

Supporting Information

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Materials and Methods

1. Chemicals & Reagents

The following chemical reagents were purchased from the indicated suppliers and used as received unless otherwise stated: Zinc chloride (Alfa, anhydrous, 98+%), 1,4-Dicyanobenzene (DCB)(Alfa, 98%), Sodium cyanide (Aldrich, 97%) and Cyanuric chloride (Alfa, 98%). 2,4,6-Tricyano-1,3,5-triazine (TCT) was prepared according to the literature. Solvents (e.g. MeCN, CH₂Cl₂) were dried or purified according to standard procedures prior to use.

2. Characterization

Elemental Analysis was performed with an Elemental Analyser 1112 FlashEA. The ¹³C solid-state cross-polarization magic angle spinning (CP-MAS) NMR spectrum was obtained on a 100 MHz NMR Varian Spectrometer. Fourier transform infrared (FTIR) spectra were collected with a FTIR 2000 Perkin Elmer spectrometer. Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-7600F SEM operating at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (PXRD) data were recorded on a SHIMADZU XRD-6000 diffractometer from $2\theta = 5^\circ$ up to 70° with 0.02° increment. Gas sorption isotherms were obtained with Quantachrome Autosorb-iQ-MP. The samples were degassed overnight at 150 °C. Thermogravimetric analyses (TGA) were performed on a TGA 500 thermogravimetric analyzer by heating the samples at 5 °C min⁻¹ to 800 °C in the atmosphere of nitrogen. ICP-MS analysis was carried out on the Agilent 7700-Japan equipment. The Raman spectra were carried out with Renishaw - inVia Raman system, with excitation laser wavelength of 514 nm and 100× objective lens, and the laser power at sample is below 1 mW to avoid possible laser heating induced sample damage. High resolution 300kV TEM with DX4 EDS system + Gatan Filter, CM300 Feg (Philips) was employed to examine the particulate properties. AFM spectra was recorded on the Dimension ICON Atomic Force Microscope with ScanAsyst. XPS was measured on the XPS VG 220i-XL (ESCALab). Electron Spin Researonce Spectra were carried out on the Bruker A300 EPR Spectrometer

3. Synthesis of 2,4,6-Tricyano-1,3,5-triazine (TCT)

The synthesis is referenced by the previous reports [S1-S2] with necessary modifications : 27.6 g (0.15 mol) of cyanuric chloride was suspended in 500 ml anhydrous MeCN at 0 °C, then 29.4 g (0.60 mol, 4eq) NaCN was added with stirring. The system was sealed and vigorously stirred for 12 hrs at 0 °C, then at room temperature for another 48 hrs. The resulting NaCl and unreacted NaCN were filtered and destroyed in a KMnO₄ and H₂O₂ mixture bath; and the brown filtrate was concentrated to dryness under reduced pressure

in a rotary evaporator at room temperature. The oily residue was stirred vigorously with 250 ml anhydrous CH_2Cl_2 for 12 hrs at room temperature to extract the crude product. After filtering off insoluble material, the filtrate is concentrated to dryness under reduced pressure in a rotary evaporator at room temperature, yielding the dry brown powders of crude TCT, which was purified by sublimation in the reduced pressure distillation system at 110 °C to give white prismatic crystals. Yield: 49.7% FTIR (KBr, cm^{-1}) 2255, 1653, 1516, 1338, 939, 821. ^{13}C -NMR (100 MHz, CDCl_3 , ppm) 154, 110.

4. *Synthesis of 2D polymer model from DCB monomer*

The synthesis is following the previous reports [21]: 1,4-dicyanobenzene (1.0 g, 7.8 mmol) and ZnCl_2 (5.32 g, 39.0 mmol) were transferred into the quartz ampule under an inert atmosphere. The ampule was evacuated, sealed, and heated to 400 °C for 40 hrs. The ampule was then cooled down to room temperature and opened. The reaction mixture was subsequently grounded and then washed thoroughly with water to remove most of the ZnCl_2 . Further stirring in diluted HCl (1 mol/L) overnight was carried out to remove the residual salt. The resulting black powder was filtered, washed successively with water and THF, and dried in vacuum at 150 °C. Elemental Analysis Found: C 59.17; H 4.45; N 12.11. FTIR (KBr, cm^{-1}) 3184, 1618, 1521. Solid ^{13}C -NMR (100 MHz, ppm) 128.

