Supporting Information

Tessellation strategy for the interfacial synthesis of an anthracene-based 2D polymer via [4 + 4]-photocycloaddition

Renzeng Chen,[a] Danbo Wang,[a] Wenbo Hao,[a] Feng Shao,[b] and Yingjie Zhao[a]**

[a] College of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

[b] Department of Physics and Astronomy, National Graphene Institute, University of Manchester, Manchester, M13 9PL, UK

[*] Corresponding Authors: feng.shao@manchester.ac.uk; yz@qust.edu.cn

Table of Contents

1. Supporting Methods

1.1 General materials and methods

The reagents and solvents employed were commercially available and used without further purification. ^{1}H and ^{13}C NMR spectra were performed on 500 MHz spectrometers (Bruker AVANCE-III 500) or 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. Chemical shifts were reported in δ (ppm) relative to TMS ($\delta = 0$). Unless stated otherwise, column chromatography was carried out on silica gel (200-300 mesh). Thin-layer chromatography (TLC) analysis was performed on precoated silica gel plates (0.2 mm thick). Scanning electron microscopy (SEM) images were collected at an accelerating voltage of 5.0 kV (JEOL, JSM-7500F). Atomic Force Microscope (AFM) images were recorded on Bruker Multimode 8 setup with Nanoscope V controller. Raman spectra were recorded from the HORIBA Raman spectrometer (LabRAM HR Evolution), with an excitation wavelength of 532 nm and a spot diameter of 1 μm. The LB trough used in the experiment was KSV Mediumtrough (KSV NIMA, Finland) with 243 cm^2. The trough was made of Teflon, and the two symmetrical barriers were made of Delrin. For BAM measurements, a 659 nm laser from the MicroBAM (KSV NIMA, Finland) was used. In order to collect total reflection without membrane, a piece of black glass was placed inside the Langmuir trough (Teflon). The microscope images of all the images were acquired by an optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera.

1.2 Synthesis

Compounds **3**, **4**, **5** were synthesized according to the literature.[1]

Compound **3**: 1,2,4,5-tetramethylbenzene (6.72 g, 0.05 mol) was dissolved in 500 mL of carbon tetrachloride. The solution was heated to reflux and irradiated with a 200 W sun lamp. Bromine (25 mL, 0.5 mmol) was slowly added to the stirring solution. After 48 h, the product was collected by filtration, washed with water and then with boiling chloroform to provide 32.5 g (0.042 mol) of compound **3** (85% yield).

Compound **4**: Compound **3** (7.65g, 0.01 mol), N-Phenylmaleimide (3.50 g, 0.02 mol) and dry NaI (15 g, 0.1 mol) were placed in a 250 mL flask with 80 mL DMAc under nitrogen. After 10 h, a yellow precipitate formed. The precipitate was filtered, triturated once with boiling water and three times with boiling *p*-dioxane, and dried, provided 1.5 g of compound **4** (30% yield).

Compound **5**: Compound **4** (2.00 g, 4.1 mmol) and 50 mL of 20% NaOH aqueous solution were charged into a round-bottomed flask and refluxed under nitrogen for 12 h. The resulting solution was decolorized with charcoal and extracted with ether. The aqueous solution was acidified and the resulting yellow precipitate was isolated by centrifugation, washed with distilled water, recentrifuged, and dried in vacuo, provided 1.2 g of compound **5** (80% yield).

Compound **1** was synthesized according to the literature.[2]

A mixture of compound **5** (1 g, 2.85 mmol) and Ac_2O/AcOH (1:1 v/v, 20 mL) was heated under reflux for 12 h. The reaction mixture was then cooled to room temperature, and the precipitate was isolated by filtration to provided compound **1** (0.8 g, 88%).

Tri-ADI: (1*R*,2*R*)-1,2-Diaminocyclohexane (**2**) (30 mg, 0.26 mmol) and compound **1**

(85 mg, 0.26 mmol) were refluxed in acetic acid (5 mL) for 3 days. The solvent was removed in vacuo and the residue was digested by refluxing with dichloromethane for 1 h. The crude product was removed from the dichloromethane extract by filtration and the filtrate was concentrated to dryness. Column chromatography of the residue on silica gel eluting with CH_2Cl_2/10% Acetone afforded **Tri-ADI** as a light yellow solid (15 mg yield 15%). ^{1}H NMR (300 MHz, Chloroform-*d*) 8.48 (s, 6H), 8.26 (s, 12H), 5.35 (m, 6H), 2.11 (m, 6H), 2.03 – 1.73 (m, 12H), 1.59 (m, 6H); HRMS (MALDI, +ve): calcd. for $C_{72}H_{49}N_6O_{12}$ ($[M + H]^+$): 1189.3408, found: 1189.3396; $C_{72}H_{48}N_6NaO_{12}$ ($[M + H]^+$): 1211.3228, found: 1211.3215.

