Layered microporous polymers by solvent knitting method

Shaolei Wang,1 Chengxin Zhang,1 Yu Shu,1 Shulan Jiang,2 Qi Xia,2 Linjiang Chen,3 Shangbin Jin,1 Irshad Hussain,4,5 Andrew I. Cooper,3 Bien Tan1*

Two-dimensional (2D) nanomaterials, especially 2D organic nanomaterials with unprecedentedly diverse and controlled structure, have attracted decent scientiﬁc interest. Among the preparation strategies, the top-down approach is one of the considered low-cost and scalable strategies to obtain 2D organic nanomaterials. However, some factors of their layered counterparts limited the development and potential applications of 2D organic nanomaterials, such as type, stability, and strict synthetic conditions of layered counterparts. We report a class of layered solvent knitting hyper-cross-linked microporous polymers (SHCPs) prepared by improving Friedel-Crafts reaction and using dichloroalkane as an economical solvent, stable electrophilic reagent, and external cross-linker at low temperature, which could be used as layered counterparts to obtain previously unknown 2D SHCP nanosheets by method of ultrasonic-assisted solvent exfoliation. This eﬁcient and low-cost strategy can produce previously unreported microporous organic polymers with layered structure and high surface area and gas storage capacity. The pore structure and surface area of these polymers can be controlled by tuning the chain length of the solvent, the molar ratio of AlCl3 and the size of monomers. Furthermore, we successfully obtain an unprecedentedly high-surface area HCP material (3002 m2 g−1), which shows decent gas storage capacity (4.82 mmol g−1 at 273 K and 1.00 bar for CO2; 12.40 mmol g−1 at 77.3 K and 1.13 bar for H2). This finding provides an opportunity for breaking the constraint of former knitting methods and opening up avenues for the design and synthesis of previously unknown layered HCP materials.

INTRODUCTION

Graphene, being the first two-dimensional (2D) nanomaterials with atomic thickness, shows many intriguing properties, including extreme mechanical strength and exceptionally high electronic and thermal conductivity (1), triggering enormous research interest in 2D nanomaterials (2–9). Unlike the graphene and 2D inorganic nanomaterials, single- or few-layered 2D organic nanomaterials have unprecedentedly diverse and controlled structure by tailoring their building blocks and introducing functional groups, endowing themselves with tunable properties, especially electronic and optoelectronic properties, and have also attracted decent scientiﬁc interest (10–13).

Inspired by the excellent properties and potential applications of 2D organic nanomaterials, two approaches (that is, “bottom-up” and “top-down”) have been developed for their production. The on-surface polymerization is an important bottom-up strategy to obtain 2D organic nanomaterials by diverse organic reactions, such as Ullmann coupling, boronic anhydridization reaction, acylation reaction, imine formation, etc. (10–19). Another bottom-up strategy, topochemical polymerization (such as air/water interface polymerization), is also of great signiﬁcance to obtain large 2D organic nanomaterials (20–22). However, the bottom-up synthetic strategy is generally associated with challenges (such as the requirement of ultrahigh vacuum, expensive substrates, and speciﬁcally designed monomers), which impede their large-scale production and real applications in the ﬁeld (18, 20, 23).

Numerous exfoliation attempts of layered bulk materials are deﬁned as a top-down approach, which is considered low-cost and scalable to produce 2D organic nanomaterials (13, 24–26). Because of the control over the geometry and proximity of the reactive sites of monomers, the 2D polymer crystals prepared by single-crystal approach can function as layered bulk materials to produce 2D organic nanomaterials (26, 27). Recently, combining the use of reversible reactions, solvothermal synthetic conditions, and dynamic covalent chemistries, the covalent organic frameworks (COFs) with layered crystals and porosity have also been prepared and used as layered organic crystals (28). The direct exfoliation of bulk COFs also resulted in a series of the single- and even multilayered 2D organic nanomaterials (23, 29–32). Compared with 2D polymer crystals, COFs have many advantages such as being low-cost and easily synthesized, but their hydrothermal instability and high sensitivity to exfoliation limit their overall stability, development, and potential applications in the ﬁeld (23, 28, 32). Therefore, it is highly desirable to develop cost-effective synthetic strategies to produce layered bulk materials with high hydrothermal stability.

