

A novel chiral porous metal–organic framework: asymmetric ring opening reaction of epoxide with amine in the chiral open space†

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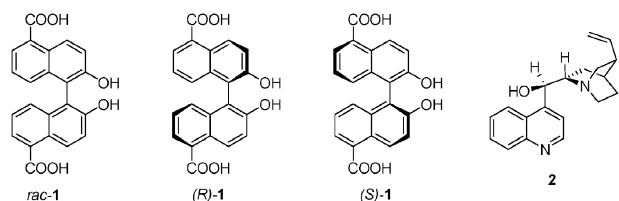
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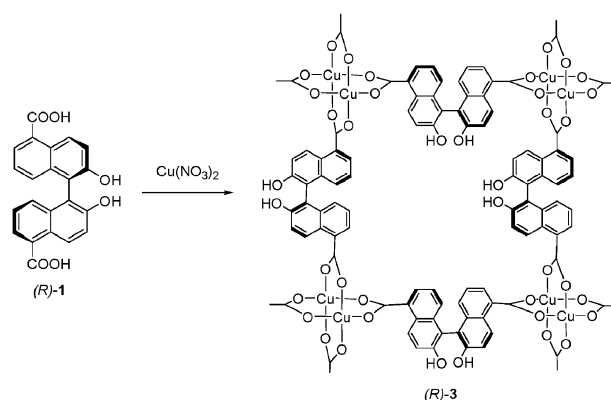
A novel chiral metal–organic framework, $[\text{Cu}_2(5,5'\text{-BDA})_2]$ was synthesized by treating chiral 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid (5,5'-H₂BDA) with a Cu(II) ion, in which the asymmetric ring opening reaction of an epoxide with amine proceeds efficiently under solvent-free conditions.

The field of metal–organic frameworks (MOFs) has grown explosively in recent years¹ and numerous studies have been reported owing to their potential applications in gas storage,² separation³ and heterogeneous catalysis.⁴ While a large number of MOF are being discovered, so far only a few examples of chiral MOF for enantioselective separations or heterogeneous asymmetric catalysis have been investigated.⁵ For example, Lin *et al.* reported the enantioselective addition of diethylzinc to 1-naphthaldehyde catalysed by a Ti modified chiral MOF under heterogeneous conditions in high ee. Here, we wish to report the synthesis of a novel chiral porous metal–organic framework (**3**) through the reaction of C₂-symmetric 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid (**1**) and a Cu(II) ion and its function as a chiral heterogeneous catalyst for the asymmetric ring opening reaction of an epoxide with amine.



The enantiopure ligand, 5,5'-H₂BDA (**1**) was prepared by optical resolution of *rac*-**1**⁶ through complexation with cinchonidine. When a solution containing a 1 : 2 mixture of *rac*-**1** and cinchonidine (**2**) in MeOH was kept at room temperature, a 1 : 2 complex of (*R*)-**1** of 91% ee and **2** was obtained as colorless prisms. Recrystallization of the complex from MeOH gave almost pure 1 : 2 complex crystals, which upon decomposition with dil. HCl afforded (*R*)-**1** of >99% ee in 35% yield. The absolute configuration of (*R*)-**1** was determined,

referred to that already known of **2**, by X-ray analysis of the 1 : 2 complex.† From the MeOH solution left after the separation of the complex crystals, (*S*)-**1** of 74% ee was obtained. (*S*)-**1** (74% ee) was then mixed with 1,4-diazabicyclo[3.3.3]octane (DABCO) in MeOH to give a 1 : 1 complex of *rac*-**1** and DABCO. From the filtrate left after separation of the complex, (*S*)-**1** of >99% ee was obtained in 32% yield.



