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Preparation and photo-physical characterisation of nanocomposites obtained by intercalation and co-intercalation of organic chromophores into hydrotalcite-like compounds†

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Several chromophores with donor–acceptor properties and containing a carboxylic or sulfonic group [coumarin-3-carboxylic acid (3-CCA), 9-anthracenecarboxylic acid (9-ACA), 4-benzoylbenzoic acid (4-BBA) and 2-naphthalenesulfonic acid (2-NSA)] have been intercalated into Mg–Al hydrotalcite-like compounds, both *via* anion exchange procedures and by using the "memory effect" of the hydrotalcites. The obtained intercalation compounds have been characterised by X-ray diffractometry, thermal analysis and chemical composition. Data obtained indicate that the guest species are accommodated in the interlayer region as a monofilm of interdigitaded anions with the C–COO$^-$ or C–SO$_3$$^-$ bond almost perpendicular to the layer plane. The pairs of chromophores investigated, 3-CCA–9-ACA and 4-BBA–2-NSA, can give rise to energy transfer processes because of the characteristics of their excited states. Co-intercalation of the above-mentioned pairs of chromophores has been achieved with different synthetic procedures. The mono-intercalated and co-intercalated systems were investigated by absorption and emission spectroscopy and by laser flash photolysis. The absorption spectrum of MgAl-9-ACA shows an unexpected band around 490 nm that was attributed to an aggregate. The fluorescence characteristics of the various co-intercalated samples depend on the excitation wavelength and on the preparation methods, which control the relative amounts of the two fluorophores in the interlayer region. In all the samples containing 9-ACA excitation around 500 nm generates an emission attributed to the anthracene aggregate. In mono-intercalated and co-intercalated samples, the fluorescence decays satisfactorily fit bi-exponential and tri-exponential functions, respectively. Laser flash photolysis experiments showed that excitation of the intercalated chromophores produces transients which can be attributed to the guest triplets and, in the case of co-intercalated 4-BBA–2-NSA composite, the probable occurrence of an energy transfer process.

Introduction

The design, synthesis and study of functionalised solids is a topic of great interest that involves solid-state and materials chemistry.[1,2] Layered solids have interesting physical properties, because of their structural anisotropy, and can be easily functionalised by intercalation of species with specific properties. It should be pointed out that these properties generally differ from those of the pure guest species, being affected by guest organisation in the interlayer region as well as by the host–guest interactions.[3] Among layered solids, hydrotalcite-like anionic clays (HTlc) occupy a special position due to their structural and compositional features, which make them rare examples of layered solids with positively charged layers balanced by exchangeable anions.[4–6] HTlc are represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{z-}_{x/z}]\cdot nH_2O$, where M^{III}, typically Al, Cr or Fe, partially replaces M^{II} cations, *i.e.* Mg, Zn, Ni and Co, in the brucite-type layer. The layer is formed by octahedral units with shared edges. Each octahedron consists of M^{II} or M^{III} cations surrounded by six OH$^-$ ions. The presence in the layer of M^{III} cations induces excess positive charge which is balanced by exchangeable anions (A^{z-}) accommodated in the interlayer region, where water molecules are also located. Therefore, functional organic or organometallic species with anionic groups (carboxylate, phosphonate, sulfonate) can be intercalated *via* anion exchange processes in this class of layered hosts only.[7] These considerations have induced many research groups to use HTlc for the intercalation of species with magnetic, photochemical and optical properties in order to immobilise them on a solid support and/or modulate their properties by confining them in a constrained medium.[8–11] Our previous studies have shown that hydrotalcites are able to intercalate, *via* ion-exchange procedures, anionic dyes such as methyl orange,[12] fluoresceine[13] and phenolphthalein.[14] The fluorescence emission of samples with these dyes intercalated and/or taken up on the surface of the microcrystals showed a considerable red shift of the fluorescence maxima when compared with the maxima of the free dyes in solution. This marked bathochromic effect has been attributed to intermolecular interactions between the intercalated dye anions.[12,13] It is known that intermolecular energy transfer can also take place between a chromophore (the sensitiser or donor, D) that absorbs the excitation light and another species, the acceptor, A. In some cases, the interaction between the donor and the

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Electronic supplementary information (ESI) available: thermogravimetric curves (Fig. S1 and S2); pictorial representation of MgAl-2-NSA intercalation compound (Fig. S3); absorption, emission and time-resolved absorption spectra of several MgAl-HTlc intercalation compounds (Fig. S4–S6). See http://www.rsc.org/suppdata/jm/b2/b204393a/

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acceptor involves electron transfer, with the formation of a high-energy charge-separated state (D^+A^-), and the light is converted into chemical energy. Supramolecular assemblies of donor–acceptor species are responsible for natural photosynthetic processes. The design of systems that could be developed for light energy storage and conversion involves the incorporation and organisation of the donor–acceptor pair into the same material.[15] Approaches towards organising the D–A pairs into one material include assembling the participating molecules into zeolites,[16] clays,[17] micelles and other host systems.[18]

In this paper, attempts to organise donor and acceptor chromophores into the interlayer region of Mg–Al hydrotalcite-like compounds are described. The chromophore pairs coumarin-3-carboxylic acid (3-CCA)–9-anthracenecarboxylic acid (9-ACA) and 4-benzoylbenzoic acid (4-BBA)–2-naphthalenesulfonic acid (2-NSA), with carboxylate or sulfonate groups that can compensate for the positive charge of the HTlc layers have been employed. This contribution reports data on the intercalation of the individual chromophores, and data on the co-intercalation of D–A pairs, achieved *via* different synthetic procedures. After a preliminary photophysical characterisation of the mono-intercalated materials formed by 3-CCA, 9-ACA, 4-BBA and 2-NSA, and MgAl-HTlc, the absorption and emission spectra of the co-intercalated samples, prepared by different procedures and containing the pairs 3-CCA–9-ACA and 4-BBA–2-NSA, were measured. Fluorescence decays obtained by the phase-shift technique and transient spectra by laser flash photolysis are also reported.

Experimental

Chemicals

The chromophores were supplied by Fluka and used without any further purification. All other chemicals were C. Erba RP-ACS products.

