Supporting Information

Antimalarial activity of ruthenium(II) and osmium(II) arene complexes with mono- and bidentate chloroquine analogue ligands

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Contents

Electrochemistry

Table S-1. Oxidation potentials for Ru complexes.

Complex	Volts vs Ferrocene	Hammet value
Ru-HL[7], OMe	0.2568	-0.268
Ru-HL[2], F	0.4972	0.062
Ru-HL[3], Cl	0.5439	0.227
Ru-HL[5], I	0.5957	0.276
Ru-HL[6], NO2	0.7795	0.778

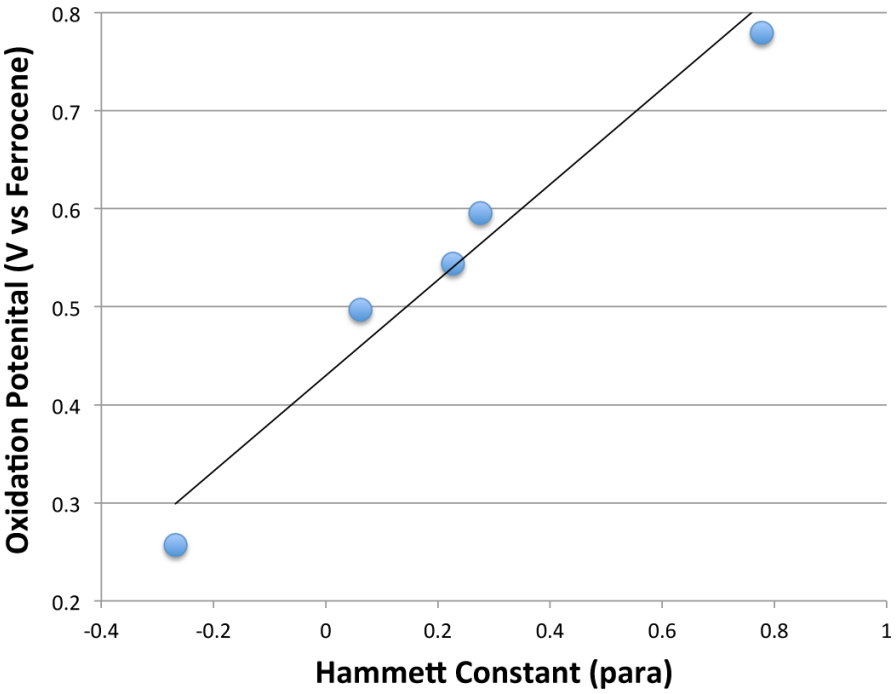

Figure S-1. The oxidation potentials for Ru^{II} to Ru^{III} correlate with the Hammett constants, as the greater electron-withdrawing groups raise the oxidation potential. The data is also shown in Table 1.

