Porous Crystalline Olefin-Linked Covalent Organic Frameworks

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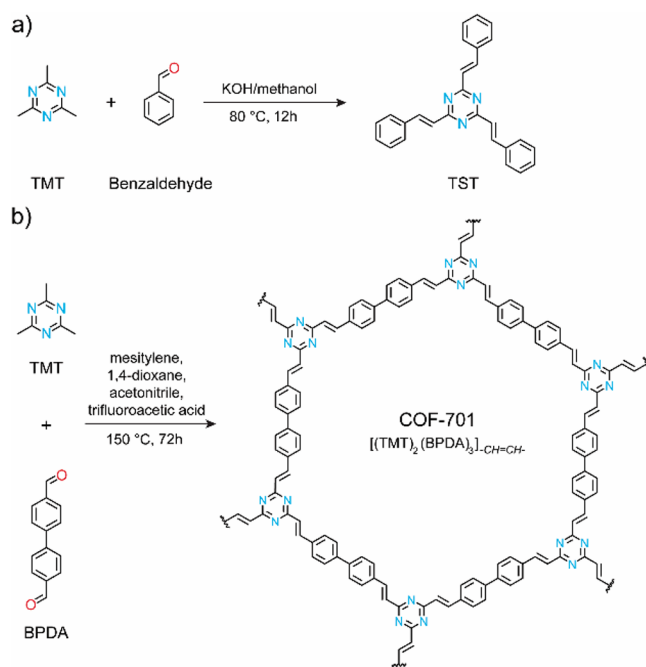
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S *Supporting Information*

ABSTRACT: The first unsubstituted olefin-linked covalent organic framework, termed COF-701, was made by linking 2,4,6-trimethyl-1,3,5-triazine (TMT) and 4,4′-biphenyldicarbaldehyde (BPDA) through Aldol condensation. Formation of the unsubstituted olefin (-CH=CH-) linkage upon reticulation is confirmed by Fourier transform infrared (FT-IR) spectroscopy and solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy of the framework and of its ^{13}C-isotope-labeled analogue. COF-701 is found to be porous (1715 m^2 g^{-1}) and to retain its composition and crystallinity under both strongly acidic and basic conditions. The high chemical robustness is attributed to the unsubstituted olefin linkages. Immobilization of the strong Lewis acid $BF_3 \cdot OEt_2$ in the pores of the structure yields $BF_3 \subset COF-701$. In the material, the catalytic activity of the guest is retained, as evidenced in a benchmark Diels−Alder reaction.

Scheme 1. (a) Aldol Condensation between TMT and Benzaldehyde To Yield Model Compound TST and (b) Synthesis of COF-701 by Aldol Condensation between TMT and BPDA

Covalent organic frameworks (COFs) expand organic chemistry from discrete molecules into the realm of crystalline 2D and 3D extended structures.[1−4] The nature of the covalent linkages joining the molecular building blocks of COFs dictates the crystallinity and the physical and chemical properties of the resulting material.[5] Thus far, linkages ranging from reversible boroxine,[1] imine,[6] or hydrazone[7] to less reversible triazine,[8] phenazine,[9] oxazole,[10,11] or dioxin[12] have been reported. In this context, chemically robust structures that maintain high crystallinity are of particular interest. One strategy to address this is to construct frameworks using C=C bond formation, which is much less reversible and promises high stability of the COF toward nucleophilic attack. To date, the only example for such COFs involves substituted acrylonitrile [-CH=C(CN)-] based on the Knoevenagel condensation[13] between aryl acetonitriles and aromatic aldehydes.[14−18] However, the strong electron-withdrawing substitution of nitriles appended to the C=C bond makes the linkage reversible, and therefore the stability of the resulting COFs is compromised. Here, we report a new strategy of constructing unsubstituted olefin (-CH=CH-)-linked COFs through Brønsted acid-catalyzed Aldol condensation between the activated methyl groups of 1,3,5-triazine and aryl aldehydes (Scheme 1a).[19] Specifically, the con-

