Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Structural, Redox and Photophysical Properties of Tris-(2,5-di(2-pyridyl)pyrrolide) Lanthanide Complexes

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Electronic Supplementary Information

SC-XRD structures

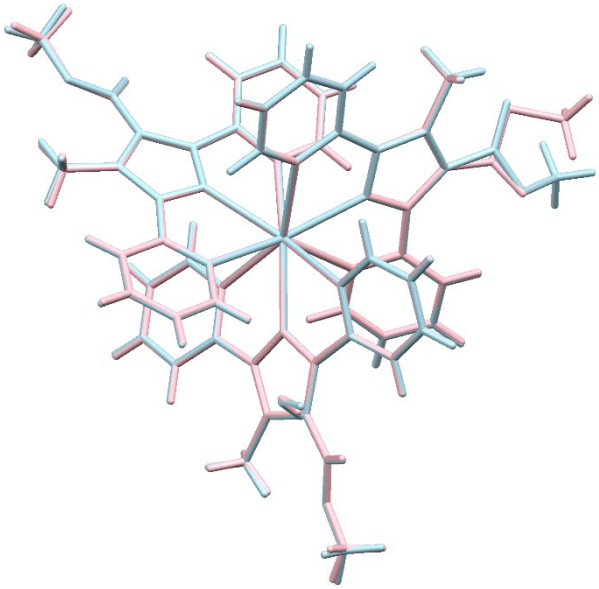

Fig S1. Overlaid SC-XRD structures of [Sm(dpp^{CO_2Me,Me})$_3$] (pink) and [Eu(dpp^{CO_2Me,Me})$_3$] (light blue) by matching the Ln(III) centre and 9 coordinating N atoms (RMSD = 0.0119 Å).

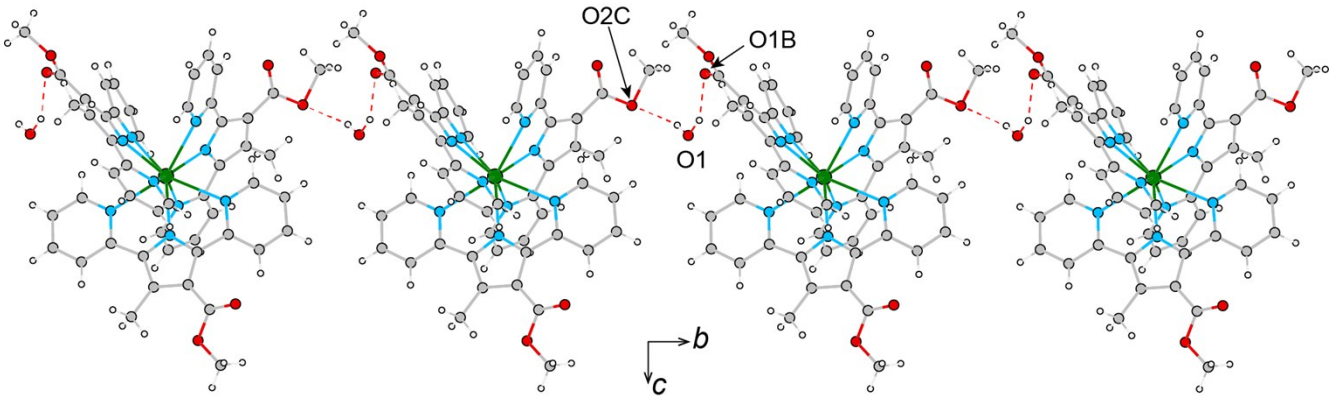

Fig S2. H-bonding network with the lattice water molecule linking neighbouring [Ln(dpp^{CO_2Me,Me})$_3$] complex molecules (Ln = Sm, Eu) down the *b* axis. Key distances and angles: Ln = Sm: O2C…O1 2.90(1) Å, O1…O1B 2.91(1) Å, and O2C–O1–O1B 92.8(4); Ln = Eu: O1C′…O1 2.91(3) Å, O1…O1B 2.92(2) Å, and O1C′–O1–O1B 98.3(7)º.

Table S1. Experimental details

Complex	[La(dpp^{Me,Me})$_3$]	[Sm(dpp^{CO2Me,Me})$_3$]	[Eu(dpp^{CO2Me,Me})$_3$]
CIF name	p1bar_a	james_sm1_a	James_Eu_June18_0m_a
Crystal data			
Chemical formula	$C_{48}H_{42}LaN_9 \cdot 1.5(C_6H_6)$	$2(C_{51}H_{42}N_9O_6Sm) \cdot H_2O$	$C_{51}H_{42}EuN_9O_6 \cdot 0.5(H_2O)$
M_r	1000.98	2072.58	1066.48
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	100	99.95
a, b, c (Å)	12.928 (3), 13.980 (3), 14.100 (3)	17.177 (3), 13.222 (3), 19.402 (4)	17.3254(12), 13.3245(9), 19.4895(13)
α, β, γ (°)	80.97 (3), 83.88 (3), 70.72 (3)	90.85 (3)	90.717(2)
V (Å^3)	2371.5 (9)	4406.0 (15)	4498.8(5)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo K□
μ (mm^{-1})	0.95	1.40	1.458
Crystal size (mm)	0.02 × 0.01 × 0.01	0.02 × 0.02 × 0.02	0.1 × 0.04 × 0.01
Data collection			
Diffractometer	ADSC Quantum 210r	ADSC Quantum 210r	Bruker D8 Quest
Absorption correction	–	–	SADABS
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39500, 10228, 9722	65218, 9559, 8469	146595, 7935
R_{int}	0.018	0.029	0.1555
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.658	0.641	0.595
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.061, 1.07	0.039, 0.103, 1.14	0.0479, 0.1249, 1.076
No. of reflections	10228	9559	7935
No. of parameters	611	651	653
No. of restraints	–	11	49
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.51, -1.40	0.92, -1.16	0.94, -0.85

Computer programs: BluIce (McPhillips, 2002), XDS (Kabsch, 1993), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

NMR Spectra

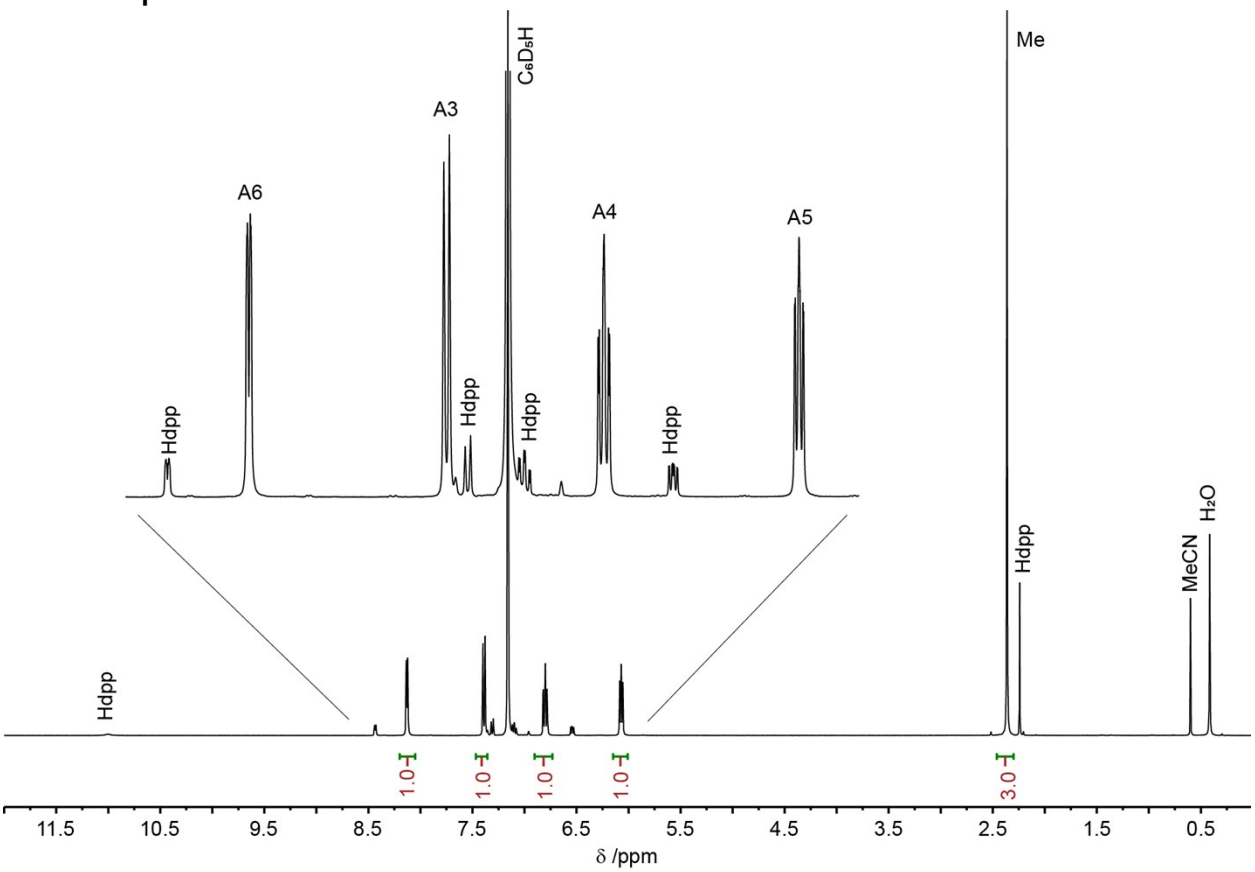

Fig. S3. ^{1}H NMR (400 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$].

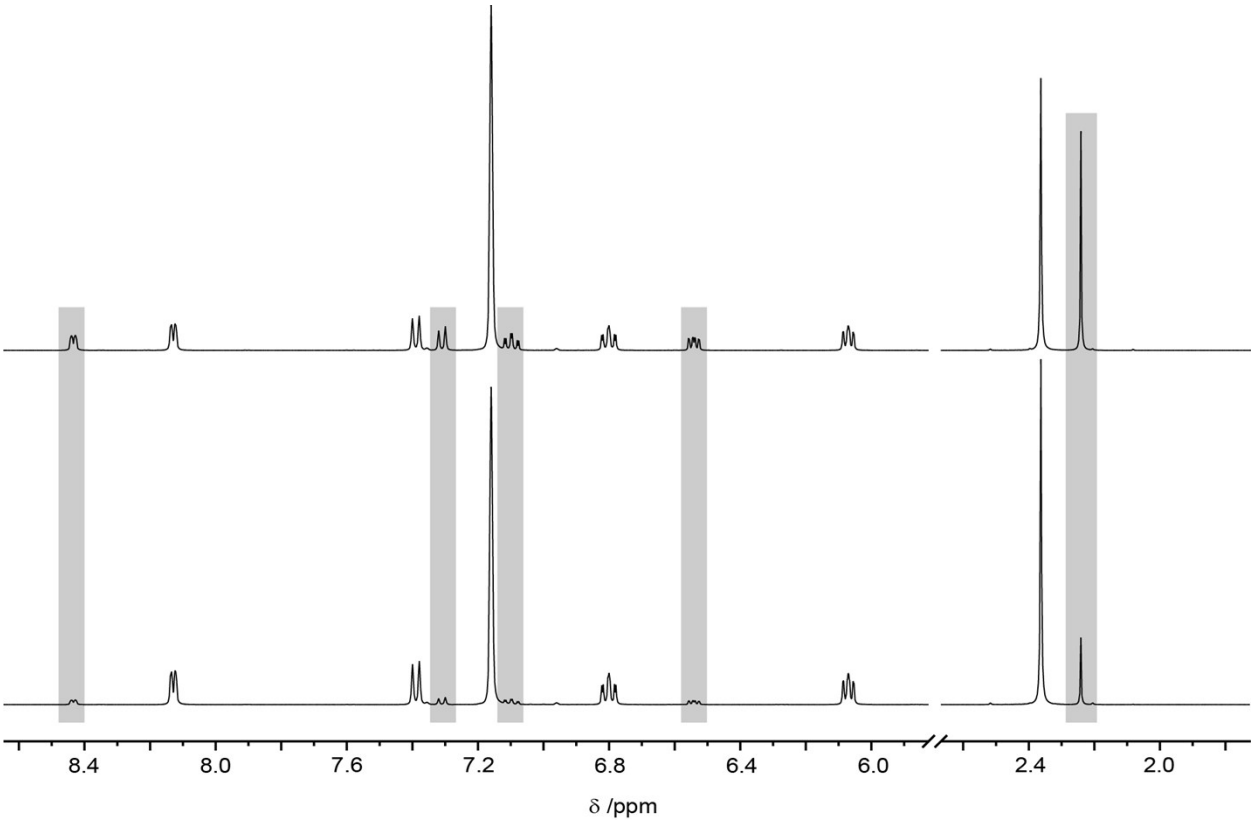

Fig. S4. ^{1}H NMR (400 MHz, C_6D_6) spectra of [La(dpp^{Me,Me})$_3$]: after 20 minutes in solution (bottom) and after 6 hours in solution (top). The signals, which correspond to unbound dpp^{Me,Me}H—and increase over time—have been highlighted by grey regions.

