

Supporting Information

Synthesis and Mechanical Exfoliation of Imine-Linked Two-Dimensional Conjugated Polymers

Haining Liu,^{‡[b]} Qing Li,^{‡[a]} Yiming Zhu,^[b,c] Mei Zhang,^[b] Runjing Liu,^{*[a]} Xiaoming Li,^[a]
Xiao Kang,^[a] Zheng Li,^[a] Shanlin Qiao,^{*[a]}

[a] College of Chemistry and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China

[b] CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience National Center for Nanoscience and Technology Beijing 100190, P. R. China

[c] Department of Applied Physics Chongqing University Chongqing 401331, P. R. China

[‡] These authors contributed equally to this work

*Corresponding author, E-mail: qiaosl@qibebt.ac.cn

Materials

All starting materials and solvents, unless otherwise specified, were obtained from Aldrich Chemical Co. and used without further purification. 1, 3, 6, 8-Tetrakis(p-formylphenyl)pyrene (TFPP) was synthesized refer to the references.^{1,2}

Synthesis of PryDA

1, 3, 6, 8-Tetrakis(p-formylphenyl)pyrene (TFPP, 25 mg, 0.04 mmol) were dissolved in 2 mL of mixture solvent (mesitylene / anhydrous 1, 4-dioxane / 3:7 v/v) within a Pyrex tube (o.d × i.d = 10 mm × 8 mm) which pre-filled argon, then the tube was sealed with Parafilm and under sonication until get a homodisperse phase, another monomer p-Phenylenediamine (PPDA, 8.7 mg, 0.08 mmol) was added and sealed again, after sonication for 30 s, the mixture was then quickly frozen with liquid N₂ and 6M acetate (100 uL) carefully added to the tube with a microsyringe, the tube then connected to vacuum pump through a short rubber hose with stopcock, after three times of freeze-pump-thaw cycles, the frozen tube was sealed with a torch reducing the length of the tube into 18-20 cm under vacuum condition. The sealed tube then put into a constant temperature oven at 130 °C for 6 days under undisturbed state. After polymerization, the tube was cooled to 50 °C, and a yellow block of precipitation under the tube was take out and dipped into pure reactive solvent for three times, then immersed in anhydrous THF and anhydrous acetone until the residuum was fully removed. The obtained polymer was tested by P-RXD to make sure there without unconverted reactant. The target polymer then slowly drying under vacuum. Yielding bright-yellow powder 21 mg, Elemental analysis: Calcd. for C₅₆H₃₄N₄: C, 86.79; H, 5.98, N, 7.23. Found: C, 85.01; H, 6.5; N, 5.1%.

Characterization

FT-IR spectra were collected in attenuated total reflection (ATR) mode on a Thermo Nicolet 6700 FT-IR spectrometer.

Raman and PL spectrum were collected on a Renishaw (514.4 nm) and Horiba(325 nm) spectrometer.

Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 μ L platinum pans under atmosphere of air (heating rate 5 °C/min).

AFM images and height sections of mechanical exfoliated nano-sheet were measured on a Veeco Dimension 3100 Atomic Force Microscope, using Tapping Mode.

Friction force microscopy (FFM, Asylum Research Atomic Force Microscopes) were scanning in hybrid mode and imaging in contact mode. The scan speed was 450 nm/s for 20 nm scan size, the lateral force was calibrated by a diamagnetic lateral force calibrator.

Scanning electron microscopy (SEM) was recorded using a Hitachi S4800 with acceleration voltage 1.0 kV and working distance ~10 mm.

Powder X-ray diffraction patterns were collected on a D/MAX-TTRIII(CBO) diffractometer with Cu K α radiation ($\lambda = 1.542$ Å) operating at 40 kV and 200 mA, sample was mounted on a sample holder and measured with a 2θ range from $2\theta = 3^\circ$ up to 40° with 1.0° increment.

Porosity and gas sorption experiment were collected using a Quantachrome Autosorb-iQ-MP-VP volumetric adsorption analyzer. PryDA was degassed at 120 °C for 800 min under vacuum before analysis. BET surface areas and pore size distribution of PryDA was measured by nitrogen adsorption-desorption at 77 K.

Device fabrication and electrical measurement

PryDA thin sheets were mechanical exfoliated on the 300-nm SiO₂/Si substrates using the scotch-tape method. A bottom-gate top-contact device geometry was employed to fabricated the FET transistors. 3-nm-Ti/50-nm-Au source and drain electrodes were deposited by electron beam evaporation. After removing the photoresist by acetone, the fabricated device was tested with probe station under high vacuum ($\sim 10^{-6}$ mbar) at room temperature using Agilent B1500 A.

