Synthesis of Vinylene-Linked Covalent Organic Frameworks by Monomer-Self-Catalyzed Activation of Knoevenagel Condensation

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ABSTRACT: Reticular chemistry on the basis of thermodynamically controlled linking modes and numerous organic building blocks has constituted versatile crystalline frameworks in molecular-level precision. However, vinylene-linked organic frameworks (COFs) are still quite far from flexible tailoring either in their structures or topologies, due to the lack of monomers with sufficient activities. Herein, we established a strategy to synthesize vinylene-linked COFs via Knoevenagel condensation of a tetratopic monomer 2,2',6,6'-tetramethyl-4,4'-bipyridine (TMBP) with linear aromatic dialdehydes in a mixed solvent of benzoic anhydride and benzoic acid. Mechanism investigation suggested that the condensation was promoted by a pyridine-self-catalyzed benzylation upon the cleavage of benzoic anhydride solvent molecules. The layered structures of the resultant COFs were highly crystallized into orthorhombic lattice with vertically aligned AA stacking mode, delivering high surface areas up to 1560 m² g⁻¹. The π-extended conjugated skeletons comprising para-bipyridyl units and vinylene linkages endow these COFs with substantial semiconducting properties, releasing visible light-stimulated catalytic activity in water-splitting hydrogen evolution with a rate as high as 3300 μmol g⁻¹ h⁻¹.

INTRODUCTION

Covalent organic frameworks (COFs) represent an emerged class of high crystalline porous polymers with well-defined periodic structures, which not only allows one to rationally design and tailor their chemical structures or topologies, but also readily manipulate them in various applications on the basis of establishing the essential structure-property relationships and understanding the related mechanism. Among them, vinylene-linked organic frameworks (COFs) feature prominent stability and π-electron communication, likely helpful for expanding the potential applications of COFs, in particular, in the field of semiconductor. Thermodynamically controlled Knoevenagel condensation is one of the most powerful tools in the formation of carbon-carbon double bond linkage. Unlike those traditional dynamic covalent chemistry, such condensation involves the generation of active intermediates, such as, carbon anions, which is crucial for efficiently boosting chain growth and correcting defect through self-healing processes for a COF. Typically, an available monomer bearing aryl α-carbon atoms, has to be enough electron-deficient for enhancing the α-proton acidity and stabilizing the reactive intermediate, commonly achieved by the introduction of multiple electron-withdrawing moieties, such as cyano group, pyridyl nitrogen. However, these modifications normally means a tedious preparation and the utilization of toxic reagent (e.g. NaCN or CuCN), meanwhile, significantly constrains the accessible reaction sites of a monomer, severely limiting its linking modes. Correspondingly, on the basis of very few monomers, vinylene-linked COFs with hexagonal crystal system occupied the major ratio, and several single-pore orthorhombic skeletons were originating from the ditopic monomer 1,4-phenylenediacetonitrile. While, a monomer with more α-carbon atoms (≥ 4) suitable for Knoevenagel condensation could not be found so far.

Pyridyl nitrogen-containing molecules are widely used in catalysis, supramolecular chemistry, and organic semiconducting materials, associated with their intrinsic Lewis basicity, substantial physical properties, and self-assembling behaviors. Knoevenagel reaction holds some merits in the preparation of vinylene-linked pyridine-based small molecules or linear conjugated polymers using methyl-substituted pyridine, due to low-cost, environmentally friendly reagents, less unidentified reactive intermediates, and only trans-alkene formation. Unfortunately, the mechanism of such traditional reaction seems never to be investigated.

Typically, functionalization at nitrogen to generate pyridinium cations, makes pyridine ring favorable for electrophilic and/or nucleophilic substitution. Very recently, we reported a Knoevenagel condensation at the three methyl carbons in one pyridine promoted upon quaternization, leading to the formation of several pyridinium-cored vinylene-linked COFs with high crystallinities and quite large surface areas, suggesting an excellent efficiency in the activation of a multi-topic monomer. N-acyl pyridinium has been found as a highly active intermediate formed in the process of pyridine-catalyzed hydrolysis of acid anhydride, or as one type of efficient acylation reagent from the treatment of pyridine with an acyl donor. With these reasons in our mind, our effort is to explore a much lower-cost, less-toxic and concise method to construct vinylene-linked COFs by virtue of methyl substituted pyridine-based monomer, and attempt to establish the optimized reaction conditions and corresponding thermodynamically controlled mechanism.
In this work, we present the preparation of two vinylene-linked COFs with orthorhombic reticular topology by condensation of \( D_2 \)-symmetric 2,2′,6,6′-tetratopic monomer with the ditopic linear aromatic dialdehydes in benzoic anhydride and benzoic acid. The reaction mechanism manifested that the pyridine units in monomer TMBP enable catalyzing their benzylation via the cleavage of benzoic anhydride solvent molecules, thus helpfully activating the aryl α-carbon atoms for Knoevenagel reaction. The resulting COFs with high crystallinities and surface areas, were considerably characterized. Their π-extended conjugated skeletons endow them with excellent semiconducting properties and corresponding application, such as, visible light catalysis of water splitting hydrogen evolution.

