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A Family of Chiral Metal–Organic Frameworks

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Abstract: Chiral metal–organic frameworks with a three-dimensional network structure and wide-open pores (>30 Å) were obtained by using chiral trifunctional linkers and multinuclear zinc clusters. The linkers, H₃ChirBTB*n*, consist of a 4,4',4"-benzene-1,3,5triyltribenzoate (BTB) backbone decorated with chiral oxazolidinone substituents. The size and polarity of these substituents determines the network topology formed under solvothermal synthesis conditions. The resulting

Keywords: aldol reaction • chirality • dyes/pigments • enantioselectivity • metal–organic frameworks chiral MOFs adsorb even large molecules from solution. Moreover, they are highly active Lewis acid catalysts in the Mukaiyama aldol reaction. Due to their chiral functionalization, they show significant levels of enantioselectivity, thereby proving the validity of the modular design concept employed.

Introduction

Recently, metal–organic frameworks (MOFs) have emerged as a new class of porous materials with extraordinarily large accessible surface areas and pore sizes that exceed those of traditional adsorbents such as zeolites and activated carbons.^[1] The crystallinity renders these materials to be promising specific catalysts due to the possibility of localizing the active sites in the structure, but also due to monomodal pore-size distribution available to achieve size-selective effects.^[2] The rational building block approach of MOFs is ideally suited for the integration of functionalities into the framework, particularly for the design of porous chiral MOF catalysts or adsorbents.

Asymmetric catalysis is of increasing importance, since the demand for enantiomerically pure compounds is rising. An initial breakthrough in the area of chiral catalysis that

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employs MOFs was achieved with POST-1, which was used to catalyze the kinetic resolution of *rac*-1-phenyl-2-propanol by means of a transesterification process.^[3] Later, some privileged chiral ligands of asymmetric catalysis were modified and employed as linkers for MOF formation.^[4-6] 1,1'-Bi-2naphthol (BINOL)-based ligands in particular were extensively studied by Lin et al., recently resulting in the formation of the first isoreticular series of chiral MOFs.^[7] The resulting highly enantioselective catalysts were used with success; however, these catalysts use the established mode of action of the corresponding homogeneous catalysts, and in addition, the coordination polymers were not highly crystalline.^[5] Thus, the full structural characterization of chiral MOFs remains a challenge.^[4,5]

MOFs represent a three-dimensional platform that allows the design of completely new catalyst architectures. They offer a family of building blocks, namely, nodes and linkers with a wide range of different connectivity. In addition, the pore diameter can be adjusted by changing the length of the linker.^[8] However, whereas linker functionality determines rather rigorously its connectivity, the formation of multinuclear clusters used as MOF building blocks (nodes) is often hard to predict. Thus, in zinc carboxylates, di-, tri-, and tetranuclear clusters are observed as the predominant species that serve as 4- or 6-connecting nodes. Another ambiguity in MOF design is interpenetration.^[9] Even though rules have been found that rationalize interpenetration,^[10] for more complex and substituted linkers, the packing is difficult to predict and solvent-linker interaction will affect the degree of interpenetration.

Besides such limitations, in our view, the rational building-block approach is applicable to the design of porous chiral MOF catalysts, and a new strategy seems to be attractive: the attachment of chiral groups/auxiliaries to linkers successfully used for MOF synthesis, thereby leading

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to the formation of unprecedented chiral MOF catalysts with no homogenous analogue. Moreover, these chiral auxiliaries, placed in close vicinity to the open accessible metal nodes as an integral part of the MOF structure, could induce enantioselectivity in Lewis acid or metal-catalyzed reactions. A related synthetic approach was pursued by Fujita et al. by decorating molecular $Pd_{12}L_{24}$ cages (L=1,3bis(pyridin-4-ylethynyl)benzene) with amino acids or peptides.^[11] However, the obtained material was not tested in asymmetric catalysis. For MOF catalysts, one requirement is the presence and accessibility of active metal centers. Such active sites are found in M_2 paddle-wheel units (M = Cu, Zn, Ni, Co, Mo) and can be used as Lewis acid catalysts.^[12] Three-dimensional networks with very large pores in which accessible sites are not blocked are formed in combination with tricarboxylates. The combination of square and triangular building blocks allows for the formation of two different topologies,^[13] the twisted boracite topology as is found in HKUST-1 (Cu₃(BTC)₂; BTC=1,3,5-benzene tricarboxylate)^[14] and in $[Cu_3(TATB)_2(H_2O)_3]$ (TATB = 4,4',4''-s-triazine-2,4,6-trivltribenzoate),^[15] and the Pt₃O₄ topology with BTB $(Cu_3(BTB)_2; BTB = 4,4',4''-benzene-1,3,5-triyltriben$ zoate) in MOF-14.[16,17]

