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Synthesis, Complexation and Spectrofluorometric Studies of a New NS_3 Anthracene-Containing Macrocyclic Ligand

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A new fluorescent device for detecting protons and metal ions, 11-(9-anthracenylmethyl)-1,4,7-trithia-11-azacyclotetradecane (**L**), has been synthesised. In addition, the photophysical properties of both the free and protonated species have been examined by absorption and fluorescence titrations of dichloromethane solutions of **L** with methanesulfonic acid. The coordinating properties of **L** toward Pd^{II}, Zn^{II}, Ni^{II} and Co^{II} have been studied both in solution and in the solid state. Different behaviours have been observed in the absorption and fluorescence titrations of **L** with the above-mentioned transition-metal ions. To evaluate whether these differences were due to the existence of equilibria between protonated and complexed species, such titrations have been repeated in the presence of an equivalent amount of acid. The structure of the $[Pd(\mathbf{L})](BF_4)_2$ complex has been solved by X-ray crystallography.

Introduction

The design of new fluorescence chemosensors capable of signalling the presence of metal ions is a subject of particular interest for chemists.[1] These systems usually consist of a fluorescent moiety (signalling unit), covalently connected to a binding site (receptor unit).[2] The more specific the interaction between the receptor unit and the analyte, the greater the selectivity of the chemosensor. Many fluorescence chemosensors have macrocycles as receptor units, as the coordinating properties of macrocycles have been shown to be more effective than those of the analogous acyclic ligands. Most of these chemosensors are made up of polyoxa,[3] polyaza[4] and oxa-azamacrocycles,[5] which have been used for the detection of alkali and *hard* metal ions. However, less attention has been paid to the study of thiamacrocycle-containing chemosensors, which could be useful for detecting *soft* transition-metal ions.[6] On the other hand, the stronger the effects of the ion on the properties of the fluorophore, the greater the sensitivity of the chemosensor. Aliphatic amines closely bonded to anthracene moieties are known to be involved in electron transfer quenching, which facilitates the signalling of the presence of metal ions in amine-containing systems.[7] Taking these considerations into account, we here report the synthesis of a new fluorescence device 11-(9-anthracenylmethyl)-1,4,7-trithia-11-azacyclotetradecane (**L**), which consists of an azathiamacrocycle connected by its aliphatic amine to an anthracene moiety. Protonation and coordination properties towards Pd^{II}, Zn^{II}, Ni^{II} and Co^{II} have also been studied, with the crystallographic data of the $[Pd(\mathbf{L})](BF_4)_2$ complex analysed as well.

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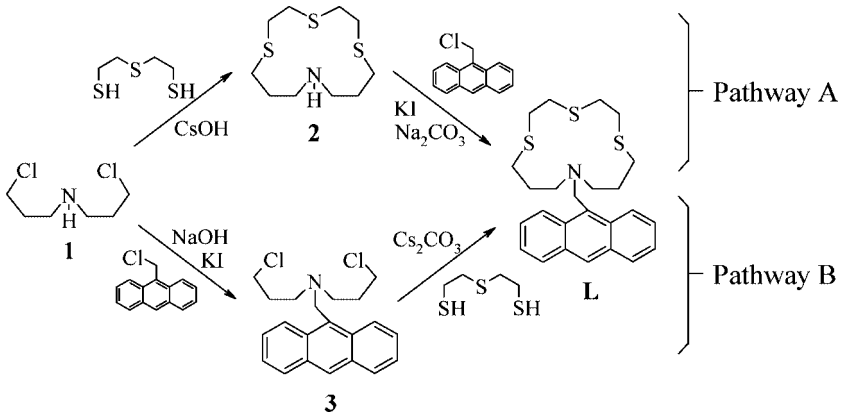
Results and Discussion

Synthesis of Ligands

Scheme 1 shows the two methods used to synthesise the anthracene-containing macrocycle **L**. The first method (pathway A in Scheme 1) is based on using macrocycle **2** as a precursor of **L**. Compound **2** was obtained by cyclisation of 2,2′-thiobis(ethanethiol) with the dichloride precursor **1**, following a procedure similar to that described by Buter and Kellogg for the synthesis of sulfur-containing macrocycles. This method is based on the simultaneous reaction between aliphatic α,ω-dithiols and α,ω-dihalides, using DMF as a solvent and Cs_2CO_3 as a base.[8] In our case, CsOH was used instead of Cs_2CO_3, as the carbonate ions react with **1** to produce 3-(3-chloropropyl)-[1,3]oxazin-2-one.[9] This modification allowed us to obtain **2** in 62% of the yield. The preparation of **2** was previously reported in the literature using other methods.[10] Those methods avoid the reaction between the carbonate ions and the dihalide **1** by using protection–deprotection strategies, which increase the number of synthetic steps and decrease the final yields. The last step in synthetic procedure A is the functionalisation of **2** with an anthracene derivative. This was performed by a reaction of **2** with 9-(chloromethyl)anthracene in the presence of KI, as we have recently shown that iodide



Scheme 1.

ions can be used as catalysts for the nucleophilic substitution reactions of 9-(chloromethyl)anthracene and secondary aliphatic amines.[11] The overall yield of pathway A was 45%.

