Electronic Supplementary Information (ESI)

Substantial luminescence enhancement in ternary europium complexes by coordination of different ionic ligands

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Excitation Spectra

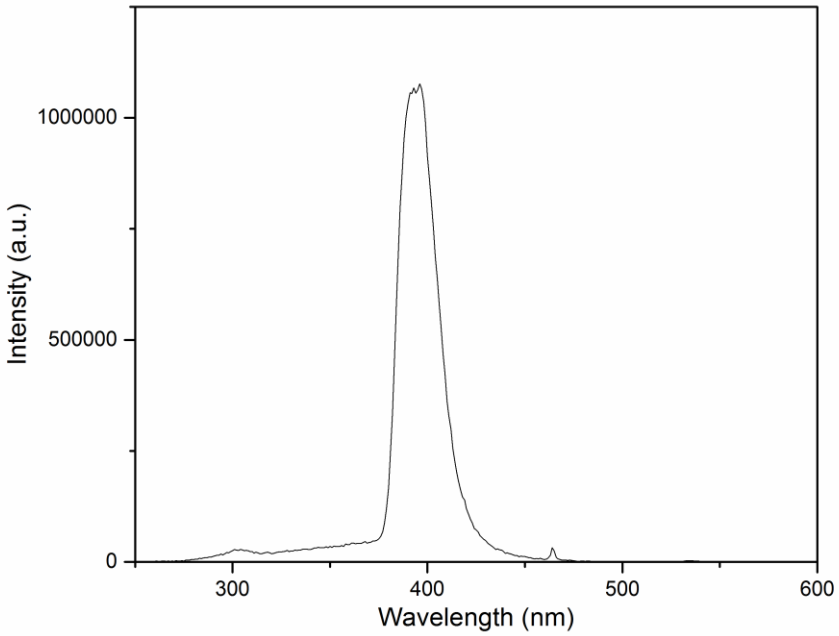


Figure S1. Excitation spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.

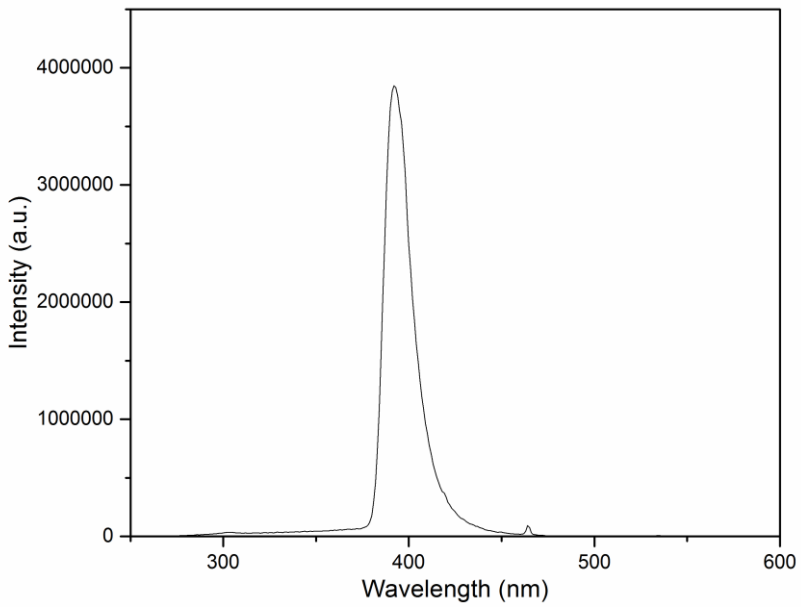


Figure S2. Excitation spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.

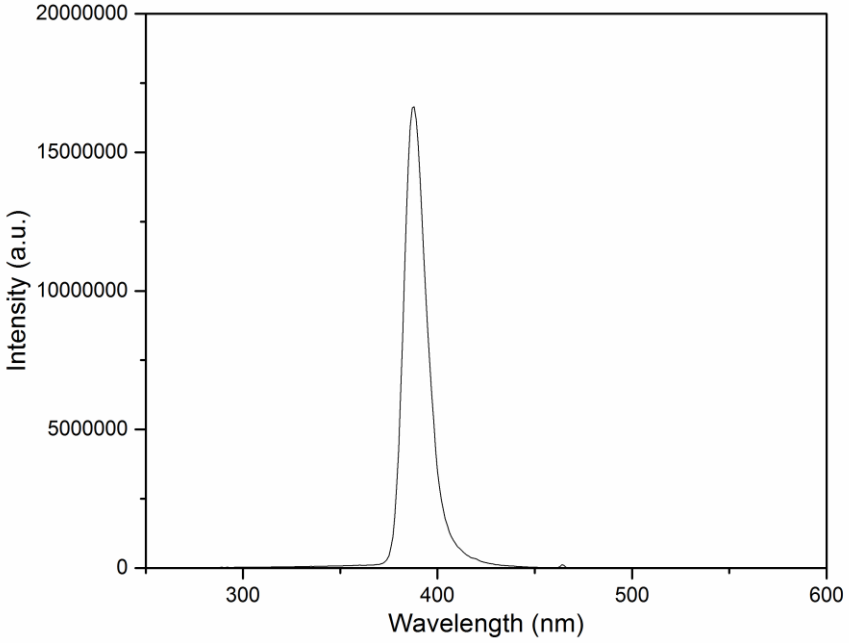


Figure S3. Excitation spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.

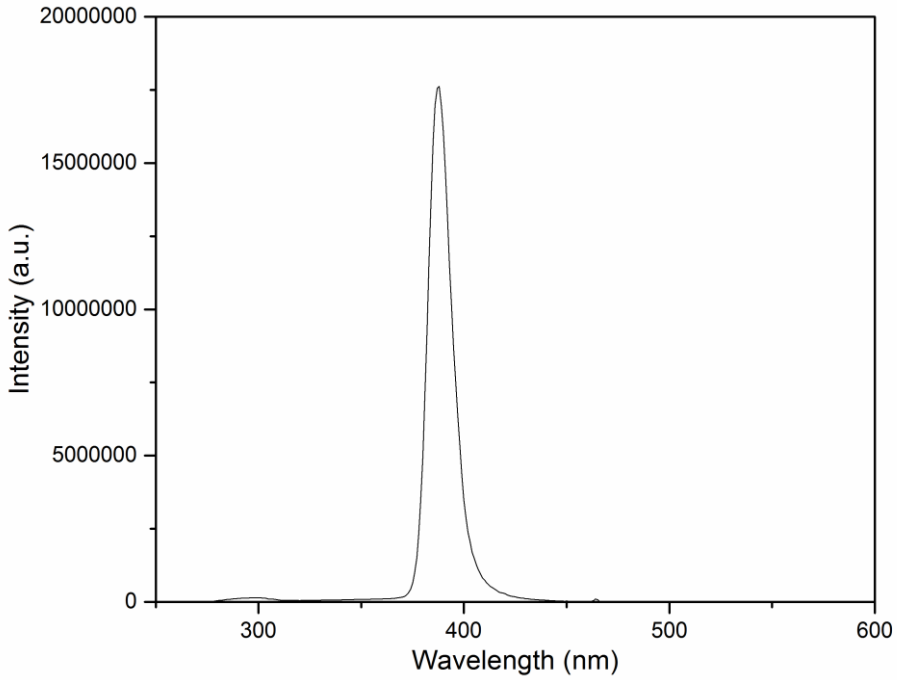


Figure S4. Excitation spectrum of $Eu(TTA)_2(BTFA)(TPPO)_2$.

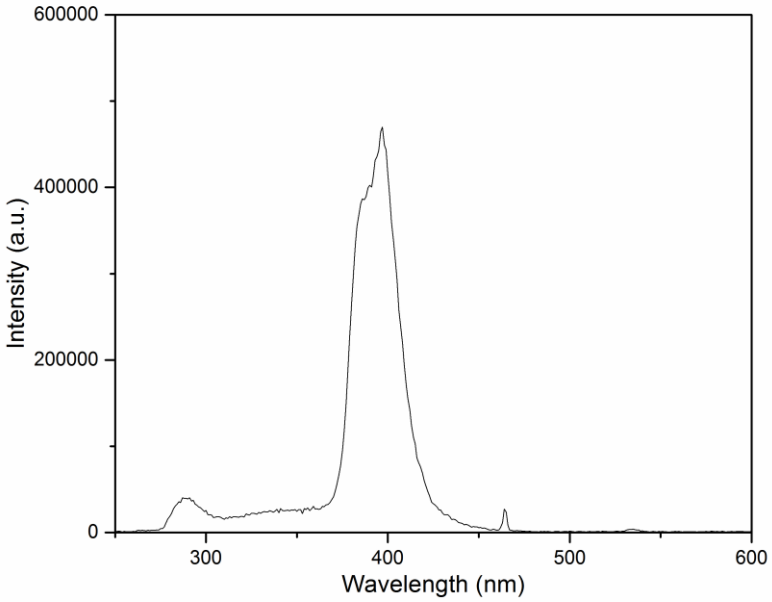


Figure S5. Excitation spectrum of $Eu(DBM)_2(BTFA)(TPPO)_2$.

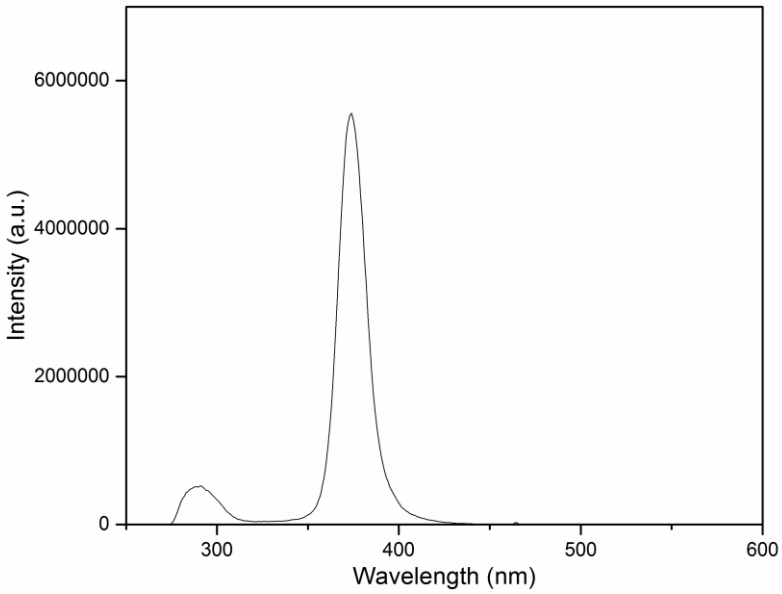


Figure S6. Excitation spectrum of $Eu(BTFA)_2(DBM)(TPPO)_2$**.**

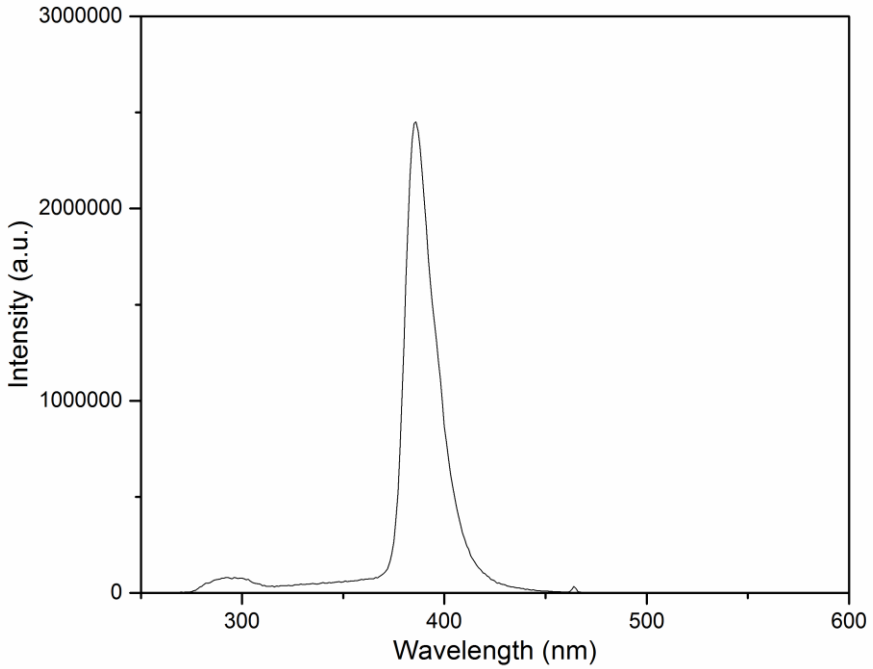


Figure S7. Excitation spectrum of Eu(DBM)(BTFA)(TTA)$(TPPO)_2$.

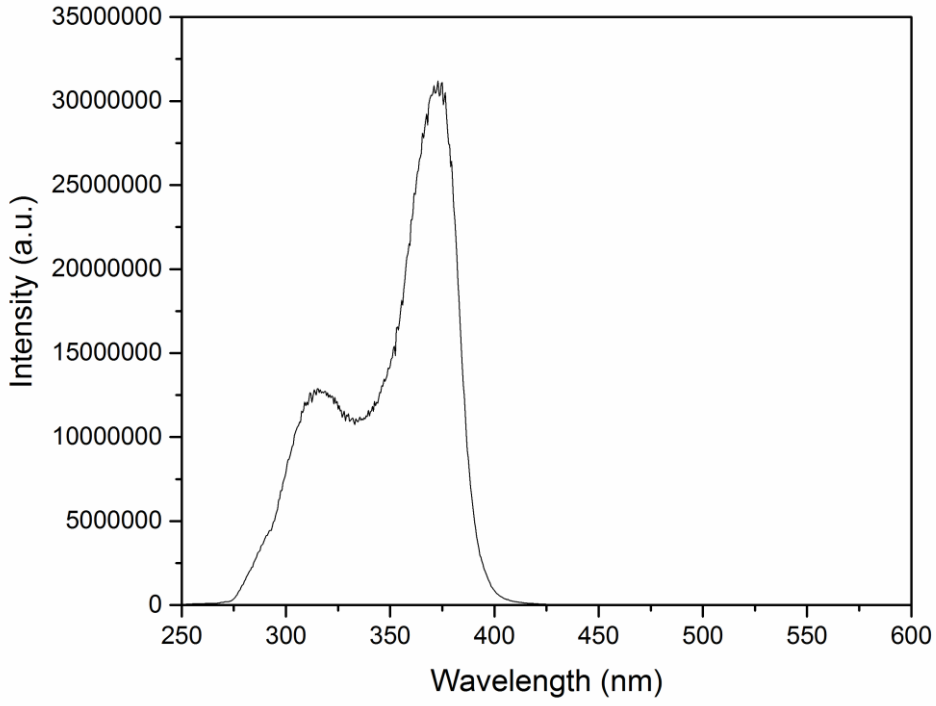


Figure S8. Excitation spectrum of Eu(DBM)(BTFA)(TTA)(PHEN).

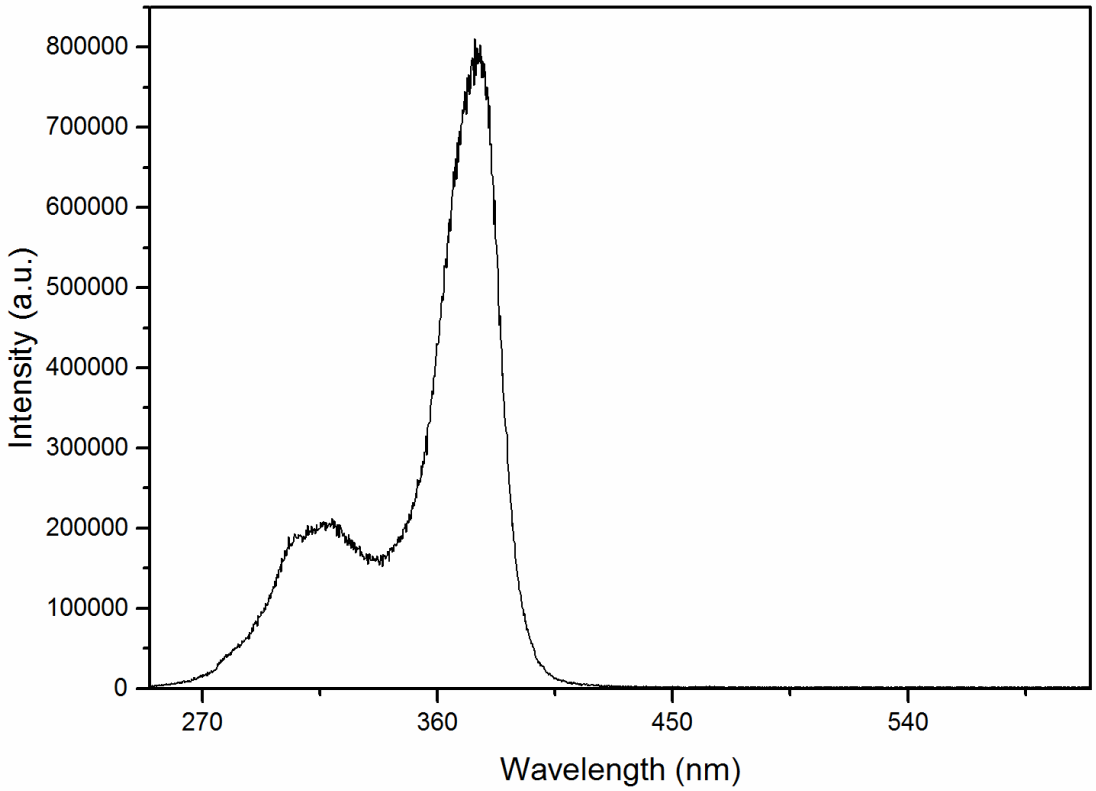


Figure S9. Excitation spectrum of Eu(DBM)(BTFA)(TTA)(BIPY).

Emission Spectra

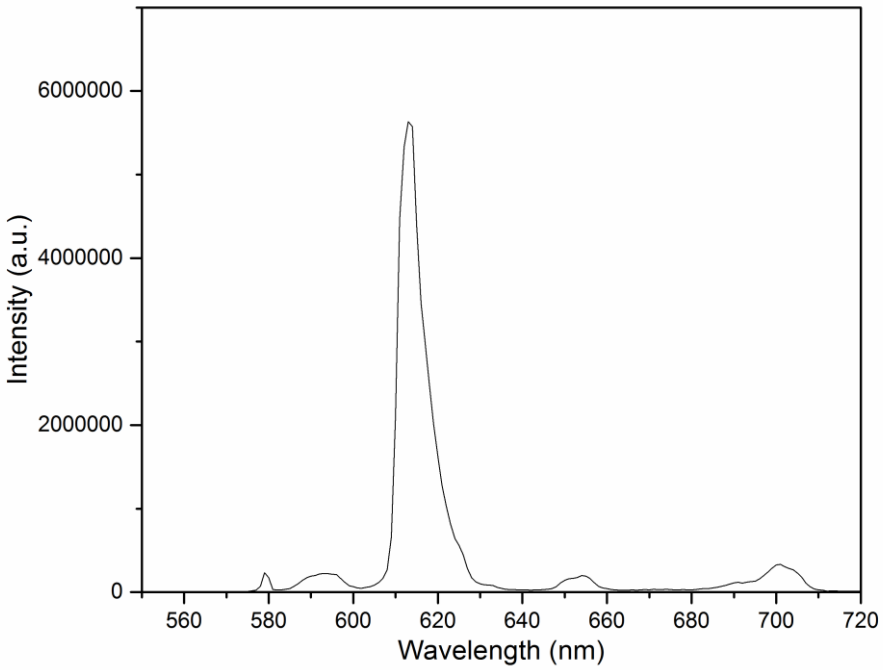


Figure S10. Emission spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.