Preparation of hydrotalcite-like compounds

MgAl-CO_3-HTlc. A large batch of Mg–Al hydrotalcite-like compound, with the formula $[Mg_{0.65}Al_{0.35}(OH)_2](CO_3)_{0.175}\cdot 0.5H_2O$, was prepared by the urea method.[19] A clear solution, obtained by mixing 100 mL of 0.50 M $AlCl_3$ (aq.) solution, 200 mL of 0.50 M $MgCl_2$ (aq.) solution and 30 g of urea, was maintained at reflux temperature for 3 days. The precipitate obtained was filtered, washed with de-ionised water and equilibrated, under stirring, with 100 mL of 0.1 M Na_2CO_3 (aq.) solution for 1 day to exchange the chloride ions (sometimes incorporated during the synthetic procedure) with carbonate ions. After equilibration, the solid was recovered, washed with de-ionised water and finally dried over P_4O_{10}.

MgAl-Cl-HTlc. The chloride form, having the formula $[Mg_{0.65}Al_{0.35}(OH)_2]Cl_{0.35}\cdot 0.68H_2O$, was obtained by titrating the carbonate form, dispersed in a 0.1 M NaCl (aq.) solution, with a 0.1 M HCl (aq.) solution by means of a Radiometer automatic titrator operating in pH stat mode at pH 5.

MgAl-ClO_4-HTlc. The perchlorate form, with the formula $[Mg_{0.65}Al_{0.35}(OH)_2](ClO_4)_{0.35}\cdot 0.6H_2O$, was obtained by equilibrating the chloride form with a 2 M $NaClO_4$ (aq.) solution (mass/volume ratio: 1 g/50 cm^3) at room temperature for 2 days. After the Cl^-–ClO_4^- exchange, the solid was washed with de-ionised, CO_2-free water and dried in a desiccator containing P_4O_{10}.

$MgAlO_x$. The mixture of magnesium and aluminum oxides used for the memory effect procedure was obtained by calcination of the Mg–Al hydrotalcite in carbonate form in a muffle furnace at 500 °C for 18 h, and stored over P_4O_{10}.

Preparation of the intercalation compounds

MgAl-3-CCA and MgAl-9-ACA. An equimolar physical mixture of 0.76 g coumarin-3-carboxylic acid (3-CCA) and 0.5 g $MgAlO_x$ was suspended in 80 ml of CO_2-free distilled water. The suspension was kept under N_2 and stirred for one day at room temperature. The solid was filtered, washed with CO_2-free distilled water and dried at room temperature (75% R.H.). The same procedure was employed to obtain MgAl-9-ACA, using 0.43 g of 9-anthracenecarboxylic acid.

MgAl-4-BBA. $MgAlO_x$ (0.5 g) was re-hydrated in 50 ml of CO_2-free distilled water at room temperature for 5 days. The suspension was maintained under an N_2 atmosphere in a well-sealed vessel. The $[Mg_{0.65}Al_{0.35}(OH)_2]OH_{0.35}\cdot 0.6H_2O$ thus obtained was separated from the solution, washed with anhydrous acetone three times and then suspended in 24 ml of a 0.1 M acetone solution of 4-benzoylbenzoic acid (4-BBA) for 5 days at room temperature. Finally, the products were filtered, washed with anhydrous acetone and dried over P_4O_{10}.

MgAl-2-NSA. Intercalation compounds containing 2-naphthalenesulfonate were prepared starting from both 2-naphthalenesulfonic acid (2-NSA1) and sodium 2-naphthalenesulfonate (2-NSA2). In the former case, 0.3 g of MgAl-CO_3 were titrated with 0.1 M aqueous 2-naphthalenesulfonic acid solution by means of an automatic titrator operating in pH stat mode at pH 5. In the latter case, 0.5 g of MgAl-Cl was dispersed in 35 ml of water–acetone 50% v/v solution 0.12 M in sodium 2-naphthalenesulfonate for 2 days at room temperature. The recovered solids were washed with water and water–acetone mixture, respectively, and dried at room temperature (75% R.H.).

Preparation of co-intercalates

MgAl 9-ACA and 3-CCA system. A series of co-intercalation compounds were prepared by ion-exchange and reconstruction procedures. Sample **1** was prepared by equilibrating 1 g of MgAl-ClO_4 with 33 ml 0.05 M aqueous 9-ACA sodium salt solution at 80 °C for one day. The recovered solid, after washing, was again equilibrated with 33 ml of 0.05 M 3-CCA sodium salt solution and maintained at 80 °C for one day. The composite obtained was washed with CO_2-free distilled water and dried at room temperature (75% R.H.). Sample **2** was prepared using the same procedure, but the MgAl-ClO_4 was first equilibrated with 3-CCA and then with 9-ACA. Sample **3** was obtained by suspending 1 g of MgAl-ClO_4 in 66 ml of an aqueous solution containing 16.5 mmol of 3-CCA and 16.5 mmol of 9-ACA sodium salts at 80 °C for one day. The composite obtained was washed with CO_2-free distilled water and dried at room temperature (75% R.H.).

The memory effect was also used to prepare sample **4**. $MgAlO_x$ (1 g) was mixed with an equimolar mixture of solid 9-ACA and 3-CCA (3-CCA + 9-ACA/Al molar ratio equal to 1) in a mortar. The solid mixture was suspended in 167 ml of CO_2-free distilled water at 80 °C for 3 days. The composite was filtered, washed with de-ionised CO_2-free water and dried in a desiccator containing P_4O_{10}.

MgAl 4-BBA and 2-NSA system. $MgAlO_x$ (0.5 g) was re-hydrated in 50 ml of CO_2-free distilled water at room temperature for 5 days. The suspension was maintained under an N_2 atmosphere in a well-sealed vessel. The MgAl-OH thus obtained was separated from the solution and washed with anhydrous acetone three times. The solid was first equilibrated at room temperature for 1 day with 4.8 ml of a 0.05 M acetone solution of 4-BBA, recovered, washed with anhydrous acetone three times and then equilibrated, again for 1 day, with 4.8 ml of 0.05 M

2-NSA solution. This sequence was repeated five times to reach the ion-exchange capacity of the hydrotalcite. Finally, the product (sample **5**) was filtered, washed with anhydrous acetone and dried over P_4O_{10}.

Analytical procedures

A weighed amount of the sample ($\sim$100 mg) was dissolved in a few drops of concentrated HCl and diluted with water to 50 ml. The Mg and Al content of the HTlc was then obtained with standard EDTA titrations. Water, carbonate and chromophore contents of the solids were obtained by thermogravimetry. The quantification of chromophores in the various samples was performed spectrophotometrically by dissolving a weighed amount of the intercalated solids, as above. The extinction coefficients of each organic compound were obtained from standard solutions at the pH value corresponding to that of the dissolution mixture. The sum of the amounts of the intercalated guests was found to be in good agreement with that obtained by thermogravimetry. Chloride and perchlorate anion contents were analysed by ion chromatography.

