# SUPPLEMENTARY INFORMATION

# The application of circular dichroism spectroscopy in the study of mixed valence asymmetric ruthenium polypyridyl complexes.

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The structures of the four diastereoisomers of $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ (**1**) are sketched in Figure SI1.

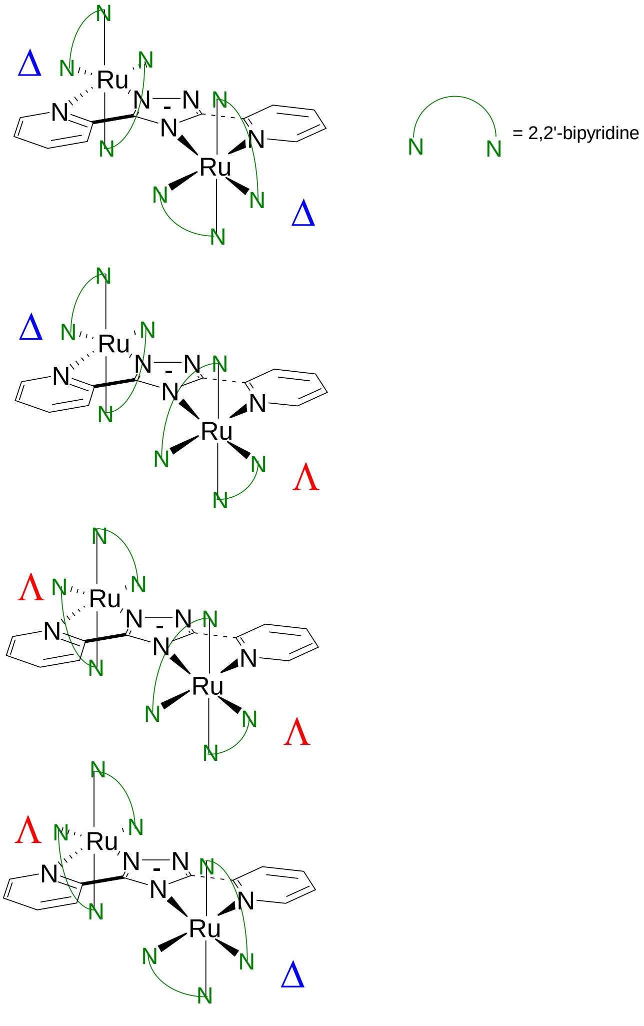


***Figure SI1.*** *From top to bottom, structures of ΔΔ, ΔΛ, ΛΛ and ΛΔ diastereoisomers of complex* ***1****.*

**Suplementary Information.**

## EXPERIMENTAL DETAILS

Preparation and HPLC separation of all four diastereoisomers of **1** (Figure SI1), as well as their CD spectroscopic characterization were reported previously in ref.SI 1 and references therein. UV-vis absorption spectra were taken with a Hewlett-Packard HP 8453 spectrophotometer. CD spectra were recorded on a JASCO J-715 spectropolarimeter using Uvasol-grade solvents (Merck). Spectroelectrochemical measurements were performed as described in SI 2 with potential control provided by a CH Instruments CHI630B electrochemical workstation. The spectroelectrochemical properties of the **1** have been reported previously.[SI1] The separation between the first and second oxidation waves is sufficient to allow for the generation of the mixed valent state by applying a potential intermediate of the two oxidation steps. In all cases simultaneous recording of both UV/Vis absorption and CD spectra allowed for the extent of oxidation to be determined spectroscopically by monitoring the extent of change in the absorption in the visible region. Irradiation at 365 nm employed a Spectroline hand held UV lamp.

