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A Thermochromic Thin Film Based on Host−Guest Interactions in a Layered Double Hydroxide

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Optically transparent thin films with thermochromic properties have been fabricated by means of cointercalation of different molar ratios of 4-(4-anilinophenylazo)benzenesulfonate (AO5) and sodium dodecylbenzene sulfonate (SDS) into the galleries of a ZnAl layered double hydroxide (LDH). The X-ray diffraction (XRD) patterns of these thin films show that they are assembled in a highly *c*-oriented manner, and the basal spacing ranges from 2.95 to 2.63 nm with varying AO5/SDS molar ratio. The preferential orientation of AO5 in the galleries of 10% AO5-LDH (AO5/SDS = 10:90, molar percentage) was evaluated by the fluorescence polarization technique; the results show that AO5 anions are accommodated between sheets of ZnAl-LDH as monomeric units with a tilt angle Ψ (defined as the angle between the transition dipole moment of the AO5 anion with respect to the normal to the LDH layer) of 74°. It was found that the composite film exhibits marked thermochromic behavior (light yellow ⇄ reddish-orange) in the temperature range of 35−65 °C, which is reversible over a number of heating−cooling cycles. It has been demonstrated that the thermochromic behavior results from tautomerism of interlayer AO5 and furthermore that both the host−guest and guest−guest interactions are key factors, since pristine AO5 shows no thermochromic performance. The 10% AO5-LDH film shows the highest thermochromic efficiency of all the films examined. Furthermore, a reversible contraction and expansion of the LDH basal spacing was also observed for this thin film over the same temperature range.

1. Introduction

Materials that exhibit reversible properties, such as thermochromism or photochromism, are of both theoretical and practical interest.[1] Thermochromic phenomena[2] have evoked much interest because of their wide range of potential applications, ranging from temperature sensors to coatings, including writable/rewritable optical data storage, security markers for monetary notes and government documents, thermal printing, and color-variable clothing.[3] A variety of thermochromic materials, including liquid crystalline, single-component organic or inorganic, and multicomponent organic systems, have been developed.[4] However some inherent demerits, such as relatively poor thermal or optical stability, very high thermochromic transition temperature, and toxicity of noble metals employed, limit the practical utility of materials prepared to date.[5] Therefore, it is important to search for novel thermochromic materials with high stability, that have reversible and repeatable behavior at a desirable thermochromic transition temperature.

In recent years, considerable interest has been focused on the fabrication of inorganic−organic host−guest composite materials, because they may show novel functionalities that are not present in the individual components alone.[6] The assembly of such supramolecular architectures relies upon intermolecular interactions such as hydrogen bonding, proton transfer or charge-transfer interactions that are determined by the chemical structures and properties of both host and guest. Aromatic azo dyes with electron donor substituents at the 4-position, such as 4-(4-anilinophenylazo)benzenesulfonate (AO5) have been widely used as thermal sensors, pH indicators, and for molecular memory storage because of the tautomerism between the azo *A*-form and hydrazone *H*-form, as shown in Scheme 1.[7] This tautomeric equilibrium is very sensitive to the microenvironment and can be affected by many factors (substituents, solvents, temperature, pH, UV-irradiation, etc.), resulting in halo-, photo-, and thermochromic properties.[8−11] Therefore, an effective solution for enhancing the thermochromic properties of a 4-substituted azo dye is to choose an appropriate inorganic material as the host matrix to tune its molecular environment.

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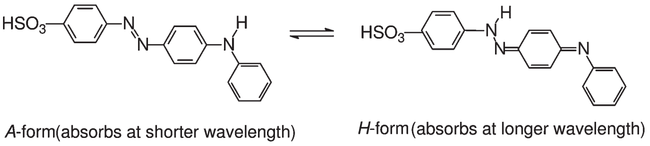
Scheme 1. Tautomeric Equilibrium between the *A*-Form and *H*-Form of AO5



Layered double hydroxides (LDHs), whose structure can be generally expressed as $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ (where M^{II} are divalent and M^{III} trivalent metals respectively, and A^{n-} is an *n*-valent anion), are two-dimensional (2-D) layered materials consisting of positively charged host layers with charge balancing guest anions.[12] As a result of their anisotropic layered structure, LDH crystallites have a platelet morphology where the crystallite dimensions in the *a* and *b* directions are much larger than that in the orthogonal *c* direction (the thickness of the platelets). One of the most interesting features of these materials is their role as a host matrix for the orientation and dispersion of interlayer anions, in order to afford tailored optical, thermal, and electrical functional materials as well as devices.[13,14] Therefore, it can be anticipated that the incorporation of a 4-substituted azo dye into an LDH matrix will give rise to one kind of novel thermochromic material with the following advantages. First, the LDH host layers impose an isolation effect and provide a rigid and ordered microenvironment for the distribution and alignment of the azobenzene group within the available free space, which should reduce the barrier to tautomerization. Second, the presence of water molecules in the LDH gallery can serve as a proton donor and may result in enhanced thermochromic performances. Finally, the presence of the inorganic LDH host matrix may improve the thermal and optical stability of the intercalated organic dye.

In this work, we report the fabrication of transparent thin films of acid orange 5 (4-(4-anilinophenylazo)benzenesulfonate or AO5, shown in Scheme 1) and sodium dodecylbenzene sulfonate (SDS) cointercalated in LDH, which show repeatable thermochromic behavior. We investigate the effect of tuning the free volume available to AO5 in the interlayer galleries by varying the molar ratio of AO5 and dispersant anions (SDS) and propose a mechanism for the thermochromic process involving tautomerism of the AO5. To the best of our knowledge, there have been no previous reports of such repeatable thermochromic films based on host−guest and guest−guest interactions. It is expected that the strategy reported here can be employed to fabricate a variety of film materials with interesting thermochromic properties based on regular arrangements of organic chromophores within an inorganic matrix.

