

Supporting Information for

Facile access to efficiently luminescent Ln³⁺ phosphonic ester coordination polymers (Ln = Eu, Tb, Dy)

Kristijan Krekić, Dieter Klintuch and Rudolf Pietschnig

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Experimental details

All chemical were purchased from Sigma-Aldrich or TCI and used without further purification. NMR measurements were done on Varian 400 MHz and 500 MHz spectrometers. Infrared spectroscopy was done using Bruker ATR IR device with diamond probe. The microwave assisted synthesis was performed in a CEM DISCOVER-SP reactor in pyrex vessels closed with Activent-lids. Excitation and emission spectra as well as luminescent quantum yields (absolute method) measurements were carried out using a Hamamatsu C11347 system. For the refinement of the data ORIGIN 2017 was used. X-ray diffraction was performed using either STOE IPDS 2 with image plate (diameter 34 cm) using Mo-GENIX source ($\lambda=0.71073$ nm) or STOE StadiVari with DECTRIS PILATUS 200K using Mo-GENIX source ($\lambda=0.71073$ nm). Structures were solved using dual space method (SHELXT¹) and are refined against F^2 with SHELXL-2014². All non-hydrogen atoms are refined anisotropically. Hydrogen atoms were placed on adjacent atoms using a riding model. In case of mix metal structure some atoms are refined isotropically due to very large disorder on said atoms. Further programs used in structure analysis consists of WinGX³, Mercury⁴ and Platon⁵. Details of the structure determinations and refinement for **L**, **1a-d**, **1e** are summarized in Table S1. CCDC-1562260-1562264, 1569994 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of tetraisopropyl biphenyl-4,4'-diylbis(methylene) diphosphonate (L). In microwave flask 5 g (20 mmol) of 4,4'-di(chloromethyl)biphenyl was placed together with 20 mL (80 mmol) of triisopropyl phosphite. The reaction mixture was heated in a microwave reactor at 200 °C (200 W) under autogenous pressure for 1.5 hours. After cooling colorless crystalline material was formed. The resulting solid was washed with large amount of cold water and dried under reduced pressure. The product was recrystallized from acetone giving 9.6 g of crystalline product affording 94% yield based on bis(chloromethyl)biphenyl.

¹H NMR (400 MHz, acetone) δ : 7.61 (d, $J = 8.1$ Hz, 4H), 7.42 (dd, $J = 8.1, 2.4$ Hz, 4H), 4.65 – 4.51 (m, 1H), 3.14 (d, $J = 21.8$ Hz, 4H), 1.21 (dd, $J = 34.8, 6.2$ Hz, 24H) ppm. ³¹P NMR [¹H] (202 MHz, acetone) δ : 24.0 (m br) ppm. ESI-MS: $m/z=533.13$ [M+Na]⁺. IR(ATR): 1105 cm⁻¹ (m, P-O), 1232 cm⁻¹ (st, P=O). Elemental analysis calc (%) : C 61.17, H 7.90; found: C 61.45 H 8.03

Synthesis of lanthanide(III) coordination polymers: The ligand (500 mg, 1 mmol) was dissolved in 5 mL of EtOH. To the solution of ligand a solution of Ln(NO₃)₃ · xH₂O (0.66 mmol) in the same solvent was added under heavy stirring at room 20°C. Slow evaporation of the solvent yields colorless crystalline material. (Yield: **1a**: 600 mg, 82 %; **1b**: 550 mg, 74 %; **1c**: 570 mg, 77%; **1d**: 580 mg, 84 %; **1e**: 512 mg, 71%)

Analysis of **1a**:

IR (ATR): 1097 cm⁻¹ (m, P-O), 1165 cm⁻¹ (s, P=O)

MALDI-MS of reaction solution: $m/z=1719.25$ [(Eu(NO₃)₃L)₂+Na]⁺, $m/z=1634.28$ [(Eu₂(NO₃)₅L₂)⁺, $m/z=2438.30$ [(Eu₃(NO₃)₈L₃)⁺

Elemental analysis calc (%) : C 42.44, H 5.48, N 3.81; found: C 42.37, H 5.46, N 3.92

Analysis of **1b**:

