

A breathing chiral molecular solid for enantioseparation via single-crystal-to-single-crystal transformation

Jun-Liang Liu · Wei Liu · Guo-Zhang Huang ·
Ming-Liang Tong

Received: 20 November 2014 / Accepted: 15 December 2014 / Published online: 23 January 2015
© Science China Press and Springer-Verlag Berlin Heidelberg 2015

Abstract Two chiral supramolecular porous solids derived from novel cluster-based structures of $[\text{Mn}_4^{\text{III}}\text{Mn}^{\text{II}}]$ and $[\text{Mn}_7^{\text{III}}\text{Mn}_3^{\text{II}}]$ were synthesized. Driven by the distinct pores and host–guest interactions, they exhibited either selective gas adsorption ability for the former or the ability of enantioselective separation via reversible single-crystal-to-single-crystal transformation for the latter.

Keywords Manganese(II,III) · Chiral · Supramolecular · Porous solids · Enantioselective separation

1 Introduction

Metal–organic hosts with cavities have provided a feasible way for separating gas or liquid molecules in different sizes [1–5] or resolving racemic compounds [6–15] under mild conditions. Enantioseparation of racemates is a significantly important yet highly challenging topic in the fields of supramolecular chemistry, materials science, and pharmaceutical industries as well [11, 12]. Supramolecular interactions between the host and the guest molecules, e.g., coordinate interaction, hydrogen bonding, and/or π – π interaction, have been well known to play a vital role in

enantioselective separation [7, 13–17]. Pecoraro and co-workers [16, 17] have discussed on how intramolecular and supramolecular interactions play in tandem to achieve effective chiral separation. If the crystals of metal–organic compounds can keep single crystalline after dramatic molecular movement such as guest molecule removal and re-adsorption or ion/solvent exchange, the structural information obtained from the single-crystal-to-single-crystal (SCSC) transformation [5, 10, 13–15, 18–23] may provide direct and clear clues on the processes of enantioseparation. Recently, Cui group [13–15] and Kim group [10] reported the separation of racemic alcohols with the chiral metal–organic compounds.

Herein, we report two chiral manganese molecular solids, $[\text{Mn}_4^{\text{III}}\text{Mn}^{\text{II}}(\text{L1-2H})_2(\text{L1-3H})_2(\text{OAc})_4] \cdot 0.5\text{CH}_3\text{CN} \cdot 8.5\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_7^{\text{III}}\text{Mn}_3^{\text{II}}\text{O}_5(\text{L1-2H})_2(\text{L2-4H})(\text{OAc})_9(\text{H}_2\text{O})] \cdot \text{G}$ (**2**), where $\text{G} = 0.5\text{CH}_3\text{CN} \cdot 3.5\text{H}_2\text{O}$ for **2** ($\supset\text{CH}_3\text{CN}$) (Figs. 1, 2, and S1). The ligands **L1** and **L2** were produced from in situ condensation of 2-hydroxy-5-methyl-isophthalaldehyde and enantiopure 2-hydroxy-propanolamine (*R* or *S*). The similar type of the core topology of compound **1** has been reported previously [24], while compound **2** is novel and unprecedented structures.

Compound **1** has selective gas adsorption toward CO_2 and exhibits a typical ferroelectric property, while compound **2** can enantioselectively absorb racemic 2-butanol with the enantiopure alcohols intercalating in the channels via a reversible SCSC transformation, which is characterized by single-crystal X-ray diffraction. The abundant hydrogen bonds (HBs) existed within the channels, which leads to a chiral and hydrophilic environment, are important for enantioseparation. Furthermore, the single crystals of **2** are stable enough to undergo several desorption–absorption cycles. From that point, the breathing solid can be a potential candidate for chiral resolution.

Electronic supplementary material The online version of this article (doi:10.1007/s11434-015-0728-9) contains supplementary material, which is available to authorized users.

J.-L. Liu · W. Liu · G.-Z. Huang · M.-L. Tong (✉)
Key Laboratory of Bioinorganic and Synthetic Chemistry
of Ministry of Education, School of Chemistry and Chemical
Engineering, Sun Yat-sen University, Guangzhou 510275, China
e-mail: tongml@mail.sysu.edu.cn

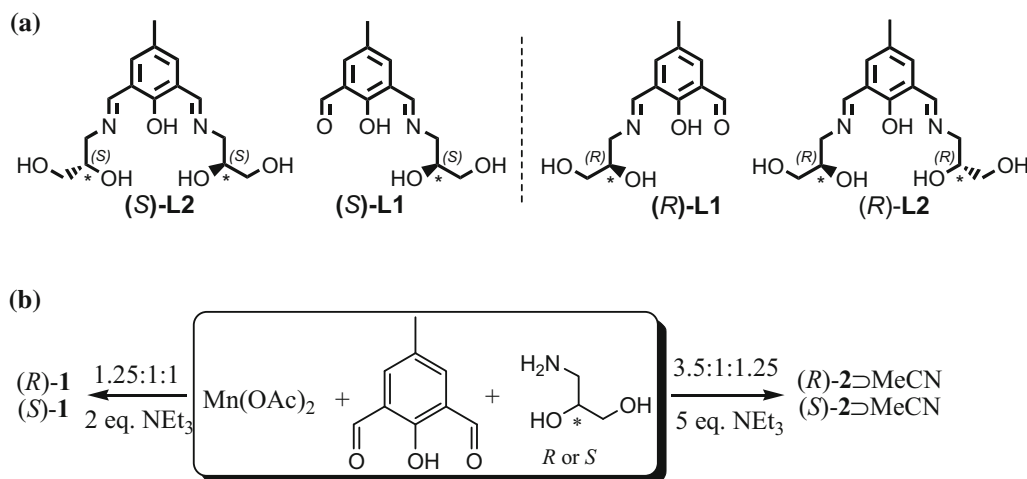


Fig. 1 In situ generated ligands **L1** and **L2** (a) and synthetic routes of **1** and **2** (b)

