1 →LUMO+2	0.20	Ru → Terpy	MLCT
413	2.99	0.0529	HOMO-1 → LUMO+3	0.40	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+4	0.25	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+6	0.27	Ru → Terpy	
			HOMO-3 → LUMO	0.45	Ru → Obbp(L^3)	
397	3.11	0.0066	HOMO-3 → LUMO+1	0.50	Ru → Terpy	MLCT
			HOMO → LUMO+1	-0.12	Ru → Terpy	

Table E.3.9 First 10 excitations of $[Ru(L^3)(Terpy)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
717	1.72	0.0139	HOMO → LUMO	0.67	Ru → Terpy	MLCT
603	2.05	0.0045	HOMO-2 → LUMO	0.21	Ru → Terpy	MLCT
			HOMO → LUMO+1	0.66	Ru → Terpy	
496	2.49	0.0093	HOMO-2 → LUMO	-0.10	Ru → Terpy	MLCT
			HOMO-1 → LUMO+1	0.66	Ru → Terpy	
			HOMO → LUMO+3	0.13	Ru → Obbp(L^3)	
494	2.50	0.0445	HOMO-2 → LUMO	0.16	Ru → Terpy	MLCT
			HOMO-2 → LUMO+1	0.58	Ru → Terpy	
			HOMO-1 → LUMO+1	0.13	Ru → Terpy	
			HOMO → LUMO+3	-0.25	Ru → Obbp(L^3)	
493	2.51	0.0894	HOMO-2 → LUMO	-0.25	Ru → Terpy	MLCT
			HOMO-2 → LUMO+1	0.33	Ru → Terpy	
			HOMO-1 → LUMO+1	-0.13	Ru → Terpy	
			HOMO → LUMO+3	0.49	Ru → Obbp(L^3)	
			HOMO → LUMO+6	0.10	Ru → Terpy	

Table E.3.9 Continued First 10 excitations of $[Ru(L^3)(Terpy)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.43	Ru → Terpy	
			HOMO-1 → LUMO	-0.10	Ru → Terpy	
			HOMO-1 → LUMO+2	0.31	Ru → Terpy	
483	2.56	0.0624	HOMO-1 → LUMO+4	-0.13	Ru → Phosphazene	MLCT
			HOMO → LUMO+1	-0.12	Ru → Terpy	
			HOMO → LUMO+3	0.30	Ru → Obbp(L^3)	
			HOMO → LUMO+6	-0.17	Ru → Terpy	
			HOMO-2 → LUMO+2	0.11	Ru → Terpy	
			HOMO-1 → LUMO+2	0.49	Ru → Terpy	
424	2.92	0.1156	HOMO → LUMO+3	-0.19	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+6	0.36	Ru → Terpy	
			HOMO-3 → LUMO+2	-0.14	Obbp(L^3) → Terpy	
418	2.95	0.0220	HOMO-1 → LUMO+3	0.66	Ru → Obbp(L^3)	MLCT
417	2.96	0.0024	HOMO-2 → LUMO+3	0.69	Ru → Obbp(L^3)	MLCT
			HOMO-3 → LUMO	0.68	Obbp(L^3) → Terpy	
414	2.99	0.0035	HOMO → LUMO+3	-0.14	Ru → Obbp(L^3)	ILCT

Table E.3.10 First 10 excitations of $[Ru(L^3)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
564	2.18	0.0141	HOMO → LUMO+1	0.65	Ru → PhTerpy	MLCT
			HOMO → LUMO+2	-0.21	Ru → Obbp(L^3)	
513	2.41	0.0032	HOMO-2 → LUMO	0.34	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+2	0.18	Ru → Obbp(L^3)	
			HOMO → LUMO+3	0.57	Ru → PhTerpy	
486	2.55	0.0330	HOMO-1 → LUMO+1	-0.43	Ru → PhTerpy	MLCT
			HOMO → LUMO+3	0.53	Ru → PhTerpy	
472	2.62	0.0062	HOMO-1 → LUMO+1	0.25	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+2	0.62	Ru → Obbp(L^3)	
			HOMO-1 → LUMO+3	0.10	Ru → PhTerpy	
			HOMO → LUMO+3	0.11	Ru → PhTerpy	

Table E.3.10 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.37	Ru → Obbp(L^3)	
			HOMO-1 → LUMO+1	0.29	Ru → PhTerpy	
464	2.66	0.3935	HOMO-1 → LUMO+2	-0.23	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+2	-0.22	Ru → Obbp(L^3)	
			HOMO → LUMO+3	0.32	Ru → PhTerpy	
			HOMO-2 → LUMO+1	0.19	Ru → PhTerpy	
458	2.70	0.0520	HOMO-2 → LUMO+2	0.64	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+3	0.10	Ru → PhTerpy	
			HOMO-1 → LUMO+2	-0.10	Ru → PhTerpy	
442	2.80	0.0380	HOMO-1 → LUMO+3	0.67	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO	0.37	Ru → Obbp(L^3)	
			HOMO-1 →LUMO+1	-0.27	Ru → PhTerpy	
			HOMO-1 →LUMO+2	0.10	Ru → Obbp(L^3)	
400	3.09	0.0179	HOMO → LUMO+2	-0.17	Ru → Obbp(L^3)	MLCT
			HOMO → LUMO+3	-0.25	Ru → PhTerpy	
			HOMO → LUMO+6	0.26	Ru → PhTerpy	

Table E.3.10 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
375	3.30	0.0032	HOMO → LUMO+4	0.69	Ru → Phosphazene	MLCT
			HOMO→ LUMO+38	0.10	Ru → Obbp(L^3) + Phosphazene	
			HOMO→ LUMO+41	0.53	Ru → PhTerpy	
360	3.44	0.0021	HOMO→ LUMO+42	-0.28	Ru → Obbp(L^3)	MLCT
			HOMO→ LUMO+43	0.12	Ru → Obbp(L^3)	
			HOMO→ LUMO+47	-0.14	Ru → Obbp(L^3)	

Table E.3.11 First 10 excitations of $[Ru(L^3)(PhTerpy)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
650	1.90	0.0125	HOMO → LUMO	0.61	Ru → PhTerpy	MLCT
			HOMO → LUMO+1	0.29	Ru → Obbp(L^3)	
618	2.00	0.0064	HOMO → LUMO	-0.27	Ru → PhTerpy	MLCT
			HOMO → LUMO+1	0.60	Ru → Obbp(L^3)	
			HOMO → LUMO+3	0.11	Ru → Obbp(L^3)+ Phosphazene	
521	2.27	0.0013	HOMO-3 → LUMO	0.12	Ru → PhTerpy	MLCT
			HOMO-2 → LUMO	0.53	Ru → PhTerpy	
			HOMO-2 → LUMO+1	0.30	Ru → Obbp(L^3)	
			HOMO-1 → LUMO	0.13	Ru → PhTerpy	
			HOMO-1 → LUMO+1	-0.20	Ru → Obbp(L^3)	
515	2.40	0.0039	HOMO-2 → LUMO	0.11	Ru → PhTerpy	MLCT
			HOMO-2 → LUMO+1	-0.31	Ru → Obbp(L^3)	
			HOMO → LUMO+3	0.55	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+4	0.17	Ru → Obbp(L^3) + Phosphazene	

Table E.3.11 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^+$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.17	Ru → PhTerpy	
			HOMO-2 → LUMO+1	-0.29	Ru → Obbp(L^3)	
			HOMO-2 → LUMO+2	0.15	Ru → PhTerpy	
488	2.53	0.3260	HOMO-1 → LUMO	0.38	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+1	0.28	Ru → Obbp(L^3)	
			HOMO → LUMO+2	0.17	Ru → PhTerpy	
			HOMO → LUMO+3	-0.16	Ru → Obbp(L^3) + Phosphazene	
			HOMO-1 → LUMO+1	0.10	Ru → Obbp(L^3)	
472	2.62	0.0430	HOMO-1 → LUMO+2	0.66	Ru → PhTerpy	MLCT
			HOMO-3 → LUMO+2	0.11	Ru → PhTerpy	
			HOMO-2 → LUMO	-0.11	Ru → PhTerpy	
466	2.65	0.0162	HOMO-2 → LUMO+1	0.23	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+1	0.62	Ru → Obbp(L^3)	
			HOMO → LUMO+2	0.11	Ru → PhTerpy	

Table E.3.11 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-3 → LUMO+3	0.13	Ru → Obbp(L^3) + Phosphazene	
			HOMO-2 → LUMO	0.15	Ru → PhTerpy	
			HOMO-2 → LUMO+1	-0.25	Ru → Obbp(L^3)	
			HOMO-2 → LUMO+2	0.16	Ru → PhTerpy	
			HOMO-2 → LUMO+3	0.41	Ru → Obbp(L^3) + Phosphazene	
450	2.75	0.0341	HOMO-2 → LUMO+4	-0.13	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO-1 → LUMO	-0.21	Ru → PhTerpy	
			HOMO-1 → LUMO+1	-0.13	Ru → Obbp(L^3)	
			HOMO → LUMO+2	-0.11	Ru → PhTerpy	
			HOMO → LUMO+3	-0.14	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+6	0.13	Ru → Obbp(L^3)	
			HOMO-2 → LUMO+3	0.24	Ru → Obbp(L^3) + Phosphazene	
426	2.91	0.0063	HOMO → LUMO+3	0.26	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO → LUMO+4	0.56	Ru → Obbp(L^3) + Phosphazene	

Table E.3.11 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
411	3.01	0.0593	HOMO-2 → LUMO+1	0.14	Ru → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+2	-0.13	Ru → PhTerpy	
			HOMO-2 → LUMO+3	0.41	Ru → Obbp(L^3) + Phosphazene	
			HOMO-1 → LUMO	0.11	Ru → PhTerpy	
			HOMO → LUMO+4	-0.33	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+6	-0.24	Ru → Obbp(L^3)	

Table E.3.12 First 10 excitations of $[Ru(L^3)(PhTerpy)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
732	1.69	0.0112	HOMO → LUMO	0.67	Ru → PhTerpy	MLCT
612	2.02	0.0017	HOMO-1 → LUMO	-0.22	Ru → PhTerpy	MLCT
			HOMO → LUMO+1	0.66	Ru → PhTerpy	
506	2.44	0.0448	HOMO-1 → LUMO	-0.10	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+1	0.66	Ru → PhTerpy	
			HOMO → LUMO+5	-0.10	Ru → PhTerpy	
499	2.48	0.2429	HOMO-1 → LUMO	0.47	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO+1	0.14	Ru → PhTerpy	
			HOMO → LUMO+1	0.16	Ru → PhTerpy	
			HOMO → LUMO+3	-0.36	Ru → Obbp(L^3)	
			HOMO → LUMO+6	0.17	Ru → PhTerpy	
488	2.53	0.0237	HOMO-2 → LUMO+2	0.33	Ru → Obbp(L^3) + Phosphazene	MLCT
			HOMO-2 → LUMO+4	-0.13	Ru → Obbp(L^3) + Phosphazene	
			HOMO-1 → LUMO	0.25	Ru → PhTerpy	
			HOMO → LUMO+3	0.52	Ru → Obbp(L^3)	

Table E.3.12 Continued First 10 excitations of $[Ru(L^3)(PhTerpy)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+2	0.50	Ru → Obbp(L^3) + Phosphazene	
			HOMO → LUMO+3	-0.20	Ru → Obbp(L^3)	MLCT
426	2.90	0.1330	HOMO → LUMO+5	0.12	Ru → PhTerpy	
			HOMO → LUMO+6	-0.34	Ru → PhTerpy	
			HOMO-3 → LUMO	0.68	Obbp(L^3) → PhTerpy	ILCT
421	2.94	0.0023	HOMO → LUMO+5	0.10	Ru → PhTerpy	
			HOMO-3 → LUMO+2	-0.16	Obbp(L^3) → Obbp(L^3) + Phosphazene	MLCT
419	2.95	0.0201	HOMO-2 → LUMO+3	0.66	Ru → Obbp(L^3)	
			HOMO-3 → LUMO	-0.12	Obbp(L^3) → PhTerpy	
416	2.97	0.0987	HOMO → LUMO+5	0.65	Ru → PhTerpy	MLCT
			HOMO → LUMO+7	-0.10	Ru → PhTerpy	
			HOMO-4 → LUMO+2	0.10	Obbp(L^3) → Obbp(L^3) + Phosphazene	
			HOMO-2 → LUMO+2	0.27	Ru → Obbp(L^3) + Phosphazene	
383	3.23	0.0084	HOMO-2 → LUMO+5	0.41	Ru → PhTerpy	MLCT
			HOMO-1 → LUMO	-0.11	Ru → PhTerpy	
			HOMO → LUMO+6	0.41	Ru → PhTerpy	

