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Polyoxometalate-based homochiral metal-organic frameworks for tandem asymmetric transformation of cyclic carbonates from olefins

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Currently, great interest is focused on developing auto-tandem catalytic reactions; a substrate is catalytically transferred through mechanistically distinct reactions without altering any reaction conditions. Here by incorporating a pyrrolidine moiety as a chiral organocatalyst and a polyoxometalate as an oxidation catalyst, a powerful approach is devised to achieve a tandem catalyst for the efficient conversion of CO₂ into value-added enantiomerically pure cyclic carbonates. The multi-catalytic sites are orderly distributed and spatially matched in the framework. The captured CO₂ molecules are synergistically fixed and activated by well-positioned pyrrolidine and amine groups, providing further compatibility with the terminal W=O activated epoxidation intermediate and driving the tandem catalytic process in a single workup stage and an asymmetric fashion. The structural simplicity of the building blocks and the use of inexpensive and readily available chemical reagents render this approach highly promising for the development of practical homochiral materials for CO₂ conversion.

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Recently, the selective and efficient conversion of light olefins with CO₂ as a C₁ building block into value-added enantiomerically pure cyclic carbonates has attracted great interest from chemists and governments due to its tremendous potential economic and environmental impact, especially considering the increasing worldwide greenhouse effect¹. The general synthetic procedure includes two mechanistically distinct catalytic processes consisting of the asymmetric epoxidation of olefins, based on the research of Sharpless and others, and the asymmetric coupling epoxide with CO₂ (refs 2–5). Both of the catalytic processes require asymmetric (or associated) catalysts to ensure enantioselectivity, as well as a sequential separation and purification process of the products from the reagents, the catalysts and the associated materials. Because light olefins are the most inexpensive and readily available chemical building blocks, a one-pot procedure that processes an olefin through a chain of discrete catalytic steps with multiple transformations using a single workup stage is highly desirable for the environmentally benign conversion of carbon dioxide to fine chemicals⁶.

Inspired by natural enzymatic processes, chemists have attempted to emulate natural reaction cascades by developing auto-tandem catalytic reactions in which a substrate is catalytically transferred through two or more mechanistically distinct reactions without the addition of reactants or catalysts and without altering the reaction conditions^{7,8}. Recently, homogeneous organo- and organometallic auto-tandem catalysts have been found to show high efficiency in solution⁹. This feature can be advantageous for separation and catalyst recovery by creating heterogenized catalysts using linkers to attach them to a support, such as high surface-area metal oxide materials, or alternatively, incorporating them within porous metal-organic frameworks (MOFs). One of the key advantageous of MOFs lies in their easily tunable composition in which the constituents' geometry, size and functionality can be widely varied^{10–12}. Thus, an ongoing challenge for the development of auto-tandem catalytic processes has been beyond the selection and incorporation of two or more catalytic sites by modifying these moieties in the building block of the original MOFs, but includes the achievement of compatibility between the reaction intermediates and synergy of the multiple catalytic cycles^{13–15}.

Polyoxometalates (POMs) are well-known catalysts studied in olefin epoxidation, with excellent thermal and oxidative stability towards oxygen donors^{16–18}. By combining chiral organic catalysts and POM components in a single MOF (POMOF), these POMOF materials can initiate the asymmetric dihydroxylation of aryl olefins with excellent stereoselectivity¹⁹. Because MOFs have exhibited unrivalled efficiency as heterogeneous Lewis acid catalysts for the chemical conversion of CO₂^{20–23}, we envision that the combination of chiral organic catalysts, Lewis acid catalysts and oxidation catalysts would be a powerful approach to devise a tandem catalytic process for the chemical transformation of olefins to chiral cyclic carbonate.

By incorporating Keggin-type [ZnW₁₂O₄₀]^{6–} anions, zinc(II) ions, NH₂-functionalized bridging links, NH₂-bipyridine (NH₂-BPY) and asymmetric organocatalytic groups, pyrrolidine-2-yl-imidazole (PYI) within one single MOF, herein we report the design and synthesis of two new enantiomorphs of POMOFs, ZnW-PYI1 and ZnW-PYI2, for the efficient conversion of CO₂ into value-added enantiomerically pure cyclic carbonates. Because the intrinsic crystalline properties could provide precise knowledge about the nature and distribution of catalytically active sites and about the potential interactions between the catalytic sites and the adsorbed substrates, the use of POM-based homochiral MOFs offers the potential to facilitate analysis of the intermediates and the catalytic processes of each step of the tandem asymmetric transformation.

