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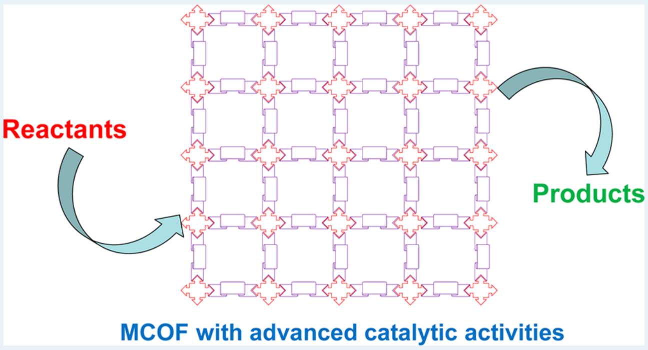
Main-Chain Organic Frameworks with Advanced Catalytic Functionalities

Yugen Zhang* and Jackie Y. Ying*

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos Singapore 138669 Singapore



ABSTRACT: Over the past 10 years, there have been remarkable advances in the development of porous organic frameworks, which include covalent organic framework (COF), conjugated microporous polymer (CMP), porous aromatic framework (PAF), and covalent triazine framework (CTF). The emergence of organic frameworks brings about tremendous possibilities for heterogeneous catalyst development. In addition to well-controlled surface chemistry and porosity, these materials possess high physicochemical stability, high density or loading of functional groups with homogeneous distribution, and high surface area. These allow the organic framework catalysts to have potentially high activity and reusability. In particular, main-chain organic frameworks (MCOFs) represent a class of organic materials whereby the functionalities are directly embedded in the framework. They are generally synthesized through the "bottom-up" approach. In catalytic MCOFs, the functional moieties can have direct interactions with the main framework, leading to unique properties beyond the general advantages associated with porous polymer heterogeneous catalysts. Higher activity, selectivity, and stability can be attained with MCOF catalyst designs. This mini Review summarizes recent developments of MCOFs that have demonstrated superior catalytic properties as compared with their homogeneous analogs. The synthesis, structure and advanced functionalities of these MCOF catalysts are discussed, along with perspectives for future development.

KEYWORDS: *main-chain organic framework, porous organic framework, heterogeneous catalyst, functional material, synergistic effect*

1. INTRODUCTION

The rapid growth in organic frameworks has been fueled by potential applications in the areas of gas storage, molecular separation, energy transformation, and catalysis.[1−17] Using the "bottom-up" approach, polymeric frameworks are synthesized from selected monomers or structural linkers via covalent bond formation, such as condensation and coupling reactions. The key to bottom-up construction of organic frameworks is the use of rigid building units with multiconnectivities.[1−9] The introduction of catalytic moieties into the frameworks[14−17] may involve a postsynthesis strategy or a bottom-up strategy. Catalytic moieties are frequently introduced into the frameworks via postsynthesis modification, such as chemical transformation and coordinative incorporation. Such an approach is versatile and easy to accomplish synthetically; however, the functionalities in the framework may be difficult to utilize. In the case of postsynthesis via coordinative incorporation, metal catalysts are hard to optimize in loading and dispersion. This in turn limits the possibility of attaining high activity with the loaded catalysts.[18,19]

The bottom-up approach is a straightforward, but more challenging, strategy for the construction of organic frameworks.[20] The catalytic functionalities are pre-embedded or attached onto the building units before assembly into the polymer frameworks.[21] The polymer frameworks usually possess a homogeneous distribution of functional moieties, a high density of functional groups, and high hydrothermal and chemical stabilities from the direct, one-step synthesis. The challenge in the bottom-up approach is the design of building modules, which need to include the catalytic functionality as well as to fulfill the construction requirements.

There are two types of functional models for framework structures: a side-chain organic framework (SCOF) and a main-chain organic framework (MCOF) (Scheme 1). In the former, the catalytic functionalities are dangled onto the main organic framework via postsynthesis or bottom-up approach. Although the side-chain moieties are still affected by the microenvironment of the framework, they do not have a high level of synergism with the framework. The SCOF-based heterogeneous catalysts can provide excellent stability and recyclability. However, in most of the cases, they do not display catalytic activities comparable to their homogeneous analogs, which is mainly due to the limited accessibility of the active center.[18,19,22] MCOF can be designed with synergistic effects that can promote the catalytic activity. This would alter the

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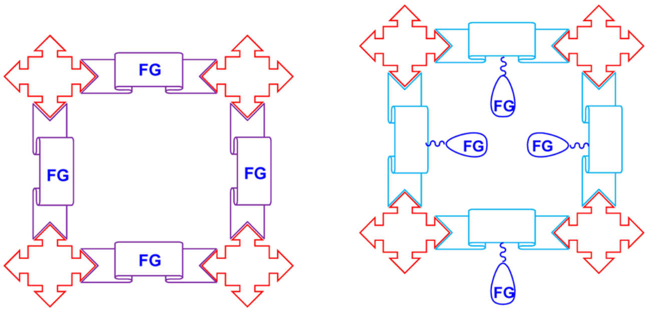
Scheme 1. Structural Schematics of (a) MCOF and (b) SCOF



(a) (b)

properties of the catalytic species, which is difficult to achieve with SCOF.

In MCOFs, the functionalities are directly embedded into the framework.[23] Different linker groups in the framework would affect the embedded functionalities. The functional moieties can have direct interactions and synergisms with the main framework, providing possibilities for designing advanced or enhanced properties. There have been a few excellent reviews on the synthesis and applications of polymer frameworks in the past few years.[1−17,20] This mini Review focuses on MCOFs that have demonstrated advanced catalytic functionalities. The study of their structures and functionalities may provide useful information for understanding structure−property−activity relationships and ideas for designing new functional materials and catalysts.

