Energy Transfer Between Eu^{3+} and Nd^{3+} in Near-Infrared Emitting *β*-Triketonate Coordination Polymers

Laura Abad Galán,[a] Alexandre N. Sobolev,[b] Brian W. Skelton,[b] Eli Zysman-Colman,*[c] Mark I. Ogden,*[a] and Massimiliano Massi*[a]

[a] *Department of Chemistry and Curtin Institute of Functional Molecules and Interfaces, Curtin University, Kent Street, Bentley 6102 WA, Australia.*

[b] *School of Molecular Sciences, University of Western Australia, 35 Stirling Highway, Crawley, Perth, WA 6009, Australia.*

[c] *Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom*

Supplementary Information

Table of Contents

X-ray diffraction studies

*[{Ln(Rb)(**mtbm**)$_4$}$_2$]$_n$*

Intermolecular interactions between chains are present between two methyl groups (C327-C327) and the free keto oxygen and a phenyl ring (O13-C325 and 033-C132) with distances shorter than 3.3Å in every case. This interactions bring two lanthanoid centres between chains relatively close with distances of 15.314 Å and 14.938 Å for Nd^{3+} and Eu^{3+}, respectively.

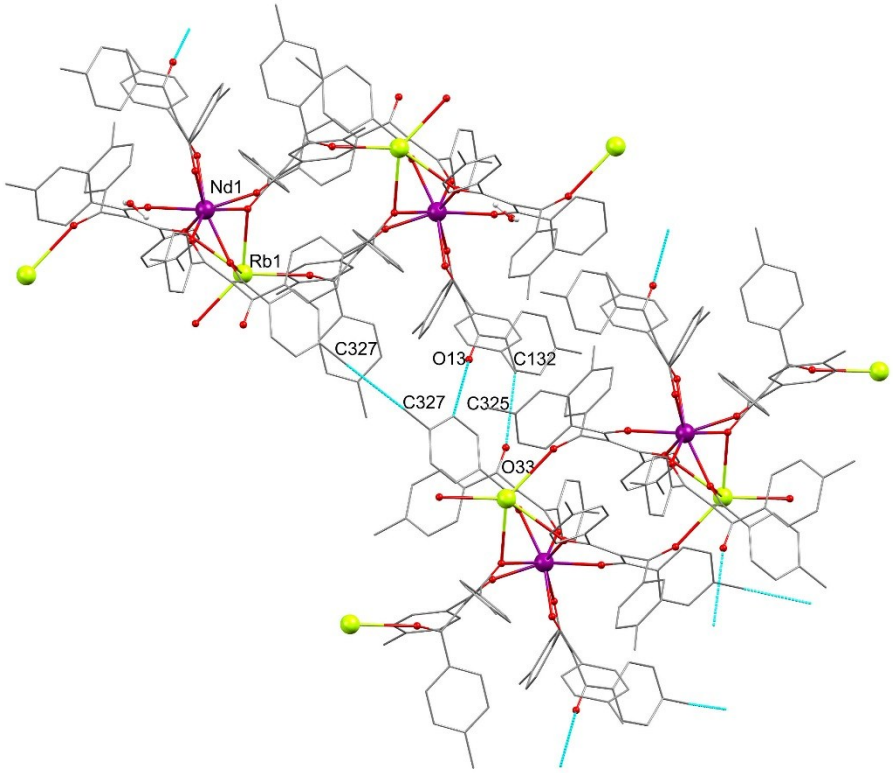

*Figure S1 Representation of the X-ray crystal structure of [{Nd(Rb)(**mtbm**)$_4$}$_2$]$_n$ where intermolecular interactions have been highlighted and the hydrogen atoms are omitted for clarity.*

*[Yb(**mtbm**)$_3$(H$_2$O)$_2$]$_2$*

This complex crystallises as a dimer formed by a hydrogen bond between the water coordinated to one Yb^{3+} centre and the uncoordinated oxygen atom O(13), with a distance of 1.84(2) Å. Each Yb^{3+} is seven coordinated being best described as distorted pentagonal bipyramid.