2. Experimental Section

2.1. Materials. Analytical grade chemicals AO5 and SDS were purchased from Aldrich. $Zn(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, and NaOH were obtained from Beijing Chemical Co., Ltd, and used without further purification. Deionized and decarbonated water was used in all the experimental processes.

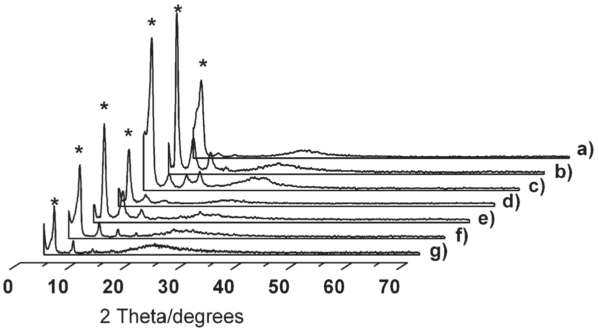


Figure 1. XRD patterns of thin film samples: (a) SDS-LDH; (b) 2% AO5-LDH; (c) 5% AO5-LDH; (d) 10% AO5-LDH; (e) 50% AO5-LDH; (f) 75% AO5-LDH; (g) 100% AO5-LDH (*x*% represents the molar percentage of AO5: $[AO5^-]/([AO5^-]+[SDS^-])$; asterisks denote the 003 reflections).

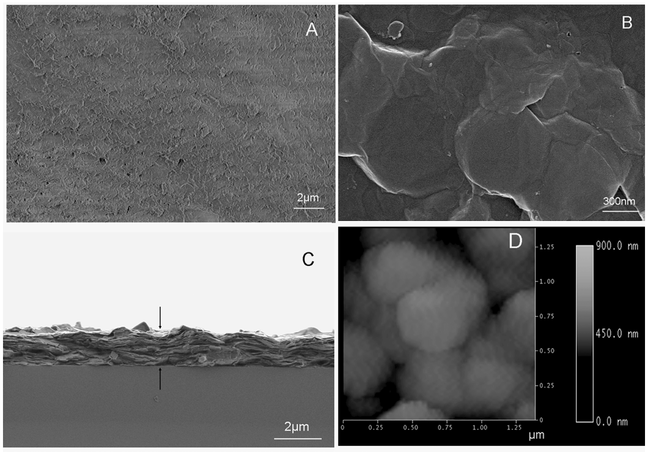


Figure 2. The morphology of the 10% AO5-LDH film in top-view SEM images at (A) low and (B) high magnification. (C) The side-view SEM image. (D) Tapping-mode AFM image of the film.

2.2. Synthesis of the AO5/SDS Cointercalated ZnAl-LDH. The AO5/SDS-LDH composite was synthesized using a method involving separate nucleation and aging steps (SNAS) developed in our laboratory. This method involves a very rapid mixing and nucleation process in a modified colloid mill, followed by a separate aging process.[15] Solution A: $Zn(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H2O$ with a Zn^{2+}/Al^{3+} molar ratio of 2.0 were dissolved in deionized water to give a solution with a Zn^{2+} concentration of 0.05 M. Solution B: NaOH, AO5, and SDS were dissolved in deionized water. The alkali concentration was related to the concentration of metal ions in solution A as follows: $[NaOH] = 2[Zn^{2+}] + 2[Al^{3+}]$, $[AO5^-] + [SDS^-] = [Al^{3+}]$, and $[AO5^-]/[Al^{3+}] = 0.02, 0.05, 0.1, 0.5, 0.75$, or 1.0, in different reactions. Solution A (80 mL) and solution B (80 mL) were simultaneously added to a modified colloid mill[16] with a rotor speed of 3000 rpm and mixed for 2 min. The resulting slurry was transferred to a 50 mL Teflon-lined autoclave and heated at 100 °C for 12 h. The final precipitate was filtered, washed thoroughly with deionized water, and dried at 70 °C for 24 h.

2.3. Fabrication of AO5/SDS-LDH Thin Films. Thin films of AO5/SDS-LDH were fabricated by the solvent evaporation method. The AO5/SDS-LDH powder (0.01 g) was suspended in ethanol (20 mL) in a glass flask and treated in an ultrasonic bath

