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

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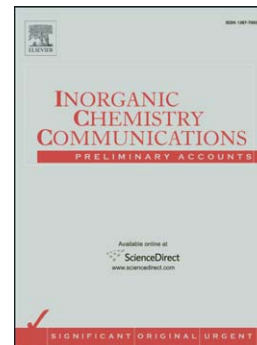
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The first substituted macrocyclic ligand $\text{Py}_2\text{N}_4\text{S}_2$ containing four naphthylmethylene pendant-armed groups: synthesis and photophysical properties

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Abstract

The synthesis of a pendant donor emissive macrocyclic ligand $\text{Py}_2\text{N}_4\text{S}_2$ 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^+ .

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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

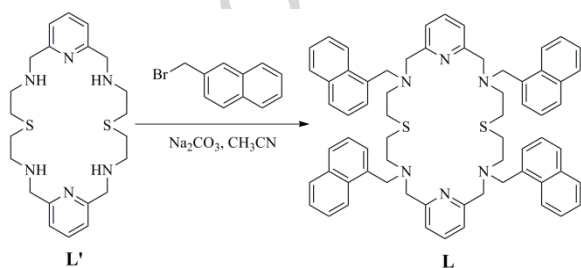
A particularly large range of macrocycles are derived from triaza or tetraazamacrocycles. However, less is known about N-functionalized derivatives of binucleating polyaza-macrocycles.²

As a part of our research, we are interested in polyamine macrocycles with a large number of nitrogen atoms substituted with several pendant-arms.³ However, macrocyclic ligands incorporating nitrogen and sulfur in their framework are not as numerous, and reviews including macrocycles with sulfur are not common in the literature.⁴

Furthermore, in the field of transition metal complexes with different macrocyclic ligands, we have previously reported the synthesis, characterization, and study of cobalt(II), copper(II)⁵ and nickel(II)⁶ complexes with the potential octadentate sulfur- and nitrogen-containing macrocyclic ligand Py₂N₄S₂ (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 two⁸ and four⁹ pendant-arms as naphthalene. It is well known that the coordination ability of these ligands increases when the macrocycles incorporate chelating moieties such as phenanthroline¹⁰ and pyridine¹¹ 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 Py₂N₄S₂ (L in scheme 1).¹²



Scheme 1. Synthetic pathway of macrocyclic ligand **L**.

Ligand **L** was isolated as an air-stable brown solid in 68% yield and was characterized by elemental analysis, ESI-MS, IR and ¹H NMR spectroscopy (see Supporting Information).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 confirms 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 field 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⁺ were 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 acetone, led to the formation of compounds of the type [M₂L](X)₄·nH₂O (X = ClO₄⁻, NO₃⁻) for M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺, [M₂L](X)₂·nH₂O (X = NO₃⁻) for M = Ag⁺, and [ML](CF₃SO₃)₂·nCH₃CN·nEt₂O·nH₂O 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 an intense band at 1384 cm⁻¹, suggesting the presence of ionic nitrate groups.¹⁵ This result is probably due to the displaced by the Br⁻ ion of the KBr disc. In the perchlorate complexes, the intense band at *ca.* 1110 cm⁻¹ is associated with ν(ClO₄⁻) and these clearly identify the ionic perchlorate groups.¹⁶

The MALDI mass spectra for all the complexes indicate the presence of the macrocyclic ligand and the metal ion. The results for the dinuclear complexes of Ni²⁺ provide important evidence to confirm the 2:1 stoichiometry of the complexes as they feature peaks attributable to the species [Ni₂LX₃]⁺.

The molar conductance values for the complexes of **L**, measured at room temperature using acetonitrile as solvent, showed the presence of ionic counterions, since they are in the range reported for solvents for 2:1 electrolytes.¹⁷

The absorption, emission and excitation spectra of **L** in CH₂Cl₂ and at 298 K are presented in Figure 1.¹⁸ The absorption spectrum of ligand **L** displays the characteristic absorption band of the naphthalene chromophore with absorption in the spectral range of 220 nm to 330 nm, formed by two electronic transitions the ¹L_a and ¹L_b bands, and maxima at *ca.* 272 nm. For naphthalene in non-polar solvents the absorption maximum is at 276 nm¹⁹ and its ¹A→¹L_b transition at ~310 nm. As shown in Figure 1, the absorption spectrum of chemosensor **L** in dichloromethane shows these characteristic bands with, however, some energetic shifts: 272 nm and for the forbidden ¹A→¹L_b at ~340 nm.