After preparation and column chromatography of **1** on alumina with acetonitrile as eluent, compound **1** was recrystallized from acetone:water (2:1) mixture. The recrystallised compound was further purified and the homo and heterochiral complexes were separated using a Semiprep HPLC *Varian – Prostar* series (Mod.230 and 330). The semi-preparative separation was carried out using a Luna strong cation exchange (SCX) column from Phenomenex (particle size 5 μm, pore size 100 Å). The mobile phase used was an acetonitrile:water mixture (volume ratio 80:20) with $KNO_3$ 0.12 M, and the flow rate is 2 $cm^3$ $min^{-1}$ with a detection wavelength of 280 nm

*HPLC behaviour of homo- and heterochiral fractions of compound 1.* Using the chromatographic conditions outlined above two signals, peaks A and B could be identified (See Figure SI2)

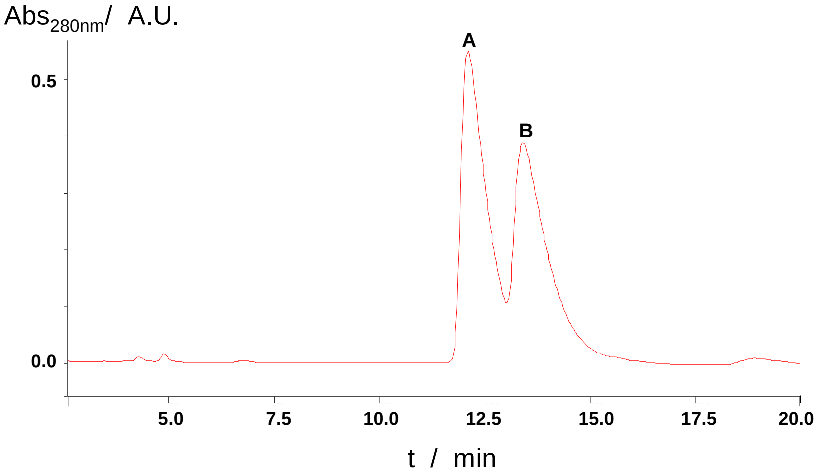


***Figure SI2.*** *Chromatogram of {[Ru(bpy)$_2$]$_2$(bpt)}$^{3+}$ (**1**) on Luna SCX column. On Y-axis the ordinate represents the absorbance of the sample at 280 nm.*

These two sets of sets of isomers could be separated and were identified by their $^1$H NMR spectra as shown in Figure SI3. See Reference SI 1c