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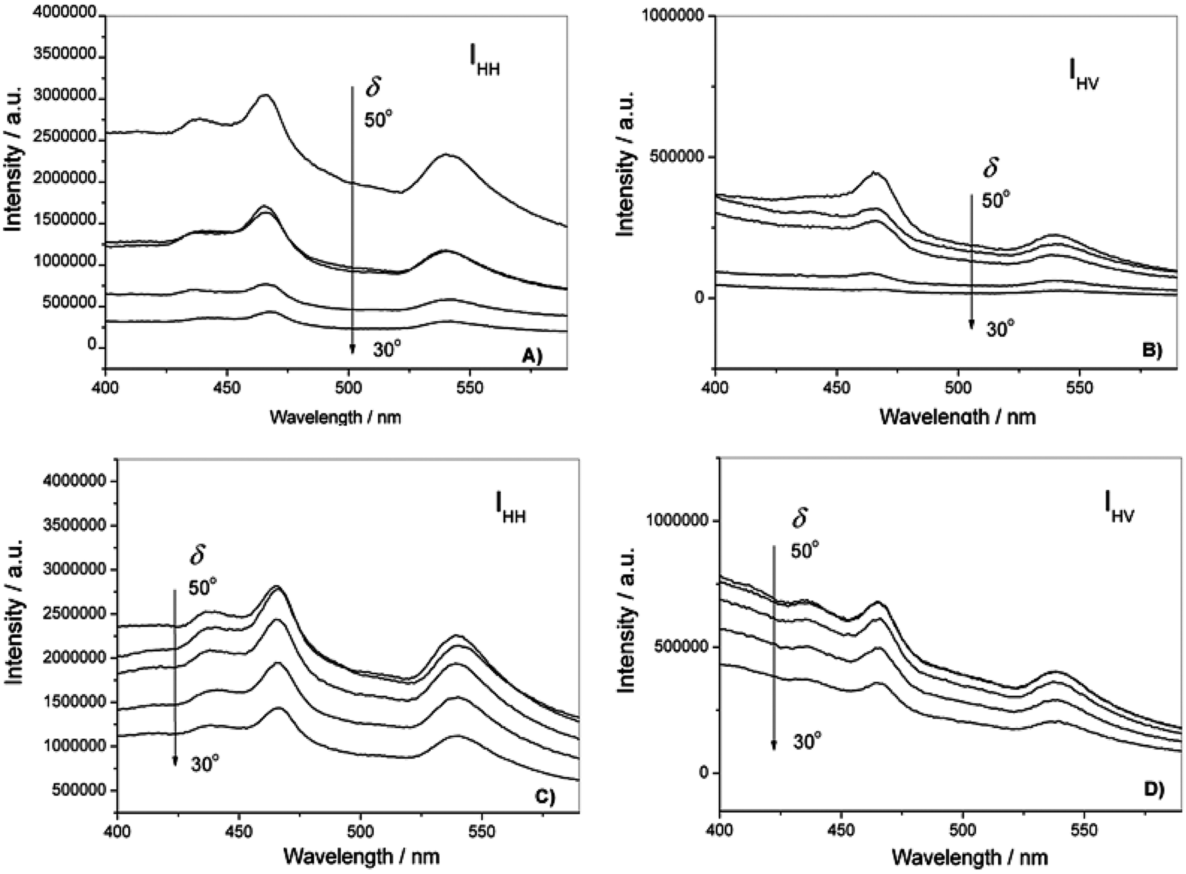

Figure 3. Evolution of the H (A) and V (B) polarized fluorescence spectra of a 10% AO5-LDH suspension in ethanol with the twist angles δ of the sample varied from 50° to 30°; evolution of the H (C) and V (D) polarized fluorescence spectra of the 10% AO5-LDH film with the twist angles δ of the sample varied from 50° to 30°. Spectra were recorded after excitation with horizontal polarized light.

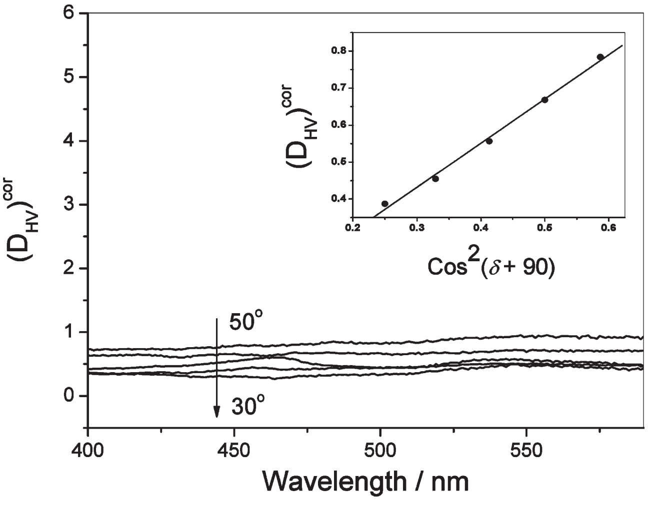

Figure 4. Evolution of the fluorescence dichroic ratio of the 10% AO5-LDH film with the emission wavelength for different twist angles δ of the sample. The linear relationship between the dichroic ratio and $\cos^2(\delta + 90)$ at 468 nm is included in the inset graph.

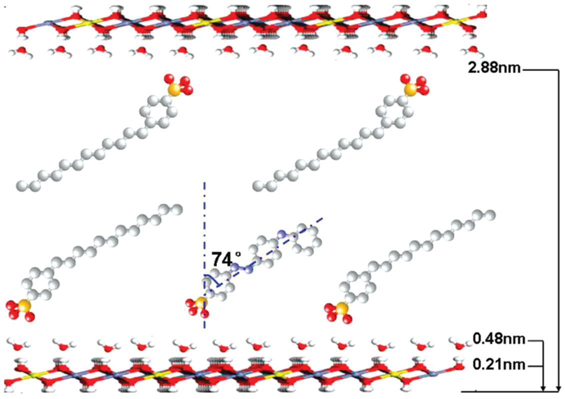

Figure 5. Proposed illustration of the orientation of interlayer anions in the 10% AO5-LDH (Zn black, C gray, H white, Al yellow, O red, N blue, S orange).

