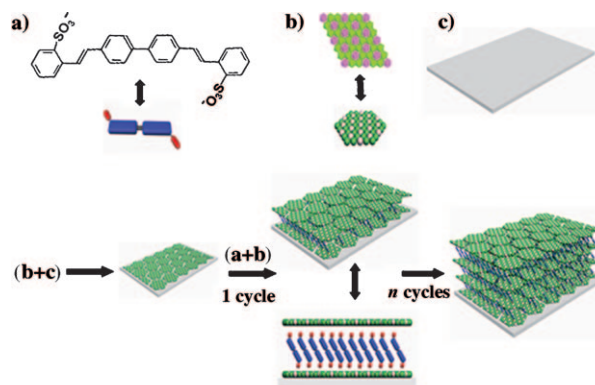


Reversibly Thermochromic, Fluorescent Ultrathin Films with a Supramolecular Architecture**

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Tunable luminescent materials that respond to different external stimuli have attracted great attention during the last few years, owing to their potential applications in fluorescent switches, sensors, and optical recording devices.^[1] Mechanisms responsible for the change in luminescence include chemical reactions^[2] and alteration of the molecular packing mode.^[3] Since solid-state chemical reactions frequently have low conversion efficiency, recent attention has focused on controlling and tuning the molecular packing mode as a strategy for the design and preparation of intelligent luminescent materials.^[4] To date, although several types of responsive luminescent materials have been developed (e.g., piezochromic,^[3a] deformation-induced chromic,^[3b] photochromic,^[3c] thermochromic,^[3d] and humidity-related colorimetric luminescent^[3e] systems), challenges remain. For instance, to meet the requirements of luminescent devices or sensors, it is important to be able to assemble ordered thin films with regular molecular orientation and intermolecular packing mode on two-dimensional surfaces. Switching of solid-state luminescence based on such ordered thin films is rather rare, however.^[3a,c] Therefore, it is of crucial importance to develop new ways to fabricate ordered film systems with fluorescent properties which respond to environmental stimuli. Furthermore, fast response, facile reversibility, and stable repeatability are all necessary from the viewpoint of practical application of such materials in sensors. Therefore, there is an urgent demand to develop new types of solid-state responsive materials as well as sensors with high efficiency, stability, and reproducibility.

Herein we present a supramolecular ultrathin film (UTF) system with thermochromic luminescence (TCL) based on the layer-by-layer (LBL) assembly of anionic bis(2-sulfonatostyryl)biphenyl (BSB, Scheme 1a) and positively charged layered double hydroxide (LDH, Scheme 1b) nanosheets as



Scheme 1. Assembly process for the (BSB/LDH)_n UTF. a) Chemical structure and schematic representation of BSB. b) Schematic illustrations of one Mg–Al–LDH monolayer. c) Quartz glass substrate.

basic building blocks. BSB is generally used as a fluorescent brightener in the chemical industry; moreover, the phenylenevinylene unit in BSB also has attracted considerable interest because of its excellent optical and electronic properties.^[5] LDHs are a class of layered anionic clays which have been widely used in the fields of catalysis, biology, and optical materials.^[6] LDHs can be exfoliated into positively charged nanosheets which can be fabricated into functional ultrathin films (UTFs) by LBL deposition of alternate layers of the LDH and polymers^[6a–c] or metal complexes.^[6d] However, LBL assembly of LDH nanosheets with small anions has rarely been reported because of the tendency of the small anions to escape from the nanosheets. Herein we describe fabrication of ordered BSB/LDH UTFs (Scheme 1) with a fast and reversible TCL response at ambient temperature. The TCL behavior of the assembled BSB anions, which is absent for their pristine form, originates from the host–guest interactions within the UTF system. Molecular dynamics (MD) and periodic density functional theoretical (PDFT) studies demonstrate that the TCL process of the BSB/LDH system is related to the changes in the orientation and aggregation of BSB anions between LDH monolayers. Moreover, coassembly of BSB with other luminescent anions into a UTF allows fabrication of responsive TCL film systems, in which the ratio of the luminescence at two different wavelengths can be reversibly transformed by varying the temperature, thus altering the luminescent color of the film. Therefore, this work provides a feasible route for designing and constructing luminescent supramolecular structures with potential applications in sensors and switching.

