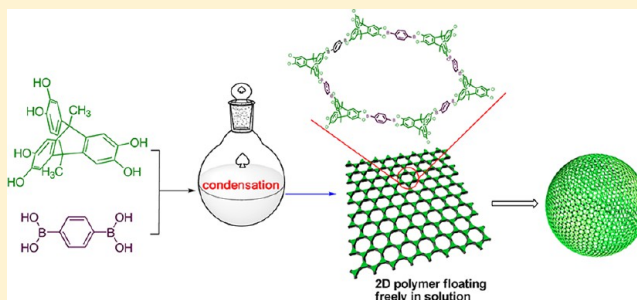


Single-Step Solution-Phase Synthesis of Free-Standing Two-Dimensional Polymers and Their Evolution into Hollow Spheres

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S Supporting Information

ABSTRACT: Interest in two-dimensional (2D) polymers has increased rapidly since the isolation of graphene. However, approaches to the preparation of graphene-like materials still face great challenges. Herein we report a facile method to prepare single molecular thick 2D polymers by simply running the polymerization reaction in a flask without the aid of any templates and postmodification techniques. The strategy is to use the triptycene scaffold, a rigid three-dimensional skeleton, as one monomeric unit to substantially suppress the interlayer interaction between the as-formed polymeric 2D monolayers. The new individual monolayered 2D polymers float freely in solution and can be further transferred onto solid surface for characterization. It is also found that the resulting 2D polymeric monolayers can further evolve into monolayered or multilayered hollow spheres, which might be regarded as a model for the transformation of graphene to fullerene.



■ INTRODUCTION

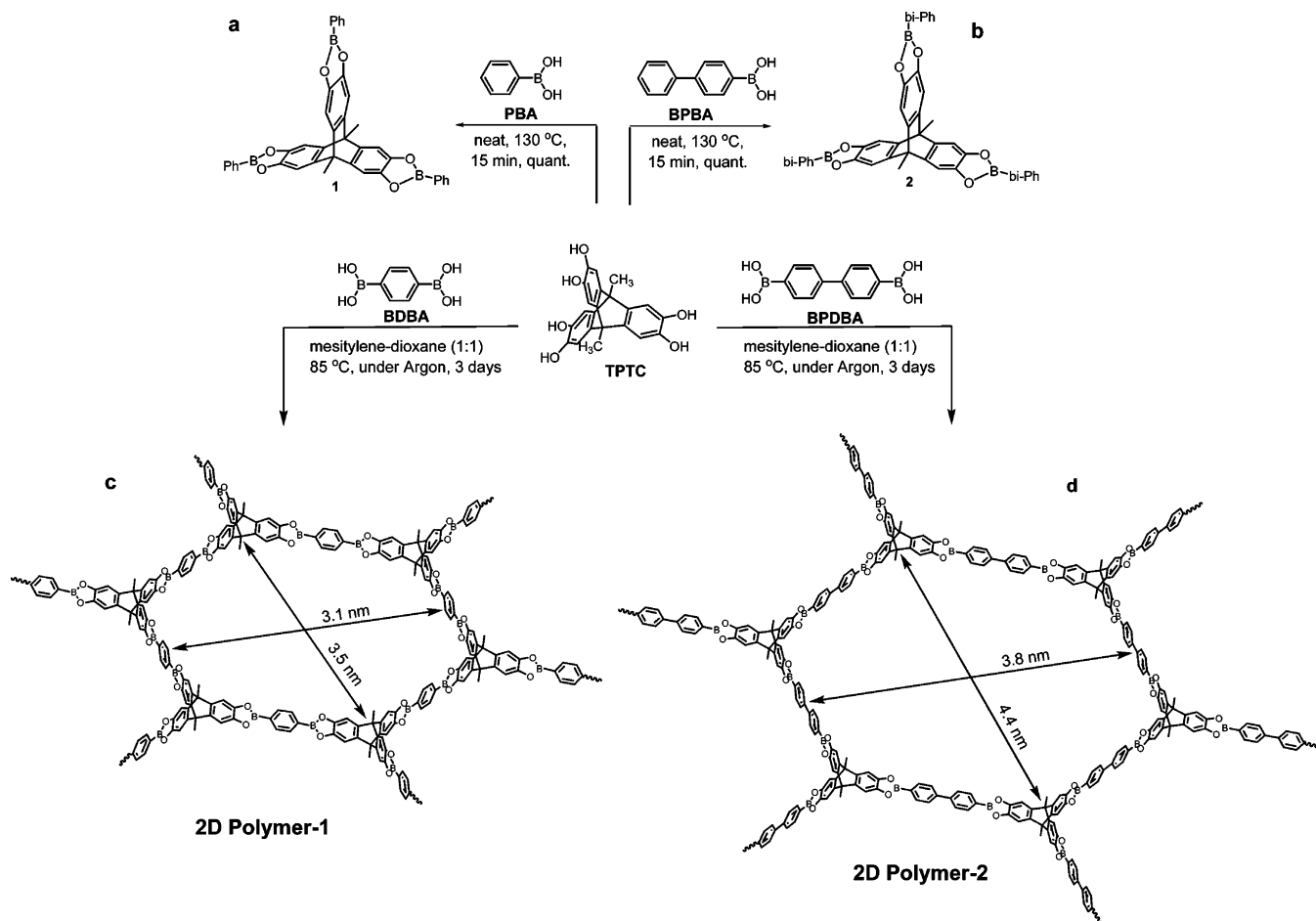
Inspired by the pioneering work of Gee and co-workers over 70 years ago,¹ efforts to fabricate two-dimensional (2D) polymers in which covalently bound monomeric units periodically extend in only two dimensions with the thickness being as thin as that of one atom or molecule have never stopped and recently been largely boosted by the discovery of graphene, the first free-standing single-atom-thick 2D polymer ever isolated.^{2–4} 2D materials have been believed to exhibit unusual behaviors that are different from those of common three-dimensional (3D) materials in electronic,^{5,6} optical,^{7,8} and mechanical⁹ properties because of the restriction of their sizes in the 2D space and the absence of interlayer interactions. Generally the fabrication of these unique structures can be designed through the top-down or bottom-up strategies. A typical example of the first strategy is the obtention of graphene via micromechanical exfoliation of highly ordered pyrolytic graphite,² which has also been further extended to the preparation of unilamellar sheets of other inorganic layered materials such as BN and MoS₂.¹⁰ Although this method has achieved great success in the isolation of graphene, it suffers from low yield of monolayers and thus is not suitable for larger production of other 2D materials. Furthermore, a prerequisite for this strategy is that highly ordered 3D layered structures must be available as starting materials for the application of the micromechanical exfoliation technique. In most cases, especially for organic materials, the preparation of such exfoliable precursors is a great challenge. The bottom-up strategy, by which 2D structures are constructed directly from small molecules via chemical synthesis, is theoretically more straightforward. On the basis