Results

Synthesis and characterization of the POMOFs. The solvothermal reaction of TBA₄W₁₀O₃₂, Zn(NO₃)₂·6H₂O, NH₂-BPY and L-N-*tert*-butoxy-carbonyl-2-(imidazole)-1-pyrrolidine (L-BCIP) in a mixed solvent of acetonitrile and H₂O gave compound ZnW-PYI1 in a yield of 68% (Supplementary Fig. 1). Elemental analyses and powder X-ray diffraction (PXRD) indicated the pure phase of the bulk sample (Supplementary Fig. 2). Circular dichroism spectrum of the bulk sample of ZnW-PYI1 presented positive cotton effects at 276 nm ($\theta = 146$ mdeg) and negative cotton effects at 340 nm ($\theta = -41.2$ mdeg). The entire spectrum was different from the spectra of the chiral adducts L-BCIP and L-PYI (Supplementary Fig. 3). ZnW-PYI2 was prepared similarly to ZnW-PYI1, except that D-BCIP replaced L-BCIP. The circular dichroism spectrum of ZnW-PYI2 exhibited the cotton effects that were opposite to ZnW-PYI1, as expected for a pair of enantiomers with a mirror-imager relationship (Fig. 1a). Single-crystal structural analysis revealed that ZnW-PYI1 and ZnW-PYI2 shared the same cell dimensions crystallized in the chiral space group *P*2₁ (Supplementary Data 1 and 2, Supplementary Fig. 14–21).

The crystal structures of POMOFs. The asymmetric unit of ZnW-PYI1 consists of the Keggin anion ZnW₁₂O₄₀^{6–} and the cation [Zn₂(NH₂-BPY)₂(HPYI)₂(H₂O)(CH₃CN)]⁶⁺ (Supplementary Fig. 4). The precursor W₁₀O₃₂^{4–} anion is labile under hydrothermal conditions and favours to rearrangement into the more stable Keggin-type ZnW₁₂O₄₀^{6–} anion. Each of these ZnW₁₂O₄₀^{6–} anions connects to four zinc ions through the terminal oxygen atoms and acts as a four connector (Supplementary Fig. 5). Each of the two crystallographically independent zinc ions adopts a distorted octahedral geometry (Supplementary Fig. 6,7) and coordinates to two terminal oxygen atoms from different ZnW₁₂O₄₀^{6–} anions, forming a two-dimensional square grid sheet (Fig. 1b,c, Supplementary Fig. 8,9). Each of the NH₂-BPY ligands coordinates to two different zinc ions and further bridges the sheets to form a three-dimensional framework with one-dimensional chiral channels along the *b* axis (Fig. 1d, Supplementary Fig. 10,11). The accessible empty space of the framework is approximately 289.1 Å³ (8.1%), as calculated from PLATON analysis, suggesting the possibility that the MOF-based material ZnW-PYI1 can absorb substrates within its pores²⁴. Chiral PYI was located in the pores of the MOF, with the butoxycarbonyl of L-BCIP removed simultaneously in the reaction and the pyrrolidine nitrogen was protonated. The unique redox properties of ZnW₁₂O₄₀^{6–}, with its oxygen-enriched surface, provide sufficient driving force for the transformation of the catalytic precursors to the active intermediate of the epoxidation^{25,26}. The chiral PYIs act as cooperative catalytic sites to forge a crucial reaction centre that enhances the activities of the oxidants and drives the catalysis asymmetrically^{27,28}. Detailed structural analyses reveal that one zinc ion has a water molecule at its sixth coordination position, while the other is associated with an acetonitrile molecule. The removability of the coordinated water molecules indicates the potential of ZnW-PYI1 to act as an active Lewis acid catalyst (Supplementary Fig. 12). These amine groups in NH₂-BPY are positioned around the inner surface of the channels and act as accessible sites to activate CO₂ directly, enabling the catalytic performance in the coupling of carbon dioxide with epoxide under relatively mild conditions (Fig. 2)^{29–32}.

Separated tandem catalysis. The transformation of asymmetric epoxidation was initially examined using styrene and *t*-butylhydroperoxide (TBHP, 70% in decane) as the oxidant, along with

