

Reticular Chemistry Directed “One-Pot” Strategy to in situ Construct Organic Linkers and Zirconium-Organic Frameworks

Chao-Qin Han, Lei Wang, Jincheng Si, Kang Zhou, and Xiao-Yuan Liu*

Zirconium-based metal–organic frameworks (Zr-MOFs) have emerged as one of the most studied MOFs due to the unlimited numbers of organic linkers and the varying Zr-oxo clusters. However, the synthesis of carboxylic acids, especially multitopic carboxylic acids, is always a great challenge for the discovery of new Zr-MOFs. As an alternative approach, the in situ “one-pot” strategy can address this limitation, where the generation of organic linkers from the corresponding precursors and the sequential construction of MOFs are integrated into one solvothermal condition. Herein, inspired by benzimidazole-contained compounds synthesized via reaction of aldehyde and *o*-phenylenediamine, tri-, tetra-, penta- and hexa-topic carboxylic acids and a series of corresponding Zr-MOFs can be prepared via the in situ “one-pot” method under the same solvothermal conditions. This strategy can be utilized not only to prepare reported Zr-MOFs constructed using benzimidazole-contained linkers, but also to rationally design, construct and realize functionalities of zirconium-pentacarboxylate frameworks guided by reticular chemistry. More importantly, in situ “one-pot” method can facilitate the discovery of new Zr-MOFs, such as zirconium-hexacarboxylate frameworks. The present study demonstrates the promising potential of benzimidazole-inspired in situ “one-pot” approach in the crystal engineering of structure- and property-specific Zr-MOFs, especially with the guidance of reticular chemistry.

because of abundant of carboxylic acids typed linkers and multiple connectivities of Zr-oxo clusters.^[14–19] Up to now, the majority of Zr-MOFs are constructed using Zr₆ cluster as the second building unit (SBU), although several works have been reported to construct Zr-MOFs using Zr₈,^[20] Zr₉^[21] and Zr₁₂^[22] clusters, even coexisted Zr₆&Zr₈,^[23] Zr₆&Zr₉^[24] and Zr₆&Zr₁₂^[25–27] clusters can also be formed in one single crystal matrix of Zr-MOFs. Compared with SBUs, organic linkers undoubtedly have more important effects on the structures and properties of resultant Zr-MOFs due to unlimited species and diversity. Di-,^[28–33] tri-^[34–40] and tetra-topic^[41–52] carboxylic acids have been widely used to prepare Zr-MOFs with different underlying nets and applications. Therefore, to construct Zr-MOFs with new topologies and/or properties, it is essential to design and synthesize unique organic linkers.

Generally, the main and conventional strategy to construct Zr-MOFs is the use of commercially available or pre-synthesized organic building units to react with inorganic building units (Scheme 1a). Therefore, extensive organic synthesis has been

made to design and synthesize suitable and predetermined organic linkers in order to prepare MOFs with demanded structures and properties. However, the construction of MOFs using elongated and/or multitopic carboxylic acids is still a great challenge due to the multistep organic syntheses to prepare linkers,^[53] such as hexa-^[54–57] and octa-topic^[58,59] carboxylic acids.

As an alternative approach, hydro/solvothermal *in situ* metal-ligand reactions, namely the “one-pot” approach, involving in situ organic synthesis and MOFs construction, are growing interesting, which has been proven to be a promising approach in crystal engineering of functional coordination materials.^[60–63] In this method, the linker precursors are employed in place of linkers to coordinate with inorganic building units directly to generate single crystals of MOFs (Scheme 1b). On the other hand, the “one-pot” strategy might be a useful approach to generating novel structures that are inaccessible or not easily obtainable from a direct reaction of organic and inorganic building units. This in situ “one-pot” approach can also avoid the time-consuming, complex and unsustainable isolation and purification of organic linkers.