The second method for the synthesis of **L** (pathway B in Scheme 1) is based on the functionalisation of the dichloride precursor **1**, prior its use in the cyclisation reaction with 2,2′-thiobis(ethanethiol). Although the cyclisation conditions of pathway B are very close to those optimised for the synthesis of sulfur-containing macrocycles,[8] as Cs_2CO_3 could be used as a base,[12] the overall yield of this second pathway (38%) was not significantly different from that found in pathway A.

Complexation of L

The reaction of equimolar amounts of **L** and $Pd(BF_4)_2 \cdot 4CH_3CN$ in acetonitrile yielded a light brown solution. The addition of diethyl ether to this solution led to the precipitation of a crystalline product, whose elemental analysis is consistent with the formula $Pd(\mathbf{L})(H_2O)_2(BF_4)_2$. Its IR spectrum confirmed the presence of **L**, tetrafluoroborate ions and water molecules, as well as the absence of acetonitrile, as no signal was observed between 2250 and 2350 cm^{-1}. This compound behaves as a 2:1 electrolyte in acetonitrile solution, which indicates that the tetrafluoroborate anions are not coordinated with the metal ions. The ^1H NMR spectrum of this complex in acetonitrile solution shows a complex pattern in the aliphatic region, as most of the signals become multiplets because of the nonequivalence of the hydrogen atoms. However, its $^{13}C\{^1H\}$NMR spectrum shows the same number of signals as that of the free ligand, which indicates that although the two protons bonded to each carbon atom are magnetically nonequivalent, each pair of carbon atoms is chemically equivalent. On the other hand, those carbons directly bonded to a donor atom of **L** show downfield displacement compared with those of the free ligand, which suggests that the Pd^{II} ion is coordinated to all four donor atoms of **L**. This fact, together with the ESI-MS and electronic spectra of this complex, points to the presence of the $[Pd(\mathbf{L})]^{2+}$ unit, which was confirmed by X-ray analysis of the pale brown crystals obtained by slow diffusion of hexane into a dichloromethane solution of $[Pd(\mathbf{L})](BF_4)_2 \cdot 2H_2O$. It is important to note that although the elemental analysis, as well as the IR spectrum of this complex, indicates the presence of water molecules, these are not present in the crystal lattice of the complex. Therefore, they were probably lost during the crystallisation process.

The crystal structure of this complex consists of discrete $[Pd(\mathbf{L})]^{2+}$ cations and tetrafluoroborate anions. A displacement ellipsoid representation of the cation complex and a list of selected bond lengths and angles are given in Figure 1. The metal coordination geometry is square-planar with the N2, S6, S9, S12 and Pd atoms on a plane. The largest deviation from this plane is 0.0941 Å for the S9 atom. The Pd–N distance [2.133(2) Å] is slightly larger than that of the analogous Pd^{II} complex without the pendant arm.[10b] The Pd–S bond lengths [2.2718(9), 2.306(3) and

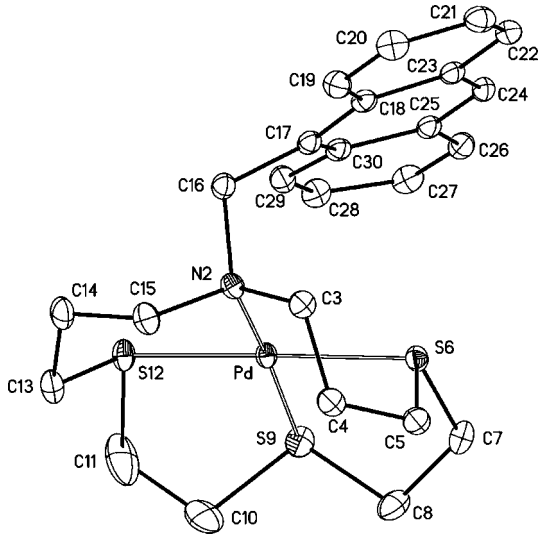


Figure 1. Displacement ellipsoid representation of the $[Pd(\mathbf{L})]^{2+}$ cation with the atom-numbering scheme adopted. Tetrafluoroborate counterions and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–N2 2.133(2), Pd–S9 2.2718(9), Pd–S12 2.306(3), Pd–S6 2.3221(9), N2–Pd–S9 174.34(6), N2–Pd–S12 94.45(9), S9–Pd–S12 85.56(7), N2–Pd–S6 93.10(6), S9–Pd–S6 87.21(3), S12–Pd–S6 171.92(8). Ellipsoids are shown at the 30% probability level.

