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Supporting Information

Microwave synthesis of a rare $[Ru_2L_3]^{4+}$ triple helicate and its interaction with DNA†

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Section S1: Selected HR-ESI-MS and theoretical isotopic distributions.

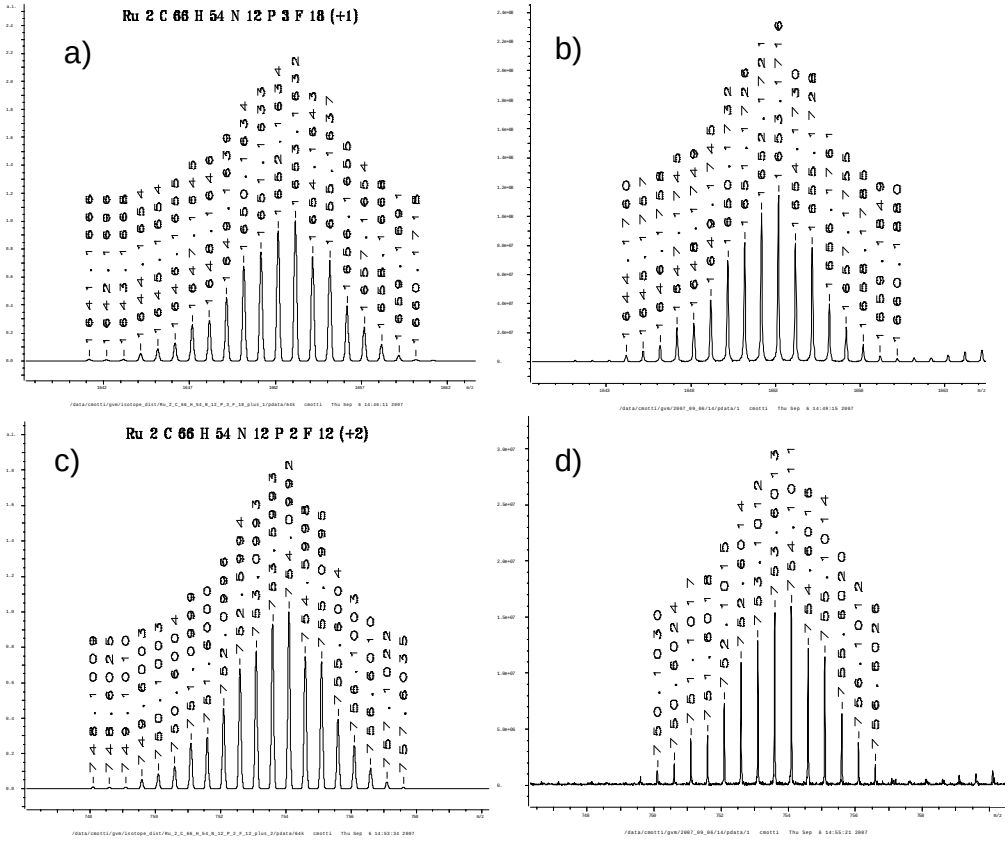

Fig. S1 Partial high resolution ESMS of $[Ru_2L_3](PF_6)_4$; a) and b) are the theoretical and experimental isotopic distributions for $\{[Ru_2L_3](PF_6)_3\}^{1+}$, respectively; c) and d) are the theoretical and experimental isotopic distributions for $\{[Ru_2L_3](PF_6)_2\}^{2+}$, respectively.

Section S2: X-ray analysis.

X-ray structural data for were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ? and *?* scans.[1] Data were collected at 150 K to approximately 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP [1] and subsequent computations were carried out using the WinGX-32 graphical user interface.[2] The structures were solved by direct methods using SIR97.[3] Multi-scan

empirical absorption corrections were applied to the data set using the program SADABS.[4] Data were refined and extended with SHELXL-97.[5] All non-hydrogen atoms with occupancies greater than 0.25, were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model, oxygen-bound hydrogen atoms could not be located in the Fourier difference map and were not included in the model. The crystals employed in the study were unstable (rapid solvent loss) and rapid mounting (<1 min) at 200 K prior to quenching in the cryostream was required to enable data collection. Three of the PF_6^- anions are disordered. Two of them (the P(1) and P(6) containing anions) were modelled over two overlapping positions employing a rigid body refinement. One of the fluorine atoms of the P(3) containing anion were modelled as disordered over two positions. Present within the lattice are four acetonitrile solvent molecules and four water molecules. Only one of the acetonitrile molecules is full occupancy (that containing N(1A)). The water molecules are also less than full occupancy. The final model contains 1.125H_2O and 2.25MeCN molecules per unit cell. A number of restraints and constraints were required in order to facilitate realistic modelling of the solvent molecules and anions. Perhaps reflecting both the crystal instability and disorder in the lattice, the diffraction properties of the crystal were less than ideal and despite long exposure times and a high power X-ray source good quality data could only be obtained to ~50 º 2?.