5. *Synthesis of 2D polymer from TCT monomer*

Similar with above procedures: TCT monomer (1.0 g, 6.4 mmol) and ZnCl_2 (5.32 g, 39.0 mmol) were transferred into the quartz ampule under an inert atmosphere. The ampule was evacuated, sealed, and heated to 400 °C for 40 hrs. The ampule was then cooled down to room temperature and opened. The reaction mixture was subsequently grounded and then washed thoroughly with water to remove most of the ZnCl_2 . Further stirring in diluted HCl (1 mol/L) overnight was carried out to remove the residual salt. The resulting black powder was filtered, washed successively with water and THF, and dried in vacuum at 150 °C. Elemental Analysis Found: C 39.51; H 4.17; N 44.71. FTIR (KBr, cm^{-1}) 3141, 2986, 1700, 1653, 1520. Solid ^{13}C -NMR (100 MHz, ppm) 161.

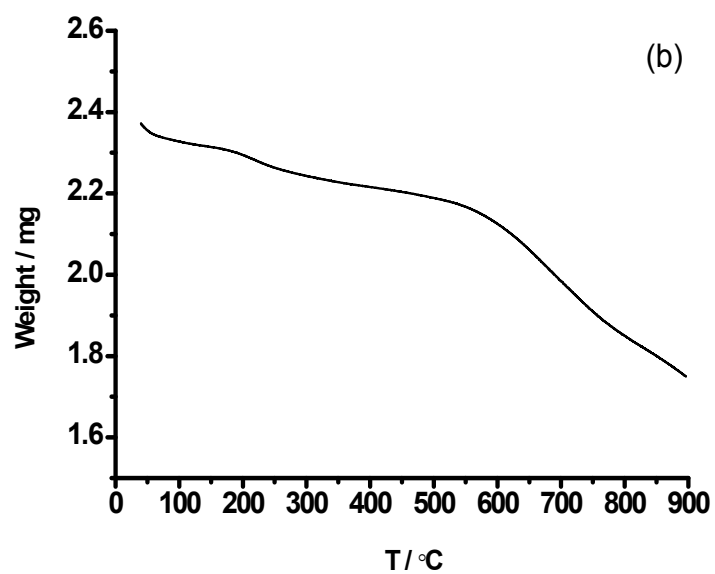
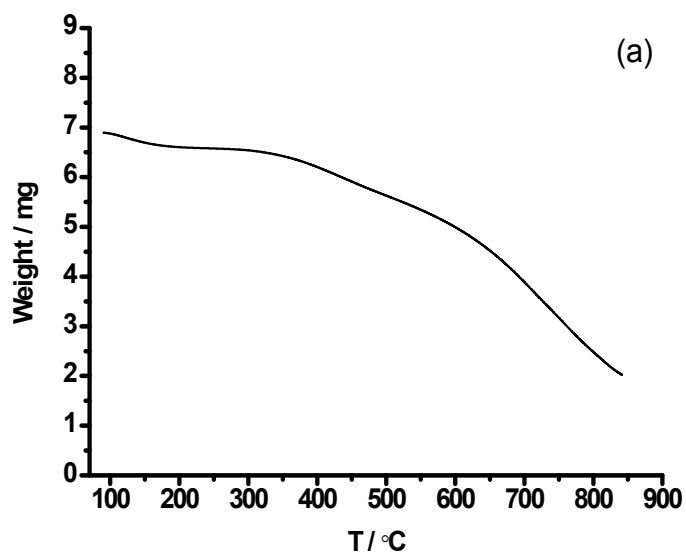


Figure S1. TGA trace for: (a) TCT based 2D polymer; (b) DCB based 2D polymer. Experimental conditions: nitrogen atmosphere, heating rate of 5 °C min⁻¹ in the temperature range of 50-850 °C.

