

Toward a Single-Layer Two-Dimensional Honeycomb Supramolecular Organic Framework in Water

Kang-Da Zhang,[†] Jia Tian,[‡] David Hanifi,[§] Yuebiao Zhang,^{||} Andrew Chi-Hau Sue,^{||} Tian-You Zhou,[†] Lei Zhang,[§] Xin Zhao,^{*,†} Yi Liu,^{*,§} and Zhan-Ting Li^{*,†,‡}

[†]Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200043, China

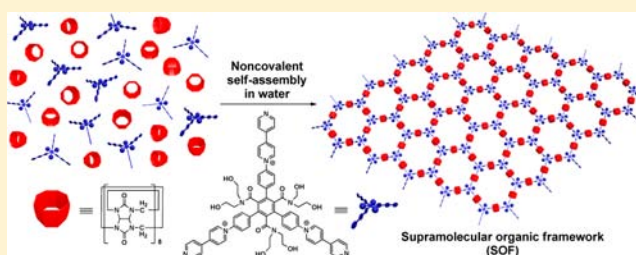
[‡]Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

[§]The Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720, United States

^{||}Department of Chemistry, University of California, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The self-assembly of well-defined 2D supramolecular polymers in solution has been a challenge in supramolecular chemistry. We have designed and synthesized a rigid stacking-forbidden 1,3,5-triphenylbenzene compound that bears three 4,4'-bipyridin-1-ium (BP) units on the peripheral benzene rings. Three hydrophilic bis(2-hydroxyethyl)carbamoyl groups are introduced to the central benzene ring to suppress 1D stacking of the triangular backbone and to ensure solubility in water. Mixing the triangular preorganized molecule with cucurbit[8]uril (CB[8]) in a 2:3 molar ratio in water leads to the formation of the first solution-phase single-layer 2D supramolecular organic framework, which is stabilized by the strong complexation of CB[8] with two BP units of adjacent molecules. The periodic honeycomb 2D framework has been characterized by various ¹H NMR spectroscopy, dynamic light scattering, X-ray diffraction and scattering, scanning probe and electron microscope techniques and by comparing with the self-assembled structures of the control systems.



INTRODUCTION

The rise of graphene as a two-dimensional (2D)-structured material has greatly stimulated the search for single-layer ordered materials.¹ In this context, the “top-down” exfoliation strategy has been developed for the preparation of unilamellar sheets of “hard” inorganic materials, and the “bottom-up” strategy has been applied for building monolayered periodic soft networks through controlling the polymerization^{2–4} or self-assembly⁵ of organic monomers on solid surfaces or employing shape-directed covalent self-assembly of disk-shaped building blocks in solution.⁶ Single-layer 2D supramolecular organic frameworks (SOFs) not only are structurally attractive but also hold great promise for applications in sensing, separation, and environmental fields. Although the last decades have witnessed tremendous progress in supramolecular polymer chemistry,^{7–17} little has been done in the construction of solution-phase periodic soft supramolecular networks.

Inclusion-enhanced dimerization represents a general approach for the design of strong binding motifs for creating advanced supramolecular architectures.^{18–22} In recent years, cucurbit[8]uril (CB[8]) has been demonstrated as a robust rigid macrocycle for stabilizing dimers of aromatic components in aqueous media,^{23–26} which has been used for developing linear, cross-linked, or hyperbranched supramolecular polymers.^{27–29} However, the ordering of these supramolecular polymers in 2D or three-dimensional space (3D) is uncertain

due to the flexibility of the backbones. In the last two decades, a large number of metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have been prepared using rigid preorganized organic molecules.^{30–39} Despite the great progress in achieving crystalline extended frameworks, confining the continuous frameworks into a single-layer one still remains challenging. Recent example by Dichtel’s group demonstrated the formation of a thin film of 2D COF on graphene, which shows great control of growth of 2D porous structures and is one step closer toward single-layer nanostructures.⁴⁰ Herein, we report a solution-phase self-assembly strategy to realize the formation of a single-layer periodic honeycomb-shaped 2D SOF in water.

RESULTS AND DISCUSSION

The formation of a single-layer SOF requires holding together a large number of individual building blocks with noncovalent forces in a 2D space. Thus, the noncovalent forces should be strong, highly directional, and cooperative. In aqueous media, aromatic building blocks are excellent choices because they can be driven to stack by hydrophobicity. We thus designed and prepared tritopic molecule **1** for assembling honeycomb SOF by utilizing the 1:2 binding motif between CB[8] and 4,4’-

Received: August 21, 2013

Published: September 30, 2013

bipyridin-1-ium (BP) (Figure 1).⁴¹ Three hydrophilic bis(2-hydroxyethyl)carbamoyl groups were introduced as steric-

