

Synthesis, Characterization and Spectroscopic Studies of two new Schiff-base bithienyl pendant-armed 15-crown-5 molecular probes.

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Abstract

Two new ligands provided with a 15-crown-5 as receptor unit and bithiophen unit as emissive probe have been synthesized and characterized in order to evaluate the coordination capabilities and their sensor effect. Ligand L1 presents an aromatic crown ether moiety directed linked to the imine-2,2'-bithiophene π -conjugated system and ligand L2 is constituted by an aliphatic crown ether moiety linked to the same imine-2,2'-bithiophene system through a methylene unit. Solid metal complexes of Ni(II), Pd(II), Hg(II) and Na(I) have been synthesized using both macrocyclic compounds, and have been studied in solution in the presence of the same metal ions. All solid compounds have been characterized by common analytical and spectroscopic techniques. The sensorial effect has been studied using absorption, emission and MALDI-TOF-MS spectroscopy.

Keywords: Nickel(II); Palladium(II); Mercury(II); Sodium(I); Bithiophene; Crown ether, Schiff base, Luminescence

Very recently G. W. Gokel and coworkers [1] and S. Fery-Forgues and coworker [2] have reviewed the importance of the crown ethers as molecular sensors for ions, molecular scaffolds and complexing agents. Many of these systems are provided with rigid binding units, molecular tweezers, butterfly structures, molecular rods, etc, presenting two well defined coordination units.

These compounds are very appealing due to the potentially application for simultaneous recognition of such as a transition metal ion and an alkaline or alkaline-earth metal ion [3-6]. The interaction with two metal ions normally modulates several interesting properties, as it has been reported previously. For example in compound I [3] (Scheme 1) the complexation capability was modulated by the alkaline Na(I), in compounds II and III the redox behavior of the Ni(II) and Re(I) complexes respectively was modulated by the alkaline and alkaline earth metals [4, 5]. Finally, the liquid crystal property in compound III has been also modulated with the presence of Na(I) [6]. Recently, we have synthesized and characterized several heterocyclic compounds functionalized with (oligo)thiophene π -conjugated systems for sensor applications [7]. Tertiary amines functionalized with a methylene crown ether moiety and two (oligo)thiophene pendants are one of the most recent examples of new heterocyclic sensors reported by us. In this case Na(I) or H⁺ modulated the intensity of the emission shown by the Pd(II) complexes [7d].

Active molecules that interact with analytes through the enhancement of any particular property are very appealing for analytical applications; particularly active molecules to be detected and used by spectrometry techniques are very interesting for their further use as MS-active matrices [8].

As a part of our research project in multifunctional/multisensorial molecular probes and keeping this alkaline/alkaline-earth modulation properties idea in mind, we report here two new compounds, **L1** and **L2**, (Scheme 2) provided with a bithiophene emissive unit covalently linked through an imine bond to a

15-crown-5 chelating unit (Scheme 2) [9]. We were particularly interested in explore the effect of the flexibility of the chemical spacer between the bithiophene heterocyclic system and the crown ether moiety and the influence of Na(I) on the spectroscopic properties. Moreover, solid metal complexes have been obtained by direct reaction between ligands **L1** and **L2** and Nickel(II) perchlorate, Palladium(II) tetrafluoroborate and Mercury(II) triflate salts respectively [10]. In all cases, mononuclear complexes have been isolated except when sodium(I) was added to the palladium(II) complexes, where dinuclear compounds Na(I)Pd(II) were obtained in both cases. The synthesis and characterization have been performed as reported [11]

The electronic absorption characterization of **L1** and **L2** were performed in acetonitrile solution and are shown in Figure 1A. The absorption spectrum of **L1** shows two bands centered at 380 nm and 250 nm with molar extinction coefficients of 34.8×10^3 and $16.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1} \text{ L}$ respectively.

Semi-empirical ZINDO/S electronic structure calculations indicated that these low energy transitions are predominantly π - π^* from the imine-bithiophene units directly linked to the crown-ether and also with some contribution of the benzene group in **L1**.

L2 shows the most intense absorption band blue shifted with respect to **L1** with a maximum centered at 340 nm ($11.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and appear in the same region for the bithiophene precursor band (Figure 1B).

Excitation of ligand **L1** at 380 and 402 nm does not show any fluorescence emission. On the other hand, excitation of **L2** at 340 nm shows a very low emission centered at 405 nm with a Stock shift of 65 nm (Figure 1). This emission is very similar in shape to the emission observed for the 2,2'-bithiophene precursor (Figure 1B), but with a red-shift in 50 nm due to the electronic delocalization impose by the imine bond.

The fluorescence quantum yield of **L2** in acetonitrile was 0.028 determined using a solution of quinine sulphate in H_2SO_4 0.5M as standard reference ($\phi = 0.546$). [12]

The effect of Ni(II), Pd(II) and Hg(II) complexation on absorption, fluorescence and MALDI-TOF-MS spectra were studied dissolving both ligands in acetonitrile and titrating with the metal ions.

The absorption spectra of **L1** in the presence of Pd(II) shows a small red-shift after the addition of one equivalent of metal. The bands are shifted from 250 to 270 nm, and from 380 to 405 nm. For the other metals studied no change was observed. Excitation of the complexes of **L1** at 380 or 405 nm any emission was observed in all cases.

Ligand **L2** proves to be useful as absorption and fluorescence molecular probe for Ni(II), Pd(II) and Hg(II). Addition of Ni(II) and Hg(II) induced a red shift in *ca.* 15 nm in the absorption spectra while Pd(II) shows a *ca.* 45 nm red-shift. (See Figure 2A). At the same time a very strong emission was observed upon Pd(II) complexation. The intensity of emission observed upon Ni(II) and Hg(II) addition was very small when compared with the Pd(II) complex. This emission is not affected after the addition of an excess of Na(I) (up to 100 equivalents).

