

Supporting Information

Single-Step Solution-Phase Synthesis of Free-Standing Two-Dimensional Polymers and Their Evolution into Hollow Spheres

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Synthesis.

General. All solvents were dried following the standard procedures before use. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and used without further purification.

Synthesis of model compound 1. Triptycene tricatechol (TPTC) (0.16 g, 0.42 mmol) and phenylboronic acid (PBA) (0.16 g, 1.27 mmol) were dissolved in methanol (7 mL) and then the solution was evaporated to remove the solvent. The resulting residue was quickly heated to 130 °C under vacuum for 1 h to give compound **1** as a yellow solid (0.26 g, 97 %). Note: the borate ester **1** is labile and should be preserved under dry condition. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.0 Hz, 6H), 7.54 (t, *J* = 7.4 Hz, 3H), 7.45 (t, *J* = 7.4 Hz, 6H), 7.37 (s, 6H), 2.49 (s, 6H). MS (MALDI): *m/z* 636.2 [M]⁺.

Synthesis of model compound 2. This compound was obtained as a yellow solid (0.36 g, 98.5 %) by following the procedure described for the synthesis of compound **1**. Note: the borate ester **2** is labile and should be preserved under dry condition. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 6H), 7.69 (d, *J* = 8.0 Hz, 6H), 7.63 (d, *J* = 7.4 Hz, 6H), 7.46 (t, *J* = 7.7 Hz, 6H), 7.39 (s, 6H), 7.38 (d, *J* = 7.7 Hz, 3H), 2.51 (s, 6H). MS (MALDI): *m/z* 864.3 [M]⁺.

Procedure for the polymerization reaction of TPTC and BDBA: Triptycene tricatechol (TPTC) (3.5 mg, 9.25 μmol) and 1,4-benzenediboronic acid (BDBA) (2.4 mg, 14.5 μmol) were dissolved in dioxane/mesitylene (40 mL, v/v = 1:1) in a 100 mL Schlenk tube. After being degassed in a liquid nitrogen bath for 40 min, the tube was purged with argon and then sealed. The tube was kept at 85 °C for 3 days without disturbance. After being cooled to room temperature, the as-prepared mixture was submitted to characterization.

Procedure for the polymerization reaction of TPTC and 4,4'-biphenyldiboronic acid (BPDBA) is same as that of TPTC and BDBA described above.

Procedure for the polymerization reaction of TPTC and BDBA conducted at higher concentration: TPTC (0.10 g, 0.26 mmol) and benzenediboronic acid (BDBA, 66 mg, 0.4 mmol) were dissolved in dioxane/mesitylene (15 mL, v/v = 1:1) in a 25 mL

Schlenk tube. After being degassed in a liquid nitrogen bath for 40 min, the tube was purged with argon and then sealed. The tube was kept at 85 °C without disturbance for 4 days to yield a white solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dioxane for 3 times and then dried under dynamic vacuum at 150 °C for 4 h to afford a white powder (80 mg, 58.8%), which was insoluble in common organic solvents such as acetone, ethanol and N, N-dimethylformamide. Anal. Calcd. For $C_{31}H_{18}B_3O_6$: C, 71.75; H, 3.50. Found: C, 67.74; H, 4.09. Note: organoboron compounds typically give lowered carbon values in elemental microanalysis due to the formation of non-combustible boron carbide byproducts.¹

Procedure for the polymerization reaction of TPTC and BPDBA conducted at higher concentration is same as that of TPTC and BDBA described above. Anal. Calcd. for $C_{40}H_{24}B_3O_6$: C, 75.89; H, 3.82. Found: C, 69.3; H, 4.63. Note: organoboron compounds typically give lowered carbon values in elemental microanalysis due to the formation of non-combustible boron carbide byproducts.¹

Instruments and Methods.

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets.

Atomic force microscopy (AFM)

Atomic force microscopy was carried out with a Nano scope IIIa MultiMode microscope. The samples were prepared by slowly pipetting a drop of the corresponding reaction solution (diluted with distilled toluene) on mica or silicon wafers, dried under vacuum for 2 h, and then submitted to AFM characterization.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a JSM-6390LV scanning electron

microscope or a Philips XL30FEG Scanning electron microscope (for field emission (FE)-SEM). For solid samples (Microsphere-1 and Microsphere-2), they were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in a nitrogen atmosphere, sputtered for 30 s from a solid gold target at a current at 30 mA) before being submitted to SEM characterization. For the samples in solution (Monolayer-1, Monolayer-2, Nanosphere-1 and Nanosphere-2), aliquots of the corresponding solution were dropped onto silicon wafers followed by removal of the solvent under vacuum, coated with gold using a sputter coater (ambient temperature, 60 torr pressure in a nitrogen atmosphere, sputtered for 200 s from a solid gold target at a current at 30 mA), and then was submitted to SEM characterization.

Transmission electron microscopy (TEM)

Transmission electron microscopy was performed on a Philips CM 200/FEG transmission electron microscope. For solid samples (Microsphere-1 and Microsphere-2), they were dispersed over the carbon coated copper grid. For the samples in solution (Monolayer-1, Monolayer-2, Nanosphere-1 and Nanosphere-2), they were prepared by carefully dropping the corresponding solution onto the carbon coated copper grid followed by removal of the solvent under vacuum.

