Highly Efficient Preparation of Single-Layer Two-Dimensional Polymer Obtained from Single-Crystal to Single-Crystal Synthesis

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ABSTRACT: A two-dimensional polymer (2DP) single crystal (T-2DP) with submillimeter size was synthesized by single-crystal to single-crystal transformation based on photochemical [2 + 2]-cycloaddition. A successful conversion from monomer to polymer was achieved in the single-crystal state. The structure information with an atomic resolution of both the monomer and 2DP was given through single-crystal X-ray diffraction. By simply treated with trifluoroacetic acid (TFA) under mild conditions, an unprecedented efficiency of exfoliation was achieved. The triazine core in T-2DP could be protonated by TFA, which resulted in a solution-like sample with >60% of monolayers. The size of the exfoliated monolayer reaches to several hundreds of μm². This is another precious example of 2DP single crystal with nearly perfect structure and large enough size. The successful preparation of the highly desirable 2DP “solution” for a long time containing large sized and large amount of 2DP monolayers may open up new prospects for the basic properties study and the applications of 2DPs.

Two-dimensional polymers (2DPs) are a new kind of macromolecule with novel, topologically planar repeat units.1−4 2DPs are generally accepted as materials with atomic-thick or monolayer, covalently linked, highly ordered 2D topological structures.5−10 Compared with the traditional 1D linear polymers, 2DPs have attracted considerable attention due to their very different sheet-like structure, which presents a long-range ordered array of nanometer-sized holes. This unique combination of repeat units in two spatial directions brings superior properties and promising applications in the fields of field-effect transistors,11−12 catalysts,13−16 energy conversion,17−19 ion separation,20−23 and sensing devices.24−26 However, increasing the dimensionality from 1D to 2D is still a challenge to synthesis.27 The polymerization not only has to be confined within a 2D plane but also has to be performed so as to create simultaneously long-range order.1−10 The successful preparation of covalent organic frameworks (COFs) facilitated the development of organic 2D materials.24−26 Especially the use of dynamic covalent bonds makes the synthesis of ordered 2D or 3D structures in solution possible.26−29 In 2014, Schlüter’s and King’s groups reported single-crystal to single-crystal (SCSC) approaches to obtain 2DP single crystals through photochemically triggered [4 + 4]-cycloaddition.30−32 For the first time, one could resolve the precise structure of 2DPs down to atomic scale by routine XRD analysis.32 These two pioneering works were published back-to-back and gained high attention. Subsequently, by using the same SCSC strategy, another single-crystal 2DP was obtained on the basis of photochemical [2 + 2]-cycloaddition.33

Although the nearly perfect large size 2DPs single crystal has been obtained in the synthesis lab, the control over the exfoliation process to gain good dispersity of 2DPs is still a challenge.34−37 A “solution” of monolayered 2DPs is highly attractive for applications of gas and ion separation as membrane materials. However, achieving a dispersion with a large number of single layers remains a great challenge. This problem also exists in the field of inorganic 2D materials. Recently, Schlüter and Backes found that the LPE/LCC-based exfoliation/fractionation method can efficiently exfoliate 2DP crystals to single layers, albeit with an overall low yield.38 Besides these “top-down” strategies, the “bottom-up” synthesis has also been adopted to achieve the goal of single layer 2DPs preparation. The interfacial synthesis is a typical “bottom-up” strategy to obtain ultrathin, large-area, and free-standing 2DPs by preassembling the monomers at an air/water interface before the polymerization.39−44 However, the limitations of the large amount synthesis and the choice of the characterization methods remain.

