Supporting information for

In situ Fabrication of Pyrene Derivative Nanorods inside Polyelectrolytes Microcapsules with Tunable Fluorescent Properties

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Experimental section:

Materials: PAH (Mn~56kDa), PSS (Mn~70kDa), Py-CHO, calcium nitrate tetrahydrate, sodium carbonate and EDTA were purchased from Aldrich. HCl solution (1mol/L) was purchased from Merck Company and diluted to the desired concentration. Other chemicals were used as received. The water used in all experiments was prepared *via* a Millipore Milli-Q purification system and had a resistivity higher than 18MΩ.cm.

Fabrication of PAH-Py-doped $CaCO_3$ microparticles: The PAH-doped $CaCO_3$ particles were fabricated according to literature.[1] Briefly, PAH was dissolved in 100 mL of 0.33 M calcium nitrate solution in a beaker under magnetic agitation (~600 rpm), into which an equal volume of 0.33 M sodium carbonate solution was rapidly poured at room temperature. The final PAH concentration was adjusted between 2 mg/mL. After 20 min, the PAH doped $CaCO_3$ particles were centrifuged and washed 3 times to remove the free PAH and salts. The as-prepared PAH-doped $CaCO_3$ microparticles were dispersed in ethanol and mixed with excess Py-CHO/ethanol solution. After the mixture was kept in a vessel under mild agitation for 2h, centrifugation and washing by ethanol were performed several times until the excess Py-CHO

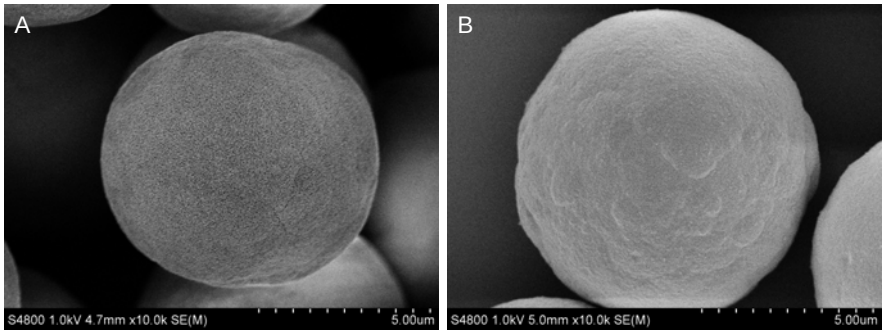
was washed away. The as-prepared PAH-Py-doped $CaCO_3$ microparticles were finally kept in ethanol.

Fabrication of PAH-Py/$(PSS/PAH)_n$ double-shells microcapsules: A suspension of the as-prepared PAH-Py-doped $CaCO_3$ microparticles (concentration ca. 5 wt %) were alternately incubated in the PSS and PAH solutions (1mg/mL, [NaCl] = 0.5M) for 10min, respectively. Three washings were applied after each adsorption to remove the excess polyelectrolytes. After adequate number of PSS/PAH bilayers were deposited, the microparticles were incubated in 0.2 M EDTA solution for 15min under shaking to obtain the PAH-Py/$(PSS/PAH)_n$ double-shells MCs. The MCs were further washed with fresh EDTA solution and water, each for 3 times using centrifugation (2000g, 3 min).

Fabrication of Py-CHO NRs in $(PSS/PAH)_n$ MCs: The as-prepared PAH-Py/$(PSS/PAH)_n$ MCs suspension (0.1mL, concentration ca. 10^8 microcapsules/mL) was incubated in 10mL 0.01 M HCl solution under shaking. After 1 h, the Py-CHO NRs were grown in the $(PSS/PAH)_n$ MCs which were separated by gentle centrifugation (2000g, 3 min) and washing with water for 3 times. The products were kept in water for further characterization.

