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Synthesis and spectroscopy of anionic tridentate benzimidazole-pyridine carboxylate and tetrazolate chromophore ligands

Nail M. Shavaleev *, Svetlana V. Eliseeva

École Polytechnique Fédérale de Lausanne, Institut des Sciences et Ingénierie Chimiques, Avenue Forel 2, BCH, CH-1015 Lausanne, Switzerland

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ABSTRACT

We report on seven new anionic benzimidazole-pyridine carboxylate and tetrazolate tridentate N^N^O and N^N^N ligands that are modified with chromophore (phenyl, biphenyl, naphthyl) and solubilizing groups. The ligands are UV chromophores with the lowest-energy absorption maxima at 312–335 nm and with the molar absorption coefficients of (20–25) $\times 10^3$ M^{-1} cm^{-1} in DMSO solution. The ligands form neutral complexes with trivalent lanthanides and sensitize the red luminescence of europium. The triplet state energies of the deprotonated ligands, which were measured from the phosphorescence spectra of their lanthanum complexes at 77 K, are in the range of (18.8–21.1) $\times 10^3$ cm^{-1}. We also describe synthesis of non-symmetric pyridines that are 2,6- and 2,4,6-substituted with hydroxymethyl, carboxaldehyde, and carbonitrile groups.

1. Introduction

Luminescent lanthanide(III) complexes are used in lighting and analytical applications [1–3]. Polydentate carboxylate [4–20] and tetrazolate [21–24] ligands are strong chelators for lanthanide ions and efficient sensitizers of their luminescence. Here, we report on synthesis and spectroscopy of anionic tridentate carboxylate and tetrazolate benzimidazole-pyridine ligands **HL1**–**HL7** that are functionalized with chromophore and solubilizing groups (Schemes 1 and 2). We developed these tridentate ligands to make neutral homoleptic *tris*-complexes of the lanthanides. The lanthanide ion in this type of complexes is expected to be nine-coordinate [7–12,23]. We also report on the synthesis of non-symmetric pyridines **P2**–**P4** that are 2,6- or 2,4,6-substituted with hydroxymethyl, carboxaldehyde, and carbonitrile groups (Scheme 3).

2. Results and discussion

The five new carboxylate N^N^O ligands **HL1**–**HL5** were prepared in three steps (Scheme 1) [23]. The formation of the benzimidazole heterocycle by the reaction of the carboxaldehyde-6-hydroxymethylpyridine **P1** or **P2** with *o*-nitroaniline [25] was followed by step-wise oxidation of the pyridine-2-methanol first to the carboxaldehyde with SeO_2 [23] and then to the carboxylic acid with H_2O_2 in formic acid [26]. The *n*-octyloxy chain and the *N*-methylene aryl group are not oxidized during this synthesis.

The two new tetrazolate N^N^N ligands **HL6** and **HL7** were prepared in four steps [23]. The first two steps were the same as for the carboxylate ligands. In the third step, the carboxaldehyde was converted into the carbonitrile with $NH_2OH{\cdot}HCl$ in formic acid [27]. Finally, reaction of the carbonitrile with NaN_3 in DMF gave the target tetrazoles [28].

We introduced the phenyl, biphenyl, and naphthyl chromophores via the *N*-methylene linker into the ligands **HL1**–**HL5**. The *N*-methylene linker prevents conjugation of the aryl chromophore with the benzimidazole. If required, any chromophore can be attached in the same way. We previously reported *N*-alkyl and *N*-aryl analogs of **HL1**–**HL5** [23].

The ligands **HL3**–**HL7** were modified with an *n*-octyloxy group to increase the solubility of the ligands and their complexes in organic solvents. If required, the *n*-octyloxy group can be replaced with other solubilizing and chromophore alkyloxy- and aryloxy-groups. Chart 1 shows the three known reference ligands **HR1**–**HR3** [23,29].

New 2,4,6-trisubstituted pyridine **P2** was obtained by mono-oxidation of bis-methanol **3** (itself prepared from chelidamic acid in three multi-gram steps by modified literature procedures [5–7,30–32]) with SeO_2 in dioxane (Scheme 3) [12]. Until now, only one report described an analogue of **P2** as a by-product of bis-oxidation of a substituted bis-methanol-pyridine by SeO_2 [33]. We note that mono-oxidation of bis-methanol-pyridines to carboxaldehyde can also be achieved with MnO_2 as oxidant [34].

* Corresponding author. Tel.: +7 (347) 254 84 38.
E-mail address: shava@mail.ru (N.M. Shavaleev).