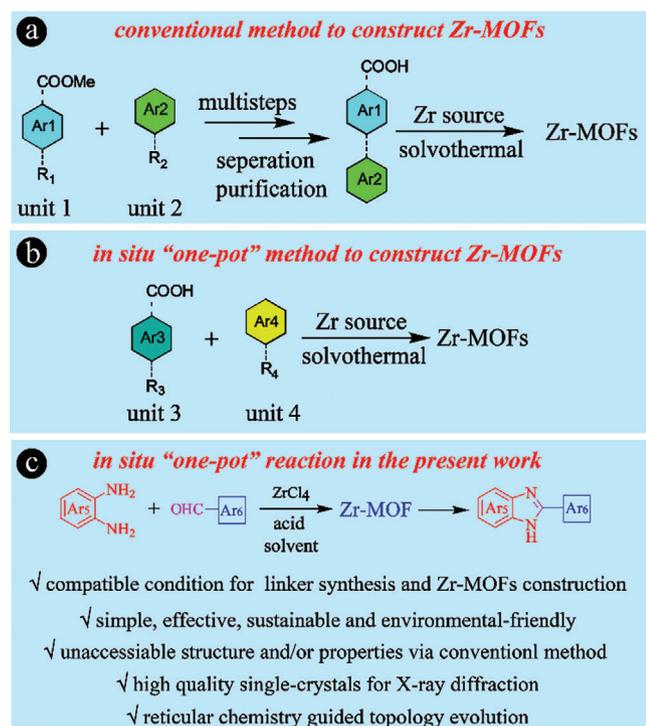
1. Introduction

Metal–organic frameworks (MOFs) have witnessed explosive development in the past three decades.^[1,2] The intrinsic porosity, tunable compositions and structures, high surface area, and mendable thermal and chemical stability endow MOFs with promising practical applications in areas including but not limited to chemical capture and separation,^[3–6] catalysis^[7–10] and sensing.^[11–13] Among these MOFs, zirconium-based MOFs (Zr-MOFs) exhibit predicted and various underlying structures

C.-Q. Han, L. Wang, J. Si, K. Zhou, X.-Y. Liu
Hoffmann Institute of Advanced Materials
Shenzhen Polytechnic University
7098 Liuxian Blvd, Nanshan, Shenzhen 518055, P. R. China
E-mail: liuxiaoyuan1989@szpu.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/sml.202402263>

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Scheme 1. a) The conventional method to construct Zr-MOFs; b) the in situ “one-pot” strategy to construct Zr-MOFs; c) schematic diagram illustrating benzimidazole inspired in situ “one-pot” approach to constructing Zr-MOFs via integrating organic reaction between aldehyde- and *o*-phenylenediamine-based precursors and the sequential coordination reaction.

In addition, the slow formation of linkers will ensure the growth of suitable single crystals for X-ray diffraction (Scheme 1c).

Although the in situ “one-pot” approach has been adopted in the preparation of MOFs since the first reported by Champness and Schröder in 1997,^[64] most previous works were mainly focused on nitrogen-contained linkers to form MOFs using low-valency metal ions, such as Ag^+ , Cu^{2+} , Zn^{2+} ,^[60–63] where it is very difficult to predict the resultant structures and only limited structures can be generated. Up to now, only a few of examples have been reported to construct Zr-MOFs using the in situ “one-pot” strategy.^[65–68] In 2019, Li et al. reported the construction of BUT-104 to BUT-109 via in situ “one-pot” strategy using organic reactions of diazo coupling of nitro-compounds, condensation of boronic acids, and imidization between amines and anhydrides.^[65] At the year, Farha et al. and Kaskel et al. also reported several UiO-typed Zr-MOFs constructed via in situ reaction of amines and aldehydes.^[66,68] The in situ “one-pot” strategy has great advantages to construct Zr-MOFs, however, its development is sluggish. The most challenging task is how to in situ synthesize organic linkers, namely which type of organic reactions can be adopted into the “one-pot” approach with excellent compatibility with the solvothermal conditions of Zr-MOFs preparation and have the universal to be extended to obtain organic linkers with various geometries, length, carboxylic group and functionalities.

It is well-known that the benzimidazole-contained organic compounds can be easily synthesized via the reaction of alde-

hyde and *o*-phenylenediamine (Scheme 1c), which has been reported for synthesizing carboxylic acid-contained organic linkers to construct Zr-MOFs, such as BUT-39^[36] and HIAM-4017.^[69] These organic linkers can be synthesized under mild conditions using dichloromethane, acetonitrile or *N,N*-dimethylformamide (DMF) as the solvent, and ZrCl_4 as the catalyst, which is highly compatible with the solvothermal conditions for Zr-MOFs construction. However, no work has been done to prepare Zr-MOFs using “one-pot” strategy via in situ formation benzimidazole-contained carboxylic acids from aldehyde- and *o*-phenylenediamine-based precursors.^[70] Herein, inspired by the organic chemistry of *o*-diamine and aldehyde, various aldehyde-contained carboxylic acids and *o*-phenylenediamine-based compounds are employed to in situ generate organic building units and sequentially construct different kinds of Zr-MOFs. Using the “one-pot” approach, tri-, tetra-, penta- and hexa-topic carboxylic acids can be in situ generated under the solvothermal conditions through the judicious selection of precursors, which is important for the practical synthesis and applications of Zr-MOFs. The present study demonstrates the promising potential of benzimidazole-inspired “one-pot” approach in the crystal engineering of structure- and property-specific MOFs, especially with the guidance of reticular chemistry. The in situ “one-pot” strategy might be extended to other organic reaction systems to in situ synthesize organic linkers and construct MOFs with demanded structures and properties.

