

Article

# Conversion of Carbon Dioxide into Molecular-based Porous Frameworks

Published as part of Accounts of Chemical Research special issue "Physical Phenomena in Porous Frameworks". Kentaro Kadota\* and Satoshi Horike\*



**CONSPECTUS:** The conversion of carbon dioxide  $(CO_2)$  to value-added functional materials is a major challenge in realizing a carbon-neutral society. Although  $CO_2$  is an attractive renewable carbon resource with high natural abundance, its chemical inertness has made the conversion of  $CO_2$  into materials with the desired structures and functionality difficult. Molecular-based porous materials, such as metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs), are designable porous solids constructed from molecular-based building units. While MOF/COFs attract wide attention as functional porous materials, the synthetic methods to convert  $CO_2$  into MOF/COFs have been unexplored due to the lack of synthetic guidelines for converting  $CO_2$  into molecular-based building units.



In this Account, we describe state-of-the-art studies on the conversion of  $CO_2$  into MOF/COFs. First, we outline the key design principles of  $CO_2$ -derived molecular building units for the construction of porous structures. The appropriate design of reactivity and the positioning of bridging sites in  $CO_2$ -derived molecular building units is essential for constructing  $CO_2$ -derived MOF/COFs with desired structures and properties. The synthesis of  $CO_2$ -derived MOF/COFs involves both the transformation of  $CO_2$  into building units and the formation of extended structures of the MOF/COFs. We categorized the synthetic methods into three types as follows: a one-step synthesis (*Type-II*); a one-pot synthesis without workup (*Type-III*); and a multistep synthesis which needs workup (*Type-III*).

We demonstrate that borohydride can convert  $CO_2$  into formate and formylhydroborate that serve as a bridging linker for MOFs in the Type-I and Type-II synthesis, representing the first examples of  $CO_2$ -derived MOFs. The electronegativity of coexisting metal ions determines the selective conversion of  $CO_2$  into formate and formylhydroborate. Formylhydroborate-based MOFs exhibit flexible pore sizes controlled by the pressure of  $CO_2$  during synthesis. In pursuit of highly porous structures, we present the Type-I synthesis of MOFs from  $CO_2$  via the in situ transformation of  $CO_2$  into carbamate linkers by amines. The direct conversion of diluted  $CO_2$  (400 ppm) in air into carbamate-based MOFs is also feasible. Coordination interactions stabilize the intrinsically labile carbamate in the MOF lattice. A recent study demonstrates that the Type-III synthesis using alkynylsilane precursors enables the synthesis of highly porous and stable carboxylate-based MOFs from  $CO_2$ , which exhibit catalytic activity in  $CO_2$  conversion. We also extended the synthesis of MOFs from  $CO_2$  to COFs. The Type-III synthesis using a formamide monomer affords stable  $CO_2$ derived COFs showing proton conduction properties. The precise design of  $CO_2$ -derived building units enables expansion of the structures and functionalities of  $CO_2$ -derived MOF/COFs. Finally, we propose future challenges in this field: (i) expanding structural diversity through synthesis using external fields and (ii) exploring unique functionalities of  $CO_2$ -derived MOF/COFs, such as carriers for  $CO_2$  capture and precursors for  $CO_2$  into porous materials.

# KEY REFERENCES

 Kadota, K.; Duong, N. T.; Nishiyama, Y.; Sivaniah, E.; Horike, S. Synthesis of porous coordination polymers using carbon dioxide as a direct source. *Chem. Commun.* 2019, 55, 9283–9286.<sup>1</sup> This work demonstrates the conversion of CO<sub>2</sub> into formate- and formylhydroboratebased MOFs by control of reactivity of borohydrides. Received:August 9, 2024Revised:September 9, 2024Accepted:September 20, 2024Published:October 14, 2024





3206



Figure 1. Molecular structures of the  $CO_2$ -derived building units for MOF/COFs. Carbon and oxygen atoms derived from  $CO_2$  are highlighted, respectively.

Table 1 Synt	thetic Methods	Gravimetric CO	Contents an	d Porosity of	Selected CO	Derived MOE/COEs
1 able 1. Sylli	menic memous,	Gravillettic CO	- Contents, an	a Porosity or	selected UU <sub>1</sub>	Derived MOT/COTS

Entry	Compositions	Material types <sup>g</sup>	Synthetic methods	CO <sub>2</sub> -derived building units	CO <sub>2</sub> contents (wt %)	$\binom{S_{\text{BET}}}{(\text{m}^2\text{g}^{-1})}$	ref.
1	$[Zn_3(OCHO)_6]$	c-MOF	Type-I	formate	56.6	225	1
2	[Mg <sub>3</sub> (OCHO) <sub>6</sub> ]	c-MOF	Type-II	formate	77.0	504	1
3	$[Mn_3(OCHO)_6]$	c-MOF	Type-II	formate	60.7	N.A.	1
4	[Fe <sub>3</sub> (OCHO) <sub>6</sub> ]	c-MOF	Type-II	formate	60.4	346	1
5	$[Co_3(OCHO)_6]$	c-MOF	Type-II	formate	59.1	324	1
6	$[Mg_{13}[BH(OCHO)_3]_{12}[BO_3]_4[B(OMe)_3][EtNH]_2]$	a-MOF	Type-I	fomylhydroborate	68.5	179-383	1
7	$[Zn_4O(PDC)_3]^a$	c-MOF	Type-I	carbamate	33.3	1525	2
8	$[Zn_4O(S-mPDC)_3]^b$	c-MOF	Type-I	carbamate	31.6	2366	2
9	$[Zn_4O(R-mPDC)_3]^c$	c-MOF	Type-I	carbamate	31.6	1943	2
10	$[Zn_4O(dmPDC)_3]^d$	c-MOF	Type-I	carbamate	30.1	1270	2
11	$[Cu_{0.5}(PDC)]$	c-MOF	Type-I	carbamate	N.A. <sup>i</sup>	88	31
12	[Cu(PDC)]	a-MOF	Type-I	carbamate	N.A.	56	31
13	$[\mathrm{Zr}_6\mathrm{O}_4(\mathrm{OH})_4(\mathrm{PDP})_6]^e$	c-MOF	Type-III	carboxylate	20	2702	36
14	$[Zr_6O_4(OH)_4(BPDP)_6]^f$	c-MOF	Type-III	carboxylate	24	3688	36
15	$[PZ(CH)_2]_3[(C_3N_3)N_3]_2$	c-COF	Type-III	caboxaldehyde	12.6	945	3
16	$[PZ(CO)_2]_3[(C_3N_3)(NH)_3]_2$	c-COF	Type-III	caboxaldehyde	10.8	731	3

<sup>a</sup>PDC = piperazine dicarbamate. <sup>b</sup>S-mPDC = S-(+)-2-methylpiperazine dicarbamate. <sup>c</sup>R-mPDC = R-(-)-2-methylpiperazine dicarbamate. <sup>d</sup>dmPDC = trans-2,5-dimethylpiperazine dicarbamate. <sup>e</sup>H<sub>2</sub>PDP = 3,3'-(1,4-phenylene)dipropiolic acid. <sup>f</sup>H<sub>2</sub>BPDP = 3,3'-([1,1'-biphenyl]-4,4'diyl)dipropiolic acid. <sup>g</sup>The prefixes "c-" and "a-" indicate that materials are either crystalline or amorphous in PXRD. <sup>h</sup>Calculated from N<sub>2</sub> adsorption isotherms at 77 K. <sup>i</sup>N.A. = Not Available.

