Supplementary Material (ESI) for *Soft Matter*

Robust, Fluorescent, and Nanoscale Freestanding Conjugated Films

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Supporting Information

1. Materials

Poly(allylamine hydrochloride) (PAH, MW = 65,000) was purchased from Aldrich and used as received. Water soluble conjugated polymer MPS-PPV (MW=175K; PDI = 2.56 as evaluated from GPC runs) was synthesized according to the suggested routine (see Figure 1 for chemical structure).[1] 5-Methoxy-2-[3-(chlorosulfonyl)propoxy]-1,4-xylene dibromide (Aldrich) 150 mg was dissolved in 4.5 ml DMF and 7.5 ml THF. The mixture was bubbled with Argon for 15 minutes. Then, 3 ml of t-BuOK THF solution (1M; Aldrich) was injected swiftly. The reaction mixture was stirred in dark for 16 hours under argon. The reaction was terminated by the addition of 45 ml Nanopure water (Nanopure system, resistivity 18 MΩ cm). The reaction mixture was further diluted to 180 ml and purified to remove low molar weight fraction and excessive DMF and THF by dialysis (MWCO 3,500) with Nanopure water.

2. AFM and Photoluminescence (PL) emission spectrum measurements

Film thickness on a silicon substrate was obtained with AFM scans along the film edge. The independent UV-visible spectra were obtained with a Shimadzu-1601 spectrometer. Photoluminescence spectra were taken on a LEICA DM 4000M microscope and attached CRAIC QDI202 microscopic spectrophotometer. The samples were excited at 365 nm and the emission spectra were collected within 400 - 1000 nm.

For measuring of the emission spectra in the rest state and after applying pressure, we combined the bulging setup with the fluorescence microscope so that it is possible to measure the in-situ fluorescence of LbL film under pressure. A hydrostatic pressure was applied to one side of an LbL film that covered a copper plate with 150 μm hole on the

LEICA DM 4000M microscope samples stage. Pressure pumps and pressure gauge were combined with the LEICA DM 4000M microscope to collect fluorescence spectra at different pressure applied to the LbL films. The insignificant effect of film tilt on the fluorescence spectra was confirmed by measuring the fluorescence spectra of LbL films under different tilting conditions.

3. Bulging and buckling measurements

The bulging test was conducted by applying a hydrostatic pressure to one side of an LbL film. The applied pressure was controlled with a motorized pump and the monitored by DPM-0.1 digital pressure module (SI Pressure Instruments Ltd. Birmingham UK) with an accuracy of ±2 Pa. The film deflection was measured using a custom-built interference optical set-up with a helium–neon laser (632.8nm). The elastic modulus of free-standing films was calculated as described earlier. The experimental data was fit with the equation for the elastic membrane deformation as tested in our earlier publications and at least 5 different specimens with same composition were tested. The buckling instability was observed for the film transferred to PDMS substrate after lateral compression. The buckling pattern formed under compressive stress was obtained with the LEICA DM 4000M microscope in either bright field mode or DIC mode.

References

[1] A. D. Smith, C. K. F. Shen, S. R. Roberts, R. Helgeson, B. J. Schwartz, http://www.chem.ucla.edu/dept/Faculty/schwartz/schwartz_complete_pubs.htm