The multilayer assembly process of the BSB/LDH UTFs was monitored by UV/Vis absorption spectra, which showed

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that the intensities of the absorption bands at about 204 and 349 nm attributed to BSB increase linearly with the number of bilayers n (Figure 1a, inset), that is, growth of the film is

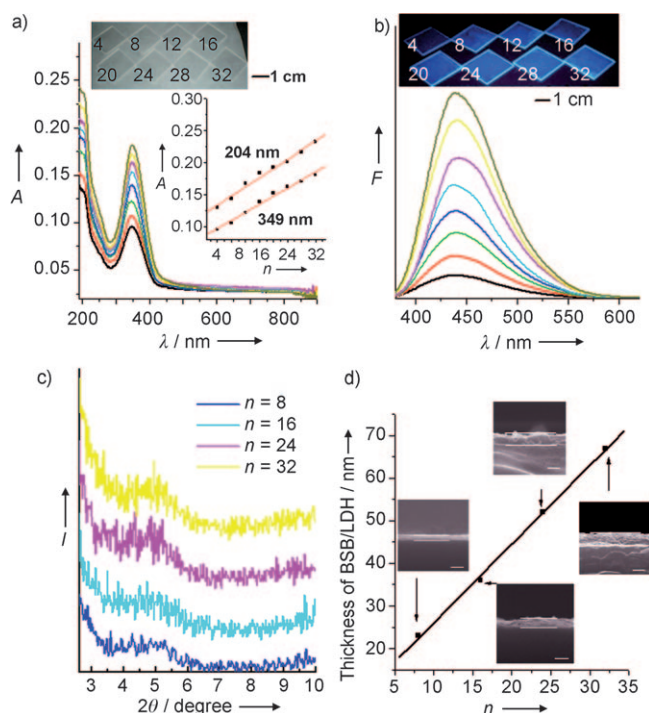


Figure 1. Characterization of $(\text{BSB/LDH})_n$ ($n=4-32$) UTFs. a) UV/Vis absorption spectra (inset: plots of the absorbance at 204 and 349 nm versus the number of bilayers, n). b) Fluorescence spectra; the insets in (a) and (b) are photographs of UTFs with different n under daylight and UV light (365 nm), respectively. c) XRD patterns. d) Thickness of the $(\text{BSB/LDH})_n$ UTFs as a function of n ; the insets show the side-view SEM images. Scale bars: 100 nm.

regular and uniform. The UTFs are colorless and highly transparent, as shown by the lack of visible absorption between 400 and 800 nm and photographs of the films in normal daylight (Figure 1a, inset). The UTFs display photo-emission spectra with a luminescence maximum at 444 nm, and the intensity shows a monotonic increase with n (Figure 1b). There is no shift or broadening of the emission band for different values of n , thus suggesting that no obvious changes in intermolecular interactions or microenvironment of BSB occur throughout the whole assembly process. Moreover, the photographs of the UTFs under UV illumination (Figure 1b, inset) show visible blue luminescence with brightness increasing as a function of increasing n . The XRD patterns (Figure 1c) of the UTFs were recorded in order to study the periodic structure. The increasing intensity of the reflection at about $2\theta = 5^\circ$ with increasing n indicates that the UTFs have an ordered periodic structure in the direction normal to the film, with a period of about 2 nm. This value is similar to that for the basal spacing of a BSB-intercalated LDH composite prepared by the co-precipitation method (Supporting Information: Figure S1a). Figure 1d illustrates the dependence of the thickness of the BSB/LDH UTFs on the value of n . The approximately linear increase (from 23 nm

for 8 bilayers to 67 nm for 32 bilayers) suggests that the average thickness of one BSB/LDH unit is about 2.2 nm, which is very close to the value indicated by XRD. The morphological features of the BSB/LDH UTFs were further studied by SEM and AFM. The top-view SEM images (Supporting Information: Figure S2) show that the surfaces of the BSB/LDH UTFs are microscopically smooth and homogeneous. The AFM images (Supporting Information: Figure S3 and Table S1) also show uniform and continuous film surfaces with root mean square roughness ranging from 1.163 ($n=1$) to 11.397 nm ($n=32$).

The UTFs undergo a significant change in luminescence color on heating for a short period of time (1–2 min). On heating the $(\text{BSB/LDH})_8$ UTF from 20 to 100°C , the photo-emission band moves from 444 to 473 nm with a concomitant gradual decrease in the luminescence intensity (Supporting Information: Figure S4). The emission color changes from blue (CIE 1931 color coordinates: 0.157, 0.129) to bluish-green (CIE 1931 color coordinates: 0.146, 0.271) on heating the UTF, and the color change is also visible to the naked eye. When the UTF was cooled to 20°C over 2 min, the fluorescence emission (Figure 2a, inset) recovered its original blue color completely together with the associated reverse spectral changes. The reversible change in luminescence color can be readily repeated (Figure 2a, inset). To obtain information about the excited states of the UTFs at different temperatures, we measured the fluorescence lifetimes of the BSB/LDH UTF at 20 and 100°C . The fluorescence decay at high temperature is much slower than that at low temperature (Figure 2b), and this suggests formation of an excimer in the BSB/LDH UTFs.^[3b] The fluorescence lifetime of the UTFs at