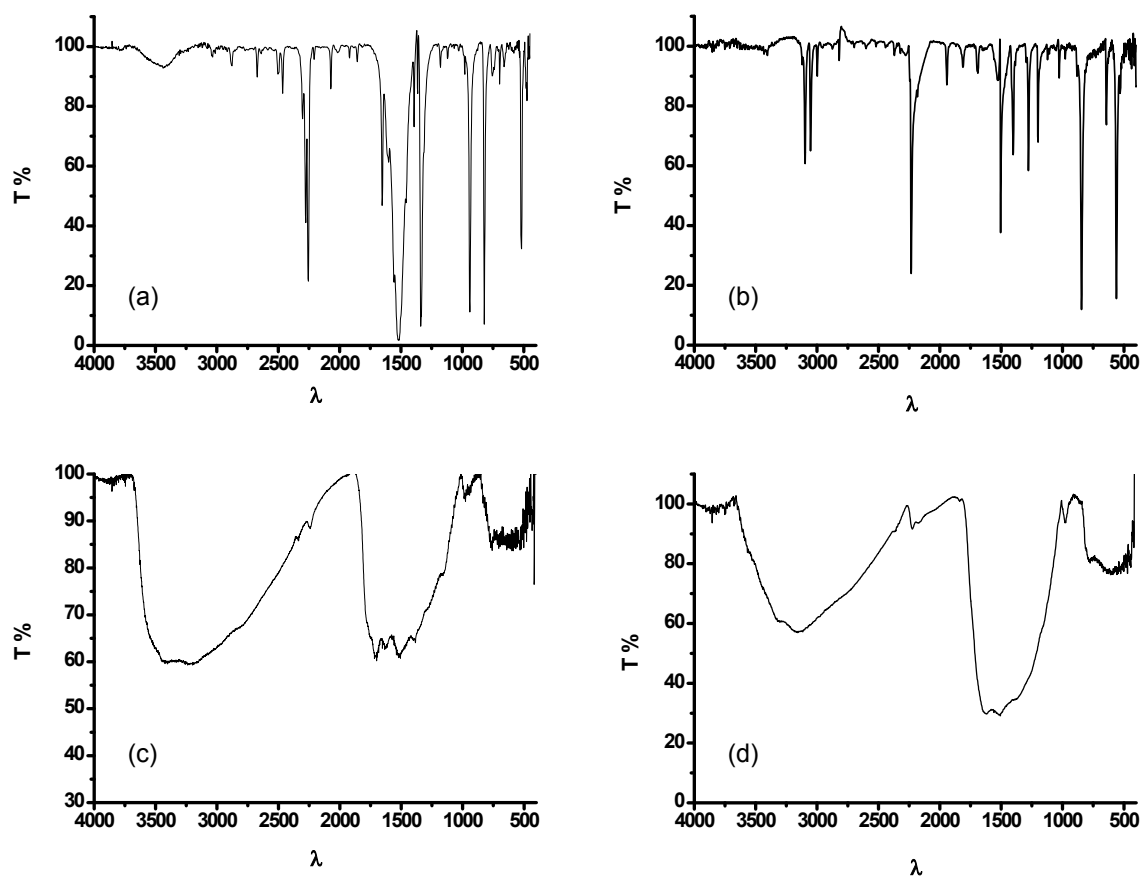


Figure S2. FT-IR spectra of: (a) TCT monomer; (b) DCB monomer; (c) TCT based 2D polymer; and (d) DCB based 2D polymer.

