

Supporting Information

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**Ion-Specific Oil Repellency of Polyelectrolyte Multilayers in Water:
Molecular Insights into the Hydrophilicity of Charged Surfaces****

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Supporting Information

1. Experimental Details

Materials.

PDDA (M_w 100 000-200 000), PSS (M_w 70 000), PAH (M_w 58 000), PAA (M_w 100 000), n-hexadecane, oil red O, and methylene blue were purchased from Sigma-Aldrich. NaCl, NaBr, KCl, HCl (37%), NaOH, acetone, isopropanol, ethanol, chloroform and cyclohexane were purchased from Chem-Supply, Australia. All the chemicals were used as received without purification. Stainless steel meshes with apertures of 25 μm were purchased from Sefar Pty Ltd, Australia. Si wafers were purchased from Si-Mat Silicon Materials, Germany. CaF_2 prisms were purchased from Altos Photonics (Bozeman, MT).

Growth of (PDDA/PSS)_n PEMs on different substrates via LbL deposition.

Silicon wafers were cleaned via immersion in Piranha solution (1:3 (v/v) mixture of 30% H_2O_2 and 98% H_2SO_4), followed by heating until no bubbles were released. *Note that Piranha solution reacts violently with organic materials and should be handled carefully.* Afterwards, the Si wafers were thoroughly rinsed with water and dried with N_2 flow. (PDDA/PSS)_n PEMs were grown on the freshly cleaned silicon wafers by alternating immersion of the wafers into the aqueous solutions of PDDA and PSS for 20 min. Each immersion step was followed by thorough rinsing with water. After the desired layer number was reached, the resulting PEMs were thoroughly rinsed by water and gently dried with N_2 flow. In the polyelectrolyte aqueous solutions used for LbL deposition, the concentrations of PDDA and PSS were 1.0 mg/mL and the concentration of NaCl was varied from 0.10, 0.50, 0.25, and 1.0 M NaCl.

After (PDDA/PSS)_{3,0} PEMs were obtained via LbL deposition in 1.0 M NaCl, they were immersed in the aqueous solution of PDDA (1.0 mg/mL) in the presence of 1.0 M NaBr or in the aqueous solution of PAH (1.0 mg/mL) in the presence of 1.0 M NaCl for 20 min, followed by thorough rinse with water and gentle drying with N_2 flow. The resulting PEMs were denoted as (PDDA/PSS)_{3,0}/PDDA(NaBr) and (PDDA/PSS)_{3,0}/PAH PEMs. Note that prior to electrostatic deposition, the pH of the aqueous solution of PAH in 1.0 NaCl were adjusted by 1.0 M HCl to 3.5 to ensure that the PAH chains in solutions were fully protonated (positively charged).

After (PDDA/PSS)_{3,5} PEMs were obtained via LbL deposition in 1.0 M NaCl, they were immersed in the aqueous solution of PSS (1.0 mg/mL) in the presence of 1.0 M KCl or in the aqueous solution of PAA (1.0 mg/mL) in the presence of 1.0 M NaCl for 20 min, followed by thorough rinse with water and gentle drying with N_2 flow. The resulting PEMs were denoted as (PDDA/PSS)_{3,5}/PSS(KCl) and (PDDA/PSS)_{3,5}/PAA PEMs. Note that prior to electrostatic deposition, the pH of the aqueous solution of PAA in 1.0 NaCl were adjusted by 1.0 M NaOH to 9.5 to ensure that the PAA chains in solutions were fully deprotonated (negatively charged).

Following the identical protocol, the (PDDA/PSS)_n PEMs were also grown on plasma cleaned CaF₂ prisms for sum frequency generation vibrational spectroscopy (SFG) measurement.

Stainless steel meshes were cleaned by successive sonication in acetone, isopropanol, ethanol and water. The cleaned stainless steel meshes were further cleaned by oxygen plasma to enhance the surface hydrophilicity. The freshly cleaned stainless steel meshes were coated by (PDDA/PSS)_n PEMs following the protocol described above.