IR (ATR): 1097 cm⁻¹ (m, P-O), 1165 cm⁻¹ (s, P=O)

Elemental analysis calc (%) : C 42.17, H 5.44, N 3.78; found: C 42.15, H 5.37, N 3.80

Analysis of **1c**:

IR (ATR): 1097 cm⁻¹ (m, P-O), 1165 cm⁻¹ (s, P=O)

Elemental analysis calc (%) : C 42.06, H 5.43, N 3.77; found: C 41.92, H 5.45, N 3.74

Analysis of **1d**:

IR (ATR): 1097 cm⁻¹ (m, P-O), 1165 cm⁻¹ (s, P=O)

Elemental analysis calc (%) : C 45.01, H 5.81, N 4.04; found: C 45.26, H 5.92, N 4.28

Analysis of **1e** (trimetallic):

IR (ATR): 1097 cm⁻¹ (m, P-O), 1168 cm⁻¹ (s, P=O)

Elemental analysis calc (%) : C 42.61, H 5.50, N 3.82; found: C 42.62, H 5.46, N 3.77

Mass spectra from the reaction solution during the formation of **1a**:

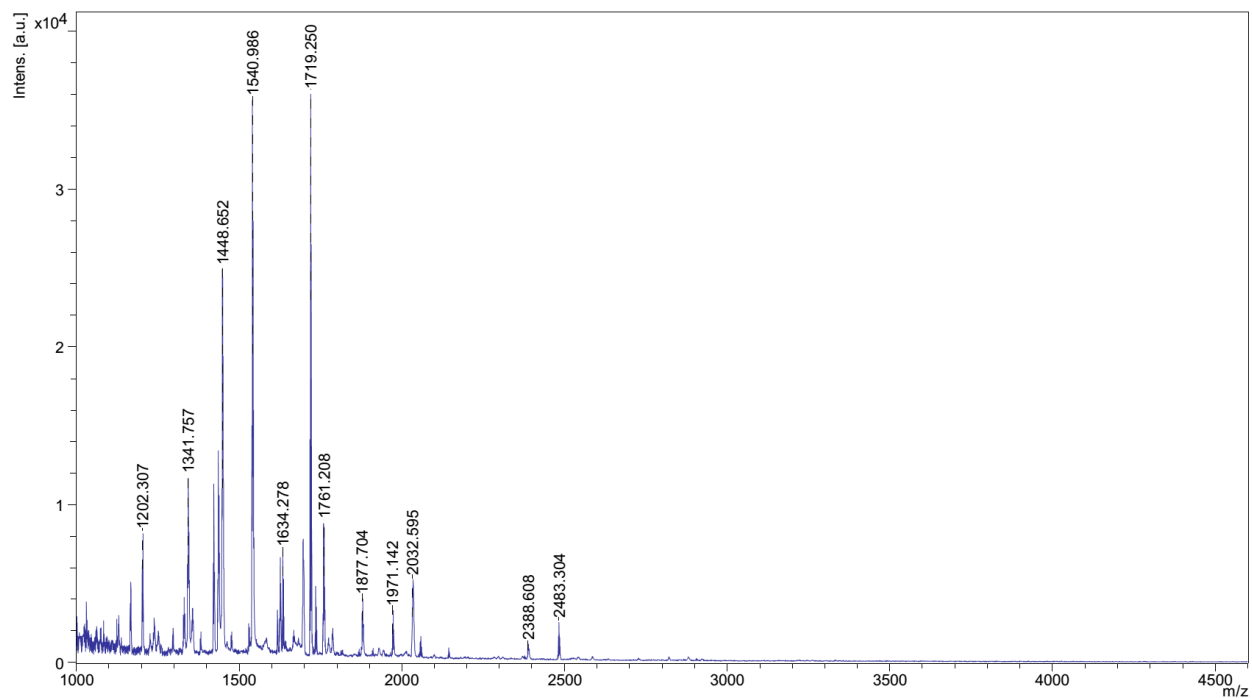


Figure s1. Mass spectrum of 1a reaction solution. Whole range.

