

# Article

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# Temperature Controlling Polymorphism and Polymorphic Interconversion in Sublimation Crystallization of 5-Methoxy-salicylaldhyde Azine

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ABSTRACT: Traditional growth of organic crystals is mostly based on solution processing techniques, but facile crystal preparation of compounds with poor solubility or polymorphic characters remains a challenge. Here we demonstrate an in-air sublimation method for strategical preparation of 5-methoxy-salicylaldhyde azine (compound 1) in two polymorphic crystal forms by controlling sublimation temperature. The kinetic stable one was offered under 180 °C with the opposite orientation of methoxy group with respect to the longest chain in the molecule (termed 1-anti), while the thermodynamic stable one was offered above 200 °C with that in same orientation (termed 1-syn). Moreover, the overall dynamic forming and interconversion between 1-anti and 1-syn crystals in sublimation process were well studied by powder X-ray diffraction,

IR, emission spectra and DFT calculations. All the results revealed this sublimation crystallization technique should be helpful for detection and even selective preparation of pure organic crystals with polymorphic characters.

### INTRODUCTION

 The performance of organic crystalline materials are known to have great relationship with their molecular arrangement in crystals.<sup>1-6</sup> As such, effective preparation of organic crystals in desired packing modes will definitely provide benefits to many frontier fields, including advanced optical materials,<sup>7-10</sup> electronic devices,<sup>11-14</sup> biomedical appliances.<sup>15-17</sup> Generally, crystal growth methods are mostly focused on solution evaporation/cooling,<sup>18-22</sup> liquid diffusion,<sup>16,23-25</sup> vapor diffusion and hydrothermal/solvothermal,<sup>24,26,27</sup> and all those solvents-involved methods are economical, simple, highly processable and largely favor the growth of functional pseudopolymorph crystals which incorporating guest solvents.<sup>28-31</sup> Although state-of-the-art, these methods still face the challenge in the preparation of those materials with poor solubility or polymorphic characters.<sup>32,33</sup>

Recently, more and more attentions have been paid to sublimation growth organic materials, which turned out to be more applicable in preparing those guest-free single crystals or insoluble organic crystal materials.<sup>32,33</sup> Moreover, high-quality crystals and undiscovered polymorphs of organic materials can also be achieved under certain sublimation conditions.<sup>12,33-36</sup> For instance, Koga and co-workers obtained the syn conformer crystals of 1,8-naphthyridine derivative by subliming anti counterparts.<sup>37</sup> Besides, a sublimation method to grow new polymorphs of 2,6-dichloro-naphthalene diimide was also first reported by Würthner and colleagues.<sup>38</sup> In fact, it is conceivable and intriguing for controlling polymorphism in the crystallization of organic

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compounds by adjusting sublimation temperature,<sup>39-41</sup> through which two polymorphic crystal forms of 1,1-bis(4-hydroxyphenyl)cyclohexane can be confirmed.<sup>42</sup> Impressively, McArdle 'group had revealed the use of low-temperature gradient sublimation to attain two pure samples of polymorphic stanozolol in vacuum.<sup>43</sup> Still and all, it remains a challenge but of great importance to discover and effectively isolate polymorphic organic crystals by sublimation.

In this paper, we first discovered and decoded the polymorphism of 5-methoxy-salicylaldhyde azine (1) by controlling the sublimation temperature under ambient conditions, which has been attained in one crystal form by Yousuf and co-workers.<sup>44</sup> With the sublimation temperature increased, the sublimed crystal structures gradually change from the kinetically stable crystals (termed 1-anti crystal) to thermodynamically stable one (termed 1-syn crystal), accompanying with the emission color changed from orange yellow to red. Single crystal X-ray diffraction revealed the two polymorphs were distinguished from each other in the orientation of methoxy group with respect to the longest chain in the molecule, thereby leaded to significantly different molecular arrangements. To the best of our knowledge, this is the first report in controlling crystallization of polymorphic salicylaldehyde azine derivatives through sublimation temperature adjustment in air. By photoluminescence (PL), IR spectra, X-ray diffraction analysis and DFT calculations, the overall dynamic forming and interconversion between 1-anti and 1-syn crystals in sublimation process were illustrated in detail.

