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Luminescent N-heterocycles based molecular backbone interleaved into LDH and polymer: for an extensive study

- 3
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Graphical Abstract



| 11 | Highlights |
|----|--|
| 12 | • Pyrazino-1,3a,6a-triazapentalene dye type structure was intercalated into LDH by co- |
| 13 | precipitation method |
| 14 | Absolute photoluminescent quantum yields of pristine dye and LDH nanohybrid were |
| 15 | compared |
| 16 | • Luminescent composite films were prepared with the LDH nanohybrid filler |
| 17 | • Optical properties of the composite films were characterized for potential lighting |
| 18 | devices |
| 19 | Keywords |
| 20 | Layered double hydroxides; Dye; Intercalation; Fluorescence; Composite films. |
| 21 | Abstract |
| 22 | A pyrazino-1,3a,6a-triazapentalene dye-based molecule was intercalated by direct co- |
| 23 | precipitation method into the galleries of negatively charged layered double hydroxide (LDH) |
| 24 | to form a new luminescent LDH filler. The materials of cation composition Zn/Al = 2 lead to |
| 25 | well-defined organic inorganic assemblies. The structure of the hybrid materials was |
| 26 | characterized by X-ray diffraction (XRD), Fourier-transform infrared spectra (FTIR) and UV- |
| 27 | visible spectra. Optical properties of the materials, at both solid state and slurry state, were |
| 28 | also recorded and absolute photoluminescent quantum yields (PLQY) were determined |
| 29 | showing that the nanohybrid LDH slurry exhibited higher luminescence properties under UV |

31 films by dispersion in both hydrophobic or hydrophilic polymer matrix such as poly(dimethyl

excitation than the corresponding LDH powder. LDH fillers were used to prepare composite

30

32 siloxane) (PDMS) and poly(ethylene oxide) (PEO), respectively. Composite films were

characterized by Small Angle X-ray Scattering (SAXS) and PLQY were recorded in order to
compare the behaviour of the nanohybrid LDH filler in both polymer matrices. It was found
that the aggregation of particles is still observed by SAXS.

36 1. Introduction

It is a long-time tradition to use/mix clay minerals with dye molecules, this in particular for coloring used in Egyptian, Maya time, as beautifully exemplified with the famous «blue Maya» as well as for the dye immobilization for water treatment. Both domains were extensively covered with book chapters and reviews(Schoonheydt et al., 2018; Sen, 2017) and are beyond the scope of the present study focusing on advanced sustainable development in lighting devices.

It is known that optical properties may inform on the location and accommodation of the
guest organic molecule into or onto the clay mineral as recently reported for laponite and
fluorescent dye Safranine simply aggregated or built as Langmuir-Blodgett film (Saha et al.,
2017).

As far as clay mineral and organic dye molecule are concerned, polymer may also play a role in dispersion the aggregated assembly as in polyamide fibers for clothes application using montmorillonite (Mmt) (Almasian et al., 2019) or layered double hydroxide (LDH) with azodye (Hajibeygi and Omidi-Ghallemohamadi, 2017). Interesting work is also focused on very specific application as those regarding active food packaging polymer, where fluorescent hemicyanine dye-modified Mmt is solvent cast with chitosan to yield bio-nanocomposite films (Mekhzoum et al., 2016).

54 Concerning LDH, their structure is referred to the natural hydrotalcite mineral, and described 55 with the ideal formula, $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]$ $[A^{m}_{x/m} \cdot nH_{2}O]$, where M^{II} and M^{III} are metal cations,

A^{m-} the interlayered anions, the x value determines the charge density of the LDH and n mol of water molecules per formula weight are also located. Indeed, the isomorphic substitution of M^{II} with M^{III} cations in the brucite-like sheet gives rise to positive electrical charges balanced by exchangeable anions (A^{m-}) leading to the well-known anion exchange/uptake LDH ability.

61 To date, pioneer works conducted by the group of U. Costantino were at first performed to 62 better understand the host / guest interaction and sometimes to address the location of the 63 organic dye, adsorption versus intercalation by scrutinizing the emission fluorescence and 64 the associated emitting state energy coming from the possible interactions between the 65 excited species of the dye molecule and the neighboring unexcited LDH host structure. This was exemplified with azoic dye methyl orange (MO) into LDH (Zn₂Al cation composition) for 66 67 which the fluorescence of MO interleaved into LDH was found close to MO itself but shifted at higher energies (Costantino et al., 1999), with the xanthene dye fluorescein surface-68 69 immobilized or intercalated into LDH (Zn₂Al), where a dual approach using computer 70 modeling and diffuse reflectance experiments helped in describing guest arrangement 71 (Costantino et al., 2000). Their approach was extended to phenolphthalein Zn₂Al hybrid 72 materials for which space-resolved fluorescence imaged the dyes distribution and their interactions with LDH platelets (Latterini et al., 2002), to a series of chromophores, 73 74 coumarin-3-carboxylic acid (3-CCA), 9-anthracenecarboxylic acid (9-ACA), 4-benzoylbenzoic 75 acid (4-BBA) and 2-naphthalenesulfonic acid (2-NSA) (Aloisi et al., 2002), as well as covering 76 the emerging aspect of fluorescent filler mostly for hydrophobic polymers with antimicrobial and photo-catalytic applications (Costantino et al., 2013) or simply for mechanical 77 78 reinforcement (Marangoni et al., 2008).

79 After this gain in understanding the interaction between LDH and organic dye molecules, more recent study focus merely on applicative properties such as emphasizing on the 80 81 tunable photoluminescent film using both fluorescein (FLU) and 1-heptanesulfonic acid 82 sodium (HES) / Zn2Al hybrid materials for the electro-catalysis of dopamine (Shi et al., 2010). 83 A step further concerns multicolor light-emitting ultrathin films that were built from Mg₂Al 84 LDH hosting photo-functional anions such as bis(N-methylacridinium)@polyvinylsulfonate 85 ion pairs and derivatives of poly(p-phenylene), poly(phenylenevinylene), and 86 poly(thiophene) showing a well-defined multicolor polarized fluorescence in association to 87 high polarization anisotropy thus making them of interest in light displays and optoelectronic 88 devices (Yan et al., 2011). In the same vein, flexible and robust free-standing films including 89 LDH platelets disposed between poly(vinyl alcohol) (PVA) and a styrylbiphenyl derivative 90 (BTBS) via layer-by-layer (LBL) were found to exhibit luminescent anisotropy (Dou et al., 91 2013).

