

## Electronic Supporting Information

# Nanosegregation in Arene-Perfluoroarene $\pi$ -Systems for Hybrid Layered Dion–Jacobson Perovskites

Masaud Almalki<sup>1#</sup>, Algirdas Dučinskas<sup>1,2#</sup>, Loï C. Carbone<sup>1#</sup>, Lukas Pfeifer<sup>1</sup>, Laura Piveteau<sup>3</sup>, Weifan Luo<sup>4</sup>, Ethan Lim<sup>4</sup>, Patricia A. Gaina<sup>4</sup>, Pascal A. Schouwink,<sup>5</sup> Shaik M. Zakeeruddin<sup>1</sup>, Jovana V. Milic<sup>1,4\*</sup> and Michael Grätzel<sup>1\*</sup>

<sup>1</sup>Laboratory of Photonics and Interfaces, EPFL, 1015 Lausanne, Switzerland

<sup>2</sup>Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

<sup>3</sup>Institute of Chemistry and Chemical Engineering, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.

<sup>4</sup>Adolphe Merkle Institute, University of Fribourg, 1700 Fribourg, Switzerland

<sup>5</sup>Institute of Chemistry and Chemical Engineering, École Polytechnique Fédérale de Lausanne, 1951 Sion, Switzerland

Email Correspondence: [michael.gratzel@epfl.ch](mailto:michael.gratzel@epfl.ch), [jovana.milic@unifr.ch](mailto:jovana.milic@unifr.ch)

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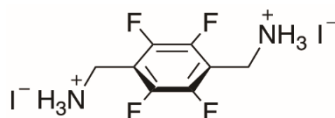
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All data presented here can be accessed at the DOI:10.5281/zenodo.6194713 and it is available under the license CC-BY-4.0 (Creative Commons Attribution 4.0 International).

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## S1. Materials and Methods

The spacers were synthesized by protonation (PDMAI<sub>2</sub>)<sup>1</sup> and reduction followed by protonation (F-PDMAI<sub>2</sub>), as detailed below. The starting materials were commercially available and conditions based on previous reports.<sup>2-3</sup>



(Perfluoro-1,4-phenylene)dimethanaminium iodide (F-PDMAI<sub>2</sub>): A solution of 2,3,5,6-tetrafluoroterephthalonitrile (506.1 mg, 2.53 mmol) under nitrogen was suspended in anhydrous tetrahydrofuran (TFH) (15 mL) in an ice-water bath and treated with borane tetrahydrofuran complex solution (12 mL, 1.0 M in THF, 12 mmol). The reaction mixture was stirred for 24 h at ambient temperature. The solution of the resulting amine intermediate was quenched with EtOH (25 mL), treated with HI (1.5 mL, 57% aqueous solution, 11.4 mmol) in an ice-water bath and stirred for 6 h. The resulting suspension was then concentrated *in vacuo*, re-dispersed into EtOH (5 mL) and poured dropwise into diethyl ether (200 mL). The obtained precipitate was filtered, extensively washed with diethyl ether and isopropanol, and dried to afford **F-PDMAI<sub>2</sub>** (278 mg, 24%) as a crystalline white solid.

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 8.33 (bs, 6H), 4.22 (s, 4H) ppm; <sup>13</sup>C NMR (101 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 144.9 (d, *J* = 247.4 Hz), 114.3, 30.9 ppm; <sup>19</sup>F NMR (377 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = -140.6 ppm.

**Perovskite thin films were prepared** based on *n* = 1 S<sub>2</sub>PbI<sub>4</sub> compositions (S = PDMA; F-PDMA and 1:1 PDMA:F-PDMA, denoted as PF) through solution processing. Specifically, stoichiometric amounts of PbI<sub>2</sub> and the spacers (or their 1:1 mixture) were dissolved in a solvent mixture of *N,N*-dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) (4:1 v/v). The solution was heated at 60 °C for a few minutes to facilitate this process and the resulting solution was obtained with a concentration of 0.4 M. Both solution preparation and spin-coating/annealing procedures were carried out in an argon atmosphere glovebox (0.5 ppm < O<sub>2</sub> and 0.5 ppm < H<sub>2</sub>O). Prior to perovskite deposition the substrates were ultrasonically cleaned sequentially with acetone and ethanol for 5 min. Thereafter, the samples were cleaned by UV-Ozone for 15 min. The films were deposited on microscope slides (Assitent 50) by spin-coating 30 μL of the solution by using a two-step program with an acceleration of 100 rpm/s for 10 s and 2000 rpm/s up to 4000 rpm/s for 20 s followed by annealing at 150 °C for 10 min.

