chem2Dmat
AUGUST 31 - September 03, 2021 • ONLINE

# 2D polymers synthesis and 2D-polymer-based vdW heterostructure fabrication at air-water interface

Kejun Liu, Renhao Dong, Xinliang Feng

Center for Advancing Electronics Dresden (cfaed) & Department of Chemistry and Food Chemistry, Chair of Molecular Functional Materials, Technical University of Dresden, 01062 Dresden, Germany
Department of Synthetic Materials and Functional Devices, Max Planck Institute of Microstructure Physics, 06120 Halle, Germany

## Objectives

- the on-water surface synthesis of monolayer 2D polymer and its assembly with graphene for the construction of **2DP-based vdWHs.**
- Increase the interlayer interaction using the **strong interlayer cation-π interaction** between protonated H-2DPI and graphene
- Investigate the emerging physics in the vdW heterostructure in terms of optical, electronic, magnetic and layer structure

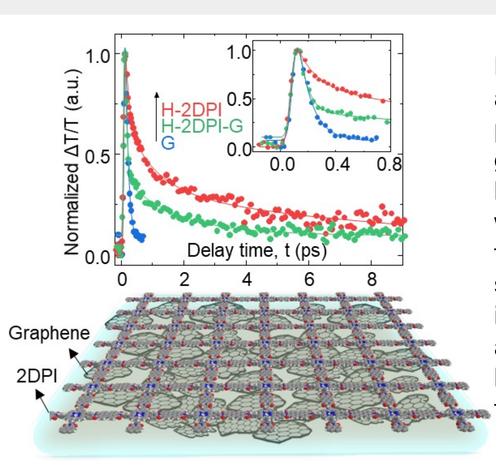


**Figure 1.** Bottom: on-water synthesis and assembly strategy toward the preparation of 2D polyimide (2DPI)-graphene (G) van der Waals heterostructures (vdWHs) on the water surface is demonstrated. Top: femtosecond transient absorption spectroscopy reveals an ultra-fast interlayer charge transfer (~60 fs) after protonation in the heterostructure, which is among the fastest reports of vdWHs.

