

ESI

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Enantioselective regulation of a metal complex in reversible binding to serum albumin: dynamic helicity inversion signalled by circularly polarised luminescence

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1. Experimental

Details of luminescence, CPL and MR instrumentation may be traced through references 11 and 12.

For (SSS)- Δ -[Tb.L^{1a}]³⁺, at 545 nm the g_{lum} value is + 0.27 (Figure 2 ESI and main text, Figure 2); for (SSS)- Δ -[Eu.L^{1a}]³⁺, the g_{lum} values at 589 and 595 nm are + 0.19 and – 0.16 respectively (Fig. 1 ESI and Fig. 3 main text). These allow calibration of the other transitions observed in these and related Figures. The scale used in each CPL figure in the ESI refers to ($I_L - I_R$) and is on a scale of x60 with respect to ($I_L + I_R$).

2. List of Supplementary Figures

Figure 1

Mirror image CPL spectra for (SSS)- Δ -[Eu.L^{1a}]³⁺ and (RRR)- Λ -[Eu.L^{2a}]³⁺; (red = (Δ), blue = (Λ); 295K, D₂O, 15 μ M)

Figure 2

Mirror image CPL spectra for (SSS)- Δ -[Tb.L^{1a}]³⁺ and (RRR)- Λ -[Tb.L^{2a}]³⁺; (red = (Δ), blue = (Λ); 295K, D₂O, 15 μ M)

Figure 3

CPL spectra for (RRR)- Λ -[Eu.L^{2a}]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (blue = without; green = with BSA)

Figure 4

CPL spectra for (RRR)- Λ -[Tb.L^{2a}]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (blue = without; green = with BSA)

Figure 5

CPL spectra for (SSS)- Δ -[Tb.L^{1b}]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (red = without; green = with BSA)

Figure 6

CPL spectra for (SSS)- Δ -[Eu.L³]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of 10 equivalents of BSA (red = without; green = with BSA)

Figure 7

CPL spectra for (RRR)- Λ -[Tb.L³]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of 10 equivalents of BSA (blue = without; green = with BSA)

Figure 8

CPL spectra for (SSS)- Δ -[Tb.L⁵]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of 10 equivalents of BSA (red = without; green = with BSA); ligand L⁵ replaces the dpqC chromophore in L¹ (bidentate moiety) for a unidentate 2-methyl-aza-xanthone moiety, and in this complex the macrocyclic ligand is octadentate and one water molecule is bound in an axial site¹³

Figure 9

Variation of the observed dissymmetry factor, g_{em} , with added BSA for (SSS)- Δ -[Eu.L^{1a}]³⁺; (295K, D₂O, 15 μ M); (blue triangles = 589 nm, red squares = 593 nm).

Figure 10

Variation of the measured relaxivity of (SSS)- Δ -[Gd.L^{1a}]³⁺ and (RRR)- Λ -[Gd.L^{2a}]³⁺; (310K, D₂O, 1.6 mM complex) as a function of added HSA (Red triangles = (Δ), blue squares = (Λ)).

Figure 11

Variation of the measured relaxivity of (SSS)- Δ -[Gd.L^{1a}]³⁺ and (RRR)- Λ -[Gd.L^{2a}]³⁺; (310K, D₂O, 1.6 mM complex) as a function of added warfarin (Red triangles = (Δ), blue squares = (Λ)).

Figure 12

Total emission spectra for (SSS)- Δ -[Eu.L^{1a}]³⁺; (295K, D₂O, 15 μ M) in the presence (red; scaled x 3) and absence (blue) of 10 equivalents of BSA.

