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# New emissive dopamine derivatives as fluorescent chemosensors for metal ions: A CHEF effect for Al(III) interaction

Elisabete Oliveira<sup>a,b,\*</sup>, Hugo M. Santos<sup>a,c,d,e</sup>, José Luis Capelo<sup>a,e</sup>, Carlos Lodeiro<sup>a,e</sup>

<sup>a</sup> BIOSCOPE Group, Faculty of Science, Physical-Chemistry Department, Ourense Campus, University of Vigo, 32004 Ourense, Spain

<sup>b</sup> Veterinary Science Department, CECAV, University of Trás-os-Montes and Alto Douro, 5001-801 Vila Real, Portugal

<sup>c</sup> Institute for Biotechnology and Biomedicine, University Autònoma of Barcelona, 08193 Bellaterra, Spain

<sup>d</sup> Institute for Biotechnology and Bioengineering, Centre of Genomics and Biotechnology, University of Trás-os-Montes and Alto Douro, 5001-801 Vila Real, Portugal

e REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnología, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal

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# ABSTRACT

Three new Schiff-base ligands **1–3** derivatives from neurotransmitter dopamine, bearing an indazole (**1**), methylimidazole (**2**) or hydroxynaphthaldehyde (**3**) units were successfully synthesized and characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR (infrared), ESI-TOF (electrospray ionization-time of flight-mass), UV–Vis absorption and emission spectroscopy. The interaction with the metal ions Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> has been explored by absorption and fluorescence emission spectroscopy. Compound **3** shows to be the most emissive one, with a quantum yield of 0.022, followed by compound **2** ( $\phi = 0.009$ ) and **1** ( $\phi = 0.001$ ). Compound **1** reveals quite selective for Al<sup>3+</sup>, generating an emissive complex formed by three units of **1** per metal ion. On the other hand compound **3**, shows a ratiometric effect with Al<sup>3+</sup> appearing as a new emission band centred at 530 nm. With the other transition and post-transition metal ions, a quenching in the emission was observed, being **3** the most sensitive one, being quenched by 0.34 ppm of Zn<sup>2+</sup> and Cu<sup>2+</sup>, 0.48 ppm of Ni<sup>2+</sup>, 0.061 ppm of Fe<sup>3+</sup> and 0.047 ppm of Al<sup>3+</sup>. In most cases a stoichiometry of three ligands by one metal ion was postulated. In order to study the fluorescence properties in the solid state, the Al<sup>3+</sup> metal complexes of **1** (**4**) and **3** (**5**) were synthesized as new emissive materials. In both cases a very strong emissive systems were obtained, with a quantum yield of 0.01 and 0.04 for **4** and **5**.

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# 1. Introduction

Nowadays, the design of new efficient chemosensors capable of selective recognition of guest species is an area of a huge research in biological, analytical and environmental fields [1,2]. Selective detection with an enhancement of the fluorescence emission of metal ions like Al<sup>3+</sup>, is extremely important because of the well-known neurotoxicity of aluminium(III) and also due to its possible relationship in the appearance of Alzheimer's disease [3]. Also, compound derivatives from aluminium are widely used in water treatment, in food additives and in medicine [3].

On the other hand, the catecholamines such as, dopamine, adrenaline, noradrenaline and L-dopa are neurotransmitters that act in the nervous system. The decrease of the dopamine neurotransmitter in the brain also leads to neurodegenerative diseases, like Alzheimer, Wilson and Parkinson [4]. Neurotransmitters are organic molecules,

\* Corresponding author at: BIOSCOPE Group, Faculty of Science, Physical-Chemistry Department, Ourense Campus, University of Vigo, 32004 Ourense, Spain. Fax: +34 988 387001. which often form adducts, like metal complexes. The metal interaction of dopamine with Fe<sup>3+</sup> is well reported in literature [5], which describes the metal ion coordination in hydroxyl groups. Furthermore, other metal ions sensing lead us to the design of new efficient chemosensors. Due to the presence of an electron donor imine and two hydroxyl sites, Schiff-bases are really important for metal ions complexation, resulting in highly stable complexes [6]. The elimination of pollutant metal ions in drinking water or waste water is normally realized *via* interaction with organic molecules such as, humic substances, Schiff-bases or diazo compounds [7]. In the same way, compounds containing indazole moieties are considered to have pharmacology properties, exhibiting activity as HIV protease inhibitors, serotonin 5-HT<sub>1 $\alpha$ </sub>, 5-HT<sub>2</sub> and 5-HT<sub>3</sub> receptor antagonists and aldol reductase inhibitors [8]. Their properties could be improved when metal ions coordinate to the organic compound [9].

Following our interest in fluorimetric chemosensors [10], here we report the synthesis of three new Schiff-bases **1**, **2**, and **3**, derivatives from the neurotransmitter dopamine, bearing indazole, methylimidazole and hydroxynaphthaldehyde, respectively (see Scheme 1). All compounds were fully characterized and their sensing ability with metal ions such as, Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>,





E-mail address: e.oliveira@uvigo.es (E. Oliveira).

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Scheme 1. Chemical structure of compounds 1-3.

 $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$ ,  $Fe^{3+}$  and  $Al^{3+}$ . Moreover, new metal complexes of aluminium(III) with compounds **1** and **3** were also synthesised and characterized as new emissive materials.