Following the synthetic concept of COFs, the reversible bond formation is the key feature, which advances many other reversible reactions, including Friedel–Crafts reactions feasible for the synthesis of layered structure synthetic materials (33). Recently, hyper-cross-linked polymers (HCPs) prepared by Friedel–Crafts alkylation based on strategies such as post-cross-linking of “Davankov-type” resins, self-polycondensation of multifunctional monomers, and knitting aromatic compound polymers using external cross-linkers are receiving more attention due to their easier preparation, high chemical and thermal stability, and low-cost and sustainable mass production (34, 35). However, the open reaction system, high temperature, and poor stability of carbocation intermediates as electrophilic reagents generally result in the production of amorphous HCP materials. Therefore, the development of efﬁcient protocols for the synthesis of layered HCP materials is still a formidable scientiﬁc challenge.

Herein, we combine the growing need for 2D organic nanomaterials with the scientiﬁc challenge of HCP materials and propose a previously unknown synthetic strategy to knit the ﬁrst HCPs with layered structure,
high surface area, and gas uptake to produce 2D SHCP nanosheets by ultrasonic-assisted solvent exfoliation method. It resulted in great improvement in the Friedel-Crafts reaction conditions upon introduction of dichloroalkane as an economical solvent, stable electrophilic reagent and external cross-linker with a relatively less air-controlled environment, low temperature and gradient heating to control the rate of reaction of highly reactive carbocation intermediates. This process will overcome the constraint of previous knitting method and open a path for the design and synthesis of previously unreported layered HCP materials.

RESULTS AND DISCUSSION
To the best of our knowledge, the Friedel-Crafts alkylation reaction used to produce HCPs with layered structure using dichloroalkane as an economical solvent has not been previously reported (34–36). The HCPs show excellent thermal stability, high surface area, and gas uptake and could be used as layered bulk materials to produce 2D SHCP nanosheets by the ultrasonic-assisted solvent exfoliation method.

Structural characterization and simulations
Surprisingly, the yield of polymers was very high, which is probably due to the favorable reaction of solvent with various aromatic precursors in the presence of AlCl3 catalyst (37, 38). The Fourier transform infrared (FTIR) spectroscopy confirms the existence of alkyl groups in the chemical structure of polymers by strong C–H stretching vibrations near 2920 cm⁻¹ (figs. S1 to S7 and table S1). The 13C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra of all these polymers show resonance peaks near 140 and 133 parts per million (ppm) due to the substituted aromatic carbon and unsubstituted aromatic carbon, respectively. The resonance peaks near 37 ppm can be ascribed to the carbon of methylene linkers [stemmed from dichloromethane (DCM) as solvent and cross-linker] or ethylene linkers [stemmed from 1,2-dichloroethane (DCE) as solvent and cross-linker] formed after a Friedel-Crafts reaction (Fig. 1 and figs. S8 to S14) (39).

To elucidate the mechanism of the polymerization process, we successfully isolated some dimers at the initial stage of polymerization and characterized them by 1H and 13C NMR, which clearly showed a resonance peak from methylene at about 4.10 ppm and thus confirmed the formation of methylene linkage in the polymers (figs. S15 and S16). On the basis of these analytical data, we believe that dichloroalkane is knitting the aromatic compounds to yield highly porous networks with methylene/ethylene as linkers under AlCl3 catalysis, thus breaking the traditional cognitive of dichloroalkane as a solvent for HCP knitting strategies. Moreover, the low residual chlorine contents in methylene-based SHCP-3 (0.5%) and ethylene-based SHCP-6 (0.01%) and almost no catalyst residues in the polymers under ambient conditions suggest that the high yield of polymers is because of extensive cross-linking and incorporated abundant alkyl groups (fig. S17).

We further investigated the morphology and texture of polymers by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). These polymers show block particles with layered structures, which are very different from the reported morphologies of HCPs figs. S18 to S24 (39–41). These polymers exhibited high thermal stability with thermal degradation of up to 400°C under nitrogen, and the residual weight of methylene-based polymers was more than that of ethylene-based polymers, indicating their higher thermal stability (fig. S17).

