Chinese Journal of
POLYMER SCIENCE 高分子科学

Soluble Two-dimensional Supramolecular Organic Frameworks (SOFs): An Emerging Class of 2D Supramolecular Polymers with Internal Long-range Orders

Jiang Shu-Yan, Zhao Xin

Cite this article as:
Jiang Shu-Yan, Zhao Xin. Soluble Two-dimensional Supramolecular Organic Frameworks (SOFs): An Emerging Class of 2D Supramolecular Polymers with Internal Long-range Orders[J]. *Chinese J. Polym. Sci*, 2019, 37(1): 1-10. doi: 10.1007/s10118-019-2189-0

View online: https://doi.org/10.1007/s10118-019-2189-0

Articles you may be interested in

Synthetic Two-dimensional Organic Structures
Chinese J. Polym. Sci. 2018, 36(4): 425 https://doi.org/10.1007/s10118-018-2070-6

Two-dimensional Nitrogen-doped Mesoporous Carbon/Graphene Nanocomposites from the Self-assembly of Block Copolymer Micelles in Solution
Chinese J. Polym. Sci. 2018, 36(3): 266 https://doi.org/10.1007/s10118-018-2091-1

Rate of Intra-Molecular Contact Formation in Short Two-Dimensional Compact Polymers Chains
Chinese J. Polym. Sci. 2006, 24(1): 13

超分子有机框架:具有周期性孔结构的超分子聚合物
Supramolecular Organic Frameworks: Porous Periodic Supramolecular Polymers
高分子学报. 2017(1): 19 https://doi.org/10.11777/j.issn1000-3304.2017.16234

二维自组装聚合制备寡层有机-氧化硅纳米杂化材料
Preparation of Few-layered Organic-silica Hybrid Nanomaterials by Two-dimensional Self-assembly and Polymerization
高分子学报. 2018(12): 1507 https://doi.org/10.11777/j.issn1000-3304.2018.18104

一种具有二维状组装体结构的氢键结合超分子水凝胶的制备
PREPARATION OF A HYDROGEN BONDED SUPRAMOLECULAR HYDROGELS WITH TWO DIMENSIONAL AGGREGATE STRUCTURE
高分子学报. 2007(4): 397

Chinese Journal of
POLYMER SCIENCE

REVIEW

https://doi.org/10.1007/s10118-019-2189-0
Chinese J. Polym. Sci. **2019**, *37*, 1–10

Soluble Two-dimensional Supramolecular Organic Frameworks (SOFs): An Emerging Class of 2D Supramolecular Polymers with Internal Long-range Orders

Shu-Yan Jiang and Xin Zhao*

CAS Key Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Abstract Two-dimensional (2D) materials have been demonstrated to exhibit unique properties originating from its 2D nature. In recent years, the construction of 2D materials has become a topic of great interest. This article summarizes the recent advance of 2D supramolecular organic frameworks (SOFs) which are homogeneously constructed in solution phase through self-assembly of rationally designed building blocks. These 2D SOFs are soluble and still maintain stable network structures in solutions, which exhibit uniqueness not only in structures but also in properties. In this concise review, the SOFs-related background is briefly introduced firstly, followed by outlining the research progress of soluble 2D SOFs from the perspective of monomer design, assembly, and structural characterization. The article ends with a personal outlook on the future development of this new class of supramolecular polymers.

Keywords Supramolecular organic frameworks (SOFs); Self-assembly; Two-dimensional; Supramolecular polymers

Citation: Jiang, S. Y.; Zhao, X. Soluble two-dimensional supramolecular organic frameworks (SOFs): an emerging class of 2D supramolecular polymers with internal long-range orders. *Chinese J. Polym. Sci.* **2019**, *37*, 1–10.

INTRODUCTION

Supramolecular chemistry originates from the research on crown ethers and their complexing properties with alkali metal ions.[1] Pioneered by C. L. Peterson, D. J. Cram, and J. M. Lehn, the early research leads to the emergence of many aspects of supramolecular chemistry such as molecular recognition, self-assembly, host-guest chemistry, and so on.[2] Over the past decades, it has become a science as well as a technology which is crossed by many disciplines such as chemistry, biology, physics, materials science, information science, nanotechnology, and environmental science. Self-assembly is the core of supramolecular chemistry which focuses on the construction of advanced architectures by linking individual molecules or macromolecules through non-covalent interactions, and the formation and regulation of well-ordered aggregates.

In 1990, J. M. Lehn *et al*. proposed the first supramolecular polymer by linking monomeric repeat units with hydrogen bonds in solution.[3] Since then, this field has become a fast-growing aspect of supramolecular chemistry. Thanks to their distinct properties such as solution-processibility, self-healing capability, and feasibility of recycling, supramolecular polymers show great potentials in the fabrication of advanced soft materials, especially smart materials that can respond to external stimuli.[4–7] Through rational designs of supramolecular monomers and selection of bonding forces, a myriad of supramolecular polymers with various structures have been constructed.[8–10] However, most of those materials are linear (one dimensional, 1D) and some of them exhibit three-dimensional (3D) structures so far.[11–15] As far as supramolecular polymers strictly extending in two dimensions (2D) are concerned, to construct this kind of materials is still a challenge due to the great difficulty in confining a self-assembly process only in a 2D plane.

Since the isolation of graphene from graphite,[16] 2D materials have received extensive attention. Among them, 2D metal organic frameworks (MOFs)[17,18] and covalent organic frameworks (COFs)[19,20] are two kinds of popular topics in materials science. Typically, they all have high ordered internal periodicity and porosities with large specific surface areas. Although both the framework polymers are constructed by assembling building blocks *via* robust coordination interactions (for MOFs) or dynamic covalent bonds (for COFs), the as-formed products are isolated as insoluble solid crystals or crystalline powders from solutions. In view of self-assembly, their supramolecular congeners should also be constructed in solution phase through less robust noncovalent interactions. However, this concept has not been realized until the first soluble 2D supramolecular organic framework (SOF) was successfully fabricated in 2013.[21] Similar to MOFs and COFs, SOFs also possess periodic framework structures. However, they do exhibit some distinct features, of which the most impressive one is the solubility and sub-

* Corresponding author: E-mail xzhao@sioc.ac.cn

Received August 8, 2018; Accepted September 16, 2018; Published online November 2, 2018

© Chinese Chemical Society
Institute of Chemistry, Chinese Academy of Sciences
Springer-Verlag GmbH Germany, part of Springer Nature 2018

sequent homogeneity in solution phase. The ability to dissolve while maintaining stable network structures endows them with some unique properties. This concise review summarizes the development of soluble 2D SOFs. The progress of SOFs has also been summarized in several nice reviews recently,[22–24] in which both 2D and 3D SOFs are included. This concise review focuses specifically on 2D SOFs and provides the state-of-the-art development of this emerging research field. The design principles, characterization, properties, and applications of 2D SOFs are introduced. In the last part, a personal perspective on the future development of 2D SOFs has also been discussed.

2D SOFs with Hexagonal Pores Assembled from C_3-Symmetric Building Blocks

The first successful construction of a SOF which is soluble and stable in solution phase has been demonstrated by Zhao, Liu, and Li in 2013.[21] To achieve the original idea, a rigid 1,3,5-triphenylbenzene motif that bears three 4,4′-bipyridin-1-ium (BP) units on the peripheral benzene rings was designed and synthesized (Fig. 1). The design principle of such supramolecular building block is based on the following considerations. Firstly, the C_3-symmmetric rigid skeleton is expected to dictate the direction of supramolecular polymerization in a plane *via* its preorganization feature. Secondly, the BP units are excellent guest molecules for cucurbit[8]uril (CB[8]) which can form a 2:1 complex between them with a high binding constant.[25] Thirdly, the water solubility of this cationic molecule could be boosted by introducing three hydrophilic bis(2-hydroxyethyl)carbamoyl groups in the inner benzene unit. On the other hand, these bulky chains also play a crucial role in inhibiting the face-to-face stacking effectively between the as-formed layers and thus secure the existence of monolayered SOF in solution.