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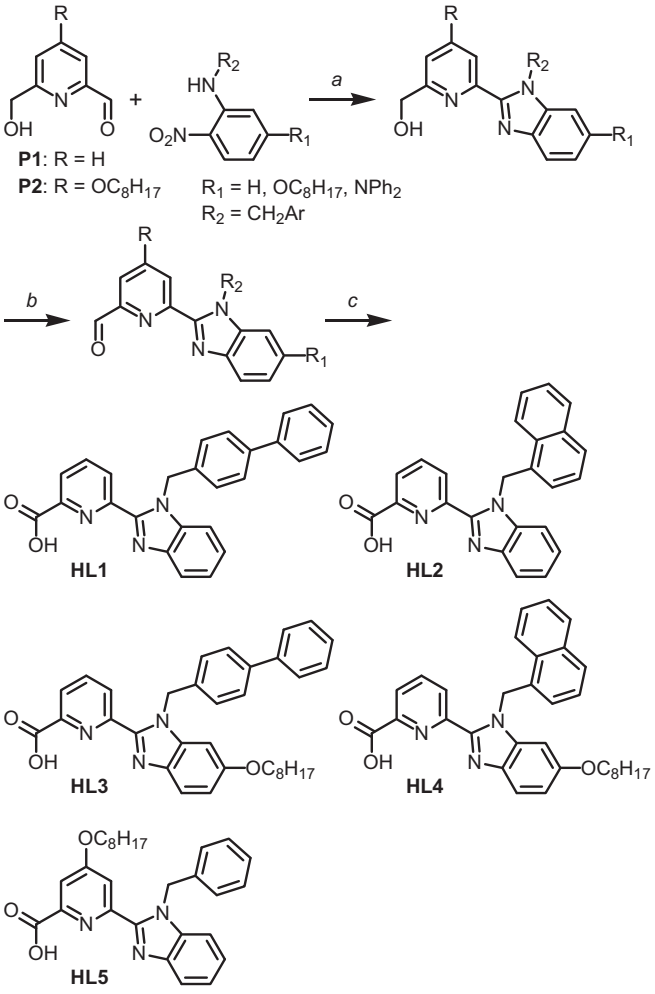
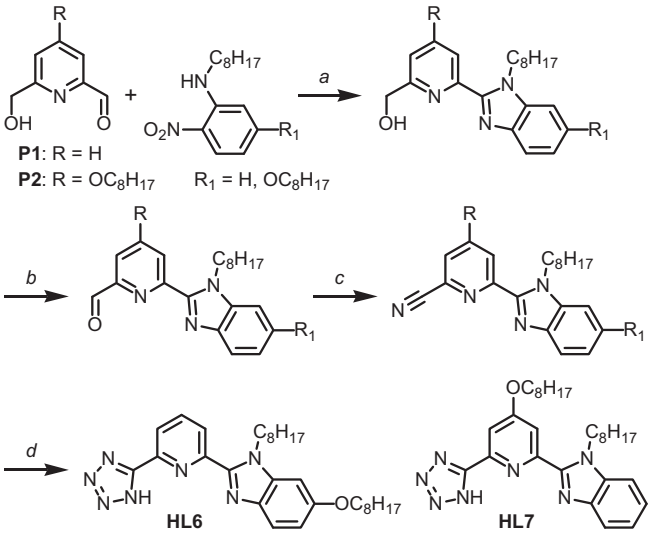


Scheme 1. Synthesis of carboxylic acids **HL1**–**HL5**: (a) $Na_2S_2O_4$, DMF/H_2O, under N_2, 110–120 °C; (b) SeO_2, dioxane, under N_2, 110 °C; (c) H_2O_2, formic acid, under air, 0 °C (this reaction does not work when R, R_1, and R_2 are H, NPh_2, and C_8H_{17}, respectively).

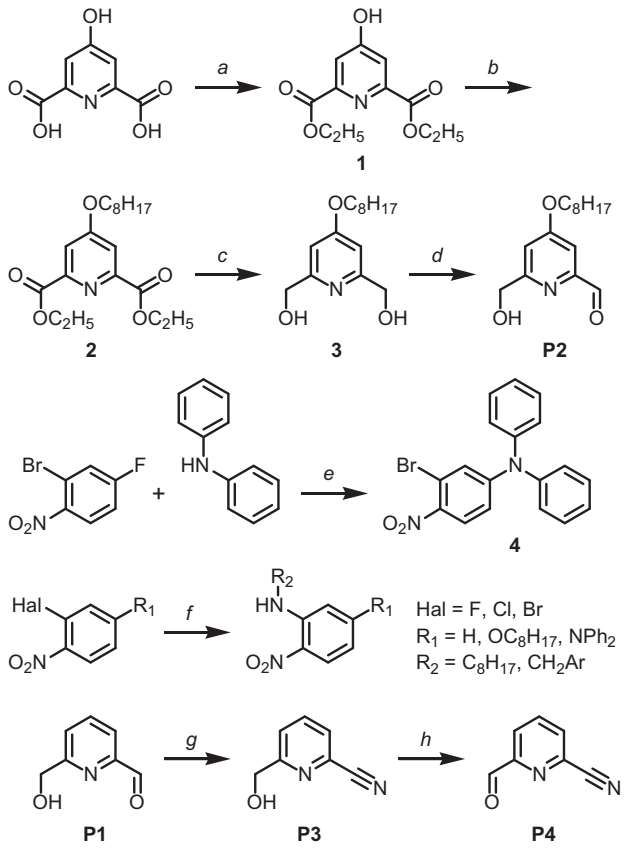
The known 2,6-disubsituted pyridines **P3** [35–37] and **P4** [36–38], which we planned to use in the synthesis of tetrazoles, were prepared from **P1** (we described its multi-gram synthesis before [12]) by conversion of the carboxaldehyde into the carbonitrile **P3** with $NH_2OH{\cdot}HCl$ in DMSO [39], and by oxidation of the pyridine-2-methanol to the carboxaldehyde **P4** with SeO_2 (Scheme 3).

The *N*-substituted *o*-nitroanilines were prepared by reaction of 2-halonitrobenzenes with an excess of amine in DMSO on heating (Scheme 3).