1.3 DFT calculations

Theoretical Raman spectra were calculated using the Gaussian 09 software (Gaussian, Wallingford, USA) by means of DFT. All calculations, including full geometry optimizations and frequency predictions, were performed using B3LYP/6-31+G(d) basis. The keyword Integral = (Grid=UltraFine, Acc2E=11) was used to increase the two-electron integral accuracy when SCF calculations failed to converge using default run parameters. All calculated frequencies were scaled with proper factors compared to confocal Raman spectra. The optimized geometry and the calculated vibrational modes were visualized using the Gaussview 5 package.[3]

1.4 References

1. J. L. Morris, C. L. Becker, F. R. Fronczek, W. H. Daly and M. L. McLaughlin, *J. Org. Chem.*, 1994, **59**, 6484-6486.
2. Z.-H. Wu, Z.-T. Huang, R.-X. Guo, C.-L. Sun, L.-C. Chen, B. Sun, Z.-F. Shi, X. Shao, H. Li and H.-L. Zhang, *Angew. Chem. Int. Ed.*, 2017, **56**, 13031-13035.
3. F. Shao, W. Dai, Y. Zhang, W. Zhang, A. D. Schlüter and R. Zenobi, *ACS Nano*, 2018, **12**, 5021-5029.

2. Supporting Figures

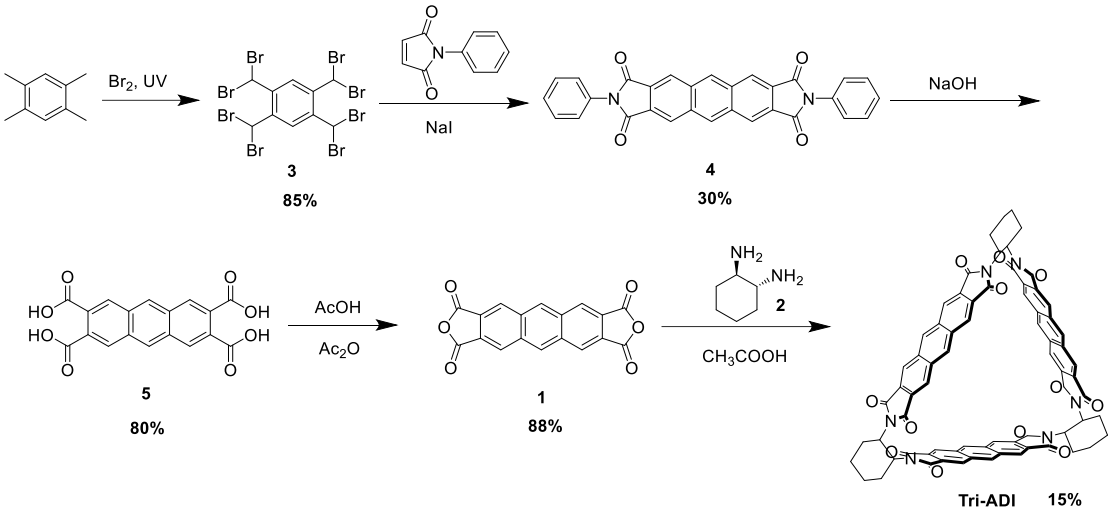

Figure S1. Synthetic scheme of **Tri-ADI**.

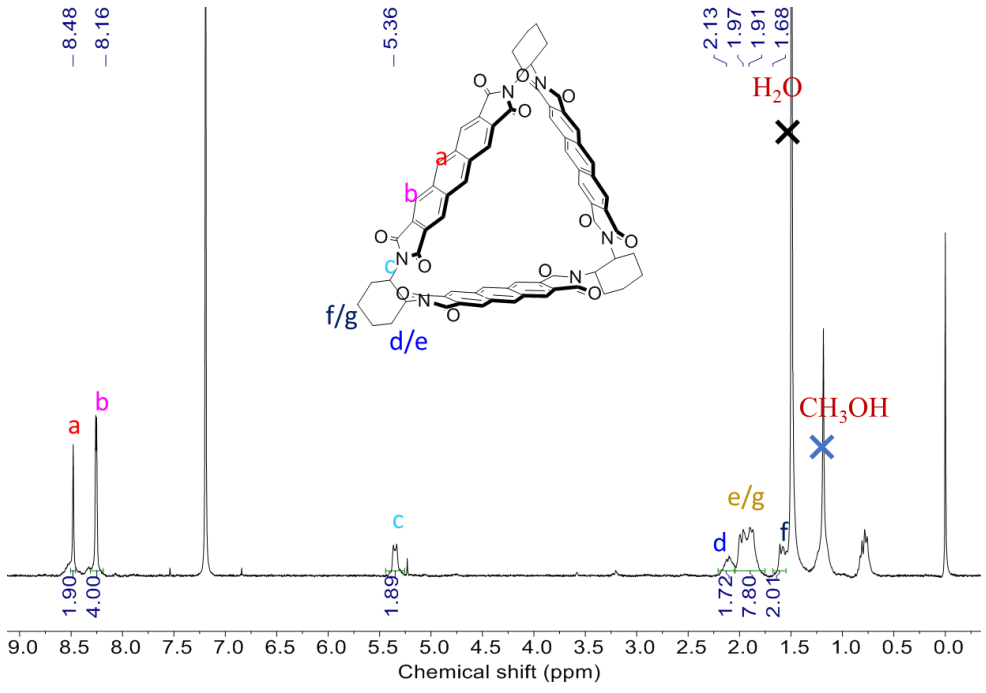

Figure S2. ^{1}H NMR (400 MHz) spectrum of **Tri-ADI** in $CDCl_3$.