Figure 2A shows the absorption titration of ligand **L2** at different concentrations of Pd(II) after the addition of one equivalent of Na(I). Isosbestic points were observed at 296 and 362 nm, suggesting at least two species in solution, the complex L2-Na(I) and the Pd(II)Na(I) complex. The inset show the absorption maxima for the bands corresponding to these two species; changes in absorbance finished after addition of one equivalent of metal ion, results that are in agreement with the mononuclear complexes obtained by direct synthesis [10].

Fluorescence titration is represented in Figure 2B upon excitation in the isosbestic point at 360 nm. The stoichiometry was also confirmed from this titration, panel B figure 2; significant enhancement of the fluorescence intensity and a strong red shift was observed upon addition of one equivalent of Pd(II). Addition of the second equivalent of Pd(II) produce a partial quenching of the emission. The inset of Figure 2B depicts the emission at 410 nm (ligand band) and at 480 nm (complex band); this effect could be attributed to a conformational change in the position and involvement of the bithiophene chromophore with the metal center, where the S-donor atoms have some

interaction with the Pd(II). Similar effect was reported recently by us with a family of tertiary amines bearing (oligo)thiophene and crown ether moieties. [7d]. This result suggests that ligand **L2** could be used as a new active emissive probe to detect Pd(II) by fluorescence spectroscopy in organic solvents, and point out the future application of **L2** as a probe for Pd(II) detection during organic synthesis with Pd(II) as catalyst. Also is very important to mention that due to the open-shell electronic property of Pd(II) (d^8 element) a positive probe for Pd(II) detection is not common [13,7] because normally Pd(II) complexation produces a quenching in the fluorescence intensity.

A MALDI-TOF-MS study was performed using ligands **L1** and **L2**. The samples were dissolved in acetonitrile ($1-2\mu\text{g}/\mu\text{L}$) and no matrix was added to obtain the mass spectra [11].

Figure 3A shows the MALDI-TOF-MS spectrum without matrix of ligand **L1** after addition of one equivalent of Na(I) metal ion. The spectrum shows strong peaks at 483.5 and 460.5 m/z attributable to the fragments $[\text{L1Na}]^+$ and $[\text{L1H}]^+$ respectively. Two small fragmentations peaks at 306.7 and 242.8 m/z can also be observed due to the fragmentation of the ligand.

Figure 3B presents the bimetallic titration with Na(I) and Pd(II) by MALDI-TOF-MS spectrometry. The spectrum of ligand **L1** after the Na(I) and Pd(II) addition shows strong peaks at 460.5, 483.5, 566.4 m/z attributable to the fragments $[\text{L1H}]^+$, $[\text{L1Na}]^+$, $[\text{L1PdH}]^+$. Other peaks due to fragmentation are observed. At higher mass value two peaks at 917.4 and 1023.4 m/z attributable to the association fragments of two ligands $[\text{2L1}]^+$ and metal complex $[\text{2L1Pd}]^+$ are also observed.

The same experiments have been carried out with ligand **L2**. Figure 4A and Figure 4B show the MALDI-TOF-MS spectra of **L2** after sodium(I) addition and after sodium(I) and palladium(II) titration. In both experiments the ligand acts as chemosensor and as MALDI-TOF-MS active matrix.

Figure 4A shows the most intense peaks at 426.7 and 448.7 m/z attributable to the $[\text{L2H}]^+$ and $[\text{L2Na}]^+$ fragments. At higher values a peak at 890.1 m/z was

observed. This peak is attributable to with the specie containing two ligands, one sodium atom and one water molecule.

Peaks at 585.0 and 780.7 corresponding to the species $[\mathbf{L2Pd}(\text{H}_2\text{O})_3]^+$ and $[\mathbf{L2NaPd}(\text{ClO}_4)(\text{BF}_4)(\text{CH}_3\text{CN})]^+$ can also be observed (see Figure 4B).

Upon titration of **L2** with Ni(II), a peak at 583.5 *m/z*, attributed to the species $[\mathbf{L2Ni}(\text{ClO}_4)]^+$, appears in the spectrum as the most intense one. In the presence of Hg(II) three peaks at 426.6, 448.6 and 662.2 *m/z* have been observed; these peaks can be attributed to the fragments $[\mathbf{L2H}]^+$, $[\mathbf{L2Na}]^+$ and $[\mathbf{L2Hg}(\text{H}_2\text{O})_2]^+$ respectively.

In order to compare these results with the solid complexes synthesized, all the metal complexes have been characterized by MALDI-TOF-MS spectrometry using the same procedure, and their results are summarized in the experimental section.

In conclusion two new molecular probes containing a 15-crown-5 as receptor unit and bithiophen unit as emissive chromophore have been synthesized and characterized. Their coordination and sensor capabilities using absorption, emission and MALDI-TOF-MS spectroscopies were explored.

All results shows that ligands **L1** and **L2** can be used as a new actives probes for Pd(II), Pd(II)Na(I), Hg(II) and Ni(II) by absorption (**L1** and **L2**), Fluorescence emission (**L2**) and MALDI-TOF-MS (**L1** and **L2**).

Acknowledgments

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Captions for Figures

Scheme 1.- Examples of crown ether ligands used for transition metal-alkaline metal combinations.

Scheme 2.- Synthesis of **L1** and **L2** receptors, and computer drawn structures for both ligands produced with HYPERCHEM version 7.0, for illustration purposes only (bottom).

