

# A Porous Crystalline Nitron-Linked Covalent Organic Framework

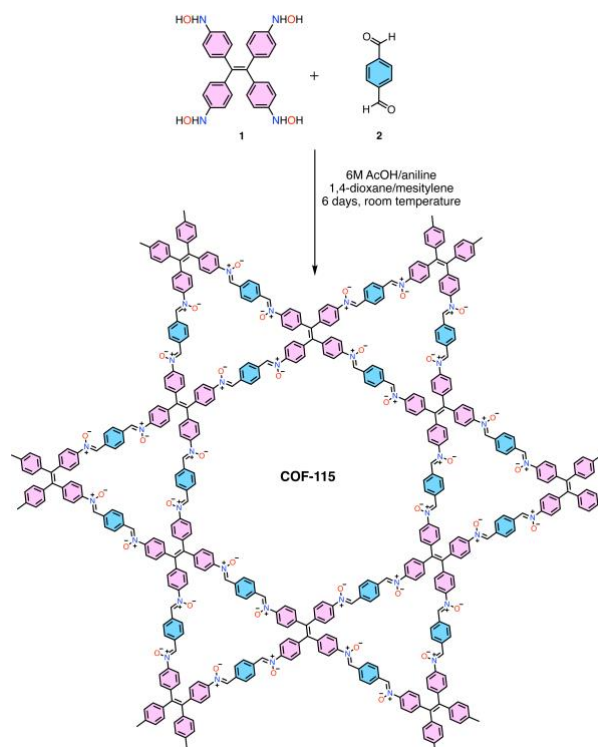
Daria Kurandina,<sup>+</sup> Banruo Huang,<sup>+</sup> Wentao Xu, Nikita Hanikel, Andrea Darù, Gautam D. Strocio, Kaiyu Wang, Laura Gagliardi,<sup>\*</sup> F. Dean Toste,<sup>\*</sup> Omar M. Yaghi<sup>\*,#</sup>

**Abstract:** Herein, we report the synthesis of a nitron-linked covalent organic framework, COF-115, by combining *N, N, N, N'*-(ethene-1,1,2,2-tetrayl)tetrakis(benzene-4,1-diyl)tetrakis(hydroxylamine) and terephthalaldehyde via a polycondensation reaction. The formation of the nitron functionality was confirmed by solid-state <sup>13</sup>C multi cross-polarization magic angle spinning NMR spectroscopy of the <sup>13</sup>C-isotope-labeled COF-115 and Fourier-transform infrared spectroscopy. The permanent porosity of COF-115 was evaluated through low-pressure N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub> sorption experiments. Water vapor and carbon dioxide sorption analysis of COF-115 and the isorecticular imine-linked COF indicated a superior potential of *N*-oxide-based porous materials for atmospheric water harvesting and CO<sub>2</sub> 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.

