Supplementary material (ESI) for Dalton Transactions

Tricarbonylrhenium(I) complexes of highly symmetric hexaazatrinaphthlene ligands (HATN): structural, electrochemical and spectroscopic properties.

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Figure S1. Intermolecular π-π stacking in 1 in the unit cell.

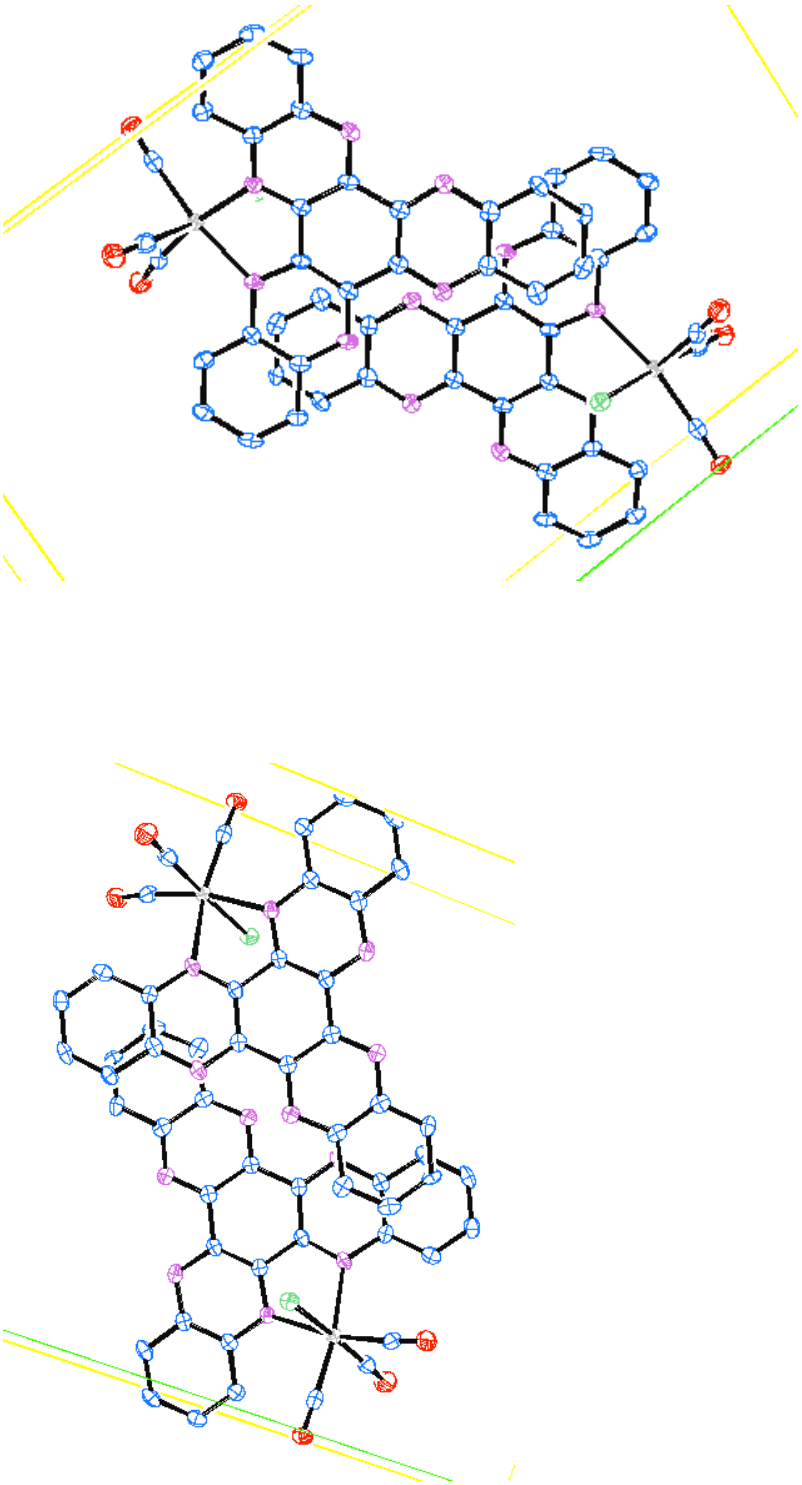


Figure S2. Solvent trapping in the unit cell by **2**-Cl_2, Space filling and ellipsoid model shows trapped $CHCl_3$ molecules in a unit cell.