Consequently, to introduce chiral groups in the vicinity of the connecting and catalytically active paddle-wheels, we prepared chiral tricarboxylic acids with a BTB backbone substituted by chiral oxazolidinones (H₃ChirBTB-*n*): 1,3,5tri{4-[2-(4-isopropyl-2-oxooxazolidin-3-yl)]benzoate}benzene (**5a**, H₃ChirBTB-1) and 1,3,5-tri{4-[2-(4-benzyl-2-oxooxazolidin-3-yl)]benzoate}benzene (**5b**, H₃ChirBTB-2) (Scheme 1). We reasoned that oxazolidinones, established chiral auxiliaries in stereoselective synthesis,^[18] might be a good group because these rigid cyclic system exhibit a significant dipole moment and should be tolerant of the conditions of MOF formation. On the other hand, the rigid and extended nature of the BTB ligand is ideally suited for the formation of wide-open structures for accessibility of the active sites. At the same time, chiral oxazolidinone substitution with varying steric demand in close vicinity to the coordinating carboxylate group introduces a new modular concept for the synthesis of enantioselective MOF catalysts.

Results and Discussion

Synthesis of chirally substituted 4,4',4"-benzene-1,3,5-tribenzoic acids: The chiral acids were synthesized in five steps from commercially available 4-iodoacetophenone 1 (Scheme 1). The 4-iodoacetophenone was brominated selectively in the 3-position, and then the iodide was converted into ethyl ester 2 by palladium-catalyzed carbonylation. The chiral oxazolidinone was introduced by a copper-catalyzed coupling of the aryl bromide. Finally, acetophenone derivatives 3a and 3b were trimerized with SiCl₄ and the ester was cleaved under basic conditions to give the chiral H₃BTB derivatives 5a and 5b.

Synthesis and crystal structure of metal-organic frameworks: Crystals of $[Zn_3(ChirBTB-1)_2]$ (6) were obtained by treating H₃ChirBTB-1 (5a) with an excess amount of zinc nitrate in diethylformamide (DEF) at 100 °C for 20 h. The structure analysis of the resulting cubic structure of 6 (space group F432, a=47.515(2) Å, Figure 1c) is a challenge on its own due to the large cell volume and extremely open structure with meso- and micropores. Finally, single-crystal synchrotron data provided the basis for a successful refinement of the complex structure. Zinc paddle-wheels in 6 are surrounded by four ChirBTB-1 ligands (Figure 1a). The axial sites of the paddle-wheel are occupied by oxygen atoms of solvent molecules. The BTB is not planar and rather screwlike. As expected, the structure of 6 has a twisted boracite topology analogous to HKUST-1^[13] (see Figure S3a in the



Scheme 1. Synthesis of the chiral H₃BTB-derivatives **5a** and **5b** starting from 4-iodoacetophenone (1). MEDA = N,N'-dimethylendiamine.

Supporting Information). Three types of pores are present (Figure 1c). A larger pore (LP) approximately 33.7 Å in diameter (Zn-Zn atom center distance) exhibits accessible Zn sites that point towards the center of the pore. The LP has windows of 12.8 Å and is polar in character. The small pore (\approx 13.7 Å in diameter) is formed by four ChirBTB-1 linkers. In addition, a third type of pore only slightly smaller than the large pore is present. This pore is also confined by ChirBTB-1 linkers and represents the interstitial space between the large and the small pores (this pore is not being shown in Figure 1c).

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Figure 1. a) Paddle-wheel unit within the crystal structure of $[Zn_3(ChirBTB-1)_2]$ (6). The oxazolidinone subunit is disordered over two positions. b) $Zn_3(RCOO)_2$ cluster in $[Zn_3(ChirBTB-2)_2]$ (7). For reasons of clarity the carbon atoms of both linkers are represented in two different colors. c) Crystal structure of 6 exhibiting two different pores, represented in orange. d) Channels in the crystal structure of 7, represented in orange. Only one oxazolidinone subunit is shown. Zn: green, O: red, N: blue, C: (dark) gray.