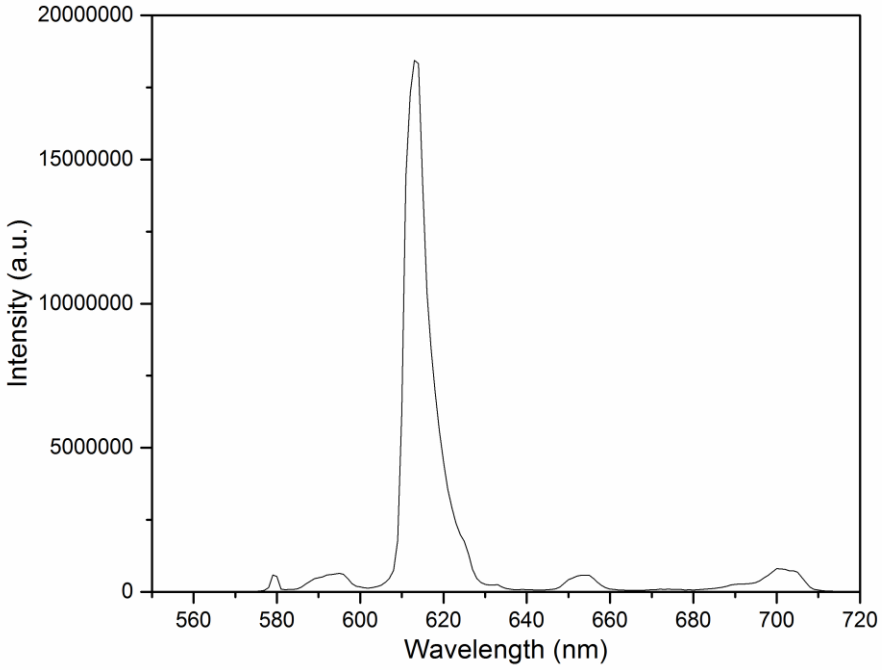


Figure S11. Emission spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.

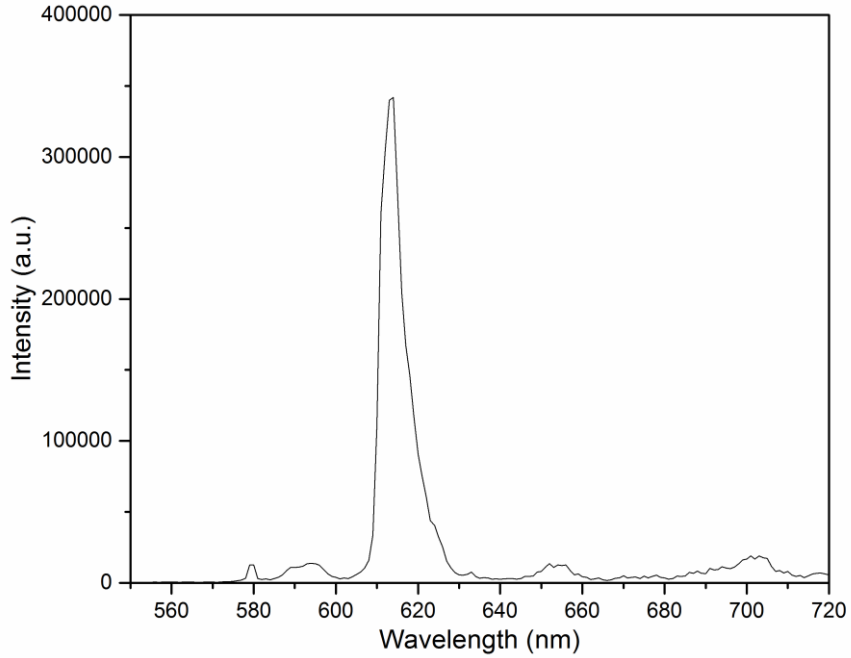


Figure S12. Emission spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.

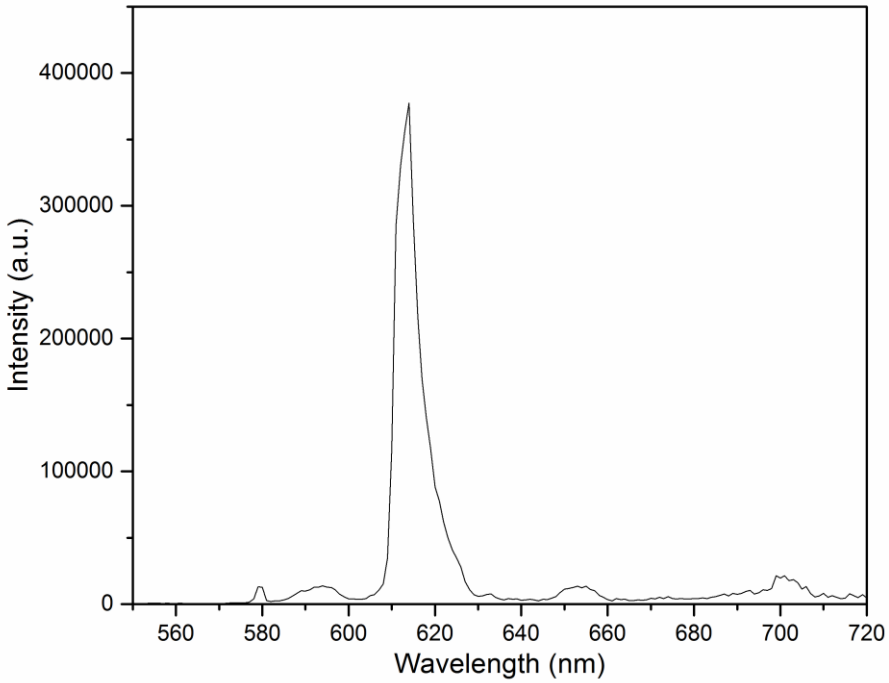


Figure S13. Emission spectrum of $Eu(TTA)_2(BTFA)(TPPO)_2$.

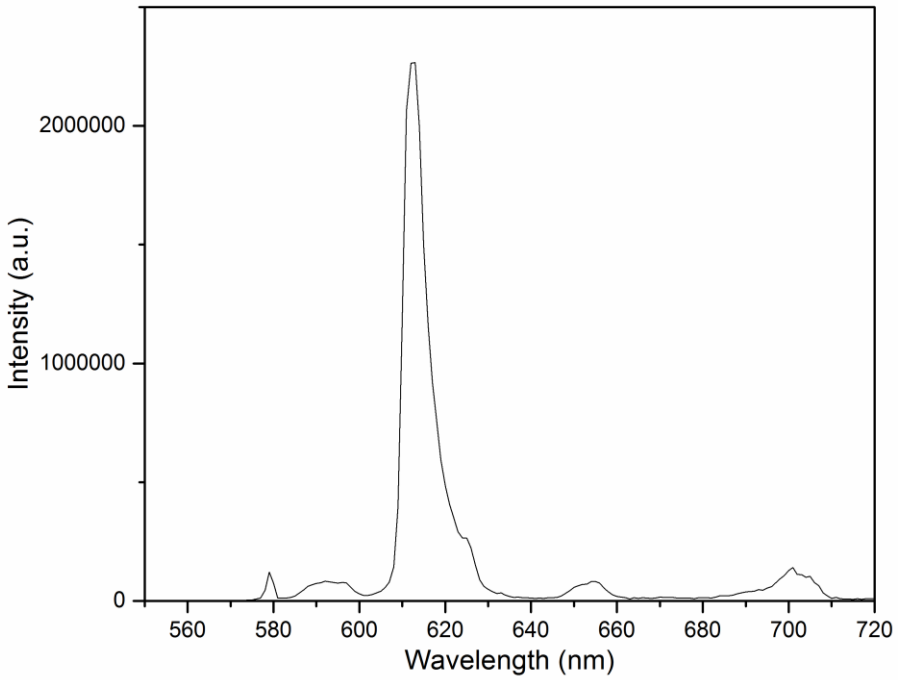


Figure S14. Emission spectrum of $Eu(DBM)_2(BTFA)(TPPO)_2$.

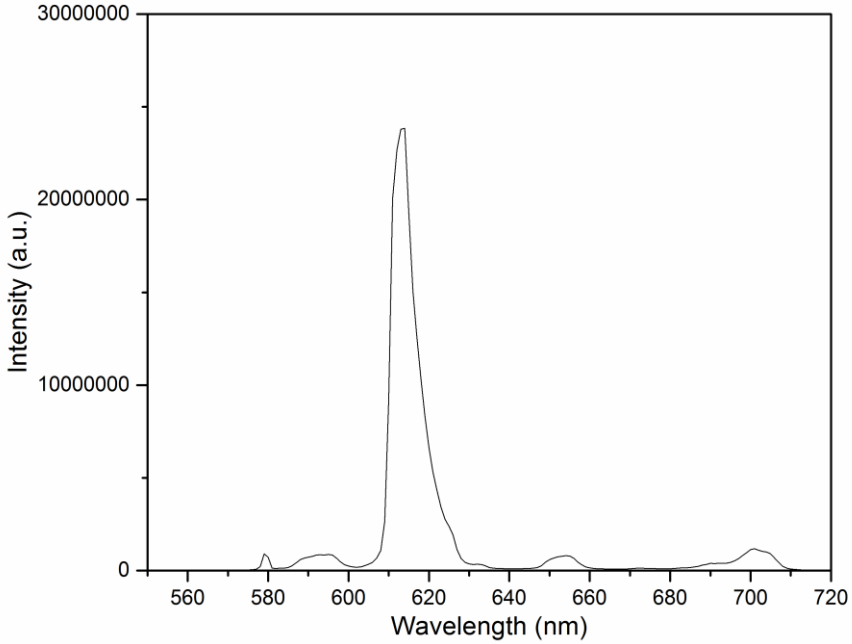


Figure S15. Emission spectrum of $Eu(BTFA)_2(DBM)(TPPO)_2$**.**

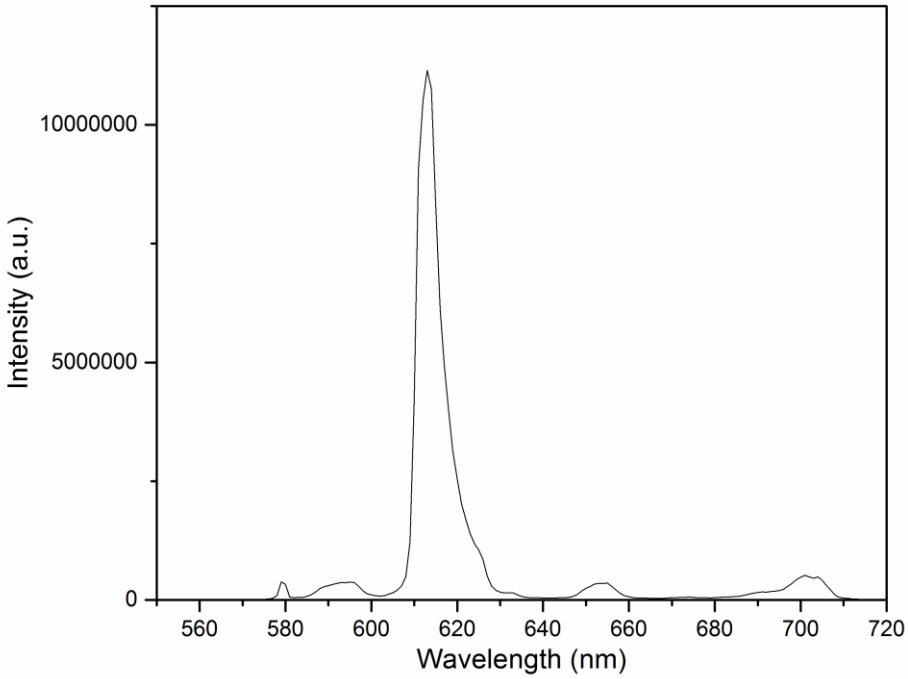


Figure S16. Emission spectrum of Eu(DBM)(BTFA)(TTA)$(TPPO)_2$.

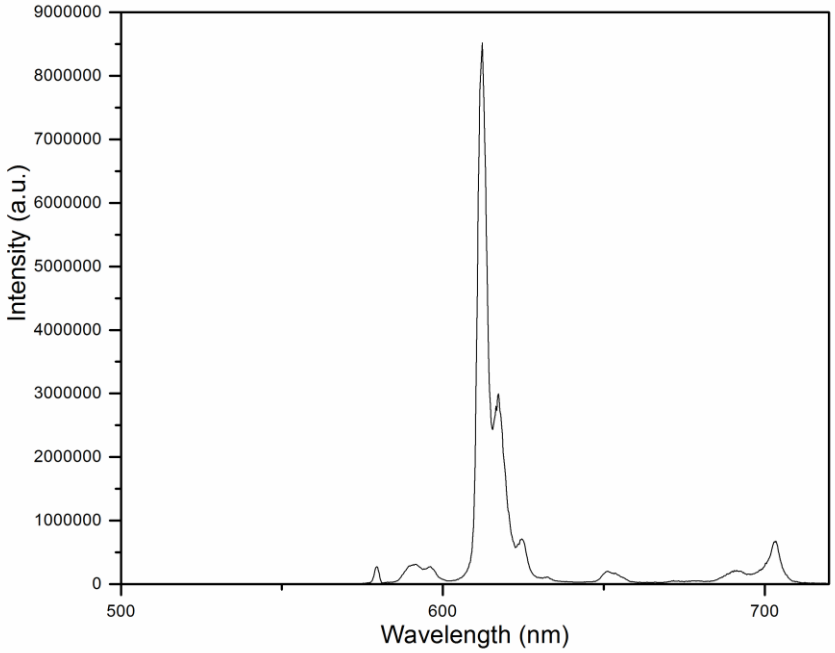


Figure S17. Emission spectrum of Eu(DBM)(BTFA)(TTA)(PHEN).

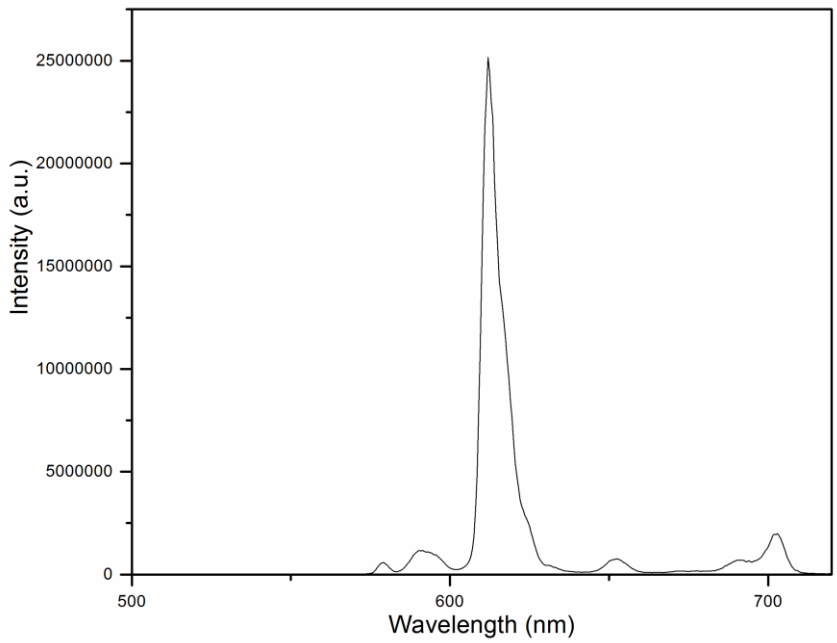


Figure S18. Emission spectrum of Eu(DBM)(BTFA)(TTA)(BIPY).

Lifetime Curves

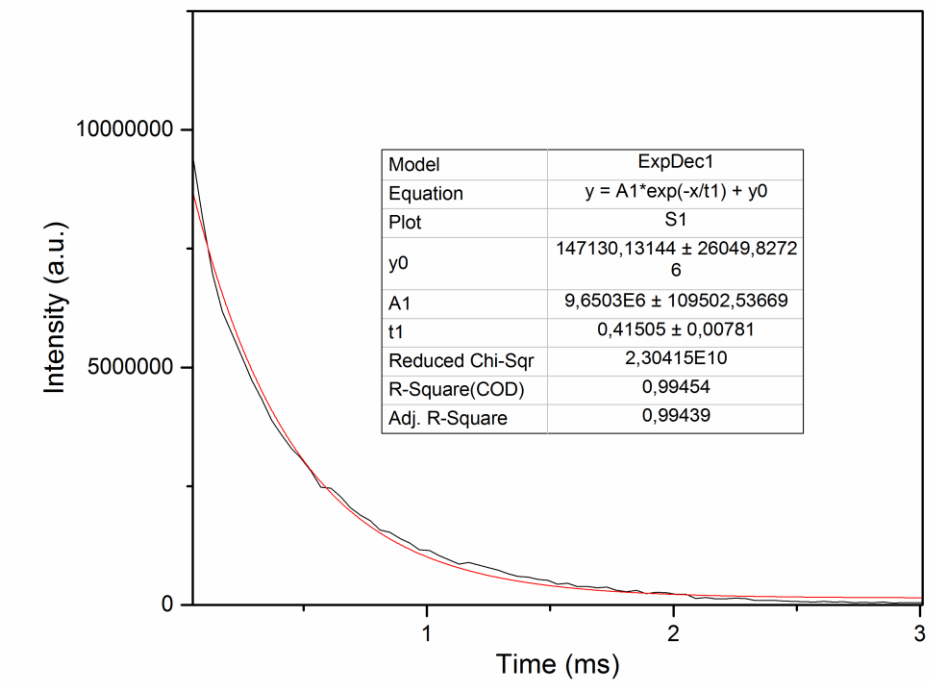


Figure S19. Lifetime curve of $Eu(DBM)_2(TTA)(TPPO)_2$**.**

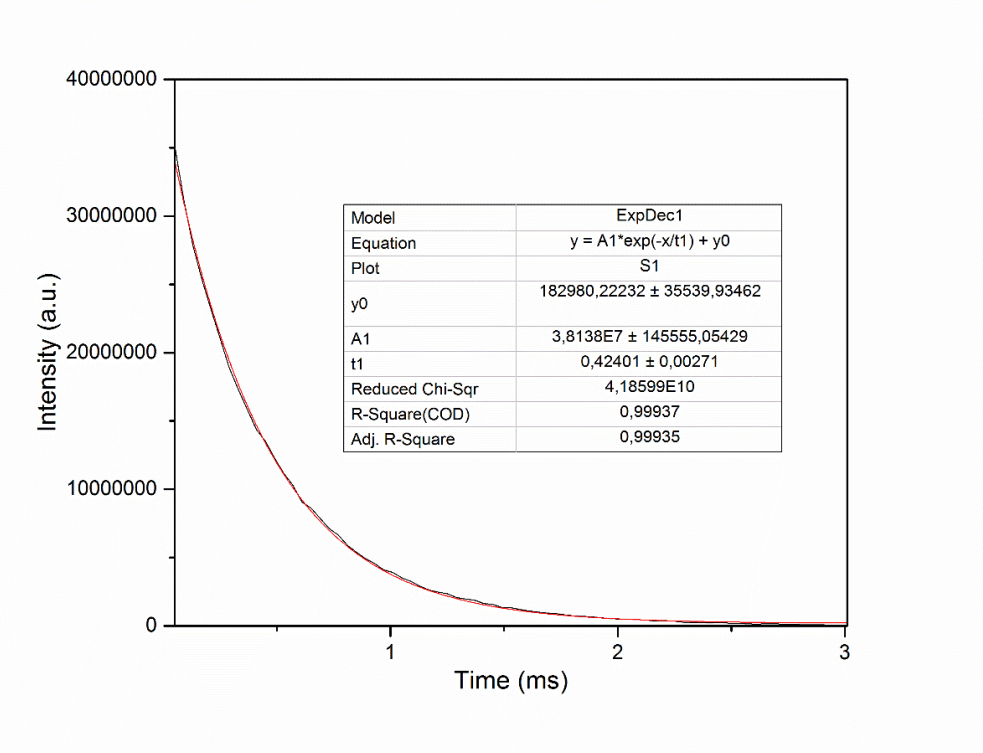


Figure S20. Lifetime curve of $Eu(TTA)_2(DBM)(TPPO)_2$.

