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# New Fluorescence PET Systems Based on $N_2S_2$ Pyridine-Anthracene-Containing Macrocyclic Ligands. Spectrophotometric, Spectrofluorimetric, and Metal Ion Binding Studies

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Three new fluorescent devices for protons and metal ions have been synthesized and characterized, and their photophysical properties have been explored; these are the macrocycles 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L1) and 7-(10-methyl-9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L2) and the bis macrocycle 7,7′-[9,10-anthracenediylbis(methylene)]-bis-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L3). All these systems have a pyridil-thioether-containing macrocycles as a binding site and an anthracene moiety as a signaling agent. The coordination properties of these ligands toward Cu(II), Co(II), Ni(II), Zn(II), and Pd(II) have been studied in solution and in the solid state. The addition of these metal ions to dichloromethane solutions of L1, L2, and L3 produce strong changes in the absorption and emission spectra of these ligands. The stoichiometry of the species, formed at 298 K, have been determined from absorption and fluorescence titrations. The Co(II) and Cu(II) complexes of L1 have been studied by EPR spectroscopy. This last complex and its free ligand have also been characterized by X-ray crystallography.

## Introduction

Selective detection of ions and molecules by using fluorescence techniques is an object of special attention for the chemical community. The design of new supramolecular fluorescence chemosensors is important for the development of more efficient complexing agents which might be used as selective metal ionophores in several areas of industrial, environmental, biological, or analytical interest.[1] These functionalized systems usually have a receptor unit (host site), covalently connected to a signaling unit (fluorophore), through a linking group (spacer). In 1994, A. W. Czarnik[2] gave these systems the general name of *conjugate chemosensors*. A great number of the conjugate chemosensors described are made up of polyoxa,[3] polyaza,[4]

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and oxa-aza macrocycles[5] as receptor units, but few examples of thia macrocycles can be found in the literature.[6] Of all these systems, those including two different protonable groups (i.e., pyridine and aliphatic amines) are of special interest. It is well-known that pyridine-containing conjugate chemosensors are able to quench the fluorescence of anthracene units only when they are complexed or protonated (pyridinium cation),[7] whereas aliphatic-amine-containing conjugate chemosensors switch off the emission of anthracene units only when they are neither protonated nor coordinated.[8] Systems with these two types of moieties can generate devices capable of displaying "off−on−off" fluorescence emission upon variation of pH, a phenomenon that is possible through two opposite photoinduced electron-transfer (PET) processes.[1a,9]

Several researchers have studied pyridine- or phenanthroline-containing thia-aza and phospha-thia-aza macrocycles and their interaction with different *soft* transition-metal ions.[10] Because of the interest in the coordination chemistry of these ions and in the analytical applications of fluorescence chemosensors, we have extended this research to fluorescence systems based on pyridine-containing thia-aza macrocycles. The present paper describes the synthesis and the coordination properties of the three new conjugate chemosensors, 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L1), 7-(10-methyl-9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L2), and 7,7′-[9,10-anthracenediylbis(methylene)]bis-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L3). All these systems have a pyridil-thioether macrocycle as a receptor unit and an anthracene moiety as a fluorophore. Protonation and coordination properties toward Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) are studied. The crystal structures of ligand L1 and complex $[CuL1(ClO_4)](ClO_4)$ are also discussed.

## Experimental Section

**General Remarks.** All reactions were carried out using standard Schlenk techniques. Elemental analyses were performed using a Carlo Erba EA-1108 instrument provided by the Chemical Analysis Service of the Universitat Autònoma de Barcelona or a Thermo Finnigan-CE Flash-EA 1112-CHNS instrument provided by the Chemical Analysis Service of the REQUIMTE, DQ, Universidade Nova de Lisboa. Mass spectra were recorded using a HP298S GC/MS system. NMR spectra were recorded on a Bruker 250 MHz AC instrument. IR spectra were recorded using a Perkin-Elmer FT-1710 instrument. EPR measurements were taken using a Bruker EMX spectrometer and an Oxford continuous flow cryostat. EPR spectra were simulated using the WINEPR Simfonia V.1.2. program from Bruker Instruments, Inc. Organic reagents and transition-metal salts were purchased from Merck and Aldrich and used as received. Compounds 3,11-ditia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),-13,15-triene[11] (**4**), 9,10-bis(chloromethyl) anthracene[12] (**5**), and *N*,*N*,*N*′,*N*′-tetramethyl-9,10-bis(aminomethyl)anthracene[13] (**6**) were prepared as reported in the literature. *N*,*N*-Bis(3-chloropropyl)amine (**1**) was also prepared according to a method described in the literature[14] but using chloroform instead of benzene as a solvent.

**Spectrophotometric and Spectrofluorimetric Measurements.** Absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer and fluorescence emission on a Horiba-Jobin-Yvon SPEX Fluorolog 3.22 spectrofluorimeter. The linearity of the fluorescence emission versus the 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 ligands (ca. $5 \times 10^{-3}$ M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with dichloromethane UVA-sol. The titration solutions ($[L1] = 4.73 \times 10^{-5}$ M, $[L2] = 4.59 \times 10^{-5}$ M, and $[L3] = 5.55 \times 10^{-5}$ M) were prepared by appropriate dilution of the stock solutions. Titrations of the ligands were carried out by addition of microliter amounts of standard solutions of the ions in acetonitrile or absolute ethanol. The absorbances and emissions of these solutions were read after each addition ($\lambda$exc = 368 nm, $\lambda$em = 422 nm for L1; $\lambda$exc = 376 nm, $\lambda$em = 433 nm for L2; and $\lambda$exc = 377 nm, $\lambda$em = 434 nm for L3). The stock solution of each cation (ca. $3 \times 10^{-3}$ M) was prepared by dissolving an appropriate amount of the metal salt in a 10 mL volumetric flask and diluting to the mark with the appropriate solvent. Luminescence quantum yields were measured using a solution of sublimated anthracene in cyclohexane as a standard [$\Phi_F = 0.36$].[15]

**X-ray Crystal Structure Determinations.** Crystallographic measurements were performed on a Bruker Smart CCD apparatus at 293 K, using a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) provided by the Rede de Infraestructuras de Apoio á Investigación e ó Desenvolvemento Tecnolóxico of the Universidade de Santiago de Compostela. Crystallographic data were corrected for Lorentz and polarization effects. The frames were integrated with the Bruker SAINT[16] software package, and the data

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were corrected for absorption using the SADABS program.[17] The structures were solved by direct methods using the SIR-97 program.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on $F^2$ using the SHELXL97 program.[19] Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. The coordinated perchlorate ion of the structure of $[Cu(ClO_4)(L1)](ClO_4)$ was modeled with disorder. Special computations for the crystal structure discussions were carried out with PLATON.[20] Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 263783 and 263784 for L1 and $[Cu(ClO_4)(L1)](ClO_4)$, respectively. These data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

***N*,*N*-Bis(3-chloropropyl)-9-anthracenemethanamine (2).** A total of 200 mL of $CH_3CN$ and 30 mL of $CH_2Cl_2$ were added to a round-bottom flask charged with **1** (2.00 g, 11.77 mmol), NaOH (0.24 g, 6.00 mmol), KI (0.49 g, 2.95 mmol), and 9-(chloromethyl)-anthracene (1.33 g, 5.86 mmol). The suspension was refluxed for 5 h and then filtered to remove the inorganic salts. The organic layer was evaporated to dryness under a vacuum. The resulting yellow residue was purified by column chromatography on silica gel using a mixture of $CHCl_3$−$CH_3OH$ (9:1 v/v ratio) as an eluent to afford 2.00 g of **2** (95% yield). Anal. Calcd for $C_{21}H_{23}Cl_2N$: C, 70.00; H, 6.45; N. 3.90. Found: C, 69.85; H, 6.55; N, 3.80. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 1.87$ (m, 4H, Cl−$CH_2$−C$\mathit{H}_2$−$CH_2$−N−), 2.70 (t, $^3J_{H,H} = 6.69$ Hz, 4H, Cl−$CH_2$−$CH_2$−C$\mathit{H}_2$−N−), 3.37 (t, $^3J_{H,H} = 6.53$ Hz, 4H, Cl−C$\mathit{H}_2$−$CH_2$−$CH_2$−N−), 4.54 (s, 2H, An−C$\mathit{H}_2$−N−), 7.49 (m, 4H, *An*−$CH_2$−N−), 8.01 (d, $^3J_{H,H} = 7.85$ Hz, 2H, *An*−$CH_2$−N−), 8.42 (s, 1H, *An*−$CH_2$−N−), 8.44 (t, $^3J_{H,H} = 8.70$ Hz, 2H, *An*−$CH_2$−N−). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.42$ (Cl−$CH_2$−*C*$H_2$−$CH_2$−N−); 43.05 (Cl−*C*$H_2$−$CH_2$−$CH_2$−N−); 51.05 (Cl−$CH_2$−$CH_2$−*C*$H_2$−N−); 51.63 (An−*C*$H_2$−N−); 124.71, 124.82, 125.61, 127.63, 129.08, 129.95, 131.23, 131.41 (*An*−$CH_2$−N−) ppm. UV−vis ($CH_2Cl_2$): $\lambda = 333$ ($\epsilon = 2792$), 349 (5680), 368 (9068), 388 nm (8714 $M^{-1}$ $cm^{-1}$).

