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Synthesis and photophysical studies of two luminescent chemosensors based on catechol and 8-Hydroxyquinoline chromophores, and their complexes with group 13 metal ions

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ABSTRACT

Two ligands, L^1 and L^2, derived from 2,3-dihydroxybenzaldehyde and 8-hydroxyquinoline-2-carbaldehyde using 4,4′-methylene-dianiline as spacer have been used to study their interaction with the group 13 metals, Al^{3+}, Ga^{3+} and In^{3+}. In all cases, emissive dinuclear metal complexes were synthesized and characterized. The complexation reactions with the diiminic ligands were obtained by direct reactions between ligand and metal ions. The complexes have been characterized by elemental analyses, mass spectrometry, IR, UV–vis and fluorescence spectroscopy. The interaction towards metal ions has been explored in solution by absorption and fluorescence emission spectroscopy, obtaining results that support the solid-state helicate-type complexes.

Much attention has been focused on the development of chemosensors for the selective and efficient detection of chemically and biologically important metal ions [1]. A fluorescent chemosensor for metal ions consists of a molecule incorporating fluorophores linked to complexing units [2]. There are three main classes of fluorescent molecular sensors for cation recognition which differ by the nature of the cation-controlled photoinduced processes: a) sensors based on control of photoinduced electron transfer (PET), b) those based on cation control of photoinduced charge transfer (PCT), and c) systems based on cation control of excimer formation or disappearance [2].

Since the discovery of the double-stranded helical structure of DNA by Watson and Crick [3], chemists have been searching for simple linear molecules that could be able to form artificial double helices through noncovalent interactions, such as π-stacking, electrostatic interactions, hydrogen bonding, or metal coordination [4]. In artificial analogs of DNA, the hydrogen bonding interaction between the two strands can be substituted by metal coordination. There are numerous reports on coordination polymers that exhibit double-helical motifs in the crystal [5]. A special class of well-defined molecular double-stranded helical metal complexes was introduced in 1987 by J.-M. Lehn and was termed double-stranded helicates [6].

Of the factors integral to helicate formation, the geometric preferences of the metal and the group that separates and links the donor atoms of the ligand are particularly influential. Chirality is introduced upon wrapping of the helicating ligands around the metal centers. In the case of the *meso*-helicates [7–12] (“side-by-side complexes” [13] or “mesocates” [14]) an achiral supermolecule is obtained that bears two oppositely configured chiral units. Different factors can be responsible for the stereocontrol in the formation of the helicate-type complexes [15,16]. Templating effects might influence the diastereoselective formation of helicates [17,18]. Chiral units in the ligand spacer can control the stereochemistry at the metal complex units [19–21], or steric constraints enforce one of the two possible diastereomeric forms of coordination compounds [22,23].

Ligands with an odd number of methylene units in the spacer possess a “horizontal” mirror plane as the most influential symmetry element of the idealized C_{2v} symmetry, which mirrors the two attached chiral metal-complex moieties onto each other. This symmetry transformation leads to an opposite configuration at the complex units, and thus the ligand is predisposed to form the achiral dinuclear meso-helicate [24]. However, to preserve this symmetry in a

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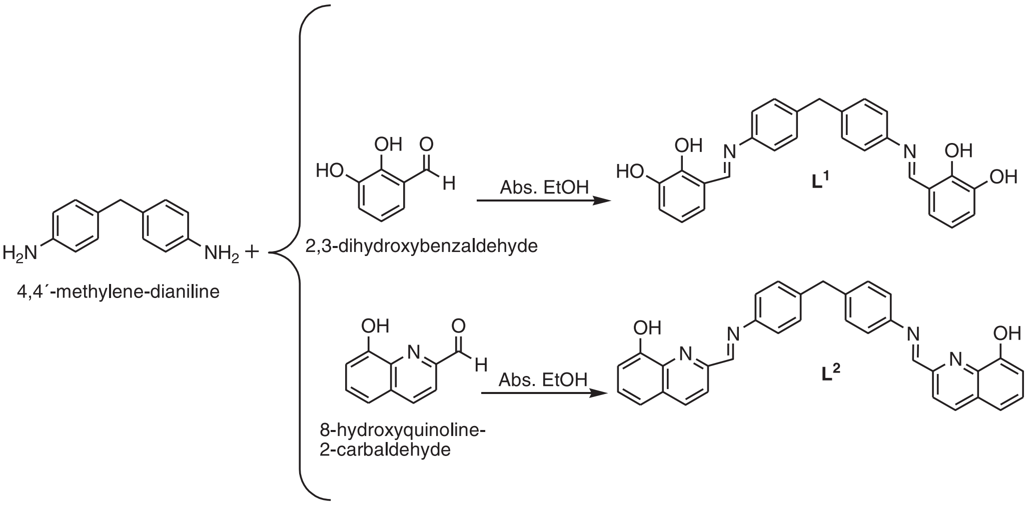

Scheme 1. Schematic synthetic route for ligands L^1 and L^2 in absolute ethanol.

dinuclear complex with short spacers, the ligand has to adopt an unfavorable conformation for complex formation. If long spacers are present, this conformation should not be "unfavorable" (vide infra).