The SCSC transformation is undoubtedly a fascinating approach to prepare 2DPs with a low number of defects and will help pave the way to these new organic 2D materials.30,31,45−47 It is necessary to mention that a linear polymer single crystal could also be prepared by this strategy.48−55 Besides the SCSC strategy, some other strategies were also developed to prepare the large-sized single crystal of 1D, 2D, and 3D COFs and other organic structures.56−59 Recently, two examples of single-crystal COFs obtained by solution polymerization were also published with consecutive pages that are considered to be a breakthrough in COFs area.57,58 The large-sized single crystals of covalent organic 2D or 3D structures are still scarce due to the difficulties of
controlling crystallization and polymerization both at the same time. SCSC transformation provides new thinking for preparing such kinds of single-crystal materials. However, the SCSC transformation is also hard to realize. The first step is called “monomer ordering”. It means that the monomers have to pack in a layered structure. In each layer, a reactive geometry is required such that polymerization can occur later between monomers. The distance between the layers has to be large enough to avoid cross-linking. To predict the crystallization of the monomer mainly depends on chemical intuition and trial-and-error most of the time. Only slight changes in the monomer structure may bring about a different packing or stacking mode in the crystals.\textsuperscript{33,44} The second step is the “polymerization” in a single-crystalline state. The possible contractions and expansions upon polymerization may cause the single crystals to crack, which can render single-crystal XRD analysis inapplicable. Thus, to the best of our knowledge, there are only very few single-crystal examples of 2DPs reported until now. It is thus an important task to broaden the structural diversity of 2DPs by exploring other monomers and reactions.

More importantly, to realize the highly efficient exfoliation of the 2DPs single crystal and obtain a large amount of the single layers of the 2DPs is certainly a milestone in this research area. Herein, we synthesized another example of 2DP single crystal (T-2DP) by using the SCSC approach through [2 + 2]-cycloaddition dimerization. A millimeter-sized 2DP single crystal was obtained under mild conditions. Single-crystal XRD analysis established unequivocal structural proof for this synthetic 2D polymer. In addition, the triazine as a core in the 2D polymer could be protonated to facilitate the exfoliation process. By simple acid treatment, a 2DP "solution" with unprecedented >60% of single layers was obtained. The sizes of the 2DP single layers reach >200 \( \mu \text{m}^2 \).

The design of the monomer M1 bears a close resemblance to Schütz’s monomer 3 (Figure 1a)\textsuperscript{33,38} Instead of the central benzene ring, however, it carries a triazine unit. While this may appear like a minor change, it is actually a key step in terms of exploitability. We anticipated that the protonation of its nitrogen atoms would render acid-induced exfoliation a much smoother process than currently encountered. The synthesis of monomer M1 is very straightforward. For the details see the Supporting Information (section 1.2).

M1 was designed to contain triazine as core and styryl pyrylium as three arms. The dimerization of the “arms” (control molecule R1) in single-crystalline state has been well identified (Figure 1b)\textsuperscript{52,60} The single crystal of M1 could be easily obtained by recrystallization in the mixture of acetic acid and formic acid and is rather stable in the air (for detail see Supporting Information section 1.3). In the resulting crystal structure (space group \( R_3 \)), M1 adopted the desired C3-symmetry, and the three arms were packed in a head-to-tail fashion to form hexagonal plane tiling (Figures 1d and 2a). The distance between neighboring styryl units is 3.919 Å, which implies the photochemical [2 + 2]-cycloaddition may occur since this distance satisfies the geometry criterion of Schmidt for [2 + 2]-cycloaddition reaction in the solid-state (Figure 1c).\textsuperscript{64} Seen from the a- or b-axis direction (side view), a layered structure was clearly formed that adopted a six membered ring as the new layer A in the crystal lattice (Figure 1i). An ABC stacking mode formed and the distance between the layers is \( \sim 0.56 \text{ nm} \) (Figure 2i). In each layer, a perfectly hexagonal honeycomb porous structure was obtained with a pore size of \( \sim 2.7 \text{ nm} \) (Figure 2i). The T-2DP crystal lattice volume shrunk only 0.42% compared to the monomer crystal (from 10442.4 to 10398.0 \( \text{Å}^3 \)) (Table S1).

Further evidence for the successful polymerization of monomer crystals to 2D polymer crystals was provided by \( ^{13} \text{C} \) CP/MAS NMR spectroscopy (Figure S7), which shows the complete disappearance of olefinic carbon signals of M1 at 144 and 118 ppm together with the appearance of the cyclobutane carbon signals at 40–50 ppm. IR spectroscopy showed a vanishing of C=C olefin stretching at 1608 cm\(^{-1}\) and an emerging peak at 1620 cm\(^{-1}\), which also indicated the success of the polymerization (Figure S8). This is highly consistent with the dimerization of the reference compound R1 and D1 (Figure S8). The time-dependent/kinetic experi-

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**Figure 1.** a) Chemical structure of monomer M1. (b) Dimerization of the model compound R1. (c) Dimerization of two adjacent monomer molecules in the single-crystalline state. (d) Polymerization of M1 to T-2DP in the single-crystalline state.
ment was also done to monitor the polymerization process. As shown in Figure S9, the [2 + 2]-cycloaddition was completed in 12 h.