Table E.3.13 First 10 excitations of $[Ru(L^1)(bbp)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
596	2.07	0.0113	HOMO → LUMO	0.68	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO	-0.27	Ru → OTerpy(L^1)	
514	2.40	0.0010	HOMO → LUMO+1	0.20	Ru → bbp	MLCT
			HOMO → LUMO+2	0.60	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.36	Ru → bbp	
482	2.56	0.0024	HOMO-1 → LUMO+2	-0.11	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+3	0.57	Ru → bbp	
			HOMO-2 → LUMO	0.51	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	-0.25	Ru → bbp	
459	2.69	0.2552	HOMO-1 → LUMO+2	0.11	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	0.21	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.17	Ru → bbp	
			HOMO-1 → LUMO+1	0.23	Ru → bbp	
454	2.72	0.0016	HOMO-1 → LUMO+2	0.64	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+4	-0.12	Ru → Phosphazene	

Table E.3.13 Continued First 10 excitations of $[Ru(L^1)(bbp)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	0.21	Ru → bbp	
453	2.73	0.0381	HOMO-2 → LUMO+2	0.64	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+3	-0.12	Ru → bbp	
			HOMO-1 → LUMO+2	0.11	Ru → OTerpy(L^1)	
430	2.87	0.0495	HOMO-1 → LUMO+3	0.67	Ru → bbp	MLCT
			HOMO-2 → LUMO+2	0.11	Ru → OTerpy(L^1)	
429	2.88	0.0010	HOMO-2 →LUMO+3	0.68	Ru → bbp	MLCT
			HOMO-2 → LUMO	0.22	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.37	Ru → bbp	
395	3.13	0.0439	HOMO-1 → LUMO+2	-0.15	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+3	-0.28	Ru → bbp	
			HOMO → LUMO+6	0.30	Ru → OTerpy(L^1)	
			HOMO → LUMO+4	0.62	Ru → Phosphazene	
367	3.37	0.0353	HOMO → LUMO+5	0.25	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+30	0.12	Ru → Ru	

Table E.3.14 First 10 excitations of $[Ru(L^1)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
696	1.78	0.0096	HOMO → LUMO	0.67	Ru → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO	0.16	Ru → OTerpy(L^1)	
599	2.06	0.0059	HOMO → LUMO+1	0.66	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	-0.13	Ru → bbp	
			HOMO-2 → LUMO	0.10	Ru → OTerpy(L^1)	
			HOMO → LUMO+1	0.12	Ru → OTerpy(L^1)	
581	2.13	0.0030	HOMO → LUMO+2	0.65	Ru → bbp	MLCT
			HOMO → LUMO+3	-0.12	Ru → bbp	
			HOMO-3 → LUMO+1	0.16	Ru → OTerpy(L^1)	
501	2.47	0.0020	HOMO-2 → LUMO	-0.15	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+1	0.64	Ru → OTerpy(L^1)	
490	2.53	0.0372	HOMO-2 → LUMO+1	0.68	Ru → OTerpy(L^1)	MLCT

Table E.3.14 Continued First 10 excitations of $[Ru(L^1)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-3 → LUMO+2	-0.10	Ru → bbp	
			HOMO-2 → LUMO	0.46	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.16	Ru → OTerpy(L^1)	
482	2.56	0.1358	HOMO-1 → LUMO+2	-0.38	Ru → bbp	MLCT
			HOMO → LUMO+1	-0.10	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	-0.12	Ru → bbp	
			HOMO → LUMO+6	0.11	Ru → OTerpy(L^1)	
478	2.59	0.0034	HOMO-2 → LUMO+2	0.68	Ru → bbp	MLCT
			HOMO-2 → LUMO	0.26	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.26	Ru → bbp	
470	2.63	0.0611	HOMO → LUMO+3	0.54	Ru → bbp	MLCT
			HOMO → LUMO+6	0.10	Ru → OTerpy(L^1)	

Table E.3.14 Continued First 10 excitations of $[Ru(L^1)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-3 → LUMO+3	0.17	Ru → bbp	
			HOMO-2 → LUMO	0.15	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.42	Ru → bbp	
427	2.90	0.0476	HOMO-1 → LUMO+3	0.21	Ru → bbp	MLCT
			HOMO → LUMO+2	-0.10	Ru → bbp	
			HOMO → LUMO+3	-0.31	Ru → bbp	
			HOMO → LUMO+6	0.20	Ru → OTerpy(L^1)	
			HOMO-4 → LUMO	0.50	Ru → OTerpy(L^1)	
417	2.97	0.0174	HOMO → LUMO	-0.10	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+4	-0.45	Ru → Phosphazene	

Table E.3.15 First 10 excitations of $[Ru(L^1)(bbp)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
770	1.60	0.0098	HOMO → LUMO	0.67	Ru → OTerpy(L^1)	MLCT
655	1.89	0.0030	HOMO-2 → LUMO	-0.19	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+1	0.67	Ru → OTerpy(L^1)	
520	2.38	0.0015	HOMO-2 → LUMO+1	-0.11	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+1	0.23	Ru → OTerpy(L^1)	
			HOMO → LUMO+3	0.64	Ru → bbp	
520	2.38	0.0405	HOMO-2 → LUMO+1	0.66	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+3	0.10	Ru → bbp	
491	2.52	0.1528	HOMO-2 → LUMO	0.55	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+3	-0.12	Ru → bbp	
			HOMO → LUMO+1	0.15	Ru → OTerpy(L^1)	
			HOMO → LUMO+4	0.14	Ru → bbp	
			HOMO → LUMO+6	-0.24	Ru → OTerpy(L^1)	
452	2.74	0.0215	HOMO-1 → LUMO+3	0.11	Ru → bbp	MLCT
			HOMO → LUMO+2	0.62	Ru → Phosphazene	
			HOMO → LUMO+4	0.25	Ru → bbp	

Table E.3.15 Continued First 10 excitations of $[Ru(L^1)(bbp)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-1 → LUMO+3	0.24	Ru → bbp	
452	2.74	0.0124	HOMO → LUMO+2	-0.28	Ru → Phosphazene	MLCT
			HOMO → LUMO+4	0.57	Ru → bbp	
411	3.01	0.0771	HOMO → LUMO+5	0.67	Ru → OTerpy(L^1)	MLCT
409	3.02	0.0013	HOMO-4 → LUMO+1	0.69	bbp → OTerpy(L^1)	ILCT
			HOMO-1 → LUMO+3	-0.45	Ru → bbp	
404	3.06	0.1218	HOMO → LUMO+4	0.15	Ru → bbp	MLCT
			HOMO → LUMO+6	0.47	Ru → OTerpy(L^1)	

Table E.3.16 First 10 excitations of $[Ru(L^2)(bbp)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
580	2.13	0.0108	HOMO → LUMO	0.62	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	0.28	Ru → bbp	
579	2.14	0.0029	HOMO → LUMO	-0.28	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	0.62	Ru → bbp	
497	2.48	0.0292	HOMO-1 → LUMO	0.40	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+2	0.43	Ru → OPhTerpy(L^2) + bbp	
			HOMO → LUMO+3	0.48	Ru → OPhTerpy(L^2) + bbp	
490	2.52	0.0019	HOMO-2 → LUMO+1	-0.37	Ru → bbp	MLCT
			HOMO → LUMO+2	-0.33	Ru → OPhTerpy(L^2) + bbp	
			HOMO → LUMO+3	0.48	Ru → OPhTerpy(L^2) + bbp	
465	2.66	0.4319	HOMO-2 → LUMO+1	0.28	Ru → bbp	MLCT
			HOMO-1 → LUMO	0.43	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+2	-0.41	Ru → OPhTerpy(L^2) + bbp	
			HOMO → LUMO+3	-0.10	Ru → OPhTerpy(L^2) + bbp	
452	2.74	0.0345	HOMO-1 → LUMO+2	0.39	Ru → OPhTerpy(L^2) + bbp	MLCT
			HOMO-1 → LUMO+3	0.55	Ru → OPhTerpy(L^2) + bbp	

Table E.3.16 Continued First 10 excitations of $[Ru(L^2)(bbp)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
440	2.81	0.0264	HOMO-2 → LUMO+3	0.69	Ru → OPhTerpy(L^2) + bbp	MLCT
439	2.82	0.0308	HOMO-2 → LUMO+2	0.69	Ru → OPhTerpy(L^2) + bbp	MLCT
398	3.11	0.0202	HOMO-2 → LUMO+1	0.41	Ru → bbp	MLCT
			HOMO-1 → LUMO	-0.22	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+3	0.30	Ru → OPhTerpy(L^2) + bbp	
			HOMO → LUMO+6	0.28	Ru → OPhTerpy(L^2)	
359	3.44	0.0636	HOMO-18 → LUMO	-0.14	OPhTerpy(L^2) → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+4	-0.25	Ru → Phosphazene	
			HOMO → LUMO+5	0.61	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+7	-0.10	Ru → OPhTerpy(L^2)	

Table E.3.17 First 10 excitations of $[Ru(L^2)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
670	1.84	0.0121	HOMO → LUMO	0.68	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	-0.43	Ru → OPhTerpy(L^2)	
588	2.10	0.0062	HOMO → LUMO+2	0.51	Ru → bbp	MLCT
			HOMO → LUMO+3	-0.14	Ru → bbp	
			HOMO-2 → LUMO	-0.10	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+1	-0.42	Ru → OPhTerpy(L^2)	
498	2.48	0.0011	HOMO-1 → LUMO+2	0.53	Ru → bbp	MLCT
			HOMO-1 → LUMO+3	-0.10	Ru → bbp	
			HOMO-2 → LUMO+2	0.39	Ru → bbp	
			HOMO-1 → LUMO	0.49	Ru → OPhTerpy(L^2)	
488	2.53	0.2451	HOMO → LUMO+1	0.14	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+6	0.11	Ru → OPhTerpy(L^2)	
			HOMO-1 → LUMO+1	0.53	Ru → OPhTerpy(L^2)	
483	2.56	0.0397	HOMO-1 → LUMO+2	0.41	Ru → bbp	MLCT

Table E.3.17 Continued First 10 excitations of $[Ru(L^2)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	0.29	Ru → OPhTerpy(L^2)	
			HOMO-2 → LUMO+2	0.33	Ru → bbp	
473	2.61	0.0864	HOMO-1 → LUMO	-0.21	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	-0.11	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+3	0.45	Ru → bbp	
			HOMO-3 → LUMO+3	0.15	bbp → bbp	
			HOMO-2 → LUMO+1	-0.18	Ru → OPhTerpy(L^2)	
			HOMO-2 → LUMO+2	0.37	Ru → bbp	
			HOMO-2 → LUMO+3	0.29	Ru → bbp	
429	2.88	0.0386	HOMO-1 → LUMO+3	-0.15	Ru → bbp	MLCT
			HOMO → LUMO	-0.12	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+2	-0.29	Ru → bbp	
			HOMO → LUMO+6	-0.19	Ru → OPhTerpy(L^2)	

Table E.3.17 Continued First 10 excitations of $[Ru(L^2)(bbp)]^+$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-3 → LUMO+1	0.11	bbp → OPhTerpy(L^2)	
			HOMO-2 → LUMO+2	-0.10	Ru → bbp	
398	3.11	0.0912	HOMO-2 → LUMO+3	0.55	Ru → bbp	MLCT
			HOMO → LUMO+3	0.13	Ru → bbp	
			HOMO → LUMO+6	0.31	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+4	-0.35	Ru → Phosphazene	
397	3.12	0.0799	HOMO → LUMO+5	0.57	Ru → OPhTerpy(L^2)	MLCT
			HOMO-3 → LUMO+1	0.67	bbp → OPhTerpy(L^2)	
385	3.21	0.0301	HOMO-2 → LUMO+1	-0.11	Ru → OPhTerpy(L^2)	ILCT

