

## **Covalent Organic Polyrotaxanes based on $\beta$ -cyclodextrin towards iodine capture**

Xia Guo,<sup>#a</sup> Jie Yu,<sup>#c</sup> Lianru Ma,<sup>#c</sup> Jingsong Yuan,<sup>c</sup> Taoyan Guo,<sup>c</sup> Yingying Ma,<sup>c</sup>  
Jingkun Bai,<sup>d</sup> Shengshun Xiao,<sup>b\*</sup> Baolong Zhou<sup>c\*</sup>

*<sup>a</sup> School of Mathematics and Statistics, Weifang University, Weifang, 261061, Shandong, PR China*

*<sup>b</sup> Weifang People's Hospital, Shandong Second Medical University, Weifang, 261000 Shandong, PR China.*

*<sup>c</sup> School of Pharmacy, Weifang Medical University, Weifang, 261053, Shandong, PR China*

*<sup>d</sup> School of Bioscience and Technology, Weifang Medical University, Weifang 261053, China*

\*Correspondence author

*E-mail: zhoubaolong@sdsu.edu.cn (B. Zhou)*

## **Contents**

### **Section 1. Experimental Section**

### **Section 2. Removal of iodine from water by $\beta$ -CD.**

### **Section 3. Removal of iodine from hexane by COPRs.**

### **Section 4. Adsorption-elution cycles of COPRs**

### **Section 5. Desorption of COPRs.**

## Section 1. Experimental Section

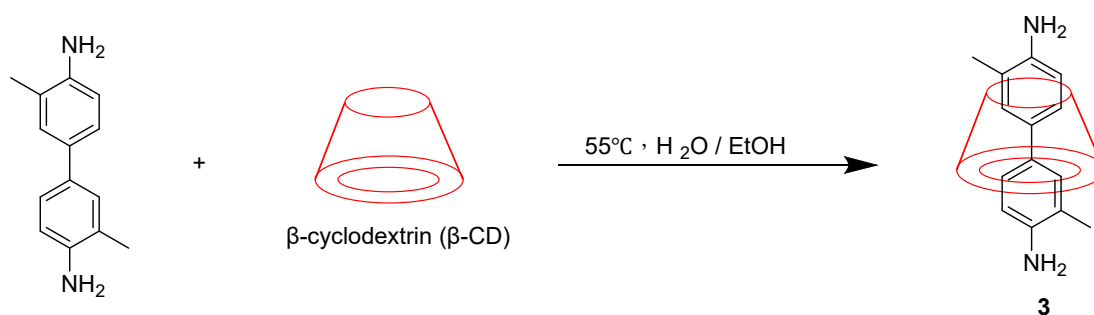
### Materials

All the reagents including the reactants (*e.g.* hexamethylenetetramine, phloroglucinol) and reactants (*e.g.* trifluoroacetic acid, HCl, acetone, tetrahydrofuran and dichloromethane) were purchased from the commercial supplier and directly used without further purifications.

### Characterization

Liquid  $^1\text{H}$  NMR spectra of prepared monomers were recorded on an Avance Bruker DPX 400 (400 MHz) in the solvent of  $\text{D}_2\text{O}$ . The solid-state  $^{13}\text{C}$  CP/MAS NMR of as-synthesized samples were collected on Bruker SB Avance III 500 MHz spectrometer. Fourier Transform Infrared Spectroscopy (FTIR) was performed on KBr pellets in the range from 4000 to 400  $\text{cm}^{-1}$  using Spectrum Spotlingt 400. Thermogravimetric analysis (TGA) were recorded using NETZSCH STA 449C analyzer from 25 to 800  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C min}^{-1}$  under the protection of  $\text{N}_2$ . The morphologies of powder samples were evaluated by field-emission transmission electron microscopy (TEM, Tecnai G2 20 TWIN) via dipping the prepared samples on a Cu-net. X-ray diffraction (XRD) parameters were obtained using a Rigaku-DMAX 2500 diffractometer at a rate of 5 $^\circ \text{min}^{-1}$  from 5 to 80 $^\circ$ .

