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New gallium(III) corrole complexes as colorimetric probes for toxic cyanide anion

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ABSTRACT

Demand for new colorimetric sensors for toxic anions has widely increased in the last ten years, because it is an inexpensive technique, in which the analyte is naked-eye detectable. Regarding this issue, two new corrole derivatives **2** and **3** were successfully synthetized and characterized by elemental analysis, ^{1}H and 19F-NMR, MALDI-TOF-MS, UV–Vis absorption and emission spectra. β-Vinyl-corrole **1** was prepared by the Wittig reaction of β-formyl-corrole with phosphorus ylide. Subsequent treatment of β-vinyl-corrole with dimethyl acetylenedicarboxylate afforded compounds **2** and **3**. The sensorial ability of the two new corrole derivatives towards fluoride, cyanide, acetate and phosphate anions was carried out by absorption and emission spectroscopy. Compound **2** shows to be colorimetric to cyanide, whereas a change of colour from *green* to *colourless* was visualized. In addition the highest association constants were obtained for compounds **2** and **3** in the presence of cyanide that are able to quantify a minor amount of cyanide (*ca.* 1.00 μM).

1. Introduction

Nowadays, a huge number of colorimetric and fluorescent chemosensors have been developed targeting the anions detection, which have a widely application on chemical and biological processes [1]. Among all anions, fluoride and cyanide are the most attractive targets, because of their significant importance in health and environmental matters [2]. Fluoride is an essential anion being widely used in toothpaste for dental caries prevention and in osteoporosis treatment, as well. Like for the other anions, an excess of fluoride anion could induce several diseases, such as fluorosis, which might cause nephorotoxic alterations in humans leading to urolithiasis [3]. The detection and quantification of fluoride anion is often controlled in urine samples, and the standard amount of this anion in water given by the United States Environmental Protection Agency (EPA) [4] must be around 2 and 4 mg L^{-1}.

Cyanide is one of the most poison and toxic anion for the environmental and human health [5]. Despite its toxicity cyanide is up to now applied in industrial fields, such as in gold and silver mining, in nitriles and nylon polymers and in acrylic plastic production [6,7]. Its quantification is really important and due to its high toxicity the highest allowable level of cyanide according to the World Health Organization in drinking water is around 1.9 μM [8,9]. There are many techniques to detect cyanide such as spectrophotometric analysis, electrochemical and optical sensors [10]. The most inexpensive methods are the use of colorimetric sensors, which allows the naked-eye detection of cyanide by a change of colour. As an example, Kang et al. [11] reported a specific naked eye sensor for cyanide over other competitive anions in protic solvents, whereas a colour change from colourless to yellow in the presence of cyanide was observed.

Consequently, the search for methods that can rapidly detect such few amount of anions is a challenge, where the used of high sensitive techniques as absorption and emission fluorescence spectroscopy enable their detection.

The design and synthesis of chemosensors with fluorophores visible excitable have increased due to their highly application *in vivo* and in the environment [12].

Corroles, porphyrins and metalloporphyrins are excellent multifunctional candidates for a great variety of sensing material applications.

Corroles have many advantages such as high radiative rate constants, large Stoke's shift, absorption and emission bands in the visible and high luminescent quantum yield [13]. Also, corrole derivatives are reactive to anions because of their high N–H acidity [14]. However, most part of the supramolecular interactions between the fluorophore and the anion are mainly hydrogen bond,

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acid–base and anion–π interactions [15]. The anions used for analysis are highly competitive with water molecules, being their detection mainly realized in organic solvents [16]. The anions with the tetrabutylammonium counter ion are the salts commonly used.

Following our interest, on the functionalization of corroles via cycloaddition rections [17] and the study of fluorescent chemosensors [18], herein we present the synthesis and the sensorial ability of new corrole derivatives **2** and **3** towards fluoride, cyanide, acetate and phosphate anions by absorption and emission spectroscopy.

2. Results and discussion

2.1. Synthesis

The synthetic route used to prepare the precursors **2** and **3** is outlined in Scheme 1. The corrole precursors 5,10,15-tris(pentafluorophenyl)corrole and 5,10,15-tris(pentafluorophenyl)corrolatogallium(III)(pyridine) were synthesized, according to procedures described in literature [19,20].