#### 2. Experimental

### 2.1. Chemicals and starting materials

CH<sub>3</sub>SO<sub>3</sub>H (methanosulfonic acid), C<sub>16</sub>H<sub>37</sub>NO (tetrabutylammonium hydroxide), LiBF<sub>4</sub>·xH<sub>2</sub>O, NaBF<sub>4</sub>·xH<sub>2</sub>O, Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, Zn(BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O, Ca(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, Cd(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, Cu(BF<sub>4</sub>)<sub>2</sub>·x-H<sub>2</sub>O, Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, AgNO<sub>3</sub>·xH<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O and Fe (NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O, salts have been purchased from Strem Chemicals, Sigma–Aldrich and Solchemar. Triethylamine, HCl Dopamine, 1H-indazole-6-carboxaldehyde, 4-methyl-5-imidazole carboxaldehyde, and 2-hydroxy-1-naphthaldehyde were from Sigma–Aldrich. All were used without previous purification.

#### 2.2. Physical measurements

Mass spectrometry analyses of the ligands were performed at the "C.A.C.T.I. – Unidad de Espectrometria de Masas" at the University of Vigo, Spain (ESI-TOF). Elemental analyses were carried out on a Fisons EA-1108 analyser in the University of Vigo Elemental analyses Service.

NMR spectra of the ligands were obtained on a Bruker Spectrometer operating at frequency of 400 MHz for <sup>1</sup>H NMR and <sup>13</sup>C NMR using the solvent peak as internal reference, in the facilities of the University of Santiago de Compostela, Spain. Melting points were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded in KBr windows using JASCO FT/IR-410 spectrophotometer.

#### 2.3. Spectrophotometric and spectrofluorimetric measurements

Absorption spectra were recorded on a JASCO V-650 UV-Vis spectrophotometer and fluorescence emission spectra on a spectrofluorimeter HORIBA JOBIN YVON Fluoromax-4. The linearity of the fluorescence emission vs. concentration was checked in the concentration used ( $10^{-4}$ – $10^{-6}$  M). A correction for the absorbed light was performed when necessary. The spectrometric characterizations and titrations were performed as follows: the stock solutions of the compounds (*ca*.  $10^{-3}$  M) were prepared by dissolving an appropriate amount of the complex in a 10 ml volumetric flask and diluting to the mark with absolute ethanol. The solutions were prepared by appropriate dilution of the stock solutions still  $10^{-5}$ - $10^{-6}$  M. Titrations of the ligands **1–3** were carried out by the addition of microlitre amounts of standard solutions of the ions in absolute ethanol. All the measurements were performed at 298 K. Luminescence quantum yields were measured using a solution of benzene in cyclohexane as a standard  $[\phi] = 0.05$  [11] for **1** 

and **2**, and fluorescein in absolute ethanol  $[\phi] = 0.79$  [12] for **3**, and were corrected for different refraction indexes of solvents.

Fluorescence spectra of solid samples were recorded using a fibre optic system connected to the Horiba-Jovin Ybon Fluoromax 4 spectrofluorimetric exciting at appropriate  $\lambda$  (nm) of the solid compounds. All the measurements were performed at 298 K.

### 2.4. Synthesis of compounds 1-3

#### 2.4.1. General synthesis

HCl. Dopamine  $(0.1045 \text{ g}, 5.51 \times 10^{-4} \text{ mol})$  was neutralized with triethylamine  $(77 \,\mu\text{l}, 5.51 \times 10^{-4} \text{ mol})$  in absolute ethanol for 30 min. The solution was filtered and the filtrate was added to the corresponding aldehyde  $(5.51 \times 10^{-4} \text{ mol})$ , and the mixture was gently refluxed with magnetic stirring for *ca.* 4 h. The solvent was evaporated under reduced pressure and the residue was washed several times with diethyl ether (10 mL) and dried under vacuum.

2.4.1.1. 4-(2-(((1H-indazol-6-yl)methylene)amino)ethyl)benzene-1,2diol. Colour: Pale Yellow powder. Melting point: 113.9-117.1 °C. Yield 0.14 g, (92%), FW = 317.3. Anal. Calc. for  $C_{16}H_{15}N_3O_2 \cdot 2H_2O$ : C, 60.6; H, 5.9; N, 13.2. Found: C, 60.5; H, 6.1; N, 13.9%. IR (KBr cm<sup>-1</sup>): 3420 (-OH broad) 2980 (N-H bond), 1682 (-CH=N), 1512 (C=C). <sup>1</sup>H NMR (DMSO, 400 MHz):  $\delta_{\rm H} = 2.94 - 2.96$  (d, I = 4 Hz, 2H,  $\beta$ -CH<sub>2</sub> dopamine), 3.20–3.21 (d, J = 2 Hz, 2H,  $\gamma$  CH<sub>2</sub> dopamine), 5.45 (s, 1H, OH), 5.70 (s, 1H, OH), 6.59-6.60 (d, 2 Hz, 1H, H5), 6.77-6.79 (d, J = 4 Hz, 1H, H6), 7.04 (s, 1H, H9), 7.68-7.70 (d, J = 4 Hz, 1H, H6'), 7.72–7.75 (m, 1H, H5'), 7.88–7.90 (s, 1H, H3'), 8.19 (s, 1H, HC=N), 8.36 (s, 1H, NH). <sup>13</sup>C NMR (DMSO, 400 MHz):  $\delta_{c} = 25.78$  (C3), 36.88 (C2), 54.25 (C8), 59.69 (C7), 110.97 (C9), 115.60 (C6), 118.90 (C5), 121.06 (C6'), 121.84 (C5'), 122.17 (C3'), 133.78 (C8'), 124.23 (C, HC=N). UV-Vis in absolute ethanol ( $\lambda$ nm): Bands at 282 nm ( $\log \varepsilon = 3.81$ ). Emission spectra in absolute ethanol ( $\lambda_{exc}$  = 282 nm,  $\lambda_{emis}$  = 318 nm). ESI-TOF calc.(found): [1] H<sup>+</sup> 282.3 (282.1).

