Supporting Information

Systematic Study of the Optical Properties of Mononuclear Hybrid Organo-Inorganic Lanthanoid Complexes.

Matias Zapata-Lizama^{a,b}, Patricio Hermosilla-Ibáñez^{a,b}, Diego Venegas-Yazigi^{a,b}, Guillermo Mínguez Espallargas^c, Lauro June Queiroz Maia^d, Gisane Gasparotto^d, Ricardo Costa de Santana^d*, Walter Cañón-Mancisidor^{a,b}*.

- a. Facultad de Química y Biología, Depto. de Química de los Materiales, Universidad de Santiago de Chile, USACH, Chile.
- b. Centre for the Development of Nanoscience and Nanotechnology, CEDENNA, Chile.
- c. Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Paterna, Spain.
- d. Instituto de Física, Universidade Federal de Goiás, Goiânia (GO), Brazil.

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1. Synthesis

All chemical reagents were directly used without further purification. [NBu₄]₄[PW₁₁O₃₉H₃] was synthesized according to a previously reported method.¹ Hydrothermal synthesis was done using a Parr reactor of 23 ml model 4749.

The corresponding hydrated Ln^{III} acetates (0.1 mmol), LnAc₃·XH₂O where Ln^{III} = Dy^{III} (LM⁴-1-Dy), Tb^{III}(LM⁴-1-Tb), Eu^{III}(LM⁴-1-Eu), Nd^{III}(LM⁴-1-Nd), Er^{III}(LM⁴-1-Er), Ho^{III}(LM⁴-1-Ho) and Gd^{III}(LM⁴-1-Gd) were mixed with [NBu₄]₄[PW₁₁O₃₉H₃] (365 mg, 0.1 mmol) and phenanthroline (0.036 mg, 0.2 mmol) in 10 mL of water in a Parr reactor and heated under autogenous pressure at 160 °C for 48 hours. The reaction mixture was filtered off, and pale pink crystals of LM⁴-1-Ln, suitable for X-ray diffraction, were obtained by mechanical separation. Then, these crystals were wash with water and acetone. The synthesis was done according to a previously reported method².

2. Compound Characterization.

 $[NBu_4]_3 [DyH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Dy): FTIR v (cm^{-1}): 3548 (w), 2964 (m), 2878 (m), 1470 (m), 1382 (s), 1077 (s), 1047 (w), 973 (m), 893 (s), 857 (s), 806 (s), 795 (s), 511 (s). Elem. Anal. for Dy_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,91%(21.76%), N = 2.48%(2.58%), H = 3.24%(3.33%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Dy : W : P = (1.07)1 : (10.96)11 : (0.95)1.$

 $[NBu_4]_3[TbH(PW_{11}O_{39})(phen)_2]\cdot H_2O (LM^4-1-Tb): FTIR v (cm^{-1}): 3540 (m), 2966, (m), 2929(m), 2869 (m), 2339 (w), 1981 (w), 1622 (w), 1518, (w), 1466(m), 1455 (m), 1377 (m), 1070 (m), 975 (s), 891 (s), 791 (s), 742 (s), 594 (s), 510 (s). Elem. Anal. for Tb_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,93%(21.85%), N = 2.49%(2.38%), H = 3.25\%(3.27\%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Tb : W : P = (0.99)1 : (10.95)11 : (0.99)1.$

 $[NBu_4]_3[EuH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Eu): FTIR v (cm^{-1}): 3566 (w), 2964 (m), 2870 (m), 1458 (m), 1143 (s), 1084 (s), 1046 (w), 953 (m), 885 (s), 812 (s), 715 (s), 512 (s). Elem. Anal. for Eu_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,91%(21.76%), N = 2.48%(2.58%), H = 3.24%(3.33%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Eu : W : P = (1.02)1 : (11.10)11 : (1.05)1.$

 $[NBu_4]_3[NdH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Nd): FTIR v (cm^{-1}): 3541 (w), 2959 (m), 2926 (m), 1468 (m), 1077 (s), 970 (s), 887 (w), 793 (s), 590 (s), 515 (s). Elem. Anal. for Nd_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,91%(21.76\%), N = 2.48\%(2.58\%), H = 3.24\%(3.33\%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Nd : W : P = (1.07)1 : (10.92)11 : (1.05)1.$