(99 W, 28 kHz) under N_2 atmosphere for 15 min. After filtration using a membrane filter (0.2 μm, Millipore), 5 mL of AO5/SDS-LDH ethanol suspension was dropped onto quartz substrates and dried in vacuum at ambient temperature for 5 h. All the quartz substrates were pretreated in an aqueous H_2O-NH_4OH (3:7 v/v) solution for 30 min, followed by a thorough rinsing with deionized water.

2.4. Characterization. To determination the AO5 and SDS contents in the resulting materials, CHN analysis was conducted using an Elementar vario elemental analyzer. The amounts of Zn and Al were analyzed by inductively coupled plasma atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument using a dilute hydrochloric acid solution. Powder X-ray diffraction (PXRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer under the following conditions: Cu Kα radiation (λ = 1.542 Å, 2θ = 2−70°), 40 kV, 30 mA. The in situ variable temperature PXRD measurements were performed on a Philip X'Pert Pro MPD X-ray diffractometer operating at 40 kV, 40 mA in the temperature range 25−65 °C in ambient air, with Cu Kα radiation. X'celerator was used for recording the data. The heating rate was 1 °C/min with a holding time of 5 min before each

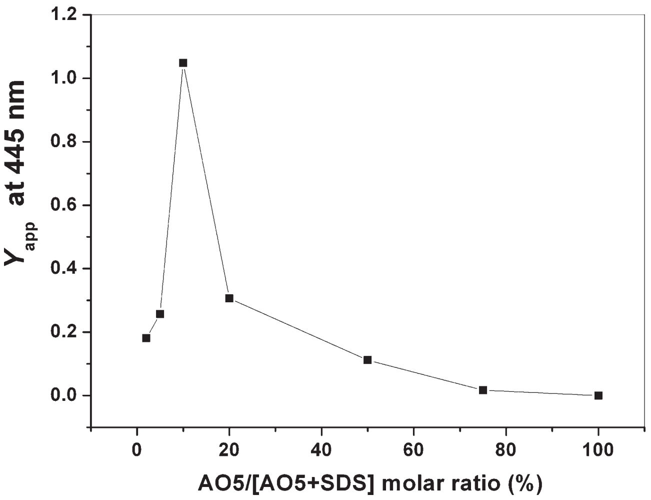

Figure 6. The tautomerization efficiency of the AO5/SDS-LDH film as a function of the relative content of AO5.

measurement. The morphology of AO5/SDS-LDH thin film was investigated by using a scanning electron microscope (SEM Hitachi S-3500) equipped with an energy-dispersive X-ray (EDX) attachment (EDX Oxford Instrument Isis 300), and the accelerating voltage applied was 20 kV. The surface roughness data were obtained by using atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). The fluorescence polarization spectra were recorded on a QuantaMaster spectrofluorometer (model QM-4), equipped with automated polarizers in both the excitation and the emission beams (see Figure S1 in the Supporting Information).

Thermochromic behavior of the samples was recorded on a UV/visible absorption spectrophotometer (Shimadzu UV-2100S) equipped with a temperature controller (CPS-260, 25−65 °C) in a darkroom.

3. Results and Discussion

3.1. Structural and Orientation Characteristics of AO5/SDS-LDH Films. SDS was chosen as the dispersant in this work to modulate the AO5−AO5 guest−guest interactions, since it has the same sulfonate group as AO5 and similar dimensions in its long direction. Powdered samples of ZnAl-LDHs cointercalated with different molar ratios of AO5 and SDS were prepared using a method employing the SNAS method. The advantage of this method is that particles with a very narrow size distribution can be obtained, whereas, with conventional coprecipitation methods, a much wider crystallite size distribution results.[16] We have previously shown that the uniform size distribution allows the preparation of robust, transparent, well-oriented LDH films that cannot be obtained using materials produced by conventional coprecipitation.[17] The chemical compositions for AO5/SDS-LDH with different molar ratios of AO5/SDS are listed in Table S1. ZnAl-LDH films were fabricated on quartz glass substrates by solvent evaporation of ethanol suspensions of the powdered materials. The PXRD patterns of the films are shown in Figure 1. In each case, the XRD pattern, which can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, exhibits the characteristic reflections of the LDH structure with a series of 00l peaks appearing as narrow, symmetric, strong lines at low angle. The basal spacing (d_{003}) of AO5/SDS-LDH (x%) decreases from 2.95 nm ($x = 0$) to 2.63 nm ($x = 100\%$), comparable to the value of 2.85 nm reported for SDS-intercalated LDHs,[18] indicating that AO5 and SDS were cointercalated into the galleries of LDH. The variation of interlayer spacing can be attributed to the different arrangements of interlayer guests with different ratios of AO5/SDS. The absence of any nonbasal reflections (h, $k \neq 0$) at high angle for the films is as expected for extremely well c-oriented assemblies of LDH platelets.[17] Moreover, the SEM images (Figure 2A−C) confirm that that the LDH lamellar crystallites are stacked with their ab-planes parallel to the substrate (c-axis perpendicular to the substrate), with an average film thickness of ca. 1.4−1.8 μm. The AFM topographical image (scan = 1.375 μm × 1.375 μm) of a thin film is illustrated in Figure 2D, and the average root-mean-square (rms) roughness was found to be 27 nm, indicating a relatively smooth surface of the film. Both the high SEM magnification (Figure 2B) and the AFM topographical image (Figure 2D) reveal that the individual round-like AO5/SDS-LDH platelets with dimensions of 400−600 nm, are densely packed with a high degree of c-orientation of LDH platelets in the 2-D plane of the substrate, consistent with the XRD results in Figure 1.