Following our ongoing research project in fluorescent materials and emissive compounds and complexes [25], in the present work we have reported the synthesis of a new helicate-type ligand L^2 derived from 4,4′-methylene-dianiline and 8-hydroxyquinoline-2-carbaldehyde and the derived aluminum(III), gallium(III) and indium(III) complexes. For comparative purposes the corresponding cathecol ligand L^1 was also synthesized following the method described previously by M. Albrecht [26] and complexed with the same metal ions, Al^{3+}, Ga^{3+} and In^{3+}.

Compounds L^1 and L^2 were synthesized following a one-pot reaction, by direct condensation of 4,4′-methylene-dianiline and the commercial carbonyl precursors 2,3-dihydroxybenzaldehyde and 8-hydroxyquinoline-2-carbaldehyde, respectively [27]. The reactions were performed by a conventional method, heating an ethanolic solution during 4 h. Both compounds were isolated as air-stable yellow solids, with ca. 63 and 53% yields, respectively. The reaction pathways are shown in Scheme 1.

The elemental analysis of the Schiff-bases L^1 and L^2 isolated as a dry orange and yellow powders, respectively, confirmed the purity of our sample. The infrared spectrum (in KBr) in both cases shows bands at 1623 and 1627 cm^{-1}, respectively, corresponding to the imine bond $\nu(C{=}N)_{imine}$ and no peaks attributable to unreacted amine or carbonyl groups were present. The ESI-MS spectra of both sensors show parent peaks at 439.1 and 531.2 m/z, corresponding to the protonated imine forms of the ligands $[L^1+H]^+$ and $[Na+L^2+H]^+$, respectively. The ^1H NMR spectra of compounds L^1 and L^2 were recorded using DMSO-d^6 as a solvent. As it could be expected for a Schiff-base, the ^1H NMR spectra show peaks corresponding to the imine protons *ca.* 9–8 ppm.

The presence of six potential donor atoms (N_2O_4) in the ligand structure of L^1 and (N_4O_2) in the ligand structure of L^2, gives strong recognition ability towards metal ions. For the preparation of the complexes $Na_6[(L^1)_3M_2]$, the ligand L^1-H_4 (3 equiv.), $[MO(acac)_2]$ (2 equiv.) ($M{=}Al^{3+}$, Ga^{3+} and In^{3+}) and $NaHCO_3$ (2 equiv.) were mixed in ethanol. For the preparation of the complexes $[(L^2)_3M_2]$, the ligand L^1-H_2 (3 equiv.), $[MO(acac)_2]$ (2 equiv.) ($M{=}Al^{3+}$, Ga^{3+} and In^{3+}) and $NaHCO_3$ (2 equiv.) were mixed in the same solvent. After 4 h the resulting solutions were concentrated in a rotary evaporator and diethyl ether were slowly infused into the solution producing powdery precipitates that were separated by centrifugation and dried under vacuum [28].

The complexes were characterized by elemental analysis, IR, and ESI MS spectra [29]. Electro-spray Ionization Mass Spectrometry (ESI-MS) in negative ion mode of the metal complexes displays peaks that confirm the formation of the metal complexes. The IR spectra of the