The synthesis of the gallium(III) complex of 3-vinyl-5,10,15-tris(pentafluorophenyl)corrole **1** involved the Vilsmeier–Haack formylation of 5,10,15-tris(pentafluorophenyl)corrolatogallium(III)(pyridine) using $POCl_3$/DMF, followed by a Wittig reaction using CH_3PPh_3Br/NaH/THF [15].

The reactivity of the 3-vinyl-corrole **1** as a diene in Diels–Alder reactions was studied using dimethyl acetylenedicarboxylate as dienophile. The reaction was carried out by heating corrole **1** with an excess of the dienophile (2 equiv.) in refluxing toluene, and were finished when the control by TLC showed the total consumption of the starting reagent. After the usual work up and purification, two novel compounds were isolated and identified, as the benzocorrole **2** ($[M+H]^+$ m/z 1029) obtained in 81% yield and compound **3** ($[M+H]^+$ m/z 1171) obtained in 16% yield (Scheme 1). The synthesis of compound **2** results from a Diels–Alder reaction followed by oxidation. However the formation of compound **3** via a cyclotrimerization process is quite surprising, since a similar reaction with a β-vinylporphyrin and the same dienophile only afforded the expected adduct [21]. This result shows a clear difference in the reactivity of porphyrins and corroles, and further studies will be performed in order to clarify this unexpected transformation.

The structures of the new compounds were established by spectroscopic data, namely NMR, UV–Vis, MS and elemental analysis.

The ^1H NMR spectrum of the adduct **2** showed in the aromatic region two doublets at δ 9.46 and δ 8.91 ppm due to the resonance of protons H-18 and H-17, respectively. The multiplet existing at δ 8.86–8.67 ppm was attributed to the ressonances of other β-pyrrolic protons. The signals at δ 8.53 and 8.17 ppm were assigned to the resonances of the aromatic protons H-5′ and H-4′.

In the aliphatic region were identified two singlets at δ 4.58 and 4.09 ppm, that are due to the resonance of the methyl ester groups.

From the ^1H NMR spectra of compound **3** it was possible to assign in the aromatic region, two singlets at δ 10.52 and 9.66 ppm corresponding to the resonances of protons H-6′ and H-2 and a doublet at δ 9.12 ppm due to the resonance of proton H-18. In the same region, it was also possible to identify four signals, three doublets at δ 8.68, 8.52 and 8.48 ppm and a multiplet at 8.77–8.73 ppm corresponding to the resonances of the remaining five β-pyrrolic protons. In the aliphatic region were identified four singlets at δ 4.23, 3.95, 3.86 and 3.80 ppm, corresponding to the resonances of the methylester groups.

2.2. Photophysical characterization

The photophysical characterization of compounds **2** and **3** was performed in toluene solution at 298 K and the main photophysical data are reported in Table 1. The benzocorrole **2** shows the highly intense Soret band at 440 nm and two weak Q bands at 590 and 614 nm. The β-substituted corrole **3** exhibits the Soret band at 443 nm and the two weak Q bands at 596 and 616 nm. The emission bands of highest energy of the compounds **2** and **3** are centered between 616 and 618 nm, respectively.

As an example, Fig. 1 shows the absorption, emission and excitation spectra in toluene of compound **2**. The same photophysical characterization was performed in toluene for compound **3.**

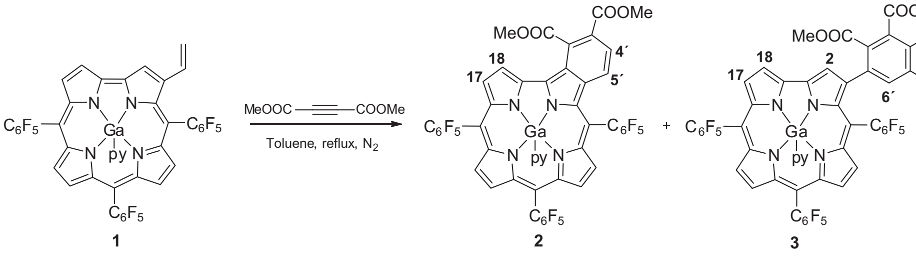
A careful inspection of Fig. 1 rules out for the absence of any emissive impurity due to the total overlap between the absorption and excitation spectra. The fluorescence quantum yield of β-substituted corrole **3** ($\phi = 0.08$) is relatively lower than that obtained with the benzocorrole **2** ($\phi = 0.24$). The high value shown by derivative **2**, is probably related with conformation issues. Compound **2** is the most planar one having then a major value of fluorescent quantum yield.