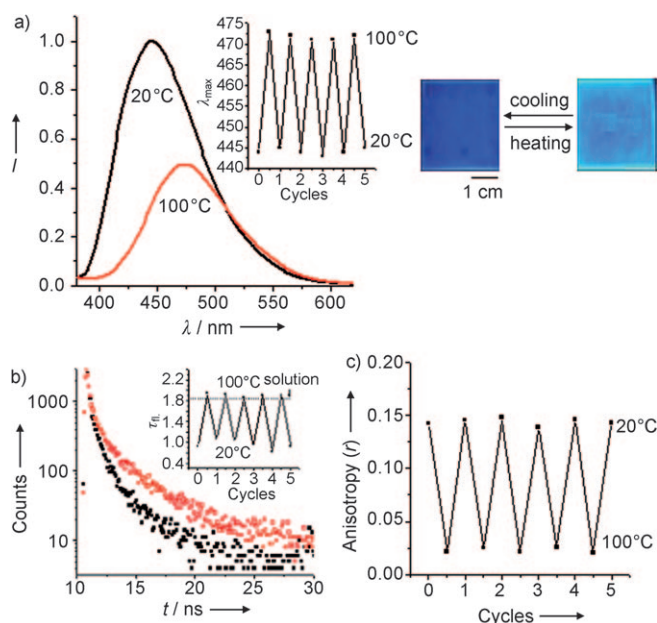


Figure 2. TCL of the $(\text{BSB/LDH})_8$ UTF at 20 and 100°C . a) Fluorescence spectra (inset: the reversible fluorescence response over five consecutive cycles, and photographs of the UTF before and after heating). b) Typical fluorescence decay curve (inset: fluorescence lifetimes τ_{fl} over five consecutive cycles). Black ■: 20°C ; red □: 100°C . c) Fluorescence anisotropy over five consecutive cycles.

100 °C is about 1.9 ns (close to the value of 1.8 ns for an aqueous solution of BSB), about twice the value observed at 20 °C (0.9 ns). These changes in fluorescence lifetime are repeatedly observed on cycling between the two typical temperatures (Figure 2b, inset). To further study the degree of structural order of the BSB/LDH UTFs, polarized fluorescence measurements with a glancing-incidence excitation beam were employed to probe the fluorescence anisotropy r .^[61,7] At 20 °C, the BSB/LDH UTF shows well-defined fluorescence anisotropy between directions parallel and perpendicular to the polarization direction of the excitation radiation, with an r value of 0.15 (Supporting Information: Figure S5). However, the r value decreases dramatically at 100 °C (ca. 0.02). This indicates that the degree of ordering of BSB anions is lower at higher temperature, with associated increased energy of molecular vibrations; this was also confirmed by in situ FTIR measurements (Supporting Information: Figure S6). Furthermore, a reversible change in the anisotropy of the UTF can also be obtained by repeated cycles of heating and cooling (Figure 2c), that is, the changes with temperature of the degree of order of the BSB anions between the LDH nanosheets are reversible. Additionally, no significant changes in the morphology of the UTF can be observed in the fluorescence microscopy images during the heating–cooling treatment (Supporting Information: Figure S7). These temperature-dependent properties can be ascribed to changes in the molecular packing of BSB between LDH nanosheets (see theoretical study below).

Good photo- and thermostability are extremely important criteria if a material is to have practical applications as a TCL film. Thermogravimetric/differential thermal analysis (Supporting Information: Figure S8) showed no weight loss below 100 °C for the BSB/LDH UTF and that, compared with pure BSB, the thermostability of BSB anions was enhanced by assembly with LDH nanosheets. In situ photoluminescence measurements showed that the BSB/LDH UTF has better UV stability than the pristine BSB film (Supporting Information: Figure S9). Moreover, after the heating–cooling process between 20 and 100 °C was repeated for 90 cycles, the BSB/LDH UTF still had TCL properties (Supporting Information: Figure S10). These results demonstrate the high thermostability and reversibility of the BSB/LDH UTF; it is thus a promising material for future practical applications.

Based on the TCL properties of the BSB/LDH UTF, we can fabricate other luminescent systems according to the three-primary-color principle. Blue/yellow two-color photo-emissive UTFs were constructed by assembling the (APPV/LDH)_{*n*} bilayer unit ($n=1-18$, where APPV^[7] is anionic poly(*p*-phenylenevinylene), which has $\lambda_{em}=547$ nm) on top of the as-prepared (BSB/LDH)₈ UTF. The UV/Vis and fluorescence spectra and SEM observations all confirm assembly of ordered (BSB/LDH)₈(APPV/LDH)_{*n*} UTFs (Supporting Information: Figures S11, S12). White-light emission occurs for (BSB/LDH)₈(APPV/LDH)₁₅ (CIE 1931: 0.257, 0.302), and the ratio of the fluorescence intensities at 445 and 547 nm undergoes a reversible transformation between about 2.4 at 20 °C and 1.0 at 100 °C (Figure 3). The photographs (Figure 3, inset) illustrate the different luminescence color responses of the (BSB/LDH)₈(APPV/LDH)₁₅ UTF at two