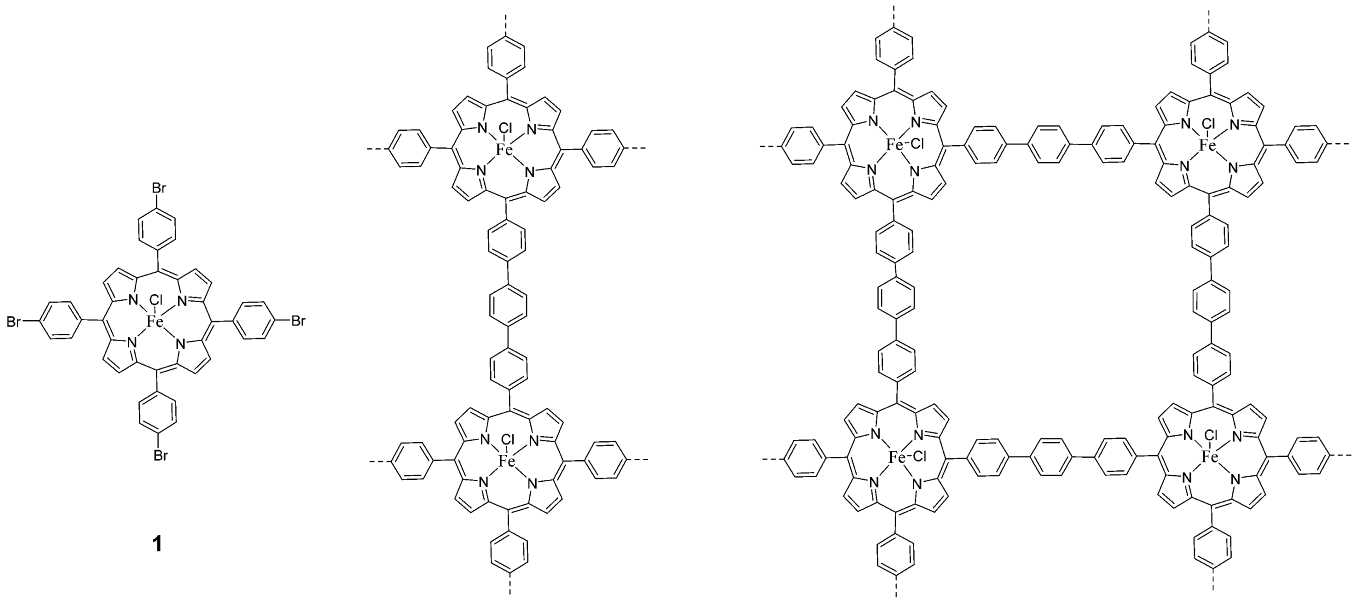
2. ISOLATED HETEROGENEOUS LIGANDS FOR SINGLE-SITE CATALYSTS

In a small-molecule catalyst system, it is difficult to manipulate ligand−metal coordination morphology and to control the interactions between ligands and complexes. However, these issues can be resolved in MCOF systems to achieve advanced catalytic functionalities via the design of building units and the bottom-up synthetic approach. In MCOFs, the entire framework can be seen as part of the functionality (Scheme 1a). The framework skeleton is analogous to a multidentate ligand system, yet the individual ligand is isolated in a fixed location. The porous framework can stabilize a catalytically active single-site metal center with a single ligand that is embedded in the framework. It represents a coordination environment that is clean and isolated and has no homogeneous analogs. Such a unique structure can lead to unusual properties and activities.

Metalloporphyrins and related compounds facilitate many important biological processes; this has led to intensive research on porphyrins in catalysis.[24,25] Porphyrin catalysts have been heterogenized by immobilization or encapsulation in porous solids, such as zeolites and polymers.[25] Because of their unique macrocyclic structure, they can be easily incorporated into organic frameworks by forming interlinks with rigid units and by forming porous organic polymers (POPs). The macrocycles can then bind to various metal ions to form heterogeneous metalloporphyrin catalysts.[26] By embedding the prophyrin units into MCOFs, catalyst deactivation commonly associated with porphyrin aggregation can be avoided.

Jiang's group has synthesized metalloporphyrin polymers with an entirely aromatic skeleton by the Suzuki−Miyaura cross-coupling polycondensation of iron(III) tetrakis(4′-bromophenyl)prophyrin derivative **1** and 1,4-phenyldiboronic acid in the presence of Pd(0) catalyst.[27] The two-dimensional (2D) aromatic framework **3** has a 2.69 nm pore width and a large surface area of 1270 m^2/g. This organic framework has an exceptionally high loading of catalytic sites. It was applied as a heterogeneous catalyst for converting various sulfides to sulfoxides under oxygen or air at room temperature in toluene with 3 equiv of isobutyraldehyde (IBA) (Scheme 2). A high turnover number (TON) of up to 97 320 in 40 h was achieved with very high selectivity, with little or no overoxidized products. MCOF catalyst **3** was much more active than

Scheme 2. Structure of Monomer 1, Linear Polymer 2 and MCOF 3 of Iron Porphyrins

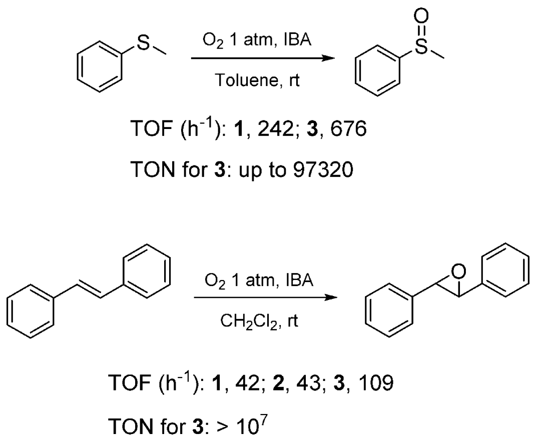


1 **2** **3**

monomeric metalloporphyrin **1**. The increased activity could be attributed to the MCOF framework system with aromatic skeleton and high surface area.

MCOF catalyst **3** was also found to activate molecular oxygen in the epoxidation of olefins with a very high TON (6.7 × 10^7) and turnover frequency (TOF) (9300 min^{-1}).[28] These values were close to those achieved by enzyme cytochrome P450. Catalyst **3** catalyzed the selective epoxidation of *trans*-stilbene with IBA and O_2 under ambient pressure and temperature. With 1 mg of **3**, *trans*-stilbene oxide was produced in 98% conversion with 97% selectivity after 9 h without any formation of *cis*-stilbene oxide. In contrast, monomeric metalloporphyrin homogeneous complex showed a low activity (Scheme 3).[29] It was also found that the catalytic activity increased with catalyst surface area. A linear control polymer **2** was synthesized and exhibited a much lower activity than **3**. The results also demonstrated that the main-chain framework was important to attaining high catalytic activity. For the same framework system, a higher surface area could be achieved with a higher ordered structure and a more conjugated skeleton. A 2D framework would present a more conjugated system than a 1D polymer.

Scheme 3. Catalytic Oxidation of Thioanisole and Stilbene over 1−3



TOF (h^{-1}): **1**, 242; **3**, 676

TON for **3**: up to 97320

TOF (h^{-1}): **1**, 42; **2**, 43; **3**, 109

TON for **3**: > 10^7

In another report, 3D conjugated porphyrin framework **5** was synthesized by the condensation of presynthesized free-base porphyrin monomer **4** and tetraamine.[30] Next, metal ions, such as Fe(II) and Mn(II), were incorporated into the macrocycles to form metalloporphyrin polymer. Compared with the homogeneous analogs, meso-tetrapentafluorophenylporphyrin (TPFPP)−MnCl (**5-Mn**) showed a slower initial conversion, but a much higher overall TON (2000 vs 780 in 30 h) for the epoxidation of styrene with iodosylbenzene as oxidant (Scheme 4). This example again demonstrated the advanced catalytic property of the porous organic framework. The 3D porphyrin framework provided clean, well-dispersed, single-site active species that contributed to the high catalytic activity.