2.3. Sensorial ability towards fluoride, cyanide, acetate and phosphate anions in toluene

The sensorial ability of compounds **2** and **3** for spherical (F^-), linear (CN^-) and bulky anions (CH_3COO^- and $H_2PO_4^-$) was carried out by the increasing addition of the tetrabutylammonium salts to a solution of each corrole derivatives. The titrations were followed by absorption and emission fluorescence measurements in toluene. The addition of F^- anion produces spectral changes in the ground and excited states of compounds **2** and **3**. Fig. 2 shows the spectrophotometric and spectrofluorimetric titrations of compounds **2**

Table 1
Selected photophysical data of compounds **2** and **3** in toluene.

Compounds	λ_{max}(nm):log ε	λ_{em} (nm)	Δλ (nm)	Φ
2	590:3.82	616	26	0.24
3	596:3.78	618	22	0.08



Scheme 1.

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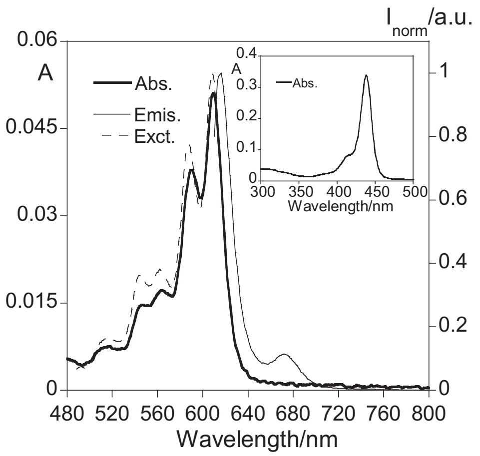

Fig. 1. Room temperature absorption (bold line), normalized emission (full line, λ_{exc} = 590 nm) and excitation spectra (dotted line, λ_{em} = 620 nm) of compound **2** in toluene. Inset: Absorption spectrum of compound **2**.

and **3** in the presence of fluoride anions in toluene. Upon addition of F^- to derivative **2** a red shift from 590 to 600 nm and from 616 to 620 nm is detected in the absorption, as well as, an increase in the absorbance at 600 and 620 nm (see Fig. 2A). In the emission spectra a red shift from 616 to 630 nm, accompanied by a quenching of 40% is visualized (see Fig. 2B). A similar behaviour was observed for compound **3**. Considering the absorption spectrum of **3** (see Fig. 2C) the titration with F^- is responsible for a decrease in the band at 596 nm and an increase in the one at 606 nm, accompanied by a red-shift from 596 to 606 nm and from 618 to 624 nm. In the excited state a quenching at 618 nm of ca. 40% occurred, followed by a red-shift from 618 to 635 nm (see Fig. 2D).

The most interesting results arise from cyanide interaction, where the compound **2** shows to be colorimetric, being its interaction with the anions naked-eye detectable.

Fig. 3 shows the absorption (ground state; Q band region) and emission (excited state) spectra of compounds **2** and **3** with the increasing amount of cyanide. In all compounds in the ground state a red shift from *ca* 440 to 450 nm followed by a decrease in the absorbance is noticed in the Soret type band. For compound **2** in the Q band region, a red shift from 590 to 605 nm and from 616 to 630 nm, with an absorbance increased at 630 nm are detected. These alterations are accompanied by a colour change from *green* to *colourless* (see Fig. 3A). A red shift in the emission spectra of **2** from 616 to 637 nm, and an emission quenching at 616 nm is detected, as well (see Fig. 3B). For compound **3** in the ground state it is also detected a red shift from 596 to 607 nm (see Fig. 3C). Subsequently, in the excited state a red shift from 618 to 636 nm, is