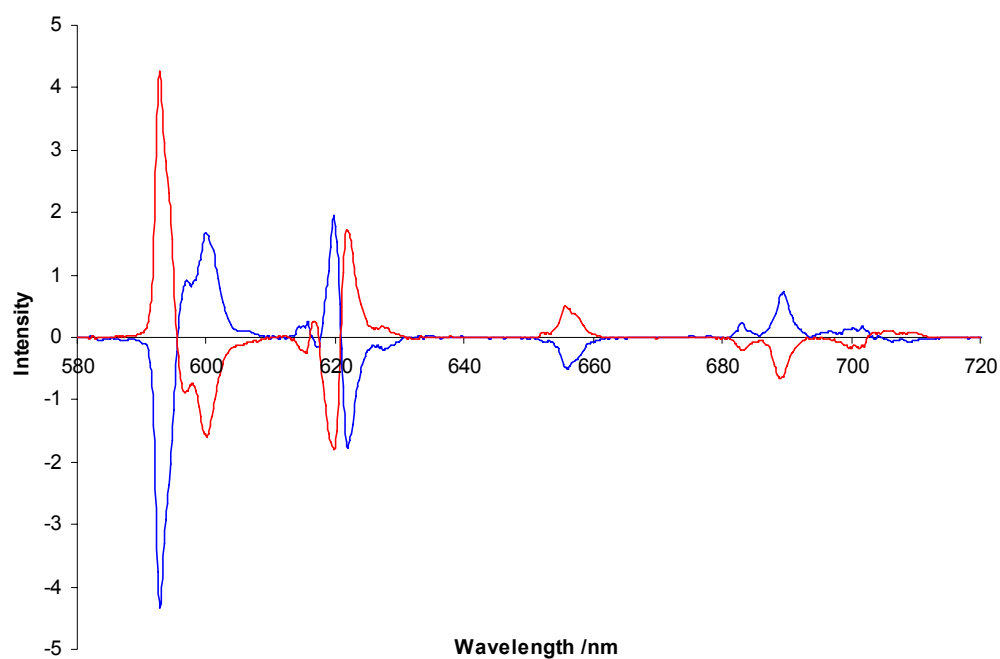


Figure 1 (above)

Mirror image CPL spectra for (SSS)- Δ -[Eu.L^{1a}]³⁺ and (RRR)- Λ -[Eu.L^{2a}]³⁺; (red = (Δ), blue = (Λ); 295K, D₂O, 15 μ M)

