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Introduction

In the past two decades, metal-organic frameworks (MOFs), as an important class of porous materials, have stimulated tremendous interest on account of their diversified architectures¹ as well as a wide range of potential applications, including catalysis,² luminescent sensors,³ gas adsorption/separation,⁴ magnetism,⁵ etc. Generally, the practical applications of materials are closely related to their architectural characteristics. However, it still remains a great challenge to design and synthesize preferable crystalline materials with desired structures and properties due to lots of factors in the determination of building block packing and growth, such as the reaction solvents,⁶ pH value,⁷ ratio of the reactants and reaction temperature.8 Subtle changes may play decisive roles in the formation of the final topology and geometry structure.⁹ Importantly, a reaction solvent is a crucial component in the domain of both kinetic and thermodynamic aspects in the coordination process, which can directly influence the crystal growth,¹⁰ structural interpenetration,¹¹ crystalline dimensionality and morphology.¹² Several examples of solvent-dependent MOFs

Solvent-dependent variations of both structure and catalytic performance in three manganese coordination polymers[†]

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Three new manganese 4'-(3,5-dicarboxyphenyl)-2,2':6',2'''-terpyridine (H₂DATP) metal–organic framework materials have been generated through regulating the ratios of a binary solvent mixture (DMA/H₂O) under solvothermal conditions. Compound **1** {[$Mn_2(DATP)(HDATP)(H_2O)_4$](OH)·10H₂O}_n displaying a onedimensional (1D) chainlike structure was crystallized from the DMA/H₂O mixture with a molar ratio of 1:1, while the two-dimensional (2D) layer species, {[$Mn(DATP)(H_2O)$]·2H₂O}_n (**2**) was produced by increasing the ratio of DMA/H₂O to 5:1. Interestingly, the crystallization in pure DMA yields a three-dimensional (3D) interpenetrating network {[Mn(DATP)]·4H₂O}_n (**3**), featuring higher solvent stability and pH stability than compounds **1** and **2**. It is proved that solvent not only influences the structural transformation process of crystals but also has a significant effect on their properties. These three compounds present different catalytic performances in the CO₂ cycloaddition to epoxides with various substituent groups into corresponding cyclic carbonates, and only **3** can serve as an efficient and recyclable catalyst at mild temperature.

> have been reported so far and solvents play different roles in the coordination chemistry:¹³ (1) solvent as a ligand; (2) solvent as a guest molecule; (3) solvent as both ligand and guest molecule; and (4) solvent as a template-directed agent. Hence, rationally controlling the ratio of solvents may yield various coordination polymers with different properties.

> On the other hand, carbon dioxide (CO_2) , one of the major greenhouse gases in the atmosphere, and industrial and human activities, should be responsible for climate change and global warming.¹⁴ At the same time, as a nontoxic, cheap, abundant, renewable and attractive C1 building block, CO₂ can be used potentially in synthetic chemistry.¹⁵ Recently, the CO₂ transformation, as an effective method for CO₂ capture and sequestration, has gained considerable attention due to the generation of high-value chemicals, including cyclic carbonates, urethanes, formic acid, dimethyl carbonate and others.¹⁶ In these investigations, one of the most promising catalysis transformations is the CO₂ cycloaddition with epoxides to form five-membered cyclic carbonates by a 100% atom-economical reaction. In particular, the desired target cyclic carbonates could be utilized as an important chemical intermediate as well as a large number of fine chemicals, making them useful in wide application.¹⁷ As far as we know, although various catalysts have been applied in the CO₂ coupling reaction, including zeolites, metal oxides, functional polymers and silica-supported salts, most of them own high catalytic reaction temperature and pressure.¹⁸ Based on the catalytic mecha-

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nism proposed in corresponding reports, Lewis-acid active sites play a key role in CO_2 transformation. In comparison, MOFs possessing some Lewis-acid active sites can be treated as efficient catalysts for CO_2 cycloaddition into cyclic carbonates at mild temperature and 0.1 MPa.¹⁹ Importantly, the CO_2 transformation without byproducts is in accordance with green chemistry and atom economy.²⁰