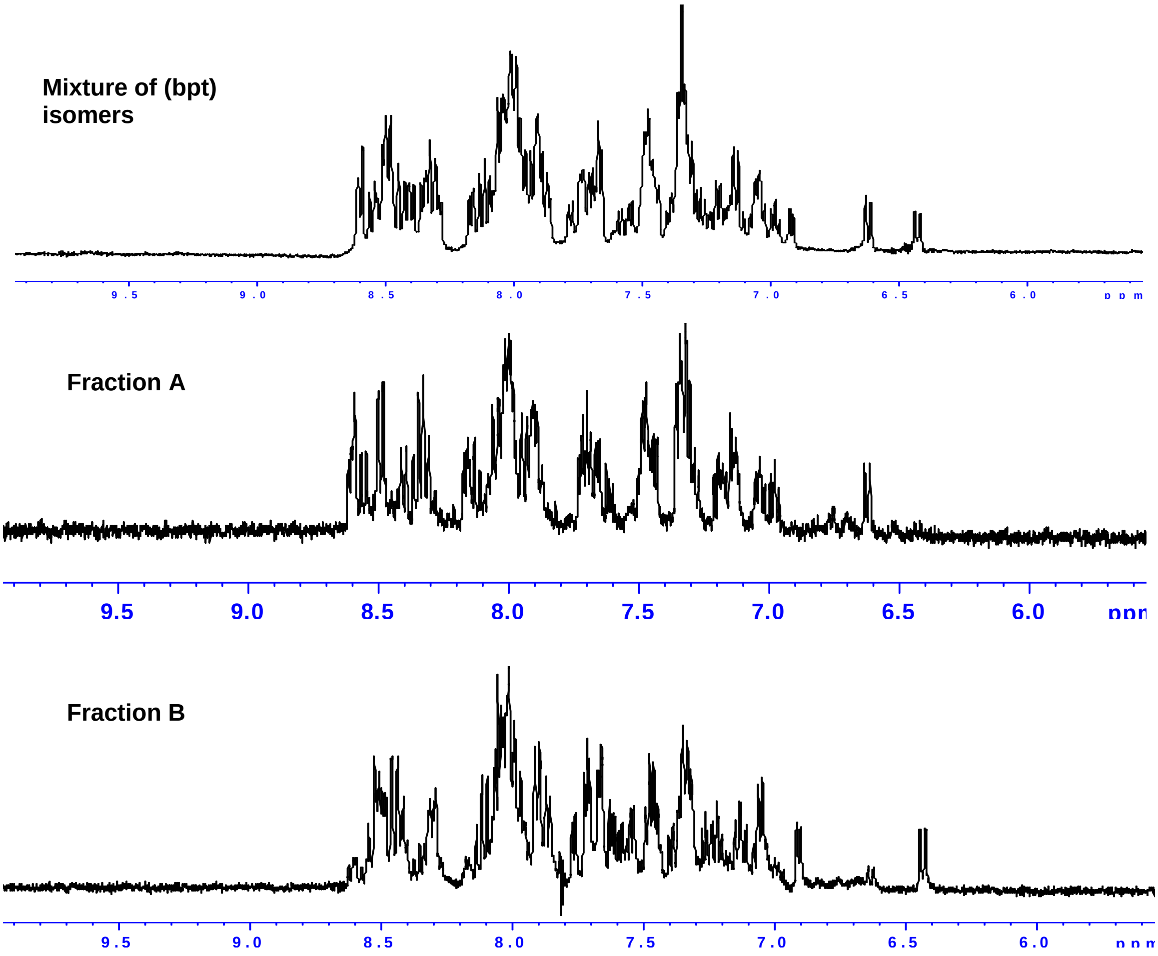


***Figure SI3.*** *$^1$H-NMR spectra of fraction A (upper profile) and fraction B (lower profile) for complex {[Ru(bpy)$_2$]$_2$(bpt)}$^{3+}$ (**1**) and mixture in deuteriated acetonitrile.*

These spectra show that the  column allows for the separation of the two racemic mixtures, the homochiral Λ,Λ/Δ,Δ  (peak A)  andthe heterochiral Λ,Δ/Δ,Λ, (peak B). The full separation of the four diastereoisomers (Figure SI1) was not possible. See refs  SI 1, SI 2, SI 3, SI 4.

*Photochemical Behaviour*.

Figures SI4 and SI5 show the photochemical behaviour of the two fractions in acetonitrile.

In case of $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ (**1**), after three hours of irradiation at 430 nm the isomers constituting fraction A are converted into the isomers forming fraction B as confirmed by $^1$H NMR spectroscopy (Figure SI6).