Scanning tunneling microscopy (STM)

Scanning tunneling microscopy was performed with a NanoScope IIIa MultiMode Scanning probe microscope (SPM) (Veeco Inc. USA) with Pt–Ir (80/20) tips in ambient conditions. The MultiMode SPM was charged with a Low Current STM Converter (Veeco Inc. USA). The samples were prepared by slowly pipetting a drop of the corresponding reaction solution (diluted with distilled toluene) on freshly cleaved highly oriented pyrolytic graphite (HOPG) surface, dried under vacuum for 2 h, and then submitted to STM characterization. It should be noted that conducting the STM experiment on the new materials reported in this work faces several challenges

because of the unique feature of “standing up” of the repeated units. The first challenge is to transfer monolayers formed in solution to the STM surface. Damage or curling of the monolayer might occur in this process. The second challenge is, differing from the reported STM images of COFs in which the in situ formed COF monolayers were tiled on the STM substrate (a planar adsorption, fabricated by sublimation of BDBA and HHTP under ultrahigh vacuum from two molybdenum crucible evaporators onto a clean Ag (111) surface, Zwaneveld et al. *J. Am. Chem. Soc.* **2008**, *130*, 6678.), in our case the vertical alignment of the COF monolayer on the STM substrate (HOPG) results in very low conductivity of the sample (as illustrated in Scheme 1). Thirdly, the vertical alignment should lead to very weak interactions between the sample and the HOPG surface and thus STM-induced or thermal drifts might exert a tremendous influence on the STM imaging (Wilson et al. *Nature* **1990**, *348*, 621.). The fourth challenge is that boronate ester is moisture sensitive. Thus, the new COF structures might partly collapse due to the part hydrolyzation of the B-O bonds during the time of conducting the STM experiment. After trying numerous times, we eventually obtained the STM images of Monolayer-2 with an acceptable resolution.



Scheme 1. Illustration for tiled (left) and vertical (right) alignments of COF structures on STM substrates.

Powder X-ray diffraction

Wide-angle X-ray diffraction measurements were carried out with an X'Pert PROX system using monochromated Cu/K α ($\lambda = 0.1542$ nm). Small-angle X-ray diffraction measurements were performed on a Bruker D8 powder diffractometer with Cu/K α radiation. The samples were spread on the square recess of XRD sample holder as a thin layer, respectively.

Small-angle X-ray scattering

Small-angle X-ray scattering experiments were conducted at room temperature in SAXSess mc² system (Anton Paar, Austria) with Ni filtered Cu K_α radiation source. The power of X-ray source was operated at 30 mA and 50 kV. The SAXS data was first corrected by subtracting a background scattering value and then desmeared.

Nitrogen adsorption-desorption isotherm measurements

The measurements were carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared samples (ca. 80 mg) were activated by being immersed in anhydrous dioxane for 1 h. The solvent was decanted and the sample was dried under dynamic vacuum at 250 °C for 10 h. The resulting sample was then used for gas adsorption measurements from 0 to 1 atm at 77 K.

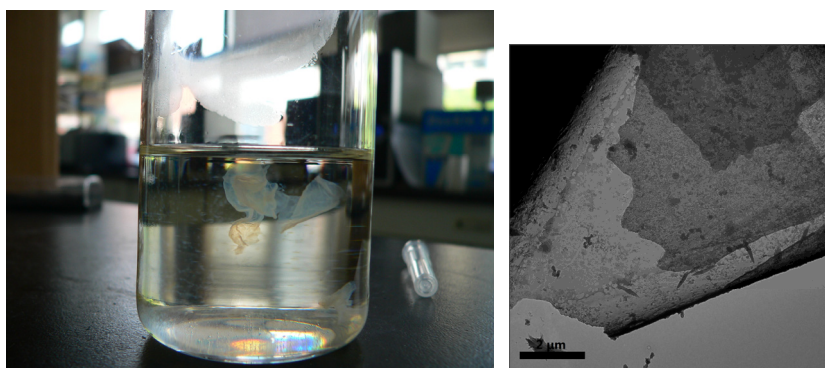


Figure S1. Picture (left) and TEM image (right) of the film-like materials floating in the reaction solution which were generated by heating a mixture of triptycene tricatechol (**TPTC**) and 4,4'-biphenyldiboronic acid (**BPDBA**) (2:3, molar ratio) in dioxane/mesitylene (1:1, v/v). The acceleration voltage used in the TEM experiment was 160 kV.

