

Postfunctionalized Covalent Organic Frameworks for Water Harvesting



Cite This: <https://doi.org/10.1021/acscentsci.2c00710>



Read Online

ACCESS |



Metrics & More



Article Recommendations

Patrick W. Fritz and Ali Coskun*

Improved atmospheric water harvesting through the postfunctionalization of hydrazine-linked covalent organic frameworks toward mixed hydrazine-hydrazide frameworks.

■ SMALL CHANGES, BIG IMPACT—HOW A POSTSYNTHETIC FUNCTIONAL GROUP CONVERSION AFFECTS WATER HARVESTING PROPERTIES

As framework materials such as covalent organic frameworks (COFs) continue to soar in popularity, an ever-growing number of researchers are working on endowing these frameworks with improved stability to enable a wider range of applications. In this issue of *ACS Central Science*, Yaghi and co-workers investigate hydrazine-hydrazide-linked frameworks obtained through postsynthetic oxidation and explore the effect of the transformation on the framework's water sorption properties.¹

Since their conception by Yaghi et al. in 2005, COFs have seen ample interest in the community due to their exceptional chemical and physical properties.² Although initially plagued by their relatively low stability, the past several years have seen the rise of a plethora of new linking moieties and functionalities; however, one of the highest potentials to overcome physicochemical limitations lies in the postsynthetic modification of framework materials.

Postsynthetic modifications have been known to COF chemistry for quite some time and have been exploited to improve the stability of the frameworks by transforming otherwise labile linkers.^{3–5} The conversion of imines, especially, has been heavily investigated due to the wide range of literature-known procedures involving imines. For example, Lotsch et al. employed a formic acid-mediated reduction of various imine-linked COFs toward aminal-linked

Although initially plagued by their relatively low stability, the past several years have seen the rise of a plethora of new linking moieties and functionalities; however, one of the highest potentials to overcome physicochemical limitations lies in the postsynthetic modification of framework materials.

systems, thus improving their chemical stability and providing ample opportunities for further functionalization.⁵ Similarly, the direct and postsynthetic conversion of imines toward thiazoles or oxazoles has been employed to significantly improve the stability and functionality of COFs (Figure 1).^{6,7}

■ A KEY ASPECT OF POSTSYNTHETIC MODIFICATIONS LIES IN MAINTAINING OR IDEALLY IMPROVING THE FUNCTIONALITY AND STABILITY OF THE OBTAINED FRAMEWORK MATERIALS

Water harvesting is an upcoming area in porous materials science aiming to tackle problems arising from extreme droughts and has seen increasing interest from industrial partners (Figure 2).^{8,9}

In this issue of *ACS Central Science*, the authors present the synthesis and characterization of three hydrazine-linked COFs and describe their postsynthetic oxidation toward

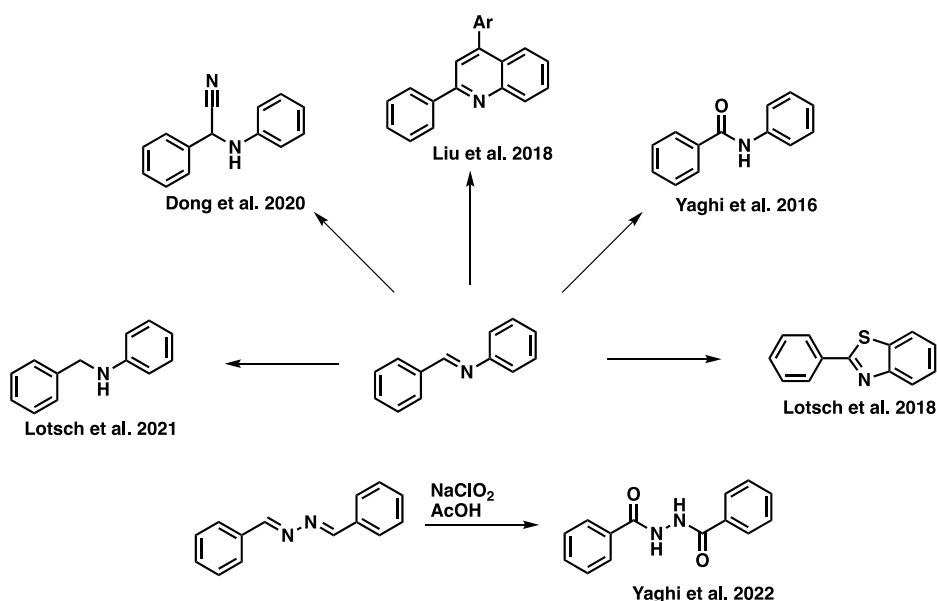


Figure 1. Selected postsynthetic modification strategies of imine and hydrazone-linked COFs.

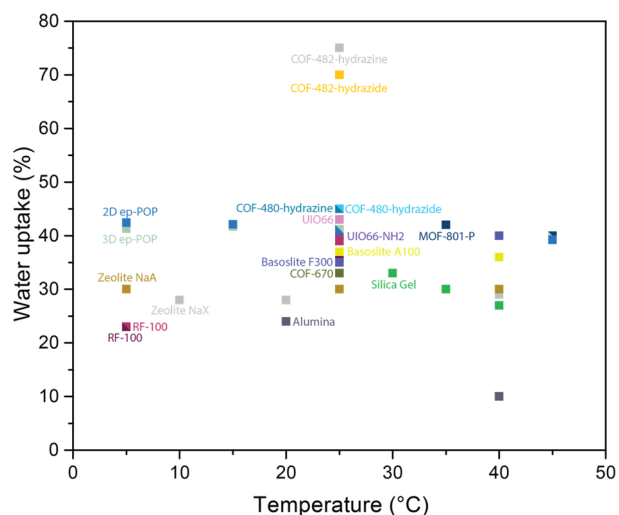


Figure 2. Comparison of temperature-dependent water uptake capacities (at RH = 0.9–0.95) of various organic, inorganic, and metal–organic framework materials.

