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Synthesis of Flexible Bis-Intercalating Ruthenium(II) Complexes

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We report the synthesis, resolution and characterisation of a number of novel ruthenium(II) complexes. Four mononuclear complexes, $[Ru(dpq)_2(3\text{-Br-phen})]^{2+}$, $[Ru(dpq)_2(4\text{-Cl-phen})]^{2+}$, $[Ru(dpq)_2(5\text{-Cl-phen})]^{2+}$ and $[Ru(dpq)_2(phen)]^{2+}$ were synthesised (dpq = dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline, phen = 1,10-phenanthroline, 3-Br-phen = 3-bromo-1,10-phenanthroline, 4-Cl-phen = 4-chloro-1,10-phenanthroline, 5-Cl-phen = 5-chloro-1,10-phenanthroline). These complexes were resolved using the chiral TRISPHAT anion, [tris(tetrachlorocatecholato)phosphate(V)]$^-$. Racemic mononuclear complexes were used in the synthesis of the racemic dinuclear complexes, $[\{Ru(dpq)_2\}_2\mu\text{-(phen-}n\text{-SOS-}n\text{-phen)}]^{4+}$ (SOS = 2-mercaptoethyl ether, n = 3, 4 or 5). Resolved mononuclear complexes were used to synthesise stereoselectively the ΔΔ- and ΛΛ-enantiomers of their respective dinuclear complexes. All metal complexes were characterised by ^{1}H NMR, ESI-MS, UV/Vis and luminescence spectroscopy. Resolved metal complexes were further characterised using CD spectroscopy and chiral ^{1}H NMR titrations.

Introduction

The widespread interest in ruthenium(II) complexes as DNA probes was initially sparked by the study of these complexes as potential anticancer agents.[1] Since then, ruthenium(II) complexes have displayed potential as medical diagnostic tools through their ability to act as "molecular light switches"; complexes which exhibit fluorescence only in the presence of DNA,[2–4] while others have been shown to induce the breakage of DNA strands by photocleavage.[5–9] By incorporating certain ligands, such as dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline (dpq), it is possible to produce ruthenium(II) complexes that display some measure of DNA sequence selectivity,[8,10] enantioselectivity[11–14] and/or preference for DNA base mismatches.[15]

Mononuclear ruthenium(II) complexes are relatively small, can only span 2–4 DNA base pairs, and bind to the double helix over a range of $K_b \approx 10^4$–10^6 M^{-1}, depending on the intercalating ligand such as dpq $K_b = 5.9 \times 10^4$,[16] dpqc $K_b = 8.5 \times 10^4$[17] and dppz $K_b > 10^6$.[8,18] Researchers have theorised that it may be possible to increase the DNA binding affinity, and therefore biological efficacy of ruthenium complexes, by producing complexes of higher nuclearity. There have been relatively few examples, however, of the application of dinuclear complexes as DNA probes.

Flexibly linked dinuclear ruthenium(II) complexes incorporating 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) ligands bind to DNA with a ca. 50-fold increase in K_b compared to the mononuclear analogues of these complexes.[19,20] The length of the linking chain was found to be a critical factor in determining binding strength,[21] with n = 7 being the optimal chain length. Nordén et al.[22–27] have focused on metal complexes derived from $[Ru(phen)_2(dppz)]^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine). The two-component metal-based units are linked through an intercalating dppz ligand and their DNA binding was found to be extremely strong (ca. 10^{11}–10^{13} M^{-1}).[26,28] Other dinuclear ruthenium complexes, where the metal centre is linked by a rigid bridge,[29] such as 2,2′-bipyrimidine,[30–33] display modest affinity for DNA bulge sites,[33] with significant enantioselectivity being observed between the three stereoisomeric forms ΔΔ, ΛΛ and *meso* (ΔΛ = ΛΔ).[30–33]

We have synthesised flexibly linked dinuclear complexes incorporating the intercalating ligand, dpq, in the hope of achieving high DNA binding strength and some measure of sequence selectivity (Figure 1). The dpq ligand is known to possess some purine-purine base specificity,[10] and adding flexibility to dinuclear intercalators may enhance the DNA binding ability of the complexes as they will be better able to fit within the DNA grooves. While only one intercalating ligand (dpq) per complex may be needed to increase the DNA affinity, two dpq ligands may allow for a more effective intercalation geometry given the specific orientation of each metal complex to DNA is not known. It is anticipated that these resolved dinuclear intercalating complexes, linked by a flexible linker and with a 4+ charge, will bind with a higher binding affinity than a mononuclear

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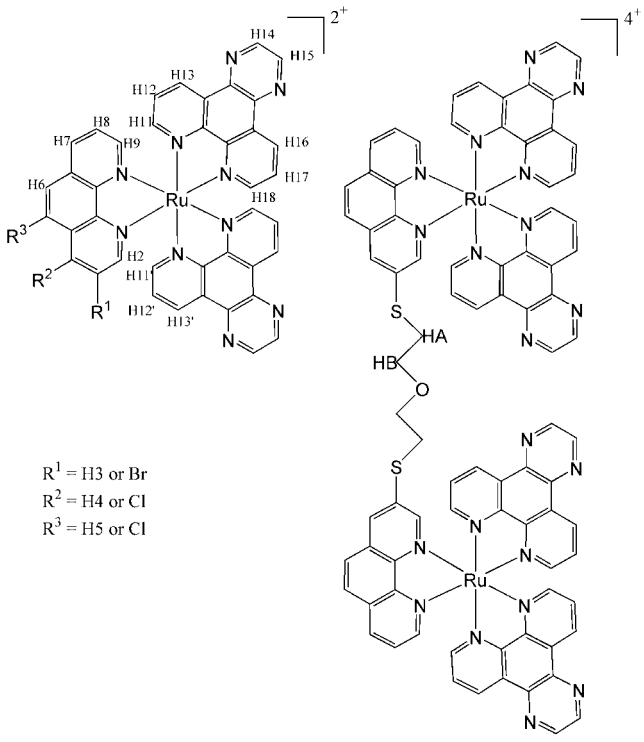

Figure 1. $[Ru(dpq)_2(R\text{-phen})]^{2+}$ and $[\{Ru(dpq)_2\}_2\mu\text{-(phen-3-SOS-3-phen)}]^{4+}$ showing the proton numbering scheme used in ^1H NMR assignments. Anions have been omitted for clarity.

complex.[34] It is also possible that the presence of additional intercalating ligands could cause unfavourable steric hindrance when the metal complex is bound to DNA. Varying the position of linker attachment (3-, 4- or 5-position on the phenanthroline ligand) causes subtle variations in the distance between the metal centres and complex geometry, which may affect the nature of the DNA adduct formed and the overall binding affinity.

Herein we expand an earlier communication[34] on the DNA binding of *rac*-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-}n\text{-SOS-}n\text{-phen)}]^{4+}$ (n = 3, 4 or 5, SOS = bis(2-mercaptoethyl) ether). We now report the synthesis of the mononuclear precursors to these complexes, the synthsis of *rac*/*meso* dinuclear complexes, the resolution of the mononuclear precursors and the stereo-retentive synthesis of the dinuclear complexes as their ΔΔ- and ΛΛ-enantiomers (see Figures 1, 2 and 3).

Results and Discussion

Synthesis of Mononuclear Complexes

Synthesis and Characterisation of $[Ru(dpq)_2(pp')](PF_6)_2$. $[Ru(dpq)_2(pp')]^{2+}$ (pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen) were synthesised by refluxing $[Ru(dpq)_2Cl_2]$ with pp′ in water. Purification was achieved using silica gel and alumina chromatography. Assignment of the ^1H NMR

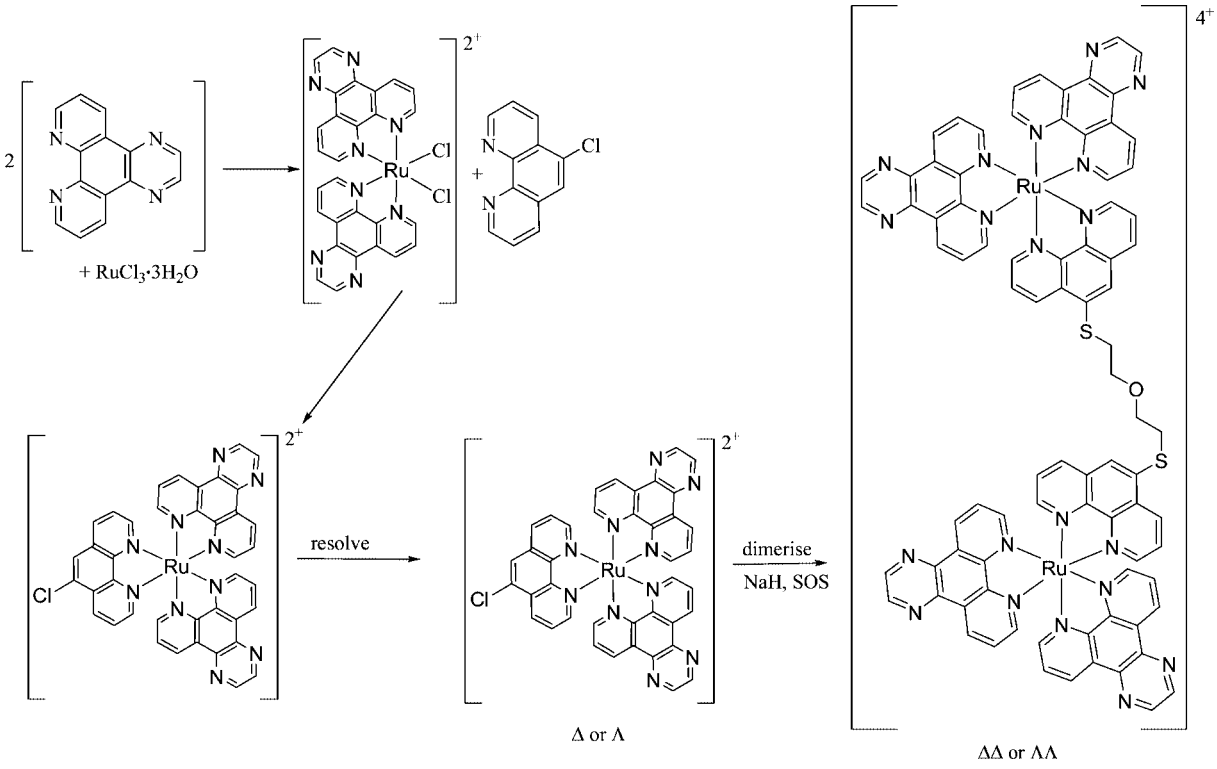

Figure 2. Synthetic route for the synthesis of dinuclear complexes of $[\{Ru(dpq)_2\}_2(\mu\text{-phen-5-SOS-5-phen})]^{4+}$. The same Scheme was also applied to synthesise $[\{Ru(dpq)_2\}_2(\mu\text{-phen-3-SOS-3-phen})]^{4+}$ and $[\{Ru(dpq)_2\}_2(\mu\text{-phen-4-SOS-4-phen})]^{4+}$. The resolution is described further in Figure 3.

