

Supplementary Material

Investigation of the photophysical properties of a Eu^{3+} coordination polymer bearing an α -nitrile substituted β -diketonate ligand via emission and ultrafast transient absorption spectroscopy

Brodie L. Reid,^a Evan G. Moore,^{b,*} Brian W. Skelton,^c Mark I. Ogden,^{a,*} and Massimiliano Massi^{a,*}

^a *Department of Chemistry, and Nanochemistry Research Institute, Curtin University, Kent Street, Bentley 6102 WA, Australia.*

^b *School of Chemistry and Molecular Biosciences, University of Queensland, St Lucia 4072 QLD, Australia.*

^c *Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Crawley 6009 WA, Australia.*

Corresponding Authors

*E-mail: m.massi@curtin.edu.au; m.ogden@curtin.edu.au; egmoore@uq.edu.au.

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1.0 SHAPE Analysis

Reciprocal shape measures were calculated using SHAPE Version 2.1 software,¹ relative to the regular tricapped trigonal prismatic (r-TCTPR, D_{3h}) and capped square antiprismatic (r-CSAPR, C_{4v}) polyhedra. The coordination sphere of Eu^{3+} in $[\text{Eu}(\text{Phen})(\text{L})_3]_{\infty}$ does not lie along the lowest energy interconversion pathway (black trace) with a deviation of 93.1% (1.028, 1.151 – blue spot). This indicates a distortion away from these regular polyhedra, but the distortion is close to that of the s-TCTPR polyhedron (1.295, 1.077 – red spot).²

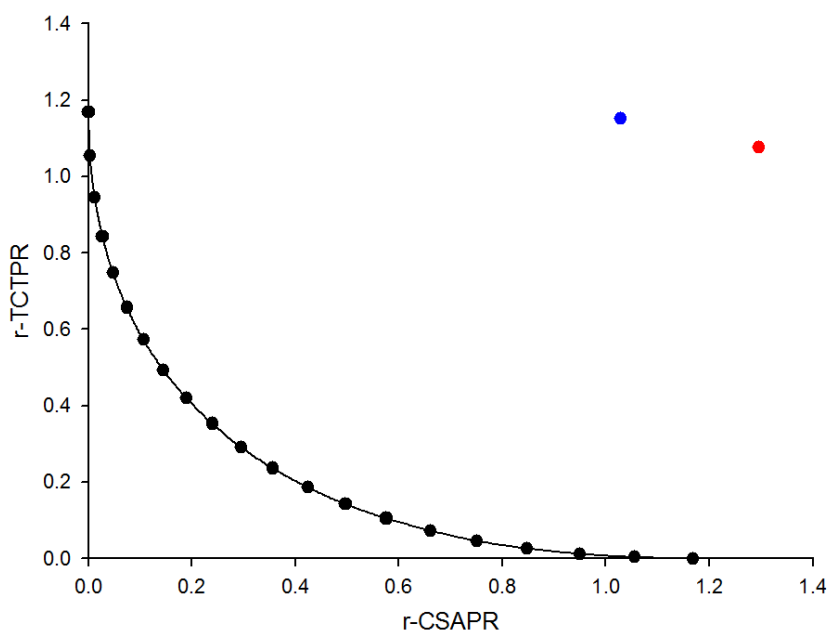


Figure S1 – Shape map relative to the regular r-CSAPR and r-TCTPR polyhedral (interconversion pathway (black line). The reciprocal shape measures of $[\text{Eu}(\text{Phen})(\text{L})_3]_{\infty}$ (1.028, 1.151 – blue spot) and the reference s-TCTPR (1.295, 1.077 – red spot) are plotted.

2.0 Photophysical Data

2.1 UV-Visible Absorption Spectra

The UV-Visible absorption spectra reveal a broad band centred at ~330 nm, which may be attributed to a ${}^1\pi\pi^*$ absorption, however this band could also have some ${}^1n\pi^*$ absorption character.

