Electronic Supporting Information (ESI)

Hybrid CdSe-Dendron Nanoparticle and Polymer Blend Knodels at the Interface

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1. Experimental

1.1. Materials

Poly(9-vinylcarbazole) (PVK, M_w =72,000 g/mol) was obtained from Aldrich and hybrid cadmium selenide (CdSe) quantum dots with second-generation poly(benzyl ether) dendrons (2GPO) containing peripheral carbazoles were synthesized in our group.[12] To investigate the interfacial behavior and morphological changes of both materials and their blend at the air-water interface, three solutions were prepared in chloroform: CdSe-2GPO (1.0 mg/mL), CdSe-2GPO and PVK blend (weight fraction, f = 0.1, 1.0 mg/mL), and PVK (3.0 mg/mL).

1.2. Langmuir Monolayer

A KSV 2000 LB system was used for all isotherm measurements and film depositions. The Teflon trough and barriers were cleaned with chloroform (spectroscopic grade) and ethanol. The trough was then filled with Millipore quality water and the surface of the subphase was carefully cleaned with an aspirator to remove contaminants. A platinum (Pt) Wilhelmy plate was used for measuring the surface pressure. Each as-prepared solution (50-150 μl) was evenly spread over the water surface and the solvent was allowed to evaporate for 15 min. Surface pressure-mean molecular area (π-A) isotherms were collected at a constant barrier speed (10 mm/min) until the barriers reached the maximum compressing position. In order to examine the stability of the Langmuir monolayer at the air-water interface, compression and expansion cycles were performed. The two barriers were compressed to a certain target surface pressure and then expanded to a return surface pressure of zero at a constant rate (10.0 mm/min) repeatedly. Another method to investigate the physical stability, i.e. isobaric creep measurements, was carried out. For this purpose, the barriers reached to target surface pressure and were held for 15-25 min. During this period, the surface molecular area change was measured.

1.3. Langmuir-Schaefer (LS) Film

For the LS film deposition, silicon substrates were rinsed with Millipore water (resistivity > 18 MΩ.cm) and acetone several times. After drying the substrates, they were immersed in 48% hydrofluoric acid (HF) solution for 50 seconds to render the surfaces hydrophobic. Such substrates were rinsed with an excess of water and then air-dried. Before the barriers were retracted and the tested material spread over the subphase, the prepared hydrophobic silicon substrate was attached to the balance's dipper whose surface was parallel to the subphase. The dipper then lowered the substrate a few millimeters above the subphase. A compression rate (10.0 mm/min) and a certain target pressure (5, 15, or 30 mN/m) were then set. Once the desired surface pressure was reached, the substrate was lowered at a rate of 5.0 mm/min. After coming into contact with the surface of the liquid, the substrate was immediately raised and air dried.

1.4. Instrumentation

In order to investigate the optical properties of the Cdse-2GPO QDs, UV/Vis spectrum was recorded using an Agilent 8453 spectrometer. Fluorescence spectra were recorded with a Perkin-Elmer LS45 luminescence spectrometer. Atomic force microscopy (Agilent 5500 AFM/SPM System, Agilent Technologies) was used to investigate the surface morphologies and surface analysis. Commercially available tapping mode tips (TAP300, Silicon AFM Probes, TedPella, Inc.) were used on cantilevers with a resonance frequency in the range of 290-410 kHz. All images (AFM topography, Tapping mode) were filtered, and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com). TEM imaging was done using a JEOL JSM 3010F. PM-RRAS measurements were done (courtesy of Biolin Scientific) using a KSV-NIMA with a spectral resolution of 8 cm-1 and incident angle of 55 degrees using a ZnSe photoelastic modulator at frequency of 100 Hz. Isotherm measurements were correlated with a KSV minitrough.

