Electronic Supplementary Material (ESI) for Dalton Transactions

Preparation and photophysical studies of [Ln(hfac)$_3$DPEPO], Ln= Eu, Tb, Yb, Nd, Gd; interpretation of total photoluminescence quantum yields.†

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Supplementary Information

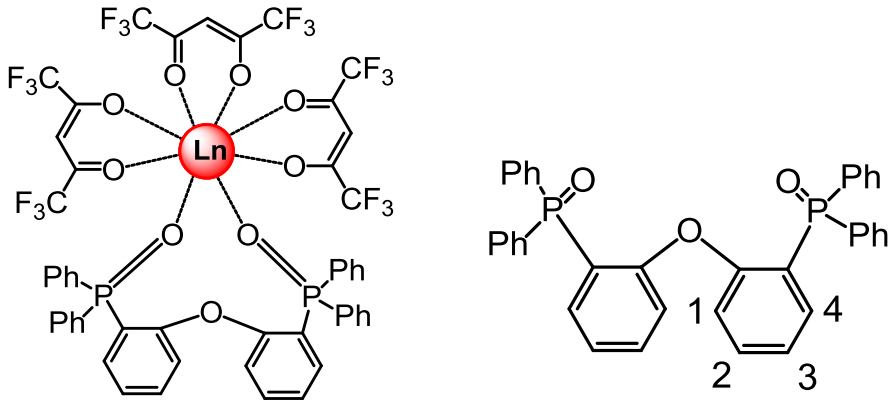

Fig. S1: (left) General molecular diagram of the complexes [Ln(hfac)$_3$(DPEPO)]: Ln = Eu, Tb, Yb, Nd, Gd. (right) Molecular formula of DPEPO, bis(2-(diphenylphosphino)phenyl)ether oxide with numbering scheme for the protons of the phenylether ring.

Figures S2 – S6: ^{1}H NMR (500MHz) in *d*-chloroform solution.

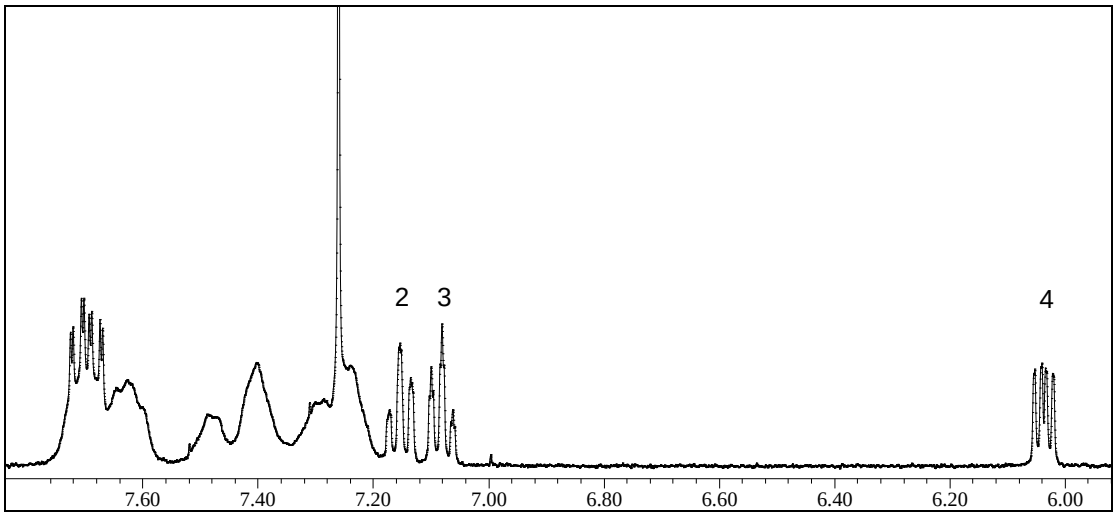

Fig. S2: DPEPO - bis(2-(diphenylphosphino)phenyl)ether oxide

The range between 7.75 and 7.20 ppm is attributed to the four phenyl groups bonded to the phosphorus and the proton at the 1 position in the diphenyl ether group. Two triplets at 7.15ppm and at 7.08ppm are assigned to the protons at the 2 and 3 positions of the diphenyl group, whereas the four-line pattern 6.04ppm is attributable to the proton at the 4 position which couples with the phosphorus atom (H. Xu, L. H. Wang, X. H. Zhu, K. Yin, G. Y. Zhong, X. Y. Hou and W. Huang, *Journal of Physical Chemistry B-Condensed Phase*, 2006, **110**, 3023-3029).

