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Contents lists available at SciVerse ScienceDirect

Tetrahedron



journal homepage: www.elsevier.com/locate/tet

New coumarin–corrole and –porphyrin conjugate multifunctional probes for anionic or cationic interactions: synthesis, spectroscopy, and solid supported studies

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ARTICLE INFO

Article history: Received 14 May 2013 Received in revised form 2 July 2013 Accepted 8 July 2013 Available online xxx

Keywords: Corroles Porphyrins Coumarins Chemosensors Mercury Fluoride Cyanide Acetate ion Agarose Cellulose

ABSTRACT

Corroles and porphyrins are very promising probes to be used as materials for anion and metal ion detection. Here, we present the synthesis and characterization of two new corrole–coumarin derivatives **7–8** and some porphyrin–coumarin analogs **3–6**.

The sensing ability of the metalloconjugates was studied in the presence of spherical (F^- , Cl^-), linear (CN^-), and bulky anions (CH_3COO^-). The porphyrin free-base conjugates were studied with Na⁺, Ca²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Fe²⁺, Ba²⁺, Cu²⁺, Ag⁺, and Hg²⁺, showing a colorimetric effect (color change from purple to yellow) and an unprecedented selectivity for Hg²⁺.

The insertion of coumarin moiety confers an unusual solubility of these conjugates in ethanol. One of the porphyrin free-base conjugate was fully studied in a mixture $EtOH/H_2O$ (50:50) and showed a similar behavior with Hg^{2+} . Under these conditions, the conjugate presented a higher association constant than in toluene and was able to detect and quantify a minimal amount of 0.6 ppm and 1.2 ppm of Hg^{2+} , respectively. Having in mind the biological and environmental application of these conjugates, non-expensive solid supports, like agarose and natural cellulose polymers were developed. In the cellulose support material (filter paper) the colorimetric effect for Hg^{2+} reveals a similar behavior as in solution. In addition pH studies carried out with the same conjugate showed a green color at low pH and a yellow color at high pH values in solution and in solid supports.

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1. Introduction

Corroles and porphyrins are excellent candidates for a great variety of sensing material applications. Chemosensors based on these tetrapyrrolic macrocycles are being pursued as active materials owing to their large absorption coefficient and well tunable fluorescence emission.^{1–6}

Porphyrin combined with other classes of molecules have been used as fluorophores in the detection of heavy metals like Cd(II), Pb(II), and Hg(II).⁷ Also, metalloporphyrins, depending on the metal ion incorporated into the inner core of the complex, offer an

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0040-4020/\$ — see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.07.022 excellent method to develop ion-selective electrode and optical sensor devices. $^{\rm 8}$

In particular, optical sensors based on porphyrinic complexes of Zn(II), Cd(II), and Hg(II) with amide functionality have shown higher anion binding abilities in more competitive solvent medium than those with metals like Fe(III), Co(III), Ni(II), and Cu(II).⁹ For instance, a cage receptor based on tetra-triazole Zn(II) metal-loporphyrin shows a naked-eye colorimetric response when strongly bound to anions.¹⁰ Also, a Zn(II)—porphyrin bearing naphthalimide or aza-crown ether-capped moieties created a fluoride ion-triggered dual fluorescence molecular switch,¹¹ or color change in the presence of sodium cyanide.¹²

In the case of corroles, these macrocycles coordinate with a large number of metals,¹³ and are very promising materials for optical and sensing applications.¹⁴ Although a few number of free-base corroles or their derivatives are being explored as selective

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sensors for Hg(II) ion, 5,15 the Ga(III) complex is presently a selective sensor for F⁻ and CN⁻ ions, 6 which empowers newer corrole derivatives to be explored as sensors for anion selectivity.

A good fluorescent chemosensor must have a strong affinity and selectivity for the analyte, no environmental interferences with the fluorescence signal, and it must be photostable. It should also be Recently we reported the hetero Diels–Alder reaction of 2-vinyl-5,10,15,20-tetraphenylporphyrinatozinc(II) **1a** with *o*-quinone methides (*o*-QM) generated in situ from Knoevenagel reaction of 4-hydroxycoumarin or 4-hydroxy-6-methylcoumarin with paraformaldehyde that afforded, respectively, derivatives **3** and **4** (Scheme 1).³⁰



Scheme 1. Functionalization of 1a with coumarin units.³⁰

easily accessible by organic reactions and be robust in nature. A good strategy to develop new probes or chemosensors is the coupling of two different molecules with well-established sensory activities.

Coumarin derivatives have been utilized as sensors for Hg(II),¹⁶⁻¹⁸ F^{-,19-23} and CN^{-24,25} ions either in organic solvents or aqueous mixtures at biological pH.

The inclusion of the coumarin nucleus in the porphyrin or corrole frameworks can enhance the fluorescence emission and furnish better solubility in aqueous medium. It is reported that coumarins transfer energy to the porphyrin molecule and increase the fluorescence lifetimes.^{26,27} Similarly, corroles coumarin dyads also have shown efficient energy transfer from the coumarin moiety to corrole.^{28,29}

Using this methodology we were able to functionalize 5,10,15,20-tetraphenylporphyrinatozinc(II) **1b** at the β -pyrrolic position with coumarin units. Thus, using similar approach we envisaged the design of corroles with coumarin moieties from the recently developed gallium(III) complex of 3-vinyl-5,10,15-tris(pentafluorophenyl)corrole **2**.⁶

Following our interest, in the development of sensing materials,³¹ we synthesized the new corrole–coumarin derivatives **7** and **8** (Scheme 2). The photophysical characterizations of compounds **3–6** and **7–8** were also carried out.

The sensing ability of the metalloconjugates towards the spherical halide ions F^- , Cl^- , the linear anion CN^- , and the bulky anion CH_3COO^- was evaluated. Interaction studies of the porphyrins **5** and **6** with the metal ions Na⁺, Ca²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Cu²⁺,



Scheme 2. Synthesis of corrole coumarin ligands 7 and 8.

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Tab

 Pb^{2+} , Hg^{2+} , Zn^{2+} , Ag^+ were realized. Additionally, pH studies were also performed with these two free-base porphyrins (**5** and **6**).

