# A combined study based on experiment and molecular dynamics: perylene tetracarboxylate intercalated in a layered double hydroxide matrix<sup>†</sup>

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This paper describes a combined experimental and theoretical simulation investigation on the photophysical properties, thermolysis, and orientation of 3,4,9,10-perylene tetracarboxylate (PTCB) intercalated Mg-Al-layered double hydroxide (PTCB/Mg-Al-LDH). UV-vis absorption and fluorescence spectroscopy show the existence of PTCB aggregates within the gallery of LDH, indicative of H-type (blue-shifted absorption band) and J-type dimers (red-shifted absorption band). In situ high-temperature X-ray diffraction (HT-XRD), thermogravimetry and differential thermal analysis (TG-DTA) and elemental analysis were used to study the thermal decomposition properties of PTCB/Mg-Al-LDH, and it was found that the decomposition temperature of the intercalated PTCB is lower than its pristine form (460 vs 565 °C), indicating that the strong  $\pi$ - $\pi$  interaction among PTCB was weakened by the positively charged LDH host layers. Molecular dynamics (MD) calculations were employed to simulate the molecular arrangement and aggregation behavior of intercalated PTCB in the gallery of Mg-Al-LDH. The simulation results show that the intercalated PTCB anions exhibit a tendency from tilted to vertical orientation with respect to the layers as the interlayer water content increases, furthermore, the H and J-type dimer species are most likely populated under low and high hydration conditions, respectively. Moreover, the distribution of interlayer water molecules are also discussed.

## 1. Introduction

Layered double hydroxides (LDHs) are a large family of host materials, whose formula can be described as:  $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]^{z+}A^{n-}_{z/n}yH_{2}O.$   $M^{II}$  and  $M^{III}$  are divalent and trivalent metal ions, respectively;  $A^{n-}$  is an anion. The host structure consists of brucite-like layers of edge-sharing M(OH)<sub>6</sub> octahedra, and the partial substitution of M<sup>3+</sup> for M<sup>2+</sup> induces positively-charged host layers, balanced by the interlayer anions. Recently, LDHs have received much attention for their potential applications in the fields of catalysis,<sup>1</sup> separation processes,<sup>2</sup> moreover, LDH can be a special "molecular container" for the novel two dimensional confined effect, which has been applied to the storage and delivery of biological molecules,<sup>3</sup> or to control the racemization of chiral pharmaceutical molecules.<sup>4</sup> Furthermore, syntheses of organic-inorganic hybrid materials based on LDHs have attracted much attention, for these materials may show some special physicochemical characteristics compared with their individual counterparts.

Dve incorporated LDHs system is an important type of layered organic-inorganic hybrid materials, for dye molecules may exhibit novel photophysical behavior in a confined microenvironment that is absent in solution or solid state. It is believed that the hybrid structure based on host-guest interactions will offer a higher mechanical, thermal and chemical stability for the dye molecules; moreover, the immobilization of dye in the hybrid materials for better optical performance also reduces the environmental pollution or operational risk, which is favorable for their application in solid-state optoelectronic devices.<sup>5</sup> Many dye molecules, such as methyl orange,  $5^{a}$  fluorescein,  $5^{b}$  anthracene,  $5^{c}$  rhodamine B,  $5^{d}$  pyrene derivatives<sup>5e,g</sup> and pervlene chromophores,<sup>5f</sup> have been intercalated into LDHs to achieve the immobilization of the dye molecules and the enhancement of luminous efficiency. However, dye aggregates can still be found in some dye intercalated LDH systems, e.g., dye dimers were found coexisting with monomers in 1-pyrenesulfonate (PS) intercalated Zn-Al-LDH.<sup>5e</sup> Martínez et al.<sup>6a</sup> reported that the properties of the host, host-dye interactions as well as dye-dye interactions, may affect the distribution, orientation and aggregates of dye molecules in the host material. Generally, there are two kinds of typical aggregates of dye dimer, depending on the angle  $\theta$  between the transition dipole vector and the lineation of centers vector of the two dye molecules. They are named as H-type ( $\theta > 54.7^{\circ}$ ) or J-type ( $\theta < 54.7^{\circ}$ ) dimers, responsible for the blue or red shift, respectively in the optical absorption of dye molecules, and the formation of dye aggregates also results in poor optical properties

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(*e.g.* absorption broadening and/or fluorescence quenching).<sup>6b</sup> Detailed information on dye aggregation is essential to reveal the host–guest, guest–guest interactions, and to optimize the optical properties for the dye incorporated LDHs materials. Up to now, although dye aggregation behavior on solid surfaces has been widely studied by optical absorption and emission observation experimentally, it is still not further understood, especially in the two dimensional confined region of LDHs matrix.