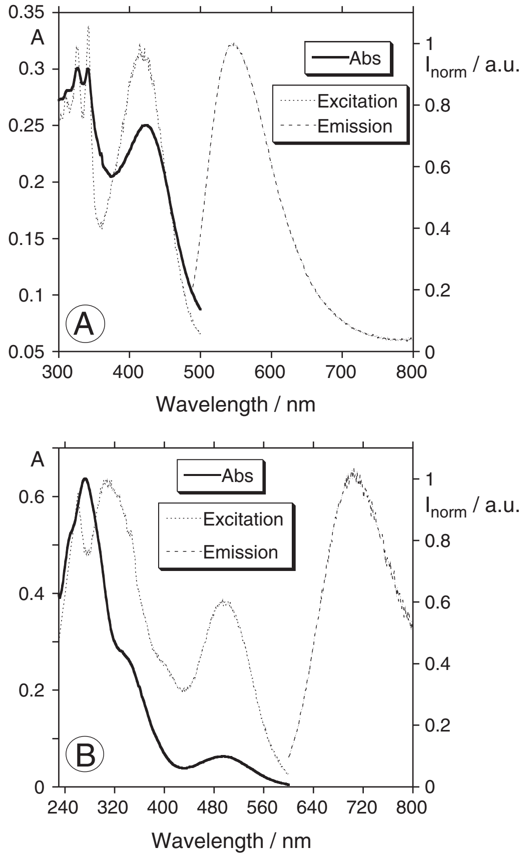

Fig. 1. Absorption (full line), emission (broken line) and excitation (dotted line) spectra of compound L1 after the addition of 5 equivalents of (Bu4N)OH (λexc = 425 nm; λem = 542 nm, [L1] = 1.07 10^{-5} M) in CH3CN at room temperature (A). Spectra of compound L^2 after the addition of 20 equivalents of (Bu4N)OH (λexc = 470 nm; λem = 710 nm, $[L^2]$ = 1.14 10^{-5} M) in CH2Cl2 at room temperature (B).

complexes were recorded as KBr disks. In the case of metal complexes derived from ligand L^1, the band due to the imine bond $[\nu(C{=}N)_{imine}]$ and the $[\nu(C{=}C)_{ar}]$ stretching modes of aromatic rings are shifted to higher wavenumbers when compared to its position in the spectrum of the free ligand. In the case of metal complexes derived from ligand L^2, the band due to the imine bond $[\nu(C{=}N)_{imine}]$ is shifted to lower wavenumbers and the $[\nu(C{=}C)_{ar}$ and $\nu(C{=}N)_{py}]$ stretching modes are shifted to higher wavenumbers when compared to its position in the spectrum of the free ligand. Both effects suggest that in solid state the N_{iminic} atom could be involved in the coordination to the metal ion, and in the case of metal complexes derived from ligand L^2 the N_{py} are involving in the coordination in solid state [30].

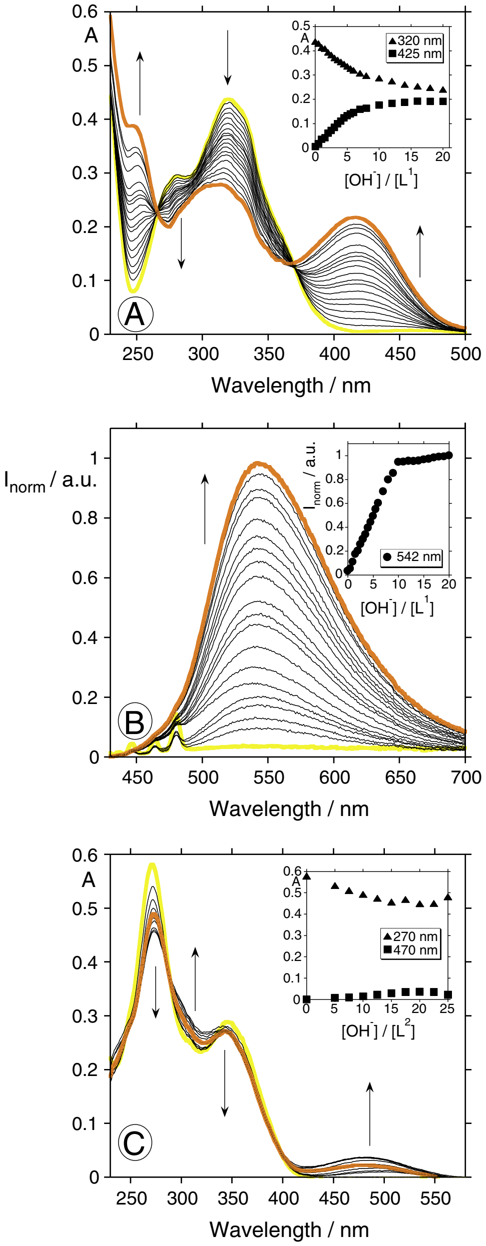

Fig. 2. Spectrophotometric (A) and spectrofluorimetric (B) titrations of ligand L^1 (yellow line) in CH3CN as a function of added (Bu4N)OH (orange line). The insets show the absorption at 320 and 425 nm; and the normalized fluorescence intensity at 542 nm ($[L^1] = 1.07{*}10^{-5}$ M; λexc = 425 nm). Spectrophotometric titration (C) of ligand L^2 (yellow line) in CH3CN as a function of added (Bu4N)OH (orange line). The insets show the absorption at 270 and 470 nm ($[L^2] = 1.14\ 10^{-5}$ M).