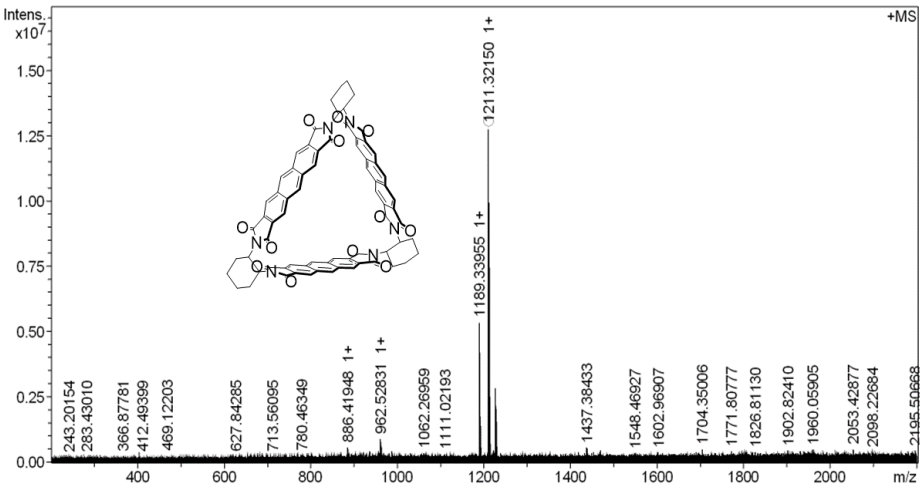

Figure S3. The high-resolution mass spectrum of **Tri-ADI**.

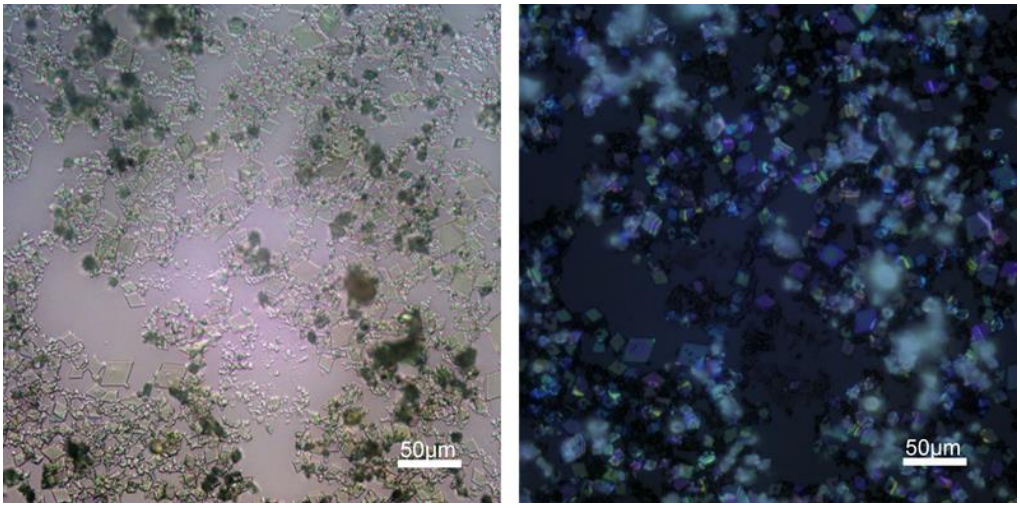

Figure S4. Optical microscope images of **Tri-ADI** single crystals. Left: transmission mode. Right: reflection mode.