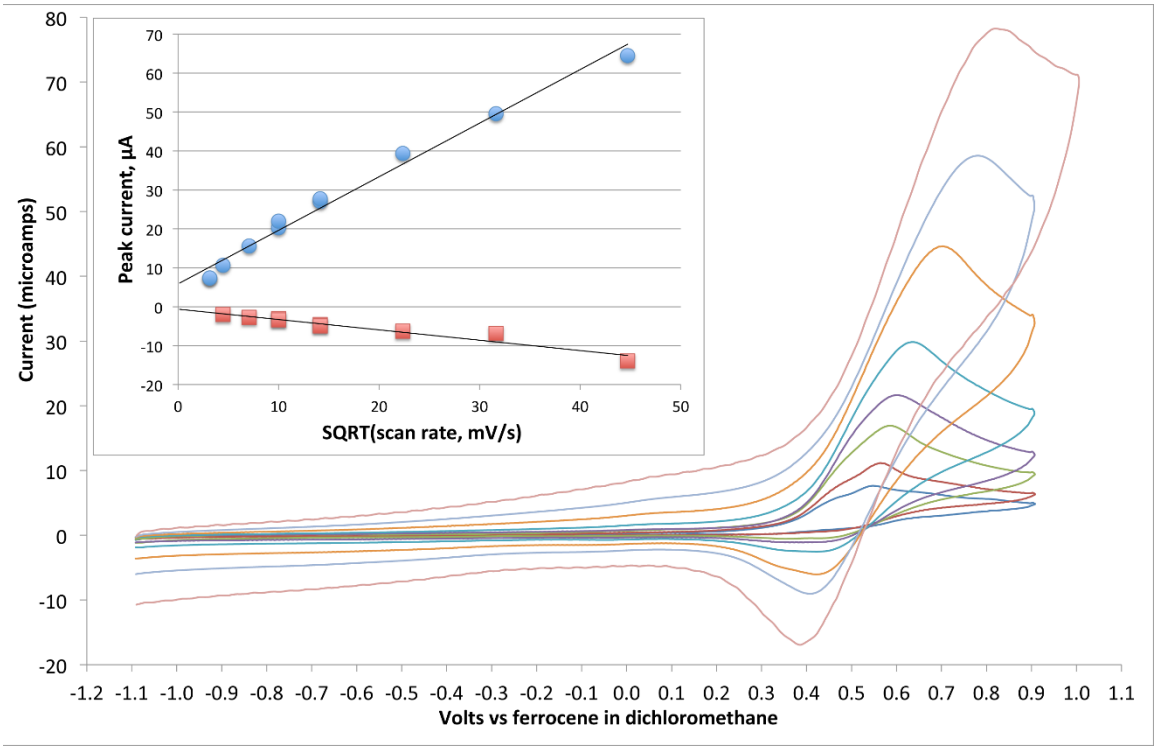

Figure S-2. The ruthenium complexes have a quasi-reversible oxidation with the cyclic voltammetry return wave having a smaller peak current. The figure shows the data for Ru-**HL**^{2} at 10, 20, 50, 100, 200, 500, 1000, and 2000 mV/s scan rates. The peak current for the return wave is only 20% of that for the forward wave.

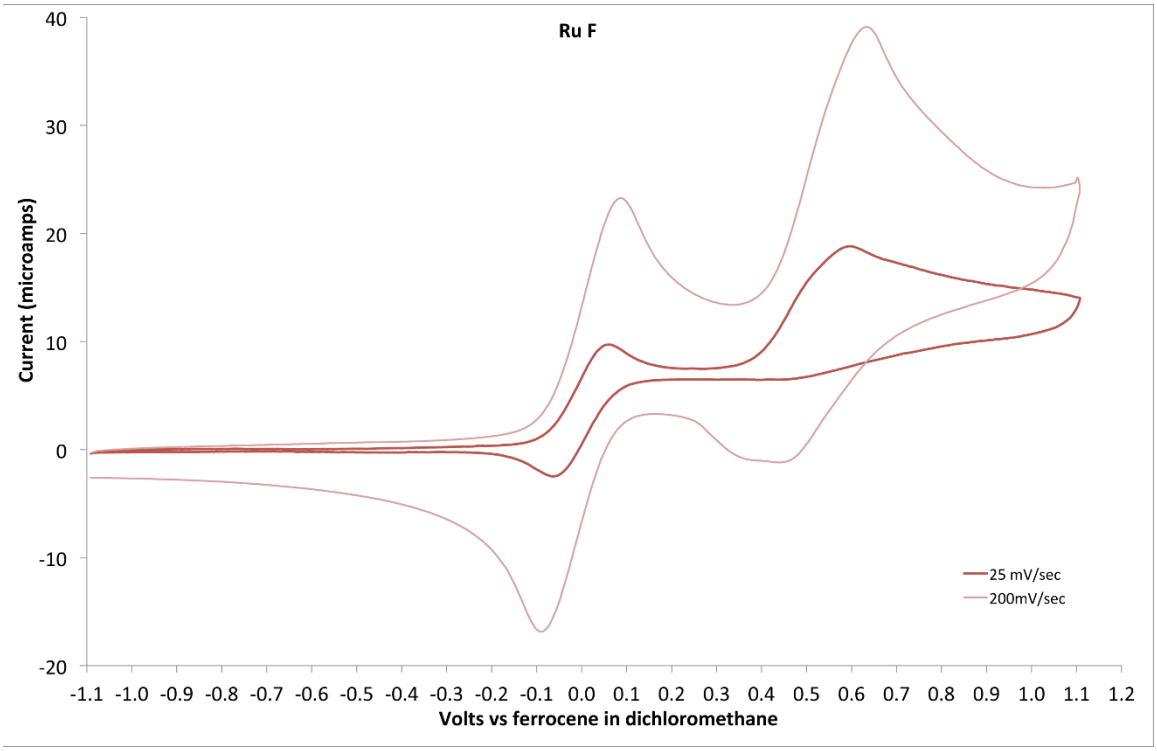

Figure S-3. Peak separations were similar to that of ferrocene. The cyclic voltammogram of Ru-**HL**^{2} in dichloromethane is shown with added ferrocene at 25 and 200 mV/s scan rates.