2. Results and Discussion

2.1. Construction Tri- and Tetra-topic Carboxylic Acids-Based Zr-MOFs via Benzimidazole-Inspired “One-Pot” Approach

Benzimidazole-contained carboxylic acids have been synthesized and used to prepare Zr-MOFs, such as BUT-39,^[36] HIAM-4017,^[69] HIAM-4033 and HIAM-4034.^[71] Therefore, to prove our hypothesis, we intended to construct these four Zr-MOFs via the in situ “one-pot” approach, in which 2',3'-diamino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (H_2DATC) (Figure 1a) reacted with different kinds of aldehydes (Figure S1, Supporting Information) to generate the target organic linkers along with the sequential formation of resultant Zr-MOFs. The four aldehyde precursors are 4-formylbenzoic acid (Figure 1b, for BUT-39-op, op: one-pot), 5-formylthiophene-2-carboxylic acid (Figure 1c, for HIAM-4033-op), 5-formylthiophene-3-carboxylic acid (Figure 1d, for HIAM-4034-op) and 5'-formyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (Figure 1e, for HIAM-4017-op), which are all commercially available (HIAM = Hoffmann Institute of Advanced Materials, 40 = Zirconium).

A general procedure for in situ “one-pot” synthesis of Zr-MOFs as follows: a 5 mL vial containing 1 mL 0.02 mM H_2DATC , 23.3 mg ZrCl_4 , 1 mL 0.03 mM aldehydes, different volume of formic or benzoic acid and 1 mL DMF was placed in a preheated oven at 120 °C for 3 days. Single crystals of BUT-39-op were successfully obtained by using H_2DATC and 4-formylbenzoic acid as the precursors (Figure 1b), which was confirmed via the well-matched powder X-ray diffraction patterns between as-synthesized BUT-39-op and simulated BUT-39 (Figure 1f).^[36] It should be noted that UiO-68-typed MOFs might also be formed using H_2DATC as organic linkers during

