**NANOMATERIALS**

**Wafer-scale synthesis of monolayer two-dimensional porphyrin polymers for hybrid superlattices**

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The large-scale synthesis of high-quality thin films with extensive tunability derived from molecular building blocks will advance the development of artificial solids with designed functionalities. We report the synthesis of two-dimensional (2D) porphyrin polymer films with wafer-scale homogeneity in the ultimate limit of monolayer thickness by growing films at a sharp pentane/water interface, which allows the fabrication of their hybrid superlattices. Laminar assembly polymerization of porphyrin monomers could form monolayers of metal-organic frameworks with Cu2+ linkers or covalent organic frameworks with terephthalaldehyde linkers. Both the lattice structures and optical properties of these 2D films were directly controlled by the molecular monomers and polymerization chemistries. The 2D polymers were used to fabricate arrays of hybrid superlattices with molybdenum disulfide that could be used in electrical capacitors.

Monolayer two-dimensional polymers (2DPs), which are one-molecule-thick, freestanding films composed of periodically linked monomers (1–4), offer an ideal material system with two key advantages. First, their properties can be tuned at the molecular level by using different monomers and polymerization chemistries (5, 6). Second, as the molecular analogs of 2D atomic crystals [e.g., graphene and transition metal dichalcogenides (TMDs)] (7–9), 2DPs can be assembled through van der Waals (vdW) interactions into heterostructures and superlattices, layer by layer. vdW heterostructures generated from 2D atomic crystals have produced properties not observed in individual building blocks (10, 11). Adding the chemical tunability of the 2DPs to such vdW heterostructures will lead to the properties and functionalities designed at the molecular level and further tuned by the interlayer interactions. However, it has remained an unmet challenge to scalably synthesize monolayer 2DP films and subsequently integrate them with other materials with monolayer precision (12, 13). This is due to the difficulty of controlling reactions in the monolayer limit with large-scale uniformity and to the lack of facile methods for the transfer and integration of monolayer 2DPs because of their fragility. Previous experiments have reported progress toward large-scale synthesis of 2DPs (14–22) but with limited success with regard to wafer-scale homogeneity, microscopic characterization of crystalline structures, and scalable thin-film integration (23).

Here, we report the wafer-scale synthesis and integration of monolayer 2DPs for the fabrication of their hybrid heterostructures with monolayer precision. We developed an interfacial synthesis technique, laminar assembly polymerization (LAP), that is compatible with various molecular building blocks and two primary polymerization chemistries (coordination and covalent). This approach incorporated key features necessary for scalable and facile processing, including large-area synthesis, ambient growth conditions, and compatibility with established patterning and integration methods. These characteristics enabled the fabrication of superlattices based on monolayer 2DPs and 2D atomic crystals.

The design approach for the 2DP monolayers was based on porphyrin building blocks (Fig. 1A). These molecules had two variation sites: one at the center of the porphyrin ring [M = 2H, Fe(III), or Pt(II)] that tuned the optical spectra (Fig. 1B) and the other on the phenyl groups (R = -COOH or -NH2) that controlled the monomer–monomer bonds. The monomers were cross-linked either through coordination bonds via a copper paddle wheel structure in the presence of Cu2+ ions (Fig. 1A, left, and fig. S1; R = -COOH) (14) or through covalent bonds via the Schiff base reaction in the presence of terephthalaldehyde (TPA) (Fig. 1A, right, and fig. S1; R = -NH2) (22). The former forms coordination 2DPs (2DP I, -II, and -III; M = 2H, Pt2+, or Fe3+, respectively), also known as monolayer metal-organic frameworks (MOFs), whereas the latter forms covalent 2DPs (2DP IV; M = 2H), also known as monolayer covalent organic frameworks (COFs). The linkage chemistry for all the 2DPs was confirmed by Fourier-transform infrared spectroscopy (FTIR) (fig. S2).

