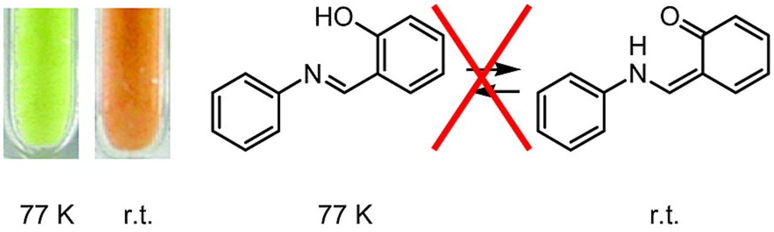
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Crucial Role of Fluorescence in the Solid-State Thermochromism of Salicylideneanilines

Jun Harada, Toshikatsu Fujiwara, and Keiichiro Ogawa

J. Am. Chem. Soc., **2007**, 129 (51), 16216-16221 • DOI: 10.1021/ja076635g



J|A|C|S
ARTICLES

Crucial Role of Fluorescence in the Solid-State Thermochromism of Salicylideneanilines

Jun Harada,* Toshikatsu Fujiwara, and Keiichiro Ogawa*

Contribution from the Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153-8902, Japan

Received September 4, 2007; E-mail: ogawa@ramie.c.u-tokyo.ac.jp; harada@ramie.c.u-tokyo.ac.jp

Abstract: The thermochromism of salicylideneanilines in the solid state has been so far explained only in terms of the temperature-induced change of light absorption, which is caused by the shift of the tautomeric equilibrium between the enol and cis-keto forms. In this study, we measured variable temperature diffuse reflectance and fluorescence spectra of the crystalline powders of salicylideneanilines. We also determined their fluorescence quantum yields. The chromaticity coordinates at each temperature were calculated from these data and compared to the perceived colors of the powders. We found that the temperature-induced shift of the tautomeric equilibrium is not the main cause of the thermochromic color change of the thermochromic crystals and that the thermochromism can be explained only by taking account of the temperature-induced change of fluorescence.

Reversible color change of substances with variation of temperature is known as thermochromism.[1−4] Thermochromism has been observed in many substances: inorganic,[2] organic,[1] metal−organic,[5−7] and macromolecular compounds.[8] It appears both in solution and the solid-state. A variety of mechanisms are known to be responsible for the thermochromism, for example, a change of electron configuration in spin-crossover complexes,[9] a change of coordination geometry and coordination number in transition-metal complexes,[10,11] a variation of the band gap in semiconductors,[3,12] a variation of the crystal field as in ruby,[13] a change of tautomeric equilibrium,[14−17] reversible molecular rearrangement reactions,[1,4,18] interchange between stereoisomers that have different colors,[1,4,19] and change of layer gratings in cholesteric liquid crystals.[3,20]

All the above mechanisms explain thermochromisms only in terms of the changes in absorption spectra. However, when the substances are luminescent, their colors could be influenced by luminescence as well as absorption. Therefore, the temperature dependence of both the absorption and luminescence spectra must be taken into account to understand the thermochromism of luminescent compounds. The absorption and luminescence spectra can give the chromaticity coordinate of the compounds as a numerical representation of the color, by which the influence of absorption and luminescence on the color could be quantitatively evaluated.[3,21] The use of the chromaticity coordinate would, therefore, serve to explain the thermochromism of luminescent substances, although no such attempt has been reported previously. In this study, we utilized chromaticity coordinates to investigate the solid-state thermo-

---

(1) Day, J. H. *Chem. Rev.* **1963**, *63*, 65−80.

(2) Day, H. J. *Chem. Rev.* **1968**, *68*, 649−657.

(3) Nassau, K. *The Physics and Chemistry of Color*, 2nd ed.; John Wiley and Sons: New York, 2001.

(4) Samat, A.; Lokshin, V. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Kluwer Academic: New York, 1999; Vol. 2, pp 415−466.

(5) Bloomquist, D. R.; Willett, R. D. *Coord. Chem. Rev.* **1982**, *47*, 125−164.

(6) Sorai, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2223−2253.

(7) Fukuda, Y., Ed. *Inorganic Chromotropism*, Springer: New York, 2007.

(8) (a) Chance, R. R.; Baughman, R. H.; Müller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616−3618. (b) Eckhardt, H.; Eckhardt, C.; Yee, K. C. *J. Chem. Phys.* **1979**, *70*, 5498. (c) Chance, R. R. *Macromolecules*, **1980**, *13*, 396−398. (d) Beckham, H. W.; Rubner, M. F. *Macromolecules* **1989**, *22*, 2130−2138.

(9) (a) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174−2178. (b) Kröber, J.; Codjovi, E.; Kahn, O.; Grolière, F.; Jay, C.; *J. Am. Chem. Soc.* **1993**, *115*, 9810−9811.