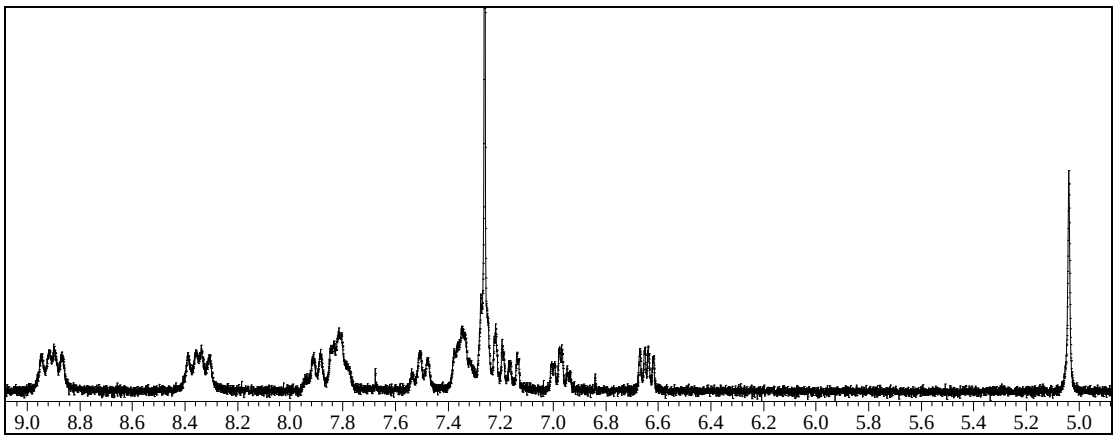

Fig. S3: [Eu(hfac)$_3$(DPEPO)]