- Kadota, K.; Hong, Y. L.; Nishiyama, Y.; Sivaniah, E.; Packwood, D.; Horike, S. One-Pot, Room-Temperature Conversion of CO<sub>2</sub> into Porous Metal–Organic Frameworks. J. Am. Chem. Soc. 2021, 143, 16750–16757.<sup>2</sup> This work demonstrates one-pot conversion of CO<sub>2</sub> into highly porous MOFs via in situ transformation of CO<sub>2</sub> into carbamate linkers.
- Zhang, S.; Lombardo, L.; Tsujimoto, M.; Fan, Z.; Berdichevsky, E. K.; Wei, Y.-S.; Kageyama, K.; Nishiyama, Y.; Horike, S. Synthesizing Interpenetrated Triazinebased Covalent Organic Frameworks from CO<sub>2</sub>. Angew. Chem. Int. Ed. 2023, e202312095.<sup>3</sup> This work demonstrates the synthesis of highly crystalline and stable COFs from CO<sub>2</sub> with proton conduction properties.

## 1. INTRODUCTION

Developing techniques to convert carbon dioxide  $(CO_2)$  into value-added molecules and materials is key to achieving a carbon-neutral society.<sup>4,5</sup> CO<sub>2</sub> is an attractive renewable resource with advantages such as high natural abundance and lower toxicity. The synthetic methods to convert CO<sub>2</sub> into functional materials, such as organic polymers and carbon materials, have been extensively studied.<sup>6,7</sup> On the other hand,

little is known about converting  $CO_2$  into molecular-based porous materials. Molecular-based porous materials are a class of porous solids constructed from molecular organic building units and encompass both molecular-based porous frameworks with extended networks, e.g., metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs), and discrete porous molecules, e.g., metal–organic polyhedra (MOPs) and porous organic cages. We focus on MOFs/COFs among molecularbased porous frameworks in this Account.

MOF/COFs are a class of molecular-based porous frameworks with high structural designability and demonstrate versatile functionality, such as gas storage/separation, heterogeneous catalysts, and ionic/electronic conduction.<sup>8–10</sup> While MOF/COFs attract much attention as functional materials, the synthesis of MOF/COFs using CO<sub>2</sub> as a feedstock remains unexplored. CO<sub>2</sub> hardly serves as a building unit of MOF/COFs by itself, and the chemical transformation of CO<sub>2</sub> into a building unit for MOF/COFs is necessary. The structures of CO<sub>2</sub>derived building units crucially impact the resultant structures and properties of the CO<sub>2</sub>-derived MOF/COFs. We developed key requirements of CO<sub>2</sub>-derived building units in the design for MOF/COFs. In this Account, we will elaborate on the design principle of a CO<sub>2</sub>-derived building unit for MOF/COFs,

3207

Article



Figure 2. Schematic representation of classification of synthetic methods for MOFs from CO<sub>2</sub>.

synthetic protocols, structures, and functionality of  $\rm CO_2$  -derived MOF/COFs.

# 2. DESIGN OF CO<sub>2</sub>-DERIVED BUILDING UNITS TOWARD POROUS SOLIDS

 $CO_2$ , being the most oxidized state of carbon, is often regarded as an inert molecule. Meanwhile, ample studies suggest that CO<sub>2</sub> demonstrates various reactivities with appropriate choice of reactants, catalysts, and reaction conditions.<sup>11</sup> This is because the carbon atom of CO<sub>2</sub> exhibits an affinity for nucleophiles and electron-donating reactants. The chemical transformation of  $CO_2$  into small organic molecules, such as carbon monoxide, organic carbonates, and carboxylic acids, are widely studied.<sup>4,1</sup> To construct porous structures of MOF/COFs, the CO<sub>2</sub>derived molecules need to satisfy the following two requirements: (i) reactivity and (ii) positioning of bridging sites. First, the CO<sub>2</sub>-derived building unit must possess functional groups that exhibit sufficient reactivity to work as bridging sites. CO2derived building units serve as bridging linkers for MOFs and monomers for COFs. CO<sub>2</sub>-derived bridging linkers need to form a coordination bond with metal ions. The oxygen atoms originating from CO<sub>2</sub> typically work as coordination sites due to the localized electrons with affinity toward metal ions. The CO<sub>2</sub>derived monomer needs to form a covalent bond with another monomer. Condensation is a typical reaction to form COF structures, and the oxygen atoms from CO<sub>2</sub> serve as reactive sites.<sup>10</sup> Second, the positioning of bridging sites is essential for determining porous structures, e.g., network topology and pore sizes. Two or more bridging sites are required in the building unit to construct the extended network. Ditopic and tritopic linkers and monomers are suitable for the formation of porous structures according to the conventional design of MOF/ COFs.<sup>12</sup> Meanwhile, incorporating multiple bridging sites, i.e., a reaction with multiple CO<sub>2</sub> molecules, in the targeted positions is challenging because precise chemo- and regioselectivity are required.<sup>13</sup> The requirements of molecular design have rendered the synthesis of MOF/COFs from CO<sub>2</sub> difficult.

We developed the conversion of  $CO_2$  into various building units that satisfy the requirements (Figure 1). Table 1 summarizes the key parameters of synthesis and physical properties of selected  $CO_2$ -derived MOF/COFs, e.g., synthetic methods, gravimetric  $CO_2$  contents, and Brunauer–Emmett– Teller surface areas ( $S_{BET}$ ). In the following sections, the  $CO_2$ -

derived MOF/COFs are referred to by their entry numbers in Table 1. The synthesis of  $CO_2$ -derived MOF/COFs inherently involves two processes: chemical transformation of CO<sub>2</sub> into building units and the formation of extended networks of MOF/ COFs. We categorized synthetic methods of CO<sub>2</sub>-derived MOF/COFs into three types (Figure 2): a one-step synthesis (Type-I); a one-pot synthesis without workup (Type-II); and a multistep synthesis which needs workup (Type-III). The reaction that involves the transformation of CO<sub>2</sub> is regarded as the first step of the entire synthesis procedure. Type-I synthesis is ideal and most challenging, because it requires optimizing the reaction conditions for both processes simultaneously. Therefore, Type-I synthesis occasionally produces amorphous MOFs (Entry 6 and 12). In contrast, Type-III synthesis can produce chemically and thermally robust MOF/COFs (Entry 13 and 16). Carrying out individual  $CO_2$ transformations enables the synthesis of stable CO2-derived molecular building units, although the multistep reactions can be fraught with laborious synthetic hurdles. The appropriate selection of CO<sub>2</sub>-derived molecular building units and associated synthetic methods tailored to the aims, e.g., feasibility of synthesis and stability of CO<sub>2</sub>-derived MOF/COFs, is essential. The precursors for the CO2-derived building units and detailed synthetic conditions are described in the following sections. CO<sub>2</sub> content is defined as a ratio of molecular weight derived from CO<sub>2</sub> divided by the molecular weight of CO<sub>2</sub>derived MOF/COFs. Higher CO<sub>2</sub> content is desired from the viewpoint of atom economy and CO<sub>2</sub> utilization. Meanwhile, it is a challenge to compromise the high CO<sub>2</sub> content and targeted structure and functionality. The  $CO_2$  contents of the MOF/ COFs largely range between 12.6 to 77.0 wt %, and the contents exceeding 20 wt % are generally considered high compared to those of CO<sub>2</sub>-derived organic polymers.<sup>14</sup>

## 3. CO<sub>2</sub>-DERIVED MOFS: SYNTHESIS, STRUCTURE ANALYSIS, AND FUNCTIONALITY

#### 3.1. Formate

Borohydrides ( $BH_4^-$ ), a hydride-based anion, exhibits versatile reactivity toward CO<sub>2</sub> depending on the reaction conditions, e.g., temperatures, pressures, and coexisting metal ions.<sup>15</sup> The reactions between  $BH_4^-$  and CO<sub>2</sub> are classified into (i) hydride transfer and (ii) CO<sub>2</sub> insertion. Hydride transfer from  $BH_4^-$  to CO<sub>2</sub> forms formate (OCHO<sup>-</sup>), whereas stepwise CO<sub>2</sub> insertion



**Figure 3.** Schematic illustration of (A) Type-I synthesis of 1 from  $CO_2$  via hydride transfer from  $BH_4^-$  and (B) Type-II synthesis of 2–5 from  $CO_2$  via the formation of OCHO<sup>-</sup> from  $[BH(OCHO)_3]^-$ .



