Vapor Switching of Photochromism of Methylenebis{*N*-(3,5-di-*tert*-butylsalicylidene)aniline} Crystals

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Photochromic behavior of 5,5′-methylenebis{2-(3,5-di-*tert*-butylsalicylideneamino)phenol} crystal, which exhibited vapochromism, was completely controlled by contact with methanol vapor. Maintenance of a reaction room in the crystal was the key to start solid-state photoinduced isomerizaton of Schiff base.

Solid-state photochromism has been an attractive research subject because of the potential applications for photoelectronic devices as well as the usefulness for a model system to elucidate molecular motion in the crystal state.[1,2] Although design and synthesis of host molecules which form crystalline inclusion compounds have been actively developed,[3] control of photoproperties of solid systems by inclusion phenomena is hardly investigated irrespective of its deeper interest. Thus far few crystalline hosts that can give optical signal response to the inclusion behavior are known. Among them some inclusion hosts which exhibit guest-dependent fluorescence are investigated,[4] while little is known about photochromic hosts.[5–7] Crystals of *N*-salicylideneamine and its derivatives (Schiff bases) exhibit thermochromism or photochromism for which adequate rooms are supposed to be required in the crystal lattice.[1,8] Some years ago, we found that a certain *N*-salicylideneaniline derivative with bulky substituents captured some small organic molecules and exhibited guest-dependent photochromism.[6] A decisive condition for exhibiting crystalline photochromism of Schiff bases might be to maintain enough room for the photoinduced isomerization in the crystal. According to this idea, we designed 4,4′-methylenebis{*N*-(3,5-di-*tert*-butylsalicylidene)-2,6-dimethylaniline} (**1**) and 5,5′-methylenebis{2-(3,5-di-*tert*-butylsalicylideneamino)phenol} (**2**) as photosensitive host molecules (Figure 1). We now report the first example of vapor-switching photochromism with the host Schiff base.

Compound **1** was synthesized by the condensation of 3,5-di-*tert*-butylsalicylaldehyde and 4,4′-methylenebis(2,6-dimethylaniline) in methanol.[9] Resultant crude product was recrystallized from acetone to yield acetone-inclusion crystal **1A**. From the inspection of the ^{1}H NMR peaks intensity ratios and elemental analysis, guest (acetone)/host (Schiff base **1**) stoichiometric ratio for **1A** was determined to be 3/2.[10] Although we could not obtain suitable crystals of **1A** for X-ray crystallography, the crystal structure of parent 4,4′-methylenebis(*N*-salicylidene-2,6-dimethylaniline) (**3**) has been well studied;[11] thus, we can discuss appropriately on the structure of **1A**. In the crystal lattice of **3**, there is a cavity between two aminoaromatic rings of the molecule, which allows the salicylidene moiety of neighboring molecule to locate in two presumed orientations in it. In the course of recrystallization of **1** from acetone, the cavity between the aminoaromatic rings must be occupied by acetone molecules rather than the salicylidene moiety of neighboring molecule due to bulky *tert*-butyl substituents on the salicylidene rings. When crystal **1A** was exposed to the atmosphere at room temperature, acetone molecules were gradually liberated in part and guest/host stoichiometric ratio reached to the final value of 1/2 for the crystal (**1A′**);[12] residual acetone molecules could not be removed even in vacuo. When **1A** and **1A′** were placed in a vessel saturated with methanol vapor, complete exchange of guest molecules occurred and methanol-inclusion crystal (**1M**) was obtained. According to ^{1}H NMR spectral inspection and elemental analysis the guest (methanol)/host (**1**) stoichiometric ratio for **1M** was 2/1.[13] By standing of **1M** in the atmosphere the crystal released methanol to yield guest-free crystal **1F**,[14] which was found to be a polymorphic form of **1** by the inspection of photochromic character. Since the color of each crystal of **1A**, **1M**, and **1F** was the same and their reflectance spectra in the visible region were closely similar to each other, the molecular structure of host **1** might be retained for all crystals.

Compound **2** was prepared by the condensation of 3,5-di-*tert*-butylsalicylaldehyde and 5,5′-methylenebis(2-aminophenol) in methanol and was obtained as methanol inclusion crystals (**2M**). According to the intensity ratios of ^{1}H NMR peaks and elemental analysis the guest (methanol)/host (**2**) stoichiometric ratio was 1/1.[15] By standing of crystal **2M** in the atmosphere, methanol molecules were liberated slowly to yield guest-free crystal **2F** and the color of the crystal changed gradually from orange to yellow.[16] When guest-free crystal **2F** was exposed orange of **2M**; the color alteration was repeated reversibly upon exposure of **2** either to the atmosphere or to methanol vapor (Figure 2). Such reversible coloration or vapochromism of organic crystals has been scarcely reported though vapochromism of crystalline metal complexes has been extensively studied.[17] ^{1}H NMR experiment showed that guest (methanol)/host (**2**) stoichiometric ratio for the orange crystal was 1/1 in every case; therefore, a guest molecule was suggested to be embedded in a certain room of the crystal in the similar fashion of **1**. The definite methanol inclusion crystal **2M** could

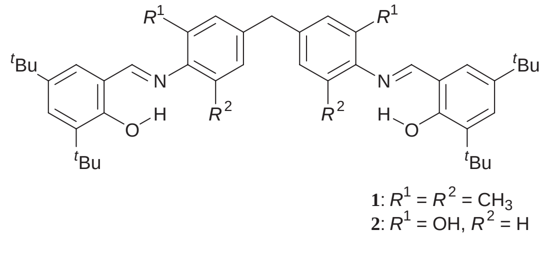

Figure 1. Schematic representation of 4,4′-methylenebis{*N*-(3,5-di-*tert*-butylsalicylidene)-2,6-dimethylaniline} (**1**) and 5,5′-methylenebis{2-(3,5-di-*tert*-butylsalicylideneamino)phenol} (**2**).