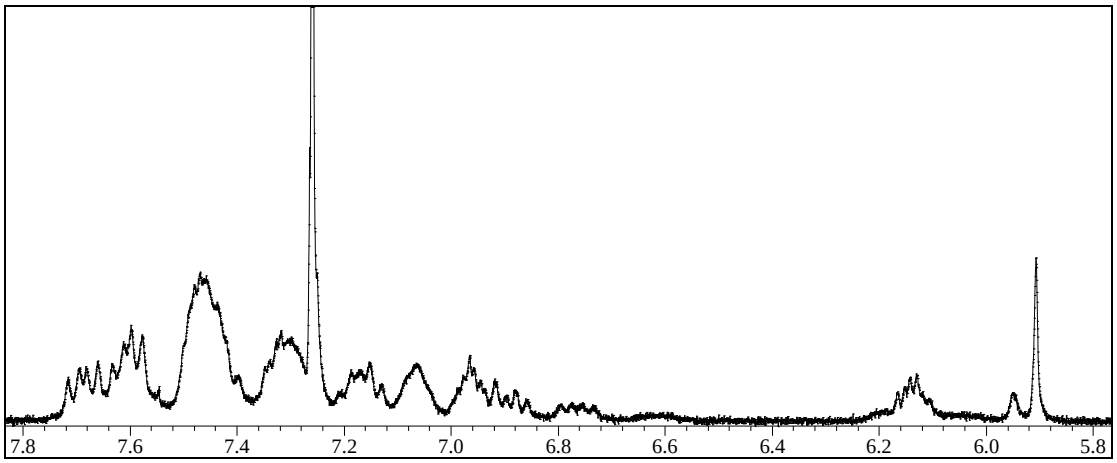

Fig. S4: [Tb(hfac)$_3$(DPEPO)**]**

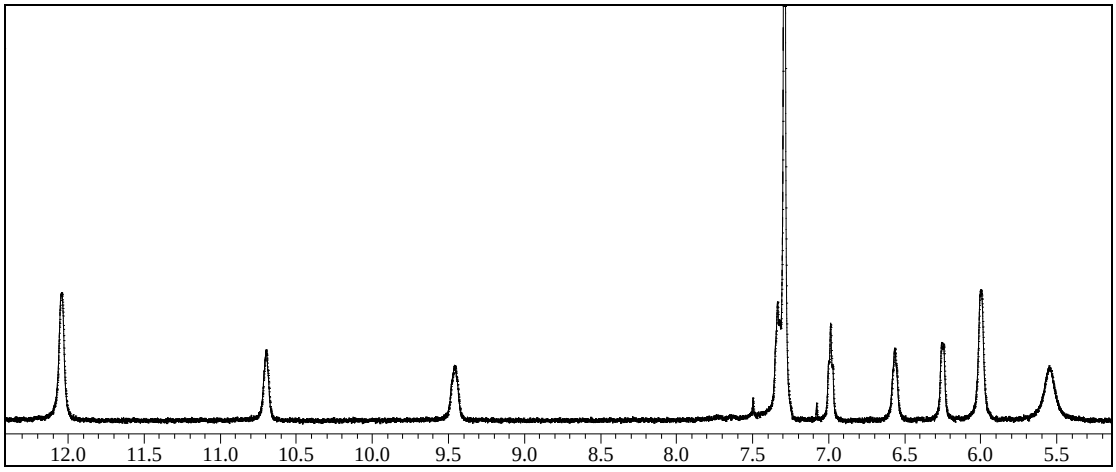

Fig. S5: [Yb(hfac)$_3$(DPEPO)]

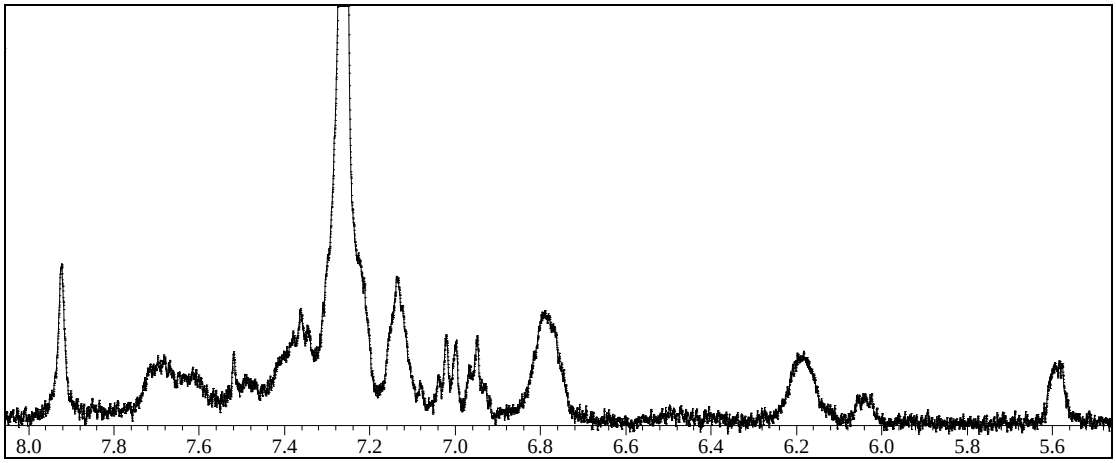

Fig. S6: [Nd(hfac)$_3$(DPEPO)]

