

Supporting Information

Eu(III) Emission Band Changes Caused by Peripheral C-H/O Hydrogen Bonding

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General Methods. Acetone- d_6 (D, 99.9%) and $CDCl_3$ (D, 99.8%) were obtained from Cambridge Isotope laboratories, Inc. All chemicals and solvents were of commercial reagent quality and were used without further purification. 1H (500 MHz), ^{19}F (470 MHz) and ^{31}P NMR (200 MHz) spectra were recorded on JEOL ECP-500. Chemical shifts were reported in δ ppm, referenced to internal tetramethylsilane standard for 1H NMR, external hexafluorobenzene standard for ^{19}F NMR and external 85% H_3PO_4 standard for ^{31}P NMR. ESI-mass spectra were measured on JEOL JMS-700MStation. The observed and calculated values refer to the most abundant peak. IR spectra were recorded on JASCO FT/IR-420 spectrometer. Elemental analyses were performed by Perkin Elmer 2400II.

Preparation of [tris(diphenylphosphinyl)methane]tris(hexafluoroacetylacetonato)-europium(III): Eu(hfa) $_3$ (TPPM). TPPM (302 mg, 4.9×10^{-4} mol) and $EuCl_3 \cdot 6H_2O$ (577 mg, 1.6×10^{-3} mol) were placed in a 20 mL flask, and the flask was purged with Ar gas. Acetonitrile (15 mL) was added and the solution was stirred for 5 h at room temperature. The resulting white suspension was added by hexafluoroacetylacetonone (hfa- H_2 ; 0.67 mL, 4.7×10^{-3} mol) and ethanol (3 mL). The reaction mixture became a clear solution and was then stirred for 16 h at room temperature. The reaction mixture was evaporated to dryness, and the residue was extracted with toluene (20 mL). After the suspension was stirred for 1 h, the insoluble material was removed by filtration and the filtrate was evaporated to dryness. A pale yellow solid was recrystallized from chloroform/hexane to attain colorless crystals (260 mg, 38% based on TPPM): IR (ATR) ν_{max} / cm^{-1} 1649, 1556, 1531, 1483, 1442, 1252, 1200, 1137, 1097, 798, 768, 733, 692, 685, 660; ^{19}F NMR (470 MHz, $CDCl_3$, C_6F_6) δ -79.4, -80.0; ^{31}P NMR (200 MHz, $CDCl_3$, H_3PO_4) δ 9.17; ESI-Mass (m/z) calcd for $C_{47}H_{33}EuF_{12}O_7P_3$ ($Eu(hfa)_2(TPPM)^+$) 1183.046 (^{153}Eu), found 1183.043 (^{153}Eu); elemental analysis calcd for $C_{52}H_{34}EuF_{18}O_9P_3 \cdot 5CHCl_3$: C, 34.46; H, 1.98%; found: C, 34.46; H, 1.62%.

Preparation of [tris(diphenylphosphinyl)methane]tris(hexafluoroacetylacetonato)-samarium(III): Sm(hfa) $_3$ (TPPM). The Sm(III) complex was synthesized by the same procedure as that used for $Eu(hfa)_3(TPPM)$, except for the use of $SmCl_3 \cdot 6H_2O$ instead of $EuCl_3 \cdot 6H_2O$. Colorless crystals were isolated (193 mg, 43% based on TPPM). IR (ATR) ν_{max} / cm^{-1} 1649, 1558, 1523, 1506,

1473, 1441, 1253, 1198, 1138, 1112, 1093, 799, 791, 769, 732, 697, 686, 660; ^{19}F NMR (470 MHz, CDCl_3 , C_6F_6) δ -76.0, -76.1; ^{31}P NMR (200 MHz, CDCl_3 , H_3PO_4) δ 40.78; ESI-Mass (m/z) calcd for $\text{C}_{47}\text{H}_{33}\text{F}_{12}\text{O}_7\text{P}_3\text{Sm}(\text{Sm}(\text{hfa})_2(\text{TPPM})^+)$ 1182.0 (^{152}Sm), found 1182.0 (^{152}Sm); elemental analysis calcd for $\text{C}_{52}\text{H}_{34}\text{F}_{18}\text{O}_9\text{P}_3\text{Sm}\cdot 2\text{CHCl}_3$: C, 39.87; H, 2.23%; found: C, 39.74; H, 2.05%.

