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Single-crystal UV-Vis spectroscopic examination of a striking odd-even effect on structure and chromic behaviour of salicylidene alkylamines

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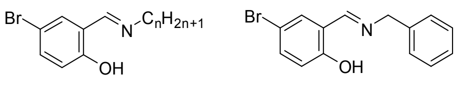
Hirohiko Houjou,* Hana Ikedo, Isao Yoshikawa

We have found that a series of *N*-(5-bromosalicylidene) alkylamines exhibited distinct chromic behaviour depending on the parity of their alkyl chain length. A group with an even number of carbon atoms in the alkyl chain showed photochromism, while another group with odd number showed thermochromism.

The prototropic isomerisation of salicylidene amines has been extensively studied in relation to their thermochromic and photochromic effects.[1–5] Specifically, the colour change is attributed to the alteration of the abundance ratio between enol-imine (OH) and keto-enamine (NH) forms.[6,7] The expression of chromic properties depends on the molecular structure, especially when substituents can directly influence the electronic state of the chromophore, while the effects of intermolecular interactions are not satisfactorily understood.[8–16] One reason for this may be the difficulty in separating these two effects with respect to the chromic behaviour: namely, the introduction of substituents normally causes a considerable change in the molecular packing structure of the crystal, and therefore, induces changes in intermolecular interactions. Some groups are trying to give a sophisticated solution to this problem by using co-crystallisation techniques.[16–20] Meanwhile, we have recently found a remarkable effect of the alkyl chain length on the chromic behaviour of *N*-(5-bromosalicylidene) alkylamines (**1Cn**, where n is the number of carbon atoms in the alkyl group): the even-numbered chains induced photochromism, while the odd-numbered chains induced thermochromism. For this series of molecules, it is unlikely that the difference in alkyl chain length directly influences the electronic state of the chromophore. Thus, we can expect that a thorough examination of these compounds will provide a clue on the long-term controversy regarding the structural criteria that determine photo- or thermochromism.[2–5] Additionally, we have found that *N*-(5-bromosalicyllidene) benzylamine (**1BN**) showed simultaneous photo- and thermochromism, although **1BN** had been reported to show photochromism exclusively.[8,21] This discrepancy may stem from polymorphism (regrettably, the crystal structures have not yet been reported). In this study, we employed single-crystal UV-Vis absorption spectroscopy system in combination with an optical microscope equipped with a temperature-controllable stage.[22–25] This method allowed us to observe crystallographically pure samples, and hence, we were able to prevent ambiguity that may arise from the contamination of the polymorph.

The target compounds **1Cn** (n = 13–18) and **1BN** were prepared in high yield by stirring 5-bromosalicylaldehyde and the respective amines in dichloromethane, followed by evaporating and recrystallising the product in methanol. The compounds were readily categorised into two groups based on appearance: **1C13**, **1C15**, **1C17** were yellow needles, while **1C14**, **1C16**, and **1C18** were colourless thin plates (Figure 1 (a)). Namely, a distinct odd-even effect with respect to the chain length was observed in the colour and morphology of **1Cn**s. The 'odd group' showed intense luminescence around 520 nm in the solid state upon UV irradiation, while the 'even group' did not. At first sight, **1BN** obtained as yellow plates appeared to belong to the odd group, except that it showed only minor photoluminescence. However, **1BN** demonstrated somewhat 'amphoteric' behaviour between that of the even and odd groups, which will be discussed later.



1Cn (n = 13, 14, 15, 16, 17, 18) **1BN**

Scheme 1 Structures of salicylideneamines studied

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[a] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan.

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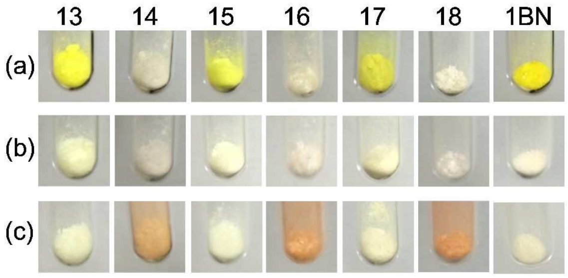

Figure 1 Photographs of **1Cn** (n = 13–18, indicated at upper row) and **1BN**: (a) at ambient temperature, (b) cooled by dipping in liquid nitrogen, (c) irradiated with handy UV lamp (325 nm) during the cooling.

A distinct odd-even effect was observed for the chromic behaviour of the Schiff bases examined. When a small portion (ca. 10 mg) of the crystalline samples in test tubes was dipped in liquid nitrogen, the odd-group samples exhibited apparent discolouration, whereas the even-group samples remained colourless (Figure 1(b)). In addition, the even-group samples showed no colour change upon heating until reaching their melting points. When the test tubes were irradiated with a UV lamp during cooling by liquid nitrogen, the even-group samples turned a reddish orange while the odd-group samples showed intensified luminescence but no recognizable colour change (Figure 1(c)). Among the even-group samples, only **1C14** showed photochromism at ambient temperature while the others reacted to UV irradiation only at low temperatures. Interestingly, **1BN** showed discolouration during cooling with liquid nitrogen and photochromism at ambient temperature. Similar phenomena regarding the coexistence of photo- and thermochromism have been so far reported.[17,18,26] We observed an apparent hysteresis with respect to the photochromism: cooling the sample under continuous UV irradiation from ambient to liquid nitrogen temperatures results in reddish-orange colouration whereas irradiation of the sample after cooling does not lead to obvious colouration (Figure S1).