2D polymer single crystals were then subjected to exfoliation to explore how single- or few-layered sheets of 2DP can be obtained. A liquid-phase exfoliation was applied here, which is a gentle method relying on solvent-diffusion. As we know, the solvent molecules can diffuse into the crystal weakening the intralayer interactions of the 2D polymer to the point when adjacent layers separate from each other. For a typical exfoliation experiment, the T-2DP single crystals were immersed in a suitable solvent (0.1−1 mg/mL) and stirred at room temperature. For routine checking, the dispersion was drop cast on a SiO₂ (280 nm)/Si wafer, dried and investigated via optical microscopy. Varying colors indicate different thicknesses due to thin-film interference (Figure 3e). The common NMP (N-methylpyrrolidone) or GBL (γ-butyrolactone) as a solvent was first employed for exfoliation. However, only minor swelling was observed and little delamination occurred.

It is noted that the monomer was designed to contain triazine units as cores. These units can be protonated by acid to introduce repulsive forces between layers due to charge and/or sterical effects, which may facilitate the exfoliation process. Trifluoroacetic acid (TFA) was then employed to protonate the triazine and achieve the exfoliation. As expected, TFA is particularly effective in the swelling and exfoliation of the 2D polymer crystals. 1.0 mg 2D polymer crystals were dispersed into 1 mL of TFA and stirred at room temperature. At the very beginning, an obvious swelling of the polymer crystal was observed (Figure 3a,b, Figure S10). With increasing time, a uniform dispersion formed (Figure S11). A slight increase in viscosity was also observed, which could be caused by the interactions between thin sheet stacks. A video of the exfoliation process in the vial was also provided in the Supporting Information. However, even after 1 month of exfoliation, no clear solution state was observed. To our surprise, when we diluted the TFA dispersion with GBL (TFA : GBL = 3 : 50), a clear yellow solution-like state was observed (Figure 3c,d). Inspired by this phenomenon, we speculate that the TFA could exfoliate the 2D layers efficiently; however, it could not dissolve or disperse them. On the other hand, GBL serves as a good solvent for the separated 2D layers.
We then tried to confirm the composition and structure of the obtained exfoliated 2DP layers. The IR spectra of the T-2DP before and after the exfoliation in TFA show almost no difference, which indicates that no chemical alterations occurred during the exfoliation (Figure S12). UV−vis spectroscopy was then employed to investigate the photophysical properties of the 2D polymer solution. The spectra displayed a maximum absorption wavelength at 290 nm (Figure S13). The obvious blue shift compared with the monomer solution (412 nm) indicates the transformation from conjugated vinylene units to nonconjugated cyclobutanes. The same tendency was observed for model compounds R1 and D1 (Figure S13).

The morphology of the exfoliated 2D polymer was studied next. A solution of T-2DP was dropped on a SiO2 (280 nm)/Si wafer, dried, and investigated via optical microscopy (OM). The OM showed that the whole wafer substrate surface was covered by significant amounts of uniform thin polymer films (Figure 3e). TEM characterization shown in Figure 3f revealed continuous sheet morphology. Transmission electron microscopy (TEM) and low-dose selected area electron diffraction (SAED) were then employed to accomplish the structural characterization of the exfoliated 2D polymer. We first tried the mechanically exfoliated samples by using the routine adhesive tape method.65 As shown in Figure 4a, a bright-field TEM image of T-2DP after micromechanical exfoliation with obvious film morphology was presented. The corresponding SAED pattern (Figure 4b) reveals a hexagonal symmetry with nearest reflections at 0.75 nm−1, which is in agreement with the simulated SAED pattern based on single-crystal XRD data (Figure 4c). However, for the T-2DP obtained from the chemical exfoliation, we observed only an extremely diffusive ring instead of hexagonal patterns, (Figure 4d−f) The disappearance of Bragg reflections despite chemical connectivity can be attributed to the flexibility of the 2D polymer network. In the single-crystal of T-2DP, the monolayers are arranged in ABC stacking order. The interlayer locking via van der Waals force could stabilize the hexagonal network structure, giving rise to clear reflections in single-crystal XRD measurements. However, in a monolayer, the pore size is as large as 2.7 nm. Due to the large pores on the extended 2D structure, the framework is not rigid and may undergo distortion/crumpling when the layer is isolated from the bulk. Note that isolation refers to the loss of interlayer locking force, but not necessarily peeling off from the bulk. During chemical exfoliation, as long as the TFA-induced swelling (i.e., an increase of interlayer distance) leads to reduction/vanish of van der Waals interaction, structural distortion/crumpling may occur. Even if the layers restack together, the long-range order is lost due to the distortions in each single monolayer.

