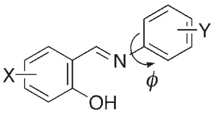
DOI: 10.1002/anie.200700999

Porous Networks

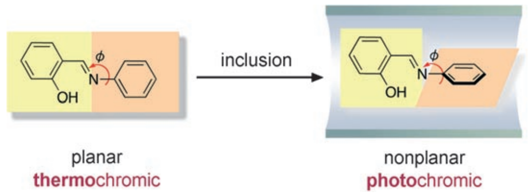
Thermo-to-Photo-Switching of the Chromic Behavior of Salicylideneanilines by Inclusion in a Porous Coordination Network**

Tsuyoshi Haneda, Masaki Kawano, Takahiro Kojima, and Makoto Fujita**



1

Salicylideneanilines (**1**) are unique chromic compounds that show either photo- or thermochromic properties depending on the substitution patterns of the aromatic rings.[1] In general, the derivatives with nonplanar conformation ($\phi > 25°$) are photochromic whereas those with planar conformation ($\phi < 25°$) are thermochromic.[2] To control the chromic properties of **1**, numerous derivatives have been synthesized by introducing various substituents on the chromophore. Another unique way to control their chromic behavior is their inclusion in matrices such as polymers,[3] zeolites,[4] cyclodextrins,[5] and bile acids.[6] Although crystallographic studies are essential to correlate the structure with chromic properties, the precise structural information of **1** within these matrices cannot be obtained with high precision even by employing the most reliable single-crystal X-ray diffraction methods. Herein we report the switching of the chromic properties of **1** by inclusion in a porous coordination network.[7,8] We reveal that an otherwise thermochromic derivative becomes photochromic when included in the clathrate network because the dihedral angle (ϕ) of the chromophore is significantly twisted as a result of inclusion (Scheme 1).



Scheme 1. Thermo-to-photo-switching of salicylideneanilines by inclusion.

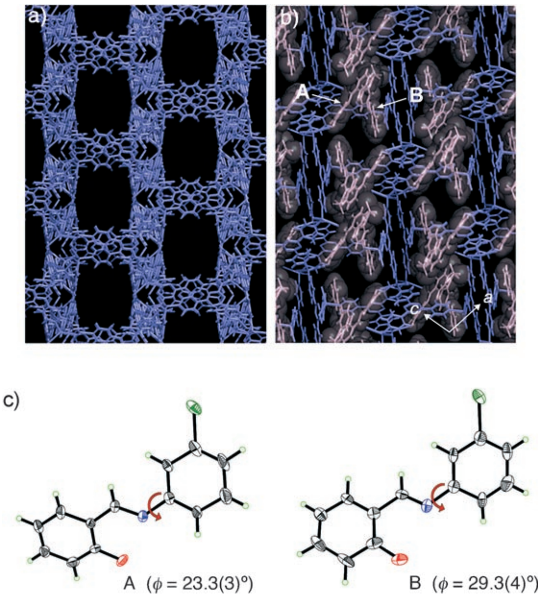


Figure 1. Crystal structure of the porous network $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\}_n]$ including **1a** in the pore: a) View in the (101) direction. Molecules of **1a** and solvent molecules in the pores are omitted. b) View along the *b* axis. The porous network of $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\}_n]$ is shown in blue in stick form. Two crystallographically independent molecules of **1a** (A and B), packed in the pore of the network, are shown in pink as a stick and translucent space-filling model. Solvent *t*BuOH molecules in the pores are omitted for clarity. c) Thermal ellipsoid plots of **1a**. The ellipsoids are drawn at the 30% probability level. The arrows represent the dihedral angle (ϕ) defined by the two planes of C=N and *m*-chlorophenyl groups.

