

## Supporting Information

### Selective Water Uptake within Micelle-Containing Layer-by-Layer Films of Various Architectures: a Neutron Reflectometry Study

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**Table S1.** Model parameters for BPEI/PSS/[(BCM/PSS)<sub>4</sub>/BCM/dPSS]<sub>3</sub>/(BCM/PSS)<sub>4</sub> measured in a dry state.

| Layer                  | $Nb$ ( $\text{\AA}^{-2}$ ) | $d$ ( $\text{\AA}$ ) | $s$ ( $\text{\AA}$ ) |
|------------------------|----------------------------|----------------------|----------------------|
| (BPM/PSS) <sub>4</sub> | 1.10E-06                   | 145.0                | 145.0                |
| dPSS                   | 1.68E-06                   | 110.0                | 110.0                |
| (BPM/PSS) <sub>4</sub> | 1.18E-06                   | 165.0                | 110.0                |
| dPSS                   | 1.68E-06                   | 110.0                | 110.0                |
| (BPM/PSS) <sub>4</sub> | 1.18E-06                   | 165.0                | 110.0                |
| dPSS                   | 1.63E-06                   | 105.0                | 105.0                |
| (BPM/PSS) <sub>4</sub> | 1.02E-06                   | 109.0                | 105.0                |
| BPEI                   | 5.50E-08                   | 10.0                 | 2.0                  |
| SiO <sub>2</sub>       | 3.60E-06                   | 8.0                  | 8.0                  |
| Si                     | 2.07E-06                   | 100.0                | 2.0                  |

**Table S2.** Model parameters for BPEI/PSS/[(BCM/PSS)<sub>4</sub>/BCM/dPSS]<sub>3</sub>/(BCM/PSS)<sub>4</sub> film measured *in situ* in 0.01 M phosphate buffer solution at pH 6.0 and 25 °C.

| Layer                  | $Nb$ ( $\text{\AA}^{-2}$ ) | $d$ ( $\text{\AA}$ ) | $s$ ( $\text{\AA}$ ) |
|------------------------|----------------------------|----------------------|----------------------|
| Si                     | 2.07E-06                   | 100.0                | -                    |
| SiO <sub>2</sub>       | 3.40E-06                   | 4.0                  | 4.0                  |
| BPEI                   | 4.00E-07                   | 9.0                  | 9.0                  |
| (BPM/PSS) <sub>4</sub> | 2.60E-07                   | 169.0                | 9.0                  |
| BPM/dPSS               | 9.40E-07                   | 155.0                | 155.0                |
| (BPM/PSS) <sub>4</sub> | 4.00E-07                   | 200.0                | 155.0                |
| BPM/dPSS               | 9.40E-07                   | 162.0                | 162.0                |
| (BPM/PSS) <sub>4</sub> | 4.00E-07                   | 200.0                | 162.0                |
| BPM/dPSS               | 9.40E-07                   | 162.0                | 162.0                |
| (BPM/PSS) <sub>4</sub> | 2.30E-07                   | 185.0                | 162.0                |

**Table S3.** Model parameters for stacked BPEI/dPSS/(PDMA/dPSS)<sub>3</sub>/(BCM/dPSS)<sub>n</sub>/(PDMA/dPSS)<sub>3</sub> system with n = 1 system measured in a dry state.

| Layer                    | $Nb$ (Å <sup>-2</sup> ) | $d$ (Å) | $s$ (Å) |
|--------------------------|-------------------------|---------|---------|
| (dPSS/PDMA) <sub>3</sub> | 2.76E-06                | 82.0    | 78.0    |
| Micelles stack           | 2.52E-06                | 62.0    | 35.0    |
| (dPSS/PDMA) <sub>3</sub> | 2.80E-06                | 64.0    | 9.0     |
| BPEI                     | 8.53E-07                | 11.0    | 7.0     |
| SiO <sub>2</sub>         | 3.20E-06                | 10.0    | 4.0     |
| Si                       | 2.07E-06                | 100.0   | 4.0     |

**Table S4.** Model parameters for stacked BPEI/dPSS/(PDMA/dPSS)<sub>3</sub>/(BCM/dPSS)<sub>n</sub>/(PDMA/dPSS)<sub>3</sub> system with n = 1 film *in situ* in 0.01 M phosphate buffer solution at pH 6.0 and 25 °C.