In recent years, the molecular dynamic (MD) simulation method has been widely used to study and predict the structures and properties of functional materials beyond experimental observations, due to the limitation of the experimental characterizations. This theoretical method has the advantage of dealing with more complicated systems than the quantum mechanical calculation. Compared with the Monte Carlo (MC) simulation method, MD simulation follows Newton's second law, which can be used to simulate the real movement of atom ensembles. Greenwell  $et al.^7$  have reviewed a number of molecular simulation details and results for cationic and anionic clay systems, and it has been confirmed that MD simulation provides an effective and complementary method to investigate the important properties of LDHs-based composite materials,<sup>8</sup> e.g., Newman et al. have reported the radial distribution functions (RDFs) of water molecules between LDH layers,<sup>8b</sup> and the self-diffusion properties of inorganic anions were also probed. Moreover, the hydration energies were calculated for predicting the optimal hydration state and swelling behavior of clavs.<sup>8d</sup> The arrangement and orientation of anions within the LDH galleries, such as carboxymethyl  $\beta$ -cyclodextrin,<sup>8g</sup> some drugs (ibuprofen), <sup>8h</sup> inorganic molecules  $(CO_3^{2-})$ , <sup>8i</sup> and biological molecules (DNA),<sup>8m</sup> were also studied, which can not be by the current experimental techniques.

Perylene and its derivatives are a family of the most attractive luminescence dyes,<sup>9a,b</sup> owing to their high quantum yields and excellent photochemical stability. They have been employed in various applications in the fields of electronics and optoelectronics devices such as organic light emitting diodes,<sup>9c</sup> photovoltaic devices<sup>9d</sup> and dye lasers.<sup>9e</sup> Compared with other non-planar dye molecules (e.g., rhodamine), the perylene molecules are symmetrical and planar conjugated, which allows aggregates to form easily due to the  $\pi$ - $\pi$  or dipole-dipole interactions. Bauer et al.<sup>5f</sup> reported that perylene bisimidetetrasulfonate (PBITS) exhibits a J-type arrangement between layers of Zn-Al-LDH, accounting for its complete fluorescence quenching. As a result, it is important to investigate the states of perylene in a confined environment of LDHs for optoelectronics applications. In this work, the thermal decomposition and spectroscopic properties of pervlene 3,4,9,10-tetracarboxylate (PTCB) intercalated LDH were studied by in situ high-temperature X-ray diffraction (HT-XRD), thermogravimetry and differential thermal analysis (TG-DTA), FT-IR, UV-vis absorption and fluorescence spectroscopy. Moreover, MD simulation was performed by employing a modified cff91 forcefield<sup>8i,10</sup> to analyze the orientations and aggregation of the confined PTCB anions. The simulation results are in reasonable agreement with those of the experimental ones, demonstrating the feasibility of MD simulation for this dye/LDH system.

# 2. Experimental

## Materials

3,4,9,10-perylenetetracarboxylic dianhydride (PTCD, 99%) was purchased from Sigma Chemical Co. Ltd. NaOH (AR),  $Mg(NO_3)_2$ ·6H<sub>2</sub>O (AR) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (AR) were purchased from Beijing Chemical Co. Ltd. and used without further purification. All the aqueous solutions were prepared with deionized and CO<sub>2</sub>-free water.

## Preparation of PTCB and PTCB intercalated Mg-Al-LDH

PTCB was prepared by hydrolysis of PTCD following Sun's previous work.<sup>11</sup> PTCB intercalated Mg-Al-LDH was prepared by the coprecipitation method. The matched molar ratio of Mg<sup>2+</sup>/Al<sup>3+</sup>/OH<sup>-</sup>/PTCB was 2.0:1.0:6.0:0.5 in this experiment. A 100 ml of solution containing Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.05 mol) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.025 mol) was slowly added dropwise to a 100 ml of solution containing NaOH (0.15 mol) and PTCB (0.0125 mol) with vigorous agitation under a nitrogen flow. The pH value at the end of addition was adjusted to 8.0 by further addition of 2.4 mol/L NaOH solution. The reaction mixture was subsequently heated at 70 °C for 12 h, washed thoroughly with deionized water and dried at 50 °C for 18 h. Elemental analysis gave C 22.13 %, N 0.0 %, H 4.33 %, and atomic emission spectroscopy showed the ratio of Mg/Al was 2.06, so the chemical composition of PTCB/Mg-Al-LDH can be determined as: Mg<sub>2.02</sub>Al<sub>0.98</sub>(OH)<sub>6</sub>(C<sub>24</sub>H<sub>8</sub>O<sub>8</sub>)<sub>0.245</sub>·1.98H<sub>2</sub>O (It should be noted that the water content was determined by TG-DTA analysis).

## Characterization

The sample of PTCB/Mg-Al-LDH was characterized on a Rigaku D/MAX2500VB2+/PC X-ray diffractometer under air conditions, using Cu Ka radiation (0.154184 nm) at 40 kV, 30 mA with a scanning rate of 5  $^{\circ}$  C/min, a step size of 0.02 $^{\circ}$ /s, and a  $2\theta$  angle ranging from 3 to  $70^{\circ}$ . The *in situ* hightemperature powder X-ray diffraction (in situ HT-XRD) measurements were performed on a Philip X'Pert Pro MPD X-ray diffractometer in the temperature range 30-580 °C under air conditions, with Cu Ka radiation (0.154184 nm) operating at 40 kV, 40 mA. X'celerator was used for acquiring data. The heating rate was 30 °C/min with a holding time of 5 min before each measurement. Typical measurement conditions were in the  $2\theta$  range  $4-70^{\circ}$ ; the step width is  $0.0167^{\circ}$  (2 $\theta$ ) and the step counting time is 20 s. The Fourier transform infrared spectra were recorded using a Nicolet  $605 \text{ XB FT-IR spectrometer in the range } 4000-400 \text{ cm}^{-1} \text{ with}$ a 4 cm<sup>-1</sup> resolution under air conditions. The standard KBr disk method (1 mg of sample in 100 mg of KBr) was used. The solution and solid UV-vis absorption spectra were collected on a Shimadzu U-3000 spectrophotometer, with a slit width of 1.0 nm and BaSO<sub>4</sub> as the reference. The solution and solid state fluorescence spectra were performed on an RF-5301PC fluorospectrophotometer under the conditions with an excitation wavelength of 420 nm. The width of both the excitation and emission slit is 3 nm. TG-DTA curves were measured on a PCT-1A thermal analysis system under an ambient atmosphere with a heating rate of 10 °C/min. Content

