Enhanced Eu^{III} ion luminescence and efficient energy transfer between lanthanide chelates within the polymeric structure in aqueous solutions

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Four new binucleating symmetric bis(4-pyridine-2,6-dicarboxylic acids) have been synthesized and luminescence enhancement of their Eu^{III} complexes by Y^{III} ions observed. The results indicate that the mechanism of enhancement is based on the formation of a polymeric structure where Eu^{III} ions and Y^{III} ions are linked together by the ligands with the consequent transfer of absorbed energy along the polymer chain through several ligands toward the Eu^{III} ion. The mechanism of energy transfer is probably different from the previously reported micellar co-luminescence where energy transfer occurs *via* the Förster dipole–dipole mechanism.

In recent years there has been a growing interest in the luminescence properties of lanthanide chelates because of their potential use as probes and labels for a variety of chemical and biological applications.[1–3] Especially Eu^{III}, Tb^{III} and Sm^{III} ions have excellent luminescence properties, but their absorption bands are weak and narrow. In order to enhance absorption, lanthanide (Ln^{III}) ions are usually chelated with ligands that have broad intense absorption bands. In these systems intense ion luminescence originates from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide ion.[4] The intensity of the luminescence depends directly on the absorptivity of the ligand, on the efficiency of energy transfer from the ligand to the lanthanide ion and on the co-ordination of the ligand to the Ln^{III} ion. Because these properties depend mostly on the structure of the ligands, a great deal of synthetic work has been done with them.[5–9]

New methods have also been developed to increase lanthanide ion luminescence. Hemmilä *et al.*[2] have observed luminescence enhancement of Eu^{III} and Tb^{III} by adding either Gd^{III} or Y^{III} to a micellar solution of β-diketone, Triton X-100 and phenanthroline. This phenomenon was termed co-luminescence. The luminescence enhancement by co-luminescence is based on the Förster type of intermolecular energy transfer from the chelates of the enhancing ion (such as Gd^{III} and Y^{III}) to the chelates of the emitting ion (such as Eu^{III}, Sm^{III} and Tb^{III}). The co-luminescence is observed in a micellar environment, but is absent in microhomogeneous solution. In benzene, *e.g.* there is no co-luminescence enhancement because the chelates exist as separate molecules and the long distance between them makes intermolecular energy transfer impossible.[2]

The aim of our work was to build up an energy antenna, which has a simpler structure and is therefore easier to investigate than the previously developed systems for co-luminescence. Also, our interest was to produce enhanced Eu^{III} ion luminescence in aqueous solutions using energy transfer between ligands, which are linked together by Ln^{III} ions, without other additives and micelle formation. In order to form a structure where energy transfer between different lanthanide chelates would be possible, we synthesized four new binucleating complexing agents (BCA): 1,2-bis(2,6-dicarboxypyridin-4-yl)ethyne (ligand **1**); 1,4-bis[2-(2,6-dicarboxypyridin-4-yl)ethynyl]benzene (ligand **2**); 1,4-bis(2,6-dicarboxypyridin-4-yl)buta-1,3-diyne (ligand **3**) and 1,4-bis(2,6-dicarboxypyridin-4-yl)benzene (ligand **4**).

Results and discussion

Synthesis

Ligand BCA1 was synthesized by coupling dimethyl 4-iodopyridine-2,6-dicarboxylate[10] with acetylene in the presence of palladium(II) acetate, triphenylphosphine and CuI. The tetramethyl ester was hydrolysed with KOH in EtOH. An organometallic coupling reaction of diethyl 4-ethynylpyridine-2,6-dicarboxylate[8] with 1,4-diiodobenzene and saponification of the tetramethyl ester gave ligand BCA2. The dimer of diethyl 4-ethynylpyridine-2,6-dicarboxylate was prepared by oxidative coupling of the alkyne with oxygen and Cu_2Cl_2.[11] Condensing four 2-acetylfurans with terephthalaldehyde gave a ketone which was converted to 1,4-bis[2,6-bis(2-furyl)pyridin-4-yl]-benzene with ammonium acetate in MeOH and oxidized with $KMnO_4$ to BCA4.[12]

Energy transfer and luminescence

All the synthesized BCA ligands have symmetric, conjugated structures and are capable of co-ordinating simultaneously two cations, each through two carboxylic acid oxygens and one nitrogen atom of the pyridine ring. One Ln^{III} ion, which has a co-ordination number nine, can then be complexed by three such ligands. These BCA ligands facilitate the formation and growth of a polymeric structure, where Ln^{III} ions are linked together through BCA ligands. An infinitely large polymer would then correspond to a 3:2 ligand-to-metal ratio. A schematic representation of the structure around Eu^{III} ion in the formed polymeric structure is shown in Fig. 1.