Instrumentation

X-Ray powder diffraction (XRPD) patterns were recorded with a computer-controlled Philips 1710 diffractometer (40 kV, 20 mA), using a graphite monocromator.

Thermoanalytical characterisations were performed with a Stanton Redcroft 781 thermoanalyser operating with a 5 °C min^{-1} heating rate, under a flow of air.

UV-VIS absorption spectra were measured using a Perkin-Elmer Lambda 16 spectrophotometer equipped with an integration sphere for reflectance spectra recording. Excitation and emission spectra, corrected for the instrumental response, were acquired on a Spex Fluorolog F112 spectrophotofluorimeter. Fluorescence lifetimes were measured with a Spex Fluorolog-τ2 system, which uses the phase modulation technique (excitation wavelength modulated in the 1–300 MHz range; time resolution *ca.* 10 ps).

The frequency-domain intensity decay (phase angle and modulation *vs.* frequency) was analysed with global analysis software, which uses the L-M algorithm, as discussed by Beeckem *et al.*[20]

The ns laser photolysis experiments were performed using the third harmonic of a Nd:Yag laser (λ_{exc} = 355 nm, pulse width *ca.*10 ns and energy *ca.*1.5 mJ $pulse^{-1}$[13]). Diffuse reflectance laser flash photolysis spectra and triplet lifetimes were measured with a home-made accessory for reflectance measurements.

Results and discussion

Structural and chemical characteristics of the host and molecular formulae of guests. The layered host used in the present work belongs to the family of hydrotalcite-like anionic clays and was prepared by thermally induced hydrolysis of urea in a clear solution containing magnesium and aluminum chlorides[19] in the molar ratio 2 to 1. The well-crystallised solid obtained has the empirical formula $[Mg_{0.65}Al_{0.35}(OH)_2]$-$(CO_3)_{0.175}·0.5H_2O$. The composition of the brucite-type layer is reported in square brackets and the charge balancing carbonate anions, located in the interlayer region, in round brackets. Notwithstanding the relatively high Al content of the brucite layer, there is no evidence of phase separation of boehmite. In fact, the XRPD patterns of the compound, shown in Fig. 1(a), can be indexed on the basis of a hexagonal unit cell with parameters a = 3.044 and c = 22.703 Å. Furthermore, the stoichiometric molar ratio between aluminum and carbonate of 2 indicates that, within the experimental errors, all the Al cations are located in the brucite layer. The 003 X-ray reflection gives an interlayer distance of 7.58 Å. Taking into account that the thickness of the brucite-type layer is evaluated[4,21] at 4.4 Å, the gallery, where the carbonate ions are located, has a height of 3.2 Å. It is 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 reactions.[5] Two procedures have been followed to insert the chromophore anions into the interlayer region of the layered host. The first procedure involves the replacement of carbonate anions with chloride or perchlorate anions (see Experimental) to obtain MgAl-Cl- and MgAl-ClO_4-HTlc, whose XRPD patterns are reported in Fig. 1(b) and (c). These compounds with counter anions more easily exchangeable than carbonates were then used as starting materials for the incorporation of chromophores *via* ion-exchange reactions. The second procedure takes advantage of the so-called "memory effect" of hydrotalcites.[22] This effect, typical of MgAl-CO_3, concerns the possibility of reconstructing the layered structure when the HTlc, previously heated at 350–500 °C, is dispersed in water or in a solution of anions. At these temperatures, the MgAl-CO_3 transforms into a mixture of magnesium and aluminum oxides that have "memory" of the original layered structure.[22,14] In the presence of water, the mixture of oxides regenerates the double hydroxide in the form of brucite-like sheets and the positive charges are balanced by OH^- counter ions. If the reconstruction is conducted in a solution containing the chromophores, these can be incorporated between the layers to produce the intercalation compounds.

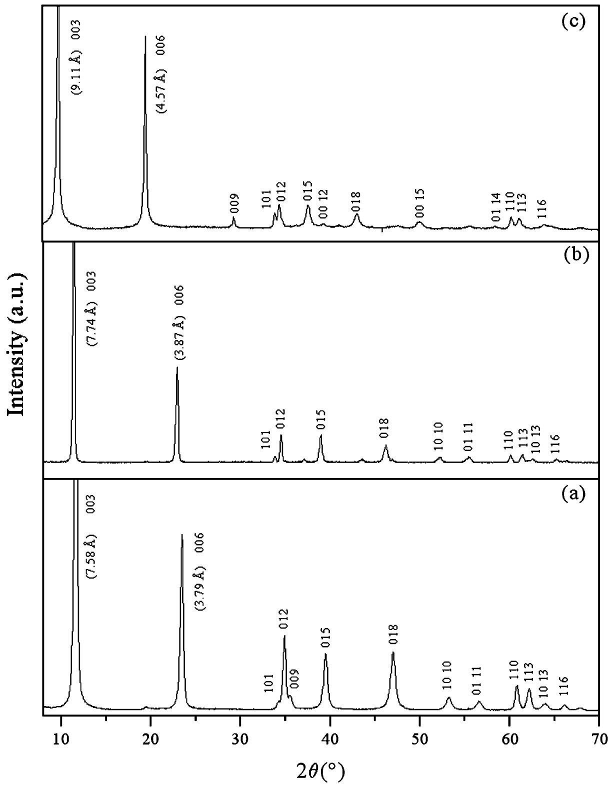

Fig. 1 XRPD patterns of (a) $[Mg_{0.65}Al_{0.35}(OH)_2](CO_3)_{0.175}·0.5H_2O$, (b) $[Mg_{0.65}Al_{0.35}(OH)_2]Cl_{0.35}·0.68H_2O$ and (c) $[Mg_{0.65}Al_{0.35}(OH)_2]$-$(ClO_4)_{0.35}·0.6H_2O$.