2.4.1.2. 4-(2-(((4-methyl-1H-imidazol-5-yl)methylene) amino)ethyl) benzene-1,2-diol. Colour: Pale yellow powder. Melting point: 182.1-185.0 °C. Yield 0.13 g, (98%), FW = 299.3. Anal. Calc. for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O: C, 52.1; H, 7.0; N, 14.0. Found: C, 51.9; H, 7.0; N, 14.5%. IR (KBr cm<sup>-1</sup>): 3420 (-OH broad) 2980 (N-H bond), 1645 (-CH=N), 1506 (C=C). <sup>1</sup>H NMR (DMSO, 400 MHz):  $\delta_{\rm H}$  = 2.45 (s, 3H, -CH<sub>3</sub>), 2.60–2.70 (d, J = 4 Hz, 2H, β-CH<sub>2</sub> dopamine), 2.72– 2.90 (d, I = 2 Hz, 2H,  $\gamma$  CH<sub>2</sub> dopamine), 5.40 (s, 1H, OH), 5.55 (s, 1H, OH), 6.15-6.17 (m, 1H, H5), 6.50-6.53 (m, 1H, H6), 6.60 (s, 1H, H9), 7.5 (s, 1H, H2'), 7.70 (s, 1H, HC=N), 7.82 (s, 1H, NH). <sup>13</sup>C NMR (DMSO, 400 MHz):  $\delta_c = 16.76 (-CH_3)$ , 37.88 (C3), 62.50 (C2), 116.01 (C6), 116.80 (C9), 122.10 (C6), 137.40 (C2'), 144.01 (C7), 144.16 (C8), 138.01 (C, HC=N). UV-Vis in absolute ethanol ( $\lambda$ nm): Bands at 282 nm ( $\log \varepsilon = 3.81$ ). Emission spectra in absolute ethanol ( $\lambda_{exc}$  = 270 nm,  $\lambda_{emis}$  = 320 nm). ESI-TOF calc. (found): [2] H<sup>+</sup> 246.1 (246.1).

2413 4-(2-(((2-hydroxynaphthalen-1-yl)methylene)amino)ethyl) benzene-1,2-diol. Colour: Brown powder. Melting point: 106.4-108.5 °C. Yield 0.14 g, (85%), FW = 361.3. Anal. Calc. for C<sub>19</sub>H<sub>17</sub>NO<sub>3</sub>·3H<sub>2</sub>O: C, 63.1; H, 6.4; N, 3.9. Found: C, 62.9; H, 6.4; N, 4.1%. IR (KBr cm<sup>-1</sup>): 3420 (-OH broad) 2980 (N-H bond), 1650 (-CH=N), 1540 (C=C). <sup>1</sup>H NMR (DMSO, 400 MHz):  $\delta_{\rm H}$  = 2.74–2.76 (d, J = 4 Hz, 2H,  $\beta$ -CH<sub>2</sub> dopamina), 2.99–3.01 (d, J = 4 Hz, 2H,  $\gamma$ CH<sub>2</sub> dopamine), 6.49–6.50 (d, J = 2 Hz, 1H, H5), 6.61–6.62 (d, I = 2 Hz, 1H, H6), 7.12-7.14 (m, 1H, H6'), 7.30-7.33 (m, 1H, H7'), 7.55–7.57 (d, J = 4 Hz, H, H5'), 7.58–7.59 (m, 1H, H8'), 7.61 (s, 1H, HC==N), 7.93-7.95 (d, J = 4 Hz, 1H, H3'), 8.96-8.98 (d, J = 4 Hz, 1H, H2'), 13.91 (s, 1H, OH1'). <sup>13</sup>C NMR (DMSO, 400 MHz):  $\delta_c$  = 36.34 (C2), 52.66 (C3), 116.68 (C6), 118.78 (C3'), 119.88 (C5), 122.43 (C6'), 126.13 (C7'), 128.22 (C8'), 129.49 (C5'), 137.43 (HC=N), 159.22 (C2'). UV–Vis in absolute ethanol ( $\lambda$  nm): Bands at 420 nm ( $\log \varepsilon = 3.54$ ). Emission spectra in absolute ethanol  $(\lambda_{exc} = 420 \text{ nm}, \lambda_{emis} = 480 \text{ nm}. \text{ ESI-TOF calc. (found): [5] H}^+ 308.3$ (308.1).

# 2.5. Synthesis of the metal complexes

 $0.047 \text{ g}(1.68 \times 10^{-4} \text{ mol}) \text{ of ligands 1 or 3 was dissolved in absolute ethanol followed by the addition of 0.021 g (<math>5.60 \times 10^{-3}$ ) of the Al<sup>3+</sup> salt. The solution was stirred and refluxed for 2 h. The solvent was evaporated under reduce pressure, yielding an oil. Diethyl ether was added drop wise and then dried under vacuum, yielding a dark green powder (1 Al<sup>3+</sup> – (4)) and a brown powder (3 Al<sup>3+</sup> – (5)).