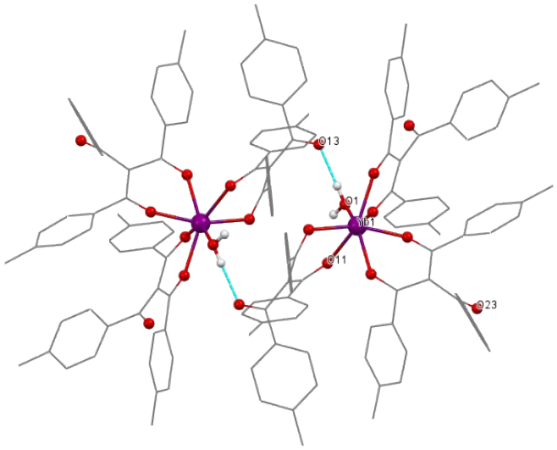

*Figure S2 Representation of the X-ray crystal structure of [Yb(**mtbm**)$_3$(H$_2$O)$_2$]$_2$ where the hydrogen atoms are omitted for clarity.*

*[Cs(**mtbm**)]$_n$*

This complex crystallises as one-dimensional polymer parallel to the a-axis. Each Cs^+ atom is bound to four carbonyl oxygen atoms and one phenyl ring from three different molecules. Each **mtbm** molecule acts as a bridge between to different Cs^+ atoms with a bidentate coordination through two of the carbonyl oxygen atoms or one oxygen and one phenyl ring.

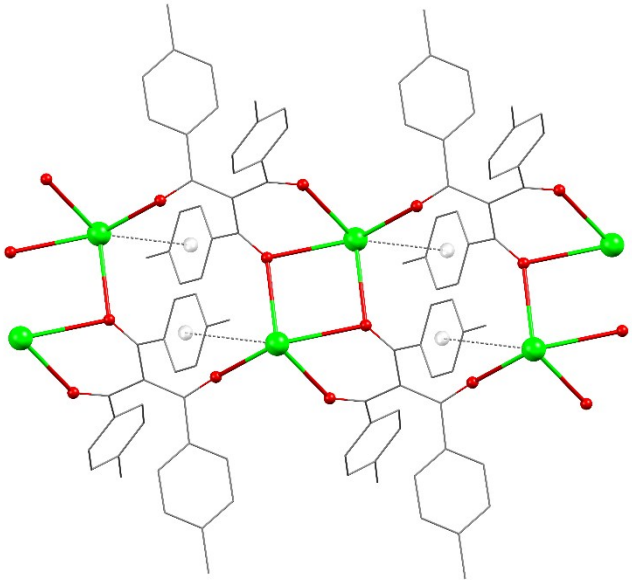

*Figure S.3 Representation of the X-ray crystal structure of [Cs(**mtbm**)]$_n$ where the hydrogen atoms are omitted for clarity.*

*[Nd(Cs·2HOEt)(**dbm**)$_4$]$_n$*

This complex crystallises as a linear polymer where Nd(**dbm**)$_4^-$ units are linked by Cs^+ cations analogously to the previously reported [{Nd(Cs)(**dbm**)$_4$}]$_n$, with the difference of two molecules of EtOH directly coordinated to the Cs^+ cation. Each Nd^{3+} centre is eight coordinated being best described as distorted triangular dodecahedron.

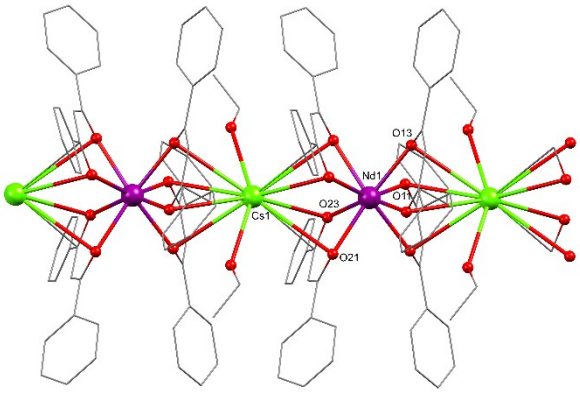

*Figure S4 Representation of the X-ray crystal structure of [Nd(Cs·2HOEt)(**dbm**)$_4$]$_n$ where the hydrogen atoms are omitted for clarity.*

Shape analysis studies

Determination of the geometrical parameters for the coordination sphere of the lanthanoid cations in the main assemblies. The analysis has been carried out considering the degree of distortion with respect to two ideal geometries: square antiprism and triangular dodecahedron.

Table S1 Selected data from shape analysis of the coordination geometries for square antiprism (SAPR-8) and triangular dodecahedron (TDD-8) polyhedral.

