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In-situ Photochromism Switching with Crystal Jumping through the Deammoniation of *N*-Salicylideneaniline Ammonium Salt

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Abstract

N-Salicylideneaniline (SA) derivatives are traditional organic photochromic compounds whose properties are closely related to their molecular conformations and crystal structures. We herein present the photochromic property switching phenomenon of SA ammonium salt crystals using a deammoniation reaction. The *N*-salicylidene-4-carboxyaniline ammonium salt crystal (**1-Sα**) was found to exhibit photochromism upon irradiation with UV light. Upon heating, **1-Sα** desorbed ammonia gas and transformed into a non-ionic SA crystal (**1-N**) with non-photochromic properties. Surprisingly, this phase transition induced the "jumping crystal" phenomenon. Thus, the crystal structures both before and after the phase transition were determined, and it was revealed that the switching phenomenon of photochromism (photochromism switching) was caused by the crystal structural and molecular conformational changes that took place upon deammoniation. In addition, **1-N** reverted to **1-Sα** by exposure to aqua-ammonia vapor for a few minutes. These results suggested that such SA crystals could be applicable as switching materials or chemical sensors.

Keywords: Photochromism switching, *N*-Salicylideneaniline, Deammoniation

1. Introduction

Photochromic compounds,[1] which exhibit reversible color changes upon photo-irradiation, have received significant attention due to their application in photo-switching materials,[2] optical data storage,[3] and sensors.[4] For example, *N*-salicylideneaniline (SA) is a well-known organic photochromic compound,[5–8] and the crystals of SA derivatives have been found to change color from yellow to red upon UV light irradiation, and subsequently back to their original color upon heating or visible light irradiation. This photochromic color change corresponds to a photo-isomerization from the enol to the *trans*-keto form via the *cis*-keto form, as shown in Scheme 1.[9–15]

The photochromic properties of such compounds have been found to depend on their crystal structures, including their molecular conformations and arrangements.[16] For example, SA crystals exhibiting a non-planar molecular conformation and/or loose molecular packing exhibit photochromism, while a planar molecular conformation and/or close packing leads to non-photochromic crystals. In this context, studies into the threshold dihedral angle between two aromatic rings of SA molecules to determine whether they are planar or non-planar in nature showed that a dihedral angle of <20° leads to non-photochromic properties, while a dihedral angle >30° results in photochromic properties (i.e., the "SA planarity rule").[17] Moreover, the molecular planarity affects the population of enol and *cis*-keto tautomers within the crystal, which are colorless and yellow, respectively. As non-planar molecules exhibit an overlap of the electron cloud between the lone pair of an imine N atom and the π-electrons of an aniline ring, this overlap weakens the basicity of the imine N atom and stabilizes the colorless enol form. Thus, SA crystals containing non-planar molecules commonly exhibit a pale yellow color.[18,19]

As an interesting relationship exists between the molecular conformation within the SA crystals and their resulting photochromic properties, several advanced studies were performed to modify the SA molecular conformations and in turn their photochromic properties.[20–22] In terms of chemical modification,[23] SA derivatives bearing *tert*-butyl groups favored non-planar molecular conformations due to the presence of these bulky groups. In addition, a change in the environment surrounding the SA molecule can also induce a change in the molecular conformation of SA. Thus, the formation of mixed materials with glasses[24] or polymers,[25] in addition to the production of clathrate compounds with zeolites,[26] bile acids,[27] cyclodextrins,[28] and molecular organic frameworks,[29] has been reported. Furthermore, mixed crystal formation[30] and co-crystallization are key crystal engineering methods for altering the crystalline environment via supramolecular synthons.[31–33]

Although the above methods have been successfully applied and reported in the literature, they lack the ability to offer in-situ changes in the photochromic properties, since this property is permanently fixed upon formation of the desired material or crystal complex. An alternative method to impart in-situ changes is therefore a desolvation-driven structural transformation of solvated crystals. Such a transformation causes changes in the crystalline environment, which in turn alters the molecular structure, and could cause in-situ changes in the physicochemical properties.[34,35] Indeed, the synthesis of an SA derivative composed of two SA moieties bridged by a methylene group has been reported, and its methanol solvated crystal dynamically changed the photochromic properties through the desorption and absorption of methanol molecules.[36] However, the crystal structure of this species could not be analyzed due to difficulties in preparing the necessary single crystals.

We therefore expect that the solid-state phase transition induced by molecular desorption, such as dehydration,[37] desolvation, and deammoniation, could be a promising method to dynamically alter the crystal structures and photochromic properties of such species. Moreover, it could allow clarification of the mechanism of photochromic property changes with relation to the crystal structures.

We herein report our study into the photochromic switching phenomenon of an SA derivative crystal through the examination of two polymorphic ammonium salt crystals of *N*-salicylidene-4-carboxyaniline (Chart 1). During heating of both polymorphs, a deammoniation phase transition was induced that resulted in the jumping crystal phenomenon[38,39] due to structural changes in the crystals; both the deammoniation phase transition and the jumping crystal phenomenon were examined. The photochromic properties of the deammoniated SA crystal was also determined. Furthermore, the crystal structures of all forms were examined and the relationship between the crystal structure and the physicochemical properties was discussed.

2. Experimental Section

Preparation of the *N*-salicylideneaniline derivatives

Salicylaldehyde (1.0 mmol) and 4-aminobenzoic acid (1.0 mmol) were dissolved in methanol (50 mL) and the resulting solution was stirred for 10 min at 25 °C. After this time, the solution was evaporated under reduced pressure, and the precipitate containing the crude product was obtained. Pure crystals of *N*-salicylidene-4-carboxyaniline (**1**) were obtained by recrystallization from methanol.

Preparation of the ammonium salt crystals

N-Salicylidene-4-carboxyaniline ammonium salt crystals **(1-Sα)** were obtained by cooling the hot methanolic solution of **1** with benzophenone imine in a molar ratio of 1:1. **1-Sα** gradually transformed over two weeks into the polymorphic crystal **(1-Sβ)** while standing in the methanolic solution. Interestingly, crystal structure analyses revealed that the SA molecule formed salt crystals with ammonia molecules, which were generated by the decomposition of benzophenone imine in the solution. Elemental analysis also supported these results: **1-Sα** ($C_{28}H_{25}N_3O_6$) expected: C, 67.33; H, 5.04; N, 8.41; O, 19.22; found: C, 67.28; H, 5.07; N, 8.40; O, 19.26, and for **1-Sβ** ($C_{28}H_{25}N_3O_6$) expected: C, 67.33; H, 5.04; N, 8.41; O, 19.22; found: C, 67.27; H, 5.05; N, 8.43; O, 19.25.

Identification of photochromism by UV-Vis measurements

The UV-Vis spectra of the SA crystals (**1-Sα**, **1-Sβ**, and **1-N**) were measured at 25 °C using a JASCO V-560 spectrometer equipped with the option (ISV-469) for diffuse reflectance spectroscopy. The measurement samples were prepared by mixing the SA crystals (7 mg) in barium sulfate powder (350 mg). Photo-irradiation was then carried out at 365 nm through a glass filter (HOYA UV360) using a high-pressure mercury lamp.

