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Non-Centrosymmetric Coordination Polymer with a Highly Hindered Octahedral Copper Center Bridged by Mandelate

Makoto Moriya,[†,‡] Shingo Tominaga,[†] Takayoshi Hashimoto,[§] Kazuki Tanifuji,[§] Tsuyoshi Matsumoto,[§] Yasuhiro Ohki,[§] Kazuyuki Tatsumi,[§] Junichi Kaneshiro,[∥] Yoshiaki Uesu,[∥] Wataru Sakamoto,[†] and Toshinobu Yogo*[,†]

[†]EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

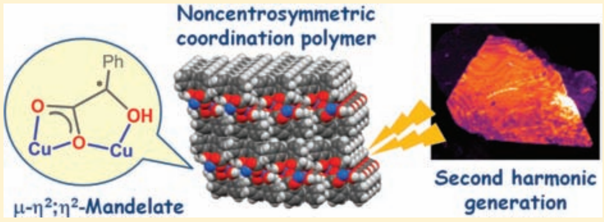
[‡]Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

[§]Department of Chemistry, Graduate School of Science, and Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602 Japan

[∥]Department of Physics, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

S *Supporting Information*

ABSTRACT: A novel chiral coordination polymer, [Cu($C_6H_5CH(OH)COO$)(μ-$C_6H_5CH(OH)COO$)] (**1**-L and **1**-D), was synthesized through a reaction of copper acetate with L-mandelic acid at room temperature. Although previously reported copper mandelate prepared by hydrothermal reaction was a centrosymmetric coordination polymer because of the racemization of mandelic acid, the current coordination polymer shows noncentrosymmetry and a completely different structure from that previously reported. The X-ray crystallography for **1**-L revealed that the copper center of the compound showed a highly distorted octahedral structure bridged by a chiral mandelate ligand in the unusual coordination mode to construct a one-dimensional (1D) zigzag chain structure. These 1D chains interdigitated each other to give a layered structure as a result of the formation of multiple aromatic interactions and hydrogen bonds between hydroxyl and carboxylate moieties at mandelate ligands. The coordination polymer **1**-L belongs to the noncentrosymmetric space group of C2 to show piezoelectric properties and second harmonic generation (SHG) activity.



INTRODUCTION

Noncentrosymmetric coordination polymers (CPs) have attracted considerable attention due to their useful electrical and optical properties.[1] Naturally occurring chiral α-hydroxy acids are useful bridging blocks for the construction of noncentrosymmetric CPs and metal complexes because these molecules are readily available without any need for complicated synthetic procedures.[2−21] Mandelic acid, which consists of a hydrophobic phenyl group and hydrophilic hydroxyl and carboxyl groups at a chiral methine carbon (Figure 1a), possesses suitable characters to synthesize chiral CPs. Owing to these functional groups, the mandelate ligand forms inter- and intramolecular interactions through aromatic interactions and hydrogen bonds to stabilize the highly ordered self-assembled structure of CPs.[2−4,16−20] Thus, the synthetic route to noncentrosymmetric metal−mandelate CPs has been studied through the alteration of auxiliary ligands.[2−4,18]

The discovery of a new coordination mode of a multidentate ligand brings a new strategy to construct novel coordination polymers. Since α-hydroxy carboxylates contain multiple coordination sites, including oxygen atoms at the carboxylate moiety and hydroxyl group, various coordination patterns have been observed, as shown in Figure 1. Chelate coordination of mandelate ligands commonly results in the formation of a five-membered ring via interactions with the oxygen atoms of the carboxylate and hydroxyl moieties (Figure 1b).[2−14] Some mandelate ligands also bridge the metal center as shown in

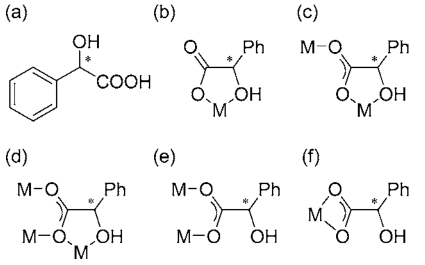


Figure 1. The structure of mandelic acid and the reported coordination modes of mandelate. (a) Molecular structure of mandelic acid. (b) Chelate coordination mode to form a five-membered ring with metal center. (c) μ-Bridging coordination with the formation of a five-membered ring. (d) μ_3-Bridging coordination with the formation of a five-membered ring. (e) μ-Bridging coordination mode via carboxylate moiety. (f) Chelate coordination mode to form a four-membered ring with a metal center.

