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## ARTICLE

# Characterization of interaction between organic molecules and Co-Al-LAH, using photo-physical techniques

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In this paper, 4-benzoylbenzoic acid (4-BBA) and 2-naphthalenesulfonic acid (2-NSA) were intercalated or co-intercalated into the layered double hydroxide (LDH), $[Co_{0.66} Al_{0.34} (OH)_2]$ $(CO_3)_{0.17}$ $0.49H_2O$ by the method of ion-exchange procedures. The powder X-ray diffraction, Fourier transform infrared spectroscopy, TG-DTA，X-ray photoelectron spectroscopy and photoluminescence spectra were used to characterize the structural and photophysical properties of the obtained compounds. It was found that $Co^{2+}$ ion in the layers was coordinated with the guest molecule 2-NSA among the interlayer region, resulting in the intercalation compound Co-Al-2-NSA-LDH enhancing the blue emission of 2-NSA at 460nm. The geometry and electronic structure of the guest molecules and their singlet vertical excitation energies and oscillator strengths were investigated at B3LYP/6-31G level by density functional theory (DFT) and time dependent DFT calculations using G03w. Fluorescence polarization method was applied to test the preferential orientation of the interlayer 4-BBA and 2-NSA molecules. It indicated that spatial distribution of the guest molecules in the layer was rather ordered arrangement and believed that 4-BBA and 2-NSA were intercalated or co-intercalated between sheets of Co-Al-LDH as a bilayer interdigitated form. There was a coordinate possibility between Co-Al-LDH and organic chromophores of containing sulfonic group, and intermolecular energy transfer from 2-NSA to 4-BBA in the layers might be happened for the co-intercalation compound. So, this work provides new opportunities to design functional material by the combination of Co-Al-LDH with various types of organic chromophores, which will be very valuable.

## 1. Introduction

Composites of organic chromophores and inorganic matrices offer a number of synergistic effect.[1] Layered double hydroxides (LDHs) or hydrotalcite, as anionic clays, are an important class of host-guest materials and receive considerable attention because of their structural anisotropy, and can be easily functionalized by intercalating some species with specific properties.[1-9] The empirical formula of LDH is generally expressed as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n}$ $mH_2O]$, where $M^{II}$ and $M^{III}$ are di- and tri-valent metal cations, respectively, occupying octahedral positions in hydroxide layers. $A^{n-}$ is the exchangeable anion between the brucite-like layers to compensate the positive charge.[2] Therefore, functional species with anionic groups can be intercalated into this class of layered hosts *via* anion exchange processes.[2, 3] These considerations have induced many research groups to use LDH for the intercalation of species with magnetic,[6] photochemical and optical properties[3-12] in order to immobilize them on a solid support or modulate their properties by confining them in a constrained medium. The intercalation of azoic and xanthenic dyes in LDHs have been recently reported by Costantino et al.[5, 10, 11] and our group.[12] It has been confirmed that the incorporation of dyes in the LDH gallery improves the

photophysical properties of dyes compared with those of their solutions and pure solids. However, it could be noted that most of studies on organic chromophores into LDH focus on the Mg-Al-LDH or Zn-Al-LDH modified by traditional method, like anion exchange method. Few researches contribute to the organic chromophores into other kind of LDH. Transition metal-bearing Co-Al-LDH is known to have broader technological applications due to their special catalytic,[13] electronic, optical, and magnetic properties.[14] Hou et al.[15] have recently reported that there was the existence of photoluminescence phenomenon of pure Co-Al-LDH. However, few the photophysical properties of the solid-state organic chromophores intercalated Co-Al-LDH system are reported and how to combine the layered double hydroxides with photoluminescence property of guest to fabricate a novel, fluorescent, hydrotalcite-like compound might be a challenge.

In this work, the intercalation or co-intercalation of 4-benzoylbenzoic (4-BBA⁻) and 2-naphthalenesulfonic (2-NSA⁻) anions with donor-acceptor properties into Co-Al-LDH are described. The investigation aims to achieve information on the photophysical of 4-benzoylbenzoic acid and 2-naphthalenesulfonic acid guests on the Co-Al-LDH crystals and, in particular, to study the influences of host-guest and guest-guest interactions on the orientation of interlayer chromophore

guest, the fluorescence properties of those guests in the inorganic constrained microenviroment, and how to combine the host with the guest photoluminescence properties to fabricate a novel, fluorescent, hydrotalcite-like compound. It was well known that fluorescence resonance energy transfer (FRET) is a non radiative process whereby an excited state donor (D, usually a fluorophore) transfers energy to a proximal ground state acceptor (A) through long-rang dipole-dipole interactions. [16] The energy transfer rate is generally related to the extent of the spectral overlap, the relative orientation of transition dipoles, and the distance between the donor and acceptor molecules. [16] This work provides a helpful methodology to the fabrication of optical materials with Co-Al-LDH and the chromophore anions bring a beneficial pathway to further develop such electronic and optical materials.

