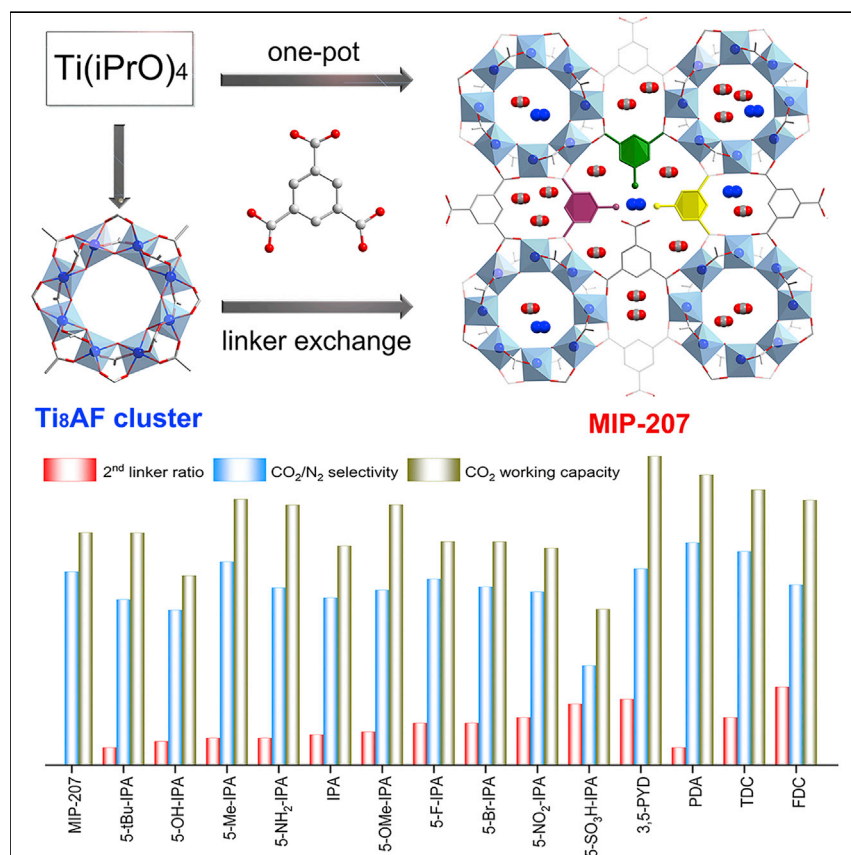


Article

Toward a Rational Design of Titanium Metal-Organic Frameworks



Titanium metal-organic framework (Ti-MOF) is an unexploited area due to its unpredictable chemistry in solution and, thus, the challenge of controlling the reaction process and product. By linker exchange with a Ti₈O₈ cluster precursor, the first green scalable controlled synthesis of a Ti-MOF structure is achieved following both post-synthetic and one-pot reaction routes. The chemical functionality and environment of the MOF pore could be tuned easily by mixed linker, resulting in an adjustable performance in CO₂ capture over N₂.

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HIGHLIGHTS

Controlled synthesis of Ti-MOF is achieved by post-synthetic and one-pot reactions

The chemical environment of the MOF pore was tuned following mixed-linker strategy

CO₂ adsorption working capacity and selectivity over N₂ could be adjusted

Ti₈AF and MIP-207 feature facile green scalable preparations under mild conditions



Benchmark

First qualification/assessment of material properties and/or performance

Wang et al., Matter 2, 1–11
February 5, 2020 © 2019 Elsevier Inc.
<https://doi.org/10.1016/j.matt.2019.11.002>

Article

Toward a Rational Design of Titanium Metal-Organic Frameworks

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SUMMARY

The complexity of Ti chemistry in solution not only leads to the difficulty of isolating crystalline titanium metal-organic frameworks (Ti-MOFs) but also brings the challenge of controlled assembly of the crystal structure. We report here the first example of a controlled synthesis of a Ti-MOF structure through a linker-exchange strategy directly from a preformed Ti-O cluster. A Ti_8O_8 cluster precursor with terminal formate and acetate ligands (Ti_8AF) was reacted with trimesic acid (BTC) under green and mild conditions, generating a microporous Ti-MOF (MIP-207) while preserving the connection and configuration of the Ti_8O_8 core. In addition, due to the ditopic meta-positional connection mode of the linker, the chemical environment and functionality of the structural voids could be easily tuned by substituting trimesate moieties with isophthalate-type linkers via concise one-pot reactions. This finally resulted in an adjustable performance in CO_2 capture over N_2 .