**2,6-Bis(mercaptomethyl)pyridine (3).** This compound was synthesized by a previously reported method with a slight modification.[21] The product was not extracted with dichloromethane but isolated with a separatory funnel.

***N*,*N*-Dimethyl-10-methyl-9-anthracenemethanamine (7).** This compound was obtained as a byproduct in the synthesis of **6**. It was isolated from the first fraction of the chromatographic purification process. Yield: 1.64 g, 12%. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.70; N, 5.60. Found: C, 86.35; H, 7.60; N, 5.45. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H, C$\mathit{H}_3$−An−$CH_2$−), 3.12 [s, 6H, −N(C$\mathit{H}_3$)$_2$], 4.41 (s, 2H, $CH_3$−An−C$\mathit{H}_2$−N−), 7.54 (m, 4H, $CH_3$−*An*−$CH_2$−N−), 8.35 (m, 4H, $CH_3$−*An*−$CH_2$−N−). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.01$ (*C*$H_3$−An−$CH_2$); 45.51 [−N(*C*$H_3$)$_2$]; 55.26 ($CH_3$−An−*C*$H_2$−N−); 124.64, 125.17, 125.27, 125.40, 128.27, 129.83, 130.91 ($CH_3$−*An*−$CH_2$−N−).

***N*,*N*,*N*-Trimethyl-10-methyl-9-anthracenemethanammonium Iodide (8).** A round-bottom flask charged with a solution of compound **7** (1.22 g, 4.90 mmol) dissolved in the minimum amount of acetonitrile was cooled in an ice bath. A solution of methyl iodide (0.36 mL, 5.70 mmol) in acetonitrile (20 mL) was added dropwise to this solution. The resulting mixture was refluxed for 10 min and then cooled at room temperature. The addition of diethyl ether produced precipitation of **8** as a deep yellow solid, which was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 1.42 g, 74%. Anal. Calcd for $C_{19}H_{22}IN$: C, 58.30; H, 5.70; N, 3.60. Found: C, 57.95; H, 5.80; N, 3.55. $^1H$ NMR (250 MHz, DMSO-$d_6$): $\delta = 3.07$ [s, 9H, (C$\mathit{H}_3$)$_3$−N−$CH_2$−], 3.17 (s, 3H, C$\mathit{H}_3$−An−$CH_2$−), 5.72 (s, 2H, −An−C$\mathit{H}_2$−N−), 7.68 (m, 4H, $CH_3$−*An*−$CH_2$−), 8.52 (d, 2H, $^3J_{H,H} = 8.42$ Hz, $CH_3$−*An*−$CH_2$−), 8.52 (d, 2H, $^3J_{H,H} = 8.78$ Hz, $CH_3$−*An*−$CH_2$−). $^{13}C\{^1H\}$ NMR (250 MHz, DMSO-$d_6$): $\delta = 14.74$ (*C*$H_3$−An−$CH_2$−); 52.79 [(*C*$H_3$)$_3$−N−$CH_2$−]; 58.92 (−An−*C*$H_2$−N−); 125.23, 125.33, 125.84, 126.91, 129.49, 132.34 ($CH_3$−*An*−$CH_2$−).

***N*,*N*,*N*,*N*′,*N*′,*N*′-Hexamethyl-9,10-anthracenedimethanammonium Iodide (9).** This compound was prepared according to the same procedure as described for **8**, but using compound **6** (2.81 g, 9.62 mmol) and methyl iodide (1.49 mL g, 23.95 mmol) as starting products. Yield: 3.40 g, 61%. Anal. Calcd for $C_{22}H_{30}I_2N_2$: C, 45.85; H, 5.25; N, 4.85. Found C, 46.00; H, 5.30; N, 4.75. $^1H$ NMR (250 MHz, DMSO-$d_6$): $\delta = 3.09$ [s, 18H, (C$\mathit{H}_3$)$_3$−N−$CH_2$−], 5.80 (s, 4H, −An−C$\mathit{H}_2$−N−), 7.76 (m, 4H, $^3J_{H,H} = 7.16$ Hz, −$CH_2$−*An*−$CH_2$−), 8.85 (m, 4H, $^3J_{H,H} = 6.98$ Hz, −$CH_2$−*An*−$CH_2$−). $^{13}C\{^1H\}$ NMR (DMSO-$d_6$): $\delta = 52.98$ [(*C*$H_3$)$_3$−N−$CH_2$−]; 58.32 (−An−*C*$H_2$−N−); 124.39, 125.62, 127.13, 132.41 (−$CH_2$−*An*−$CH_2$−).

**7-(9-Anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene (L1). Preparation from 2.** A solution of **2** (1.79 g, 5.00 mmol) in DMF (50 mL) and a solution of **3** (0.85 g, 5.00 mmol) in DMF (50 mL) were added simultaneously at 4 mL/h to a suspension of $Cs_2CO_3$ (1.78 g, 5.50 mmol) in DMF (700 mL). The reaction mixture was stirred for an additional 24 h under nitrogen. After that, the solvent was removed and the residue was extracted with diethyl ether (3 × 100 mL). The combined extracts were dried over $Na_2SO_4$ and evaporated to dryness to yield a yellow oil. This residue was purified by column chromatography on silica gel using $CHCl_3$ as an eluent to afford L1 as a yellow solid. Yield: 0.92 g, 40%.

**Preparation from 4.** A mixture of anhydrous $Na_2CO_3$ (0.20 g, 1.88 mmol), KI (0.16 g, 0.96 mmol), 9-(chloromethyl)anthracene (0.43 g, 1.90 mmol), and **4** (0.42 g, 1.56 mmol) in $CH_3CN$ (60 mL) was refluxed for 4 h. After that, the mixture was filtered and the solvent was evaporated under a vacuum. The resulting yellow residue was purified by column chromatography on silica gel using $CHCl_3$ as an eluent to afford 0.49 g of L1. Yield: 68%. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of L1. Anal. Calcd for $C_{28}H_{30}N_2S_2$: C, 73.30; H, 6.60; N, 6.10; S, 14.00. Found: C, 73.10; H, 6.55; N, 6.10; S, 14.05. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 1.52$ (m, 4H, −S−$CH_2$−C$\mathit{H}_2$−$CH_2$−N−), 2.23 (t, $^3J_{H,H} = 7.97$ Hz, 4H, −S−C$\mathit{H}_2$−$CH_2$−$CH_2$−N−), 2.43 (t, $^3J_{H,H} = 6.00$ Hz, 4H, −S−$CH_2$−$CH_2$−C$\mathit{H}_2$−N−), 3.76 (s, 4H, −Py−C$\mathit{H}_2$−S−), 4.33 (s, 2H, An−C$\mathit{H}_2$−N−), 7.24 (d, $^3J_{H,H} = 7.70$ Hz, 2H, −*Py*−$CH_2$−S−), 7.41 (m, 4H, *An*−$CH_2$−N−), 7.65 (t, $^3J_{H,H} = 7.70$ Hz, 1H, −*Py*−$CH_2$−S−), 7.96 (m, 2H, *An*−$CH_2$−N−), 8.30 (m, 2H, *An*−$CH_2$−N−), 8.36 (s, 1H, *An*−$CH_2$−N−). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 27.78$ (−S−$CH_2$−*C*$H_2$−$CH_2$−N−); 29.13

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$(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 37.75 $(-Py-\mathit{C}H_2-S-)$; 51.51 $(An-\mathit{C}H_2-N-)$; 53.65 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 121.21, 137.32, 158.53 $(-\mathit{Py}-CH_2-S-)$; 124.59, 124.81, 125.33, 127.22, 128.77, 130.03, 131.05, 131.14 $(\mathit{An}-CH_2-N-)$. UV−vis ($CH_2Cl_2$): $\lambda = 333$ ($\epsilon = 2935$), 350 (5929), 368 (9361), 388 nm (9034 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 459.1 $[L1+H]^+$.