In this polymeric network the enhancement of Eu^{III} ion luminescence is based on two factors. First, a great excess of energy donors (BCA ligands) relative to energy acceptors (Eu^{III} ion) is used. Excess of BCA ligands is added to obtain maximum absorption and excess of Y^{III} ion is added to link the ligands and enhance intersystem crossing to triplet state in these extra ligands. Secondly, the energy absorbed by BCA ligands coordinated to Y^{III} ions is transferred toward Eu^{III} ions *via* triplet–triplet migration. The proposed mechanism of the energy transfer process is illustrated in Fig. 2. One Eu^{III} ion is able to be excited either by the energy absorbed by three BCA ligands, which are coordinated directly to it, or by several other BCA ligands, which transfer their energy to this Eu^{III} ion through ligands coordinated directly to it. In practice this means that when energy is lost non-radiatively during the energy transfer

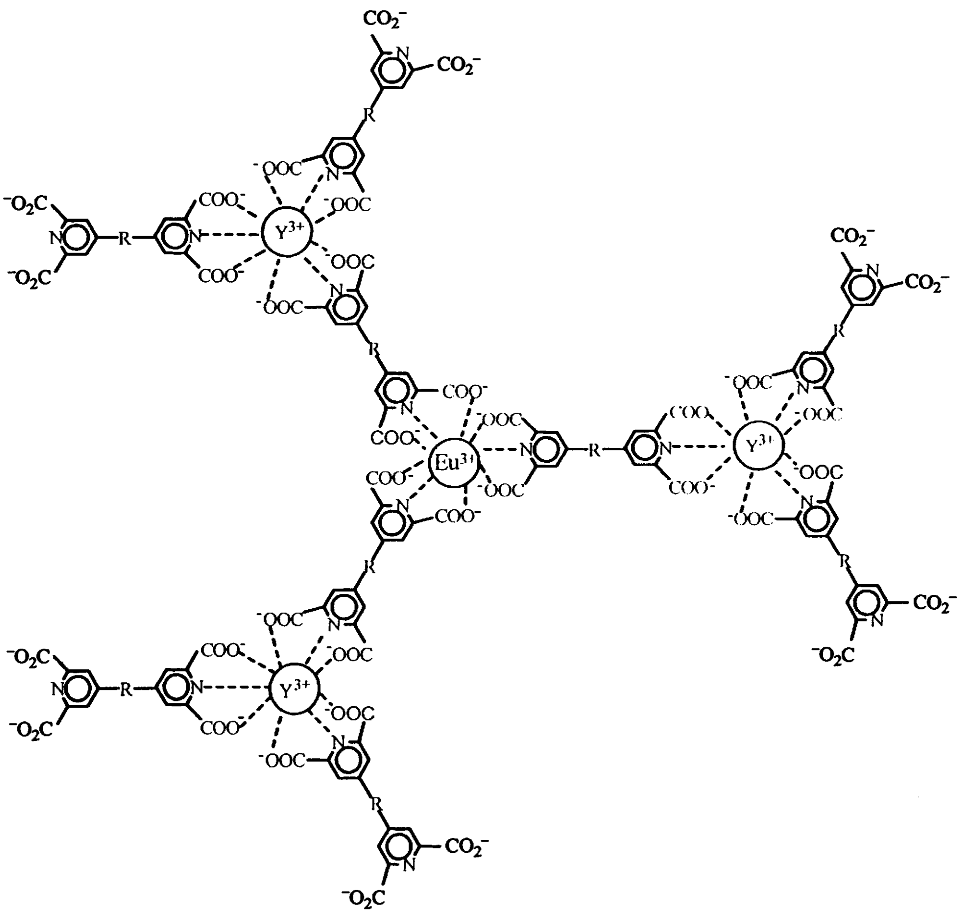
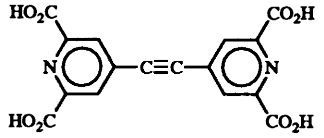