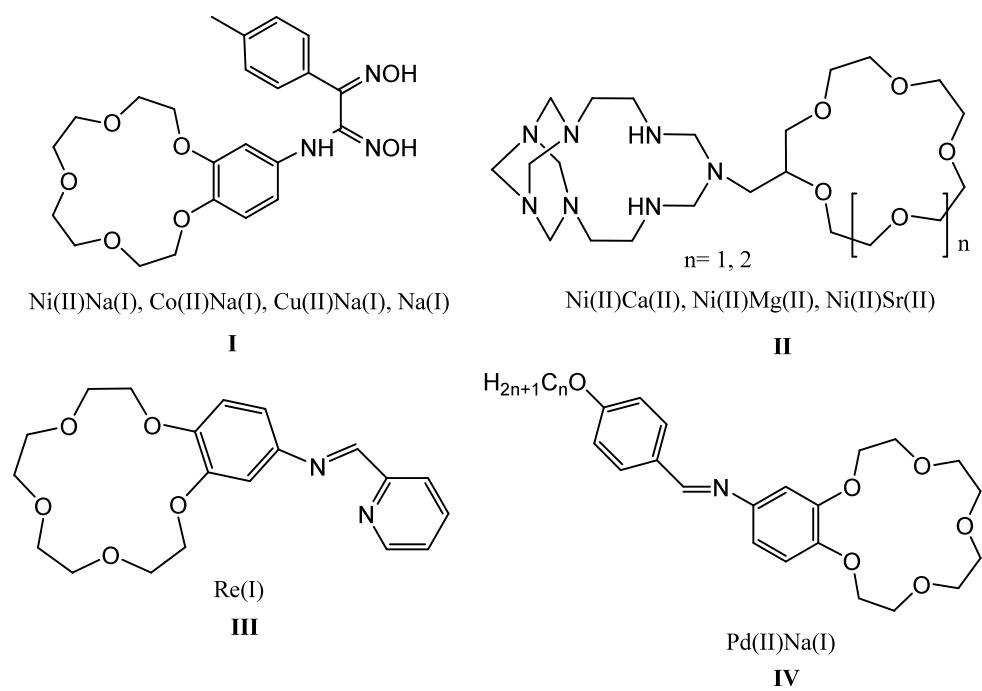
Figure 1.- A) Absorption spectrum of **L1** and absorption and emission spectra of **L2** in acetonitrile solution ($[\mathbf{L1}] = 1.04 \times 10^{-5} \text{M}$; $[\mathbf{L2}] = 4.02 \times 10^{-5} \text{M}$, $\lambda_{\text{exc}} = 361 \text{nm}$). B) Absorption (\circ) and emission (\square) spectra of the organic precursor 2,2'-bithiophene-5-carbaldehyde. ($[\text{BTP}] = 4.65 \times 10^{-6} \text{M}$, $\lambda_{\text{exc}} = 354 \text{nm}$) and absorption (\bullet) and emission (\blacksquare) spectra of the precursor 4'-aminobenzo-15-crown-5 [**4AMC**] = $8.82 \times 10^{-6} \text{M}$, $\lambda_{\text{exc}} = 298 \text{nm}$) in acetonitrile.

Figure 2.- Absorption (A) and Emission(B) titration of **L2** in the presence of Pd(II) after addition of an initial one equivalent of Na(I) in acetonitrile solution ($[\mathbf{L2}] = 4.02 \times 10^{-5} \text{M}$, $\lambda_{\text{exc}} = 361 \text{nm}$). The insets show the absorption at λ_{abs} 341 and 385 nm (Pd(II) complex) and fluorescence emission at 410 and 481 nm (Pd(II) complex).

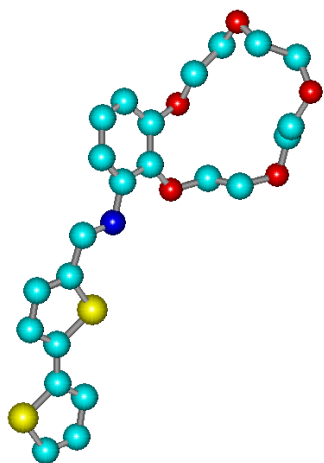
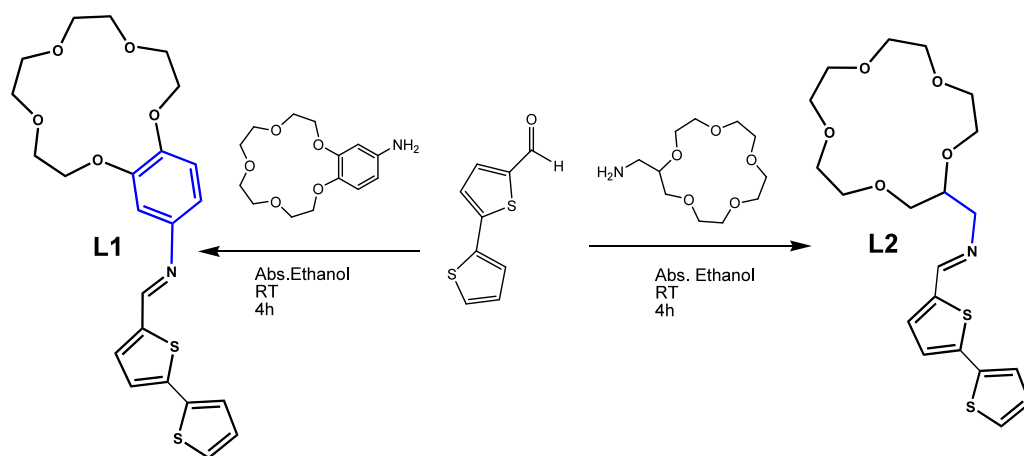
Figure 3.- A) MALDI-TOF-MS spectra of **L1** in the presence of one equivalent of Na(I) without matrix in acetonitrile solution. B) MALDI-TOF-MS spectra of **L1Na** after the addition of one equivalent of Pd(II).

Figure 4.- A) MALDI-TOF-MS spectra of **L2** in the presence of one equivalent of Na(I) without matrix in acetonitrile solution. B) MALDI-TOF-MS spectra of **L2Na** after titration with one equivalent of Pd(II).