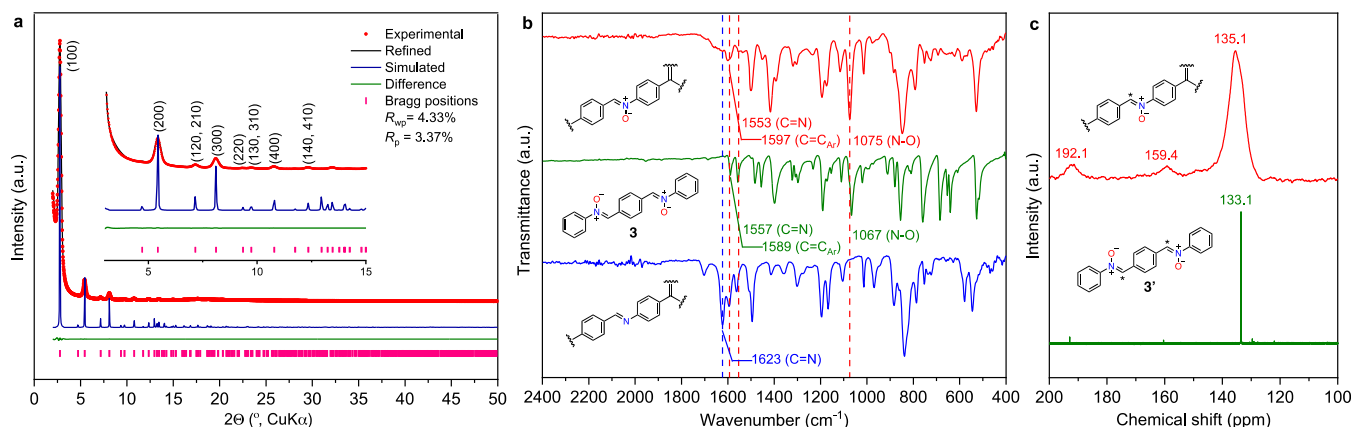
Development of new linkages to broaden the scope of covalent organic frameworks (COFs) has been one of the major drivers of the research field.<sup>[1,2]</sup> The diversity of linkage functionalities plays a critical role in tuning the material properties including its chemical stability,<sup>[3]</sup> adsorption behavior,<sup>[4]</sup> and catalytic activity.<sup>[5]</sup> Despite the ubiquitous usage of the imine linkage in various studies, its oxidized counterpart, the nitron functionality, remains elusive as a linkage in COFs.<sup>[2]</sup> Nitron compounds, featuring 1,3-dipolar structures, are versatile synthetic intermediates that can undergo nucleophilic additions, cycloaddition reactions, and photochemical rearrangements. Additionally, nitrons can serve as spin traps to detect short-lived radicals and their therapeutic potential against oxidative stress has been actively studied.<sup>[6]</sup> Thus, synthesis of porous, crystalline nitron-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 nitron functionality has largely been unexplored to constitute backbones of polymers.<sup>[7]</sup> This can partially be attributed to the difficulty of synthesizing multidentate

- [#] Prof. Dr. Omar M. Yaghi\*  
Department of Chemistry, Kavli Energy Nanoscience Institute and Bakar Institute of Digital Materials for the Planet, Division of Computing, Data Science, and Society  
University of California, Berkeley, California 94720, United States  
UC Berkeley–KACST Joint Center of Excellence for Nanomaterials for Clean Energy Applications, King Abdulaziz City for Science and Technology, Riyadh 11442, Saudi Arabia  
E-mail: yaghi@berkeley.edu; orcid.org/0000-0002-5611-3325
- Prof. Dr. F. Dean Toste,\* Dr. Banruo Huang\*  
Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States  
E-mail: fdtoste@berkeley.edu; orcid.org/0000-0001-8018-2198
- Dr. Daria Kurandina,<sup>+</sup> Dr. Wentao Xu, Dr. Nikita Hanikel  
Department of Chemistry and Kavli Energy Nanoscience Institute  
University of California, Berkeley, Berkeley, California 94720, United States
- Prof. Dr. Laura Gagliardi,\* Dr. Andrea Darù, Dr. Gautam D. Strocio  
Department of Chemistry  
Pritzker School of Molecular Engineering, and Chicago Center for Theoretical Chemistry  
University of Chicago, Chicago, Illinois 60637, United States  
E-mail: lgagliardi@uchicago.edu; orcid.org/0000-0001-5227-1396
- Kaiyu Wang  
Department of Chemistry, Kavli Energy Nanoscience Institute, and Bakar Institute of Digital Materials for the Planet, Division of Computing, Data Science, and Society  
University of California, Berkeley, California 94720, United States
- [+] These authors contributed equally  
[\*] Corresponding authors



**Scheme 1.** Synthesis of the nitron-linked COF-115 by connecting *N, N, N, N'*-(ethene-1,1,2,2-tetrayl)tetrakis(benzene-4,1-diyl)tetrakis(hydroxylamine) (1) and terephthalaldehyde (2) via a polycondensation reaction.