2.3221(9) Å] are similar to those found for other Pd^{II} complexes of thioether-containing macrocycles.[10b,13] In this structure, **L** adopts a conformation in which all carbon atoms of the macrocyclic unit lie below the plane defined by the four heteroatoms, whereas the whole anthracene moiety lies over this plane. As expected, the anthracene unit is essentially planar. In fact, the largest deviation from the least-squares plane calculated using all 14 aromatic atoms is 0.126 Å for the C29 atom. A ring of the anthracene moiety is located over the Pd^{II} ion. The distance between the centroid of such a ring [Cg(1): C25–C26–C27–C28–C29–C30] and the metal ion is 3.635 Å, whereas the angle between the normal of the ring and the Cg(1)···Pd vector is 41.26°. These considerations may suggest a weak intramolecular cation···π interaction.[14] On the other hand, nonclassical C–H···F hydrogen bonds lead to the formation of a 2D supramolecular network along the crystallographic *ab* plane (Figure 2).

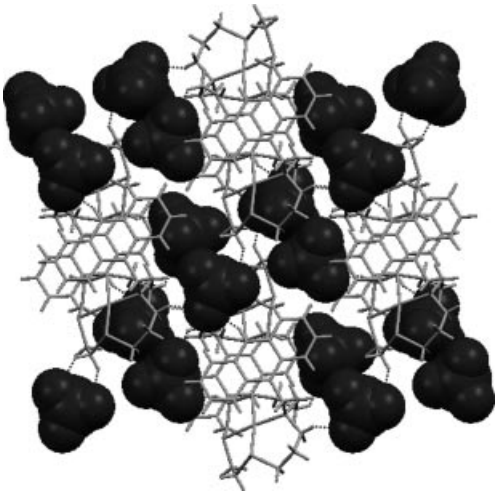


Figure 2. A fragment of an infinite 2D network through C–H···F hydrogen bonds of $[Pd(\mathbf{L})](BF_4)_2$ showing the close packing in the plane *ab*. Tetrafluoroborate counterions in space-filling mode.

All attempts to obtain solid complexes with Ni^{II}, Co^{II} and Zn^{II} were unsuccessful, as no homogeneous products were isolated. This fact could be attributed to the protonation of **L**, as was also observed in the titrations of other tertiary amine-containing ligands with these metal ions.[11]

Spectrophotometric and Spectrofluorometric Studies

Ligand Protonation

The absorption spectrum of a dichloromethane solution of **L** shows the characteristic band of the anthracene derivatives above 330 nm. The absorption band of **L** has a vibrational fine structure with maxima at 333, 350, 368 and 388 nm. The effect of the protonation on the absorption spectrum of this ligand was determined by titration with methanesulfonic acid (Figure 3, A). This absorption titration revealed seven isosbestic points at 335, 342, 352, 361, 371, 380 and 391 nm, which suggests the presence of two species in equilibrium. The protonation induced a red shift of the absorption maxima, as well as a decrease in the absorption coefficient of this band. As can be seen in the inset of Figure 3 (A), an equivalent amount of acid is required to complete the protonation of **L**.

The fluorescence emission and excitation spectra of **L** show the characteristic bands of the anthracene systems (Figure 3, B). An "off–on" behaviour is observed when a dichloromethane solution of **L** is titrated with acid, as the nonprotonated ligand is slightly emissive in dichloromethane, whereas the protonated form is at least 30 times more

Table 1. Quantum yields in dichloromethane at 298 K.

	Φ
L	0.010
L + H^+	0.341
L + Pd^{2+}	0.005
L + Zn^{2+}	0.254
L + Ni^{2+}	0.203
L + Co^{2+}	0.208

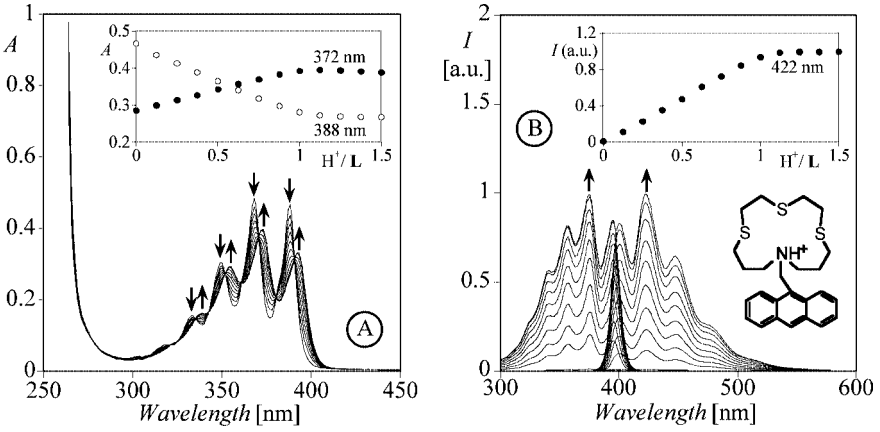


Figure 3. (A) Absorption spectra of a dichloromethane solution of **L** as a function of added CH_3SO_3H. The inset shows the absorbances at 372 and 388 nm. (B) Excitation and emission spectra of a dichloromethane solution of **L** as a function of added CH_3SO_3H. The inset shows the normalised fluorescence intensity at 422 nm ($[\mathbf{L}] = 5.14 \times 10^{-5}$ M, T = 298 K, λ_{exc} = 368 nm; λ_{em} = 423 nm).

emissive than the free ligand. This increase in the fluorescence intensity is also reflected by comparing the quantum yield of the nonprotonated and protonated ligands (see Table 1), and is due to the fact that protonation prevents photoinduced electron transfer (PET) from the lone pair of electrons of the nitrogen atom to the anthracene moiety.

