

## 12

## The Applications of Reticular Framework Materials

Metal-organic frameworks (MOFs) and other reticular framework materials prepared following the principles outlined in this book have become the largest class of crystalline materials. Today, a large community of scientists and engineers is working in the field of reticular chemistry, expanding it beyond the synthesis and characterization of new materials by exploring a manifold of applications. This wide range of applications of such materials (MOFs, zeolitic imidazolate framework (ZIFs), and covalent organic frameworks (COFs)) is made possible by their crystalline structures with exceptional surface areas, tailorable pore openings and pore sizes, and their extensive structural diversity [1]. As illustrated throughout this book, reticular materials can be modified on an atomic scale, allowing for precise chemical modifications as well as the formation of structural motifs not accessible in the realm of molecular or classical solid-state chemistry. Knowledge of the local structure facilitates the determination of adsorption sites within the pores, a key factor for the design of MOFs with ultrahigh porosity. Controlling the surrounding of catalytically active sites by crafting the sterics and electronics of such sites gives tailored materials with outstanding properties [2].

The development of reticular chemistry has allowed chemists to synthesize materials by design whose properties surpass those of traditional porous materials. Among such properties are ultrahigh gas storage capacities, high selectivity in gas separations, and the capability to harvest water from air [3]. Employing the principles of reticular chemistry not only allows to tune the metrics and composition of the resulting materials but also to create structural arrangements such as precisely designed catalytic centers for highly selective transformations and small molecule activation not accessible any other way [4]. Such tunability is also advantageous for adjusting the electronic properties, which led to the discovery of porous conductive frameworks [5]. The ability to make materials that are both conductive and porous opens new fields of applications such as supercapacitors or electrocatalysis; both have been proved fruitful for conductive MOFs and COFs alike [6].

Gaining control over the particle size and being able to process materials into specific shapes facilitates the preparation of thin films, membranes, and shaped bodies for gas separation and catalytic applications, as well as the synthesis of colloidal materials for biomedical applications such as drug delivery systems [7]. Knowledge of the precise crystal structures plays a key role in the development

of hybrid materials such as encapsulated metal nanocatalysts [8]. Both modeling and quantum chemical calculations lead to a deeper understanding of many phenomena found in porous framework materials and will, without a doubt, become increasingly important for both the discovery of new materials and the understanding of their properties [3], 9].

Some of the materials covered in this book are being produced on an industrial scale. BASF SE is now scaling up the synthesis of a variety of MOFs and multiple start-up companies produce MOFs for different applications such as gas storage tanks. This illustrates that research in reticular chemistry with respect to possible applications is not limited to research programs at universities worldwide but major chemical and automobile companies are also focusing on the development and commercialization of these porous materials [10]. We will focus on applications of MOFs and ZIFs as these two classes of materials are well developed and many applications have been tested. The study of COFs in various applications is beginning to emerge and will most certainly constitute a major direction in the future. We will also limit our discussion to applications based on the adsorption of gases and vapors since such applications have been studied in detail and a solid understanding of the underlying process has been established. The principles discussed in the following chapters are however also applicable to other reticular materials such as COFs.

## References

- (a) Farha, O.K., Eryazici, I., Jeong, N.C. et al. (2012). Metal-organic framework materials with ultrahigh surface areas: is the sky the limit? *Journal of the American Chemical Society* 134 (36): 15016–15021. (b) Furukawa, H., Ko, N., Go, Y.B. et al. (2010). Ultrahigh porosity in metal-organic frameworks. *Science* 329 (5990): 424–428. (c) Wang, T.C., Bury, W., Gómez-Gualdrón, D.A. et al. (2015). Ultrahigh surface area zirconium MOFs and insights into the applicability of the BET theory. *Journal of the American Chemical Society* 137 (10): 3585–3591. (d) El-Kaderi, H.M., Hunt, J.R., Mendoza-Cortés, J.L. et al. (2007). Designed synthesis of 3D covalent organic frameworks. *Science* 316 (5822): 268–272. (e) Ascherl, L., Sick, T., Margraf, J.T. et al. (2016). Molecular docking sites designed for the generation of highly crystalline covalent organic frameworks. *Natural Chemistry* 8 (4): 310–316. (f) Deng, H., Grunder, S., Cordova, K.E. et al. (2012). Large-pore apertures in a series of metal-organic frameworks. *Science* 336 (6084): 1018–1023. (g) Spitler, E.L., Koo, B.T., Novotney, J.L. et al. (2011). A 2D covalent organic framework with 4.7-nm pores and insight into its interlayer stacking. *Journal of the American Chemical Society* 133 (48): 19416–19421. (h) Ferey, G., Mellot-Draznieks, C., Serre, C. et al. (2005). A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science* 309 (5743): 2040–2042. (i) Wang, B., Cote, A.P., Furukawa, H. et al. (2008). Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs. *Nature* 453 (7192): 207–211. (j) Cui, X., Chen, K., Xing, H. et al. (2016). Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science* 353 (6295): 141–144. (k) Yaghi, O.M., O’Keeffe, M.,