Figure 4. Schematic illustration of the Type-III synthesis of [Na(DME)][BH(OCHO)<sub>3</sub>] from CO<sub>2</sub>.

into the B-H bond affords formylhydroborate ( $[BH_{4-x}(OCHO)_x]^-$ , x = 1, 2, 3) with B-O bond formation. Previous studies suggest a trend that the electronegativity of coexisting metal ions affects the reactivity of BH<sub>4</sub><sup>-</sup> toward CO<sub>2</sub>.<sup>16</sup> The electronegative/intermediate metal ions lead to hydride transfer, whereas the electropositive metal ions lead to CO<sub>2</sub> insertion, e.g., Zn<sup>2+</sup>, Ni<sup>2+</sup> vs Na<sup>+</sup>, K<sup>+</sup>. This is because the polarization of BH<sub>4</sub><sup>-</sup> induced by electrostatic interaction with metal ions influences the reactivity of BH<sub>4</sub><sup>-.17</sup> In 2019, we reported the synthesis of MOFs consisting of OCHO<sup>-</sup> and  $[BH(OCHO)_3]^-$ , respectively, from CO<sub>2</sub> based on the appropriate choice of counter metal ions and reaction conditions as the first examples of CO<sub>2</sub>-derived MOFs.

OCHO<sup>-</sup> with a small steric hindrance displays various coordination modes with metal ions, e.g., Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, and Zr<sup>4+</sup>, to construct porous MOFs showing gas capture and separation.<sup>18-20</sup> The synthetic methods of an OCHO<sup>-</sup>-based MOF typically employ either formic acid or in situ formation of an OCHO<sup>-</sup> from hydrolysis of DMF as a solvent. Despite extensive studies on the conversion of  $CO_2$  into formic acid, the synthesis of OCHO<sup>-</sup>-based MOFs from CO<sub>2</sub> remained unexplored. We focused on intermediate  $Zn^{2+}$  to convert  $CO_2$ into OCHO<sup>-</sup> based on the reactivity trend of BH<sub>4</sub><sup>-</sup> toward CO<sub>2</sub>. In 2019, we reported the Type-I synthesis of porous  $[Zn_3(OCHO)_6]$  from the reaction between CO<sub>2</sub> and (PPh<sub>4</sub>)- $[Zn_2(BH_4)_5]$  at 25 °C (Entry 1, Figure 3A).<sup>1</sup> CO<sub>2</sub> at atmospheric pressure into a solution of  $(PPh_4)[Zn_2(BH_4)_5]$ produces a crystalline powder of 1 with a yield of 58.4%. The  $S_{\text{BET}}$  of 1 is comparable to that of  $[\text{Zn}_3(\text{OCHO})_6]$  obtained from HCOOH (225 vs 243 m<sup>2</sup> g<sup>-1</sup>). In contrast to the porosity, 1 displays rod-shaped particles smaller than those obtained from HCOOH (4–20 vs 15–70  $\mu$ m). The high reactivity of BH<sub>4</sub><sup>-</sup>

toward CO<sub>2</sub> accelerates the reaction kinetics, resulting in rapid crystal growth. To expand the availability of metal ions for OCHO<sup>-</sup>-based MOFs from CO<sub>2</sub>, we carried out the Type-II synthesis of  $[M_3(OCHO)_6]$  (Entry 2, 3, 4, and 5;  $M = Mg^{2+}$ , Mn<sup>2+</sup>, Fe<sup>2+</sup>, and Co<sup>2+</sup>, Figure 3B) using tetraethylammonium borohydride (TEAB) as a  $BH_4^-$  source. (NEt<sub>4</sub>)[BH(OCHO)<sub>3</sub>] was first prepared from the reaction between TEAB and CO<sub>2</sub> pressurized at 2.0 MPa at 25 °C. The subsequent solvothermal reaction with  $MCl_2$  converts  $(NEt_4)[BH(OCHO)_3]$  into OCHO<sup>-</sup> and affords the corresponding OCHO<sup>-</sup>-based MOFs. The S<sub>BET</sub> values of the OCHO<sup>-</sup>-based MOFs obtained from  $CO_2$  are comparable to those obtained from HCOOH (2: 504, 4: 346, and 5:  $324 \text{ m}^2 \text{ g}^{-1}$ ). The Type-II synthesis method using TEAB is also applicable to the diluted  $CO_2$  in the air. Bubbling of the dried air containing 400 ppm of CO<sub>2</sub> into a solution of TEAB, instead of the pressurized CO2, and subsequent solvothermal reaction affords crystalline  $[Mn_3(OCHO)_6]$  (Entry 3). The selective reactivity of BH<sub>4</sub><sup>-</sup> toward CO<sub>2</sub> enables the synthesis of OCHO<sup>-</sup>-based MOFs from the diluted CO<sub>2</sub>. OCHO<sup>-</sup>-based MOFs exhibit high CO<sub>2</sub> contents ranging from 55.6 to 77.0 wt % due to the high CO<sub>2</sub> content of OCHO<sup>-</sup>. In contrast, the  $S_{\rm BET}$  values are relatively lower, ranging from 225 to 504 m<sup>2</sup> g<sup>-1</sup> (Table 1) because the shorter bridging distance by OCHO<sup>-</sup> results in smaller pore sizes. OCHO<sup>-</sup>-based MOFs are expected to be more suitable for selective gas adsorption due to their well-defined smaller pore sizes.<sup>18</sup>

#### 3.2. Formylhydroborate

In contrast to that of OCHO<sup>-</sup>, the limited number of coordination complexes consisting of  $[BH_{4-x}(OCHO)_x]^-$  are reported regardless of porosity. In 2015, Cummins et al.

Article



Figure 5. (A) Schematic illustration of the Type-I synthesis of 6 from  $CO_2$ . (B)  $N_2$  adsorption isotherms and (C) pore size distributions of 6 synthesized at 2.0, 3.0, and 4.0 MPa, respectively.



**Figure 6.** (A) Schematic illustration of the Type-I synthesis of  $[Cu_3(CO_3)_2(bpac)_3](ClO_4)_2$  from CO<sub>2</sub>.  $ClO_4^-$  is omitted for clarity. (B) Hexagonal  $[Cu_3(CO_3)_2]^{2+}$  lattice. (C) Pyridyl linkers of  $CO_3^{2-}$ -based MOFs synthesized from CO<sub>2</sub>.

reported the Type-III synthesis of Na(DME)[BH(OCHO)<sub>3</sub>] (DME = 1,2-dimethoxyethane) through the crystallization of Na[BH(OCHO)<sub>3</sub>] in DME at -40 °C (Figure 4).<sup>21</sup> Na[BH-(OCHO)<sub>3</sub>] was formed by the reaction between pressurized CO<sub>2</sub> and NaBH<sub>4</sub>. Single-crystal X-ray diffraction (SC-XRD) indicated that Na<sup>+</sup> exhibits a pseudo-octahedral geometry and a three-dimensional (3D) dense structure is formed by bridging [BH(OCHO)<sub>3</sub>]<sup>-</sup>. The porosity of Na(DME)[BH(OCHO)<sub>3</sub>] is not reported. In 2016, Filinchuk et al. reported the Type-I mechanochemical synthesis between solid CO<sub>2</sub>, i.e., dry ice, and KBH<sub>4</sub> provides K[HB(OCHO)<sub>3</sub>].<sup>22</sup> The crystal structure of K[BH(OCHO)<sub>3</sub>] was determined by Rietveld refinement as a 3D dense structure without porosity. The formation of a porous structure consisting of [BH(OCHO)<sub>3</sub>]<sup>-</sup> remains a challenge due to the conformational flexibility of [BH(OCHO)<sub>3</sub>]<sup>-</sup>.