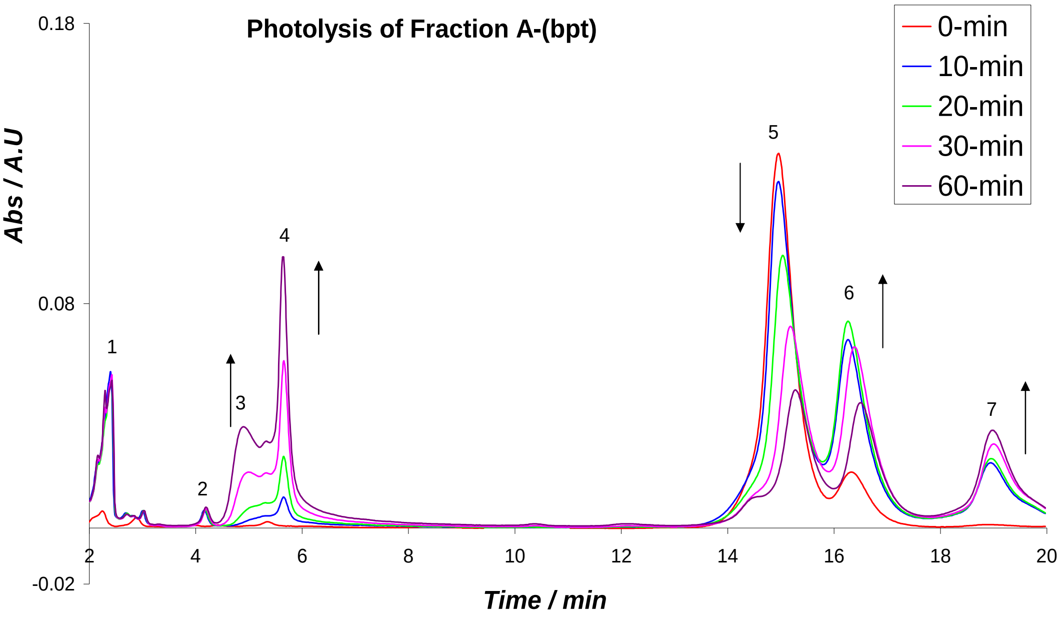


***Fig SI4***. *HPLC trace during Photolysis of fraction A of $\{[Ru(bpy)_2]_2\ bpt\}^{3+}$ in $CH_3CN$.  (mobile phase  $CH_3CN$: $H_2O$: $CH_3OH$ with volume ratio 75:15:10 containing 0.12 M $KNO_3$). Flow rate: 2.0 $cm^3\ min^{-1}$; detection wavelength: 280 nm.*

The chromatograms show the decrease of peak 5, fraction A  with the grow in of peak 6 that is assigned to fraction B.  The other material formed are decomposion products such as the $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ and $[Ru(bpy)_2bpt]^+$. See ref SI 5.

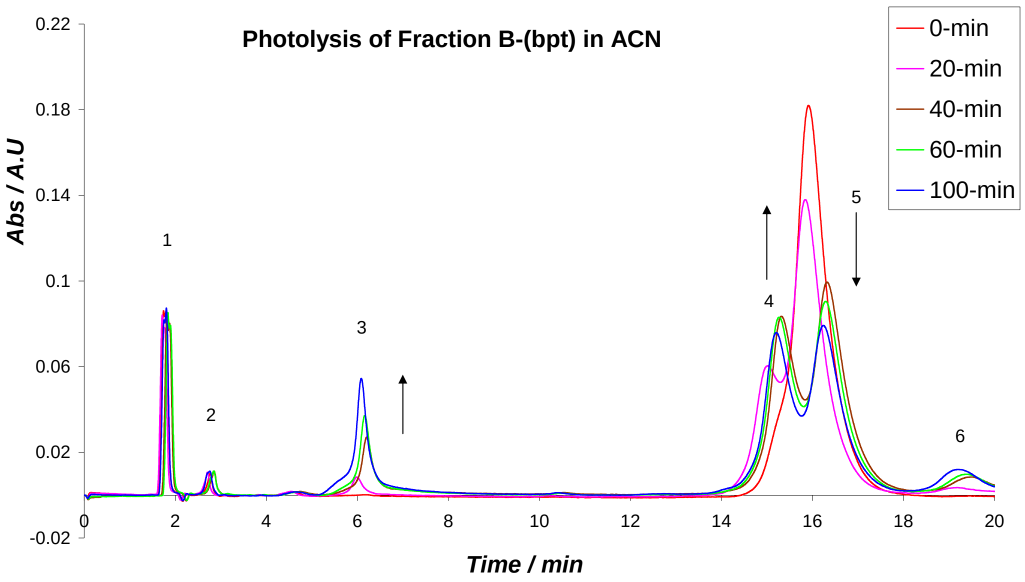


***Figure SI5*** *HPLC traces taken during Photolysis of Fraction* ***B*** *in* $CH_3CN$*, (mobile phase* $CH_3CN$*:* $H_2O$*:* $CH_3OH$ *with volume ratio 75:15:10 containing 0.12 M* $KNO_3$*). Flow rate: 2.0* $cm^3\ min^{-1}$*; detection wavelength: 280 nm.*

Similar information can be obtained from $^1$HNMR spectroscopy as shown in Figure SI6.