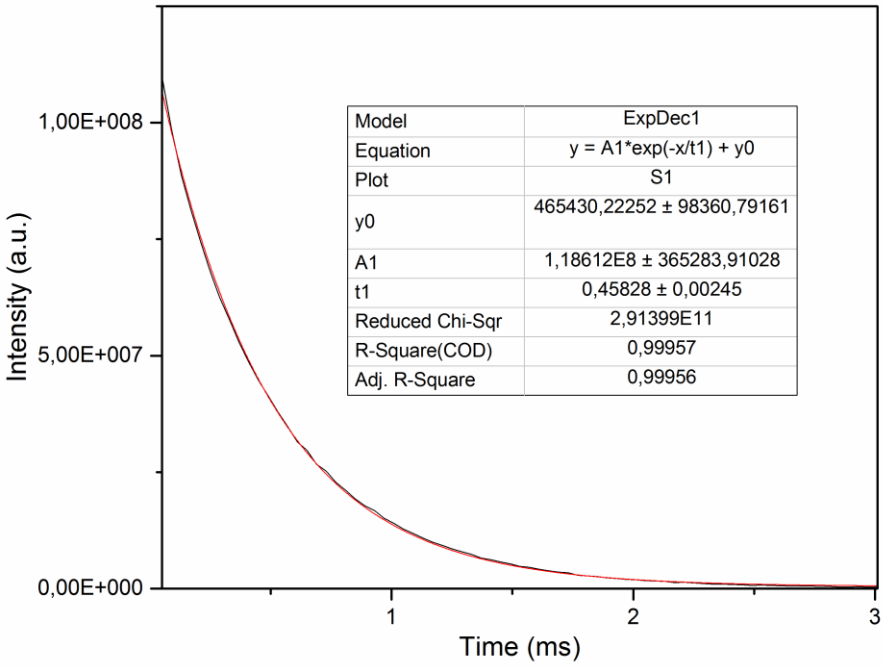


Figure S21. Lifetime curve of $Eu(BTFA)_2(TTA)(TPPO)_2$.

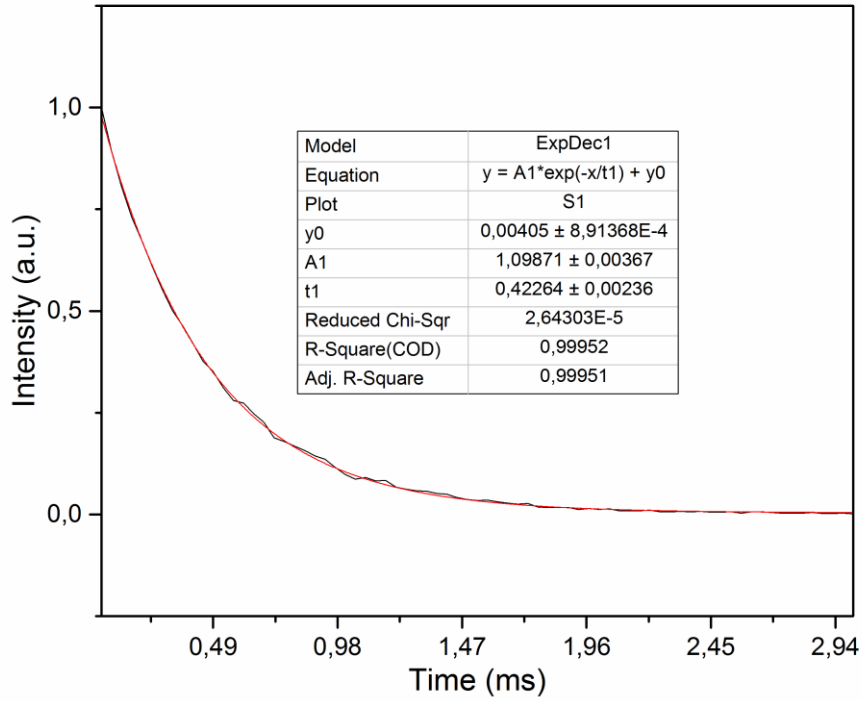


Figure S22. Lifetime curve of $Eu(DBM)_2(BTFA)(TPPO)_2$.

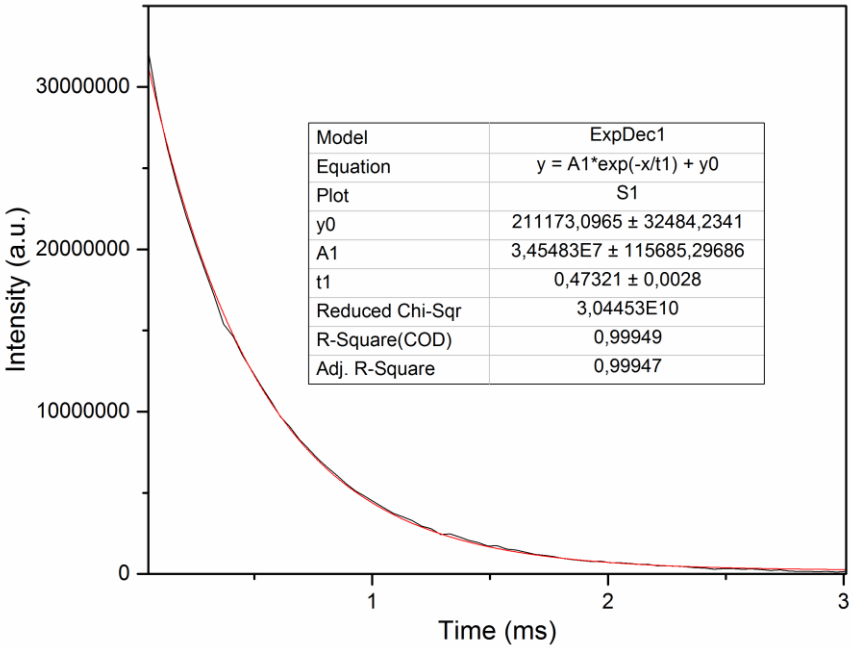


Figure S23. Lifetime curve of $Eu(BTFA)_2(DBM)(TPPO)_2$**.**

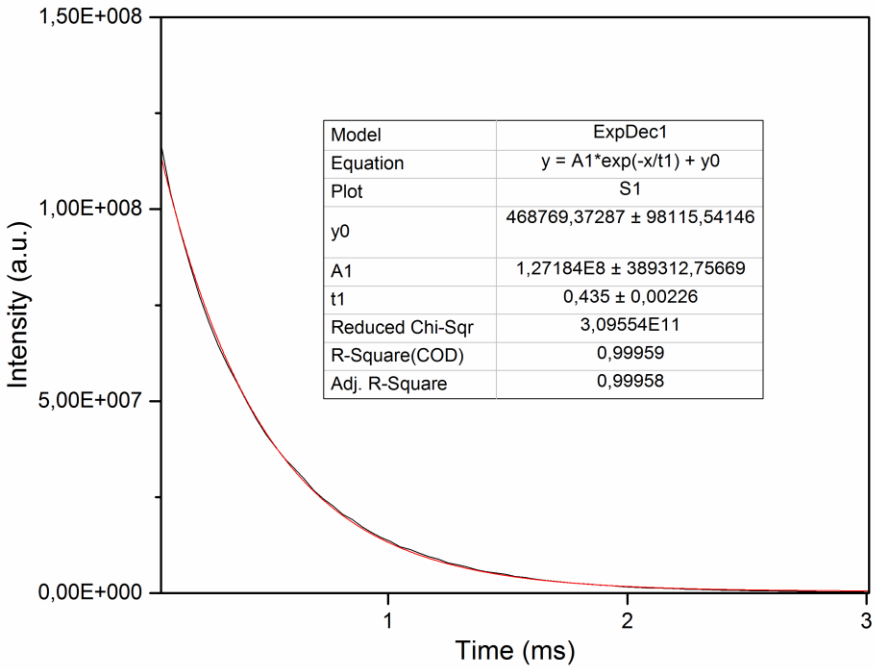


Figure S24. Lifetime curve of $Eu(TTA)_2(BTFA)(TPPO)_2$.

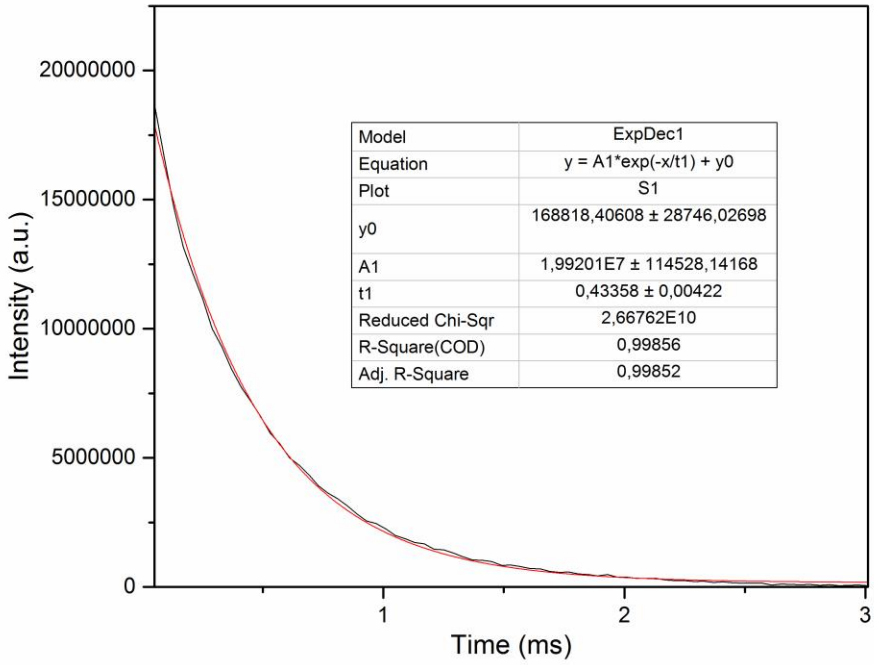


Figure S25. Lifetime curve of Eu(DBM)(BTFA)(TTA)$(TPPO)_2$.

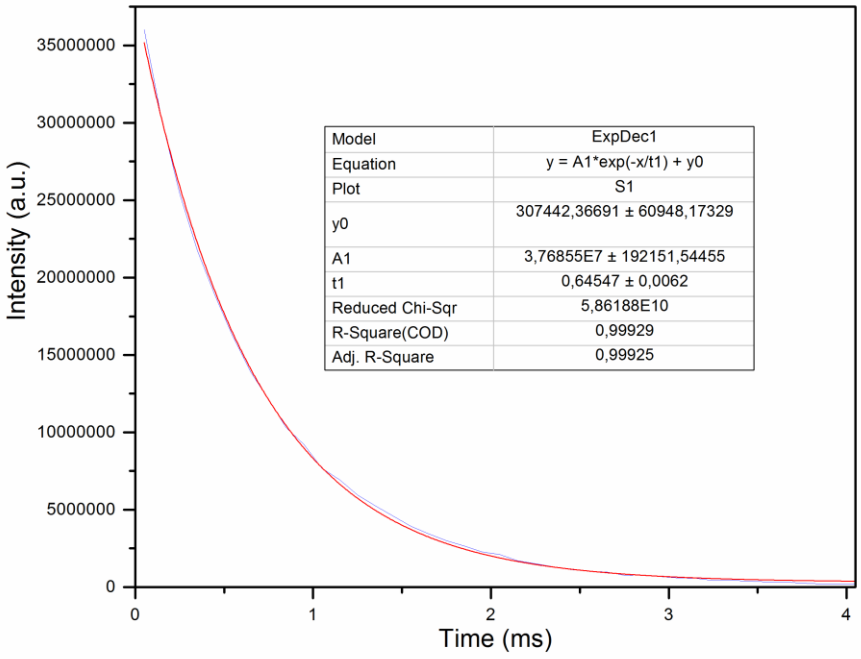


Figure S26. Lifetime curve of Eu(DBM)(BTFA)(TTA)(PHEN).

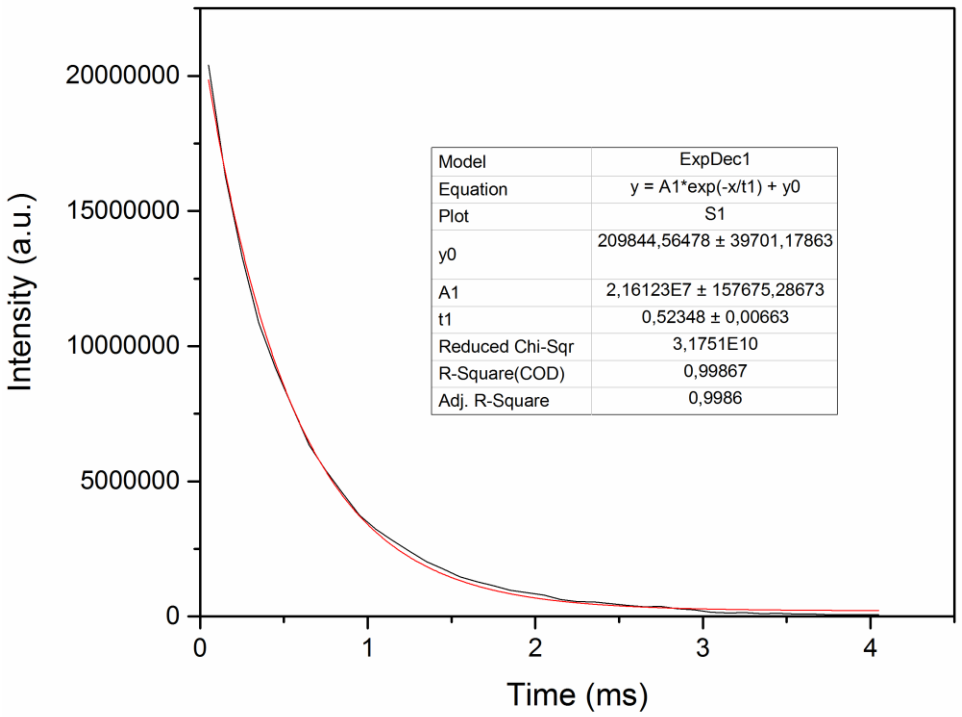


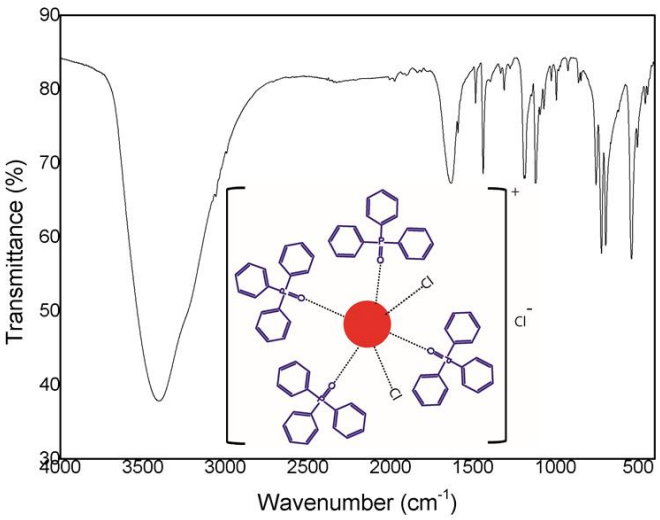
Figure S27. Lifetime curve of Eu(DBM)(BTFA)(TTA)(BIPY).

Table S1. Q, D, C and D/C values for all complexes computed via Sparkle/RM1, with electronic densities and electrophilic superdelocalizabilities, together with calculated and experimental Ω_λ values. Units are: *Q* (au^{-1}); *D* ($au^{-1}\cdot Å^3$); *C* ($Å^3$); *D/C* (au^{-1}); Ω_λ ($10^{-20}cm^2$) as described in Dutra et al[1].