Complex	**TTD-8**	**SAPR-8**
[{Eu(Rb)(**mtbm**)$_4$}$_2$]$_n$	1.415	2.357
[{Nd(Rb)(**mtbm**)$_4$}$_2$]$_n$	1.306	2.295
[Nd(Rb)(**tbm**)$_4$]$_2$	0.539	2.921
[Nd(Cs·2HOEt)(**dbm**)$_4$]$_n$	0.951	1.269

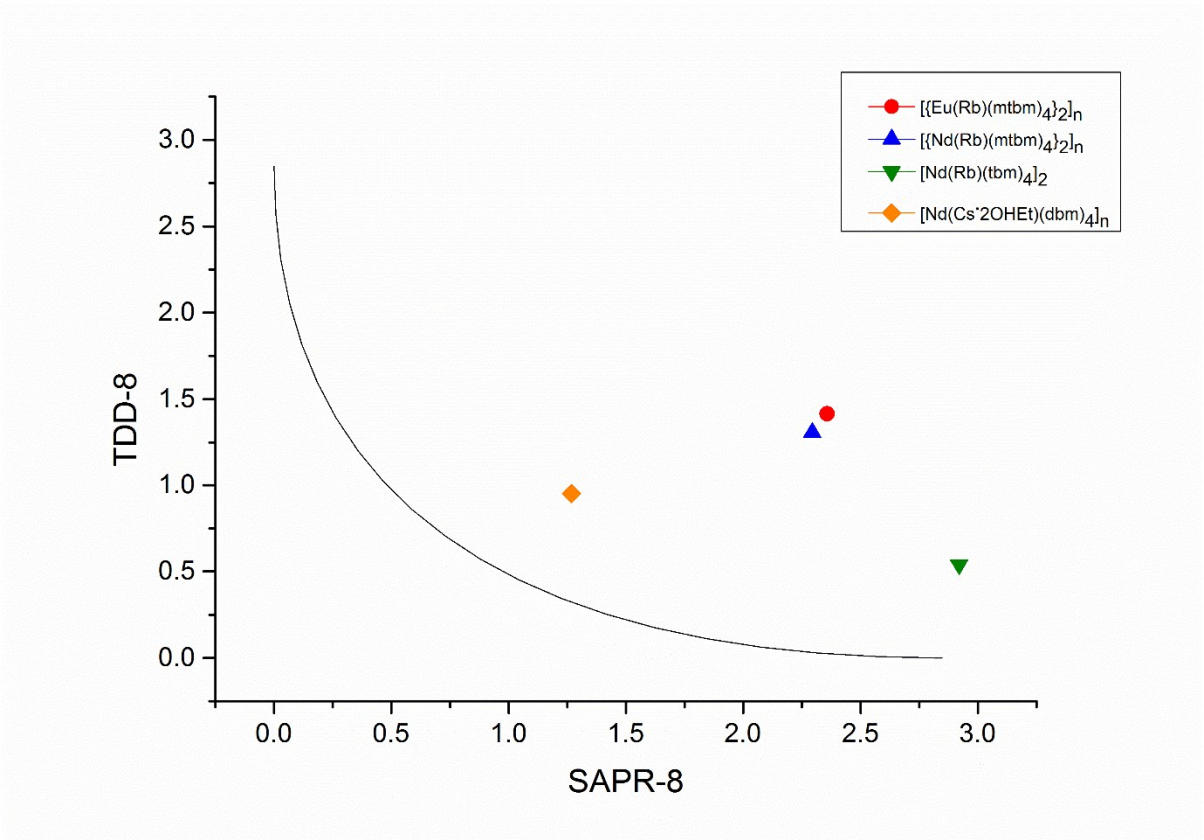

Figure S5 Shape analysis plot for square antiprism (SAPR-8) and triangular dodecahedron (TDD-8) polyhedral.