Considering the environmental monitoring of heavy metals⁷ and pH³² the potential of compound **5** was tested using nonexpensive natural solid supports, with simple fabrication and handling towards Hg(II) and pH studies. The polymeric materials selected were agarose³³ used in gel electrophoresis, and cellulose. Also, the use of these compounds for on-site Hg(II) detection, was carried out by immersing a filter paper in the compound solution and drying in air.

2. Results and discussion

2.1. Synthesis

The synthetic strategy to obtain the new corrole-coumarin conjugates 7 and 8 is shown in Scheme 2. The gallium(III) complex of 3-vinyl-5,10,15-tris(pentafluorophenyl)corrole 2 was reacted with the o-quinone methides, generated in situ from ca. 1.4 equiv of 4-hydroxycoumarins and 11 equiv of paraformaldehyde, under reflux in 1,4-dioxane. The reaction of vinyl corrole 2 showed complete consumption in 1 h (TLC) and after the workup and preparative purification the adducts 7 (92% yield) and 8 (87% yield) were isolated. The structures of these corrole-coumarin conjugates were confirmed by NMR (1D and 2D), UV-vis, and high resolution mass spectrometry. In particular, from the analysis of ¹H NMR spectra of 7 (for numbering see Scheme 2) it was possible to assign, the four multiplets between δ 2.65 and 3.02 to the H-3' and H-4' protons of the dihydropyran ring and the double doublet at δ 5.83 to the H-2' proton (this feature is due to the non-equivalence of H-3' protons). In the aromatic region, the multiplet at δ 7.19–7.24 was assigned to the H-9' of coumarin nucleus, the ones at δ 7.38–7.42 and δ 7.66–7.68 to H-7' and H-8', respectively, and finally the doublet at δ 7.84 to H-10'. The beta substitution pattern of the corrole nucleus was confirmed by the presence of the singlet at δ 9.40 due to H-2 proton resonance. The analysis of the ¹³C NMR spectrum of **7** showed the signal at δ 163.2 and δ 75 assigned to the coumarin carbonyl (C5') and C2', respectively, which is in accordance with the proposed structure; this shows that the addition occurred selectively at the 3,4-position of the coumarin nucleus.³⁰ In the ¹H NMR spectrum of compound **8**, the presence of the methyl group on the coumarin moiety was confirmed by the appearance of a singlet at δ 2.27.

Similarly, the reaction of 2-vinyl-5,10,15,20-tetraphenylporphyrin natozinc(II) (**1a**) with the *o*-quinone methide, generated in situ from 4-hydroxycoumarins and paraformaldehyde afforded the porphyrin–coumarin conjugates **3** (88% yield) and **4** (95% yield).³⁰ The decomplexation of porphyrin–coumarin conjugates **3** and **4** in 5% TFA/CHCl₃ gave the corresponding free-bases **5** (97% yield) and **6** (92% yield). The structures of these coumarin conjugates were confirmed by NMR, UV–vis, and high resolution mass spectrometry. The NMR profile of the free-bases was similar to the metalloporphyrinic forms. The presence of the inner N–*H* of the macrocycle at δ –2.69 confirmed the success of the metal removal.

2.2. Photophysical studies

The photophysical characterization of compounds **3** to **8** were performed in dichloromethane, DMSO, toluene, and ethanol solutions at 298 K. Compound **5** was characterized in the solvents referred above and also in a mixture of ethanol/water (50:50). In Table 1, the main photophysical data for all compounds in toluene are reported and the results obtained in the other solvents are presented in Supplementary data (Table SN1).

In toluene and in the other solvents, the absorption spectra of the metalloporphyrin conjugates ${\bf 3}$ and ${\bf 4}$ showed the Soret band

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Photophysical data of compounds 3-8 in toluene at 298 K

Compds.	λ_{\max} (nm):log ϵ	$\lambda_{em} (nm)$	Stoke's shift (nm)	Φ
3	426:5.23; 565:3.95; 599:3.21	599,646	47	0.02
4	426:5.28; 560:4.15; 599:3.31	599,646	47	0.01
5	421:5.32; 523:4.15; 557:3.85;	652,719	67	0.02
	603:3.78; 652:3.56			
6	420:5.38; 519:4.15; 560:3.86;	652,713	61	0.02
	607:3.72; 652:3.40			
7	427:5.51; 580:4.30; 601:3.81	602,650	48	0.06
8	426:5.53; 582:4.27; 601:3.76	602,651	49	0.09

between 423 and 426 nm (due to the allowed transition from $S_0 \rightarrow S_2$) and two weak Q bands (due to the transition from $S_0 \rightarrow S_1$) at ca. 560–565 and 599 nm. The free-base derivatives **5** and **6** exhibit the Soret band between 417 and 424 nm and four Q bands centered between 519 and 654 nm. The absorption spectra of corroles **7** and **8** present the Soret-type band between 426 and 430 nm and two Q bands at ca. 580 and 603 nm except for compound **8** in DMSO. In the case of compound **8** a bathochromic shift was visualized with polarity increase, being the absorbance band centered at ca. 582 nm (toluene)<585 nm (CH₂Cl₂)<587 nm (EtOH)<605 nm (DMSO). This positive solvatochromic effect can be detected by naked eye for compound **8**, which shows different colors in different solvents (colorless; yellow and purple—Fig. 1).



Fig. 1. Solvatochromic effect of compound 8.

In order to characterize quantitatively this solute—solvent interaction the multiparametric fitting of Kamlet—Taft equation³⁴ was realized by using of solvent parameters gathered in Table SN2. Through this fitting a liner plot of v_{exp} versus v_{calcd} was determined for compound **8**, being the fitted parameters $v_0=17,887 \text{ cm}^{-1}$, $a=-2274 \text{ cm}^{-1}$, $b=2156 \text{ cm}^{-1}$, and $p=-2283 \text{ cm}^{-1}$ with a correlation factor of 1. The negative value of p shows that the contribution of dipolarity/polarizability decreases the stabilization of the excited state in compound **8**. The ground (μ_g) and excited (μ_e) states dipole moments were estimated based on Kawski theory,^{35,36} whereas, a linear curve fitting of v_a-v_f and v_a+v_f as a function of $f(\varepsilon,n)$ and $f(\varepsilon,n)+2g(n)$. Values of $\mu_g=0.42$ D and $\mu_e=0.15$ D were determined, which indicate that in compound **8**, the ground state is slightly more polar than the excited state.