# 2.5.1. [Al1<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O (4)

Colour: Dark green. Yield: 90%. *Anal.* Calc. for  $C_{48}H_{57}AlN_{12}O_{21}$  (MW: 1165.01): C, 49.50; H, 4.95; N, 14.43. Found: C, 49.80; H, 5.10; N, 14.20%. IR (KBr, cm<sup>-1</sup>): 1621 [ $\nu$ (C=N)], 1570 [ $\nu$ (C=C)], 1455 [ $\nu$ (-CH<sub>2</sub>  $\delta$ )], 1336 [ $\nu$ (C=O st)], 1460–1452 ( $\nu$ <sub>5</sub>), 1300 ( $\nu$ <sub>1</sub>) and 1028 ( $\nu$ <sub>2</sub>) cm<sup>-1</sup> [ $\nu$  nitrate counterions], 1380 cm<sup>-1</sup> [ $\nu$  ionic nitrate].

UV–Vis in abs. ethanol ( $\lambda$  nm): 290 nm, ( $\varepsilon \approx 4.16$ ). Fluorescence emission band in abs. ethanol ( $\lambda_{exc} = 290$  nm);  $\lambda_{emis} = 320$  nm.

### 2.5.2. [Al**3**<sub>3</sub>] (NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O (**5**)

Colour: Brown. Yield: 88%. *Anal.* Calc. for  $C_{57}H_{63}AlN_6O_{24}$  (MW: 1243.11): C, 55.07; H, 5.11; N, 6.76. Found: C, 54.80; H, 4.90; N, 6.95%. IR (KBr, cm<sup>-1</sup>): 1662 [ $\nu$ (C=N)], 1618 [ $\nu$ (C=C)], 1361 [ $\nu$ (C-O st)], 1460–1452 ( $\nu_5$ ), 1300( $\nu_1$ ) and 1028( $\nu_2$ ) cm<sup>-1</sup> [ $\nu$  nitrate counterions], 1380 cm<sup>-1</sup> [ $\nu$  ionic nitrate].

UV–Vis in abs. ethanol ( $\lambda$  nm): 420 nm, ( $\epsilon \approx$  4.03). Fluorescence emission band in abs. ethanol ( $\lambda_{exc}$  = 420 nm);  $\lambda_{emis}$  = 530 nm.

# 3. Results and discussion

# 3.1. Synthesis

Dopamine. HCl was neutralized with triethylamine, followed by the addition of an equimolar amount of the corresponding aldehyde compounds, 1*H*-indazole-6-carboxaldehyde (1), 4-methyl-5imidazolecarboxaldehyde (2) and 2-hydroxy-1-naphthaldehyde (3), yielding compounds 1, 2 and 3, respectively. The solution was stirred and refluxed for 2 h. After 2 h the solvent was evaporated under reduced pressure and the product purified with diethyl ether yielding a powder. All compounds synthesized were obtained in an excellent yield, 92% (1), 96% (2) and 85% (3).

All ligands were characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, ESI-TOF, absorption and fluorescence emission spectroscopy.

A careful inspection of elemental analysis evidences that the values fit perfectly with the expected chemical formula postulated. This fact was also confirmed by ESI-TOF where the spectra show

peaks corresponding to  $[1H]^+$  282.3 (282.1),  $[2H]^+$  246.1 (246.1) and  $[3H]^+$  308.3 (308.1). The IR spectra of the three compounds present a band at 1645–1682 cm<sup>-1</sup> corresponding to the imine bond and a band at 2980 cm<sup>-1</sup> assignable to the N–H bond [13].

The <sup>1</sup>H NMR spectra of compounds **1**, **2** and **3** evidences that the signal corresponded to the imine HC=N, the  $\beta$ CH<sub>2</sub> and  $\gamma$ CH<sub>2</sub> of the dopamine amino acid and the aromatic signals between 6.5 and 7.9 ppm, as well. In the <sup>13</sup>C NMR spectra, the formation of the amide linkage was also confirmed by the appearance of the signal at about 125–140 ppm.

# 3.2. Photophysical studies

Compounds **1**, **2** and **3** were characterized in absolute ethanol and the main photophysical data are gathered on Table 1. Compounds **1**, **2** and **3** show absorption bands at 282 nm, 270 nm, 420 nm, and emission bands at 318 nm, 320 nm and 480 nm, respectively (see Fig. 1). Compound **3** is the most emissive compound, with a quantum yield of 0.022, followed by compound **2** ( $\phi = 0.009$ ) and **1** ( $\phi = 0.001$ ) (see Table 1).

There are many signalling mechanisms involving the excited state of the molecules, which can decrease or affect the emission fluorescence signal of the chemosensors, such as, photoinduced electron/energy transfer (PET) [14], metal ligand charge transfer (MLCT) [15], intramolecular charge transfer (ICT) [16] and others.

In spite of the good properties of Schiff-bases, usually they present very weak emission signal, due to the isomerization around the imine linkage C=N [17], allowing a free rotation with a consequent quenching of the emission intensity. It is well known that chelating groups as C=N or C=O have a higher affinity for transition and post-transition metal ions [17].