Metal Ion Titrations

To explore the utility of **L** as a fluorescence device, titrations with several transition-metal ions were performed. Two different behaviours were observed as a function of the used metal ion.

Pd^{II} Titrations

To identify the absorption bands that exclusively resulted from the interactions between the Pd^{II} cations and the macrocyclic moiety of **L**, we first performed a titration of the nonfunctionalised macrocycle **2** with this metal ion. The addition of $Pd(BF_4)_2 \cdot 4CH_3CN$ to a dichloromethane solution of **2** led to the formation of two absorption bands at 258 and 330 nm, assigned to MLCT and *d*–*d* bands respectively.[15] The inset of Figure 4 shows that the titration was completed after the addition of 1 equiv. of metal ion, which is in agreement with the formation of mononuclear species.

Figure 5 (A) shows the absorption spectra of the titration of **L** with $Pd(BF_4)_2$. The addition of the metal ion causes a

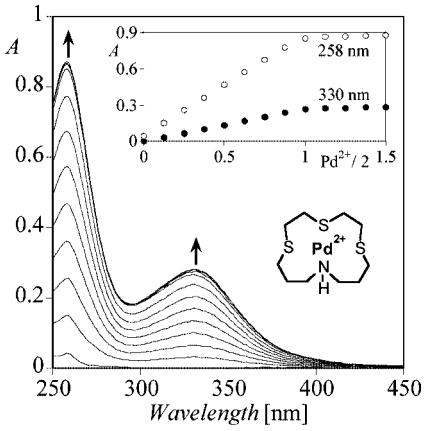


Figure 4. Absorption spectra of a dichloromethane solution of **2** as a function of added $Pd(BF_4)_2$. The inset shows the absorbances at 258 and 330 nm ([**2**] = 5.50×10^{-5} M, T = 298 K).

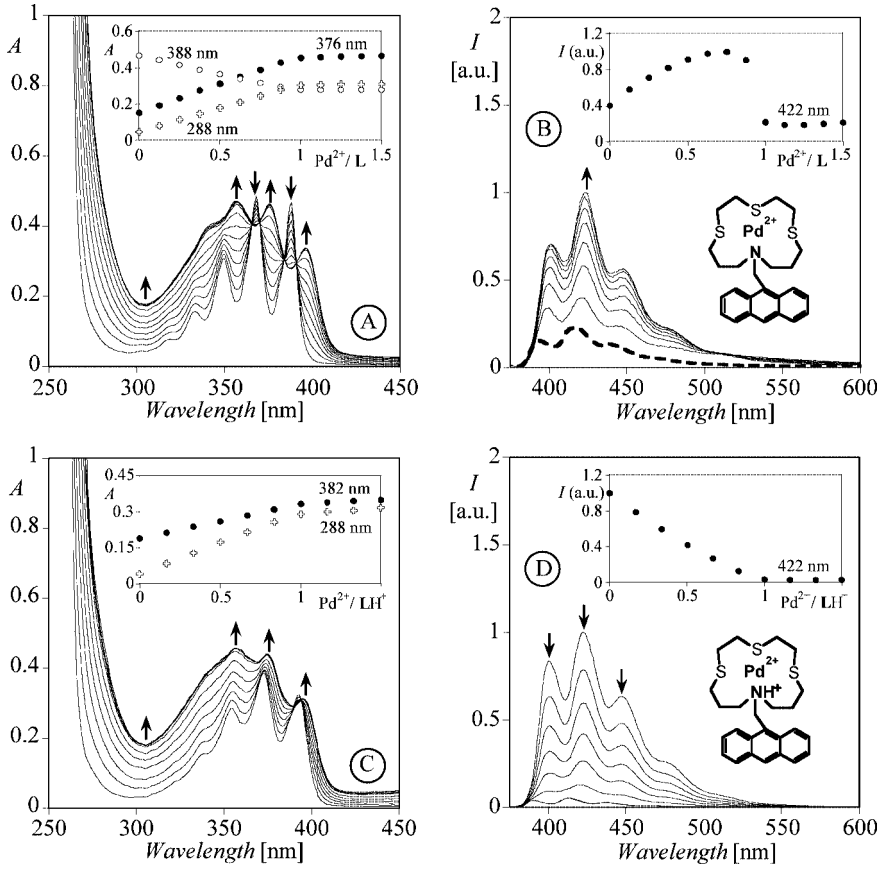


Figure 5. (A) Absorption spectra of **L** as a function of increasing amounts of $Pd(BF_4)_2$. The inset shows the absorbances at 288, 376 and 388 nm. (B) Emission spectra of **L** as a function of added $Pd(BF_4)_2$. Those spectra between the maximum and the end of the titration have been omitted for clarity. The last spectrum of each titration is shown as a dotted line. The inset shows the normalised fluorescence intensity at 422 nm. (C) Absorption spectra of $\mathbf{LH}^+$ as a function of increasing amounts of $Pd(BF_4)_2$. The inset shows the absorbances at 288 and 382 nm. (D) Emission spectra of $\mathbf{LH}^+$ as a function of added $Pd(BF_4)_2$. The inset shows the normalised fluorescence intensity at 422 nm (dichloromethane solution, [**L**] = [$\mathbf{LH}^+$] = 5.14×10^{-5} M, T = 298 K, λ_{exc} = 368 nm).

