Electronic supplementary information

Phosphonium based tetrakis dibenzoylmethane Eu(III) and Sm(III) complexes: synthesis, crystal structure and photoluminescence properties in weakly coordinating phosphonium ionic liquid

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Content:

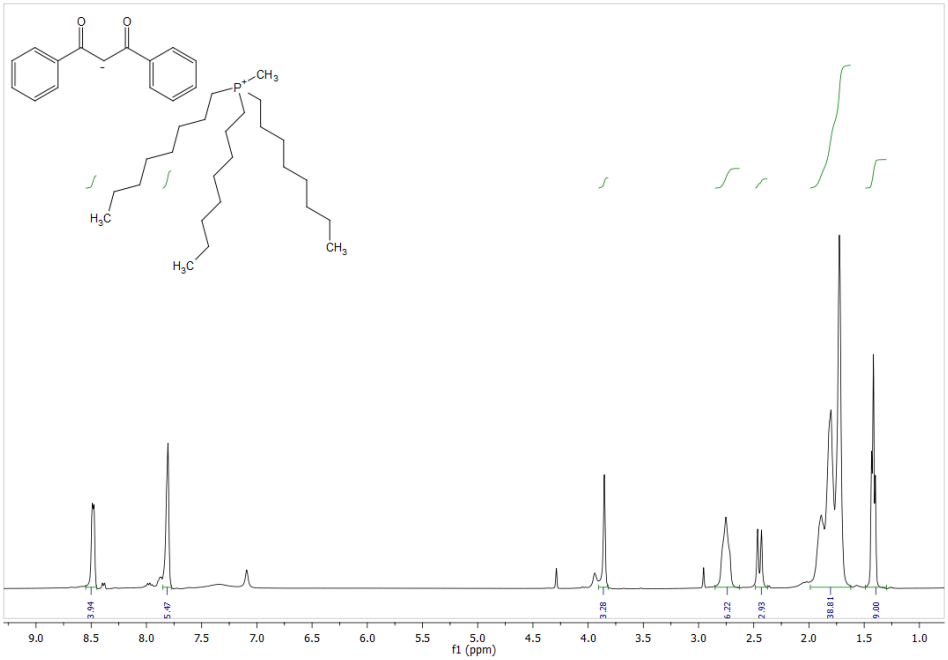

Figure S1: ^{1}H NMR $[P_{8,8,8,1}][dbm]$

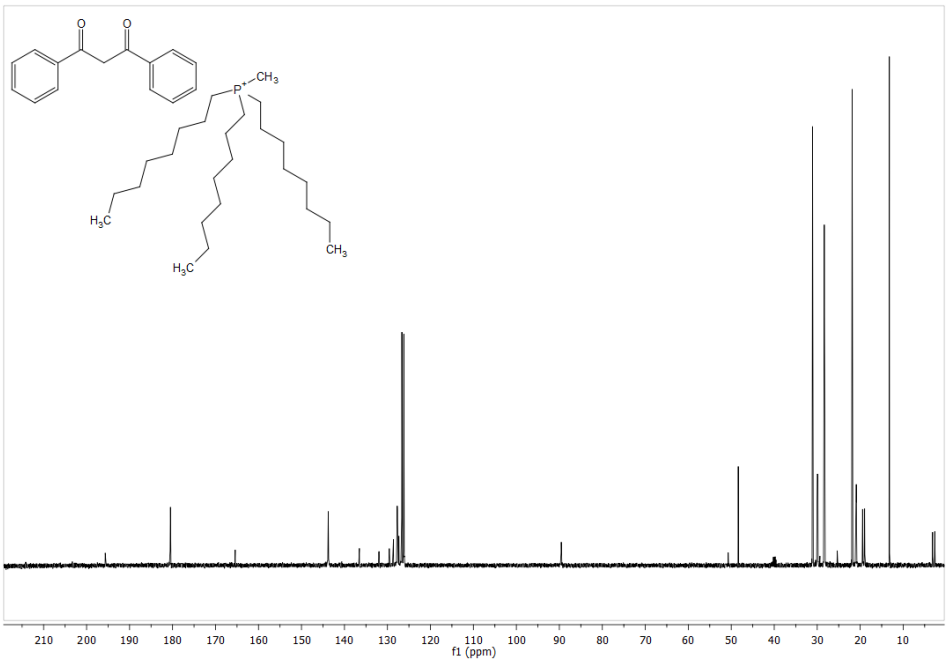

Figure S2: ^{13}C NMR $[P_{8,8,8,1}][dbm]$

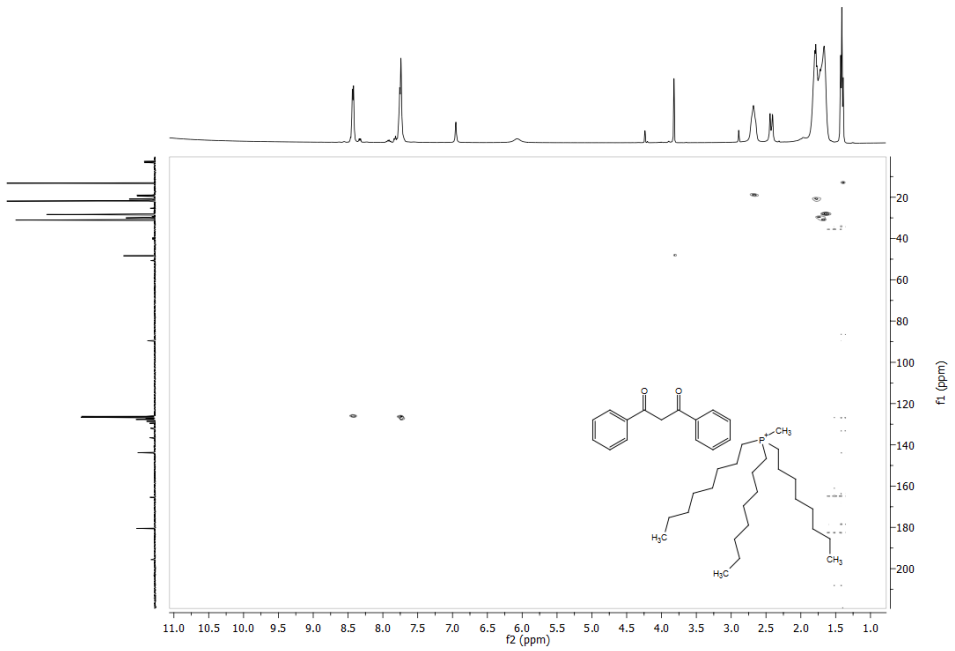