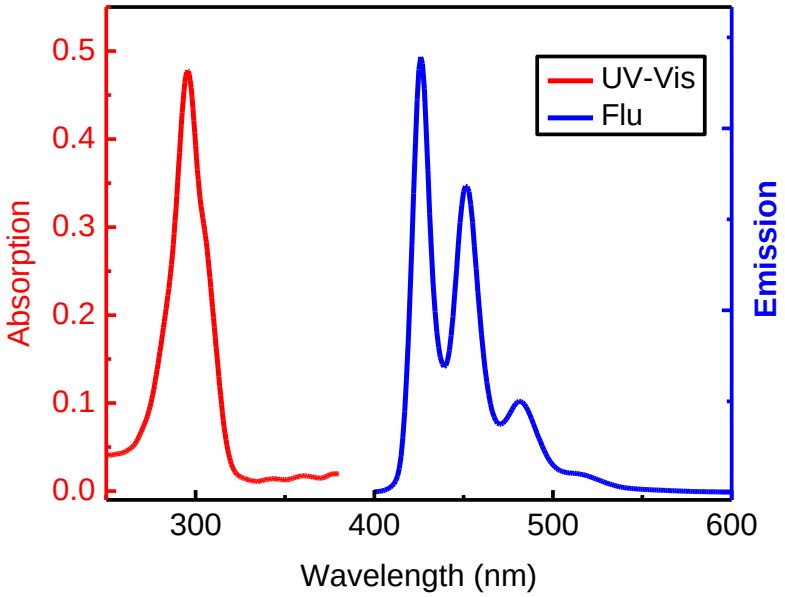

Figure S5. UV-Vis and fluorescence spectra of **Tri-ADI** in $CHCl_3$ at room temperature (Concentration of **Tri-ADI** for the UV-Vis spectrum measurement is 1.5×10^{-6} M. Concentration of **Tri-ADI** for the fluorescence spectrum is 2×10^{-5} M with an excitation wavelength of 300 nm).

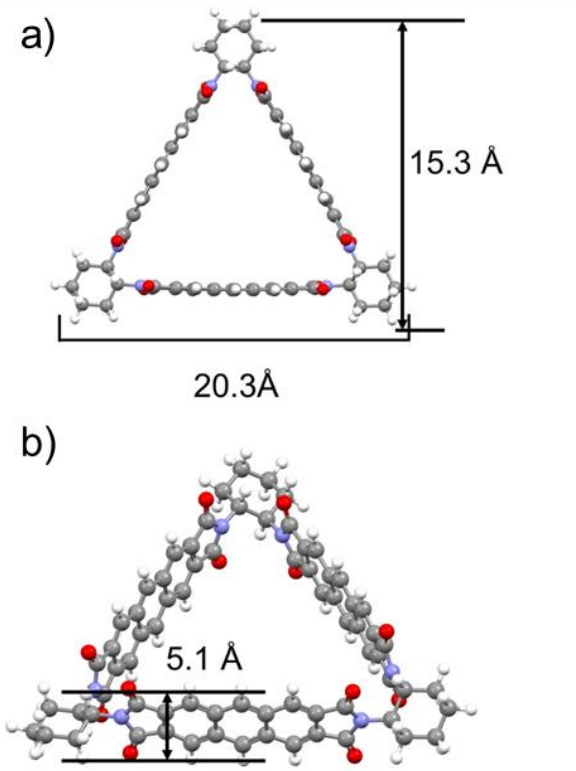

Figure S6. DFT optimized dimensions of **Tri-AID.**

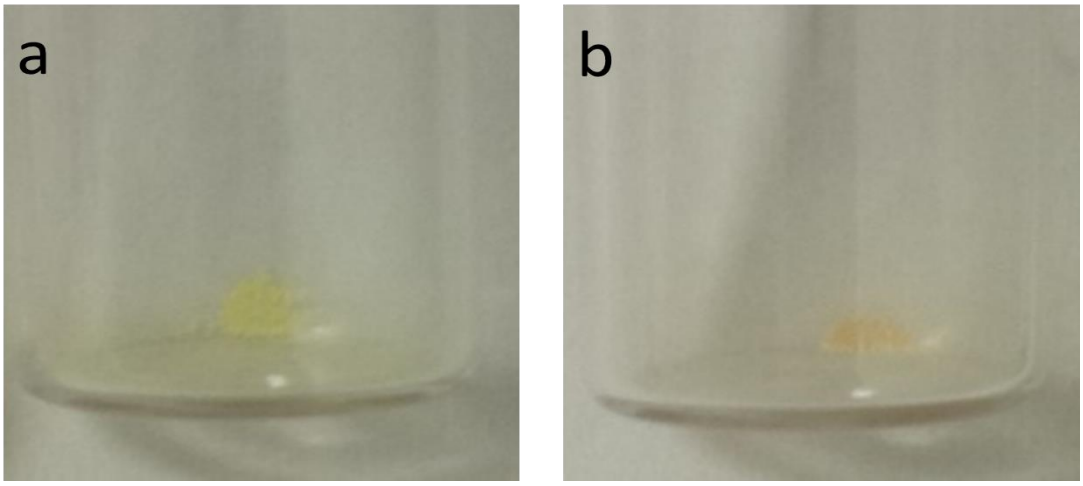

Figure S7. The color change of the **Tri-ADI** to the 2DP single-crystals before and after 450 nm LED irradiation for 24 h. a: before irradiation; b: after irradiation. To avoid the influence of oxygen, the photo-irradiation experiment was performed under the N_2 atmosphere.