Even though similar reaction conditions were used for the preparation of $[Zn_3(ChirBTB-2)_2]$ (7), the crystal structure differs completely from that found for [Zn₃(ChirBTB-1)₂] (6). Compound 7 crystallizes in the tetragonal, chiral space group $P4_32_12$ (Figure 1d). Trinuclear $M_3(RCO_2)_6$ (M=Zn, Mg) clusters, a common secondary building unit (SBU) in porous MOFs such as MOF-3 and TUDMOF-2 and -3^[19] form the nodes of the network. The three zinc atoms of the SBU form a nearly linear array (Zn-Zn-Zn-angle 175.8(3)°; Figure 1b). The central zinc atom has octahedral coordination, whereas the terminal zinc atoms are distorted tetrahedral, thereby resulting in a 6-connecting node. The SBUs are connected by the chiral linker to form a chiral 3D net with cys topology (every net has a name consisting of three characters, in this case "cys". The different network topologies were collected by the Center for Reticular Chemistry (http://rcsr.anu.edu.au/), see Figure S3b in the Supporting Information). The linkers are stacked pairwise (Figure 1b) due to the strong π - π interactions between two face-to-face stacked ligands,^[20] thus resulting in a relatively dense structure with two types of channels that run through all three directions of the crystals. The rectangular channels along the *c*-axis are 18×18 Å (as measured from atom center to atom center) and are partially occupied by the benzyl groups of the oxazolidinone substituents (Figure 1d). The solvent-accessible volume calculated by using PLATON^[21] is 60.3% of the unit cell volume for 6 and 50.7% for 7.

Host-guest systems: The powder X-ray diffraction patterns of freshly made samples of 6 and 7 (see Figures S4 and S5 in

the Supporting Information) match the patterns calculated from the crystal structure. Slight differences can be assigned to the fact that the enclosed solvent molecules could not be taken into account for the calculation of the theoretical patterns.

The composition of the frameworks was further confirmed by thermal analysis (see Figures S8 and S9 in the Supporting Information) combined with elemental analysis. In both cases, the solvent molecules bound to the metal centers could not be removed by solvent exchange with CH₂Cl₂ and subsequent drying in vacuum. In addition, several molecules of water are included, thereby leading to the final framework compositions of [Zn₃(ChirBTB- $1)_2(DEF)_3(H_2O)_5$] for 6 and [Zn₃(ChirBTB-2)₂(DEF)₂- $(H_2O)_3$ for 7. The presence of

DEF and water was also verified by the IR spectra of compounds 6 and 7 (see Figures S10 and S11), indicated by strong bands around 1643 cm⁻¹ (IR spectrum of 6) and 1657 cm^{-1} (IR spectrum of 7) for the C=O valence vibration of DEF and broad bands between 3000 and 3700 cm⁻¹ (H₂O), respectively. Furthermore, bands caused by symmetric valence vibrations of the carboxylate groups were identified (6: 1402 and 1433 cm⁻¹, 7: 1400, 1435 and 1456 cm⁻¹). The presence of the oxazolidinone subunits is proven by very strong bands at 1732 and 1761 cm^{-1} (6) and 1734 and 1763 cm⁻¹ (7), respectively, which can be assigned to the C= O stretching vibration of the oxazolidinone ring. The bands between 2800 and 3000 cm⁻¹ caused by aliphatic C-H vibrations support this finding, too. In the case of MOF 7, additional bands at 3028, 3062, and 3086 cm⁻¹ are observed (aromatic valence vibrations) that are caused by the presence of the benzyl group.

Due to the internal stress caused upon the drying of such highly porous structures, thus resulting in pore collapse, gas physisorption that requires activation in vacuum was not the method of choice. According to Monte Carlo integration, the accessible surface area for **6** and **7** is 2278 and $1990 \text{ m}^2\text{g}^{-1}$, respectively.^[22] Even though nitrogen or argon physisorption is usually used for determination of porosity of the materials, for catalytic applications in fine chemical production, not the access of gases but rather pore access for large molecules in solution is essential. Thus, to prove the permanent porosity and accessibility for larger molecules of **6** and **7**, three different dye molecules were adsorbed in solution (Table 1). Both metal–organic frame-

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Table 1. Adsorption of different dyes within the pores of 6 and 7.