After addition of tetrabutylammonium hydroxide, the spectrophotometric characterization of receptors L^1 and L^2 are reported in Fig. 1. The absorption, emission and excitation spectra of this deprotonated species were studied in CH_3CN at 298 K [31]. The absorption spectrum of ligand L^1 shows two bands with the maxima centered at 325 and 425 nm, coincident with the excitation spectrum. In the case of ligand L^2 this bands appeared at 270, 340 and 470 nm. Only after deprotonation, a very low emission was observed; the luminescence of ligands L^1 and L^2 appears centered at 542 nm and 710 nm, respectively.

Titration of chemosensors L^1 with tetrabutylammonium hydroxide in CH_3CN solution at 298 K (Fig. 2), can be followed by the formation of a new band centered at *ca.* 425 nm assigned to a charge transfer (CT) process and a decrease in the band assigned to the π–π* transition of the chromophores centered at 325 nm. In the case of chemosensor L^2 this new band appeared at *ca.* 470 nm and a decrease in the bands centered at 270 and 340 nm was observed.

The weak luminescence of compounds L^1 and L^2 could be attributed to the competition between the intramolecular photoinduced proton transfer (PPT) from the hydroxyl groups present in both compounds, and the photo-induced electron transfer (PET) from the imines [32]. After addition of tetrabutylammonium hydroxide, the deprotonation effect prevents the PPT process, resulting in a short enhancement of the fluorescence signal.

The sensing behavior of L^1 and L^2 toward Al^{3+}, Ga^{3+} and In^{3+} has been studied by UV–vis spectroscopy in CH_3CN and CH_2Cl_2 as the solvent for compounds L^1 and L^2, respectively.

As it can be seen in Figs. 3A, 4A and B, addition of increasing amounts of anhydrous aluminum, gallium and indium nitrates to an

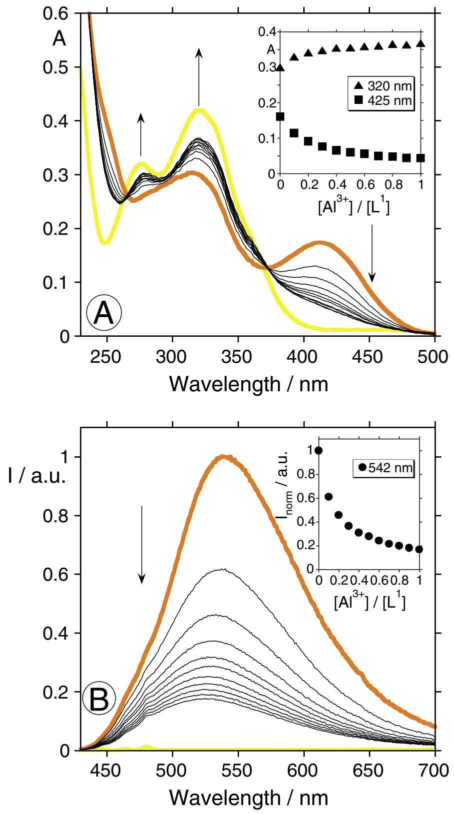

Fig. 3. Spectrophotometric (A) and spectrofluorimetric (B) titrations of ligand L^1 (yellow line) in CH3CN as a function of added Al3+, after the addition of 5 equivalents of (Bu4N) OH (orange line). The insets show the absorption at 320 and 425 nm; and the normalized fluorescence intensity at 542 nm ($[L^1] = 1.07\ 10^{-5}$ M).

acetonitrile solution of the deprotonated ligand L^1 ($1.07\ 10^{-5}$ M), at 298 K, led to an increase in the absorption bands centered at 320 nm, and an decrease in the bands centered at 425 nm. Addition of increasing amounts of the same metal ions to a dichloromethane solution of the deprotonated ligand L^2 ($1.14\ 10^{-}$ M), at 298 K, led to an increase in the absorption bands centered at 270 nm, and a decrease in the bands centered at 470 nm (Fig. 4C and D).

Simultaneously, upon addition of increasing amounts of anhydrous aluminum, gallium and indium nitrates to the deprotonated ligands L^1 ($1.07\ 10^{-5}$ M) and L^2 ($1.14\ 10^{-5}$ M), at 298 K, respectively, the emission disappears (Fig. 3B). This quenching can be attributed to the coordination effect towards the hydroxyl groups.

The stability constants for the interaction of ligands L^1 and L^2 with OH^-, Al^{3+}, Ga^{3+} and In^{3+} followed by absorption and fluorescence titrations were calculated using HypSpec software and are summarized in Table 1. Taking into account these values, the sequence of the strongest interaction expected for compound L^1, in decreasing order is $Al^{3+} > Ga^{3+} > In^{3+}$; and the decreasing order for system L^2 is $Al^{3+} > In^{3+} > Ga^{3+}$.

