Multi-Channel Receptors and Their Relation to Guest Chemosensing and Reconfigurable Molecular Logic Gates

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The synthesis and characterisation of a family of multi-channel receptors containing crown-cation binding sites anchored to a 1-aminophenyl-1,2,2-tricyanoethylene group is reported. The ligands L^1–L^6 bear a 1-aminophenyl-1,2,2-tricyanoethylene scaffolding which is simultaneously a redox-active group (showing reduction processes at moderately modest potentials) and an acceptor moiety in the 1-aminophenyl-1,2,2-tricyanoethylene chromophore. Additionally, dyes L^1–L^6 also show fluorescence emission. The colour variation of L^1–L^6 in acetonitrile in the presence of the metal cations Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+} and Zn^{2+} has been studied. Selective hypsochromic shifts were found for the systems L^4-Pb^{2+}, L^5-Hg^{2+} and L^6-Hg^{2+}. For Hg^{2+} with L^5 and L^6 and Pb^{2+} with L^4, emission fluorescence enhancements most likely associated with metal coordination to the anilinium nitrogen were observed. The electrochemical behaviour of receptors L^1–L^6 was studied in acetonitrile with platinum as working electrode and $[Bu_4N][BF_4]$ as supporting electrolyte. This family of receptors shows a one-electron reversible reduction process at around –0.70 V vs. SCE, attributed to the reduction of the tricyanovinyl group. Additionally, all the receptors also show the oxidation of the anilinium moiety at about 1.2–1.4 V vs. SCE. Significant anodic shifts of both reduction and oxidation waves were found in the presence of certain metal cations. The relationship of these multiple-channel signalling receptors with guest chemosensing and reconfigurable molecular-based logic gates is discussed.

Introduction

One of the most interesting and expanding fields in supramolecular chemistry is related to the management of input/output signals and their relationship with molecular information. This double "signal-information" concept has, for instance, been applied to different research fields, such as those of molecular logic gates[1] and chemosensing.[2] In the former, chemical species are used as inputs and the output is usually a light signal (emission or colour variation). In chemosensing protocols, light (emission or colour variation) or an electrochemical signal can be considered as input events which are related to the presence of certain chemical species (output information). In many cases these molecular input/output transducers have in common the presence of "binding sites" and "signalling" units.

In the development of chemosensors, the binding site is specifically designed to achieve a high degree of complementarity with target ions, whereas the signalling unit is capable of transducing the (usually selective) binding event into a signal.[3] Following this approach, a number of examples have been described in recent years on the synthesis of cation[4] and anion chemosensors.[5] A large number of coordination sites have been designed that are dependent on the nature of the guest. Three groups of reporters have been mainly used as signalling units: fluorescent groups[6] (the signal is an emission fluorescence change), dyes (the signal is a colour variation) and redox-active groups[7] (the signal upon guest coordination is a shift in the redox potential of the redox-active groups). Advances in this area have been described as important for the selective and sensitive development of target molecular probes.

However and despite the development of individual chromogenic, fluorogenic and electrochemical molecular sensors, there are few examples of receptors capable of displaying two or more output signals upon guest binding. Towards the development of multi-signalling receptors, we have recently reported chemosensors containing both anthracene (as fluorescent) and ferrocene (as electroactive) subunits.[8] Some other recent examples of multi-signalling include the work of Delavaux-Nicot et al., who have developed cation chemosensors containing ferrocene and *N*,*N*-diethylbenzene fluorescent groups.[9] A similar approximation has been used by Beer et al. by synthesising redox-

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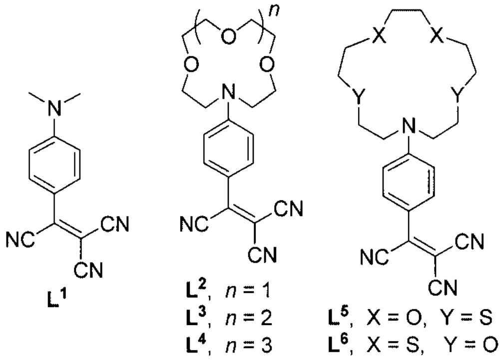
active and photoactive ruthenium(II) and osmium(II) bipyridylferrocene and -cobaltocene-containing macrocycles capable of sensing anionic guests by electrochemical and fluorescence techniques.[10] Also remarkable are the papers published by Shimidzu and Lehn.[11] Chemosensors functionalised with only one subunit capable of displaying two or more observable events (usually two-channel fluorescence – colour changes) upon addition of a certain guest are commonly observed in the so-called intrinsic sensors, in which at least one coordination atom from the binding site is also part of the signalling subunit (usually a dye scaffolding). For example, Fabbrizzi et al. recently reported the synthesis of a chemodosimeter for copper(II), composed of a cyclam unit functionalised with 7-nitrobenzo[1,2,5]oxadiazol-4-ylamine chromophore, which operates through two different channels − colour change and fluorescence quenching of the chromophore.[12] A pH sensor operating through both absorption and emission and based on 1,3-diaryl-5-pyridyl-4,5-dihydropyrazole has been reported by de Silva.[13] However, as far we know, chemosensors operating through three different channels (colour, fluorescence and redox) are very rare and are not common in the literature.[14] We report here the synthesis and characterisation of a family of multichannel receptors containing different crown cation binding sites anchored to a 1-aminophenyl-1,2,2-tricyanoethylene group, which is simultaneously a redox-active group (showing reduction processes at moderately modest potentials) and an acceptor moiety in the 1-aminophenyl-1,2,2-tricyanoethylene chromophore. Additionally, the synthesised receptors also show fluorescence emission. An advance report of the results shown here has recently been published.[14] These multi-signalling systems are not only of interest in sensing protocols but could also be of importance for the development of “reconfigurable” molecular-based logic gates.

Results and Discussion

Receptors L^2–L^6 are built of macrocyclic binding sites (of different sizes, also containing different heteroatoms; nitrogen, oxygen and sulfur) and an (aminophenyl)tricyanovinyl signalling reporter (Scheme 1). Ligands L^1 and L^3 have previously been synthesised by Charles[15a] and Beer,[15b] respectively. Receptor L^1 has an *N*,*N*-dimethylamino moiety and was selected as a model compound in order to study the selectivity towards metal cations imposed by the nature of the binding rings. The Richman–Atkins procedure was used to synthesise the phenyl-functionalised macrocyclic subunits.[16] Aza-oxa macrocycles were synthesised in high dilution procedures by deprotonation of *N*,*N*-phenyldiethanolamine (**3**) with sodium hydride followed by reaction with the methylsulfonyl ester derived from the corresponding polyethylene glycol (**2a**–**2c**; see Scheme 2). The macrocycles used to obtain receptors L^3 and L^4 were previously synthesised in 1978 by Vögtle.[17] The macrocycles used to obtain receptors L^5 and L^6, which contain sulfur atoms in their structures, were synthesised by a modified procedure in which 3,6-dioxaoctane-1,8-dithiol (**6a**) and 3,6-dithiaoctane-1,8-diol (**6b**) were deprotonated with potassium carbonate and sodium hydride, respectively, followed by treatment with the methylsulfonyl ester of *N*,*N*-phenyldiethanolamine (**5**) to give the sulfur-containing macrocycles **7a** and **7b**. *N*,*N*-Dimethylaniline and the synthesised phenyl-containing macrocycles were treated with tetracyanoethylene in warm DMF (60 °C) to give the corresponding receptors L^1–L^6, which were isolated as dark-reddish solids.