Crystallography. Colorless single crystals of $\text{Eu}(\text{hfa})_3(\text{TPPM})$ obtained from chloroform/hexane and acetone/water solutions were mounted on a glass fiber using epoxy resin glue. All measurements were made with a graphite monochromated Mo-K α radiation on a Rigaku RAXIS RAPID utilizing its imaging plate as the area detector. The data were collected at a temperature of -80 ± 1 °C to a maximum 2θ value of 54.9° . Corrections for decay and Lorentz-polarization effects were made with empirical absorption correction solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the crystal structure crystallographic software package. We confirmed the CIF data by using the checkCIF/PLATON service. The supplementary crystallographic data for this paper are contained in CCDC-852900 (crystal 1) and 852901 (crystal 2). Their data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Optical Measurements. Emission spectra of Eu(III) complexes were measured with a Hitachi F-4500 spectrometer. Emission spectra at various temperatures were measured using a nitrogen cryostat (Oxford Instruments, Optistat DN). Emission quantum yields of Eu(III) complexes were obtained and compared with emission signal integration (570–640 nm) of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ as a reference ($\Phi = 0.65$ in acetone- d_6) using an excitation wavelength of 465 nm.^{1,2} Emission quantum yield of Sm(III) complex was obtained and compared with emission signal integration (530–680 nm) of $\text{Sm}(\text{hfa})_3(\text{phen})_2$ as a reference ($\Phi = 0.014$ in acetone) using an excitation wavelength of 360 nm.^{2,3} Emission lifetimes were measured with the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, $\lambda = 1064$ nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a

digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. High-resolution emission spectra were obtained with SPEX FluoroLog-3.

References

- 1 K. Nakamura, Y. Hasegawa, H. Kawai, N. Yasuda, Y. Tsukahara and Y. Wada, *Thin Solid Films*, **2008**, *516*, 2376-2381.
- 2 J. N. Demas and G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991-1024.
- 3 Y. Hasegawa, S. Tsuruoka, T. Yoshida, H. Kawai and T. Kawai, *J. Phys. Chem. A* **2008**, *112*, 803-807.

