Solution Synthesis of Semiconducting Two-Dimensional Polymer via Trimerization of Carbonitrile

Jingjing Liu,†,‡ Wu Zan,†,‡ Ke Li,† Yang Yang,† Fanxing Bu,† and Yuxi Xu*,†,‡

†State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
‡State key Laboratory of Application Specific Integrated Circuit and System, School of Microelectronics, Fudan University, Shanghai 200433, China

ABSTRACT: The synthesis of crystalline two-dimensional polymers (2DPs) with proper bandgaps and well-defined repeating units presents a great challenge to synthetic chemists. Here we report the first solution synthesis of a single-layer/few-layer triazine-based 2DP via trimerization of carbonitrile at the interface of dichloromethane and trifluoromethanesulfonic acid. The processable triazine-based 2DP can be assembled into mechanically strong layered free-standing films with a high specific surface area via filtration. Moreover, the highly crystalline triazine-based 2DP can function as the active semiconductor layer in a field-effect transistor via drop coating and exhibits slightly bipolar behavior with a high on/off ratio of $10^3$ and a remarkable mobility of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$.

Two-dimensional polymers (2DPs) with internal periodicity composed of areal repeat units is an new extension of Staudinger’s polymerization concept. As a prototypical example of 2DPs, graphene, an atomic layer of sp$^2$-hybridized carbon, exhibits a variety of exceptional physicochemical properties. The discovery and prosperity of the natural 2D graphene has stimulated great interest in rational organic synthesis of 2DPs at the atomic or molecular level, which will offer a versatile family of 2DPs with desired structures, properties and functions. As a first attempt, 2D monolayers of molecular networks have been constructed through aryl–aryl coupling on crystalline metal surfaces under ultrahigh vacuum conditions. However, the synthesized 2D monolayers are limited to nanometers in size and it is difficult to release them from the substrate. As an alternative approach, 2D 2DPs have been recently achieved by exfoliation of presynthesized 2D covalent organic frameworks or crystalline polymers via polymerization between 2D-confined monomers in single crystals. Another major method is performing 2D polymerization such as photochemical cycloaddition and Schiff-base condensation reactions at two-phase interfaces typically at air–liquid interface of a Langmuir–Blodgett trough to synthesize single ultrathin 2DP films. Despite the current progress, the types and the synthetic routes of 2DPs are still very limited, which greatly impede their fundamental and applied research. Moreover, the functionality of π-conjugation for organic electronics/optoelectronics has rarely been demonstrated in these synthetic 2DPs. Therefore, it is highly desirable but remains a significant challenge to develop versatile and scalable synthetic methodology to access crystalline 2DPs with new linkage motifs and excellent processability.

Herein we demonstrate the first one-pot solution synthesis of a crystalline single-layer/few-layer triazine-based 2DP through cyclotrimerization reaction of nitrile moieties of 1,4-dicyanobenzene (DCB) at the interface of dichloromethane and trifluoromethanesulfonic acid (Figure 1a–c and Figure S1). The lateral size of obtained triazine-based 2DP is typically several micrometers and can be as large as several hundred micrometers. Remarkably, the excellent dispersity of triazine-based 2DP in organic solvents allows the 2DP to be assembled into mechanically strong layered free-standing films with a high specific surface area of 102 m$^2$/g via filtration. By dropping coating, the crystalline triazine-based 2DP with high π-conjugation can easily function as the active semiconducting channel in field-effect transistor (FET) devices and exhibits slightly bipolar behavior with a high on/off ratio of $10^3$ and a superb mobility of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$.

In a typical synthesis process, CH$_2$Cl$_2$ performed as the good solvent for the DCB monomer and CF$_3$SO$_3$H was employed as...
the catalyst for the nitrile cyclotrimerization. Under the stirring, abundant dynamic CH₂Cl₂/CF₃SO₃H interfaces originating from the immiscibility between CH₂Cl₂ and CF₃SO₃H played a vital role in the synthesis of 2DP. In this case, it is easy to control the reaction reversibility and the van der Waals epitaxial effect, which is helpful for 2DP growth. The overall reaction can be accomplished after tens of minutes (for experimental details, see Supporting Information), much faster than previously reported methods which usually take ten or more hours to several days. The yield of 2DP was about 68%. Controlled experiments under the same experimental conditions involving only CF₃SO₃H failed to obtain 2DP but yielded amorphous triazine-based nanoparticles aggregates, highlighting the importance of the interface (Figure S2). We have also used benzene, another good solvent for DCB monomer and also immiscible with CF₃SO₃H, and obtained similar 2DP in the C₆H₆/CF₃SO₃H solution system (Figure S3). We have also found that the monomer concentration could exert significant effect on the 2D polymerization (Figure S4 and S5).