**7-(10-Methyl-9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L2).** A mixture of **4** (0.91 g, 3.39 mmol), $Na_2CO_3$ (1.18 g, 11.13 mmol), and **8** (1.33 g, 3.38 mmol) in DMF (250 mL) was refluxed for 24 h. The solvent was removed under a vacuum to obtain L2, which was purified by column chromatography on silica gel using a mixture of $CH_2Cl_2-CH_3OH$ (5:1 v/v ratio) as an eluent. Yield: 0.88 g, 55%. Anal. Calcd for $C_{29}H_{32}N_2S_2\cdot H_2O$: C, 70.95; H, 6.95; N, 5.70; S, 13.10. Found: C, 70.50; H, 6.80; N, 5.70; S, 12.90. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 1.53$ (m, 4H, $-S-CH_2-C\mathit{H}_2-CH_2-N-$), 2.24 (t, $^3J_{H,H} = 8.06$ Hz, 4H, $-S-C\mathit{H}_2-CH_2-CH_2-N-$), 2.45 (t, $^3J_{H,H} = 6.18$ Hz, 4H, $-S-CH_2-CH_2-C\mathit{H}_2-N-$), 3.09 (s, 3H, $C\mathit{H}_3-An-CH_2-$), 3.76 (s, 4H, $-Py-C\mathit{H}_2-S-$), 4.37 (s, 2H, $CH_3-An-C\mathit{H}_2-N-$), 7.26 (d, $^3J_{H,H} = 7.70$ Hz, 2H, $-\mathit{Py}-CH_2-S-$), 7.43 (m, 4H, $CH_3-\mathit{An}-CH_2-N-$), 7.67 (t, $^3J_{H,H} = 7.70$ Hz, 1H, $-\mathit{Py}-CH_2-S-$), 8.33 (m, 4H, $CH_3-\mathit{An}-CH_2-N-$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.29$ $(\mathit{C}H_3-An-CH_2)$; 27.92 $(-S-CH_2-\mathit{C}H_2-CH_2-N-)$; 29.29 $(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 37.90 $(-Py-\mathit{C}H_2-S-)$; 51.71 $(CH_3-An-\mathit{C}H_2-N-)$; 53.58 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 121.34, 137.45, 158.71 $(-\mathit{Py}-CH_2-S-)$; 124.61, 124.89, 125.10, 127.57, 128.34, 129.73, 130.61, 130.95 $(CH_3-\mathit{An}-CH_2-N-)$. UV−vis ($CH_2Cl_2$): $\lambda = 341$ ($\epsilon = 2605$), 359 (5168), 376 (8395), 399 nm (8237 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 473.1 $[L2+H]^+$.

**7,7′-[9,10-Anthracenediylbis(methylene)]bis-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L3). Preparation from 5.** A solution of **5** (0.49 g, 1.78 mmol) in $CHCl_3$ (180 mL) was added dropwise to a stirred refluxing mixture of KI (0.29 g, 1.75 mmol), $Na_2CO_3$ (0.55 g, 5.19 mmol) and **4** (1.00 g, 3.73 mmol) in $CH_3CN$ (200 mL). After the addition was completed, the resulting suspension was refluxed for an additional 24 h. The mixture was filtered, and the solvent was removed under a vacuum to yield a brown oil, which was purified by column chromatography on silica gel using $CHCl_3$ as an eluent. Yield: 0.80 g, 61%.

**Preparation from 9.** L3 was also prepared from **4** (1.00 g, 3.73 mmol) and **9** (1.00 g, 1.74 mmol) by the procedure described above but using DMF as the solvent. Yield: 0.68 g, 53%. Anal. Calcd for $C_{42}H_{50}N_4S_4$: C, 68.25; H, 6.80; N, 7.60; S, 17.35. Found: C, 68.50; H, 6.70; N, 7.65; S, 17.05. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 1.50$ (m, 8H, $-S-CH_2-C\mathit{H}_2-CH_2-N-$), 2.21 (t, $^3J_{H,H} = 8.06$ Hz, 8H, $-S-C\mathit{H}_2-CH_2-CH_2-N-$), 2.44 (t, $^3J_{H,H} = 6.09$ Hz, 8H, $-S-CH_2-CH_2-C\mathit{H}_2-N-$), 3.76 (s, 8H, $-Py-C\mathit{H}_2-S-$), 4.37 (s, 4H, $-N-C\mathit{H}_2-An-C\mathit{H}_2-N-$), 7.26 (d, $^3J_{H,H} = 7.70$ Hz, 4H, $-\mathit{Py}-CH_2-S-$), 7.34 (m, 4H, $-N-CH_2-\mathit{An}-CH_2-N-$), 7.67 (t, $^3J_{H,H} = 7.70$ Hz, 2H, $-\mathit{Py}-CH_2-S-$), 8.32 (m, 2H, $-N-CH_2-\mathit{An}-CH_2-N-$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 27.97$ $(-S-CH_2-\mathit{C}H_2-CH_2-N-)$; 29.30 $(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 37.91 $(-Py-\mathit{C}H_2-S-)$; 51.80 $(-N-\mathit{C}H_2-An-\mathit{C}H_2-N-)$; 53.80 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 121.35, 137.46, 158.72 $(-\mathit{Py}-CH_2-S-)$; 124.82, 125.42, 130.63, 130.79 $(-N-CH_2-\mathit{An}-CH_2-N-)$. UV−vis ($CH_2Cl_2$): $\lambda = 341$ ($\epsilon = 3386$), 358 (6530), 377 (10568), 398 nm (10 800 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 370.1 $[L3+2H]^{2+}$, 739.2 $[L3+H]^+$.

**Synthesis of Metal Complexes. General Procedure.** A dichloromethane solution of the corresponding macrocycle (0.22 mmol, 4 mL) was added dropwise to an acetonitrile solution of $M(ClO_4)_2$ or $M(BF_4)_2$ (0.22 mmol, 4 mL). The resulting solution was stirred at room temperature for 2 h, and the solvent was partially removed to ca. 3 mL. Diethyl ether was slowly infused into the solution, producing powdery precipitates. The products were filtered off, washed with diethyl ether, and recrystallized by the diffusion of diethyl ether into ethanol or acetonitrile solutions.

**$[Pd(L1)](BF_4)_2$.** Yield: 0.12 g, 73%. Anal. Calcd for $C_{28}H_{30}N_2S_2PdB_2F_8\cdot H_2O$: C, 44.45; H, 4.25; N, 3.70; S, 8.45. Found: C, 44.35; H, 4.25; N, 3.80; S, 8.40. Conductivity ($CH_3CN$, $1 \times 10^{-3}$ M): 221 $\mu S\ cm^{-1}$. $^{13}C\{^1H\}$ NMR ($CD_3CN$): $\delta = 26.75$ $(-S-CH_2-\mathit{C}H_2-CH_2-N-)$; 37.49 $(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 46.43 $(-Py-\mathit{C}H_2-S-)$; 57.69 $(An-\mathit{C}H_2-N-)$; 62.15 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 123.11, 141.39, 162.61 $(-\mathit{Py}-CH_2-S-)$; 122.67, 124.00, 125.81, 128.09, 130.04, 131.17, 132.59 $(\mathit{An}-CH_2-N-)$. UV−vis ($CH_2Cl_2$): $\lambda = 357$ ($\epsilon = 6745$), 376 (7626), 396 nm (6119 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 651.0 $[PdL1BF_4]^+$.

**$[Pd(L2)](BF_4)_2$.** Yield: 0.13 g, 78%. Anal. Calcd for $C_{29}H_{32}N_2S_2PdB_2F_8\cdot 2H_2O$: C, 44.10; H, 4.60; N, 3.55; S, 8.15. Found: C, 43.50; H, 4.30; N, 3.85; S 8.35. Conductivity ($CH_3CN$, $1 \times 10^{-3}$ M): 230 $\mu S\ cm^{-1}$. $^{13}C\{^1H\}$ NMR ($CD_3CN$): $\delta = 15.19$ $(\mathit{C}H_3-An-CH_2)$; 27.34 $(-S-CH_2-\mathit{C}H_2-CH_2-N-)$; 37.99 $(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 47.19 $(-Py-\mathit{C}H_2-S-)$; 58.59 $(CH_3-An-\mathit{C}H_2-N-)$; 62.55 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 124.08, 141.96, 163.39 $(-\mathit{Py}-CH_2-S-)$; 122.08, 125.57, 126.50, 127.02, 128.28, 131.05, 133.05, 136.27 $(CH_3-\mathit{An}-CH_2-N-)$. UV−vis ($CH_2Cl_2$): $\lambda = 367$ ($\epsilon = 5569$), 385 (6984), 406 nm (5868 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 665.0 $[PdL2BF_4]^+$.

