Supplementary Materials: Optical Properties of Heavily Fluorinated Lanthanide Tris β-Diketonate Phosphine Oxide Adducts

Adam N. Swinburne, Madeleine H. Langford-Paden, Tsz Ling Chan, Simon Randall, Fabrizio Ortu, Alan M. Kenwright and Louise S. Natrajan

Table S1. Single crystal X-ray data collection and structural refinement for the complexes and unit cell parameters for **5**.

Parameter	3 (CCDC 1472376)	4 (CCDC 1472377)	5	6 (CCDC 1472378)	7 (CCDC 1472379)	9 (CCDC 1472380)	CCDC 1472382	10 (CCDC 1472381)
Formula	$C_{33}H5F_{33}O_8PTb$	$C_{33}H_5F_{33}O_8PEr$	$C_{33}H_5F_{33}O_8PYb$	$C_{52}H_2Cl_2F_{51}O_8P_2Sm$	$C_{52}H_2Cl_2F_{51}O_8P_2Eu$	$C_{52}H_2Cl_2F_{51}O_8P_2Er$	$C_{52}H_2Cl_2F_{52}O_8P_2Tm$	$C_{52}H_2Cl_2F_{51}O_8P_2Yb$
Fw	1346.22	1354.60	1358.30	2006.73	2008.34	2023.64	2025.31	2029.42
cryst size, mm	0.21 × 0.45 × 0.73	0.05 × 0.10 × 0.30	-	0.40 × 0.50 × 0.80	0.25 × 0.40 × 0.50	0.40 × 0.40 × 0.80	0.50 × 0.70 × 1.00	0.20 × 0.30 × 0.40
crystal syst	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P-1$	$P-1$	$P-1$	Cc	$P2_1$	Cc	Cc	Cc
a, Å	11.8690(4)	11.8993(6)	11.8505(16)	19.5641(4)	11.8578(2)	19.4879(3)	19.5041(3)	19.4803(13)
b, Å	13.0006(5)	12.9623(6)	12.9958(16)	14.7311(4)	22.9499(4)	14.7720(2)	14.7989(2)	14.8269(10)
c, Å	16.0853(5)	16.1082(8)	15.980(2)	21.5669(6)	11.9125(2)	21.4793(3)	21.4651(3)	21.4352(15)
α, °	110.653(3)	110.744(5)	110.828(12)°	90	90	90	90	90
β, °	94.658(3)	94.010(4)	94.655(11)°	90.046(3)	104.640(2)	90.3530(14)	90.3628(12)	90.484(2)
γ, °	114.343(4)	114.162(5)	115.026(13)°	90	90	90	90	90
V, Å^3	2039.92(16)	2051.6(2)	2004.8(6)	6215.6(3)	3136.56(10)	6183.24(15)	6195.55(15)	6191.0(7)
Z	2	2	2	4	2	4	4	4
ρcalcd, g·cm^3	2.192	2.193	-	2.145	2.126	2.174	2.171	2.177
μ, mm^{-1}	1.976	2.286	-	1.291	1.343	5.786	1.779	6.057
$F(000)$	1288	1294	-	3852	1928	3876	3880	3884
No. of reflections (unique)	12681(7470)	14628(7318)	-	14238(8632)	11452(1045)	67392(9617)	28875(14561)	28875(14561)
S [a]	1.03	1.21	-	1.03	1.11	1.05	1.04	1.08
$R1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0396(0.0818)	0.0593(0.1129)	-	0.0356(0.1059)	0.0335(0.0838)	0.0323(0.0832)	0.0285(0.0743)	0.0310(0.0829)

*R*int	0.044	0.046	-	0.036	0.036	0.032	0.027	0.045
min., max. diff map, e Å^{-3}	−0.79, 1.14	−1.15, 1.52	-	−1.45, 1.47	−0.58, 1.12	−1.41, 1.41	−1.38, 1.49	−1.29, 1.27

[a] Conventional $R = \Sigma||F_O| - |F_C||/\Sigma|F_O|$; $R_W = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$; $S = [\Sigma w(F_O^2 - F_C^2)^2/\text{No. data} - \text{No. params})]^{1/2}$ for all data.