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Figure 1c–e.[15−17,19,20] Chelate coordination to form a four-membered ring (Figure 1f) has also been reported.[18]

The versatility of the coordination mode of mandelate is useful for the construction of highly ordered structures. In fact, the discovery of a new bridging mode of mandelate corresponds to the development of a novel building block for functional coordination polymers. Hydrothermal reactions are generally used to obtain CPs. However, the method tends to restrict the coordination mode of the ligands to the thermodynamically stable form due to the high reaction temperature. Moreover, hydrothermal reactions often give centrosymmetric CPs as a result of racemization of chiral mandelic acid due to the severe reaction conditions.[16,17]

Hence, we attempted to synthesize a novel coordination polymer with the mandelate ligand by the control of reaction conditions. In order to inhibit the racemization of the mandelate ligand, we performed the synthesis under room temperature and ambient pressure without the use of a base (Scheme 1). Moreover, it is expected that the structural change in the coordination mode of mandelate ligand occurs as a result of the kinetic reaction control under mild conditions. We herein report the synthesis of novel noncentrosymmetric coordination polymers with chiral mandelate ligands and a copper center, [Δ-Cu(μ-η^2;η^2-(L)-$C_6H_5CH(OH)COO$)(η^2-(L)-$C_6H_5CH(OH)COO$)] (**1**-L) and [Δ-Cu(μ-η^2;η^2-(D)-$C_6H_5CH(OH)COO$)(η^2-(D)-$C_6H_5CH(OH)COO$)] (**1**-D), by the reaction between aqueous copper acetate with mandelic acid under ambient conditions. This compound possesses the crystal structure of **1**-L with the mandelate ligands bridging highly hindered octahedral copper centers in an unusual coordination mode. This coordination polymer is given as one-dimensional zigzag chains interdigitated to form a layered structure. We also describe the piezoelectricity and second harmonic generation (SHG) activity of the obtained coordination polymer.

Scheme 1. Ligand Exchange Reaction between Copper Acetate and L- or D-Mandelic Acid

$$\mathrm{Cu(CH_3COO)_2\cdot 2H_2O + 2(L\ or\ D)\text{-}C_6H_5CH(OH)COOH}$$

$$\xrightarrow[\text{rt, 2-3 d}]{}\ \underset{\textbf{1}\text{-L or }\textbf{1}\text{-D}}{\mathrm{Cu((L\ or\ D)\text{-}C_6H_5(OH)COO)_2}} + \mathrm{2CH_3COOH + 2H_2O}$$

water,

■ EXPERIMENTAL SECTION

Copper acetate hydrate (98.5%) was purchased from Kishida Chemical Industry Inc. L- and D-Mandelic acid (99%) were purchased from Tokyo Chemical Industry Co. These reagents were used as received.