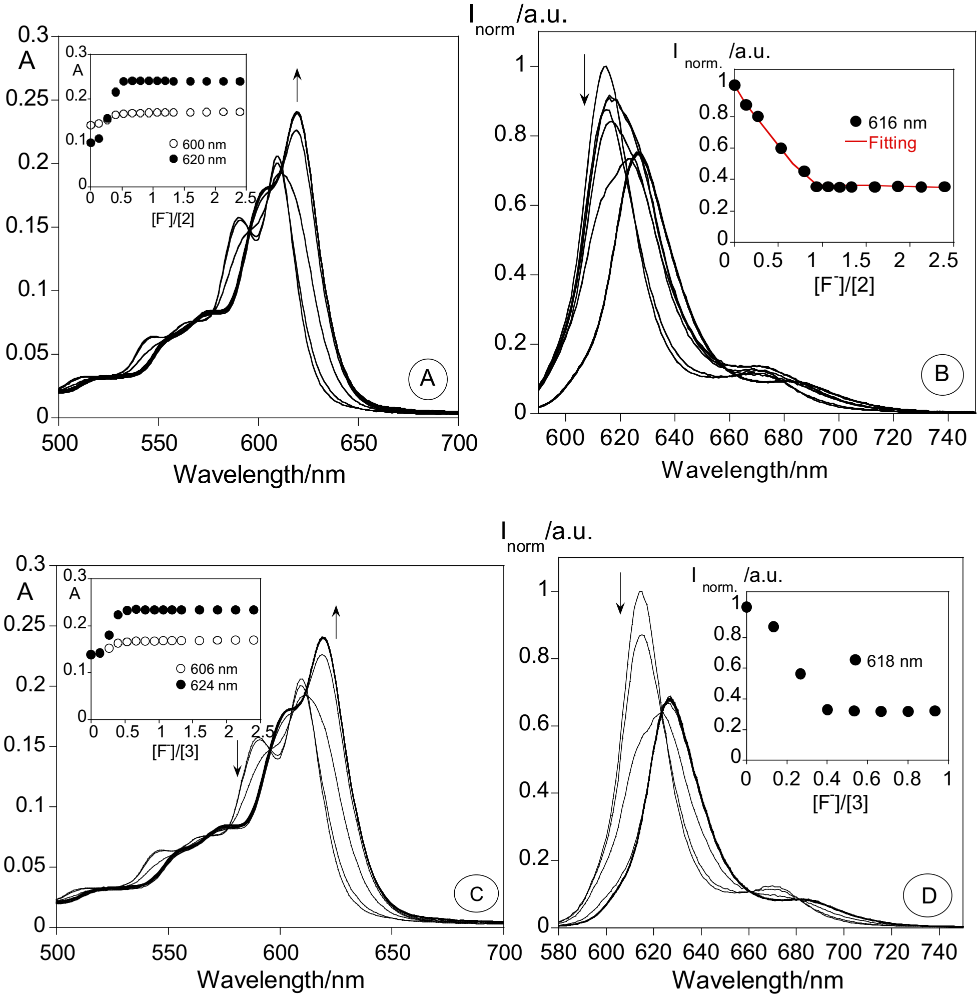

Fig. 2. Spectrophotometric (A, C) and spectrofluorimetric (B, D) titration of compounds **2** (A, B) and **3** (C, D) with the addition of F^- in toluene. The inset represents the absorption at 600, 620 nm (A), 606, 624 nm (C) and the emission intensity at 616 nm (B), 618 nm (D) as a function of $[F^-]/[2]$, $[F^-]/[3]$ ($[2] = [3] = 1 \times 10^{-5}$ M, λ_{exc2} = 590 nm, λ_{exc3} = 596 nm, T = 298 K).