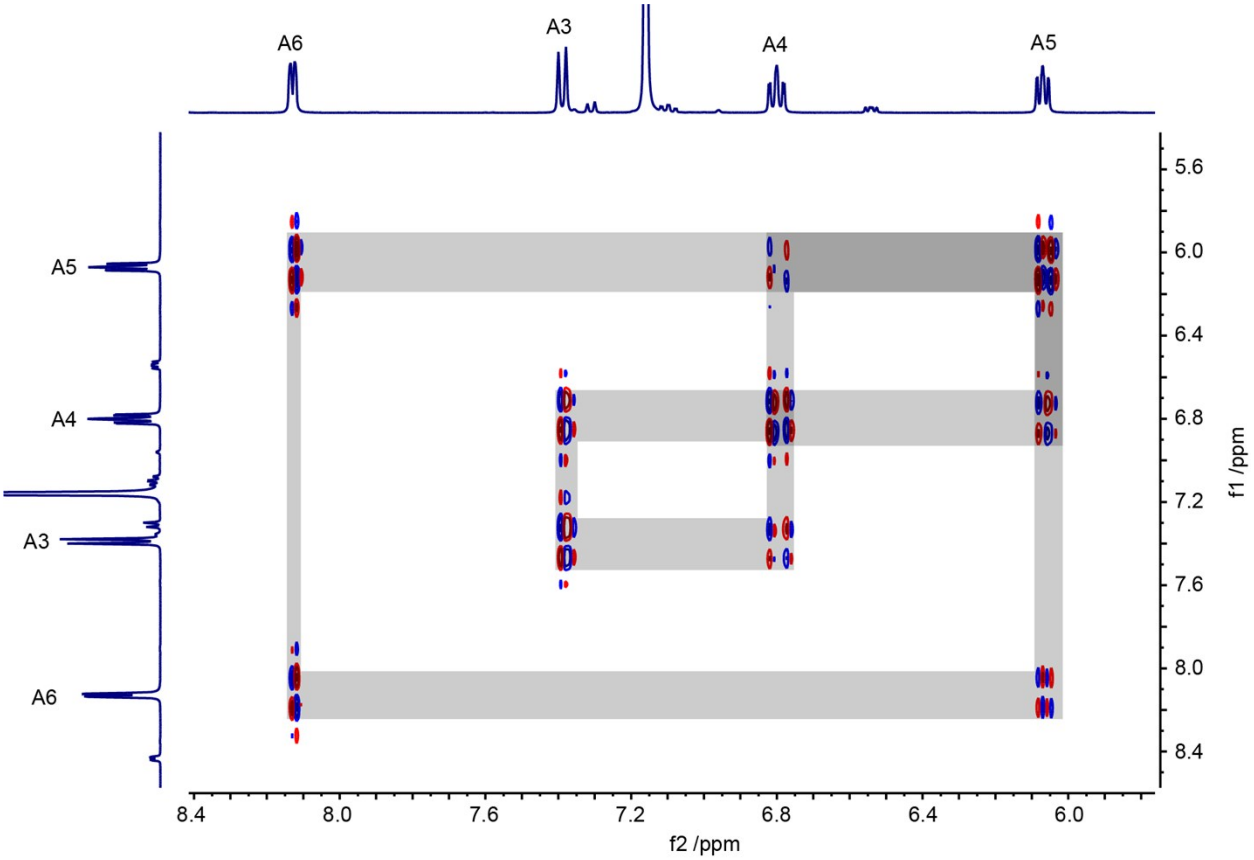

Fig S5. ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$].

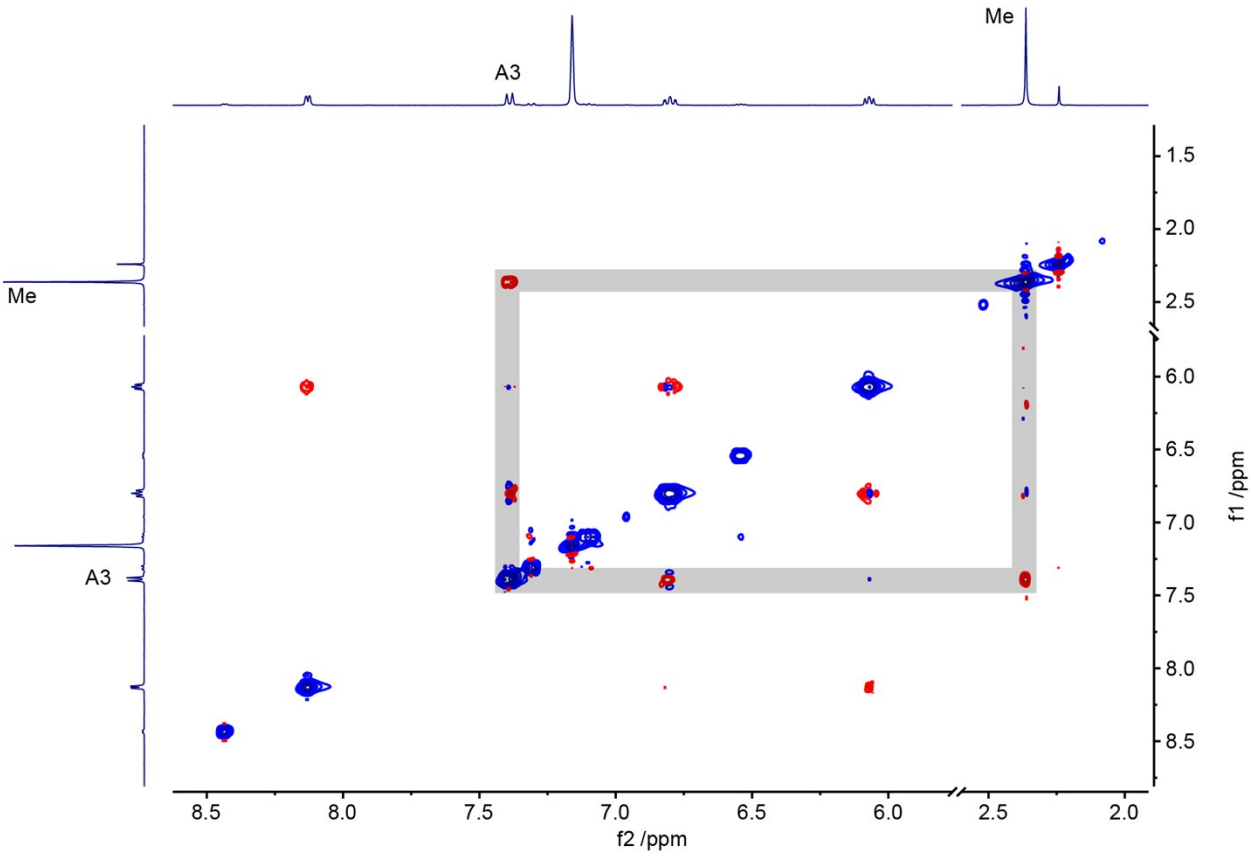

Fig S6. ^{1}H-^{1}H nOeSY NMR (400 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$]. The key interaction (A3 – Me) has been highlighted.

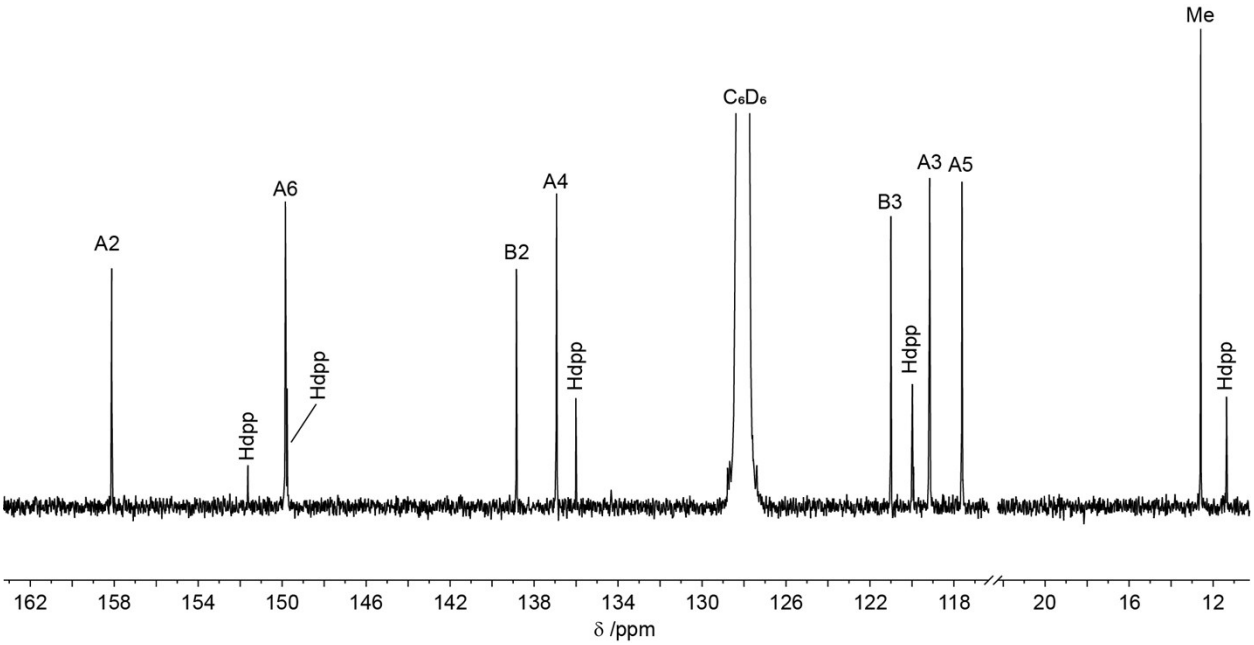

Fig. S7. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$].

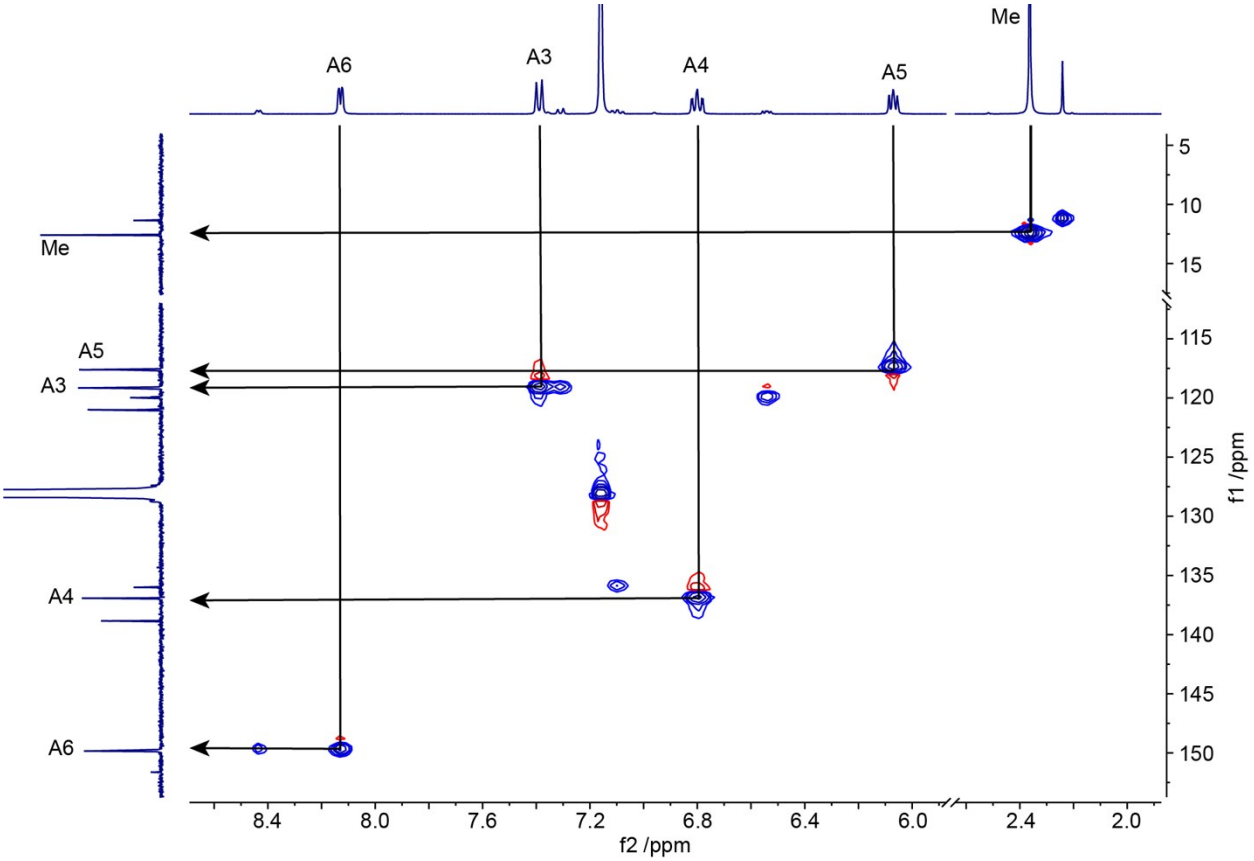

Fig S8. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (400 MHz, 101 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$].

