

Supplementary Information

Template polymerization of columnar architectures based on the salts of a carboxylic acid and 2-amino alcohols: application to the molecular recognition of 2-amino alcohols

Yasuhiro Ishida,^a Sayaka Amano^b and Kazuhiko Saigo^{*ab}

^a Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

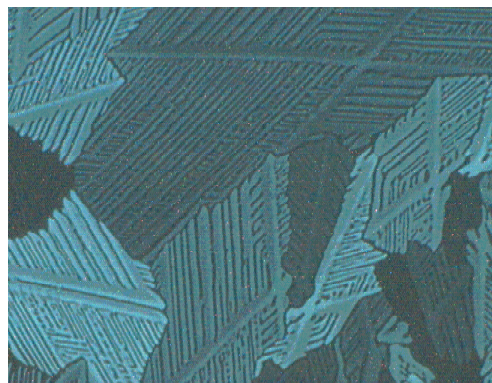
^b Department of Integrated Biosciences, Graduate School of Frontier Sciences, The University of Tokyo, Bioscience Bldg. 702, Kashiwa, Chiba 277-8562, Japan

Optical textures of the salts

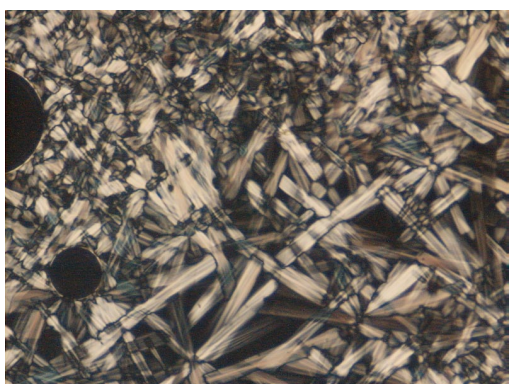
(a) 1·3



(b) 1·(+)-8



(c) 2·(+)-8



Phase behavior of the salts^a

salt	phase transition (°C) and corresponding enthalpy changes (kcal/mol)
1-3	K ₁ 16 (0.30) K ₂ , K ₃ , K ₄ 33, 41, 53 (9.44) ^b LC 105 (0.08) I
1·(-)-4	K ₁ , K ₂ 26, 31 (-1.53) ^b K ₃ , K ₄ 36, 40 (2.37) ^b K ₅ , LC ₁ 54, 65 (9.08) ^b LC ₂ 87 (0.26) I
1·(+)-5	K, LC ₁ 42, 50 (11.26) ^b LC ₂ 83 (0.07) I
1·(-)-6	K ₁ 30 (2.29) K ₂ 35 (-0.57) K ₃ , K ₄ 49, 58 (12.31) ^b I
1·(-)-7	K ₁ 48 (9.60) K ₂ , LC 80 ^c , 91 (4.31) ^b I
1·(+)-8	K ₁ 26 (-0.74) K ₂ 41 (-2.17) K ₃ 57 (2.65) K ₄ 88 (0.31) LC 104 (2.46) I
1·(+)-9	K 63 (8.68) I
1·(-)-10	K 124 (10.09) I
1-11	K ₁ 34 (3.92) K ₂ 66 (0.31) LC 94 (9.51) I
1-12	K ₁ 41 (12.95) K ₂ 64 (1.74) I
1·(-)-13	K ₁ 33 (-2.51) K ₂ 64 (12.6) I
1-14	K ₁ 21 (-0.28) K ₂ 67 (15.99) I
2-3	K 9 (4.23) I
2·(-)-4	K, LC 3, 12 (9.75) ^b I
2·(+)-5	K 4 (8.27) LC 38 (0.84) I
2·(-)-7	K -14 (5.00) ND, LC 19, 26 (1.67) ^b I
2·(+)-8	K -15 (3.32) LC 60 (2.65) I