In order to unambiguously elucidate the structure of the homogeneous self-assembled entities formed in the aqueous solution, a variety of techniques including ^{1}H-NMR spectroscopy, dynamic light scattering (DLS), small angle X-ray scattering (SAXS), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were applied. While ^{1}H-NMR spectroscopy is used to reveal the binding manner of the host-guest complex between CB[8] and the BP units, the size of self-assembled entity is revealed by DLS. Generally speaking, 2D materials should possess sheet-like structures, which could be characterized by the electron microscopes. Besides, as far as a 2D polymer is concerned, the long-range ordered periodicity is a key criterion, and such feature is investigated typically by SAXS and PXRD. In details, the DLS experiment revealed that D_H of the aggregates formed from **1** (1.0 mmol/L) and CB[8] (1.5 mmol/L) in water was as high as 69 nm and the D_H value further increased with the increasing concentration of the monomers, indicating the formation of large aggregates in the aqueous solution. Morphology study with SEM and TEM showed that sheet-like structure was generated. The height of the sheets was revealed by AFM to be 1.72 nm (Fig. 2), which perfectly matched the diameter of CB[8] (1.75 nm). All the microscopic evidences supported the formation of a soluble monolayer 2D SOF. The solution-phase SAXS experiment in water revealed a scattering peak with a *d*-spacing of 3.61 nm. A peak corresponding to *d*-spacing of 3.78 nm was observed by synchrontron SAXS for a dry sample of 2:3 mixture of **1** and CB[8] after evaporation of water. Moreover, the PXRD pattern of the dried sample revealed a broad (100) peak with a *d*-spacing of 3.7 nm. All of these results strongly suggested the formation of long-range ordered polymeric structures and were consistent with the pore diameter (3.7 nm) calculated for the monolayer SOF assembled from **1** and CB[8] (Fig. 3).

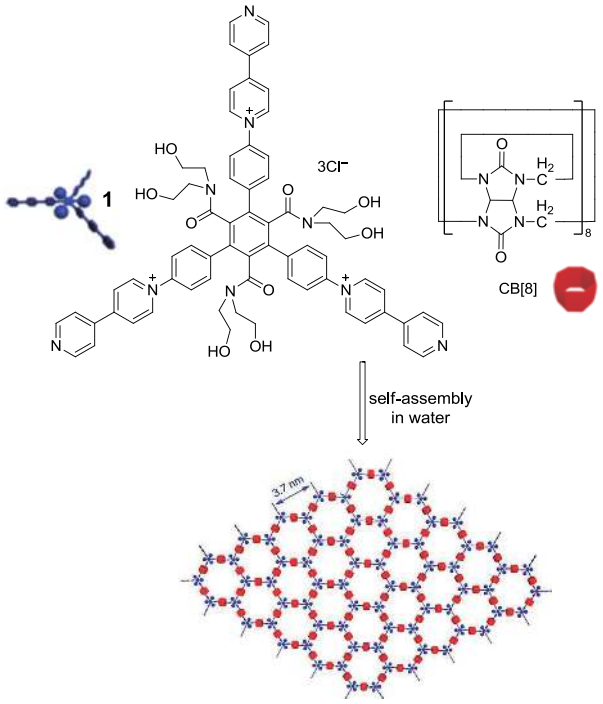


Fig. 1 The structures of supramolecular monomer **1** and CB[8] and schematic representation of the 2D SOF formed by **1** and CB[8] in 2:3 ratio in water (Adapted with permission from Ref. [21]; Copyright (2013) American Chemical Society)

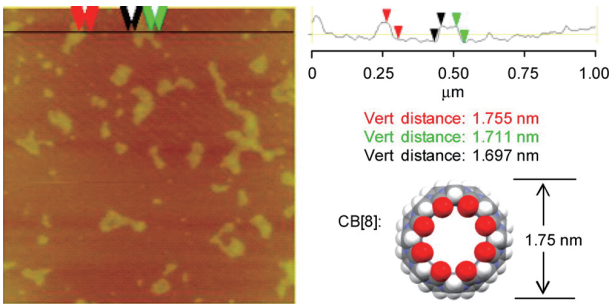


Fig. 2 Tapping-mode AFM image (1 μm × 1 μm) and section analysis of the aggregates on mica from dried solution of compound **1** (1.0 mmol/L) and CB[8] (1.5 mmol/L) in H_2O. Height analysis versus distance along the black line in the image showed an average thickness of 1.72 nm, consistent with the thickness of the expected monolayer framework, which is equivalent to the diameter of CB[8]. (Reproduced with permission from Ref. [21]; Copyright (2013) American Chemical Society)

https://doi.org/10.1007/s10118-019-2189-0

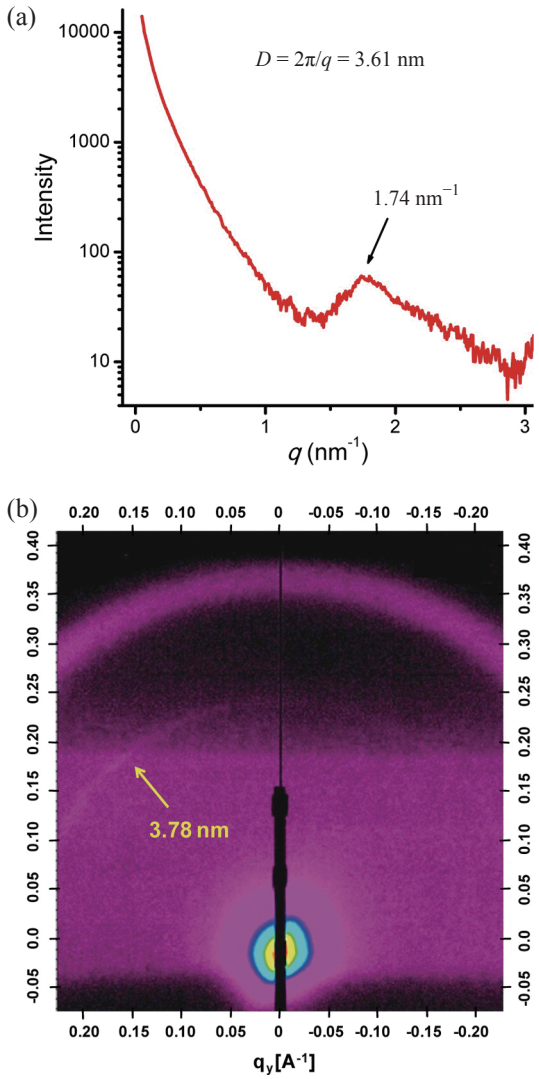


Fig. 3 (a) Solution-phase SAXS profile of the 2:3 mixture of compound **1** (1.0 mmol/L) and CB[8] in water; (b) Synchrotron X-ray scattering of the 2:3 mixture of **1** and CB[8] upon the evaporation of the abovementioned solution. The broader diffusion signal is from Kapton background. (Reproduced with permission from Ref. [21]; Copyright (2013) American Chemical Society)

After reacting with iodine methane and ion exchange, **1** can be changed into $BIPY^{2+}$ derivative **2** (Fig. 4). It is well established that viologen radicals dimerize in water and the dimerization could be further enhanced by encapsulation of CB[8].[26] Thus the viologen units of **2** were readily reduced to the radical cation **3** by sodium dithionite in water. Driven by the dimerization of the radical cations, 2D single-layer SOF was produced.[27] Furthermore, in the presence of CB[8], the monolayer network was stabilized due to the encapsulation of the radical cation dimer within CB[8] (Fig. 5). Both the 2D SOFs formed without and with CB[8] were thoroughly charactzeized with UV-Vis spectroscopy, eletron paramagnetic resonance, DLS, SAXS, and AFM, which confirmed the formation of the predicated network structures.

