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Authors

Yu, Shang-Bo

Lin, Furong

Tian, Jia

et al.

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Two-Dimensional Covalent and Supramolecular Polymers: from Monolayer to Bilayer and the Thicker

Shang-Bo Yu,^[a] Furong Li,^[a] Jia Tian,^[a] Yi Liu,^{*,[b]} Dan-Wei Zhang,^[c] Zhan-Ting Li^{*,[a,c]}

[a] Dr. S.-B. Yu, Dr. F. Li, Prof. J. Tian, Prof. Z.-T. Li
Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032 (China)

[b] Dr. Y. Liu
The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720 (United States)
E-mail: yliu@lbl.gov

[c] Prof. D.-W. Zhang, Prof. Z.-T. Li
Department of Chemistry, Fudan University, 2205 Songhu Road, Shanghai 200438 (China)
E-mail: ztli@fudan.edu.cn

Abstract: Selective preparation of two-dimensional polymers (2DPs) and supramolecular polymers (2DSPs) with defined thickness is crucially important for controlling and maximizing their functions, yet it has remained as a synthetic challenge. In the past decade, several approaches have been developed to allow selective preparation of discrete monolayer 2DPs and 2DSPs. Recently, crystal exfoliation and self-assembly strategies have been employed to successfully prepare bilayer 2DP and 2DSP, which represent the first step towards the controlled “growth” of 2D polymers from the thinnest monolayers to thicker few-layers along the third dimension. This Concept review discusses the concept of accurate synthesis of 2D polymers with defined layers. Advances in this research area will pave the way to rational synthetic strategies for 2D polymers with controlled thickness.

Introduction

Synthetic polymers permeating modern society are mainly one-dimensional polymers consisting of topologically linear chains. Two-dimensional polymers (2DPs), defined as monolayered, periodic and covalent 2D materials,^[1] represent another class of topologically unique architectures with covalent bonds confined to two orthogonal directions. In 1941, Talmud described the first attempt of 2D polymerization through interfacial coupling of aldehydes and amines.^[2] For many years since then, 2D polymerization had not been vigorously explored due to the lack of both synthetic and analytical means. In a review paper in 2009, Schlüter and co-workers noted that the making of such monolayer 2DPs by then was “still a dream of many organic and polymer chemists”.^[3] Since 2012, several 2D polymerization strategies, including crystal exfoliation/ delamination,^[4] air/water interface^[5] and solution-phase polymerization,^[6] have been developed, allowing the synthesis of a variety of discrete 2DPs.

Chemists’ interests in 2DPs come from their uniqueness as novel topological structures, the challenges as synthetic targets, as well as their expected novel mechanical, physical and chemical properties.^[7] The preparation of 2DPs in two orthogonal directions within flat monolayer space requires unprecedented control of covalent bond formation.^[7] “Bottom-up” self-assembly provides another powerful

approach for constructing monolayer 2D architectures.^[8] In 2013, Zhao and co-workers reported the self-assembly of the first 2D monolayer supramolecular organic framework (SOF) by utilizing cucurbit[8]uril (CB[8]) encapsulation-enhanced dimerization of a rigid tritopic monomer in water,^[9] which features anti-parallel stacking of the appended aromatic units of the monomer.^[10] Referring to the definition of 2DPs, this and other related SOFs can be considered as a special kind of 2D supramolecular polymers (2DSPs).^[11] Different from 2DPs, 2DSPs constructed by such methods are typically water-soluble due to the introduction of multiple cationic units in the monomers.