We focused on  $Mg(BH_4)_2$  as a precursor to construct porous  $[BH(OCHO)_3]^-$ -based MOFs. The electropositive  $Mg^{2+}$  was selected to prioritize the formation of  $[BH(OCHO)_3]^-$  over that of OCHO<sup>-</sup> according to the trend of reactivity. The reactions between  $Mg(BH_4)_2$  and  $CO_2$  pressurized at 2.0, 3.0,

and 4.0 MPa at 25 °C afford amorphous solids (Entry 6, Figure 5A). The pair distribution function (PDF) profile of 6synthesized at 3.0 MPa displays a peak at 11.1 Å which is assigned as a correlation of Mg-Mg bridged by [BH- $(OCHO)_3$ ]<sup>-</sup>. The permanent porosity of 6 synthesized at each CO<sub>2</sub> pressure was confirmed by N<sub>2</sub> adsorption at 77 K (Figure 5B). The key to the successful formation of the porous structure in **6** is attributed to that  $BO_3^{3-}$  and  $[B(OMe)_3]$  serve as a rigid tritopic linker in addition to  $[BH(OCHO)_3]^-$  with conformational flexibility to prevent the formation of a dense structure. The  $S_{\text{BET}}$  of 6 increases as the CO<sub>2</sub> pressure in the synthesis increases (179, 356, and  $383 \text{ m}^2 \text{ g}^{-1}$  for 2.0, 3.0, and 4.0 MPa, respectively). The pore size distribution of 6 was obtained by the nonlocal density functional theory (NLDFT) method (Figure 5C). The pore size distribution indicates that the higher pressure of CO<sub>2</sub> in the synthesis results in the formation of a mesopore at 2.7 nm, while the micropore at 0.7 nm shows no significant difference. The results indicate that a higher pressure of CO<sub>2</sub> kinetically induces the formation of mesoporous structures. The high  $CO_2$  content of 68.5 wt % for 6 is due to



**Figure 7.** (A) Schematic illustration of the Type-I synthesis of 7 from  $CO_2$ . (B) Molecular structures of PDC type linkers used in 8 to 10. (C) SEM image of compound 8. (D) Potential curve as a function of Zn–O distance. Inset: the model structures calculated by DFT at the Zn–O distances of 1.96 and 4.43 Å, respectively.

the high  $CO_2$  content of  $[BH(OCHO)_3]^-$  that consists of three molecules of  $CO_2$  per  $BH_4^-$ .

# 3.3. Carbonate

Carbonate  $(CO_3^{2-})$  is a ubiquitous anion that exists on Earth as metal carbonates, such as calcite  $(CaCO_3)$ . From the viewpoint of coordination chemistry, CO<sub>3</sub><sup>2-</sup> displays various coordination numbers and geometries due to its low steric hindrance.<sup>23</sup> Meanwhile, CO<sub>3</sub><sup>2-</sup>-based MOFs are limited, regardless of whether CO<sub>2</sub> is used as a feedstock. This limitation arises because the shorter linker length is not suitable for constructing porous structures. Previous studies have employed a coligand to construct CO<sub>3</sub><sup>2-</sup>-based MOFs. A series of CO<sub>3</sub><sup>2-</sup>-based MOFs consisting of Cu<sup>2+</sup> and a pyridyl ligand are reported through Type-I synthesis from  $CO_2$  in the air. For instance,  $NH_3$  aqueous solution containing Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and 4,4'-bipyridylacetylene (bpac) reacts with  $CO_2$  in the air at 25  $^{\circ}C$  to afford  $[Cu_3(CO_3)_2(bpac)_3](ClO_4)_2$  (Figure 6A).<sup>24</sup>  $[Cu_3(CO_3)_2(bpac)_3](ClO_4)_2$  exhibits a 3D structure where the 2D Kagome-type  $[Cu_3(CO_3)_2]^{2+}$  lattice is bridged by bapc coordinated in the axial position of Cu<sup>2+</sup> (Figure 6B). Most  $CO_3^{2-}$ -based MOFs display Kagome-type  $[Cu_3(CO_3)_2]^{2+}$ , and the packing structures vary depending on the coordination modes of pyridyl linkers (Figure 6C). Nonbridging pyridyl linkers, e.g., 4-aminopyridine (4-apy)<sup>25</sup> and 2,4'-bipyridyl (2,4'bipy),<sup>26</sup> afford 2D packing structure, while bridging 1,2-di(4pyridyl)ethane (dpe)<sup>27</sup> affords 3D packing structure. All of the studies focus on the magnetic interaction derived from the Kagome-type  $[Cu_3(CO_3)_2]^{2+}$  lattice. The reported porosity is limited to the H<sub>2</sub>O adsorption of  $[Cu_3(CO_3)_2(bpac)_3](ClO_4)_2$ at 298 K ( $0.9 \text{ mol mol}^{-1}$ ).<sup>24</sup> This is consistent with the fact that crystallographic void space is not observed because ClO<sub>4</sub>occupies it as a counteranion. Nevertheless, the direct conversion of  $CO_2$  in air into MOFs is of interest. Functionalities that do not require porosity, e.g., ionic and electronic conduction, are promising in addition to the magnetism studied in the reports.

#### 3.4. Carbamate

Carbamate  $(R_2NCO_2^{-})$  is formed by the nucleophilic reaction of amines  $(R_2NH)$  with CO<sub>2</sub> at ambient temperatures and pressures.<sup>28</sup> Carbamates are typically thermodynamically labile and readily release CO<sub>2</sub> upon heating. The inherent thermal instability has hampered the utilization of carbamates as building units for materials. We focused on piperazine dicarbamate (PDC) as a bridging linker to construct carbamate-based MOFs. Piperazine ( $H_2PZ$ ), a cyclic secondary amine, reacts with CO<sub>2</sub> at 25 °C to afford PDC salts.<sup>29</sup> In 2021, we reported the Type-I synthesis of cubic carbamate-based MOFs from CO<sub>2</sub> (Entry 7, Figure 7A).<sup>2</sup> 7 is a structural analogue of MOF-5,  $[Zn_4O (BDC)_3$ ] (H<sub>2</sub>BDC = benzene-1,4-dicarboxylic acid).<sup>30</sup> The key design of PDC is structural similarity to BDC, with comparable molecular lengths of 5.7 vs 5.5 Å. Bubbling CO<sub>2</sub> into a solution of  $Zn(OAc)_2 \cdot 2H_2O$  (OAc<sup>-</sup> = acetate),  $H_2PZ$ , and 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) quickly forms crystalline powder of 7. The synthesis of 7 using the diluted  $CO_2$  in air (400 ppm) is also feasible. The structural analogues of 7 are obtained using methyl piperazine derivatives (Entry 8 to 10, Figure 7B). The crystal structures of 7 to 10 were confirmed by Rietveld refinement using synchrotron PXRD. The presence of methyl groups in the linkers affects the crystallinity and porosity of the carbamate-based MOFs. The full width at half-maximum study indicates 8 exhibits the highest crystallinity among the structural analogues. The SEM image of 8 displays well-shaped, cube-like particles with a particle size of 200-500 nm, which aligns well with the cubic crystal system of 8 (Figure 7C). The  $S_{\text{BET}}$  values were calculated as 1525, 2366, 1943, and 1270 m<sup>2</sup>  $g^{-1}$  for 7 to 10, respectively. The carbamate-based MOFs with moderately high CO<sub>2</sub> contents from 30.1 to 33.3 wt % exhibit higher S<sub>BET</sub> compared to other CO<sub>2</sub>-derived MOF/COFs (Table 1). The formation of a highly porous structure is attributed to the well-defined coordination direction and the suitable bridging distance of PDC<sup>2-</sup>. While carbamates exhibit thermal instability to release  $CO_2$  upon heating, the carbamate-