**$[Pd_2(L3)](BF_4)_4$.** This compound was obtained by the general procedure using 0.11 mmol of L3 in order to maintain an appropriate L/M molar ratio. Yield: 0.08 g, 57%. Anal. Calcd for $C_{42}H_{50}N_4S_4Pd_2B_4F_{16}\cdot 3H_2O$: C, 37.30; H, 4.15; N, 4.15; S, 9.50. Found: C, 37.35; H, 4.20; N, 4.15; S, 9.40. Conductivity ($CH_3CN$, $1 \times 10^{-3}$ M): 495 $\mu S\ cm^{-1}$. $^{13}C\{^1H\}$ NMR ($CD_3CN$): $\delta = 27.19$, 27.29 $(-S-CH_2-\mathit{C}H_2-CH_2-N-)$; 37.98, 38.55 $(-S-\mathit{C}H_2-CH_2-CH_2-N-)$; 47.16, 47.68 $(-Py-\mathit{C}H_2-S-)$; 59.01 $(-\mathit{C}H_2-An-\mathit{C}H_2-)$; 62.92 $(-S-CH_2-CH_2-\mathit{C}H_2-N-)$; 123.97, 124.07, 141.96, 163.46, 163.82 $(-\mathit{Py}-CH_2-S-)$; 126.52, 127.39, 127.98, 128.75, 128.90, 132.96 $(-CH_2-\mathit{An}-CH_2-)$. UV−vis ($CH_2Cl_2$): $\lambda = 372$ ($\epsilon = 9495$), 390 (10 041), 410 nm (8984 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 1211.9 $[Pd_2L3(BF_4)_3]^+$.

**$[Cu(ClO_4)(L1)](ClO_4)$.** This compound was obtained by the general procedure using ethanol instead of acetonitrile in order to avoid formation of Cu(I) species. Yield: 0.11 g, 71%. Anal. Calcd for $C_{28}H_{30}N_2S_2CuCl_2O_8$: C, 46.65; H, 4.20; N, 3.90; S, 8.90. Found: C, 46.40; H, 4.30; N, 3.70; S 8.65. Conductivity ($CH_3NO_2$, $1 \times 10^{-3}$ M): 154 $\mu S\ cm^{-1}$. UV−vis ($CH_2Cl_2$): $\lambda = 356$ ($\epsilon = 8466$), 375 (10 550), 395 nm (9896 $M^{-1}$ $cm^{-1}$). MS-ESI (*m/z*): 621.0 $[CuL1ClO_4]^+$.

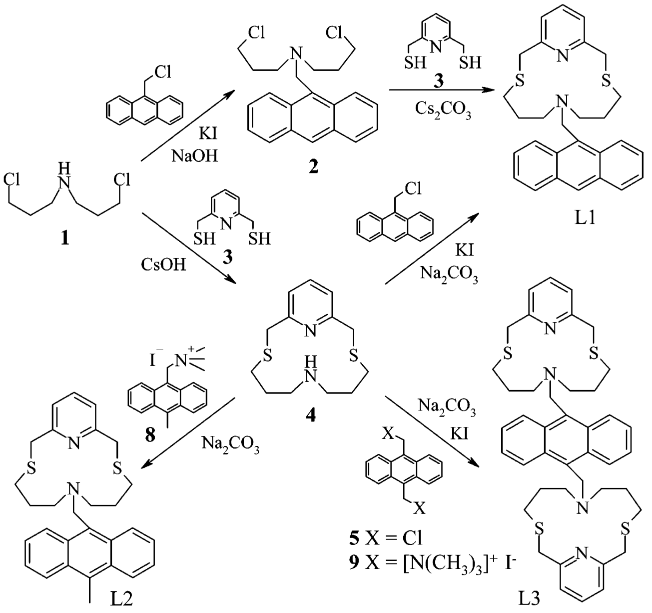
**$[CoCl_2(L1)]$.** This compound was obtained by the general procedure using hydrated $CoCl_2$ as a metal precursor. Yield: 0.10 g, 79%. Anal. Calcd for $C_{28}H_{30}N_2S_2CoCl_2\cdot H_2O$: C, 55.45; H, 5.30; N, 4.60; S, 10.55. Found: C, 55.60; H, 5.30; N, 4.50; S 10.40. Conductivity ($CH_3NO_2$, $1 \times 10^{-3}$ M): 14 $\mu S\ cm^{-1}$. MS-ESI (*m/z*): 552.0 $[CoL1Cl]^+$.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution.

## Results and Discussion

**Synthesis of Macrocyclic Ligands.** The synthetic pathways for L1, L2, and L3 are summarized in Scheme 1. The initial purpose was to obtain the desired conjugate chemosensors by reacting an appropriate anthracene derivative with compound **4**, because this macrocycle can be easily obtained

**Scheme 1**



by reacting the dichloride **1** with the dithiol **3**.[11] We expected that the nucleophilic attack of the aza-dithia macrocycle **4** on anthracene-containing alkyl halides would lead to the desired products. The preparation of L1 was initially attempted by reacting equimolar amounts of **4** and 9-(chloromethyl)anthracene in the presence of $Na_2CO_3$. Compound L1 was obtained under these conditions, but the yield was lower than expected (19%). This fact was attributed to the relatively low efficiency of the chloride moiety as a leaving group. To improve this yield, the same reaction was carried out in the presence of halide salts, which could act as a catalyst in the reaction. The first attempt was made by using tetrabutylammonium bromide as a catalyst because this halide salt is very soluble in acetonitrile. The $^1H$ NMR spectrum of the crude product showed that the presence of this salt led to an increase in the yield of L1. However, several problems were found in their purification, and the tetrabutylammonium bromide was replaced with KI. In this case, the synthesis and the purification processes for L1 were successful and the product was obtained in higher yield (68%). It is interesting to note that, although an efficient synthesis of the lepidopterene **11** has been reported by refluxing 9-(chloromethyl)anthracene in the presence of NaI, no evidence of this compound was found as a byproduct of this reaction (Scheme 2).[22]

Macrocycle L1 was characterized by analytical and spectroscopic techniques, and these results were confirmed by solving its crystal structure. The crystal structure and the crystallographic data for L1 are displayed in Figure 1 and Table 1, respectively. The bond lengths and angles of L1 are within expected ranges. This ligand adopts a conformation in which all aliphatic atoms define a pseudo-plane almost perpendicular to the plane of the pyridine ring. This situation leaves the lone pairs of the sulfur atoms pointing outward from the macrocyclic cavity at a distance of ca. 6.68 Å from one another, a fact which reflects the poor preorganization of the free ligand in the solid state. C−H···π interactions were found in the crystal packing of L1.[23] These interactions, between the methylene group (C15) and the central ring of the anthracene moiety of another molecule (symmetry code i: $1 - x$, $1 - y$, $1 - z$), join two macrocyclic molecules leading to the formation of dimers (Figure 1b). The C−H·

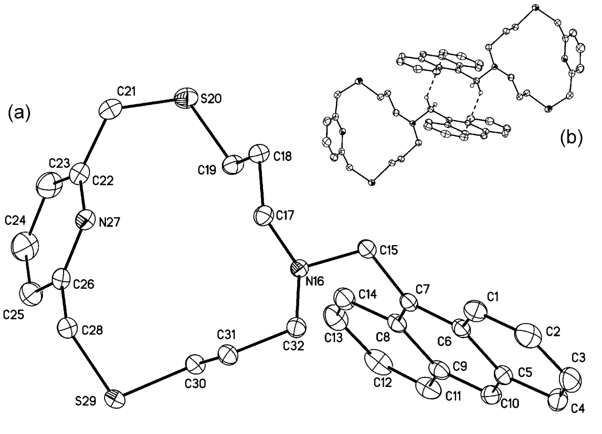


**Figure 1.** (a) Displacement ellipsoid representation (at the 40% probability level) of L1, with the atom-numbering scheme adopted. Hydrogen atoms were omitted for clarity. (b) Perspective view of L1 dimers showing the C−H···π interactions.

**Scheme 2**

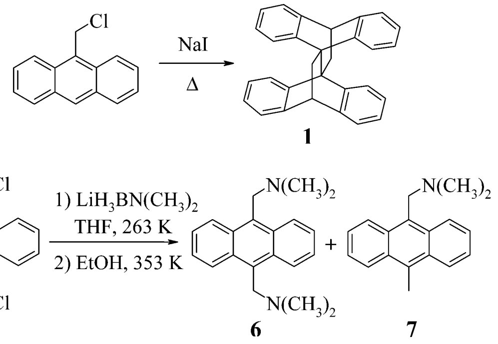


**Table 1.** Crystallographic Data for L1 and $[Cu(ClO_4)(L1)](ClO_4)$

| | L1 | $[Cu(ClO_4)(L1)](ClO_4)$ |
|---|---|---|
| empirical formula | $C_{28}H_{30}N_2S_2$ | $C_{28}H_{30}CuCl_2O_8N_2S_2$ |
| fw | 458.66 | 721.10 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 12.237(5) | 8.901(3) |
| $b$ (Å) | 15.088(5) | 9.145(3) |
| $c$ (Å) | 13.302(5) | 35.075(10) |
| $\beta$ (deg) | 100.598(5) | 95.403(5) |
| vol (Å$^3$) | 2414.1(16) | 2842.4(16) |
| Z, $\rho_{calc}$ (g cm$^{-3}$) | 4, 1.262 | 4, 1.685 |
| $F$(000) | 976 | 1484 |
| cryst size (mm$^3$) | 0.65 × 0.57 × 0.34 | 0.42 × 0.19 × 0.06 |
| abs coeff (mm$^{-1}$) | 0.239 | 1.160 |
| $\theta$ range (deg) | 2.06−29.01 | 1.17−26.46 |
| max/min transmission | 0.922/0.777 | 0.933/0.570 |
| reflns collected | 22 428 | 23 500 |
| independent reflns ind($R_{int}$) | 5938 (0.0235) | 5843 (0.0748) |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0345, wR2 = 0.0866 | R1 = 0.0485, wR2 = 0.1092 |
| final $R$ indices (all data) | R1 = 0.0447, wR2 = 0.0946 | R1 = 0.1012, wR2 = 0.1421 |

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··centroid distance and angle are 2.90 Å and 145.4°, respectively.