Beyond synthetic curiosity, several 2DSPs have been shown to exhibit interesting functions, such as fluorescence sensing,^[11c] chiral recognition,^[11d] and cell imaging.^[11b] From the point of chemical synthesis, exploration of methods of synthesizing bilayers is a logical advance to create complex matters beyond monolayers. Once strategies for the synthesis of bilayers are established, they may be applied more broadly to thicker few-layer architectures, and possibly enable the controlled growth of 2D architectures into 3D ones, an untamed challenge using currently available synthetic tools, even although confined growth of ordered organic frameworks have been extensively studied at interfaces.^[12] This Concept review will firstly summarize the approaches for the construction of monolayered 2D covalent and supramolecular architectures. We then highlight two recent strategies for the synthesis of bilayer 2DP and 2DSP.^[4d,13] Following these highlights, we will discuss potential approaches to realizing 2D materials with more than two layers. Finally, we will provide our perspectives on challenges and potentials related to such layered 2D covalent and supramolecular polymers.

Monolayer 2DPs and 2DSPs

Topochemical polymerization by a single-crystal to single-crystal transformation has been the optimal approach to synthesizing 2DPs. In 2012, Sakamoto and co-workers reported the preparation of the first 2D polymer **2DP-1** from compound **M1** (Scheme 1).^[4a] In order to facilitate 2D polymerization, **M1** was first crystallized as lamellar sheets and then subjected to photochemical cross-linking via [4 + 2] cycloaddition

between adjacent anthracenes and ethynyl subunits, which led to the formation of layered crystals. Upon heating, the crystals delaminated to give individual monolayers (Figure 1), which was confirmed by atomic force microscopic (AFM) height analysis. In 2014, King, Schlüter and their co-workers separately reported the 2D polymerization of compounds **M2** and **M3** through photoinduced [4 + 4] cycloaddition of the anthracene units in single crystals (Scheme 1).^[4b, 4c] In these two examples, both monomers and resulting **2DP-2** and **2DP-3** were obtained as single crystals, which could be characterized by single crystal X-ray diffraction. Again, exfoliation of the polymer crystals afforded the corresponding monolayer 2DPs (Figure 1). This approach can be further applied to **M4** and **M5** through photoinduced [2 + 2] cycloaddition of their styrylium units (Scheme 1).^[4e, f] Treating the resulting polymer crystals with ammonia or trifluoroacetic acid induces the crystals to delaminate to afford the corresponding 2DPs (Figure 1).

Scheme 1. Compounds **M1–M5** and the related cycloaddition motifs (right) used for photochemically triggered topochemical 2D polymerization.

Although topochemical 2D polymerization affords 2DPs of high quality, it requires crystallization of the monomers and preservation of crystallinity in targets, which is challenging experimentally. However, monomers developed for this approach can be further modified to undergo 2D polymerization at air/water interface to directly produce monolayer 2DPs.^[5] For example, Zhang and co-workers showed that imine-based 2DP can be prepared from **M6** and **M7** (3:2) at air/water interface through imine formation (Scheme 2).^[5b] Moreover, this strategy has been extended to the formation of several different architectures.^[14]