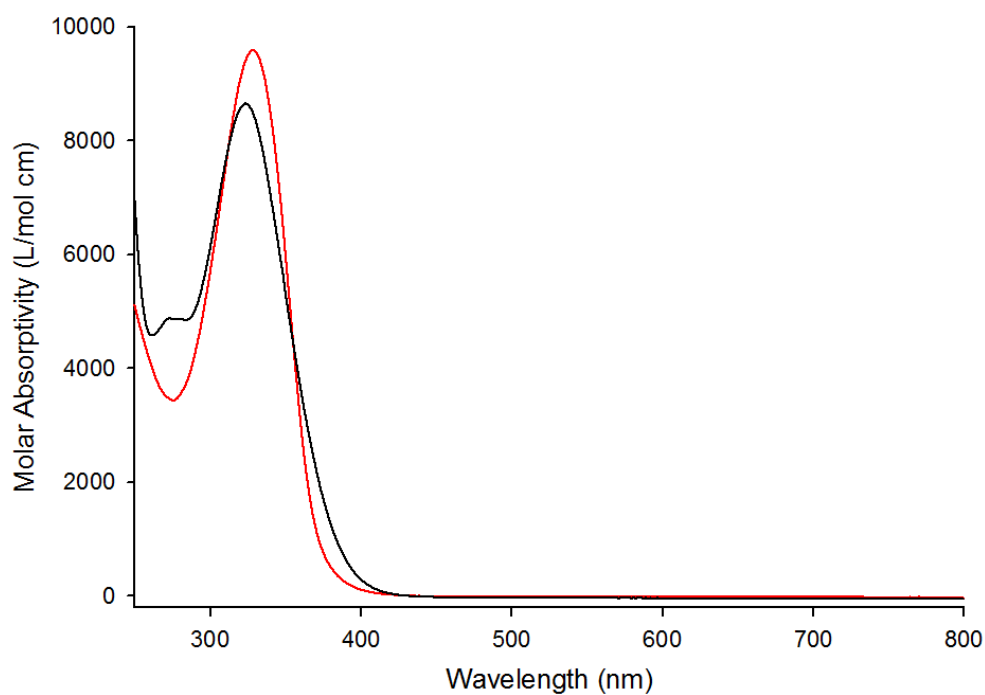


Figure S2 – UV-visible absorption spectra of **LH** (black trace), and **L⁻** (excess triethylamine, red trace) in acetonitrile.

2.2 LH and L⁻ Emission Spectra

The emission spectra in Figure S3 can be attributed to emission from the $^1\pi\pi^*$ from the LH and L⁻ ligand. Thus the emission spectrum can be fit to a series of overlapping Gaussian functions, using commercially available software (Igor, Version 6.1.2.1, Wavemetrics), with the highest energy function (Gaussian band 4) attributed to the 0-0 phonon transition of the $^1\pi\pi^*$ state.

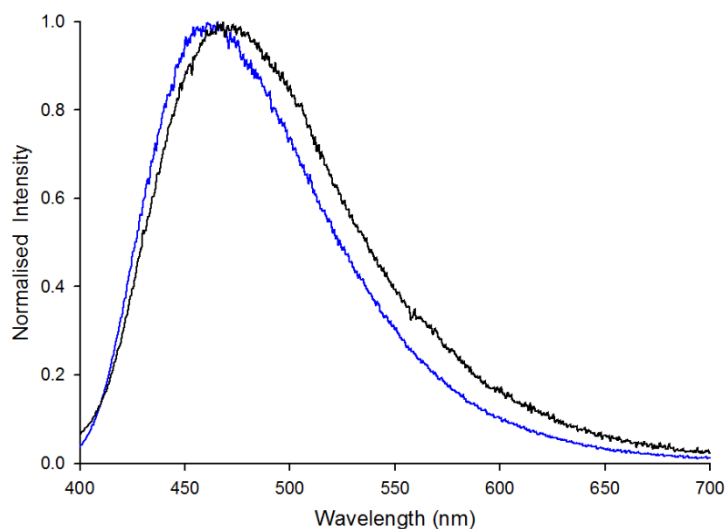


Figure S3 – Emission spectra of LH (black trace), and L⁻ (blue trace) in the presence of excess Gd³⁺ and triethylamine, in acetonitrile at 77K, $\lambda_{ex} = 325$ nm.

