

## Supporting Information

### Switching of Structural Order in a Cross-linked Polymer Triggered by the Desorption/Adsorption of Guest Molecules

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#### Materials

The carboxylic acid **1** was prepared according to the literature with some modification.<sup>1</sup> The amino alcohols (–)-**2**, (+)-**2**, and (+)-**4** were purchased from Tokyo Chemical Industry and purified by distillation before use. The amino alcohols (–)-**3** and (+)-**3** were prepared from (–)-**2** and (+)-**2**, respectively, according to the procedure in a literature.<sup>2</sup> Diethyl ether was distilled from sodium/benzophenone ketyl before use.

#### Methods

X-ray diffraction (XRD) profiles were obtained with a Rigaku R-Axis IV, using monochromated Cu K $\alpha$  radiation (40 kV, 30 mA). The liquid crystalline salt **1**•(–)-**2** and the cross-linked polymers were transferred to a quartz capillary tube and used for XRD analyses. IR spectra were recorded on a JASCO model FT/IR-480plus. High-pressure liquid column chromatography (HPLC) experiments were performed at 0 °C on a JASCO PU-980 intelligent HPLC pump equipped with a UV-970 intelligent UV/VIS detector: Column, Daicel CHIRALCEL CROWNPAK CR (+) (4.6  $\times$  153mm); eluent, aqueous HClO<sub>4</sub> solution (pH 1.0); flow rate, 0.60 mL min<sup>–1</sup>; detection of **2** and **3**, UV absorption (190 nm); detection of **4**, UV absorption (345 nm) of a derivative formed by the post-column derivatization with *o*-phthalaldehyde.

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1 Smith, R. C.; Fischer, W. M.; Gin, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4092.

2 Colman, B.; de Sausa, S. E.; O'Brien, P.; Towers, T. D.; Watson, W. *Tetrahedron: Asymmetry* **1999**, *10*, 4175.

### Preparation of the cross-linked polymer

A diethyl ether solution (10 mL) of **1** (843 mg, 1.00 mmol) and (–)-**2** (151 mg, 1.00 mmol) was partitioned into three glass tubes (length 100 mm, diameter 20 mm), and the solvent was removed by argon flow and subsequent evaporation under reduced pressure at room temperature to afford the liquid crystalline salt **1**•(–)-**2**.  $^{60}\text{Co}$   $\gamma$ -ray induced polymerization was conducted at room temperature (dose rate, 1.7 kGy h<sup>-1</sup>; irradiation time, 48 h) in evacuated and sealed glass tubes. The irradiated samples detached from the glass tubes were combined, mechanically ground, washed with CHCl<sub>3</sub>, and collected by filtration (Advantec T050A047A PTFE membrane filter, 0.5  $\mu\text{m}$  mesh). In the CHCl<sub>3</sub> washing, only small amounts (<2%) of **1** and (–)-**2** were contained, which was confirmed by an HPLC analysis. The resultant white powder was dried in *vacuo* to give the cross-linked polymer (952 mg, 96%).