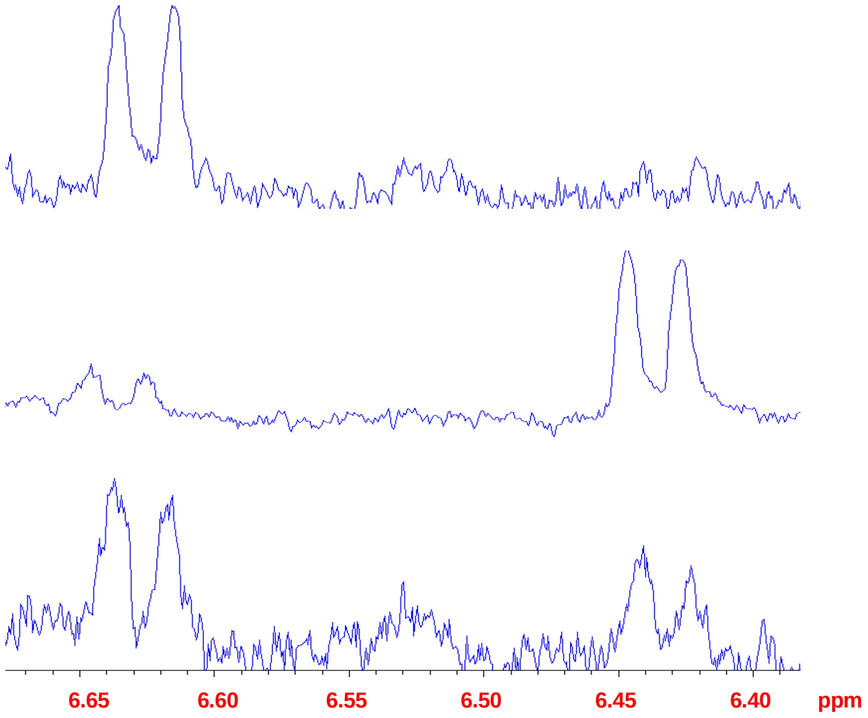
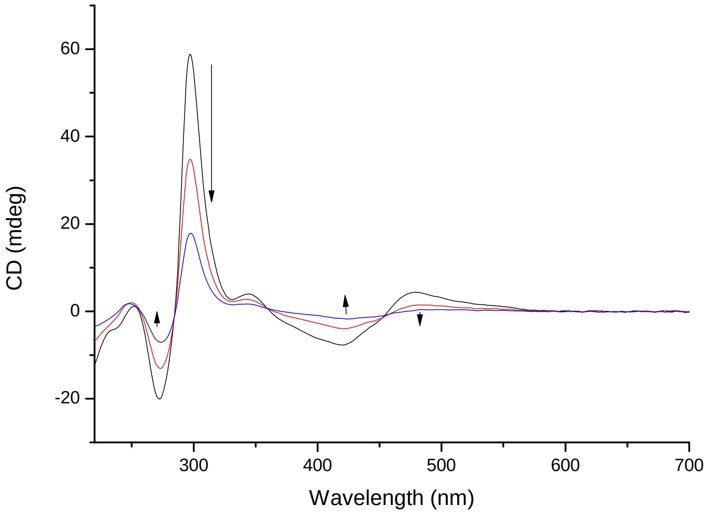


***Figure SI6.*** *Comparison of the* $^1$*H NMR spectra in deuteriated acetonitrile of fractions A (upper profile), B (middle) and fraction A of* $\{[Ru(bpy)_2]_2(bpt)\}(PF_6)_3$ *(**1**) after three hours of irradiation at 430 nm (lower profile) showing the photoisomerization process of fraction A.*

## Photoracemization

The photochemistry of the dinuclear complex **1** is typical or ruthenium(II) polypyridyl complexes in that irradiation leads ultimately to ligand dissociation. For bidentate ligands the dissociation is less obvious due to the competition between reformation of the photocleaved Ru-N bond and the thermolysis of the second Ru-N bond. For **1** dissociation leads to formation of both possible mononuclear complexes (bound via the N4 or N2 of the triazole ring). However a more efficient process which is not observed in the racemic mixture is the interconversion of the stereoisomers upon photoexcitation. As can be seen in Figure SI7, for **1a** the rate of racemisation is far in excess of that of photodissociation to form the mononuclear complex.



