Electronic Supplementary Material (ESI) for Analytical Methods

Support Information

Enantioselective Chromatographic Resolution Using A Homochiral Metal–organic Frameworks

Mei Zhang,[a] Xu-Dong Xue,[b] Jun-Hui Zhang,[a] Sheng-Ming Xie,[b] Yan Zhang[b], and Li-Ming Yuan*[a, b]

[a] Department of Chemistry, East China Normal University, Shanghai 200241, P.R. China
[b] Department of Chemistry, Yunnan Normal University, Kunming 650500, P.R. China

1. Chemicals and Reagents. All chemicals were at least of analytical grade. Ultrapure water (18.2 MΩ cm) was obtained from a ELGA LabWater water purification system (UK), Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%), 4,4'-bipyridine (4,4'-bpy, 98%), and D-(+)-camphoric acid (D–Cam, 99%) were purchased from Adamas. $Na_2CO_3 \cdot 10H_2O$, Hexane, dichloromethane (DCM) were from Tianjin Fengchuan Fine Chemical Research Institute (Tianjin, China). For the nine racemates, 1-(9-Anthryl)-2,2,2-trifluoroethanol, 1,1'-bi-2-naphthol, benzoin, and trans-stilbene oxide were obtained from Acros, furoin and troger's base from Aldrich, while 1-(1-Naphthyl)ethanol, 3,5-dinitro-N-(1-phenylethyl)benzamide, and Metoprolol are purchased from Fluka.

2. Instrumentation. The powder X-ray diffraction (PXRD) patterns were obtained with a D/max-3B diffractometer (Rigaku, Japan) using Cu_{ka} radiation. The TGA experiment was performed on a ZRY-1P Simultaneous Thermal Analyzer (Shanghai, China) from room temperature to 700 ℃ at a ramp rate of 10 ℃ min^{-1}. The scanning electron microscopy (SEM) images were recorded on a Philip model XL30ESEMTMP scanning electron microscope at 30.0 kV.

Stainless steel empty column (250 mm long × 4.6 mm i.d.) and 1/3 HP liquid pump were purchased from Alltech (USA). The HPLC system consisted of a LabTech LC600 liquid delivery pump and UV–vis detector (USA). A LabTech HPLC Workstation for the LC system was used to process the chromatographic data. The Auto science AT-330 column heater (± 0.1 ℃) was used to control the column temperature during HPLC separation.

3. Synthesis of 1. 1 was synthesized according to the method of Jian Zhang et al.[s1]. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (0.2217 g), $Na_2CO_3 \cdot 10H_2O$ (0.1449 g), 4,4'-bipyridine (0.0791 g), and D-(+)-camphoric acid (0.1110 g) which in a molar ratio of 1.5:1:1:1 and ultrapure water (8.7244g) were stirred for 20 min in a 23 mL Teflon-lined bomb. Then, the Teflon-lined bomb was heated at 120 ℃ for 2 days. After being cooled to room temperature, transparent colorless crystals were obtained. The crystals were washed thoroughly with distilled water and ethanol and dried at room temperature. The yield is 186 mg. The as-synthesized crystals was characterized by Powder X-ray diffraction (PXRD) spectrometry, thermal gravimetric analysis (TGA), and scanning electronmicroscopy (SEM).

4. Column Packing Procedure for HPLC Measurement. Before packing the column, the as-synthesized **1** was passed through the sample screening (280 mesh) with the help of hexane in order to discard exogenous impurity. According to the conventional high-pressure slurry packing procedure, the dried crystals were suspended in a mixture of hexane and dichloromethane (DCM). Then the suspension was packed into the empty column under 40 MPa for 2 min with hexane/DCM (9:1, v/v) as the slurry solvent. By changing the pressure to press the slurry into the column, the crystals could dispose slowly to get a better packing, then column **MOF** was obtained. Before chromatographic experiments, column **MOF** was equilibrated with hexane/DCM (9:l, v/v) until the baseline stabilized.

5. The van't Hoff equation:[S2]

$$\ln k' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \Phi \qquad (1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

where R is the gas constant, T is the absolute temperature, and Φ represents the column phase ratio.

Reference

[S1] Jian Zhang, Yuan-Gen Yao, Xian-hui Bu. *Chem. Mater.* 2007, 19, 5083–5089.

[S2] M. Maes, F. Vermoortele, L. Alaerts, S. Couck, C. E. A. Kirschhock, J. F. M. Denayer, D. E. De Vos, *J. Am. Chem. Soc.* **2010**, 132, 15277 –15285.

Table S1. Values of column void time, column pressure, k_1' and α for the HPLC separation of troger's base on a column packed with **1** and using hexane/DCM (95:5) as the mobile phase at 30 °C in the flow rate range of 0.5 – 2.5 mL min^{-1}.

