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Efficient route to hybrid polypyridine–carboxylate ligands for lanthanide complexation

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Abstract—An efficient methodology for the preparation of aminobutyl-bromo-terpyridine is described using a preformed imine prepared from a *gem*-dibromomethyl terpyridine derivative and the primary amine and further reduced to the secondary amine. Alkylation with pyridine, bipyridine, or terpyridine residues in the presence of a mineral base provides highly functionalized asymmetrical and symmetrical N-heterocyclic ligands. All bromo-containing products were subjected to a carboalkoxylation/hydrolysis sequence of reactions, providing the desired carboxylic acids. Stable Eu complexes were prepared under neutral aqueous conditions and some of them display interesting spectroscopic properties.

Polypyridine ligands (e.g., bipyridine, phenanthroline, and terpyridine) have been widely studied for their unique coordination abilities toward transition metals and lanthanide salts.[1] The stability of the resulting complexes depends on the acidity of the metal center and on the steric crowding provided by the ligand around the cations. Recently, these polypyridine complexes have been discussed as potential candidates for optoelectronic devices,[2] π-conjugated functional materials.[3] In addition, these lanthanide complexes have potential applications in electroluminescence.[4]

In fluid solution the lanthanide scaffoldings appear to be more fragile and the luminescence is effectively quenched by vibronic deactivation processes. This is particularly true in aqueous solution.[5] The engineering of molecular architectures (macrocyclic loops, flexible multitopic podands, preorganized, and rigid frameworks...) has blossomed over the last decade and spectacular increase in stability and improvement of spectroscopic properties have been successfully reached.[6] In particular, the design of highly absorbing ligands for the antenna effect and the presence of multiple donor atoms largely excluding water from the first coordination sphere were effective tools in reaching quantum yields over 10% for Eu and Tb and lifetimes longer than 1 ms.[6,7]

However, if luminescent lanthanide chelates are to be used as tags in more advanced technologies such as homogeneous fluoroimmunoassays, fluorescence imaging, immuno-histochemistry, or in situ hybridization techniques, additional strict requirements are needed, namely: (i) high thermodynamic and kinetic stability, (ii) hydrophilicity, (iii) very efficient cation emission and high absorption at a suitable wavelength, (iv) a chemical structure allowing proper linkage via a covalent bond between the label and the targeted biomolecule, (v) the affinity and specific binding properties of the labelled biomolecules must be retained and (vi) the possible effects that the attachment of the label to the biological species may have on the photophysical properties of the tag must be taken into account.[8] As a consequence of these requirements for the optimal stability and luminescence properties only a few viable labels have been nowadays developed and tested.[9]

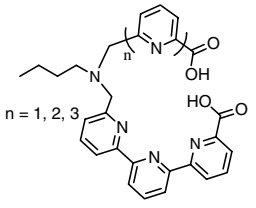

Chart 1.

One suitable possibility to prepare very stable complexes is to use negatively charged pendant arms such

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as methyl-acetate a tenet used in DOTA (1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) for the complexation of gadolinium cations and their application in magnetic resonance imaging.[10] We have recently introduced the possibility of combining within a simple design the donor center, the chromophoric unit, and an anionic side function directly fused to the N,N chelating unit. This ideal anionic tridendate pocket provides various preorganized platforms for lanthanide complexation.[11] Several of these complexes have been structurally characterized and have proven to be exceptionally stable in aqueous and biological solutions. However, the use of anionic auxiliaries in the field of luminophoric labels is less extensive than one might expect. This shortcoming is largely due to the difficulties in preparing the prerequisite starting building blocks and in introducing the carboxylic functions directly on the aromatic scaffold. Furthermore, terpyridine derivatives have received little attention despite their appropriate absorption wavelengths and high extension coefficients.[12]

Herein, we wish to report the convenient preparation of asymmetrical and symmetrical terpyridine based podands bearing useful carboxylic functions suitable for the preparation of lanthanide complexes (Chart 1). Within this new series of terpy based ligands, the number of pyridine rings is increased from one to three and the influence on the photophysical properties of the Eu complexes is scrutinized.