Crystal data for **1**-L: $C_{16}H_{14}O_6Cu$; monoclinic; $C2$ (No. 5); a = 30.032(16), b = 5.718(3), c = 9.294(5) Å, β = 103.177(8) °, V = 1553.9(14) Å^3; Z = 4; F(000) = 748; μ = 1.433 cm^{-1}; ρ_{calcd} = 1.564 g cm^{-3}; 5445 reflections ($2\theta < 55.0°$); 2669 unique (R_{int} = 0.070); Flack parameter = 0.03(3); R_1 = 0.0523 ($I > 2\sigma(I)$), wR_2 = 0.1245 (all data), GoF = 1.005. The crystallographic data and refinement parameters of **1**-L are summarized in Table S1. A single crystal was mounted on a loop using oil (CryoLoop, Immersion Oil, Paratone, Hampton Research Corp.) and set on a Rigaku AFC10 instrument equipped with a Saturn CCD detector. The measurement was made using graphite monochromated Mo Kα radiation (λ = 0.71070 Å) under a cold nitrogen stream. The frame data were integrated and corrected for absorption with the Rigaku/MSC CrystalClear program package. The structures were solved using direct methods (SIR-92 or SIR-97) and standard difference map techniques and refined with full-matrix least-squares procedures on F^2 by the Rigaku/MSC CrystalStructure package. Anisotropic refinement was applied to all non-hydrogen atoms. All of the hydrogen atoms were placed at calculated positions.

CD spectra of **1**-L and **1**-D dissolved in dimethyl sulfoxide were measured with JASCO J-720WN. Thermogravimetry-differential thermal analysis (TG-DTA) was performed using a Rigaku Thermo Plus EVO TG8120 at a heating rate of 10 °C/min in O_2 using Al_2O_3 as the reference. IR spectra were measured using a Nicolet Nexus 470 FT-IR spectrometer. The UV–vis spectrum was measured with a JASCO V-570. The powder X-ray diffraction pattern of **1**-L was collected with a Rigaku RINT 2500 diffractometer using Cu Kα radiation with a monochromator. Elemental analysis was performed on a Perkin-Elmer 2400II. The piezoelectric properties were measured on a single crystal of **1**-L on a silicon substrate using an atomic force microscope (AFM: SII SPI3800N) in piezoresponse mode at room temperature. AFM measurements were carried out along the thickness direction of the **1**-L crystal plate at a driving frequency of 1 Hz. The emission of second harmonic light was observed using a second harmonic generation (SHG) interference microscope of the confocal transmission type according to a previously reported setup.[22] Field-emission scanning electron microscopy (SEM) images were taken on a JEOL JSM-6330 electron microscope at 5 kV.

The procedure for the synthesis of **1**-L was as follows: The reaction flask was charged with 0.2 mmol of L-mandelic acid and 4 mL of water. To this flask was added 0.1 mmol of $Cu(CH_3COO)_2{\cdot}H_2O$ dissolved in 1 mL of water. From this reaction solution, pale blue crystals of **1**-L in the form of a thin plate were given at room temperature in a few days (yield: 23%). IR (KBr cm^{-1}): 694, 698, 820, 953, 1022, 1054, 1187, 1261, 1441, 1581, 2580, 3047. Anal. Calcd for $C_{16}H_{14}CuO_6$: C, 52.53; H, 3.86. Found: C, 52.38; H, 3.40. The chiral compound **1**-D was obtained through the same procedure as that of **1**-L by the use of D-mandelic acid instead of L-mandelic acid.

■ RESULTS AND DISCUSSION

The reaction of aqueous copper acetate dihydrate with two equivalents of L-mandelic acid occurred at room temperature to afford a novel coordination polymer **1**-L as pale blue single crystals in the form of thin plates like fish scales. The magnified image of **1**-L is shown in Figure S1. The enantiomer **1**-D was obtained by using D-mandelic acid instead of L-mandelic acid for this reaction. The circular dichroism (CD) spectra of **1**-L and **1**-D measured in dimethylsulfoxide (DMSO) were mirror images of one another, which proves the enantiomeric relationship of the two compounds (Figure 2). We confirmed that these CD spectra differ completely from those of L- and D-mandelic acid.

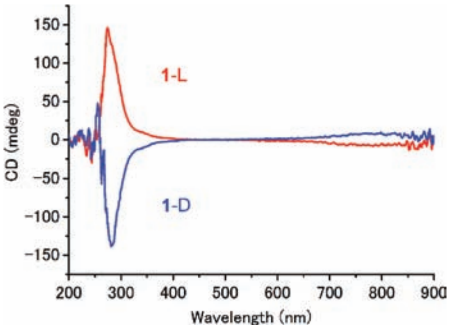


Figure 2. CD-spectra of **1**-L (red) and **1**-D (blue).

