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Covalent Organic Frameworks | Hot Paper

A Porous Crystalline Nitrone-Linked Covalent Organic Framework**

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Abstract: Herein, we report the synthesis of a nitrone-linked covalent organic framework, COF-115, by combining *N*, *N′*, *N′*, *N′′′*-(ethene-1, 1, 2, 2-tetrayltetrakis(benzene-4, 1-diyl))tetrakis(hydroxylamine) and terephthaladehyde via a polycondensation reaction. The formation of the nitrone functionality was confirmed by solid-state ^{13}C multi cross-polarization magic angle spinning NMR spectroscopy of the ^{13}C-isotope-labeled COF-115 and Fourier-transform infrared spectroscopy. The permanent porosity of COF-115 was evaluated through low-pressure N_2, CO_2, and H_2 sorption experiments. Water vapor and carbon dioxide sorption analysis of COF-115 and the isoreticular imine-linked COF indicated a superior potential of *N*-oxide-based porous materials for atmospheric water harvesting and CO_2 capture applications. Density functional theory calculations provided valuable insights into the difference between the adsorption properties of these COFs. Lastly, photoinduced rearrangement of COF-115 to the associated amide-linked material was successfully demonstrated.

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Development of new linkages to broaden the scope of covalent organic frameworks (COFs) has been one of the major drivers of the research field.[1,2] The diversity of linkage functionalities plays a critical role in tuning the material properties including its chemical stability,[3] adsorption behavior,[4] and catalytic activity.[5] Despite the ubiquitous usage of the imine linkage in various studies, its oxidized counterpart, the nitrone functionality, remains elusive as a linkage in COFs.[2] Nitrone compounds, featuring 1,3-dipolar structures, are versatile synthetic intermediates that can undergo nucleophilic additions, cycloaddition reactions, and photochemical rearrangements. Additionally, nitrones can serve as spin traps to detect short-lived radicals and their therapeutic potential against oxidative stress has been actively studied.[6] Thus, synthesis of porous, crystalline nitrone-linked frameworks will provide an invaluable opportunity to expand the linkage chemistry of COFs potentially diversifying their properties and applications.

Although being widely utilized in side chains in polymer chemistry, the nitrone functionality has largely been unexplored to constitute backbones of polymers.[7] This can partially be attributed to the difficulty of synthesizing multidentate hydroxylamine monomers.[8] Herein, we found an easy synthetic route (Supporting Information, Section S2) to access *N*, *N′*, *N′*, *N′′′*-(ethene-1, 1, 2, 2-tetrayltetrakis(benzene-4, 1-diyl))tetrakis(hydroxylamine) (**1**) and to reticulate it with terephthaladehyde (**2**) via a polycondensation reaction leading to COF-115 (Scheme 1). Previous studies showing reversibility of the condensation reaction between aromatic hydroxylamines and aldehydes[9] were encouraging that a successful framework crystallization is feasible. However, due to thermal sensitivity of the nitrone functionality,[7a] we expected that the typical conditions for the crystallization of imine-linked COFs (120 °C, 3 days) would be unsuitable for COFs bearing nitrone linkages. After comprehensive screening of the reaction conditions, COF-115 was synthesized in a 1,4-dioxane/mesitylene mixture at room temperature for 6 days using an aqueous solution of acetic acid as a catalyst. Furthermore, the use of aniline as a modulator was essential for high crystallinity of the target COF. The material was found to be sensitive to moisture in the air (Supporting Information, Figure S1d), therefore anhydrous 1,4-dioxane and acetone were used for the washing procedure to remove any impurities within the COF pores. After supercritical CO_2 drying and activation, COF-115 had to be stored under inert atmosphere.