Figure S3: hmqc $[P_{8,8,8,1}][dbm]$

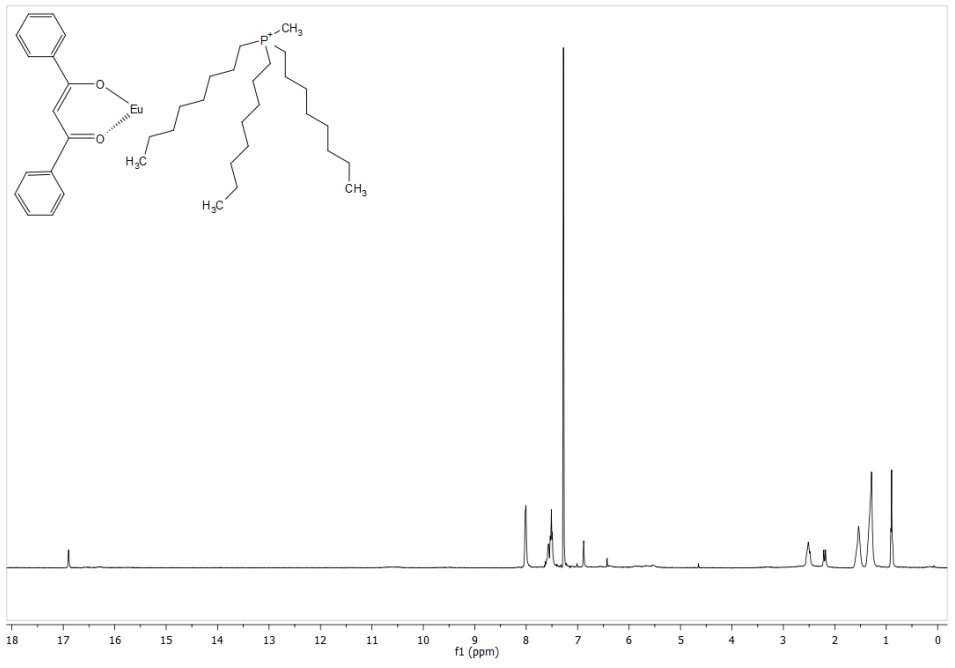

Figure S4: ^{1}H NMR $[P_{8,8,8,1}]$ $[Eu(dbm)_4]$ (400 MHz, $CDCl_3$)

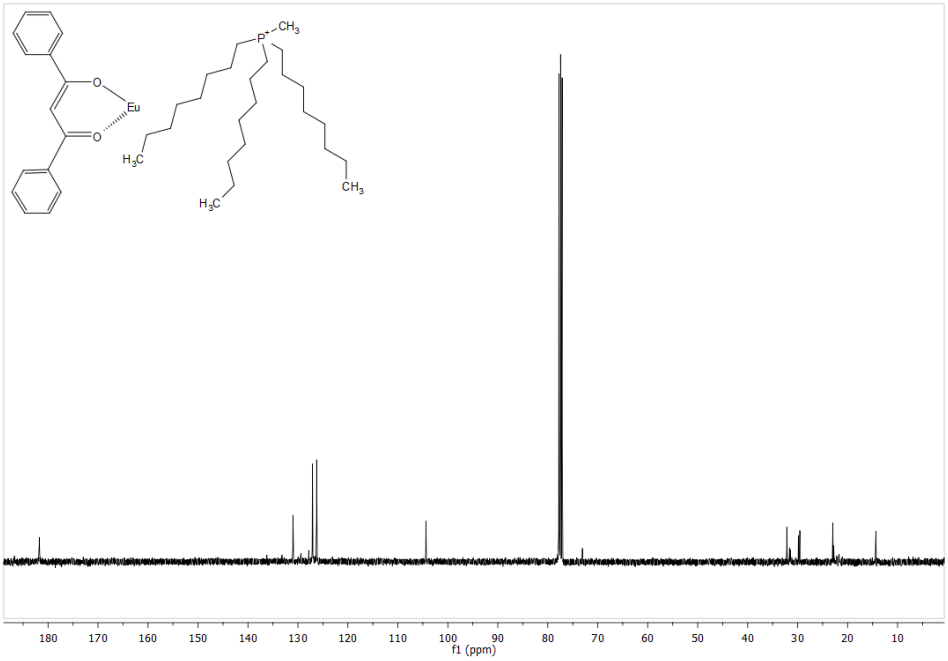

Figure S5: ^{13}C NMR $[P_{8,8,8,1}][Eu(dbm)_4]$ (400 MHz, $CDCl_3$)