In this contribution, three coordination polymers have been obtained by varying the ratio of a binary solvent mixture (DMA/H₂O): a 1D chain species ({[Mn₂(DATP)(HDATP)(H₂O)₄] $(OH) \cdot 10H_2O_{ln}$ (1)), a 2D sheet structure ({[Mn(DATP)] (H_2O)]·2H₂O $_n$ (2)), and a 3D net framework ({[Mn(DATP)]·4H₂O} $_n$ (3) (4'-(3,5-dicarboxyphenyl)-2,2':6',2"'-terpyridine) (H₂DATP)) (see in Scheme S1[†]). As the ratio of DMA/H₂O changes, the number of H₂O molecules as ancillary ligands coordinated to the manganese ion decreases, and all the water molecules are fully replaced by H₂DATP gradually. Interestingly, the variation of solvents leads to the architectural transformation of these three compounds from a 1D chain to a 3D framework, and from nonpenetration to interpenetration. Furthermore, there are differences in the stabilities of 1-3, and compound 3 is more stable than 1 and 2 in various organic solvents and acid/base solutions with the pH range from 2 to 13. Diverse catalytic activities of 1-3 were observed in the CO₂ cycloaddition with epoxides into five-membered cyclic carbonates, but only compound 3 can be reused six times at mild temperature.

Experimental section

Materials and general methods

All chemicals and solvents used for the syntheses are reagent grade without further purification. The new ligand (H₂DATP) was characterized by IR and ¹H NMR analyses (Fig. S1 and S2†). Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-2500 diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å), with a scan speed of 5° min⁻¹ in the $2\theta = 3-60^{\circ}$ region. The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 spectrophotometer using KBr pellets in the range of 400–4000 cm⁻¹. Elemental analyses (EA) for C, H, and N were performed by a PerkinElmer elemental analyzer. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG 209 TG-DTA analyzer with heating the crystal-line samples from room temperature to 700 °C at a rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Syntheses of compounds 1-3

Synthesis of {[$Mn_2(DATP)(HDATP)(H_2O)_4$](OH)·10 H_2O }_n (1). A mixture of 0.03 mmol Mn(Ac)₂·2H₂O (0.0073 g), 0.025 mmol H₂DATP (0.0099 g), 3 mL H₂O and 3 mL DMA (*N*,*N*'-dimethyl-acetamide), together with 100 µL HNO₃, was sealed in a 7 mL capped vial. The vial was heated at 100 °C for 72 h under autogenous pressure and then cooled slowly down to room temperature at 2 °C h⁻¹. Bright yellow block single crystals were obtained. The yield was 92% (based on Mn(Ac)₂·2H₂O). Elemental analysis (%) for compound 1 (C₄₆H₅₆Mn₂N₆O₂₃, M = 1170.68, calcd: C 47.15, H 4.78, N 7.17. Found: C 47.86, H 4.79, N 7.11. IR (KBr, cm⁻¹) (Fig. S3a⁺): 3201(s), 1606(vs), 1553(vs), 1441(s), 1358(vs), 1241(s), 1159(m), 1088(m), 1005(s), 770(s), 723(s), 659(vs), 571(w).

Synthesis of {[Mn(DATP)(H₂O)]·2H₂O}_n (2). The synthesis of compound 2 is similar to that of {[Mn₂(DATP)(HDATP)(H₂O)₄] (OH)·10H₂O}_n (1), excepting that 3 mL H₂O and 3 mL DMA are replaced by 1 mL H₂O and 5 mL DMA. The mixture was sealed in a 7 mL capped vial and was heated at 100 °C for 3 days under autogenous pressure and then cooled gradually down to room temperature at the rate of 2 °C h⁻¹. Bright yellow block single crystals were collected (yield: 95%). Elemental analysis (%) for compound 2 (C₂₃H₁₉MnN₃O₇, M = 504.34), calcd: C 54.72, H 3.77, N 8.33. Found: C 54.78, H 3.78, N 8.48. IR (KBr, cm⁻¹) (Fig. S3b†): 3401(m), 3071(w), 1606(s), 1547(vs), 1436(s), 1353(vs), 1247(m), 1159(w), 1088(m), 1012(s), 870(m), 788(s), 730(vs), 652(s), 588(w).