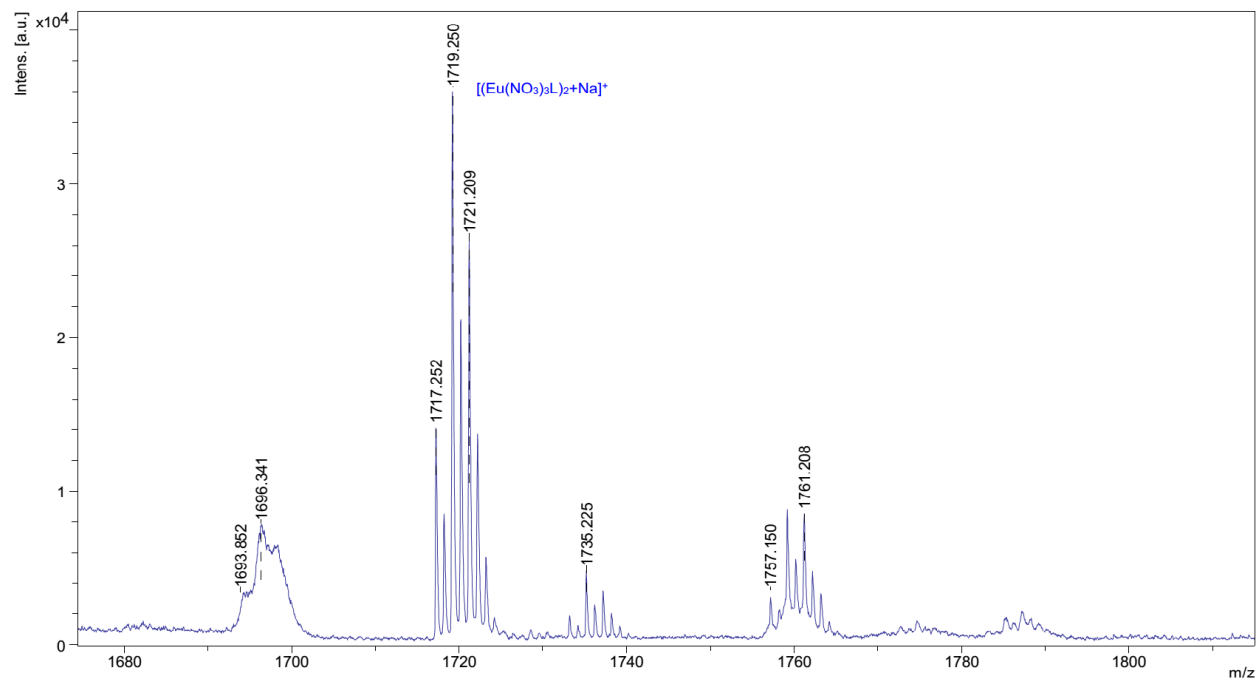


Figure s2. Mass spectrum of 1a reaction solution. $[(\text{Eu}(\text{NO}_3)_3)_2 + \text{Na}]^+$.

