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The construction of single-layer two-dimensional supramolecular organic frameworks in water through the self-assembly of rigid vertexes and flexible edges

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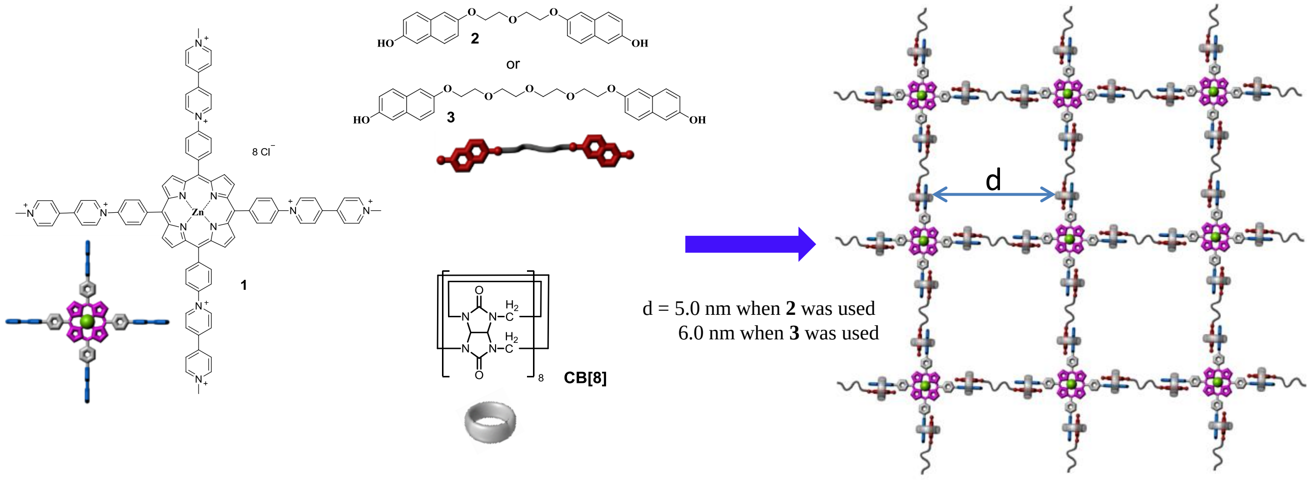
Single-layer two-dimensional supramolecular organic frameworks have been constructed in water through three-component self-assembly of rigid cross-shaped vertexes, flexible oligoethylene glycol edges, and cucurbit[8]uril (CB[8]) hosts, driven by CB[8]-encapsulation-enhanced donor-acceptor interaction between viologen unit and 2,6-dihydroxynaphthalene segment which were peripherally incorporated into the vertex and edge, respectively.

Since the discovery of graphene,[1,2] a prototype of two-dimensional (2D) polymers, the fabrication of synthetic 2D polymers has aroused considerable interest because it provides an access to exploring the unique properties and practical applications of 2D materials.[3-6] To date many efforts have been devoted to developing efficient methods to fabricate 2D materials, in which exfoliation of layered precursors and surface-assisted growth have gained great success. [1,7-12] However, in spite of these progresses, only a few reliable methods have been developed to produce free-standing single-monomer-thick 2D polymeric structures with macroscopic dimensions in solution phase,[13,14] which severely limits the availability of 2D materials for further applications. Since solution-based processing has many advantages in mass production, developing general methods to fabricate 2D materials in solution phase is highly desired. As a powerful bottom-up method to construct polymeric structures in solution phase,[15-26] self-assembly should be very promising in taking this task.

In the construction of 2D materials, the realization of long-range internal order and confinement to 2D dimensions still face great challenges. Very recently we and coworkers reported the first free-standing monolayered 2D supramolecular polymer named as supramolecular organic framework (SOF) in water.[27] Sequentially, a 2D SOF bearing similar structure but driven by different noncovalent interaction has also been constructed.[28] In both cases, wholly rigid tritopic skeletons were used to control the growing directions of the building blocks in 2D space, through which the 2D networks were self-assembled from two-component systems driven by cucurbit[8]uril (CB[8])-encapsulation-enhanced dimerization of bonding motifs. It has been generally accepted that rigid building blocks have good direction controllability in self-assembling processes because of the preorganization of rigid backbones. As for flexible building blocks, however, with their flexibility increasing, controlling the degree of order and dimensions of self-assembled architectures become more and more challenging. Moreover, the complexity of self-assembled systems is expected to significantly increase with the increase of the component of building blocks, which will also decrease the controllability over self-assembling processes. Thus a question arises: is it possible to construct well-ordered 2D structures through multi-component self-assembly of flexible building blocks? To address this question, we designed a three-component system which consisted of a rigid cross-shaped tetraphenylporphyrin peripherally bearing four methyl viologen (**MV**) (**1**) units, a 2,6-dihydroxynaphthalene (**DAN**) derivative linked by flexible oligoethylene glycols (**2** or **3**), and a macrocycle CB[8] (Scheme 1). We herein demonstrate that well-ordered 2D SOFs could also be constructed from flexible building blocks in solution phase, which was evidenced by a variety of characterization techniques.

