

Controllable Photoluminescence Properties of an Anion-Dye-Intercalated Layered Double Hydroxide by Adjusting the Confined Environment

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Supporting Information

ABSTRACT: This article reports a novel method to tune the photoluminance properties of ammonium 1-anilinonaphthalene-8-sulfonate (ANS) in a 2D matrix of layered double hydroxide (LDH) by changing the interlayer microenvironment. ANS and a series of surfactants with different alkyl chain lengths (pentanesulphonate (PES), hexanesulphonate (HES), heptanesulphonate (HPS), decanesulphonate (DES), and dodecylsulphonate (DDS)) were respectively cointercalated into the galleries of ZnAl-LDH by the anion exchange method. Thin films of ANS/ surfactant-LDHs obtained by the solvent evaporation method possess good *c* orientation as revealed by XRD and SEM. It was found that the ANS/HPS-LDH film showed the maximum fluorescence efficiency and the longest intensity-average lifetime among these ANS/surfactant-LDH composites owing to the "size-matching" rule between the organic dye and



surfactant. Moreover, the fluorescence properties can be tuned by changing the relative molar ratio of ANS/HPS, and the film containing 20% ANS (molar percentage, expressed as ANS(20%)/HPS-LDH) exhibits the maximum fluorescence efficiency, the longest average lifetime, and significantly enhanced photo and thermal stability. In addition, the composite films show fluorescence anisotropy, attributed to the preferential orientation of ANS in the LDH gallery. Therefore, this work demonstrates a feasible approach to tuning the photoluminescence properties of a dye confined in an inorganic 2D matrix via changing the interlayer microenvironment, which may be considered to be a good candidate for solid photoluminescence materials, nonlinear optics, and polarized luminescence materials.

1. INTRODUCTION

Fluorescent dyes have attracted much attention owing to their broad use in paint, inks, textiles, and optical devices as a result of their vivid color, broad spectra, strong fluorescence intensity, and high quantum yield.¹ In addition, they have rather specialized applications in biodiagnostic assays. For instance, a series of amorphous fluorescence materials based on the triphenylamino core with strong emission from blue to red in the solid state under single UV wavelength excitation have been reported.² Rhodamine and its derivatives have been used not only in the laser field for technological application³ but also as a fluorescent probe for optical imaging in medicine.⁴ However, the application of fluorescent dyes was limited because of the decomposition or discoloration upon heat treatment or irradiation by UV light for a long period of time; moreover, fluorescence quenching induced by aggregation is another primary reason for limiting the application of fluorescent dyes. Therefore, much effort was focused on the incorporation of photoactive molecules into inorganic matrixes such as montmorillonite, phyllosilicate, zinc hydroxide, zirconium phosphate, and layered double hydroxide in order to improve the thermal, photostable, and fluorescence properties.⁵

Among the solid inorganic matrices used to accommodate organic dye molecules, layered double hydroxide (LDH) materials

have attracted much interest. The LDHs generally expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}](A^{n-})_{x/n} \cdot mH_{2}O$ (where M^{II} and M^{III} are divalent and trivalent metals, respectively, and A^{n-} is an *n*-valent anion) represent a large versatility in terms of their ability to construct 2D-organized intercalated compounds.⁶ 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.⁷ Recently, it has been reported that photoactive molecules were intercalated into LDHs, and the resulting chromophore/ LDH composites showed enhanced stability and photophysical behavior.⁸ However, the aggregation of fluorescent dyes was still inevitable in some dye-LDH systems, resulting in a decrease in the fluorescence capability and photonic facilities.⁹ Therefore, how to inhibit dye aggregation effectively and improve its photoluminescence properties in a confined region of the LDH gallery remains a challenge.