In conclusion, chemosensor L^1 and the new ligand (L^2) containing two 8-HQ units have been synthesized and fully characterized. The deprotonation behavior and sensing capability of these ligands toward trivalent Al^{3+}, Ga^{3+} and In^{3+} metal ions have been studied by UV–vis and fluorescent emission spectroscopy. The fluorescence of chemosensors L^1 and L^2 is weak but an *Enhancement of the Fluorescence* (EF) effect was observed in both cases after addition of tetrabutylammonium hydroxide. Titration of ligands L^1 and L^2 with trivalent Al^{3+}, Ga^{3+} and In^{3+} metal ions led to a decrease in the fluorescence emission. This effect in solution is due to the coordination of the oxygen atoms and the uncoordinated nitrogen donor atoms present in the ligands, activating the quenching through the PET phenomena. All of these results support our hypothesis of the formation of helicate-type structures.

Table 1
Stability constants for compounds L^1 and L^2 in the presence of OH^-, $Al3^+$, $Ga3^+$ and $In3^+$ in acetonitrile.

Ligand	Interaction	Σ log β (absorption)	Σ log β (emission)
L^1	OH^- (1:1)	–	$3.91 \pm 2.41.10^{-2}$
	OH^- (1:2)	$7.88 \pm 1.28.10^{-2}$	–
	OH^- (1:3)	$12.29 \pm 1.56.10^{-2}$	–
	OH^- (1:4)	$16.65 \pm 1.76.10^{-2}$	–
L^1	Al3 + (1:1)	–	$4.23 \pm 4.31.10^{-3}$
	Al3 + (1:2)	$6.98 \pm 6.93.10^{-2}$	$7.09 \pm 5.08.10^{-3}$
L^1	Ga3 + (1:1)	–	–
	Ga3 + (1:2)	$6.36 \pm 4.93.10^{-2}$	–
L^1	In3 + (1:1)	–	–
	In3 + (1:2)	$5.56 \pm 3.36.10^{-2}$	–
L^2	OH^- (1:1)	$4.56 \pm 4.68.10^{-3}$	–
	OH^- (1:2)	$8.38 \pm 4.53.10^{-3}$	–
L^2	Al3 + (1:1)	$4.96 \pm 1.41.10^{-3}$	–
	Al3 + (1:2)	$9.55 \pm 1.44.10^{-3}$	
L^2	Ga3 + (1:1)	$3.57 \pm 6.98.10^{-3}$	–
	Ga3 + (1:2)	$6.79 \pm 7.04.10^{-3}$	–
L^2	In3 + (1:1)	$4.06 \pm 8.64.10^{-3}$	–
	In3 + (1:2)	$7.28 \pm 8.47.10^{-3}$	–

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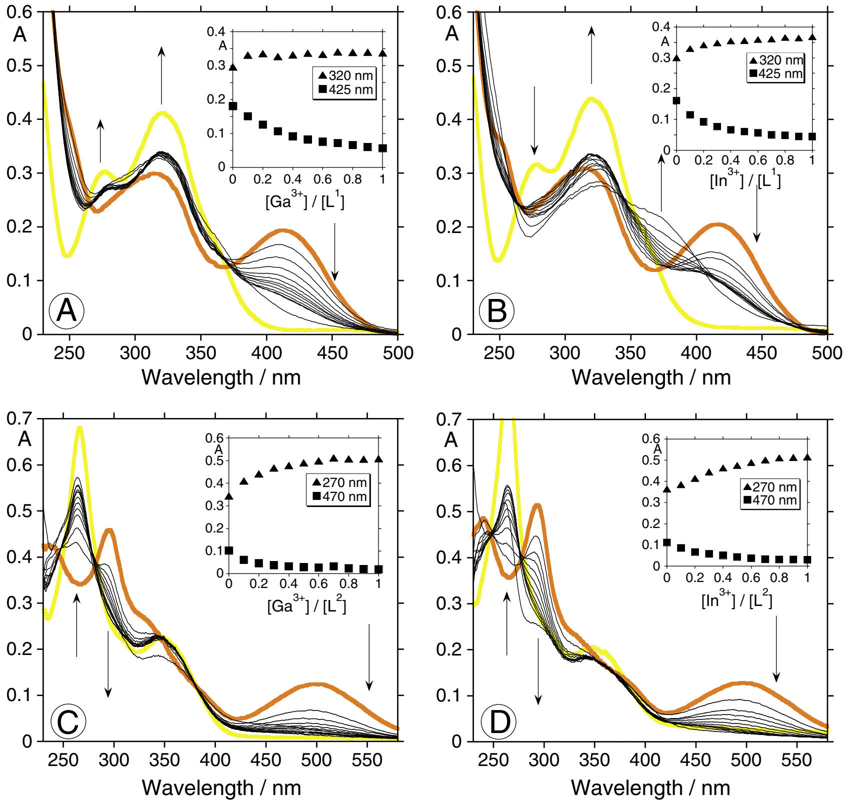

Fig. 4. Spectrophotometric titrations of ligand L^1 and L^2 (yellow lines) in CH3CN as a function of added $Ga3^+$ (A and C) and $In3^+$ (B and D), after the addition of 5 equivalents of (Bu4N) OH (orange lines). The insets show the absorption at 320 and 425 nm ($[L^1] = 1.07\ 10^{-5}$ M) and the absorption at 270 and 470 nm ($[L^2] = 1.14\ 10^{-5}$ M).