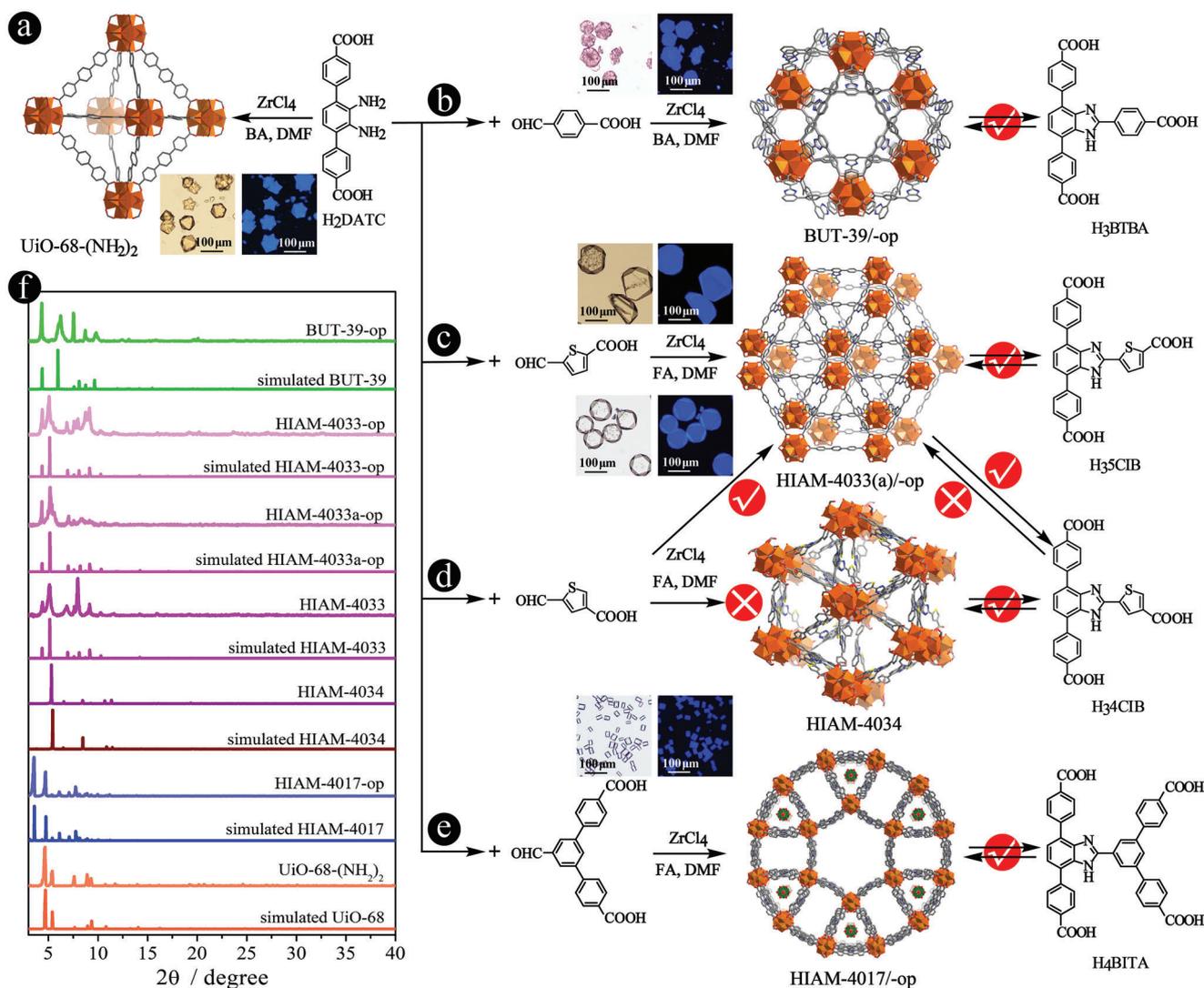


Figure 1. The linker structure of H₂DATC and corresponding crystal structure of UiO-68-(NH₂)₂ (a); in situ “one-pot” strategy and conventional approach to constructing BUT-39-op and BUT-39 (b), HIAM-4033-op and HIAM-4033 (c), HIAM-4033a-op and HIAM-4034 (d), HIAM-4017-op and HIAM-4017 (e) with their single crystal structures and the molecular structures of corresponding organic linker; the simulated and experimental PXRD patterns of UiO-68, UiO-68-(NH₂)₂, HIAM-4017, HIAM-4033, HIAM-4034, HIAM-4033a-op and BUT-39-op constructed using conventional and “one-pot” strategy.

the solvothermal conditions. H₂DATC-based Zr-MOF, UiO-68-(NH₂)₂, was thus prepared for comparison (Figure 1a). As shown in Figure 1f, no PXRD patterns belonging to UiO-68-(NH₂)₂ were observed for the samples of BUT-39-op, indicating the phase purity of BUT-39-op using the in situ “one-pot” approach. The successful formation of BUT-39-op initially proves the feasibility of benzimidazole-inspired in situ “one-pot” approach to constructing Zr-MOFs via the reaction of aldehyde- and *o*-phenylenediamine-based precursors.

To evaluate the universality of this in situ “one-pot” strategy and discover novel Zr-MOFs, other two aldehyde precursors, 5-formylthiophene-2-carboxylic acid (Figure 1c) and 5-formylthiophene-3-carboxylic acid (Figure 1d), were chosen to in situ react with H₂DATC to form 4,4’-(2-(5-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H₃5CIB)

and 4,4’-(2-(4-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H₃4CIB), which subsequently coordinate with ZrCl₄ to obtain corresponding Zr-MOFs. H₃5CIB and H₃4CIB have been used to construct two (3,9)-c Zr-MOFs, HIAM-4033 and HIAM-4034, in our previous work.^[71] As expected, great single crystals, namely HIAM-4033-op (Figure 1c) and HIAM-4033a-op (Figure 1d), were obtained using 5-formylthiophene-2-carboxylic acid and formylthiophene-3-carboxylic acid as the aldehyde precursors, respectively. The HIAM-4033-op and HIAM-4033a-op exhibit almost the same PXRD patterns (Figure 1f), which indicates these two MOFs have the isorecticular structures. The sc-XRD analyses reveal that both HIAM-4033-op and HIAM-4033a-op crystallize in trigonal crystal system with P₃21 space groups (Tables S1 and S2, Supporting Information). As shown in Figure 1c and Figures

