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1 **Reliability study under thermal and photonic stresses of sulforhodamine B**  
2 **(SRB) confined in layered double hydroxide (LDH).**

3 Paul Legentil<sup>1</sup>, Fabrice. Leroux<sup>1\*</sup>, Sandrine Therias<sup>1</sup>, Damien Boyer<sup>1</sup>, François Reveret<sup>2</sup>, Geneviève  
4 Chadeyron<sup>1\*</sup>

5 <sup>1</sup> *Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 Clermont–Ferrand,*  
6 *France.*

7 <sup>2</sup> *Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Pascal, F-63000 Clermont–*  
8 *Ferrand, France.*

9 \*e-mail [genevieve.chadeyron@sigma-clermont.fr](mailto:genevieve.chadeyron@sigma-clermont.fr), [fabrice.leroux@uca.fr](mailto:fabrice.leroux@uca.fr)

10 **ABSTRACT**

11 When sulforhodamine B (SRB) is entrapped in a tightly packed hybrid material composed of  
12 dodecylsulfate anions interleaved in layered double hydroxide, the organic dye is considered as a  
13 possible red-emitting phosphor for white light-emitting diodes (WLEDs). To confirm such promising  
14 potential, a reliability study is here undertaken and the materials and their associated silicone films  
15 are subjected to different thermal and photonic stresses. Optical properties, photoluminescence  
16 quantum yields and emission spectra are recorded after photo-aging studies. Interestingly, the  
17 composite silicone film is found to be completely stable under blue LED excitation, while in the  
18 absence of the hybrid LDH the emission of SRB decays rapidly, thus underlining the protective role of  
19 the LDH hybrid cargo. At this stage, these results confirm the potential offered by a system consisting  
20 of such an emitter film and a blue LED. This system also opens up new possibilities for interesting  
21 organic dyes that are sensitive to photonic and/or thermal stresses.

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## 34 1. Introduction

35 In lighting applications, white light-emitting diodes (WLED) are now emerging very strongly and  
36 constitute a reference in solid-state lighting sources because of their excellent properties, such as  
37 high light efficiency, energy-saving properties, long lifetime and absence of toxic mercury or other  
38 heavy metals. A commercial WLED consists of a blue chip, emitting between 450 and 480 nm,  
39 combined with a yellow-emitting phosphor (Nair et al., 2020), YAG:Ce<sup>3+</sup> (yttrium aluminium garnet  
40 doped with Ce<sup>3+</sup> cations), and a red-emitting phosphor is commonly added to improve the  
41 colorimetric characteristics of light (Xia et al., 2016). A recent study concerning a well-known organic  
42 dye, sulforhodamine B (SRB), underlined its interest as a red phosphor and its potential under  
43 commercial blue LED excitation when highly dispersed in a host structure, layered double hydroxide  
44 (LDH) (Legentil et al., 2020). Indeed, the inorganic LDH vessel intercalated with surfactant molecules  
45 (dodecylsulfate (DS)) is found to display a suitable arrangement for SRB to be well ensconced,  
46 avoiding intermolecular interactions deleterious for the red emission as well as providing an affinity  
47 with silicone in the preparation of homogeneous films. The properties of an optimized system  
48 composed of alternating a blue chip, a YAG: Ce<sup>3+</sup>/silicone composite film and a LDH-DS-SRB/silicone  
49 composite film are satisfactorily met, with a correlated color temperature (T(K)) associated with a  
50 color rendering index (CRI) suitable for a commercial WLED application.

51 LEDs are known to have an operating temperature of up to 100 or 120°C, and hence phosphors  
52 must have the ability to sustain such harsh conditions without any degradation

53 Several studies have been undertaken on inorganic phosphors. Da Lago et al.(Dal Lago et al.,  
54 2012) published one of the first reliability studies concerning a commercial YAG: Ce phosphor under  
55 thermal stresses (between 85 and 145 °C) for remote-phosphor technology. Thus, it was  
56 demonstrated that the heat generated can significantly limit the lifetime as well as the performance  
57 of the phosphor. We can also mention the works of Shao et al (Shao et al., 2014), which have shown  
58 the modification of the color coordinates and the spectral shift of BaSiO<sub>4</sub>: Eu<sup>2+</sup> emission (a green-  
59 emitting phosphor under blue LED excitation) with respect to temperature. In order to provide better  
60 thermal stability, they suggested substituting the Ba sites by Sr atoms in this phosphor, and in this  
61 way they succeeded in lowering thermal quenching. Since then, other works have reported the  
62 limited stability of phosphors formulated with rare earth elements under thermal stresses (Yazdan  
63 Mehr et al., 2014; Zhou et al., 2014).

64 However, the reliability of organic phosphors has scarcely been reported so far. Indeed, the use  
65 of organic dyes for WLED applications is appealing in terms of their luminescence properties but the  
66 stability studies are only superficial (Boonsin et al., 2015; Kajjam et al., 2018). As mentioned before,  
67 to further address a practical application in commercial lighting devices, a major specification  
68 required of the fluorophore and its associated system is to present long-term stability with respect to  
69 various types of stress in real operating conditions. Several published works mentioned the use of  
70 fluorophore with a potential application for replacing traditional phosphors with rare earth elements  
71 in commercial WLED, such as fluorescein, pyranine, rhodamine or triphenylamine derivatives for  
72 instance (Das and Manam, 2018; Legentil et al., 2019; Nyalosaso et al., 2019; Zhang et al., 2008).  
73 However, the authors do not usually pay attention to the reliability of the dyes in stressful  
74 conditions.

75 Traditionally, LDH materials find applications as precursors in catalysis and as scavengers in  
76 environmental science, but are also finding renewed interest in the domain of energy (Wu et al.,  
77 2018; Yin et al., 2019) as well as in biology as vessels for drug delivery (Conterposito et al., 2016;  
78 Lonkar et al., 2013; Yan et al., 2014). Their general chemical formula is as follows

79  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$  where M(II) is a divalent cation such as  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ , etc... and  
80 M(III) a trivalent cation such as  $Al^{3+}$ ,  $Fe^{3+}$ , etc. and  $A^{n-}$  is an interleaved anion. The anisotropic two-  
81 dimensional structure is built from edge-sharing octahedral. Compared to brucite  $Mg(OH)_2$ , the  
82 partial substitution of divalent cations by trivalent cations implies for LDH sheets a net positive  
83 charge. To ensure electroneutrality, anions of interest, here the dye molecules together with the  
84 surfactant molecules, are located in the interlayer space of the LDH with the presence of water  
85 molecules.