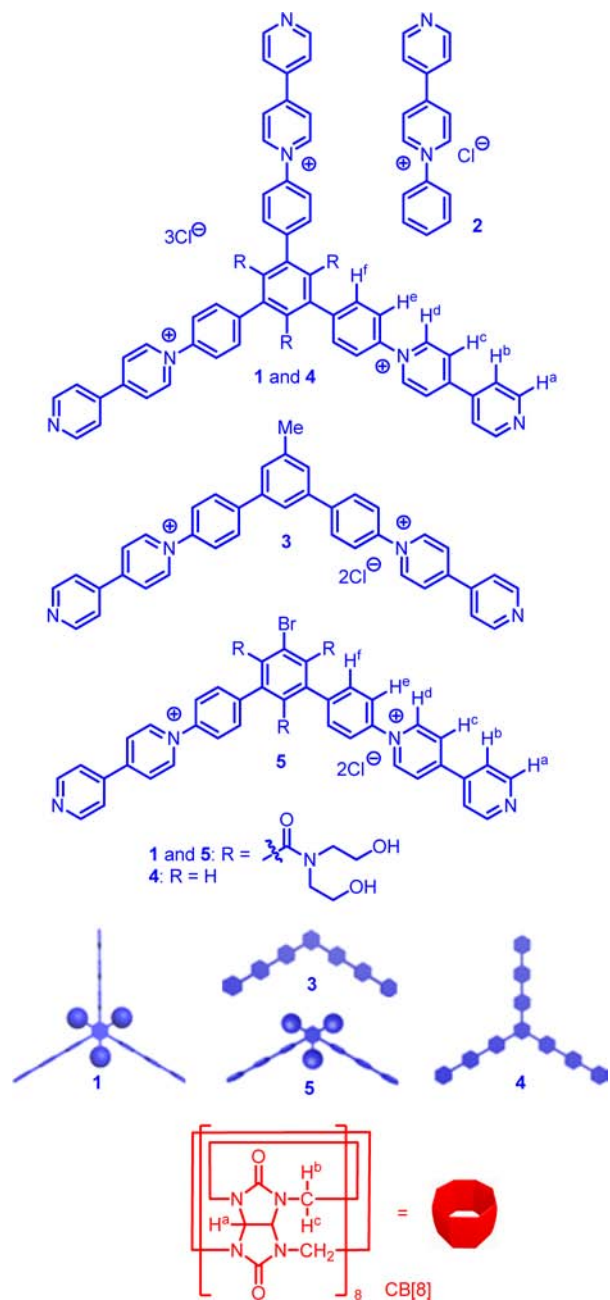


Figure 1. Structures of compounds 1–5 and CB[8] and cartoon representations of 1, 3–5, and CB[8].

generating groups to suppress the stacking between layers.⁴² Several other BP-containing compounds 2–5 were also prepared in order to establish self-assembly conditions for the desired structures (Figure 1).

The 1:2 binding pattern between CB[8] and the 1-aryl-BP 2 in water was confirmed by X-ray diffraction analysis of suitable single crystals, which were grown from the 1:2 aqueous solution of CB[8] and 2. The crystal structure showed that the BP units of two independent molecules of 2 were entrapped in the cavity of CB[8] in a head-to-tail orientation (Figure 2a), with the attached phenyl groups pointing away from each other (Figure 2b). This binding pattern serves well for our design of extended

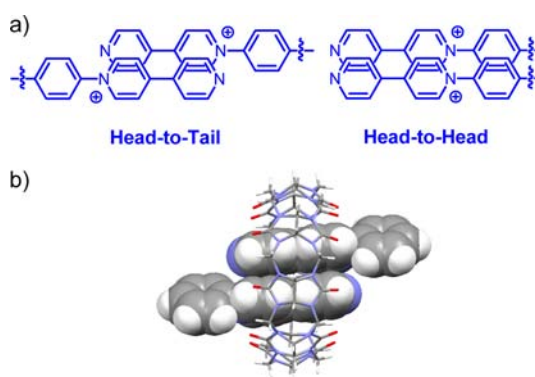


Figure 2. (a) Illustration of head-to-tail and head-to-head stacking arrangements between two BP units within the CB[8] cavity. (b) Crystal structure of the 2:1 complex between 2 and CB[8].

supramolecular networks. By using the competition ¹H NMR method and 1-adamantanamine as a competing guest,⁴³ we determined the association constant (K_a) of this 2:1 complex to be $8.4 \times 10^{10} \text{ M}^{-2}$ in 50 mM $\text{CD}_3\text{CO}_2\text{Na}$ -buffered D_2O (pD = 4.74).