**Figure 8.** (A) Schematic illustration of the Type-III synthesis of **13** from CO<sub>2</sub>. (B) Crystal structure of compound **14**. (C) HR-TEM image and zoomin view overlaid with a structure model (inset) and (D) SAED pattern of **13** along the [110]. Adapted from ref **36**. Copyright 2024 American Chemical Society.

based MOFs preserve the crystalline porous structure at 80 °C under a vacuum. The stabilization of carbamate was studied by density functional theory (DFT) calculations with a simplified two-cluster model structure (Figure 7D). The total energy of the model structure was calculated by varying the distance between  $Zn^{2+}$  and oxygen atoms of PDC in the range of 1.51 to 4.43 Å. The potential energy decreases and reaches a minimum of -583 kJ mol<sup>-1</sup> at the Zn–O distance of 1.96 Å, which matches with the crystallographically observed Zn–O bond. The results indicate that stabilization by the coordination interaction between  $Zn^{2+}$  and PDC enables one to employ thermodynamically unstable carbamates as a stable building unit of MOFs.

In 2024, Peng et al. reported the Type-I synthesis of crystalline and amorphous carbamate-based MOFs consisting of Cu<sup>2+</sup> and PDC from CO<sub>2</sub> at 25 °C (Entry 11 and 12).<sup>31</sup> The crystallinity of the carbamate-based MOFs, Cu<sub>x</sub>PDC, was tuned by the ratio between metal ions and PDC; crystalline 11 at x =0.33 to 0.75, and amorphous 12 at x = 1 to 1.5. The PXRD pattern of crystalline 11 is reported to be similar to that of CuBDC. The  $S_{\text{BET}}$  values of 11 and 12 are comparable (88 and 56 m<sup>2</sup> g<sup>-1</sup>). The catalytic activity of **12** for the CO<sub>2</sub> cycloaddition is superior to that of 11 (92.2% vs 81.5%, styrene oxide with TBAB as a cocatalyst, CO<sub>2</sub> at 0.1 MPa, 70 °C, 8 h). The higher performance of amorphous 12 is due to the defective metal site in the amorphous structure. In the Type-I synthesis, the direct conversion of  $CO_2$  is likely to cause amorphization due to the difficulty in controlling the crystallization kinetics, which is consistent with the results of 6. The results demonstrate that the defective structure of the CO2-derived MOFs is leveraged for catalytic activity.

#### 3.5. Carboxylates

Di- and tricarboxylates are most commonly used as a bridging linker, and various types of MOFs are reported to date:  $H_2BDC$ for MOF-5<sup>30</sup> and UiO-66,  $[Zr_6O_4(OH)_4(BDC)_6]$ ,<sup>32</sup> and 1,3,5benzene tricarboxylic acid  $(H_3BTC)$  for HKUST-1,  $[Cu_3(BTC)_2]$ .<sup>33</sup> Meanwhile, the synthesis of carboxylatebased MOFs from CO<sub>2</sub> has not been explored because facile alternative synthesis methods of carboxylates without using CO<sub>2</sub> have been already established. For instance,  $H_2BDC$  is industrially produced by oxidation of *p*-xylene with O<sub>2</sub> in the air.<sup>34</sup> Although the synthesis of  $H_2BDC$  from CO<sub>2</sub> is possible using a conventional Grignard reagent, it requires rigorously moisture-free conditions and multiple steps.<sup>35</sup> This synthetic difficulty makes the synthesis of carboxylate-based MOFs from CO2 impractical. In 2024, Liu et al. reported the Type-III synthesis of carboxylate-based MOFs from CO<sub>2</sub> by the sequential desilylation-carboxylation (Entry 13 and 14, Figure 8A, B).<sup>36</sup> Alkynylsilanes, 1,4-di[(trimethylsilyl)ethynyl]phenyl (DTMSEP) for **13** and 1,4-di[(trimethylsilyl)ethynyl]diphenyl (DTMSEDP) for 14, were selected as a precursor with higher reactivity toward CO<sub>2</sub> in the carboxylation reaction. CsF promotes cleavage of the C-Si bond of alkynylsilanes as a base, and  $CO_2$  is subsequently inserted into the terminal alkynes to form dipropiolic acids: H<sub>2</sub>PDP for 13 and H<sub>2</sub>BPDP for 14. The subsequent solvothermal reactions with ZrOCl<sub>2</sub>·8H<sub>2</sub>O afford cubic UiO-66 type MOFs. The high-resolution transmission electron microscopy (HR-TEM) image indicates regular pore arrangement in good agreement with the simulated structure of 13 along [110] (Figure 8C). The corresponding selected-area electron diffraction (SAED) pattern of 13 along the [110] shows diffraction spots with  $d_{-111} = 1.65$  nm and  $d_{020} =$ 1.43 nm, which corresponds to the lattice spacing in the HR-TEM image (Figure 8D). The gravimetric  $CO_2$  contents are 24 and 20 wt % for 13 and 14, respectively. The S<sub>BET</sub> of 13 and 14 are 2702 and 3688 m<sup>2</sup> g<sup>-1</sup>, which is the highest  $S_{\text{BET}}$  among the reported CO<sub>2</sub>-derived MOF/COFs (Table 1). To impart catalytic activity, Ag<sup>+</sup> ion was incorporated into the carboxylate-based MOFs driven by the  $\pi$ -coordinating affinity of alkyne groups of the linkers toward metal ions. Ag<sup>+</sup>-embedded 13 and 14 exhibit high catalytic activity on the conversion of CO<sub>2</sub> and propargylic alcohols into cyclic carbonates, achieving 86-99% yield under ambient conditions (DBU as a cocatalyst, CO<sub>2</sub> at 0.1 MPa, 25 °C, 6 h). The results demonstrate that alkynylsilane precursors enable the conversion of  $CO_2$  into robust and highly porous carboxylate-based MOFs.