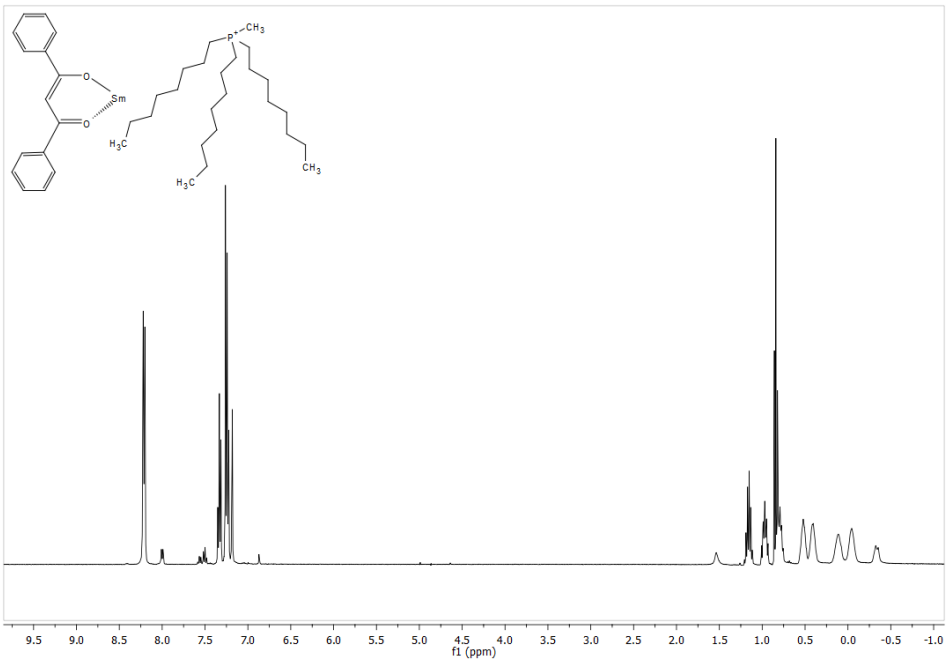

Figure S6: ^{1}H NMR $[P_{8,8,8,1}][Sm(dbm)_4]$ (400 MHz, $CDCl_3$)

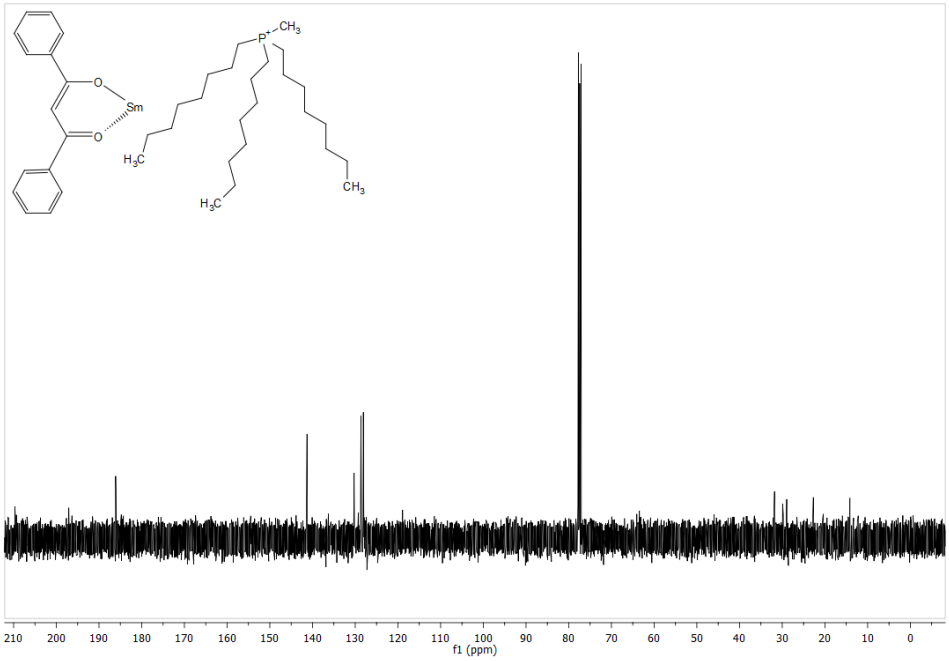

Figure S7: ^{1}H NMR $[P_{8,8,8,1}][Sm(dbm)_4]$ (400 MHz, $CDCl_3$)