hydrazine-hydrazide-linked COFs for the first time. With water harvesting in mind, hydrazine-linked parent frameworks were chosen for their good water sorption properties and their relative ease of synthesis. Subsequently, a sodium chlorite-mediated oxidation—similar to a previously conducted study on the oxidation of imines to amides¹⁰—was employed to oxidize the hydrazines to hydrazide. A drawback of postsynthetic modifications lies in the accessibility of the functional units that should be converted. In their manuscript, Yaghi and co-workers describe conversions between 9.4% and 26.3%, evidenced by ¹⁵N multi-CP-MAS NMR and elemental analysis, depending on the parent framework. Despite the relatively low conversion, COF-480, which featured the lowest hydrazine to hydrazide conversion, showed a significant

change in its water uptake properties, shifting the steep pore-filling step from around 23% relative humidity (RH) to 18% RH, while preserving its total water uptake capacity of 0.45 g g⁻¹. Although showing higher overall conversions, COF-482-hydrazide and COF-670-hydrazide showed a lower impact on their water harvesting properties compared to COF-480-hydrazide; however, in the hydrazide version of COF-482, water uptake at lower relative humidity could be achieved. Surprisingly, no clear correlation between the calculated pore sizes, the degree of oxidation, and water harvesting capacity could be found, pointing toward the many variables such as mass transport that need to be optimized. Overall, these findings showcase both the intriguing potential of postpolymerization modifications of framework materials and its biggest problem in partial conversions owing to the inaccessibility of functional units. Nonetheless, COF-480-hydrazide especially demonstrates the immense impact that functional group conversions can have on the properties of a material. Given that the global average temperature will continue to rise over the upcoming years, simple and adaptable methodologies such as the one presented by Yaghi and co-workers can and will help provide pure drinking water to humans living in arid environments.

A drawback of postsynthetic modifications lies in the accessibility of the functional units that should be converted.

Furthermore, considering the wide range of applications that amide-linked frameworks found enabled through their hydrogen-bonding interactions, it can be envisioned that

hydrazide-linked frameworks could also find applications in catalysis or precious metal recovery.

Author Information

Corresponding Author

Ali Coskun – Department of Chemistry, Université de Fribourg, 1700 Fribourg, Switzerland; orcid.org/0000-0002-4760-1546; Email: ali.coskun@unifr.ch

Author

Patrick W. Fritz – Department of Chemistry, Université de Fribourg, 1700 Fribourg, Switzerland

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acscentsci.2c00710>

REFERENCES

- (1) Nguyen, H. L.; Gropp, C.; Hanikel, N.; Möckel, A.; Lund, A.; Yaghi, O. Hydrazine-Hydrazide-Linked Covalent Organic Frameworks for Water Harvesting. *ACS Cent. Sci.* **2022**, in press. DOI: [10.1021/acscentsci.2c00398](https://doi.org/10.1021/acscentsci.2c00398)
- (2) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, crystalline, covalent organic frameworks. *Science* **2005**, *310* (5751), 1166–70.
- (3) Li, X.-T.; Zou, J.; Wang, T.-H.; Ma, H.-C.; Chen, G.-J.; Dong, Y.-B. Construction of Covalent Organic Frameworks via Three-Component One-Pot Strecker and Povarov Reactions. *J. Am. Chem. Soc.* **2020**, *142* (14), 6521–6526.
- (4) Li, X.; Zhang, C.; Cai, S.; Lei, X.; Altoe, V.; Hong, F.; Urban, J. J.; Ciston, J.; Chan, E. M.; Liu, Y. Facile transformation of imine covalent organic frameworks into ultrastable crystalline porous aromatic frameworks. *Nat. Commun.* **2018**, *9* (1), 2998.
- (5) Grunenberg, L.; Savasci, G.; Terban, M. W.; Duppel, V.; Moudrakovski, I.; Etter, M.; Dinnebier, R. E.; Ochsenfeld, C.; Lotsch, B. V. Amine-Linked Covalent Organic Frameworks as a Platform for Postsynthetic Structure Interconversion and Pore-Wall Modification. *J. Am. Chem. Soc.* **2021**, *143* (9), 3430–3438.
- (6) Haase, F.; Troschke, E.; Savasci, G.; Banerjee, T.; Duppel, V.; Dörfler, S.; Grundei, M. M. J.; Burow, A. M.; Ochsenfeld, C.; Kaskel, S.; Lotsch, B. V. Topochemical conversion of an imine- into a thiazole-linked covalent organic framework enabling real structure analysis. *Nat. Commun.* **2018**, *9* (1), 2600.
- (7) Waller, P. J.; AlFaraj, Y. S.; Diercks, C. S.; Jarenwattananon, N.; Yaghi, O. M. Conversion of Imine to Oxazole and Thiazole Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140* (29), 9099–9103.
- (8) Byun, Y.; Je, S. H.; Talapaneni, S. N.; Coskun, A. Advances in Porous Organic Polymers for Efficient Water Capture. *Chem.—Eur. J.* **2019**, *25* (44), 10262–10283.
- (9) Byun, Y.; Coskun, A. Epoxy-Functionalized Porous Organic Polymers via the Diels–Alder Cycloaddition Reaction for Atmospheric Water Capture. *Angew. Chem., Int. Ed.* **2018**, *57* (12), 3173–3177.
- (10) Waller, P. J.; Lyle, S. J.; Osborn Popp, T. M.; Diercks, C. S.; Reimer, J. A.; Yaghi, O. M. Chemical Conversion of Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138* (48), 15519–15522.