Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

for

Solvent-Dependent Properties of Poly(vinylidene fluoride) Monolayers at the Air–Water Interface

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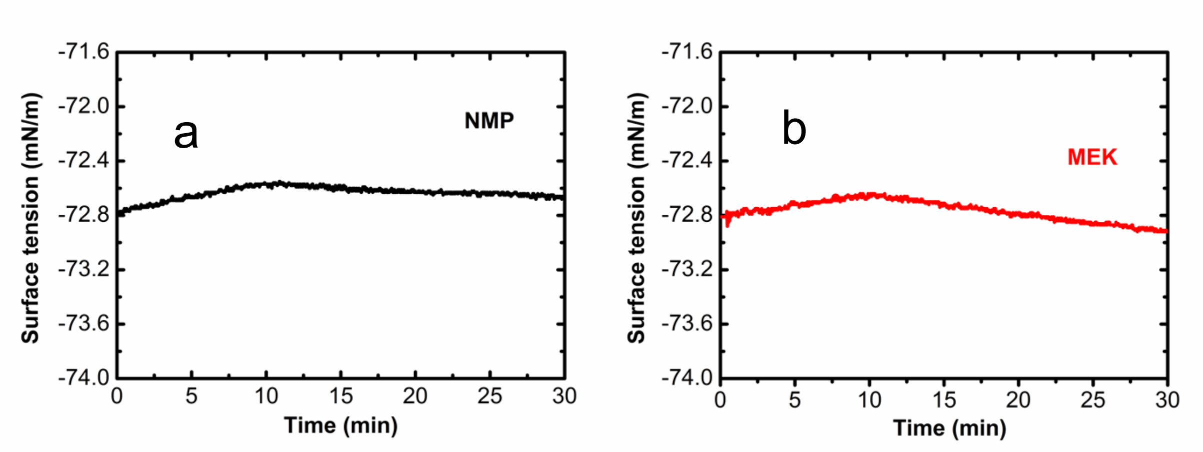

Figure S1. Water surface tension changes during the waiting time (30 minutes).

As shown in Figure S1, it is enough to remove the solvent from the water surface by waiting for 30 minutes under the air draft before compression, because the surface pressure after 30 minutes is almost identical to that of water.

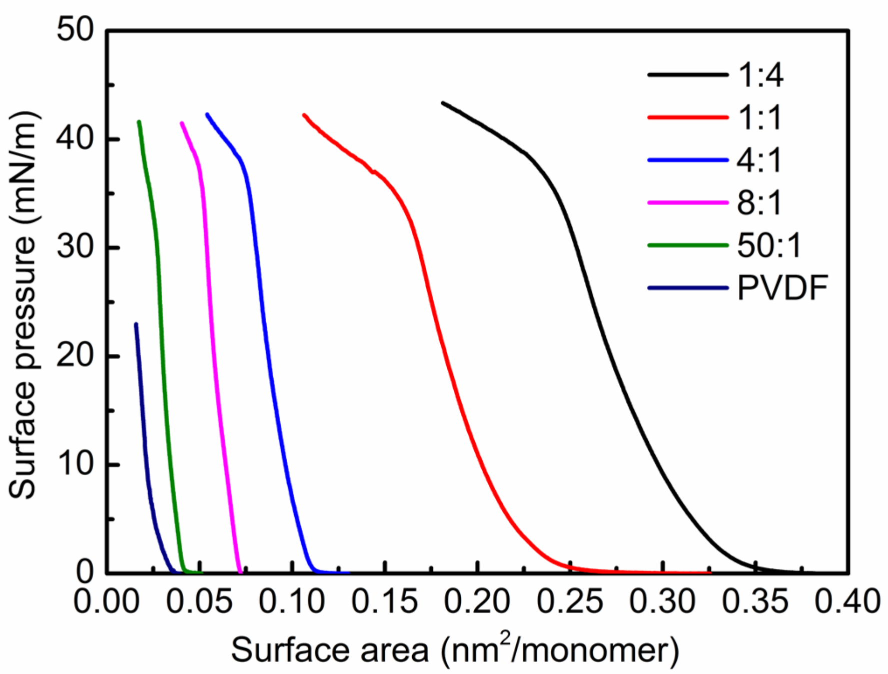

Figure S2. *π–A* isotherms of PVDF(DMF)/pDDA Langmuir films at different molar mixing ratios (PVDF:pDDA): 1:4 (black line), 1:1 (red line), 4:1 (blue line), 8:1 (pink line), 50:1 (green line) and pure PVDF(DMF) (navy line).