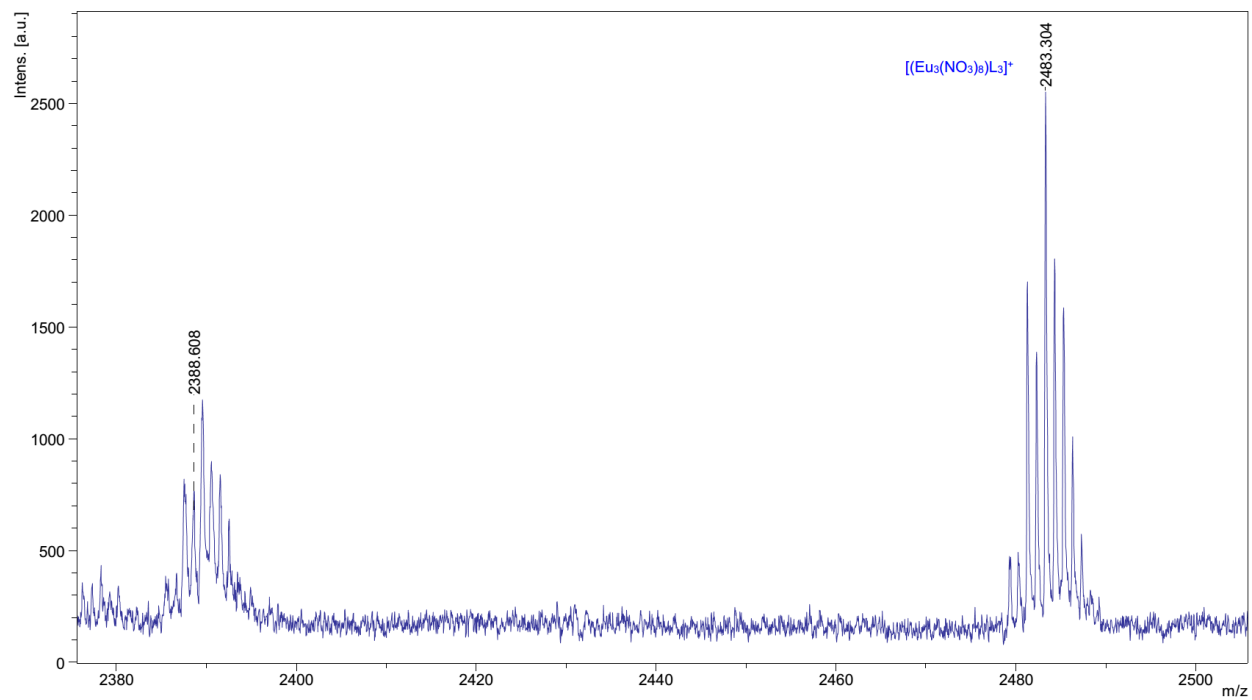


Figure s3. Mass spectrum of 1a reaction solution. $[(Eu_3(NO_3)_8)L_3]^+$

X-Ray diffraction

Table s1. Crystal data for the coordination polymers and ligand.

	L	1a	1b	1c	1d	1e
CCDC	1562260	1562261	1562262	1562263	1562264	1569994
Empirical formula	C26 H40 O6 P2	C39 H60 Eu N3 O18 P3	C39 H60 N3 O18 P3 Tb	C39 H60 Dy N3 O18 P3	C39 H60 N3 O18 P3 Y	C39 H60 Eu0.16 N3 O18 P3 Tb0.70 Y0.14
Formula weight	510.52	1103.77	1110.73	1114.31	1040.72	1099.97
Crystal description	colorless plate	colorless plate	colorless plate	colorless plate	colorless block	colorless plate
Crystal size [mm]	0.300 X 0.090 X 0.020	0.300 X 0.130 X 0.080	0.050 X 0.050 X 0.040	0.300 X 0.130 X 0.080	0.190 X 0.180 X 0.110	0.150 X 0.110 X 0.040
Crystal system, space group	monoclinic P 21/n	monoclinic P 21/n	monoclinic P 21/n	monoclinic P 21/n	monoclinic P 21/n	monoclinic 'P 21/n'
Radiation and λ [Å]	Mo K α 0.71073	Mo K α 0.71073	Mo K α 0.71073	Mo K α 0.71073	Mo K α 0.71073	'Mo K α ' 0.71073
Monochromator	plane graphite	plane graphite	plane graphite	plane graphite	plane graphite	'Graded multilayer mirror'
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Unit cell dimensions:						
a [Å]	21.8266(18)	16.2689(6)	16.4639(6)	16.4696(6)	16.4785(6)	16.5126(5)
b [Å]	5.8487(3)	13.2684(7)	13.4794(3)	13.4724(3)	13.3577(3)	13.4910(4)
c [Å]	23.1849(18)	22.3097(9)	22.5915(8)	22.5458(6)	22.5110(6)	22.5623(7)
a [°]	90	90	90	90	90	90
b [°]	109.753(6)	103.599(3)	104.281(3)	104.209(2)	103.528(2)	104.149(2)
g [°]	90	90	90	90	90	90
Volume [Å ³]	2785.6(4)	4680.8(4)	4858.7(3)	4849.5(2)	4817.5(2)	4873.8(3)
Z	4	4	4	4	4	4
Calculated density	1.217	1.566	1.518	1.526	1.435	1.499
F(000)	1096	2268	2276	2280	2172	2260
Linear absorption coefficient $\hat{\mu}$ [mm ⁻¹]	0.192	1.518	1.627	1.712	1.383	1.560
Absorption correction	integration	integration	integration	integration	integration	integration
Unit cell determination	STOE X-area	STOE X-area	STOE X-area	STOE X-area	STOE X-area	STOE X-area
Diffractometer	STOE IPDS 2	STOE IPDS 2	STOE IPDS 2	STOE IPDS II	STOE IPDS 2	STOE STADIVARI
Radiation source	Genix Mo HF	Genix Mo HF	Genix Mo HF	Genix Mo HF	Genix Mo HF	Mo Genix
Scan type	Omega scan	Omega scan	Omega scan	Omega scan	Omega scan	Omega scan