Characterization.

Contact angle measurements were implemented on a Dataphysics OCA 20 contact angle system at ambient temperature using a 2 μ L liquid droplet as indicator. Colorimeter glass cells, purchased from Starna, were used for measurement of the $\theta_{o/w}$ and $\theta_{w/o}$ on solid surfaces. Atomic force microscopy (AFM) imaging was performed with a MultiMode 8 AFM from Bruker in a ScanAsyst mode at ambient condition using Si cantilevers. XPS analysis was carried out on a Kratos Axis Ultra with a Delay Line Detector photoelectron spectrometer using an Aluminium monochromatic X-ray source. Scanning electron microscopy (SEM) images were obtained on FEI Quanta 450 operated at 10-20 kV. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 300 MHz NMR Spectrometer. SFG measurement was conducted according to the method reported by Chen et al.^[1] Typically, the visible and infrared (IR) input beams penetrated a right angle CaF₂ prism and overlap spatially and temporally at the sample surfaces. The incident angles of the visible and IR beams are 60° and 54° with respect to the surface normal, and the pulse energies of the visible and IR beams are 30 and 100 μ J, respectively. The reflected SFG signal is collected by a monochromator along with a photomultiplier tube. All SFG spectra were collected using the ssp (SFG output, visible input, and IR input) polarization combination.

[1] Leng, C.; Han, X. F.; Shao, Q.; Zhu, Y. H.; Li, Y. T.; Jiang, S. Y.; Chen, Z. In Situ Probing of the Surface Hydration of Zwitterionic Polymer Brushes: Structural and Environmental Effects. *J. Phys. Chem. C* **2014**, *118*, 15840-15845.

2. Supplementary Schemes, Figures, and Tables.

Scheme S1. Schematic sketch of the molecular structures of PDDA, PSS, PAA, and PAH.

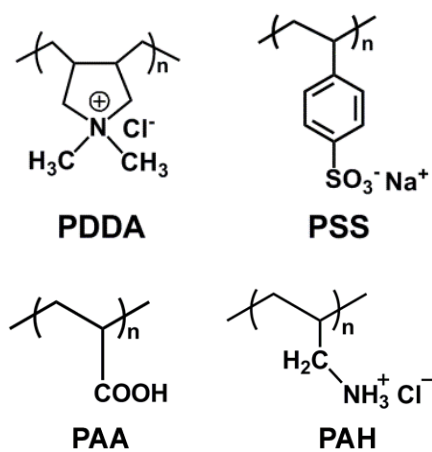


Figure S1. Atomic force microscopy (AFM) images of the (PDDA/PSS)_n PEMs, coated on silicon wafer via LbL deposition in the presence of 1.0 M NaCl. The PEM bilayer numbers (n) are 3.5 (a), 4.0 (b), 5.5 (c), 6.0 (d), 7.5 (e) and 8.0 (f).