The previously described synthesis of L1 from the dichloride **1** allowed us to obtain this macrocycle in an overall yield of 37%. An attempt was made to improve the yield of L1 by reacting the dithiol **3** and the anthracene-containing dichloride **2**. This dihalide was obtained in high yield by reaction of **1** with 9-(chloromethyl)anthracene in similar conditions to those used in the functionalization of **4**, but replacing $Na_2CO_3$ with NaOH. This modification prevents the formation of 3-(3-chloropropyl)-[1,3]oxazolidine-2-one, a byproduct resulting from the reaction of **1** with carbonate ions.[24] L1 was obtained by reaction of **2** with **3** in a yield of 40%. Therefore, the overall yield of L1 from the dichloride **1** via this second pathway was 38%, which is almost identical to that obtained by the first pathway. However, the second synthetic way allowed us to obtain dihalide **2**, which can be a useful synthon for the synthesis of new anthracene-containing chemosensors.

The bis macrocycle L3 was initially obtained in a yield of 61% by functionalization of **4** with 9,10-bis(chloromethyl)anthracene (**5**) in the presence of KI. As in the case of L1, we searched for other synthetic ways to improve the yield of this product. The option selected was to use an anthracene derivative with neutral leaving groups because this kind of molecule often increases the yield of nucleophilic substitution reactions.[25] We chose the anthracene-containing quaternary ammonium salt **9**, which was easily obtained by methylation of the diamine **6**. The preparation of this last compound was accomplished by a double nucleophilic attack of lithium *N*,*N*-dimethylaminoborohydride on the dichloride **5** (Scheme 2).[13]

This reaction was performed at −10 °C, and the resulting products were the desired diamine **6** in a 51% yield and the asymmetric methylamino derivative **7** in a yield of 19%. The formation of **7** can be explained when taking into account that the *N*,*N*-dialkylaminoborohydrides can behave as a nucleophile or reducing agent, depending on the temperature of the reaction.[26] The amines **6** and **7** were easily quaternized with methyl iodide to afford the ammonium salts **9** and **8**, respectively. The reaction of the macrocycle **4** with the diammonium salt **9** produced the desired bis macrocycle L3 in a yield of 53%. Although this yield is lower than that obtained using **5** as a starting product, this pathway allowed the preparation of an interesting synthon, the quaternized derivative **9**.

Compound **8** was used in the preparation of the conjugate chemosensor L2 in similar conditions to those used in the synthesis of L3 but using this ammonium salt as a starting product.

## Solid State Complexes

**Reaction of Pd(II) and L1, L2, and L3.** The reaction of equimolar amounts of $Pd(BF_4)_2$ and L1 or L2 produced yellow microcrystalline complexes which behaved as 2:1 electrolytes in acetonitrile solution. The same reaction was performed with L3 but using a 1:2 L/M molar ratio, and the resulting complex behaved as a 4:1 electrolyte in acetonitrile. Taking into account these data, the elemental analyses, and the ESI-MS spectra of these compounds, these complexes should be formulated as $[PdL](BF_4)_2$ (L = L1, L2) and $[Pd_2L_3](BF_4)_4$. The $^1H$ NMR spectra of these three compounds show a complex pattern in the aliphatic region because coordination increases the rigidity of the macrocyclic units, so all protons become magnetically nonequivalent, giving rise to broad signals. The $^{13}C\{^1H\}$ NMR spectra of these complexes show a single signal for each aliphatic carbon. Those carbons directly bonded to the donor atoms exhibit significant downfield displacement (6−9 ppm) with respect to the free ligands, whereas the position of the central methylene carbons of the propyl linkers does not vary significantly. It can be assumed that the coordinating behavior of the three ligands in relation to Pd(II) is very similar, and in all cases, the metal ion probably adopts a square-planar geometry defined by the four donor atoms of the macrocyclic ring.

**Reaction of Co(II) and L1.** Taking into account the identical donor sets of atoms of all three ligands, and the equivalent coordinating behaviors observed in their complexations with Pd(II), it was assumed that these ligands have similar coordinating properties; therefore, the rest of the coordination studies were performed using only ligand L1 as a coordinating agent.

The reaction of L1 with Co(II) perchlorate or tetrafluoroborate led to the formation of reddish solutions which gradually changed to green. Only heterogeneous precipitates could be isolated from these solutions. However, the reaction with $CoCl_2{\cdot}6H_2O$ produced a violet solid whose elemental analysis, ESI-MS spectrum, and electrolytic behavior suggest that it should be formulated as $[CoCl_2(L1)]$. The absorption of the anthracene moiety prevents the observation of the d−d transition bands corresponding to the Co(II) ion, and therefore, the UV−visible spectrum of this complex cannot be used to make structural assignments.

The EPR spectrum of a microcrystalline sample of $[CoCl_2(L1)]$ at 4 K (Figure 2A) is typical for Co(II) ions in a high-spin configuration ($S = {}^3/_2$), in which this spin state is split into two Kramer doublets ($S = \pm{}^1/_2, \pm{}^3/_2$). The resonance lines broaden at higher temperatures and disappear at ca. 50 K. This spectrum corresponds to the transitions between the doublet $S = \pm{}^1/_2$, which are highly anisotropic, as expected for Co(II) ions in distorted octahedral or square-pyramidal coordinations. Simulation of this spectrum assuming an effective Zeeman Hamiltonian yields the EPR parameters $g_{max} = 4.9$ (500), $g_{med} = 3.0$ (2000), and $g_{min} = 2.0$ (200) (line width between parenthesis). No hyperfine splitting with the cobalt nucleus ($I = {}^7/_2$) has been observed, which suggests that the exchange interaction between Co(II) ions is large enough to collapse this interaction into a single line. The EPR parameters obtained for $[CoCl_2(L1)]$ are within the

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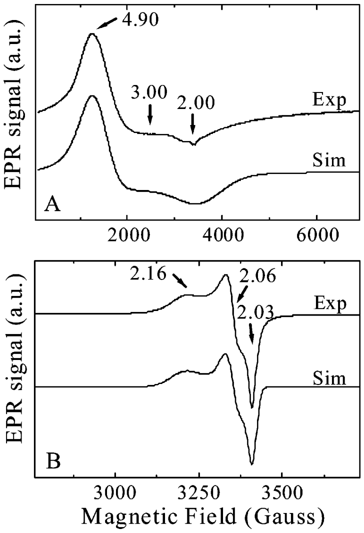

**Figure 2.** X-band EPR spectra of polycrystalline samples of [$CoCl_2$(L1)] at 4 K (A) and of [$Cu(ClO_4)$(L1)]($ClO_4$) at room temperature (B).

typical values found for Co(II) compounds, in which the zero-field splitting is larger than the microwave energy.[27]

**Reaction of Cu(II) and L1.** The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with L1 afforded a blue microcrystalline product whose elemental analysis fits the formula Cu(L1)$(ClO_4)_2$. This compound behaves as a 2:1 electrolyte in a nitromethane solution. As in the case of the Co(II) complex, the UV−visible spectrum of this compound is unable to give any useful information about the coordination geometry of the metal ion.