analysis of metals was performed by ICP atomic emission spectroscopy on a Shimadzu ICPS-7500 instrument using the solutions prepared by dissolving the samples in dilute nitric acid. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer Elementarvario elemental analysis instrument.

## 3. Structural model and simulation method

Generally, a model with  $6 \times 3 \times 1^{8b,d,i}$  or  $6 \times 6 \times 1^{8g}$ rhombohedral supercell for LDH was chosen by most researchers when performing MD simulations. Taking the four negative charges of PTCB into account and reducing the computational complexity without affecting the precision, an ideal LDH layer model with tetragonal superlattice was selected from the rhombohedral supperlattice, whereas the *R*-3*m* space group was unchanged (shown in Fig. 1A and B). The layer containing 16 Mg atoms and 8 Al atoms was built based on the following rule: each [AlO<sub>6</sub>] octahedron is surrounded by six [MgO<sub>6</sub>] octahedra and each [MgO<sub>6</sub>] octahedron is, in turn, surrounded by three [AlO<sub>6</sub>] octahedra, ensuring that Al atoms will not occupy adjacent octahedra. Therefore, every octahedral layer has 24 metal atoms and 48 OH groups under the conditions of  $\alpha = \beta = 90^{\circ}$ . The distance between adjacent metal atoms is 3.05 Å, in accordance with the literature<sup>12</sup> and our experimental results below. Based on the model of the host layer, a supercell was constructed, with lattice parameters a = 21.132 Å, b = 9.150 Å, c = 18.45 Å (experimental result),  $\alpha = \beta = \gamma = 90^{\circ}$ . The supercell was treated as P1 symmetry and all of the lattice parameters were considered as independent variables in the simulation. A 3-dimensional periodic boundary condition<sup>13</sup> was applied to the system, and the simulated supercell can be repeated infinitely in three directions. Perylene tetracarboxylate (PTCB) anion is of high symmetry with the symmetric center at the molecular centre. For maintaining the whole system electrically neutral, two PTCB anions (shown in Fig. 1C) were introduced into the simulated supercell with the long axis normal to the layer as an initial configuration. Furthermore, different numbers of water molecules were located in the supercell randomly based on the assumption that these molecules occupy the whole available interlayer space as much as possible. As a result, the formula of the simulated structure can be expressed as: Mg<sub>16</sub>Al<sub>8</sub>(OH)<sub>48</sub>(C<sub>24</sub>H<sub>8</sub>O<sub>8</sub>)<sub>2</sub>·*n*H<sub>2</sub>O.

A modified cff91 forcefield was employed to perform an MD simulation in the whole process. Forcefield parameters for Al, O and H in the layer were derived from Li *et al.*'s work;<sup>8i</sup> the



**Fig. 1** The superlattice layer model for Mg–Al-LDH (Color codes: white: H; pink: Al; red: O; green: Mg) (A)  $6 \times 6 \times 1$  rhombohedral supercell; (B) tetragonal supercell; (C) structural model of perylene 3,4,9,10-tetracarboxylate (PTCB).

bond length parameters of Mg-O were adopted from the modified Dreiding forcefield;<sup>8n</sup> the bond angle parameters of Mg-O-Mg or O-Mg-O were assigned the same as those of Al atoms; Lennard-Jones (LJ) 9-6 potential parameters of Mg atom were obtained by curve-fitting method based on consistent-valence forcefield (CVFF) given by Kim et al.<sup>8q</sup> (see the ESI<sup>†</sup>). The Charge Equilibration (QEq) method<sup>14</sup> was used to calculate atomic charges of the layer, in which the partial charges are +0.703 e for Mg, +1.363 e for Al, -0.537 e for O and +0.243 e for H. Other forcefield parameters for the anions and water molecules were referred to the cff91 forcefield.<sup>10</sup> The NBO analysis<sup>15</sup> was employed to calculate the partial charges of perylene tetracarboxylate anion on the B3LYP/6-31G\*\* level using the Gaussian 03 programs.<sup>16</sup> For the water molecule, the partial charges came from the Simple point charge (SPC) water model reported by Berendsen.<sup>17</sup> In potential energy calculations, the long range Coulomb interactions between partial charges were computed by the Ewald summation technique<sup>13</sup> and a "spline cutoff" method was used to calculate van der Waals interaction. After energy minimization was applied on the initial model, MD simulations were performed in isothermal-isobaric (NPT) ensemble with the temperature of 300 K and the pressure of 0.1 MPa (about 1 atm). The Andersen method<sup>18</sup> and Berendsen method<sup>19</sup> were used to control temperature and pressure, respectively. The total simulation time was 50 ps with the simulation time step of 1 fs. The result shows that the system reached equilibrium with lattice parameters and total potential energy fluctuating around a constant value within the first 10-15 ps, so the dynamic trajectories were recorded every 10 fs in the remaining 35 ps in order to analyze the ensemble average values. All the simulations were performed using the Discover module in the Material Studio software package.<sup>20</sup>