Taking into account this fact, several titrations of compounds 1, 2 and 3 with  $H^+$ ,  $OH^-$ ,  $Li^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$ ,  $Fe^{3+}$  and  $Al^{3+}$  were performed.

The study of the acid–base behaviour of compounds **1–3** was carried out with increasing amounts of protons using metanosulfonic acid, CH<sub>3</sub>SO<sub>3</sub>H, and fluoride ion as basic anion. Protonation induces in compound **1** a decrease and a red-shift of the absorption band from 282 to 293 nm ( $\Delta\lambda = 11$  nm) followed by an absorbance decrease of a shoulder at 330 nm (see Fig. 2A). On the other hand, an intense increase of the emission fluorescence in **1** upon protonation is also observed, wherever the fluorescence quantum yield changes from 0.001 to 0.02 (20-fold) (see Fig. 2B). An inspection of Fig. 2(B) indicates that 2 equivalents of proton are necessary for stabilizing the system. Protonation takes place on the nitrogen groups on the molecule, avoiding then the photoinduced electronic transfer phenomena from the lone-pair of electrons to the excited chromophore [18].

In a basic environment, compound **1** is not affected, without changes in the absorption and emission spectra.

Contrary to compound **1**, compounds **2** and **3** are highly pH dependent presenting spectral changes in acid and basic media (see Fig. SN1). Upon addition of one equivalent of acid, compound **2** shows a decrease and a red-shift from 270 to 294 nm ( $\Delta \lambda = 24$  nm) on the absorption band, followed by a decrease of about 40% in the emission fluorescence (see Fig. SN1). However, with the addition of base compound **2** is practically not affected.

The same quenching behaviour on the absorption and emission spectra in compound **2** was observed for compound **3**, but the percentage of the emission quenching with the addition of one equivalent of proton was higher (*ca.* 60%) (see Fig. SN1). This result suggests that the observed quenching in the fluorescence emission is probably due to the formation of hydrogen-bonds between the protonated nitrogen located in the aromatic ring and the oxygen atoms on the dopamine amino acid [19]. Furthermore in a basic media, **3** shows a decrease in the emission intensity, probably

Table 1		
UV-Vis and fluorescence da	ta for 1, 2 and 3	3 in absolute ethanol.

Compounds	UV-Vis		Fluorescence		
	$\lambda_{\rm exc} (nm)$	Log $\varepsilon$	$\lambda_{\rm em}$ (nm)	Stokes'shift (cm <sup>-1</sup> )	Quantum yield $\phi$
1	282	3.81	318	4014	0.001
2	270	3.72	320	5787	0.009
3	420	3.54	480	2976	0.022



**Fig. 1.** Absorption and emission spectra of compounds **1–3** in absolute ethanol (*T* = 298 K, **[1**] =  $5.9 \times 10^{-5}$  M, **[2**] =  $4.0 \times 10^{-5}$  M, **[3**] =  $3.25 \times 10^{-5}$  M,  $\lambda_{exc1}$  = 282 nm,  $\lambda_{exc2}$  = 270 nm,  $\lambda_{exc3}$  = 420 nm).

due to the deprotonation of the oxygen and nitrogen atoms, allowing a photoinduced electronic transfer phenomenon [18,20].

# 3.2.1. Alkali and alkali-earth metal ions

Although all compounds show two oxygen atoms in a catechol unit specially designed for metal ion complexation, and according to the Pearsons rules [21] are preferred for hard metal ions, it is expected that for alkali and alkali earth metal ions, the binding affinity will be higher. However, compounds **1–3** did not show any change in the ground (absorption) and excited (emission) states after the addition of alkali metals  $Li^+$ ,  $Na^+$  and alkali earth  $Mg^{2+}$  and  $Ca^{2+}$ .

# 3.2.2. Transition and post-transition metal ions

Taking into account the previous results, we explored the interaction with the transition and post-transition metal ions,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$ ,  $Fe^{3+}$  and  $Al^{3+}$ .

Compound **1** did not show spectral changes with the addition of the metal ions aforementioned. However, compound **2** presented spectral changes in the excited state (emission) in the presence of  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$  and  $Fe^{3+}$ . In the ground state (absorption), were observed changes only in the presence of  $Ag^+$  metal ion. Simultaneously, a quenching on the emission intensity was observed in all cases. In Fig. 3(A and B) the emission titration of compound **2** in the presence of  $Ag^+$  (see Fig. 3C and D).

As stated above, the addition of  $Cu^{2+}$  and  $Fe^{3+}$  to compound **2** induces a quenching of the emission intensity being necessary less than half equivalent of metal ion to quench the system. Based on the high affinity of the  $Cu^{2+}$  and  $Fe^{3+}$  for oxygens [21], we believe that the metal ion coordination occurs in the catechol's presenting in the dopamine amino acid [22]. The complexation constants with both metals were calculated using the HYPSPEC [23] program, and are summarized in Table 2. In both cases the complexation constants suggest a complex of three ligands for one metal ion with an association constant of (L:M, 3:1),  $logK_{ass.} = 17.12 \pm 0.02$  for  $Cu^{2+}$  and  $logK_{ass.} = 13.47 \pm 0.02$  for  $Fe^{3+}$ . It is important to note that, compound **2** gave a higher stability complex for  $Cu^{2+}$  than for  $Fe^{3+}$  metal ion. Moreover, the interaction of **2** with Ag<sup>+</sup> induces a small quenching in the absorbance at 270 nm and an increase at 420 nm. This new band can be attributed to a metal to ligand



**Fig. 2.** Absorption (A) and emission (B) titration of compound **1**, with the addition of methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) (T = 298 K, [**1**] =  $5.9 \times 10^{-5}$  M, [CH<sub>3</sub>SO<sub>3</sub>H] =  $1.00 \times 10^{-2}$  M,  $\lambda_{exc} = 282$  nm.