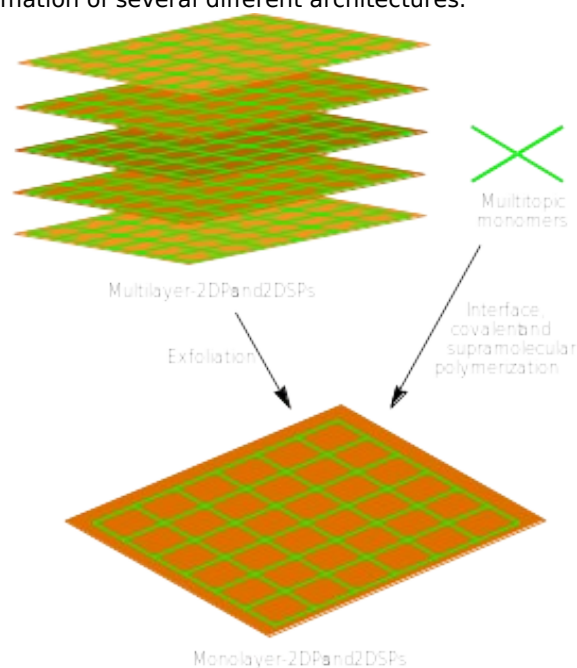
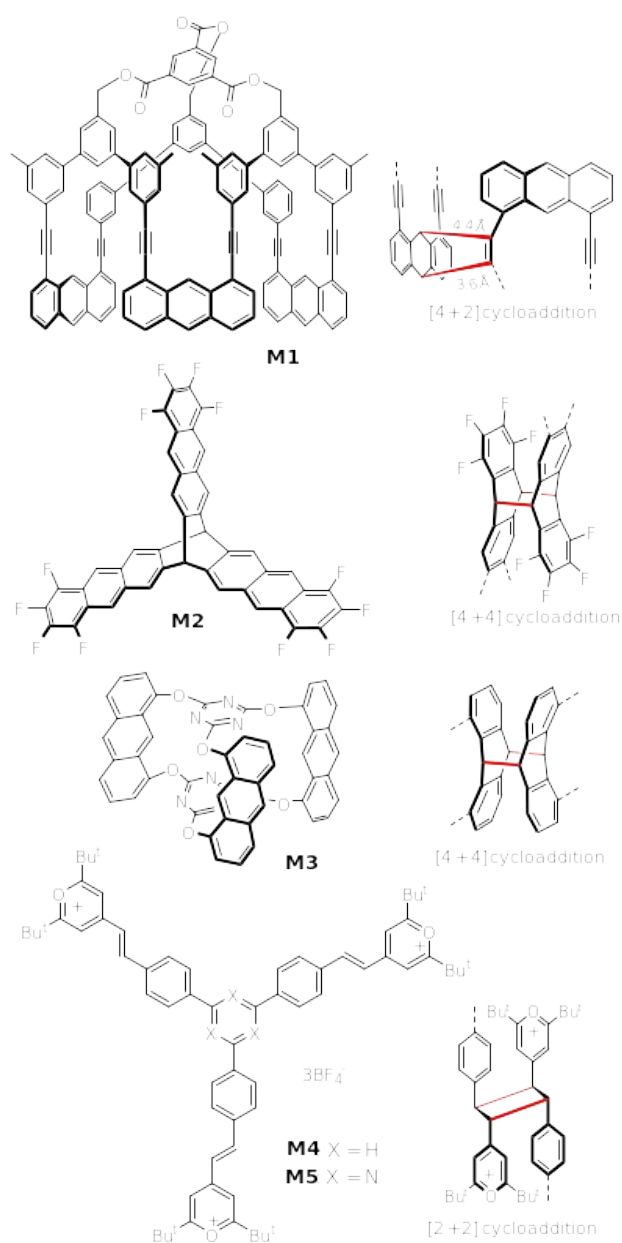
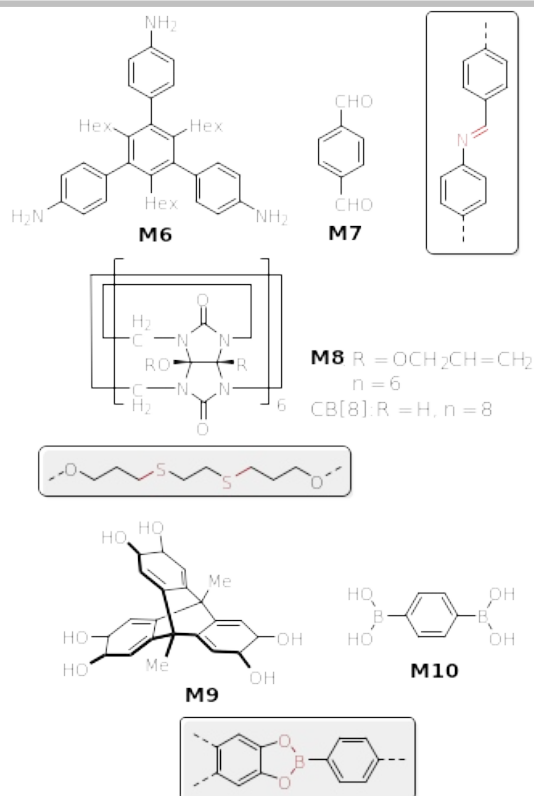


Figure 1. Cartoon representation of strategies for the construction of monolayer 2DPs and 2DSPs through crystal exfoliation (left, upper) and interface, covalent and supramolecular polymerizations (right, upper). Monomers may be tetra-, tri- or hexatopic.



