Self-organized Nanofibers and Nanorods of Porphyrins Bearing Hydrogen Bonding Motifs

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Scheme S1. 3-dimensional renderings of the $\alpha\alpha\alpha\beta$ atropisomers of the two compounds: TUrP (left, with hydrogen atoms omitted for clarity) and TPyrP (right), computed with ChemBio3D Ultra © CambridgeSoft. N=blue, O=red, C=grey, H=white.

I. Experimental

Instrumentation and Reagents. Tetraphenylporphyrin, tetrahydrofuran (THF) and toluene were purchased from Sigma Aldrich. Solvents were distilled using standard procedures. 200 proof ethyl alcohol was from Pharmaco Products, Inc. Glass slides and cover slips were purchased from Fisher Scientific. Mica substrate was from SPI Supplies. A Cary 3-Bio UV-visible spectrophotometer, a Spex Tau-3 fluorescence spectrophotometer, and a Leica fluorescence microscope were used. The atomic force microscope used was a Veeco Multimode SPM. A home-built ozone cleaner was used.

Synthesis of compounds. The porphyrins were prepared as previously described. ZnTUrP: Shi, X.; Barkigia, K. M.; Fajer, J.; Drain, C. M. J. Org. Chem., 2001, 66, 6513-6522; TUrP: by demetalation on the zinc complex, X. Shi, Ph.D. Thesis, City University of New York 2002; TPyrP: Knor, G. Inorg. Chem. Com., 2001, 4, 160-163.

Preparation of glass and mica substrates. The glass substrate was ozone cleaned for 20 min in a home-made ozone cleaner, and then rinsed with water and 200 proof ethanol. The slides were finally dried with a nitrogen stream at RT. Mica and HOPG substrates were cleaved just prior to use without any further preparation. The concentrations of the porphyrin solutions in THF were calculated to be 10 μ M and 100 μ M from UV-visible absorption data (absorption values ~ 2.0 and 0.2) using a 1 mm glass cuvette and an approx. extinction coefficient of 2x10 ⁵ M⁻¹cm⁻¹ at the maximum Soret absorbance. The concentration of solutions of TPyrP in toluene were calculated to be 5 μ M and 20 μ M from UV-visible absorption data (absorption values ~ 2.0) using 1 cm and 1 mm glass cuvettes and an approx. extinction coefficient of 4.1 x10 ⁵ M⁻¹cm⁻¹ at the Soret band maximum. (Knor, G. *Inorg. Chem. Com.*, **2001**, *4*, 160-163.)

Preparation of AFM, UV-vis and fluorescence samples. A drop of solution was cast on the substrates and let dry overnight at RT in a closed glass cell culture dish. To slow the rate of evaporation of the solvent and give the porphyrins more time to self-organize on the substrate, a few drops of THF were placed in the closed dish next to the sample. The low boiling point of THF enables the samples to dry in ca. 3 minutes and 30 minutes, respectively. When completely dried, samples were rinsed with THF to remove amorphous aggregates at the edge of deposited area. After drying them again at RT in a cell culture dish, samples were ready for AFM measurements. The same samples were used for fluorescence microscopy studies. The same conditions for preparation of samples for UV-visible and fluorescent measurements were used for the glass slides. The same sample preparation was used for TPyrP in toluene, but the samples were not rinsed after deposition because of the weak interactions between these molecules and glass and mica surfaces. The same experimental conditions were used for the free base TUrP in THF as well as for TPP in toluene as control molecules. In the text we refer to "dry" THF as freshly distilled THF, and "wet" with approx. 5% of water. Because of the difficulties in obtaining accurate UV-visible spectra on mica, those on glass are shown (Bazzan, G.; Smith, W.; Francesconi, L.; Drain, C. M. Langmuir 2007. 24, 3244 - 3249.)



II. 5,10,15,20 - tetrakis(1-butyl-6-uracyl) porphyrinato zinc(II) (ZnTUrP)

Figure S1. **A.** Absorption spectra of a 100 μ M solution of ZnTUrP in THF in a 1.0 mm glass cuvette (blue); Soret band 424 nm, Q bands 555 nm, and 591 nm (expanded 10 times in pink). **B.** Deposition of a 100 μ M ZnTUrP solution in THF on ozone cleaned glass. The Soret band and Q bands are shifted ca. 5 nm and 3 nm, respectively.