## Synthesis of monolayer 2DP and fabrication of vdWHs

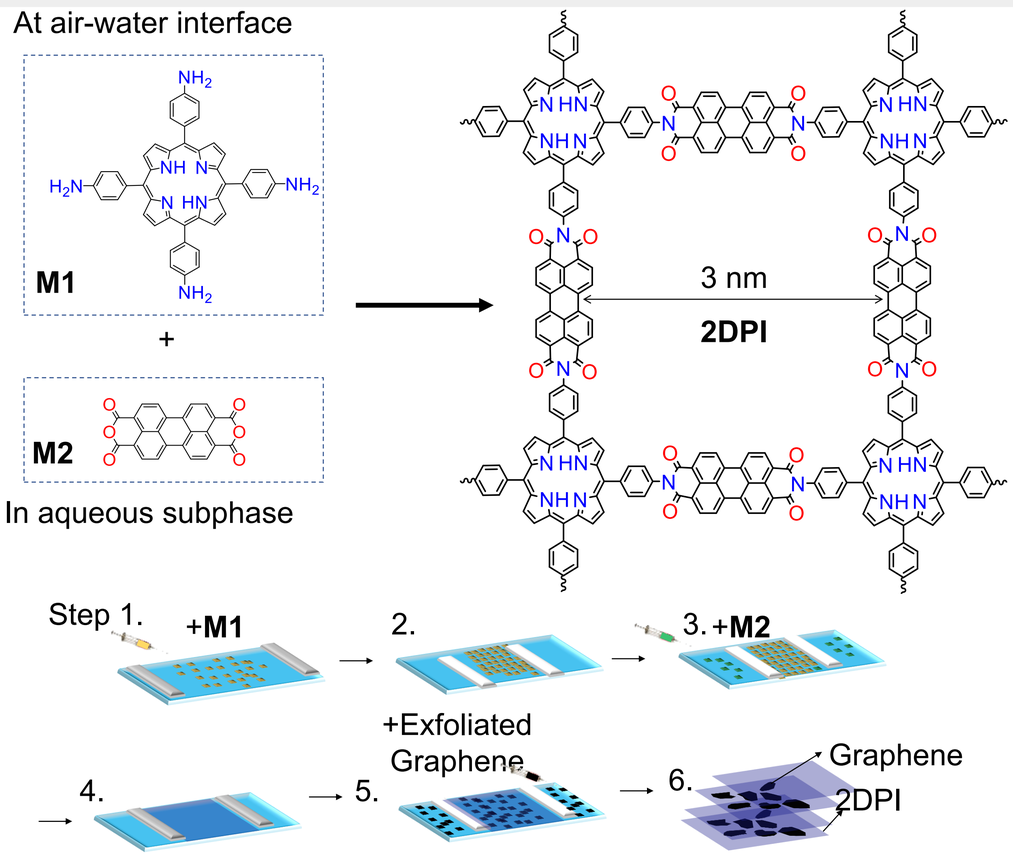


**Figure 2.** Reaction scheme of the 2DPI by the LB method and schematic illustration of 2DPI-G vdWH. (a) Reaction scheme of 2DPI. (b) Schematic illustration of the 2DPI-G fabrication on the water surface by LB method. There are six steps Step 1: spread **M1** onto the water surface; Step 2: well-controlled compression induces the pre-organization of **M1**; Step 3: Inject **M2** into water subphase; Step 4: **M2** is absorbed onto pre-organized **M1**, triggering assembly and reaction; Step 5: disperse exfoliated graphene (EG) into the subphase; Step 6: 2DPI-G formation via interfacial co-assembly and subsequent annealing process.