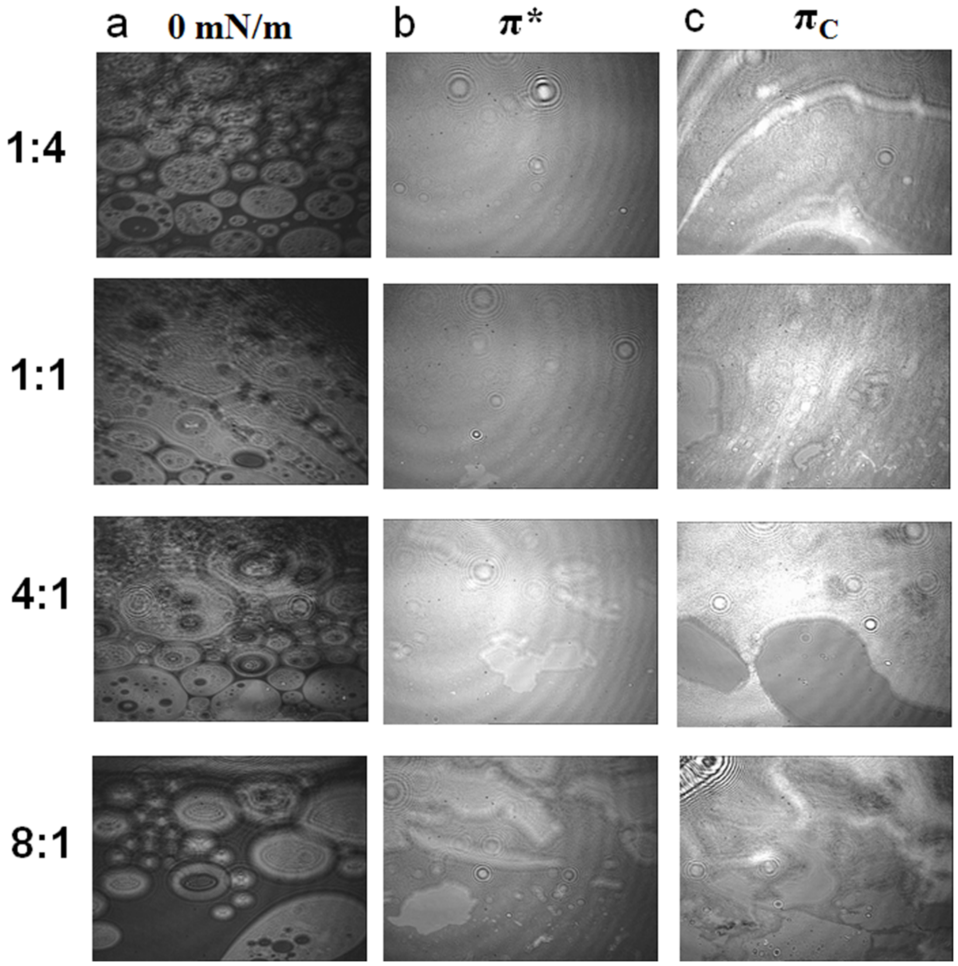

Figure S3. BAM images of PVDF(NMP)/pDDA Langmuir films at different mixing ratios (PVDF:pDDA). (a) π = 0 mN/m, (b) π*, and (c) the collapsed phase at π_c. The area of each image is 400 × 300 μm^2.

Table S1. The Cs^{-1} values at different mixing ratios and their corresponding surface area and surface pressures for the small peaks after C_s^{-1}*.

PVDF(NMP):pDDA	**0:1**	**1:4**	**1:1**	**4:1**	**8:1**	**50:1**	**1:0**
Cs^{-1}(mN/m)	187.2	138.1	117.3	134.3	125.8	–	–
A (nm^2/monomer)	0.23	0.22	0.13	0.061	0.043	–	–
π (mN/m)	36.8	36.3	36.7	35.4	35.8	–	–