Again, facing new concerns for possible development of optical devices such as to be
economic, environmental friendly, rare-earth-free, and to address the life cycle assessment
and shelf-life and durability of use, all these prompt us to further study hybrid pigments.

These last years, a lot of interest has been carried out to design organic molecules with optical properties for sustainable alternatives of inorganic luminophores, usually composed with rare-earth elements. A lot of organic molecules exhibit very high luminescence property such as N-Heterocyclic compounds and find applications in wide range such as lighting devices (Weber et al., 2015; Zhang et al., 2008), cell imaging sensors (Gogoi and Sen Sarma, 2015; Mahajan et al., 2019; Volpi et al., 2018) or even dye-sensitized solar cells (Lu et al., 2018; Wu et al., 2019). Particularly, pyrazino-1,3a,6a-triazapentalene type organic backbone 102 has been identified and substituents are possibly attached to tune the optical properties 103 (antenna effect, shift of the absorption/emission spectra) (Sirbu et al., 2019). In terms of 104 tethering to any host structure, such substituents are the functional groups. Indeed, many 105 researches have proven that both the alkyl chain length and the nature of functional groups 106 could subtly and significantly impact the intermolecular interactions and molecular packing 107 and consequently the optical properties of the dye at solid state or in concentrated solutions 108 (Davis et al., 2008; Kumar et al., 2014). The present study is focus on a dye with a pyrazino-109 1,3a,6a-triazapentalene based molecular backbone and 5-hexynoic acid as substituent, this 110 dye hereafter called compound "PTPH" in the following. The functionalized antenna of PTPH 111 allows its intercalation within a LDH matrix thanks to the bonds occurring between the 112 hydroxyl layers and the carboxylic acid function. Other substituents are also possible such as 113 formic acid and benzoic acid but the PTPH is the only one which presents luminescence 114 property under solid state. Organic molecules at solid state exhibiting luminescence are very 115 rare. Usual dyes such as fluorescein, eosin or rhodamine form aggregates at solid state 116 responsible of the quenching of luminescence (De et al., 2005; Math et al., 2006).

117 Thus, the dye PTPH has been incorporated into a Zn₂Al LDH matrix by one pot 118 coprecipitation method. The nanohybrid LDH-PTPH was characterised by X-Ray diffraction 119 and FT-IR spectroscopy. The photophysical properties of the pristine dye PTPH and hybrid 120 LDH-PTPH are also scrutinized by UV–visible absorption and fluorescence emission as well as 121 by recording the absolute photoluminescence quantum yield (PLQY). Consequently, 122 composite thin films are prepared by dispersing the LDH-PTPH filler into silicon-type polymer 123 matrix or poly(ethylene oxide). The photophysical properties of the resulting films are also 124 determined in correlation with their morphology analysed by SAXS.

125 2. Materials and Methods

126 2.1. Chemicals

127 The reagents $Zn(NO_3)_2$.6H₂O (purity 99.9+%), Al(NO₃)₃ .9H₂O (purity 99.9+%) and NaOH 128 (97%) were obtained from Sigma Aldrich. The two-component silicon polymer, Bluesil RTV 129 141 part A and part B, were supplied by Elkem. The poly(ethylene oxide) (Mw 100,000 g.mol⁻ 130 ¹) was supplied by Scientific Polymer Products.

131 2.2. Synthesis of PTPH

The N-heterocycles dye called PTPH was synthetized starting from the recently reported bromo derivative **1** (Sirbu et al., 2019). For this purpose, compound **1** was first engaged in a Sonogashira cross-coupling reaction with the methyl-5-hexynoate. The resulting ester **2** was then hydrolysed under basic conditions to afford the desired PTPH (Figure 1).



136

137

Figure 1 : Synthesis of PTPH

138 2.3. Synthesis of dye co-intercalated in Zn₂AL LDH

The hybrid layered double hydroxide phase, $Zn_2Al-Dye$, was prepared by the co-precipitation method. The synthesis of $[Zn_2Al_1(OH)_6]^+[NO_3^-]_{1-x}[PTPH^-]_x \cdot mH_2O$, where PTPH⁻ is the anionic dye, was performed using the target dye in 50 mL of deionized water. 50 mL of an aqueous solution of Zn^{2+} (1.6 mmol) and Al^{+3} (0.8 mmol) was added dropwise during 3 hours under magnetic stirring. For instance, to prepare the sample LDH-PTPH $[Zn_2Al_1(OH)_6]^+[NO_3^-]_{0.60}[PTPH^-]_{0.4} \cdot mH_2O$, 0.32 mmol of the dye was used. The pH was maintained at 9 by adding 145 0.25 M NaOH during all the addition process. The co-precipitation was performed under 146 nitrogen at 20°C. The mixture was centrifuged at 5 000 rpm during 10 minutes; the 147 sedimented solid on the bottom of the flask was washed several times with deionized water 148 until to obtain a clear and transparent supernatant. A paste was recovered and stored at 149 5°C. A small amount was dried over night at room temperature to obtain a powder for 150 further characterizations and to determine the proportion of the dry extract as well as the 151 uptake of PTPH in LDH-(NO₃⁻/PTPH⁻).