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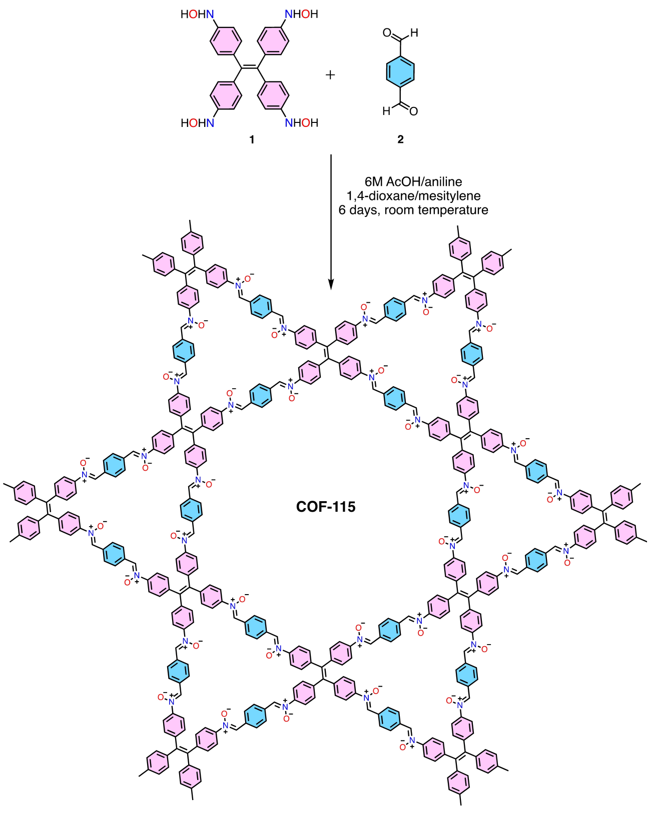

Scheme 1. Synthesis of the nitrone-linked COF-115 by connecting *N*, *N*′, *N*′, *N*′′′- (ethene- 1, 1, 2, 2- tetrayltetrakis(benzene-4,1-diyl))-tetrakis(hydroxylamine) (**1**) and terephthaladehyde (**2**) via a polycondensation reaction.

The structure of COF-115 was evaluated by powder X-ray diffraction (PXRD) analysis (Figure 1a). The framework was modeled in the *P*6 space group (No. 168), with the layers assuming the **kgm** topology stacked in an eclipsed fashion. Three different linker orientations were analyzed by conducting periodic DFT calculations (Supporting Information, Section S7.1). Using the most stable optimized structural model (COF-115-**3**), Pawley refinement was performed against the experimental pattern to provide the unit cell parameters (a=38.2 Å, and c=5.3 Å) with reasonable agreement factors (R_{wp}=3.43 %, R_p=2.66 %).

The presence of the nitrone functionality in the framework was first assessed by Fourier-transform infrared (FT-IR) spectroscopy (Figure 1b). The prominent peak at 1075 cm^{-1}, which is absent in the FT-IR spectrum of the isoreticular imine-linked COF that was synthesized by using a previously published procedure,[3a,10] was assigned to the N–O stretch.[11] Based on isotope labeling analyses of COF-115 and the model compound **3** (Supporting Information, Figure S2), the stretches at 1553 and 1597 cm^{-1} were attributed to the vibrations of the C=N and aromatic C=C bonds, respectively. The C=N bond stretch of the nitrone functionality is naturally shifted to a lower frequency compared to the imine C=N stretch (1623 cm^{-1}).[11]

Next, the ^{13}C-labeled COF-115 was synthesized via a polycondensation reaction between a ^{13}C-labeled terephthaladehyde (**2**′) and the hydroxylamine-linker **1**. The resulting product was analyzed by solid-state ^{13}C multi cross-polarization magic angle spinning (multiCP-MAS) NMR spectroscopy. The major peak at 135.1 ppm evidently showed that the COF is mainly connected via the nitrone linkage (Figure 1c),[7a] which was in good agreement with the respective shift of ^{13}C-labeled model compound **3**′ (133.1 ppm). Based on a previous report,[3a] the minor peaks at 159.4 and 192.1 ppm were assigned to imine and aldehyde defects (8 % each), respectively.[12]

The porosity of COF-115 was studied via nitrogen sorption analysis at 77 K (Figure 2). A Type IV adsorption isotherm was observed, thus indicating the presence of mesopores in the framework structure. A surface area of 1387 m^2/g was estimated using the Brunauer–Emmett–Teller (BET) model. DFT analysis of the nitrogen adsorption isotherm provided a bimodal pore size distribution, which further confirmed the structure of COF-115 exhibiting micro- and mesopores (Figure 2, inset). This was further validated by the water vapor sorption isotherm of COF-115 that exhibited a characteristic two-step profile indicative of