Synthesis of {[Mn(DATP)]-4H₂O}_{*n*} (3). The synthesis of compound 3 is similar to that of 1, excepting that the mixed solvent is substituted by 6 mL pure DMA. The reactants were sealed in a 7 mL capped glass container and were heated at 100 °C for 72 hours under autogenous pressure. After cooling slowly to room temperature, bright yellow block-shaped crystals of 3 were obtained (yield: 94%). Elemental analysis (%) for compound 3 (C₂₃H₂₁MnN₃O₈, M = 522.30), calcd: C 52.84, H 4.02, N 8.04. Found: C 52.91, H 3.97, N 8.10. IR (KBr, cm⁻¹) (Fig. S3c†): 3389(m), 3059(w), 612(s), 1553(vs), 1436(s), 1353(vs), 1247(m), 1159(w), 1088(w), 1012(s), 870(m), 782(s), 730(vs), 652(vs), 594(w).

Crystallographic determination

Suitable single crystals of 1-3 were selected for single-crystal X-ray diffraction analysis under a nitrogen atmosphere. The crystal data were recorded on an Oxford diffractometer SuperNovaTM equipped with a graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) using a $\omega - \phi$ scan technique and corrected for Lorentz-polarization effects. The single-crystal structures of 1-3 were solved by directed methods and refined by full-matrix least-squares techniques based on F^2 using SHELXS-97 and SHELXL-97 programs.^{21,22} All the non-hydrogen atoms were refined with anisotropic thermal parameters while H atoms attached to C atoms were placed in calculated positions and refined using the riding model. The water H atoms were located from the difference maps. The SQUEEZE routine within the PLATON software package was employed to remove the solvent contribution in compounds 1-3²³ and the guest molecules could be confirmed by elemental analysis and thermogravimetric analysis. All crystallographic data and refinement details for 1-3 are listed in Table 1 and selected bond lengths and angles are shown in Table S1.† All the crystal data of 1-3 have been deposited with the Cambridge Crystallographic Data Centre (1821375, 1822245, 1822246†).

Catalysis

The general procedure for the CO_2 coupling reaction with epoxide to form cyclic carbonates is described as follows: first,

	1	2	3
Empirical formula	$C_{46}H_{56}Mn_2N_6O_{23}$	C ₂₃ H ₁₉ MnN ₃ O ₇	C ₂₃ H ₂₁ MnN ₃ O ₈
Formula weight	1170.68	504.34	522.30
Temperature/K	293(2)	113(15)	293(2)
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	C2/c	P41212
a/Å	11.3671(5)	27.489(5)	17.3875(12)
b/Å	11.6113(3)	12.3570(16)	17.3875(12)
c/Å	20.9861(7)	13.6835(17)	18.3017(9)
$\alpha/^{\circ}$	80.625(3)	90	90
β/\circ	74.837(3)	118.528(3)	90
γ/°	73.183(3)	90	90
Volume/Å ³	2547.68(16)	4083.7(10)	5533.0(8)
Ζ	2	8	8
$\rho_{\rm calc} {\rm g}{\rm cm}^{-3}$	1.269	1.523	1.081
μ/mm^{-1}	0.557	0.689	0.503
F(000)	1216	2072.0	2152.0
2θ range for data collection/°	5.972 to 50.02	6.04 to 50.018	6.464 to 50.012
Reflections collected	17 050	25 670	11 972
R _{int}	0.0207	0.0289	0.0856
Goodness-of-fit on F^2	1.028	1.061	0.988
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0421, wR_2 = 0.1118$	$R_1 = 0.0359, wR_2 = 0.1002$	$R_1 = 0.0688, wR_2 = 0.1338$
Final <i>R</i> indices [all data]	$R_1 = 0.0534, wR_2 = 0.1198$	$R_1 = 0.0391, wR_2 = 0.1022$	$R_1 = 0.1025, wR_2 = 0.1495$
$\Delta \rho_{\text{max/min}} (e \text{ Å}^{-3})$	0.617 / -0.464	0.772 / -0.444	0.498 / -0.299
Flack parameter	_		0.08(3)

2 mmol of the corresponding epoxide, 0.025 mmol tetrabutylammonium bromide (TBAB) (16.2 mg), and 3.05 mol% catalyst (based on Mn) were slowly added to a glass vial (10 mL). Then CO_2 (0.1 MPa) was introduced into the vial using a balloon and the resulting reaction mixture was stirred at different temperatures. After 12 h, when the reaction was cooled down to room temperature, 0.025 mmol 1,3,5-trimethoxybenzene (42 mg) and 3 mL CH₂Cl₂ were added to the reaction products. The mixture was stirred for 5 min and the supernatant was obtained after centrifugation. The yield of the product was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard and the relational expression is shown in detail in Fig. S4.†

Results and discussion

Syntheses

Three new Mn-based MOFs were prepared by the solvothermal method with good reproducibility (Fig. S5†) and characterized by single-crystal X-ray diffraction, PXRD, EA, TGA and IR analyses.