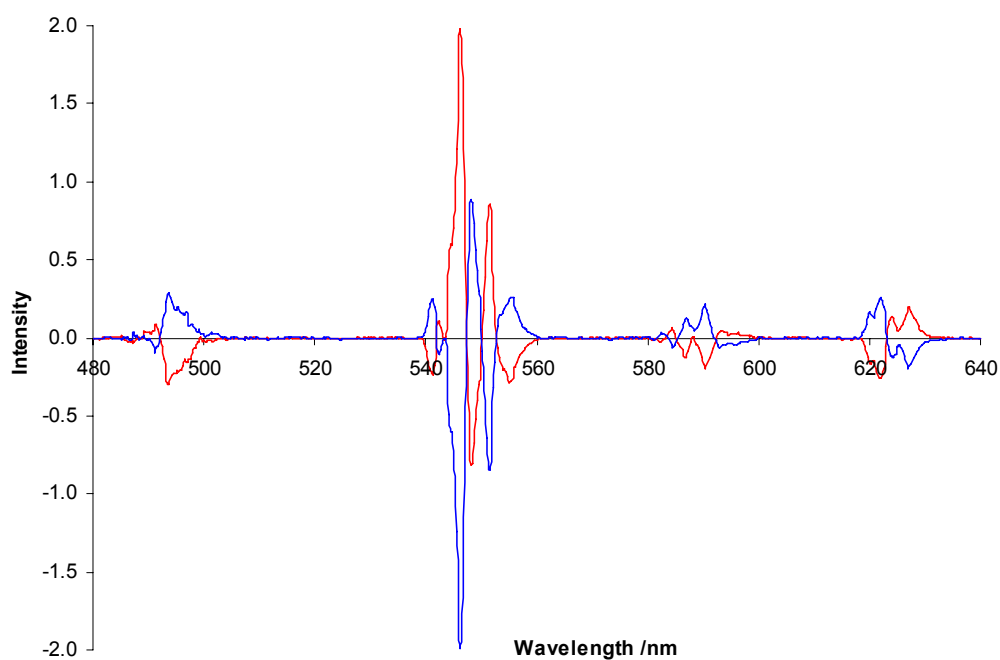


Figure 2

Mirror image CPL spectra for (SSS)- Δ -[Tb.L^{1a}]³⁺ and (RRR)- Λ -[Tb.L^{2a}]³⁺; (red = (Δ), blue = (Λ); 295K, D₂O, 15 μ M)

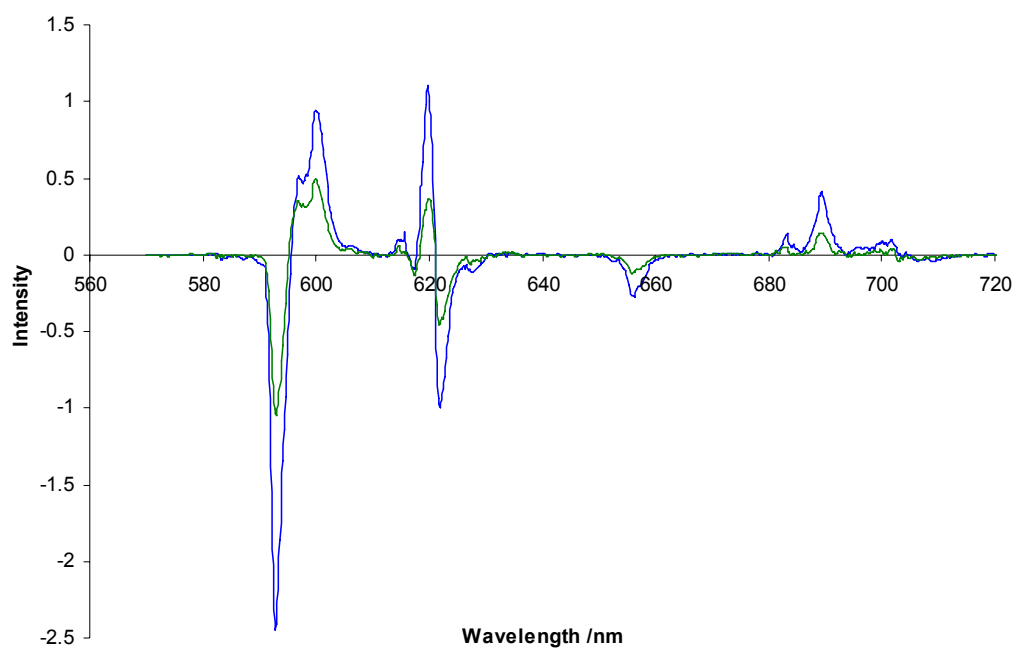


Figure 3

CPL spectra for $(RRR)\text{-}\Lambda\text{-[Eu.L}^{2a}\text{]}^{3+}$; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (blue = without; green = with BSA)