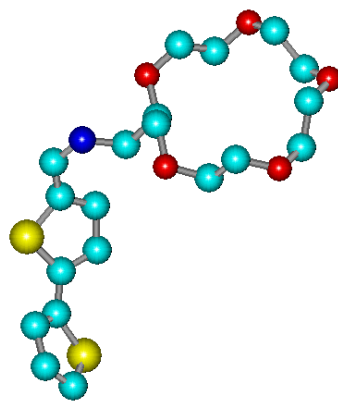
Figures



Scheme 1



L1



L2

Scheme 2

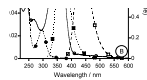
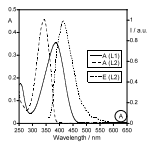


Figure 1

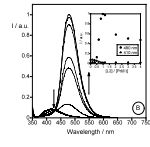
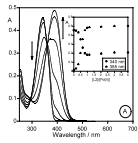


Figure 2

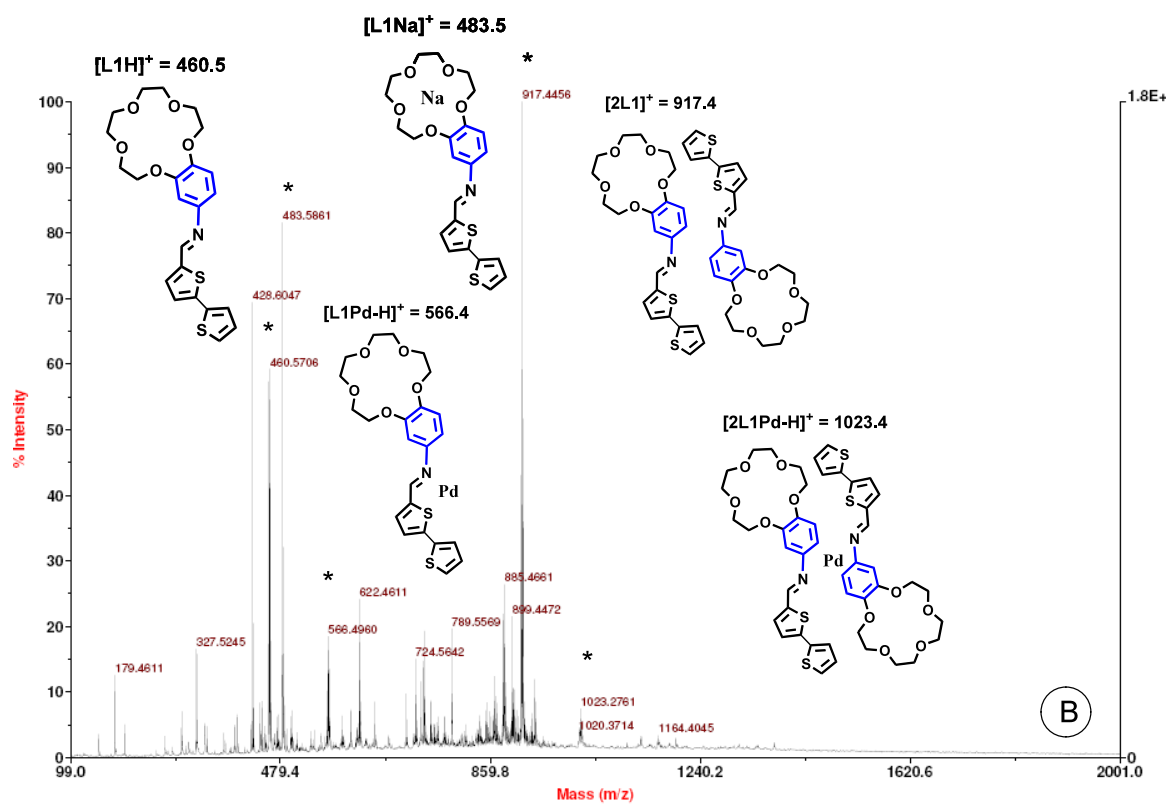
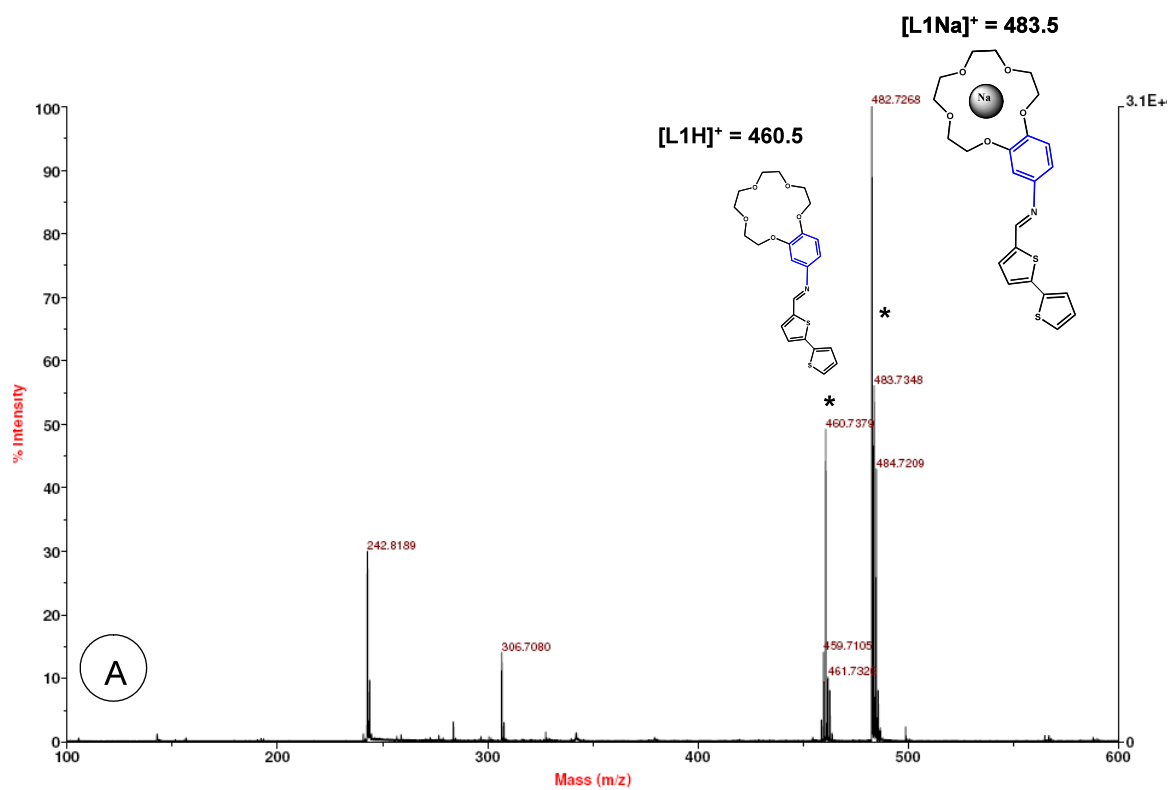