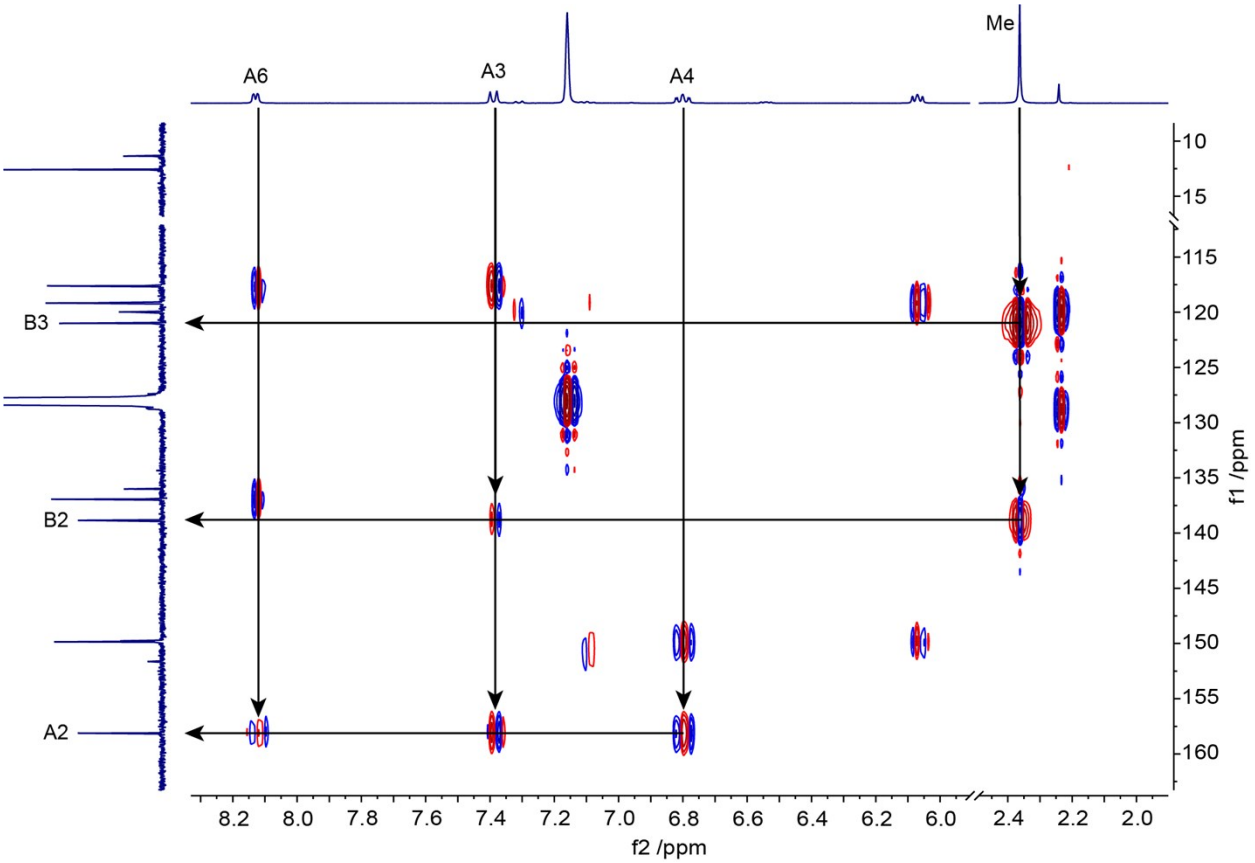

Fig S9. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR (400 MHz, 101 MHz, C_6D_6) spectrum of [La(^{Me,Me}dpp)$_3$].

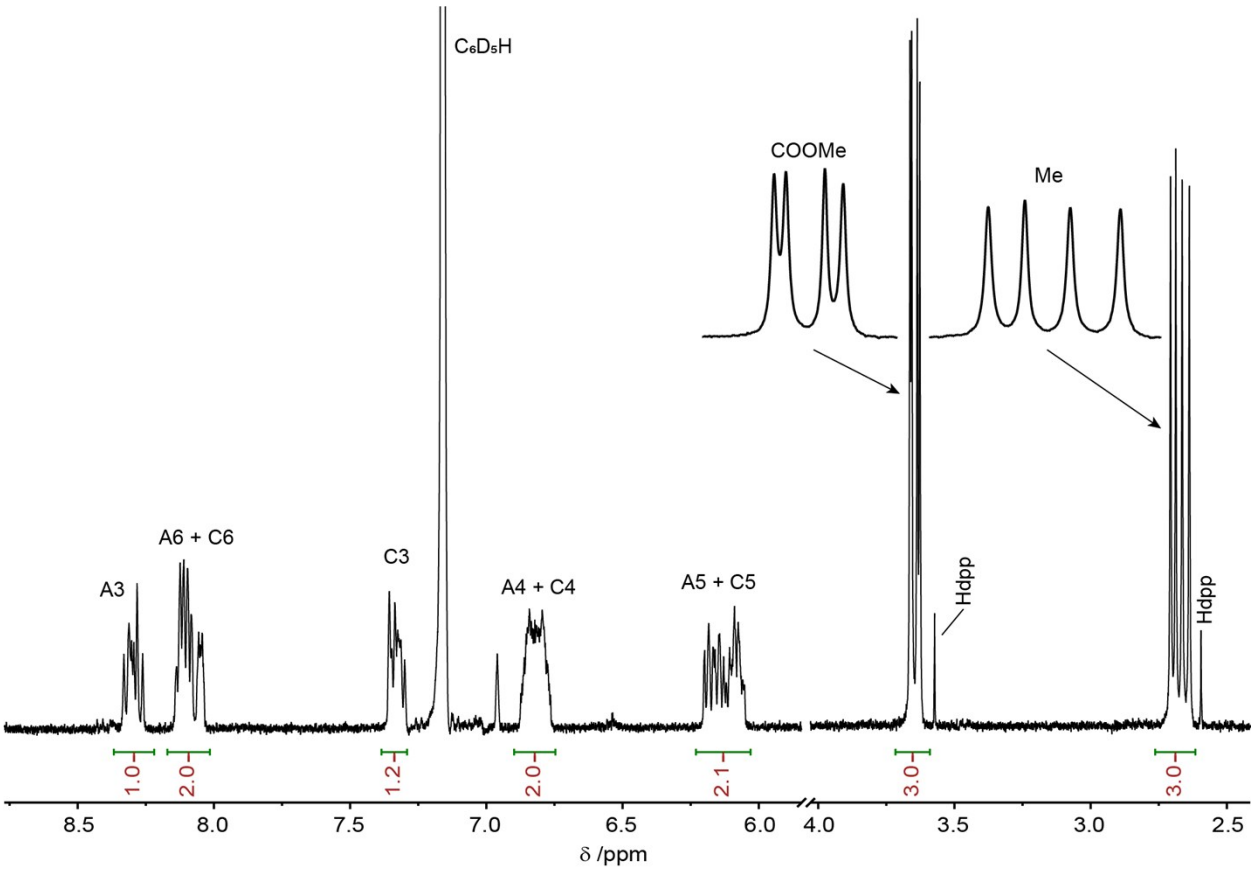

Fig. S10. ^{1}H NMR (400 MHz, C_6D_6) spectrum of [La(dpp^{CO_2Me,Me})$_3$].

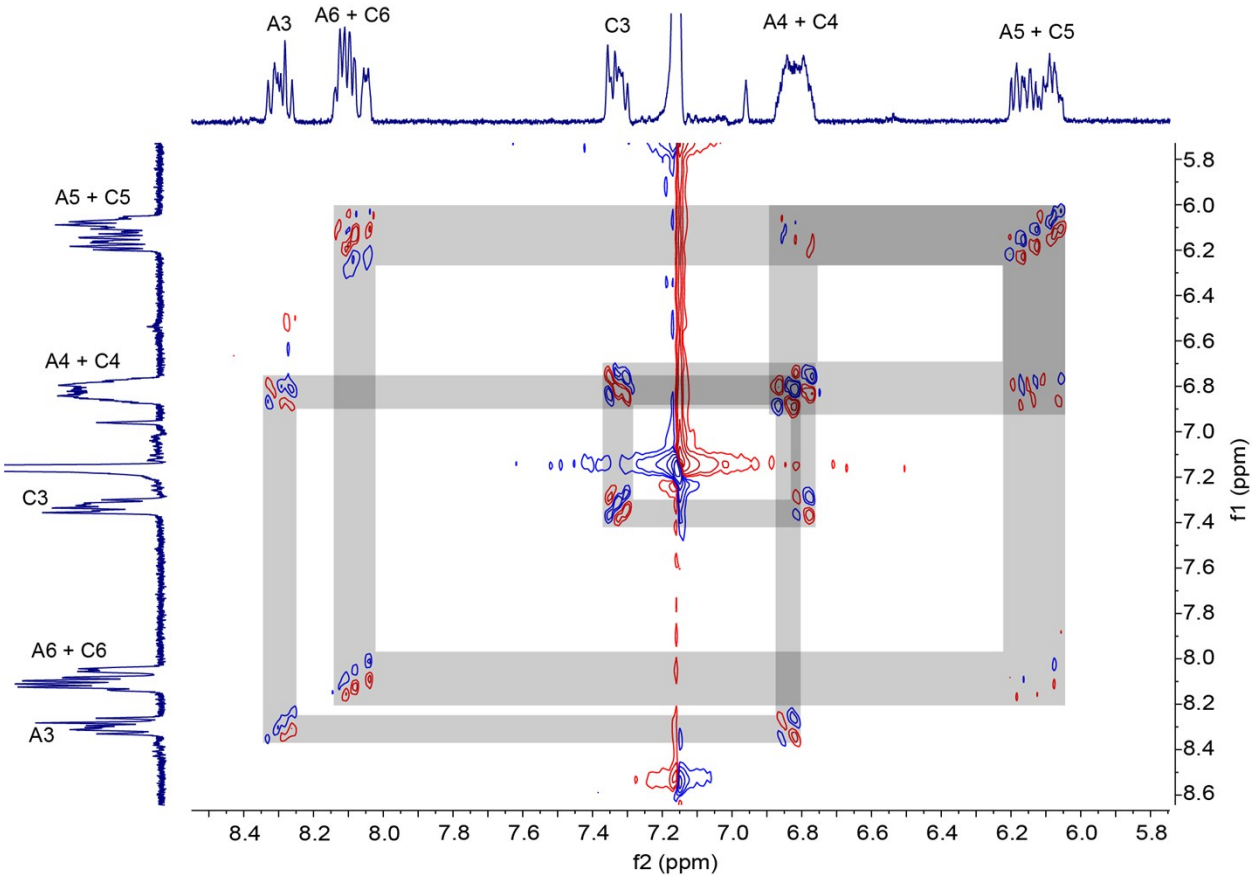

Fig S11. ^{1}H-^{1}H COSY NMR (400 MHz, C_6D_6) spectrum of [La(dpp^{CO_2Me,Me})$_3$].

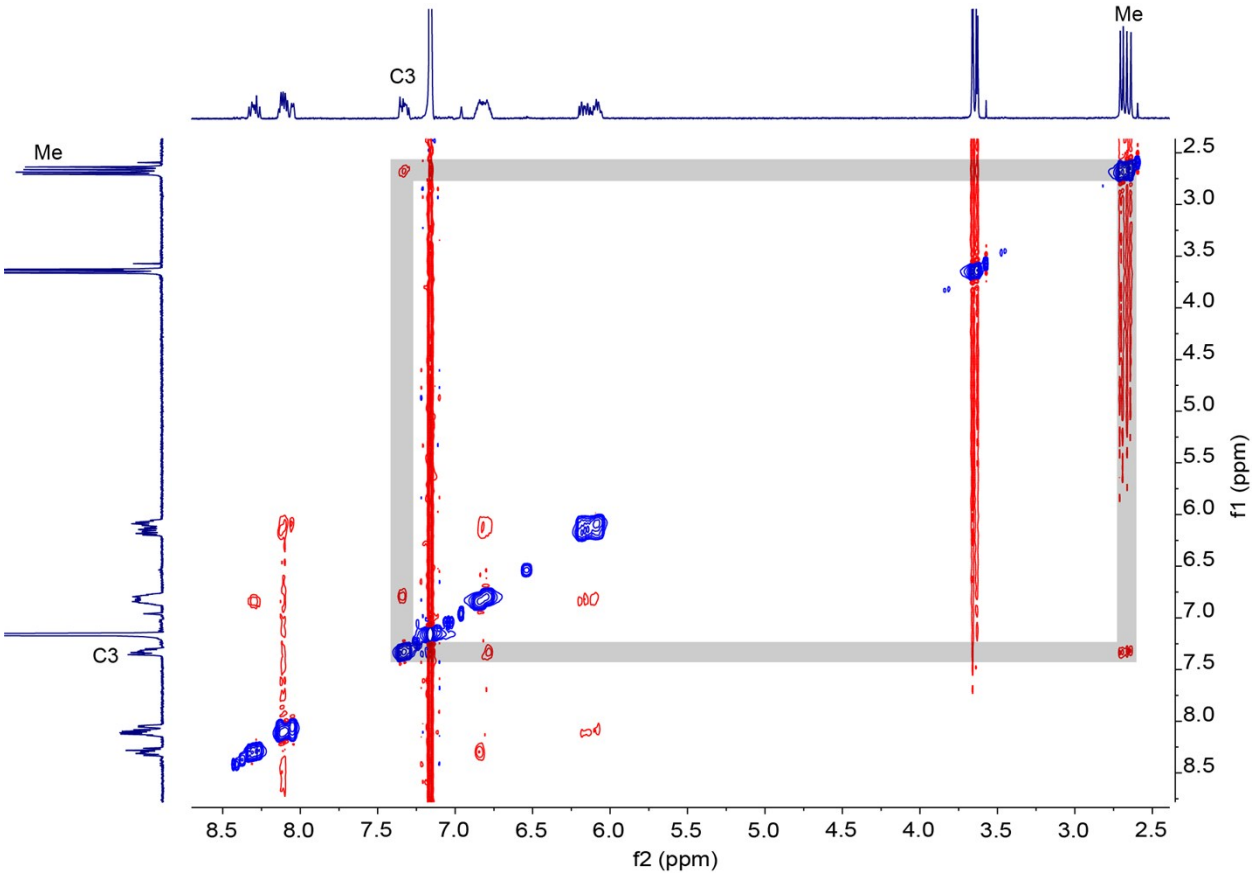

Fig S12. ^{1}H-^{1}H nOeSY NMR (400 MHz, C_6D_6) spectrum of [La(dpp^{CO_2Me,Me})$_3$].