Ammonium 1-anilinonaphthalene-8-sulfonate (ANS, Scheme 1) was widely used as a fluorescent probe with excellent fluorescence properties. In our previous work, ANS-intercalated ZnAl-LDH

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Scheme 1. Molecular Structures for PES, HES, HPS, DES, DDS, and ANS Optimized by Gaussian 03^{*a*}



^a C, gray; H, white; O, red; S, yellow.

showed a stronger fluorescence intensity and a higher thermal stability than did ANS-intercalated MgAl-LDH.¹⁰ However, the aggregation of ANS molecules was still unavoidable and uncontrollable in the LDH gallery. It has been reported that the immediate surroundings play a key role in determining the aggregate state and fluorescence properties of ANS.^{10–12} For instance, ANS showed particular fluorescence behavior through the formation of inclusion complexes with α -, β -, and γ -cyclodextrin.^{11a} These previous reports inspire us to challenge the goal of tuning the photoluminescence properties of ANS immobilized in the LDH gallery via changing the interlayer microenvironment.

In this work, ammonium 1-anilinonaphthalene-8-sulfonate (ANS) and a series of surfactants with different alkyl chain lengths (pentanesulphonate (PES), hexanesulphonate (HES), heptanesulphonate (HPS), decanesulphonate (DES) and dodecylsulphonate (DDS) shown in Scheme 1) were respectively cointercalated into the galleries of ZnAl-LDH by the anion exchange method. It was found that the luminescence properties of the composites can be tuned by changing the surfactant polarity as well as the relative ratio of ANS/surfactant, demonstrating that the coexisting surfactant serves as an efficient regulator of the microenvironment in the LDH gallery. The results show that the ANS/HPS-LDH film exhibits the maximum fluorescence efficiency and the longest intensity-average lifetime among the five ANS/surfactant-LDH composites, owing to the size matching between the organic dye and surfactant molecule. The dependence of the luminescence behavior on the concentration of ANS (x) was also explored, and the optimal fluorescence efficiency and the longest lifetime were obtained at x = 20%. Furthermore, the ANS(20%)/HPS-LDH film shows significantly improved photo- and thermal stability as well as anisotropy. Therefore, this work provides a facile method for designing and preparing tunable photoluminescence materials that can be potentially applied in laser materials, nonlinear optics, and polarized luminescence materials.

2. EXPERIMENTAL SECTION

2.1. Materials. ANS, sodium pentanesulphonate (PES), sodium hexanesulphonate (HES), sodium heptanesulphonate (HPS), sodium decanesulphonate (DES), and sodium dodecylsuphonate (DDS) were purchased from J&K Chemical Ltd. Analytical-grade chemicals including $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and NaOH were used without further purification. Deionized, decarbonated water was used in all preparation processes.

2.2. Synthesis of ANS/Surfactant-LDH Composites. The ZnAl-LDH precursor was synthesized by the hydrothermal method reported previously.¹² The ANS- and surfactant-cointercalated LDHs were prepared by the ion-exchange method as follows: ANS (0.001 mol) and PES (0.004 mol) were dissolved in a mixture of ethanol—water (1:1 v/v) with the pH adjusted to 7.5 by a NaOH solution (0.1 M), and then 1.5 g of freshly prepared ZnAl-NO₃-LDH was added. The mixture was stirred at 70 °C under a N₂ atmosphere for 48 h. The resulting precipitate ANS/PES-LDH composite was centrifuged and washed thoroughly with ethanol and water. ANS/HES-LDH, ANS/HPS-LDH, ANS/DDS-LDH were synthesized by a similar procedure.

2.3. Synthesis of ANS(*x*%)/HPS-LDH Composites with Different Contents of ANS. ANS (*a* mols) and HPS (*b* mols in which a + b = 0.005 mol; x% = a/(a + b); x% = 10, 15, 20, 25, 30, 50, 75, and 100% respectively) were dissolved in 150 mL of ethanol—water (1:1 v/v) solvent, and then 1.5 g of freshly prepared Zn₂Al-NO₃-LDH was added. The mixture was stirred at 70 °C under a N₂ atmosphere for 48 h. The resulting ANS(*x*%)/HPS-LDH composite was centrifuged, and washed thoroughly with ethanol and water.