The FT-IR spectra of **1**-L and L-mandelic acid are depicted in Figure 3. The peak attributable to carboxylic acid at 1728 cm^{-1} in the spectrum of mandelic acid is not evident in the spectrum of **1**-L. Instead, new signals assignable to a carboxylate moiety appear at 1442 and 1581 cm^{-1} in the spectrum of **1**-L. The spectrum of **1**-L also features absorptions associated with the

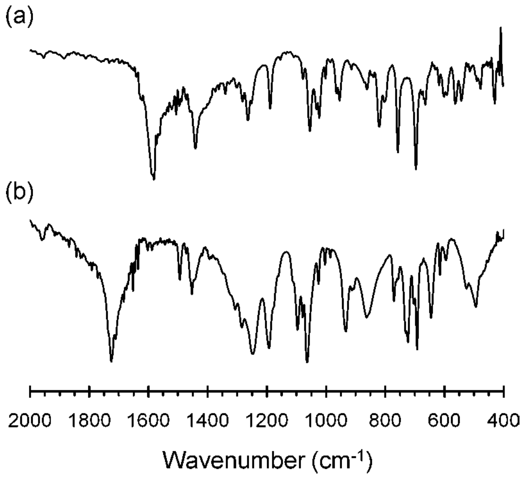


Figure 3. IR spectra. (a) The obtained coordination polymer **1**-L. (b) L-mandelic acid.

bending vibration of hydrogen–oxygen bonds and the stretching vibration of carbon–oxygen bonds of the hydroxyl group at 1264 and 1055 cm^{-1}, respectively. These results indicate that the mandelate ligands in coordination polymer **1**-L exist in the carboxylate form with hydroxyl groups.

The thermogravimetry (TG) curve of **1**-L measured under an oxygen atmosphere revealed a dramatic weight loss at 215 °C and moderate weight loss at 280 °C (Figure 4). The thermal behavior of **1**-D is similar to that of **1**-L (Figure S2). The total weight loss ratio was estimated to be 79% with the remaining product being CuO, as confirmed from the X-ray diffraction pattern. This weight loss is in good agreement with the calculated ratio for the transformation of $Cu(C_6H_5CH(OH)\text{-}COO)_2$ to CuO. Elemental analysis also supports the formula of the obtained products.

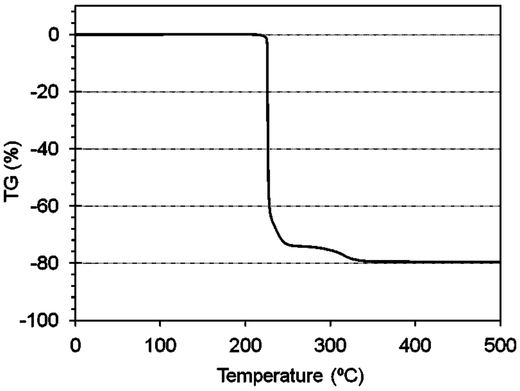


Figure 4. TG curve of **1**-L.

Powder XRD measurements for **1**-L and **1**-D show the same diffraction patterns to suggest the formation of the compound with a layered structure (Figure S3). The interlayer distances of **1**-L and **1**-D were determined to be 1.49 nm. As single crystals of **1**-L suitable for X-ray structural analysis were obtained, the measurement for X-ray crystallography was performed. The structure of **1**-L and its noncentrosymmetric space group of C2 were determined as shown in Figure 5. Interestingly, the copper center of **1**-L features a highly hindered octahedral structure consisting of mandelate ligands in two types of coordination modes. The Cu1–O4# bond length at 2.570 Å is quite long relative to the other Cu–O distances (Figure 6a). One coordination mode of mandelate in **1**-L is a bridging structure, while the other is a terminal structure. Since the Cu1–O4–C11–O5 torsion angle is only 0.2(5)°, the copper centers and oxygen atoms of the bridging mandelate ligand are located in the same plane. In the crystal of **1**-L, all copper centers show Δ-form chirality, and all mandelate ligands are in the L-configuration. The bridging mandelate ligand forms a four-membered ring through the two oxygen atoms of the carboxylate moiety and a five-membered ring through the hydroxyl group and an oxygen atom of the carboxylate moiety. Owing to the strained chelation of the carboxylate, an extraordinarily small bond angle of 56.3(2)° is observed at O4#–Cu1–O5# (Figure 6b). The formation of both the four-membered and five-membered rings in **1**-L causes the highly hindered octahedral structure of the copper center.