- Ockwig, N.W. et al. (2003). Reticular synthesis and the design of new materials. *Nature* 423 (6941): 705–714.
- 2 (a) Rowsell, J.L.C., Spencer, E.C., Eckert, J. et al. (2005). Gas adsorption sites in a large-pore metal-organic framework. *Science* 309 (5739): 1350–1354. (b) Düren, T., Sarkisov, L., Yaghi, O.M., and Snurr, R.Q. (2004). Design of new materials for methane storage. *Langmuir* 20 (7): 2683–2689.
- 3 (a) Spanopoulos, I., Tsangarakis, C., Klontzas, E. et al. (2016). Reticular synthesis of HKUST-like tbo-MOFs with enhanced CH<sub>4</sub> storage. *Journal of the American Chemical Society* 138 (5): 1568–1574. (b) Jiang, J., Furukawa, H., Zhang, Y.-B., and Yaghi, O.M. (2016). High methane storage working capacity in metal-organic frameworks with acrylate links. *Journal of the American Chemical Society* 138 (32): 10244–10251. (c) Gándara, F., Furukawa, H., Lee, S., and Yaghi, O.M. (2014). High methane storage capacity in aluminum metal-organic frameworks. *Journal of the American Chemical Society* 136 (14): 5271–5274. (d) Mason, J.A., Oktawiec, J., Taylor, M.K. et al. (2015). Methane storage in flexible metal-organic frameworks with intrinsic thermal management. *Nature* 527 (7578): 357–361. (e) Alezi, D., Belmabkhout, Y., Suyetin, M. et al. (2015). MOF crystal chemistry paving the way to gas storage needs: aluminum-based soc-MOF for CH<sub>4</sub>, O<sub>2</sub>, and CO<sub>2</sub> storage. *Journal of the American Chemical Society* 137 (41): 13308–13318. (f) Li, B., Wen, H.-M., Wang, H. et al. (2014). A porous metal-organic framework with dynamic pyrimidine groups exhibiting record high methane storage working capacity. *Journal of the American Chemical Society* 136 (17): 6207–6210. (g) Peng, Y., Krungleviciute, V., Eryazici, I. et al. (2013). Methane storage in metal-organic frameworks: current records, surprise findings, and challenges. *Journal of the American Chemical Society* 135 (32): 11887–11894. (h) Mason, J.A., Veenstra, M., and Long, J.R. (2014). Evaluating metal-organic frameworks for natural gas storage. *Chemical Science* 5 (1): 32–51. (i) Fracaroli, A.M., Furukawa, H., Suzuki, M. et al. (2014). Metal-organic frameworks with precisely designed interior for carbon dioxide capture in the presence of water. *Journal of the American Chemical Society* 136 (25): 8863–8866. (j) McDonald, T.M., Mason, J.A., Kong, X. et al. (2015). Cooperative insertion of CO<sub>2</sub> in diamine-appended metal-organic frameworks. *Nature* 519 (7543): 303–308. (k) Nguyen, N.T.T., Furukawa, H., Gándara, F. et al. (2014). Selective capture of carbon dioxide under humid conditions by hydrophobic chabazite-type zeolitic imidazolate frameworks. *Angewandte Chemie International Edition* 53 (40): 10645–10648. (l) Mason, J.A., McDonald, T.M., Bae, T.-H. et al. (2015). Application of a high-throughput analyzer in evaluating solid adsorbents for post-combustion carbon capture via multicomponent adsorption of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. *Journal of the American Chemical Society* 137 (14): 4787–4803. (m) Nugent, P., Belmabkhout, Y., Burd, S.D. et al. (2013). Porous materials with optimal adsorption thermodynamics and kinetics for CO<sub>2</sub> separation. *Nature* 495 (7439): 80–84. (n) Furukawa, H., Gándara, F., Zhang, Y.-B. et al. (2014). Water adsorption in porous metal-organic frameworks and related materials. *Journal of the American Chemical Society* 136 (11): 4369–4381. (o) Canivet, J., Fateeva, A., Guo, Y. et al. (2014). Water adsorption in MOFs: fundamentals and applications. *Chemical Society Reviews* 43 (16): 5594–5617. (p) Henninger, S.K., Habib,