Thermal analysis

Thermal gravimetric and differential thermal analysis (TG-DTA) were performed using a Rigaku Thermo Plus EVO (TG8120) instrument for **1-Sα** and **1-Sβ**. The TG-DTA curves were recorded up to final temperatures of 250 and 300 °C, respectively (Figs. 3 and 4). Thermogravimetry-differential thermal analysis and mass spectrometry (TG-DTA-MS) were performed using a Rigaku Thermo Plus Photo instrument to analyze the thermal ammonia gas desorption for **1-Sα** and **1-Sβ** (Figs. S3 and S4). Powder X-ray diffraction and differential scanning calorimetry (XRD-DSC) were simultaneously carried out on a Rigaku D/MAX 2400 diffractometer coupled with a Rigaku Thermo Plus 2 instrument (Figs. S5 and S6).

Powder X-ray diffraction

To confirm the deammoniation of both **1-Sα** and **1-Sβ**, powder X-ray diffraction (PXRD) was carried out using a Bruker D8 ADVANCE diffractometer with Cu-*Kα* radiation (λ=1.54184 Å) from a sealed tube source.

Single-crystal X-ray diffraction

Single crystal X-ray diffraction data were collected in ω-scan mode with R-AXIS RAPID II Imaging Plate cameras (Rigaku) using Cu-*Kα* radiation (λ=1.54186 Å) from a rotating anode source equipped with a confocal multilayer mirror. The data were collected at 20 °C to correspond with the conditions required for observing the photochromic properties. The integrated and scaled data were empirically corrected for absorption effects using *ABSCOR*.[40] The initial structures were solved by direct methods using *SHELXS 97* and refined on F_0^2 with *SHELXL*-2018/1.[41] Non-hydrogen atoms were refined anisotropically. All H atoms of the hydroxyl group, methine group, and ammonium cation were picked from the differential Fourier map. The crystal structure of **1-Sα** was solved with the space group of *C*2/*c*, where an inversion center of symmetry was present. One independent SA molecule and half an ammonium cation were present in an asymmetric unit. As shown in Fig. 1a, the SA molecules form a strong hydrogen bond (O···O = 2.497(2) Å), and the H atom is on the inversion center. Thus, the carboxyl group of the SA molecule has an average structure of a carboxylate and a carboxyl group.

In contrast, the crystal structure of **1-Sβ** was solved with the space group of *Cc,* which does not contain an inversion center. In Fig. 1b, the C-O bond distances and C-O-O angles clearly indicate that the left SA molecule is neutral, while the other is cationic. The H atom of the carboxyl group was also picked up from the differential Fourier map, and refined without any restraints or constraints.

Interestingly, although the local catemer-like structures of **1-Sα** and **1-Sβ** are similar, inversion symmetry was present only in **1-Sα** (*C*2/*c*). This was attributed a strong negative-charge-assisted hydrogen bond forming a symmetric single well-type proton transfer profile, which generated a higher symmetry in the crystal structure of **1-Sα** than in that of **1-Sβ**. In contrast, the corresponding hydrogen bond is weaker in **1-Sβ** than in **1-Sα** (O···O = 2.591(2) Å in **1-Sβ**), and the H atom was located on one of the SA molecules. Therefore, the carboxyl group and carboxylate were distinguishable, and the space group was *Cc* without an inversion center. The molecular dihedral angles (Φ) between two benzene rings of the SA molecule were calculated using the PLATON program.[42] Detailed crystal data are given in Table S1.

3. Results and Discussion

Polymorphs of *N*-salicylidene-4-carboxyaniline ammonium salt

Polymorphic ammonium salt crystals of *N*-salicylidene-4-carboxyaniline, namely **1-Sα** and **1-Sβ**, were recrystallized from methanol and their crystal structures were determined by single crystal X-ray structural analyses. The crystals contained one neutral and one anionic SA molecule with one ammonium cation. **1-Sα** and **1-Sβ** were found to belong to the different space groups of *C*2/*c* and *Cc*, respectively. In the crystal structure of **1-Sα**, the observed SA molecule was an average structure between neutral and anionic SA molecules (Fig. 1a), where the C-O distances in the carboxyl group were 1.290(2) and 1.236(2) Å, and the C-C-O angles were 116.9(2) and 120.4(2)°. However, the neutral and anionic SA molecules were distinguishable in the crystal structure of **1-Sβ** (Fig. 1b), with the neutral molecule having C-O distances of 1.314(5) and 1.227(6) Å, and C-C-O angles of 114.2(4) and 122.5(4)°, while the anionic molecule had C-O distances of 1.284(5) and 1.256(6) Å, and C-C-O angles of 118.3(4) and 117.4(4)°. These C-O distances and C-C-O angles of the carboxyl groups differed significantly between the neutral and cationic SA molecules, which supported the assignation of space group *Cc*.

In addition, the carboxylic groups in **1-Sα** and **1-Sβ** exhibited catemer-like hydrogen bonding patterns due to the presence of both neutral and anionic SA molecules. This catemer-like motif is not uncommon, with 38 different crystal structures being found with this motif in the CSD database (Version 5.40; search details are given in the Supporting Information). We also note that the hydrogen bonding distance ($O2\cdots O2^{\#1}$, #1: -x, y+2, -z+1) is 2.497(2) Å in **1-Sα**, and which is similar to those of previously reported structures (Fig. S7). However, in the case of **1-Sβ**, a significantly longer hydrogen bonding distance of 2.591(2) Å was detected.

Furthermore, the SA molecular pairs formed 1D chain structures with ammonium cations along the *c*-axis via hydrogen bonding, and the interatomic distance between SA molecules and ammonium cations was 2.776(2) Å in **1-Sα**. In contrast, the distances between the neutral and cationic SA molecules to the ammonium cations were 2.895(4) and 2.751(3) Å in **1-Sβ**, respectively. This difference in interatomic distances stabilizes the crystal structure where one neutral and one cationic SA molecule are present independently.

We also found that the molecular arrangements viewed along the *b*-axis were similar (Figs. S1 and S2). However, the molecular packing motifs viewed along the *c*-axis, as shown in Figs. 2a and 2b, differed between **1-Sα** and **1-Sβ**. Although the SA molecules were arrayed almost parallel along the *b*-axis in **1-Sα**, they were arrayed in a herringbone pattern in **1-Sβ**. Importantly, the molecular conformations of SA differed significantly between the non-planar conformation in **1-Sα** and the planar conformation in **1-Sβ**. When the **1-Sα** crystals were allowed to stand in the methanol solution, they gradually disappeared, and crystals of **1-Sβ** were formed. This observation shows that the unstable kinetic polymorph (**1-Sα**) dissolved, and the thermodynamically stable polymorph (**1-Sβ**) was formed. Indeed, the stabilities of these polymorphs were confirmed by the density rule, with crystal densities of 1.386 g·cm^{-3} for **1-Sα** and 1.444 g·cm^{-3} for **1-Sβ**.