152 2.4. Fabrications of composites thin film Silicon/LDH

The LDH hybrid powder was used to elaborate the polymer/hybrid material composite with 153 154 different loadings. The two-component silicone polymer (silicone Bluesil-RTV 141 A&B) was 155 composed of a viscous liquid called part A cured by polyaddition reaction with a catalyser, 156 part B. The silicone film was prepared following the process: a mixture of the part A and 10 157 phr of part B was prepared, homogenised with mechanical mixer (Planetary Centrifugal 158 vacuum Mixer "Thinky Mixer") during 10 minutes at 500 rpm then pressed in a three rolls 159 mill Exakt 80E. Next, the final composite film was prepared by casting onto a Teflon surface 160 using an Elcometer 4340 automatic film applicator. The blade knife height was fixed at 200 161 µm and the casting speed was 30 mm/s. This two-component silicone polymer was cured at 162 80°C for 2 hours. The film thickness was measured using an Elcometer 456 coating thickness 163 gauge.

164 2.5. Fabrications of composites thin film PEO/LDH

165 The LDH hybrid paste obtained after the last cleaning of LDH-PTPH synthesis was used to 166 elaborate the polymer/hybrid material composite. Hydrophilic poly(ethylene oxide) (PEO) 167 with Mw = $100,000 \text{ g.mol}^{-1}$ was used. 1.0 g of PEO powder was dispersed into 10 mL of deionized water under magnetic stirring during 2 hours. 0.4 g of the LDH-PTPH paste was added to 5.0 g of the previous mixture and then homogenised during 1 hour. The final mixture was poured directly onto a Teflon surface and dried overnight to obtain the composite film PEO-LDH-PTPH.

- **172** 2.6. Techniques of characterization
- 173 2.6.1. X-ray diffraction

174 LDH powders were characterised by X-Ray Diffraction, the patterns were measured with a 175 Philips X-Pert Pro diffractometer operating with Cu-K α radiation (λ =1.5418 Å). The data were 176 collected in a 20 range from 5° to 70° with a step size of 1°/min.

177 2.6.2. SAXS

Small Angle X-ray Scattering (SAXS) experiments were performed on an Empyrean Panalytical equipment with a ScatterX78 using a θ/θ goniometer and Cu anode (45 kV and 40 mA). An elliptic W/Si focusing X-ray mirror for Cu radiation was used, and divergence fixed slit of 1/32 °. The distance form incident beam to sample was 140 mm. The detector GaliPIX3D was at a distance of 240 mm from the sample. SAXS curves were recorded in continuous scan mode. The background (no sample) was removed in each case.

184 2.6.3. Fourier transformed-infrared spectroscopy

185 The infrared spectra were recorded with a Nicolet 5700-FTIR spectrometer with Omnic

- 186 software. Spectra were obtained using a summation of 32 scans and a resolution of 4 cm^{-1} .
- 187 Powders of LDH and fluorescein were studied by using the KBr pellet technique.

188 2.6.4. UV-Visible absorption

189 The UV–visible absorption spectra of the samples were recorded in the wavelength range of 190 200 to 800 nm with a UV–vis spectrophotometer (SP-3000 Plus) equipped with an 191 integrating sphere with UV-Probe software.

192 2.6.5. Luminescence

193 Quantum yields efficiencies were measured using an integrating sphere C9920-02G PL-QY 194 measurement system from Hamamatsu Photonics. The setup consisted of a 150 W 195 monochromatized Xe lamp, an integrating sphere (Spectralon coating, Ø= 3.3 in.) and a high 196 sensibility CCD camera. Excitation and blue-excited emission spectra were recorded with a 197 Jobin-Yvon set-up consisting of a Xe lamp operating at 400 W coupled with two 198 monochromators (Triax 550 and Triax 180) and a cryogenically cold charge coupled device 199 (CCD) camera (Jobin–Yvon Symphony LN2 series) for emission spectra and Hamamatsu 980 200 photomultiplicator for excitation ones. Excitation spectra were corrected for instrument 201 response and Xe lamp intensity using sodium salicylate. The resolution of the system was 202 better than 0.1 nm in both emission and excitation configurations. Luminescence decays 203 were recorded using a second-harmonic generation on a pulsed Nd:YAG OPO Ekspla NT342A laser (3-5 ns pulse duration, 10 Hz, 5 cm⁻¹ line width, 0.3 mJ - 20 mJ in the UV-blue). The 204 205 emitted photons were detected at right angle from the excitation and analysed through 206 Edinburgh FLS980 spectrometer (Czerny-Turner monochromator, 300 mm focal length, 1200 groove mm⁻¹ grating and minimum band-pass of 0.1 nm) equipped with Hamamatsu R928P 207 208 PMT (200-850 nm range).

209

2.6.6. Scanning electron microscopy (SEM)

Scanning electron microscopy was performed using a ZEISS Supra 55 VP scanning electron
microscope in high vacuum, at 20 kV using a back-scatter electron detector (QBSD).

212 3. Results and Discussion

213 3.1. Characterisation of the pristine dyes and the LDH-Dye

The organic molecule PTPH is represented in Figure 2 a). It is composed of a pyrazino-214 215 1,3a,6a-triazapentalene molecular backbone with a 4-hexynoic acid substituent chain. 216 Carboxylic acid group is attached to allow the intercalation of the dye molecules between 217 the LDH sheets (Yan et al., 2014). The sample LDH-PTPH powder was synthetized by 218 coprecipitation method. The XRD patterns of LDH-PTPH powder as well as pristine PTPH 219 powder and reference LDH-NO₃ powder where nitrate anions are intercalated in a Zn_2AI LDH 220 matrix, are represented in the Figure 3. Diffraction planes (00ℓ) are the fingerprints of the 221 layered structure of LDH. For the reference sample LDH-NO₃, the positions of $2\theta = 10.1^{\circ}$ and 20.2° (i.e. 0.78 nm and 0.39 nm) are characteristic of a nitrate LDH phase and assigned to 222 (003) and (006) diffraction planes, respectively (Mahjoubi et al., 2017). The basal spacing 223 224 given by the Scherrer equation (Scherrer, 1912) is 0.78 nm for a (003) diffraction plan at a position of $2\theta = 10.1^{\circ}$. (110) and (113) diffraction plans are partially overlapped around $2\theta =$ 225 60.5° leading to a the metal-to-metal distance within the cationic hydroxide layers of a = 226 227 $2d_{(110)}$ = 3.1 Å, this in agreement with a ratio Zn : Al of 2 : 1 (Vial et al., 2006).