Pioneering research by Kim et al. has proved that CB[8] could simultaneously and selectively accommodates an electron-deficient guest and an electron-rich guest in its hydrophobic cavity to form a stable 1:1:1 ternary complex.[29] This binding model has been widely utilized to construct supramolecular systems with diverse topologies.[30-34] In our design, CB[8] was employed to glue rigid **1** (as vertexes) and flexible **2** or **3** (as edges) together to generate 2D network structures (Scheme 1).

^{1}H NMR titration experiment was firstly performed to probe the formation of ternary complex between **MV**, **DAN** and CB[8] and to determine their stoichiometry (Figure 1). Adding 2 equiv of **2** into a solution of **1** in D_2O led to almost no change of the spectrum of **1** because of the extremely low solubility of compound **2** in D_2O. However, upon the addition of CB[8] into the above mixture, the solution turned from cloudy to clear gradually, accompanied with progressive disappearance of the signals of **MV** units of free **1** and growth of a group of new peaks which were attributed to the encapsulated **MV** units. The peaks of **MV** became broad after being encapsulated, suggesting the formation of polymeric structures.[35,36] The original peaks corresponding to H_1-H_5 of **MV** units in **1** disappeared completely



Scheme 1 Chemical structures of compounds **1**, **2**, **3**, and CB[8] and schematic representation of 2D supramolecularly polymeric pattern from the self-assembly of them.

and only the broad peaks remained when 4 equiv of CB[8] was introduced, indicating a 1:2:4 stoichiometry for **1**, **2** and CB[8] (Fig. 1a). Same phenomenon was observed while **2** was replaced by **3** (Fig. 1b), indicating the same binding pattern for them. .

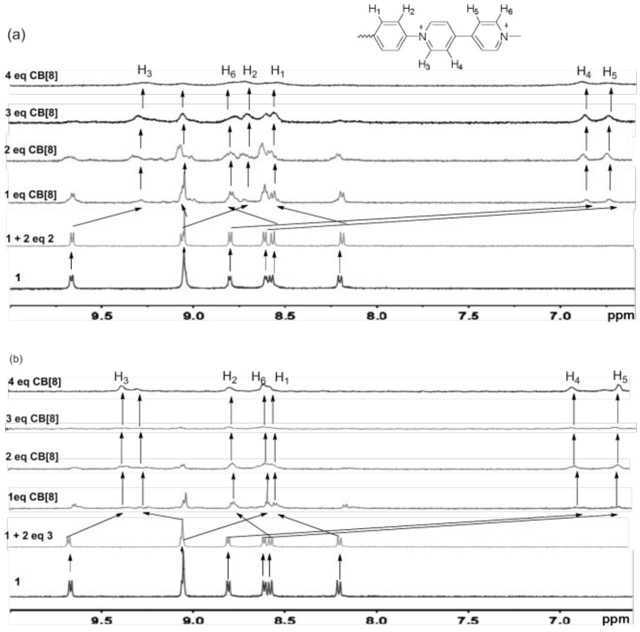


Fig. 1 Partial ^{1}H NMR spectra (500 MHz) of **1** (0.20 mM) and mixtures of **1** and (a) **2** or (b) **3** with different amounts of CB[8] in D_2O at 25 °C.

The host-guest interaction in the ternary complex was further investigated through UV-vis experiment. Upon the addition of 2 equiv of **2** and 4 equiv of CB[8] into a solution of **1** in water, its peaks centred at 257 nm and 280 nm, which corresponded to the absorption of **MV** unit, decreased significantly, accompanied with a slight increase of the peak at 356 nm and a bathochromic shift of the Soret absorption band of porphyrin unit from 421 nm to 427 nm (Fig. S1a, ESI). When **3** and CB[8] were added into a solution of **1**, similar transition was observed, except that the Soret band of porphyrin unit exhibited an increase in intensity instead of bathochromic shift (Fig. S1b, ESI). The ternary complex was also studied by fluorescence spectroscopy. Since **1** and CB[8] were fluorescence silent, **DAN** unit of **2** (or **3**) was selected as probe. It exhibited a emission peak centred at 350 nm, which was significantly quenched upon the addition of 1 equiv of **1** and **4** equiv of CB[8] (Fig. S2, ESI). The quenching of fluorescence could be ascribed to charge transfer between electron-rich **DAN** unit and electron-deficient **MV** unit after they were co-encapsulated in the cavity of CB[8].[29]