Θ range for data collection	1.58 - 26.31	1.40 - 26.35	1.51 - 26.14	1.51 - 26.35	1.52 - 26.27	1.75 - 29.15
Index ranges	-26 <h< 26	-19 <h< 19	-19 <h< 20	-18 <h< 20	-18 <h< 20	-19 <h< 19
	-6 <k< 7	-14 <k< 16	-16 <k< 14	-16 <k< 16	-16 <k< 16	-16 <k< 15
	-28 <l< 27	-27 <l< 25	-27 <l< 27	-27 <l< 27	-27 <l< 27	-26 <l< 20
Refl. collected / unique	12393 / 5233	22264 / 8816	22107 / 9122	24710 / 9125	23678 / 9036	30749 / 8568
Significant unique refl.	3407	6729	6262	7666	7678	6587
R(int), R(sigma)	0.1167, 0.0927	0.0348, 0.0379	0.0560, 0.0648	0.0366, 0.0320	0.0261, 0.0252	0.0649, 0.0539
Completeness to Θ = 26.0Å°	0.983	0.99	0.985	0.986	0.986	0.998
Refinement method	SHELXL-2014/7	SHELXL-2014/7	SHELXL-2014/7	SHELXL-2014/7	SHELXL-2014/7	SHELXL-2014/7
Data/parameters/restraints	5233 / 286 / 0	8816 / 475 / 1	9122 / 577 / 0	9125 / 577 / 0	9036 / 577 / 0	8568 / 564 / 4
Goodness-of-fit on F2	1.704	1.175	1.03	1.053	1.03	2.572
Final R indices [I > 2σ(I)]	0.1503	0.0696	0.0601	0.0588	0.0498	0.1848
R indices (all data)	0.1863	0.0912	0.0935	0.0694	0.0603	0.212

