Porous Materials

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Porous Carbon Fibers Containing Pores with Sizes Controlled at the Ångstrom Level by the Cavity Size of Pillar[6]arene

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Abstract: *We report a new synthesis method of fibrous carbon material with pores sizes that are precisely controlled at the Ångstrom level, by carbonization of two dimensional (2D) porous sheets of pillar[6]arenes. The 2D porous sheets were prepared by 2D supramolecular polymerization induced by oxidation of hydroquinone units of pillar[6]arenes. Owing to the hexagonal structure of pillar[6]arene, the assembly induced by 2D supramolecular polymerization gave hexagonal 2D porous sheets, and the highly ordered structure of the 2D porous sheets formed regular fibrous structures. Then, carbonization of the 2D porous sheets afforded fibrous carbon materials with micropores. The micropore size of the fibrous porous carbon prepared from pillar[6]arene was the same size as that of the starting material pillar[6]arene assembly.*

Porous carbon materials, which contain over 90% carbon and have micro- and mesopores, have been widely investigated because they have high mechanical and chemical stability, heat and abrasion resistances, and can be applied for various fields, for example as adsorbents, catalyst supports, and electrode materials.[1,2] One of the most common and effective ways to tailor the pore structure of carbon materials is template carbonization method, in which various porous carbons can be molded to reflect the shape of the inorganic templates.[1] Though the template carbonization is a straightforward method to control the pore structure, it is very difficult to tune pore size at an accuracy of the Ångstrom level. Ångstrom-level pore control can be achieved using molecular-based porous frameworks, such as porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). Carbonization of such molecular-based porous frameworks has been intensively investigated with a purpose of more precise pore control.[2] But, the carbonization process severely destroys the original ordered structure, resulting in a failure to retain the original pore structure at the Ångstrom level in most of cases. The template carbonization method and carbonization of PCPs/MOFs have another problem, that of removing inorganic templates or residues, which can be costly. Herein, we report a new synthesis method of fibrous carbon materials with pores sizes that are precisely controlled at the Ångstrom level without the inorganic templates. We discovered that carbonization of organic porous supramolecular assemblies constructed from pillar[6]arenes led to fibrous carbon materials with pores sizes that are precisely controlled at the Ångstrom level. This is a new method to synthesize porous carbon materials containing controlled pores without the inorganic templates. Pillar[*n*]arenes, first reported by our groups in 2008,[3a] are important macrocyclic hosts in supramolecular chemistry.[3] Pillar[*n*]arenes can be functionalized by various organic reactions. Among various functionalizing pillar[*n*]arenes, cyclic pentamer pillar[5]arene (**OH[5]**)[3a] and hexamer pillar[6]arene (**OH[6]**),[3g] containing 10 and 12 phenolic moieties, respectively, were used in this study (Figure 1a). We speculated that supramolecular assembly of these pillar[*n*]arenes would be a potential candidate as a source for the synthesis of carbon material, because they have many phenolic moieties, as in the case of good carbon sources, such as phenolic resins.[4] In the present study, using **OH[6]** as a starting compound in a two-step processes, we obtained a fibrous carbon material with pores sizes that are precisely controlled at the Ångstrom level. The first step is two-dimensional (2D) supramolecular polymerization of **OH[5]** or **OH[6]** by oxidation of the hydroquinone units (Figure 1b). The formation of intermolecular charge-transfer complexes between hydroquinone and benzoquinone (quinhydrone) produced supramolecular assemblies constructed from charge-transfer complexes (**CT[5]** and **CT[6]**). Owing to the hexagonal structure of **OH[6]**, **CT[6]** assembly induced by the 2D supramolecular polymerization gave 2D porous sheets by hexagonal packing of **CT[6]**, and the highly ordered structure of the 2D sheets formed regular fibrous structures. The second step is carbonization of the 2D porous sheets (Figure 1c). Pleasingly, the fibrous structures of **CT[6]** were completely retained after carbonization, and the carbon material (**PC[6]**) prepared by the process has precisely controlled pores at Ångstrom level which result from the cavity size of **OH[6]**. Carbonization of organic compounds generally affords non-porous materials, thus retaining the cavity of the pillar[6]arene as micropores after carbonization is an unexpected result and a first example.