The structural formulae, chemical names and acronyms of the chromophores used are reported in Fig. 2. The molecules possess a carboxylic or sulfonic acid group and the corresponding anions may be located in the interlayer region of the host to compensate for the positive layer charge. Furthermore, 3-CCA and 9-ACA can act as an energy donor–acceptor pair and 4-BBA acts as an energy donor towards 2-NSA, which acts as an acceptor.[23]

Intercalation compounds of Mg-Al-HTlc and chromophores with carboxylic acid functions. Intercalation by ion-exchange

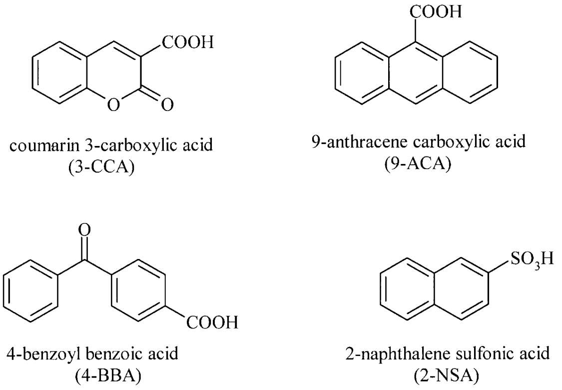

Fig. 2 Structural formulae, chemical names and acronyms of the chromophores intercalated into Mg–Al hydrotalcites.

procedures of these guests requires pH values at which the deprotonated forms of the guests are the predominant species. At these pH values, generally higher than 9, contamination by carbonates may be a problem, and a slight dissolution of the host may occur. Incorporation of chromophores with carboxylic acid functions was attempted, taking advantage of the above-mentioned "memory effect" of the HTlc. The host, in carbonate form, was calcined at 500 °C and the mixture of oxides obtained was regenerated in water in the presence of a stoichiometric amount of the chromophores (see Experimental).

Fig. 3 shows the XRPD patterns of the composites obtained. Note the loss in crystallinity degree of the composites when compared with that of the pristine host in carbonate form [see Fig. 1(a)]. The quality of the patterns does not permit a structural analysis of the materials. However, it is generally accepted that the intercalation compounds maintain the structure of the layers of the original host and that the layers move apart to make room for guest species.[3] Therefore, the first strong reflection at a low 2θ value in the XRPD pattern is attributed to the scattering of the dense layer planes and the corresponding d value gives the interlayer distance. In many instances, two or more strong reflections at low 2θ values are observed, and these are attributed to intercalated phases that may differ either in the amount of guest per mol of host, or in hydration or orientation of the guest. If the intercalation process is incomplete, it is possible to find from the XRPD pattern the interlayer distances of both the intercalated and original phases. In the present case, intercalation of 3-CCA and 9-ACA gives rise to single phases (see Fig. 3) with interlayer distances of 17.9 and 20.4 Å, respectively. The XRPD pattern of MgAl-4-BBA shows two basal spacings (and their second order reflections), indicating the presence of two different phases with interlayer distances of 21 and 26 Å, respectively, probably due to a different orientation of the guest anion in the interlayer region.

Thermogravimetric analysis (see Fig. S1, ESI) indicates that all the samples reach a constant weight at temperatures higher than 600 °C, due to the formation of MgO and $MgAl_2O_4$. The decomposition of the organic components occurs with a marked exothermic effect between 250 and 600 °C. The loss of co-intercalated water occurs between room temperature and 250 °C. Table 1 reports the compositions of the materials, derived from weight loss curves, their interlayer distances and gallery heights, obtained by subtracting the sheet thickness (4.4 Å) from the interlayer distance. A possible arrangement of the guest species in the interlayer region may be obtained by assuming that (i) the layer structure of the host remains practically unchanged after the reconstruction and intercalation procedures and (ii) the carboxylate anion of the guest is oriented with the $C–COO^-$ bond almost perpendicular to the layer plane and interacts with the positive charge due to the presence of aluminum atoms. According to these hypotheses, and with the aid of the Hyperchem programme, it was possible to build up models of the intercalates that reproduce the experimental interlayer distances. As an example, Fig. 4 shows a model of the MgAl-3-CCA intercalate. The guests are accommodated as a monofilm of interdigitated species and interact with each others through π–π interactions between the coumarin benzene rings. A similar disposition of the guest species was found in the case of the ZnAl-HTlc Methyl Orange intercalate.[12]

Intercalation compounds of Mg-Al-HTlc and 2-naphthalene-sulfonate. Two different composites were prepared. The

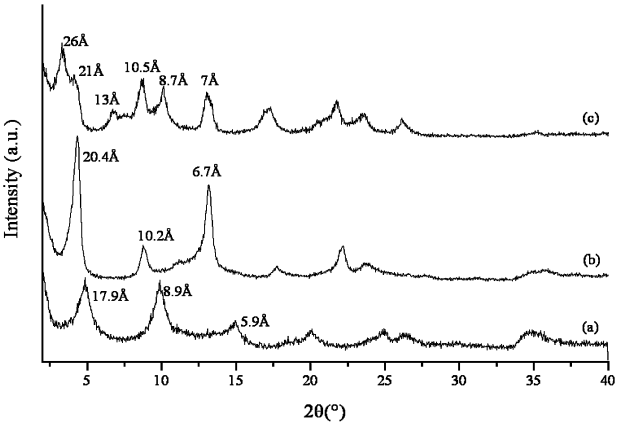

Fig. 3 XRPD patterns of dried intercalation compounds: (a) MgAl-3-CCA, (b) MgAl-9-ACA, (c) MgAl-4-BBA.

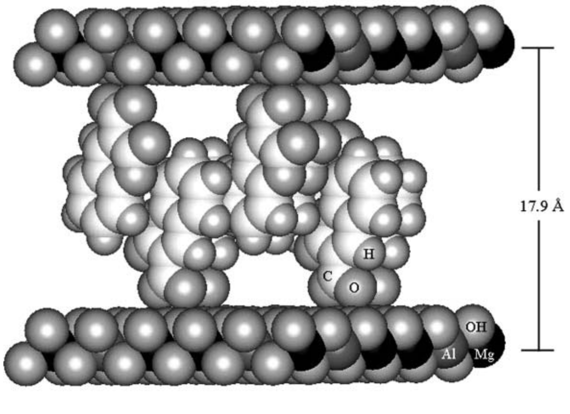

Fig. 4 Computer-generated model, showing the most probable arrangement of 3-CCA anions between the HTlc layers.