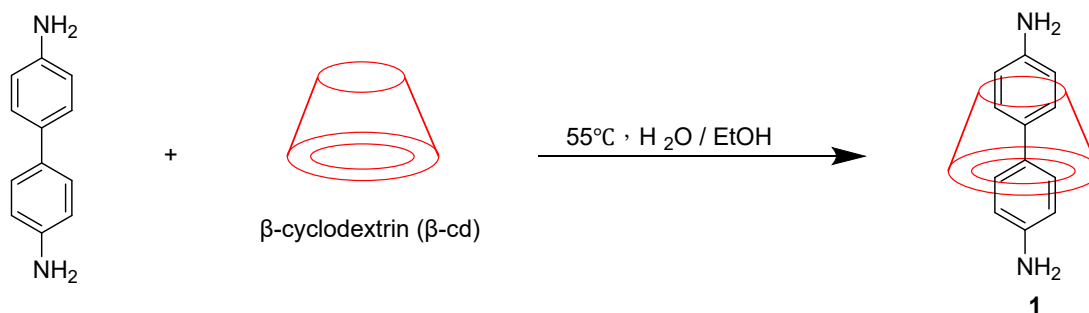
### Synthesis of $\beta$ -CD-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2)<sup>[2]</sup>



$\beta$ -CD (11.347 g 10 mmol) was added to a 500 ml reaction bottle containing 300 ml of distilled water, which was heated until all the  $\beta$ -CD was dissolved. Then, bis-o-toluidine (2.2 g) which was predissolved in 100 mL of ethanol solution, was slowly added dropwise to the bottle and stirred for 5 h at 55 $^\circ\text{C}$ . Afterwards, the solvent was evaporated under reduced pressure. The remaining powder was collected by filtering.

The crude product was recrystallized from water and vacuum dried to give compound **3** (Yield: 70%). <sup>1</sup>H NMR (400 MHz, Deuterium Oxide): δ 7.11 (d, J = 11.1 Hz, 4H), 6.82 (d, J = 7.9 Hz, 2H), 5.00 (s, 7H), 3.66 (ddd, J = 56.4, 13.8, 5.3 Hz, 42H), 2.23 (s, 6H).

### 1.1. Synthesis of β-CD- 4, 4-biphenylenediamine (**1**)



Compound **1** was synthesized similarly to compound **3**. β-CD (11.35 g, 10 mmol) and 300 ml of distilled water were added to a 500 ml three-necked round bottom reaction bottle, which was heated to 55°C until all the CD was fully dissolved. Biphenylenediamine (1.8463 g 10 mmol) which was pre-dissolved in 100 ml of ethanol, was added dropwise to the reaction bottle with stirring for 5 h at 55°C. The crude product was recrystallized from water and dried under vacuum to give compound **1** (74% yield). <sup>1</sup>H NMR (400 MHz, Deuterium Oxide) δ 7.28 (d, J = 7.6 Hz, 4H), 6.87 (d, J = 7.4 Hz, 4H), 4.99 (s, 7H), 3.81-3.45 (m, 42H).