#### 4. Results and discussion

#### 4.1 Experimental

A Structural characterization of PTCB intercalated Mg–Al-LDH. The powder XRD pattern of PTCB/Mg–Al-LDH is shown in Fig. 2. In this case, all the reflections can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, which is commonly used for the description of



Fig. 2 Powder XRD pattern of PTCB/Mg-Al-LDH.

3R-type LDH structure. The main characteristic reflections of the PTCB intercalated LDH appear at 4.77° (003), 9.64° (006), 14.33° (009), 19.12° (0012), 23.82° (0015) and 61.17° (110), respectively. It was found that  $d_{003}$  (1.851 nm),  $d_{006}$  (0.917 nm) and  $d_{009}$  (0.618 nm) of PTCB/LDH gave a good multiple relationship between the basal, second and third-order reflections. The parameter c is related to several factors (such as the van der Waals radii of PTCB, arrangement of interlayer guest anions and the hydration state), and it can be calculated from averaging the positions of the three harmonics: c = 1/3 $(d_{003} + 2d_{006} + 3d_{009}) = 1.845$  nm. It should be noted that the 006 reflection is stronger than 003, implying that the PTCB molecules are accommodated with the symmetric center located in the half-way plane within the interlayer region. Additionally, a shoulder peak was observed at ca. 5.78° (1.53 nm), which may be attributed to a different arrangement of PTCB anions in the gallery of LDH. The lattice parameter a, which stands for the shortest distance of adjacent metal atoms with identical chemical environments in the LDH layer, can be calculated by:  $a = 2d_{110} = 3.03$  Å. This is in accordance with other reported Mg2Al-LDH systems (3.04 or 3.05 Å).<sup>12</sup> The values of a and c are referenced in the computer simulation section.

Fig. 3 shows the FT-IR spectra of pristine PTCD, PTCB, the sodium salt of PTCB and PTCB/LDH samples. For the pristine PTCD (Fig. 3a), the bands at 3442 and 3120  $\text{cm}^{-1}$  are attributed to the O-H stretching vibrations of the water molecules from air. The strong band at 1773  $\text{cm}^{-1}$  corresponds to the characteristic CO-O-CO stretching vibration of the anhydride, and the bands at 1595 and 1507  $cm^{-1}$  due to the skeleton vibration of benzene can also be observed. The bands at 809 and 734 cm<sup>-1</sup> represent the out-of-plane bending of =C-H within arene derivatives. The symmetry and asymmetry bands of C-O-C in the lactone bond of the anhydride are located at 1236 and 1301 cm<sup>-1</sup>, respectively. When the PTCD hydrolyzed into PTCB, two bands corresponding to the vibrations of C=O in the -COOH group can be observed at 1769 and 1697  $\text{cm}^{-1}$ (Fig. 3b), and the in-plane deformation vibration of O-H appears at 1433 cm<sup>-1</sup>. The sodium salt of PTCB shows the vibration of C=O in



**Fig. 3** FT-IR spectra for (a) PTCD, (b) PTCB (c) sodium salt of PTCB and (d) PTCB/Mg-Al-LDH.

the –COO<sup>-</sup> group at 1765 cm<sup>-1</sup> (Fig. 3c). The FT-IR spectrum of PTCB/Mg–Al-LDH is displayed in Fig. 3d. Compared with that of the sodium salt of PTCB, the band was resolved as the vibration of C=O of the –COO<sup>-</sup> group, and it is shifted from 1765 to 1758 cm<sup>-1</sup> ( $\Delta = -7$  cm<sup>-1</sup>), indicating the strong interactions between the four carboxylate of PTCB and Mg–Al-hydroxyl layers. The bands at 1544 and 1421 cm<sup>-1</sup> are assigned to the antisymmetric and symmetric stretching vibration of C–O<sup>-</sup> in the –COO<sup>-</sup> group. The skeleton vibration of the phenyl ring also appears at 1599 cm<sup>-1</sup>. Finally, the lattice vibration of the inorganic LDH layers appears in the range from 400 to 800 cm<sup>-1</sup>.