of this strategy, many approaches have been proposed. However, most of them turned out to be unsuccessful in obtaining true monolayered 2D structures, even though their thicknesses could be made extremely thin.³ A limited number of successful examples in constructing monolayered 2D polymers relied on surface-assisted *in situ* growth technique,^{11–13} by which polymerization reaction takes place on a template surface to direct the growth of 2D structures. However, this approach has the drawback of tedious procedure and usually requires high temperature and ultrahigh vacuum conditions. Furthermore, whether the monolayered 2D entities can be removed from the solid surface as free-standing ones is still questionable. In 2012, Sakamoto and co-workers reported an elegant approach to preparing 2D polymers.¹⁴ In their procedure, a photochemical reaction within a layered organic crystal was first induced by photoirradiation, and then the resulting layered 3D material was delaminated in hot organic solvent to give monolayered 2D polymers. Undoubtedly, this approach represents a great progress in the preparation of 2D polymers by organic synthesis. The generality of this solid-phase approach, however, still needs to be further demonstrated because it requires that monomers must be aligned in a specific manner in the solid state to facilitate the photoinduced polymerization reaction, which is hard to realize in crystal engineering. Very recently, Kim et al. demonstrated the fabrication of single-monomer-thick layers in solution via

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Scheme 1. Scheme for the Synthesis of Model Compounds and 2D Polymers^a

^aThe pore widths of the "honeycomb units" were obtained by semiempirical calculation at the PM3 level.

photoinduced covalent self-assembly.¹⁵ In their case electrostatic repulsion was employed to prevent the as-prepared monolayers from stacking. In the absence of ammonium salts, aggregation of monolayers was observed due to the strong face-to-face stacking of the layers. Despite this progress, construction of 2D polymers is in its infancy, and developing efficient and general approaches for the construction of real 2D polymers still faces great challenges. We herein report a novel solution-phase approach to preparing free-standing, single-molecule-thick 2D polymers and their evolution into hollow spheres, which might remind of the formation of fullerene from graphene.¹⁶

