

Controlling the Self-Assembly and Optoelectronic Properties of Porphyrin Nanostructures

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Porphyrins are highly conjugated macrocyclic organic compounds which, due to their rich photophysical properties, have found numerous applications in areas ranging from catalysis, to optoelectronics, to photodynamic cancer therapies.[1,2] To tune their described structural and electronic properties, self-organizing porphyrins into hierarchical structures is often desirable.[3] Here, utilizing simply electrostatic interactions via the acidification of tetra(*p*-carboxyphenyl)porphyrin (TCPP) using hydrochloric acid, we have created porphyrin nanostructures, whose structural and optical properties are found to be pH dependent. From combinations of UV-visible absorption spectroscopy and atomic force microscopy (AFM) we have observed that after the carboxylate groups of TCPP were protonated (at ca. pH 5), the porphyrins form J-aggregate nanoplatelets. These structures further evolve, and by lowering pH to ca. pH 2, nanotubes ranging from ca. 30 - 300 nm in diameter with aspect ratios of > 400:1 are formed, with the absorption spectrum of the porphyrin nanotubes showing a collapse of the Q bands, revealing that protonation of the central nitrogens on the porphyrin macrocycle has occurred. Both in solution and on surfaces, these structures can be formed and cycled between, simply by changing solution pH. The porphyrin nanotubes have been observed by cryo-TEM to exhibit a highly organized lattice, and elemental mapping, as well as X-ray photoelectron spectroscopy (XPS) shows that chloride is intercalated within the porphyrin nanotubes at low pH, but not in the mid-pH range platelet structures. Photoconductivity of the porphyrin nanofibers was measured by four point probe and two-terminal current voltage (I-V) measurements and show the material to be semi-conducting in nature. As in solution, the structures on the surface can be tuned from platelet to nanofiber structures, simply by local pH changes, and using capillary condensation around an AFM tip, we can pattern these structures spatially on the surface.

[1] N.V.S.D.K. Bhupathiraju, W. Rizvi, J.D. Batteas and C.M. Drain, *Organic and Biomolecular Chemistry*, **14** (2016) 389-408.

[2] M. Jurow, A.E. Schuckman, J.D. Batteas and C.M. Drain, *Coord. Chem. Rev.* **254** (2010) 2297-2310.

[3] C. Xu, A. Wan, X. Gong, N.V.S.D.K. Bhupathiraju, J.D. Batteas and C.M. Drain, *J. of Porphyrins and Phthalocyanines* **20** (2016) 439-443.

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