

Synthesis of [Bis(pyridine)salen]Zn^{II}-based Coordination Polymers and Their Application in Enantioselective Separations

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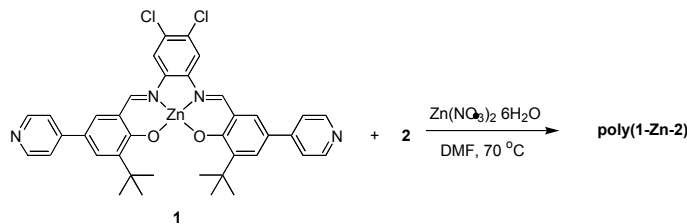
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INTRODUCTION

Coordination polymers were first introduced in the early 1960s¹ and have since been the subject of intensive research.² Versatile synthetic approaches to construct coordination polymers—especially *crystalline* polymers (metal-organic frameworks (MOFs))—from molecular building blocks have been developed and hold promise for eventual industrial applications, especially for gas storage, catalysis, and selective sorptions/separations.³ Of the many potential properties envisioned for these polymeric materials, enantioselectivity is one of the most challenging to incorporate.^{4,5} Along with applications in enantioselective catalysis, applications in enantioselective sorption/separation are often anticipated.^{5,6} Ideally, porous polymeric materials with chiral functionalities along their pores can be utilized to separate a racemic mixture into optically pure compounds. Despite substantial effort in this area, a completely satisfactory demonstration of the synthesis of materials with desired chiral-open pores and application of such materials in enantioselective separations has not yet been realized.

Our laboratory has been investigating the post-synthetic modification of MOFs as a route into optically active materials. Otherwise suitable non-chiral MOFs are synthesized and then modified with chiral moieties to create new MOFs with asymmetric sites. In this context, we envisioned that materials obtained from coordinatively unsaturated non-chiral (salen)Zn^{II} compounds could be post-synthetically modified with a coordinating enantiopure ligand to engender the desired enantioselective behavior. Toward this aim, the complex [bis(pyridine)salen]Zn^{II} (**1**) was combined with biphenyl-4,4'-dicarboxylic acid (**2**) in the presence of Zn^{II}(NO₃)₂·6H₂O to generate a crystalline framework material that was subsequently modified with a chiral pyridine ligand, bis((—)-neomenthyl)pyridine-3,5-dicarboxylate (**3**). Closely related materials, not described here, were also prepared from other ditopic carboxylate-terminated struts and other chiral modifiers. The modified materials hold potential for enantioselective sorption and separation.



EXPERIMENTAL

General Information. All materials were purchased from the Aldrich Chemical Company unless otherwise noted. [1,2-Diamino-4,5-dichlorobenzene-*N,N'*-bis(3-*tert*-butyl-5-(4-pyridyl)-salicylidene)]Zn^{II} (**1**) was synthesized according to a literature procedure with a slight modification⁷ and bis((—)-neomenthyl)pyridine-3,5-dicarboxylate (**3**) was obtained from (—)-menthol via Mitsunobu reaction.⁸ Bis((—)-menthyl)isophthalate (**4**) was synthesized by ester formation between (—)-menthol and isophthalic acid using 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine as reagents. A Perkin Elmer TGA7 thermogravimetric analyzer was used for TGA measurements.

Polymerization of 1. In a 500-mL glass bottle were mixed Zn(NO₃)₂·6H₂O (0.212 g, 1.12 mmol), **1** (0.200 g, 0.280 mmol), **2** (0.136 g, 0.560 mmol), and dimethylformamide (DMF, 150 mL). The bottle was capped and heated at 70 °C in an oven for one week over which time red plate-shaped crystals of **poly(1-Zn-2)** slowly formed. The solids were collected by filtration, washed with DMF (3 × 20 mL), and dried under vacuum for 18 h before ligand modification. Powder X-ray diffraction (PXRD) measurements established that the material is crystalline.

Post-synthetic modification of poly(1-Zn-2) with ligand 3. To a 20-mL glass vial were added the evacuated **poly(1-Zn-2)** (0.2 g), ligand **3** (1.0 g, 2.2 mmol), and toluene (10 mL). The vial was capped and heated at 70 °C in an oven for 18 h. The solids were collected by filtration and washed with toluene (3 × 20 mL) and hexanes (2 × 10 mL) consecutively to give **poly(1-Zn-2)·3** (0.22 g). PXRD pointed to loss of crystallinity upon functionalization.