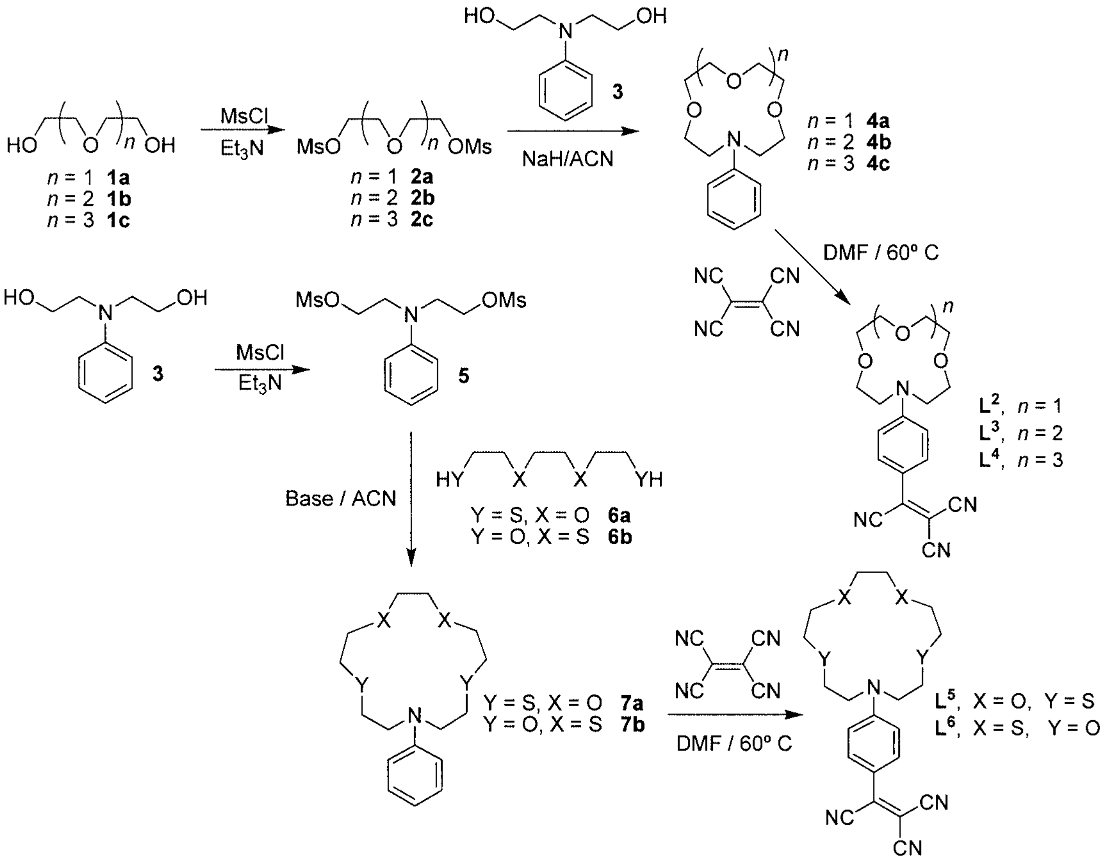


Scheme 1.

The ^{1}H NMR spectra of receptors L^2–L^6 show macrocyclic protons in the range of δ = 2.6 to 3.8 ppm, with two clearly defined zones − the methylene protons adjacent to the sulfur atoms at δ = 2.6–2.9 ppm and the methylene protons adjacent to nitrogen and oxygen atoms in the range δ = 3.5–3.8 ppm. Two doublets at δ = 6.70 and 8.00 ppm indicate the presence of a 1,4-disubstituted aromatic benzene ring. In the ^{13}C NMR spectrum the methylenes adjacent to the sulfur atoms appear in the range δ = 30–35 ppm, whereas the methylenes adjacent to nitrogen and oxygen show signals in the δ = 51–73 ppm range. The aromatic and cyanide carbons appear in the δ = 113–155 ppm range. The most significant signals are the three cyanide carbons centred at δ = 113.7, 114.0 and 114.5 ppm and the signals at δ = 117.8 and 137.3 ppm attributed to the quaternary carbons of the tetrasubstituted double bond.

Despite their easy synthesis and extensive application in different fields, such as optical recording materials or in electrophotography,[18] tricyanovinyl dyes have scarcely been used for sensing purposes. Phenyltricyanoethylene dyes coupled with a phenylboronic acid have previously been used as chromogenic reagents for carbohydrate sensing.[19] Additionally, receptors L^1 and L^3 have previously been used for electrochemical studies in the presence of Na^+, K^+ and Mg^{2+} cations.[15b]

The crystal structure of receptor L^5 was solved by single-crystal X-ray procedures. Suitable crystals for X-ray diffraction were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the receptor L^5. The compound crystallises in the space group $P\bar{1}$ with two molecules of L^5 per asymmetric unit. Figure 1 shows a view of one of the two molecules. The aromatic ring, the double bond and the three cyanide moieties that form the chromogenic subunit are planar within the experimental error. This chromo-



Scheme 2.

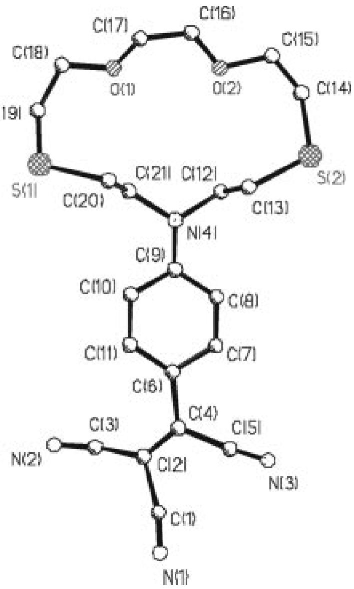


Figure 1. Crystal structure of receptor L^5. Two molecules of L^5 were found in the asymmetric unit but only one is shown. Selected distances [Å]: C(1)–N(1) 1.118(9), C(3)–N(2) 1.115(9), C(5)–N(3) 1.130(8), C(2)–C(1) 1.434(10), C(2)–C(3) 1.419(11), C(4)–C(2) 1.356(10), C(4)–C(5) 1.497(10), C(4)–C(6) 1.431(19), C(9)–N(4) 1.350(8), S(1)–C(19) 1.772(8), S(1)–C(20) 1.848(9), S(2)–C(14) 1.781(7), S(2)–C(13) 1.794(7).

genic subunit is linked to the macrocycle by a nitrogen atom.

Chromogenic Signaling

The visible spectrum of the chemosensors L^1–L^6 in acetonitrile solutions (5.0×10^{-5} M) is characterised by a band centred at about 520 nm which can tentatively be assigned to a charge-transfer band from the donor anilinium group to the acceptor tricyanovinyl moiety.[20] This visible band is responsible for the red-pink colour shown by the receptors in acetonitrile solution.

Addition of equimolar quantities of alkali (Li^+, Na^+, K^+) or alkaline-earth (Ca^{2+}, Ba^{2+}, Mg^{2+}) cations to acetonitrile solutions of receptors L^1–L^6 produced negligible changes in this band. The visible behaviour was also studied in the presence of the metal cations Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Ag^+. The model compound L^1, without a macrocyclic cavity in its structure, shows three different behaviours (see Figure 2 and Table 1); namely no changes with Ag^+ and Cd^{2+}, a slight hyperchromic effect (intensity enhancement of the visible band centred at 516 nm) in the presence of Zn^{2+}, Pb^{2+} and Hg^{2+}, and the apparition of a shoulder at 468 nm in the presence of Fe^{3+} and Cu^{2+} (see Figure 2) attributed to metal coordination with the donor nitrogen atom of the aniline group.[6] Upon titration of a solution of receptor L^1 with Cu^{2+} cation, clear isosbestic points were obtained. The presence of these isosbestic points is indicative of the formation of only one complex, with a 1:2 stoichiometry (cation:receptor). Monitoring the changes at 468 nm upon Cu^{2+} addition, a logarithm of the stability constant of 4.53 ± 0.03 for the formation of the $[Cu(L^1)_2]^{2+}$ complex was obtained.[21] Studies with Fe^{3+} gave no clear isosbestic points, most likely due to the simultaneous formation of complexes with different stoichiometries.

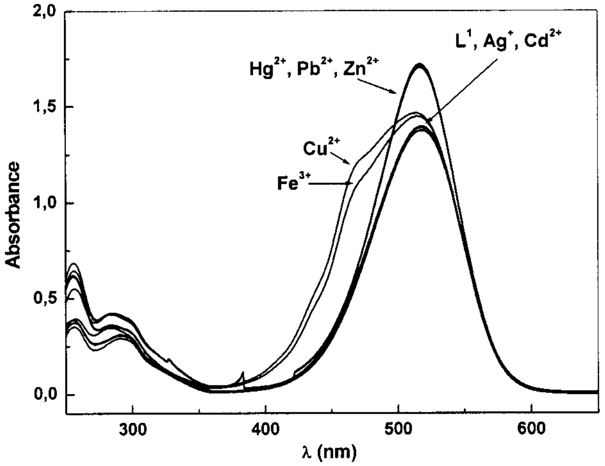


Figure 2. Changes in the UV/Vis spectra of receptor L^1 upon addition of equimolar quantities of metal cations in acetonitrile (5.0×10^{-5} M).

Table 1. Absorption λ_{max} [nm]and ε [$L\,mol^{-1}\,cm^{-1}$] for receptors L^1 to L^6 and their variation upon addition of metal cations in acetonitrile solutions.

	L^1	L^2	L^3	L^4	L^5	L^6
λ_{max}	517	523	518	520	520	518
ε	32500	47300	29900	33500	35200	37500
Ag^+	517	523	518	520	520	518
Cd^{2+}	517	523	518	520	520	518
Cu^{2+}	↓ 490[a]	523	518	520	520	518
Fe^{3+}	↓ 490[a]	↓ 519[a]	↓ 518[a]	↓ 513[a]	520	518
Hg^{2+}	517	523	518	520	394	504
Pb^{2+}	517	523	518	475	520	518
Zn^{2+}	517	523	518	520	520	518

[a] The downward pointing arrows indicate a significant hypochromic change in the visible band with respect to that of the free ligand.