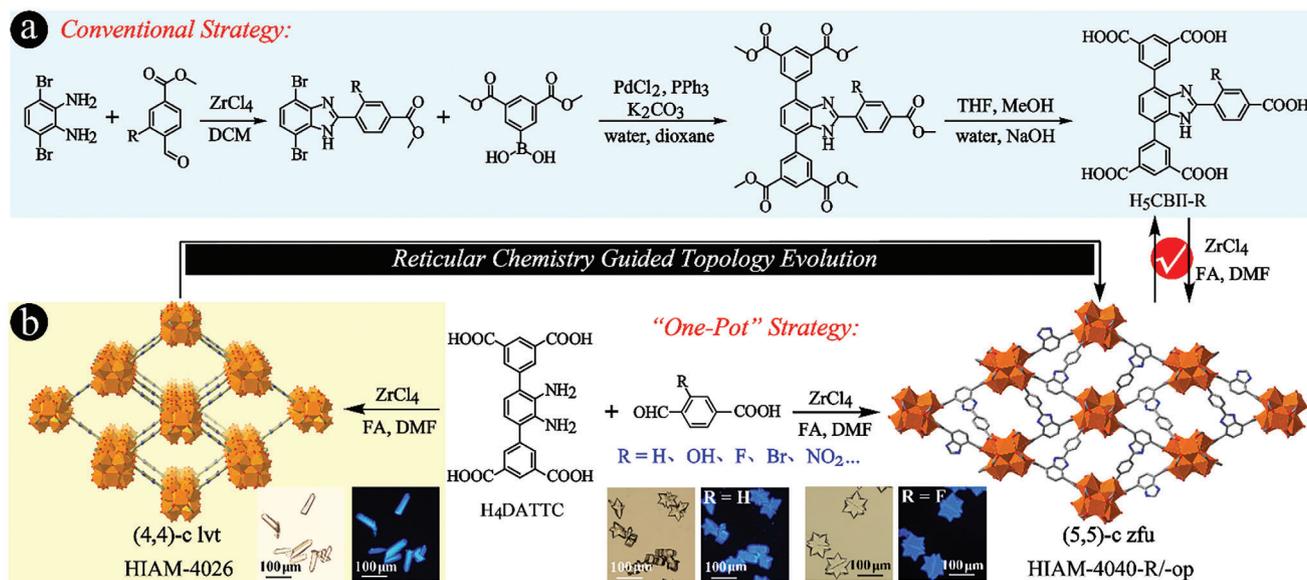


Figure 2. The conventional synthetic routes of H₅CBII-R and the corresponding structure of (5,5)-c HIAM-4040-R with zfu topology (a); the molecular structure of H₄DATTC and the corresponding single crystal structure of (4,4)-c HIAM-4026 with lvt underlying net (b); reticular chemistry guided in situ “one-pot” strategy to construct HIAM-4040-R-op and the corresponding single crystal structure (c).

S2–S5 (Supporting Information), each Zr₆ cluster is connected by nine fully deprotonated H₃5CIB/H₃4CIB linkers, in which six carboxylic groups are from the benzene rings and the other three are located on the thiophene rings. Each H₃5CIB/H₃4CIB is coordinated to three Zr₆ clusters. As a result, (3,9)-c underlying net is generated in HIAM-4033-op and HIAM-4033a-op. The aforementioned structure features are the same as HIAM-4033 directly constructed using H₃5CIB.⁷⁰ While, as we reported, a different Zr-MOF, HIAM-4034, can be generated directly using H₃4CIB as the organic linker (Figure 1d). HIAM-4034 is also a (3,9)-c underlying nets but possesses totally different topology compared with HIAM-4033a-op constructed via the in situ “one-pot” method, although they are formed using the same organic linker, H₃4CIB. To have a deep understanding of the “one-pot” and direct synthesis strategy-induced structure diversity of HIAM-4033a-op and HIAM-4034, we analyzed H₃4CIB conformations in these two Zr-MOFs. As shown in Figure S6 (Supporting Information), completely different linker conformations were observed for H₃4CIB in HIAM-4033a-op and HIAM-4034, which indicates that the “one-pot” approach can cause different H₃4CIB conformation during in situ synthesis compared with directly dissolved H₃4CIB in DMF solution.

Using the similar synthesis conditions, the suitable single-crystal of HIAM-4017-op can also be constructed (Figure 1e) via the in situ linker synthesis between H₂DATC and 5'-formyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid, which exhibits almost identical PXRD patterns with the simulated HIAM-4017 directly constructed using the tetratopic carboxylic acid, 5'-(4,7-bis(4-carboxyphenyl)-1H-benzo[d]imidazol-2-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (H₄BITA) and ZrCl₄ (Figure 1f).⁶⁹ The phase purities of these Zr-MOFs via in situ “one-pot” and direct synthesis strategy were confirmed by the almost identical PXRD patterns of the simulated and experimental one (Figure 1f). The above results demonstrate that the in situ

“one-pot” approach indeed can be used to construct Zr-MOFs via the in situ formation benzimidazole-contained carboxylic acids from reaction between aldehyde- and o-phenylenediamine-based precursors.

