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AUGUST 31 - September 03, 2021 ONLINE

How to image the structural details in molecular framework of the imine-based 2D polymers

Baokun Liang, Yingying Zhang, Christopher Leist, Zhiyong Wang, Renhao Dong, Thomas Heine, Xinliang Feng, Haoyuan Qi, Ute Kaiser

universität ulm

TECHNISCHE UNIVERSITÄT DRESDEN

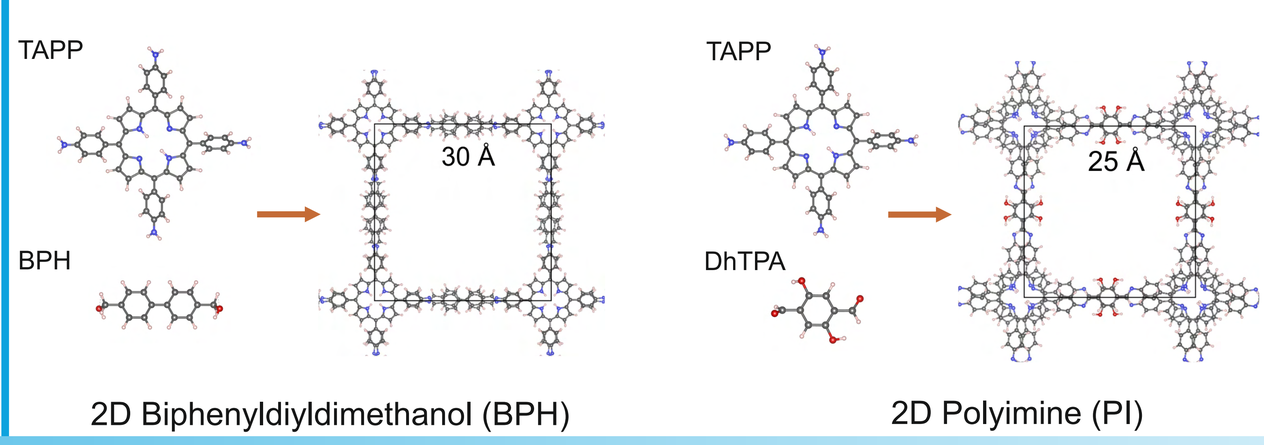
Introduction

Due to the high electron beam sensitivity of 2D polymers (2DPs), TEM imaging of their single molecular building blocks remains a challenging task. Here we quantitatively analyzed the dependence between the acceleration voltage and the available structural information [1]. A systematic analysis of the 2DPs at the acceleration voltages of 80, 120, 200, and 300 kV was applied. Our results demonstrated that 120 kV is superior to the traditionally applied high acceleration voltages of 300 kV .

By utilizing 120 kV and combined with low-dose technique, we have successfully imaged imine-based 2DPs with sub-2 Å resolution which enables the direct observation of the structural details in the moleculer framework. The enhanced image contrast allowed for image acquisition with low defocus values, this greatly facilitates direct image interpretation and avoids confusion due to delocalization under high defocus. The HRTEM images of glassy 2DP is also obtained with high image contrast, for an efficient quantitative image analysis, a neuro-network was applied.

2D polymer samples

Samples produced by surfactant-monolayer-assisted interfacial synthesis(SMAIS) method [2].(grey: C, blue: N, pink: H, red: O).

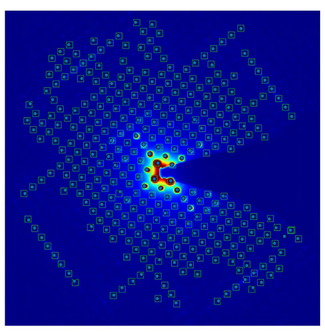


2D Biphenyldiyldimethanol (BPH) 2D Polyimine (PI)

Determination of optimal acceleration voltage for HRTEM characterization

1. Critical fluence (F_{cr})

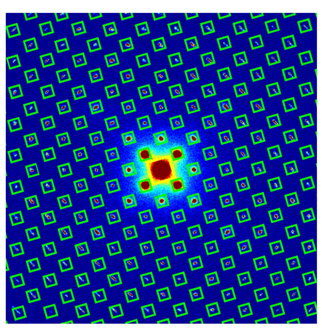
Determined by monitoring the decreasing of the reflections' intensities, 1/e of the initial intensity is the threshold for critical dose.