Starting materials **1a**[13] and **2**[14] were prepared according to the literature (see Chart 2). The monobromo- and dibromomethyl derivatives **3a** (25%) and **3b** (65%) were prepared in one pot by conventional radical bromination of 6-bromo-2″-methyl-2,2′:6′,2″-terpyridine[15] using NBS (5 equiv), and AIBN (4 mol %) in refluxing benzene using a 100 W halogen lamp as the heat source. The yield for the synthesis of **3a** was increased to 65% using 1 equiv of NBS and a shorter reaction time. The dibromo compound **3b** was a very interesting starting material for the synthesis of secondary amine derivatives (Scheme 1).

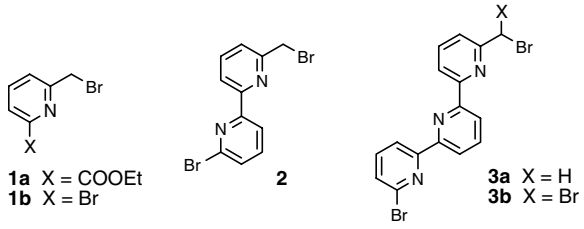
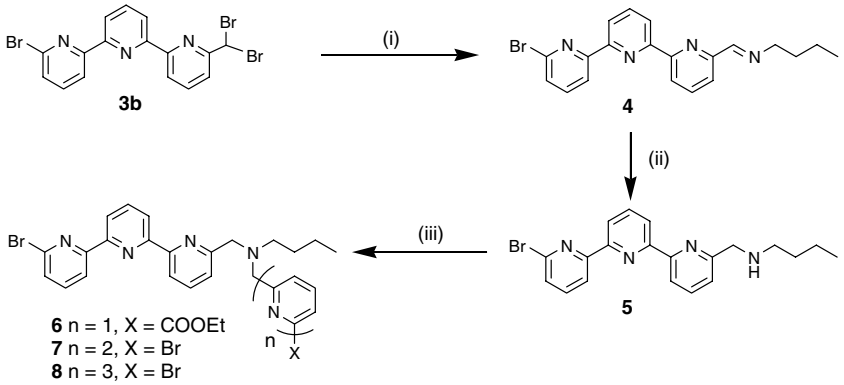


Chart 2.

For the preparation of the key compound **5**, the Schiff base route proved to be the most adapted. When the *gem*-dibromo derivative **3b** was allowed to react with *n*-butylamine under anhydrous conditions,[16] the imino species **4** was obtained quantitatively. The desired secondary amino compound **5** was then obtained by reduction with $NaBH_4$ in ethanol. An alternative route consisted in the reaction of the monobromo derivative **3a** in neat *n*-butylamine. However, this reaction afforded an intractable mixture of derivatives which could not be separated by column chromatography. The addition of K_2CO_3 to the mixture did not improve the reaction. It was our hypothesis that despite the high concentration of the primary amine, multiple substitution processes occurred, possibly on the bromopyridine. As a consequence, the best alternative to synthesize the secondary amine **5** is the route presented in Scheme 1.

Subsequent work focused on optimizing of the nucleophilic substitution at the bromomethylene function of compounds **1a**, **2**, and **3a** by the secondary amine **5**. After some experimentation, it was found that the substitution was effective under strict anhydrous conditions, using equimolar quantities of reactants at a mild temperature over long reaction times. The asymmetrically and symmetrically substituted compounds **6** and **7**, and **8**, respectively, were prepared in acceptable yields after column chromatography (respectively, 87%, 82%, and 87%). Nevertheless, in all cases this protocol generated trace amounts of the triply alkylated ammonium compounds which complicated the purification procedure.