**Perovskite thin films for grazing incidence wide angle X-ray scattering** measurements were prepared based on *n* = 1 S<sub>2</sub>PbI<sub>4</sub> compositions (S = PDMA; F-PDMA and 1:1 PDMA:F-PDMA, denoted as PF) through solution processing. Stock solutions of PbI<sub>2</sub>, PDMA, and F-PDMA with a concentration of 0.4 M were prepared followed by mixing these stock solutions to obtain the resulting perovskite precursor solutions. The subsequent spin-coating/annealing procedures were in accordance with the previous procedure. In this case, we observed excess PbI<sub>2</sub> in the measurements.

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**Perovskite powders were prepared** based on  $n = 1$   $S_2PbI_4$  compositions (S = PDMA; F-PDMA and 1:1 PDMA:F-PDMA, denoted as PF) through mechanosynthesis. Stoichiometric amounts of  $PbI_2$  and the corresponding spacers were ground with beads in a ball mill (Retsch Ball Mill MM-200) using a grinding jar (10 mL) and a ball ( $\varnothing 10$  mm) for 1 h at 25 Hz followed by subsequent annealing in an oven at 150 °C for 30 min to get the final powder.

**Powder X-Ray diffraction measurements** were carried out using a PANalytical Empyrean Series 2 instrument in Bragg-Brentano configuration with Cu  $K\alpha$  radiation at 40 kV voltage and 40 mA current. For the grazing incidence measurements, the X-ray incidence angle was set at 2°. Under both conditions diffracted X-rays were detected using a PIXcel3d detector.

**Grazing incidence wide angle X-ray scattering (GIWAXS)** of the thin films on microscope glass was measured at 1.5° incidence angle with a D8 Discover Plus TXS (Bruker) equipped with a rotating anode (Cu), a Dectris Eiger2 2D detector, and using a point-collimated beam of approx. 300  $\mu$ m, at a power of 5.4 kW.

**UV-vis measurements** were performed using a Shimadzu UV-2600 spectrophotometer.

**Steady-state photoluminescence (PL) spectra** were recorded with a Fluorolog 322 spectrometer (Horiba Jobin Yvon iHr320 and a CCD) with a bandpass of 5 nm upon excitation at 350 nm (Xenon lamp) with a band pass of 2 nm.

**Solid-state NMR spectra** of mechanochemically prepared powders were recorded on a 500 MHz Bruker spectrometer (11.7 T) equipped with an Avance III console and a 3.2 mm three-channel low temperature MAS probe. Samples were packed into 3.2 mm zirconia rotors under ambient conditions and spun at a frequency up to 20 kHz using nitrogen gas.

*<sup>19</sup>F NMR spectra* were acquired using a Hahn echo pulse sequence with  $\pi/2$  pulses of 4.5  $\mu$ s, echo delays of four rotor periods and 128 accumulated transients. Recycle delays were set to 1.3 times  $T_1$ . <sup>19</sup>F chemical shifts were referenced to the secondary reference polytetrafluoroethylene (PTFE, -121 ppm). <sup>13</sup>C CP MAS spectra were obtained by transferring polarization either from <sup>1</sup>H or from <sup>19</sup>F to <sup>13</sup>C nuclei by cross polarization (CP)<sup>4</sup> with variable amplitude during a contact time of 1.5 and 2.0 ms respectively.<sup>5</sup> Heteronuclear decoupling of either <sup>1</sup>H or <sup>19</sup>F nuclei was achieved using the spinal64 pulse sequence<sup>6</sup> (<sup>1</sup>H) or continuous wave irradiation (<sup>19</sup>F) at 64 or 80 kHz, respectively. Recycle delays were set to 1.3 times  $T_1$  of the <sup>1</sup>H, respectively <sup>19</sup>F signal and 1024 scans were accumulated for every spectrum. <sup>13</sup>C chemical shifts were referenced to the secondary reference adamantane (left peak at 38.48 ppm).