Figure 3

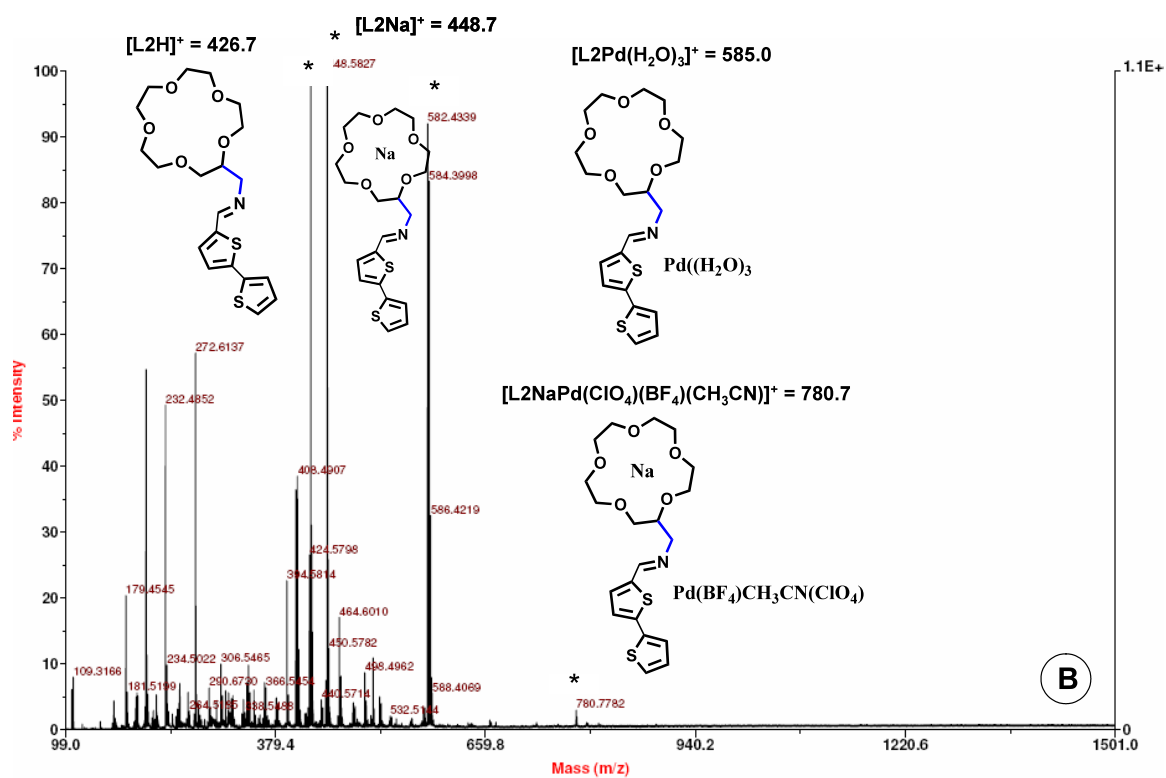
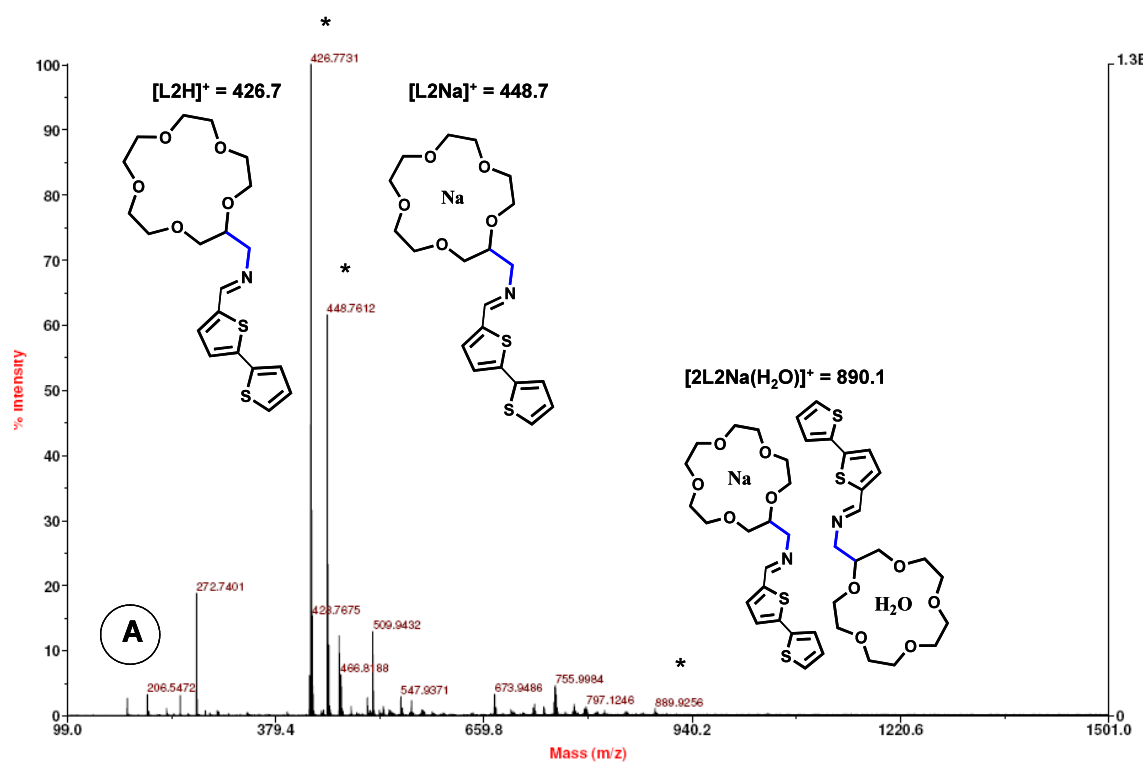


