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Ionic self-assembly reactions of a porphyrin octacation

Christian Frigerio [a], João P.G. Santos [a], Pedro Quaresma [a], Susana L.H. Rebelo [b], Ana Gomes [a], Peter Eaton [a], Eulalia Pereira [a], Patrícia A. Carvalho [c,d], John A. Shelnutt [e], Lin Jiang [f], Hong Wang [f], Craig J. Medforth [a,*]

[a] UCBIO/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Porto, Portugal
[b] LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Porto, Portugal
[c] Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-100 Lisboa, Portugal
[d] SINTEF Materials and Chemistry, Forskningsveien 1, Oslo, Norway
[e] Department of Chemistry, University of Georgia, Athens, GA 30602, United States
[f] Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, United States

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ABSTRACT

To determine if ionic self-assembly can be used to produce nanomaterials from unusual porphyrin ions we have investigated the reactions of a novel octacationic porphyrin. A range of nanomaterials are obtained depending upon the tetra(4-sulfonatophenyl)porphyrin (**TPPS**) anion(s) used in the reaction: binary ionic solids (from reactions with metal **TPPS** complexes), ternary ionic solids (from reactions with two different metal **TPPS** complexes) and binary solids with variable compositions (from reactions with diprotonated **TPPS**).

1. Introduction

Porphyrins and related tetrapyrroles possess a combination of optical, electronic and catalytic properties that make them attractive components for a wide range of functional materials. For example, they have been investigated in artificial photosynthesis systems[1,2] and dye-sensitized solar cells,[3] and have been intensively studied in model donor–acceptor systems for electron transfer processes.[4] Porphyrins have also been investigated as components of photonic devices[5] and LEDs,[6] and in optoelectronics.[7] The desirable properties and well-developed synthetic chemistry of porphyrins also make them useful as components of organic nanomaterials, and recently the use of self-assembly methods to produce porphyrin-based nanomaterials has generated considerable interest.[8–13] Reprecipitation or coordination polymerization reactions have been used to obtain porphyrin nanostructures from single porphyrin species.[12,10] Ionic self-assembly (ISA)[14] of oppositely-charged porphyrin ions in water has been used to produce binary porphyrin nanomaterials.[15]

ISA is a useful method for preparing porphyrin nanostructures because it can generate materials where the porphyrin ions have complementary properties. These include electron donor and electron acceptor porphyrins,[16] light-harvesting and catalytic porphyrins,[17] or two variants of cobalt porphyrin catalyst for oxygen-reduction reactions.[18] ISA has been used to prepare a number of nanoscale structures including nanotubes,[19] nanorods[20] and bundles of nanofibers,[21] as well as micron-sized clovers[16,22] or hyperbranched materials[23] with nanoscale features. Nanoscale porphyrin ionic solids have been investigated as sensors[24] and as photocatalysts for the production of hydrogen using a sacrificial electron donor.[22] Nanomaterials have also been produced by ISA at liquid–liquid interfaces,[18,21] and 'rafts' of interfacial material have been used as oxygen-reduction catalysts.[18]

To date, ISA studies have largely focused on the synthesis of discrete binary nanomaterials using commercially available tetraarylporphyrins such as **TMPyP** (**1**) and **TPPS** (**2**) (Fig. 1).[15] This allows the production of a range of functional materials via variation of the aryl substituents and/or the central metal ion (e.g., the use of zinc porphyrin electron donors and tin porphyrin electron acceptors to produce photoconductive materials).[16] Recent advances include a detailed investigation of the growth of crystals formed by ionic self-assembly of **TPPS** (M=2H) and **TMPyP** (M=2H).[25] The effect of porphyrin concentration and the reaction temperature were explored and a model was developed to simulate growth of the crystals. In addition, the first measurement of the

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* Corresponding author. E-mail address: craig.medforth@fc.up.pt (C.J. Medforth).

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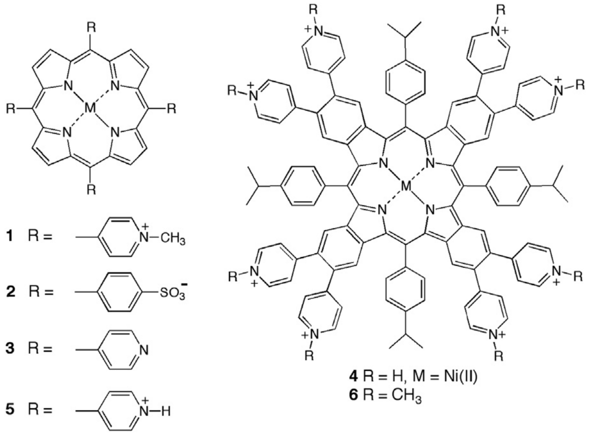

Fig. 1. Structures of the porphyrins discussed in this work.

elastic properties of a porphyrin ionic solid have been reported.[26] The Young's modulus for nanorods prepared at pH 2 from **TPPS** and **TPyP** (**3**) was reported as 6.5±1.3 GPa.

In this work, we investigate whether ISA can be used to produce nanomaterials from porphyrin ions with unusual structural features, specifically the octacationic porphyrin **NiTBTAP** (**4**).[27] This porphyrin has an extended π-system of the tetrabenzoporphyrin class, a structural modification that significantly alters its optical and electronic properties. Interactions between the aryl substituents at the *meso* positions and the benzo groups also deform the porphyrin ring into a nonplanar conformation (see Fig. 2). Nonplanarity is known to alter many properties of porphyrins, including their UV–vis absorption maxima, excited state lifetimes, and oxidation potentials.[28–30]

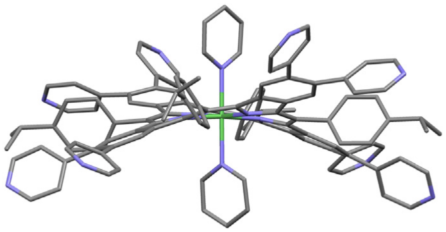

Fig. 2. Crystal structure of the unprotonated form of **NiTBTAP**.[27] Two axial pyridine ligands are coordinated to a high-spin nickel(II) ion. The DFT structure of the unprotonated low-spin nickel(II) complex shows an even more nonplanar structure.[27.]