**Figure 1.** Characterization of COF-115: a) Pawley refinement of COF-115 (eclipsed, AA-H) 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  $^{13}\text{C}$  multiCP-MAS NMR spectrum of the  $^{13}\text{C}$ -labeled COF-115 and  $^{13}\text{C}$ -labeled model compound **3'**.

hydroxylamine monomers.<sup>[8]</sup> 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 terephthalaldehyde (**2**) via a polycondensation reaction leading to COF-115 (Scheme 1). Previous studies showing reversibility of the condensation reaction between aromatic hydroxylamines and aldehydes<sup>[9]</sup> were encouraging that a successful framework crystallization is feasible. However, due to thermal sensitivity of the nitrone functionality,<sup>[7a]</sup> 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  $\text{CO}_2$  drying and activation, COF-115 had to be stored under inert atmosphere.

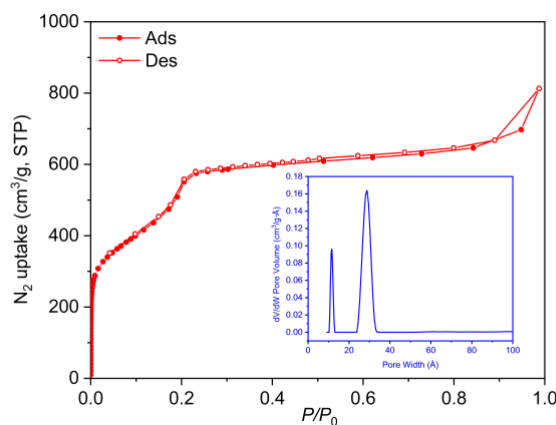
The structure of COF-115 was evaluated by powder X-ray diffraction (PXRD) analysis (Figure 1a). The framework was modeled in the *P6* space group (No. 168), with the layers assuming the *kgm* topology stacked in an eclipsed fashion. Using this structural model, a Pawley refinement was performed against the experimental pattern to provide the unit cell parameters ( $a = 38.3 \text{ \AA}$ , and  $c = 6.9 \text{ \AA}$ ) with reasonable agreement factors ( $R_{\text{wp}} = 4.33\%$ ,  $R_{\text{p}} = 3.37\%$ ). This structure was further optimized using periodic DFT calculations and found to be the most stable among the other two potential structural variants of COF-115 (see Section S7.1 in the Supporting Information).

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  $1075 \text{ cm}^{-1}$ , which is absent in the FT-IR spectrum of the isoreticular imine-linked COF that was synthesized by using a previously published procedure,<sup>[3a,10]</sup> was assigned to the N-O stretch.<sup>[11]</sup> Based on

isotope labeling analyses of COF-115 and the model compound **3** (Figure 1b, Supporting information, Figure S2), the stretches at  $1553$  and  $1597 \text{ cm}^{-1}$  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 ( $1623 \text{ cm}^{-1}$ ).<sup>[11]</sup>

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

The porosity of COF-115 was studied via nitrogen sorption analysis at  $77 \text{ K}$  (Figure 2). A Type IV adsorption isotherm was observed, thus indicating the presence of mesopores in the framework structure. A surface area of  $1387 \text{ m}^2/\text{g}$  was



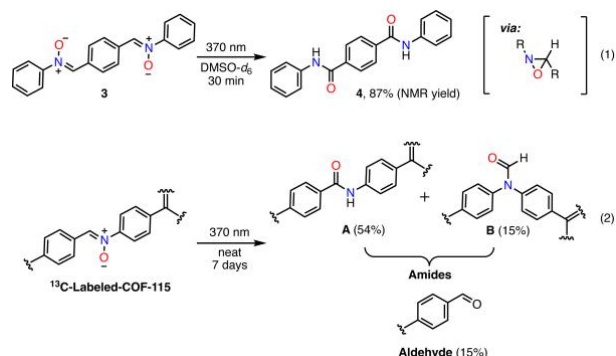
**Figure 2.**  $\text{N}_2$  sorption isotherm of COF-115 at  $77 \text{ K}$  and its pore size distribution profile (inset).