densation between 2,4,6-trimethyl-1,3,5-triazine (TMT) and 4,4′-biphenyldicarbaldehyde (BPDA) yields a layered **hcb** topology framework, termed COF-701 (Scheme 1b). The olefin linkage of COF-701 was unambiguously confirmed by Fourier transform infrared (FT-IR) spectroscopy and solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy on both unlabeled and ^{13}C-isotope-labeled samples. The unsubstituted olefin linkage endows COF-701 with exceptionally high stability toward Brønsted acids and bases, organolithium reagents, and Lewis acids. To highlight the stability of this linkage, we immobilized $BF_3 \cdot OEt_2$, a strong Lewis acid, within the pores of COF-701. A benchmark Diels−Alder reaction[20] was used to show that COF-701 retains its crystallinity and chemical composition in the presence of the
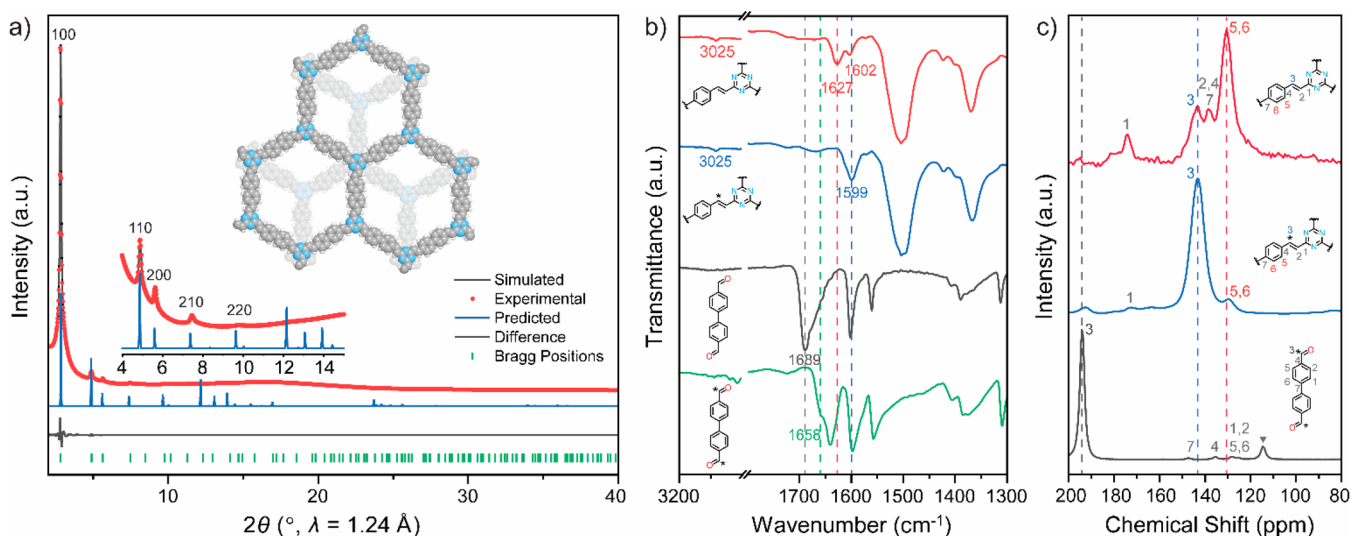
Figure 1. WAXS, FT-IR, and solid-state ^{13}C CP-MAS NMR data of COF-701. (a) Pawley refinement of COF-701 (staggered, AB) against the experimental WAXS pattern. Color code of the structure model: H, white; C, gray; N, blue. (b) FT-IR spectra of unlabeled (red) and labeled (blue) COF-701, as well as unlabeled (black) and labeled BPDA (green). Transmittance spectrum between 2900 and 1800 cm^{-1} was omitted for clarity. * indicates ^{13}C-labeled atom. (c) Solid-state ^{13}C CP-MAS NMR of unlabeled (red) and labeled (blue) COF-701, and ^{13}C-labeled BPDA (black) for comparison. * indicates ^{13}C-labeled atom. ▼ marks spinning sideband.

BF$_3$ species and that the immobilized Lewis acid in turn retains its catalytic activity.

The molecular reaction of the Aldol condensation between TMT and aryl aldehydes has been employed in the synthesis of a series of star-shaped fluorophores (e.g., 2,4,6-tri((E)-styryl)-1,3,5-triazine, TST, Scheme 1a).[21] The reaction is typically performed in a methanolic KOH solution under reflux. However, direct application of these reaction conditions to the synthesis of COFs results in amorphous materials, indicating insufficient reversibility or the formation of side products. By extensive screening of reaction conditions, COF-701 was successfully crystallized through the condensation between TMT and BPDA under solvothermal conditions in a mixture of mesitylene, 1,4-dioxane, and acetonitrile, with trifluoroacetic acid as a catalyst (Scheme 1b, Supporting Information (SI) Section S2). It was also confirmed that these conditions yield the molecular compound TST (Scheme 1a, SI Section S2).