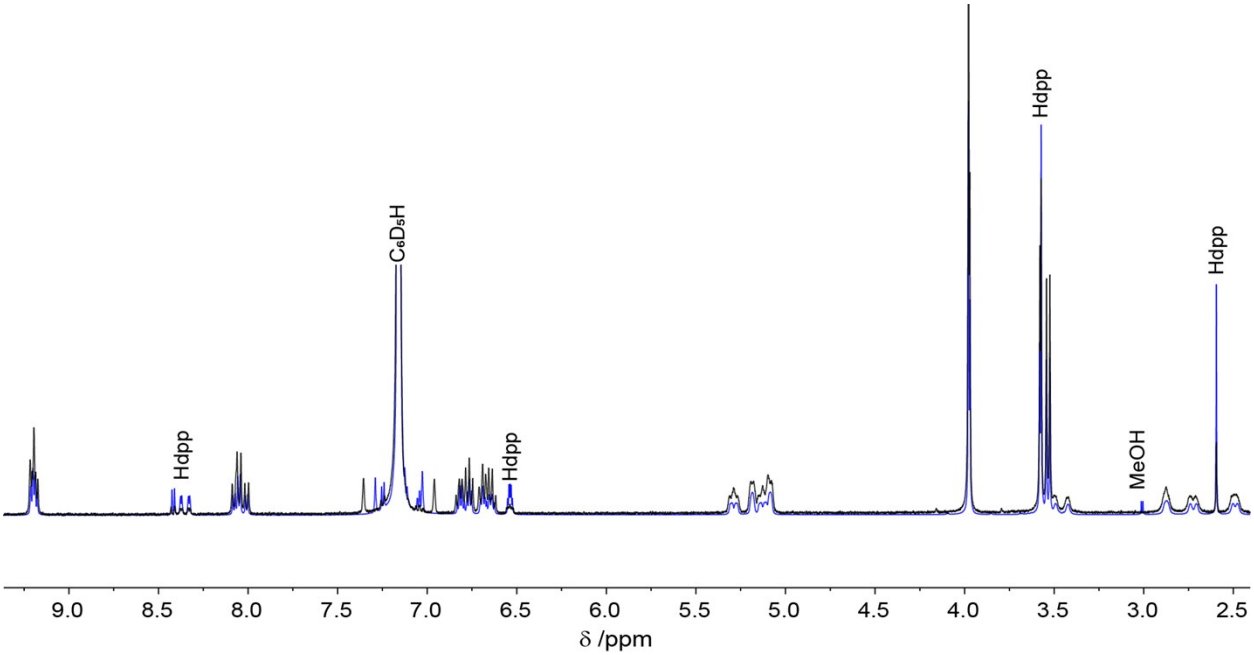

Fig. S13. Superimposed ^{1}H NMR (C_6D_6) spectra of solutions of [Sm(dpp^{CO_2Me,Me})$_3$] prepared separately at different fields (600 MHz in blue, 400 MHz in black).

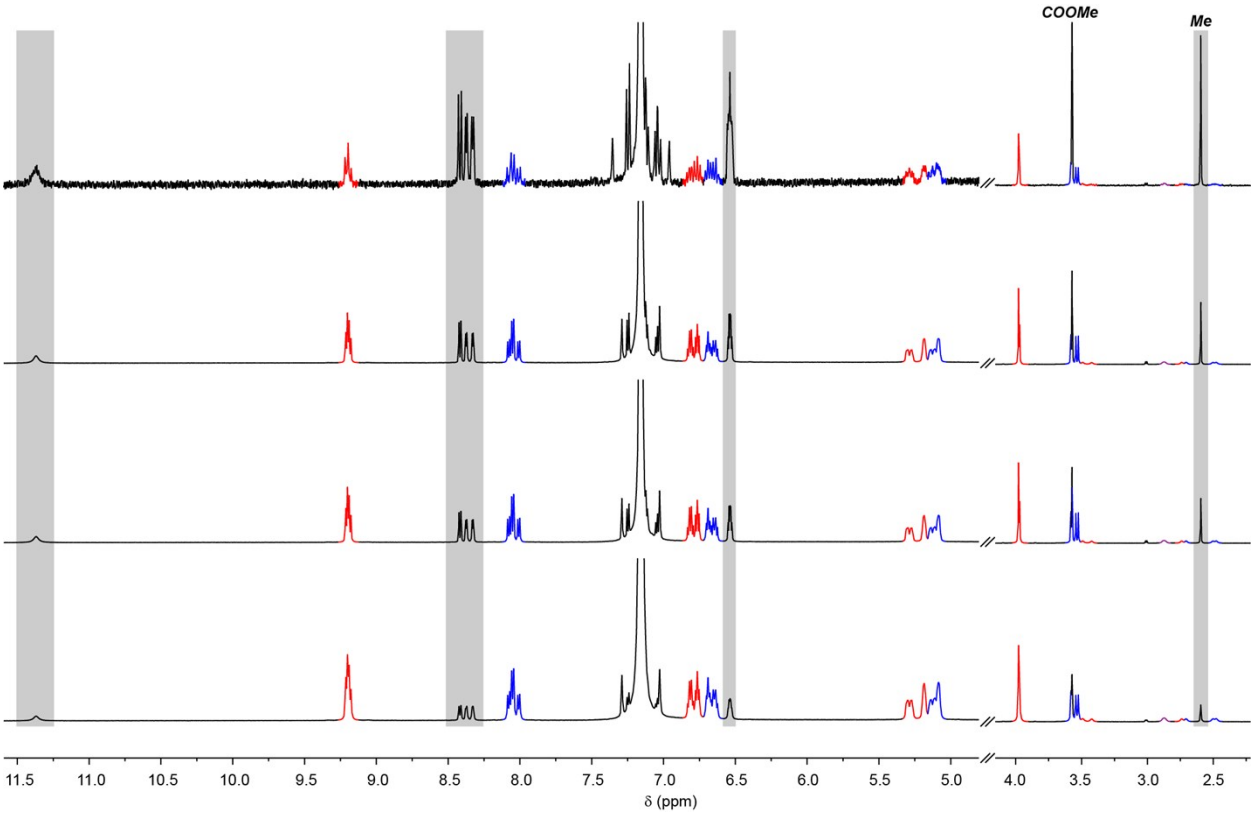

Fig. S14. From bottom to top, ^{1}H NMR (C_6D_6) spectra of [Sm(dpp^{CO_2Me,Me})$_3$]: after 20 minutes in solution (600 MHz, bottom), [Sm(dpp^{CO_2Me,Me})$_3$] after 4 hours in solution (600 MHz, second from the bottom), after 12 hours in solution (600 MHz, second from the top); and after 9 days in solution (400 MHz, top). Selected signals, which correspond to unbound Hdpp^{CO_2Me,Me} and increase over time, have been highlighted by grey regions, while the signals assigned to the [Sm(dpp^{CO_2Me,Me})$_3$] complex (and decrease over time) are coloured red and blue according to their assignment (Fig. X) for clarity. Note – a break in scale occurs between 4–5 ppm.

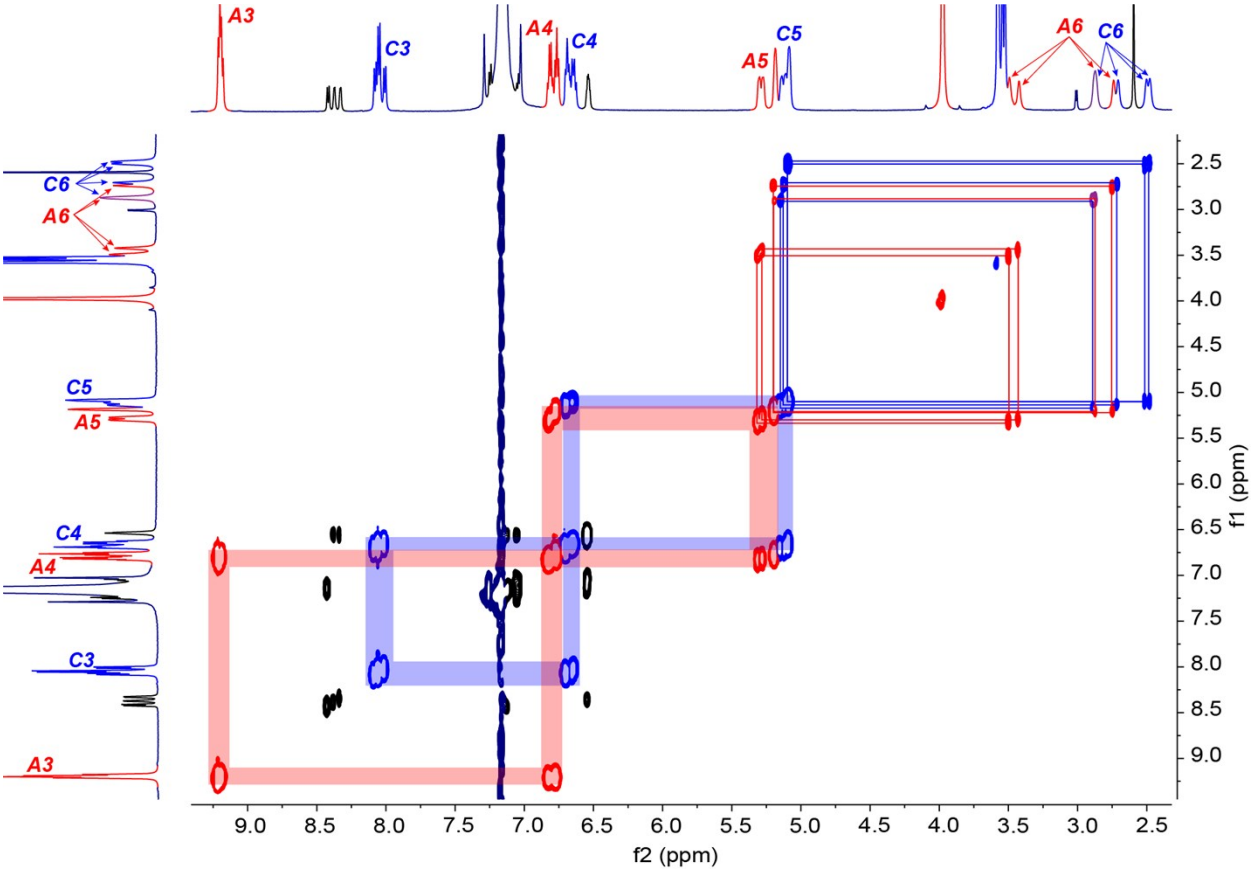

Fig. S15. ^{1}H-^{1}H COSY NMR (600 MHz, C_6D_6) of [Sm(dpp^{CO_2Me,Me})$_3$]. In black are signals corresponding to free Hdpp^{CO_2Me,Me} which has dissociated during the course of the solution state NMR studies.

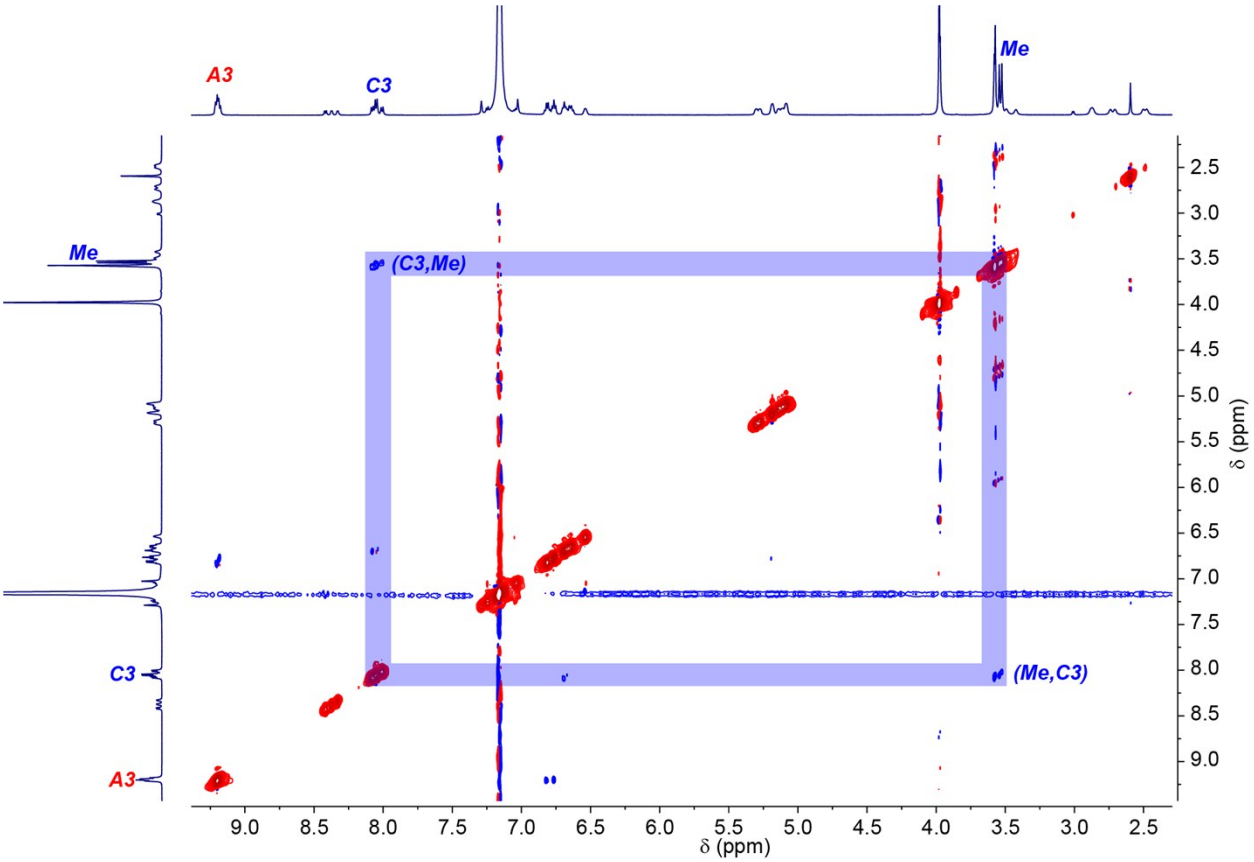

Fig. S16. ^{1}H-^{1}H nOeSY NMR (600 MHz, C_6D_6) of [Sm(dpp^{CO_2Me,Me})$_3$] highlighting the key nOe interactions (opposite phase to diagonal peaks) between *C3* and the 4-methyl pyrrolide proton environments.