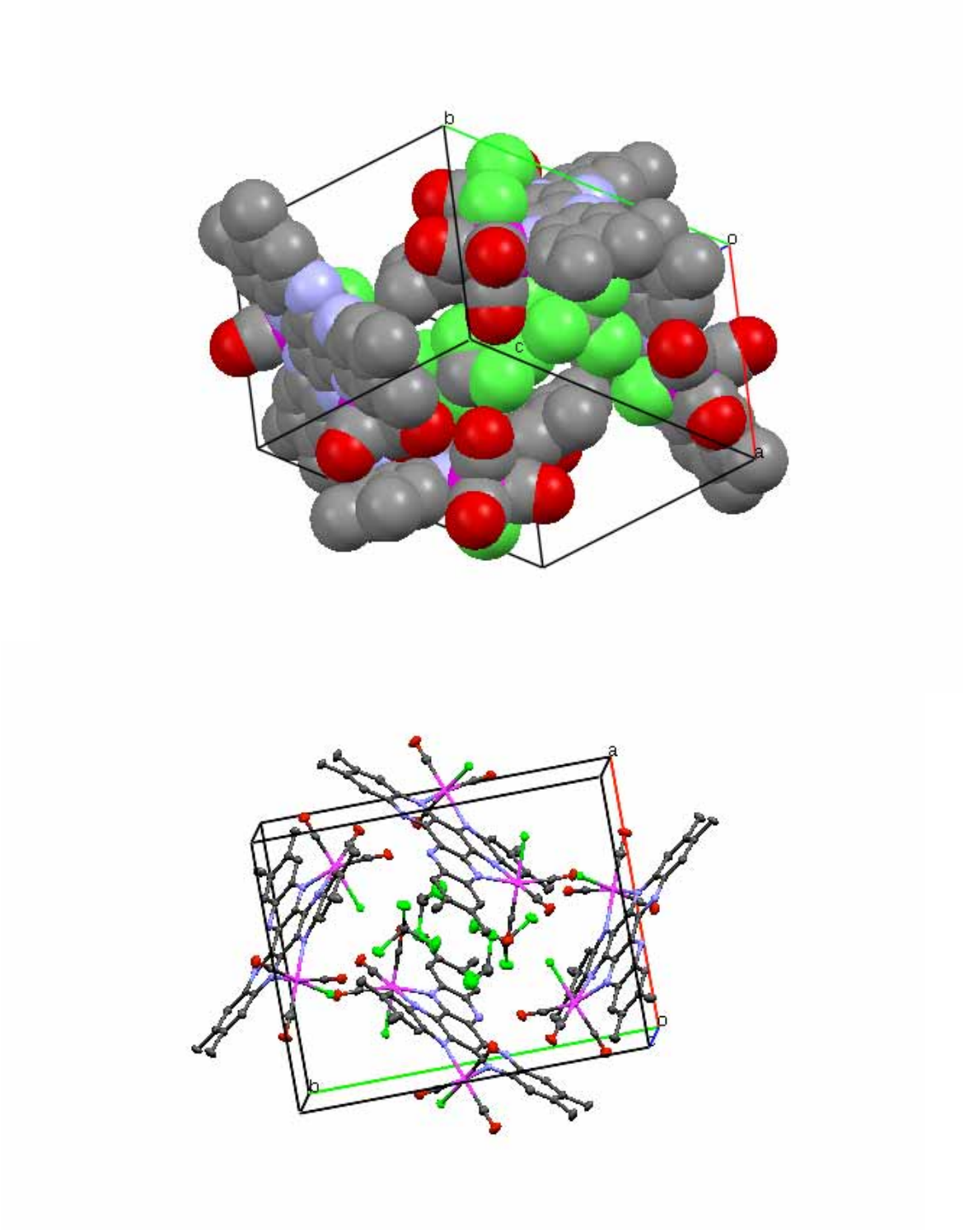


Figure S3. Computer simulation of the 1950 cm^{-1} peak in the IR spectrum of **1**-OTf.