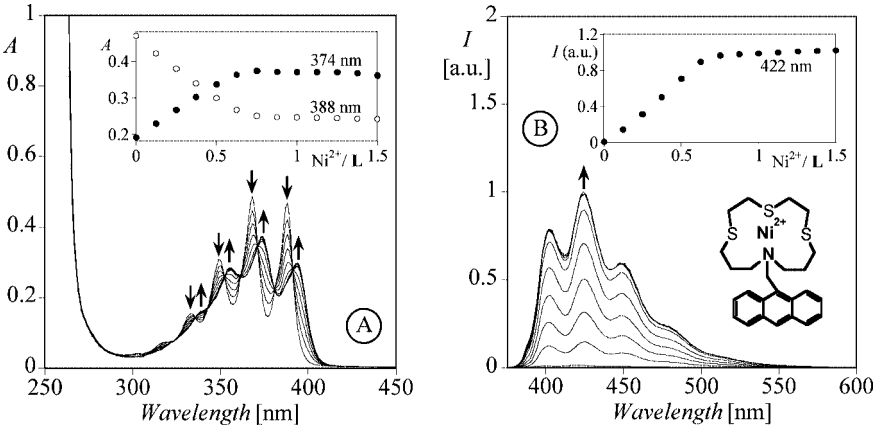


Figure 6. (A) Absorption spectra of a dichloromethane solution of **L** as a function of increasing amounts of $Ni(BF_4)_2$. The inset shows the absorbances at 374 and 388 nm. (B) Emission spectra of a dichloromethane solution of **L** as a function of added $Ni(BF_4)_2$. The inset shows the normalised fluorescence intensity at 422 nm. ([**L**] = 5.14×10^{-5} M, T = 298 K, λ_{exc} = 368 nm).

red shift of the anthracene band, as well as an incremental increase in the molar absorption coefficient in the region around 300 nm. This increment is attributed to the formation of the absorption bands analogous to those observed in the titration of **2**. As can be seen in the inset of Figure 5 (A), a plateau is reached after the addition of an equivalent amount of metal ion, which suggests that each macrocyclic unit is coordinated to one metal ion. Figure 5 (B) shows the fluorescence titration of **L** with $Pd(BF_4)_2$. Although initial additions of the metal ion increase the fluorescence of the ligand, supplementary additions cause a strong quenching of the fluorescence, as well as a blue shift of about 6 nm. The *chelation enhancement of the quenching* (CHEQ) effect can be explained by assuming that Pd^{II}, as well as other transition-metal ions with partially filled d orbitals, is known to induce fluorescence quenching through photoinduced electron transfer or energy transfer mechanisms.[16] The initial increase of the fluorescence could be explained by the protonation of the amine, which prevents PET from its nitrogen atom to the anthracene moiety. This protonation is probably due to the presence of water in the metal ion solutions, which acts as an acid.

To verify this hypothesis, both absorption and fluorescence titrations of **L** were repeated in the presence of 1 equiv. of methanesulfonic acid (see parts C and D in Figure 5). The absorption titration of $\mathbf{LH}^+$ with $Pd(BF_4)_2$ followed the same pattern as that observed for **L**. On the other hand, the fluorescence titration of $\mathbf{LH}^+$ was significantly different from that of **L**, as the intensity of fluorescence decreased after each addition of metal ion. These results are in agreement with the simultaneous presence of protonated and complexed species in the early stages of the titration of **L** with $Pd(BF_4)_2$, and with the presence of only complexed species in the last stages of this titration. The insets of Figure 5 (parts C and D) show that 1 equiv. of Pd^{II} is required to complete the complexation of $\mathbf{LH}^+$, which indicates that the Pd^{II} ions can efficiently replace the protons of the $\mathbf{LH}^+$ moieties.

Zn^{II}, Ni^{II} and Co^{II} Titrations

No significant differences were found in the absorption or in the fluorescence titrations of **L** when this ligand was titrated with $Zn(CF_3SO_3)_2$, $Ni(BF_4)_2$ or $Co(BF_4)_2$. As a representative example, Figure 6 shows both the absorption and fluorescence titrations of **L** with Ni^{II}. The addition of any of these salts causes a red shift in the anthracene absorption maximum of **L**, as well as a decrease in its molar absorption coefficient. These changes occur until the addition of 0.6 equiv. of Zn^{II} or Ni^{II} or 0.7 equiv. of Co^{II}.

