

Supporting Information

New Nanoscale Insights into the Internal Structure of Tetrakis(4-sulfonatophenyl) Porphyrin Nanorods

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Raman. The diacid RR spectrum is compared to that of aggregate in solution and on gold substrate in Figure 1 below. All solutions were 50 μM in porphyrin concentration. The intensities have been normalized to the strongest peak in each spectrum: (top) RR spectrum of $\text{H}_2\text{TSPP}^{2-}$ in solution excited at 458 nm, pH 3.48; (middle) RR spectrum of TSPP aggregate in 1.5M HCl solution excited at 488 nm, and (bottom) SERRS spectrum of TSPP aggregates in 1.5M HCl deposited on gold, excited at 488 nm.

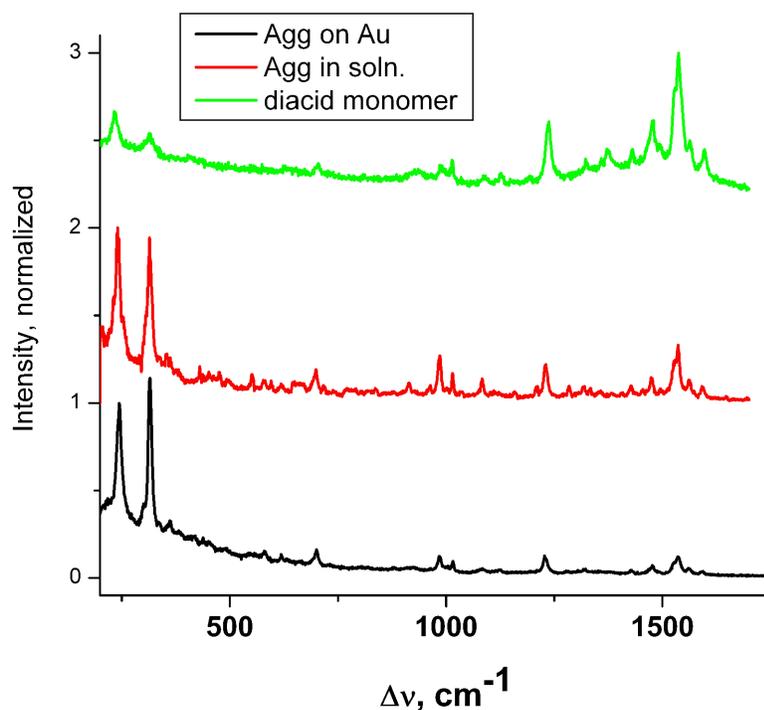


Figure 1

Table 1. Raman vibrational mode positions ($\Delta\nu$ in cm^{-1}) and assignments of different forms of TSPP.

Free Base	Diacid Monomer	Aggregate	Assignments
	234	240 (soln)	oop C_m - ϕ
312	316	245 (Au)	
		314 (soln)	pyr tilt or swivel
		316 (Au)	
~400	~400	360	pyr swivel
		380	phenyl
		420	phenyl
		436	phenyl
		453	pyr rot
		~490 (br)	phenyl $\tau(\text{CC})$, $\gamma(\text{CCH})$
		550	$\gamma(\text{C}_\alpha\text{-C}_m)$
		580	$\gamma(\text{C}_\alpha\text{-C}_m)$
623	weak	620	phenyl
733	703	700	$\delta(\text{N-C}_\alpha\text{-C}_m)/\nu(\text{C}_\alpha\text{-N})$
806		806	pyr fold
		820	$\delta(\text{pyr def})$
885		880	$\delta(\text{pyr def})$
	~925 (br)	~915 (br)	phenyl
965	993	984	$\nu(\text{pyr breath})$
1003	1015	1015	$\nu(\text{pyr breath})$
1084	1083	~1082	$\delta(\text{C}_\beta\text{-H})$
1124	1120	~1120	$\delta(\text{C}_\beta\text{-H})$
1234	1238	1229 (soln)	$\nu(\text{C}_m\text{-}\phi)$
		1231 (Au)	
1293			$\nu(\text{pyr half-ring})$
	1327	1320	$\nu(\text{pyr quarter-ring})$
1364	1370	1355,1380 (soln)	$\nu(\text{pyr half-ring})$
		1340 (Au)	
1440	1428	1428	phenyl
	1476	1477	$\nu(\text{C}_\alpha\text{-C}_m)$
1549	1539	1536, ~1530 sh (soln)	$\nu(\text{C}_\beta\text{-C}_\beta)$
	~1530 (sh)	1538, ~1530 sh (Au)	
	1564	1561	$\nu(\text{C}_\alpha\text{-C}_m)$
1601	1600	1591	phenyl

For specific carbon atom labels refer to Figure 1 in the main paper; pyr: pyrrole; oop: out of plane; (Au): TSPP deposited on gold.

STM. Medium resolution 400nm^2 images in Figure 2 depict two different nanorods samples of TSPP aggregates deposited on Au(111) from $5\mu\text{M}$ porphyrin solutions in 0.75M HCl. Both images were acquired at room temperature employing similar scan parameters: 1.3V and 10 pA . The z heights scale in the images (a) and (d) are 11.8 nm and 6.19 nm , respectively. Image (a) in Figure 2 reveals that the body of the nanorod has small relatively uniform corrugations that almost appear to run parallel along the long axis of the aggregate. In Figure 2b we observe that a section of the rod was disrupted by the STM probe as evidenced by a band of small fragments spread across that area. As we make the scan size smaller, the quality of our images becomes more variable because in the absence of moisture the rods are less stable and more prone to disintegration with the repeated probing by the STM tip.