The triazine-based 2DP can be well dispersed in organic solvents such as N,N-dimethylformamide (DMF) (inset in Figure 2a and Figure S6) and ethanol, which implies its excellent processability. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images (Figure 2a, f) revealed a lateral size of several micrometers and transparent appearance for the triazine-based 2DP similar to graphene, indicating an ultrathin thickness. In some places, the 2DP sheet was crumpled or scrolled, suggesting that the sheets were highly flexible. High-resolution TEM (HR-TEM) revealed the 2DP in sight is few-layer thick (three layers, Figure 2b) and the higher-magnification HR-TEM image (Figure 2c) and the sharp selected area electron diffraction (SAED) pattern (Figure 2d) strongly proved the high structural ordering and a hexagonal lattice for the triazine-based 2DP, in accordance with the structure derived from density functional based tight binding (DFTB) calculation (Figure 1b). Furthermore, on the basis of theoretical simulation (Figure S7) and its comparison with the HR-TEM image (Figure 2c), we proposed that the few-layer triazine-based 2DP has a staggered AB stacking structure (Figure 2e). The distance between two diagonal atomic groups from the HR-TEM image is measured to be 1.4 nm (Figure 2e), in agreement with the DFTB value (Figure 1a) and further demonstrating the ordered lattice within the 2DP. Additionally, the homogeneous distribution of carbon and nitrogen elements were revealed by the elemental mapping on the selected area of triazine-based 2DP (insets in Figure 2f). The atomic ratio of C to N obtained from SEM energy-dispersive spectroscopy was 100:24 for the 2DP, which is very close to the theoretical value of 100:25 and confirms the highly efficient 2D polymerization proposed in Figure 1a. Furthermore, the uniformity of sheet thickness was also demonstrated.

Figure 2. (a) TEM image of triazine-based 2DP. Inset is a photograph of 2DP dispersion in DMF (~0.1 mg mL⁻¹). (b) HR-TEM image of 2DP showing few-layer (three-layer) thickness. (c) Higher-magnification HR-TEM image and (d) SAED pattern of the 2DP. (e) Staggered AB stacking model structure matching with the HR-TEM image of 2DP. (f) SEM image of 2DP. The insets are the element mapping of C and N of the selected area. (g) Optical microscopy of 2DP. (h) AFM images of single-layer and (i) few-layer 2DP. (j) Fluorescent microscopy and (k) polarizing microscopy images of a super large 2DP sheet.
Communication

Figure 3. XPS N 1s spectra (a) and FT-IR spectra (b) of DCB and 2DP. (c) UV−vis spectra of DCB and 2DP. The inset shows the photographs of 2DP dispersion before and after excitation under UV light. (d) Steady state photoluminescence spectra of 2DP and DCB upon excitation at λ = 374 nm.

Figure 4. (a) Photograph of the free-standing 2DP film with the inset showing its fluorescent image under UV light. (b) N2 adsorption and desorption isotherms of the 2DP film and its pore size distribution calculated by nonlocal DFT modeling (inset). (c, d) Cross-sectional SEM images of the 2DP film.

by the uniform color contrast in the optical microscope image of 2DP (Figure 2g). AFM images clearly demonstrated that the thickness of micrometer-size triazine-based 2DP is about 0.9−3 nm (Figure 2h,i and Figure S8), providing solid evidence for the formation of single-layer and few-layer sheets based on consideration that the typical AFM thickness of monolayer graphene is 0.8−1 nm.25 Interestingly, we can even occasionally obtain a superlarge 2DP sheet up to several hundred micrometers shown in fluorescent microscopy (Figure 2j), polarizing microscopy (Figure 2k) and SEM (Figure S9).

X-ray photoelectron spectroscopy (XPS) (Figure 3a and Figure S10) and Fourier transform infrared spectroscopy (FT-IR) (Figure 3b) revealed that the −C==N of the monomer was almost fully transformed to −C≡N of the 2DP, suggesting the high efficiency of the 2D polymerization. Relative to the monomer, the crystalline 2DP showed significantly improved thermal stability with an ~80% weight retention at 800 °C in thermogravimetric analysis due to its robust polymer framework (Figure S11). The triazine-based 2DP displayed a much broader absorbance range from the ultraviolet to visible regions (Figure 3c) and red-shifted fluorescence emission (Figure 3d) compared to DCB monomer, indicating an extended delocalization of the π-conjugated skeleton after polymerization. The optical band gap of the triazine-based 2DP determined by UV−vis spectrum is 2.48 eV, in accordance with DFT calculation value of 2.46 eV (Figure 1d and Figure S12), further confirming the high crystallinity and low defect within the triazine-based 2DP. Under UV light irradiation, the triazine-based 2DP showed bright blue-green fluorescence (inset in Figure 3c), consistent with the fluorescence emission spectrum in Figure 3d and suggesting its potential in optoelectronic applications.