Figure 4

References

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- [1] G. W. Gokel, W. M. Leevy, M. E. Weber, *Chem. Rev.* 104 (2004) 2723
- [2] S. Fery-Forgues, F. Al-ali, *J. Phot. Photobiol. C. Photochem. Revs.* 5 (2004) 139
- [3] (a) E. Karapinar, E. Özcan, *J. Incl. Phen. Mac. Chem.*, 47 (2003) 59.
- [4] (b) J-E. Jee, M. C. Chang, C-H. Kwak, *Inorg. Chem. Commun.*, 7 (2004) 614.
- [5] (c) K. M-C. Wong, W-P. Li, K. K-K. Cheung, V. W-W. Yam, *New. J. Chem.*, 29 (2005) 165.
- [6] (d) J. Arias, M. Bardají, P. Espinet, *J. Organomet. Chem.*, 691 (2006) 4990.
- [7] (a) R. M. F. Batista, E. Oliveira, S. P. G. Costa, C. Lodeiro, M. M. M. Raposo, *Org. Lett.* 9 (2007), 3201; (b) S. P. G. Costa, E. Oliveira, C. Lodeiro, M. M. M. Raposo, *Sensors* 7 (2007) 2096; (c) S. P. G. Costa, E. Oliveira, C. Lodeiro, M. M. M. Raposo, *Tetrahedron Lett.* 49 (2008) 5258; (d) R. M. F. Batista, E. Oliveira, S. P. G. Costa, C. Lodeiro, M. M.M. Raposo, *Tetrahedron Letters* 49 (2008) 6575. (e) R. M. F. Batista, E. Oliveira, C. Nunez, S. P. G. Costa, C. Lodeiro, M. M. M. Raposo, *J. Phys. Org. Chem.* (2008) DOI 10.1002/poc.1440.
- [8] B. Pedras, H. M. Santos, L. Fernandes, B. Covelo, A. Tamayo, E. Bértolo, T. Avilés, J. L. Capelo, C. Lodeiro, *Inorg. Chem. Commun.*, 10 (2007) 925.
- [9] Ligands **L1** and **L2** were prepared as follows. A solution of 4'-aminobenzo-15-crown-5 (**L1**) (1 mmol) or 2-(aminoethyl)-15-crown-5 (**L2**) (0.5 mmol) in absolute ethanol (30 mL) was added dropwise to a solution of 2,2'-bithiophene-5-carbaldehyde (1.0 (**L1**) or 0.5 (**L2**) mmol) in the same solvent (30 mL). The resulting solution was gently refluxed with magnetic stirring for ca. 8 h. As no changes were observed, the solution was cooled to room temperature and

kept under stirring 24h. A yellow solution was obtained in both cases, which after solvent removal rendered compounds **L1** and **L2** as a solid powder and an oil respectively. Both compounds were washed twice with diethyl ether (10 mL) and dried under vacuum.

L1: Colour: Yellow. Yield 0.429 g (94 %). Anal. Calcd for $C_{23}H_{25}NO_5S_2 \cdot 2EtOH$: C, 58.78; H, 6.75; N, 2.55; S, 11.62. Found: C, 58.32; H, 6.20; N, 2.90; S, 11.54. IR (cm^{-1}): $\nu_{(C=Nimine)}$, 1610. 1H NMR (400 MHz, CD_3CN): $\delta = 8.62$ (s, 1H)_{imine}. $\delta = 7.70-6.70$ (m, 8H), $\delta = 4.40-3.54$ (m, 16H). MS (EI) m/z : 459.10 [**L1**]⁺; 460.50 [**L1H**]⁺

L2: Colour: Orange. Yield 0.179 g (84%). Anal. Calcd for $C_{20}H_{27}NO_5S_2 \cdot 1.5H_2O$: C, 53.10; H, 6.68; N, 3.10; S, 14.17. Found: C, 53.00; H, 6.30; N, 2.90; S, 14.28. IR (cm^{-1}): $\nu_{(C=Nimine)}$, 1628; 1H NMR (400 MHz, CD_3CN): $\delta = 8.24$ (s, 1H)_{imine}, $\delta = 7.34$ (d, 1H), $\delta = 7.27$ (d, 1H), $\delta = 7.22$ (d, 1H), $\delta = 7.15$ (d, 1H), $\delta = 7.02-7.00$ (m, 1H), $\delta = 3.70-3.40$ (m, 21H). MS (EI) m/z : 425.13 [**L2**]⁺; (MALDI-TOF-MS): 426.61 [**L2H**]⁺

[10] Metal complexes. General Procedure.

L1: A solution of the corresponding metal salt (0.1 mmol, 25 mL) in acetonitrile was added to a solution of **L1** (0.1 mmol, 20 mL) in the same solvent. On the addition of the metal salt the solution changed from yellow to orange for Ni(II), yellow to red for Pd(II), and yellow to orange for Hg(II). The reaction mixture was stirred overnight at room temperature. In the case of the heterodinuclear compound of Pd(II)Na(II) after half an hour of the Pd(II) addition a solution of $NaClO_4 \cdot H_2O$ (0.1 mmol) in acetonitrile was added.

As no further changes were observed, the solvent was evaporated and a solid was obtained. All compounds were washed twice with cold diethyl ether (10 mL) and dried under vacuum.