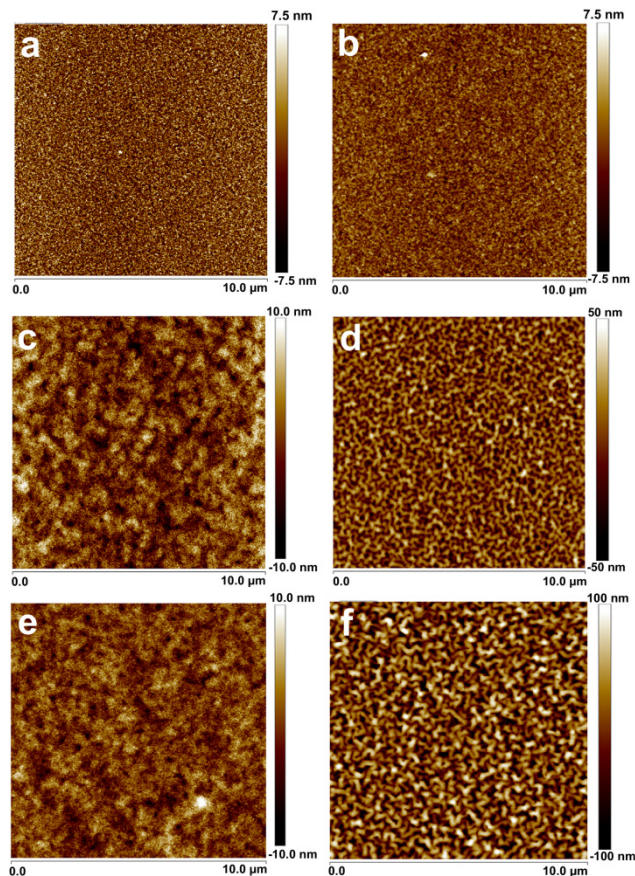


Figure S2. XPS wide scan spectra of (PDDA/PSS)_n PEMs with the bilayer number (n) varying from 3.5 (a) to 4.0 (b), 5.5 (c), 6.0 (d), 7.5 (e) and 8.0 (f). The PEMs are prepared via LbL deposition in the presence of 1.0 M NaCl. The insets are the corresponding high-resolution spectra for Cl and Na elements.

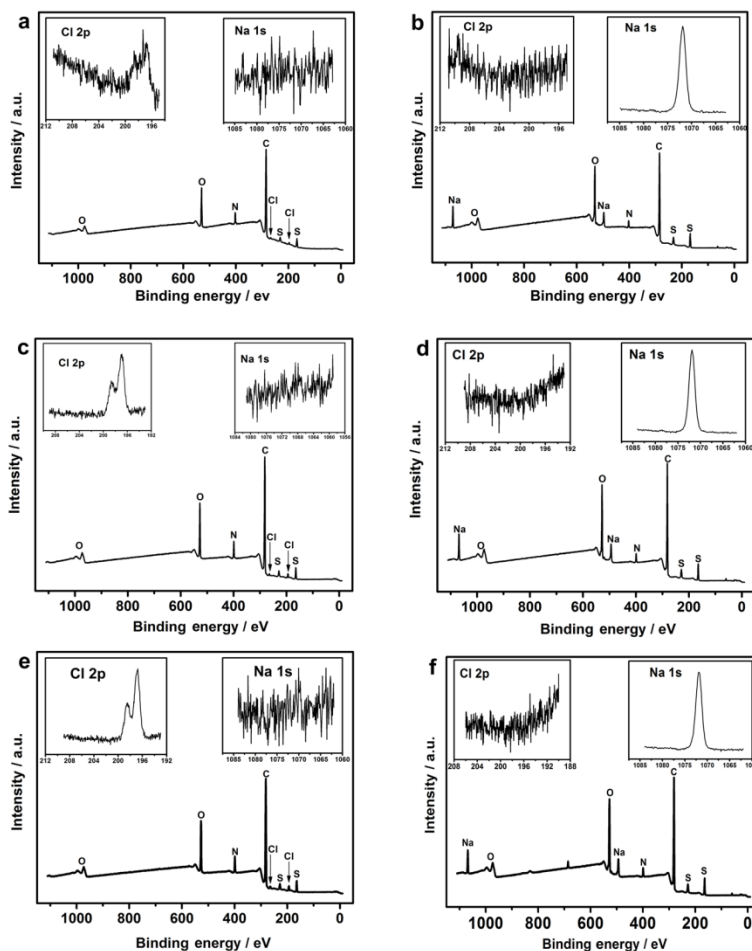


Table S1. Summary of the atomic concentrations of the different elements on the (PDDA/PSS)_n PEMs, obtained via LbL deposition in the presence of 1.0 M NaCl. The surface atomic concentrations are deduced from the XPS spectra of the corresponding PEMs, shown in Figure S2.