We have previously reported that the complexation of tris(4-pyridyl)triazine (**2**) with $\mathrm{ZnI_2}$ gives a porous 3D coordination network $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\}_n]$ (Figure 1a).[9] This network complex was typically prepared in a nitrobenzene/methanol solvent mixture and isolated in high yield as nitrobenzene clathrate $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot 5.5\,(\mathrm{C_6H_5NO_2})\}_n]$ (**3**), in which the large channel of the $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\}_n]$ network is filled with loosely packed nitrobenzene molecules. An intriguing feature of clathrate complex **3** is the facile uptake of large organic guests by single-crystal-to-single-crystal guest exchange.[10] By this guest-exchange method, we obtained the inclusion complexes of several salicylideneanilines in the $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\}_n]$ network.

We studied in detail the inclusion complex of $(o\text{-}\mathrm{HOC_6H_4})\mathrm{CH{=}N}(m\text{-}\mathrm{ClC_6H_4})$ (**1a**), which is a thermochromic compound in the crystalline state. This inclusion compound was prepared by single-crystal-to-single-crystal guest exchange from nitrobenzene clathrate **3**.[9] When single crystals of **3** were immersed in a saturated solution of **1a** in *t*BuOH at room temperature for 3 days, the colorless crystal of **3** turned pale yellow. Elemental analysis of the isolated

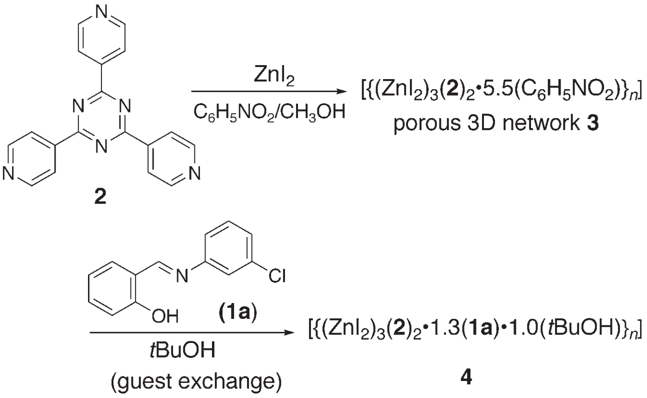
---

[*] T. Haneda, Dr. M. Kawano, Dr. T. Kojima, Prof. Dr. M. Fujita
Department of Applied Chemistry
School of Engineering
The University of Tokyo and Genesis Research Institute, Inc.
Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7257
E-mail: mkawano@appchem.t.u-tokyo.ac.jp
mfujita@appchem.t.u-tokyo.ac.jp

[**] This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2006G284).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

crystal showed the composition $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot1.3(\mathbf{1a})\cdot1.0(t\mathrm{BuOH})\}_n]$ (**4**) (Scheme 2). After guest exchange, the crystals showed no change in size and morphology and diffracted well, remaining suitable for single-crystal X-ray analysis.



Scheme 2. Preparation of clathrate complex **4** by guest exchange.

Crystallographic analysis of clathrate complex **4** revealed the exchange of nitrobenzene in **3** for a mixture of **1a** and *t*BuOH in a single-crystal-to-single-crystal fashion (Figure 1b). The guest molecule **1a** exists in two crystallographically independent positions (A and B) within a column parallel to the $a+c$ direction. The 3D net remains unchanged and the cell parameters are almost the same as those of **3**. Notably, the dihedral angles of **1a** in the coordination network are considerably distorted ($\phi = 23.3(3)°$ and $29.3(4)°$ at positions A and B, respectively) from that found at the single-crystal X-ray analysis of **1a** alone ($\phi = 5°$).[11] Thus, the restricted space in the channel significantly twisted the conformation of **1a** (Figure 1c).