2. Additional Results

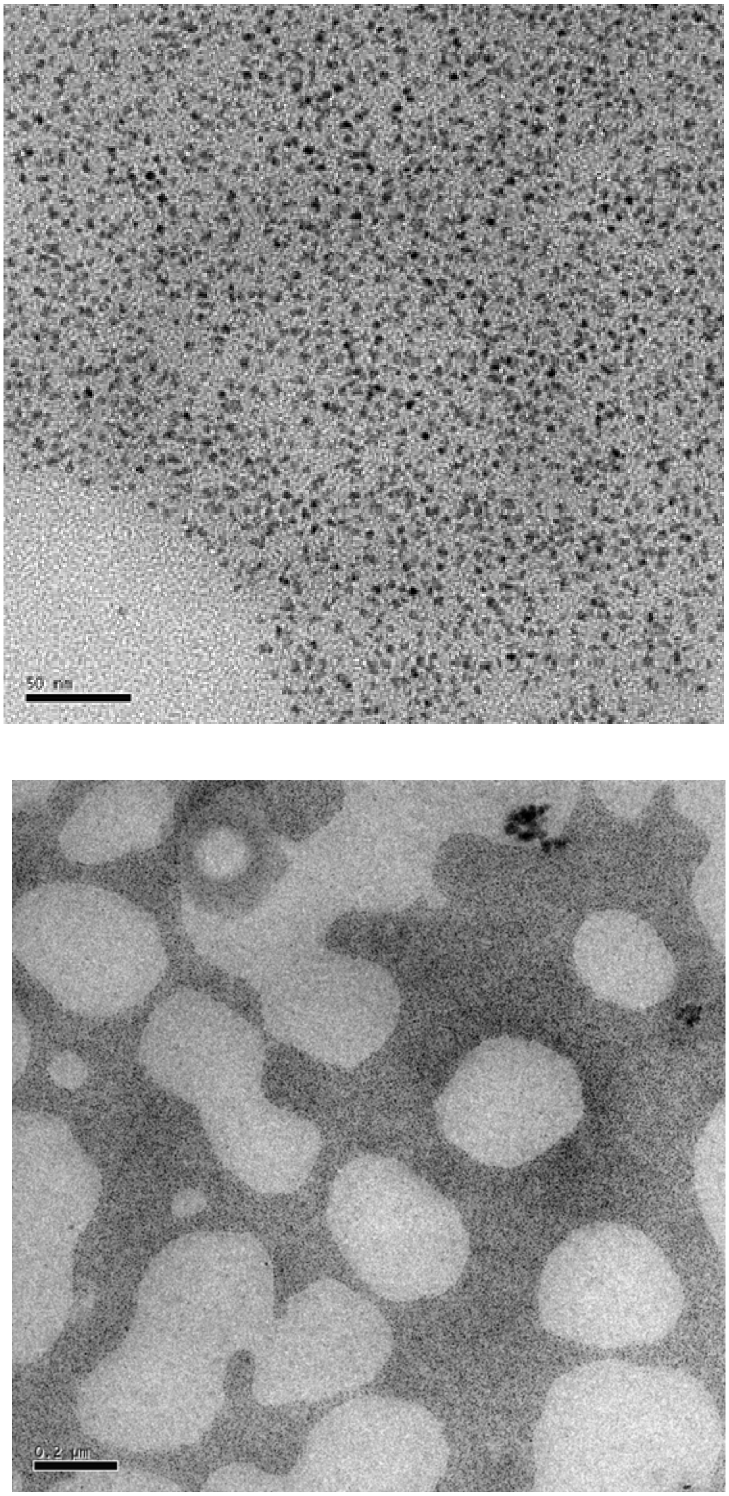
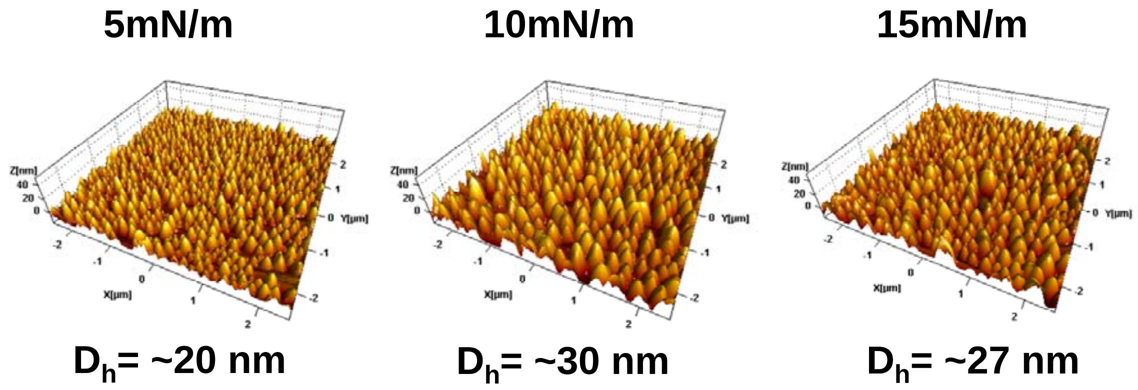


Fig. S1 TEM images of CdSe-2GPO QDs.