The powder x-ray diffraction (PXRD) pattern of these previously unknown polymers with layered structure showed a broad diffraction peak at 2θ = 23° to 27° (figs. S25 to S28). Unlike the reported morphologies of HCPs (such as polymer 3), SHCP-3 and SHCP-6 showed obvious features of layered structures by HR-TEM and scanning TEM (STEM) at a high resolution, confirming the existence of layered structures in these polymers (Fig. 2 and fig. S29). We further evaluated the propensity of 1,3,5-triphenylbenzene (TPB), in its molecular form...
and in the form of oligomers (fig. S30), to construct layered structures by calculating the energy required to create 1 unit of surface area relative to the bulk (see details in the Supplementary Materials). Intrinsically, surfaces are less energetically favorable than the bulk material overall, and the surfaces characterized by higher surface energies are less likely to be present or they are not very stable. Our calculations suggest that it is equally likely to form 2D slabs with the model TPB oligomers and with the TPB molecules. The surface energy is the same (that is, 0.10 J m$^{-2}$) for both the amorphous packing of the TPB oligomers and the crystalline packing of the TPB molecules, as shown in figs. S31 and S32, respectively. Thus, we assume that the layered structures might have been formed by the formation of chloroalkyl-substituted aromatic monomers at low temperature, followed by their bridging and formation of larger rings, and finally knitting the layered structure at high temperature.

**AFM information of SHCP nanosheets**

To further confirm the existence of layered nanosheet-like structures, we used ultrasonic-assisted solvent exfoliation method to exfoliate bulk SHCP-3 and SHCP-6. The atomic force microscopy (AFM) measurements further confirmed the precise information of SHCP-3 and SHCP-6 nanosheets. As shown in Fig. 3, the lateral dimensions of SHCP-3 nanosheets are fully consistent with its HR-TEM result, and the height of SHCP-3 nanosheets varies from 2 to 50 nm (figs. S33 and S34). Meanwhile, the nanosheets of SHCP-6 also show similar characteristics to the nanosheets of SHCP-3, which suggests that all the SHCP materials have layered structure. The reproducibility of SHCP nanosheets is marked by this exfoliation method. Moreover, the ionic liquid exfoliation also produces SHCP nanosheets under ultrasonic conditions (fig. S34, C and D) (42).

**Porosity of layered microporous polymers**

After confirming the chemical and layered structure of polymers, we further investigated the porosity parameters of polymers by nitrogen sorption analysis at 77.3 K. As shown in Fig. 4 (A and C), the isotherms of polymers exhibited a type I character with a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$), thus reflecting an abundant microporous structure, and the existence of hysteresis for nitrogen sorption isotherm of polymers suggests that polymers also have mesopores (43, 44). With an increase in monomer size, the Brunauer-Emmett-Teller (BET) surface area of polymers increased from 575 to 1808 m$^2$ g$^{-1}$ for methylene-based polymers and from 731 to 935 m$^2$ g$^{-1}$ for ethylene-based polymers (Table 1).
It is also worth mentioning that the surface area of methylene-based polymers increased markedly and that of ethylene-based polymers decreased by increasing the molar ratio of AlCl₃ (Table 1, table S2, and Fig. 4C). This result may be due to a faster rate of cross-linking and the low degree of free packing for building blocks, leading to abundant mesopores and macropores and a much higher surface area for methylene-based polymers (Fig. 4C). The decrease in the microporosity of TPB-based polymers from 44 to 18% also supports the proposed explanation (Table 1). However, the ethylene-based polymers with much higher yield have high ethylene content in their unit mass, leading to a more efficient packing and thus compromising the surface area. Most notably, SHCP-3b has abundant ultramicropores (centered at 0.5 and 0.59 nm) and an extremely high specific surface area of 3002 m² g⁻¹, which is unprecedented in HCP materials reported thus far (39, 40, 45–47).

On the basis of the pore size distribution analysis data, the chain length of solvent can effectively tune the pore size of polymers from 0.5 to 0.59 nm for benzene-based polymers, 0.64 nm for biphenyl-based polymers, and 0.68 nm for TPB-based polymers. Moreover, the size of monomers can also be controlled to tune the pore size from 0.59 nm for SHCP-4 to 0.64 nm for SHCP-5 and to 0.68 nm for SHCP-6 (Fig. 4B and table S3). Therefore, this knitting method shows significant advantages, including the systematic tuning of the porosity of layered structured HCPs, by varying the chain length of the solvent, the size of monomers, and the molar ratio of AlCl₃.