Inspired by previous work performed on carboalkoxylation of oligopyridine compounds,[17] the bromopyridine functions of **6**, **7**, and **8** were transformed into carboxylic ester derivatives. The reaction was promoted by



Scheme 1. Reagents and conditions: (i) ^{n}BuNH$_2$, CH_3CN, K_2CO_3, 80 °C, 26 h, 99%. (ii) $NaBH_4$, EtOH, 65 °C, 35 h, 99%. (iii) For **6**, 1 equiv of **1a**, for **7**, 1 equiv of **2**, for **8**, 1 equiv of **3a**, anhydrous CH_3CN, K_2CO_3, 80 °C, 93 h, yield range 82–87%.

$[Pd(PPh_3)_2Cl_2]$ (10 mol %). Optimized conditions used ethanol as solvent and reactant, triethylamine as base, and a continuous flow of CO at atmospheric pressure. The pure carboethoxy esters were isolated after column chromatography in 80–94% yield. Interestingly, this kind of protocol was first attempted using the tertiary amine obtained from nucleophilic substitution of **5** with 6-bromomethyl-2-bromopyridine **1b**, but as previously observed,[18] the carboalkoxylation reaction proved to be far less efficient for the simple bromopyridine, justifying the use of compound **1a**. Hydrolysis of the esters to the acids was straightforward using concentrated HCl at 70 °C to afford the target compounds **10**, **12** and **14**[19] in 70%, 95%, and 94% yields, respectively (Chart 3).

On the basis of the above optimization efforts, the secondary aminodiacetate derivative **15** was used as a starting material to incorporate a pendant methylterpyridine arm (Scheme 2).

The first reaction proceeded smoothly under anhydrous conditions leading to **16** in 70% isolated yield. Conversion of the bromo derivative was conducted under conditions similar to those used in the carboalkoxylation reaction described above, to afford **17** in 93% isolated yield. Simultaneous hydrolysis of the three ester functions provided **18** in 85% yield. The phosphorylation reaction was carried out using $[Pd(PPh_3)_4]$ and diethylphosphite at higher temperature using Hünig's base.[20] The use of excess PPh_3 was required to insure a 72% yield. Likewise, both the carboxylic and the phosphoric esters were hydrolyzed with concentrated HCl providing compound **20** in 95%.[21]

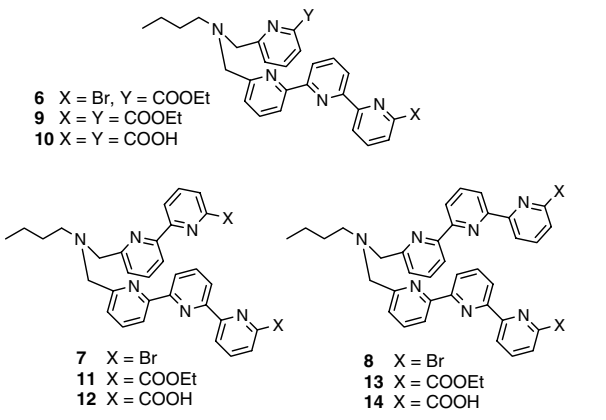
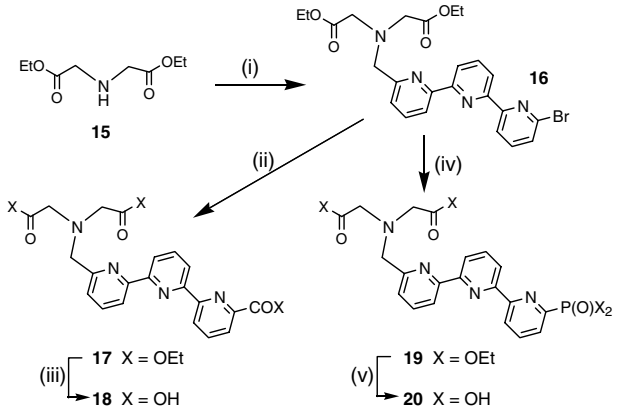


Chart 3.