Scheme 2. Compounds **M6–M10** and the corresponding bonds, highlighted in boxes, for covalent polymerization to afford 2DPs.

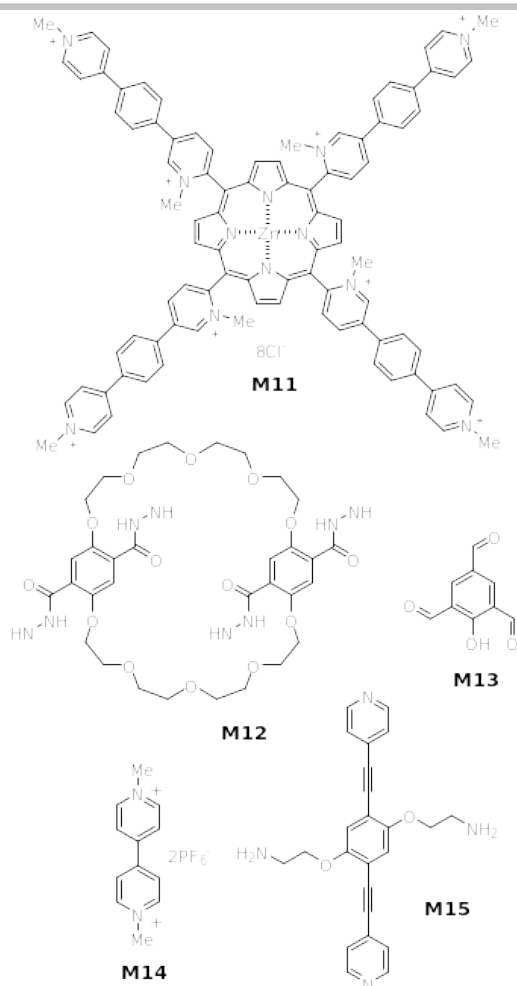
Crystalline 2DPs prepared using the above two approaches are of high regularity, but generally insoluble, which may restrict their scalability, processability and functionality. Kim, Zhao and their co-workers have separately demonstrated that solution-phase polymerization can also afford free-standing 2DPs (Figure 1).^[6] In Kim's instance,^[6a] twelve laterally predisposed allyloxy groups of cucurbit[6]uril derivative **M8** were treated with 1,2-ethanedithiol to afford **2DP-8** (Scheme 2), whose monolayer feature was defined by the height of CB[6]. Protonated spermine was used to suppress the stacking of **2DP-8** by threading through CB[6] to introduce electrostatic repulsion. This is a rare example of flexible 2DPs due to the introduction of the dithioether chains. Further exploration of this approach may lead to more 2DPs of high processability. In another effort, Zhao and co-workers reported the condensation of **M9** and **M10** to produce free-standing **2DP-9/10** through the formation of borates (Scheme 2).^[6b]

Self-assembly via supramolecular interactions serves as another efficient approach to generating 2DSPs (Figure 1). The first example was reported in 2013 by Zhao and co-workers,^[9] which involved the co-assembly of a tritopic monomer and CB[8] in water, induced by CB[8]-enhanced dimerization of the aromatic units of tritopic monomers. Since then, this supramolecular motif has been applied towards many tri- or tetratopic building blocks.^[11] Very recently, Yu and co-workers showed that zinc porphyrin **M11** and CB[8] (1:2) co-assembled to afford 2D supramolecular polymer **2DSP-11/CB[8]** (Scheme 3).^[13] Different from covalent 2DPs, the building blocks of 2DSPs are cationic. Their electrostatic

repulsion can suppress the stacking of the monolayers and endow the monolayers with good water-solubility.