Fig. 2 shows the absorption (only Q band region), excitation, and emission spectra, of compound **3** (Fig. 2A) as an example of metalloporphyrin series and of compound **7** (Fig. 2B) as an example of the corrole series.

The perfect match between the absorption and excitation spectra in Fig. 3, indicates the absence of any emissive impurity in all cases.

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Fig. 2. Absorption, normalized emission and excitation spectra of porphyrin **3** (A) and corrole **7** (B) in toluene, (**[3]**=**[7]**= 5.0×10^{-6} M, λ_{exc} (full line)**3**=565 nm, λ_{exc} (full line)**7**=580 nm and λ_{emiss} (dotted line)**3**=646 nm λ_{emiss} (dotted line)**7**=650 nm).



Fig. 3. Spectrofluorimetric titrations of compound **3** (A) and **7** (B) with the addition of Cl⁻ and F⁻ in toluene at room temperature. ([**3**]=[**7**]=1.0×10⁻⁵ M, $\lambda_{exc. 3}$ =565 nm, $\lambda_{exc. 7}$ =580 nm).

The fluorescence emission spectra of zinc porphyrins **3** and **4** obtained after excitation at ca. 560–565 nm, present two bands centered at 599 and 646 nm that are characteristic of metal-loporphyrins derivatives (see Table 1 and Table SN1). Otherwise, the excitation of **5** and **6** at ca. 605 nm afforded two emission bands, one centered at ca. 652 nm and the other between 713 and 719 nm. In the case of corrole derivatives **7** and **8** the emission bands are centered between 602 nm and 652 nm.

As can been seen in Table 1 and SN1, the excited state of conjugates **3**–**7** are not affected by the dipole moment of the solvent. The fluorescence quantum yields of porphyrin and corrole derivatives were determined by the internal reference method with respect to a solution of crystal violet in methanol as a standard ([ϕ]=0.54) and the values are presented in Table 1 and Table SN1. The fluorescence quantum yields of porphyrinic conjugates **3**–**6** (0.01< ϕ <0.03) are relatively lower than those obtained with the corrole derivatives (0.04< ϕ <0.13), being the highest value determined for compound **8** in an ethanolic solution. This behavior can be due to the inherent differences of the tetrapyrrolic macrocycle.³⁷ On the other hand, a better solubility conferred by the coumarin unit to corrole may favor the decay of excited molecules by fluorescence in ethanol.

2.3. Spectrophotometric and spectrofluorimetric sensing studies

Corroles, porphyrins, and metalloporphyrins as it was already referred are excellent multifunctional candidates for a great variety of sensing material applications. These molecules are rather stable compounds and their properties can be finely tuned by simple modifications of their basic molecular structure. These macrocycles offer a large variety of interaction mechanisms that can be exploited for chemical sensing. Hydrogen bonds, polarization, and polarity interactions are expected to take place between analyte molecules and these tetrapyrrolic macrocycles.

For these reasons it was decided to study the potentialities of these macrocycles in conjunction with coumarins in the signaling of different anions and metals. The measurement of sensory activity is generally undertaken in purely organic solvents or less efficiently in aqueous mixtures. The combination of the corrole or porphyrin macrocycles with coumarin moiety, conferred solubility to all synthesized compounds in ethanol and in ethanol/water mixtures. This fact also prompted us to perform pH sensing studies.

2.3.1. Anion sensing effects. The sensorial ability of metallocompounds **3**, **4**, **7**, and **8** towards the spherical (F^- , CI^-), linear (CN^-), and bulky anions (CH_3COO^-) was carried out by ligand titrations with the addition of small amounts of the adequate anion as tetrabutylammonium salt.

The titrations were followed by UV—vis and fluorescence measurements in toluene and the most significant data are gathered in Table 2.

Fluoride ion is added in drinking water and dental hygiene products for the purpose of reducing the frequency of dental caries. However, its ingestion in high or in low levels may result in fluorosis, nephrotoxic changes, and urolithiasis in human.³⁸ The

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 Table 2

 Association constants of conjugates 3, 4, 7, and 8 in toluene

Compound	Analyte (A)	$Log K_{ass}$ (A:L)
3	Cl-	5.43±0.03 (1:1)
	CN^{-}	6.57±0.01 (1:1)
	CH ₃ COO ⁻	4.87±0.02 (1:1)
4	Cl-	5.40±0.03 (1:1)
	CN ⁻	6.53±0.01 (1:1)
	CH ₃ COO [−]	4.85±0.02 (1:1)
7	F	5.28±0.01 (1:1)
	CN^{-}	6.11±0.01 (1:1)
	CH ₃ COO ⁻	4.32±0.01 (1:1)
8	F	5.04±0.01 (1:1)
	CN^{-}	6.08±0.01 (1:1)
	CH_3COO^-	4.11±0.01 (1:1)

fluoride anion is known to be used in many industrial applications, and in human diet, but, recently it has been accused for several human pathologies (osteoporosis and poor dental health).³⁹ The EPA-recommended F^- level in drinking water is 1 ppm, and over 2 ppm is considered a health-risk.⁴⁰ The chloride ion has significant role in biological, medical and environmental fields. The addition of Cl⁻ to chemosensors **3** and **4** was responsible for mild alterations in their emission spectra. No spectral alterations were detected in

determined for compound **3** and **7**, respectively. Similar interactions were found for compounds **4** and **8**.

On the other hand, cyanide is one of the most poisonous and toxic anions. It is a lethal anion for humans, as well as for aquatic life.⁴³ Most environmental cyanides are released by industries involved in gold mining, electroplating, and metallurgy.⁴⁴ Due to its high toxicity, the highest allowable level of cyanide in drinking water by the World Health Organization (WHO) is 1.9 μ M.⁴⁵

The cyanide anion interacts with all metallocorroles and metalloporphyrins conjugates. The addition of CN⁻ to **3** promotes in the absorption spectrum (Fig. SN1A) a small red-shift from 426 to 429 nm ($\Delta\lambda$ =3 nm), accompanied by an increase of ca. 40% in the band at 429 nm. An isosbestic point at 427 nm was also observed. A similar behavior was observed in the case of Q-bands. Initially there was a decrease in the intensity of the band centered at 550 nm, and an increase at 573 nm, with an isosbestic point at 560 nm. A new band appears at 600 nm (Fig. SN1B). Considering the emission spectrum of **3** (Fig. 4A), the titration with CN⁻ was responsible for a decrease of intensity of ca. 60% at 599 nm and also at 646 nm (ca. 80%), followed by a red-shift from 599 to 605 nm and from 646 to 656 nm. Similar spectral modifications were also observed in compound **4**.