It has been reported that the arrangement and orientation of guest molecules within the host matrix plays an important role in determining the optical, electronic, and magnetic properties of the resulting composite.[19,20] Polarized fluorescence, resulting from the ordered arrangement of chromophores, was employed in this work to shed light on the structural orientation of interlayer AO5. According to the literature,[21] the transition dipole moment of AO5 is oriented along its long axis. The horizontal (H) and vertical (V) polarized fluorescence spectra of the 10% AO5-LDH film were recorded with a common horizontally polarized excitation light source as a function of the twist angle δ of the thin film with respect to the excitation beam. The experimental setup is shown in Figure S1. A linear relationship between the fluorescence dichroic ratio (D_{HV} is defined as the ratio of H and V polarized emission spectra, $D_{HV} \equiv I_{HH}/I_{HV}$) and the twist angle δ (with a right-angle configuration between the excitation and the emission beam) was established by means of[22]

$$(D_{HV})^{cor} = \frac{I_{HH}}{I_{HV}} \times G = 2\cot^2\psi + (1 - 2\cot^2\psi)\cos^2(90 + \delta) \qquad (1)$$

where G is the instrumental factor determined by the recorded fluorescence anisotropy of an isotropic system, $G \equiv (I_{HV}/I_{HH})^{iso}$. In this work, a suspension of 10% AO5-LDH in ethanol was used as the isotropic system, and the fluorescence spectra are shown in Figure 3A,B. Figure 3C displays the fluorescence spectra of the 10% AO5-LDH film recorded with the emission polarizer in the H (I_{HH}) and V (I_{HV}) directions for different twist δ angles. The fluorescence intensity for the emission H polarizer decreases upon decreasing the twist angle δ from 50° to 30°. Analogous changes were also observed for the V polarized emission light (Figure 3D). For a given emission wavelength, the dichroic ratio of the 10% AO5-LDH film sample linearly correlates with the $\cos^2(90 + \delta)$

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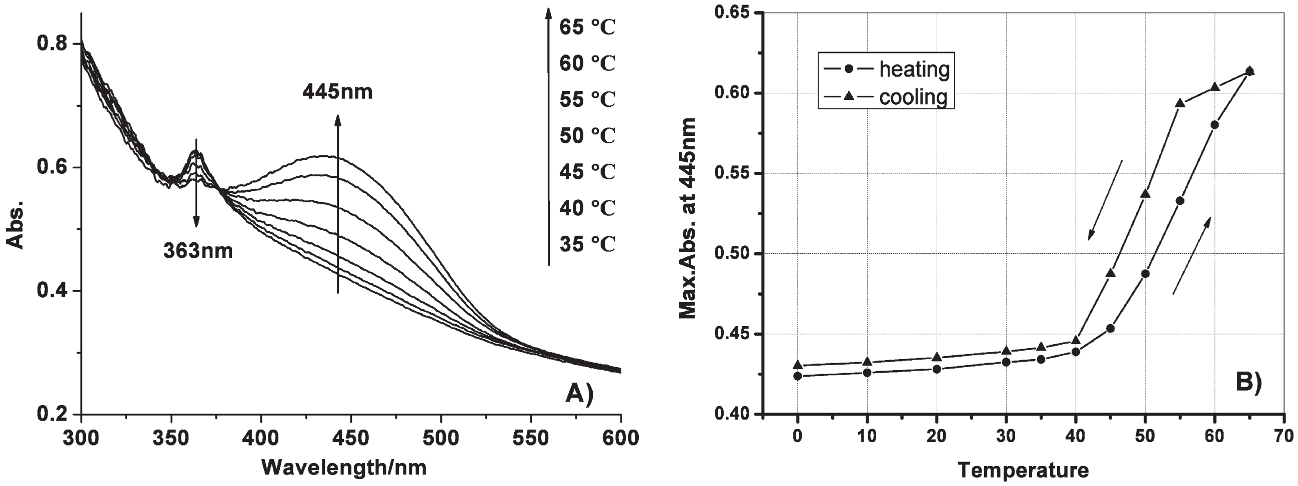

Figure 7. (A) In situ absorption spectra of the 10% AO5-LDH film during heating in the temperature range 35−65 °C. (B) The correlation between the absorbance of the band at 445 nm and temperature over a complete heating−cooling cycle.

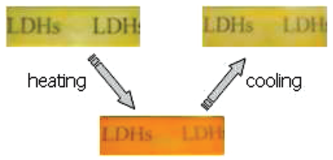

Figure 8. Digital photographs of the 10% AO5-LDH film in a heating−cooling cycle.

value, as shown in the inset of Figure 4. A good linear relationship was observed in this representation with a correlation coefficient $r > 0.997$, indicating the absence of any depolarization phenomena during the excited state lifetime of the 10% AO5-LDH film sample. This indicates that AO5 molecules in the LDH inorganic matrix exist mainly as the monomer form. According to eq 1, from the slope and intercept of the linear plot of $(D_{HV})^{cor}$ versus $\cos^2(90 + \delta)$ shown in the inset of Figure 4, the orientation angle Ψ (defined as the angle between the transition dipole moment of the fluorescent species AO5 and the normal to the LDH layer) was calculated to be 74°.

On the basis of the results of fluorescence polarization, the length of AO5 and SDS as well as the thickness of the LDH layer (0.21 nm[23]) and the hydrogen bonding space (0.27 nm[23]), a proposed illustration for the orientation of the 10% AO5-LDH is shown in Figure 5. The AO5 and SDS anions are accommodated in the galleries of LDH as an interdigitated bilayer arrangement, with the sulfonate group of individual anions attached alternately to the upper and lower hydroxide layers by hydrogen bonding.

