Synthesis and characterization of a 2D covalent organic framework (COF) of hexagonal topology using boronate linkages

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Abstract. A covalent organic framework (COF) has been designed and synthesized successfully by a condensation reaction between hexahydroxytriphenylene hydrate and tetrahydroxydiborane. The characterisation studies reveal that it has good thermal stability and high crystallinity. This is a mesoporous material having a pore size of 2.8 nm and also having a B–B linkage with prospect of potential applications in future.

Keywords. Covalent organic framework; porosity; mesoporous; crystallinity.

1. Introduction

The field of porous covalent-organic frameworks (COFs)¹ has been developing rapidly due to their multi-chemical functionality. The salient features that make COFs one of the most attractive field now are predetermined and periodic diverse structures,² permanent high porosities with low density and high surface area,³ high chemical and thermal stabilities,⁴ and semiconducting properties.⁵ All these features enable COFs to play a major role in various applications like gas adsorption, optoelectronics, catalysis, gas separation, proton conductivity, chemical sensing, drug delivery, energy storage and chromatographic separations.⁶ 2D COFs constructed from π -conjugated systems with short inter-layer distances could exhibit electronic interactions between different sheets, and hence potentially become conducting materials.⁷ The intrinsic cavities in COFs bear unique advantage in selective binding and separation.⁸ These are the materials which mainly consist of light elements (B, C, N, O, and H).⁹ The concepts behind COFs are the design and synthesis of 2D or 3D crystalline organic extended porous structures in which the building blocks are linked by covalent bonds. Here, the various organic units are precisely integrated to create predesigned skeletons.¹⁰ Several linkages in

organic reactions have been used successfully in synthesizing COFs, namely imine, boronate ester, borazine, hydrazine, boroxine, borosilicate, triazine, squaraine, and azodioxide.¹¹ The chemical and physical properties of COFs can be easily tuned through a selection of building blocks and linkage motifs. The porous COFs can be classified into two sub-classes: crystalline and amorphous porous materials.¹² The crystalline porous materials are prepared by dynamic covalent controlled reactions, where a rapid equilibrium allows the coexistence of a variety of different species among which molecules can be selected with desired properties. So, it possesses reactions with reversible characteristics having the property of self-assembly, error correction and editing. But preparation of amorphous porous materials is done by kinetically-controlled covalent reactions, which form covalent bonds irreversibly. Because of this, unlike amorphous materials, crystalline porous materials form ordered structures.

Since Yaghi and co-workers reported the first 2D COF material in 2005,¹³ COFs have attracted increasing worldwide attention in several areas. In order to obtain predetermined COFs using building blocks and linkage motifs, the synthetic procedure plays an extremely vital role. Since COFs are prepared by dynamically-controlled covalent reactions, regulating the conditions of thermodynamic equilibrium during covalent bond formation is extremely essential in

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Scheme 1. The synthetic reaction of hexahydroxytriphenylene hydrate (HHTP) and tetrahydroxydiboron (THDB) to form HTCOF with a hexagonal mesoporous pore.

forming highly ordered covalent frameworks. Especially the reaction media (including solvent mixture) and conditions (temperature, pressure, and presence or absence of template) are significant. Yaghi and co-workers exploited solvothermal methods to get success in the synthesis of the first COF.¹³ Since then, different new types of synthetic procedures have been reported by various research groups. Amongst these, solvothermal, ionothermal, and microwave methods are most widely applied synthetic procedures for COF synthesis. Research is under progress to achieve room-temperature synthesis for COFs.¹⁴ Most of the COFs reported till now are synthesized by solvothermal method.

Herein, we report the synthesis of 2D hexagonal mesoporous COF (HTCOF) by employing a mixture of C_3 -symmetric 2,3,6,7,10,11-hexahydroxytriphenylene hydrate (HHTP) and C_2 -symmetric tetrahydroxydiboron (THDB) monomers in 2:3 stoichiometric ratio (Scheme 1). Both HHTP and THDB are planar molecules that display the capability to form ordered 2D porous periodic networks that are analogous to graphene material. This is the first COF ever reported having a B–B linkage with good crystalline peaks. It forms a mesoporous material having a pore size of 2.8 nm.