[a] Fluorescein@MOF under UV irradiation.

works are able to adsorb fluorescein (8) and merocyanine 9 from solution. The adsorption behavior differs, however, when Reichardt's dye (10),^[23] a very large molecule $(1.26 \times$ $1.01 \times 0.81 \text{ nm}^3)^{[24]}$ is used. Dye **10** was previously employed to probe the enormous pore size in MOF-177^[16] and is completely adsorbed by 6 (see Figure S12 in the Supporting Information). As determined by ¹H NMR spectroscopy (see Figures S13 and S14), one molecule of Reichardt's dye (10) is adsorbed per formula unit $[Zn_3(ChirBTB-1)_2]$ (6), whereas MOF-177 adsorbs only $\frac{1}{8}$ molecules of Reichardt's dye (10) per formula unit Zn₄O(BTB)₂.^[16] Compound 7 is not able to adsorb the large Reichardt's dye (10, Table 1). Though the crystal structure of 7 exhibits rectangular channels (Figure 1d), these channels are not accessible for the larger dye since they are occupied by benzyl groups as described above. Furthermore, the solvatochromic Reichardt's dye (10) shows a color change from green in the less-polar solvent CH₂Cl₂ towards violet in the MOF (see Figure S12), thus indicating adsorption in the hydrophilic LP of 6, which exposes polar functional groups such as Zn sites and amide groups. Besides that, dye@MOF materials exhibit an exceptional long-term stability if one judges from the powder Xray diffraction pattern of merocyanine $9@Zn_3(ChirBTB-2)_2$ (7) obtained two years after loading (see Figure S5d).

Application in Mukaiyama aldol reactions: Since the pores of **6** and **7** are accessible even for large molecules, the Lewis acidic metal sites can be used for the catalytic conversion of organic substrates. Compounds **6** and **7** were tested in the Mukaiyama aldol reaction of benzaldehyde (**11a**) and 1-naphthaldehyde (**11b**) with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (**12**) (Scheme 2; for details, see the Exper-



Scheme 2. Mukaiyama aldol reactions with 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene (12) and benzaldehyde (11a) or 1-naphthaldehyde (11b).

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imental Section and Supporting Information) that required relatively strong Lewis acid catalysts.^[25] The application of metal-organic frameworks in Mukaiyama aldol reactions was first investigated by Long and co-workers. They used a MOF with exposed manganese sites in the catalytic conversion of different aldehydes and silyl enol ethers.^[25] After four days' reaction time, they obtained a moderate yield of 63% by using benzaldehyde (11a) and silvl enol ether 12. In this case, the metal atoms that formed the nodes of the framework were themselves used as catalytic active sites. Cohen et al. successfully employed a postsynthetic approach to synthesize an active MOF catalyst by fixation of an iron complex at the framework of UMCM-1.^[26] The catalyst thus formed was able to convert the bulky aldehydes 1-naphthaldehyde (11b) and mesitylaldehyde. But, up to now, the successful application of chiral MOF catalysts in the enantioselective Mukaiyama aldol reaction has not been reported to the best of our knowledge.

The catalytic performance of **6** and **7** was compared with that of zinc nitrate tetrahydrate (**15**), a homogeneous analogue; MOF-177 (**16**), a well-known zinc-based MOF with a large accessible pore volume;^[16] and MIL-101 (**17**),^[27] an MOF that exhibits high catalytic activity in Lewis acid mediated reactions.^[28] For reasons of comparison, the quantity of MOF employed was calculated in a way that the number of metal sites with regard to the amount of aldehyde was the same. The conversion of benzaldehyde (**11a**) in the Mukai-yama aldol reaction with silyl enol ether **12** by the aforementioned catalysts is presented in Figure 2a. As expected, the highest initial catalytic performance is found for MIL-101 (**17**) but it is surpassed by that of **6** after only one day of

reaction time and reached by **7** after seven days. The performance of $[Zn(NO_3)_2(H_2O)_4]$ (**15**) is comparable to that of **7** and thus unexpectedly low, probably due to the low solubility of zinc nitrate in *n*-heptane. The poorest performance in the Mukaiyama aldol reaction was with benzaldehyde (**11 a**) and MOF-177 (**16**). Since this material has only coordinatively saturated zinc atoms, this finding seems to be rational. The catalytic activity of **16** can be explained by defects in the crystal structure^[29] or a short lifetime expansion of the coordination number, as was already observed for DUT-7, a Zn_4O -based chiral MOF.^[30] Judging from the observed conversion rates, the new chiral MOFs **6** and **7** show competitive catalytic performances, especially with regard to MIL-101 (**17**).