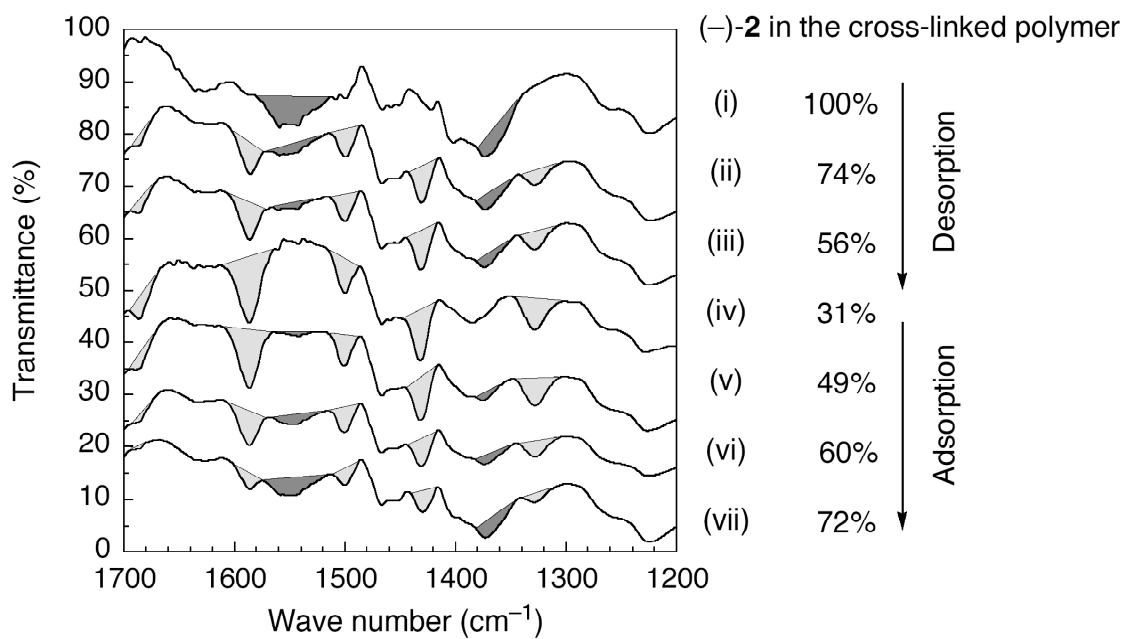
### Desorption of (–)-**2** from the cross-linked polymer

The cross-linked polymer prepared by the above procedure (45.0 mg, calculated to contain 45  $\mu\text{mol}$  of the carboxylic acid–amine pair) was soaked in a mixture of 3.0 M aqueous HCl (2.5 mL) and methanol (2.5 mL) and left to stand at room temperature. The amount of (–)-**2** desorbed from the cross-linked polymer was estimated by an HPLC analysis; a fraction of the supernatant (10  $\mu\text{L}$ ) was directly injected to an HPLC system. The cross-linked polymer was separated from the supernatant by centrifugation (3000 rpm, 3 min). Residual HCl in the solid was removed by repeating the following process twice; the solid was suspended in methanol (5.0 mL) and collected by centrifugation (3000 rpm, 3 min). The cross-linked polymer thus obtained was dried in *vacuo* and used for FT-IR and XRD analyses and re-adsorption experiments.

### Re-adsorption of amino alcohols **2–4** to the apo-polymer

The apo-polymer obtained by the above procedure (35.5 mg, calculated to contain 40 and 12  $\mu\text{mol}$  of the carboxylic acid unit and (–)-**2**, respectively) was soaked in a methanol solution of (–)-**2** (16 mM, 5.0 mL) and left to stand at room temperature. The amount of (–)-**2** adsorbed to the cross-linked polymer was estimated by the HPLC analysis of the supernatant, and the reconstituted polymer was recovered from the mixture by centrifugation, as described for the desorption process. The re-adsorptions of the other amino alcohols, (+)-**2**, (–)-**3**, (+)-**3**, and (+)-**4**, were conducted in the same procedure as that of (–)-**2**.

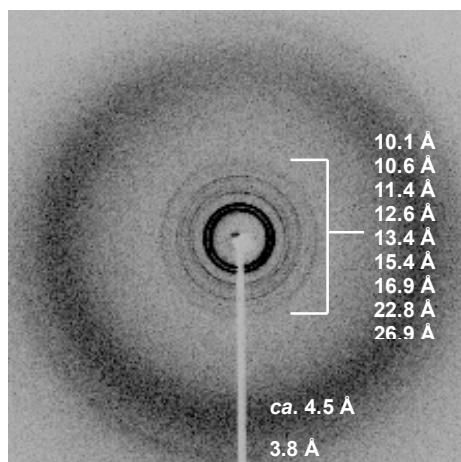
## Changes in FT-IR spectra of the cross-linked polymer through the desorption/adsorption of (–)-2



Dark-shaded and bright-shaded peaks were attributable to the absorption of the ammonium-carboxylate salt and the free carboxylic acid, respectively.