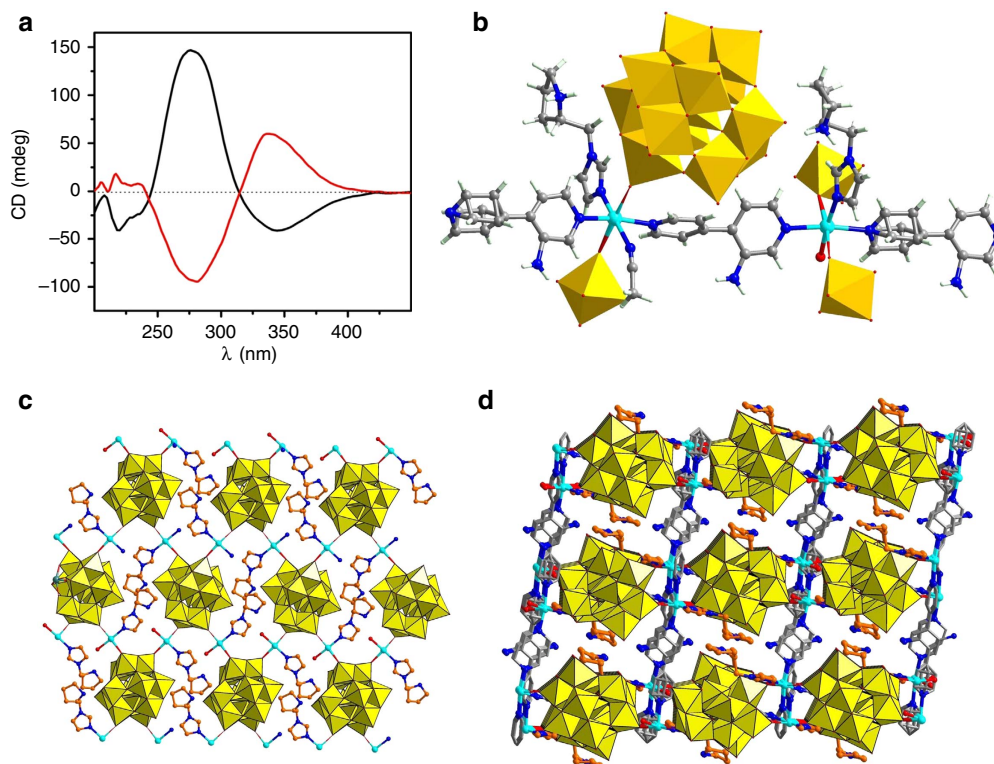


Figure 1 | The structure and characterization of ZnW – PYIs. (a) Circular dichroism spectra of bulk crystals of ZnW – PYI1 (black) and ZnW – PYI2 (red), respectively. (b) Plot of the one-dimensional connections between the bipyridine ligands and the zinc centres, showing the coordination mode of the zinc centres. (c) Perspective view of the two-dimensional sheet connected by the polyoxometalate clusters and the zinc centres, the bipyridine ligands were omitted for clarity. (d) 3D open network of ZnW – PYI1 viewed down the *b* axis. H atoms and solvent molecules are omitted for clarity. Carbon, nitrogen and zinc are drawn in gray (orange for PYI), blue, and cyan, respectively, with $\text{ZnW}_{12}\text{O}_{40}^{6-}$ shown as polyhedra.

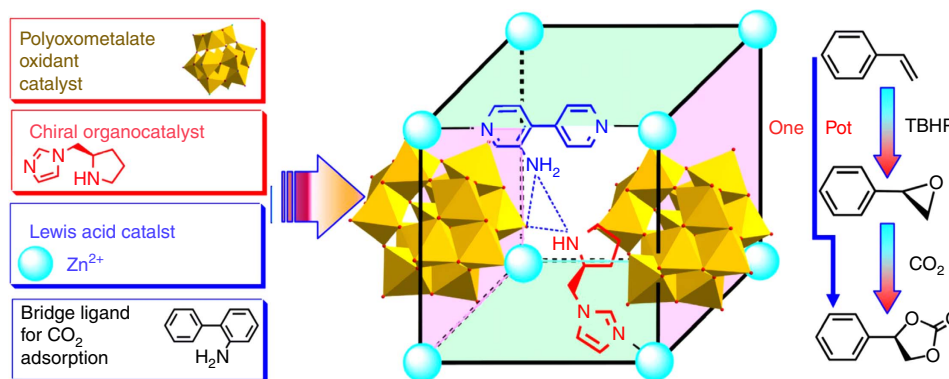
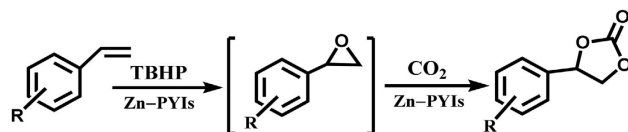


Figure 2 | The design concept of achieving a tandem catalyst. Synthetic procedure of the metal-organic framework, showing the constitutive/constructural fragments of the MOF; and the schematic representation of tandem catalysis for the asymmetric cyclic carbonate transformation from olefins and carbon dioxide.