Figure 2: a) Molecular structure of the studied dye: a pyrazino-1,3a,6a-triazapentalene type structure; b) 3D molecular
 structure of the dye a with calculated size of the molecule

231 The diffraction plan (003) and (006) of the XRD pattern of LDH-PTPH are observed at 232 lower 2 θ , the peak positions are 4.0° and 8.1° meaning that the basal spacing (2.21 nm) is 233 larger than for the LDH-NO₃ (I. Khan and O'Hare, 2002), thus indicating that the large 234 molecules PTPH are intercalated into the LDH host. Moreover, the geometry of the dye was 235 optimized with Avogadro software and the length of the molecule is estimated to be 1.32 236 nm (Figure 2 b)). The basal spacing agrees well the accommodation of the interleaved dye 237 PTPH. The XRD pattern of the pristine sample PTPH is also represented, a narrow intense 238 peak is observed at 2θ = 26.8° which is not observed for the XRD pattern of LDH-PTPH that 239 excludes the structural packing of free PTPH molecules onto the sample. The mean 240 crystallite size (L) was calculated according to the Scherrer equation $L = k\lambda/(B\cos\theta)$, where B 241 is the full width at half maximum (FWHM) of the diffraction peak (003) and k is the shape 242 factor of the average crystallite and fixed to k = 0.9 (assuming a spherical shape) (Cullity, 243 1978). A coherence length Lc along the stacking direction of 17 nm was found for the LDH-244 PTPH powder meaning that LDH aggregates are composed in average by less than ten 245 stacked layers.



Figure 3: X-Ray Diffractogram (XRD) of the pristine dye PTPH and intercalated in a Zn₂Al LDH matrix LDH-PTPH as well as a reference Zn₂Al LDH matrix with nitrate anions intercalated: LDH-NO₃

The FTIR spectra of PTPH and LDH-PTPH recorded between 400 and 4000 cm⁻¹ (Figure 4). 249 Several characteristic bands are observed for the pristine powder PTPH at 1300 cm⁻¹ (C-N 250 aromatic), 1515 cm⁻¹ (C=C aromatic), 1715 cm⁻¹ (stretching bond C=O from carboxylic acid) 251 and around 3100 cm⁻¹ (C-H aromatic). These bands are also visible in the spectra of the LDH-252 253 PTPH powder that confirms the presence of PTPH in the sample. However, the IR band at 1715 cm⁻¹ (stretching bond C-O from carboxylic acid) disappears from the LDH-PTPH IR 254 spectra while a new band appears around 1560 cm⁻¹ which is characteristic of stretching 255 256 bond C=O from carboxylate. Thus, XRD data as well as FTIR spectra confirm the intercalation 257 and its interaction, respectively, of the molecule PTPH under carboxylate form into the LDH 258 matrix.



*Figure 4: FTIR spectra of the pristine dye PTPH and intercalated in a Zn₂AI LDH matrix LDH-PTPH recorded into KBr pellets*The UV-Vis absorption spectra of PTPH and LDH-PTPH powders recorded into KBr pellets
(Figure 5). Both powders present a large absorbance domain between 200 and 500 nm
without a specific absorbance band. The intercalation of PTPH in the LDH matrix does not
affect its own absorbance properties.

265



Figure 5: UV-visible spectra of the pristine dye PTPH and intercalated in a Zn2Al LDH matrix LDH-PTPH recorded into KBr
 pellets

268 3.2. Photoluminescence of the pristine dye and the LDH-Dye

The absolute PLQY of the dye recorded between 250 and 500 nm for the compound PTPH in aqueous solution and in dichloromethane solution at three concentrations $(10^{-3}, 10^{-4} \text{ and } 10^{-5} \text{ M})$ is displayed in Figure 6. Thanks to the carboxylate group and the polarity of the dye, PTPH is soluble in water. It is also soluble in organic polar solvent such as dichloromethane or DMSO. The absolute PLQY of PTPH in water is silent; the quenching of luminescence properties occurs whatever the concentration. On the other hand, PTPH in dichloromethane exhibits high absolute PLQY. In a high diluted system (10^{-5} M), PTPH shows absolute PLQY between 340 and 465 nm, the absolute PLQY_{max} is 20.3 % for λ_{exc} = 315 nm, whereas the absolute PLQY reaches 40.3 % for 10^{-4} M concentration. At 10^{-3} M, compound PTPH displays a saturation step between 370 and 450 nm due to high concentration.





280 Figure 6: Absolute PLQY in function of the wavelength for solution of PTPH in water and in dichloromethane at three different concentration: 10^{-3} , 10^{-4} and 10^{-5} M

The absolute photoluminescence quantum yield (PLQY) of the pristine powder PTPH is 282 illustrated on the Figure 7. The PLQY has been recorded between 250 and 500 nm as if the 283 284 dye was associated with an UV-LED. The PLQY varies between 6 and 11 % and the maximum 285 is reached at λ_{exc} = 315 nm. The values are weak for a potential lighting application but in fact 286 they are very interesting for pristine solid organic dye. Indeed, most of the organic dyes at the solid state such as fluorescein or eosin do not present any luminescent properties at 287 all.(De et al., 2005; De and Kundu, 2011; Yaguchi et al., 2012). The absolute PLQYs of LDH-288 289 PTPH under powder and paste form are also reported on the Figure 6. As reported in 290 Experimental section, the paste is obtained after the washing/centrifugation process and 291 before the drying process. The absolute PLQY of the LDH-PTPH powder is almost constant as

292 a function of the wavelength (around 2 %) and are much weaker than the absolute PLQY of 293 the pristine powder PTPH. Expectedly, the dispersion of the dye into LDH matrix would allow 294 to reproduce a solid state mixed into a solvated system as in a liquid solution to increase the 295 absolute PLQY. However, the desired effect is not occurring as for the fluorescein(Legentil et 296 al., 2019). The absolute PLQY of the LDH-PTPH paste is higher than the absolute PLQY of the 297 powder, the absolute PLQY_{max} is 11.9 % for λ_{exc} = 320 nm. Counter intuitively, the paste, 298 which is just the powder dispersed in a small quantity of water, displays higher absolute 299 PLQY than the powder, while the luminescence is guenched for PTPH dispersed in water.