In the first step, the composition of COF-701, especially the presence and complete formation of olefin linkages, were confirmed (Figure 1). ^{13}C-labeled COF-701 was synthesized using ^{13}C carbonyl-labeled BPDA to complement spectroscopic studies. Labeled and unlabeled COF-701 were subsequently characterized by FT-IR and solid-state ^{13}C CP-MAS NMR spectroscopy. In the FT-IR spectrum, unlabeled COF-701 displays a characteristic absorbance at 1627 cm^{-1}, which was not found in the TMT or BPDA starting materials (Figure S2). Consequently, it was assigned to the $^{12}C\!=\!^{12}C$ stretch of the formed olefin linkage. In addition, the characteristic absorbance at 1689 cm^{-1} of the $^{12}C\!=\!^{16}O$ stretch is extensively attenuated in COF-701. Comparison between IR spectra of labeled and unlabeled samples (Figure 1b, full spectrum in Figure S3) was based on treating the vibration normal modes as diatomic harmonic oscillators (SI Section S3). The experimental data was found to be in good agreement with predicted values based on this assumption; the $^{12}C\!=\!^{13}C$ stretch of the ^{13}C-labeled COF appears at 1599 cm^{-1} (expected 1595 cm^{-1}), as opposed to absorption at 1627 cm^{-1}

for the unlabeled material. Similarly, the $^{12}C\!=\!^{16}O$ stretch in unlabeled BPDA at 1689 cm^{-1} was shifted to 1658 cm^{-1} (expected 1651 cm^{-1}).

Further support for the presence of the olefin linkage was obtained by solid-state ^{13}C CP-MAS NMR analysis of labeled and unlabeled COF-701 and comparison to labeled BPDA (Figure 1c, SI Section S4). In the unlabeled COF-701, the unambiguous assignment of the alkene carbon peaks proved difficult due to overlapped signals of aromatic and olefinic carbons of the backbone of the structure. The peak of the labeled BPDA aldehyde starting material is observed around 192 ppm. In labeled COF-701, the labeled peak around 192 ppm is largely attenuated, and a new prominent peak at 144 ppm is observed, which is assigned to the newly formed alkene carbons.

The crystallinity of COF-701 was confirmed by wide-angle X-ray scattering (WAXS, Figure 1a). Based on the planar geometry of the model compound TST (Scheme 1a) and its analogs in single-crystal structures, structural models of COF-701 were constructed in an **hcb** topology.[22,23] Several interlayer stacking modes were modeled and compared to the experimental WAXS pattern, among which the model with a staggered (AB) stacking mode in space group $P6_3/m$ provided the best fit (SI Section S5). Full profile Pawley refinement of the model against the experimental pattern yielded a unit cell of $a = b = 29.1$ Å, $c = 6.9$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$ with good agreement factors ($R_{wp} = 2.92\%$, $R_p = 1.73\%$). In the structure, 1.1 nm wide rhombic channels run along the crystallographic c-axis (Figure 1a inset).

The porosity and surface area of COF-701 were evaluated after removal of solvent molecules from the pores of the structure (SI Section S2). In thermogravimetric analysis (TGA) under anaerobic (N$_2$) conditions, no significant weight loss was recorded up to 400 °C (Figure S16). The N$_2$ sorption isotherm of COF-701 was measured at 77 K (Figure S9), giving a Langmuir surface area of 1715 m^2 g^{-1}, and a Brunauer−Emmett−Teller (BET) area of 1366 m^2 g^{-1}, respectively. Fitting of the isotherm using a quenched solid

density functional theory (QSDFT) slit/cylindrical pore model[24] resulted in a pore size distribution with a maximum centered around 1.14 nm, close to the expected 1.1 nm based on the van der Waals surface of the structure model (Figure S10).

