

A Porous Covalent Organic Framework with Voided Square Grid Topology for Atmospheric Water Harvesting

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ABSTRACT: Atmospheric moisture is a ubiquitous water resource available at any time and any place, making it attractive to develop materials for harvesting water from air to address the imminent water shortage crisis. In this context, we have been exploring the applicability of covalent organic frameworks (COFs) for water harvesting and report here a new porous, two-dimensional imine-linked COF with a voided square grid topology, termed COF-432. Unlike other reported COFs, COF-432 meets the requirements desired for water harvesting from air in that it exhibits an S-shaped water sorption isotherm with a steep pore-filling step at low relative humidity and without hysteretic behavior—properties essential for energy-efficient uptake and release of water. Further, it can be regenerated at ultra-low temperatures and displays exceptional hydrolytic stability, as demonstrated by the retention of its working capacity after 300 water adsorption–desorption cycles.

Developing new materials for water production from air is an important endeavor in addressing the global water crisis.¹ Ideally, water harvesting materials should have (i) high hydrolytic stability and retention of capacity upon long-term water uptake and release cycling, (ii) an S-shaped water sorption isotherm with a steep pore-filling step (IUPAC Type IV or V) at low relative humidity (<40% relative humidity, RH) with minimal to no hysteresis, and (iii) a low regeneration temperature to allow for use of low-grade heating to enable facile release of water molecules from the material.²

Reticular structures, that is metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), are ideally suited to address the water shortage crisis because of their exceptional porosity, as well as the large diversity of chemical compositions and accessible topologies; aspects that allow to tune their water sorption properties in a great variety of ways.^{2,3} Indeed, MOFs have been identified, studied, and practically employed for water harvesting from air.^{2,4–9} COFs, however, remain largely unexplored for this application.¹⁰ This could potentially be explained by the relatively lower crystallinity exhibited by COFs, in particular those constructed from hydrolytically robust linkages,¹¹ which precludes the formation of highly ordered molecular water networks within the porous framework—an important prerequisite for obtaining S-shaped water isotherm profiles.

Herein, we sought to explore COFs as water-harvesting materials. Accordingly, we report a new, highly crystalline framework, constructed from the tetratopic 1,1,2,2-tetrakis(4-aminophenyl)ethene [ETTA, C₂₆H₁₆(NH₂)₄] and the tritopic 1,3,5-triformylbenzene [TFB, C₆H₃(CHO)₃], termed COF-432 [(ETTA)₃(TFB)₄]_{imine}, which exhibits the **mtf** topology—a net hitherto not reported in COF chemistry (Figure 1).^{11–13} This COF displays a water sorption isotherm without hysteretic behavior and with a steep pore-filling step at low relative humidity (<40% RH), exceptionally high water

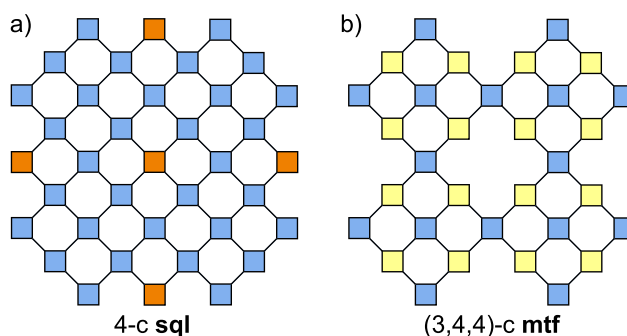


Figure 1. Juxtaposition of the 4-c uninodal **sql** net (a) and the (3,4,4)-c trinodal **mtf** net (b). The **mtf** net is conceptually constructed by removing 1/8 of the nodes (orange) from the **sql** net, and can be perceived as a voided **sql** net. The nodes in both nets are depicted as squares. Blue/orange squares represent 4-c and yellow squares 3-c nodes.

sorption cycling stability, and a low heat of adsorption. All these factors establish COF-432 as a long-term hydrolytically stable water-harvesting material with a low regeneration energy barrier and relatively high working capacity within a small partial pressure range; with the latter enabling efficient use of a small temperature gradient for water uptake and release cycling.