Table 1 Compositions, interlayer distances and gallery heights of intercalation compounds of MgAl-HTlc with the indicated chromophores

Sample	Composition	Interlayer distance/Å	Gallery height/Å
MgAl-3-CCA	$[Mg_{0.65}Al_{0.35}(OH)_2](3CC)_{0.35}\cdot 2H_2O$	17.9	13.5
MgAl-9-ACA	$[Mg_{0.65}Al_{0.35}(OH)_2](9CAN)_{0.35}\cdot 0.2H_2O$	20.4	16
MgAl-4-BBA	$[Mg_{0.65}Al_{0.35}(OH)_2](4BB)_{0.35}$	26–21	21.6–16.6
MgAl-2-NSA1	$[Mg_{0.65}Al_{0.35}(OH)_2](2\text{-}NSA)_{0.22}(SO_4)_{0.065}\cdot 1.42H_2O$	18	13.6
MgAl-2-NSA2	$[Mg_{0.65}Al_{0.35}(OH)_2](2\text{-}NSA)_{0.22}(Cl)_{0.13}\cdot 0.73H_2O$	18	13.6

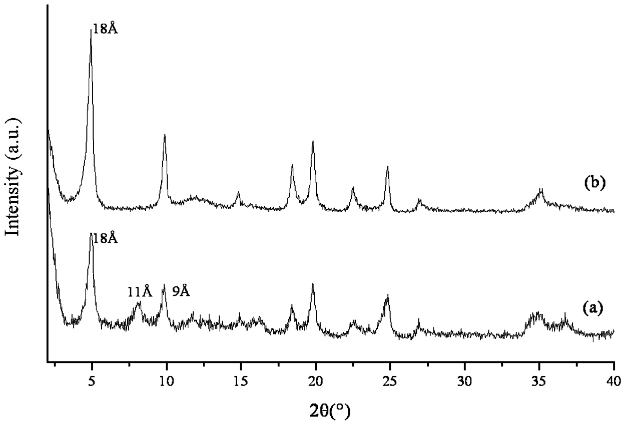

Fig. 5 XRPD patterns of the (a) MgAl-2-NSA1 and (b) MgAl-2-NSA2 intercalation compounds.

sample MgAl-2-NSA1 was obtained by titrating MgAl-CO_3 with a solution of 2-naphthalenesulfonic acid (this commercial solution contains about 25% free sulfuric acid) at pH stat = 5. Complete replacement of the carbonates by naphthalenesulfonate and sulfate anions was obtained, and the XRPD patterns of the sample, reported in Fig. 5(a), show the co-existence of the sulfate (interlayer distance 11 Å) and naphthalenesulfonate (interlayer distance 18 Å) forms of the HTlc. The sample MgAl-2-NSA2 was obtained by equilibrating MgAl-Cl with a sodium 2-naphthalenesulfonate solution. Almost complete exchange of chloride with sulfonate anions was attained. The XRPD pattern [see Fig. 5(b)] of the sample shows the presence of a single phase with an interlayer distance of 18 Å, and good crystallinity. The weight loss below 250 °C can be attributed to the loss of co-intercalated water, whereas the weight loss between 250° and 600 °C is due to combustion of the organic component; the abrupt weight loss at 950 °C can be attributed to the thermal decomposition of $MgSO_4$. At 1000 °C, the solid consists of MgO and $MgAl_2O_4$ (see Fig. S2, ESI). Table 1 reports the chemical compositions of the solids derived from thermogravimetry, their interlayer distances and gallery heights (see Fig. S3, ESI).

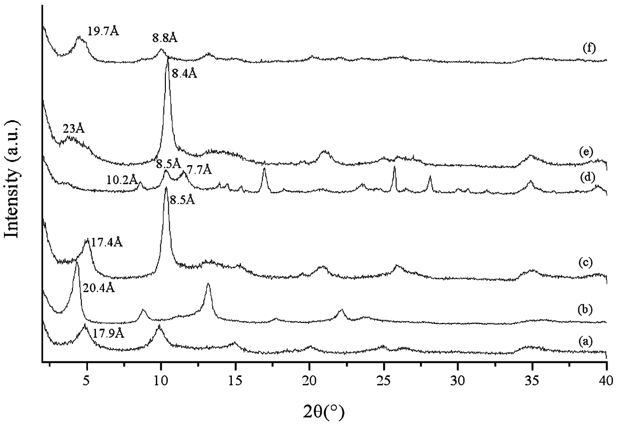

Fig. 6 XRPD patterns of the (a) MgAl-3-CCA and (b) MgAl-9-ACA intercalation compounds, and (c) sample **1**, (d) sample **2**, (e) sample **3** and (f) sample **4** (see Table 2).

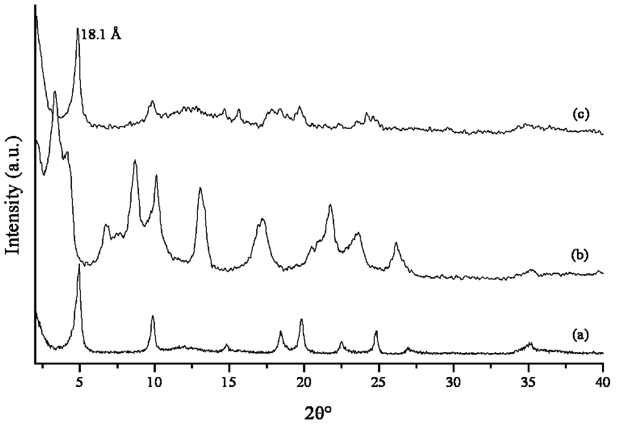

Fig. 7 XRPD patterns of the (a) MgAl-2-NSA2 and (b) MgAl-4-BBA intercalation compounds, and (c) sample **5** (see Table 2).

Nanostructured materials obtained by co-intercalation of 3-CCA and 9-ACA. The various attempts to co-intercalate the donor–acceptor pair of chromophores 3-CCA and 9-ACA into Mg-Al HTlc are described in detail in the Experimental. Table 2 reports the synthetic procedures used, the chemical compositions of the products, and the identifying numbers of the samples. Fig. 6 shows the XRPD patterns of the different samples and those of MgAl-3-CCA and MgAl-9-ACA. In samples **1**, **2** and **3**, obtained by ion-exchange procedures, the amount of intercalated 3-CCA is much higher than the 9-ACA content, even though equimolar amounts of guests were present in the equilibrating solution. This indicates that the host has a strong preference for coumarin. The XRPD patterns of these samples are difficult to interpret. The crystallinity is very low, indicating disorder in the packing of the anions. However, the XRPD patterns of the co-intercalated samples show the presence of MgAl-9-ACA and MgAl 3-CCA phases, the latter phase being predominant. Sample **4**, obtained by taking advantage of the "memory effect", contains an equimolar amount of the guests. Moreover, its XRPD patterns [Fig. 6(f)] indicate the presence of a phase with interlayer distance 19.7 Å, a value intermediate between the interlayer distances of coumarin (17.9 Å) and anthracene (20.4 Å) intercalates.