Figure 7: Absolute PLQY of powders PTPH and LDH- PTPH as well as paste LDH-PTPH and both composite thin films TF-PTPH
 and TF-LDH-PTPH

303 3.3. Characterisation of the thin film

300

Two composite thin films with a silicon matrix (PDMS) was prepared (Deng et al., 2016). The first one, TF-PTPH, was prepared with pristine powder PTPH with a loading rate of 5 wt. % whereas the second one, TF-LDH-PTPH, was elaborated with the LDH-PTPH powder with a loading rate of 20 % to get around 5 % of PTPH. Both films under UV radiation and under daylight are illustrated in the Figure 8. First of all, one may observe that the dispersion of PTPH molecule in the polymer matrix is quite inhomogeneous, as small aggregates are visible in the thin film TF-PTPH leading to a granular aspect. On the contrary, the dispersion in TF- LDH-PTPH is homogeneous without any aggregates. Thus, LDH matrix has a real additional value in dispersing of the dye PTPH into a polymer matrix. However, TF-PTPH seems to be more luminescent than TF-LDH-PTPH under UV radiation where luminescence is completely turned-off.



Figure 8: Composite thin films of TF-LDH-PTPH and TF-PTPH under daylight and UV irradiation (λ=265 nm)
The FTIR spectra of LDH-PTPH and TF-LDH-PTPH recorded between 400 and 4000 cm⁻¹
(Figure 9). For TF-LDH-PTPH, several IR bands can be attributed to the PDMS polymer (28802960, 2140, 1945, 1445, 1415 cm⁻¹) (Bodas and Khan-Malek, 2006). Only two bands, relating
to compound PTPH, at 1515 et 1560 cm⁻¹ are observed. Thus, the dispersion in the matrix
polymer does not modify or degrade the LDH-PTPH powder.

315



Figure 9: FTIR spectra of powder LDH-PTPH recorded into KBr pellets and the composite thin film TF-LDH-PTPH between 400 and 4000 cm⁻¹

325 The small-angle X-ray scattering data of both composite films TF-LDH-PTPH and reference silicon film are presented in Figure 10. Scattered intensity I is plotted versus the scatter 326 vector g, where g = $4\pi \sin(\theta)/\lambda$. For TF-LDH-PTPH, a characteristic LDH pattern is observed 327 328 (Schaefer and Justice, 2007; Seftel et al., 2015). Two diffraction peaks are observed at 0.26 and 0.53 Å⁻¹ corresponding to distances of 2.42 and 1.18 nm, the first one is the basal 329 spacing of the LDH matrix. For PEO-HDL-PTPH, only one diffraction peak is observed at 0.33 330 $Å^{-1}$ corresponding to a basal spacing of 1.90 nm. These values are closed and match with 331 data obtained from X-ray diffractogram of the powder LDH-PTPH (2.21 nm). According with 332 333 other SAXS investigations (Jarzębski et al., 1997; Tokudome et al., 2016; Wu et al., 2007), the 334 mean size (L) of secondary aggregated particles, i.e. LDH pellets, can be calculated from the 335 scatter vector found between the slop modifications of the curve. $L_2 = 27.3$ nm and $L_1 = 23.1$ 336 nm were measured, respectively for TF-LDH-PTPH and for PEO-HDL-PTPH. These values are 337 slightly higher than the size (Lc = 17 nm) obtained through the Scherrer equation from the X-338 ray diffractogram of the powder HDL-PTPH. It could be explained by a modification of the 339 environment into the basal spacing or a swelling effect due to the polymer matrices.



341 Figure 10: Small-angle X Ray scattering (SAXS) of thin composite film TF-LDH-PTPH and a reference silicone film

342 3.4. Photoluminescence of the thin film

The absolute PLQY of both composite films TF-LDH-PTPH and TF-PTPH are presented on Figure 7. The PLQY of TF-PTPH are close to those of the pristine powder PTPH with a maximum of 11 % for λ_{exc} = 315 nm. The PLQY of the composite film TF-LDH-PTPH is extremely weak, between 1 and 2 %. The luminescence of the thin film is barely observed under UV irradiation. These results show that the intercalation of the molecule PTPH into LDH host is not suitable for the luminescence properties, this is also the case after dispersion into a PDMS-type polymer.

A hydrophilic polymer PEO is then used to prepare a second composite film with the LDH-PTPH paste which presents decent photoluminescence property. The absolute PLQY of the film PEO-LDH-PTPH were presented on Figure 11. The PLQY between 250 and 500 nm are perfectly matching with the PLQY of LDH-PTPH paste. The photoluminescence property of the paste is preserved through its dispersion into a hydrophilic polymer such as PEO, then yielding a luminescent composite film. Further studies are needed to unravel the unexpected behaviour of the observed stable luminescence in such medium.