Normalised excitation and emission plots

*[{Eu(Rb)(**mtbm**)$_4$}$_2$]$_n$(**1**)*

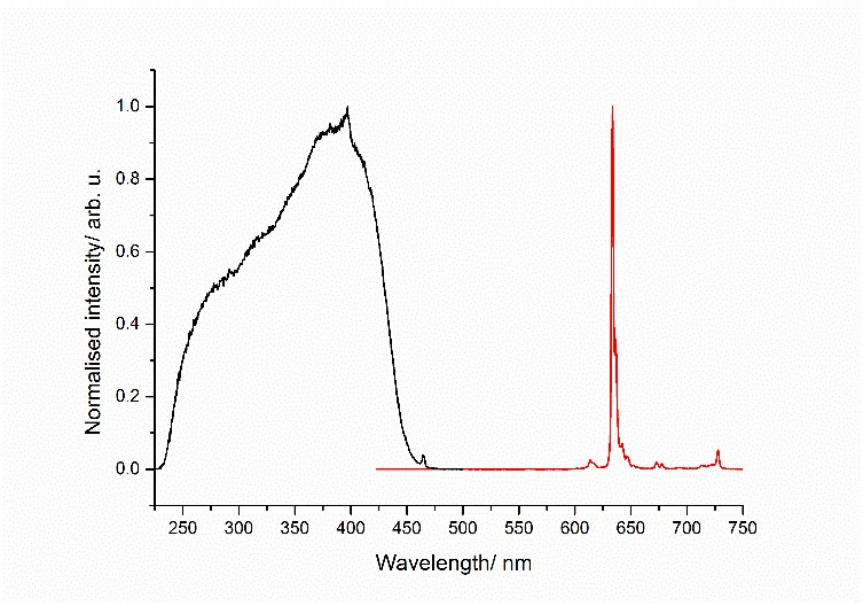

*Figure S6 Excitation (black trace) and emission spectra (red trace) for complex **1** with excitation wavelength at 350nm in the solid state.*

*[{Nd(Rb)(**mtbm**)$_4$}$_2$]$_n$(**2**)*

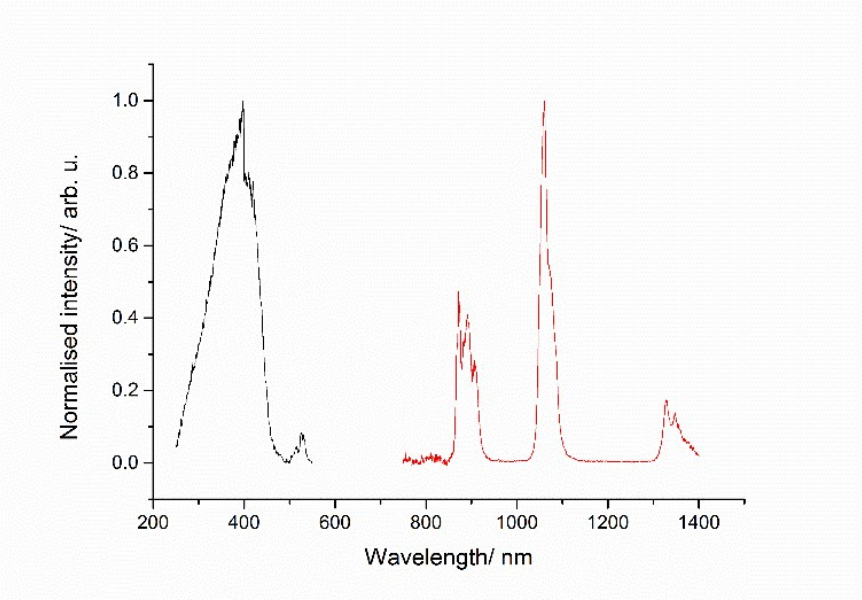

*Figure S7 Excitation (black trace) and emission spectra (red trace) for complex **2** with excitation wavelength at 350nm in the solid state.*