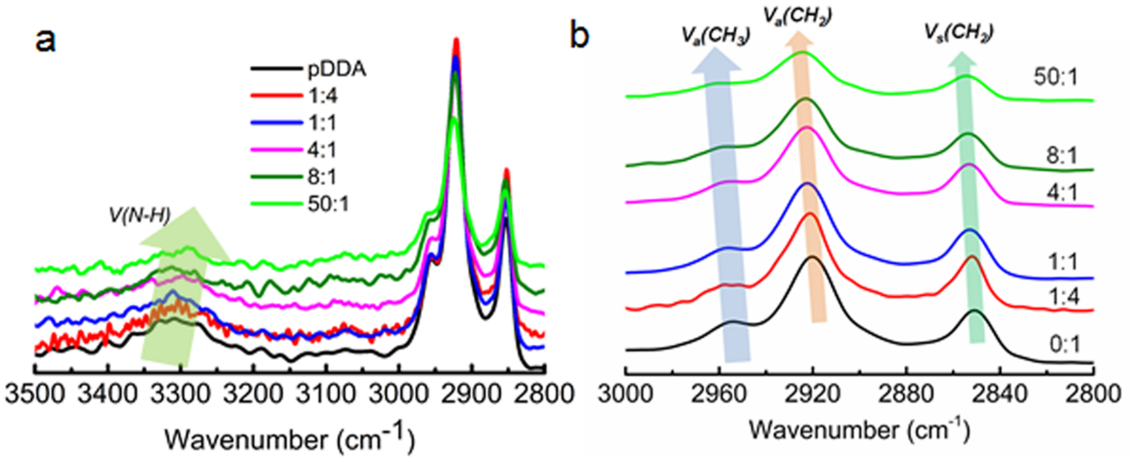

Figure S4. FTIR spectra in the regions: a) 3500-2800 cm^{-1} and b) 3000-2800 cm^{-1} of 20-layer PVDF(NMP)/pDDA LB films at different mixing ratio deposited at 30.0 mN/m.

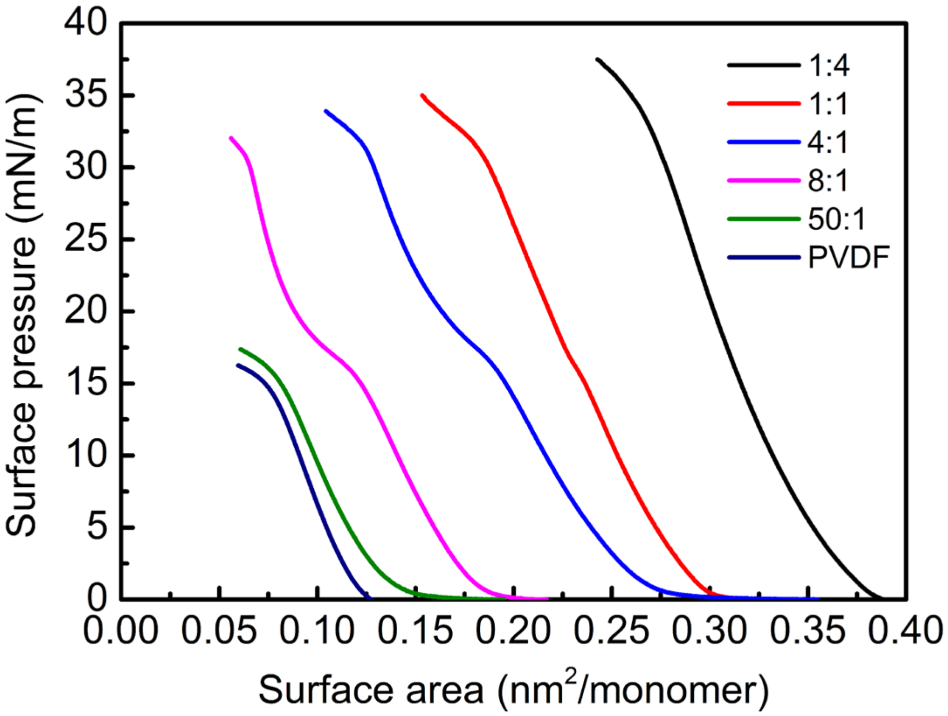

Figure S5. *π–A* isotherms of PVDF(acetone)/pDDA Langmuir films at different molar mixing ratios (PVDF:pDDA): 1:4 (black line), 1:1 (red line), 4:1 (blue line), 8:1 (pink line), 50:1 (green line) and pure PVDF(acetone) (navy line).