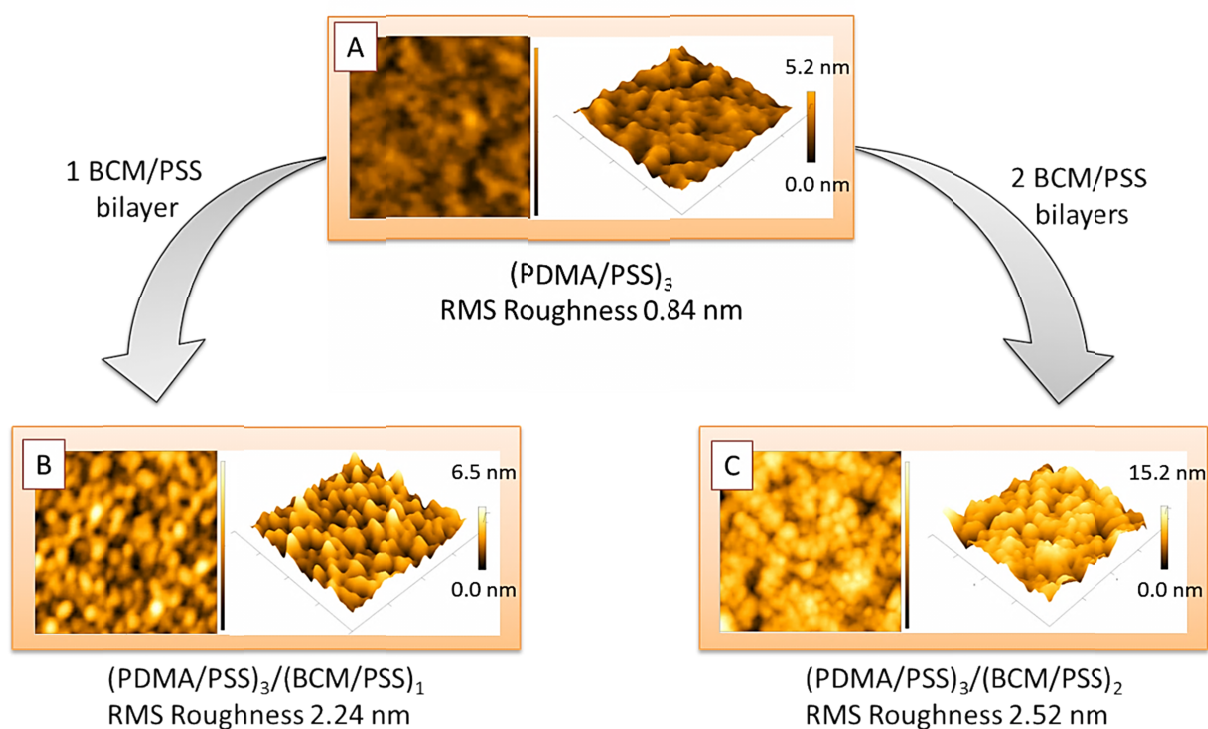
| Layer                    | $Nb$ (Å <sup>-2</sup> ) | $d$ (Å) | $s$ (Å) |
|--------------------------|-------------------------|---------|---------|
| Si                       | 2.07E-06                | 100.0   | -       |
| SiO <sub>2</sub>         | 3.20E-06                | 10.0    | 10.0    |
| BPEI                     | 5.53E-07                | 11.0    | 5.0     |
| (dPSS/PDMA) <sub>3</sub> | 2.45E-06                | 73.0    | 11.0    |
| Micelles stack           | 1.73E-06                | 84.0    | 45.0    |
| (dPSS/PDMA) <sub>3</sub> | 1.60E-06                | 117.0   | 82.0    |

**Table S5.** Model parameters for stacked BPEI/dPSS/(PDMA/dPSS)<sub>3</sub>/(BCM/dPSS)<sub>n</sub>/(PDMA/dPSS)<sub>3</sub> system with n = 2 system measured in a dry state.