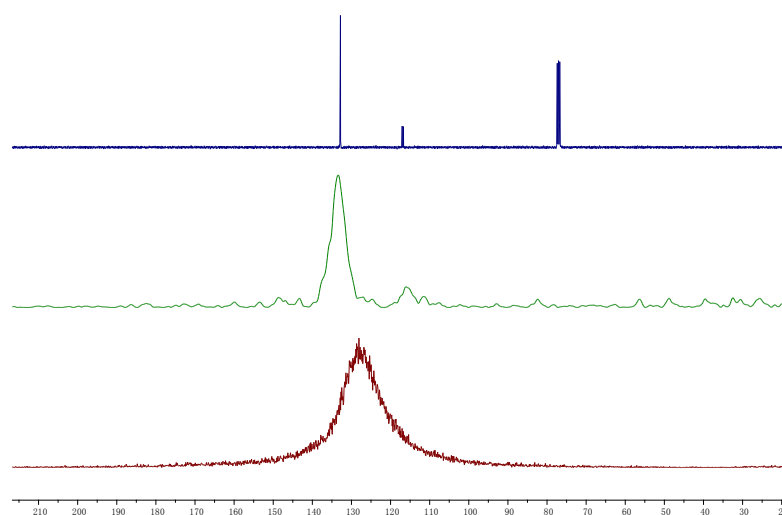


Figure S3. ^{13}C -NMR spectrum of the DCB monomer and polymer: ^{13}C -NMR spectrum of DCB monomer in CDCl_3 (Top line), ^{13}C CP-MAS NMR spectrum of the DCB monomer (Middle line), ^{13}C CP-MAS NMR spectrum of the DCB based polymer (Down line).