(10) Willett, R. D.; Haugen, J. A.; Lebsack, J.; Morrey, J. *Inorg. Chem.* **1974**, *13*, 2510−2513.

(11) Roberts, S. A.; Bloomquist, D. R.; Willet, R. D.; Dodgen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2603−2610.

(12) (a) Coogan, C. K.; Ress, A. L. *J. Chem. Phys.* **1952**, *20*, 1650−1651. (b) Mollwo, E. *Z. Angew. Phys.* **1954**, *6*, 257−260.

(13) Orgel, L. E. *Nature* **1957**, *179*, 1348−1348.

(14) Inoue, M.; Tsuchiya, K.; Kitao, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 204−205.

(15) (a) Schönberg, A.; Mustafa, A.; Asker, W. *Nature* **1953**, *171*, 222. (b) Hendon, J. E.; Gordon, A. W.; Gordon, M. *J. Org. Chem.* **1972**, *37*, 3184−3185.

(16) Miura, M.; Harada, J.; Ogawa, K. *J. Phys. Chem. A* **2007**, *111*, 9854−9858.

(17) Corval, A.; Kuldova, K.; Eichen, Y.; Pikramenou, Z.; Lehn, J. M.; Trommsdorff, H. P. *J. Phys. Chem.* **1996**, *100*, 19315−19320.

(18) (a) Yitzchaik, S.; Berkovic, G.; Krongauz, V. *Chem. Mater.* **1990**, *2*, 162−168. (b) Sheng, Y.; Leszczynski, J.; Garcia, A. A.; Rosario, R.; Gust, D.; Springer, J. *J. Phys. Chem. B* **2004**, *108*, 16233−16243.

(19) (a) Korenstein, R.; Muszkat, K. A.; Sharafy-Ozeri, S. *J. Am. Chem. Soc.* **1973**, *95*, 6177−6181. (b) Tapuhi, Y.; Kalisky, O.; Agranat, I. *J. Org. Chem.* **1979**, *44*, 1949−1952.

(20) Bamfield, P. *Chromic Phenomena*; Royal Society of Chemistry: Cambridge, U.K., 2001.

(21) Zollinger, H. *Color Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

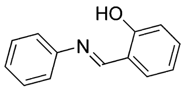
(22) Luminescence from many multinuclear copper(I) complexes changes with variation of the temperature and the resulting color change has been known as luminescence thermochromism.[23] These compounds are, however, colorless unless they are exposed to UV light and they are not thermochromic under the normal light. Therefore, the luminescence thermochromism ever reported is totally different from the thermochromism of SAs described here, which occurs under the normal light.

(23) (a) Hardt, H. D.; Gechnizdjani, H. *Z. Anorg. Allg. Chem.* **1973**, 397, 23−30. (b) Hardt, H. D. *Naturwissenschaften*, **1974**, *61*, 107−110. (c) Ford, P. C.; Cariati, E.; Boursassa, J. *Chem. Rev.* **1999**, *99*, 3625−3647. (d) Dias, H. V. R.; Diyabalanage, V. K.; Rawashdeh-Omary, M. A.; Franzman, M. A.; Omary, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 12072−12073.

10.1021/ja076635g CCC: $37.00 © 2007 American Chemical Society

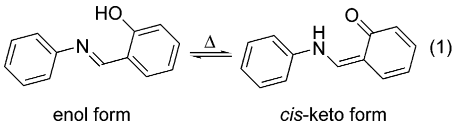
chromism of salicylideneanilines (hereafter abbreviated as SAs) and discovered that the thermochromic color strongly depends on the fluorescence.[22,23]

Salicylideneaniline (**1**) and its congeners belong to a class of the best known organic compounds that exhibit thermochromism and photochromism in the solid state.[1,3,4,20,24] The crystals of SAs have been classified into two types, thermochromic (TC) and photochromic (PC).[25,26]

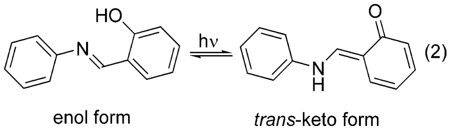


1

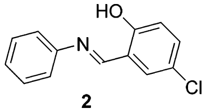
TC crystals have been reported to have the following features. They are deeply colored at room temperature and become paler as the temperature is lowered. They are not photochromic but fluorescent. The fluorescence is weak at room temperature but increases in intensity when the temperature is decreased. The molecules of SAs in TC crystals are planar. It has been demonstrated that there is a tautomeric equilibrium between the enol and cis-keto forms in TC crystals [eq 1] and that the cis-keto form is usually less stable than the enol form. The cis-keto form has an absorption band in the visible region, while the enol form does not. When the temperature is lowered, the cis-keto form decreases in population. The thermochromism of TC crystals has been, therefore, explained in terms of the absorption change caused by the temperature-induced shift of the tautomeric equilibrium. This explanation has been widely accepted for more than 40 years.[27]