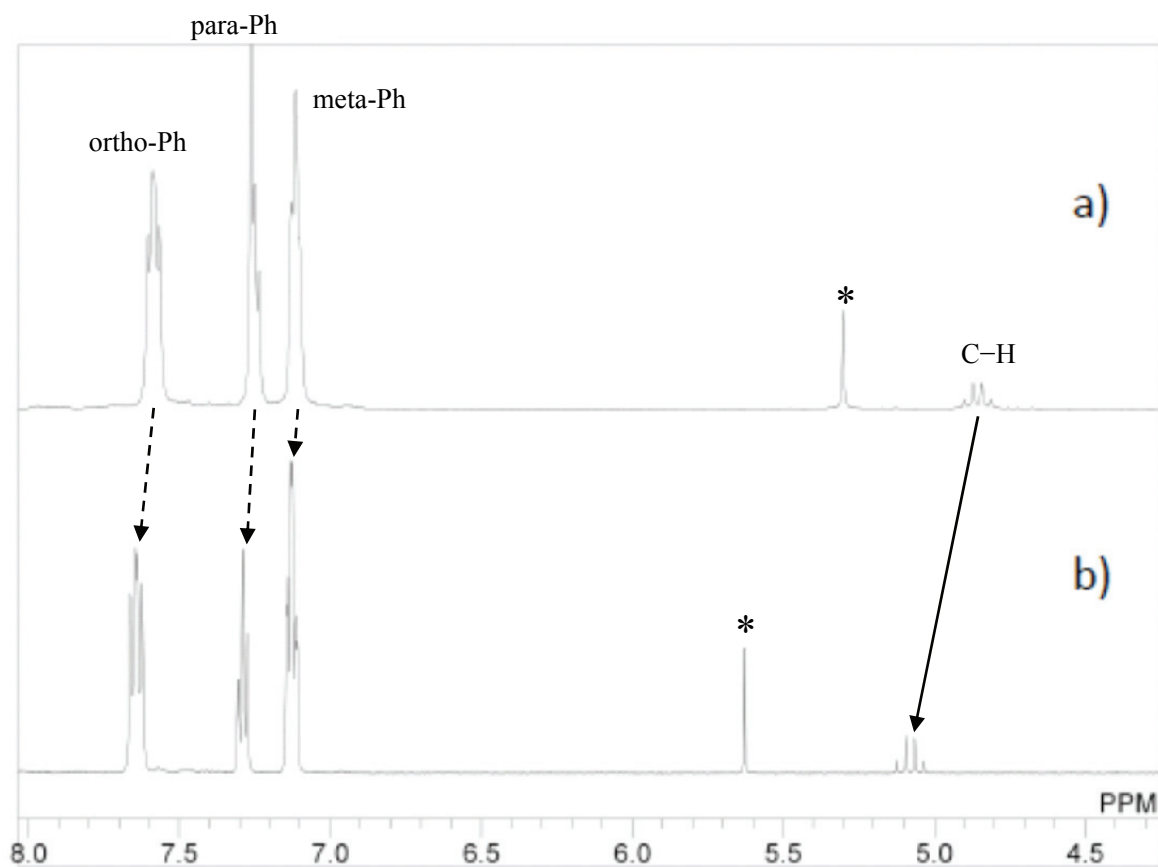
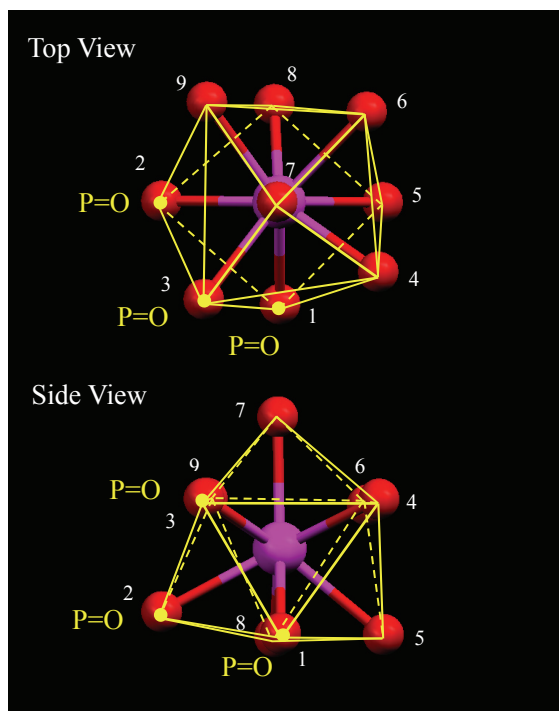
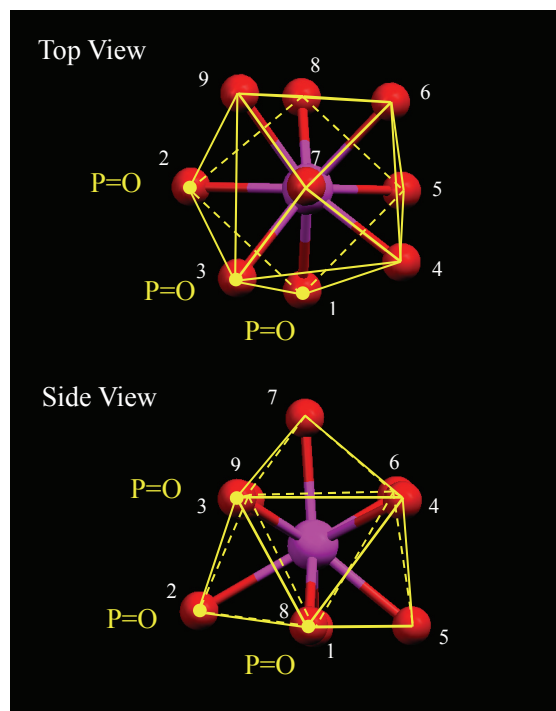


Figure S1. ¹H NMR spectra of TPPM in a) CDCl₃ and b) [D₆]acetone. The asterisks (*) correspond to dichloromethane: H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512.

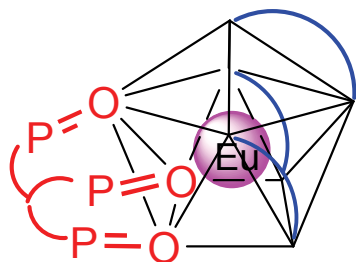
a) Crystal 1



b) Crystal 2



c)



d)

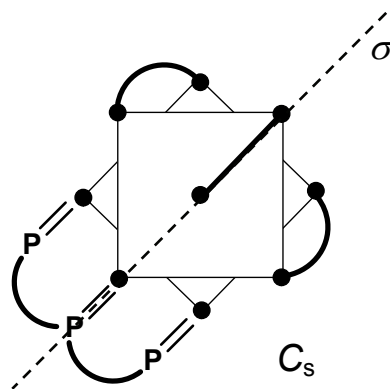


Figure S2. Coordination polyhedrons of a) **crystal 1** and b) **crystal 2**. c) Simplified diagram of the coordination structure of **crystal 1** and **crystal 2**. d) Geometrical image of $\text{Eu}(\text{hfa})_3(\text{TPPM})$ as viewed from above. Coordinated oxygen atoms are shown as dots in the images and the curved lines between oxygen atoms represent the hfa linkages.