The intermediate **4** was obtained by a non-catalyzed exothermic reaction of 2-bromo-4-fluoronitrobenzene with diphenylamine in the presence of potassium *tert*-butoxide in DMSO (Scheme 3) [40]. This reaction takes advantage of the high reactivity of C–F bond in electron-deficient arenes [40–42]. An attempt to make carboxylate ligand '**HL8**' from **4** worked for the first three steps (see the intermediates **L8-NO$_2$**, **L8-CH$_2$OH**, **L8-CHO** and the structure of ligand '**HL8**' in the Supplementary material); however, oxidation of the carboxaldehyde **L8-CHO** to the carboxylic acid '**HL8**' with H_2O_2 in formic acid [26] resulted in oxidative decomposition, probably because of the presence of electron-rich diphenylamino group (Supplementary material). The benzimidazole-pyridines **L8-CH$_2$OH** and **L8-CHO** (Supplementary material) can be used as ligands themselves and as precursors to polydentate ligands [20]. The ligands derived from **4** are likely to exhibit low-energy intra-ligand diphenylamine-to-benzimidazole charge-transfer absorption transition.



Scheme 2. Synthesis of tetrazoles **HL6** and **HL7**: (a) $Na_2S_2O_4$, 2-methoxyethanol/H_2O or DMF/H_2O, under N_2, 110–120 °C; (b) SeO_2, dioxane, under N_2, 110 °C; (c) $NH_2OH{\cdot}HCl$, sodium formate, formic acid, under N_2, 120 °C; (d) NaN_3, NH_4Cl, DMF, under N_2, 110 °C.



Scheme 3. Synthesis of precursors: (a) ethanol, H_2SO_4, 100 °C; (b) 1-octylbromide, K_2CO_3, DMF, under N_2, 60 °C; (c) $NaBH_4$, CH_3OH/THF, under N_2, room temperature; (d) SeO_2, dioxane, under N_2, 60 °C; (e) KO^{t}Bu, DMSO, under N_2, room temperature; (f) amine, DMSO, under N_2, 90–100 °C; (g) $NH_2OH{\cdot}HCl$, DMSO, under N_2, 100 °C; (h) SeO_2, dioxane, under N_2, 110 °C.

Tris-complexes of the ligands **HL1**–**HL7** with lanthanum(III) and europium(III) were obtained as air- and moisture-stable solids from hot ethanol/water solutions with a 3:3:1 M ratio of the ligand, NaOH (base), and $LnCl_3{\cdot}nH_2O$. Elemental analysis indicates that these

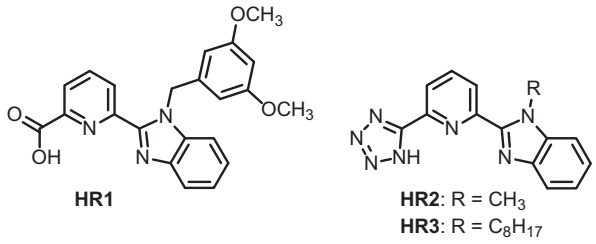


Chart 1. Reference ligands [23,29].

complexes have the composition $Ln(Ligand)_3 \cdot nH_2O \cdot mC_2H_5OH$, where $n = 0.5–4$ and $m = 0–1$. The complexes are soluble in dichloromethane.

The new europium complexes exhibit the line-like red *f*–*f* luminescence from the $^5D_0$ excited state of europium (Fig. S2, Supplementary material). The photophysical study of the neat solid europium complexes indicate that they are a mixture of species because (a) the luminescence decays are bi-exponential at 298 K (short and long components of 0.05–0.87 ms and 0.24–2.52 ms; ligand-sensitized quantum yield 0.3–61%) and at 10 K (short and long components of 0.43–0.83 ms and 1.65–2.77 ms), and (b) the $^5D_0 \leftarrow {}^7F_0$ transition in the high resolution excitation spectrum exhibits multiple, and often broad, components [3]. This mixture is probably made of the hydrated complex [Eu(κ^3-Ligand)$_2$(κ^1-Ligand)$(H_2O)_x$], where one of the ligands is monodentate-bound to the europium through the anionic carboxylate oxygen or the tetrazolate nitrogen, and of the anhydrous complex [Eu(κ^3-Ligand)$_3$]. Both types of these lanthanide complexes are known for tridentate N^N^O and N^N^N ligands [12,23]. The excited states of europium are quenched by water [14,15]. The hydrated and the anhydrous complexes give rise to the short and the long components in the luminescence decay, respectively. The europium complexes were not studied further, because it is difficult to make a quantitative characterization of europium-centred luminescence for mixtures of species.

The new lanthanum complexes are probably a mixture of species too; however, this should not change the ligand-centred spectroscopy of these complexes, which is discussed below. The ligands **HL1**–**HL7** may provide pure anhydrous *tris*-complexes with lanthanides [Ln(κ^3-Ligand)$_3$] when the synthesis is conducted in anhydrous conditions.

The absorption spectra of the ligands **HL1**–**HL7** in DMSO solution exhibit the lowest-energy band centred at 312–335 nm with molar absorption coefficient of $(20–25)\times10^3\ M^{-1}\ cm^{-1}$, which corresponds to $\pi \rightarrow \pi^*$ transition of the benzimidazole chromophore (Fig. 1 and Table 1). For the lanthanum and europium complexes,

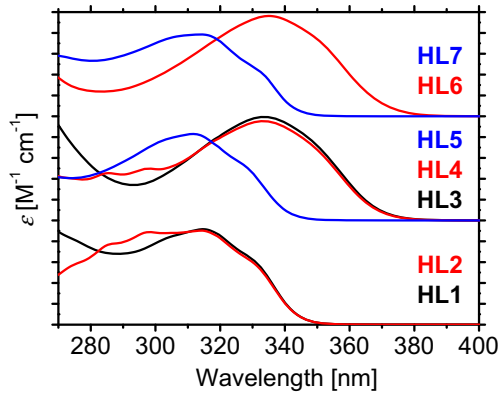


Fig. 1. Absorption spectra of ligands **HL1**–**HL7** in DMSO. The unit on the vertical axis is $5 \times 10^3\ M^{-1}\ cm^{-1}$.

