



Review

Click chemistry as a versatile reaction for construction and modification of metal-organic frameworks

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ABSTRACT

Intriguing porous architectures, fascinating physical and chemical properties, and wide application potentials have made metal-organic frameworks (MOFs) a class of highly promising functional materials. The inherent feature of incorporating decorative organic components as building blocks has facilitated MOF constructions by ingenious pre-design and post-synthetic modifications of the organic moieties through appropriate reactions. Meanwhile, the click chemistry has become an effective and robust tool in the fabrication and modification of various functional materials. The azide-alkyne 1,3-dipolar cycloaddition is usually conducted in mild conditions using diversely available substrates to generate 1,4-regioisomers of 1,2,3-triazoles as sole products in high yields, which meets the characteristics of the conceptual click chemistry and has been referred as the premier example of a click reaction. In 2007, the azide-alkyne 1,3-dipolar cycloaddition as a representative reaction of the click chemistry was introduced into the field of MOFs. In the past decade, utilizing the azide-alkyne 1,3-dipolar cycloaddition, not only lots of organic ligands have been designed and synthesized for MOF constructions, but also diverse functional groups have been grafted into/onto MOF networks for targeted applications. Although other click reactions, such as Diels-Alder click reaction and thiol-ene click reaction, have also been introduced into the MOF field, more and more successful examples have undoubtedly demonstrated that the azide-alkyne 1,3-dipolar cycloaddition is a highly efficient click reaction in the MOF construction and modification toward purposed applications. Herein, we highlight representative research progresses on MOFs derived from the azide-alkyne 1,3-dipolar cycloaddition along with their attractive applications.

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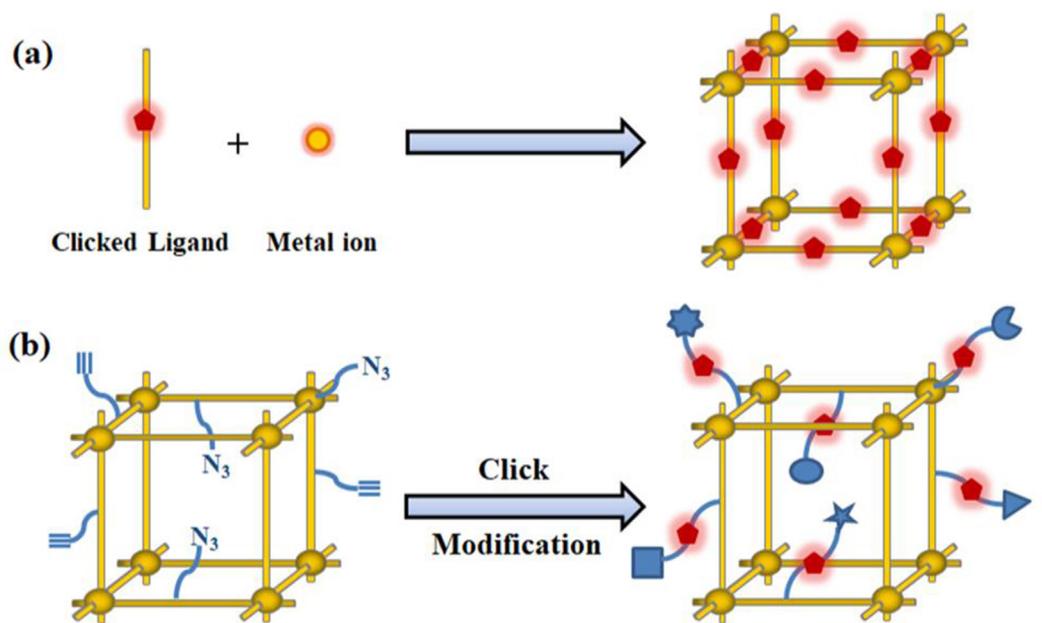
1. Introduction

Metal–organic frameworks (MOFs) are a class of highly promising functional materials owing to their intriguing porous architectures, fascinating physical and chemical properties, and wide application potentials [1–5], especially in the adsorption and separation of gases or small molecules including H₂ [6,7], CO₂ [8,9], CH₄ or other hydrocarbons [10,11] and toxic chemicals [12,13], heterogeneous catalysis [14,15] or catalyst supports [16,17], drug delivery and bioimaging [18,19], and electronic and photophysical aspects [20,21]. Distinct from other inorganic porous materials such as zeolites and activated porous carbons, crystallographically infinite lattices and perspicuous topologies of MOFs are typically derived from the modular combination of polytopic organic bridging ligands and metal ions or *in situ* generated metal clusters [22,23]. Although a large library of porous MOF architectures has been developed so far by judicious coordination of diverse organic linkers [24–29] and abundant inorganic nodes [30–37] under various synthetic processes [38,39], more and more examples have demonstrated that their properties and applications show high dependency on the sophisticated organic moieties reticulated in the frameworks [24–29,40]. For instance, by modifying the length of organic backbones, isoreticular MOFs with different pore sizes could be achieved [41–43]; by introducing chiral centers into organic ligands, MOFs for enantiomer separation and asymmetric catalysis were constructed [44,45]; by utilizing fluorinated compounds as organic precursors in the ligand synthesis, moisture-resistant and superhydrophobic MOFs were assembled [46,47]; and by taking biocompatible natural products as ligands, edible MOFs were obtained [48]. The inherent feature of incorporating decorative organic components as building blocks has facilitated MOF fabrications by ingenious pre-design and synthesis of functional organic ligands [49,50] or post-synthetic modification of the organic moieties by grafting functional groups into the pristine networks [51,52]. Therefore, a rational selection of efficient and reliable reactions to synthesize and/or modify organic ligands becomes a pivotal step to construct unique MOF architectures or composites toward targeted applications.

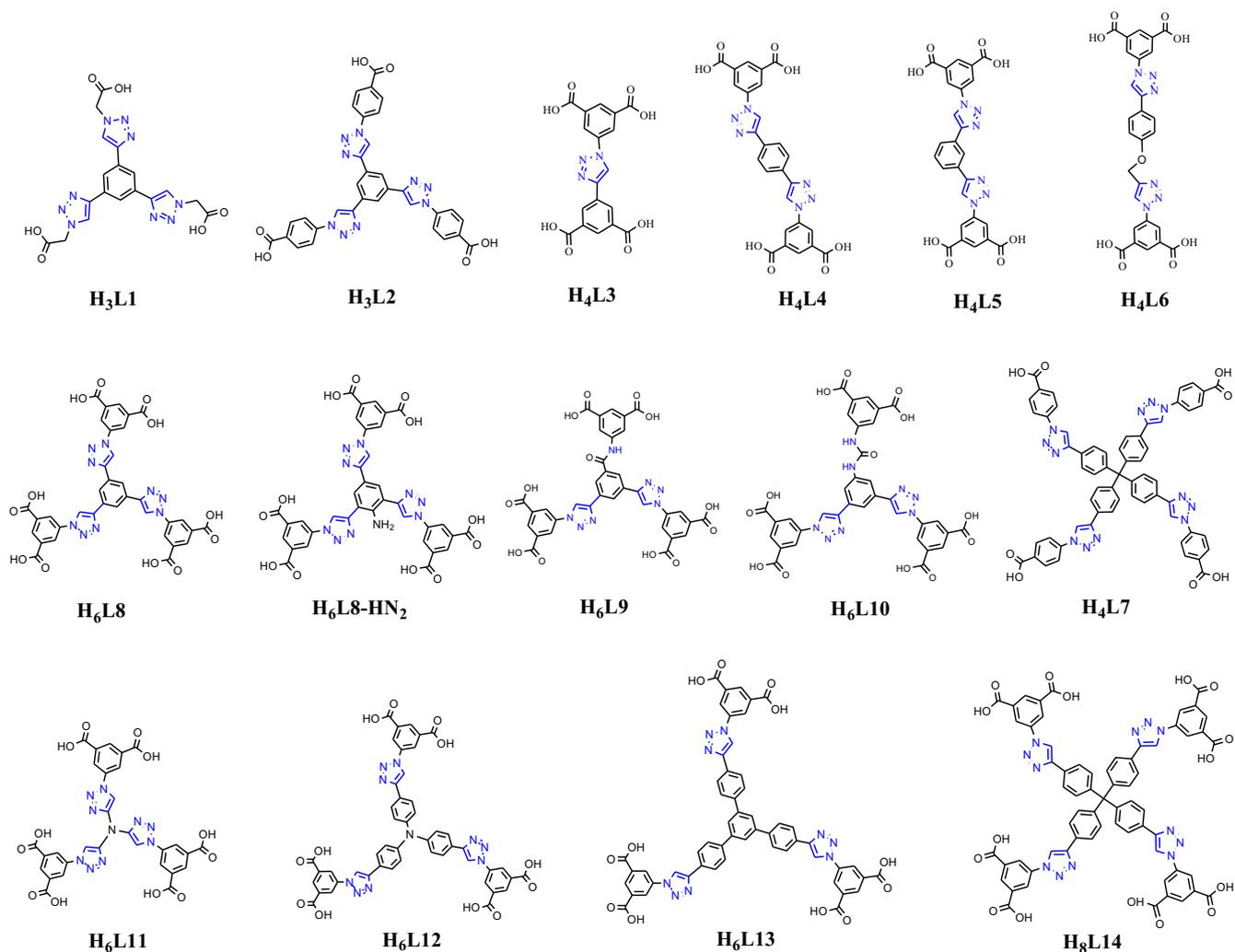
The click chemistry has become a group of effective and robust reactions since it was proposed in 2001 [53]. Such reactions could be carried out in non-stringent conditions with wide scopes of reactants to generate highly yielded (stereospecific) products

[53,54]. Among these unique reactions, azide-alkyne 1,3-dipolar cycloaddition is usually conducted in mild conditions using diverse available substrates, highly yielding 1,4-regioisomers of 1,2,3-triazoles as sole products instead of regiorandom triazole adducts [55,56], which complies fully with the definition of the conceptual click chemistry and has been referred as the premier example of a click reaction [57]. The investigation of azide-alkyne cycloaddition could be traced back to 1960s [58], but its affirmatory breakthrough is based on the landmark event of introducing copper(I) as a catalyst into the reaction systems reported in 2002 [55,56]. In recent years, copper(I)-free clicked azide-alkyne 1,3-dipolar cycloaddition was also well developed to overcome the cytotoxic challenge of copper(I) ion, especially in biological systems [59]. Here, azide-alkyne 1,3-dipolar cycloaddition is adopted instead of the terms of copper(I)-catalyzed azide-alkyne cycloaddition, copper(I)-free azide-alkyne 1,3-dipolar cycloaddition, or Huisgen 1,3-dipolar cycloaddition for fully describing and summarizing this type of reactions in this review. Since the toxicity of copper(I)-catalyzed azide-alkyne cycloaddition restricts its practical applications in certain situations, e.g., bioconjugation, the development of copper-free click reaction would overcome this issue. So far, the azide-alkyne 1,3-dipolar cycloaddition has been broadly exploited in the fabrication and modification of various functional molecules and materials [60–62], such as small organic compounds [63,64], drugs and bio-active molecules [56,65,66], dendritic compounds [67], and organic polymers [68–72], which have been widely used in molecular recognition, heterogenous catalysis, bioconjugation, pharmaceutical industry and so on. In recent years, the click reaction of azide-alkyne 1,3-dipolar cycloaddition was also employed in the research field of porous organic polymers (POPs) and covalent-organic frameworks (COFs) [73–82]. While some POPs or COFs with crystallizing frameworks could be easily modified by the click chemistry [81,82], the POPs or COFs constructed by direct click reaction of two modular building blocks are often amorphous with low- or non-porosity and irregular pore distribution, probably due to its feature of irreversible reaction [73–80]. Since the azide-alkyne 1,3-dipolar cycloaddition is the most widely used reaction among all the click reactions, it has been often referred as the “click reaction”.

In 2007, the azide-alkyne 1,3-dipolar cycloaddition as the representative reaction of the click chemistry was introduced into the research field of MOFs by Devic and coworkers [83]. Since then,



Scheme 1. Illustrations of MOFs (a) derived from the pre-designed clicked ligands and metal ions, and (b) modified by clicked post-synthetic modification.



Scheme 2. Commonly used clicked polytopic-carboxylate ligands in MOF constructions.

lots of MOFs have been pre-designed, constructed (Scheme 1a) or post-synthetically modified (Scheme 1b) by this user-friendly and robust reaction. Although other click reactions, such as Diels–Alder click reaction and thiol–ene click reaction, have also been employed in the MOF field, more and more successful examples have undoubtedly demonstrated that the azide-alkyne 1,3-dipolar cycloaddition is a powerful click reaction in both pre-design and post-synthetic modification of MOFs toward purposed applications. Previous reviews have focused on either prosperous MOFs [1–40] or click chemistry [59–72] separately. A very few reports have briefly covered the topic of MOFs derived from the click reaction. For instance, some MOFs constructed by the clicked 1,2,3-triazole-containing ligands were discussed in reviews regarding (i) coordination materials constructed from triazoles and tetrazoles reported by Gameza and coworkers in 2011, and (ii) metal azolate frameworks reported by Chen et al. in 2012 [24,25]. Several MOFs post-synthetically modified by the click reaction were also mentioned in some reviews [51,84,85]. However, the research progresses on MOFs based on this versatile click chemistry have still not been comprehensively summarized so far, to the best of our knowledge.

In this review, we highlight recent significant research progresses on the pre-design, construction and post-synthetic modification of MOFs by the click reaction of azide-alkyne 1,3-dipolar cycloaddition along with their attractive applications. In the section of clicked ligands and constructed MOFs, various types of organic ligands including (i) clicked carboxylate ligands, (ii) clicked triazolates, (iii) clicked carboxylate-containing triazolates, and (iv) click-extended bipyridine ligands, and related triazole-containing MOF architectures are discussed in detail. In addition to the MOF construction *via* clicked pre-design, lots of MOFs were also post-synthetically modified by the click chemistry. Thus, four sections including (i) azide-tagged MOFs modified by alkynes, (ii) alkyne-tagged MOFs modified by azides, (iii) one-pot, two-step click modification of amino-derived MOFs by alkynes, and (iv) copper-free strain-promoted click modification of MOFs are separately discussed. The versatile azide-alkyne 1,3-dipolar cycloaddition not only enriches the library of MOF structures, but also widely broadens the application of MOFs by incorporating functional groups into the frameworks during the processes of ligand pre-design and MOF post-synthetic modification. Therefore, various attractive applications of MOFs derived from the azide-alkyne 1,3-dipolar cycloaddition in (i) gas adsorption, (ii) heterogeneous catalysis, (iii) large-molecule capture and separation, (iv) drug delivery and cancer therapy, and (v) templated polymer-gel fabrications are summarized in this review.

2. Clicked ligands and related MOF structures

In the ligand design and syntheses, the click reaction of azide-alkyne 1,3-dipolar cycloaddition not only affords an effective combination between polytopic-symmetrical organic moieties and electron donor coordination groups to produce diverse triazole-containing carboxylates for MOF constructions, but also leads to the generation of coordinative 1,2,3-triazole ring. Since 1,2,3-triazole ring is an electron donor group, the coordination between metal ions and the triazole ring could be formed [24,25,33]. Therefore, various types of organic ligands including clicked carboxylate ligands, clicked triazolates, clicked carboxylate-containing triazolates, and clicked pyridine ligands were successfully synthesized *via* the modular click combinations of polytopic-symmetrical acetylene-containing organic components and azide-containing components. Subsequently, diverse triazole-containing MOF architectures were constructed through the coordination of these clicked organic ligands with suitable metal ions.

2.1. MOFs derived from clicked carboxylate ligands

Among several types of clicked ligands, clicked carboxylate ligands are one of the most well studied groups. Diverse clicked carboxylate ligands (Scheme 2) including tricarboxylic acids, tetracarboxylic acids, hexacarboxylic acids, and octacarboxylic acids were successfully synthesized *via* the clicked combinations of dual-, triple-, or tetrapolar-symmetrical acetylene-containing organic components with azide-containing carboxylates, such as 4-azidobenzoates and 5-azidoisophthalates. Subsequently, various MOFs with coordination-free triazole groups were constructed after the coordination between these clicked organic ligands and metal ions.

2.1.1. MOFs derived from clicked tri-carboxylate ligands

Utilizing the azide-alkyne 1,3-dipolar cycloaddition as the core reaction through the conjugation between triple-symmetrical acetylene-containing 1,3,5-triethynylbenzene and the azide precursor of azidoglycine ethylester, a flexible tricarboxylic acid, {4-[3,5-bis-(1-carboxymethyl-1H-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}acetic acid (H_3L1 in Scheme 2), was synthesized by Devic and coworkers in 2007 [83]. After solvothermal reaction with Td(III) ions, a triazole-containing MOF, denoted as MIL-112 (Fig. 1), was then obtained as a counterexample of isoreticular chemistry [41–43]. On account of the flexibility of the clicked tri-topic carboxylate linker, a 4^4 network (Fig. 1b) instead of an isotopic hexagonal 6^3 network in prototypical MIL-103 (a MOF

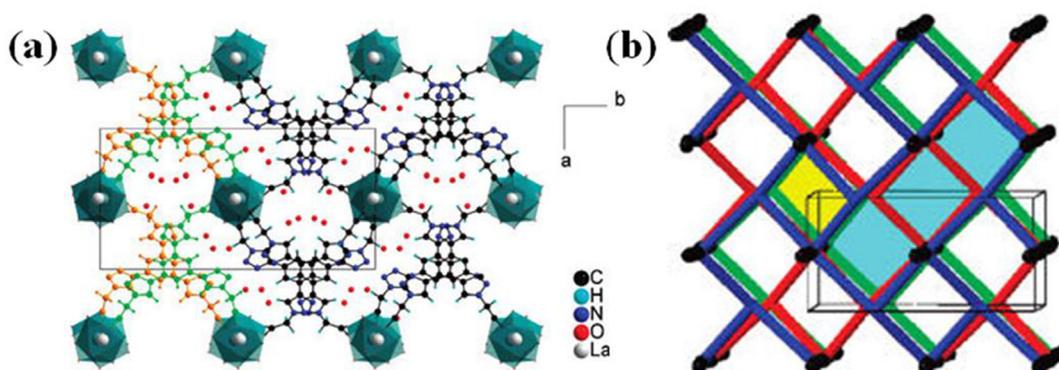


Fig. 1. (a) Porous framework of MIL-112 and (b) its topological 4^4 network. Adapted with permission from Ref. [83]. Copyright 2007, American Chemical Society.

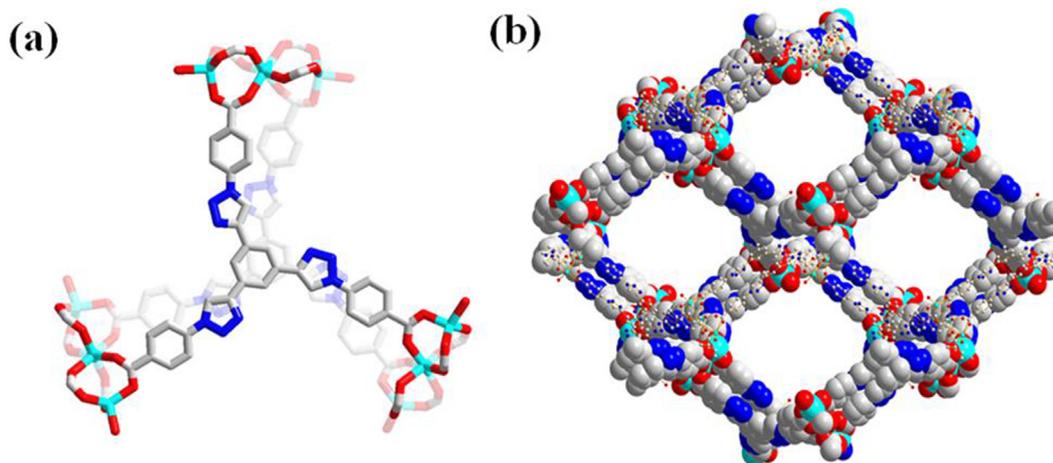


Fig. 2. (a) L2 connected three Zn_3 units and (b) 1D porous channels along c -axis in NTU-130. Adapted with permission from Ref. [87]. Copyright 2017, Royal Society of Chemistry.

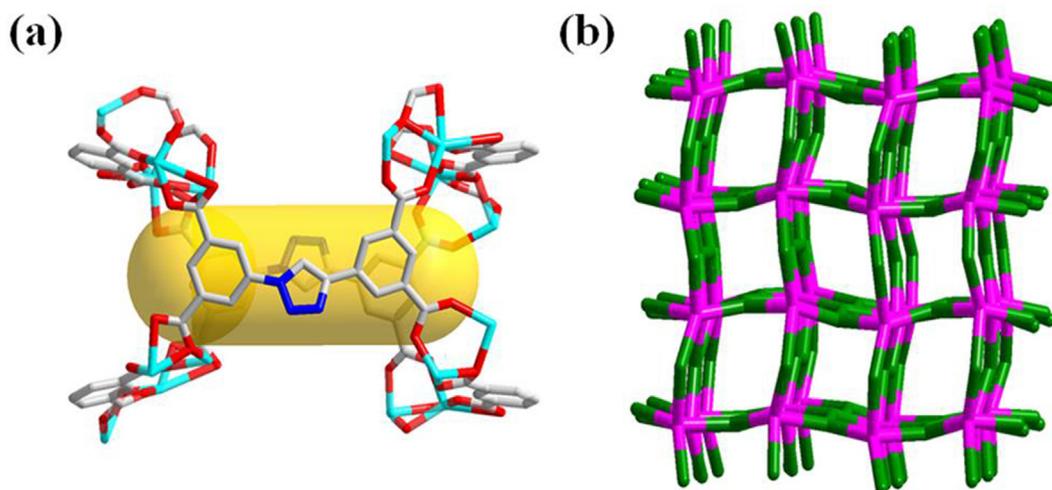


Fig. 3. (a) Wire-and-stick representation of L3 linked four Zn_2 clusters in NTU-101-Zn, and (b) simplified PtS-type network of NTU-101-Zn. Adapted with permission from Ref. [90]. Copyright 2012, Royal Society of Chemistry.

based on Td and benzene-tricarboxylic acid) [86] was presented in MIL-112, although infinite one-dimensional (1D) secondary building units (SBUs) similar to that in MIL-103 was also observed in MIL-112.

Replacing the azide precursor of azidoglycine ethylester by 4-azidobenzoate to react with triple-symmetrical 1,3,5-triethynylbenzene followed by the deprotection, a tricarboxylate ligand, 4,4',4''-benzene-1,3,5-tryl-tri(1*H*-1,2,3-triazol-1-yl)benzoic acid (H_3L_2 , Scheme 2), was synthesized by our group [87]. After solvothermal reaction with Zn(II) ion in DMF, block colorless crystals of a MOF, denoted as NTU-130, with a framework formula of $[Zn_6(L_2)_4(H_2O)_3]_n$ were obtained. Structural analysis reveals that, in NTU-130, linear Zn_3 clusters [88,89] were *in-situ* generated by six distributed carboxylate groups from six different L2 ligands coordinated with three neighboring Zn(II) ions (Fig. 2a). Although two-fold interpenetrated uninodal (10,3)-net with intrinsically chiral $SrSi_2$ topology in an *srs* symbol [89] was formed by the coordination of click-extended L2 and Zn_3 clusters, a framework with a Brunauer-Emmett-Teller (BET) surface area of $2819 \text{ m}^2 \text{ g}^{-1}$, and large pores having opening windows of $14.8 \times 19.9 \text{ \AA}^2$ along a -axis (Fig. 2b), and channels with opening diameters of about 10.2 \AA perpendicular to the (110) plane was successfully

constructed, attributed to enough length of click-extended organic backbone of the tricarboxylate ligand.