Treatment of enantiopure 5,5'-H₂BDA (*R*)-**1** with Cu(NO₃)₂ in aqueous MeOH solution by slow diffusion of *N,N*-dimethylaniline at room temperature for several days afforded $[\text{Cu}_2(5,5'\text{BDA})_2(\text{H}_2\text{O})_2] \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}$, (*R*)-**3**, as green needles in 33% yield. Similarly, (*S*)-**3** was also prepared using (*S*)-**1**. The product was characterized by IR and CD spectroscopy, thermogravimetric analysis (TGA), and finally X-ray analysis. The IR spectra of **3** exhibited peaks of νOH at 3367 and νCO₂⁻ at 1610 cm⁻¹, respectively. The enantiomeric nature of (*R*)- and (*S*)-**3** in the solid state was demonstrated by solid-state CD spectra, which showed almost mirror image of each other (Fig. 1).

A single crystal X-ray diffraction study revealed that (*R*)-**3** is formulated as $[\text{Cu}_2(5,5'\text{BDA})_2(\text{H}_2\text{O})_2] \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}$ which crystallized in a space group *P*2₁(#4).§ (Fig. 2) In (*R*)-**3**, each Cu(II) ion is coordinated by four carboxylate oxygen atoms of (*R*)-**1** and each pair of Cu(II) ions is bridged by four carboxylate groups to form 2D dinuclear square grid coordination networks with a Cu...Cu distance of 15.62(2) Å; the void space is filled by one MeOH and two H₂O guest molecules through hydrogen bonding. The 2D square grids stuck to form layers along the *b*-axis. (Fig. 3) Thermogravimetric analysis (TGA) of (*R*)-**3** showed that 19.5% of its mass is lost in the temperature range 25–120 °C, corresponding to the loss of all solvent molecules per formula unit. N₂ adsorption

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† Electronic supplementary information (ESI) available: Optical resolution of **1**, synthesis of **3** and general procedure for the asymmetric ring-opening reaction of epoxide, and Fig. S1–S4. See DOI: 10.1039/b714083e

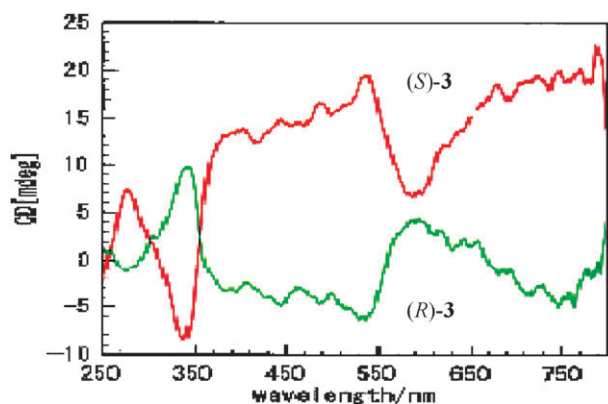


Fig. 1 CD spectra of (*R*)- and (*S*)-3 as Nujol mulls.

measurements indicated that an evacuated sample of (*R*)-3 had BET surface area of $1.71 \text{ m}^2 \text{ g}^{-1}$.

X-ray powder diffraction (XRPD) patterns for (*R*)-3 are shown in Fig. 4. After removal of the guest MeOH and water *in vacuo*, the crystalline (*R*)-3 changes to an amorphous solid. Interestingly, however, the evacuated solid (*R*)-3 readily adsorbs the guest MeOH and water to form the original crystalline phase upon exposure to their vapours.

The catalytic activity of (*R*)-3 toward asymmetric ring opening reactions of epoxides with aromatic amines was examined. (Table 1) For example, when a solution of a mixture of cyclohexene oxide (**4a**), aniline (**5a**) and 0.05 equiv. of evacuated (*R*)-3 was stirred at 25°C for 48 h in toluene, an optically active β -amino alcohol (**6a**) of 40% ee was obtained in 47% yield. Similarly, cyclopentene oxide (**4b**) reacted with **5a** to give an optically active **6b** of 43% ee in 15% yield. After the experiments, the crystals of (*R*)-3 were recovered by simple filtration and reused in the next cycles of the reaction without appreciable loss of reactivity and enantioselectivity. It is interesting to note that remarkable improvements both in the reactivity and enantioselectivity were achieved when the