## 2. Experimental section

### 2.1 Materials.

4-benzoylbenzoic acid （ $C_{14}H_{10}O_3$,>99% ） and 2-naphthalene-sulfonic acid（$C_{10}H_8SO_3$, >98%）were purchased from Alfa Aesar Chemical Co. Ltd. NaOH (AR), $Na_2CO_3$ (AR), $CoSO_4 \cdot 7H_2O$ (AR), $Al_2(SO_4)_3 \cdot 18H_2O$(AR) and ethylene glycol(AR) were purchased from Beijing Chemical Co. Ltd and used without further purification. All the aqueous solution was prepared with de-ionized and $CO_2$-free water.

### 2.2 Preparation of the intercalation compounds

The layered host, used for the chromophore uptake is Co-Al-LDH in carbonate form with a Co/Al molar ratio of 2.0. The Co-Al-LDH was synthesized by the co-precipitation method reported previously.[17] Elemental analysis indicated the LDH composition was [$Co_{0.66}$ Al $_{0.34}$ (OH) $_2$] ($CO_3$) $_{0.17}$ 0.49$H_2O$. 0.68 g Co-Al-$CO_3$-LDH was dispersed in 50 mL of ethylene glycol dissolving 0.93 g 4-BBA at 70 ℃ for 7 h. The solid was filtered, washed with de-ionized water and dried at 60 ℃ for 24 h to obtain Co-Al-4-BBA-LDH. The same procedure was employed to obtain Co-Al-2-NSA-LDH using 0.83 g 2-NSA.

A co-intercalation compound was prepared by suspending 0.68 g Co-Al-$CO_3$-LDH in 50 mL of ethylene glycol dissolving 0.46 g 4-BBA and 0.42 g 2-NSA (4-BBA /2-NSA molar ratio 1:1). The suspension was stirred for 7 h at 70 ℃. Then the solid was filtered, washed with de-ionized water and dried at 60 ℃ for 24 h.

### 2.3 Measurements

The powder X-ray diffraction (XRD) measurement was performed on a Rigaku D/Max-3B powder X-ray diffractometer （30 kV, 20 mA）, using Cu Kα radiation, and a scanning rate of 5 °min⁻¹, a 2θ angle ranging from 3 ° to 70 °. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Bruker VECTDR22 spectrophotometer using a KBr pellet technique in the range 400-4000 cm⁻¹. TG-DTA was performed at a rate of 10 ℃ /min under air atmosphere using an SPSIC ZRY-1P thermal analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a V.G. Scientific ESCALAB Mark II system high vacuum electron spectrometer with residual gas pressure better than $2 \times 10^{-8}$ Pa and Al Kα (E = l486.6 eV) as X-ray source. The binding energies (BE) were referenced to the C1s peak at 284.6 eV. The experimental curve was fitted with a program that made use of a combination of Gaussian–Lorentzian lines. The solid state UV-VIS absorption spectra were measured in the range from 200 to 500 nm using a

Hitachi U-3010/3310 spectrophotometer equipped with an integration sphere for reflectance spectrum recording. The width of the slit is 1.0 nm, and $BaSO_4$ was used as reference. The solid state fluorescence spectra of powders and steady-state polarized photoluminescence measurements were recorded on an Edinburgh Instruments' FLS 920 fluorospectrophotometer, equipped with automated polarizers in both the excitation and emission beams, under identical conditions with excitation wavelength of 310 nm and emission spectra in the range 330-800 nm. The width of the excitation and emission slit is 3 and 5 nm, respectively. The organic guest contents of the obtained compounds were obtained by the standard curves of UV-Vis absorption spectra (see ESI Fig.S1-S4） by dissolving a weighed amount of the compounds in a concentrated HCl and diluting with de-ionized water to 50 mL.

### 2.4 Theoretical calculations

Density Functional Theory （ DFT ） [18-20] calculations were performed using Gaussian 03 program package. [21] The B3LYP has been widely used and proved to be accurate. [22] The guest molecular geometries have been fully optimized at the B3LYP/6-31G theoretical level. [23] Further time dependent density functional theory (TDDFT) calculations have been performed at the same level to obtain singlet vertical excitation energies and oscillator strengths on the ground state optimized geometries. [24]

## 3. Results and discussion

### 3.1 Structural characterization of compounds

XRD patterns of Co-Al-$CO_3$-LDH, Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH and Co-Al-4-BBA-2-NSA-LDH are shown in Fig.1. FTIR spectra of Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH, Co-Al-4-BBA-2-NSA-LDH, 4-BBA and 2-NSA are shown in Fig.2.

The X-ray diffraction pattern of the Co-Al-$CO_3$-LDH ( Fig. 1, curve a) exhibits the characteristic pattern of the LDH layered structure with a series of 00l peaks, such as (003), (006)，and (009) with sharp, symmetrical lines at low angle, and some asymmetrical peaks at high angle due to diffraction by planes (015) and （018）.[7] In addition, a doublet close to 60°(2θ), where the maximum at 0.154 nm corresponds to diffraction by plane (110) was observed.[25, 26] The absorption peak at 1363 cm⁻¹ (see ESI Fig. S5) is the vibration of $CO_3^{2-}$, which indicates the existence of $CO_3^{2-}$ between the layers. The (003) reflection of Co-Al-$CO_3$-LDH at 2θ = 11.67° (Fig. 1, curve a) shows an interlayer distance [25-28] of 0.763 nm, typical of a LDH containing carbonate as the interlayer anion ， which is consistent with the result reported previously. [29]