Table E.3.18 First 10 excitations of $[Ru(L^2)(bbp)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
743	1.66	0.0120	HOMO → LUMO	0.67	Ru → OPhTerpy(L^2)	MLCT
509	2.41	0.0439	HOMO-1 → LUMO+1	0.67	Ru → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+5	0.11	Ru → OPhTerpy(L^2)	
497	2.49	0.2462	HOMO-2 → LUMO+3	0.13	Ru → bbp	MLCT
			HOMO-1 → LUMO	0.55	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+1	-0.19	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+4	0.14	Ru → bbp	
			HOMO → LUMO+6	-0.23	Ru → OPhTerpy(L^2)	
458	2.70	0.0044	HOMO-2 → LUMO+3	-0.27	Ru → bbp	MLCT
			HOMO → LUMO+4	0.63	Ru → bbp	
435	2.84	0.0175	HOMO → LUMO+2	0.67	Ru → Phosphazene	MLCT
			HOMO → LUMO+5	-0.18	Ru → OPhTerpy(L^2)	
418	2.96	0.1030	HOMO → LUMO+2	-0.19	Ru → Phosphazene	MLCT
			HOMO → LUMO+5	0.63	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+7	-0.14	Ru → OPhTerpy(L^2)	

Table E.3.18 Continued First 10 excitations of $[Ru(L^2)(bbp)]^0$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+3	-0.45	Ru → bbp	
407	3.03	0.1467	HOMO → LUMO+4	0.16	Ru → bbp	MLCT
			HOMO → LUMO+5	0.46	Ru → OPhTerpy(L^2)	
			HOMO-3 → LUMO+3	0.14	bbp → bbp	
399	3.10	0.0277	HOMO-2 → LUMO+2	0.66	Ru → Phosphazene	MLCT
			HOMO-1 → LUMO+2	0.61	Ru → Phosphazene	
380	3.26	0.0759	HOMO-1 → LUMO+5	-0.32	Ru → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	-0.20	Ru → bbp	
			HOMO-1 → LUMO	0.10	Ru → OPhTerpy(L^2)	
370	3.34	0.0377	HOMO-1 → LUMO+2	0.28	Ru → Phosphazene	MLCT
			HOMO-1 → LUMO+5	0.48	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+6	0.26	Ru → OPhTerpy(L^2)	

Table E.3.19 First 10 excitations of $[Ru(L^4)(Terpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
530	2.33	0.0169	HOMO → LUMO	0.69	Ru → Terpy	MLCT
480	2.57	0.0117	HOMO → LUMO+1	0.68	Ru → OPhbpp(L^4)	MLCT
435	2.84	0.5189	HOMO-2 → LUMO	0.30	Ru → Terpy	MLCT
			HOMO-1 → LUMO+1	0.53	Ru → OPhbpp(L^4)	
			HOMO → LUMO+2	-0.21	Ru → Terpy	
			HOMO → LUMO+3	0.20	Ru → OPhbpp(L^4)	
432	2.86	0.0011	HOMO-2 → LUMO+1	0.69	Ru → OPhbpp(L^4)	MLCT
416	2.97	0.0619	HOMO-2 → LUMO	-0.35	Ru → Terpy	MLCT
			HOMO-1 → LUMO+1	0.14	Ru → OPhbpp(L^4)	
			HOMO → LUMO+2	0.26	Ru → Terpy	
			HOMO → LUMO+3	0.48	Ru → OPhbpp(L^4)	
			HOMO → LUMO+6	-0.11	Ru → Terpy	
413	3.00	0.0447	HOMO-2 → LUMO+2	0.68	Ru → Terpy	MLCT
395	3.13	0.0288	HOMO-14 → LUMO+1	0.11	OPhbpp(L^4) → OPhbpp(L^4)	MLCT
			HOMO-1 → LUMO+3	0.67	Ru → OPhbpp(L^4)	

Table E.3.19 Continued First 10 excitations of $[Ru(L^4)(Terpy)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.21	Ru → Terpy	
			HOMO-1 → LUMO+1	-0.32	Ru → OPhbpp(L^4)	
373	3.31	0.2169	HOMO → LUMO+2	-0.13	Ru → Terpy	MLCT
			HOMO → LUMO+3	0.42	Ru → OPhbpp(L^4)	
			HOMO → LUMO+6	0.28	Ru → Terpy	
			HOMO-14 → LUMO	0.10	OPhbpp(L^4)→ Terpy	
339	3.65	0.0207	HOMO-13 → LUMO	0.23	OPhbpp(L^4)→ Terpy	MLCT
			HOMO → LUMO+5	0.65	Ru → Terpy	
			HOMO-6 → LUMO	-0.16	OPhbpp(L^4) → Terpy	
330	3.75	0.0014	HOMO-3 → LUMO	0.66	Ru + OPhbpp(L^4) → Terpy	MLCT
			HOMO-1 → LUMO	0.13	Ru → Terpy	

Table E.3.20 First 10 excitations of $[Ru(L^4)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
535	2.31	0.0155	HOMO → LUMO	0.69	Ru → PhTerpy	MLCT
480	2.58	0.0115	HOMO → LUMO+1	0.68	Ru → OPhbpp(L^4)	MLCT
464	2.66	0.0679	HOMO-2 → LUMO	-0.46	Ru + PhTerpy → PhTerpy	MLCT
			HOMO → LUMO+2	0.51	Ru → PhTerpy	
441	2.80	0.0060	HOMO-2 → LUMO+1	0.68	Ru + PhTerpy → OPhbpp(L^4)	MLCT
440	2.81	0.6985	HOMO-2 → LUMO	0.29	Ru + PhTerpy → PhTerpy	MLCT
			HOMO-1 → LUMO+1	0.47	Ru + OPhbpp(L^4) → OPhbpp(L^4)	
			HOMO → LUMO+2	0.36	Ru → PhTerpy	
			HOMO → LUMO+3	0.12	Ru → OPhbpp(L^4)	
425	2.91	0.0368	HOMO-2 → LUMO+2	0.68	Ru + PhTerpy → PhTerpy	MLCT
419	2.95	0.0296	HOMO-2 → LUMO	-0.27	Ru + PhTerpy → PhTerpy	MLCT
			HOMO-1 → LUMO+1	0.25	Ru + OPhbpp(L^4) → OPhbpp(L^4)	
			HOMO → LUMO+2	-0.26	Ru → PhTerpy	
			HOMO → LUMO+3	0.50	Ru → OPhbpp(L^4)	
			HOMO → LUMO+6	0.10	Ru → PhTerpy	

Table E.3.20 Continued First 10 excitations of $[Ru(L^4)(PhTerpy)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
397	3.12	0.0293	HOMO-16 → LUMO+1	0.10	OPhbpp(L^4) + PhTerpy → OPhbpp(L^4)	MLCT
			HOMO-1 → LUMO+3	0.67	Ru + OPhbpp(L^4) → PhTerpy	
374	3.30	0.2139	HOMO-2 → LUMO	0.18	Ru + PhTerpy → PhTerpy	MLCT
			HOMO-1 → LUMO+1	-0.33	Ru + OPhbpp(L^4) → OPhbpp(L^4)	
			HOMO → LUMO+2	0.12	Ru → PhTerpy	
			HOMO → LUMO+3	0.44	Ru → OPhbpp(L^4)	
			HOMO → LUMO+6	-0.27	Ru → PhTerpy	
342	3.61	0.0319	HOMO-17 → LUMO	-0.18	OPhbpp(L^4) + PhTerpy → PhTerpy	MLCT
			HOMO-16 → LUMO	-0.12	OPhbpp(L^4) + PhTerpy → PhTerpy	
			HOMO → LUMO+5	0.65	Ru → PhTerpy	
			HOMO → LUMO+8	-0.10	Ru → PhTerpy	

Table E.3.21 First 10 excitations of $[Ru(L^1)(bpp)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
550	2.25	0.0129	HOMO → LUMO	0.68	Ru → OTerpy(L^1)	MLCT
475	2.60	0.0019	HOMO-2 → LUMO	-0.30	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+1	0.62	Ru → OTerpy(L^1)	
458	2.70	0.0139	HOMO-2 → LUMO	0.11	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	0.67	Ru → bpp	
425	2.91	0.2538	HOMO-2 → LUMO	0.53	Ru → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO+2	0.25	Ru → bpp	
			HOMO → LUMO+1	0.27	Ru → OTerpy(L^1)	
			HOMO → LUMO+7	-0.11	Ru → OTerpy(L^1)	
423	2.92	0.0345	HOMO-2 → LUMO+1	0.68	Ru → OTerpy(L^1)	MLCT
411	3.01	0.0019	HOMO-1 → LUMO+2	0.38	Ru → bpp	MLCT
			HOMO → LUMO+3	0.57	Ru → bpp	
410	3.02	0.0016	HOMO-2 → LUMO+2	0.68	Ru → bpp	MLCT
382	3.24	0.0384	HOMO-8 → LUMO+2	-0.12	OPh → bpp	MLCT
			HOMO-1 → LUMO+3	0.67	Ru → bpp	

Table E.3.21 Continued First 10 excitations of $[Ru(L^1)(bpp)]^{2+}$

λ/nm	E/eV	f	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.12	Ru → OTerpy(L^1)	
			HOMO-1 → LUMO+2	-0.39	Ru → bpp	
363	3.41	0.0648	HOMO → LUMO+3	0.31	Ru → bpp	MLCT
			HOMO → LUMO+7	-0.29	Ru → OTerpy(L^1)	
			HOMO → LUMO+17	0.23	Ru → OPh	
			HOMO-1 → LUMO+2	0.15	Ru → bpp	
			HOMO → LUMO+3	-0.12	Ru → bpp	
363	3.41	0.0103	HOMO → LUMO+7	0.11	Ru → OTerpy(L^1)	MLCT
			HOMO → LUMO+16	0.13	Ru → OPh	
			HOMO → LUMO+17	0.59	Ru → OPh	

Table E.3.21 First 10 excitations of $[Ru(L^2)(bpp)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
533	2.32	0.0154	HOMO → LUMO	0.69	Ru → OPhTerpy(L^2)	MLCT
464	2.67	0.0715	HOMO-1 → LUMO	0.47	Ru + OPhTerpy(L^2) → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	0.49	Ru → OPhTerpy(L^2)	
463	2.67	0.0168	HOMO → LUMO+2	0.68	Ru → bpp	MLCT
431	2.87	0.4712	HOMO-2 → LUMO+2	-0.25	Ru → bpp	MLCT
			HOMO-1 → LUMO	-0.40	Ru + OPhTerpy(L^2) → OPhTerpy(L^2)	
			HOMO → LUMO+1	0.45	Ru → OPhTerpy(L^2)	
431	2.87	0.0052	HOMO-2 → LUMO+1	0.69	Ru → OPhTerpy(L^2)	MLCT
429	2.88	0.0080	HOMO-3 → LUMO+2	0.15	Ru + OPhTerpy(L^2) → bpp	MLCT
			HOMO-1 → LUMO+2	0.66	Ru + OPhTerpy(L^2) → bpp	
426	2.90	0.0313	HOMO-1 → LUMO+1	0.67	Ru + OPhTerpy(L^2) → OPhTerpy(L^2)	MLCT
388	3.19	0.0419	HOMO-13 → LUMO+2	0.11	OPh → bpp	MLCT
			HOMO-2 → LUMO+3	0.68	Ru → bpp	

Table E.3.21 Continued First 10 excitations of $[Ru(L^2)(bpp)]^{2+}$

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+2	0.41	Ru → bpp	
			HOMO-1 → LUMO	-0.13	Ru + OPhTerpy(L^2) → OPhTerpy(L^2)	
365	3.39	0.0557	HOMO → LUMO+3	-0.35	Ru → bpp	MLCT
			HOMO → LUMO+6	-0.29	Ru → OPhTerpy(L^2)	
			HOMO → LUMO+17	-0.10	Ru → OPh	
			HOMO → LUMO+17	0.66	Ru → OPh	
364	3.39	0.0012	HOMO → LUMO+21	0.11	Ru → Ru	MLCT

E.4 Assignment of vibrational modes

Table E.4.1 Assignment of rR and IR for $[Ru(L^1)_2](PF_6)_2$

$\nu_{FT\text{-}IR}$ /cm^{-1}	$\nu_{rR}\lambda_{488\ nm}$ /cm^{-1}	$\nu_{rR}\lambda_{514\ nm}$ /cm^{-1}	ν_{Calc} /cm^{-1}	Assignment from Gauss View
500			500	OTerpy(L^1) and phosphazene out-of-plane ring def. ν. delocalised
556			553	OPh and phosphazene out-of-plane ring def. ν. delocalised
	657	658	663	OTerpy(L^1) and phosphazene in-plane ring def. ν. delocalised; out-of-plane H-wag
687	685	684	684	OTerpy(L^1) and phosphazene in-plane ring def. ν. delocalised; OPh out-of-plane ring def.
771			769	OPh out-of-plane ring def. and out-of-plane H-wag
	840	840	849	Phosphazene in-plane ring def.
845			PF_6^-	
880			882	OTerpy(L^1), OPh and phosphazene in-plane ring def. ν. delocalised
955			955	Phosphazene in-plane ring def.
	1017	1018	1018	Phosphazene in-plane ring def. and OTerpy(L^1) out-of-plane H-wag
	1045	1045	1048	OTerpy(L^1) in-plane ring def. and in-plane H-wag
1050			1055	OTerpy(L^1) in-plane ring def.; symm Ru-N stretch and in-plane H-wag
	1060		1078	OTerpy(L^1) in-plane ring def. and in-plane H-wag
1090			1094	OTerpy(L^1) in-plane ring def. and in-plane H-wag