INTRODUCTION

Titanium metal-organic frameworks (Ti-MOFs) have attracted considerable and continuous attention over the past decade, mainly due to the low toxicity and rich natural abundance of elemental Ti, the well-recognized specialty of Ti-MOFs in photocatalysis,^{1–4} and their great promise in gas separation.^{5,6} However, the complexity of Ti chemistry in solution has led so far to notable difficulties in controlling the Ti-MOF structures. For all the published Ti-MOFs obtained from direct synthesis using simple Ti precursors, including MIL-91,⁷ MIL-125,⁸ NTU-9,⁹ MIL-101,¹⁰ COK-69,¹¹ Ti-CAT-5,¹² MIL-167,¹³ MIP-177,¹⁴ MIL-100,¹⁵ Ti-TBP,¹⁶ and ZSTUs,¹⁷ their inorganic building units range from discrete Ti-O clusters to infinite chains, showing the highly unpredictable feature of Ti reaction. In this regard, only post-synthetic cation exchange between MOFs built with various metal centers of known secondary building units (SBUs) and Ti ions has led to Ti-MOFs in a structurally controlled manner.^{18–20}

To achieve a better structure control of the resulting MOF during direct synthesis, Zhou and co-workers firstly tried to prepare PCN-22 in *N,N*-diethylformamide (DEF)/benzoic acid under solvothermal conditions involving a preformed Ti_6 cluster compound as precursor, which efficiently slowed down the crystallization and thus gave rise to a single-crystal product.²¹ Nonetheless, a break of the pristine Ti_6 cluster and its reorganization into a Ti_7 one was revealed by single-crystal structure analysis. Later, using the same Ti_6 cluster complex in methanol, an exciting progress in synthesizing Ti-MOF while under control was achieved by Yaghi and co-workers by applying a combined MOF and covalent-organic framework (COF) strategy. MOF-901 was successfully assembled via the imine formation from the amino group of the Ti_6 cluster-protecting ligand and the aldehyde groups of the organic spacer,

Progress and Potential

Rational design and synthesis of metal-organic frameworks (MOFs) is of particular interest in fine-tuning the crystalline structures for given targeting applications. Considerable advance of this topic has been achieved for MOFs built with a large number of metal species but not titanium. The complex and unpredictable titanium chemistry in solution not only leads to the difficulty of isolating crystalline Ti-MOFs via direct synthesis but also results in the challenge of maintaining control over ordered structures. We demonstrated a Ti-O cluster guided green scalable preparation of a Ti-MOF (MIP-207) in a controlled manner with both post-synthetic and one-pot reaction routes. The chemical environment and functionality of the MOF structural void could be easily tuned by adopting the mixed-linker strategy, which finally resulted in an adjustable performance in CO_2 capture over N_2 . This provides a new avenue for the rational design of Ti-MOFs in energy- and environment-related applications.

during which the connection of the Ti_6 cluster core was not disturbed.²² This method was proven to tolerate other dialdehyde spacers by the preparation of MOF-902, which represents the first example of reticular chemistry in Ti-MOFs.²³ The challenge remaining is to realize the controlled formation of Ti-MOF by modulating the Ti-O coordination bond of the cluster instead of the organic covalent bonds from the protective ligand, as in the cases reported previously for the other metal-based MOFs such as Fe^{24-26} and Zr^{27-29} MOFs.

Recently, Park and co-workers reported DGIST-1, which displays an infinite Ti-O chain inorganic building block resulting from the reorganization of the pristine Ti_6 or Ti_8 clusters in the DEF/benzoic acid reaction system.³⁰ Similarly, Lin and co-workers found that a Ti_3 building unit was generated in *N,N*-dimethylformamide (DMF)/acetic acid mixture when the same Ti_6 cluster precursor reacted with a 4,4'-biphenyl-dicarboxylic acid (BPDC) linker.³¹ It further supported that alternative solvent systems other than the conventional one, i.e., DEF or DMF with modulators, could be an important factor in helping the preservation of the original connectivity in the Ti-O cluster precursor during reactions.

In addition, the configuration of the Ti-O cluster precursor, such as the chemical component and connection mode, could represent another essential determinant for the linker-exchange process during the MOF formation. All the aforementioned Ti-O clusters reported so far feature large terminal monocarboxylate ligands with bulky aromatic moieties in a densely arranged configuration, which could possibly impede the effective bonding exchange between the protective species and the targeting linker for MOF formation. In this case, Ti-O connections of the cluster have to be reorganized to preferentially facilitate the linker exchange. Therefore, selection of a Ti-O cluster precursor with adequate space flexibility, particularly protected by small and appropriate terminal ligands such as formate or acetate, could be a feasible solution. However, to our knowledge, controlled synthesis of Ti-MOF starting from such Ti-O clusters with adapted reactivity and directly via linker exchange has never been achieved to date.