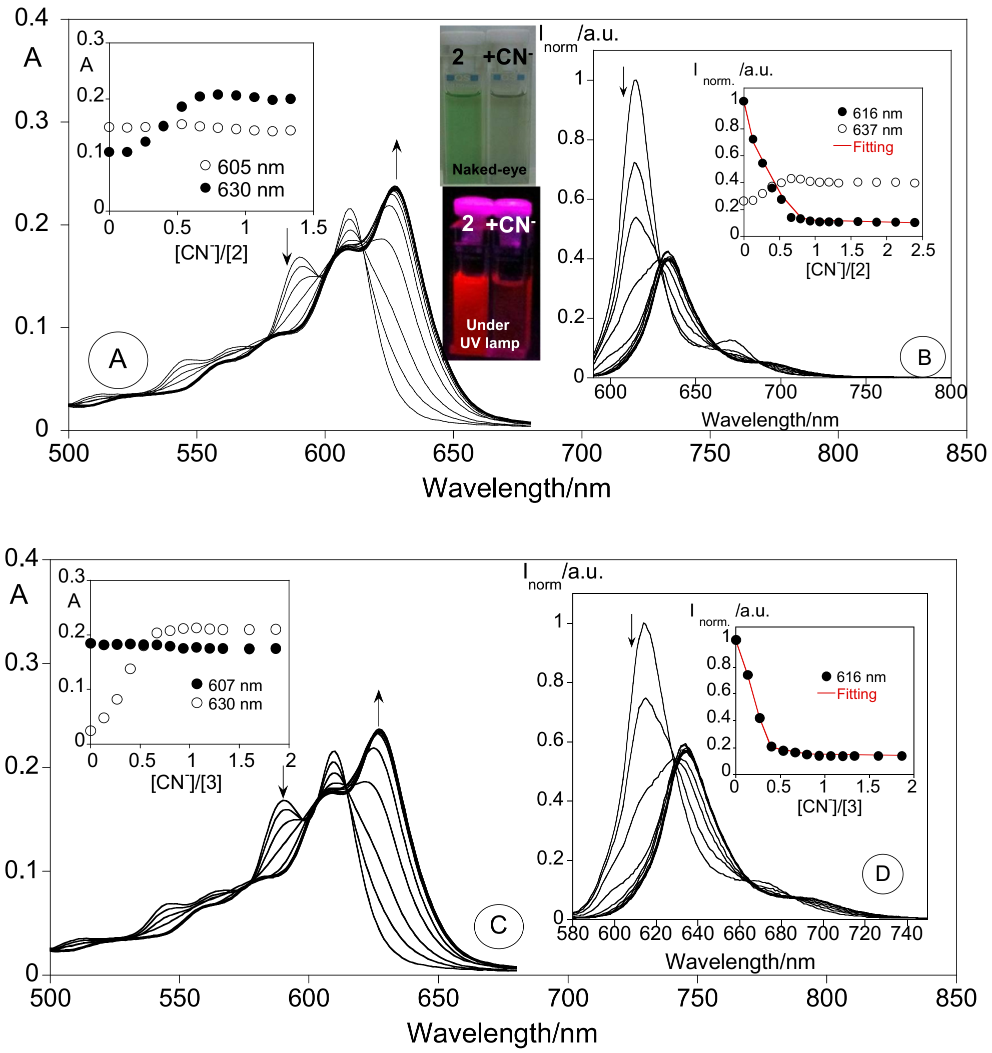

Fig. 3. Spectrophotometric (A, C) and spectrofluorimetric (B, D) titration of compounds **2** (A, B) and **3** (C, D) with the addition of CN^- in toluene. The inset represents the absorption at 605, 630 nm (A), 607, 630 nm (C) and the emission intensity at 616, 637 nm (B), 616 nm (D) as a function of $[CN^-]/[2]$, $[CN^-]/[3]$ ($[2] = [3] = 1 \times 10^{-5}$ M, $\lambda_{exc2} = 590$ nm, $\lambda_{exc3} = 596$ nm, $T = 298$ K).

perceived, as well as, a turn-off in the emission intensity at 618 nm (see Fig. 3D).

The bulky anions as acetate and phosphate can be found in food additives and in agricultural fertilizers [8]. Their interactions with corrole **2** did not produce changes in the ground state (see Fig. 4A and C). However, in the excited state a quenching of ca. 40% at 616 nm was observed for macrocycle **2** in the presence of CH_3COO^- and $H_2PO_4{}^-$ anions (see Fig. 4B and D). A different situation occurs with corrole **3** where no changes in the ground and excited state were observed, during the titrations performed with the anions above referred.