As in the case of the fluorescence titration of **L** with Pd^{II}, initial additions of Zn^{II}, Ni^{II} or Co^{II} increase the fluorescence of **L**. However, further additions cause neither the shift nor the quenching of the emission band. These observations suggest that the addition of Zn^{II}, Ni^{II} or Co^{II} also leads to the initial protonation of **L**, after which no interaction between **L** and these metal ions can occur. This hypothesis was confirmed when the titrations were repeated in the presence of an equivalent amount of acid, as the addition of these ions to dichloromethane solutions of $\mathbf{LH}^+$ did not cause significant changes either in the absorption or in the emission spectrum of the ligand, which indicates that these metal ions cannot efficiently replace the protons in the protonated macrocycles.

The different behaviour observed between the titrations with Pd^{II} and those with Zn^{II}, Ni^{II} or Co^{II} is probably due to the different affinity between the metal ion and the donor atoms of **L**. This is in agreement with the fact that the *soft* nature of the NS_3 set of **L** leads to the formation of complexes with only the *softest* of these metal ions, that of Pd^{II}.

Conclusions

The azathiamacrocycle **2** can be synthesised by reacting *N*,*N*-bis(3-chloropropyl)amine with 2,2′-thiobis(ethanethiol) in the presence of CsOH. This new method allowed

us to obtain **2** without using any amine-protecting group, which decreases the number of synthetic steps and improves the final yield. The anthracene-containing macrocycle **L** can be obtained either by functionalisation of **2** with 9-(chloromethyl)anthracene or by cyclisation of *N*,*N*-bis(3-chloropropyl)-9-anthracenemethanamine with 2,2′-thiobis-(ethanethiol). Both methods allow the synthesis of **L** in moderately high yields.

As observed in the spectra of the fluorescence titration of **L** with methanesulfonic acid, the protonation of this ligand greatly increase its fluorescence. This protonation also occurs when **L** is titrated with Pd^{II}, Zn^{II}, Ni^{II} or Co^{II} solutions, as the water molecules present in such solutions are acidic enough to produce the protonation of the ligand, which reflects the basic nature of its tertiary amine group.

Only the Pd^{II} ions can efficiently remove the protons from the protonated $\mathbf{LH}^+$ molecules to yield complexed species, which indicates that the interactions between **L** and the Pd^{II} ions are stronger than those between **L** and protons, whereas the interactions between **L** and the Zn^{II}, Ni^{II} or Co^{II} ions are weaker than those between **L** and the proton ions. These differences explain why only characterisable species with Pd^{II} could be isolated. The high affinity of **L** towards Pd^{II} could be potentially useful in the development of new molecular devices.

Experimental Section

General Remarks: Elemental analyses were performed with a Carlo–Erba EA-1108 instrument by the Chemical Analysis Service at the Universitat Autònoma de Barcelona. Mass spectra were recorded with a HP298S GC–MS system. NMR spectra were recorded with a Bruker 250 MHz AC instrument. Conductivity measurements were carried out with a Cyberscan 500 conductimeter. IR spectra were recorded with a Perkin–Elmer FT-1710 instrument. Organic reagents and transition-metal salts were purchased from Aldrich and used as received. All syntheses were carried out using standard Schlenk techniques. *N*,*N*-Bis(3-chloropropyl)amine (**1**) was prepared from 3-amino-1-propanol and 3-chloro-1-propanol according to the published method but using chloroform instead of benzene as solvent.[17] *N*,*N*-Bis(3-chloropropyl)-9-anthracenemethanamine (**3**) was prepared from **1** and 9-(chloromethyl)anthracene as previously reported in the literature.[11]

X-ray Crystal Structure Determinations: A single crystal of $[Pd(\mathbf{L})](BF_4)_2$ was mounted on a glass fibre and used for data collection. A summary of the crystallographic data is reported in Table 2. Crystallographic measurements were performed with a Bruker Smart CCD apparatus at 293 K, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) in RIAIDT (University of Santiago de Compostela, Spain). Crystallographic data were corrected for Lorentz and polarisation effects. The frames were integrated with the Bruker SAINT Software package,[18] and the data were corrected for absorption using the SADABS program.[19] The structure was determined by direct methods using the SIR-97 program.[20] All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the SHELXL97 program.[21] Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Tetrafluoroborate anions and the S12 sulfur atom of the macrocyclic ligand were modelled with disorder. Special computations for the crystal structure discussions were carried out with PLATON.[22]

Table 2. Crystallographic data for $[Pd(\mathbf{L})](BF_4)_2$.