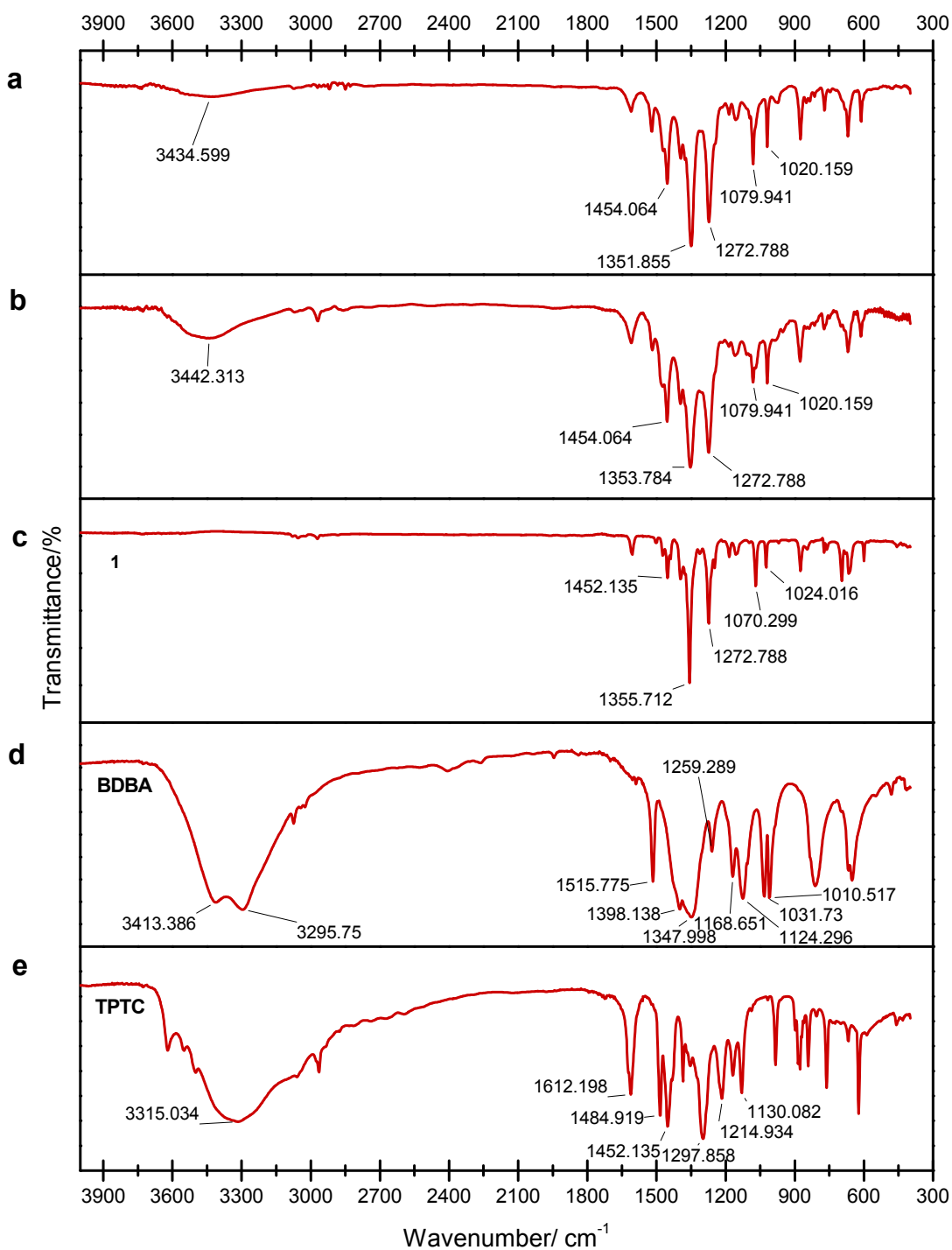


Figure S2. FT-IR spectra ($400\text{--}4000\text{ cm}^{-1}$) of (a) The mixture of Monolayer-1 and Nanosphere-1, (b) Microsphere-1, (c) model compound **1**, (d) BDBA, and (e) TPTC. The bands of 3413.4 , 3295.8 and 3315.0 cm^{-1} are attributed to the O-H stretching vibrations of BDBA and TPTC. For model compound **1**, these bands disappear and the characteristic B-O stretching band (1355.7 cm^{-1}) and C-O stretching band (1272.8 cm^{-1}) of borate ester are observed. For Monolayer-1 and Nanosphere-1, the band

corresponding to O–H stretching are attenuated dramatically (The weak peaks in this region are attributed to the residual OH groups at the peripheral of polymers). The characteristic B-O and C-O stretching bands of borate ester are observed at 1351.9 and 1272.8 cm^{-1} respectively, which are very close to those observed for model compound **1**, confirming the formation of borate ester. The FT-IR spectrum of Microsphere-1 displays similar pattern as that of model compound **1**, also confirming that it consists of borate ester.

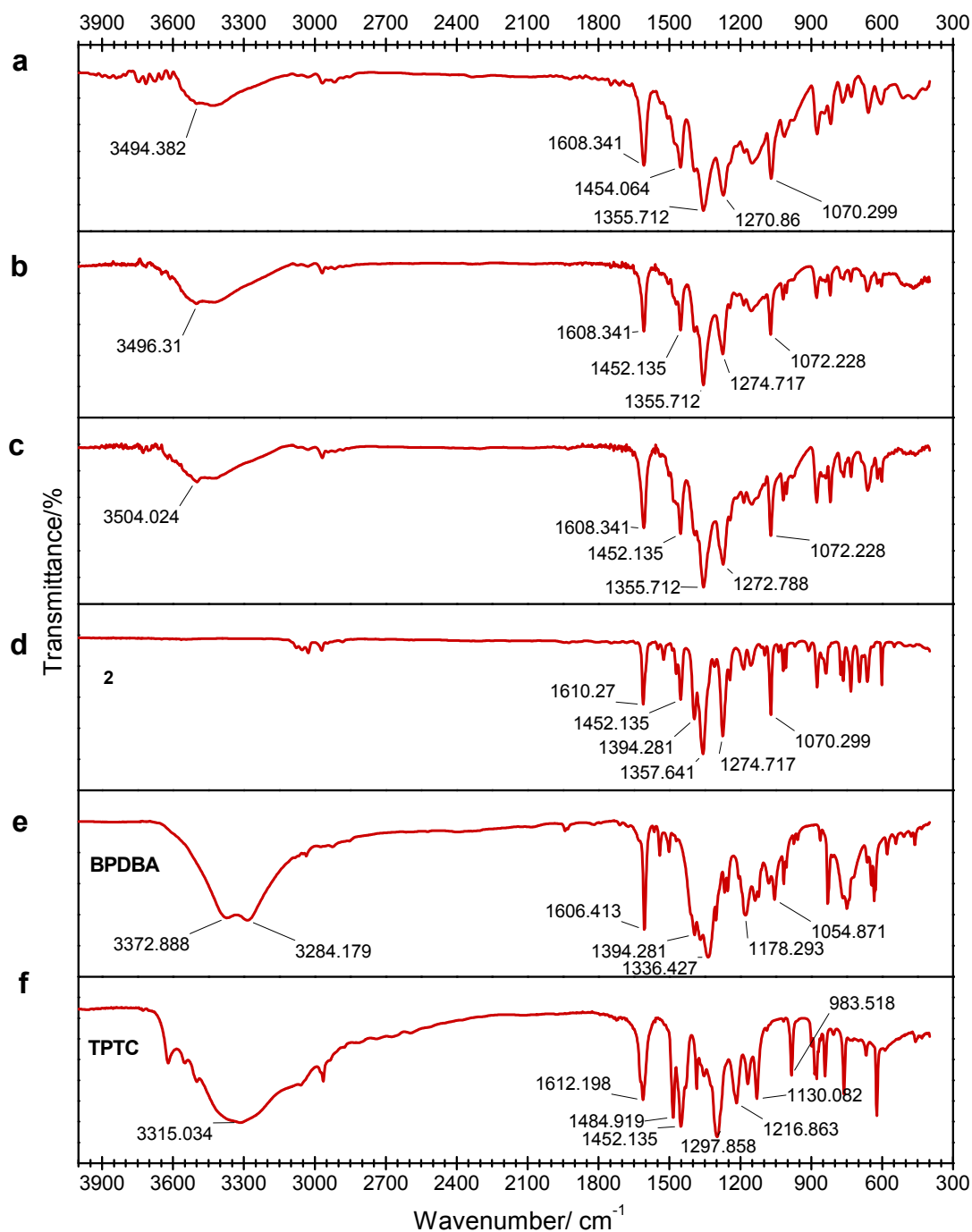


Figure S3. FT-IR spectra ($400\text{--}4000\text{ cm}^{-1}$) of (a) The visible floating films, (b) the mixture of Monolayer-2 and Nanosphere-2, (c) Microsphere-2, (d) model compound **2**, (e) BPDBA, and (f) TPTC. The visible floating films and both the samples obtained from solution (Monolayer-2 and Nanosphere-2) and the precipitate (Microsphere-2) display similar IR patterns as that of model compound **2**, confirming that they consist of boronate ester. The weak peaks in the region of O–H stretching vibration in figures **a** and **b** are attributed to the residual OH groups at the peripheral of polymers.

