Supporting Information

# Hyperbranched Crystalline Nanostructures Produced from Ionic $\pi$ -Conjugated Molecules

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### Synthesis of TAPP: TSPP Sheaf-like Structures

**Materials and Sample Preparation:** The meso-tetra(4-aminophenyl)porphyrin H<sub>2</sub>TAPP and the diacid form of meso-tetra(4-sulfonatophenyl)porphyrin were purchased from Frontier Scientific and used without further purification. Concentrated trace-metal grade HCl from Fisher was used for pH adjustment. Nanopure (18.1 M $\Omega$ /cm) water was used in all of the syntheses.

The sheaf-like TAPP:TSPP nanostructures were prepared as follows. A 500  $\mu$ M TAPP stock solution at pH 2 was prepared by first partially dissolving the TAPP crystals in a lower pH smaller volume of water followed by partial dilution and further dissolving of the TAPP crystals. Once completely dissolved the solution was diluted to the final concentration. The solution was maintained at pH 2 to ensure the TAPP remains in solution at these higher concentrations. The stock TSPP was also prepared at 500  $\mu$ M concentration following the procedure outlined elsewhere.<sup>1</sup> In order to prepare stoichiometric TAPP:TSPP sheaf-like nanostructures, equal volume pH 3 solutions of TAPP and TSPP at twice the final mixed concentration were prepared by adding a calculated amount of the TAPP or TSPP stock solution followed by the addition of 1 M HCl (1:1000 by volume where the latter is the final solution volume). These solutions were then quickly diluted to the final volume. The equal volume solutions were then mixed always adding the TSPP to the TAPP to make the final concentration solutions. Solutions of TAPP: TSPP at room temperature were prepared using this procedure for 3.7:1, 2.8:1, 1.8:1, 1:1, 1:2.2, and 1:3.2 ratios.

Extinction coefficients for each molecule were obtained by weighing out a known mass and preparing a series of dilute solutions at pH 3. The extinction coefficients at the maximum of the B-band or Soret peak were used,  $\varepsilon_{455nm} = 152,000 \text{ M}^{-1} \text{ cm}^{-1}$  for TAPP and  $\varepsilon_{434nm} = 435,000 \text{ M}^{-1} \text{ cm}^{-1}$  for TSPP. The extinction coefficient for TSPP is within 2% of the literature value (443,000 M<sup>-1</sup> cm<sup>-1</sup>).<sup>2</sup> An extinction coefficient for TAPP in aqueous solutions at pH 3 has not been reported elsewhere.

Equimolar heated solutions of TAPP:TSPP were prepared at a variety of temperatures and concentrations. The TAPP and TSPP solutions were brought to the desired reaction temperature in a thermally insulated hot water bath. The heated solutions were then mixed and allowed to react while sitting in the hot water bath for 2 hours. After 2 hours the heater on the bath was shut off and the entire bath was allowed to cool slowly to room temperature. Final solution concentrations were either 2.5:2.5  $\mu$ M, 5:5  $\mu$ M, 10:10  $\mu$ M, or 25:25  $\mu$ M and temperatures were 30, 40, 50, 60, and 75 °C.

Solid samples of the TAPP:TSPP nanosheaves were filtered following the same procedure as previously performed.<sup>1</sup>

**UV-Vis Spectral Acquisition:**Spectra of the TAPP, TSPP, and TAPP:TSPP solutions were obtained using 1 cm path length quartz cuvettes on either a Perkin-Elmer 330 dual-beam spectrometer or a Thermo Scientific Evolution 260 Bio UV-Visible spectrometer. Solutions were allowed to stand for sufficient time to allow the spectral intensities of the solutions to become constant.



**Figure S1.** Plot of the absorbance spectra of TSPP, TAPP, and 1:1 TAPP:TSPP at pH 3. The diacid spectrum of TSPP is shown in blue. The hyperporphyrin spectrum of TAPP is shown in red. The 1:1 mixture of TAPP and TSPP exhibits a blue shifted peak typical of an "H-aggregate" resulting from excitonic coupling of face-to-face stacked porphyrins.