Wafer-scale 2DP films were all produced at a sharp pentane-water interface and then transferred onto a substrate (e.g., fused silica in Fig. 1) placed underneath by slowly draining the bottom solution (more details are in the supplementary text). We visualized these films using a custom color-coding scheme based on the hyperspectral optical transmission images (Fig. 1C and fig. S3). Images of four transferred 2DP monolayers that covered an entire 2-inch (5-cm) fused silica substrate are shown in Fig. 1D. The films displayed uniform contrast over entire wafers, suggesting macroscopic continuity and homogeneity (a higher-resolution analysis is shown in fig. S4). The MOF-based 2DP I, -II, and -III with different M had distinct absorption spectra (Fig. 1B), resulting in markedly different colors (shown in Fig. 1D).

These monolayer 2DPs were synthesized using the LAP explained in Fig. 2. It is based on monomer self-assembly and polymerization at the sharp interface formed between two immiscible solvents (pentane/water) that strictly confined the monomers in a monolayer limit, which was critical for precise control of the thickness (Fig. 2, A and B). Laminar flow of the assembled monomers led to large-scale continuity and homogeneity in thickness (Fig. 2A and fig. S7 describe the LAP synthesis and the in situ optical characterization apparatus; additional details are in the supplementary text).

There are three phases in the LAP process (illustrated in Fig. 2, A and B): injection, self-assembly, and polymerization. During injection, the monomers were introduced from the edge of the reactor (width W) and directly delivered onto the sharp pentane/water interface by a continuous stream of carrier solution through the pentane layer (within 1 cm from the edge, movie S1). The pentane-mediated delivery has two key advantages. First, the mass flow of the precursor is continuous at the interface, which is achieved by using microsyringe pumps and carefully choosing the combination of the carrier solvents. Second, the pentane/water interface is steady during the growth, resulting in minimal disturbance. This contrasts with dropwise delivery through the air, which disturbs the interface. Once delivered to the interface, the porphyrin-based monomers self-assembled at the interface because of their amphiphilicity and then spread, while being restricted by the longer sidewalls.
The monolayer nature of the 2DPs was confirmed by optical images that showed unidirectional movement of the monolayer assembly parallel to the longer sidewalls (Fig. 2C and movie S2) with little mixing perpendicular to this direction (Fig. 2F), confirming a laminar flow. This monolayer remained intact upon solvent washing after a complete polymerization (~30 min); in contrast, unpolymerized films were washed away (Fig. 2D). Quantitative measurements of the synthesized area of 2DP I (R = −COOH and M = 2H with Cu²⁺ ions) as a function of the injected volume of the monomer solution closely followed a linear growth model consistent with a near-unity monomer-to-monolayer yield (Fig. 2E and movie S3).

Fig. 1. Wafer-scale monolayer 2DPs. (A) Schematic of monolayer 2DPs and corresponding chemical structures of the molecular precursors. (B) Absorption spectra of monolayer 2DPs on fused silica substrates. (C) Hyperspectral transmission images and resulting false-color images of 1-inch-square 2DP I on a 2-inch fused silica substrate. Transmission images taken at the wavelengths of 405, 420, and 440 nm were assigned red, green, and blue channels, respectively, to generate the false-color image. A linear transmission scale of 50 to 95% was applied to all of the channels. (D) False-color images of monolayer 2DPs covering entire 2-inch fused silica wafers. The same color code was applied in (C) and (D).

COF-based 2DP IV, no evidence for long-range order could be collected (through GIXRD or selected area electron diffraction), similar to other monolayer covalent 2DPs reported previously (26).