Empirical formula	$C_{25}H_{31}B_2F_8NPdS_3$
Formula mass	721.71
Crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	17.614(5)
b [Å]	14.495(5)
c [Å]	21.754(5)
β [°]	97.310(5)
V [Å^3]	5509(3)
Z, ρ_{calcd} [g/cm^3]	8, 1.740
F(000)	2912
Crystal size [mm]	0.34 × 0.31 × 0.14
Absorption coefficient [mm^{-1}]	0.974
θ range [°]	1.83–28.32
Max./min. transmission	0.873–0.748
Reflections collected	25542
Independent reflections (R_{int})	6677 (0.0331)
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0330, wR_2 = 0.0768
Final *R* indices (all data)	R_1 = 0.0468, wR_2 = 0.0840

CCDC-266369 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

Spectrophotometric and Spectrofluorometric Measurements: Absorption spectra were recorded with a Shimadzu UV-2501PC spectrophotometer and fluorescence emissions on a Horiba–Jobin–Yvon SPEX Fluorolog 3.22 spectrofluorimeter at the Universidade Nova de Lisboa. The linearity of the fluorescence emission versus concentration was verified for the concentration range used (10^{-4} to 10^{-6} M). A correction for the absorbed light was performed when necessary. The absorption and fluorescence titrations were performed by adding microlitre amounts of acetonitrile, or ethanol solutions of the corresponding titrating agent, to dichloromethane solutions of the ligand. [**2**] = 5.50×10^{-5} M. [**L**] = 5.14×10^{-5} M, λ_{exc} = 368 nm; λ_{em} = 423 nm. Luminescence quantum yields were measured using a solution of sublimated anthracene in cyclohexane as a standard [Φ_F = 0.36].[23]

1,4,7-Trithia-11-azacyclotetradecane (2): A solution of **1** (3.32 g, 15.54 mmol) in deoxygenated DMF (50 mL) and a solution of 2,2′-thiobis(ethanethiol) (3.02 g, 15.54 mmol) in deoxygenated DMF (50 mL) were added simultaneously (at 2 mL/h using a perfusor) to a round-bottomed flask equipped with a magnetic stirrer and charged with CsOH (6.45 g, 39.06 mmol) and deoxygenated DMF (700 mL). Subsequently, the solvent was removed and the residue was dissolved in $CHCl_3$ (200 mL). The solution was filtered off and the solvent was removed to obtain a pale brown oil. This residue was purified by column chromatography on silica gel using a mixture of $CHCl_3$/CH_3OH (10:1 v/v ratio) as eluent. Yield 3.07 g, 62%. $C_{10}H_{21}NS_3$ (251.48): calcd. C 47.76, H 8.42, N 5.57, S 38.25; found C 47.55, H 8.30, N 5.55, S 37.80. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.18 (s, 1 H, -CH_2-N*H*-CH_2-), 1.72 (m, $^3J_{H,H}$ = 6.23 Hz, 4 H, -S-CH_2-C*H*$_2$-CH_2-NH-), 2.63–2.74 (m, 8 H, -S-C*H*$_2$-CH_2-C*H*$_2$-NH-), 2.74 (m, 8 H, -S-C*H*$_2$-C*H*$_2$-S-) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 28.9 (-S-CH_2-*C*H$_2$-CH_2-NH-), 30.4 (-S-*C*H$_2$-CH_2-CH_2-NH-), 31.9 (-S-CH_2-*C*H$_2$-S-*C*H$_2$-CH_2-S-), 32.5 (-S-*C*H$_2$-CH_2-S-CH_2-*C*H$_2$-S-), 46.9 (-S-CH_2-CH_2-*C*H$_2$-NH-) ppm. UV/Vis (CH_2Cl_2): λ = 258 nm (ε = 769 M^{-1}/cm). ESI-MS: *m*/*z* (%) = 252.4 [**2** + H]$^+$. IR (KBr pellet): $\tilde{\nu}$ = 3316, 2925, 2819, 1675, 1424, 1265, 1191, 1122, 693 cm^{-1}.

11-(9-Anthracenylmethyl)-1,4,7-trithia-11-azacyclotetradecane (L). Preparation from 2: A mixture of anhydrous Na_2CO_3 (0.31 g, 2.94 mmol), KI (0.20 g, 1.20 mmol), 9-(chloromethyl)anthracene (0.49 g, 2.15 mmol) and **2** (0.65 g, 1.47 mmol) in CH_3CN (100 mL) was refluxed for 4 h. The mixture was filtered off and the solvent was removed with a rotary evaporator. The resultant yellow residue was purified by column chromatography on silica gel using $CHCl_3$ as eluent. Yield 1.14 g, 73%.