86 Importantly, organic dyes are known to be sensitive to different stresses (thermal, photonic...)  
87 (Lamouche et al., 1999; Sultana, 2018). To overcome such issues, an elegant solution consists in  
88 immobilizing the SRB molecules in an inorganic host lattice like layered double hydroxide (LDH) as  
89 previously reported (Legentil et al., 2020). Pioneer research has underlined the benefit of confining  
90 photoactive species to a restricted space such as a two-dimensional host in terms of 1) their strong  
91 adsorption through host-guest interaction to avoid possible migration and aggregation within a  
92 polymer, and 2) their dispersion with the presence of co-adsorbates to avoid as far as possible guest-  
93 guest interactions (Ogawa and Kuroda, 1995). However, a reliability study of such a hybrid organic  
94 dye/LDH host matrix for LED applications must be conducted before considering any practical  
95 application; this aspect has never been published to the best of our knowledge.

96 In the following, a reliability study of the SRB dye in the presence of thermal and photonic  
97 stresses in different conditions when placed in a LED set-up is presented in order to confirm the  
98 promising features of the synthesized hybrid LDH-SRB. To address this issue, comparative studies  
99 were performed, first on the hybrid LDH/SRB powder and then on a composite film by dispersing the  
100 powder in silicone polymer. In the first case only temperature effects were studied. Then, both  
101 thermal and photonic stresses were concomitantly applied and recorded for silicone films. Behaviour  
102 in accelerated photo-aging was also observed. Photoluminescence properties such as emission  
103 spectra and photoluminescence quantum yields were scrutinized during all the different tests to  
104 better understand the mechanisms involved in the loss of optical properties.

## 105 **2. Experimental section**

### 106 **2.1. Materials**

107 Sulforhodamine B sodium salt  $C_{27}H_{30}N_2NaO_7S_2$ , sodium dodecylsulfate  $CH_3(CH_2)_{11}OSO_3Na$  and  
108 terephthalic acid  $C_8H_6O_4$  were purchased from Sigma-Aldrich, and YAG:Ce<sup>3+</sup> from Phosphortech.  
109  $Zn(NO_3)_2 \cdot 6H_2O$  (purity 99.9+%),  $Al(NO_3)_3 \cdot 9H_2O$  (purity 99.9+%) and NaOH (97%) were obtained from  
110 Sigma Aldrich. The two-component silicone elastomer, Bluesil RTV 141 part A and part B, was  
111 supplied by Elkem.

### 112 **2.2. Synthesis procedure for LDH hybrid materials using the coprecipitation method**

113 The sulforhodamine B (SRB)-dodecylsulfate (DS) LDH phase,  $Zn_2Al-DS-SRB$ , called LDH-DS-SRB, was  
114 prepared using the coprecipitation method. The synthesis of  $[Zn_2Al_1(OH)_6]^+[DS^-]_{1-x}[SRB^-]_x \cdot mH_2O$  was  
115 performed using 50 mL of sulforhodamine B and dodecylsulfate aqueous solution (with de-ionized  
116 water). 50 mL of an aqueous solution of  $Zn^{2+}$  (3.2 mmol) and  $Al^{+3}$  (1.6 mmol) was added dropwise  
117 over a period of 3 hours under magnetic stirring. To synthesize the  $[Zn_2Al_1(OH)_6]^+[DS^-]$   
118  $]_{0.9995}[SRB^-]_{0.0005} \cdot mH_2O$  sample,  $0.8 \times 10^{-3}$  mmol and 1.5992 mmol were used for SRB salt and sodium  
119 dodecylsulfate, respectively. This formulation was determined in a previous article as that leading to  
120 the best optical performance under commercial blue LED and UV excitation (Legentil et al., 2020).

121 The pH was maintained at 8.5 by adding 0.25 M NaOH during the synthesis process.  
122 Coprecipitation was performed under nitrogen at 20 °C. The mixture was centrifuged at 5,000 rpm  
123 for 5 minutes and the slurry on the bottom of the flask was then washed several times with de-  
124 ionized water until a clear and transparent supernatant was obtained. A paste was recovered and  
125 dried overnight at room temperature to obtain the LDH-DS-SRB powder.

126 The post-synthesis hydrothermal treatment was performed by dispersing the paste, obtained  
127 before the drying step, in 20 ml of de-ionized water in a sealed container at 110 °C under autogenous  
128 pressure during 48 hours. The slurry was then centrifuged (5 minutes at 5,000 rpm) and the paste  
129 was dried overnight at room temperature to obtain the LDH-DS-SRB-TH powder.

130 Similarly, the terephthalate LDH phase, Zn<sub>2</sub>Al-TP-SRB, was prepared by following the method  
131 previously described for LDH-DS-SRB by replacing DS by terephthalic acid (TP). However, TP being  
132 dianionic, the input of TP was half the molar concentration compared to DS.

### 133 **2.3. Elaboration of Silicone/HDL-DS-SRB composite films**

134 The LDH-DS-SRB powder was used to produce the silicone/hybrid composite material. A loading  
135 rate of 40 wt. % was chosen (beyond this loading rate, it was difficult to obtain a homogeneous  
136 distribution of the powder in the polymer matrix, as shown in figure S1). The two-component silicone  
137 elastomer (silicone Bluesil-RTV 141 A&B) was composed of a viscous liquid, called part A, cured by a  
138 polyaddition reaction with a catalyser, part B.