3.2. Thermochromic Behavior of AO5/SDS-LDH Films. Actually, we first tried the ultraviolet−visible (UV−vis) irradiation to invoke *cis*−*trans* isomerization of AO5 in the AO5/SDS-LDH film owing to high research interest on photochromism of azobenzene materials, but no obvious photochromic properties can be observed for the film. Then the thermochromic behavior of AO5/SDS-LDH films with different molar ratios was evaluated using an *in situ* UV/visible absorption spectrophotometer with a temperature controller in a darkroom. It was found that the 10% AO5-LDH film shows the highest efficiency of thermochromism, characterized by the appearance of the *H*-form at 65 °C. The apparent extent of thermochromism is determined by

$$Y_{app} = (A_t - A_0)/A_0 \qquad (2)$$

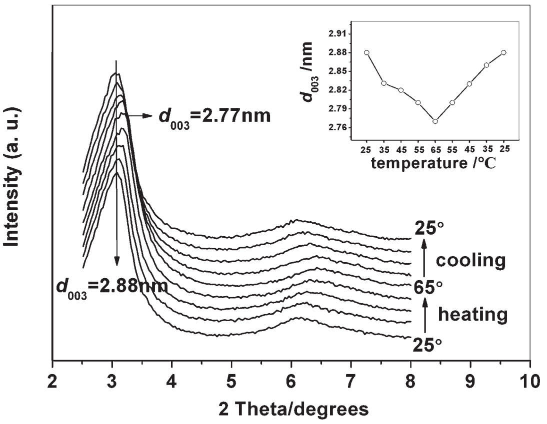

Figure 9. In situ XRD patterns of the 10% AO5-LDH thin film over a heating−cooling temperature cycle in the range 25−65 °C. Inset: the change in the d_{003} basal spacing over the whole cycle.

where A_0 and A_t correspond to the absorbance at 445 nm of the film at 35 and 65 °C, respectively. As shown in Figure 6, the film containing 10% AO5 exhibits the optimal tautomerization efficiency. The explanation for this is straightforward. Lower contents of AO5 lead to undetectable thermochromic phenomena, whereas much higher content of the chromophore reduces the volume available for AO5 to undergo tautomerization. When the molar ratio of AO5 is 100%, the thermochromism disappears completely. Therefore, the cointercalated SDS plays an important role in determining the thermochromic properties of AO5/SDS-LDH film since it supplies sufficient volume and a weakly polar interlayer space for tautomerization to occur.

According to the result above, the 10% AO5-LDH film was chosen to describe the thermochromic behavior. At ambient temperature, the thin film has a maximal absorption at 363 nm (Figure 7A). As the temperature is increased, a spectral change occurs with a progressive decrease in the intensity of the band at 363 nm, and a new band appears with increasing intensity at 445 nm (shown in Figure 7A). Visually, a color change from light yellow to reddish-orange can be observed upon heating the 10% AO5-LDH film from 35 to 65 °C. As the film is cooled to room temperature, it recovers its original color completely with the associated converse spectral changes. Digital photographs for a complete thermochromic cycle (shown in Figure 8) illustrate the color changes and also highlight the high degree

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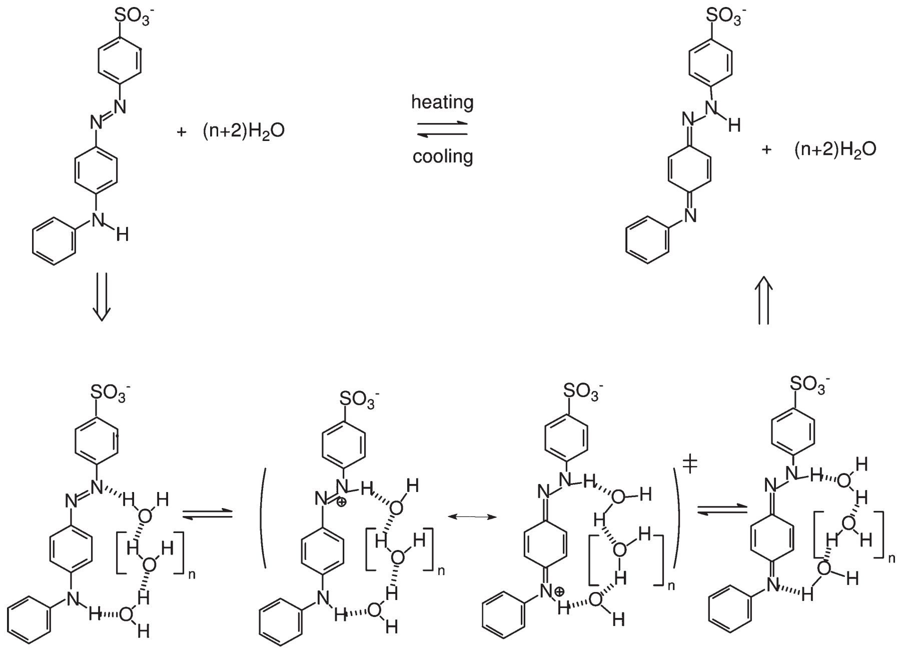
[23] Allmann, R. *Chimia* **1970**, *24*, 99.