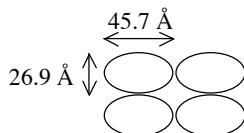
## Two dimensional images of the X-ray diffractions

### (i) Liquid crystalline salt **1**•(–)-**2**<sup>3</sup>



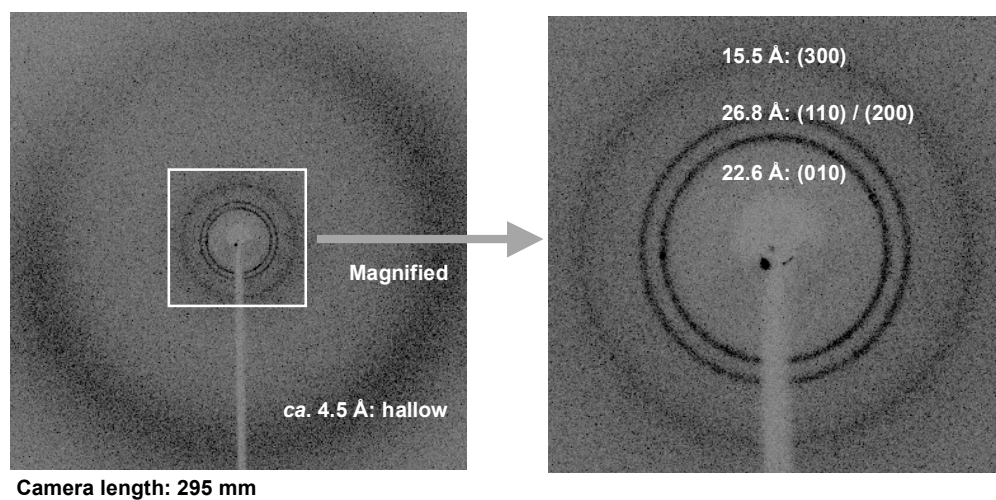
Camera length: 150 mm

mesophase	lattice constant/Å	Miller indices	<i>d</i> -spacing/Å	
			calcd.	found
Col <sub>rec</sub> ( <i>P</i> 2m)	<i>a</i> = 45.7 <i>b</i> = 26.9	(010)	26.9	26.9
		(110)	23.2	22.8
		(200)	22.9	22.8
		(210)	17.4	16.9
		(300)	15.2	15.5
		(020)	13.5	13.4
		(310)	13.3	13.4
		(120)	12.9	12.6
		(220)	11.6	11.4
		(400)	11.4	11.4
		(410)	10.5	10.6
		(320)	10.1	10.1
		(001)	3.8	3.8

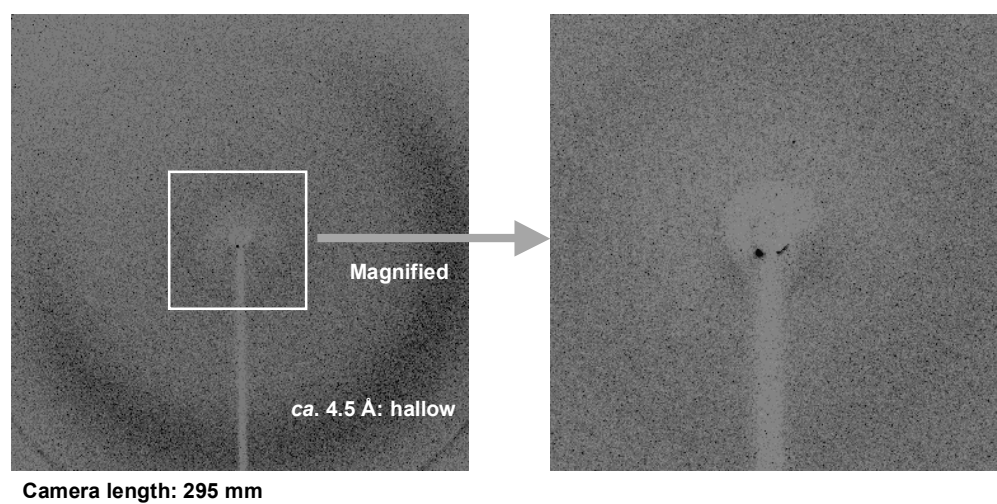


3 For more information about the liquid crystalline salt **1**•(–)-**2**, see: Ishida, Y.; Amano, S.; Saigo, K. *Chem. Commun.* **2003**, 2338 and its supplementary information.

(ii) Cross-linked polymer: initial state



(iii) Cross-linked polymer: after the desorption of (-)-2



(iv) Cross-linked polymer: after the re-adsorption of (-)-2