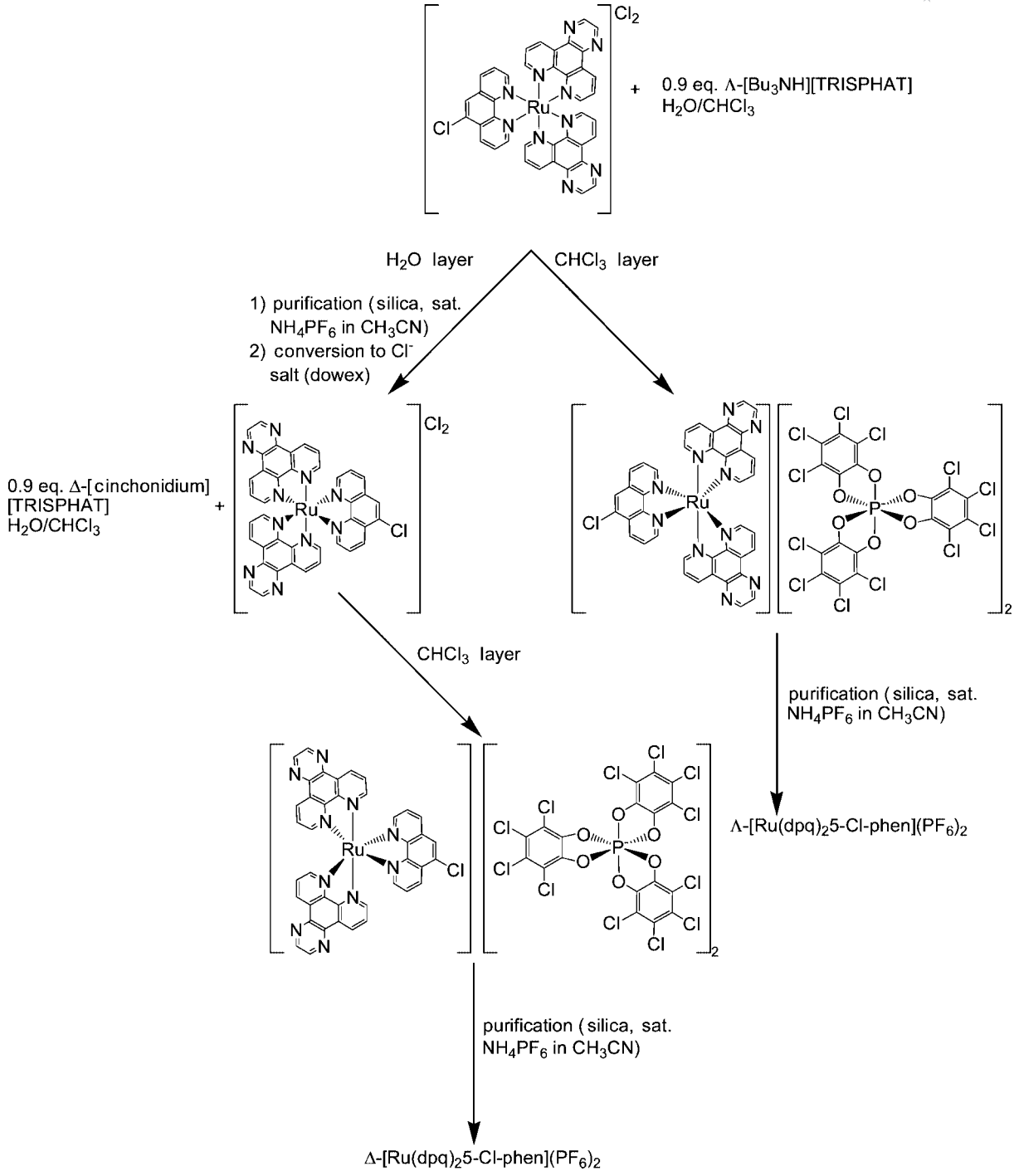

Figure 3. Resolution of $[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$ using the TRISPHAT anion.

spectra of the mononuclear complexes was made using NOESY and g-DQCOSY experiments. Each of the metal complexes exhibit similar resonances with comparative chemical shifts and splitting patterns observed for protons at the same relative positions. $[Ru(dpq)_2(phen)]^{2+}$ is an octahedral complex with two different types of bidentate ligands, and as such it belongs to point group C_2. This complex exhibits the simplest ^1H NMR spectrum of all the mononuclear complexes due to the presence of the C_2 axis. Since the halide substituent occupies the 3-, 4- and 5-position in the 3-Br-phen, 4-Cl-phen and 5-Cl-phen ligands, the complexes of these ligands feature C_1 symmetry (i.e. are dissymmetric) and the spectra for $[Ru(dpq)_2(pp')]^{2+}$ are slightly more complicated (see Supporting Information).

Resolution of Mononuclear Complexes. Attempts to resolve the $[Ru(dpq)_2(pp')]^{2+}$ complexes using solvent recycled chromatography employing SP-Sephadex® as the stationary phase and the chiral anions *O*,*O*′-dibenzoyl-L-tar-

taric acid and *O*,*O*′-ditoluoyl-L-tartaric acid by the methods of Rutherford et al.[35] were unsuccessful. Likewise, fractional recrystallisation employing (+)- and (–)-antimonyl tartrate was also unsuccessful.

The method of [(tris(tetrachlorocatecholato)phosphate(V))]$^-$ (TRISPHAT) extraction was developed from the technique of Lacour et al.[36] for analogous ruthenium(II) complexes. $[Ru(dpq)_2(pp')]Cl_2$ in water was added to a solution of $[Bu_3NH][\Lambda$-TRISPHAT] (0.9 equiv.) in chloroform. The solutions were stirred to allow complete equilibration to occur and the layers separated, with the organic layer containing $[Ru(dpq)_2(pp')][(\Lambda$-TRISPHAT$)_2]$. The reaction was subsequently repeated on the remaining aqueous layer using [cinchonidium][Δ-TRISPHAT] to give $[Ru(dpq)_2(pp')][(\Delta$-TRISPHAT$)_2]$.

The CD spectrum of each sample was obtained and the Δε values calculated as a means of characterising the optical properties of the metal complexes. The assignment of the absolute configurations of the resolved complexes in this study is based on CD and comparison with similar complexes whose absolute configuration has been determined by X-ray crystallography, such as the complex $[Ru(phen)_2(dpq)](PF_6)_2$.[35] In this work, relative enantiomeric purity of the chloride salt was determined by CD to be 99.0–93.3% for the monomers (Tables 1 and 2). The CD spectra for Δ- and Λ-$[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$ are shown in Figure 4 and those of Δ,Λ-$[Ru(dpq)_2(phen)]^{2+}$, Δ,Λ-$[Ru(dpq)_2(3\text{-Br-phen})]^{2+}$ and Δ,Λ-$[Ru(dpq)_2(4\text{-Cl-phen})]^{2+}$ are shown in the Supporting Information. As expected for a pair of enantiomers, there is a mirror–image relationship between the CD curves of the Δ- and Λ-enantiomers as well as the presence of isosbetic points, where the spectra of the Δ- and Λ-enantiomers intercept on the *x*-axis.

The enantiopurity of the samples was also confirmed by the use of a ^{1}H NMR TRISPHAT titration.^{1}H NMR experiments using chiral shifting agents have been applied previously[37] and were necessary in order to confirm that complete resolution had been achieved. The TRISPHAT anion has previously been shown to be a successful chiral shift reagent, specifically with complexes such as $[Ru(phen)_3]$.[38,39] The TRISPHAT titration was performed initially on *rac*/*meso* mixtures of the metal complexes to demonstrate that selective resonance shifts would be induced in the ^{1}H NMR spectrum of each metal complex. As can be

Table 1. CD data obtained for the metal complexes. All measurements conducted in CH_3CN at 25 °C.

Metal complex	CD, λ / nm (Δε, mdeg M^{-1} cm^{-1})
Δ-$[Ru(dpq)_2(phen)](PF_6)_2$	462.5 (–24.9), 415.5 (+21.2), 298.0 (–139.7), 265.0 (–189.9), 248.5, (+109.4), 216.0, (+73.7)
Λ-$[Ru(dpq)_2(phen)](PF_6)_2$	462.5, (+21.8), 415.0 (–20.4), 298.0 (+123.3), 265.5 (+188.5), 249.0, (–109.6), 216.0, (–66.6)
Δ-$[Ru(dpq)_2(3\text{-Br-phen})](PF_6)_2$	463.0 (–23.2), 414.5 (+22.7), 300.0 (–148.1), 275.0 (–109.8), 247.0 (+45.5), 219.0, (+51.8)
Λ-$[Ru(dpq)_2(3\text{-Br-phen})](PF_6)_2$	463.0 (+24.8), 414.5 (–23.4), 300.0 (+155.3), 275.0 (+112.8), 247.0 (–47.6), 216.5, (–55.9)
Δ-$[Ru(dpq)_2(4\text{-Cl-phen})](PF_6)_2$	465.0 (–26.7), 415.5 (+22.8), 299.0 (–139.5), 267.5 (–175.5), 249.5 (+95.6), 218.5, (+60.9)
Λ-$[Ru(dpq)_2(4\text{-Cl-phen})](PF_6)_2$	465.5 (+24.8), 417.0 (–21.1), 299.0 (+129.8), 267.5 (+163.9), 249.5 (–90.0), 216.5, (–57.1)
Δ-$[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$	463.5 (–26.2), 414.5 (+23.1), 299.0 (–140.0), 270.5 (–171.4), 250.5 (+88.0), 216.0, (+69.5)
Λ-$[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$	463.5 (+26.7), 414.5 (–22.9), 298.5 (+141.4), 271.0 (+176.5), 251.0 (–90.3), 217.0, (–68.6)
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-3-SOS-3-phen)}](PF_6)_4$	464.0 (–48.3), 415.0 (+46.1), 299.0 (–269.6), 260.0 (–188.3), 242.0 (+188.9), 213.0, (+111.8)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-3-SOS-3-phen)}](PF_6)_4$	463.0 (+54.9), 415.5 (–55.1), 299.0 (+317.1), 260.0 (+222.8), 242.0 (–220.4), 212.0, (–133.1)
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-4-SOS-4-phen)}](PF_6)_4$	470.0 (–44.9), 419.0 (+35.1), 298.5 (–218.6), 263.5 (–293.0), 247.0 (+163.6), 213.5, (+152.4)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-4-SOS-4-phen)}](PF_6)_4$	468.5 (+45.5), 418.5 (–36.2), 298.5 (+213.3), 263.5 (+280.5), 247.5 (–169.3), 213.5, (–149.6)
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-5-SOS-5-phen)}](PF_6)_4$	464.0 (–59.2), 415.0 (+43.7), 299.0 (–309.1), 260.5 (–101.1), 241.0 (+25.1), 216.5, (+163.0)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-5-SOS-5-phen)}](PF_6)_4$	464.0 (+53.5), 416.0 (–49.4), 299.0 (+307.6), 260.5 (+101.6), 240.0 (–35.1), 216.5, (–173.2)

Table 2. Relative enantiomeric purity, quantum yield, emission and absorption data of the metal complexes. All measurements conducted in CH_3CN at 25 °C.