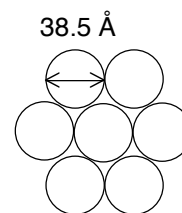
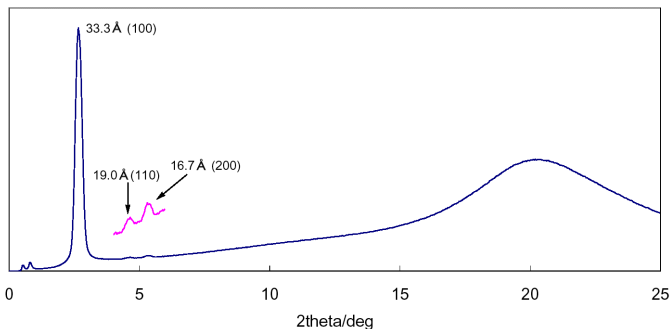
a The transition temperatures (°C) and the enthalpy changes, in parentheses (kcal/mol), were determined during the second heating scan (scan rate 10 °C/min). The designations K, LC, I, and ND represent crystal, liquid crystal, isotropic, and not determined phases, respectively.

b Combined enthalpy changes are represented for overlapped transitions.

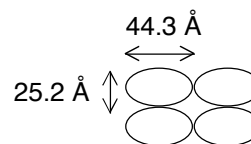
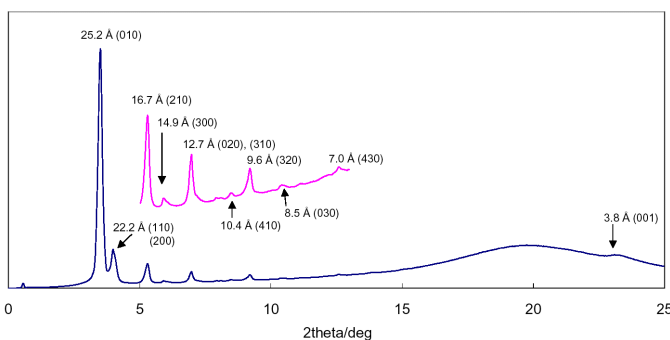
c Transitions determined by optical microscopy.

Powder X-ray diffraction patterns of the salts

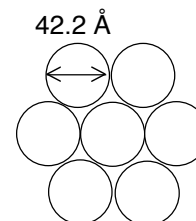
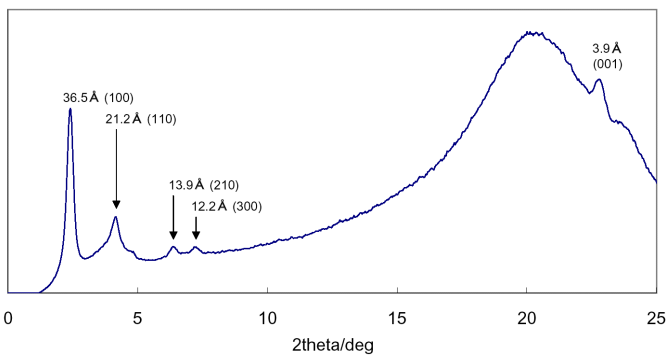
(a) **1·3** (at 70 °C)



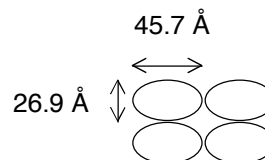
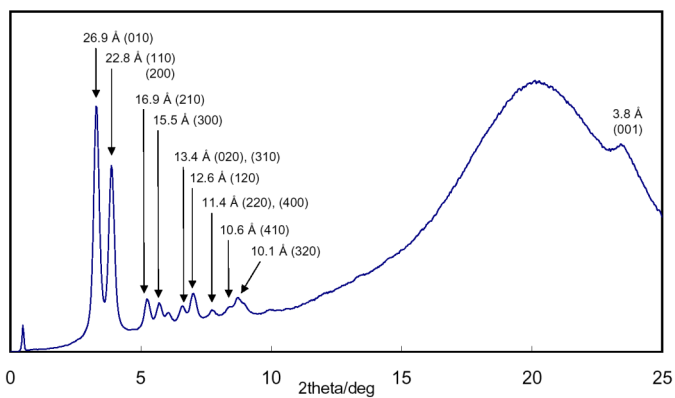
(b) **1·(+)-8** (at 90 °C)