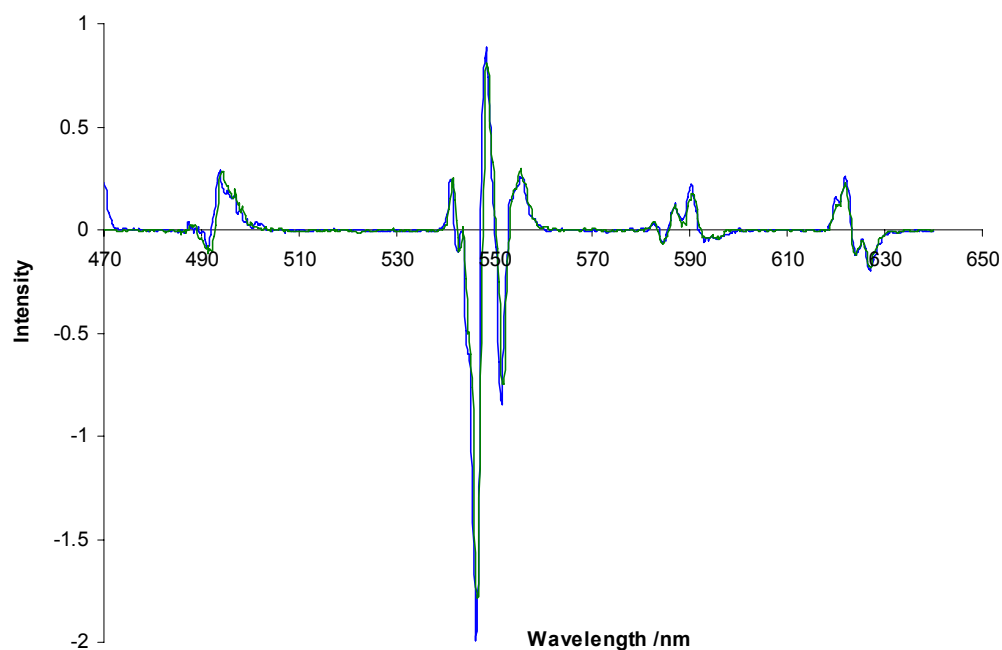


Figure 4

CPL spectra for $(RRR)\text{-}\Lambda\text{-[Tb.L}^{2a}\text{]}^{3+}$; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (blue = without; green = with BSA)

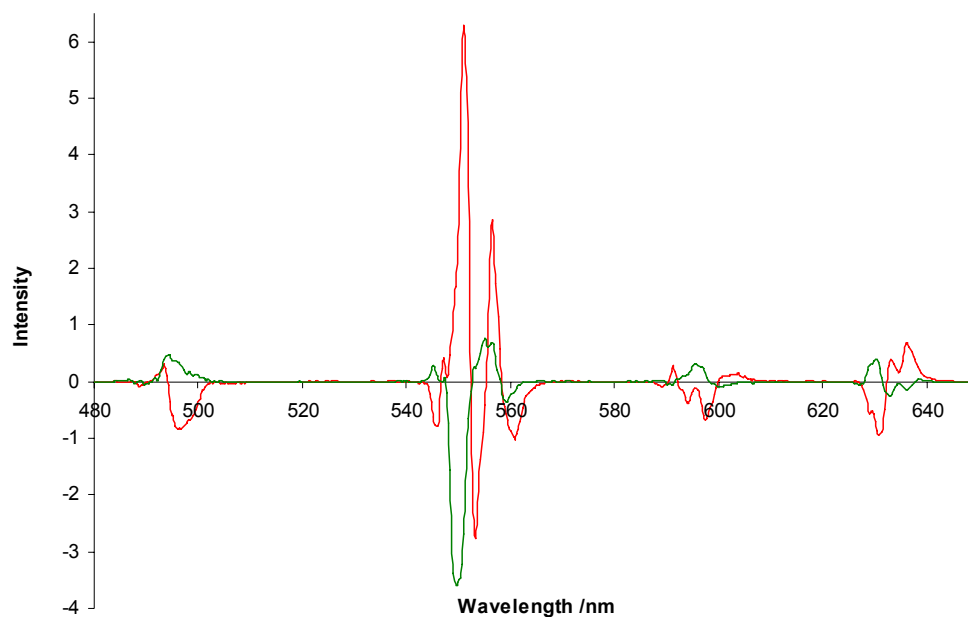


Figure 5

CPL spectra for (SSS)- Δ -[Tb.L^{1b}]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of one equivalent of BSA (red = without; green = with BSA)