Metal complex	Relative enantiomeric purity %[a]	Quantum yield Φ	Emission λ_{max} / nm	Absorption λ_{max} / nm ($\varepsilon \times 10^4$ mol^{-1} dm^3 cm^{-1})
Δ-$[Ru(dpq)_2(phen)](PF_6)_2$	93.9 ± 5.3			447 (1.7), 290 (4.6) sh[b], 258 (10.6), 206 (6.7)
Λ-$[Ru(dpq)_2(phen)](PF_6)_2$		0.061	604–608	
Δ-$[Ru(dpq)_2(3\text{-Br-phen})](PF_6)_2$	95.3 ± 1.9			447 (1.9), 257 (10.0), 207 (7.8)
Λ-$[Ru(dpq)_2(3\text{-Br-phen})](PF_6)_2$		0.042	590–600	
Δ-$[Ru(dpq)_2(4\text{-Cl-phen})](PF_6)_2$	93.3 ± 0.6			449 (2.1), 291 (5.4) sh, 257 (12.0), 207 (8.1)
Λ-$[Ru(dpq)_2(4\text{-Cl-phen})](PF_6)_2$		0.050	590–600	
Δ-$[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$	99.0 ± 1.8			448 (2.0), 291 (5.1) sh, 257 (11.6), 207 (7.7)
Λ-$[Ru(dpq)_2(5\text{-Cl-phen})](PF_6)_2$		0.059	598–598	
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-3-SOS-3-phen)}](PF_6)_4$	85.1 ± 1.6			448 (3.7), 255 (20.8), 215 (13.6)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-3-SOS-3-phen)}](PF_6)_4$		0.062	603–608	
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-4-SOS-4-phen)}](PF_6)_4$	99.9 ± 3.2			452 (4.8), 257 (20.5), 215 (15.1)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-4-SOS-4-phen)}](PF_6)_4$		0.053	607–610	
ΔΔ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-5-SOS-5-phen)}](PF_6)_4$	94.1 ± 13.3			450 (4.8), 256 (20.2), 217 (14.1)
ΛΛ-$[\{Ru(dpq)_2\}_2\mu\text{-(phen-5-SOS-5-phen)}](PF_6)_4$		0.048	602–603	

[a] The relative enantiomeric purity has been determined by dividing the intensity of each of the peaks of one enantiomer by the corresponding peaks of the other. The averages for all the peaks in the spectrum are given as percentage purity along with the standard deviation. [b] sh = shoulder band.

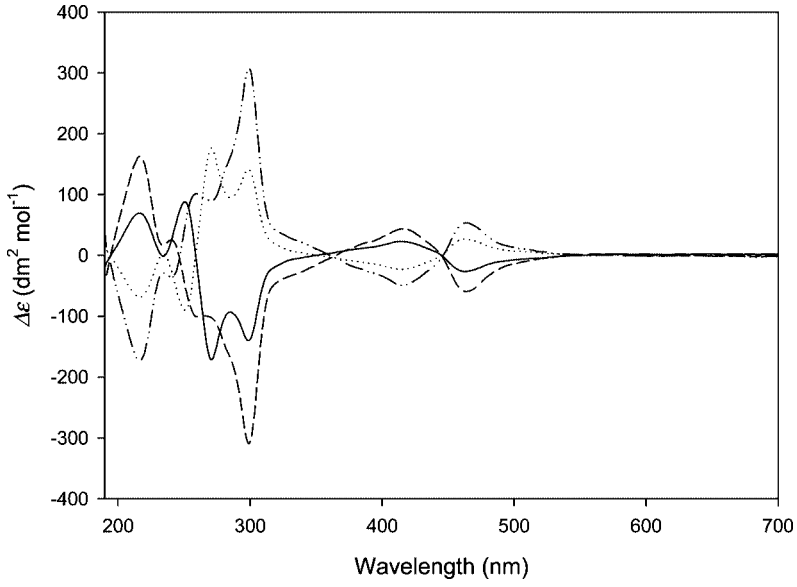

Figure 4. CD spectra (CH_3CN) of Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ (solid line), Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ (dotted line), ΔΔ-[{Ru(dpq)$_2$}$_2$-μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$ (dashed line) and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$ (dashed and dotted line).

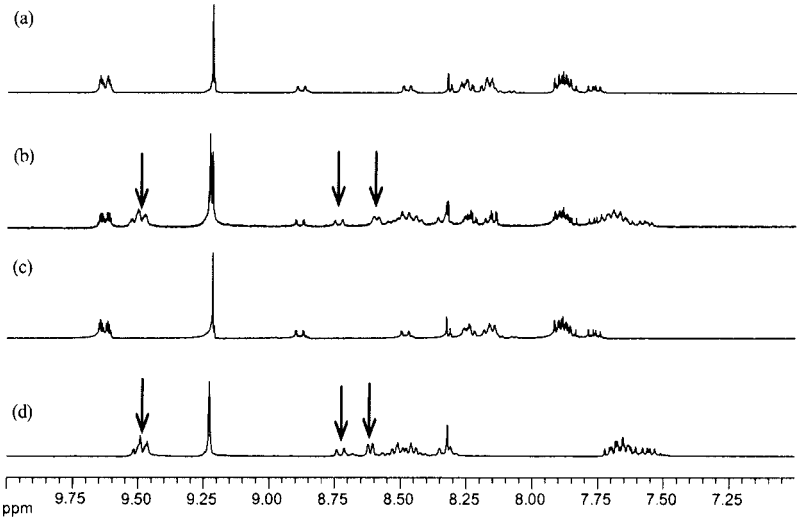

Figure 5. ^{1}H NMR (CD_3CN, 25 °C) titration of [Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ with [Bu$_3$NH][Λ-TRISPHAT]. Arrows indicate the splitting and shifting of the Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ proton resonances from the Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ proton resonances; (a) *rac*-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$, (b) *rac*-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ + 1 mol-equiv. of [Bu$_3$NH][Λ-TRISPHAT], (c) Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ + 1 mol-equiv. of [Bu$_3$NH][Λ-TRISPHAT] and (d) Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ + 1 mol-equiv. of [Bu$_3$NH][Λ-TRISPHAT].

seen in Figure 5, the addition of 1 mol-equiv. of [Bu$_3$NH][Λ-TRISPHAT] to *rac*-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ causes the resonances for the metal complex to broaden and split into two groups – one complete set of resonances for each enantiomer.

The three most downfield resonances, corresponding to the H13/16, H14/15 and H4 protons are the signals most easily used for the assessment of optical purity, because each of them is isolated from other overlapping resonances. The resonance for H13/16 splits into two multiplets, one resonance (due to Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$) remains at δ = 9.63 ppm while the resonance for Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ shifts upfield to 9.50 ppm. Similarly, the H14/15 and H4 resonances also split, with separations of 0.01 ppm and 0.15 ppm, respectively, observed between the Δ- and Λ-resonances. The addition of 1 mol-equiv. of [Bu$_3$NH][Λ-TRISPHAT] does not induce any change in the ^{1}H NMR spectrum of Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$, while the addition of [Bu$_3$NH][Λ-TRISPHAT] to Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ induces chemical shift changes in all resonances of the metal complex.

The results from the chiral ^{1}H NMR titration experiment shown in Figure 5 agree with those published previously for [Ru(4,7-Me$_2$phen)$_3$]$^{2+}$ and [Ru(Me$_2$bpy)$_3$]$^{2+}$, where it was shown that Λ-TRISPHAT will interact more strongly with the Λ-enantiomer of a metal complex than with the Δ-en-

Table 3. Summary of the MS data obtained for the metal complexes. All measurements conducted in CH_3CN at 25 °C.

Metal complex	ESI-MS (calcd., found) (*m*/*z*)
Δ-[Ru(dpq)$_2$(phen)](PF$_6$)$_2$	[M(PF$_6$) + H]$^+$ (891.7, 891.2), [M]$^{2+}$ (372.9, 372.4)
Λ-[Ru(dpq)$_2$(phen)](PF$_6$)$_2$	[M(PF$_6$) + H]$^+$ (891.7, 891.4), [M]$^{2+}$ (372.9, 371.0)
Δ-[Ru(dpq)$_2$(3-Br-phen)](PF$_6$)$_2$	[M(PF$_6$) + H]$^+$ (970.7, 970.5), [M]$^{2+}$ (412.3, 412.7)
Λ-[Ru(dpq)$_2$(3-Br-phen)](PF$_6$)$_2$	[M(PF$_6$) + H]$^+$ (970.7, 970.5), [M]$^{2+}$ (412.3, 412.7)
Δ-[Ru(dpq)$_2$(4-Cl-phen)](PF$_6$)$_2$	[M(PF$_6$)]$^+$, (925.2, 924.6). [M]$^{2+}$ (390.1, 390.0)
Λ-[Ru(dpq)$_2$(4-Cl-phen)](PF$_6$)$_2$	[M(PF$_6$)]$^+$ (925.2, 924.6), [M]$^{2+}$ (390.1, 390.0)
Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$	[M(PF$_6$)]$^+$ (925.2, 924.7), [M]$^{2+}$ (390.1, 390.0)
Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$	[M(PF$_6$)]$^+$ (925.2, 924.7), [M]$^{2+}$ (390.1, 390.0)
ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)](PF$_6$)$_4$	[M(PF$_6$)$_2$]$^{2+}$ (957.8, 958.0), [M(PF$_6$)]$^{3+}$ (590.2, 590.7), [M]$^{4+}$ (406.4, 407.0)
ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)](PF$_6$)$_4$	[M(PF$_6$)$_2$]$^{2+}$ (957.8, 958.1), [M(PF$_6$)]$^{3+}$ (590.2, 590.4), [M]$^{4+}$ (406.4, 406.6)
ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$	[M(PF$_6$)$_2$]$^{2+}$ (957.8, 958.3), [M(PF$_6$)]$^{3+}$ (590.2, 590.7), [M]$^{4+}$ (406.4, 407.0)
ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$	[M(PF$_6$)$_2$]$^{2+}$ (957.8, 958.3), [M(PF$_6$)]$^{3+}$ (590.2, 590.7), [M]$^{4+}$ (406.4, 406.9)
ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$	[M(PF$_6$)$_4$ + H]$^+$ (2206.6, 2206.4), [M(PF$_6$)$_3$]$^+$ (2060.6, 2061.3), [M(PF$_6$)$_2$]$^{2+}$ (957.8, 958.4), [M(PF$_6$)]$^{3+}$ (590.2, 590.7), [M]$^{4+}$ (406.4, 406.9)
ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$	[M(PF$_6$)$_2$]$^{2+}$ (957.8, 957.3), [M(PF$_6$)]$^{3+}$ (590.2, 589.7), [M]$^{4+}$ (406.4, 406.3)

antiomer of the same metal complex.[35] The TRISPHAT titrations were repeated for all the resolved metal complexes and similar results were observed for each.