 $[NBu_4]_3 [ErH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Er): FTIR v (cm^{-1}): 3544 (w), 2961 (m), 2934(m), 1458 (m), 1377 (s), 1078 (s), 973 (m), 884 (s), 794 (s), 592 (s), 666 (s), 521 (s). Elem. Anal. for Er_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,89%(21.96\%), N = 2.48\%(2.34\%), H = 3.24\%(3.15\%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Er : W : P = (0.98)1 : (11.03)11 : (0.97)1.$

 $[NBu_4]_3[HoH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Ho): FTIR v (cm^{-1}): 3550 (w), 2958 (m), 2934 (m), 1472 (m), 1376 (s), 1073 (s), 964 (w), 889 (s), 806 (s), 730 (s), 504 (s). Elem. Anal. for Ho_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,90%(21.82\%), N = 2.48\%(2.34\%), H = 3.24\%(3.30\%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Ho : W : P = (1.07)1 : (11.07)11 : (1.11)1.$

 $[NBu_4]_3[GdH(PW_{11}O_{39})(phen)_2] \cdot H_2O (LM^4-1-Gd): FTIR v (cm^{-1}): 3547 (w), 2965 (m), 2925 (m), 2870 (m), 1463 (m), 1378(w), 1064 (s), 972 (s), 888 (w), 796 (s), 612 (s), 505 (s). Elem. Anal. for Gd_1P_1W_{11}O_{40}C_{72}H_{127}N_7; Teo. (Exp) C = 21,94%(21.88%), N = 2.49%(2.51%), H = 3.25%(3.29%). Elemental ratio estimated by electron probe microanalysis (EPMA): (Exp) Teo Gd : W : P = (0.97)1 : (1.02)1 : (11.03)1.$

2.1. Fourier transform infrared spectroscopy (FTIR)



Fig. S1 Infrared Spectra of compounds $[NBu_4]_3[LnH(PW_{11}O_{39})(phen)_2] \cdot H_2O$, where $Ln^{III} = Dy^{III} (LM^4-1-Dy)$, $Tb^{III}(LM^4-1-Tb)$, $Eu^{III}(LM^4-1-Eu)$, $Nd^{III}(LM^4-1-Nd)$, $Er^{III}(LM^4-1-Er)$, $Ho^{III}(LM^4-1-Ho)$ and $Gd^{III}(LM^4-1-Gd)$.

2.2. Electron Probe Microanalysis

Table S1. Atomic relation obtained of tungsten, phosphorous and lanthanide by electron probe microanalysis for the crystalline materials of compounds $[NBu_4]_3[LnH(PW_{11}O_{39})(phen)_2]\cdot H_2O$, where $Ln^{III} = Dy^{III} (LM^4-1-Dy)$, $Tb^{III}(LM^4-1-Tb)$, $Eu^{III}(LM^4-1-Eu)$, $Nd^{III}(LM^4-1-Nd)$, $Er^{III}(LM^4-1-Er)$, $Ho^{III}(LM^4-1-Ho)$ and $Gd^{III}(LM^4-1-Gd)$. In parenthesis expected value.

Compound	Tungsten	Phosphorous	Lanthanide
LM ⁴ -1-Dy	10.96 (11)	0.95 (1)	1.07 (1)
LM ⁴ -1-Tb	10.95 (11)	0.99 (1)	0.99 (1)
LM ⁴ -1-Eu	11.10 (11)	1.05 (1)	0.98 (1)
LM ⁴ -1-Nd	10.92 (11)	1.05 (1)	1.07 (1)
LM ⁴ -1-Er	11.03 (11)	0.97 (1)	0.98 (1)
LM ⁴ -1-Ho	11.07 (11)	1.11 (1)	1.07 (1)
LM ⁴ -1-Gd	11.03 (11)	1.02 (1)	0.97 (1)

3. X-Ray Diffraction

3.1. Single Crystal X-Ray Diffraction

A single crystal for each compound was taken directly from the synthesis vessel and examined under microscope, suggesting acceptable quality. It was then mounted on the tip of a glass fibre. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-1951517 for LM⁴-1-Tb, CCDC-1962564 for LM⁴-1-Eu, CCDC-1962563 for LM⁴-1-Nd and CCDC-1951518 for LM⁴-1-Ho. The crystallographic data of LM⁴-1-Dy, LM⁴-1-Er and LM⁴-1-Gd has been reported previously².

Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

Table S2 Crystallography data and structure refinement for $[NBu_4]_3[Ln(HPW_{11}O_{39})(phen)_2] \cdot H_2O$, where $Ln^{III} = Tb^{III}(LM^4-1-Tb)$, $Eu^{III}(LM^4-1-Eu)$, $Nd^{III}(LM^4-1-Nd)$ and $Gd^{III}(LM^4-1-Ho)$.

Complex	LM4-1-Tb	LM ⁴ -1-Eu	LM ⁴ -1-Nd	LM ⁴ -1-Ho
CCDC	1951517	1962564	1962563	1951518
Formula weight	3942.94	3935.07	3927.35	3948.94
Temperature/K	297(2)	297(2)	297(2)	297(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P21/c	P21/c
a/Å	23.604(2)	23.6618(19)	23.735(2)	23.5545(17)
b/Å	15.5757(13)	15.5649(12)	15.5531(14)	15.5860(11)
c/Å	28.605(3)	28.600(2)	28.628(3)	28.588(2)
β/°	97.252(2)	97.2580(10)	97.055(2)	97.2360(10)
Volume/ų	10432.6(15)	10448.9(14)	10488.1(16)	10411.5(13)
Z	4	4	4	4
ρ _{calc} g/cm ³	2.509	2.500	2.486	2.517
µ/mm⁻¹	12.835	12.738	12.588	12.941
F(000)	7276.0	7268.0	7256.0	7284.0
Crystal size/mm ³	$0.21 \times 0.19 \times 0.09$	$0.17 \times 0.16 \times 0.09$	$0.16 \times 0.07 \times 0.06$	$0.23 \times 0.16 \times 0.08$
20 range for data collection/°	3.14 to 55.982	3.14 to 52	2.986 to 51.998	2.982 to 56.05
	-31 ≤ h ≤ 31,	-29 ≤ h ≤ 29,	-29 ≤ h ≤ 29,	-31 ≤ h ≤ 31,
Index ranges	-20 ≤ k ≤ 20,	-19 ≤ k ≤ 19,	-19 ≤ k ≤ 19,	-20 ≤ k ≤ 20,
	-37 ≤ ≤ 37	-35 ≤ l ≤ 35	-35 ≤ l ≤ 35	-37 ≤ l ≤ 35
Reflections collected	86559	80934	81269	86617
Independent reflections	25719[R(int) =	20509[R(int) =	20601[R(int) =	25207[R(int) =
Independent reflections	0.0558]	0.0905]	0.1014]	0.0828]
Data/restraints/parameters	25719/175/907	20509/173/907	20601/175/907	25207/164/907
Goodness-of-fit on F ²	1.014	1.008	1.025	1.015
Einal Pindovos [I>-2a (I)]	$R_1 = 0.0620$, $wR_2 =$	$R_1 = 0.0670$, $wR_2 =$	R ₁ = 0.0757, wR ₂ =	$R_1 = 0.0695$, $wR_2 =$
	0.1651	0.1679	0.1836	0.1778
Final P indoxos [all data]	$R_1 = 0.1019$, $wR_2 =$	R ₁ = 0.1258, wR ₂ =	R ₁ = 0.1380, wR ₂ =	R ₁ = 0.1310, wR ₂ =
rinai n inuexes [all uata]	0.1934	0.2061	0.2181	0.2146

3.2. Structural Analysis



Fig. S2 View along the *c*-axis of the crystalline packing of hybrid organic-inorganic complexes $[LnH(PW_{11}O_{39})(phen)_2]^{3^-}$. Hydrogen atoms, water molecule and $[n-NBu^4]^+$ ions have been omitted for clarity. Hydrogen atoms, water molecule and $[n-NBu_4]^+$ ions are omitted for clarity. Colour label: Ln (cyan), W (yellow), N (blue), C (grey) O (red) and P (green).

Continuous shape measurement (CShM's) calculations using the SHAPE code 3,4 show that the geometry of the Ln complexes of this family can be described as a square antiprism (sa), which mean that the Ln centres present a pseudo D_{4d} symmetry (**Fig. S3**).