On changing from the receptor L^1 to those containing macrocycles, important changes in the selectivity trends were found. Thus, addition of equimolar quantities of Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} or Ag^+ to acetonitrile solutions of L^2 produced negligible changes in the UV/Vis spectrum, whereas the presence of equimolar quantities of Fe^{3+} resulted in a remarkable hypochromic change (diminution of the visible band intensity of 60% for Fe^{3+}). A concomitant unremarkable hypsochromic shift of the band centred at 523 nm to 519 nm was also observed for Fe^{3+}. Studies on the variation of the intensity at 523 nm upon addition of increasing amounts of this cation suggested the formation of well-defined 1:1 complexes. A log K value of 4.69 ± 0.09 was determined for the formation of the $[Fe(L^2)]^{3+}$ complex (see Table 2).[21] These results for L^2, which has a relatively small coordination ring, are somehow related to the characteristics of the Fe^{3+} metal cation, which is, of all the metal cations studied, that with the smallest ionic radius (0.64 Å). The perfect fitting of the Fe^{3+} cation within the macrocyclic subunit of L^2 probably induces Fe–N interactions that could be the responsible for the hypsochromic shift observed. The lack of response in the presence of Cu^{2+} shown by L^2 (when compared to L^1) could be due to the poorer tendency of the Cu^{2+} cation to fit within the macrocyclic cavity (Cu^{2+} ionic radius = 0.69 Å), although steric constraints could make the Cu–N interaction less effective.

For L^3 – the macrocycle in L^3 contains one oxygen atom and one methylene unit more than the macrocycle in L^2 – only Fe^{3+} is able to induce a hypochromic change in the visible band at 518 nm similar to that observed for L^2 (no hypsochromic shifts were found). A log K of 4.63 ± 0.15 for the formation of the $[Fe(L^3)]^{3+}$ complex was obtained from the intensity changes of the 518 nm band (see Figure 3). The addition of equimolar quantities of the other metal cations tested induced negligible changes.

A more selective and remarkable behaviour was found for chemosensor L^4, which contains the largest macrocyclic cavity of all the receptors studied. A selective colour variation from red-pink to yellow-orange (hypsochromic shift from 520 to 475 nm) was observed upon addition of the heavy metal cation Pb^{2+} (see Figure 4).[22] This result is in agreement with the larger radius of Pb^{2+}, which apparently fits well into the large binding cavity of L^4. The correct combination of ring and cation size would result in a suitable coordination to the nitrogen atom of the macrocyclic subunit, thus inducing the hypsochromic shift of the charge-transfer band.[6] UV/Vis titration experiments for the system Pb^{2+}-L^4 showed clear isosbestic points indicative of the formation of 1:1 ligand-to-metal species. The log K for the formation of the $[Pb(L^4)]^{2+}$ complex, obtained by nonlinear least-squares treatment of the titration profile, is 6.42 ± 0.03 (see Figure 5).[21] The presence of Fe^{3+} results in

Table 2. Logarithm of the stability constant for the formation of $[M(L^n)]^{m+}$ complexes.

	L^1	L^2	L^3	L^4	L^5	L^6
Cu^{2+}	4.53 ± 0.03[a]	–	–	–	–	–
Fe^{3+}	–	4.69 ± 0.09	4.63 ± 0.15	4.97 ± 0.10	–	–
Hg^{2+}	–	–	–	–	7.57 ± 0.02	5.60 ± 0.05
Pb^{2+}	–	–	–	6.42 ± 0.03	–	–

[a] 2:1 (receptor:cation) stoichiometry for the complex formed between L^1 and Cu^{2+}.

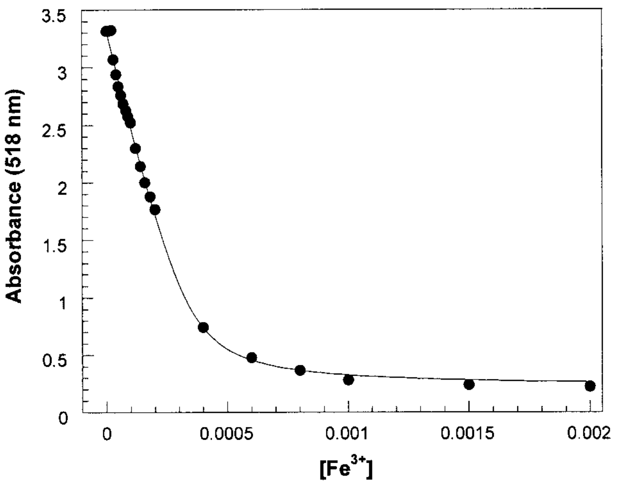


Figure 3. Variation of the intensity at 518 nm for receptor L^3 upon addition of increasing amounts of Fe^{3+} cation in acetonitrile (5.0×10^{-5} M).

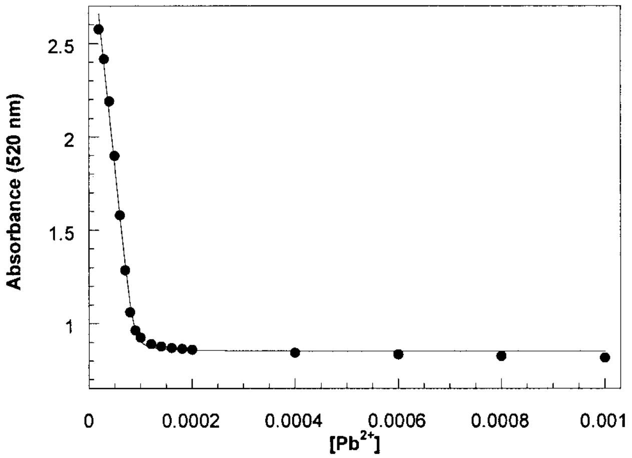


Figure 5. Variation of the intensity at 520 nm for receptor L^4 upon addition of increasing amounts of Pb^{2+} cation in acetonitrile (5.0×10^{-5} M).

a hypochromic effect and an unremarkable hypsochromic shift of less than 10 nm. Monitoring the intensity changes at 520 nm upon addition of Fe^{3+} gave moderate log K values (4.97 ± 0.10). Addition of other metals such as Ag^+, Cu^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+} and Zn^{2+} to acetonitrile solutions of L^4 gave no change in the colour of the solutions.

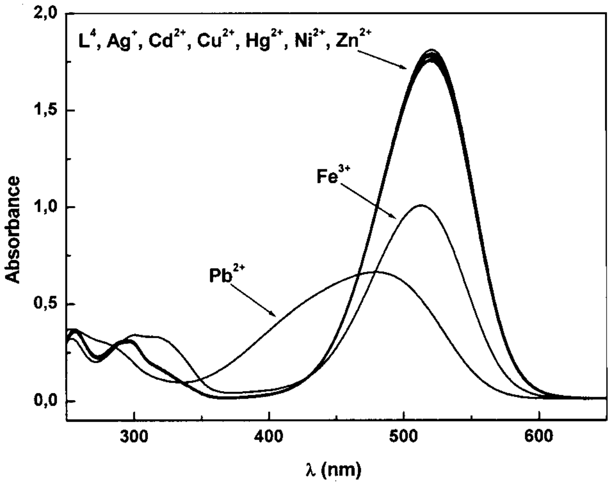


Figure 4. Changes in the UV/Vis spectra of receptor L^4 upon addition of equimolar amounts of metal cations in acetonitrile (5.0×10^{-5} M).

The receptors L^5 and L^6, which bear oxathiaaza crowns, were synthesised in an attempt to colourimetrically recognise additional thiophilic cations such as Hg^{2+}.[23] Thus, red-pink acetonitrile solutions of L^5 changed to yellow upon addition of Hg^{2+} due to a hypsochromic shift of the visible band upon cation binding (see Figure 6). Other metal cations (Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, Mg^{2+},Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Fe^{3+}) induced no significant changes.[24] The behaviour of acetonitrile solutions of receptor L^6 in the presence of equimolar quantities of metal cations was very similar to that found for L^5: only Hg^{2+} induced a significant hypsochromic shift of the band centred at 518 nm to 504 nm associated with a change in colour from pink to orange. This lesser hypsochromic shift shown by L^6 when compared to L^5 can be ascribed to the position of the sulfur atoms in the macrocyclic subunit. Hypsochromic shifts of a charge-transfer band are observed upon a suitable interaction (for instance coordination) with the donor group. In receptor L^5, the sulfur atoms are placed in the vicinity of the anilinium nitrogen that is part of the chromogenic unit. This spatial proximity might favour the interaction (orbital overlap) of the nitrogen with the Hg^{2+} cation. In receptor L^6, however, the sulfur atoms are separated from the anilinium nitrogen by oxygen atoms and the corresponding methylene subunits. In this case, a preferential coordination of the highly thiophilic Hg^{2+} cation with these sulfur atoms would result in a weaker interaction with the anilinium nitrogen, with concomitant smaller changes in the UV/Vis spectra. As in the above cases, the hypsoch-