The mononuclear metal complexes were also analysed using electrospray ionisation mass spectrometry (ESI-MS) as an additional method of characterisation (Table 3). Although the parent ions, [M(PF$_6$)$_2$ + H]$^+$ were not observed, peaks were generally observed for the [M(PF$_6$)]$^+$ and [M]$^{2+}$ ions of each complex (e.g. Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ ([M(PF$_6$)]$^+$ *m*/*z* calcd. 925.2, found 924.7); ([M]$^{2+}$ *m*/*z* calcd. 390.1, found 390.0)), confirming the molecular weights of the metal complexes. The isotopic splitting patterns observed agree closely with those calculated. The peak due to the [M(PF$_6$)]$^+$ ion was approximately twice the intensity of that due to the [M]$^{2+}$ ion, and this ratio was observed for all the mononuclear complexes studied.

Dinuclear Complexes

Synthetic Method Development: Synthesising [{Ru(dpq)$_2$}$_2$μ-(phen-*n*-SOS-*n*-phen)](PF$_6$)$_4$ (*n* = 3, 4 or 5) by reacting the bridging SOS linker with the mononuclear complexes (DMF, $N_{2(g)}$, NaH, 25 °C) resulted in a number of side-products, in addition to the required complex. The impurities were characterised by TLC and ^{1}H NMR spectroscopy. The simplest component in the mixture was the unreacted mononuclear complex [Ru(dpq)$_2$(5-Cl-phen)]$^{2+}$. A mononuclear ruthenium complex with a non-bridging dithiol linker attached, that had not dimerised with a second monomer of [Ru(dpq)$_2$(phen-*n*-SOS-H)]$^{2+}$ was also identified. A third species was also found in which the linker had reacted with itself forming a dinuclear ruthenium(II) complex, bridged by a disulfide-bonded linker, forming a 14 unit chain instead of the desired seven. The desired dinuclear ruthenium(II) complexes were isolated from solution by precipitation with diethyl ether followed by silica gel chromatography.

In the initial method development the synthesis of the dinuclear metal complexes using racemic (unresolved) mononuclear precursors was tried and it was expected that this would afford a mixture consisting of 25% of each of the two homochiral enantiomers, ΔΔ and ΛΛ, and 50% of the *meso* (ΔΛ/ΛΔ) diastereoisomer. The ^{1}H NMR spectra of the ΔΔ- and ΛΛ-enantiomers of the metal complexes are

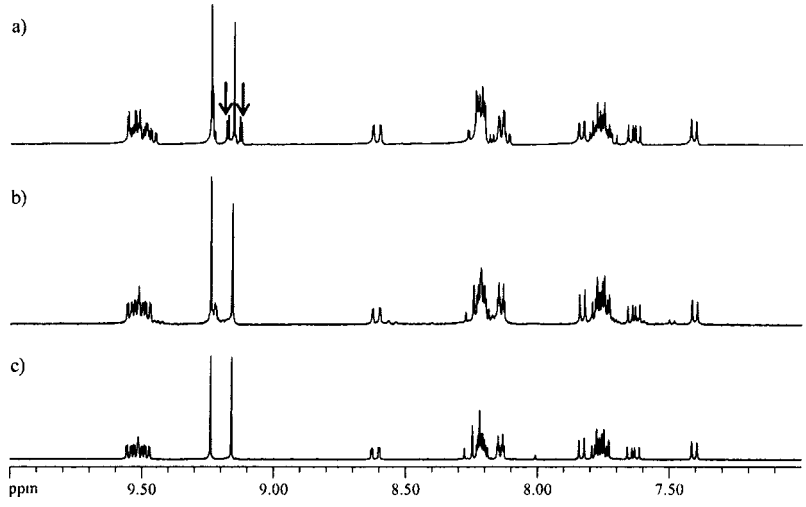

Figure 6. ^{1}H NMR spectra (CD_3CN, 25 °C) of the stereoisomers of [{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$; (a) *rac*/*meso* (ΔΔ/ΛΛ/ΔΛ/ΛΔ-), (b) ΔΔ- and (c) ΛΛ- showing the presence of the *meso* (ΔΛ/ΛΔ-) complex (indicated by arrows).

slightly different from those of the *meso* (ΔΛ/ΛΔ)-diastereoisomer, giving rise to overlapping resonances due to the chemically identical ΔΔ- and ΛΛ- enantiomers with the *meso* (ΔΛ/ΛΔ) form. Due to resonance overlap, it was not possible to determine the ratio of the enantiomers formed in these experiments.

When the dinuclear metal complexes were synthesised using enantiopure starting materials, resonances due to the *meso* diastereoisomer were absent from the ^{1}H NMR spectra of the ΔΔ- and ΛΛ complexes (Figure 6).

UV/Vis: The extinction coefficients for ΔΔ- and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)]$^{4+}$ exhibited an increase in intensity of 220% compared to *rac*-[Ru(dpq)$_2$(3-Br-phen)]$^{2+}$. The extinction coefficients for the ΔΔ- and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)]$^{4+}$ and ΔΔ- and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)]$^{4+}$ complexes also increased by 180 and 200%, respectively, compared to their mononuclear analogues ([Ru(dpq)$_2$(4-Cl-phen)]$^{2+}$ and [Ru(dpq)$_2$(5-Cl-phen)]$^{2+}$). Three main peaks were observed in the UV/Vis spectra of the metal complexes, in the ranges of 206–217 nm, 256–258 nm and 447–452 nm. For the mononuclear metal complexes, the transitions observed in the region of 447–452 nm are attributed to metal-to-ligand charge transfer (MLCT). For both the mono- and dinuclear metal complexes, the bands in the region of 206–256 are attributed predominantly to overlapping π→π* transitions. In the spectrum of each of the dinuclear complexes, the MLCT bands were observed at slightly higher wavelength (lower energy) than the MLCT bands of the analogous mononuclear complexes.

Luminescence Quantum Yields: The luminescence quantum yields of the complexes were determined and are shown in Table 2. Excitation at 450 nm of the metal complexes in CH_3CN at 25 °C results in an emission maximum at 600 ± 10 nm (depending on the position of substitution shown in Table 2) and is due to both the phen and dpq ligands. The luminescence quantum yields of the mononuclear metal complexes are in the range of $\Phi = 4.2 \times 10^{-2}$ to 5.9×10^{-2} and for the dinuclear complexes are in the range of $\Phi = 4.8 \times 10^{-2}$ to 6.2×10^{-2}. It is not expected that the excitation and emission maxima and Φ would vary significantly between the mono- and dinuclear complexes (as was the case with ε_{max}). The metal centres in the dinuclear complexes are separated by a relatively long aliphatic linker and therefore the electronic configuration of the ruthenium(II) centres is not significantly changed upon dimerisation.

Circular Dichroism: The CD spectrum of each of the resolved dinuclear metal complexes was obtained and the Δε values calculated as a means of characterising the optical properties of the complexes (see Tables 1 and 2, Figure 4 and Supporting Information). The relative enantiomeric purity of the chloride salt of each of the complexes was determined by CD spectroscopy to be 99.9–85.1% for the dimers. Each pair of enantiomers shows a mirror–image relationship between the CD curves of the ΔΔ and ΛΛ enantiomers and the presence of isosbetic points, but when compared with the spectra of the corresponding mononuclear complex subtle differences are observed.

The main CD features for the mononuclear complexes Δ-[Ru(dpq)$_2$(phen)]$^{2+}$, Δ-[Ru(dpq)$_2$(4-Cl-phen)]$^{2+}$ and Δ-[Ru(dpq)$_2$(5-Cl-phen)]$^{2+}$ are two sets of bisignate curves due to the excition coupling of the π–π* transitions of the diimine chromophores that are centred around 250 nm. The two bands between 200–250 nm are positive, the two bands between 250–350 nm are negative and the intensities between the monomeric complexes are comparable. The CD spectra of Δ-[Ru(dpq)$_2$(4-Cl-phen)]$^{2+}$ and Δ-[Ru(dpq)$_2$(5-Cl-phen)]$^{2+}$ show very slight differences, about 10% in intensity in peaks at ca. 265, 247 and 216 nm. Δ-[Ru(dpq)$_2$(3-Br-phen)]$^{2+}$ has a similar CD spectrum, however, the intensities are significantly reduced for the peaks (% reduction) at 275 (58%), 247 (42%) and 219 (70%) nm when compared with Δ-[Ru(dpq)$_2$(phen)]$^{2+}$.

Telfer et al.[29] have shown that the energy ordering of the positive and negative Cotton effects is related directly to the absolute configuration of the metal centre. The contribution of intranuclear excition coupling to the CD spectra is dependent strongly upon the length of the bridging ligand and is not simply double the intensity of the appropriate mononuclear complex, as one might expect, even though a flexible linker connects the two metal complexes in this case. The CD spectra that are produced are uniquely different for each of the dimers indicating that although the linker does not rigidly orientate the molecules there must be some coupling between the chromophores and that the resulting CD spectra are not simply additive.

The CD spectrum of Δ-[Ru(dpq)$_2$(phen)]$^{2+}$ contains four intraligand π–π* transitions, between 190–300 nm (216, 248, 265 and 298 nm at Δε = 73, 109, –190, and –140 respectively), while the weak band at 462.5 nm is most likely to be an MLCT transition. The intense CD bands at ca. 298 and 265 nm (long-axis polarization transition) for Δ-[Ru(dpq)$_2$(phen)]$^{2+}$ is strongly negative and the CD bands at higher energy (ca. 247 and 216 nm) positive, confirming the assignment as the Δ-enantiomer.[35] As expected, the CD spectrum of Λ-[Ru(dpq)$_2$(phen)]$^{2+}$ exhibits peaks of opposite intensity.