Fig. S3 Results of the SHAPE measurements for the $[Ln(PW_{11}O_{39})(phen)_2]^3$ complexes, where $Ln^{III} = Dy^{III}$ (LM^4-1-Dy), $Tb^{III}(LM^4-1-Tb)$, $Eu^{III}(LM^4-1-Eu)$, $Nd^{III}(LM^4-1-Nd)$, $Er^{III}(LM^4-1-Er)$, $Ho^{III}(LM^4-1-Ho)$ and $Gd^{III}(LM^4-1-Gd)$.

3.3. Powder X-Ray Diffraction

Crystalline and microcrystalline samples of all compounds were slightly grounded with a pestle in an agate mortar and filled into 0.5 mm borosilicate capillaries prior to being mounted and aligned on an Empyrean PANalytical powder diffractometer, using Cu K α radiation ($\lambda = 1.54056$ Å). For each sample, two or three repeated measurements were collected at room temperature ($2\theta = 2 - 40^{\circ}$) and merged into a single diffractogram. The XRPD pattern of [NBu₄]₃[LnH(PW₁₁O₃₉)(phen)₂]·H₂O is quite similar for all the Ln complexes, but some differences exist that are due to the existence of amorphous material. The crystalline products of [NBu₄]₃[LnH(PW₁₁O₃₉)(phen)₂]·H₂O, where Ln^{III} = Dy^{III} (LM⁴-1-Dy), Tb^{III}(LM⁴-1-Tb), Eu^{III}(LM⁴-1-Eu), Nd^{III}(LM⁴-1-Rr), Ho^{III}(LM⁴-1-Ho) and Gd^{III}(LM⁴-1-Gd) are isostructural and also are in agreement with their simulated patterns, which demonstrates that the crystal structures of the compounds are truly representative of the bulk materials. The differences in intensity are due to the preferred orientation of the powder samples (**Fig. S4 and S5**).



Fig. S4 PXRD patterns of the crystalline phase of compound, $[NBu_4]_3[DyH(PW_{11}O_{39})(phen)_2] \cdot H_2O$ (**LM⁴-1-Dy**), in black, and the theoretical pattern of compounds **LM⁴-1-Dy**.



Fig. S5 PXRD patterns of the different crystalline phases of the compounds $[NBu_4]_3[Ln(HPW_{11}O_{39})(phen)_2] \cdot H_2O$, where $Ln^{III} = Dy^{III} (LM^4-1-Dy)$, $Tb^{III} (LM^4-1-Tb)$, $Eu^{III} (LM^4-1-Eu)$, $Nd^{III} (LM^4-1-Nd)$, $Er^{III} (LM^4-1-Er)$, $Ho^{III} (LM^4-1-Ho)$ and $Gd^{III} (LM^4-1-Gd)$.

4. Solid State Absorption Spectra



Fig. S6. UV-Vis-NIR solid state absorption spectra of LM⁴-1-Ln, complexes, taken at room temperature.



Fig. S7 Solid state absorption spectra for $[NBu_4]_4[PW_{11}O_{39}H_3]$ (a, UV-VIS range and b, complete range), for 1,10-phenanthroline (c) showing the absorption bands in the UV range, $[NBu_4]_4[PW_{11}O_{39}H_3]$ and for **LM⁴-1-Gd** complex, showing the absorption bands of the organic and inorganic ligands.

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5. Solid State Emission Spectra



Fig. S8 Excitation monitored at 435 nm (black line) and emission spectra, excited at 290 nm of LM⁴-1-Gd measure at room temperature.



Fig. S9 Emission spectra of LM⁴-1-Dy (a), LM⁴-1-Tb (b), LM⁴-1-Eu (c) and LM⁴-1-Nd (d) under different excitations.



Fig. S10 Emission spectra for LM^4 -1-Eu, [NBu₄]₄[PW₁₁O₃₉H₃] and 1,10-phenanthroline under excitation at 350 nm, measure at room temperature. It is possible to observed that both types of ligands (phen and LPOM) have emission bands in practically all the same spectral range (c.a. 330 to 500 nm).



Fig. S11 Y/B, G/B and R/O ratios for LM⁴-1-Dy (a), LM⁴-1-Tb (b) and LM⁴-1-Eu (c) as a function of the temperature, respectively.



Fig. S12 Judd-Ofelt (a) radiative lifetimes and decay rates and (b) branching ratios values as a function of temperature for LM⁴-1-Eu.



Fig. S13 Emission spectra in the UV-VIS region for **LM⁴-1-Er** (a) and **LM⁴-1-Ho** (b). All spectra are taken at room temperature.

6. References

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