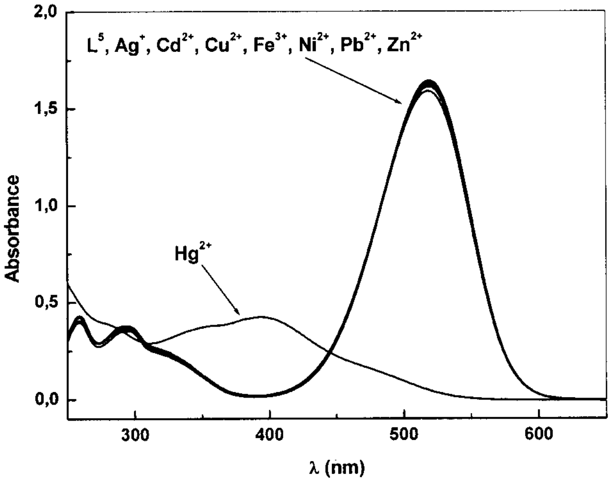


Figure 6. Changes in the UV/Vis spectra of receptor L^5 upon addition of equimolar amounts of metal cations in acetonitrile (5.0×10^{-5} M).

romic shift of the visible band upon Hg^{2+} coordination is consistent with a decrease in the donor strength of the donor group.[6] UV/Vis titrations showed clear isosbestic points, indicating the formation of 1:1 L^5-to-Hg^{2+} complexes. A log *K* of 7.57 ± 0.02 was calculated for the formation of the $[Hg(L^5)]^{2+}$ complex (see Figure 7); 1:1 complexes were also formed between L^6 and Hg^{2+}. In this case, log *K* for the formation of the $[Hg(L^6)]^{2+}$ complex, calculated by nonlinear least-squares treatment of the titration profiles, was 5.60 ± 0.05.

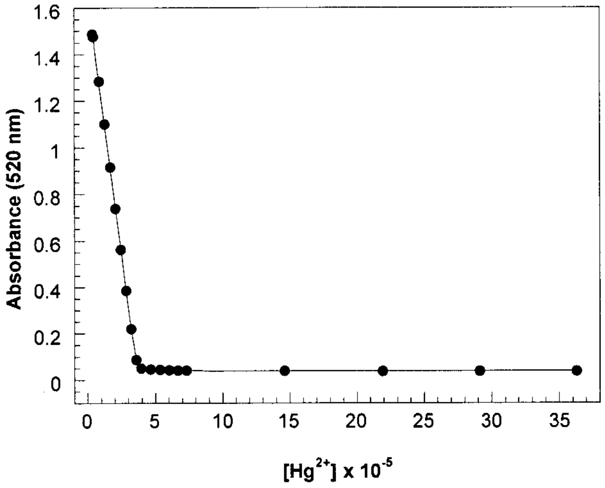


Figure 7. Variation of the intensity at 518 nm for receptor L^5 upon addition of increasing amounts of Hg^{2+} cation in acetonitrile (5.0×10^{-5} M).

Fluorogenic Signalling

The 1-aminophenyl-1,2,2-tricyanoethylene chromophore also shows fluorescence emission upon excitation at the visible absorption band. Fluorescence studies were carried out with acetonitrile solutions (ca. 3.0×10^{-5}M) of the receptors by addition of equimolar quantities of the corresponding metal cation. L^1 shows dual emission features in acetonitrile upon excitation at 517 nm, with a broad, unstructured emission band centred at 610 nm and another more-intense, red-shifted band centred at 690 nm. This red-shifted emission can tentatively be ascribed to formation of an excimer by interaction of an excited state fluorophore with a fluorophore in the ground state.[25] Addition of Ag^+, Pb^{2+}, Zn^{2+}, Ni^{2+} or Cd^{2+} resulted in no significant variation in the emission intensity profiles, whereas the presence of Fe^{3+}, Hg^{2+} or Cu^{2+} inhibited the formation of the excimer and caused an almost complete quenching of the red-shifted band centred at 690 nm.

The emission behaviour of receptors functionalised with macrocyclic subunits (L^2–L^6) is somewhat different to that of L^1 and, upon excitation, only an emission band centred at 600 nm was found; the red-shifted emission found in L^1 was not observed. This could be related to steric factors due to the presence of the bulky macrocyclic moieties, which might prevent excimer formation in the L^2–L^6 receptors. The emission behaviour of acetonitrile solutions of L^2 and L^3 (excitation at 518 and 515 nm for L^2 and L^3, respectively) upon addition of metal cations was unexciting, with only minor changes in the emission intensity (centred at 610 nm) upon addition of the Fe^{3+} cation (see Table 3).

Table 3. Fluorescence emission intensity variation (as % of that of the receptor) obtained for L^1–L^6 upon addition of metal cations in acetonitrile solutions.

	L^1[a]	L^2[a]	L^3[a]	L^4[a]	L^5[a]	L^6[a]
Ag^+	<5	<5	<5	<5	<5	<5
Cd^{2+}	<5	<5	<5	<5	<5	<5
Cu^{2+}	↓ 90[b]	<5	<5	↓ 16[b]	<5	<5
Fe^{3+}	↓ 90[b]	↓ 11[b]	↓ 18[b]	↓ 22[b]	<5	<5
Hg^{2+}	↓ 90[b]	<5	<5	<5	↑ 90[b]	↑ 20[b]
Pb^{2+}	<5	<5	<5	↑ 45[b]	<5	<5
Zn^{2+}	<5	<5	<5	↑ 10[b]	<5	<5

[a] Excitation wavelengths of 517, 518, 515, 467, 450 and 470 nm for L^1, L^2, L^3, L^4, L^5 and L^6, respectively. [b] The upward and downward pointing arrows indicate increase and quenching, respectively, of the emission intensity (690 nm for L^1 and 610 nm for L^2–L^6).

A more significant and selective behaviour was observed with receptors L^4 and L^5. The isosbestic points obtained in the UV/Vis titrations of L^4 with Pb^{2+} (467 nm) and L^5 with Hg^{2+} (450 nm) were chosen as excitation wavelengths. Upon excitation unstructured emission bands centred at 610 and 605 nm were observed for L^4 and L^5, respectively. The results obtained upon addition of one equivalent of the corresponding metal cations are shown in Table 3. The most remarkable effect was the selective enhancement of the emission intensity (90%), coupled with a moderate 10-nm hypsochromic shift of the emission band (from 605 to 595 nm) observed upon addition of Hg^{2+} to solutions of L^5 (Figure 8). Other metal cations tested (Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+}) induced negligible variations (less than 5%) in the fluorescence emission of this receptor. The excitation spectra (λ_{exc} = 610 nm) measured upon addition of one equivalent of Hg^{2+} cation to an acetonitrile solution of receptor L^5 show the apparition of a band centred at 380 nm, indicating that the $[Hg(L^5)]^{2+}$ complex is the emissive species that induces the apparition of the emission band centred at 605 nm. With L^4, the addition of equimolar quantities of Pb^{2+} or Zn^{2+} induced enhancement in the emission intensity (45% with Pb^{2+} and 10% with Zn^{2+}) with a very low hypsochromic shifts in the emission band (2 nm for Pb^{2+} and negligible with Zn^{2+}), whereas the presence of Cu^{2+} or Fe^{3+} induced moderate quenching and hypsochromic shifts (5 and 10 nm for Cu^{2+} and Fe^{3+} respectively). The fluorescent behaviour of receptor L^6 in the presence of metal cations is very similar to that found for L^5. Upon excitation at the isosbestic point obtained from UV/Vis titrations of L^6 with the mercuric cation (470 nm), a broad emission band centred at 614 nm developed. Of all the metal cations tested, only Hg^{2+} induces a 20% enhancement of the emission intensity, with a hypsochromic shift of the emission band to 604 nm.

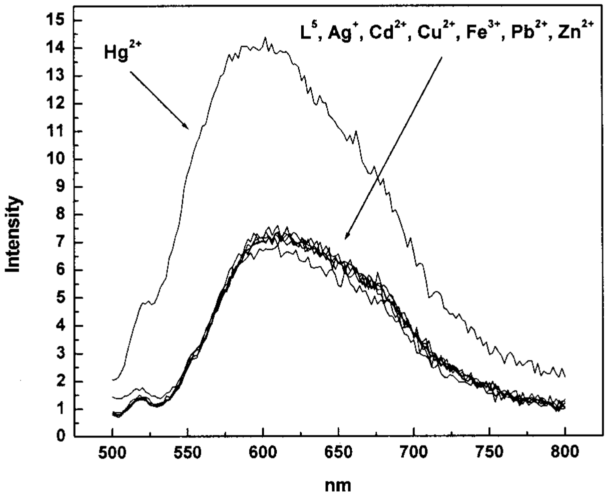


Figure 8. Emission spectra of receptor L^5 (λ_{ex} = 450 nm) upon addition of equimolar amounts of metal cations in acetonitrile (3.0×10^{-5} M).