Bilayer No.	Capping layer	Na	S	Cl	N	O	C
3.5	PDDA	0	2.93	1.33	5.27	11.60	78.86
4.0	PSS	3.47	4.74	0	3.26	17.66	70.86
5.5	PDDA	0	2.84	1.74	5.52	12.04	77.86
6.0	PSS	3.66	4.60	0	3.06	17.85	70.83
7.5	PDDA	0	2.98	2.05	5.88	11.89	77.20
8.0	PSS	3.27	4.64	0	3.31	17.86	70.93

Figure S3. XPS wide scan spectra of the (PDDA/PSS)_n PEMs prepared via LbL deposition at NaCl concentrations of 0.50 M (a and b), 0.25 M (c and d) and 0.10 M (e and f). The PEM bilayer numbers (n) are 5.5 (a), 6.0 (b), 9.5 (c), 10.0 (d), 14.5 (e) and 15.0 (f). These PEMs show similar thickness and roughness to those of the (PDDA/PSS)_{3.5} and (PDDA/PSS)_{4.0} PEMs obtained in 1.0 NaCl. The insets are corresponding high-resolution spectra for Cl and Na elements.

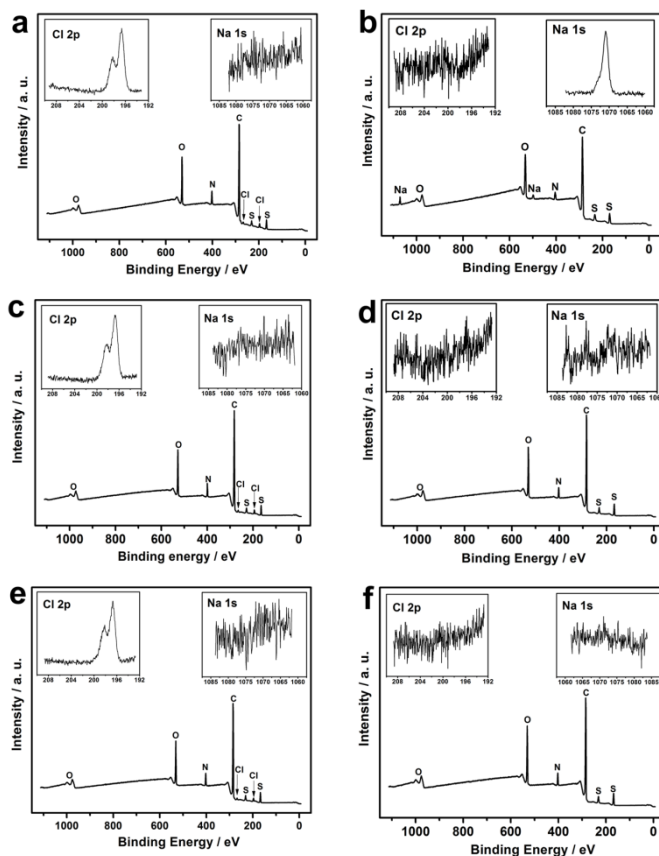


Table S2. Summary of the atomic concentrations of the different elements on the (PDDA/PSS)_n PEMs, obtained via LbL deposition in the presence of 0.50, 0.25 and 0.10 M NaCl. The surface atomic concentrations are deduced from the XPS spectra of the corresponding PEMs, shown in Figure S3.

NaCl Concentration	Bilayer No.	Capping Layer	Na	S	Cl	N	O	C
0.50 M	5.5	PDDA	0	3.05	1.93	5.24	12.65	77.13
	6.0	PSS	1.15	4.08	0	4.14	15.04	75.58
0.25 M	9.5	PDDA	0	2.90	2.08	5.2	12.03	77.79
	10.0	PSS	0	3.72	0	4.41	14.22	77.65
0.10 M	14.5	PDDA	0	3.12	1.83	5.22	12.80	77.03
	15.0	PSS	0	3.77	0	4.66	14.54	77.03

Figure S4. A series of photos taken when the silicon wafers, coated with the (PDDA/PSS)_{3,5} (a) and (PDDA/PSS)₄ (b) PEMs via LbL deposition in 1.0 M NaCl, are approaching (a₁, a₂, b₁, b₂) and leaving (a₃, a₄, b₄, b₅) a droplet of n-hexadecane (2 μL) pending on a needle in water. The photo in Figure a₅ is taken 30 min after the photo in Figure a₄. The photo in Figure b₃ is taken 12 h after the photo in Figure b₂. The arrows indicate the direction of the silicon wafer movement.