Fig. 1 Schematic representation of the structure around the Eu^{III} ion in aqueous solution



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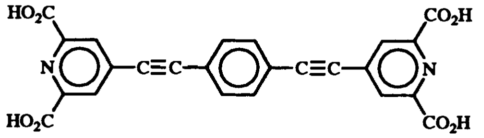

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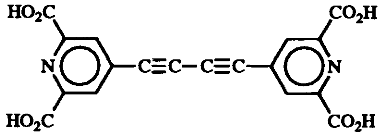

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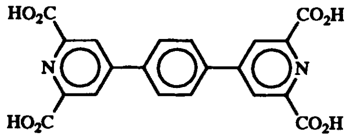

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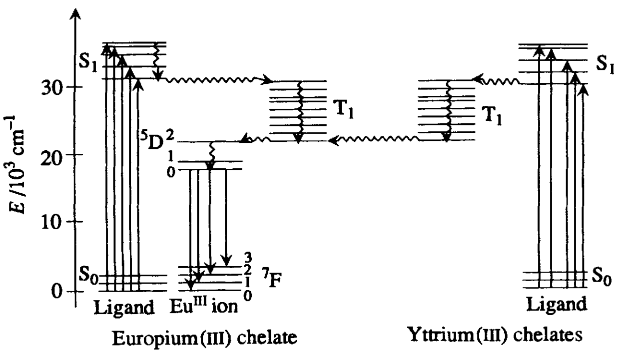

Fig. 2 Schematic diagram of the energy flow in polymer structure co-luminescence (PSCL)

process from the ligand to the Eu^{III} ion, this specific Eu^{III} ion can still be excited by one of the several energy transfer processes from other ligands coordinated to Y^{III} ions.

In all our measurements Eu^{III} ion is the luminescent lanthanide ion and various BCA ligands are added to obtain optimum absorption of excitation energy. Because the Y^{III} ion has the same coordination number as Eu^{III} ion and has no energy levels suitable for accepting energy from the triplet levels of BCA ligands, it is used as a non-luminescent ion to increase both intersystem crossing to triplet levels and consequent triplet–triplet energy transfer between BCA ligands.

The luminescence intensity of the Eu^{III} ion is plotted against time passed after mixing together ligand **1**, Y^{III} and Eu^{III} (Fig. 3). The growth of the luminescence signal is quite rapid in the beginning, but slowed down after 3 min. This is probably due to the growth of the polymer network after mixing the components. In all BCA ligands except in the case of **3** this kind of growth was observed. In solutions of ligand **3** the luminescence signal started to decrease after a few hours. For all BCA ligands optimization of ligand concentration, Y^{III} ion concentration and pH has been made. In all BCA solutions the effect of pH was

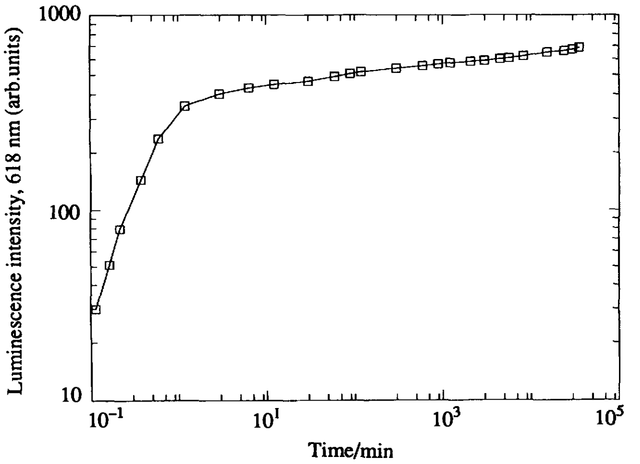

Fig. 3 Eu^{III} ion luminescence intensity *vs.* time passed after mixing all components. Conditions: Eu^{III} 1×10^{-7}, Y^{III} 1.3×10^{-5}, ligand **1** 2×10^{-5} mol dm^{-3}, pH 9, λ_{em} = 618 and λ_{ex} = 307 nm.