2D supramolecular polymerization was induced by oxidation of hydroquinone units of **OH[5]** and **OH[6]**, using hypervalent iodine, an efficient reagent for the oxidation of

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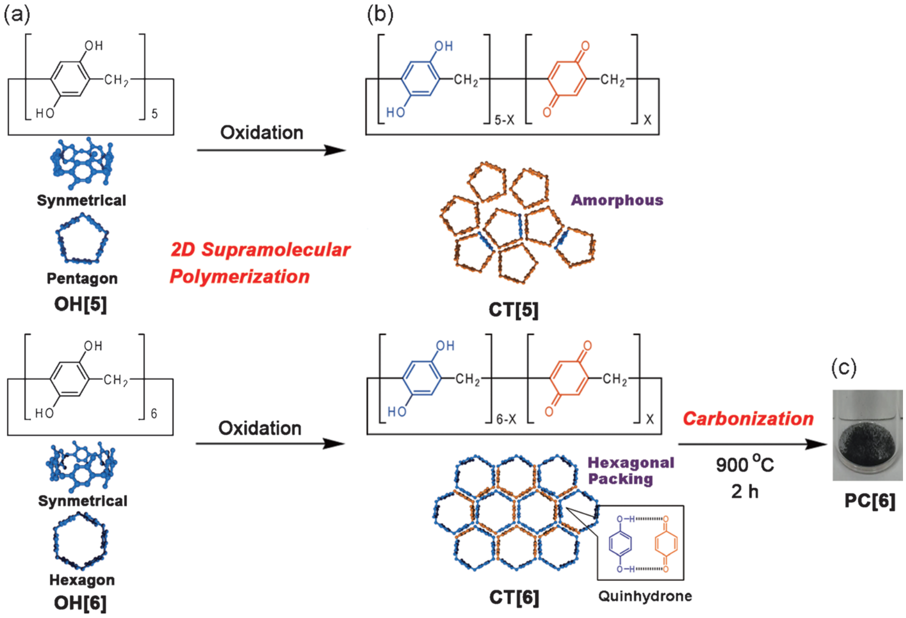

Figure 1. a) Pentagonal and hexagonal structures of **OH[5]** and **OH[6]**, b) 2D supramolecular polymerization by oxidation of hydroquinone units, and c) porous carbon (**PC[6]**) prepared by carbonization of **CT[6]**.

hydroquinone to benzoquinone under mild conditions.[5] The addition of bis[(trifluoroacetoxy)-iodo]benzene to a homogeneous solution of **OH[5]** or **OH[6]** in methanol immediately afforded precipitates. These precipitates were poorly soluble in organic solvents, including methanol, acetone, *N*,*N*-dimethylformamide and dimethyl sulfoxide, which are good solvents for **OH[5]** and **OH[6]**. To remove **OH[5]** and **OH[6]**, the precipitates were washed with methanol. The precipitates were characterized using Fourier-transform infrared (FT-IR) spectroscopy (Supporting Information Figure S1). For both samples, new strong bands at 1651 cm^{-1} were observed, which correspond to the C=O stretching band of the charge-transfer complex between hydroquinone and benzoquinone (Figure 1 b, quinhydrone).[6] Pillar[*n*]arenes have pillar-shaped three-dimensional (3D) structures, therefore the intermolecular formation of quinhydrone between pillar[5]arenes or pillar[6]arenes contributed to the 2D supramolecular polymerization. The 2D supramolecular polymerization gave insoluble assemblies. Elemental analyses of the assemblies showed that the number of benzoquinone units in **CT[6]** was 2.0 ± 0.12. In the case of **CT[5]**, almost all the hydroquinone was converted into benzoquinone. Quinhydrone was formed more efficiently in pillar[6]arene than in pillar[5]arene; this is consistent with the colors of the precipitates. **CT[5]** was yellow (Figure 2 a, inset), indicating benzoquinone mainly forms.

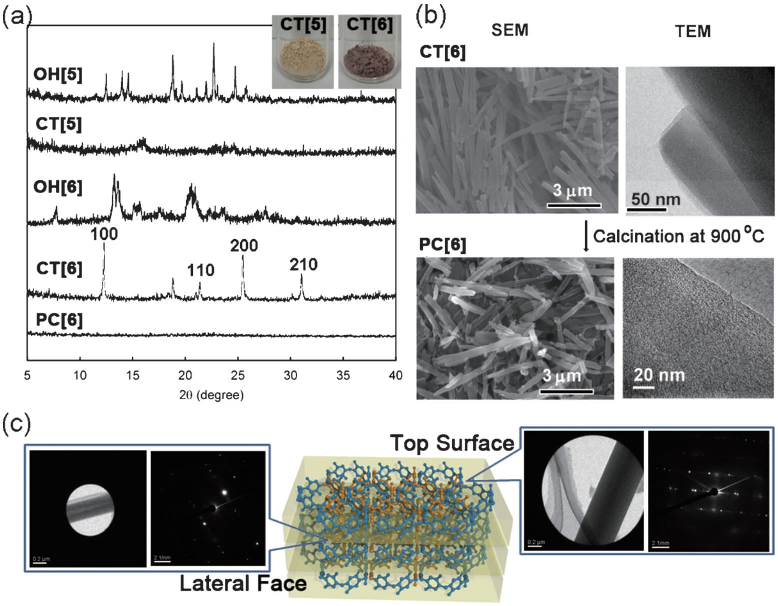

Figure 2. a) PXRD patterns and photographs (inset), b) SEM and TEM images of **CT[6]** and **PC[6]**, and c) selected-area electron diffraction patterns from top surface and lateral face of **CT[6]**.