### Synthesis of COPR-1

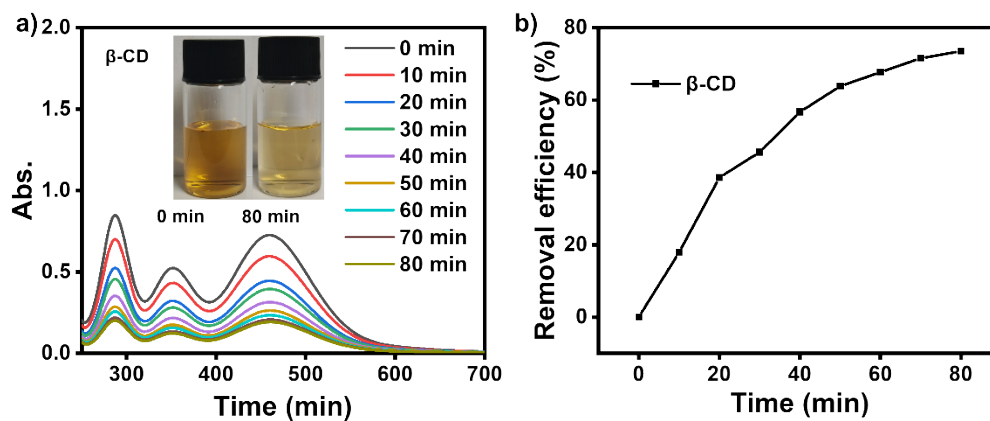
Polymerization of trialdehyde phloroglucinol and β-cyclodextrin p-phenylenediamine inclusion complex: p-benzenesulfonic acid (475.5 mg, 2.5 mmol) and β-cyclodextrin p-biphenylenediamine inclusion compound (598.9 mg, 0.45 mmol) was finely grind in a mortar for 15 min. After grinding, trialdehyde phloroglycerol (63 mg, 0.3 mmol) was added and continued grinding for 15 min. After grinding, the compound was transferred to a Pyrex tube equipped with a magnetic stirrer containing the mixed solvents of mesitylene (1.5 mL), 1, 4-dioxane (1.5 mL), and 3M acetic acid aqueous solution (0.5 mL). The Pyrex tube was ultrasonic treated for 10 minutes, followed by rapid freezing in liquid nitrogen bath, and degassed through three freeze-pump-thawing cycles. After the degassing was completed, the container was sealed and

heated at 120 degrees for 72 hours. After centrifugation and extraction, the brown and black precipitate was collected and cleaned with acetone, tetrahydrofuran and dichloromethane 3-5 times each until the solution was clarified, and the COF was obtained by drying under 100 degrees vacuum for 12 hours.

### **Synthesis of COPR-2:**

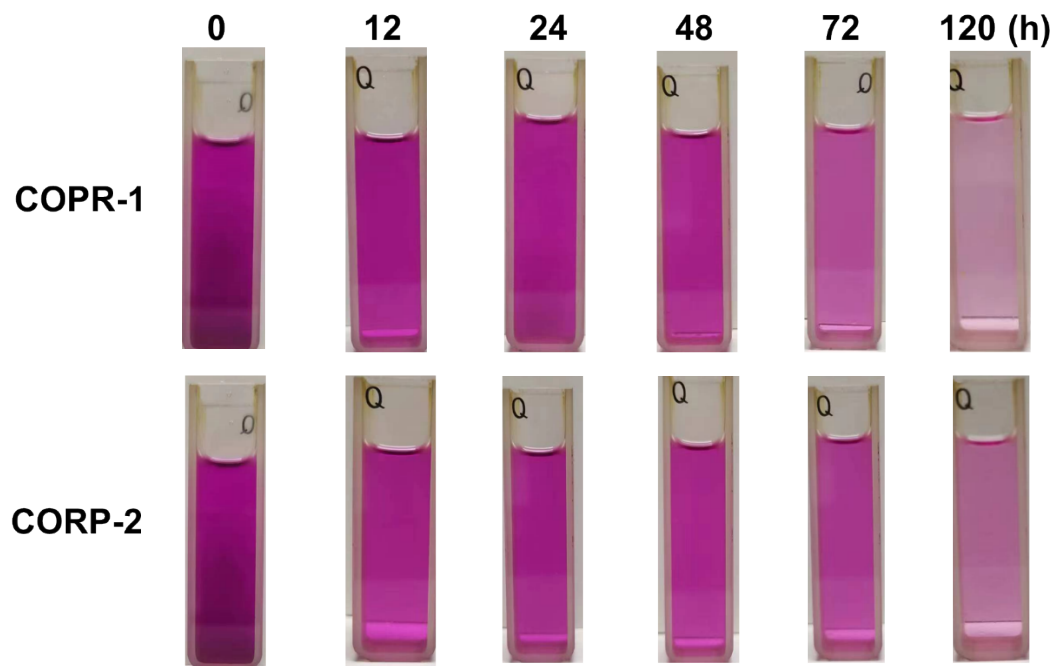
Polymerization of trialdehyde phloroglucinol and  $\beta$ -cyclodextrin o-toluidine inclusion complexes. P-benzoisulfonic acid (475.5 mg, 2.5 mmol) and  $\beta$ -cyclodextrin o-toluidine inclusion compound (606 mg, 0.45 mmol) were finely grind in a mortar for 15 min. After grinding, trialdehyde phloroglycerol (63 mg, 0.3 mmol) was added and the mixture was continued grinding for 15 min. Then, the compound was transferred to a Pyrex tube equipped with a magnetic stirrer, and solvents were added to the container (1.5 mL mesitylene, 1.5 mL 1, 4-dioxane, 0.5 mL 3M acetic acid aqueous solution). The Pyrex tube was treated by ultrasonic for 10 minutes, followed by rapid freezing in liquid nitrogen bath, and degassed through three freeze-pump-thawing cycles. After, the container was sealed and heated at 120 degrees for 72 hours. After centrifugation and extraction, the brown and black precipitate was collected and washed subsequently with acetone, tetrahydrofuran and dichloromethane 3-5 times each until the solution was clarified, and the COF was obtained by drying under 100 degrees vacuum for 12 hours