(c) **2·(+)-5** (at 25 °C)



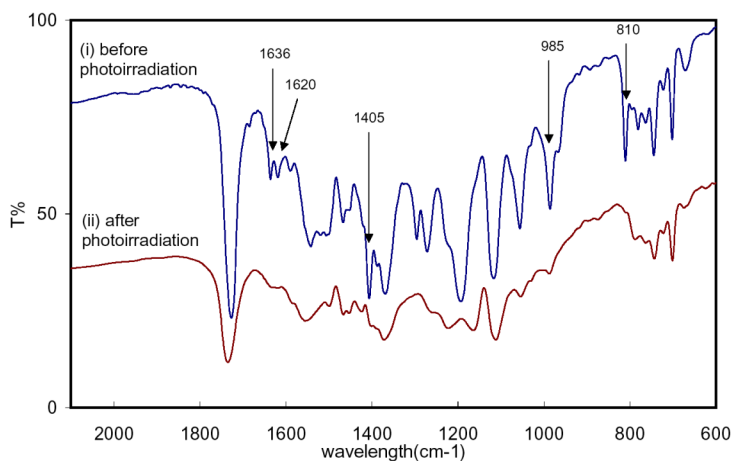
(d) **2·(+)-8** (at 40 °C)



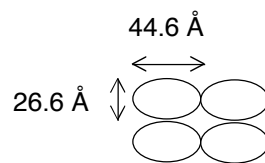
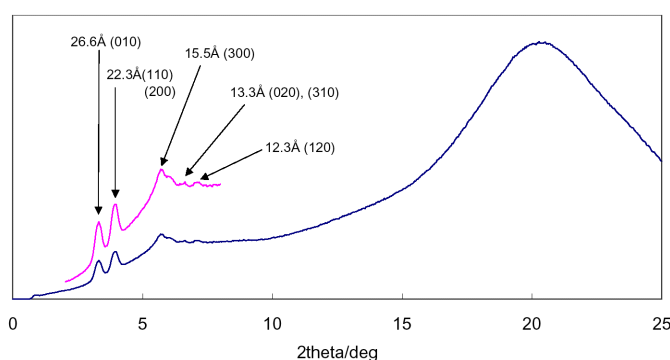
Cross-linking of 2·8

The salt of **2** with (+)-**8** (102.0 mg, 103 μmol), and 2-hydroxy-2-methylpropiophenone (2.3 mg, 13.8 μmol) were dissolved in distilled chloroform (1.0 mL), and the solvent was removed from the mixture under reduced pressure. The residual oil was placed on a quartz plate and irradiated with > 300 nm light (500 W high-pressure mercury lamp) under argon at 16 $^{\circ}\text{C}$ for 48 h to afford a hard insoluble film. The extent of the polymerization was confirmed by the loss of the olefinic bands in the IR spectrum. The sample was detached from the quartz plate, milled, and washed successively with methanol and chloroform. The resulting solid was dried in *vacuo* to afford cross-linked **2·(+)-8** as a white powder (88.8 mg). The retention of the LC phase architecture was confirmed by comparing the X-ray diffraction profiles of the samples before and after the photoirradiation.