Table 1
Absorption spectra of the ligands.[a]

	λ_{abs}/nm ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$)
HL1	315 (23)
HL2	314 (23), 298 (22)
HL3	334 (25)
HL4	334 (24), 298 (12), 286 (11)
HL5	312 (21)
HL6	335 (24)
HL7	314 (20)
HR3[b]	320 (22)

[a] See Fig. 1. λ_{abs} and ε in DMSO solution at 250–500 nm at $(1.25–1.96) \times 10^{-4}$ M at 298 K. Errors: ±1 nm for λ_{abs}; ±5% for ε.
[b] Data from [23].

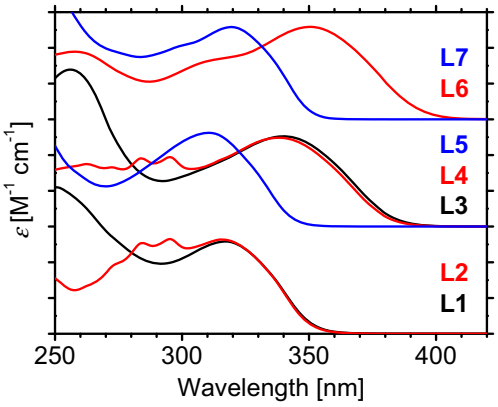


Fig. 2. Absorption spectra of lanthanum complexes in dichloromethane. The unit on the vertical axis is $20 \times 10^3\ M^{-1}\ cm^{-1}$.

Table 2
Ligand-centered absorption and phosphorescence of lanthanum complexes.

	λ_{abs}/nm ($\varepsilon/10^3\ M^{-1}\ cm^{-1}$)[a]	$E_T(0–0)/10^3\ cm^{-1}$[b]
La(**L1**)$_3 \cdot 2H_2O$	317 (52), 251 (82)	20.5
La(**L2**)$_3 \cdot 3H_2O \cdot C_2H_5OH$	316 (53), 295 (53), 285 (51)	19.2 (sh)
La(**L3**)$_3 \cdot 2H_2O$	340 (50), 256 (88)	18.9
La(**L4**)$_3 \cdot 3H_2O$	338 (50), 295 (39), 284 (38), 273 (33), 263 (35)	18.8
La(**L5**)$_3 \cdot 2H_2O$	311 (52)	20.8
La(**L6**)$_3 \cdot 4H_2O$	350 (52), 258 (38)	18.9 (sh)
La(**L7**)$_3 \cdot 4H_2O$	319 (52), 244 (90)	21.1
[La(**R3**)$_3$]$\cdot 2.5H_2O$[c]	322 (68), 269 (45)[d]	20.7

[a] See Fig. 2. λ_{abs} and ε in dichloromethane solution at 250–500 nm at $(3.79–5.79) \times 10^{-5}$ M at 298 K. Errors: ±1 nm for λ_{abs}; ±5% for ε.
[b] See Fig. 3. Triplet state energies, $E_T(0–0)$, from 0–0 transition of phosphorescence spectra of neat solid complexes at 77 K. Error: $\pm200\ cm^{-1}$.
[c] Data from [23].
[d] In DMSO solution.

the lowest-energy ligand-centred absorption maxima and molar absorption coefficients are 311–352 nm and $(46–53)\times10^3\ M^{-1}\ cm^{-1}$ in dichloromethane solution (Fig. 2 and Table 2, and Fig. S1 and Table S1, Supplementary material).

The ligand-to-lanthanide energy transfer in lanthanide complexes usually occurs from the triplet state of the ligand [13]. The triplet state energies of the ligands (E_T) were determined to be $(18.8–21.1) \times 10^3\ cm^{-1}$ from the 0–0 transition of the phosphorescence spectra of their neat solid lanthanum complexes at 77 K (Fig. 3 and Table 2).

The ligands **HL1**–**HL7** exhibit intense UV absorption and their triplet state energies are sufficiently high to sensitize the red luminescence of europium [13]; therefore, these ligands can be used as sensitizer chromophores in luminescent lanthanide complexes

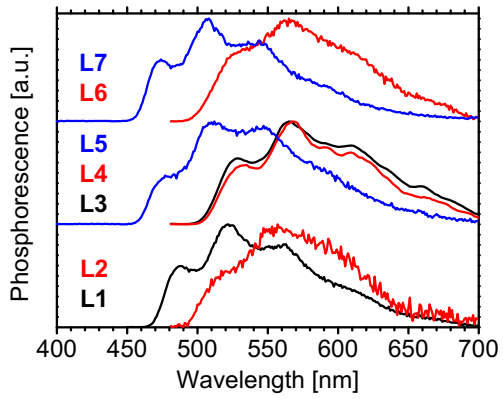


Fig. 3. Phosphorescence spectra of lanthanum complexes in neat solids at 77 K.

(Fig. S2, Supplementary material) [20]. The lowest-energy absorption transition and the triplet state of the new ligands and their lanthanum complexes exhibit the following trends (Figs. 1–3 and Tables 1 and 2):

(a) the absorption transition is unchanged, but the triplet state is red-shifted when biphenyl at the *N*-methylene is replaced by naphthyl from **HL1** to **HL2**, because the triplet state energy of the naphthyl is lower than that of the biphenyl and benzimidazole [43];
(b) both are unchanged when the biphenyl at the *N*-methylene is replaced by naphthyl from **HL3** to **HL4** (the only changes in the absorption spectra are observed at <310 nm), because the triplet state energy of the alkoxy-benzimidazole in **HL3** and **HL4** is lower than that of the biphenyl and naphthyl;
(c) both are red-shifted when electron-donor *n*-octyloxy group is attached to the benzimidazole from **HL1** to **HL3**, from **HL2** to **HL4**, and from **HR3** to **HL6** because of generation of low-energy benzimidazole-centered "alkoxy"-to-imine charge-transfer excited state;
(d) both are blue-shifted when *n*-octyloxy group is attached to the 4-position of pyridine, from **HL1** to **HL5** and from **HR3** to **HL7**.