It is well known that carbonate anions are strongly held in the interlayer region and it is difficult to replace them with other counter anions by ion-exchange reaction. [3] However, it is found that the reaction of Co-Al-$CO_3$-LDH with 4-BBA or 2-NSA in ethylene glycol at 70 ℃ can easily obtain the intercalation compounds Co-Al-4-BBA-LDH or Co-Al-2-NSA-LDH, and the co-intercalation compound Co-Al-4-BBA-2-NSA-LDH, which might be related to the delamination of Co-Al-$CO_3$-LDH in ethylene glycol. [29] It can be seen from Fig.1, curve b, c, and d that the XRD patterns still exhibit the characteristic pattern of the LDH layered structure with a series of 00l peaks. The diffraction peaks corresponding to the basal spacing of the obtained compounds (Fig.1, curve b, c, and d) were shifted toward the lower 2θ side compared with those of the parent Co-Al-$CO_3$-LDH (Fig.1, curve a). The increase of the interlayer distance in the (003) reflection was estimated to be approximately 1.904, 1.800, 1.820 nm (Fig.1, curve b, c, and d), respectively, indicating that these two anions have been intercalated into the

interlayer space of Co-Al-CO$_3$-LDH, and corresponding to the formation of Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH, and the co-intercalation compound Co-Al-4-BBA-2-NSA-LDH.[2,3,25,26] Since XRD analysis of the intercalated LDH did not exhibit any reflections ascribable to the pure 4-BBA and 2-NSA (see ESI Fig.S6 and S7), it might be that the crystalline domains were very small or the compounds were intercalated in an amorphous phase .[25, 26]
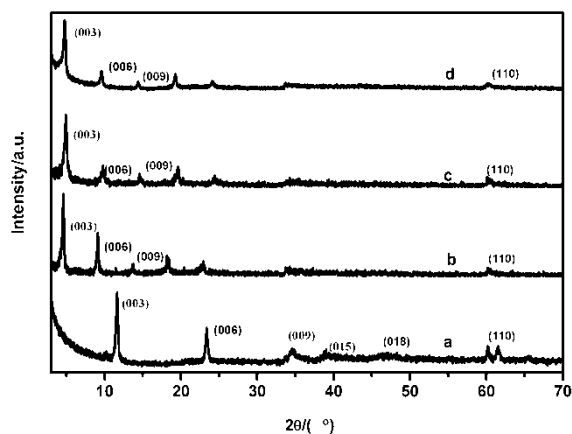


Fig. 1 XRD patterns of (a) Co-Al-CO$_3$-LDH, (b)Co-Al-4-BBA-LDH, (c) Co-Al-2-NSA-LDH, (d) Co-Al-4-BBA-2-NSA-LDH
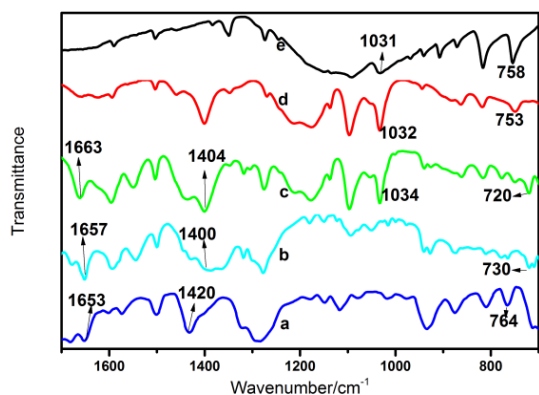


Fig. 2 FTIR spectra of (a) 4-BBA, (b) Co-Al-4-BBA-LDH,(c) Co-Al-4-BBA-2-NSA-LDH (d) 2-NSA, (e) Co-Al-2-NSA-LDH

The effective intercalation of anions can also be confirmed by FTIR spectrum as shown in Fig. 2 curve b, c, e. The characteristic bands of organic chromophores anions, i.e. sulfonic group bending frequency in 1040-1030 cm$^{-1}$, carboxylate group the asymmetric stretching vibration in 1670-1550 cm$^{-1}$ and the symmetric stretching vibration in 1415-1391 cm$^{-1}$, were clearly observed. At the same time, the phenyl group vibration in 700-880 cm$^{-1}$ was also seen. In addition, the peak characteristic of CO$_3^{2-}$ at about 1360 cm$^{-1}$ in Fig. 2 curve b, c, e is almost absent, indicating that the ion-exchange process might be complete.

FTIR spectra have been extensively used to probe host-guest interaction or guest-guest interaction such as π-π interaction existence from the vibration bands change.[5, 30] It was found that the wave number of the sulfonic group and phenyl group vibration in

Co-Al-2-NSA-LDH was almost similar to the pure 2-NAS (from 1032 to 1031 cm$^{-1}$, and 753 to 758 cm$^{-1}$), indicating that host-guest or guest-guest interactions were weak. However, phenyl group and carboxylate group were shifted to lower wave numbers (from about 764 to 730 cm$^{-1}$,1420 to 1400 cm$^{-1}$ ) in the Co-Al-4-BBA-LDH than in pure 4-BBA, which might provide the evidence that after 4-BBA anions are intercalated into the layers, there is π-π interaction between guest-guest,[5] and the electrostatic interactions with the positively-charged layers of host, or the hydrogen bonding interactions between COO$^-$ and OH planes of host.[5, 30] In addition, for the co-intercalation compound Co-Al-4-BBA-2-NSA-LDH, it showed that there was a possibility of π-π interaction between 4-BBA and 2-NSA[5] due to phenyl group wave numbers from about 750 to 720 cm$^{-1}$.