The nonplanar conformation of **1a** when included in the clathrate suggests the emergence of photochromic properties. Indeed, photoirradiation ($\lambda = 366$ nm) of the crystal of the inclusion complex at 120 K induced chromism from pale yellow to red (Figure 2).[12] The photoisomerization of **1a** (*cis*-enol form) into **1a′** (*trans*-keto form; Figure 2c), which causes the photochromism, was confirmed by single-crystal microscopic IR spectroscopy. The difference FTIR spectra before and after UV irradiation for 20 minutes clearly showed the conversion of **1a** into **1a′**.[13] The band at 1616 cm^{-1} (attributable to C=N stretching mode of **1a**) decreased, and instead a new band appeared at 1651 cm^{-1} attributable to the C=O stretching mode of **1a′** (Figure S10 in the Supporting Information). The degree of photoisomerization was estimated to be approximately 20% from the decrease in the area of the absorption band at 1282 cm^{-1}.[14,15] Unfortunately, a crystal structure of the photoproduct could not be determined in situ because of severe disorder.

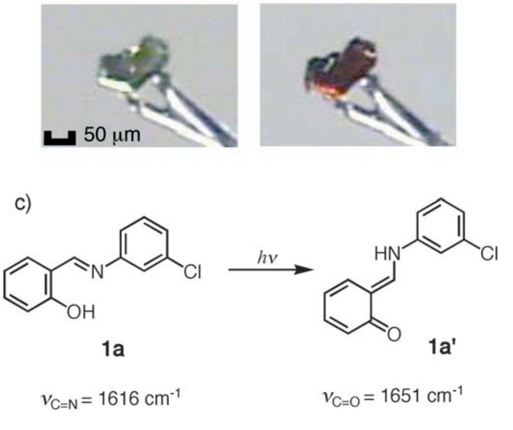


Figure 2. Photographs of a single crystal of clathrate **4** before (a) and after (b) irradiation ($\lambda = 366$ nm) for 80 min at 120 K. c) The photoisomerization of **1a** (*cis*-enol form) into **1a′** (*trans*-keto form).

Interestingly, the degree of the photoisomerization was significantly decreased to around 5% upon guest exchange of *t*BuOH with cyclohexane. Clathrate complex $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot1.8(\mathbf{1a})\cdot0.8(c\text{-}\mathrm{C_6H_{12}})\}_n]$ (**5**) was obtained without deterioration of crystallinity by immersing the single crystals of **3** in a saturated solution of **1a** in cyclohexane. The crystal structure of the cyclohexane clathrate **5** reveals that the packing of the guest molecules and the 3D net is very similar to that of the *t*BuOH clathrate **4** (Figure S4 in the Supporting Information).[16] However, the dihedral angles of **1a** in the cyclohexane clathrate **5** (18.0(2)° and 40.5(2)°) are considerably different from those in the *t*BuOH clathrate **4** (23.3(3)° and 29.3(4)°). This result suggests that the photochromism of **1a** can be tuned in the network by changing the nature of the solvent that coexists with this guest in the channels.[17]

We also examined the behavior of $(o\text{-HOC}_6\mathrm{H}_4)\mathrm{CH{=}N}(p\text{-ClC}_6\mathrm{H}_4)$ (**1b**) in $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot1.4(\mathbf{1b})\cdot1.0(t\mathrm{BuOH})\}_n]$ (**6**). Similarly, thermochromic **1b** turned photochromic through inclusion within the clathrate network. We found that the dihedral angle (originally $\phi = 6°$) changed to 2.5(3)° and 42.8(5)° in the two crystallographically independent **1b** molecules upon inclusion (see the Supporting Information).

In summary, we could control the chromic properties of **1** by inclusion in a coordination network. Thanks to the crystalline nature of the network, the relationship between the dihedral angle and the chromic behavior of **1** can be studied by single-crystal X-ray analysis without any chemical modification of **1**. Our approach of inclusion in the channel of a coordination network could be used to control the physical properties of labile chromic compounds.

Experimental Section

Elemental analysis (%) for **4**: Calcd for $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot1.3(\mathbf{1a})\cdot1.0(t\mathrm{BuOH})\}_n]$: C 34.91, H 2.42, N 9.52; found: C 34.61, H 2.68, N 9.43.