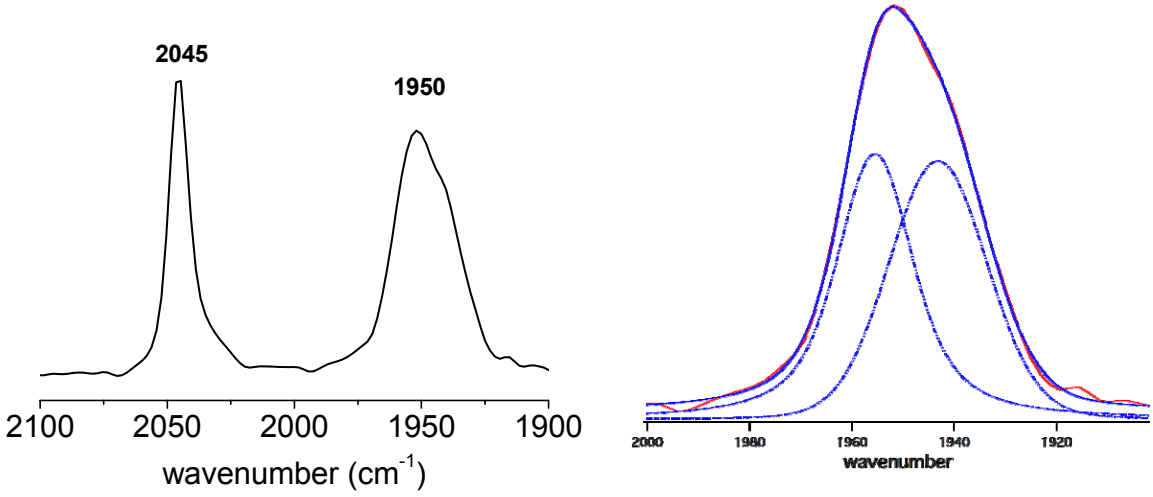


Figure S4. Computer simulation of the 1950 cm^{-1} peak in the IR spectrum of **2**-OTf_2.

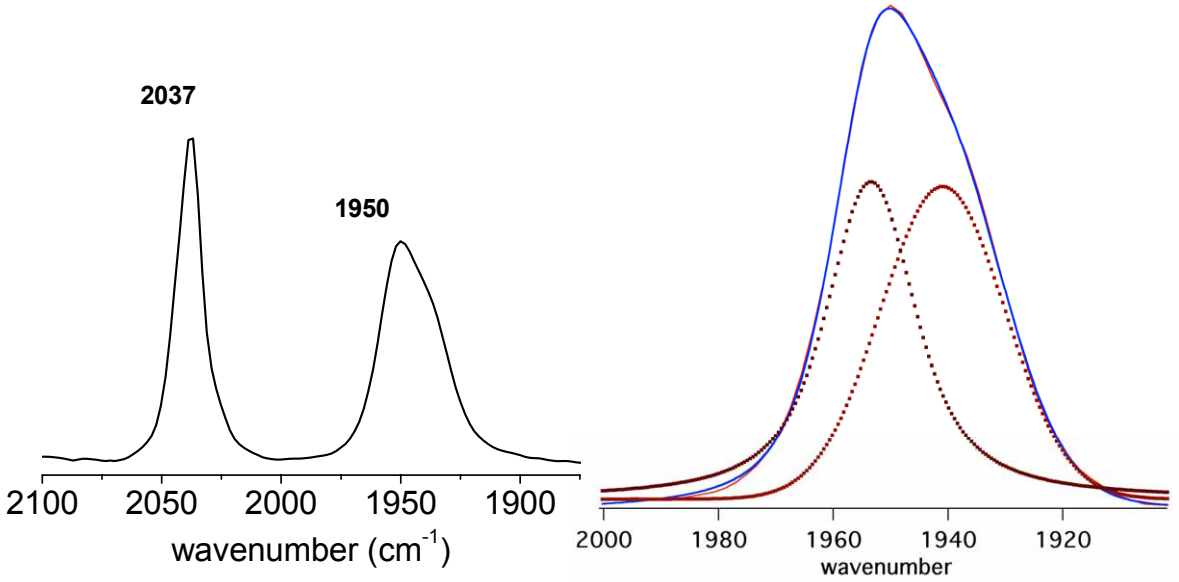


Figure S5: UV-vis spectrum of **1**-Cl (red) and **2**-Cl_2 (black) in CH_2Cl_2.