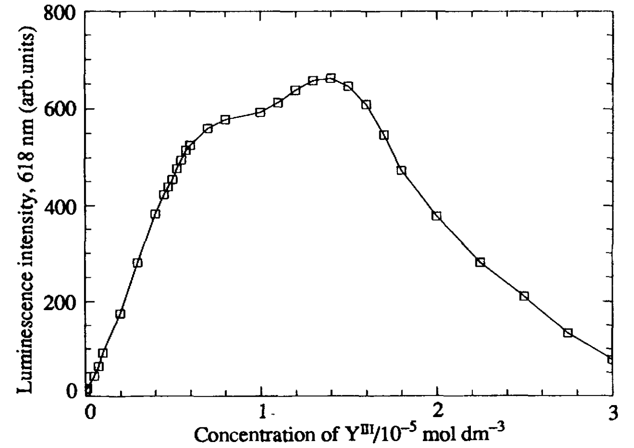

Fig. 4 The effect of concentration of Y^{III} on the luminescence of Eu^{III}. Conditions: Eu^{III} 1×10^{-7}, ligand **1** 2×10^{-5} mol dm^{-3}, pH 9, λ_{em} = 618 and λ_{ex} = 307 nm.

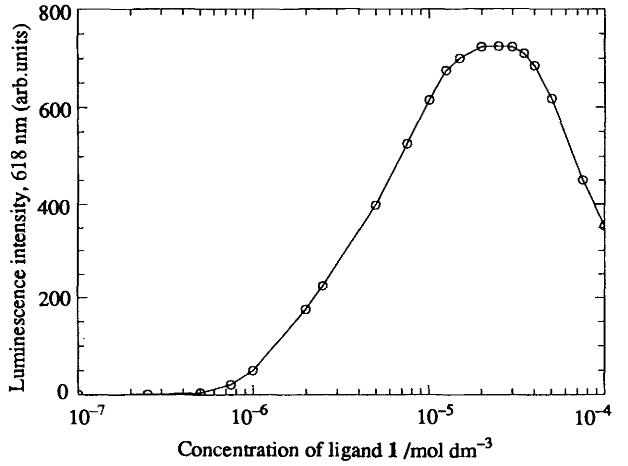

Fig. 5 The dependence of the emission intensities of Eu^{III} on concentration of ligand **1**. Conditions: Eu^{III} 1×10^{-7}, Y^{III} 1.3×10^{-5} mol dm^{-3}, pH 9, λ_{em} = 618 and λ_{ex} = 307 nm.

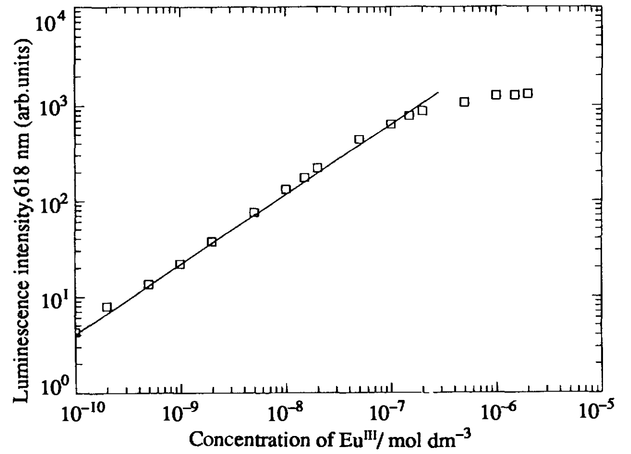

Fig. 6 The dependence of the emission intensities of Eu^{III} on Eu^{III} concentration of Eu^{III}–Y^{III}–ligand **1** system. Conditions: Y^{III} 1.3×10^{-5}, ligand **1** 2×10^{-5} mol dm^{-3}, pH 9, λ_{em} = 618 and λ_{ex} = 307 nm.