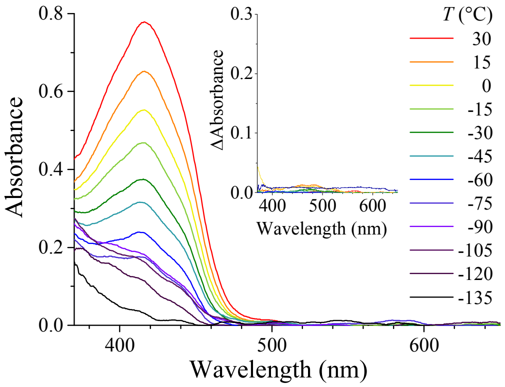

Figure 2 Temperature-dependent UV-Vis absorption spectra measured for a single crystal of **1C15** under microscope. Inset: the difference between spectra measured with and without UV irradiation. The colours of the plots correspond to varying temperatures (from –135 to 30 °C with 15 °C increment).

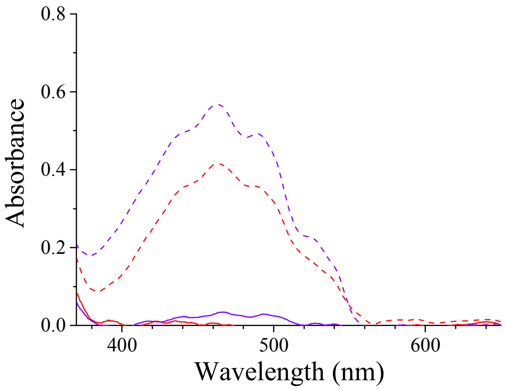

Figure 3 Temperature-dependent UV-Vis absorption spectra measured for the single crystal of **1C14** under microscope (selected). Dashed lines indicate measurement ca. 1 sec after UV irradiation with a Hg lamp. For full version, see Figure S3. The colour code (red = 30°C, violet = –90°C) is the same as in Figure 2.

As representatives of the odd- and even-group samples, **1C15** and **1C14** were examined with microscopic UV-Vis absorption spectroscopy. Figure 2 shows the temperature-dependent spectra measured for the single crystal of **1C15**. In the range from –75 °C to 30 °C, the absorbance around 416 nm increases in proportion to the temperature (Figure S2). Below –75 °C, the spectral profile is slightly changed, and the intensity of the absorption band was slightly weakened as the temperature was lowered. At each temperature, UV irradiation did not influence the spectral profile (Figure 2, inset). Figure 3 shows the temperature-dependent spectra measured for the single crystal of **1C14**. Without UV irradiation, the spectra showed no notable absorption band in the visible region, so it was not possible to discern whether the slight changes in the baseline are meaningful. Upon UV irradiation, the spectra drastically changed to reveal an intense band over the 400–550 nm region. This new band disappeared within a few seconds when the UV source was removed. As temperature decreased, the band gently intensified and its vibronic structure became slightly sharpened. The rate of colouration and decolouration did not noticeably change with temperature.

Figure 4 shows the absorption spectra measured for the single crystal of **1BN** under conditions similar to **1C15** and **1C14**. The spectra at 15 °C showed a moderate absorption band around 425 nm, together with a weak, structured edge toward 550 nm. When the sample was cooled to –75°C, the band around 425 nm was considerably diminished, while the low-energy edge was almost unchanged. Upon UV irradiation, the absorbance drastically increased, especially in the range from 450 to 550 nm. The difference spectra (Figure 4, inset) is quite similar to that observed for **1C14** after UV irradiation. The spectral profile reverted after the UV irradiation was stopped. In contrast to **1C14**, the UV-induced spectral change became small as temperature decreased. Also, the colouration and decolouration processes were both decelerated at low temperatures. These properties seemed to be a cause of the apparent hysteresis in the photochromic behaviour of **1BN** (Figure S1).

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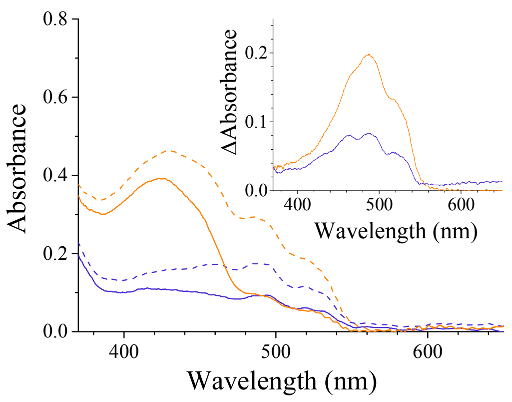

Figure 4 Temperature-dependent UV-Vis absorption spectra measured for the single crystal of **1BN** under microscope (solid lines). Dashed lines indicate measurement ca. 1 sec after UV irradiation with a Hg lamp. Inset: the difference between spectra measured with and without UV irradiation. The colour code (orange = 15°C, dark blue = 75°C) is the same as in Figure 2.