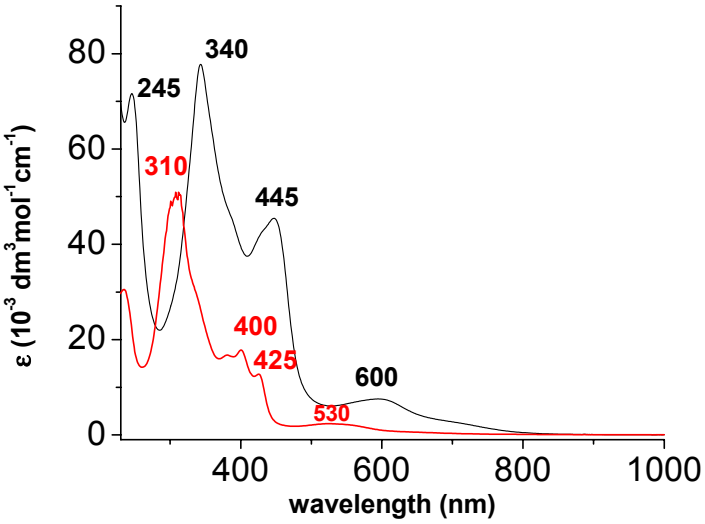


Figure S6: UV-vis spectrum of **1**-OTf (red) and **2**-OTf_2 (black) in CH_3CN.

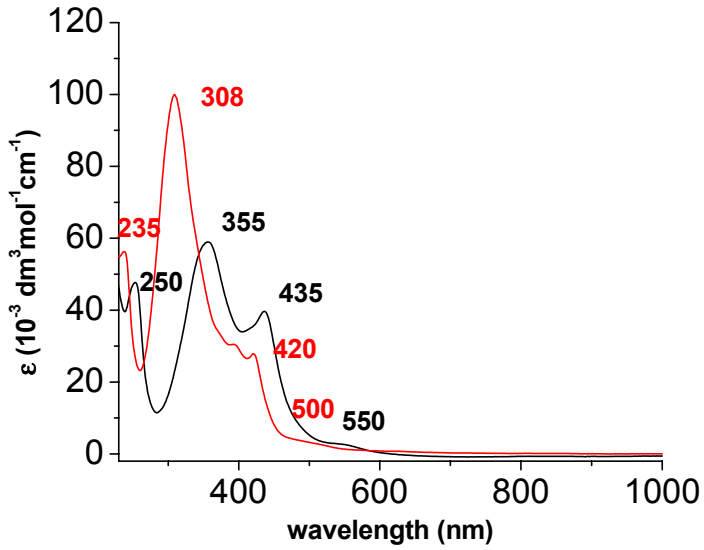


Figure S7: UV-vis-NIR spectra of **2**-Cl_2 (black) and (**2**-Cl_2)$^{\cdot-}$ (red).

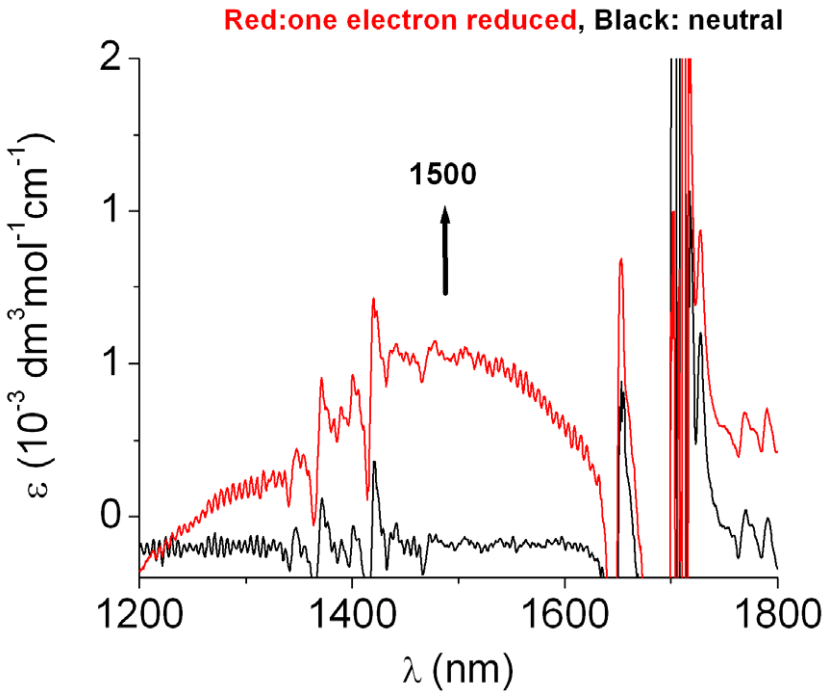


Figure S8: Cyclicvoltammogram of **1**-OTf (red) and **2**-OTf_2 (black) in 0.1 M Bu_4NPF_6/CH_3CN at RT.