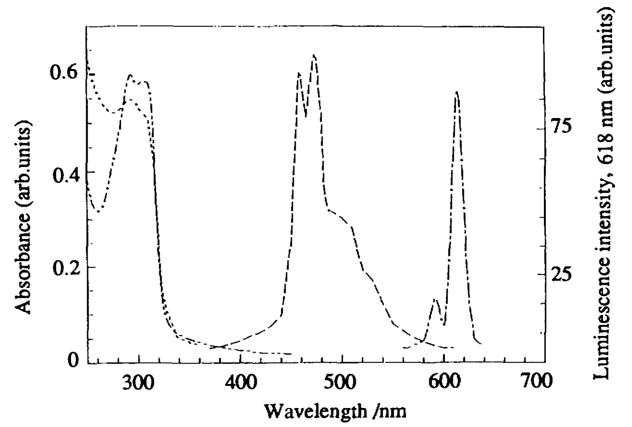

Fig. 7 Absorption (– – – –), excitation (- - - -), phosphorescence (— — —) and luminescence emission (— - —) spectra of Eu^{III}–Y^{III}–ligand **1** solution. Phosphorescence spectra were measured without Eu^{III} at 77 K. Conditions: Eu^{III} 1×10^{-7}, Y^{III} 1.3×10^{-5}, ligand **1** 2×10^{-5} mol dm^{-3}, pH 9, λ_{em} = 618 and λ_{ex} = 295 nm.

investigated in the range 1.5–11. The luminescence signal was observed to be highest at pH 9. The effects of Y^{III} ion concentration and ligand **1** concentration on Eu^{III} ion luminescence are shown in Fig. 4 and in Fig. 5, respectively. In the case of **1**, the luminescence intensity of Eu^{III} ion was highest when the Y^{III} : ligand **1** ratio was close to the theoretical value 2 : 3. When the luminescence intensity of Eu^{III} is plotted against the concentration of Eu^{III} ion (Fig. 6), it can be seen that there is a quite good linearity from 1×10^{-10} to 5×10^{-7} mol dm^{-3}, which enables the method to be used in the determination of small amounts of Eu^{III}. Absorption, luminescence excitation, luminescence emission and phosphorescence spectra of Eu^{III}–Y^{III}–BCA chelates were also measured and in the case of **1** these spectra are illustrated in Fig. 7. Phosphorescence spectra were measured without Eu^{III} ion.

Table 1 shows the optimum concentrations of BCAs and Y^{III} ions, the energies of the triplet levels, the wavelengths of maximum excitation and emission, the relative luminescence yields (log *R* values) for Eu^{III}–Y^{III}–BCA solutions and relative luminescence yields for these solutions without Y^{III} ions. In addition, the relative luminescence yield for Delfia® Enhancement solution (β-naphthoyltrifluoroacetone, trioctylphosphine oxide and Triton X-100 in acetate buffer), which is known to produce the very stable and high Eu^{III} ion luminescence[13] is shown in Table 1. When comparing log *R* values of Eu^{III}–Y^{III}–ligand **1** solution and the same solution without Y^{III} ions, it can be observed that adding Y^{III} ions increases the Eu^{III} ion luminescence by a factor of 80. This increased and strong Eu^{III} ion luminescence is most likely due to the presence of efficient migration of the ligand triplet state through several ligands towards the Eu^{III} ion. The same kind of enhancement of Eu^{III} ion luminescence was reported before in crystalline samples by Piguet *et al.*[14] As seen from Table 1, the optimum

Table 1 Wavelengths of the maximum excitation and emission, relative luminescence values (log *R*), energy of triplet levels and optimum concentrations of the components of BCA–Eu^{III}–Y^{III} systems in water solutions[a] compared with Delfia® Enhancement solution. The concentration of Eu^{III} was 1.0×10^{-7} mol dm^{-3}

Ligand	[Ligand]/ mol dm^{-3}	$[Y^{III}]$/ mol dm^{-3}	λ_{ex}/nm	λ_{em}/nm	T_1/cm^{-1}	log *R*	log *R* without Y^{III}
1	2.0×10^{-5}	1.4×10^{-5}	290	618	21 690	8.9	7.0
2	2×10^{-6}	6×10^{-7}	338	618	20 750	7.9	6.8
3	3.0×10^{-5}	1.3×10^{-5}	278	618	21 740	6.8	5.9
4	1.5×10^{-4}	9.0×10^{-6}	305	618	21 500	8.1	6.9
Delfia®	—	—	338	618	—	8.0	—

[a] Solutions were buffered to pH 9 with 2-(cyclohexylamino)ethanesulfonic acid (CHES).