ZnW – PYI1 (0.1% mol ratio) in a heterogeneous reaction at 50 °C for 5 days. As shown in Table 1 (entries 1–4), the result revealed the successful execution of our POMOF design, showing excellent yield (92%) and enantioselectivity (79% enantiomer excess (ee)) for (*R*)-styrene oxide (Supplementary Fig. 22, Supplementary Table 6). The control experiments showed that *L*–PYI and its hydrochloride salt could not initiate the reaction under similar conditions. The use of *L*–PYI and $\text{Zn}_3[\text{ZnW}_{12}\text{O}_{40}]$ as homogeneous catalysts gave a conversion of 55% and an ee value of 18%. The higher conversion in the case of the ZnW – PYI1 system was attributed to the suitable distribution of pairs of the chiral PYI moiety and the $\text{ZnW}_{12}\text{O}_{40}^{6-}$ oxidant

catalyst. Infrared of the catalyst impregnated with TBHP revealed a new $\nu(\text{O}-\text{O})$ band at 821 cm^{-1} , which indicated that the active intermediate peroxotungstate was formed during the epoxidation process (Fig. 3a)³³. From a mechanistic perspective, the formation of hydrogen bonds between the pyrrolidine N atom and the terminal oxygen atoms of the $\text{ZnW}_{12}\text{O}_{40}^{6-}$ with the interatomic separation $\text{N}(12) \cdots \text{O}(7)$, approximately 2.8 Å, initially activated the corresponding $\text{W}=\text{O}_t$ (O_t = terminal oxygen) and generated an active peroxide tungstate intermediate, ensuring the smooth progress of the reaction (Supplementary Table 2–5). These hydrogen bonds then enforced the proximity between the conventional electrophilic oxidant and the chiral directors to

Table 1 | Yields and enantiomer excess (ee) in the asymmetric epoxidation of the olefins*, in the coupling of CO₂ to styrene oxide†, and in the asymmetric auto-tandem catalysis of olefins to cyclic carbonates over ZnW – PYI catalysts‡.

Entry	Substrate	Product	Yield(%) ^[§]	ee(%) ^[]
1			92(94)	79(-76)
2			87(88)	75(-74)
3			76(79)	75(-76)
4			87(85)	93(-70)
5			>99	trace
6			>99	90
7			>99	-96
8			28	-
9			92(90)	80(-77)
10			83(85)	70(-73)
11			72(70)	55(-59)
12			25	-

*Entries 1–4: Conditions: olefin: 10 mmol, ZnW – **PYI**s: 0.01 mmol; TBHP(70% in decane): 20 mmol, 50 °C, 120 h.

†Entries 5–8: Conditions: styrene oxide: 10 mol, catalyst: 0.01 mmol, TBABr 0.1 mmol, CO₂, 0.5 MPa, 50 °C, 48 h.

‡Entries 9–12: conditions: olefin: 10 mmol, catalyst: 0.01 mmol, TBHP 20 mmol, CO₂, 0.5 MPa, 50 °C, 96 h.

§The yield was determined by ¹H NMR spectroscopy of crude products. Yields catalysed by ZnW – **PYI**2 were listed in the parentheses.

||The ee value was determined by chiral HPLC on a Chiralcel OD – H column. The ee values catalysed by ZnW – **PYI**2 were listed in the parentheses.

provide additional steric orientation, driving the catalysis to proceed in a stereoselective manner^{19,34}.

Solids of ZnW – **PYI**2 exhibited similar catalytic activities but gave products with the opposite chirality in the asymmetric epoxidation of styrene. The use of such a catalyst can be extended to other substituted styrene substrates and α , β -unsaturated aldehydes with comparable activity and asymmetric selectivity. The presence of a C=O stretching vibration at 1,675 cm⁻¹ (cf. 1682 cm⁻¹ of the free aldehyde) in the infrared spectra of the catalyst impregnated with a CH₂Cl₂ solution of cinnamaldehyde suggested the absorbance and activation of cinnamaldehyde in the cavities of ZnW – **PYI**1 (Fig. 3b).

The transformation of the asymmetric coupling of CO₂ to styrene oxide was examined using the racemic styrene oxide and CO₂ in free solvent, along with ZnW – **PYI**1 (0.1% mol ratio)

and cocatalyst TBABr (1% mol ratio), in a heterogeneous mixture at 50 °C and 0.5 MPa for 48 h, as shown in Table 1 (entry 5). The result exhibited excellent reaction efficiency (>99% yield) for phenyl(ethylene carbonate) (Supplementary Table 7). The control experiments demonstrated that no detectable conversion was observed for the model reaction in the absence of ZnW – **PYI**1 or the ammonium salt cocatalyst. It is postulated that the directed coordination of the ZnW₁₂O₄₀⁶⁻ anion to the zinc ions results in significant activation of the MOF on the acid surface, facilitating the coupling step because of its additional labile ligand sites, possibly through the provision of a carbon dioxide. The surface properties of the nanocation also meet a number of criteria for the carbon dioxide coupling reaction, such as an overall positive charge, the presence of coordinated water and the presence of functional groups for acid catalysis.

