Ionic Self-Assembly Reactions of a Porphyrin Octacation

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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). **KEYWORDS:** Porphyrin; Ionic Self-Assembly; Nanomaterial; Octacation

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 devices⁵ 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 nanorods²⁰ and bundles of nanofibers,²¹ as well as micron-sized clovers^{16,22} or hyperbranched materials²³ with nanoscale features. Nanoscale porphyrin ionic solids

have been investigated as sensors²⁴ 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 **TMPP** (**1**) and **TPPS** (**2**) (Figure 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 **TMPP** (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 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 **NiBTAP** (**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 Figure 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. 1. Structures of the porphyrins discussed in this work.

Fig. 2. Crystal structure of the unprotonated form of **NiBTAP**.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 **NiBTAP** with metal complexes of **TPPS** (**MTPPS**, $M = \text{Sn}^{\text{IV}}$, 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 **NiBTAP** 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 **NiBTAP** and **MTPPS** 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 **NiBTAP** 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 **H₄TPPS** ($M = 4\text{H}$ in Figure 1). **H₄TPPS** 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 **H₄TPPS** 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 **NiBTAP** and **H₄TPPS** therefore represent a rare example of self-assembly between two very nonplanar porphyrin ions.

In Section 3.3, the reactions of **NiBTAP** with two different **TPPS** complexes are investigated as a method for producing nanomaterials containing three different porphyrin ions. Little is known about the formation of ternary ionic porphyrin nanomaterials, although the synthesis of bimetallic materials containing Fe^{III} and Cu^{II} complexes of **THPyP** and **H₄TPPS** at pH 2 (porphyrin ratios 2:2:9) has been reported.³⁸ In our experiments, equimolar amounts of **NiBTAP** are reacted with two metal complexes of **TPPS** (**CuTPPS** and **MTPPS** ($M = \text{Fe}$, Sn or Mn)) with the goal of producing trimetallic ternary nanomaterials. **NiBTAP** is also reacted with one equivalent of **MTPPS** ($M = \text{Cu}$, Fe , Sn) and two equivalents of **H₄TPPS** with the aim of producing bimetallic ternary nanomaterials.

2. Experimental Methods

2.1 Materials

$\text{Sn}^{\text{IV}}\text{TPPS}$ dichloride, $\text{Mn}^{\text{III}}\text{TPPS}$ chloride, $\text{Fe}^{\text{III}}\text{TPPS}$ chloride, **CuTPPS** and **H₂TPPS** tetrasodium salt dodecahydrate were obtained commercially (Frontier Scientific) and used without further purification. The unprotonated form of **NiBTAP** was prepared using a literature procedure.²⁷ Nanopure™ water was used in the preparation of all reagents.

Stock solutions of the porphyrins (100 micromolar **NiBTAP**, 400 micromolar **MTPPS**, 400 and 1600 micromolar **H₄TPPS**) were prepared in 0.01 M HCl. The unprotonated form of **NiBTAP** 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 **NiBTAP** was dissolved in chloroform (1 mL) in a round-bottom flask, 2 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 minutes.

For the example of a 2:1 **MTPPS-NiBTAP** reaction, 0.8 mL of 100 micromolar **NiBTAP** was diluted to 1 mL with 0.01 M HCl and 0.4 mL of 400 micromolar **MTPPS** 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 **NiBTAP** and **MTPPS** in the reaction mixture were 40 and 80 micromolar, respectively. **MTPPS-NiBTAP** reactions with other ratios (1:1, 3:1 or 4:1) were prepared by adjusting the volume of **MTPPS** stock solution used to prepare the reaction solution.