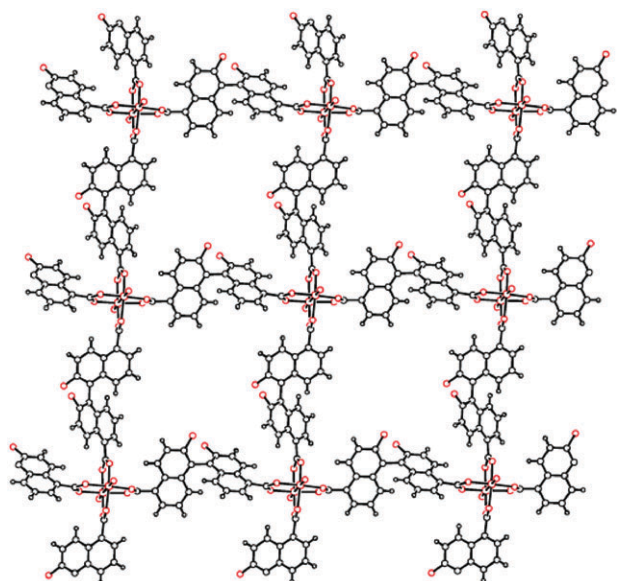


Fig. 2 2D chiral open framework of (*R*)-3 viewed down the *b*-axis. (all the solvent molecules are omitted for clarity).

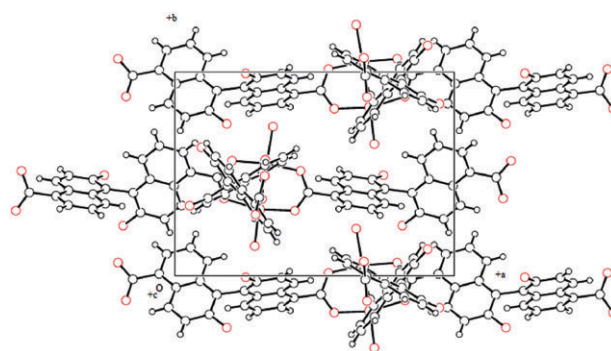


Fig. 3 Crystal structure of (*R*)-3 viewed down the *c*-axis.

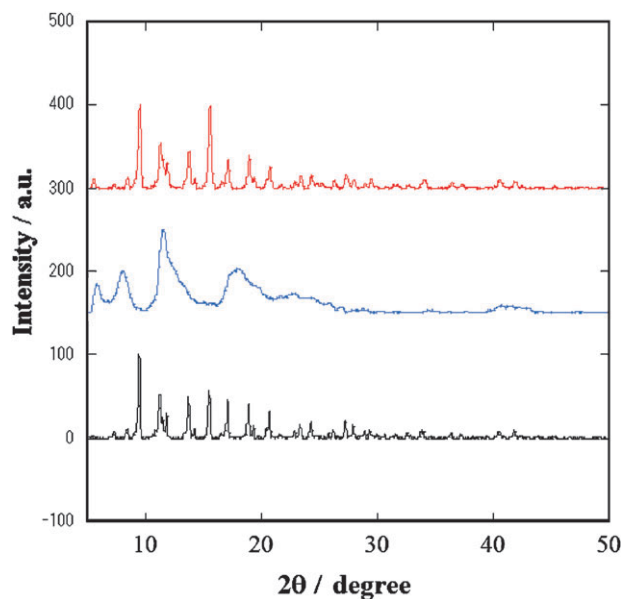
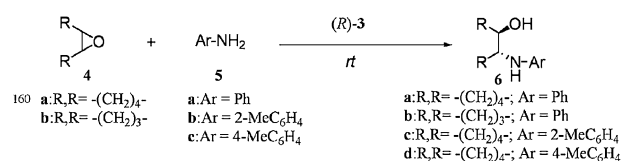


Fig. 4 XRPD patterns of (*R*)-3 before (bottom) and after (middle) the removal of guest methanol and water and after exposure of evacuated solid to methanol and water vapours (top).