Our strategy is to construct monolayered covalent organic frameworks (COFs) in solution. COFs are a class of porous polymer materials generated by linking organic building units into predetermined network structures.^{17–20} In the context of 2D COFs, although several methods have been developed for the production of COF architectures of nanoscaled thickness or even monolayered networks by making use of the surface-assisted in-situ growth technique,^{21–23} fabricating COFs in solution phase without a template always produces insoluble microcrystalline powders, which are 3D laminar structures resulting from strong interlayer stacking between the formed 2D COF monolayers,²⁴ as observed for exfoliated graphene sheets.⁴ We conjectured that, if interlayer interactions between the monolayers can be efficiently suppressed, we might create free-standing monolayered 2D COFs in solution. A direct

method to suppress the interlayer interactions in COFs is to eliminate π – π stacking between aromatic units of the COF monolayers, which, as we anticipated, could be realized by upright arrangement of the benzene units of COFs. El-Kaderi et al. recently also reported that π – π interactions between the COF monolayers could be weakened by integrating triptycene²⁵ unit into the backbone of COFs.²⁶ However, in their system, although π – π interactions was weakened, 3D laminar structures were still obtained. This result suggested that interlayer interactions between those COF monolayers were still strong enough to hold the monolayers together. To realize our purpose, we have introduced two methyl groups into the 9,10-positions of triptycene tricatechol (TPTC) to further increase the distance between monolayers (Scheme 1). We envisioned that the unique geometry of TPTC and the existence of the methyl groups would make it impossible for TPTC-derived 2D networks to undergo strong interlayered stacking, and thus monolayered COF materials might form and exist stably in solution.

RESULTS AND DISCUSSION

The preparation of 2D COF polymers was carried out under a condition similar to the procedure reported in previous literatures,^{18,19} under which the condensation reaction between boronic acids and 1,2-diols is reversible and should be favorable to the generation of the expected shape-persistent honeycomb structures (Scheme 1). Heating a mixture of triptycene