Manipulating the coordination environment of organometallic sites is critical in the design of highly active organometallic catalysts. Creating an unsaturated organometallic site is one of the key strategies to achieve active catalysts; however, this is very challenging for homogeneous, small-molecule catalysts.[31] For example, homogeneous metal catecholate complexes frequently form bis- or tris-chelated complexes to stabilize the metal center. Such complexes lack reactive sites and are often catalytically inactive or susceptible to ligand loss or deactivation.[32] MCOFs provide an ideal platform to design a unique single-site coordination environment for the organometallic sites with stabilized and unsaturated catalysts; this is typically not possible in the homogeneous, supramolecular or zeolitic systems.

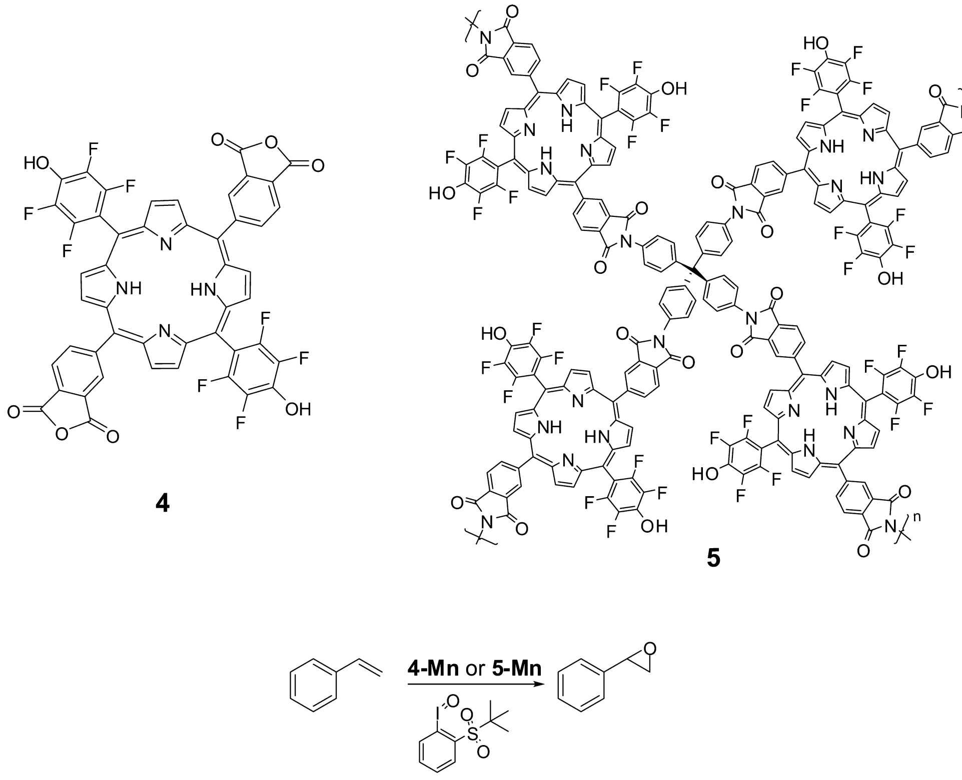
Nguyen's group recently reported a catechol-containing MCOF **7**.[33,34] In this design, catechol units **6** were embedded into the main chain of a 3D organic skeleton. The framework was built with rigid aromatic units. It provided an isolated catechol environment that could bind single metal atoms, resulting in monocatecholated metal sites with a high degree of coordination unsaturation. Fe(II) was incorporated into the framework of **7** for catalytic hydrosilylation of ketones and aldehydes (Scheme 5).[35] The resulting Fe-cat-MCOF **9** was extremely sensitive to oxygen, but stable in the absence of O_2 when suspended in solution or stored as a solid. In contrast, the Fe(II) source, $Fe[N(SiMe_3)_2]_2$, was unstable in solution. In the hydrosilylation of benzaldehyde with diphenylsilane, **9** showed a TOF of 1.11 s^{-1}, which was much higher than $Fe[N(SiMe_3)_2]_2$ (0.007 s^{-1}). Catalyst **9** could also be recovered as a solid and easily reused. The molecular analog of Fe-cat-MCOF was prepared by mixing $Fe[N(SiMe_3)_2]_2$ with 3,6-di-*tert*-butyl catechol; the resulting system, **8**, showed very low activities for catalytic hydrosilylation. The rapid hydrosilylation of benzaldehyde over **9** was unusual for iron-based catalysts and could be attributed to the isolated and unsaturated metallic sites. This catalyst further accommodated a broad range of substrates. This example of low-coordination, single-site metal catecholate with enhanced catalytic functionality demonstrated the great potential of functional MCOFs. A similar concept has also been applied to several other catalytic systems.[36,37]

3. THE EFFECT OF POROSITY ON CATALYTIC ACTIVITY

One of the important characteristics for porous organic frameworks is that porosity can be controlled via bottom-up synthesis. It is well-known that pore structure is important to mass transfer in heterogeneous catalysis.[1−17] A well-designed pore structure can provide a positive synergistic effect and advanced catalytic functionality in porous organic frameworks.

A recent report presented conjugated microporous polymers (CMPs) with embedded Salen-Co/Al/Zn complexes **10−12** (Scheme 6).[38,39] These polymers have high BET surface areas (>750 m^2/g) and high pore volumes (1.81−2.81 cm^3/g). They demonstrated good CO_2 capture capacity as a result of their microporosity. Al-CMP and Co-CMP achieved CO_2 uptakes of 79.3 and 76.5 mg/g, respectively, at 298 K and 1 atm. Salen-Co/Al/Zn-containing CMPs were also excellent catalysts for the conversion of propylene oxide to propylene carbonate with CO_2. These materials were capable of both CO_2 capture and conversion because of their porous structure and metal−organic moieties. Co-CMP has a TON of 201 (yield = 98.1%), which was higher than the homogeneous catalyst Salen-Co-OAc **13** (TON = 173, yield = 84.6%) under the same reaction conditions (Scheme 6). Its microporous structure captured CO_2 under reaction conditions, concentrating CO_2 around the catalytic active sites. Similar enhancement of catalytic activity in the conversion of epoxides to carbonates was also observed with other porous organic-framework-based catalysts.[40−44] The concept of using a porous structure of organic framework to concentrate the reactants to achieve advanced catalytic functionality has also been applied to several other cases.

