The first substituted macrocyclic ligand Py$_2$N$_4$S$_2$ containing four naphthylmethylene pendant-armed groups: Synthesis and photophysical properties

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Abstract

The synthesis of a pendant donor emissive macrocyclic ligand Py$_2$N$_4$S$_2$ with up to four naphthylmethylene arms (L) has been achieved. Their derivative solid metal complexes (Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$ and Ag$^{+}$) have been isolated and characterized. The photophysical properties of the free ligand L and their complexation behaviour have been investigated in solution. In dichloromethane, the free ligand presents two emission bands which are related to the monomer naphthalene emission and a red-shifted band attributable to ground state dimers (interaction between two naphthalene chromophores), which was further validated from time-resolved data, with bi-exponential decay with absence of dynamic components. UV−Vis spectroscopy has revealed a 2:1 binding stoichiometry for Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Hg$^{2+}$ and Ag$^{+}$.

Keywords: Macrocycles, Dinuclear complex, Stability constant, Naphthalene, Pendant-arms, Sensor.

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Macrocyclic ligands bearing pendant donor arms have attracted considerable attention in recent years owing to their potential applications in catalysis, metal ion recognition, solvent extraction, mimicry of enzymes and radionuclide therapy [1].

A particularly large range of macrocycles are derived from triaza or tetrazamacrocycles. However, less is known about N-functionalized pendant-arms [3]. However, macrocyclic ligands incorporating nitrogen and sulfur in their framework are not as numerous, and reviews including flexible naphthylmethylene pendant-arms to study their photophysical properties in organic solution. We therefore, report what is, to our best knowledge, the first example of a pendant-armed derivative of the binucleating macrocyclic ligand Py$_2$N$_4$S$_2$ (L') [7], which has the capability of forming dinuclear complexes (Scheme 1).

During the recent years, we have also been involved in the investigation of several acyclic and macrocyclic ligands bearing two [8] and four [9] pendant-arms as naphthalene. It is well known that the coordination ability of these ligands increases when the macrocycles incorporate cheletating moieties such as phenanthroline [10] and pyridine [11] as unit heads.

In the present work we have combined the good coordination capability towards metal ions shown by ligand L with the introduction of four emissive flexible naphthylmethylene pendant-arms to study their photophysical properties in organic solution. We therefore, report what is, to our best knowledge, the first example of a pendant-armed derivative of the binucleating macrocyclic ligand Py$_2$N$_4$S$_2$ (L in Scheme 1) [12].

Ligand L was isolated as an air-stable brown solid in 68% yield and was characterized by elemental analysis, ESI-MS, IR and $^1$H NMR spectroscopy (see Fig. 1S in the Supplementary Material) [13]. The infrared spectrum (KBr disc) of L contains three bands at 854, 818 and 752 cm$^{-1}$, corresponding to the ν(C−H) out of the plane
bending vibrations for β-substituted naphthalenes. The other absorption bands corresponding to ν(C=N) and ν(C=C) vibrations from pyridine groups appear in their expected positions at 1589 and 1454 cm⁻¹, respectively.

The ESI-MS of L presents a peak at m/z 1007 and another at 504 confirming the presence of the ligand. The ¹H NMR spectra confirm the integrity and stability of the ligand in solution. The spectrum shows that the four quadrants of the macrocyclic ligand are chemically equivalent, as it would be expected for this kind of system. The ¹H-NMR spectrum at room temperature gives to unresolved broad signals, by reducing the temperature to 0 °C the signals appearing at higher resolution are better resolved.

The coordination ability of ligand L towards hydrated nitrate, perchlorate or triflate salts of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Ag⁺ was explored [14]. The complexes were characterized by elemental analysis, IR, MALDI-MS spectra and conductivity measurements [13]. The reaction of L with the metal salts in a 2:1 metal:ligand ratio, in ace tone, led to the formation of compounds of the type [M₂L]((X)₂·n H2O) (X = ClO₄⁻, NO₃⁻, Zn²⁺ and Cd²⁺, [M₂L]((X)₃·n H₂O) (X = NO₃⁻) for M = Ag⁺, and [ML]((CF₃SO₃)₂·n MeCN·n Et₂O·n H₂O for M = Hg²⁺).