Crystal jumping induced by deammoniation

TG-DTA measurements (Figs. 3 and 4) showed that **1-Sα** and **1-Sβ** deammoniated at 161.0 and 135.8 °C, respectively. In addition, TG-DTA-MS measurements supported the desorption of an ammonium cation from the crystal structure as a neutral ammonia molecule upon heating (Figs. S3 and S4). This resulted in the SA molecule switching from a cationic to a neutral state. In addition, Fig. 5 shows the PXRD patterns both before and after heating at the deammoniation temperatures, and the changes in the PXRD patterns suggest that the salt crystals of **1-Sα** and **1-Sβ** transformed to the same SA crystal of **1-N**. The crystal structure of **1-N** is well known and has been reported previously.[31] XRD-DSC measurements confirmed that **1-Sα** and **1-Sβ** directly transformed into **1-N** without passing through any other crystalline phase (Figs. S5 and S6). While heating at the deammoniation temperatures using a hot plate, crystals of both **1-Sα** and **1-Sβ** exhibited the jumping crystal phenomenon (Fig. 6). Movies of the jumping crystals are available in the Supporting Information. These mechanical phenomena induced by thermal stimuli are classified as a thermosalient effect.[43] Indeed, in the past few decades, several crystals have been reported to exhibit this interesting phenomenon. Such thermosalient crystals have attracted considerable attention due to their potential use in the development of molecular actuators, molecular machines, and mechanical sensors. Moreover, **1-Sα** and **1-Sβ** are classified into rare types of jumping crystals that are related to molecular desorption.[44,45]

To account for the jumping crystal phenomena in **1-Sα** and **1-Sβ**, we compared crystal structures before and after deammoniation. In the case of jumping crystal **1-Sα**, a linear-chain structural motif was formed by neighboring molecules along the *a*-axis (Fig. 7a). In contrast, in **1-N**, the molecules formed a zigzag-chain structural motif with neighboring molecules (Fig. 7b), thereby indicating that deammoniation produced a significant structural change in the crystal. In contrast, **1-Sβ**, which also exhibited the jumping crystal phenomenon upon heating, formed a zigzag-chain structural motif. When **1-Sβ** was deammoniated and transformed into **1-N**, the zigzag-chain pattern, which is highlighted in blue in Figs. 7c and 7d, slips half of a unit cell length. These large crystal structural changes induced by deammoniation were therefore responsible for the jumping crystal phenomena. Thus, we selected and examined the lattice parameters of single crystals of **1-Sα** and **1-Sβ** as soon as the crystals jumped upon heating with a hot plate. Contrary to our expectations, these crystals appeared to be present in their original ammonium salt phase, thereby suggesting that deammoniation occurred on the crystal surface that was in contact with the hot plate. We note that the crystal structural change taking place upon deammoniation causes a partial crystal deformation, which generates mechanical stress, and results in the jumping crystal phenomenon. Indeed, not all crystals jumped upon heating, which suggested that only crystals that had a suitable contact with the hot plate could jump. In addition, **1-Sα** and **1-Sβ** were completely transformed into **1-N** upon further heating, under which conditions the crystals did not retain their single crystal state.

In-situ photochromism switching via deammoniation and crystal color changes

We found that the photochromic properties differed between **1-Sα** and **1-Sβ**. More specifically, as shown in Fig. 8a, **1-Sα** exhibited photochromism from pale yellow to red upon UV light irradiation, where the increase in the absorption band at approximately 500–600 nm corresponds to isomerization from the colorless enol to the red *trans*-keto form. The dihedral angle of the SA molecule in **1-Sα** was 45.15(9)°, which is within the photochromic range (i.e., >30°). In contrast, **1-Sβ** did not exhibit photochromism (Fig. 8b), and its molecular dihedral angles were 2.1(2) and 1.9(2)°, which are lower than the threshold value of 20°. These results indicate that both ammonia salt crystals conformed to the previously mentioned SA planarity rule. Interestingly, **1-Sα** lost its photochromic properties upon heating due to deammoniation to **1-N**. Actually, as shown in the UV-Vis. spectrum of **1-N**, no differences were observed following UV irradiation (Fig. 8c). In the case of **1-N**, the molecular dihedral angle was 5.1(1)°, which is significantly lower than the non-photochromic threshold of 20°. It was therefore apparent that the photochromic properties were switched off due to a change in the SA molecular conformation from a photochromic non-planar conformation to a non-photochromic planar conformation upon deammoniation from **1-Sα** to **1-N** (Fig. 9). As mentioned previously, SA molecules switched their ionic state from anionic to neutral through deammoniation, which did not affect the photochromic properties due to the photochromic mechanisms of SA.[31,46]

To investigate the reversibility of the deammoniation reaction, we stored the crystalline sample of **1-N** with a 28–30% concentrated aqueous ammonia solution, such that **1-N** was exposed to the aqua-ammonia vapor. In this context, we note that a gas-solid reaction with aqua-ammonia vapor is a common method for ammonium salt formation with an organic acid.[47,48] Based on the PXRD results, it was found that **1-N** transformed into **1-Sα** when exposed to aqua-ammonia vapor for a few minutes (Fig. S8). Thus, the in-situ photochromism switching phenomenon appeared to be reversible upon exposure to external stimuli, such as heating and aqua-ammonia vapor. Indeed, a few reports describe the successful reversible transformation from ammonium salt crystals to deammoniated neutral SA crystals.[49,50] Recently, these crystals are called “soft crystals”,[51] which can changes their structure and properties flexibly by external stimuli.

As shown in Figs. 8a, 8b, and 8c, the crystal color of **1-Sα** clearly differed from those of **1-Sβ** and **1-N** prior to UV light irradiation, and this was attributed to differences in the molecular conformations. More specifically, **1-Sα** exhibited a paler yellow color than the other samples, which was accounted for by the fact that SA crystals containing non-planar molecules tend to exhibit a paler yellow color than those containing planar molecules.[18,19] The color differences between **1-Sα**, **1-Sβ**, and **1-N** were therefore supported by this observation. In addition, the UV-Vis spectra of **1-Sβ** and **1-N** showed large absorption bands at ~500 nm, which were not observed for **1-Sα**. Indeed, the absorption of light by the *cis*-keto form was responsible for the orange crystal color, thereby confirming that the molecular conformation change induced by deammoniation resulted in changes to both the crystal color and the photochromic properties of **1-Sα**.

4. Conclusion

N-Salicylideneaniline (SA) derivatives are photochromic compounds in which the properties are closely related to their molecular conformations and crystal structures. We herein demonstrated that the photochromic properties of an SA derivative crystal **1-Sα** were successfully switched via deammoniation, which can be explained by the in-situ molecular conformation change from a photochromic non-planar conformation to a non-photochromic planar conformation within the crystal. Interestingly, the deammoniation phase transition with photochromism switching was reversible; **1-N** reverted to **1-Sα** by exposure to aqua-ammonia vapor. In addition, the two polymorphs of the ammonium salt crystal, namely the photochromic **1-Sα** and the non-photochromic **1-Sβ**, exhibited different crystal colors that depended on the molecular conformation. Moreover, both polymorphs exhibited the jumping crystal phenomenon upon heating. This thermosalient effect may be induced by the partial mechanical strains caused by deammoniation. Our results therefore confirm that ammonium salt crystals containing SA derivatives exhibit dynamic mechanical and chemical property changes upon deammoniation. These crystals that can undergo changes in their structure and properties upon exposure to external stimuli are known soft crystals, and could be potentially useful in applications such as switching materials or chemical sensors.

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: xxxxxxx.

TG-DTA-MS data, XRD-DSC data, X-ray crystallographic data, and powder X-ray diffraction (PDF)

Accession Codes

CCDC 1884035 and 1884036 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12

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References

(1) Heinz Dürr, H. B.-L. *Photochromism: Molecules and Systems*; Elsevier Science; 1 edition, 2003; p 1218.

(2) Li, Y.; Zhang, H.; Qi, C.; Guo, X. Light-Driven Photochromism-Induced Reversible Switching in P3HT–Spiropyran Hybrid Transistors. *Journal of Materials Chemistry* **2012**, 22, 4261.

(3) Kawata, S.; Kawata, Y. Three-Dimensional Optical Data Storage Using Photochromic Materials. *Chemical reviews* **2000**, 100, 1777–1788.