The association constants for anions interaction were determined using the HYPSPEC program [22] and the main results are gathered in Table 2. For both compounds the highest association constants were obtained for cyanide anion (corrole **3** $\text{Log}K_{\text{ass.}} = 6.82 \pm 0.02$) and (corrole **2** $\text{Log}K_{\text{ass.}} = 6.73 \pm 0.02$). A stoichiometry of two complexes per anion was postulated for both derivatives. Concerning the sensorial ability of compounds **2** and **3** studied towards cyanide anion and future application of these probes, the detection (LOD) and quantification (LOQ) limits for the analyte (CN^-) were also determined (see Table 2). It was found that compounds **2** and **3** are able to detect and quantify a fewer amount of cyanide with values of 0.33–0.34 μM and of 1.00–1.01 μM, respectively.

3. Experimental

3.1. Materials

$(CH_3CH_2CH_2CH_2)_4NF$, $(CH_3CH_2CH_2CH_2)_4N(CN)$, $(CH_3CH_2CH_2CH_2)_4N(CH_3CO_2)$, $(CH_3CH_2CH_2CH_2)_4NCl$, $(CH_3CH_2CH_2CH_2)_4N(H_2PO_4)$ salts were purchased from Sigma–Aldrich and dimethyl acetylenedicarboxylate were obtained from Alfa Aesar. All these chemicals were used without further purification. The solvents were obtained from Panreac and Riedel-de Haen and used as received or distilled and dried using standard procedures.

3.2. Physical measurements

Elemental analyses were carried out with a Fisons Instruments EA1108 microanalyser at the University of Vigo (CACTI), Spain. ^1H NMR spectra were recorded on Bruker Avance 300 (at 300 and 75 MHz, respectively) spectrometers. ^{19}F NMR spectra were also

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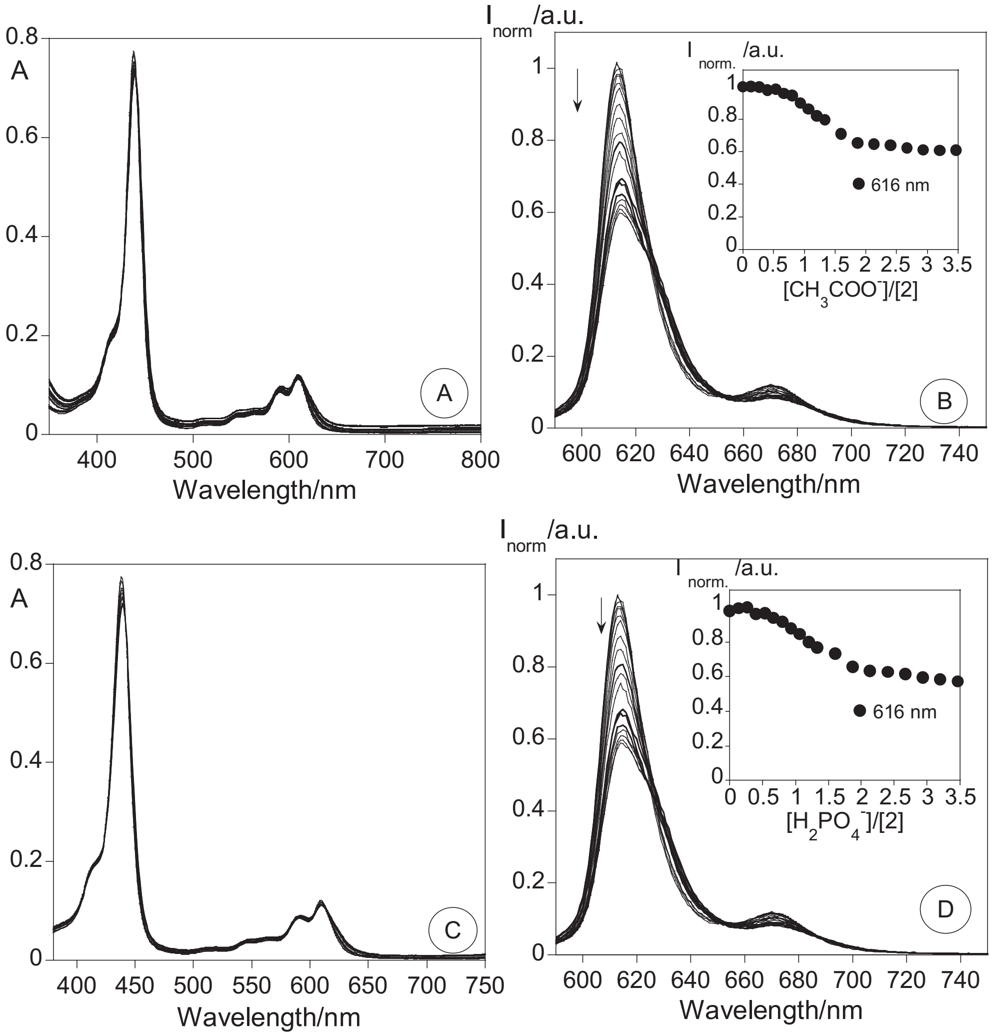