In order to provide more information about the self-assembled structures, 2D ^{1}H NMR diffusion ordered spectroscopy (DOSY), a commonly used technique for characterization of supramolecular entities in solution,[37] was conducted by correlating chemical resonances with diffusion coefficients (D). The collected data revealed comparable D values for the solution of mixture of **1**, **2**, and CB[8] (1:2:4) (1.17×10^{-10} m^2/s) and the solution of mixture of **1**, **3**, and CB[8] (1:2:4) (1.22×10^{-10} m^2/s), respectively (Fig. S3b-c, ESI). Both the values were approximately half of the D value of free **1** (2.19×10^{-10} m^2/s) (Fig. S3a, ESI), which strongly supported the formation of large aggregates in solution, most likely, supramolecular polymers. ^{1}H NMR dilution experiments were further carried out to examine the stability of the self-assembled architectures. No obvious change of chemical shifts or appearance of the signals of free **1** was observed with progressively diluting the mixtures (Fig. S4, ESI), suggesting both the self-assembled structures were quite stable in solution. Dynamic light scattering (DLS) investigation revealed that the hydrodynamic diameters (D_H) recorded for the solution of mixture of **1**, **2**, and CB[8] and the solution of mixture of **1**, **3**, and CB[8] in water increased with the increase of their concentrations. The D_H values reached 76 and 86 nm for **1**-**2**-CB[8] and **1**-**3**-CB[8] at 0.20 mM (for **1**), respectively (Fig. S5, ESI), indicating again the formation of polymeric structures.

In the next step the morphology of the as-formed self-assembled structures was characterized. The aggregates were investigated by transmission electron microscopy (TEM), which clearly demonstrated the existence of film-like structures with some corrugations (Figure 2 and Fig. S6 in ESI for additional TEM images). This result strongly suggested the formation of 2D supramolecular polymers from the self-assembly of **1**, **2** (or **3**), and CB[8]. The corrugations suggested pliable feature of the films, which might be attributed to the flexible building blocks. Scanning electron microscopy (SEM) study also provided evidence for the formation of film-like materials from the three-component self-assemblies (Fig. S7, ESI). Since TEM and SEM could not reveal the thicknesses of the films, atomic force microscopy (AFM) experiment was further conducted. As can be seen in Figure 3, film-like structures were also observed by AFM. Cross-section analysis revealed that the lateral sizes of the films could be as large as several microns and they were quite flat. The heights of the selected films were measured to be 1.32 and 1.24 nm for the films formed from **1**-**2**-CB[8] and **1**-**3**-CB[8], respectively. As illustrated in Scheme 1, the thickest part of the expected 2D networks self-assembled from the three components should be CB[8] and the thickness of the other part should be less than the outer diameter of CB[8]. Since the outer diameter of CB[8] was 1.75 nm,[38] the films were believed to be monolayers.

After obtaining above morphological evidence for the formation of 2D supramolecular organic frameworks, the internal order of the 2D structures was of our particular interest because the existence of long-range ordered periodicity in two dimensions is a key criterion for a true 2D structure. It was studied with the aid of small angle x-ray scattering (SAXS), As shown in Figure 4a, a broad scattering peak corresponding to *d* spacing around 7.52 nm was observed for the solution of mixture of **1**, **3**, and CB[8] (1:2:4). For the sample fabricated from **1**, **2** and CB[8], although a clearly assignable scattering peak could not be identified, a broad peak centred around 5.46 nm was observed (Fig. 4b). The broadening of the scattering peaks in both cases could mainly be attributed to the flexible nature of the oligoethylene glycol edges and dynamic characteristic of the self-assembled structures. CPK modelings were performed to estimate the pore sizes of the expected 2D networks as illustrated in Scheme 1. The theoretical sizes of the quadrangular pores were estimated to be 5.0 nm and 6.0 nm for the 2D structures self-assembled from **1**-**2**-CB[8] and **1**-**3**-CB[8], respectively. These values were close to the experimental results if the dynamic nature of the self-assembled networks was taken into consideration. This founding not only established the microstructure information for 2D SOFs formed in water but also clearly pointed to the presence of relatively long-range ordered periodic arrangement of the pore units in the 2D structures.

