

Procedure for preparation of Co/Al coordinated conjugated microporous polymer

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Method Article

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Abstract

Co/Al coordinated conjugated polymers (Co/Al-CMPs) have been synthesized to achieve bifunctional properties, i.e., capture and conversion of CO₂ at room temperature and pressure. Here we report the protocol for synthesizing Co-CMP and Al-CMP.

Introduction

This protocol describes a procedure for preparation of Co/Al-coordinated conjugated microporous polymer (Co-CMP and Al-CMP). The protocol requires four components: Co(OAc)₂, Al(OEt)₃, 1,3,5-triethynylbenzene and Salen [(R,R)-N,N'-bis(5-bromo-3-tert-butyl-salicylidene)-1,2-cyclohexanediaminate]. Co-CMP was synthesised via two steps as follows: First, the Salen-Co-OAc was synthesised by complexation reaction of Co(OAc)₂ and Salen; Second, the Co-CMP was prepared by Pd(0)-catalysed cross-coupling of 1,3,5-triethynylbenzene with Salen-Co-OAc. Al-CMP was synthesised via two steps as follows: We first prepared a CMP by Sonogashira-Hagihara cross-coupling of Salen and 1,3,5-triethynylbenzene in the presence of Pd(0) as a catalyst. The precursor CMP was treated with Al(OEt)₃ in toluene under reflux to obtain the polymer Al-CMP.

Reagents

1,3,5-triethynylbenzene was purchased from Alfa-Aesar. Co(OAc)₂ (anhydrous) was purchased from Alfa-Aesar. Al(OEt)₃ was purchased from Alfa-Aesar.

Equipment

Etelux Lab 2000 glove box standard Schlenk line Magnetic stirrer Soxhlet extraction apparatus

Procedure

A typical example of the synthesis Co-CMP is given below: 1. Synthesis of 5-bromo-3-tert-butyl-2-hydroxybenzaldehyde.² A solution of Br₂ (0.44 ml, 8.45 mmol) in CH₃COOH (2 ml) was added dropwise at room temperature over 30 min to a solution of 3-tert-butyl-2-hydroxybenzaldehyde (1.50 g, 8.41 mmol) in CH₃COOH (5 ml). After 2 hours, the reaction mixture was diluted with CH₂Cl₂ (50 ml) and washed with water (20 ml), saturated aqueous Na₂S₂O₅ (20 ml), saturated aqueous NaHCO₃ (10 ml), and saturated sodium chloride (20 ml). The organic phase was dried with anhydrous Na₂SO₄, and the solvents were evaporated, leaving the target compound as a yellow solid. The crude product was further purified through crystallisation from CH₃OH (10 ml) on an analytically pure sample. 2. Synthesis of Salen.¹ A solution of (R,R)-1,2-diaminocyclohexane (0.48 ml, 4 mmol) in ethanol (60 ml) was placed in a three-neck flask tube (250 ml) maintained under vacuum. The solution was stirred for 30 minutes under an argon atmosphere at ambient temperature. After the reaction solution was added to 80°C, the solution of 5-bromo-3-tert-butyl-salicylidene [(2.056 g, 8 mmol) 5-bromo-3-tert-butyl-salicylidene

dissolved in 10 ml THF] was slowly added to the reaction solution over 30 minutes. The mixture solution was then stirred for 4-5 hours at 80°C, cooled to room temperature and combined with 60 ml of water, after which it was continually stirred at ambient temperature. The insoluble precipitate was filtered and dissolved in ether, and this solution was washed 2-3 times with saturated sodium chloride solution and water to remove any unreacted residues. Removing the solvent yielded a yellow powder, which was dried in a vacuum for 24 hours at 50 °C (yield: 1.91 g, 80.2%).

3. Synthesis of Salen-Co(II).¹ A solution of Co(OAc)₂ (170 mg, 0.96 mmol) in CH₃OH (10 ml) was added to a solution of Salen (400 mg, 0.675 mmol) in toluene (10 ml) under argon with a syringe, resulting in a dark red precipitate. The reaction mixture was heated to 80-85°C and stirred for 5-6 hours, then cooled down to room temperature and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (80 ml) and passed through a Celite pad to remove the excess Co(OAc)₂. Removing the solvent of the filtrate yielded a dark red powder (yield: 390 mg, 89.1%).

5. Synthesis of Salen-Co-OAc.¹ Acetic acid (0.35 ml) was added to a solution of Salen-Co(II) (390 mg, 0.6 mmol) in toluene (6 ml) and CH₂Cl₂ (18 ml). The solution quickly changed from red to brown. After 5-6 hours, all solvents and excess acetic acid were removed, and the residue was dried in a vacuum for 24 hours at 70°C, yielding a brown powder.

6. Synthesis of Co-CMP. 1,3,5-triethynylbenzene (180 mg, 1.2 mmol), Salen-Co-OAc (400 mg, 0.6 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg) and CuI (50 mg) were dissolved in a mixture of toluene (15 ml) and triethylamine (6 ml). The reaction mixture was heated to 40 °C and stirred for 1 hour under an argon atmosphere (to exclude oxygen and prevent any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 80 °C, stirred for 72 hours, then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol and dichloromethane (volume ratio = 1:1) for 48 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (yield: 460 mg, 79.3%).

A typical example of the synthesis Al-CMP is given below:

1. Synthesis of 5-bromo-3-tert-butyl-2-hydroxybenzaldehyde.² same as above

2. Synthesis of Salen.¹ same as above

3. Synthesis of CMP. 1,3,5-triethynylbenzene (300 mg, 2 mmol), Salen (296 mg, 0.5 mmol), tetrakis-(triphenyl phosphine)palladium(0) (120 mg) and CuI (80 mg) were dissolved in a mixture of toluene (10 mL) and Et₃N (5 mL). The reaction mixture was heated to 40 °C and stirred for 1 hour under an argon atmosphere (to exclude oxygen and prevent any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 85°C, stirred for 72 hours, then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with water, dichloromethane, acetone and methanol (volume ratio = 1:1:1:1) for 24 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (yield: 481 mg, 80.8%).