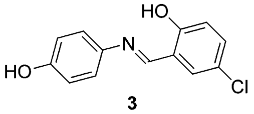
PC crystals have been reported to have the following features. They are pale yellow and not fluorescent at room temperature. The molecules in PC crystals are nonplanar; the N-aryl bond is twisted substantially. When PC crystals are irradiated with UV light, they turn red; when they are left in the dark or irradiated with visible light, they revert to the original color. It has been demonstrated that the photoinduced colored species is the trans-keto form and that the photochromism is due to the transformation between the enol and trans-keto forms [eq 2].[28] PC crystals had not been regarded as thermochromic for a long time since Cohen and co-workers classified them as non-thermochromic on the basis of their spectroscopic criterion.[26] Their criterion for the thermochromism was an increase of the absorption band of the cis-keto form in intensity with increase of temperature. Such an increase of the absorption band was not observed for PC crystals, although Senier had reported that their color becomes paler when the temperature is decreased.[29] We recently discovered that PC crystals also exhibit the thermochromism caused by the temperature-induced shift of the tautomeric equilibrium between the enol and cis-keto forms [eq 1].[30]



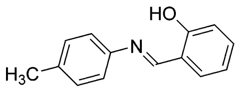
In this study, we investigated the cause of the thermochromism of TC crystals using chromaticity coordinates of the crystalline powders of some SAs, **2**, **3**, and **4** and revealed that the thermochromism can be explained only by considering the temperature-induced change of the fluorescence.



2



3



4

Results and Discussion

Thermochromism of *N*-(5-Chloro-2-hydroxybenzylidene)aniline (2). Absorption Spectra. The crystal of **2** has been known as a typical TC crystal extensively studied by the Weizman Institute group in 1960s.[25,26] Cohen and Schmidt measured the variable temperature UV−vis absorption spectra of **2** in the crystalline film and found that the absorption band of the cis-keto form ($\lambda_{\max} = 470$ nm) decreases in intensity when the temperature is decreased. The spectral change proved that the tautomeric equilibrium between the enol and cis-keto forms takes place in the crystals of SAs.

Our variable-temperature diffuse reflectance spectra of the crystalline powder of **2** reproduced similar spectral changes, when they are converted into the absorption spectra by the Kubelka−Munk transformation (Figure 1). At 298 K, the Kubelka−Munk spectrum exhibits the absorption band assigned to the cis-keto form ($\lambda_{\max} = 470$ nm). When the temperature is decreased, the intensity of this band decreases. The spectral changes confirm the tautomeric equilibrium in the crystals of **2**.

Color of the Crystals. TC crystals including **2** were reported to be "red" at room temperature and "yellow" at low temperatures.[31] However, the actual colors of the crystalline powder of **2** are different from the reported ones. At room temperature, the color should be called "orange". At 77 K, the color is not yellow but yellowish *green* (Figure 2). Although the thermochromism of **2** has been explained in terms of the absorption

---

[24] (a) Dürr H.; Bouas-Laurent H., Eds. *Photochromism. Molecules and Systems*, rev. ed.; Elsevier, Amsterdam, 2003. (b) Brown, G. H., Ed. *Photochromism*; Wiley: New York, 1971.

[25] Cohen, M. D.; Schmidt, G. M. *J. Phys. Chem.* **1962**, *66*, 2442−2445.

[26] Cohen, M. D.; Schmidt, G. M.; Flavian, S. *J. Chem. Soc.* **1964**, 2041−2051.

[27] (a) Hadjoudis, E.; Mavridis, I. M. *Chem. Soc. Rev.* **2004**, *33*, 579−588. (b) Chatziefthimiou, S. D.; Lazarou, Y. G.; Hadjoudis, E.; Dziembowska, T.; Mavridis, I. M. *J. Phys. Chem. B* **2006**, *110*, 23701−23709.

[28] Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809−5810.

[29] Senier, A.; Shepheard, F. G. *J. Chem. Soc.* **1909**, *95*, 1943−1955.

[30] Fujiwara, T.; Harada, J.; Ogawa, K. *J. Phys. Chem. B* **2004**, *108*, 4035−4038.

[31] Bregman, J.; Leiserowitz, L.; Schmidt, G. M. *J. Chem. Soc.* **1964**, 2068−2085.