139 The silicone/hybrid composite material was manufactured by mixing the LDH powder with part  
140 A of the silicone elastomer using a mechanical mixer ("Thinky Mixer") for 10 min at 1200 rpm. Then  
141 the obtained mixture was processed through a three-roll Exakt80E (spacing of 30 µm between the  
142 first two rolls and 50 µm between the last two rolls) to achieve a better dispersion of the LDH  
143 platelets by shearing and to obtain a homogeneous hybrid component. Part B was added at 10phr  
144 and further homogenised using the mechanical mixer for 10 min at 1200 rpm.

145 The silicone/hybrid composite film (Si-LDH) was prepared by casting onto a Teflon surface using  
146 an Elcometer 4340 automatic film applicator. The knife blade height was set at 200 µm and the  
147 casting speed was 30 mm/s. This two-component silicone film was cured at 80 °C for 2 hours.

148 A reference film composed of SRB powder dispersed in the silicone, called Si-SRB, was also  
149 performed by dispersing 100 µL of an SRB solution in ethylene glycol (10 g.L<sup>-1</sup>) in 4.45 g of part A of  
150 the silicone elastomer using the "Thinky Mixer" mechanical mixer for 10 min at 1200 rpm. Then 0.45  
151 g of part B was added and homogenised with the mechanical mixer for 10 min at 1200 rpm. The film  
152 was prepared by casting onto a Teflon surface in the same way as for Si-LDH mentioned above.

153 Film thickness was measured using an Elcometer 456 coating thickness gauge.

## 154 **2.4. Characterisation**

### 155 **2.4.1. X-ray diffraction**

156 LDH powders were characterised by X-Ray Diffraction; the XRD patterns were recorded with a  
157 Philips X-Pert Pro diffractometer operating with Cu-Kα radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The data were  
158 collected in a 2θ range between 5° and 70° with a step size of 1°/min.

159           **2.4.2. Thermogravimetric analysis**

160           Thermogravimetric (TG) analyses were performed on a Setaram TGA 92 instrument with a linear  
161 heating rate of 5 °C.min<sup>-1</sup> under air.

162           **2.4.3. UV-Visible absorption**

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

166           **2.4.4. Luminescence**

167           Quantum yield efficiencies and emission spectra were measured using a C9920–02G PL-QY  
168 integrating sphere measurement system from Hamamatsu Photonics. The setup consisted of a 150 W  
169 monochromatized Xe lamp, an integrating sphere (Spectralon coating,  $\varnothing= 3.3$  in.) and a high-  
170 sensitivity CCD camera.

171           **2.4.5. Emission stability of films under LED irradiation**

172           A photo-aging study was performed in a SEPAP 12/24 unit. This system was designed to achieve  
173 accelerated artificial weathering conditions related to natural ageing. The composite films were  
174 placed on a rotating carousel positioned in the centre, and four polychromatic mercury lamps (400  
175 W) with wavelengths higher than 300 nm (90 W.m<sup>-2</sup>) were installed at the corners of the chamber.  
176 The temperature was set at 60 °C.

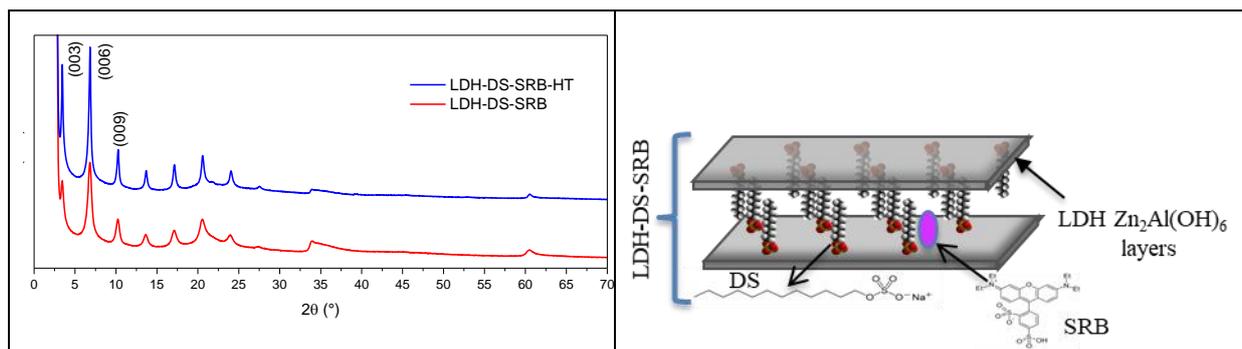
177 Reliability studies were carried out using a home-made setup consisting of a power-controlled blue  
178 LED emitting at 460 nm as the excitation source and a HR4000 high resolution spectrometer (Ocean  
179 Optics) as the PL analyser. The samples were positioned on a heating element whose temperature  
180 was adjusted to 80°C. The emission spectra of the composite films were acquired every 20 min for 24  
181 hours. Their area was integrated to obtain the total emission intensity. LED power was measured  
182 using a Scientech Model Mentor MA 10 with a MC2501 calorimetric head unit (25.4 mm aperture).  
183 The measurement was performed by centring the head unit over the LED source and measuring the  
184 power of the LED light emitted through the aperture. The blue LED power was 183 mW. The LED  
185 power density can be expressed in W/m<sup>2</sup> and was calculated by LED power (in watt) per unit surface  
186 of the sample (0.25 cm<sup>2</sup>). The power density of the blue LED was 9300 W/m<sup>2</sup>; for our experiments, a  
187 filter was used in order to reduce this value to 2480 W/m<sup>2</sup>.

188           **3. Results and discussion**

189           **3.1. Hydrothermal post-treatment**

190           **3.1.1. Structural effect**

191           X-ray diffractogram patterns of both LDH-DS-SRB and LDH-DS-SRB-HT powders before and after  
192 hydrothermal treatment respectively are plotted in Fig. 1. The two patterns closely overlap, and the  
193 associated diffraction peaks are located at similar angles in 2 $\theta$ . The observed interlamellar space is  
194 2.58 nm for both powders. However, thinner diffraction peaks are observed for LDH-DS-SRB-HT than  
195 for LDH-DS-SRB powder, in particular the peaks with  $h$  Miller peak indices, underlining the fact that  
196 the hydrothermal treatment induced more ordered platelet stacking.