(4) Mizuno, H.; Mal, T. K.; Wälchli, M.; Kikuchi, A.; Fukano, T.; Ando, R.; Jeyakanthan, J.; Taka, J.; Shiro, Y.; Ikura, M.; et al. Light-Dependent Regulation of Structural Flexibility in a Photochromic Fluorescent Protein. *Proceedings of the National Academy of Sciences of the United States of America* **2008**, 105, 9227–9232.

(5) Senier, A.; Shepheard, F. G. Arylidene- and Naphthylidene-Amines. *Journal of the Chemical Society, Transactions* **1909**, 95, 1943–1955.

(6) Senier, A.; Shepheard, F. G.; Clarke, R. Arylideneamines. *Journal of the Chemical Society, Transactions* **1912**, 101, 1950–1958.

(7) Cohen, M. D.; Schmidt, G. M. J. PHOTOCHROMY AND THERMOCHROMY OF ANILS. *Journal of Physical Chemistry* **1962**, 66, 2442–2446.

(8) Cohen, M. D.; Schmidt, G. M. J.; Flavian, Experiments on Photochromy and Thermochromy of Crystalline Anils of Salicylaldehydes. *Journal of the Chemical Society* **1964**, 2041–2051.

(9) Nakagaki, R.; Kobayashi, T.; Nakamura, J. Spectroscopic and Kinetic Studies of the Photochromism of N-Salicylideneanilines and Related Compounds. *Bulletin of the Chemical Society of Japan* **1977**, 50, 1909–1912.

(10) Lewis, J. W.; Sandorfy, C. A Spectroscopic Study of Proton Transfer and Photochromism in N -(2-Hydroxybenzylidene)Aniline. *Canadian Journal of Chemistry* **1982**, 60, 1738–1746.

(11) Turbeville, Wayne.; Dutta, P. K. Spectroscopic Studies of the Photochromic Molecule N-(2-

Hydroxybenzylidene)Aniline and Its Photoproduct. *The Journal of Physical Chemistry* **1990**, 94, 4060–4066.

(12) Yuzawa, T.; Takahashi, H.; Hamaguchi, H. Submicrosecond Time-Resolved Infrared Study on the Structure of the Photoinduced Transient Species of Salicylideneaniline in Acetonitrile. *Chemical Physics Letters* **1993**, 202, 221–226.

(13) Kownacki, K.; Mordzinski, A.; Wilbrandt, R.; Grabowska, A. Laser-Induced Absorption and Fluorescence Studies of Photochromic Schiff Bases. *Chemical Physics Letters* **1994**, 227, 270–276.

(14) Harada, J.; Uekusa, H.; Ohashi, Y. X-Ray Analysis of Structural Changes in Photochromic Salicylideneaniline Crystals. Solid-State Reaction Induced by Two-Photon Excitation. *Journal of the American Chemical Society* **1999**, No. 10, 5809–5810.

(15) Sliwa, M.; Mouton, N.; Ruckebusch, C.; Poisson, L.; Idrissi, A.; Aloïse, S.; Potier, L.; Dubois, J.; Poizat, O.; Buntinx, G. Investigation of Ultrafast Photoinduced Processes for Salicylidene Aniline in Solution and Gas Phase: Toward a General Photo-Dynamical Scheme. *Photochemical & Photobiological Sciences* **2010**, 9, 661–699.

(16) Bregman, J.; Leiserowitz, L.; Osaki, K. The Crystal and Molecular Structures of 2-Chloro-N-Salicylideneaniline. *Journal of the Chemical Society* **1964**, 2086–2100.

(17) Johmoto, K.; Ishida, T.; Sekine, A.; Uekusa, H.; Ohashi, Y. Relation between Photochromic Properties and Molecular Structures in Salicylideneaniline Crystals. *Acta Crystallographica Section B Structural Science* **2012**, 68, 297–304.

(18) Chatziefthimiou, S. D.; Lazarou, Y. G.; Hadjoudis, E.; Dziembowska, T.; Mavridis, I. M. Keto Forms of Salicylaldehyde Schiff Bases: Structural and Theoretical Aspects. *The Journal of Physical Chemistry B* **2006**, 110, 23701–23709.

(19) Hadjoudis, E.; Dziembowska, T.; Rozwadowski, Z. Photoactivation of the Thermochromic Solid Di-Anil of 2-Hydroxy-5-Methyl-Isophthalaldehyde in β-Cyclodextrin. *Journal of Photochemistry and Photobiology A: Chemistry* **1999**, 128, 97–99.

(20) Kawato, T.; Koyama, H.; Kanatomi, H.; Isshiki, M. Photoisomerization and Thermoisomerization I: Unusual Photochromism of N-(3, 5-Di-Tert-Butyl-Salicylidene) Amines. *Journal of photochemistry* **1985**, 28, 103–110.

(21) Fukuda, H.; Amimoto, K.; Koyama, H.; Kawato, T. Crystalline Photochromism of N-Salicylidene-2,6-Dialkylanilines: Advantage of 2,6-Dialkyl Substituents of Aniline for Preparation of Photochromic Schiff Base Crystals. *Organic & biomolecular chemistry* **2003**, 1, 1578–1583.

(22) Amimoto, K.; Kawato, T. Photochromism of Organic Compounds in the Crystal State. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2005**, 6, 207–226.

(23) Kawato, T.; Kanatomi, H.; Koyama, H.; Igarashi, T. Photoisomerization and Thermoisomerization II: Steric Requirements for Photochromism and Thermochromism of N,N'-Bis (Salicylidene)Diamines. *Journal of Photochemistry* **1986**, 33, 199–208.

(24) Higelin, D.; Sixl, H. Spectroscopic Studies of the Photochromism of N-Salicylideneaniline Mixed Crystals and Glasses. *Chemical Physics* **1983**, 77, 391–400.

(25) Hadjoudis, E.; Vittorakis, M.; Mavridis, I. M. Photochromism and Thermochromism of Schiff Bases in the Solid State and in Rigid Glasses. *Tetrahedron* **1987**, 43, 1345–1360.

(26) Casades, I.; Álvaro, M.; García, H.; Pillai, M. N. Photochemistry of Anils in NaY Zeolite. *European Journal of Organic Chemistry* **2002**, 2002, 2074–2079.

(27) Kawato, T.; Amimoto, K.; Maeda, H.; Koyama, H.; Kanatomi, H. Photochromism of Guest N-Salicylideneaniline in the Rooms of Host Bile Acid Derivatives. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals* **2000**, 345, 57–62.

(28) Pistolis, G.; Gegiou, D.; Hadjoudis, E. Effect of Cyclodextrin Complexation on Thermochromic Schiff Bases. *Journal of Photochemistry and Photobiology A: Chemistry* **1996**, 93, 179–184.

(29) Haneda, T.; Kawano, M.; Kojima, T.; Fujita, M. Thermo-to-Photo-Switching of the Chromic Behavior of Salicylideneanilines by Inclusion in a Porous Coordination Network. *Angewandte Chemie* **2007**, 46, 6643–6645.

(30) Cohen, M. D. The System: 4-Chloro-N-Salicylideneaniline—4-Bromo-N-Salicylideneaniline. *J. Chem. Soc. B* **1968**, 0, 373–376.

(31) Johmoto, K.; Sekine, A.; Uekusa, H. Photochromism Control of Salicylideneaniline Derivatives by Acid–Base Co-Crystallization. *Crystal Growth & Design* **2012**, 12, 4779–4786.