Table E.4.1 Continued Assignment of rR and IR for $[Ru(L^1)_2](PF_6)_2$

$\nu_{FT\text{-}IR}$ /cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ /cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ /cm^{-1}	ν_{Calc} /cm^{-1}	Assignment from GaussView
	1097		1097	OTerpy(L^1) in-plane ring def. and in-plane H-wag
	1166	1165	1164	OTerpy(L^1) in-plane H-wag
1172			1177	OTerpy(L^1) and OPh in-plane ring def. and in-plane H-wag
	1253	1254	1253	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1265			1271	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
	1288	1289	1291	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
	1356	1355	1371	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1406			1406	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
	1473	1473	1464	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1488			1503	OTerpy(L^1) in-plane ring def., Ru-N wag and in-plane H-stretch
	1536	1534	1532	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
		1558	1575	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
	1564		1577	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1590			1578	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
	1610	1609	1584	OTerpy(L^1) in-plane ring def. and in-plane H-stretch

Table E.4.2 Assignment of rR and IR for $[Ru(L^1)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\ nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
526			529	Phosphazene, Terpy(L^1), Terpy and OPh out-of- plane ring def. v. delocalised
557			551	Phosphazene, Terpy(L^1) and OPh out-of-plane ring def. v. delocalised
	671	670	671	Phosphazene, Terpy(L^1) and OPh in-plane ring def. v. delocalised
689			689	OPh out-of-plane ring def.
	725		730	Terpy(L^1) out-of-plane ring def. and Ru-N(Terpy(L^1)) wag
772			770	OPh out-of-plane ring def. and out-of-plane H-wag
		802	808	Terpy in-pane ring def. and Ru-N(Terpy) wag
		837	835	OPh out-of-plane H-wag
850				PF_6^-
877		875	875	P-O stretch, Terpy(L^1) and OPh in-plane ring def.
		917	914	Terpy(L^1) in-plane ring def. and C-O stretch
955			972	Terpy(L^1) out-of-plane H-wag
	1017	1020	1020	Terpy(L^1) and Terpy in-plane ring def.; out-of-plane H-wag and Ru-N symm. stretch
1025			1025	Terpy in-plane ring def. and Ru-N(Terpy) stretch
		1046	1041	Terpy in-plane ring def. and in-plane H-wag

Table E.4.2 Continued Assignment of rR and IR for $[Ru(L^1)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1057		1058	OPh in-plane ring def. and in-plane H-wag
	1095		1096	Terpy(L^1) and Terpy in-plane ring def.; in-plane H-wag
		1124	1122	Terpy in-plane ring def. and in-plane H-wag
	1162		1162	Terpy(L^1) and Terpy in-plane ring def.; in-plane H-wag
		1170	1168	Terpy(L^1) in-plane ring def. and in-plane H-wag
1177			1173	OPh in-plane H-wag
	1258	1257	1256	Terpy(L^1) and Terpy in-plane ring def.; in-plane H-stretch
1261			1261	Terpy in-plane ring def., in-plane H-stretch and Ru-N(Terpy) wag
	1285	1287	1284	Terpy in-plane ring def., in-plane H-stretch and Ru-N(Terpy) wag
	1329		1335	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1351	1356	1357	Terpy in-plane ring def. and in-plane H-stretch
1404			1406	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1473	1472	1463	Terpy in-plane ring def. and in-plane H-stretch
1487	1487		1505	Terpy(L^1) in-plane ring def., in-plane H-stretch and Ru-N(Terpy(L^1)) wag
		1539	1534	Terpy(L^1) and Terpy in-plane ring def.; in-plane H-stretch

Table E.4.2 Continued Assignment of rR and IR for $[Ru(L^1)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\,\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\,\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from Gauss View
	1549		1535	Terpy(L^1) and Terpy in-plane ring def.; in-plane H-stretch
1590			1578	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1608	1609	1581	Terpy(L^1) in-plane ring def. and in-plane H-stretch

Table E.4.3 Assignment of rR and IR for $[Ru(L^1)(PhTerpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
501			502	Phosphazene, Terpy(L^1) and PhTerpy out-of-plane ring def. v. delocalised
556			550	Phosphazene and Terpy(L^1) out-of-plane ring def. v. delocalised
	660	663	672	Phosphazene and Terpy(L^1) in-plane ring def. v. delocalised
688	690		693	PhTerpy(Ph) out-of-plane ring def.
765			765	OPh out-of-plane ring def. and out-of-plane H-wag
		804	808	PhTerpy in-plane ring def. and Ru-N(PhTerpy) stretch
	829	832	829	PhTerpy(Terpy) out-of-plane ring def. and P-O stretch
845				PF_6^-
888			893	Out-of-plane H(Terpy)-wag
956			953	Phosphazene in-plane ring def.
	1017	1020	1020	PhTerpy in-plane ring def. and sym Ru-N stretch
		1045	1041	PhTerpy in-plane ring def. and Ru-N(PhTerpy) stretch
	1057		1050	H(Terpy)-wag in-plane and Ru-N(Terpy(L^1)) stretch
	1094		1096	Terpy(L^1) and PhTerpy in-plane ring def.; in-plane H-wag
1159			1159	Terpy(L^1) and PhTerpy in-plane ring def.; in-plane H-wag

Table E.4.3 Continued Assignment of rR and IR for $[Ru(L^1)(PhTerpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1163	1163	1163	Terpy(L^1) and PhTerpy in-plane ring def.; in-plane H-wag
1196			1184	PhTerpy(Ph) in-plane ring def. and in-plane H-wag
1258	1257	1257	1258	Terpy(L^1) and PhTerpy in-plane ring def.
		1283	1272	PhTerpy in-plane ring def. and in-plane H-stretch
	1288		1275	Terpy(L^1) in-plane ring def. and Ru-N(Terpy(L^1)) wag
	1355	1354	1338	PhTerpy in-plane ring def. and in-plane H-stretch
1404			1407	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1474	1476	1474	C-C (PhTerpy) stretch and in-plane H-stretch
1486			1494	PhTerpy in-plane ring def., Ru-N(PhTerpy) wag and in-plane H-stretch
		1543	1534	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1548		1559	PhTerpy(Ph) in-plane ring def.
1589			1582	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1610	1608	1585	PhTerpy in-plane ring def. and in-plane H-stretch

Table E.4.4 Assignment of rR and IR for $[Ru(L^2)_2](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\,\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\,\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
498			498	OPhTerpy(L^2) out-of-plane ring def.
556			556	OPhTerpy(L^2) in-plane ring def.
	658		665	OPhTerpy(L^2) in-plane ring def. and P-O bond stretch
		662	668	OPhTerpy(L^2) in-plane ring def. and P-O bond stretch
	685		685	OPhTerpy(L^2) in-plane ring def. and P-O bond stretch
689			689	OPh out-of-plane ring def.
		754	756	OPhTerpy(L^2) out-of-plane ring def. and out-of-plane ring wag
772			772	OPh out-of-plane ring def. and out-of-plane H-wag
		797	802	OPhTerpy(L^2) in-plane ring def. and sym. Ru-N stretching
	839	842	841	OPhTerpy(L^2) out-of-plane ring def. and out-of-plane ring wag
846				PF_6^-
883			879	Phosphazene in-plane ring def.
956			953	Phosphazene in-plane ring def.
	1017	1020	1022	OPhTerpy(L^2) in-plane ring def. and asym. Ru-N stretching
	1048	1047	1040	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag

Table E.4.4 Continued Assignment of rR and IR for $[Ru(L^2)_2](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\,nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1097		1097	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
1159			1160	OPh in-plane ring def. and in-plane H-wag
	1163	1165	1165	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
1177			1179	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
	1257	1257	1257	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1264			1270	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1288	1286	1286	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1355	1353	1340	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1403			1400	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1474	1475	1487	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1488			1492	OPhTerpy(L^2) in-plane ring def. and Ru-N wag in-plane H-stretch
	1548	1546	1542	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1590			1578	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1609	1608	1594	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch

Table E.4.5 Assignment of rR and IR for $[Ru(L^2)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
555			577	Phosphazene, OPh and OPhTerpy(L^2) out-of-plane ring def. v. delocalised
	672	671	668	Phosphazene, OPh and OPhTerpy(L^2) out-of-plane ring def. v. delocalised
688			688	OPh out-of-plane ring def.
	726		729	OPhTerpy(L^2) out-of-plane ring def.
764			767	Out-of-plane H(OPh)-wag
		803	805	OPhTerpy(L^2) in-plane ring def. and Ru-N(Terpy(L^2)) stretch
	835	838	835	OPhTerpy(L^2)(Ph) and OPh in-plane ring def.; P-O stretch
841			PF_6^-	
880		878	875	Phosphazene and OPhTerpy(L^2)(Ph) in-plane ring def.
		915	908	OPhTerpy(L^2) out-of-plane ring def.
951			955	Phosphazene in-plane def.
	1018	1019	1014	OPhTerpy(L^2) and Terpy in-plane ring def.; symm Ru-N stretching
	1050	1049	1043	OPhTerpy in-pane ring def and in-plane H-wag
	1098		1096	OPhTerpy(L^2) and Terpy in-plane ring def.; in-plane ring H-wag
		1124	1122	Terpy in-plane ring def., Ru-N(Terpy) wag and in-plane H-wag

Table E.4.5 Continued Assignment of rR and IR for $[Ru(L^2)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1160			1159	OPh in-plane H-wag
	1164	1166	1164	Terpy in-plane H-wag
1176			1177	OPhTerpy(L^2)(Ph) in-plane H-wag
	1256	1256	1256	OPhTerpy(L^2) and Terpy in-plane ring def.
1266			1269	Terpy in-plane H-stretch
	1288	1288	1288	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1328		1341	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1358	1356	1358	OPhTerpy in-plane ring def. and in-plane H-stretch
1388			1387	OPhTerpy(L^2) in-plane ring def., Ru-N(OPhTerpy(L^2)) and in-plane H-stretch
1407			1410	Terpy in-plane def and in-plane H-stretch
1449			1449	OPhTerpy(L^2) and Terpy in-plane ring def.; in-plane H-stretch
	1473	1472	1463	Terpy in-plane def. and H-stretch
1487			1492	OPhTerpy(L^2)(Ph) in-plane ring def. and C-O stretch
	1536		1534	Terpy in-plane ring def., Ru-N(Terpy) wag and in-plane H-stretch
		1546	1539	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch

Table E.4.5 Continued Assignment of rR and IR for $[Ru(L^2)(Terpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1590			1580	OPhTerpy(L^2)(Ph) and (Terpy) in-plane ring def.; in-plane H-stretch
	1609	1608	1594	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch

Table E.4.6 Assignment of rR and IR for $[Ru(L^2)(PhTerpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from Gauss View
499			499	OPhTerpy(L^2) out-of-plane ring def. v. delocalised
556			553	Phosphazene and OPhTerpy(L^2) in-plane ring def.; Ru-N(OPhTerpy(L^2)) stretch v. delocalised
		662	668	Phosphazene and OPhTerpy(L^2) in-plane ring def. v. delocalised
	671		678	PhTerpy in-plane def.
689			689	OPh out-of-plane ring def.
	726		729	OPh out-of-plane ring def. and Ru-N wag
732			732	OPhTerpy(L^2) out-of-plane ring def. and Ru-N wag
764			767	OPh out-of-plane H-wag
	835	834	836	OPhTerpy(L^2) and OPh in-plane ring def.; P-O stretch
837				PF_6^-
880			875	OPhTerpy(L^2) and OPh in-plane ring def.; P-O stretch
955			956	Phosphazene in-plane ring def.
	1016	1018	1014	OPhTerpy(L^2) and PhTerpy in-plane ring def.; symm Ru-N stretch
1049		1046	1042	PhTerpy in-plane ring def. and Ru-N(PhTerpy) stretch