197

198 *Figure 1. X-ray patterns of LDH-DS-SRB and LDH-DS-SRB-HT powders and on the right an idealized*  
 199 *scheme of the LDH-DS-SRB.*

200

201 The average size of crystallites can be calculated using the Scherrer equation  $L = k\lambda / (B \cdot \cos\theta)$   
 202 where B is the FWHM (Full Width at Half Maximum) of diffraction peak (003),  $\lambda$  is the Cu  $K_{\alpha}$  radiation  
 203 wavelength in nm,  $\theta$  is the diffraction angle of (003) in radian et k is the shape factor ( $k = 0,9$ ) (Cullity,  
 204 1978). The sizes calculated for LDH-DS-SRB and LDH-DS-SRB-HT are 27.2 nm and 42.3 nm  
 205 respectively, these values corresponding roughly to 11 and 16 structurally coherent stacked layers,  
 206 thus confirming a better crystallisation in the stacking direction for LDH-DS-SRB-HT.

207 As shown in a previous paper (Legentil et al., 2020) and illustrated on the scheme of the  
 208 Fig.1(right), the sulfonate groups are in the vicinity of the hydroxyl-covered LDH layers, thus leaving  
 209 the benzene and xanthene rings close to the surfactant alkyl chains. The relative amount of SRB per  
 210 DS is very small, SRB is highly diluted in the LDH-DS environment.

### 211 **3.1.2. Optical properties**

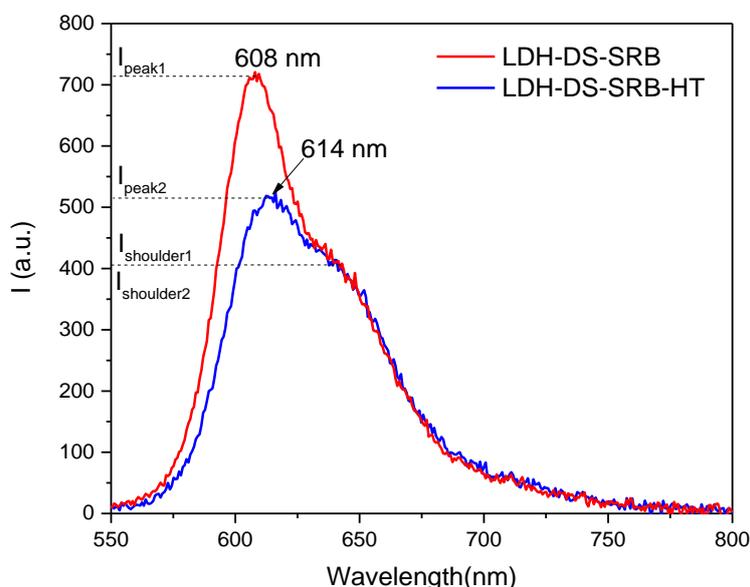
212 Internal photoluminescence quantum yields (PL  $QY_{int}$ ) were recorded from the samples  
 213 before and after hydrothermal treatment to know whether a change in the ordered stacking may  
 214 affect the optical response of the interleaved dye molecules (Table 1). Rather counter-intuitively,  
 215 LDH-DS-SRB-HT powder exhibits lower PL  $QY_{int}$  than LDH-DS-SRB. Even if the hydrothermal treatment  
 216 leaves intact the confinement of the SRB molecules inside the host structure (similar basal spacing is  
 217 observed), a significant decrease in the luminescence properties is observed for the three excitation  
 218 wavelengths of interest (570 nm is the excitation wavelength leading to the best PL  $QY_{ab}$  and  $int$ ,  
 219 (Legentil et al., 2020) (365 nm and 480 nm wavelengths correspond to UV and commercial blue  
 220 LED, respectively).

221 **Table 1.** PL  $QY_{int}$  of LDH-DS-SRB and LDH-DS-SRB-HT powder for three excitation wavelengths (570  
 222 nm, 480 nm and 365 nm). Three wavelengths are of interest: the 365 nm and 480 nm wavelengths  
 223 correspond to UV and commercial blue LED respectively, while 570 nm is the excitation wavelength  
 224 leading to the best PL  $QY_{ab}$ .

	Excitation wavelength	LDH-DS-SRB	LDH-DS-SRB-HT
PL $QY_{int}$ (%)	570 nm	73.1 ± 3.5	52.6 ± 2.5
	480 nm	68.9 ± 3.5	42.8 ± 2.1
	365 nm	73.1 ± 3.7	39.0 ± 2.0

225 We can note that the PL  $QY_{ab}$  recorded for these samples before and after hydrothermal  
226 treatment (which corresponds to the ratio between the number of photons emitted by the phosphor  
227 and the number of photons emitted by the excitation source) leads to the same conclusion (Table  
228 S2).

229 To better understand the modification undergone by the dye molecule, the emission spectra  
230 under blue excitation (480 nm) were recorded for both LDH-DS-SRB and LDH-DS-SRB-HT powders  
231 (Fig. 2). The emission spectra being similar for the other two excitation wavelengths, they are not  
232 presented here. The maximum intensity of the emission band is shifted towards higher wavelengths  
233 (from 608 to 614 nm) after the hydrothermal treatment, thus indicating a modification of the  
234 environment for the SRB molecules. In detail, the intensity ratio between the main emission peak  
235 and the associated shoulder is also modified, with the values of  $I_{\text{shoulder1}}/I_{\text{peak1}} = 0.58$  and  $I_{\text{shoulder2}}/I_{\text{peak2}} = 0.67$   
236 before and after the hydrothermal treatment, respectively. Since the main peak is attributed  
237 to SRB monomer molecules and the shoulder peak to SRB aggregates (dimer and trimer) (Ray and  
238 Nakahara, 2002; Yan et al., 2009), the hydrothermal treatment leads to a greater aggregation of the  
239 SRB molecules into the LDH-DS hybrid material.