Fig. 4. Spectrofluorimetric (A, B) titrations of compounds **3** and **7**, in toluene, with the addition of CN^- in DMSO. The insets show the normalized emission intensity at 599 and 646 nm (A) and at 601 and 613 nm (B) ([**3**]=[**7**]= 1.0×10^{-5} M, $\lambda_{exc. 3}$ =565 nm, $\lambda_{exc. 7}$ =580 nm, T=278 K).

their absorption spectra, suggesting that their ground state is not affected by the interaction with this spherical halide ion. Fig. 3A shows the spectral changes, in the excited state, obtained for compound 3 during the titration with Cl⁻. This addition leads to an emission quenching of ca. 40% at 599 and of ca. 60% at 646 nm, followed by a red-shift from 599 to 605 nm and from 646 to 656 nm. A similar spectral behavior was obtained for compound **4**. Considering the addition of F⁻ to these two chromophores **3** and **4** no significant spectral changes were detected. In the case of corrole conjugates 7 and 8 no spectral modifications were observed, in the ground state, during the titrations with these anions and in the excited state with Cl⁻. However, the titrations of these compounds with F^- were responsible for a quenching of ca. 40% at 602 nm. Fig. 3B, shows the spectrofluorimetric titration of compound 7, in toluene, in the presence of F⁻. Similar spectral changes were detected for compound **8** with the addition of fluoride.

The association constants for the interaction of F^- and Cl^- with the different ligands were determined using the HypSpec⁴¹ program and are summarized in Table 2.

Looking at Table 2, for the anions chloride and fluoride a stoichiometry of one ligand per anion was postulated, and was confirmed by Job's plot method (SI).⁴² Thus, a value of Log $K_{ass.}$ $_{Cl}$ =5.43±0.03 (1:1); and of Log $K_{ass.}$ _F=5.28±0.01 (1:1), were In the presence of CN⁻, compounds **7** and **8**, undergo strong changes in the ground state. The addition of the anion produces a decrease in the intensity of the initial bands centered at ca. 580 nm and 601 nm, with the concomitant appearance of two new bands centered at 588 nm and 613 nm. Two isosbestic points were detected at 586 nm and 607 nm (Fig. SN1C). Taking into account the emission spectra (excited state), a quenching of ca. 40% at 601 nm was observed (Fig. 4B) followed by a red-shift of 12 nm.

With respect to the association constants a value of Log $K_{ass}=6.57\pm0.01$ (1:1) and of Log $K_{ass}=6.11\pm0.01$ (1:1) were determined for compound **3** and **7**, respectively (Table 2).

Compounds **3**, **4**, and **7**, **8** were titrated with the acetate anion (CH₃COO⁻), and spectral changes in the ground and excited state were observed, in both macrocycles. In compound **3**, like in **4**, a red-shift in the absorption spectra from 426 nm to 430 nm, as well as, an emission quenching of ca. 80% at 599 nm and 646 nm, was observed, with the addition of 1 equiv of the anion (see Fig. SN2). With respect to the interaction of compound **7** and **8** with acetate a similar behavior to the one observed for cyanide was found (see Fig. SN3). An association constant of Log $K_{ass.}$ =4.87±0.02 and of Log $K_{ass.}$ =4.32±0.01, with a stoichiometry of one ligand per anion was determined for compounds **3** and **7**, respectively. Similar interactions were found for compounds **4** and **8**.

It is to be noted that the sensing ability of porphyrin precursor **1b** was also evaluated for all the anions and under the experimental conditions used, no changes in the ground and excited states were observed (see Fig SN4). These results are in accordance with literature.⁹

Additionally, the detection (LOD) and quantification (LOQ) limits for the anions studied were determined and the values gathered in Table 3 show that the lowest values for LOD (0.09 and 0.10 ppm) and LOQ (0.18 and 0.19) were obtained for compound **3** and **4**, respectively, with the addition of chloride anion.

Table	3
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Detection (LOD) and quantification (LOQ) limits of conjugates 3, 4, 7, and 8 in toluene

Compound	Analyte (A)	LOD (ppm)	LOQ (ppm)
3	Cl-	0.09	0.18
	CN ⁻	0.13	0.27
	CH ₃ COO [−]	0.20	0.40
4	Cl ⁻	0.10	0.19
	CN^{-}	0.13	0.27
	CH ₃ COO ⁻	0.21	0.42
7	F	0.52	0.87
	CN^{-}	0.18	0.27
	CH ₃ COO [−]	0.40	0.60
8	F	0.50	0.85
	CN^{-}	0.19	0.28
	CH ₃ COO [−]	0.41	0.62

2.3.2. Metal sensing effects. The sensorial ability of compounds **5** and **6** towards the metal ions Na⁺, Ca²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Fe²⁺, Ba²⁺, Cu²⁺, Ag⁺, and Hg²⁺ was investigated by the titration of the ligands, dissolved in toluene, with small amounts of the adequate metal salt dissolved in acetonitrile. These experiments were followed by UV/ vis and fluorescence emission spectroscopy. It is worth to refer that, mercury ions are environmentally toxic ions and are responsible for pollution and adverse effects to human health.⁴⁶

In these conditions, only the Hg(II) cation caused significant changes in the ground and excited states of porphyrins **5** and **6**. No changes were detected upon addition of the other metal ions to the derivatives **5** and **6**. Fig. 5A, B and C shows the alterations observed in the absorption and emission spectra of compound **5** with the increasing addition of Hg²⁺, in toluene.

In the absorption spectra, the addition of Hg^{2+} to **5** results in a decrease in the band at 421 nm and an increase at 434 nm. A colorimetric effect was observed (a change of color from purple to yellow), which allows a naked-eye detection of Hg^{2+} (see Fig. 5A). In the emission spectra a quenching in the emission intensity at 654 nm was visualized (Fig. 5C). The association constant was determined by HypSpec program and the value of Log $K_{ass.}$ $Hg^{2+}=5.51\pm0.01$, was obtained with a stoichiometry of one ligands per one metal ion.