2. Structural Information (P_{el})

The proportion of the elastically scattered electrons:

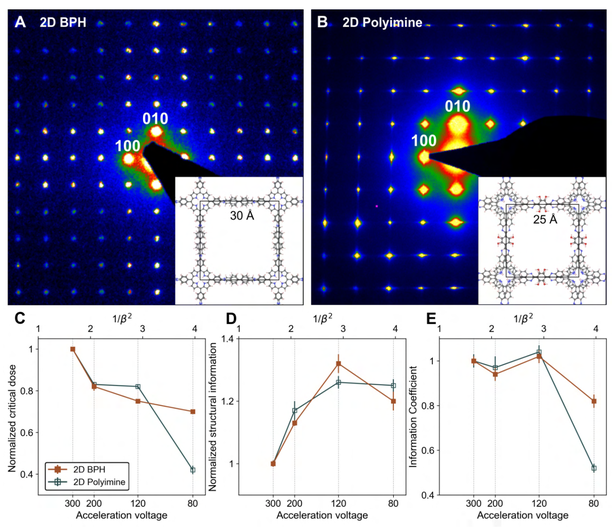
$$P_{el} = I_{Bragg} / I_{total}$$



3. Information coefficient (ζ)

The representation of the avaible structural information with regard to the damage rate of the sample:

$$\zeta = F_{cr} \cdot P_{el}$$



SAED and acceleration voltage optimization of 2D BPH and PI.

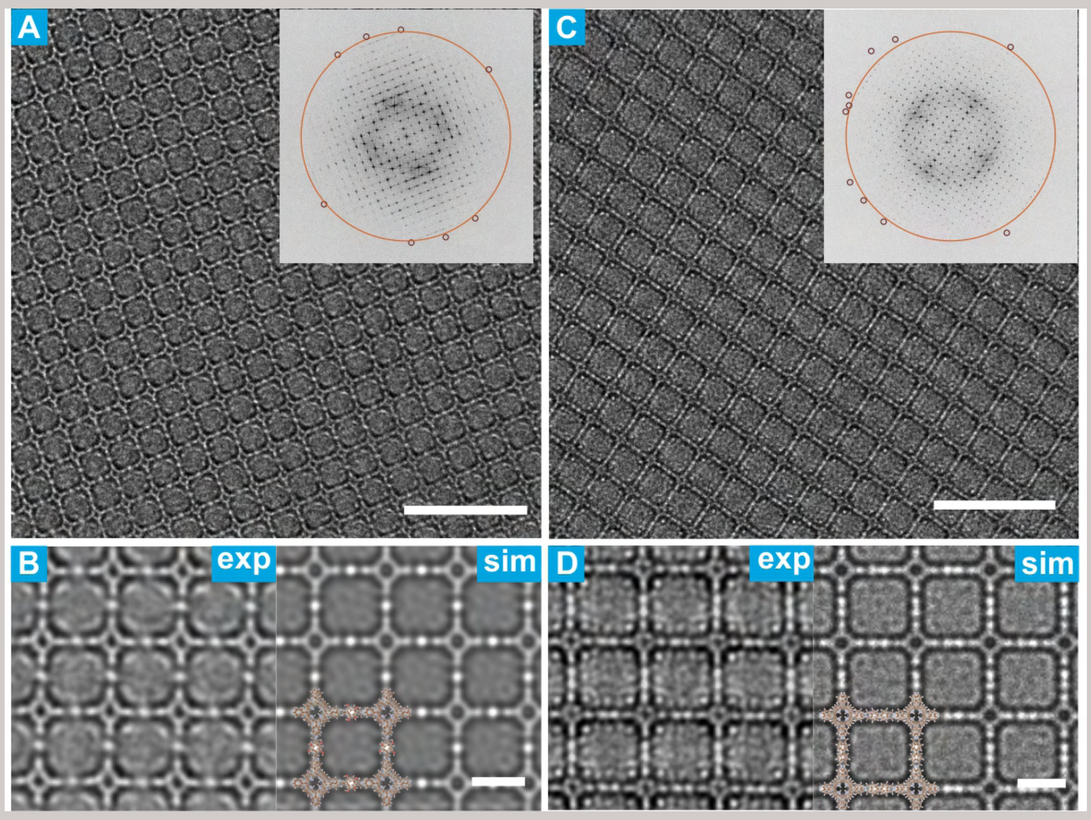
(A), (B) SAED of 2D-BPH and PI, the schematic structures are the insets.

(C) The diagram shows the normalized results of the critical dose under different acceleration voltages.

(D) shows the structural information proportion.

(E) demonstrates the information coefficient as a function of acceleration voltage, and the information coefficient is obtained by the multiplication of the normalized critical dose and structural information.