(32) Carletta, A.; Buol, X.; Leyssens, T.; Champagne, B.; Wouters, J. Polymorphic and Isomorphic Cocrystals of a *N* -Salicylidene-3-Aminopyridine with Dicarboxylic Acids: Tuning of Solid-State Photo- and Thermochromism. *The Journal of Physical Chemistry C* **2016**, 120, 10001–10008.

(33) Hutchins, K. M.; Dutta, S.; Loren, B. P.; MacGillivray, L. R. Co-Crystals of a Salicylideneaniline: Photochromism Involving Planar Dihedral Angles. *Chemistry of Materials* **2014**, 26, 3042–3044.

(34) Varughese, S.; Desiraju, G. R. Using Water as a Design Element in Crystal Engineering. Host−Guest Compounds of Hydrated 3,5-Dihydroxybenzoic Acid. *Crystal Growth & Design* **2010**, 10, 4184–4196.

(35) Fujii, K.; Sakon, A.; Sekine, A.; Uekusa, H. Reversible Color Switching of an Organic Crystal Induced by Organic Solvent Vapors. *Crystal Growth & Design* **2011**, 11, 4305–4308.

(36) Taneda, M.; Koyama, H.; Kawato, T. Vapor Switching of Photochromism of Methylenebis{ *N* -(3,5-Di-*Tert* -Butylsalicylidene)Aniline} Crystals. *Chemistry Letters* **2007**, 36, 354–355.

(37) Sugiyama, H.; Johmoto, K.; Sekine, A.; Uekusa, H. Reversible on/off Switching of Photochromic Properties in *N*-Salicylideneaniline Co-Crystals by Heating and Humidification. *CrystEngComm* **2019**, *21*, 3170–3175.

(38) Nath, N. K.; Panda, M. K.; Sahoo, S. C.; Naumov, P. Thermally Induced and Photoinduced Mechanical Effects in Molecular Single Crystals—a Revival. *CrystEngComm* **2014**, 16, 1850–1858.

(39) Lusi, M.; Bernstein, J. On the Propulsion Mechanism of “Jumping” Crystals. *Chemical Communications* **2013**, 49, 9293–9295.

(40) Higashi, T. ABSCOR, Empirical Absorption Correction Based on Fourier Series Approximation. *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation, Rigaku Corporation* **1995**.

(41) Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallographica Section C Structural Chemistry* **2015**, 71, 3–8.

(42) Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Crystallographica Section D Biological Crystallography* **2009**, 65, 148–155.

(43) Skoko, Ž.; Zamir, S.; Naumov, P.; Bernstein, J. The Thermosalient Phenomenon. “Jumping Crystals” and Crystal Chemistry of the Anticholinergic Agent Oxitropium Bromide. *Journal of the American Chemical*

Society **2010**, 132, 14191–14202.

(44) Shibuya, Y.; Itoh, Y.; Aida, T. Jumping Crystals of Pyrene Tweezers: Crystal-to-Crystal Transition Involving π/π-to-CH/π Assembly Mode Switching. *Chemistry - An Asian Journal* **2017**, 12, 811–815.

(45) Singh, M.; Bhandary, S.; Bhowal, R.; Chopra, D. Observation of Bending, Cracking and Jumping Phenomena on Cooling and Heating of Tetrahydrate Berberine Chloride Crystals. *CrystEngComm* **2018**, 20, 2253–2257.

(46) Jacquemin, P.-L.; Robeyns, K.; Devillers, M.; Garcia, Y. Photochromism Emergence in *N*-Salicylidene *p*-Aminobenzenesulfonate Diallylammonium Salts. *Chemistry - A European Journal* **2015**, 21, 6832–6845.

(47) Chen, X.; Li, T.; Morris, K. R.; Byrn, S. R. Crystal Packing and Chemical Reactivity of Two Polymorphs of Flufenamic Acid with Ammonia. *Molecular Crystals and Liquid Crystals* **2002**, 381, 121–131.

(48) Chen, X.; Morris, K. R.; Griesser, U. J.; Byrn, S. R.; Stowell, J. G. Reactivity Differences of Indomethacin Solid Forms with Ammonia Gas. *Journal of the American Chemical Society* **2002**, 124, 15012–15019.

(49) Braga, D.; Cadoni, M.; Grepioni, F.; Maini, L.; Rubini, K. Gas–Solid Reactions between the Different Polymorphic Modifications of Barbituric Acid and Amines. *CrystEngComm* **2006**, 8, 756–763.

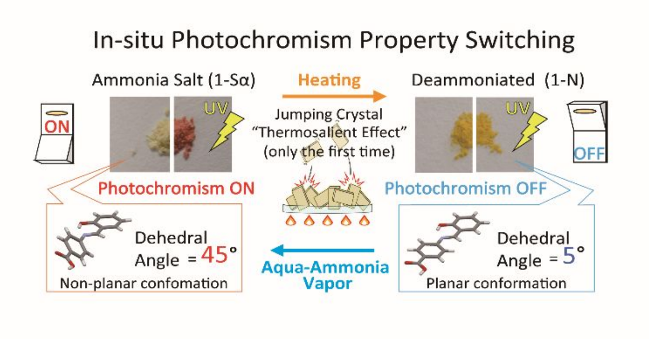
(50) Akhbari, K.; Morsali, A. Solid-State Structural Transformations of Two Ag^{I} Supramolecular Polymorphs to Another Polymer upon Absorption of HNO_3 Vapors. *Inorganic Chemistry* **2013**, 52, 2787–2789.

(51) Kato, M.; Ito, H.; Hasegawa, M.; Ishii, K. Soft Crystals -Flexible Response Systems with High Structural Order. *Chemistry - A European Journal* **2019**, 25, 1–9.

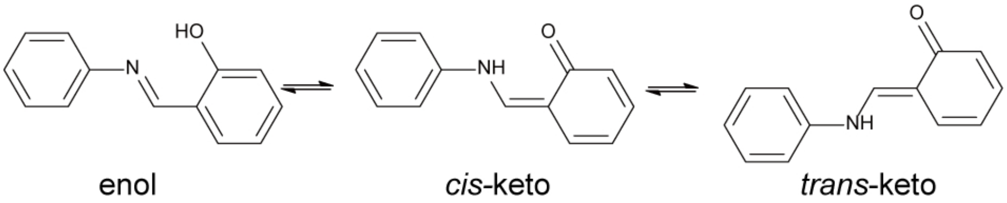
For Table of Contents Use Only

In-situ Photochromism Switching with Crystal Jumping through the Deammoniation of *N*-Salicylideneaniline Ammonium Salt

Haruki Sugiyama,[1, 2] Kohei Johmoto,[2] Akiko Sekine,[2] and Hidehiro Uekusa[2]*

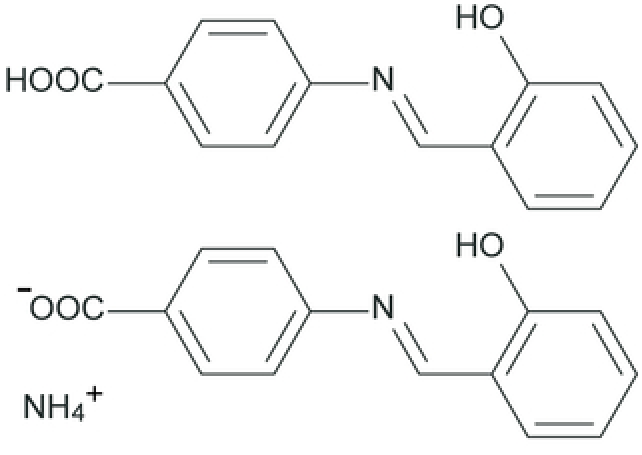


N-Salicylideneaniline ammonium salt crystals **1-Sα** exhibited the jumping crystal phenomenon, and the photochromic properties were switched off due to the molecular conformation change through the deammoniation transition upon heating.