Table S1. Observed Dihedral Angles (δ_i), Dihedral Angles of Ideal Monocapped Square Antiprism (θ_i) and Measure Shape Criterion, $S(C_{4v})$ for Crystal 1

Edge	δ_i	θ_i	$\delta_i - \theta_i$
O2–O5	12.95	0.0	13.0
O1–O5	78.72	69.1	9.6
O5–O8	76.07	69.1	7.0
O8–O2	72.88	69.1	3.8
O2–O1	70.00	69.1	0.9
O4–O5	53.91	53.0	0.9
O5–O6	50.26	53.0	-2.7
O6–O8	45.00	53.0	-8.0
O8–O9	50.48	53.0	-2.5
O9–O2	59.75	53.0	6.8
O2–O3	61.75	53.0	8.8
O3–O1	58.66	53.0	5.7
O1–O4	43.93	53.0	-9.1
O4–O6	44.51	37.6	6.9
O6–O9	47.66	37.6	10.1
O9–O3	19.91	37.6	-17.7
O3–O4	38.80	37.6	1.2
O7–O4	56.12	59.0	-2.9
O7–O6	48.99	59.0	-10.0
O7–O9	63.49	59.0	4.5
O7–O3	67.53	59.0	8.5

$S(C_{4v}) = 7.88$

Table S2. Observed Dihedral Angles (δ_i), Dihedral Angles of Ideal Monocapped Square Antiprism (θ_i) and Measure Shape Criterion, $S(C_{4v})$ for Crystal 2

Edge	δ_i	θ_i	$\delta_i - \theta_i$
O2–O5	9.57	0.0	9.6
O1–O5	74.65	69.1	5.6
O5–O8	75.90	69.1	6.8
O8–O2	71.75	69.1	2.7
O2–O1	71.13	69.1	2.0
O4–O5	54.82	53.0	1.8
O5–O6	49.80	53.0	-3.2
O6–O8	45.01	53.0	-8.0
O8–O9	48.48	53.0	-4.5
O9–O2	61.93	53.0	8.9
O2–O3	60.54	53.0	7.5
O3–O1	55.74	53.0	2.7
O1–O4	47.52	53.0	-5.5
O4–O6	44.36	37.6	6.8
O6–O9	47.28	37.6	9.7
O9–O3	17.47	37.6	-20.1
O3–O4	38.65	37.6	1.1
O7–O4	54.25	59.0	-4.8
O7–O6	53.61	59.0	-5.4
O7–O9	62.36	59.0	3.4
O7–O3	68.38	59.0	9.4