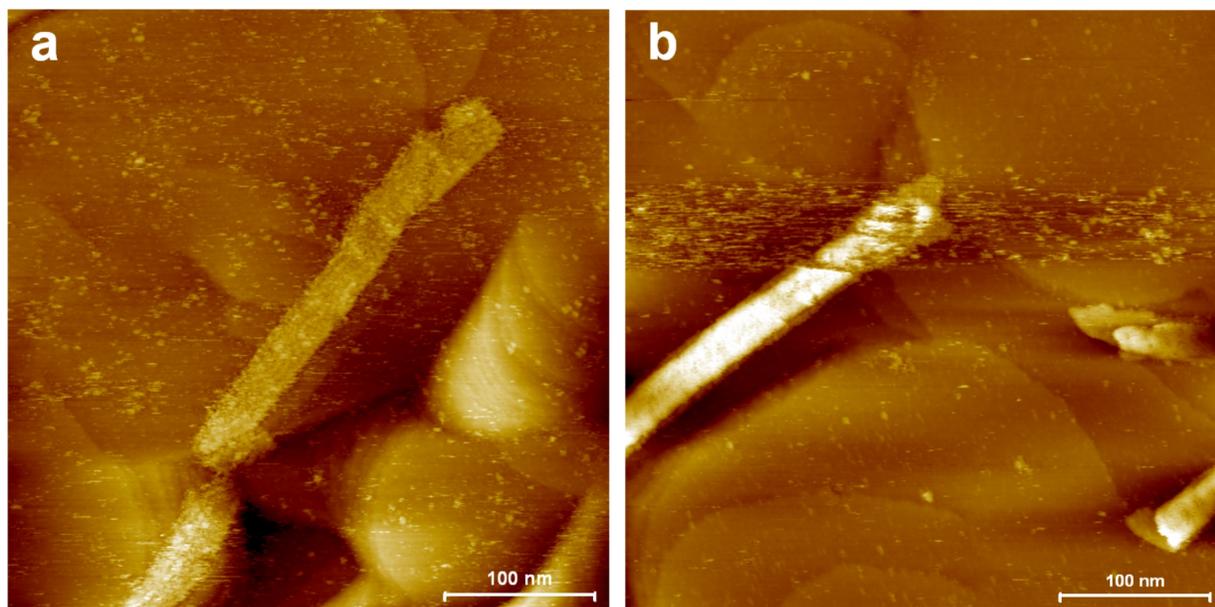


Figure 2.

UV-visible. Electronic absorption spectra of a 50 μM TSPP solution at different pH is shown are in Figure 3: free-base (black trace), diacid (red trace) and the aggregate (green trace) of TSPP. The 490 nm absorbance is assigned to the J-aggregate transition and the 420 nm band is attributed to the H-aggregate. Spectra were collected using 1mm cuvettes.

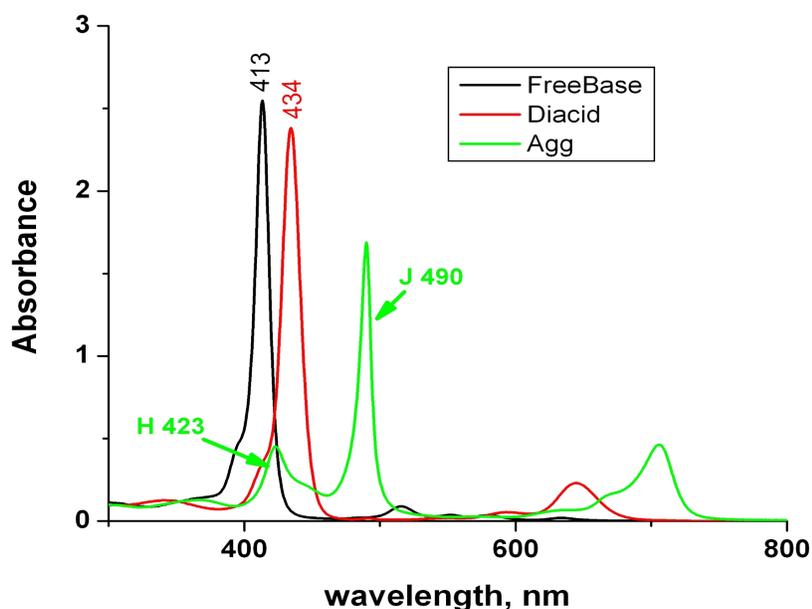


Figure 3.

Figure 4 compares solution electronic absorption spectrum of 5 μM TSPP in 0.75M HCl (pH 0.125) at room temperature (black trace) and after heating to reflux and cooling to 24 C (red trace).

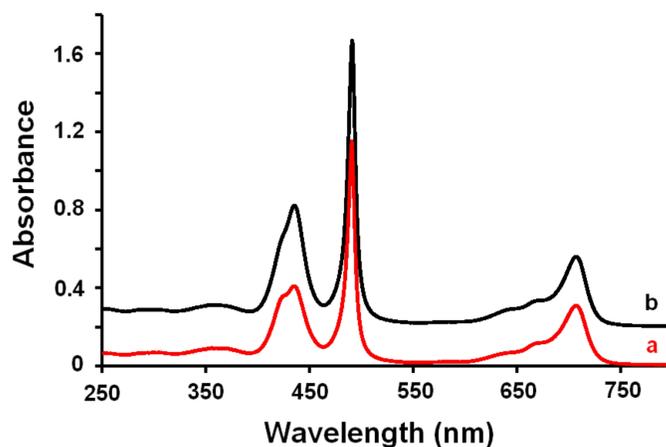


Figure 4.