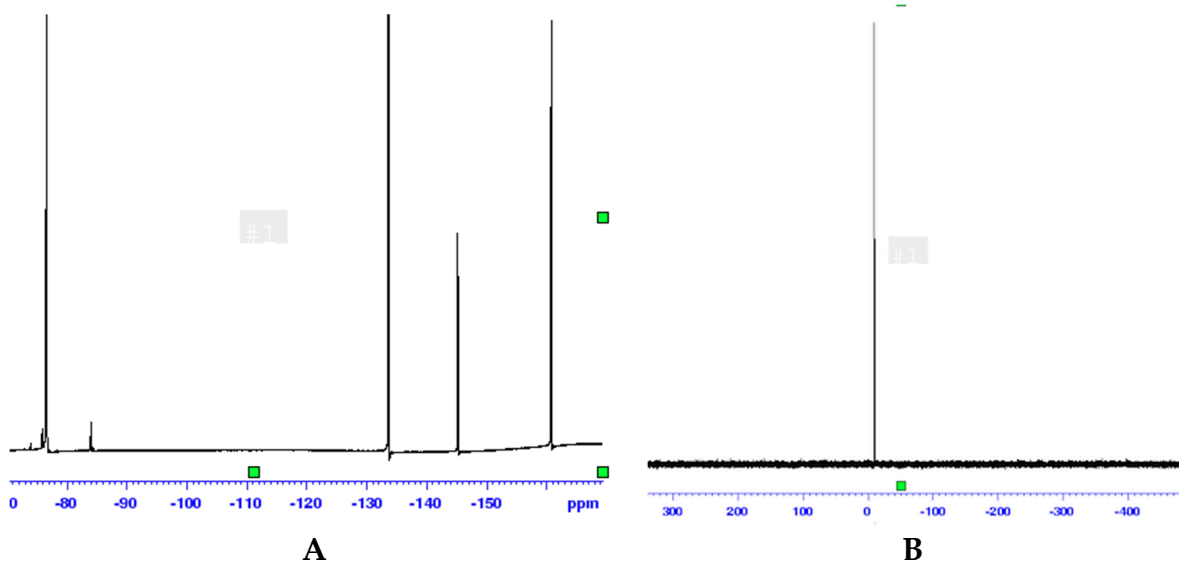

Figure S1. ^{19}F (**A**) and $^{31}P\{^{1}H\}$ (**B**) NMR spectra of $[Sm(hfac)_3\{(Ar^F)_3PO\}(H_2O)]$ (**1**) recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer at 295 K.