*[{Eu$_{1-x}$Nd$_x$(Rb)(**mtbm**)$_4$}$_2$]$_n$ (**3**,**4**,**5**)*

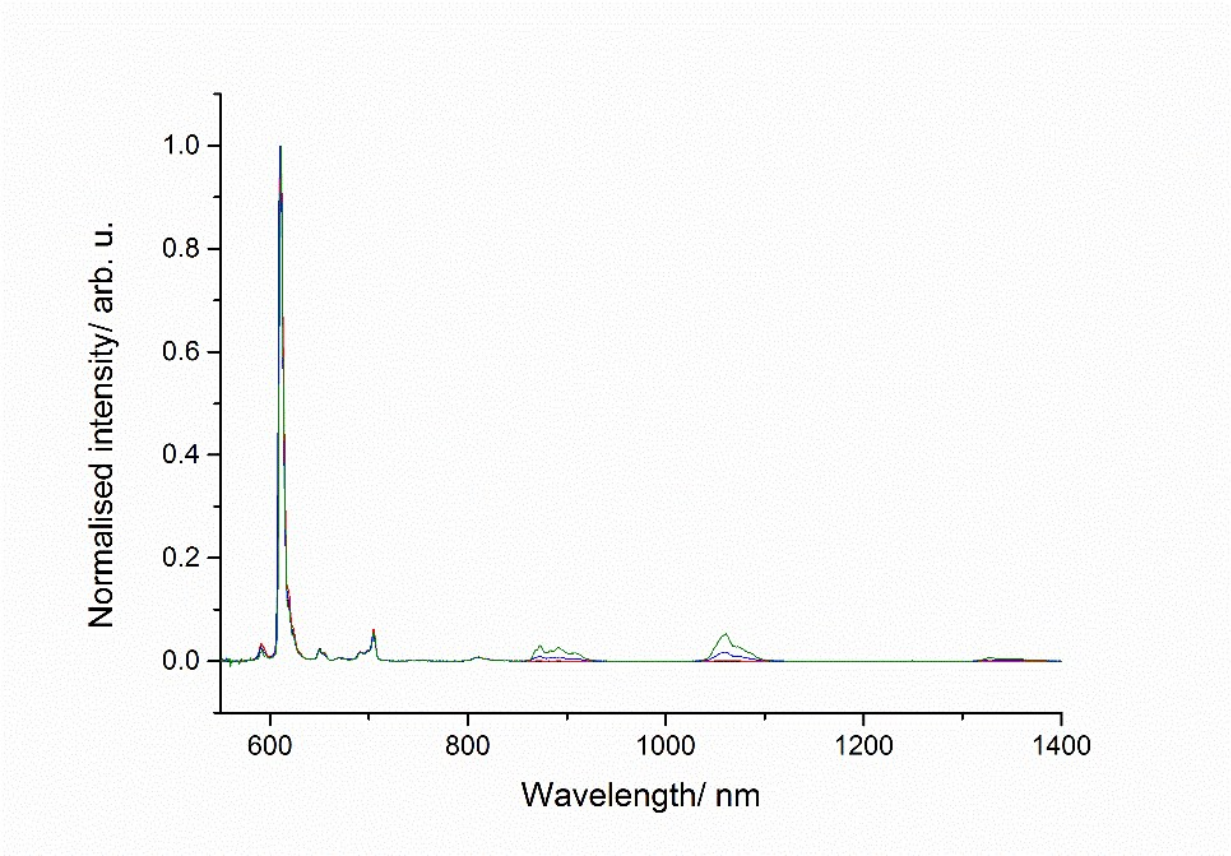

*Figure S8 Whole emission spectra comparison for complexes **1** (black trace), **3** (red trace), **4** (blue trace) and **5** (green trace) with excitation wavelength at 350nm in the solid state.*

*[Nd(Rb)(**tbm**)$_4$]$_2$(**6**)*

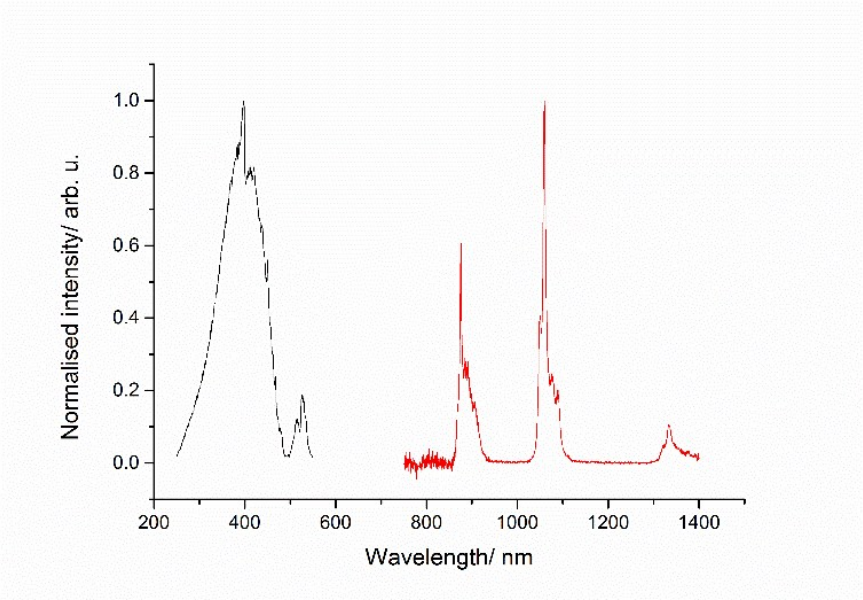

*Figure S9 Excitation (black trace) and emission spectra (red trace) for complex **6** with excitation wavelength at 350nm in the solid state.*