Figure 11: Absolute PLQY of composite films PEO-LDH-PTPH and TF-LDH-PTPH as well as paste LDH-PTPH

359 4. Conclusion

360 The study demonstrates that the organic molecule PTPH (pyrazino-1,3a,6a-triazapentalene 361 type structure) exhibits efficient photoluminescence property for an organic molecule at 362 solid state. The cumbersome organic guest PTPH is well intercalated into LDH matrix Zn₂Al 363 using a coprecipitation method, enough ensconced to get a hybrid luminescent material. 364 Counter intuitively, the LDH-PTPH powder does not emit any radiation under blue/UV 365 excitation (absolute PLQY lower than 2 %) whereas the LDH-PTPH paste produces 366 luminescence with an absolute PLQY_{max} of 11.9 % for λ_{exc} = 320 nm. The dispersion of the 367 LDH-PTPH powder in a polymer (PDMS) occurs readily thanks to the compatible LDH host 368 matrix. However, such dispersion is not able to produce luminescence enough. When 369 hydrophilic polymer such as poly(ethylene oxide) is combined with the LDH-PTPH paste, the 370 absolute PLQY is similar to LDH-PTPH paste values, reaching an absolute PLQY_{max} of 11.5 % 371 for λ_{exc} = 315 nm, and showing that the continuous phase; i.e. polymer, may play a role at 372 nanoscale.

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380 References

- Almasian, A., Mirjalili, M., Maleknia, L., Giahi, M., 2019. Preparation of Multi-Functional Polyester
 Fabrics with the Use of a New Organo-Clay Nanopigment in High Temperature/High Pressure
- Fabrics with the Use of a New Organo-Clay NanopigCondition. Fibers and Polymers 20, 1387-1395.
- Aloisi, G.G., Costantino, U., Elisei, F., Latterini, L., Natali, C., Nocchetti, M., 2002. Preparation and
- 385 photo-physical characterisation of nanocomposites obtained by intercalation and co-
- intercalation of organic chromophores into hydrotalcite-like compounds. Journal of Materials
- **387** Chemistry 12, 3316-3323.
- Bodas, D., Khan-Malek, C., 2006. Formation of more stable hydrophilic surfaces of PDMS by
 plasma and chemical treatments. Microelectronic Engineering 83, 1277-1279.
- 390 Costantino, U., Coletti, N., Nocchetti, M., Aloisi, G.G., Elisei, F., 1999. Anion Exchange of Methyl
- Orange into Zn–Al Synthetic Hydrotalcite and Photophysical Characterization of the Intercalates
 Obtained. Langmuir 15, 4454-4460.
- 393 Costantino, U., Coletti, N., Nocchetti, M., Aloisi, G.G., Elisei, F., Latterini, L., 2000. Surface Uptake
- and Intercalation of Fluorescein Anions into Zn–Al–Hydrotalcite. Photophysical Characterization
- of Materials Obtained. Langmuir 16, 10351-10358.
- 396 Costantino, U., Costantino, F., Elisei, F., Latterini, L., Nocchetti, M., 2013. Coupling physical
- chemical techniques with hydrotalcite-like compounds to exploit their structural features and
- **398** new multifunctional hybrids with luminescent properties. Physical Chemistry Chemical Physics
- **399** 15, 13254-13269.
- 400 Cullity, B.D., 1978. Elements of X-ray Diffraction. Addison-Wesley Publishing Company.
- 401 Davis, R., Saleesh Kumar, N.S., Abraham, S., Suresh, C.H., Rath, N.P., Tamaoki, N., Das, S., 2008.
 402 Molecular Packing and Solid-State Fluorescence of Alkoxy-Cyano Substituted
 403 Diphenylbutadienes: Structure of the Luminescent Aggregates. The Journal of Physical
 404 Chemistry C 112, 2137-2146.
- 405 De, S., Das, S., Girigoswami, A., 2005. Environmental effects on the aggregation of some xanthene
- 406 dyes used in lasers. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 61,407 1821-1833.
- 408 De, S., Kundu, R., 2011. Spectroscopic studies with fluorescein dye—Protonation, aggregation
 409 and interaction with nanoparticles. Journal of Photochemistry and Photobiology A: Chemistry
 410 223, 71-81.
- 411 Deng, S., Binauld, S., Mangiante, G., Frances, J.M., Charlot, A., Bernard, J., Zhou, X., Fleury, E., 2016.
- Microcrystalline cellulose as reinforcing agent in silicone elastomers. Carbohydrate Polymers
 151, 899-906.
- 414 Dou, Y., Liu, X., Shao, M., Han, J., Wei, M., 2013. Flexible and transparent free-standing films with 415 enhanced magnetic and luminescent anisotropy. Journal of Materials Chemistry A 1, 4786-4792.
- 416 Gogoi, B., Sen Sarma, N., 2015. Curcumin-cysteine and curcumin-tryptophan conjugate as
- fluorescence turn on sensors for picric Acid in aqueous media. ACS applied materials &interfaces 7, 11195-11202.
- Hajibeygi, M., Omidi-Ghallemohamadi, M., 2017. One-step synthesized azo-dye modified Mg-Al
 LDH reinforced biobased semi-aromatic polyamide containing naphthalene ring; study on
 thermal stability and optical properties. Journal of Polymer Research 24, 61.
- 422 I. Khan, A., O'Hare, D., 2002. Intercalation Chemistry of Layered Double Hydroxides: Recent
 423 Developments and Applications.
- 424 Jarzębski, A.B., Lorenc, J., Pająk, L., 1997. Surface Fractal Characteristics of Silica Aerogels.
 425 Langmuir 13, 1280-1285.
- 426 Kumar, S., Singh, P., Srivastava, R., Koner, R., Pramanik, A., Mathew, J., Sinha, S., Rawat, M., Anand,
- R., Ghosh, S., 2014. Engineering Fused Coumarin Dyes: Molecular Level Understanding of
 Aggregation Quenching and Tuning Electroluminescence via Alkyl Chain Substitution.
- 429 Latterini, L., Elisei, F., Aloisi, G.G., Costantino, U., Nocchetti, M., 2002. Space-resolved fluorescence
- 430 properties of phenolphthalein-hydrotalcite nanocomposites. Physical Chemistry Chemical
- 431 Physics 4, 2792-2798.