Besides the conversion of the starting material 11a, the nature and enantiomeric excess (ee) of the formed products is of greater interest. For all catalysts that exhibit open metal sites, a considerable amount of 14a (the desilylated form of 13a) is formed (6: 22%, 7: 20%, 17: 27%). This diminishes the yield of 13a expected from the conversion rates (Figure 2c, solid lines) to 77% for 6 (conversion: 99%), 74% for 7 (conversion: 98%), and 69% for MIL-101 (17, conversion: 98%). But on the whole, both compounds 13a and 14a are products of the Mukaiyama aldol reaction (Figure 2c, dotted lines), thereby resulting in good product selectivities for the new chiral MOF materials 6 and 7. This finding is also supported by the small amount of unidentified side products formed during the reaction (<1% for 6 and $\approx 4\%$ for 7; see Figure S15 in the Supporting Information). The yield of 13a observed during the performance studies is also supported by the isolated yields after column



chromatography (Table 2). MOF-177 (16) is the best catalyst in terms of the selectivity of formed product 13a, since only 4% of desilylated product 14a and 2% further side products are formed. This finding is in accordance with the poor performance in terms of the conversion of benzaldehyde (11a).

As discussed in the foregoing sections, $[Zn_3(ChirBTB-1)_2]$ (6) is an efficient catalyst for the Mukaiyama aldol reaction that uses benzaldehyde (11a). Interestingly, the enantioselectivity of 6 as catalyst during catalysis depends on the solvent used. If *n*-heptane is used as solvent, an enantiomeric excess of 9% is detected (Table 2, entry 7) but no influence on the enantioselectivity of the formed product could be observed when dichloromethane used was

Figure 2. Catalytic performances of $[Zn_3(ChirBTB-1)_2]$ (6) and $[Zn_3(ChirBTB-2)_2]$ (7) relative to $[Zn(NO_3)_2(H_2O)_4]$ (15), MOF-177 (16), and MIL-101 (17) in *n*-heptane at room temperature. a) Conversion of benzalde-hyde (11a). b) Conversion of 1-naphthaldehyde (11b). c) Yield of 13a. The dotted gray line represents the sum of the yields of 13a and 14a. d) Yield of 13b. Catalyst 6: triangles; catalyst 7: squares with crosshair; catalyst 15: circles; catalyst 16: squares; catalyst 17: diamonds.

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Table 2. Results of Mukaiyama aldol reactions using dichloromethane or n-heptane as solvent.

Entry	Aldehyde	MOF	Solvent	Yield [%]	ee value [%]	
		/R	eaction time	tion time		
		dicl	nloromethane	9		
1	11 a	6	48 h	83 ^[a]	0	
2	11b	6	17 d	31 ^[a]	40 ^[b,c]	
3	11b	6	17 d	22 ^[a]	10 ^[b,d]	
4	11 a	7	13 d	66 ^[a]	8 ^[e]	
5	11 a	7	13 d	54 ^[a]	8 ^[e,d]	
6	11b	7	14 d	0 ^[a]	-	
			<i>n</i> -heptane			
7	11 a	6	48 h	77 (98) ^[f]	9 ^[e]	
8	11b	6	48 h	77 ^[f]	16 ^[b]	
			7 d	84 ^[f]		
9	11 a	7	48 h	43 (82) ^[f]	6 ^[e]	
			12 d	74 (94) ^[f]		

[a] Isolated yield of **13a** after column chromatography. [b] Determined by chiral HPLC. [c] However, a different batch of material gave a 10% *ee* in the first cycle. [d] Second cycle. [e] Determined by chiral GC. [f] Yield of **13a** determined during kinetic measurements; yield of **13a**+ **14a** in parentheses.

(Table 2, entry 1). $[Zn_3(ChirBTB-2)_2]$ (7) catalyzes the reaction of benzaldehyde (11 a) and the silyl enol ether 12 with a decreased reaction rate and a small but reproducible enantiomeric excess of the product 13a of 6% (*n*-heptane) and 8% (dichloromethane), respectively, was measured (Table 2, entries 4, 5, and 9).