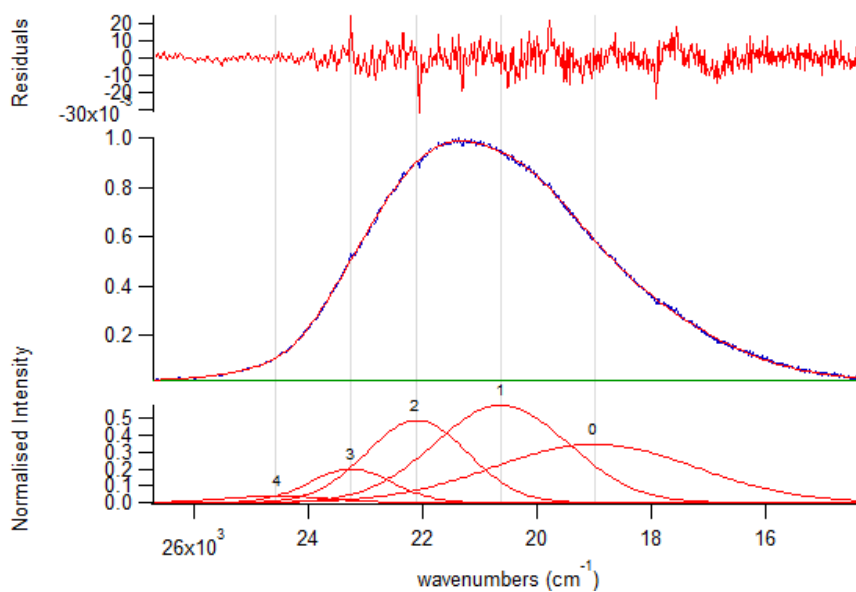


Figure S4 – Emission of LH in acetonitrile at 77K, fit to a series of overlapping Gaussian functions. The 0-0 phonon energy of the singlet state can be estimated from the maximum of the Gaussian labelled 4 ($\sim 24,576$ cm^{-1}).

2.3 Solution State Excitation Spectra

After dissolution of the $[\text{Eu}(\text{Phen})(\text{L})_3]_\infty$ complex in acetonitrile, the solution state excitation spectra at 298 K and 77 K reveal a trace very similar to the UV-Visible absorption spectra of the L^- ligand (Figure S2), suggesting sensitisation of the Eu^{3+} *via* the antenna effect.

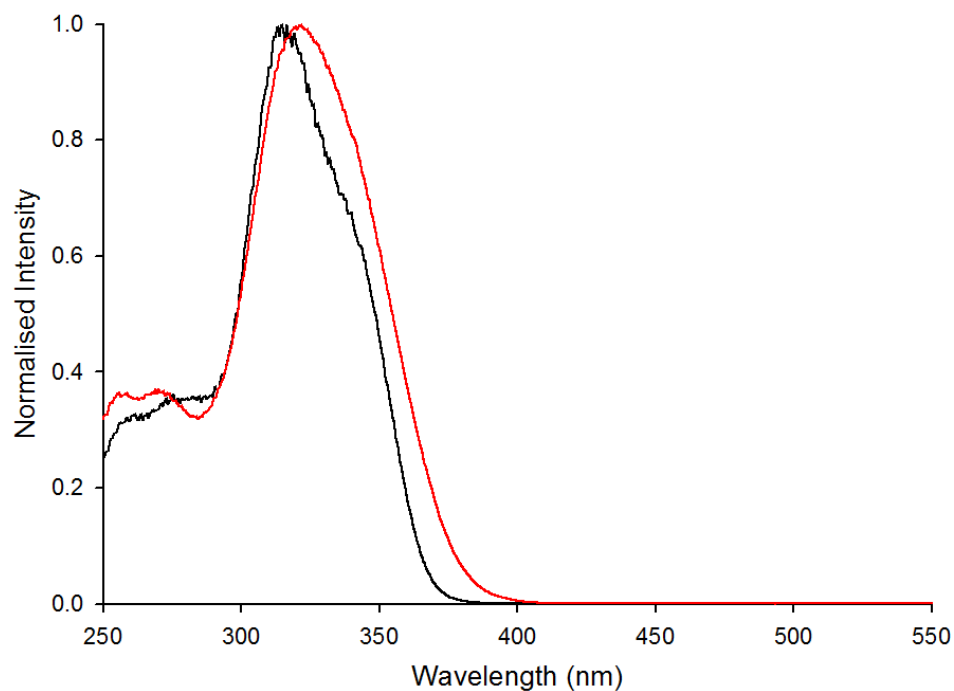


Figure S5 – Excitation spectra of $[\text{Eu}(\text{Phen})(\text{L})_3]_\infty$ after dissolution in acetonitrile at 298K (red trace) and 77K (black trace), monitoring $\lambda_{\text{em}} = 612$ nm.