To evaluate the chemical stability of the olefin linked COF, the material was exposed to a series of Brønsted acids and bases, organolithium reagents, and Lewis acids. Specifically, activated COF-701 was suspended in 12.1 mol L^{-1} aqueous HCl (35 wt%), saturated aqueous KOH (55 wt%), and saturated methanolic KOH (35 wt%) at room temperature for 24 h. The structural integrity of the treated COF-701 powders was examined by WAXS and FT-IR (Figure 2a,b, SI Section S10). COF-701 was found to retain its crystallinity and chemical composition under all aforementioned conditions. This is evidenced by the fact that both the WAXS patterns and FT-IR spectra of all treated samples retained largely unaltered. It must be noted that the stability of COFs to aqueous NaOH or KOH solutions can also be due to the hydrophobic nature of the material and the concomitant poor contact of aqueous solutions with the COF particles. As such, COF-701 was exposed to saturated solutions of KOH in methanol (Figure 2a,b), where the material was well suspended, and again retained its crystallinity and chemical composition.

To further probe the stability of COF-701, the material was treated with different organolithium reagents (Figure 2c,d, SI Section S10). After exposure of COF-701 to 1.0 mol L^{-1} *n*-BuLi in THF/hexanes and 0.8 mol L^{-1} MeLi in THF/Et$_2$O at −78 °C for 24 h, the reagents were quenched, and the materials isolated. WAXS and FT-IR measurements demonstrated that COF-701 remained intact. The materials were further exposed to solutions containing 1 equiv of tetramethylethylenediamine (TMEDA) to dissociate the tetrameric species they form in ethereal solvents. Upon treatment with MeLi/TMEDA in THF/Et$_2$O, COF-701 remains intact, and only a minor loss of crystallinity is observed with samples exposed to *n*-BuLi/TMEDA in THF/hexanes. Notably, the FT-IR spectrum of the treated material shows that the chemical composition remains unaltered. The fact that even under such harsh conditions COF-701 remains intact suggests a pronounced stability of the structure to strong acids and bases, which we attribute to the low polarity of the C=C bonds of its olefin linkages.

To make use of the pronounced chemical stability of olefin-linked COF-701, BF$_3$·OEt$_2$ was immobilized within the material as a strategy toward heterogenizing strong Lewis acid catalysts. BF$_3$·OEt$_2$ was loaded into the framework by mixing with the COF powder, followed by drying under dynamic vacuum. The resultant material, termed BF$_3$⊂COF-701, displays a significant color change which persists after vacuum drying, indicative of interactions of the BF$_3$ species with the framework. The WAXS pattern of the material displays a significant broadening of the (220) and (221) diffractions, likely due to the presence of disordered species in the pores of the framework. This is supported by the fact that upon removal of the guests, the crystallinity of the parent framework can be recovered (Figure 3a). To prove that not only the COF remains intact but that the BF$_3$ species also retain their catalytic activity, BF$_3$⊂COF-701 was tested in a benchmark Lewis acid catalyzed Diels−Alder cycloaddition reaction.[18] The acceleration over the non-catalyzed reaction was quantified by recording the increase in yield at a fixed reaction time (8 h). It was found that the immobilized BF$_3$ species remained active and retained 86% of the activity of free BF$_3$·OEt$_2$ (Table 1). After isolation from the reaction media and removal of the guest elements, confirmed by inductively coupled plasma−optical emission spectroscopy (ICP-OES) and SEM energy-dispersive X-ray spectroscopy (EDS), the solid residue displayed a WAXS pattern and FT-IR spectrum identical to that of parent COF-701 (SI Section S11 and Figure 3b). These experiments prove that BF$_3$ species can be immobilized in COF-701 and retain their Lewis acidity.