(a) IR spectra of **2·(+)-8** before (i) and after (ii) the photoirradiation



(b) X-ray diffraction patterns of **2·(+)-8** after the photoirradiation

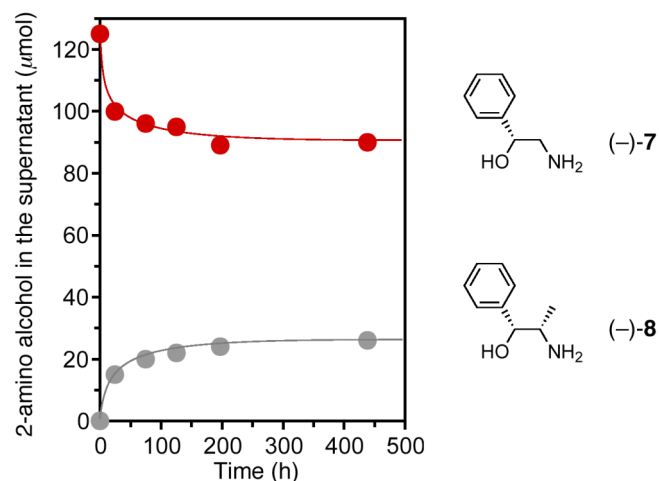


The exchange reaction of the amine units of the cross-linked 2·(-)-8

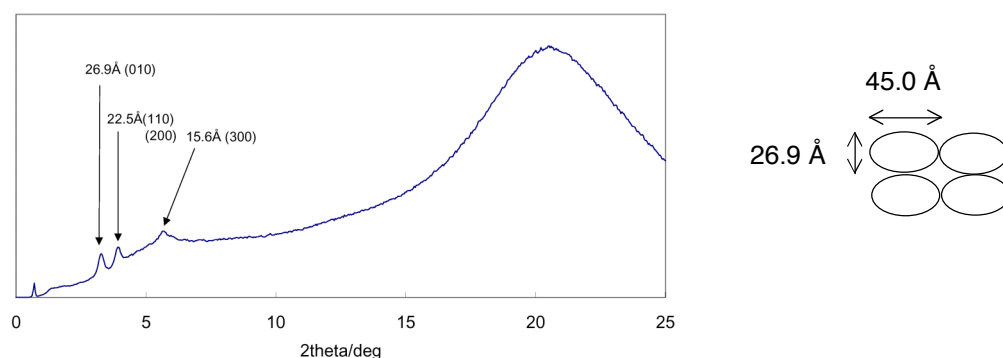
For the experiments of the guest exchange reaction, (-)-8 was used as the template instead of (+)-8, since (+)-8 and (-)-7 were eluted with similar elution times under the HPLC condition we used (Daicel CHIRALCELL CROWNPAK CR(+), at 0 °C, UV detection at 254 nm). Elution time: (+)-7 = 42 min; (-)-7 = 34 min; (+)-8 = 34 min; (-)-8 = 22 min.

(a) Exchange with (-)-7

The cross-linked 2·(-)-8 (62.1 mg, 63 μmol monomer units) was soaked in a methanol solution (5.0 mL) of (-)-7 (25.0 mM, 125 μmol) at 4 °C. The concentrations of (-)-8 and (-)-7 in the supernatant were determined by HPLC.

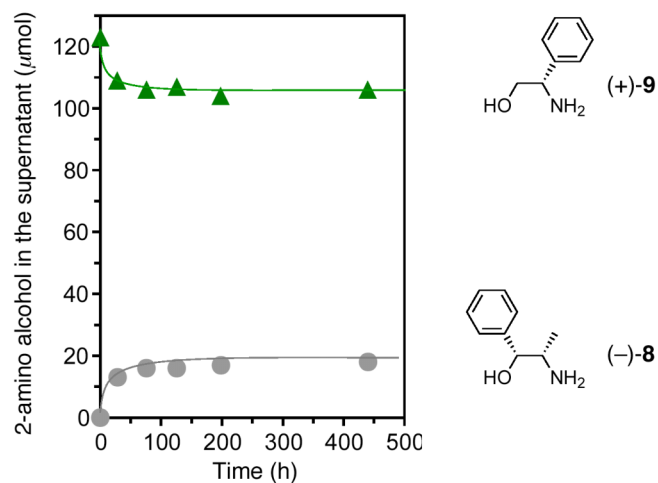


The cross-linked material after the guest exchange was collected by centrifugation, dried *in vacuo*, and subjected to X-ray diffraction measurement.