Monomer **2** was further used by Li and co-workers to construct two kinds of 2D honeycomb-like single-layer SOFs through the CB[8]-encapsulation-enhanced donor-acceptor

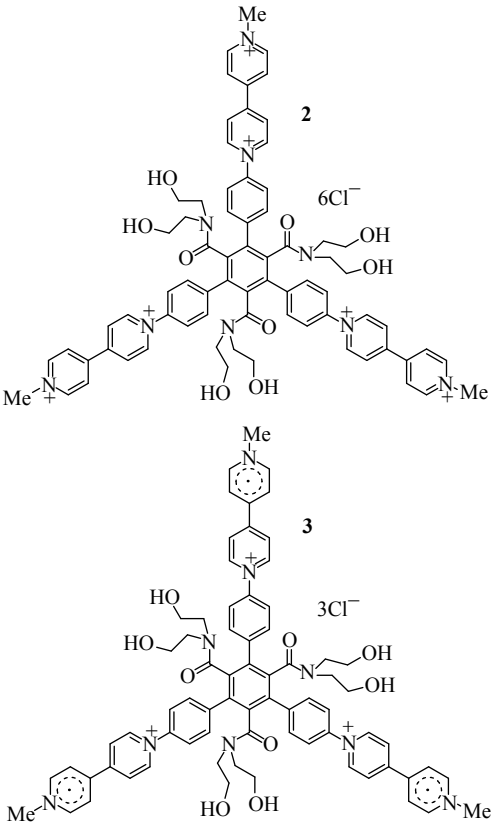


Fig. 4 The structures of monomers **2** and **3**

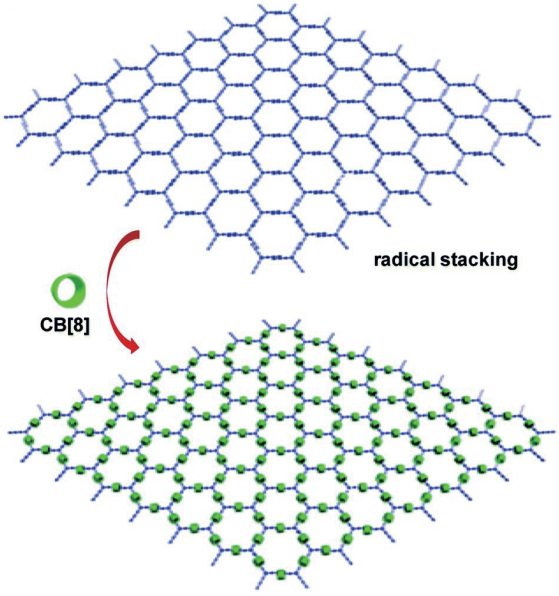


Fig. 5 Schematic illustration of the honeycomb 2D SOF formed by **3** through $BIPY^{\cdot+}$ stacking (top), which was further promoted by CB[8] (bottom) (Reproduced with permission from Ref. [27]; Copyright (2014) The Royal Society of Chemistry)

interaction.[28] In that work, electron-rich naphthalene-incorporated linear flexible monomers **4a** and **4b** were used as the edge of the SOFs, while the rigid C_3-symmetric monomer **2** was used as the vertex (Fig. 6). 2D SOFs with pore size as large as 7 nm were generated in water driven by the donor-

acceptor interaction between the electron-rich naphthalene units and the electron-deficient viologen segments. Taking advantage of protonation and deprotonation of the amine groups on **4b**, for the first time, a pH-responsive SOF was realized by adding HCl and NaOH into the SOF solution alternately. Interestingly, the two SOFs displayed antibacterial activities which were revealed by agar diffusion assays of methicillin-resistant *Staphylococcus aureus* (MRSA) as a test strain. In contrast, none of compounds **2**, **4a**, **4b** or CB[8] with the identical concentration showed any detectable activity. The activity of the two SOFs may be due to the ion enriching effect by their periodic frameworks.

Feng *et al*. have developed an interface self-assembly approach to fabricate 2D SOF monolayers with large areas.[29]

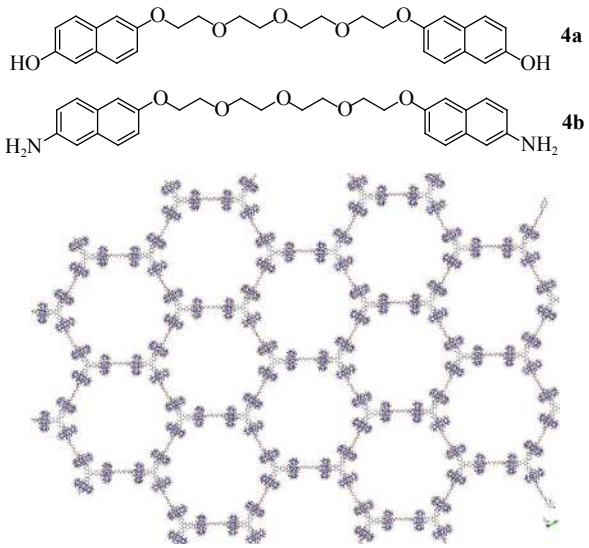


Fig. 6 The chemical structures of **4a** and **4b** and schematic representation of the 2D honeycomb monolayer SOFs assembled from **2**, CB[8], and **4a**/**4b** (Adapted with permission from Ref. [28] Copyright (2016) The Royal Society of Chemistry)

In their work, a C_3-symmetric rigid tris(methoxynaphthyl)-substituted truxene (**Np-Trx**) was selected as the vertex of the honeycomb framework and the edge was designed by connecting two viologen units to naphthalene diimide (**MV-NDI**) (Fig. 7). The self-assembly process is different from the previous ones which are homogeneous. As shown in Fig. 8, over an aqueous solution of **MV-NDI** and CB[8], a solution of **Np-Trx** in toluene was placed. In such way, the building blocks could assemble at the liquid-liquid interface, driven by CB[8]-encapsulation-enhanced donor-acceptor interactions. After draining the solution through the trough bottom, the SOF layers were isolated. This approach endows SOF monolayers with dimensions as large as 0.25 cm^2.

Using a triphenylamine skeleton as the core, we designed two C_3-symmetric building blocks (**5a** and **5b**) by introducing three phenyl-pyridinium (PP) units at the three branches (Fig. 9).[30] As indicated by our previous work, CB[8] can enhance the dimerization of PP units by the encapsulation of two PP units with head-to-tail arrangement in its cavity.[31] As expected, these two building blocks co-assembled with CB[8] to form monolayer 2D SOFs in water, respectively. When the concentrations of SOFs further increased, the formation of hydrogels was observed. Very surprisingly, these hydrogels exhibited extremely high thermal stability, as demonstrated by temperature-dependent rheological experiments, which revealed that both storage modulus and loss modulus of the hydrogels remained nearly constant over the range of 30−180 °C (Fig. 10). This was also clearly indicated by the inverse experiment at 175 °C. It is a rare case for hydrogels fabricated by the self-assembly of small organic molecules, whose thermal stabilities are usually quite low. Molecular dynamic simulations revealed that the high thermal stability of the hydrogels could be attributed to the extraordinarily large surface areas of the 2D sheets, which provide a maximum number of interaction sites for the formation of hydrogen bonds between water molecules and the SOF skeletons.