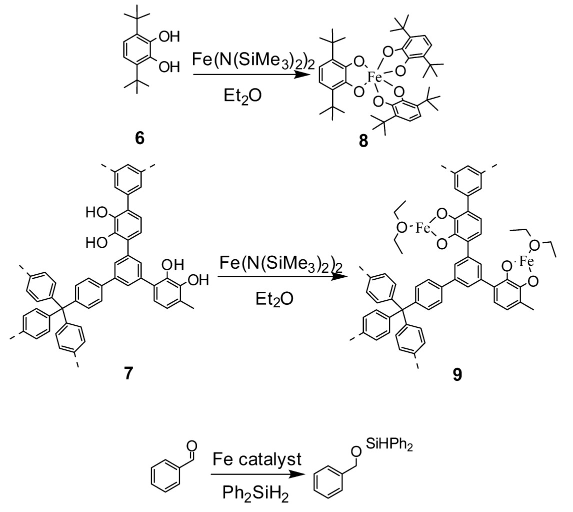
Scheme 4. Structure of Porphyrin Monomer 4 and Porphyrin-MCOF 5[a]



TON: **4-Mn**, 780; **5-Mn**, 2000

[a]Their Mn-complexes catalyzed styrene oxidation.

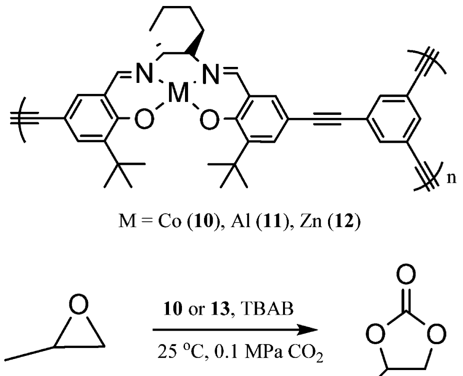
Scheme 5. Structure and Coordination Motif of Catechols 6 and 8, and Catechol-Containing MCOFs 7 and 9[a]



TOF (S^{-1}): **9**, 1.11; **8**, 0; $Fe(N(SiMe_3)_2)_2$, 0.007

[a]Hydrosilylation of aldehyde was successfully catalyzed by **9**.

Scheme 6. Salen/Metal-Containing MCOFs 10, 11, and 12 and Their Application in the Conversion of Epoxide to Carbonate with CO_2



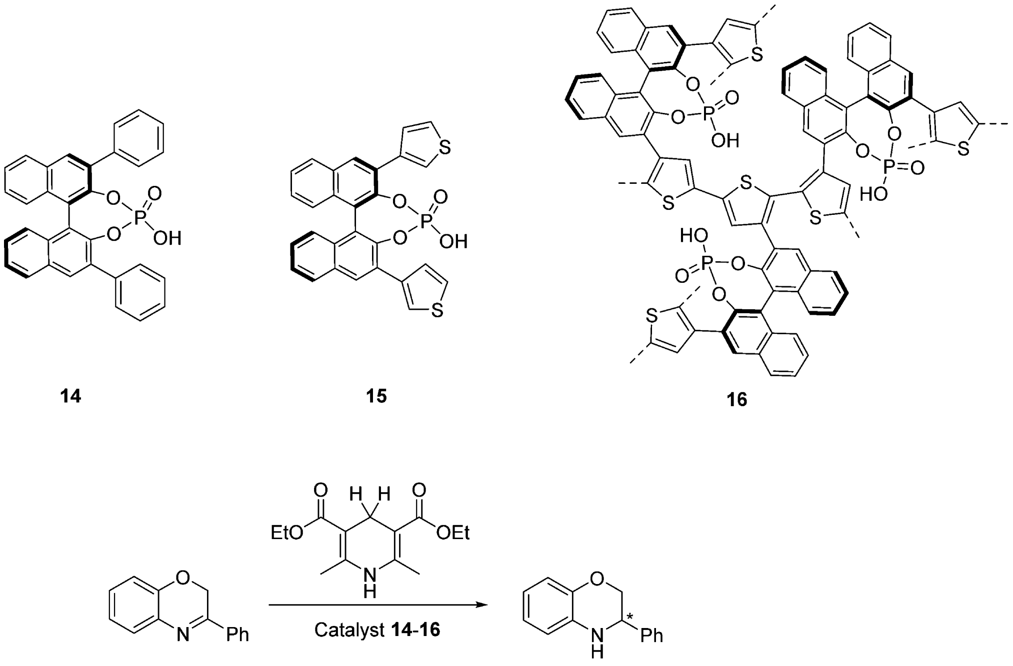
M = Co (**10**), Al (**11**), Zn (**12**)

10: TON 197, yield 96.0%
13: TON 173, yield 84.6%

McKeown et al. reported a heterogeneous organocatalyst system that was assembled from triamino-triptycene monomers using a Troger's base formation process.[45] This porous organic framework has significant microporosity with a surface area of up to 1000 m^2/g. It has a high density of amino groups that could be used as basic catalytic sites. This catalyst was tested in the Knoevenagel reaction between malononitrile and benzaldehyde and attained a much higher catalytic activity than the homogeneous analog (TON = 37 vs 15, TOF = 2.5 vs 1.0). The enhancement of activity was attributed to the rapid adsorption of malononitrile within the porous framework, where the catalytic active sites were located, thereby accelerating the reaction.

In another example, microporous polyisocyanurate (PICU) organic framework was synthesized by trimerization of diisocyanate.[46,47] PICU-supported iron catalyst was tested in the oxidation of benzyl alcohol to benzaldehyde with H_2O_2 in aqueous solution under mild reaction conditions. PICU-Fe

Scheme 7. Structure of Chiral Monomer Catalysts 14 and 15, and Chiral MCOF Catalyst 16, and the Application of 14−16 in Transfer Hydrogenation



Conversion (%): **14**, low; **15**, 99; **16**, 99
ee (%): **14**, 6; **15**, 34; **16**, 47-56

showed selectivity and activity superior to that of the other Fe catalysts. This was attributed to the microporosity and excellent absorption capacity of PICU-Fe. Benzyl alcohol was believed to be concentrated in the micropores of PICU, promoting the catalytic conversion over the active Fe sites. High selectivity was also achieved in an oxidizing environment of a dilute aqueous H_2O_2 solution. This example demonstrated again the potential of achieving advanced catalytic functionality via the well-controlled pore structure of organic framework.

4. EMBEDDING CHIRAL MOTIFS IN POROUS ORGANIC FRAMEWORKS

Because of the high cost of chiral ligands, heterogenization of asymmetric catalysts has been of high interest. Most studies were focused on a postsynthesis approach to graft chiral ligands onto the frameworks or solid surfaces, that is, using a side-chain model.[48,49] The chiral centers have loose interactions with each other as well as with the framework. In most cases, this resulted in a decrease in catalytic activity and selectivity. In contrast, in MCOFs, chiral ligands were fixed in the framework.[50−54] The coordinated metal catalytic sites or the framework organocatalysts have minimal undesired self-interactions and interactions with the framework surface. On the other hand, embedding chiral motifs in the framework would create chiral pore structures, which could induce enantioselectivity.[55] Catalytic activity and selectivity could be tuned by adjusting the microenvironment of the catalytic sites with different building units.