For AFM measurements, ~100 nanosheets were randomly measured from five different SiO2 (280 nm)/Si wafers. A large number of monolayers were observed with a thickness of 0.7−0.8 nm and a homogeneous surface. Figure 5a−h shows four typical examples of folded monolayers. More examples are presented in the Supporting Information (Figure S14). We

![Figure 4. Structural characterization of the exfoliated T-2DP layers. (a) Bright-field TEM image of a micromechanically exfoliated nanosheet of the T-2DP. (b) Selected area electron diffraction (SAED) pattern of the circled area in (a) (electron dose: 0.5 e Å−2) showing good crystallinity and nearest reflections at 0.75 nm−1. (c) Simulated diffraction pattern based on X-ray diffraction on T-2DP single crystals. (d), (e) Bright-field TEM images of T-2DP produced from exfoliation in TFA. (f) SAED of circled area in (e) (electron dose: 0.5 e Å−2).](https://doi.org/10.1021/jacs.1c00907)

![Figure 5. AFM images of T-2DP (a, c, e, g) and related height analysis (b, d, f, h). (i) Statistical analysis of ~100 nanosheets.](https://doi.org/10.1021/jacs.1c00907)
then did a statistical analysis of the ∼100 nanosheets. The obviously folded sheets from the monolayer were considered to be the monolayer. The proportion of monolayers accounted for >60% (Figure S1). To provide a better overview of all features in the sample, we have performed large-scale optical microscope imaging of the exfoliated samples on 280 nm SiO2/Si wafers (Figure S15). No substantial agglomeration was observed and the fairly uniform contrast of the nanosheets revealed a narrow thickness distribution. The demonstration of dispersed and uniform nanosheets on a larger scale further supports the high efficacy and efficiency of the exfoliation.

In summary, a new example of 2DP single crystal was synthesized by using the SCSC approach through a [2 + 2]-cycloaddition dimerization. Single-crystal XRD analysis with the atomic resolution gives clear evidence of the ABC stacking 2D layered structure. In addition, an efficient exfoliation was achieved by TFA because of the presence of the triazine as a core. We propose the exfoliation process to be facilitated by the protonation of triazine. The introduction of the ion pairs in the structure of 2DP effectively improved the exfoliation efficiency. Finally, a clear solution-like sample of T-2DP in TFA/GBL was obtained, which contained more than 60% of the monolayered 2D polymer. The feasibility and efficiency of the reported exfoliation method may pave the way for real-life applications of 2D polymers obtained via the top-down approach. We envisage that the production of large-sized 2DP nanosheets would continue to benefit from the ever-growing quality and size of the 2DP single crystals. Meanwhile, systematic studies on the 2DP-solvent interactions as well as the structural and chemical evolution of the 2D polymer nanosheets in solution would be indispensable to achieve a deeper understanding of the liquid-phase exfoliation, particularly on the microscopic scale. In addition, delicate monomer design and more sophisticated exfoliation protocols, e.g., liquid cascade centrifugation, will be of vital importance to boost the monolayer yield to an even higher level.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00907.

Synthetic procedures; Figures S1–S15 of NMR, FT-IR, and UV–vis spectra, cooling-rate curve, pictures and optical microscope images, time-dependent/kinetic study of the cycloaddition, exfoliation images, AFM images and height profiles; table of crystal data (PDF)

Accession Codes

CCDC 2025582 and 2025669 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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