Since the catalytically active sites of 6 and 7 are blocked by solvent molecules, which cannot be removed in vacuum without a collapse of the framework, the influence of these coordinated solvent molecules was studied for MIL-101 (17). A portion of 17 equivalent to the amount used in the standard reaction described in the Experimental Section was completely soaked with an excess amount of dry DEF for one day. Afterwards, the supernatant DEF was removed and the sample treated with dry dichloromethane to eliminate DEF molecules occluded in the pores of MIL-101 but not the ones coordinated to chromium centers. After activation in vacuum at room temperature, the obtained material denoted as DEF@MIL-101 (18) was used in the Mukaiyama aldol reaction with benzaldehyde (11a) and silylenol ether 12 (Scheme 2). As expected, the initial reaction rate drops significantly (see Figure S17 in the Supporting Information). In contrast to pure MIL-101, the kinetic curve does not reach a plateau after three days' reaction time but a lower rate is observed until it reaches the same conversion after 12 days. This steady increase in conversion indicates the successive replacement of the coordinated DEF molecules by benzaldehyde (11a). This result supports the assumption that the catalytic activity of 6 and 7 arises from the open zinc centers at the nodes of the frameworks and not from defects in the crystal structure. In comparison to MIL-101 (17), the use of DEF@MIL-101 (18) suppresses the formation of the desilvlated product 14a (see Figure S18) and further side products (see Figure S19).

Using the larger 1-naphthaldehyde (11b) in the Mukaiyama aldol reaction with silylenol ether 12 results in a drop of the conversion rates for all catalysts (Figure 2b). Compound 7 showed no conversion at all. Again, compound 6 shows the best performance (conversion: 97%), but in contrast to the conversion of benzaldehyde (11a), the gap between 6 and the other catalysts— $[Zn(NO_3)_2(H_2O)_4]$ (15, conversion: 65%), MOF-177 (16, conversion: 61%), and MIL-101 (17, conversion: 60%)—is significant. As already found for **11a**, a large number of side products are formed if catalysts with open metal sites (6, 17) are employed (see Figure S16 in the Supporting Information), thus leading to decreased yields in comparison to the observed conversions (6: 86%, 17: 36%). In contrast to the use of benzaldehyde (11a), in the case of 1-naphthaldehyde (11b) none of the peaks in the chromatogram could be assigned to the desilylated product 14b, thus the effective yields are possibly higher. The isolated yield of 13b after column chromatography is significantly lower (31%, Table 2, entry 2) than that observed during the kinetic measurements (Figure 2d and Table 2, entry 8), but a significant enantiomeric excess of 40% was observed in the first run, which decreased to 10%in a second one (both dichloromethane as solvent, Table 2, entries 2 and 3). If *n*-heptane is used as solvent, an enantiomeric excess of 16% is detected (Table 2, entry 8).

The different behavior of **6** and **7** in the Mukaiyama aldol reaction is consistent with their crystal structures that exhibit completely different pore systems. A filtration test proved the assumed heterogeneity of the reaction mechanism. The framework of all MOF catalysts remains intact on the basis of the powder X-ray diffraction patterns before and after the catalytic reactions, since they do not show significant changes (see Figure S4–S7 in the Supporting Information).

Conclusion

In the present contribution, we describe the successful synthesis of metal-organic frameworks derived from two new chiral organic tricarboxylates of the 4,4',4"-benzene-1,3,5-tribenzoic acid (H₃BTB) family. Two new metal-organic frameworks, [Zn₃(ChirBTB-1)₂] (6) and [Zn₃(ChirBTB-2)₂] (7), were obtained by the reaction of the aforementioned acids with an excess amount of zinc nitrate in diethylformamide. Depending on the nature of the chiral oxazolidinone, either substituted by an isopropyl or by a benzyl group, two completely different framework topologies were observed. The isopropyl-substituted oxazolidinone ligand causes the formation of a structure analogous to that of Cu₃(BTC)₂. Introduction of the benzyl-substituted oxazolidinone, on the other hand, has a striking effect on the crystal structure formed. The $[Zn_3(RCOO)_6]$ nodes identified in the crystal structure of 7 are interconnected by ChirBTB-2 linkers stacked pairwise due to π - π interactions. The crystal structures of 6 and 7 show large pore systems accessible even for large substrates proven by dye adsorption from solution. Compound 6 is even capable of adsorbing the extraordinarily large Reichardt's dye (10) since the pore size is in the mesopore range (2-50 nm). In contrast to this finding, the space in the channels found in the crystal structure of 7 is not sufficient for the adsorption of 10, probably because these channels are occupied by a third of the oxazolidinone moieties. Both MOFs exhibit metal sites accessible for potential substrates, since they are occupied by solvent molecules. These metal sites are surrounded by the chiral oxazolidinone subunits fixed at the BTB linker (see Figures S1 and S2 in the Supporting Information). In the Mukaiyama aldol reactions catalyzed by 6 and 7, enantiomeric excesses of up to 40% were obtained. Thus the preparation of chiral MOF catalysts by the incorporation of auxiliaries known from homogeneous catalysis into linkers not yet established in MOF synthesis has been proven to be successful. Even though the selectivity in these few test reactions was low, the enantioselectivity is a proof of the validity of this new concept. Further development and understanding of linkersubstrate interactions is required for enhancing enantioselectivity and yield.