concentrations of BCA ligands and Y^{III} ions and their mutual relation varies considerably. In the case of **1** the ratio between the concentration of Y^{III} and concentration of ligand **1** is 2:3 as expected, and the concentrations are quite near the limit where the inner filter effect due to high absorption starts to decrease the luminescence signal. In the case of **2** the optimum concentrations are much lower and in the case of **4** the optimum concentration of the ligand is much higher and the concentration of Y^{III} ion much lower compared with those of **1**. According to Table 1 the relative luminescence yield (log *R* value) is highest for ligand **1**. This might be the result of several factors. This structure has the shortest distance between different Ln^{III} centres and the lowest triplet energy level (see Fig. 7, phosphorescence spectra and Table 1) suitable for transferring energy to the $^5D_2$ resonance level ($\approx$21 500 cm^{-1}) of Eu^{III} ion. It is totally conjugated and planar so that all ligands in the polymer structure are equal and have equal energy levels, which enables the effective energy transfer between ligands. The structure in ligand **2** is longer, which probably lowers energy transfer. Also the energy of the triplet level in **2** chelates is below $^5D_2$ level of Eu^{III} ion. The energy is probably transferred to the $^5D_1$ level of Eu^{III} ion (*ca.* 19 000 cm^{-1}) and the energy gap between the triplet level of ligand **2** and $^5D_1$ level of Eu^{III} ion may be too large for the effective energy transfer. The ligand **3** is able to rotate around the carbon–carbon single bond in which case ligands are not equal and energy transfer along the polymer structure may be partly prevented. The ligand **4** is not conjugated or planar (see NMR data) and this may be responsible for the diminished energy transfer compared with the ligand **1**.

Conclusions

The advantages of polymer enhanced co-luminescence (PECL) are that the ligands are highly soluble in water and it requires less components than micellar co-luminescence solutions. In addition more precise knowledge about structure can be obtained in comparison with the rather unknown structure inside micelles. In PECL the mechanism of energy transfer is probably different from micellar Ln^{III}–β-diketone–phenanthroline complexes,[15] where π-stacking interactions are responsible for the synergistic co-ordination of the complexes and energy is transferred *via* the Förster dipole–dipole mechanism. In PECL the ligands are linked together so that energy transfer along the polymer chain is possible. In addition a part of the energy can be transferred in PECL *via* the Förster dipole–dipole mechanism.

In this work the enhanced Eu^{III} ion luminescence and effective energy transfer through several ligands was achieved. There are still many unresolved questions, such as the effectiveness of the triplet–triplet migration, the maximum distance where energy still can be transferred to a certain Eu^{III} ion, the optimum length of the ligand, stability of the polymer structures and the average size of the polymeric structure. So far we have not made exact studies of the effect of replacing yttrium with other lanthanides such as Gd^{III}, Tb^{III}, La^{III} and Lu^{III} but we have noticed that Tb^{III} also enhances Eu^{III} ion luminescence in this polymer structure. The possibility to enhance also the luminescence of Tb^{III} and Sm^{III} ions in this way is also interesting. In the future our research will be focussed on these questions.

Experimental

Stock solutions (1.00×10^{-3} mol dm^{-3}) of Eu^{III} ion (Eu_2O_3, Aldrich, 99.95%), Y^{III} ion (Y_2O_3, Johnson Matthey, 99.999%) and Gd^{III} ion (Gd_2O_3, Koch-Light, 99.9%) were obtained by dissolving the oxides in dilute hydrochloric acid. Working solutions were prepared by dilution with triply-distilled water.

All synthesized ligands were dissolved in a 0.1 mol dm^{-3} boric acid buffer, pH 9.0, to prepare 1.00×10^{-3} mol dm^{-3} stock solutions. Working solutions were prepared by dilution with buffer solutions of a known pH-value. Buffer solutions were made by mixing a suitable acid and sodium hydroxide (Merck, Titrisol®). The acids used were 4-morpholinoethanesulfonic acid (MES, Aldrich, 98%), 4-morpholinopropanesulfonic acid (MOPS, Aldrich, 99%), 2-(cyclohexylamino)ethanesulfonic acid (CHES, Aldrich, 99%), 3-(cyclohexylamino)propane-1-sulfonic acid (CAPS, Aldrich, 99%), boric acid (Merck, pa), acetic acid (Merck, Titrisol®) and formic acid (Merck, pa). All reagents were used without further purification.

The measuring solutions contained 1×10^{-10}–1×10^{-6} Eu^{III} ion, 5×10^{-6}–2×10^{-5} Y^{III} ion, 5×10^{-6}–2×10^{-4} BCA ligand and 0.1 mol dm^{-3} buffer solution. In order to avoid contamination, all luminescence measurements were made in disposable acrylic luminescence cuvettes except for excitation and emission spectra, which were recorded in silica cuvettes.