The IR spectra of the complexes are similar. The vibrations ν(C=N) and ν(C=C) for pyridine groups appear to higher wavenumbers, suggesting pyridine nitrogen coordination to the metal atoms. The bands corresponding to the naphthalene groups are also slightly shifted to higher wavenumbers. The IR spectra of the nitrate complexes show the bending vibrations for (C=C) for pyridine groups appear to higher wavenumbers, ν(C=N) and ν(C=C) for pyridine groups appear to higher wavenumbers, suggesting pyridine nitrogen coordination to the metal atoms.

The MALDI mass spectra for all the complexes indicate the presence of the ligand. The ¹H NMR spectra confirm the presence of the ligand. The ¹H NMR spectra confirm the integrity and stability of the ligand in solution. The spectrum shows that the four quadrants of the macrocyclic ligand are chemically equivalent, as it would be expected for this kind of system.

Further knowledge on the species present in solution comes from time-resolved data. We have obtained the fluorescence decays of ligand L in dichloromethane with τ_max = 282 nm and λ_max = 325 and 450 nm (without degassing the solutions, i.e., in the presence of oxygen). These are therefore experimental conditions where we are exciting both the monomer and also the (possible) dimer existing in the ground state (see Fig. 2).

The decays are best fitted with a sum of two exponentials with decay times of 1.8 ns and 6.6 ns, which mirrors the fact that we are in the presence of two species, according to Eqs. (1) to (3).

Indeed the absence of a rising component (usually associated with a negative pre-exponential factor) at 450 nm shows that the long wavelength maxima at 322 nm) with a shoulder at ~390 nm suggesting the presence of an excimer [20]. The excitation spectrum collected in the monomer emission band (325 and 340 nm) matches the absorption spectrum.

The MALDI mass spectra for all the complexes indicate the presence of the ligand. The ¹H NMR spectra confirm the presence of the ligand. The ¹H NMR spectra confirm the integrity and stability of the ligand in solution. The spectrum shows that the four quadrants of the macrocyclic ligand are chemically equivalent, as it would be expected for this kind of system. The ¹H-NMR spectrum at room temperature gives to unresolved broad signals, by reducing the temperature to 0 °C the signals appearing at higher resolution are better resolved.

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The reaction of L with the metal salts in a 2:1 metal:ligand ratio, in acetone, led to the formation of compounds of the type [M₂L]((X)₂·n H₂O) (X = ClO₄⁻, NO₃⁻, Zn²⁺ and Cd²⁺, [M₂L]((X)₃·n H₂O) (X = NO₃⁻) for M = Ag⁺, and [ML]((CF₃SO₃)₂·n MeCN·n Et₂O·n H₂O for M = Hg²⁺).

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emission band is likely to be due to a ground state dimer rather than to an excited dimer (excimer).

Based on the bi-exponential nature of the decays, with absence of rising component and of the relatively invariance of the pre-exponential factors at the two emission wavelengths (the fluorescence decays are identical at the two emission wavelengths) we have faced a difficulty in the attribution of the decay times to each one of the species: monomer and dimer.

\[ I_\lambda(t) = \sum_{i=1}^{n} a_{i,j} e^{(-t/\tau_i)} \]

where for emission at 370 nm and 450 one obtains respectively

\[ I_{370\,nm}(t) = a_{1,1} e^{(-t/\tau_1)} + a_{1,2} e^{(-t/\tau_2)} \]

\[ I_{450\,nm}(t) = a_{2,1} e^{(-t/\tau_1)} + a_{2,2} e^{(-t/\tau_2)} \]

with \( \tau_1 = 1.8 \) ns and \( \tau_2 = 6.6 \) ns, \( a_{1,1} = 0.732, a_{1,2} = 0.268, a_{2,1} = 0.799 \) and \( a_{2,2} = 0.201 \).