The emission spectrum of chemosensor **L** displays again the characteristic spectrum of the naphthalene monomer, with maxima at ~338 nm, (for naphthalene, Np, the literature data indicates a 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.

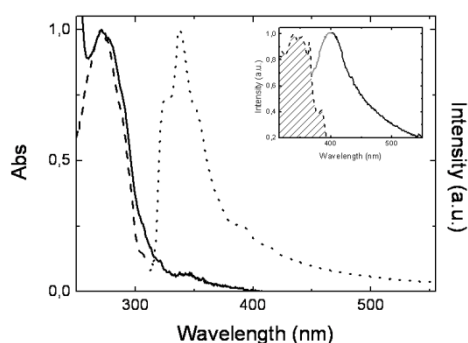


Figure 1. Absorption (full line), emission (dotted line) and excitation (dashed line) spectra of ligand **L** ($\lambda_{\text{exc}}=282$ nm; $\lambda_{\text{em}}=325$ nm) in CH_2Cl_2 at room temperature. Inset: emission (full line obtained with $\lambda_{\text{exc}}=282$ nm) and excitation (dashed line, obtained with $\lambda_{\text{em}}=410$ nm) spectra of ligand **L**. In the inset magnified and partial regions of the excitation and emission spectra are shown to show the mirror-image relationship between the dimer absorption and emission spectra.

However, one interesting feature comes when the excitation spectrum is collected at 410 nm, i.e., in the emission region of the excimer. It can now be observed that besides the match between the monomer band (at ~272 nm) a new band ranging between 320 and 390 nm is now obtained. This band most likely mirrors the fact that the interaction between the Np chromophores is occurring in the ground state, i.e., we are in the presence of ground state dimers.

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 $\lambda_{\text{exc}}=282$ nm and $\lambda_{\text{em}}=325$ 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 Figure 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 Equation 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 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.

$$I_{\lambda}(t) = \sum_{i=1}^n a_{i,j} e^{(-t/\tau_i)} \quad \text{Equation 1}$$

where for emission at 370 nm and 450 nm one obtains respectively

$$I_{370\text{nm}}(t) = a_{1,1} e^{(-t/\tau_1)} + a_{1,2} e^{(-t/\tau_2)} \quad \text{Equation 2}$$

$$I_{450\text{nm}}(t) = a_{2,1} e^{(-t/\tau_1)} + a_{2,2} e^{(-t/\tau_2)} \quad \text{Equation 3}$$

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.

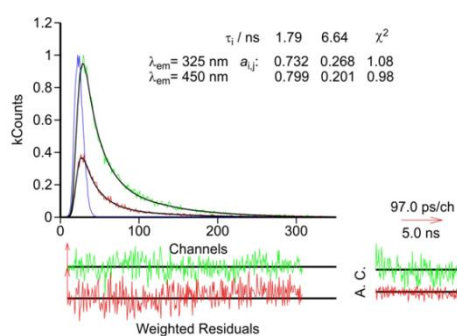


Figure 2. Fluorescence decays of ligand **L** in dichloromethane obtained with $\lambda_{\text{exc}}=282$ nm and $\lambda_{\text{em}}=325$ and 450 nm, $T=293$ K.

Fluoroboric acid (HBF_4) and tetrabutylammonium hydroxide ($[(\text{Bu})_4\text{N}]\text{OH}$) 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 HBF₄ at room temperature, but different behaviour was observed after the addition of tetrabutylammonium hydroxide (see Figure 3).

Figure 3 shows the absorption and emission spectra of **L** in dichloromethane as a function of increasing amounts of [(Bu)₄N]OH at room temperature. The inset of Figure 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.

Figure 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 photoinduced electron transfer quenching of the naphthalene emission.²¹ The inset of Figure 3B also shows how the intensity of the dimer band at 426 nm increases with the addition of OH⁻.