240

241 **Figure 2.** Emission spectra of LDH-DS-SRB and LDH-DS-SRB-HT for  $\lambda_{\text{exc}} = 480$  nm

242 From these observations, the LDH-DS-SRB sample without hydrothermal treatment is selected in the  
243 following.

### 244 3.2. Effect of thermal stress

#### 245 3.2.1. Powder LDS-DS-SRB

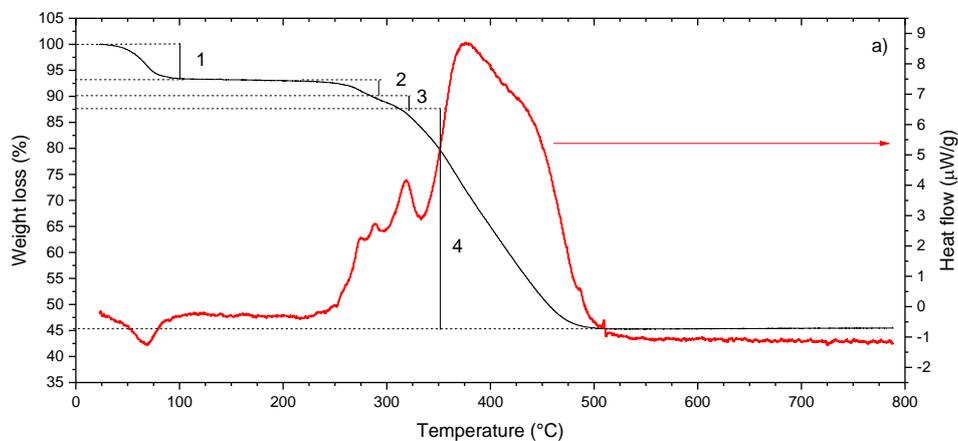
246

#### 247 Thermogravimetric analyses (TGA)

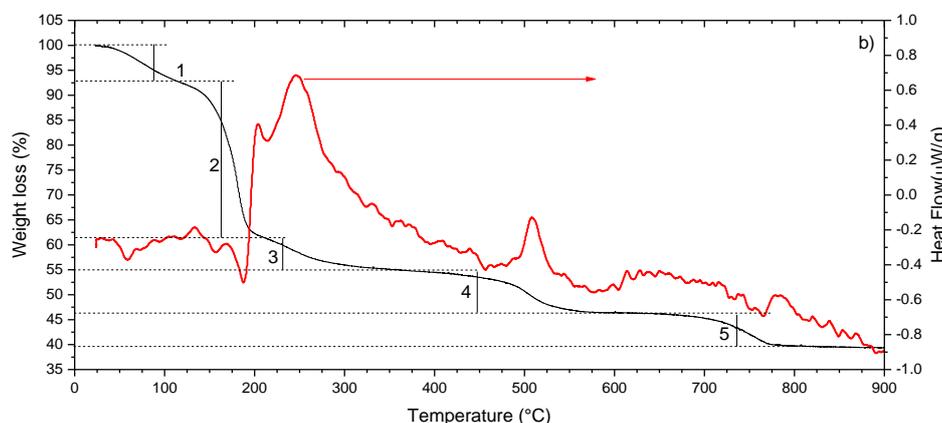
248 Thermogravimetric analysis shows that the SRB molecule is stable up to about 220 °C (Fig. 3a).  
249 Below 100 °C, the mass loss can be attributed to the departure of the weakly-adsorbed water

250 molecules (weight loss n°1 of 6,8% around 80-100 °C). After 220 °C, decomposition of the SRB  
251 molecules (weight loss n°2, 3 and 4) occurs until the final mass loss observed at 500 °C.

252



253



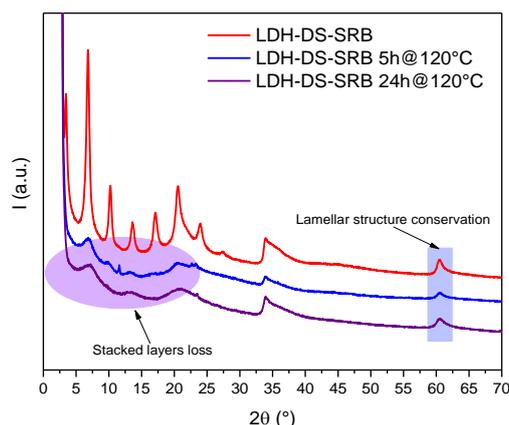
254

255 **Figure 3.** Thermogravimetric analysis and heat flow of a) SRB (2 °C/min, 25 °C- 800 °C, under air) and  
256 b) LDH-DS-SRB powder (2 °C/min, 25 °C-1000 °C, under air).

257 For the hybrid LDH-DS-SRB material, several mass losses are observed. After the water  
258 molecules that are weakly bound to the surface of the HDL platelets have been removed (weight  
259 loss 1), deshydroxylation of the LDH layers occurs from 180 up to 300 °C, concomitantly with the  
260 decomposition of the interleaved organic molecules (weight losses 2 and 3). This is consistent with  
261 DS decomposition, well documented in the literature (Degoutin et al., 2008; El-kharrag et al., 2011).  
262 The associated mass loss starts at 200 °C and continues up to 400 °C. The mass loss observed at 500  
263 °C is attributed to the final decomposition of the organic residue, while the mass loss at around 740  
264 °C is assigned to the decomposition of ZnSO<sub>4</sub> formed during the thermal treatment with the collapse  
265 of the LDH layers reacting with the functionalized head of the surfactant (as well as possibly SRB).

#### 266 Thermal stress in oven (120 °C)

267 The thermal stability study was completed in static conditions by placing the LDH-DS-SRB in an  
268 oven at 120 °C for 24 hours. X-ray diffraction patterns were recorded after 5 and 24 hours (Fig. 4).