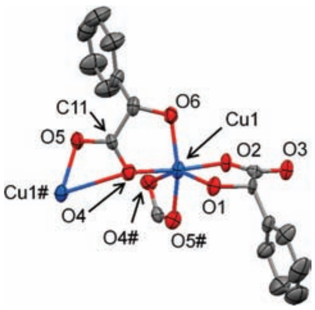


Figure 5. Thermal-ellipsoid (40% probability) representation of **1**-L (blue, copper; red, oxygen; gray, carbon; hydrogen atoms omitted for clarity).

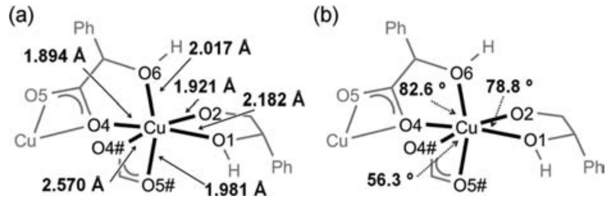
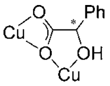


Figure 6. Schematic diagram of **1**-L with structural parameters around the copper center. (a) Cu–O distances. (b) O–Cu–O angles.

The coordination mode of the mandelate ligand in **1**-L shown in Scheme 2 is quite rare not only for mandelate but also for hydroxyl carboxylates in general. Although α-hydroxycarboxylates are widely used as building blocks for CPs, these ligands generally coordinate to metal centers to form a five-membered ring with a hydroxyl group and an oxygen atom at carboxylate similar to the bonding of the terminal mandelate ligand in **1**-L.

Scheme 2. Bridging Coordination Mode of Mandelate in 1-L



As a result of the bridging coordination of mandelate, the copper atoms in **1**-L are arranged in one-dimensional (1D) zigzag chains along the *b* axis as shown in Figure 7. The aromatic rings of the mandelate ligands are arranged in a herringbone structure to reinforce the 1D array with inter- and intramolecular edge-to-face aromatic interactions. The average

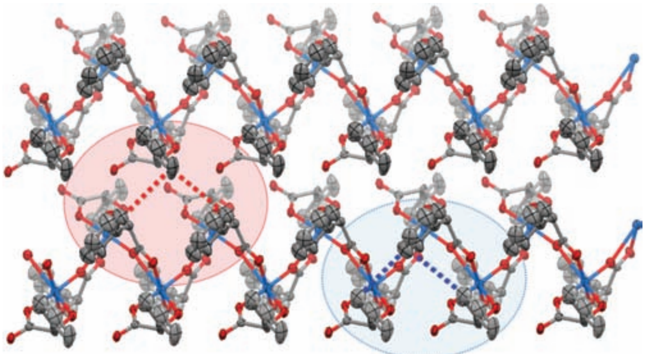


Figure 7. Plain view of the zigzag chains of **1**-L exhibiting intermolecular aromatic interactions (red circle region) and intramolecular ones (blue circle region; blue, copper; red, oxygen; gray, carbon; hydrogen atoms omitted for clarity).

distances of the inter- and intramolecular aromatic interactions were estimated to be 3.91 and 4.08 Å, respectively. Hydrogen bonds are also present between the hydroxyl and carboxylate moieties to form the two-dimensional (2D) ordered arrangements of the zigzag chains (Figure 8). The length of the hydrogen bond was calculated to be 2.539 Å. These intra- and intermolecular interactions stabilize not only the 1D arrangement of highly hindered copper centers coordinated by bridging mandelate ligands but also the 2D array of copper mandelate zigzag chains. This 2D arrangement of copper chains afforded a layered structure by the stacking as a result of the self-assembled stacking as shown in Figure 9.