Flow rate (mL / min)	Column void time (t_0 / min)	Column pressure (psi)	Retention factor (k_1')	Separation factor (α)
0.5	4.01	42	1.75	1.42
1	2.35	80	2.09	1.38
1.5	1.48	140	2.57	1.36
2	1.11	203	2.70	1.49
2.5	0.89	259	2.82	1.35

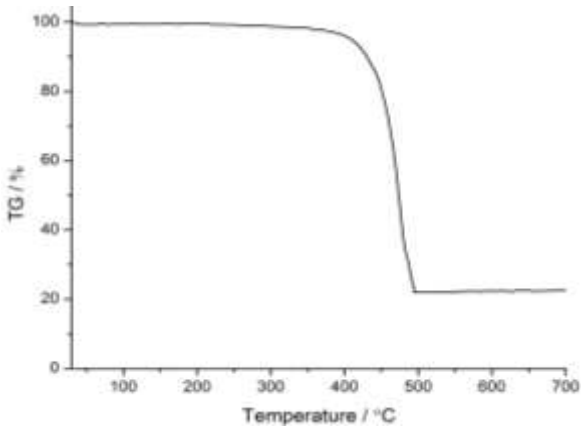

Figure S1. TG curve of **1**

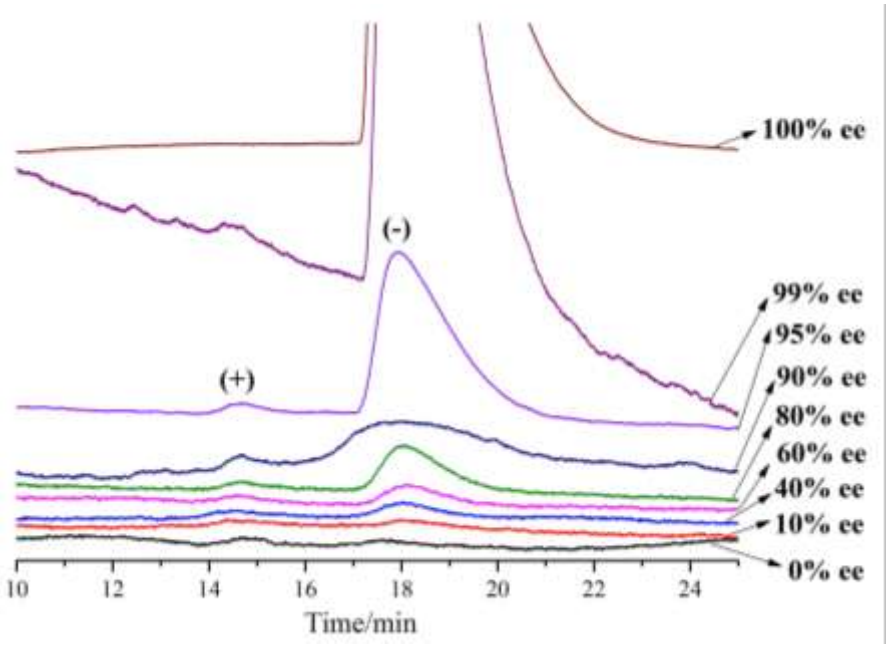

Figure S2. HPLC chromatograms of 1-(1-Naphthyl)ethanol which with different ee values. By using hexane as the mobile phase at a flow rate of 0.4 mL min^{-1}. The signals were monitored with a UV detector at 254 nm.

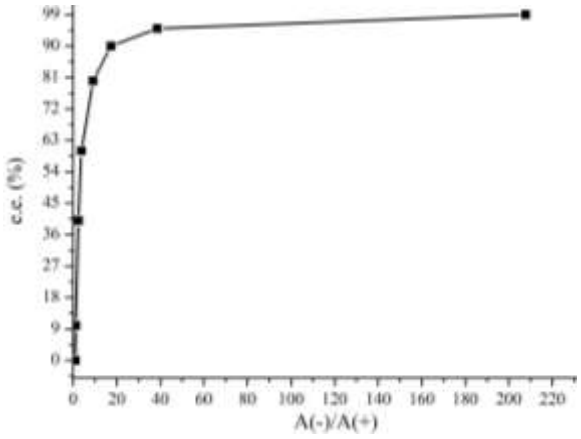

Figure S3. The relationship between ee values of nonracemic (0 – 99 %) and the ratio of peak area for two enantiomers.

Figure S4. Gridlike homochiral 2-D layers in crystal **1**.

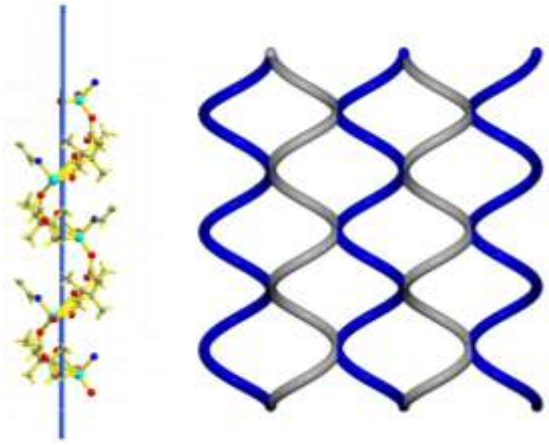

Figure S5. 2_1 helix in homochiral layer structure and the orderly arrangement of left- and right-handed helices.