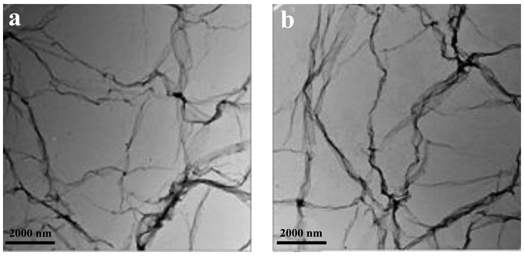


Fig. 2 TEM images of the aggregates fabricated from (a) **1**-**2**-CB[8] and (b)**1**-**3**-CB[8] in water. The concentration of **1** was 6.25 × 10^{-6} M and the molar ratio for **1**, **2** (or **3**), and CB[8] was 1:2:4.

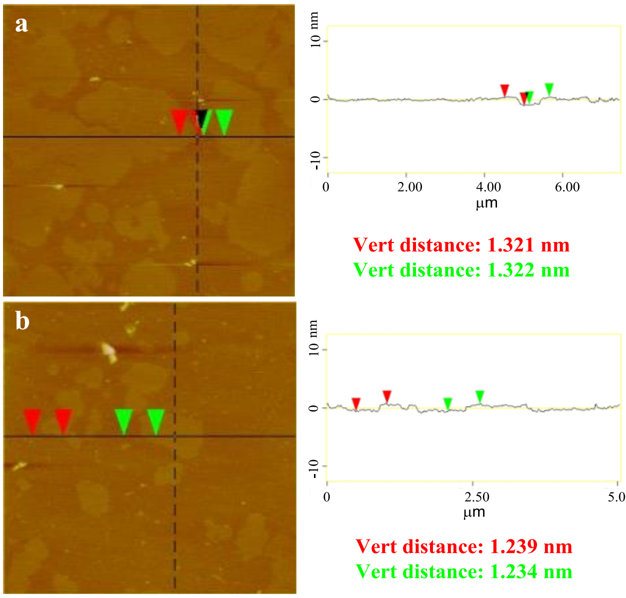


Fig. 3 Tapping-mode AFM images and section analyses of the aggregates on mica surface fabricated from(a) **1**-**2**-CB[8] and (b)**1**-**3**-CB[8] in water. The concentration of **1** was 6.25 × 10^{-6} M and the molar ratio for **1**, **2** (or **3**), and CB[8] was 1:2:4.

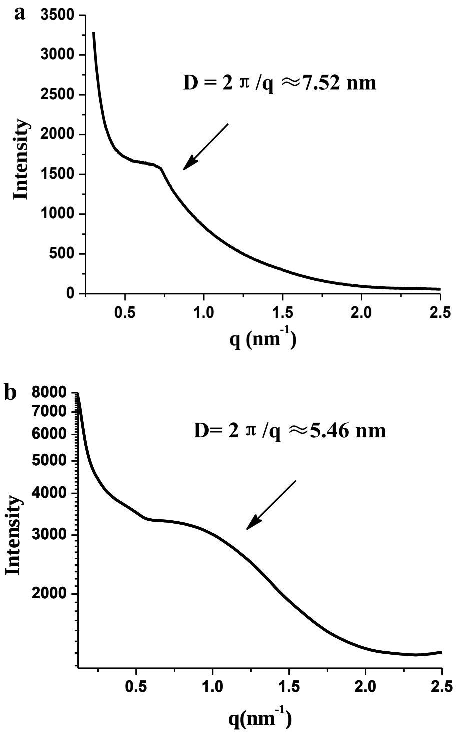


Fig. 4 Solution-phase SAXS profiles of a) the mixture of **1**, **3**, and CB[8] and b) the mixture of **1**, **2**, and CB[8] in water. The concentration of **1** was 0.80 mM and molar ratio for **1**, **2** (or **3**) and CB[8] was 1:2:4. Synchrotron radiation was used for (a).

In summary, two single-layer 2D supramolecular organic frameworks with different internal pores sizes have been successfully constructed through three-component self-assembly in water. Different from the previously reported 2D networks which were fabricated from two-component self-assembly of rigid building blocks, the 2D structures reported herein were generated by connecting flexible edges and rigid vertexes by macrocycle host. The as-prepared 2D materials exhibited pliable feature as a result of the introduction of flexible segments. This work well demonstrates that supramolecular 2D materials could also be constructed from flexible building blocks and through multi-component self-assembly, although controllability over such systems become much more difficult compared to those from rigid building blocks and less components. Since flexible skeletons are more accessible and diverse than rigid ones, this strategy might open a new window for the construction of 2D supramolecular materials with diversified topologies and intriguing properties. This potential is now under investigation in our laboratory.

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Notes and references

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