Scheme 2. Reagents and conditions: (i) **3a** (1 equiv), CH_3CN, K_2CO_3, 80 °C, 23 h, 70%. (ii) $[Pd(PPh_3)_2Cl_2]$ (10%), CO (1 atm), EtOH, Et_3N, 70 °C, 21 h, 93%. (iii) Concd HCl, 80 °C, 3 h, 85%. (iv) $HP(O)(OEt)_2$, $[Pd(PPh_3)_4]$, PPh_3, $(i\text{-}Pr)_2EtN$, MePh, 110 °C, 18 h, 72%. (v) Concd HCl, 80 °C, 36 h, 95%.

To test the effectiveness of terpyridine ligands to sensitize lanthanide emission,[12,22] Eu complexes of ligands **10**, **12**, and **14** were prepared by mixing equimolar amounts of the ligands and $EuCl_3{\cdot}6H_2O$ in aqueous solutions. The isolated complexes have the generic formulae $[Eu(\mathbf{L})Cl]{\cdot}3H_2O$ and were characterized by elemental analysis, infrared spectroscopy and mass spectrometry. The latter confirmed a one to one metal to ligand stoichiometry in all cases.[23] All complexes displayed significant europium emission in water upon UV excitation, confirming an efficient ligand to metal energy transfer (Fig. 1). Nevertheless, this transfer is not quantitative, as shown by the presence of a weak residual fluorescence signal of the ligand in the 350–450 nm region.

Table 1 summarizes the main photophysical properties of the Eu complexes in aqueous conditions. In all cases, the luminescence decay of Eu could be perfectly fitted with a mono-exponential function (Fig. 1), confirming the presence of single species in solution. From the analysis of the luminescence lifetimes of Eu in water and deuterated water, it was possible to calculate the number of water molecules directly linked to the first

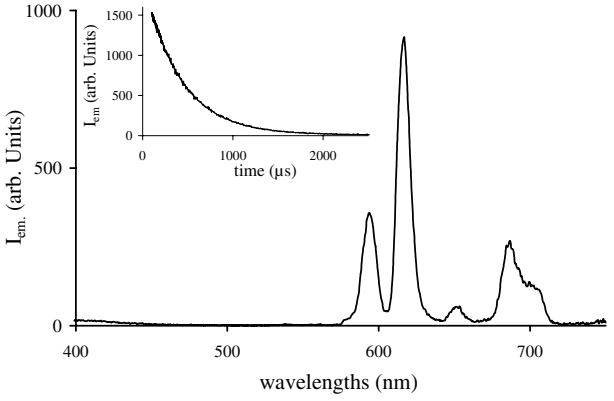


Figure 1. Emission spectrum of $[Eu(\mathbf{12})Cl]^+$ in water (Tris/HCl, 0.01 M, pH 7.0, $\lambda_{exc} = 337$ nm, cut-off filter at 390 nm). Inset: intensity decay profile of Eu and its mono-exponential fitting ($\lambda_{exc} = 290$ nm, $\lambda_{em} = 609$ nm).

Table 1. Emission properties of the Eu complexes of ligands **10**, **12**, and **14**

	ϕ_{H_2O} (%)	τ_{H_2O} (τ_{D_2O}) (µs)	q (±0.5)
$[Eu\mathbf{10}]^+$	5.7	390 (2060)	2.0
$[Eu\mathbf{12}]^+$	3.7	410 (2180)	1.9
$[Eu\mathbf{14}]^+$	0.5	360 (2060)	2.2

coordination sphere of the cations (hydration number q in Table 1).[24]

Surprisingly, despite the increase of the number of potentially coordinating pyridyl rings from **10** to **14**, the hydration number remains constant at two water molecules within the series. It is noteworthy that the gradual increase of denticity of the ligands resulted in a decrease of the luminescence quantum yield of the Eu complexes. Increasing the size of the second coordination arm concomitantly increases the steric constraints, favoring non-radiative deactivation pathways and resulting in a lower overall luminescence quantum yield. Remarkably, the hybrid terpy/py ligand **10** bearing seven donor atoms (2O/5N) gives an europium complex that displays the most attractive properties, combining the large absorption of tepyridine with the strong chelation of 6-carboxypyridine.[25] Preliminary results on the Tb complexes also revealed interesting properties with quantum yields larger than 10%.[26]

The present work describes the synthetic approach to new ligands for lanthanide complexation based on asymmetric terpyridines containing carboxylate or phosphonate coordinating functions. The podand type structures were obtained by an original protocol for the synthesis of secondary amines. The synthesis is based on the condensation of an amine on *gem*-dibromo derivatives to form imines under basic conditions, followed by reduction of the imines. Europium complexes of some of these terpyridines were prepared and displayed interesting luminescence properties in aqueous solutions.