Preparation from 3: A solution of 2,2′-thiobis(ethanethiol) (0.77 g, 4.98 mmol) in deoxygenated DMF (50 mL) and a solution of **3** (1.79 g, 4.98 mmol) in deoxygenated DMF (50 mL) were added simultaneously at 2 mL/h using a perfusor to a round-bottomed flask equipped with magnetic stirrer and charged with a solution of Cs_2CO_3 (1.78 g, 5.50 mmol) in deoxygenated DMF (700 mL). The solvent was removed and the residue was dissolved in $CHCl_3$. This solution was filtered off and the solvent was removed to yield a yellow oil that was purified by column chromatography on silica gel using $CHCl_3$ as eluent to afford 0.90 g (40% yield) of yellow solid. $C_{25}H_{31}NS_3$ (441.72): calcd. C 67.98, H 7.07, N 3.17, S 21.78; found C 67.55, H 7.10, N 3.10, S 21.40. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.73 (m, 4 H, -S-CH_2-CH_2-CH_2-N-), 2.26 (t, $^3J_{H,H}$ = 7.93 Hz, 4 H, -S-CH_2-CH_2-CH_2-N-), 2.59 (t, $^3J_{H,H}$ = 6.19 Hz, 4 H, -S-CH_2-CH_2-CH_2-N-), 2.69 (s, 8 H, -S-CH_2-CH_2-S-), 4.51 (s, 2 H, An-CH_2-N-), 7.50 (m, 4 H, *An*-CH_2-N-), 8.00 (m, 2 H, *An*-CH_2-N-), 8.44 (m, 3 H, *An*-CH_2-N-) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 28.5 (-S-CH_2-CH_2-CH_2-N-), 29.8 (-S-CH_2-CH_2-CH_2-N-), 31.1 (-S-CH_2-CH_2-S-CH_2-CH_2-S-), 31.8 (-S-CH_2-CH_2-S-CH_2-CH_2-S-), 52.0 (An-CH_2-N-), 53.7 (-S-CH_2-CH_2-CH_2-NH-), 124.8, 125.6, 127.6, 129.1, 130.1, 131.2, 131.4 (*An*-CH_2-N-) ppm. UV/Vis (CH_2Cl_2): λ = 333 (ε = 3024), 350 (5902), 368 (9418), 388 nm (9096 M^{-1}/cm). ESI-MS: *m*/*z* (%) = 442.7 [**L** + H]$^+$. IR (KBr pellet): $\tilde{\nu}$ = 3048, 2949, 2922, 2810, 1677, 1622, 1444, 1436, 1426, 1336, 1279, 1190, 1023, 893, 735, 541 cm^{-1}.

[Pd(L)](BF$_4$)$_2$·2H$_2$O: A dichloromethane solution of **L** (90 mg, 0.20 mmol, 4 mL) was added dropwise to an acetonitrile solution of $Pd(BF_4)_2$·4CH_3CN (91 mg, 0.20 mmol, 4 mL). The resulting solution was stirred at room temperature for 2 h, and the solvent was partially removed to about 3 mL. Diethyl ether was slowly infused into the solution producing a powdery precipitate, which was filtered off and washed with diethyl ether. This complex was recrystallised by diffusion of diethyl ether into acetonitrile solutions. The yield was 130 mg (88%). Crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a dichloromethane solution. $C_{25}H_{31}B_2F_8NPdS_3$·2H_2O (757.72): calcd. C 39.63, H 4.66, N 1.85, S 12.69; found C 39.40, H 4.85, N 1.80, S 12.25. Conductivity (CH_3CN, 1×10^{-3} M): 231 μS/cm. ^{1}H NMR (250 MHz, CD_3NO_2, 25 °C): δ = 2.29 (m, 2 H, -S-CH_2-CH_2-CH_2-N-), 2.47 (m, 2 H, -S-CH_2-CH_2-CH_2-N-), 2.70 (m, 2 H, -S-CH_2-CH_2-CH_2-N-), 3.03 (m, 2 H, -S-CH_2-CH_2-CH_2-N-), 3.11 (m, 4 H, -S-CH_2-CH_2-CH_2-N-), 3.32 (m, 4 H, -S-CH_2-CH_2-S-CH_2-CH_2-S-), 3.35 (m, 2 H, -S-CH_2-CH_2-S-CH_2-CH_2-S-), 3.84 (m, 2 H, -S-CH_2-CH_2-S-CH_2-CH_2-S-), 5.02 (s, 2 H, An-CH_2-N-), 7.46 (m, 2 H, *An*-CH_2-N-), 7.63 (m, 2 H, *An*-CH_2-N-), 8.04 (d, $^3J_{H,H}$ = 8.40 Hz, 2 H, *An*-CH_2-N-), 8.56 (d, $^3J_{H,H}$ = 8.95 Hz, 2 H, *An*-CH_2-N-), 8.61 (s, 1 H, *An*-CH_2-N-) ppm. ^{13}C{^{1}H} NMR (CD_3NO_2, 25 °C): δ = 24.6 (-S-CH_2-CH_2-CH_2-N-), 32.6 (-S-CH_2-CH_2-CH_2-N-), 39.8 (-S-CH_2-CH_2-S-CH_2-CH_2-S-), 41.1 (-S-CH_2-CH_2-S-CH_2-CH_2-S-), 57.5 (An-CH_2-N-), 61.0 (-S-CH_2-CH_2-CH_2-NH-), 123.3, 123.4, 125.9, 128.4, 130.1, 131.1, 131.7, 132.5 (*An*-CH_2-N-) ppm. UV/Vis (CH_2Cl_2): λ = 357 (ε = 9154), 376 (9019), 397 nm (6542 M^{-1}/cm). ESI-MS: *m*/*z* (%) = 634.9 [Pd(BF$_4$)(**L**)]$^+$. IR (KBr pellet): $\tilde{\nu}$ = 3424, 2923, 1623, 1446, 1295, 1084, 1063, 1038, 739, 534, 521 cm^{-1}.

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