Nanostructured materials obtained by co-intercalation of 4-BBA and 2-NSA. As already described, the intercalation compound containing 4-BBA was obtained by means of the "memory effect" of the hydrotalcite. For this reason, the co-intercalation of 4-BBA and 2-NSA was carried out with the same procedure (see Experimental). The XRPD pattern of the composite obtained (sample **5**) is reported in Fig. 7 and compared with those of the MgAl-4-BBA and MgAl-2-NSA2 samples. It can be seen that the XRPD spectrum of the co-intercalated sample [Fig. 7(c)] is similar to that of the

Table 2 Synthetic procedure, composition and molar ratio of the chromophores in the solid of the indicated co-intercalation composites

Sample	Synthetic procedure[a]	Composition	Molar ratio of the chromophores in the solid
1	I.E.	$[Mg_{0.65}Al_{0.35}(OH)_2](9\text{-}ACA)_{0.043}(3\text{-}CCA)_{0.232}(CO_3)_{0.034}\cdot 0.38H_2O$	5.4[b]
2	I.E.	$[Mg_{0.65}Al_{0.35}(OH)_2](9\text{-}ACA)_{0.06}(3\text{-}CCA)_{0.254}(CO_3)_{0.018}\cdot 0.21H_2O$	4.2[b]
3	I.E.	$[Mg_{0.65}Al_{0.35}(OH)_2](9\text{-}ACA)_{0.058}(3\text{-}CCA)_{0.192}(CO_3)_{0.05}\cdot 0.24H_2O$	3.3[b]
4	H	$[Mg_{0.65}Al_{0.35}(OH)_2](9\text{-}ACA)_{0.143}(3\text{-}CCA)_{0.152}(CO_3)_{0.028}\cdot 0.34H_2O$	1.1[b]
5	H	$[Mg_{0.65}Al_{0.35}(OH)_2](4\text{-}BBA)_{0.133}(2\text{-}NSA)_{0.135}(SO_4)_{0.041}\cdot 0.46H_2O$	1[c]

[a] I.E.: ion exchange; H: re-hydration. [b] 3-CCA/9-ACA. [c] 2-NSA/4-BBA.

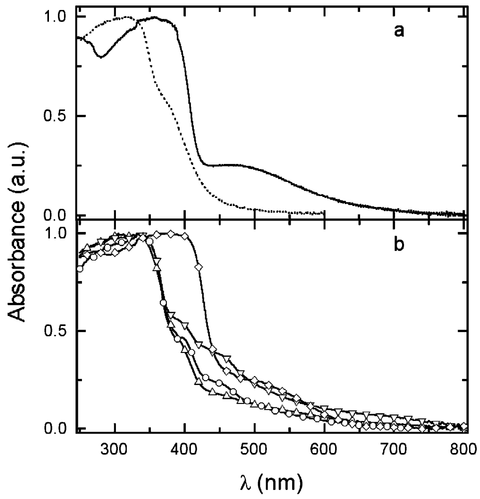

Fig. 8 Absorption spectra of (a) intercalation compounds of MgAl-HTlc with 9-ACA (full line) and 3-CCA (dashed line), and (b) co-intercalation composites reported in Table 2: sample **1** (○), sample **2** (Δ) sample **3** (∇) and sample **4** (◊).

compound containing only 2-NSA. However, thermogravimetric and chemical analyses indicate that 2-NSA and 4-BBA are present in the molar ratio 1 (see Table 2). It seems that the MgAl-2-NSA phase is able to solubilise the 4-BBA guest with little change in the crystal structure.

Photophysical characterisation

Absorption and emission spectra. The absorption spectra of 9-ACA and 3-CCA intercalated into MgAl-HTlc are reported in Fig. 8(a). The spectrum of intercalated 3-CCA, located in the same spectral region as that of the pure solid, has a maximum (λ_{max}) around 350 nm and a shoulder near 380 nm. The absorption of intercalated 9-ACA results in a main maximum at 360 nm (50 nm blue-shifted compared to that for pure microcrystals) and a second maximum at about 490 nm. The latter band is broad and unstructured, and might indicate the formation of anthracene aggregates favoured by the confinement of the aromatics within the restricted space of the host interlayer region. The red-shifted absorption and emission spectra in Shpolskii solutions,[24] in vitreous solutions of non-polar aliphatic hydrocarbons[25] and in zeolites[26] were explained by the formation of anthracene aggregates. It should be noted that the interlayer region has a specific role in inducing the formation of aggregates, since, for pure solid anthracene, no spectral evidence of aggregation could be observed.

The absorption spectra of co-intercalated systems (3-CCA–9-ACA), prepared in four different ways, are reported in Fig. 8(b). The spectra reflect the relative amounts of the two guests, which depend on the preparation method (see Experimental). However, in the 400–500 nm range, there are spectral features which cannot be explained by the sum of the relative contributions of the two singly intercalated chromophores. In particular, the spectrum obtained by weighted summation of the absorption spectra of the singly intercalated compounds did not reproduce the spectrum recorded for the co-intercalated compounds in the 400–500 nm region, thus indicating the occurrence of specific interactions between the 9-ACA and 3-CCA molecular anions.

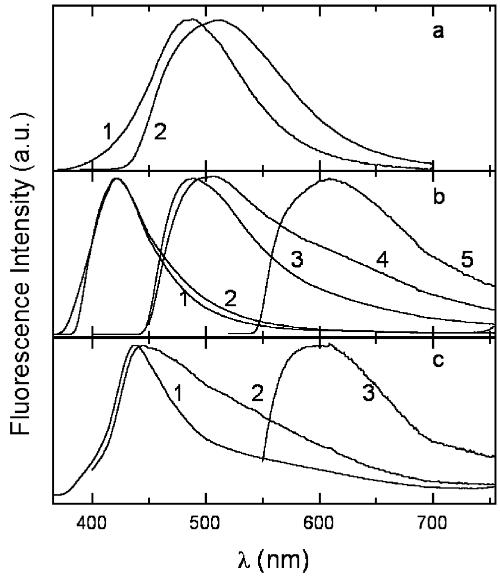

Fig. 9 Emission spectra of (a) intercalation compounds of MgAl-HTlc with 3-CCA (1) and 9-ACA (2) using λ_{exc} = 366 nm, (b) sample **2** composite (see Table 2) excited at λ_{exc} = 313 (1), 366 (2), 403 (3), 420 (4) and 500 nm (5), and (c) sample **4** composite (see Table 2) excited at: λ_{exc} = 313 (1), 366 (2) and 520 nm (3).