Scheme 2. Schematic Representation of the Tautomerization of AO5 upon Heating and Cooling the AO5/SDS-LDH Film



of optical transparency of the films before and after thermal treatment; as noted above, this can be attributed to the narrow distribution of crystallite sizes obtained using the SNAS method.[17]

Figure 7B displays the correlation between the absorbance at 445 nm and temperature over a complete heating−cooling cycle, confirming the reversibility of the thermochromic performance for the film, despite the existence of some spectral lag. Moreover, the absorbance at 363 and 445 nm for five heating−cooling cycles shown in Figure S2 (see Supporting Information) indicates the rather good repeatability of the spectral changes.

During the thermochromic process, the expansion and contraction of the basal spacing of the 10% AO5-LDH film can be detected by in situ variable-temperature XRD. As shown in Figure 9, the basal spacing (d_{003}) decreases from 2.88 to 2.77 nm during the heating process from 25 to 65 °C, and increases to 2.88 nm again after cooling treatment. Similar to the changes in the absorption spectra, this reversible change in basal spacing can be performed repeatedly. The thermochromism of the intercalated guests is therefore clearly associated with a change in the basal spacing, which can be regarded as a novel thermomechanical response.[24]

3.3. The Stability of the Thermochromic Thin Film. Both the thermal and photostability of the 10% AO5-LDH film were also studied. After preheating treatment of the 10% AO5-LDH film at temperatures as high as 250 °C for 30 min, it still showed a thermochromic performance (see Supporting Information Figure S3). Comparison of the thermal and photostability revealed that the 10% AO5-LDH sample exhibited higher stability to thermal aging and UV irradiation than pristine AO5 (see Figures S4 and S5 in the Supporting Information and the associated discussion). Moreover, the storage life was also tested, and the results showed that the film still retained its thermochromic properties after being kept for as long as one year. These results indicate that both the thermal and photostability of the 10% AO5-LDH film are enhanced significantly as a result of the host−guest interactions in the composite material. Compared with conventional thermochromic materials (inorganic, liquid crystalline, and organic systems),[25] the thin film in this work possesses the advantages of enhanced thermal stability, long storage time, easy manipulation, low cost, and environmental friendliness.

3.4. Study of the Mechanism of Thermochromism in the 10% AO5-LDH Film. In order to further understand the thermochromic mechanism of the 10% AO5-LDH film, a series of comparative experiments were carried out.

(1) It has been reported in the literature that free AO5 exists predominantly in the *A*-tautomer in aqueous solution[11a] and that, for a variety of azo dyes in solution, conversion of the *A*-tautomer to the *H*-tautomer results in a red-shift in the absorption maximum by ~80−100 nm.[11a] These data suggest that the decrease in the intensity of the band at 363 nm and concomitant increase in the intensity of the band at 445 nm observed on heating the 10% AO5-LDH film (shown in Figure 7A) can be attributed to tautomerism of *A*-AO5 to give *H*-AO5 within the interlayer galleries. The tautomerism presumably involves proton transfer from the terminal −NHPh group to the β-azo nitrogen atom via a network of hydrogen-bonded water molecules in a Grotthuss-type mechanism as shown in Scheme 2. The exsitence of interlayer water molecules is a key factor for the tautomerism of AO5. For LDH materials, because the deintercalation and regain of interlayer water is a reversible process below 250 °C in air atmosphere,[12a,26] a preheating treatment at 250 °C does not influence the themochromic behavior of the 10% AO5-LDH film, as mentioned in section 3.3.

(2) In order to provide additional evidence that tautomerism is responsible for the thermochromic behavior of AO5/SDS-LDH film, we prepared an analogous material containing methyl orange (MO) in place of AO5. The structure of MO (Figure 10A) differs from AO5 only in that the −NHPh group in the latter is replaced by an $-NMe_2$ group in the former. MO therefore lacks a labile >NH proton able to take part in a tautomerism process similar to that shown in Scheme 2. An MO/SDS-LDH film was

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[24] Itoh, T.; Shichi, T.; Yui, T.; Takahashi, H.; Inui, Y.; Takagi, K. *J. Phys. Chem. B* **2005**, *109*, 3199.

[25] (a) Fujiwara, T.; Harada, J.; Ogawa, K. *J. Phys. Chem. B* **2004**, *108*, 4035. (b) Hatada, M.; Katanosaka, A.; Minami, N. *J. Photopolymer Sci. Tech* **2006**, *19*, 63.

[26] Evans, D. G.; Duan, X. *Structure and Bonding: layered double hydroxides*; Springer: Verlag Berlin Heidelberg, 2005.