Determination of the Py-CHO NRs amount in $(PSS/PAH)_n$ MCs: The $(PSS/PAH)_n$ MCs containing Py-CHO NRs (concentration ca. 10^8 microcapsules/mL) were ruptured by means of ultrasonication for 2 min and followed by centrifugation (5000g, 5 min) to remove the ruptured microcapsules. The released Py-CHO NRs in the filtrate were then measured by UV-visible (UV-vis) spectroscopy (Cary 4E) and calculated into Py-CHO NR amount percentage in the microcapsules.

Characterizations: Scanning electron microscopy (SEM) images were recorded with a Gemini Leo 1550 microscope at an acceleration voltage of 3kV. Transmission electron microscopy (TEM) images were obtained with a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV. Confocal laser scanning microscopy (CLSM) images were taken on a LEICA TCS system (Aristoplan, Germany, 100 × oil immersion using commercial software). The samples were dropped onto copper grids with a carbon film (for TEM), silicon wafers (for SEM), and glass slides (for CLSM), and air-dried in case needed, respectively. Steady-state fluorescence spectra were measured on a Fluoromax-4 spetrofluorometer (Horiba, Jobin Yvon).



PAH-Py-doped $CaCO_3$ PAH-Py-doped $CaCO_3$ covered with $(PSS/PAH)_n$

Figure S1. SEM images of PAH-Py-doped $CaCO_3$ microparticles before (A) and after LbL assembly of $(PSS/PAH)_{12}$ (B).

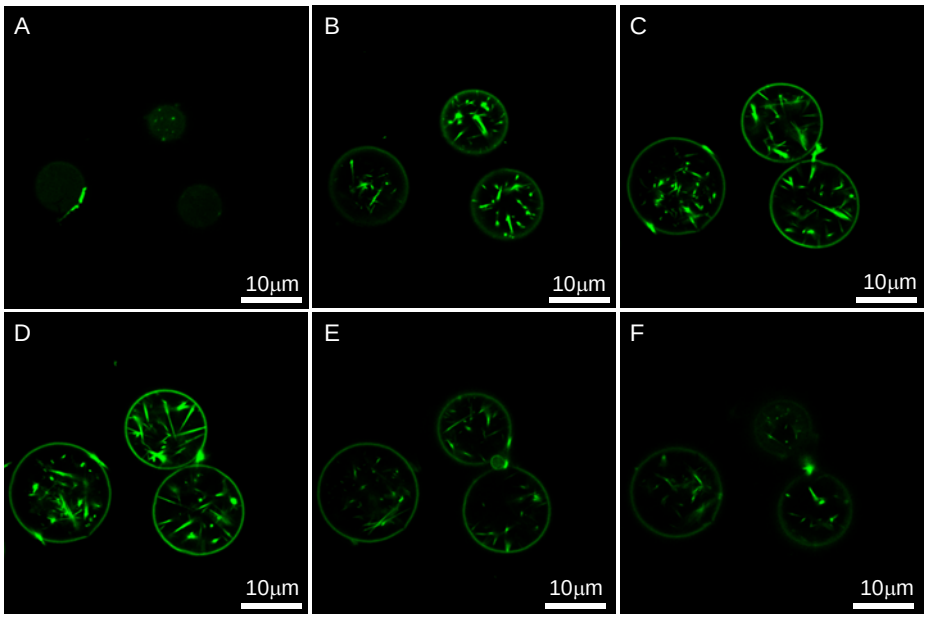


Figure S2. Z direction scanning CLSM images (A-F) of Py-CHO NRs in $(PSS/PAH)_{12}$ MCs after incubation of PAH-Py/$(PSS/PAH)_{12}$ double-shells MCs in pH 2 HCl solution for 1h.