Asymmetric nonporous heterogeneous organocatalysts have been synthesized with a bottom-up approach recently.[56−58] Bleschke et al. derived the first porous heterogeneous chiral organocatalyst by introducing chiral 1,1′-bi-2-naphthol (BINOL) derivatives into a MCOF via polymerization of two thienyl-substituted BINOLs.[59] The polymer skeleton was used to provide steric hindrance to influence the enantioselectivity of the chiral sites. BINOL-MCOF was examined for transfer hydrogenation of dihydro-2*H*-benzoxazine (Scheme 7). It demonstrated an activity similar to that of the homogeneous catalysts, but an enhanced enantioselectivity. The latter could be due to the greater steric hindrance of the skeleton and the electronic effect associated with an extended thiophene ring system.

Jorgensen-Hayashi (JH) catalyst has been embedded in a MCOF by $Co_2(CO)_8$-mediated trimerization of ethynyl-modified JH catalyst and tetra(4-ethynylphenyl)methane.[60] High surface area (881 m^2/g), wide openings, and interconnected pores were achieved for JH-MCOF **18**. In the asymmetric Michael addition of aldehydes to nitroalkenes (Scheme 8), **18** achieved product yields of up to 96%, high enantioselectivities (93−99% ee), and high diastereoselectivities (d.r.) (74:26 to 97:3); **18** also showed higher activity and selectivity than the homogeneous JH catalyst **17** and could be easily reused.

For the chiral porous organic framework organocatalyst, the catalytic sites are directly embedded in the framework. The framework structure has a direct impact on the catalytic site. The modification of the chiral catalytic center would also change the interaction with the substrates, thereby altering the catalytic activity and selectivity. Thus, the manipulation of catalyst microenvironment could affect both the catalytic activity and selectivity, as illustrated by heterogeneous catalysts **16** and **18**, noted above. In contrast, chiral, porous, organic-framework-ligated organometallic catalysts have indirect interaction with the main-chain framework. In such a case, it would be more difficult to improve the activity and selectivity via framework structure modification. As shown in the two examples below, although the activities were greater for the

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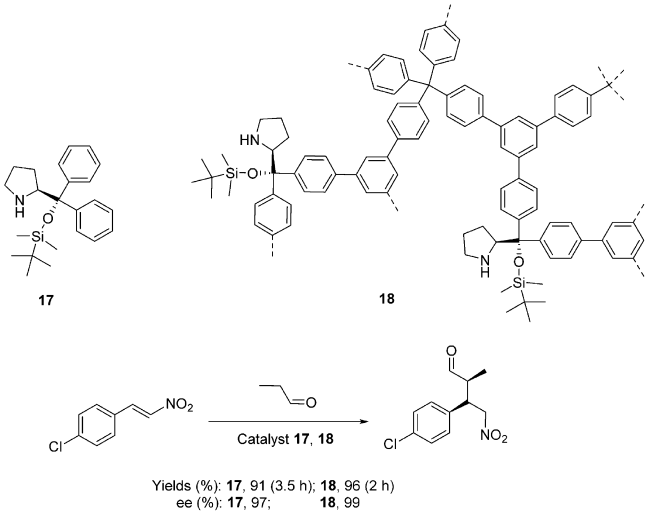
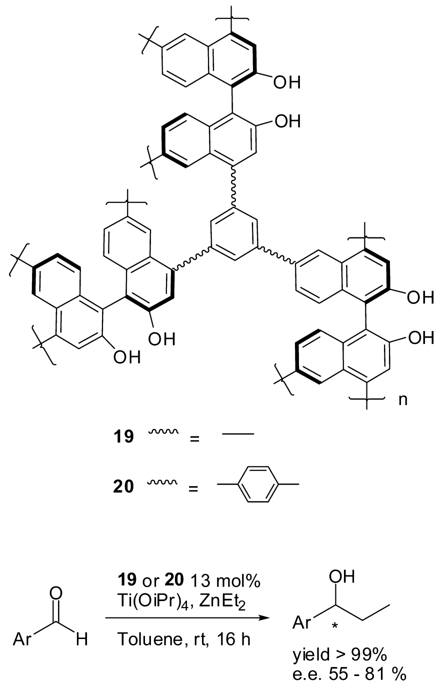
Scheme 8. Asymmetric Michael Addition Catalyzed by JH Catalyst 17 and JH MCOF Catalyst 18



heterogeneous systems (**20** and **22**), the selectivities were still slightly lower than the homogeneous analogs.[61−63]

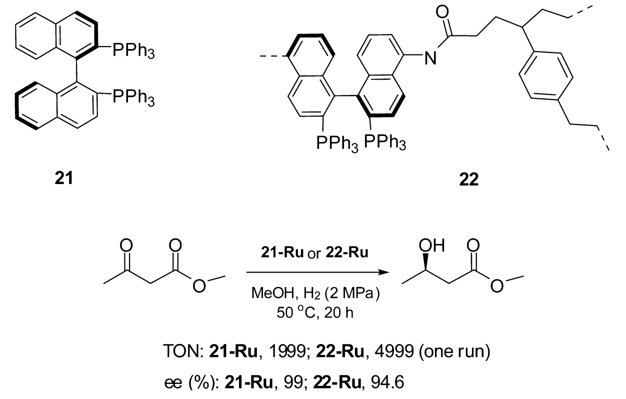
Lin et al. reported the synthesis of a series of chiral, cross-linked, main-chain polymers based on 1,1′-binaphthyl building blocks.[64] Chiral POPs **19** and **20** were synthesized on the basis of alkyne trimerization. They have surface areas of 689−974 m^2/g, pore volumes of 0.84−1.23 cm^3/g, and very high densities of chiral dihydroxyl groups in the main chain. These materials were treated with $Ti(O^iPr)_4$ to generate chiral Lewis acid catalysts. Catalysts **19** and **20** with $Ti(O^iPr)_4$ showed high activities for the asymmetric diethylzinc addition to various aryl aldehydes with almost quantitative yield for secondary alcohols, but modest to good enantioselectivity (55−81%) (Scheme 9).

Scheme 9. Structure of Chiral MCOF Catalysts 19 and 20 and the Application of 19 and 20 in Catalytic Asymmetric Diethylzinc Addition to Aldehyde



Recently, a mesoporous polymer, **22**, with BINAP ligands in the framework was synthesized by copolymerization of divinylbenzene and divinylbinaphthyl phosphine.[65] It has a surface area of ∼550 m^2/g. $[RuCl_2(benzene)]_2$ coordinated effectively to the framework. In asymmetric hydrogenation over **22-Ru**, a number of *β*-ketone esters was completely converted to the corresponding chiral alcohols with up to 95% ee and TONs of up to 5000 (Scheme 10). The higher activity of **22-Ru** as compared with the homogeneous **21-Ru** catalyst and the excellent enantioselectivity could be attributed to the incorporation of chiral BINAP ligands into the polymer backbone. Catalyst **22-Ru** also demonstrated remarkable recyclability in the hydrogenation of methyl acetoacetate.