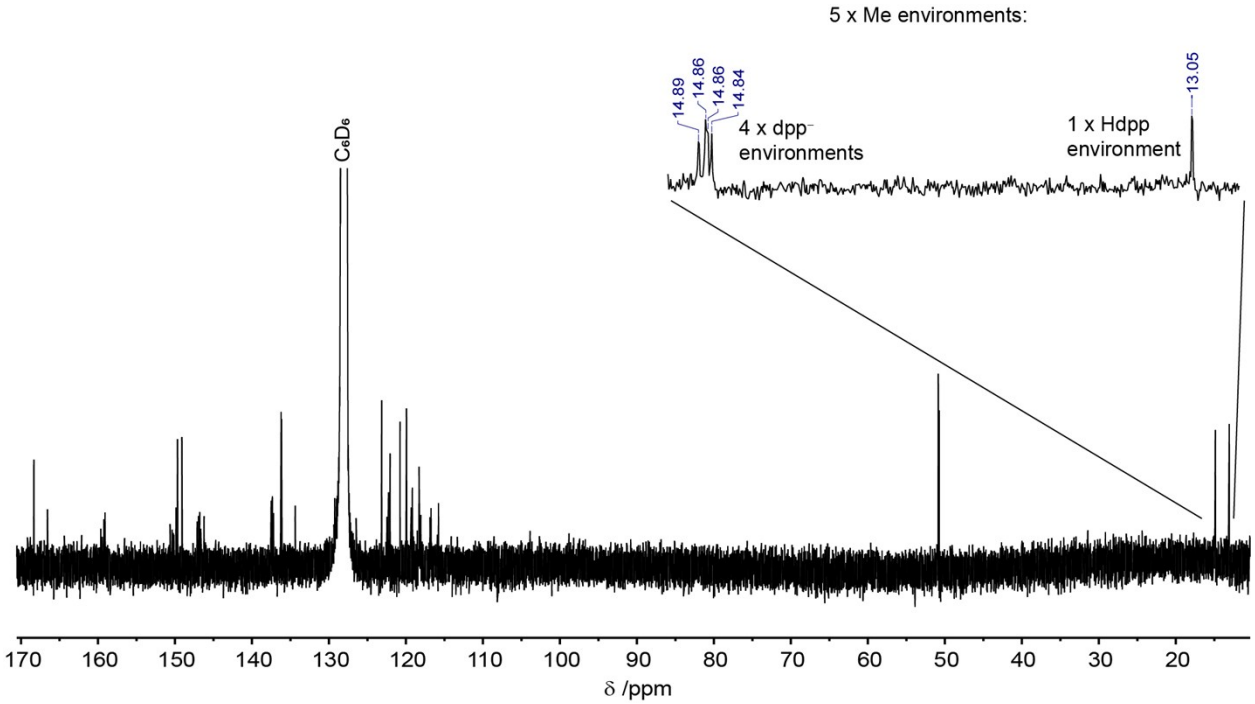

Fig. S17. $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6) spectrum for [Sm(dpp^{CO_2Me,Me})$_3$]. Shown inset are the five ^{13}C environments associated with the pyrrole methyl substituent.

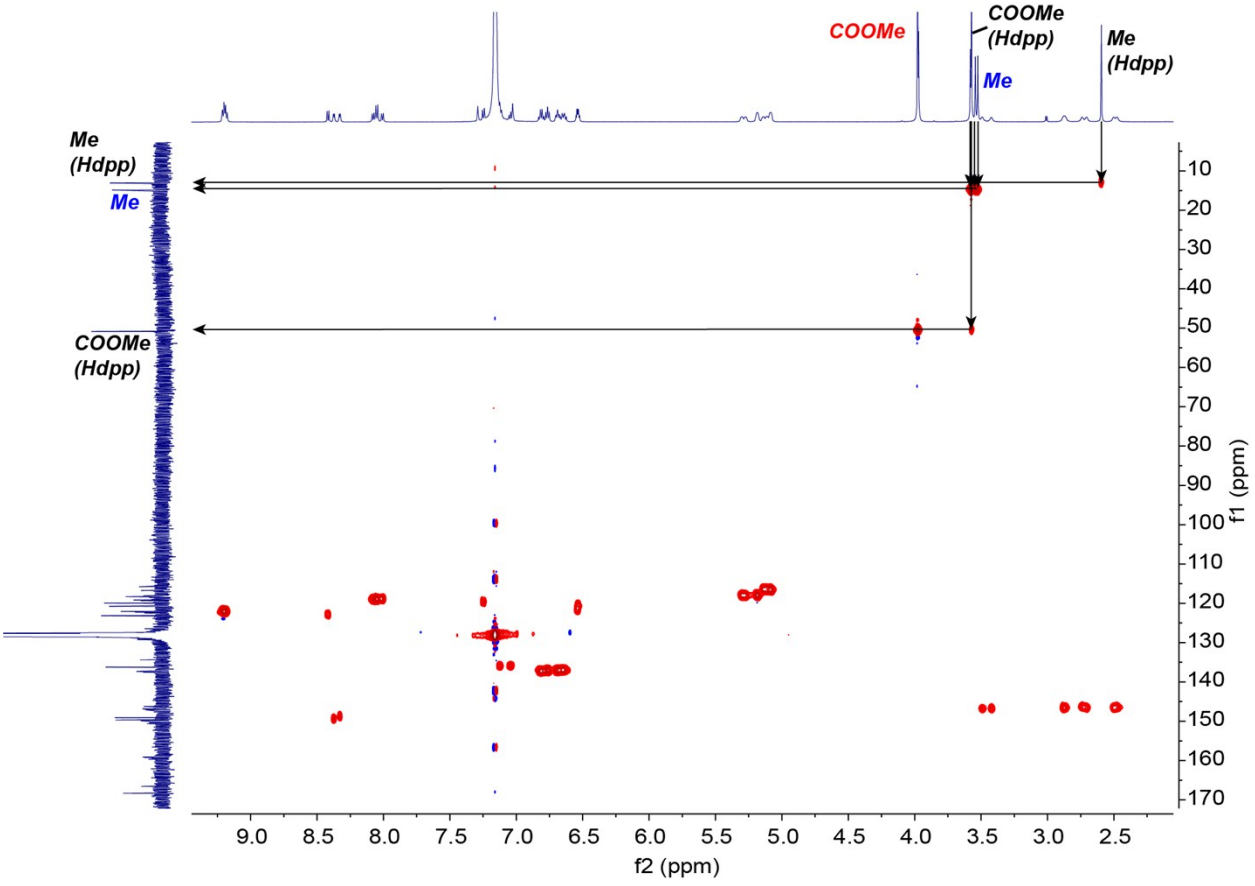

Fig. S18. ^{1}H-^{13}C HSQC NMR (600 MHz, 151 MHz, C_6D_6) spectrum of [Sm(dpp^{CO_2Me,Me})$_3$].

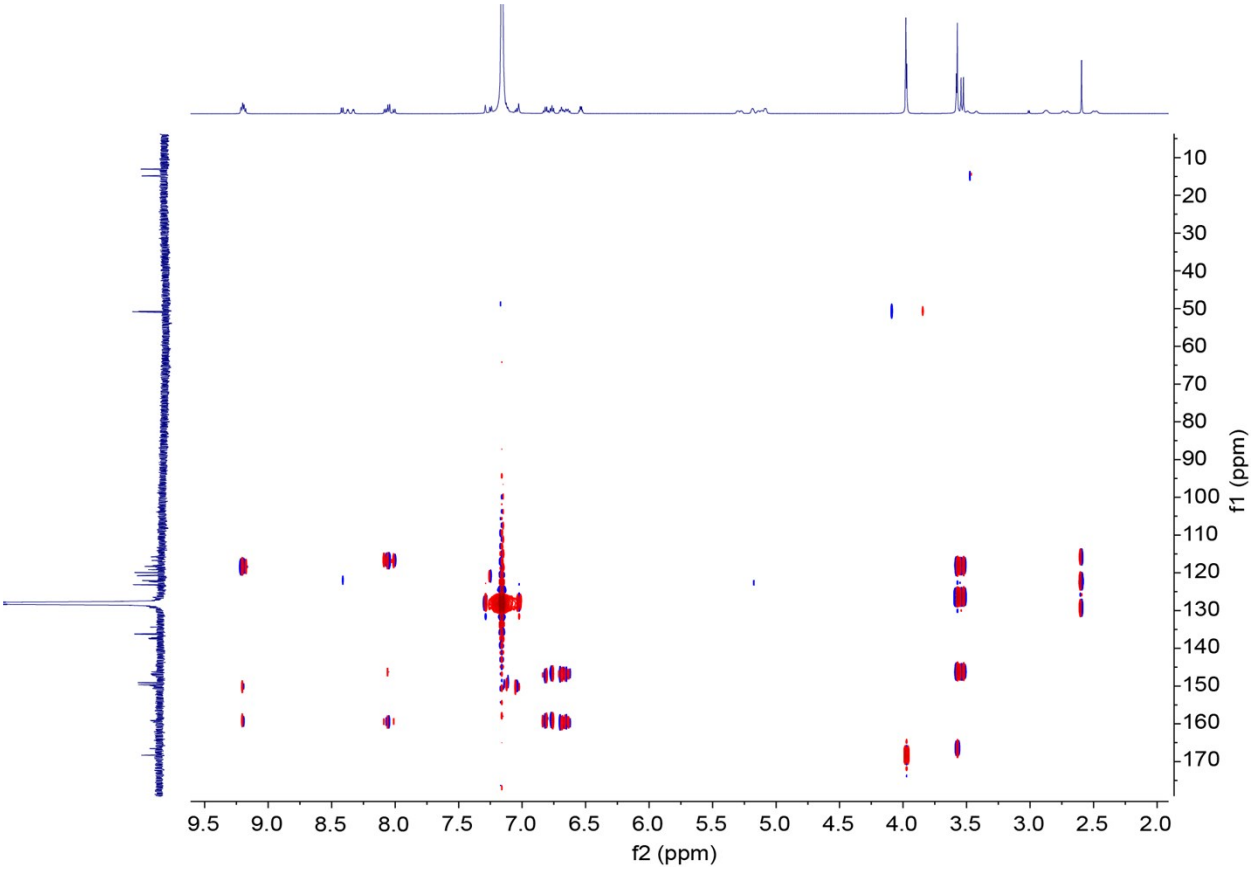

Fig. S19. ^{1}H-^{13}C HMBC NMR (600 MHz, 151 MHz, C_6D_6) spectrum of [Sm(dpp^{CO_2Me,Me})$_3$].