B Photophysical properties of PTCB/Mg-Al-LDH. Fig. S1A in the ESI<sup>†</sup> shows the UV-vis absorption spectra of PTCB aqueous solution with various concentrations. The absorption band at *ca*. 217 nm can be attributed to the  ${}^{1}E_{11}$ transition of the phenyl ring; the one at 260 nm originates from the transition along the short axis of PTCB anions  $(S_0-S_4)$ , and the absorption band ranging from 400 to 475 nm (the absorption peaks at 438 nm  $(S_0-S_1)$  and 466 nm) is due to the long-axis transition of PTCB chromophore.<sup>21</sup> For the sample of PTCB/LDH (Fig. S1C in the ESI<sup>+</sup>), a broad strong absorption ranging in 400-600 nm dominates the whole absorption spectrum, and two maximum absorption bands are mainly populated at ca. 450 and 550 nm. These results illustrate that PTCB anions may form aggregates within the LDH gallery (H-type: blue-shifted absorption; J-type: red-shifted absorption). Similar dimer aggregation was also observed in the system of Rhodamine B intercalated LDH with high dye concentration.<sup>5d</sup>

The photoluminescence spectra of PTCB aqueous solutions are shown in Fig. S1B. The emission peaks of PTCB in solution (1 µM, Fig. S1B, curve a in the ESI<sup>+</sup>) locate at 480  $(S_0-S_1 \text{ emission})$  and 510 nm. When the concentration increases to 10 µM, the emission intensity increases nearly two times with the peak at 480 nm red-shifted to 492 nm  $(\Delta = 12 \text{ nm})$ . Furthermore, the intensity of 510 nm decreases greatly for 30 µM solution. These phenomena confirm the formation of J dimers (red-shifted emission) upon the increase of concentration. Compared with the PTCB aqueous solution, the poor luminescence for the PTCB/LDH sample can be detected (Fig. S1D in the ESI<sup>†</sup>), due to the severe aggregation of dye molecules. Compared with Bauer et al.'s work,<sup>5f</sup> the intercalated PTCB shows weak luminescence centered at 462 ( $\Delta = -18$  nm) and 498 nm ( $\Delta = -12$  nm). This blue-shift behavior can be mainly attributed to two factors. Firstly, the formation of dye aggregation is responsible for this phenomenon as UV-Vis absorption spectra suggested. Secondly, the state of interlayer PTCB anions is based on the H-bond, electrostatic attraction, and/or van der Waals interactions between the electropositive Mg-Al-layer and PTCB anions, which is totally different from the one in aqueous solution. In the confined and electrostatic microenvironment, the electronic energy level of PTCB is different from the free one, which imposes influence on the emission spectrum of PTCB.



Fig. 4 In situ XRD patterns of PTCB intercalated Mg–Al-LDH in the temperature range 30-430 °C.

C Thermal decomposition of PTCB/Mg-Al-LDH. The in situ high-temperature XRD patterns of the intercalation product PTCB/Mg-Al-LDH and the dependence of the interlayer spacing on the temperature are displayed in Fig. 4. It can be observed that the 00l reflections of PTCB/Mg-Al-LDH systematically move to a higher  $2\theta$  angle from 30 °C to 330 °C, with the gradual decrease in intensity. This indicates the decrease both in interlayer spacing and crystallinity of the composite, which is mainly related to the deintercalation of interlayer water molecules and the decomposition of the PTCB anions. At 480 °C, the characteristic reflections of MgO were observed at ca. 42.8° and 63.4° (Fig. S2a in ESI<sup>†</sup>), accompanied by the disappearance of LDH reflections.<sup>4a</sup> This is due to the combustion of the PTCB anions and dehydroxylation of LDH layers under air conditions.

Thermolysis behavior of PTCB was studied as a reference to compare with PTCB/Mg-Al-LDH, and its TG-DTA curves are displayed in Fig. 5A. A weight loss of ca. 2.5% occurs below 150 °C, with an endothermic peak in the DTA curve, which corresponds to the loss of crystalline water. No obvious thermolysis can be observed until the temperature increases to 400 °C. The sharp weight loss (420-580 °C) with the peak at *ca.* 565 °C in the DTA curve is attributed to the decomposition and combustion of PTCB. In the case of the PTCB/Mg-Al-LDH sample (Fig. 5B), its thermal decomposition process is characterized by three weight loss steps. The first one from room temperature to 190 °C with a broad endothermic peak is the removal of surface adsorbed and interlayer water molecules. The second one with a gradual weight loss (190-400 °C) includes both the decomposition of the PTCB anions and the dehydroxylation of the brucite-like layers as in situ XRD suggested, accompanying with an exothermic peak from 250 to 350 °C in the DTA curve. The third one corresponds to the collapse of the LDH layer and combustion of PTCB, with a strong exothermic peak at ca. 460 °C. Based on the comparison study on the thermolysis process, it was found that the decomposition or combustion temperature of the intercalated PTCB is lower than its pristine form. This is possibly due to the different states of PTCB in the two



Fig. 5 TG and DTA curves for (A) PTCB, (B) PTCB/Mg-Al-LDH.

samples. For the pristine PTCB sample, the strong  $\pi$ - $\pi$  and H-bond interactions among the planar PTCB anions dominate in the whole crystal lattice, whereas in the case of PCTB/LDH, the host-guest interaction (mainly electrostatic interaction) determines the arrangement of PTCB, and the guest-guest interaction (mainly  $\pi$ - $\pi$  interaction) is depressed largely. A similar behavior has also been observed in the system of polystyrene sulfonate/Ni-Al-LDH.<sup>80</sup>

#### 4.2 Molecular dynamics simulation

A Swelling and hydration properties. The swelling behavior and hydration state are key information in understanding the hydrophobic/hydrophilic environment and distribution of water molecules in the gallery of LDH. Fig. 6 shows an almost linear dependence of simulated interlayer spacing on the water content in the LDH matrix, which is similar to the results of



Fig. 6 Variation of interlayer spacing as a function of water content in the supercell (inset: the experimental and computational interlayer spacing. The data corresponds to temperatures of 70 °C, 90 °C, 110 °C, 130 °C, 150 °C and 170 °C).

other anions intercalated Mg–Al-LDH systems.<sup>8b,i-k</sup> As described in the experimental section, the comparison study between experimental and simulated results for interlayer spacing with different hydration states was carried out based on the elemental analysis, TG-DTA and *in situ* HT-XRD technique. In addition, the temperature range of 90–170 °C was chosen to make the comparison (shown in the inset of Fig. 6), in order to eliminate the influence of surface adsorbed water.