Scheme 10. Structure of BINAP 21 and Chiral MCOF 22 and the Application of 21 and 22 in Catalytic Asymmetric Hydrogenation

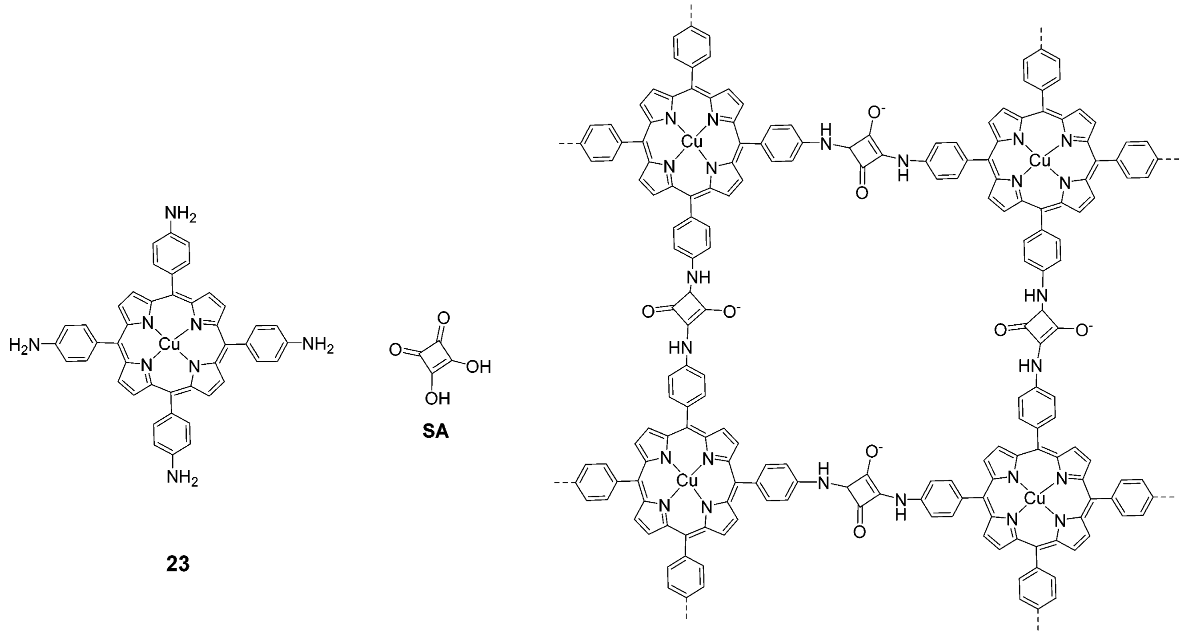


5. CONJUGATED MCOFS FOR EFFICIENT PHOTOCATALYSIS

Highly conjugated organic frameworks are versatile materials that can be applied in gas separation, gas storage, and catalysis, as well as in optoelectronics and for energy applications because of their highly conjugated skeleton.[66,67] By embedding small-molecule photocatalysts into a highly conjugated MCOF, novel heterogeneous photocatalysts have been created.[68−74]

Unlike a 3D framework, the layered structure of 2D organic networks can provide periodic arrays of *π* clouds that greatly facilitate charge-carrier transport. Such characteristics change the catalytic functionality because the photoactive moieties are embedded into the main chain of the skeleton. Recently, a highly crystalline and conjugated 2D MCOF linked by squaraine (SQ) and porphyrin was reported.[75] Squaraines are interesting dyes with a zwitterionic resonance structure and have broad applications in imaging, nonlinear optics, photovoltaics, photodynamic therapy, and ion sensing. 2D MCOF was synthesized by condensation between copper(II) 5,10,15,20-tetrakis(4-aminophenyl) **23** and squaric acid (SA). It has a planar but zigzag zwitterionic resonance skeleton **24** (Scheme 11). The SQ linkage was unique because it extended the *π* conjugation over the 2D skeleton and provided a new molecular motif for charge-carrier transfer. The improved light-harvesting capacity, lowered band gap, layered *π*-stacking porphyrin arrays, and open mesopores were useful features for the development of functional molecular systems. For example, Cu-porphyrin MCOF **24** was an excellent photocatalyst for the activation of molecular oxygen. It could harvest visible photons for photocatalysis through its conjugated

Scheme 11. Structure of Cu-Porphyrin 23 and Conjugated Cu-Porphyrin MCOF 24



23

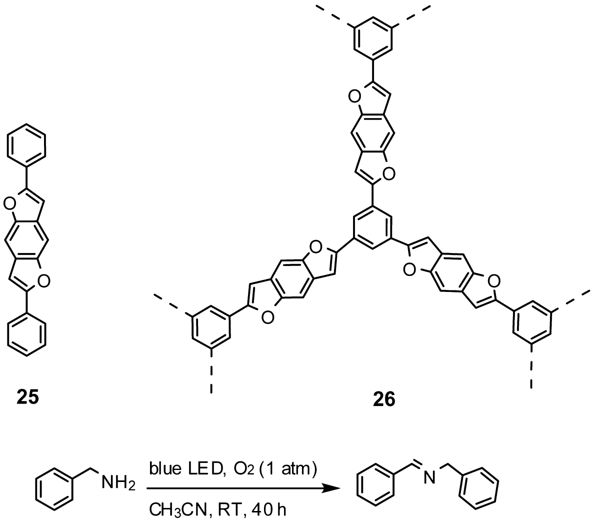
SA

24

structure. Singlet oxygen could be generated rapidly with the MCOF catalyst, but sluggishly with Cu-porphyrin **23** catalyst. The significant difference in the catalytic activities of monomeric **23** and MCOF **24** illustrated that a well-defined, ordered main-chain, conjugated skeleton was important in controlling the photogenerated excited states and enhancing the catalytic functionality.

In another report, photoactive benzodifuran (BDF) moieties were built in an aromatic MCOF through tandem synthetic processes.[76] BDFs have unique optical and electrical properties and were applied in organic light-emitting devices (OLEDs), solar cells, and organic field-effect transistors. DBF-MCOF **26** was synthesized by conventional Sonogashira coupling reaction of 1,3,5-triethynylbenzene and 2,5-diiodo-1,4-hydroquinone using diisopropylamine as a base (Scheme 12). It was employed in the photocatalytic transformation of amines under irradiation with a blue LED. Catalyst **26** catalyzed 97% conversion of benzylamine into the imine in 40 h, whereas 2,6-diphenylbenzodifuran **25** showed only 29% conversion; **26** was also reusable and tolerant to various benzylic amine substrates. This example clearly demonstrated the enhancement in photocatalytic activity by main-chain conjugated framework.