2.4 Lifetime Decays

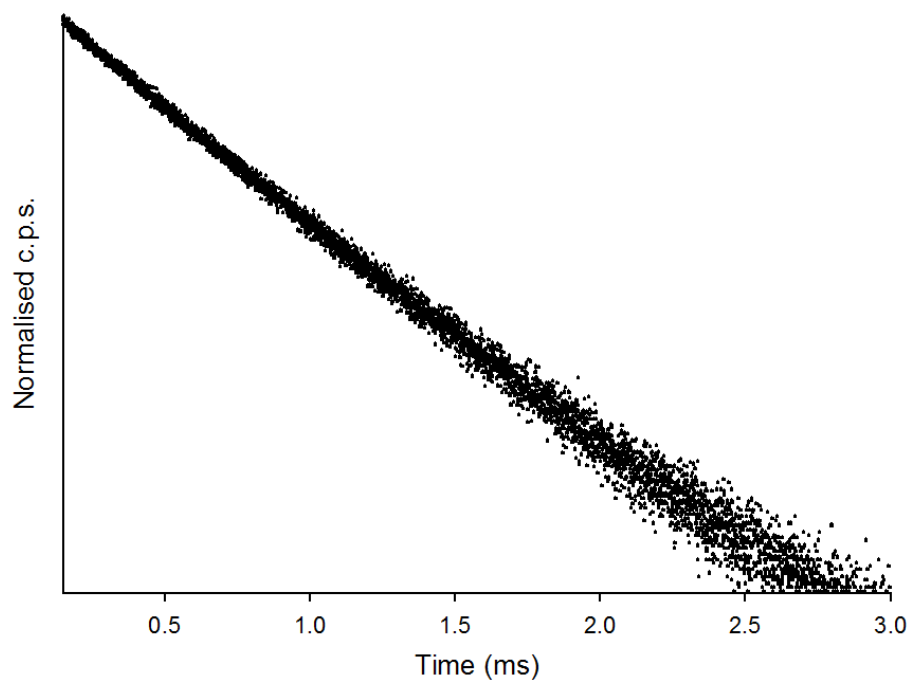


Figure S6 – Lifetime decay of [Eu(Phen)(L)₃]_∞ in the solid state, $\lambda_{\text{ex}} = 350 \text{ nm}$, $\lambda_{\text{em}} = 612 \text{ nm}$.