A similar procedure was used for the **H₄TPPS-NiBTAP** reactions at 1:1, 2:1, 3:1 and 4:1 ratios. The **H₄TPPS-NiBTAP** reactions were also carried out using selected porphyrin ratios between 2:1 and 50:1. For these reactions the concentration of **NiBTAP** in the reaction mixture was reduced to 10 micromolar to avoid the need for very concentrated stock solutions of **H₄TPPS**. Reaction solutions were prepared by diluting 0.2 mL of 100 micromolar **NiBTAP** to 1 mL with 0.01 M HCl and by diluting aliquots of either the 400 or 1600 micromolar stock solutions of **H₄TPPS** to 1 mL with 0.01 M HCl. The concentration of unreacted (monomeric) **H₄TPPS** in the supernatant was determined by UV-Vis spectroscopy and used to calculate the amount of **H₄TPPS** in the precipitate.

For the synthesis of ternary porphyrin materials, the porphyrin concentrations in the reactions were as follows: (1) **NiBTAP-CuTPPS-MTPPS**, 40 micromolar for each metaloporphyrin, and (2) **NiBTAP-H₄TPPS-MTPPS**, 40 micromolar for each metaloporphyrin and 80 micromolar for **H₄TPPS**. Stock solutions were diluted to produce three reaction solutions each containing three times the required porphyrin concentration. The **NiBTAP** was added to the reaction vessel, followed by the **CuTPPS** (reaction 1) or **MTPPS** (reaction 2) and then the third porphyrin. The mixtures were left to react for 1 week, and the precipitates collected as described previously.

A series of control reactions were carried out using solutions of the porphyrin ions. No precipitates were observed for either the stock solutions (100 micromolar **NiBTAP**, 400 micromolar **MTPPS**, 400 and 1600 micromolar **H₄TPPS**) or selected reaction solutions (40 micromolar **NiBTAP**, 80 micromolar **MTPPS** and 160 micromolar **H₄TPPS**) that were left in the dark and undisturbed for one week.

2.3 ICP-AES analysis, UV-vis spectroscopy and electron microscopy

Samples for ICP-AES were harvested as described above. After removing the supernatant, 1 mL of 68% nitric acid (TraceSELECT® grade) was added, the sample transferred to a 5 mL volumetric flask and the volume adjusted to 5 mL using water. Control samples were

made by diluting 1 mL of the 68% nitric acid to 5 mL using water. ICP-AES analysis was carried out at the REQUIMTE Analysis Laboratory in the Department of Chemistry at the Universidade Nova de Lisboa.

UV-vis spectra of a small amount of the precipitate suspended in 0.01 M HCl were measured using a Shimadzu UV-3600 spectrophotometer. For the electron microscopy studies, a small amount of the precipitate was suspended in 0.01 M HCl and one drop of this suspension placed on a carbon-coated copper grid. The grid was then allowed to air dry at room temperature. TEM was performed using a HITACHI H-8100 microscope operated at 200 kV. SEM was performed using an FEI Quanta 400 FEG scanning electron microscope (CEMUP, University of Porto) typically operated at 15 kV, with around 10 mm working distance. All SEM data shown are secondary electron images.

3. Results and discussion

3.1 Self-assembly of **NiBTAP** and **MTPPS**

The self-assembly of **NiBTAP** and **MTPPS** was carried out at pH 2 (0.01 M HCl) where the pyridine groups of **NiBTAP** should be fully protonated to form the octacationic species. The concentration of **NiBTAP** was fixed at 40 micromolar and the **MTPPS:NiBTAP** ratio varied (1:1, 2:1, 3:1 and 4:1, see Experimental methods). For an ISA reaction the composition of the product should be independent of the ratio of the reactants.

Previous studies have shown that the ratios of the porphyrin ions in tetraarylporphyrin-based nanomaterials are related to the charges of the porphyrin ions.^{19,21,16,39,20,23,26,25} Other (non-porphyrinic) ions do not neutralize the charges of the porphyrins to a significant degree. For example, ISA of 4- and 4+ porphyrin ions produces an ionic solid with a 1:1 stoichiometry.³⁹ For **MTPPS** (charge 4-, assuming any charge arising from the central metal ion is neutralized by axial anions) and **NiBTAP** (charge 8+), ionic self-assembly should produce a solid of formula (**MTPPS**)₂(**NiBTAP**).