Excited state lifetime decay plots

Eu^{3+}

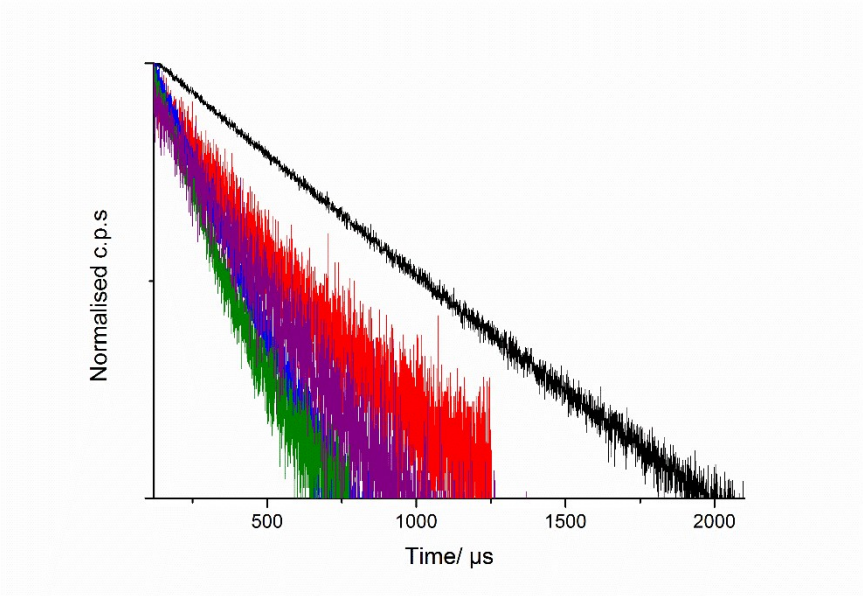

*Figure S10 Lifetime decay at 612nm for complexes **1** (black trace), **3** (red trace), **4** (blue trace), **5** (green trace) and **1+2** (purple trace) in the solid state at 298K.*

Nd^{3+}

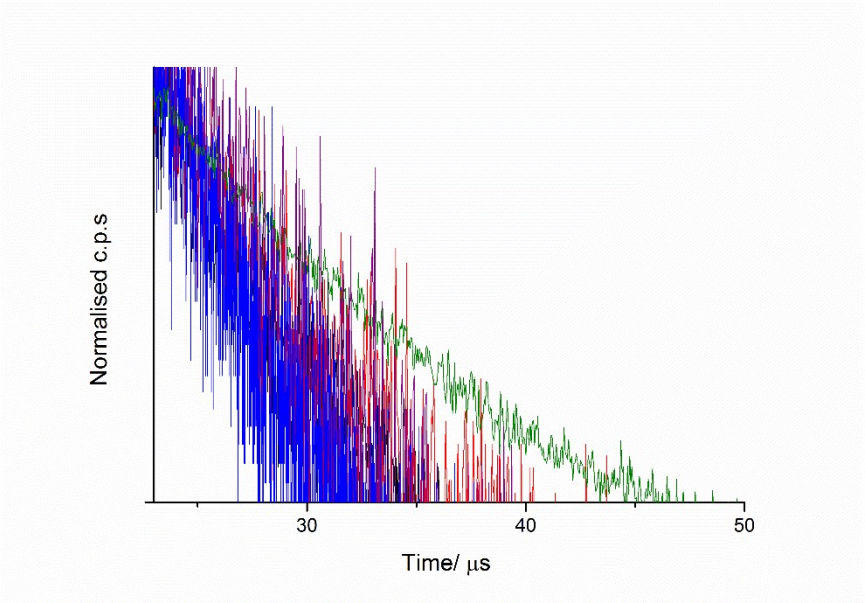

*Figure S11 Lifetime decay at 1060 nm for complexes **2** (black trace), **3** (red trace), **4** (blue trace), **5** (green trace) and **1+2** (purple trace) in the solid state at 298K.*