Here, we report a controlled preparation of a microporous Ti-MOF, denoted MIP-207 (MIP stands for the Materials of the Institute of porous materials from Paris), via direct ligand exchange between the small terminal monocarboxylate species of a Ti_8O_8 cluster (Ti_8 -acetate-formate, Ti_8AF) and the targeting trimesic acid (BTC) for MOF fabrication. MIP-207 can be synthesized not only under solvothermal conditions by using the pre-formed Ti_8 cluster as precursor, but also in reflux reaction under ambient pressure by the assembly of the *in situ* generated Ti_8O_8 cluster and BTC, which is concise and facile for scale-up preparation. The BTC linker in the structure adopts a meta-connection mode leaving the free carboxylic group pointing toward the pore, which allows a successful partial substitution of trimesate linker by different isophthalates with diverse functional groups, so that the chemical environment of the MOF pore can be tuned. It is noteworthy that the Ti_8AF cluster features an appropriate reactivity and a green scalable production, which makes it a suitable precursor for rational design and direct synthesis of Ti-MOFs. Furthermore, MIP-207 displays good water stability at room temperature (RT) and a promising adsorptive selectivity of carbon dioxide (CO_2) over nitrogen, suitable for future CO_2 working adsorption processes.

RESULTS AND DISCUSSION

Considerable progress in crystalline Ti-O clusters has been achieved during the past few decades, leading to diverse structures with different numbers of Ti centers.³²⁻³⁶

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<https://doi.org/10.1016/j.matt.2019.11.002>

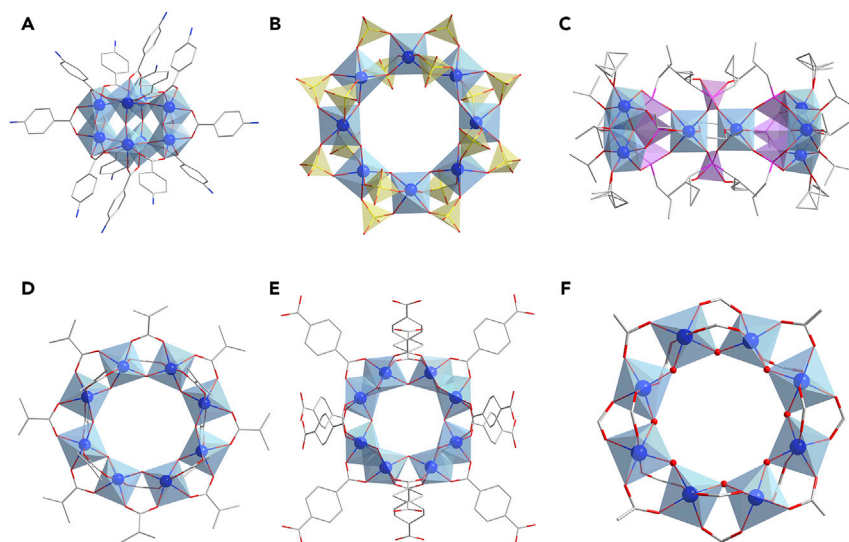


Figure 1. Selected Ti_8 Clusters

Comparison of some Ti_8 clusters reported with protection ligands of (A) 4-aminobenzoic acid, (B) sulfate, (C) a phosphorous acid derivative, (D) isobutyric acid, (E) terephthalic acid, and (F) the Ti_8AF in this work. Ti is shown in blue, C in gray, O in red, S in yellow, and P in pink.

In most cases, the syntheses of Ti-O clusters require hydrolysis of Ti precursor under solvothermal conditions, which is always limited by long reaction time, low reaction yield, and small scale for further applications. In contrast, the Ti_8AF cluster was prepared under reflux conditions with ambient pressure for a short duration, simply by heating the mixture of $Ti(iPrO)_4$, formic acid, and acetic anhydride in a round-bottomed flask in contact with air. This facile process allows easy scale-up preparation.

The crystal structure of the $Ti_8(\mu_2-O)_8(acetate)_{12}(formate)_4$ (Ti_8AF) cluster was solved *ab initio* from high-resolution powder X-ray diffraction (PXRD) data (Figures S1 and S2; Tables S1 and S2). As shown in Figure 1, different from the reported Ti_8 clusters, the protective ligands of the Ti_8AF cluster are bridging formates and acetates, which are of much less steric hindrance or weaker bonding interactions with the Ti(IV) ions in comparison with those reported, such as 4-aminobenzoic acid, terephthalic acid, isobutyric acid, and sulfate, to name a few. It not only provides adequate space and freedom for the surrounding coordination but also possesses appropriate coordination strength between the ligands and Ti-O core, as it is well demonstrated that both formate and acetate are good modulators for MOF synthesis and are thus replaced smoothly by multitopic carboxylate linkers.^{37–39} Hence, a much easier installation of the MOF linker molecule can be promoted via an efficient linkage exchange when the Ti_8AF cluster is used as precursor (see Figures S6–S9 for the detailed characterizations).