**Ionic Self-Assembly of TAPP:TSPP Studied by UV-Visible Spectroscopy:** The electronic spectra of TSPP, TAPP, and a 1:1 ratio of TAPP:TSPP in pH 3 aqueous solutions is shown in Figure S1. The absorbance spectrum of TSPP is indicative of the diacid form with a Soret band at 434 nm resulting in a net -2 charge for the entire porphyrin. This is expected by reason of the pKa = 4.8 of the inner pyrrole nitrogens resulting in a +2 center due to the addition of the 2 extra protons on the porphyrin core and a -4 charge on the periphery due to the SO<sub>3</sub><sup>-</sup> groups.<sup>3</sup>

The absorbance spectrum of the TAPP at pH 3 is typical for what is known as a hyperporphyrin spectrum with even further red shifted Soret and Q-bands compared to typical diacid spectra. At this pH we observe a broad Soret band at 454 nm and a broad Q-band at 720 nm. In pH 3 solutions the TAPP is expected to exist in the diacid form. The imino nitrogens of the porphyrin core have a pKa of 4.57. The aminophenyl nitrogens are believed to protonate in pairs with a pKa of 1.86 and 0.37 respectively with the latter forming the completely protonated  $H_4[H_4TAPP]^{6+}$  species.<sup>4</sup> Thus at pH 3 we expect a 1  $H_4TAPP^{2+}$ : 1  $H_4TSPP^{2-}$  neutral species to be formed. The optical spectrum of the 1:1 TAPP:TSPP adduct show the presence of a broad band at 409 nm followed by a peak at 434 nm and 2 overlapping peaks at around 645 nm and 700 nm. The peaks at 434, 645, and 700 nm are similar to those for the Soret band of the TSPP, the Q-band of the TSPP, and the hyperporphyrin Q-band of the TAPP respectively. The blue shifted



**Figure S2.** Plot of the calculated excess porphyrin concentrations versus the mole fraction of TSPP. The filled squares are the concentrations of the excess porphyrin measured by taking the UV-Vis spectrum of the supernatant solution above the formed and settled precipitate. The extinction coefficients of the Soret peak maxima for TAPP and TSPP were used in the calculations. The open circles are the calculated excess porphyrin concentration based off a 1:1 ratio of TAPP to TSPP.

peak at 409 nm may be called an *H*-aggregate band suggesting a face-to-face stacking of the porphyrins which undergo excitonic coupling.

We studied the stoichiometry of the TAPP:TSPP solution at pH 3 by measuring the excess porphyrin concentration after mixing the solutions of different ratios. The solutions were allowed to sit for at least 5 days. Excess porphyrin concentration was determined by pipetting the supernatant solution above the settled precipitate into a quartz cuvette. The UV-Vis spectrum of the supernatant for each ratio was taken. The excess porphyrin concentration was then determined using the absorbance of the Soret maxima for the TAPP and the TSPP. The calculated excess porphyrin concentration plotted against the mole fraction of the TSPP in solution is shown in Figure S2. A plot of the expected porphyrin concentration based off of the starting porphyrin stock solution and volume added to make each solution is shown for comparison. From this plot we observe that the TAPP:TSPP system interacts in a 1:1 ratio to form the precipitate. This is in agreement with what is expected by the pKa values.

**AFM Sample Preparation and Imaging:** AFM samples were prepared by depositing 1-2 drops by Pasteur pipette of the TAPP:TSPP nanocrystal solution onto freshly peeled HOPG for 1 minute followed by a 30 second spin at 3900 rpm. This process was repeated 10 times to create a well dispersed sample for AFM imaging.

AFM images were taken using a Bruker Multimode 8 AFM with Nanoscope V controller and a "J" vertical scanner. Bruker's Nanoscope 8.15 software was used to acquire data. Antimony doped silicon cantilevers with 116  $\mu$ m length, 130 kHz resonance frequency, and 3 N/m spring constant purchased from Bruker were used. Highly oriented pyrolytic graphite (HOPG) purchased from SPI Supplies Inc. was used as a substrate.



**Figure S3.** High resolution tapping mode AFM image of TAPP: TSPP nanosheaves prepared from equimolar ( $5\mu$ M) porphyrin solutions at pH 3 and 75 °C. Sample was deposited onto highly ordered pyrolytic graphite. Image was acquired under ambient conditions.

**X-ray Powder Diffraction Acquisition:** X-ray powder diffraction was acquired using a Krystalloflex XRD in  $\theta/2\theta$  Bragg-Brentano (BB) geometry and a Rigaku Miniflex in BB geometry at room temperature (~22 °C). For the data using the Krystalloflex XRD, the filtered and dried flaky sample was sprinkled on the flat backside of an aluminum sample plate and wet with a drop of ethanol to adhere it to the surface. The sample was allowed to completely dry before analysis. Copper K $\alpha$  X-rays ( $\lambda = 1.5406$  Å) at 35 kV and 20 mA emission with a scintillation detector was used for the analysis. A  $\theta/2\theta$  scan was run from 2° to 40° in step mode with a step size of 0.05° and a 60 s per pt dwell time. The total time for analysis was 12.67 hours.

**Table S1.** Lattice spacings calculated for a body centered structure based on electron diffraction patterns of individual TAPP : TSPP nanoribbons. Sample was prepared at 75  $^{\circ}$  C.