In conclusion, the new tridentate anionic ligands **HL1**–**HL7**, which combine 'hard' oxygen and 'soft' nitrogen donor atoms and which can be modified with solubilizing and chromophore groups, can be used for lanthanides and actinides [4–24], for lanthanide/actinide separation [24], and for any 'hard' or 'soft' metal ion with square-planar or octahedral coordination geometry [44–46].

3. Experimental

Elemental analyses were performed by Dr. E. Solari, Service for Elemental Analysis, Institute of Chemical Sciences and Engineering (EPFL). ESI MS were recorded on a Q-TOF Ultima (Waters) or TSQ7000 (Thermo Fisher) spectrometers at the Mass Spectrometry Service of the Institute of Chemical Sciences and Engineering (EPFL). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 400 MHz and Bruker Avance II 800 MHz spectrometers.

Absorption spectra were measured on a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer. Luminescence was measured with a previously described instrumental setup [23]. Spectroscopic studies were conducted in optical cells of 2-mm path length or in 2-mm i.d. quartz capillaries under air. The solutions in DMSO (Fluka, >99.9%, ACS spectrophotometric grade) and in CH_2Cl_2 (Fisher Scientific, analytical reagent grade) were freshly prepared before each experiment.

Commercial reagents were used without purification. Chromatography was performed on a column with an i.d. of 30 mm on silica gel 60 (Fluka, Nr 60752). The progress of reactions and the elution of products were followed on TLC plates (silica gel 60 F_{254} on aluminum sheets, Merck).

Caution: Tetrazole derivatives and other nitrogen-rich heterocycles are known to be explosive hazard. We did not encounter any problems in the handling of small quantities of the new tetrazole ligands and their complexes; however, we did not perform stress tests on these materials.

3.1. Synthesis of pyridines

P2: The reaction was performed under nitrogen. SeO_2 (182 mg, 1.64 mmol; 99.8%, Acros) and **3** (900 mg, 3.37 mmol, small excess) were stirred in dioxane (30 mL; neither dried nor degassed) at 60 °C (bath temperature) for 48 h (we note that the use of higher temperature and of the excess of SeO_2 in this reaction will lead to undesired bis-oxidation). The mixture was filtered through Celite to remove precipitated selenium. Celite was washed with CH_2Cl_2. Chromatography was performed on silica (20 g) with CH_2Cl_2 to remove the bis-aldehyde and with 2–2.5% CH_3OH in CH_2Cl_2 to recover the product. The product shows one spot on TLC (silica; ethyl acetate). It is soluble in organic solvents, and it remains soluble even after long storage as a solid (in contrast to the non-substituted analog **P1** [12]). Pale yellow solid: 804 mg (3.03 mmol; 90%; $C_{15}H_{23}NO_3$; MW 265.35). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.89 (s, 1H, CHO), 7.3–7.2 (m, 2H), 5.61 (s, br, 1H, OH), 4.60 (s, 2H, CH_2OH), 4.14 (t, J = 6.4 Hz, 2H), 1.79–1.68 (m, 2H), 1.46–1.20 (m, 10H), 0.85 (t, J = 7.2 Hz, 3H) ppm.

P3: For alternative syntheses, see [35–37]. The reaction was performed under nitrogen. Hydroxylamine hydrochloride (600 mg, 8.63 mmol; excess) and **P1** (750 mg, 5.47 mmol) were stirred in DMSO (3 mL; 99.7%, degassed, extra dry, over mol. sieve, water <50 ppm, Acros) at 100 °C (bath temperature) for 2 h to give dark red solution. It was extracted with CH_2Cl_2 and sat. aq. solution of NaCl. The organic layer was extracted with sat. aq. solution of NaCl to remove the residual DMSO. The aqueous extracts were back-extracted with CH_2Cl_2. The aim of the extraction is to remove DMSO without losing the product (it is soluble in water). The combined organic extracts were evaporated and purified by chromatography on silica (20 g) with CH_2Cl_2 to remove the impurities and with 0.5% CH_3OH in CH_2Cl_2 to recover the product. Pale yellow solid: 446 mg (3.32 mmol; 61%; $C_7H_6N_2O$; MW 134.14). It can be checked for the presence of DMSO by recording ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 4.83 (d, J = 5.2 Hz, 2H, CH_2OH), 3.13 (t, J = 5.2 Hz, 1H, OH) ppm.

P4: For alternative syntheses, see [36–38]. The reaction was performed under nitrogen. SeO_2 (386 mg, 3.48 mmol) and **P3** (933 mg, 6.96 mmol) were stirred in dioxane (30 mL; neither dried nor degassed) at 110 °C (bath temperature) for 24 h to give a dark yellow solution and black precipitate of selenium. The mixture was filtered through Celite to remove selenium. Celite was washed with CH_2Cl_2. Purification by chromatography (10 g of silica; CH_2Cl_2) gave pale yellow eluate of the product. White solid: 692 mg (5.24 mmol; 75%; $C_7H_4N_2O$; MW 132.12). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 8.16 (dd, J = 8.0, 1.2 Hz, 1H), 8.07 (td, 1H), 7.92 (dd, J = 7.6, 0.8 Hz, 1H) ppm.