Elemental analysis (%) for **5**: Calcd for $[\{(\mathrm{ZnI_2})_3(\mathbf{2})_2\cdot1.8(\mathbf{1a})\cdot0.8(\mathrm{C_6H_{12}})\}_n]$: C 37.31, H 2.52, N 9.35; found: C 37.29, H 2.57, N 9.19.

Crystallographic data for **4**: The diffraction data were measured on a Bruker APEX-II/CCD diffractometer equipped with a focusing mirror ($\mathrm{Mo_{K\alpha}}$ radiation $\lambda = 0.71073$ Å) with a cryostat system equipped with a $\mathrm{N_2}$ generator (Japan Thermal Eng. Co., Ltd.). $\mathrm{C_{58.9}H_{35.7}Cl_{1.3}I_6N_{13.3}O_{2.8}Zn_3}$, $M_r = 1978.10$, crystal dimensions $0.05\times0.02\times0.01$ mm^3, monoclinic, space group $C2/c$, $a = 35.91(4)$, $b = 14.83(2)$, $c = 32.04(3)$ Å, $\beta = 102.98(2)°$, $V = 16628(33)$ Å^3, $T = 80$ K, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.580$ g cm^{-3}, 12140 unique reflections out of 19645 with $I > 2\sigma(I)$, 865 parameters, $1.54 < \theta < 28.49°$, final R factors $R_1 = 0.0680$ and $wR_2 = 0.2088$.

Crystallographic data for **5**: Synchrotron radiation ($\lambda = 0.6890$ Å) was used at PF-AR (NW2 beamline) of the High Energy Accelerator Research Organization (KEK). Data were collected on RIGAKU/MSC Mercury CCD X-ray diffractometer. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) by using the SHELX-TL program package. Hydrogen atoms were fixed at calculated positions and refined by using a riding model. $C_{71.4}H_{64.2}Cl_{1.8}I_6N_{13.8}O_{1.8}Zn_3$, $M_r = 2165.69$, crystal dimensions $0.1 \times 0.05 \times 0.03$ mm^3, monoclinic, space group $C2/c$, $a = 35.648(7)$, $b = 14.809(3)$, $c = 31.842(6)$ Å, $\beta = 102.75(3)°$, $V = 16395(6)$ Å^3, $T = 150$ K, $Z = 8$, $\rho_{\text{calcd}} = 1.755$ g cm^{-3}, 10956 unique reflections out of 20149 with $I > 2\sigma(I)$, 937 parameters, $1.88 < \theta < 27.33°$, final R factors $R_1 = 0.0364$ and $wR_2 = 0.0996$.

CCDC 631665 (**4**), CCDC 631664 (**5**), and CCDC 631666 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: March 7, 2007
Revised: June 26, 2007

Keywords: coordination networks · host–guest systems · photochromism · structure elucidation · thermochromism

---

[1] a) M. D. Cohen, G. M. Schmidt, *J. Phys. Chem.* **1962**, *66*, 2442–2445; b) M. D. Cohen, G. M. Schmidt, S. Flavian, *J. Chem. Soc.* **1964**, 2041–2051; c) E. Hadjoudis, *Mol. Eng.* **1995**, *5*, 301–337; d) J. Harada, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1999**, *121*, 5809–5810; e) T. Fujiwara, J. Harada, K. Ogawa, *J. Phys. Chem. B* **2004**, *108*, 4035–4038.

[2] According to a search of the Cambridge Structural Database (see the Supporting Information).

[3] E. Hadjoudis, M. Vittorakis, I. M. Mavridis, *Tetrahedron* **1987**, *43*, 1345–1360.

[4] I. Casades, M. Álvaro, H. García, M. N. Pillai, *Eur. J. Org. Chem.* **2002**, *13*, 2074–2079.