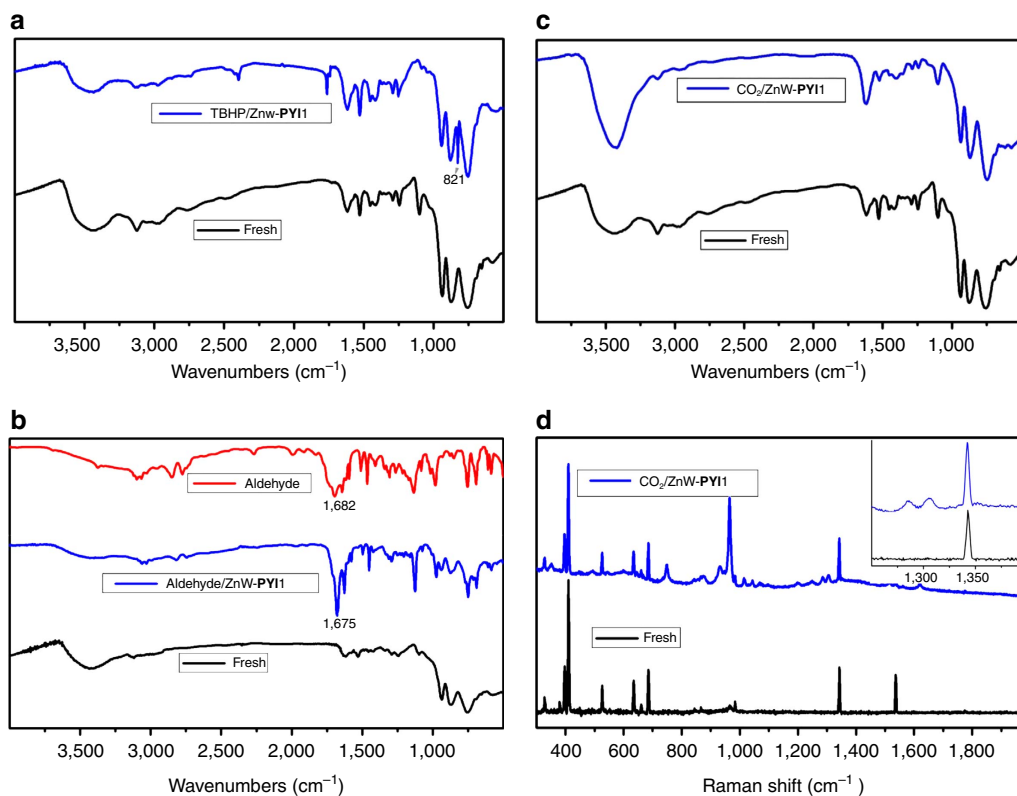


Figure 3 | The spectroscopic studies of ZnW – PYI1. (a) Infrared (IR) spectra of fresh and TBHP-oxidized ZnW – PYI1. (b) IR spectra of fresh and cinnamaldehyde-incorporated ZnW – PYI1. (c,d) IR spectra and Raman spectra of fresh (dark line) and CO₂-adsorbed ZnW – PYI1 (blue line), respectively.

Enantiospecific phenyl(ethylene carbonate) could be obtained through the coupling of CO₂ to the (*R*) or (*S*)-styrene oxide, catalysed with excellent reaction efficiency (>99% yield) and high enantioselectivity (>90% ee) (Supplementary Fig. 23, Supplementary Table 8) by ZnW – PYIs (Table 1, entries 6,7). The retention of chirality through the asymmetric coupling process demonstrated that selective ring opening occurred preferentially at the methylene C–O bond of the terminal epoxides^{5,32}. The high selectivity of the asymmetric transformation reflected that CO₂ molecules were also activated, providing favourable conditions for a fast reaction with epoxide by nucleophilic attack, avoiding the racemization of the epoxide through premature ring opening. It is postulated that these NH₂ molecules in channels not only enhanced the reaction rate by increasing the concentration of CO₂ substrate around its reactive centre but also increased the electron cloud density of activated CO₂, enabling the cyclic carbonate ring formation³⁵. In contrast to Ahn's group reported that combination of Lewis acid and base give highly active for the CO₂ cycloaddition to epoxide because of cooperative activation of epoxide by acid-base²², the Lewis acid catalytic zinc centres restricted within the ZnW–PYIs channels have the potential to interact synergistically with CO₂ in view of spatial location matching of catalytic sites in MOFs, such that an intramolecularly cooperative catalysis is proposed to contribute to the high activity and excellent stereochemical control of the given reactions³⁶.