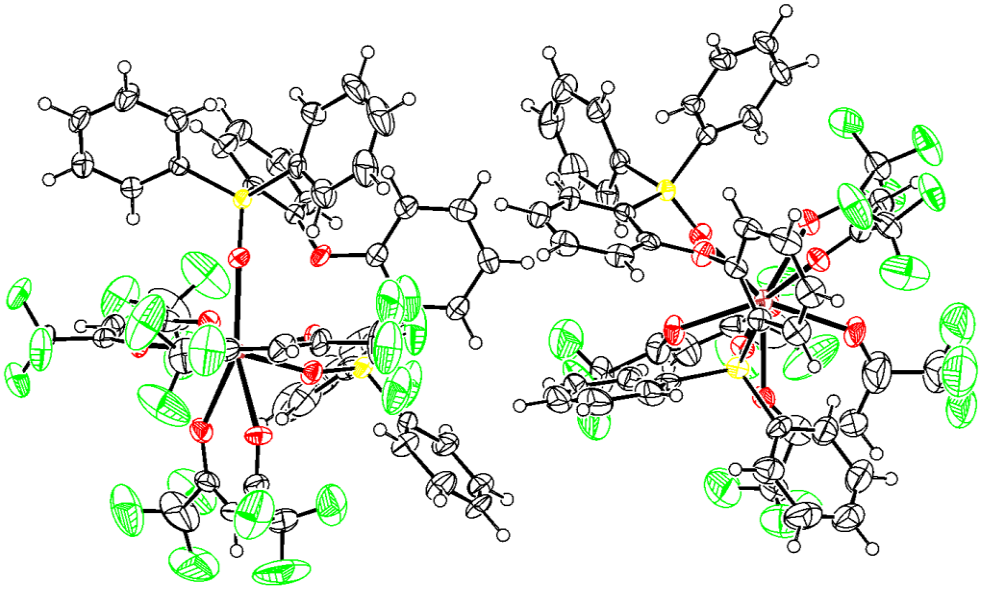

Figure S7: Asymmetric unit of [Gd(hfac)$_3$DPEPO]

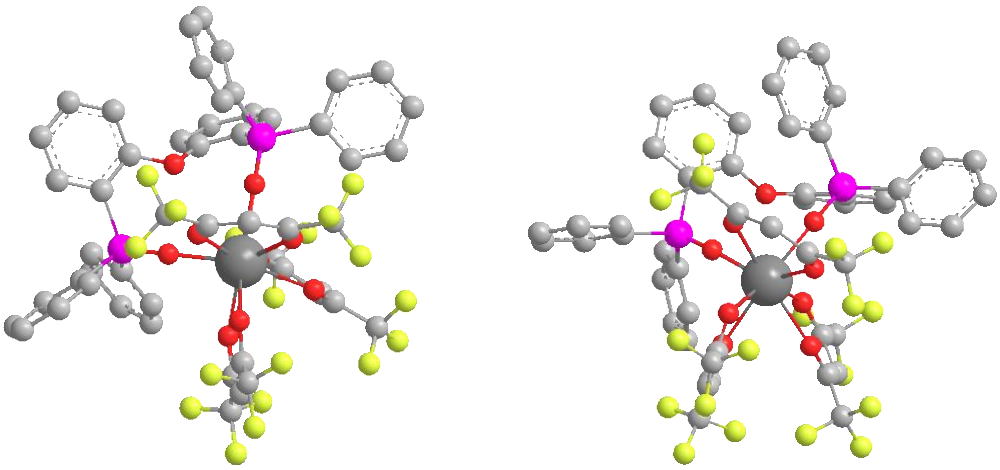

Fig. S8: Optimised structures of the ground (singlet spin) state (left) and of the lowest energy triplet spin state (right) of the [Eu(hfac)$_3$(DPEPO)].