Table E.4.6 Continued Assignment of rR and IR for $[Ru(L^2)(PhTerpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1057		1060	OPhTerpy(L^2) and PhTerpy in-plane ring def.; say Ru-N(OPhTerpy(L^2), PhTerpy) stretch and in-plane H-wag
	1126		1115	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-wag
	1162	1164	1165	OPhTerpy(L^2) and PhTerpy in-plane H-wag
1180			1178	OPhTerpy(L^2)(Ph) in-plane ring def.; in-plane H-wag and C-O stretch
	1256	1253	1253	PhTerpy in-plane ring def. and in-plane H-stretch
1267			1268	PhTerpy in-plane ring def., in-plane H-stretch and Ru-N(PhTerpy)-wag
	1288	1288	1288	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1329		1330	PhTerpy(Ph) in-plane ring def. and in-plane H-stretch
	1357	1355	1340	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1406			1400	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1471	1473	1475	C-C(PhTerpy) stretch in-plane ard in-plane H-stretch
1487			1492	C-O stretch C-C(PhTerpy) stretch in-plane and in-plane H-stretch
	1533	1534	1532	OPhTerpy PhTerpy in-plane H wag ring def.
	1548		1540	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch

Table E.4.6 Continued Assignment of rR and IR for $[Ru(L^2)(PhTerpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1591			1586	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch
	1607	1610	1594	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch

Table E.4.7 Assignment of rR and IR for $[Ru(L^3)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
556			557	Phosphazene, Obbp(L^3), Terpy and OPh out-of-plane ring def. v. delocalised
	673		672	Phosphazene, Obbp(L^3) and Terpy out-of-plane ring def. v. delocalised
		676	677	Phosphazene, Obbp(L^3) and Terpy out-of-plane ring def. v. delocalised
698			691	Phosphazene and OPh out-of-plan ring def.
	733		736	Phosphazene, Obbp(L^3) and Terpy out-of-plane ring def. v. delocalised
767			767	Benz and OPh out-of-plane H-wag
848				PF_6^-
	918		919	Obbp(L^3) in-plane ring def. and C-O stretching
		922	923	Obbp(L^3) in-plane ring def. and C-O stretching
956			956	Obbp(L^3) out-of-plane H-wag
		1018	1018	Obbp(L^3) and Terpy in-plane ring def. and symm Ru-N(Obbp and Terpy) stretch
	1020		1022	Obbp(L^3) and Terpy in-plane ring def. and symm Ru-N(Obbp and Terpy) stretch
	1162		1163	Obbp(L^3) in-plane ring def. and Ru-N(Obbp) rock
1177			1171	OPh in-plane H-wag
1267			1267	Obbp(L^3) and Terpy in-plane ring def.; in-plane H-stretch

Table E.4.7 Continued Assignment of rR and IR for $[Ru(L^3)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{RR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{RR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1287		1286	Terpy in-plane ring def. and in-plane H-stretch
	1328	1331	1341	Obbp(L^3) in-plane ring def. and in-plane H-stretch
		1377	1363	Obbp(L^3) in-plane ring def. and in-plane H-stretch
1380	1380		1372	Obbp(L^3) in-plane ring def. and in-plane H-stretch
1450			1450	OPh in-plane ring def. and in-plane H-stretch
	1465	1460	1461	Obbp(L^3) in-plane ring def. and in-plane H-stretch
1488	1486	1486	1500	Obbp(L^3) in-plane ring def., in-plane H-stretch and Ru-N(Obbp(L^3)) wag
		1545	1572	Terpy in-plane ring def. and in-plane H-stretch
1590			1579	Terpy in-plane ring def. and in-plane H-stretch
		1614	1590	Obbp(L^3) in-plane ring def. and in-plane H-stretch

Table E.4.8 Assignment of rR and IR for $[Ru(L^3)(PhTerpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	658		646	PhTerpy in-plane ring def.
		666	675	Obbp(L^3), phosphazene and OPh out-of-plane ring def. ν. delocalised
688			686	OPh out-of-plane ring def.
762			758	Obbp(L^3) and PhTerpy H-wag out-of-plane
	831		823	PhTerpy in-plane ring def. and Ru-N(PhTerpy) wag
		835	837	Obbp(L^3) in-plane ring def. and Ru-N(Obbp(L^3)) wag
836				PF_6^-
	917	922	920	Obbp(L^3) in-plane ring def. and H-wag out-of-plane
956			957	Obbp(L^3) H-wag out-of-plane
	1019	1020	1020	Obbp(L^3) and PhTerpy in-plane ring def.; sym Ru-N stretching
		1044	1042	PhTerpy in-plane ring def. and in-plane H-wag
		1091	1085	Obbp(L^3) in-plane ring def. and in-plane H-wag
	1094		1096	PhTerpy in-plane ring def. and in-plane H-wag
1160	1162	1160	1155	Obbp(L^3) in-plane H-wag
1176			1172	OPh in-plane H-wag

Table E.4.8 Continued Assignment of rR and IR for $[Ru(L^3)(PhTerpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	ν_{rR} $\lambda_{488\,nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1249		1250	PhTerpy in-plane ring def. and in-plane H-stretch
		1254	1255	PhTerpy in-plane ring def. and in-plane H-stretch
1267			1267	PhTerpy in-plane ring def. and in-plane H-stretch
	1286	1286	1287	PhTerpy in-plane ring def. and in-plane H-stretch
	1355	1355	1362	Obbp(L^3) in-plane ring def. and in-plane H-stretch
1455			1455	PhTerpy in-plane ring def. and in-plane H-stretch
	1471	1473	1474	PhTerpy in-plane ring def. and in-plane H-stretch
1487			1496	PhTerpy in-plane ring def.; in-plane H-stretch and Ru-N(Obbp(L^3)) wag
	1535	1534	1533	PhTerpy in-plane ring def. and in-plane H-stretch
1591			1591	Obbp(L^3) in-plane ring def. and in-plane H-stretch
	1607	1609	1601	Obbp(L^3) in-plane ring def. and in-plane H-stretch
1611			1604	Obbp(L^3) in-plane ring def. and in-plane H-stretch

Table E.4.9 Assignment of rR and IR for $[Ru(L^1)(bbp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	685		683	OPh out-of-plane ring def.
688		689	689	OPh and Phosphazene out-of-plane ring def.
772			772	OPh out-of-plane ring def.
	800	803	804	bbp out-of-plane ring def. and Ru-N(bbp) wag
845			PF_6^-	
	917	921	918	OTerpy(L^1) in-plane ring def. and C-O stretch
959			959	Bbp out-of-plane ring def. and out-of-plane H-wag
	1017		1016	Phosphazene in-plane ring def.
		1020	1019	Sym. Ru-N(bbp and OTerpy(L^1)) stretching
		1049	1050	OTerpy(L^1) in-plane ring def. and in-plane H-wag
	1156	1154	1155	Bbp in-plane H-wag
1159			1159	OPh in-plane H-wag
1176			1173	OPh and OTerpy(L^1) in-plane H-wag
	1255		1256	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1261		1261	1259	OTerpy(L^1) in-plane ring def. and in-plane H-stretch

Table E.4.9 Continued Assignment of rR and IR for $[Ru(L^1)(bbp)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	ν_{rR} $\lambda_{488\,nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1279		1285	bbp in-plane ring def., in-plane H-stretch and Ru-N(bbp) wag
	1350	1351	1361	bbp in-plane ring def. and in-plane H-stretch
1403			1404	bbp in-plane ring def., in-plane H-stretch and Ru-N(bbp) wag
1460			1458	bbp in-plane ring def. and in-plane H-stretch
	1473	1474	1463	bbp in-plane ring def. and in-plane H-stretch
1487			1488	bbp in-plane ring def. and in-plane H-stretch
	1547	1544	1534	OTerpy(L^1) in-plane ring def. and in-plane H-stretch
1591			1580	bbp in-plane ring def. and in-plane H-stretch
	1607	1608	1601	bbp in-plane ring def. and in-plane H-stretch

Table E.4.10 Assignment of rR and IR for $[Ru(L^2)(bbp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
557			557	OPhTerpy(L^2), OPh, and Phosphazene out-of-plane ring def.; and Ru-N(OPhTerpy(L^2)) stretch v. delocalised
	656		664	bbp in-plane ring def. and Ru-N(bbp) stretch
	684		684	Phosphazene and OPh out-of-plane ring def.
		689	689	Phosphazene and OPh out-of-plane ring def.
747			740	bbp out-of-plane ring def., out of plane H-wag and Ru-N(bbp) wag
770			770	bbp and OPh out-of-plane ring def., out-of-plane H-wag
		803	804	bbp out-of-plane H-wag
	837		835	OPhTerpy(L^2) out-of-plane ring def., out-of-plane H-wag and P-O stretch
844				PF_6^-
		921	922	OPh out-of-plane ring def. and out-of-plane H-wag
952			950	bbp in-plane ring def. and Ru-N(bbp) stretch
	1016		1012	OPhTerpy(L^2) and Phosphazene in-plane ring def.
		1020	1024	OPhTerpy(L^2) in-plane ring def. and Ru-N(OPhTerpy(L^2)) stretch
	1044	1049	1041	OPhTerpy(L^2) in-plane ring def. and Ru-N(OPhTerpy(L^2)) stretch

Table E.4.10 Continued Assignment of rR and IR for $[Ru(L^2)(bbp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1095		1097	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
		1154	1155	bbp in-plane H-wag
	1158		1158	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
1177			1175	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
	1248		1234	bbp in-plane ring def. and in-plane H-stretch
1267		1261	1263	bbp in-plane ring def. and in-plane H-stretch
	1286		1286	bbp in-plane ring def., in-plane H-stretch and Ru-N(bbp) wag
		1351	1342	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1355		1362	bbp in-plane ring def. and in-plane H-stretch
1460			1458	bbp in-plane ring def. and in-plane H-stretch
	1470	1474	1463	bbp in-plane ring def. and in-plane H-stretch
1488			1488	bbp in-plane ring def. and in-plane H-stretch
	1533		1534	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
		1544	1542	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch
	1553		1567	OPhTerpy(L^2)(Ph) and bbp in-plane ring def. and in-plane H-stretch

Table E.4.10 Continued Assignment of rR and IR for $[Ru(L^2)(bbp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1591			1594	OPhTerpy(L^2)(Ph) in-plane ring def. and in-plane H-stretch
	1607	1608	1602	bbp in-plane ring def. and in-plane H-stretch

Table E.4.11 Assignment of rR and IR for $[Ru(L^4)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	674	676	674	OPhbpp (L^4) in-plane ring def. and phosphazene out-of-plane ring def.
689			693	Phosphazene and OPh out-of-plane ring def.
	727		730	OPhbpp (L^4) out-of-plane ring def. and Ru-N(OPhbbp) wag
		732	737	OPhbpp (L^4) in-plane ring def.
763			763	OPhbpp (L^4) out-of-plane H-stretch
844			PF_6^-	
880			876	OPhbpp (L^4) out-of-plane ring def.
952			953	Phosphazene in-plane ring def.
	1017	1017	1013	OPhbpp (L^4) and Terpy in-plane ring def. sym Ru-N(OPhbpp (L^4) and Terpy) stretch
1049			1044	Terpy in-plane ring def. and in-plane H-wag
	1058	1057	1053	OPhbpp (L^4) in-plane ring def. and Ru-N(OPhbpp (L^4)) stretch
		1090	1098	OPhbpp (L^4) and Terpy in-plane ring def. and in-plane H-wag
	1094		1099	OPhbpp (L^4) and Terpy in-plane ring def. and in-plane H-wag
	1161	1159	1164	Terpy in-plane H-wag
1179	1180		1175	OPhbpp (L^4) in-plane H-wag

Table E.4.11 Continued Assignment of rR and IR for $[Ru(L^4)(Terpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1267			1268	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
	1270	1272	1269	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
	1327	1328	1340	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
		1355	1361	Terpy in-plane ring def. and in-plane H-stretch
1415			1413	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
	1468		1466	Terpy in-plane ring def. and in-plane H-stretch
1486	1489	1487	1482	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
		1548	1537	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch
1590			1577	OPh in-plane ring def. and in-plane H-streich
	1605		1578	Terpy in-plane ring def. and in-plane H-stretch
		1615	1578	Terpy in-plane ring def. and in-plane H-stretch
	1621		1599	OPhbpp (L^4) in-plane ring def. and in-plane H-stretch