COF-432 was synthesized solvothermally through the condensation of ETTA and TFB in a mixture of chloroform, methanol, and aqueous acetic acid (Figure 2 and Supporting

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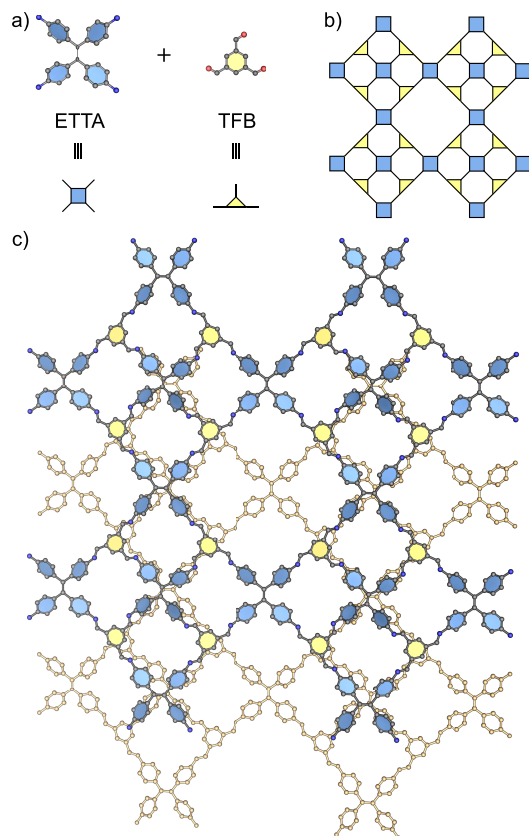


Figure 2. Reaction of 1,1,2,2-tetrakis(4-aminophenyl) ethane (ETTA) and 1,3,5-triformylbenzene (TFB) (a), which represent a 4-c and a 3-c node, respectively, yields COF-432 (c). This framework exhibits the (3,4,4)-c mtf topology, shown in its augmented form (b). Atom colors: C, gray; N, blue; O, red. H atoms are omitted for clarity. The second layer of the staggered structure of COF-432 is depicted in light orange.

Information (SI), Section S2. The structure of COF-432 was determined by powder X-ray diffraction (PXRD) and supported by elemental analysis (EA), Fourier-transform infrared (FTIR) spectroscopy, ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy, thermogravimetric analysis (TGA) and N_2 sorption analysis. FTIR spectroscopy of COF-432 showed the absence of aldehyde ($\nu_{\text{C=O}} = 1692 \text{ cm}^{-1}$) and amine ($\nu_{\text{N-H}} = 3352 \text{ cm}^{-1}$) stretches, present in the starting materials ETTA and TFB. Also, the emergence of an imine ($\nu_{\text{C=N}} = 1628 \text{ cm}^{-1}$) stretch indicated the formation of an extended imine-linked network (SI, Section S3). Formation of the imine linkage was further corroborated by ^{13}C CP-MAS NMR spectroscopy, with the characteristic ^{13}C imine resonance observed at 158 ppm (SI, Section S4).

Due to the small crystal size (ca. $100 \times 100 \times 300 \text{ nm}^3$; SI, Section S5) of COF-432, its structure was determined by analysis of its PXRD pattern (SI, Section S6). Indexing of the PXRD pattern using TOPAS 4.2¹⁴ identified the space group $I4_1/a$ (No. 88). Next, a charge flipping method¹⁵ was used to calculate the electron density map (EDM) of COF-432, generating a valid result in the respective space group. Finally, the structure of COF-432 was determined by locating the fragments of ETTA observed in the EDM (SI, Section S6) and linking those into an extended network. In this structure, the ETTA and TFB building units (Figure 2a) are connected

through imine bonds to form an extended two-dimensional (2D) framework of mtf topology (Figures 1 and 2b, and SI, Section S7). The unit cell parameters of COF-432 were refined by the Le Bail method using wide-angle X-ray scattering (WAXS) data ($I4_1/a$; $a = 30.65 \text{ \AA}$, $c = 12.85 \text{ \AA}$) with residual factors of $R_p = 2.88\%$ and $R_{wp} = 3.96\%$ (Figure 3 and SI, Section S6).