Figure S2. A. Absorption spectra of 10 μ M solution ZnTUrP in THF in a 1.0 mm glass cuvette (blue); Soret band 424 nm, Q bands 555 nm and 591 nm (expanded 10 times in pink). **B.** Deposition of a 10 μ M ZnTUrP solution in THF on ozone cleaned glass. The Soret band is shifted by 5 nm (429 nm), while Q bands are hard to observe due to the low concentration.



Figure S3. A. Emission spectra of a 10 μ M solution ZnTUrP in THF, excited in the Soret band at 425 nm, exhibits characteristic bands at 600 nm and at 656 nm. A small broadening of the 656 nm band (shoulder at 636 nm) and the band at ca. 700 nm shows presence of < 10% of free base porphyrin. **B**. Front face emission spectra of ZnTUrP on a glass surface; bands at 600 nm and 658 nm correspond to the solution. The 636 nm free base peak is observed though the ZnTUrP is excited preferentially (ca. 2-fold); this shows some energy transfer to the < 10% free base in this sample because the emission band at 600 nm is diminished and the bands at 631 nm and 656 nm are enhanced. **C**. Fluorescence microscopy image of ZnTUrP fibers formed by drop casting on glass slide, 20 x. The slide was also scanned with AFM and showed formation of bundles of nanofibers (see AFM images below). Image C is taken six months after fiber formation and indicates that the structures are robust and remain fluorescent.

Dynamic Light Scattering

Dynamic Light Scattering (DLS) analysis of the solutions indicates the presence of rod-shaped species that are 400-800 nm in length in 100 μ M solutions in dry THF. In 10 μ M solutions, the rods are 150-250 nm in length. In 100 μ M wet THF solutions, DLS indicates the presence of 80-200 nm diameter aggregates, whereas 10 μ M solutions in wet THF particles are not observed.

AFM Studies

Representation of additional images of the morphology arising from drop casted ZnTUrP solution from "dry" THF on mica and glass surface, controlled via evaporation rate of the solvent. We also show the histograms of the distribution of sizes of nanofibers and nanorods and AFM images indicating how we measured the vertical distances for nanofibers and both vertical and horizontal sizes for nanorods. See figures S4 to S11.





Figure S4. A. Distribution of vertical distances for nanofibers deposited from a 100 μ M dry THF solution on mica substrates. **B.** Diagrams of the sorted values of heights of individual nanofibers ranging from 1.75 nm to 43 nm for a slow rate of evaporation, and 2.97 nm to 50.21 nm for fast evaporation rates. Slightly greater heights are observed for fast rate of evaporation. The minimum unit seems to be a single porphyrin for the fibers formed from slow evaporation and two porphyrin molecules for the faster rates of evaporation. **C.** AFM height image and **D.** distribution (nm) of the vertical distances for materials deposited from 100 μ M solutions of ZnTUrP on mica substrates, deposited from freshly distilled, dry THF with slow evaporation rates.



Figure S5. Images indicating that different surface energetic do not influence formation of very dense bundles of nanofibers from a 10 μ M ZnTUrP solution drop cast from dry THF on mica (left) and glass slides (right) with a faster rate of evaporation. The smallest heights in these figures correspond to one ZnTUrP unit of 2 nm (see Figure S6).





Figure S6. Distribution of vertical distances for nanofibers deposited from a 10 μ M solution on glass substrates with slower evaporation rate. The lower plots the sorted heights values of individual nanofibers ranging from 2.04 nm to 45.58 nm. Slightly greater heights are observed for fast rate of evaporation. No obvious subunit or minimal structure is observed.



Figure S7. Distribution of vertical distances for nanofibers deposited from a 10 μ M solution on mica substrates. Fibers are formed no matter of the evaporation rate. Inset plots the sorted values of the heights of individual nanofibers ranging from 1.8 nm to 24.1 nm for slow rates of evaporation, and 4.2 nm to 51.6 nm for faster evaporation rates. Slightly greater heights are observed for fast rate of evaporation. In this case the 1.8 nm height is consistent with a single porphyrin laying flat on the surface.