The solvothermal syntheses of MOFs generally undergo a complicated process, which is influenced by lots of synthesis parameters, including reaction temperature, concentration of reactants, pH, counterion and types of solvents. As a primary component for the reaction, solvents play key roles in the growth of crystals and the structural transformation of MOFs. In our work, **1–3** were obtained *via* the hydrothermal reaction of Mn(Ac)₂ and the H₂DATP ligand in a binary solvent mixture of DMA and H₂O. In the presence of 0.1 mL HNO₃ in DMA–H₂O (6 mL, v/v = 1:1), compound **1** was produced at 100 °C,

while the reaction results in the generation of 2 in the DMA– H_2O ratio of 5 : 1. With the concentration of DMA increasing, the number of water molecules coordinated to the central metal ion decreases. When a pure DMA solvent was used, all the coordinated H_2O molecules were fully replaced by H_2DATP and 3 was isolated (see in Scheme 1). It is worth noting that 0.1 mL HNO₃ is applied to improve the yield and crystalline quality.

Crystal structure description

 $\{[Mn_2(DATP)(HDATP)(H_2O)_4](OH)\cdot 10H_2O\}_n$ (1). Single-crystal diffraction analysis reveals that compound 1 crystallizes in the triclinic system with the space group P1. Each asymmetric unit is completed by two crystallographically independent Mn²⁺, one independent DATP²⁻ and HDATP⁻, four coordinated water molecules and ten free water molecules. As shown in Fig. 1a, the seven-coordinated Mn2+ is connected by three N atoms and two carbonyl oxygen atoms from one H₂DATP, as well as two coordinated water molecules, presenting an irregular decahedron coordination geometry. The Mn-N distances fall into the range of 2.2755(19)-2.355(2) Å. The Mn-O_{COO}- average value is 2.3681(18) Å, while Mn–O_{H,O} bond lengths are slightly shorter [Mn1-O1 = 2.211(2) and Mn1-O2 = 2.242(2) Å], which is similar to those in related Mn-based MOFs.²⁴ A one-dimensional chain structure is generated by end-on coordination modes of three N atoms and two carbonyl oxygen atoms from H₂DATP (Fig. 1b). The guest DATP²⁻ and HDATP⁻ anions form intermolecular charge-assisted hydrogen bonds between the negatively charged and neutral carboxylate groups with a short O···O distance of 2.487(3) Å. Then, abundant O_{H_2O} ···O_{COO}- and O-H…O hydrogen bonds between the neighboring chains extend the chains into the 3D supramolecular framework







Fig. 1 (a) The coordination environment of Mn^{2+} in 1. (b) The chainlike structure of 1. All hydrogen atoms are omitted for clarity. Green: Mn; red: O; blue: N; gray: C. (c) The 3D supramolecular framework of compound 1 through the H-bond interactions between the neighboring chains.



(Fig. 1c). The distance of O6…H12 is 1.683 Å and the angle of O6…H12–O12 is 166.447°.

{[**Mn(DATP)(H₂O)]·2H₂O**}_{*n*} (2). When the ratio of DMA/H₂O was tuned to 5 : 1, the dimensionality of 2 changes correspondingly. Single-crystal diffraction analysis demonstrates that compound 2 crystallizes in the monoclinic system with the space group *C*2/*c*. As shown in Fig. 2, 2 presents a two-dimensional (2D) layer structure, and mononuclear Mn^{2+} bonds to one crystallographically independent DATP²⁻, one oxygen atom from the other DATP²⁻ and one water molecule. Each DATP²⁻ possesses three N atoms and two carboxylate groups, leading to a double negative charge on the ligand. The Mn-O_{COO}-average distance is 2.2795(46) Å and the Mn-O_{H₂O</sup> bond length is 2.1758(13) Å. Additionally, the O–Mn–O bond angles range}