The CD spectra of Δ- and Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$, and ΔΔ- and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$ are shown in Figure 4. The spectra of both the mono- and dinuclear metal complexes are characterised by the peak wavelengths and their intensity in the 190 to 500 nm region. The two peaks at higher wavelength (465 to 415 nm), due to the MLCT, are similar in shape for both the mono- and dinuclear metal complexes and the peaks are approximately double (2.26 and 1.89 times intensity respectively) the intensity for the dinuclear metal complexes compared to the mononuclear complexes. The peaks at 299 and 216 nm also are approximately double (2.21 and 2.35 times intensity respectively) however, the peaks at 261 and 241 nm are considerably less (0.59 and 0.29 times intensity, respectively) than the mononuclear complex.

The CD spectra of Δ- and Λ-[Ru(dpq)$_2$-(4-Cl-phen]$^{2+}$, ΔΔ- and ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)]$^{4+}$ are provided in the Supporting Information. For ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)]$^{4+}$ the two peaks at higher

wavelength (468 to 418 nm), due to the MLCT, are similar in shape for both the mono- and dinuclear metal complexes and the peaks are 1.68 and 1.54 the intensity, respectively, for the dinuclear metal complexes compared to the mononuclear complexes. The peaks at 289, 263 and 247 nm have all similarly increased in intensity (1.57, 1.67 and 1.71 times, respectively) whereas the peak at 213 nm is the only peak which is approximately double (2.50 times) in intensity when compared to Δ-$[Ru(dpq)_2$-(4-Cl-phen)$]^{2+}$.

The CD spectra of Δ- and Λ-$[Ru(dpq)_2$-(3-Br-phen)$]^{2+}$, ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-3-SOS-3-phen)$]^{4+}$ are provided in the Supporting Information. For ΔΔ-$[\{Ru(dpq)_2\}_2\mu$-(phen-3-SOS-3-phen)$]^{4+}$ the two peaks at higher wavelength (463 to 415 nm), due to the MLCT, are similar in shape for both the mono- and dinuclear metal complexes and the peaks are more than double (2.21 and 2.35) the intensity, respectively, for the dinuclear metal complexes compared to the mononuclear complexes. The peaks at 299, 260 and 212 nm are also about double the intensity (2.04, 1.98 and 2.38 times intensity, respectively) whereas the peak at 242 nm is 4.63 times the intensity when compared to Δ-$[Ru(dpq)_2$-(3-Br-phen)$]^{2+}$.

These differences in the CD spectra indicate that the location of the flexible linker attachment in the 3-, 4- or 5-positions on the phenanthroline ligand contribute differently to internuclear excitation coupling. The transitions at ca. 216 and 299 nm and the intensity of the MLCT band for all of the complexes are about double that of the mononuclear complex indicating that the linker position has a limited effect on these transitions. The transitions at ca. 241 and 261 nm are particularly sensitive to the orientation of the coordinated ligands when the linker attachment is in the 3- (0.29 and 0.29 times the mononuclear respectively), 4- (1.71 and 1.67 times the mononuclear respectively) or 5- (4.65 and 1.98 times the mononuclear respectively) positions.

For ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-3-SOS-3-phen)$]^{4+}$ the distance between the complexes and the orientation with respect to one another is sufficient for all of the transitions to be additive and in the case of the transition at 242 nm four times. For ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-4-SOS-4-phen)$]^{4+}$ the internuclear excitation coupling is 1.5–2 for all transitions indicating that in this case each of the observed transitions for the complexes is almost independent. In the case of ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-5-SOS-5-phen)$]^{4+}$ the distance between the complexes appears to be adequate to produce a reduction in the band intensity which is accompanied by a wavelength shift of –10 nm for the dinuclear complex at 240 nm (the mononuclear complex peak occurs at 250 nm).

ESI-MS: As with the mononuclear complexes, the racemic and resolved dinuclear complexes were also characterised by ESI-MS (Table 3). The parent ions, $[M(PF_6)_4 + H]^+$ were not observed for any of the complexes. In the case of ΔΔ-$[\{Ru(dpq)_2\}_2\mu$-(phen-5-SOS-5-phen)$](PF_6)_4$, the mass spectrum displayed $[M(PF_6)_2]^{2+}$ (*m*/*z* calcd. 957.8, found 958.4), $[M(PF_6)]^{3+}$ (*m*/*z* calcd. for 590.2, found 590.7) and $[M]^{4+}$ (*m*/*z* calcd. 406.4, found 406.9). The intensity of the peaks increased as the charge on the metal complexes increased, such that the order of intensity was $[M]^{4+} > [M(PF_6)]^{3+} > [M(PF_6)_2]^{2+}$ (100%, 50% and 18%, respectively). The other dinuclear metal complexes also exhibited isotopic patterns for the $[M(PF_6)_2]^{2+}$, $[M(PF_6)]^{3+}$ and $[M]^{4+}$ ions, in similar ratios to those observed for ΔΔ-$[\{Ru(dpq)_2\}_2\mu$-(phen-5-SOS-5-phen)$](PF_6)_4$. The *m*/*z* values and isotopic ratios for the peaks observed in the ESI-MS of all the metal complexes are in close agreement with the calculated values.

Conclusions

Here we have demonstrated that the mononuclear complexes Δ,Λ-$[Ru(dpq)_2$(3-Br-phen)$]^{2+}$, Δ,Λ-$[Ru(dpq)_2$(4-Cl-phen)$]^{2+}$, Δ,Λ-$[Ru(dpq)_2$(5-Cl-phen)$]^{2+}$ and Δ,Λ-$[Ru(dpq)_2$-(phen)$]^{2+}$ can be used to produce enantiomerically pure dinuclear complexes ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-3-SOS-3-phen)$]^{4+}$, ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-4-SOS-4-phen)$]^{4+}$ and ΔΔ- and ΛΛ-$[\{Ru(dpq)_2\}_2\mu$-(phen-5-SOS-5-phen)$]^{4+}$. The resolution of the mononuclear complexes could only be achieved using the chiral TRISPHAT anion, as column chromatography and classical resolution techniques were not effective in this case. Resolution of the mononuclear metal complexes was confirmed by CD and chiral ^{1}H NMR titrations using the TRISPHAT anion. The production of the enantiomerically pure dinuclear complexes was assessed by CD. When compared to the monomeric form, the intensity of the peaks in the CD spectra the dinuclear complexes were not simply double that of their mononuclear analogues. This suggests that the position of attachment of the flexible linker affects the internuclear excitation coupling between the chromophores located on each of the metal centres differently. Binding studies using the dinuclear metal complexes are under way for these potential DNA probes.

Experimental Section

Materials Dowex® 1X8–200 (Cl^- form), 1,10-phenanthroline, lithium chloride, 5-chloro-1,10-phenanthroline, aluminium oxide (activated, neutral, Brockman I), potassium hexafluorophosphate, ammonium hexafluorophosphate, anhydrous *N*,*N*′-dimethylformamide (99.9%), NaH, KNO_3 and silica gel (TLC grade) were all obtained from the Aldrich chemical company. Ruthenium trichloride $(RuCl_3)\cdot xH_2O$ was purchased from Precious Metals Online. Silica gel 60 (0.040–0.063 mm) for column chromatography was obtained from Merck. Bis(2-mercaptoethyl) ether was purchased from Lancaster. Deuterated solvents, [D_2O (99.9% D), CD_2Cl_2 (99.8% D) and CD_3CN (99.8% D)] were purchased from Cambridge Isotope Laboratories. 3-Br-phen was made by the method of Tzalis et al.,[40] 4-Cl-phen was made by the method of Snyder and Freier,[41] dpq was made by the method of Collins et al.[17] Tetrachlorocatechol was made by the method of Renner and Hopfer,[42] TRISPHAT was synthesised and resolved by the methods of Favarager et al.[43] and $[Ru(dpq)_2Cl_2]$ was synthesised by the method of Anderson et al.[44] as for the analogous bpy complex. All general reagents and solvents were used as received (unless specifically stated) and were of analytical reagent grade or higher.

NMR Spectroscopy: Routine NMR was carried out on a 300-MHz Varian Mercury spectrometer equipped with a variable temperature accessory. For one-dimensional ^{1}H spectra, a spectral width of 4500 Hz was used with 18000 data points and relaxation delay of 1 s, with the temperature kept constant at 25 °C. The spectra were referenced internally to the solvent resonances. Two dimensional NOESY spectra were accumulated using a 4200 Hz spectral width with 256 increments in the t_1 dimension, 2048 points in the t_2 dimension and mixing times of 300–800 ms. Two dimensional g-DQCOSY experiments were recorded over a spectral width of 4200 Hz using 256 increments in the t_1 dimension, 2048 points in the t_2 dimension and a pulse repetition delay of 1.5–2.0 s.

ESI-MS: Electrospray ionisation mass spectrometry was carried out by the mass spectroscopic service provided by the Research School of Chemistry, Australian National University.

Circular Dichroism: Circular dichroism spectra were recorded using a Jasco J-810 CD spectropolarimeter at room temperature. Samples of metal complexes (approx. 0.22 mg) were weighed directly into a 1-cm cell. The samples were dissolved by the addition of CH_3CN (3.000 mL) then diluted so that the absorbance maximum was in the range 2.2 ± 0.2 absorbance units. The spectrum of each sample was then reacquired (in the range of 190–700 nm), the data pitch was set at 0.5 nm, the scan speed at 500 nm/min and the response time at 1 s. Spectra are shown as an average of 20 accumulations. The value of the molar absorptivity ($\Delta\varepsilon$) was calculated according to Equation (1).[45]

$$\Delta\varepsilon = \frac{\theta}{32.982 \times c \times l} \quad (1)$$

TRISPHAT Titrations: Samples of metal complexes $[Ru(dpq)_2(pp')]^{2+}$ (pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen) (approx. 4.4×10^{-4} mmol) were weighed out and dissolved in CD_2Cl_2 (650 μL) in NMR tubes. A solution of [Bu_3NH][Λ-TRISPHAT] was also prepared in CD_2Cl_2 at such a concentration that 25 μL of this solution would be 1 equiv. of the metal complex. ^{1}H NMR spectra were acquired for each sample before and after the addition of [Bu_3NH][Λ-TRISPHAT].

UV/Vis: Absorption spectra were measured at 25 °C in the range 200–800 nm using a Varian Cary 300 Bio UV/Vis double-beam spectrophotometer referenced to H_2O. Extinction coefficients were determined by repeated measurements of the absorbance of aqueous metal complex solutions of known concentration. The solutions were serially diluted so that for all peaks, three measurements within the range 0.3–0.8 were obtained. The gradient of the lines of best fit of a plot of concentration vs. absorbance at each λ_{max} gave the extinction coefficients, ε_{max}.