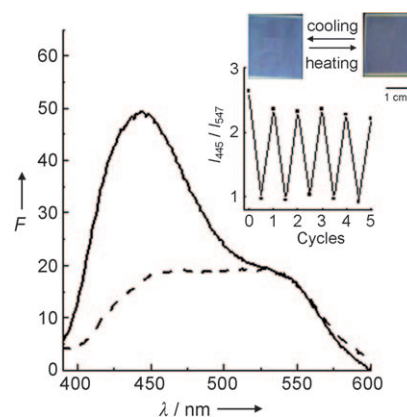


Figure 3. Fluorescence responses of the (BSB/LDH)₈(APPV/LDH)₁₅ UTF at 20 °C (—) and 100 °C (----) (inset: changes in the ratio of fluorescence intensities at 445 and 547 nm over five consecutive cycles).

typical temperatures. Based on the response of the intensity ratio to the temperature, these UTFs can serve as new types of molecular temperature sensors or molecular thermometers.^[3d]

To further understand the TCL behavior of the BSB/LDH system, MD simulations^[7] were performed for an ideal BSB/LDH model at thermodynamic temperatures of 293 and 373 K (corresponding to the values used in the experiment). At 293 K, the most probable angle of BSB relative to the LDH monolayer is about 28°. At 373 K, the orientational distribution broadens, ranging from 16 to 43°, and the distribution of dihedral angles of BSB also becomes broader (Supporting Information: Figures S13, S14). This suggests the distribution of BSB anions becomes more disordered at high temperature, consistent with the polarized fluorescence and in situ FTIR data. Additionally, the BSB anions are arranged almost parallel to each other, and the average distance (Supporting Information: Figure S15) between the centers of adjacent anions decreases from about 5.9 (293 K) to 5.1 Å (373 K), which facilitates formation of a chromophore excimer at high temperature. The distribution of the relative orientations of two neighboring BSB anions at 373 K is mainly populated in the range 15–40° (Supporting Information: Figure S16), and thus indicates formation of J-type BSB dimers between the LDH nanosheets. This is in agreement with the red-shift of the luminescence of the BSB/LDH UTF at high temperature. Total and partial electronic densities of states (Supporting Information: Figures S17, S18) calculated by the PDFT method^[7] show that the BSB/LDH system has a small band gap of 2.4 eV (Supporting Information: Figure S19), and HOMO and LUMO are completely localized on the 2p(π) and 2p(π^*) carbon atomic orbitals in BSB anions (Figure 4, Supporting Information: Figure S20). The results demonstrate that the blue fluorescence arises solely from BSB, and no energy or electron transfer occurs between BSB and the LDH nanosheets during the TCL process. The LDH monolayer, with a band gap of 5.7 eV, plays an energy-blocking role which prevents any interactions between BSB anions in adjacent bilayers. It thus can be concluded that the TCL performance is mainly associated with the variations in

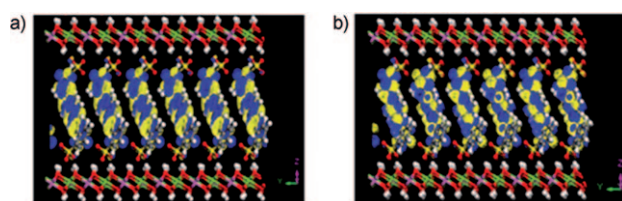


Figure 4. HOMO (a) and LUMO (b) profiles for the BSB/LDH system (the two colors donate $+/ -$ wavefunctions).

orientation, molecular packing, and aggregation state of BSB confined between the LDH nanosheets.

In summary, we have fabricated TCL UTF systems based on a supramolecular architecture comprising BSB anions and LDH nanosheets. In the temperature range 20–100 °C, the UTFs exhibit fast luminescence response and reversible transformations, including color, fluorescence lifetime, and anisotropy. Their high photo-/thermostability and effective reversibility promise long service lifetimes of the UTFs under practical conditions. MD and PDFT calculations demonstrate that the TCL properties of UTFs are related to changes in relative orientation and packing mode of the chromophores in the LDH matrix during heating–cooling cycles. Moreover, by combining suitable luminescent building blocks, the TCL UTF system is also applicable to other multicolor systems, which can be potentially used as luminescent sensors, molecular thermometers, and fluorescent antiforgery devices. It is anticipated that design and assembly principles based on versatile LBL methods can be utilized to fabricate other new types of luminescent materials sensitive to external stimuli.

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