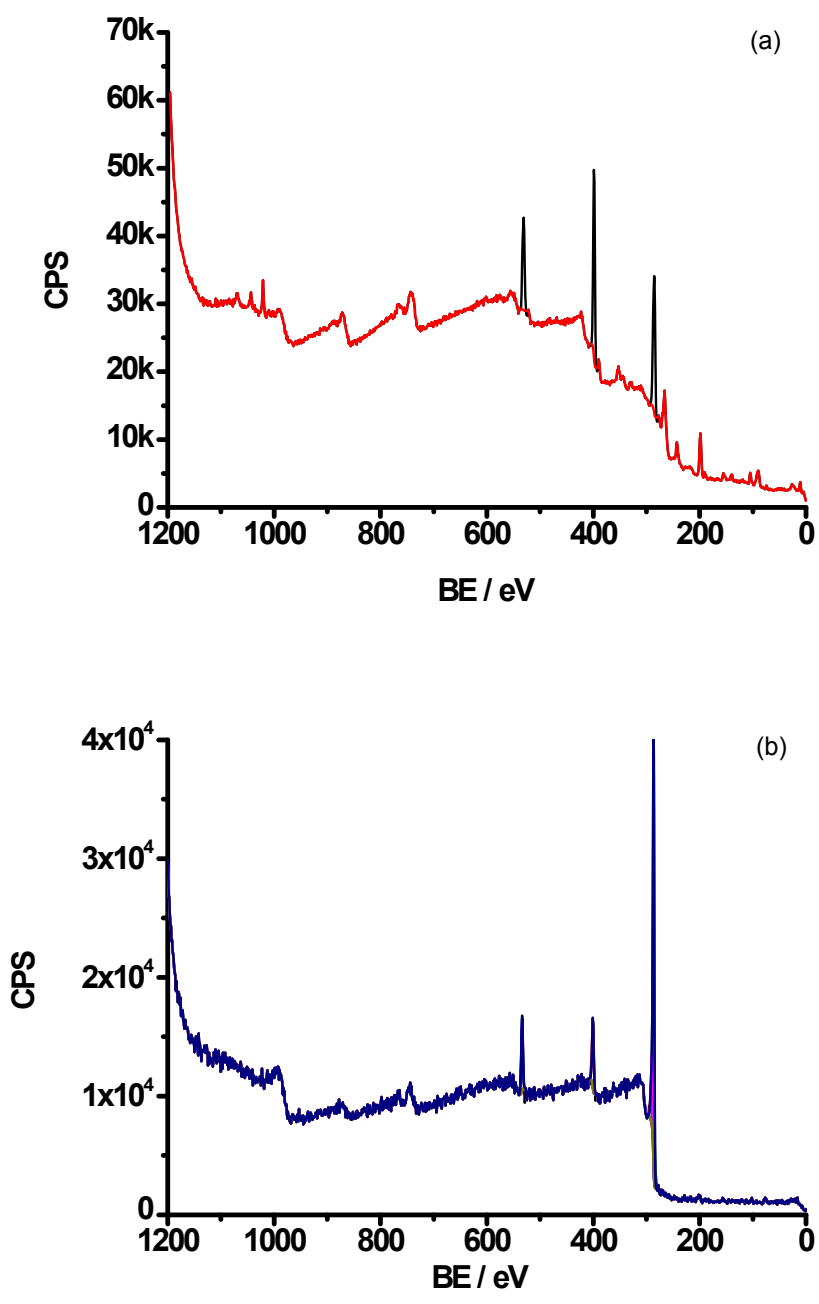


Figure S4. Broad scan survey XPS spectra of: (a) TCT based 2D polymer; (b) DCB based 2D polymer.

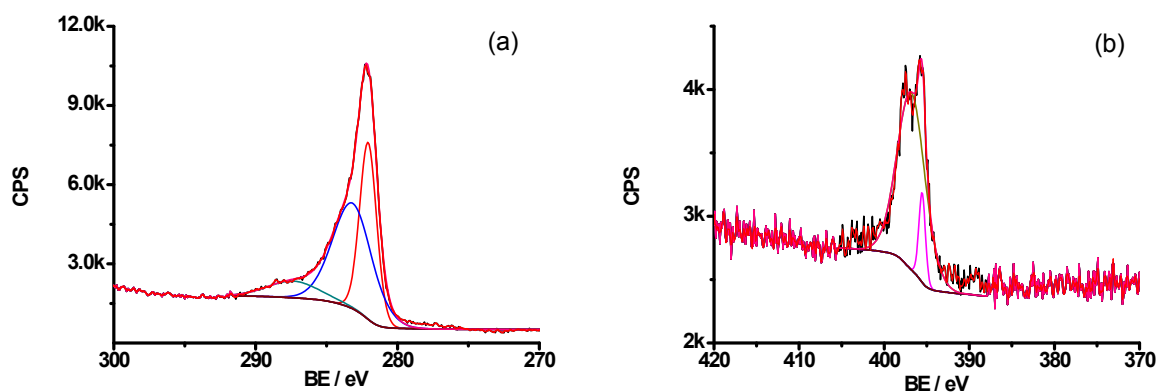
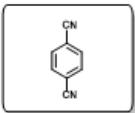
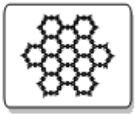
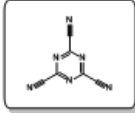
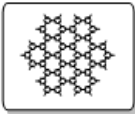


Figure S5. High-resolution C 1s and N 1s XPS spectra: (a) C 1s spectrum of DCB based 2D polymer; (b) N 1s spectrum of DCB based 2D polymer.

Table 1. Main peak positions of high-resolution C 1s and N 1s XPS spectra

	C			N	
	—			—	
	287.5	283.3	282.1	397.1	395.6
	287.9	284.0		399.7	398.4
	286.7	284.0		398.4	

Note: (a) DCB monomer will sublime at low pressure;

(b) Unit: eV.