It can be seen from Fig. 6 that the simulated interlayer spacing with the experimental hydration state is systematically less than that of the experimental value by ca. 2 Å, and a similar result was also found in the vinyl-benzenesulfonate (VBS)/Ni-Al-LDH system.<sup>80</sup> The experimental variation of the interlayer spacing under different hydration conditions is less sensitive than that of the simulation one. Linear regression analysis shows that the simulated interlayer spacing increases by about 0.041 Å with as one interlayer water molecule is increased in our model, whereas 0.026 Å was obtained for the experimental one. This may imply that the host-guest interaction in a real system is stronger than that of the ideal model in this work. The differences between the experimental and computational results may be attributed to the following reasons. Firstly, the real system with some lattice defects and different stacking modes of the layers is more complex than the ideal and simplified LDH supercell model. Secondly, in our simulation process, the parameters of atomic charges or Lennard-Jones potentials in the cff91 forcefield also influence the calculation of the host-guest interaction, since it is known that a stronger attraction between the host layer and anions leads to a lower interlayer spacing. Finally, since the hydration state can transform to each other as the hydration energy suggested below, the experiment-determined hydration state may also be responsible for the error. It should be noted that the simulation temperature in the range 70-170 °C hardly affects the calculated results deviated from the real system based on our previous work.80

The hydration energy is an important index to estimate the hydration behavior and swelling properties of materials,  $^{8a,dj,k}$  and the most common function form is defined as:

$$\Delta U = \frac{\langle U(N) \rangle - \langle U(0) \rangle}{N}$$

where N is the number of interlayer water molecules;  $\langle U(N) \rangle$  is the average potential energy of hydrated LDH containing N water molecules in the interlayer gallery and  $\langle U(0) \rangle$  is the average potential energy of anhydrous LDH.

The hydration energy in the system of PTCB/Mg–Al-LDH is negative, indicating that the hydration of the intercalated composite is a spontaneous process. It increases upon the increase of the water content (shown in Fig. 7), which is similar to the results reported for citrate and monocarboxylate intercalated Mg–Al-LDH system.<sup>8j,k</sup> No local minimal energy was found under different hydration states. It was found that when a small energy barrier is surmounted for n = 72, the hydration energy curve reaches another relatively stable stage, gradually approaching the hydration energy value of SPC water ( $\sim -10$  kcal/mol). The experimentally-determined water



Fig. 7 Hydration energy of PTCB/Mg–Al-LDH with different water content.

content is ~16 water molecules, close to the stable stage of hydration energy with n equal to 9–18.

To further understand the hydration state, the distribution of interlayer water molecules, and the interlayer hydrophobic/ hydrophilic character, the distribution of H<sub>2</sub>O along the direction normal to the LDH layer were calculated. Three typical density profiles under different hydration conditions are shown in Fig. 8A. It was observed that the water profiles display nearly symmetric distribution in the gallery of LDH. For the low water content, all of the water molecules are populated close to the LDH layers as seen from the two sharp peaks in the case of 12 water molecules, suggesting the prevailing hydrogen-bond interaction between the water and LDH host layers. Upon the increase of water content, some water molecules are located near the gallery centre of LDH, which is a nonpolar environment created by PTCB anions, as a result, multilayer water distribution is observed, although most water molecules are still present close to the LDH layers. Furthermore, the maximal distribution of interlayer water is closer to the LDH layers with higher hydration state (as shown in Fig. 8B), suggesting some water molecules migrate to the hydrophilic layers upon increasing the hydration state. Fig. 8C displays the density profiles of the carboxylate group of PTCB in the z direction, and its distribution is consistent with the electrostatic interaction mode between the carboxylate group and the LDH host layer. It was found that the occupied zone of PTCB in the LDH gallery in the z direction increases (from 9 Å to 12 Å) with increasing water molecules (from 12 to 90 H<sub>2</sub>O), which is related to the orientation change of PTCB in the LDH matrix. On comparison of the density profiles of Fig. 8A with 8C, it was found that most of the water molecules are close to the carboxylate groups based on hydrogen-bond interaction, whereas a few are populated in the central zone, which contributes to the hydrophobic interaction between perylene and water molecules. This indicates that the intercalated  $\pi$ -conjugated molecules, e.g. PTCB, can effectively transform the hydrophilic interlayer gallery into a hydrophobic one by adjusting the distribution of water molecules.