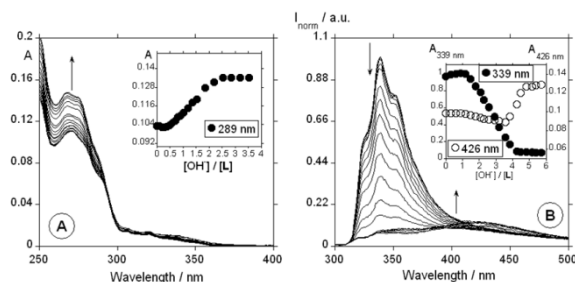


Figure 3. Absorption (A) and emission (B) spectra of dichloromethane solutions of **L** as a function of increasing amounts of [(Bu)₄N]OH. The insets show in (A) the absorption read at 289 nm and in (B) the normalized fluorescence intensity at 339 and 426 nm. ([L]= 1.00 × 10⁻⁵ M, λ_{exc}= 289 nm).

In order to explore the behaviour of compound **L** as a chemosensor towards Co²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Ag⁺ several metal titrations followed by absorption and emission were performed. All complexation studies have been performed in dichloromethane.¹⁸

As an example, Figure 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 (Figure 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 ca. 426 nm increases in intensity. This result suggests that coordination to the metal ion increases the level of ground-state dimer absorption and therefore the level of dimer emission.

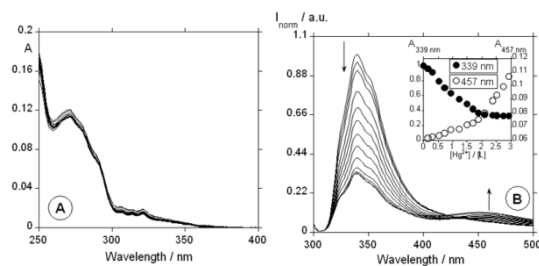


Figure 4. Absorption (A) and emission (B) spectra of **L** in dichloromethane as a function of increasing amounts of Hg(CF₃SO₃)₂. The inset shows the normalized fluorescence intensity at 339 and 457 nm. ([L]= 1.00 × 10⁻⁵ M, λ_{exc}= 289 nm).

The stability constants for the interaction of **L** with Co²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Ag⁺ were calculated using HypSpec software and are summarized 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⁺.

Table 1. Stability constants for chemosensor **L** in the presence of Co²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Ag⁺ in CH₂Cl₂ for an interaction 2:1 (metal:L).

Compound	Interaction (M:L)	Σ log β
L	Co ²⁺ (2:1)	5.14 ± 1.22 × 10 ⁻³
	Cu ²⁺ (2:1)	5.52 ± 1.72 × 10 ⁻³
	Zn ²⁺ (2:1)	5.46 ± 1.96 × 10 ⁻³
	Hg ²⁺ (2:1)	6.58 ± 1.23 × 10 ⁻³
	Ag ⁺ (2:1)	5.19 ± 1.58 × 10 ⁻³

In summary, we have reported the first substituted macrocyclic ligand Py₂N₄S₂ containing four naphthylmethylene pendant-armed groups. In solid state, ligand **L** leads to the formation of dinuclear complexes after the interaction with Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Ag⁺. Only with Hg²⁺, the formation of the mononuclear complex is observed. 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 Co²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Ag⁺ in solution, being the strongest interaction for sensor **L** with Hg²⁺.

Supporting Information. (see footnote on the first page of this article): magnified emission (λ_{exc}= 282 nm) and excitation (λ_{em}= 410 nm) spectra.

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The first substituted macrocyclic ligand $\text{Py}_2\text{N}_4\text{S}_2$ containing four naphthylmethylene pendant-armed groups: synthesis and photophysical properties

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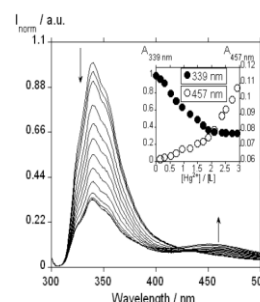
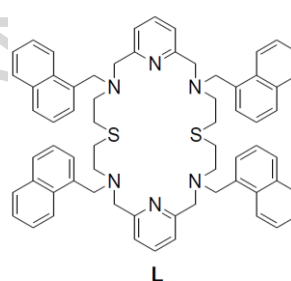
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Graphical Abstract



Synopsis

Synthesis of a novel emissive macrocyclic ligand **L** containing four naphthylmethylene arms and their derivative solid metal complexes (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Ag^+).

The photophysical properties of the free ligand **L** and their complexation behaviour have been investigated in organic solution.