Table 1. Composition and porosity of the polymers.

<table>
<thead>
<tr>
<th>Number</th>
<th>Monomer</th>
<th>Solvent</th>
<th>S BET (m² g⁻¹)*</th>
<th>S L (m² g⁻¹)†</th>
<th>Pore volume (cm³ g⁻¹)‡</th>
<th>MPV (cm³ g⁻¹)§</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHCP-1</td>
<td>Benzene</td>
<td>DCM</td>
<td>575</td>
<td>769</td>
<td>0.32</td>
<td>0.15</td>
</tr>
<tr>
<td>SHCP-2</td>
<td>Biphenyl</td>
<td>DCM</td>
<td>1475</td>
<td>1944</td>
<td>0.79</td>
<td>0.43</td>
</tr>
<tr>
<td>SHCP-3</td>
<td>TPB</td>
<td>DCM</td>
<td>1808</td>
<td>2407</td>
<td>1.08</td>
<td>0.48</td>
</tr>
<tr>
<td>SHCP-4</td>
<td>Benzene</td>
<td>DCE</td>
<td>731</td>
<td>981</td>
<td>0.80</td>
<td>0.16</td>
</tr>
<tr>
<td>SHCP-5</td>
<td>Biphenyl</td>
<td>DCE</td>
<td>536</td>
<td>724</td>
<td>0.35</td>
<td>0.12</td>
</tr>
<tr>
<td>SHCP-6</td>
<td>TPB</td>
<td>DCE</td>
<td>935</td>
<td>1281</td>
<td>0.88</td>
<td>0.15</td>
</tr>
<tr>
<td>SHCP-3a</td>
<td>TPB</td>
<td>DCM</td>
<td>2525</td>
<td>3480</td>
<td>2.10</td>
<td>0.43</td>
</tr>
<tr>
<td>SHCP-3b</td>
<td>TPB</td>
<td>DCM</td>
<td>3002</td>
<td>3896</td>
<td>2.33</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*Surface area calculated from nitrogen adsorption isotherms at 77.3 K using the BET equation. †Surface area calculated from nitrogen isotherm at 77.3 K and P/P₀ = 0.995. ‡Pore volume calculated from nitrogen isotherm at P/P₀ = 0.050. §Micropore volume calculated from the nitrogen isotherm at P/P₀ = 0.050. ||The amount of Lewis acid is 12 molar ratio to TPB. ¶The amount of Lewis acid is 24 molar ratio to TPB.
Gas uptake of layered microporous polymers

The high specific surface area and abundant ultramicroporous nature of the polymers inspire us to investigate their gas uptake capacities. On the basis of the CO$_2$ isotherms of polymers, the CO$_2$ uptake of ethylene-based polymers is lower than that of methylene-based polymers (Fig. 5, A and B, and Table 2) because of lower surface area and micropore volume (MPV) of ethylene-based polymers. Of these SHCP polymers, SHCP-3 with much higher microporosity exhibits the highest CO$_2$ uptake at 4.84 mmol g$^{-1}$ (273 K and 1.00 bar). The CO$_2$ uptake of SHCP-3 is much higher than that of other HCP materials under similar conditions, such as TPB-based HCPs (3.61 mmol g$^{-1}$) (39), binaphthol-based HCPs (3.96 mmol g$^{-1}$) (40), and C1M1-Al (4.34 mmol g$^{-1}$) (46), with the highest CO$_2$ uptake capacity for HCP materials reported thus far.

Moreover, the CO$_2$ uptake capacity of SHCP-3 is comparable to that of the best porous materials reported, such as CPOP-10 ($S_{\text{BET}}$ = 3337 m$^2$g$^{-1}$, <2.27 mmol g$^{-1}$, at 298 K and 1.00 bar) (48–50). Different from most porous materials with open metal sites and CO$_2$-philic active sites such as heteroatoms and functional groups, the ultramicropores of SHCP-3 may endow itself with the outstanding CO$_2$ capture performance, which is comparable to the kinetic diameter of CO$_2$, to increase interactions between CO$_2$ and the pore walls (51). In addition, the CO$_2$ uptake of SHCP-2 with lower surface area is higher than that of SHCP-3 (298 K and 1.00 bar), which further proves the assumption that the ultramicropores play a major role in the high CO$_2$ uptake of these SHCP polymers.