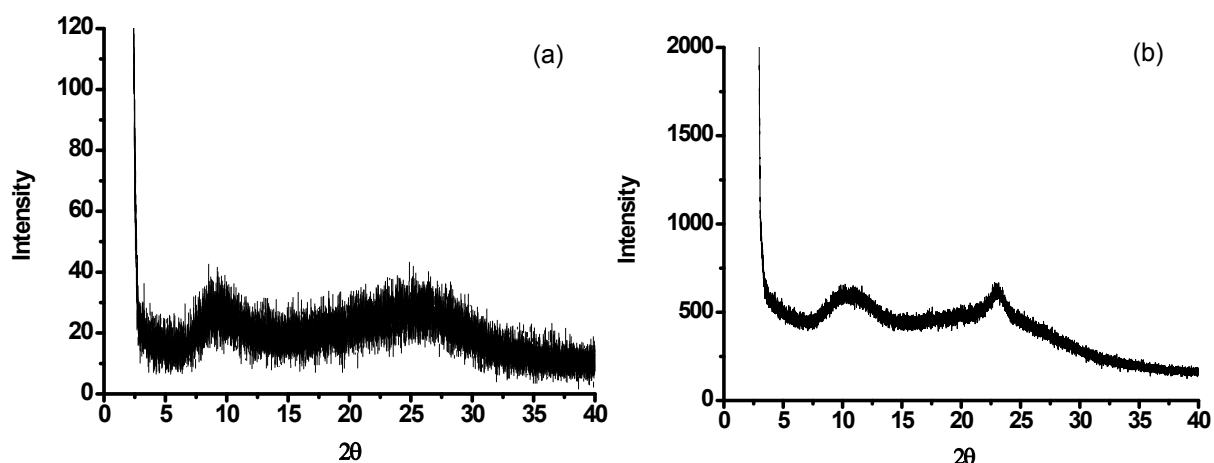


Figure S6. Powder XRD spectra of: (a) TCT based 2D polymer and (b) DCB based 2D polymer.

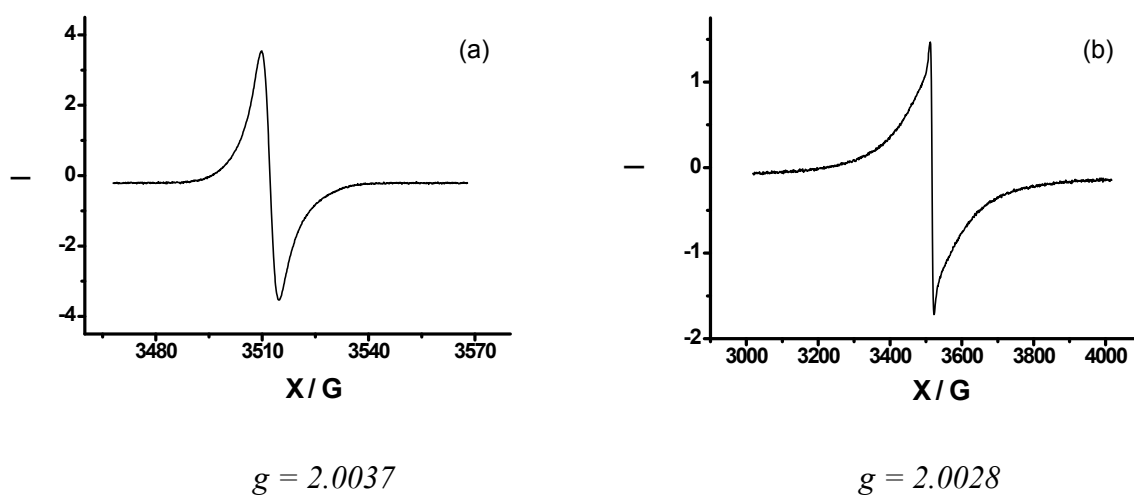


Figure S7. ESR spectra of (a) TCT based 2D polymer; (b) DCB based 2D polymer. Experimental conditions: 2 mg polymer suspending in 5 ml DMF, then ultrasonicated for 30 mins and collecting the polymer from the resulting solution by centrifuge. Drying the polymer in vacuum oven at 100 °C for 12 hrs.