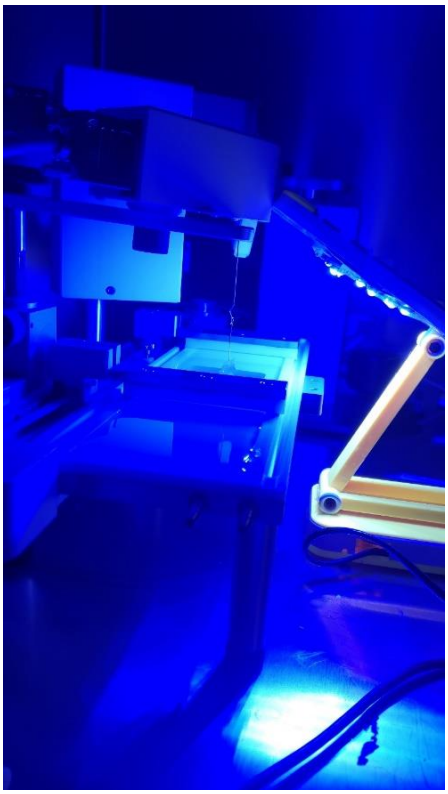

Figure S8. Photopolymerization progress of the pre-assembled monomers under the irradiation with a home-made 450 nm LED lamp (36 W)

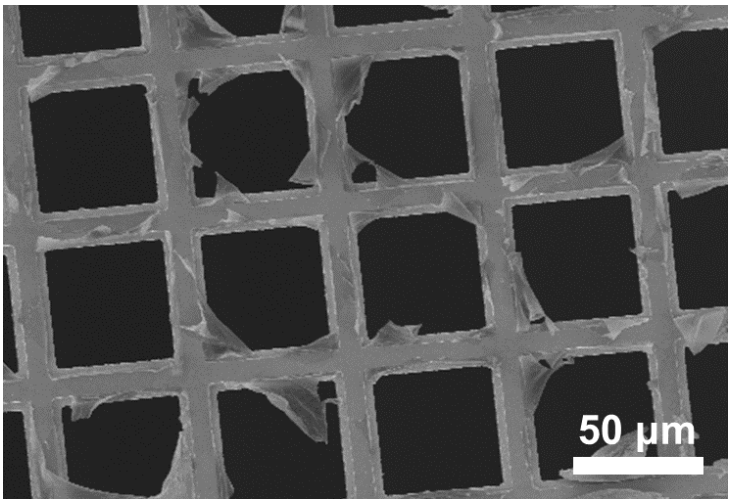

Figure S9. SEM images of the monomer films under compression with a surface pressure of 10 mN/m.