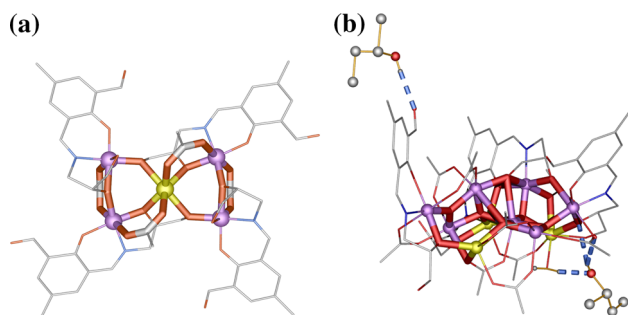


Fig. 2 Structures of *(R)*-**1** (a) and *(S)*-**2** with *(S)*-2-butanol (b). Color code: Mn^{II} yellow, Mn^{III} violet, O red, N blue, C gray. Hydrogen bonds are highlighted as blue dash. H atoms are omitted for clarity

2 Experimental

2.1 Materials and physical measurements

The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range 4,000–400 cm^{-1} with a Bruker-EQUINOX 55 FTIR spectrometer. The powder X-ray diffraction (PXRD) intensities for polycrystalline samples were measured at room temperature on a Bruker D8 Advance diffractometer (Cu $K\alpha$, $\lambda = 1.54056 \text{ \AA}$) by scanning over the range 5° – 60° with step $0.2^\circ/\text{s}$. The calculated patterns were generated with mercury [25]. The gas chromatography–mass spectrometry measurements were taken using a Thermo Finnigan Voyager GC/MS.

2.2 Synthesis

Synthesis of 1: 2-hydroxy-5-methylisophthalaldehyde (0.4 mmol) and 2-hydroxy-propanolamine [*(R)* or *(S)*-,

0.4 mmol] dissolved in CH_3CN (15 mL), and then, the mixture was heated to 75°C for 15 min. It was then added with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol) and triethylamine (0.8 mmol). After stirring for another hour, the solution turned black. Black crystals of **1** were obtained from the filtration in $\sim 60\%$ yield based on Mn. Anal. Calcd. (%) for **1**: N, 3.88; C, 42.17; H, 5.00; Found (%) for *(R)*-**1**: N, 3.75; C, 42.71; H, 5.42. Found (%) for *(S)*-**1**: N, 3.67; C, 42.24; H, 5.24. IR data for **1** (KBr, cm^{-1}): 3,417 s, 2,924 m, 2,861 m, 1,670 s, 1,365 s, 1,548 vs, 1,418 s, 1,324 m, 1,289 m, 1,235 m, 1,047 m, 841 w, 653 w, 621 w, 536 w.

Synthesis of 2 CH_3CN : 2-hydroxy-5-methylisophthalaldehyde (0.2 mmol) and 2-hydroxy-propanolamine (*(R)* or *(S)*-, 0.25 mmol) dissolved in CH_3CN (8 mL) and then covered with cyclohexane (5 mL). The mixture was heated to 50°C for 30 min. It was then added with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.7 mmol) and triethylamine (1.0 mmol). After stirring for another hour, the solution turned black. Black crystals of **2** CH_3CN were obtained from the filtration (CH_3CN only) in $\sim 20\%$ yield based on Mn. Anal. Calcd. (%) for **2** CH_3CN : N, 3.09; C, 34.16; H, 4.03; Found (%) for *(R)*-**2** CH_3CN : N, 2.92; C, 33.67; H, 3.85. Found (%) for *(S)*-**2** CH_3CN : N, 2.99; C, 33.90; H, 4.09. IR data for **2** (KBr, cm^{-1}): 3,406 s, 2,925 m, 1,639 s, 1,563 vs, 1,403 vs, 1,339 s, 1,290 m, 1,235 m, 1,130 m, 1,052 s, 875 w, 661 s, 626 s, 532 m.

SCSC transformation: The enantiopure single crystals of *(R)*-**2** CH_3CN or *(S)*-**2** CH_3CN were immersed into CH_2Cl_2 , 1-butanol/cyclohexane (1:4, v:v), racemic 2-butanol/ CH_2Cl_2 (1:4, v:v), and racemic 2-butanol/cyclohexane (1:4, v:v), respectively, in a sealed vial at 25°C . After ~ 3 days, the single crystals were characterized by single-crystal XRD measurements.

Download English Version:

<https://daneshyari.com/en/article/5789350>

Download Persian Version:

<https://daneshyari.com/article/5789350>

[Daneshyari.com](https://daneshyari.com)