Anti-malarial activities as a function of σ_{para}

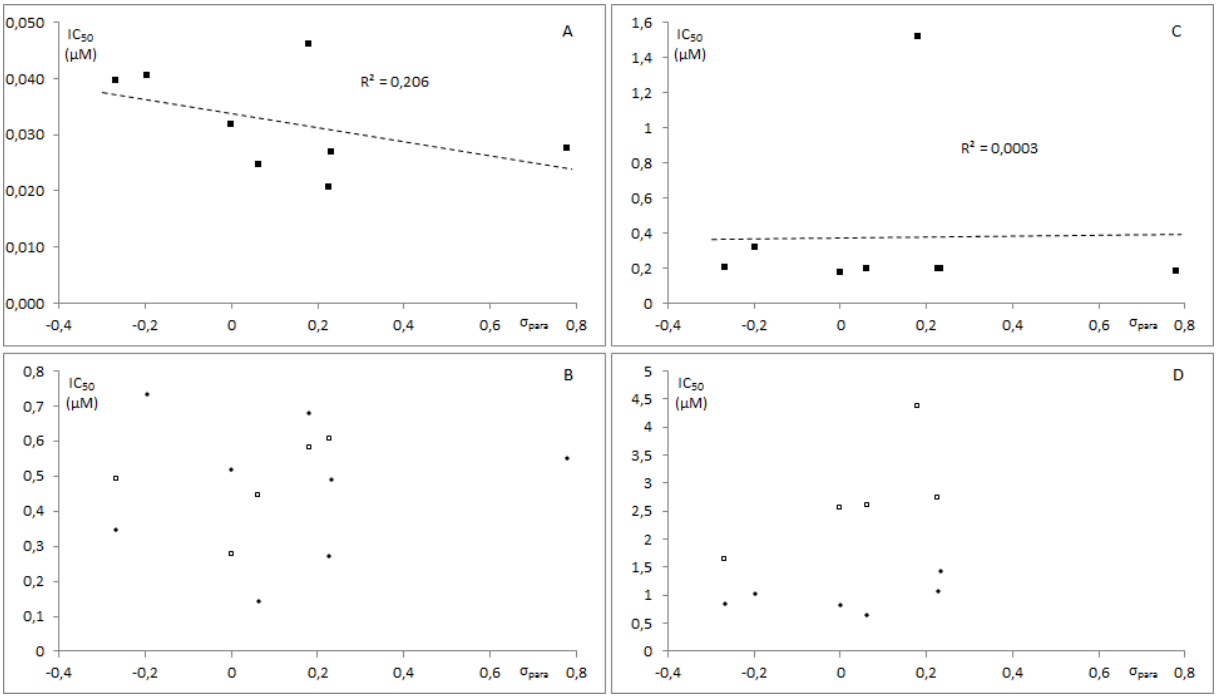

Figure S-4. Antimalarial activities as a function of Hammett σ-para values. A) Ligands **HL**[1] to **HL**[8] (solid squares), NF54 strain (CQS), B) Complexes Ru-**1** to **8** (solid diamonds) and Os-**1**,**2**,**3**,**5** and **7** (white squares) NF54 strain (CQS), C) Ligands **HL**[1] to **HL**[8] (solid squares), Dd2 strain (CQR), D) Complexes Ru-**1** to **8** (solid diamonds) and Os-**1**,**2**,**3**,**5** and **7** (white squares), Dd2 strain (CQR). Notice the weak negative correlation between antimalarial activity versus the CQS strain for the ligands **HL**[1] to **HL**[8] and the absence of the same trend in the the corresponding complexes.

^{1}H-NMR assignments used in the characterization of Ru-HL^9 and Os-HL^9

Table S-2. Selected ^{1}H NMR data (Δδ, ppm) for complexes Ru-**HL**^{9} and Os-**HL**^{9} in CD_2Cl_2.[a]

	Ru-HL^9	Os-HL^9
H1	0.03	0.04
H3	-0.04	-0.05
H5	0.00	0.00
H8	-0.03	-0.04
H9	-0.10	-0.18
H11	0.31	0.33
H12	-0.34	-0.35
H14	0.68	0.77
H16	-0.35	-0.43
H17	-0.36	-0.48
H29	0.01	-0.01
H30	-0.02	-0.02
H31	0.09	0.14

[a] Δδ is the displacement of the signal in the coordinated ligand with respect to the corresponding signal in the free ligand. Positive values denote downfield shifts. See figure S-5 for numbering.