- Legentil, P., Leroux, F., Therias, S., Mahiou, R., Chadeyron, G., 2019. Revisiting fluorescein and
 layered double hydroxide using a synergistic approach: A complete optical study. Journal of
- 433 layered double hydroxide u434 Luminescence 215, 116634.
- 435 Lu, T.-F., Li, W., Zhang, H.-X., 2018. Rational design of metal-free organic D- π -A dyes in dye-
- 436 sensitized solar cells: Insight from density functional theory (DFT) and time-dependent DFT
 437 (TD-DFT) investigations. Organic Electronics 59, 131-139.
- 438 Mahajan, P.G., Dige, N.C., Vanjare, B.D., Eo, S.-H., Kim, S.J., Lee, K.H., 2019. A nano sensor for
- sensitive and selective detection of Cu2+ based on fluorescein: Cell imaging and drinking water
- 440 analysis. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 216, 105-116.
- Mahjoubi, F.Z., Khalidi, A., Abdennouri, M., Barka, N., 2017. Zn–Al layered double hydroxides
 intercalated with carbonate, nitrate, chloride and sulphate ions: Synthesis, characterisation and
 dye removal properties. Journal of Taibah University for Science 11, 90-100.
- Marangoni, R., Taviot-Guého, C., Illaik, A., Wypych, F., Leroux, F., 2008. Organic inorganic dye
 filler for polymer: Blue-coloured layered double hydroxides into polystyrene. Journal of Colloid
 and Interface Science 326, 366-373.
- Math, N.N., Naik, L.R., Suresh, H.M., Inamdar, S.R., 2006. Dual fluorescence and laser emissions
 from fluorescein-Na and eosin-B. Journal of Luminescence 121, 475-487.
- 449 Mekhzoum, M.E.M., Essassi, E.M., Qaiss, A., Bouhfid, R., 2016. Fluorescent bio-nanocomposites
- 450 based on chitosan reinforced hemicyanine dye-modified montmorillonite. RSC Advances 6,451 111472-111481.
- 452 Saha, M., Shil, A., Hussain, S.A., Bhattacharjee, D., 2017. Clay induced changes in the aggregation
- pattern of Safranine-O in hybrid Langmuir-Blogdgett (LB) films. Journal of Photochemistry and
 Photobiology A: Chemistry 348, 199-208.
- 455 Schaefer, D.W., Justice, R.S., 2007. How Nano Are Nanocomposites? Macromolecules 40, 8501-456 8517.
- 457 Scherrer, P., 1912. Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels
- 458 Röntgenstrahlen, Kolloidchemie Ein Lehrbuch. Springer Berlin Heidelberg, Berlin, Heidelberg,
 459 pp. 387-409.
- 460 Schoonheydt, R., Johnston, C.T., Bergaya, F., 2018. Surface and interface chemistry of clay 461 minerals.
- 462 Seftel, E., Niarchos, M., Vordos, N., Nolan, J., Mertens, M., Mitropoulos, A.C., Vansant, E., Cool, P.,
- 2015. LDH and TiO2/LDH-type nanocomposite systems: A systematic study on structuralcharacteristics.
- 465 Sen, T.K., 2017. Clay minerals : properties, occurrence, and uses. Nova Science Publishers.
- Shi, W., Sun, Z., Wei, M., Evans, D.G., Duan, X., 2010. Tunable Photoluminescence Properties of
 Fluorescein in a Layered Double Hydroxide Matrix by Changing the Interlayer
 Microenvironment. The Journal of Physical Chemistry C 114, 21070-21076.
- 469 Sirbu, D., Diharce, J., Martinić, I., Chopin, N., Eliseeva, S.V., Guillaumet, G., Petoud, S., Bonnet, P.,
- 470 Suzenet, F., 2019. An original class of small sized molecules as versatile fluorescent probes for471 cellular imaging. Chemical communications 55, 7776-7779.
- 472 Tokudome, Y., Morimoto, T., Tarutani, N., Vaz, P.D., Nunes, C.D., Prevot, V., Stenning, G.B.G.,
- Takahashi, M., 2016. Layered Double Hydroxide Nanoclusters: Aqueous, Concentrated, Stable,
 and Catalytically Active Colloids toward Green Chemistry. ACS Nano 10, 5550-5559.
- 475 Vial, S., Ghanbaja, J., Forano, C., 2006. Precipitation of Zn2Al LDH by urease enzyme. Chemical
 476 communications, 290-292.
- Volpi, G., Lace, B., Garino, C., Priola, E., Artuso, E., Cerreia Vioglio, P., Barolo, C., Fin, A., Genre, A.,
 Prandi, C., 2018. New substituted imidazo[1,5-a]pyridine and imidazo[5,1-a]isoquinoline
- 479 derivatives and their application in fluorescence cell imaging. Dyes and Pigments 157, 298-304.
- 480 Weber, M.D., Niklaus, L., Proschel, M., Coto, P.B., Sonnewald, U., Costa, R.D., 2015. Bioinspired
- 481 Hybrid White Light-Emitting Diodes. Advanced materials 27, 5493-5498.
- Wu, H., Huang, Z., Hua, T., Liao, C., Meier, H., Tang, H., Wang, L., Cao, D., 2019. Metal-free organic
- 483 dyes with di(1-benzothieno)[3,2-b:2',3'-d]pyrrole as a donor for efficient dye-sensitized solar
- 484 cells: Effect of mono- and bi-anchors on photovoltaic performance. Dyes and Pigments 165, 103-
- 485 111.