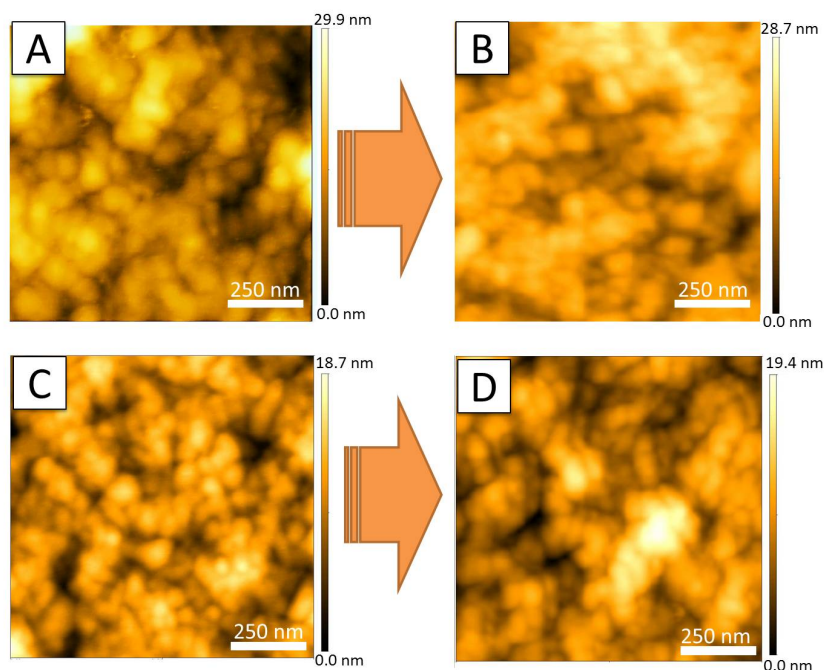
| Layer                    | $Nb$ (Å <sup>-2</sup> ) | $d$ (Å) | $s$ (Å) |
|--------------------------|-------------------------|---------|---------|
| (dPSS/PDMA) <sub>3</sub> | 2.16E-06                | 122.0   | 96.0    |
| Micelles stack           | 2.16E-06                | 84.0    | 45.0    |
| (dPSS/PDMA) <sub>3</sub> | 2.27E-06                | 132.0   | 85.0    |
| BPEI                     | 8.51E-07                | 7.0     | 6.0     |
| SiO <sub>2</sub>         | 3.50E-06                | 13.5    | 3.0     |
| Si                       | 2.07E-06                | 100.0   | 2.0     |

**Table S6.** Model parameters for stacked BPEI/*d*PSS/(PDMA/*d*PSS)<sub>3</sub>/(BCM/*d*PSS)<sub>*n*</sub>/(PDMA/*d*PSS)<sub>3</sub> system with *n* = 2 system measured *in situ* in 0.01 M phosphate buffer solution at pH 6.0 and 25 °C.