Figure S8. A 100 μ M ZnTUrP solution drop cast from dry THF on a glass substrate with a slow evaporation rate results in a few fibrous nanostructures and a preponderance of island. No fibers or rods are observed using faster evaporation rates.



Figure S9. Vertical and horizontal distance of a nanorod formed from a 100 μ M ZnTUrP solution in dry THF cast on mica using a slow evaporation rate.



Figure S10. Distribution of vertical distances for nanorods deposited out of a 10 μ M THF solution on mica. The lower plot shows the sorted values of heights of individual nanorods ranging from 6.0 nm to 25.4 nm for slow rates of evaporation.





Figure S11. Distribution of horizontal distances for nanorods deposited out of 10 μ M THF solutions on mica using a slow rate of evaporation. The lower plot shows the sorted values of length of individual nanorods ranging from 215 nm to 629 nm.

III. Free base 5,10,15,20-tetrakis(1-butyl-6-uracyl)porphyrin (TUrP)



Figure S12. A. Absorption spectra of a 100 μ M solution of free base TUrP in THF in a 1.0 mm glass cuvette (orange); Soret band 417 nm, Q bands 509 nm, 543 nm, 585 nm and 648 nm (expanded 10 times in blue). **B**. Deposition of a 100 μ M TUrP solution in THF on ozone cleaned glass. The Soret band is shifted by 4 nm to 421 nm, the 509 nm band is red shifted to 515 nm, and the remaining Q bands are hard to observe due to the low concentration.



Figure S13. A. Absorption spectra of a 10 μ M solution of free base TUrP in THF in a 1.0 mm glass cuvette (orange); Soret band 417 nm, Q bands 509 nm, 543 nm, 585 nm and 648 nm (expanded 10 times in blue). **B.** Deposition of 10 μ M TUrP solution in THF on ozone cleaned glass. The Soret band is shifted by 3 nm to 420 nm, the 509 nm band is shifted to the red to 515 nm, and the remaining Q bands are hard to observe due to the low concentration.



Figure S14. A. Front face emission spectra of a THF solution of TUrP excited in the Soret band 417 nm exhibits bands at 650 and 714 nm; the presence of < 10% ZnTUrP is indicated by the weak band at 600 nm and a shoulder at 658. **B.** Emission spectra of free base TUrP cast on an ozone cleaned glass substrate shows peaks that correspond to the solution phase. Blank sample of glass substrate (blue), 10 µM solution on glass (pink) and 100 µM solution on glass (green).



Figure S15. top: Phase image (2.75 μ m x 2.75 μ m) of free base TUrP deposited on mica surface from a 10 μ M solution in THF with slow evaporation rate yield some fibers that are ca. 5 nm high, and **bottom:** thin films of no more that 2 nm in height.



Figure S16. **Top**: A nanorod from a 10 μ M solution of free bas TUrP has a horizontal distance of 620 nm and a height of 37 nm; **bottom:** on glass surfaces only aggregates and flat islands form.

IV. 5,10,15,20-tetrakis(1-pyrenyl)porphyrin (TPyrP)

TPyrP precipitates out of solutions of $> 20 \mu$ M.



Figure S17. A. UV-visible spectra of 20 μ M TPyrP toluene solution in 1 mm cuvette (blue); the Soret band is at 435 nm and Q bands are at 520 nm, 554 nm, 593 nm, 651 nm (represented in pink and expanded 10 x); **B.** TPyrP drop cast on glass substrate; the Soret band red shifts by 20 nm to 450 nm, and Q bands are at 529 nm, 562 nm, 597 nm, 655 nm.



Figure S18. **A.** Emission spectra of TPyrP in toluene solution excited at 336 nm where the pyrene moieties absorb ca. 23-fold more than the porphyrin shows energy transfer from the four antenna pyrene moieties to the porphyrin core, and the emission is observed at 660 nm and 724 nm (blue). The "peak" at 672 nm is scattering of the excitation light (2x336 nm). When excited in the 435 nm porphyrin Soret band only the porphyrin emission bands are observed at 660 nm and 724 nm (pink). **B.** Comparison of absorption spectra of TPP and TPyrP shows ca. 23 times greater absorption at the pyrene maximum absorption at 336 nm versus TPP.