5mN/m 10mN/m 15mN/m

D_h= ~20 nm D_h= ~30 nm D_h= ~27 nm

Fig. S2 Three-dimensional (3-D) AFM topographical images of the PVK LS films transferred at (d) 5, (e) 10, and (f) 15 mN/m. Scan size: 5× 5 μm^2.

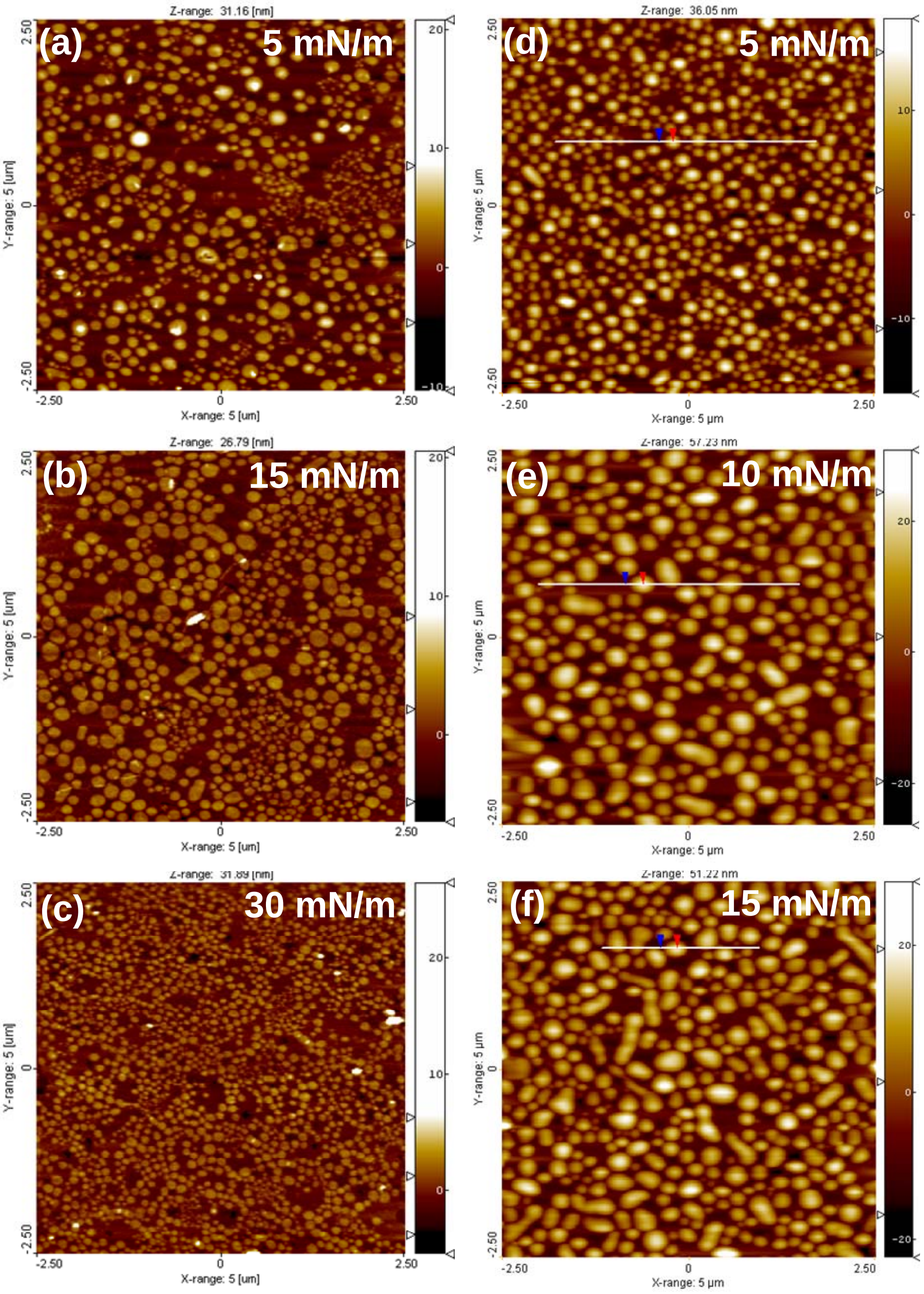


Fig. S3 (a)Enlarged AFM Images for comparison of LS films o CdSe-GPO Nanoparticles and PVK alone