2.4. Fabrication of Thin Films of ANS/Surfactant-LDH and ANS(x%)/HPS-LDH Composites. The thin film of the ANS/surfactant-LDH composite was prepared by the solvent evaporation method. The suspension of the ANS/surfactant-LDH composite in ethanol (1 mg/mL) was thoroughly dispersed by an ultrasonicator under a N₂ atmosphere for 15 min. After filtration using a membrane filter ($0.2 \mu m$, Millipore), 5 mL of the ANS/surfactant-LDH ethanol suspension was dropped onto a silicon substrate and dried in vacuum at ambient temperature for 5 h. The ANS(x%)/HPS-LDH thin films were fabricated using a similar procedure.

2.5. Techniques of Characterization. The powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer using Cu K α radiation (λ = 0.15418 nm) at 40 kV and 30 mA with a scanning rate of 5°/min and a 2 θ angle ranging from 3 to 70°. FT-IR spectra were recorded on a Bruker Vector 22 Fourier transfer infrared spectrophotometer using the KBr disk method in the range from 4000 to 400 cm^{-1} with a resolution of 2 cm⁻¹ and an accumulation of 32 scans. SEM images were obtained using a Zeiss Supra 55 scanning electron microscope operating at 20 kV. Metallic elemental analysis was performed by atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument. The C, H, and N contents was determined using an Elementar vario elemental analysis instrument. Thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained on a Beifen PCT-IA instrument in the temperature range of 25–700 °C. The solid UV-vis absorption spectra were collected in the range of 250-550 nm on a Pupkinje General TU-1901 with a slit width of 1.0 nm, and BaSO₄ was used as a reference. The fluorescence spectra were recorded on an RF-5301PC fluorospectrophotometer under identical conditions at an excitation wavelength of 370 nm with emission spectra in the range of 400-600 nm. Steady-state and time-decay polarized photoluminescence measurements were recorded with an Edinburgh Instruments FLS 920 fluorimeter, which is equipped with a solid sample holder and an emission double monochromator. The emission spectra and lifetime were measured by exciting the samples to 370 nm with a 450 W Xe lamp and a nanosecond flashlamp, respectively. The percentage contribution of each lifetime component to the total decay was calculated with the F900 Edinburgh Instruments software. Photobleaching was tested by UV light with a CHF-XQ 500 W.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Study of ANS/Surfactant-LDH Films. The XRD patterns for the films of the LDH precursor, ANS-LDH, ANS/PES-LDH, ANS/HES-LDH, ANS/ HPS-LDH, ANS/DES-LDH, and ANS/SDS-LDH are shown in Figure 1. In each case, the reflections can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, which is commonly used for the description of the LDH structure. The interlayer spacing can be calculated from averaging the positions of the three harmonics: $c = \frac{1}{3}(d_{003} + 2d_{006} + 3d_{009})$. For the ZnAl-LDH precursor (Figure 1a), the (003) reflection gives an interlayer distance of 8.92 Å, in accordance with the reported value for NO₃-LDH.¹³ After the anion-exchange reaction, the basal reflection (003) of ANS/surfactant-LDH composites (Figure 1c-g) shifted to lower 2θ angles and the basal spacing expanded gradually from 17.4 to 24.1 Å upon increasing the length of the surfactant molecules (from 0.85 to 1.73 nm, Scheme 1). The results indicate that ANS and surfactant anions were cointercalated into the LDH lamella. Fourier transform infrared (FT-IR) spectra (Figure S1 in Supporting Information), and chemical compositions of the LDH precursor and resulting ANS/surfactant-LDH composites (Table S1) further confirm the cointercalation structure and the presence of NO_3^{-} in the ANS/surfactant-LDH composites. The half-peak width (fwhm) of the (003) reflection (0.27-0.35°) for all of the ANS/ surfactant-LDH samples (Table S1 in Supporting Information) is less than that of ANS-LDH (0.40°) (i.e., no broadening of the (003) reflection occurs after the cointercalation of ANS and surfactant molecules). This indicates that ANS and the surfactant disperse uniformly in the galleries of LDH, forming a homogeneous phase. In the case of the ANS-LDH sample, it was found