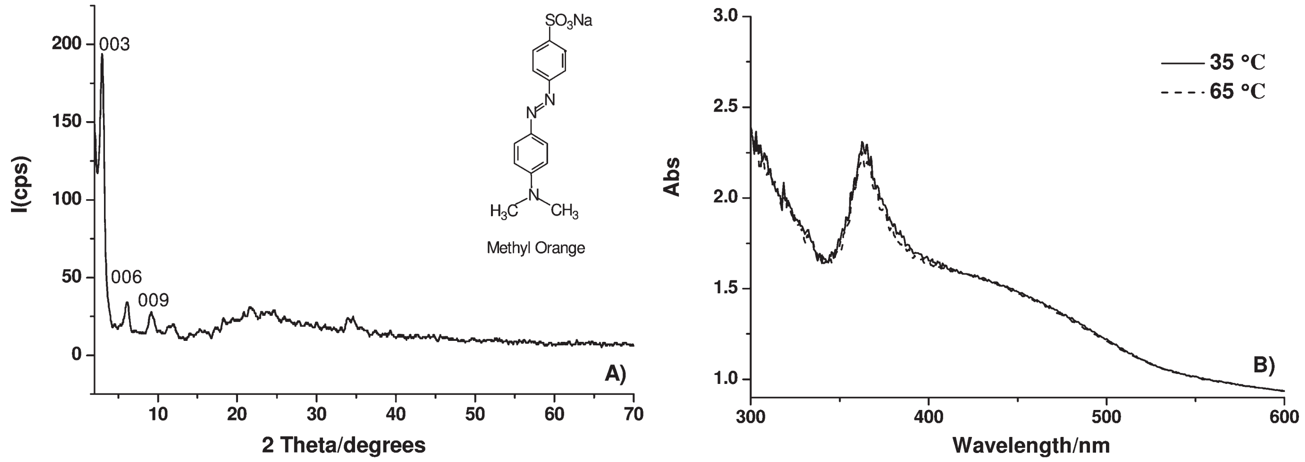

Figure 10. (A) XRD pattern of the 10% MO-LDH film. Inset: chemical structure of MO. (B) In situ UV/visible absorption spectra for the 10% MO- LDH film at 35 and 65 °C.

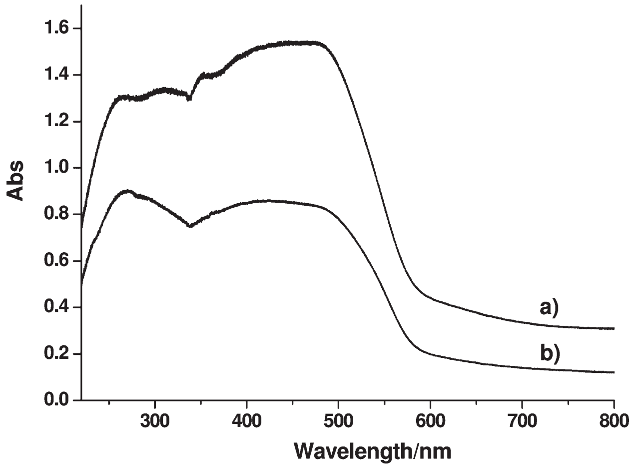

Figure 11. In situ absorption spectra for (a) pristine AO5 and (b) a physical mixture of AO5 and SDS (molar percentage of AO5: 10%) at 25 °C. No any change can be observed as the temperature rises to 65 °C for the two samples.

fabricated and characterized by exactly the same procedures as for the AO5/SDS-LDH film. The PXRD pattern of the 10% MO/SDS-LDH film exhibits the characteristic reflections of the LDH structure with a series of $00l$ peaks (Figure 10A). The interlayer spacing of the 10% MO/SDS-LDH film is 2.90 nm, comparable to that of 10% AO5/SDS-LDH. At ambient temperature, the UV spectrum of the 10% MO-LDH thin film (Figure 10B) has an absorption maximum at 365 nm. This is very similar to that of the 10% AO5-LDH film (Figure 7A), suggesting that the *A*-form of MO is also the predominant tautomer in the interlayer galleries of the LDH. However, no significant spectral change was observed on heating the sample to 65 °C and subsequently cooling to room temperature (Figure 10B). The absence of thermochromic behavior for the MO/SDS-LDH film provides support for the tautomerism mechanism of the thermochromism of the 10% AO5-LDH film shown in Scheme 2.

(3) For comparison, the UV−visible spectra of pristine AO5 and a physical mixture of AO5 and SDS (molar percentage of AO5: 10%) were measured under the same conditions as for the film, as shown in Figure 11. At ambient temperature, the pristine AO5 has a broad absorption peak centered at 450 nm (Figure 11a), which shows no change when the sample is heated to 65 °C. The color of the AO5 is orange at both temperatures, with no difference discernible to the naked eye on heating and cooling. A similar phenomenon was also observed in a physical mixture of AO5 and SDS (Figure 11b). It can be concluded from the above comparison studies that the thermochromic behavior for the 10% AO5-LDH film is attributed to the synergic effect of both host−guest and guest−guest interactions. They are necessary conditions that facilitate the tautomeric processes of interlayer AO5.

4. Conclusions

The 10% AO5-LDH film showed significant and reversible thermochromism in the temperature range of 35−65 °C. It was found that the tautomerization reaction of AO5 is responsible for the thermochromism and involves cointercalated water molecules. The presence of cointercalated SDS provides excess space, which facilitates the deprotonation−protonation processes of AO5 through the formation of hydrogen bonding with interlayer water molecules. The film material also shows rather high thermal and photostability resulting from the host−guest structure. Moreover, as the temperature range for the thermochromism of this film covers the body temperature of human beings and the atmosphere, it is expected that this film material should have potential applications in the field of physiological and environmental temperature designation and temperature warning. By virtue of the wide variety of anionic azo dyes capable of being intercalated into an LDH matrix, the simple process described here can be expanded to prepare functional thin film materials with a range of thermochromic properties.

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Supporting Information Available: Chemical compositions of AO5/SDS-LDH materials with different AO5 contents (Table S1). Three-dimensional perspective for the experimental setup to record fluorescence spectra (Figure S1). Thermochromism cycles of the 10% AO5-LDH film at different wavelengths (Figure S2). Thermal and photostability comparison between pristine AO5 and the 10% AO5-LDH material (Figures S3, S4, and S5). This material is available free of charge via the Internet at http://pubs.acs.org.