The binding of ditopic 3 and tritopic 4 with CB[8] in D_2O was then investigated. The ¹H NMR spectra of the respective 1:1 and 1:1.5 solutions in D_2O both displayed one set of sharp signals, with complete disappearance of the signals of free 3 or 4 (Figures S1 and S2 in Supporting Information), which indicated the formation of a single complex in both solutions. Job's plots confirmed that the two complexes had a 1:1 and 2:3 stoichiometry (Figures S15 and S16 in Supporting Information), respectively. Further information for the complex formation was obtained from 2D ¹H NMR diffusion ordered spectroscopy (DOSY), a technique that has been widely used to characterize supramolecular structures in solution by correlating chemical resonances with diffusion coefficients (D).⁴⁴ The DOSY NMR spectra of the two solutions revealed that all the signals of the two components gave rise to comparable D values ($\sim 2.5 \times 10^{-10}$ (Figure S3) and $2.0 \times 10^{-10} \text{ m}^2/\text{s}$ (Figure S4), respectively), which further confirmed the formation of a single complex in both cases. On the basis of competition ¹H NMR experiments, we also determined the apparent K_a of the 2:1 complexes formed between their BP units and CB[8] in 50 mM $\text{CD}_3\text{CO}_2\text{Na}$ -buffered D_2O to be 5.6×10^{11} and $3.2 \times 10^{13} \text{ M}^{-2}$, respectively. Both values are substantially higher than that of the complex of 2 and CB[8], which thus excluded the possibility of the formation of linear supramolecular polymers.

The BP units of rigid 3 and 4 are arranged at an angle of around 120° . Due to the geometric constraint⁴⁵ and a head-to-tail orientation between two stacking BP units as observed in the complex between CB[8] and 2, a [6 + 6] hexagonal macrocycle (Figure 3c) was expected for the complex between 3 and CB[8]. However, the electrospray ionization mass spectrometry (ESI-MS) of the 1:1 mixture of 3 and CB[8] clearly indicated the formation of a [2 + 2] complex instead (m/z 941.8234, calcd value 941.8210 for $[\text{M} - 4\text{Cl}]^{4+}$, Figure S8 in Supporting Information). The corresponding structure of the [2 + 2] supramolecular entity is illustrated in Figure 3a, in which the BP units from two independent guest molecules were forced to stack in a head-to-head arrangement (Figure 2a) while maintaining maximum face-to-face overlapping. This head-to-head arrangement was also observed in the assembly between tritopic 4 and CB[8], which resulted in the formation