$S(C_{4v}) = 7.39$

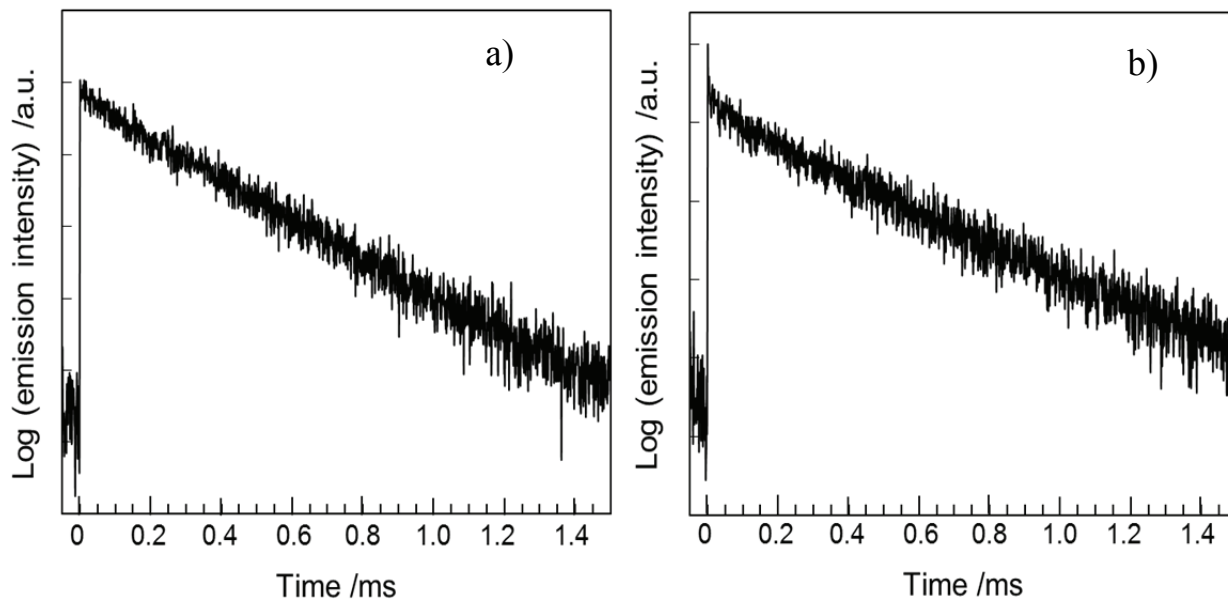


Figure S3. Decay profiles of $\text{Eu}(\text{hfa})_3(\text{TPPM})$ in a) CDCl_3 and b) $[\text{D}_6]\text{acetone}$.

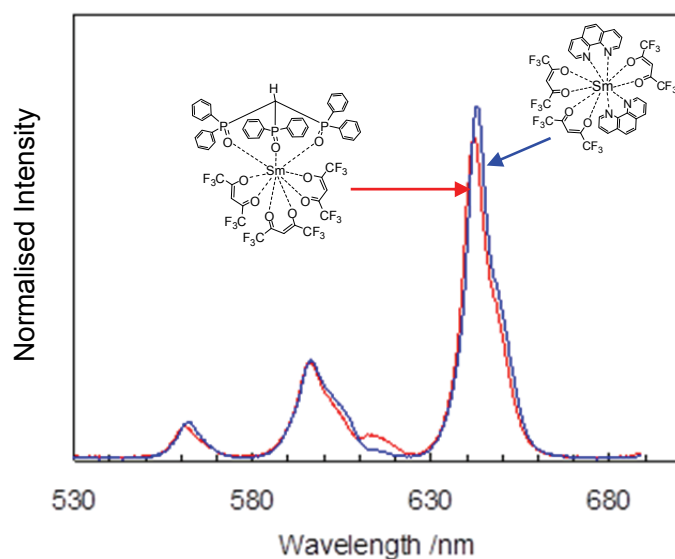


Figure S4. Emission spectra of $\text{Sm}(\text{hfa})_3(\text{TPPM})$ and $\text{Sm}(\text{hfa})_3(\text{phen})_2$ in acetone at room temperature. The spectral intensity is normalised to the magnetic dipole transition (${}^4\text{G}_{5/2}-{}^6\text{H}_{7/2}$).
 $\text{Sm}(\text{hfa})_3(\text{phen})_2$: Y. Hasegawa, S. Tsuruoka, T. Yoshida, H. Kawai, T. Kawai, *J. Phys. Chem. A* **2008**, *112*, 803.

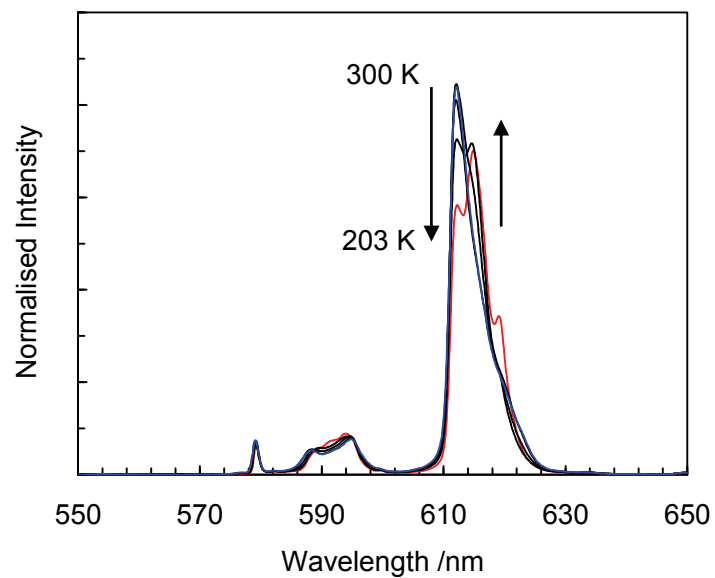


Figure S5. Emission spectra of Eu(hfa)₃(TPPM) at 300, 273, 253, 223, 203 K (1.36 M acetone /dichloromethane, $\lambda_{\text{ex}} = 350$ nm). The spectral intensity is normalised to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (magnetic-dipole) transition.