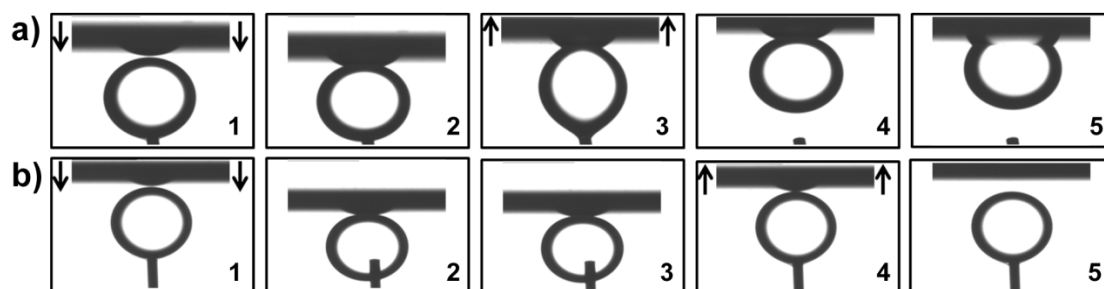


Figure S5. Temporal evolution profiles of the $\theta_{o/w}$ values of the (PDDA/PSS)_n PEMs obtained via LbL deposition in 0.25 M (a) and 0.1 M (b) NaCl. The bilayer numbers are marked in the legends.

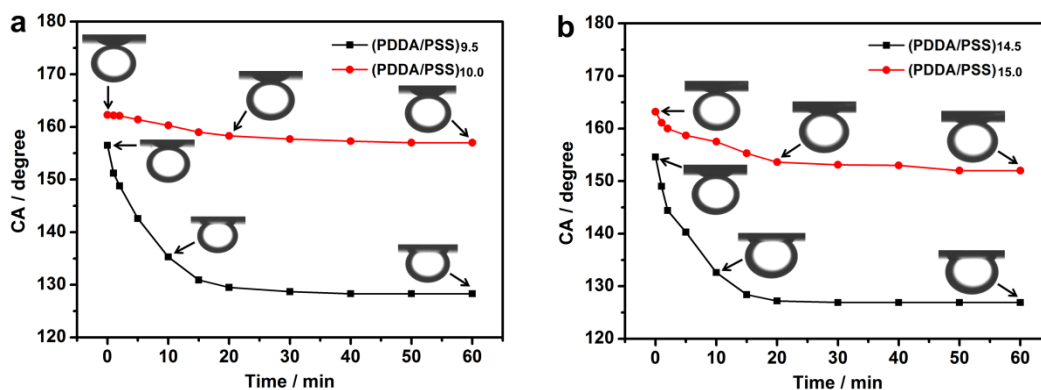


Figure S6. XPS wide scan spectra of the (PDDA/PSS)_n PEMs capped with the outmost layers of PDDA (a), PSS (b), PAH (c), and PAA (d). (PDDA/PSS)_{3.0} PEMs, obtained via LbL deposition in 1.0 M NaCl, are used as primer layers for deposition of the PDDA capping layers in 1.0 M NaBr and the PAH capping layers in 1.0 M NaCl at pH 3.5. The resulting PEMs are denoted as (PDDA/PSS)_{3.0}/PDDA(NaBr) and (PDDA/PSS)_{3.0}/PAH. (PDDA/PSS)_{3.5} PEMs, obtained via LbL deposition in 1.0 M NaCl, are used as primer layers for deposition of the PSS capping layers in 1.0 M KCl and the PAA capping layers in 1.0 M NaCl at pH 9.5. The resulting PEMs are denoted as (PDDA/PSS)_{3.5}/PSS(KCl) and (PDDA/PSS)_{3.5}/PAA PEMs. The insets present the signals of Br 3d, Cl 2p, K 2p, and Na 1s observed in the corresponding XPS spectra.