B The arrangement of PTCB and  $H_2O$  in the gallery. In this section, four orientation angles were defined to describe



Fig. 8 (A) Distribution probability of water molecules in the hydrated PTCB/Mg–Al-LDH system. (B) Distribution probability of water molecules in the hydrated PTCB/Mg–Al-LDH system with normalized coordinate (the abscissa of Fig. 8A was divided by the interlayer height of each sample). (C) The distribution probability for the carboxylate group of PTCB in the *z* direction. The center of the interlayer gallery is chosen as the origin of coordinates.

the geometries of guest molecules (shown in Fig. 9): angle  $\theta_1$  stands for the orientation angle of the long axis of PTCB with respect to the LDH layer, which is also the direction of the  $S_0$ - $S_1$  transition dipole; angle  $\theta_2$  stands for the angle between the  $S_0$ - $S_1$  transition dipole vector of PTCB and the lineation of centers vector of two dye molecules, and two different  $\theta_2$  in the system are analyzed; angle  $\theta_3$  stands for the orientation angle of dipole vector of water molecule with respect to the layer; and angle  $\theta_4$  represents the orientation angle of H–H vector of water molecule with respect to the



Fig. 9 Definitions of four orientation angles in the gallery of LDH.

layer. The four orientation angles under different hydration states were probed in the MD simulation.

Fig. 10A displays the distribution of  $\theta_1$  under four typical hydration states. The orientation varies between 23 and 34° with the most probable angle of *ca*. 26° in the anhydrous state. Under this state, all of the guest molecules are inclining to the layers, which can be attributed to the strong electrostatic interaction between the positive-charged host layers and the



Fig. 10 The distributions of four orientation angles under different hydration states (A, B, C, D displays the distributions of  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  and  $\theta_4$ , respectively).

PTCB anions. When the molar ratio of H<sub>2</sub>O to PTCB is 15:1 (30 H<sub>2</sub>O molecules per supercell), the distribution of  $\theta_1$  is mainly populated from 33 to 52°, indicating that PTCB become less tilted with respect to the layer. When the molar ratio increases to 30:1 (60 H<sub>2</sub>O molecules per supercell), the distribution of  $\theta_1$  broadens in the range 46–73° and exhibits nearly normal distribution with the maximum likelihood angle of 61°. As the molar ratio increases to 45:1 (90 H<sub>2</sub>O molecules per supercell), the angle distribution from 53 to 88° is observed, indicating that the PTCB anions are nearly perpendicular to the host layers under a high hydration state. It can be concluded from Fig. 10A that the guest molecules have a tendency to move from a tilted to a vertical arrangement with respect to the layers as the interlayer water increases, and similar results were also found in the system of terephthalate/ LDH.<sup>8b</sup> Two snapshots of the simulation for PTCB intercalated Mg-Al-LDH in anhydrous and hydrous states are shown in Fig. 11, which can help to further understand the structure and orientation of PTCB in the gallery of Mg-Al-LDH. Another important fact is that the distribution of  $\theta_1$  becomes broad upon the increase of water molecules, indicating that the involvement of water molecules supplies a more flexible space for the guest molecules. Specific attention has been focused on the state with 16 water molecules in the supercell corresponding to the experimental hydration condition. The computational interlayer spacing is 15.53 Å, which is between the one with 12 H<sub>2</sub>O (15.41 Å) and 18 H<sub>2</sub>O (15.68 Å) as expected. This result is lower than the experimental value by ca. 3 Å. Moreover, the orientation of the PTCB was also investigated, and the distribution is mainly populated in the orientational angle of  $25-32^{\circ}$  with the most probable angle of *ca*.  $28^{\circ}$  under this state (Fig. S3 in the ESI<sup>†</sup>).

Angle  $\theta_2$ , which is related to configuration of the dye dimer aggregate in the gallery of LDH, was calculated under different hydration states. The H or J-type dimer was estimated by the criterion as follows: H-type dimer comes into formation if  $\theta_2 > 54.7^\circ$ , while the J-type forms if  $\theta_2 < 54.7^\circ$ . As a result the percentages of H and J-type species in the LDH layers dependent on water molecules can be estimated, as shown in Fig. 10B. It was found that coexistence of both types of dimers occurs in the LDH layers. For the anhydrous PTCB/LDH system, the J-type dimer accounts for ca. 2/3 of the total aggregation. When the interlayer H<sub>2</sub>O molecules increase to 30, the percentages of two types of dimers are nearly equal, and the maximal distribution of  $\theta_2$  is populated at ca.  $50^{\circ}$ . Additionally, more H-type dimers (63.30%) can be observed with 60 H<sub>2</sub>O molecules in the gallery of LDH. In this case,  $\theta_2$  mainly distributes at *ca*. 70°. Furthermore, nearly



Fig. 11 Snapshots of the simulation for PTCB intercalated Mg-Al-LDH under two hydration conditions (A: anhydrous, B: 60 water in the supercell).