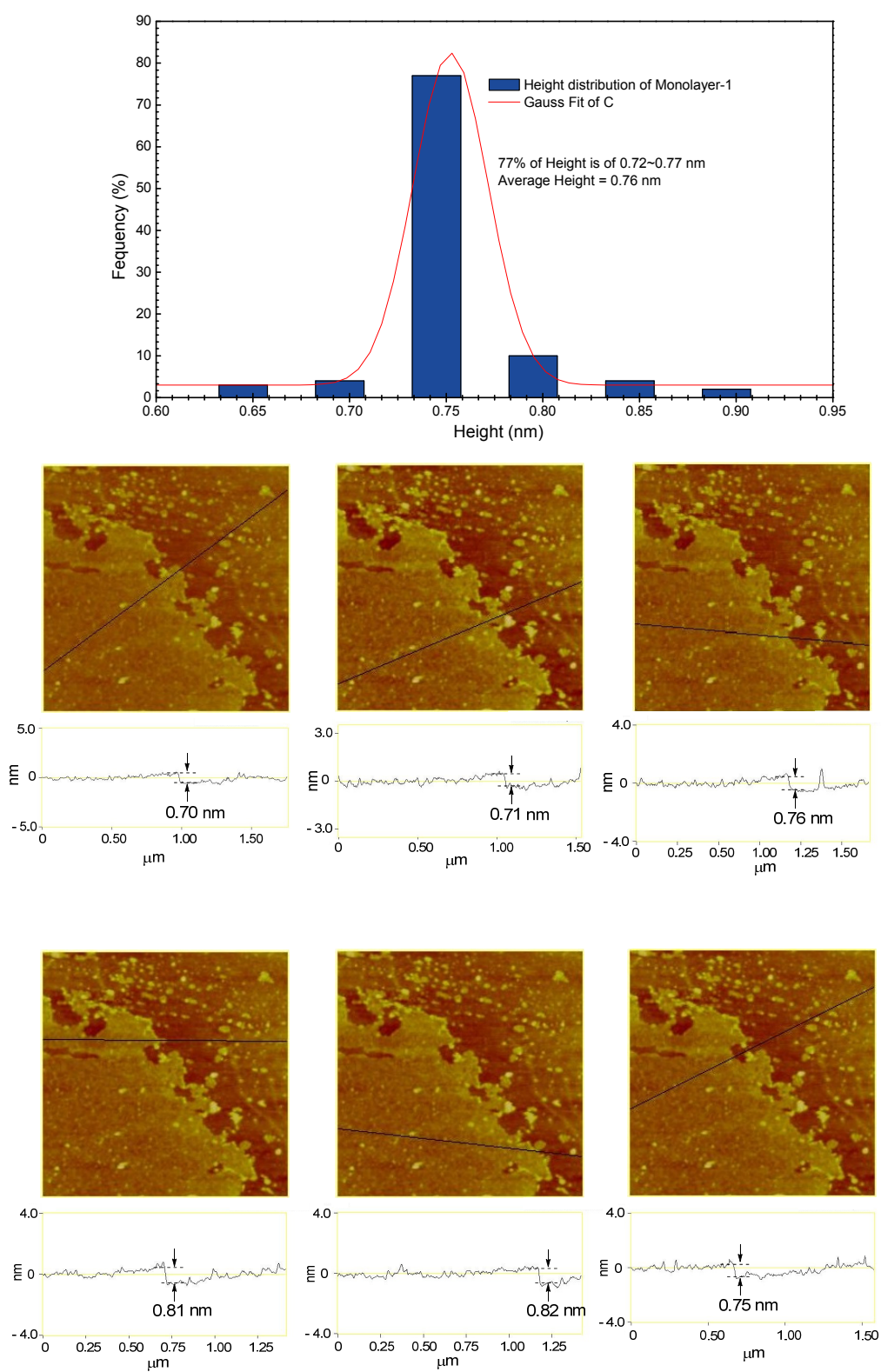


Figure S4. Height histogram of Monolayer-1 (top) obtained from 100 different sites in the AFM image (Fig. 2b) and the representative sites selected in the AFM image (middle and bottom).