The porphyrin ratios determined for the precipitates using ICP-AES to measure the metal concentrations are shown in Table 1. For precipitates from the 2:1, 3:1 or 4:1 reactions of **SnTPPS**, **FeTPPS** or **CuTPPS** with **NiBTAP**, the **MTPPS:NiBTAP** ratios are all approximately 2:1. This is consistent with **NiBTAP** and **MTPPS** being present as octacations and tetraanions, respectively, and the reactions producing ionic solids. A corollary to these results is that the **Sn^{IV}TPPS** and **Fe^{III}TPPS** have two and one anions, respectively, coordinated to the metal ions. The slight increases seen for the **MTPPS:NiBTAP** ratios for 3:1/4:1 **SnTPPS** reactions or 2:1/3:1/4:1 **FeTPPS** reactions may arise from difficulties in completely separating the precipitates from the supernatants (which in the case of the 3:1 and 4:1 reactions contain a high concentration of the **MTPPS** complex).

The ratios for the solids with **MnTPPS** (2.45±0.02) suggest the presence of a species other than the tetraanionic form (which is presumably **Mn^{III}TPPS(OH)(H₂O)**). The protonated form **Mn^{III}TPPS(H₂O)₂** with a charge of

3- and an expected ratio of 2.66:1 is a likely candidate. The experimentally observed ratio (2.45) indicates a mixture of these two ions in the solid, with $\text{Mn}^{\text{III}}\text{TPPS}(\text{H}_2\text{O})_2$ being the dominant form.

Changes in the compositions of porphyrin-based ionic solids due to protonation of the axial ligands have previously been reported for tin porphyrins in tetraarylporphyrin ISA reactions.^{39,19} For example, the reactions of ZnTPPS and SnTMPyP produce a 1.27:1 solid at pH 6 and a 1.01:1 solid at pH 5. This was interpreted in terms of the ions $\text{Sn}^{\text{IV}}\text{TMPy}(\text{OH})(\text{H}_2\text{O})$ (5+) and $\text{Sn}^{\text{IV}}\text{TMPyP}(\text{OH})_2$ (4+) being present in the respective solids.³⁹ The absence of a similar protonated species for FeTPPS may be due to the much lower $\text{pK}_{\text{a}1}$ values noted for iron porphyrins versus manganese porphyrins⁴⁰.

Table 1. MTPPS-NiBTAP Ratios Determined by ICP-AES Analysis for the Metals in the Porphyrins.

M	1:1	2:1	3:1	4:1
Sn^{IV}	^a	^b	1.93	2.12
Fe^{III}	^a	1.90	1.99	2.23
Mn^{III}	^a	^b	2.47	2.43
Cu^{II}	^a	1.98	^a	^a

^aNegligible amount of precipitate collected. ^bTrace amount of precipitate collected, sufficient for UV-vis characterization.

The UV-vis spectrum of the SnTPPS-NiBTAP precipitate suspended in 0.01 M HCl is shown in Figure 3 (Main Image) together with the spectra of the starting materials. The Soret band of NiBTAP is red-shifted by approximately 70-80 nm compared to the MTPPS complexes ($\text{M} = \text{Sn, Fe, Cu}$). This reflects the extended π -system and nonplanar macrocycle of NiBTAP . The absorption bands of SnTPPS and NiBTAP are nicely complementary and the spectrum of the suspended precipitate shows significant absorption across most of the visible region. Note that in the solid the Soret band for SnTPPS is much more intense than that of NiBTAP . This is related to the >5 times larger extinction coefficient for SnTPPS ($\epsilon = 620,000$ ⁴¹ versus $110,000 \text{ M}^{-1} \text{ cm}^{-1}$) and its 2-fold higher abundance in the ionic solid.