Fig. 2 (a) The coordination environment of Mn^{2+} in 2. (b) The 2D layer structure of compound 2. (c) The 3-connected fes topological structure for 2 with the Schläfli symbol of {4.8^2}. All hydrogen atoms are omitted for clarity. Green: Mn; red: O; blue: N; gray: C.

from 56.10(4) to 170.90(5)°, which agrees well with those reported.²⁵ In order to simplify the structure of 2, the 2D framework was constructed by the freely available TOPOS software package. Then, each Mn ion acts as a 3-connected node, and each H₂DATP also serves as a 3-connected node linking three Mn ions. As a result, such connectivity affords a 3-connected **fes** topological framework with the Schläfli symbol of $\{4.8^{2}\}$ (Fig. 2c).

 ${[Mn(DATP)]}\cdot 4H_2O_n$ (3). Compound 3 was obtained in pure DMA solvent, featuring a 3D framework structure (Fig. 3b).



Fig. 3 (a) Coordination mode of the Mn²⁺ ion in 3. (b) The 3D network of compound 3. (c) Representation of the two-fold interpenetrating structure with a SrSi₂ (srs) topology from two identical and independent 3D networks. All hydrogen atoms were omitted for clarity. Green: Mn; red: O; blue: N; gray: C.

Single-crystal diffraction analysis displays that 3 crystallizes in the tetragonal system with the space group $P4_12_12$. The asymmetric unit consists of one isolated Mn²⁺, one independent DATP²⁻ as well as four free water molecules. As shown in Fig. 3a, each central Mn²⁺ adopting a six coordinated geometry occupies one crystallographic site, which is coordinated by three N atoms with the Mn-N distances from 2.248(6) to 2.349(6) Å and three carbonyl oxygen atoms. The Mn-O bond lengths fall in the range between 2.133(6) and 2.270(5) Å, and the O-Mn-O bond angles change from 57.72(18)° to 158.7(2)°, which matches well with those reported previously.²⁶ In compound 3, a cavity with the pore of an independent network is $12.142 \times 12.142 \text{ Å}^2$ (Fig. 1c). Two identical and independent 3D frameworks interdigitate into each other, generating a two-fold interpenetrating architecture. The 1D channels are observed along the [001] direction in 3, presenting the solvent-accessible volume of 40.3%, calculated by the PLATON program.²³ Better insight into the 3D network can be attained by topology analysis. In this network, each Mn ion can be regarded as a 3-connected node that coordinates to three H₂DATP ligands, and each H₂DATP ligand belongs to a 3-connected spacer, which is linked by three Mn ions. Thus, the two-fold interpenetrating framework of 3 can be simplified into a 3-connected $SrSi_2$ (srs) topology with the point symbol of $\{10^3\}$ (Fig. 3d). Comparing compound 3 with 1 and 2, the absence of coordinated water molecules determines the coordination modes, giving rise to different structures.

Influence of the solvents on the assembly of frameworks

H₂DATP as a novel building linker was chosen for constructing new MOFs on account of its multidentate characteristic to provide versatile coordination modes and the close relationship of coordination natures with the reaction parameters. It is found that the ratio of solvents is of great importance in the assembly of metal ions and ligands by the comparison of summarizing synthetic conditions and architectures of 1-3. The 1D chain structure was generated under the condition of DMA/ $H_2O = 1:1$ while the 2D layer structure was produced in a rich-DMA environment. When the pure DMA was used, the 3D 2-fold interpenetrating network was obtained. Due to the strong competition between the H₂DATP ligand and the water, the number of coordinated water molecules acting as ancillary ligands around the Mn(II) center (2 in 1, 1 in 2, 0 in 3) depends on the water ratio in mixed solvents (see in Scheme S2[†]). The high dimensional (3D) framework is inclined to form in pure DMA environment, which may be explained by more stronger metal-ligand coordination than metal-water interaction. Therefore, the subtle change of solvents plays a crucial role in regulating the dimensionality and interpenetration of structures.