3.2. Synthesis of carboxylic acids

The reaction was performed under air [26]. The required aldehyde (its synthesis is described in the Supplementary material) was dissolved in formic acid at room temperature to give a pale yellow solution (it might be cloudy due to the presence of red solid, which is residual Se from the previous synthetic step). It was

cooled to 0 °C. Cold H_2O_2 was added (30% wt. solution in water). The mixture was stirred at 0 °C for 6 h and kept overnight in the refrigerator at 3 °C to give colorless or pale yellow solution. Ice-cold water (30 mL for **HL1** and **HL2**; 15 mL for **HL3**; 20 mL for **HL4** and **HL5**) was added drop-wise to precipitate the product. The suspension was stirred for 1 h at 0 °C. It was filtered. The product was washed with water and organic solvent [ether for **HL1** and **HL2**; hexane, hexane/ether (1/1, 50 mL), and, again, hexane for **HL3**; hexane for **HL4** and **HL5**]. It was dried under vacuum. Further details are provided below.

HL1: Aldehyde (642 mg, 1.65 mmol), formic acid (6 mL, 7.32 g, 0.16 mol), and H_2O_2 (0.9 mL, 300 mg of H_2O_2, 8.81 mmol) gave white solid: 585 mg (1.44 mmol, 87%). *Anal.* Calc. for $C_{26}H_{19}N_3O_2$ (MW 405.45): C, 77.02; H, 4.72; N, 10.36. Found: C, 76.97; H, 5.16; N, 10.32%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.58 (dd, J = 7.6, 1.2 Hz, 1H), 8.17 (t, J = 7.6 Hz, 1H), 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.43–7.24 (m, 7H), 6.46 (s, 2H) ppm; CO_2H proton not observed.

HL2: Aldehyde (528 mg, 1.45 mmol), formic acid (6 mL, 7.32 g, 0.16 mol), and H_2O_2 (0.8 mL, 266 mg of H_2O_2, 7.83 mmol) gave white solid: 349 mg (0.92 mmol, 63%). *Anal.* Calc. for $C_{24}H_{17}N_3O_2$ (MW 379.41): C, 75.97; H, 4.52; N, 11.08. Found: C, 76.06; H, 4.66; N, 10.98%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.58 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.13 (td, J = 8.0, 1.2 Hz, 1H), 8.02 (dd, J = 8.0, 1.2 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.65–7.53 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.35–7.22 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 6.98 (s, 2H), 6.34 (d, J = 7.2 Hz, 1H) ppm; CO_2H proton not observed.

HL3: Aldehyde (665 mg, 1.28 mmol), formic acid (4 mL, 4.88 g, 0.11 mol), and H_2O_2 (0.75 mL, 250 mg of H_2O_2, 7.34 mmol) gave white solid: 512 mg (0.96 mmol, 75%). *Anal.* Calc. for $C_{34}H_{35}N_3O_3$ (MW 533.66): C, 76.52; H, 6.61; N, 7.87. Found: C, 76.55; H, 6.66; N, 7.84%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.47 (d, J = 7.2 Hz, 1H), 8.12–8.02 (m, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.28–7.21 (m, 3H), 6.89 (dd, J = 8.8, 2.4 Hz, 1H), 6.41 (s, 2H), 4.00 (t, J = 6.4 Hz, 2H), 1.75–1.65 (m, 2H), 1.44–1.15 (m, 10H), 0.82 (t, J = 6.8 Hz, 3H) ppm; CO_2H proton not observed.

HL4: Aldehyde (227 mg, 0.46 mmol), formic acid (4 mL, 4.88 g, 0.11 mol), and H_2O_2 (0.35 mL, 117 mg of H_2O_2, 3.43 mmol) gave pale orange solid: 154 mg (0.30 mmol, 66%). *Anal.* Calc. for $C_{32}H_{33}N_3O_3$ (MW 507.62): C, 75.71; H, 6.55; N, 8.28. Found: C, 75.19; H, 6.67; N, 8.12%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.49 (dd, J = 8.0, 1.2 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.07 (t, J = 8.0 Hz, 1H), 7.96 (dd, J = 7.6, 0.8 Hz, 1H), 7.92 (d, J = 8.4, 1.6 Hz, 1H), 7.75–7.67 (m, 2H), 7.64–7.53 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.94 (s, 2H), 6.91 (dd, J = 8.8, 2.4 Hz, 1H), 6.33 (d, J = 7.2 Hz, 1H), 3.85 (t, J = 6.8 Hz, 2H), 1.67–1.56 (m, 2H), 1.37–1.15 (m, 10H), 0.83 (t, J = 7.2 Hz, 3H) ppm; CO_2H proton not observed.

HL5: Aldehyde (490 mg, 1.11 mmol), formic acid (4 mL, 4.88 g, 0.11 mol), and H_2O_2 (0.65 mL, 217 mg of H_2O_2, 6.36 mmol) gave pale yellow solid: 397 mg (0.87 mmol, 78%). *Anal.* Calc. for $C_{28}H_{31}N_3O_3$ (MW 457.56): C, 73.50; H, 6.83; N, 9.18. Found: C, 73.31; H, 7.06; N, 9.06%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02 (d, J = 2.4 Hz, 1H), 7.79–7.73 (m, 1H), 7.72–7.66 (m, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.35–7.26 (m, 2H), 7.24–7.12 (m, 5H), 6.39 (s, 2H), 4.24 (t, J = 6.4 Hz, 2H), 1.83–1.72 (m, 2H), 1.50–1.22 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H) ppm; CO_2H proton not observed.