Selected UV-vis data for the MTPPS-NiBTAP precipitates and the starting materials are shown in Table 2. The absorbance bands for the metal TPPS complexes and NiBTAP are shifted and broadened in the ionic solids compared to the starting materials. In most cases, the Soret bands show a red shift, except for CuTPPS where a small blue shift is observed. The largest shifts for both the MTPPS and NiBTAP bands are seen with FeTPPS (21 and 23 nm, respectively).

Additional UV-vis spectroscopy studies were undertaken to investigate the stability of the precipitates harvested from the reactions. The Inset of Figure 3 shows the Soret band region of the supernatant from the 2:1 SnTPPS-NiBTAP reaction (which yields only a trace amount of precipitate). The spectrum (black line) shows

two Soret bands at 418 and 426 nm. In the case of the suspended ionic solid (blue line) there is only a single band at 419 nm. No Soret band at 426 nm is observed even after 1 day. This suggests that the SnTPPS-NiBTAP ionic solid does not readily re-equilibrate to form the mixture of species seen in the supernatant of the 2:1 reaction. UV-Vis spectra of suspensions of precipitates from the other MTPPS-NiBTAP reactions, together with spectra of the starting porphyrins, are provided in Figures S1-S3. In these cases, the supernatants of the 2:1 reactions do not show two Soret bands for the MTPPS so dissociation of the precipitates could not be investigated using the method employed for SnTPPS .

Figure 3. Main Image: UV-vis spectra in 0.01 M HCl of SnTPPS , NiBTAP and suspended SnTPPS-NiBTAP precipitate. Inset: Soret band region of the supernatant from a 2:1 reaction (black), SnTPPS (red), suspended SnTPPS-NiBTAP precipitate (blue) and the 1:1 reaction (green). All sample concentrations were chosen to best illustrate the spectral features.

The UV-vis spectra in the Inset of Figure 3 also provide insights into the 1:1 reactions of SnTPPS and NiBTAP which do not produce any precipitate. The 1:1 reactions show a single Soret band at 425 nm (green line) which is red-shifted compared to the bands seen for SnTPPS (red line) and the ionic solid (blue line). The band seen for the 1:1 reaction is in a similar position to the red-shifted Soret band of the supernatant of the 2:1 reaction (black line). These red-shifted Soret bands may arise from water-soluble aggregates with a different arrangement of the porphyrin subunits compared to the ionic solids obtained by centrifugation. One possibility is the formation of a strong ion pair between SnTPPS

and **NiBTAP** with the net charged species staying in solution.

Table 2. Soret Bands (nm) for the Starting Materials (in parentheses) and the MTPPS-NiBTAP Ionic Solids.

TPPS Complex	MTPPS	NiBTAP
Sn^{IV}TPPS	(416) 419	(474) 484
Fe^{III}TPPS	(395) 416	(474) 497
Mn^{III}TPPS	(467) ^a 472 ^b	(474) 472 ^b
Cu^{II}TPPS	(412) 410	(474) 493

^aFor the most intense band of the hyper type spectrum of **MnTPPS**. ^bOnly a single band at 472 nm is present in the spectrum of the precipitates.

TEM images obtained for the ionic solids from the **MTPPS-NiBTAP** reactions show two types of material in varying proportions, as illustrated for the **MnTPPS-NiBTAP** reactions in Figure 4. The first consists of nanoparticles and clusters of nanoparticles (Figure 4(a)). In the case of the reactions of **MnTPPS**, the smallest particles discernible in the images are approximately 10 nm. Most of the nanoscale material however is in the form of larger nanoparticle clusters. The presence of only a small number of 10 nm particles on the TEM grid may result from aggregation of the particles upon drying or inefficient separation of the 10 nm particles under the centrifugation conditions employed.

An estimate of the number of porphyrins in the 10 nm particles was obtained using the approximate dimensions of the porphyrin ions (2 x 2 x 0.5 nm for **MTPPS**, and 2 x 2 x 1.5 nm for **NiBTAP**²⁷). The shape of the particles is difficult to discern so they were modelled as both 10 nm spheres and 10 nm cubes. The solid was assumed to have a **MTPPS:NiBTAP** ratio of 2:1, corresponding to a volume of 10 nm³ for the trimeric unit (packing effects were not considered). The 10 nm spheres and cubes are calculated to contain 52 trimers (156 porphyrins) and 100 trimers (300 porphyrins), respectively.