Nevertheless the shorter component has a contribution of 42% to the total emission contribution at 325 nm whereas it increases to 51% at 450 nm. The longer (6.6 ns) component decreases its contribution from 58% to 49% upon going from 325 nm to 450 nm. From the emission spectra, it can be seen that the dimer has a higher contribution at longer emissions (\( \lambda > 400 \) nm). This together with the fact that at 325 nm (an emission region where the monomer emission is likely to be dominant) the 6.6 ns component contributes more suggests that the shorter component should be identified with the dimer lifetime and the longer with the monomer.

Therefore there is a ground-state equilibrium involving a monomer and dimer which are simultaneously excited at 282 nm leading to the emission of these two species.

Fluoroboric acid (HBF\(_4\)) and tetrabutylammonium hydroxide ([[(Bu)\(_4\)N]OH]) were used to change the acidity conditions of the solutions of ligand \( L \) in dichloromethane [18]. No changes were observed in the absorption and emission spectra of \( L \) in dichloromethane as a function of increasing amounts of HBF\(_4\) at room temperature, but different behaviour was observed after the addition of tetrabutylammonium hydroxide (see Fig. 3).

Fig. 3 shows the absorption and emission spectra of \( L \) in dichloromethane as a function of increasing amounts of [[(Bu)\(_4\)N]OH] at room temperature. The inset of Fig. 3A shows how, at 289 nm (which is not the absorption maximum), the absorbance increases with the number of equivalents of base added to the solution, stabilizing after the addition of two hydroxyl equivalents.

Fig. 3B shows the deprotonation effect in the fluorescence intensity. In the inset, the emission band at 339 nm, attributable to the naphthalene, decreases in intensity with basification until the fourth hydroxyl equivalent is added. The decrease in intensity can be attributed to the
As an example, Fig. 4 depicts the absorption and emission spectra of a dichloromethane solution of L in the presence of increasing amounts of Hg(CF3SO3)2. Addition of increasing amounts of Hg2+ to a solution of ligand L (1.00 × 10−5 M) at 298 K led to a small decrease in the fluorescence intensity. Results with additions of Co2+, Cu2+, Zn2+ and Ag+ were similar and are, therefore, not presented.

The absorption spectrum (Fig. 4A) is not affected by complexation. The inset shows the normalized fluorescence intensity at 339 nm (monomer emission). Upon addition of 2 equiv. metal ion, the monomer emission decreases; and at the same time, in all cases, the red-shifted band now seen to be centred at 480 nm increases.

The stability constants for the interaction of L with Co2+, Cu2+, Zn2+, Hg2+ and Ag+ were calculated using HypSpec software and are shown in Table 1. Taking into account the values obtained, the strongest interaction expected for sensor L is with Hg2+. This result could be due to the strong thiophilic affinity presented by Hg2+.

In summary, we have reported the first substituted macrocyclic ligand Py2N4S2 containing four naphthylmethylene pendant-armed groups postdoctoral Contracts SFRH/BD/75134/2010. C.S.d.C. thanks the Financial support. The authors thank the Xunta de Galicia (Spain) for the project PGI1D10PXIB209028PR, IN845B-2010-057, and 10CSA383009PR (Bio-medicine) for financial support. The authors thank the Scientific Association Proteomass (Portugal) for financial support. C.N. thanks Xunta de Galicia for their postdoctoral contract (I2C program). C.S.d.C thanks the Fundação para a Ciência e a Tecnologia/FEDER (Portugal/EU) programme postdoctoral Contracts SFRH/BD/75134/2010.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Interaction (M:L)</th>
<th>logβ</th>
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<tbody>
<tr>
<td>L</td>
<td>Co2+ (2:1)</td>
<td>5.14 ± 1.22 × 10−3</td>
</tr>
<tr>
<td></td>
<td>Cu2+ (2:1)</td>
<td>5.52 ± 1.72 × 10−3</td>
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<tr>
<td></td>
<td>Zn2+ (2:1)</td>
<td>5.46 ± 1.96 × 10−4</td>
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<tr>
<td></td>
<td>Hg2+ (2:1)</td>
<td>6.58 ± 1.23 × 10−4</td>
</tr>
<tr>
<td></td>
<td>Ag+ (2:1)</td>
<td>5.19 ± 1.58 × 10−10</td>
</tr>
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</table>