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, insert). This was further validated by the water vapor sorption isotherm of COF-115 that exhibited a characteristic two-step profile indicative of the presence of two significantly different-sized pores (Supporting Information, Figure S6).

The zwitterionic nature of the nitron 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 (*vide infra*). To probe this hypothesis, we compared the water vapor and carbon dioxide sorption behavior of the two isorecticular 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 S5). The water vapor sorption isotherm of COF-115 was significantly shifted to lower relative pressures ( $-0.2 P/P_{\text{sat}}$ ) compared with the isotherm of the imine-linked COF (Figure S6). This result showcases an unexplored potential of *N*-oxide-containing materials for atmospheric water harvesting applications.<sup>[13]</sup> Likewise, COF-115 demonstrated superior CO<sub>2</sub> capture properties (Figures S7). The volumetric CO<sub>2</sub> uptake of COF-115 was 37 cm<sup>3</sup>/g t 1 bar and 298 K, while it was 26 cm<sup>3</sup>/g for the imine-linked COF (Figure S7a). Furthermore, the higher isosteric heat of adsorption ( $Q_{\text{st}}$ ) values estimated for COF-115 are indicative of stronger interactions of carbon dioxide molecules with the nitron framework compared to the imine-linked COF (Figure S7b). Finally, the hydrogen sorption isotherm of COF-115 at 77 K revealed an overall uptake capacity of 151 cm<sup>3</sup>/g (1.34 wt.%) at 1 bar (Figure S8), which is comparable to the uptake of its imine-based analog (1.37 wt.%),<sup>[10]</sup> which can be ascribed to the similar porosity of the two materials. Interestingly, the zero-loading  $Q_{\text{st}}$  value for COF-115 was determined to be 7.4 kJ mol<sup>-1</sup>, which is higher than the values obtained for some imine-<sup>[14]</sup> and most boroxine-linked COFs (4.4–7 kJ mol<sup>-1</sup>).<sup>[15]</sup>

To get insight into the superior adsorption behavior of COF-115, the interactions of both nitron- and imine-based frameworks with water and CO<sub>2</sub> molecules were studied computationally. First, pristine COF structures (three potential structural variants of COF-115 and the reported imine-COF structure<sup>[3a]</sup>) were optimized using periodic DFT calculations with the PBEsol-D3BJ functional<sup>[16]</sup> (see Section S7.1 in the Supporting Information). Following the structure optimization, we investigated the primary adsorption sites of water and CO<sub>2</sub> for the COFs at a loading of one guest molecule per linkage. As a result, the most stable COF-115 structure binds a water molecule stronger by about 1.3 kcal/mol in free energy terms (computed via the SCAN-D3BJ functional<sup>[17]</sup>) 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<sup>[18]</sup> predicted stronger interactions of COF-115 with CO<sub>2</sub> molecules compared to the imine-linked COF (see Section S7.2 in the Supporting Information).

Lastly, we explored the photochemical properties of the nitron-linked COF. It was reported that small-molecule nitron 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.<sup>[6a,19]</sup> 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 after 30 min (Scheme 2, (1)). The photoreactivity of COF-115 was studied under neat conditions under inert atmosphere employing an activated sample of <sup>13</sup>C-labeled COF-115. The sample was irradiated for 4-7 days and analyzed by FT-IR, PXRD and <sup>13</sup>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 <sup>13</sup>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.<sup>[20, 21]</sup>



**Scheme 2.** Photoinduced rearrangement reactions of model compound **3** (1) and <sup>13</sup>C-labeled COF-115 (2).

In summary, this report demonstrates the first direct, one-step synthesis of a crystalline, porous COF with nitron linkages. We believe it will pave the way for other nitron-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<sub>2</sub> capture applications compared to their well-known imine-based analogs. Through DFT calculations, preferential interactions with the nitron 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.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[22-27]</sup>

## 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.

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