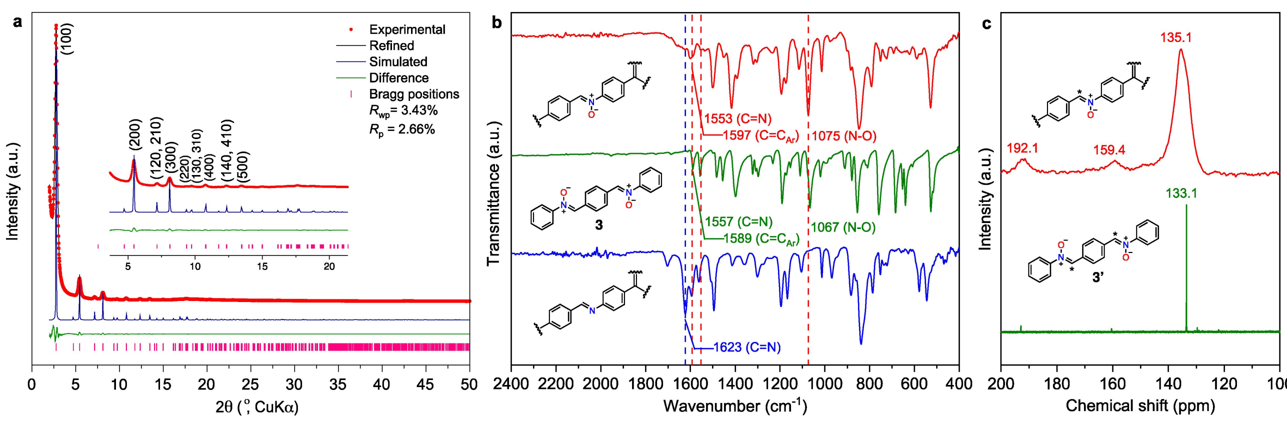

Figure 1. Characterization of COF-115: a) Pawley refinement of COF-115 (eclipsed, AA) against the experimental PXRD pattern; b) FT-IR spectra of COF-115 (red), its isoreticular imine-linked COF (blue), and model compound **3** (green); c) Solid-state ^{13}C multiCP-MAS NMR spectra of the ^{13}C-labeled COF-115 and ^{13}C-labeled model compound **3’**.

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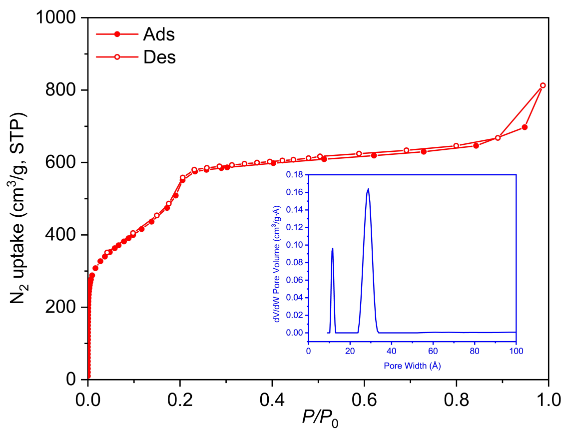


Figure 2. N_2 sorption isotherm of COF-115 at 77 K and its pore size distribution profile (inset).

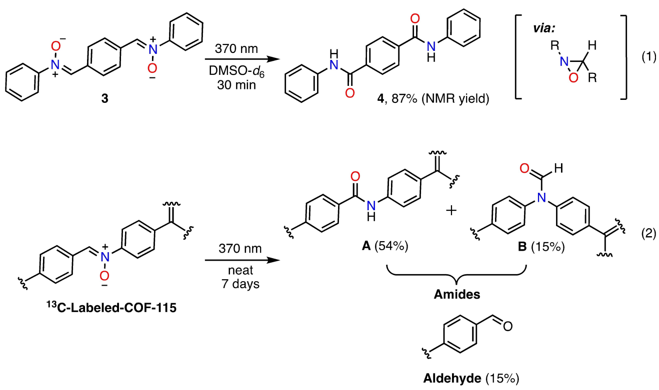
the presence of two significantly different-sized pores (Supporting Information, Figure S5).