References

[1] (a) C. Lodeiro, J.L. Capelo, J.C. Mejuto, E. Oliveira, H.M. Santos, B. Pedras, C. Nuñez, Chem. Soc. Rev. 39 (2010) 2948;
  (b) Z.C. Xu, J. Yoon, D.R. Spring, Chem. Soc. Rev. 39 (2010) 1996;
  (c) C. Bazzicalupi, A. Bencini, S. Biagini, A. Bianchi, E. Faggi, C. Giorgi, M. Marchetta, F. Totti, B. Valtancoli, Chem. Eur. J. 15 (2009) 8049.

[2] (a) A. Prassana de Silva, H.Q.N. Gunartne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515;
  (b) K. Rurack, Spectrochim. Acta A 57 (2001) 2161.

[3] J.D. Watson, F.C.H. Crick, Nature 171 (1953) 737.

[4] I.E. Rowan, R.J.M. Nolte, Angew. Chem. 110 (1998) 65;
Angew. Chem. Int. Ed. 37 (1998) 62.

[5] (a) O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli, Angew. Chem. 111 (1999) 3129;
  O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli, ibid, Angew. Chem. Int. Ed. 38 (1999) 2945;
  (b) A. Erxleben, Inorg. Chem. 40 (2001) 2928.

[6] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, Proc. Nat. Acad. Sci. U.S.A. 84 (1987) 2565.

[7] M. Albrecht, S. Kotila, Chem. Commun. (1996) 2309.

[8] M. Albrecht, S. Kotila, Angew. Chem. 107 (1995) 2285;
Angew. Chem. Int. Ed Engl. 34 (1995) 2134.

[9] M. Albrecht, C. Riether, Chem. Ber. 129 (1996) 829.

[10] M. Albrecht, M. Schneider, H. Röttele, Chem. Ber. 130 (1997) 615.

[11] M. Albrecht, Chem. Eur. J. 6 (2000) 3485.

[12] E.C. Constable, M. Neuburger, L. Whall, M. Zehnder, New J. Chem. 22 (1998) 219.

[13] W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, Helv. Chim. Acta 74 (1991) 1843.

[14] J. Xu, T.N. Parac, K.N. Raymond, Angew. Chem. 111 (1999) 3055;
Angew. Chem. Int. Ed. 38 (1999) 2878.

[15] A. Bilyk, M.M. Harding, P. Turner, T.W. Hambley, J. Chem. Soc. Dalton Trans. (1994) 2783.

[16] A.L. Airey, G.F. Swiegers, A.C. Willis, S.B. Wild, J. Chem. Soc. Chem. Commun. (1995) 695.

[17] A. Bilyk, M.M. Harding, J. Chem. Soc. Chem. Commun. (1995) 1697.

[18] A. Bilyk, M.M. Harding, P. Turner, T.W. Hambley, J. Chem. Soc. Dalton Trans. (1995) 2549.

[19] E.J. Corey, C.L. Cywin, M.C. Noe, Tetrahedron Lett. 35 (1994) 69.

[20] E.J. Enemark, T.D.P. Stack, Angew. Chem. 107 (1995) 1082;
Angew. Chem. Int. Ed Engl. 34 (1995) 996.

[21] E.J. Enemark, T.D.P. Stack, Angew. Chem. 110 (1998) 977;
Angew. Chem. Int. Ed. 37 (1998) 932.

[22] M. Meyer, B. Kersting, R.E. Powers, K.N. Raymond, Inorg. Chem. 36 (1997) 5179.

[23] M. Albrecht, M. Schneider, R. Fröhlich, New J. Chem. 22 (1998) 753.

[24] M. Albrecht, S. Kotila, Chem. Commun. (1996) 2309.