The TG-DTA curves of Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH, and co-intercalation compound are shown in Fig. S8, S9, S10. All TG-DTA curves in Fig.S8, S9, S10 exhibit three stages of weight loss corresponding to one endothermal peak and two or three exothermal peaks. The first stage corresponding to the endothermal peaks in the temperature region from room temperature to 200 ℃ were attributed to the removal of interlayer water molecules and adsorbed water molecules.[2,3,15] The weight loss amount is the water content of the solid products. The second and third large stages corresponding to two or three exothermal peaks, over 200 ℃, are due to the decomposition and oxidation of the absorbed (former) and intercalated (later) anions that overlaps with the dehydroxylation of the LDH basal layer.[31] Obviously, the exothermal peak temperatures of the co-intercalation compound in Fig.S10 are much higher than those of Co-Al-4-BBA-LDH and Co-Al-2-NSA-LDH in Fig.S8, S9, indicating increment in the stability of co-intercalation compound. It should be closely related to not only the electrostatic interactions between the host and the two guests, but also the two guests interactions each other, which supports the above FTIR spectrum analysis results. In addition, the DTA curves of co-intercalation compound present three exothermal peaks, which correspond to decompositions and oxidation of the absorbed and intercalated 4-BBA and 2-NSA anions. The organic guest contents of the obtained compounds were obtained by the standard curves of UV-Vis absorption spectra（see ESI Fig.S1-S4）by dissolving a weighed amount of the compounds in a concentrated HCl and diluting with de-ionized water to 50 mL. The analysis results show that the amount of 4-BBA, 2-NSA intercalated into Co-Al-CO$_3$-LDH is 0.395mg 4-BBA/mg Co-Al-4-BBA-LDH, 0.396 mg 2-NSA /mg Co-Al-2-NSA-LDH, respectively, and 4-BBA-2-NSA co-intercalated into Co-Al-CO$_3$-LDH is 0.422 mg 4-BBA and 2-NSA/mg Co-Al-4-BBA-2-NSA-LDH. Although there is the possibility of the co-existence of partially intercalated and surface adsorbed Co-Al-LDH, it is difficult to be evaluated the two amounts of absorbed and intercalated clearly.

In order to support the above FTIR and the TG-DTA results, we have performed X-ray photoelectron spectroscopy (XPS) measurements. The whole scanning spectra of 4-BBA, 2-NSA , Co-Al-CO$_3$-LDH, Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH and Co-Al-4-BBA-2-NSA-LDH surfaces are shown in Fig.S11, and the peaks correspond to the electronic states of Co2p, O1s and Cls, respectively. Fig.3, 4, 5 show the fine spectra of Co2p and O1s, respectively. It was found that the Co2p peak intensity in Co-Al-4-BBA-LDH, Co-Al-2-NSA-LDH and Co-Al-4-BBA-2-NSA-LDH (Fig.3, curve a, b, c) became lower than that of in Co-Al-CO$_3$-LDH (Fig.3, curve d). In Fig3, compared with Co-Al-CO$_3$-LDH (781.4 eV), the average binding energy of Co atoms in the Co-Al-4-BBA-LDH (781.55 eV), Co-Al-2-NSA-LDH (781.60 eV), and Co-Al-4-BBA-2-NSA-LDH (781.65 eV) increases 0.15 eV, 0.2 eV, and 0.25 eV, respectively. However, the O1s peak intensity of the intercalation

and co-intercalation compounds (Fig.4, curve b, c, and Fig.5,curve b, c) became higher than that of in 4-BBA (Fig.4, curve a) or 2-NSA(Fig.5, curve a), respectively. Compared with Fig.4, curve a (531.95 eV), the binding energy of O atoms of carboxyl group in Fig.4, curve b (532.15 eV) increases about 0.2 eV, and Fig.4, curve c (532.1 eV) increases 0.15 eV. On the contrary, the binding energy of O atoms of sulfonic group in both Fig. 5, curve b（532.1 eV）and Fig. 5, curve c (532.1 eV) decreases about 0.4 eV, when compared with Fig. 5, curve a (532.5 eV). These variations imply that the ambient environment around the atoms has changed; this may affect the shield effect of the electron cloud [32, 33]. It indicates that after 4-BBA anions are intercalated into the layers, there was no interaction between Co2p and O1s, since Co2p increases $\Delta E_b$=0.15 eV, O1s also increases $\Delta E_b$=0.2 eV in Co-Al-4-BBA-LDH, which implies that guest-guest interaction may exist. Guest-guest interaction can make electrons around the O atoms of carboxyl group in Co-Al-4-BBA-LDH transferred to the phenyl group due to co-plane between the carboxyl group and benzene ring (see the following section 3.3), which causes the binding energy increases. However, in Co-Al-2-NSA-LDH, Co2p increases $\Delta E_b$=0.2 eV, O1s decreases $\Delta E_b$=0.4 eV. This phenomenon may be related to the fact that fewer electrons around the O atoms in Co-Al-2-NSA-LDH are transferred to the outer empty orbit of $Co^{2+}$, which leads to a decrease in the charge density of the outer orbit and an increase in the binding energy. In addition, the binding energy change of O atoms of sulfonic group in Co-Al-2-NSA-LDH is similar to that in Co-Al-4-BBA-2-NSA-LDH ($\Delta E_b$=0.4 eV). It was concluded that there is a coordinate bond between the $Co^{2+}$ in the hydroxide basal layer of host and guest 2-NSA in Co-Al-2-NSA-LDH or Co-Al-4-BBA-2-NSA-LDH, and guest-guest interactions exist in Co-Al-4-BBA-LDH or Co-Al-4-BBA-2-NSA-LDH. XPS analysis further supports the above FTIR spectrum analysis and TG-DTA results. Furthermore, it implies that there is a coordinate possibility between Co-Al-LDH and organic chromophores of containing sulfonic group.