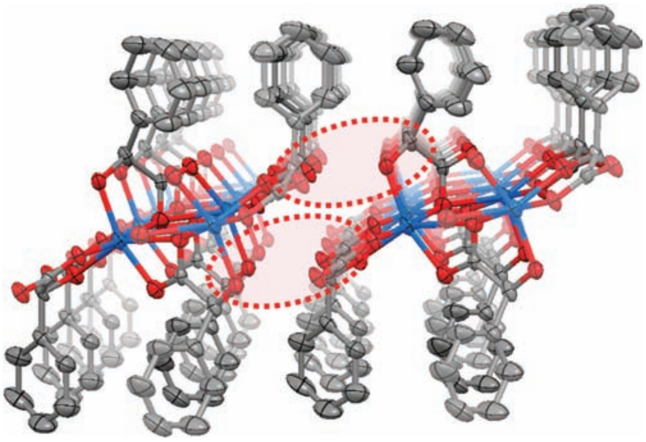


Figure 8. Front view of the zigzag chains of **1**-L displaying intermolecular hydrogen bonds between the hydroxyl group at bridging mandelate ligands and carboxyl group of terminal ones as red dashed circles (blue, copper; red, oxygen; gray, carbon; hydrogen atoms omitted for clarity.).

Previously, centrosymmetric copper mandelate described as Cu(μ-η;η^2-$C_6H_5CH(OH)COO)_2$ (**2**)[16,17] was already obtained using the hydrothermal method with $CuCl_2{\cdot}2H_2O$ as the starting material in the presence of sodium hydroxide at 170 °C. Although complex **2** has the same chemical formula as **1**-L, the color of **1**-L was different from that of **2.** While **1**-L is pale blue, complex **2** was described as blue-green. This indicates that the coordination mode of the mandelate ligand in **1** is different from that in **2**. The X-ray crystallography clearly shows the differences between the structure of **1-L** and that of **2**. As mentioned above, **2** possesses the centrosymmetric space group of $P2_1/a$ as a result of racemization of the mandelate due to the severe reaction conditions. The copper center of **2** features a strain-free octahedral structure: the O−Cu−O bond angles of **2** were in the range from 83 to 97°. The bridging coordination modes of mandelate in **1**-L are completely different from those in **2.** The mandelate ligands in **2** bridge the copper centers in a monodentate coordination mode through the oxygen atom of the carboxylate group and chelation to form a five-membered ring through the hydroxyl group and the oxygen atom of the carboxylate group.[16,17] This result suggests that the novel coordination polymer **1**-L with a noncentrosymmetric structure is afforded as a result of the kinetic reaction control under mild conditions.

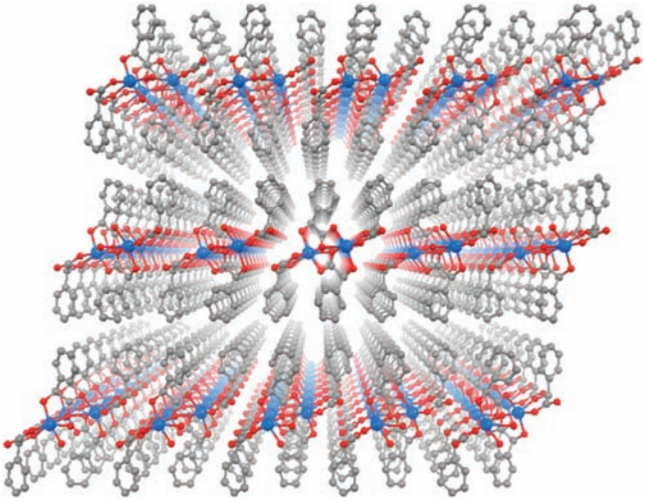


Figure 9. Perspective view of the sheet structure of **1**-L along the *b* axis. (blue, copper; red, oxygen; gray, carbon; hydrogen atoms omitted for clarity).