2.1.2. MOFs derived from clicked planar tetracarboxylate ligands

Reacting two isophthalate compounds, *i.e.*, dimethyl 5-azidoisophthalate and dimethyl 5-ethynylisophthalate, followed by the hydrolysis, a sandwich-type tetracarboxylate ligand, 5,5'-(1*H*-1,2,3-triazole-1,4-diyl)di-isophthalic acid (H_4L_3 in Scheme 2), was also synthesized by our group [90]. Colorless block-shaped crystals of a MOF, denoted as NTU-101-Zn, was then constructed under solvothermal reaction of the ligand with Zn(II) ion. Structure analysis reveals that Zn_2 clusters are *in situ* formed within the framework by three DMF and four carboxylates coordinated with two neighboring Zn ions, four of which are then connected by one tetracarboxylate L3 (Fig. 3a) to finally give the formation of a three-dimensional (3D) framework of NTU-101-Zn. By simplifying the tetracarboxylate L3 into a 4-connected square-planar linker and four carboxylate coordinated Zn_2 clusters into a tetrahedral node, a topological PtS-type network could be obtained (Fig. 3b).

By replacing the Zn ion by lanthanide ions (Ln(III)) and reacting with the clicked H_4L_3 , a family of isostructural MOFs with a framework formula of $[Ln(HL_3)(H_2O)_4] \cdot xH_2O$ (Ln = La, Eu, Tb, and Er;

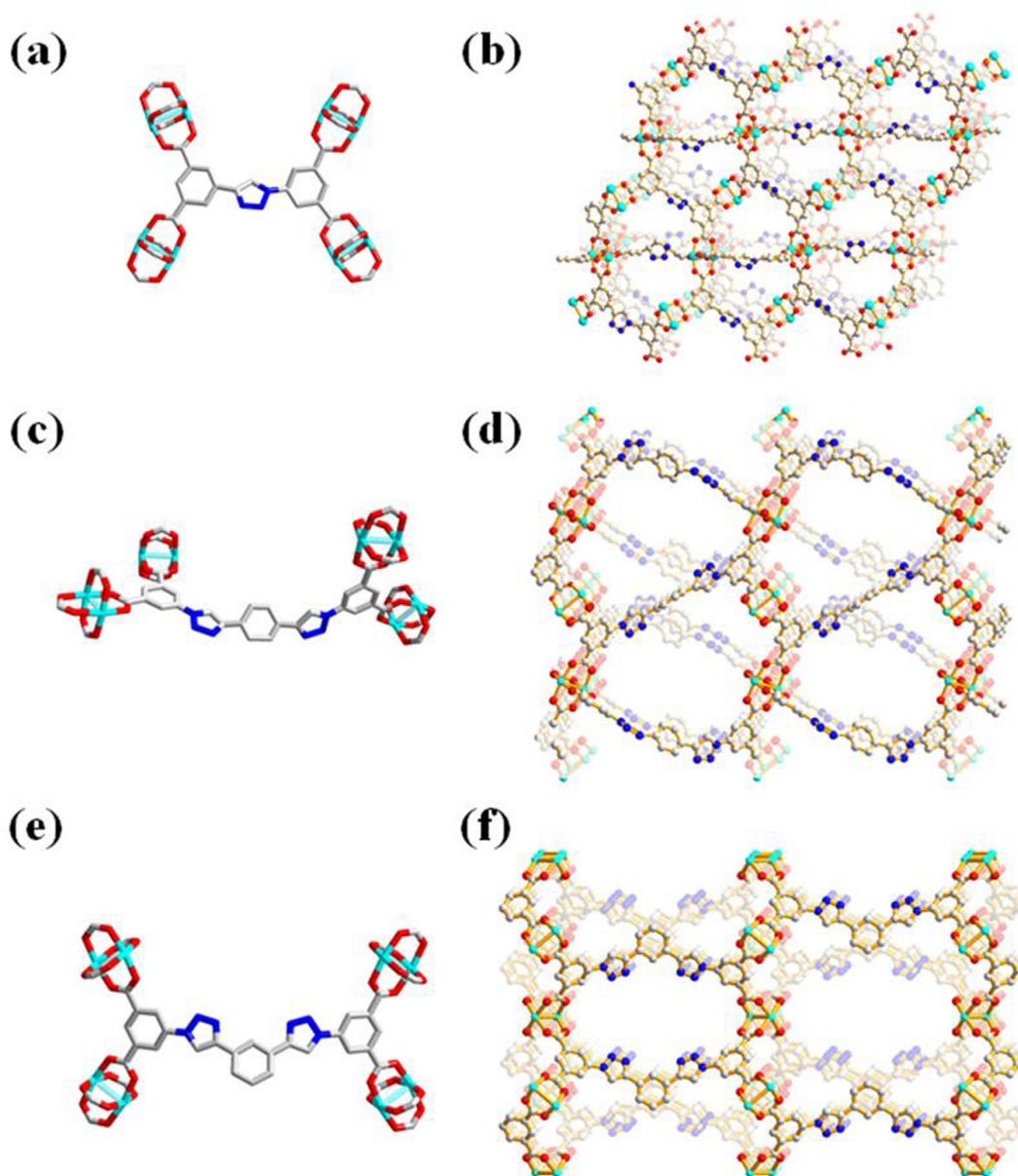


Fig. 4. Wire-and-stick representation of L3, L4, or L5 linked four paddlewheel Cu_2 clusters and porous frameworks of corresponding MOFs. (a and b) NTU-111, (c and d) NTU-112, and (e and f) NTU-113. Coordinated water molecules and hydrogen atoms are omitted for the clarity. Adapted with permission from Ref. [92]. Copyright 2014, Royal Society of Chemistry.

$2 < x < 2.5$) and 3,6-connected rutile topology was hydrothermally synthesized by Liang and coworkers [91]. Luminescent studies show that Eu- and Tb-based MOFs present characteristic emission of Eu(III) and Tb(III), and Tb-based MOF exhibits selective luminescent sensing for Cu(II) ion in aqueous solution. The authors also found that Tb- and Er-based MOFs exhibit distinct magnetic behavior in different temperature regions.

Subsequently, other two longer tetra-carboxylate ligands, 5,5'-(benzene-1,4-diyl)di(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid ($\text{H}_4\text{L4}$ in Scheme 2) and 5,5'-(benzene-1,3-diyl)di(1H-1,2,3-triazole-1,4-diyl)diisophthalic acid ($\text{H}_4\text{L5}$ in Scheme 2), were also designed and synthesized by our group via the click extension of diisophthalates with two different diethynyl-benzenes, i.e., 1,4-diethynylbenzene and 1,3-diethynylbenzene, respectively [92]. The three ligands $\text{H}_4\text{L3}$, $\text{H}_4\text{L4}$, and $\text{H}_4\text{L5}$ were then reacted directly with Cu(II) ions to afford blue crystals of three MOFs, denoted as NTU-111, 112, and 113, respectively. Structure analysis shows that

all three MOFs possess 3D porous frameworks with the same basic framework formula of $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2]_n$, in which typical unsaturated paddlewheel Cu_2 clusters were formed (Fig. 4a,c,e) [26,93] and coordination-free clicked triazole rings as the extending spacer in the tetra-carboxylate ligands were uniformly located (Fig. 4b,d,f) [22,23]. On the other hand, topological analysis indicates that NTU-111 shows an NbO-type network with $6^4 \cdot 8^2$ topology, while NTU-112 exhibits a rare acs net and NTU-113 gives a PtS-type network with $4^2 \cdot 8^4$ topology. Such detailed investigation demonstrated that subtle variation of clicked extension on the model tetracarboxylate ligand, i.e., di-isophthalate, could lead to a high diversity of the target frameworks

A longer tetra-carboxylate ligand, $\text{H}_4\text{L6}$ in Scheme 2, was prepared *in situ* using an unconventional approach to generate the MOF structure [94]. Verpoort and coworkers integrated the synthetic steps for the formations of organic linker and metal-organic self-assembly into one stride, and blue block crystals of a porous

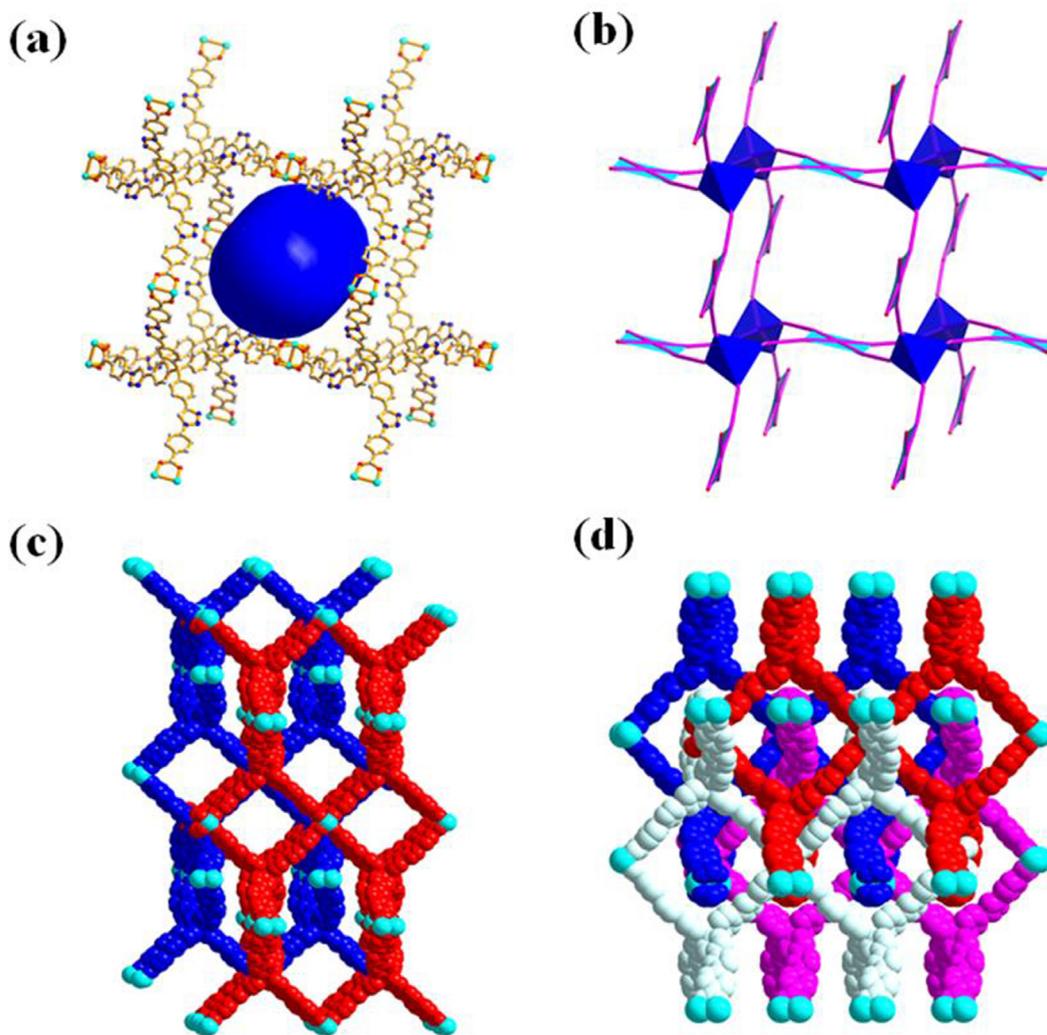


Fig. 5. (a) Coordination of L7 ligands with paddlewheel Cu_2 units in the framework, (b) simplified PtS-type basic network in two MOFs, and (c and d) perspective view of 2-fold (for NTU-140) and 4-fold (for NTU-141) interpenetrations of basic networks in the two MOFs. Adapted with permission from Ref. [104]. Copyright 2014, Royal Society of Chemistry.

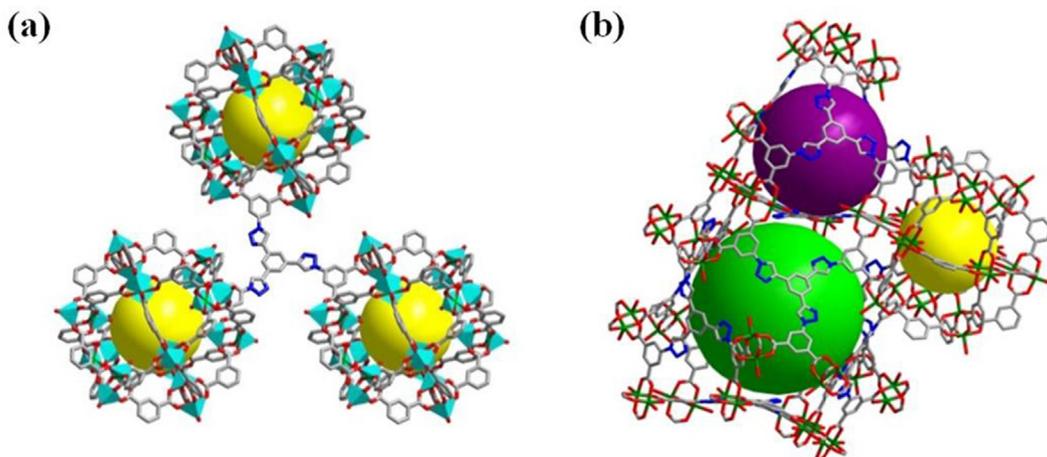


Fig. 6. (a) Constructed (3,24)-connected *rht*-type framework of NTU-105, and (b) three types of polyhedrons in NTU-105. Adapted with permission from Ref. [121]. Copyright 2013, Springer Nature Limited.

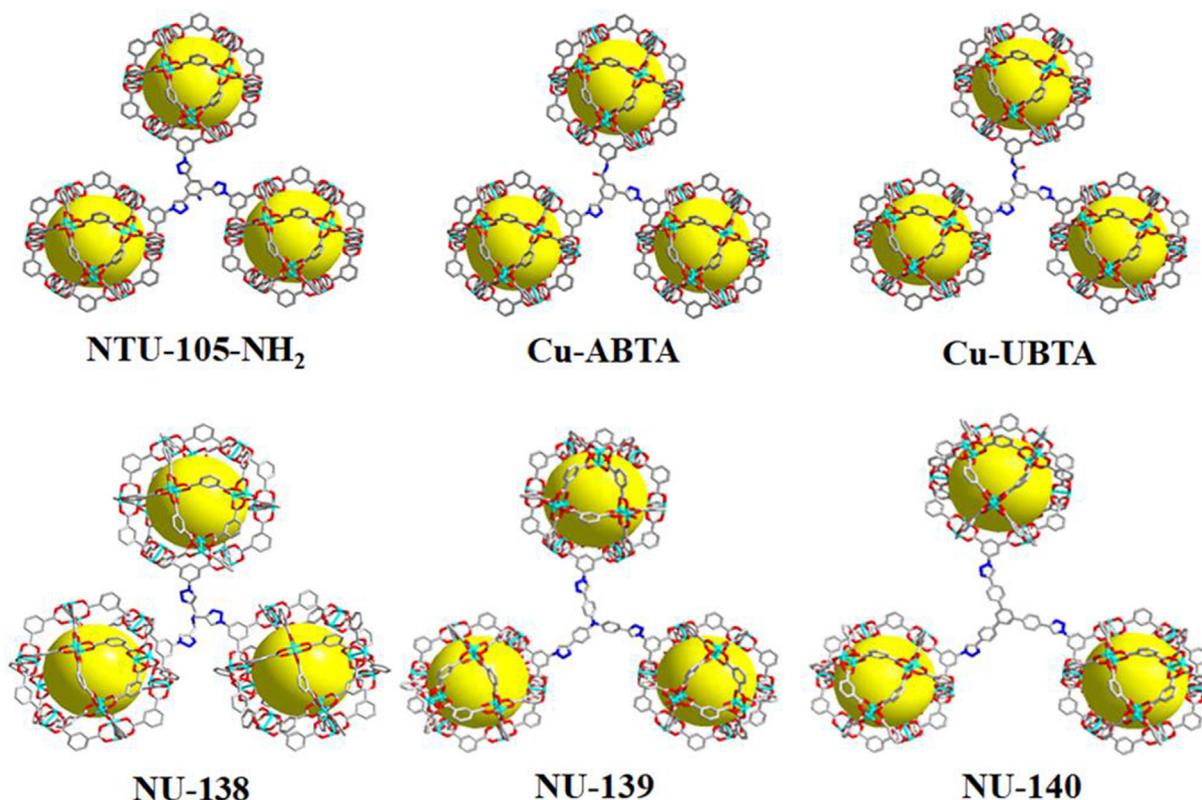


Fig. 7. (a) Triazole-containing (3,24)-connected frameworks of NTU-105-NH₂ [124], Cu-ABTA [125], Cu-UBTA [126], NU-138, NU-139, and NU-140 [127]. These structures are drawn based on their crystal data.

Cu-MOF were obtained. Structure analysis reveals that this framework has a 3,4-coordinated net with the *fof* topology. When they changed the metal ion from Cu(II) to Zn(II), this unconventional approach was failed to afford the Zn-MOF due to the absence of the catalytic Cu ion. While coordinating the pre-clicked ligand H₄L6 with Zn ion, Zn-MOF crystallized in the monoclinic chiral space group *P2*₁ was obtained.

2.1.3. MOFs derived from clicked tetragonal tetra-carboxylate ligands

Similar to other tetragonal tetracarboxylate ligands [95–103], a tetragonal tetracarboxylate ligand, 4,4',4'',4'''-((methane-tetrayl-tetrakis(benzene-4,1-diyl))tetrakis(1*H*-1,2,3-triazole-4,1-diyl))tetrabenzoic acid (H₄L7 in Scheme 2), was synthesized through the click combination of 4-azidobenzoate with a tetrapolar-symmetrical

acetylene-containing organic precursor, tetrakis(4-ethynylphenyl) methane by our group [104]. Interestingly, high quality blue crystals of two kinds of MOFs, denoted as NTU-140 and 141, were obtained when solvothermal reacting H₄L7 with Cu(II) ion in different solvents. Structure analysis shows that both MOFs share the same typical PtS-type network with a framework formula of [Cu₂(L7)]_n constructed by the coordination of clicked L7 and *in situ* generated paddlewheel Cu₂ cluster (Fig. 5a and b), similar to those reported Cu-MOFs with tetragonal tetracarboxylate ligands [95–98]. Interestingly, 2-fold interpenetration of basic networks in NTU-140 (Fig. 5c) and 4-fold interpenetration in NTU-141 (Fig. 5d) were presented. As a result, porous channels with a diameter of ~20 Å in NTU-140 and close-packing with nearly no pores in NTU-141 were observed.

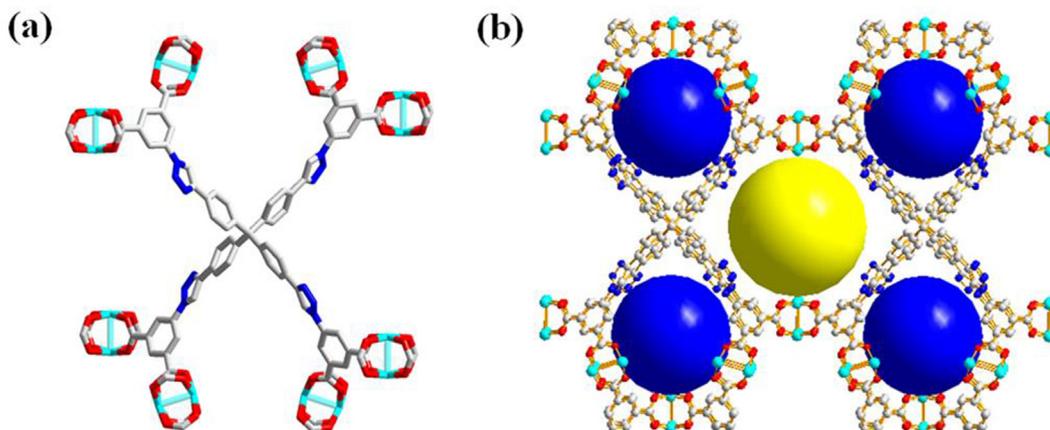


Fig. 8. (a) Clicked oct-carboxylate linked four pairs of paddlewheel Cu₂ units, and (b) perspective view of the framework of NTU-180 with two kinds of cages (yellow and blue balls). Adapted with permission from Ref. [137]. Copyright 2016, American Chemical Society.

2.1.4. MOFs derived from clicked hexa-carboxylate ligands

Inspired by diverse examples of highly porous MOFs constructed by dendritic hexacarboxylate ligands with Cu(II) ions [105–120], a triazole-containing hexacarboxylate ligand, 5,5',5''-(4,4',4''-(benzene-1,3,5-triyl)tris(1*H*-1,2,3-triazole-4,1-diyl))triiisophthalic acid (H₆L8 in Scheme 2), was prepared in our group via the clicked combination of 1,3,5-triethynylbenzene and pre-synthesized di-*tert*-butyl 5-azidoisophthalate followed by the deprotection [121]. After solvothermal reaction of ligand H₆L8 with Cu(II) ion, high quality blue crystals of a MOF, denoted as NTU-105, were obtained. As expected, structure investigation reveals that NTU-105 shares the same (3,24)-connected network as prototypical *rht*-type MOFs with coordination-free triazole groups uniformly embedded (Fig. 6a), in which three types of metal-organic polyhedrons, *i.e.*, cuboctahedron (*cub*-Oh), truncated tetrahedron (*T*-Td), and truncated octahedron (*T*-Oh) with theoretical inner sphere diameters of about 12, 15, and 20 Å respectively, were synchronically constructed (Fig. 6b). Nearly at the same time, the same structure but denoted as NOTT-122 and NU-125 was also reported by Schröder and Hupp, respectively [122,123]. In their reports, both CO₂ and CH₄ adsorption of the MOFs was investigated. In particular, high-pressure CH₄ adsorption was measured at 298 K using NU-125 in gram scale.

After that, an amine-functionalized H₆L8 ligand, ascribed as H₆L8-NH₂ in Scheme 2 [124], and two symmetry-reduced dendritic hexacarboxylate ligands, *i.e.*, 5,5'-(4,4'-(5-(3,5-dicarboxyphenyl-carbamoyl)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))diisophthalic acid (abbreviated as ABTA or H₆L9 in Scheme 2) [125] and 5,5'-(4,4'-(5-(3-(3,5-dicarboxyphenyl)ureido)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))diisophthalic acid (abbreviated as UBTA or H₆L10 in Scheme 2) [126], were also designed and synthesized by our group via click reactions. X-ray diffraction analyses reveal that all three constructed Cu-based MOFs (denoted as NTU-105-NH₂, Cu-ABTA and Cu-UBTA, respectively) possess the same prototypical *rht*-type network as shown in Fig. 7.

Three other triazole-containing H₆L ligands, *i.e.*, 5,5',5''-((tripropargylamine-triyl)-tris(1*H*-1,2,3-triazole-4,1-diyl))-tri-*iso*-phthalic acid (H₆L11 in Scheme 2), 5,5',5''-(4,4',4''-((triphenylamine)-4,4',4''-triyl)-tris(1*H*-1,2,3-triazole-4,1-diyl))tri-*iso*-phthalic acid (H₆L12 in Scheme 2), and 5,5',5''-(4,4',4''-((1,3,5-triphenylbenzene)-4',4'',4'''-triyl)-tris(1*H*-1,2,3-triazole-4,1-diyl))tri-isophthalic acid (H₆L13 in Scheme 2) were synthesized by Farha and coworkers via clicked combinations of dimethyl 5-azidoisophthalate with three triethynyl-containing precursors, tripropargylamine, tris(4-ethynylphenyl)amine, and 1,3,5-tris(4-ethynylphenyl)benzene, respectively [127]. Then, three MOFs, denoted as NU-138, 139, and 140, were constructed after reacting these ligands with Cu(II) ion (Fig. 7). Structure analyses show that these MOFs have isoreticular *rht*-type network but different pore sizes. Similar to NU-125, these three MOFs also show high capability for CH₄ uptake.

Facilitated by the conceptual approach of reticular chemistry, three types of transparent crystals of MOFs, denoted as NTU-161, 162 and 163, were successfully assembled after reacting H₆L8, H₆L12 and H₆L13 with Zn(II) ion [128]. Structure analyses reveal that they are isoreticular framework of NTU-105 with the same inner sphere diameters of the *cub*-Oh polyhedron (approximately 11.0 Å), but their apertures of both *T*-Td and *T*-Oh polyhedrons expand from 13.0 and 20.0 Å in NTU-161 to 14.0 and 23.0 Å in NTU-162, and to 15.0 and 25.0 Å in NTU-163, respectively.