With the Ti_8AF cluster in hand, controlled synthesis of Ti-MOF using it as precursor was carried out. Based on the influence of the reported solvent systems, acetic anhydride was selected because it is a widely used solvent in organic synthesis and has been proven to be efficient for MOF preparation.⁴⁰ A highly crystalline Ti-MOF of chemical formula $Ti_8(\mu_2-O)_8(acetate)_8(BTC)_4$, named MIP-207, was obtained in the solvent mixture of formic acid and acetic anhydride under solvothermal conditions (Figure S10). The crystal structure was initially solved from PXRD data and further refined with the geometry optimization performed at the density functional theory

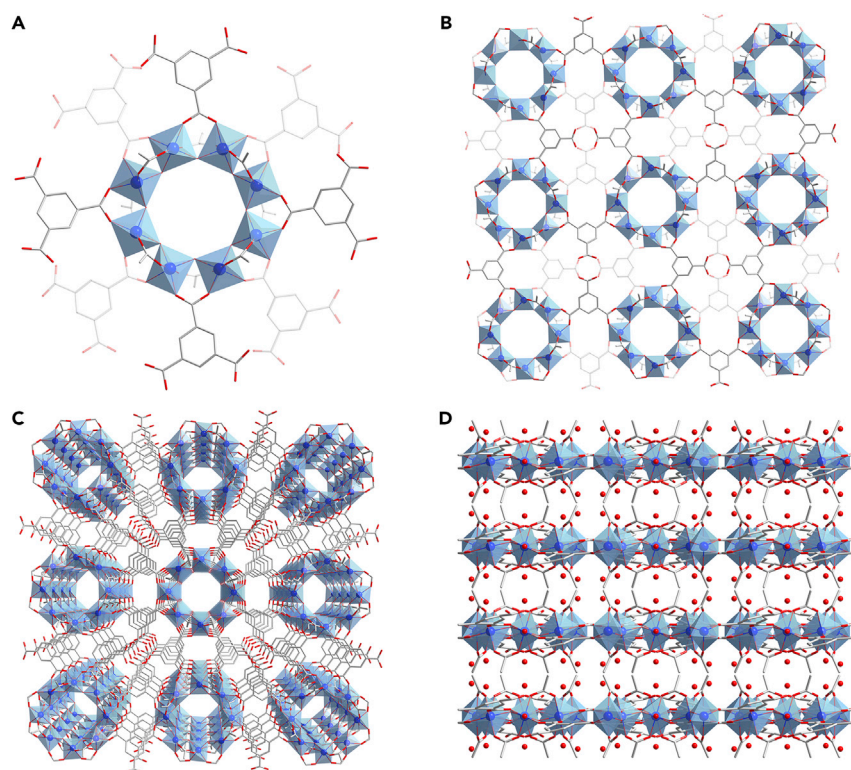


Figure 2. Crystal structure of MIP-207

(A) A $\text{Ti}_8(\mu_2\text{-O})_8(\text{acetate})_8(\text{BTC})_4$ cluster SBU.

(B) A single 2D layer viewed along the *c* axis.

(C) Micropore system viewed along the *c* axis.

(D) Adjacent 2D layers closely packed with a large amount of guest water molecules in between to stabilize the crystal structure. Ti is shown in blue, C in gray, and O in red.

(Tables S3 and S4; Figures S3–S5). This reveals that the MIP-207 structure crystallizes in a tetragonal $P4/nbm$ space group with unit-cell parameters of $a = b = 24.2224(15)$ Å, $c = 7.8291(5)$ Å, and $V = 4,593.5(6)$ Å³. As shown in Figure 2A, the entire arrangement and configuration of the Ti_8 cluster core is maintained in the SBU of MIP-207. A thorough ligand exchange was observed for all of the terminal formates. Eight carboxylate groups from the BTC molecules occupy the adjacent positions of formates and acetates in an up-and-down mode above and below the symmetrical plane of the cluster core, which could be due to the steric hindrance repulsion effect. Each Ti_8 cluster is interconnected with neighboring four SBUs by using a meta-position carboxylate group of the BTC linker, forming a two-dimensional (2D) layer with a large amount of free carboxylic acid groups facing the voids (Figure 2B). The presence of both acetate and BTC moieties is confirmed by the ¹³C solid-state nuclear magnetic resonance (NMR) spectrum (Figures S13 and S14), in which all carboxylic carbon atoms are clearly distinguished. The presence of the free carboxylic groups is validated by the ¹H solid-state NMR spectrum that displays a characteristic acidic proton at 13.3 ppm (Figure S13). Contiguous layers stack against each other in a strictly ordered fashion so that the channel of about 6 Å (Figure S12) inside the Ti_8 cluster and between SBUs remains when viewed along the *c* axis of the structure (Figure 2C), resulting in a Brunauer-Emmett-Teller (BET) area of 570 m² g^{−1} and a free pore volume of 0.34 cm³ g^{−1} deduced from the nitrogen porosimetry data collected at 77 K (Figure S11 and Table S5). There is a considerable amount of guest water

molecules accommodated between layers, supplying intermolecular hydrogen bonding for guest-guest and guest-host interactions to further stabilize the crystal structure of MIP-207 (Figure 2D).