Compound **5** was also titrated with Hg^{2+} in a mixture of EtOH/ H₂O (50:50), and in the emission spectra (see Fig. SN5B) a similar behavior, to the one found in toluene was detected. In the ground state a slight decrease in the absorbance at 421 nm was observed (see Fig. SN5A). A higher association constant for Hg^{2+} was obtained for EtOH/H₂O with respect to toluene, yielding a value of Log $K_{ass.}$ =7.13±0.01. At 654 nm the detection (LOD) and quantification (LOQ) limits were of 1.05±0.11 and 1.31±0.40, respectively. Thus, the minimal amount of Hg^{2+} detectable in an aqueous solution (EtOH/H₂O/50:50) by compound **5** was 0.6 ppm and the minimal amount quantified was 1.2 ppm.

In competitive studies with compound **5** in toluene a higher affinity and an unprecedented selectivity for Hg^{2+} metal was seen (Fig. 6), where a normalized emission intensity towards the addition of 2 equiv of metal ions studied is showed. A similar conduct was observed during the titrations with compound **6**.



Fig. 5. Spectrophotometric (A and B) and spectrofluorimetric (C) titration of compound **5** with the addition of Hg²⁺ in toluene. The inset represents the absorption (A, B) at 421 nm, 434 nm for (A) and 520 nm for (B); and represents the emission intensity (C) at 654 and 714 nm, as function of $[Hg^{2+}]/[5]$. ([**5**]=1×10⁻⁵ M, λ_{exc} =592 nm, *T*=298 K).



Fig. 6. *Black bar*: normalized relative emission intensity of compound **5** upon the addition of 2 equiv of a (Na⁺), b (Ca²⁺), c (Zn²⁺), d (Cd²⁺), e (Pb²⁺), f (Fe²⁺), g (Ag⁺) and h (Hg²⁺). *Red bar*: normalized emission intensity of **5** with Hg²⁺ upon addition of 100 equiv of the metal ions a to g. ([**5**]= 1×10^{-5} M, λ_{exc} =603 nm).

2.3.3. Solid supports and pH studies. Several pH studies with compound **5** were carried out in mixtures of ethanol/water (50:50). Fig. SN6 shows the absorption spectra of compound **5** at different pH's. Compound **5** behaves as a colorimetric sensor with the change in pH. Increasing the pH, compound **5** change its color from green (low pH) to yellow (high pH) (see Fig. 7A). This behavior is typical of *meso*-tetraarylporphyrins like 5,10,15,20-tetraphenylporphyrin

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Fig. 7. A. Color change (from green to yellow) at different pH, of compound **5** in EtOH/ H_2O (50:50). B. Agarose gel doped with compound **5** exposed at different pH (from pH 0.8–12).

(the free-base of **1b**),⁴⁷ but the great advantage of conjugate **5** is its high solubility in polar solvent, such as ethanol and water, which allows its use in non-expensive solid supports. The green color at very low pH, according with literature,⁴⁸ is due to the formation of dicationic species, confirmed by the appearance of a band at 650 nm, in the absorption spectra (Fig. SN6). During the pH experiments with compound 5, two low-cost polymers, agarose and cellulose, were tested (see Fig. 7B and SN7). Thus, an agarose and a natural cellulose polymer (carboxymethylcellulose sodium salt) doped with compound 5 were exposed to different pH's (from 0.8 to 12). The same color changes (green at low pH to yellow at higher pH) were observed in solution EtOH/H₂O (50:50) when the compound 5 was doped in the agarose and cellulose polymers. The emission of both polymers at different pH's was also recorded in solid state, using a fiber optic system connected to the Horiba Jobin-Yvon Fluoromax 4. As can be seen in Fig. SN8 with the pH, the emission intensity of the polymers doped with 5 was practically not affected. From these results compound 5 can be considered as a colorimetric pH probe, which can be applied in low cost materials, such as agarose and cellulose. It is worthwhile to mention that under the same conditions (EtOH/H₂O) the free-base of 1b showed limited solubility.

In order to explore the colorimetric properties of compound **5** and its application in solid support materials, cellulose paper, in this case filter paper, containing compound **5** was exposed to different amounts of mercury(II) metal ion. As can be seen in Fig. 8, the cellulose paper with **5** was purple and showed a strong red emission under a UV lamp λ_{exc} =365 nm. After the addition of Hg²⁺ metal ion, the color of the cellulose paper changes from purple to yellow, and under the UV lamp the strong red emission disappears.

This emission quenching in solid state was monitored using a fiber optic system and the results are presented in Fig. 8A.

3. Conclusions

New corrole–coumarin derivatives **7** and **8**, and the porphyrin–coumarin conjugates **3–6** were successfully obtained and fully characterized. The compounds were photophysically characterized in dichloromethane, DMSO, toluene, and ethanol. Compound **8** is slightly more polar in the ground state (μ_g =0.42 D) than in the excited state (μ_e =0.15 D), showing a positive solvatochromic effect, while the other conjugates were practically not affected by the solvent. A strong color change from purple to yellow (colorimetric effect) and an unprecedented selectivity for Hg²⁺ was detected for compound **5** in EtOH/H₂O (50:50); the association constant in EtOH/H₂O (50:50) was higher than in toluene (Log *K*_{ass. EtOH/} water=7.13±0.01; Log *K*_{ass. toluene}=5.51±0.01). In addition, compound **5** was able to detect and quantify the minimal amount of 0.6 ppm and 1.2 ppm of Hg²⁺ in aqueous solution (EtOH/H₂O, 50:50).

The naked eye sensorial ability of the colorimetric effect of **5** for Hg^{2+} was successfully applied in a solid support material, a cellulose paper (filter paper).

The sensorial ability of conjugate **5** for Hg^{2+} was maintained when applied in cellulose paper allowing naked eye detection.

Moreover, pH studies carried out with conjugate **5** showed a green color at low pH and a yellow color at high pH values in solution and solid supports.