Complex	Q	D	C	D/C	Ω_2^{calc}	Ω_2^{exp}	Ω_4^{calc}	Ω_4^{exp}	Ω_6^{calc}
$Eu(DBM)_2(TTA)(TPPO)_2$	0.0858	44.7	26.6	1.68	33.27	33.28	6.90	6.91	0.215
$Eu)(TTA)_2(DBM)(TPPO)_2$	0.2733	43.0	23.7	1.81	29.90	30.17	10.24	9.58	0.204
$Eu(DBM)_2(BTFA)(TPPO)_2$	0.0841	36.8	21.7	1.70	30.74	30.75	6.69	6.70	0.222
$Eu(BTFA)_2(DBM)(TPPO)_2$	0.0804	45.2	24.5	1.84	35.55	35.55	6.06	6.05	0.222
$Eu(BTFA)_2(TTA)(TPPO)_2$	0.1336	36.9	23.4	1.58	31.87	31.87	7.44	7.44	0.223
$Eu(TTA)_2(BTFA)(TPPO)_2$	0.0976	40.3	23.4	1.72	33.19	33.19	7.30	7.31	0.257
$Eu(DBM)(BTFA)(TTA)(TPPO)_2$	0.0954	40.6	23.2	1.75	30.87	30.87	7.73	7.73	0.235
Eu(DBM)(BTFA)(TTA)(PHEN)	0.0793	23.5	13.4	1.75	25.78	25.78	6.70	6.70	0.201
Eu(DBM)(BTFA)(TTA)(BIPY)	0.0841	21.8	13.0	1.68	26.45	26.45	7.32	7.33	0.201
$Eu(DBM)_3(TPPO)_2^2$	0.0673	17.4	11.9	1.46	6.92	6.92	7.69	7.69	0.137
$Eu(BTFA)_3(TPPO)_2^2$	0.0045	81.7	43.3	1.89	28.7	28.6	1.41	7.73	0.179
$Eu(TTA)_3(TPPO)_2^2$	0.145	42.9	20.8	2.06	24.7	24.8	6.53	6.47	0.323

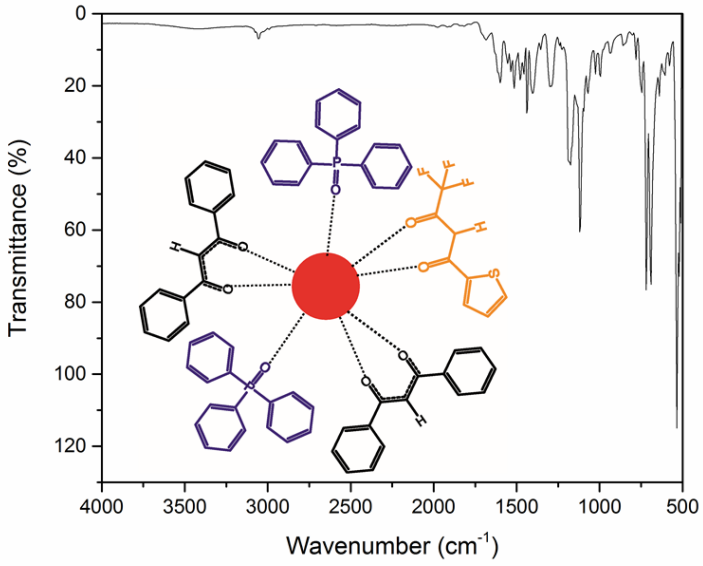
Characterization

Infrared Spectra



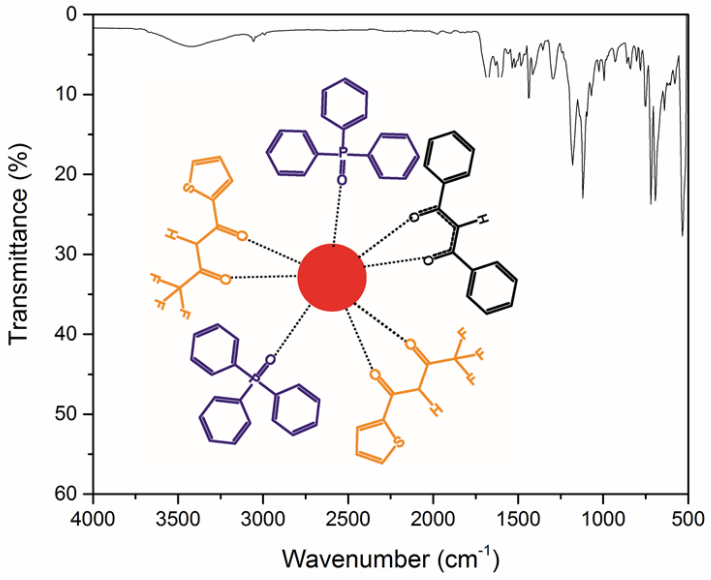
$[EuCl_3(TPPO)_4].3H_2O$ (KBr disk): υO-H 3461 cm^{-1}; υ=C–H 3090 cm^{-1} - 3015 cm^{-1}; υP=O 1087 cm^{-1}.

Figure S28. Infrared spectrum of $[EuCl_3(TPPO)_4].3H_2O$.



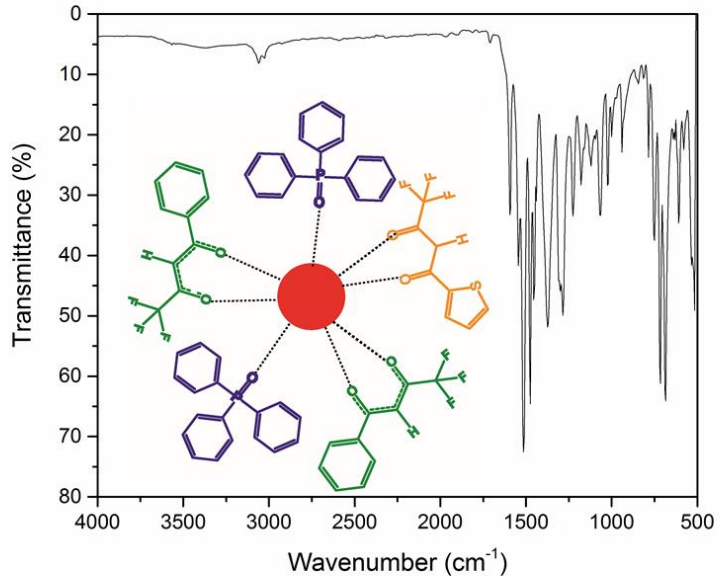
$Eu(DBM)_2(TTA)(TPPO)_2$ (KBr disk): υ=C-H 3075 cm^{-1} - 3054 cm^{-1}; υC–H 2990 cm^{-1}; υC=O 1685 cm^{-1}; υC=O 1600 cm^{-1}; υP=O 1113 cm^{-1}; υC=F 1179 cm^{-1}.

Figure S29. Infrared spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.



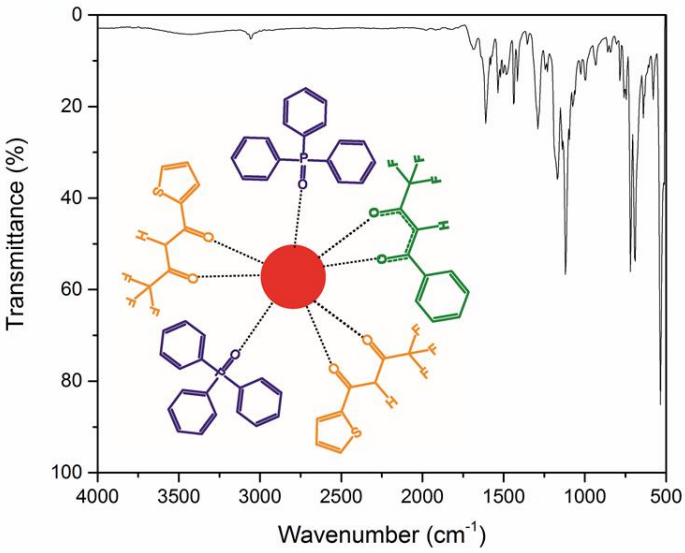
$Eu(TTA)_2(DBM)(TPPO)_2$ (KBr disk): υ=C-H 3076 cm^{-1} - 3056 cm^{-1}; υC–H 2989 cm^{-1}; υC=O 1680 cm^{-1}; υC=O 1608 cm^{-1}; υP=O 1118 cm^{-1}; υC=F 1182 cm^{-1}.

Figure S30. Infrared spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.



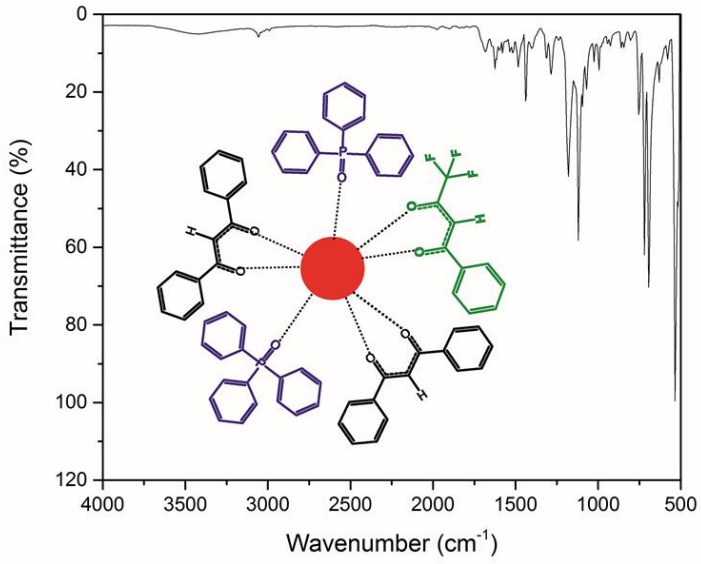
$Eu(BTFA)_2(TTA)(TPPO)_2$ (KBr disk): υ=C-H 3061 cm^{-1} - 3026 cm^{-1}; υC=O 1595 cm^{-1}; υC=O 1545 cm^{-1}; υP=O 1068 cm^{-1}; υC=F 1177 cm^{-1}; υC=F 1118 cm^{-1}.

Figure S31. Infrared spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.



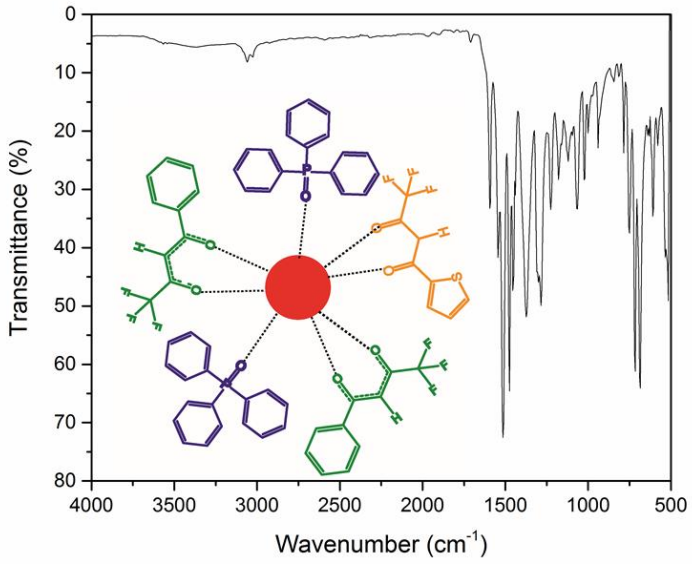
Eu(TTA)$_2$(BTFA)(TPPO)$_2$ (KBr disk): υ=C-H 3074 cm^{-1} - 3056 cm^{-1}; υC=O 1684 cm^{-1}; υC=O 1610 cm^{-1}; υP=O 1120 cm^{-1}; υC=F 1188 cm^{-1}; υC=F 1168 cm^{-1}.

Figure S32. Infrared spectrum of Eu(TTA)$_2$(BTFA)(TPPO)$_2$.



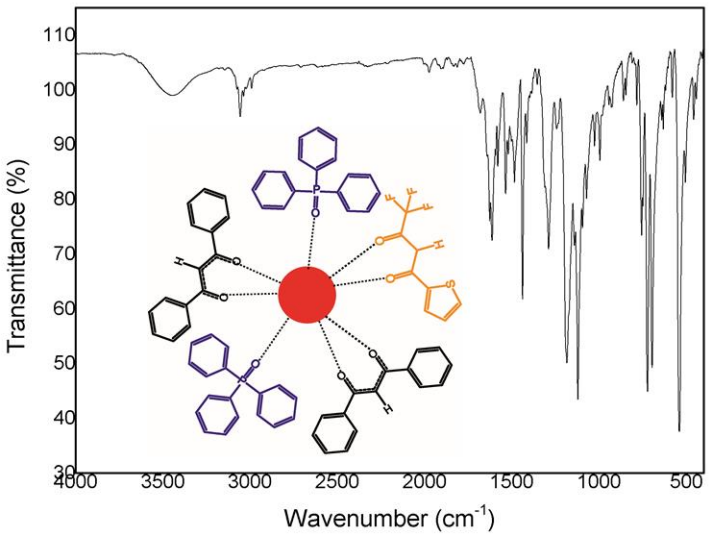
Eu(DBM)$_2$(BTFA)(TPPO)$_2$ (KBr disk): υ=C-H 3078 cm^{-1} - 3055 cm^{-1}; υC=O 1684 cm^{-1}; υC=O 1621 cm^{-1}; υP=O 1118 cm^{-1}; υC=F 1184 cm^{-1}.

Figure S33. Infrared spectrum of Eu(DBM)$_2$(BTFA)(TPPO)$_2$.



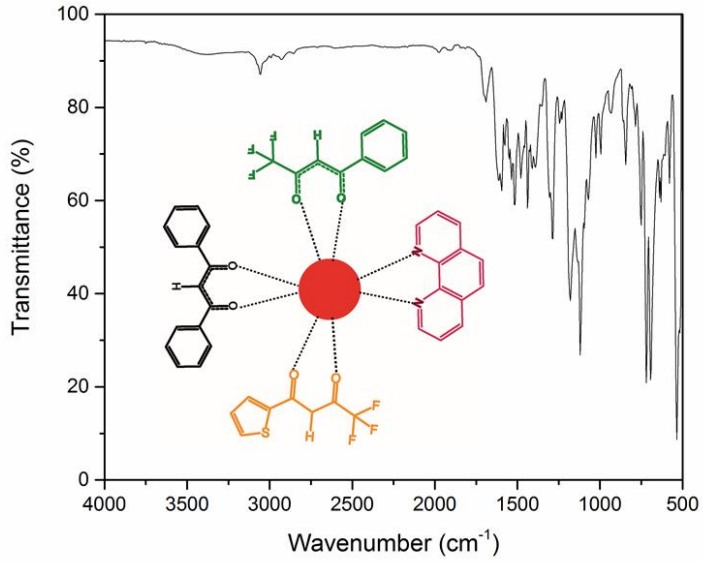
$Eu(BTFA)_2(DBM)(TPPO)_2$ (pastilha de KBr): υ=C-H 3076 cm^{-1} - 3054 cm^{-1}; υC=O 1681 cm^{-1}; υC=O 1625 cm^{-1}; υP=O 1117 cm^{-1}; υC=F 1181 cm^{-1}.

Figure S34. Infrared spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.



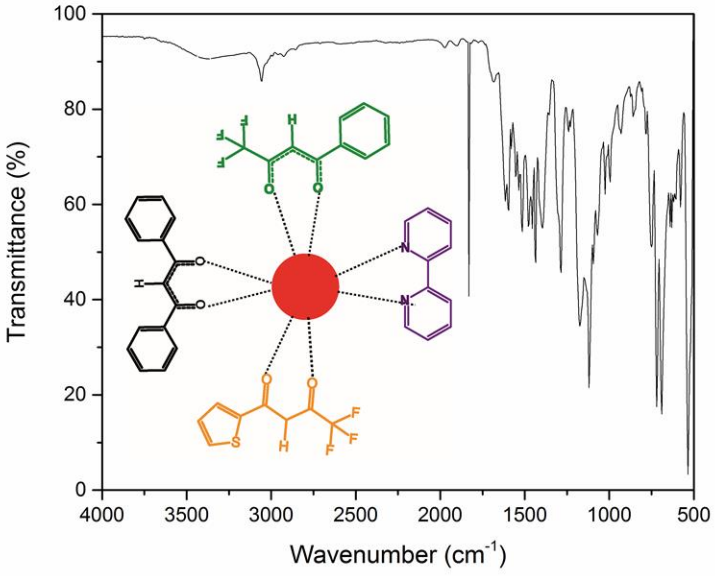
$Eu(DBM)(BTFA)(TTA)(TPPO)_2$ (KBr disk): ν=O-H 3452 cm^{-1}, νC-H 3060–3039 cm^{-1}, νC=O 1619 cm^{-1}, νP=O 1115 cm^{-1}; υC=F 1182 cm^{-1}; υC=F 1174 cm^{-1}.

Figure S35. Infrared spectrum of $Eu(DBM)(BTFA)(TTA)(TPPO)_2$.



Eu(DBM)(BTFA)(TTA)(PHEN) (KBr disk): ν=C-H 3079cm^{-1}-3049 cm^{-1}, νC=N 1615cm^{-1}, νC-F 1179cm^{-1}, νC=O 1694cm^{-1}.

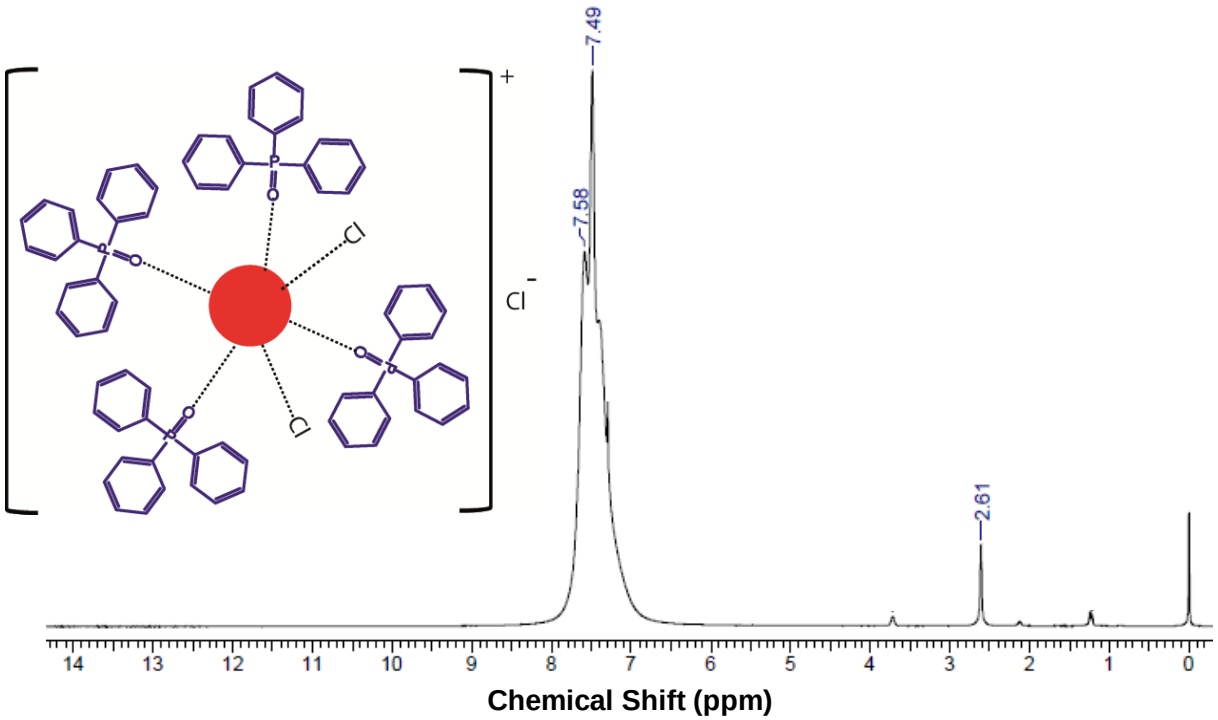
Figure S36. Infrared spectrum of Eu(DBM)(BTFA)(TTA)(PHEN).