2.1.5. MOFs derived from clicked oct-carboxylate ligands

Similar to other reported oct-carboxylate ligands [129–136], a triazole-containing octcarboxylate ligand, 5,5',5'',5'''-((methanetetrayltetrakis-(benzene-4,1-diyl))tetrakis(1*H*-1,2,3-triazole-4,1-diyl))tetrakisophthalic acid (H₈L14 in Scheme 2), was designed and syn-

thesized via the click reaction followed by the deprotection [137]. Blue crystals of the MOF, denoted as NTU-180, were successfully obtained after solvothermal reaction with Cu(II) ion. Structure analysis reveals that NTU-180 is a 3D porous network with a basic framework formula of [Cu₄(L14)(H₂O)₄]_n constructed by the connection of “clicked” L14 ligands with *in situ* generated paddlewheel Cu₂ clusters (Fig. 8a), in which two kinds of pores in diameters of 7.9 Å and 12.6 Å were observed (Fig. 8b).

2.2. MOFs derived from clicked triazolate ligands

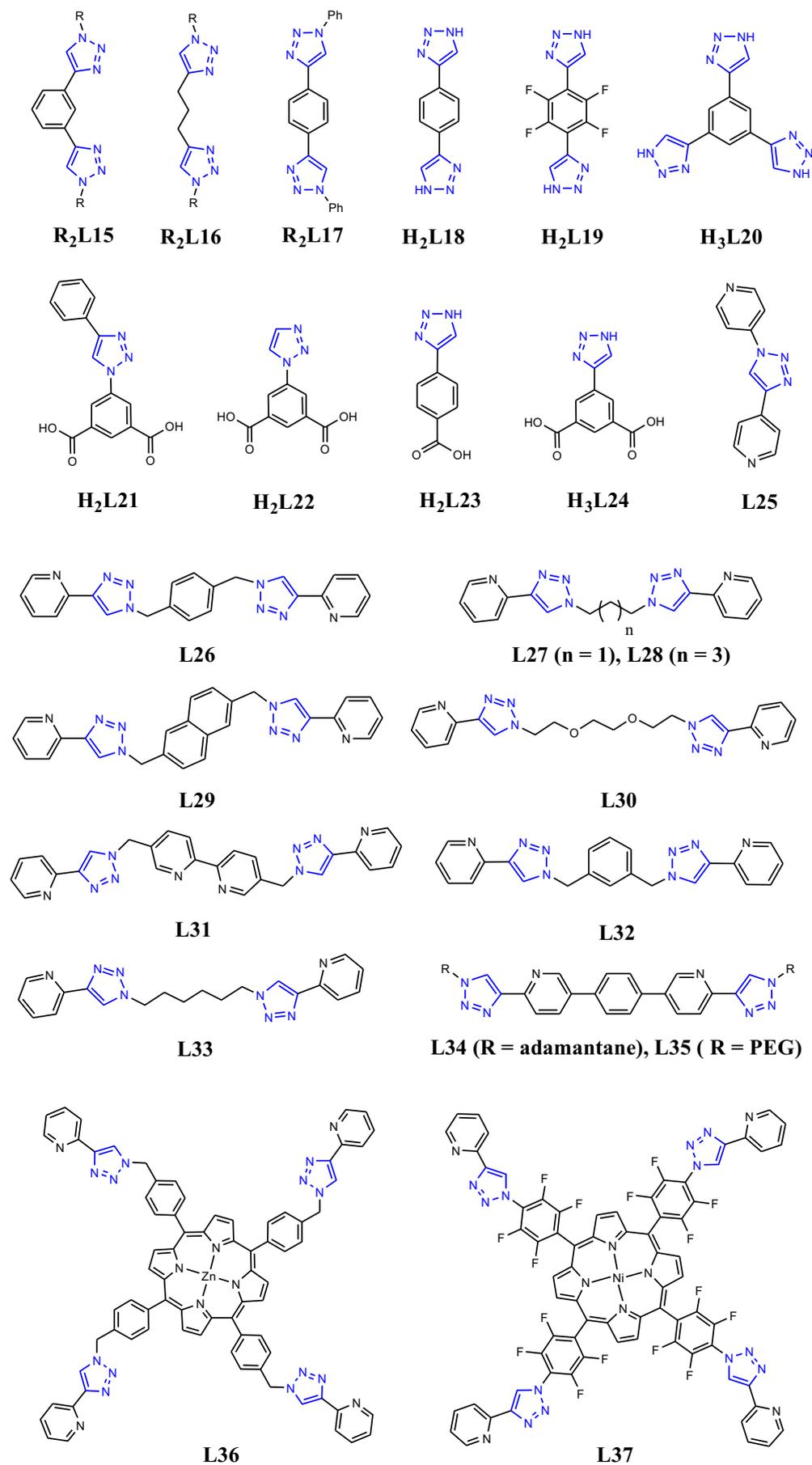
In addition to carboxylate-containing ligands, nitrogen-containing heterocyclic organic compounds, such as pyrazolates, triazoles and tetrazoles, are another large group of organic ligands for constructions of coordination materials [24,25,138–145]. The azide-alkyne 1,3-dipolar cycloaddition can easily give the generation of nitrogen-containing heterocyclic triazoles. Thus, organic ligands having coordinative triazolates were also synthesized via the click reaction of dual-, or triple-symmetrical acetylene-containing organic components and azide components such as trimethylsilyl azide. Taking the generated triazole group as an electron donor group, metal-organic polyhedrons (MOPs), cages, coordination polymers, and other coordinated complexes were constructed. For example, by taking 1,3-diethynylbenzene, 1,6-heptadiyne, and 1,4-diethynylbenzene as spacers in the click reaction with azide compounds, a series of triazolates were synthesized (R₂L15–R₂L17 in Scheme 3) [146,147]. After assemblies with Pd(II) ion, a group of [Pd₂L₄](BF₄)₄ cages were successfully obtained.

Recently, organic ligands having terminal triazolates, such as benzeneditriazolate and benzenetris-triazolate, were synthesized via the click reaction. Subsequently, MOFs with fascinating networks were constructed through strong coordination between the clicked polytopic triazolates and metal ions.

2.2.1. MOFs derived from clicked benzeneditriazolates

A ditopic triazolate ligand, 1,4-benzenedi(1*H*-1,2,3-triazole) (H₂L18 in Scheme 3, abbreviated as H₂BDTri), was designed and synthesized via the click reaction of pre-synthesized 1,4-diethynylbenzene with azide-containing precursor by Long and coworkers [148]. After solvothermal reactions with Cu(II) in different solvents (*N,N*-dimethylformamide (DMF) or *N,N*-diethylformamide (DEF)), two 3D flexible microporous MOFs possessing the same structure type but with different coordinated solvent molecules in a formula of Cu(BDTri)L (L = DMF or DEF) were obtained. The crystal structural transformation featuring the “breathing” behavior through single-crystal to single-crystal conversion was observed (Fig. 9), similar to some MOFs having the structure feature such as MIL-53 and Co(1,4-benzenedipyrazolate) [138,149–151]. Upon the exposure of the single crystals of Cu(BDTri)(DMF) in ambient atmosphere, 1D channels along the [0 1 0] direction gradually become narrow along with the crystal color change from green to blue and finally gray. On account of strong coordination between metals and the clicked triazolates, the initial and final structures together with an intermediate state of highly stable triazolate-bridged framework were well characterized by the X-ray analyses for detailed understanding of the structural deformations associated with framework breathing (Fig. 9). During the N₂ and O₂ adsorption investigations, two-step isotherm based hysteresis was also observed, further revealing the flexibility of the framework.

When replacing the organic ligand in Cu(BDTri)(DMF) by another clicked ditopic triazolate ligand, 2,3,5,6-tetrafluoro-1,4-benzeneditriazolate (H₂L19 in Scheme 3, abbreviated as TFBDTri²⁻) [152], its fluorinated analogue, Cu(TFBDTri)(DMF), was constructed, in which the framework flexibility was once again observed during the solvent exchange by DEF and DMSO.



Scheme 3. Clicked polytopic triazolates (L15–L20), carboxylate-containing triazolates (L21–L24), and pyridines (L25–L35). PEG = polyethylene glycol.

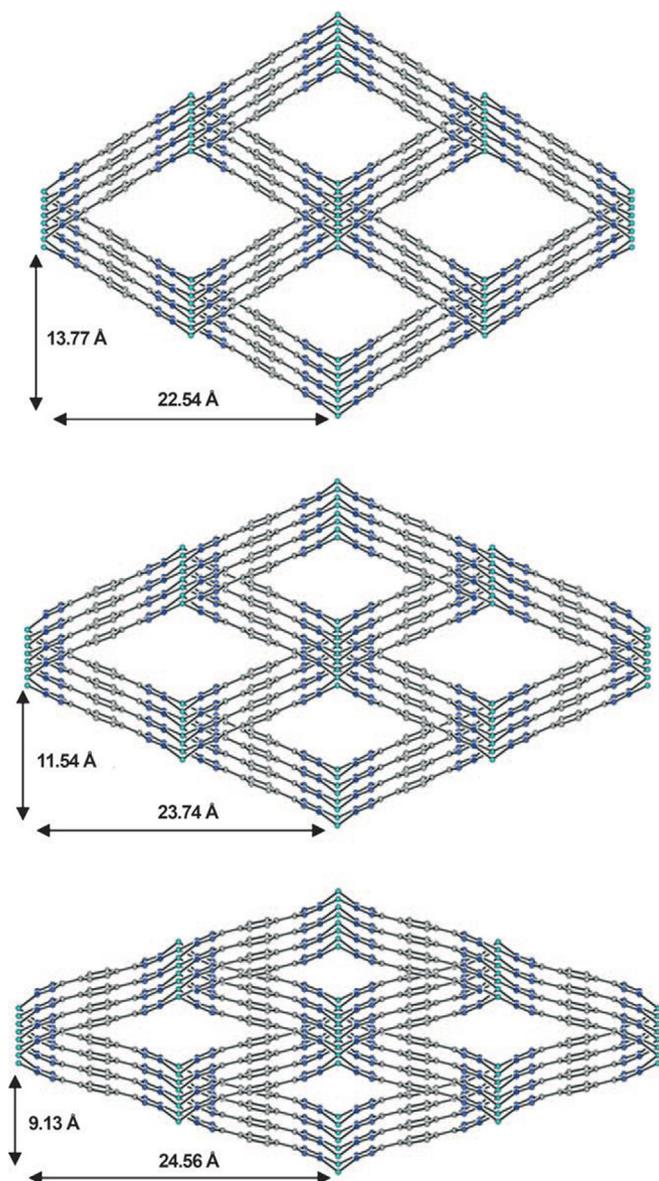


Fig. 9. Framework transformations of Cu(BDTri) showing the “breathing” behavior through single-crystal to single-crystal conversions. Adapted with permission from Ref. [148]. Copyright 2010, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2.2. MOFs derived from clicked benzenetriazolates

1,3,5-Tris(1H-1,2,3-triazol-5-yl)benzene (H_3L20 in Scheme 3, abbreviated as H_3BTri) was designed and synthesized *via* click reaction of pre-synthesized 1,3,5-triethynylbenzene with trimethylsilyl azide in 2009 [153]. After the coordination with Cu(II) under solvothermal reaction, a porous MOF, denoted as CuBTri, was successfully constructed by BTri-bridged *in situ*-generated chloride-centered $[Cu_4Cl]^{7+}$ square. Structure analysis reveals that the MOF possesses a cubic sodalite-type framework (Fig. 10). Characterization measurements indicate that it shows both remarkable chemical and thermal stability. Immersion experiments and powder X-ray diffraction (XRD) measurements show that it is highly stable in air, boiling water, methanol and even acidic media. Its framework could be well maintained until at least 270 °C. High porosity together with the remarkable stability makes the constructed CuBTri an excellent MOF in wide applications.

By replacing Cu(II) ion with Fe(II) or Co(II) ions, two structural analogous of CuBTri, *i.e.*, Fe-BTtri and Co-BTtri, were also

constructed by Long and coworkers [154,155]. Investigations of gas adsorption reveal that Fe-BTtri not only is highly selective toward CO over a variety of other gas molecules, but also exhibits readily reversible CO binding (Fig. 11), rendering it a promising adsorbent for CO scavenging from gas molecules such as H_2 , N_2 , CH_4 , and ethylene. The desolvated Co-BTtri exhibits a strong preference for binding O_2 over N_2 , with the isosteric heat of adsorption (Q_{st}) value of $-34(1)$ and $-12(1)$ kJ/mol, respectively. The high stability, selectivity, and O_2 adsorption capacity of Co-BTtri make it highly useful for the air separation.

2.3. MOFs derived from clicked carboxylate-containing triazolate ligands

By employing the versatile click chemistry, bifunctional carboxylate-containing triazolate ligands were synthesized for MOF constructions. In 2007, a carboxylate-containing triazolate, 1-(3,5-dicarboxyphenyl)-4-phenyl-1H-1,2,3-triazole (H_2dcppt , H_2L21 in Scheme 3), was synthesized *via* click reactions of 3,5-dicarboxyphenyl azide with azidobenzene [156]. After the solvothermal reaction with Co(II) ion, a (3,10)-connected 2D coordination polymer was successfully constructed. 1-(3,5-Dicarboxyphenyl)-4-carboxy-1H-1,2,3-triazole was also synthesized *via* click reaction, but when it was reacted with Mn(II) or Co(II) ion, *in situ* hydrothermal decarboxylation happened and it was transformed into 1-(3,5-dicarboxyphenyl)-1H-1,2,3-triazole (H_3dcpct , H_3L22 in Scheme 3) in the finally constructed four coordination polymers [157].

A ditopic bifunctional organic ligand, 4-(1,2,3-triazol-4-yl)-benzoate (abbreviated as *tab*, H_{23} in Scheme 3) including both 1,2,3-triazolate and carboxylate donor groups, was synthesized by Ma and coworkers [158–160]. Then, a porous MOF, denoted as MTAF-1, was constructed by the coordination between the *tab* ligand and *in situ* generated pentanuclear zinc cluster (Fig. 12a) [159]. Gas adsorption investigations reveal that the activated MTAF-1 shows a high porosity with a Langmuir surface area of 2300 m^2/g , exhibiting high performance on selective uptake of CO_2 over N_2 . After that, a MOF, denoted as MTAF-4, with a rare (6,9)-connected network was also constructed by the coordination of the *tab* ligand with *in situ* generated tetranuclear and heptanuclear zinc cluster (Fig. 12b) [160]. The microporous MTAF-4 exhibits a BET surface area of $\sim 1600 m^2 g^{-1}$ and a high capability for adsorbing CO_2 , H_2 and CH_4 under high pressure.

Subsequently, a triazole-containing ligand, 5-(1H-1,2,3-triazol-4-yl)isophthalic acid (abbreviated as H_3TAIP , H_3L24 in Scheme 3) [161], was also synthesized *via* clicked reaction in order to replace the tetrazole moiety of 5-tetrazolylisophthalic acid in *rht*-MOF-1 [105]. A new *rht*-type MOF, denoted as *rht*-MOF-tri (tri is short for triazolate), was then constructed (Fig. 13) by the assembly of the ligand with Cu(II) ion, which as expected exhibited high porosity and remarkably enhanced water/chemical stability by incorporating *in situ* generated triangular inorganic building unit $[Cu_3O(Tri)_3]$. These studies successfully demonstrate that employing bifunctional linkers incorporating both the azolate and carboxylate groups as donor units provide a promising way to construct highly stable MOFs for various applications.

2.4. MOFs incorporating click-extended bipyridine

In addition to the pyrazolates, triazoles and tetrazoles, pyridine derivatives are also a large group of nitrogen-heterocyclic organic ligands in the construction of coordination complexes [162–173]. Taking click reaction as an effective approach, some pyridine derivatives, such as L25–L37 in Scheme 3, were synthesized and subsequently used for assemblies of coordination complexes. Among these clicked pyridines, polytopical 1,2,3-triazol-4-

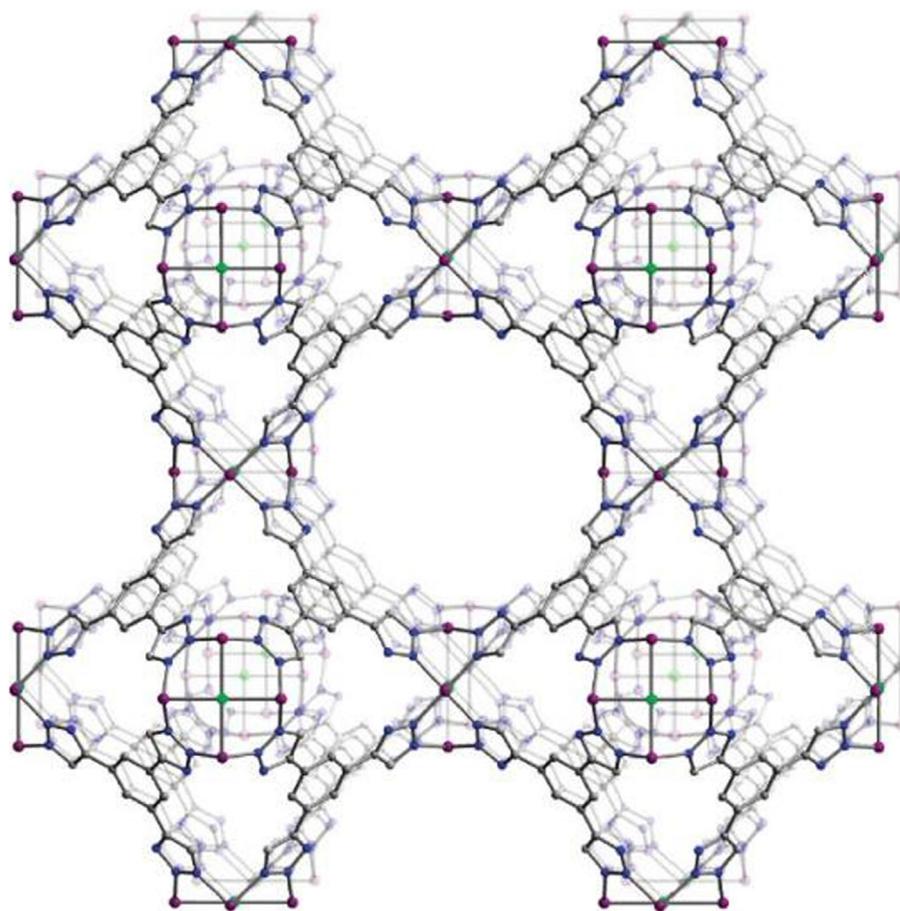


Fig. 10. Sodalite-type framework of CuBTri. Adapted with permission from Ref. [153]. Copyright 2009, American Chemical Society.

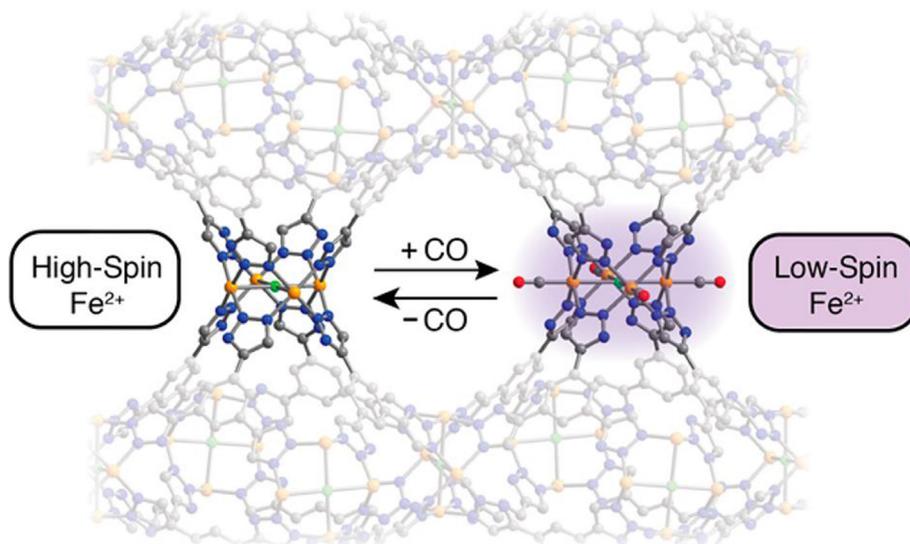


Fig. 11. Framework of Fe-BTtri showing reversible CO adsorption by unsaturated Fe(II) site and the spin-state exchange of Fe(II) during the adsorption and desorption of CO molecule. Adapted with permission from Ref. [154]. Copyright 2016, American Chemical Society.

ylpyridyl ligands can strongly chelate with metal ions through the nitrogen atoms of triazole and pyridine units, and thus, these ligands have been intensively investigated for synthesizing coordination compounds. For example, helicates were constructed by coordinating metal ions with the clicked pyridine derivatives (L26–L33 in Scheme 3) [174–178] and cages were also assembled

via the coordination between metal ions and the clicked triazole-containing pyridines (L34–L37 in Scheme 3) [179–182].

In the MOF construction, a custom-designed ligand, 4,4'-(2H-1,2,3-triazole-2,4-diyl)di-pyridine, was synthesized via click chemistry by Ma and coworkers [183]. Introducing the clicked new ligand into a prototypal pillared MOF, i.e., MOF-508 [184], to

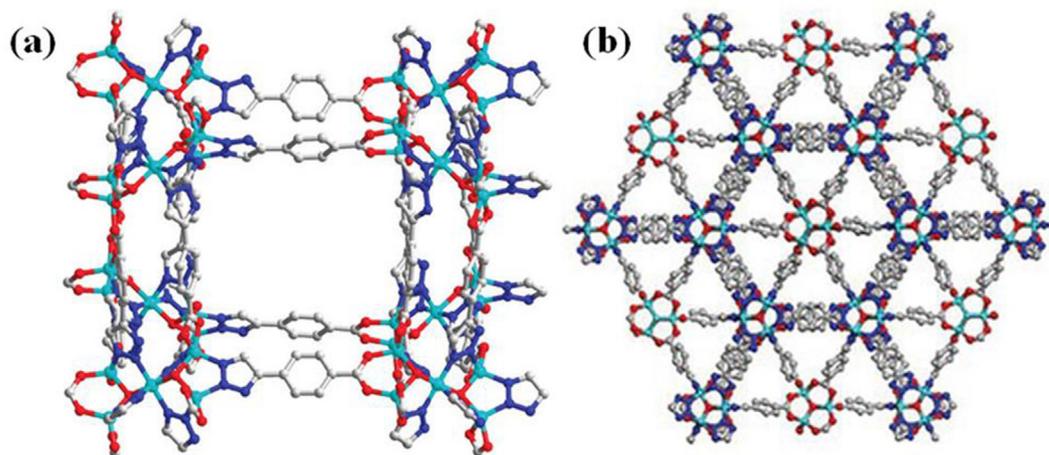


Fig. 12. Framework structures of (a) MTAF-1 and (b) MTAF-4. Adapted with permission from Ref. [160]. Copyright 2013, Royal Society of Chemistry.