### 3.2 Absorption Emission Spectra of compounds

The UV-Vis absorption spectra of 4-BBA (or 2-NSA), Co-Al-4-BBA (or 2-NSA)-LDH, and co-intercalation compound were measured and reported in Fig.6. There is one absorption band in these solid compounds, which is assigned to the π-π* transition. [12, 34] The absorption rang of Co-Al-4-BBA (200-300 nm or 2-NSA 200-330 nm)-LDH is about 30 nm (or 20 nm) blue-shifted when compared to the pure solid 4-BBA (200-330 nm or 2-NSA 200-350 nm), implying that the change was related to the host-guest interaction or guest-guest interaction. The spectrum of the co-intercalation compound was difficult to be interpreted. It seems that the 2-NSA is in much less quantity than 4-BBA in Co-Al-4-BBA-2-NSA-LDH.
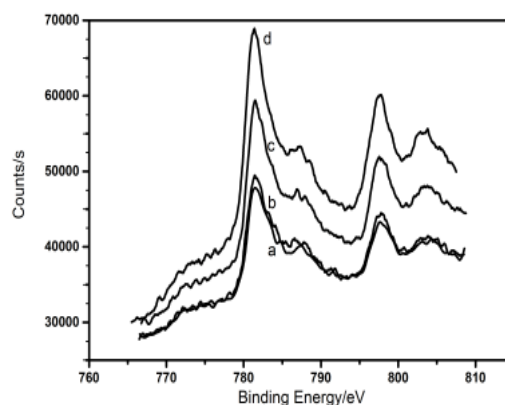


Fig.3 The XPS spectra of Co2p for (a) Co-Al-4-BBA-LDH，(b) Co-Al-2-NSA-LDH，(c) Co-Al-4-BBA-2-NSA-LDH，(d) Co-Al-CO₃-LDH
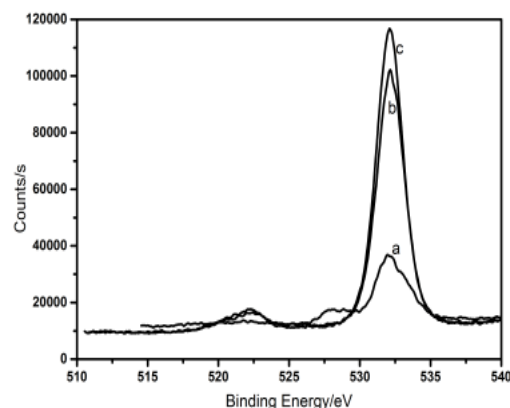


Fig.4 The XPS spectra of O1s of carboxyl group in 4-BBA(a) 4-BBA，(b) Co-Al-4-BBA-LDH，(c) Co-Al-4-BBA-2-NSA-LDH
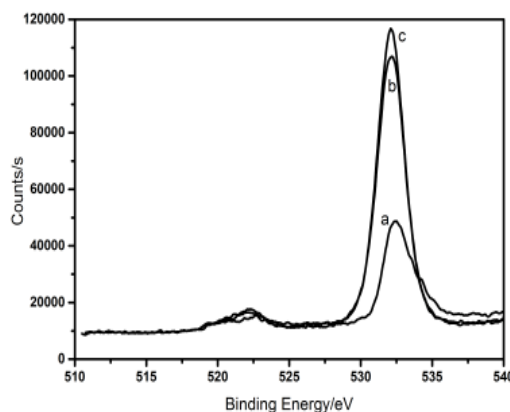


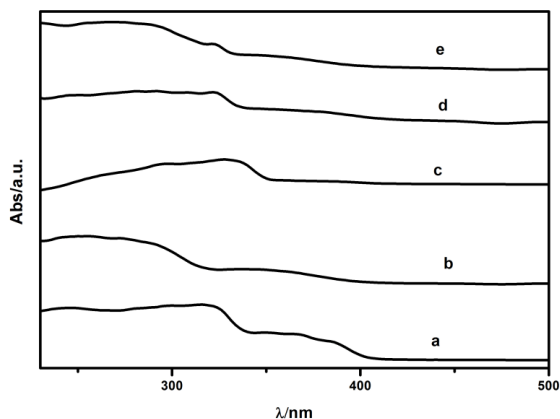Fig.5 The XPS spectra of O1s of sulfonic group in 2-NSA (a) 2-NSA ，(b) Co-Al-2-NSA-LDH ，(c) Co-Al-4-BBA-2-NSA-LDH