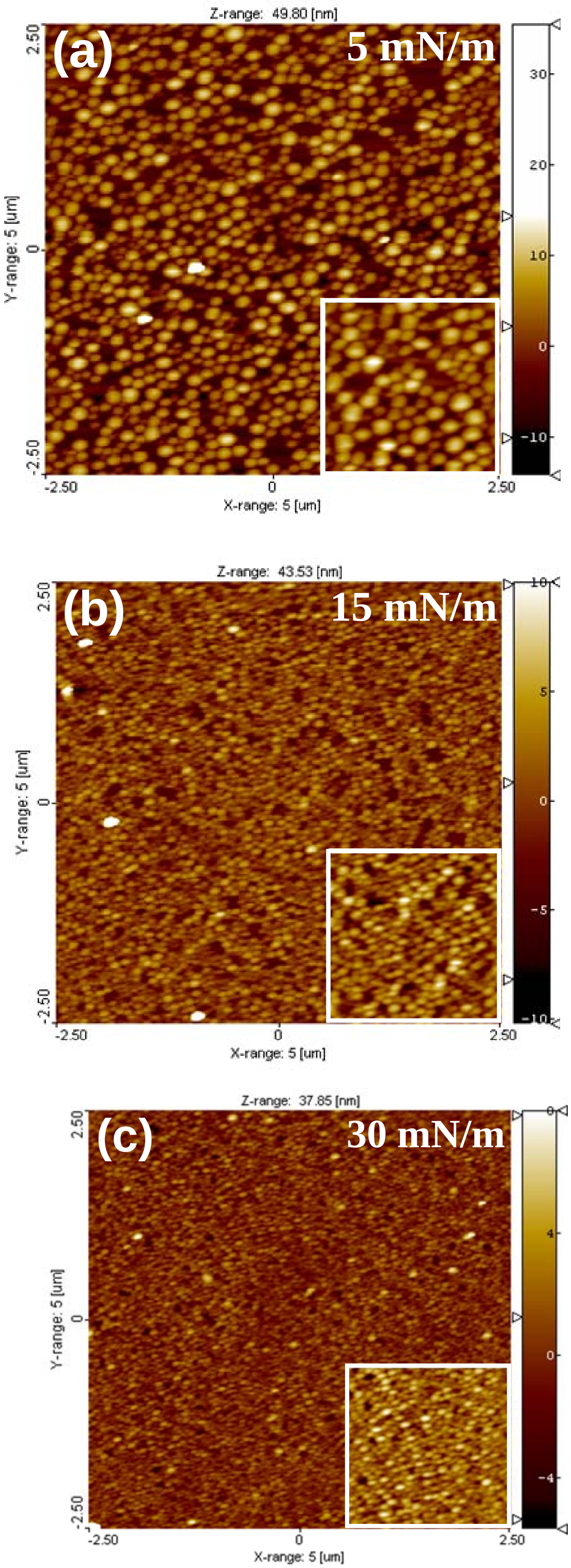


Fig. S3 (b) Enlarged AFM topographical images of the CdSe-2GPO QDs/PVK LS films transferred at (a) 5, (b) 15, and (c) 30 mN/m. Scan size: 5× 5 μm^2 and 1.5× 1.5 μm^2 (inset).

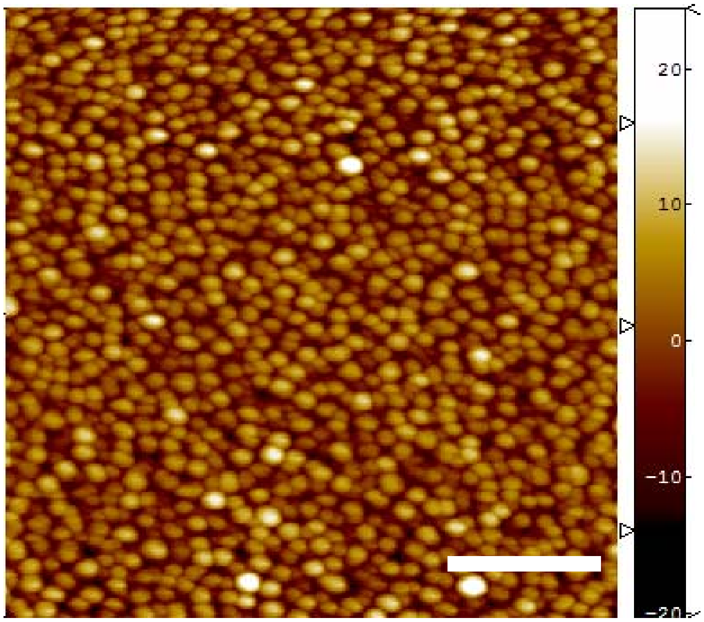


Fig. S3 (c) Enlarged AFM topographical image of the CdSe-2GPO LB multilayer film (6 layers) transferred at 40 mN/m. The scale bar is 1μm.