**Fig. 3.** Spectrofluorimetric titrations of compound **2** with the addition of  $Cu^{2+}(A)$ ,  $Fe^{3+}(B)$  and  $Ag^{+}(D)$  in absolute ethanol. The inset shows the emission as function of  $[Cu^{2+}]/[2](A)$ ,  $[Fe^{3+}]/[2](B)$  and  $[Ag^{+}]/[2](D)$  at 320 nm. Spectrophotometric titration (C) of compound **2** with the addition of  $Ag^{+}$  in absolute ethanol. The inset shows the absorption as function of  $[Ag^{+}]/[2](C)$  at 320 nm ( $[2] = 4.1 \times 10^{-5}$  M, T = 298 K).

charge band [15]. A decrease in the emission intensity at 320 nm was observed, as well. The association constant suggests a mononuclear complex formation with a small constant of (L:M, 1:1), log- $K_{ass.} = 4.72 \pm 0.01$  (see Table 2) when compared with Cu<sup>2+</sup> or Fe<sup>3+</sup>.

Compound **3** appears to be the most reactive system, presenting similar spectral changes with  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$  and  $Fe^{3+}$  metal ions. Here we will focus on  $Zn^{2+}$  and  $Fe^{3+}$  metal ions.

In Fig. 4, the absorption and emission spectra of compound **3** upon addition of  $Zn^{2+}$  metal ion is presented.

A similar behaviour is observed for all metals, wherever in the absorption spectra (Fig. 4(A)) a decrease in the absorbance at 420 nm and an increase at 470 nm is shown. On the other hand, a quenching in the emission intensity at 480 nm is also observed. The amount of metal ion necessary to quench the system is less than half equivalent.

In the same way upon addition of  $Fe^{3+}$  metal ions, a decrease in the absorbance at 420 nm and an increase at 560 nm is observed in the absorption spectra (see Fig. 5A). In emission spectra, a quenching in the emission intensity is observed, as well.

The association constants for the transition and post-transition metal ions mentioned above were determined by the program HYP-SPEC [23], which revealed several complexes formed by three ligands and one metal ion, L:M; 3:1 for  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$  and Fe<sup>3+</sup> and L:M; 2:1 for Cd<sup>2+</sup> metal ion. The association constants

#### Table 2

Complexation constants of compounds 1-3 in the presence of metal ions, calculated by Hypspec program (log  $K_{ass.}$ ).

Compounds	Metal ion	(L:M) $\log K_{ass.}$
1	Al <sup>3+</sup>	3:1-11.33 ± 0.01
2	Ni <sup>2+</sup>	2:1-9.198 ± 0.006
	Cu <sup>2+</sup>	$3:1-17.12 \pm 0.02$
	Al <sup>3+</sup>	2:1-9.06 ± 0.04
	Ag <sup>+</sup>	1:1-4.723 ± 0.001
	Fe <sup>3+</sup>	3:1-13.47 ± 0.02
3	Zn <sup>2+</sup>	3:1-15.499 ± 0.002
	Ni <sup>2+</sup>	$3:1-14.98 \pm 0.01$
	Cd <sup>2+</sup>	2:1-8.65 ± 0.01
	Cu <sup>2+</sup>	$3:1-15.26 \pm 0.02$
	Al <sup>3+</sup>	$3:1-13.384 \pm 0.002$
	Ag <sup>+</sup>	$3:1-12.96 \pm 0.01$
	Fe <sup>3+</sup>	3:1-13.691 ± 0.1

are presented in Table 2. A detailed analysis of these constants suggests that a more stable complex is formed by  $Zn^{2+}$  (log $K_{ass.} = 15.50 \pm 0.01$ ) >  $Cu^{2+}$  (log $K_{ass.} = 15.26 \pm 0.02$ ) >  $Ni^{2+}$  (log $K_{ass.} = 14.98 \pm 0.01$ ) >  $Fe^{3+}$  (log $K_{ass.} = 13.69 \pm 0.1$ ) >  $Ag^+$  (log $K_{ass.} = 12.96 \pm 0.01$ ) >  $Cd^{2+}$  (log $K_{ass.} = 4.72 \pm 0.01$ ).

The most interesting results arise from the interaction with  $Al^{3+}$  using compounds **1** and **3**, where an enhancement in the emission



**Fig. 4.** Spectrophotometric (A) and spectrofluorimetric (B) titrations of compound **3** with the addition of  $Zn^{2+}$  in absolute ethanol. The inset (A) shows the absorption as function of  $[Zn^{2+}]/[3]$  at 420 nm. The inset (B) shows the emission as function of  $[Zn^{2+}]/[3]$  at 480 nm ([**3**] =  $3.25 \times 10^{-5}$  M, T = 298 K).



