



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



Carla I.M. Santos^a, Elisabete Oliveira^{b,c,†}, José C.J.M.D.S. Menezes^{a,†}, Joana F.B. Barata^a, M.Amparo F. Faustino^a, Vitor F. Ferreira^d, José A.S. Cavaleiro^a, M.Graça P.M.S. Neves^{a,*}, Carlos Lodeiro^{b,*}

^a Chemistry Department and QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

^b BIOSCOPE Group, REQUIMTE-CQFB, Chemistry Department, Faculty of Science and Technology, University Nova of Lisbon, 2829-516 Monte de Caparica, Portugal

^c Veterinary Science Department and CECAV, University of Trás-os-Montes and Alto Douro, 5001-801 Vila Real, Portugal

^d Instituto de Química, Departamento de Química Orgânica, Universidade Federal Fluminense, 24020-150 Niterói-RJ, Brazil

ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form 2 July 2013

Accepted 8 July 2013

Available online 20 July 2013

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^+ , Ca^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Fe^{2+} , Ba^{2+} , Cu^{2+} , Ag^+ , and Hg^{2+} , showing a colorimetric effect (color change from purple to yellow) and an unprecedented selectivity for Hg^{2+} .

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/H₂O (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.

© 2013 Elsevier Ltd. All rights reserved.

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

excellent method to develop ion-selective electrode and optical sensor devices.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) metalloporphyrin 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

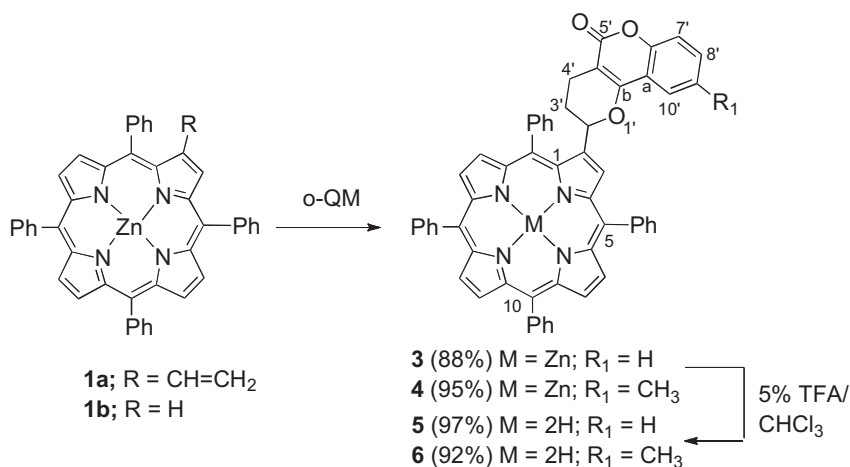
* Corresponding authors. Tel.: +351 212948550; fax: +351 212948300; e-mail addresses: gneves@ua.pt (M.G.P.M.S. Neves), cle@fct.unl.pt (C. Lodeiro).

† E. Oliveira and J. C. J. M. D. S. Menezes contributed equally to this work.

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.

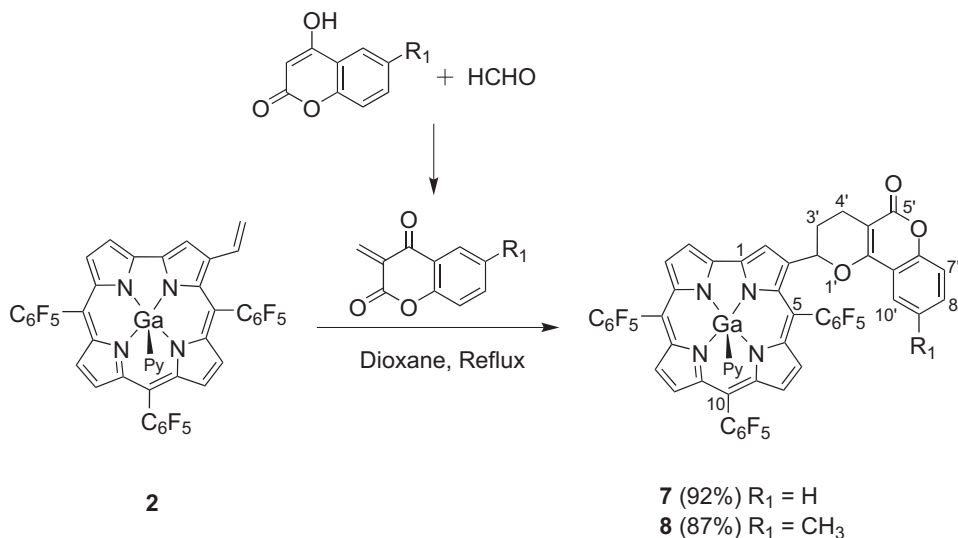
Coumarin derivatives have been utilized as sensors for Hg(II),^{16–18} F⁻,^{19–23} and CN⁻^{24,25} ions either in organic solvents or aqueous mixtures at biological pH.

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 CH₃COO⁻ 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**.

Download English Version:

<https://daneshyari.com/en/article/5215865>

Download Persian Version:

<https://daneshyari.com/article/5215865>

[Daneshyari.com](https://daneshyari.com)