3.3. Synthesis of tetrazoles

The reaction was performed under nitrogen [28]. The required 2-pyridinecarbonitrile (its synthesis is described in the Supplementary material), NaN_3 (small excess), and NH_4Cl (small excess) were stirred in dry degassed DMF (2.5 mL, absolute, puriss >99.8% GC, over molecular sieves, Fluka) at 110 °C (bath temperature) for 24 h to give yellow suspension. It was cooled to room temperature. Water (30 mL) was added to give a suspension of the product. Further details are provided below.

HL6: The reaction was performed with 2-pyridinecarbonitrile (503 mg, 1.09 mmol), NaN_3 (78 mg, 1.20 mmol), and NH_4Cl (64 mg, 1.20 mmol). pH of the suspension was adjusted to 3–4. It was extracted with H_2O/CH_2Cl_2 and purified by chromatography (7 g of silica; with 0.3% CH_3OH in CH_2Cl_2 to remove the impurities; with 2.5% CH_3OH in CH_2Cl_2 to recover the crude product). The product was dissolved in CH_2Cl_2 (20 mL). Hexane (20 mL) was added. CH_2Cl_2 was rotor-evaporated to leave a suspension of the pure product in hexane. The suspension was filtered. The product was washed with ice-cold hexane. White solid: 370 mg (0.73 mmol; 67%). *Anal.* Calc. for $C_{29}H_{41}N_7O$ (MW 503.68): C, 69.15; H, 8.20; N, 19.47. Found: C, 69.07; H, 8.05; N, 19.72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.39 (d, J = 7.2 Hz, 1H), 8.29–8.17 (m, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 6.90 (dd, J = 8.8, 2.0 Hz, 1H), 4.95 (t, J = 6.8 Hz, 2H), 4.07 (t, J = 6.4 Hz, 2H), 1.82–1.72 (m, 2H), 1.66–1.55 (m, 2H), 1.52–1.40 (m, 2H), 1.40–1.22 (m, 8H), 1.18–0.92 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H), 0.74 (t, J = 7.2 Hz, 3H) ppm; NH proton not observed. ^{13}C NMR (200 MHz, DMSO-d_6): δ = 156.7, 151.4, 148.1, 143.8, 139.6, 137.8, 137.0, 126.3, 123.2, 120.7, 113.4, 95.0, 68.5, 44.8, 31.7, 31.4, 29.9, 29.3, 29.24, 29.18, 28.9, 28.7, 26.3, 26.1, 22.6, 22.4, 14.4, 14.3 ppm; one of the aromatic carbons not observed. ESI$^+$ TOF MS: m/z 504.5 {M+H}$^+$.

HL7: The reaction was performed with 2-pyridinecarbonitrile (406 mg, 0.88 mmol), NaN_3 (63 mg, 0.97 mmol), and NH_4Cl (54 mg, 1.01 mmol). The suspension was stirred for 1 h. The solid was filtered. It was thoroughly washed with water and with ice-cold hexane (2 × 10 mL). It was dried under vacuum. It was purified by chromatography (6 g of silica; with 0.3% CH_3OH in CH_2Cl_2 to remove the impurities; with 3% CH_3OH in CH_2Cl_2 to recover the product). Pink oil that crystallizes to white solid: 273 mg (0.54 mmol; 62%). *Anal.* Calc. for $C_{29}H_{41}N_7O$ (MW 503.68): C, 69.15; H, 8.20; N, 19.47. Found: C, 69.16; H, 8.15; N, 19.28%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.89 (d, J = 1.6 Hz, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 4.98 (t, J = 7.2 Hz, 2H), 4.29 (t, J = 6.8 Hz, 2H), 1.86–1.76 (m, 2H), 1.69–1.58 (m, 2H), 1.52–1.41 (m, 2H), 1.41–1.21 (m, 8H), 1.18–0.92 (m, 10H), 0.86 (t, J = 7.2 Hz, 3H), 0.74 (t, J = 7.2 Hz, 3H) ppm; NH proton not observed. ESI$^+$ TOF MS: m/z 504.3 {M+H}$^+$.

3.4. Synthesis of lanthanide complexes

The reactions were performed under air with a 3:3:1 M ratio of the ligand (**HL1** to **HL7**), NaOH (base), and $LnCl_3{\cdot}nH_2O$ (Ln = La, Eu). The ligand was suspended in hot ethanol (65–75 °C, 5 mL; the same temperature was kept throughout the reaction). A solution of NaOH in water was added (0.5–1 mL, used as a stock solution with 100 mg of NaOH per 10 mL of water). The mixture was stirred for 5 min to give a solution. A solution of $LnCl_3{\cdot}nH_2O$ (Ln = La, n = 7; Ln = Eu, n = 6; 99.9%, Aldrich) in water (2 mL) was added drop-wise over 5 min. The mixture was stirred for further 5 min. Usually, a solid or an oily precipitate of the complex appeared on stirring. If it was required, water was added to induce and complete precipitation of the complex or to crystallize the oily precipitate. The suspension was further stirred for 5 min at 65–75 °C. It was allowed to cool to 40–50 °C. It was filtered while it was warm. The product was washed with ethanol/water (1/1) and either ether or hexane. It was dried under vacuum at room temperature. The complexes are white or pale colored solids. They are soluble in dichloromethane and DMSO. They are insoluble in hexane and water. Elemental analysis indicates that the complexes have the composition

$Ln(Ligand)_3 \cdot nH_2O \cdot mC_2H_5OH$, where $n = 0.5–4$ and $m = 0–1$. The new lanthanide complexes are mixtures of species (see the main text for discussion). The complexes did not give suitable crystals for X-ray structure analysis. ^1H NMR spectra of lanthanum complexes in CD_2Cl_2 (a non-coordinating solvent) at room temperature are broad and non-informative. Further details for the lanthanum complexes are provided below. The europium complexes are described in the Supplementary material.

