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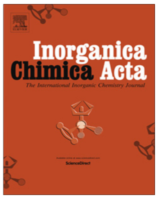

Synthesis and spectroscopy of anionic tridentate benzimidazole-pyridine carboxylate and tetrazolate chromophore ligands

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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].

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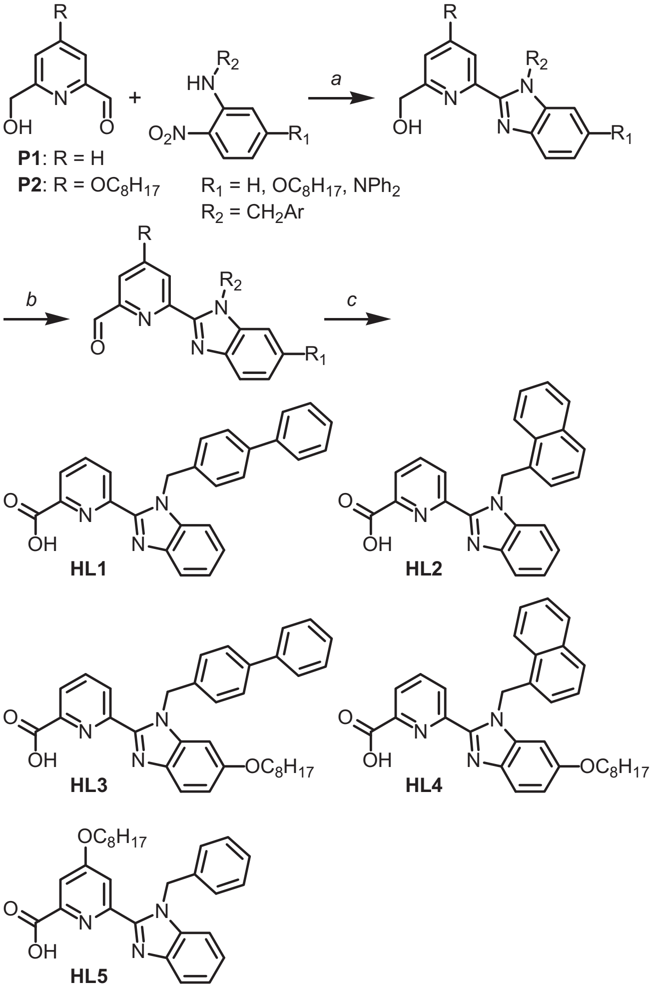
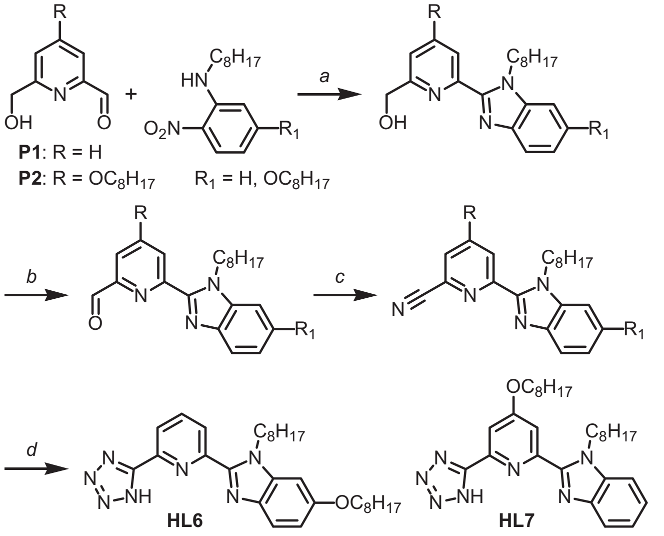


Scheme 1. Synthesis of carboxylic acids **HL1**–**HL5**: (a) $Na_2S_2O_4$, DMF/H_2O, under N_2, 110–120 °C; (b) SeO_2, dioxane, under N_2, 110 °C; (c) H_2O_2, formic acid, under air, 0 °C (this reaction does not work when R, R_1, and R_2 are H, NPh_2, and C_8H_{17}, respectively).

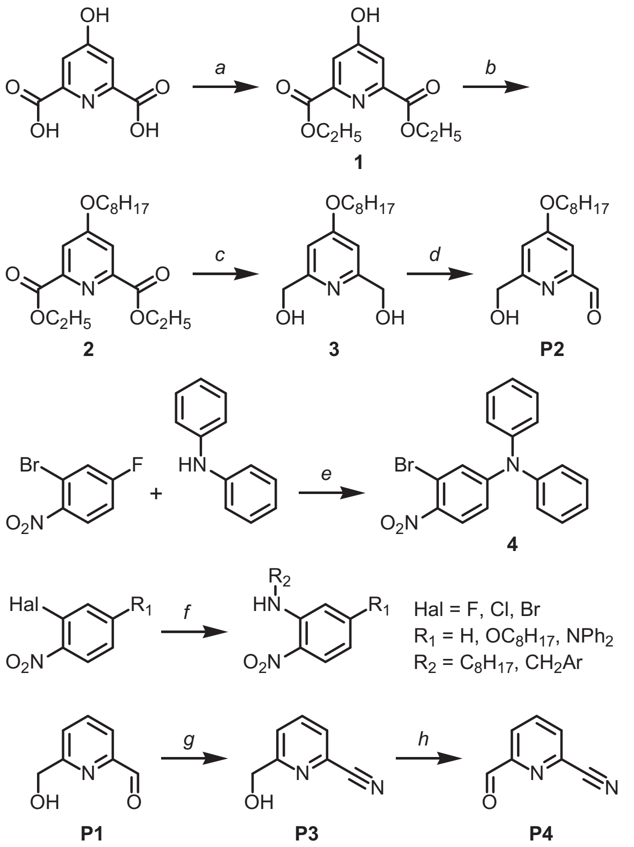
The known 2,6-disubsituted pyridines **P3** [35–37] and **P4** [36–38], which we planned to use in the synthesis of tetrazoles, were prepared from **P1** (we described its multi-gram synthesis before [12]) by conversion of the carboxaldehyde into the carbonitrile **P3** with $NH_2OH{\cdot}HCl$ in DMSO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