Bending behavior of isomorphic salicylideneaniline crystals by photoirradiation

(¹School of Advanced Science and Engineering, Waseda University, ²Graduate School of Advanced Science and Engineering, Waseda University, ³Research Organization for Nano & Life Innovation, Waseda University) OKazuya Hirata, ¹Shodai Hasebe, ²Yuki Hagiwara, ²Toru Asahi, ^{1,2,3} Hideko Koshima³

Keywords: Isomorphic Crystals; Bending Behavior; Salicylideneaniline; Photoisomerization; Photothermal Effect

Mechanically responsive materials, which exhibit macroscopic motion by external stimuli such as light and heat, have attracted attention from perspective of both basic research and applications to actuators and soft robots.¹ Over the past decade, we have developed many mechanically responsive crystals based on photoisomerization.^{2,3} Some crystals are known to form isomorphic crystals which different components are crystallized in the same crystal

structure. However, photomechanical motions of isomorphic crystals have been scarcely studied so far. We have found that salicylideneaniline derivatives with 4-Cl (1a) and 4-Br (1b) substituents form isomorphic crystals. Here we report the photomechanical motions of the isomorphic crystals (Scheme 1).



Scheme 1 Photoisomerization of enol-1.

Single crystals of **1a** and **1b** were obtained by recrystallization from methanol solutions. X-ray crystallographic analysis revealed that both crystals belong to the same space group $P2_1/c$. **1a** and **1b** crystals had almost the same unit cell constants, and there existed one independent molecule in an asymmetric unit, showing **1a** and **1b** are isomorphic crystals each other. Both crystals showed similar and smooth photoisomerization properties due to almost the same crystal structures.

Upon UV light (375 nm) irradiation, both thin crystals exhibited similar bending motions towards the light source. The mechanical behavior depended on crystal thickness; the thin (3 μ m) **1a** crystal bent 12° after 1.5 s (a)

thin (3 μ m) **1a** crystal bent 12° after 1.5 s due to the photoisomerization (Fig. 1a). Then, the crystal returned to the initial straight shape 9.3 s after stopping UV light. On the other hand, the thick (227 μ m) **1a** crystal quickly bent away from the light source 0.3° after 0.3 s due to photothermal effect⁴ (Fig. 1b). The crystal returned to the initial straight shape 0.3 s after UV stopping. In addition, slightly thick (83 μ m) **1a** crystal exhibited twostep bending by the combination of photoisomerization and photothermal effect.



Fig. 1 (a) Large bending toward the light source of the thin 1a crystal by photoisomerization, and (b) fast bending away from the light source of the thick 1a crystal by photothermal effect.

Mechanically Responsive Materials for Soft Robotics, ed. H. Koshima, Wiley-VCH, Weinheim, 2020.
H. Koshima, N. Ojima, H. Uchimoto, J. Am. Chem. Soc. 2009, 131, 6890–6891. 3) H. Koshima, K. Takechi, K. Uchimoto, M. Shiro, D. Hashizume, Chem. Commun. 2011, 47, 11423–11425. 4) Y. Hagiwara, T. Taniguchi, T. Asahi, H. Koshima, J. Mater. Chem. C. 2020, 8, 4876–4884.