# **RESULTS AND DISCUSSION**

**Synthesis of 1.** 2-hydroxy-5-methoxybenzaldehyde was refluxed with hydrazine hydrate at a molar ratio of 2:1 at 80 °C for 5 hours. The resulting product was filtrated and washed with ethanol to give yellowish powder (1, Scheme 1). The powder was then dried in vacuum at low temperature.



Scheme 1. Synthesis of 5-methoxy-salicylaldhyde azine (1).

Preparation and Crystallography of Polymorphs. Since the powders were stable and unchanged after being exposed to air at room temperature for several days, it was assumed whether the single crystals can be prepared by sublimation.<sup>33,34,43</sup> The device employed in the sublimation experiments was consists of an electricity hot jacket and a micro sublimator. As schematized in Figure 1a, the obtained yellowish powders were put in the bottom of the micro sublimator in air, then placed inside the electricity hot jacket. After that, setting the temperature and adding the adjustable lid at the top of the electricity hot jacket to ensure constant temperature. At the meanwhile, the sublimation temperature was also monitored by a thermometer attached to the sublimator to ensure the same temperature as the settings. By controlling the temperature, the powders of 1 will be sublimed, and then the sublimate was collected on quartz tube wall with cooling water. In order to explore the feasibility of this experiment and the appropriate temperature for sublimation, we first raised the temperature every 10 °C and stop for 1 hour to reach the melting point. Results revealed that only small crystals appeared on quartz tube wall until heated to 160 °C in apparatus and grew larger to display rodlike shapes at 170 °C. When the temperature in the micro sublimator reached 170 °C and kept for 2 hours, the collected sublimates were rodlike crystals (polymorph A) while it turned to be lamellar crystals (polymorph **B**) with temperature at 220  $^{\circ}$ C, illustrated in Figure 1b and 1c. More importantly, the collected sublimate were crystals with lengths of several hundreds

of micrometers, fitting for single crystal X-ray diffraction. Further increasing the temperature is not recommended since the substrates in the bottom of sublimator had all melted at 220 °C.



**Figure 1.** Sublimation crystallization growth of polymorphous **1**. (a) Schematic drawing of the applied sublimation apparatus for crystal growth. (b) Fluorescence microscope images of polymorph **A** in the solid state under UV light excitation. (c) Fluorescence microscope images of polymorph **B** in the solid state under UV light excitation.

With the aid of single crystal X-ray diffraction analysis, the main difference of the two polymorphs was the mutual orientation of the two methoxy groups correspond to the hydroxyl groups, in which the methoxy and the hydroxyl groups were oriented in the opposite direction for polymorph **A** (Figure 2a, termed **1-anti**), and oriented in the same direction for polymorph **B** (Figure 3a, termed **1-syn**). In both forms, the molecules all located inversion centers which are at the midpoint of the N-N bond. The crystal data of the two crystals were summarized in Figure S1 and Table S1-4 (Supporting Information).

As shown, **1-anti** crystal belonged to monoclinic space group  $P2_1/c$  with two crystallographically independent half molecules per asymmetric unit and four molecules per unit cell. The O-H…N hydrogen bonding interaction between H atoms on the hydroxyl groups and adjacent N atoms was 1.723 Å (Figure 2a). As for **1-syn** crystal, it crystallized in the monoclinic space group  $P2_1/c$  with one half molecule per asymmetric unit and two molecules per unit cell

according to X-ray analysis. The O-H···N hydrogen bonding interaction between H atoms on the hydroxyl groups and adjacent N atoms was 1.788 Å (Figure 3a). While **1-anti** crystal emitted intense orange yellow color (Figure 1b,  $\Phi = 11.70$  %) at  $\lambda_{em} = 580$  nm (Figure 4), the **1-syn** crystal emitted weak red fluorescence (Figure 1c,  $\Phi = 1.70$  %) at  $\lambda_{em} = 650$  nm (Figure 4). For **1-anti** and **1-syn** crystals, the adjacent parallel-packed molecules were observed with the interplanar distance of 3.297 Å and 3.475 Å and slipping angles along the long axis of 46.1° and 32.1°, respectively, both resulted in typical face-to-face  $\pi$ - $\pi$  stackings. (Figure 2f and 3f). From the top view of the adjacent parallel-packed molecules, the overlaps ratio in **1-anti** crystal was larger than **1-syn** ones (Figure 2c and 3c). However, the strong  $\pi$ - $\pi$  interactions caused by higher degree of overlap in **1-anti** crystal did not result in general observed red-shifted emission in common fluorescence materials, which brought an investigation in its fluorescence mechanism at single molecular level.