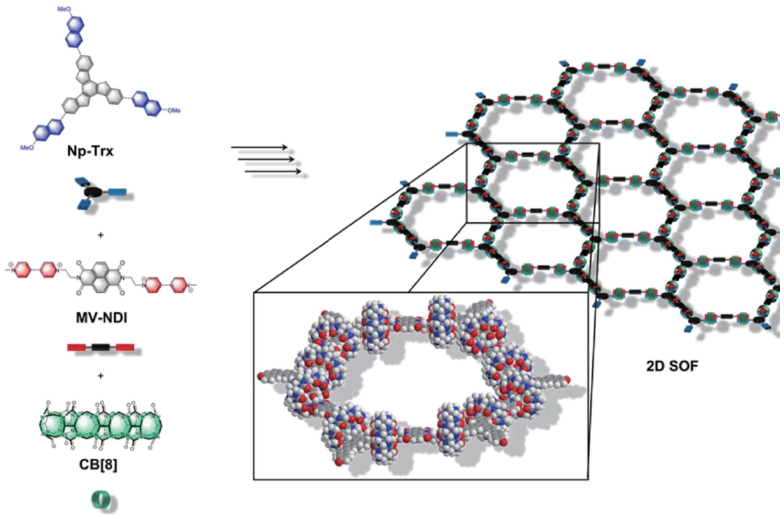


Fig. 7 Schematic illustration of the 2D SOF assembled in water from **Np-Trx**, **MV-NDI**, and CB[8] (Reproduced with permission from Ref. [29]; Copyright (2015) American Chemical Society)

https://doi.org/10.1007/s10118-019-2189-0

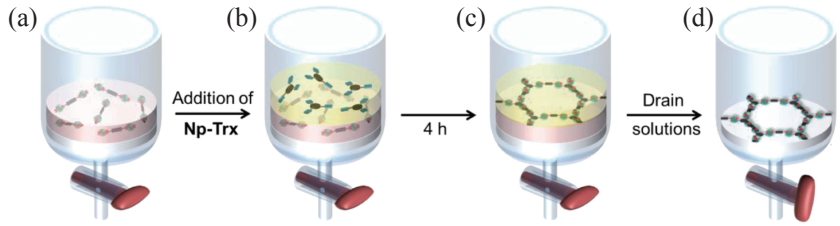


Fig. 8 Schematic illustration of the interface self-assembly process and the isolation of the 2D SOF films (Reproduced with permission from Ref. [29]; Copyright (2015) American Chemical Society)

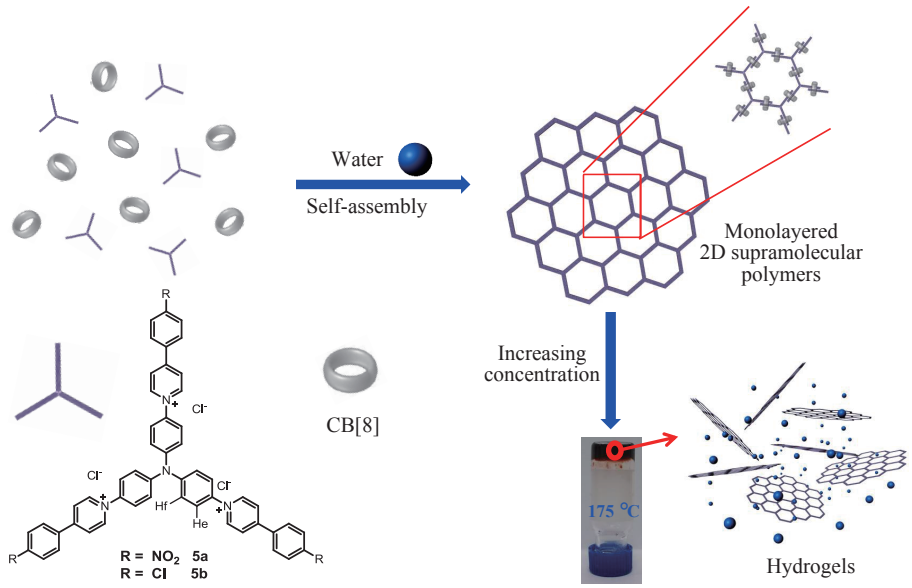


Fig. 9 Cartoon representations of the formation of 2D SOFs and hydrogels from the self-assembly of CB[8] with **5a** and **5b**, respectively (Adapted with permission from Ref. [30]; Copyright (2015) The Royal Society of Chemistry)

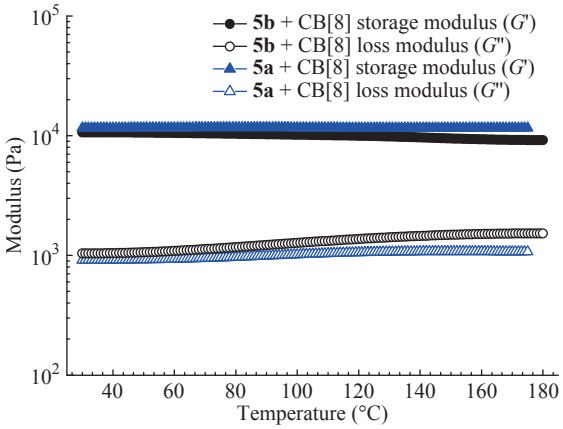


Fig. 10 Temperature-dependent storage modulus (G') and loss modulus (G'') for the hydrogels fabricated from CB[8] and **5a** or **5b** (50 bar, 1 Hz; 2 °C/min) (Reproduced with permission from Ref. [30]; Copyright (2015) The Royal Society of Chemistry)

When the substituents (R) in the monomer **5a** (or **5b**) were replaced by methoxy groups, a new building block **5c** was produced. The soluble SOF built by **5c** and CB[8] (2:3 molar ratio) in water exhibited a strong fluorescence emision.[32] In contrast, compound **5c** itself was almost non-emissive in water. This turn-on fluorescence phenomenon was attributed to the block of charge-transfer by the encapsulation of PP units in cavity of CB[8] and/or the aggregation-induced emission (AIE) effect.[33] The fluorescent 2D SOF was further used as a fluorescent chemosensor to detect nitroaromatic explosives. It was found that the SOF exhibited very high selectivity and sensitivity toward picric acid over the other 12 nitroaromatics by displaying a dramatic fluorescence quenching (Fig. 11). The recognition mechanism was explained by the charge-transfer between the highly electron-deficient picric acid and the electron-rich triphenylamine core.

Very recently, Park and co-workers also designed a trilateral cationic cyanstilbene molecule **6** as the monomer for the construction of a fluorescent 2D SOF (Fig. 12).[34] Synthesized by the Knoevenagel reaction of 1,3,5-benzenetriacetonitrile with 4-(pyridine-4-yl)benzaldehyde, **6** gave rise to nanosized structures in aqueous solution with moderate fluorescence emission forced by hydrophobic effect. The fluorescence emission can be gradually enhanced by dropwise adding CB[8] aqueous solution into aqueous solution of **6**, with its emission peak red shifting from 520 nm to 585 nm. The fluorescence characterization also indicated that the 2D SOF has a higher fluorescent emission efficiency and a longer fluorescent lifetime (Φ_f = 0.60, τ_f = 19.7 ns). As revealed

by the DLS measurement, the size of the 2D SOF made from 1 mmol/L aqueous solution of **6** was close to 1 μm. This 2D SOF was further used for photolysis of water. When it was used as a photosensitizer template in a visible-light-driven H_2 evolution system, the 2D SOF improved the turnover number (TON) of a colloidal Pt catalyst up to 300 in 6 h.