In summary, we have presented the synthesis of the two new chiral linkers H_3 ChirBTB-1 (**5a**) and H_3 ChirBTB-2 (**5b**) and their successful use for the synthesis of chiral MOF catalysts for asymmetric catalysis. Although compound **6** has the same topology as HKUST-1, slight changes in the oxazolidinone substituent lead to a completely different topology in **7**. The pore systems of both materials are accessible to even large molecules. Both MOFs are active Lewis acid catalysts and show enantioselectivity in the Mukaiyama aldol reaction.

Experimental Section

Synthesis of H_3 ChirBTB-1 and -2: A detailed description of the synthesis route is given in the Supporting Information.

Synthesis and crystal structure of $[Zn_3(ChirBTB-1)_2]$ -3DEF (6): H₃ChirBTB-1 (5a, 85.0 mg 0.104 mmol) and zinc nitrate tetrahydrate (82.0 mg, 0.314 mmol, Merck 98.5%) were dissolved in DEF (2.5 mL). The solution was heated in a Pyrex tube at 100 °C for 20 h. The resulting yellowish crystals were washed with fresh DEF and subsequently exchanged with dichloromethane within three days. The product was further collected by filtration under argon and dried in vacuum at room temperature. Yield: 58 mg (52% referred to the amount of H₃ChirBTB-1). IR: $\tilde{\nu}$ = 658 (w), 725 (w), 769 (w), 798 (m), 825 (w), 850 (w), 877 (w), 976 (w), 1014 (w), 1053 (w), 1082 (w), 1119 (m), 1149 (m), 1236 (m), 1263 (w), 1402 (s), 1433 (s), 1643 (s), 1732 (s), 1761 (s), 2875 (w), 2931 (m), 2960 (m), 2700–3700 cm⁻¹ (br); elemental analysis calcd (%) for $2n_3(ChirBTB-1)_2(DEF)_3(H_2O)_5.^{128}$ C 56.7, H 5.76, N 5.67, O 23.0, Zn 8.82; found: C (56.2±0.2), H (5.98±0.09), N (5.72±0.07), O (23.5±0.4), Zn (8.35±0.03).

Crystal data: Zn₃(C₄₅H₄₂O₁₂N₃)₂·3 C₅H₁₁NO; M_r =2133.27 gmol⁻¹; cubic, F432 (no. 209); a=47.515(2) Å; V=107271(9) Å³; Z=16; ρ_{calcd} = 0.527 gcm⁻³; synchrotron λ =0.88561 Å; T=20°C; θ_{max} =32.30°; reflections collected/unique 71285/8014; R_{int} =0.0534, R_1 =0.0686, wR_2 = 0.2214; Flack parameter x=-0.13(2); largest diff. peak and hole: 0.397 and -0.895 eÅ⁻³.

Synthesis and crystal structure of $[Zn_3(ChirBTB-2)_2]$ -2DEF (7): H₃ChirBTB-2 (5b, 75.3 mg, 0.078 mmol) and zinc nitrate tetrahydrate (61.5 mg, 0.236 mmol, Merck 98.5%) were dissolved in DEF (2.1 mL). The solution was heated in a Pyrex tube at 100 °C for 20 h. The resulting yellowish crystals were washed with fresh DEF and subsequently exchanged with dichloromethane within three days. The product was fur-