## Section 2. Removal of iodine from water by $\beta$ -CD.



**Figure S1.** Removal of iodine from water by  $\beta$ -CD.

### Section 3. Removal of iodine from hexane by COPRs.



**Figure S2.** Change in colour of iodine solution in hexane.

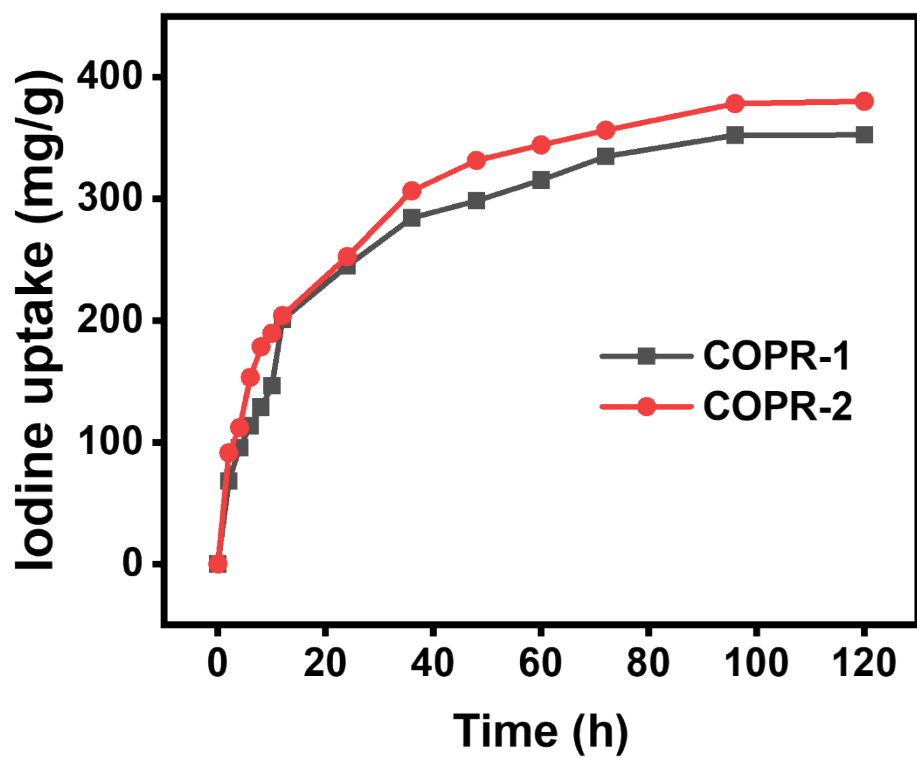


Figure S3. Adsorption monitoring of COPRs in hexane.