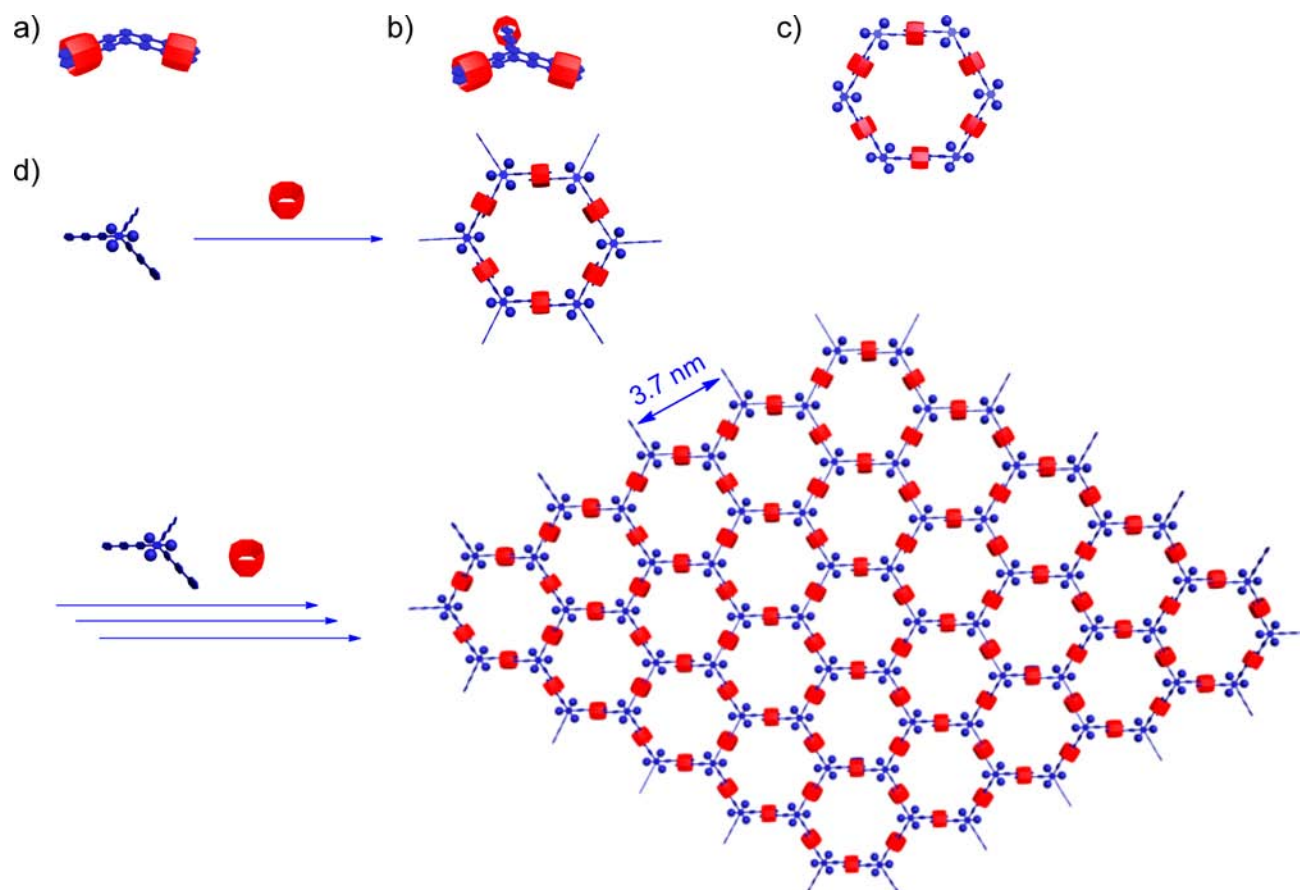


Figure 3. Schematic representation of the self-assembly patterns of different building blocks with CB[8] in water: (a) [2 + 2] complex formed by 3; (b) [2 + 3] complex formed by 4; (c) [6 + 6] complex formed by 5; (d) formation of 2D honeycomb SOF formed by 1.

of a [2 + 3] five-component complex (Figure 3b). The complexation motif was confirmed by ESI-MS of the 2:3 mixture of 4 and CB[8], which revealed the m/z peaks of the hexacation of the [2 + 3] complex (m/z 921.6400, calcd value 921.6381 for $[M - 6Cl]^{6+}$, Figure S9 in Supporting Information). In both cases, the BP units were situated inside the cavity of CB[8] in a face-to-face manner. From dynamic light scattering (DLS) experiments, we measured the hydrodynamic diameter (D_H) of the two complexes to be 0.96 and 1.12 nm, respectively (Figure 4), which was consistent with their relative size and D value obtained from the DOSY NMR experiments.

The above results suggest that guests containing more than one BP unit prefer to stack in the head-to-head manner within the CB[8] cavity to form smaller complexes rather than larger macrocycles or supramolecular polymers where head-to-tail stacking takes place. In order to cross-link these host-guest complexes into polymeric framework structures, the head-to-tail stacking, which lives in the complex between 2 and CB[8], has to be restored. We thus introduced auxiliary groups to impose steric influence on the stacking geometry. The model ditopic 5 bears two bulky hydrophilic bis(2-hydroxyethyl)carbamoyl groups for suppressing head-to-head stacking of the BP units while ensuring water solubility. The 1H NMR spectra of 5 in D_2O are shown in Figure 5a. The slow rotation of the (Ar)C–C(=O) bonds caused broadening of the H-e and H-f signals, while the H-a–d signals remained sharp. Adding 1.0 equiv of CB[8] to the guest solution caused the signals of free 5 to disappear completely and one new set of signals to emerge,

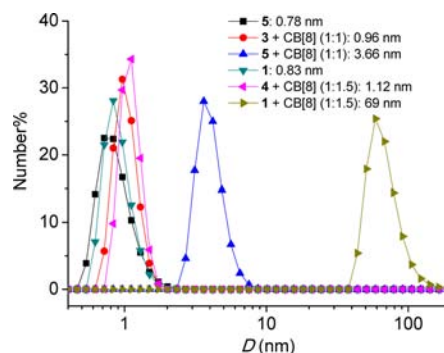


Figure 4. DLS results of different compounds and their mixture with CB[8] in water. The data represent the hydrodynamic diameters (D_H) in water at 25 °C. The concentration was 1.0 mM for compounds 1, 3, 4, and 5.

illustrating the formation of a new single complex. The apparent K_a of the 2:1 complex between the BP unit of 5 and CB[8] in 50 mM CD_3CO_2Na -buffered D_2O was measured to be $1.8 \times 10^{10} M^{-2}$, indicating that this complex was also highly stable. The 2D NOESY spectrum of the mixture revealed a NOE contact between H-b and H-d of 5 (Figure S7 in Supporting Information), which was stronger than that of pure 5 of the same concentration recorded under identical conditions, supporting that the BP units of two molecules of 5 entrapped in the same cavity of CB[8] were arranged in a head-to-tail fashion. The D value of the 1:1 solution of 5 and CB[8] was determined by DOSY NMR spectroscopy to be 7.2