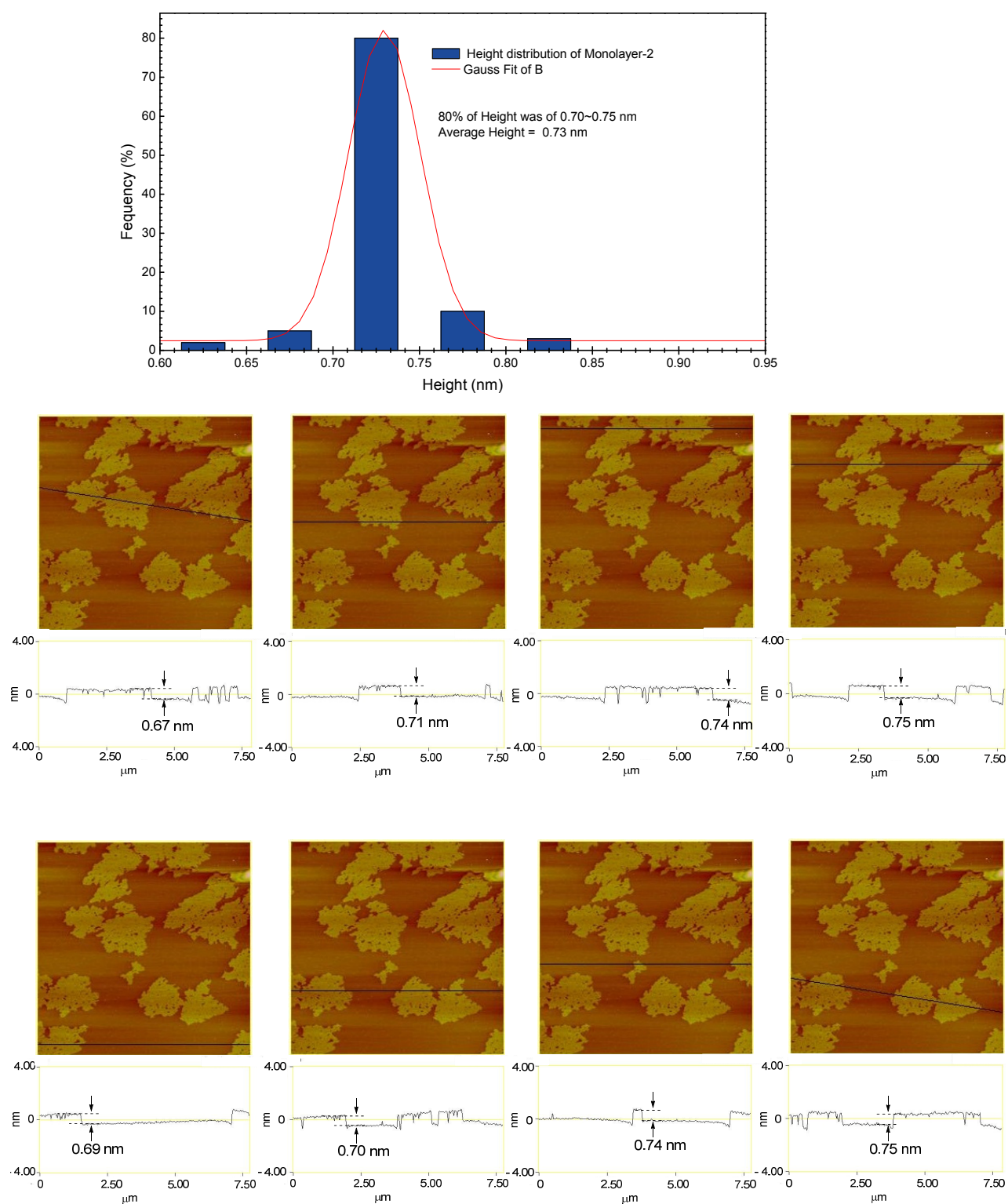


Figure S5. Height histogram of Monolayer-2 (top) obtained from 100 different sites in the AFM image (Fig. 2c) and the representative sites selected in the AFM image (middle and bottom).

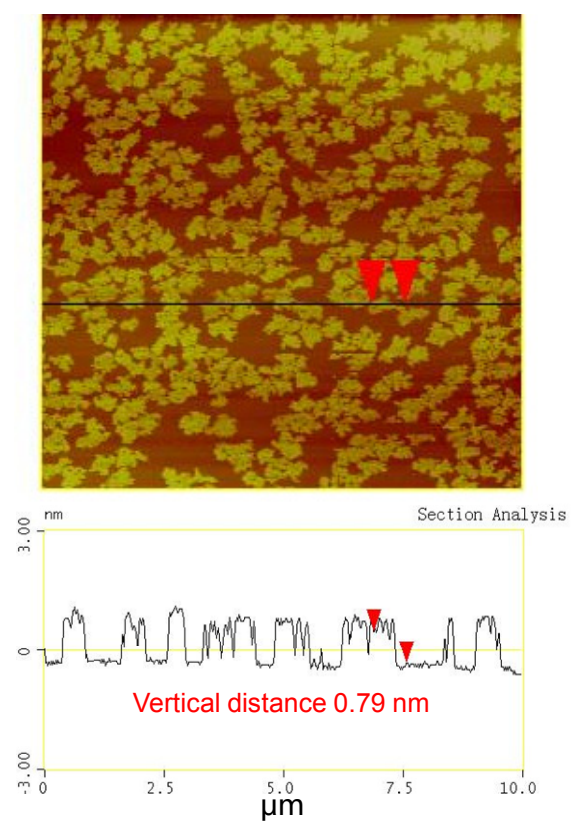


Figure S6. Lower magnification AFM image of Monolayer-2.