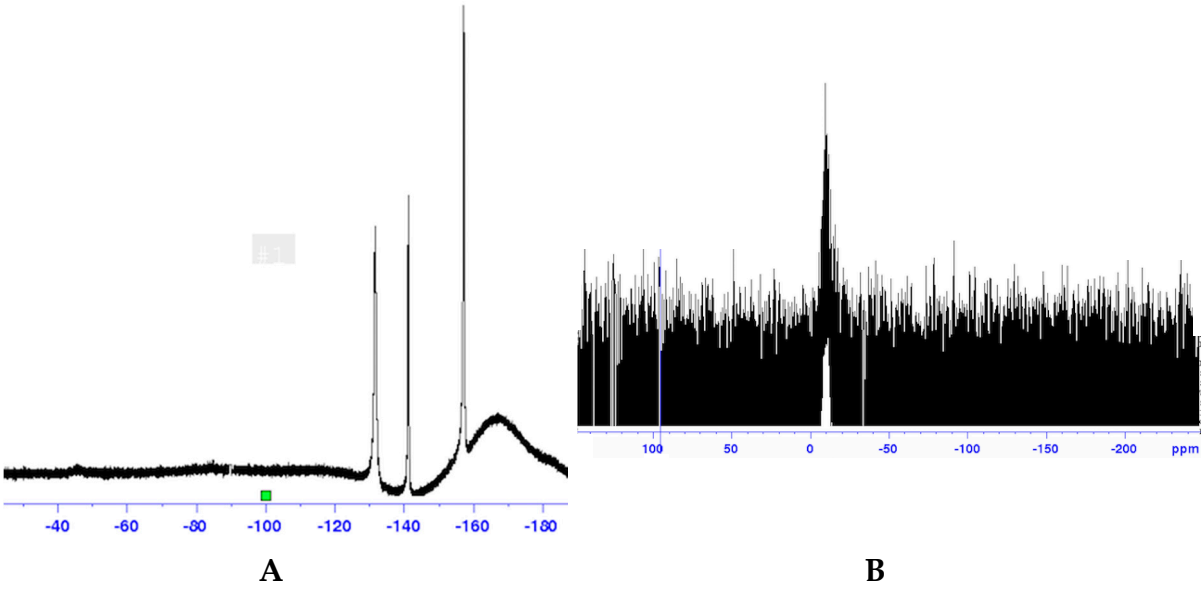

Figure S2. ^{19}F (**A**) and $^{31}P\{^{1}H\}$ (**B**) NMR spectra of $[Tb(hfac)_3\{(Ar^F)_3PO\}(H_2O)]$ (**3**) recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer at 295 K. Undulations in the baseline are due to the presence of Teflon™ that could not be satisfactorily corrected using baseline correction functions.

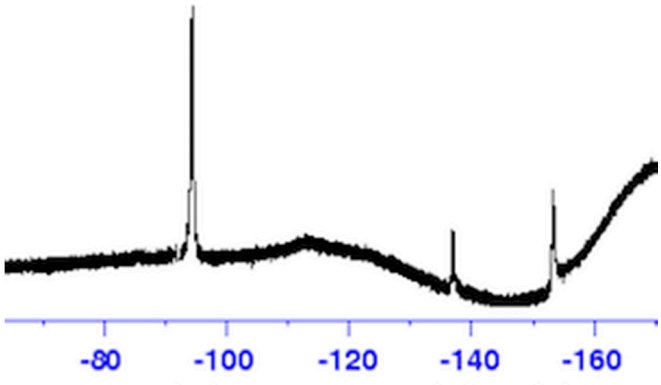

Figure S3. ^{19}F NMR spectrum of [Erhfac)$_3${$(Ar^F)_3PO$}(H_2O)] (**4**) recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer at 295 K. The $^{31}P\{^1H\}$ resonance of this compound was too broad to observe. Undulations in the baseline are due to the presence of Teflon™ that could not be satisfactorily corrected using baseline correction functions.

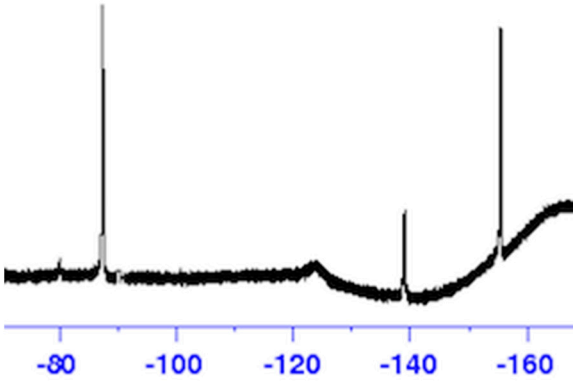

Figure S4. ^{19}F NMR spectrum of [Ybhfac)$_3${$(Ar^F)_3PO$}(H_2O)] (**5**) recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer at 295 K. The $^{31}P\{^1H\}$ resonance of this compound was too broad to observe.

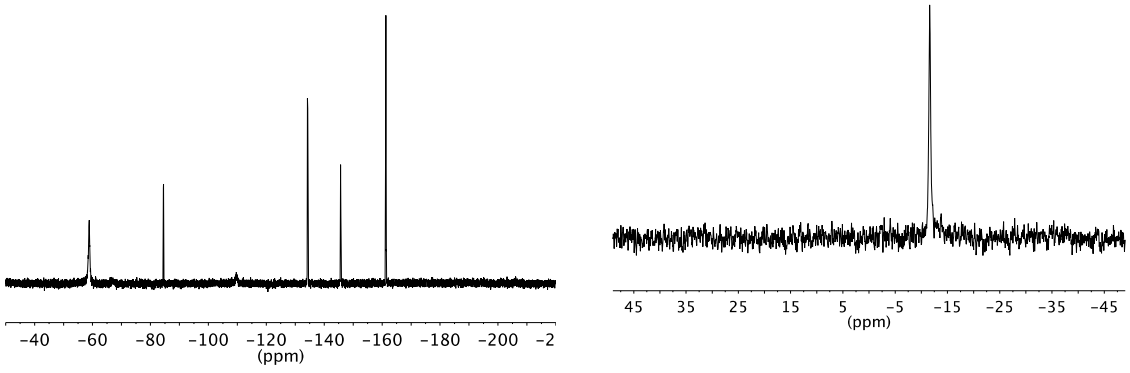

Figure S5. ^{19}F (**A**) and $^{31}P\{^1H\}$ (**A**) NMR spectra of [Tb(F_7-acac)$_3${$(Ar^F)_3PO$}$_2$] (**8**) recorded in d_6-acetone on a Varian Mecury-200 spectrometer at 298 K.