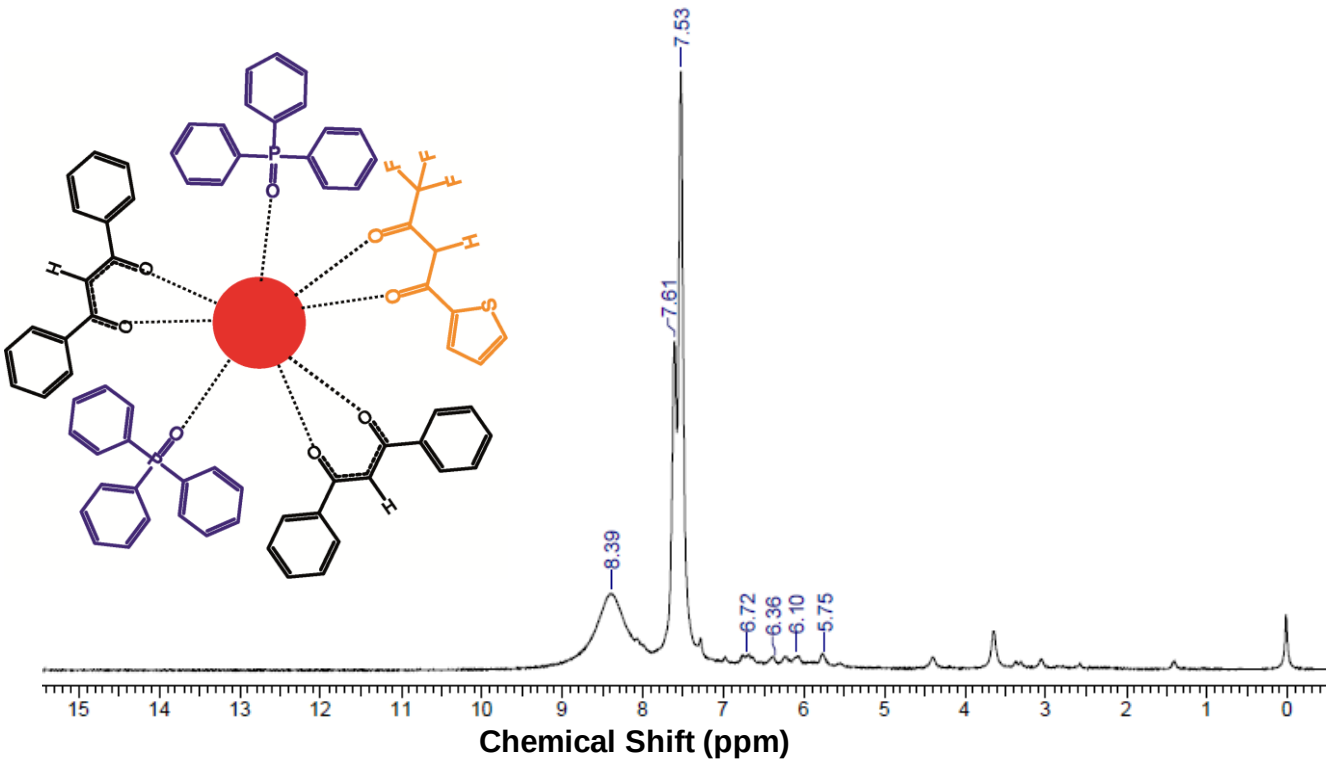
Eu(DBM)(BTFA)(TTA)(BIPY) (KBr disk): ν=C-H 3062cm^{-1}-3048 cm^{-1}, νC=N 1625 cm^{-1}, νC-F 1170cm^{-1}, νC=O 1684cm^{-1}.

Figure S37. Infrared spectrum of Eu(DBM)(BTFA)(TTA)(BIPY).

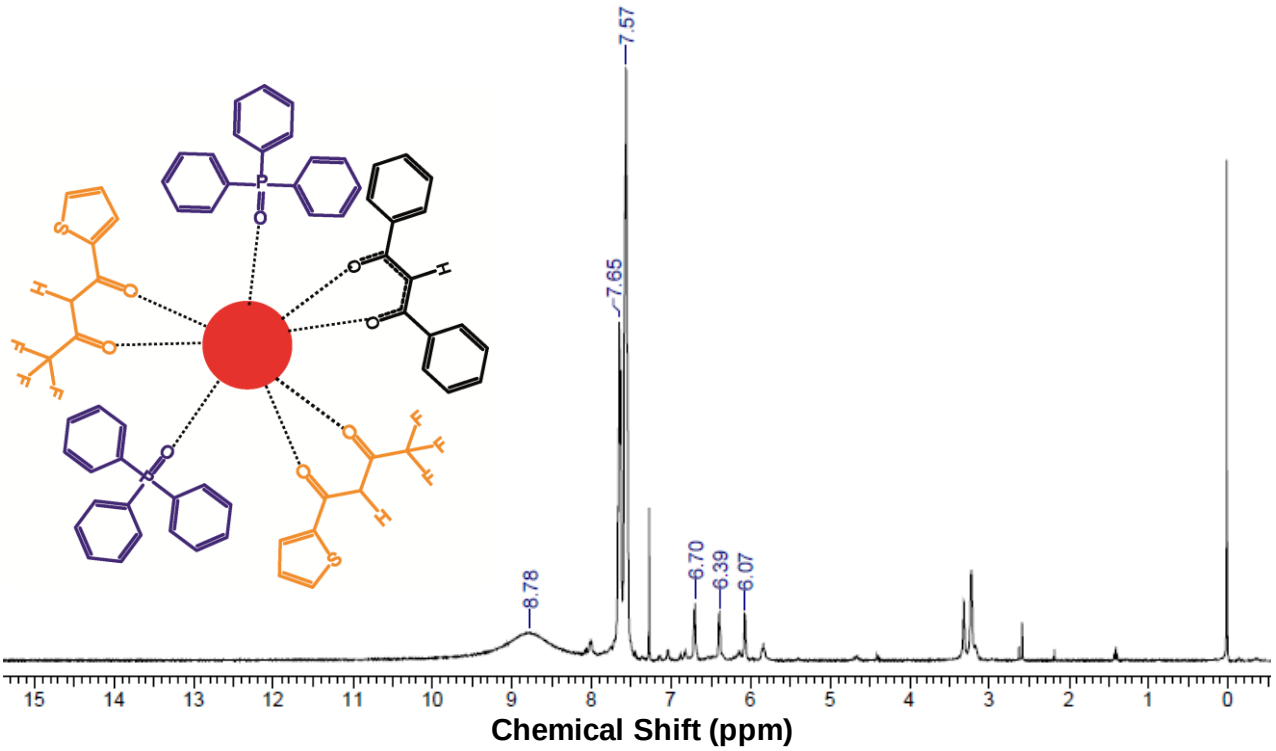
^{1}H NMR Spectra



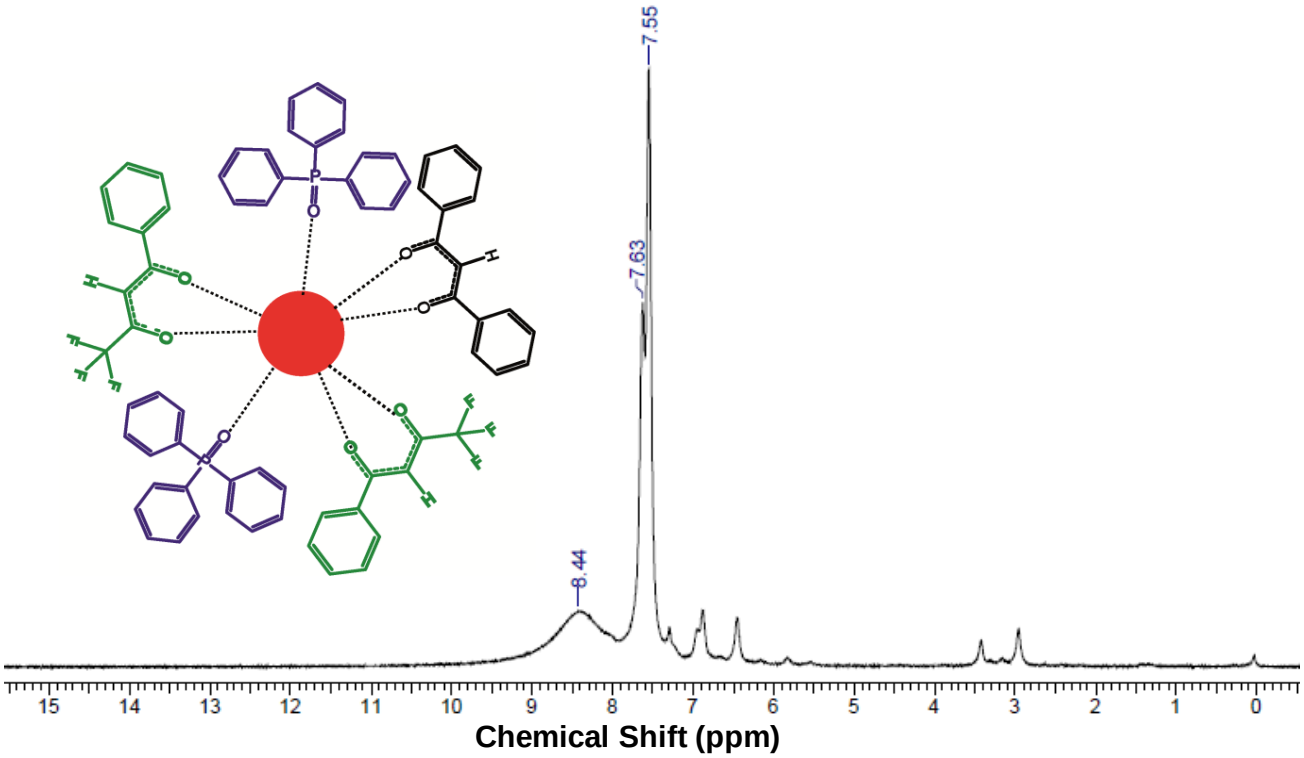
^{1}H NMR (400 MHz, $CDCl_3$): δ7.60-7.31 (m, Ar.), 2.61 (s, OH).
Figure S38. ^{1}H NMR spectrum of $EuCl_3(TPPO)_4.3H_2O$.



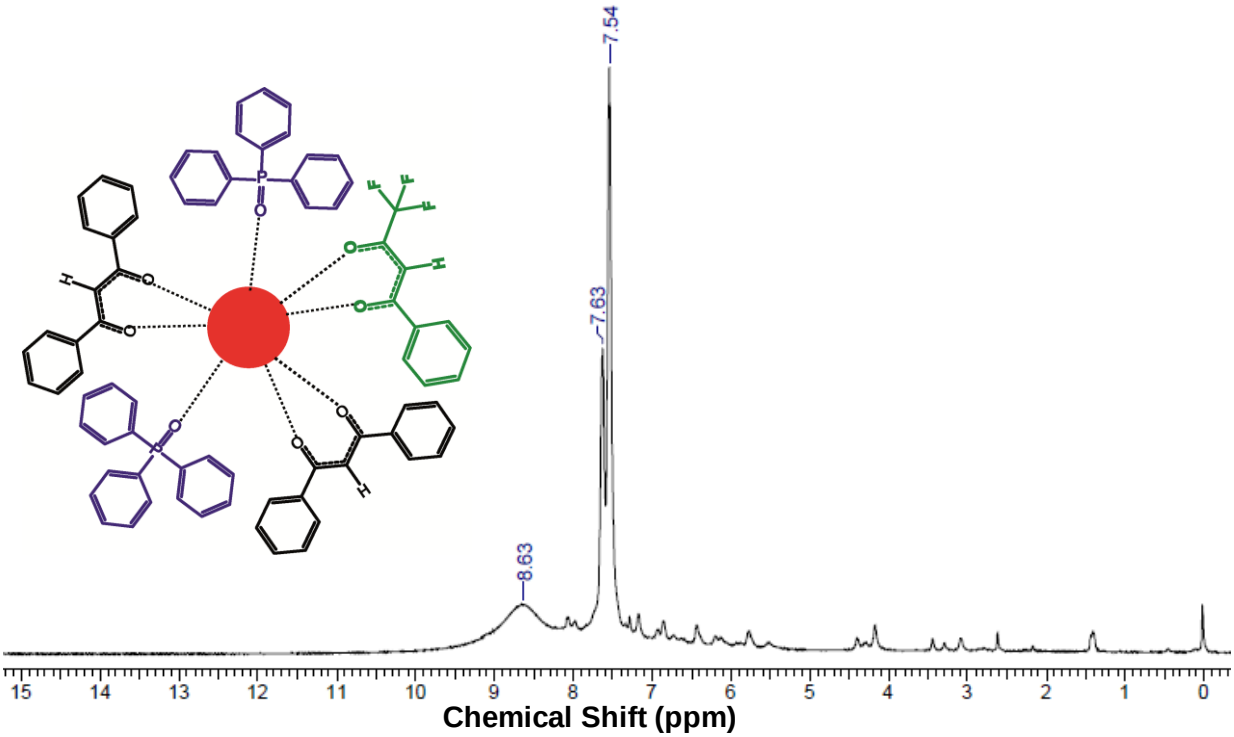
H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, CH), 7.85-5.75 (m, Ar.).
Figure S39. ^{1}H NMR spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.



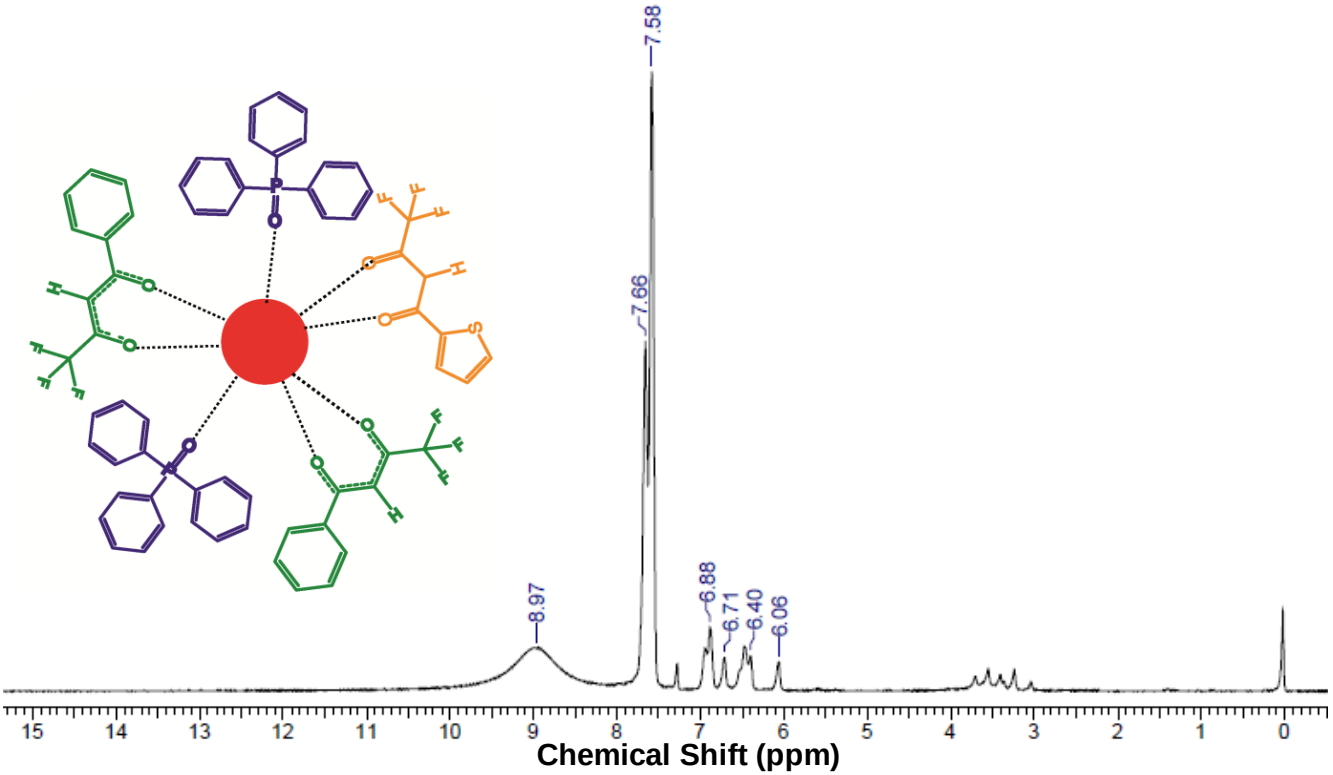
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, CH),7.82-6.07 (m, Ar.).
Figure S40. ^{1}H NMR spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.