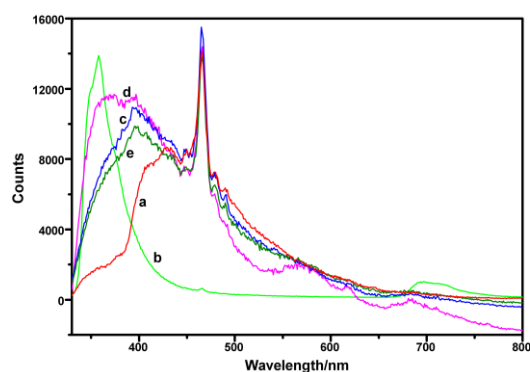Fig. 6 UV spectra of (a) 4-BBA (b) Co-Al-4-BBA-LDH(c) 2-NSA (d) Co-Al-2-NSA-LDH (e) Co-Al-4-BBA-2-NSA-LDH



Fig.7 Emission spectra ($\lambda_{exc}$=310 nm) of (a) 4-BBA (b) 2-NSA (c) Co-Al-4-BBA-LDH (d) Co-Al-2-NSA-LDH (e) Co-Al-4-BBA-2-NSA-LDH

The importance of these interactions is confirmed by the emission spectra measurements on the samples. From the UV spectra of Fig.6, the excitation wavelength of 310 nm was applied to measure the emission spectra of the samples in order to compare with each other. Fig.7 shows the emission spectra ($\lambda_{exc}$=310 nm) of 4-BBA (or 2-NSA), Co-Al-4-BBA (or 2-NSA)-LDH, and co-intercalation compound. It can be seen that except the emission peak at 460 nm due to the 4-BBA, the emission spectra of Co-Al-4-BBA-LDH (Fig.7 curve c) has a structured emission peak centered at 400 nm, also assigned to the 4-BBA, and is about 40 nm blue-shifted compared with the pure 4-BBA (Fig.7 curve a). However, the emission spectra of Co-Al-2-NSA-LDH (Fig.7 curve d) is quite different from the pure 2-NSA (Fig.7 curve b). The emission spectra of the pure 2-NSA has strong emission peak (Fig.7 curve b) at around 360 nm, a very weak peak at about 460 nm, and a broader peak in the range of 670-740 nm. It is interesting to note that after the intercalation of 2-NSA anion into Co-Al-LDH, the first emission peak around 360 nm, assigned to the 2-NSA, becomes broader and is about 50 nm red-shifted (Fig.7 curve d), while the second emission peak intensity around 460 nm becomes much stronger than that of the pure solid 2-NSA (Fig.7 curve b), since the existence of coordination structure of Co-Al-2-NSA-LDH was confirmed by XPS analysis. Moreover, it was reported that Co-Al-LDH appeared the

maximum emission peak at 430 nm after 370 nm excitation,[15] this can result in the intercalation compound Co-Al-2-NSA-LDH enhancing the blue emission at 460 nm. These results were quite different from the result of Mg-Al-2-NSA-LDH reported only having one emission peak centered at 420 nm in the literature[11] due to the different layered chemical composition. Co is a transition metal, it has lots of empty electric orbit, which can cause the interaction between host and guest such as the above mentioned host-guest coordination interactions. In addition, 4-BBA and 2-NSA are a pair of chromophores with donor (2-NSA)-acceptor (4-BBA) properties due to the overlapping of the 2-NSA emission and 4-BBA absorption within 320-400 nm (see ESI Fig.S12). Moreover, both 4-BBA and 2-NSA absorb in the same region within 320-350 nm (see ESI Fig. S12). The emission spectrum of co-intercalation compound (4-BBA/2-NSA molar ratio 1:1) was recorded in Fig.7 curve e on excitation at 310 nm. It was interesting to note that Fig.7 curve e was almost identical to that of Co-Al-4-BBA-LDH (Fig.7 curve c), and the emission peak of 2-NSA was not observed. It seems that a prominent FRET process occurred at the 310 nm intrinsic excitation energy of 4-BBA and 2-NSA, resulted in the predominant fluorescence emission of 4-BBA at 400 nm, being accompanied with a fluorescence quench of 2-NSA at 360 nm, which is in accordance with other reported Mg-Al-LDH system.[11] These findings of co-intercalation compound (Fig.7 curve e) suggest that intermolecular energy transfer from 2-NSA to 4-BBA might be take place between sheets of Co-Al-LDH. The reason should be relate to the host composition, selective photo-excitation, and the different arrangement of the interlayer molecule. In order to understand the relationship between the guest molecular structure and its photophysical property in the host, we have performed DFT calculations on the guest ions at B3LYP/6-31G level by G03w.