The photochromism mechanism in *N*-salicylideneanilines.

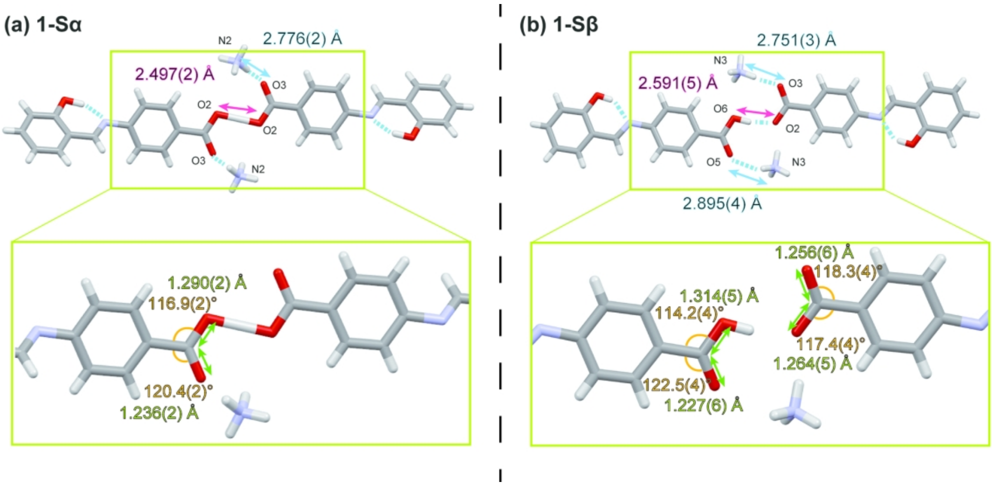
80x16mm (300 x 300 DPI)



1-Sα and 1-Sβ

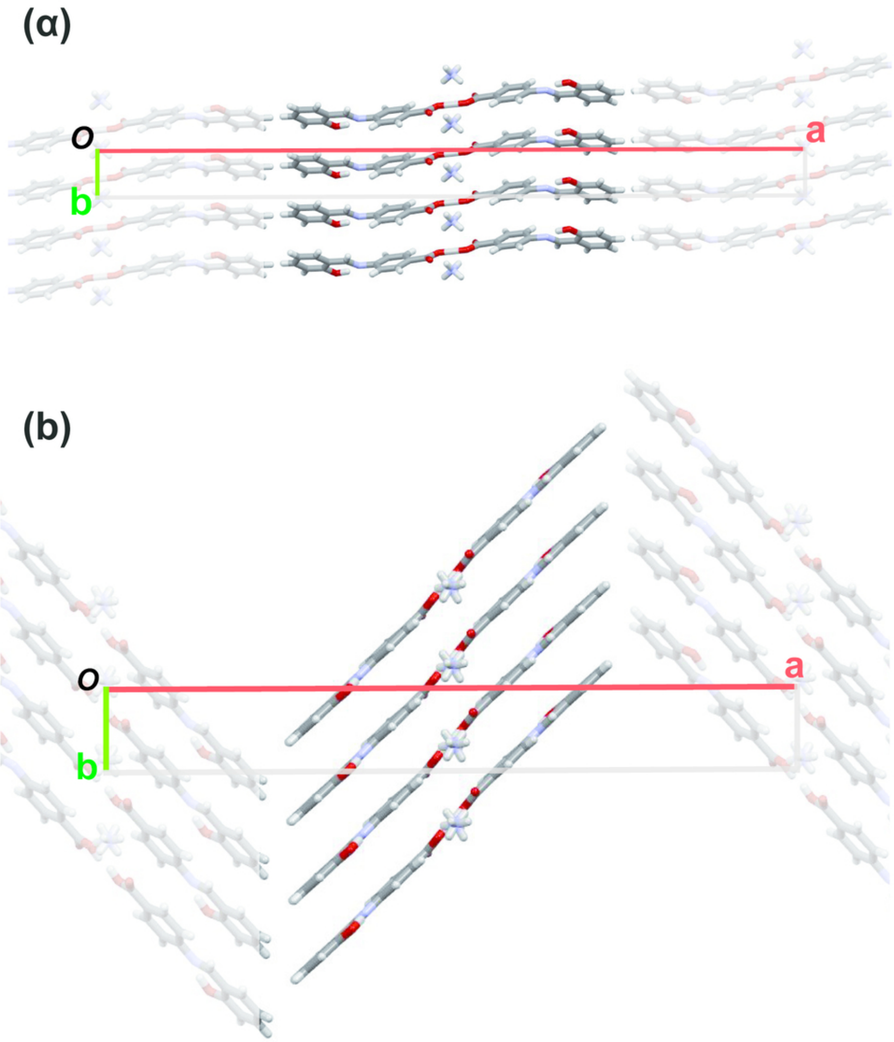
The chemical structures of **1-Sα** and **1-Sβ**.

26x23mm (300 x 300 DPI)



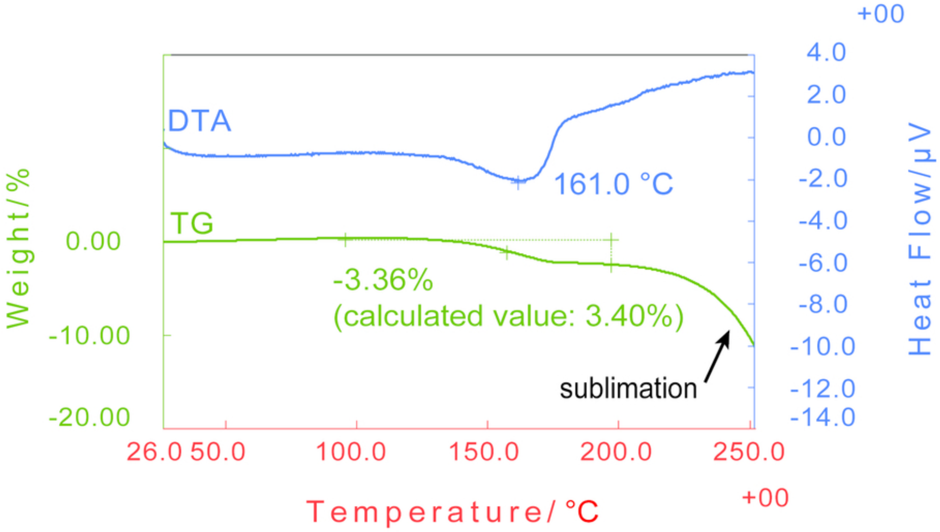
The crystal structures of **1-Sα** (a) and **1-Sβ** (b). Hydrogen bonds are highlighted with blue dotted lines.