## Characterization of monolayer 2DPI

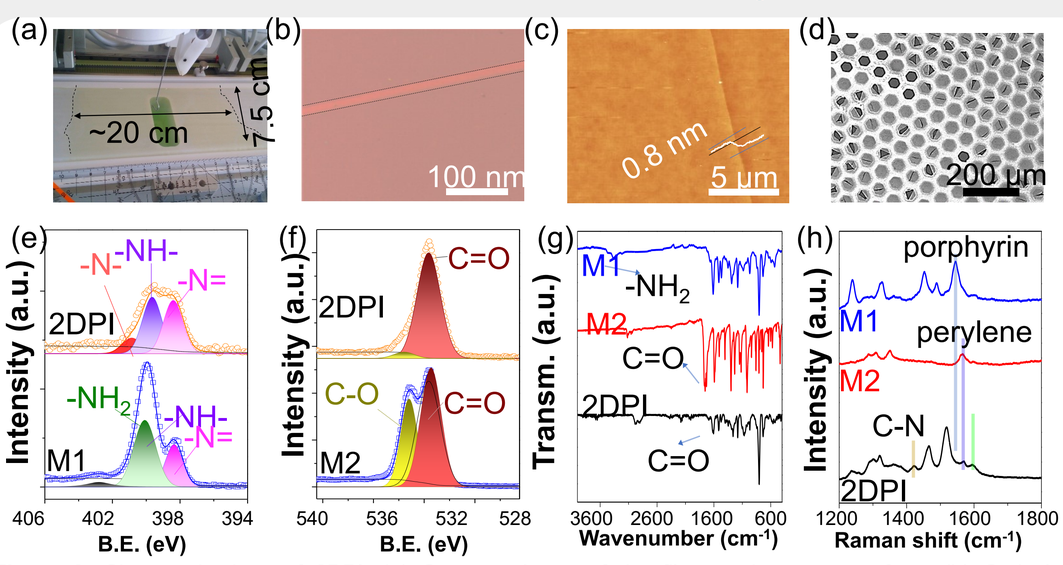


**Figure 3.** Characterizations of 2DPI. (a) Camera picture of the film on the water surface. (b) Optical microscope image of the film with a rupture on a $SiO_2$/Si substrate (c) AFM image on a $SiO_2$/Si substrate. (d) SEM image on a copper grid with the hexagonal pores of 18 μm diameter (e) High-resolution XPS spectrum of N 1s region of **M1** (bottom) and 2DPI (top). Nitrogen species of -$NH_2$ (400.0 eV), imide (400.8 eV), and porphyrin core (including -N- at 398.4 eV and -NH- at ~400 eV) are marked in green, red, magenta, and violet, respectively. (f) High-resolution XPS spectrum at O1s region of **M2** and 2DPI, the marked peaks at 533.18 eV (brown), and 531.58 eV (green) correspond to the character peaks of oxygen in C-O-C and C=O, respectively. (g) ATR-FTIR spectrum with marked reactive functional groups. (h) Raman spectra of **M1**, **M2**, and 2DPI.

## Optical properties

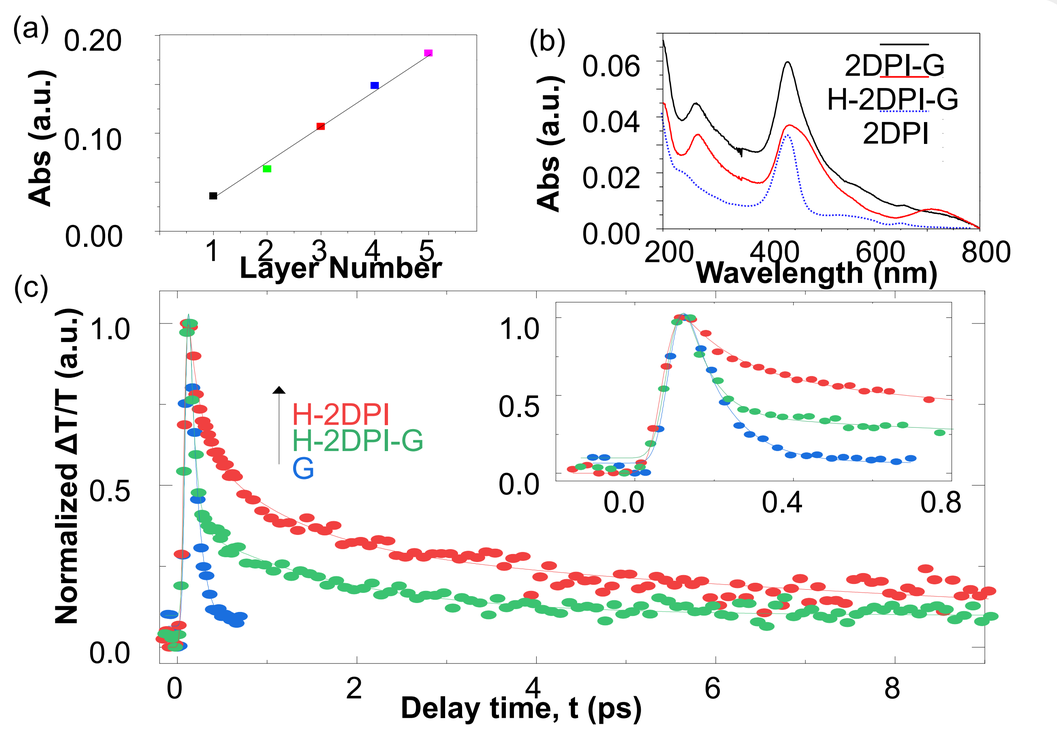


**Figure 5.** Optical properties of 2DPI-G heterostructure. (a) The absorbance intensity of Soret bands versus layer numbers, showing a linear relationship. (b) UV-vis absorption spectra of 2DPI-G (black) and H-2DPI-G (red). The spectrum of 2DPI (blue dash) is also added as the reference. (c) Dynamics of transient absorption in multi-layer graphene (blue dots), protonated 2DPI (red dots) and protonated 2DPI-G (green dots) measured using a degenerate pump-probe spectroscopy setup with fs pulses at 470 nm. The inset shows the sub-ps dynamics immediately after the photoexcitation.