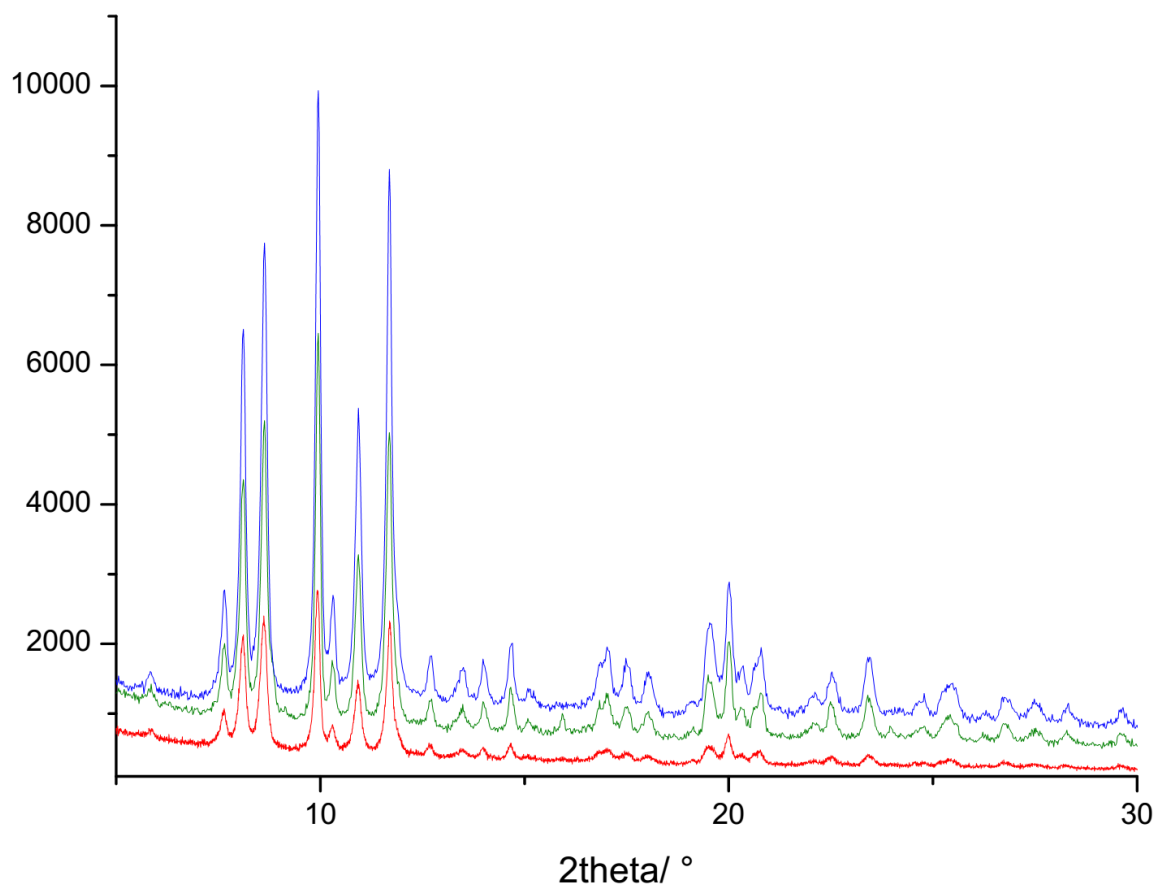


Figure s4. Powder diffraction of bulk **1e** (green) vs. **1a** (Red) vs **1b** (blue)

Selected emission spectra

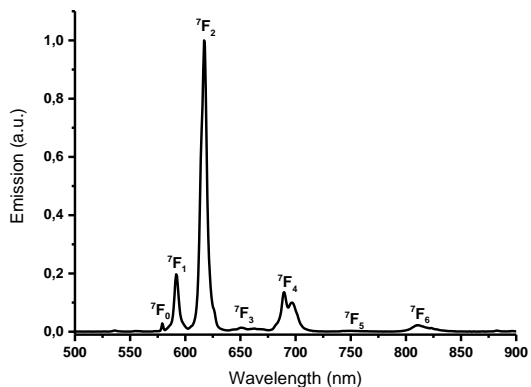


Figure s5. Normalized emission spectrum of **1a** at 330 nm excitation wavelength with the observed ${}^5D_0 \rightarrow {}^7F_n$ transitions.

Table s2. Transitions observed in luminescence spectrum of **1a**

Transition	Wavelength [nm]	Comment
${}^5D_0 \rightarrow {}^7F_0$	579	Due to C_1 symmetry
${}^5D_0 \rightarrow {}^7F_1$	592	
${}^5D_0 \rightarrow {}^7F_2$	617	High intensity due to ligand
${}^5D_0 \rightarrow {}^7F_3$	651	Forbidden transition
${}^5D_0 \rightarrow {}^7F_4$	690/697	Doublet
${}^5D_0 \rightarrow {}^7F_5$	749	Forbidden transition
${}^5D_0 \rightarrow {}^7F_6$	811	

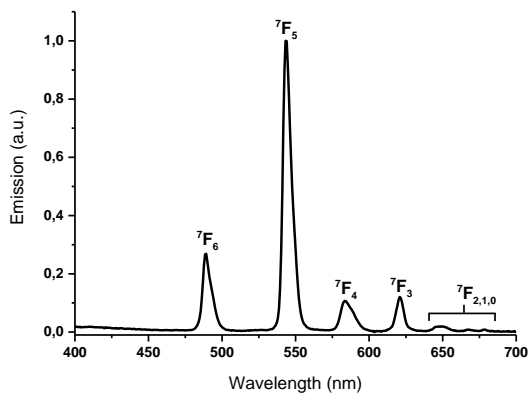


Figure s6. Normalized emission spectrum of **1b** at 318 nm excitation wavelength with the observed ${}^5D_4 \rightarrow {}^7F_n$ transitions.