166x79mm (300 x 300 DPI)



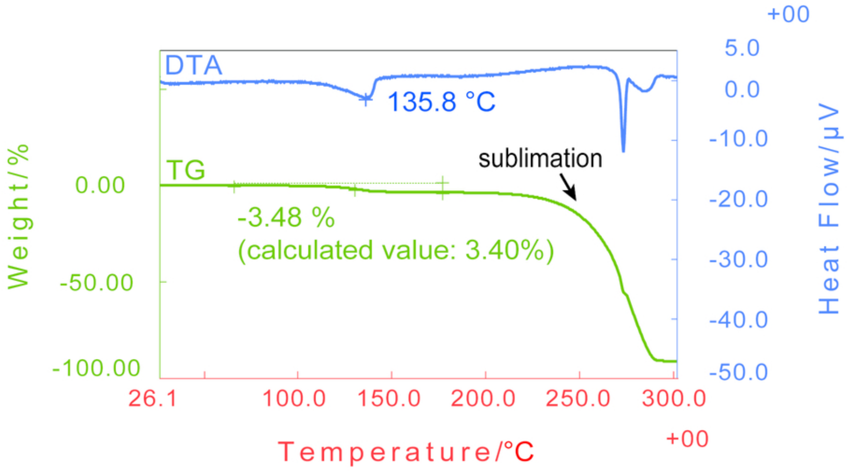
The crystal structure of **1-Sα** (a) and **1-Sβ** (b) viewed along the *c*-axis.

90x107mm (300 x 300 DPI)



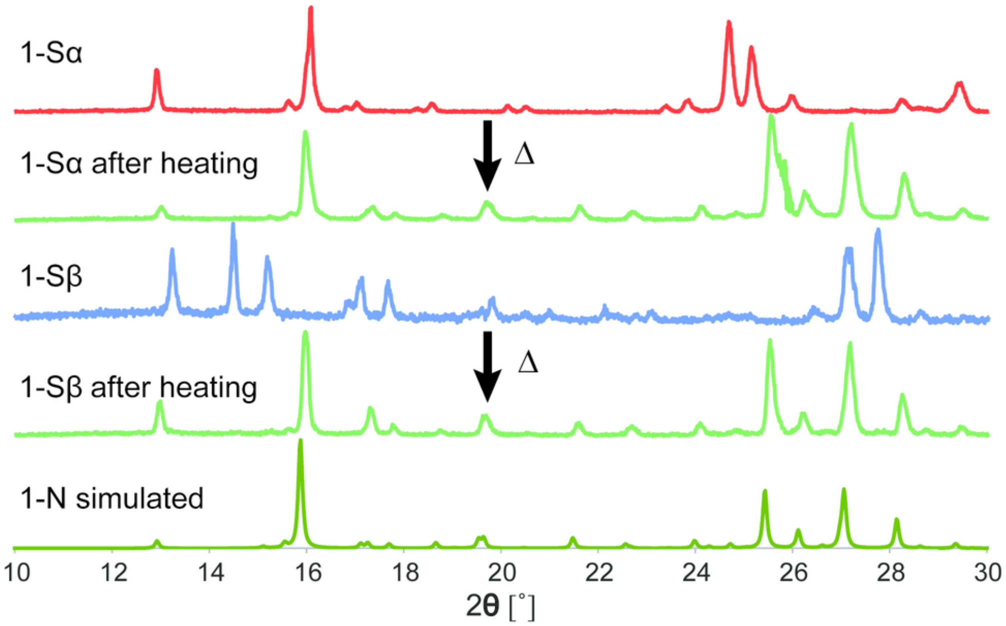
TG-DTA curves of **1-Sα**. **1-Sα** deammoniated to **1-N** at 161.0 °C with a weight loss of 3.45 % (the ideal mass percentage of 0.5 ammonia molecules is 3.40%).

81x47mm (300 x 300 DPI)



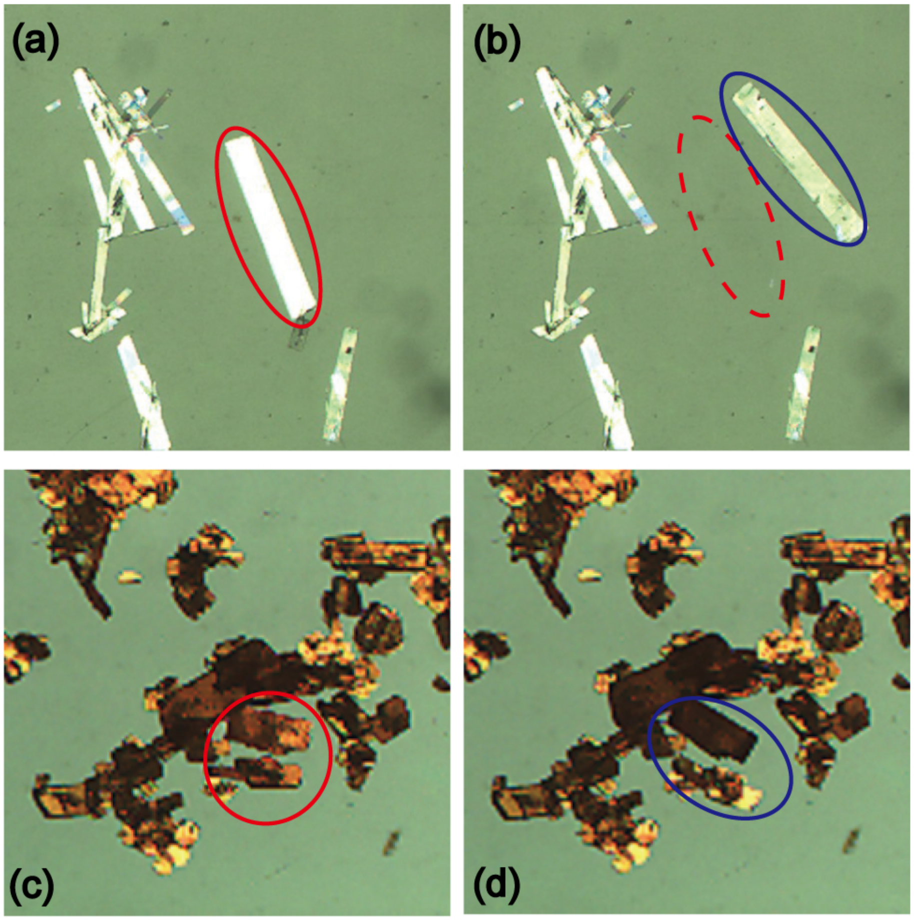
TG-DTA curves of **1-Sβ**. **1-Sβ** deammoniated to **1-N** at 135.8 °C with a weight loss of 3.48 % (the ideal mass percentage of 0.5 ammonia molecules is 3.40%).

90x51mm (300 x 300 DPI)



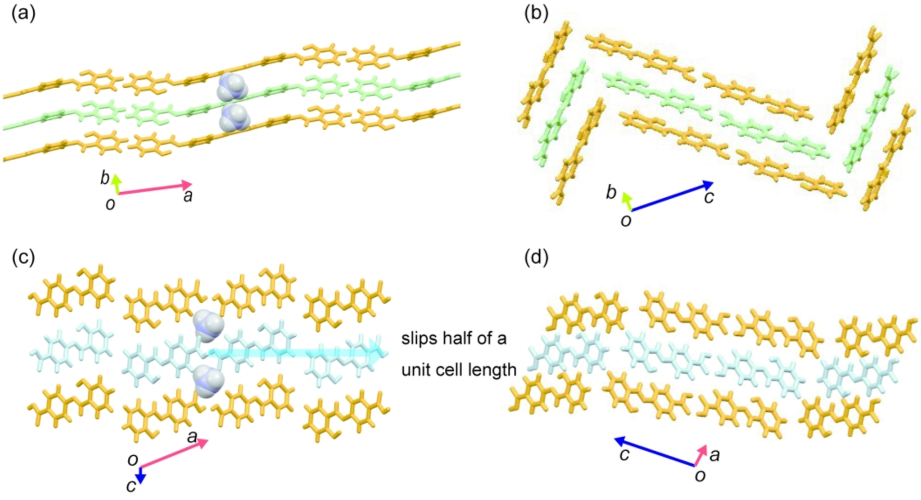
The PXRD patterns of **1-Sα** (red), after the heating of **1-Sα** (green), **1-Sβ** (blue), after the heating of **1-Sβ** (green), and **1-N** (dark green) calculated from the crystal data.