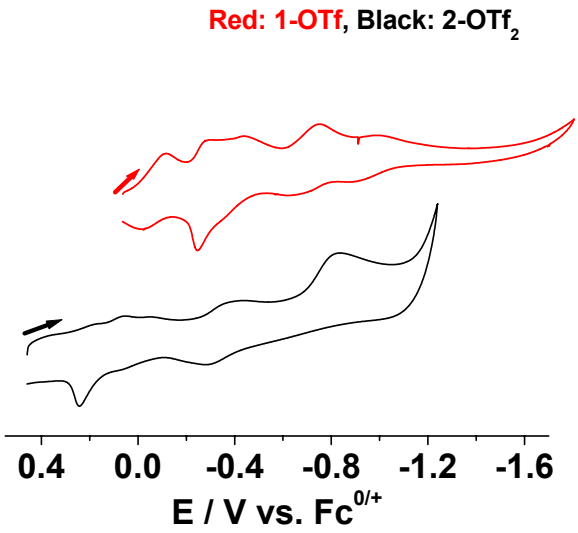


Figure S9: IR spectroelectrochemical reduction of **1**-Cl to (**1**-Cl)$^{\bullet-}$.

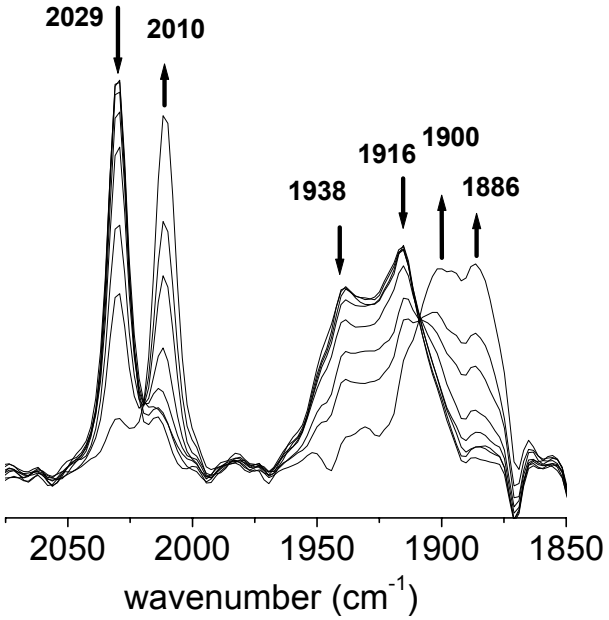


Figure S10: IR spectroelectrochemical reduction of **1**-OTf to **1**$^{\cdot-}$ and **1**$^{\cdot-}$ to **1**$^{2-}$.