Table 1 Asymmetric ring-opening reaction of epoxide with amine



Catalyst	Epoxide	Amine	Solvent	Time/h	Yield (%) ^a	Ee (%) ^a
(<i>R</i>)-3	4a	5a	Toluene	48	54	45
(<i>R</i>)-3	4b	5a	Toluene	48	15	43
(<i>R</i>)-3	4a	5a	None	24	51	51
(<i>R</i>)-3	4b	5a	None	24	30	50
(<i>S</i>)-BINOL ^b	4a	5a	None	24	3	2
(<i>S</i>)-BINOL	4b	5a	None	24	1	0
(<i>R</i>)-3	4a	5b	None	24	3	2
(<i>R</i>)-3	4a	5c	None	24	13	0

^a Determined by HPLC. ^b 2,2'-Dihydroxy-1,1'-binaphthalene.

reaction was carried out under solvent-free conditions. For example, the reaction of **4a** with **5a** without using toluene afforded **6a** of 51% ee in 51% yield. Similarly, **4b** was converted to **6b** in 30% yield and 50% ee under solvent-free conditions. In contrast, when the reaction was performed using (*S*)-BINOL as catalyst instead of (*R*)-**3**, no reactivity and enantioselectivity were observed (Table 1). It was also found that the reaction is very sensitive to the structure of nucleophile. In this case of the reactions between cyclohexene oxide (**4a**) and *o*- (**5b**) or *p*-methylaniline (**5c**) under the same conditions, the conversion as well as the enantioselectivity dropped dramatically.

In summary, a novel chiral metal–organic framework has been synthesized and structurally characterized. In the presence of the chiral metal–organic framework, asymmetric ring opening reactions of epoxides with amines proceeded to give optically active β -amino alcohols under solvent-free conditions. Continued efforts to apply this strategy to other asymmetric reactions are presently under way.

Notes and references

† X-ray single crystal diffraction data for (*R*)-**1**·**2** was collected on a Rigaku RAXIS RAPID imaging plate diffractometer using Cu K α radiation. Crystal data: formula C₆₂H₇₄N₄O₁₄, formula weight 1099.28, space group *P*2₁2₁2(#18), *a* = 13.7716(6), *b* = 15.0164(7), *c* = 15.8042(8) Å, *V* = 3268.3(3) Å³, *Z* = 2, ρ = 1.117 g cm⁻³, $2\theta_{\max}$ = 136.5°, *R*1 = 0.1250 (calculated on *F*² for 2503 reflections with *I* > 2 σ (*I*)), *wR*2 = 0.3256 (calculated on *F* for 3303 reflections), GOF = 1.066. The structure was solved by SHELXS97⁷ and refined by SHELXL97⁸. The molecule of **1** lies on a 2-fold axis in the crystal. The absolute configuration of **1** was determined based on that of **2**. CCDC 660911. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714083e

§ X-ray single crystal diffraction data for (*R*)-**3** was collected on a Rigaku RAXIS RAPID imaging plate diffractometer using Mo K α radiation. Crystal data: formula C₄₅H₃₆Cu₂O₁₉, formula weight 1007.86, space group *P*2₁(#4), *a* = 15.620(5), *b* = 11.377(4), *c* = 15.620(5) Å, β = 94.88(5)°, *V* = 2766(2) Å³, *Z* = 2, ρ = 1.210 g cm⁻³, $2\theta_{\max}$ = 50.0°, *R*1 = 0.0745 (for 6750 reflections with *I* > 2 σ (*I*)), *wR*2 = 0.1946 (for 8263 reflections), GOF = 1.039, Flack parameter = -0.05(2) (refined using 3212 Friedel pairs). The structure was solved by SHELXS97 and refined by SHELXL97. The absolute configuration was determined based on the Flack parameter. At the first stage of the structure analysis, it was suggested that the unit cell corresponded to C-centered orthorhombic cell and its space group was *C*222₁(#20). After successive trials were failed in the structure determination, we supposed that the compound might be crystallized in merohedrally twinning form with two domains of the space group *P*2₁(#4). The unit cell transformation matrix was 0.5 0.5 0 0 0 1 -0.5 0.5 0 (according to the representation in SHELXL). The structures composed of the two domains related by the matrix of 0 0 -1 0 -1 0 -1 0 0 was successfully solved and refined to *R*1 = 0.0751. The twin fraction at the last stage of the refinement was 0.510(3). CCDC 660912. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714083e

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