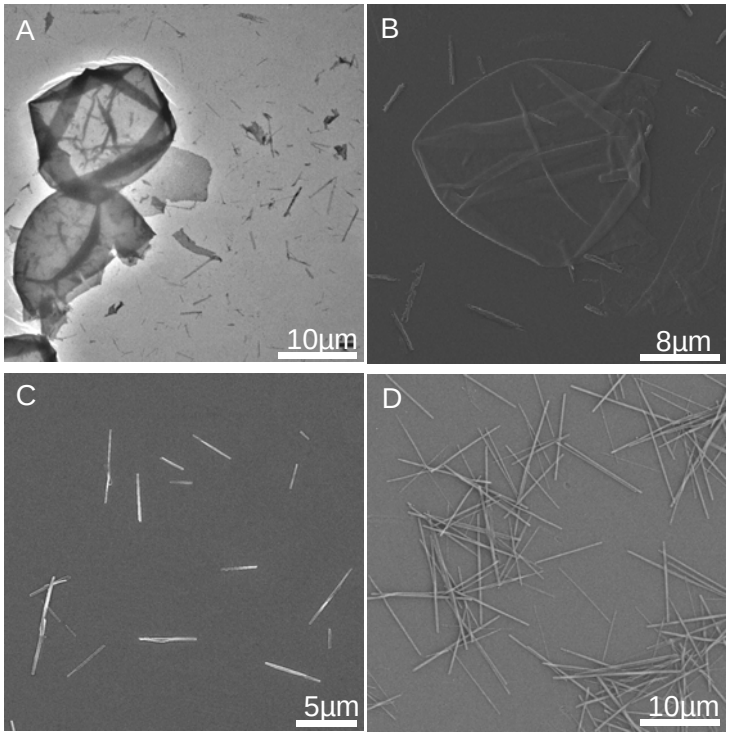


Figure S3. TEM (A) and SEM (B) images of Py-CHO NRs released from $(PSS/PAH)_{12}$ MCs after ultrasonication. (C) SEM image of Py-CHO NRs collected after ultrasonication. (D) SEM image of Py-CHO NRs formed in PAH-Py aqueous solution.

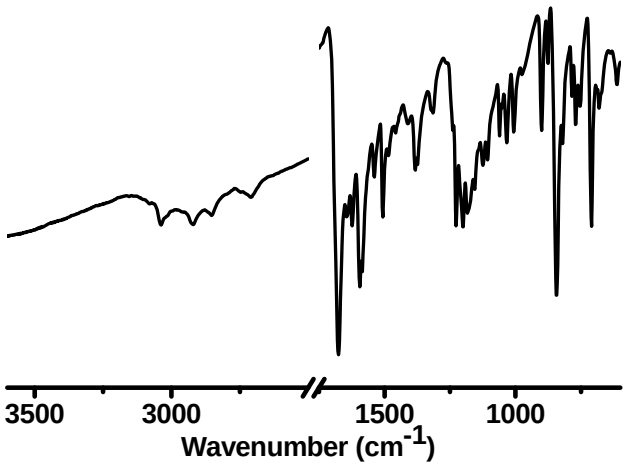


Figure S4. FTIR spectrum of Py-CHO NRs collected after ultrasonication.

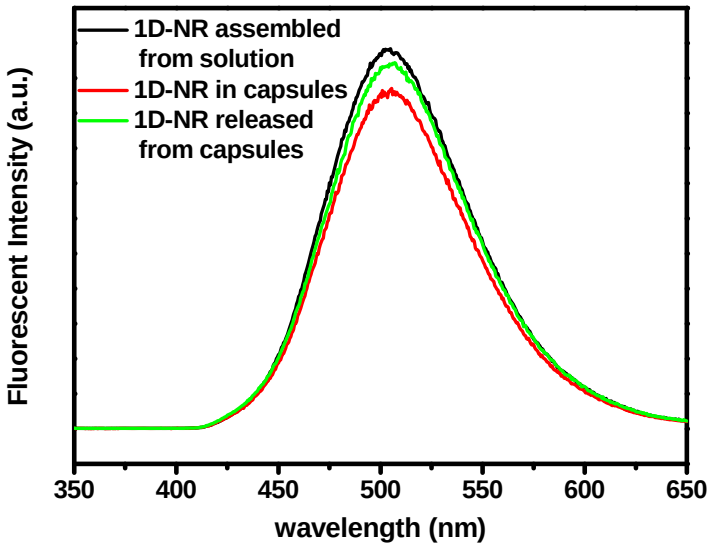


Figure S5. Fluorescent emission spectra of Py-CHO NRs assembled from solution, in $(PSS/PAH)_{12}$ MCs, and released from the MCs.