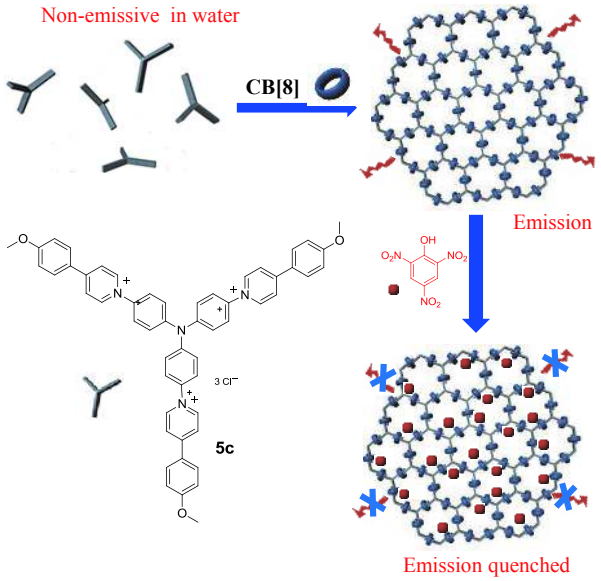


Fig. 11 Cartoon representation for the 2D SOF assembled from **5c** and CB[8] and its application as a highly selective picric acid sensor (Adapted with permission from Ref. [32]; Copyright (2016) The Royal Society of Chemistry)

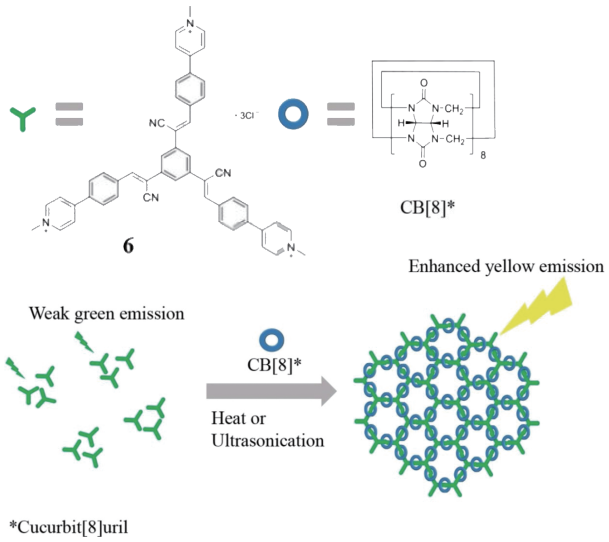


Fig. 12 Structures of cationic cyanostilbenes (**6**), CB[8], and cartoon representation for the 2D SOF (Reproduced with permission from Ref. [34]; Copyright (2018) Wiley-VCH)

2D SOFs with Other Topological Structures

In addition to the SOFs with hexagonal pores described above, 2D SOFs bearing other topological structures have also been constructed over the past several years. In 2015, we reported two SOFs with square-shaped pores through three-component self-assembly.[35] In these SOFs, rigid cross-shaped tetraphenylporphyrin units (**7**) were used as vertexes, and the flexible oligoethylene glycols (**8** and **9**) were used as edges (Fig. 13). They were drawn together by CB[8] through host-guest interactions between viologen and naphthalene units to give rise to 2D SOFs in water. In contrast to the previous SOFs which were constructed through rigid building blocks, these two SOFs exhibited a flexible feature. AFM measurements revealed that the heights of the as-prepared SOFs were only 1.32 and 1.24 nm for the samples of **7**-**8**-CB[8] and **7**-**9**-CB[8], respectively. These values are lower than the outer diameter of CB[8] (1.75 nm), suggesting collapsing of the films on the solid supporter, as a result of the flexibility of the building blocks. Their flexibility also resulted in more corrugations of the SOF films and broadened SAXS peaks, as shown by the TEM images and SAXS patterns. Although the internal order of the SOFs was lower than those fabricated from wholly rigid monomers, this work demonstrates for the first time that complete rigidity is not necessarily required for building blocks to construct SOFs. And such strategy might be extended to other framework structures such as MOFs and COFs, and might boost up structural diversity of framework materials since flexible skeletons are more accessible and diverse.

A 2D SOF with parallelogram pores has also been assembled by our group recently.[36] In 2015, we reported a tetraphenylethene (TPE)-based 2D SOF (Fig. 14), since TPE is a widely used scaffold which exhibits unique AIE phenomenon.[33] Holding an AIE-effect skeleton, the TPE-based building block (**10**) has no fluorescence emission in aqueous solution. However, after the 2D SOF was generated through the self-assembly of monomer **10** and CB[8] in water, fluorescence emission could be detected. This fluorescence turned-on phenomenon could be attributed to restriction of free rotation of the TPE structure after self-assembled. Since 2D layers are prone to stack into layered structures, organic solvents such as THF, acetone, 1,4-dioxane, and acetonitrile were added into the aqueous SOF solution to push the single layers to aggregate through solvophobic interactions between the ionic network and the organic solvents. With the increased amount of organic solvents, the fluorescence emission of SOF increased remarkably. The enhancement of fluorescence emission after the addition of organic solvents could be attributed to the stacking of the monolayer SOF, which resulted in further inhibition of the rotation of TPE units in the stack layers. The aggregation of the SOF layers was revealed by TEM and DLS.

This system was also studied by Liu and co-workers, who found that the self-assembly of **10** and CB[8] could lead to the formation of a hydrogel with distinct orange fluorescence (Fig. 15).[37] The as-formed hydrogel has been detailedly investigated with rheological analysis and microscopy. This hydrogel is highly thermostable and the gel phase could be maintained even at 200 °C. Another interesting feature of this hydrogel is the mutistimuli-responsiveness to acid-base, competitive guests, and mechanical force. It also exhibits brilliant loading and removal capability to anionic dyes, which shows potential applications in waste water treatment and environmental protection.

https://doi.org/10.1007/s10118-019-2189-0

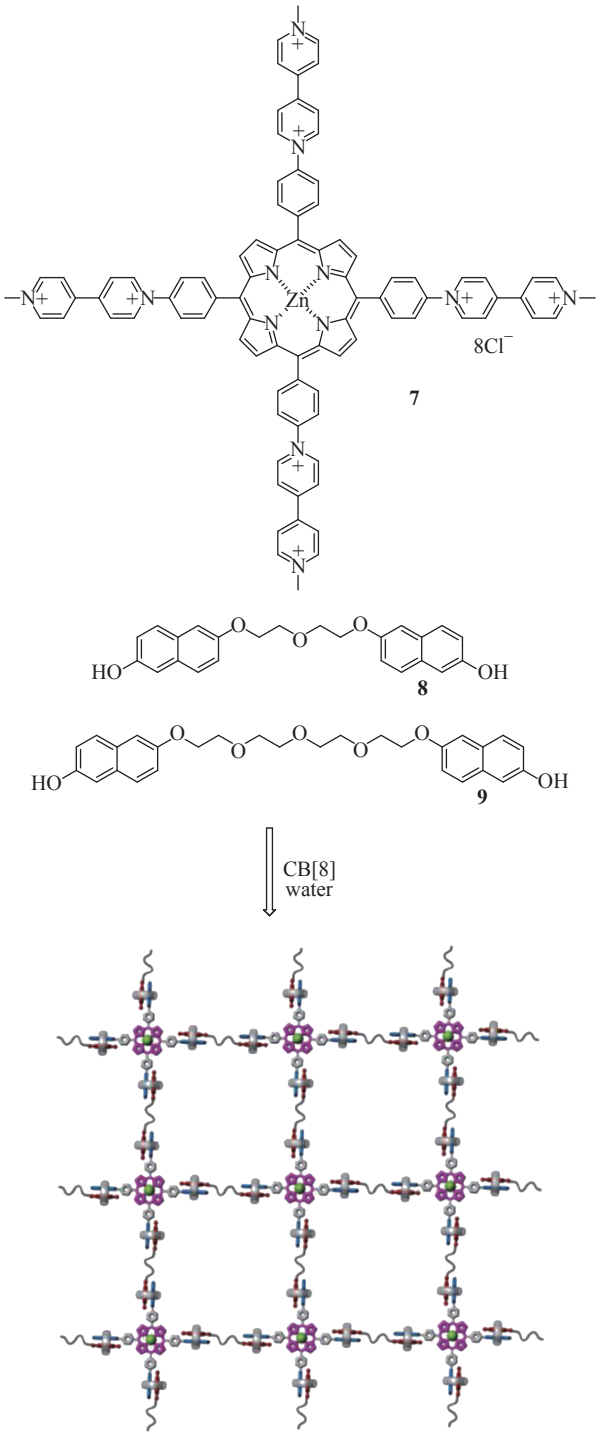


Fig. 13 Chemical structures of compounds **7**, **8**, **9** and schematic representation of 2D supramolecularly polymeric pattern from the self-assembly of these compounds and CB[8] (Adapted with permission from Ref. [35]; Copyright (2015) The Royal Society of Chemistry)