Following the increasing environmental concerns and energy demand, porous materials are extensively being searched for the H$_2$ storage; therefore, we also set out to explore the potential of these polymers for H$_2$ uptake. As shown in Fig. 5C, all the isotherms of polymers for H$_2$ adsorption are fully reversible and exhibit a steep rise and unsaturation at low pressures. The methylene-based polymers exhibit higher H$_2$ uptake capacity than ethylene-based polymers. For example, the SHCP-3b showed the highest H$_2$ uptake of up to 12.40 mmol g$^{-1}$ (77.3 K and 1.13 bar), which is also the highest H$_2$ uptake of HCP materials reported to date (39, 46). The hydrogen storage capacity of SHCP-3b is also higher than that of many reported microporous organic polymers (MOPs) under similar conditions (28, 34, 52–54) but slightly lower than that of the CPOP-1 (14 mmol g$^{-1}$) in MOP materials (55).

---

**Table 2. Gas adsorption of the polymers.**

<table>
<thead>
<tr>
<th>Number</th>
<th>Monomer</th>
<th>Solvent</th>
<th>H$_2$ uptake (mmol g$^{-1}$; wt %)*</th>
<th>CO$_2$ uptake (mmol g$^{-1}$; wt %)$^+$</th>
<th>CO$_2$ uptake (mmol g$^{-1}$; wt %)$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHCP-1</td>
<td>Benzene</td>
<td>DCM</td>
<td>4.80 (0.96)</td>
<td>1.95 (8.6)</td>
<td>1.14 (5.0)</td>
</tr>
<tr>
<td>SHCP-2</td>
<td>Biphenyl</td>
<td>DCM</td>
<td>10.55 (2.11)</td>
<td>4.64 (20.4)</td>
<td>2.77 (12.2)</td>
</tr>
<tr>
<td>SHCP-3</td>
<td>TPB</td>
<td>DCM</td>
<td>10.70 (2.14)</td>
<td>4.84 (21.3)</td>
<td>2.64 (11.6)</td>
</tr>
<tr>
<td>SHCP-3a</td>
<td>TPB</td>
<td>DCM</td>
<td>11.80 (2.36)</td>
<td>4.75 (20.9)</td>
<td>2.52 (11.1)</td>
</tr>
<tr>
<td>SHCP-3b</td>
<td>TPB</td>
<td>DCM</td>
<td>12.40 (2.48)</td>
<td>4.82 (21.2)</td>
<td>2.57 (11.3)</td>
</tr>
<tr>
<td>SHCP-4</td>
<td>Benzene</td>
<td>DCE</td>
<td>5.90 (1.18)</td>
<td>2.11 (9.3)</td>
<td>1.23 (5.4)</td>
</tr>
<tr>
<td>SHCP-5</td>
<td>Biphenyl</td>
<td>DCE</td>
<td>4.40 (0.88)</td>
<td>2.02 (8.9)</td>
<td>1.18 (5.2)</td>
</tr>
<tr>
<td>SHCP-6</td>
<td>TPB</td>
<td>DCE</td>
<td>6.30 (1.26)</td>
<td>2.43 (10.7)</td>
<td>1.43 (6.3)</td>
</tr>
</tbody>
</table>

*H$_2$ uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.13 bar and 77.3 K. $^+$CO$_2$ uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.00 bar and 273.15 K. $^\dagger$CO$_2$ uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.00 bar and 298.15 K.

**Fig. 5. Gas uptake data of polymers.** (A) Volumetric CO$_2$ adsorption and desorption isotherms up to 1.00 bar at 273.15 K, (B) volumetric CO$_2$ adsorption and desorption isotherms up to 1.00 bar at 298.15 K, and (C) volumetric H$_2$ adsorption and desorption isotherms up to 1.13 bar at 77.3 K of polymers. wt %, weight percent.
CONCLUSION
In summary, we demonstrated a previously unreported solvent knitting strategy to produce layered HCPs with high surface area and gas storage. This strategy has several outstanding characteristics: (i) The method can produce porous materials with high surface area, abundant microporous structure, and high gas storage; (ii) the simple synthesis conditions, cheap reagents, and high yield could allow economical and larger-scale production of such materials; and (iii) a tunable porous structure and surface area can be achieved by controlling the solvent chain length, molar ratio of AlCl₃, and monomer size. Another merit of this strategy is the demonstration of a previously unknown formation of layered structure of HCP materials. The very thin SHCP-3 nanosheets were obtained by ultrasonic-assisted solvent exfoliation method, which suggests that this exfoliation method has the potential to form 2D nanosheets of other SHCPs. We are now trying to apply this strategy to develop new materials and explore intriguing properties and applications of this previously unreported strategy by “knitting” aromatic heterocyclic compounds (for example, carbazole and thiophene) and functionalized large conjugated aromatic rings (for example, grapheme) and small-aromatic molecular catalysts (for example, porphyrin).