**Fig. 5.** Spectrophotometric (A) and spectrofluorimetric (B) titrations of compound **3** with the addition of  $Fe^{3+}$  in absolute ethanol. The inset (A) shows the absorption as function of  $[Fe^{3+}]/[3]$  at 420 nm and 560 nm. The inset (B) shows the emission as function of  $[Fe^{3+}]/[3]$  at 480 nm ([**3**] = 3.25 × 10<sup>-5</sup> M, *T* = 298 K).

intensity was observed. In Fig. 6, the absorption and emission spectra of compounds 1-3 with Al<sup>3+</sup> is presented.

In compound **1** upon addition of Al<sup>3,+</sup> a decrease and a red-shift in the absorption band from 282 to 293 nm ( $\Delta\lambda = 11$  nm) was observed, followed by an absorption increase at 330 nm. The emission spectra show an enhancement in the intensity band at 318 nm, increasing the quantum yield of *ca*. 18-fold, from 0.001 to 0.018. Based on Upadhyay's [24] work, we suggest that the complexation probably involves the nitrogen atoms from the imine bond, completing the coordination sphere with some of the nitrogens from the indazole, and the hydroxyl groups from the dopamine. As stated above, usually Schiff-bases have low emission due to the isomerization reaction around the imine linkage C=N [17], being a non-planar molecule, but upon complexation by a metal, this isomerization is inhibited and an emissive planar complex is formed. This result was not observed for the other metal ions reported.

It is interesting to note that relatively to compound  $\mathbf{2}$ , the opposite effect was observed in the presence of Al<sup>3+</sup>. A quenching of 60% in the emission intensity upon addition of one equivalent of metal ion was observed. Moreover, in the absorption spectra was observed a decrease in the absorbance and a red-shift from 270 to 292 nm ( $\Delta\lambda$  = 22 nm) (see Fig. 6C and D). Similar to the other metal ions studied for this compound, probably the metal complexation takes place on the catecholate of dopamine.

Finally, Fig. 6(E and F) show the absorption and emission spectra of compound **3** with Al<sup>3+</sup>. A decrease in the absorption at 410 nm is evidenced, and in the emission spectra, a fast quench of emission at 480 nm (free ligand), was observed, followed by the appearance of new intense emissive band at 530 nm relative to the aluminium complex. These spectral changes suggest that we are in the presence of a ratiometric fluorescent compound for Al<sup>3+</sup>. Upon complexation, the quantum yield of **3** increases from  $\phi = 0.02$  to  $\phi = 0.04$  (see the complexation by the metal ion on the imine bond and hydroxyl group picture 1). As explained for compound **1**, the enhancement of emission intensity arises from the dopamine and hydroxynaphthalene, avoing then the C=N isomerization (see Fig. 7).

The association constants for  $Al^{3+}$  interaction were determined using the HYPSPEC program and complexes of three ligands for one metal ion were found for compounds **1** and **3** with a log- $K_{ass.} = 11.33 \pm 0.01$  and  $\log K_{ass.} = 13.38 \pm 0.01$ , respectively. For



**Fig. 6.** Spectrophotometric (A, C) and spectrofluorimetric (B, D) titrations of compound **1** and **3** with the addition of  $AI^{3*}$  in absolute ethanol. The inset (A and C) shows the absorption as function of  $[AI^{3*}]/[1]$  (A) at 280 and 330 nm; and as function of  $[AI^{3*}]/[3]$  (C) at 420 nm. The inset (B and D) shows the emission as function of  $[AI^{3*}]/[1]$  (B) at 318 nm; and as function of  $[AI^{3*}]/[3]$  (D) at 480 nm and 530 nm ([1] =  $5.9 \times 10^{-5}$  M, [3] =  $3.25 \times 10^{-5}$  M,  $\lambda_{exc1}$  = 282 nm,  $\lambda_{exc3}$  = 420 nm, *T* = 298 K).



Fig. 7. Proposed interaction mode of compound 3 with  $Al^{3+}$  and the fluorescence image with and without  $Al^{3+}$ , under UV lamp  $\lambda_{exc}$  = 365 nm.

compound **2**, a complex formation of two ligands for one metal with a  $\log K_{\rm ass.} = 9.06 \pm 0.04$  was postulated. The most stable aluminium complex was obtained with compound **3**.

In order to study the potential analytical application of these compounds, the detection (LOD) and quantification (LOQ) limits were determined in absolute ethanol. For compound **1**, the values at 318 nm were of  $1.016 \pm 0.026$  (DL),  $1.078 \pm 0.09$  (QL); for com-

pound **2** at 320 nm were of  $1.035 \pm 0.045$  (DL),  $1.140 \pm 0.150$  (QL); and for compound **3** at 480 nm and 530 nm were of  $1.086 \pm 0.13$  (DL),  $1.40 \pm 0.45$  (QL) and  $1.093 \pm 0.12$  (DL),  $1.379 \pm 0.41$  (QL), respectively.

In conclusion, compound **1** shows to be quite selective for Al<sup>3+</sup>, with a strong enhancement of the emission intensity, (see Fig. 8) while with the other metal ions did not show any spectral changes.