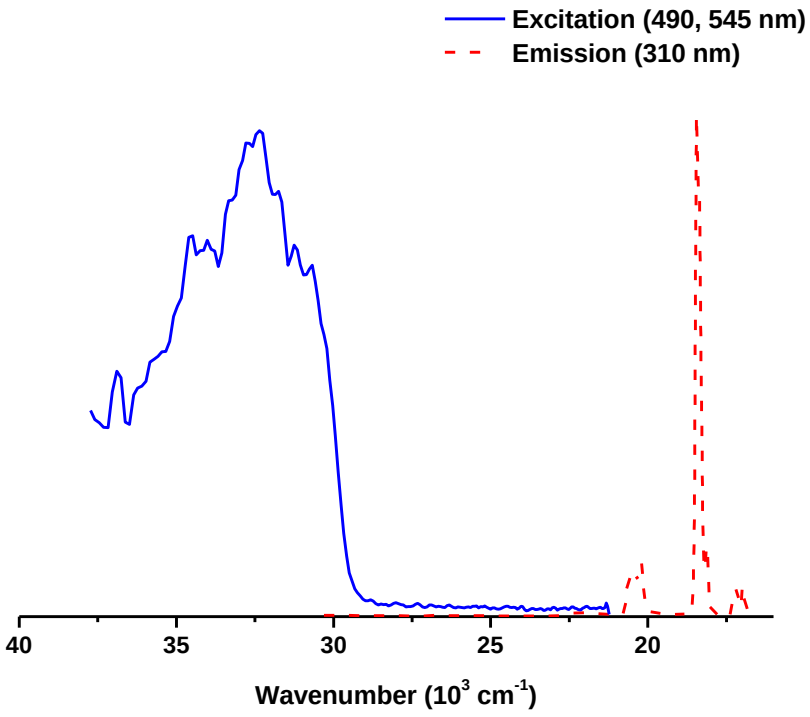

Fig. S9: Emission and excitation spectra of [Tb(hfac)$_3$DPEPO] at 77 K in degassed DCM solution.

Table S1 Selected bond lengths (Å) and angles (◦) for the complex $Gd(hfac)_3DPEPO$

Bond lengths/Å			
Gd(1)-O(1)	2.281(5)	Gd(101)-O(101)	2.298(5)
Gd(1)-O(2)	2.304(5)	Gd(101)-O(102)	2.264(4)
Gd(1)-O(3)	3.686(5)	Gd(101)-O(103)	3.935(4)
Gd(1)-O(4)	2.444(5)	Gd(101)-O(104)	2.376(5)
Gd(1)-O(5)	2.385(5)	Gd(101)-O(105)	2.438(5)
Gd(1)-O(6)	2.381(5)	Gd(101)-O(106)	2.414(5)
Gd(1)-O(7)	2.420(5)	Gd(101)-O(107)	2.376(5)
Gd(1)-O(8)	2.403(4)	Gd(101)-O(108)	2.365(5)
Gd(1)-O(9)	2.418(5)	Gd(101)-O(109)	2.425(5)
Angles/◦			
O(8)-Gd(1)-O(9)	69.21(17)	O(108)-Gd(101)-O(109)	72.15(18)
O(4)-Gd(1)-O(5)	71.51(16)	O(105)-Gd(101)-O(104)	69.96(19)
O(6)-Gd(1)-O(7)	71.93(16)	O(107)-Gd(101)-O(106)	70.53(15)
O(1)-Gd(1)-O(2)	103.41(17)	O(101)-Gd(101)-O(102)	89.87(17)

Table S2 Selected calculated bond-lengths (Å) and angles (°) for the complex $Eu(hfac)_3DPEPO$ in the lowest singlet state

Eu(1)-O(1)	2.360
Eu(1)-O(2)	2.332
Eu(1)-O(3)	4.076
Eu(1)-O(4)	2.479
Eu(1)-O(5)	2.405
Eu(1)-O(6)	2.435
Eu(1)-O(7)	2.460
Eu(1)-O(8)	2.466
Eu(1)-O(9)	2.421
O(8)-Eu(1)-O(9)	69.35
O(4)-Eu(1)-O(5)	70.21
O(6)-Eu(1)-O(7)	71.04
O(1)-Eu(1)-O(2)	91.18

Table S3 Selected calculated bond-lengths (Å) and angles (°) for the complex $Eu(hfac)_3DPEPO$ in the lowest triplet state

Eu(1)-O(1)	2.365
Eu(1)-O(2)	2.332
Eu(1)-O(3)	4.122
Eu(1)-O(4)	2.447
Eu(1)-O(5)	2.417
Eu(1)-O(6)	2.432
Eu(1)-O(7)	2.463
Eu(1)-O(8)	2.484
Eu(1)-O(9)	2.427
O(8)-Eu(1)-O(9)	70.44
O(4)-Eu(1)-O(5)	70.23
O(6)-Eu(1)-O(7)	71.12
O(1)-Eu(1)-O(2)	88.20