81x59mm (300 x 300 DPI)



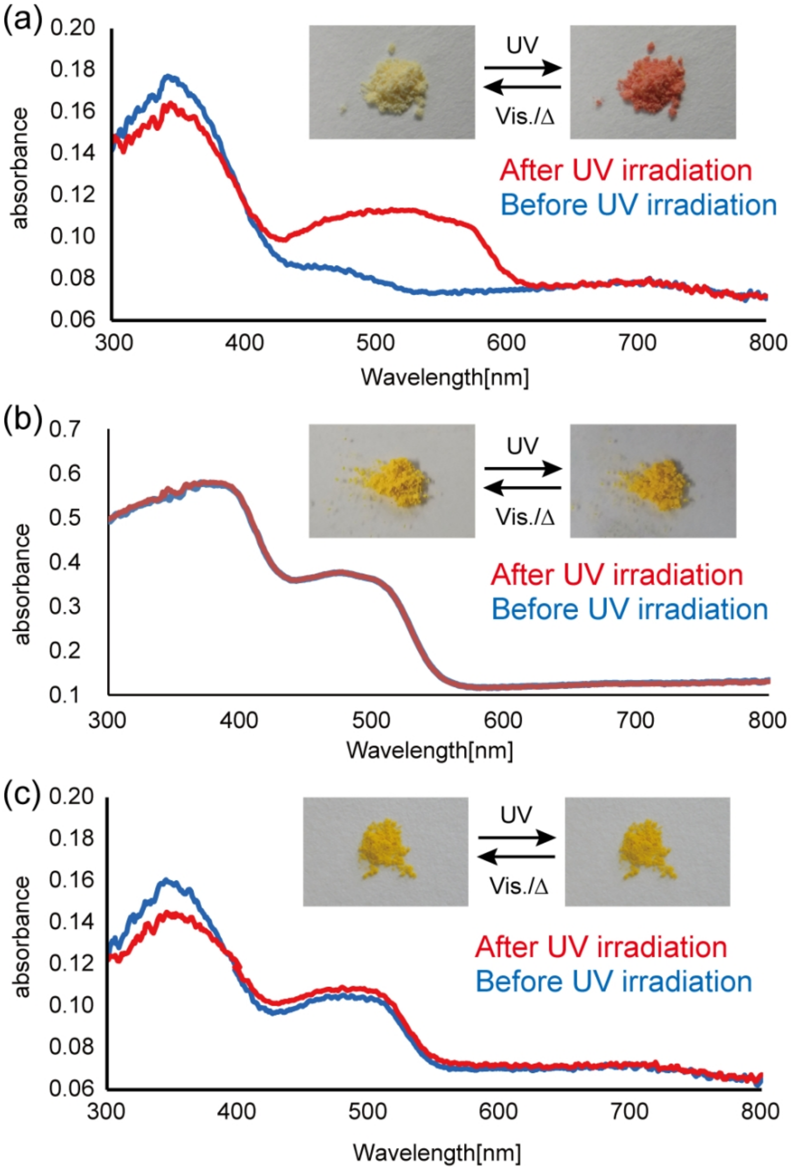
Photographic images showing before (a, c) and after (b, d) crystal jumping of **1-Sα** and **1-Sβ**, respectively, upon heating using a hot plate. The crystal circled by a red line jumped up to the position circled by a blue line.

90x90mm (300 x 300 DPI)



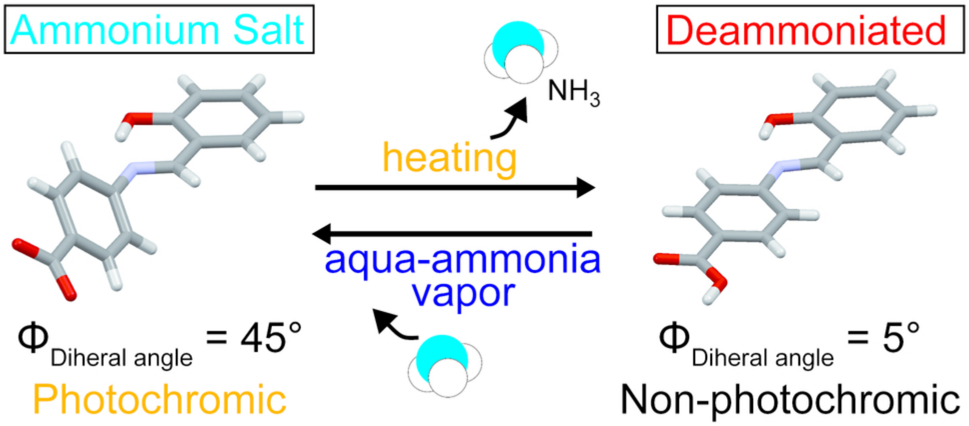
(a) The straight chain in **1-Sα** viewed along the *c*-axis. (b)The zigzag chain in **1-N** viewed along the *a*-axis. (c)The zigzag chain pattern in **1-Sβ** viewed along the *b*-axis. (d) The zigzag chain in **1-N** viewed along the *b*-axis.

175x99mm (300 x 300 DPI)



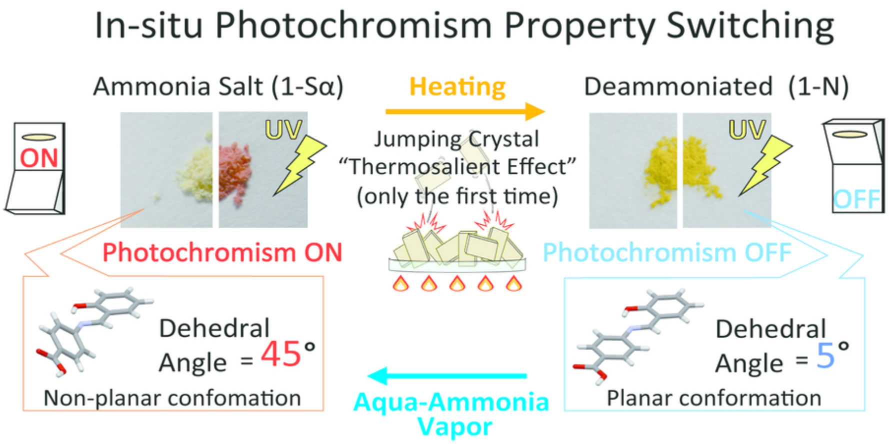
The UV/Vis. diffuse reflectance spectra before (blue) and after (red) UV irradiation for (a) **1-Sα**, (b) **1-Sβ**, and (c) **1-N**. The inset photographs show the color changes of the powdery crystalline samples before and after UV irradiation.

84x127mm (300 x 300 DPI)



Structural changes upon deammoniation from **1-Sα** to **1-N**. The molecular conformation converted from non-planar to planar, and the photochromic properties changed.

84x38mm (300 x 300 DPI)



N-Salicylideneaniline ammonium salt crystal **1-Sα** exhibited the jumping crystal phenomenon upon heating, and the photochromic properties were switched off due to the molecular conformation change through the deammoniation transition.

86x46mm (300 x 300 DPI)