The zwitterionic nature of the nitrone functionality in COF-115 was anticipated to have more favorable interactions with polar or polarizable gas molecules compared with an isostructural imine-linked COF of the same pore size. To probe this hypothesis, we compared the water vapor and carbon dioxide sorption behavior of the two isoreticular COFs, COF-115 and the imine-linked COF. Importantly, both COFs featured similar pore sizes and BET surface areas, as evaluated by the nitrogen sorption analysis at 77 K (Supporting Information, Figure S4). The water vapor sorption isotherm of COF-115 was significantly shifted to lower relative humidity (by ~20% RH) compared with the isotherm of the imine-linked COF (Figure S5). This result showcases an unexplored potential of *N*-oxide-containing materials for atmospheric water harvesting applications.[13] Likewise, COF-115 demonstrated superior CO_2 capture properties (Figures S6). The volumetric CO_2 uptake of COF-115 was 37 cm^3/g at 1 bar and 298 K, while it was 26 cm^3/g for the imine-linked COF (Figure S6a). Furthermore, the higher isosteric heat of adsorption (Q_{st}) values estimated for COF-115 are indicative of stronger interactions of carbon dioxide molecules with the nitrone framework compared to the imine-linked COF (Figure S6b). Finally, the hydrogen sorption isotherm of COF-115 at 77 K revealed an overall uptake capacity of 151 cm^3/g (1.34 wt.%) at 1 bar (Figure S7), which is comparable to the uptake of its imine-based analog (1.37 wt.%).[10] The nearly identical hydrogen sorption properties can be ascribed to the similar porosity of the two materials. Interestingly, the zero-loading Q_{st} value for COF-115 was determined to be 7.4 kJ mol^{-1}, which is higher than the values obtained for some imine-[14] and most boroxine-linked COFs (4.4–7 kJ mol^{-1}).[15]

To get insight into the superior adsorption behavior of COF-115, the interactions of both nitrone- and imine-based frameworks with water and CO_2 molecules were studied computationally. First, pristine COF structures (three potential structural variants of COF-115 and the reported imine-COF structure[3a]) were optimized using periodic DFT calculations with the PBEsol-D3BJ functional[16] (Supporting Information, Section S7.1). Following the structure optimization, we investigated the primary adsorption sites of water and CO_2 for the COFs at a loading of one guest molecule per linkage. As a result, the most stable COF-115 structure (COF-115-**3**) binds a water molecule stronger by about 1.3 kcal/mol in free energy terms (computed via the SCAN–D3BJ functional[17]) compared to the imine-linked COF. This difference is likely responsible for the experimentally observed shift of the water sorption isotherm of the former COF towards lower RH values. Likewise, the SCAN functional-based computations[18] predicted stronger interactions of COF-115 with CO_2 molecules compared to the imine-linked COF (Supporting Information, Section S7.2).

Lastly, we explored the photochemical properties of the nitrone-linked COF. It was reported that small-molecule nitrone compounds can undergo photoisomerization reactions to afford oxaziridine products. The stability of the latter greatly depends on the nature of substituents, and in the case of aryl groups, oxaziridines are known to readily decompose to amides and aldehyde products.[6a,19] First, we subjected model compound **3** to irradiation conditions (30 min, 370 nm) and observed the formation of compound **4** in 87 % NMR yield and traces of terephthalaldehyde (Scheme 2, (1)). The photoreactivity of COF-115 was studied under neat conditions under inert atmosphere employing an activated sample of ^{13}C-labeled COF-115. The sample was irradiated for 4–7 days and analyzed by FT-IR, PXRD and ^{13}C multiCP-MAS NMR (Supporting Information, Section S10). The crystallinity was found to gradually decrease upon prolonged irradiation (Figure S14a), with conversion reaching 84 % after 7 days according to solid-state ^{13}C multiCP-MAS NMR (Figure S15b). The main products of this reaction were identified as amide **A** (54 %), amide **B** (15 %) and aldehyde (15 %) (Scheme 2, (2)). This skeletal rearrangement represents a rare example of a post-synthetic COF modification induced by light.[20,21]

In summary, this report demonstrates the first direct, one-step synthesis of a crystalline, porous COF with nitrone linkages. We believe it will pave the way for other nitrone-



Scheme 2. Photoinduced rearrangement reactions of model compound **3** (**1**) and ^{13}C-labeled COF-115 (**2**).

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linked COFs of different topologies. Water vapor and carbon dioxide sorption analyses of this COF showcased an untapped potential of *N*-oxide-based porous materials for atmospheric water harvesting and CO_2 capture applications compared to their well-known imine-based analogs. Through DFT calculations, preferential interactions with the nitrone functionality are identified as the origin of its favorable absorption properties. In addition, the demonstrated photoinduced isomerization of COF-115 to the corresponding amide-linked material is a promising avenue for post-synthetic framework modifications.

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Conflict of Interest

The authors declare the following competing financial interest(s): O.M.Y. is cofounder of Water Harvesting Inc. and ATOCO Inc., aiming at commercializing related technologies.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article. The raw solid-state NMR data associated with this work are available at https://doi.org/10.6078/D14M8R.

Keywords: Atmospheric Water Harvesting · Covalent Organic Frameworks · Light Rearrangement · Nitrone

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