Table s3. Transitions observed in luminescence spectrum of **1b**

Transition	Wavelength [nm]
${}^5D_4 \rightarrow {}^7F_6$	489
${}^5D_4 \rightarrow {}^7F_5$	543
${}^5D_4 \rightarrow {}^7F_4$	584
${}^5D_4 \rightarrow {}^7F_3$	621
${}^5D_4 \rightarrow {}^7F_2$	649
${}^5D_4 \rightarrow {}^7F_1$	668
${}^5D_4 \rightarrow {}^7F_0$	678

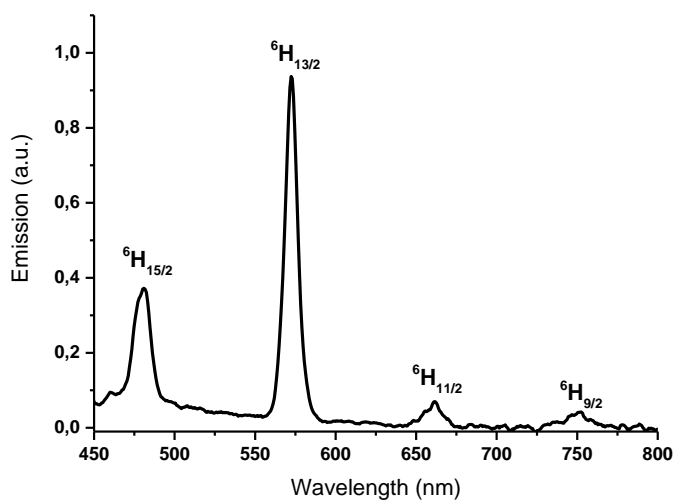


Figure s7. Normalized emission spectrum of **1c** at 399 nm excitation wavelength with the observed ${}^5F_{9/2} \rightarrow {}^6H_{n/2}$ transitions.

Table s4. Transitions observed in luminescence spectrum of **1c**

Transition	Wavelength [nm]
${}^5F_{9/2} \rightarrow {}^6H_{15/2}$	481
${}^5F_{9/2} \rightarrow {}^6H_{13/2}$	573
${}^5F_{9/2} \rightarrow {}^6H_{11/2}$	661
${}^5F_{9/2} \rightarrow {}^6H_{9/2}$	750

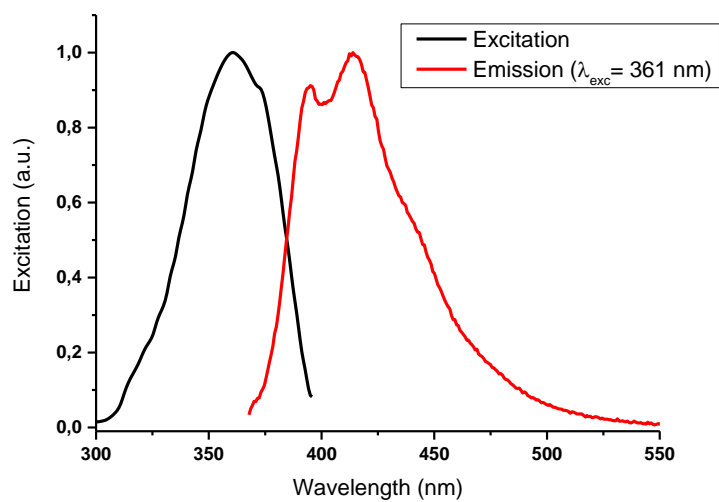


Figure s8. Excitation and emission spectra of $[Y(NO_3)_3]_2L_3$ at 361 nm excitation wavelength.

References

- (1) Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta. Crystallogr. A.* **2015**, *71* (1), 3.
- (2) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta. Crystallogr. C.* **2015**, *71* (1), 3.
- (3) Farrugia, L. J. WinGXandORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012**, *45* (4), 849.
- (4) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39* (3), 453.
- (5) Spek, A. L. Structure validation in chemical crystallography. *Acta. Crystallogr. D.* **2009**, *65* (Pt 2), 148.