The irreversible CO₂-adsorption and desorption isotherms of ZnW – PYI1 may be attributed to the chemical adsorption onto the amine of NH₂-BPY (Supplementary Fig. 13) (ref. 37). The infrared spectrum of activated ZnW – PYI1 in a vacuum and after the introduction of 1 bar of CO₂ at room temperature clearly shows the loss of the NH stretching vibration peak at 3,126 cm⁻¹, confirming that the CO₂ was adsorbed and

activated by NH₂ groups in the channels of ZnW – PYI1 (Fig. 3c) (refs 38,39). The Raman spectra of the MOF in a vacuum and after the introduction of 1 bar of CO₂ showed peaks at 1,285 cm⁻¹ (ref. 40), further supporting that CO₂ molecules were adsorbed within the MOFs (Fig. 3d). Mechanistically, this reaction is based on a nucleophilic cocatalyst that activates the epoxide to form an alkoxide. This intermediate can then react with activated carbon dioxide to ultimately yield the cyclic carbonate.

One-pot asymmetric catalysis. Because chiral ZnW – PYIs demonstrated their ability as effective catalysts in the epoxidation of styrene and the coupling reaction, the one-pot synthesis was applicable to a range of different substrates. As shown in Table 1 (entries 9–11), by heating a reaction mixture of styrene, TBHP and CO₂ with catalyst ZnW – PYI1 to 50 °C, the asymmetric epoxidation and the CO₂ asymmetric coupling could be smoothly completed with a single workup stage. The target (*R*)-phenyl(ethylene carbonate) was obtained in 92% yield with 80% ee (Supplementary Fig. 24, Supplementary Table 9). The removal of ZnW – PYI1 by filtration after 48 h stopped the reaction, and the filtrate afforded nearly no additional conversion after stirring for another 48 h. These observations suggest that ZnW – PYI1 is a true heterogeneous catalyst. ZnW – PYI1 solids could be isolated from the reaction suspension by simple filtration. The catalysts could be reused at least three times with moderate loss of activity (from 92 to 88% yield) and with a slight decrease in selectivity (from 80 to 77% ee) (Supplementary Table 10). The index of PXRD patterns of the ZnW – PYI1 bulky sample filtered from the catalytic reaction revealed that the crystallinity was maintained. The ZnW – PYI2 solids exhibited similar catalytic activities but

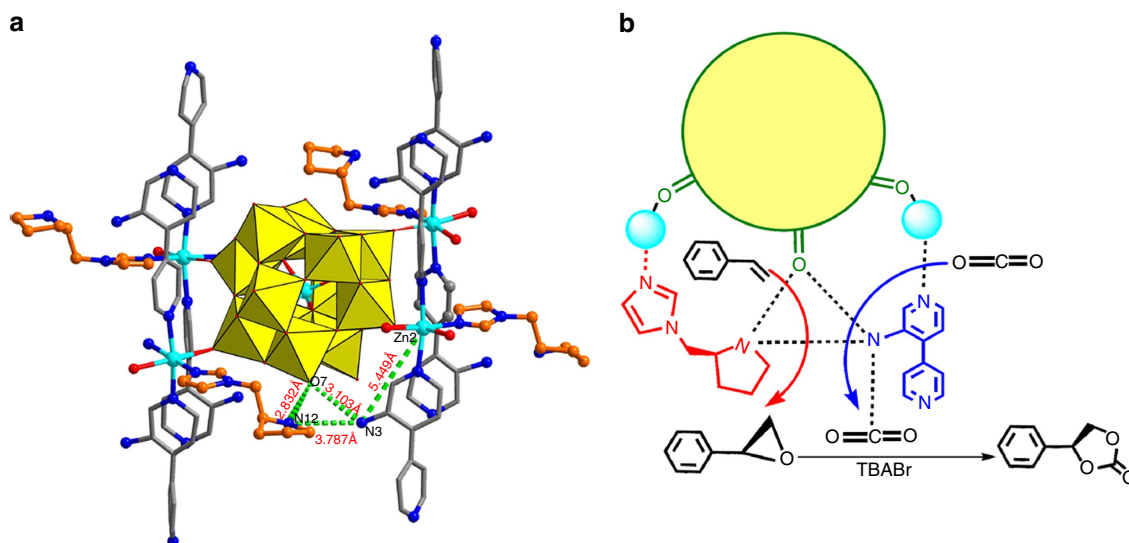


Figure 4 | The spatial relationship of multiple catalytic sites and synergistic catalysis. (a) Schematic diagram of the catalytic site distribution in ZnW – PYI, showing the interactions of the catalytic sites. (b) Diagram of potential mechanism for the auto-tandem catalysis.

gave products with opposite chiralities in the asymmetric auto-tandem epoxidation/coupling of styrene.