Figure S19. Emission spectra of a TPyrP drop cast from a toluene solution on glass substrate excited at 520 nm exhibits peaks that correspond to the porphyrin emission in solution.

DLS and AFM studies on mica, glass and HOPG surface

DLS: For solution $<20~\mu\text{M},$ no observable aggregates in solution are observed for TPyrP in toluene.

AFM: We observed formation of particles on mica substrates but no film formation. On glass surface both films and particles of various sizes are observed, see below.



Figure S20. Small particles formed from 20 μ M solution of TPyrP in toluene deposited on a mica substrate. The particles have heights of < 5nm.



Figure S21. **A.** TPyrP cast from a 5 μ M toluene solution on a glass substrate forms μ m islands under normal solvent evaporation rates. Vertical distances range from 11.23 nm to 18.33 nm. **B.** A 5 μ M solution of TPP drop cast under same conditions forms a few <10 nm particles.



Figure S22. A 5 μ M solution of TPyrP in toluene drop cast on an ozone cleaned glass substrate and evaporated slowly forms thin films of 4.8 nm to 8.8 nm thickness.

A. m Π B. 0.2 0.4 0.6 0.8 1.2 1.4 1.6

Figure S23. A. AFM image of 20 μ M TPyP in toluene drop cast on glass from dry toluene with fast evaporation rates (left); the particles size range from 35 nm to 178 nm in height (right). **B.** AFM image of 20 μ M TPyP drop cast solution on cleaned glass from dry toluene with fast evaporation rate (left). Histograms show that the particles sizes range from 293 nm to 703 nm in the horizontal direction.



Figure S24. A. AFM of a 20 μ M TPyrP drop cast on glass from dry toluene with slower evaporation rate leads to formation of larger domains. The domain sizes range from 42.7 nm to 185 nm in height and 437 nm to ca. 1180 nm in the horizontal direction. **B**. AFM of a TPP 20 μ M solution drop cast under same conditions does not organize on glass substrates, thus indicating the significance of pyrene π - π interactions in nanostructured aggregate formation.





Figure S25. Top: AFM measured distribution of vertical distances for TPyrP nanoparticles deposited from a 20 μ M solutions on glass with fast and slow evaporation rates. Bottom: plot of the sorted heights values of particles ranging from 42.7 nm to 185 nm for slow and 35.3 nm to 177.6 nm for fast evaporation.



Figure S26. A. and B. AFM of the film-like structures resulting from a 20 μ M solution of TPyrP in toluene cast on HOPG (image size 5x5 μ m); left fast and right slow evaporation rates. **C.** Control TPP 20 μ M solution in toluene drop cast on HOPG with slow evaporation. TPP forms much less dense nanostructures compared to TPyrP on HOPG.



Figure S27. A. AFM of a 5 μ M solution of TPyrP in toluene cast on HOPG forms < 5 nm thick films (image size 1.5 x 1.5 μ m) and **B.** islands (image size 5x5 μ m) with fast and slow evaporation rate, respectively. **C.** TPP 5 μ M solution in toluene drop cast on HOPG with fast evaporation. Neither TPP nor TPyrP show significant organization on HOPG surfaces under these conditions.

Notes:

- TPyrP is a good control for the porphyrins with the uracyls in terms of: (a) examining the role of water, (b) both have atropisomers, (c) the equatorial pi-pi interactions are somewhat comparable, (d) the disposition of the bulky substitutents the atropisomers make a difference in that the majority of the molecules have both faces blocked by at least one meso substituent.
- (2) The observation that the free base TUrP forms rods and fibers indicates axial binding is not a priori necessary for formation of these structures. Axial coordination by the uracyl carbonyl opposite the tertiary amine into the zinc center is possible, but the increase electron density on the uracyl moieties upon binding zinc leading to somewhat stronger H-bonds may be a better explanation. This may be in analogy to what is observed for pyridylporphyrins [12].

V. Bibliography

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