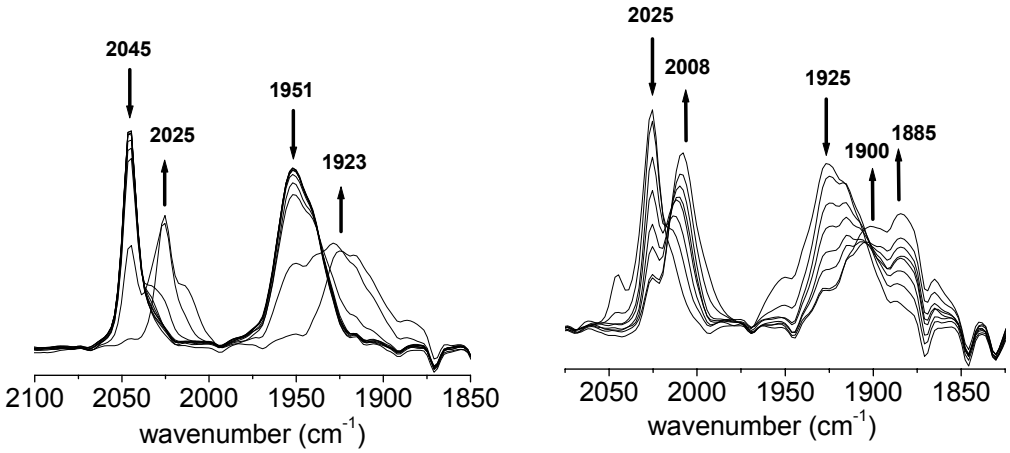
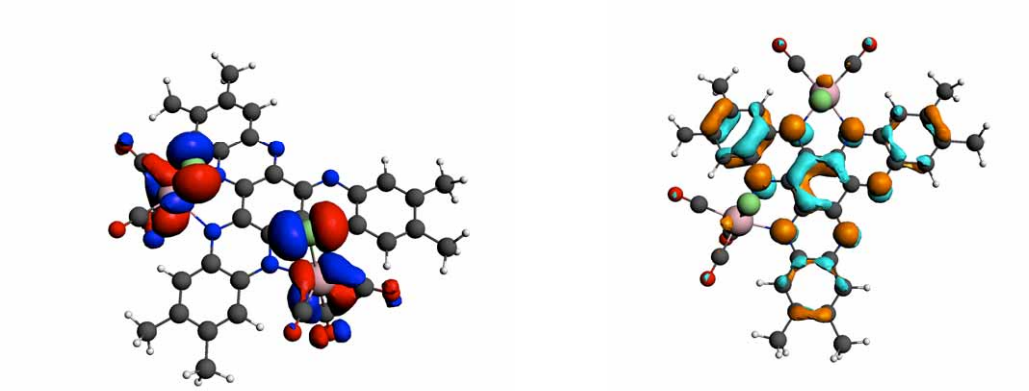


Figure S11: Spin density plot. HOMO of **2**-Cl_2 in neutral state and SOMO of (**2**-Cl_2) after one electron reduction.



HOMO of **2**-Cl_2 SOMO of (**2**-Cl_2)$^{\bullet-}$

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Table S1: Experimental and theoretical Bond lengths (Å).

Complexes	Bonds	Experimental bond lengths (Å)	Calculated bond lengths (Å)
1-Cl	Re-N1	2.178(5)	2.193
	Re-N2	2.188(5)	2.196
	Re-Cl1	2.479(2)	2.479
	C1-O1	1.136(8)	1.160
	C2-O2	1.153(8)	1.167
	C3-O3	1.139(8)	1.160
2-Cl_2	Re1-N1	2.200(3)	2.217
	Re1-N2	2.176(3)	2.198
	Re1-Cl2	2.473(1)	2.462
	C1-O1	1.147(6)	1.160
	C2-O2	1.151(5)	1.167
	C3-O3	1.146(5)	1.162
	Re2-N3	2.174(4)	2.200
	Re2-N4	2.199(3)	2.208
	C4-O4	1.144(6)	1.160
	C5-O5	1.150(6)	1.167
	C6-O6	1.151(6)	1.162
	Re2-Cl1	2.471(1)	2.460

Table S2: Experimental and theoretical bond angles (°).

Complexes	Angles	Experimental bond angles (°)	Calculated bond angles (°)
1-Cl	N1-Re1-N2	74.1(2)	74.52
	C1-Re1-C2	87.7(3)	87.42
	C2-Re1-Cl4	88.4(2)	87.82
	C1-Re1-Cl4	85.6(2)	87.08
	C2-Re1-C3	91.6(3)	90.89
	C1-Re1-C3	92.0(3)	91.63
	N1-Re1-C3	97.1(2)	97.08
	N2-Re1-C3	98.9(3)	99.39
	C3-Re1-Cl4	177.6(2)	177.91
2-Cl_2	N1-Re1-N2	75.52(12)	74.85
	C3-Re1-C2	86.64(18)	86.05
	C3-Re1-C1	91.64(19)	91.98
	C2-Re1-C1	88.55(19)	89.66
	C3-Re1-N2	95.58(15)	97.43
	C2-Re1-N2	177.14(16)	179.81
	C1-Re1-N2	93.18(16)	94.85
	C2-Re1-N1	101.98(15)	98.34
	C1-Re1-N1	98.89(16)	98.94
	N3-Re2-N4	75.56(13)	74.73
	C5-Re2-C4	95.37(19)	91.23
	C5-Re2-C6	84.17(19)	86.62
	C4-Re2-C6	87.49(19)	88.52
	C5-Re2-N3	97.56(16)	97.12
	C4-Re2-N3	94.91(16)	94.39
	C4-Re2-N4	97.96(16)	98.52
	C6-Re2-N4	102.18(16)	100.07