Bilayer 2DP and 2DSP

Bi- or thicker few-layer 2DPs and 2DSPs represent fascinating 2D architectures with tailor-made pores and functionalities. However, their selective fabrication has been a forbidding challenge. In 2020, Loh and coworkers reported the first example of bilayer 2DPs through exfoliation of COF crystals.^[4d] For this aim, macrocycle **M12** bearing four acylhydrazone groups was used to condense with triol **M13** to afford hydrazone-linked **COF-12/13** (Scheme 3), which had unique bilayer repeats defined by the stacking electron-rich 1,4-dioxybenzene units of **M12**. Remarkably, this COF spontaneously exfoliated to afford bilayer **2DP-12/13** when treated with electron-deficient viologen **M14** (Figure 2a), driven by donor-acceptor interaction between **M14** and the 1,4-dioxybenzene units to impose cross-layer electrostatic repulsion. **2DP-12/13** cannot be further separated as the two monolayers are covalently connected by glycol chains. Nonetheless, this system represents a formal bilayer with high regularity. In 2021, Yu and co-workers demonstrated that coordination could be used to guide two **2DSP-11/CB[8]** monolayers to form bilayer structures.^[13] In order to achieve this structure, ditopic ligand **M15** was prepared to coordinate the zinc porphyrins of the monolayer (Scheme 3). At a **M15**/porphyrin ratio of 0.5, the penta-coordination geometry of Zn^{2+} enabled selective formation of the corresponding bilayer **2DSP-M11/CB[8]** (Figure 1), as was confirmed by AFM investigations.



Scheme 3. Compounds **M11**~**M15** used to construct mono- and bilayer 2DPs and 2DSPs.

Towards Construction of Tri- and Tetralayer 2DPs and 2DSPs

Exfoliation of 2DP polymer crystals is effective to produce monolayer 2DPs, but less so in giving 2DPs with controlled thicknesses beyond monolayer. Bottom-up construction of trilayer or even thicker few-layers from monolayer “building blocks” may be more challenging, because it requires accurate control of the layer number of a specific few-layer in a fashion like selective formation of an oligomer among others. As of now, selective generation of few-layers is still not accessible. Nevertheless, thicker few-layers have been observed during the synthesis and manipulation of the above-mentioned covalent and supramolecular bilayers. AFM studies of thickness distribution showed that, within a film with a lateral size of $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$, the above bilayer **2DP-12/13** constituted 82% of the overall content, while the tetralayer 2DP was obtained in 15% yield (Figure 2a).^[4d] Separately, during the synthesis of bilayer **2DSP-M11/CB[8]** from the monolayers and **M15**, within a film with a lateral size of $15\ \mu\text{m} \times 15\ \mu\text{m}$, bilayer **2DSP-M11/CB[8]** was obtained in 94.4% yield, together with 3.1% trilayer (Figure 2b).^[11] It is expected

that, with the optimization of the conditions, these thicker layers may be formed in higher percentage.