The fluorescence spectra of the mono-intercalated materials in the 450–600 nm range are reported in Fig. 9(a). Both of them are unstructured and present large half-widths (3940 and 4500 cm^{-1} for 3-CCA and 9-ACA, respectively). As observed for the absorption spectrum, the emission spectrum of MgAl-9-ACA is red-shifted compared to the corresponding spectrum of MgAl-3-CCA. Unlike the cases for Methyl Orange[12] and fluorescein[13] both 9-ACA- and 3-CCA-intercalated systems present red-shifted emission spectra with respect to the pure solids (40 and 80 nm for 9-ACA and 3-CCA, respectively). Therefore, the matrix is able to impose a spacial arrangement on the molecules. Since the fluorescence maximum of pure 3-CCA microcrystals is coincident with that at pH 5 (where the acid form is prevalent), and that of the intercalated sample is the same as that at pH 12, it seems likely that 3-CCA is present in anionic form in the mono-intercalated material. For the co-intercalated materials, the features of the emission spectra are strongly dependent on the excitation wavelength and on the 3-CCA/9-ACA ratio inside the interlayer region.

Sample **2** containing 3-CCA and 9-ACA in the molar ratio 4.2, excited at 313 and 366 nm, gives rise to an emission around 420 nm that resembles that of 3-CCA in the acidic form. Excitation at 403 nm produces an emission that seems to be a mixture of the emission spectra of the two intercalated dyes because the fluorescence of 3-CCA looks like that of the anionic form (λ_{max} = 500 nm). The emission spectrum becomes more similar to that of 9-ACA, with a shoulder at about 600 nm, when the sample is excited at 420 nm. This shoulder becomes an intense and large band on excitation at 460 nm [Fig. 9(b), curve 5], where the presumed absorbing species (see discussion on the absorption spectra) is an aggregate of 9-ACA. The fluorescence spectra confirm that the interlayer region forces anthracene molecules to aggregate. A similar emission, but at shorter wavelengths, was reported for anthracene in zeolites and was attributed to anthracene dimers whose formation was favoured by the presence of Na^+ ions.[26]

Fig. 9(c) shows the emission spectra of sample **4**, which has increased 9-ACA concentration compared to 3-CCA (see Table 2). This is reflected in the spectrum obtained by excitation at 313 nm, where, in addition to the 3-CCA emission around 420 nm, a low shoulder is observable in the emission region of 9-ACA. The 9-ACA fluorescence increases on excitation at 366 nm (curve 2), while when the excitation is at 520 nm, the emission of aggregate appears.

Fluorescence lifetime measurements were carried out on mono-intercalated solids and on co-intercalated samples **1** and **4**. The results are reported in Table 3.

The fluorescence decays are, in general, multi-exponentials. The decays of the mono-intercalated samples fit a bi-exponential

Table 3 Fluorescence decay times of MgAl-9-ACA, MgAl-3-CCA and of composites obtained by co-intercalation in MgAl-HTlc (see Table 2)

Sample	λ_{exc}/nm	λ_{em}/nm	τ_F/ns	A_i (%)
3-CCA	333		$\tau_1 = 0.81 \pm 0.05$	61
			$\tau_2 = 4.7 \pm 0.4$	39
9-ACA	366		$\tau_1 = 0.14 \pm 0.03$	62
			$\tau_2 = 5.1 \pm 0.4$	38
	480	>490	$\tau_1 = 0.038 \pm 0.006$	99
			$\tau_2 = 150 \pm 50$	1
Sample **1**	370	>390	$\tau_1 = 0.29 \pm 0.03$	99.1
			$\tau_2 = 3.9 \pm 0.02$	0.7
			$\tau_3 = 180 \pm 30$	0.2
	420	>440	$\tau_1 = 0.22 \pm 0.03$	91.4
			$\tau_2 = 2.66 \pm 0.15$	8.4
			$\tau_3 = 210 \pm 30$	0.2
	470	>490	$\tau_1 = 0.49 \pm 0.04$	93.6
			$\tau_2 = 3.6 \pm 0.4$	6.2
			$\tau_3 = 77 \pm 25$	0.2
Sample **4**	360	>390	$\tau_1 = 0.037 \pm 0.006$	99.2
			$\tau_2 = 1.7 \pm 0.07$	0.75
			$\tau_3 = 18 \pm 1.4$	0.05
	420	>440	$\tau_1 = 0.17 \pm 0.04$	95.4
			$\tau_2 = 2.6 \pm 0.3$	4.4
			$\tau_3 = 66 \pm 13$	0.2
	470	>490	$\tau_1 = 0.24 \pm 0.02$	97.5
			$\tau_2 = 2.97 \pm 0.30$	2.38
			$\tau_3 = 154 \pm 40$	0.08

function satisfactorily. The pre-exponential factors show that, in both cases, the shorter-lived contribution is predominant. Presumably, the bi-exponential decay is the result of a distribution of lifetimes caused by the different environments. When the MgAl-9-ACA sample is excited in the band attributed to the anthracene aggregate and the emission is recorded at $\lambda > 490$ nm, the fluorescence decay is dominated (99%) by a species (probably the anthracene aggregate) with 0.038 ns lifetime.

The decays of the two co-intercalated samples satisfactorily fit a tri-exponential function. However the short-lived component has an abundance higher than 90%.

The fluorescence decay has a complex behaviour originated by the different microenvironments of the fluorophores and the different preparation methods. For instance, it can be seen that in both cases (samples **1** and **4**), for observation at $\lambda > 490$ nm (excitation at 470 nm) the lifetimes are much longer than those measured for mono-intercalated samples. This behaviour should be determined by the interactions between the two different chromophores in the interlayer region.