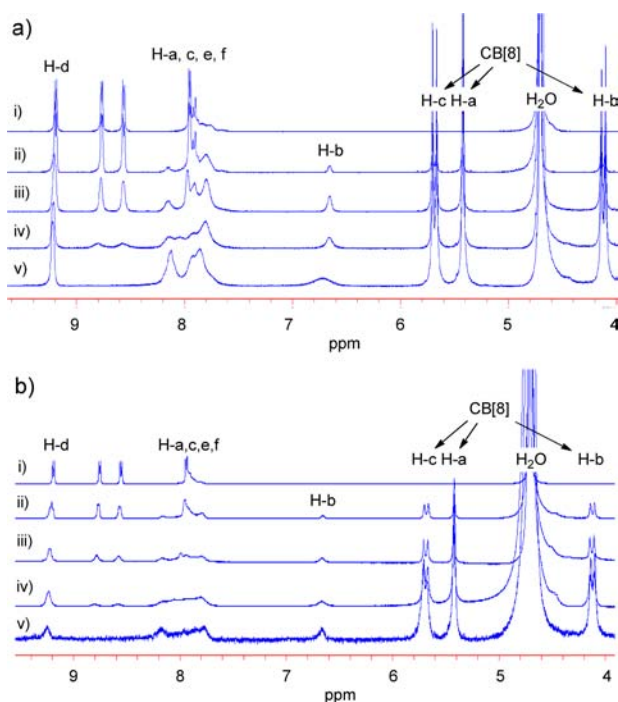


Figure 5. ¹H NMR spectra (400 MHz, 25 °C): (a) **5** (3.0 mM) in D₂O in the presence of (i) 0, (ii) 0.12, (iii) 0.30, (iv) 0.50, and (v) 1.0 equiv of CB[8]; (b) **1** (2.0 mM) in D₂O in the presence of (i) 0, (ii) 0.45, (iii) 0.75, (iv) 1.0, and (v) 1.5 equiv of CB[8].

$\times 10^{-11}$ m²/s, which was significantly lower than that of pure **5** (2.8×10^{-10} m²/s) measured at the identical concentration (Figures S5 and S6 in Supporting Information). The D_H of the complex was determined to be 3.66 nm by DLS measurement (Figure 4). This large value clearly pointed to the formation of a [6 + 6] hexagonal macrocyclic entity (Figure 3c) as it agreed very well with the calculated value (3.70 nm) of the 12-component macrocycle obtained on the basis of the crystal structure of the complex between **2** and CB[8]. The DOSY NMR spectra of the 1:1 solution of **5** and CB[8] also revealed that the signals of the two components all gave rise to the identical D value, further confirming the selective formation of the hexagonal complex.

Encouraged by the above result, we then exploited the possibility of forming 2D honeycomb networks from steric modified tritopic **1** and CB[8]. Adding 1.5 equiv of CB[8] to the solution of **1** in D₂O caused the signals of free **1** to vanish and a new set of signals to form (Figure 5b). The spectrum in the downfield area was very similar to that of the **5**/CB[8] solution, implying that they possessed the same binding pattern. The apparent K_a , which was determined to be 1.9×10^{10} M⁻², of the 2:1 complex of the BP unit of **1** with CB[8] in 50 mM CD₃CO₂Na-buffered D₂O was also close to that of the **5**/CB[8] system, reflecting a comparable thermodynamic stability. However, the DLS experiment revealed that the D_H of the complex formed between **1** (1.0 mM) and CB[8] (1.5 mM) in water was as high as 69 nm (Figure 4), which was 19 times that of the 1:1 mixture of **5** and CB[8] (1.5 mM) and 83 times that of **1** (1.0 mM). This result strongly supported that **1** and CB[8] formed a 2D honeycomb SOF (Figure 3d). Assuming that the SOF was single-layer and the repeating hexagonal unit had a diameter of 3.70 nm, we found that one framework would contain about 350 hexagonal pores. It was also found that the D_H values reduced substantially with the

decrease of the concentration (Figure S41 in Supporting Information). When the concentration was further increased, much larger aggregates ($D_H > 200$ nm) were formed, while the solution was still transparent. These very large aggregates might be generated due to the further aggregation of smaller supramolecular entities. When the concentration of **1** and CB[8] was increased to 2.1 and 3.15 mM, respectively, the mixture turned into a hydrogel. This phenomenon was not observed for other CB[8]–guest mixtures even at higher concentrations, corroborating the network nature of the complex formed between **1** and CB[8].

The microstructural information for the single-layer supramolecular framework as-formed in water was revealed by the solution-phase small-angle X-ray scattering (SAXS) experiment.⁴⁶ As shown in Figure 6a, a scattering peak corresponding to d spacing of 3.61 nm was observed.