2.2. Reticular Chemistry Guided Construction Zirconium-Pentacarboxylate Frameworks via Benzimidazole-Inspired “One-Pot” Approach

Inspired by the successful construction of aforementioned four Zr-MOFs, we attempt to prepare zirconium-pentacarboxylate frameworks guided by reticular chemistry using the in situ “one-pot” strategy.^{72,73} As we reported, (5,5)-c zirconium-pentacarboxylate frameworks with zfu underlying net, HIAM-4040 and HIAM-4040-OH, can be precisely constructed by reticular chemistry guided structure evolution from (4,4)-c NU-1400 possessing lvt topology.^{74–76} Conventionally, to prepare HIAM-4040, the organic linker, namely 5,5'-(2-(4-carboxyphenyl)-1H-benzo[d]imidazole-4,7-diyl)diisophthalic acid (H₅CBII), has to be synthesized via a three-step route as shown in Figure 2a. It is obvious that if we intend to investigate substituent properties of resultant MOFs, fifteen-step organic synthesis has to be conducted to obtain the five organic linkers, which is time-consuming and unsustainable. Alternatively, 2',3'-diamino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid (H₄DATTC) (Figure 2b) was then designed and synthesized by two-step reaction with which five HIAM-4040 type Zr-MOFs with different functional groups can be facily constructed via the in situ “one-pot” method. The reasons to use H₄DATTC as the precursor are: i) H₄DATTC might be utilized to prepare Zr-MOFs with (4,4)-c lvt topology (Figure 2b), which is essential for the structure evolution from lvt to zfu; ii) this investigation will be a good example

to further prove the universality of the present in situ “one-pot” strategy in another linker system; iii) the successful construction of zirconium-pentacarboxylate frameworks will further confirm the importance of reticular chemistry guided structure transformation from (4,4)-c *lvt* topology to (5,5)-c *zfu* underlying net constructed using H_4 DATTC inspired pentacarboxylic acids.

Light yellow single crystals of H_4 DATTC-based Zr-MOF, HIAM-4026, were obtained using formic acid as the modulator (Figure 2b). The sc-XRD analysis indicates that HIAM-4026 crystallizes in the orthorhombic crystal system with an *Imma* space group (Table S3, Supporting Information). As expected, in the structure of HIAM-4026, each Zr_6 cluster is connected to four fully deprotonated DATTC and each DATTC is coordinated to four Zr_6 clusters (Figure 2b; Figure S7, Supporting Information), which is the same with NU-1400 possessing *lvt* underlying net and is essential for the topology evolution from *lvt* to designed zirconium-pentacarboxylate frameworks via the in situ “one-pot” approach.

A procedure for in situ “one-pot” synthesis of zirconium-pentacarboxylate frameworks is as follows: a 5 mL vial containing 1 mL 0.02 mM H_4 DATTC, 1 mL 0.03 mM 4-formylbenzoic acid with five different substituent groups (Figure 2c), 23.3 mg $ZrCl_4$, different volume of formic acid and 1 mL DMF was placed in a preheated oven at 120 °C for 3 days. Single crystals HIAM-4040-op, HIAM-4040-OH-op, HIAM-4040-F-op, HIAM-4040-Br-op and HIAM-4040-NO₂-op were obtained using appropriate concentrations of formic acid, in which the excellent single crystals can be obtained for HIAM-4040-op and HIAM-4040-F-op (Figure 2c). As expected, both of them crystallize in an orthorhombic crystal system with a *P2₁2₁2₁* space group (Tables S4 and S5, Supporting Information). In these two structures, each Zr_6 cluster is coordinated by five fully deprotonated organic linkers (Figure 2c and Figures S8–S11, Supporting Information). Each organic linker is connected to five Zr_6 clusters. As a result, HIAM-4040-op and HIAM-4040-F-op possess a rarely reported (5,5)-c *zfu* underlying net, which is identical to HIAM-4040 directly constructed using H_5 CBII as the organic linker.^[76] These results further prove the universality of the in situ “one-pot” approach and the infinite potential of reticular chemistry for achieving the structure evolution and predicting new underlying nets in MOFs.

Then PXRD patterns of HIAM-4026 and these five zirconium-pentacarboxylate frameworks synthesized via conventional and in situ “one-pot” approach were measured and compared with the simulated PXRD patterns. As shown in Figure 3a, the well-matched PXRD patterns between simulated HIAM-4026, HIAM-4040, HIAM-4040-op, HIAM-4040-F-op and as-synthesized Zr-MOFs are not only indicated their phase purity, but also demonstrated that the (5,5)-c zirconium-pentacarboxylate frameworks indeed can be constructed using the in situ “one-pot” method under the guidance of reticular chemistry. Then the solid-state emission and absorption spectra of these five Zr-MOFs were measured. The substituent groups indeed have significant effects on the optical behaviors of resultant Zr-MOFs (Figure 3b,c), which might enhance their performances in various applications. Compared with HIAM-4040-op, the remarkable emission redshift of HIAM-4040-OH-op can be ascribed to the excited-state intramolecular proton transfer (ESIPT), which is consistent with MOFs constructed using the traditional method.^[76]