Since the Ti_8AF cluster and MIP-207 share the same solvent system for preparation, a direct synthesis using $\text{Ti}(\text{iPrO})_4$ as the Ti(IV) precursor was considered. As expected, MIP-207 was obtained from heating the mixture of $\text{Ti}(\text{iPrO})_4$ and BTC in the presence of formic acid and acetic anhydride under solvothermal conditions. A further attempt at performing the same reaction under reflux conditions worked as well, although with a slightly less crystalline product. Additionally, the absence of formate in the MIP-207 structure inspired us to replace formic acid by acetic acid, since acetic acid is much more cost-effective and of less risk when handled in large quantity in comparison with formic acid. To this end, a product of the same phase but with a slightly worse crystallinity was obtained by applying acetic acid instead of formic acid. Thus, the preparation of MIP-207 was improved to a green scalable chemistry level, which could be of remarkable benefit for its future applications on an industrial scale.

Water stability is an important concern for MOFs when real application conditions are considered. Therefore, stability of MIP-207 in contact with water was checked (Figure S15). First, a long-duration (18 months) exposure of an MOF sample in open-air atmosphere was carried out. The PXRD pattern of the corresponding product did not show obvious change in comparison with that of the pristine compound, suggesting good stability of MIP-207 in air at RT. Similar observations were made when the MOF sample was soaked in water for 3 days at RT. Nevertheless, MIP-207 displays limited hydrothermal resistance, similar to other reported Ti-MOFs. Both hot water vapor (100°C) and hot liquid water (80°C) could destroy the long-range order of MIP-207 crystal structure within 24 h. Therefore, MIP-207 presents moderate water stability at the same level of $\text{NH}_2\text{-MIL-125}$, which is adequate for applications involving water vapor at low temperatures.^{14,41,42}

Thermal stability of MIP-207 was evaluated by a combined analysis of thermogravimetric data and temperature-dependent PXRD data (Figures S16 and S17). A continuous weight loss was observed from RT to 325°C in the thermogravimetric analysis (TGA) curve before the sharp drop, which could be ascribed to the gradual departure of guest solvent molecules and terminal acetates. The PXRD patterns confirm the successful maintenance of the long-range order of the MOF crystal structure up to 300°C, with slight alterations in relative intensity of some peaks. Further increase of heating temperature leads to a fast decomposition of the MOF structure, evidenced by a steep weight loss in TGA and a significant decrease of crystallinity in PXRD. Therefore, MIP-207 is among the best thermally stable Ti-MOFs reported so far.

The BTC molecule in the MIP-207 structure uses two carboxylate groups at meta-positions on the benzene ring for the linkage of SBUs and leaves the third carboxylic acid group free from coordination, so it could be considered as an isophthalate-type linker. Thus, to make the chemical environment of the MOF cavity diverse and tunable, we can envisage partial or even entire replacement of the BTC by other functional linkers with similar molecular size and angles between the two connection sites as that of the isophthalic acid (IPA). Accordingly, various similar linkers have therefore been tested under the same reaction conditions (acetic acid/acetic anhydride solvent system, reflux), and the corresponding results are shown in Figure 3 and listed in Table 1.

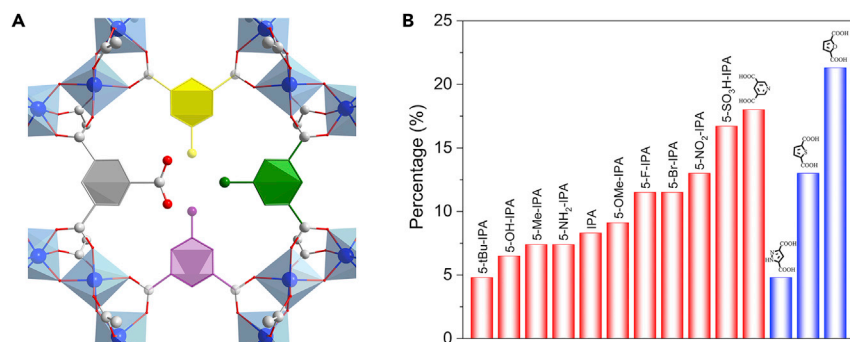


Figure 3. Summary of Secondary Linker Substitution in MIP-207 Structure

(A) Illustration of linker substitution in MIP-207 crystal structure; the functional isophthalate-type linkers are marked with colors.

(B) Linker substitution ratio determined by ¹H NMR data collected with the decomposed MOF samples in D₂O/KOH solution. Standard conditions for all the reactions involving mixed linkers: Ti(iPrO)₄ (3 mmol), BTC (3 mmol), secondary linker (1 mmol), acetic acid (10 mL), acetic anhydride (10 mL), reflux overnight.