Table E.4.12 Assignment of rR and IR for $[Ru(L^4)(PhTerpy)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	660	663	674	OPhbpp(L^4) in-plane ring def.
688			688	OPh out-of-plane ring def. out-of-plane H-wag
763			763	OPhbpp(L^4) in-plane ring def. out-of-plane H-wag
		799	794	PhTerpy out-of-plane ring def. out-of-plane H-wag
	830	832	827	OPhbpp(L^4) out-of-plane ring def. out-of-plane H-wag
844				PF_6^-
950			953	Phosphazene in-plane ring def.
	1003		1000	OPhbpp(L^4) and PhTerpy in-plane ring def.; asym Ru-N stretch
		1009	1006	OPhbpp(L^4) and PhTerpy in-plane ring def.
		1049	1051	OPhbpp(L^4) in-plane ring def. and in-plane H-wag
	1058		1055	OPhbpp(L^4) in-plane ring def. and in-plane H-wag
		1091	1097	PhTerpy in-plane ring def. and in-plane H-wag
	1094		1099	OPhbpp(L^4) in-plane ring def. and in-plane H-wag
1160	1162	1162	1162	OPh in-plane ring def. and in-plane H-wag
1177			1175	OPhbpp(L^4) in-plane ring def. and in-plane H-wag

Table E.4.12 Continued Assignment of rR and IR for $[Ru(L^4)(PhTerpy)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\ \lambda_{488\ nm}$ / cm^{-1}	$\nu_{rR}\ \lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1252	1253	1252	PhTerpy in-plane ring def. and in-plane H-stretch
1266			1267	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch
	1289	1288	1286	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch
	1355	1355	1341	OPhbpp(L^4) and PhTerpy in-plane ring def.; in-plane H-stretch
1415			1412	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch
	1472	1472	1474	PhTerpy in-plane ring def. and in-plane H-stretch
1487			1482	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch
	1536	1535	1534	PhTerpy in-plane ring def. and in-plane H-stretch
	1563		1566	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch
1590			1586	PhTerpy in-plane ring def. and in-plane H-stretch
	1607	1608	1598	OPhbpp(L^4) in-plane ring def. and in-plane H-stretch

Table E.4.13 Assignment of rR and IR for $[Ru(L^1)(bpp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\,nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from Gauss View
557			557	bpp in-plane ring def. and Ru-N(bpp) wag
	652	654	646	Terpy(L^1) in-plane ring def.
690			690	OPh out-of-plane ring def.
773			772	OPh out-of-plane H-wag
	801	803	793	Terpy(L^1) in-plane ring def.
849			PF_6^-	
	920	918	923	bpp in-plane ring def. and Ru-N(bpp) stretch
	950	948	942	bpp out-of-plane ring def. and phosphazene in-plane ring def.
956			972	OPh in-plane ring def.
		1021	1022	Terpy(L^1) and bpp in-plane ring def.; sym Ru-N(Terpy(L^1) and bpp) stretch
	1037		1032	Terpy(L^1) in-plane ring def.
	1162	1162	1163	Terpy(L^1) in-plane H-wag
1177			1182	Bpp in-plane ring def. and in-plane H-wag
1259	1262	1261	1259	Terpy(L^1) in-plane ring def.
	1283		1278	Terpy(L^1) in-plane ring def. and Ru-N(Terpy(L^1))

Table E.4.13 Continued Assignment of rR and IR for $[Ru(L^1)(bpp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{488\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1357	1355	1337	Terpy(L^1) in-plane ring def., in-plane H-stretch and C-O stretch
1405			1406	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1411		1414	Terpy(L^1) in-plane ring def. and in-plane H-stretch
	1478	1475	1462	Terpy(L^1) in-plane ring def. and in-plane H-stretch
1485			1483	bpp in-plane ring def. and in-plane H-stretch
	1554	1551	1540	bpp in-plane ring def., in-plane H-stretch and Ru-N(bpp) wag
1591			1577	Terpy(L^1) in-plane H-stretch
	1610	1607	1583	bpp in-plane ring def., in-plane H-stretch and Ru-N(bpp) wag

Table E.4.14 Assignment of rR and IR for $[Ru(L^2)(bpp)](PF_6)_2$

ν_{FT-IR} / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from Gauss View
556			556	OPhTerpy(L^2) and phosphazene in-plane ring def. v. delocalised
		651	640	OPhTerpy(L^2) and phosphazene in-plane ring def. v. delocalised
	654		646	OPhTerpy(L^2) and phosphazene in-plane ring def. v. delocalised
	685		685	OPhTerpy(L^2) and phosphazene in-plane ring def. v. delocalised
688			688	OPh out-of-plane ring def.
		713	714	OPhTerpy(L^2) and phosphazene in-plane ring def. v. delocalised
		750	752	OPhTerpy(L^2) out-of-plane ring def. and out-of-plane H-wag
773			770	OPh out-of-plane ring def. and out-of-plane H-wag
		789	790	bpp out-of-plane ring def. and out-of-plane H-wag
		803	805	OPhTerpy(L^2) in-plane ring def.
	837	839	845	OPhTerpy(L^2) in-plane ring def. and P-O stretching
845				PF_6^-
	918		913	bpp out-of-plane ring def. and out-of-plane H-wag
		921	923	bpp in-plane ring def. and in-plane H-wag
	950	949	954	OPhTerpy(L^2) and phosphazene in-plane ring def.

Table E.4.14 Continued Assignment of rR and IR for $[Ru(L^2)(bpp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from Gauss View
954			954	Phosphazene in-plane ring def.
		1025	1025	OPhTerpy(L^2) in-plane ring def. and Ru-N asym. stretching
	1031		1031	OPhTerpy(L^2) and Phosphazene in-plane ring def.
		1045	1041	OPhTerpy(L^2) in-plane ring def. and Ru-N asym. stretching
	1048		1050	bpp in-plane ring def. and in-plane H-wag
	1164		1165	OPhTerpy(L^2) in-plane H-wag
		1168	1170	bpp in-plane H-wag
1178			1177	OPhTerpy(L^2) in-plane ring def. and in-plane H-wag
	1219	1222	1225	OPhTerpy(L^2) in-plane ring def., in-plane H-stretch and C-O stretch
	1256	1256	1255	OPhTerpy(L^2) in-plane ring def., in-plane H-stretch and Ru-N wag
1269			1273	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1290	1288	1286	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1358	1358	1343	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1471		1454	bpp in-plane ring def. and in-plane H-stretch
		1475	1481	bpp in-plane ring def. and in-plane H-stretch

Table E.4.14 Continued Assignment of rR and IR for $[Ru(L^2)(bpp)](PF_6)_2$

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{488\ nm}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1487			1492	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1539	1538	1539	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
1591			1580	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch
	1610	1610	1594	OPhTerpy(L^2) in-plane ring def. and in-plane H-stretch

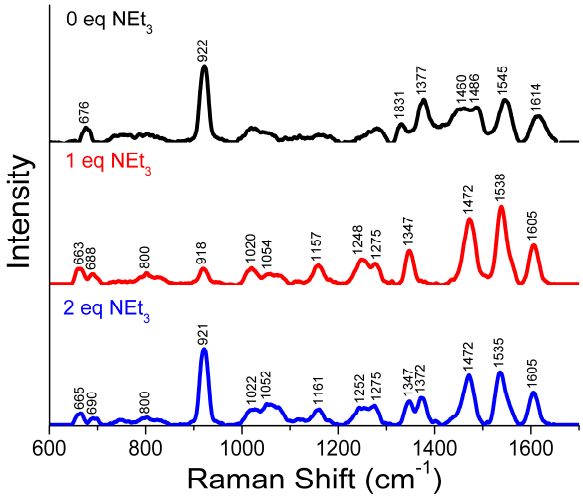

Figure E.4.1 rR collected with λ_{ex} = 514 nm. Titration of NEt_3 with $[Ru(L^3)(Terpy)](PF_6)_2$.

Appendix F: Chapter 7 Supplementary

F.1 Instrumentation

F.1.1 Electrochemistry

Cyclic voltammetry was obtained using a glassy carbon working electrode, Pt counter electrode and Ag/AgCl reference electrode, $\nu = 0.1$ V s^{-1} on a BAS 100B Electrochemical Workstation (Bioanalytical System Inc.), calibrated with ferrocene. $[Fe(L^1)_2](PF_6)_2$ and $[Fe(L^2)_2](PF_6)_2$ were recorded in acetonitrile, 0.1 M tetrabutylammonium hexfluorophosphate ($TBAPF_6$) at 10^{-3} M; $[Fe(L^1)_2](ClO_4)_2$, $[Fe(L^2)_2](ClO_4)_2$, $[Fe(L^3)_2](ClO_4)_2$ and $[Fe(L^4)_2](ClO_4)_2$ were recorded in acetonitrile, 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) at 10^{-3} M; $[Fe(L^3)_2](BF_4)_2$ was recorded in acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) at 10^{-3} M.

F.1.2 UV-Visible spectroscopy

UV-Visible absorbance spectra were recorded on an Oceans Optics USB2000+UV-Vis spectrophotometer with a variable temperature cell holder ± 0.05°C with a Quantum Northwest controller.

Small molecule complexes ($[Fe(L^1)_2](ClO_4)_2$, $[Fe(L^1)_2](PF_6)_2$, $[Fe(L^2)_2](ClO_4)_2$, $[Fe(L^2)_2](PF_6)_2$, $[Fe(L^3)_2](ClO_4)_2$, $[Fe(L^3)_2](BF4_4)_2$ and $[Fe(L^4)_2](ClO_4)_2$) were in acetonitrile at 10^{-5} M for the room temperature measurements and benzonitrile at 10^{-5} M for the variable temperature measurements. The thermal expansion of the solutions was based on the density of the solvent as described in the literature.

The polymeric complexes ($[Fe(L^{1P})_2](ClO_4)_2$, $[Fe(L^{2P})_2](ClO_4)_2$, $[Fe(L^{3P})_2](ClO_4)_2$ and $[Fe(L^{4P})_2](ClO_4)_2$) were recorded in chloroform at 10^{-5} M for all temperatures. The thermal expansion of the solutions was based on the density of the solvent as described in the literature.

F.1.3 Vibrational spectroscopy

All ground state vibrational measurements were taken using KBr disks on a Nicolet 5700 FT-IR spectrometer. Resonance Raman spectra were recorded by Raphael Horvath and Keith Gordon at Otago University. Resonance Raman measurements were carried out based on a modified version of a system described previously.[1-3] Spectra were acquired of solid-state samples at 79 K, 298 K and 362 K with a number of excitation wavelengths. Temperature control was achieved by utilising a variable temperature cell (Specac, Woodstock, GA, USA) and a high stability temperature controller (Specac, Woodstock, GA, USA). Vacuum-purging of the cell was used to minimise condensation and frosting of the quartz window of the variable temperature cell. For excitation at 350.7 and 568.1 nm, a continuous-wave Innova I-302 krypton-ion laser (Coherent, Inc.) was used. For excitation at 457.9 and 514.5 nm an Innova Sabre DBW argon-ion laser (Coherent, Inc.). The beam was passed through either a Pellin-Broca prism (for 350.7, 457.9 and 514.5 nm) or a holographic laser bandpass filter (Kaiser Optical Systems, Inc.) and subsequently two irises in order to remove unwanted laser-lines. The beam-power was adjusted between 20 - 40 mW at the sample, depending on the wavelength used. The sample and collection lens were arranged in a 180˚ backscattering geometry where the collection lens also served to focus the excitation beam on the sample. The Raman photons were focussed on the entrance slit of an Acton Research SpectraPro500i spectrograph (Princeton Instruments, Inc.) with a 1200 grooves mm^{-1} grating. The slit width was set to 50 µm, giving a resolution of *ca.* 2 cm^{-1}. Radiation from Raleigh and Mie-scattering was attenuated using a notch filter (Kaiser Optical Systems, Inc.) for 568.1 nm and RazorEdge filters (Semrock, Inc.) for other wavelengths. The dispersed photons were detected using a Princeton Instruments liquid nitrogen cooled 1152-EUV charge-coupled detector controlled by a Princeton Instruments ST-130 controller. WinSpec/32 software (Roper Scientific, Inc.) was used to control the CCD, and spectra were analysed using GRAMS/32 (Galactic Industries Corp.) software. Wavelength calibration was achieved using a reference sample made from 1:1 Toluene:Acetonitrile and general alignment was done using a solid sample of carbamazepine.

F.1.4 Magnetic susceptibility

Magnetic susceptibility data was recorded by Dr. Boujemaa Moubaraki at Monash University. Measurements were made using a Quantum Design MPMS 5 SQUID magnetometer operating with an applied field of 1T. The samples were loaded into a gelatine capsule held in the centre of a drinking straw fixed to the end of the sample rod.