95.07% of the aggregates belong to the H-type one as the molar ratio of H<sub>2</sub>O/PTCB increases to 45:1. It thus can be concluded that the value of  $\theta_2$  increases upon increasing H<sub>2</sub>O molecules, and the H and J-type dimers are populated under low and high hydration states, respectively. This property can also be understood in terms of the orientation of dve molecules in the gallery (*i.e.*,  $\theta_1$ ). The dye molecules prefer tail-to-tail stacking (J dimer) due to their tilted arrangement with respect to the LDH layer under a low hydration state, whereas they are apt to face-to-face stacking (H dimer) due to a nearly perpendicular arrangement with respect to the layers under a high hydration state. In our experimental work, the PTCB/ LDH sample with ca. 16 water molecules was obtained (low hydration state), so it can be deduced that most of the aggregates belong to J-type dimers for the synthesized sample. This accounts for the broad absorption of 500-600 nm as shown in its UV-vis spectrum. Actually, the dependence of dye aggregates on the water content has been studied by some researchers. Mohanambe et al.<sup>5g</sup> have observed that the dye excimer disappears or reappears under anhydrous or hydrous conditions when investigating the pyrene and dodecylsulfate co-intercalated Mg-Al-LDH. Costantino et al.<sup>5a</sup> reported that the absence of the hydration state causes a red-shift of ca. 50 nm in the fluorescence spectrum for the methyl orange/Zn-Al-LDH system, which is very similar to our simulated result. These observations confirm that the hydration state is a significant factor for the formation of dye aggregates and their spectral features. Moreover, eliminating aggregation of dyes is a key factor to improving the photoluminescence performances of these composite materials, and the introduction of co-intercalated surfactant in the galleries of LDH may be a good choice.

Taking into account the difference in chemical environment between multilayer water distributions in the LDH layers, the water molecules in the gallery of LDH can be divided into two types based on their distance to the LDH host layer. Type 1 is the water layer closest to the LDH layers; type 2 is the rest of the water molecules located near the gallery centre. Fig. 10C displays the distribution of the orientation angle for the dipole vector of water molecules relative to host layers ( $\theta_3$ ) under three hydration states. The  $\theta_3$  for water molecules of type 1 mainly distributes in the range from 20 to  $90^{\circ}$  and the maximum likelihood angle appears at  $\sim 60^{\circ}$  without shifting to a higher or lower angle direction as the interlayer water increases. This suggests that with the increase of water content. the plane of water molecules keeps the tilt at  $ca. 60^{\circ}$  to the layers, since the force induced by the positive-charged LDH layer was nearly unchanged. The  $\theta_3$  of type 2 water molecules ranges from 0 to  $90^{\circ}$ , and the maximum likelihood angle is present at ca. 40° with 48 water molecules between the layers. When the number of waters increase to 90, however, the distribution probability at *ca*.  $40^{\circ}$  decreases and the most probable angle is mainly populated from 0 to  $30^{\circ}$  with approximately uniform distribution, indicating that the plane of type 2 water molecules is more likely parallel to the LDH layers in the state of high hydration.

Fig. 10D exhibits the distribution of the orientation angle  $(\theta_4)$  for the H–H vector of water molecule relative to the host layers in three hydration states. The distribution of the type 1

water from 0 to  $45^{\circ}$  represents an exponential decay and the one from 45 to 90° hardly appears in each hydration state, which is similar to the simulation results of the  $SO_4^{2-}/LDH$  system.<sup>8*i*</sup> However, the type 2 water molecules are mainly populated in the range 0–80°. This indicates that the H–H vector of type 1 is more likely parallel to the LDH layer compared with type 2 water, which meets the requirements of force equilibrium in different hydration states.

## Conclusions

In this work, the photophysical properties, thermolysis behavior and orientation arrangements of perylene tetracarboxylate (PTCB) in the Mg-Al-LDH matrix have been investigated. Obvious absorption broadening and poor fluorescence were found for the PTCB/LDH system, which indicates the formation of dye aggregates in the LDH gallery. The decomposition temperature of the intercalated PTCB is lower than its pristine form, indicating that the strong  $\pi - \pi$ interaction between PTCB anions was weakened by the positive charge of LDHs layers. Molecular dynamics simulation was employed to study the hydration state, dye arrangement, aggregation of the PTCB/Mg-Al-LDH system. The interlayer spacing of different hydration states was investigated in terms of both experimental technique and MD simulation. The experimentally-determined interlayer spacing is less affected by interlayer water molecules than the simulated one, which suggests that the host-guest interaction between the LDH layers and PTCB anions in the real state is stronger than that of the model system. To probe the arrangement of guest molecules, four orientation angles have been defined. PTCB exhibits a tendency from a tilting to a vertical arrangement with respect to the layers with increasing water content. The H and J-type dimer species are most likely populated under low and high hydration conditions respectively, which is in agreement with the results of absorption and fluorescence spectra for PTCB/LDH. The simulation also indicates that the intercalated  $\pi$ -conjugated PTCB can effectively transform the hydrophilic interlayer gallery into a hydrophobic one by adjusting the distribution of water molecules. The water molecules and the carboxylate groups of PTCB are populated close to the LDH host layers via hydrogen bond and electrostatic interactions. Therefore, by virtue of a combination of experimental technique and theoretical calculation, this work not only gives a detailed investigation on the photophysical properties, thermolysis of dye molecules confined in the LDH matrix, but also provides a further understanding of the orientations, dye aggregation and hydrophobic/hydrophilic properties in the gallery of LDH. It can be expected that MD simulation can be used to explain and predict structural and spectral information for LDH-based dye composites and/or an ordered assembly of dye molecules, for the purposes of designing and preparing solid-state optoelectronic devices with high-quality performance.

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