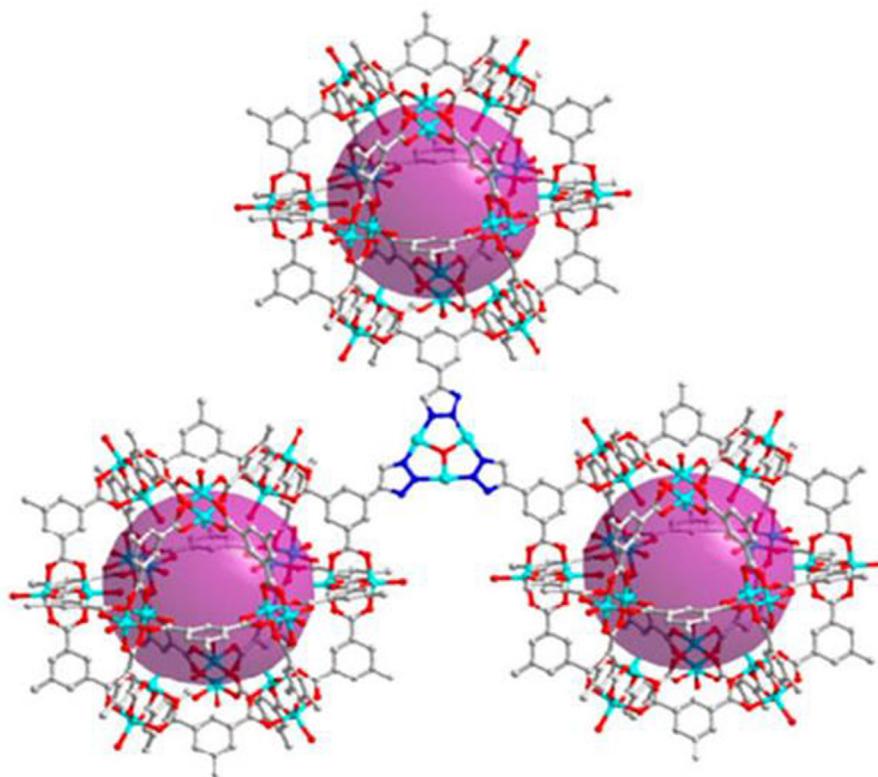


Fig. 13. C_3 symmetric building moiety of *rht*-MOF-tri. Adapted with permission from Ref. [161]. Copyright 2015, American Chemical Society.

replace 4,4'-bipyridine, a triazole-containing MOF, denoted as MTAF-3, was successfully constructed (Fig. 14). Since the incorporated 1,2,3-triazolate moieties feature exposed nitrogen atoms, the constructed MTAF-3 exhibits a remarkable enhancement of uptake capacity as well as significantly boosted Q_{st} toward CO_2 . These interesting results well demonstrate that incorporating 1,2,3-triazole functional groups to act as relatively moderate Lewis base centers is a feasible strategy for constructing novel porous MOFs with enhanced CO_2 uptake performance.

3. MOFs modified by click reaction

In addition to the direct synthesis of MOFs through the coordination of pre-designed polytopic organic ligands with inorganic

metal ions, an effective approach to achieve functional MOFs is post-synthetic modification. By incorporating functional groups into pristine MOFs that usually cannot be achieved during the direct synthesis processes, the modified MOFs often exhibit unique physical and chemical properties that are rarely presented in the pristine MOFs. Thus, post-synthetic modification has become a powerful strategy for the rational functionalization of the readily-available MOFs. Since the post-synthetic modification was introduced into MOFs in 2007 [185], a variety of MOFs have been post-synthetically modified so far [51,52,85,186,187]. For instance, amino-derived MOFs were intensively modified by various synthons such as aldehydes, isocyanates, and acid anhydrides. As aforementioned, the azide-alkyne 1,3-dipolar cycloaddition is an efficient reaction with wide readily-available reactants, which

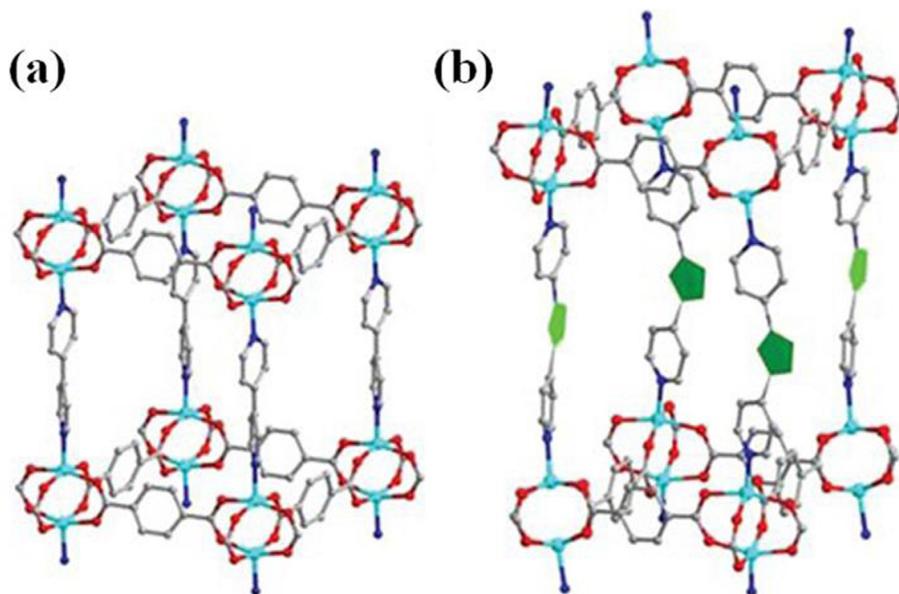


Fig. 14. Building units of (a) MOF-508 [184] and (b) MTAF-3. Adapted with permission from Ref. [183]. Copyright 2012, Royal Society of Chemistry.

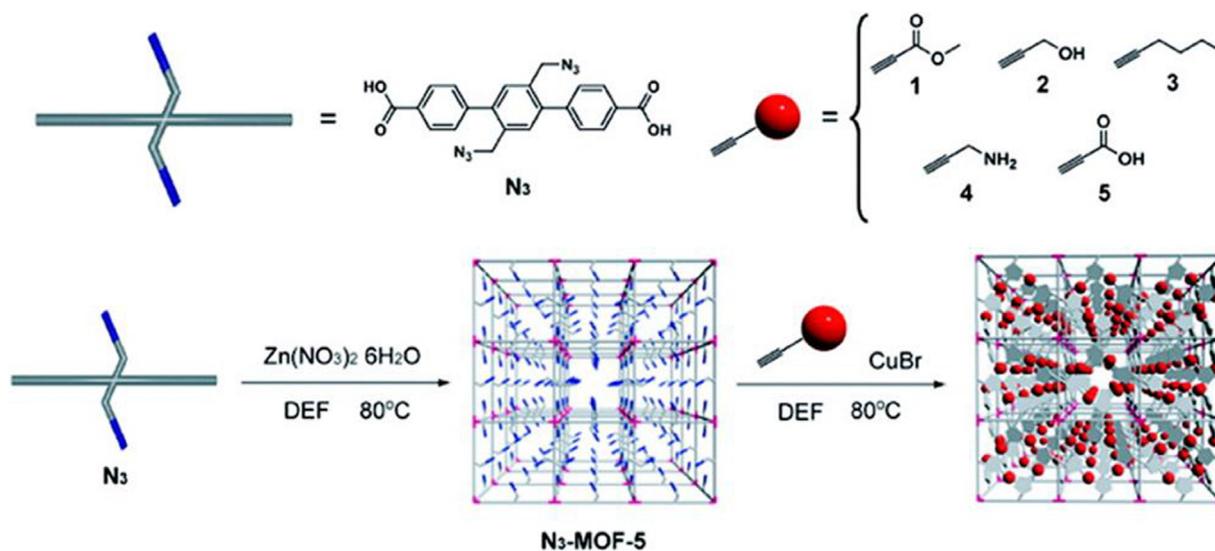


Fig. 15. Schematic illustration of a MOF bearing the azide group (N_3) for the click post-modification by alkyne substrates (1–5). Adapted with permission from Ref. [188]. Copyright 2008, American Chemical Society.

broadens the selectivity of reaction conditions and substrates. By using post-synthetic modification approach, a lot of functional groups including alkyne and azide derivatives have been grafted into or onto MOFs for diverse applications. When classifying these click post-synthetic modifications, four main types of reactions were developed as discussed below: (a) azide-tagged MOFs click-modified by alkynes, (b) alkyne-tagged MOFs click-modified by azides, (c) one-pot, two-step click modification of amino-derived MOFs by alkynes, and (d) copper-free strain-promoted click modification.

3.1. Click modification of azide-tagged MOFs by alkynes

Soon after the click chemistry being introduced into the process of ligand synthesis for the MOF construction, it was also used for post-synthetic modifications of MOFs. In 2008, Sada and coworkers investigated the click modification of a MOF (an analogue of

IRMOF-16) bearing the azide group on the organic linker (denoted as N_3 -MOF-16) by five small external alkynes, *i.e.*, methyl propargylate, propargyl alcohol, 1-hexyne, propargylamine, and propionic acid (1–5 in Fig. 15) [188]. After copper(I)-catalyzed click reaction of N_3 -MOF-16 with methyl propargylate, characterizations were carried out to check whether the host MOF was clickable or not. IR spectra reveal that the MOF was thoroughly modified, due to the complete disappearance of the feature peak of azide stretching band at 2100 cm^{-1} . The solution $^1\text{H NMR}$ spectrum of the decomposed product after click reaction illustrates that the corresponding triazole derivative as the major product was formed and no starting material was detected. Powder XRD patterns indicate that the framework was still well maintained after the click reaction. Reactions with substrates 2 and 3 in Fig. 15 further confirm the feasibility of the MOF modification by the effective click chemistry, although the framework decomposition was observed during the reactions with substrates 4 and 5 in Fig. 15.

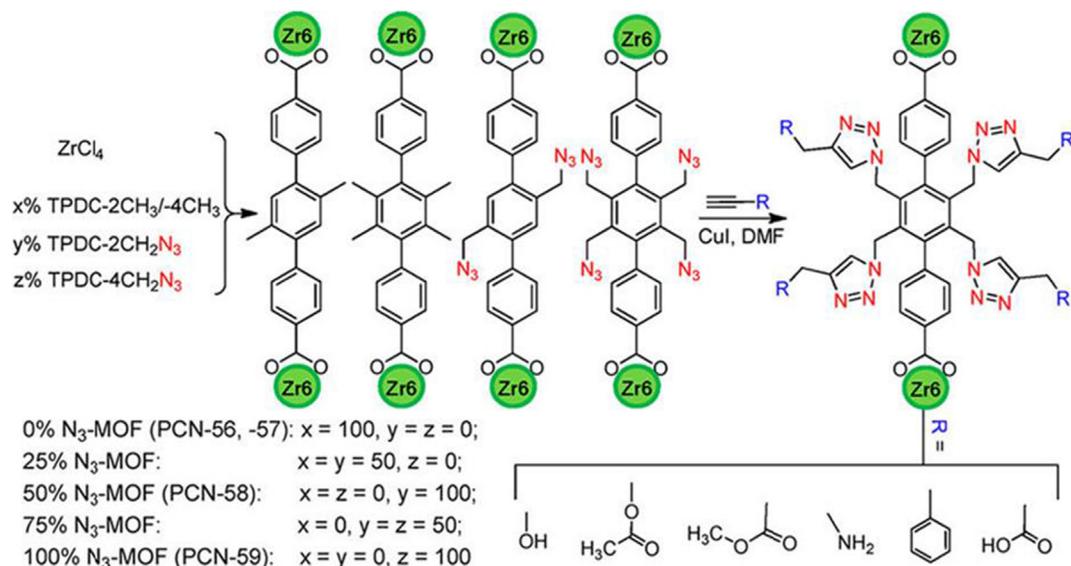


Fig. 16. Schematic illustration of Zr-based PCN-58 and PCN-59 “click”-modified by a series of acetylene compounds containing various functional groups. Adapted with permission from Ref. [189]. Copyright 2012, American Chemical Society.

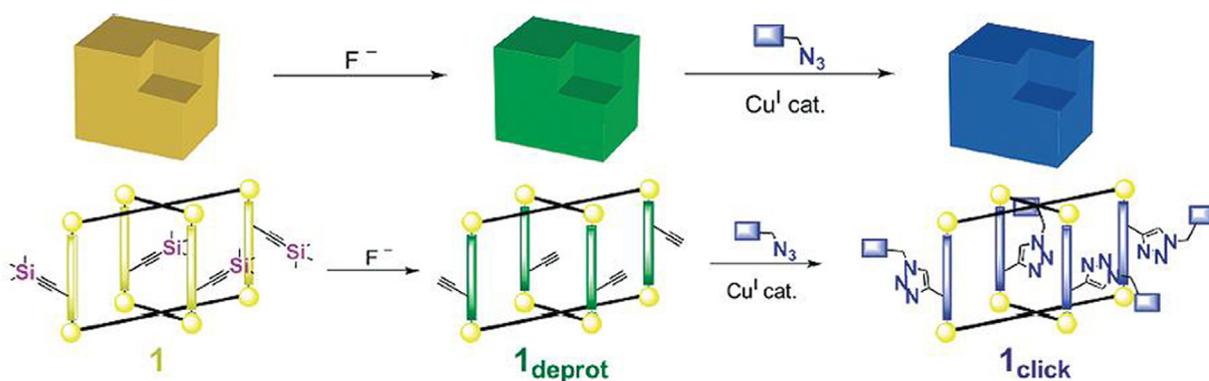


Fig. 17. Schematic illustration of the click post-modification of a MOF through functionalizing internal and external surfaces by different azides. Adapted with permission from Ref. [195]. Copyright 2009, American Chemical Society.

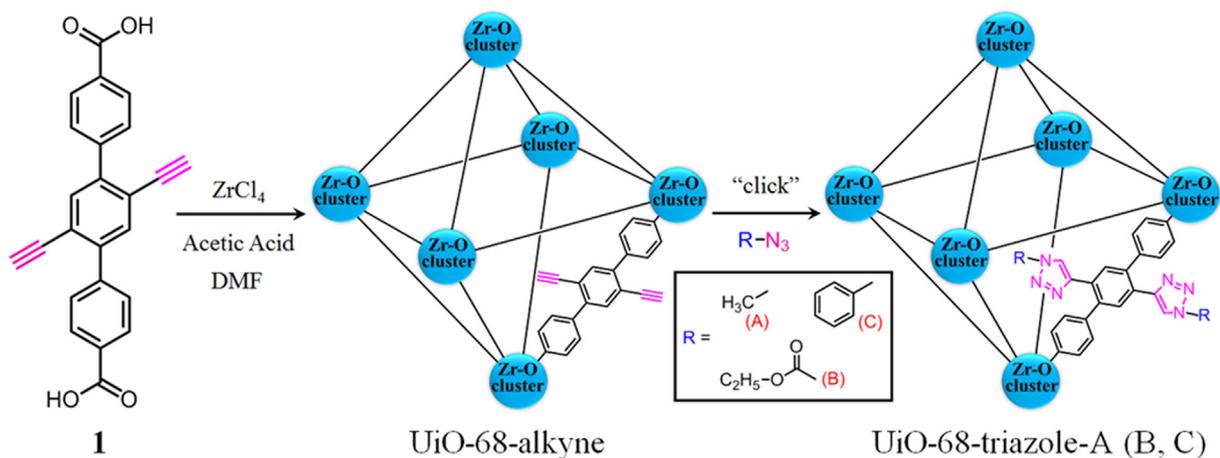


Fig. 18. Schematic illustration for the click post-modification of an alkyne-tagged UiO-68 (UiO-68-alkyne). Adapted with permission from Ref. [197]. Copyright 2015, American Chemical Society.

By following this method, Zr-based PCN-58 and PCN-59 were then click-modified by a series of acetylene-containing compounds with different functional groups, and the obtained modified MOFs were used for CO_2 adsorption by Zhou et al. (Fig. 16) [189]. After that, some highly stable MOFs were also click-modified by acetylene

compounds [190–193]. For instance, azide-tagged UiO-66 (UiO-66- N_3) was modified by phenylacetylene [193], and the resulted MOF was used as a fluorescent probe for selective detection of mercury(II) in aqueous media. Subsequently, clicked post-synthetic modification of azide-bearing MOFs by polytopical acetylene



Fig. 19. One-pot, two-step functionalization of an amine-containing MOF, DMOF-NH₂. Reproduced with permission. Adapted with permission from Ref. [199]. Copyright 2010, American Chemical Society.

ylene compounds for the fabrication of polymer gels was also investigated, as discussed in Section 4.5.

3.2. Click modification of alkyne-tagged MOFs by azides

Nearly at the same time when the azide-tagged MOFs were reported to be click-modified by alkynes, alkyne-tagged MOFs were also click-modified by azides. The surface of a MOF bearing trimethylsilyl (TMS) protected alkyne was post-synthetically modified with azides reported by Nguyen and coworkers in 2008 [194]. After solvothermal reaction of 3-[(trimethylsilyl)ethynyl]-4-[2-(4-pyridinyl)ethenyl]pyridine, 2,6-naphthalene-di-carboxylic acid, and Zn(II) ion, a two-fold interwoven MOF containing TMS-protected acetylenes was obtained. Characterizations reveal that when employing tetrabutylammonium fluoride (TBAF) as the desilylation reagent, only the MOF surface was desilylated due to large molecule size of tBu₄N⁺ counterion and pore-size limitation of the two-fold interwoven MOF. Copper(I)-catalyzed click reaction with an azide-containing dye, ethidium bromide monoazide, further confirm that the reaction only occurred on the crystal surface of contracted MOF, since the fluorescence from the clicked azide-containing dye was exclusively observed on the surface. Inspired by the surface-selective modification, azide-containing polyethylene glycol (PEG) was then grafted onto the surface of contracted MOF by click post-synthetic modification, changing the MOF crystal to be hydrophilic and wettable.

Subsequently, the authors synthesized an acetylene-bearing and non-catenated MOF, termed as TO-MOF, after solvothermal reaction of 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB) and 3-[(trimethylsilyl)ethynyl]-4-[2-(4-pyridinyl)ethenyl]pyridine with Zn(II) ion [195]. When employing TBAF as the fluoride source

for the removal of the TMS group, characterizations reveal complete desilylation in the internal MOF (Fig. 17). The conclusion was further confirmed after copper(I)-catalyzed click reaction of deprotected TO-MOF with benzyl azide. Interestingly, when changing the fluoride source from TBAF to KF, selective external surface deprotection was detected due to poor solubility of KF in organic solvents (Fig. 17). When click-modifying the surface deprotected TO-MOF by organic moieties, MOF composites in a core-shell fashion were achieved. In these processes, the MOF framework was determined both powder XRD and N₂ adsorption analyses, and the results show that the MOF crystallinity was well maintained.

Some other alkyne-tagged MOFs were also post-synthetic modified by copper(I)-catalyzed click reactions with azide-containing compounds. For example, azide groups were introduced into the network of NU-1000 by click reaction with pre-incorporated alkyne-containing compounds [196], and an alkyne-tagged Zr-based MOF, UiO-68-alkyne, was also click-modified with azidoethane, ethyl azidoacetate, and azidomethylbenzene by Wang and coworkers (Fig. 18) [197,198].

3.3. One-pot, two-step click modification of amino-derived MOFs by alkynes

Due to the unavailability and instability of most azide linkers, a one-pot, two-step functionalization method using easier-available amino-derived MOFs was developed by Farrusseng et al. for smoothly clicked post-synthetic modification of MOFs (Fig. 19). Taking DMOF-NH₂ [Zn(bdc-NH₂) (DABCO)] (DABCO = 1,4-diazabicyclo(2.2.2)octane) as a starting MOF, an alternative approach involving stable, nonexplosive compounds under mild conditions instead of reacting with diazonium salts in acidic conditions was conducted [199]. The azide intermediate MOF, DMOF-N₃, was obtained after treating the freshly dried DMOF-NH₂ with tBuONO and TMSN₃ in THF at room temperature overnight. Subsequently, copper(I)-catalyzed clicked post-synthetic modification was carried out in the same vessel by adding excess phenylacetylene in the presence of Cu^I(CH₃CN)₄PF₆ for 24 h. IR spectroscopy, solution ¹H NMR analysis and powder XRD patterns confirm the formation of azide intermediate and final product of DMOF-fun without the loss of long-range order of crystallinity of parent DMOF-NH₂. The feasibility of such a method was further confirmed by the one-pot, two-step clicked-modification of MIL-68(In)-NH₂. Finally, a combinatorial library of 24 functionalized MOFs was obtained by the one-pot,

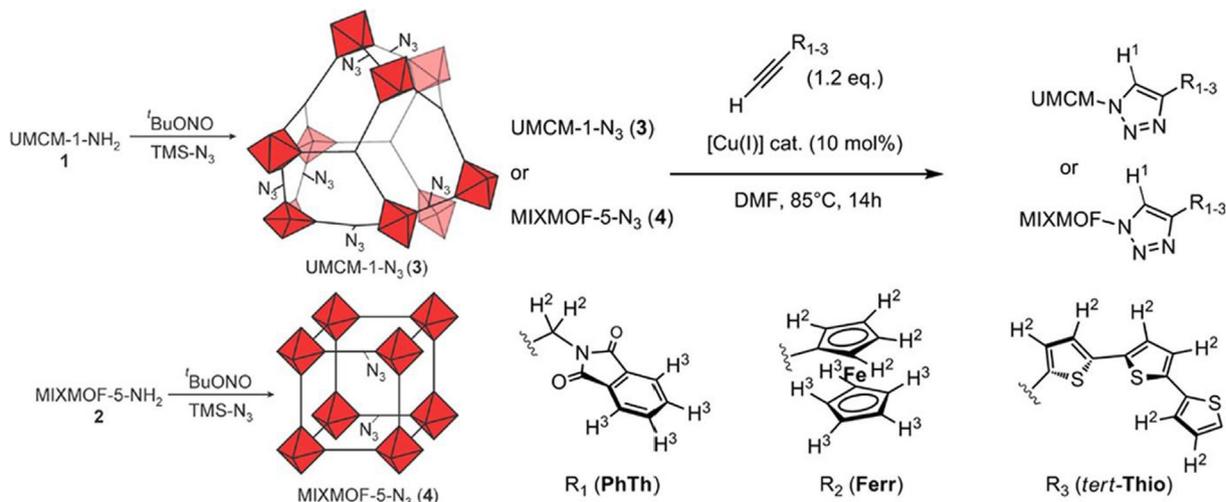


Fig. 20. Two-step clicked post modification of amine-functionalized UMCM-1 and MIXMOF-5. Adapted with permission from Ref. [84]. Copyright 2013, American Chemical Society.

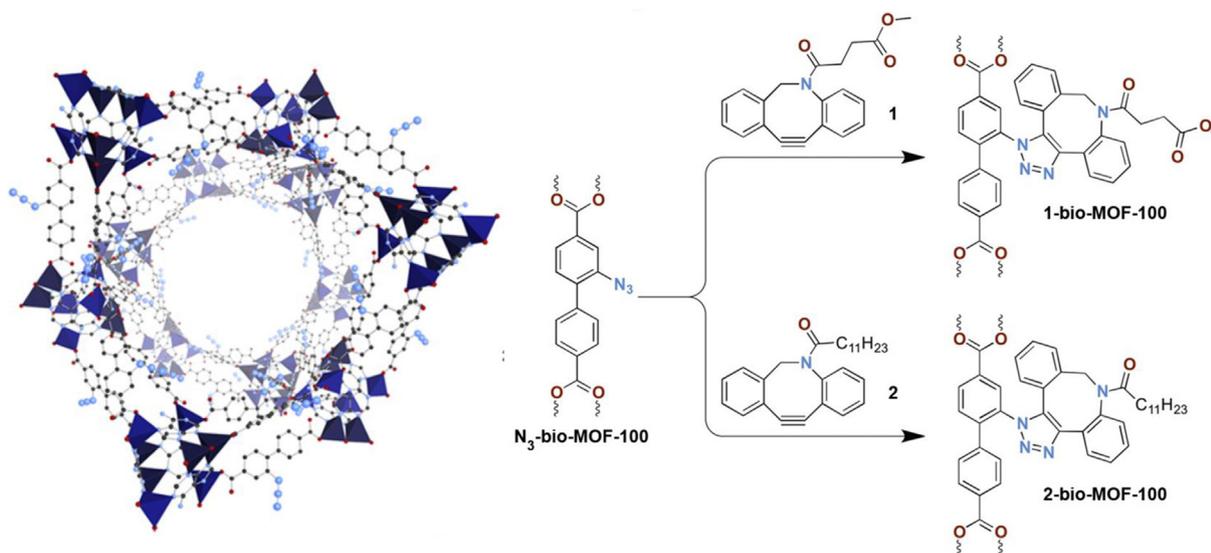


Fig. 21. Crystal structure of azide-decorated N_3 -bio-MOF-100, and schematic illustration for the strain-promoted click modification of N_3 -bio-MOF-100 with 4-(11,12-didehydrodi benzo[b,f]-azocin-5(6H)-yl)-4-oxobutanoate (1) and *N*-dodecanoyl-5,6-dihydro-11,12-didehydrodibenzo[b,f]azocine (2) to afford 1-bio-MOF-100 and 2-bio-MOF-100, respectively. Adapted with permission from Ref. [205]. Copyright 2012, American Chemical Society.