4. Experimental section

4.1. Chemicals

NaCH₃SO₃, Ca(CH₃SO₃)₂, Ba(CH₃SO₃)₂, Cd(CH₃SO₃)₂, Cu(BF₄)₂· 6H₂O, Pb(BF₄)₂·6H₂O, Hg(CH₃SO₃)₂, Zn(CH₃SO₃)₂, Fe(CH₃SO₃)₂ AgCH₃SO₃, (CH₃CH₂CH₂CH₂O₄)₄NF, (CH₃CH₂CH₂CH₂)₄NCl, (CH₃CH₂CH₂CH₂)₄N(CN), (CH₃CH₂CH₂CH₂)₄N(CH₃CO₂) salts, paraformalde hyde, methanesulfonic acid (CH₃SO₃H), carboxymethylcellulose sodium salt, agarose, 4-hydroxycoumarin, and 4-hydroxy-6-methyl coumarin were purchased from Sigma–Aldrich. 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.

4.2. Physical measurements

HRMS were carried out at the University of Vigo (CACTI), Spain. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 (at



Fig. 8. Spectrofluorimetric titration of compound 5 in a cellulose paper with the addition of 0-4 equiv of the metal ions Hg²⁺ in water, λ_{exc} =592 nm.

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500 and 125 MHz, respectively) and 300 (at 300 and 75 MHz, respectively) spectrometers. ¹⁹F NMR spectra were also obtained on a Bruker Avance 300 at 282 MHz. CDCl₃ and pyridine- d_5 were used as solvents with tetramethylsilane (TMS) as the internal reference; the chemical shifts are expressed in δ (parts per million) with the coupling constants (*J*) in Hertz (Hz). Unequivocal ¹H assignments were made using 2D COSY experiments (mixing time of 800 ms), while ¹³C assignments were made on the basis of 2D HSQC and HMBC experiments (delay for long-range *J* C–H couplings was optimized for 7 Hz). 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).

4.3. Photophysical measurements

Absorption spectra were recorded on JASCO V-650 spectrophotometer and fluorescence emissions were performed on a Spectrofluorimeter HORIBA-JOBIN-YVON Fluoromax 4. The linearity of the fluorescence emission versus concentration was checked in the concentration range used (10^{-4} to 10^{-6} M). A correction for the absorbed light was performed when necessary. The spectroscopic characterizations and titrations were performed using stock solutions of the studied compounds (ca. 10^{-3} M), prepared by dissolving the appropriate amount of porphyrin/corrole derivatives in toluene, dichloromethane, ethanol or DMSO in a 10 mL volumetric flask. The studied solutions were prepared by appropriate dilution of the stock solutions up to 10^{-5} to 10^{-6} M. Titrations of the ligands **3–8** were carried out by the addition of microliter amounts of standard solutions of cations in acetonitrile and anions in DMSO or toluene, respectively. All the measurements were performed at 298 K. Fluorescence quantum yields were measured using a solution of cresyl violet perchlorate in absolute ethanol as a standard ($[\phi]$ 0.54),¹⁸ and were corrected for different refraction indexes of solvents. Fluorescence spectra of the doped solid supports were recorded using a fiber optic system connected to a Horiba Jobin-Yvon Fluoromax 4 spectrofluorimeter, exciting at appropriate λ (nm) for the solid supports. The limit of detection (LOD) and the limit of quantification (LOQ) for the analytes were performed, having in mind their use for real ions detection and 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: $y_{dl}=y_{blank}+3$ std where $y_{dl}=$ signal detection limit and std=standard deviation.

4.4. Synthesis of organic ligands

The precursors 2-vinyl-5,10,15,20-tetraphenylporphyrinatozinc (II) **1a** and gallium(III) complex of 3-vinyl-5,10,15-tris(pentafluoro phenyl)corrole **2** were synthesized according to the procedures described within the literature.^{6,30}

4.4.1. General procedure for preparing **3**, **4**, **7**, and **8**. In a roundbottom flask, equipped with a magnetic stirring bar, a solution of 4-hydroxycoumarin (5.7 mg, 35.5 μ mol)/4-hydroxy-6-methylcou marin (6.2 mg; 35.5 μ mol), 1,4-dioxane (5 mL), paraformalde hyde (8.5 mg, 284 μ mol), and porphyrin **1a** (25 mg, 35.5 μ mol)/ corrole **2** (25 mg, 25.8 μ mol) was heated at reflux until consumption of the starting porphyrin **1a**/corrole **2** (1 h). 1,4-Dioxane was then removed under reduced pressure, chloroform (50 mL) was added to the residue and the mixture was washed with saturated aqueous sodium bicarbonate (2×20 mL). The organic phase was concentrated under vacuum and the porphyrin residue was purified by column chromatography on silica gel and subsequently by preparative TLC using chloroform as the eluent. The corrole compounds were purified by preparative TLC using hexane/ethyl acetate/pyridine (150:50:1) system.

4.4.1.1. Compound **3**. {2-(5-Oxo-2,3,4,5-tetrahydro-2*H*-pyrano [3,2-c]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II).³⁰ 88%, ¹H NMR (CDCl₃, 500 MHz): δ 2.25–2.29 (m, 2H, H-3' and H-4'), 2.61–2.67 (m, 2H, H-3' and H-4'), 5.04 (d, 1H, J=8.5 Hz. H-2'), 7.19 (ddd, 1H, I=8.1, 7.2, 1.0 Hz, H-9'), 7.34 (dd, 1H, I=8.5, 1.0 Hz, H-7'), 7.40-7.45 (m, 1H, Hp-Ph), 7.49 (ddd, 1H, J=8.5, 7.2, 1.4 Hz, H-8'), 7.71-7.81 (m, 12H, Hm,p-Ph, H-10'), 8.16-8.23 (m, 8H, Ho-Ph), 8.75 (d, 1H, *I*=4.6 Hz, H-β), 8.90 (d, 1H, *I*=4.6 Hz, H-β), 8.94 (s, 2H, H-12 and H-13), 8.95 (d, 1H, *J*=4.6 Hz, H-β), 8.97 (d, 1H, J=4.6 Hz, H- β), 9.15 (d, 1H, J=0.5 Hz, H-3); ¹³C NMR (CDCl₃, 125 MHz): δ 20.9 (C-4'), 30.03 (C-3'), 75.9 (C-2'), 101.2(C-4'a), 115.9 (C-10'a), 116.5(C-7'), 120.5, 121.1, 121.3, 121.6, 122.5 (C-10'), 123.7 (C-9'); 126.4, 126.5, 126.6, 126.7, 127.6, 127.7, 128.5 (C-m,p); 131.2 (C-8'); 131.7, 132.3, 132.35, 132.6 (C-β); 133.4, 133.5, 134.37, 134.4, 134.42, 134.47, 134.5 (C-o); 142.3, 142.4, 142.5, 142.7, 143.5 (C-1), 145.6, 147.8, 150.2, 150.4, 150.5, 150.6, 150.9, 152.4 (C-6'a), 160.7 (C-10'b), 163.4 (C-5'); HRMS-ESI-TOF m/z calcd for C₅₆H₃₇N₄O₃ Zn [M+H]⁺ 877.2152, found 877.2116.