If no crystalline MOF comprising the pure isophthalate ligands could be obtained, a good tolerance toward a large range of functional groups of this substitution reaction was observed when partial substitution of trimesate by IPA derivatives was applied (Table 1, entries 2–12; Figures S18–S21). Interestingly, the electronic effect of the functional group plays an important role in determining the final ratio of the secondary linker included. Compared with the electron-withdrawing free carboxyl group in the pure MIP-207 structure, the electron-donating functions including H, Me, OH, NH₂, OMe, and tBu on the IPA moiety all result in replacing ratios below 10% (Table 1, entries 2–7; Figure S22). In sharp contrast, electron-withdrawing functional groups, such as -NO₂, -SO₃H, -F, -Br, and pyridyl (Table 1, entries 8–12; Figure S23), give rise to elevated substitution proportions (i.e., 12–18 mol %). In particular, the higher replacing rates of the bulky -NO₂ and -SO₃H derivatives compared with the less hindered -H and -Me ones indeed highlight the key role of the influence of electronic effect. It is noteworthy that dicarboxylic acids with heterocyclic five-membered rings could also substitute BTC efficiently (Table 1, entries 13–15; Figure S24). Especially the fact that 2,5-furan-dicarboxylic acid shows notably higher ratio (21 mol %) than that of the 2,5-thiophene-dicarboxylic acid (13 mol %) supports well the decisive role of electronic effect, since the thiophene ring is well known to be more electron-rich than furan. In addition, the substitution ligand could be extended to multicomponent with different functional groups. For instance, both IPA and 5-NO₂-IPA could be included in the MOF framework at the same time, further enriching the local chemical environment of the pore (Table 1, entry 16; Figure S24).

Linker substitution not only generates a rich chemical environment in the cavity but also produces a pronounced effect on the surface area and pore volume of the MOF structure (Tables 1 and S6; Figures S25–S27). In comparison with the pure MIP-207, some secondary linkers could lead to a slight increase of the BET area and pore volume. For example, 5-NO₂-IPA substitution (entry 10) results in an increase of BET area of up to 32% while introduction of 2,5-thiophene-dicarboxylic acid raises the pore volume by 54%. However, some functional groups that might form strong binding with Ti(IV) ion decrease the surface area and pore content notably, possibly due to the trapping of coordinated Ti complex impurities, as is the case for 5-SO₃H-IPA (entry 11). The changes in BET area and pore volume for a given secondary linker do

Table 1. Summary of Secondary Linker Substitution and Corresponding Selective CO₂ Sorption Performance

Entry	Substitution Linker	Ratio ^a (mol %)	S _{BET} ^b (m ² g ⁻¹)	S _{BET} ^b (m ² cm ⁻³)	CO ₂ Uptake 298 K, 0.15 bar (mmol g ⁻¹)	CO ₂ Working Capacity 298 K (mmol g ⁻¹)	CO ₂ Working Capacity 298 K (μmol g ⁻¹ m ⁻²)	IAST Selectivity CO ₂ /N ₂ = 15:85, 298 K, 1 bar
1	–	–	590	820	0.89	0.63	1.07	52.8
2	5-tBu-IPA	5	680	950	0.88	0.63	0.93	45.2
3	5-OH-IPA	7	530	740	0.69	0.52	0.98	42.3
4	5-Me-IPA	7	750	1,040	1.04	0.73	0.97	55.5
5	5-NH ₂ -IPA	7	630	880	1.00	0.71	1.13	48.4
6	IPA	8	670	930	0.82	0.60	0.90	45.7
7	5-OMe-IPA	9	750	1,040	1.01	0.71	0.95	47.8
8	5-F-IPA	12	560	780	0.86	0.61	1.09	50.8
9	5-Br-IPA	12	620	870	0.85	0.61	0.98	48.6
10	5-NO ₂ -IPA	13	780	1,090	0.81	0.59	0.76	47.3
11	5-SO ₃ H-IPA	17	420	590	0.52	0.43	1.02	27.2
12	PYD ^c	18	680	930	1.21	0.84	1.24	53.6
13	PDA ^d	5	730	1,010	1.14	0.79	1.08	60.7
14	TDC ^e	13	770	1,060	1.09	0.75	0.97	58.3
15	FDC ^f	21	750	1,020	1.02	0.72	0.96	49.2
16	IPA	5	680	940	0.96	0.69	1.01	43.0
	5-NO ₂ -IPA	5						

^aThe ratio of the secondary linker was determined by the NMR data obtained with decomposed MOF product in D₂O/KOH solution.

^bData obtained from the nitrogen adsorption isotherm collected at 77 K.

^c3,5-Pyridine-dicarboxylic acid.

^d3,5-Pyrazole-dicarboxylic acid.

^e2,5-Thiophene-dicarboxylic acid.

^f2,5-Furan-dicarboxylic acid.

not correlate with its steric hindrance, molecular weight, and replacing ratio, which could be possibly explained by different linker defects.