**RESULTS AND DISCUSSION**

Traditionally, in order to activate the methyl groups of pyridine ring for Knoevenagel condensation, incorporation of the electron-withdrawing substituents or quaternization at pyridine ring is necessary. Here, our attempt is to take use of the Lewis basicity of pyridine moiety for promoting the Knoevenagel reaction of a newly designed pyridine-based monomer 2,2′,6,6′-tetratopic monomer (TMBP), bearing four pyridinium terminal groups. Some previous works reported that methyl-substituted pyridine derivatives were facile to conduct Knoevenagel reaction with aromatic aldehydes in a mixture solvent of acetic anhydride and acetic acid at ca. 135 °C with moderate yield (< 60%)\(^{23}\). Considering the relatively weak reversibility of such carbon-carbon double bond formation reaction, we decided to raise the reaction temperature in a mixed solvent of benzoic anhydride and benzoic acid for the preparation of model compound and COFs\(^{26}\).

The key monomer TMBP was prepared via a facile one-step Yamamoto coupling in high yield\(^{27}\). The Knoevenagel condensation between TMBP and benzaldehyde was performed in a mixture of benzoic acid and benzoic anhydride under 180 °C, affording the model molecule 2,2′,6,6′-tetrastryl-4,4′-bipyridine in a yield of 85% (synthesis detailed in the Supporting Information). The structures of these new compounds were unambiguously characterized by NMR, MALDI-TOF MS and single crystal X-ray diffraction analyses. The packing diagram of the model molecule showed a π-dimer arrangement of the neighbouring molecules with a distance of 3.43 Å, manifesting the distinct π-π interaction. By using the condition of the model reaction, TMBP was copolymerized with 1,4-diformylbenzene (DFB) or 4,4′-biphenyldialdehyde (BPDA), respectively, to synthesize COFs. In a typical protocol, TMBP, DFB, benzoic anhydride and benzoic acid in a molar ratio of 1:2:2:0.2 was sealed in glass ampoule and heated at 180 °C for 3 days (Scheme 1), leading to the generation of large amount of red-brown precipitates. After washed with base solution and organic solvents (methanol, THF and DCM), the resultant crude product was converted to yellow powder in 90 % isolated yield (term COF-DFB). Similarly, another COF (COF-BPDA) were derived from a larger aldehyde monomer (BPDA) as yellow powders in 94 % yield.

It is well-known that, acylation or alkylation at the pyridyl nitrogen always leads to nucleophilic attack on the pyridine ring due to the strengthened electron deficiency\(^{18, 28}\). Alkylation at the pyridyl nitrogen has been verified to efficiently promote a Knoevenagel condensation at the pyridylmethyl carbon atoms\(^{22, 29}\). Considering that pyridine can act as Lewis base for catalyzing hydrolysis of acetic anhydride through the formation of the \( \text{N}^{+} \) acetyl pyridinium ion intermediate\(^{25}\), under our circumstance, the proposed mechanism could begin with the benzylation of methylpyridine moieties by benzoic anhydride to give the benzyol pyridinium salt. The electron-deficient character of pyridine ring was significantly increased by the benzylation, thus favorable for the enhancement of C-H acidity on the pyridyl methyl. Meanwhile, the generated conjugated base benzoate also could capture the protons at the methyl groups, leading to the formation of enamine intermediate. Subsequently, electrophilic attack of the protonated aldehyde in the presence of benzoic acid, to the above
enamine intermediates, followed by the elimination of molecular water, affords the carbon-carbon double bond linkages. For further illustration, several controlled experiments were conducted. First, the formation of the key intermediate benzyl pyridinium moiety in a reaction of benzoic anhydride and trimethylpyridine was confirmed by GC-MS analysis, somehow, supporting the self-catalyzed cleavage of benzoic anhydride by the pyridine-based monomer during the preparation of COFs (Figure S1, detailed see the Supporting Information). Additionally, the aforementioned model molecule 2,2',6,6'-tetrastyryl-4,4'-bipyridine could be efficiently achieved by the reaction of TMP and benzaldehyde in a mixture of benzoic chloride as acylation reagent and sodium benzoate as conjugated base, indicative of the acylation-activated Knoevenagel condensation. Notably, similar to those previous reports, such intermediate benzyl pyridinium is quite unstable, which readily recovered to pyridine even in the presence of trace water.

**Figure 1.** PXRD patterns of (a) COF-DFB and (b) COF-BPDA. Comparison between the experimental profiles (red cross), Pawley refined profiles (black line), the simulated patterns for eclipsed (AA) stacking mode (blue line), the Bragg positions (green bar) and the refinement differences (violet line). Inset: Corresponding refined 2D crystal structural models of COF-DFB and COF-BPDA assuming the eclipsed (AA) stacking mode.