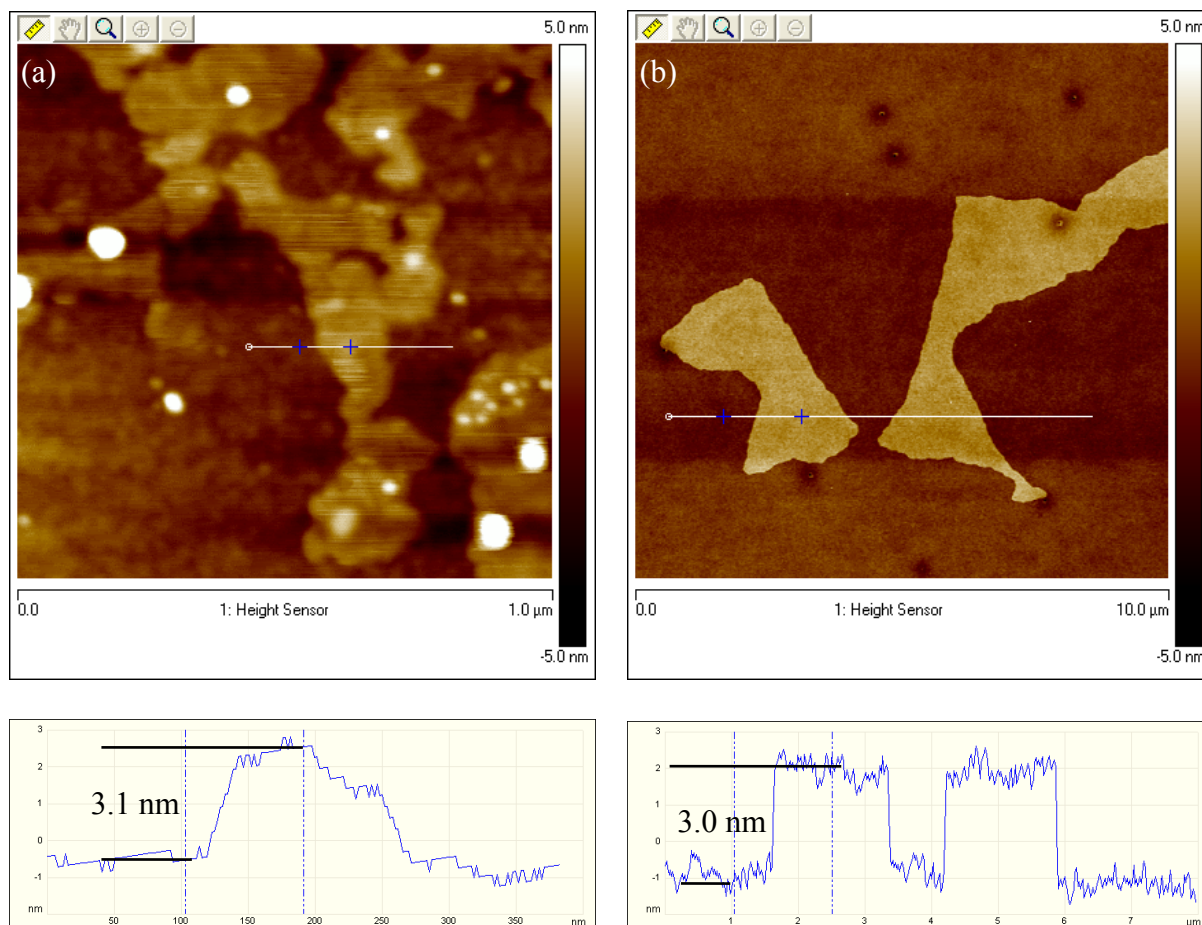


Figure S8 AFM images and thickness measurements of exfoliated two-dimensional polymers: (a) TCT based 2D polymer; (b) DCB based 2D polymer.

References:

- S1. G. Beck, Leverkusen, United States Patent, Patent Number: 5,086,172, Date of Patent: Feb. 4, 1992.
 S2. R. E. Del Sesto, A. M. Arif, J. J. Novoa, I. Anusiewicz, P. Skurski, J. Simons, B. C. Dunn, E. M. Eyring, J. S. Miller, *J. Org. Chem.*, 2003, **68**, 3367.