Formula $C_{70.50}H_{63}F_{24}N_{14.25}O_{1.125}P_4Ru_2$, *M* 1909.87, trigonal, space group $P6_3$(#173), *a* 13.6600(7), *b* 13.660, *c* 57.016(3) Å, *g* 120.00º, *V* 9213.6(7) $Å^3$, D_c 1.377 g cm^{-3}, *Z* 4, crystal size 0.20 by 0.18 by 0.02 mm, color orange, habit plate, temperature 150(2) Kelvin, *l*(MoKα) 0.71073 Å, *m*(MoKα) 0.492 mm^{-1}, $T(SADABS)_{min,max}$ 0.863, 0.990, $2q_{max}$ 56.48, *hkl* range -14 14, -17 17, -75 75, *N* 47169, N_{ind} 14750(R_{merge} 0.0322), N_{obs} 12114(I > 2σ(I)), N_{var} 799, residuals* *R*1(*F*) 0.0984, *wR*2(F^2) 0.2675, GoF(all) 1.116, $\Delta r_{min,max}$ -3.936, 3.324 e^- $Å^{-3}$.

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.1201P)^2+63.1133P]$ where $P=(F_o^2+2F_c^2)/3$

Section S3: Cyclic Voltammetry.

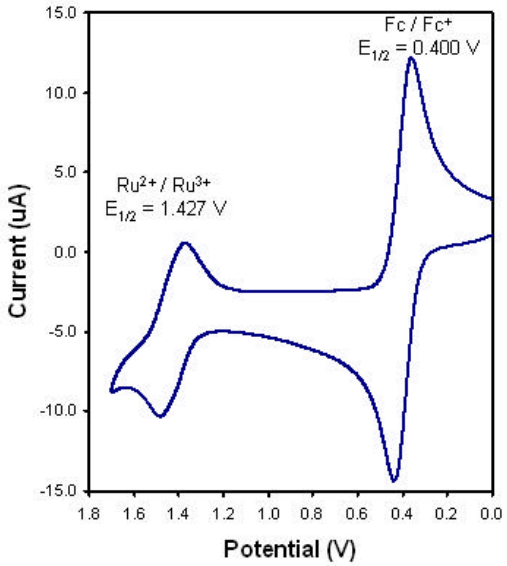

Fig. S2 Cyclic voltammogram of $[Ru_2L_3](PF_6)_4$ with two redox couples belonging to Ru^{2+} / Ru^{3+} (1.427 V) and Fc / Fc^+ (0.400 V).

Section S4: DNA binding affinity chromatography:

A 20 mM sodium phosphate/0.15 M sodium chloride/pH 7.5 buffer solution was used as eluent for all chromatographic separations. The DNA sequences employed included, an immobilised AT duplex DNA 12-mer, tridecanucleotide possessing an unpaired adenine base (or "bulge") $d(CCGAGAATTCCGG)_2$, an icosamer featuring a 6-base CT hairpin loop, d(CACTGGTCTCTCTACCAGTG), and GC duplex DNA 12-mers. Enantiomeric purity of the separated *M* and *P* $[Ru_2L_3]^{4+}$ resulting from the various chromatography experiments were assessed by CD spectroscopy. See Smith et al.[21] for general chromatography details.

Section S5: Dialysis experimental method:

A 300 uM ct-DNA solution was made up in Tris buffer and placed on the inside of a 1 ml cellulose ester membrane Spectra/Por® DispoDialyzer®. This ct-DNA loaded

dialysis tube was then submerged in a 20 uM racemic mixture of $[Ru_2\mathbf{L}_3]Cl_4$ made up in Tris buffer. The dialysis was left for 18 h and the complex solution was inspected using CD spectroscopy to determine if enrichment of an enantiomer was evident. The *M*-helicate was observed to be enriched (Fig. S4), thus indicating that the *P* helicate is preferentially bound to the ct-DNA.

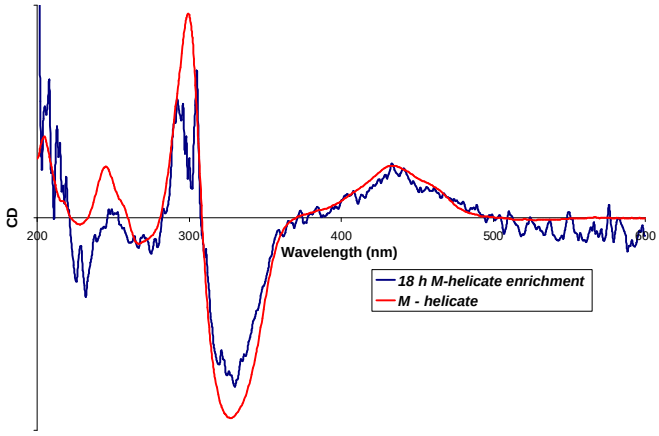

Fig. S4 CD of the $[Ru_2\mathbf{L}_3]Cl_4$ solution after 18 h of dialysis indicating an enrichment in the *M*-helicate.