The second type of material observed is porous micron-sized wafers with nanoscale features (Figure 4(b)). The wafers are large enough to be observed on the dried TEM grid using optical microscopy (Figure S4). However, they could not be detected when solutions of the completed reactions were examined by optical microscopy. This suggests that the wafers form when the sample is dried on the TEM grid.

Overall, the ISA reactions of **MTPPS** and **NiBTAP** are more complicated than those reported for tetraarylporphyrin ions. For example, the 1:1 reactions produce negligible amounts of precipitate whereas for ISA they are expected to yield 2:1 (or 2.5:1 for **MnTPPS**) solids with the excess **NiBTAP** remaining in solution. The yield of precipitate for a 2:1 reaction also shows a strong dependence on the metal in the **TPPS** complex, being low for **SnTPPS** and **MnTPPS** but very high for **CuTPPS**

(98%, as determined by UV-vis spectroscopy of the supernatant). Given the very high yield for the 2:1 **CuTPPS-NiBTAP** reaction it is also surprising that a negligible amount of precipitate is formed in the 3:1 and 4:1 reactions of these porphyrins.

Figure 4. TEM images of **MnTPPS-NiBTAP** precipitate showing (a) nanoparticles and clusters of nanoparticles, and (b) porous micron-sized wafers.

3.2 Self-assembly of **NiBTAP** and **H₄TPPS**

The self-assembly of **NiBTAP** with the dication of **TPPS** (**H₄TPPS**) was then investigated using the same experimental conditions described for **NiBTAP** and **MTPPS**. A charge of 2- has been observed for the **H₄TPPS** ion in tetraarylporphyrin ionic solids.^{19,20,26,23} The 2- charge results from the four negative charges of the peripheral sulfonate groups and the two positive charges from the protons in the porphyrin core. Ionic self-assembly of **H₄TPPS** (2-) and **NiBTAP** (8+) was therefore expected to produce the solid (**H₄TPPS**)₄(**NiBTAP**). For the reaction of a 4:1 mixture of **H₄TPPS** and **NiBTAP** the ratio of the porphyrins in the solid was determined by ICP-AES analysis of the precipitate (99% of the Ni expected for complete precipitation of the **NiBTAP**) and UV-Vis spectroscopy of the supernatant (9% of the **H₄TPPS** was present as the monomeric form). The ratio of the porphyrins in the solid (~3.7:1) is thus similar to that expected for formation of an ionic solid.

Figure 5 shows the UV-vis spectrum of precipitate from a 4:1 reaction of H_4TPPS with $NiBTAP$. The bands at 432, 490 and 704 nm indicate that J-aggregates of H_4TPPS ³³⁻³⁵ are present in the solid. Two previously characterized porphyrin ionic solids containing H_4TPPS ^{19,20} also show J-aggregate type UV-vis spectra, suggesting that this is a preferred structure for H_4TPPS in ionic solids. The absence of a Soret band for $NiBTAP$ in Figure 5 is probably due to its low intensity (the ratio of the H_4TPPS : $NiBTAP$ Soret bands is 3.2:1, and the ratio of H_4TPPS : $NiBTAP$ in the precipitate is 3.7:1) and its overlap with the 490 nm band for the J-aggregate. Electronic coupling of $NiBTAP$ to the J-aggregate seems unlikely as resonance Raman studies⁴² of nanotubes prepared by ISA of $SnTHPyP$ and H_4TPPS at pH 2¹⁹ indicate that the J-aggregate bands arise solely from the H_4TPPS .