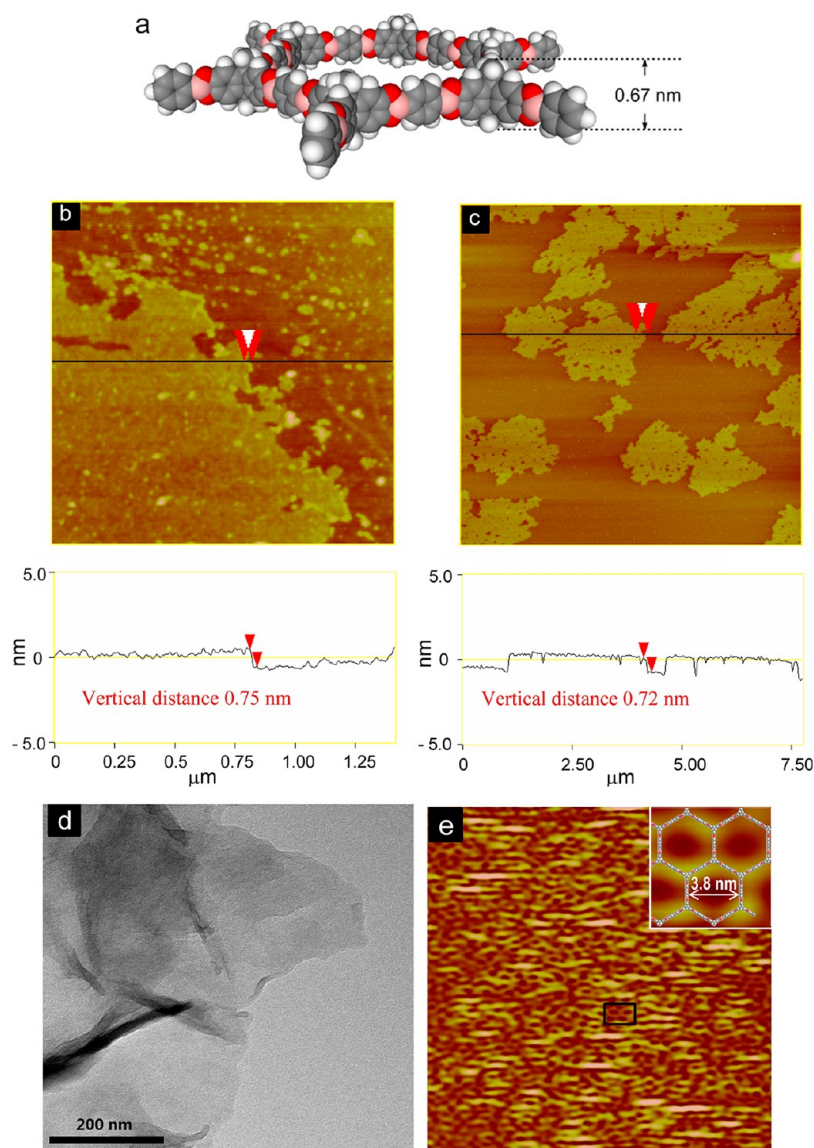


Figure 1. (a) Theoretical thickness of one monolayer. (b, c) AFM images and cross-section analysis of monolayer 1 (b) and monolayer 2 (c). (d) TEM (130 kV) image of monolayer 2. (e) STM image of monolayer 2 recorded in ambient conditions. The inset is magnification of the area marked by the black rectangle, well illustrating the hexagonal units of the honeycomb structure of monolayer 2. The tunneling conditions were $I = 15$ pA and $V = 4.0$ V, recorded in a constant current mode.

tricatechol (TPTC) and 1,4-benzenediboronic acid (BDDBA) or 4,4'-biphenyldiboronic acid (BPDBA) in mesitylene–dioxane (1:1, v/v) at 85 °C under argon for several days without disturbance afforded a solution containing floating film-like materials (Supporting Information, Figure S1). Transmission electron microscopy (TEM) also revealed their sheet-like morphology (Figure S1). The floating films should not be of monolayer since a single-molecule layer is expected to be transparent.⁴ Therefore, the clear solutions were examined to see if soluble 2D monolayered polymers were formed.

Both the visible floating films and the materials obtained upon evaporation of the solvent were first characterized by Fourier transform infrared spectroscopy (FTIR), which confirmed the formation of condensation products because they exhibited a dramatic attenuation of the hydroxyl bands of the starting materials and the appearance of the characteristic B–O and C–O stretching vibrations of the boronate ester,

which was in agreement with those of model compounds **1** and **2** (Figures S2 and S3).

The as-prepared polymers in solution were then investigated by tapping-mode atomic force microscopy (AFM), which showed the formation of film-like structures with lateral sizes of up to several micrometers (Figure 1b,c). Cross-section analysis indicated that the films were very flat and uniform. The heights of the films were measured to be ~ 0.75 nm (statistically average height being 0.76 nm based on 100 different sites, Figure S4) for the sample obtained from TPTC and BDDBA (named as monolayer 1) and ~ 0.72 nm (statistically average height being 0.73 nm based on 100 different sites, Figure S5) for the sample fabricated from TPTC and BPDBA (named as monolayer 2), respectively. These values agreed very well with the theoretical thickness of the expected polymeric monolayer (0.67 nm, Figure 1a, calculated by semiempirical method at the PM3 level), strongly suggesting the formation of single-layer sheets. The lower magnification AFM image of the film was also