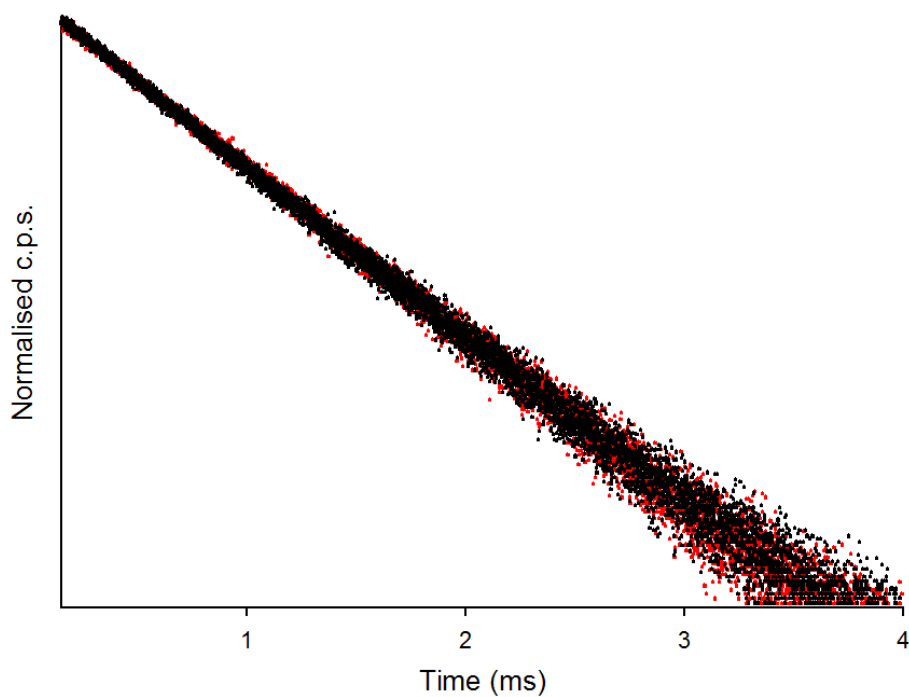


Figure S7 – Lifetime decays of [Eu(Phen)(L)₃]_∞ after dissolution in acetonitrile at 298K (red) and 77K (black), $\lambda_{\text{ex}} = 350 \text{ nm}$, $\lambda_{\text{em}} = 612 \text{ nm}$.

3.0 Transient Absorption Data

3.1 UV-Visible Absorption Spectra

The samples used for transient absorption experiments were characterised by the absorption spectra presented in Figure S8. For excitation at 330 nm, the absorption values are ~0.5-0.8.

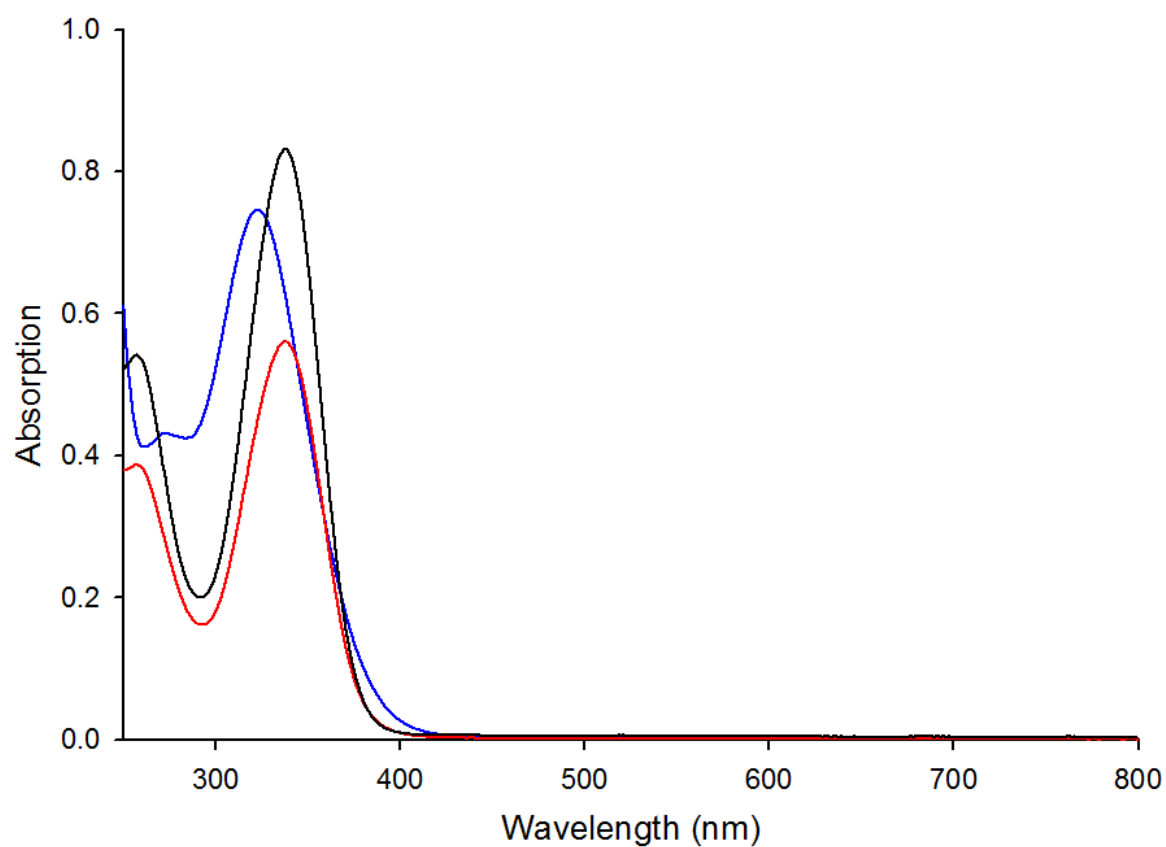


Figure S8 – UV-visible absorption spectra of L^- (blue trace), and L^- in presence of excess Gd^{3+} (black trace) and Eu^{3+} (red trace) in acetonitrile.