- Wu, Q., Sjåstad, A.O., Vistad, Ø.B., Knudsen, K.D., Roots, J., Pedersen, J.S., Norby, P., 2007.
 Characterization of exfoliated layered double hydroxide (LDH, Mg/Al = 3) nanosheets at high concentrations in formamide. Journal of Materials Chemistry 17, 965-971.
- 489 Yaguchi, K., Furube, A., Katoh, R., 2012. Aggregate formation of eosin-Y adsorbed on 490 nanocrystalline TiO2 films. Chemical Physics Letters 551, 96-100.
- 491 Yan, D., Lu, J., Wei, M., Qin, S., Chen, L., Zhang, S., Evans, D.G., Duan, X., 2011. Heterogeneous
- 492 Transparent Ultrathin Films with Tunable-Color Luminescence Based on the Assembly of
- 493 Photoactive Organic Molecules and Layered Double Hydroxides. Advanced Functional Materials494 21, 2497-2505.
- 495 Yan, L., Wang, Y., Li, J., Kalytchuk, S., Susha, A.S., Kershaw, S.V., Yan, F., Rogach, A.L., Chen, X.,
- 496 2014. Highly luminescent covalently bonded layered double hydroxide–fluorescent dye 497 nanohybrids. Journal of Materials Chemistry C 2, 4490.
- 498 Zhang, L., Li, B., Lei, B., Hong, Z., Li, W., 2008. A triphenylamine derivative as an efficient organic
- 499 light color-conversion material for white LEDs. Journal of Luminescence 128, 67-73.

Supporting information

504

505 Materials and methods

506 Nuclear Magnetic Resonance (NMR) spectra were recorded on a 250 or 400 MHz 507 Bruker NMR spectrometers in CDCl₃ or DMSO. All chemical shift values are reported in parts 508 per million (ppm) with coupling constant (J) values reported in Hz. All spectra were referenced to the CDCl₃ residual solvent peak CHCl₃ (δ = 7.26 ppm) for ¹H NMR and the CDCl₃ 509 solvent peak (δ = 77.16 ppm) for ¹³C NMR. The notation of signals is: Proton: δ chemical shift 510 511 in ppm (multiplicity, J value(s), number of protons). Carbon: δ chemical shift in ppm. 512 Fluorine: δ chemical shift in ppm. Splitting patterns are assigned s = singlet, b = broad, d = 513 doublet, td = triplet of doublet, dt = doublet of triplet, t = triplet, q = quartet, app= apparent.

514

All reaction were monitored by thin-layer chromatography (TLC) analysis using silica 515 516 gel (60 F254). Solvents, unless otherwise stated, were purchased in reagent grade or 517 anhydrous quality and used as received. Reagents were either purchased directly from 518 commercial suppliers or prepared according to literature procedures. Yields of all the 519 compounds refer to isolated compounds. Chromatography: Separations were carried out on 520 Silica gel 60, (40-63 µ, 60 Å) purchased from Sigma Aldrich. High Resolution Mass 521 Spectrometry (HRMS) were recorded on Maxis Bruker 4G. Melting points (mp [C°]) were taken on open capillary tubes using a Electrothermal IA 9100 apparatus. 522

523 Reactants were purchased from commercial suppliers and were used without further 524 purification. Compound **1** was synthesized following reported synthesis (Sirbu et al., 2019).

525 Experimental procedures



526

527 In a round bottom flask, the bromopyridazinotriazapentalene **1** (Sirbu et al., 2019) (1.0 g, 528 4.20 mmol) was solubilized in Et₃N (10 mL) with methyl-5-hexynoate (1.060 g, 8.40 mmol, 2 529 eq.) and Pd(PPh₃)₂Cl₂ (294.8 mg, 0.42 mmol, 10 mol%). The mixture was stirred at room 530 temperature for 20 min and then Cul (72.4 mg, 0.38 mmol, 9 mol%) was added. The mixture 531 was stirred at 90°C for 3h. Solvent was removed under vaccum and crude compound purified 532 by column chromatography (DCM/AcOEt 1/1) to give pure **2** (900 mg, 76%) as a yellow solid. 533 Pf : 99°C

534 IR *v*(cm⁻¹) : 3138, 3078, 2959, 1721, 1507, 1424, 1382, 1368, 1336, 1256, 1186.

¹H NMR (400 MHz, Chloroform-d) δ 8.35 (d, J = 2.7 Hz, 1H), 8.03 (s, 1H), 7.83 (d, J = 2.7 Hz,

536 1H), 7.78 (s, 1H), 3.63 (s, 3H), 2.45 (td, J = 7.2, 5.4 Hz, 4H), 1.89 (p, J = 7.2 Hz, 2H).

- ¹³C NMR (101 MHz, CDCl₃) δ 173.27, 152.43, 143.33, 130.43, 128.94, 111.86, 110.52, 107.83,
 93.28, 70.19, 51.66, 32.81, 23.49, 18.86.
- 539 HRMS (ESI) m/z : calculated for C₁₄H₁₄N₅O₂ [M+H]⁺ 284.1142 ; found 284.1141.



542

In a round bottom flask, **2** (500 mg, 1.77 mmol) was solubilized in MeOH (4 mL) with NaOH 10N (1 mL, 10 mmol, 5.6 eq.). The mixture was stirred at room temperature for 2h. Solvents were removed under vaccum and the crude mixture solubilized in DCM and water (1/1). Aqueous phase was extracted and washed with DCM (3 x 20 mL) and then acidified with HCl 2N until pH 4-5. Organic phase was extracted with DCM, washed with water and concentrated under vacuo to give pure **TPTH** (377 mg, 1.40 mmol, 79%).

- 549 Pf: ~175°C (decomp.)
- 550 IR v(cm⁻¹) : 3143, 3074, 2960, 1715, 1512, 1382, 1336, 1250, 1176, 1016.

¹H NMR (400 MHz, DMSO-d6) δ 12.14 (s, 1H), 8.85 (s, 1H), 8.58 (s, 1H), 8.36 (d, J = 2.7 Hz,
1H), 7.90 (d, J = 2.7 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.38 (t, J = 7.3 Hz, 2H), 1.78 (p, J = 7.2 Hz,
2H).

- ¹³C NMR (101 MHz, DMSO) δ 173.96, 152.08, 142.65, 129.59, 128.92, 113.90, 111.37,
 106.68, 92.99, 70.80, 32.60, 23.46, 18.16.
- 556 HRMS (ESI) m/z: calculated for C₁₃H₁₂N₅O₂ [M+H]⁺ 270.0985; found 270.0984.

557

560 NMR spectra