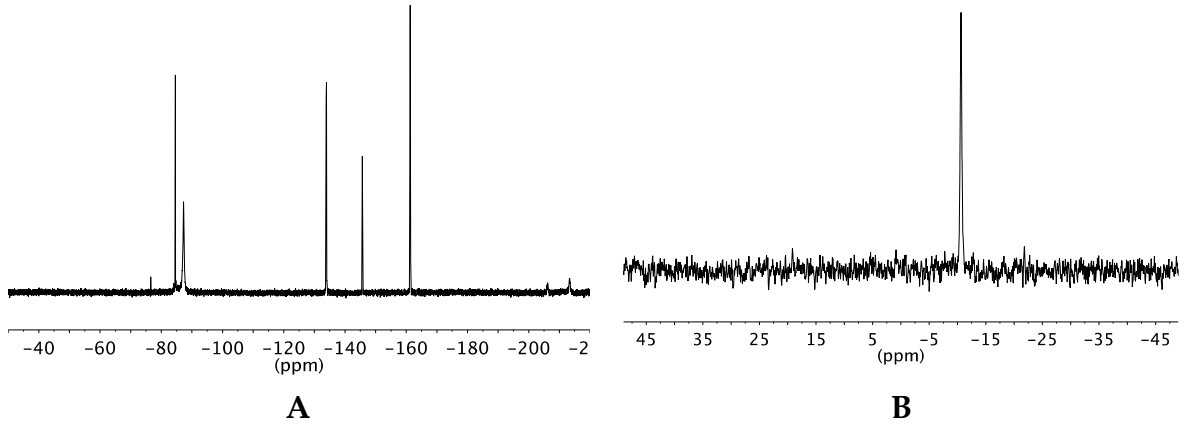

Figure S6. ^{19}F (**A**) and $^{31}P\{^{1}H\}$ (**B**) NMR spectra of [Er(F7-acac)3{(Ar^{F})3PO}2] (**9**) recorded in *d*6-acetone on a Varian Mecury-200 spectrometer at 298 K.

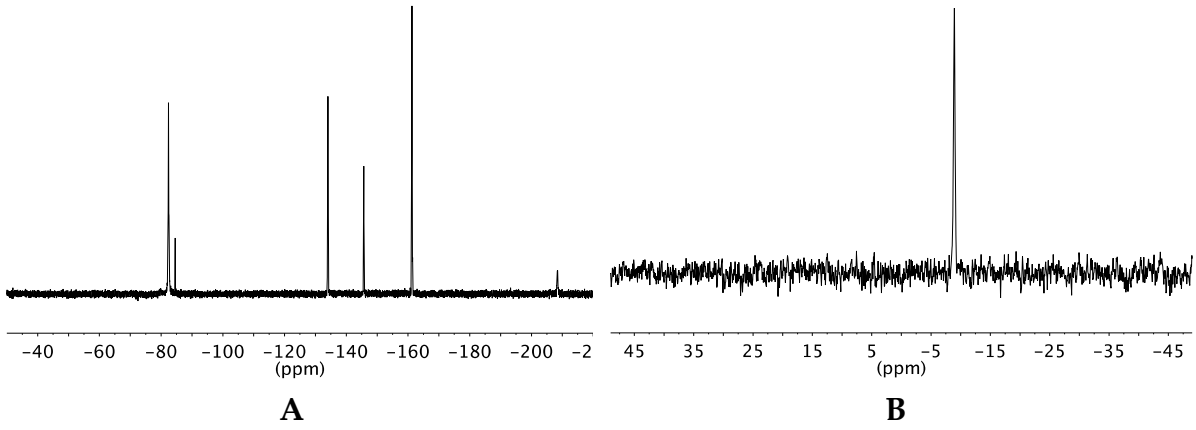

Figure S7. ^{19}F (**A**) and $^{31}P\{^{1}H\}$ (**B**) NMR spectra of [Yb(F7-acac)3{(Ar^{F})3PO}2] (**10**) recorded in *d*6-acetone on a Varian Mecury-200 spectrometer at 298 K.