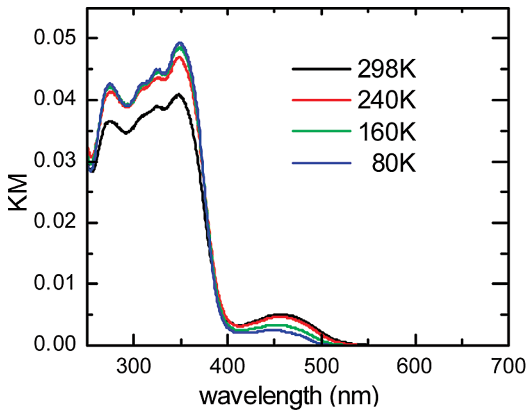
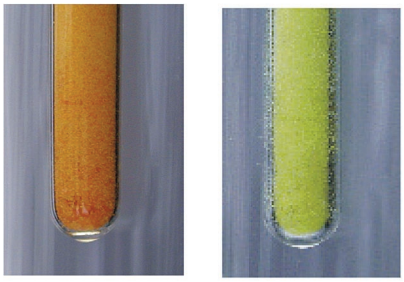


Figure 1. The Kubelka−Munk spectra of *N*-(5-chloro-2-hydroxybenzylidene)-aniline (**2**) in NaCl (0.1 wt %) at different temperatures.



r.t. 77 K

Figure 2. Photographs of the crystalline powders of *N*-(5-chloro-2-hydroxybenzylidene)aniline (**2**).

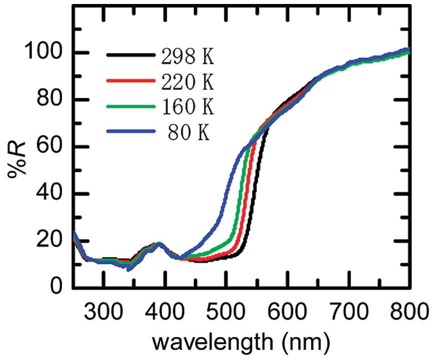


Figure 3. Diffuse reflectance spectra of *N*-(5-chloro-2-hydroxybenzylidene)-aniline (**2**) at different temperatures.

spectral change caused by the tautomerization, this explanation was found to be insufficient, as shown below. We propose here a new explanation that the color change is mainly caused by the change of the fluorescence with variation of the temperature.

Diffuse Reflectance Spectra. To quantitatively examine the color of a powder sample, its diffuse reflectance spectra are essential. Figure 3 shows the variable temperature diffuse reflectance spectra of the nondiluted powder, in which the spectral distortion caused by the fluorescence is eliminated by the use of an appropriate optical filter. At 298 K, the reflectance decreases rapidly in the wavelength region shorter than 575 nm. When the temperature is decreased, the reflectance increases considerably in the region between 400 and 575 nm. These spectra show that the powder of **2** absorbs the light between 400 and 575 nm and that the magnitude of the absorption decreases when the temperature is decreased. This spectral change is consistent with that of the Kubelka−Munk spectra of the diluted powder (Figure 1), indicating the occurrence of the temperature-induced shift of the tautomeric equilibrium in the powder of **2**.

Chromaticity Coordinate (I). The chromaticity coordinate of a sample under a specific illuminating light can be calculated from the diffuse reflectance spectrum of the sample, the spectrum of the illuminating light, and the spectral sensitivity of the human eye.[3,21] Among these spectra, the spectrum of the illuminating light, which depends on the lamp used, is given by the Commission International de l'Eclairage (CIE).[32] The spectral sensitivity of the human eye is also given by CIE as a set of color matching functions. Therefore, only the diffuse reflectance spectrum is necessary for the calculation of the chromaticity coordinates.

By the use of the diffuse reflectance spectra (Figure 3), the chromaticity coordinates of the powder of **2** were calculated. The coordinates and the corresponding color[33] are listed in Table 1. The coordinates at room-temperature lie in the region of orange and those at 80 K lie in the region of pale yellow in the chromaticity coordinate diagram. This indicates that the color expected from the diffuse reflectance spectra is orange at room temperature and pale yellow at 80 K. Although the perceived color at room temperature (orange) almost agrees with the expected one (orange), the perceived one at 80 K (yellowish green) does not agree with the expected one (pale yellow). The discrepancy of the colors at 80 K is likely due to the neglect of the fluorescence, because the fluorescence is eliminated in the measurement of the diffuse reflectance spectra. This suggests that the colors at low temperature cannot be explained only in terms of absorption and that they are significantly influenced by fluorescence.

Variable-Temperature Fluorescence Spectra. To evaluate the influence of the fluorescence on the temperature-induced color changes, fluorescence spectra of the crystalline powder of **2** were measured (Figure 4) and the fluorescence quantum yields were determined at various temperatures (Table 2).

The fluorescence spectra are essentially the same as those reported by Cohen and Schmidt;[25,26,34] the spectra exhibit a weak band with $\lambda_{max} = 560$ nm at room temperature. The fluorescence has been assigned to the emission from the cis-keto form, which is produced through the proton transfer in the excited-state of the enol form. Therefore, an anomalously large Stokes shift is observed.