F.1.5 Mössbauer spectroscopy

Under argon iron-57 (95% I.E.) powder was obtained from Isoflex. Fe-57$(ClO_4)_2 \cdot 6H_2O$ was produced by dissolving iron power (200 mg, 3.5 mmol) in acetonitrile (4 mL) and perchloric acid (2.5 mL, 17.5 mmol) was added. The solution was filtered and diethyl ether was added. The solution was cooled for -4°C yielding pale green crystals. The crystals were filtered and washed with diethyl ether.

^{57}Fe Mössbauer spectra were recorded by Dr. Guy N. L. Jameson at the University of Otago. Approximately 20 mg of sample was placed in a nylon sample holder (12.8 mm diameter, 1.6 mm thickness) with Kapton windows. Mössbauer spectra were measured on a Mössbauer spectrometer from SEE Co. (Science Engineering & Education Co., MN) equipped with a closed cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.). Data were collected in constant acceleration mode in transmission geometry with an applied field of 47 mT perpendicular to the γ-rays. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 μm metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co., Edina, MN).

F.2 Computational

F.2.1 Bond lengths

Table F.2.1.1 Average bond length difference for the cationic DFT models.

Level	Average bond length difference (Å)		
	$[Fe(L^1)_2]^{2+}$	$[Fe(L^2)_2]^{2+}$	$[Fe(L^3)_2]^{2+}$
B3LYP	0.021	0.021	0.021
OLYP	0.005	0.006	0.003

F.2.2 MAD values

Table F.2.2.1 A comparison of MAD values for B3LYP and OLYP.

Level	MAD values		
	$[Fe(L^1)_2]^{2+}$	$[Fe(L^2)_2]^{2+}$	$[Fe(L^3)_2]^{2+}$
B3LYP	4.52	4.08	7.70
OLYP	4.27	4.17	5.36

F.3 Electronic spectra assignment

On the basis that the OLYP/6-31G(d) provided the most accurate model of the cationic complex the electronic spectra were assigned by calculating each of the electronic transitions associated with the MLCT band. Shown in Tables F.3.1-4 are the first ten transitions with a non-zero oscillator strength.

Table F.3.1 Summary of the first ten transitions calculated for the cationic complex $[Fe(L^1)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+3	0.14	Fe → OTerpy(L^1)	
657	1.88	0.0014	HOMO-1 → LUMO	0.24	Fe → OTerpy(L^1)	MLCT
			HOMO → LUMO	0.62	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+2	0.26	Fe → OTerpy(L^1)	
653	1.89	0.0014	HOMO-1 → LUMO	0.59	Fe → OTerpy(L^1)	MLCT
			HOMO → LUMO	-0.25	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+1	-0.16	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+2	-0.12	Fe → OTerpy(L^1)	
643	1.92	0.0086	HOMO-1 → LUMO+3	-0.16	Fe → OTerpy(L^1)	MLCT
			HOMO → LUMO+1	0.64	Fe → OTerpy(L^1)	

Table F.3.1 continued. Summary of the first ten transitions calculated for the cationic complex $[Fe(L^1)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	-0.12	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+1	-0.13	Fe → OTerpy(L^1)	MLCT
628	1.97	0.0081	HOMO-1 → LUMO+3	0.12	Fe → OTerpy(L^1)	
			HOMO → LUMO+2	0.65	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+1	0.14	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.22	Fe → OTerpy(L^1)	MLCT
619	2.00	0.0079	HOMO-1 → LUMO+3	0.55	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+4	-0.29	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+1	0.59	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+2	0.19	Fe → OTerpy(L^1)	
614	2.01	0.0030	HOMO-2 →LUMO+3	0.10	Fe → OTerpy(L^1)	MLCT
			HOMO-1 →LUMO	-0.22	Fe → OTerpy(L^1)	
			HOMO-1 →LUMO+2	-0.12	Fe → OTerpy(L^1)	

Table F.3.1 continued. Summary of the first ten transitions calculated for the cationic complex $[Fe(L^1)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+1	-0.17	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+2	0.63	Fe → OTerpy(L^1)	
602	2.05	0.0030	HOMO-2 → LUMO+3	0.18	Fe → OTerpy(L^1)	MLCT
			HOMO-1 → LUMO	0.11	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.13	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+2	0.22	Fe → OTerpy(L^1)	
577	2.14	0.0339	HOMO-1 → LUMO+3	0.57	Fe → OTerpy(L^1)	MLCT
			HOMO → LUMO+1	0.20	Fe → OTerpy(L^1)	
			HOMO-2 → LUMO+2	-0.19	Fe → OTerpy(L^1)	MLCT
			HOMO-2 → LUMO+3	0.62	Fe → OTerpy(L^1)	
567	2.18	0.0297	HOMO-1 → LUMO+4	0.10	Fe → OTerpy(L^1)	
			HOMO → LUMO	-0.12	Fe → OTerpy(L^1)	

Table F.3.1 continued. Summary of the first ten transitions calculated for the cationic complex $[Fe(L^1)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.40	Fe → OTerpy(L^1)	
			HOMO-1 → LUMO+1	0.39	Fe → OTerpy(L^1)	
549	2.25	0.1629	HOMO-1 → LUMO+2	-0.20	Fe → OTerpy(L^1)	MLCT
			HOMO → LUMO+2	0.17	Fe → OTerpy(L^1)	
			HOMO →LUMO+5	0.11	Fe → OTerpy(L^1)	

Table F.3.2 Summary of the first ten transitions calculated for the cationic complex $[Fe(L^2)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
669	1.85	0.0086	HOMO-2 → LUMO+3	-0.10	Fe → OPhTerpy(L^2)	MLCT
			HOMO → LUMO	0.67	Fe → OPhTerpy(L^2)	
658	1.88	0.0090	HOMO-1 → LUMO+3	0.14	Fe → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	0.67	Fe → OPhTerpy(L^2)	
618	2.00	0.0106	HOMO-2 → LUMO	-0.25	Fe → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO+1	-0.20	Fe → OPhTerpy(L^2)	
			HOMO → LUMO+2	0.60	Fe → OPhTerpy(L^2)	
614	2.01	0.0025	HOMO-1 → LUMO+2	0.69	Fe → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO+3	0.10	Fe → OPhTerpy(L^2)	
598	2.07	0.0088	HOMO-2 → LUMO+2	0.60	Fe → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	-0.34	Fe → OPhTerpy(L^2)	
588	2.10	0.0267	HOMO-2 → LUMO	-0.15	Fe → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO+1	0.37	Fe → OPhTerpy(L^2)	
			HOMO → LUMO+2	0.13	Fe → OPhTerpy(L^2)	
			HOMO → LUMO+3	0.52	Fe → OPhTerpy(L^2)	

Table F.3.2 Continued Summary of the first ten transitions calculated for the cationic complex $[Fe(L^2)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	0.38	Fe → OPhTerpy(L^2)	
			HOMO-2 →LUMO+2	0.10	Fe → OPhTerpy(L^2)	
			HOMO-2 → LUMO+3	0.17	Fe → OPhTerpy(L^2)	
572	2.16	0.4578	HOMO-1 → LUMO+1	0.30	Fe → OPhTerpy(L^2)	MLCT
			HOMO-1 → LUMO+3	-0.13	Fe → OPhTerpy(L^2)	
			HOMO → LUMO+2	0.26	Fe → OPhTerpy(L^2)	
			HOMO → LUMO+3	-0.19	Fe → OPhTerpy(L^2)	
			HOMO-1 → LUMO+2	-0.10	Fe → OPhTerpy(L^2)	
571	2.16	0.0421	HOMO-1 → LUMO+3	0.64	Fe → OPhTerpy(L^2)	MLCT
			HOMO → LUMO+1	-0.10	Fe → OPhTerpy(L^2)	
			HOMO-2 → LUMO	-0.13	Fe → OPhTerpy(L^2)	
570	2.17	0.0745	HOMO-2 → LUMO+2	0.29	Fe → OPhTerpy(L^2)	MLCT
			HOMO-2 → LUMO+3	0.56	Fe → OPhTerpy(L^2)	

Table F.3.3 Summary of the first ten transitions calculated for the cationic complex $[Fe(L^3)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	-0.10	Fe → Obbp(L^3)	
			HOMO → LUMO	0.48	Fe → Obbp(L^3)	MLCT
779	1.59	0.0042	HOMO → LUMO+1	-0.41	Fe → Obbp(L^3)	
			HOMO → LUMO+2	-0.23	Fe → Obbp(L^3)	
			HOMO → LUMO+1	-0.37	Fe → Obbp(L^3)	
770	1.61	0.0032	HOMO →LUMO+2	0.53	Fe → Obbp(L^3)	MLCT
			HOMO → LUMO+3	-0.20	Fe → Obbp(L^3)	
			HOMO → LUMO	0.14	Fe → Obbp(L^3)	
757	1.64	0.0268	HOMO → LUMO+2	0.26	Fe → Obbp(L^3)	MLCT
			HOMO → LUMO+3	0.60	Fe → Obbp(L^3)	
			HOMO-2 → LUMO	0.51	Fe → Obbp(L^3)	
			HOMO-2 → LUMO+1	0.11	Fe → Obbp(L^3)	
613	2.02	0.0436	HOMO-2 → LUMO+2	0.31	Fe → Obbp(L^3)	MLCT
			HOMO-2 → LUMO+3	0.28	Fe → Obbp(L^3)	

Table F.3.3 Continued Summary of the first ten transitions calculated for the cationic complex $[Fe(L^3)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-1 → LUMO	-0.18	Fe → Obbp(L^3)	
609	2.03	0.0434	HOMO-1 → LUMO+1	-0.37	Fe → Obbp(L^3)	MLCT
			HOMO-1 → LUMO+3	0.53	Fe → Obbp(L^3)	
			HOMO-2 → LUMO	-0.24	Fe → Obbp(L^3)	
			HOMO-2 →LUMO+1	0.27	Fe → Obbp(L^3)	
			HOMO-2 → LUMO+2	0.24	Fe → Obbp(L^3)	
548	2.26	0.1370	HOMO-1 → LUMO+1	-0.24	Fe → Obbp(L^3)	MLCT
			HOMO-1 → LUMO+2	0.32	Fe → Obbp(L^3)	
			HOMO-1 → LUMO+3	-0.18	Fe → Obbp(L^3)	

Table F.3.4 Summary of the first ten transitions calculated for the cationic complex $[Fe(L^4)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
659	1.87	0.0064	HOMO → LUMO	0.68	Fe → OPhbpp(L^4)	MLCT
656	1.88	0.0064	HOMO → LUMO+1	0.68	Fe → OPhbpp(L^4)	MLCT
			HOMO-2 → LUMO	0.14	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+1	0.17	Fe → OPhbpp(L^4)	
553	2.23	0.0141	HOMO-1 → LUMO+1	-0.10	Fe → OPhbpp(L^4)	MLCT
			HOMO → LUMO+3	-0.39	Fe → OPhbpp(L^4)	
			HOMO → LUMO+4	0.50	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+1	-0.14	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO	0.23	Fe → OPhbpp(L^4)	
543	2.27	0.0037	HOMO-1 →LUMO+1	-0.15	Fe → OPhbpp(L^4)	MLCT
			HOMO → LUMO+3	0.47	Fe → OPhbpp(L^4)	
			HOMO → LUMO+4	0.37	Fe → OPhbpp(L^4)	

Table F.3.4 continued Summary of the first ten transitions calculated for the cationic complex $[Fe(L^4)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO	-0.27	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+1	-0.31	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO	-0.30	Fe → OPhbpp(L^4)	
512	2.42	0.9471	HOMO-1 → LUMO+1	0.27	Fe → OPhbpp(L^4)	MLCT
			HOMO → LUMO+3	-0.10	Fe → OPhbpp(L^4)	
			HOMO → LUMO+4	0.24	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+2	0.32	Fe → Fe	
			HOMO-2 → LUMO+4	-0.14	Fe → OPhbpp(L^4)	
507	2.44	0.0031	HOMO-2 → LUMO+5	-0.11	Fe → Fe-N*	MLCT
			HOMO-1 → LUMO+2	0.14	Fe → Fe	
			HOMO-1 → LUMO+3	0.55	Fe → OPhbpp(L^4)	

Table F.3.4 continued Summary of the first ten transitions calculated for the cationic complex $[Fe(L^4)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+3	0.30	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+4	0.38	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+2	-0.38	Fe → Fe	MLCT
504	2.45	0.0150	HOMO-1 → LUMO+3	0.20	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+4	-0.10	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+5	-0.18	Fe → Fe-N*	
			HOMO-2 → LUMO+2	0.35	Fe → Fe	
			HOMO-2 → LUMO+4	-0.19	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+5	-0.31	Fe → Fe-N*	
493	2.51	0.0050	HOMO-1 → LUMO+2	-0.22	Fe → Fe	MLCT
			HOMO-1 → LUMO+3	-0.23	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+4	0.28	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+5	-0.14	Fe → Fe-N*	

Table F.3.4 continued Summary of the first ten transitions calculated for the cationic complex $[Fe(L^4)_2]^{2+}$. Only transitions with nonzero oscillator strengths are shown.