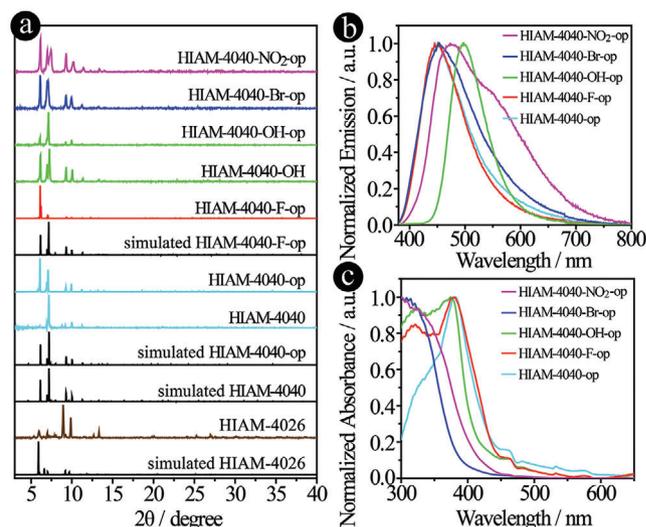


Figure 3. The simulated and experimental PXRD patterns of HIAM-4026 and HIAM-4040-R-op series (a); solid-state emission spectra (b) and UV-vis absorption spectra (c) of HIAM-4040-R-op series.

2.3. In Situ “One-Pot” Approach to Constructing Zirconium-Hexacarboxylate Framework and Characterization

Due to the great challenge in the synthesis of multitopic carboxylic acids and limitations in constructing corresponding Zr-MOFs, such as low solubility of organic linkers, up to now only four works have been reported to synthesize zirconium-hexacarboxylate frameworks with *pbz* and *alb-a* underlying nets, respectively.^[54–57] Therefore, to enrich the diversity of zirconium-hexacarboxylate frameworks and confirm the universality of the “one-pot” in situ strategy for constructing multitopic carboxylic-acid-based Zr-MOFs, herein, 5',5''-(2,3-diaminophenyl)-bis((1,1':3',1''-terphenyl)-4,4''-dicarboxylic acid) (H_4 APTC)^[77] (Figure 4a) were chosen to react with 5'-formyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (Figure 4a) to in situ synthesize hexacarboxylic acids for constructing zirconium-hexacarboxylate frameworks, HIAM-4060-op.

As expected, large single crystals of HIAM-4060-op were obtained with bright blue emission (Figure 4b). The sc-XRD analysis reveals that HIAM-4060-op crystallizes in an orthorhombic crystal system with an *Fddd* space group (Table S6, Supporting Information). In HIAM-4060-op, each Zr_6 cluster is coordinated by eight deprotonated organic linkers, 5',5''',5''''-(1H-benzod[*d*]imidazole-2,4,7-triyl)tris((1,1':3',1''-terphenyl)-4,4''-dicarboxylic acid) (H_6 BITTCA) and four DMF molecules (Figure 4c-e; Figures S12 and S13, Supporting Information). In these eight organic linkers, four of them are connected with the Zr_6 cluster via bidentate coordination using one of six carboxyls from the in situ formed linker. The most interesting structural feature is that for the rest four organic linkers, two of the six carboxyls from a single linker are connected with the Zr_6 cluster, in which one carboxylic group employed bidentate coordination and the other one is in a monodentate fashion (Figure 4d; Figure S13, Supporting Information). Each hexacarboxylate is connected to four Zr_6 clusters (Figure 4d; Figure S13, Supporting Information). This