Powder X-ray diffraction (PXRD) studies and thermal behavior (TGA)

The PXRD patterns of 1-3 are shown in Fig. S6.[†] Good consistency between the simulated and experimental peaks demonstrates high phase purity of 1-3. In order to evaluate the solvent and pH stabilities of 1-3, these crystal samples were immersed in various common solvents for about 12 h but only the PXRD patterns of 3 agree well with the simulated one (Fig. S7[†]). Then 1-3 were treated with different acid/base solutions for 12 h, respectively, but the comparison of simulated results with experimental ones revealed that only 3 can remain intact in the solutions with the pH range from 2.0 to 13.0 (Fig. S8[†]). Therefore, compound 3 possesses higher solvent stability and pH stability than 1 and 2. Moreover, the thermal stabilities of 1-3 were explored (Fig. S9[†]). For compound 1, the TGA curve displays a weight loss of 21.78% (calculated 21.53%) in the range from 25 °C to 347 °C, which is attributed to the removal of ten free and four coordinated water molecules. 2 and 3 were observed to lose 10.65% (calculated 10.71%) and 13.42% (calculated 13.78%) weight, respectively, before the collapse of their structures, corresponding to the removal of free and coordinated water molecules. Then, these frameworks begin to collapse at nearly 355 °C (346 °C for 1, 355 °C for 2, and 361 °C for 3), indicating the good thermal stabilities of 1-3.

Catalytic studies

Given the manganese Lewis-acid sites in 1-3, the catalytic performances are evaluated for the cycloaddition of CO₂ with epoxides as a model reaction under 1 atm CO₂ pressure at different temperatures with 2.5 mmol% TBAB as a co-catalyst for 12 h. Styrene oxide is selected as a probe substrate to investigate the optimized conditions, and the corresponding results show that the yields of the desired products rise first and then fall from 50 to 100 °C using 3.05 mol% 1-3 as a catalyst (based on Mn), respectively (Tables S2a and S2b[†] and Table 2). Both lower and higher temperatures can reduce the catalytic activity. The optimum value (99%) of styrene carbonate can be observed at a mild temperature of 70 °C for 1 and 3 (entry 3 in Table S2a[†] and Table 2), while the highest yield (98%) of the desired product was obtained at 90 °C for 2 (entry 3 in Table S2b[†]), which may be attributed to the different structures of 1-3. However, only 48% conversion to 4-phenyl-1,3-dioxolan-2-one was obtained using 2.5 mol% TBAB alone in the absence of a catalyst at 70 °C (entry 10, Table 2), indicating that the nucleophilic attack of Br⁻ to epoxide will be enhanced tremendously with the help of manganese Lewis-acid sites.

Under the optimized conditions, the catalytic coupling of CO_2 with other epoxides substituted by different functional groups has been conducted to examine the effectiveness of **1–3**. A relatively high catalytic activity has been observed for the cycloadditions of epoxy chloropropane and glycidyl phenyl ether with CO_2 into corresponding cyclic carbonates (95% and 92% yields in **1** (entries 2 and 3 in Table S3a[†]), 90% and 91% yields in **2** (entries 2 and 3 in Table S3b[†]), and 94% and 92%

Table 2 Cycloaddition reaction of CO_2 with styrene oxide under different conditions^a

P	$^{\circ}$ + $^{\circ}$ CO ₂	Catalyst 3 TBAB	Ph	
Entry	Catalyst 3 [mg]	TBAB [%]	$T [^{\circ}C]$	Conv. ^b [%]
L	32	2.5	50	59
2	32	2.5	60	73
3	32	2.5	70	99
ł	32	2.5	80	94
5	32	2.5	90	93
5	32	2.5	100	91
7 ^C	0	2.5	70	13
3^d	0	2.5	70	11
)	32	0	70	15
10	0	2.5	70	48

^{*a*} Reaction conditions: styrene oxide (240.2 mg, 2.0 mmol), solvent-free, catalyst 3 (32 mg, 0.061 mmol), TBAB (16.2 mg, 0.025 mmol), CO₂ (0.1 MPa), 12 h, 32 mg catalyst 3 loading (based on Mn, about 3.05 mol%). ^{*b*} Yield of the product determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*} MnCl₂ (12.07 mg, 0.061 mmol). ^{*d*} Mn(Ac)₂ (10.55 mg, 0.061 mmol).