Electron microscopy images of the precipitates from 4:1 reactions of H_4TPPS - $NiBTAP$ reveal structures similar to those seen for the $MTPPS$ - $NiBTAP$ ionic solids. Some of the material consists of nanoparticles and collections of particles (Fig. S5). Micron-sized wafers with nanoscale features are also observed in TEM images (Figure 6(a)) where the porous nature of the wafers is readily apparent. Micron-sized structures were not seen in suspensions of the precipitates imaged using optical microscopy, again indicating that they probably result from a drying effect. SEM images (Figures 6(b) and S6) show that in some cases the wafers form in large numbers and are densely packed. Many of the wafers are oriented approximately perpendicular to the surface of the grid. This arrangement is also consistent with the wafers having grown on the surface of the grid rather than being deposited from solution.

Figure 5. UV-Vis spectra in 0.01 M HCl of H_4TPPS , $NiBTAP$ and suspended precipitate from a 4:1 reaction. Sample concentrations were chosen to best illustrate the spectral features.

Figure 6. (a) TEM and (b) SEM images showing wafers obtained from 4:1 H_4TPPS - $NiBTAP$ reactions.

Experiments with H_4TPPS : $NiBTAP$ ratios varying from 2:1 (an excess of $NiBTAP$) to 50:1 (a large excess of H_4TPPS) unexpectedly produced precipitates with variable stoichiometries rather than the 4:1 ratio characteristic of an ionic solid. ICP-AES analysis for Ni was used to establish the amount of $NiBTAP$ in the precipitate, and UV-vis spectroscopy the amount of monomeric H_4TPPS in the supernatant. The H_4TPPS : $NiBTAP$ ratios in the precipitates ranged from ~2:1 for a 2:1 reaction to ~30:1 for a 50:1 reaction and the syntheses were reproducible. The UV-vis spectra of the precipitates again show bands indicative of H_4TPPS J-aggregates (data not shown). The absolute amount of J-aggregate in the precipitate increases for higher reactant ratios, as shown for the 490 nm band in the Inset of Figure 7, consistent with the results described above.

To the best of our knowledge, this is the first time that the products from "ionic self-assembly" reactions of porphyrins have been found to possess such variable compositions. A plot of the ratio in the precipitate versus the reactant ratio is shown in Figure 7 (blue line) together with the precipitate compositions expected for ISA (green line) and for complete reaction of H_4TPPS and $NiBTAP$ (red line). The gap between the blue and red lines corresponds to the amount of free (monomeric) H_4TPPS in the reaction supernatant. The amount of free H_4TPPS increases with the reactant ratio, from a very low value for the 2:1 reaction (2%), to 9% for a 4:1 reaction and 23% for a 20:1 reaction. A limiting $H_4TPPS:NiBTAP$ ratio was not observed up to the highest reaction ratio studied in our experiments (50:1). No precipitates are observed in control experiments containing only H_4TPPS (see Experimental methods) consistent with homo-aggregation of H_4TPPS being weak in 0.01 M HCl.

These results clearly show that $NiBTAP$ does not react with H_4TPPS via ISA as previously observed for other porphyrins.^{19,20} One explanation for the formation of precipitates with $H_4TPPS:NiBTAP$ ratios higher than 4:1 is that $NiBTAP$ acts as a template that stabilizes H_4TPPS J-aggregates, perhaps as a result of its high positive charge. In this case, some of the H_4TPPS molecules in the J-aggregates will have non-porphyrinic counterions associated with their sulfonate groups to provide charge neutrality. Interestingly, H_4TPPS also reacts with $NiBTAP$ to produce solids with $H_4TPPS:NiBTAP$ ratios *lower* than expected given the charges of the ions. The lowest $H_4TPPS:NiBTAP$ reactant ratio that produces a large amount of precipitate is 2:1, where essentially all of the H_4TPPS and $NiBTAP$ react. Such behaviour has not previously been reported for ionic self-assembly reactions of porphyrins under aqueous conditions. One possible explanation for the formation of a 2:1 solid is ISA of the free base form of $TPPS$ (H_2TPPS , charge 4-) with $NiBTAP$ (charge 8+). However, this seems unlikely given that the 2:1 precipitate shows UV-vis bands characteristic of H_4TPPS J-aggregates. Another possibility is that the charge in the solid is balanced by anions (presumably chlorides) associated with the protonated pyridine groups of $NiBTAP$ i.e., the solid consists H_4TPPS (2-) and $NiBTAP \cdot 4Cl$ (4+).