Nitrogen adsorption isotherm

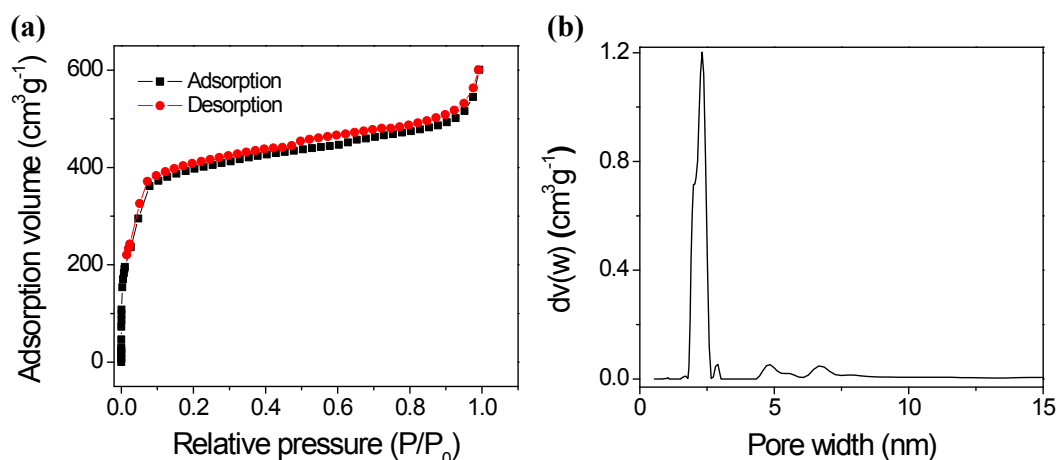


Fig. S1 N₂ adsorption isotherm of as-synthesized PryDA (a) and differential pore volume (b) derive from the N₂ adsorption isotherm.

Raman spectrum

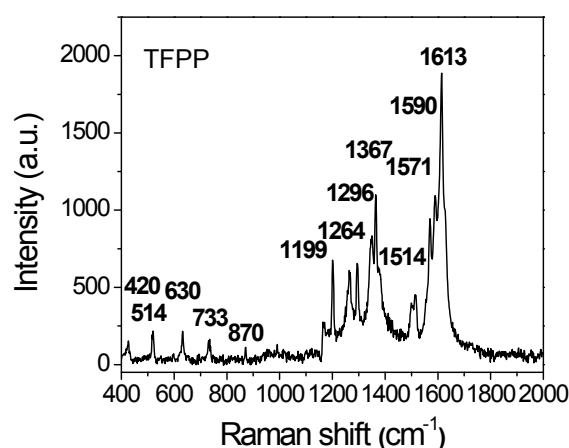


Fig. S2 Raman spectra of monomer TFPP (325 nm laser, Grating: x1200; Objective amplification: x100; Powder: 0.2 mW; Accumulation: 10 s)

Raman spectrum of TFPP was observed at 325 nm excitation. The intense bands 1624–1640 cm⁻¹ is the distortion of aromatic rings toward a rectangular shape. 1613 cm⁻¹ (a_{1g}), 1590 cm⁻¹ (b_{2u}) and 1571 cm⁻¹ (b_{1g}) are ring stretching mode mixed with little CH-in-plane bending. 1514 cm⁻¹ (b_{1g}, phenyl) and 1498 cm⁻¹ (b_{1g}, pyrenyl) peaks are the ring stretching deformation modes. 1367 cm⁻¹ and 1346 cm⁻¹ (b_{2u}) peaks are the strong o-CH and m-CH in-plane bend plus weak ring stretching deformation vibration. 1296 cm⁻¹ and 1264 cm⁻¹ is the p-substituted ring breathing stretching mode. 1157 cm⁻¹ and 1199 cm⁻¹ (b_{2u}) are the o-CH and m-CH in-plane rocking. Characteristic 870 cm⁻¹ (a_{1u}) and 731 cm⁻¹ (b_{1g}) two low-frequency modes assign to the C-C-C angle bending. 631 cm⁻¹ is the linked C-C wag mode. 520 cm⁻¹ (b_{2g}) is a breathing mode of symmetric pyrenyl.

