



Metalloporphyrin triads: Synthesis and photochemical characterization

Sara M.A. Pinto¹, Ângela C.B. Neves¹, Mário J.F. Calvete¹, Artur R. Abreu¹, Mário T.S. Rosado¹,
Telma Costa¹, Hugh D. Burrows*, Mariette M. Pereira*

Departamento de Química, Universidade de Coimbra, Coimbra, Portugal

ARTICLE INFO

Article history:

Received 14 March 2012
Received in revised form 23 May 2012
Accepted 30 May 2012
Available online 7 June 2012

Keywords:

Metalloporphyrins
Triad
Photophysics

ABSTRACT

A porphyrin triad has been synthesized by reaction of 5-(3-hydroxyphenyl)-10,15,20-triphenylporphyrin with the *tris*(triflate) ether of 2-(hydroxymethyl)-2-methylpropane-1,3-diol in dimethylformamide in the presence of cesium carbonate. This has been fully characterized, and the zinc(II), palladium(II), platinum(II) and manganese(III) metallated triads were prepared from it by modified Alder reactions. Semiempirical (PM6) calculations indicate that the lowest energy geometries of the triads are not strongly influenced by the metal and suggest free access of reagents to the porphyrin units. This is supported by acid–base titrations of the free-base porphyrins with trifluoroacetic acid. Detailed photophysical studies are reported on both free base and metallated triads and suggest little interaction between porphyrin moieties, although molar absorption coefficients are higher than in the corresponding monomers, probably due to decreased symmetry. With the Pd(II) and Pt(II) derivatives, room temperature phosphorescence is observed in solution. This is quenched by oxygen, and it is suggested that these may be good candidates for ratiometric sensing. The mechanism of quenching of triad triplets by oxygen depends on the metal ion, and both type-I, which involves hydrogen-atom abstraction or electron-transfer between the excited sensitizer and a substrate yielding free radicals and type II, in which singlet oxygen is generated via an energy transfer process during a collision of the excited sensitizer with triplet oxygen processes, may be involved. The good solubility and photophysical characteristics of the platinum(II) triad may make this useful as a phosphor in organic light emitting diodes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Dendron-type materials are of current interest within the scenario of increasingly more complex and sophisticated molecules for a multitude of highly specific applications [1–7]. Their unique structural features, arising from their three-dimensional architecture, can be tailored and controlled, while the size, shape of the molecule and the orientation of functional groups can be designed for specific applications [8].

Multiporphyrin arrays have also been the focus of considerable attention, resulting, in particular, from possibilities of incorporating different functionalities [9,10]. The combination of synthetic accessibility, excellent electronic properties and their ability to complex many types of metal ions, makes porphyrins matchless as building blocks for the synthesis of both straight-chain and branched extended molecular systems designed for specific advanced applications, including optoelectronic gates [11], molecular photonic wires [12], optical switches [13] and light harvesting arrays [6].

Since dendritic architectures allow interaction between chromophores, leading to corresponding effects on their properties, construction of branched multiporphyrin structures is expected to provide an efficient and alternative approach for the synthesis of porphyrin triads [14], which can maximize these interactions by taking advantage of the synergy between the individual porphyrin moieties.

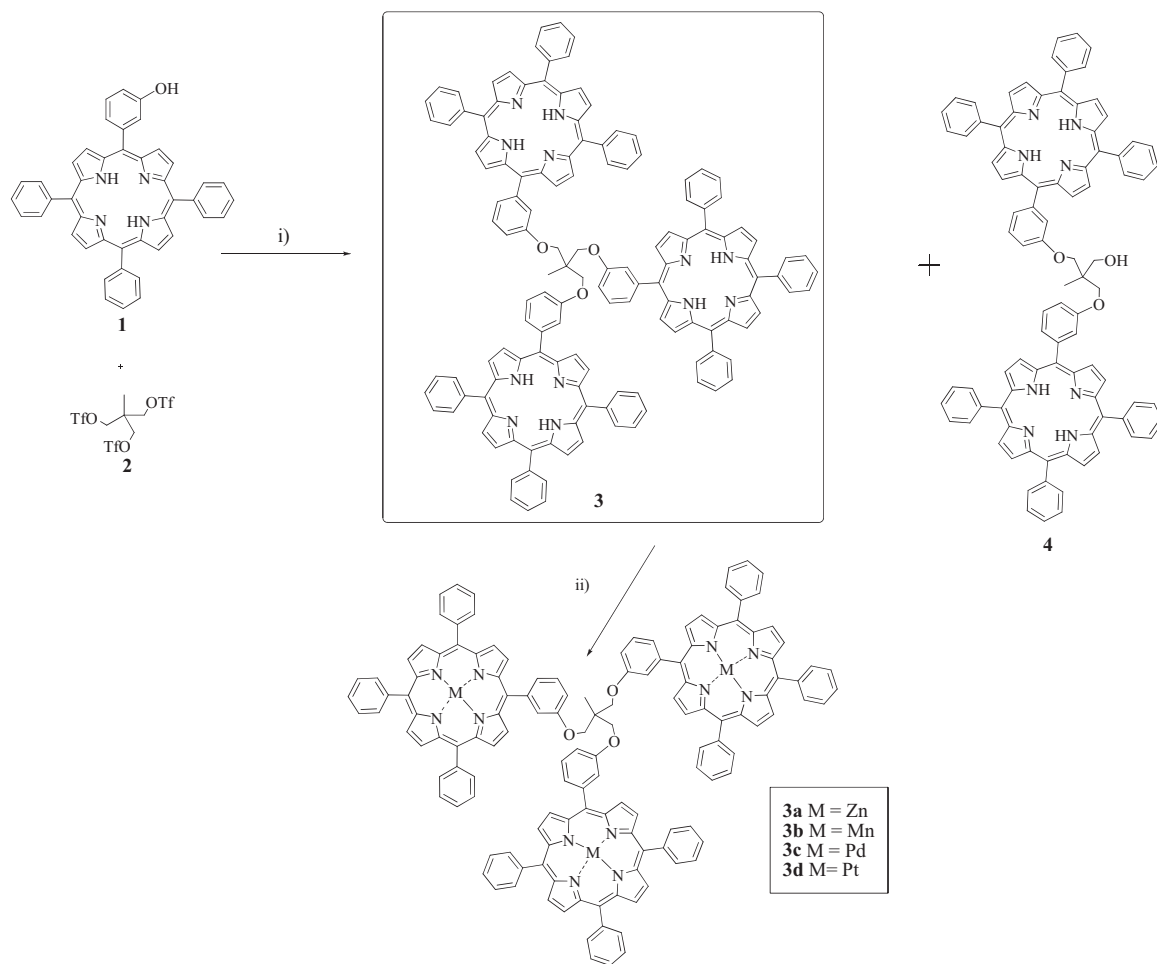
It seems appropriate to use this synergic effect, to devise a versatile methodology for preparation of highly branched dendron-based multiporphyrin systems, which can be further directed for specific applications, including chemical sensing. The propensity and selectivity of each system to a certain analyte can be drastically modified by changing the metal in the porphyrin core. The combination of a strongly interacting system with a highly conjugated structure, whose electronic distribution, either in central or radial porphyrin sites [15,16], is affected upon interaction with analytes (e.g. amines, oxygen and peroxides) is expected to allow their sensing at low concentrations. These can be conveniently studied spectroscopically, as recently reported by us [17].