Scheme 12. Structure of Benzodifuran 25 and Benzodifuran MCOF 26, and the Application of 25 and 26 in Photocatalysis



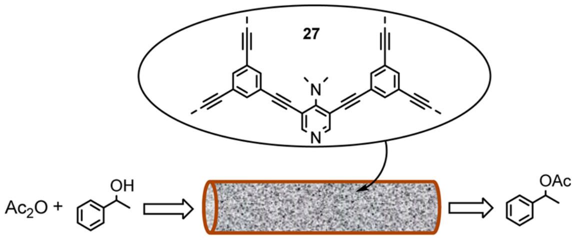
Yields: **25**, 29%; **26**, 97%

6. ROBUST MCOF ORGANOCATALYST FOR FLOW REACTOR

Organocatalysts have been widely developed for use in organic synthesis, especially toward green chemistry. Significant efforts have been devoted toward generating heterogeneous organocatalysts via a postsynthesis approach and with a side-chain structure.[48−52] However, this method often suffers from tedious synthesis, nonuniform distribution of catalytic functionalities, poor stability, and undesired interactions. These problems can be resolved by employing an all-in-one construction of heterogeneous organocatalysts directly from the condensation of well-designed functional building units through a bottom-up strategy.[77] Direct embedding of catalytic motifs into the rigid main-chain framework would also provide additional advantages for heterogeneous organocatalysts, such as isolated catalytic sites, porosity, high surface area, a stable network, and a skeleton with tunable functionalities.[21]

Embedding small organocatalysts into a highly stable MCOF could produce heterogeneous organocatalysts with high robustness and long lifetime. Recently, Wang's group reported a conjugated organic framework embedded with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) by palladium-catalyzed Sonogashira−Hagihara coupling of 3,5-dibromo-*N*,*N*-dimethylpyridin-4-amine and 1,3,5-triethynylbenzene.[78] The resulting DMAP-MCOF **27** has a surface area of 508 m^2/g and was stable up to 295 °C in air. It demonstrated yields of 92−99% in the acylation of alcohols (Scheme 13). Catalyst **27** could be recovered from the reaction mixture and reused for at least 14

Scheme 13. DMAP-MCOF 27 catalyzed alcohol acylation reaction under a continuous flow condition



Flow rate = 0.2 mL/h, RT, conversion > 97% for up to 540 h

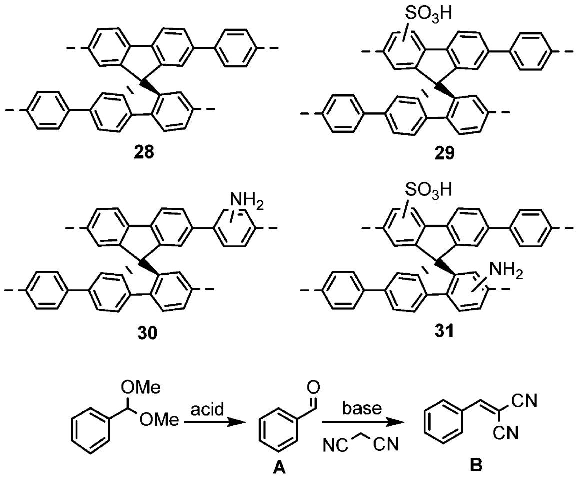
consecutive cycles without loss in activity. Under a continuous flow condition, it maintained high activity for at least 536 h. This indicated that the strong main-chain framework led to a robust heterogeneous organocatalyst that could potentially be used in industrial processes.

7. MULTIPLE FUNCTIONALITIES AND SYNERGISTIC EFFECTS WITHIN MCOF

MCOF provides an excellent platform for material functionality design. One attractive possibility is to embed multiple functionalities in one skeleton. The embedded functionalities are fixed and isolated on different positions in the framework, allowing for multiple functionalities to be achieved for heterogeneous catalysts.

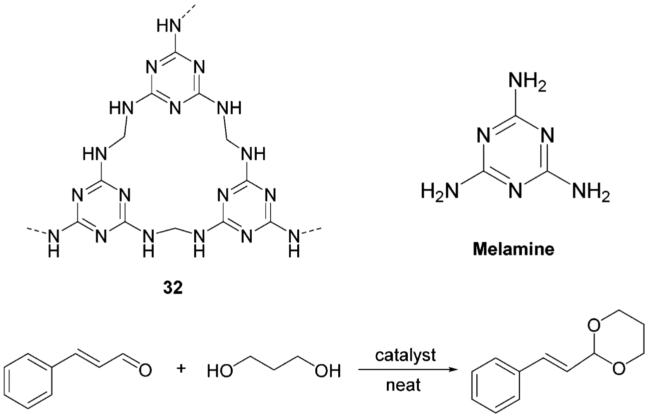
Recently, Corma's group reported a porous aromatic organic framework **28** synthesized by Suzuki coupling of 2,2′,7,7′-tetraiodo-9,9′-spirobisfluorene and 1,4-phenylenediboronic acid using microwave heating.[79] Catalyst **28** was functionalized with acid groups by treatment with chlorosulfonic acid in chloroform, yielding PPAF−SO$_3$H **29**. Next, basic sites were introduced by functionalization of PPAF−SO$_3$H with amino groups in two steps, first introducing the nitro group and then reducing it to amine to produce PPAF−SO$_3$H−NH$_2$ **31**. The bifunctional catalyst **31** was applied in a cascade reaction that involved (i) acid-catalyzed hydrolysis of benzaldehyde dimethylacetal to benzaldehyde, and (ii) base-catalyzed Knoevenagel reaction with malononitrile to yield 2-benzylidenemalononitrile. Remarkably, it gave 100% conversion and 100% selectivity toward the final product. This excellent result could not be achieved using an individual solid acid catalyst and solid base catalyst, or one solid catalyst with another homogeneous catalyst (see Scheme 14). The bifunctional heterogeneous catalyst was stable and robust, allowing several recycles with only a minor loss in activity. This study demonstrated the interesting potential for embedding different organic functional groups in the framework for catalyzing one-pot and cascade reactions. A dual functional porous framework similar to the advanced heterogeneous cascade catalyst has also been reported by Zhang et al.[80]

Scheme 14. Cascade Reaction Catalyzed by Bifunctional MCOF 31



Catalyst	Yield of **A**	Yield of **B**
28	0	0
29 + aniline	50	50
30 + p-CH$_3$Ph-SO$_3$H	75	25
29 + **30**	9	91
31	0	100

Scheme 15. mPMF 32 Demonstrated Much Higher Catalytic Activity than Melamine in Acetalization Reaction