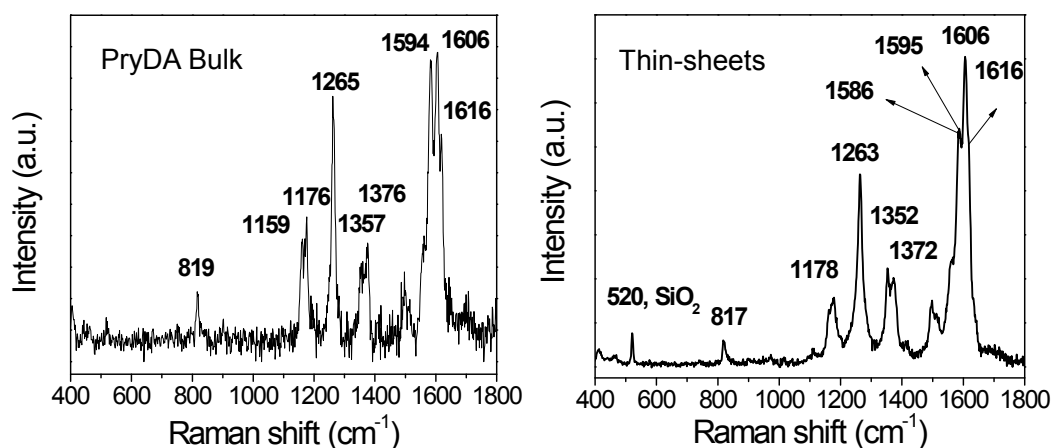


Fig. S3 Raman spectra of PryDA (a) and exfoliated thin-sheet (b) (For clear, the baseline was deducted. 514.5 nm laser, Grating: x1200; Objective amplification: x100; Powder: 0.2 mW; Accumulation: 10 s)

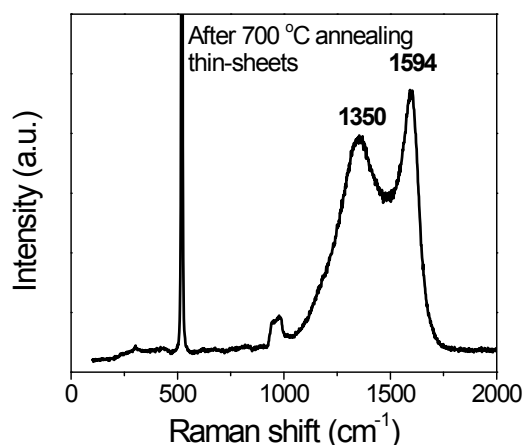


Fig. S4 Raman spectrum of annealed PryDA thin-sheets excited by 514.5 nm laser. (Raman intensity of annealed thin-sheet are homogeneous over a large area, measured at on 300 nm SiO₂/Si substrates, sheets have a height ~20 nm (Grating: x 1800; Objective amplification: x100; Powder: 0.2 mw, Accumulation: 10 s).