- H.A., and Janiak, C. (2009). MOFs as adsorbents for low temperature heating and cooling applications. *Journal of the American Chemical Society* 131 (8): 2776–2777. (q) Henninger, S.K., Jeremias, F., Kummer, H., and Janiak, C. (2012). MOFs for use in adsorption heat pump processes. *European Journal of Inorganic Chemistry* 2012 (16): 2625–2634. (r) Küsgens, P., Rose, M., Senkowska, I. et al. (2009). Characterization of metal-organic frameworks by water adsorption. *Microporous and Mesoporous Materials* 120 (3): 325–330. (s) Seo, Y.-K., Yoon, J.W., Lee, J.S. et al. (2012). Energy-efficient dehumidification over hierarchically porous metal-organic frameworks as advanced water adsorbents. *Advanced Materials* 24 (6): 806–810. (t) Ehrenmann, J., Henninger, S.K., and Janiak, C. (2011). Water adsorption characteristics of MIL-101 for heat-transformation applications of MOFs. *European Journal of Inorganic Chemistry* 2011 (4): 471–474. (u) Akiyama, G., Matsuda, R., and Kitagawa, S. (2010). Highly porous and stable coordination polymers as water sorption materials. *Chemistry Letters* 39 (4): 360–361. (v) Kim, H., Yang, S., Rao, S.R. et al. (2017). Water harvesting from air with metal-organic frameworks powered by natural sunlight. *Science* 356 (6336): 430–434.
- 4 (a) Manna, K., Ji, P., Lin, Z. et al. (2016). Chemoselective single-site earth-abundant metal catalysts at metal-organic framework nodes. *Nature Communications* 7: 12610. (b) Wang, C., Xie, Z., deKrafft, K.E., and Lin, W. (2011). Doping metal-organic frameworks for water oxidation, carbon dioxide reduction, and organic photocatalysis. *Journal of the American Chemical Society* 133 (34): 13445–13454. (c) Wu, C.-D., Hu, A., Zhang, L., and Lin, W. (2005). A homochiral porous metal-organic framework for highly enantioselective heterogeneous asymmetric catalysis. *Journal of the American Chemical Society* 127 (25): 8940–8941. (d) Metzger, E.D., Brozek, C.K., Comito, R.J., and Dincă, M. (2016). Selective dimerization of ethylene to 1-butene with a porous catalyst. *ACS Central Science* 2 (3): 148–153. (e) Mondloch, J.E., Katz, M.J., Isley, W.C. III, et al. (2015). Destruction of chemical warfare agents using metal-organic frameworks. *Nature Materials* 14 (5): 512–516. (f) Xiao, D.J., Bloch, E.D., Mason, J.A. et al. (2014). Oxidation of ethane to ethanol by N<sub>2</sub>O in a metal-organic framework with coordinatively unsaturated iron(II) sites. *Natural Chemistry* 6 (7): 590–595. (g) Feng, D., Gu, Z.-Y., Li, J.-R. et al. (2012). Zirconium-metalloporphyrin PCN-222: mesoporous metal-organic frameworks with ultrahigh stability as biomimetic catalysts. *Angewandte Chemie International Edition* 51 (41): 10307–10310. (h) Dang, D., Wu, P., He, C. et al. (2010). Homochiral metal-organic frameworks for heterogeneous asymmetric catalysis. *Journal of the American Chemical Society* 132 (41): 14321–14323. (i) Manna, K., Zhang, T., Greene, F.X., and Lin, W. (2015). Bipyridine- and phenanthroline-based metal-organic frameworks for highly efficient and tandem catalytic organic transformations via directed C-H activation. *Journal of the American Chemical Society* 137 (7): 2665–2673.
- 5 (a) Sun, L., Miyakai, T., Seki, S., and Dincă, M. (2013). Mn<sub>2</sub>(2,5-disulfhydrylbenzene-1,4-dicarboxylate): a microporous metal-organic framework with infinite (–Mn–S–)<sup>∞</sup> chains and high intrinsic charge mobility. *Journal of the American Chemical Society* 135 (22): 8185–8188.