#### Section 4. Adsorption-elution cycles of COPRs

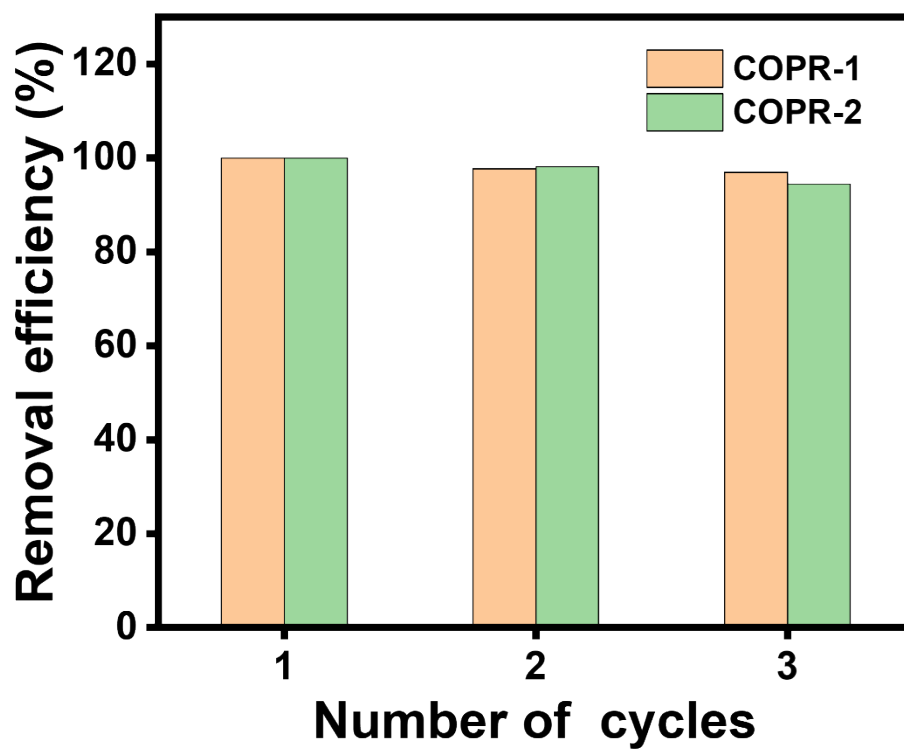


Figure S4. Variation of adsorption of COPRs with the number of cycles.



Section 5. Desorption of COPRs.

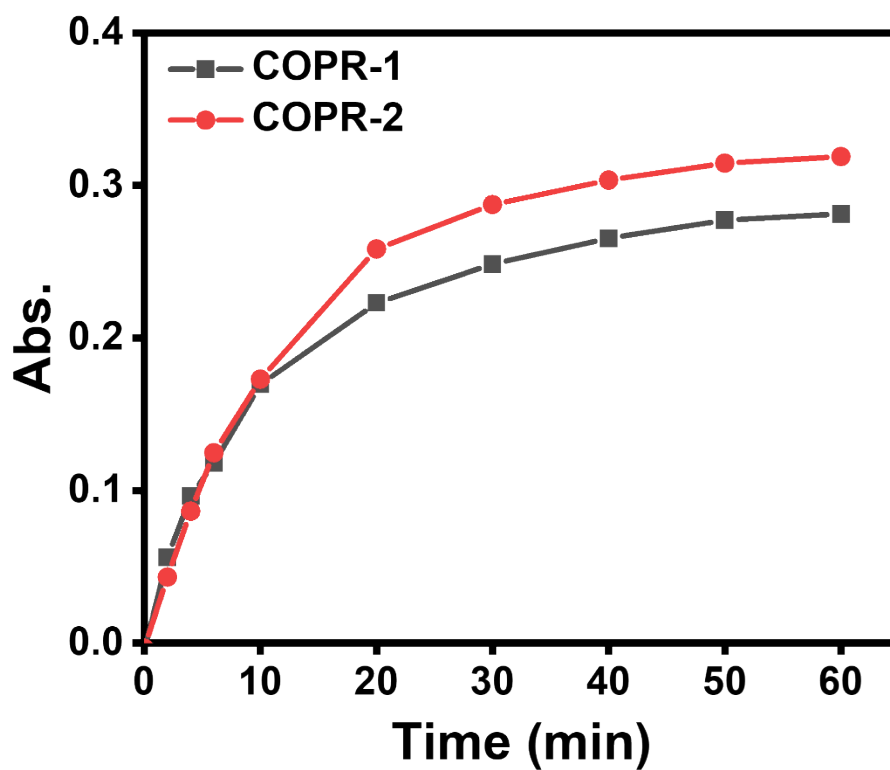


Figure S5. The adsorbent elutes iodine in MeOH.