*<sup>13</sup>C CP spectra* were obtained by transferring polarisation from either <sup>1</sup>H (dark blue spectra in Figure 5c) or from <sup>19</sup>F nuclei (black spectra in Figure 5c). The <sup>1</sup>H $\rightarrow$ <sup>13</sup>C CP NMR spectrum of neat PDMA exhibits two signals, one from -CH<sub>2</sub>- (44 ppm) and another from aromatic carbons (134 ppm). In the equivalent spectrum of fluorinated spacers, there are two signals from aromatic carbons (145, 113 ppm) and the -CH<sub>2</sub>- signal is shifted (34 ppm) due to the presence of the fluorine atoms. The <sup>1</sup>H $\rightarrow$ <sup>13</sup>C CP NMR spectrum of

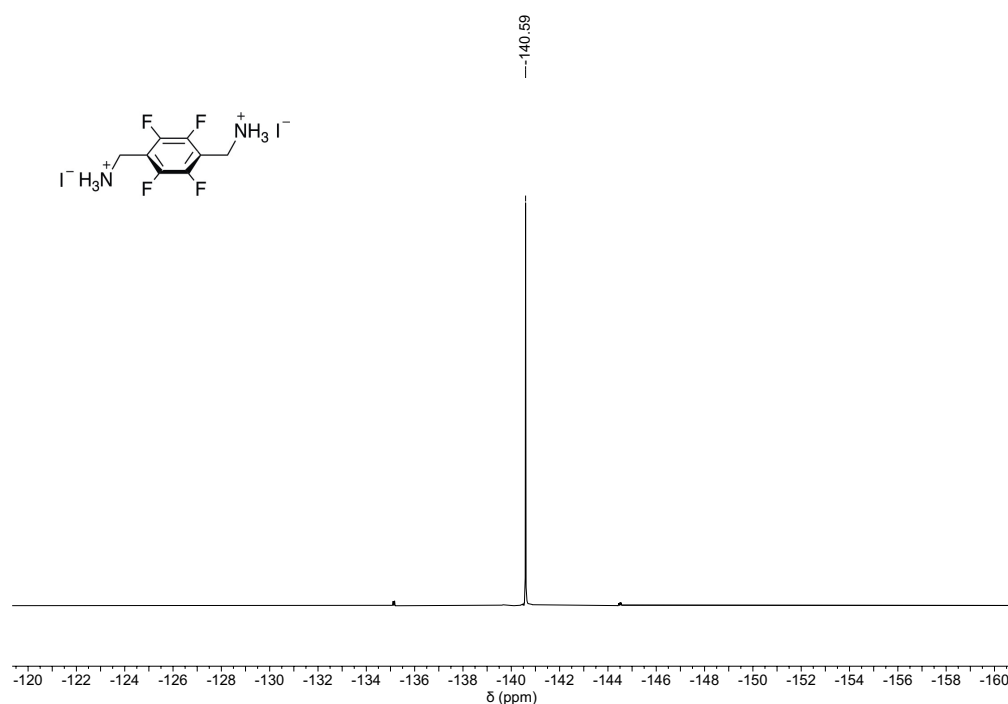
the mixture of the two spacers is a linear combination of the spectra of the individual spacers. The spectra of the two perovskite samples are almost identical to the spectra of the pristine spacers used for the synthesis.

The  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP NMR spectra are composed of significantly broader signals, with more than an order of magnitude larger line width. This is explained by residual dipolar interactions of the protons, which remains significant at the applied magnetic field strength (11.7 T) and the used spinning speed (20 kHz magic angle spinning). For technical reasons, decoupling of  $^1\text{H}$  is not possible in the experimental configuration in which  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP transfer is conducted. An increase of the applied magnetic field and the spinning speed should lead to sufficient reduction of the residual dipolar interaction of the  $^1\text{H}$  spins which is necessary to record better resolved  $^{13}\text{C}$  spectra after polarization transfer from  $^{19}\text{F}$  nuclei.