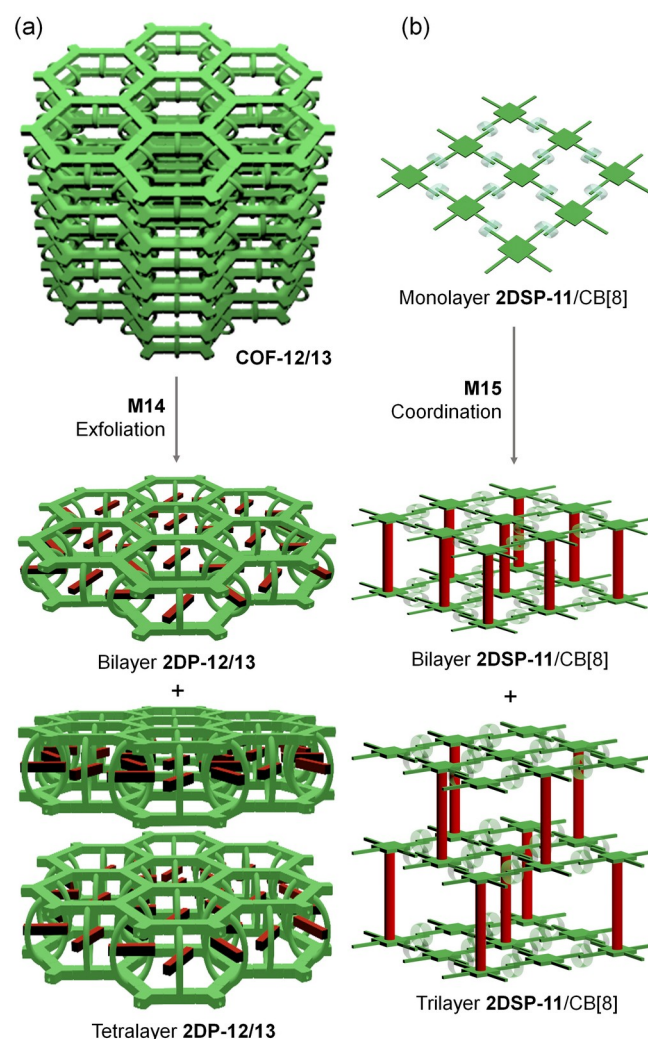


Figure 2. Cartoon representations for the preparation of (a) bi- and tetralayer **2DP-12/13** formed from **COF-12/13** and (b) bi- and trilayer **2DSP-11/CB[8]** from monolayer **2DSP-11/CB[8]**.

Summary and Perspectives

The Concept review briefly summarizes major approaches for the generation of monolayer 2D (supramolecular) polymers and the state-of-the-art for the generation of bilayer structures. Two approaches have been discussed for the generation of bilayer 2DPs and 2DSPs, respectively. The fact that thicker tri- and tetralayers are also observed suggest that few- or multilayer structures may be produced more efficiently or selectively by developing new methodologies or optimizing the current methods. A straightforward strategy is to synthesize linear precursors that contain a fixed number of monomeric units for simultaneous and parallel formation of 2DPs or 2DSPs of the identical layer numbers. By making use of dynamic covalent or supramolecular chemistry, the bottom-up self-assembly strategy may be developed as a more robust and versatile tool to enable the fabrication of previously unattainable 2D layered materials. As a new family of porous polymers with controlled thickness, they are

expected to exhibit new properties and functions beyond currently available 2D polymers.

Acknowledgements

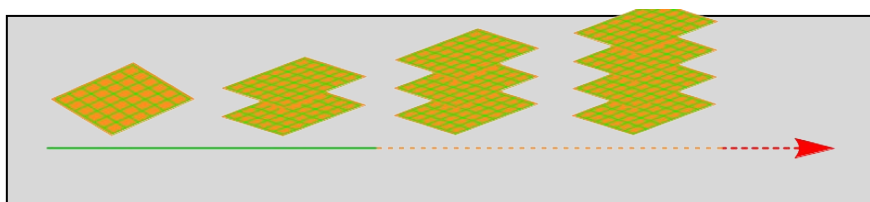
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Keywords: 2D polymer • bilayer • monolayer • self-assembly • supramolecular polymer

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With the synthetic strategies of monolayer 2D covalent and supramolecular polymers being available, synthetic chemistry for bilayer 2D polymers has emerged, which holds promises for attaining well-defined, few-layer 2D polymers. The advances will lead to a bridge to transform 2D materials to 3D materials in a controllable manner.