The first substituted macrocyclic ligand $\text{Py}_2\text{N}_4\text{S}_2$ containing four naphthylmethylene pendant-armed groups: synthesis and photophysical properties

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Highlights

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Synthesis of an emissive macrocyclic ligand **L** with four naphthylmethylene arms.

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Synthesis of the derivative solid metal complexes (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Ag^+) of **L**.

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Photophysical properties of the free ligand **L** and study of the complexation properties in organic solution.

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¹² **Synthesis of L.** The macrocycle **L'** (0.89 g, 2 mmol) was dissolved in acetonitrile (50 mL) and Na₂CO₃ (2.12 g; 20 mmol) was added. The mixture was refluxed and 2-(bromomethyl)naphthalene (2.43 g; 20 mmol), dissolved in acetonitrile (10 mL), was added dropwise to the refluxing solution. The mixture was refluxed with magnetic stirring for 24 h and the hot solution was filtered off to eliminate 2-(bromomethyl)naphthalene in excess. The crude solid was then extracted with chloroform (50 mL) and brown oil was obtained. The oil residue was extracted with water/chloroform, and the

organic phase was dried (Na₂SO₄), filtered, and solvent removal gave brown solid.

L. Anal. Calcd for C₆₆H₆₆N₆S₂·0.5·CHCl₃ (MW: 1065.4): C, 74.8; H, 6.3; N, 7.9; S, 6.0. Found: C, 75.2; H, 6.2; N, 7.3; S, 5.7. Yield: 68%. IR (KBr, cm⁻¹): 1589, 1454 [ν(C=N) and ν(C=C)], 854, 818, 752 ν(C-H)_{naft}. ESI-MS (*m/z*): 1007 [L+H]⁺, 867 [L-1Pendant]⁺, 727 [L-2Pendant]⁺, 504 [L+2H]²⁺. ¹H NMR (500 MHz, CDCl₃) δ 2.5-2.7 (m, 16H), 3.6-3.8 (m, 16H), 7.4-7.8 (m, 34H). P_T: 63-65 °C. Color: brown.

¹³ Elemental analyses were performed on a Fisons Instruments EA1108 microanalyser by the Universidade de Santiago de Compostela. Infra-red spectra were recorded as KBr discs on a BIO-RAD FTS 175-C spectrometer. ESI mass spectra were recorded using a micrOTOF spectrometer. The ¹H NMR spectrum of **L** was recorded in CDCl₃ solutions on a Bruker 500 MHz spectrometer.

Conductivity measurements were carried out in 10⁻³ mol dm⁻³ acetonitrile solutions at r.t. using a Crison Basic 30 conductivimeter. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis was performed in a MALDI-TOF-MS model Bruker Ultraflex II workstation equipped with a nitrogen laser radiating at 337 nm from Bruker (Germany) at the BIOSCOPE Group. 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 5.60×10⁻⁷ Torr, respectively. The MALDI-MS spectra of the soluble samples (1 or 2 mg/mL), such as the ligand and metal complexes, were recorded using the conventional sample preparation method for MALDI-MS.

¹⁴ **Synthesis of the Metal Complexes of L.** *General Procedure.* A solution of the appropriate metal salt (0.08 mmol) in acetone (5 mL) was added dropwise to a stirred solution of the ligand **L** (0.042 g, 0.04 mmol) in the same solvent (20 mL). The solution was stirred for 4 h, and the solvent was partially removed to ca. 5 mL. Diethyl ether was infused into the solution, producing powdery precipitates. The precipitates formed were isolated by centrifugation and dried under vacuum, yielding the metal complexes of the ligand.

[Co₂L](ClO₄)₄·H₂O. Anal. Calcd for C₆₆H₆₈N₈O₁₇S₂Cl₄Co₂ (MW: 1538.2): C, 51.4; H, 4.5; N, 5.5; S, 4.2. Found: C, 51.1; H, 4.3; N, 5.3; S, 4.3. Yield: 87%. IR (KBr, cm⁻¹): 3440 [ν(OH)], 1607, 1458 [ν(C=N)_{py} and ν(C=C)_{py}], 1119, 625, [ν(ClO₄)], 862, 823, 794 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1007 [L+H]⁺, 1164 [CoL(ClO₄)]⁺. Λ_M/Ω⁻¹·cm²·mol⁻¹ (in acetonitrile): 218 (2:1). Color: brown.