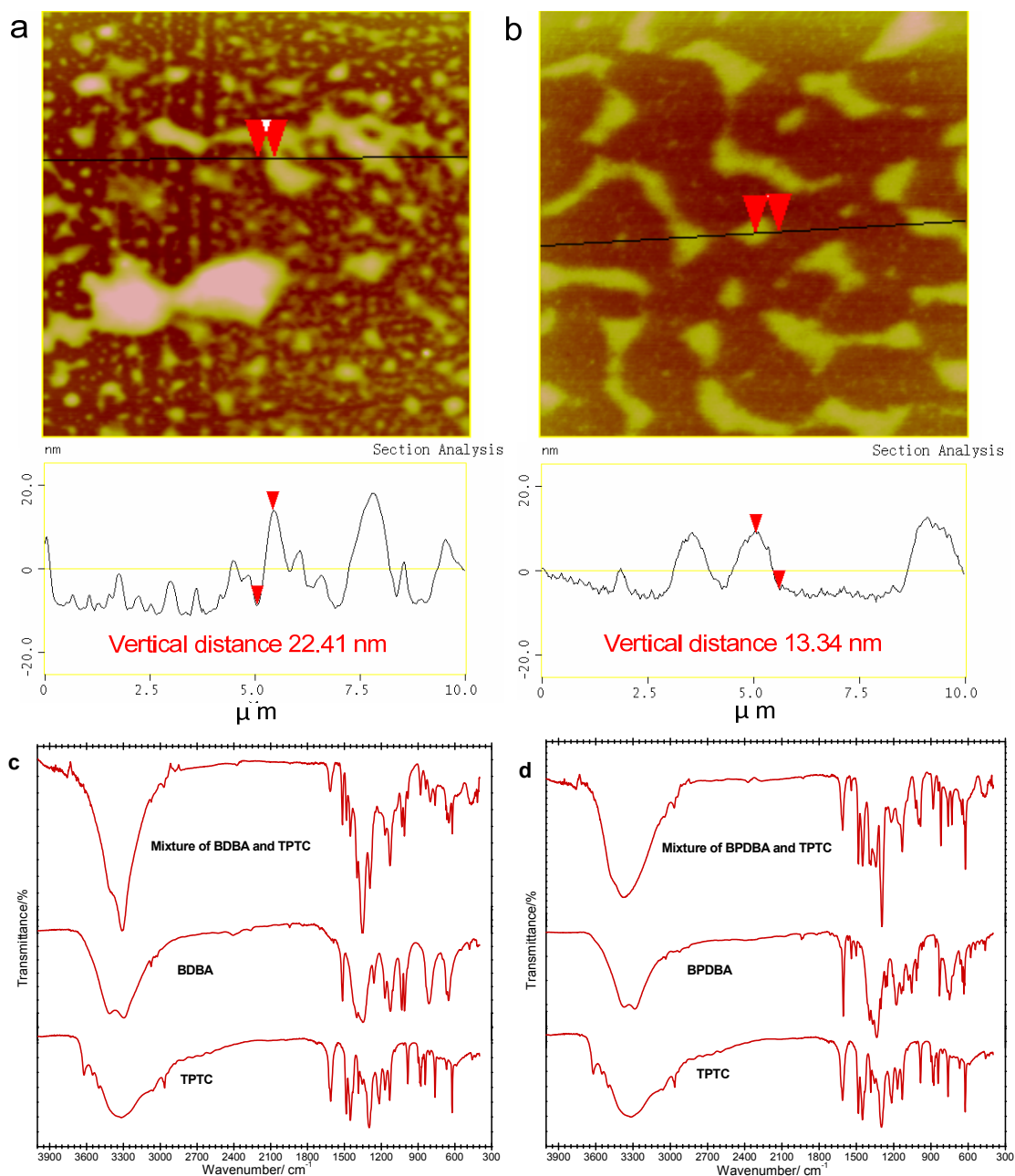


Figure S7. AFM images and cross-section analysis of (a) the mixture of TPTC and BDBA (2:3, molar ratio), and (b) the mixture of TPTC and BPDBA (2:3, molar ratio), in dioxane/mesitylene (1:1, v/v) without heating show characterless morphology, revealing that both Monolayer-1-2 and Nanosphere-1-2 were not generated by the self-assembly of unreacted starting materials. And (c) and (d) IR spectra of the above mixtures after evaporation of the solvent at room temperature. The IR spectra show hydroxyl signals with intensive intensity, indicating that the extent of condensation (if occurs) between TPTC and BDBA or BPDBA is quite low upon evaporation of the solvent under such condition.

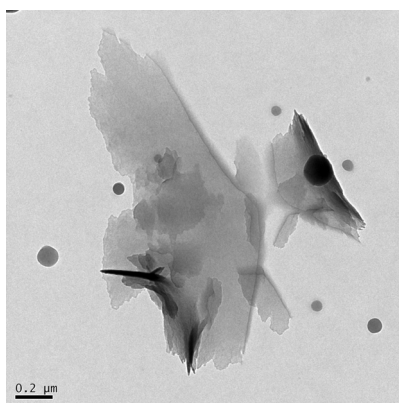


Figure S8. TEM image of Monolayer-1. The acceleration voltage used in the TEM experiment was 80 kV.

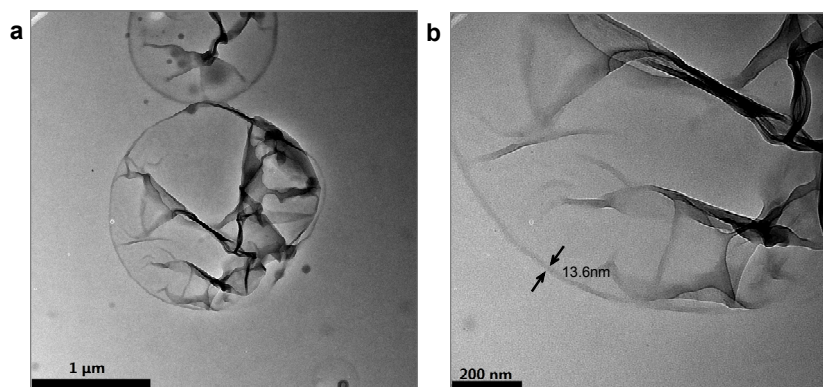


Figure S9. (a) HR-TEM image of multilayered spheres generated from TPTC and BPDBA, and (b) partial magnification of the figure a. The wall thickness is estimated to be ca. 13.6 nm.