4. Synthesis of Al-CMP. CMP (150 mg) was added to a solution of Al(OEt)₃ (300 mg) in 30 ml toluene, and the suspension was then refluxed for 24 hours. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed four times with dichloromethane, water, methanol, and acetone to remove the unreacted aluminium complex. Further purification of the polymer was carried out using a Soxhlet extraction with water, acetone, dichloromethane and methanol for 24 h.

The product was then dried under vacuum for 24 hours at 70 °C to yield 280 mg of brown powder (Al-CMP) (yield: 280 mg, 62.2%).

Timing

A typical synthesis of Co-CMP requires 8 days. A typical synthesis of Al-CMP requires 7 days.

Troubleshooting

a) During polymerization procedure, the precursor must be stirred for 40min-1hour under 40°C to prevent from the self-polymerization of 1,3,5-triethynylbenzene. Then the temperature was increased to 80-85°C for polymerization. b) Further purification of the polymer carried out by Soxhlet extraction requires 24hours or longer to obtain the polymer with large BET surface.

Anticipated Results

The synthesized Co-CMPs have BET surface ranging from 810-960m²/g. The synthesized Al-CMPs have BET surface ranging from 700-800m²/g.

References

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Figures

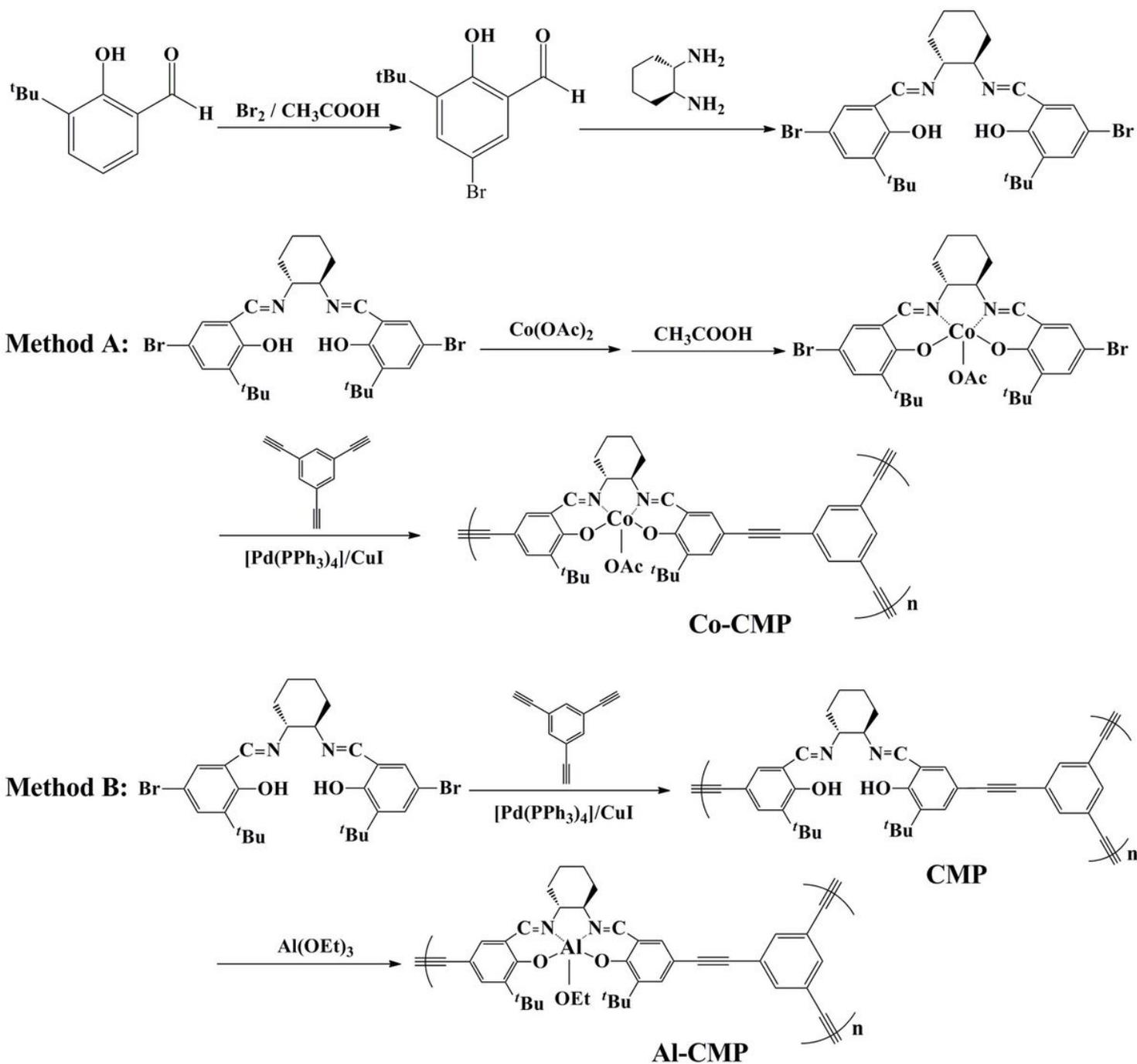


Figure 1

Synthesis of Co-CMP and Al-CMP Synthesis routes for Co-CMP (Method A) and Al-CMP (Method B).