As the temperature is lowered, the shorter wavelength region of the fluorescence band increases in intensity and a new fluorescence band ($\lambda_{max} = 535$ nm) appears at 80 K. The quantum yields of the fluorescence increases from 0.29 at 298 K to 0.46 at 80 K (Table 2). Similar fluorescence spectral changes were reported for **1** in the solid state[35] and the frozen solution,[36] and they were explained in terms of the conformational change of the cis-keto form in the excited state. Accordingly, the spectral change in **2** can be explained in a similar way: the band at the longer wavelength is due to the emission from the more stable and relaxed conformation of the cis-keto

---

(32) CIE Home Page. http://www.cie.co.at/cie/ (accessed Aug. 27, 2007).
(33) Kelly, K. L. *J. Opt. Soc. Am.* **1943**, 33, 627−632.
(34) Cohen, M. D.; Flavian, S. *J. Chem. Soc. B* **1967**, 334−340.
(35) Higelin, D.; Sixl, H. *Chem. Phys.* **1983**, *77*, 391−400.
(36) (a) Barbara, F. P.; Rentzepis, P. M.; Brus, L. E. *J. Am. Chem. Soc.* **1980**, *102*, 2786−2791. (b) Knyazhansky, M. I.; Metelitsa, A. V.; Bushkov, A. Ja.; Aldoshin, S. M.; *J. Photchem. Photobiol. A* **1996**, *97*, 121−126.

Table 1. Calculated Chromaticity Coordinates and Corresponding Colors of the Powders of Salicylideneanilines *N*-(5-Chloro-2-hydroxybenzylidene)-aniline (**2**), 4-Hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)-aniline (**3**), and 4-Methyl-*N*-(2-hydroxybenzylidene)-aniline (**4**) at Different Temperatures

	2		**3**		**4**	
T (K)	without fluorescence[a]	with fluorescence[a]	without fluorescence[a]	with fluorescence[a]	without fluorescence[a]	with fluorescence[a]
298	0.48, 0.41 orange	0.49, 0.44 yellowish orange	0.47, 0.42 yellowish orange	0.47, 0.43 yellowish orange	0.46, 0.44 yellowish orange	0.46, 0.47 yellow
220		0.42, 0.50 yellow/yellowish orange[b]				
160		0.45, 0.48 greenish yellow/yellow green[b]				
80	0.42, 0.44 pale yellow	0.42, 0.49 greenish yellow/yellow green[b]	0.43, 0.46 yellow	0.42, 0.49 greenish yellow	0.38, 0.44 pale yellow	0.37, 0.50 yellow green

[a] Chromaticity coordinate (*x*, *y*) calculated with and without taking account of the fluorescence, respectively. [b] The coordinates lie on the boundary between the two colors.

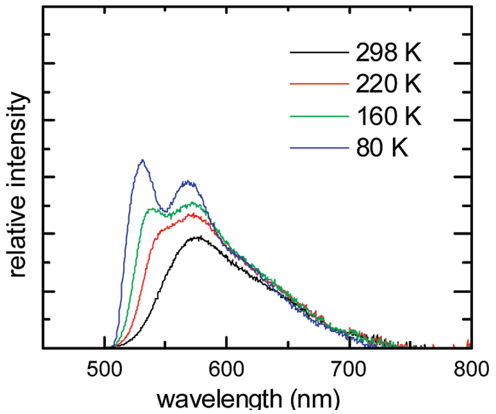


Figure 4. Fluorescence spectra of the powder of *N*-(5-chloro-2-hydroxybenzylidene)-aniline (**2**) at different temperatures (excitation wavelength is 420 nm).

Table 2. Quantum Yields of Fluorescence of Salicylideneanilines *N*-(5-Chloro-2-hydroxybenzylidene)-aniline (**2**), 4-Hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)-aniline (**3**), and 4-Methyl-*N*-(2-hydroxybenzylidene)-aniline (**4**) in the Solid State at Different Temperatures

	compound		
T (K)	**2**	**3**	**4**
298	0.29	0.02	0.38
220	0.38	0.06	0.61
160	0.41	0.11	0.80
80	0.46	0.22	0.99

form, which is preferred at higher temperature, and the band at the shorter wavelength ($\lambda_{max} = 535$ nm) is due to the emission from the less stable, planar conformation.

Chromaticity Coordinate (II). The chromaticity coordinates were recalculated by taking account of the fluorescence spectra (Table 1). The corresponding colors are yellowish orange at 298 K, the boundary between yellow and yellowish orange at 220 K, the boundary between yellow and greenish yellow at 160 K, and the boundary between greenish yellow and yellow-green at 80 K. Each of these colors agrees well with the perceived color at each temperature (Figure 5). This clearly shows that the color at low temperatures can be reproduced only when the fluorescence is taken into account. Thus, the change of the fluorescence with variation of the temperature is a dominant cause in the thermochromic color change of **2** in the solid-state.

Thermochromism of 4-Hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)aniline (3). Investigation of the color change of compound **3** in the solid state has reinforced the above idea. The population ratio of the enol and cis-keto forms was reported to change with temperature:[37] from 37:63 at room temperature to 10:90 at 90 K. The direction of this temperature-induced tautomeric shift is opposite to that in **2**, where the cis-keto form decreases in population with lowering of the temperature. It is accordingly expected that the color of **3** becomes deeper with lowering of the temperature, if the color change is strongly influenced by the temperature-induced tautomeric shift. However, the color of **3** becomes paler with lowering of the temperature. The powder of **3** is yellowish orange at room temperature and yellowish green at 77 K (Figure 6).