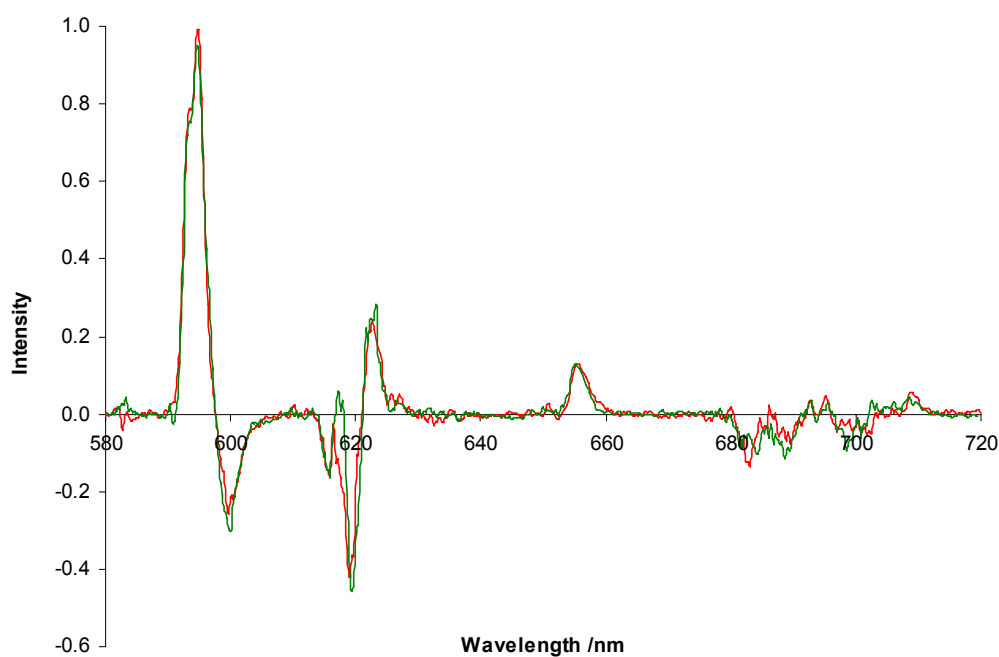


Figure 6

CPL spectra for (SSS)- Δ -[Eu.L³]³⁺; (295K, D₂O, 15 μ M) in the presence and absence of 10 equivalents of BSA (red = without; green = with BSA); note the absence of any quenching of emission following protein addition.