**Contact angle measurements** were recorded with a drop shape analyzer (KRÜSS, DSA100) at ambient temperature to assess hydrophilicity of surfaces.

**Photoluminescence quantum yield (PLQY)** was measured using an integrating sphere (Fluorolog, Horiba Jobin Yvon), an Andor Kymera 193i spectrograph, and a 660 nm continuous-wave laser (OBIS, Coherent) set at 1-Sun equivalent photon flux (1.1  $\mu\text{m}$  beam full-width half-maximum, 632  $\mu\text{W}$ ); photoluminescence was collected at normal incidence using a 0.1 NA, 110  $\mu\text{m}$ -diameter optical fiber. For the absolute spectral calibration of the PLQY measurement system, we used a radiometrically calibrated halogen lamp (HL-3 plus CAL from Ocean Optics). PLQY is defined as the emitted photon flux divided by the absorbed photon flux measured under open circuit; the emitted photon flux is limited by non-radiative recombination processes under this condition.<sup>7</sup>

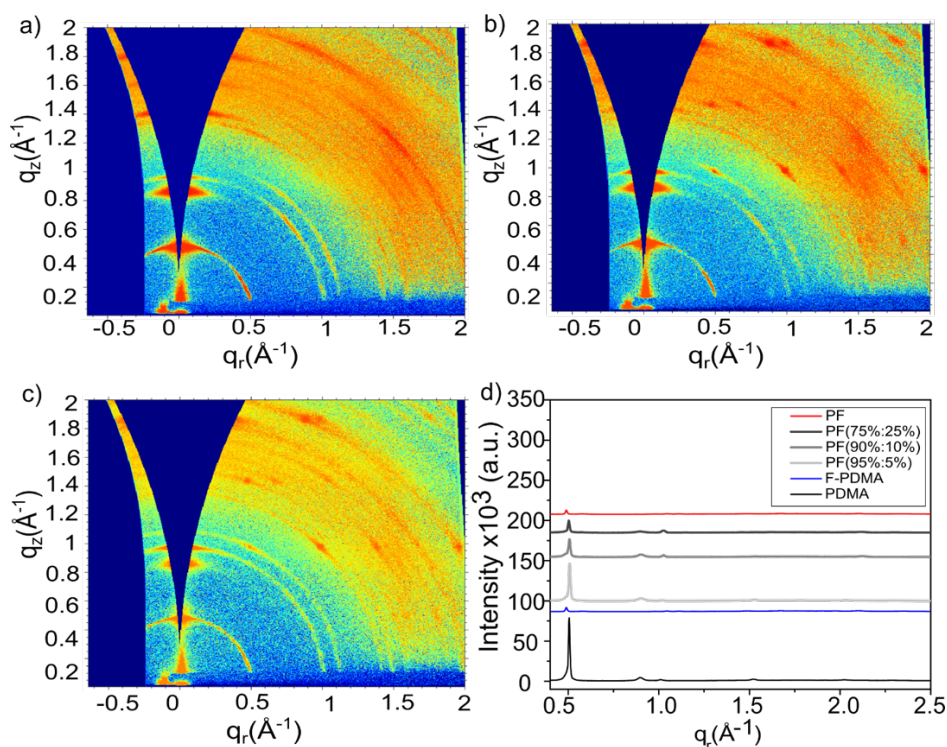
