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Supplementary Information

Spectroscopic Imaging Studies of Nanoscale Polarity and Mass Transport Phenomena in Self-Assembled Organic Nanotubes

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Additional details on the measurements of the NR-OH pK_a are provided, along with representative nanotube video data.

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Determination of pK_a of NR-OH dye

A pH titration experiment was conducted to determine the pK_a of the phenolic proton on the NR-OH dye. The pK_a of the protonated amine groups on the nanotube inner surface was previously reported to be 7.27 in aqueous solution.[1] To directly compare with this pK_a, the present titration was performed in water as well. During the titration, small aliquots of 0.2 wt% NaOH aqueous solution were added to the NR-OH dye solution continuously. The pH was measured using a pH meter after each addition of NaOH. The NR-OH absorption spectra were recorded on a UV-vis spectrometer during the titration.

As a solvatochromic dye, the absorption peak of NR-OH shifts as the polarity of the environment changes. It has been reported earlier that the absorption peak of NR-OH shifted upon the addition of 9.9 mM tetrabutylammonium hydroxide (Bu_4NOH) in methanol.[2] The peak shift was assigned to the deprotanation of the phenolic OH group on NR-OH in the presence of base. Thus, in this experiment, we determined the pK_a of NR-OH by plotting the peak absorption wavelength as a function of pH. **Figure S1** shows the absorption peak shift upon the addition of base. The pK_a of the phenolic proton was determined to be 9.21 from these data. The relatively large pK_a of the phenolic proton on NR-OH suggests that it will not be deprotonated by interaction with the amine groups on the tube inner surface.

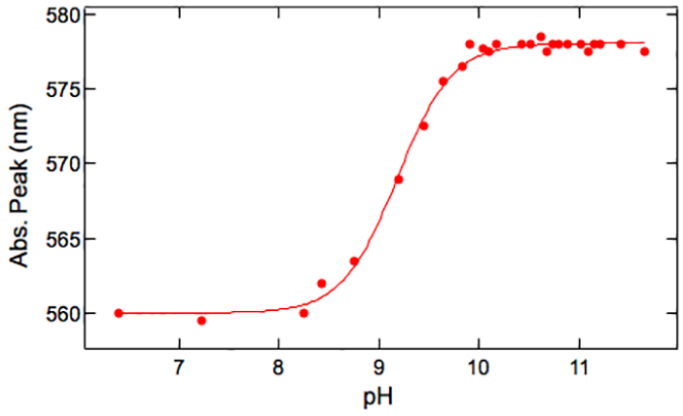

Figure S1 The NR-OH absorption peak shift as a function of solution pH.

Video S1. Fluorescence video (20000 frames, 149 frames/s) depicting imaging-FCS measurement on one nanotube. Clear photobleaching in the long time range can be observed in the video. The data shown in Figure 6 were derived from this video.

REFERENCES

(1) Kameta, N.; Minamikawa, H.; Masuda, M.; Mizuno, G.; Shimizu, T. Controllable Biomolecule Release from Self-assembled Organic Nanotubes with Asymmetric Surfaces: pH and Temperature Dependence. *Soft. Matter.* **2008**, *4*, 1681-1687.

(2) Nagy, K.; Göktürk, S.; Biczók, L. Effect of Microenvironment on the Fluorescence of 2-Hydroxy-Substituted Nile Red Dye: a New Fluorescent Probe for the Study of Micelles. *J. Phys. Chem. A* **2003**, *107*, 8784-8790.