- (b) Sun, L., Hendon, C.H., Minier, M.A. et al. (2015). Million-fold electrical conductivity enhancement in  $\text{Fe}_2(\text{DEBDC})$  versus  $\text{Mn}_2(\text{DEBDC})$  ( $E = \text{S}, \text{O}$ ). *Journal of the American Chemical Society* 137 (19): 6164–6167.
- (c) Gándara, F., Uribe-Romo, F.J., Britt, D.K. et al. (2012). Porous, conductive metal-triazolates and their structural elucidation by the charge-flipping method. *Chemistry A European Journal* 18 (34): 10595–10601.
- (d) Sheberla, D., Sun, L., Blood-Forsythe, M.A. et al. (2014). High electrical conductivity in  $\text{Ni}_3(2,3,6,7,10,11\text{-hexaiminotriphenylene})_2$ , a semiconducting metal-organic graphene analogue. *Journal of the American Chemical Society* 136 (25): 8859–8862.
- (e) Ōkawa, H., Sadakiyo, M., Yamada, T. et al. (2013). Proton-conductive magnetic metal-organic frameworks,  $\{\text{NR}_3(\text{CH}_2\text{COOH})\}[\text{M}_a^{\text{II}}\text{M}_b^{\text{III}}(\text{ox})_3]$ : effect of carboxyl residue upon proton conduction. *Journal of the American Chemical Society* 135 (6): 2256–2262.
- (f) Nguyen, N.T.T., Furukawa, H., Gándara, F. et al. (2015). Three-dimensional metal-catecholate frameworks and their ultrahigh proton conductivity. *Journal of the American Chemical Society* 137 (49): 15394–15397.
- (g) Wan, S., Gándara, F., Asano, A. et al. (2011). Covalent organic frameworks with high charge carrier mobility. *Chemistry of Materials* 23 (18): 4094–4097.
- 6 (a) Sheberla, D., Bachman, J.C., Elias, J.S. et al. (2017). Conductive MOF electrodes for stable supercapacitors with high areal capacitance. *Nature Materials* 16 (2): 220–224. (b) Mulzer, C.R., Shen, L., Bisbey, R.P. et al. (2016). Superior charge storage and power density of a conducting polymer-modified covalent organic framework. *ACS Central Science* 2 (9): 667–673. (c) Lin, S., Diercks, C.S., Zhang, Y.-B. et al. (2015). Covalent organic frameworks comprising cobalt porphyrins for catalytic  $\text{CO}_2$  reduction in water. *Science* 349 (6253): 1208–1213. (d) Miner, E.M., Fukushima, T., Sheberla, D. et al. (2016). Electrochemical oxygen reduction catalysed by  $\text{Ni}_3(\text{hexaiminotriphenylene})_2$ . *Nature Communications* 7: 10942.
- 7 (a) Chen, Y., Li, S., Pei, X. et al. (2016). A solvent-free hot-pressing method for preparing metal-organic-framework coatings. *Angewandte Chemie International Edition* 55 (10): 3419–3423. (b) Li, Y.-S., Liang, F.-Y., Bux, H. et al. (2010). Molecular sieve membrane: supported metal-organic framework with high hydrogen selectivity. *Angewandte Chemie International Edition* 49 (3): 548–551. (c) Guo, H., Zhu, G., Hewitt, I.J., and Qiu, S. (2009). “Twin copper source” growth of metal-organic framework membrane:  $\text{Cu}_3(\text{BTC})_2$  with high permeability and selectivity for recycling  $\text{H}_2$ . *Journal of the American Chemical Society* 131 (5): 1646–1647. (d) Bux, H., Liang, F., Li, Y. et al. (2009). Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *Journal of the American Chemical Society* 131 (44): 16000–16001. (e) Bae, T.-H., Lee, J.S., Qiu, W. et al. (2010). A high-performance gas-separation membrane containing submicrometer-sized metal-organic framework crystals. *Angewandte Chemie International Edition* 49 (51): 9863–9866. (f) Rodenas, T., Luz, I., Prieto, G. et al. (2015). Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nature Materials* 14 (1): 48–55. (g) Zornoza, B., Martínez-Joaristi, A., Serra-Crespo, P. et al. (2011). Functionalized flexible MOFs as fillers in mixed matrix membranes for highly