# CO<sub>2</sub>-DERIVED COFS: SYNTHESIS, STRUCTURE ANALYSIS, AND FUNCTIONALITY

While the synthetic methods of organic polymers from  $CO_2$  have been extensively studied, the synthesis of COFs from  $CO_2$  remains unexplored due to the lack of design of suitable  $CO_2$ -derived monomers to construct the porous structure. The typical monomers for  $CO_2$ -derived organic polymers are



**Figure 9.** (A) Schematic illustration of Type-III synthesis of 15 from  $CO_2$  and postsynthetic oxidation of 15 to provide 16. (B) SAED pattern and (C) HR-TEM image of 15. (D) Schematic illustration of the Type-I synthesis of alkynoate-based organic polymers from  $CO_2$  as an example of potential building for  $CO_2$ -derived COFs.

aliphatic, e.g., alkyl carbonates.<sup>6</sup> The high flexibility of the aliphatic building unit renders the formation of crystalline and porous structures difficult.37 We focused on formamide (N-CHO) as a CO<sub>2</sub>-derived monomer and melamine to construct a stable triazine unit. In 2023, we reported the Type-III synthesis of triazine-based COFs from CO<sub>2</sub> (Entry 15, Figure 9A).<sup>3</sup>  $Na[BH_{4-x}(OCHO)_x]$  was obtained from  $NaBH_4$  and  $CO_2$  at 25 °C, and subsequently reacted with H<sub>2</sub>PZ under the solvothermal condition to afford 1,4-piperazine dicarboxaldehyde (PZ- $(CHO)_2$ ). The synthesis of highly crystalline triazine-based COFs from N-CHO has been a challenge due to the lower reactivity of N-CHO than the corresponding aldehydes (C-CHO).<sup>38</sup> The triazine-based COF was synthesized from  $PZ(CHO)_2$  and melamine in mixed solvents at 165 °C. The key to the successful synthesis of crystalline COF from N-CHO was the appropriate choice of the ratio of mixed solvents to control the polymerization kinetics. The stacking structure of 15 was identified as the 3-fold interpenetrated structure with hcb topology by Pawley refinement. The SAED pattern and HR-TEM image of 15 exhibit the triangular prism channels corresponding to the [101] facet and the layered packing corresponding to the [201] facet, confirming the formation of a regular hexagonal lattice (Figure 9B, C). The  $S_{\text{BET}}$  of 15 was calculated as 945 m<sup>2</sup> g<sup>-1</sup> from the  $N_2$  adsorption isotherm at 77 K. The high chemical and thermal stability of 15 was confirmed by treatment in boiling water, acidic, and basic conditions. The proton  $(H^+)$  conductivity of 15 and 16 oxidized by postsynthesis was studied. The postsynthetic treatment using potassium peroxymonosulfate, a strong oxidant, converts the amidine group to an amide group (N-CO-N) in the COF (Entry 16, Figure 9A). The electrochemical impedance spectroscopy confirmed the H<sup>+</sup> conductivity of 15 and 16 are  $3.1 \times 10^{-4}$ and  $2.5 \times 10^{-2}$  S cm<sup>-1</sup> under the relative humidity of 95% at 85 °C. The enhanced H<sup>+</sup> conductivity of 16 is attributed to the hydrogen-bonded network induced by the larger amount of adsorbed H<sub>2</sub>O.<sup>39</sup> While the CO<sub>2</sub> contents of the COFs are relatively lower (10.8 and 12.6 wt %) because CO2-derived oxygen atoms are removed upon condensation reaction, the high stability is advantageous over the CO<sub>2</sub>-derived MOFs. In

addition to the carboxaldehyde system, the knowledge of design for  $CO_2$ -derived organic polymers suggests that several  $CO_2$ derived building units potentially serve as monomers of the COFs. For instance, Tang et al. reported the Type-I synthesis of organic polymers from diynes (HC=C-R<sup>1</sup>-C=CH), alkyl dihalides (X-R<sup>2</sup>-X), and CO<sub>2</sub> (Figure 9D).<sup>40</sup> The incorporation of rigid multitopic components, such as 1,3,5triethynylbenzene, is expected to construct porous COF networks. Although the optimization on the crystallization kinetics is a challenge, the facile Type-I synthesis is attractive for CO<sub>2</sub>-deirved COF synthesis.

In addition to COFs, hydrogen-bonded organic frameworks (HOFs) are also an essential class of molecular-based porous frameworks consisting of organic building units. There are several reports of the Type-I synthesis of nonporous HOFs synthesized from CO<sub>2</sub> via hydrogen bonding between carbamate and protonated amine;<sup>41</sup> CO<sub>3</sub><sup>2-</sup> or bicarbonate and guanidium.<sup>42</sup> Rigid and multitopic building units would enable to construct CO<sub>2</sub>-derived HOFs with porosity, e.g., CO<sub>2</sub>-derived aromatic carboxylates.

#### 5. PERSPECTIVE

We summarize recent developments in the conversion of CO<sub>2</sub> into MOF/COFs with an emphasis on the design of CO<sub>2</sub>-derived building units. The precise design of CO<sub>2</sub>-derived building units, e.g., the reactivity and positioning of bridging sites, enables the synthesis of CO<sub>2</sub>-derived MOF/COFs with various structures. The results provide a synthetic guideline for CO<sub>2</sub>-derived molecular-based porous frameworks. On the other hand, several challenges must be addressed for future advancement in this field.

First, further exploration of the structural diversity of the  $CO_2$ derived MOF/COFs is necessary. Structural analogues of the reported  $CO_2$ -derived MOF/COFs can be obtained by alternating the constituting metal ions or monomers; however, expanding structural libraries of  $CO_2$ -derived building units remains a fundamental bottleneck and an essential synthetic challenge. One future approach is to utilize external stimuli, e.g., light, electricity, and pressure, in the synthesis of  $CO_2$ -derived



Figure 10. Proposed future ideas. Schematic representation of (A) a  $CO_2$ -derived MOF as a carrier for  $CO_2$  capture and (B) transformation of  $CO_2$  using  $CO_2$ -derived MOFs as a predesigned precursor.

MOF/COFs. Ample studies demonstrate that the synthesis using external stimuli can convert CO<sub>2</sub> into various molecules under ambient conditions without the need for stoichiometric amounts of reactive reagents. Examples include the photo-induced synthesis of carboxylates,<sup>43</sup> electrochemical synthesis of oxalate,<sup>44</sup> and mechanochemical synthesis of carbamates.<sup>45</sup> In particular, the Type-I electrochemical conversion of CO<sub>2</sub> into MOF is an interesting approach by integrating electrochemical CO<sub>2</sub> transformation and electrochemical MOF synthesis which have been separately studied.<sup>46</sup> The well-developed chemistry of transformation of CO<sub>2</sub> using external stimuli would provide a clue for the design of CO<sub>2</sub>-derived molecular-based porous frameworks.

Second, exploring the unique functionalities of the CO<sub>2</sub>derived MOF/COFs is essential for advancing this field. Currently, the functionalities being studied, e.g., porosity, catalysis, and H<sup>+</sup> conduction, are also achievable by conventional MOF/COFs. One future challenge is to employ CO<sub>2</sub>derived MOF/COFs as carriers for the capture of  $CO_2$  (Figure 10A). The formation and degradation of CO<sub>2</sub>-derived materials, e.g., metal carbonates and organic carbamates, serve as processes for CO<sub>2</sub> capture and release.<sup>28,47</sup> The high structural designability of MOF/COFs offers advantages in controlling CO<sub>2</sub> capture and release properties, e.g., reaction temperatures and kinetics, compared to conventional materials. Understanding the mechanisms behind the formation and degradation of CO<sub>2</sub>-derived MOF/COFs could provide a tunable platform for CO<sub>2</sub> capture. In addition to CO<sub>2</sub> capture, a recent study demonstrates CO<sub>2</sub>-mediated capture of metal ions through the formation of CO<sub>2</sub>-derived discrete carbamate complexes.<sup>48</sup> CO2-derived MOF/COFs readily precipitate upon reacting with CO<sub>2</sub> due to their extended network, which is attractive for the capture of metal ions and organic molecules through phase separation. Another future challenge is to utilize CO2-derived MOF/COFs as predesigned precursors of CO<sub>2</sub> for the further transformation of  $CO_2$  (Figure 10B). The  $CO_2$  molecules in

CO<sub>2</sub>-derived MOF/COFs can be regarded as being periodically immobilized with metal ions and molecules. The chemical environment of CO<sub>2</sub> adsorbed on the metal surface affects the reaction pathway and selectivity.<sup>49</sup> By predesigning the chemical environment of CO<sub>2</sub> in MOF/COFs, it may be possible to achieve unprecedented CO<sub>2</sub> transformations, e.g., high chemoand regioselectivity and high reactivity under ambient conditions. Although some CO<sub>2</sub>-derived MOFs exhibit catalytic activity for CO<sub>2</sub> transformation, the CO<sub>2</sub> molecules fixed in the MOFs do not participate in the catalytic reactions (Entry 11 to 14). If we can employ the  $CO_2$  predesigned in the MOF/COFs for catalytic reactions, it would differentiate them from other catalysts for CO<sub>2</sub> transformation. It is crucial to consider CO<sub>2</sub>derived MOF/COFs not only as an end-product but also as a designable carrier and precursor. While developing the design principle to synthesize robust MOF/COFs from CO<sub>2</sub> is essential at this early stage, it will inevitably involve competition with numerous conventional MOF/COFs. Therefore, exploring functionalities that leverage the advantages of using CO<sub>2</sub> as a feedstock is crucial. We hope that the findings described in this Account will contribute to advancements in the field of CO<sub>2</sub>derived molecular-based porous frameworks.