Discussion

It was found that performing the reaction through a one-pot process could greatly shorten the reaction time to 4 days, and the configuration was maintained throughout both of the steps. It is clear from the crystal structures of the ZnW – PYIs that the smooth and stereoselective conversion of the olefins into the epoxide can be attributed to the hydrogen bonding interaction between the spatially matched organocatalyst PYI and the oxidation catalyst ZnW₁₂O₄₀⁶⁻ and to the potential π - π interaction between the benzene ring of styrene oxide and the imidazole ring of PYI. Because the CO₂ molecules adsorbed in the channels of ZnW – PYI are activated by NH₂ groups, the weak hydrogen bonding interactions between the chiral amine group N(12) and the amino group N(3) (interatomic separation of 3.79 Å) is believed to enforce the proximity between the activated CO₂ and the terminal epoxide (Fig. 4). The well-matched positions and the suitable interactions provide a promising route for nucleophilic attack at the methylene C – O bond, ensuring chiral retention in the coupling process. The Lewis acid catalytic zinc centres restricted within the MOF channels have the potential to interact synergistically with CO₂ such that the compatibility between the reaction intermediates and the synergy of the multiple catalytic cycles allow the auto-tandem reaction to proceed smoothly and efficiently³⁶. Most importantly, the multi-catalytic sites with orderly distribution and spatial matching in the three-dimensional open framework provide favourable conditions for the auto-tandem reaction and avoid cross-interference.

The use of this catalyst can be extended to other styrene derivatives with comparable activity and asymmetric selectivity. In contrast to the smooth reaction of substrates 9–11, the one-pot catalytic reaction in the presence of cinnamaldehyde only gave 25% conversion under the same reaction conditions (Table 1, entry 12). It is suggested that the aldehyde group has the potential to interact with the NH₂ group, inactivating these sites for the activation and concentration of CO₂, which further substantiates the pivotal role of NH₂ in the one-pot process.

We have developed an asymmetric auto-tandem epoxidation/cycloaddition catalytic reaction catalysed solely by chiral POMOFs, which proceeds in a highly enantioselective manner for the efficient conversion of light olefins into value-added enantiomerically pure cyclic carbonates in a one-pot procedure. The results demonstrated that asymmetric auto-tandem catalysis is an atom-economical and environmentally benign synthetic method for producing useful chiral compounds.

Future work will focus on design structurally diverse chiral POMOFs and optimizing such reactions. The structural simplicity of catalyst and the use of inexpensive and readily available chemical reagents render this approach highly promising for the development of practical homochiral materials for asymmetric catalytic reactions.

Methods

Reagents and Syntheses. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. All epoxides were purchased from Acros and distilled under a nitrogen atmosphere from CaH₂ prior to use. Carbon dioxide (99.995%) was purchased from Dalian Institute of Special Gases and used as received. All manipulations involving air- and/or water-sensitive compounds were carried out in glove box or under dry nitrogen using standard Schlenk techniques. L- and D-*N*-*tert*-butoxycarbonyl-2-(imidazole)-1-pyrrolidine (L- or D-BCIP) (ref. 41), 3-amino-4,4'-bipyridine (NH₂-BPY) (ref. 42), and [(n-C₄H₉)₄N]₄[W₁₀O₃₂] (ref. 43) were prepared according to the literature methods.

Elemental analyses. Elemental analyses of C, H and N were performed on a Vario EL III elemental analyser.

Inductively coupled plasma. W and Zn analyses were performed on a Jarrel-AshJ-A1100 spectrometer.

Fourier translation infrared spectrum (FT-IR). FT-IR spectra were recorded as KBr pelletson JASCO FT/IR-430.

Powder X-ray diffractograms. PXRDs were obtained on a Rigaku D/Max-2,400 X-ray diffractometer with Cu sealed tube ($\lambda = 1.54178$ Å).

Circular dichroism spectrum. Circular dichroism spectra were measured on JASCO J-810 with solid KBr tableting.

Laser-Raman spectrum. Raman spectroscopy (Lab Raman HR Evolution) measurements were performed using a solid state 785 nm laser. A laser power of

1–2.5% was used to avoid degradation of the sample under the laser beam during the Raman measurements.

Thermogravimetric analysis. Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851 instrument and recorded under N₂ or under air, upon 14 equilibration at 100 °C, followed by a ramp of 5 °C min⁻¹ up to 800 °C.