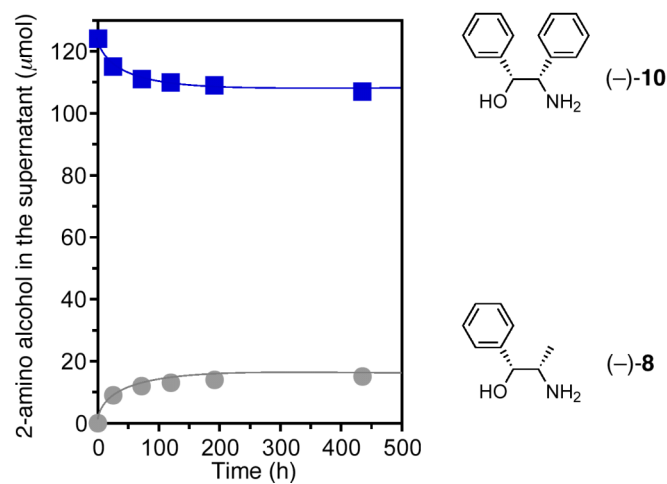
(b) Exchange with (+)-**9**

The cross-linked **2**·(-)-**8** (61.4 mg, 62 μ mol monomer units) was soaked in a methanol solution (5.0 mL) of (+)-**9** (23.0 mM, 123 μ mol) at 4 °C, and the exchange reaction was monitored by HPLC as described above.



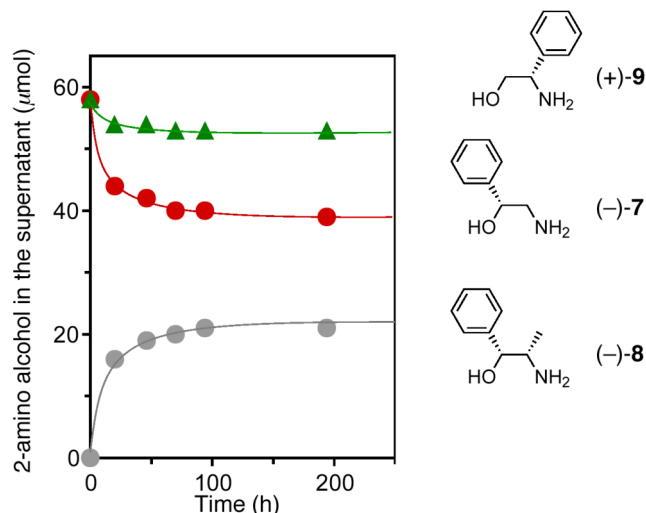
(c) Exchange with (-)-**10**

The cross-linked **2**·(-)-**8** (61.9 mg, 62 μ mol monomer units) was soaked in a methanol solution (5.0 mL) of (-)-**10** (24.8 mM, 124 μ mol) at 4 °C, and the exchange reaction was monitored by HPLC as described above.



(d) Exchange with (–)-**7** and (+)-**9** under a competitive condition

The cross-linked **2**·(–)-**8** (57.0 mg, 57 μmol monomer units) was soaked in a methanol solution (5.0 mL) of (–)-**7** (11.6 mM, 58 μmol) and (+)-**9** (11.6 mM, 58 μmol) at 4 °C, and the exchange reaction was monitored by HPLC as described above.



(e) Exchange with (+)- and (–)-**7** under a competitive condition

The cross-linked **2**·(–)-**8** (58.7 mg, 59 μmol monomer units) was soaked in a methanol solution (5.0 mL) of racemic **7** (23.4 mM, 117 μmol) at 4 °C, and the exchange reaction was monitored by HPLC as described above. At the equilibrium, **7** in the supernatant was (+)-enriched (2% ee).

After the equilibrium was attained, the insoluble fraction was collected by centrifugation, and extensively washed with aqueous HCl. The HPLC analysis revealed that 9.5 μmol of **7** (25% with respect to the adsorbed **7**) was recovered, which was (–)-enriched (7% ee).