Figure 1. Powder XRD patterns for the films of (a) ZnAl-LDH, (b) ANS-LDH, (c) ANS/PES-LDH, (d) ANS/HES-LDH, (e) ANS/HPS-LDH, (f) ANS/DES-LDH, and (g) ANS/DDS-LDH.

that its d_{003} (19.6 Å) is close to that of ANS/HPS-LDH (19.7 Å). The ANS/surfactant-LDH thin films (Figure 1) display only one series of (00*l*) reflections, indicating a highly ordered stacking of the *ab* plane of LDH platelets parallel to the substrate.

The morphology of the thin films revealed by SEM is shown in Figure 2. The thin films of ANS/surfactant-LDH exhibit a smooth, continuous surface in the top view (Figure 2a-e). High-magnification SEM images (Figure $2a_1-e_1$) demonstrate that the individual ANS/surfactant-LDH platelets are densely packed on the substrate with good *c* orientation (*ab* plane of LDH platelets parallel to the substrate), consistent with their XRD results in Figure 1.

3.2. Photoluminescence Properties of the ANS/Surfactant-LDH Thin Films

3.2.1. UV–Vis Absorption and Fluorescence Emission Spectra. The UV–vis absorption spectra of pristine ANS and ANS/ surfactant-LDH composites are shown in Figure 3A. Compared with pristine ANS (curve f, 406 nm), a blue shift of ~15 nm was observed for the ANS/surfactant-LDH samples, indicating that the LDH matrix provides a rigid, constrained environment for ANS, resulting in an ordered, dense packing of ANS molecules and an intramolecular charge-transfer character of the π - π transition.¹⁴

Figure 3B displays the fluorescence emission spectra for pristine ANS and the ANS/surfactant-LDH thin films, and the corresponding fluorescence photographs are illustrated in Figure S2. Compared with pristine ANS (curve f), the maximum emission of ANS/PES-LDH, ANS/HES-LDH, and ANS/HPS-LDH (curves a-c, respectively) moves to low wavelength gradually (blue shift) from 490 to 464 nm, indicating that the dilution effect of surfactant facilitates the dispersion of ANS and thus suppresses its aggregation. The fluorescence efficiency¹⁵ increases at first to a maximum and then decreases as the surfactant length increases (shown in the inset of Figure 3B). ANS/HPS-LDH (curve c) exhibits the maximum fluorescence efficiency among the ANS/surfactant-LDH composites, which is much higher than that of pristine ANS (Table 1). The changes in the fluorescence spectra of these samples were further demonstrated by their photographs with irradiation by UV light (Figure S2), from which ANS/HPS-LDH shows the strongest brightness in blue among these composites, in accordance with the results of the fluorescence spectra (Figure 3B). This indicates that the cointercalation of HPS is effective at inhibiting the aggregation of interlayer ANS, which can be explained by the "size-matching" rule between ANS and HPS (Scheme 1, calculated by Gaussian 03; ANS, 1.13 nm; HPS, 1.10 nm.). A shorter-chain surfactant (PES, HES) cannot effectively prevent the aggregation of ANS molecules, whereas longer chains (DES, DDS) possess strong



Figure 2. SEM images for the film samples: (a) ANS/PES-LDH, (b) ANS/HES-LDH, (c) ANS/HPS-LDH, (d) ANS/DES-LDH, and (e) ANS/DDS-LDH. (a-e) Low magnification; (a_1-e_1) high magnification.