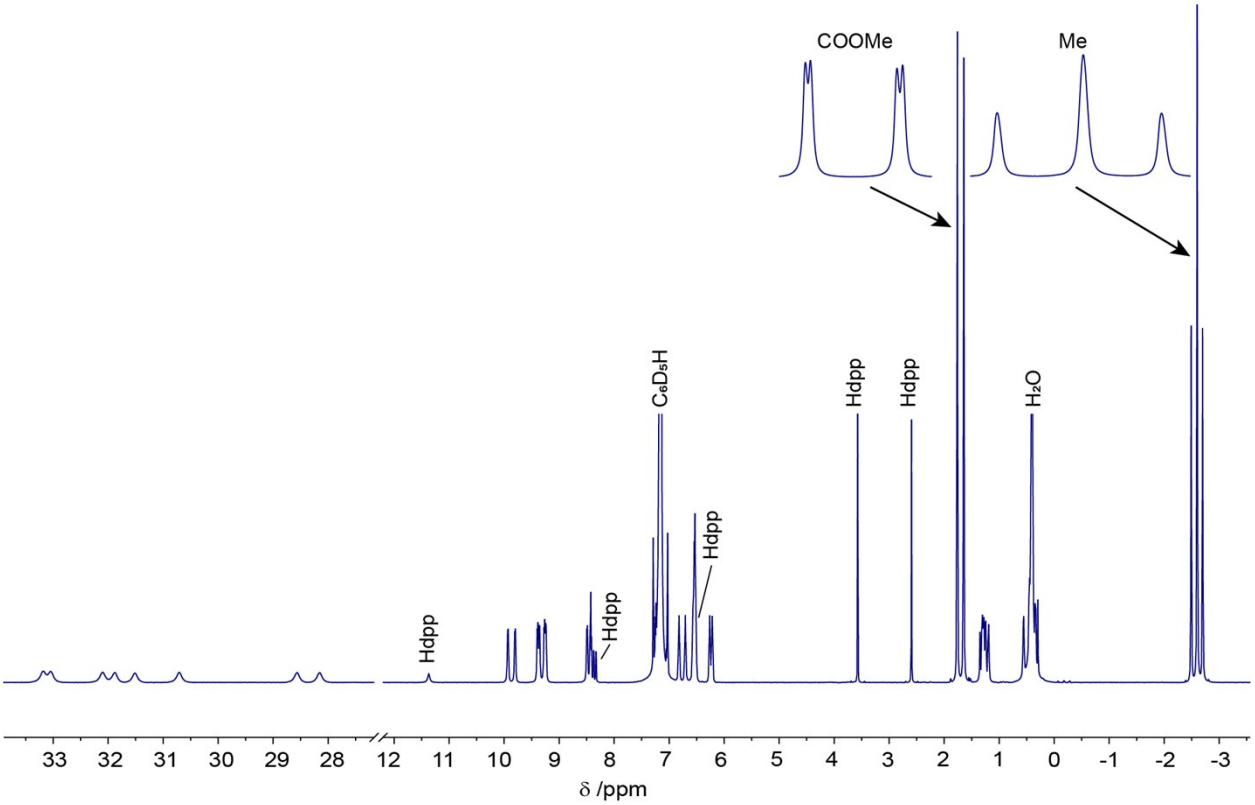

Fig. S20. ^{1}H NMR (400 MHz, C_6D_6) spectrum of [Eu(dpp^{CO_2Me,Me})$_3$].

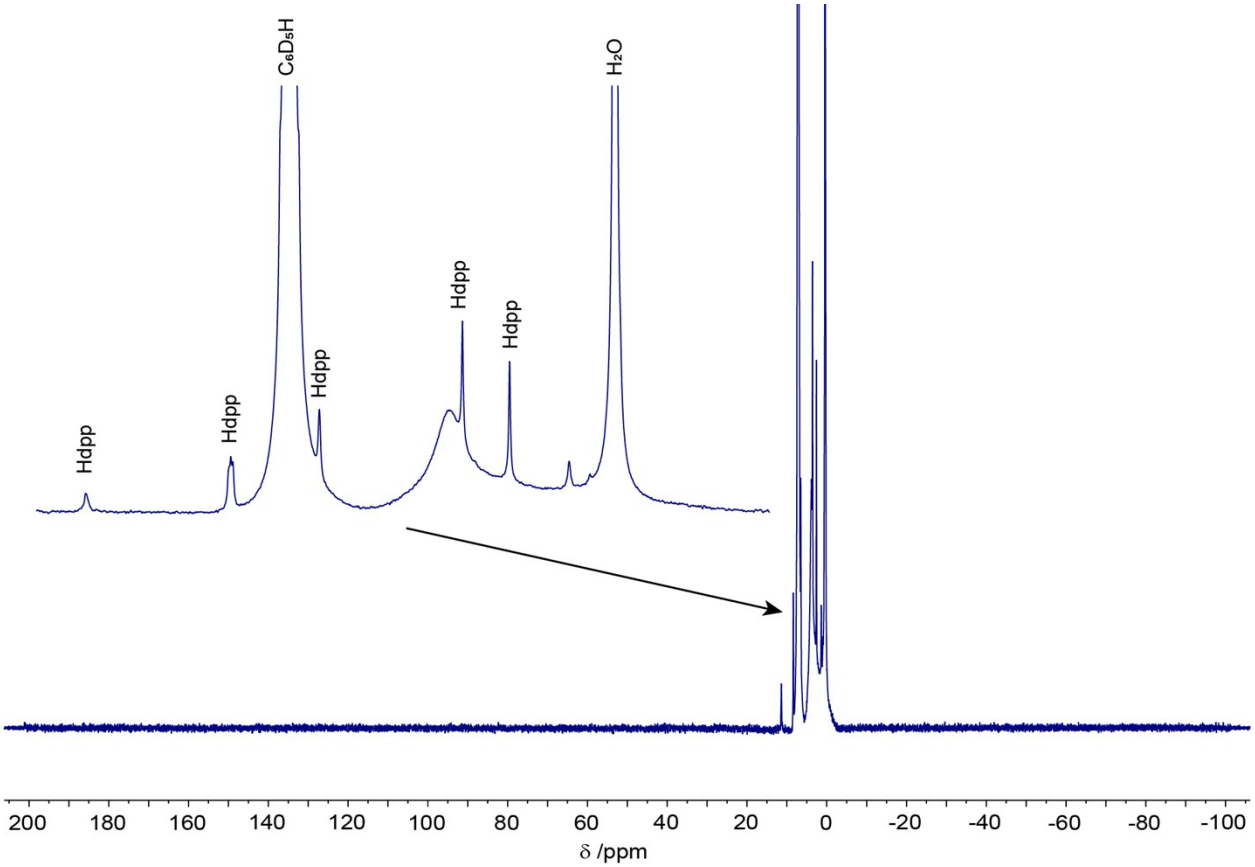

Fig. S21. ^{1}H NMR (400 MHz, C_6D_6) spectrum of [Gd(dpp^{CO_2Me,Me})$_3$].

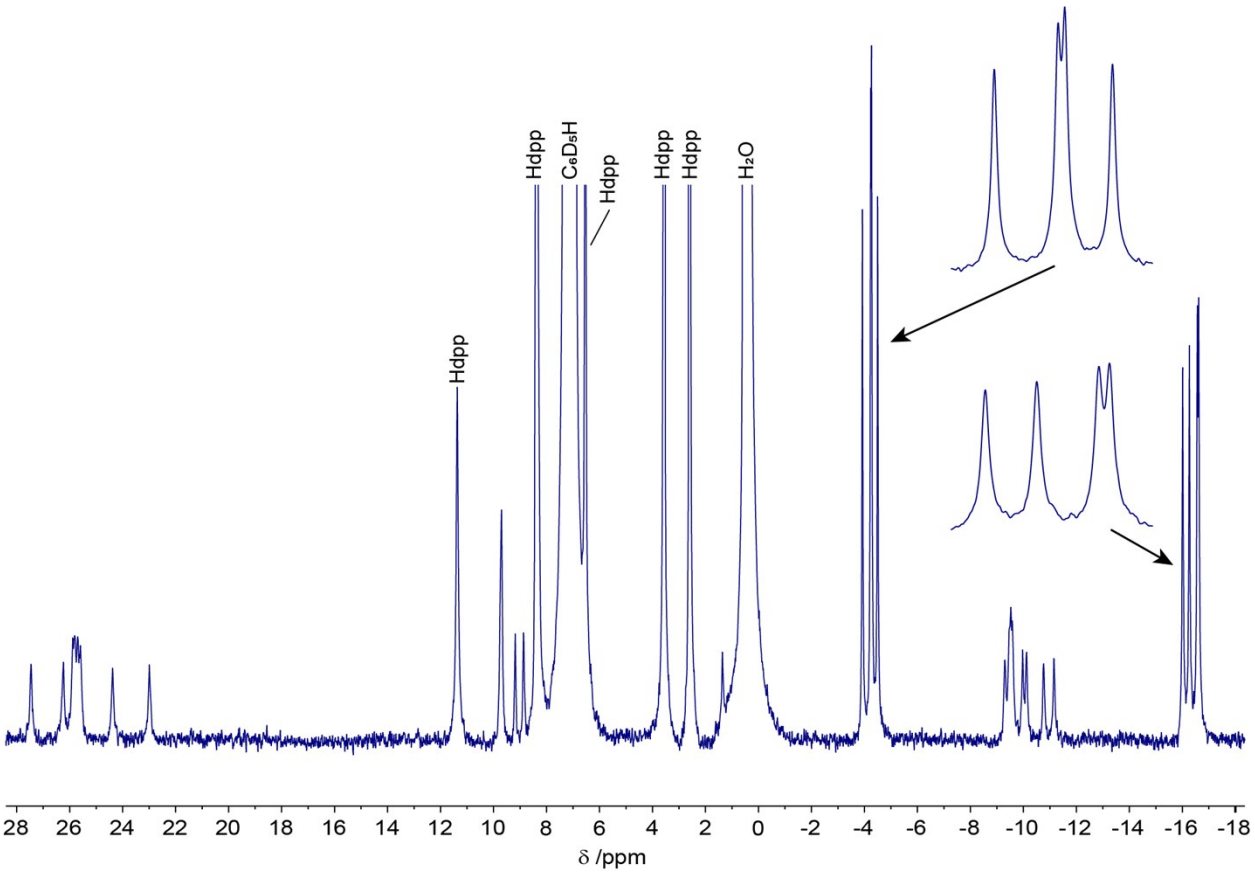

Fig. S22. ^{1}H NMR (400 MHz, C_6D_6) spectrum of [Yb(dpp^{CO_2Me,Me})$_3$].

Mass Spectra

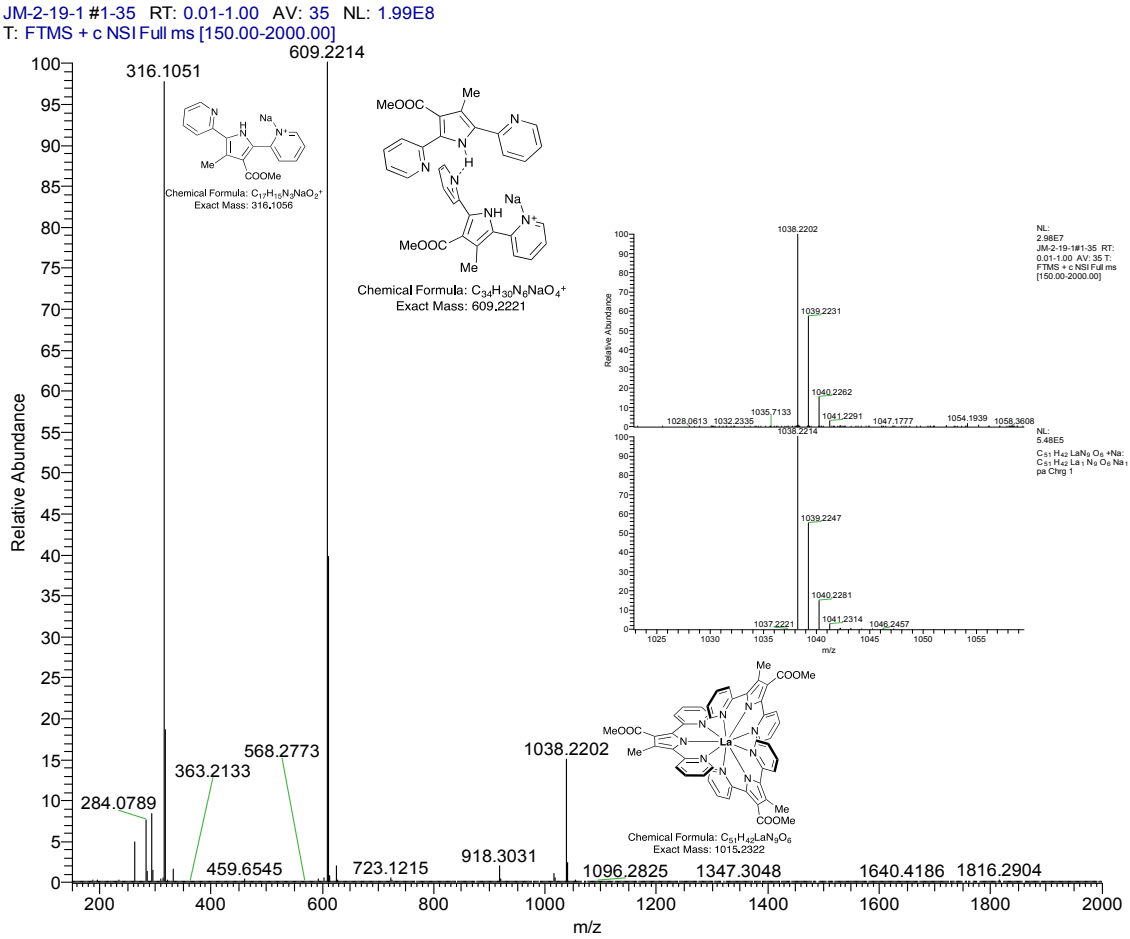

Fig. S23. (+)-HR-NSI-MS of [La(dpp^{CO_2Me,Me})$_3$] in acetonitrile. Shown inset is the observed isotopomers (top) against the simulated isotopic distribution for [La(dpp^{CO_2Me,Me})$_3$ + Na]$^+$.