[Co₂L](NO₃)₄·3H₂O. Anal. Calcd for C₆₆H₇₂N₁₀O₁₅S₂Co₂ (MW: 1426.3): C, 55.5; H, 5.1; N, 9.8; S, 4.5. Found: C, 55.2; H, 4.8; N, 9.4; S, 4.6. Yield: 77%. IR (KBr, cm⁻¹): 3440 [ν(OH)], 1606, 1469 [ν(C=N)_{py} and ν(C=C)_{py}], 1384 [ν(NO₃)], 860, 822, 756 [ν(C-H)_{naft}]. MALDI-MS (*m/z*):

1127 [CoL(NO₃)]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 220 (2:1). Color: pink.

[Ni₂L](ClO₄)₄·H₂O. Anal. Calcd for C₆₆H₆₈N₆O₁₇S₂Cl₄Ni₂ (MW: 1536.2): C, 51.5; H, 4.5; N, 5.5; S, 4.2. Found: C, 51.2; H, 4.4; N, 5.4; S, 3.9. Yield: 67%. IR (KBr, cm⁻¹): 3440 [ν(OH)], 1606, 1450 [ν(C=N)_{py} and ν(C=C)_{py}], 1108, 624, [ν(ClO₄⁻)], 862, 823, 794 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1163 [NiL(ClO₄)⁺], 1419 [Ni₂L(ClO₄)₃⁺]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 215 (2:1). Color: brown.

[Ni₂L](NO₃)₄·2H₂O. Anal. Calcd for C₆₆H₇₀N₁₀O₁₀S₂Ni₂ (MW: 1406.3): C, 56.3; H, 5.0; N, 9.9; S, 4.5. Found: C, 56.6; H, 5.3; N, 9.2; S, 3.9. Yield: 59%. IR (KBr, cm⁻¹): 3443 [ν(OH)], 1607, 1459 [ν(C=N)_{py} and ν(C=C)_{py}], 1384 [ν(NO₃⁻)], 861, 823, 754 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1007 [L+H]⁺, 1308 [Ni₂L(NO₃)₃]⁺. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 205 (2:1). Color: brown.

[Cu₂L](ClO₄)₄·H₂O. Anal. Calcd for C₆₆H₆₈N₆O₁₇S₂Cl₄Cu₂ (MW: 1546.1): C, 51.1; H, 4.4; N, 5.4; S, 4.1. Found: C, 51.1; H, 4.6; N, 4.8; S, 4.2. Yield: 89%. IR (KBr, cm⁻¹): 3448 [ν(OH)], 1607, 1454 [ν(C=N)_{py} and ν(C=C)_{py}], 1119, 625, [ν(ClO₄⁻)], 859, 823, 795 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1168 [CuL(ClO₄)⁺]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 214 (2:1). Color: green.

[Cu₂L](NO₃)₄·3H₂O. Anal. Calcd for C₆₆H₇₂N₁₀O₁₅S₂Cu₂ (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(C=C)_{py}], 1384 [ν(NO₃⁻)], 860, 823, 757 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1068 [L(NO₃)⁺], 1194 [CuL(H)(NO₃)₂]⁺. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 283 (2:1). Color: green.

[Zn₂L](ClO₄)₄·H₂O. Anal. Calcd for C₆₆H₆₈N₆O₁₇S₂Cl₄Zn₂ (MW: 1548.2): C, 51.0; H, 4.4; N, 5.4; S, 4.1. Found: C, 51.1; H, 4.7; N, 5.7; S, 4.2. Yield: 63%. IR (KBr, cm⁻¹): 3445 [ν(OH)], 1606, 1452 [ν(C=N)_{py} and ν(C=C)_{py}], 1108, 624, [ν(ClO₄⁻)], 862, 823, 794 [ν(C-H)_{naft}]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 235 (2:1). Color: brown.

[Zn₂L](NO₃)₄·4H₂O. Anal. Calcd for C₆₆H₇₄N₁₀O₁₆S₂Zn₂ (MW: 1454.3): C, 54.4; H, 5.1; N, 9.6; S, 4.4. Found: C, 54.4; H, 4.7; N, 9.2; S, 4.5. Yield: 71%. IR (KBr, cm⁻¹): 3447 [ν(OH)], 1609, 1470 [ν(C=N)_{py} and ν(C=C)_{py}], 1384 [ν(NO₃⁻)], 860, 821, 756 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1007 [L+H]⁺, 1132 [ZnL(NO₃)⁺]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 249 (2:1). Color: brown.