Table 3 shows that only Hg^{2+}, Pb^{2+} and Zn^{2+} display fluorescence enhancement effects. This is in agreement with their d^{10} electronic configuration, for which electron-transfer or energy-transfer processes usually do not occur.[26] For Hg^{2+} with L^5 and L^6, and Pb^{2+} with L^4, the emission fluorescence enhancement is remarkable and is most likely associated with a strong metal coordination to the anilinium nitrogen (this is also supported by the UV/Vis studies, see above). On the other hand, quenching was observed with the redox-active metal cations Fe^{3+} and Cu^{2+}, for which electron-transfer processes involving the d-orbitals of the metals and the excited state of the fluorophore can occur.[26]

Electrochemical Signalling

The electrochemical behaviour of the tricyanovinyl receptors was studied in acetonitrile with platinum as working electrode and $[Bu_4N][BF_4]$ as supporting electrolyte. This family of receptors shows a one-electron reversible reduction process at about –0.70 V vs. SCE attributed to the reduction of the tricyanovinyl group.[15b] They also show a reversible oxidation process at 1.2–1.4 V vs. SCE due to the oxidation of the anilinium moiety.[27] This electrochemical interpretation is in agreement with molecular modelling and orbital calculations performed on L^1 at the PM3 level.

A detailed electrochemical study in the presence of the metal cations Ag^+, Cd^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+} and Zn^{2+} was carried out with ligands L^4, L^5 and L^6, which are those that show a more remarkable optical behaviour (see above). A summary of the electrochemical responses is shown in Table 4. For ligand L^5, three different cation-induced electrochemical behaviours were observed. The first type of behaviour was found in the presence of Hg^{2+}, with a remarkable anodic shift (340 mV) of the reduction wave of L^5 along with a significant drop in the reduction wave intensity. Additionally, in the presence of this metal cation the oxidation peak of L^5 "disappears" (the wave is shifted anodically out of the solvent redox window). As is well-known, cation coordination with redox-active molecules results in significant electrochemical anodic shifts of either oxidation or reduction processes.[28] A simple explanation of this effect is related to the idea that it is easier to reduce and more difficult to oxidize the positively charged $[Hg(L^5)]^{2+}$ complex than the corresponding neutral ligand. Therefore, coordination of Hg^{2+} to the oxathiaaza ring would give rise to both an anodic shift in the oxidation wave of the aniline (the shift is so large that the new wave is not observed) and an anodic shift of the reduction process (340 mV). This strong Hg^{2+}–N interaction in L^5, suggested by the electrochemical results, is in agreement with the selective chromogenic results found for this cation (see above).

Table 4. Anodic shifts of the reduction wave (ΔE in mV) obtained for L^4, L^5 and L^6 in the presence of metal cations in acetonitrile solutions.

	$\Delta E(L^4)$[a]	$\Delta E(L^5)$[a]	$\Delta E(L^6)$[a]
Ag^+	10	17	<10
Cd^{2+}	170	120	80
Cu^{2+}	40	25	20
Fe^{3+}	340	240	<10
Hg^{2+}	370	340	200
Pb^{2+}	360	330	160
Zn^{2+}	160	140	20

[a] $\Delta E(L^n) = E(L^n + M^{n+}) - E(L^n)$.

A second sort of electrochemical behaviour was observed for L^5 upon addition of cations such as Pb^{2+}, Zn^{2+}, Fe^{3+} and Cd^{2+}. In this case, there is also a significant anodic shift of the reduction wave, but there is no significant shift of the oxidation peak of L^5. A drop of the peak intensity was found for both the oxidation and reduction waves. This intensity drop (attributed to the formation of species with a lower diffusion coefficient), along with the anodic shift of the reduction wave suggests that there must be some kind of interaction between these metal cations and L^5. Additionally, the absence of changes in the oxidation wave suggests that this interaction is not with the anilinium nitrogen. Tentatively, this interaction can be assigned to a weak coordination of the metal cations with either remote donor atoms from the ring, such as S or O, or due to some interaction with the electron-rich cyano groups. The absence of significant shifts observed in the oxidation wave is often indicative of CE (chemical electrochemical) processes (decoordination and oxidation of the free ligand) favoured by a weak metal–ligand interaction in these cases. Finally, for cations such as Ag^+, Al^{3+} and Cu^{2+} no remarkable changes were observed in either the oxidation or reduction peaks of L^5.

Ligand L^6 shows a somehow similar behaviour to L^5, although in this case, in general, smaller anodic shifts of the reduction wave are observed. The most remarkable are the anodic shifts of 200 and 160 mV of the reduction wave observed for L^5 in the presence of Hg^{2+} and Pb^{2+} cations, respectively.

L^4 shows a notably large anodic shift of the reduction wave of 370 mV with the metal cations Hg^{2+}, Pb^{2+} and

Fe^{3+}. Addition of Cd^{2+} and Zn^{2+} cations induced a less-important redox shift (170 and 160 mV for Cd^{2+} and Zn^{2+}, respectively). Of all these metal cations, Pb^{2+} is the only one capable of inducing a significant anodic shift of the oxidation peak (140 mV), strongly suggesting coordination of the Pb^{2+} cation with the anilinium nitrogen, in agreement with the chromogenic results. Ag^+ and Cu^{2+} cations gave unremarkable variations of the electrochemical behaviour of L^4.

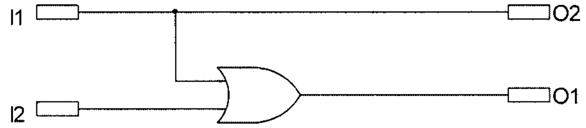
Triple Signalling

A very remarkable aspect is that, in their molecular interaction with metal cations, the receptors gave a somewhat different response depending on the transduction channel studied (electrochemical, chromogenic or fluorogenic). In order to explain this effect, it has to be taken into account that the specific response observed in each case strongly depends on the particularities of each coordination-transduction process. Thus, for instance, chromogenic transduction (hypsochromic shift) would be expected when there is a strong enough interaction of a certain metal cation with the anilinium nitrogen (the donor group involved in the anilinotricyanoethylene chromophore). On the other hand, the electrochemical transduction is related to a coulombic-type interaction between the reduced form of the redox-active group (the tricyanovinyl moiety in this case) and the metal cation. This means that the interaction of a certain metal cation with "remote" binding sites, such as the oxygen and sulfur atoms or the cyano groups, might result in an electrochemical response, but in a poor optical variation. Also remarkable is that, in certain cases, the response obtained by fluorescence is also somehow different to that found chromogenically. Thus, for L^4 the coordination of d^{10} cations such as Pb^{2+} induces emission enhancement, whereas redox-active cations such as Fe^{3+} induce significant quenching, probably by interaction with the photo-excited L^4 receptor through energy or photoelectron transfer processes.

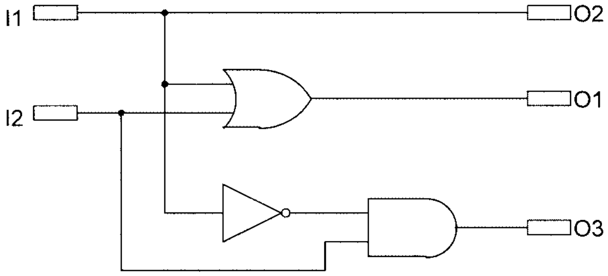
As we have commented above, there is a recent interest in the development of molecules with intrinsic logic capabilities. This concept has become widespread since it was realized that the interaction of a receptor molecule with certain species (input) and the observed response (output) can follow Boolean logic rules.[29] Since then a number of examples have been described, most of them using two inputs (usually the presence of protons and a certain metal cation) that cooperatively control the output observed (usually an optical signal). It is also common to many described molecular logic systems to be related to just one Boolean function, whereas it is less common to observe different logical expressions from one unique molecular entity. However the development of "reconfigurable" molecular logic gates could be of interest.[30] In this context, some of the multi-channel signalling chemosensors described above might lead to the expression of different logical truth tables by selecting different types of output. This is, for instance, observed in Table 5, which shows the changes in receptor L^4 upon addition, as inputs, of the metal cations Pb^{2+} and Hg^{2+}. A two-input OR logic gate is observed when the output is electrochemical, whereas a TRANSFER gate is found for colour variation outputs. Table 5 also shows changes in L^4 upon addition of Pb^{2+} and Fe^{3+} input cations. An OR, TRANSFER and INHIBIT logic gate is obtained when the electrochemical, colour and emission quenching outputs are selected, respectively. These multi-channel systems can be seen as reconfigurable versatile logic systems. More-complex, three-input reconfigurable molecular logic systems can also be obtained, as shown in Table 6, where the logic gates OR, TRANSFER and INHIBIT are found for just one molecular entity (receptor L^4) by selecting the output channel.

Table 5. Two-input logical truth tables associated with electrochemical, colour and emission quenching measurements using receptor L^4 and different metal cations as input signals.