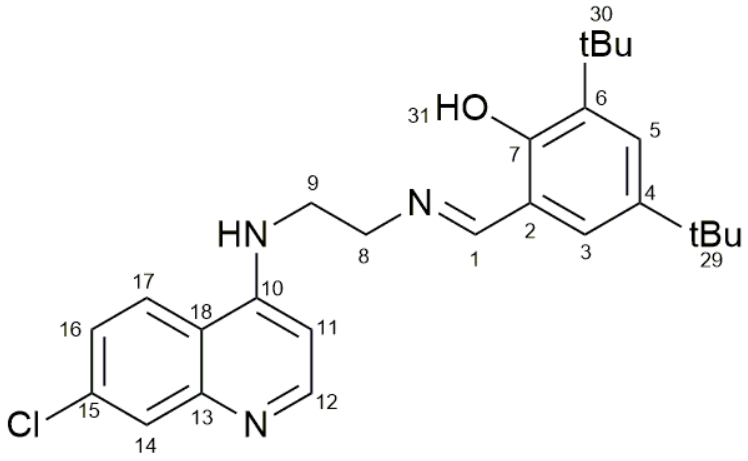

Figure S-5. Numbering scheme used for ^{1}H-NMR assignments in Table S-2. The same numbering is used for all crystal structures.

Stacking fault in Ru-1

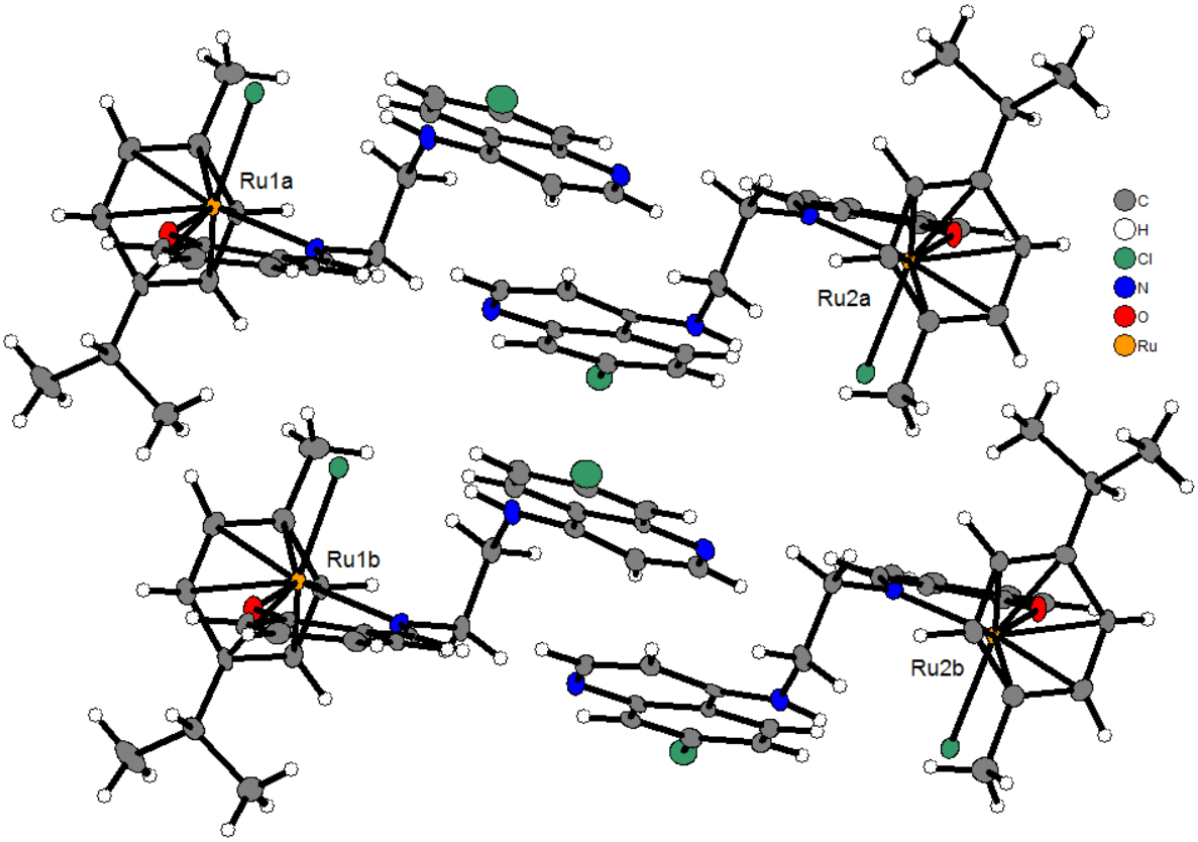

Figure S-6. Structure of the two different domains of Ru-**1**. Ru1a and Ru2a is in the main polymorph, Ru1b and Ru2b in the minor polymorph. Notice the local centrosymmetry at the interface between the polymorphs.