MATERIALS AND METHODS

Materials
Benzene, biphenyl, AlCl₃ (anhydrous), FeCl₃ (anhydrous), ethanol, HCl, DCM, DCE, and N-methylpyrrolidone (NMP) were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. TPB (syn-PhPh₃, Alfa Aesar, 98%), FDA (Alfa Aesar, 98%), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (Alfa Aesar, 98%) were also used as received.

Synthesis of SHCP-1 (methylenated-based polymer)
Under a N₂ atmosphere, the catalyst (AlCl₃; 0.02 mol, 2.67 g) was added to a solution of benzene (0.78 g, 0.01 mol) in DCM (8 ml) and then the system connected the nitrogen package to form a relatively less air-controlled environment. The reaction system was then stirred for 4 hours at 0°C, for 8 hours at 30°C, for 12 hours at 40°C, for 12 hours at 60°C, and for 24 hours at 80°C to obtain a microporous polymer. The resulting precipitate was quenched using HCl-H₂O [2:1 (v/v)], washed thrice with water and twice with ethanol, extracted with ethanol for 48 hours, and finally dried in a vacuum oven for 24 hours at 65°C (yield, 134%; elemental analysis: C, 88.82; H, 5.94).

Synthesis of SHCP-1a (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating benzene (0.78 g, 0.01 mol) with AlCl₃ (0.04 mol, 5.33 g) in DCM (8 ml) (yield, 141%).

Synthesis of SHCP-1b (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating benzene (0.78 g, 0.01 mol) with AlCl₃ (0.08 mol, 10.67 g) in DCM (8 ml) (yield, 147%).

Synthesis of SHCP-2 (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.02 mol, 2.67 g) in DCM (8 ml) (yield, 145%; elemental analysis: C, 86.24; H, 5.90).

Synthesis of SHCP-2a (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.04 mol, 5.33 g) in DCM (8 ml) (yield, 149%).

Synthesis of SHCP-2b (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.08 mol, 10.67 g) in DCM (8 ml) (yield, 151%).

Synthesis of SHCP-3 (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.018 mol, 2.40 g) in DCM (8 ml) (yield, 142%; elemental analysis: C, 85.74; H, 6.19; Cl, 0.5%).

Synthesis of SHCP-3a (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.036 mol, 4.80 g) in DCM (8 ml) (yield, 146%).

Synthesis of SHCP-3b (methylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.072 mol, 9.60 g) in DCM (8 ml) (yield, 151%).

Synthesis of SHCP-4 (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating benzene (0.78 g, 0.01 mol) with AlCl₃ (0.02 mol, 2.67 g) in DCE (8 ml) (yield, 256%; elemental analysis: C, 86.66; H, 7.86).

Synthesis of SHCP-4a (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating benzene (0.78 g, 0.01 mol) with AlCl₃ (0.04 mol, 5.33 g) in DCE (8 ml) (yield, 284%).

Synthesis of SHCP-4b (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating benzene (0.78 g, 0.01 mol) with AlCl₃ (0.08 mol, 10.67 g) in DCE (8 ml) (yield, 313%).

Synthesis of SHCP-5 (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.02 mol, 2.67 g) in DCE (8 ml) (yield, 265%; elemental analysis: C, 85.33; H, 7.08).

Synthesis of SHCP-5a (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.04 mol, 5.33 g) in DCE (8 ml) (yield, 291%).

Synthesis of SHCP-5b (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating biphenyl (0.77 g, 0.005 mol) with AlCl₃ (0.08 mol, 10.67 g) in DCE (8 ml) (yield, 322%).