## Characterization of vdWH

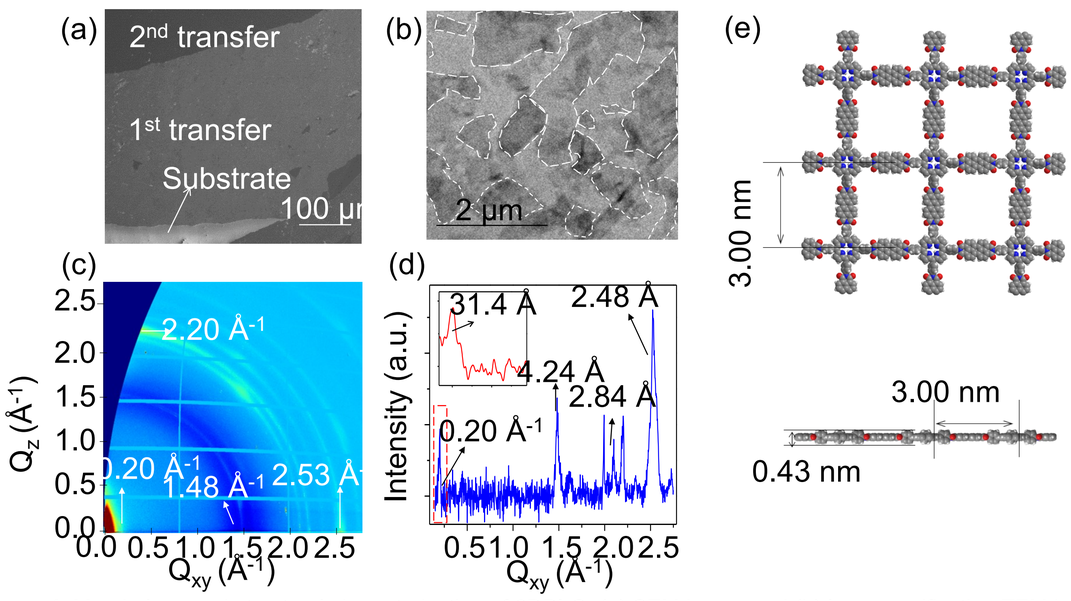


**Figure 4.** Morphology and structural characterization of 2DPI-G. (a) SEM image and (b) low-magnification TEM images of 2DPI-G heterostructure after twice deposition. (c) 2D-GIWAXS pattern of 2DPI-G. (d) The profile of integrated intensity of GIWAXS pattern with a zoom-in view of low $Q_{xy}$ region. (e) The model from DFT calculation.

## CONTACT PERSON

Dr. Kejun Liu
liu.kejun@tu-dresden.de
Dr. Renhao Dong
renhao.dong@tu-dresden.de
Prof. Dr. Xinliang Feng
xinliang.feng@tu-dresden.de

## REFERENCES

1. **Kejun Liu**#, Haoyuan Qi#, Renhao Dong#, Rishi Shivhare, Matthew Addicoat, Tao Zhang, Hafeesudeen Sahabudeen, Thomas Heine, Stefan Mannsfeld, Ute Kaiser*, Zhikun Zheng* and Xinliang Feng*: *On-water surface synthesis of crystalline two-dimensional polymers assisted by surfactant monolayers*. **Nature Chemistry** 2019, 11, 994–1000.
2. **Kejun Liu**, Jiang Li, Haoyuan Qi, Mike Hambsch, Jonathan Rawle, Adrián Romaní Vázquez, Ali Shaygan Nia, Alexej Pashkin, Harald Schneider, Mirosllav Polozij, Thomas Heine, Manfred Helm, Stefan C. B. Mannsfeld, Ute Kaiser, Renhao Dong*, Xinliang Feng*: "*A Two-Dimensional Polyimide-Graphene Heterostructure with Ultra-fast Interlayer Charge Transfer*." **Angewandte Chemie International Editioin**, 2021, 60, 13859–13864.

chem2Dmat
AUGUST 31 - September 03, 2021 • ONLINE