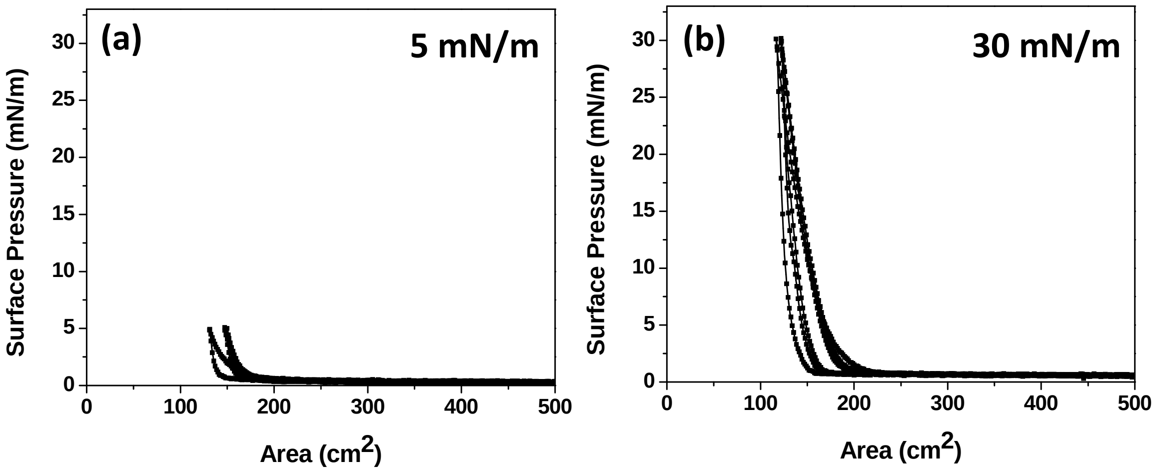


Fig. S4 Compression and expansion cycles of the CdSe-2GPO/PVK blend monolayer at (a) 5 mN/m and (b) 30 mN/m.