Blue crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into an ethanol solution of this complex. The crystal structure consists of discrete [$Cu(ClO_4)$(L1)]$^+$ cations and perchlorate anions, so the solid complex should be formulated as [$Cu(ClO_4)$(L1)]($ClO_4$). The representation and selected bond lengths and angles of the [$Cu(ClO_4)$(L1)]$^+$ cation are given in Figure 3. The metal coordination geometry is distorted square-pyramidal with the N16, S20, N27, and S29 atoms of the macrocyclic ring on the basal plane and one oxygen atom of a perchlorate ion in the apical position. The value of the angular parameter of trigonal distortion is 0.35,[28] which indicates that, in this structure, the Cu(II) ion mostly lies within the macrocyclic cavity. In contrast, this situation is not possible with $N_2S_2$ 12-membered pyridine-containing macrocycles, because the size of the cavity is not large enough to accommodate this metal ion.[6c] The Cu−$N_{py}$ and Cu−$N_{aliphatic}$ distances (2.008 and 2.057 Å, respectively) are within expected ranges for 14-membered pyridine-containing macrocycles.[29] Both Cu−S distances (2.311 and 2.322 Å) are shorter than those observed in the Cu(II) complexes of 12-membered macrocycles.[6c] The Cu−O bond length (2.364 Å) is shorter than the sum of the van der Waals radii [$r_{vdw}(Cu) = 1.40$ Å and $r_{vdw}(O) = 1.50$ Å].[30] $\pi \cdots \pi$ interactions[31] have been found in the crystal packing (Figure 3b). These interactions between two pairs of aromatic rings [Cg(1): C5−C6−C7−C8−C9−C10 and Cg(2): C8−C9−C11−C12−C13−C14] join two macrocyclic complexes, leading to formation of supramolecular dimers. {d[Cg(1)$\cdots$Cg(2)$^i$] = d[Cg(2)$\cdots$Cg(1)$^i$] = 3.881 Å; dihedral angle α: 1.46°; symmetry code i: $1 - x, -y, 1 - z$}.

The EPR spectrum of a microcrystalline sample of [$Cu(ClO_4)$(L1)]($ClO_4$) (Figure 2B) was recorded at room temperature, and no significant differences were found in the range between 4 K and room temperature. The spectrum departs slightly from the axial symmetry which is usually found in Cu(II) ions having a distorted square-pyramidal coordination. The hyperfine structure produced by the Cu(II) nucleus ($I = {}^1/_2$) was not observed, since it is presumably collapsed by exchange interactions between Cu(II) ions. These exchange interactions should be the $\pi \cdots \pi$ interactions between two anthracene moieties. The EPR parameters ($g_1 = 2.155$, $g_2 = 2.060$, $g_3 = 2.025$) are in agreement with those expected for Cu(II) ions in a square-pyramidal geometry and sulfur and nitrogen atoms as basal ligands. However, it should be kept in mind that exchange interaction might collapse the resonance of the two nonequivalent copper ions present in the unit cell of [$Cu(ClO_4)$(L1)]($ClO_4$),[32] and therefore, the spectrum shown in Figure 2B should be considered as an average of the individual magnetic properties of the nonequivalent copper ions.[33]

All attempts to obtain solid complexes of Ni(II) and Zn(II) have been unsuccessful. Only the monoprotonated ligand has been isolated from the reaction of L1 with Ni(II) chloride or perchlorate. In the case of Zn(II), the same kind of reactions produced heterogeneous products.

## Spectrophotometric and Spectrofluorimetric Studies

**Photophysical Properties of the Ligands.** The electronic spectra of L1, L2, and L3 were recorded in dichloromethane at room temperature. These spectra show the characteristic bands of the anthracene derivatives above 330 nm. The absorption band of L1 has a vibrational fine structure with maxima at 333, 350, 368, and 388 nm. The absorption spectra of L2 and L3 also show this kind of band but red-shifted (ca. 11 nm), since the anthracene moieties are not 9-alkyl- but 9,10-dialkyl-substituted. The effect of the protonation

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[27] Pilbrow, J. R. *Transition Ion Electron Paramagnetic Resonance;* Clarendon Press: Oxford, U. K., 1990.

[28] The value of the angular parameter of trigonal distortion $\tau$ ranges from 0 for a perfect square pyramid to 1 for a perfect trigonal bipyramid. Addison, A. W.; Rao, T. N.; Reedjik, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, *7*, 1349−1356.

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[32] Systems of the space group *P*21/*c* have two magnetically nonequivalent metal sites per unit cell related by a *C*2*b* symmetry axis.

[33] Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Springer-Verlag: Berlin, 1990.

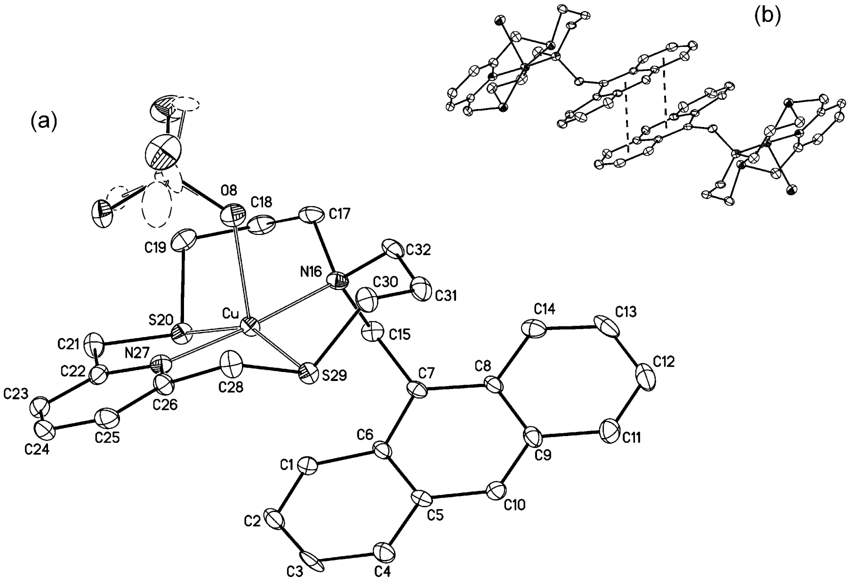

**Figure 3.** (a) Displacement ellipsoid representation (at the 40% probability level) of the $[Cu(ClO_4)(L1)]^+$ ion, with the atom-numbering scheme adopted. Noncoordinated counterions and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu−N27 2.008(4), Cu−N16 2.057(4), Cu−S29 2.3114(15), Cu−S20 2.3223(15), Cu−O8 2.364(3), N27−Cu−N16 175.95(15), N27−Cu−S29 84.09(12), N16−Cu−S29 98.76(12), N27−Cu−S20 84.47(12), N16−Cu−S20 94.00(12), S29−Cu−S20 154.53(5), N27−Cu−O8 89.36(14), N16−Cu−O8 87.72(14), S29−Cu−O8 90.89(10), S20−Cu−O8 111.66(10). (b) Perspective view of dimers of $[Cu(ClO_4)(L1)]$ showing the $\pi\cdots\pi$ interactions.