- selective separation of CO<sub>2</sub> from CH<sub>4</sub> at elevated pressures. *Chemical Communications* 47 (33): 9522–9524. (h) Bachman, J.E., Smith, Z.P., Li, T. et al. (2016). Enhanced ethylene separation and plasticization resistance in polymer membranes incorporating metal-organic framework nanocrystals. *Nature Materials* 15 (8): 845–849. (i) Rieter, W.J., Taylor, K.M.L., and Lin, W. (2007). Surface modification and functionalization of nanoscale metal-organic frameworks for controlled release and luminescence sensing. *Journal of the American Chemical Society* 129 (32): 9852–9853. (j) Rieter, W.J., Taylor, K.M.L., An, H. et al. (2006). Nanoscale metal-organic frameworks as potential multimodal contrast enhancing agents. *Journal of the American Chemical Society* 128 (28): 9024–9025. (k) Horcajada, P., Chalati, T., Serre, C. et al. (2010). Porous metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging. *Nature Materials* 9 (2): 172–178. (l) Wuttke, S., Braig, S., Preiß, T. et al. (2015). MOF nanoparticles coated by lipid bilayers and their uptake by cancer cells. *Chemical Communications* 51 (87): 15752–15755. (m) Zhuang, J., Kuo, C.-H., Chou, L.-Y. et al. (2014). Optimized metal-organic-framework nanospheres for drug delivery: evaluation of small-molecule encapsulation. *ACS Nano* 8 (3): 2812–2819. (n) Zheng, H., Zhang, Y., Liu, L. et al. (2016). One-pot synthesis of metal-organic frameworks with encapsulated target molecules and their applications for controlled drug delivery. *Journal of the American Chemical Society* 138 (3): 962–968.
- 8 (a) Choi, K.M., Na, K., Somorjai, G.A., and Yaghi, O.M. (2015). Chemical environment control and enhanced catalytic performance of platinum nanoparticles embedded in nanocrystalline metal-organic frameworks. *Journal of the American Chemical Society* 137 (24): 7810–7816. (b) Rungtaweeworanit, B., Baek, J., Araujo, J.R. et al. (2016). Copper nanocrystals encapsulated in Zr-based metal-organic frameworks for highly selective CO<sub>2</sub> hydrogenation to methanol. *Nano Letters* 16 (12): 7645–7649. (c) Zhao, M., Yuan, K., Wang, Y. et al. (2016). Metal-organic frameworks as selectivity regulators for hydrogenation reactions. *Nature* 539 (7627): 76–80. (d) Lu, G., Li, S., Guo, Z. et al. (2012). Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nature Chemistry* 4 (4): 310–316. (e) Zhao, M., Deng, K., He, L. et al. (2014). Core-shell palladium nanoparticle@metal-organic frameworks as multifunctional catalysts for cascade reactions. *Journal of the American Chemical Society* 136 (5): 1738–1741. (f) Kuo, C.-H., Tang, Y., Chou, L.-Y. et al. (2012). Yolk-shell nanocrystal@ZIF-8 nanostructures for gas-phase heterogeneous catalysis with selectivity control. *Journal of the American Chemical Society* 134 (35): 14345–14348.
- 9 (a) Boyd, P.G., Moosavi, S.M., Witman, M., and Smit, B. (2017). Force-field prediction of materials properties in metal-organic frameworks. *The Journal of Physical Chemistry Letters* 8 (2): 357–363. (b) Yang, D., Bernales, V., Islamoglu, T. et al. (2016). Tuning the surface chemistry of metal organic framework nodes: proton topology of the metal-oxide-like Zr<sub>6</sub> nodes of UiO-66 and NU-1000. *Journal of the American Chemical Society* 138 (46): 15189–15196. (c) Dzubak, A.L., Lin, L.-C., Kim, J. et al. (2012). *Ab initio*

- carbon capture in open-site metal-organic frameworks. *Nature Chemistry* 4 (10): 810–816. (d) Tsivion, E., Long, J.R., and Head-Gordon, M. (2014). Hydrogen physisorption on metal-organic framework linkers and metalated linkers: a computational study of the factors that control binding strength. *Journal of the American Chemical Society* 136 (51): 17827–17835. (e) Lin, L.-C., Berger, A.H., Martin, R.L. et al. (2012). *In silico* screening of carbon-capture materials. *Nature Materials* 11 (7): 633–641. (f) Frost, H., Düren, T., and Snurr, R.Q. (2006). Effects of surface area, free volume, and heat of adsorption on hydrogen uptake in metal-organic frameworks. *The Journal of Physical Chemistry B* 110 (19): 9565–9570. (g) Fairen-Jimenez, D., Moggach, S.A., Wharmby, M.T. et al. (2011). Opening the gate: framework flexibility in ZIF-8 explored by experiments and simulations. *Journal of the American Chemical Society* 133 (23): 8900–8902.
- 10 Furukawa, H., Müller, U., and Yaghi, O.M. (2015). “Heterogeneity within order” in metal-organic frameworks. *Angewandte Chemie International Edition* 54 (11): 3417–3430.