It has been well documented that the presence of polar functional groups, such as -hydroxyl, -carboxyl, and -amino, in the MOF structure could notably improve its CO₂-capture performance.^{43–46} Nevertheless, it is very difficult to obtain Ti-MOFs with useful and accessible functional groups within the crystal framework. To date, only the NH₂-MIL-125 that contains^{41,47} free amino group has been successfully synthesized as the analog of MIL-125 despite its average performance in selective CO₂ adsorption, probably due to the large open pore system of the framework and/or lack of strong adsorption sites. This fact somehow largely limits the possible application of Ti-MOFs in CO₂ separation and capture processes. As the first Ti-MOF with free carboxyl in the crystal structure, MIP-207 thus motivated us to investigate its performance in the application of selective CO₂ adsorption and separation.

Single-component CO₂ and nitrogen (N₂) adsorption isotherms were collected on the MIP-207 sample to determine the CO₂ adsorption working capacity and calculated ideal adsorbed solution theory (IAST) selectivity of CO₂/N₂ for a typical post-combustion condition of vacuum swing adsorption (VSA) process (CO₂/N₂ = 15/85, 298 K, 0.1–1 bar; see [Supplemental Information](#)). It is worth noting that the desorption branch of CO₂ sorption isotherm is fully reversible for both temperatures ([Figure 4A](#)), indicating that regeneration of the MIP-207 sample could be realized under mild conditions. Hence, the strong interaction with CO₂ and relatively small

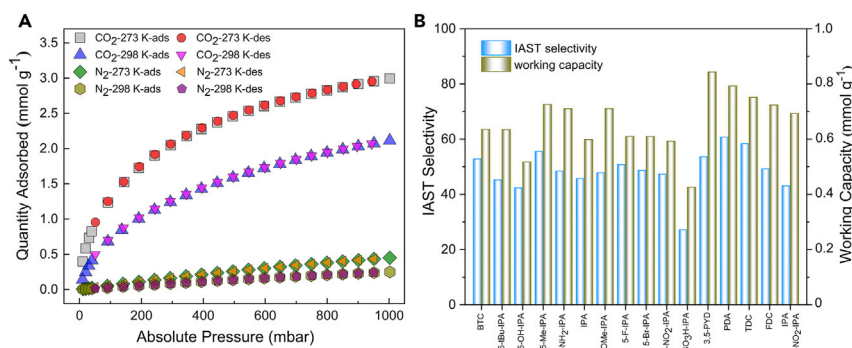


Figure 4. CO₂/N₂ Separation Performance of MIP-207s

(A) CO₂ and N₂ sorption isotherms of MIP-207 collected separately at 273 K and 298 K.

(B) Comparison of IAST selectivity (CO₂/N₂ = 15:85 v/v, 298 K, 1 bar) and CO₂ adsorption working capacity (CO₂/N₂ = 15:85 v/v, 298 K, 0.1–1 bar) between MIP-207 and samples with different substituted linkers.

pore volume of the structure result in the CO₂ adsorptive uptake of MIP-207 at 298 K of 0.89 and 2.11 mmol g⁻¹ for 0.15 bar and 1 bar, respectively, associated with an adsorptive working capacity of 0.63 mmol g⁻¹. To the best of our knowledge, these values are the highest among all the reported MOF structures with free carboxyl groups. Additionally, the calculated IAST selectivity is 52.8 and 81.2 for 298 K and 273 K, respectively, when a binary gases mixture of CO₂/N₂ = 15:85 (v/v) was considered, which is evidently higher than that of all the other Ti-carboxylate MOFs and comparable with that of MIL-91(Ti).

Furthermore, the adsorptive separation property of the MIP-207 framework on CO₂/N₂ could be easily adjusted by tuning the cavity chemical environment via secondary linker substitution (Figures 4B and S28; Table 1). On one hand, it is of great interest to improve the working capacity while keeping the selectivity. For example, introduction of the pyridyl moiety by partially replacing BTC with 3,5-pyridine-dicarboxylic acid (PYD) significantly enhanced the working capacity to 0.84 mmol g⁻¹ (33.3% increase) with a slightly increased IAST selectivity (Table 1, entry 12) in comparison with pure MIP-207. On the other hand, promotion in selectivity could be another aspect of interest. The highest IAST selectivity (60.7) among all the modified samples was achieved by inclusion of a small amount of 3,5-pyrazole-dicarboxylic acid (PDA), whose adjacent N/-NH- pair from the heterocyclic ring could possibly play an important role in enhancing the working capacity as well (entry 13). To confirm these results obtained by IAST, we performed real co-adsorption measurements with a home-made breakthrough apparatus (see Supplemental Information) on the parent sample (MIP-207, Figure S30), the sample with the highest working capacity (MIP-207 substituted with PYD, Figure S31), and the sample with the highest selectivity (MIP-207 substitutes with PDA, Figure S32). The experimental selectivity and working capacity values are in a very good agreement with those determined by IAST (Table S7). Therefore, MIP-207 provides a tunable scaffold regarding working capacity and selectivity for adsorptive separation of CO₂ over N₂.