HRTEM and image simulation results



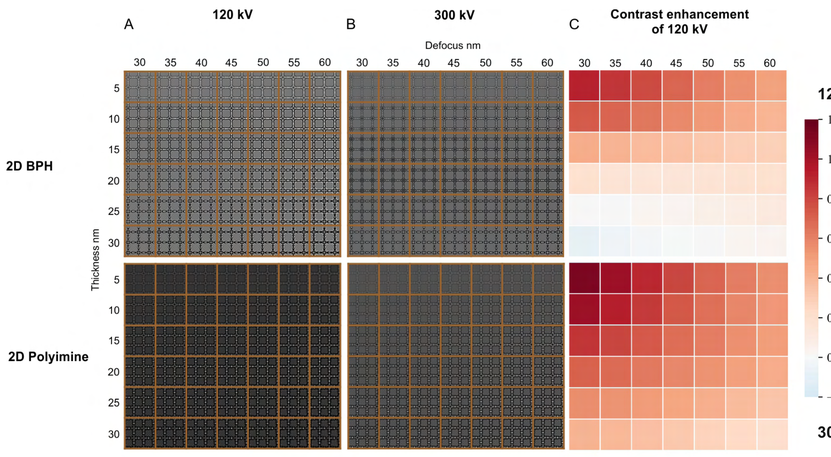
Experimental HRTEM images and simulations of 2D polyimine (PI) and biphenyldiyldimethanol (BPH).

(A) shows the HRTEM image of 2D PI, scale bar: 10 nm. Inset: fast Fourier transform (FFT) patterns. The orange circle marks the spatial resolution of 2 Å.

(B) includes enlarged experimental image and simulation result, scale bar: 2 nm. The atomic model is overlaid.

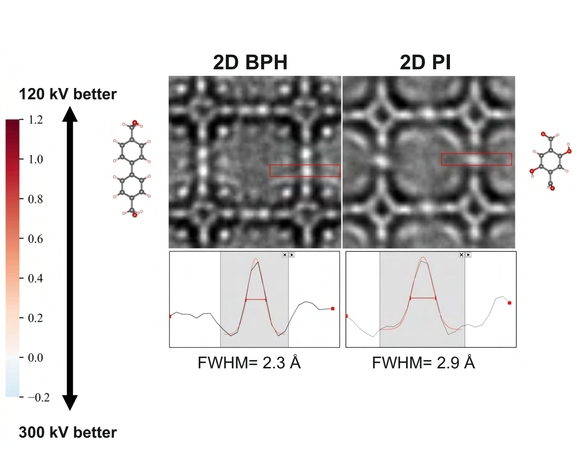
(C) the HRTEM image of 2D BPH, scale bar: 10 nm. Inset: FFT patterns. The orange circle marks the spatial resolution of 2 Å.

(D) enlarged experimental image and simulation, scale bar: 2 nm. The atomic model is overlaid. The DFT caculations were conducted for the atomic models.



Comparison of the image contrast between 120 and 300 kV

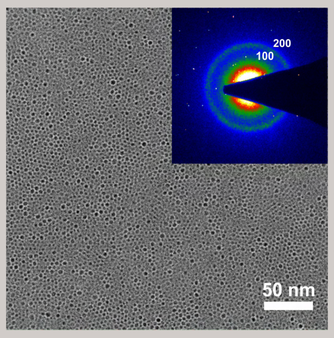
The comparison in the last column is defined as $(Contrast_{120}-Contrast_{300})/Contrast_{300}$.
120 kV is the optimum voltage for high-contrast HRTEM imaging of thin 2D polymer samples.



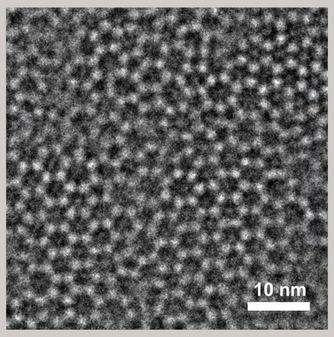
Comparison of the width of the linkers

Statistical results demonstrate that the linker width of 2D PI is on average 0.9 Å broader that the linker of 2D BPH.

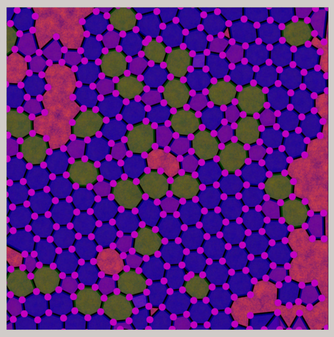
120 kV imaging applied to glassy 2D polymer



120 kV TEM overview image and SAED as inset.



120 kV AC-HRTEM image.



Analysis of the distribution of hte polygons in the AC-HRTEM by a neural network of U-net architecture.

CONTACT PERSON

Baokun Liang
baokun.liang@uni-ulm.de

REFERENCES

[1] Peet, M. J., Henderson, R. & Russo, C. J. , Ultramicroscopy, 203 (2019) 125–131 The energy dependence of contrast and damage in electron cryomicroscopy of biological molecules.

[2] Nature Chemistry volume 11, pages 994–1000 (2019).

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