Very recently, another two TPE-based building blocks (**11** and **12**) were reported by Cao and co-worker. Two kinds of shape-controllable and fluorescent 2D SOFs have been constructed through the self-assembly of CB[8] with **11** and **12**, respectively.[38] As shown in Fig. 16, **11** and **12** contain a TPE core appended by four pyridinium(vinyl) arms. The difference between the two blocks is that **11** is rigid while **12** is more flexible and rotatable due to its longer pyridiniumvinyl arms. Such difference leads to different morphologies of the aggregates of the SOFs. While the SOF from **11** and CB[8] produces planar networks which further stack into supramolecular cuboids, the SOF of **12**·CB[8] gives rise to curved networks which further aggregate into spheroids. Furthermore, compared to the monomers, the SOFs of $\mathbf{11}_n$·CB[8]$_{2n}$ and $\mathbf{12}_n$·CB[8]$_{2n}$ exhibited large red-shifts of maximum emission peaks and stimuli-responsive turn-off/turn-on fluorescence was also realized. Such feature was further applied in cellular imaging. Upon the addition of competitive guest, 3,5-dimethyl-1-adamantylamine, the fluorescence of the building blocks can be recovered in HeLa cells by releasing **12** from the SOF.

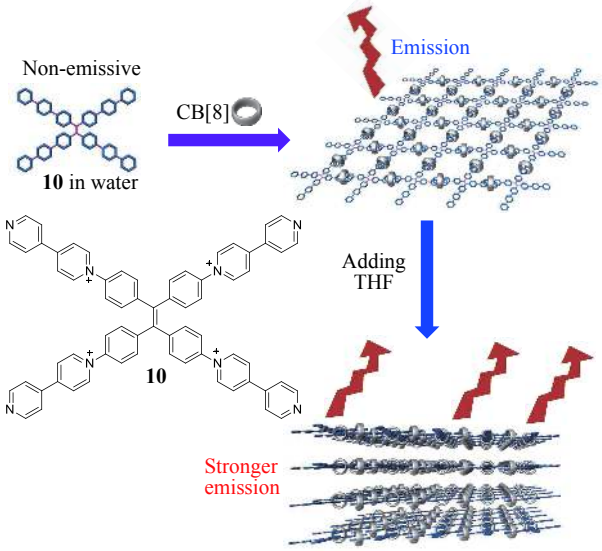


Fig. 14 Cartoon representation for the formation of a 2D SOF assembled from **10** and CB[8] in water, and stepwise fluorescence enhancement (Adapted with permission from Ref. [36]; Copyright (2015) The Royal Society of Chemistry)

In 2016, Wu and co-workers reported a new strategy to build soluble single-layer SOFs *via* electrostatic interaction and steric effect.[39] First, they chose polyoxometalates (POMs) $PW_{11}VO_{40}^{4-}$(PWV^{4-}) as a link nod in the SOF network because the negative charge in POMs is delocalized and moveable. Meanwhile, there is enough space to accommodate four CD-shielded cations packing in one plane, which is the prerequisite for the formation of 2D frameworks. Then, the mutual recognition of azo group, Azo-TrEG·2Br, and α-cyclodextrin was used to construct a pseudorotaxane structure with positive charges on both ends (Fig. 17). This ionic single-layer 2D framework was assembled by mixing Azo-TrEG@CD·2Br and PWV^{4-} at 2:1 molar ratio in aqueous solution driven by electrostatic interaction between pyridinium and PWV^{4-} (Fig. 18). The formation of a 1.4 nm-thick single-layered SOF with 3.7 nm quadrilateral pores is supported by the experimental results of DLS, TEM, AFM, and XRD experiments. Stable membranes containing nanoporous structure were fabricated by filtration of the SOF solution through a polycarbonate filter

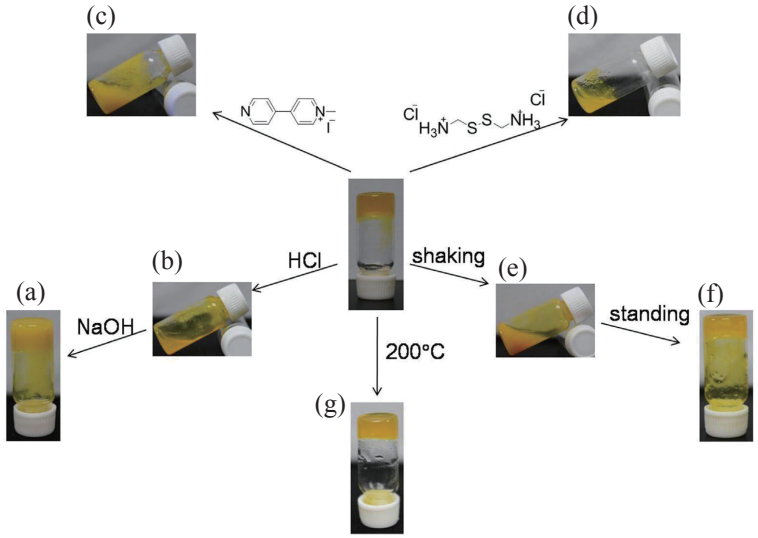


Fig. 15 Multistimuli-responsiveness of the supramolecular hydrogel formed by **10** (5 mmol/L, 0.5 wt%) and CB[8] (10 mmol/L, 1.3 wt%) and its thermal stability at 200 °C (Adapted with permission from Ref. [37]; Copyright (2016) Taylor and Francis)

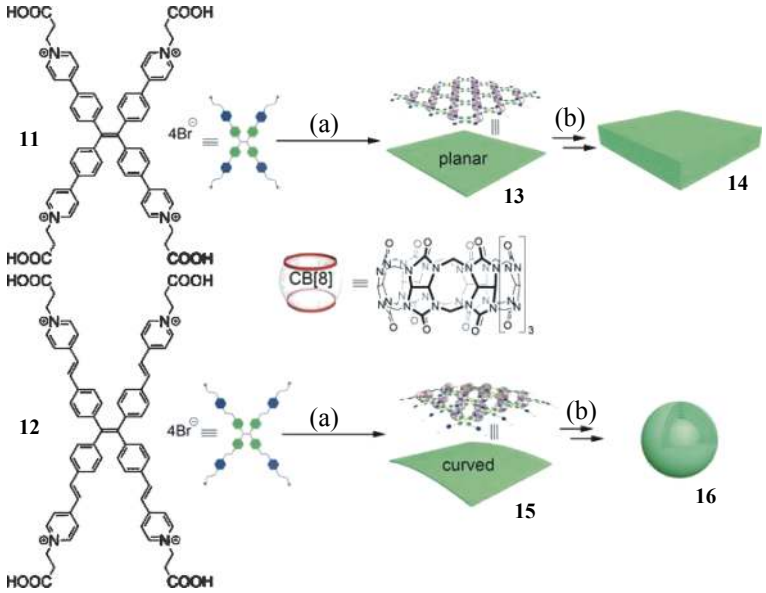


Fig. 16 Chemical structures of **11**, **12**, and CB[8], and cartoon illustrations of the hierarchical formation of supramolecular network-type layers (**13** and **15**) and frameworks (**14** and **16**): (a) host-guest complexation; (b) Stacking or aggregating (Reproduced with permission from Ref. [38]; Copyright (2018) Wiley-VCH)

under reduced pressure. The as-obtained membranes are quite stable and demonstrate precisely size-selective separation of quantum dots with very high accuracy and efficiency, suggesting great potentials in selective transport, molecular separation, and dialysis systems.

