Porous Networks

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

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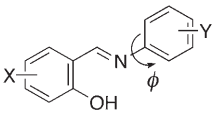
Salicylideneanilines (**1**) are unique chromic compounds that show either photo- or thermochromic properties depending on the substitution patterns of the aromatic rings.[1] In general, the derivatives with nonplanar conformation ($\phi > 25°$) are photochromic whereas those with planar conformation ($\phi < 25°$) 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).



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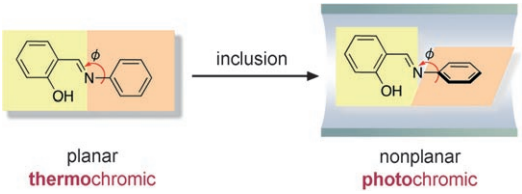
We have previously reported that the complexation of tris(4-pyridyl)triazine (**2**) with ZnI_2 gives a porous 3D coordination network $[\{(ZnI_2)_3(\mathbf{2})_2\}_n]$ (Figure 1a).[9] This network complex was typically prepared in a nitrobenzene/methanol solvent mixture and isolated in high yield as nitrobenzene clathrate $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}5.5\,(C_6H_5NO_2)\}_n]$ (**3**), in which the large channel of the $[\{(ZnI_2)_3(\mathbf{2})_2\}_n]$ 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 $[\{(ZnI_2)_3(\mathbf{2})_2\}_n]$ network.



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

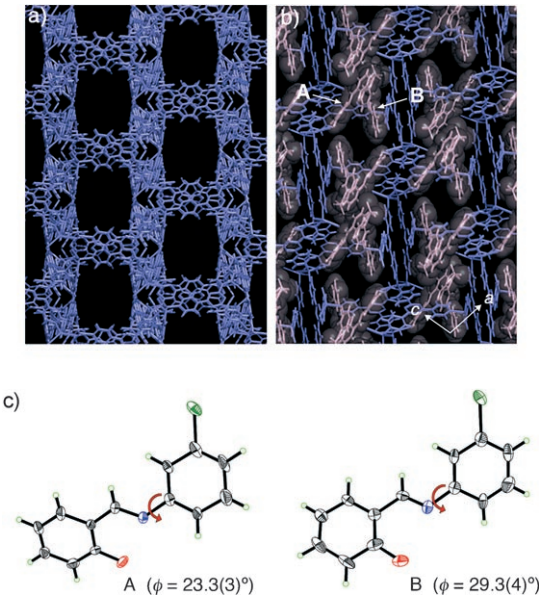


Figure 1. Crystal structure of the porous network $[\{(ZnI_2)_3(\mathbf{2})_2\}_n]$ including **1a** in the pore: a) View in the (101) direction. Molecules of **1a** and solvent molecules in the pores are omitted. b) View along the *b* axis. The porous network of $[\{(ZnI_2)_3(\mathbf{2})_2\}_n]$ is 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 studied in detail the inclusion complex of (*o*-HOC_6H_4)CH=N(*m*-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

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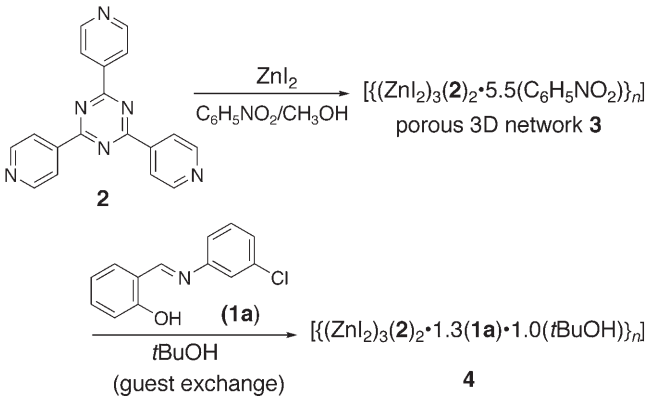
crystal showed the composition $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}1.3(\mathbf{1a}){\cdot}1.0(t\text{BuOH})\}_n]$ (**4**) (Scheme 2). After guest exchange, the crystals showed no change in size and morphology and diffracted well, remaining suitable for single-crystal X-ray analysis.



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.

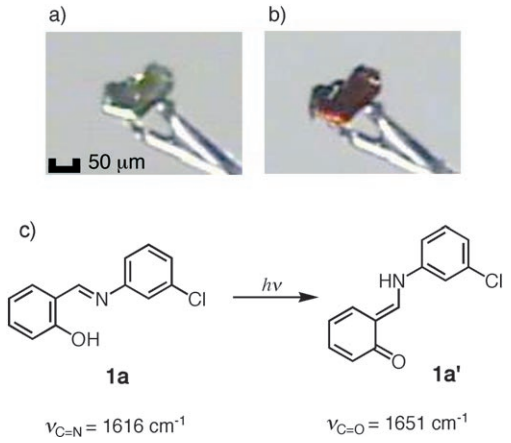


Figure 2. Photographs of a single crystal of clathrate **4** before (a) and after (b) irradiation ($\lambda = 366$ nm) for 80 min at 120 K. c) The photoisomerization of **1a** (*cis*-enol form) into **1a′** (*trans*-keto form).

Interestingly, the degree of the photoisomerization was significantly decreased to around 5% upon guest exchange of *t*BuOH with cyclohexane. Clathrate complex $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}1.8(\mathbf{1a}){\cdot}0.8(c\text{-}C_6H_{12})\}_n]$ (**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 $(o\text{-}HOC_6H_4)CH{=}N(p\text{-}ClC_6H_4)$ (**1b**) in $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}1.4(\mathbf{1b}){\cdot}1.0(t\text{BuOH})\}_n]$ (**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 $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}1.3(\mathbf{1a}){\cdot}1.0(t\text{BuOH})\}_n]$: 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 $[\{(ZnI_2)_3(\mathbf{2})_2{\cdot}1.8(\mathbf{1a}){\cdot}0.8(C_6H_{12})\}_n]$: 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 ($Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å) with a cryostat system equipped with a N_2 generator (Japan Thermal Eng. Co., Ltd.). $C_{58.9}H_{35.7}Cl_{1.3}I_6N_{13.3}O_{2.8}Zn_3$, $M_r = 1978.10$, crystal dimensions $0.05 \times 0.02 \times 0.01$ 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, $Z = 8$, $\rho_{calcd} = 1.580$ $g\,cm^{-3}$, 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, $Z = 8$, $\rho_{calcd} = 1.755$ 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.

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[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.

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[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.