In Fig. 4, we further demonstrate the potential of LAP by presenting an array of vertically programmed hybrid vdW superlattices. These superlattices were produced by repeatedly stacking in vacuum hybrid 2D building units 2DP/(MoS2)ᵣ each made of a 2DP monolayer and n monolayers of MoS2. Examples of a 2DP II/(MoS2)₃ superlattice and a 2DP II/ MoS2 film are shown in Fig. 4, A and B, respectively (detailed methods are shown in figs. S14 and S15) (27, 28). Figure 4A shows a cross-sectional annular dark field (ADF) scanning transmission electron microscope (STEM) image of a representative 2DP II/(MoS2)₃ superlattice—an 11-layer stack—constructed by alternating one layer of 2DP II and three layers of MoS2. The image shows three bright bands separated by two dark lines. Each of the bright bands consisted of three layers of MoS2, and the dark layer in between corresponds to the hybrid 2DP II monolayer, as confirmed by the composite ADF and electron energy loss spectroscopy (EELS) mapping (Fig. 4A and fig. S16). The films ran parallel to each other with sharp interfaces and a uniform layer thickness over the entire 100-nm view of the ADF STEM image, indicating a high level of uniformity. In addition, the composition of the superlattice could be tuned by using a different 2DP, as demonstrated with the 2DP III/(MoS2)₃ superlattice shown in Fig. 4C. EELS data confirmed the chemical composition of each constituting layer, where 2DP III was identified by a strong carbon signal and MoS2 by a strong sulfur signal (Fig. 4C and fig. S16).

The vertical structure and composition of the hybrid vdW superlattices could be directly engineered by using different hybrid building units. Figure 4D (left) shows a series of vdW superlattices with varied superlattice periodicity d made of 2DP II/(MoS2)ₙ repeating units, with n = 1, 2, or 3. The grazing incidence wide-angle x-ray scattering (GIWAXS) data presented in Fig. 4D (middle and right) and figs. S17 and S18 show the distinctive diffraction peaks for each superlattice. By radially integrating the 2D GIWAXS images along the out-of-plane direction, 1D spectra were obtained in reciprocal space and used to measure d (fig. S19). For example, the superlattice with n = 3 showed d = 3.5 nm and a vdW thickness of 1.5 nm for 2DP II, which was close to the
Fig. 3. Structural characterizations of 2DPs.

(A) SEM image of monolayer 2DP I on a holey silicon nitride TEM grid. The white arrow indicates a hole not covered by monolayer 2DP I. Scale bar, 5 μm. (Bottom left inset) Schematic of monolayer 2DP I suspended over a hole on a silicon nitride TEM grid. (Top right inset) Magnified SEM image of monolayer 2DP I suspended over a 2-μm hole. (B) AFM height image of monolayer 2DP I. Scale bar, 500 nm. (Inset) AFM height profile. (C) Experimental and calculated in-plane XRD profiles for 2DP II. The experiment was conducted on a stacked 2DP II of 147 layers on sapphire. (Inset) Crystal structure of 2DP II. (D) Constant-current STM topography image of a single-crystalline domain of monolayer 2DP II on a thin film of Au(111) on mica. (Inset) 2D FFT of the image. (E) Constant-current STM topography image of multiple-crystalline domains of monolayer 2DP II. Boundaries between different domains are manually identified by the white dashed line. (F) 2D FFT of (E) showing square lattices of three major orientations. (G) Color-coded inverse 2D FFT image generated using the three sets of square lattice spots in (F). One spot from each set is circled with the corresponding color in (F).

Fig. 4. 2DP/TMD vertical superlattices.