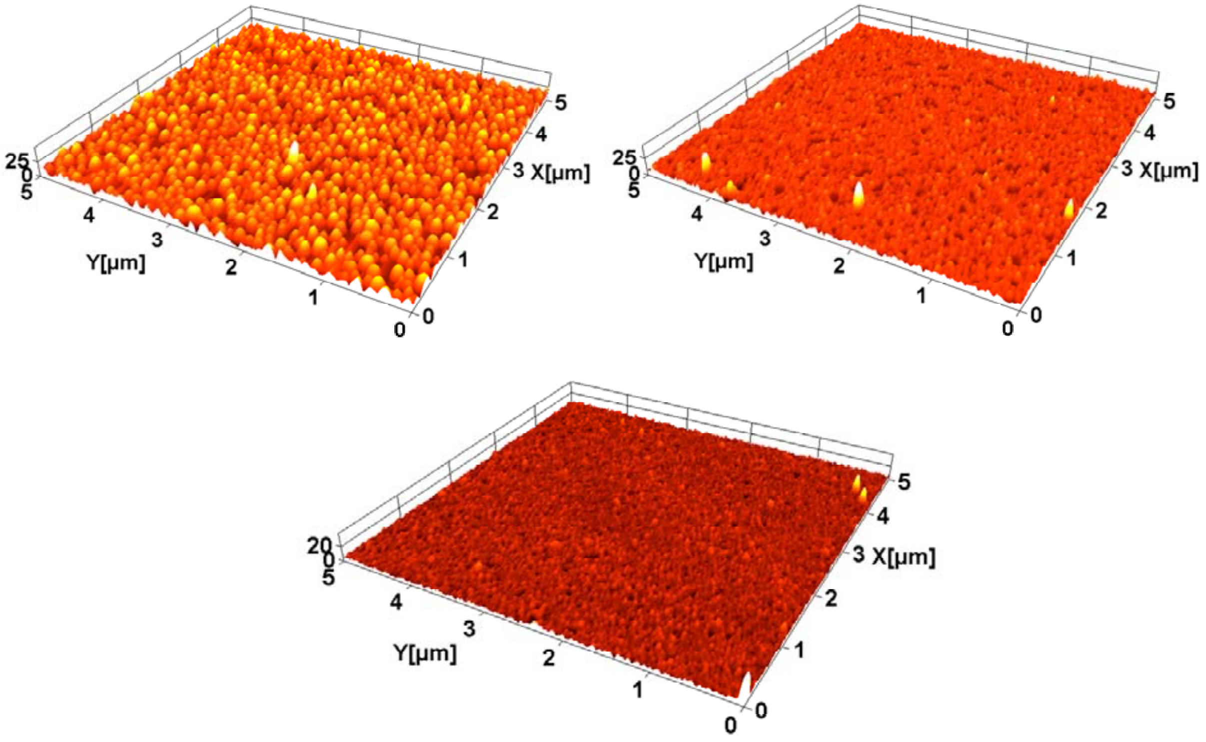


Fig. S5 Three-dimensional (3-D) AFM topographical images of the CdSe-2GPO/PVK LS films transferred at (a) 5, (b) 15, and (c) 30 mN/m. Scan size: 5× 5 µm^2.

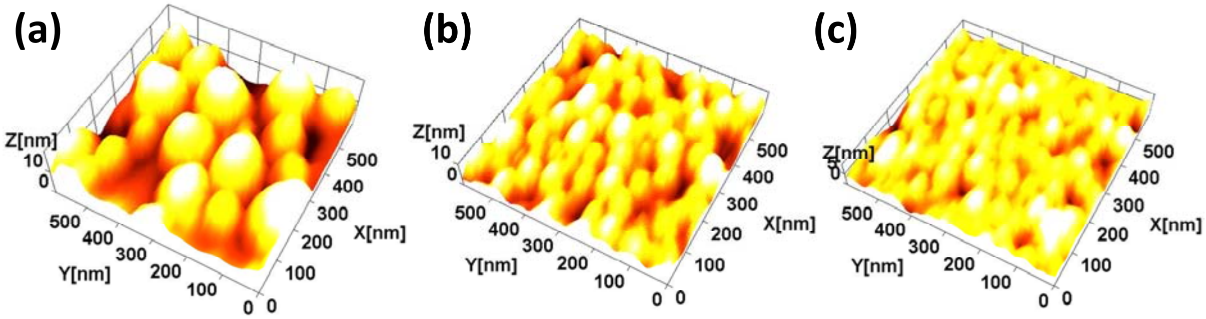


Fig. S6 Three-dimensional (3-D) AFM topographical images of the CdSe-2GPO/PVK LS films transferred at (a) 5, (b) 15, and (c) 30 mN/m. Scan size: 600 × 600 nm^2.

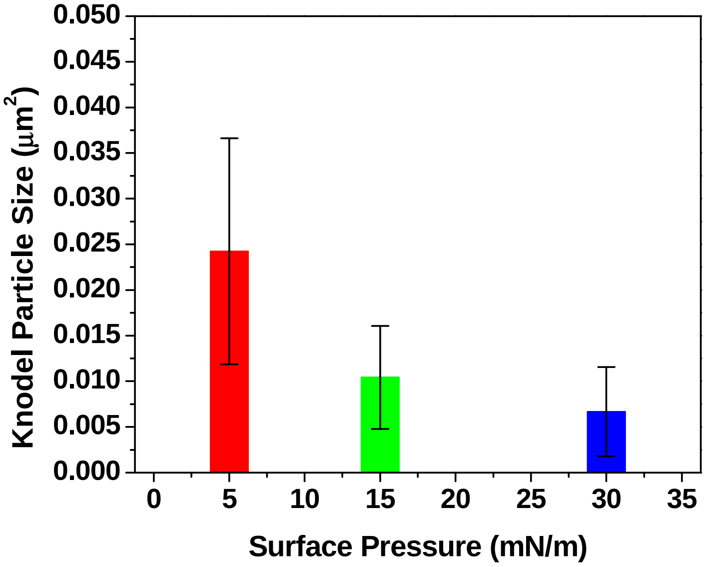


Fig. S7 A histogram of knodel particle size at each surface pressure (0.02424, 0.01042, and 0.00667 μm^2 at 5, 15, and 30 mN/m, respectively).