4.4.1.2. Compound **4**. {2-(9-Methyl-5-oxo-2,3,4,5-tetrahydro-2H-pyrano[3,2-c]chromen-2-yl)-5,10,15,20tetraphenylporphyrinato}zinc(II). 95%, ¹H NMR (CDCl₃, 500 MHz): δ 2.17–2.31 (m, 2H, H-3' and H-4'), 2.33 (s, 3H, CH₃), 2.61–2.68 (m, 2H, H-3' and H-4'), 5.06 (d, 1H, J=10.4 Hz, H-2'), 7.24 (d, 1H, *J*=8.4 Hz, H-7′), 7.31 (dd, 1H, *J*=8.4, 1.7 Hz, H-8′), 7.44–7.45 (m, 1H, Hm,p-Ph), 7.49 (d, 1H, J=1.7 Hz, H-10′), 7.71–7.79 (m, 11H, Hm,p-Ph). 8.15-8.28 (m, 8H, Ho-Ph), 8.76 (d, 1H, *J*=4.7 Hz, H-β), 8.90 (d, 1H, *J*=4.7 Hz, H-β), 8.94 (s, 2H, H-12 and H-13), 8.96 (d, 1H, *J*=4.7 Hz, Hβ), 8.97 (d, 1H, I=4.7 Hz, H-β), 9.15 (s, 1H, H-3); ¹³C NMR (CDCl₃, 125 MHz): δ 20.9 (Ar–CH₃), 21.0 (C-4'), 30.2 (C-3'), 76.0 (C-2'), 101.1 (C-4'a), 115.6 (C-10'a), 116.3 (C-7'), 120.5, 121.05, 121.3, 121.6, 122.2 (C-10'), 126.4, 126.5, 126.6, 126.8, 127.6, 127.66, 128.6 (C-m,p); 131.7, 132.2, 132.3, 132.4, 132.5, 132.6 (C-8' and all C-β); 133.37, 133.4, 133.6, 134.37, 134.41, 134.44, 134.6 (C-o); 142.2, 142.5, 142.8, 143.6, 145.5, 147.8, 150.2, 150.4, 150.5, 150.6, 150.7, 150.8, 160.7 (C-10'b), 163.6 (C-5'); HRMS-ESI-TOF m/z calcd for C₅₇H₃₈N₄O₃Zn [M]⁺• 890.2230, found 890.2236.

4.4.1.3. Compound 7. {3-(5-Oxo-2,3,4,5-tetrahydro-2H-pyrano [3,2-c]chromen-2-yl)-5,10,15-tris(pentafluorophenyl)corrolato} gallium(III). 92%, ¹H NMR (CDCl₃, a few drops of pyridine-*d*₅, 500 MHz): § 2.65-2.72, 2.75-2.81, 2.85-2.89, 2.98-3.02 (4m, 4H, H-3' and H-4'), 2.97-3.04 (m, 2H, H-3' and H-4'), 5.83 (dd, 1H, *J*=9.7, 1.8 Hz, H-2'), 7.22 (dt, 1H, *J*=7.8, 1.0 Hz H-9'), 7.40 (dd, 1H, J=8.4, 0.6 Hz, H-7'), 7.66-7.68 (m, 1H, H-8'), 7.84 (dd, J=7.8 Hz, H-10'), 8.63–8.64 (m, 2H, H- β), 8.72 (d, 1H, J=4.5 Hz, H- β), 8.83 (d, 1H, *I*=4.0 Hz, H-17), 8.87 (d, 1H, *I*=4.5 Hz, H-β), 9.25 (d, 1H, *I*=4.0 Hz, H-18), 9.40 (s, 1H, H-2); ¹³C NMR (CDCl₃, a few drops of pyridine-*d*₅, 125 MHz): § 22.6 (C-4'), 29.3 (C-3'), 75.0 (C-2'), 101.1, 115.4, 116.4 (C-7'), 116.5 (C-2), 118.0 (C-18), 122.5 (C-10'), 124.2 (C-9'), 124.4 (C-β), 124.5 (C-β), 125.6 (C-17), 127.6 (C-β), 128.3 (C-β), 131.5, 131.7, 131.8, 131.9, 132.0, 133.4 (C-8'), 135.7, 137.0, 137.4, 140.8, 141.4, 143.7, 147.6, 152.3, 160.4 (C-10'b), 163.2 (C-5'); $^{19}{\rm F}$ NMR (CDCl₃, a few drops of pyridine- d_5 , 282 MHz): δ –161.3 to –161.4 (m, 6F, Fortho), –177.2 to -177.5 (m, 3F, Fpara), -185.7 to -186.2 (m, 6F, Fmeta); HRMS-ESI-TOF m/z calcd for C₄₉H₁₆F₁₅N₄O₃Ga [M]⁺• 1062.3830, found 1062.3617.