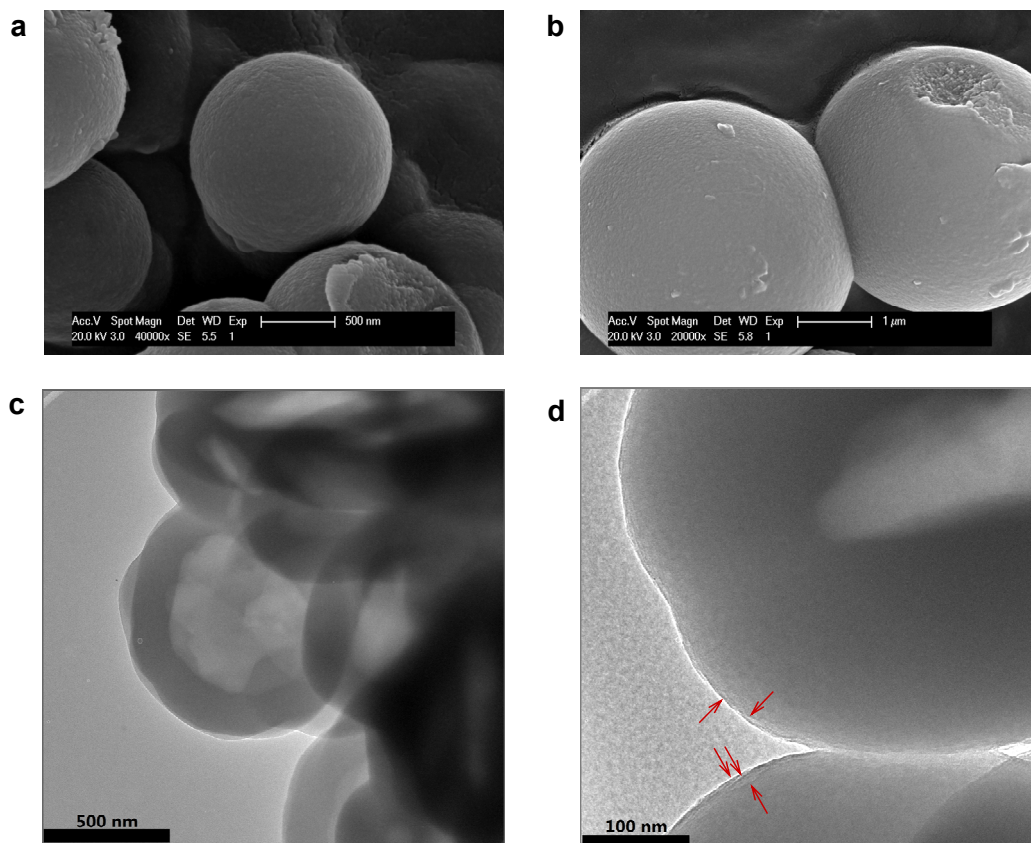


Figure S10. FE-SEM images of Microsphere-1 (**a**) and Microsphere-2 (**b**), showing their regular spherical morphology with smooth surface. And high resolution TEM images of Microsphere-1 (**c**) and Microsphere-2 (**d**). The layered structure is showed by red arrows, which gives the evidence that the stack between layers is disordered. The acceleration voltage used in the TEM experiment was 160 kV.

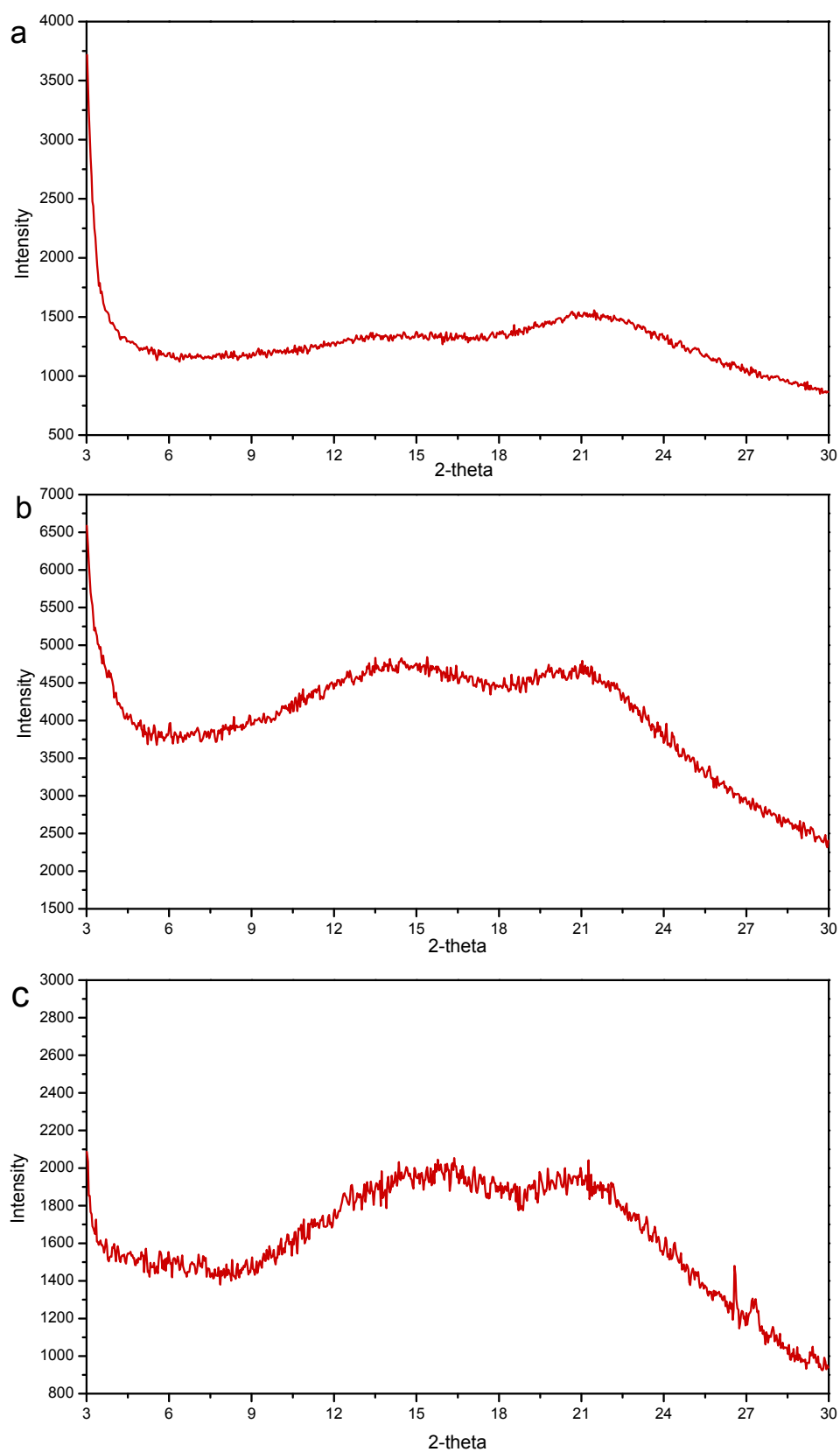


Figure S11. Wide-angle XRD patterns of the visible floating films (a), Microsphere-1 (b), and Microsphere-2 (c). The structure-less diffraction patterns suggest disordered aggradation between the monolayers.