Acknowledgments

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19. *Compound* **10**: ^{1}H NMR (methanol-d_4): $\delta = 0.96$ (t, 3H, $^3J = 7.0$ Hz), 1.42–1.52 (m, 2H), 1.9–2.0 (m, 2H), 3.53 (t, 2H, $^3J = 8.0$ Hz), 4.90 (s, 2H), 4.91 (s, 2H), 7.67 (d, 1H, $^3J = 7.0$ Hz), 7.72 (d, 1H, $^3J = 8.0$ Hz), 7.97 (d, 1H, $^3J = 8.0$ Hz), 8.03 (t, 1H, $^3J = 7.0$ Hz), 8.13 (t, 1H, $^3J = 8.0$ Hz), 8.30 (d, 2H, $^3J = 8.0$ Hz), 8.39 (t, 1H, $^3J = 8.0$ Hz), 8.60 (d, 1H, $^3J = 8.0$ Hz), 8.72 (d, 1H, $^3J = 8.0$ Hz), 8.78 (d, 1H, $^3J = 8.0$ Hz), 8.80 (d, 1H, $^3J = 8.0$ Hz). MS (FAB$^+$): $m/z = 497.2$ ([M]$^+$, 100%). Anal. Calcd for $C_{28}H_{27}N_5O_4{\cdot}3HCl{\cdot}3H_2O$: C, 50.88; H, 5.49; N 10.60. Found: C, 50.43; H, 5.68; N, 10.55.
Compound **12**: ^{1}H NMR (methanol-d_4): $\delta = 0.99$ (t, 3H, $^3J = 7.0$ Hz), 1.44–1.52 (m, 2H), 1.93–2.04 (m, 2H), 3.61 (t, 2H, $^3J = 7.0$ Hz), 4.99 (s, 2H), 5.00 (s, 2H), 7.53 (d, 1H, $^3J = 8.0$ Hz), 7.69 (d, 1H, $^3J = 8.0$ Hz), 7.72 (d, 1H, $^3J = 8.0$ Hz), 7.94 (t, 1H, $^3J = 8.0$ Hz), 8.03 (dd, 1H, $^3J = 7.0$ Hz, $^4J = 1.0$ Hz), 8.12 (t, 1H, $^3J = 8.0$ Hz), 8.21 (d, 1H, $^3J = 8.0$ Hz), 8.26 (d, 1H, $^3J = 8.0$ Hz), 8.32 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 2.0$ Hz), 8.39 (d, 1H, $^3J = 8.0$ Hz), 8.43 (d, 1H, $^3J = 8.0$ Hz), 8.53 (d, 1H, $^3J = 8.0$ Hz), 8.62 (d, 1H, $^3J = 7.0$ Hz), 8.67 (d, 1H, $^3J = 7.0$ Hz), 8.68 (d, 1H, $^3J = 7.0$ Hz). MS (FAB$^+$): $m/z = 575.2$ ([M + H]$^+$, 100%). Anal. Calcd for $C_{33}H_{30}N_6O_4{\cdot}HCl{\cdot}2H_2O$: C, 61.25; H, 5.45; N, 12.99. Found: C, 61.10; H, 5.33; N, 12.74.
Compound **14**: ^{1}H NMR (methanol-d_4): $\delta = 0.98$ (t, 3H, $^3J = 7.0$ Hz), 1.44–1.54 (m, 2H), 1.96–2.06 (m, 2H), 3.67 (t, 2H, $^3J = 8.0$ Hz), 5.08 (s, 4H), 7.72 (d, 2H, $^3J = 8.0$ Hz), 8.07 (t, 2H, $^3J = 8.0$ Hz), 8.12–8.16 (m, 2H), 8.23 (d, 2H, $^3J = 8.0$ Hz), 8.29 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.0$ Hz), 8.37 (d, 2H, $^3J = 8.0$ Hz), 8.46 (d, 2H, $^3J = 8.0$ Hz), 8.56 (t, 4H, $^3J = 7.0$ Hz). Anal. Calcd for $C_{38}H_{33}N_7O_4{\cdot}3HCl{\cdot}3H_2O$: C, 55.99; H, 5.19; N, 12.03. Found: C, 56.19; H, 5.05; N, 11.92.
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21. *Compound* **20**: ^{1}H NMR (DMSO-d_6): $\delta = 3.94$ (s, 4H), 4.43 (s, 2H), 7.68 (d, 1H, $^{3}J = 8.0$ Hz), 7.89 (t, 1H, $^{3}J = 7.0$ Hz), 8.08 (d, 1H, $^{3}J = 8.0$ Hz), 8.11 (t, 1H, $^{3}J = 8.0$ Hz), 8.19 (t, 1H, $^{3}J = 8.0$ Hz), 8.49 (d, 1H, $^{3}J = 7.0$ Hz), 8.56 (d, 1H, $^{3}J = 8.0$ Hz), 8.62 (d, 1H, $^{3}J = 8.0$ Hz), 8.70 (d, 1H, $^{3}J = 8.0$ Hz). ^{31}P NMR (CD_6SO): $\delta = 7.7$. MS (FAB$^+$): $m/z = 459.2$ ([M + H]$^+$, 100%). Anal. Calcd for $C_{20}H_{19}N_4O_7P{\cdot}2HCl{\cdot}H_2O$: C, 43.73; H, 4.22; N, 10.20. Found: C, 44.28; H, 4.62; N, 10.19.