La(**L1**)$_3 \cdot 2H_2O$: The complex precipitated on addition of water (1 mL). It was washed with ethanol/water (1/1) and ether. White solid: 33 mg (0.024 mmol, 58%) from **HL1** (50 mg, 0.123 mmol), NaOH (4.93 mg, 0.123 mmol), and $LaCl_3 \cdot 7H_2O$ (15.3 mg, 0.041 mmol). *Anal.* Calc. for $C_{78}H_{54}LaN_9O_6 \cdot 2H_2O$ (MW 1388.26): C, 67.48; H, 4.21; N, 9.08. Found: C, 67.73; H, 4.31; N, 8.93%.

La(**L2**)$_3 \cdot 3H_2O \cdot C_2H_5OH$: The complex precipitated on addition of water (3 mL). It was washed with ethanol/water (1/1) and ether. Pale pink solid: 28 mg (0.020 mmol, 46%) from **HL2** (50 mg, 0.132 mmol), NaOH (5.27 mg, 0.132 mmol), and $LaCl_3 \cdot 7H_2O$ (16.3 mg, 0.044 mmol). *Anal.* Calc. for $C_{72}H_{48}LaN_9O_6 \cdot 3H_2O \cdot C_2H_5OH$ (MW 1374.23): C, 64.68; H, 4.40; N, 9.17. Found: C, 65.07; H, 4.41; N, 8.89%.

La(**L3**)$_3 \cdot 2H_2O$: The complex precipitated as oil on mixing of the reagents. It crystallized on cooling and scratching. It was washed with ethanol/water (1/1) and hexane. Cream solid: 44 mg (0.025 mmol, 80%) from **HL3** (50 mg, 0.094 mmol), NaOH (3.75 mg, 0.094 mmol), and $LaCl_3 \cdot 7H_2O$ (11.6 mg, 0.031 mmol). *Anal.* Calc. for $C_{102}H_{102}LaN_9O_9 \cdot 2H_2O$ (MW 1772.89): C, 69.10; H, 6.03; N, 7.11. Found: C, 69.24; H, 6.25; N, 7.05%.

La(**L4**)$_3 \cdot 3H_2O$: The complex precipitated as oil on mixing of the reagents and on addition of water (1 mL). It crystallized on cooling and scratching. It was washed with ethanol/water (1/1) and hexane. Pale brown solid: 38 mg (0.022 mmol, 67%) from **HL4** (50 mg, 0.099 mmol), NaOH (3.94 mg, 0.099 mmol), and $LaCl_3 \cdot 7H_2O$ (12.2 mg, 0.033 mmol). *Anal.* Calc. for $C_{96}H_{96}LaN_9O_9 \cdot 3H_2O$ (MW 1712.80): C, 67.32; H, 6.00; N, 7.36. Found: C, 67.36; H, 6.03; N, 7.26%.

La(**L5**)$_3 \cdot 2H_2O$: The complex precipitated as oil on addition of water (1 mL). It crystallized after decanting of the mother liquor and after washing with ethanol/water (1/1). It was washed with ethanol/water (1/1) and hexane. White solid: 32 mg (0.021 mmol, 58%) from **HL5** (50 mg, 0.109 mmol), NaOH (4.37 mg, 0.109 mmol), and $LaCl_3 \cdot 7H_2O$ (13.5 mg, 0.036 mmol). *Anal.* Calc. for $C_{84}H_{90}LaN_9O_9 \cdot 2H_2O$ (MW 1544.60): C, 65.32; H, 6.13; N, 8.16. Found: C, 65.65; H, 6.21; N, 8.09%.

La(**L6**)$_3 \cdot 4H_2O$: The complex precipitated as oil on addition of water (1 mL). It crystallized on cooling and stirring. It was washed with ethanol/water (1/1) and hexane. White solid: 31 mg (0.018 mmol, 55%) from **HL6** (50 mg, 0.099 mmol), NaOH (3.97 mg, 0.099 mmol), and $LaCl_3 \cdot 7H_2O$ (12.3 mg, 0.033 mmol). *Anal.* Calc. for $C_{87}H_{120}LaN_{21}O_3 \cdot 4H_2O$ (MW 1718.99): C, 60.79; H, 7.51; N, 17.11. Found: C, 60.54; H, 7.16; N, 17.08%.

La(**L7**)$_3 \cdot 4H_2O$: The complex precipitated as oil on addition of water (1.5 mL). It crystallized on cooling and stirring. It was washed with ethanol/water (1/1) and hexane. White solid: 28 mg (0.016 mmol, 49%) from **HL7** (50 mg, 0.099 mmol), NaOH (3.97 mg, 0.099 mmol), and $LaCl_3 \cdot 7H_2O$ (12.3 mg, 0.033 mmol). *Anal.* Calc. for $C_{87}H_{120}LaN_{21}O_3 \cdot 4H_2O$ (MW 1718.99): C, 60.79; H, 7.51; N, 17.11. Found: C, 60.34; H, 7.04; N, 17.43%.

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Appendix A. Supplementary material

Synthesis of intermediates and europium complexes; absorption, luminescence, and ^1H NMR spectra. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.11.037.

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