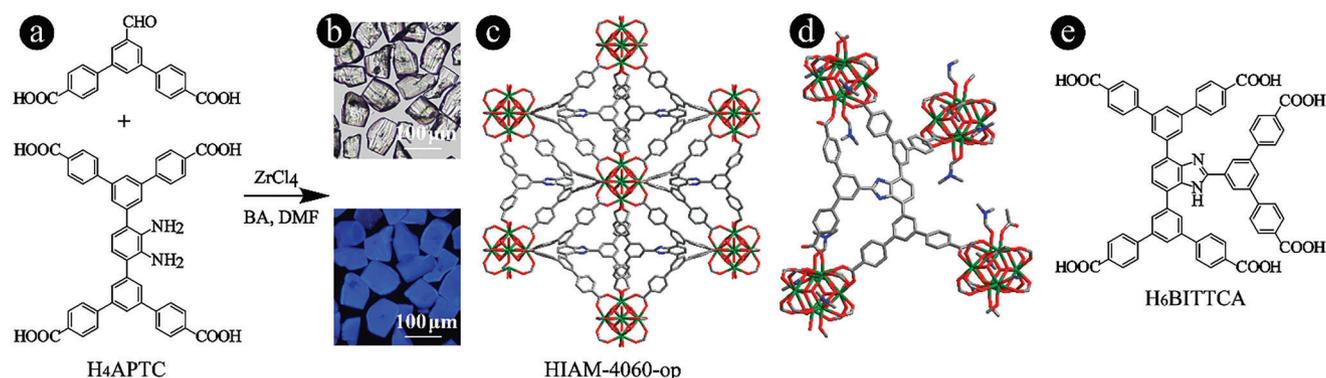


Figure 4. a) The molecular structures of H₄APTC and 5'-formyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid; b) the single crystals of HIAM-4060-op under daylight and 365 nm excitation; c) the single-crystal structure of HIAM-4060-op; d) the connection model of organic linker and Zr₆ clusters; e) the molecular structure of H₆BITTCA.

kind of structural feature is distinct from all reported Zr-MOFs. As a result, HIAM-4060-op is a 2-nodal (4,8)-c net with the point symbol of $\{4^{10} \cdot 6^{14} \cdot 8^4\}\{4^5 \cdot 6\}_2$ and represents a rarely reported topology of **alb-4,8-Fddd** in MOFs with chemical formula of Zr₆O₄(OH)₄(DMF)₂(H₂O)₂(BITTCA)₂. These aforementioned results demonstrate that the in situ “one-pot” strategy has the capacity to synthesize multitopic carboxylic acids and sequential construct the corresponding Zr-MOFs.

The phase purity of the bulk HIAM-4060-op was confirmed by the well-matched PXRD patterns of simulated and as-synthesized samples (Figure 5a). As observed from the PXRD pattern, the framework maintained its structural integrity after solvent-exchange and thermal activation under a dynamic vacuum at 120 °C for 12 h, indicating the rigid structural nature of HIAM-4060-op. Then the permanent porosity of HIAM-4060-op was examined by N₂ sorption experiments at 77 K. As depicted in Figure 5b, HIAM-4060-op shows typical type I isotherms. The corresponding Brunauer–Emmett–Teller (BET) surface area of HIAM-4060-op is 2047 m² g⁻¹ calculated from the sorption data. The experimental total pore volume is 0.92 cm³ g⁻¹ for HIAM-4060-op. Based on the N₂ sorption data, the pore size distribution analysis using density functional theory (DFT) method revealed the micropores at 11.3 Å for HIAM-4060-op (Figure 5b).

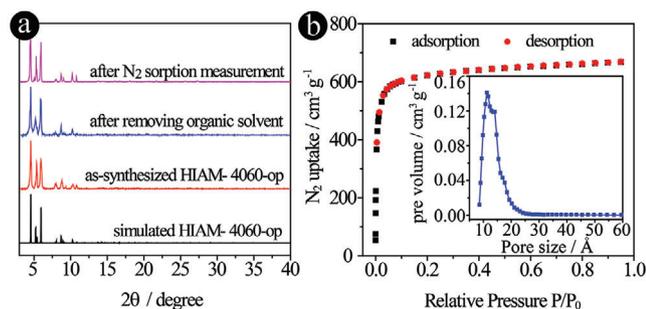


Figure 5. a) The PXRD patterns of the simulated, as-synthesized, desolvated and after sorption measurement of HIAM-4060-op; b) the N₂ adsorption–desorption isotherms at 77 K and the corresponding pore size distribution of HIAM-4060-op.

3. Conclusion

In conclusion, we have developed a “one-pot” approach to constructing different kinds of Zr-MOFs via in situ synthesis of benzimidazole-contained carboxylic acids, generated from the reaction of benzimidazole aldehyde- and *o*-phenylenediamine-typed precursors, and subsequently coordination with Zr₆ clusters. The benzimidazole-contained organic linkers can be extended from tritopic, tetratopic, pentatopic to hexatopic carboxylic acids. Guided by the reticular chemistry, zirconium-pentacarboxylate frameworks can be rationally designed and constructed via the in situ “one-pot” strategy with various functionalities. The present study opens a new avenue toward the construction of Zr-MOFs, especially for these multitopic carboxylic acids based Zr-MOFs, which will not only enrich the structure diversity of Zr-MOFs, but also extend the pool of functional luminescent MOFs for target specific applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

benzimidazole, metal–organic frameworks, multitopic carboxylic acids, one-pot strategy, reticular chemistry

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