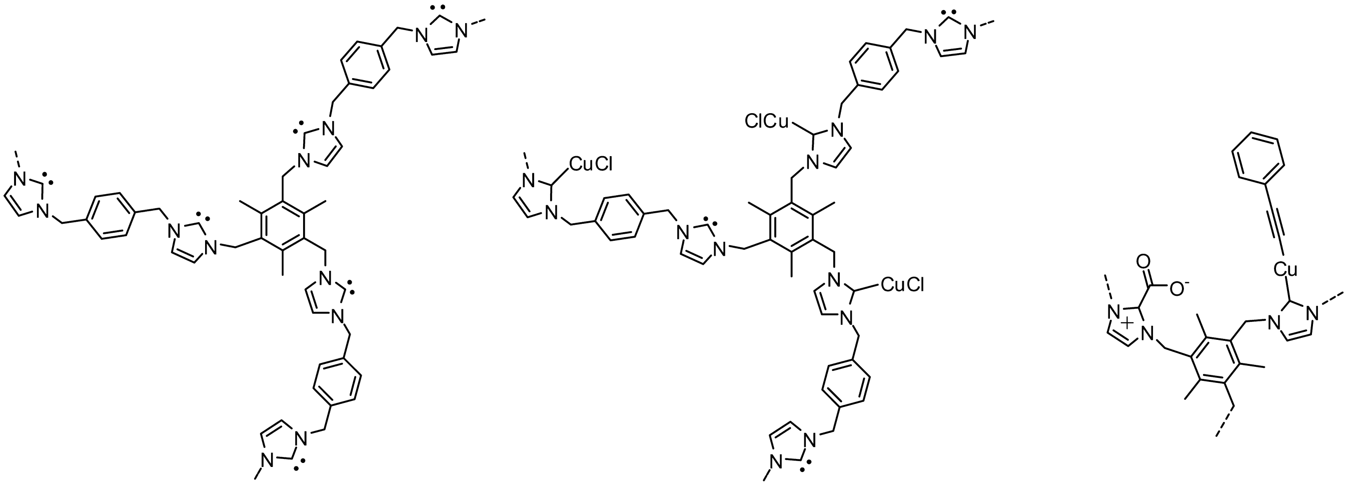


TOF$_{32}$ / TOF$_{Mel}$ > 240

MCOF could also be designed to promote synergistic effects between different functionalities loaded in high densities on the main chain. For example, a mesoporous polymelamine−formaldehyde (mPMF), **32**, has been synthesized by mixing melamine and paraformaldehyde in hot dimethyl sulfoxide (Scheme 15).[81] It possessed a high surface area of 930 m^2/g and an average pore size of ∼16 nm. Catalyst **32** was found to catalyze the acetalization of *trans*-cinnamaldehyde with a TOF that was 240 times higher than the homogeneous catalyst, melamine. It catalyzed a variety of substrates, including aliphatic and aromatic aldehydes, with good to excellent yields and showed excellent reusability. The high activity of **32** could be attributed to its condensed network structure with a high density of aminal groups and triazine rings, which presented dual functionalities of Brønsted acidity and Lewis basicity. These unique characteristics led to multiple types of hydrogen bonding interactions and synergism, which catalyzed the acetalization reaction efficiently.

In another example, synergistic effects were demonstrated between MCOF and its coordinated metal sites.[83,84] A main-chain NHC framework **33** and its coordinated copper cocatalyzed CO$_2$ transformation to carboxylic acids via C−H bond activation of terminal alkynes.[83] Catalyst **33** was synthesized by condensation between bis-imidazole precursor and 2,4,6-tris(bromomethyl)mesitylene in hot dimethylformamide, followed by deprotonating imidazolium.[23,77] A unique NHC-Cu cocatalyst was designed by using main-chain poly-N-heterocyclic carbene (PNHC) both as a ligand and a catalyst.

Scheme 16. Poly-NHC 33 and Poly-NHC-Cu Dual-Functional Catalyst 34[a]



33 (PNHC)

34 (P(NHC)$_{0.5}$(NHC-Cu)$_{0.5}$)

synergistic effect of dual functional catalyst

[a]The synergistic effect of **34** catalyzed carboxylation of alkyne with CO_2.

The carbene units were located and fixed in the backbone of PHNC (Scheme 16). P(NHC)$_{0.5}$(NHC-Cu)$_{0.5}$ catalyst **34** was prepared by reacting 1 equiv of CuCl with 2 equiv of PHNC such that only half of the carbene species coordinated with copper and the other half of the species remained as free carbenes. This heterogeneous catalyst showed 70% yield in catalyzing carboxylation of the challenging substrate 4-nitro-1-ethynylbenzene with CO_2. The high activity could not be achieved with other copper catalysts. In contrast, P-(NHC)$_0$(NHC-Cu)$_1$ gave only 18% yield, and P-(NHC)$_1$(NHC-Cu)$_0$ showed no activity. The high activity of heterogeneous catalyst **34** was attributed to synergistic effect. The copper center activated the terminal alkyne with a base to form the copper acetylide intermediate, while the free carbene activated CO_2 to form the NHC-carboxylate (Scheme 16). Next, the NHC-carboxylate would coordinate to the nearby copper center to induce the formation of the new C−C bond. This system demonstrated an interesting synergistic effect between an organocatalyst and an organometallic catalyst on the same main-chain framework.

8. CONCLUSIONS AND PERSPECTIVES

The area of organic framework polymers has witnessed significant growth over the past decade. In general, they possess high porosity and surface area, high catalyst loading, and high structural stability. Such characteristics are important in the design of heterogeneous catalysts with high catalytic efficiency and recyclability.

MCOFs that are constructed via the bottom-up approach may possess more functionalities beyond those generally associated with heterogeneous catalysts. They may be derived with interactions between the embedded functionalities and the main framework so that synergistic properties can be achieved for complex catalytic applications. Compared with homogeneous or SCOF catalysts, MCOF catalysts can provide higher activity, selectivity, and stability with strategic structural design. In particular, chiral MCOF synthesis with catalytic functionality is still at an early stage of research. The tuning of activity and selectivity of asymmetric catalyst by designing building units with various structural flexibility and bulkiness holds a great deal of promise. To further advance these systems, it would be useful also to develop computational models that can provide insights into structural design and functionalization. By combining new synthetic approaches and computational modeling, we can expect to see more and more sophisticated MCOFs tailored with well-defined microstructures and pore structures and controlled dispersion of a variety of functional groups. This new class of robust, solid-state systems would not only promote the use of heterogenized catalysts in industrial processes, but also serve as advanced materials in optoelectronics, energy, gas separation, gas storage, and sensor applications.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ygzhang@ibn.a-star.edu.sg.
*E-mail: jyying@ibn.a-star.edu.sg.

Notes

The authors declare no competing financial interest.

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