# AUTHOR INFORMATION

#### **Corresponding Authors**

- Kentaro Kadota Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan; Email: kadota.kentaro.7a@kyoto-u.ac.jp
- Satoshi Horike Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan; Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan; Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong

21210, Thailand; orcid.org/0000-0001-8530-6364; Email: horike.satoshi.3r@kyoto-u.ac.jp

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.accounts.4c00519

#### **Author Contributions**

The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

#### **Biographies**

Kentaro Kadota received his Ph.D. in chemistry from Kyoto University in 2020, followed by a postdoctoral fellowship at the University of Oregon from 2020 to 2022. He returned to Kyoto in 2022 as an Assistant Professor at Kyoto University. His research interest focuses on the design and synthesis of molecular-based frameworks for  $CO_2$ related applications.

**Satoshi Horike** received his Ph.D. in chemistry from Kyoto University in 2007, followed by a postdoctoral fellowship at the University of California, Berkeley, from 2007 to 2009. He returned to Kyoto in 2009 as an Assistant Professor and has been an Associate Professor/PI at Kyoto University from 2017 to 2023. He is currently a Professor at the Graduate School of Science, Kyoto University, and the Vidyasirimedhi Institute of Science and Technology, Thailand. His research interest is the synthesis of glass and liquid states of molecular framework materials.

## ACKNOWLEDGMENTS

This work was supported by the Japan Society of the Promotion of Science (JSPS) for a Grant-in-Aid for Early-Career Scientists (JP24K17696), Scientific Research (B) (21H01950), Transformative Research Areas (A) "Supraceramics" (JP22H05147) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and research grant funded by Amano Institute of Technology.

# REFERENCES

(1) Kadota, K.; Duong, N. T.; Nishiyama, Y.; Sivaniah, E.; Horike, S. Synthesis of porous coordination polymers using carbon dioxide as a direct source. *Chem. Commun.* **2019**, *55*, 9283–9286.

(2) Kadota, K.; Hong, Y. L.; Nishiyama, Y.; Sivaniah, E.; Packwood, D.; Horike, S. One-Pot, Room-Temperature Conversion of CO<sub>2</sub> into Porous Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2021**, *143*, 16750–16757.

(3) Zhang, S.; Lombardo, L.; Tsujimoto, M.; Fan, Z.; Berdichevsky, E. K.; Wei, Y.-S.; Kageyama, K.; Nishiyama, Y.; Horike, S. Synthesizing Interpenetrated Triazine-based Covalent Organic Frameworks from CO<sub>2</sub>. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202312095.

(4) Artz, J.; Muller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **2018**, *118*, 434–504.

(5) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the valorization of exhaust carbon: from  $CO_2$  to chemicals, materials, and fuels. technological use of  $CO_2$ . *Chem. Rev.* **2014**, *114*, 1709–1742.

(6) Grignard, B.; Gennen, S.; Jerome, C.; Kleij, A. W.; Detrembleur, C. Advances in the use of  $CO_2$  as a renewable feedstock for the synthesis of polymers. *Chem. Soc. Rev.* **2019**, *48*, 4466–4514.

(7) Cheng, X.; Wu, M.; Li, J.; Wang, W.; Mitsuzaki, N.; Chen, Z. Conversion of carbon dioxide into solid carbon materials - a mini review. *Catal. Sci. Technol.* **2023**, *13*, 3891–3900.

(8) Horike, S.; Kitagawa, S. The development of molecule-based porous material families and their future prospects. *Nat. Mater.* **2022**, *21*, 983–985.

(9) Diercks, C. S.; Kalmutzki, M. J.; Diercks, N. J.; Yaghi, O. M. Conceptual Advances from Werner Complexes to Metal-Organic Frameworks. *ACS Cent. Sci.* **2018**, *4*, 1457–1464.

(10) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **2020**, *120*, 8814–8933.

(11) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933.

(12) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. *Nature* **2003**, *423*, 705–714.

(13) Tortajada, A.; Ninokata, R.; Martin, R. Ni-Catalyzed Site-Selective Dicarboxylation of 1,3-Dienes with CO<sub>2</sub>. J. Am. Chem. Soc. **2018**, 140, 2050–2053.

(14) Rapagnani, R. M.; Dunscomb, R. J.; Fresh, A. A.; Tonks, I. A. Tunable and recyclable polyesters from  $CO_2$  and butadiene. *Nat. Chem.* **2022**, *14*, 877–883.

(15) Lombardo, L.; Yang, H.; Horike, S.; Züttel, A. Complex hydrides for CO<sub>2</sub> reduction. *MRS Bull.* **2022**, *47*, 424–431.

(16) Kadota, K.; Sivaniah, E.; Horike, S. Reactivity of borohydride incorporated in coordination polymers toward carbon dioxide. *Chem. Commun.* **2020**, *56*, 5111–5114.

(17) Łodziana, Z.; Błoński, P.; Yan, Y.; Rentsch, D.; Remhof, A. NMR Chemical Shifts of <sup>11</sup>B in Metal Borohydrides from First-Principle Calculations. *J. Phys. Chem. C* **2014**, *118*, 6594–6603.

(18) Evans, H. A.; Mullangi, D.; Deng, Z.; Wang, Y.; Peh, S. B.; Wei, F.; Wang, J.; Brown, C. M.; Zhao, D.; Canepa, P.; et al. Aluminum formate,  $Al(HCOO)_3$ : An earth-abundant, scalable, and highly selective material for  $CO_2$  capture. *Sci. Adv.* **2022**, *8*, No. eade1473.

(19) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. Microporous Manganese Formate: A Simple Metal-Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties. J. Am. Chem. Soc. **2004**, 126, 32–33.

(20) Choi, J. I.; Chun, H.; Lah, M. S. Zirconium-Formate Macrocycles and Supercage: Molecular Packing versus MOF-like Network for Water Vapor Sorption. *J. Am. Chem. Soc.* **2018**, *140*, 10915–10920.

(21) Knopf, I.; Cummins, C. C. Revisiting  $CO_2$  Reduction with NaBH<sub>4</sub> under Aprotic Conditions: Synthesis and Characterization of Sodium Triformatoborohydride. *Organometallics* **2015**, *34*, 1601–1603.

(22) Picasso, C. V.; Safin, D. A.; Dovgaliuk, I.; Devred, F.; Debecker, D.; Li, H.-W.; Proost, J.; Filinchuk, Y. Reduction of CO<sub>2</sub> with KBH<sub>4</sub> in solvent-free conditions. *Int. J. Hydrog. Energy* 2016, 41, 14377–14386.
(23) Sołtys-Brzostek, K.; Terlecki, M.; Sokołowski, K.; Lewiński, J. Chemical fixation and conversion of CO<sub>2</sub> into cyclic and cage-type metal carbonates. *Coord. Chem. Rev.* 2017, 334, 199–231.