## S2. NMR Spectroscopy



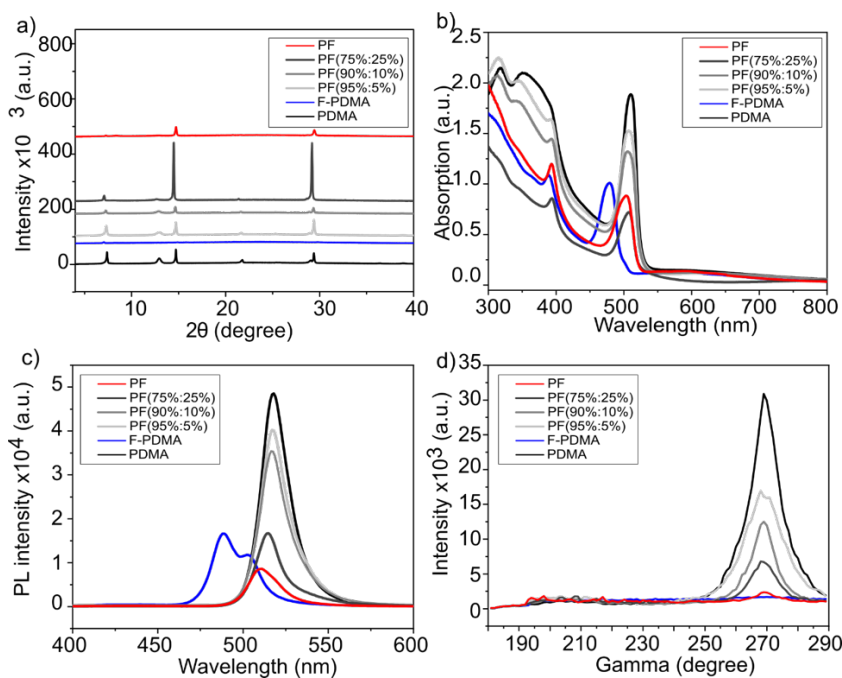
**Figure S1.**  $^{19}\text{F}$  NMR spectrum of F-PDMAI<sub>2</sub> in (CD<sub>3</sub>)<sub>2</sub>SO (400 MHz, 298 K).



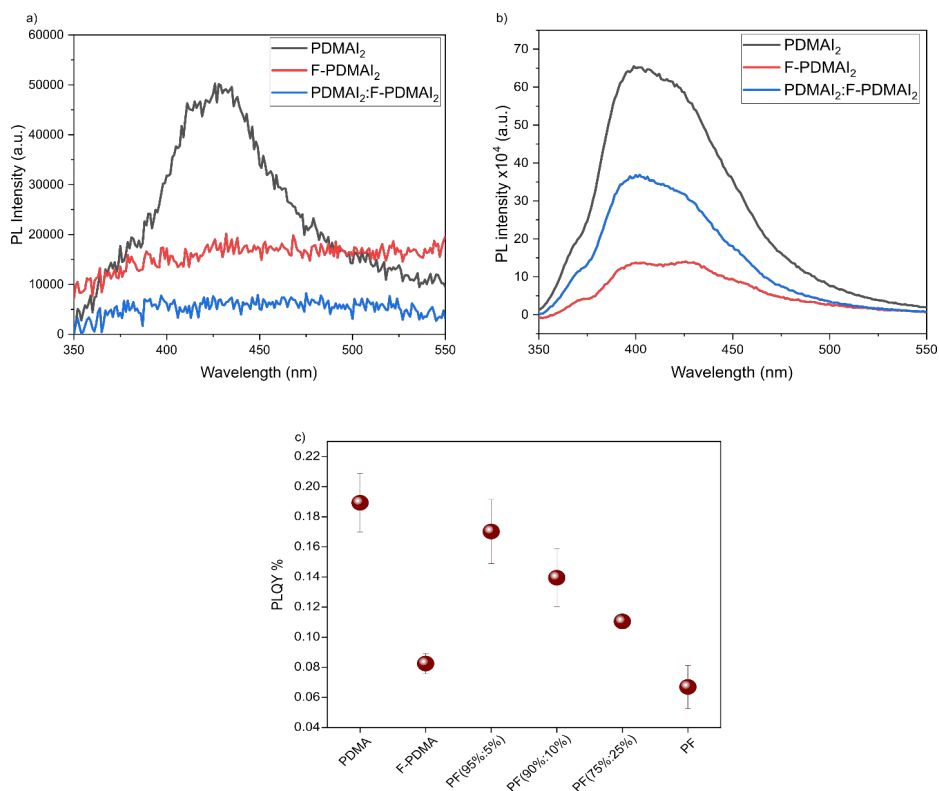
### S3. Supplementary Data



**Figure S4.** Grazing incidence wide angle X-ray scattering (GIWAXS) data at incidence angles of ca.  $1.5^\circ$  map of the films with F-PDMA content of a) 5%, b) 10%, and c) 25%. d) Integrated diffraction patterns (from GIWAXS images) for thin films containing PDMA (black), F-PDMA (blue), and their mixtures (PF) based on F-PDMA content of 5% (light grey), 10% (medium grey), 25% (dark grey), and 50% (red) compositions. The data for 2D perovskites based on PF mixtures with 1:1 PDMA and F-PDMA are presented in Figure 2 of the main manuscript.