Radiative Quantum Yield: Radiative quantum yield (Φ) measurements were performed using an adaptation of the method of Damrauer et al.[46] UV spectra were recorded on a Varian Cary 300-Bio spectrophotometer equipped with temperature controller set at 298 K. Luminescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer, also equipped with a temperature controller at 298 K. All metal complexes were used as PF_6^- salts in CH_3CN. Values of Φ are reported relative to $[Ru(bpy)_3]^{2+}$ in CH_3CN ($\Phi_r = 0.062$)[47] and were calculated using Equation (2),[48] where Φ_{unk} is the radiative quantum yield of the sample, Φ_{std} is the radiative quantum yield of the standard, I_{unk} and I_{std} are the integrated emission intensities of the sample and standard, respectively. A_{unk} and A_{std} are the absorbance of the sample and standard, respectively, at the wavelength of excitation (450 nm). η_{unk} and η_{std} are the indices of refraction of the sample and standard solutions, respectively. Values of η corresponding to the pure solvent are generally used. Since all measurements were conducted in the same solvent, $\eta_{unk}/\eta_{std} = 1$.

$$\Phi_{unk} = \Phi_{std}\left(\frac{I_{unk}}{A_{unk}}\right)\left(\frac{A_{std}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \quad (2)$$

Metal Complex Synthesis

Synthesis of $[Ru(dpq)_2(pp')](PF_6)_2$ (pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen): In a typical experiment, $[Ru(dpq)_2Cl_2]$ (1.0 g, 1.58 mmol) was suspended in H_2O (800 mL) and the solution heated to reflux (30 min). The ligand pp′ (1.16 mmol) was dissolved in CH_3CH_2OH (200 mL) and added dropwise over a period of 1 h. The mixture was kept at reflux for another 48 h, during which time it changed colour from black to deep red. After cooling, the solution was reduced in volume to ca. 100 mL before the addition of saturated KPF_6 solution (3 mL), which caused precipitation of the complex. The suspension was extracted with CH_2Cl_2 (5×200 mL), into which the orange complex redissolved and the combined extracts were dried with anhydrous Na_2SO_4. The solution was evaporated to dryness to give the crude product as a red solid, which was purified on silica gel (eluent: 89% CH_3CN, 1% saturated KNO_3 solution, 10% H_2O). The fractions containing pure $[Ru(dpq)_2(pp')](PF_6)_2$ were identified by ^{1}H NMR, combined and extracted with CH_2Cl_2. The compound was dissolved in acetone and then precipitated by the addition of H_2O. The complex was collected by vacuum filtration, washed with diethyl ether and air-dried. The complex was subsequently purified by column chromatography on alumina, eluting with CH_3CN. The single fraction was collected and the solvents evaporated to dryness to yield the product as an orange solid.

***rac*-$[Ru(dpq)_2(phen)](PF_6)_2$:** Yield 0.11 g (30%). UV (CH_3CN): λ_{max} ($\varepsilon \times 10^4$, $mol^{-1}\,dm^3\,cm^{-1}$) = 447 (1.7), 290 (4.6), 258 (10.6), 206 (6.7) nm. Quantum luminescence yield (Φ): 0.061. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.57 (dd, J = 1.4 Hz, 4 H, H13/16), 9.26 (d, J = 1.4 Hz, 4 H, H14/15), 8.66 (ddd, J = 1.3, 1.3, 8.3 Hz, 4 H, H4/7), 8.30 (d, J = 1.3 Hz, 2 H, H5/6), 8.26 (d, J = 5.4 Hz, 4 H, H2/9), 8.16 (dddd, J = 1.3, 1.3, 2.6, 5.2 Hz, 4 H, H11/18), 7.80 (m, 4 H, H12/17), 7.67 (ddd, J = 1.3, 5.3, 8.3 Hz, 2 H, H3/8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}F_6N_{10}PRu$ $[M(PF_6) + H]^+$, 891.7, found 891.4, m/z calcd. for $C_{40}H_{24}N_{10}Ru$ $[M]^{2+}$, 372.9, found 371.0.

***rac*-$[Ru(dpq)_2(3\text{-}Br\text{-}phen)](PF_6)_2$:** Yield 0.75 g (45%). UV (CH_3CN): λ_{max} ($\varepsilon \times 10^4$, $mol^{-1}\,dm^3\,cm^{-1}$) = 447 (1.9), 257 (10.0), 207 (7.8). Quantum luminescence yield (Φ): 0.042. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (m, 4 H, H13/16), 9.24 (d, J = 3.0 Hz, 4 H, H14/15), 8.88 (d, J = 1.9 Hz, 1 H, H4), 8.65 (dd, J = 1.2, 8.3 Hz, 1 H, H7), 8.33 (d, J = 8.9 Hz, 1 H, H5), 8.24 (m, 4 H, H11/18), 8.14 (dd, J = 1.2, 9.1 Hz, 1 H, H2), 8.14 (dd, J = 1.3, 1.3 Hz, 1 H, H6), 8.10 (dd, J = 1.3, 5.3 Hz, 1 H, H9), 7.80 (m, 4 H, H12/17), 7.68 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}BrF_6N_{10}PRu$ $[M(PF_6) + H]^+$, 970.7, found 972.2, m/z calcd. for $C_{40}H_{23}BrN_{10}Ru$ $[M]^{2+}$, 412.3, found 409.9.

***rac*-$[Ru(dpq)_2(4\text{-}Cl\text{-}phen)](PF_6)_2$:** Yield 0.44 g (52%). UV (CH_3CN): λ_{max} ($\varepsilon \times 10^4$, $mol^{-1}\,dm^3\,cm^{-1}$) = 449 (2.1), 291 (5.4), 257 (12.0), 207 (8.1). Quantum luminescence yield (Φ): 0.050. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (m, 4 H, H13/16), 9.24 (d, J = 0.9 Hz, 4 H, H14/15), 8.67 (dd, J = 1.3, 8.3 Hz, 1 H, H7), 8.52 (d, J = 9.1 Hz, 1 H, H5), 8.40 (d, J = 9.2 Hz, 1 H, H6), 8.20 (m, 4 H, H11/18), 8.12 (dd, J = 1.3, 5.3 Hz, 2 H, H2/9), 8.03 (d, J = 5.8 Hz, 1 H, H3),

7.78 (m, 4 H, H12/17), 7.68 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 926.1, m/z calcd. for $C_{40}H_{23}BrN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.3.

***rac*-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$:** Yield 0.587 g (58%). UV (CH_3CN): λ_{max} ($\varepsilon \times 10^4$, $mol^{-1}\,dm^3\,cm^{-1}$) = 448 (2.0), 291 (5.1), 257 (11.6), 207 (7.7). Quantum luminescence yield (Φ): 0.059. ^1H NMR (300 MHz, CD_3CN): δ = 9.57 (ddd, J = 1.5, 2.9, 8.3 Hz, 4 H, H13/16), 9.26 (d, J = 0.7 Hz, 4 H, H14/15), 8.89 (dd, J = 1.2, 8.5 Hz, 1 H, H4), 8.58 (dd, J = 1.2, 8.3 Hz, 1 H, H7), 8.48 (s, 1 H, H6), 8.24 (m, 3 H, H2/11), 8.15 (m, 3 H, H9/18), 7.80 (m, 4 H, H12/17), 7.75 (d, J = 5.3 Hz, 1 H, H3), 7.68 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 925.6, m/z calcd. for $C_{40}H_{23}ClN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.2.

Resolution of Mononuclear Complexes: TRISPHAT extraction was carried out using modifications of the methods of Lacour et al.[36] In a typical experiment, [Ru(dpq)$_2$(pp′)](PF$_6$)$_2$ pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen) (approx. 0.83 mmol, 1 equiv.) was suspended in H_2O (1.8 L) and the solution stirred with Dowex® 1X8–200 (2.0 g) for 4 h to convert the metal complex to a chloride salt. The solution was filtered to remove the resin and [Bu_3NH][Λ-TRISPHAT] (approx. 0.75 mmol, 0.9 equiv.) in chloroform (600 mL) was added. The solution was stirred in darkness for 4 h, and then filtered to remove any precipitate. The organic layer was removed, dried with anhydrous $MgSO_4$ and the solvents evaporated to dryness to give an orange solid (first isolate, Λ-[Ru(dpq)$_2$(pp′)](Λ-TRISPHAT)$_2$).

To the remaining aqueous layer was added saturated KPF_6 (5 mL), causing the formation of an orange precipitate which was subsequently extracted with CH_2Cl_2 (3 × 250 mL). The extracts were dried with anhydrous $MgSO_4$ and the solvents evaporated to dryness to give an orange solid (Δ-[Ru(dpq)$_2$(pp′)](PF$_6$)$_2$) (pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen). This complex was dissolved in CH_3CN and purified on silica gel using saturated NH_4PF_6 in CH_3CN as eluent. A single orange band was collected and the solvents evaporated to dryness (intermediate isolate).

The intermediate isolate was suspended in H_2O (900 mL) and converted into the chloride salt by stirring with Dowex® 1X8–200 (1.0 g) for 4 h. The solution was filtered to remove the resin and a suspension of [cinchonidium][Δ-TRISPHAT] (approx. 0.75 mmol, 0.9 equiv.) in chloroform (600 mL) was added. The solution was stirred in darkness for 4 h, and then filtered to remove any precipitate. The organic layer was separated, dried with anhydrous $MgSO_4$ and the solvents evaporated to dryness to give an orange solid (second isolate, Δ-[Ru(dpq)$_2$(pp′)](Δ-TRISPHAT)$_2$).

The removal of TRISPHAT counterions and conversion of the metal complexes back to PF_6^- salts was achieved using flash chromatography. The two isolates were separately pre-absorbed onto silica gel (5 g) using CH_2Cl_2 (50 mL). The CH_2Cl_2 was removed under reduced pressure prior to dry loading each of the fractions onto separate pre-prepared columns of silica gel equilibrated with CH_3CN. The complexes were eluted from the columns as a single orange band in each case using saturated NH_4PF_6 in CH_3CN. H_2O (50 mL) was added to each fraction and the CH_3CN was removed under reduced pressure to precipitate the complex as a finely divided orange solid. The solid was collected under vacuum, washed with diethyl ether (50 mL) and air dried. The first isolate was found to contain Λ-[Ru(dpq)$_2$(pp′)](PF$_6$)$_2$ while the second isolate contained Δ-[Ru(dpq)$_2$(pp′)](PF$_6$)$_2$. The information gained from the characterisation of Δ- and Λ-[Ru(dpq)$_2$(pp′)](PF$_6$)$_2$ (where pp′ = phen, 3-Br-phen, 4-Cl-phen or 5-Cl-phen) is detailed below.