Luminescence and phosphorescence excitation and emission spectra, luminescence intensities and emission decay times were measured on a Perkin-Elmer LS-5 spectrofluorometer using phosphorescence mode. Phosphorescence measurements have been made at 77 K. The absorption spectra of the solutions were determined on a Perkin-Elmer Lambda 2 spectrophotometer.

For the purpose of fast comparison of the luminescence properties of the lanthanide chelates, the parameter relative luminescence yield (*R*) was developed by Mukkala and Kankare.[12] We have used log *R* values in our measurements for mutual comparison of the luminescence yields.

1,2-Bis[2,6-bis(methoxycarbonyl)pyridin-4-yl]ethyne

A mixture of dimethyl 4-iodopyridine-2,6-dicarboxylate[10] (1.0 g, 3.1 mmol), palladium(II) acetate (7.0 mg, 31 μmol), triphenylphosphine (16 mg, 62 μmol), copper(I) iodide (6.0 mg, 31 μmol) and dry triethylamine (20 cm^3) was deaerated with N_2. Acetylene was slowly bubbled through the stirred mixture for 24 h, the mixture was filtered and washed with diethyl ether. The solid material was dissolved in chloroform (50 cm^3), washed with water (3×20 cm^3) and dried (Na_2SO_4). The product was crystallized from dichloromethane. Yield 0.4 g (63%); ν(KBr)/cm^{-1} 1730, 1720 and 1270 (C=O, C–O); δ(400 MHz; CDCl$_3$) 4.05 (s, 12 H) and 8.39 (s, 4 H).

1,2-Bis(2,6-dicarboxypyridin-4-yl)ethyne (ligand 1)
A mixture of 1,2-bis[2,6-bis(methoxycarbonyl)pyridin-4-yl]-ethyne (0.35 g, 0.85 mmol) and 0.5 mol dm^{-3} KOH in ethanol (10 cm^3) was stirred for 2 h at room temperature. Water was added (15 cm^3), the pH adjusted to 1.5 with 6 mol dm^{-3} HCl, the product was filtered, washed with water and crystallized from a mixture of DMF and water. Yield 0.23 g (77%), mp > 250 °C (decomp.); ν(KBr)/cm^{-1} 1735, 1415 and 1260 (C=O, C–O).

1,4-Bis{[2,6-bis(ethoxycarbonyl)pyridin-4-yl]ethynyl}benzene
A mixture of diethyl 4-ethynylpyridine-2,6-dicarboxylate[8] (1.00 g, 4.04 mmol), 1,4-diiodobenzene (0.59 g, 1.80 mmol), dry triethylamine (15 cm^3) and dry tetrahydrofuran (30 cm^3) was deaerated with N$_2$. Bis(triphenylphosphine)palladium(II) chloride (51 mg, 0.07 mmol) and copper(I) iodide (27 mg, 0.14 mmol) was added and the mixture was stirred for 5 h at room temperature. The mixture was filtered, the filtrate evaporated, the residue dissolved in chloroform (30 cm^3), washed with water (2 × 10 cm^3), dried (Na$_2$SO$_4$) and the product purified by flash chromatography (silica gel, light petroleum (40–60 °C)–ethyl acetate 5:3). Yield 0.13 g (13%); ν(KBr)/cm^{-1} 2210 (C≡C), 1720 and 1237 (C=O, C–O); δ(400 MHz; CDCl$_3$) 1.48 (t, *J* 7.1, 12 H), 4.51 (q, *J* 7.1, 8 H), 7.62 (s, 4 H) and 8.35 (s, 4 H).

Tetrapotassium salt of 1,4-bis[(2,6-dicarboxypyridin-4-yl)-ethynyl]benzene (ligand 2)
The ligand was prepared from 1,4-bis{[2,6-bis(ethoxycarbonyl)-pyridin-4-yl]ethnyl}benzene as **1**, but after hydrolysis the product was filtered and washed with ethanol. Yield 100%, mp could not be detected; ν(KBr)/cm^{-1} 2213 (C≡C), 1616, 1409 and 1349 (C=O, C–O); δ(400 MHz; D$_2$O) 7.56 (s, 4 H) and 7.90 (s, 4 H).