RESULTS AND DISCUSSION

Under solvothermal synthetic conditions,⁹ MOF **poly-1** can be formed in good yields from a mixture of **1**, **2**, and Zn(NO₃)₂·6H₂O. The polymerization was allowed to run at 70 °C for one week, during which time red, plate-shaped crystalline **poly(1-Zn-2)** MOFs formed. Thermal gravimetric analysis (TGA) reveals that the freshly synthesized **poly(1-Zn-2)** holds ~15% of solvent by weight. The framework itself is stable to ~360 °C (Figure 1).

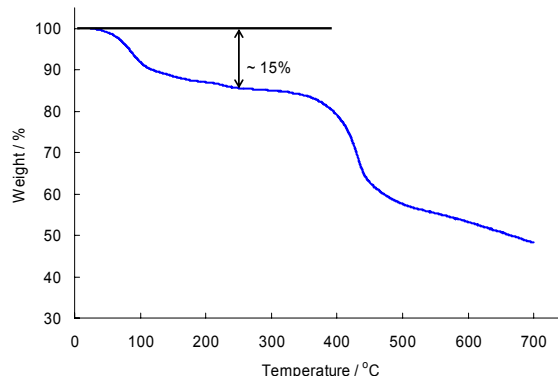


Figure 1. TGA trace for freshly synthesized **poly(1-Zn-2)**.

The functionalization of **poly(1-Zn-2)** with a chiral ligand was attempted by immersing the solid polymer in a toluene solution containing compound **3** at 70 °C overnight. The objective was to axially ligate the available Zn(II) site with ligand **3**.

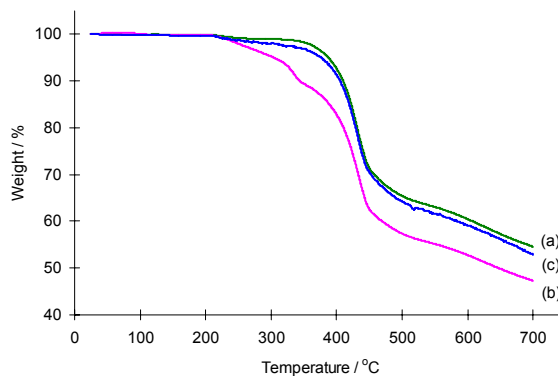


Figure 2. TGA traces for solvent-evacuated (a) **poly(1-Zn-2)**, (b) **poly(1-Zn-2)·3**, and (c) **poly(1-Zn-2)** after being exposed to **4**.

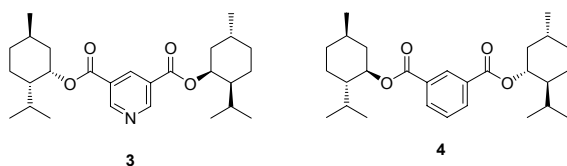


Figure 2 shows the TGA traces for solvent-evacuated forms of naked **poly(1-Zn-2)** and **poly(1-Zn-2)** that has been modified with **3** (**poly(1-Zn-2)•3**) (Figure 2, curves (a) and (b), respectively). Relative to the unmodified polymer, **poly(1-Zn-2)•3** exhibited ~11% weight loss between 200-350 °C. This observed weight loss is tentatively attributed to the liberation of compound **3**. Notably, immersion of **poly(1-Zn-2)** in a toluene solution of **4**, the benzene derivative of **3**, showed no significant evidence for modification of the material, as verified by TGA (Figure 2, curves (c)). The contrasting behavior between **poly(1-Zn-2)** materials that has been exposed to **3** versus **4** underscores the importance of the Lewis acid-Lewis base coordinative interactions in achieving modification with chiral ligands.

The enantioselective sorption/separation ability of **poly(1-Zn-2)•3** was subsequently evaluated using *rac*-2-phenethylalcohol. When a hexanes solution of this racemic substrate was carefully passed through a column packed with **poly(1-Zn-2)•3**, it eluted with up to 36% enantiomeric excess. Similar behavior was seen for closely related framework materials.

CONCLUSIONS

We have demonstrated that non-chiral [bis(pyridine)salen]Zn^{II}-based coordination polymers can be formed and later modified with chiral ligands to impart enantioselective properties. The empty coordination site at the Zn core in complex **1** was essential to carry out the post-synthetic modification successfully. Optimization of the polymer's pore-size and surface area are crucial in the development of materials with higher enantioselectivity. Our preliminary analysis suggests that separation is achieved mainly by interaction of the analyte molecules with the surface of the coordination polymers rather than its interior. The design and synthesis of related materials featuring large, tailorable, substrate-permeable pores is a current objective.

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