3.2 Global Analysis

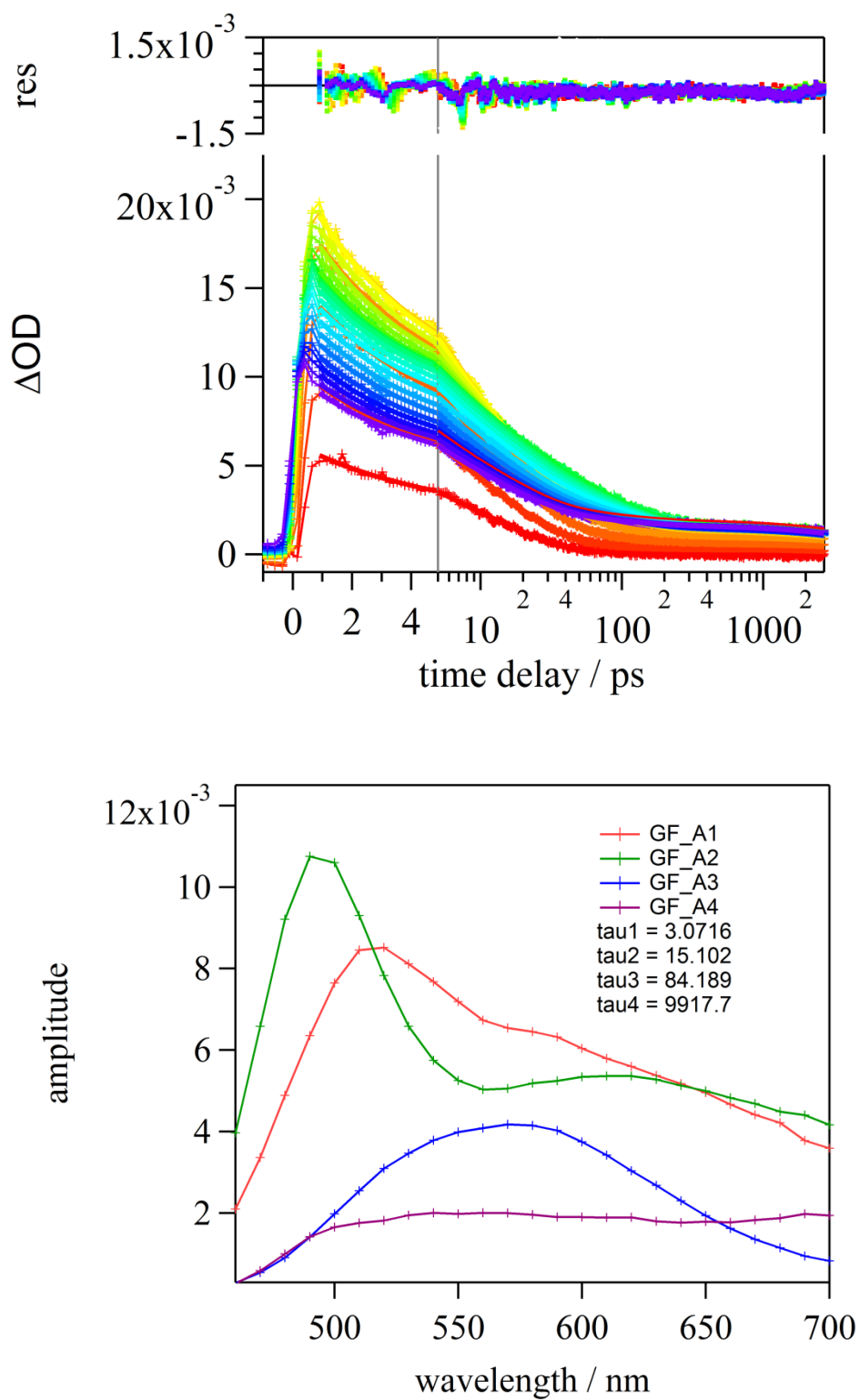


Figure S9 – Results of global fitting the observed TA data across all wavelengths for **L** in acetonitrile solution.