**Figure 2.** The molecular structures and stackings in **1-anti** crystal. (a,b) The molecular conformation in front and side view, respectively. (c) The molecular overlap between adjacent

molecules. (d) Molecular stacking structures. (e) Front view with the illustration of pitch angle and interplanar distance. (f) Side view with the illustration of roll angle and interplanar distance.



**Figure 3.** The molecular structures and stackings in **1-syn** crystal. (a,b) The molecular conformation in front and side view, respectively. (c) The molecular overlap between adjacent molecules. (d) Molecular stacking structures. (e) Front view with the illustration of pitch angle and interplanar distance. (f) Side view with the illustration of roll angle and interplanar distance.



Figure 4. Normalized PL spectra of compound 1 in solid state. ( $\lambda_{ex}$ = 365 nm)

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In terms of the salicylaldehyde azine derivatives were extensively used in probing its excitedstate intramolecular proton transfer (ESIPT) process in the photoluminescence procedure.<sup>45-48</sup> Further studies were conducted by solid UV absorption spectrum and time-correlated singlephoton counting (TCSPC) technique method shown in Figure S2 and S3 (Supporting Information) and Table S5 (Supporting Information). Combining the large stokes shifts of 1-anti and 1-syn crystals with the fluorescence decay properties, it was deduced that an ESIPT process had taken place in the two polymorphs after photoexcitation.<sup>49-53</sup> From TDDFT calculation to reveal this ESIPT mechanism, the optimized geometric conformations of the enol ( $ES_0$ ), enol\* ( $ES_1$ ), keto  $(KS_0)$  and keto\*  $(KS_1)$  forms and the results are shown in Figure S4 (Supporting Information). It can be seen that both for 1-anti and 1-syn crystals, upon excitation of the S<sub>1</sub> state, the OH bond would be prolonged, and then transferred to one of N atom to form  $KS_1$  state. Eventually, the excited KS<sub>1</sub> structure decayed to the ground state KS<sub>0</sub> by radiative processes followed by a reverse proton transfer, returning to the original ES<sub>0</sub> state. Therefore, the smaller energy gap of 1-syn compared to 1-anti (Figure S4, Supporting Information) was consistent with the observed red shift of the ESIPT fluorescence.

Temperature controlled sublimation crystallization. Since two polymorphic crystals of 1 were obtained in different sublimation temperatures, it was reasonable to deduce that the temperature should play a crucial role in the growth of the crystal structures. We raised the temperature at each subsequent 5 °C interval with 2 hours stopovered from 170 to 220 °C, and then collected each interval samples for further characterization. It was worth mentioning that whether the substrates for sublimation was 1-anti, 1-syn crystals or the mixture of the two polymorphs, the characteristics of the sublimate in the sublimation process were the same.



**Figure 5.** Characterization of crystallization conversion of sublimate. (a) Powder X-ray diffraction (PXRD) patterns of sublimate at different sublimation temperature. (b) PL spectra of sublimate in the solid state at different sublimation temperature ( $\lambda_{ex} = 365$  nm).