CONCLUSIONS AND OUTLOOK

The advances made in 2D SOFs soluble in aqueous solution phase have been summarized. These self-assembled architectures represent a new class of 2D supramolecular polymers which exhibit high long-range internal orders. In contrast to their framework analogues, MOFs and COFs, which are insoluble in solution phase and regarded to be "hard" porous materials, the 2D SOFs described in this article are homogeneous and soluble "soft" porous polymers, which have the advantage of solution processibility. Moreover, while the synthesis of MOFs and COFs usually requires harsh solvothermal conditions, the construction of 2D SOFs processes through molecular self-assembly in solutions, which is quite mild and suitable for mass production.

However, although impressive progress on soluble 2D SOFs has been made since the first example was reported in 2013, this research field is still in its infancy. The following aspects should be focused for future development. Firstly, the topological structures of 2D SOFs are quite limited. Currently, most 2D SOFs reported possess hexagonal porosity,

https://doi.org/10.1007/s10118-019-2189-0

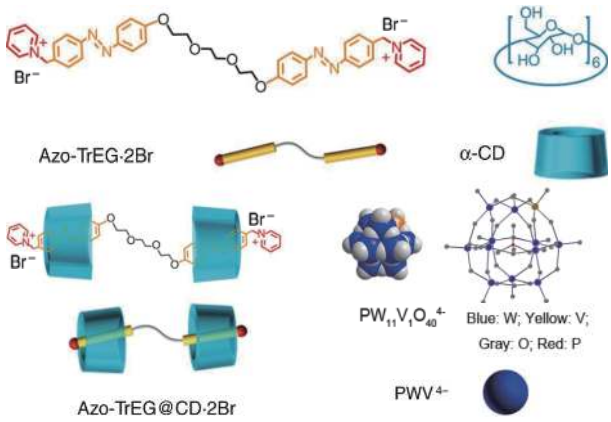


Fig. 17 Schematic representation of chemical structures and building blocks[39]

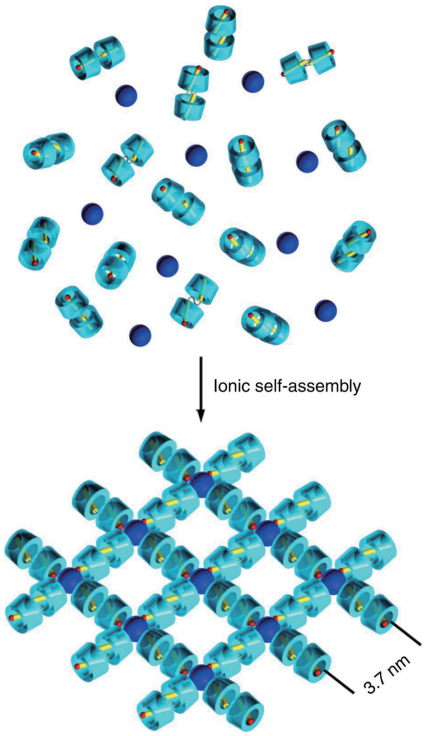


Fig. 18 Schematic representation of the formation of 2D SOF *via* ionic self-assembly[39]

albeit a few examples of 2D SOFs bearing square and parallelogram pores have also been demonstrated recently. In this context, construction of 2D SOFs with diversiform pore topologies and even those with heterogeneous porosity[40–42] is highly desired and crucial for pushing forward the development of this exciting research field. Secondly, the driven force for the assembly of the SOFs is mainly CB[8]-based host-guest interactions so far. While this kind of interaction has some advantages such as high binding constants and aqueous phase friendliness, other noncovalent bonds should also have potentials to construct soluble 2D SOFs in a variety of solvents. To achieve this goal, building blocks must be elegantly designed. Thirdly, due to the extremely thin feature of SOF monolayers, characterization of these soft materials is a very challenging task, especially the periodicity, which is a key criterion to define 2D polymers. Although a toolkit for convinced structural elucidation has been established in the research summarized in this article, the processes are fussy and the solution phase scattering/diffraction peaks are too weak in some cases to provide useful information. Therefore, advanced and simplified characterization techniques require urgent development. At last, exploring applications of this class of unique homogeneous 2D materials will become the center of attention. Some interesting properties and applications have already been demonstrated above. However, we believe that this is just the tip of the iceberg. Thanks to the structural uniqueness of 2D SOFs, versatile applications can be expected for exploitation. For example, taking advantage of the extremely thin SOF singlelayers with the ordered internal periodicity, excellent platforms can be obtained for functionalization through postsynthetic modification on frameworks. In such way, arrays of functional units anchored on the surface of 2D SOFs with highly ordered arrangements can be realized. In addition to surface functionalizations, the porosity of 2D SOFs is another key aspect for applications. In this context, 2D SOF films may serve as ultrafiltration membranes, as their pore size and shape can be precisely designed and constructed. For such application, a nice example has been already demonstrated by Wu and coworkers[39] and more elegant designs are highly expected.

Based on the unique structures and properties as well as the advantages of 2D SOFs, it is undoubtedly that research on this new class of 2D supramolecular polymers will spring up in the near future.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21472225, 21725404) and the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDAB20000000).

REFERENCES

1 Pedersen, C. J. Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **1967**, *89*, 7017−7036.
2 Lehn J. M. in *Supramolecular Chemistry: Concepts and Perspectives*. Wiley VCH, Weinheim, **2006**.
3 Fouquuey, C.; Lehn, J. M.; Levelut, A. M. Molecular recognition directed self-assembly of supramolecular liquid crystalline polymers from complementary chiral components. *Adv. Mater.* **1990**, *2*, 254−257.
4 Aida, T.; Meijer, E. W.; Stupp, S. I. Functional supramolecular polymers. *Science* **2012**, *335*, 813−817.
5 Yang, L.; Tan, X.; Wang, Z.; Zhang, X. Supramolecular polymers: Historical development, preparation, characterization, and functions. *Chem. Rev.* **2015**, *115*, 7196−7293.
6 Qu, D. H.; Wang, Q. C.; Zhang, Q. W.; Ma, X.; Tian, H. Photoresponsive host-guest functional systems. *Chem. Rev.* **2015**, *115*, 7543−7588.
7 Guo, D. S.; Liu, Y. Calixarene-based supramolecular polymerization in solution. *Chem. Soc. Rev.* **2012**, *41*, 5907−5921.
8 Xu, J. F.; Zhang, X. Study on supramolecular polymers in China: An overview and outlook. *Acta Polymerica Sinica* (in Chinese) **2017**, 37−49.