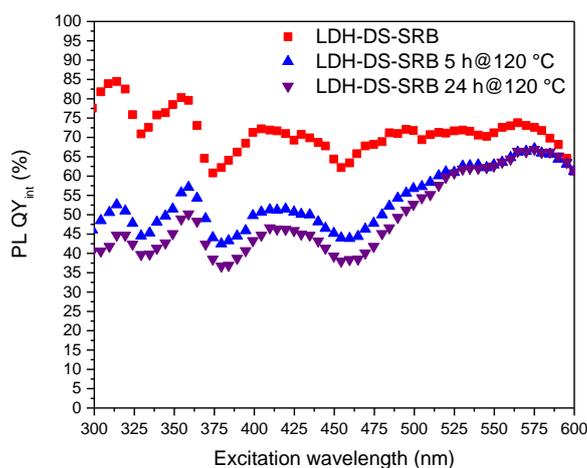


269

270 **Figure 4.** X-ray diffraction patterns of LDH-DS-SRB powder before after thermal treatment (5 and 24  
271 hours)

272 After both exposure times at 120 °C, the LDH-DS-SRB powder exhibits a similar XRD pattern. As  
273 the peak at 61 ° in 2θ assigned to the diffraction peak (110) merged with (113) is still observed, this is  
274 indicative that the LDH layer structure is maintained. However, the harmonic peaks (00 $l$ ), visible at  
275 angles lower than 25 ° (2θ) attributed to the strongly pronounced stacking for LDH-DS-SRB disappear  
276 after the thermal treatment at 120 °C. Only a few peaks of relatively low intensity are observed; the  
277 first peak located at 2θ = 7.5 ° corresponds to a basal spacing of 11.8 nm. Unexpectedly at this low  
278 temperature, this strong modification can be explained by the decomposition of the interleaved  
279 organic DS molecules. Even if the decomposition of DS occurs at slightly higher temperatures under  
280 dynamic mode (TGA), the surfactant is found to be thermally unstable in static conditions. A basal  
281 spacing of 11 to 12 nm for the degraded hybrid phase seems to indicate the presence of interleaved  
282 sulfate anions (Sotiles and Wypych, 2019) in association with a significant loss of coherent stacking,  
283 which can be further interpreted by a process of exfoliation.

284 Variations in internal photoluminescence quantum yields (PL QY<sub>int</sub>) as a function of the  
285 excitation wavelengths are shown for the samples treated 5 and 24 h at 120°C and for  
286 pristine LDH-DS-SRB powder in Fig. 5.



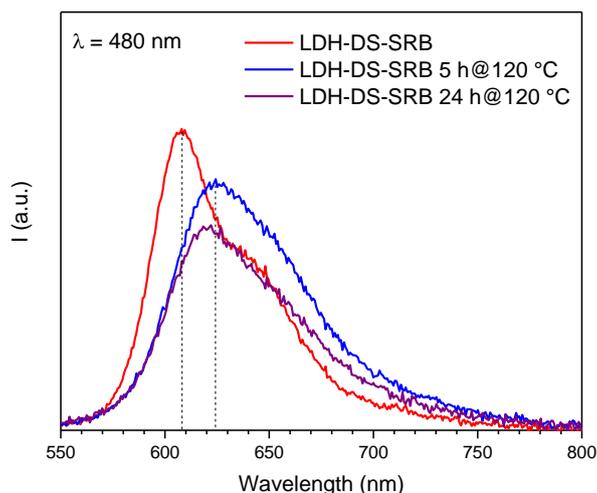
287

288 **Figure 5.** Variation in PL QY<sub>int</sub> as a function of the excitation wavelength for LDH-DS-SRB powders,  
289 before and after thermal treatment at 120 °C.

290 The PL  $QY_{int}$  slightly decreases after the thermal treatment (for both exposure times) while the  
291 SRB molecule is not expected to decompose in this temperature range (Fig. 3 a). The partial loss of  
292 the stacked structure reduces the optical properties, most probably by changing the local  
293 environment of the SRB molecules. Indeed, initially stabilised by the LDH host structure as well as  
294 well dispersed and ensconced within the space supplied by the interleaved DS, the modification may  
295 cause the SRB molecules to move closer to each other. This could explain the decrease in the  
296 photoluminescence properties due to the non-radiative de-excitations.

297 Emission spectra of the LDH-DS-SRB powder before and after thermal treatment are compared  
298 (Fig. 6). In both cases, a wide and asymmetric emission band is observed. The maximum intensity is  
299 strongly shifted (by about 15 nm) after treatment at 120 °C. Moreover, emission intensity is found to  
300 decrease and the contribution associated with the SRB aggregates increases. At this temperature the  
301 loss of the lamellar structure, as explained before, leads to significant interactions between the SRB  
302 molecules, which are close to each other and are prone to aggregation by  $\pi$ -stacking (parallel  
303 stacking) due to conjugated xanthene rings or by hydrogen bonding (head-to-tail). Xanthene dyes  
304 such as SRB or fluorescein are well known to interact mutually, resulting in luminescence quenching  
305 (De and Kundu, 2011).

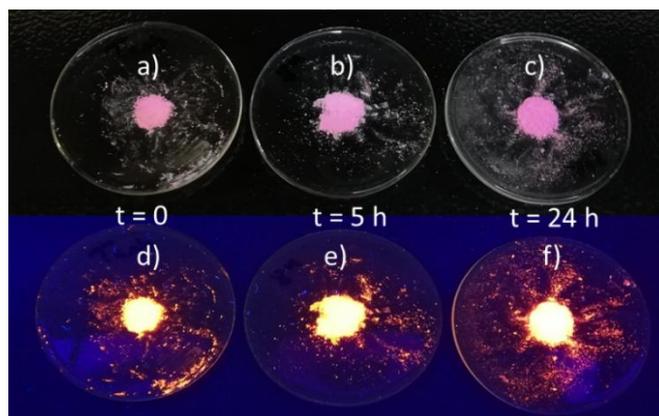
306



307

308 **Figure 6.** Emission spectra of the LDH-DS-SRB powder before and after thermal treatment at 120 °C  
309 for 5 h and 24 h ( $\lambda_{exc} = 480$  nm).