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The collected sublimate were measured for PXRD patterns directly without further treatment, as shown in Figure 5a. The strong preferred orientation and the small number of observed peaks in the PXRD patterns were ascribed to the needle shapes of the sublimed crystals.<sup>41,43</sup> The needle-shaped sublimates collected at 170 °C showed four peaks at 10.3°, 13.2°, 14.9° and 19.3° of simulate **1-anti** crystal (which are marked with '×' in Figure 5a). After rising the temperature to 220 °C, the diffraction peaks of the collected sublimate showed characteristics of simulated 1syn crystal at 11.3°, 13.4°, 14.3°, 17.4°, 21.4°, 22.6° (which are marked with 'o' in Figure 5a). During the heating process, the sublimate collected at 170-180 °C had characteristic peaks of 1anti crystal according to the simulated XRD patterns. The diffraction peaks of the gathered sublimate at 185-195 °C began displayed peaks of both 1-anti and 1-syn crystals, indicating the existence of mixed crystals. When the sublimate was collected at 200 °C, its PXRD pattern exhibited both sharp and intense peaks of **1-syn** crystal at 14.3° and 22.6°, and weak characteristic peak of 1-anti crystal at 13.2°, which indicated that 1-syn crystal occupied the majority. As the temperature increased to 210 °C, the diffraction peaks of the collected sublimate showed higher purity, all the characteristic peaks of 1-anti crystal were nearly negligible, accompanied by an increase in intensity of characteristic peaks of **1-syn** crystal. There no peaks indicative of the existence of **1-anti** crystal when the temperature reached at 220 °C.

The fluorescence changes were recorded by PL spectra in detail. As shown in Figure 5b, the fluorescence intensity at 580 nm declined with the sublimation temperature increasing. During the process from 180 to 210 °C, the emission band at 580 nm of the sublimate gradually expanded toward 650 nm. While heating at 220 °C, the sublimate behaved red fluorescence (Figure S5, Supporting Information) and the sole emission peak at 650 nm had revealed instead of a broad emission band. The trend of PL spectra changes were well accordance with the red

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shifted emission and low quantum yield of **1-syn** crystals. Moreover, the composition of sublimate were also supported by IR spectra shown in Figure 6. The absorption originated from C-O-C and C-O stretching of the sublimate at 1161 cm<sup>-1</sup> and 1188 cm<sup>-1</sup> underwent unperceived shift when the sublimation temperature increased to 180 °C. When the sublimation temperature increased to 185 °C, the observed absorption intensity of C-O-C and C-O became stronger and the stretching gradually shifted to low wavenumber, finally, shifted to 1151 cm<sup>-1</sup> and 1176 cm<sup>-1</sup> at 220 °C (Figure 6). As described above, the collected sublimate at 170 °C adopted the conformation of **1-anti** crystal while the sublimate at 220 °C was in the conformation of **1-syn**. It was not hard to explain that the orientation of methoxy group toward the longest chain in the molecule had quite a different effect on the  $\pi$  delocalization of a conjugated system, resulting in discrepant absorption stretching band. Hence, these results were well accordance with the change with PXRD patterns, demonstrated that the sublimate collected at different temperatures had different temperatures of growth kinetics.



**Figure 6.** C-O-C and C-O stretching of sublimate at each temperature. Dashed lines indicate the changes of stretching.



**Figure 7.** The sublimate formation and transformation. (a) The mechanism of **1-anti** and **1-syn** crystals sublimation formation studied by DFT calculation (unit: kcal mol<sup>-1</sup>). Because of difficulty in finding transition states, both from **1-anti** to **1-antis** and from **1-syn** to **1-syns**, the potential energy curves were attained by scanning the distance between two monomers based on the optimized dimers structures. (b) The reversible transformation scheme between **1-anti** and **1-syn** crystals.

In order to give deep insight into the process of temperature controlled sublimation crystallization, the DFT calculations were carried out to explore the mechanism of crystal formation. Figure 7a presented potential energy profiles for the transformation between **1-anti** and **1-syn** molecules. It was found that the transformation from **1-anti** to **1-syn** molecules was taken place via two steps, in which the twist of two C-O-C was occurred step by step via two

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transition states (TS1 and TS2). The energy barriers for two steps were 13.74 and 9.45 kcal mol<sup>-1</sup> for TS1 and TS2, respectively. And also, the energy of **1-syn** was found to be 0.94 kcal mol<sup>-1</sup> higher than that of **1-anti**, which meant **1-anti** was more stable than **1-syn** in gas phase, and the conversion from **1-anti** to **1-syn** need under certain temperature..