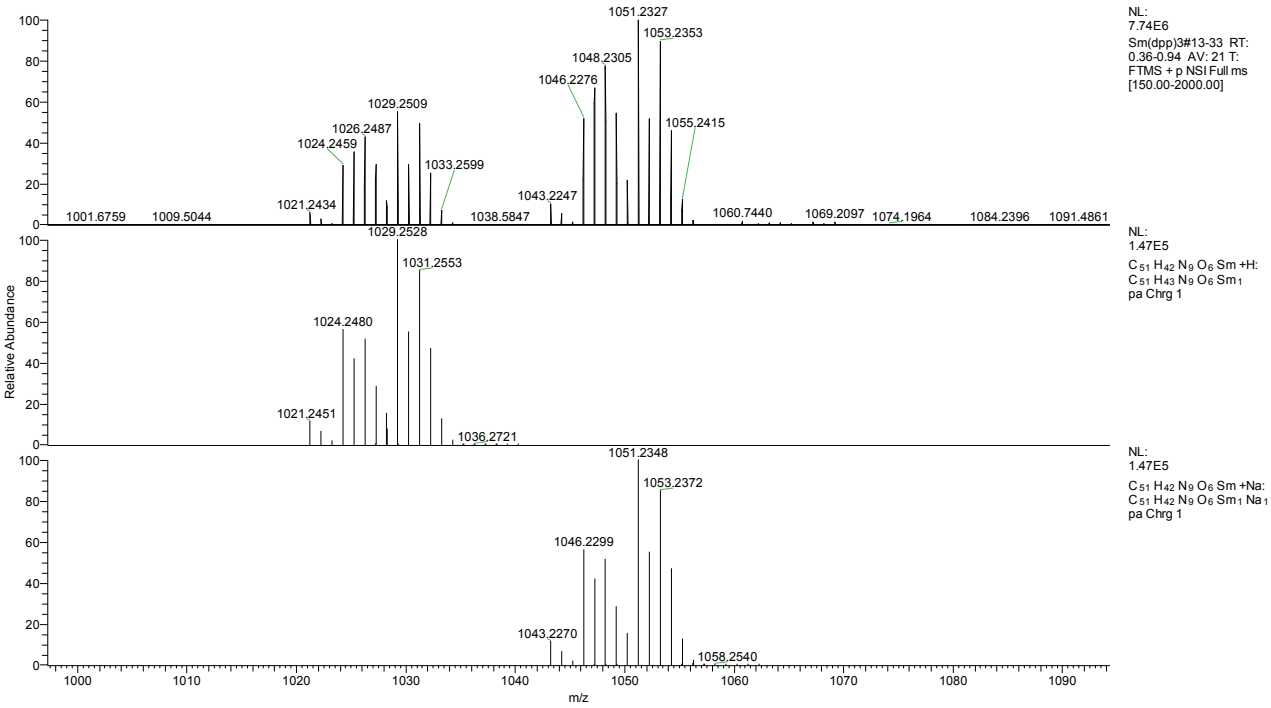

Fig. S24. (+)-HR-NSI-MS of [Sm(dpp^{CO_2Me,Me})$_3$] in acetonitrile (top), against the simulated isotopic distribution for [Sm(dpp^{CO_2Me,Me})$_3$ + H]$^+$ (middle) and [Sm(dpp^{CO_2Me,Me})$_3$ + Na]$^+$ (bottom).

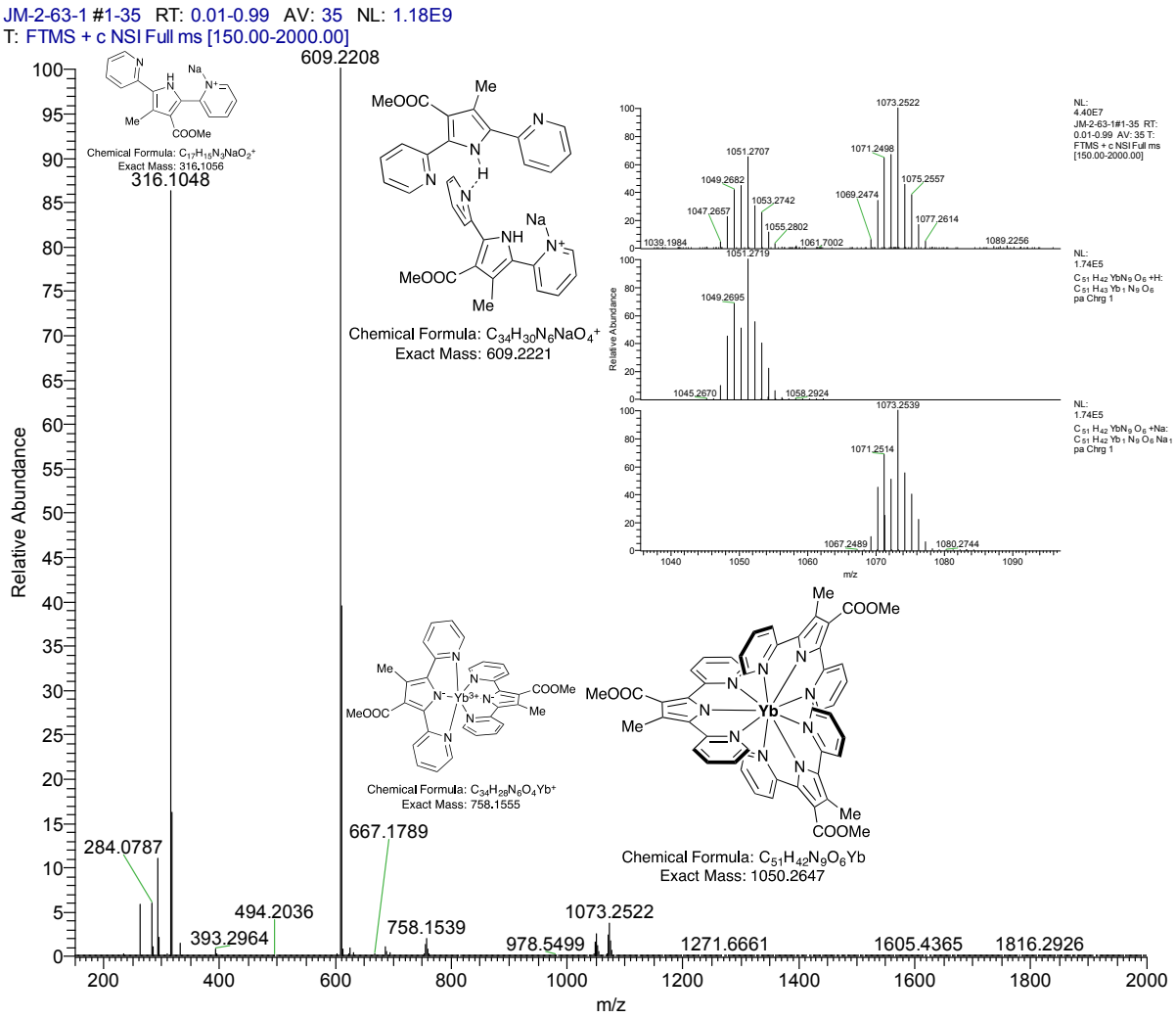

Fig. S25. (+)-HR-NSI-MS of [Yb(dpp^{CO_2Me,Me})$_3$] in acetonitrile. Shown inset is the observed isotopomers (top) against the simulated isotopic distribution for [Yb(dpp^{CO_2Me,Me})$_3$ + H]$^+$ (middle) and for [Yb(dpp^{CO_2Me,Me})$_3$ + Na]$^+$ (bottom).

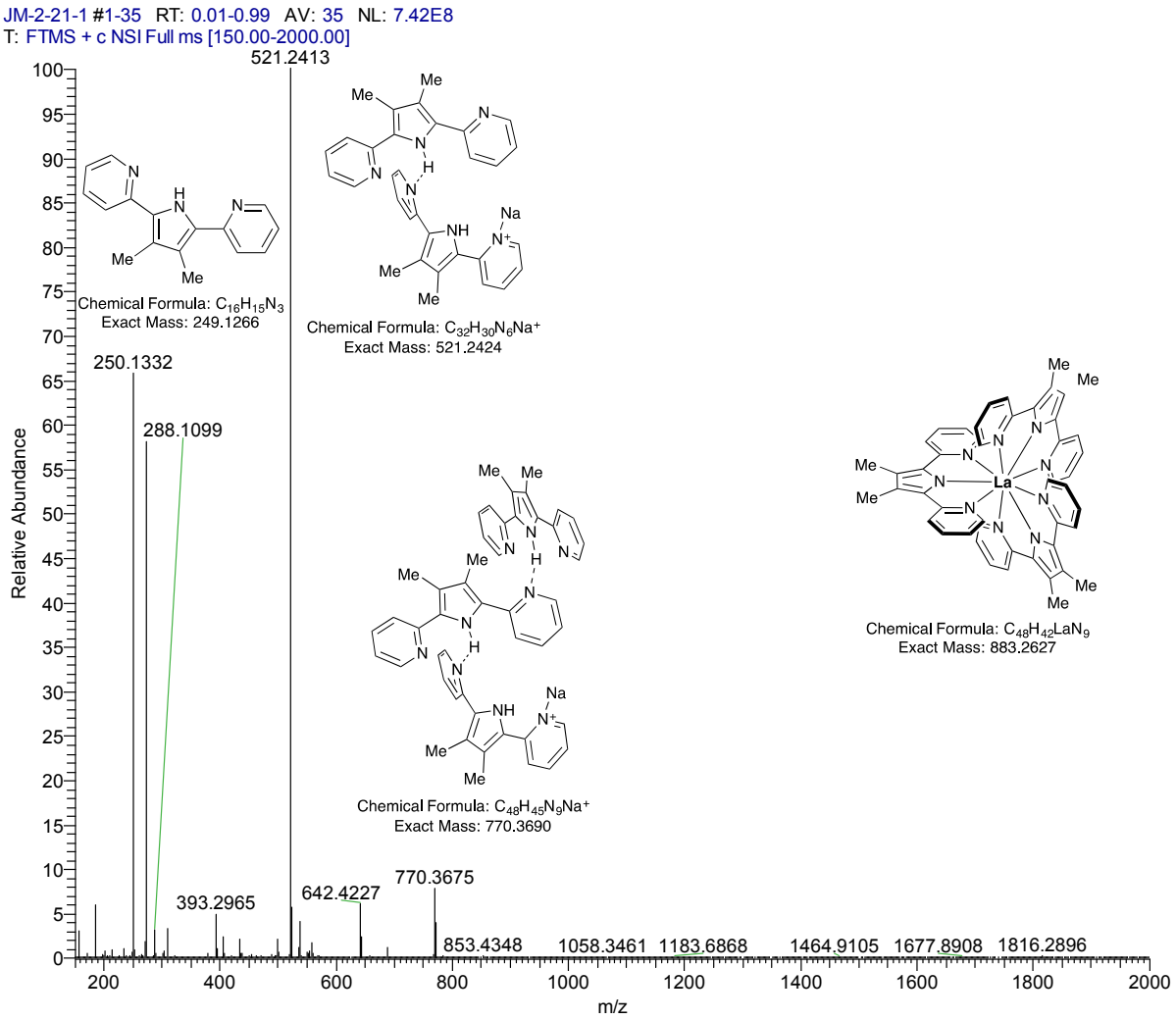

Fig. S26. (+)-HR-NSI-MS of [La(dpp^{Me,Me})$_3$] in acetonitrile.

Photophysical studies

[Eu(dpp)$_3$]:

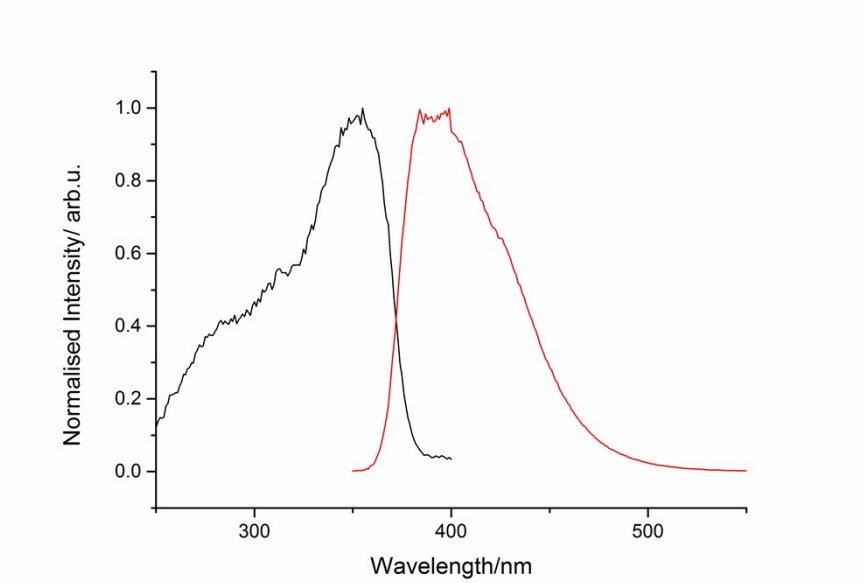

Fig. S27. Normalised excitation (λ_{em} = 612 nm) and emission (λ_{exc} = 300 nm) spectra of [Eu(dpp)$_3$] in CH_2Cl_2 at room temperature.