Diffuse Reflectance Spectra and Chromaticity Coordinates. Calculations of the chromaticity coordinates revealed that the color change is dominated by the fluorescence. Diffuse reflectance spectra of nondiluted powder, in which the spectral distortion caused by the fluorescence is eliminated by the use of an appropriate optical filter, were measured for the powder of **3** (Figure 7). The chromaticity coordinates calculated from the diffuse reflectance spectra at each temperature are shown in Table 1. The corresponding color is yellowish orange at 298 K and yellow at 80 K. The fact that the calculated color becomes paler when the temperature is decreased is ascribed to the increase of the reflectance, that is, the decrease of the absorption intensity, in the longer wavelength region (450−550 nm). This decrease seems to be inconsistent with the increase of the cis-keto form, which is responsible for the absorption of the longer wavelength light. This decrease, however, can be explained in terms of a sharpening of the absorption band of the cis-keto form, which is evidenced by the absorption spectra of the crystalline film of **3** (Figure S1). The calculation indicates that even though the colored species increases in population, the color becomes paler if the absorption band sharpens.

The observed color change was fully explained by taking into account the fluorescence. The variable temperature fluorescence spectra of the crystalline powder of **3** are shown in Figure 8, and the fluorescence quantum yields are shown in Table 2. There is a broad and weak band with $\lambda_{max} = 560$ nm at 298 K. When the temperature is lowered, the band remarkably increases in

---

(37) (a) Ogawa, K.; Kasahara, Y.; Ohtani, Y.; Harada, J. *J. Am. Chem. Soc.* **1998**, *120*, 7107−7108. (b) Ogawa, K.; Harada, J.; Tamura, I.; Noda, Y. *Chem. Lett.* **2000**, *29*, 528−529.

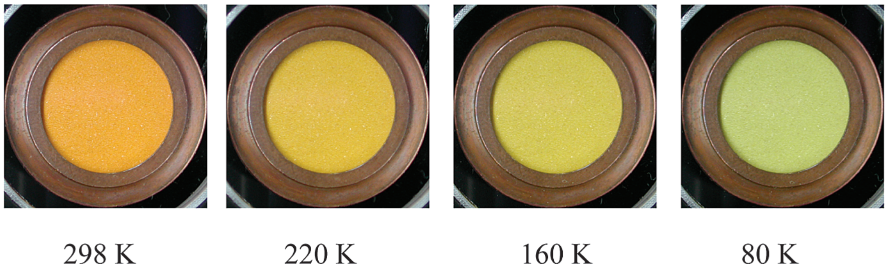


Figure 5. Photographs of the powder of *N*-(5-chloro-2-hydroxybenzylidene)-aniline (**2**) at different temperatures.

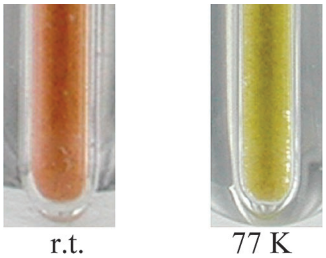


Figure 6. Photographs of the powder of 4-hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)-aniline (**3**) at different temperatures.

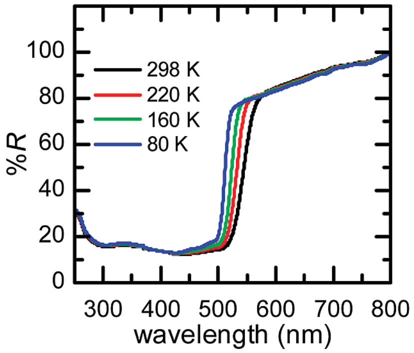


Figure 7. Diffuse reflectance spectra of 4-hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)-aniline (**3**) at different temperatures.

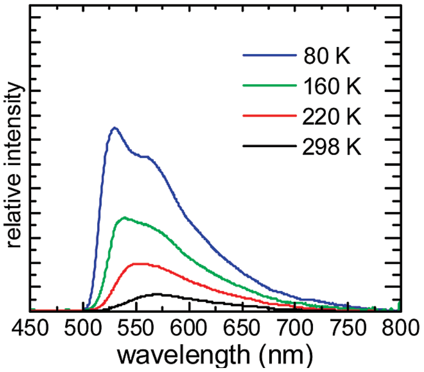


Figure 8. Fluorescence spectra of the powder of 4-hydroxy-*N*-(5-choloro-2-hydroxybenzylidene)-aniline (**3**) at different temperatures (excitation wavelength is 420 nm).

intensity and a new band (λ_{max} = 480 nm) appears at 80 K. The quantum yield of the fluorescence increases from 0.02 at 298 K to 0.22 at 80 K (Table 2).