In summary, we report controlled fabrication of a Ti-MOF (MIP-207) via direct synthesis by applying a linker-exchange and installing strategy based on a Ti₈ cluster (Ti₈AF), in which the connection and configuration arrangement of the Ti₈ cluster precursor were maintained. Due to the unique ditopic bonding mode of the BTC linker, various IPA-type secondary linkers with diverse functional groups were

introduced to the MOF framework and replaced BTC through concise one-pot reactions, allowing the rational adjustment of the tunable chemical environment of the MOF pore system. MIP-207 exhibits one of the best performances for CO₂/N₂ separation among all the reported Ti-carboxylate MOFs, with a good working capacity and an interesting selectivity of CO₂/N₂ under the typical post-combustion condition of CO₂/N₂ = 15/85, 298 K for a VSA process. As a result of the diverse chemical functions involved in the substituted secondary linkers, further improvement of CO₂/N₂ separation performance of MIP-207 could be achieved easily. Moreover, both the Ti₈AF cluster precursor and MIP-207 feature scalable green synthesis and good air stability. Thus, MIP-207 represents the first Ti-MOF example prepared while controlled under green scalable conditions. The wide tunability of the MOF pore environment and adequate stability of MIP-207 not only allow its good performance for CO₂/N₂ separation but also provide encouraging possibilities in other energy- and environment-related molecule separations.

EXPERIMENTAL PROCEDURES

MOF Syntheses

Reflux Synthesis of Ti₈AF Cluster

To a 500-mL round-bottomed flask, formic acid (200 mL), acetic anhydride (200 mL), and Ti(iPrO)₄ (40 mL) were added with stirring at RT. The mixture was refluxed at 120°C for 12 h. After cooling down to RT, the white crude product was collected by filtration or centrifugation. The final product was obtained by washing in boiling acetone and filtration or centrifugation. To keep the long-range order of the Ti₈AF cluster crystal structure for a long duration, immersing the product in acetone at RT is recommended. This procedure could be applied to either smaller or larger scale upon the request of product quantity.

Solvothermal Synthesis of MIP-207

To a 25-mL Teflon reactor, BTC (315 mg), acetic acid (2.5 mL), and acetic anhydride (2.5 mL) were added and stirred at RT. Ti(iPrO)₄ (300 μL) was added last while stirring. The reaction mixture was sealed in an autoclave and heated at 120°C for 48 h. After cooling down to RT, the crude product was collected by filtration, followed by washing it in boiling acetone for activation. The final product was obtained by filtration and air-drying.

Reflux Synthesis of MIP-207

To a 250-mL round-bottomed flask, BTC (4.2 g), acetic acid (50 mL) and acetic anhydride (50 mL) were added and mixed at RT. Ti(iPrO)₄ (4 mL) was added last while stirring. The reaction mixture was refluxed at 120°C for 12 h. After cooling down to RT, the crude product was collected by filtration, followed by washing it in boiling acetone for activation. The final product was obtained by filtration and air-drying. This procedure could be applied to either smaller or larger scale upon the request of product quantity.

Synthesis of Substituted MIP-207 with Secondary Linkers with Different Functional Groups

To a 50-mL round-bottomed flask, BTC (630 mg, 3 mmol), secondary linker (1 mmol), acetic acid (10 mL), and acetic anhydride (10 mL) were added and mixed at RT. Ti(iPrO)₄ (800 μL) was added last while stirring. The reaction mixture was refluxed at 120°C for 12 h. After cooling down to RT, the crude product was collected by filtration, followed by washing it in boiling acetone for activation. The final product was obtained by filtration and air-drying.

Co-adsorption Breakthrough Measurement

The co-adsorption breakthrough curves are measured with a home-made device (Figure S29) mainly composed of an adsorption column (5 cm height and 1 cm diameter [volume: 3.9 cm³]) placed in an oven, a gas supply system with two mass flow controllers (one for helium and one for N₂/CO₂ mixture), and a mass spectrometer to analyze gas composition at the outlet of the column.

Prior to each measurement, the adsorbent is outgassed at 423 K in the oven for 12 h under secondary vacuum. After cooling to 298 K, a helium flow is set to 2 NL h⁻¹ to pressurize the column. The breakthrough curve measurement is started by switching helium flow to N₂/CO₂ mixture (85:15) flow of 1 NL h⁻¹ (minimum set point value). The resulting pressure is 1.2 bar. The measurements are repeated twice (run 1 and run 2) for each sample.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.matt.2019.11.002>.

ACKNOWLEDGMENTS

The authors are grateful to the ANR project MeaCoPA (ANR-17-CE29-0003) for financial support.

AUTHOR CONTRIBUTIONS

Conceptualization, S.W. and C.S.; Investigation, S.W., H.R., N.H., M.W., C.M.-C., G.D.W., and G.M.; Writing – Original Draft, S.W.; Writing – Review & Editing, S.W., H.R., N.H., M.W., C.M.-C., G.D.W., G.M., and C.S. Supervision, G.D.W., G.M., and C.S.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: July 11, 2019

Revised: September 24, 2019

Accepted: October 31, 2019

Published: December 4, 2019

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