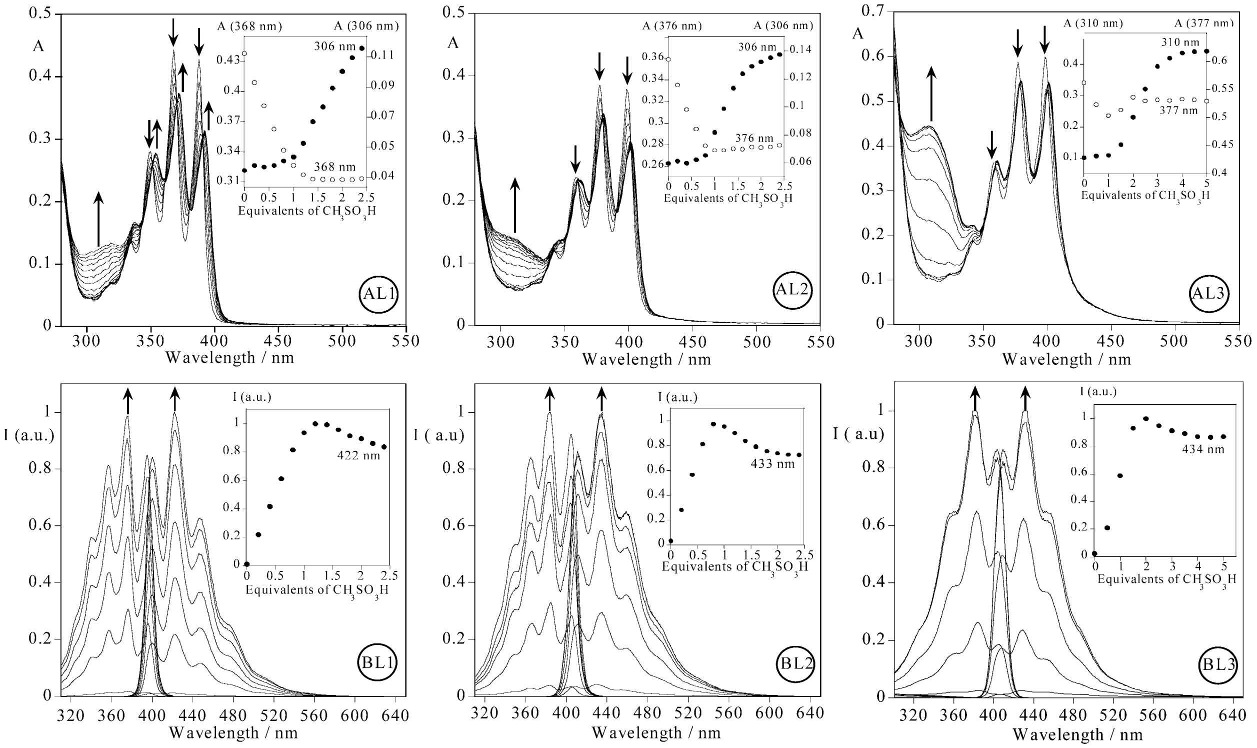

**Figure 4.** Absorption spectra of dichloromethane solutions of L1 (AL1), L2 (AL2), and L3 (AL3) as a function of added $CH_3SO_3H$. The insets show the absorbances at 306 and 368 nm (AL1), 306 and 376 nm (AL2), and 310 and 377 nm (AL3). Excitation and emission spectra of dichloromethane solutions of L1 (BL1), L2 (BL2), and L3 (BL3) as a function of added $CH_3SO_3H$ are also shown. The insets show the normalized fluorescence intensity at 422 nm (BL1), 433 nm (BL2), and 434 nm (BL3). [L1] = $4.73 \times 10^{-5}$ M, $\lambda$exc = 368 nm, $\lambda$em = 422 nm. [L2] = $4.59 \times 10^{-5}$ M, $\lambda$exc = 376 nm, $\lambda$em = 433 nm. [L3] = $5.55 \times 10^{-5}$ M, $\lambda$exc = 377 nm, $\lambda$em = 434 nm.

on the absorption spectra of the three ligands was established by titration with methanesulfonic acid (Figures 4AL1, 4AL2 and 4AL3). Two equivalents of acid are needed to protonate the aliphatic amine and the pyridine nitrogen atoms of L1 and L2. The insets of Figure 4AL1 and AL2 show that the addition of the first equivalent of acid mainly affects the absorption of the anthracene region. This reflects the fact that the first protonation process involves the aliphatic amine, which is significantly more basic than the pyridine moiety. The progressive addition of the second equivalent of acid does not affect the anthracene bands but leads to the apparition of a new absorption around 310 nm, which is assigned to the formation of the pyridinium cation.[34] Four equivalents of acid are required to protonate all the basic

**Table 2.** Quantum Yields in Dichloromethane at 298 K[a]

| | Φ L1 | Φ L2 | Φ L3 |
|---|---|---|---|
| L | 0.027 | 0.064 | 0.018 |
| L + $n$H$^+$ | 0.394 | 0.459 | 0.458 |
| L + 2$n$H$^+$ | 0.342 | 0.254 | 0.387 |
| L + $n$Cu$^{2+}$ | 0.003 | 0.004 | 0.004 |
| L + $n$Pd$^{2+}$ | 0.007 | 0.004 | 0.007 |
| L + $n$Zn$^{2+}$ | 0.255 | 0.260 | 0.445 |
| L + $n$Ni$^{2+}$ | 0.223 | 0.210 | 0.359 |
| L + $n$Co$^{2+}$ | 0.200 | 0.227 | 0.439 |

[a] $n = 1$ for L1 and L2 and $n = 2$ for L3.

sites of L3. As in the case of L1 and L2, the addition of the first equivalent of acid decreases the absorption of the anthracene band but does not affect the region around 310 nm. However, a moderate increase in the anthracene band and the apparition of the band related to the pyridinium cation is observed during the addition of the second equivalent of acid. The intensity of this second band increases until the end of the titration, whereas the anthracene band remains unaltered after the addition of the second equivalent of acid. These observations suggest that the first protonation of L3, which essentially involves one of the aliphatic amines, modifies the basicity of the other aliphatic amine and makes different both pyridine moieties, which generates a complex acid−base system.

The fluorescence spectra of the nonprotonated ligands L1, L2, and L3 show the characteristic bands of the anthracene systems. Figure 4BL1, BL2, and BL3 show the fluorescence titrations of these ligands with methanesulfonic acid. The insets of these figures illustrate that the intensity of the fluorescence increases until the ligand is half protonated. The addition of the second equivalent of acid (third and fourth for L3) produces a slight decrease in the fluorescence emission, and therefore, the global behavior observed during the titration can be identified as an "off−on−off" mechanism. This behavior is also reflected in the values of the quantum yield of the free and protonated species (Table 2) and can be explained by assuming that the initial protonation of the aliphatic amine prevents the PET from its lone pair of electrons to the anthracene moiety, whereas the protonation of the pyridine ring generates a very fast PET from the anthracene to the pyridine moiety. A similar behavior for a pyridine-anthracene-containing macrocycle has been reported by A. P. de Silva and co-workers.[35]

**Metal Ion Titrations.** It is well-known that the aliphatic amines closely bonded to fluorophore moieties are involved in the electron-transfer quenching, which makes it possible to signal the presence of metal cations in polyamine systems.[36] The stronger the involvement of these nitrogen atoms in the complexation, the stronger the effect on the luminescence of the ligand. On the other hand, protonated pyridines are known to quench the fluorescence of anthracene moieties by a PET mechanism[7] from the excited anthracene to the pyridinium. Participation of the pyridine moiety in metal complexation is expected to produce this effect. To explore the utility of these macrocyclic systems as fluorescence devices in organic solvents, titrations with different transition-metal ions were performed. Two different behaviors were observed as a function of the used metal ion.

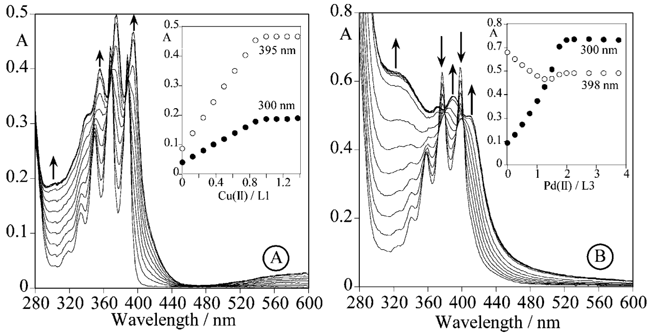

**Figure 5.** (A) Absorption spectra of a dichloromethane solution of L1 as a function of added Cu($CF_3SO_3$)$_2$. The inset shows the absorbances at 300 and 395 nm. (B) Absorption spectra of a dichloromethane solution of L3 as a function of added Pd($BF_4$)$_2$. The inset shows the absorbances at 300 and 398 nm. [L1] = $4.73 \times 10^{-5}$ M, [L3] = $5.55 \times 10^{-5}$ M.

**Pd(II) and Cu(II) Titrations.** Strong changes in the absorption and emission spectra of dichloromethane solutions of L1, L2, and L3 were observed, when they were titrated with Pd(II) or Cu(II). Parts A and B of Figure 5 show the absorption titrations of L1 with Cu(II) and L3 with Pd(II), respectively. In both titrations, the addition of the metal ion causes a red shift of the anthracene band and the apparition of a new band around 300 nm. The changes of the anthracene band are attributed to interactions between the metal ion and the aliphatic nitrogen, whereas the changes around 300 nm are attributed to the coordination of the pyridine moiety to the metal ion. The increase around 300 nm is larger in the titrations of L3 than in the titrations of L1 or L2, since each L3 molecule has two pyridine moieties. The insets of Figure 5 show that these changes occur until the addition of one equivalent of metal ion for L1 and two equivalents for L3. These data suggest that each macrocyclic moiety is coordinated to one metal ion, and therefore, each molecule of bis macrocycle L3 is coordinated to two metal ions. A new absorption band corresponding to d−d transitions was observed around 580 nm, when Cu(II) was used as the titrating agent.

Parts A and B of Figure 6 show the fluorescence titrations of L2 with Cu($CF_3SO_3$)$_2$ and Pd($BF_4$)$_2$, respectively. Initial additions of Cu(II) or Pd(II) increase the fluorescence of dichloromethane solutions of L1, L2, or L3. Subsequent additions of these metal ions cause a blue shift of ca. 10 nm, and a strong quenching of the fluorescence bands. The increase of the fluorescence is explained by the protonation of the aliphatic nitrogen atom, which prevents the PET from this atom to the anthracene moiety.[7,9] This protonation is probably due to the presence of water in the metal ion

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(34) This absorption band was also observed when the nonfunctionalized macrocycle **4** was titrated with acid (ref 11).

(35) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Chem. Commun.* **1996**, *21*, 2399−2400.