[5] a) G. Pistolis, E. Hadjoudis, I. M. Mavridis, *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 215–219; b) E. Hadjoudis, A. Botsi, G. Pistolis, H. Galons, *J. Carbohydr. Chem.* **1997**, *16*, 549–559.

[6] T. Kawato, K. Amimoto, H. Maeda, H. Koyama, H. Kanatomi, *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 57–62.

[7] Within porous coordination networks, guest absorption, removal, exchange behavior, and photoreactions have been previously reported: a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; b) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375–376; c) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2000**, *112*, 4001–4003; *Angew. Chem. Int. Ed.* **2000**, *39*, 3843–3845; d) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2002**, *114*, 3545–3548; *Angew. Chem. Int. Ed.* **2002**, *41*, 3395–3398; e) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* ***2002***, *298*, 1762–1765; f) M. P. Suh, J. W. Ko, H. J. Choi, *J. Am. Chem. Soc.* **2002**, *124*, 10976–10977; g) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; h) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288; i) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; j) B. Rather, M. J. Zaworotko, *Chem. Commun.* **2003**, 830–831; k) S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki, W. Mori, *Angew. Chem.* **2003**, *115*, 4467–4470; *Angew. Chem. Int. Ed.* **2003**, *42*, 4331–4334; l) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; m) D. Braga, F. Grepioni, *Angew. Chem.* **2004**, *116*, 4092–4102; *Angew. Chem. Int. Ed.* **2004**, *43*, 4002–4011; n) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858–2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798–2801; o) T. K. Maji, K. Uemura, H. C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 3331–3334; *Angew. Chem. Int. Ed.* **2004**, *43*, 3269–3272; p) C. Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia, H. C. zur Loye, *J. Am. Chem. Soc.* **2004**, *126*, 3576–3586; q) S. Takamizawa, E. Nakata, T. Saito, *Angew. Chem.* **2004**, *116*, 1392–1395; *Angew. Chem. Int. Ed.* **2004**, *43*, 1368–1371; r) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem.* **2004**, *116*, 5143–5146; *Angew. Chem. Int. Ed.* **2004**, *43*, 5033–5036.

[8] a) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560–564; *Angew. Chem. Int. Ed.* **2003**, *42*, 542–546; b) P. Mahata, G. Madras, S. Natarajan, *J. Phys. Chem. B* **2006**, *110*, 13759–13768; c) F. X. Llabrés i Xamena, A. Corma, H. Garcia, *J. Phys. Chem. C* **2007**, *111*, 80–85.

[9] K. Biradha, M. Fujita, *Angew. Chem.* **2002**, *114*, 3542–3545; *Angew. Chem. Int. Ed.* **2002**, *41*, 3392–3395.

[10] O. Ohmori, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 16292–16293.

[11] A. Karakas, A. Elmali, H. Unver, I. Svoboda, *J. Mol. Struct.* **2004**, *702*, 103–110.

[12] Photoirradiation at 293 K induced no color change of the crystal of **4**, probably because the reverse reaction at 293 K is too fast to be observed. We did not observe thermochromism of **4** in the range of 80 to 293 K.

[13] a) R. Nakagaki, T. Kobayashi, J. Nakamura, S. Nagakura, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1909–1912; b) T. Yuzawa, H. Takahashi, H. Hamaguchi, *Chem. Phys. Lett.* **1993**, *202*, 221–226.

[14] Interestingly, in a KBr matrix, the conversion increased to 38%, probably because of the smaller crystal size relative to that of the single crystal for the microscopic measurement.

[15] Photoirradiation ($\lambda = 560$ nm) at 250 K bleached the *trans*-keto form to the initial state.

[16] Because each *t*BuOH molecule is well separated by 3.4 Å from neighboring molecules, no hydrogen bond was found.

[17] There are three possible factors that could control the conversion efficiency: 1) the dihedral angle of **1a**; 2) the polarity of co-included solvent molecules; and 3) the shape and size of co-included solvent molecules.