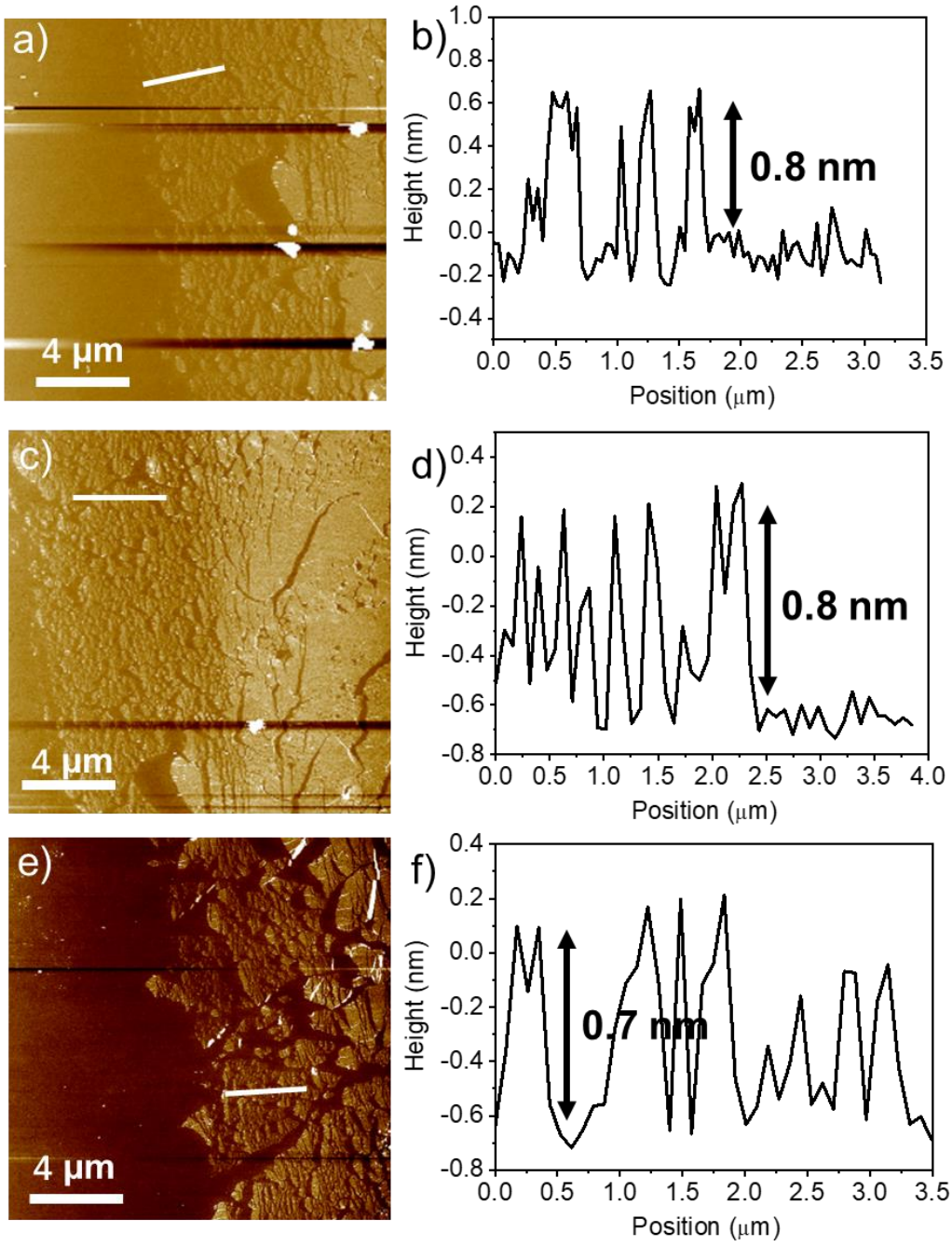

Figure S10. AFM images of the obtained 2DP films under compression with a surface pressure of 0 mN/m.

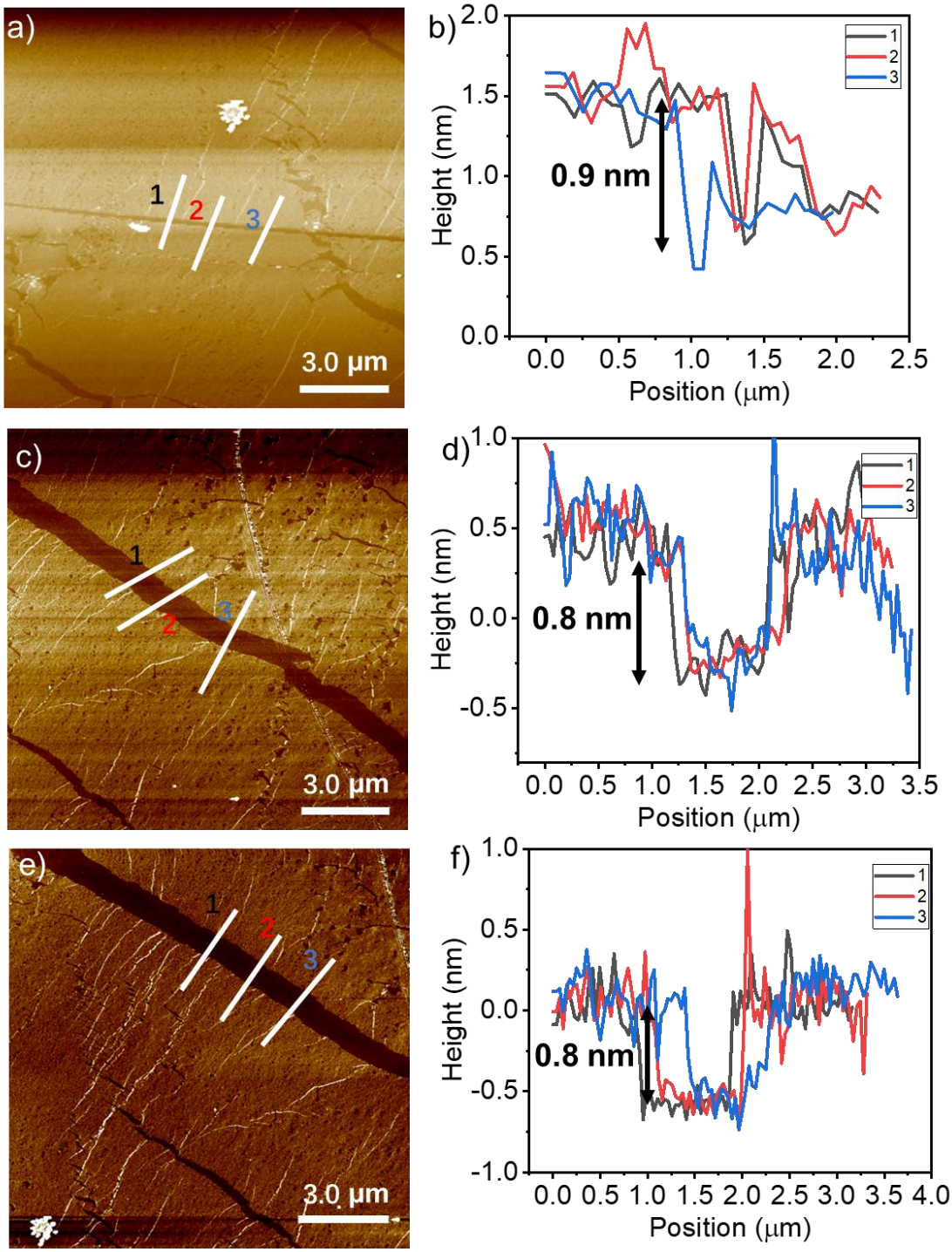

Figure S11. AFM images of the obtained 2DP films under compression with a surface pressure of 5 mN/m.