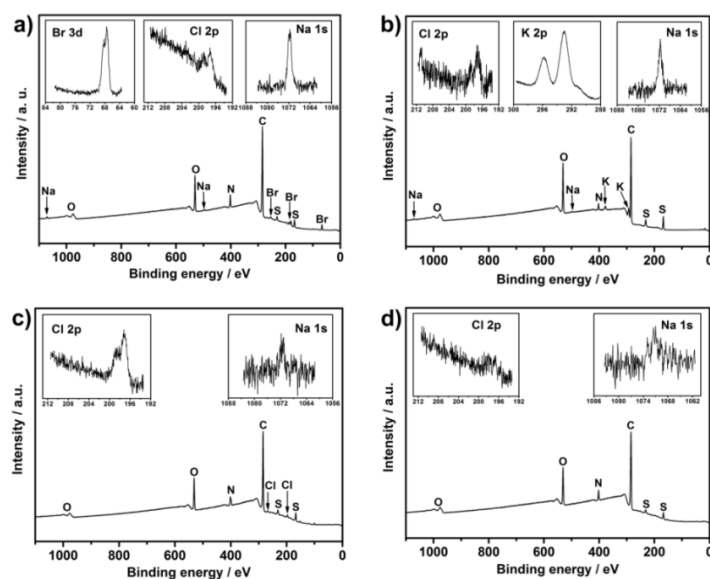


Table S3. Summary of the atomic concentrations of the different elements on the (PDDA/PSS)_{3.0}/PDDA(NaBr), (PDDA/PSS)_{3.5}/PSS(KCl) and (PDDA/PSS)_{3.0}/PAH, (PDDA/PSS)_{3.5}/PAA PEMs. The surface atomic concentrations are deduced from the XPS spectra of the corresponding PEMs, shown in Figure S6

Bilayer No.	Capping layer (Salt)	Na	K	S	Cl	Br	N	O	C
3.5	PDDA (1.0 M NaBr)	0.23	N/A	2.59	0.14	1.46	5.56	10.71	79.29
4.0	PSS (1.0 M KCl)	0.15	1.66	5.14	0	N/A	3.52	16.27	73.51
3.5	PAH (1.0 M NaCl)	0	N/A	3.37	0.74	N/A	7.18	11.35	77.36
4.0	PAA (1.0 M NaCl)	0	N/A	2.53	0	N/A	4.75	12.99	79.74

N/A = Not applicable

Figure S7. Summaries of the $\theta_{w/a}$ (a), $\theta_{w/o}$ (b), and $\theta_{o/w}$ (c) values of the resulting (PDDA/PSS)_{3.5}, (PDDA/PSS)_{4.0}, (PDDA/PSS)_{3.0}/PDDA(NaBr), (PDDA/PSS)_{3.5}/PSS(KCl), (PDDA/PSS)_{3.0}/PAH, and (PDDA/PSS)_{3.5}/PAA PEMs to assess the impact of the type of the counterions and the molecular nature of the capping layers on the surface wetting behavior of the resulting PEMs. The (PDDA/PSS)_{3.5} and (PDDA/PSS)_{4.0} PEMs are obtained via LbL deposition in 1.0 M NaCl. The (PDDA/PSS)_{3.0}/PDDA(NaBr), (PDDA/PSS)_{3.0}/PAH, (PDDA/PSS)_{3.5}/PSS(KCl), and (PDDA/PSS)_{3.5}/PAA are obtained as described in Figure S6. The bilayer numbers of the (PDDA/PSS)_{3.5}, (PDDA/PSS)_{3.0}/PDDA(NaBr), and (PDDA/PSS)_{3.0}/PAH PEMs are 3.5 and their surfaces are positively charged. The bilayer number of the (PDDA/PSS)_{4.0}, (PDDA/PSS)_{3.5}/PSS(KCl), and (PDDA/PSS)_{3.5}/PAA PEMs are 4.0 and their surfaces are negatively charged.