Synthesis of SHCP-6 (ethylenated-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.018 mol, 2.40 g) in DCE (8 ml) (yield, 279%; elemental analysis: C, 87.05; H, 7.00; Cl, 0.01%).
Synthesis of SHCP-6a (ethylene-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.036 mol, 4.80 g) in DCE (8 ml) (yield, 301%).

Synthesis of SHCP-6b (ethylene-based polymer)
Following the synthesis conditions of SHCP-1, this SHCP was produced by treating syn-PhPh₃ (0.003 mol, 0.92 g) with AlCl₃ (0.072 mol, 9.60 g) in DCE (8 ml) (yield, 323%).

Synthesis of polymer 3 (knitted by FDA as external cross-linker)
Following the synthesis conditions of Li et al. (39), polymer 3 was produced by treating syn-PhPh₃ (0.005 mol, 1.53 g) with FeCl₃ (0.03 mol, 4.87 g) and FDA (0.03 mol, 2.28 g) in DCE (10 ml).

Synthesis of TPB-based oligomer at 30°C
Under a N₂ atmosphere, AlCl₃ (0.018 mol, 2.40 g) was added to a solution of syn-PhPh₃ (0.003 mol, 0.92 g) in DCM (8 ml), then the system connected the nitrogen package to form a relatively less air-controlled environment. The reaction system was then stirred for 4 hours at 0°C and for 1 hour at 30°C and then was quenched using HCl-H₂O [2:1 (v/v)] and added 20 ml of DCM. The oil-water mixture was transferred to a 100-ml separating funnel and washed with abundant water until it reached pH 7, and the oil phase was then dried using MgSO₄. The oligomer was obtained after removing the solvent and further purified by column chromatography.

The formula for polymeric yield

\[ w = \frac{m_{\text{polymers}}}{m_{\text{monomers}}} \times 100\% \]

where \( m_{\text{polymers}} \) is the weight of the dry polymers obtained using the SHCP method, and \( m_{\text{monomers}} \) is the weight of the corresponding monomers of polymers.

The preparation of SHCP nanosheets by ultrasonic-assisted solvent exfoliation method
Take the preparation of SHCP-3 nanosheets, for example, using NMP with high surface tensions, as an exfoliation solvent, 1 mg of SHCP-3 was dispersed in 10 ml of NMP and then sonicated in an ultrasonication bath (100 W) for 10 min. Then, the resulting suspension was transferred to a 100-ml separating funnel and centrifuged at 5000 rpm for 10 min. Finally, the light yellow supernatant containing very thin 2D nanosheets was obtained, diluted 10⁶ times, and deposited by drop-casting on a silicon wafer surface (or mica wafer surface). The reactive liquids are also useful solvents to produce SHCP nanosheets under ultrasonic conditions, as demonstrated by Wang et al. (42).

Characterization
FTIR spectra were recorded on a Bruker Vertex 70 spectrometer using the KBr disk method. Solid-state \(^{13}\)C CP/MAS NMR spectra were performed on a WB 400 MHz Bruker Avance II spectrometer. The \(^{13}\)C CP/MAS NMR spectra were collected with a spinning rate of 8 kHz and using a 4-mm double-resonance MAS probe. The \(^{1}H\) and \(^{13}\)C NMR spectra of oligomers for SHCP-3 were recorded on a Bruker AV-400 spectrometer using CDCl₃ as solvent. Elemental analysis was performed on a vario MICRO cube elemental analyzer (Elementar). The data of chlorine content for polymers were offered by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Thermogravimetric analysis (TGA) was performed at room temperature to 850°C under nitrogen and air using a PerkinElmer Instrument Pyris 1 TGA with a heating rate of 10°C min⁻¹. The FE-SEM images were recorded using an FEI Sirion 200 FE-SEM operated at 10 kV. Before measurement, the samples were dried in a vacuum oven for 24 hours at 70°C and then sputter-coated with platinum. PXRD images were collected on X’Pert PRO with a scanning rate of 5° min⁻¹. The HR-TEM and STEM images of the samples were recorded on a Tecnai G2 F30 microscope (FEI Corp.). The thickness and size of the nanosheets were carried out by Bruker Innova AFM in tapping mode. Before measurement, the diluted solution containing very thin nanosheets was deposited by drop-casting on the silicon wafer (or mica wafer) and dried in a vacuum oven for 72 hours at 80°C to allow complete evaporation of NMP. Gas (H₂, N₂, and CO₂) sorption properties and specific surface area of samples were measured using a Micromeritics ASAP 2020 surface area and porosity analyzer. Before analysis, the samples were degassed for 8 hours at 110°C under vacuum of 10⁻⁵ bar. Pore size distribution was calculated by N₂ adsorption isotherm using the Tarezona nonlocal DFT model, assuming slit pore geometry. Total pore volumes \((V_{\text{total}})\) were derived from nitrogen sorption isotherms at relative pressure \(P/P_0 = 0.995\).