The chromaticity coordinates were recalculated using the fluorescence spectra (Table 1). The corresponding color is yellowish orange at 298 K and greenish yellow at 80 K. Each of these colors agrees well with the perceived color at each temperature (Figure 6). The calculated color at 80 K, greenish yellow, is reproduced only by taking into account the fluorescence. In contrast, the fluorescence does not change the calculated color at 298 K, which agrees well with the perceived one. This is because the fluorescence quantum yield is very small at 298 K. Thus, the color of **3** is strongly influenced by fluorescence at low temperatures, but virtually not at 298 K. It is therefore concluded that the temperature-induced color change of the crystalline powder of **3** is not due to the tautomeric equilibrium, but can be fully explained by taking account of the change of the fluorescence.

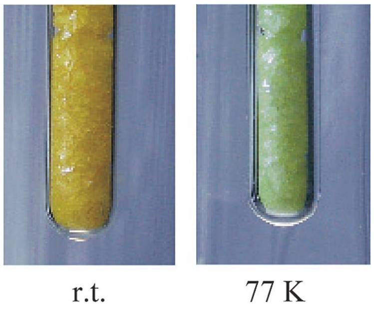


Figure 9. Photographs of the powder of 4-methyl-*N*-(2-hydroxybenzylideneaniline) (**4**) at different temperatures.

Thermochromism of 4-Methyl-*N*-(2-hydroxybenzylideneaniline) (4). The crystals of **4** have also been known to be strongly thermochromic.[26] They are yellow at room temperature and yellowish green at 77 K (Figure 9). Aldoshin and his coworkers reported UV−vis absorption spectra of the crystalline film, in which the band of the cis-keto form (λ_{max} = 475 nm) decreases when the temperature is decreased.[38] They explained the thermochromism in terms of the shift of the tautomeric equilibrium.

We measured the absorption and fluorescent spectra of **4**. The Kubelka−Munk spectra of the diluted powder (Figure S2) are consistent with the reported shift of the tautomeric equilibrium. The fluorescence spectra of the nondiluted powder of **4** (Figure S3) show that the powder of **4** strongly emits the fluorescence, which shows temperature dependence similar to that of **2** and **3**. The chromaticity coordinate analysis (Table 1) using the diffuse reflectance (Figure S4) and fluorescence spectra (Figure S3) revealed that the thermochromic color change of the crystalline powder of **4** is dominated by the change of the fluorescence (Table 2). It is notable that the color of **4** is significantly influenced by the fluorescence even at room temperature because of the strong fluorescence.

Concluding Remarks

The thermochromism of salicylideneanilines in the solid state has so far been explained only by considering the change of light absorption, which is due to the shift of the tautomeric

---

[38] Aldoshin, S. M.; Knyazhanskii, M. I.; Tymyanskii, Y. R.; Atovmyan, L. O.; Dyachenko, O. A. *Sov. J. Chem. Phys.*, **1984**, *1*, 1775−1788.

equilibrium. The following explanations have been accepted but now are proved to be oversimplified.

There is a tautomeric equilibrium between the enol and cis-keto forms in the solid state. The enol and cis-keto forms should be yellow and red, respectively, in TC crystals. The crystals are actually orange, because both the tautomers coexist in the crystals. As the equilibrium shifts with the temperature, the color of the crystals changes accordingly; for example, the orange color becomes deeper when the temperature is increased. Therefore, the thermochromism at any temperatures can be explained in this way.

It is true that the above explanation is valid at the temperatures higher than room temperature, where the fluorescence is negligibly weak. At lower temperatures, however, the fluorescence is much stronger, so that the above explanation is not applicable. When the temperature is decreased, the color changes from orange to yellow-green because of the fluorescence. This color change is much more prominent than that at higher temperatures, where the color change is only marginal. The present study has revealed that the prominent thermochromic color change of salicylideneanilines is dominated by the fluorescence.

In a previous study, we revealed that the tautomeric equilibrium exists also in PC crystals, which are scarcely fluorescent, and that the temperature-induced shift of the equilibrium causes the thermochromism in these crystals. We can now summarize the thermochromism of SAs in the solid state as follows: When the fluorescence is negligibly weak, that is, in TC crystals at the higher temperatures and in PC crystals, the thermochromism is explained in terms of the change of light absorption, which is due to the temperature-induced shift of the tautomeric equilibrium. When the fluorescence is strong, that is, in TC crystals below room temperature, the thermochromic color change is dominated by the fluorescence.

Experimental Section

Materials. Salicylideneanilines **2**−**4** were prepared according to the standard procedures and recrystallized from methanol. The crystals of **2**−**4** were each ground using an agate mortar and pestle. X-ray powder diffraction of the samples was measured using a Rigaku MultiFlex powder diffractometer and was confirmed to be identical with the patterns calculated from their crystal structures.