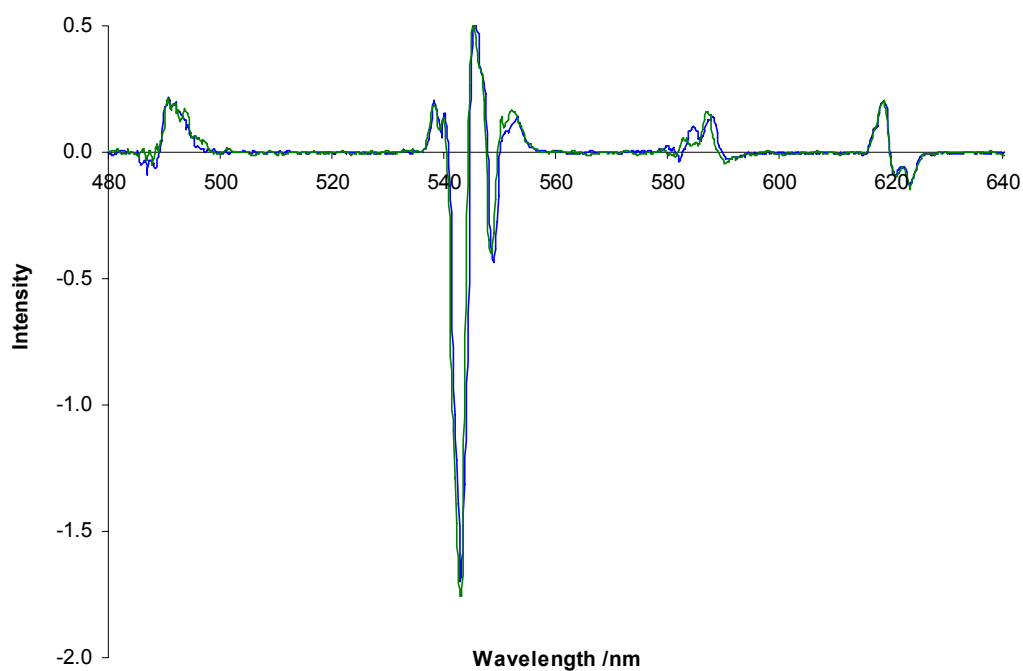


Figure 7

CPL spectra for $(RRR)\text{-}\Lambda\text{-}[\text{Tb.L}^3]^{3+}$; (295K, D_2O , $15\mu\text{M}$) in the presence and absence of 10 equivalents of BSA (blue = without; green = with BSA)

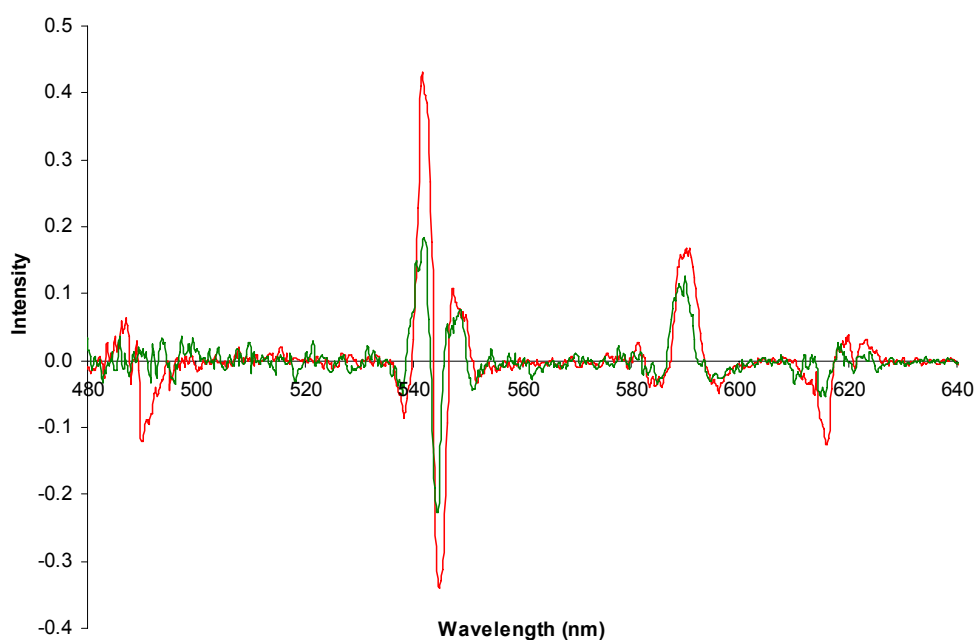


Figure 8

CPL spectra for $(SSS)\text{-}\Delta\text{-}[\text{Tb.L}^5]^{3+}$; (295K, D_2O , $15\mu\text{M}$) in the presence and absence of 10 equivalents of BSA (red = without; green = with BSA); ligand L^5 replaces the dpqC chromophore in L^1 (bidentate moiety) for a unidentate 2-methyl-aza-xanthone moiety, and in this complex the ligand is octadentate and one water molecule is bound in an axial site¹³