### 3.3 Theoretical calculations

The molecular structures of the guest anions were shown in Fig.S13 and a summary of the results of these calculations was given in Table 1. The optimized structure of 4-BBA in Fig.S13 indicated that two benzene rings was not co-plane and about 140° between them. However, the electrons around the O atoms in carboxyl group of Co-Al-4-BBA-LDH could conjugate with the phenyl group due to co-plane of the carboxyl group and benzene ring. On the contrary, the electrons around the O atoms in sulfonic group of Co-Al-2-NSA-LDH could not transfer to the phenyl group because they were not co-plane, which confirmed the above XPS results. As the layer is formed by octahedral units with shared edges each octahedron consists of $M^{II}$ or $M^{III}$ cations is surrounded by six $OH^-$ ions. The presence in the layer of $M^{III}$ cations induces excess positive charge which is balanced by exchangeable anions accommodated in the interlayer region, where water molecules are also located.[2,3,15] The sheet area equals to 3 times the basis of the hexagonal unit cell (i.e., $a^2 \times \sin 60°$, $a$ being 0.308 nm from Fig.1 curve a) contains one Al atom.[10] Consequently, the free area associated with each positive charge on both sides of layer is about 0.25 nm$^2$. The area of $COO^-$ and $SO_3^{2-}$ from the geometry optimized by G03w calculation was about 0.23 nm$^2$ and 0.21 nm$^2$, respectively, basically match each other.

Previously, we reported that both Coulombic and hydrogen bonding interactions existed between the layers and the intercalated anions, and the strength of the hydrogen bonding interaction was connected with the charge distribution of the anion and its orientation in space.[35, 36] It was expected that the principal energy consideration was the electrostatic interaction between the guest with the positively charged metal hydroxide layer. As the measured interlayer distance of Co-Al-4-BBA–LDH, Co-Al-2-NSA-LDH, and Co-Al-4-BBA-2-NSA-LDH was 1.904, 1.800,1.820 nm (Fig.1 curve

b, c, d), respectively and the thickness of the LDH hydroxide basal layer was 0.48 nm,[2] the gallery height was calculated as 1.42, 1.32, 1.34 nm, respectively. The theoretic calculation results showed that the length of 4-BBA and 2-NSA was about 1.11 and 0.83 nm (Fig.S13), respectively. From the XRD measured interlayer distance, the theoretic calculation length of 4-BBA and 2-NSA, and the principle of energy minimum, the proposed orientations of the guest ions between the layers in the intercalation or co-intercalation compounds were illustrated in Fig.8. It was believed that the planes of benzene ring connecting with the carboxyl functional group of 4-BBA were tilted approximately 45 ° to the layers and the planes of naphthalene ring with sulfonic group of 2-NSA were perpendicular to the plane of the host layer, and both of them are arranged as a bilayer of interdigitated species between the metal hydroxide layers (Fig.8). In this arrangement, the guests were easy to interact with each other through π-π interactions between the benzene ring and naphthalene ring so that the pair of chromophores, 4-BBA and 2-NSA, within the restricted space of the interlayer region of the host might give rise to FRET process because of the characteristics of their excited states, which supported the above results of the absorption, emission spectra, FTIR, and XPS analysis. Moreover, it was thought that in this arrangement the carboxyl functional groups of 4-BBA and three oxygen atoms of the sulfonic group of 2-NSA, having largely negative charge (Table 1) could form much stronger hydrogen bonds with the metal hydroxide layers, and were maximized into their electrostatic interactions with the positively-charged layers, which were likely to be the dominant energy term in controlling the guest orientation.

Table 1. Calculated charges, transitional dipoles, excitation energies and the oscillator strength for the anions

| Anions | 4-BBA | 2-NSA |
|---|---|---|
| Calculated oxygen atom charge | -0.509, -0.602 | -0.615, -0.615, -0.608 |
| Transitional dipoles(D) | 3.865 | 4.581 |
| Excited energies(eV, nm) | 3.652, 339 | 4.385, 283 |
| Oscillator strength | 0.207 | 0.349 |

The photophysical property of molecule is generally related to a molecule's polarizability, its π-electron conjugation length and donor/acceptor strength of the fluorophore's substituents.[14,37,38,39] TDDFT was used to calculate the optical properties of the guests. TDDFT also provided the mean to determine the oscillator strength (f), an indicative property for effective sensitizers.[40] The results (Table 1) showed that the wavelengths of maximum absorption were 339 nm and 283 nm for 4-BBA and 2-NSA, respectively, which were basically in the absorption range in Fig.6. The oscillator strengths (or transitional dipoles) in 4-BBA and 2-NSA were 0.207 (3.865 D) and 0.349 (4.582 D), respectively, indicating 2-NSA might be easy to be polarized at their excited states and lead to the enhancement of emission,[40] which supported the above emission spectra. Moreover, the guests arranged as a bilayer of

interdigitated species between the metal hydroxide layers should be beneficial to increase donor/acceptor strength of the pair of chromophores, 4-BBA and 2-NSA within the restricted space of the interlayer region of the host. Fluorescence spectra confirmed the analysis, since the predominant fluorescence emission of 4-BBA at 400 nm, being accompanied with a fluorescence quench of 2-NSA at 360 nm (Fig. 7 curve e).
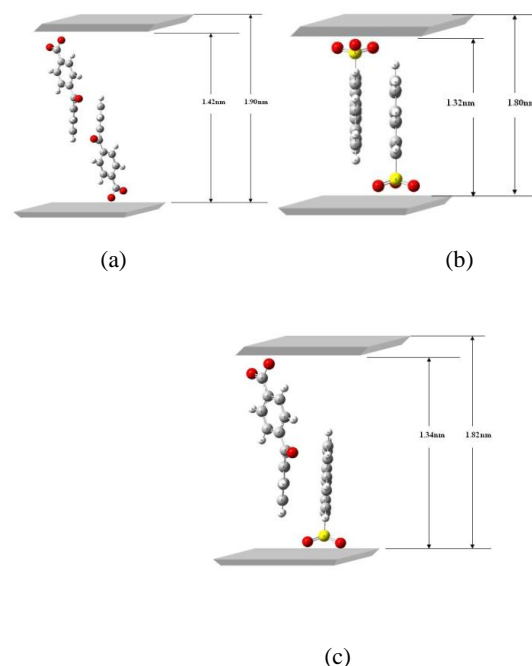