4.4.1.4. Compound **8**. {3-(9-Methyl-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15-tris(pentafluorophenyl) corrolato}gallium(III). 87%, ¹H NMR (CDCl₃, a few drops of pyridine- d_5 , 300 MHz): δ 2.27 (s, 3H, CH₃), 2.63–3.06 (m, 4H, H-3' and H-4'), 5.82–5.91 (m, 1H, H-2'), 7.21–7.37 (m, 2H, H-7' and H-8'), 7.63 (d,

1H, *J*=1.8 Hz, H-9'), 8.59–8.93 (m, 5H, H-β), 9.20–9.28 (m, 1H, H-β), 9.35–9.42 (m, 1H, H-β). ¹³C NMR (75 MHz, CDCl₃) δ 20.8 (Ar–CH₃), 22.7 (C-4'), 29.4 (C-3'), 74.9 (C-2'), 101.0, 115.1, 116.2, 116.3, 118.1, 123.7, 124.4, 125.6, 127.2, 127.8, 128.1, 128.6, 129.7, 132.6, 133.5, 133.6, 133.7, 136.0, 137.3, 140.9, 141.4, 143.2, 150.6, 160.5, 163.6. ¹⁹F NMR (CDCl₃, a few drops of pyridine-*d*₅, 282 MHz): δ –159.1 to –159.2 (dd, 1F, *J*=25.0, 7.2 Hz, Fortho), –161.0 to –161.2 (dd, 1F, *J*=25.4, 9.0 Hz, Fortho), –161.4 to –161.5 (m, 4F, Fortho), –174.9 (t, 1F, *J*=21.2 Hz, Fpara), –176.8 (t, F, *J*=21.0 Hz, Fpara), –177.0 (t, 1F, *J*=21.0 Hz, Fpara), –184.1 to –184.3 (m, 1F, Fmeta), –185.0 to –185.2 (m, 1F, Fmeta), –185.5 to –186.0 (m, 4F, Fmeta); HRMS-ESI-TOF *m/z* calcd for C₅₀H₁₈F₁₅N₄O₃Ga [M]⁺ 1076.0412, found 1076.0362.

4.4.2. General procedure for porphyrin decomplexation. Zn–porphyrins **3** and **4** (8.98 μ mol) were treated with a mixture of 5% TFA in chloroform (1 mL). The reaction mixture was stirred at room temperature for 30 min and then neutralized with a saturated solution of NaHCO₃. The aqueous phase was extracted with chloroform, and the organic phase was dried over Na₂SO₄ and evaporated under vacuum to dryness. The resulting residue was purified by preparative TLC using chloroform as eluent.

4.4.2.1. Compound **5**. 2-(5-Oxo-2,3,4,5-tetrahydro-2*H*-pyrano [3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrin, 97%, ¹H NMR (CDCl₃, 300 MHz): δ –2.69 (s, 2H, NH), 2.15–2.35 (m, 2H, H-3' and H-4'), 2.58–2.72 (m, 2H, H-3' and H-4'), 5.05 (d, 1H, *J*=9.8 Hz, H-2'), 7.18–7.23 (m, 1H, H-9'), 7.34 (d, 1H, *J*=7.7, Hz, H-7'), 7.44–7.53 (m, 2H, H-8' and H-10'), 7.70–7.79 (m, 12H, H*m*,*p*-Ph), 8.17–8.24 (m, 8H, Ho-Ph), 8.67 (d, 1H, *J*=4.8 Hz, H- β), 8.79 (d, 1H, *J*=4.8 Hz, H- β), 8.82–8.86 (m, 4H, H- β), 9.0 (s, 1H, H-3'); HRMS-ESI-TOF *m*/*z* calcd for C₅₆H₃₉N₄O₃ [M+H]⁺ 815.3017, found 815.3006.

4.4.2.2. *Compound* **6**. 2-(9-Methyl-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrin, 92%, ¹H NMR (CDCl₃, 300 MHz): δ –2.69 (s, 2H, NH), 2.07–2.31 (m, 2H, H-3' and H-4'), 2.34 (s, 3H, CH₃), 2.55–2.68 (m, 2H, H-3' and H-4'), 5.06 (d, 1H, *J*=9.3 Hz, H-2'), 7.24 (d, 1H, *J*=8.6 Hz, H-7'), 7.31 (dd, 1H, *J*=8.6, 2.0 Hz, H-8'), 7.45–7.50 (m, 1H, H*m*,*p*-Ph), 7.54 (d, 1H, *J*=2.0 Hz, H-10'), 7.71–7.82 (m, 11H, H*m*,*p*-Ph), 8.14–8.24 (m, 8H, Ho-Ph), 8.68 (d, 1H, *J*=4.8 Hz, H- β), 8.80 (d, 1H, *J*=4.8 Hz, H- β), 8.85 (d, 1H, *J*=4.8 Hz, H- β), 8.85 (d, 1H, *J*=4.8 Hz, H- β), 8.85 (s, 2H, H-12,13), 9.01 (s, 1H, H-3); HRMS-ESI-TOF *m*/*z* calcd for C₅₇H₄₁N₄O₃ [M+H]⁺ 829.3173, found 829.3162.

4.5. Preparation of the solid supports doped with compounds 5 and 6

The solid supports based on the agarose were prepared by the addition of compounds **5** or **6** (1 mg) to agarose (15%) using the conventional 1D-Gel Electrophoresis procedure described for protein separation.⁴⁹ The solid supports based on cellulose were prepared by dissolving 0.4 g of carboxymethylcellulose sodium salt in 8 mL of ca. 1×10^{-5} M solutions of **5** or **6**, and the final pH (pH=8) measured on a MeterLab 240 pH meter was slightly readjusted before gelification with the addition of small amounts of NaOH or HCl.

Acknowledgements

Authors are grateful to Xunta de Galicia (Spain) through project 10CSA383009PR and Scientific PROTEOMASS Association (Portugal) for financial support. Thanks are due to Fundação para a Ciência e a Tecnologia (FCT, Portugal), European Union, QREN, FEDER and COMPETE for funding the QOPNA research unit (project PEst-C/ QUI/UI0062/2011) and the Portuguese National NMR Network, also supported by funds from FCT. C.S., E.O. and J.B. thanks also FCT for their doctoral and post-doctoral grants, SFRH/BD/64155/2009, SFRH/BPD/72557/2010 and SFRH/BPD/63237/2009, respectively. J.C.J.M.D.S.M also thanks QOPNA for a research grant.

Supplementary data

Photophysical data of compounds **3–8** in other solvents studied. Spectroscopic polarity parameters, physical properties and polarity functions of employed solvents. Detection (LOD) and quantification (LOQ) limits of compounds **3**, **4**, **7** and **8** in toluene. Titrations of compounds **3** and **7** with cyanide and acetate. Normalized emission of **1b** with chloride, fluoride, cyanide and acetate. Titration of compound **5** with Hg²⁺ in EtOH/H₂O(50:50), absorption spectra of **5** at different pH's. Image of a cellulose polymer with **5** at pH 1, 7 and 12. Emission spectra of **5** in agarose gel and cellulose polymer at different pH's are available. The 1D and 2D NMR and HRMS spectra for compounds **3–8** are also provided. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.022.

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