Fig. 4. Spectrophotometric (A, C) and spectrofluorimetric (B, D) titration of compound **2** with the addition of CH_3COO^- and $H_2PO_4^-$ in toluene. The inset represents the emission intensity at 616 nm for (B) and (D) as a function of $[CH_3COO^-]/[2]$ and $[H_2PO_4^-]/[2]$ ($[2]=1 \times 10^{-5}$ M, λ_{exc2} = 590 nm, T = 298 K).

Table 2
Association constants, detection (LOD) and quantification (LOQ) limits of compounds **2** and **3**. [LOD and LOQ were measured at 616 and 618 nm for **2** and **3**].

Compound	Anion	Log K_{ass} A:L	LOD (μM)	LOQ (μM)
2	F^-	5.48 ± 0.02 (1:2)	–	–
	CN^-	6.73 ± 0.02 (1:2)	0.33	1.00
	CH_3COO^-	4.28 ± 0.02 (1:2)	–	–
	$H_2PO_4^-$	3.78 ± 0.02 (1:2)	–	–
3	F^-	5.86 ± 0.01 (1:2)	–	–
	CN^-	6.82 ± 0.02 (1:2)	0.34	1.01

obtained on a Bruker Avance 300 at 282 MHz. $CDCl_3$ and pyridine-d_5 were used as solvents with tetramethylsilane (TMS) as the internal reference; the chemical shifts are expressed in δ (ppm) with the coupling constants (J) in Hertz (Hz). Unequivocal ^{1}H assignments were made using 2D COSY experiments (mixing time of 800 ms). Preparative thin-layer chromatography (TLC) was carried out on 20 × 20 cm glass plates coated with silica gel (0.5 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (Merck 60, 0.2 mm thick).

3.3. Spectrophotometric and Spectrofluorimetric measurements

Absorption spectra were recorded on a JASCO V-650 Spectrophotometer and the fluorescence emission on a Spectrofluorimeter HORIBA-JY Scientific Fluromax-4. The linearity of the fluorescence emission versus the concentration was checked out 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 compounds **2** and **3** (*ca.* 10^{-3} M) were prepared by dissolving an appropriated amount of each compound in a 10 mL volumetric flask and diluting it to the mark with toluene. The solutions were prepared by appropriate dilution of the stock solutions up to 10^{-5}–10^{-6} M. Titrations of compounds **2** and **3** were carried out by adding microliter amounts of standard solutions of the anions in DMSO.

Fluorescent quantum yields of compounds **2** and **3** were measured using a solution of cresyl violet perchlorate in absolute ethanol as a standard ($[\phi]$ = 0.54) [23] and was corrected for different refraction indexes of solvents. The limit of detection (LOD) and the limit of quantification (LOQ) for the anions were performed, having in mind their use for real anion detection and for analytical applications. For these measurements, ten different analyses for the selected receptor were performed in order to obtain the LOQ. The LOD was obtained by applying the formula:

$$Y_{dl} = y_{blank} + 3std \text{ where } y_{dl} = \text{signal detection limit and std} = \text{standard deviation.}$$

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3.4. Synthesis of organic ligands

The precursor gallium(III) complex of 3-vinyl-5,10,15-tris(pentafluorophenyl)corrole **1** was synthesized according to the procedures described within the literature [15].