(A) (Left) Schematic of a 2DP/(MoS2)3 superlattice. (Middle) Cross-sectional ADF STEM image of a 2DP II/(MoS2)3 superlattice film transferred onto a SiO2/Si substrate. Each bright band consists of three MoS2 monolayers, and each dark layer between the bands is a monolayer 2DP II. (Right) Composite image of carbon (yellow) and oxygen (blue) EELS mapping and ADF STEM signal (green) taken from a different area on the sample shown in fig. S16. (B) Optical transmission image of a 2DP II/MoS2 heterostructure on fused silica taken at the wavelength of 405 nm. The diameter of the wafer is 1 inch. (C) (Left) Cross-sectional ADF STEM image of a 2DP III/(MoS2)2 superlattice film transferred onto a SiO2/Si substrate. Each bright layer consists of two layers of MoS2 stacked, and each dark layer is a 2DP III monolayer. (Right) EELS profiles of carbon and sulfur taken from a different area on the sample shown in fig. S16. Scale bar, 5 nm. (D) (Left) Structures of 2DP II/(MoS2)n vertical superlattices. (Middle) Normalized diffraction peaks corresponding to 2DP II/(MoS2)n superlattices measured by GIWAXS. (Right) 2D GIWAXS scattering patterns of 2DP II/(MoS2)n superlattices. Scale bar, 0.2 Å⁻¹. (E) Schematic of vertical capacitor device arrays and individual device geometry. (F) Optical image of a 3-by-5 capacitor device array. Scale bar, 500 μm. (G) Reciprocal of area-normalized capacitance, 1/C', as a function of N, the number of 2DP II layers in stacked (MoS2/2DP II)n(MoS2)6-N films. Each data point is averaged from 10 devices with corresponding stacked film structures shown above. Green, MoS2; yellow, 2DP II. The inset shows a capacitance histogram of 25 devices of N = 2.
value measured from Fig. 4A. The results from other superlattices agreed very well with the predicted values (Fig. S4 and table S2). In addition, x-ray reflectivity (XRR) measurements conducted on similar superlattice structures and the scattering length density profiles generated from fitting the XRR spectra clearly revealed oscillations of electron density consistent with the alternating structures of (MoS$_2$)$_n$ and 2DP II (fig. S20 and supplementary text). The thickness of the repeating units extracted from the XRR analysis matched those obtained from GIWAXS and cross-sectional STEM within a 2-Å mismatch (table S3). Both the GIWAXS and the XRR data were taken from a macroscopic area randomly chosen from 1-cm by 1-cm superlattice films, illustrating the homogeneity of the vdW superlattices on a large scale.

Vertically programmed vdW superlattices and heterostructures provide a powerful platform for fabricating uniform arrays of devices whose properties are engineered layer by layer (10, 11, 29–32). To demonstrate such potential, we chose to fabricate arrays of electrical capacitors (photo shown in Fig. 4F) from vdW heterostructures of 2DP II and MoS$_2$ (Fig. 4E), as such a process involves integration of both top and bottom electrodes and the capacitance can be directly tuned by the thickness of the superlattices. Each device in an array consisted of two gold electrodes sandwiching the vdW heterostructure dielectric (27). Figure 4G shows the results measured from a series of heterostructures, (MoS$_2$/2DP II)$_N$(MoS$_2$)$_{2m}$, where $N$ monolayers of 2DP II films were inserted in between MoS$_2$ layers of a six-layer MoS$_2$ stack (schematics in Fig. 4G). Thus, the dielectric thickness and the capacitance are directly tuned by varying the layer number of monolayer 2DP II. The measured inverse capacitance, $1/C$, where $C$ is the area-normalized capacitance, linearly increased as $N$ increased from 1 to 5. Using the classical capacitor model, we extracted the dielectric constants of 2DP II (4.1) and MoS$_2$ (2.7), and these were in agreement with reported values (33, 34). The measured capacitance from an array of devices exhibited a narrow distribution (lower inset in Fig. 4G), suggesting the spatial uniformity of the hybrid heterostructures. This spatial uniformity is comparable to what has been achieved with stacked MoS$_2$ films (27). Thus, this method offers a general platform to incorporate diverse molecular species into vdW hybrid thin films for functional devices.

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S20

Table S1 to S3

References (35–45)

Movies S1 to S3

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Single-layer porphyrin polymerization

Two-dimensional polymers can be made as monolayer sheets through controlled synthesis at an interface. However, it is often difficult to create intact sheets over large areas that can be transferred onto substrates. Zhong et al. polymerized derivatized porphyrin molecules during laminar flow at a sharp pentane-water interface to form sheets that are 5 centimeters in diameter (see the Perspective by MacLean and Rosei). The authors used electron microscopy and spectroscopy to confirm that they had produced intact monolayers. These films were then transferred onto monolayer sheets of molybdenum disulfide to form superlattices for use as capacitors. Science; this issue p. 1379; see also p. 1308.