yields in 3 (entries 2 and 3 in Table 3), respectively), revealing that the electron-withdrawing groups contribute to the ringopening of substrates by nucleophilic attack. Inversely, when 1,2-epoxyhexane and epoxy-2-methylpropane with the electrondonating group were used, a dramatic reduction in the yields of desired products was detected, as indicated by 51% formation of 1,2-epoxyhexane carbonate (entry 4 in Table 3) and 42% formation of epoxy-2-methylpropane carbonate (entry 5 in Table 3) with 3 as the catalyst (51% and 41% yields in 1 (entries 4 and 5 in Table S3a[†]), and 59% and 39% yields in 2 (entries 4 and 5 in Table S3b⁺)). Additionally, under identical conditions, the cyclohexene oxides were converted into the corresponding products with low yields (entry 6 in Table 3, Table S3a and S3b[†]) possibly due to the large steric hindrance of the substrate. The productivities of cyclic carbonates catalyzed by $MnCl_2$ and $Mn(Ac)_2$ are 13% and 11%, respectively (entries 7 and 8 in Table 2), showing that the inorganic salts with various anions can't work effectively in this catalytic reaction.

Recyclability is an essential and important factor for heterogeneous catalysts in application, and the residual products of compounds 1–3 could be separated from the reaction mixture through centrifugation and filtration, respectively. Then, the catalytic reactions of the residual products on CO_2 conversion were carried out to explore the reusability of 1–3. As illustrated in Fig. 4, 3 can be recycled at least six times without significant decrease in catalytic activity, whereas 1 and 2 can't catalyze the CO_2 cycloaddition repeatedly, which is explained by the limitation of their chemical stabilities. The PXRD patterns of used 3 are in line with the simulated ones, confirming that 3 can remain stable after six successive recycles (Fig. S10†). Then,

Table 3 Yields of the cycloaddition reaction of CO_2 with various epoxides under optimized conditions^a

^{*a*} Reaction conditions: epoxides (2.0 mmol), catalyst 3 (32 mg, about 3.05 mol%, based on Mn), TBAB (16.2 mg, 2.5 mmol%), solvent-free, CO_2 (0.1 MPa). ^{*b*} Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

the TGA curve of recycled **3** was measured to further prove the result (Fig. S11†). The inductively coupled plasma (ICP) analysis of reaction mixture filtrate demonstrated that only a trace amount of leakage (0.66 ppm) of Mn^{2+} was found (Table S4†). Consequently, compound **3** is a heterogeneous catalyst with good recyclability for synthesizing cyclic carbonates from CO_2 and epoxides efficiently.

Run 3

Fig. 4 Recycling tests of 3 for the CO₂ coupling with styrene oxide.

Run 4

Run 5

Run 6

Based on reported work,²⁷ taking 3 as an example, the plausible mechanism of the CO₂ coupling reaction has been studied carefully, as shown in Fig. S12.† First of all, the oxygen atom from epoxide bonds with unsaturated Mn Lewis-acid sites in 3 and the epoxy ring is activated. Compared with 1 and 2, more space is available for the activation of the epoxy ring by the catalytic action of 3 due to the change in coordination number from seven to six. Secondly, the ring-opening process is started by the attack of nucleophilic Br⁻ on the less-hindered C of epoxides.²⁸ Subsequently, CO₂ reacts with the oxygen anion of the opened epoxy ring to generate an alkylcarbonate anion and the corresponding cyclic carbonate is obtained finally through ring-closure. We deduce that the synergistic effect of 3 and TBAB has facilitated the chemical transformation of CO₂ into cyclic carbonates. In truth, it is necessary to examine intermediates during the CO₂ coupling and the research in this direction will be explored in the future.

In conclusion, three new coordination polymers have been prepared in the presence of mixed solvents with advisable ratios and characterized structurally, featuring a 1D chain species, 2D layer structure and 3D network with two-fold interpenetration for 1–3, respectively. Structural variation controlled by solvents further makes a difference in the properties of 1–3. The chemical stability analysis reveal that only compound 3 can resist various organic solvents and acid/base solutions with pH range from 2 to 13. Different catalytic activities are detected for compounds 1–3 in the synthesis of cyclic carbonates from CO_2 and epoxides. Importantly, only 3 can serve as a high-efficiency heterogeneous catalyst in CO_2 cycloaddition with excellent cyclic performance.

Conflicts of interest

There are no conflicts to declare.

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Run 2



100

90 80 70

60 50

40 30 20

10 0

Run 1

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