The absorption spectra of MgAl-4-BBA, MgAl-2-NSA and of the composite containing the two chromophores were recorded (see Fig. S4, ESI). The spectrum of sample **5** resembles the sum of those of the mono-intercalated samples, suggesting that no ground-state interactions occur in the co-intercalated composite, or that any that do occur are weak. In the case of the MgAl-2-NSA system, the emission spectrum centred at 420 nm is due to the fluorescence of 2-NSA, while for MgAl-4-BBA, a structured spectrum centred at 460 nm, assigned to the phosphorescence of 4-BBA, is observed (see Fig. S5, ESI). In both cases, the spectra are not affected by changes in the excitation wavelength in the range 313–366 nm. Upon excitation at these wavelengths of the co-intercalated sample **5** (molar ratio 4-BBA/2-NSA = 1.0), a spectrum is recorded, with a maximum at 420 nm (see Fig. S5, ESI), which is identical to that of mono-intercalated 2-NSA and it is not affected by the excitation wavelength. The phosphorescence of 4-BBA was not observed for sample **5**, even when exciting at 366 nm, where the major absorption is due to 4-BBA. These findings suggest a quenching process involving the triplet state of 4-BBA. The emission decay times, recorded on MgAl 2-NSA and on sample **5**, are presented in Table 4. The decays could be satisfactorily fitted by a tri-exponential function and, in both samples, the shortest living component presented the major contribution.

Table 4 Fluorescence decay times for MgAl-2-NSA and the composite obtained by co-intercalation in MgAl-HTlc (see Table 2)

Sample	λ_{exc}/nm	λ_{em}/nm	τ_F/ns	A_i (%)
2-NSA	330	>370	$\tau_1 = 0.15 \pm 0.05$	96
			$\tau_2 = 1.6 \pm 0.05$	2.9
			$\tau_3 = 8.0 \pm 0.6$	1.1
Sample **5**	330	>370	$\tau_1 = 0.20 \pm 0.03$	94.8
			$\tau_2 = 2.4 \pm 0.2$	4.9
			$\tau_3 = 30.2 \pm 4$	0.3

Comparison of the decay time values obtained for MgAl-2-NSA and sample **5** suggests that there are no singlet–singlet interactions between 2-NSA and 4-BBA in the co-intercalated composite. Therefore, the quenching of the 4-BBA phosphorescence can be tentatively assigned to an energy transfer process from the phosphorescent 4-BBA triplet to the non-phosphorescent triplet of 2-NSA.

Laser flash photolysis experiments. *3-CCA–9-ACA pair.* Laser flash photolysis experiments were performed to detect possible transient species (triplets and/or radicals) formed by laser excitation of the composite materials. Upon excitation of sample **4** (molar ratio 3-CCA/9-ACA = 1.1), a transient absorption with a lifetime of 50 μs was observed (see Fig. S6, ESI); perusal of the time-resolved spectra permits the transient to be attributed to the lowest triplet state of 9-ACA because its spectral features correspond to those of well-known triplets of anthracene derivatives.[27] On excitation of sample **1** (with a 3-CCA/9-ACA molar ratio of 5.4), in which the light is preferentially adsorbed by 3-CCA, the transient observed was attributed to 3-CCA and no trace of the 9-ACA spectrum appeared. On the basis of these observations, it is possible to conclude that in the 3-CCA and 9-ACA co-intercalated samples, no evidence of energy transfer processes could be detected.

4-BBA–2-NSA pair. Transient absorption experiments were performed for the mono- and co-intercalated samples; the time-resolved spectra are reported in Fig. 10. For the MgAl-2-NSA system, a transient with the absorption maximum at 460 nm and a lifetime of 110 μs was detected. The transient was attributed to the 2-NSA lowest triplet state on the basis of its lifetime and taking into account that, in solution, the triplet–triplet absorption of naphthalene and its derivatives is in the range 420–440 nm.[27]

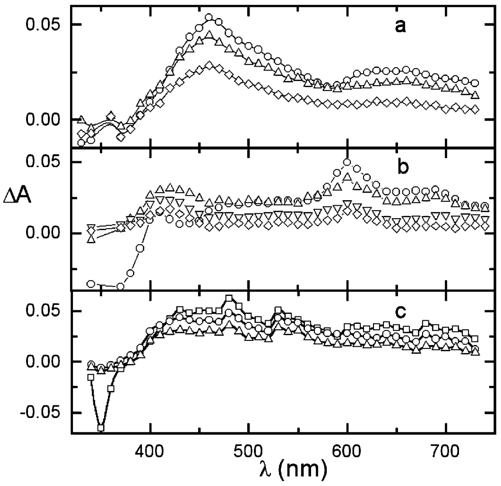

Fig. 10 Time-resolved absorption spectra: (a) MgAl-2-NSA recorded at 7.0 (○), 24 (Δ) and 76 μs (◊) after the laser pulse; (b) MgAl-4-BBA recorded at 3.0 (○), 6.0 (Δ), 40 (∇) and 80 μs (◊) after the laser pulse; (c) sample **5** (see Table 2) recorded at 5.6 (□), 33 (○) and 75 μs (Δ) after the laser pulse (λ_{exc} = 355 nm).

Laser excitation of MgAl-4-BBA produced a transient with a maximum at 600 nm which, due to the position of the triplet of benzophenone and its derivatives in several solvents (about 520–540 nm), was attributed to the 4-BBA triplet.

Excitation at 355 nm of the co-intercalated 4-BBA–2-NSA generates the spectrum shown in Fig. 10(c). Note that the maximum resembles that of 2-NSA and the absence of the 4-BBA triplet absorption. This observation could be an indication of triplet–triplet energy transfer from 4-BBA to 2-NSA, similar to the classical experiment carried out by Terenin with benzophenone and naphthalene.[28]

Conclusion

The work described herein confirms the remarkable ability of hydrotalcite-like compounds to intercalate organic chromophores of different sizes and shapes. Even pairs of chromophores with donor–acceptor properties have been inserted in the interlayer region of the MgAl HTlc. Samples containing the two chromophores in different molar ratios, as a result of different synthetic procedures, have been obtained. However, the synthetic control of the co-intercalation process requires further improvement, since homogeneous distribution of the two guests in the interlayer region was only possible for the 2-NSA–4-BBA composite.

The photophysical responses of the intercalated or co-intercalated chromophores provide details of their interlayer organisation. The absorption and emission spectra give indications that the confinement of the anthracenecarboxylic acid within the restricted space of the interlayer region of hydrotalcites favours aggregate formation. For the co-intercalated 3-CCA–9-ACA the fluorescence spectra are strongly dependent on the excitation wavelength and on the ratio of the two guests inside the interlayer region, determined by the preparation method. The fluorescence decays of mono- and co-intercalated materials are, in general, satisfactorily fit by bi-exponential and tri-exponential functions, respectively. The poly-exponential decays are probably the result of a distribution of lifetimes caused by the different environments. In the co-intercalated 4-BBA–2-NSA material, laser flash photolysis experiments seems to indicate the occurrence of an energy transfer process.

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