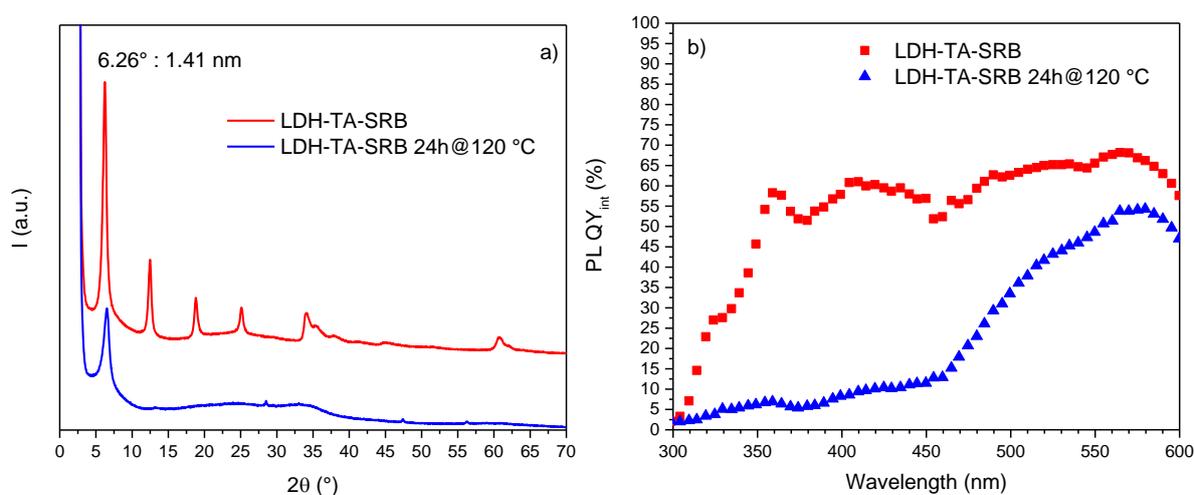
310 The LDH-DS-SRB powders treated at 120 °C for 5 and 24 hours are shown in Fig. 7 under daylight  
311 and UV excitation (365 nm). The heat-treated powder exposed for 24 hours appears slightly darker  
312 under daylight (Fig. 7 c) than the initial powder or the sample treated for 5 hours (Fig. 7 a) and b),  
313 respectively). Under UV radiation (Fig. 7 d), e) and f), the three powders are photoluminescent with  
314 no real distinction in terms of emission intensity.



315  
 316 **Figure 7.** Initial LDH-DS-SRB powder and powders treated at 120 °C for 5 and 24 hours under daylight  
 317 (a), b) and c), respectively) and under UV radiation (365 nm) (d), e) and f), respectively).

318 Replacing dodecylsulfate (DS) by terephthalate anions (TP)

319 With the aim of providing more stability, a study was performed by replacing the mono-  
 320 functional surfactant DS by terephthalate anions (TP). Pioneering work showed the pillaring effect of  
 321 such a di-anion form (Drezdzon, 1988), which should be of interest here in stabilizing the host  
 322 structure. However, the amount of interleaved TP was half the quantity of DS, while the amount of  
 323 SRB was not modified. The LDH TP SRB sample was treated at 120 °C in an oven for 24 hours. The  
 324 XRD patterns before and after this thermal treatment are presented in Fig. 8 a). Before thermal  
 325 treatment, the powder is well crystallized, leading to a basal spacing of 1.41 nm (diffraction peak  
 326 (003) at 6.3 ° in  $2\theta$ ), in agreement with the literature (Drezdzon, 1988). As before in the case of DS,  
 327 the presence of SRB molecules cannot be detected, due to the very small amount used. After  
 328 treatment, the pattern is strongly modified but the diffraction peak (003) at 6.3 ° in  $2\theta$  is still  
 329 observed, meaning that the lamellar structure, even if largely degraded, is still somehow present. As  
 330 expected, the 2D host structure is more robust under thermal stress thanks to a pillaring effect  
 331 supplied by the TP molecules. Indeed, bi-tethered TP molecules allow an increase in the cohesion  
 332 strength between layers.

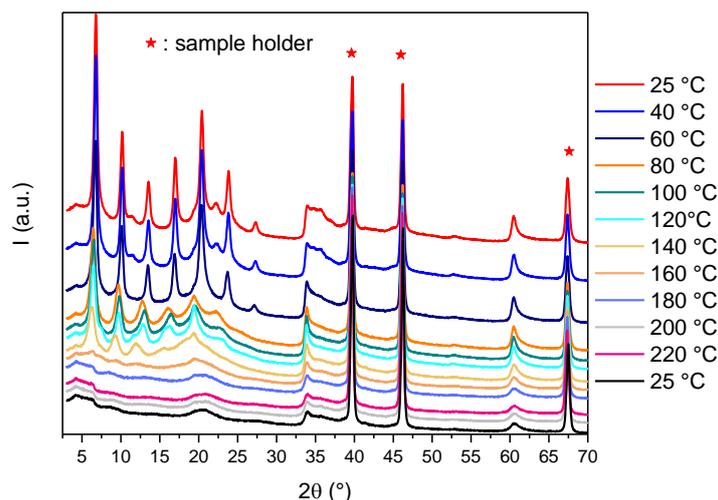


333  
 334 **Figure 8.** a) XRD patterns of LDH-TP-SRB powder and b) PL  $QY_{int}$  before and after thermal treatment  
 335 at 120 °C for 24h.

336 PL  $QY_{int}$  was recorded before and after the thermal treatment for excitation wavelengths  
337 between 300 and 600 nm (Fig. 8 b). Before thermal treatment, the optical performances of the  
338 sample LDH-TP-SRB are generally weaker than for LDH-DS-SRB (68.1 % and 73.8 % at 570 nm  
339 respectively, for example). Moreover, photoluminescence is also thermally more affected, and the PL  
340  $QY_{int}$  of LDH-TP-SRB decreases significantly after the treatment at 120°C; this is even more  
341 pronounced below 450 nm. At first glance, the structural cohesion supplied by TP molecules does not  
342 help to stabilize the photoluminescence properties more than in the case of the DS spacer. This is  
343 tentatively interpreted by the fact that the interlayer molecular packing is halved when replacing DS  
344 by TP, leaving the SRB molecules more space and more potential to diffuse freely, possibly causing  
345 their intermolecular interaction and thus optical quenching. For this reason, the focus is on LDH DS  
346 SRB in the following.