In contrast, **CT[6]** was purple (Figure 2 a, inset), corresponding to quinhydrone formation. Compared with the pentagonal structure of pillar[5]arene, the hexagonal structure of pillar[6]arene should facilitate the formation of a symmetric 2D structure, resulting in efficient formation of quinhydrone. This was clarified by powder X-ray diffraction (PXRD) studies of the assemblies (Figure 2 a). No clear peaks were detected for the **CT[5]** assembly, indicating it is amorphous. In contrast, the PXRD pattern of the **CT[6]** assembly had clear diffraction patterns, which were assigned to the hexagonal phase, (100), (110), (200), and (210) peaks. These results show that 2D supramolecular polymerization via formation of quinhydrone proceeded more efficiently for pillar[6]arene than pillar[5]arene. Pillar[6]arene has a regular hexagonal scaffold, therefore the 2D supramolecular polymerization of pillar[6]arene molecules via intermolecular formation of quinhydrone afforded a well-defined rigid hexagonal structure (d_{100} = 7.21 Å).

The structures of these **CT[5]** and **CT[6]** assemblies were investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). From the SEM image, the structure of the **CT[5]** assembly was amorphous (Figure S2). In contrast, **CT[6]** showed fibrous structures of width of approximately 300 nm and length several micrometers (Figure 2 b). The height of the fibers, determined by AFM, was around 300 nm (Figure S3), which corresponds to the width observed in the SEM image (Figure 2 b). The TEM image (Figure 2 b) shows individual 2D sheets, and these form fibrous structures. Selected-area electron diffraction patterns provide information on the stacking structures of the 2D sheets (Figure 2 c). Clear diffraction patterns from hexagonal phase (100), (110), and (200) were detected at the "top", that is, the large surface of the fibrous structure, but these diffraction patterns were not observed for the lateral face. These data indicate that stacking of the 2D sheets occurred in the short axes direction, which resulted in formation of the fibrous structure.

We used the molecular probe technique[7] to evaluate the pore-size of **CT[6]**. Molecular probes of different kinetic diameters, including CO_2 (0.33 nm), ethane (0.40 nm), *n*-butane (0.43 nm), and *n*-hexane (0.49 nm) were used for adsorption at 298 K (adsorption isotherms of **OH[6]** and **CT[6]** for these probe gases and vapor are shown in Figure S4 and S5). The pore-sizes of **OH[6]** and **CT[6]** assemblies were determined to be 4.10 and 4.04 Å (Figure 3 a,b), respectively. The micro-pore size of the **CT[6]** assembly was the same size as that of the starting material **OH[6]** assembly.

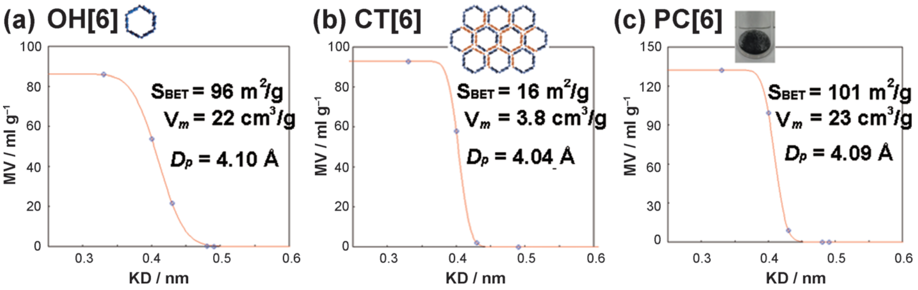

Figure 3. Micropore volumes (MV) of a) **OH[6]**, b) **CT[6]** and c) **PC[6]** estimated by the DA method, plotted against kinetic diameter (KD) of molecular probes.