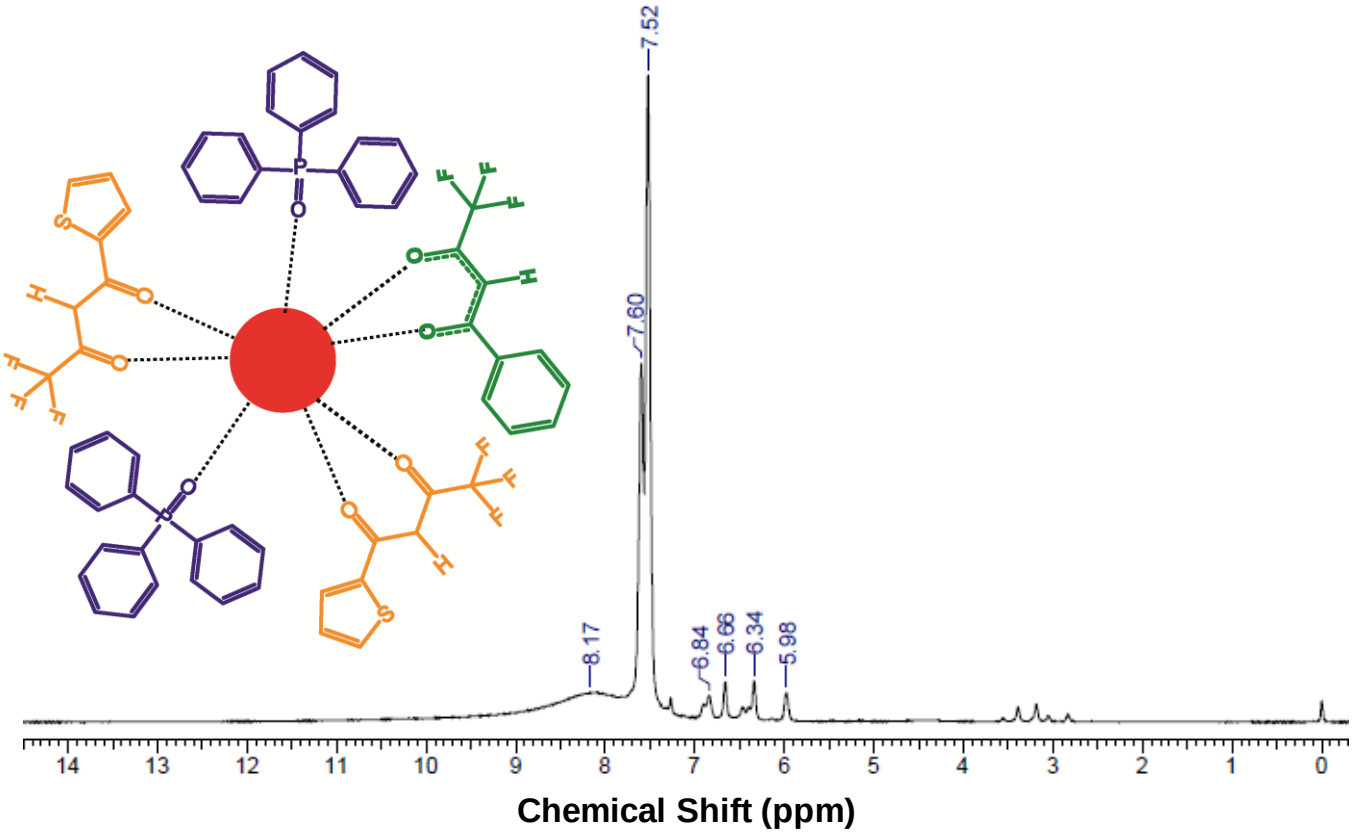
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, CH),7.91-7.55 (m, Ar.).
Figure S41. ^{1}H NMR spectrum of $Eu(BTFA)_2(DBM)(TPPO)_2$.



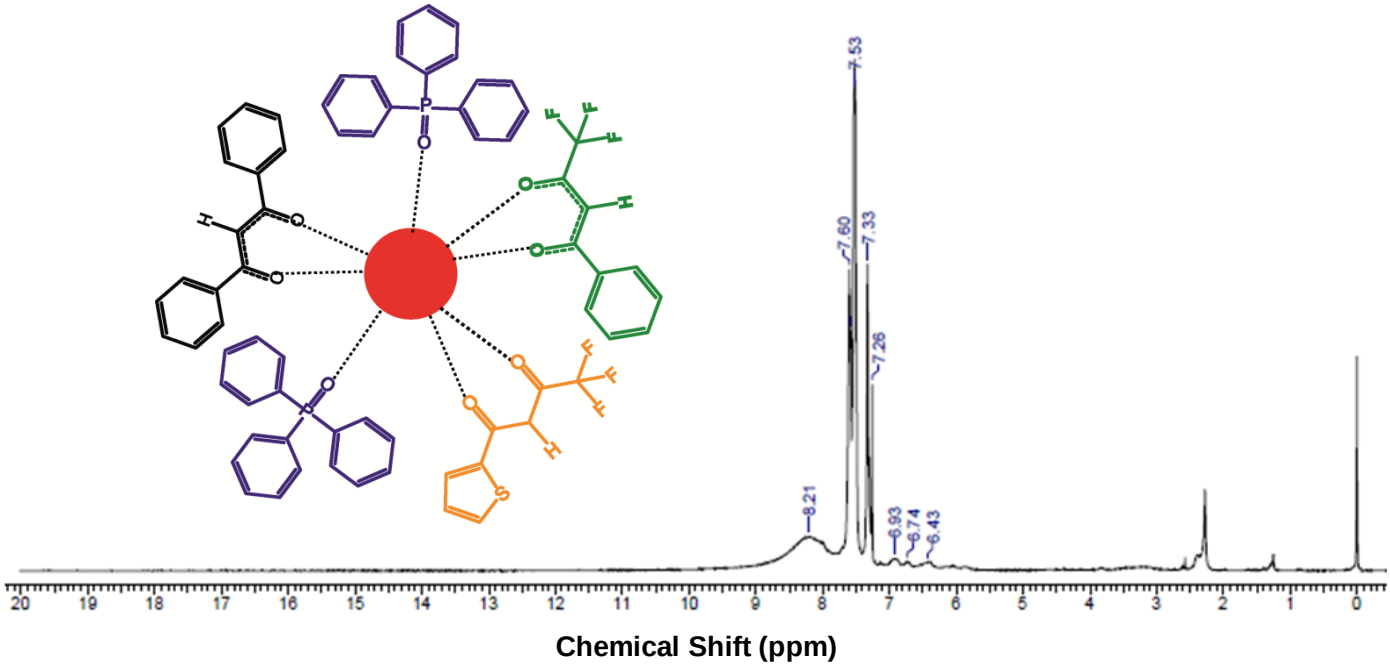
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, CH), 7.90-7.54 (m, Ar.).
Figure S42. ^{1}H NMR spectrum of $Eu(DBM)_2(BTFA)(TPPO)_2$.



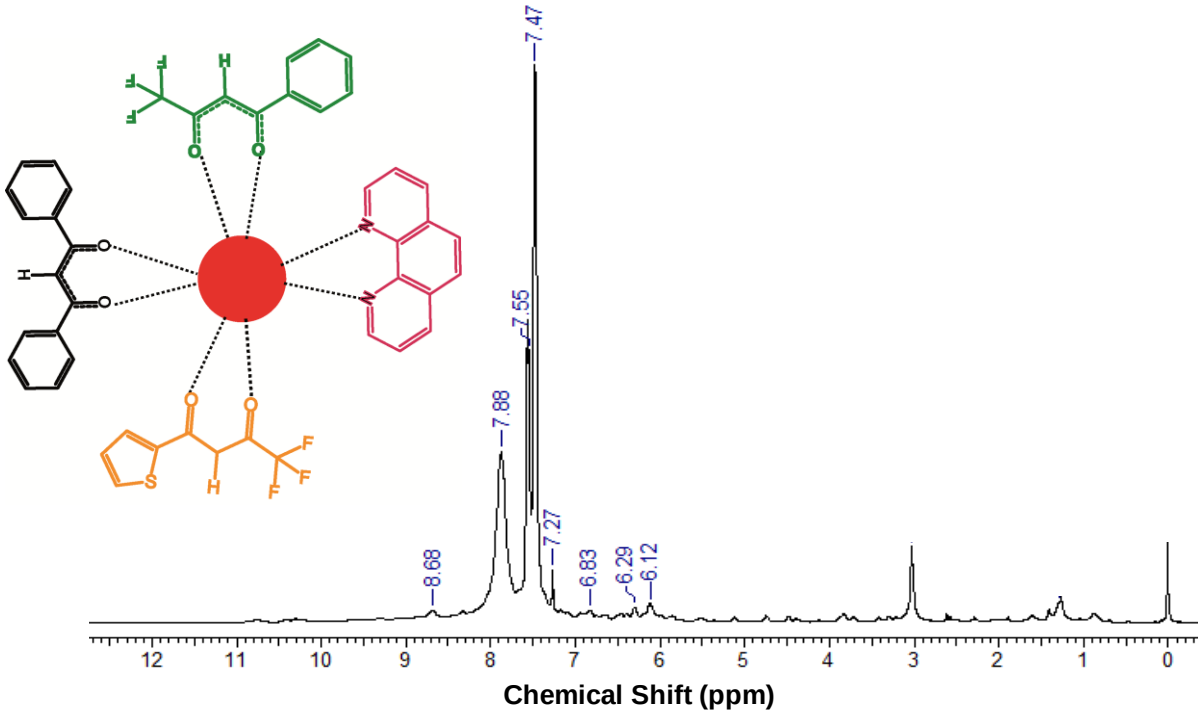
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, CH),7.84-6.06 (m, Ar.).
Figure S43. ^{1}H NMR spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, CH),7.85-7.34 (m, Ar.).
Figure S44. ^{1}H NMR spectrum of $Eu(TTA)_2(BTFA)(TPPO)_2$.

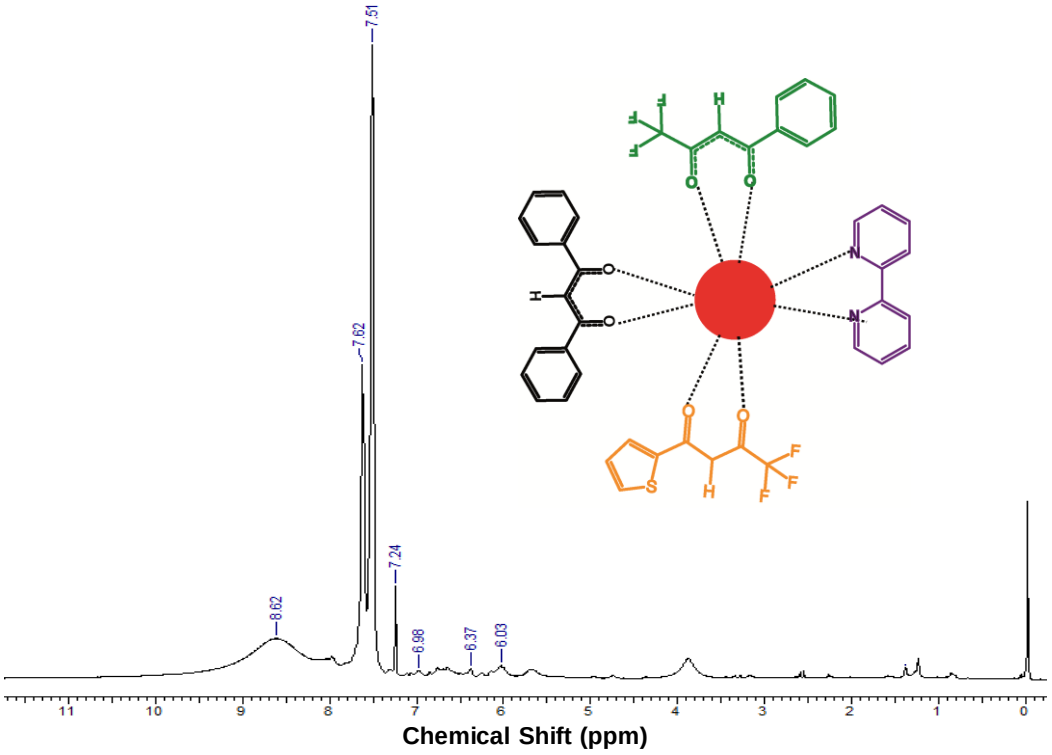


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, CH),7.79-6.43 (m, Ar.).
Figure S45. ^{1}H NMR spectrum of $Eu(DBM)(BTFA)(TTA)(TPPO)_2$.



^{1}H NMR (400 MHz, $CDCl_3$): δ8.68 (s, CH),8.27-6.12 (m, Ar.).

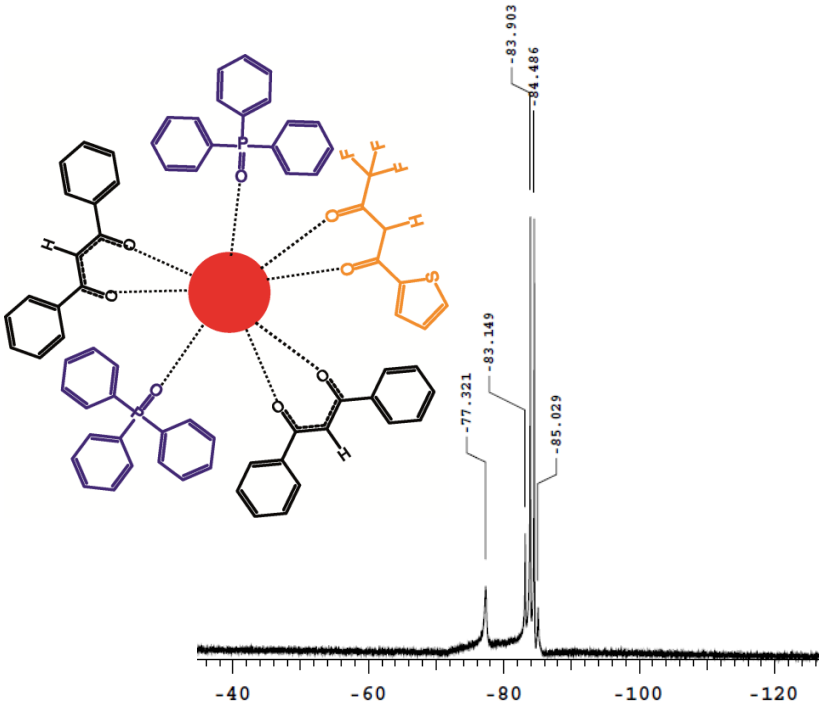
Figure S46. ^{1}H NMR spectrum of Eu(DBM)(BTFA)(TTA)(PHEN).



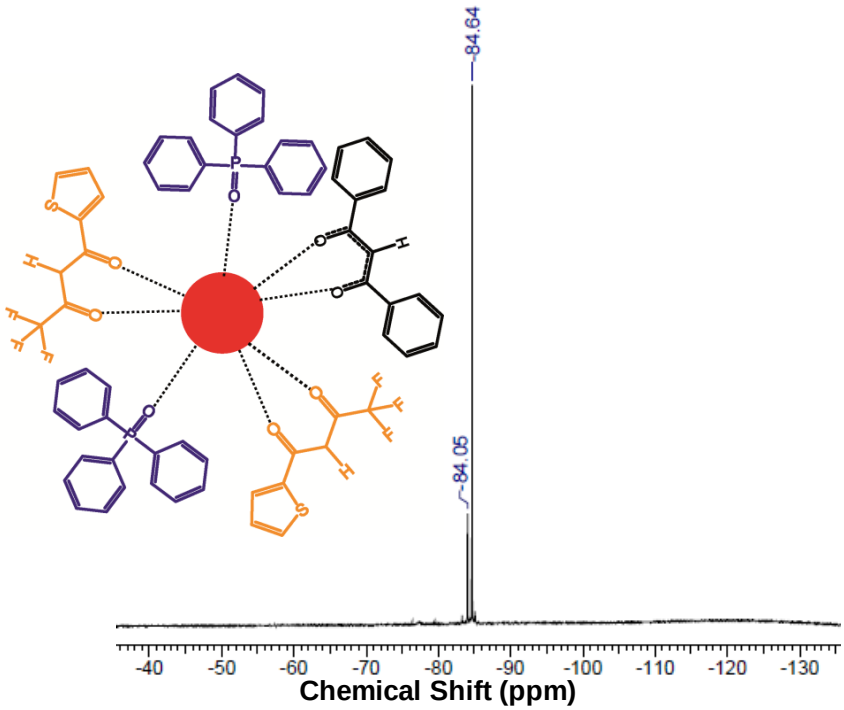
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, CH),7.86-6.03 (m, Ar.).

Figure S47. ^{1}H NMR spectrum of Eu(DBM)(BTFA)(TTA)(BIPY).

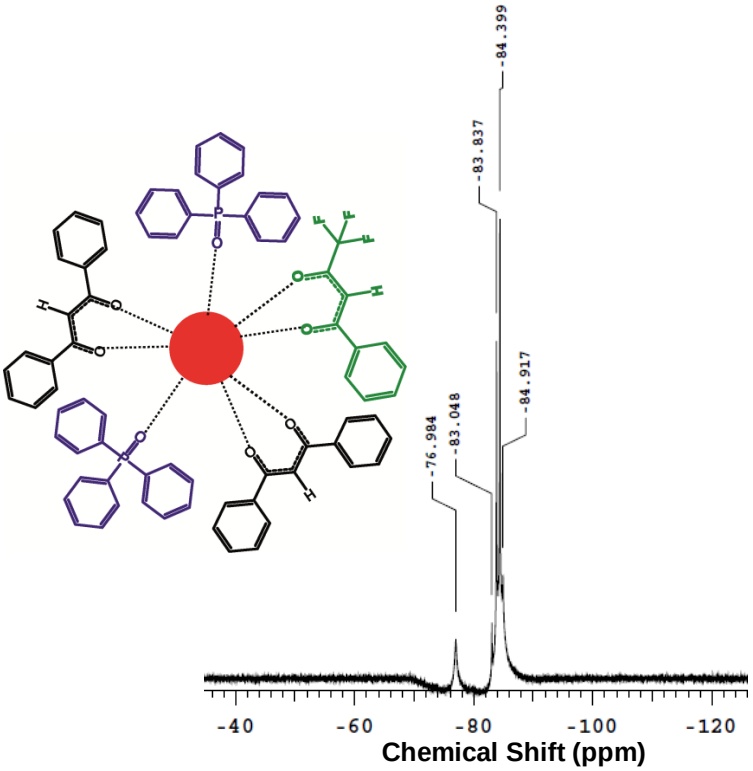
^{19}F NMR Spectra



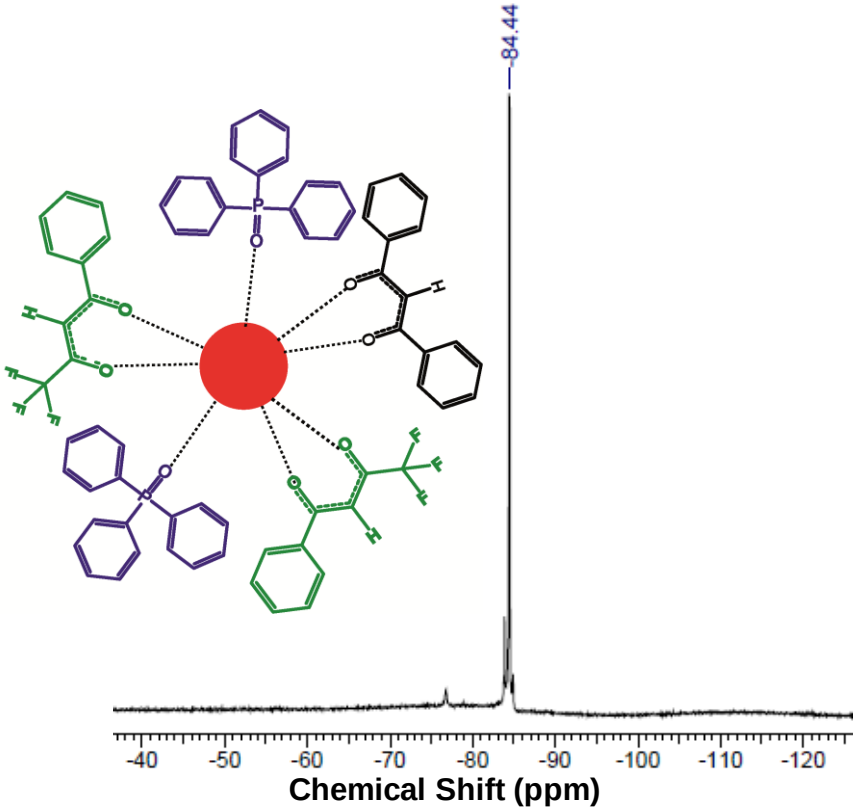
^{19}F NMR (376 MHz, $CDCl_3$): δ -83.90 ppm and -84.41 ppm.
Figure S48. ^{19}F NMR spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.