X-ray diffraction

X-ray diffraction Data collections were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy) with a Pilatus 2M image plate detector. Complete datasets have been collected at a monochromatic wavelength of 0.6525 Å through the rotating crystal method. The crystals of $[P_{8,8,8,1}][Eu(dbm)_4]$ and $[P_{8,8,8,1}][Sm(dbm)_4]$ were dipped in N-paratone and mounted on the goniometer head with a nylon loop. The diffraction datasets were collected at 100 K, using a nitrogen stream supplied through an Oxford Cryostream 700. The diffraction data were indexed and integrated and scaled using XDS.[1] The structures were solved by direct methods using SIR2011,[2] Fourier analyzed and refined by the full-matrix least-squares based on F2 implemented in SHELXL-2014.[3] Coot program has been used for modelling.[4] Empirical absorption correction has been applied as implemented in the XABS2 program.[5] Anisotropic thermal motion modelling was then applied to atoms with full occupancy. In the final refinement, all non-hydrogen atoms were treated anisotropically and the hydrogen atoms were included at calculated positions with isotropic Ufactors = 1.2 Ueq and Ufactors = 1.5 Ueq for methyl groups. All the crystals tried for the Europium complex show disorder of the whole cell contents, due to pseudo translational phenomena found in the crystals. The diffraction pattern spots were fully

predicted with the reported monoclinic cell and no bigger cells could be identified to solve the problem. The situation did not improve even after recrystallizations and fresh data collections. Electron density maps showed clearly disorder on all the atoms that constitute the asymmetric unit, with occupancy of the preponderant part greater than 80%; refinement of this model required extensive use of restrains on ligands and cation bond lengths, angles and thermal factors.

Essential crystal and refinement data are reported in table S1.

Table S1: Crystallographic data for $[P_{8,8,8,1}][Eu(dbm)_4]$ and $[P_{8,8,8,1}][Sm(dbm)_4]$

	$[P_{8,8,8,1}][Eu(dbm)_4]$	**$[P_{8,8,8,1}][Sm(dbm)_4]$**
CCDC	1051982	1051983
Empirical formula	$2 \cdot (C_{85}\ H_{98}\ O_8\ P\ Eu)$	$C_{85}\ H_{98}\ O_8\ P\ Sm$
Formula weight	2861.12 Da	1428.95 Da
Temperature	100(2) K	100(2) K
Wavelength	0.6525 Å	0.6525 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c
Unit cell dimensions	a = 32.475(2) Å b = 22.412(3) Å c = 20.852(3) Å β = 102.214(13)°	a = 16.169 (3) Å b = 22.341(4) Å c = 20.962 (2) Å β = 100.60 (2)°
Volume	14833(3) $Å^3$	7443 (2) $Å^3$
Z	4	4
Density (calculated)	1.281 Kg/dm^3	1.275 Kg/dm^3
Absorption coefficient	0.679 mm^{-1}	0.638 mm^{-1}
F(000)	6000	2996
Theta range for data collection	0.589 to 22.574°	1.176 to 21.253°
Reflections collected	320493	58479
Independent reflections	24345 [R(int) = 3.2 %]	10324 [R(int) = 6.1%]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	24345 / 3690 / 1886	10324 / 1055 / 763

Goodness-of-fit on F^2	1.006	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1434	R1 = 0.0879, wR2 = 0.2248
R indices (all data)	R1 = 0.0632, wR2 = 0.1449	R1 = 0.1197, wR2 = 0.2559

References:

1 W. Kabsch, Acta Cryst. 2010, D66, 125.
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3 G. M. Sheldrick, Acta Cryst. 2008, 64, 112.
4 P. Emsley, K. Cowtan, Acta Cryst. 2004, D60, 2126.
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