



Molecular recognition of aliphatic amines by luminescent Zn-porphyrins



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ABSTRACT

Two new porphyrins and their zinc(II) complexes have been synthesized, their photophysical properties studied, and their use in the molecular recognition of amines has been analyzed. The luminescence properties of both series of compounds show a decrease on the luminescence quantum yield of the Zn-derivatives with respect to their corresponding free base porphyrins. Attempts to probe the ability of the compounds to recognise certain biologically relevant drugs revealed that dimethylformamide (DMF) is capable of binding the zinc(II) porphyrins. This fact led us to perform sensing experiments of different aliphatic amines, the highest calculated association constant for methyl- and trimethylamine. These properties confirm the sensitivity of porphyrins to the binding of closely related analytes.

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1. Introduction

Porphyrin derivatives represent an important class of pigments in the storage of energy in both natural and artificial photosynthesis, on the making of molecular energy devices, catalysts, and more recently as photosensitizers of specific products (e.g., the singlet $^1\Delta_g$ state of molecular oxygen) [1] in photodynamic therapy (PDT) and in the photodynamic destruction of viruses [2].

Porphyrins and/or metalloporphyrins are ideal components for the construction of photoactive assemblies (supramolecular systems) designed to emulate, at the molecular level, light-induced functions typical of biological systems or of artificial macroscopic electronic devices such as photoinduced charge separation and antenna effect. In fact, porphyrins offer a variety of appealing features: rigid and planar geometries, high stability, intense electronic absorption bands in the visible region, a relatively long fluorescence decay time, facile tunability of their optical and redox properties by metallation/functionalization, and availability of a variety of synthetic strategies for supramolecular organization [3].

This planar aromatic macrocycle is composed of four pyrrole residues held together by four *meso*-carbon atoms which can allow the metallation via four M–N coordination bonds onto the corresponding anion and the functionalization at the *meso* and β -positions [4]. The porphyrin skeleton permits to attach easily four energy donor arms in the near periphery, and such a light-harvest-

ing system can be expected to show an antenna effect. Antenna systems comprising a central porphyrin linked to four peripheral photon-harvesting hydrocarbon moieties have been reported. For example, naphthalene [5], anthracene [6] or phenanthrene [7] groups have been linked directly to four *meso*-carbons of the porphyrin [8].

The search for porphyrin systems linked by π -conjugated connectors is receiving increasing attention in view of their potential application in the design of molecular wires for electronic and photonic applications and for molecular recognition purposes [9–11]. In this context, the analysis of the effect of π -conjugated substituents on the photophysical properties of porphyrins is of great relevance [12].

Related to this, we reported recently on the synthesis of biphenyl-porphyrins (Chart 1, **P1**, **ZnP1**) and their luminescence properties [13]. In this work, the structure of the substituent at the *meso*-position (Chart 1) has been modified in order to evaluate how it can affect their luminescence. Thus, we have prepared and characterized two different porphyrins **P2** and **P3**, incorporating triphenyl and stilbene substituents respectively in the *meso* positions, as well as their corresponding zinc(II) derivatives **ZnP2** and **ZnP3**. On the other hand, the high number of substrates that can be recognized by tetrapyrrolic macrocycles like porphyrins and analogues make them particularly attractive to be considered as receptors [14,15]. For this reason, we have explored their use in molecular recognition of biological relevant drugs, namely ibuprofen, piroxicam, and indomethacin. Although they do not interact significantly, we realised that the zinc(II) porphyrins do interact