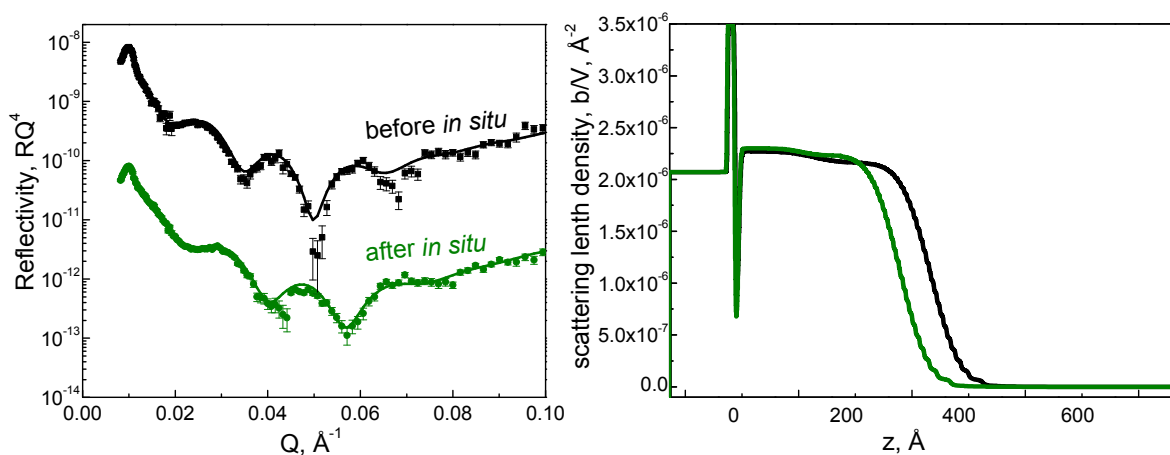
| Layer                             | <i>Nb</i> (Å <sup>-2</sup> ) | <i>d</i> (Å) | <i>s</i> (Å) |
|-----------------------------------|------------------------------|--------------|--------------|
| Si                                | 2.07E-06                     | 100.0        | -            |
| SiO <sub>2</sub>                  | 3.30E-06                     | 14.0         | 1.0          |
| BPEI                              | 5.53E-07                     | 7.0          | 5.0          |
| ( <i>d</i> PSS/PDMA) <sub>3</sub> | 1.45E-06                     | 140.0        | 10.0         |
| Micelles stack                    | 6.70E-07                     | 127.0        | 127.0        |
| ( <i>d</i> PSS/PDMA) <sub>3</sub> | 1.33E-06                     | 140.0        | 109.0        |



**Figure S1.** AFM images of a (PDMA/PSS)<sub>3</sub> film (A), and (PDMA/PSS)<sub>3</sub>/(BCM/PSS)<sub>*n*</sub> films with *n* = 1 (B) and *n* = 2 (C). For all images scanning area was 1×1 μm.



**Figure S2.** AFM images of dry  $(\text{PDMA}/\text{PSS})_{19}$  (A, B) and  $\text{BPEI}/\text{PSS}/(\text{PDMA}/\text{PSS})_3/(\text{BCM}/\text{PSS})_2/(\text{PDMA}/\text{PSS})_3$  (C, D) films before (A, C) and after (B, D) *in situ* measurements. For all images scanning area was  $1 \times 1 \mu\text{m}$ .



**Figure S3.** NR data (left) and SLD profiles (right) of the dry  $\text{BPEI}/d\text{PSS}/(\text{PDMA}/d\text{PSS})_3/(\text{BCM}/d\text{PSS})_n/(\text{PDMA}/d\text{PSS})_3$  film with  $n = 2$  before (black curve) and after (green curve) *in situ* study. The green reflectivity curve was offset two orders of magnitude for ease of visualization. Corresponding SLDs and thicknesses values are summarized in Tables S5 and S7.

**Table S7.** Model parameters for stacked BPEI/*d*PSS/(PDMA/*d*PSS)<sub>3</sub>/(BCM/*d*PSS)<sub>n</sub>/  
(PDMA/*d*PSS)<sub>3</sub> system with n = 2 system measured in a dry state after performing *in situ*  
measurement.

| Layer                             | $Nb$ ( $\text{\AA}^{-2}$ ) | $d$ ( $\text{\AA}$ ) | $s$ ( $\text{\AA}$ ) |
|-----------------------------------|----------------------------|----------------------|----------------------|
| ( <i>d</i> PSS/PDMA) <sub>3</sub> | 2.28E-06                   | 105.0                | 93.0                 |
| Micelles stack                    | 2.28E-06                   | 70.0                 | 55.0                 |
| ( <i>d</i> PSS/PDMA) <sub>3</sub> | 2.32E-06                   | 110.0                | 60.0                 |
| BPEI                              | 8.51E-07                   | 7.0                  | 6.0                  |
| SiO <sub>2</sub>                  | 3.50E-06                   | 13.5                 | 3.0                  |
| Si                                | 2.07E-06                   | 100.0                | 2.0                  |