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23. [Eu**10**$(H_2O)_2$]Cl·$2H_2O$. Yield: 97%, orange crystalline powder. IR (solid): 3361 (s), 3074 (w), 2961 (w), 2872 (w), 1620 (m), 1590 (s), 1572 (s), 1455 (m), 1378 (m), 1014 (m), 776 (m) cm^{-1}. MS (FAB$^+$): $m/z = 646.2$ ([Eu**10**]$^+$, 70%). Anal. Calcd for $C_{28}H_{25}ClN_5O_4Eu{\cdot}4H_2O$: C, 44.54; H, 4.41; N, 9.28. Found: C, 44.39; H, 4.20; N, 9.02.

[Eu**12**$(H_2O)_2$]Cl·H_2O. Yield: 86%, yellowish crystalline powder. IR (solid): 3390 (s), 1614 (s), 1591 (s), 1572 (s), 1461 (m), 1373 (m), 1011 (m), 778 (m) cm^{-1}. MS (FAB$^+$): $m/z = 723.2$ ([Eu**12**]$^+$, 85%), 725.2 ([Eu**12**]$^+$, 100%). Anal. Calcd for $C_{33}H_{28}N_6O_4Eu{\cdot}Cl{\cdot}3H_2O$: C, 48.69; H, 4.21; N, 10.32. Found: C, 48.44; H, 3.84; N, 10.16.

[Eu**14**$(H_2O)_2$]Cl·H_2O. Yield: 87%, white crystalline powder. IR (solid): 3361 (s), 2961 (w), 1627 (m), 1596 (s), 1572 (s), 1456 (m), 1372 (m), 1013 (m), 777 (s) cm^{-1}. MS (FAB$^+$): $m/z = 800.2$ ([Eu**14**]$^+$, 80%), 802.1 ([Eu**14**]$^+$, 100%). Anal. Calcd for $C_{38}H_{31}ClN_7O_4Eu{\cdot}3H_2O$: C, 51.21; H, 4.18; N, 11.00. Found: C, 51.09; H, 4.01; N, 10.73.

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