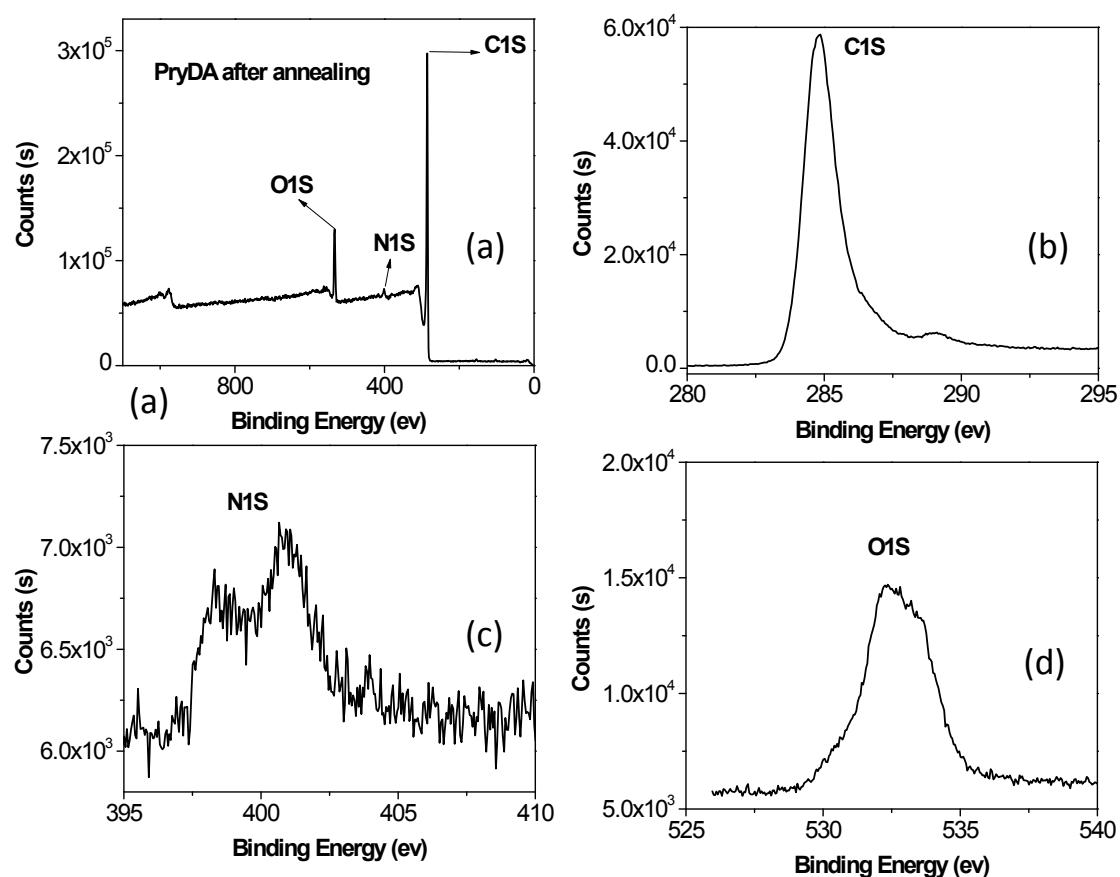


Fig. S5 (a) XPS spectrum of 700 °C annealed the COFs. (b), (c), (d) The corresponding C, N, O show the high-resolution peak.

AFM images

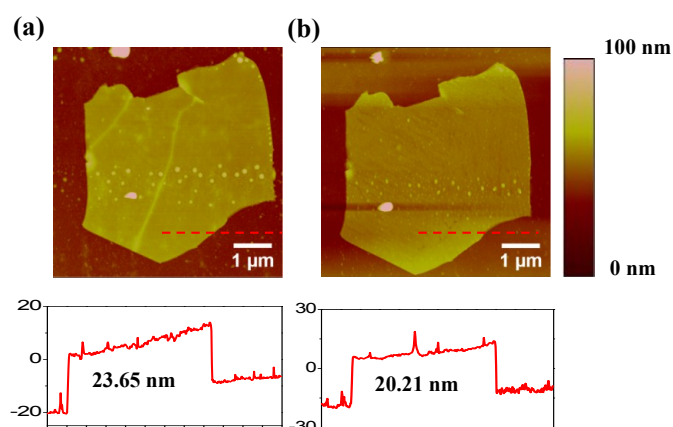


Fig. S6 AFM images and height sections of a PryDA thin sheet (a) before and (b) after 700 °C annealing.

Mechanical Exfoliation

Reference: The procedure of exfoliation graphene layers from the bulk HOPG surface is presented in **Fig. S7** (*J. Mater. Chem. A*, 2015, 3, 11700-11715). The exfoliation mechanics in this method is that Scotch tape is applied to the HOPG surface and thus

exerts normal force. If one takes great pains to repeat this normal force by numerous times, the graphitic layer becomes thinner and thinner and finally he will get a single layer graphene.

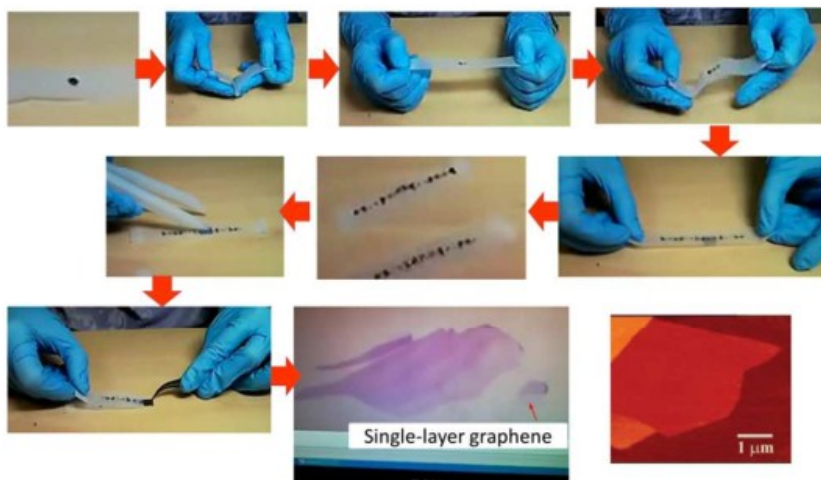


Fig. S7 The illustrative procedure of Scotch-tape based micromechanical cleavage.

Reference

1. M. G. Rabbani, A. K. Sekizkardes, Z. Kahveci, T. E. Reich, R. Ding, H. M. El-Kaderi. *Chem- Eur. J.* **2013**, 19, 3324.
2. H. F. Chang, S. H. Ye, B. R. He, Z. R. Bei, L. Y. Lin, P. Lu, B. Chen, Z. J. Zhao, H. Y. Qiu, *Chem- Asian. J.* **2013**, 2, 444.