Because the crystallization process was difficult to simulate by DFT calculation due to too many atoms, for the convenience of calculation, the dimers was used as simplified model in the calculation to measure the difference of intermolecular interaction of 1-anti and 1-syn. From Figure 7a, it was also found that the aggregate of two molecules via intermolecular interaction both for 1-syn and 1-anti undergo low barrier of 0.2 and 1.44 kcal mol<sup>-1</sup>, and released -12.25 and -14.38 kcal mol<sup>-1</sup> energy, to form the dimer **1-syn** and **1-anti**, respectively. Because of the low activation energy barrier and large reaction energy, the route from 1-anti to 1-antis (dimer of 1anti) would be the fastest and to reach the kinetically favored structure. However, from 1-anti to 1-syns (dimer of 1-syn) via 1-syn, the thermodynamically favored crystal would take longer to form because the activation barrier was much higher, but it would be more stable because the final energy state was the lowest. So, in low sublimation temperature, the kinetically favored crystal would be formed. However, when the sublimation temperature and time is high and long, the fine product would transfer to thermodynamically favored crystal. This conclusion was well agreement with the above experimental results that controlling the sublimation temperature may result in two polymorphs of compound 1 (Figure 7b and Figure S5, Supporting Information).

**Crystal-to-Crystal transformation of the polymorphs.** Notably, the fluorescence microscopy images (Figure S5, Supporting Information) witnessed that the fluorescence of the substrates of **1-anti** crystal in 160 °C was quite different from the origin samples in apparatus but resemble the fluorescence of **1-syn** crystal, while the substrates of **1-syn** crystal displayed no

fluorescence change in the heating procedure (Figure S5, Supporting Information), thus leaded to the proposal that thermal treating may induce crystals transformation. To investigate this thermochromism, the differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) of the two crystals were performed. In the first and second heating cycle, both **1-anti** and **1-syn** crystals showed one peak at 217 °C (Figure S7 and S8, Supporting Information), which was the endothermic peak of melting point. Meanwhile, an exothermic peak of **1-anti** and **1-syn** crystals upon cooling procedure appeared at 192 °C was due to solidification. The same DSC and TGA curves of **1-syn** and **1-anti** crystals suggested that heating can induce phase transition. However, due to the small energy barrier resulted from the rotation of methoxy group around the C-O bond in molecule (0.94 kcal mol <sup>-1</sup>, Figure 7a), it was assumed that the phase transition can be difficult to detect in DSC and TGA analysis.



Figure 8. Powder X-ray diffraction of 1-anti crystal under heating at different temperature.



Figure 9. Characterization of 1-anti crystal under thermal treatment. (a) PL spectra of 1-anti crystal under thermal treatment ( $\lambda_{ex}$ = 365 nm). (b) IR spectra of polymorphs 1 and change of IR spectra of 1-anti crystal upon thermal treatment.

As indicated in Figure S9a (Supporting Information), the measured PXRD spectra of pristine **1-anti** crystals have preferred orientation dominated by their 4 0 2 reflections (peaks at 19.3°),<sup>42.43</sup> while the reflection peaks from 20° to 35° became more distinct and the preferred orientation of 4 0 2 reflections was significantly weakened for the ground samples. Notably, grinding at room temperature induced no change in the crystal form. Next, we employed PXRD analysis to monitor the changes of **1-anti** crystal upon thermal treating. These pristine crystals were heated on a heating platform from 60 °C to 160 °C at each subsequent 10 °C interval with 10 minutes stopovered and then collected the crystals in each interval samples for characterization. The changes of PXRD patterns of **1-anti** crystal in the heating procedure were shown in Figure 8. When the temperature increased from 60 to 100 °C, there was no large difference in peak position but intensity changed. The intensity of peaks at 10.3° for **1-anti** crystal (denoted by circles in Figure 8) decreased to the minimum when heated at 100 °C, and the peaks finally disappeared when heated at 110 °C. Moreover, the peaks at 19.3° corresponded to