EDX studies were carried out to investigate this possibility. The chloride content of a true 4:1 ionic solid should be negligible¹⁹ whereas the 2:1 solid should contain 4 chloride ions associated with the protonated pyridine groups. Unfortunately, a definitive determination could not be made as both the 4:1 and 2:1 solids were found to contain highly variable amounts of chlorine, perhaps due to contamination by residual hydrochloric acid.

Figure 7. Main Image: Plot showing the H_4TPPS - $NiBTAP$ ratio in the precipitate versus the reactant ratio (OBS) and the plots expected for ISA and for complete reaction of H_4TPPS and $NiBTAP$. Inset: Spectra showing an increase in the absolute intensity of the J-aggregate band at 490 nm for suspended precipitates from H_4TPPS - $NiBTAP$ reactions with reactant ratios of 4:1, 8:1, 12:1 and 16:1.

3.3 Ternary nanomaterials

A feature of ISA is that it can be used to produce nanomaterials containing porphyrin ions with complementary properties. Examples of such pairings include electron donor and electron acceptor porphyrin ions,¹⁶ light-harvesting and catalytic porphyrin ions,¹⁷ and oppositely-charged catalytic cobalt porphyrin ions.¹⁸ Other potential pairings include the formation of nanomaterials containing Fe and/or Mn porphyrin ions as catalytic components for reactions such as the oxidation of saturated C-H bonds.⁴³ This which would represent a novel approach to the synthesis of heterogeneous reaction systems based on Fe or Mn porphyrins.^{44,45} We decided to investigate whether the ISA reactions of $NiBTAP$ could be used to synthesize ionic solid nanomaterials containing three different porphyrins. This increases the range of functionality present in the nanomaterial and also the potential for cooperative interactions between the porphyrin ions. The formation of ternary systems may provide a new approach to customizing the properties of porphyrin nanomaterials for applications such as light harvesting, catalysis and photocatalysis.

Our investigations focused on the synthesis of nanomaterials from $NiBTAP$ and two different $TPPS$ ions. The first study investigated the synthesis of trimetallic systems containing $NiBTAP$, $CuTPPS$ and a $MTPPS$ ($M = Fe, Sn$ or Mn). The synthesis of bimetallic systems derived from $NiBTAP$, $MTPPS$ ($M = Cu, Fe, Sn$) and H_4TPPS was also studied. It is worth noting that $TBAP$ is available with a variety of metals complexed to the porphyrin and as the metal-free form.²⁷ The N-methyl pyridiniumyl derivative Me_8TBAP (6) has also

been synthesized,²⁷ and like **TMPyP** it can be used over a much wider pH range than the non-alkylated porphyrin. This makes for an extensive range of synthetic possibilities considering just the **TBTAP** and **TPPS** ions.

For the **NiBTAP**-**CuTPPS**-**MTPPS** reactions, the concentration of **NiBTAP** was the same as in the binary reactions described in Section 3.1 (40 micromolar) and the ratio of the reactants was 1:1:1. All of the reactions gave significant quantities of precipitate which were analyzed by ICP-AES to determine the metal concentrations (Figure 8(a)). For each reaction the precipitate contains all three porphyrins, and the total **TPPS** to **NiBTAP** ratio (1.7-2.0) is consistent with the formation of ionic solids. However, the solids contain different amounts of **CuTPPS** and **MTPPS** depending upon the metal M (Figure 8(a)). The amount of **MTPPS** tracks the amount of precipitate formed for the corresponding binary reactions at 2:1 ratios (**FeTPPS** > **SnTPPS** ~ **MnTPPS**) (Table 1). A TEM image of the precipitate from a **NiBTAP**-**CuTPPS**-**FeTPPS** reaction is shown in Figure 8(b). Nanoscale materials are observed including rods, particles and clusters of these materials.