(24) Keene, T. D.; Murphy, M. J.; Price, J. R.; Sciortino, N. F.; Southon, P. D.; Kepert, C. J. Multifunctional MOFs through  $CO_2$  fixation: a metamagnetic kagome lattice with uniaxial zero thermal expansion and reversible guest sorption. *Dalton Trans.* **2014**, *43*, 14766–14771.

(25) Majumder, A.; Choudhury, C. R.; Mitra, S.; Rosair, G. M.; El Fallah, M. S.; Ribas, J. Isolation of a new two-dimensional honeycomb carbonato-bridged copper(II) complex exhibiting long-range ferro-magnetic ordering. *Chem. Commun.* **2005**, 2158–2160.

(26) Mulrooney, D. Z. T.; Clements, J. E.; Ericsson, D. J.; Price, J. R.; Kühne, I. A.; Coles, S. J.; Kepert, C. J.; Keene, T. D. Phase Control of Ferromagnetic Copper(II) Carbonate Coordination Polymers through Reagent Concentration. *Eur. J. Inorg. Chem.* **2018**, *2018*, 5223–5228.

(27) Kanoo, P.; Madhu, C.; Mostafa, G.; Maji, T. K.; Sundaresan, A.; Pati, S. K.; Rao, C. N. A planar  $Cu^{2+}$  (S = 1/2) kagome network pillared by 1,2-bis(4-pyridyl) ethane with interesting magnetic properties. *Dalton Trans.* **2009**, 5062–5064.

(28) Heldebrant, D. J.; Koech, P. K.; Glezakou, V. A.; Rousseau, R.; Malhotra, D.; Cantu, D. C. Water-Lean Solvents for Post-Combustion CO<sub>2</sub> Capture: Fundamentals, Uncertainties, Opportunities, and Outlook. *Chem. Rev.* 2017, *117*, 9594–9624.

(29) Sim, J.; Jo, E.; Jhon, Y. H.; Jang, S. G.; Shim, J.-G.; Jang, K.-R.; Paek, K.; Kim, J. Isolation and Crystal Structure Determination of Piperazine Dicarbamate Obtained from a Direct Reaction between Piperazine and Carbon Dioxide in Methanol. *Bull. Korean Chem. Soc.* **2016**, *37*, 1854–1857.

(30) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, 402, 276–279.

(31) Fang, Z.; Hu, Y.; Yao, B.; Ye, Z. Z.; Peng, X. S.  $CO_2$ -generated amorphous metal organic frameworks for efficient  $CO_2$  conversion. *J. Mater. Chem. A* **2024**, *12*, 6112–6122.

(32) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.

(33) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. A Chemically Functionalizable Nanoporous Material  $[Cu_3(TMA)_2(H_2O)_3]_n$ . Science **1999**, 283, 1148–1150.

(34) Tomas, R. A.; Bordado, J. C.; Gomes, J. F. p-Xylene oxidation to terephthalic acid: a literature review oriented toward process optimization and development. *Chem. Rev.* **2013**, *113*, 7421–7469.

(35) Dowson, G. R.; Dimitriou, I.; Owen, R. E.; Reed, D. G.; Allen, R. W.; Styring, P. Kinetic and economic analysis of reactive capture of dilute carbon dioxide with Grignard reagents. *Faraday Discuss.* **2015**, *183*, 47–65.

(36) Song, B.; Liang, Y.; Zhou, Y.; Zhang, L.; Li, H.; Zhu, N. X.; Tang, B. Z.; Zhao, D.; Liu, B. CO<sub>2</sub>-Based Stable Porous Metal-Organic Frameworks for CO<sub>2</sub> Utilization. *J. Am. Chem. Soc.* **2024**, *146*, 14835–14843.

(37) Zhang, Y.; Duan, J.; Ma, D.; Li, P.; Li, S.; Li, H.; Zhou, J.; Ma, X.; Feng, X.; Wang, B. Three-Dimensional Anionic Cyclodextrin-Based Covalent Organic Frameworks. *Angew. Chem., Int. Ed.* **2017**, *56*, 16313–16317.

(38) Bhunia, M. K.; Das, S. K.; Pachfule, P.; Banerjee, R.; Bhaumik, A. Nitrogen-rich porous covalent imine network (CIN) material as an efficient catalytic support for C-C coupling reactions. *Dalton Trans.* **2012**, *41*, 1304–1311.

(39) Tao, S.; Jiang, D. Accelerating Anhydrous Proton Transport in Covalent Organic Frameworks: Pore Chemistry and its Impacts. *Angew. Chem., Int. Ed.* **2024**, 63, No. e202408296.

(40) Song, B.; He, B.; Qin, A.; Tang, B. Z. Direct Polymerization of Carbon Dioxide, Diynes, and Alkyl Dihalides under Mild Reaction Conditions. *Macromolecules* **2018**, *51*, 42–48.

(41) Leclaire, J.; Husson, G.; Devaux, N.; Delorme, V.; Charles, L.; Ziarelli, F.; Desbois, P.; Chaumonnot, A.; Jacquin, M.; Fotiadu, F.; et al. CO<sub>2</sub> Binding by Dynamic Combinatorial Chemistry: An Environmental Selection. J. Am. Chem. Soc. **2010**, 132, 3582–3593.

(42) Seipp, C. A.; Williams, N. J.; Kidder, M. K.; Custelcean, R.  $CO_2$ Capture from Ambient Air by Crystallization with a Guanidine Sorbent. *Angew. Chem., Int. Ed.* **2017**, *56*, 1042–1045.

(43) Ishida, N.; Masuda, Y.; Imamura, Y.; Yamazaki, K.; Murakami, M. Carboxylation of Benzylic and Aliphatic C-H Bonds with CO<sub>2</sub> Induced by Light/Ketone/Nickel. J. Am. Chem. Soc. **2019**, *141*, 19611–19615.

(44) Angamuthu, R.; Byers, P.; Lutz, M.; Spek, A. L.; Bouwman, E. Electrocatalytic  $CO_2$  Conversion to Oxalate by a Copper Complex. *Science* **2010**, 327, 313–315.

(45) Al-Terkawi, A.-A.; Lamaty, F.; Métro, T.-X. Efficient CO<sub>2</sub> Sequestration by a Solid-Gas Reaction Enabled by Mechanochemistry: The Case of l-Lysine. ACS Sustain. Chem. Eng. 2020, 8, 13159–13166.
(46) Zhang, X.; Wan, K.; Subramanian, P.; Xu, M.; Luo, J.; Fransaer, J.

Electrochemical deposition of metal-organic framework films and their applications. J. Mater. Chem. A **2020**, *8*, 7569–7587.

(47) Zanatta, M. Materials for Direct Air Capture and Integrated  $CO_2$ Conversion: Advancement, Challenges, and Prospects. ACS Mater. Au 2023, 3, 576–583.

(48) Septavaux, J.; Tosi, C.; Jame, P.; Nervi, C.; Gobetto, R.; Leclaire, J. Simultaneous CO<sub>2</sub> capture and metal purification from waste streams

using triple-level dynamic combinatorial chemistry. *Nat. Chem.* 2020, *12*, 202–212.

(49) Ye, Y.; Yang, H.; Qian, J.; Su, H.; Lee, K. J.; Cheng, T.; Xiao, H.; Yano, J.; Goddard, W. A., 3rd; Crumlin, E. J. Dramatic differences in carbon dioxide adsorption and initial steps of reduction between silver and copper. *Nat. Commun.* **2019**, *10*, 1875.