the 4 0 2 reflection of **1-anti** crystal also disappeared when heated at 110 °C (denoted by circles in Figure 8). At the same time, characteristic peaks corresponding to **1-syn** crystal at 11.3°, 14.3°, 17.4° and 22.6° began to appear when heated to 110 °C (denoted as dashed circles in Figure 8). Moreover, PXRD patterns of **1-anti** crystal upon heating at 160 °C was quite different from its origin state but same with that of **1-syn** crystal (Figure S10, Supporting Information), indicating that heating might induce crystals of **1-anti** conversion into the thermodynamical phase, i.e. **1syn**. This was well agreement with the calculation results (Figure 7a) and evidenced that heatinduced Crystal-to-Crystal transformation between the two polymorphs had taken place at 100-110 °C.

This also brings the question of whether the rate of structure transition have differences between crystal state and powder state. Exposed to air at 100 °C for 5 minutes, the differences in PL spectra and PXRD patterns between the pristine crystals and ground samples were monitored. As shown in Figure S9a (Supporting Information), PXRD patterns of the ground samples exhibited similar **1-syn**-like peaks but there are still **1-anti**-like peaks on crystals samples (marked as black circles). PL spectra (Figure S9c, Supporting Information) also confirmed that the crystal transformation is easily to occur in ground samples at a certain temperature. However, few experimental clues were available for the definition of the easily rotatable C-O bonds and specific phase transition temperature. Inspired by the above fact, the pristine **1-anti** crystals were subjected to PL and IR spectroscopy analyses by heating at intervals of 10 °C for 10 minutes during 60 to 160 °C. The emission intensity of **1-anti** crystal at 580 nm decreased and the emission band exhibited red-shift from 580 nm to 650 nm. When heating at 120 °C, it began to appear a broad emission band centred at 580 nm gradually to disappear so that a new emission peak

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at 650 nm (Figure 9a) similar to the emission of **1-syn** appeared. At the meanwhile, an observed absorption of C-O-C and C-O stretching at 1161 and 1188 cm<sup>-1</sup> of **1-anti** crystal had no large difference when heating from 60 to 80 °C. However, two **1-syn**-like absorptions appeared at 1153 and 1178 cm<sup>-1</sup> when heated at 90 °C and then became more distinct at 110 °C (Figure 9b). Combining PXRD patterns and PL spectra analyses, the heating procedure can not only verified the easily rotatable of the methoxy group but also the occurrence of phase transition at 90 °C. The two distinct absorption bands at 110 °C also indicated that phase transition mostly took place at this temperature. In addition, thermal treating of **1-syn** caused no vibration changes in the C-O-C and C-O as indicated in Figure S11a (Supporting Information). We latter carried out heating at 130 °C to monitor the emission change over times (Figure S11b, Supporting Information), and interestingly to find that the phase transition process is step by step for a new emission peak emerges at 630 nm. It can be concluded that the hardly detected phase transition endothermic peak in measurements was ascribed to the little energy required process, coinciding with that theoretical calculation and DSC and TGA experimental analyses.

# CONCLUSIONS

In summary, we demonstrated and decoded here an in-air sublimation method suitable for obtaining and achieving interconversion of two polymorphs of 5-methoxy-salicylaldhyde azine (compound 1) by controlling the sublimation temperature. The sublimed rodlike crystals can be obtained at 170 °C while lamellar crystals can be attained at 220 °C, accompanying with emission color change from orange yellow to red. Single crystal X-ray analysis revealed the two polymorphs were rotational isomers, antiperiplanar (1-anti) and synperiplanar (1-syn) configurations toward the longest chain in the molecule, respectively. Both the experimental analysis and DFT calculation on the dynamic formation process validated the existence of

alternative conformations for **1** in the gas phase because of the temperature-sensitive structure arrangement. Furthermore, an occurrence of Crystal-to-Crystal transformation from **1-anti** to **1-syn** caused by the easily rotatable C-O bonds was observed under thermal treatment. Therefore, the controllable sublimation process can guide the detection and growth of polymorphic materials in regular shapes and good crystallinities.