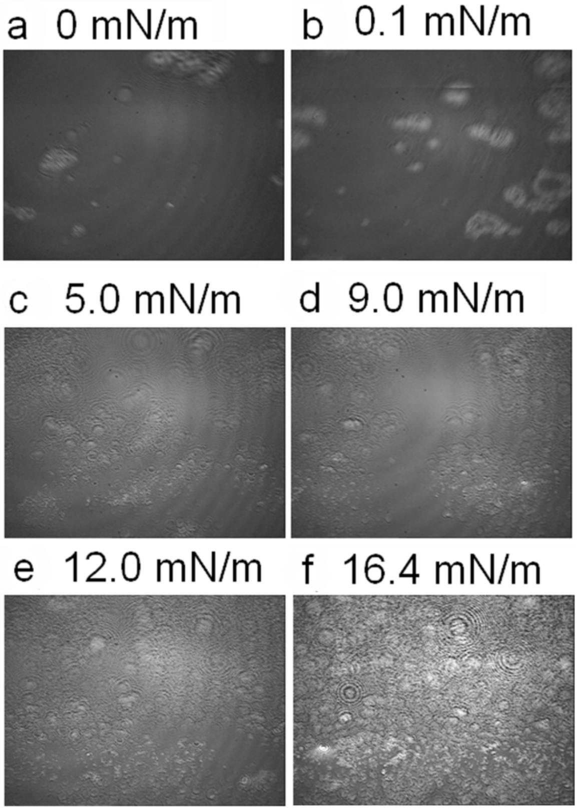

Figure S6. BAM images at different surface pressures for the PVDF(MEK)/pDDA Langmuir film at 50:1 at π = (a) 0 (after spreading), (b) 0.1 (the lift-off state), (c) 5.0, (d) 9.0 (π*), (e) 12.0 (a concentrated solid phase), and (f) 16.4 mN/m (π_c). The area of each image is 400 × 300 μm^2.

Deposition and morphological studies of pure PVDF films. We found that it was difficult to transfer pure PVDF Langmuir films onto substrates by the vertical deposition method, due to the nonamphiphilicity of PVDF. Therefore, pure PVDF Langmuir film was tried to be transferred onto substrates by the horizontal deposition method (or LS method), as reported for the preparation of PVDF copolymer LS films in the literatures.[1, 2] As discussed before, the peaks in the C_s^{-1}–A curves represent a critical concentrated state, which is a sign for the formation of stable and dense Langmuir films. Moreover, the maximum C_s^{-1*} represents the maximum arrangement of molecules at the air-water interface.[3] Therefore, the surface pressure was kept constant at $\pi^* = 9.0$ and 13.0 mN/m for depositing PVDF(MEK) and PVDF(NMP) LS films, respectively. During deposition, the silicon substrate was lifted at a dipping speed of 10 mm/min in both upstrokes and downstrokes.

The AFM images of PVDF LS monolayers are shown in Figure S7. PVDF(NMP) LS monolayer shows a surface partially covered by PVDF films because detachment happened during deposition, corresponding to a very low transfer ratio of about 0.30. However, for PVDF(MEK) Langmuir film deposition, the surface area decreasing at the air–water interface during deposition was not detected by the auto-controlled LB system. It indicates that PVDF(MEK) Langmuir film was not successfully transferred even by the horizontal deposition. The transfer ratio estimated from the decrements of the surface area was quite low. This is inconsistent with the reported result of PVDF copolymer.[1] Therefore, homopolymer PVDF is more difficult to be transferred onto substrates to obtain regular LS films than copolymers. It is necessary to find an effective way to transfer the PVDF Langmuir films onto substrates.

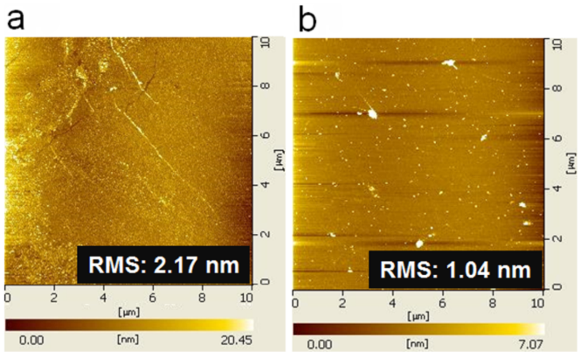

Figure S7. AFM images of PVDF monolayers (LS films) from (a) PVDF(NMP), and (b) PVDF(MEK) on the hydrophobic silicon substrates.