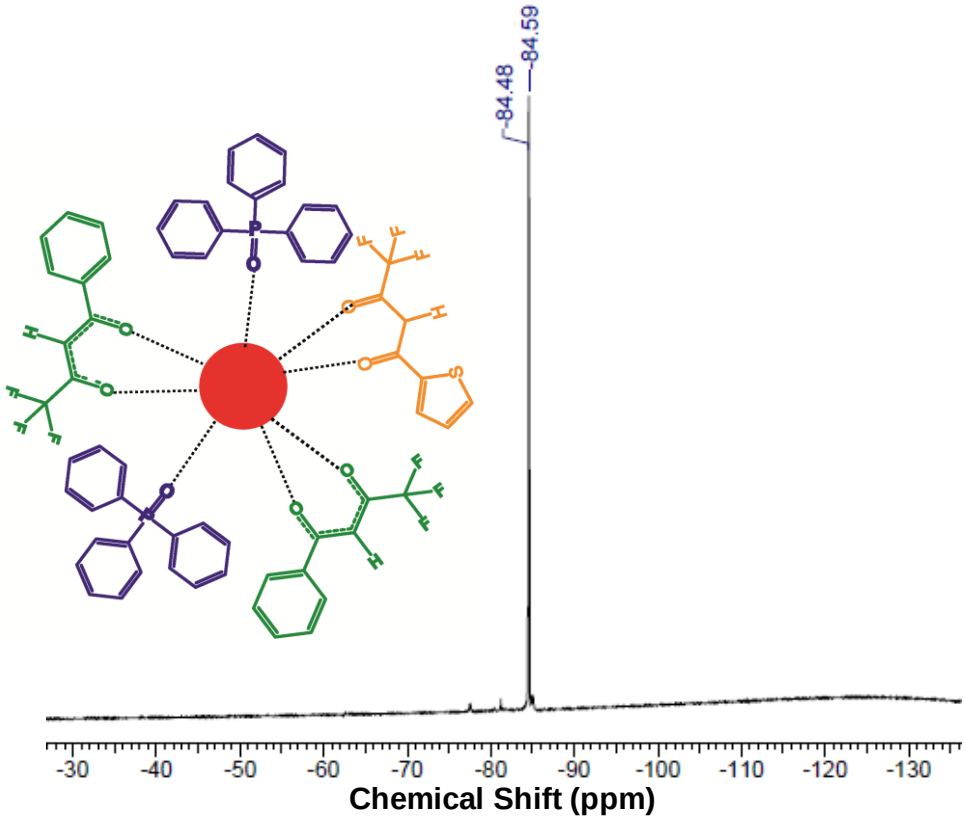
^{19}F NMR (376 MHz, $CDCl_3$): δ -84.06 ppm and -84.64 ppm.
Figure S49. ^{19}F NMR spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.



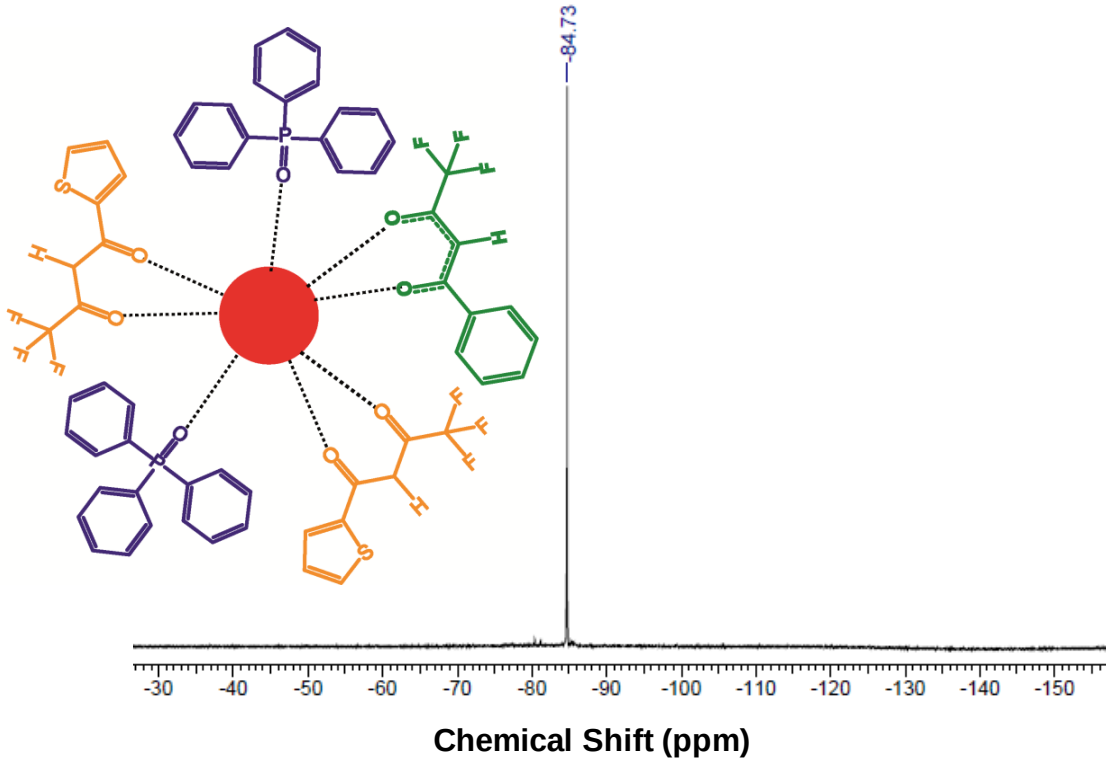
^{19}F NMR (376 MHz, $CDCl_3$): δ -83.84 ppm and -84.40 ppm.
Figure S50. ^{19}F NMR spectrum of $Eu(DBM)_2(BTFA)(TPPO)_2$.



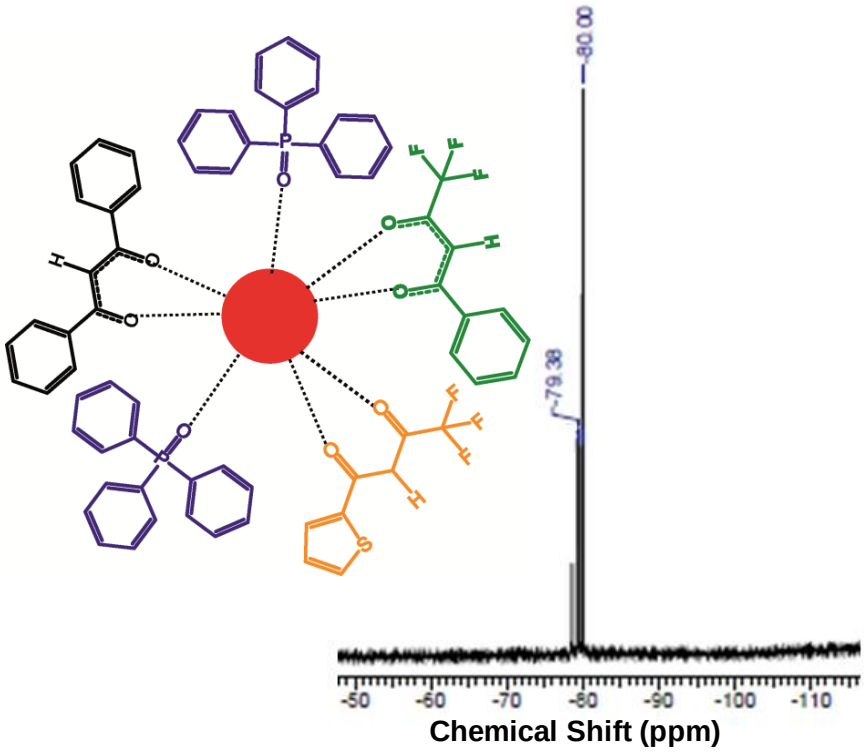
^{19}F NMR (376 MHz, $CDCl_3$): δ -84.44 ppm.
Figure S51. ^{19}F NMR spectrum of $Eu(BTFA)_2(DBM)(TPPO)_2$.



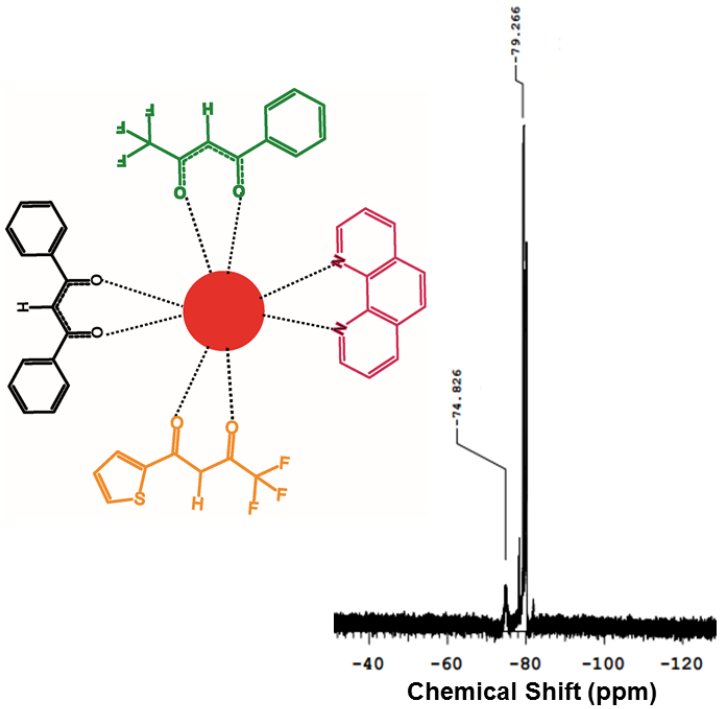
^{19}F NMR (376 MHz, $CDCl_3$): δ -84.48 ppm and -84.59 ppm.
Figure S52. ^{19}F NMR spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.



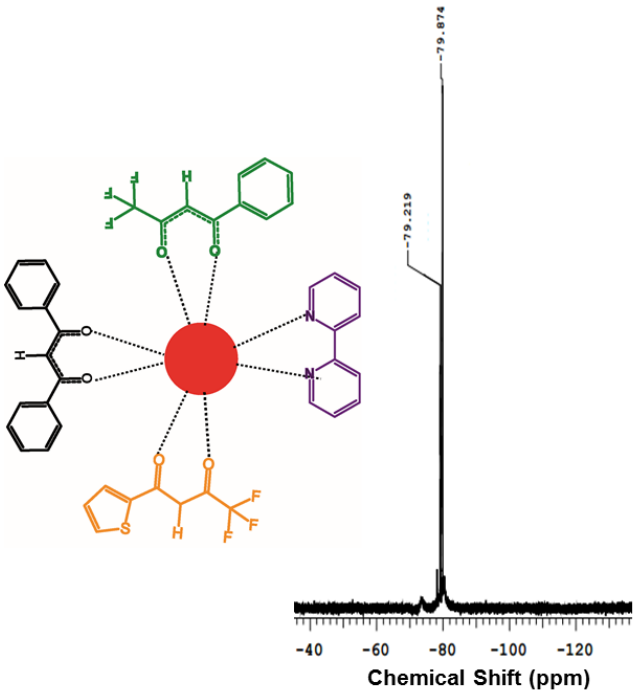
^{19}F NMR (376 MHz, $CDCl_3$): δ -84.73 ppm.
Figure S53. ^{19}F NMR spectrum of $Eu(TTA)_2(BTFA)(TPPO)_2$**.**



^{19}F NMR (282 MHz, $CDCl_3$): δ -79.38 ppm and -80.00 ppm.
Figure S54. ^{19}F NMR spectrum of Eu(DBM)(BTFA)(TTA)$(TPPO)_2$.



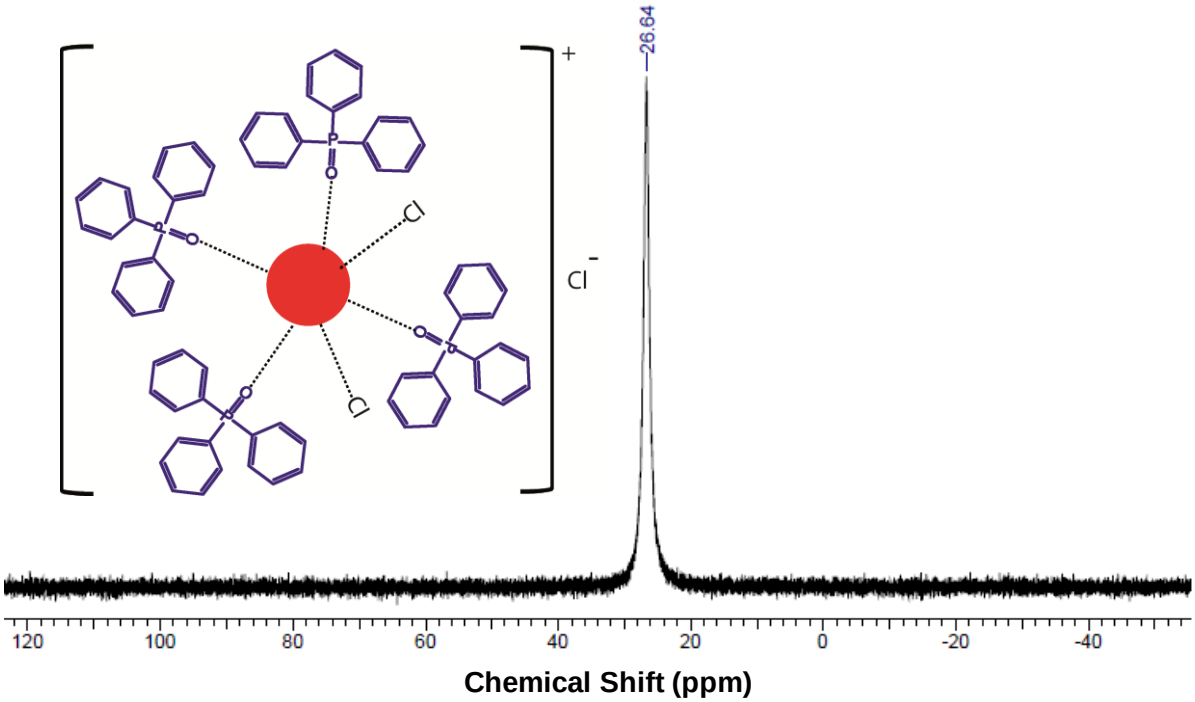
^{19}F NMR (376 MHz, $CDCl_3$): δ -79.26-74.82 ppm.
Figure S55. ^{19}F NMR spectrum of Eu(DBM)(BTFA)(TTA)(PHEN).



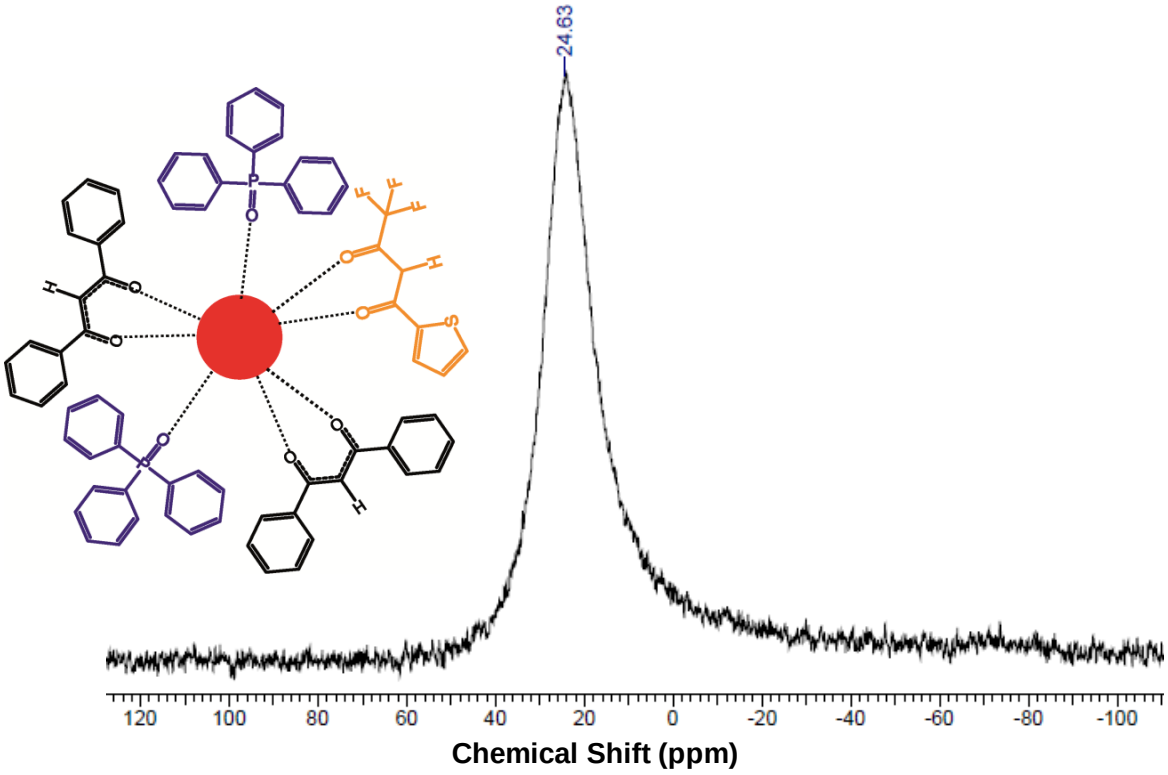
^{19}F NMR (376 MHz, $CDCl_3$): δ -79.22-79.87 ppm.

Figure S56. ^{19}F NMR spectrum of Eu(DBM)(BTFA)(TTA)(BIPY).