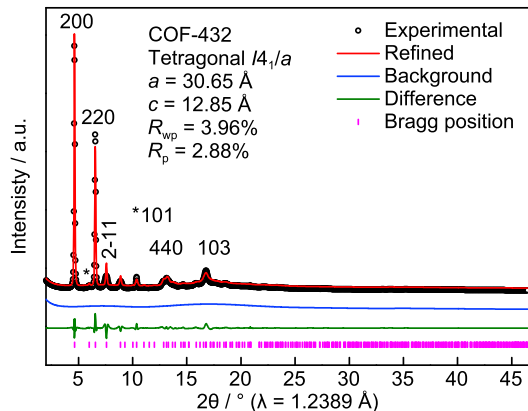


Figure 3. Wide-angle X-ray scattering (WAXS) pattern and Le Bail analysis of COF-432. The experimental pattern (black), the refined Le Bail fitting (red), the difference plot (green), background (blue), and the Bragg positions (pink) are provided.

A single layer of COF-432 (Figure 2c) has two kind of square pore apertures with diameters of ca. 10.0 and 21.0 \AA (based on van der Waals radii). Adjacent 2D layers are staggered, thus creating a 1D cylindrical pore structure with a diameter of ca. 7.5 \AA (Figure 2c). COF-432 is permanently porous with a BET surface area of $895 \text{ m}^2 \text{ g}^{-1}$. This is close to the theoretical value calculated from the structural model ($900 \text{ m}^2 \text{ g}^{-1}$), approximated by its molecularly accessible area using N_2 as the probe adsorbate (kinetic diameter = 3.6 \AA).¹⁶ The pore volume of COF-432, determined from its N_2 sorption isotherm ($0.43 \text{ cm}^3 \text{ g}^{-1}$), is in good agreement with the pore volume predicted from its structural model using the Void Calculation function in PLATON ($0.45 \text{ cm}^3 \text{ g}^{-1}$). Additionally, the pore size distribution of COF-432 calculated from its N_2 sorption isotherm indicates a single pore with a diameter of 8.0 \AA , which is in good agreement with the proposed crystal structure (SI, Section S8). The structural model is further confirmed by elemental analysis of COF-432, which matches well with the expected elemental ratio calculated for the framework (SI, Section S2).

The hydrolytic stability of COF-432 was initially investigated by immersing the activated COF in water. PXRD patterns of the framework before and after exposure demonstrated that the material retained its crystallinity for at least 20 d. Additionally, the material did not lose its surface area after extended soaking of the COF in water (90 h under stirring; SI, Section S10). We hypothesize that this stability stems from tight packing of the 2D COF layers and usage of high-connectivity linker molecules, which hampers the hydrolysis of the labile imine bonds.

The exceptional hydrolysis resistance of COF-432 encouraged us to study its water sorption properties. The framework exhibits an S-shaped water sorption isotherm with a steep pore-filling step at 34% RH (at 25 $^\circ\text{C}$; Figure 4a). The maximal water uptake at $P/P_{\text{sat}} = 0.95$ reaches 30 wt% (0.3 g

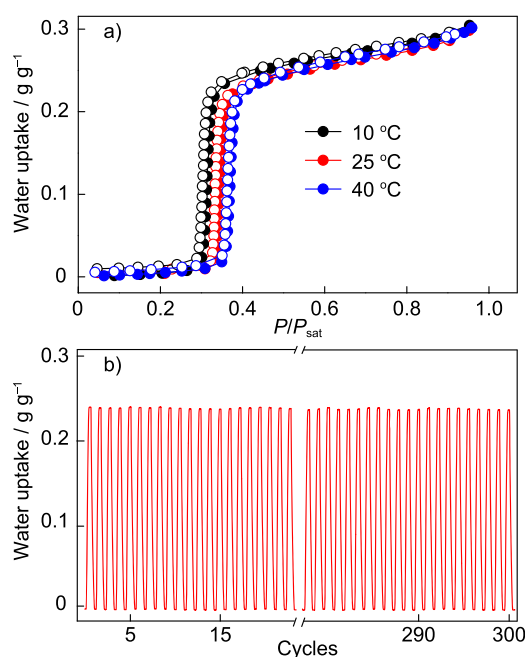


Figure 4. (a) Water sorption analysis on COF-432, measured at different temperatures (10, 25, and 40 °C). P : water vapor pressure. P_{sat} : saturation water vapor pressure at the given temperature. (b) Water cycling stability test for 300 adsorption–desorption cycles conducted on COF-432 at constant water vapor pressure (1.7 kPa). Adsorption and desorption are carried out at 30 °C (40% relative humidity, RH) and 35 °C (30% RH), respectively (full data set is displayed in the SI, Section S12).