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ther collected by filtration under argon and dried in vacuum at room temperature. Yield: 64 mg (71 % referred to the amount of H₃ChirBTB-2). IR: $\tilde{\nu} = 656$ (w), 700 (m), 729 (m), 756 (m), 796 (m), 825 (m), 864 (w), 1001 (w), 1038 (m), 1082 (m), 1115 (m), 1144 (s), 1240 (m), 1265 (m), 1311 (m), 1400 (s), 1435 (s), 1456 (s), 1498 (m), 1552 (m), 1614 (s), 1657 (s), 1734 (s), 1763 (s), 2912 (m), 2978 (w), 3028 (w), 3062 (w), 3086 (w), 2700–3700 cm⁻¹ (br); elemental analysis calcd (%) for Zn₃(ChirBTB-2)₂-(DEF)₂(H₂O)₃.^[31] C 62.7, H 4.75, N 4.72, O 19.5, Zn 8.26; found: C (62.6±0.5), H (4.97±0.05), N (4.82±0.08), O (19.2±0.2), Zn (7.92±0.04).

Crystal data: Zn₃(C₅₇H₄₂O₁₂N₃)₂2 (C₅H₁₁NO); M_r =2320.38 gmol⁻¹; tetragonal, *P*4₃2₁2 (no. 96); *a*=28.3927(4), *c*=20.3756(3) Å; *V*= 16425.7(4) Å³; *Z*=4; ρ_{calcd} =0.920 gcm⁻³; synchrotron λ =0.88561 Å; *T*= 20°C; θ_{max} =28.41°; reflections collected/unique 38101/10603; R_{int} = 0.0561, R_I =0.0963, wR_2 =0.2580; Flack parameter *x*=-0.09(2); largest diff. peak and hole: 0.085 and -0.011 e Å⁻³.

CCDC-735821 (6) and 735822 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Dye adsorption from solution: Freshly prepared samples of **6** and **7**, respectively, were transferred to concentrated solutions of fluorescein (**8**) in DEF/CH₂Cl₂, merocyanine **9** in DEF/MeOH, and Reichardt's dye (**10**) in CH₂Cl₂. After several days, the crystals were washed with fresh DEF to remove dye molecules not soaked into the MOF.

To determine the amount of adsorbed **10**, sample **6** was placed in a solution of dye in CH_2Cl_2 for 6 d and washed thoroughly with CH_2Cl_2 (see Figure S7 in the Supporting Information). The resulting dye@MOF was subsequently hydrolyzed with aqueous HCl. The ¹H NMR of the hydrolyzed MOF shows a ratio of 2:1 (linker/dye) (see Figures S13 and S14).

Performance of Mukaiyama aldol reactions: The Mukaiyama aldol reactions were performed by using 6 and 7 as catalysts, as well as by applying MIL-101 (17), MOF-177 (16), and $[Zn(NO_3)_2(H_2O)_4]$ (15) as reference catalysts. The amount of catalyst employed was calculated in a way that 15 mol% accessible metal centers were present in reference to the amount of benzaldehyde (11a) or 1-naphthaldehyde (11b). Since 6 and 7 cannot be generated in a solvent-free manner, these materials were treated in the following way prior to use. Freshly prepared samples of 6 and 7 were washed with fresh DEF and treated with absolute ethanol to exchange the occluded high-boiling solvent DEF with a solvent miscible with *n*-heptane. The mass of the MOF samples was determined using a pycnometer and the ethanol was replaced by dry n-heptane three times. The other catalysts were treated as described in the supplementary part. After transferring the respective catalyst to the reaction vessel, dry nheptane (10 mL) was introduced. Under stirring at room temperature, benzaldehyde (319 mg, 11a, 3 mmol) or 1-naphthaldehyde (469 mg, 11b, 3 mmol), respectively (each freshly distilled), and silvl enol ether (1.046 g, 12, 6 mmol) were added. The reaction was monitored by GC-MS analysis using n-octane as standard. For the determination of the isolated yields of 13a and 13b, the reaction was conducted in dichloromethane and the reaction mixture was filtered through a short pad of silica (pretreated with NEt₃), washed with EtOAc, and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica pretreated with NEt₃). The results of the catalytic test reactions are summarized in Table 2.

For the filtration test, the addition of the enol ether 12 to 11a with 6 was run again in the presence of mesitylene as an internal standard and the MOF was removed by filtration after 18 h. The ratio of product (13a) to standard was measured directly after the filtration, after 30 h, 54 h and 7 d by means of GC-MS. No more product was formed after filtration.

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