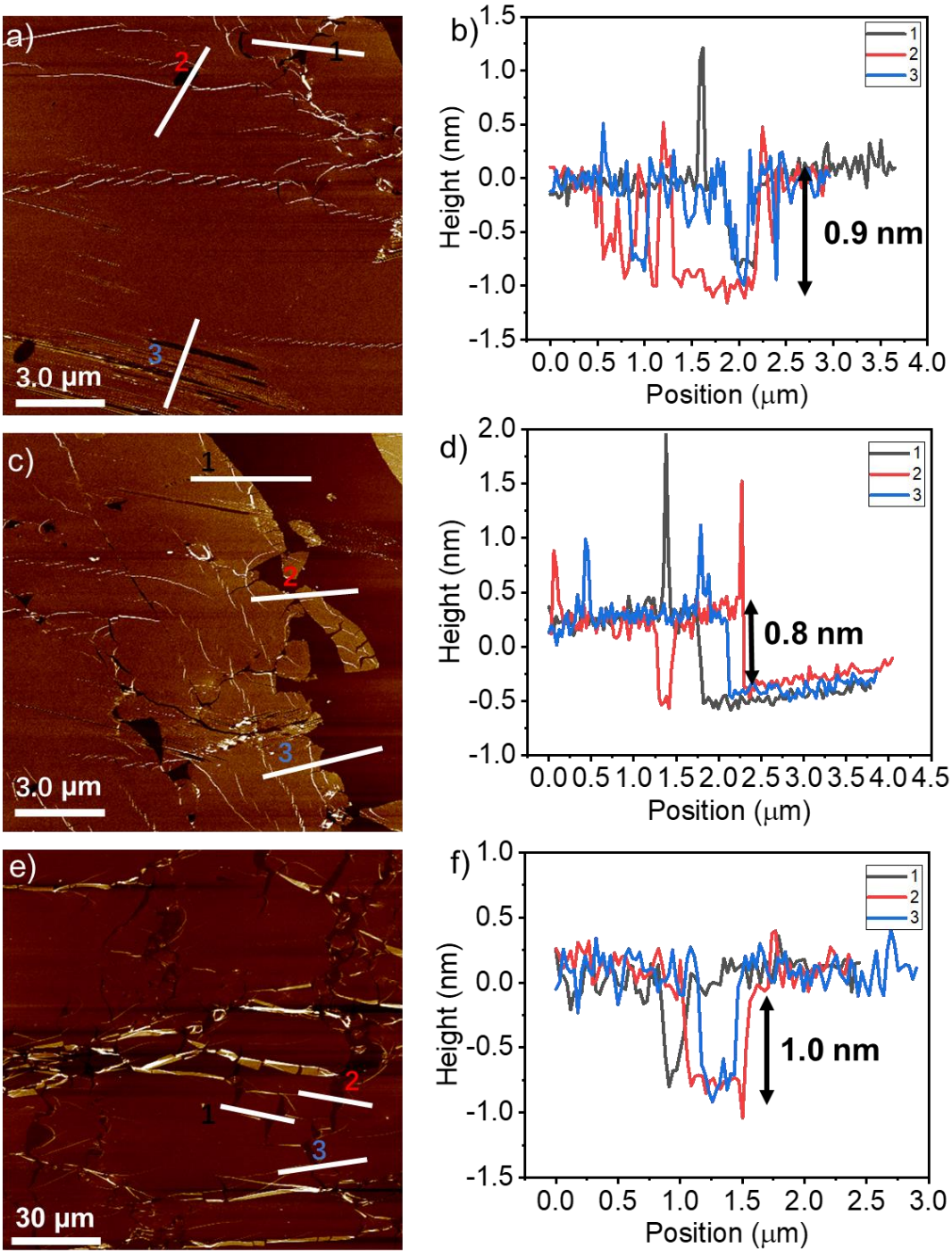

Figure S12. AFM images of the obtained 2DP films under compression with a surface pressure of 10 mN/m.