Figure 3. (A) UV-vis absorption spectra and (B) fluorescence spectra of samples: (a) ANS/PES-LDH, (b) ANS/HES-LDH, (c) ANS/HPS-LDH, (d) ANS/DES-LDH, (e) ANS/DDS-LDH, and (f) pristine ANS. The inset plot in B shows the fluorescence efficiency varying with the surfactant length.

Table 1.	Double-Exponential Fitting of the Fluorescence	e
Decay D	ita of ANS and ANS/Surfactant-LDH Composit	es

samples	$ au_i (\mathrm{ns})^a$	A_i (%)	$\langle \tau \rangle$ (ns)	$\chi^{2 b}$	$\log(I_{\rm flu}/A_{\rm exc})^c$
ANS/PES-LDH	6.67	62.59	4.80	1.030	6.07
	1.68	37.41			
ANS/HES-LDH	1.68	43.79	4.87	1.156	6.16
	7.37	56.21			
ANS/HPS-LDH	11.17	77.91	8.91	1.117	6.20
	0.92	22.09			
ANS/DES-LDH	7.83	62.31	5.70	1.000	5.52
	2.17	37.69			
ANS/SDS-LDH	0.23	83.51	1.41	1.017	5.26
	7.41	16.49			
ANS powder	6.00	54.13	3.82	1.024	4.89
	1.24	45.87			
ANS ethanol solution	8.30	93.85	7.96	1.134	5.03
	2.88	6.15			

^{*a*} τ_i (*i* = 1, 2) is the fitted fluorescence lifetime. A_i is the percentage of τ_i . In the biexponential case, $\langle \tau \rangle = A_1 \tau_1 + A_2 \tau_2$; $A_1 + A_2 = 1$. ^{*b*} The goodness of fit is indicated by the value of χ^2 . ^{*c*} $I_{\text{flu}}/A_{\text{exc}}$ is the ratio of fluorescence intensity (determined from the integral of the peak) vs absorbance at the excitation wavelength.

flexibility that reduces the confinement effect imposed by the LDH matrix. Both of them lead to a decrease in the fluorescence intensity.

3.2.2. Fluorescence Lifetime. To understand further the influence of surfactant polarity on the photoluminescence properties of dye, pristine ANS and ANS/surfactants-LDH thin film samples were studied by detecting their fluorescence decays, with an excitation wavelength of 370 nm. The fluorescence lifetimes were obtained by fitting the decay profiles with a double-exponential form, and the results are listed in Table 1. The multiexponential decay curves were usually observed in solid samples and can be attributed to a very heterogeneous environment for the molecules on the solid surface.^{16,17} Owing to the difficulty in providing an appropriate interpretation of the multiexponential decay curves, an intensity-average lifetime was used in this work. The results show that the intensity-average lifetime of ANS/surfactant-LDH increases significantly from PES to HPS whereas it decreases for DES and DDS. As a result, the longest lifetime obtained by double-exponential fitting is presented for



Figure 4. Powder XRD patterns for films (a) ZnAl-LDH and ANS/ HPS-LDH(*x*%) (b, 10; c, 15; d, 20; e, 25; f, 30; g, 50; h, 75; and i, 100%).

the ANS/HPS-LDH sample as a result of the "size-matching" rule between ANS and surfactant mentioned above.

3.3. Structure and Chemical Composition of ANS(x%)/ HPS-LDH Films. Because HPS shows the best matching with ANS anions and the ANS/HPS-LDH thin film displays the optimum fluorescence properties, we subsequently further studied the influence of the relative content of ANS on the luminous behavior of composites. Figure 4 shows the XRD patterns of ANS and HPS cointercalated LDH samples ANS(x%)/HPS-LDH, in which x% stands for the nominal molar percentage of ANS accounting for the summation of ANS and HPS. In each case, the XRD pattern exhibits the characteristic reflections of the LDH layered structure with a series of (00l) peaks appearing as narrow, strong lines at low angles. The absence of any nonbasal reflections $(h, k \neq 0)$ indicates the extremely well *c*-oriented assembly of LDH platelets. It can be observed that the interlayer spacing of ANS(x%)/HPS-LDH increases gradually from 19.6 Å (x% = 10) to 20.1 Å (x% = 100, Table S2 in Supporting Information) with the increase in x%. The expansion of interlayer spacing is attributed to the increase in the content of ANS with a slightly larger size in comparison with that of HPS.