The excellent dispersity of triazine-based 2DP in organic solvents makes it processable for various applications. We can obtain a free-standing flexible 2DP film for the first time by filtration of the 2DP dispersion (Figure 4a and Figure S13). The flexible 2DP film showed blue-green fluorescence under UV light (inset in Figure 4a). The SEM cross-sectional view of the 2DP film clearly revealed a well-packed layered structure (Figure 4c,d). The well-organized 2DP film (Figure S14) exhibited a tensile strength and modulus of 6.9 MPa and 1.6 GPa (Figure S15), respectively, comparable to those of graphite foils composed of stacked platelets of expanded graphite.26 Furthermore, the 2DP film also showed a Brunauer−Emmett−Teller (BET) surface area of 102 m2 g−1 (Figure 4b), nearly 1 order of magnitude higher than graphene oxide paper (11 cm2 g−1, Figure S16) probably due to its in-plane porosity of 2DP and interlayer porosity between 2DP sheets (inset in Figure 4b).

Our processable crystalline triazine-based 2DPs also afford a great opportunity to prepare 2DP-based FET devices. By simply drop coating of the 2DP dispersion, we can easily deposit individual 2DP sheets on a p-type Si wafer as the semiconducting layer to construct FET devices (Figure 5a and insets in Figure 5b). The atomic smooth surface of 2DP sheet can create a high-quality interface between the 2DP semiconductor, SiO2 dielectric and source/drain electrodes. Figure 5b shows the typical transfer curve (I DS vs V GS with V DS = 5 V) of triazine-based 2DP FET device. The device showed slightly bipolar behavior with an on/off ratio of 1200 and a mobility of 0.15 cm2 V−1 s−1. In the output characteristics of the 2DP-based FET device (Figure 5c), a gradual slope increased as the gate-source voltage (V GS) decreased from +10 to ~40 V, indicating the carrier concentration in the 2DP channel could be effective modulated by altering V GS. It is worth noting that the research of 2DPs-based FET devices have been very limited so far due to the multiple structural requirements for 2DPs such as dispersity/processability, π-conjugation, lateral size, and morphological/thickness uniformity. Our triazine-based 2DP demonstrated the highest mobility among all reported results (Figure 5d and Table S1), highlighting its great potential in organic electronics.

In summary, we have demonstrated the successful one-pot solution synthesis of crystalline single-layer/few-layer triazine-
Communication

Figure 5. (a) Schematic of the FET device employing triazine-based 2DP as the semiconducting layer. (b) Transfer curve of the 2DP-based FET device with the inset showing optical picture of the device. $V_{gs}$ is the gate-source voltage and $I_D$ is the drain current. (c) Output characteristics of the 2DP-based FET device as $V_D$ decreases from +10 to −40 V. (d) Comparison of mobilities of our triazine-based 2DP with recently reported 2DPs such as C$_2$N-h2D$_2$,$^{17}$ polyTB,$^{18}$ and porphyrin-contained 2DP.$^{19}$

based 2DPs with a new methodology of trimerization of carbonitrile at the interface. The 2D polymerization reaction is highly efficient and scalable. The achieved triazine-based 2DP shows a typical lateral size of several micrometers and excellent dispersity in organic solvents, which allows the processing of 2DP into mechanically strong layered free-standing films with high specific surface area via filtration-induced assembly. Furthermore, the crystalline 2DP with a high π-conjugation function as the semiconducting layer in FET and exhibits a high on/off ratio and a superb mobility. We postulate this study provides a versatile route to synthesize a new variety of 2DPs with tailored structures and properties for various applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b05025.

Experimental details and additional data (PDF)

**AUTHOR INFORMATION**

*Corresponding Author

xuyuxi@fudan.edu.cn

**ORCID**

Yuxi Xu: 0000-0003-0318-8515

**Author Contributions**

J. Liu and W. Zan contributed equally.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge support by the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (TP2015002), the National Natural Science Foundation of China (51673042) and the National Key Research and Development Program (2016YFA0203900).

**REFERENCES**

(12) Kissel, P.; Murray, D. J.; Wulfhange, W. J.; Catalano, V. J.; King, B. T. Nat. Chem. 2014, 6, 774.

**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published on July 24, 2017. Figure S9b of the Supporting Information has been corrected. The revised version was re-posted on August 21, 2017.