Post-synthetic modification of MOFs thin films

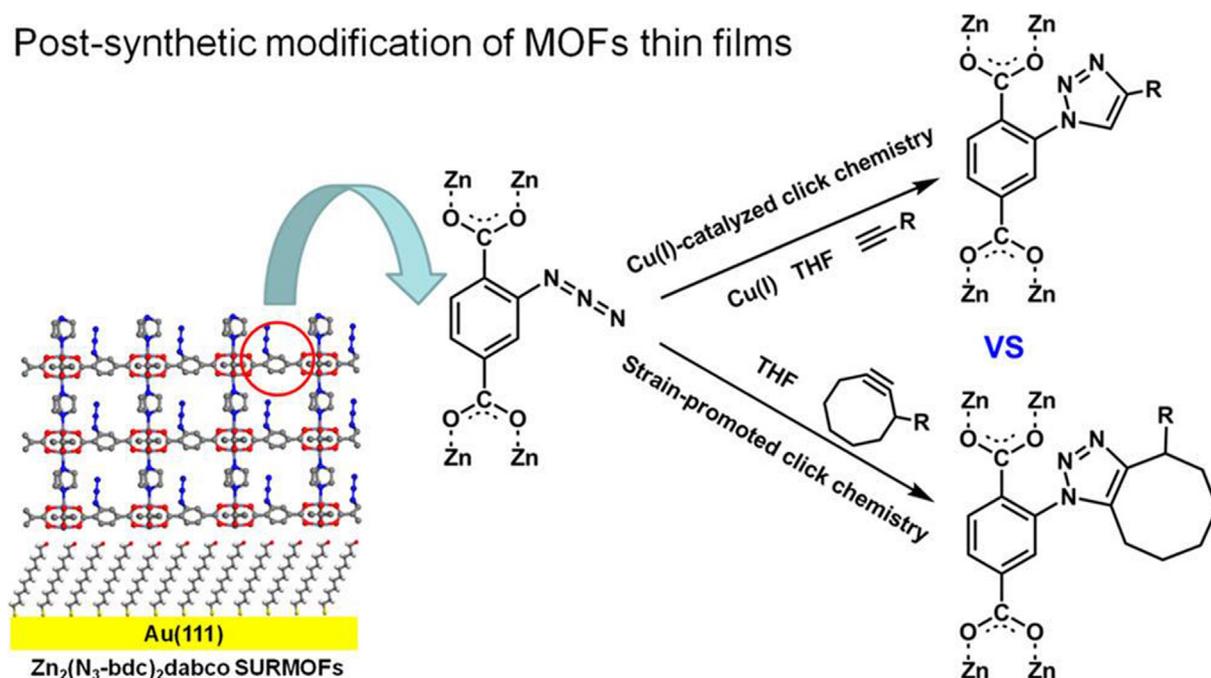


Fig. 22. Illustration of an azide-decorated MOF thin film post-synthetic modified by copper(I)-catalyzed and copper-free strain-promoted click reaction. Adapted with permission from Ref. [209]. Copyright 2013, American Chemical Society.

two-step clicked-modification of five aminoterephthalate-containing MOFs, *i.e.*, DMOF-NH₂, MIL-68(1n)-NH₂, CAU-1, MIL-53(Al)-NH₂ and MIL-101(Fe)-NH₂, with different alkynes [200]. Moreover, the grafting yields in these MOFs could be controlled from 10 to 100%.

Inspired by this method, the unconventional derivatization of N_3 -decorated MOFs was successfully demonstrated using amine-analogues as initial reactants by Giambastiani and coworkers [84]. Firstly, amine-functionalized UMCM-1 and MIXMOF-5 were treated by stable and nonexplosive *t*BuONO and TMSN₃ to afford N_3 -decorated MOFs, UMCM-1- N_3 and MIXMOF-5- N_3 , respectively. Single organic/organometallic acetylene derivatives for homodecoration, and defined binary and ternary mixtures of reactive

terminal alkynes in variable molar fractions for heterodecoration of N_3 decorated MOFs demonstrate that the single step click chemistry is a versatile reaction for a facile and convenient MOF engineering (Fig. 20).

3.4. Copper-free strain-promoted click modification of MOFs

To overcome intrinsic toxicity from conventional Cu-catalyzed azide-alkyne cycloaddition and broaden its utilization in biological field, strain-promoted Cu-free azide-alkyne cycloaddition was developed by using cycloalkyne derivatives as alkyne reagents [201], and this Cu-free method was rapidly employed in other areas [59,202–204]. The Cu-free approach was brought into MOFs

by Rosi and coworkers in 2012 [205]. In their investigation, an azide-modified mesoporous MOF, denoted as N₃-bio-MOF-100, was selected as the scaffold MOF, on account of its large interconnected channels allowing for unimpeded diffusion of large molecules (Fig. 21). Then, two cycloalkyne derivatives, i.e., methyl 4-(11,12-didehydridibenzo[*b,f*]-azocin-5(6H)-yl)-4-oxobutanoate (1 in Fig. 21) and *N*-dodecanoyl-5,6-dihydro-11,12-didehydridibenzo[*b,f*]azocine (2 in Fig. 21), were prepared to demonstrate the strain-promoted Cu(I)-free click-modification. After mixing the azide-bearing MOF with equivalent cycloalkyne derivatives in dichloromethane and standing the mixtures at room temperature overnight, characterizations indicate that the strain-promoted Cu-free click-modification was proceeded nearly quantitatively under ambient conditions without affecting the structural integrity of the MOF. The reaction was free of catalysts and byproducts, and even more efficient than the Cu-catalyzed counterpart.

After that, Woll et al. demonstrated that strain-promoted Cu-free click reaction is more effective reaction than the Cu(I)-catalyzed click reaction in the field of membrane fabrications. Utilizing strain-promoted Cu-free click-modification, a complete conversion on surface-anchored MOF (SURMOF) thin films was detected, in which the contamination of the product by cytotoxic Cu^I ion was successfully avoided (Fig. 22) [206,207]. Since then, the modifications of MOFs, such as UiO-66 and UiO-68, by the strain-promoted Cu-free click reaction were intensively investigated especially for utilizations in biological systems, as discussed in Section 4.4.

4. Applications of MOFs constructed or modified by click reaction

The azide-alkyne 1,3-dipolar cycloaddition not only enriches the library of MOF structures, but also widely broadens the applications of MOFs by introducing the *in situ* generated triazole groups and incorporating functional groups into the frameworks during either the syntheses of organic ligands or the post-synthetic modifications of pristine MOFs. Thus, diverse utilizations of MOFs derived from the azide-alkyne 1,3-dipolar cycloaddition have been investigated, including CO₂ selective adsorption, heterogeneous catalytic reactions, large-molecule capture and separation, biological research, and porous material fabrication.

4.1. Porosity and CO₂ adsorption capability

CO₂ has been cited as the primary gas leading to average temperature increase of the global surface and climate changes [8,9,208–218]. As a group of effective porous materials, lots of newly developed MOFs have been employed as CO₂ adsorbents, aiming to reduce anthropogenic CO₂ emission. Theoretical and experimental investigations have revealed that the incorporation of accessible nitrogen-donor groups into MOFs could dramatically increase the framework affinity toward CO₂ due to the dipole-quadrupole interactions between the polarizable CO₂ molecule and the accessible nitrogen site [217,218]. While the MOFs constructed *via* click reaction possess nitrogen-rich triazole groups, clicked post-synthetic modification could also introduce CO₂-philic groups into MOFs. Thus, these MOFs derived from the click chemistry have been exploited for the CO₂ adsorption.

4.1.1. MOFs containing accessible triazole groups for CO₂ adsorption

Although structural and topological analyses show that NTU-101-Zn processes a 3D porous framework, almost half of the pore channels are blocked by the coordinated DMF molecules. The removal of coordinated DMF molecules through the activation process causes the collapse of the framework [90]. As a result, NTU-101-Zn shows poor gas adsorption capacities. Surprisingly, a sharp improvement of framework stability was achieved after a process of metal ion exchange from Zn to Cu, and a remarkable increase of the framework porosity was observed after the activation of Cu exchanged NTU-101-Zn (named as NTU-101-Cu). The results of N₂ sorption at 77 K show that the activated NTU-101-Cu gives an overall N₂ uptake of 526 cm³ g⁻¹ and a calculated BET surface area of 2017 m² g⁻¹, while the pristine NTU-101-Zn shows an overall N₂ uptake of 30 cm³ g⁻¹ with a BET surface area of only 37 m² g⁻¹ (Fig. 23a). The CO₂ adsorption capability was then carried out, and the results indicate that NTU-101-Cu presents the CO₂ uptake of 101 cm³ g⁻¹ (16.6 wt%) at 1 atm and 273 K (Fig. 23b) and the Q_{st} for CO₂ was determined to be 25–20 kJ mol⁻¹. Meanwhile, NTU-101-Cu shows low N₂ and CH₄ uptake capabilities of 7 and 20 cm³ g⁻¹ at 1 atm and 273 K, respectively [90]. These results clearly demonstrate that the triazole-containing NTU-101-Cu could act as an efficient adsorbent for CO₂ selective adsorption.

The gas adsorption measurements were also carried out on the activated NTU-111, NTU-112 and NTU-113, and the results show

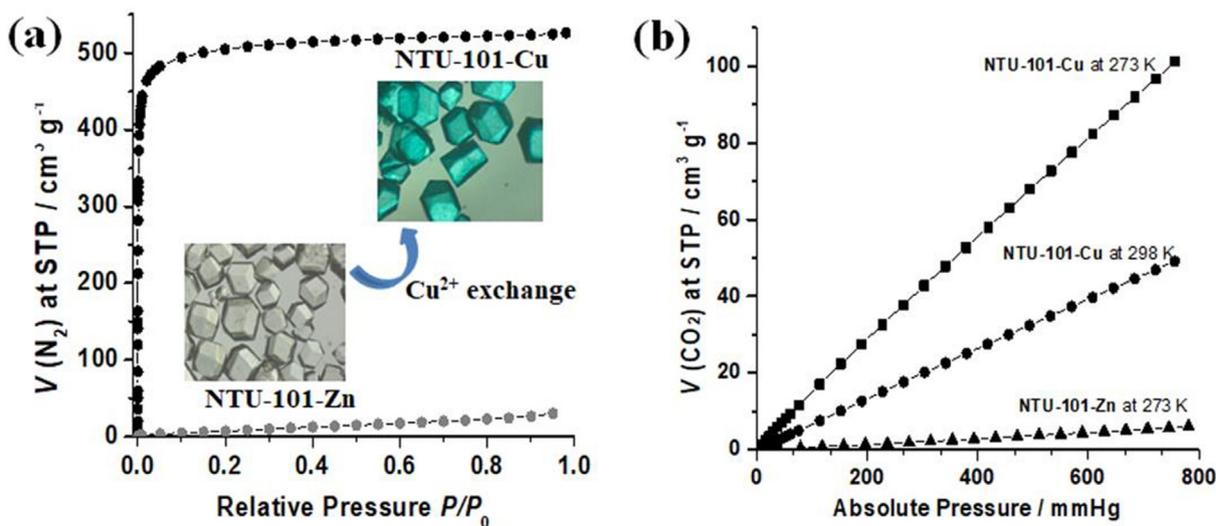


Fig. 23. (a) N₂ sorption isotherms of activated NTU-101-Zn and NTU-101-Cu at 77 K, and (b) gas sorption isotherms of activated NTU-101-Cu for CO₂ at 273 and 298 K, and N₂ at 273 K. Adapted with permission from Ref. [90]. Copyright 2012, Royal Society of Chemistry.

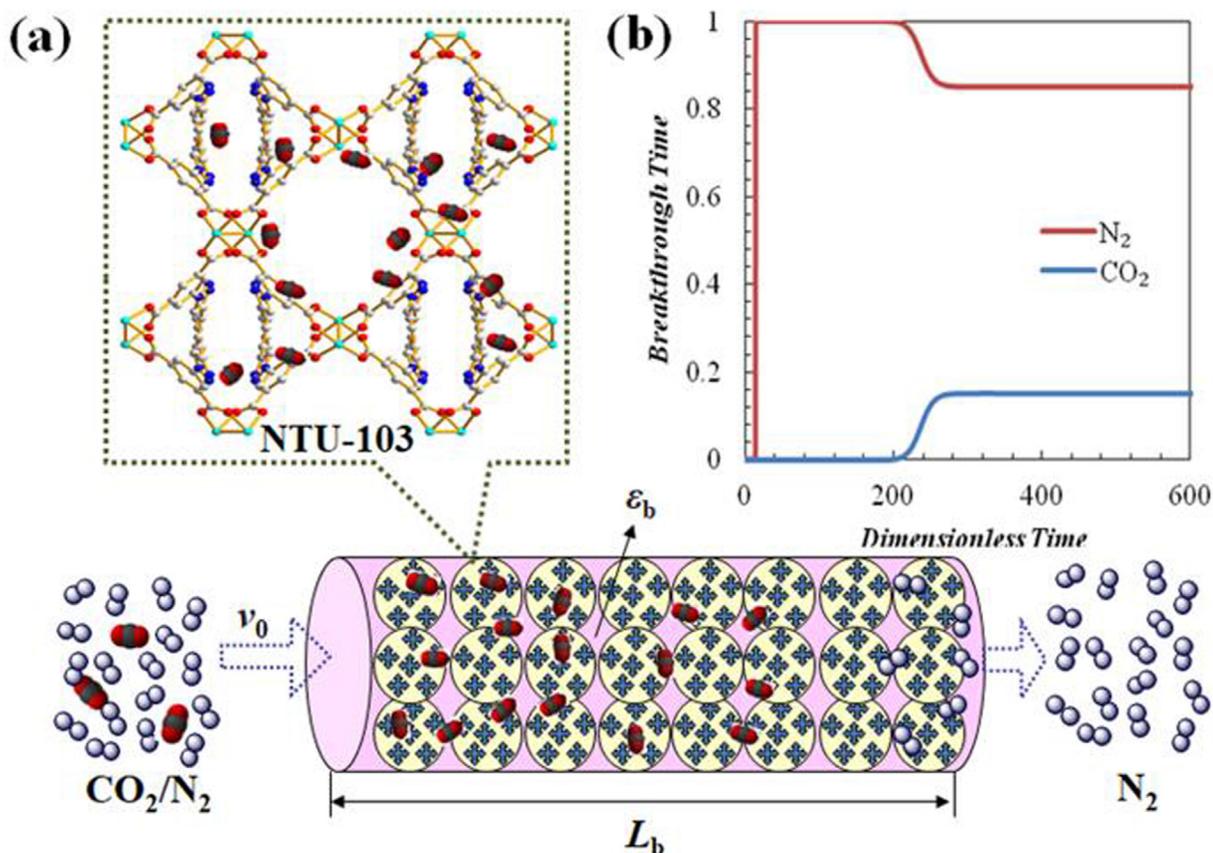


Fig. 24. (a) Illustration of an NTU-113 packed fixed-bed, and (b) simulated breakthrough curves for CO_2/N_2 mixture passing through the fixed-bed. The inlet CO_2/N_2 ratio is 0.15/0.85 at 273 K and 100 kPa. Adapted with permission from Ref. [92]. Copyright 2014, Royal Society of Chemistry.

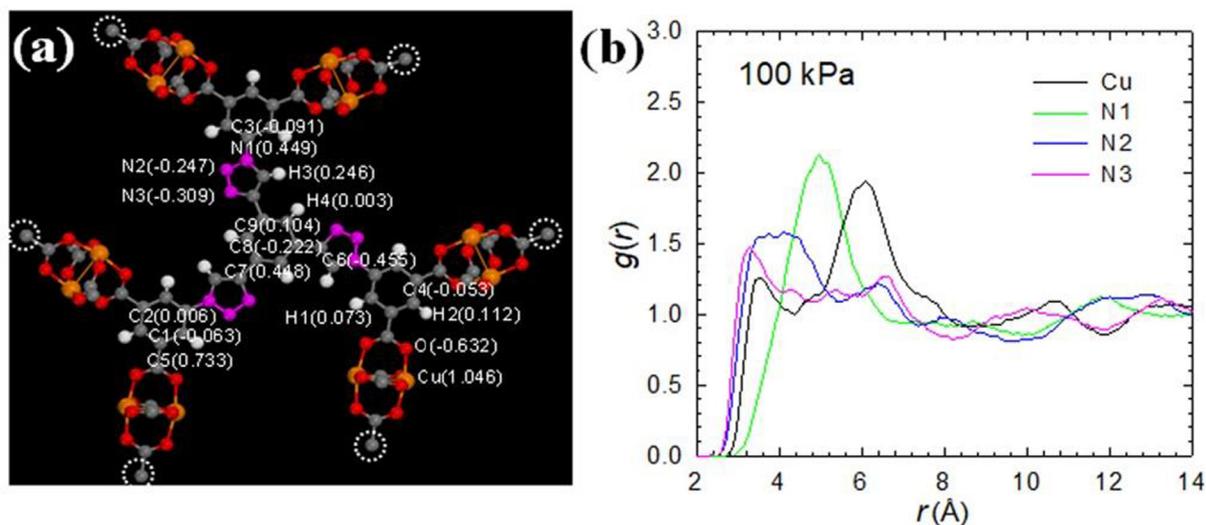


Fig. 25. (a) Atomic charges in a fragmental cluster of NTU-105. Color code: Cu, orange; O, red; N, pink; C, grey; H, white. (b) Radial distribution functions of CO_2 around Cu, N1, N2 and N3 atoms at 100 kPa. Adapted with permission from Ref. [121]. Copyright 2013, Springer Nature Limited.

that all of them possess high framework stability and high porosity with overall N_2 uptake of 660, 829, 873 $\text{cm}^3 \text{g}^{-1}$ and calculated BET surface areas of 2450, 2992 and 3095 $\text{m}^2 \text{g}^{-1}$, respectively [92]. Gas adsorption investigations indicate an increase of the CO_2 -uptake capability from NTU-111 to NTU-113. At 273 K and 1 atm, NTU-111, NTU-112 and NTU-113 give CO_2 -uptake values of 124.6, 158.5 and 166.8 $\text{cm}^3 \text{g}^{-1}$ respectively, while corresponding

N_2 -uptake values are of only 10.5, 11.0 and 11.9 $\text{cm}^3 \text{g}^{-1}$. The calculations show corresponding $Q_{\text{st}}(\text{CO}_2)$ values of ~ 30.7 , ~ 32.0 and $\sim 33.2 \text{ kJ mol}^{-1}$ at low loading range of CO_2 . All of them present high CO_2 selectivity and high CO_2 -framework interactions, especially in the case of NTU-113. Therefore, a simulation was conducted to investigate the performance of NTU-113 toward post-combustion CO_2 capture from a flue gas. The breakthrough

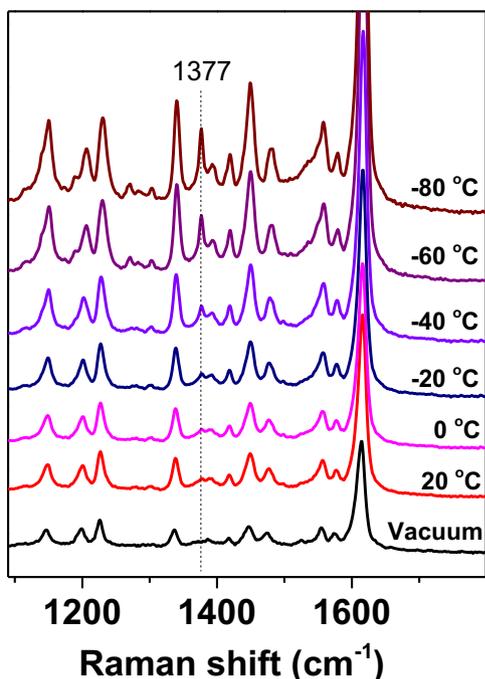


Fig. 26. Temperature dependent Raman spectra of NTU-180 (Vacuum) and CO₂-adsorbed NTU-180 (20 to -80 °C) showing obvious spectroscopic changes before and after the CO₂ adsorption. Adapted with permission from Ref. [137]. Copyright 2016, American Chemical Society.

times were calculated to be 13.8 for N₂ and 181.2 for CO₂ when the CO₂/N₂ mixture with initial molar ratio of 0.15:0.85 passes through a fixed-bed packed by NTU-113 (Fig. 24). The positive result based on the theoretical simulation clearly indicates that the clicked triazole-containing MOFs are highly useful systems for the CO₂/N₂ separation.

As the activated NTU-105 exhibits an overall N₂ uptake of 861 cm³ g⁻¹ at 1 atm with a surface area of up to 3543 m² g⁻¹, its CO₂ adsorption capability was also investigated [121]. Gas sorption isotherms reveal that it possesses an CO₂-uptake capability as high as 187 cm³ g⁻¹ (36.7 wt%) but a N₂ uptake capability of only 16 cm³ g⁻¹ at 1 atm and 273 K, making it one of top MOFs for CO₂ selective adsorption. The calculation based on isothermals reveals that it has a Q_{st} value of ~35 kJ mol⁻¹ for CO₂ at low loading range. Molecular simulation studies were further utilized to investigate the remarkable CO₂-framework interactions (Fig. 25), and the calculated radial distribution functions g(r) reveal that not only the open Cu sites but also all of the three N atoms in the coordination-free triazole ring provide high affinities to CO₂ molecule. Then, the isoreticular MOFs of NTU-105, NU-138, NU-139, NU-140 were also studied for the CO₂ adsorption. Gas adsorption experiments reveal that, among them, NU-140 exhibits not only gravimetric methane uptake of 0.34 g g⁻¹ at 65 bar and 298 K, corresponding to almost 70% of the target (0.5 g g⁻¹) set by the U.S. Department of Energy [127], but also rather high CO₂ uptake of 1.52 g g⁻¹ at 298 K and 30 bar and a significant H₂ uptake of 90 mg g⁻¹ at 65 bar at 77 K.

After the activation, NTU-180 shows a high porosity with an overall N₂ uptake of 655 cm³ g⁻¹ at 1 atm and 77 K, and a BET surface area of 2436 m² g⁻¹ [137]. It displays a CO₂-uptake value of 160.8 cm³ g⁻¹ at 273 K and 1 atm with a calculated Q_{st} of ~32.2 kJ mol⁻¹ at low loading range of CO₂. In order to monitor its affinity to CO₂ molecule, *in situ* Raman spectral measurements were then implemented to the activation NTU-180. After adsorbing CO₂, a new peak corresponding to CO₂ adsorbed in the framework clearly appears at 1377 cm⁻¹ instead of 1388 cm⁻¹ for gaseous CO₂ (Fig. 26), which gives unambiguous evidence of the framework affinity to CO₂ in the clicked triazole-containing MOF.