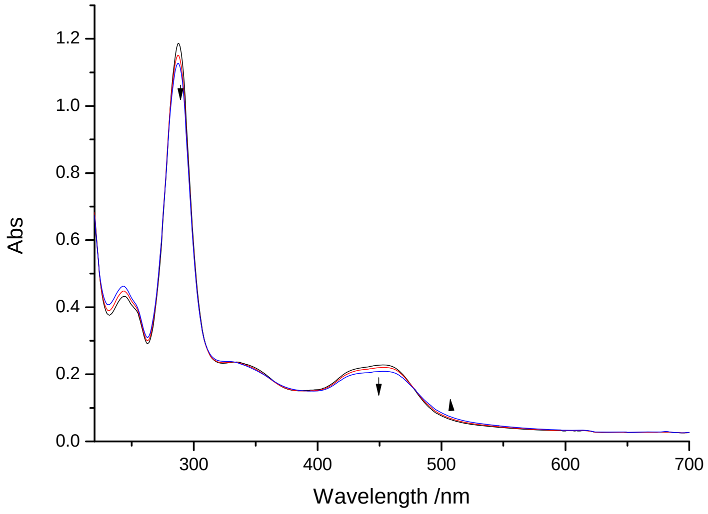


***Figure SI7*** *Changes in the CD (upper) and UV/Vis absorption spectrum of* ***1a*** *upon irradiation at 365 nm (CD and UV/Vis absorption spectra were recorded simultaneously in each case).*