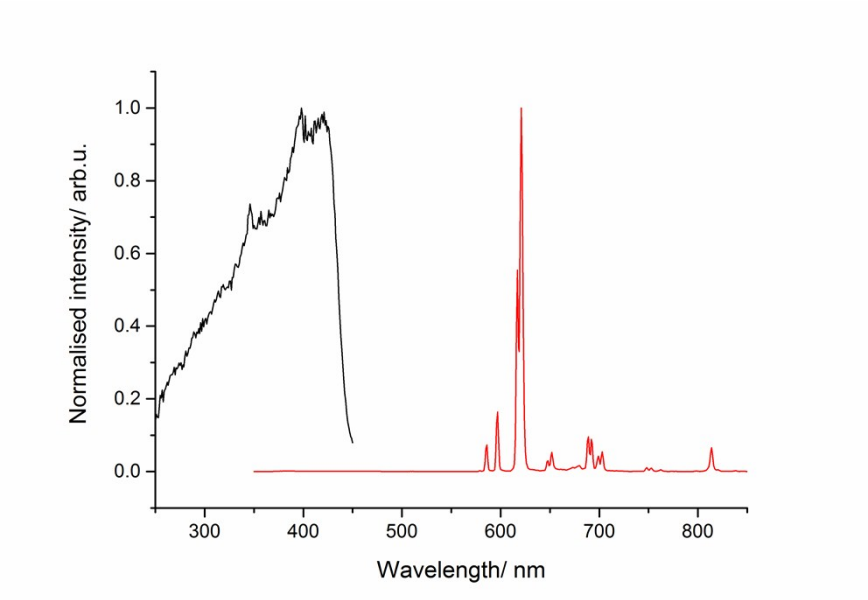

Fig. S28. Normalised excitation (λ_{em} = 612 nm) and emission (λ_{exc} = 300 nm) spectra of [Eu(dpp)$_3$] in CH_2Cl_2 at 77K.

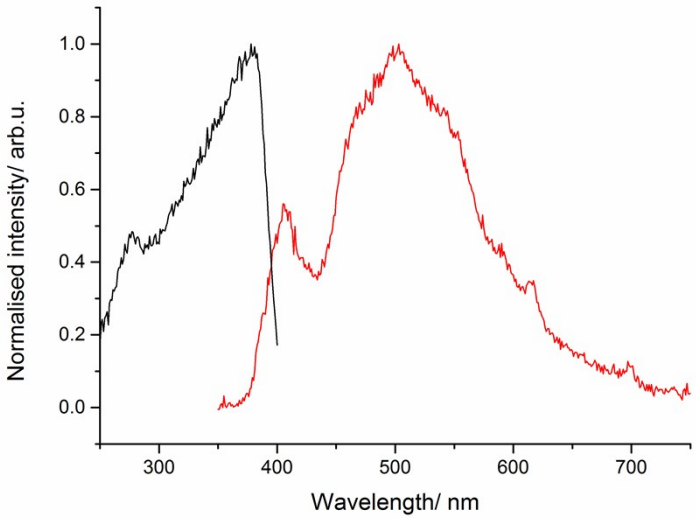

Fig. S29. Normalised excitation (λ_{em} = 612 nm) and emission (λ_{exc} = 300 nm) spectra of [Eu(dpp)$_3$] in the solid state.

[Yb(dpp)$_3$]:

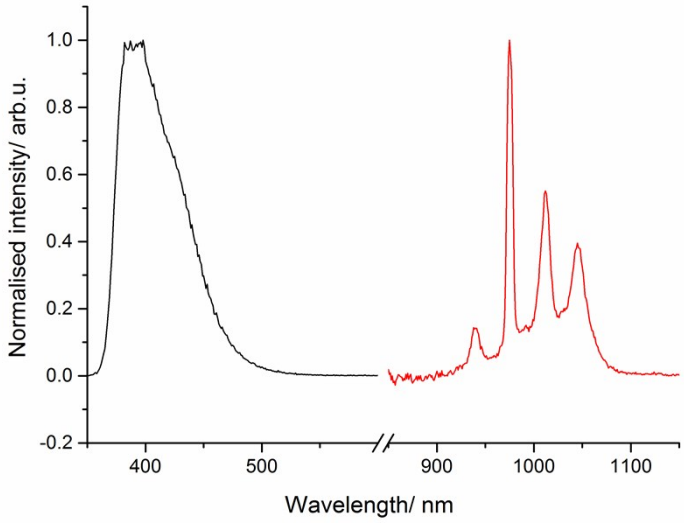

Fig. S30. Normalised excitation (λ_{em} = 980 nm) and emission (λ_{exc} = 300 nm) spectra of [Yb(dpp)$_3$] in CH_2Cl_2 at room temperature.

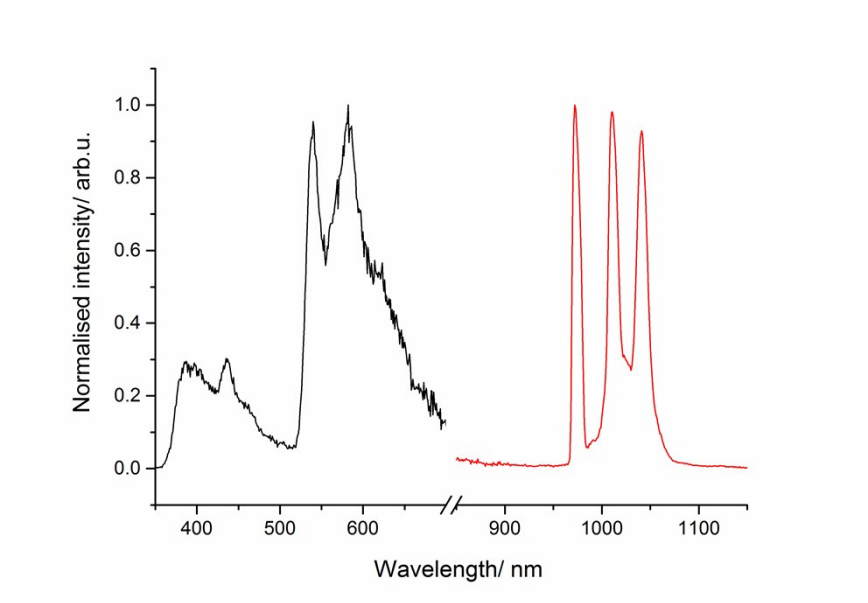

Fig. S31. Normalised excitation (λ_{em} = 980 nm) and emission (λ_{exc} = 300 nm) spectra of [Yb(dpp)$_3$] in CH_2Cl_2 at 77K.

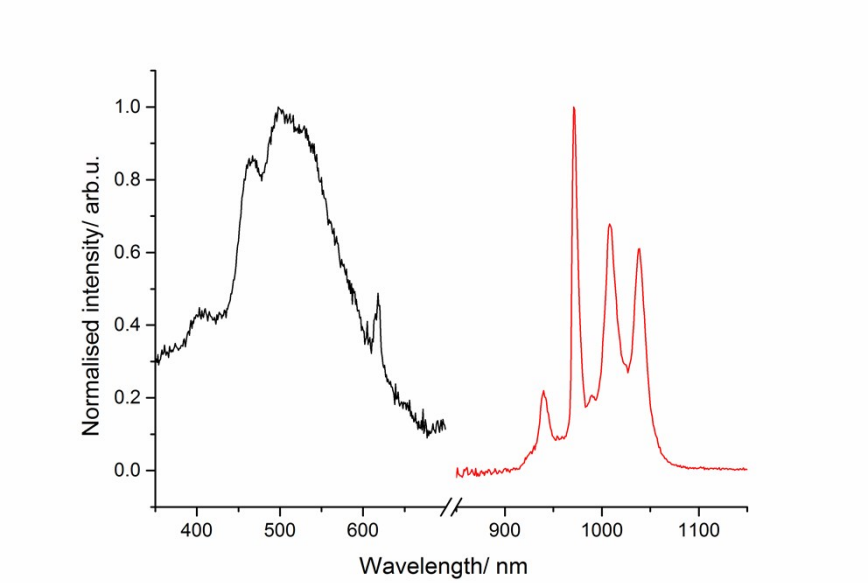

Fig. S32. Normalised excitation (λ_{em} = 980 nm) and emission (λ_{exc} = 300 nm) spectra of [Yb(dpp)$_3$] in the solid state.

Cyclic Voltammetry

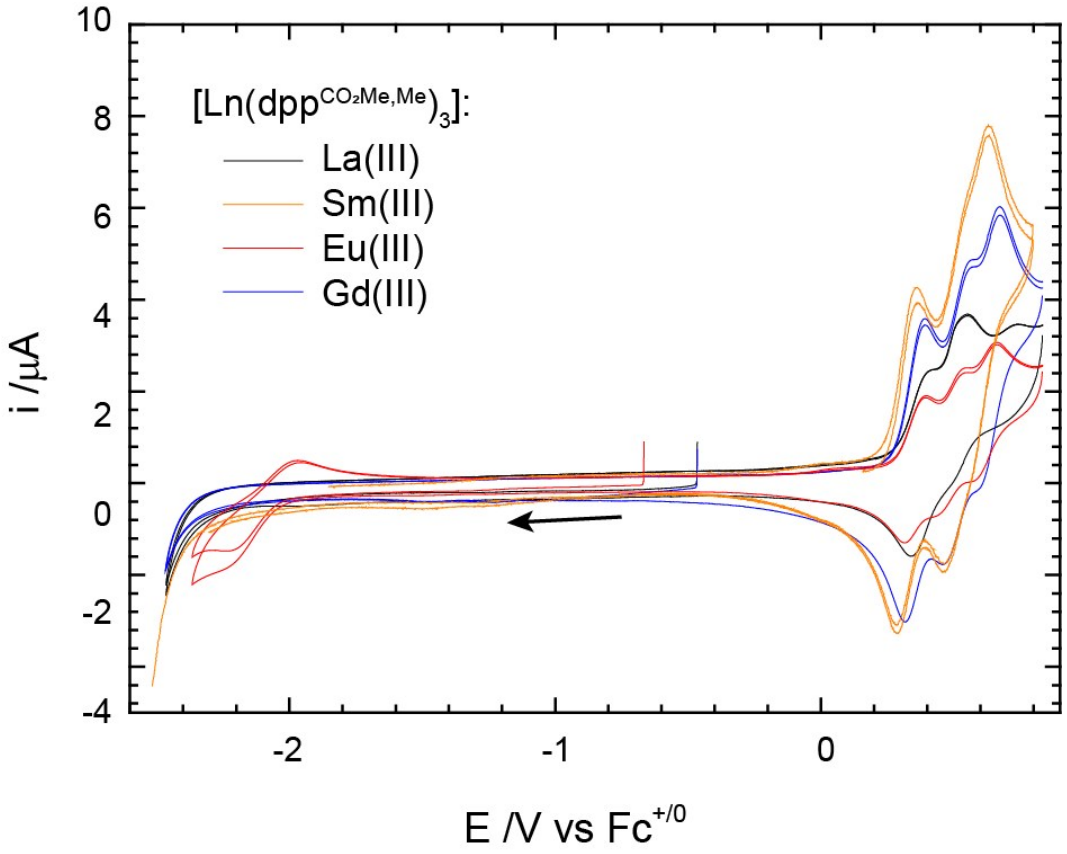

Fig. S33. Overlay of CVs for [Ln(dpp^{CO_2Me,Me})$_3$] (Ln = La(III), black trace; Sm(III), orange trace; Eu(III), red trace; and Gd(III), blue trace).

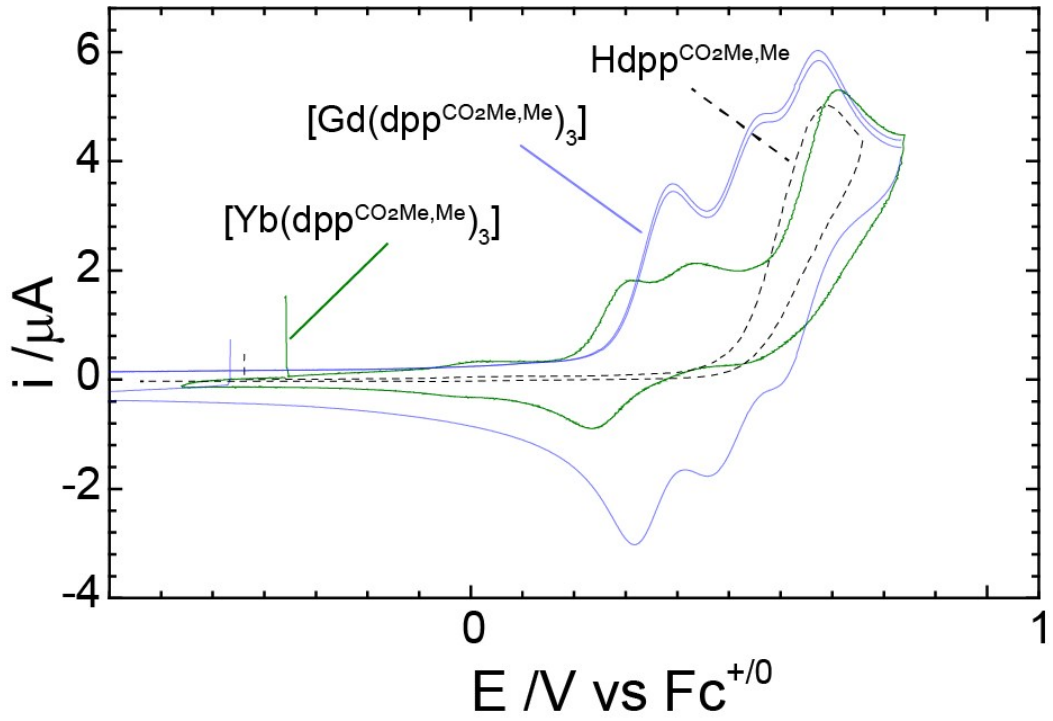

Fig. S34. CV of [Yb(dpp^{CO_2Me,Me})$_3$] (green trace) overlayed onto those for [Gd(dpp^{COOMe,Me})$_3$] (transparent blue trace) and Hdpp^{COOMe,Me} (dashed black trace).