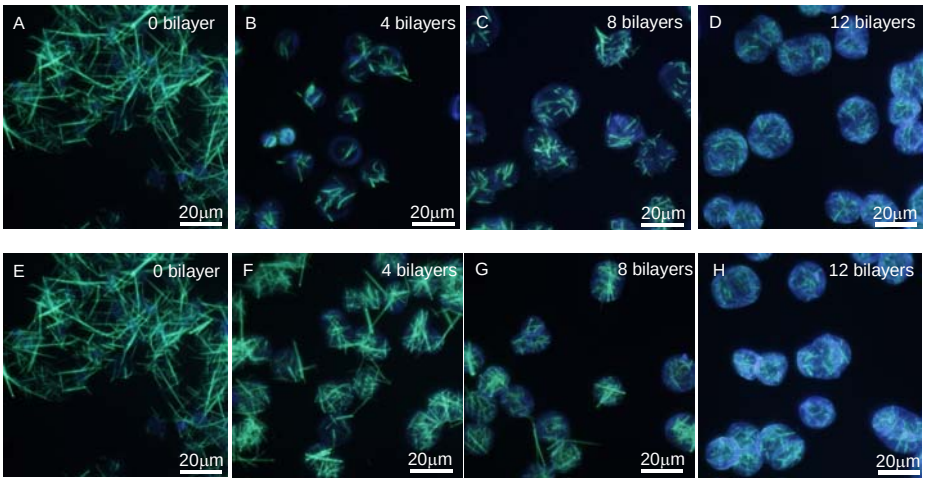


Figure S6. Fluorescent microscopy images of 1D-NRs formed in the PAH-Py/$(PSS/PAH)_n$ double-shells MCs with different bilayer numbers noted in the right-up corner of each image. (A)-(D) capsule size 10.2μm, and (E)-(H) capsule size 5.5μm.

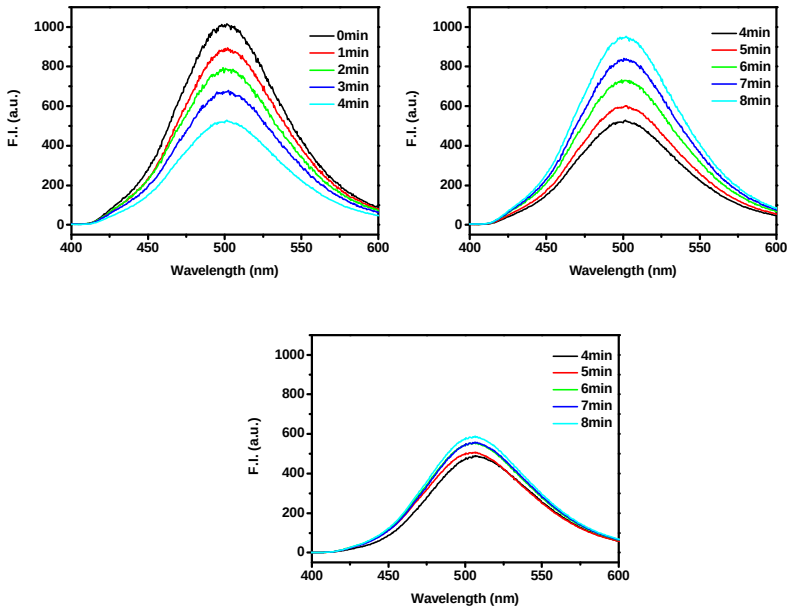


Figure S7. Fluorescent emission spectra of Py-CHO NRs inside the MCs mediated by stepwise addition of (A) MV, and then (B) PyTs or (C) water for rinsing.

Reference:

1. Z. P. Wang, H. Möhwald and C. Y. Gao, *Langmuir*, 2011, 27, 1286.