The observed difference in chromic behaviour between the even- and odd-group samples can be attributed to their crystal structures because they have the same chromophore structure and hence the same electronic state when isolated. Indeed, the solution UV-Vis absorption spectra of **1Cn** (n = 13–18) were nearly identical (Figure S4). Single crystal X-ray structure analyses were successfully conducted for odd-group samples and **1BN**. Figure 5 shows the molecular packing structure in the crystal of **1C15**. The salicylidene rings were obliquely stacked along *b*-axis to form a herringbone-like wall, and the alkyl chains were interdigitated among the walls. The salicylidene rings were surrounded by the alkyl chains and have no remarkable interatomic contact with molecules in the proximity except for close contacts (3.10 Å and 3.18 Å at 93 K) between the bromine atom and certain alkyl hydrogen atoms (Figure 5, red circle). It may be worth noting that the Br–H contacts were elongated to 3.17 Å and 3.24 Å, respectively, as temperature was raised to 253 K. We commonly observed similar features among the odd-group samples (Figure S5), suggesting that this type of packing is possible only for alkyl chains in the odd group. In the crystal structure of **1BN**, two crystallographically inequivalent molecular units have similar non-covalent contacts between Br and H atoms (Figure S6). The roles of similar interatomic contacts in the formation of supramolecular architectures have been noted by Garcia et al.[27]

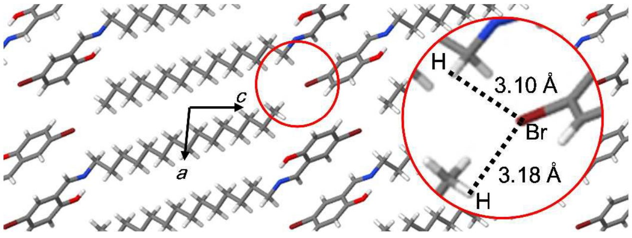

Figure 5 The molecular packing structure of **1C15** as viewed along the crystallographic *b*-axis.

Unfortunately, the structures of the even-group samples have not been clarified due to difficulty in preparing crystals suitable for the analysis. Comparing the powder diffraction patterns of the even-group samples revealed a common feature: there were a series of equally-spaced peaks in a region 3–15° of 2θ, suggesting a lamellar structure with a long period (d_{001} = 46.1 Å, 51.3 Å, 55.2 Å, for n =14, 16, 18, respectively) (Figure S7). The overall diffraction patterns were entirely distinct from those of the odd-group samples (d_{001} = 35.7 Å, 38.9 Å, and 42.4 Å, for n = 13, 15, and 17, respectively, Figure S8), indicating that the crystal structures were also classified into two groups depending on the parity of the alkyl chain. The profiles of infrared spectra were also classified into the even and odd groups, and the positions of some major peaks clearly shifted alternately with respect to the chain length (Figure S9). These results suggest that the difference in molecular environment induced the change in the molecular framework, probably due to enol–keto tautomerisation.

The above results are reminiscent of findings in our previous study that revealed a noticeable spectroscopic change associated with polymorphic change observed for a series of a naphthylmethylidene alkylamines.[28] In that work, the difference in molecular arrangement (alternate or bunting shape with respect to the hydrogen bonding network) was clearly correlated with the profiles of absorption spectra and patterns of infrared spectra. Those results suggested that the length of alkyl chain strikingly influences the molecular arrangement in the crystal, and hence the electronic state of the chromophore, through the change in the relative stability of the tautomers. However, to the best of our knowledge, it was the first observation of such a clear odd-even effect not only on the spectroscopic properties but also on the chromic behaviour of salicylidene alkylamines. We suggest that a deep insight into alkylamine Schiff bases would shed a light on the mechanism of photo- or thermochromism in the molecular system. It should be noted that the previously reported works utilised spectroscopic methods for polycrystalline films, rigid glasses, powder diluted with inorganic salts, and so on. Our present attempts provide quantitative data directly relatable to the crystal structures using single crystal microscopic UV-Vis absorption spectroscopy.

During the past few decades, there has been progress toward understanding the photochromism and thermochromism of salicylaldehyde Schiff bases. [29–36] Originally, research focused on salicylideneanilines, which are reported to show thermochromism when the phenyl ring is virtually co-planar to the salicylidene ring, but otherwise show photochromism.[1] However, this empirical rule has been broken by a number of exceptions so far.[12,16,18] It is also widely accepted that a less densely-packed structure tends to induce photochromism.[2] Salicylidene benzylamines were investigated as analogues of salicylideneanilines to explore the effects of the additional methylene spacer between the imine nitrogen and the phenyl ring. The present results, however, imply that the chromic behaviour of benzylamine Schiff bases should be understood as analogues of alkylamine Schiff bases. A comprehensive investigation on these materials is currently in progress.

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Conflicts of interest

There are no conflicts to declare.

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A simple salicylideneamine exhibits either photochromism or thermochromism depending on the number of its alkyl carbons.