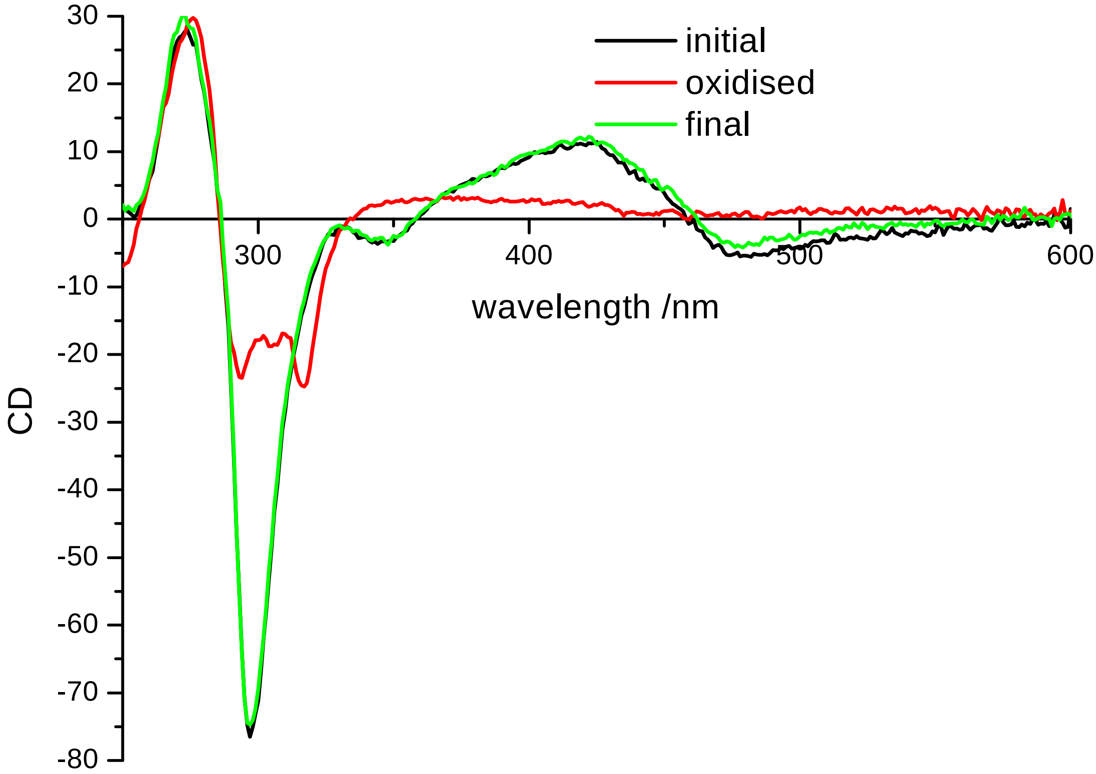


***Figure SI8***. *Retention of configuration upon oxidation and subsequent reduction*

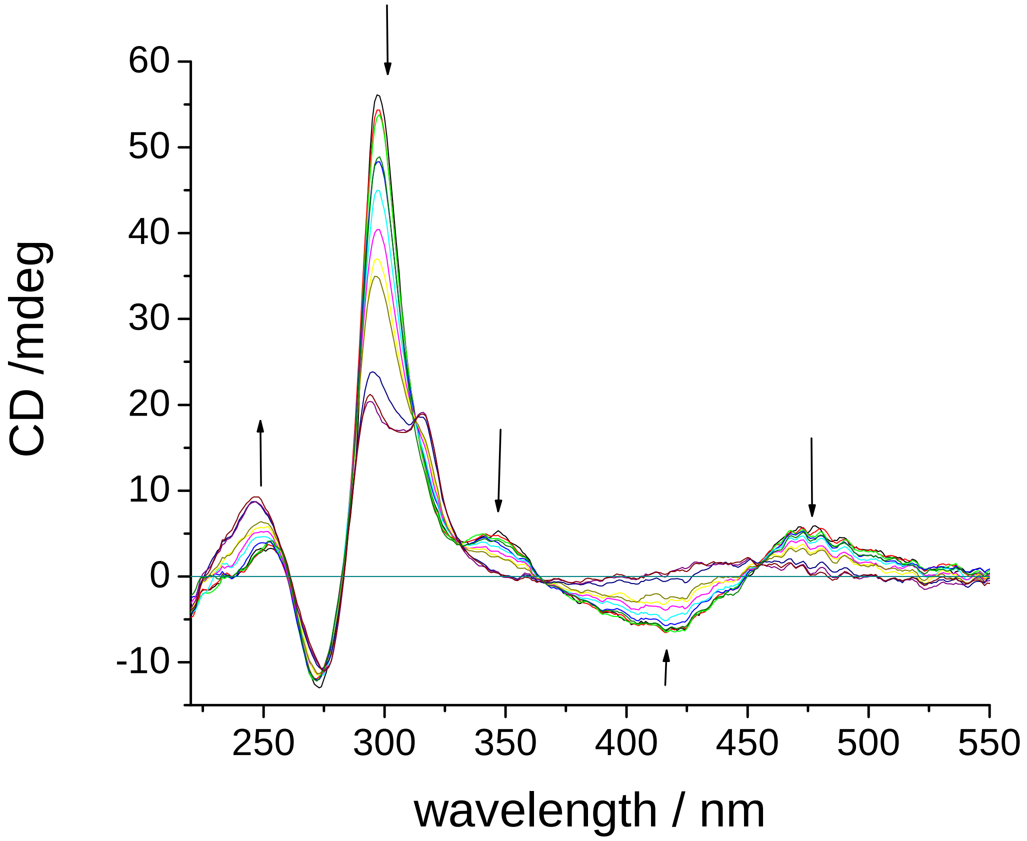


***Figure SI9***. *Conversion of the Λ,Λ stereoisomer of* ***1*** *from the Ru(II)Ru(II) to the mixed valence (Ru(II)Ru(III)) state followed by CD spectroscopy. Arrows indicate the change in CD intensity with increasing applied potential.*

## References

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