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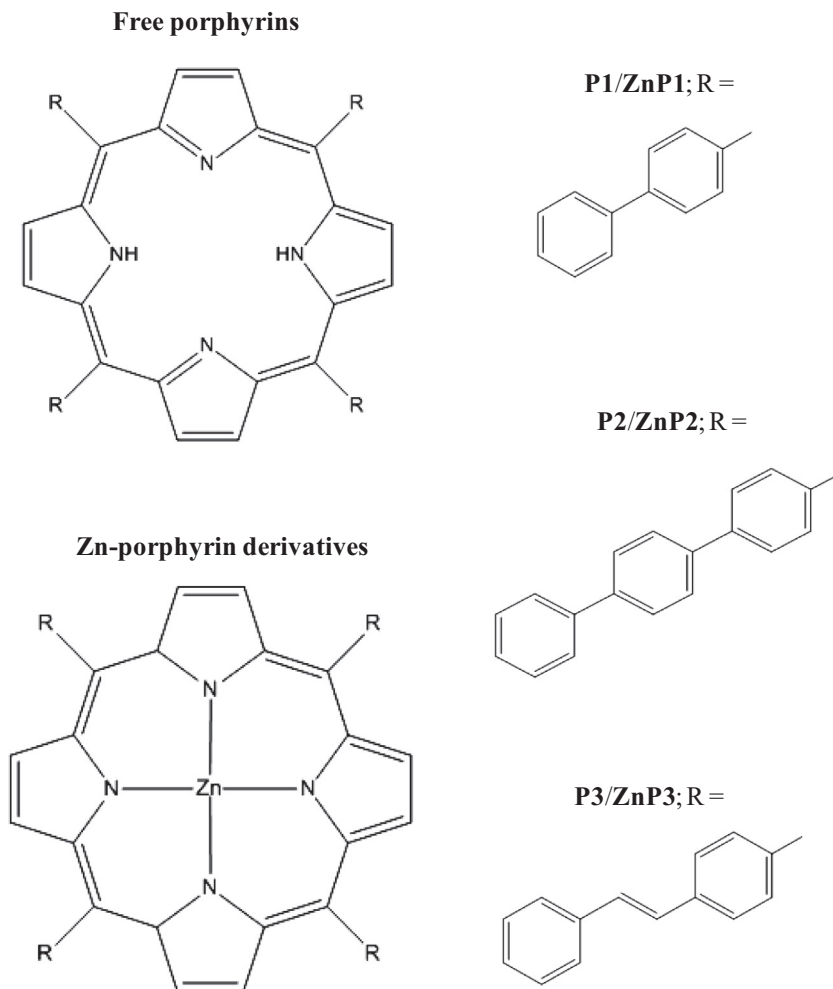


Chart 1.

well with Lewis bases, and for this reason studied their binding to a series of aliphatic amines.

2. Experimental

2.1. Materials and methods

The following are commercially available compounds: Acetic acid, 4-biphenylboronic acid, *trans*-bis(dicyclohexylamine) palladium(II) acetate (DAPCy), 4-bromobenzaldehyde, pyrrole, sodium chloride, sodium hydrogencarbonate, *trans*-4-stilbenecarboxaldehyde, zinc acetate dihydrate and all tested analytes (piroxicam, indomethacin, 8-hydroxyquinoline, sodium ibuprofenate, methylamine, trimethylamine, triethylamine and tributylamine) were purchased from Aldrich (St. Louis, USA). Potassium phosphate was purchased from Merck. All the solvents used were analytical grade.

¹H NMR spectra were recorded using a Varian-300, Varian VXR 500 (300 MHz and 500 MHz) spectrometers. NMR spectra were determined in CDCl₃ or CDCl₃/CF₃COOD, and chemical shifts are expressed in parts per million (δ) relative to the central peak of the solvent. Chromatography (TLC) was performed on Merck coated F₂₅₄ silica gel plates. Column chromatography was carried out on silica gel 60 (Merck 9385, 230–400 mesh). Melting points were recorded using a Gallenkamp apparatus and are uncorrected. IR measurements were done using a Perkin Elmer Spectrum One Fourier Transform spectrometer in the attenuated total reflection

(ATR) mode. IR spectra (KBr disks) were obtained using Thermo Nicolet Avatar 320 FT-IR. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-ToF-MS) analyses were performed using a Voyager-DE-RP (Applied Biosystems, Framingham, USA) mass spectrometer from *Centres Científics i Tècnològics de la Universitat de Barcelona* (CCiT-UB).

All spectroscopic measurements were performed in spectroscopic grade solvents which were purchased from Aldrich and used without further purification. All absorption spectra were recorded in a Shimadzu UV2501PC and UV-1800 spectrophotometer, using quartz cuvettes with a 10 mm path length. Emission/excitation spectra were recorded in either a Jobin-Yvon SPEX Fluorolog or SPEX Nanolog spectrofluorimeters equipped with a 300 W Xe lamp.

For fluorescence decay measurements, the samples were excited at 370 nm using a nanoleed (IBH). The electronic start pulses were shaped in a constant fraction discriminator (Canberra 2126) and directed into a time to amplitude converter (TAC, Canberra 2145). The emission wavelength was selected through a monochromator (Oriel 77250), imaged in a fast photomultiplier (9814B Electron Tubes Inc.), the PM signal was shaped as before and delayed before entering the TAC as stop pulses. The analogue TAC signals were digitized (ADC, ND582) and stored in multichannel analyzer installed in a PC (1024 channels, 38.1 ps/ch). The analysis of the decays is carried out with the method of modulating functions extended by global analysis as implemented by Striker [16]. The resolution of SPC measurements is approximately

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