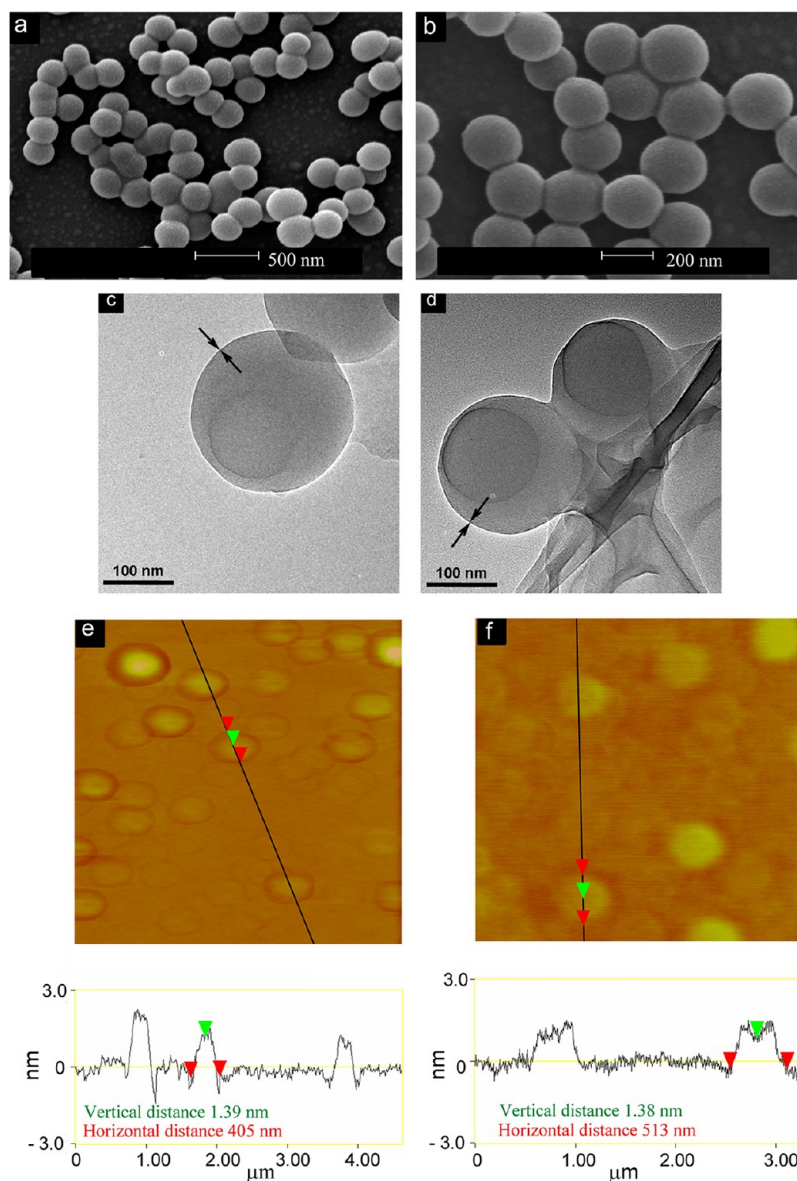


Figure 2. SEM images of (a) nanosphere 1 and (b) nanosphere 2. High-resolution TEM (130 kV) images of (c) nanosphere 1 and (d) nanosphere 2; and AFM images and cross-section analysis of (e) nanosphere 1 and (f) nanosphere 2.

provided (Figure S6), which showed good structural homogeneity. The possibility that the monolayers were generated by the self-assembly of unreacted starting materials was ruled out by control experiments, which showed that the mixture of TPTC and either of the diboric acids only afforded ill-defined aggregates (Figure S7). These results clearly indicated that our new strategy did work to construct free-standing 2D polymers of monomolecular thickness in solution, and the resulting monolayered 2D polymers were strong enough to be transferred onto a solid substrate. TEM investigation further confirmed the existence of 2D structures by displaying sheet-like structures (Figure 1d and Figure S8). Although the thickness of these sheets and films could not be estimated from TEM, their obviously transparent feature suggested that they should be extremely thin, probably several layers because an organic monolayer should be quite unstable under the condition used for the TEM experiment.

In order to obtain the structural information on the as-prepared 2D polymers at molecular resolution, scanning

tunneling microscopy (STM) investigations were carried out. As shown in Figure 1e, although being interfered by some noises, the STM image of monolayer-2 displayed the expected honeycomb network and hexagonal units of the “honeycomb”. Furthermore, polygonous structures of different shape and size were also observed, which might be attributed to the deformation of the polygons, incomplete ring closure, or cleavage of B–O bonds (see Supporting Information for detailed explanation). Similar phenomena were also reported for the COF structures fabricated from BDBA and planar 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP).²¹

In addition to the above sheet-like structures, monolayered and multilayered hollow spheres were also found to coexist in the same solution. Their spherical morphology was clearly demonstrated by scanning electron microscopy (SEM) (Figure 2a,b). The sizes of the spheres are ~ 200 nm and some of them fused each other a little bit. The hollow nature of these spheres was evidenced by high-resolution TEM (HR-TEM), which exhibited a contrast between the inner part and the peripheral

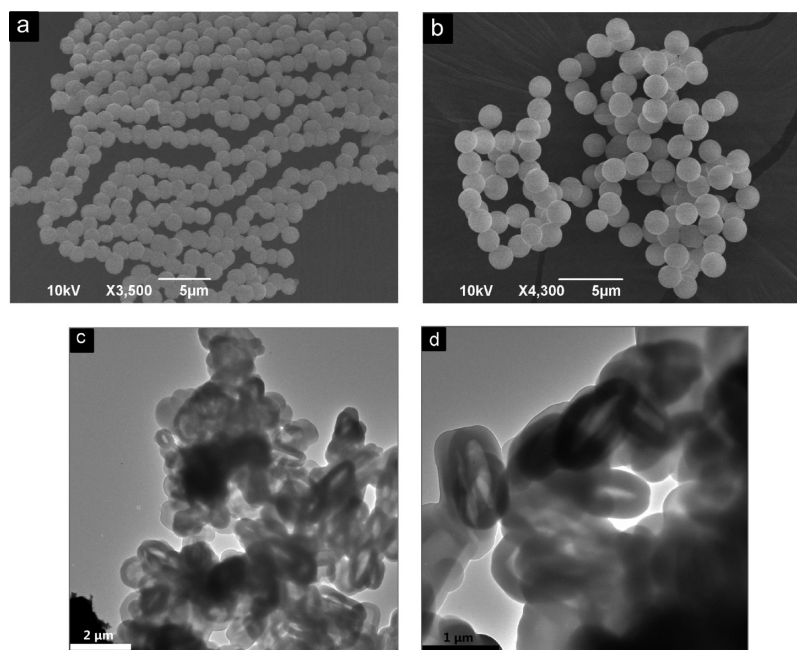


Figure 3. SEM images of (a) microsphere 1 and (b) microsphere 2 and TEM (160 kV) images of (c) microsphere 1 and (d) microsphere 2.