As aforementioned, MOFs derived from the clicked carboxylate-containing triazolate ligands and click-extended bipyridines also show high performance on CO₂ selective-adsorption [159–161,183]. Experimental measurements of CO₂ adsorption, theoretical simulations, and *in situ* Raman spectral studies clearly

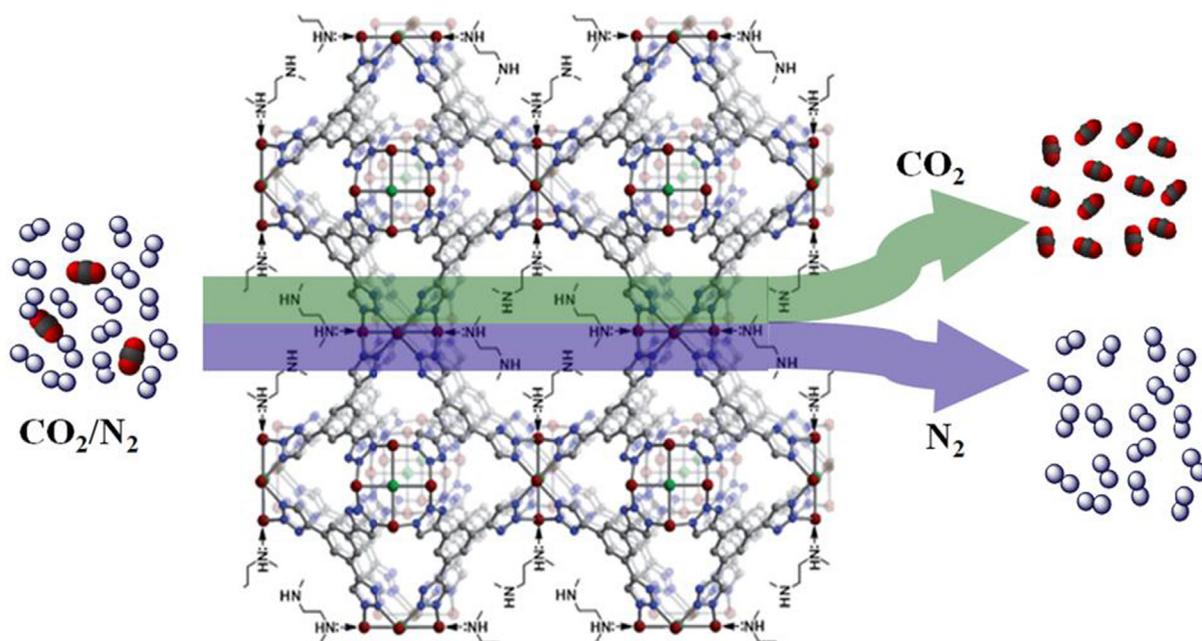


Fig. 27. Illustration of amine functionalized CuBTri (mmen-CuBTri) and its excellent selectivity for CO₂ capture. Adapted with permission from Ref. [220]. Copyright 2011, Royal Society of Chemistry.

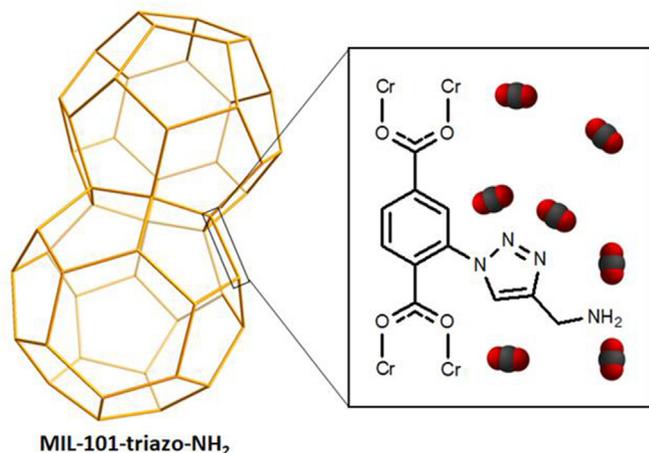
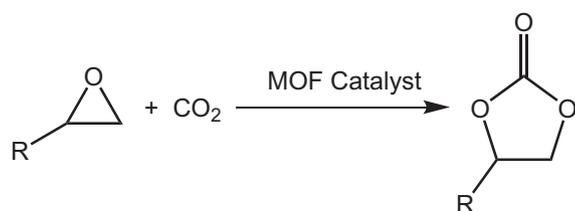


Fig. 28. Illustration of clicked adsorbent, MIL-101-triazo-NH₂, for selective CO₂ capture. Adapted with permission from Ref. [190]. Copyright 2013, Royal Society of Chemistry.

reveal that the incorporation of coordination-free triazole-containing groups into MOFs could dramatically increase the framework affinity to CO₂ molecule and the MOFs derived from the click reaction are highly promising materials for CO₂ selective adsorption.

4.1.2. Amine modified triazolate-MOFs for CO₂ adsorption

CuBTri itself is an effective adsorbent for CO₂ selective adsorption [219]. Amine derivatives were introduced into its framework to further improve the CO₂ selectivity on account of its remarkable chemical and thermal stability. Firstly, ethylenediamine (en) molecule was incorporated into CuBTri by Long and coworkers [153]. The resulting en-functionalized framework (CuBTri-en) exhibits higher uptake of CO₂ at very low pressures as compared with the non-grafted pristine MOF, and displays very high affinity for CO₂ binding with the Q_{st} value of up to 90 kJ mol⁻¹. Subsequently, they also introduced *N,N'*-dimethylethylenediamine (mmen) into the robust porous CuBTri, and the resulted mmen-CuBTri could adsorb 2.38 mmol CO₂ g⁻¹ (9.5 wt%) with a Q_{st} of up to 96 kJ mol⁻¹ and a high selectivity of up to 327 [220]. Although the chemisorption between amines and CO₂ was supported by infrared spectra, the CO₂ uptake was fully reversible, and the framework could be easily regenerated at 60 °C with a cycling time of just 27 min. Thus, mmen-CuBTri is an effective adsorbent for CO₂/N₂ separation based on the CO₂ selective adsorption (Fig. 27). Piperazine (pip) was also used to modify CuBTri by D'Alessandro et al. for the purpose of CO₂ selective adsorption [221]. The post-synthetically modified product, pip-CuBTri, exhibits an improved CO₂ uptake capability as compared with the non-grafted material, showing a Q_{st} of up to 96.5 kJ mol⁻¹ and a selectivity factor of 130 over N₂. The pip-CuBTri could also be regenerated *via* both pressure and temperature swing processes. These results clearly indicate that



Scheme 4. MOF-based catalytic cycloaddition of CO₂ with epoxides to generate various carbonates.

highly stable MOFs constructed by the coordination of clicked triazolates with metal ions could be modified by organic amines to achieve high CO₂ adsorption capabilities.

4.1.3. Click modified MOFs for CO₂ adsorption

Through Cu-catalyzed azide-alkyne cycloaddition, some highly stable azide-tagged MOFs such as Zr-based PCN-58 and PCN-59 were post-synthetically modified by alkynes and then utilized for CO₂ adsorption [189]. The results reveal that, when introducing CO₂-philic amine and hydroxyl groups into the MOF networks, increased performance on CO₂ uptake and selective adsorption was observed.

To mimic conventional amine-based aqueous absorbents in the process of CO₂ adsorption, CO₂-philic amine group and *in situ* generated triazole group were both introduced into a highly stable mesoporous MIL-101 by the Cu-catalyzed azide-alkyne cycloaddition (Fig. 28) [190]. As compared with the pristine MIL-101, MIL-101-triazo-NH₂ exhibits remarkably improved CO₂-uptake capability of up to 128.3 cm³ g⁻¹ (20.1 wt%) at 1 atm and 273 K, and significantly enhanced selectivity to CO₂ over N₂. All the results clearly demonstrate that both the triazole-containing MOFs derived from click reactions and MOFs modified by CO₂-philic groups *via* click reactions could serve as excellent adsorbents for CO₂ selective adsorption.

4.2. Heterogeneous catalytic reactions

Owing to their high surface areas, larger molecule-accessible pores, and intrinsic properties, MOFs have also been employing as a group of effective heterogeneous catalysts or catalyst supports [14–17,222]. The MOFs constructed or modified by click reaction were considered as heterogeneous catalysts for different kinds of reactions, and their applications in CO₂ chemical conversion, biomimetic catalytic NO generation, asymmetric aldol reactions, transesterification reactions, and Knoevenagel condensations were well studied.

4.2.1. Catalytic CO₂ conversion

In addition to the physical adsorption, an alternative strategy to reduce the anthropogenic CO₂ emission is the catalytically chemical conversion of CO₂ into value-added chemicals [223,224]. MOFs incorporating coordination-free triazole groups usually have a good CO₂-philic property, thus facilitating the heterogeneous reac-

Table 1

Yields of various cyclic carbonates produced from NTU-180 catalyzed CO₂ cycloaddition with small/big sized epoxides. Adapted with permission from Ref. [115]. Copyright 2016, American Chemical Society.

Entry	Epoxides	Products	Yields
<i>Small substrates</i>			
1			96
2			83
3			85
4			88
<i>Large substrates</i>			
5			8
6			6
7			5

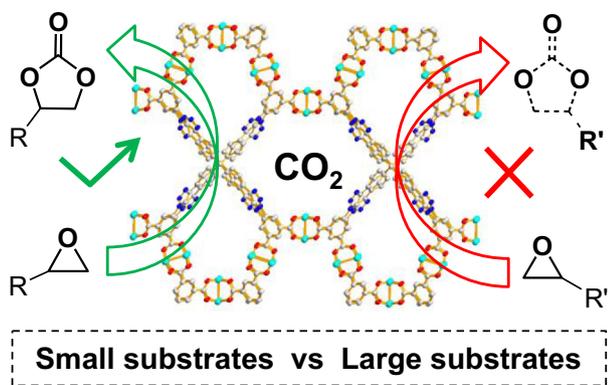


Fig. 29. Illustration of cyclic carbonates produced from the catalytic cycloaddition of CO_2 with epoxides using NTU-180 as a catalyst, and the effect of substrate-size on the reactions. Adapted with permission from Ref. [137]. Copyright 2016, American Chemical Society.

tion of CO_2 involved. Meanwhile, open Cu sites could usually be incorporated after the assembly of the clicked ligands with Cu ion. The embedded open Cu metal sites as active Lewis-acid species together with their inherent CO_2 -philic property endow these triazole-containing MOFs highly promising catalysts for CO_2 -involved reactions. The cycloaddition of CO_2 with epoxides to produce various carbonates (Scheme 4) was taken as a representative reaction for such an investigation [225–228].

When taking cuboctahedral nanoparticles of NTU-105 as a catalyst with tetra-*n*-butylammonium bromide (TBAB) as a co-catalyst and small-sized epoxides as substrates, the reaction yields after reactions at room temperature under 1 atm CO_2 pressure for 48 h were found to be 89%, 88% and 87% for 4-ethyl-1,3-dioxolan-2-one, 4-(bromomethyl)-1,3-dioxolan-2-one, and 4-(chloromethyl)-1,3-dioxolan-2-one, respectively [229]. However, the reaction gives lower yield of only 38% for 4-phenyl-1,3-dioxolan-2-one after the same process. Due to the difference of their porosity derived from different degree of the framework interpenetration, NTU-140 and 141 exhibited an obviously different catalytic activity toward the same substrates [95]. After stirring the reactions with TBAB as the co-catalyst in tubes at room temperature under 1 atm CO_2 for 60 h, the yields of cyclic carbonate products catalyzed by NTU-140 are 94%, 80%, 83% and 85% for 2-methyloxirane, 2-ethyloxirane, 2-(chloromethyl)oxirane, and

2-(bromomethyl)oxirane respectively, while corresponding yields catalyzed by NTU-141 are only 49%, 33%, 35%, and 36%.

The catalytic activity of activated NTU-180 toward CO_2 chemical conversion was also investigated with the same type reaction [137]. After catalytic reaction under 1 atm CO_2 pressure at room temperature for 48 h with TBAB as the co-catalyst, the yields of cyclic carbonates catalyzed by NTU-180 are 96%, 83%, 85%, and 88% for 2-methyloxirane, 2-ethyloxirane, 2-(chloromethyl)oxirane, and 2-(bromomethyl)oxirane, respectively (Table 1). Their related turnover frequency (TOF) values are 200.0, 172.9, 177, and 183.3 h^{-1} per paddlewheel Cu_2 cluster. In the control experiments catalyzed by HKUST-1, the yields are only 65%, 54%, 56%, and 57%, respectively. On the other hand, when larger epoxide substrates were exploited, a sharp decrease of the product yields was observed under the same catalytic process (Fig. 29). They were just 8%, 6% and 5% for 1,2-epoxyoctane, 1,2-epoxydodecane, and 2-ethylhexyl glycidyl ether, respectively (Table 1). Thus, remarkably high efficiency and selectivity to small epoxides on catalytic CO_2 cycloaddition make the Cu-based MOFs derived from clicked ligands suitable heterogeneous catalysts for carbon fixation.

4.2.2. Biomimetic catalytic NO generation

Since CuBTri has robust porosity and high stability even in media routinely used for *in vitro* and *in vivo* experiments, it has been exploited for biological application by Reynolds and coworkers (Fig. 30) [230–232]. By blending CuBTri into biomedical polyurethane matrices, a composite denoted as CuBTri-poly was firstly fabricated for use as a biomimetic catalyst to generate bioactive agent nitric oxide (NO) as therapeutic species from endogenous sources, *S*-nitrosothiols (RSNOs). The catalytic function of CuBTri in the composite was demonstrated by CuBTri catalyzed RSNO substrate, *i.e.*, *S*-nitrosocysteamine (CysamNO) [230]. The CuBTri-poly composite displays tunable NO-release kinetics proportional to the total content of CuBTri embedded into the composite. Its surface flux corresponding to the therapeutic range of 1–100 $\text{nM cm}^{-2} \text{min}^{-1}$, which is within the physiologically relevant range, was maintained in biological fluids such as blood. In order to mimic the proprietary composition of medical grade Tygon used in extracorporeal circuits, CuBTri was also embedded into a mixture of poly(vinyl chloride) (PVC) and dioctyl sebacate plasticizer to give the formation of a CuBTri/polymer composite film [231]. They found that the composite film could enhance NO-generation from the RSNO substrate, *i.e.*, *S*-nitroso-*N*-acetyl-

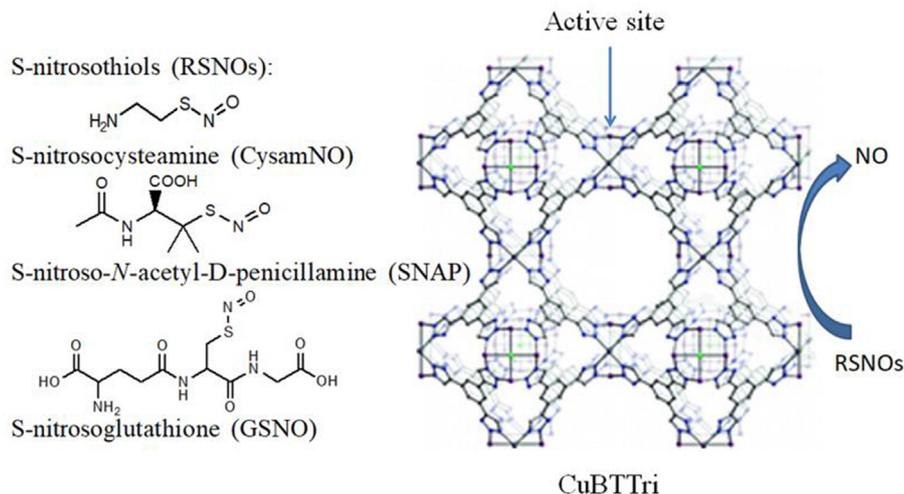


Fig. 30. Illustration of the NO generation from bioavailable substrates, *S*-nitrosothiols, catalyzed by CuBTri. Adapted with permission from Ref. [230]. Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



Fig. 31. Illustration of alkyne-bearing MOF click-modified by chiral azide (*L*- and *D*-2-azidomethylpyrrolidine) for their application of asymmetric aldol reactions. Adapted with permission from Ref. [233]. Copyright 2012, Royal Society of Chemistry.

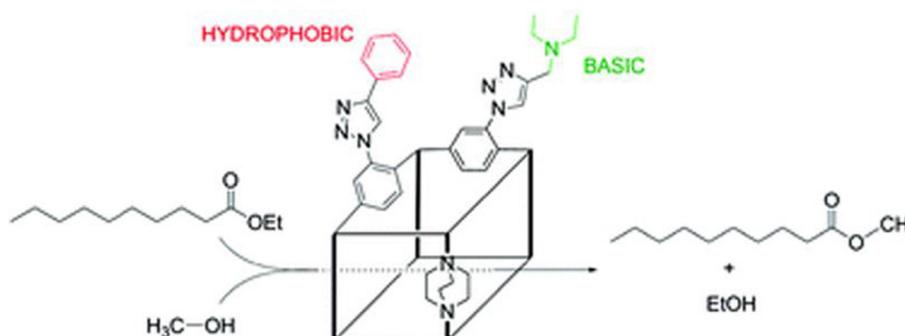


Fig. 32. Illustration of click-modified bifunctional MOF catalyst and its applications in catalytic transesterification of ethyldecanoate in methanol. Adapted with permission from Ref. [234]. Copyright 2012, Royal Society of Chemistry.

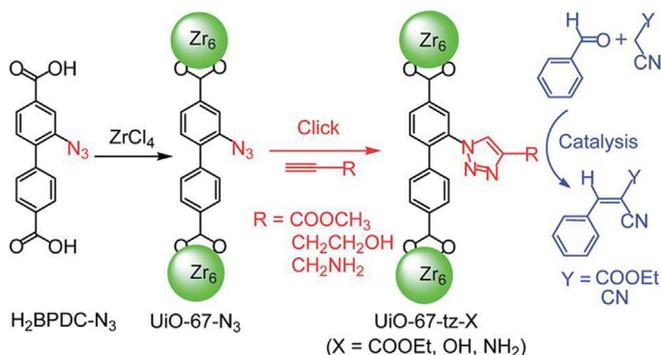


Fig. 33. Illustration for the synthesis and click-modification of UiO-67-N₃ in Knoevenagel condensation reactions. Adapted with permission from Ref. [235]. Copyright 2015, Royal Society of Chemistry.

D-penicillamine (SNAP). The cytotoxicity of CuBTTri/polymer composite film was evaluated. Cumulative copper release from the probable CuBTTri degradation during the catalytic process in both phosphate buffered saline (PBS) and cell culture media under physiological conditions for a 4-week duration was recorded to be less than 1% of theoretical copper content present in the CuBTTri/polymer composite film, and no significant toxicity was observed from *in vitro* cell studies in 3T3-J2 murine embryonic fibroblasts and primary human hepatocytes. When replacing the hydrophobic polyurethane or PVC by naturally derived polysaccharide chitosan, hydrophilic CuBTTri composite membrane was also fabricated by the same group [232], and the fabricated CuBTTri composite membrane exhibited the ability to enhance the NO generation from the most abundant small-molecule RSNO, *i.e.*, *S*-nitrosoglutathione (GSNO). All these investigations provide insight into the function and utility of CuBTTri based polymer systems in biomedical applications.

4.2.3. Heterogeneous asymmetric catalysis

An achiral alkyne-bearing MOF, denoted as Zn-DPYI, was pre-constructed by Duan et al. [233]. After clicked modification by two azide compounds with opposite chiral centers, *L*-*N*-2-azidomethylpyrrolidine (*L*-AMP) and *D*-*N*-2-azidomethylpyrrolidine (*D*-AMP), two enantiomeric Zn-MOFs with asymmetric catalytic sites were achieved (Fig. 31). Taking various aromatic aldehydes as substrates and reacting with cyclohexanone catalyzed by the click modified Zn-MOFs, decent yields with fairly high enantioselectivity were detected in all reaction systems. On the other hand, very low conversion with undetectable enantiomeric excess was obtained when taking the pristine MOF as the catalyst in the same reaction. These results indicate that introducing catalytic chiral centers into achiral MOFs by click chemistry to synthesize effective chiral catalysts could be easily achieved for heterogeneous asymmetric catalysis.

4.2.4. Transesterification reaction

Through the one-pot, two-step click modification, a strong organic base ($pK_b \approx 3$ for trialkylamines), diethylpropargylamine, as a catalytic center was grafted into an amino-derived MOF, and thus a mono-functionalized MOF catalyst was obtained by Fariuseng and coworkers [234]. A lipophilic group, *i.e.*, phenylacetylene, was respectively introduced into the amino-derived MOF and another mono-functionalized MOF with moderate basicity originated from the triazolyl group ($pK_b \approx 9.4$) and strong lipophilicity from the phenyl group. Meanwhile, modified by both diethylpropargylamine and phenylacetylene, a bifunctionalized MOF with an optimized balance between basicity and lipophilicity was also obtained (Fig. 32). Subsequently, their catalytic activities in the transesterification reactions were investigated. The results clearly show that the bifunctionalized MOF presents the highest activity toward the transesterification of ethyldecanoate in methanol, while the modification degree affects the ethyldecanoate conver-

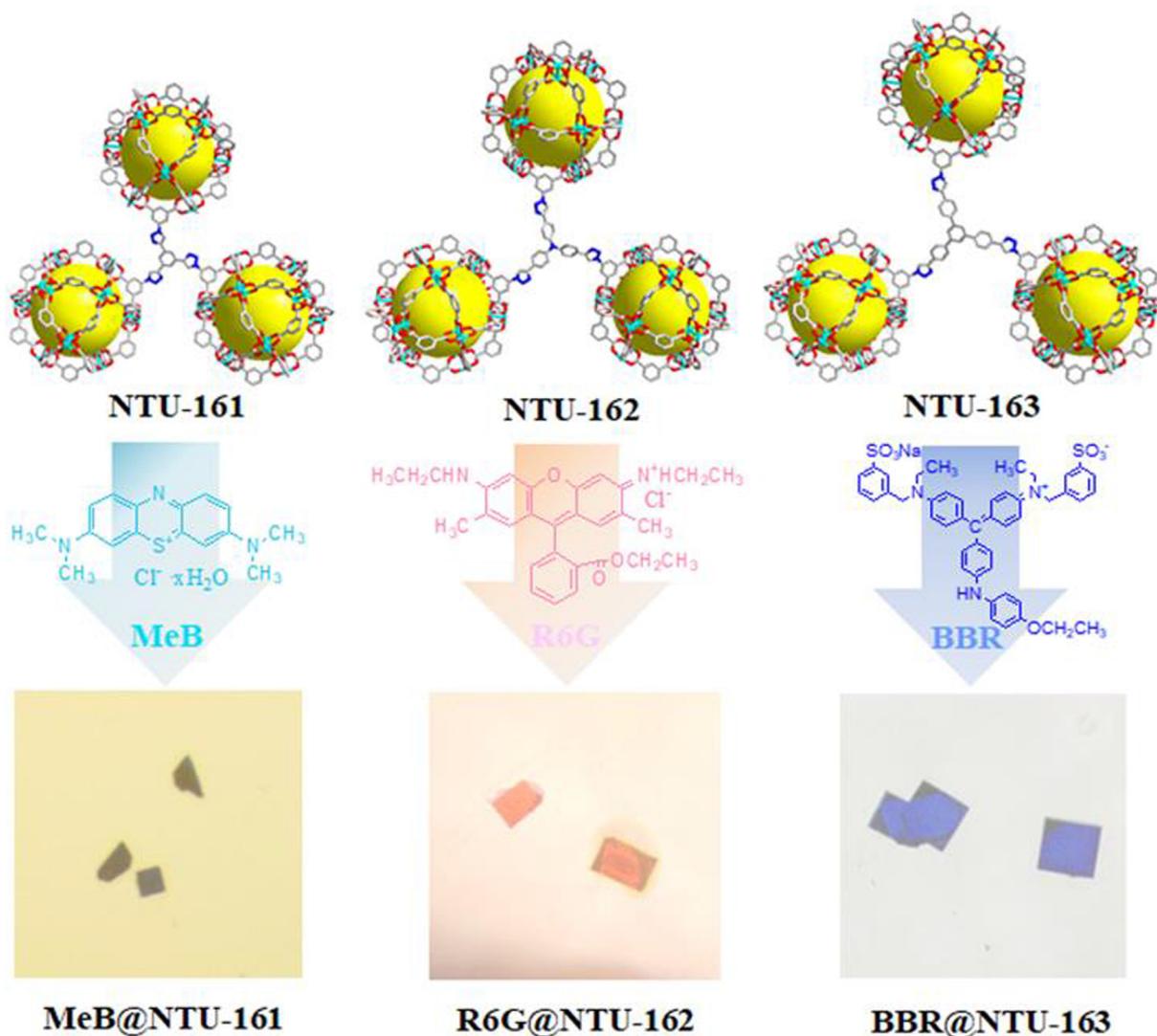


Fig. 34. Crystal colors of organic dye-adsorbed clicked isorecticular MOFs, *i.e.*, NTU-161, NTU-162, and NTU-163. MeB: Methylene Blue; R6G: Rhodamine 6G; BBR: Brilliant Blue R. Adapted with permission from Ref. [128]. Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

sion in the case of the monofunctionalized MOFs. These interesting results indicate that effective catalysts could be achieved through ingenious click modification of host MOFs.