References


Acknowledgements

We are grateful to the Xunta de Galicia (Spain) for the project PGI1D10PXIB209028PR, IN845B-2010-057, and 10CSA383009PR (Bio-medicine) for financial support. The authors thank the Scientific Association Proteomass (Portugal) for financial support. C.N. thanks Xunta de Galicia for their postdoctoral contract (I2C program). C.S.d.C thanks the Fundação para a Ciência e a Tecnologia/FEDER (Portugal/EU) programme postdoctoral Contracts SFRH/BD/75134/2010.

Appendix A. Supplementary material

Supporting Information. (see footnote on the first page of this article): magnified emission (νexc = 282 nm) and excitation (νem = 410 nm) spectra. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.07.019.
ν(C = N)py and ν(C = C)py: 1108, 624, 1384 [NO3]−, 1384 [NO3]−.

Yield: 78%. IR (KBr, cm-1): 3459 [ν(OH)], 1050, 1450 [ν(C = C)py], 1119, 625, [ν(LO)], 859, 823, 795 [ν(C–H)aryl]. MALDI-MS (m/z): 1168 [CuL(LO)]2+, ωH + cm-1 (in acetonitrile): 214 (2:1). Color: green.

Cu2L4·2H2O. Anal. Calc. for Cu6H12O7Cl2 (MW: 1546.1): C, 51.1; H, 4.4; N, 5.4; S, 4.4. Found: C, 51.5; H, 4.7; N, 5.2; S, 4.4. Yield: 80%. IR (KBr, cm-1): 3448 [ν(OH)], 1607, 1454 [ν(C = N)py] and ν(LO) = 1119, 625, [ν(LO)], 859, 823, 795 [ν(C–H)aryl]. MALDI-MS (m/z): 1168 [CuL(LO)]2+, ωH + cm-1 (in acetonitrile): 214 (2:1). Color: green.

CuL(NO3)2·3H2O. Anal. Calc. for CuH4N2O4Cl2 (MW: 1434.3): C, 55.2; H, 5.0; N, 9.8; S, 4.5. Found: C, 55.5; H, 4.9; N, 9.2; S, 4.5. Yield: 78%. IR (KBr, cm-1): 3449 [ν(OH)], 1606, 1462 [ν(C = N)py] and ν(LO) = 1119, 625, [ν(LO)], 859, 823, 795 [ν(C–H)aryl]. MALDI-MS (m/z): 1088 [LO]-, 1194 [CuH(LO)]2+; ωH + cm-1 (in acetonitrile): 283 (2:1). Color: green.

Cu2L4·2H2O. Anal. Calc. for Cu6H12O7Cl2 (MW: 1546.1): C, 51.1; H, 4.4; N, 5.4; S, 4.4. Found: C, 51.5; H, 4.7; N, 5.2; S, 4.4. Yield: 80%. IR (KBr, cm-1): 3448 [ν(OH)], 1607, 1454 [ν(C = N)py] and ν(LO) = 1119, 625, [ν(LO)], 859, 823, 795 [ν(C–H)aryl]. MALDI-MS (m/z): 1168 [CuL(LO)]2+, ωH + cm-1 (in acetonitrile): 214 (2:1). Color: green.

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