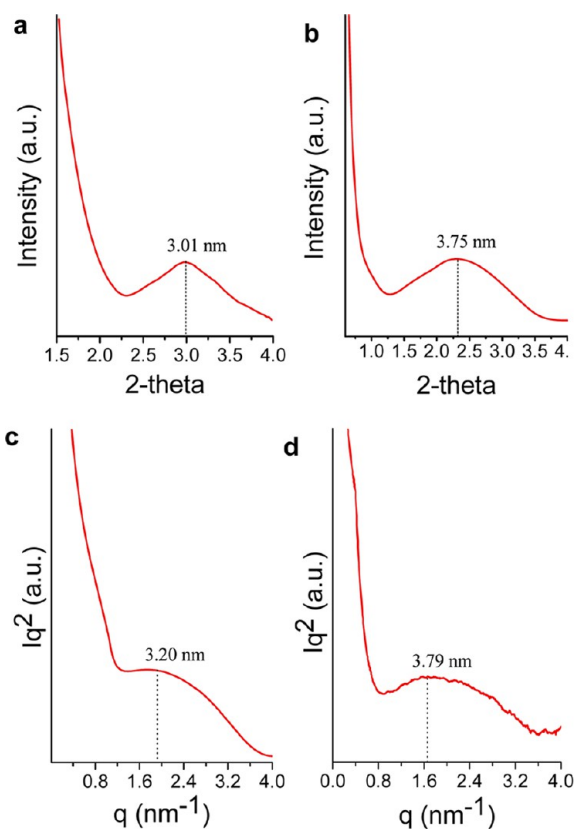


Figure 4. SAXD patterns of (a) microsphere 1 and (b) microsphere 2 and Lorentz-corrected SAXS profiles of (c) microsphere 1 and (d) microsphere 2.

of the spheres (Figure 2c,d). The wall thicknesses of the selected spheres were also revealed by HR-TEM to be less than 1.0 nm for the sample prepared from TPTC and BDDBA (named as nanosphere 1) and the sample prepared from TPTC and BPDDBA (named as nanosphere 2), which are very close to the thicknesses of the monolayered COF sheets investigated

above, suggesting that the walls of the hollow spheres consisted of monolayered polymers. AFM further supported that the hollow spheres were formed from monolayered polymers. The cross-section analysis revealed that the diameters of the spheres were in the range of several hundreds of nanometers, while the heights of the two selected spheres were measured to be only 1.39 nm for nanosphere 1 and 1.38 nm for nanosphere 2 (Figure 2e,f). Such large ratios of diameter over height indicated that the spheres were totally flattened under the high local force applied by the AFM tip, which is reasonable if one considers that the flexibility of a single-molecule-layer polymer and the expected collapse of hollow spheres after the solvent molecules were evaporated. Most importantly, the heights of the selected spheres were just twice the thickness of the expected monolayered sheet which had a thickness of 0.67 nm, suggesting that the walls of the spheres consisted of single-molecule-layer polymers. This result again strongly suggested that monolayered 2D polymers did form in solution during the dehydration process. Multilayered hollow spheres with wall thickness of more than 10 nm were also observed (Figure S9). This result suggested that aggradation between the formed monolayers could still occur, although π – π stacking between them was inhibited. This is reasonable because sheet-like objects can stack on top of one another, but in our case the formed sheets should stack less readily due to the absence of π – π stacking and the long face-to-face distance. Different from the well-ordered layer-by-layer stacking of monolayers in laminar COF materials previously reported,^{17–20} the aggradation of the formed monolayers in our system should be random and sideways movement between the layers is expected to occur easily due to the lack of π – π stacking and the long face-to-face distance between them. Moreover, it was found that the relative amounts of sheets and spheres varied with the concentrations of the starting materials. A lower concentration of TPTC (0.01–0.1 mg/mL) favored the formation of sheet-like structures, while spheres were the major products when the concentration increased (0.1–1.0 mg/mL). Furthermore, it was also found that shorter reaction time (2 days) should be