g^{-1}) and the working capacity in the relative humidity range between 20 and 40% is 0.23 g g^{-1} . Unlike other COFs, COF-432 does not exhibit hysteretic water sorption behavior (Figure 4a and SI, Section S11). This is an attractive feature because it restricts the energy requirement for regeneration of this material. To further study the interaction of the water molecules with the COF, water sorption isotherms at different temperatures (10, 25, and 40 °C; Figure 4a) were used to calculate the isosteric heat of adsorption of water in COF-432. It was estimated to account to ca. 48 kJ mol^{-1} (SI, Section S11)—close to the evaporation enthalpy of water (44 kJ mol^{-1} at 25 °C). This indicates that water–water interactions are predominant during the pore filling process.² Indeed, the pore surface of COF-432 is mostly nonpolar; however, the imine bonds could serve as primary adsorption sites for water molecules, as hydrogen bonding between imine bonds of a COF and water molecules has been observed in a previous study.¹⁷ This relatively weak hydrogen bonding and the strong confinement effect in the small framework pores (ca. 7.5 Å diameter) likely initiate the pore-filling step at low relative humidity (<40% RH). We hypothesize that the absence of highly polar functional groups and low framework flexibility through employment of high-connectivity (tri- and tetra-topic) linker molecules prevent hysteretic water sorption behavior of COF-432.^{18,19}

Importantly, COF-432 retained its crystallinity, BET surface area and water vapor capacity after seven consecutive water sorption measurements (SI, Section S12)—an impressive feat considering that other COFs reported as promising water sorbents in the literature exhibit a decrease in surface area after water exposure and/or sorption.^{20–23} These findings encour-

aged us to subject COF-432 to a long-term water adsorption–desorption cycling test: In a thermogravimetric analyzer, the framework was exposed to water vapor under isobaric conditions (1.7 kPa), and a temperature swing between 30 and 35 °C (corresponding to 40 and 30% RH, respectively) was applied to trigger water ad- and desorption. The steep pore-filling step allowed for a high working capacity of 0.23 g g^{-1} under employment of an ultra-low temperature gradient ($5 \text{ }^{\circ}\text{C}$). In total, 300 uptake and release cycles were conducted, and the working capacity remained unchanged during the experiment (Figure 4b), indicating retention of porosity and thus exceptional water cycling stability.

In summary, we have synthesized a new 2D imine-linked framework, COF-432, which exhibits attractive water sorption properties. In particular, COF-432 has (i) exceptional long-term stability upon water uptake and release cycling, (ii) a hysteresis-free water sorption isotherm with a steep uptake step at low relative humidity, and (iii) low heat of adsorption, allowing for regeneration by low-grade energy sources. Accordingly, COF-432 could be employed as a material for water harvesting from air, and potentially in heat pump systems or in desiccant-based dehumidifiers.

We note that selected reported MOFs exhibit a higher water uptake capacity than COF-432, however, its other characteristics (hydrolytic stability, isotherm profile, facile regeneration) are comparable with those of the most advanced water-harvesting MOFs,² indicating that COFs can, indeed, be competitive materials in this regard. Additionally, the usage of all-organic materials does not rely on metal cations, which may potentially exhibit toxic properties or be cost-prohibitive. In conclusion, we think that extending the scope of material classes suitable for atmospheric water extraction will be of great benefit to this technology, and we firmly believe that our findings will inspire more future research on COFs as water-harvesting materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b13094>.

Synthesis and characterization details of COF-432: powder X-ray diffraction analysis data, computational modeling, and water sorption analysis data (PDF)

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Notes

The authors declare the following competing financial interest(s): Omar M. Yaghi is co-founder of Water Harvesting Inc., aiming at commercializing related technologies.

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