Considering the dynamic feature of the noncovalent self-assembly in solution, this spacing was consistent with the expected pore diameter (3.70 nm) calculated on the basis of the

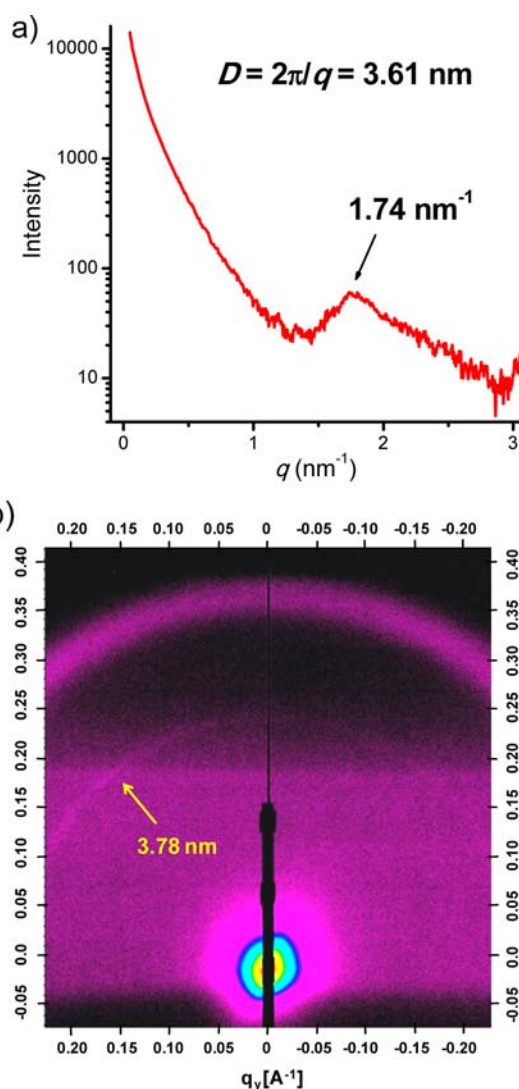


Figure 6. (a) Solution-phase small-angle X-ray scattering profile of the mixture of **1** and CB[8] (1:1.5, 3.0 mg/mL) in water. (b) Synchrotron X-ray scattering of the mixture of **1** and CB[8] upon evaporation of their 1:1.5 solution in water ($[1] = 1.0$ mM). The broader diffusion signal is from Kapton background.

crystal structure of the complex between **2** and CB[8] (Figure 2b) and clearly indicated the presence of the 2D periodic hexagonal pore array in solution. Powder X-ray diffraction experiment was also performed for the dried sample obtained by evaporating the 2:3 solution of **1** and CB[8] in water, which revealed a broad (100) peak with d spacing of 3.70 nm (Figure S10 in Supporting Information). A similar peak was not observed for the other four mixtures. Further synchrotron X-ray scattering experiment was carried out for the sample, which revealed a scattering peak with d spacing of 3.78 nm (Figure 6b). Both values matched well with the expected diameter of the repeating units in the proposed honeycomb supramolecular network (Figure 3d).

In addition to the periodic information provided by X-ray analysis, a layered structure of these samples was also clearly revealed by microscopic methods. Transmission electron microscope (TEM) images showed that the 2:3 mixture of **1** and CB[8] gave rise to layered films on surfaces (Figure S11 in Supporting Information). Cryo-scanning electron microscope (SEM) images further revealed curly layered structures, reflecting the soft nature of the 2D structures (Figure S12 in Supporting Information). SEM images also showed that increasing the concentration of the 2:3 mixture led to the formation of thicker planar flakes (Figures S12 and S13 in Supporting Information). Moreover, planar aggregates with a height around 1.72 nm were observed by atomic force microscopic (AFM) studies (Figure 7). This result strongly

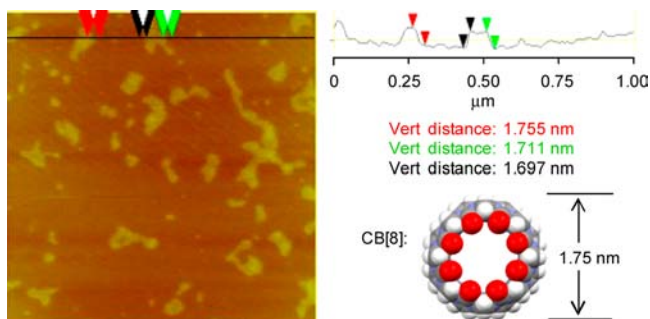


Figure 7. Tapping-mode AFM image ($1 \mu\text{m} \times 1 \mu\text{m}$) and section analysis of the aggregates on mica from dried solution of compound **1** (1.0 mM) and CB[8] (1.5 mM) in H_2O . Height analysis versus distance along the black line in the image showed an average thickness of 1.72 nm, consistent with the thickness of the expected monolayer framework, which is equivalent to the diameter of CB[8].

supported the formation of the single-layer 2D supramolecular framework as it perfectly matched the diameter of rigid CB[8] (1.75 nm), which determined the thickness of the single-layer framework (Figure 7). The shapes of the aggregates were irregular. This result implied that the formation of the hexagonal subunits was stepwise, and thus when the 2D networks “grew up” to certain size, further growing could occur randomly from different directions to lead to irregular shapes rather than the round ones. Together, all of these observations provide consistent evidence for the periodic arrangement of **1** and CB[8] in the 2D space in both solution and the solid state.