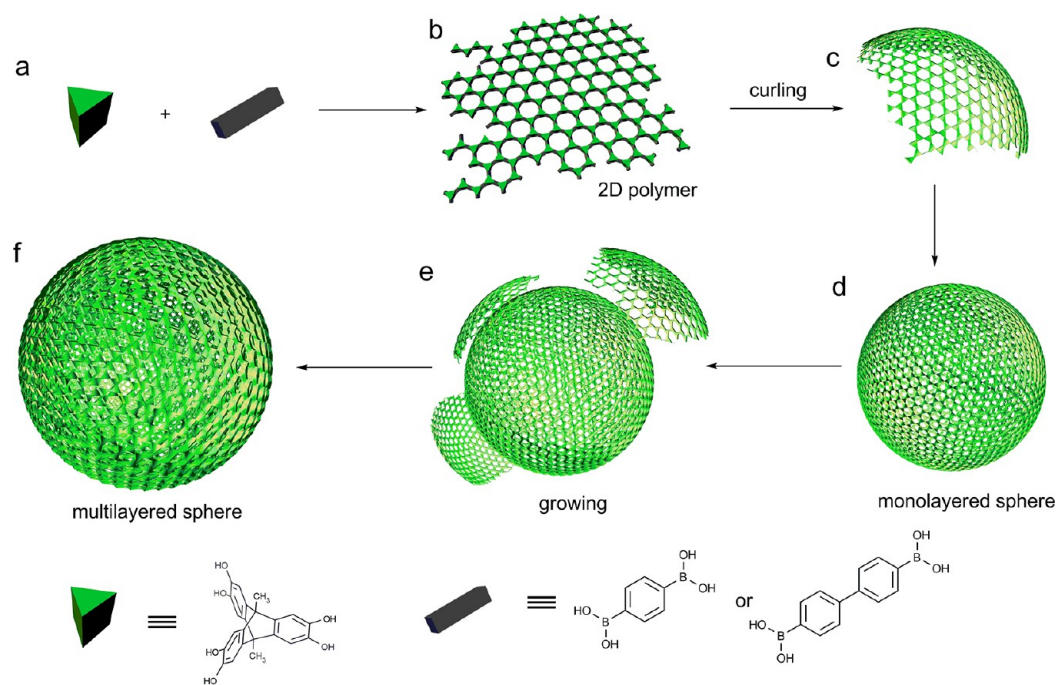


Figure 5. Proposed mechanisms for the formation of 2D polymers and hollow spheres. (a) Cartoon representation for the polymeric monomers (see the bottom of the figure for the chemical structures of the monomers). (b) Formation of monolayered 2D polymers via dehydration reactions between TPTC and boronic acids. (c) Curling of the monolayer sheet. (d) The monolayer sheet further close up into a monolayered hollow sphere. (e) Procedure of the formation of multilayered hollow sphere via enwrapping the monolayered sphere by new layers produced from the dehydration reaction in solution. (f) Representation for a multilayered hollow sphere.

adopted if monolayers were desired and extending reaction time led to more spheres.

When the initial concentration of the starting materials was increased, we observed that white precipitates formed during the reaction process. FTIR spectra of these precipitates are similar to that of model compounds **1** and **2**, suggesting they are also boronate polymers (Figures S2 and S3). Elemental analysis also revealed that the compositions of the precipitates corresponded to the formula expected for the polymeric structures (Supporting Information, synthesis part). Their morphologies were visualized by SEM and TEM. SEM images showed that the two precipitates both displayed regular spherical morphology with smooth surface and the size distribution of the spheres was uniform, with an average diameter of ca. $1.30\ \mu\text{m}$ for the sample from TPTC and BDDBA (named as microsphere 1) and ca. $1.85\ \mu\text{m}$ for the sample from TPTC and BPDDBA (named as microsphere 2), respectively (Figure 3a,b and Figure S10). TEM images revealed that the microspheres were also hollow (Figure 3c,d). The wall thickness was estimated to be ca. $150\ \text{nm}$ for microsphere 1 and ca. $250\ \text{nm}$ for microsphere 2, indicating they were multilayers. Moreover, the layered arrangement could be distinguished at the boundaries of microsphere 2 in the high-resolution TEM image (Figure S10), again suggesting that the walls of the microspheres consisted of multilayered polymers. It should be noted that most of the microspheres shrunk tremendously under high vacuum condition of TEM experiment, with the shape of the microspheres changing from being spherical to oval.