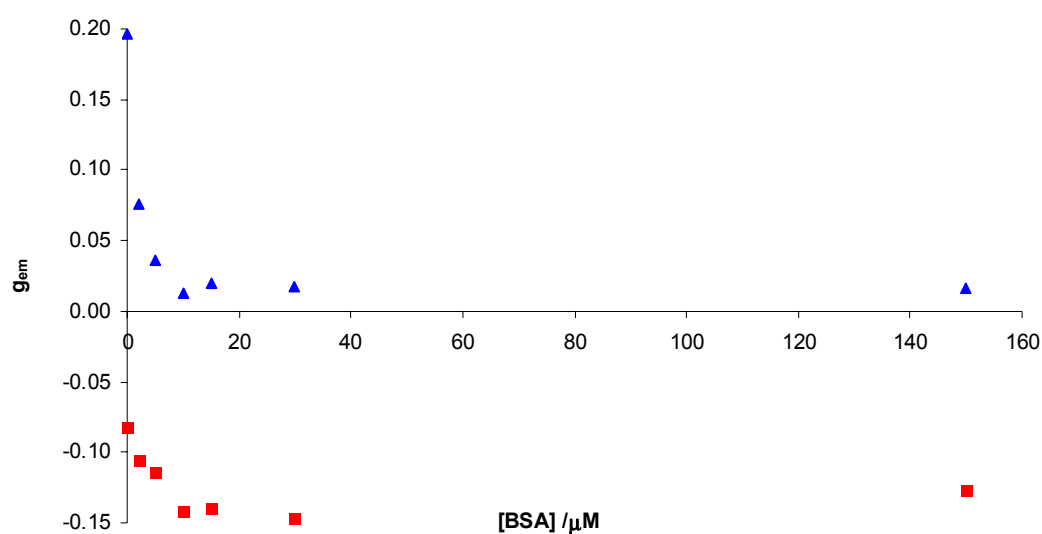


Figure 9

Variation of the observed dissymmetry factor, g_{em} , with added BSA for $(SSS)\text{-}\Delta\text{-}[\text{Eu.L}^{1a}]^{3+}$; (295K, D_2O , 15 μM) (blue triangles = 589 nm, red squares = 593 nm).

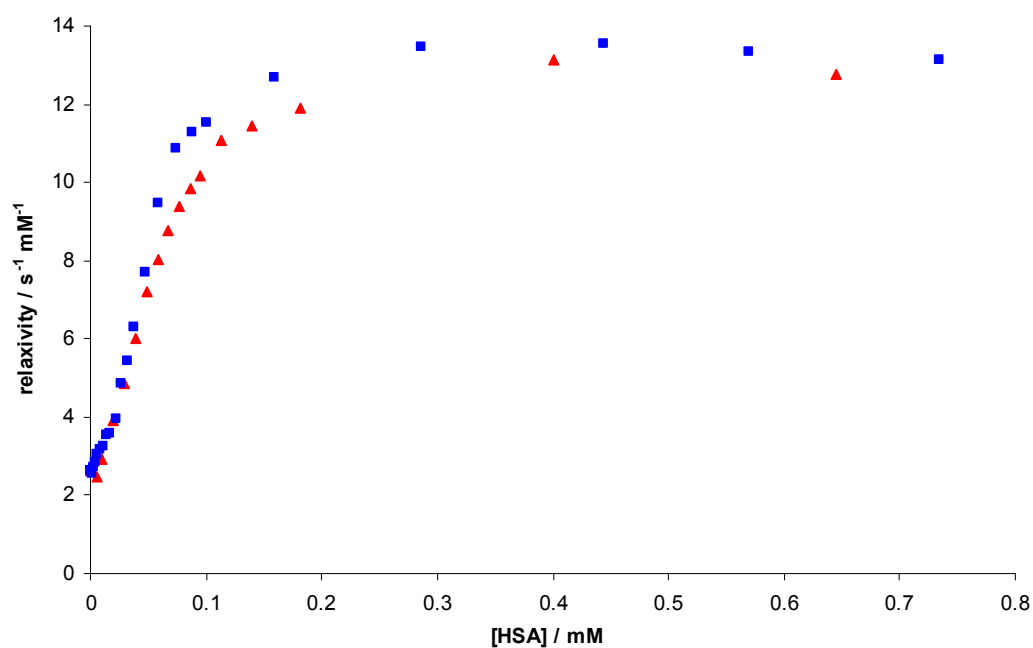


Figure 10

Variation of the measured relaxivity of $(SSS)\text{-}\Delta\text{-}[\text{Gd.L}^{1a}]^{3+}$ and $(RRR)\text{-}\Lambda\text{-}[\text{Gd.L}^{2a}]^{3+}$; (310K, D_2O , 1.6 mM complex) as a function of added HSA (Red triangles = (Δ) , blue squares = (Λ)).