CONCLUSIONS

In this work, we have demonstrated that a single-layer 2D supramolecular organic framework can be generated in solution using a robust self-assembling strategy in water. The self-assembly is facilitated by the tunable complexation between

CB[8] and BP-containing aromatic guests. In the 1:2 inclusion complex, two BP units enclosed in the same CB[8] cavity can stack in either a head-to-head or head-to-tail geometry, the selectivity of which can be effected by multivalency or the introduction of steric groups. The obtained 2D porous architecture represents a new type of supramolecular polymer, which exhibits periodic structural ordering similar to that of MOFs and COFs, despite the former being in solution while the latter is in the solid state. The concept of SOF in crystals has been illustrated to be common,⁴⁷ but in solution, periodic single-layer supramolecular frameworks have never been realized before. The formation of solution-based SOF offers unprecedented accessibility and processability of soft layered nanostructures. For example, stable ordered 2D polymers may be constructed by further covalently modifying the framework. In this way, additional functional groups of various sorts may be attached for different purposes. Multilayer 3D polymers may also be produced by performing cross-layer reactions. The ordered structures may also be expressed on surfaces by introducing adhering or reactive groups to the monomers. The resulting networks could serve as ordered platforms for producing advanced architectures. Moreover, the strategies developed for the processing of graphene, including wrapping, covering, rolling, folding, and stacking, can be tested for this new kind of 2D networks.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization, method for the determination of association constants, ^1H and ^{13}C NMR and MS spectra, SAXD profile, SEM and TEM images, Job plots, and DLS profile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

xzhao@mail.sioc.ac.cn; ztli@mail.sioc.ac.cn; yliu@lbl.gov

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Z.L. and X.Z. were supported by MOST (2013CB834501), STCSM (13NM1400200), and NSFC (91227108, 91127007, 21228203). D.H. and Y.L. were supported by the “Organic Inorganic Nanocomposites” program from Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Part of this research was performed at the Molecular Foundry as a user project. Solution SAXS and solid-state SAXS were conducted at the SIBYLS beamline and beamline 7.3.3 at Advanced Light Source (ALS), which was supported by DOE Integrated Diffraction Analysis (IDAT) grant under the same contract number. We thank Kevin Dyle, Dr. Michal Hammel, and Dr. Alexander Hexemer at ALS for their help with SAXS measurements.

REFERENCES

- (1) Geim, A. K. *Science* **2009**, *324*, 1530–1534.
- (2) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. *Nat. Nanotechnol.* **2007**, *2*, 687–691.
- (3) Lafferentz, L.; Eberhardt, V.; Dri, C.; Africh, C.; Comelli, G.; Esch, F.; Hecht, S.; Grill, L. *Nat. Chem.* **2012**, *4*, 215–220.