In Section 3.1, the reactions of **NiTBTAP** with metal complexes of **TPPS** (M**TPPS**, M=Sn^{IV}, Fe^{III}, Mn^{III}, Cu^{II}) are investigated. The reactions are carried out at pH 2 (0.01 M HCl) where the pyridine groups of **NiTBTAP** should be fully protonated to form an octacationic species (the pK_a of pyridine is 5.23).[31] Under these reaction conditions the metal complexes of **TPPS** will normally be present as tetraanions (due to the low pK_a values of aryl sulfonic acid groups)[31,32] with planar or slightly nonplanar macrocycles. The precipitates obtained are first analyzed by ICP–AES to determine the ratio of the porphyrin metal ions and thus the composition of the materials. Next, the UV–vis spectra of the precipitates are examined as suspensions in 0.01 M HCl. Finally, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used to characterize the materials obtained after drying suspensions of the precipitates on TEM grids. The reactions of **NiTBTAP** and M**TPPS** are then compared to those previously reported for ISA of tetraarylporphyrin cations and anions as typified by **TMPyP** (or **THPyP** (**5**)) and **TPPS**.

Reactions of **NiTBTAP** with the metal-free form of **TPPS** are described in Section 3.2. At pH 2 (0.01 M HCl) the metal-free form of **TPPS** is present as the diprotonated (dicationic) form H_4**TPPS** (M=4H in Fig. 1). H_4**TPPS** is largely present as the monomeric form in the 0.01 M HCl, although it is known to self-aggregate at high ionic strengths to form J-aggregates and nanostructures.[33–35] H_4**TPPS** nanotubes have been synthesized and shown to be insulators in the dark but to become photoconductive upon illumination with 488 nm light.[36] Protonated tetraarylporphyrins also adopt very nonplanar structures due to steric crowding of the protons in the porphyrin core.[37] The reactions of **NiTBTAP** and H_4**TPPS** therefore represent a rare example of self-assembly between two very nonplanar porphyrin ions.

In Section 3.3, the reactions of **NiTBTAP** with two different **TPPS** complexes are investigated as a method for producing nanomaterials containing three different porphyrin ions. Little is know about the formation of *ternary* ionic porphyrin nanomaterials, although the synthesis of bimetallic materials containing Fe^{III} and Cu^{II} complexes of **THPyP** and H_4**TPPS** at pH 2 (porphyrin ratios 2:2:9) has been reported.[38] In our experiments, equimolar amounts of **NiTBTAP** are reacted with two metal complexes of **TPPS** (Cu**TPPS** and M**TPPS** (M=Fe, Sn or Mn)) with the goal of producing trimetallic ternary nanomaterials. **NiTBTAP** is also reacted with 1 equiv of M**TPPS** (M=Cu, Fe, Sn) and 2 equiv of H_4**TPPS** with the aim of producing bimetallic ternary nanomaterials.

2. Experimental methods

2.1. Materials

Sn^{IV}**TPPS** dichloride, Mn^{III}**TPPS** chloride, Fe^{III}**TPPS** chloride, Cu^{II}**TPPS** and H_2**TPPS** tetrasodium salt dodecahydrate were obtained commercially (Frontier Scientific) and used without further purification. The unprotonated form of **NiTBTAP** was prepared using a literature procedure.[27] Nanopure™ water was used in the preparation of all reagents.

Stock solutions of the porphyrins (100 μM **NiTBTAP**, 400 μM M**TPPS**, 400 and 1600 μM H_4**TPPS**) were prepared in 0.01 M HCl. The unprotonated form of **NiTBTAP** does not readily dissolve in 0.01 M HCl so the trifluoroacetate salt was synthesized and used to make the stock solution. The required amount of unprotonated **NiTBTAP** was dissolved in chloroform (1 mL) in a round-bottom flask, two drops of trifluoroacetic acid were added, and the chloroform and trifluoroacetic acid removed using a rotavapor. After drying the sample overnight under vacuum, the resulting solid was dissolved in 0.01 M HCl to produce the stock solution.

2.2. Ionic self-assembly reactions

Self-assembly reactions were carried out using reaction solutions prepared by diluting the stock solutions with 0.01 M HCl. The reaction solutions were mixed and the reactions left in the dark and undisturbed for one week. Precipitates were then harvested from the reactions by taking 1 mL of the reaction mixture (homogenized by shaking the reaction vial) and centrifuging the sample at 18,000 g for 10 min.

For the example of a 2:1 M**TPPS**–**NiTBTAP** reaction, 0.8 mL of 100 μM **NiTBTAP** was diluted to 1 mL with 0.01 M HCl and 0.4 mL of 400 μM M**TPPS** was diluted to 1 mL with 0.01 M HCl. The reaction solutions were mixed in a glass vial and the reaction mixture left in the dark and undisturbed for one week. The concentrations of **NiTBTAP** and M**TPPS** in the reaction mixture were 40 and 80 μM, respectively. M**TPPS**–**NiTBTAP** reactions with other ratios (1:1, 3:1 or 4:1) were prepared by adjusting the volume of M**TPPS** stock solution used to prepare the reaction solution.