As an example, this can be used in amine detection, which is of particular importance [18] since both aliphatic and aromatic amines can induce toxicological responses at low concentrations [19,20]. Aliphatic amines are found in many wastewater effluents from industry, agriculture, pharmaceuticals and food processing

* Corresponding authors. Tel.: +351 239854474; fax: +351 239827703.

E-mail address: mmpereira@qui.uc.pt (M.M. Pereira).

¹ Tel.: +351 239854474; fax: +351 239827703.



Scheme 1. a) Reagents and conditions: i) for **3**: Cs_2CO_3 , DMF, R.T., 48 h; ii) for **3a**: M = Zn: $\text{Zn}(\text{OAc})_2$, DME, 70 °C, 5 h (porphyrin/salt: 1/8); for **3b**: M = Mn: $\text{Mn}(\text{OAc})_2$, DME, 70 °C, 5 h (porphyrin/salt: 1/10); for **3c**: M = Pd: $\text{Pd}(\text{OAc})_2$, DMF, 150 °C, 24 h (porphyrin/salt: 1/10); for **3d**: M = Pt: dichlorobis(acetonitrile)platinum (II), 170 °C, 30 h (porphyrin/salt: 1/10).

[21], and their easy detection is valuable in environmental and industrial monitoring, food quality control, etc. [22]. Also oxygen and carbon dioxide are analytes of interest for a variety of reasons [23], and are included in the “must have” list of applications for this type of dendron based metallated multiporphyrins. In addition, these porphyrin assemblies show great potential as receptors for a variety of entities, especially for photoinduced electron transfer [14,24].

We report a straightforward methodology for the preparation of tripodal porphyrin systems, linked through the branched triol, tris(hydroxymethyl)ethane. This represents an interesting starting material for the design of hyperbranched dendritic compounds. Metallation adjusts the characteristics for the desired applications and we extend the study to synthesis of zinc(II), manganese(III), palladium(II) and platinum(II) triads. We also report their photophysical characterization, which allows the “fingerprinting” of these materials, and is of particular importance in understanding how to modulate properties for a specific application.

2. Results and discussion

2.1. Synthesis

The syntheses of the free base triad **3** and its metallated zinc(II), manganese(III), palladium(II) and platinum(II) triads (**3a–3d**) were carried out according to Scheme 1.

Two main factors were evaluated to optimize the reaction conditions of the coupling reaction between the triol based compound and the *meso*-mono-hydroxyphenyl-triphenylporphyrin: i) the leaving group ability of the triol starting material (tosylate vs triflate); ii) type of base employed for the nucleophilic substitution. Using cesium carbonate as base, it was found that higher temperatures and longer reaction times were necessary for the reaction between the tris(tosylate) ether and the hydroxyl substituted porphyrin, when compared with the reaction starting from tris(triflate) ether, even though substantially lower yields were obtained.

The reaction was repeated using the tris(triflate) ether as starting material, and three different bases tested, tetrabutylammonium hydroxide, potassium carbonate and cesium carbonate. The yields were 20, 40 and 60%, respectively. It has previously been shown in many nucleophilic substitution reactions that the base used should have a well-balanced base strength; for this, cesium carbonate is neither too weak nor strong, thus minimizing hydrolysis of the protected group in the starting triad [25]. In addition, Cs_2CO_3 is 15 times more soluble in DMF than K_2CO_3 [26].

From these studies, the selected synthetic conditions were Cs_2CO_3 as base and tris(triflate) ether as starting material, mixed with 5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin in DMF as solvent, and stirred at room temperature for ca. 48 h, which gave 1,3-di[5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin]-2-(5-(3-hydroxyphenyl)-10,15,20-(triphenyl)porphyrin)-2-methylpropane in 60% yield, as indicated above.

Download English Version:

<https://daneshyari.com/en/article/27010>

Download Persian Version:

<https://daneshyari.com/article/27010>

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