Gas adsorption isotherms. Gas adsorption isotherms were collected using a Micromeritics 3Hex 128 instrument. As-synthesized crystals were thoroughly washed with anhydrous dichloromethane and dried under argon flow, approximately 100 mg of each sample was added into a pre-weighed sample analysis tube. The samples were degassed at 100 °C under vacuum for 24–48 h until the pressure change rate was no more than 3.5 mTorr min⁻¹. Ultra high purity (UHP) grade N₂ and CO₂ gas adsorbates (99.999 %) were used in this study.

Nuclear magnetic resonance. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Varian INOVA-400 MHz type (¹H, 400 MHz; ¹³C, 400 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (tetramethylsilane (TMS)) shifts at 0 p.p.m. for ¹H NMR and against the solvent, chloroform-D at 77.0 p.p.m. for ¹³C NMR, respectively.

High-performance liquid chromatography. High-performance liquid chromatography analysis was performed on Agilent 1,150 using a ChiralPAK OD – H column or AD – H column purchased from Daicel Chemical Industries, Ltd.

Crystallography. Data of POMOFs ZnW – PYIs were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs^{44,45}. Routine Lorentz polarization and Multi-scan absorption correction were applied to intensity data. Their structures were determined and the heavy atoms were found by direct methods using the SHELXTL-97 program package⁴⁶. The remaining atoms were found from successive full-matrix least-squares refinements on F² and Fourier syntheses. Not all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at their positions and allowed to ride on the parent atoms. Crystallographic data for ZnW – PYIs are summarized in Supplementary Table 1.

Synthesis of ZnW – PYI1. A mixture of [(n-C₄H₉)₄N]₄[W₁₀O₃₂] (66.4 mg, 0.02 mmol), Zn(NO₃)₂ · 6H₂O (60.0 mg, 0.20 mmol), NH₂-BPY (10.3 mg, 0.06 mmol) and L-BCIP (7.5 mg, 0.03 mmol) in mixed water (4.0 ml) and acetonitrile (2.0 ml) was stirred and its pH value was adjusted to 4.3 with 1 mol l⁻¹ acetic acid (HAc). The resulting suspension was sealed in a 25 ml Teflon-lined reactor and kept at 130 °C for 3 days. After cooling the autoclave to room temperature, yellow rod-like single crystals were separated, washed with water and air-dried. (Yield: calculated (calcd) 68% based on [(n-C₄H₉)₄N]₄[W₁₀O₃₂]). Elemental analyses and inductively coupled plasma calcd (%) for C₄₀H₅₄N₁₄O₄₁W₁₂Zn₃: C 12.68, H 1.44, N 5.18, Zn 5.18, W 58.22; Found: C 12.64, H 1.41, N 5.20, Zn 5.22, W 58.24 for ZnW – PYI1. IR (KBr): 3,440 (s), 3,123(w), 1,619(s), 1,532(s), 1,247 (s), 1,103(w), 938(s), 872(s), 756(versus) per cm.

Synthesis of ZnW – PYI2. The preparation of ZnW – PYI2 was similar to that of ZnW – PYI1, except that D-BCIP (50.0 mg, 0.2 mmol) replaced L-BCIP. (Yield: ca. 68% based on [(n-C₄H₉)₄N]₄[W₁₀O₃₂]). Elemental analyses and inductively coupled plasma calcd (%) for C₄₀H₅₄N₁₄O₄₁W₁₂Zn₃: C 12.68, H 1.44, N 5.18, Zn 5.18, W 58.22; Found: C 12.64, H 1.42, N 5.17, Zn 5.20, W 58.25 for ZnW – PYI2. IR (KBr): 3,443 (s), 3,124(w), 1,618(s), 1,531(s), 1,248 (s), 1,104(w), 939(s), 873(s), 757(versus) per cm.

Typical one-pot procedure for asymmetric catalysis. Catalyst (0.01 mmol), TBABr (0.1 mmol), TBHP (20 mmol) and styrene (10 mmol) was added to a Schlenk flask (50 ml) equipped with a three-way stopcock. Then CO₂ was charged into the autoclave, and the pressure (0.5 MPa) was kept constant during the reaction. The autoclave was put into a bath and heated to the 50 °C. After the expiration of the desired time, the excess gases were vented. The remaining mixture was degassed and fractionally distilled under reduced pressure or purified by column chromatography on silica gel to obtain the cyclic carbonate.

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Author contributions

Q.X.H., C.H. and C.Y.D. conceived and designed the experiments. Q.X.H., B.Q. and W.M.R. performed the experiments. C.H., J.Y.N. and C.Y.D. contributed materials and analysis tools. Q.X.H., C.H. and C.Y.D. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Accession codes: The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1063826–1063827. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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