4.2.5. Knoevenagel condensation

An azide-tagged Zr-based MOF, UiO-67-N₃, was initially constructed by Gao and coworkers [235]. Subsequently, three alkyne compounds, *i.e.*, methyl propargylate, propargyl alcohol, and propargylamine, were introduced into the framework by copper (I)-catalyzed click modification, leading to more stable MOFs, UiO-67-Tz-COOCH₃, UiO-67-Tz-OH, and UiO-67-Tz-NH₂, with different functional groups (Fig. 33). Due to moderate basicity derived from *in situ* generated triazolyl group, all three MOFs were taken as base catalysts for the Knoevenagel condensation between carbonyl and activated methylene. Catalytic reaction of benzaldehyde ethyl and cyanoacetate was conducted in DMF. The results reveal that, in the presence of UiO-67-Tz-NH₂, ethyl (E)- α -cyanocinnamate as the only product was detected and the condensation could be completely achieved within 8 h at 40 °C or only 3 h at 80 °C, while in the presence of UiO-67-Tz-COOCH₃ and UiO-67-Tz-OH, only a comparable conversion to that in the absence of any catalyst was observed, indicating that the grafted amino group,

instead of the *in situ* generated triazole group or other component of the framework, is the crucial active site for Knoevenagel condensation reaction. Further studies also demonstrate that the UiO-67-Tz-NH₂ catalyst was recyclable for the reaction with malononitrile, but not for the reaction with ethyl cyanoacetate, probably because the reaction between the amino site and the ester group of ethyl cyanoacetate leads to the formation of amide. The investigations also reveal that, although the basicity of the *in situ* generated triazolyl group is not strong enough, organic base groups could be grafted into the framework for Knoevenagel condensation by click post-synthetic modification.

4.3. Dye-probed applications toward large organic molecules

In addition to the gas adsorption and catalytic reactions, MOFs with large pores derived from the click-extended ligands or modified by the clicked reaction were also investigated in the applications toward large organic molecules.

4.3.1. Dye-probed large organic molecule capture and separation

Taking the clicked triazole group as an extending spacer, large organic ligands were successfully obtained by the click reaction

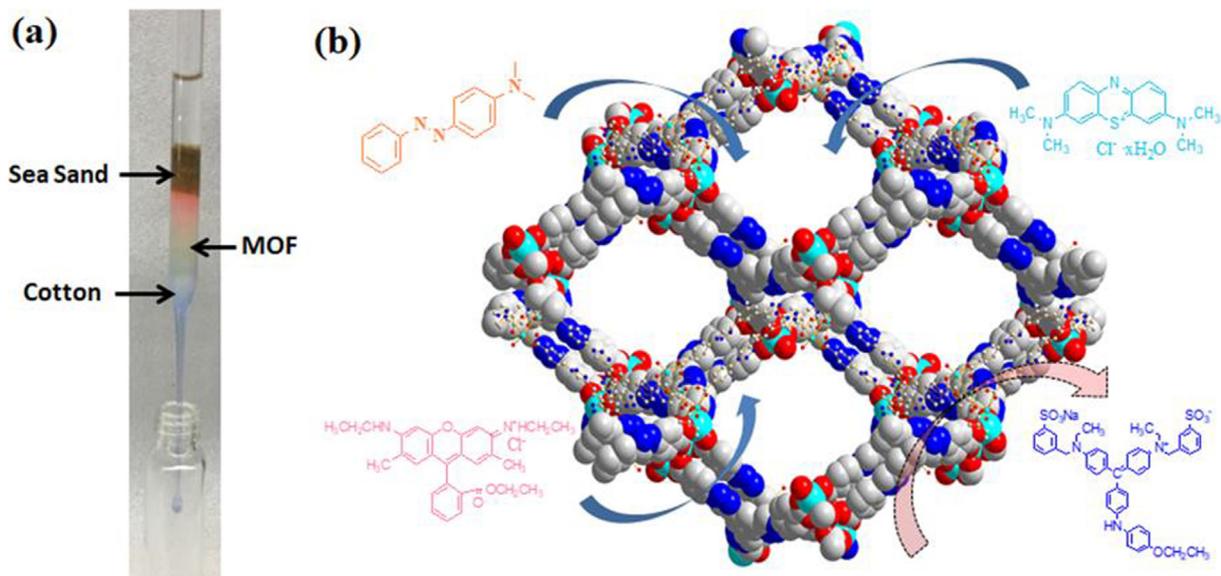


Fig. 35. (a) Column packed by the crystals of NTU-130 for the separation of dye mixture (R6G/BBR), and (b) illustration of large molecule separation based on size-selective adsorption probed by dye molecules. Adapted with permission from Ref. [87]. Copyright 2017, Royal Society of Chemistry.

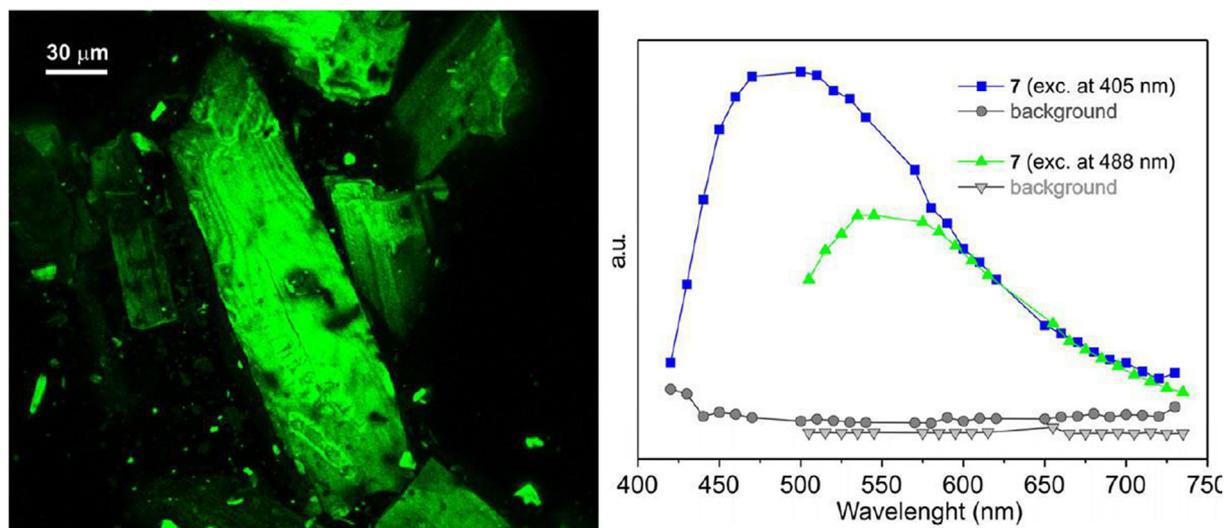


Fig. 36. Left: Maximum intensity projection (MIP) obtained for crystals of *tert*-thiophene derivative modified UCMC-1 upon excitation at 405 nm. Right: Fluorescence spectra of *tert*-thiophene derivative modified UCMC-1 (7) under the excitation at 405 and 488 nm. Adapted with permission from Ref. [84]. Copyright 2013, American Chemical Society.

of triple-symmetrical acetylene-containing organic moieties with 4-azidobenzoates or 5-azidoisophthalates. After the assembly with Zn(II) ion, transparent crystals of MOFs, *i.e.*, NTU-130, NTU-161, NTU-162, and NTU-163, with large-molecule accessible pores were achieved [87,128]. Among large organic molecules, organic dyes are a useful group of organic molecules with visible colors, which have been widely used in environmental science and biological imaging. Colorless/light-yellow transparent property and large-molecule accessible pores of these Zn-based MOF crystals and visible color feature of dye molecules jointly facilitate the investigation of the MOF applications for large-molecule capture and separation probed by organic dyes.

As previously reported [236–238], the investigation toward large molecule adsorption and capture was carried out by immersing the activated crystals of three isorecticular MOFs, *i.e.*, NTU-161, NTU-162, and NTU-163, into the DMF solution of dyes, methylene

blue (MeB, blue), rhodamine 6G (R6G, red), and brilliant blue R (BBR, blue), respectively [128]. The visible large-molecule soaking experiments clearly demonstrate that all these click-extended MOFs, especially NTU-163 with the largest pores, could be used as adsorbents for large molecule capture (Fig. 34). Subsequently, their promising applications in environmental science for pollutant removal were proven by dye capture experiments after passing-through MOF packed columns, and their potentials as drug carriers in biological applications were also demonstrated by the adsorption of an anticancer drug doxorubicin (Dox). The same capability of NTU-130 was also observed [87].

Inspired by the size-dependent adsorption of these clicked-extended MOFs toward organic dyes with different molecule size, the capabilities of size-dependent separation for the mixtures of large molecules were also examined. As shown in Fig. 35, after the DMF solution of dye mixtures, R6G and BBR, passing through

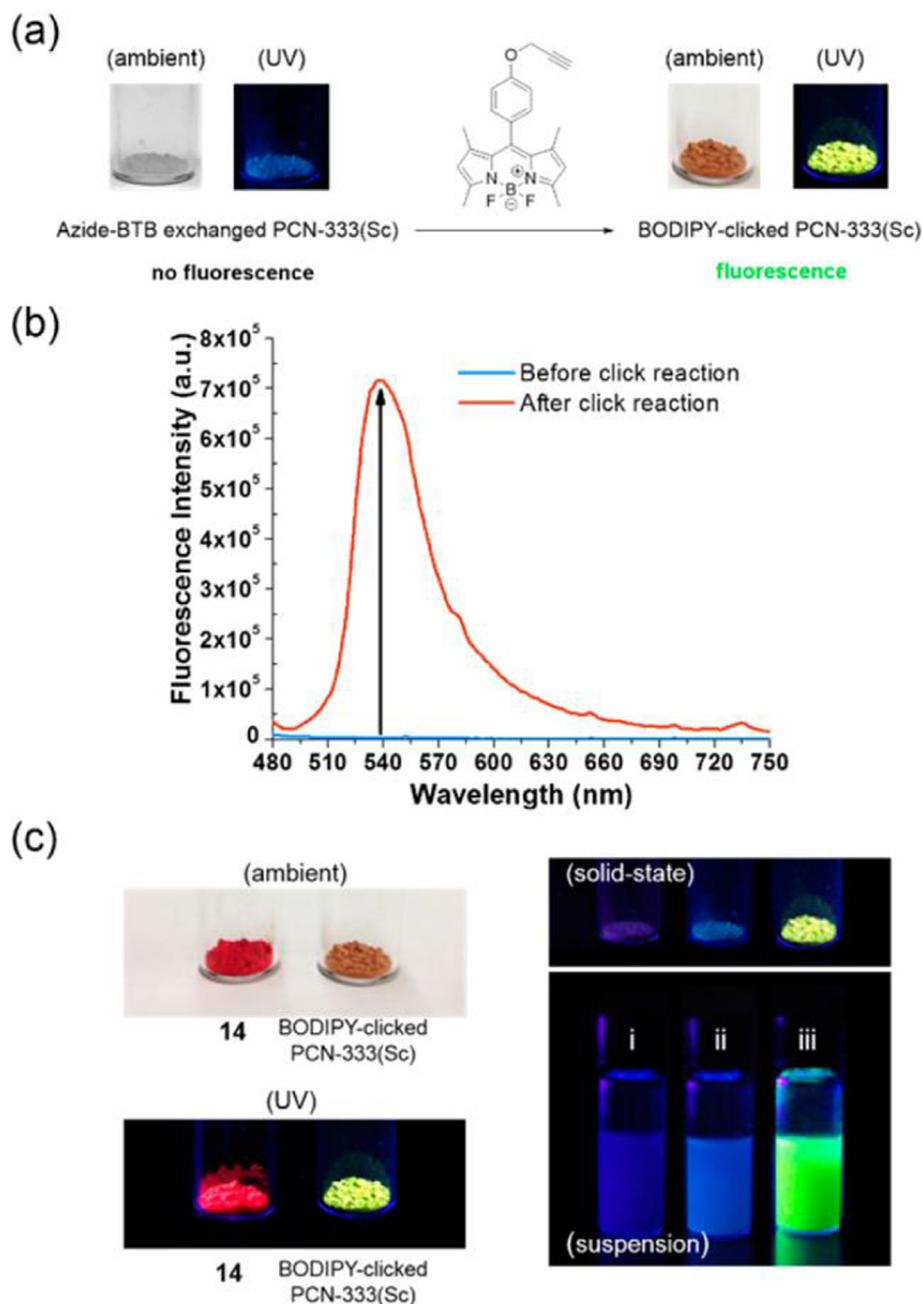


Fig. 37. (a) Photographs of PCN-333(Sc) and BODIPY fluorophore clicked PCN-333(Sc) under ambient condition and UV light irradiation. (b) Solid-state fluorescence emission spectra of azide-tagged PCN-333(Sc) and BODIPY clicked PCN-333(Sc). $\lambda_{\text{ex}} = 450$ nm. (c) Comparison of solid state alkyne-BODIPY (14) and BODIPY-clicked PCN-333(Sc) under ambient condition and UV light irradiation. Photographs of (i) pristine PCN-333(Sc), (ii) azide-tagged PCN-333(Sc), and (iii) BODIPY-clicked PCN-333(Sc) in both solid-state and suspension. Adapted with permission from Ref. [192]. Copyright 2015, American Chemical Society.

the column packed by crystals of NTU-130, the dye with small molecule size (R6G) was undoubtedly captured by the MOF, while relatively large one (BBR) was eluted [87]. Effective separation capability of the three clicked-extended isorecticular MOFs was observed during the large molecule separation experiments probed by dye mixtures [128]. These successful experiments of large-molecule capture, uptake and separation probed by dye molecules demonstrate that extending organic backbones of ligands *via* the versatile click reaction to increase the pore size of MOFs is an efficient approach to fabricate large porous MOFs toward large guest molecule based applications, such as catalysis, drug delivery, bioimaging, pollutant removal, and large organic molecule separation.

4.3.2. Dye-probed luminescence and imaging

Upon multimodal derivatization of aforementioned N_3 -decorated MOFs, UMCM-1- N_3 and MIXMOF-5- N_3 , by single organic/organometallic acetylene derivatives or defined binary and ternary mixtures [84], acetylene end-capped *tert*-thiophene derivatives were introduced into the pristine UMCM-1 and MIXMOF-5, and the obtained materials were subsequently employed as both polycyclic reagents and fluorescent probes for the monitoring of guest molecules. For the MOFs fluorescently labeled by *tert*-thiophene derivative, the studies indicate homogeneous fluorescent probe diffusion into MOF bulk materials (Fig. 36).

An organic dye, alkyne-BODIPY, was successfully grafted into the pores of azide-tagged PCN-333(Sc) *via* the click reaction in

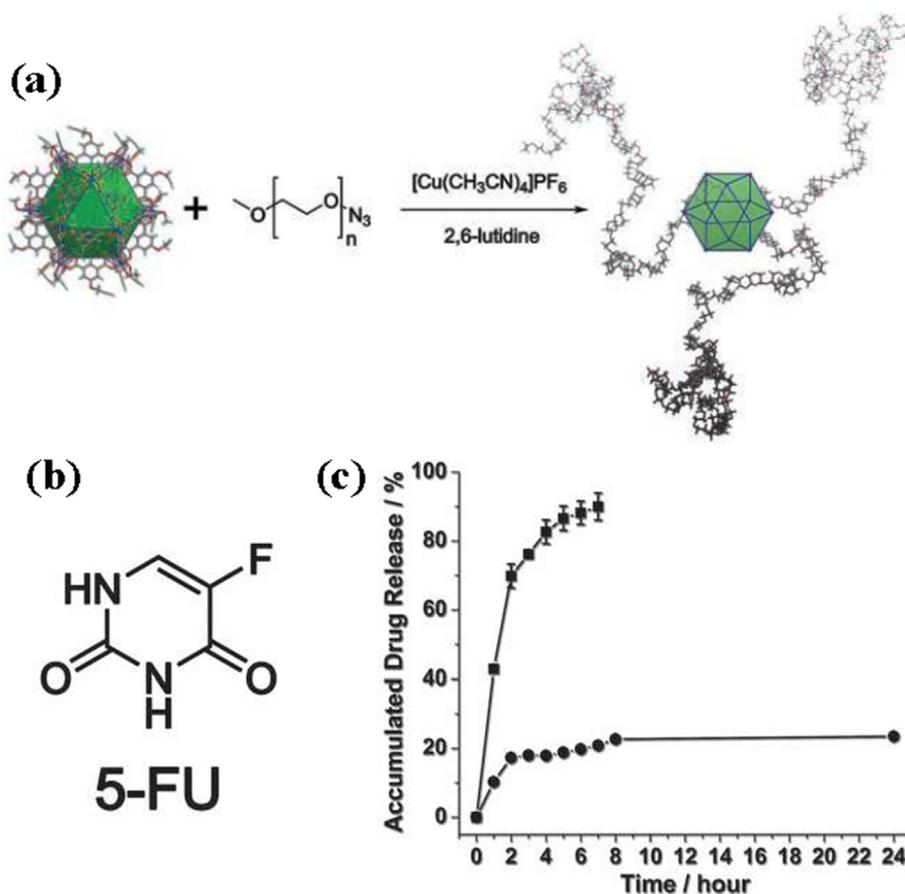


Fig. 38. (a) Click reaction for the formation of Cu(pi)-PEG5k, (b) chemical structure of 5-fluorouracil (5-FU), and (c) the release of 5-FU from control (square) and Cu(pi)-PEG5k (circle). Adapted with permission from Ref. [239]. Copyright 2010, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2015 [192]. In both suspension and solid-state of BODIPY-clicked PCN-333(Sc), strong fluorescence was observed (Fig. 37). Interestingly, dye aggregates of alkyne-BODIPY show a red emission, while the emission of BODIPY-clicked PCN-333(Sc) in the solid state is green ($\lambda = 550$ nm, Fig. 37c), suggesting that the clicked dye in PCN-333(Sc) behaves as a monomeric dye.

4.4. Drug delivery and cancer therapy

Developing drug delivery systems for cancer therapy has become one of the important tasks for the scientific community, and MOFs have been showing a high potential in this area. As click chemistry is a powerful tool for bioconjugation, lots of MOFs have been modified by click reaction for the drug delivery and cancer therapy. A nano-sized metal-organic polyhedron (MOP, one-dimensional MOF), denoted as Cu(pi), with alkyne groups covered on the surface was synthesized using 5-(prop-2-ynoxy)iso phthalic acid (H_2pi) as the ligand precursor by Zhou and coworkers in 2011 [239]. Using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ instead of CuSO_4 /sodium ascorbate as the catalyst system for clicked modification, azide-terminated PEG was successfully grafted onto the MOP surface (Fig. 38), and thus water-stable colloid Cu(pi)-PEG5k was obtained. Subsequently, Cu(pi)-PEG5k was used as a carrier for drug release studies. A widely-used anticancer drug, 5-fluorouracil (5-FU), was selected as a drug model in this investigation, and the drug-loaded Cu(pi)-PEG5k, Cu(pi)-PEG5k-5-FU, was prepared based on the solubility difference of 5-FU between chloroform and methanol. During the drug release experiments on the Cu(pi)-PEG5k-5-FU system, after the initial burst release stage (2 h), much flatter

release curve up to 24 h was observed, and around 20% of the loaded 5-FU was released. For pure 5-FU, close to 90% of the total drug was released within 7 h. This successful demonstration of drug release from post-synthetically modified MOP opens an avenue for promising applications in the drug delivery.

MOF nanoparticle-nucleic acid conjugates were fabricated via the strain-promoted Cu-free click reaction by Mirkin and coworkers in 2014 (Fig. 39) [240]. Firstly, nanoparticles of an azide-bearing MOF, UiO-66- N_3 , were prepared. Utilizing the strain-promoted Cu-free click reaction between DNA appended with dibenzylcyclooctyne and the UiO-66- N_3 nanoparticles, the surface of the MOF nanoparticles was covalently functionalized by oligonucleotides. On account of the pore size limitation, the click post-synthetic modification only occurred on the MOF surface, and the surface coverage of DNA was quantified. Characterizations reveal that the framework structure of the MOF was preserved throughout the chemical transformation, and the click modified UiO-66- N_3 nanoparticles exhibit increased stability and enhanced cellular uptake as compared to un-functionalized MOF particles with a comparable size when dispersed in aqueous NaCl.

By utilizing the strain-promoted Cu-free click reaction, nucleic acid tethers were covalently modified onto the surface of UiO-68 MOF nanoparticles, denoted as UiO-68 NMOF, by Willner et al. (Fig. 40) [241]. Firstly, dibenzocyclooctyne-sulfo-*N*-hydroxysuccinimidyl ester (DBCOSulfo-NHS ester) was conjugated to the amine-modified nucleic acid, and then the resulted DBCO-modified nucleic acid was linked with the azide group on the surface of UiO-68 MOF nanoparticles via strain-promoted click chemistry. After the dye/drug loading, two different stimuli-responsive

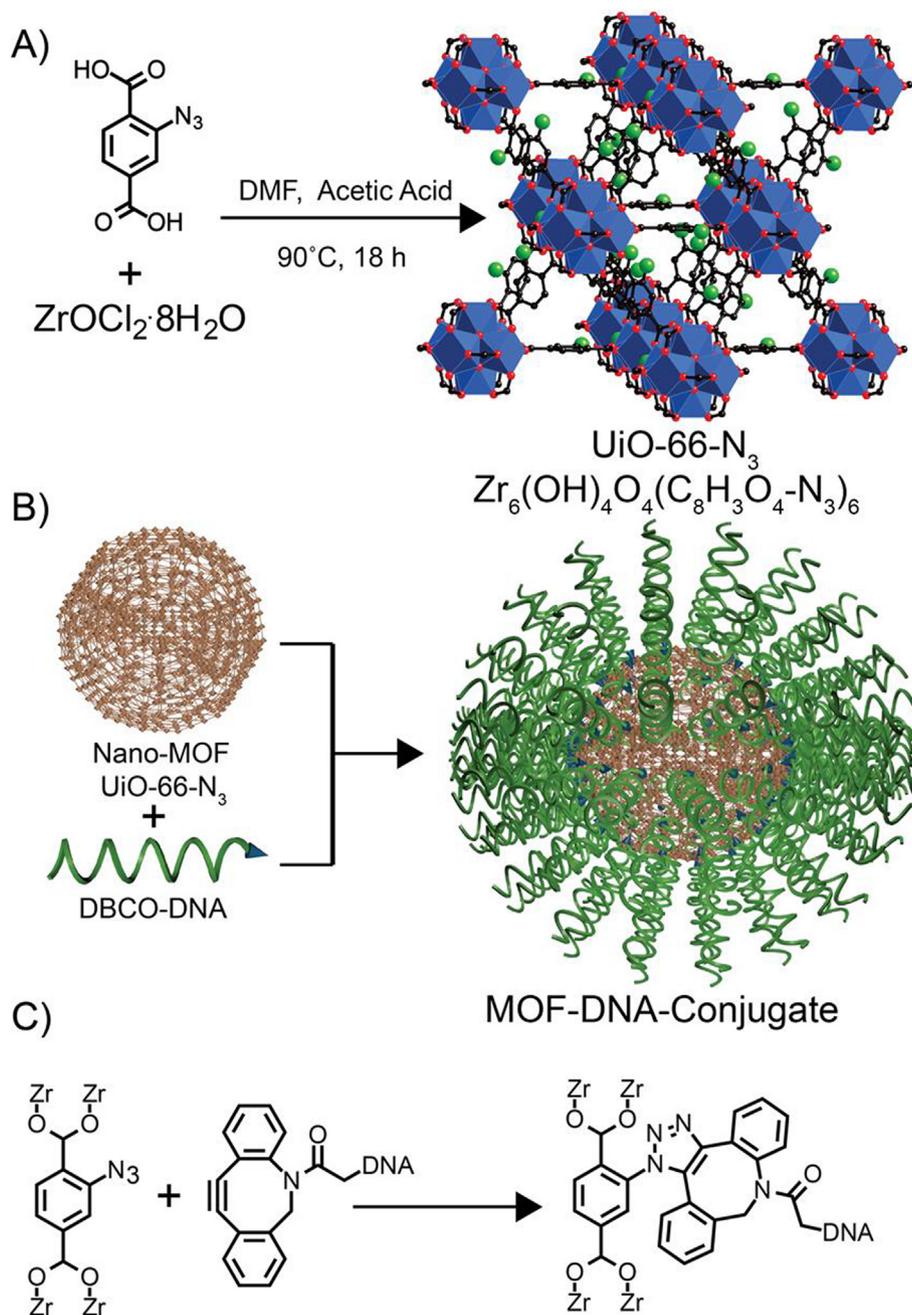


Fig. 39. (a) Synthesis of UiO-66-N₃ nanoparticles, (b) DNA functionalization of UiO-66-N₃ nanoparticles, where DNA was functionalized with DBCO, and (c) strain promoted click reaction between a MOF strut and DNA. Adapted with permission from Ref. [240]. Copyright 2014, American Chemical Society.