[25] (a) C. Lodeiro, F. Pina, Coord. Chem. Rev. 253 (2009) 1353;
  (b) M.R. Bermejo, M. Vazquez, M. Sanmartin, J. Garcia-Deibe, M. Fondo, C. Lodeiro, New J. Chem. 26 (2002) 1365;
  (c) C. Bazzicalipi, A. Bencini, E. Berni, A. Bianchi, A. Danesi, C. Giorgi, B. Valtancoli, C. Lodeiro, J.C. Lima, F. Pina, M.A. Bernardo, Inorg. Chem. 43 (2004) 5134;
  (d) A. Tamayo, B. Pedras, C. Lodeiro, L. Escriche, J. Casabo, J.L. Capelo, B. Covelo, R. Kivekas, R. Sillanpaa, Inorg. Chem. 46 (2007) 7818;
  (e) M.J. Mayoral, P. Ovejero, J.A. Campo, J.V. Heras, E. Pinilla, M.R. Torres, C. Lodeiro, M. Cano, Dalton Trans. (2008) 6912.

[26] M. Albrecht, I. Janser, H. Houjou, R. Fröhlich, Chem. Eur. J. 10 (2004) 2839.

[27] Synthesis of L^1 and L^2. The synthesis of L^1 was carried out through the slow addition of 4,4′-methylene-dianiline to an ethanolic solution of 2,3-dihydroxybenzaldehyde using the methodology reported previously Albrecht et al. [26] The synthesis of L^2 was attempted through the slow addition of 4,4′-methylene-dianiline (0.11419 g, 0.57 mmol) in absolute ethanol (20 mL) to a solution of 8-hydroxyquinoline-2-carbaldehyde (0.1766 g, 1.02 mmol) in the same solvent (30 mL). The resulting solution was gently refluxed with magnetic stirring for ca. 4 h. The colour changed from yellow to orange. The solution was then allowed to cool and an orange solid appeared. The solid was filtered off, washed with diethyl ether and methanol and dried under vacuum. This compound was characterized as $L^2.L^1$. Anal. Calcd for $C_{27}H_{22}N_2O_4$: C, 73.96; H, 5.06; N, 6.39. Found: C, 73.78; H, 5.24; N, 6.33%. Yield: 63%. IR (KBr, cm^{-1}): 1623 [$\nu(C{=}N)_{imine}$]; 1583 [$\nu(C{=}C)$]. MS (ESI^+, m/z): 439 $[L^1+H]^+$. ^1H NMR (DMSO) (L^1): $\delta = 13.25$ (s, 4 H, OH); 9.18 (s, 1 H, N=CH); 8.89 (s, ^1H, N=CH); 7.07–6.75 (m, 14 C-H, Ar); 4.01 (s, 2 H, CH2) ppm. L^2. Anal. Calcd for $C_{33}H_{26}N_4O_3$: C, 75.27; H, 4.97; N, 10.63. Found: C, 75.95; H, 4.92; N, 10.64%. Yield: 53%. IR (KBr, cm^{-1}): 1627 [$\nu(C{=}N)$imine]; 1560 [$\nu(C{=}C)$]. MS (ESI^+, m/z): 531 $[Na+L^2]+$. ^1H NMR (DMSO) (L^2): $\delta = 9.97$ (s, 2 H, N=CH); 8,78 (s, 2 H, OH); 8.41–7.14 (m, 18 C-H, Ar); 4.04 (s, 2 H, CH2) ppm.