In conclusion, we developed a new strategy to synthesize porous, crystalline olefin-linked COFs, exemplified by the layered **hcb** topology COF-701. The framework exhibits high compositional purity, porosity, and crystallinity as confirmed by spectroscopic, sorption, and scattering techniques. Due to the chemical nature of the olefin linkages, COF-701 was found to retain its crystallinity and chemical composition in the presence of concentrated Brønsted acids and bases, organo-lithium reagents, and Lewis acids. The utility of this
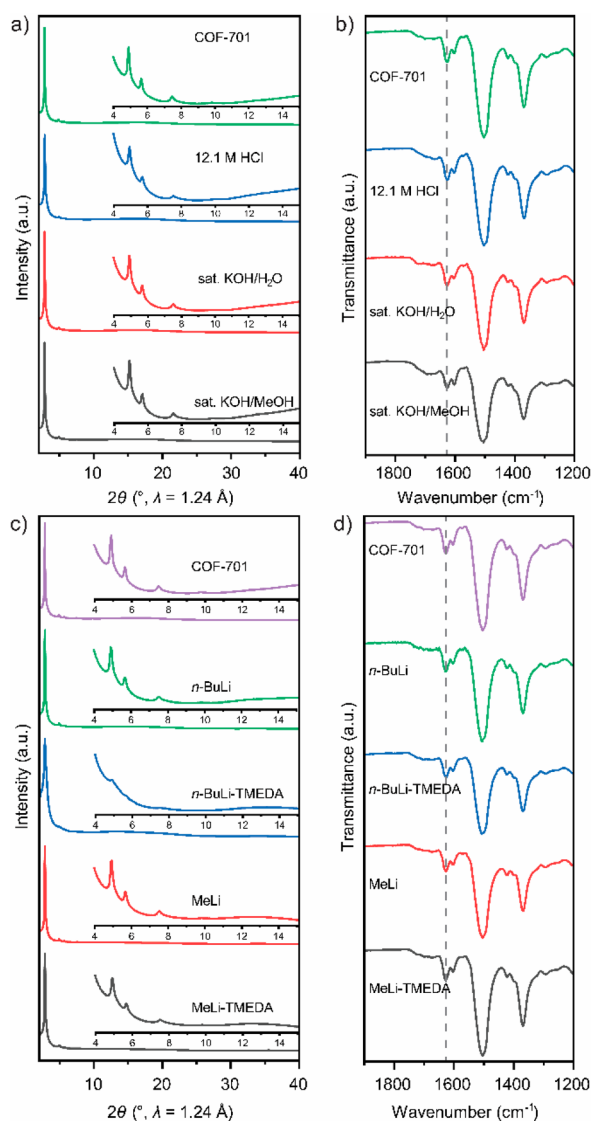

Figure 2. Chemical stability test of COF-701 with Brønsted acid and base (a, b) and organolithium reagents (c, d). WAXS patterns of treated materials with zoomed insets (a, c) and FT-IR spectra (b, d) (1900−1200 cm^{-1}) illustrate the retention of crystallinity and chemical composition of COF-701.
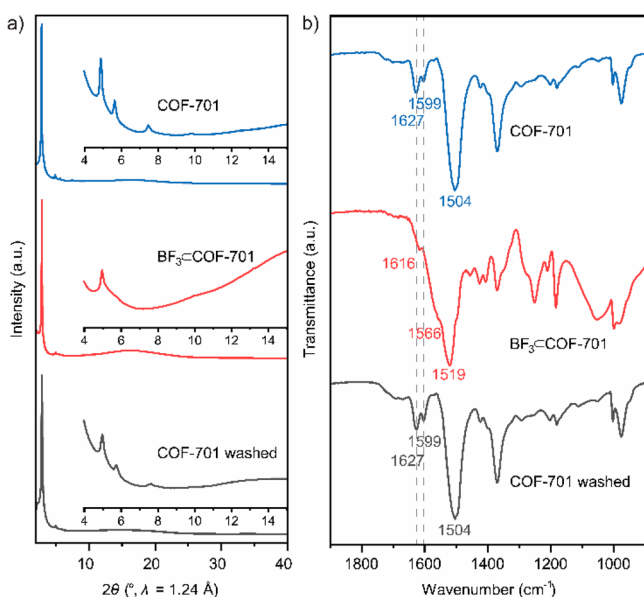
Figure 3. Chemical stability test of COF-701 against $BF_3 \cdot OEt_2$ characterized by WAXS (a) and FT-IR (b).

Table 1. Catalytic Activity of $BF_3 \subset COF$-701 in a Diels−Alder Reaction

catalytic species	time (h)	yield (%)
$BF_3 \cdot OEt_2$	8	99
$BF_3 \subset COF$-701	8	88
non-catalyzed	8	19

pronounced chemical stability was exploited for the immobilization of a strong Lewis acid catalyst within the pores of the material. The activity of the COF catalyst was confirmed by a benchmark Lewis acid-catalyzed Diels−Alder reaction. We anticipate that olefin-linked COFs, as exemplified by COF-701, will serve as a robust, functionalizable platform for a broad array of chemical transformations.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02848.

General experimental methods, supplementary spectra, and analysis details (PDF)

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Notes

The authors declare no competing financial interest.

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