Input 1 Pb^{2+}	Input 2 Hg^{2+}	$\Delta E > 300$ mV O1	Colour variation O2
0	0	0	0
1	0	1	1
0	1	1	0
1	1	1	1



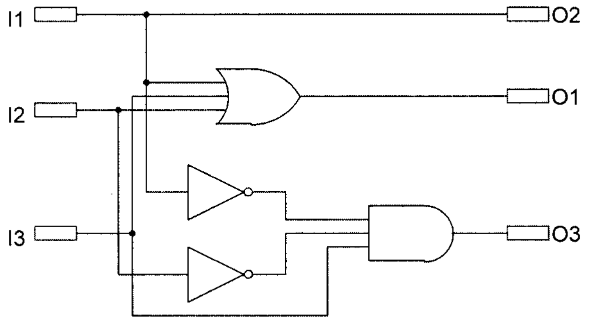
Input 1 Pb^{2+}	Input 2 Fe^{2+}	$\Delta E > 300$ mV O1	Colour variation O2	Emission quenching O3
0	0	0	0	0
1	0	1	1	0
0	1	1	0	1
1	1	1	1	0



A related aspect is that multi-channel signalling receptors such as L^4 and L^5 can give multiple signalling expressions (combination of different signals) that can be used for sensing purposes. This is also depicted in Table 6, where the equivalence between the output observed and the sensing information one can obtain can be seen. Thus a 1/1/0 output pattern (ΔE larger than 300 mV/colour variation/emission quenching) would only be observed in the presence of Pb^{2+}. In the absence of lead (no colour variation), 1/0/0 and 1/0/1 patterns would be indicative of the presence of Hg^{2+} and Fe^{3+}, respectively. Some other combinations (not shown in Table 6) are possible; for instance, and despite the

Table 6. Three-input logical truth tables associated with electrochemical, colour and emission measurements using receptor L^4.

Input 1 Pb^{2+}	Input 2 Hg^{2+}	Input 3 Fe^{3+}	$\Delta E > 300$ mV O1	Colour variation O2	Emmission quenching O3
0	0	0	0	0	0
1	0	0	1	1	0
0	1	0	1	0	0
1	1	0	1	1	0
0	0	1	1	0	1
1	0	1	1	1	0
0	1	1	1	0	0
1	1	1	1	1	0



low quenching found for copper, a 0/0/1 combination would be observed with Cu^{2+}; a 0/0/0 pattern, but with variations of ΔE of about 100 mV. can indicate the presence of Cd^{2+} or Zn^{2+} cations. L^4 therefore acts as a prototype of molecular chemosensors capable of sensing several single guests by multiple signalling combinations. Similar observations can be made with other receptors and a suitable combination of input signals.

Table 6 shows how reconfigurable logic gates or multi-channel signalling receptors are both intimately related concepts. This is indicated by using tricyanoethylene receptors, which are rare electro-optical signalling systems capable of reporting molecular interaction by a triple-channel transduction. These studies suggest that the development of receptors containing a number of reporter groups might open new perspectives in the design of a new generation of multichannel signalling molecules capable of being used as either prototypes of "reconfigurable" molecular logic gates or as multi-channel guest reporting systems by the use of different output signals from just one molecular entity.

Conclusions

A family of receptors based on functionalised tricyanoethylene moieties has been synthesised and characterised and their interaction with metal cations monitored by optical (colour and fluorescence) and electrochemical changes. A selective chromogenic response was found for the L^4-Pb^{2+}, L^5-Hg^{2+} and L^6-Hg^{2+} systems in acetonitrile, whereas fluorescence and electrochemical responses were usually less selective. A final discussion suggests that receptors containing several reporter channels (multi-channel signalling molecules) can be used for studying the intimately related concepts of multi-channel signalling and reconfigurable logic gates.

Experimental Section

General Remarks: All commercially available reagents were used without further purification. Air/water-sensitive reactions were performed in flame-dried glassware under argon. Acetonitrile was dried with CaH$_2$ and distilled prior to use.

Physical Measurements: Metal cations (Ag$^+$, Cd^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} as perchlorate salts and Cu^{2+}, Hg^{2+}, Zn^{2+} as triflate salts) were used to obtain approximately 1.0×10^{-3} M acetonitrile solutions. UV/Vis studies were carried out with a Perkin–Elmer Lambda 35 spectrometer. The concentration of ligands used in the measurements was about 5.0×10^{-5} M in acetonitrile. UV/Vis spectra were recorded in the presence of equimolar quantities of the corresponding ligand and metal cation or anion. The fluorescence behaviour was studied with an FS900CDT Steady State T-Geometry Fluorimeter from Edinburgh Analytical Instruments. All solutions for photophysical studies were previously degassed. The concentration of ligands was about 3.0×10^{-5} M in acetonitrile. Fluorescence emission spectra were recorded in the presence of equimolar quantities of ligand and the corresponding metal cation. Electrochemical data were recorded fors previously degassed dry acetonitrile solution, with a programmable function generator Tacussel IMT-1, connected to a Tacussel PJT 120–1 potentiostat. The concentration of ligands and metal ions was about 1.0×10^{-3} M in acetonitrile (the metal ions were perchlorate or triflate salts of Ag$^+$, Cd^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+} and Zn^{2+}). Electrochemical studies were carried out in the presence of equimolar quantities of ligand and the corresponding metal cation. The working electrode was platinum connected to a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent and the supporting electrolyte (0.25 M [Bu$_4$N][BF$_4$]). The auxiliary electrode was a platinum wire.

The ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini spectrometer. Chemical shifts are reported in ppm downfield from TMS signal. Spectra recorded in CDCl$_3$ were referenced to residual CHCl$_3$.

Synthetic Procedures: The syntheses of 2-(2-methylsulfonyloxyethoxy)ethyl methanesulfonate (**2a**),[31] 2-[(2-methylsulfonyloxyethyl)phenylamino]ethyl methanesulfonate (**5**),[31] 13-phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane (**4b**)[17] and 16-phenyl-1,4,7,10,13-pentaoxa-16-azacycloheptadecane (**4c**)[17] have been previously published. Compound **3** is commercially available.

Synthesis of 10-Phenyl-1,4,7-trioxa-10-azacyclododecane (4a): *N*,*N*-phenyldiethanolamine (**3**; 10 g, 0.05 mol) was dissolved in dry acetonitrile (400 mL) and then sodium hydride (3.3 g, 0.137 mol) was slowly added over 60 min with vigorous stirring at room temperature. The mixture formed was heated to reflux and then, over 4 h, 2-(2-methylsulfonyloxyethoxy)ethyl methanesulfonate (**2a**; 14.4 g, 0.055 mol) dissolved in dry acetonitrile was added. The crude reaction mixture was refluxed overnight. The mixture was then filtered and the filtrate concentrated in vacuo to dryness to give an orange sticky oil that was purified by column chromatography on aluminium oxide with dichloromethane and dichloromethane/ethanol (50:1 v/v) as eluents to give 10-phenyl-1,4,7-trioxa-10-azacyclododecane (3.8 g, 0.015 mol) as a yellowish oil. Yield: 30%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.55 (t, J = 7.5 Hz, 4 H, O-CH_2-CH$_2$-N), 3.64 (m, J = 7.5 Hz, 8 H, O-CH_2-CH_2-O-CH_2-CH_2-O), 3.83 (t, J = 7.5 Hz, 4 H, O-CH$_2$-CH_2-N), 6.68 (t, J = 6 Hz, 2 H, C$_6$H$_5$), 6.70

(d, J = 6 Hz, 1 H, C$_6$H$_5$), 7.18 (t, J = 6 Hz, 2 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 52.35 (CH$_2$-N), 69.55 (CH$_2$-O), 69.77 (CH$_2$-O), 71.46 (CH$_2$-O), 112.24 (C$_6$H$_5$), 116.03 (C$_6$H$_5$), 128.98 (C$_6$H$_5$), 148.44 (C$_6$H$_5$) ppm. MS: m/z = 251 [M$^+$], 220, 176, 162, 150, 132, 120, 105, 91 [C$_6$H$_5$N], 77 [C$_6$H$_5$]. C$_{14}$H$_{21}$NO$_3$ (251): calcd. C 66.91, H 8.42, N 5.57; found C 66.62, H 8.37, N 5.60.