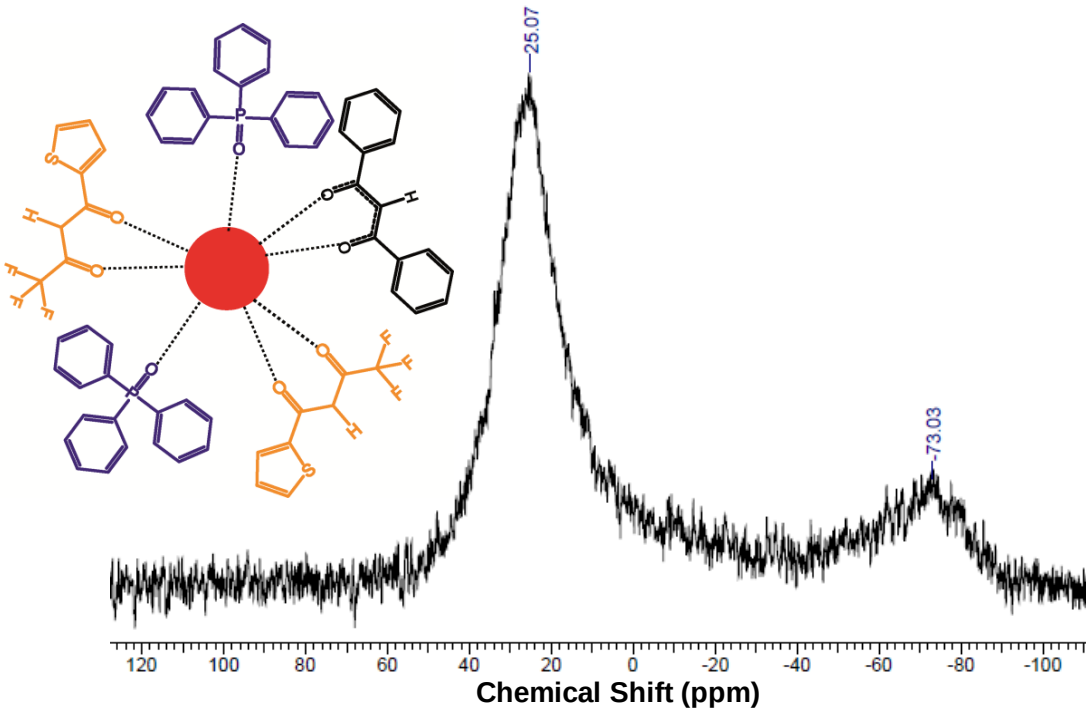
^{31}P NMR Spectra



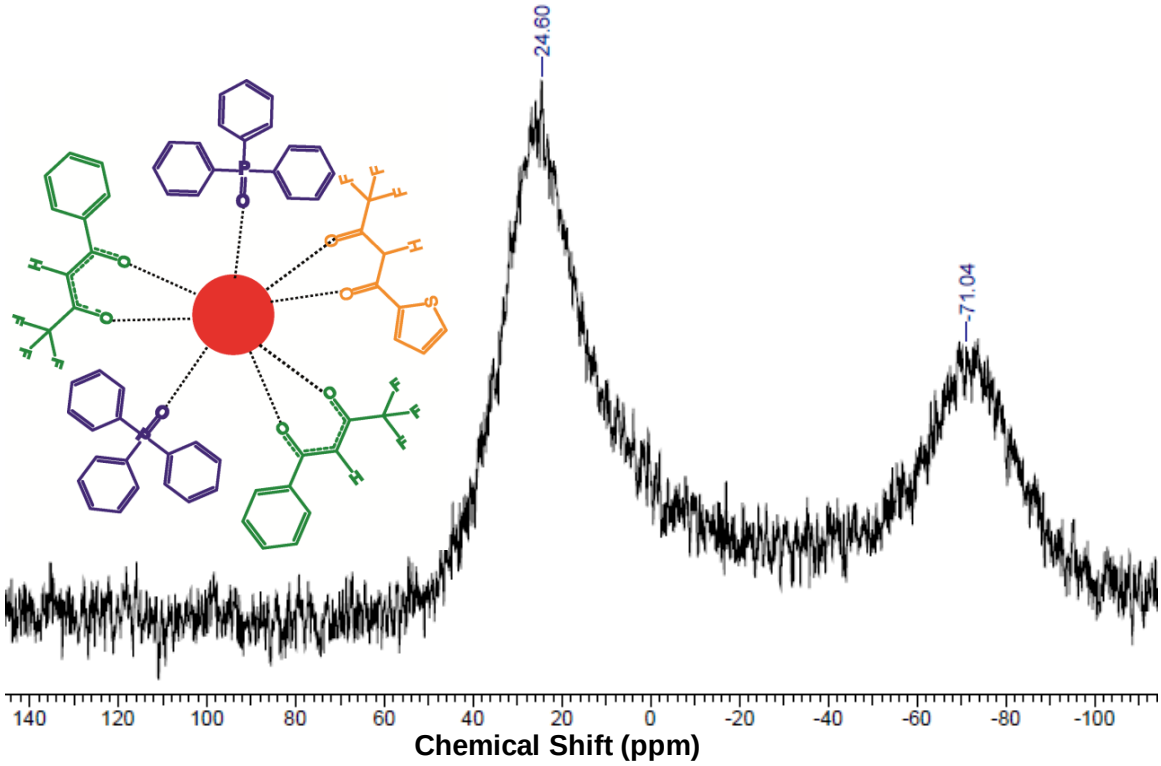
^{31}P NMR (162 MHz, $CDCl_3$): δ 27 ppm.
Figure S57. ^{31}P NMR spectrum of $EuCl_3(TPPO)_4.3H_2O$.



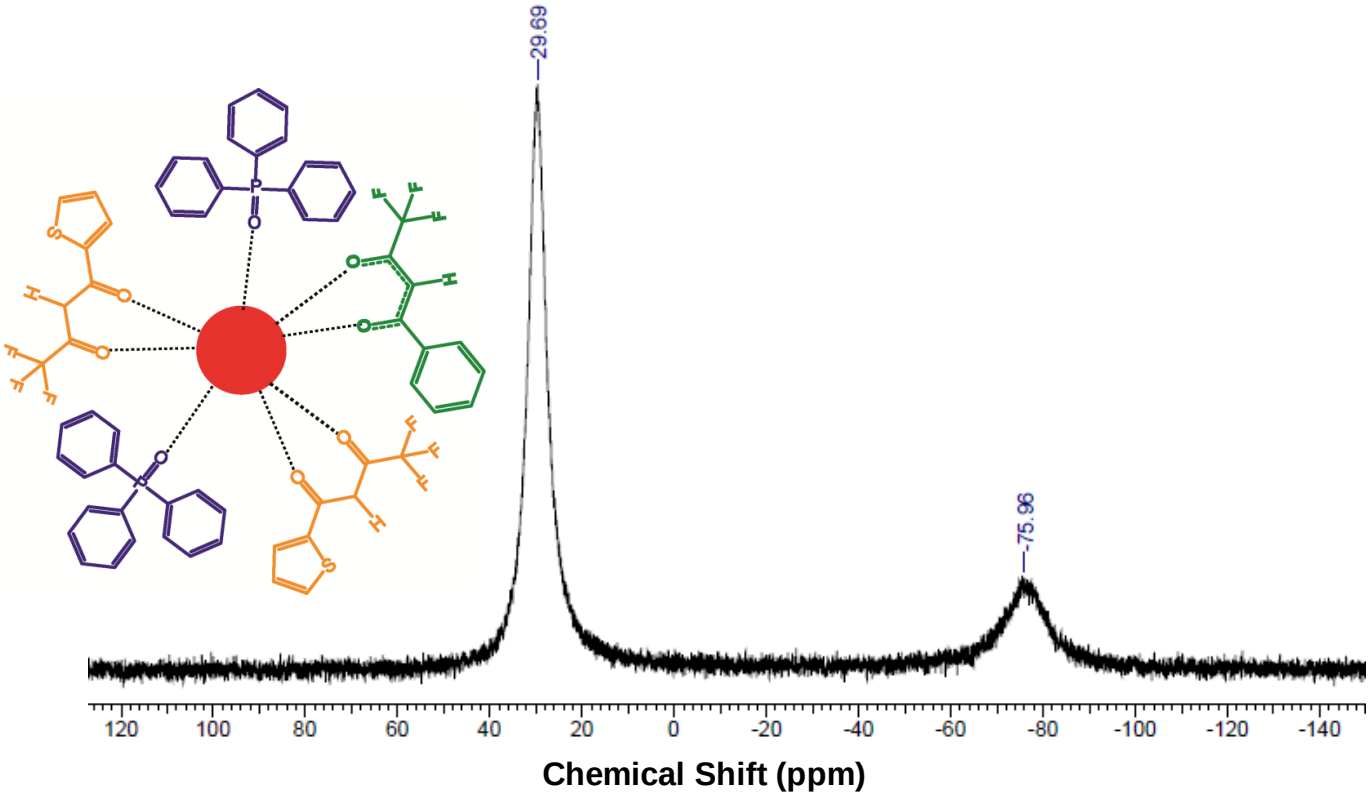
^{31}P NMR (162 MHz, $CDCl_3$): δ 25 ppm.
Figure S58. ^{31}P NMR spectrum of $Eu(DBM)_2(TTA)(TPPO)_2$.



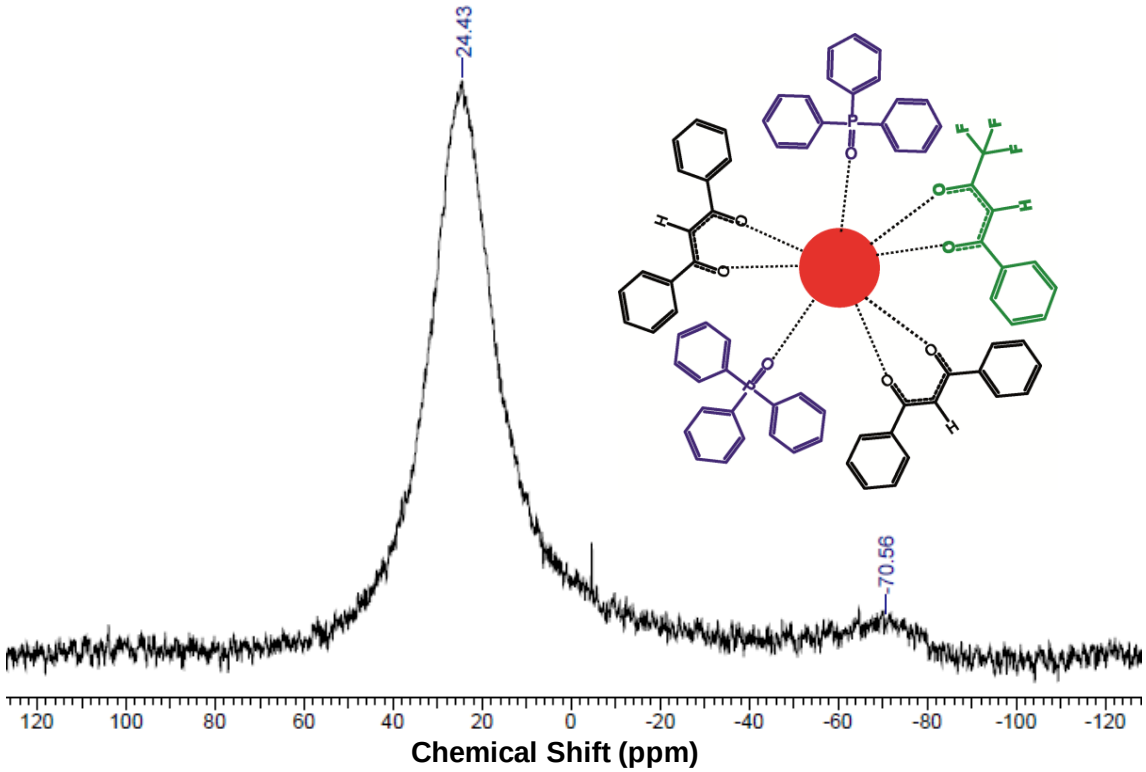
^{31}P NMR (162 MHz, $CDCl_3$): δ 25 ppm and -73 ppm.
Figure S59. ^{31}P NMR spectrum of $Eu(TTA)_2(DBM)(TPPO)_2$.



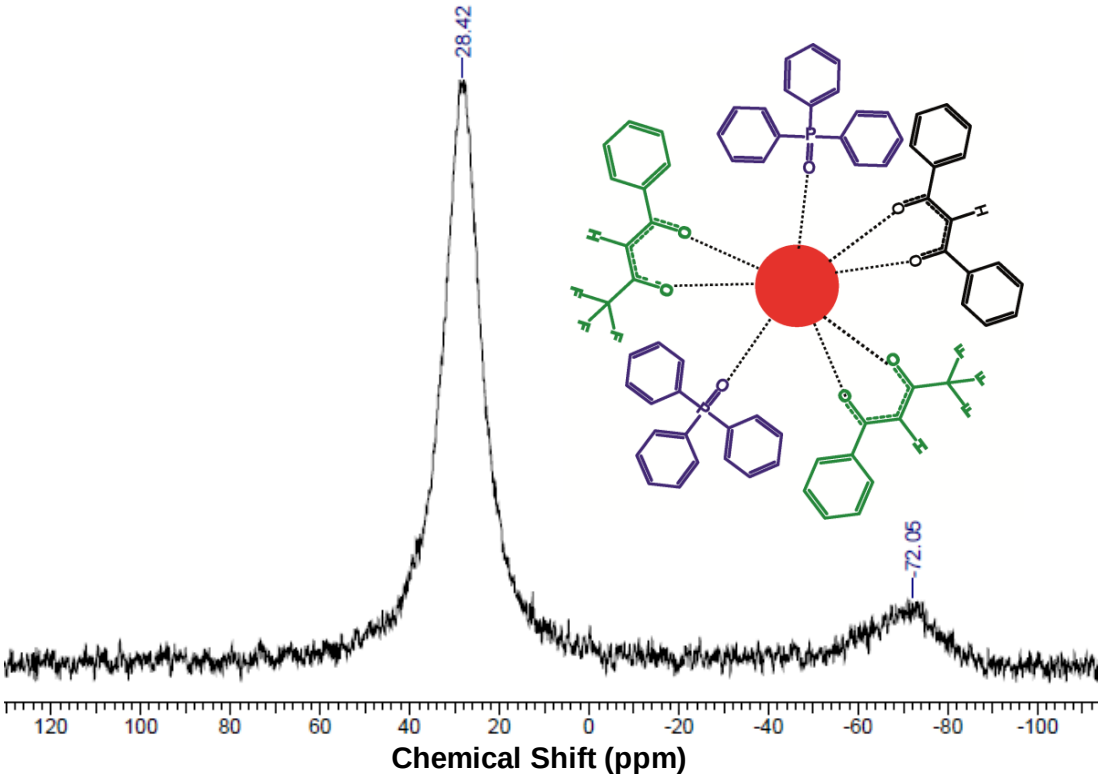
^{31}P NMR (162 MHz, $CDCl_3$): δ 25 ppm and -71 ppm.
Figure S60. ^{31}P NMR spectrum of $Eu(BTFA)_2(TTA)(TPPO)_2$.



^{31}P NMR (162 MHz, $CDCl_3$): δ 30 ppm and -76 ppm.
Figure S61. ^{31}P NMR spectrum of $Eu(TTA)_2(BTFA)(TPPO)_2$.

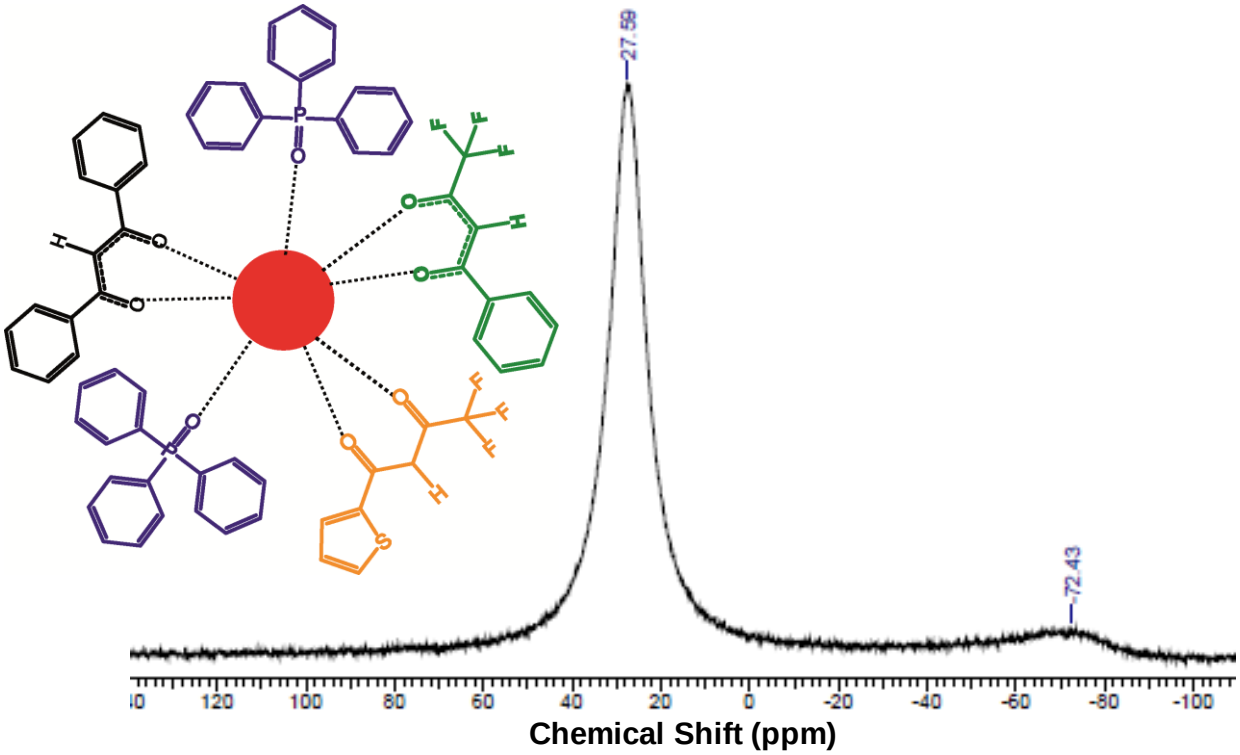


^{31}P NMR (162 MHz, $CDCl_3$): δ 24 ppm and -71 ppm.
Figure S62. ^{31}P NMR spectrum of $Eu(DBM)_2(BTFA)(TPPO)_2$.



^{31}P NMR (162 MHz, $CDCl_3$): δ 28 ppm and -72 ppm.

Figure S63. ^{31}P NMR spectrum of $Eu(BTFA)_2(DBM)(TPPO)_2$**.**



^{31}P NMR (162 MHz, $CDCl_3$): δ 28 and 72.43 ppm.

Figure S64. ^{31}P NMR spectrum of $Eu(DBM)(BTFA)(TTA)(TPPO)_2$.

References

1 J. D. L. Dutra, N. B. D. Lima, R. O. Freire and A. M. Simas, *Sci. Rep.*, 2015, **5**, 13695.

2 N. B. D. Lima, J. D. L. Dutra, S. M. C. Gonçalves, R. O. Freire and A. M. Simas, *Sci. Rep.*, 2016, **6**, 21204.