Nanorod	а	с
1*	32.09	8.17
2*	31.96	8.18
3**	30.01	7.65
4**	30.19	7.68
5**	30.15	7.70
6	31.16	8.06
7	30.98	8.09
8	31.23	8.07
9***	31.93	8.23
10***	31.82	8.20
11	31.93	8.31
12	31.89	8.32
Average (Å)	31.28	8.05
St. Dev. (Å)	0.79	0.24

\*, \*\*, \*\*\* denote measurements made on the same nanoribbon at different locations.

The sample was then gently ground on the aluminum plate and adhered to the surface with a drop of ethanol and allowed to completely dry before analysis as above. No sample degradation was observed between the two 12.67 hour scans. For the data using the Miniflex, a separate ground sample powder was placed in a 0.2 mm deep zero-background holder. Copper Ka  $(\lambda = 1.5406 \text{ Å})$  X-rays at 40 kV and 15 mA emission, with a scintillation detector and monochromator were used for the analysis. A scan was run from 2° to 35° in step mode with a step size of 0.05° and a 10 sec/pt dwell time. Total scan time was about 1.8 hours. CMPR was used to determine the possible crystal system and lattice spacings.<sup>5</sup>

#### **X-Ray Powder Diffraction:**

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X-ray powder diffraction supports the assignment of a body centered orthorhombic structure of a = 30.92 Å, b = 15.44 Å, c = 8.01 Å and  $\alpha = \beta = \gamma = 90^{\circ}$  (see Figure S3). The broad peaks are to be expected for nanocrystalline materials.<sup>6</sup> It should also be noted that there is very little amorphous background in the powder pattern, suggesting a high degree of crystallinity.



**Figure S5.** Plot showing the Arrhenius-like dependence of the TAPP:TSPP sheaf half-length on temperature (30°C -75 °C).

**TEM Sample Preparation:** Samples for high resolution transmission electron microscopy (HRTEM) were prepared by depositing 5 uL of the TAPP:TSPP onto a nickel Formvar coated TEM grid. The solution was then wicked away using a filter paper touched to the edge of the drop. A 200 kV Phillips CM200 TEM and a 200 kV FEI G2 T20 Twin TEM was used to acquire TEM images.

## TEM, HRTEM, and SAED Imaging of the TAPP:TSPP Nanosheaves

Table 1 shows electron diffraction spacings in the *a* and *c* directions calculated for a body centered orthorhombic crystal. The average distances are  $a = 31.3 \pm 0.8$  Å and  $c = 8.0 \pm 0.2$  Å with  $\alpha = \beta = \gamma = 90^{\circ}$ . These distances agree well with spacings observed by X-ray diffraction.

TEM images of the time dependent growth of the TAPP:TSPP nanosheaves is shown in Figure S4. The nanosheaves shown in Figure S4 are representative bundles found on samples prepared by pipetting out aliquots of hot (75 °C) TAPP:TSPP solution onto cold TEM grids at various times during the reaction process. We observe initial sheaf-like bundles that continue to grow and split over time with the fastest growth occurring within the first 10 minutes. We were unable to differentiate between nanoparticles formed during the cooling process on the cold TEM grid and the initial formation of the nanosheaves at times less than about 4 minutes.



**Figure S6.** Time dependent growth of the 5  $\mu$ M TAPP : 5  $\mu$ M TSPP pH 3 sheaf-like structures prepared at 75 °C showing the formation of small sheaf-like structures that continue to grow and branch over time.

#### **Details of Data Fitting in Fig 5.**

The nonlinear least squares fitting of the aspect ratio versus the  $\ln(L_{1/2})$  is performed using the Levenberg-Marquardt method in MathCAD 14 where the error on the residuals is minimized. Our function is a piecewise continuous function defined as:  $f(L,a,b,c,d) = c^* \exp(d^*L)$  if  $L < L_c$  and  $f(L,a,b,c,d) = a+b^*L$  otherwise, where L is the natural log of the Half-Length in nm  $[\ln(L_{1/2})]$ ;  $L_c$  is the point at which the transition occurs from the linear region to the logarithmic region; and a, b, c, and d are fitting parameters. The point of intersection,  $L_c$ , obeys the logarithmic matching boundary conditions:  $c^* \exp(d^*L) = a+b^*L$  and  $c^* \exp(d^*L) = b$ . We fit the average and upper and lower limits with the above function to determine the range of  $L_c$ . The typical values of  $L_c$  ranged from about 250-300 nm. The values of a ranged from -38 to -101. The values of b ranged from 8.5 to 23.5. The values of c ranged from 0.1 to 0.3. The values of d ranged from 0.81 to 0.83.

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