3.4. Fluorescence Properties of ANS(x%)/Surfactant-LDH Thin Films. 3.4.1. Fluorescence Emission Spectra. The fluorescence emission spectra for ANS(x%)/HPS-LDH with different molar ratios of ANS to HPS are shown in Figure 5. The fluorescence efficiency increases at first to a maximum (x = 20%) with the



Figure 5. (A) Fluorescence spectra of the ANS/HPS-LDH (x %) films: (a) x = 10, (b) 15, (c) 20, (d) 25, (e) 30, (f) 50, (g), 75, and (h) 100%. (B) Fluorescence efficiency (a) and the maximum emission wavelength (b) varying with the content of ANS (x%).

Table 2. Double-Exponential Fitting of the Fluorescence Decay Data of the ANS(x%)/HPS-LDH Composites

samples	$ au_i (\mathrm{ns})^a$	A_i (%)	$\left< \tau \right> (\mathrm{ns})$	$\chi^{2 b}$	$\log(I_{\rm flu}/A_{\rm exc})^c$
ANS(10%)/HPS-LDH	2.62	22.31	9.44	0.961	5.88
	11.44	77.69			
ANS(15%)/HPS-LDH	1.94	20.10	11.25	1.083	5.98
	13.59	79.90			
ANS(20%)/HPS-LDH	3.29	19.57	11.76	0.987	6.02
	13.82	80.43			
ANS(25%)/HPS-LDH	3.04	22.10	10.29	1.034	5.99
	12.35	77.90			
ANS(30%)/HPS-LDH	2.50	22.39	8.83	0.883	5.97
	10.65	77.61			
ANS(50%)/HPS-LDH	2.30	38.13	6.13	1.124	5.96
	8.46	61.87			
ANS(75%)/HPS-LDH	1.25	39.11	4.06	1.002	5.28
	5.87	60.89			
ANS-LDH	1.49	43.61	3.69	1.192	5.13
	5.40	56.39			

^{*a*} τ_i (*i* = 1, 2) is the fitted fluorescence lifetime. A_i is the percentage of τ_i . In the biexponential case, $\langle \tau \rangle = A_1 \tau_1 + A_2 \tau_2$; $A_1 + A_2 = 1$. ^{*b*} The goodness of fit is indicated by the value of χ^2 . ^{*c*} $I_{\text{flu}}/A_{\text{exc}}$ is the ratio of fluorescence intensity (determined from the integral of the peak) vs absorbance at the excitation wavelength.

emission peak appearing at 464 nm and then decreases with further increases in x (Figure 5B, curve a). A red shift of the maximum emission wavelength from 464 to 490 nm was observed along with the increase in ANS content (Figure 5B, curve b). The changes in the fluorescence of ANS(x%)/HPS-LDH were further demonstrated by their photographs with irradiation by UV light (Figure S3), from which ANS(20%)/ HPS-LDH shows the strongest brightness in blue among the composites, in accordance with the results of the fluorescence spectra (Figure 5A). This behavior can be attributed to the change in the microenvironment of the interlayer ANS chromophore. The dye exhibits a single molecular luminescence with a low ANS concentration accounting for the increase in the luminous intensity first; aggregates of dye are formed when the content of ANS increases to a certain value, resulting in the red shifts in the emission spectra and the fluorescence quenching.



Figure 6. Fluorescence average lifetime of ANS(x%)/HPS-LDH composites as a function of x%. The horizontal line represents the average lifetime of pristine ANS.