- (4) (a) Kissel, P.; Erni, R.; Schweizer, W. B.; Rossell, M. D.; King, B. T.; Bauer, T.; Göttinger, S.; Schlüter, A. D.; Sakamoto, J. *Nat. Chem.* **2012**, *4*, 287–291. (b) Liu, X.-H.; Guan, G.-Z.; Ding, S.-Y.; Wang, W.; Yan, H.-J.; Wang, D.; Wan, L.-J. *J. Am. Chem. Soc.* **2013**, *135*, 10470–10474.
- (5) (a) Wan, L.-J. *Acc. Chem. Res.* **2006**, *39*, 334–342. (b) Liu, J.; Chen, T.; Deng, X.; Wang, D.; Pei, J.; Wan, L.-J. *J. Am. Chem. Soc.* **2011**, *133*, 21010–21015. (c) Zhang, X.; Zeng, Q.; Wang, C. *RSC Adv.* **2013**, *3*, 11351–11366. (d) Yang, Y.; Wang, C. *Chem. Soc. Rev.* **2009**, *38*, 2576–2589.
- (6) Baek, K.; Yun, G.; Kim, Y.; Kim, D.; Hota, R.; Hwang, I.; Xu, D.; Ko, Y. H.; Gu, G. H.; Suh, J. H.; Park, C. G.; Sung, B. J.; Kim, K. *J. Am. Chem. Soc.* **2013**, *135*, 6523–6528.
- (7) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097.
- (8) Lehn, J.-M. *Polym. Int.* **2002**, *51*, 825–839.
- (9) (a) Park, T.; Zimmerman, S. C.; Nakashima, S. *J. Am. Chem. Soc.* **2005**, *127*, 6520–6521. (b) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 13986–13987. (c) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 14236–14237.
- (10) de Greef, T. F. A.; Meijer, E. W. *Nature* **2008**, *453*, 171–173.
- (11) Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977–980.
- (12) Harada, A.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H. *Nat. Chem.* **2011**, *3*, 34–37.
- (13) Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813–817.
- (14) Bruns, C. J.; Stoddart, J. F. *Nat. Nanotechnol.* **2013**, *8*, 9–10.
- (15) (a) Appel, E. A.; del Barrio, J.; Loh, X. J.; Scherman, O. A. *Chem. Soc. Rev.* **2012**, *41*, 6195–6214. (b) Appel, E. A.; Biedermann, F.; Rauwald, U.; Jones, S. T.; Zayed, J. M.; Scherman, O. A. *J. Am. Chem. Soc.* **2010**, *132*, 14251–14260.
- (16) (a) Liu, Y.; Huang, Z.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Commun.* **2013**, *49*, 5766–5768. (b) Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41*, 5922–5932.
- (17) (a) Ji, X.; Yao, Y.; Li, J.; Yan, X.; Huang, F. *J. Am. Chem. Soc.* **2013**, *135*, 74–77. (b) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042–6065. (c) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 1621–1636. (d) Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7011–7015. (e) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 1621–1636.
- (18) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630.
- (19) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, *38*, 875–882.
- (20) Hooley, R. J.; Rebek, J., Jr. *Chem. Biol.* **2009**, *16*, 255–264.
- (21) (a) Rebek, J., Jr. *Acc. Chem. Res.* **2009**, *42*, 1660–1668. (b) Ajami, D.; Rebek, J., Jr. *Acc. Chem. Res.* **2013**, *46*, 990–999.
- (22) Chen, G.; Jiang, M. *Chem. Soc. Rev.* **2011**, *40*, 2254–2266.
- (23) Kim, H.-J.; Heo, J.; Jeon, W. S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1574–1777.
- (24) Ko, Y. H.; Kim, E.; Hwang, I.; Kim, K. *Chem. Commun.* **2007**, 1305–1315.
- (25) (a) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870. (b) Liu, S.; Shukla, A. D.; Gadde, S.; Wagner, B. D.; Kaifer, A. E.; Isaacs, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 2657–2660.
- (26) Nau, W. M. *Nat. Chem.* **2010**, *2*, 248–250.
- (27) (a) Zhang, Z.-J.; Zhang, H.-Y.; Chen, L.; Liu, Y. *J. Org. Chem.* **2011**, *76*, 8270–8276. (b) Qian, H.; Guo, D.-S.; Liu, Y. *Chem.—Eur. J.* **2012**, *18*, 5087–5095.
- (28) (a) Rauwald, U.; Scherman, O. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3950–3953. (b) Appel, E. A.; Loh, X. J.; Jones, S. T.; Biedermann, F.; Dreiss, C. A.; Scherman, O. A. *J. Am. Chem. Soc.* **2012**, *134*, 11767–11773.
- (29) (a) Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 6576–6579. (b) Liu, Y.; Yang, H.; Wang, Z.; Zhang, X. *Chem.—Asian J.* **2013**, *8*, 1626–1632. (c) Fang, R.; Liu, Y.; Wang, Z.; Zhang, X. *Polym. Chem.* **2013**, *4*, 900–903.
- (30) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (31) Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. *Nat. Chem.* **2010**, *2*, 439–443.
- (32) Feng, X.; Ding, X.; Jiang, D. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022.
- (33) Colson, J. W.; Dichtel, W. R. *Nat. Chem.* **2013**, *5*, 453–465.
- (34) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670–4679.
- (35) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724–781.
- (36) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248–1256.
- (37) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- (38) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232–1268.
- (39) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734–777.
- (40) Colson, J. W.; Woll, A. R.; Mukherjee, A.; Levendorf, M. P.; Spitler, E. L.; Shields, V. B.; Spencer, M. G.; Park, J.; Dichtel, W. R. *Science* **2011**, *332*, 228–231.
- (41) Zhang, Z.-J.; Zhang, Y.-M.; Liu, Y. *J. Org. Chem.* **2011**, *76*, 4682–4685.
- (42) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546.
- (43) Liu, S.; Ruspic, C.; Mukhopadhyay, P.; Chakrabarti, S.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2005**, *127*, 15959–15967.
- (44) Cohen, Y.; Avram, L.; Frish, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 520–554.
- (45) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810–6918.
- (46) Hura, G. L.; Menon, A. L.; Hammel, M.; Rambo, R. P.; Poole, F. L.; Tsutakawa, S. E.; Jenney, F. E., Jr.; Classen, S.; Frankel, K. A.; Hopkins, R. C.; Yang, S. J.; Scott, J. W.; Dillard, B. D.; Adams, M. W.; Tainer, J. A. *Nat. Methods* **2009**, *6*, 606–612.
- (47) Yang, W.; Greenaway, A.; Lin, X.; Matsuda, R.; Blake, A. J.; Wilson, C.; Lewis, W.; Hubberstey, P.; Kitagawa, S.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2010**, *132*, 14457–14469.