λ/nm	*E*/eV	*f*	Orbital transition(s)	Coefficients	Major Contributors	Assignment
			HOMO-2 → LUMO+2	0.16	Fe → Fe	
			HOMO-2 → LUMO+3	-0.20	Fe → OPhbpp(L^4)	
			HOMO-2 → LUMO+4	0.53	Fe → OPhbpp(L^4)	
492	2.51	0.0092	HOMO-2 → LUMO+5	-0.11	Fe → Fe-N"	MLCT
			HOMO-1 → LUMO+2	0.20	Fe → Fe	
			HOMO-1 → LUMO+4	0.16	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+5	0.18	Fe → Fe-N"	
			HOMO-2 → LUMO+3	0.51	Fe → OPhbpp(L^4)	
			HOMO-1 → LUMO+2	0.14	Fe → Fe	
487	2.54	0.0103	HOMO-1 → LUMO+4	0.34	Fe → OPhbpp(L^4)	MLCT
			HOMO-1 → LUMO+5	0.24	Fe → Fe-N"	

F.4 Iron titration of L^3

The equilibrium of $Fe(BF_4)_2 \cdot 6H_2O$ and L^3 was studied by following the peak absorbance of the MLCT band as $Fe(BF_4)_2 \cdot 6H_2O$ was gradually added to an acetonitrile solution of L^3 at 20 ± 0.05°C (see spectra in Figure F.4.1). $Fe(BF_4)_2 \cdot 6H_2O$ was used for this investigation as it is less hydroscopic than $Fe(ClO_4)_2 \cdot 6H_2O$, allowing for an accurate calculation of concentration.

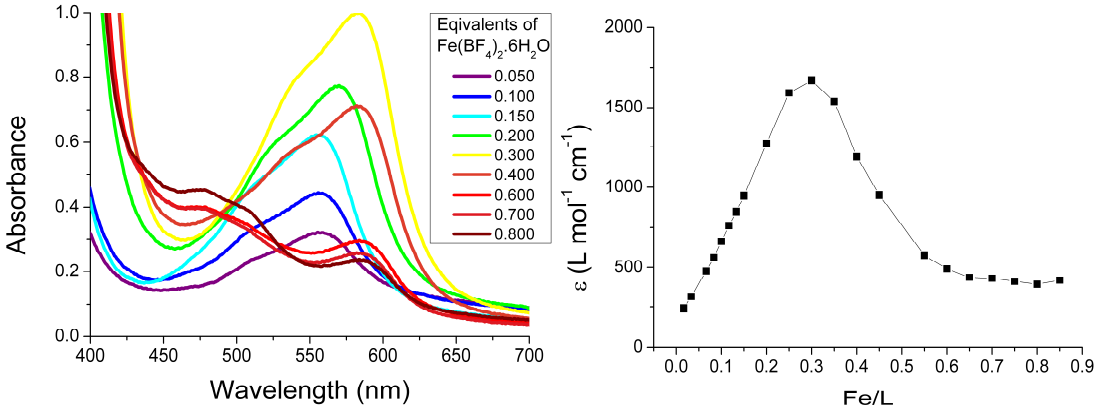

Figure F.4.1 Left: The spectra of L^3 as $Fe(BF_4)_2 \cdot 6H_2O$ was added. Right: A plot of peak absorbance vs. ratio of iron:ligand.

F.5 Assignment of vibrational modes

On the basis that the OLYP/6-31G(d) provided the most accurate model of the cationic complex the assignments of the perchlorate complexes vibrational spectra were made based on the calculated spectra (Tables F.5.1-4).

Table F.5.1 DFT assigned vibrational modes for $[Fe(L^1)_2](ClO_4)$.

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\,\lambda_{514\,nm}$ / cm^{-1}	$\nu_{rR}\,\lambda_{568nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
622			622	OTerpy(L^1) in-plane deform
		655	648	OTerpy(L^1) and CTP out of plane deform v. delocalised
689			686	OTerpy(L^1) and CTP out of plane deform v. delocalised
		694	692	OTerpy(L^1) and CTP out of plane deform v. delocalised
771			770	CTP and OPh deform v delocalised
840			841	OTerpy out-of-plan distortion
879			879	CTP out-of-plan deform and P-O stretch
955				ClO_4^-
		1020	1015	OPh ring in-plane deform and H-stretch
1092			1086	CTP in-plane deform
1159		1160	1160	OPh and OTerpy in-plane deform, H in-plane stretch
1177				ClO_4^-
		1243	1245	OTerpy(L^1) in-plane ring deform and H-stretch

Table F.5.1 Continued DFT assigned vibrational modes for $[Fe(L^1)_2](ClO_4)$.

$\nu_{FT\text{-}IR}$ / cm^{-1}	$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{568nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1262		1261	1259	OTerpy(L^1) in-plane ring deform and H-stretch
	1286	1287	1285	OTerpy(L^1) in-plane ring deform and H-stretch
	1357	1358	1338	OTerpy(L^1) and OPh in-plane ring deform and H-stretch
	1472	1471	1468	OTerpy(L^1) in-plane ring deform and H-stretch
1487	1488	1488	1498	OTerpy(L^1) in-plane ring deform, H-stretch and Fe-N wag
	1551	1551	1545	OTerpy(L^1) in-plane ring deform, H-stretch and Fe-N wag
1591			1584	OTerpy(L^1) in-plane ring deform, H-stretch and Fe-N wag
	1609	1608	1588	OTerpy(L^1) in-plane ring deform and H-stretch

Table F.5.2 DFT assigned vibrational modes for $[Fe(L^2)_2](ClO_4)$.

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{rR} λ_{568nm} / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
498			498	CTP and OPhTerpy(L^2) out-of-plane ring deform v. delocalised
624			624	OPhTerpy(L^2) in-plane deform
		653	651	CTP and OPhTerpy(L^2) out-of-plane ring deform v. delocalised
689		687	689	OPhTerpy(L^2) out-of-plane ring deform
770			771	CTP, OPhTerpy(L^2) and OPh in-plane ring deform v. delocalised
		842	842	OPhTerpy(L^2) H-wag out-of-plane
881			885	P-O stretching, CTP and OPh out-of-plane distortion
949				ClO_4^-
	1018		1014	OPhTerpy(L^2) ring breathing
		1021		ClO_4^-
		1047	1044	OPhTerpy(L^2) ring breathing
1088			1082	CTP in-plane deform
		1094	1102	OPhTerpy(L^2) in-plane deform and Fe-N symm stretch
1160			1149	OPhTerpy(L^2) in-plane deform and H-stretch
		1164	1164	OPhTerpy(L^2)(Ph) in-plane deform and H-stretch
	1265		1265	OPhTerpy(L^2) in-plane ring deform, H and C-O stretch

Table F.5.2 Continued DFT assigned vibrational modes for $[Fe(L^2)_2](ClO_4)$.

$\nu_{FT\text{-}IR}$ / cm^{-1}	ν_{rR} $\lambda_{514\ nm}$ / cm^{-1}	ν_{rR} λ_{568nm} / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
	1290	1291	1292	OPhTerpy(L^2) in-plane ring deform, H stretch
1268		1268	1268	OPhTerpy(L^2) in-plane ring deform, H and C-O stretch
	1363	1364	1391	OPhTerpy(L^2) in-plane ring deform, H and Fe-N stretch
	1471	1472	1472	OPh in-plane ring deform, H stretch
	1485	1486	1482	OPhTerpy(L^2) in-plane ring deform, H and Fe-N wag
1488			1483	OPhTerpy(L^2) in-plane ring deform, H stretch wag and Fe-N wag
	1540	1543	1543	OPhTerpy(L^2) in-plane ring deform, H stretch wag and Fe-N wag
	1561		1568	OPhTerpy(L^2) in-plane ring deform, H stretch wag and assym. Fe-N stretch
		1565	1570	OPhTerpy(L^2) in-plane ring deform, H stretch wag and assym. Fe-N stretch
1590			1595	OPhTerpy(L^2) in-plane ring deform and H stretch
	1611	1611	1597	OPhTerpy(L^2) in-plane ring deform and H stretch

Table F.5.3 DFT assigned vibrational modes for $[Fe(L^3)_2](ClO_4)$ at 80 K.

ν_{rR} $\lambda_{514\,nm}$ / cm^{-1}	ν_{rR} λ_{568nm} / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
576		575	Obbp(L^3), CTP and OPh out-of-plane ring deform v. delocalised
597		602	Obbp(L^3) in-plane ring deform
	638	630	Obbp(L^3) in-plane ring deform
	653	653	Obbp(L^3) out-of-plane ring deform and CTP in-plane ring deform
	687	687	Obbp(L^3) and CTP in-plane ring deform
	950	944	Obbp(L^3) H-bend out-of-plane
	1003	1001	Fe-N assym stretch and in-plane Obbp(L^3) ring deform
	1014	1015	Fe-N assym stretch and in-plane Obbp(L^3) ring deform
	1029	1030	Fe-N sym stretch and in-plane Obbp(L^3) ring deform
	1119	1112	Obbp(L^3) H in-plane stretch
	1149	1149	Obbp(L^3) H in-plane stretch

Table F.5.3 Continued DFT assigned vibrational modes for $[Fe(L^3)_2](ClO_4)$ at 80 K.

$\nu_{rR}\lambda_{514\,nm}$ / cm^{-1}	$\nu_{rR}\lambda_{568nm}$ / cm^{-1}	ν_{Calc} / cm^{-1}	Assignment from GaussView
1246		1255	Obbp(L^3) in-plane ring breathing and Obbp(L^3) H stretch in-plane
1276		1271	Obbp(L^3) in-plane deform and Obbp(L^3) H in-plane stretch
	1293	1296	Obbp(L^3) in-plane ring deform and Fe-N wag
	1364	1366	Obbp(L^3) in-plane ring deform Fe-N symm stretch
1393	1392	1385	Obbp(L^3) in-plane ring deform
1450	1448	1451	Obbp(L^3) in-plane ring deform
	1464	1469	Obbp(L^3) and OPh in-plane ring and Obbp(L^3) H in-plane stretch
	1491	1496	Obbp(L^3) in-plane ring deform and Fe-N wag
1496		1496	Obbp(L^3) in-plane ring deform and Fe-N wag
	1544	1534	Obbp(L^3) in-plane ring deform and Obbp(L^3) H in-plane stretch
1551		1567	Obbp(L^3) in-plane ring deform and Obbp(L^3) H in-plane stretch
1564		1561	Obbp(L^3) in-plane ring deform and Obbp(L^3) H in-plane stretch
	1616	1602	Obbp(L^3) in-plane ring deform and Obbp(L^3) H in-plane stretch
1629	1627	1606	Obbp(L^3) in-plane ring deform and Obbp(L^3) H in-plane stretch

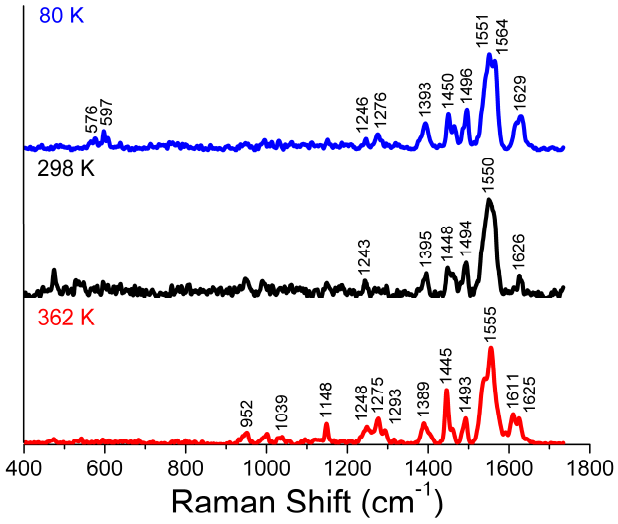

Figure F.5.1 Solid-state rR collected for $[Fe(L^3)_2](BF_4)_2$. λ_{ex} 514 nm.

F.6 References

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