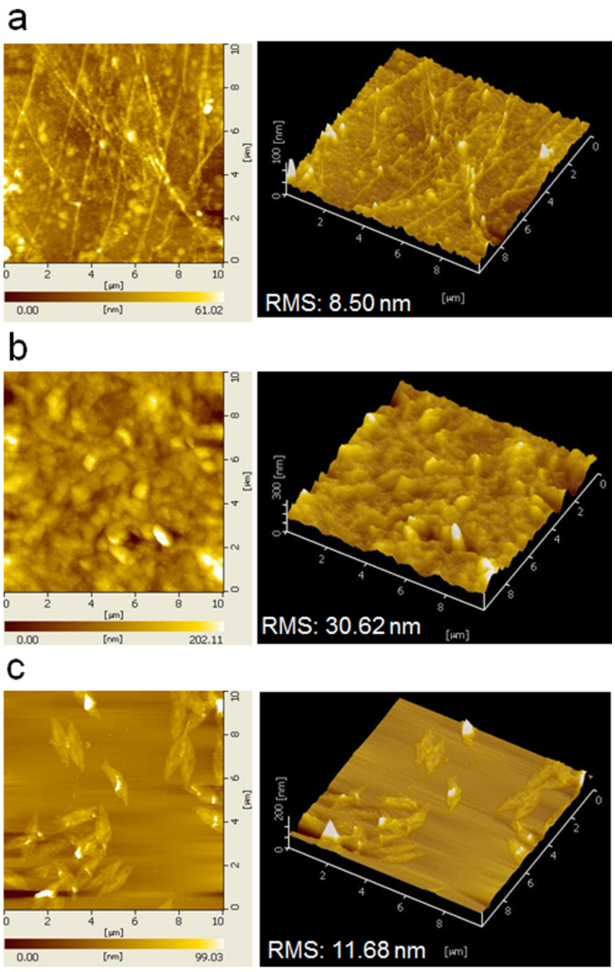

Figure S8. AFM images of PVDF/pDDA LB multilayers: (a) 20-layer PVDF(NMP)/pDDA LB films (50:1) at 30.0 mN/m, (b) 20-layer PVDF(MEK)/pDDA LB films (8:1) at 30.0 mN/m and (c) 20-layer PVDF(MEK)/pDDA LB films (8:1) at 9.0 mN/m.

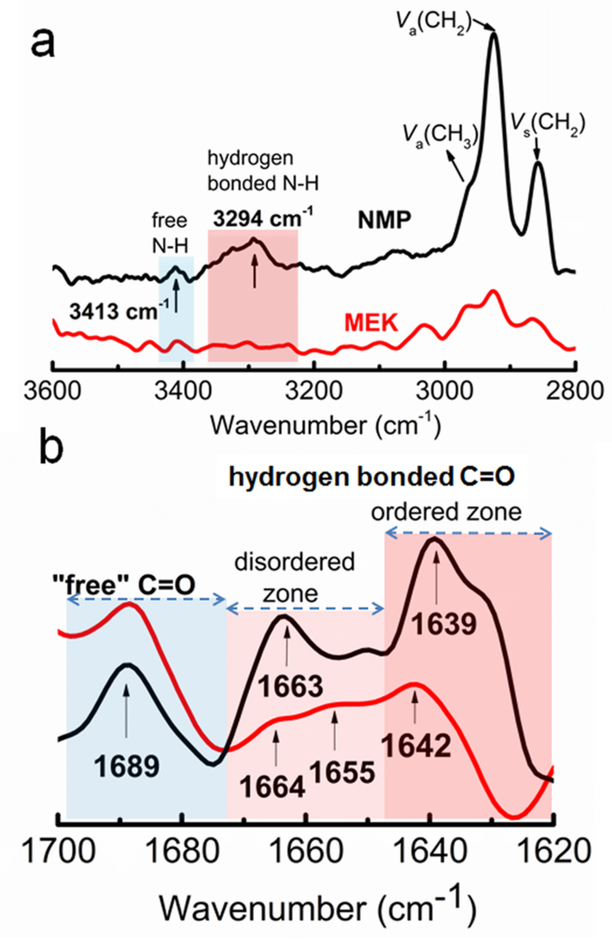

Figure S9. FTIR spectra in the regions (a) 3600-2800 cm^{-1}, and (b) 1700-1620 cm^{-1} of 20-layer PVDF(NMP)/pDDA LB films at 50:1 (black line) deposited at 30.0 mN/m and PVDF(MEK)/pDDA LB film at 50:1 (red line) deposited for 20 times at 9.0 mN/m.

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