Δ-[Ru(dpq)$_2$(phen)](PF$_6$)$_2$: Yield 36 mg, (13%). ^1H NMR (300 MHz, CD_3CN): δ = 9.57 (dddd, J = 1.5, 3.0, 5.3, 9.0 Hz, 3 H, H13/16), 9.26 (s, 2 H, H14/15), 9.25 (s, 2 H, H14/15), 8.89 (d, J = 1.9 Hz, 1 H, H2), 8.65 (dd, J = 1.3, 8.3 Hz, 1 H, H7), 8.33 (d, J = 8.9 Hz, 1 H, H6), 8.24 (m, 4 H, H11/18), 8.24 (s, 1 H, H4), 8.22 (d, J = 2.6 Hz, 1 H, H5), 8.13 (ddd, J = 1.3, 3.9, 5.2 Hz, 1 H, H9), 8.09 (dd, J = 1.3, 5.4 Hz, 1 H, H13′), 7.80 (m, 3 H, H12/17), 7.81 (d, J = 8.5 Hz, 1 H, H12′) 7.68 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}F_6N_{10}PRu$ $[M(PF_6) + H]^+$, 891.7, found 891.2, m/z calcd. for $C_{40}H_{24}N_{10}Ru$ $[M]^{2+}$, 372.9, found 372.4. CD (CH_3CN, 1.60×10^{-5} M, r.t.): λ ($\Delta\varepsilon$, $mdeg\,M^{-1}\,cm^{-1}$) = 462.5 (–24.9), 415.5 (+21.2), 298.0 (–139.7), 282.5 (–77.0), 265.0 (–189.9), 248.5, (+109.4), 232.5 (+9.4), 216.0, (+73.7) nm.

Λ-[Ru(dpq)$_2$(phen)](PF$_6$)$_2$: Yield 90 mg, (34%). ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}F_6N_{10}PRu$ $[M(PF_6) + H]^+$, 891.7, found 891.4, m/z calcd. for $C_{40}H_{24}N_{10}Ru$ $[M]^{2+}$, 372.9, found 371.0. CD (CH_3CN, 1.77×10^{-5} M, r.t.): λ ($\Delta\varepsilon$; $mdeg\,M^{-1}\,cm^{-1}$) = 462.5, (+21.8), 415.0 (–20.4), 298.0 (+123.3), 283.0, (+69.6), 265.5 (+188.5), 249.0, (–109.6), 232.0, (–9.3), 216.0, (–66.6) nm.

Δ-[Ru(dpq)$_2$(3-Br-phen)](PF$_6$)$_2$ Yield 297 mg, (64%). ^1H NMR (300 MHz, CD_3CN): δ = 9.57 (dddd, J = 1.5, 3.0, 5.3, 9.0 Hz, 3 H, H13/16), 9.26 (s, 2 H, H14/15), 9.25 (s, 2 H, H14/15), 8.89 (d, J = 1.9 Hz, 1 H, H2), 8.65 (dd, J = 1.3, 8.3 Hz, 1 H, H7), 8.33 (d, J = 8.9 Hz, 1 H, H6), 8.24 (m, 4 H, H11/18), 8.24 (s, 1 H, H4), 8.22 (d, J = 2.6 Hz, 1 H, H5), 8.13 (ddd, J = 1.3, 3.9, 5.2 Hz, 1 H, H9), 8.09 (dd, J = 1.3, 5.4 Hz, 1 H, H13′), 7.80 (m, 3 H, H12/17), 7.81 (d, J = 8.5 Hz, 1 H, H12′) 7.68 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}BrF_6N_{10}PRu$ $[M(PF_6) + H]^+$, 970.7, found 970.5, m/z calcd. for $C_{40}H_{23}BrN_{10}Ru$ $[M]^{2+}$, 412.3, found 412.7. CD (CH_3CN, 1.24×10^{-5} M, r.t.): λ ($\Delta\varepsilon$; $mdeg\,M^{-1}\,cm^{-1}$) = 463.0 (–23.2), 414.5 (+22.7), 300.0 (–148.1), 275.0 (–109.8), 247.0 (+45.5), 219.0, (+51.8) nm.

Λ-[Ru(dpq)$_2$(3-Br-phen)](PF$_6$)$_2$: Yield 288 mg, (62%). ESI-MS CH_3CN m/z calcd. for $C_{40}H_{24}BrF_6N_{10}PRu$ $[M(PF_6) + H]^+$, 970.7, found 970.5, m/z calcd. for $C_{40}H_{23}BrN_{10}Ru$ $[M]^{2+}$, 412.3, found 412.7. CD (CH_3CN, 1.18×10^{-5} M, r.t.): λ ($\Delta\varepsilon$; $mdeg\,M^{-1}\,cm^{-1}$) = 463.0 (+24.8), 414.5 (–23.4), 300.0 (+155.3), 275.0 (+112.8), 247.0 (–47.6), 216.5, (–55.9) nm.

Δ-[Ru(dpq)$_2$(4-Cl-phen)](PF$_6$)$_2$ Yield 137 mg, (81%). ^1H NMR (300 MHz, CD_3CN): δ = 9.54 (m, 4 H, H13/16), 9.23 (d, J = 0.9 Hz, 4 H, H14/15), 8.66 (dd, J = 1.3, 8.3 Hz, 1 H, H7), 8.51 (d, J = 9.1 Hz, 1 H, H5), 8.39 (d, J = 9.1 Hz, 1 H, H6), 8.19 (m, 4 H, H11/18), 8.11 (dd, J = 1.3, 5.4 Hz, 2 H, H2/9), 8.02 (d, J = 5.8 Hz, 1 H, H3), 7.77 (dddd, J = 2.0, 3.9, 5.7, 7.1 Hz, 1 H, H12/17), 7.67 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 924.6, m/z calcd. for $C_{40}H_{23}BrN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.0. CD (CH_3CN, 1.04×10^{-5} M, r.t.): λ ($\Delta\varepsilon$ $mdeg\ M^{-1}\,cm^{-1}$) = 465.0 (–26.7), 415.5 (+22.8), 299.0 (–139.5), 267.5 (–175.5), 249.5 (+95.6), 218.5, (+60.9) nm.

Λ-[Ru(dpq)$_2$(4-Cl-phen)](PF$_6$)$_2$: Yield 139 mg, (82%). ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 924.6, m/z calcd. for $C_{40}H_{23}ClN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.0. CD (CH_3CN, 1.14×10^{-5} M, r.t.): λ ($\Delta\varepsilon$; $mdeg\,M^{-1}\,cm^{-1}$) = 465.5 (+24.8), 417.0 (–21.1), 299.0 (+129.8), 267.5 (+163.9), 249.5 (–90.0), 216.5, (–57.1) nm.

Δ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$ Yield 262 mg, (73%). ^1H NMR (300 MHz, CD_3CN): δ = 9.54 (dddd, J = 1.7, 1.7, 3.8, 6.6 Hz, 4 H, H13/16), 9.23 (d, J = 0.7 Hz, 4 H, H14/15), 8.85 (dd, J = 1.2,

8.5 Hz, 1 H, H4), 8.54 (dd, J = 1.3, 8.3 Hz, 1 H, H7), 8.44 (s, 1 H, H6), 8.20 (m, 3 H, H2/11), 8.12 (m, 3 H, H9/18), 7.77 (m, 4 H, H12/17), 7.72 (d, J = 5.3 Hz, 1 H, H3), 7.64 (dd, J = 5.3, 8.3 Hz, 1 H, H8) ppm. ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 924.7, m/z calcd. for $C_{40}H_{23}ClN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.0. CD (CH_3CN, 1.08×10^{-5} M, r.t.): λ ($\Delta\varepsilon$; mdeg M^{-1} cm^{-1}) = 463.5 (–26.2), 414.5 (+23.1), 299.0 (–140.0), 270.5 (–171.4), 250.5 (+88.0), 216.0, (+69.5) nm.

Λ-[Ru(dpq)$_2$(5-Cl-phen)](PF$_6$)$_2$: Yield 231 mg, (65%). ESI-MS CH_3CN m/z calcd. for $C_{40}H_{23}ClF_6N_{10}PRu$ $[M(PF_6)]^+$, 925.2, found 924.7, m/z calcd. for $C_{40}H_{23}ClN_{10}Ru$ $[M]^{2+}$, 390.1, found 390.0. CD (CH_3CN, 1.19×10^{-5} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 463.5 (+26.7), 414.5 (–22.9), 298.5 (+141.4), 271.0 (+176.5), 251.0 (–90.3), 217.0, (–68.6) nm.

Synthesis of Racemic Dinuclear Complexes: In a typical experiment, anhydrous $(CH_3)_2NCOH$ was de-aerated prior to use by bubbling with $N_{2(g)}$ for 10 min in a round-bottomed flask fitted with a rubber septum. *rac*-[Ru(dpq)$_2$(pp′)](PF$_6$)$_2$ (pp′ = 3-Br-phen, 4-Cl-phen or 5-Cl-phen, 0.10 mmol) was dissolved in de-aerated anhydrous $(CH_3)_2NCOH$ (2 mL). In a separate vessel NaH (70% dispersion in mineral oil, 0.0024 g, 0.10 mmol) was suspended $(CH_3)_2NCOH$ (2 mL) and the solution was purged by bubbling with $N_{2(g)}$ for 5 min. Under a strong stream of $N_{2(g)}$, bis(2-mercaptoethyl) ether (SOS) (5.6 μL, 0.05 mmol) in $(CH_3)_2NCOH$ (100 μL) was added to the solution by micropipette. The solution of SOS/NaH was allowed to stir under $N_{2(g)}$ to complete dissolution of the NaH, at which point the solution went clear (c.a. 2 min). The separate solutions containing the monomer and linker were mixed using cannulation at which time the solution underwent a rapid colour change from deep red to black. The solution was allowed to stir under $N_{2(g)}$ for a further 5 min before $(CH_3CH_2)_2O$ (50 mL) was added causing a black precipitate to form. The solution was stored at 0 °C for 2 h before the product was collected under vacuum and washed with copious amounts of $(CH_3CH_2)_2O$.

The crude mixture was purified using flash chromatography on silica gel (20 × 2.5 cm, eluent: 89% CH_3CN, 10% H_2O, 1% saturated aqueous KNO_3). The fractions containing pure [{Ru(dpq)$_2$}$_2$μ-(phen-*n*-SOS-*n*-phen)]$^{4+}$ (n = 3, 4 or 5, SOS = –S–CH_2–CH_2–O–CH_2–CH_2–S–) were identified by TLC (silica gel, CH_3CN/H_2O/saturated KNO_3, 45:5:2) and were combined. Saturated KPF_6 (1 mL) was added before extraction with CH_2Cl_2 (3 × 50 mL) to remove the KNO_3. The extracts were dried with anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. The complex was purified a second time on silica gel, (20 × 2.5 cm, eluent:saturated NH_4PF_6 in CH_3CN), and the single orange band was collected and the solvents evaporated to dryness under reduced pressure. The resultant orange solid was dissolved in a minimum volume of CH_3CN and precipitated by the addition of H_2O. The complex was collected by vacuum filtration, washed with $(CH_3CH_2)_2O$ and air dried. The yields and characterisation data of the dinuclear complexes synthesised are given below.