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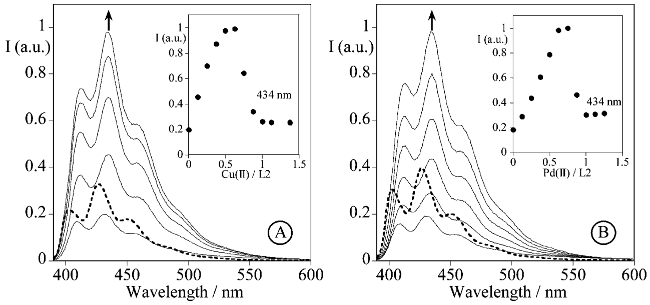

**Figure 6.** Emission spectra of L2 in dichloromethane as a function of added $Cu(CF_3SO_3)_2$ (A) and $Pd(BF_4)_2$ (B). The insets show the normalized fluorescence intensities at 434 nm. Those spectra between the maximum and the end of the titration have been omitted for clarity. The last spectrum of each titration is shown as a dotted line. $[L2] = 4.59 \times 10^{-5}$ M, $\lambda$exc = 376 nm.

solutions, which allows the hydrolysis of these ions.[37] On the other hand, the *chelation enhancement of the quenching* (CHEQ) effects can be explained by assuming that, for transition-metal ions with partially filled d orbitals, the quenching of the fluorescence emission upon complexation is mainly due to an energy transfer quenching of the $\pi^*$ emissive state, through low-lying metal-centered states.[38] Similar effects have already been reported for other anthracene-containing ligands with aliphatic amines.[7,9] However, in our case, the quenching can also be attributed to the coordination of the pyridine moiety to the metal ion, which leads to a PET mechanism from the anthracene to the pyridine moiety. The insets of Figure 6 reveal that the fluorescence of L2 changes until the addition of one equivalent of metal ion, confirming the interaction of one metal ion per macrocyclic moiety.

**Co(II), Ni(II), and Zn(II) Titrations.** No significant differences were found in the absorption titrations of L1, L2, and L3 with $Co(BF_4)_2$, $Ni(BF_4)_2$, or $Zn(CF_3SO_3)_2$. Figures 7A and 8A show the absorption titrations of L1 with Co(II) and L3 with Zn(II), respectively. The addition of these salts to dichloromethane solutions of these ligands caused a red shift of the anthracene bands, as well as a decrease of the extinction coefficient of these absorption bands. No changes were observed around 300 nm, which suggests that there were no interactions between the pyridine groups and the metal ions.

Figures 7B and 8B show the emission titrations of L1 with Co(II) and L3 with Zn(II), respectively. Although, as in the cases of Pd(II) and Cu(II), initial additions of Co(II), Ni(II), or Zn(II) increase the fluorescence of dichloromethane solutions of L1, L2, or L3, as a consequence of the partial protonation of the ligands, the following additions of these metal ions cause neither the shift nor the quenching of these emissions. The absence of CHEQ effects together with the nonappearance of absorption bands around 300 nm suggest that there is no interaction between ligands and metal ions. This could be due to the fact that the protonated forms of these ligands compete effectively with the metal ions and prevent the formation of the complexes. The different behavior of these two groups of metal ions is attributed to the different stabilities of their complexes, since the Co(II), Ni(II), and Zn(II) complexes of these ligands are probably less stable than those of Pd(II) and Cu(II). This explains why no complex could be isolated by reacting L1 with noncoordinating salts of Co(II), Ni(II), or Zn(II).

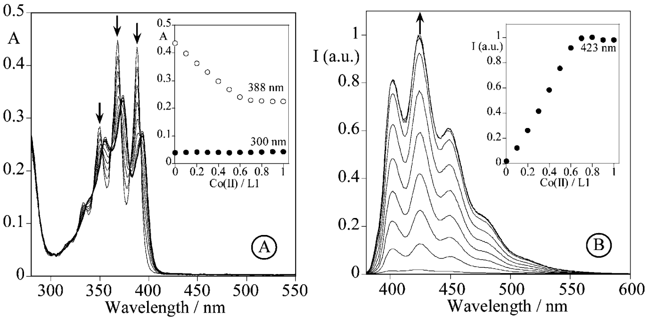

**Figure 7.** (A) Absorption spectra of a dichloromethane solution of L1 as a function of increasing amounts of $Co(BF_4)_2$. The inset shows the absorbances at 300 and 388 nm. (B) Emission spectra of a dichloromethane solution of L1 as a function of added $Co(BF_4)_2$. The inset shows the normalized fluorescence intensity at 423 nm. $[L1] = 4.73 \times 10^{-5}$ M, $[Co(BF_4)_2] = 2.90 \times 10^{-3}$ M, $\lambda$exc = 368 nm.

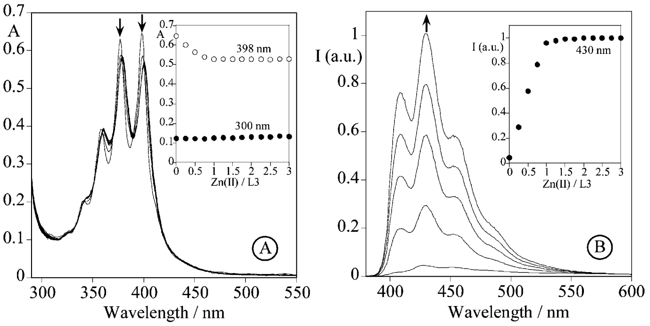

**Figure 8.** (A) Absorption spectra of a dichloromethane solution of L3 as a function of added $Zn(CF_3SO_3)_2$. The inset shows the absorbances at 300 and 398 nm. (B) Emission spectra of a dichloromethane solution of L3 as a function of added $Zn(CF_3SO_3)_2$. The inset shows the normalized fluorescence intensity at 430 nm. $[L3] = 5.55 \times 10^{-5}$ M, $[Zn(CF_3SO_3)_2] = 3.04 \times 10^{-3}$ M, $\lambda$exc = 377 nm.

## Conclusions

Two different methods have been used to synthesize three new fluorescent devices based on a $N_2S_2$ pyridine-anthracene-containing macrocycles. The first one is based on the functionalization of the secondary amine-containing macrocycle **4** with an appropriate anthracenyl synthon, via a $S_N2$ reaction. The second method is based on a cyclization reaction between a dithiol-pyridine-containing synthon and a dichloro-anthracene-containing synthon. Under the appropriate conditions, both methods make it possible to obtain the desired chemosensors in similar yields.

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(37) If a highly charged metal ion with a small volume is hydrated, it effectively attracts the bonding electron pairs in the O−H bonds of the water molecules that surround it. As a result, the hydrogen atoms in these water molecules become available as protons that can be extracted by other water molecules. The higher the charge of the cation and the smaller its volume, the more the O−H bonds are polarized and the more readily the hydrated ion donates protons to water molecules.

(38) (a) Czarnik, A. W. *Fluorescent Chemosensors for Ion and Molecule Recognition*; American Chemical Society: Washington, D. C., 1993. (b) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; Sandanayake, K. R. A. S. *Chem. Soc. Rev.* **1992**, *21*, 187−185. (c) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; McClenaghan, N. D.; Roiron, J. *Coord. Chem. Rev.* **1999**, *186*, 297−306.

The spectrophotometric and spectrofluorimetric titrations of dichloromethane solutions of L1 and L2 show two well-defined protonation processes due to the protonation of the secondary amine and the pyridine ring, respectively. However, the presence of four basic sites in the structure of bis macrocycle L3 produces a complex acid–base system, since its two macocyclic rings do not act as isolated moieties.

The absorption and fluorescence titrations of L1, L2, and L3 with Pd(II) or Cu(II) reflect the existence of ligand–metal interactions. However, these interactions have not been observed by titrating these ligands with Co(II), Ni(II), or Zn(II). This different behavior is attributed to the different stabilities of the resulting complexes, which could be useful in the design and preparation of new selective fluorescence devices.

Each Pd(II) or Cu(II) ion interacts with one macrocyclic moiety; therefore, these metals ions lead to the formation of complexes with a 1:1 stoichiometry by reaction with L1 and L2 and 1:2 L/M stoichiometry by reaction with L3.

Initial additions of ethanol or acetonitrile solutions of Pd(II), Cu(II), Co(II), Ni(II), or Zn(II) to dichloromethane solutions of L1, L2, or L3 produce an increase of the emission as a consequence of the protonation of their aliphatic amines. This protonation is attributed to the presence of water in the metal ion solutions, which permits hydrolysis of the metal ions.

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**Supporting Information Available:** Absorption and emission titrations of L1, L2, and L3 with $Pd(BF_4)_2$, $Cu(CF_3SO_3)_2$, $Co(BF_4)_2$, $Zn(CF_3SO_3)_2$, and $Ni(BF_4)_2$ not reported in this paper. X-ray crystallographic data in CIF format for L1 and $[Cu(ClO_4)(L1)](ClO_4)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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