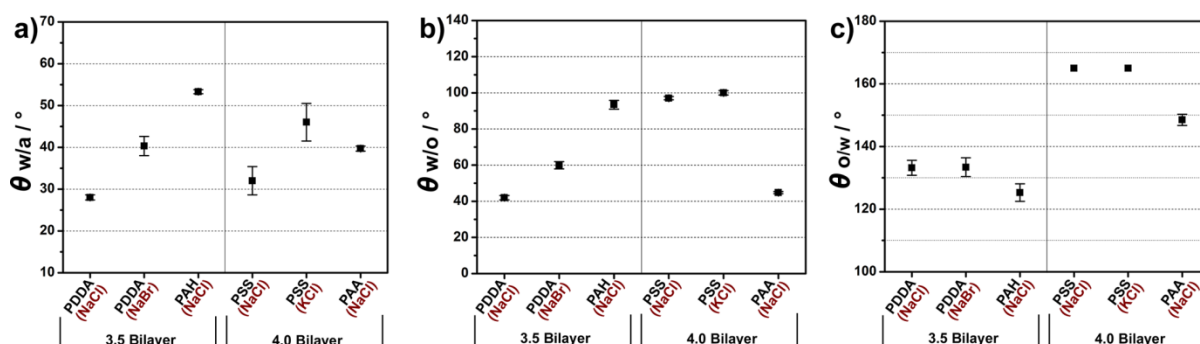


Figure S8. A series of photos taken when a silicon wafer, coated with the (PDDA/PSS)₄ (b) PEMs via LbL deposition in 1.0 M NaCl, is approaching (1, 2) and leaving (4, 5) a droplet of n-hexadecane (2 μL) pending on a needle in water. The PEMs are aged at 60°C for 72 h in air. The photo in Figure 3 is taken 12 h after the photo in Figure 2. The arrows indicate the direction of the sample movement. This figure reveals that the aged (PDDA/PSS)₄ PEM surfaces retain excellent oil-repellence in water.



Figure S9. Temporal evolution profiles of the $\theta_{o/w}$ values of the (PDDA/PSS)_n PEMs, obtained via LbL in the presence of 1.0 M NaCl. The bilayer numbers of the PEMs are 5.5 (a, black curve), 6.0 (a, red curve), 7.5 (b, black curve), and 8.0 (b, red curve).

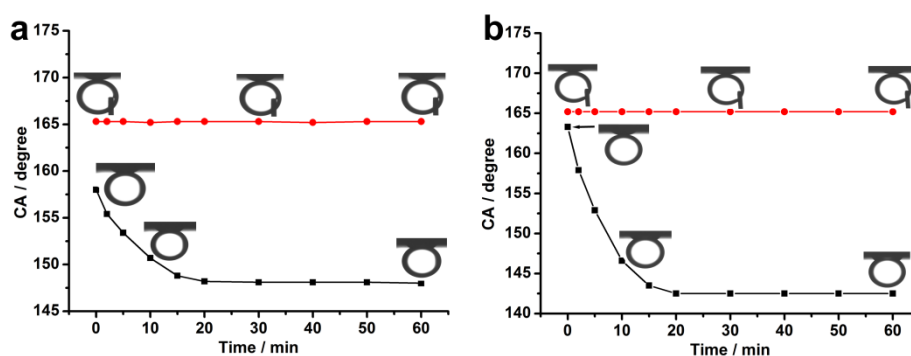


Figure S10. NMR spectra of pure chloroform (a), pure cyclohexane (b), and the extracting solution after using chloroform to extract the water phase, collected after filtration of a water/cyclohexane mixture through a (PDDA/PSS)₄-coated stainless steel mesh with aperture of 25 μm.