Wide-angle X-ray diffraction (WAXD) study on the visible floating films and the as-prepared microspheres revealed that they exhibited structure-less diffraction patterns (Figure S11), also suggesting a random aggregation of the formed

monolayers. A reasonable explanation is that no long-range ordered arrangement along the z direction occurred, although the arrangement of the repeating units of monolayered polymers in 2D (along x and y directions) should be ordered. In order to get detailed structural information for the 2D polymers which should be the precursors of the microspheres, small-angle X-ray diffraction (SAXD) studies were carried out. The SAXD patterns of microsphere 1 and microsphere 2 displayed diffraction peaks corresponding to 3.01 and $3.75\ \text{nm}$, respectively (Figure 4a,b).

Moreover, small-angle X-ray scattering (SAXS) experiments were also performed for the microspheres. While microsphere 1 exhibited a peak corresponding to $3.20\ \text{nm}$, a peak of $3.79\ \text{nm}$ was observed for microsphere 2 (Figure 4c,d). The values from SAXD and SAXS were consistent with each other and agreed well with the theoretical pore widths calculated from the expected honeycomb-like units of the polymers (Scheme 1). The SAXD and SAXS peaks observed should be caused by the ordered long periodic arrangement of the pore units, which clearly indicated the long-range internal order of the materials and confirmed again the formation of 2D polymers with the expected honeycomb-like networks. Nitrogen adsorption–desorption isotherm measurements on the microspheres revealed that they were porous materials. The maximum nitrogen uptake reached $347\ \text{cm}^3/\text{g}$ for microsphere 1 and $308\ \text{cm}^3/\text{g}$ for microsphere 2, respectively, indicating a good capacity for nitrogen storage. The apparent surface areas calculated from the Brunauer–Emmett–Teller (BET) model were $973\ \text{m}^2/\text{g}$ for microsphere 1 and $731\ \text{m}^2/\text{g}$ for microsphere 2, respectively. These results indicated that these hollow microspheres are good porous materials. The pore size distributions of the microspheres were calculated by the Barrett, Joyner, and Halenda method (Figure S12),²⁷ which showed

that the mesoporous distributions were largely populated at 3.4 nm for microsphere 1 and 4.0 nm for microsphere 2, which were consistent with the values obtained by small-angle X-ray diffraction and scattering experiments above.

On the basis of the above results, we proposed the mechanisms for the generation of our 2D polymers and hollow spheres which are shown in Figure 5. The dehydration reactions between triptycene tricatechol and boronic acids first led to the formation of reticular frameworks. In contrast to Yaghi's or El-Kaderi's systems in which the interlayer interactions are strong and thus the as-formed monolayered 2D frameworks further stack one another to generate 3D layered structures,^{17,26} in our case the stacking between the initially formed monolayers was very weak. As a result, the as-formed single-molecule-layer 2D polymers could be maintained and freely float in solution without aggregating. With the degree of polymerization becoming higher, some of the monolayers curled and finally closed up into monolayered hollow spheres, which was driven by a reduction of the surface energy.^{28,29} The monolayered spheres formed could be further enwrapped by other layers and thus grew bigger and bigger and finally precipitated out of the solution when they reached a critical size, which led to the generation of the uniform multilayered hollow microspheres. The conversion of 2D polymer sheets to hollow spheres was evidence by the observation of an unclosed sphere which might be on the way transferring from 2D sheet to hollow sphere (Figure S13).

CONCLUSIONS

A facile method for preparing free-standing, monolayered 2D polymers in solution has been developed. In these systems, the interlayer interactions between monolayers become very weak due to the lack of π - π stacking and the long face-to-face distance. Although the tendency of aggregation of monolayers still cannot be completely inhibited, such strategy does create the possibility for the existence of monolayered 2D polymers without aggregation, which is not only evidenced by the as-obtained monolayered polymeric sheets that float individually in solution but also supported by the formation of monolayered hollow nanospheres from the simple monolayers. Besides their fundamental scientific importance, the new mono/multilayered honeycomb-like sheets and hollow micro/nanospheres may perform promising applications in separation science, selective entrapment, and in other aspects which can benefit from their extraordinary large surfaces and micropores embedded in the surfaces of these unique materials. Furthermore, we believe this strategy should be more general and effective. In principle, it should also be applicable to COFs constructed by other types of bonding linkages such as imine and hydrazine,^{30,31} to supramolecular organic frameworks (SOFs),³² and even to the fabrication of monolayered metal-organic frameworks (MOFs).^{33,34}

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, additional AFM, TEM, and SEM images, FT-IR spectra, XRD experiments, and nitrogen adsorption-desorption isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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