The crystallinity of COF-DFB was examined by powder X-ray diffraction (PXRD) measurements. Theoretically, the condensation of a \( D_{2h} \) monomer and a \( C_2 \) monomer can give rise to two possible 2D COF structures, that is, an orthorhombic system that bears only a single-pore framework and a hexagonal system that possesses two different kinds of pores with Kagome lattice. Indexing of the PXRD pattern of COF-DFB identified the space group Cmmm (No. 65), indicating an orthorhombic lattice. The diffraction peaks at 5.81°, 11.67° and 25.90° could be assigned to (110), (220) and (001) facets, respectively (Figure 1a). The experimental PXRD pattern of COF-DFB was in accordance with simulated pattern of an orthorhombic lattice with AA stacking mode, whereas the staggered AB stacking model and Kagome lattices exhibit significant difference from the experimental PXRD data (Figures S21 and S22). The first dominant diffraction peak at 5.81° corresponds to the d-spacing of 1.52 nm, which was in good agreement with the calculated diameter of the rhombic pore (1.4 nm, Figure S18). Furthermore, the profile of Pawley refinement matched well with the observed signals as evident by the residual \( R_w \) and \( R_p \) values converged to 3.79 % and 2.94 %, respectively, affording unit cell parameters of \( a = 25.872 \text{ Å}, \ b = 18.625 \text{ Å}, \ c = 3.439 \text{ Å}, \alpha = \beta = \gamma = 90^\circ \).

Similarly, COF-BPDA exhibits diffraction peaks at 4.59°, 6.45°, 9.15°, 13.76°, and 26.21°, which can be assigned to the (110), (200), (220), (330) and (001) facets, respectively (Figure 1b). It can be found that the simulated orthorhombic lattice with AA stacking mode well reproduced the experimentally observed PXRD pattern in terms of peak positions and relative intensities. The unit cell parameters were refined by the Pawley method using PXRD data (\( a = b = 27.274 \text{ Å}, \ c = 3.398 \text{ Å}, \alpha = \beta = \gamma = 90^\circ \)) with residual factors of \( R_w = 8.74 \text{ %} \) and \( R_p = 6.40 \text{ %} \).

**Figure 2.** (a) FT-IR spectra of model molecule, COF-DFB and corresponding monomers. (b) \(^{13}\text{C}\) NMR spectra of COF-DFB, COF-BPDA and model molecule. (c) Raman spectra of COF-DFB and COF-BPDA. (d) Nitrogen sorption isotherms of COF-DFB and COF-BPDA. Inset: Pore size distribution calculated from quenched solid density functional theory.
CONCLUSIONS

As a proof of concept, we studied the visible light photocatalytic H₂ evolution activities of COF-DFB and COF-BPDA from water reduction. Both COF samples can be easily dispersed in water, which is related to their pyridine-rich backbones that strongly interacted with water. The photocatalysis experiments were performed by dispersing 20.0 mg of COF powder into 0.1 M aqueous ascorbic acid solution, in which ascorbic acid was applied as a sacrificial electron donor, and 3 wt% platinum was in situ photo-deposited on the COF. Upon visible light illumination, COF-BPDA showed an average hydrogen evolution rate (HER) of 3229.01 μmol h⁻¹ g⁻¹, nearly 1.54 times faster than that of COF-DFB (2099.60 μmol h⁻¹ g⁻¹) (Figure 4d). This indicated that the photocatalytic H₂ generation performance of COF-DFB and COF-BPDA were mainly influenced by their intrinsic semiconducting properties. COF-BPDA with longer conjugation length and narrower band gap delivered higher activity as compared to COF-DFB.
In conclusion, we have established an efficient synthetic strategy that can combine a $D_2h$ symmetrical building block $2,2',6,6'$-tetramethyl-4,4'-bipyridine with $C_2$ symmetrical aromatic dialdehyde linkers to construct vinylene-linked COFs through Knoevenagel condensation in a mixed solvent of benzoic anhydride/benzoic acid. The possible reaction mechanism involves the self-catalyzed benzoylation of the used pyridine-based monomer, which subsequently promoted the Knoevenagel condensation at the pyridymethyl carbon atoms of this monomer. The as-synthesized COFs were highly crystallized in orrhorhombic lattices, releasing relatively large surface areas. The fully π-conjugated structures give rise to abundant semiconducting properties of the COFs, allowing for efficiently visible light-catalyzed hydrogen evolution from water reduction. This strategy paves a low-cost, environmentally friendly pathway to enlarge the regimes of vinylene-linked COFs with complex geometric and topological structures, as well as intriguing properties.

EXPERIMENTAL SECTION
All experimental procedures are provided in the Supporting Information.

ASSOCIATED CONTENT
Supporting Information.
The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org. Detailed synthetic procedures, characterization of materials and photocatalytic experiments.

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Notes
The authors declare no competing financial interest.

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REFERENCES


24. Yanagi, M.; Imayoshi, A.; Ueda, Y.; Furuta, T.; Kawabata, T., Carboxylate Anions Accelerate Pyrrolidinopyridine (Ppy)-Catalyzed...