9 Wei, P.; Yan, X.; Huang, F. Supramolecular polymers constructed by orthogonal self-assembly based on host-guest and metal-ligand interaction. *Chem. Soc. Rev.* **2015**, *44*, 815−832.
10 Harada A. in *Supramolecular Polymers Chemistry*. Wiley VCH, Weinheim, **2012**.
11 Fan, Y.; Lin, F.; Xu, X. N.; Xu, J. Q.; Zhao, X. Construction of a rod-coil supramolecular copolymer through CB[8]-encapsulation-enhanced donor-acceptor interaction. *Acta Polymerica Sinica* (in Chinese) **2017**, 80−85.
12 Yi, Z. J.; Wu, Z. Q.; Lin, F.; Qi, Q. Y.; Xu, X. N.; Zhao, X. A supramolecular bottlebrush polymer assembled on the basis of cucurbit[8]uril-encapsulation-enhanced donor-acceptor interaction. *Chinese Chem. Lett.* **2017**, *28*, 1167−1171.
13 Chen, S. G.; Yu, Y.; Zhao, X.; Ma, Y.; Jiang, X. K.; Li, Z. T. Highly stable chiral $(A)_6$-B supramolecular copolymers: A multivalency-based self-assembly process. *J. Am. Chem. Soc.* **2011**, *133*, 11124−11127.
14 Zhou, C.; Tian, J.; Wang, J. L.; Zhang, D. W.; Zhao, X.; Liu, Y.; Li, Z. T. A three-dimensional cross-linking supramolecular polymer stabilized by the cooperative dimerization of the viologen radical cation. *Polym. Chem.* **2014**, *5*, 341−345.
15 Ji, X. F.; Wang, P.; Wang, H.; Huang, F. A fluorescent supramolecular crosslinked polymer gel formed by crown ether based host-guest interactions and aggregation induced emission. *Chinese J. Polym. Sci.* **2015**, *33*, 890−898.
16 Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. E.; Grigorieva, I. V.; Firsov, A. A. Electric field in atomically thin carbon films. *Science* **2004**, *306*, 666−669.
17 Stock, N.; Biswas, S. Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* **2012**, *112*, 933−969.
18 Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 673−674.
19 Ding, S. Y.; Wang, W. Covalent organic frameworks (COFs): From design to applications. *Chem. Soc. Rev.* **2013**, *42*, 548−568.
20 Waller, P. J.; Gandara, F.; Yaghi, O. M. Chemistry of covalent organic frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053−3063.
21 Zhang, K. D.; Tian, J.; Hanifi, D.; Zhang, Y.; Sue, A. C.; Zhou, T. Y.; Zhang, L.; Zhao, X.; Liu, Y.; Li, Z. T. Toward a single-layer two-dimensional honeycomb supramolecular organic framework in water. *J. Am. Chem. Soc.* **2013**, *135*, 17913−17918.
22 Wang, H.; Zhang, D. W.; Zhao, X.; Li, Z. T. Supramolecular organic frameworks (SOFs): Water-phase periodic porous self-assembled architectures. *Acta Chimica Sinica* (in Chinese) **2015**, *73*, 471−479 .
23 Tian, J.; Chen, L.; Zhang, D. W.; Liu, Y.; Li, Z. T. Supramolecular organic frameworks: Engineering periodicity in water through host–guest chemistry. *Chem. Commun.* **2016**, *52*, 6351−6362.
24 Wang, H.; Zhang, D. W.; Li, Z. T. Supramolecular organic frameworks: porous periodic supramolecular polymers. *Acta Polymerica Sinica* (in Chinese) **2017**, 19−26.
25 Zhang, Z. J.; Zhang, H. Y.; Chen, L.; Liu, Y. Interconversion between [5]pseudorotaxane and [3]pseudorotaxane by pasting/detaching two axle molecule. *J. Org. Chem.* **2011**, *76*, 8270−8276.
26 Jeon, W. S.; Kim, H. J.; Lee, C.; Kim, K. Control of the stoichiometry in host-guest complexation by redox chemistry of guests: Inclusion of methylviologen in cucurbit[8]uril. *Chem. Commun.* **2002**, 1828−1829.
27 Zhang, L.; Zhou, T. Y.; Tian, J.; Wang, H.; Zhang, D. W.; Zhao, X.; Liu, Y.; Li, Z. T. A two-dimensional single-layer supramolecular organic framework that is driven by viologen radical cation dimerization and further promoted by cucurbit[8]uril. *Polym. Chem.* **2014**, *5*, 4715−4721.
28 Zhang, L.; Jia, Y.; Wang, H.; Zhang, D. W.; Zhang, Q.; Liu, Y.; Li, Z. T. pH-Responsive single-layer honeycomb supramolecular organic frameworks that exhibit antimicrobial activity. *Polym. Chem.* **2016**, *7*, 1861−1865.
29 Pfeffermann, M.; Dong, R.; Graf, R.; Zajaczkowshi, W.; Gorelik, T.; Pisula, W.; Barita, A.; Müllen, K.; Feng, X. Free-standing monolayer two-dimensional supramolecular organic framework with good internal order. *J. Am. Chem. Soc.* **2015**, *137*, 14525−14532.
30 Zhou, T. Y.; Qi, Q. Y.; Zhao, Q. L.; Fu, J.; Liu, Y.; Ma, Z.; Zhao, X. Highly thermally stable hydrogels derived from monolayered two-dimensional supramolecular polymers. *Polym. Chem.* **2015**, *6*, 3018−3023.
31 Zhang, Y.; Zhou, T. Y.; Zhang, K. D.; Dai, J. L.; Zhu, Y. Y.; Zhao, X. Encapsulation enhanced dimerization of a series of 4-aryl-*N*-methylpyridinium derivatives in water: New building blocks for self-assembly in aqueous media. *Chem. Asian J.* **2014**, *9*, 1530−1534.
32 Zhang, Y.; Zhan, T. G.; Zhou, T. Y.; Qi, Q. Y.; Xu, X. N.; Zhao, X. Fluorescence enhancement through the formation of a single-layer two-dimensional supramolecular organic framework and its application in highly selective recognition of picric acid. *Chem. Commun.* **2016**, *52*, 7588−7591.
33 Zhang, S.; Yan, J. M.; Qin, A. J.; Sun, J. Z.; Tang, B. Z. The specific detection of Cu(II) using an AIE-active alanine ester. *Chinese Chem. Lett.* **2013**, *24*, 668−672.
34 Lee, H. J.; Kim, H. J.; Lee, E. C.; Kim, J.; Park, S. Y. Highly luminescent and water-soluble two-dimensional supramolecular organic framework: All-organic photosensitizer template for visible-light-driven hydrogen evolution from water. *Chem. Asian J.* **2018**, *13*, 390−394.
35 Zhang, X.; Nie, C. B.; Zhou, T. Y.; Qi, Q. Y.; Fu, J.; Wang, X. Z.; Dai, L.; Chen, Y.; Zhao, X. The construction of single-layer two-dimensional supramolecular organic frameworks in water through the self-assembly of rigid vertexes and flexible edges. *Polym. Chem.* **2015**, *6*, 1923−1927.
36 Xu, S. Q.; Zhang, X.; Nie, C. B.; Pang, Z. F.; Xu, X. N.; Zhao, X. The construction of a two-dimensional supramolecular organic framework with parallelogram pores and stepwise fluorescence enhancement. *Chem. Commun.* **2015**, *51*, 16417−16420.
37 Chen, X. M.; Zhang, Y. M.; Liu, Y. Adsorption of anionic dyes from water by thermostable supramolecular hydrogel. *Supramol. Chem.* **2016**, *28*, 817−824.
38 Li, Y. W.; Dong, Y. H.; Miao, X. R.; Ren, Y. L.; Zhang, B. L.; Wang, P. P.; Yu, Y.; Li, B.; Isaacs, L.; Cao, L. P. Shape-controllable and fluorescent supramolecular organic frameworks through aqueous host-guest complexation. *Angew. Chem. Int. Ed.* **2018**, *57*, 729−733.
39 Yue, L.; Wang, S.; Zhou, D.; Zhang, H.; Li, B.; Wu, L. X. Flexible single-layer ionic organic-inorganic frameworks towards precise nano-size separation. *Nat. Commun.* **2016**, *7*, 10742.
40 Zhou, T. Y.; Xu, S. Q.; Wen, Q.; Pang, Z. F.; Zhao, X. One-step construction of two different kinds of pores in a 2D covalent organic framework. *J. Am. Chem. Soc.* **2014**, *136*, 15885−15888.
41 Pang, Z. F.; Xu, S. Q.; Zhou, T. Y.; Liang, R. R.; Zhan, T. G.; Zhao, X. Construction of covalent organic frameworks bearing three different kinds of pores through the heterostructural mixed linker strategy. *J. Am. Chem. Soc.* **2016**, *138*, 4710−4713.
42 Qian, C.; Qi, Q. Y.; Jiang, G. F.; Cui, F. Z.; Tian, Y.; Zhao, X. Toward covalent organic frameworks bearing three different kinds of pores: the strategy for construction and COF-to-COF transformation *via* heterogeneous linker exchange. *J. Am. Chem. Soc.* **2017**, *139*, 6736−6743.

https://doi.org/10.1007/s10118-019-2189-0