Synthesis of 10-Phenyl-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (7a): 3,6-Dioxaoctane-1,8-dithiol (**6a**; 3.6 g, 0.022 mol) and anhydrous potassium carbonate (12.2 g, 0.088 mol) were dissolved in dry acetonitrile (400 mL) and heated to reflux. Then, 2-[(2-methylsulfonyloxyethyl)phenylamino]ethyl methanesulfonate (**5**; 7.4 g, 0.022 mol) was added over 4 h. The crude reaction mixture was refluxed overnight. The resultant mixture was then filtered and the filtrate concentrated in vacuo to dryness to give a yellow sticky oil that was purified by column chromatography on silica with dichloromethane as eluent to give 10-phenyl-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (2.9 g, 0.009 mol) as a white solid. Yield: 40%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.73 (t, J = 7 Hz, 4 H, O-CH$_2$-CH_2-S), 2.88 (t, J = 7 Hz, 4 H, N-CH$_2$-CH_2-S), 3.62 (s, 4 H, O-CH_2-CH_2-O), 3.64 (t, J = 7 Hz, 4 H, O-CH_2-CH$_2$-S), 3.79 (t, J = 7 Hz, 4 H, N-CH_2-CH$_2$-S), 6.63 (m, 3 H, C$_6$H$_5$), 7.20 (d, J = 6 Hz, 2 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 29.29 (CH$_2$-S), 30.95 (CH$_2$-S), 51.63 (CH$_2$-N), 70.56 (CH$_2$-O), 74.11 (CH$_2$-O), 111.57 (C$_6$H$_5$), 115.98 (C$_6$H$_5$), 129.29 (C$_6$H$_5$), 146.46 (C$_6$H$_5$) ppm. MS: m/z = 327 [M$^+$], 204, 192, 179, 164, 149, 132, 119, 105, 91 [C$_6$H$_5$N], 77 [C$_6$H$_5$]. C$_{16}$H$_{25}$NO$_2$S$_2$ (327): calcd. C 58.68, H 7.69, N 4.28; found C 58.60, H 7.61, N 4.23.

Synthesis of 4-Phenyl-1,7-dioxa-10,13-dithia-4-azacyclopentadecane (7b): 3,6-Dithiaoctane-1,8-diol (**6b**; 3.6 g, 0.022 mol) was dissolved in dry acetonitrile (400 mL) and then sodium hydride (1.6 g, 0.066 mol) was slowly added over 1 h with vigorous stirring at room temperature. The mixture formed was heated to reflux and then, over 4 h methanesulfonic acid 2-[(2-methylsulfonyloxy-ethyl)phenylamino]ethyl methanesulfonate (**5**; 7.4 g, 0.022 mol) dissolved in dry acetonitrile was added. The crude reaction mixture was refluxed overnight, filtered, and the filtrate concentrated in vacuo to dryness to give a yellow sticky oil that was purified by column chromatography on silica with dichloromethane as eluent to give 4-phenyl-1,7-dioxa-10,13-dithia-4-azacyclopentadecane (1.8 g, 0.0055 mol) as a yellowish oil. Yield: 25%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.72 (t, J = 7 Hz, 4 H, O-CH$_2$-CH_2-S), 2.88 (s, 4 H, S-CH_2-CH_2-S), 3.60–3.82 (m, 12 H, N-CH_2-CH_2-O), 6.63 (m, 3 H, C$_6$H$_5$), 7.20 (d, J = 6 Hz, 2 H, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 31.50 (CH$_2$-S), 32.72 (CH$_2$-S), 51.06 (CH$_2$-N), 69.73 (CH$_2$-O), 72.02 (CH$_2$-O), 112.02 (C$_6$H$_5$), 116.33 (C$_6$H$_5$), 129.18 (C$_6$H$_5$), 148.02 (C$_6$H$_5$) ppm. MS: m/z = 327 [M$^+$], 204, 192, 179, 164, 149, 132, 119, 105, 91 [C$_6$H$_5$N], 77 [C$_6$H$_5$]. C$_{16}$H$_{25}$NO$_2$S$_2$ (327): calcd. C 58.68, H 7.69, N 4.28; found C 58.55, H 7.73, N 4.31.

General Procedure for the Synthesis of Tricyanovinyl Dyes: *N*,*N*-Dimethylaniline or the corresponding phenyl macrocycle (1.0 mmol) and tetracyanoethylene (192 mg, 1.5 mmol) were dissolved in dry DMF (12 mL) and heated at 60 °C for 90 min. The crude reaction mixture was concentrated in vacuo to dryness and purified by column chromatography as indicated below. Receptors L^1 and L^3 were previously synthesised by Beer et al. in 1990. ***CAUTION:*** *Synthesis of* L^2 *to* L^6 *occurs with elimination of HCN.*

Receptor L^2: Flash chromatography (dichloromethane/acetonitrile, 9:1 v/v) on silica gel gave a dark reddish solid. Yield: 65%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.58 (m, 8 H, O-CH_2-CH_2-O), 3.73 (t, J = 4.9 Hz, 4 H, O-CH_2-CH$_2$-N), 3.92 (t, J = 4.9 Hz, 4 H, O-CH$_2$-CH_2-N), 6.86 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$), 8.01 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 53.19 (CH$_2$-N), 69.08 (CH$_2$-O), 69.81 (CH$_2$-O), 71.24 (CH$_2$-O), 113.41 (C$_6$H$_4$), 113.76 (CN), 114.03 (CN), 114.48 (CN), 117.79 (C=C), 132.70 (C$_6$H$_4$), 137.30 (C=C), 154.91 (C$_6$H$_4$) ppm. MS (FAB$^+$): m/z (%) = 353 (100) [M$^+$ + 1]. HRMS: calcd. for C$_{19}$H$_{20}$N$_4$O$_3$ 353.1614; found 353.1608.

Receptor L^4: Flash chromatography (dichloromethane/acetonitrile, 8:2 v/v) on silica gel gave a dark reddish oil. Yield: 68%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.53–3.64 (m, 16 H, O-CH_2-CH_2-O), 3.73 (t, J = 4.7 Hz, 4 H, O-CH_2-CH$_2$-N), 3.80 (t, J = 4.7 Hz, 4 H, O-CH$_2$-CH_2-N), 6.80 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$), 8.00 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 51.80 (CH$_2$-N), 68.40 (CH$_2$-O), 70.61 (CH$_2$-O), 70.72 (CH$_2$-O), 70.76 (CH$_2$-O), 70.92 (CH$_2$-O), 112.74 (C$_6$H$_4$), 113.84 (CN), 114.08 (CN), 114.47 (CN), 117.54 (C=C), 132.92 (C$_6$H$_4$), 137.10 (C=C), 154.31 (C$_6$H$_4$) ppm. MS (FAB$^+$): m/z (%) = 440 (100) [M$^+$ + 1]. HRMS: calcd. for C$_{23}$H$_{28}$N$_4$O$_5$ 440.2060; found 440.2057.

Receptor L^5: Flash chromatography (dichloromethane) on silica gel gave a dark reddish solid. Yield: 58%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.75 (t, J = 4.8 Hz, 4 H, O-CH$_2$-CH_2-S), 2.89 (t, J = 7.9 Hz, 4 H, N-CH$_2$-CH_2-S), 3.62 (s, 4 H, O-CH_2-CH_2-O), 3.76–3.83 (m, 8 H, O-CH_2-CH$_2$-S and N-CH_2-CH$_2$-S), 6.70 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$), 8.04 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 29.65 (CH$_2$-S), 31.88 (CH$_2$-S), 52.40 (CH$_2$-N), 70.64 (CH$_2$-O), 74.30 (CH$_2$-O), 112.54 (C$_6$H$_4$), 113.58 (CN), 113.84 (CN), 114.36 (CN), 117.76 (C=C), 133.14 (C$_6$H$_4$), 137.51 (C=C), 153.03 (C$_6$H$_4$) ppm. MS (FAB$^+$): m/z (%) = 429 (100) [M$^+$ + 1]. HRMS: calcd. for C$_{21}$H$_{24}$N$_4$O$_2$S$_2$ 429.1419; found 429.1426.

Receptor L^6: Flash chromatography (dichloromethane) on silica gel gave a dark reddish solid. Yield: 61%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.72 (t, J = 5.7 Hz, 4 H, O-CH$_2$-CH_2-S), 2.81 (s, 4 H, N-CH$_2$-CH_2-S), 3.70 (t, J = 5.7 Hz, 4 H, O-CH_2-CH_2-O), 3.77 (t, J = 4.7 Hz, 4 H, O-CH_2-CH$_2$-S), 3.85 (t, J = 4.7 Hz, 4 H, N-CH_2-CH$_2$-S), 6.78 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$), 8.03 (d, J = 9.4 Hz, 2 H, C$_6$H$_4$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 31.93 (CH$_2$-S), 32.96 (CH$_2$-S), 51.73 (CH$_2$-N), 69.23 (CH$_2$-O), 72.16 (CH$_2$-O), 112.65 (C$_6$H$_4$), 113.50 (CN), 113.78 (CN), 114.35 (CN), 117.80 (C=C), 132.93 (C$_6$H$_4$), 137.52 (C=C), 154.26 (C$_6$H$_4$) ppm. MS (FAB$^+$): m/z (%) = 429 (100) [M$^+$ + 1]. HRMS: calcd. for C$_{21}$H$_{24}$N$_4$O$_2$S$_2$ 429.1419; found 429.1413.