(a)

(b)

(c)

Fig. 8 Schematic illustration of the two anions into the interlayer of Co-Al-LDH (a) Co-Al-4-BBA-LDH (b) Co-Al-2-NSA-LDH (c) Co-Al-4-BBA-2-NSA-LDH

### 3.4 Orientation for guests in LDH matrix by polarized fluorescence

In order to have more information on the properties of microenviroment of the guests and hence on the characteristics of the supramolecular state of the three samples, respectively, fluorescence polarized spectra were recorded (see ESI Fig.S14-S18). Anisotropy value $r$ can be expressed as the formula: $r = (I_{VV}-GI_{VH})/(I_{VV}+2GI_{VH})$ where $G=I_{HV}/I_{HH}$, $I_{HV}$ stands for the photoluminescence intensity obtained with horizontally polarized light excitation and vertical polarization detection, and $I_{VV}$, $I_{HH}$, $I_{HV}$ are defined in a similar way.[38,39] Theoretically the $r$ value is in the range from -0.2 (absorption and emission transition dipoles are perpendicular) to 0.4 (two transition dipoles are parallel).[41,42] Fig.9 reported the anisotropy traces for the energy emission band (see ESI Fig.S19-S23). Pure 4-BBA (Fig.9 curve a) showed the higher anisotropy values for the 330-400 nm and 650-800 nm energy emission than that of 2-NSA (Fig.9 curve b). This is because the pure solid phase is the most ordered, the constrained microenviroment,[43] and the 4-BBA molecule length and space hindrance are larger than that of 2-NSA molecule, resulting in the large size 4-BBA molecules do not have appreciable rotational diffusion freedom. However, when intercalation into Co-Al-LDH, the anisotropy values of Co-Al-4-BBA-LDH (Fig.9 curve c), Co-Al-2-NSA-LDH (Fig.9 curve d), and Co-Al-4-BBA-2-NSA-LDH (Fig.9 curve e) were all higher than that of pure 4-BBA and 2-NSA in the 300-800 nm energy emission. It might be that spatial distribution of the guest molecules in the layer

was rather ordered arrangement and therefore dissipation processes through energy transfer might increase the anisotropy values for the 330-800 nm energy emission, which supported the above results of theoretical calculations.
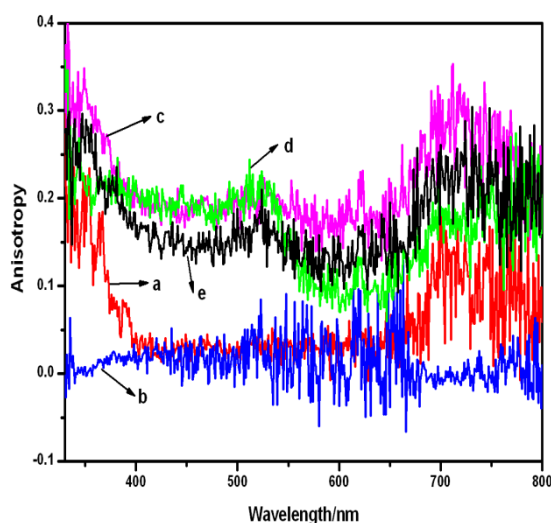


Fig. 9 Anisotropy traces of fluorescence of (a) 4-BBA (b) 2-NSA (c) Co-Al-4-BBA-LDH (d) Co-Al-2-NSA-LDH (e) Co-Al-4-BBA-2-NSA-LDH

## 4. Conclusions

4-BBA and 2-NSA with donor-acceptor properties were intercalated or co- intercalated into the Co-Al-LDH by the method of ion-exchange procedures. It was found that the guest 2-NSA intercalated into Co-Al-LDH enhanced the blue emission due to the host-guest coordination interactions. Fluorescence polarization method was applied to investigate the preferential orientation of the interlayer 4-BBA and 2-NSA molecules, and the results showed that spatial distribution of the guest molecules in the layer is rather ordered arrangement and was believed that 4-BBA and 2-NSA were intercalated or co-intercalated between sheets of Co-Al-LDH as a bilayer interdigitated form, and intermolecular energy transfer from 2-NSA to 4-BBA might be take place between sheets of Co-Al-LDH. Therefore, it is expected that such a strategy to design functional material by the combination of Co-Al-LDH with various types of containing sulfonic group organic chromophores will be very valuable.
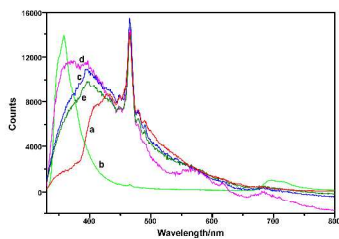
## 5. Acknowledgements

## 6. References

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