DNA duplex capping/locking units were respectively hybridized with the surface-linked nucleic acid. For the pH-responsive MOF/drug system, AS1411 aptamer-modified pH-responsive MOF nanoparticles reveal selective and targeted cytotoxicity to MDA-MB-231 breast cancer cells. For the metal ion (Mg^{2+} or Pb^{2+} ions) responsive MOF/drug system, the metal-ion-dependent DNAzyme/substrate complexes were used as locking units, and adenosine 5'-triphosphate (ATP)/ Mg^{2+} -triggered Dox-loaded NMOF reveals selective cytotoxicity to MDA-MB-231 cancer cells.

Under solvothermal condition by the addition of *p*-azidomethylbenzoic acid (L1), well-defined nontoxic UiO-66 nanoparticles in the size of around 100–200 nm coated with azide modulators were synthesized by Forgan and coworkers. Subsequently, the surface modification by Cu(I)-catalyzed azide-alkyne

cycloaddition with amphiphilic PEG (PEG2000) was carried out to afford UiO-66-L1-PEG2000 (Fig. 41) [242]. Characterizations reveal that PEG chains not only prevent the aggregation of MOF nanoparticles and further increase their solution stability, but also improve the stability of MOF nanoparticles by delaying their decomposition. When carrying out the click reaction in the presence of calcein, a calcein-loaded system (cal@UiO-66-L1-PEG2000) was obtained. The effect of the surface modification on the drug release was tested by taking calcein as a probe, showing that the release of calcein from cal@UiO-66-L1-PEG2000 could be affected by pH. The release at pH = 7.4 was drastically decreased, while rapid cargo release at pH = 5.5 was observed, which could facilitate the drug delivery selectivity because cancerous cells are typically more acidic than healthy ones. Successful internalization of cal@UiO-

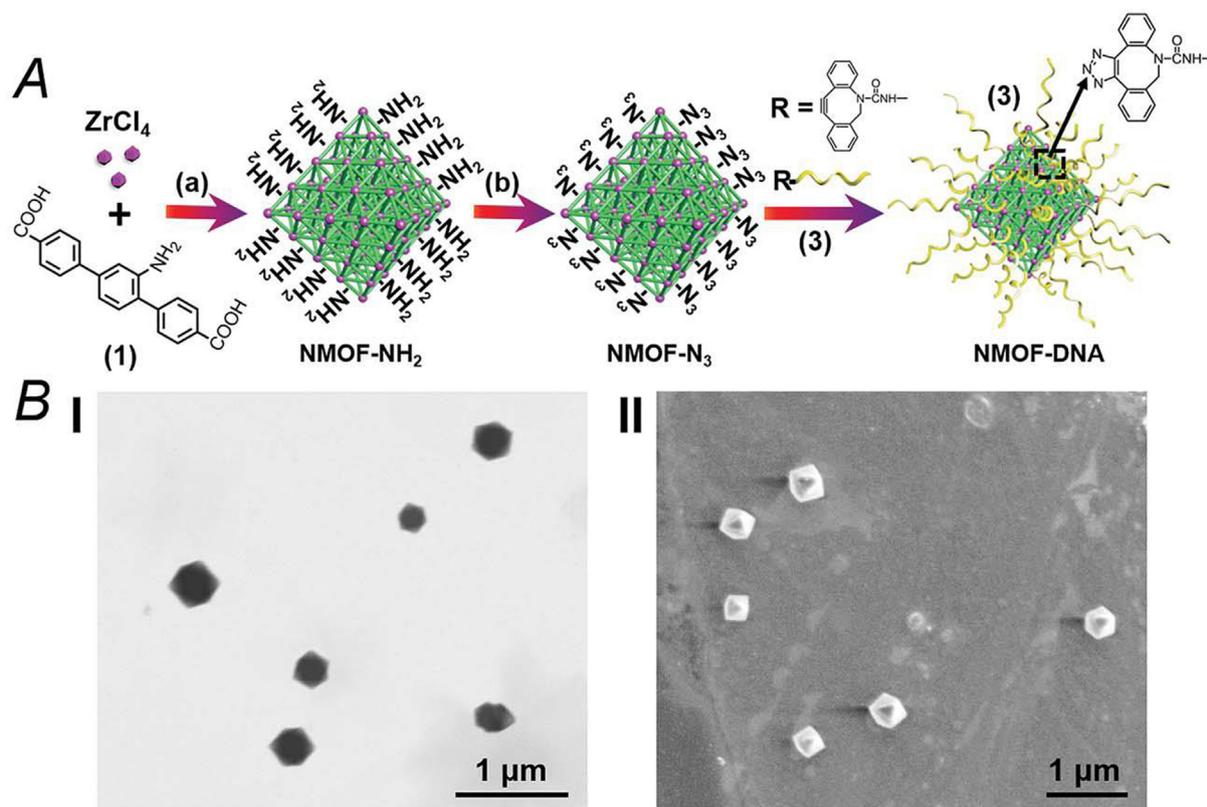


Fig. 40. (a) Illustration of the synthesis and strain-promoted click modification of UiO-68 NMOF nanoparticles by nucleic acid. (b) TEM image (I) and SEM image (II) of the UiO-68 NMOF nanoparticles. Adapted with permission from Ref. [241]. Copyright 2017, Royal Society of Chemistry.

66-L1-PEG2000 by HeLa cells and subsequent calcein release were further confirmed by confocal fluorescence microscopy. When replacing calcein by dichloroacetic acid (DCA), an anticancer drug that is cytotoxic only once it is internalized by cells, another drug loaded system DCA@UiO-66-L1-PEG2000 was constructed. Studies reveal significant cell death at the utilization concentrations of 0.75 mg mL^{-1} and above. These results indicate that a proper click modification on the surface of MOF nanoparticles by PEG could increase their stability and cellular internalization with improved therapeutic effect.

Meanwhile, a unique framework denoted as N₃-UiO-66-NH₂ was synthesized by Xue and coworkers. The pre-synthesized N₃-UiO-66-NH₂ possesses dual tunable groups, i.e., azide group and amino group. After the amidation with a carboxyl substituted zinc phthalocyanine (Pc) and click-reacted with Erlotinib (E), a dual functionalized MOF named E-UiO-66-Pc was obtained (Fig. 42) [243]. The zinc phthalocyanine is an effective photosensitizer in photodynamic therapy, while Erlotinib can target the ATP bonding region in cancer cells. Thus, the dual functionalized E-UiO-66-Pc is a promising material in photodynamic therapy. The studies on the photosensitizing efficiency show an enhanced photosensitizing activity after the conjugation of zinc phthalocyanine with UiO-66. The cytotoxicity investigation reveals that the introduction of Erlotinib into the system could significantly enhance the photodynamic activity of UiO-66-Pc. Thus, by introducing two synergistic components into MOFs by click reaction, effective anticancer systems for photodynamic cancer therapy could be achieved. At the same time, some MOF-polymer hybrids were also fabricated by clicked combination of different components and subsequently utilized for biological applications [94,244–246]. All these examples successfully demonstrate that MOFs could be applied for biological uses after suitable click modifications.

4.5. Template for polymer-gel fabrication

As an effective reaction for connecting two components, click modifiable MOFs, such as azide-bearing MOFs, were investigated as templates for the fabrication of functional materials. In 2013, Sada and coworkers demonstrated a success example of MOF templated polymer-gel fabrication via click post-synthetic modification of organic ligands pre-organized in the MOF network. Firstly, an azide-bearing MOF denoted as AzM was assembled by the coordination of azide-containing organic ligand (AzTPDC) with Zn(II) ion (Fig. 43) [247]. Then, taking tetra-acetylene cross-linker (CL4) as the guest substrate, *in situ* click reaction was carried out in the presence of Cu(I) catalyst in DEF. A cross-linked MOF (CLM) was obtained after the incubation for 1 week and washing by fresh DEF repeatedly. The decomposition of CLM by the acidification with concentrated HCl in DEF gave the final generation of a non-crystalline MOF-templated polymer (MTP) gel, and the swelling behavior was observed by immersing the resulted MTP gel in various solvents. Interestingly, the shape and size of the fabricated polymer gel were highly influenced by the shape and size of the pristine MOFs. Inspired by this success, other polymer gels were obtained by click cross-linking of other azide-bearing MOFs with various polytopic acetylene compounds. Recently, anisotropic swelling gels were also obtained by the cross-linking of organic ligands pre-organized in a pillared-layer MOF (PLMOF) through the click reaction followed by the framework decomposition [248].

A polymer gel film with homogeneous thickness was fabricated through clicked cross-linking of a surface-anchored MOF by Wöll and coworkers [249]. Subsequently, hierarchically structured MOF multi-shell encapsulated magnetic core particles (magMOFs) were synthesized by layer-by-layer synthesis. After clicked cross-linking of the MOF structure followed by the framework decompo-

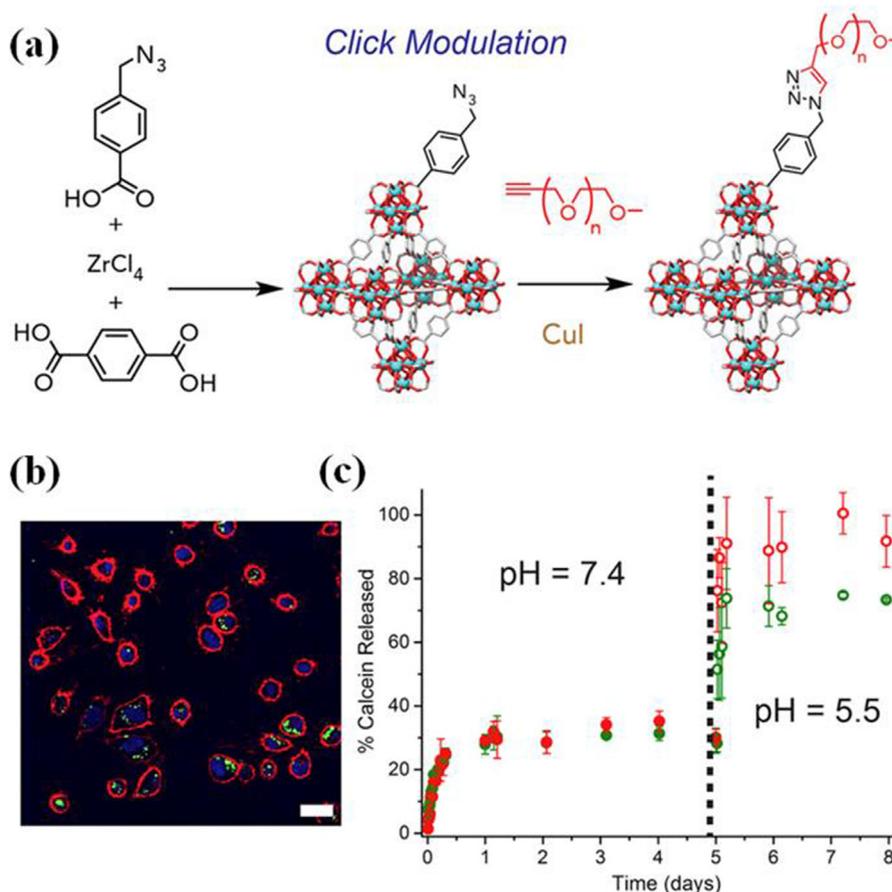


Fig. 41. (a) Click modulation of UiO-66 by PEG, (b) confocal microscopy image of HeLa cells incubated with calcein loaded UiO-66-L1-PEG2000, and (c) pH-responsive release of calcein from the PEGylated MOF. Adapted with permission from Ref [242]. Copyright 2017, Elsevier B.V.

sition, nice capsules were obtained (Fig. 44) [250]. The inner shell of these capsules could serve as a reservoir and the outer one could act as a membrane that enables the controlled release of loaded dye molecules. This interesting demonstration makes the click cross-linking reaction an effective approach for polymer gel fabrications.

More recently, highly antimicrobial active porphyrin polymer thin films were fabricated through click post-synthetic modification with surface anchored MOF (SURMOF) as the template by Tsotsalas and coworkers (Fig. 45) [251]. Firstly, the azido-porphyrin SURMOF was prepared utilizing layer-by-layer synthesis method. Click post-synthetic modification was carried out after the SURMOF was immersed into a solution of triple-acetylene, and then the process for removing metal ions by immersing the sample in ethylenediaminetetraacetic acid (EDTA) solution was conducted to finally give the generation of porphyrin-based, water-stable, surface anchored polymeric thin films. The morphology and thickness of the fabricated polymer thin films were not significantly changed during the removal process of the metal ions in the MOF template. By probing the ability of visible-light-promoted singlet O₂ generation, the antimicrobial potential of the films was investigated, showing its high antibacterial activity against pathogens. All of these interesting applications once again demonstrate that MOFs could be constructed or modified by versatile azide-alkyne cycloaddition for various applications.

5. Conclusion and outlook

This review summarizes recent development of MOFs prepared or modified through click reactions. Taking versatile azide-alkyne 1,3-dipolar cycloaddition as a core reaction during the ligand design for the MOF construction, a unique group of polytopic carboxylate ligands were synthesized *via* the modular combinations of polytopic symmetrical acetylene-containing organic moieties and azide-containing components such as 4-azidobenzoates and 5-azidoisophthalates. Subsequently, diverse triazole-containing MOFs were successfully prepared by the assemblies of these clicked organic ligands with suitable metal ions. In the post-synthetic modification of MOFs, lots of functional groups were successfully grafted into/onto pristine MOFs by the azide-alkyne 1,3-dipolar cycloaddition toward targeted applications. In addition to the azide-alkyne 1,3-dipolar cycloaddition, other click reactions, such as Diels-Alder click reaction and thiol-ene click reaction, have also been employed as effective reactions in the MOF construction and modification [207,252–257]. The versatile click chemistry through both ligand pre-design and post-synthetic modification not only makes the MOF preparation easy, but also broadens their applications by integrating functional groups into the MOF networks. These examples have successfully demonstrated that the click chemistry is a useful approach in the construction and post-synthetic modification of MOFs for purposed applications including molecular capture and separation, catalysis, drug delivery and bioimaging, materials engineering, and so on.

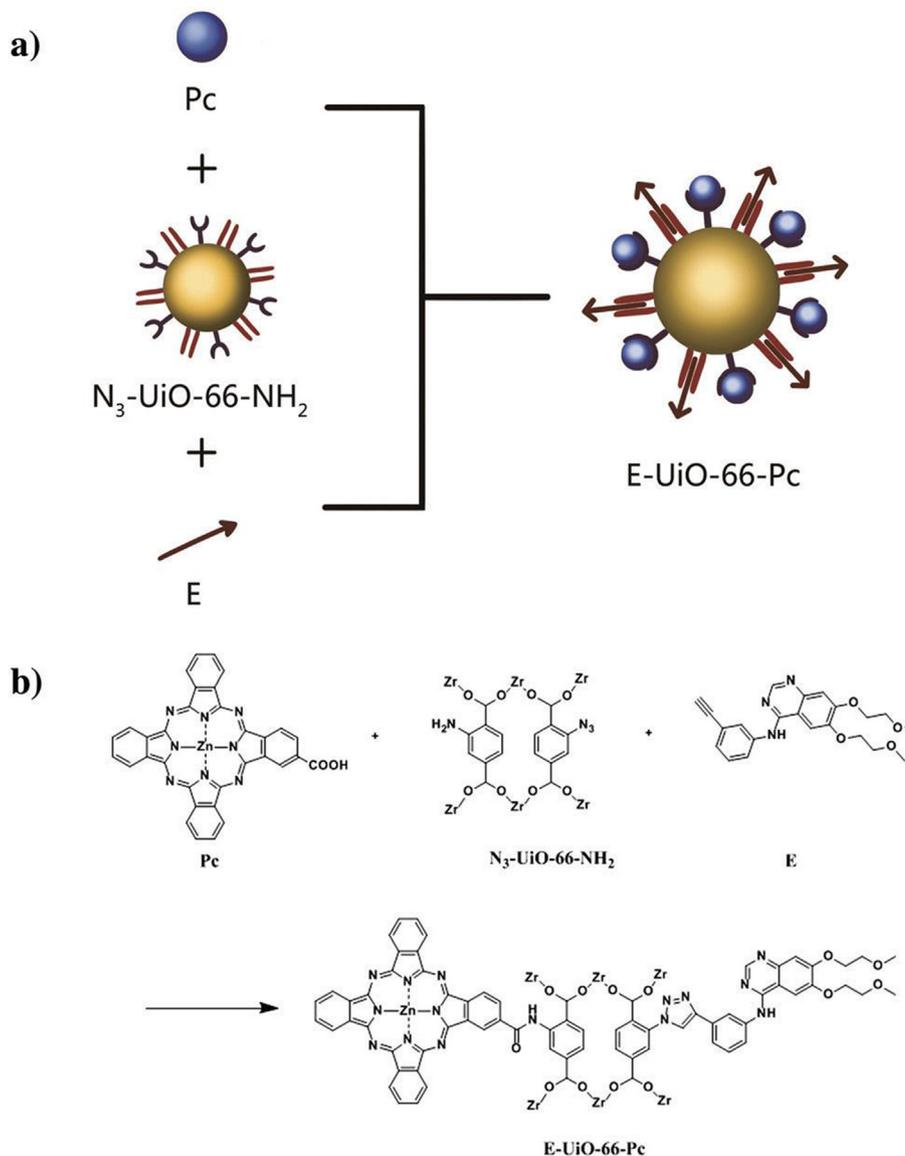


Fig. 42. (a) Schematic synthesis of $\text{N}_3\text{-UiO-66-NH}_2$ and E-UiO-66-Pc, and (b) synthesis of E-UiO-66-Pc via covalent post-synthetic modification of $\text{N}_3\text{-UiO-66-NH}_2$. Adapted with permission from Ref. [243]. Copyright 2017, Royal Society of Chemistry.

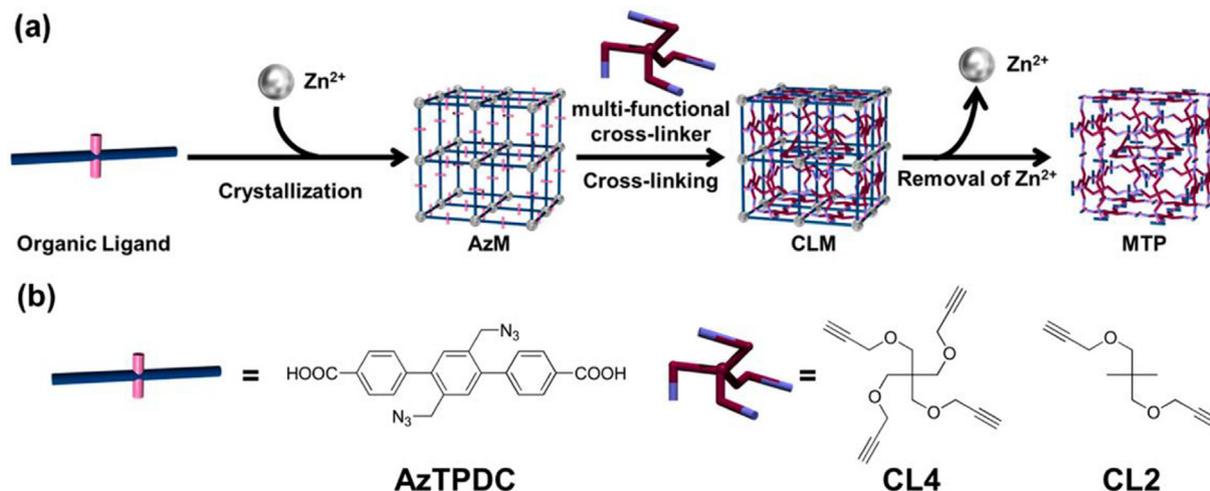


Fig. 43. (a) Schematic illustration for the cross-linking of organic linkers in azide-bearing MOF (AzM) and subsequent decomposition to obtain MOF-templated polymer (MTP) gel. (b) Molecular structures of the organic ligand (AzTPDC) and alkyne-containing cross-linkers (CL4 and CL2). Adapted with permission from Ref. [247]. Copyright 2013, American Chemical Society.

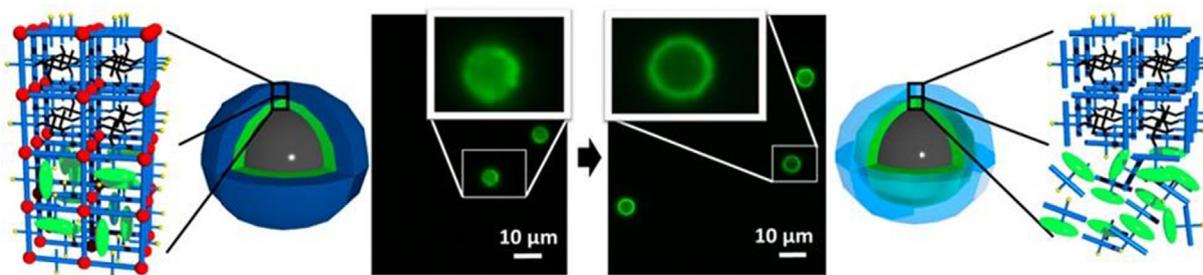


Fig. 44. Illustration of MOF multi-shell encapsulated magnetic core particles (magMOFs, left) and the finally obtained capsules with magnetic core and converted multi-shells (right). Adapted with permission from Ref. [250]. Copyright 2015, American Chemical Society.

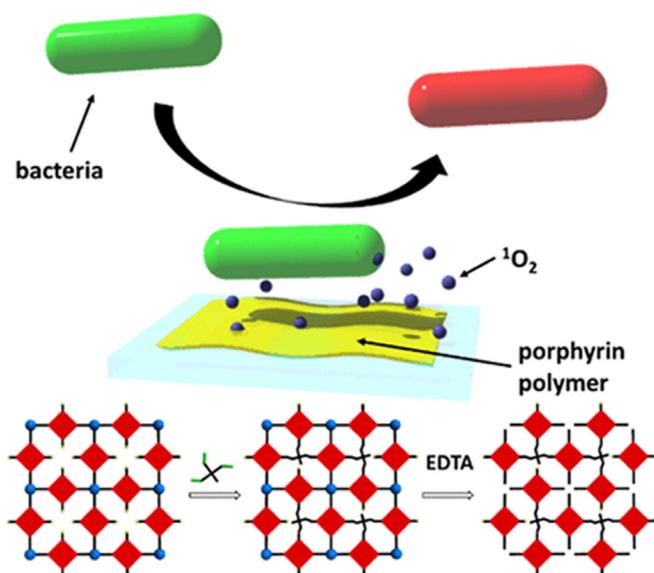


Fig. 45. Illustration of highly antimicrobial active MOF-templated porphyrin polymer thin film fabricated by click post-modification of a surface anchored MOF. Adapted with permission from Ref. [251]. Copyright 2018, American Chemical Society.

Future studies on this rapidly developing research field will be even more diverse. Assisted by computational simulations, purposely designed organic ligands suitable for click reaction will definitely boost the application scope and depth of the resulted MOFs. In particular, interfacing such MOFs with biology and medicine would broaden the research horizon. The ease of click chemistry employed for the MOF synthesis and modification also brings a high possibility for the large-scale production of MOF materials. It is expected that, by utilizing the versatile click chemistry, more and more MOFs will be constructed and post-synthetically modified toward their practical applications.

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