[Cd₂L](ClO₄)₄·H₂O. Anal. Calcd for C₆₆H₆₈N₆O₁₇S₂Cl₄Cd₂ (MW: 1648.1): C, 48.1; H, 4.2; N, 5.1; S, 3.9. Found: C, 48.2; H, 4.5; N, 5.1; S, 3.9. Yield: 60%. IR (KBr, cm⁻¹): 3429 [ν(OH)], 1608, 1460 [ν(C=N)_{py} and ν(C=C)_{py}], 1107, 624, [ν(ClO₄⁻)], 863, 824, 795 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1007 [L+H]⁺, 1219 [CdL(ClO₄)⁺]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 210 (2:1). Color: brown.

[Cd₂L](NO₃)₄·2H₂O. Anal. Calcd for C₆₆H₇₀N₁₀O₁₄S₂Cd₂ (MW: 1518.3): C, 52.3; H, 4.7; N, 9.2; S, 4.2. Found: C, 52.1; H, 4.6; N, 8.9; S, 4.2. Yield: 63%. IR (KBr, cm⁻¹): 3448 [ν(OH)], 1606, 1450 [ν(C=N)_{py} and ν(C=C)_{py}], 1384 [ν(NO₃⁻)], 862, 823, 794 [ν(C-H)_{naft}]. MALDI-MS (*m/z*): 1007 [L+H]⁺, 1182 [CdL(NO₃)⁺]. $\Lambda_M/\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (in acetonitrile): 227 (2:1). Color: brown.

[Ag₂L](NO₃)₂·2H₂O. Anal. Calcd for C₆₆H₈₀N₈O₁₃S₂Ag₂ (MW: 1470.3): C, 53.8; H, 5.6; N, 7.6; S, 4.4. Found: C, 53.3; H, 6.3; N, 7.9; S, 4.9. Yield: 53%. IR (KBr, cm⁻¹): 3453 [ν(OH)], 1603, 1458 [ν(C=N)_{py} and ν(C=C)_{py}], 1384 [ν(NO₃⁻)], 861, 821, 755 [ν(C-H)_{naft}]. Color: brown.

[HgL](CF₃SO₃)₂·3CH₃CN·2Et₂O·4H₂O. Anal. Calcd for C₇₄H₈₃N₉O₁₀S₄F₆Hg (MW: 1701.5): C, 53.2; H, 5.6; N, 6.8; S, 6.9. Found: C, 52.7; H, 6.0; N, 7.4; S, 7.2. Yield: 56%. IR (KBr, cm⁻¹): 3442 [ν(OH)], 1605, 1455 [ν(C=N)_{py} and ν(C=C)_{py}], 859, 821, 756 [ν(C-H)_{naft}]. Color: brown.

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¹⁸ Spectrophotometric and Spectrofluorimetric

Measurements: UV-vis absorption spectra were performed using a Jasco 650 or a Shimadzu 2450 UV-vis spectrophotometer; fluorescence spectra were recorded on a Horiba Jobin-Yvon Fluoromax 4 spectrometer. All of the fluorescence spectra were corrected for the wavelength response of the system. The linearity of the fluorescence emission versus concentration was checked in the concentration range used (10⁻⁵-10⁻⁶ M). A correction for the absorbed light was performed when necessary. The fluorescence decays of compound **L** were obtained with picosecond resolution with equipment described elsewhere¹⁸ and were analyzed using the method of modulating functions implemented by Striker.¹⁸ The experimental excitation pulse (FWHM= 21 ps) was measured using a LUDOX scattering solution in water. After deconvolution of the experimental signal, the time resolution of the apparatus was ca. 2 ps.

All spectrofluorimetric titrations were performed as follows: a stock solution of the ligand was prepared by dissolving an appropriate amount of the ligand in dichloromethane and diluted to the desired concentration ([L] = 1.00 x 10⁻⁵-6.84 x 10⁻⁶ M).

Titrations were carried out by the addition of microliter amounts of standard solutions of the ions dissolved in acetonitrile. All of the measurements were performed at 298 K.

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