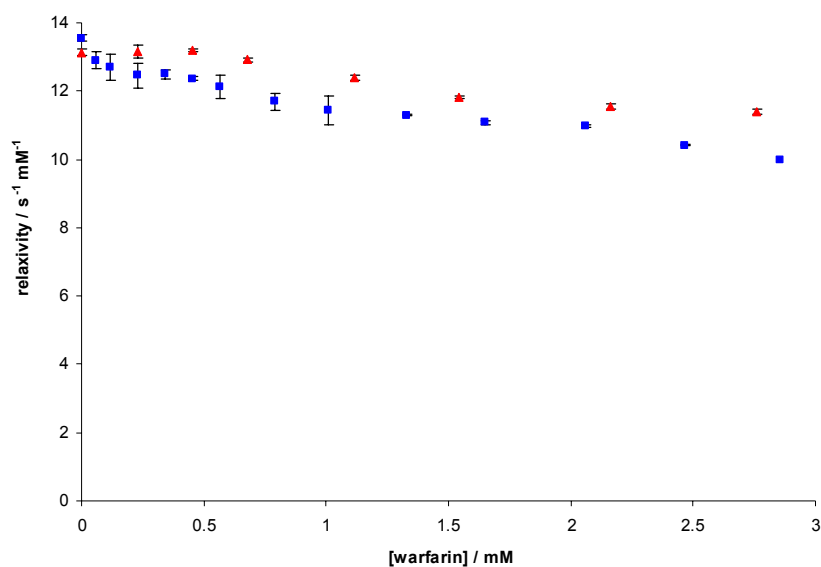


Figure 11

Variation of the measured relaxivity of $(SSS)\text{-}\Delta\text{-}[\text{Gd.L}^{1a}]^{3+}$ and $(RRR)\text{-}\Lambda\text{-}[\text{Gd.L}^{2a}]^{3+}$; (310K, D₂O, 1.6 mM complex) as a function of added warfarin (Red triangles = (Δ) , blue squares = (Λ)).

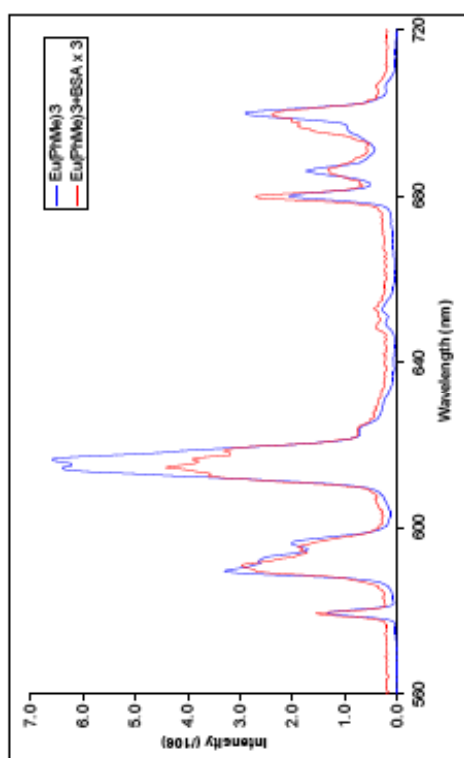


Figure 12

Total emission spectra for $(SSS)\text{-}\Delta\text{-}[\text{Eu.L}^{1a}]^{3+}$; (295K, D₂O, 15 μM) in the presence (red; scaled x 3) and absence (blue) of 10 equivalents of BSA, showing changes in spectral form in the $\Delta J = 1$ and $\Delta J = 2$ and 4 manifolds.