Figure 8. (a) Compositions of the products obtained from **NiBTAP**-**CuTPPS**-**MTPPS** reactions, as determined by ICP-AES, and (b) TEM image of the **NiBTAP**-**CuTPPS**-**FeTPPS** nanomaterial. The ratios in (a) were normalized using the concentration of nickel in **NiBTAP**.

In the case of the **NiBTAP**-**H₄TPPS**-**MTPPS** reactions the concentration of **NiBTAP** was 40 micromolar and the ratio of the reactants was 1:2:1. The reaction of two equivalents of **H₄TPPS** (charge 2-) and one equivalent of **MTPPS** (charge 4-) with **NiBTAP** was chosen to provide the potential for charge neutrality in the solids using only porphyrin ions. The reactions produced copious amounts of precipitate, and ICP-AES of the precipitate (for Ni or M) and UV-vis analysis of the supernatant (for **H₄TPPS**) yielded the porphyrin ratios shown in Figure 9(a). For all three reactions most of the

H₄TPPS (1.8-2.0 equivalents) is present in the precipitate. This is consistent with the high incorporation of **H₄TPPS** seen in the 2:1 and 4:1 **H₄TPPS**-**NiBTAP** reactions in Section 3.2. The UV-vis spectrum of the **NiBTAP**-**H₄TPPS**-**FeTPPS** precipitate shows bands at 490 and 710 nm confirming formation of J-aggregates for the **H₄TPPS** (Figure S7). The amount of **MTPPS** in the solid varies from 0.98 equivalents (M = Fe) to only 0.37 equivalents (M = Sn). In the latter case, the precipitate is clearly not a standard ionic self-assembly product. The amount of **MTPPS** in the precipitate is again related to the amount of precipitate formed for the binary reactions at 2:1 ratios (**CuTPPS** ~ **FeTPPS** > **SnTPPS**) (Table 1). A TEM image of the precipitate from a **NiBTAP**-**H₄TPPS**-**FeTPPS** reaction (Figure 9(b)) reveals a mixture of nanomaterials and some larger sheet-like structures.

Figure 9. (a) Compositions of the products obtained from **NiBTAP**-**H₄TPPS**-**MTPPS** reactions, as determined by ICP-AES and UV-vis spectroscopy, and (b) TEM images of the **NiBTAP**-**H₄TPPS**-**FeTPPS** material. The ratios in (a) were normalized using the concentration of **NiBTAP**.

4. Conclusions

We have investigated the ionic self-assembly (ISA) reactions of an octacationic porphyrin, **NiBTAP**, to determine if it is possible to produce nanomaterials from porphyrin ions with unusual structures. Nanomaterials are obtained from the reactions of **NiBTAP** with metal complexes of **TPPS** in 0.01 M HCl and the materials have stoichiometries consistent with ionic solids i.e., charge neutrality is provided by the porphyrin ions. The reactions of **NiBTAP** with the dication of **TPPS** (**H₄TPPS**) also produce nanomaterials but in this case the materials have variable **H₄TPPS**:**NiBTAP** ratios, something not previously reported for ISA of tetrarylporphyrins.

Nanomaterials with higher than expected H₄TPPS: NiBTAP ratios may result from NiBTAP stabilizing the formation of H₄TPPS J-aggregates. NiBTAP is also used to prepare new classes of *ternary* porphyrin nanomaterials. Both trimetallic (NiBTAP-CuTPPS-MTPPS) and bimetallic (NiBTAP-H₄TPPS-MTPPS) solids are synthesized. Additional studies of TBTAP, Me₈TBTAP and other highly-charged porphyrins are underway with the goal of better understanding their self-assembly reactions. In addition, investigations of the catalytic oxidation reactions of nanomaterials prepared from Fe and/or Mn complexes of TMPyP and TPPS are in progress.

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