3.4.2. Fluorescence Lifetime. To gain in-depth insight into the solid-state photophysical properties, the ANS(x%)/HPS-LDHcomposites were studied by detecting their luminescence lifetime with excitation at 370 nm. The average lifetimes of the ANS (x%)/HPS-LDH samples with x = 10-100% were obtained by fitting the decay profiles with a double-exponential form, and the results are tabulated in Table 2. Fluorescence decay curves and residual plots of the ANS(x%)/HPS-LDH film samples are displayed in Figure S4, and the fluorescence average lifetime is shown in Figure 6. Compared with the ANS powder sample (3.82 ns, Table 1), the average lifetime of ANS(x%)/HPS-LDHexhibits a remarkable increase, indicating that the cointercalation of surfactant enhanced the stability of the excited state of ANS anions. It was reported that two lifetime values can be attributed to the monomers and dimers or higher aggregates, respectively.¹⁸ In this work, the long lifetime (listed in Table 2) may correspond to the monomer state of ANS in ANS(x%)/HPS-LDH and the short one is due to its aggregates. It was found that the percentage of long-lifetime species (monomers) increases significantly as x%increases from 10 to 20 but decrease with further increases in x%. Similarly, the pre-exponential factor associated with the short decay component increases with the increase in x% whereas the short lifetime decreases in absolute value (from ~ 2.6 to ~ 1.5 ns), indicative of a high level of quenching (promoted by aggregation). The increase in the pre-exponential factor mirrors the contribution



Figure 7. Photoemission profiles in (a) HH, (b) HV, (c) VH, and (d) VV. (e) Anisotropy for (A) ANS-LDH and ANS(x%)/HPS-LDH thin film samples: (B) x = 10, (C) x = 20, and (D) x = 50%. The excitation wavelength is 370 nm.



Figure 8. (A) Photostability of the ANS(20%)/HPS-LDH thin film and pristine ANS as a function of irradiation time with UV light. (B) Thermal stability of the ANS(20%)/HPS-LDH thin film and pristine ANS as a function of the heat-treatment temperature.

from this species of ANS. The results above confirm that dye aggregates are formed when the content of ANS increases to a certain value (x = 20%), and the degree of aggregation is enhanced with further increases in x%.

3.5. Steady-State Fluorescence Polarization of the ANS (x%)/HPS-LDH Thin Films. One of the most common methods of evaluating fluorescence polarization is the measurement of the anisotropic value r, which was fully described by Valeur.¹⁹ r can be expressed by the following equation

$$r = \frac{I_{\rm P} - I_{\perp}}{I_{\rm P} + 2I_{\perp}} \text{ or } r = \frac{I_{\rm VV} - GI_{\rm VH}}{I_{\rm VV} + 2GI_{\rm VH}}$$
(1)

where I_{\parallel} and I_{\perp} are the photoluminescence intensity measured in the planes parallel and perpendicular to the excitation radiation,

respectively ($G \equiv I_{\rm HV}/I_{\rm HH}$); $I_{\rm VH}$ is the photoluminescence intensity obtained with vertical excitation polarization and horizontal detection polarization; and $I_{\rm VV}$, $I_{\rm HV}$, and $I_{\rm HH}$ are defined in a similar way. Theoretically, the value of r is in the range from -0.2(perpendicular absorption and emission transition dipoles) to 0.4 (two parallel transition dipoles, where deviation from this value indicates a reorientation of the emission dipole moment).

The polarized photoemission spectra of ANS-LDH and ANS-(*x*%)/HPS-LDH thin films are displayed in Figure 7. It was found that the anisotropic value of the ANS-LDH thin film (Figure 7A) is 0.0 ± 0.01 , whereas the anisotropic value of the ANS(*x*%)/HPS-LDH thin films increases from x = 10% ($r = 0.12 \pm 0.01$, Figure 7B) to a maximum of x = 20% ($r = 0.15 \pm 0.01$, Figure 7C) and then decreases as x = 50% ($r = 0.10 \pm 0.01$, Figure 7D). The maximum anisotropic value is present in the sample with x = 20%, confirming that ANS possesses a preferential orientation in the LDH gallery with the coexistence of HPS.