1,4-Bis[2,6-bis(ethoxycarbonyl)pyridin-4-yl]buta-1,3-diyne
Oxygen was passed for 0.5 h through a stirred mixture of copper(I) chloride (8 mg, 0.04 mmol), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethyltriamine (7 mg, 0.04 mmol) and 1,2-dimethoxyethane (10 cm^3). A solution of diethyl 4-ethynylpyridine-2,6-dicarboxylate (0.20 g, 0.80 mmol) was added within 0.5 h. After stirring for 2 h at room temperature under O$_2$, the mixture was evaporated. The cold residue was treated with cold 5% HCl (20 cm^3), filtered and washed with water and ethanol. Yield 0.07 g (30%), mp 258–259 °C; ν(KBr)/cm^{-1} 2155 (C≡C), 1715 and 1215 (C=O, C–O); δ(400 MHz; CDCl$_3$) 1.47 (t, *J* 7.1, 12 H), 4.25 (q, *J* 7.1, 8 H) and 8.37 (s, 4 H).

Tetrapotassium salt of 1,4-bis(2,6-dicarboxypyridin-4-yl)buta-1,3-diyne (3)
The ligand was prepared as **2**. Yield 81%, mp could not be detected; ν(KBr)/cm^{-1} 2160 (C≡C), 1615, 1415 and 1345 (C=O, C–O).

1,4-Bis[1,5-(di-2-furyl)-1,5-dioxopentan-3-yl]benzene
A mixture of terephthalaldehyde (6.7 g, 50 mmol), 1.5 mmol dm^{-3} NaOH (150 cm^3) and 2-acetylfuran (22 g, 200 mmol) was refluxed for 4 h. The mixture was filtered, washed with ethanol and ethyl acetate. Yield 11 g (40%); ν(KBr)/cm^{-1} 1663 (C=O); δ(400 MHz; [^{2}H$_6$]DMSO) 3.12 (dd, *J* 7.0, 16.5, 4 H), 3.20 (dd, *J* 7.0, 16.5, 4 H), 3.76 (quint, *J* 7.0, 2 H), 6.64 (dd, *J* 1.5, 3.6, 4 H), 7.17 (s, 4 H), 7.40 (d, *J* 3.6, 4 H) and 7.92 (d, *J* 1.5, 4 H).

1,4-Bis[2,6-di(2-furyl)pyridin-4-yl]benzene
A mixture of 1,4-bis[1,5-(di-2-furyl)-1,5-dioxopentan-3-yl]-benzene (5.38 g, 10 mmol), ammonium acetate (30.8 g, 0.4 mol) and methanol (200 cm^3) was refluxed for 20 h. The mixture was concentrated, a cold residue filtered and washed with cold methanol. The product was purified by flash chromatography (silica gel, ethyl acetate). Yield 1.15 g (23%); ν(KBr)/cm^{-1} 1615 (pyridine); δ(400 MHz; CDCl$_3$) 6.59 (dd, *J* 1.6, 3.4, 4 H), 7.23 (d, *J* 3.4, 4 H), 7.59 (d, *J* 1.6, 4 H), 7.86 (s, 4 H) and 7.90 (s, 4 H).

1,4-Bis(2-6-dicarboxypyridin-4-yl)benzene (ligand 4)
Potassium permanganate (9.02 g, 57 mmol) was added in small portions to a mixture of 1,4-bis[2,6-di(2-furyl)pyridin-4-yl]-benzene (1.13 g, 2.2 mmol), *tert*-butanol (300 cm^3) and water (60 cm^3) at 80–85 °C. After stirring for 16 h, the mixture was filtered, washed with water and the filtrate was evaporated. The residue was dissolved in water (30 cm^3), the pH adjusted to 1.5 with 2 mol dm^{-3} HCl and the product was filtered and washed with cold water. Yield 0.57 g (63%), mp > 250 °C (decomp.); ν(KBr)/cm^{-1} 1700, 1387, 1264 (C=O, C–O) and 1602 (pyridine); δ(400 MHz; [^{2}H$_6$]DMSO, D$_2$O) 8.05 (d, *J* 7.8, 2 H), 8.07 (s, 2 H), 8.15 (d, *J* 7.8, 2 H) and 8.54 (s, 2 H).

Acknowledgements

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