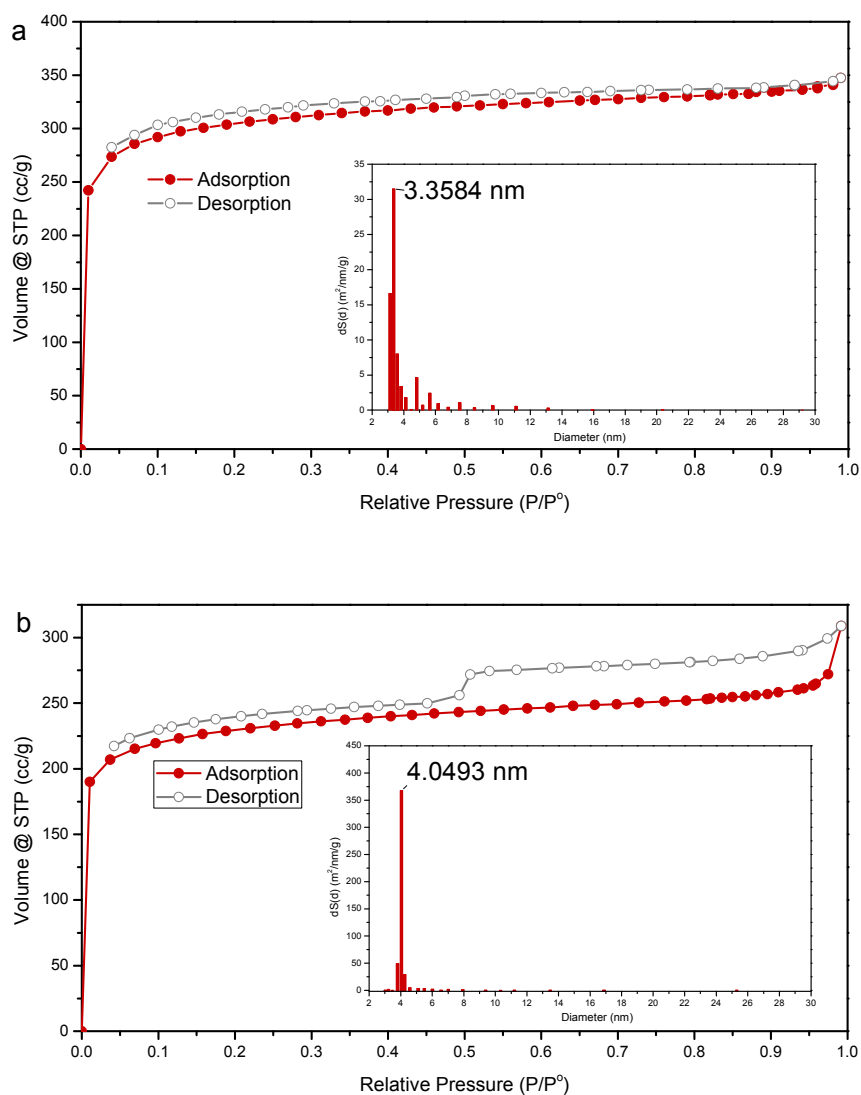


Figure S12. Nitrogen adsorption-desorption isotherms of Microsphere-1 (a) and Microsphere-2 (b). Inset: Pore size distributions. The values of pore sizes well match the theoretical pore widths calculated for the expected honeycomb-like units of the polymers, reflecting the formation of honeycomb-like frameworks.

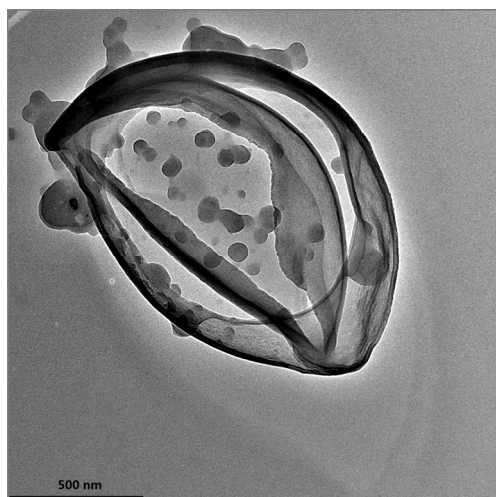


Figure S13. TEM image of a sample prepared from the polymerization reaction of TPTC and BPDBA at 24 h.

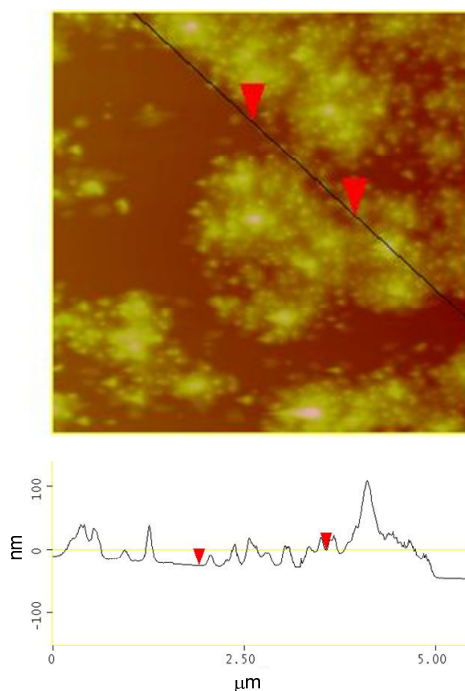


Figure S14. AFM image of the control experiment using pristine triptycene and BDBA under the same reaction condition used for preparing monolayer 2D polymers, clearly indicating that no film-like structures generated.

Supplementary reference

1. Côté, A. P. ; Benin, A. I.; Ockwig, N. W.; O'keeffe, M.; Matzger, A. J.; Yaghi, O. M.
Science **2005**, *310*, 1166–1170.