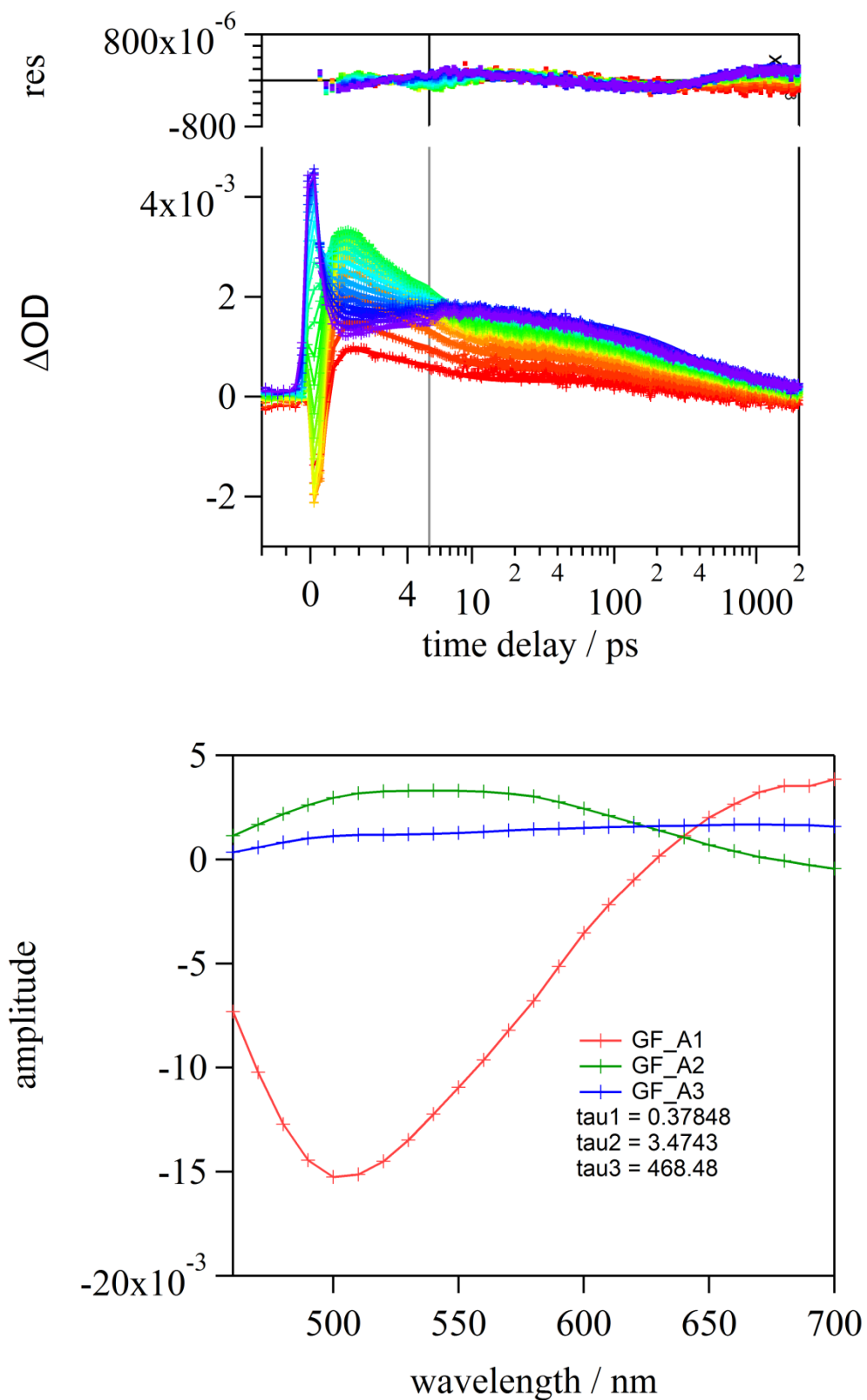


Figure S10 – Results of global fitting the observed TA data across all wavelengths for **L** in the presence of excess Gd^{3+} in acetonitrile solution.