Section S6: Spectrophotometric binding study:

UV/visible spectrophotometric measurements were made on a Cary 50 Bio UV/visible spectrophotometer. The *P* and *M* helicates were anion exchanged using Amberlite resin IRA-400 (Cl) to the $[Ru_2\mathbf{L}_3]Cl_4$ to facilitate water solubility. All solutions were made up in Tris buffer (5 mM Tris-HCl, 50 mM NaCl, 7.2 pH). Calf thymus DNA (ct-DNA) was purchased from Sigma Aldrich. The concentrations of ct-DNA solutions were determined spectrophotometrically using the molar extinction coefficient e_{260} = 6600 M^{-1} cm^{-1} (all ct-DNA concentrations with respect to base pairs). Titrations were conducted by keeping the metal complex concentration constant at 10 uM and sequentially titrating in a solution with 10 uM complex (*P* or *M* helicate) : 600 uM ct-DNA. The first spectrum was collected on the ct-DNA free 10 uM complex solution followed by the addition of successive 50ul aliquots of the complex/ct-DNA solution until an approximate 20 : 1 ratio of DNA to complex was reached. Fig. S3 is representative of *P* - $[Ru_2\mathbf{L}_3]Cl_4$ and *M* - $[Ru_2\mathbf{L}_3]Cl_4$ with ct-DNA.

In the presence of ct-DNA, hypochromicity was observed for both the *P* and *M* helicates in both the p-p* and MLCT bands (Fig. S3). An apparent binding constant (K_b) value of 2.0 x 10^5 M^{-1} for *P*-[Ru_2**L**$_3$]Cl_4 was determined from this titration data (see inset, Fig. S3). The same spectrophotometric titration conducted with *M*-$[Ru_2L_3]^{4+}$ consistently gave K_b values in the range 4.0 x 10^5 to 2.6 x 10^6 M^{-1} in apparent conflict with the chromatography data. Note that the e value for the Cl^- salt in Tris buffer was 16000 $M^{-1}cm^{-1}$ which is significantly less than that recorded for the PF_6^- salt in acetonitrile, however the general form of the absorption spectrum remains the same.

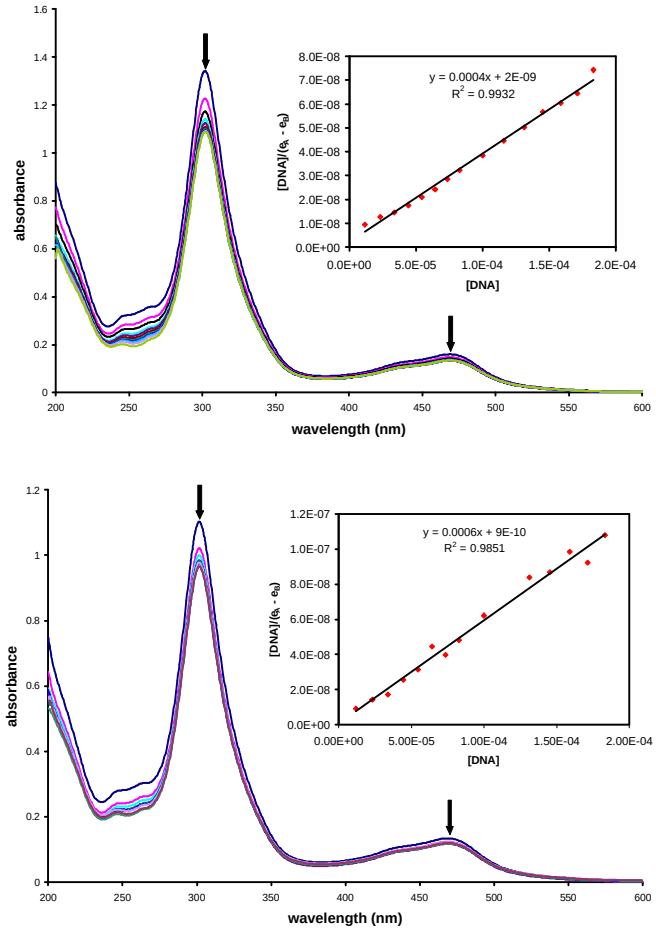

Fig. S3 Spectrophometric titration data from titrations of *P*-[Ru_2L_3]Cl_4 (top) and *M*-[Ru_2L_3]Cl_4 (below) with ct-DNA at 293 K.

References

[1] Bruker-Nonius (2003). APEX v2.1, SAINT v.7 and XPREP v.6.14. Bruker AXS Inc. Madison, Wisconsin, USA.

[2] *WinGX-32: System of programs for solving, refining and analysing single crystal X-ray diffraction data for small molecules*, L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837.

[3] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giocavazzo, A. Guagliardi, A. G. C. Moliterni, G. Polidori, S. Spagna, *J. Appl. Cryst.*, **1999**, *32*, 115.

[4] G. M. Sheldrick, *SADABS: Empirical Absorption and Correction Software*, University of Göttingen, Germany, 1999-2003.

[5] G. M. Sheldrick, *SHELXL-97: Programs for Crystal Structure Analysis*, University of Göttingen, Germany, 1997.

[6] Flack H D (1983), *Acta Cryst.* A39, 876-881.