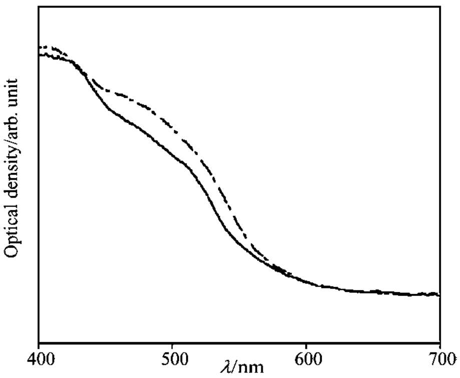

Figure 2. Solid-state reflectance spectra of **2F** (full line) and **2M** (chain line).

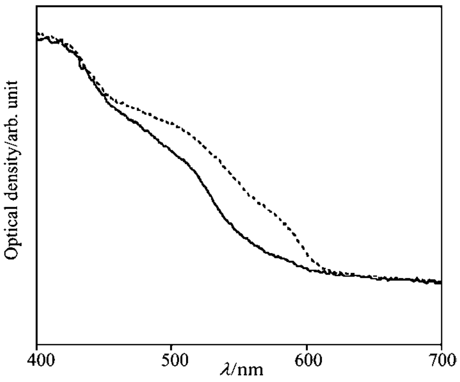

Figure 3. Reflectance spectra of **2F** before (full line) and after (dotted line) UV irradiation.

be obtained also by recrystallization of **2F** with methanol as thin plates, none of which was suited for X-ray crystallography.

Crystals of **1F**, **1A**, **1M**, and **2F** exhibited photochromism. The degree of spectral change after UV light irradiation on **1M** was smaller than those of **1A** and **1F**. It is worthwhile to note that methanol adduct **2M** is non-photochromic, while the guest-free host **2F** shows clear photochromic behavior (Figure 3). We have reported that the introduction of bulky *tert*-butyl groups into the aromatic rings of Schiff bases was effective for the satisfactory preparation of photochromic organic crystals. The bulky group can act as a space-opener in the crystal lattice in order to increase a part of the molecular thickness to allow partial framework movement.[18] In the case of **2**, guest-free crystal **2F** has a cavity and the cavity can be used for either photoisomerization room or vapor inclusion room. Therefore, **2F** shows both photochromism and vapochromism. When methanol molecule is included in the crystal, there is not enough room left for photochromism. Our success to construct a vapor-switching photochromic system is attributed to the employment of bis(Schiff base), whose total molecular movement induced by photoirradiation can be controlled even by a small neighboring molecule. Thus, methanol molecule could act as a key to lock the photochromic behavior of Schiff base **2**.

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9 **1** as pale yellow crystalline powder; mp 95.5–98.6 °C (Found: C, 81.92; H, 9.11; N, 4.33%. $C_{47}H_{62}N_2O_2$ requires C, 82.17; H, 9.10; N, 4.08%); ^{1}H NMR (270 MHz; $CDCl_3$): δ 1.33 (18H, s, $C(CH_3)_3$), 1.49 (18H, s, $C(CH_3)_3$), 2.20 (12H, s, Ar–CH_3), 3.85 (2H, s, Ar–CH_2–Ar), 6.94 (4H, s, Ar–H), 7.14 (2H, s, Ar–H), 7.48 (2H, s, Ar–H), 8.34 (2H, s, CH=N), 13.16 (2H, br, Ar–OH).

10 **1A** as pale yellow plates (Found: C, 80.13; H, 9.20; N, 3.78%. $C_{103}H_{142}N_4O_7$ requires C, 79.90; H, 9.24; N, 3.62%).

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12 **1A′** as pale yellow plates (Found: C, 81.12; H, 9.05; N, 4.05%. $C_{97}H_{130}N_4O_5$ requires C, 81.35; H, 9.15; N, 3.91%).

13 **1M** as pale yellow plates (Found: C, 78.73; H, 9.31; N, 3.77%. $C_{49}H_{70}N_2O_4$ requires C, 78.36; H, 9.39; N, 3.73%).

14 **1F** as pale yellow plates, which exhibited mp of **2F** by releasing of methanol by heating (Found: C, 81.41; H, 9.22; N, 4.19%. $C_{47}H_{62}N_2O_2$ requires C, 82.17; H, 9.10; N, 4.08%).

15 **2M** as orange plates; mp 197.8–204.8 °C (Found: C, 75.84; H, 8.34; N, 3.99%. $C_{44}H_{58}N_2O_5$ requires C, 76.05; H, 8.41; N, 4.03%); ^{1}H NMR (270 MHz, CD_3COCD_3): δ 1.32 (s, 18H, $C(CH_3)_3$), 1.46 (s, 18H, $C(CH_3)_3$), 3.49 (s, 3H, CH_3OH), 3.93 (s, 2H, Ar–CH_2–Ar), 6.93 (d, 2H, 5(H)), 7.04 (d, 2H, 6(H)), 7.26 (s, 2H, 3(H)), 7.41 (s, 2H, 4′(H)), 7.48 (s, 2H, 6′(H)), 8.34 (br, 2H, 2(OH)), 8.92 (s, 2H, CH=N), 13.9 (br, 2H, 2′(OH)).

16 **2F** as yellow plates; mp 197.8–204.8 °C (Found: C, 77.74; H, 8.23; N, 4.24%. $C_{43}H_{54}N_2O_4$ requires C, 77.91; H, 8.21; N, 4.23%).

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