EXPERIMENTAL SECTION

**Materials.** The reagents used in this research were purchased from Energy Chemical (China). Unless otherwise noted, all the solvents used in this experiment were obtained from Sinopharm Chemical Reagent (China) and were used without further purification

**Instrumentation.** <sup>1</sup>H NMR was recorded on Agilent NMR Systems 400 MHz Spectrometer (Agilent, USA). <sup>13</sup>C NMR was determined on Agilent NMR Systems 100 MHz Spectrometer using tetramethylsilane as internal standard. PL spectra were collected on a Horiba FluoroMax-4 luminescence spectrometer. The absolute fluorescence quantum efficiencies were measured using a Horiba FL-3018 Integrating Sphere. The lifetime was measured by a time-correlated single-photon counting (TCSPC) system coupled with an interchangeable NanoLEDs and a microchannel plate detection system. All excitation wavelengths were 365 nm. The solid UV/Vis diffuse reflectance spectrum was determined on Agilent Cary 60 spectrophotometer. UV-visible absorption spectra were recorded on a Lambda 750 spectrophotometer. Single crystal X-ray diffraction were collected by BRUKER SMART APEX II CCD diffractometer (Billerica, USA) operating at room temperature and their the structures were resolved and analyzed with the assistance of shelx-97 software. Powder X-ray diffraction data were collected using a XD-2 Purkinje multi crystal X-ray diffractometer in parallel beam geometry employing CuKα radiation at 40 kV and 30 mA. The diffraction data were collected in the 2 Θ range from 4 to 40° at a

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sacning speed of 1.54 s step <sup>-1</sup> with a 2  $\Theta$  step inof 0.02°. IR analysis was performed in BRUKER TENSOR II FTIR Spectrometer at room temperature. DSC analysis was performed in Dimand DSC (PerkinElmer) under argon atmosphere at a heating and cooling rate of 8 °C min <sup>-1</sup>. TG-DTA analyses were performed on Dimand TG/DTA under a dry nitrogen atmosphere at a heating rate of 5 °C min <sup>-1</sup>. Optical fluorescence images were taken by using UOP0500CC microscope at the excitation of UV (365 nm) light.

**Computational method.** All calculations were performed using Gaussian 09 package.<sup>54</sup> Theoretical calculations for the geometrical optimizations was performed by density functional theory (DFT) and time-dependent DFT (TD-DFT) using B3LYP method.<sup>55,56</sup> The -311G+(d,p) basis sets were employed for C, H, O and N atoms. We ascertained that all the transition states have only one imaginary frequency through vibrational analysis. Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the transition states led to the expected reactants and products. The vibrational frequency was calculated at the same level to characterize the nature of the stationary points as true minima (with no imaginary frequency) or transition states (with unique imaginary frequency). The zero-point vibrational energy (ZPE) and thermal corrections was also obtained by frequency calculations.

# ASSOCIATED CONTENT

# Supporting Information.

Crystallographic data for **1-anti** and **1-syn** crystals including ORTEP drawings, selected bond lengths and angles for **1-anti** and **1-syn**, UV absorption spectra, fluorescence decay profiles, TDDFT energy gaps calculation, fluorescence microscopy images of the sample under thermal treatment, powder X-ray diffraction of simulated samples and measured samples, DSC curves for **1-anti** and **1-syn** crystals, changes in PXRD patterns after samples processing, fluorescence and IR spectra under thermal treatment, and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for **1-anti** and **1-syn** crystals. These materials are available free of charge via the internet at <u>http://pubs.acs.org</u>. Full crystallographic data (CCDC 1841532 for **1-anti** crystal) has been deposited at Cambridge Crystallographic Database Center and is available free of charge via the internet at <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

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# Notes

The authors declare no competing financial interest.

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Temperature Controlling Polymorphism and Polymorphic Interconversion in Sublimation Crystallization of 5-Methoxy-salicylaldhyde Azine

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When sublimation temperature in the range between 160-180 °C, the molecules in the gas state take the conformation of **1-anti**, then, crystallized into **1-anti** crystals. Further heating to above 200 °C causes the molecules to adopt the conformation of **1-syn**. The **1-anti** crystals can also transformed into **1-syn** crystals under thermal treatment above 110 °C.