[28] General procedure for the synthesis of the metal complexes with ligands L^1 and L^2 Ligands L^1 or L^2 (3 equiv), $NaHCO_3$ (2 equiv), and the corresponding salt (Al^{+3}, Ga^{+3} and In^{+3}) were dissolved in ethanol under argon. The resulting mixture was gently heated and magnetically stirred for 4 h. The solution was then concentrated in a rotary evaporator to ca. 5 mL. A small volume of diethyl ether (ca. 3 mL) was slowly infused into the solution producing powdery precipitates. The products were separated by centrifugation and dried under vacuum. $Na_6[Al_2(L^1)_3]$. Anal. Calcd for $C_{81}H_{66}Al_2N_6Na_6O_{12}$: C, 64.54; H, 4.41; N, 5.58. Found: C, 64.74; H, 4.15; N, 4.94%. Yield: 53%. IR (KBr, cm^{-1}): 1635 [$\nu(C{=}N)_{imine}$]; 1596 [$\nu(C{=}C)_{ar}$]. MS (ESI^-, m/z): 461 $[AlL^1{-}4H]^-$, 923 $[Al_2(L^1)_2{-}7H]^-$, 945 $[Al_2(L^1)_2Na\text{-}8H]^-$, 1405 $[Al_2(L^1)_3Na_2{-}9H]^-$, 1427 $[Al_2(L^1)_3Na_3{-}10H]^-$. $Na_6[Ga_2(L^1)_3]$. Anal. Calcd for $C_{81}H_{66}Ga_2N_6Na_6O_{12}$: C, 61.08; H, 4.18; N, 5.28. Found: C, 61.66; H, 3.34; N, 5.55%. Yield: 53%. IR (KBr, cm^{-1}): 1633 [$\nu(C{=}N)_{imine}$]; 1595 [$\nu(C{=}C)_{ar}$]. MS (ESI^-, m/z): 437 $[L^1{-}1H]^+$, 459 $[L^1Na\text{-}2H]^+$, 503 $[Ga(L^1)\text{-}4H]^+$, 1009 $[Ga_2(L^1)_2{-}5H]^+$, 1031 $[Ga_2(L^1)_2Na\text{-}6H]^+$. $Na_6[In_2(L^1)_3]$. Anal. Calcd for $C_{81}H_{66}In_2N_6Na_6O_{12}$: C, 57.81; H, 3.95; N, 4.99. Found: C, 41.80; H, 3.15; N, 3.26%. Yield: 53%. IR (KBr, cm^{-1}): 1632 [$\nu(C{=}N)_{imine}$]; 1592 [$\nu(C{=}C)_{ar}$]. MS (ESI^-, m/z): 549 $[In(L^1)\text{-}4H]^+$, 1121 $[In_2(L^1)_2Na\text{-}8H]^+$. $[Al_2(L^2)_3]$. Anal. Calcd for $C_{99}H_{88}Al_2N_{12}O_{14}$: C, 68.98; H, 5.15; N, 9.75. Found: C, 68.69; H, 4.15; N, 8.89%. Yield: 53%. IR (KBr, cm^{-1}): 1612 [$\nu(C{=}N)_{imine}$]; 1567, 1460 [$\nu(C{=}C)_{ar}$ and $\nu(C{=}N)_{py}$]. MS (ESI^-, m/z): 1039 $[Al(L^2)_2{-}4H]^+$. $[Ga_2(L^2)_3]$. Anal. Calcd for $C_{98}H_{82}Ga_2N_{12}O_{11}$: C, 67.74; H, 4.71; N, 9.58. Found: C, 67.24; H, 4.21; N, 8.84%. Yield: 53%. IR (KBr, cm^{-1}): 1615 [$\nu(C{=}N)_{imine}$]; 1563, 1455 [$\nu(C{=}C)_{ar}$ and $\nu(C{=}N)_{py}$]. MS (ESI^-, m/z): 1081 $[Ga(L^2)_2{-}4H]^+$. $[In_2(L^2)_3]$. Anal. Calcd for $C_{99}H_{82}In_2N_{12}O_{11}$: C, 64.43; H, 4.48; N, 9.11. Found: C, 64.11; H, 4.26; N, 9.09%. Yield: 53%. IR (KBr, cm-1): 1623 [$\nu(C{=}N)_{imine}$]; 1594, 1447 [$\nu(C{=}C)_{ar}$ and $\nu(C{=}N)_{py}$]. MS (ESI^-, m/z): 1127 $[In(L^2)_2{-}4H]^+$.

[29] Elemental analyses were carried out at the REQUIMTE DQ Service (Universidade Nova de Lisboa), on a Thermo Finnigan-CE Flash-EA 1112- CHNS instrument. Infrared spectra were recorded as KBr discs using Bio-Rad FTS 175-C spectrophotometer. Proton NMR spectra were recorded using a Bruker WM-400 spectrometer.

[30] (a) N.S. Grill, R.H. Nuttall, D.E. Scaife, D.W. Sharp, J. Inorg. Nucl. Chem. 18 (1961) 79;
  (b) S. Aime, M. Botta, U. Casellato, S. Tamburini, P.A. Vigato, Inorg. Chem. 34 (1995) 5825.

[31] Absorption spectra were recorded on a Shimadzu UV-2501PC or in a Perkin Elmer lambda 35 spectrophotometer. Fluorescence emission spectra were recorded on a Horiba–Jobin–Yvon SPEX Fluorolog 3.22 or a Perkin Elmer LS45 spectrofluorimeters. The linearity of the fluorescence emission versus concentration was checked in the concentration range used (10^{-4} to 10^{-6} M). A correction for the absorbed light was performed when necessary. All spectrofluorimetric titrations were performed as follows: the stock solutions of the ligand (ca. 1.10^{-3} M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with acetonitrile (ligand L^1) and dichloromethane (ligand L^2) UVA-sol. All measurements were performed at 298 K. The titration solutions (ca. $[L] = 1.0.10^{-5}$ M) were prepared by appropriate dilution of the stock solutions. Titrations of the ligand were carried out by addition of microliter amounts of standard solutions of the ions in acetonitrile or dichloromethane.

[32] R.T. Bronson, M. Montalti, L. Prodi, N. Zaccheroni, R.D. Lamb, N.K. Dalley, R.M. Izatt, J.S. Bradshaw, P.B. Savage, Tetrahedron 60 (2004) 11139.