The minimum amount for **1** of  $Al^{3+}$  that might be sensed in absolute ethanol is *ca.* 4.73 ppm. Compound **2** is quite sensitive in the presence of transition and post-transition metal ions, generating nonemissive quite stable complexes with  $Cu^{2+}$  and  $Fe^{3+}$ . Moreover, this compound could sense in absolute ethanol 0.5 ppm of  $Cu^{2+}$ , 0.39 ppm of  $Fe^{3+}$  and 5.00 ppm of  $Al^{3+}$ . On the other hand, the compound **3** is the most reactive compound presenting changes with all the transition and post-transition metal ions studied. Very stable contents were obtained with  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$  and  $Al^{3+}$  metal ions. The minimal amount of these metal ions that can be quantified is of 0.34 ppm for  $Zn^{2+}$  and  $Cu^{2+}$ , 0.48 ppm for  $Ni^{2+}$ , 0.061 ppm for  $Fe^{3+}$  and 0.047 ppm for  $Al^{3+}$ .

#### 3.3. Aluminium(III) metal complexes

In order to study the emission properties in the solid state, the solid aluminium(III) complexes of **1** and **3** were obtained. The synthesis was carried out in absolute ethanol by direct reactions, leading to the formation of complexes with 3:1 metal-to-ligand ratio. The metal synthesis yields a green powder for (**1** Al<sup>3+</sup> – (**4**)) and a red-brown powder for (**3** Al<sup>3+</sup> – (**5**)) with excellent yields of 90% and 88%. Both the metal complexes were characterized by elemental analysis, IR, <sup>1</sup>H NMR, UV–Vis and fluorescence emission. The aluminium metal complexes gave the formula: [Al**1**<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O (**4**) and [Al**3**<sub>3</sub>] (NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O (**5**).

The IR spectra were recorded in KBr discs, and show bands attributed to the imine linkage C=N at  $1621-1618 \text{ cm}^{-1}$ .

The absorptions of the nitrate counterions, at *ca*. 1460–1452 ( $v_5$ ), 1300( $v_1$ ) and 1028( $v_2$ ) cm<sup>-1</sup>, suggest the presence of bidentate nitrate groups; an intense band at *ca*. 1380 cm<sup>-1</sup> attributable to ionic nitrate, is also present [25–27].

The appearance of a broad band at around  $3400 \text{ cm}^{-1}$  in all complexes suggests the presence of coordinated and/or hydrated water molecules [13].

The absorption and emission spectra of the metal complexes **4** and **5** were performed in absolute ethanol. Complexes **4** and **5** show bands at 290 and 420 nm in absorption and at 320 and 530 nm in emission spectra, respectively (see Supporting information). As, shown previously in the aluminium metal titration for **1** and **3** in solution, very strong emissive systems were also obtained for the synthesized aluminium metal complexes, with a quantum yield of 0.01 and 0.04 for **4** and **5**. However, due to their dark colour, dark green for **4** and brown for **5**, the complexes were not emissive in solid state.

# norm. /a.u. 1.4 318 nm 1.2 Zn<sup>2+</sup> Cd<sup>2+</sup> 1Al<sup>3+</sup> Ni<sup>2+</sup> Fe<sup>3+</sup> Ag 1 08 0.6 04 0.2 [LAI<sup>3+</sup>] vs [M<sup>n+</sup>]



# 4. Conclusions

Three new Schiff-base ligands **1–3** derivated from neurotransmitter dopamine, bearing an indazole, methylimidazole or hydroxynaphthaldehyde units were successfully synthesized and fully characterized. Compound **3** was revealed as the most emissive compound, with a quantum yield of 0.022, followed by compound **2** ( $\phi = 0.009$ ) and **1** ( $\phi = 0.001$ ). Compound **1** showed an enhancement in the emission after protonation and Al<sup>3+</sup> complexation, being quite selective for this metal ion. After protonation, the appearance of any PET (photoinduced electronic transfer) phenomena was prevented, and after complexation by the metal which inhibits the C=N isomerization. The minimum amount of Al<sup>3+</sup> that might be sensed by **1** in absolute ethanol is *ca.* 4.73 ppm.

Compound **2** is quite sensitive in the presence of the transition and post-transition metal ions studied, forming non-emissive quite stable complexes with Cu<sup>2+</sup> and Fe<sup>3+</sup>. This compound could sense in absolute ethanol 0.5 ppm of  $Cu^{2+}$ , 0.39 ppm of  $Fe^{3+}$  and 5.00 ppm of Al<sup>3+</sup>. On the other hand while the selectivity is lost, compound **3** is the most reactive compound presenting changes with all the transition and post-transition metal ions studied. The presence of these metal ions, induces in **3** a quenching in the emission, forming complexes of three ligands for one metal ion, as well. In these both cases, **2** and **3**, we postulated that the complexation probably takes place on the catecholate of the neurotransmitter dopamine, activating also the C=N isomerization. In compound **3**, the addition of  $Al^{3+}$  generates a very emissive and ratiometric complex with an emission band at 530 nm, with a stoichiometry of L:M; 3:1. The minimal amount sense with 3 of these metal ions can be quantified as: 0.34 ppm for Zn<sup>2+</sup> and Cu<sup>2+</sup>, 0.48 ppm for Ni<sup>2+</sup>, 0.061 ppm for Fe<sup>3+</sup> and 0.047 ppm for Al<sup>3+</sup>.

As a conclusion, very promising results were obtained for  $AI^{3+}$ , where a CHEF effect was observed in compounds **1** and **3**. Otherwise compound **3** could be explored in the future for analytical purposes since it has a very low quantification limit, as well as, ratiometric properties.

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# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.033.

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