2. Experimental

2.1 Synthesis of HTCOF

The HTCOF was synthesized using solvothermal conditions by reacting 2,3,6,7,10,11-hexahydroxytriphenylene hydrate

and tetrahydroxydiboron monomers in a 1:1 (v/v) 1,4 dioxane and mesitylene mixture (Scheme 1). Tetrahydroxydiboron was purchased from Sigma-Aldrich Chemicals, and 2,3,6,7,10,11-hexahydroxytriphenylene hydrate was purchased from TCI chemicals. These two starting materials were used without further purification. Schlenk tube of 25 mL capacity was used for COF synthesis. For washing the product, acetone was used after drying it over molecular sieves. The monomers HHTP (169.6 mg, 0.52 mmol) and THDB (70.36 mg, 0.78 mmol) were added to a Schlenk tube which is fitted with a nitrogen balloon. Solvents 1,4 dioxane (5 mL) and mesitylene (5 mL) were added to it using a syringe. The mixture was then sonicated for 2 min. The reaction system was heated at 100 °C for seven days. HTCOF was obtained in 30% yield by vacuum filtration and washed with anhydrous acetone. A green crystalline powder that was insoluble in common organic solvents was obtained.

2.2 Powder X-ray diffraction (PXRD)

The experimental powder X-ray diffraction pattern of the synthesised COF was recorded on PANalytical Empyrean X-ray diffractometer with $\text{CuK}\alpha$ radiation (1.5406 Å). The bulk powder of each sample was placed in a silica sample holder and measured by a continuous scan with a step size of 0.013103°. Pawley refinement¹⁵ was performed using Materials Studio 6.1¹⁶ on the experimental PXRD pattern.

2.3 BET surface area and porosity measurement

Nitrogen sorption measurements were conducted at 77 K to evaluate the porosity characteristics of the prepared COF. Before sorption experiments, the COF sample was degassed at 100 °C for 24 h. Gas adsorption experiments were performed on a Quantachrome Autosorb equipment in 9 mm

w/o rod Cell. These isotherms were analyzed using ASiQwin software. Pore-size distribution profile was estimated using NLDFT method.¹⁷

2.4 Transmission electron microscopy (TEM) imaging and Tyndall effect

For TEM imaging and investigating the Tyndall effect, 1 mg of HTCOF was added in 1 mL of acetone and sonicated for 15 min. The sample was coated on the carbon-coated copper grid and dried at room temperature intended for TEM imaging. High-resolution TEM images were obtained in FEI Talos F200S TEM system with an accelerated voltage of 200 kV.

3. Results and Discussion

Even though many diboronic acid derivatives have been used in synthesizing COFs, tetrahydroxydiborane has been employed by us for the first time as a building block in COF synthesis. So, it was challenging to determine the appropriate conditions required for synthesizing the crystalline product. We have optimized the synthetic procedures by performing the reaction under different solvent conditions, apparatus, and methods. After trying in various solvent combinations and their ratios (Table S1 and Figure S1 in Supplementary Information), we obtained significantly improved yields and enhanced crystallinity in dioxane: mesitylene (1:1 v/v) solvent combination. A series of experiments was carried out before optimizing the final conditions of the performed reaction, *i.e.*, the duration of heating and the temperature (Table S1 and Figure S1). Finally, we obtained the synthetic method which gives the desired COF material with higher thermal stability and decent crystallinity.

Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA 4000 instrument under N₂ atmosphere at a heating rate of 10 °C/min with a temperature range of 30–900 °C (Figure 1). HTCOF displayed good thermal stability, as revealed by TGA analysis, which indicates that it maintained about 85% of its weight up to 300 °C and 70% up to 550 °C.

The powder X-ray diffraction (PXRD) analysis of the obtained product confirmed the crystallinity of the prepared COF. It showed intense peaks at 2-theta values of 7.9°, 15.4°, 16.4°, 20.7°, 26.8°, 28.1°, and 31.9° along with some other peaks of lower diffraction intensities (Figure 2), indicating long-range ordering. The powder pattern was indexed in the hexagonal crystal system with lattice parameters $a = 23.03$ Å, $b = 23.03$ Å, $c = 5.61$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$ with $R_p = 2.76\%$ and $R_{wp} = 3.74\%$ (Figure 2). In order to confirm that the phases observed from PXRD indeed corroborate with the target, we modelled the possible extended

Figure 1. TGA plot of HTCOF@ 10 °Cmin^{−1}.