*3.5. General procedure for preparing compounds **2** and **3***

A solution of **1** (0.025 mmol) and the dienophile (acetylenedicarboxylate) (0.050 mmol) in toluene (0.5 mL) was gently refluxed for 48 h under a nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated and the compounds **2**, and **3** were separated and further purified by preparative TLC (silica: hexane–ethyl acetate–pyridine (15:5:0.1)). Compound **2** and **3** were obtained in 81% and 16% yield and were crystallized from dichloromethane/methanol.

*3.5.1. Compound **2**: ^1H NMR ($CDCl_3 + C_5D_5N$, 300.13 MHz), δ (ppm) and J (Hz):*

4.09 (s; 3H; 2′-CO_2Me), 4.58 (s; 3H; 3′-CO_2Me), 8.17 (d; 1 H; J = 8.7 Hz; H-4′), 8.53 (d; 1 H; J = 8.7 Hz; H-5′), 8.86–8.67 (m; 4 H; H-β), 8.91 (d; 1H; J = 3.6 Hz; H-17), 9.46 (d; 1 H; J = 3.6 Hz; H-18).

^{19}F NMR (282.37, $CDCl_3 + C_5D_5N$): −161.49 to −161.69 (m, 6F, Forto), −175.38 (t, 1F, J = 21.1 Hz, Fpara), -177.38 (t, 1F, J = 21.3 Hz, Fpara), −177.57 (t, 1F, J = 21.1 Hz, Fpara), −184.85 to −185.14 (m, 2F, Fmeta), −185.89 to −186.15 (m, 2F, Fmeta), −186.15 to −186.42 (m, 2F, Fmeta).

λ_{max} ($\log\varepsilon$) Toluene: 418 (sh), 440 (5.21), 590 (3.82), 614 (3.08) nm.

MALDI-MS m/z: 1029 $[M+H]^+$. *Anal.* Calc. for $C_{45}H_{14}F_{15}GaN_4O_4$: C, 52.51; H, 1.37; N, 5.44. Found: C, 52.48; H, 1.46; N, 5.47%.

*3.5.2. Compound **3**: ^1H NMR ($CDCl_3 + C_5D_5N$, 300.13 MHz), δ (ppm) and J (Hz):*

3.80 (s; 3H; CO_2Me), 3.86 (s; 3H; CO_2Me), 3. 95 (s; 3H; CO_2Me), 4.23 (s; 3H; CO_2Me), 8.48 (d; 1 H; J = 4.5 Hz; H-β), 8.52 (d; 1 H; J = 4.7 Hz; H-β), 8.68 (d; 1 H; J = 4.7 Hz; H-β), 8.77–8.73 (m; 2 H; H-β and H-17), 9.12 (d; 1 H; J = 4,1 Hz; H-18), 9.66 (s; 1 H; H-2), 10.52 (s; 1 H; H-6′).

^{19}F NMR (282.37, $CDCl_3 + C_5D_5N$): −161.41 (dt, 4F, J = 23.5, 11.8 Hz, Forto); −162.19 (dd, 2F, J = 24.5, 8,4 Hz, Forto), −176.19 to −176.40 (m, 1F, Fpara), −176.67 (t, 1F, J = 21.0 Hz, Fpara); −185.17 to −185.42 (m, 2F, Fmeta), −185.49 to −185.69 (m, 2F, Fmeta), −185.76 to −185.95 (m, 2F, Fmeta),

λ_{max} ($\log\varepsilon$) Toluene: 417 (sh), 443 (5.21), 596 (3.78), 616 (3.17) nm.

MALDI-MS m/z 1171 $[M+H]^+$. *Anal.* Calc. $C_{51}H_{20}F_{15}GaN_4O_{8.1/3}Py$: C, 52.81; H, 1.82; N, 5.07. Found: C, 52.62; H, 1.50; N, 5.39%.

4. Conclusions

Two new corrole derivatives **2** and **3** were synthetized and fully characterized. Corrole **2** shows a colorimetric behaviour in the presence of cyanide, whereas a change of colour from *green* to *colourless* was visualized. Corroles **2** and **3** shows good affinity for cyanide presenting the highest association constant for the tested anions. At the same time, the low detection and quantification limits obtained for corrole derivatives **2** and **3** opens new avenues for their future application in real environmental samples.

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