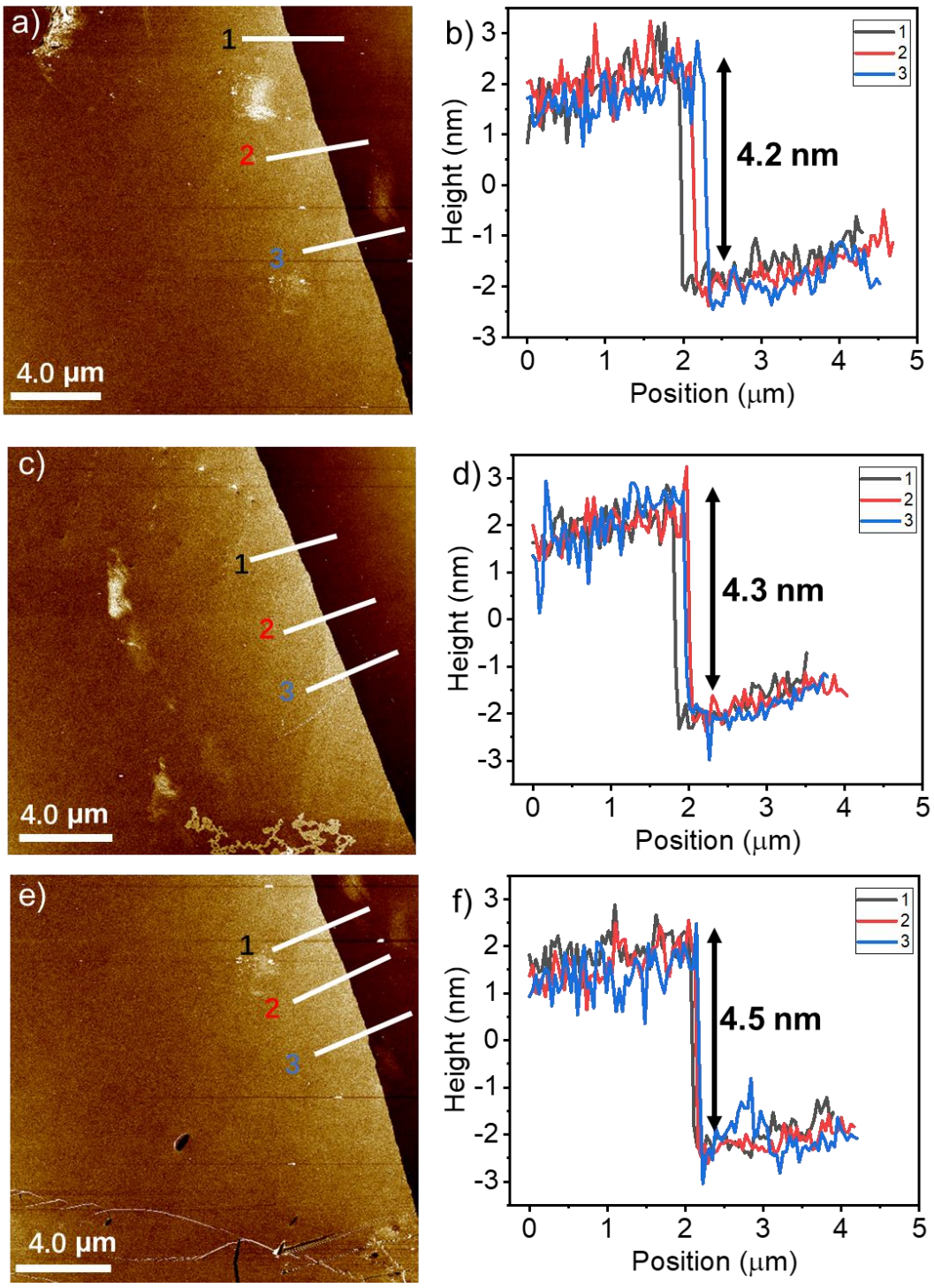

Figure S13. AFM images of the obtained 2DP films under compression with a surface pressure of 15 mN/m.

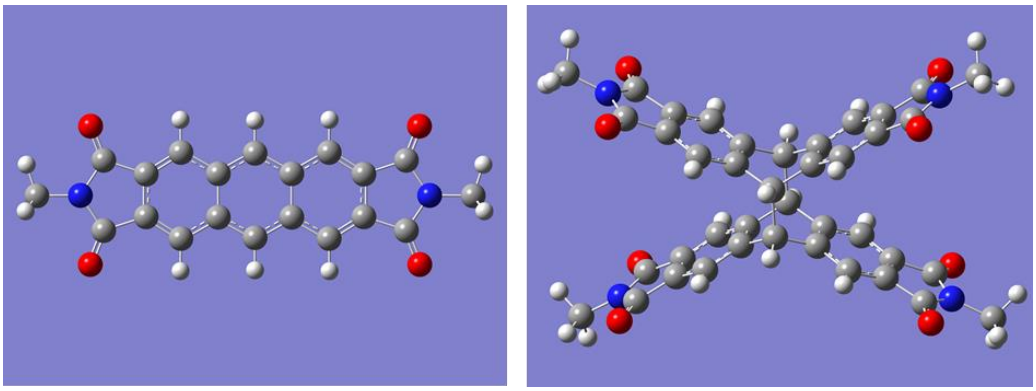

Figure S14. The monomer (left) and dimer (right) models for DFT calculations.