L1Ni(BF₄)₂·H₂O: Color: Brown/red. Yield 0.063 g (81%). Anal. Calcd for $C_{23}H_{27}B_2F_8NNiO_6S_2$: C, 38.91; H, 3.83; N, 1.97; S, 9.03; Ni, 8.27. Found: C,

39.20; H, 3.81; N, 1.66; S, 8.93; Ni, 8.37. IR (cm^{-1}): $\nu_{(\text{C}=\text{Nimine})}$, 1634; MS (MALDI-TOF-MS): 460.10 [**L1H**]⁺; 623.09 [**L1NiBF₄(H₂O)**]⁺.

L1Pd(CH₃CN)₂(BF₄)₂·5H₂O: Color: Red. Yield 0.068 g (68%). Anal. Calcd for C₂₇H₄₁B₂F₈N₃O₁₀PdS₂: C, 35.57; H, 4.53; N, 4.61; S, 7.03. Found: C, 35.14; H, 4.30; N, 4.02; S, 7.29. IR (cm^{-1}): $\nu_{(\text{C}=\text{Nimine})}$, 1650. MS (MALDI-TOF-MS): 653.80 [**L1PdBF₄**]⁺.

L1Hg(CF₃SO₃)₂·H₂O: Color: Brown. Yield 0.056 g (53%). Anal. Calcd for C₂₅H₂₇F₆HgNO₁₂S₄: C, 30.75; H, 2.79; N, 1.43; S, 13.14; Hg, 20.55. Found: C, 31.06; H, 2.58; N, 1.25; S, 13.02; Hg, 20.75 IR (cm^{-1}): $\nu_{(\text{C}=\text{Nimine})}$, 1652. MS (MALDI-TOF-MS): 847.70 [**L1Hg(CF₃SO₃)₂·2H₂O**]⁺.

L1Pd(CH₃CN)₂(BF₄)₂NaClO₄·4H₂O: Color: Dark red. Yield 0.099 g (85%). Anal. Calcd for C₂₇H₃₉B₂ClF₈N₃NaO₁₃PdS₂: C, 31.90; H, 3.87; N, 4.13; S, 6.31. Found: C, 30.86; H, 3.30; N, 3.95; S, 6.38. IR (cm^{-1}): $\nu_{(\text{C}=\text{Nimine})}$, 1650. MS (MALDI-TOF): 804.65 [**L1PdNa(BF₄)₂(CH₃CN)**]⁺.

L2: A solution of the corresponding metal salt (0.1 mmol, 25 mL) in acetonitrile or absolute ethanol was added to a solution of **L2** (0.1 mmol, 20 mL) in the same solvent. In the case of Ni(II) and Hg(II) absolute ethanol was used, while for Pd(II) acetonitrile was used, in order to avoid the Palladium(II) reduction. On the addition of the metal salt the solution changed from yellow to red-orange for Pd(II), and no change in the cases of Ni(II) and Hg(II). The reaction mixture was stirred overnight at room temperature.

As no further changes were observed, the solvent was evaporated and a solid was obtained. All compounds were washed twice with cold diethyl ether (10 mL) and dried under vacuum.

L2Ni(ClO₄)₂·5H₂O: Color: Yellow. Yield 0.116 g (44%). Anal. Calcd for C₂₀H₃₇Cl₂NNiO₁₈S₂: C, 31.10; H, 4.82; N, 1.80; S, 8.29; Ni, 7.59. Found: C, 31.53; H, 5.15; N, 1.79; S, 8.55; Ni, 7.80. IR (cm^{-1}): $\nu_{(\text{C}=\text{Nimine})}$, 1654. MS (MALDI-TOF-MS): 426.61 [**L2H**]⁺; 583.5 [**L2Ni(ClO₄)**]⁺.

L2Pd(CH₃CN)₄(BF₄)₂: Color: Red. Yield 0.049 g (55%). Anal. Calcd for C₂₈H₃₉B₂F₈N₅O₅PdS₂: C, 38.66; H, 4.52; N, 8.05; S, 7.37. Found: C, 38.25; H, 4.87; N, 7.75; S, 7.75. IR (cm⁻¹): ν_(C=Nimine), 1650. MS (MALDI-TOF-MS): 426.76 [L2H]⁺; 702.10 [L2Pd(CH₃CN)₂(BF₄)₂]⁺.

L2Hg(CF₃SO₃)₂.H₂O: Color: Green. Yield 0.090 g (95%). Anal. Calcd for C₂₂H₂₉F₆HgNO₁₂S₄: C, 28.05; H, 3.10; N, 1.49; S, 13.61; Hg, 21.29. Found: C, 28.41; H, 3.26; N, 1.62; S, 13.47; Hg, 21.60. IR (cm⁻¹): ν_(C=Nimine), 1663. MS (MALDI-TOF-MS): 426.68 [L2H]⁺; 776.53 [L2Hg(CF₃SO₃)₂]⁺.

L2Pd(CH₃CN)₂(BF₄)₂NaClO₄: Color: Red. Yield 0.100 g (98 %). Anal. Calcd for C₂₄H₃₃B₂ClF₈N₃NaO₉PdS₂: C, 31.67; H, 3.65; N, 4.62; S, 7.05. Found: C, 31.32; H, 3.90; N, 4.99; S, 6.74. IR (cm⁻¹): ν_(C=Nimine), 1656. MS (MALDI-TOF-MS): 426.75 [L2H]⁺; 730.63 [L2PdNa(BF₄)₂]⁺; 742.10 [L2PdNa(ClO₄)(BF₄)₂]⁺.

[11] Chemicals and Starting materials

4'-aminobenzo-15-crown-5, 2-(aminoethyl)-15-crown-5, 2,2'-bithiophene-5-carbaldehyde, and Ni(ClO₄)₂·6H₂O, Ni(BF₄)₂·6H₂O, Pd(BF₄)₂·4(CH₃CN) and NaClO₄ were commercial products from Aldrich used without further purification. Hg(CF₃SO₃)₂ was a commercial product from Strem-Chemicals. Solvents were of reagent grade purified by the usual methods.