Structure Determination of L^5: C$_{21}$H$_{24}$N$_4$O$_2$S$_2$, M = 428.56, triclinic space group $P\bar{1}$, a = 9.654(4), b = 13.643(6), c = 17.196(5) Å, α = 96.68(3)°, β = 102.98(3)°, γ = 97.72(3)°, Z = 4, V = 2161.7(14) Å^3, $D_{\text{calcd.}}$ = 1.317 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, T = 293(2) K, μ(Mo-K_α) = 0.271 mm^{-1}. Measurements were carried out with a Siemens P4 diffractometer with graphite-monochromated Mo-K_α radiation on a crystal of dimensions 0.17 × 0.17 × 0.15 mm^3. A total of 5963 reflections was collected of which 5558 were independent (R_{int} = 0.0468). Lorentz, polarisation and absorption (ψ-scan, max. and min. transmission 0.295 and 0.210) corrections were applied. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares analysis on F^2 (SHELXTL).[32] The refinement converged at R_1 = 0.090 [$F > 4\sigma(F)$] and wR_2 = 0.2494 (all data). Largest peak and hole in the final difference map +0.58 and –0.37 e Å^3.

CCDC-252155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) F. M. Raymo, S. Giordani, *Molecular Logic Gates, Encyclopedia of Nanoscience and Nanotechnology* **2004**, vol. 5, p. 677; b) A. P. de Silva, B. McCaughan, B. O. T. McKinney, M. Querol, *Dalton Trans.* **2003**, 1902.

[2] J. P. Desvergne, A. W. Czarnik *Chemosensors for Ion and Molecule Recognition*, NATO Asi Series, Series C, Kluwer Academic Publisher, London, **1997**.

[3] a) L. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* **1995**, 197; b) R. A. Bissell, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, K. R. A. S. Sandanayake, *Chem. Soc. Rev.* **1992**, 187.

[4] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515.

[5] a) R. Martínez-Máñez, F. Sancenón, *Chem. Rev.* **2003**, *103*, 4419; b) P. D. Beer, P. A. Gale, *Angew. Chem. Int. Ed.* **2001**, *40*, 486.

[6] a) B. Valeur, I. Leray, *Coord. Chem. Rev.* **2000**, *205*, 3; b) A. W. Czarnik, *Acc. Chem. Res.* **1994**, *27*, 302; c) K. Rurack, U. Resch-Genger, *Chem. Soc. Rev.* **2002**, *31*, 116.

[7] a) P. D. Beer, *Chem. Commun.* **1996**, 689; b) R. Martínez-Máñez, J. Soto, J. M. Lloris, T. Pardo, *Trends Inorg. Chem.* **1998**, *5*, 183; c) P. D. Beer, *Coord. Chem. Rev.* **2000**, *205*, 131.

[8] F. Sancenón, A. Benito, F. J. Hernández, J. M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, *Eur. J. Inorg. Chem.* **2002**, 866.

[9] a) J. Maynadie, B. Delavaux-Nicot, S. Fery-Forgues, D. Lavabre, R. Mathieu, *Inorg. Chem.* **2002**, *41*, 5002; b) B. Delavaux-Nicot, S. Fery-Forgues, *Eur. J. Inorg. Chem.* **1999**, 1821.

[10] a) P. D. Beer, A. R. Graydon, L. R. Sutton, *Polyhedron* **1996**, *15*, 2457; b) P. D. Beer, F. J. Szemes, *J. Chem. Soc., Chem. Commun.* **1995**, 2245; c) P. D. Beer, A. R. G. Graydon, A. O. M. Johnson, D. K. Smith, *Inorg. Chem.* **1997**, *36*, 2112.

[11] a) T. Saika, T. Iyoda, K. Honda, T. Shimidzu, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1181; b) T. Iyoda, T. Saika, K. Honda, T. Shimidzu, *Tetrahedron Lett.* **1989**, *30*, 5429; c) T. Shimidzu, T. Iyoda, K. Honda, *Pure Appl. Chem.* **1988**, *60*, 1025; d) F. P. Funeriu, J. M. Lehn, K. M. Fromm, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 2103; e) J. M. Lehn, *Chem. Eur. J.* **2000**, *6*, 2097.

[12] M. Boiocchi, L. Fabbrizzi, M. Licchelli, D. Sacchi, M. Vázquez, C. Zampa, *Chem. Commun.* **2003**, 1812.

[13] A. P. de Silva, H. Q. N. Gunaratne, M. Lynch, *J. Chem. Soc., Perkin Trans. 2* **1995**, 685.

[14] D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. Soto, *Tetrahedron Lett.* **2004**, *45*, 1257.

[15] a) R. G. Charles, *Org. Synth.* **1959**, *39*, 61; b) P. D. Beer, H. Sikanyika, *Polyhedron* **1990**, *9*, 1747.

[16] K. E. Krakowiak, J. S. Bradshaw, D. J. Zamecka-Krakowiak, *Chem. Rev.* **1989**, *89*, 929.

[17] J. P. Dix, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 857.

[18] a) S. Maeda, *Jpn. Kokai Tokkyo Koho*, **1998**, JP 10244752; b) L. Vanmaele, W. Janssens, *Eur. Pat. Appl.*, **1994**, EP 594238.

[19] C. J. Wood, P. Patel, T. D. James, *Org. Lett.* **2002**, *4*, 477.

[20] J. Aihara, K. Araya, Y. Matsunaga, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 615.

[21] J. Bourson, J. Pouget, B. Valeur, *J. Phys. Chem.* **1993**, *97*, 4552.

[22] a) A. Mason, A. Sheridan, J. O. Sutherland, A. Vincent, *J. Chem. Soc., Chem. Commun.* **1994**, 2627; b) N. J. van der Veen, R. J. M. Egberink, J. F. J. Engbersen, F. J. C. M. Van Veggel, D. N. Reinhoudt, *Chem. Commun.* **1999**, 681.

[23] a) F. Sancenón, R. Martínez-Máñez, J. Soto, *Angew. Chem. Int. Ed.* **2002**, *41*, 1416; b) A. B. Descalzo, R. Martínez-Máñez, R. Radeglia, K. Rurack, *J. Am. Chem. Soc.* **2003**, *125*, 3418.

[24] a) M. J. Choi, M. Y. Kim, S. K. Chong, *Chem. Commun.* **2001**, 1664; b) O. Brümmer, J. J. La Clair, K. D. Janda, *Org. Lett.* **1999**, *1*, 415; c) F. Sancenón, R. Martínez-Máñez, J. Soto, *Chem. Commun.* **2001**, 2262.

[25] a) *Principles of Fluorescence Spectroscopy* (Ed.: J. R. Lakowicz), Plenum Publishers Corporation, New York, **1999**; b) B. Valeur, *Top. Fluoresc. Spectrosc.* **1994**, *4*, 21.

[26] L. Fabbrizzi, M. Licchelli, P. Pallavicini, L. Parodi, A. Taglietti *Transition Metals in Supramolecular Chemistry*, John Wiley & Sons Ltd, New York, **1999**, p. 93.

[27] We have found (unpublished results) oxidation values for products **4a**, **4b**, **4c**, **7a** and **7b** of +0.8–0.9 V in acetonitrile. However, in the electrochemical studies carried out with L^1–L^6 there was no oxidation peak in this anodic region – the first anodic peak was found at +1.2–1.4 V and attributed to the oxidation of the anilinium moiety. The different nature of the ligands and the existence of CE (chemical electrochemical) mechanisms (the anilinium oxidation peak is not reversible) might account for this difference between the oxidation peaks of the anilinum crowns **4a**, **4b**, **4c**, **7a**, **7b** and those of L^1–L^6.

[28] J. M. Lloris, R. Martínez-Máñez, M. E. Padilla-Tosta, T. Pardo, J. Soto, P. D. Beer, J. Cadman, D. K. Smith, *J. Chem. Soc., Dalton Trans.* **1999**, *23*, 2359.

[29] A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, *10*, 574.

[30] a) G. J. Brown, A. P. de Silva, S. Pagliari, *Chem. Commun.* **2002**, 2461; b) F. Pina, M. J. Melo, M. Maestri, R. Ballardini, V. Balzani, *J. Am. Chem. Soc.* **1997**, *119*, 5556; c) F. M. Raymo, S. Giordani, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2003**, *68*, 4158; d) A. Saghatelian, N. H. Voelcker, K. M. Guckian, V. S.-Y. Lin, M. R. Ghadiri, *J. Am. Chem. Soc.* **2003**, *125*, 346; e) S. Ami, M. Hliwa, C. Joachim, *Chem. Phys. Lett.* **2003**, *367*, 662; f) K. Rurack, A. Kovalchuck, J. L. Bricks, J. L. Slominskii, *J. Am. Chem. Soc.* **2001**, *123*, 6205; g) S. Alves, F. Pina, M. T. Albelda, E. García-España, C. Soriano, S. V. Luis, *Eur. J. Inorg. Chem.* **2001**, 405; h) A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2002**, *8*, 4935.

[31] P. E. Stott, J. S. Bradshaw, W. W. Parish, *Heterocycles* **1981**, *15*, 179.

[32] SHELXTL, version 5.03, Siemens Analytical X-ray Instruments, Madison, WI, **1994**.

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