***raclmeso*-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)](PF$_6$)$_4$:** Yield 111 mg (56%). UV (CH_3CN): λ_{max} (ε × 10^4 mol^{-1} dm^3 cm^{-1}) = 215 (13.6), 255 (20.8), 289 (11.9), 342 (4.0), 448 (3.7) nm. Quantum luminescence Yield (Φ): 0.062. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (d, J = 8.0 Hz, 4 H), 9.48 (dd, J = 8.5, 16.8 Hz, 2 H), 9.37 (d, J = 8.2 Hz, 2 H), 9.23 (s, 4 H), 9.08 (d, J = 2.4 Hz, 2 H), 9.00 (d, J = 2.5 Hz, 1 H), 8.63 (d, J = 8.3 Hz, 2 H), 8.40 (d, J = 7.5 Hz, 2 H), 8.25 (m, 8 H), 8.14 (m, 8 H), 7.95 (dd, J = 1.7, 3.4 Hz, 2 H), 7.79 (m, 4 H), 7.69 (m, 5 H), 3.52 (m, 4 H), 2.96 (dd, J = 5.7, 12.1 Hz, 4 H) ppm. ESI-MS m/z calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.2, m/z calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.5, m/z calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.5.

***raclmeso*-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$:** Yield 62 mg (31%). UV (CH_3CN): λ_{max} (ε × 10^4, mol^{-1} dm^3 cm^{-1}) = 215 (15.1), 257 (20.5), 452 (4.8) nm. Quantum luminescence Yield (Φ): 0.053. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (m, 4 H), 9.50 (m, 2 H), 9.47 (d, J = 1.3 Hz, 1 H), 9.26 (s, 4 H), 9.17 (s, 2 H), 9.17 (dd, J = 2.2, 12.7 Hz, 2 H), 8.63 (d, J = 8.5 Hz, 2 H), 8.29 (d, J = 1.4 Hz, 1 H), 8.24 (m, 8 H), 8.20 (d, J = 3.5 Hz, 1 H), 8.16 (d, 4 H), 8.13 (d, J = 1.4 Hz, 1 H), 7.86 (d, J = 6.4 Hz, 2 H), 7.78 (m, 8 H), 7.66 (dd, J = 3.3, 5.1 Hz, 2 H), 7.43 (d, J = 6.1 Hz, 2 H), 3.74 (dd, J = 5.5, 11.6 Hz, 4 H), 2.74 (dd, J = 4.8, 5.8 Hz, 4 H) ppm. ESI-MS m/z calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.3, m/z calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.7, m/z calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.9;

***raclmeso*-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$:** Yield 95 mg (48%). UV (CH_3CN): λ_{max} (ε × 10^4, mol^{-1} dm^3 cm^{-1}) = 217 (14.1), 256 (20.2), 450 (4.8) nm. Quantum luminescence Yield (Φ): 0.048. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (dd, J = 7.3, 14.7 Hz, 7 H), 9.50 (s, 1 H), 9.26 (d, J = 1.0 Hz, 4 H), 9.24 (dd, J = 2.7, 8.5 Hz, 4 H), 8.84 (dd, J = 2.7, 8.5 Hz, 2 H), 8.50 (d, J = 7.9 Hz, 2 H), 8.24 (dd, J = 4.7, 9.9 Hz, 4 H), 8.18 (m, 8 H), 8.06 (d, J = 5.0 Hz, 2 H), 7.80 (m, 8 H), 7.63 (m, 4 H), 3.93 (dd, J = 6.1, 12.3 Hz, 4 H), 3.48 (m, 4 H) ppm. $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.2, m/z calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.5, m/z calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.5.

Synthesis of Homochiral Dinuclear Complexes: The homochiral dinuclear complexes were synthesised in a manner analogous to that used for the diastereoisomeric mixtures synthesised above using resolved mononuclear metal complexes. Their yields and characterisation data are provided below.

ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)](PF$_6$)$_4$: Yield 22 mg (31%). ^{1}H NMR (300 MHz, CD_3CN): δ = 9.54 (dd, J = 1.3, 8.3 Hz, 4 H, H13/16) 9.40 (dd, J = 1.3, 8.3 Hz, 4 H, H13/16) 9.24 (s, 4 H, H14/15) 9.11 (s, 4 H, H14/15) 8.59 (dd, J = 1.2, 8.3 Hz, 2 H, H7) 8.37 (d, J = 1.8 Hz, 2 H, H2/H4) 8.20 (m, 4 H, H11/18) 8.19 (d, J = 1.35 Hz, 4 H, H11/18) 8.15 (dd, J = 1.3, 5.3 Hz, 2 H, H5/H6) 8.10 (d, J = 1.3 Hz, 2 H, H5/6) 8.07 (m, 2 H, H9) 7.89 (d, J = 1.9 Hz, 2 H, H2/H4) 7.78 (dd, J = 1.6, 5.3, 8.3 Hz, 4 H, H12/17) 7.69 (m, J = 5.3, 8.3, 13.1 Hz, 4 H, H12/17) 7.61 (dd, J = 5.3, 8.6 Hz, 2 H, H8) 3.35 (m, J = 1.9, 6.2 Hz, 4 H, HB) 2.94 (m, J = 3.6, 6.1 Hz, 4 H, HA) ppm. ESI-MS m/z calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.0, m/z calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.7, m/z calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 407.0. CD (CH_3CN, 4.12×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 464.0 (– 48.3), 415.0 (+46.1), 299.0 (–269.6), 260.0 (–188.3), 242.0 (+188.9), 213.0, (+111.8) nm.

ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-3-SOS-3-phen)](PF$_6$)$_4$: Yield 24 mg (24%). ESI-MS m/z calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.1, m/z calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.4, m/z calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.6. CD (CH_3CN, 4.15×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 463.0 (+54.9), 415.5 (–55.1), 299.0 (+317.1), 260.0 (+222.8), 242.0 (–220.4), 212.0, (–133.1) nm.

ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$: Yield 17 mg (17%). ^{1}H NMR (300 MHz, CD_3CN): δ = 9.54 (m, J = 1.3, 5.1, 8.3, 12.4 Hz, 8 H, H13/16), 9.26 (s, 4 H, H14/15), 9.18 (s, 1 H, H14/15), 8.64 (dd, J = 1.2, 8.3 Hz, 2 H, H7), 8.24 (m, J = 3.4, 4.9,

6.4 Hz, 8 H, H11/18), 8.16 (m, J = 1.2, 1.2, 5.4 Hz, 4 H, H5/6), 7.86 (d, J = 5.9 Hz, 2 H, H2/9), 7.78 (m, 10 H, H2/9/12/17), 7.66 (dd, J = 5.2, 8.3 Hz, 2 H, H8), 7.43 (d, J = 6.0 Hz, 2 H, H3), 3.75 (dd, J = 5.8, 5.8 Hz, 4 H, HB), 3.28 (dd, J = 5.7, 10.6 Hz, 4 H, HA) ppm. ESI-MS *m/z* calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.3, *m/z* calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.7, *m/z* calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 407.0. CD (CH_3CN, 6.25×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 470.0 (–44.9), 419.0 (+35.1), 298.5 (–218.6), 263.5 (–293.0), 247.0 (+163.6), 213.5, (+152.4) nm.

ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-4-SOS-4-phen)](PF$_6$)$_4$: Yield 51 mg (50%). ESI-MS *m/z* calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.3, *m/z* calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.7, *m/z* calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.9. CD (CH_3CN, 6.88×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 468.5 (+45.5), 418.5 (–36.2), 298.5 (+213.3), 263.5 (+280.5), 247.5 (–169.3), 213.5, (–149.6) nm.

ΔΔ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$: Yield 32 mg (31%). ^{1}H NMR (300 MHz, CD_3CN): δ = 9.56 (m, 8 H, H13/16), 9.26 (m, 8 H, H14/15), 8.83 (dd, J = 1.2, 8.5 Hz, 2 H, H4), 8.50 (dd, J = 1.2, 8.3 Hz, 2 H, H7), 8.24 (m, J = 1.3, 4.2, 5.5 Hz, 4 H, H11/18), 8.20 (s, 2 H, H6), 8.16 (m, 6 H, H11/18/2/9), 8.06 (dd, J = 1.2, 5.3 Hz, 2 H, H2/9), 7.80 (m, 8 H, H12/17), 7.62 (m, J = 5.3, 8.4, 11.4 Hz, 4 H, H3/8), 3.93 (dd, J = 6.0, 6.0 Hz, 4 H, HB), 3.49 (m, J = 3.1, 6.0, 6.3 Hz, 4 H, HA) ppm. ESI-MS *m/z* calcd. for $C_{84}H_{55}F_{24}N_{20}OP_4Ru_2S_2$ $[M(PF_6)_4 + H]^+$, 2206.6, found 2206.4, *m/z* calcd. for $C_{84}H_{54}F_{18}N_{20}OP_3Ru_2S_2$ $[M(PF_6)_3]^+$, 2060.6, found 2061.3, *m/z* calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 958.4, *m/z* calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 590.7, *m/z* calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.9. CD (CH_3CN, 5.02×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 464.0 (–59.2), 415.0 (+43.7), 299.0 (–309.1), 260.5 (–101.1), 241.0 (+25.1), 216.5, (+163.0) nm.

ΛΛ-[{Ru(dpq)$_2$}$_2$μ-(phen-5-SOS-5-phen)](PF$_6$)$_4$: Yield 52 mg (51%). ESI-MS *m/z* calcd. for $C_{84}H_{54}F_{12}N_{20}OP_2Ru_2S_2$ $[M(PF_6)_2]^{2+}$, 957.8, found 957.3, *m/z* calcd. for $C_{84}H_{54}F_6N_{20}OPRu_2S_2$ $[M(PF_6)]^{3+}$, 590.2, found 589.7, *m/z* calcd. for $C_{84}H_{54}N_{20}ORu_2S_2$ $[M]^{4+}$, 406.4, found 406.3. CD (CH_3CN, 5.24×10^{-6} M, r.t.): λ ($\Delta\varepsilon$, mdeg M^{-1} cm^{-1}) = 464.0 (+53.5), 416.0 (–49.4), 299.0 (+307.6), 260.5 (+101.6), 240.0 (–35.1), 216.5, (–173.2) nm.

Supporting Information (see also the footnote on the first page of this article): Additional CD spectra of the metal complexes and a comparison of the NMR spectra of all the mononuclear complexes.

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