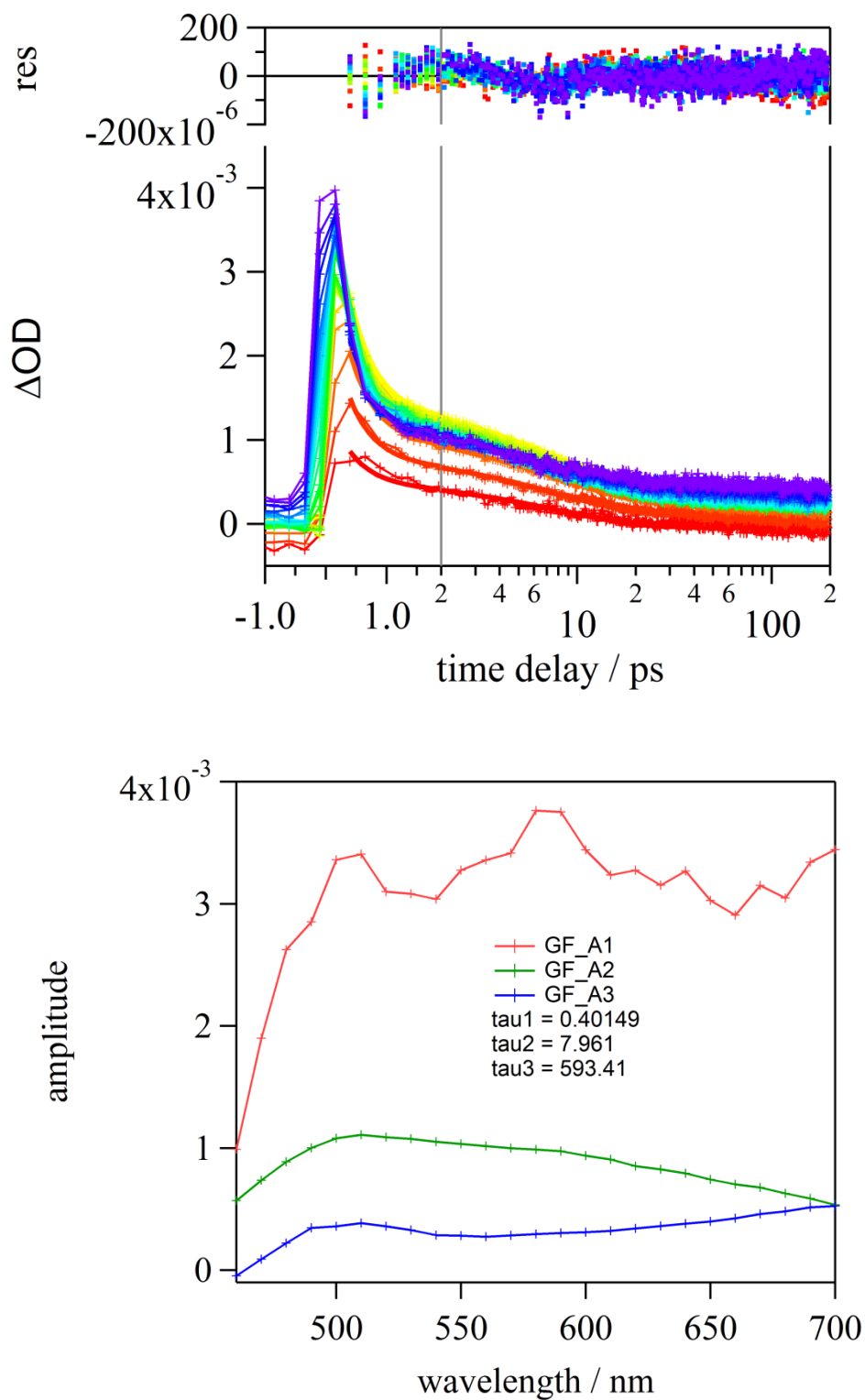


Figure S11 – Results of global fitting the observed TA data across all wavelengths for **L** in the presence of excess Eu^{3+} in acetonitrile solution.

4.0 References

- 1 M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, *Shape Version 2.1*, 2013. Available from: <http://www.ee.ub.es/index.php/news-ee/575-shape-available>.
- 2 A. Ruiz-Martínez, D. Casanova and S. Alvarez, *Chem. Eur. J.*, 2008, **14**, 1291–1303.