To assess the oil/water separation efficiency of (PDDA/PSS)₄-coated stainless steel meshes, cyclohexane was utilized as the oil phase because it has only one characteristic peak in the NMR spectrum, which can be easily identified. After a mixture of 200 mL of water and 200 mL of cyclohexane was filtrated through a (PDDA/PSS)₄-coated steel mesh with aperture of 25 μm, the water phase was mixed with 50 mL chloroform under vigorous stirring in order to extract the cyclohexane possibly left over in the water phase after oil/water separation. The resulting chloroform extracting solution was analyzed by NMR spectroscopy. Figure c is the NMR spectra of the chloroform extracting solutions, in which cyclohexane single is hardly detected, thus underlining the complete separation of water from cyclohexane.

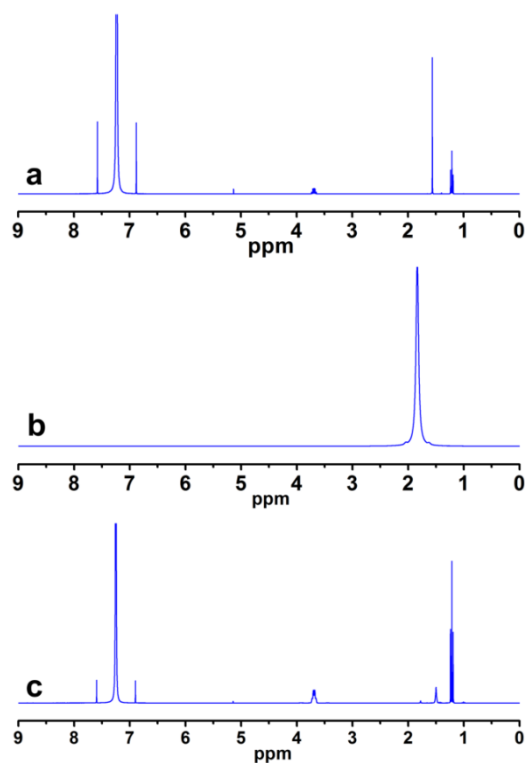
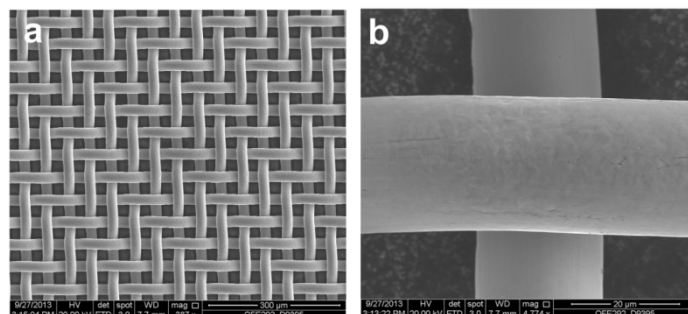


Figure S11. Low (a) and high (b) magnification SEM images of the stainless steel mesh with aperture of 25 μm , coated with (PDDA/PSS)₄ PEMs via LbL deposition in 1.0 M NaCl.



3. Supplementary movies.

- Movie S1.** Video recorded when a silicon wafer, coated with (PDDA/PSS)_{3.5} PEMs via LbL deposition in 1.0 M NaCl, is brought to approach and leave a droplet of hexadecane (2 μL) pending on a needle in water.
- Movie S2.** Video recorded when a silicon wafer, coated with (PDDA/PSS)_{4.0} PEMs via LbL deposition in 1.0 M NaCl, is brought to approach and leave a droplet of hexadecane (2 μL) pending on a needle in water.
- Movie S3.** Video of oil-water separation through a stainless steel mesh with aperture of 25 μm , coated by (PDDA/PSS)_{4.0} PEMs via LbL deposition in 1.0 M NaCl. The mixture of hexadecane, stained with Oil Red O, and water, stained with methylene blue, was poured on the (PDDA/PSS)_{4.0}-coated mesh fixed in a filtration apparatus. The volume ratio of water to hexadecane in the mixture was 1:1. It is visible that water selectively passes through the mesh whereas hexadecane is retained on top of the mesh.