Figure 2. Experimentally observed PXRD pattern (red), Pawley refined pattern (blue), their difference (black), and observed reflections (green line) of HTCOF.

structure that could be formed from the monomers using the obtained lattice parameters. To clarify the stacked configuration of the 2D sheets, two extreme possible stacking models, namely, eclipsed packing and staggered packing were modelled with *P1* space group.¹⁸ Given that planar 2D organic sheets were expected to form, layered crystal structures were modelled, in which a possibility of eclipsed stacking, where atoms of adjacent sheets lie directly over each other (Figure 3a) and in staggered arrangement three-connected vertices lie over the centre of the six-membered rings (Figure 3b). The obtained simulated PXRD pattern of the synthesized COF is shown in Figure 3(c and d) and compared with the experimental pattern. The simulated PXRD pattern shows good agreement with the experimental powder X-ray diffraction pattern. The higher angle simulated PXRD peaks ($2\theta = 10^\circ$ to 30°) of the staggered model are relatively more intense (Figure 3d) in comparison to the simulated PXRD peaks at higher angle for the eclipsed model (Figure 3c), which was in good agreement with the experimental PXRD patterns.¹⁹

Figure 3. (a) Eclipsed packing of HTCOF; (b) Staggered packing of HTCOF; (c) Simulated PXRD pattern of eclipsed HTCOF packing; and (d) Simulated PXRD pattern of staggered HTCOF packing.

Figure 4. (a) N_2 adsorption isotherm of HTCOF (black squares: adsorption; red circles: desorption). (b) Pore-size distribution profile estimated using NLDFT method (blue squares: differential pore volume; red circles: cumulative pore volume).

The N_2 gas adsorption measurement confirmed the porosity of HTCOF. Figure 4a shows the nitrogen sorption isotherm. The pore size distribution was evaluated using nonlocal density functional theory (Figure 4b), and the pore size was calculated to be 2.8 nm. This value is reliable with the theoretical pore size (2.7 nm) predicted from the modelling based on the crystal packing. The sorption curve was classified as type II isotherm, which indicates the formation of a monolayer. The Brunauer-Emmett-Teller (BET) surface area and total pore volume were estimated to be $60 \text{ m}^2/\text{g}$ and 0.132 cc/g , respectively. The hysteresis loop was observed in the whole range of HTCOF adsorption-

desorption isotherm which is reliable with the high pore size (mesoporous). We attribute the lower surface area to the presence of unreacted monomers and small branched polymers trapped within the material and interpenetration of the hexagonal network. The lower total pore volume of HTCOF is reliable with the possible staggered model. Table 1 shows the comparison between some of the reported boronate esters COFs and HTCOF in terms of pore size, surface area, and volume.

Transmission electron microscopy (TEM) images was used to investigate the morphology of the HTCOF after evaporating an acetone suspension ($c = 1.0 \text{ g/L}$) on a carbon-coated copper grid. The TEM images

Table 1. The pore size, surface area, and volume comparison between HT-COF and other reported COF materials.

Material	Reactants	Pore size (Å)	Surface area (m ² g ⁻¹)	Volume (cm ³ g ⁻¹)	Ref.
COF-18Å	Benzene-1,3,5-triboronic acid + 1,2,4,5-Tetrahydroxybenzene	18	1260	0.29	4
TP-COF	Hexahydroxytriphenylene + Pyrene-2,7-diboronic acid	32	868	0.791	7a
COF-1	Diboronic acid	15	711	0.32	13
COF-5	Hexahydroxytriphenylene+ Diboronic acid	27	1590	0.998	11a
COF-6	Hexahydroxytriphenylene + Benzenetriboronic acid	6.4	980	0.32	
COF-8	Hexahydroxytriphenylene + Benzenetris(4-phenylboronic acid)	19	1400	0.69	
COF-10	Hexahydroxytriphenylene + Biphenyldiboronic acid	34	2080	1.44	
CTC-COF	Diboronic acid + Cyclotricatechylene	23	1710	1.031	14a
HT-COF	Hexahydroxytriphenylene + Tetrahydroxydiboron	28	60	0.132	-

Figure 5. (a) TEM images of bulk HTCOF. (b) The Tyndall effect of a diluted HTCOF suspension using a laser pointer.

specified the presence of mesoscopic substances (Figure 5a). Upon introduction of a laser beam, the Tyndall scattering effect was observed for the diluted acetone suspension (Figure 5b).

4. Conclusions

In summary, we have synthesized a new 2D COF constructed by a reversible condensation reaction between hexahydroxytriphenylene hydrate and tetrahydroxydiborane. The COF obtained is highly crystalline with a pore size of 2.8 nm and also having a B–B linkage. Studies in future are directed towards increasing its surface area and porosity facilitating the exploration of enhanced gas uptake and storage.

Supplementary Information (SI)

Optimization of the reaction conditions and experimentally observed PXRD pattern for preparing the HTCOF are included. Supplementary Information is available at www.ias.ac.in/chemsci.

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