In order to measure piezoelectric properties of the coordination polymer, the deposition of a single crystal of **1**-L on a silicon substrate was investigated. The crystals of **1**-L were obtained as stacked thin plates and are significantly fragile. Hence, it was difficult to place single crystals of **1**-L on a silicon substrate to measure piezoelectricity. Therefore, silicon substrates were immersed in an aqueous solution of copper acetate and mandelic acid in the ratio of 1:2 to grow **1**-L crystals. This procedure resulted in the direct crystal growth of a few thin crystalline sheets of **1**-L on a silicon substrate.

The piezoelectric property of **1**-L was investigated using the above-mentioned single crystal on a silicon substrate with an atomic force microscope (AFM) in piezoresponse mode at room temperature. The measurements were carried out along the thickness direction of the plate-like crystal of **1**-L to give the electric-field-induced strain curve at a driving frequency of 1 Hz, which is a typical field-induced strain curve with a little hysteresis (Figure 10). The crystal **1**-L showed a piezoelectric coefficient of AFM-d_{33} (effective d_{33}), which is determined to be approximately 8 pm/V calculated from the slope of the loops between the strain maximum and the origin. Interestingly, the piezoelectric properties of **1**-L between negative and positive electric fields were asymmetric. This result indicates that the crystal of **1**-L undergoes stress from the silicon substrate, since similar asymmetric piezoelectric properties are observed for ceramic thin films on substrates.

The UV−vis spectra of **1**-L depicted a marked transparency in the range from 365 to 560 nm (Figure S4). Since the crystal

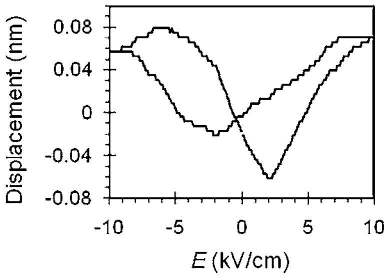


Figure 10. Piezoelectric property of **1**-L measured with AFM in piezoresponse mode.

structure of **1**-L is noncentrosymmetric and highly transparent, the SHG activity of **1**-L was analyzed using an SHG microscope. From the measurements, a polarization-dependent SHG emission from a single crystal of coordination polymer **1**-L was observed (Figure 11).

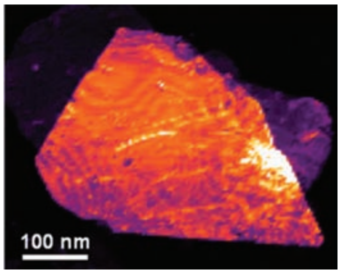


Figure 11. Photograph of single crystal of **1**-L taken by SHG microscope.

■ CONCLUSION

In conclusion, we synthesized a novel noncentrosymmetric copper−mandelate coordination polymer from copper acetate and mandelic acid under ambient reaction conditions. The obtained coordination polymer shows a layered structure obtained as a result of the self-assembly of 1D zigzag chains with the intra- and intermolecular aromatic interactions and the hydrogen bonds between the hydroxy and carboxylate groups at mandelate ligands. The 1D arrangement of the copper ions comprised a bridging mandelate ligand in a highly distorted coordination mode. Owing to the noncentrosymmetric structure, the obtained product shows piezoelectricity and SHG activity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full crystallographic description (CIF). SEM image and UV−vis spectrum of **1**-L. Powder XRD patterns of **1**-L and **1**-D. TG curve of **1**-D. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yogo@esi.nagoya-u.ac.jp.

Notes

The authors declare no competing financial interest.

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