Measurements. Diffuse UV−vis reflectance spectra were measured on a Jasco V-550 spectrometer equipped with an integrating sphere accessory, following the procedures described previously.[30] Fluorescence spectra were measured on a Perkin-Elmer LS55 spectrofluorometer. For both the measurements at low temperatures, a liquid nitrogen bath cryostat Oxford Optistat DN−V with a homemade sample holder was used. The temperature was held constant within ± 0.1 K during the measurement.

Determination of Absolute Fluorescence Quantum Yields from Reflectance Spectra. The absolute fluorescence quantum yields of the powdered samples were determined from the diffuse reflectance and fluorescence spectra, using the following equation, which was reported by Mirenda et al.:[39]

$$\Phi_{\mathrm{F,obs}} = \frac{R_{\mathrm{t,obs}}(\lambda_0) - R^{\mathrm{f}}_{\mathrm{t,obs}}(\lambda_0)}{I(\lambda_0)[1 - R^{\mathrm{f}}_{\mathrm{t,obs}}(\lambda_0)] - I^{\mathrm{f}}(\lambda_0)[1 - R_{\mathrm{t,obs}}(\lambda_0)]}$$

where

$$I(\lambda_0) = \int_\lambda f_{\mathrm{obs}}(\lambda)\,\frac{s(\lambda)}{s(\lambda_0)}\,\frac{\lambda_0}{\lambda}\,\mathrm{d}\lambda$$

$$I^{\mathrm{f}}(\lambda_0) = \int_\lambda f_{\mathrm{obs}}(\lambda)\,\frac{T(\lambda)}{T(\lambda_0)}\,\frac{s(\lambda)}{s(\lambda_0)}\,\frac{\lambda_0}{\lambda}\,\mathrm{d}\lambda$$

and $R_{\mathrm{t,obs}}(\lambda)$ is the observed diffuse reflectance (without filter), $R^{\mathrm{f}}_{\mathrm{t,obs}}(\lambda)$ is the observed diffuse reflectance (with filter), $f_{\mathrm{obs}}(\lambda)$ is the observed fluorescence spectrum, $T(\lambda)$ is the filter transmittance, $s(\lambda)$ is the relative spectral responsivity, λ_0 is the wavelength of incident light, and λ is the wavelength of fluorescent light.

Among these quantities, $R_{\mathrm{t,obs}}(\lambda)$, $R^{\mathrm{f}}_{\mathrm{t,obs}}(\lambda)$, $f_{\mathrm{obs}}(\lambda)$, and $T(\lambda)$ were obtained experimentally and $s(\lambda)$ was provided by the photomultiplier manufacturer (Hamamatsu Photonics). Thus, the absolute fluorescence quantum yields at room temperature were determined.

The quantum yield at the low temperatures was determined by comparison with that at room temperature (rt), using the following equation:

$$\phi_x = \phi_{\mathrm{rt}}\frac{\int f_x(\lambda)\,\mathrm{d}\lambda}{\int f_{\mathrm{rt}}(\lambda)\,\mathrm{d}\lambda}$$

where ϕ_x,ϕ_{rt} is the fluorescence quantum yield at x K and rt respectively, and $f_x(\lambda)$, $f_{\mathrm{rt}}(\lambda)$ is the fluorescence spectrum at x K and rt, respectively.

This equation is based on the following assumptions: (i) The sample is excited at the same wavelength and with the same intensity both at a low and the room temperature, and (ii) the absorbance at the excited wavelength is the same at both of the temperatures. We confirmed that assumption ii is satisfied, as shown in Figure 3, Figure 7, and Figure S4. Assumption i is also satisfied, because the fluorescence spectra were measured under the same conditions except for their temperatures.

Calculations of the Chromaticity Coordinates. The chromaticity coordinate of a powdered sample under a specific illumination was calculated from the spectral distribution function $R(\lambda) \times P(\lambda) + F(\lambda)$, where $R(\lambda)$ represents the reflectance spectrum, $P(\lambda)$ the spectrum of the illuminating light, and $F(\lambda)$ the fluorescence spectrum. The function of the fluorescence spectrum $F(\lambda)$ is derived from the following equation:

$$F(\lambda) = k\,f(\lambda)/\lambda^2$$

where $f(\lambda)$ is the fluorescence spectrum proportional to the number of photons and k is a scaling coefficient. The coefficient k is given by

$$k = \frac{\Phi \times \int P(\lambda) \times (1 - R(\lambda))\,\mathrm{d}\lambda}{\int (f(\lambda)/\lambda^2)\,\mathrm{d}\lambda}$$

on the assumption that Φ is independent of λ.

The colorimetric calculations were performed using a colorimetry software JASCO VWCT-615, to which $R(\lambda) + kF(\lambda)/P(\lambda)$ was input as the reflectance spectrum type function.

Acknowledgment. This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: UV−vis spectra of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA076635G

---

(39) Mirenda, M.; Lagorio, M. G.; Román, E. S. *Langmuir*, **2004**, *20*, 3960−3967.