The fibrous porous **CT[6]** assembly was heated at 900 °C for 2 h under an inert gas atmosphere to obtain carbon material (Figure 1 c, **PC[6]**). The yield of the carbon material **PC[6]** was 54 %, which is high for a char yield (TGA study of **CT[6]** and **OH[6]** is shown in Figure S6). Char yields of unit models, hydroquinone, benzoquinone and quinhydrone at 900 °C were nearly 0 % (Figure S7), thus it is the pillar[*n*]arene structure that gives rise to the high char yields. Among organic compounds, carbonization of ionic liquids afforded carbon materials in high char yields (ca. 22 %).[1g] But, these char yields are approximately two times lower than that of teh carbonization of **CT[6]**. Thus, **CT[6]** is a good carbon source among organic compounds. Calcination increased the carbon contents of the materials, determined by elemental analysis, from 65 % to 93 % going from **CT[6]** to **PC[6]**,indicating formation of carbon material. The Raman spectrum of **PC[6]** showed peaks at 1355 and 1590 cm^{-1} (Figure S8), which correspond to the D and G bands, respectively. The carbon material **PC[6]** was therefore identified as assemblies of graphene sheets. In addition to the D and G bands, we observed a broad band at 200–530 nm, in the range of the radial breathing mode vibrations of single- and multi-walled carbon nanotubes.[6] The observation of this Raman band indicates the presence of curved graphitic sheets with a small diameter of curvature (below 2–3 nm). The PXRD pattern of **PC[6]** had no clear peaks (Figure 2 a), indicating that the hexagonal-packed structure of the **CT[6]** assembly became amorphous on carbonization. We used SEM and TEM images of **PC[6]** to investigate their structures. In the SEM image of **PC[6]**, fibrous structures with widths of around 300 nm and lengths of several micrometers were observed (Figure 2 b). Thus fibrous structures of **CT[6]** were completely retained even after carbonization. The fibrous structures were also observed in the TEM image (Figure 2 b), and surprisingly, numerous micropores of size less than 1 nm (white dots) were found. We measured N_2 adsorption isotherm of **PC[6]** at 77 K (Figure S9). Adsorption of N_2 at low pressures was observed, which indicates the presence of micropores. We determined the micropore sizes using molecular-probe technique (Adsorption isotherm of **PC[6]** for these probe gases and vapor are shown in Figure S9). The pore-size of **PC[6]** was 4.09 Å (Figure 3 c), which was same as the pore-size of the **OH[6]** assembly (Figure 3 a, 4.10 Å).

We proposed a mechanism of the porous carbon formation. From a TGA study of **CT[6]** (Figure S6), we observed a first weight loss (ca. 10 wt %) from 210 to 240 °C. After annealing **CT[6]** at 210 °C, the signal from the C=O bond dissapeared from the FT-IR measurement (Figure S10). By additional heating at high temperature under an inert gas atmosphere, as with phenolic resins, the OH moiety is lost and carbonization occurred. The stable hexagonal packing structure of **CT[6]** contributes to the formation of carbon materials which have the pores the same size as the cavity of the pillar[6]arene precursor even after the carbonization process.

In conclusion, we synthesized a fibrious carbon material, with pore sizes that are precisely controlled at the Ångstrom level, by carbonization of porous 2D sheets that were formed by 2D supramolecular polymerization of the hexagonal structured **OH[6]**. Assembly of hexagonal molecules is a good method for obtaining well-defined supramolecular architectures, and is known as molecular tiling.[8] However, the concept has mainly been applied to planar polyaromatic compounds. The formation of 2D hexagonal sheets using 3D hexagonal compounds achieved in this study therefore opens up new possibilities for molecular tiling. Macrocycle-based 2D assemblies are also comparatively rare.[9] Carbonization of the fibrous assemblies of 2D porous sheets afforded fibrous porous carbon **PC[6]**. The carbon fibers in **PC[6]** had micropores of size 4.09 Å, which is the same as the micropore size of the starting material **OH[6]** (4.10 Å). Compared with template carbonization method and chemical vapor deposition on activated carbons to obtain carbon molecular sieves, this synthesis method does not need to use inorganic templates, and is a simple way for the synthesis of porous carbon fibers with pores sizes that are precisely controlled at the Ångstrom level.

Experimental Section

CT[6]. To a solution of **OH[6]** (0.300 g, 0.410 mmol) in methanol (100 mL), [bis(trifluoroacetoxy)iodo]benzene (0.530 g, 1.23 mmol) was added. Addition of [bis(trifluoroacetoxy)iodo]benzene immediately afforded precipitates. The mixture was stirred at 25°C for 30 min. The resulting precipitate was isolated by filtration (Yield: 45%). For the gas and vapor adsorption measurements, the sample was heated at 150°C for 12 h to complete remove methanol.

PC[6]. CT[6] was converted to porous carbon **PC[6]** by heating at 900°C for 2 h under an inert gas atmosphere.

Keywords: carbon · macrocyclic compounds · pillar[*n*]arene · porous materials · two dimensional sheets

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