3.6. Photo- and Thermal Stability of the ANS(20%)/HPS-LDH Thin Film. The photo- and thermal stability of a dye is of major importance because it leads to the irreversible loss of fluorescence, which limits the statistical accuracy of the detection in biological, environmental, and physiological applications.²⁰ To study the photo- and thermal stability, the fluorescence intensity of pristine ANS and the ANS(20%)/HPS-LDH thin film were recorded by the correlation between fluorescence intensity and ultraviolet/heat treatment. Figure 8A displays the fluorescence intensity of the samples as a function of bleaching time. The halflife (12.8 min) of the ANS(20%)/HPS-LDH thin film is higher than that of pristine ANS (6.9 min), indicating that the photostability of ANS was enhanced after intercalation into LDH. Figure 8B shows the variation in fluorescence intensity for the two samples along with the heat treatment temperature, from which a much slower decrease in the fluorescence intensity of ANS(20%)/HPS-LDH was observed compared with that of pristine ANS. This indicates that the thermal stability of ANS was enhanced upon intercalation into the LDH matrix, in agreement with the results of TG-DTA (Figure S5). The storage stability test of the ANS(20%)/HPS-LDH film shows that \sim 96.7% of its initial fluorescence intensity remains after 4 months (Figure S6). The enhancement of the photo-, thermal, and storage stability demonstrates that the ANS molecule is protected by both the LDH matrix and the coexisting surfactant. First, the LDH matrix offers a confined, stable microenvironment for ANS molecules, enhancing its thermal stability.²¹ Second, the surfactant molecules uniformly distribute ANS in the LDH gallery and thus reduce the fluorescence quenching effectively. Therefore, the synergistic effect of the LDH matrix and the surfactant plays an important role in obtaining luminous materials with excellent photo and thermal stability.

4. CONCLUSIONS

The ANS anion and a series of surfactants have been incorporated into a ZnAl-LDH matrix by the ion-exchange method. Thin films of ANS/surfactant-LDH with the ab plane of hexagonal platelets parallel to the substrate as verified by XRD and SEM were obtained by the solvent evaporation method on Si substrates. Both the maximum absorption and fluorescence efficiency follow the order ANS/HPS-LDH > ANS/HES-LDH > ANS/PES-LDH > ANS/DES-LDH > ANS/DDS-LDH. The optimal fluorescence properties were obtained for the sample of ANS/HPS-LDH because of the size-matching rule between the organic dye and surfactant. The photoluminescence properties of ANS and HPS cointercalated ZnAl-LDH with different molar ratios were also investigated. The fluorescence efficiency, emission wavelength, average lifetime, and anisotropy can be finely modulated by simply varying the relative content of ANS/HPS, and the ANS-(20%)/HPS-LDH sample shows the maximum fluorescence efficiency and the longest average lifetime. In addition, the photoand thermal stability of ANS(20%)/HPS-LDH is remarkably enhanced. In summary, this work provides a facile and efficient method to tune the luminescence behavior of inorganic-organic hybrid materials by changing the 2D microenvironment of the inorganic matrix. The modulation of the photoluminescence properties of a chromophore (anisotropy, wavelength, fluorescence efficiency, and lifetime) based upon the synergistic effect of the

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LDH matrix and surfactant creates new opportunities for the preparation and application of these intercalation compounds in the fields of photoluminescence materials, nonlinear optics, and polarized luminescence materials.

ASSOCIATED CONTENT

Supporting Information. FT-IR spectra, photographs, fluorescence decay curves and residual plots, TG-DTA curves, and chemical compositions. This material is available free of charge via the Internet at http://pubs.acs.org.

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