Instrumentation

Elemental analyses were carried out by the REQUIMTE DQ, Universidade Nova de Lisboa Service on a Thermo Finnigan-CE Flash-EA 1112-CHNS Instrument. Infrared spectra were recorded as KBr discs or in Nujol using Bio-Rad FTS 175-C spectrophotometer. Proton NMR spectra were recorded using a Bruker WM-450 spectrometer. Electronic Impact spectra were determined on a Micromass GCT-TOF7000 and the MALDI-TOF-MS analysis have been performed in a MALDI-TOF-MS model voyager DE-PRO biospectrometry workstation equipped with a nitrogen laser radiating at 337 nm from Applied Biosystems (Foster City, United States) at the REQUIMTE, Chemistry Department, Universidade Nova de Lisboa. The acceleration voltage was

2.0×10^4 kV with a delayed extraction (DE) time of 200 ns. The spectra represent accumulations of 5×100 laser shots. The reflectron mode was used. The ion source and flight tube pressures were less than 1.80×10^{-7} and 5.60×10^{-8} Torr, respectively. The MALDI mass spectra of the soluble samples (1 or 2 $\mu\text{g}/\mu\text{L}$) such as the metal salts were recorded using the conventional sample preparation method for MALDI-MS. $1 \mu\text{L}$ were put on the sample holder on which the chelating ligand had been previously spotted. The sample holder was inserted in the ion source. Chemical reaction between the ligand and metal salts occurred in the holder and complexed species were produced.

Absorption spectra were recorded on a Perkin Elmer lambda 35 spectrophotometer and fluorescence emission on a Perkin Elmer LS45. The linearity of the fluorescence emission vs. concentration was checked in the concentration range used (10^{-4} - 10^{-6} M). A correction for the absorbed light was performed when necessary. All spectrofluorimetric titrations were performed as follows: the stock solutions of the ligand (ca. 1.00×10^{-3} M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting to the mark with absolute EtOH or acetonitrile UVA-sol. The titration solutions ($[\text{L}] = 1.00 \times 10^{-6}$ and 1.00×10^{-5} M) were prepared by appropriate dilution of the stock solutions. Titrations of both ligands were carried out by addition of microliter amounts of standard solutions of the ions in absolute ethanol or acetonitrile.

Semi-empirical molecular orbitals calculations were carried on with use of HYPERCHEM version 7.0. Hypercube Inv., 1115 NW 4th St., Gainesville, FL. 32601-4256, USA.

Ni(II) were measured with a Varian (Cambridge, UK) atomic absorption spectrometry model Spectra AA 20 plus equipped with a 10 cm burner head. Hollow-cathode lamps operated at 4 mA were used as radiation source. The wavelength (nm) and slit width (nm) used were 352.4 and 0.5.

Mercury(II) was determined in a Flow Injection System consisting of: a four channels Gilson (Villiers le Bel, France) Minipuls 2 peristaltic pump, a four channels Ismatec (Glattbrugg, Switzerland) programmable peristaltic pump model Reglo Digital MS-4/12; a Perkin-Elmer (Uberlingen, Germany) membrane gas-liquid separator; a six-port injection valve (Supelco, Bellefonte, PA) with a

500- μL loop, and a Fisher and Porter (Warminster, PA) flow meter (0–100% N_2 , 200 ml min^{-1}). Ismatec tygon tubing type R3607 of different internal diameters (2.06 and 3.15 mm id), was used for carrying the reducing agent, carrier solution, and waste solution. The initial conditions for cold vapour generation using SnCl_2 as a reducing agent were established in a previous works [14] and were: a 5% mass v^{-1} SnCl_2 solution in 10% v.v^{-1} HCl was used as reducing stream with a 3 mL min^{-1} flow rate; a 3% v.v^{-1} HCl solution was used as carrier with a 10 mL min^{-1} flow rate. A 200 mL min^{-1} flow-rate of carrier gas (N_2) was used. Mercury atomic absorbance was measured with a Thermo (Cambridge, UK) atomic absorption spectrometer model Solar S2 equipped with a homemade quartz tube. The quartz tube was kept at room temperature during operation. A mercury hollow-cathode lamp (Thermo) operated at 4 mA was used as a radiation source. The mercury line at 253.7 nm and a slit width of 0.5 nm were used for measurements. An inorganic mercury stock standard solution (Merck, Darmstat, Germany, 1 g.L^{-1}) was used. All stock standard solutions were stored in a refrigerator at 4 °C and protected from light. Working standard solutions were prepared just before use by appropriate dilution of the stock standard solution. Sn(II) chloride used as reducing agent was prepared by dissolving the appropriate mass of Sn(II) chloride dehydrate (Panreac, Barcelona, Spain) in concentrated hydrochloric acid and diluted with ultrapure water. Diluted hydrochloric acid (Merck) was used as carrier.

[12] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, "Handbook of Photochemistry", 3th Ed. CRC Press, Taylor & Francis Group, Boca Raton, New York (2006).

[13] (a) Q. E. Cao, Z. D. Hu, *Ind. J. Chem. A* 11 (1998) 1029; (b) Q. E. Cao, Y. K. Zhao, X. J. Yao, Z. D. Hu, Q. H. Xu, *Spectrochim. Acta A* 56 (2000) 1319

[14] (a) J.L. Capelo, G. M. Rivas, L. G. Oliveira, C. Villena, A. C. Santos, T. Valada, M. Galesio, P. Oliveira, M. D. R. Gomes de Silva, E. Gaspar, S. Alves, C. Fernandez,; Vaz, C.; *Talanta*, 68 (2006) 813. (b) A. Tamayo, B. Pedras, C.

Lodeiro, L. Escriche, J. Casabo, J. L. Capelo, B. Covelo, R. Kivekäs, R. Sillampää, *Inorg. Chem.*, 46 (2007) 7818.