Surface energy calculation details
To obtain amorphous models for the TPB oligomers (fig. S32), the Amorphous Cell module in BIOVIA Materials Studio 2016 was used, in conjunction with the COMPASS II force field. The dimensions of the orthorhombic simulation box for the bulk were 4.5 nm × 4.5 nm × 4.9 nm, whereas those of the box for the slab were 4.5 nm × 4.5 nm × 6.5 nm. The thickness of the slab at the narrowest cross section was 2 nm. The atomistic bulk and slab models for the crystalline TPB were constructed on the basis of the crystal structure reported in the Cambridge Structural Database (CCDC 867818). The dimensions of the simulation box for the crystalline slab were 4.7 nm × 4.5 nm × 4.0 nm, in which the slab thickness was 2 nm and the slab surfaces were the (100) plane of the bulk crystal.

Thus, all atomistic models generated were further geometry-optimized using density functional–based tight-binding (DFTB) methods. DFTB in the self-consistent charge parameterization was used in combination with a universal force field dispersion correction (56, 57). Using these DFTB-optimized configurations, surface energies were determined using dispersion-corrected DFT. All DFT calculations made use of the Perdew-Burke-Ernzerhof exchange-correlation functional with semiempirical dispersion corrections from the DFT-D3 method (58, 59). The MOLOPT basis sets of the double-\(\zeta\) quality were used, together with the Goedecker-Teter-Hutter pseudopotentials (60–62). The charge-density cutoff for the auxiliary plane-wave expansions was set to 350 rydberg.

Surface energy calculations
We evaluated the propensity of TPB, in its molecular form and in the form of oligomers (fig. S32), to form layered structures by calculating the energy required to create 1 unit of surface area relative to the bulk, or the surface energy, given as

\[ \gamma = \frac{(U_{\text{slab}} - U_{\text{bulk}})}{2A} \]

where \(U_{\text{slab}}\) is the total energy of the 2D slab (at least 2 nm thick, with a minimum of 2 nm of vacuum region on each side), \(U_{\text{bulk}}\) is the total...
energy of the corresponding number of TPB units in bulk, and A is the surface area created on each side of the slab and is repeated periodically. Calculations were performed with first-principles DFT, using the CP2K package (www.cp2k.org).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/3/e1602610/DC1

REFERENCES AND NOTES


Acknowledgments: We thank the Analysis and Testing Center, Huazhong University of Science and Technology for assistance in characterization of materials. Funding: This work was supported by the Program for National Natural Science Foundation of China (no. 21474033/51273074/51173058), the International S&T Cooperation Program of China (2016YFE0124400), and the Program for HUST Interdisciplinary Innovation Team (2016JCTD104). Author contributions: B.T. conceived the project and supervised the experiment. S.W., C.Z., and Y.S. synthesized and characterized the SHCPs. Q.X. and S.J. performed the AFM measurement. L.C. performed the simulation of layered structure. A.I.C., I.H. and S.J., and I.H. helped in writing/improving the manuscript in addition to technical and intellectual discussion/contribution. S.W. and B.T. co-wrote the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 21 October 2016
Accepted 10 February 2017
Published 31 March 2017
10.1126/sciadv.1602610

Layered microporous polymers by solvent knitting method
Shaolei Wang, Chengxin Zhang, Yu Shu, Shulan Jiang, Qi Xia, Linjiang Chen, Shangbin Jin, Irshad Hussain, Andrew I. Cooper and Bien Tan

Sci Adv 3 (3), e1602610.
DOI: 10.1126/sciadv.1602610