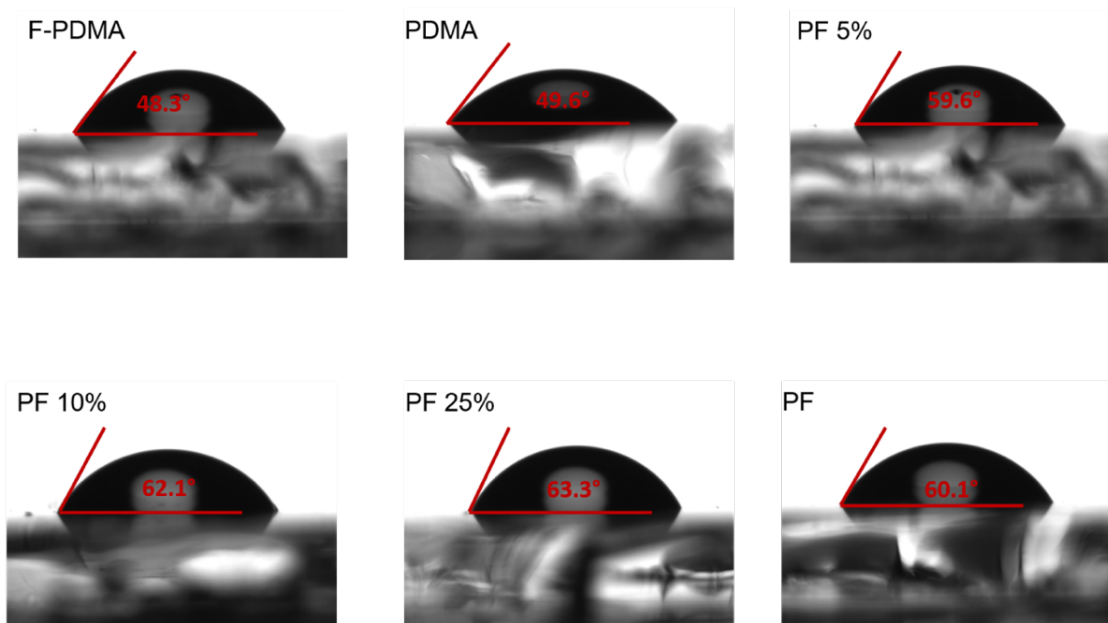


**Figure S5.** (a) XRD patterns, b) UV-vis absorption spectra, c) PL spectra d) Gamma scans integration for the peak at  $7.3^\circ$  with  $\gamma = 270^\circ$  corresponds to out-of-plane vector for thin films containing PDMA (black), F-PDMA (blue), and their mixture (PF) with F-PDMA content of 5% (light grey), 10% (medium grey), 25% (dark grey), and 50% (red).



**Figure S6.** PL spectra for neat PDMAI<sub>2</sub>, F-PDMAI<sub>2</sub> and their mixture in a) thin films and b) solution of DMSO. c) Photoluminescence quantum yield (PLQY) for thin films based on different compositions.

PDMA-based layered perovskites showed the highest PLQY of about 0.2%, whereas F-PDMA revealed a very low PLQY of 0.08%. The values of PLQY are by an order of magnitude lower as compared to 3D perovskite due to the excitonic nature of 2D structures.<sup>8</sup> For PDMA/F-PDMA mixtures, increasing the F-PDMA ratio (5, 10, 25, 50%) resulted in the reduction of the PLQY (to 0.17, 0.14, 0.11, and 0.075%, respectively), which is in the agreement with the reduction in crystallinity revealed by XRD measurements.



**Figure S7.** Contact angles of water droplets on F-PDMA (48°), PDMA (49.6°), F-PDMA 5% (59.6°), F-PDMA 10% (62.1°), F-PDMA 5% (63.3°), and F-PDMA 50% (60.1°) films.

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