#### 347 HTK-XRD analysis: thermal stability up to 220 °C

348 To unravel more precisely the structural changes occurring in the temperature domain between  
349 25 and 220 °C, the LDH-DS-SRB powder pattern was recorded with a progressive temperature rise.  
350 The series of stacked XRD patterns recorded for each 20 °C step is shown in Fig. 9.

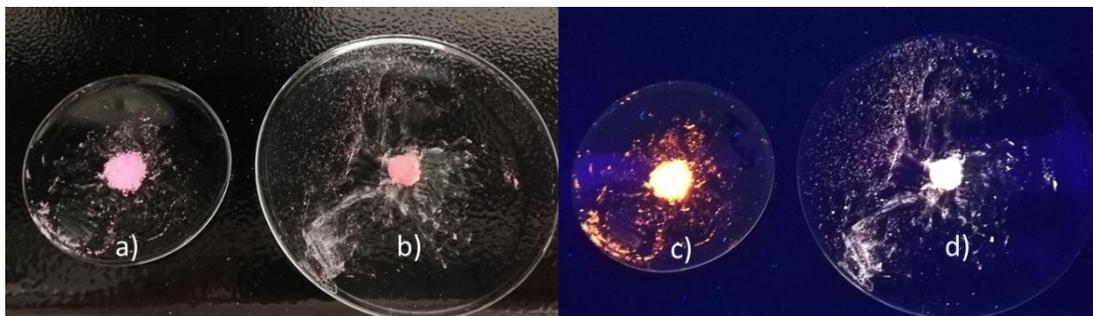


351  
352 **Figure 9.** XRD patterns of LDH-DS-SRB powder as a function of temperature (HTK-XRD): temperature  
353 elevation of 5 °C/min followed by 15 minutes of temperature stabilisation then 1 hour of acquisition.  
354 Cooling, at 15 °C/min until reaching 25 °C, is followed by a 1-hour stabilisation period; then a final  
355 acquisition for another hour is recorded. The three intense peaks at 40°, 46° and 65° in  $2\theta$  are due to  
356 the platinum holder.

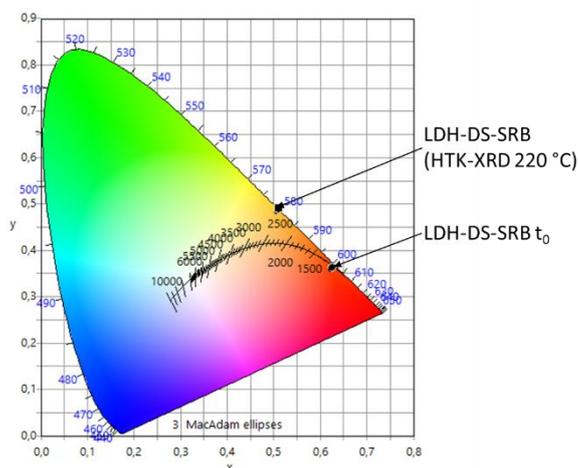
357 Between 25 and 60 °C, the XRD patterns are superimposed, then the intensity of the  
358 diffraction peaks ( $00\ell$ ) decreases with the temperature above 80°C, underlining that the LDH matrix  
359 is gradually losing its crystallinity in the stacking direction. Above 160°C, the diffraction peaks ( $00\ell$ )  
360 observed below 30 ° in  $2\theta$  disappear, thus showing the absence of any stacking. However, the LDH  
361 sheets remain intact, with the presence of diffraction peaks at 35 and 60° in  $2\theta$ . This study confirms  
362 that the layer structure of the LDH hybrid material is lost with the decomposition of the surfactant  
363 molecules, while the LDH sheets remain after treatment at 220°C.

364 Photographs of LDH-DS-SRB powder under daylight and UV excitation at 365 nm before and  
365 after HTK-XRD are presented in Fig. 10. In daylight, the powder treated at 220 °C (b) is still pink, but

366 slightly less colourful than the initial powder (a). Under UV radiation (365 nm), photoluminescence is  
 367 also still observed (d) but the emission is much weaker than initially (c). Moreover, the colour  
 368 emitted by the powder excited under UV radiation is slightly different, as shown in Fig. 11. Indeed,  
 369 the thermal treatment has an effect on the trichromatic coordinates, with a pronounced shift in the  
 370 XY CIE diagram.

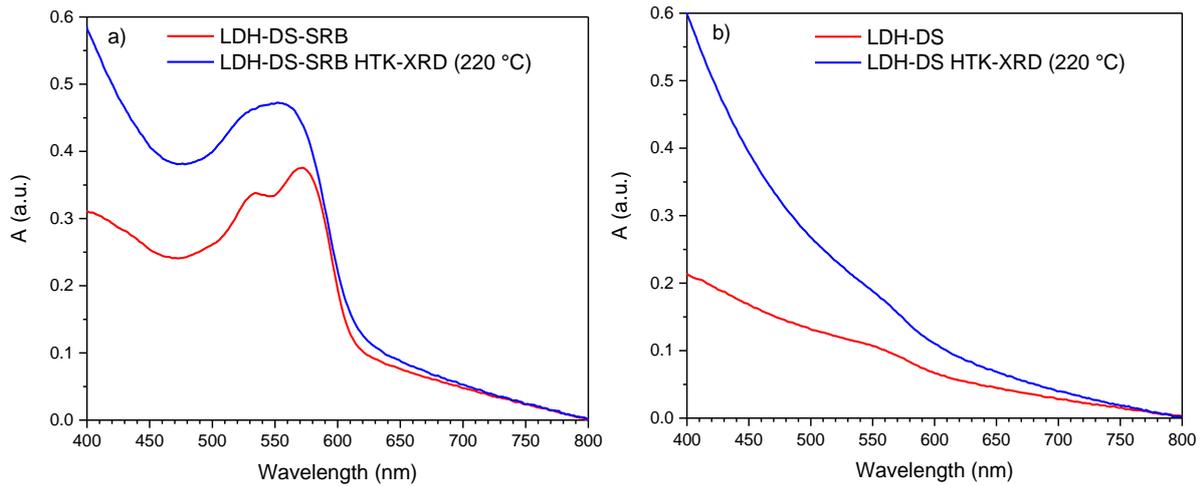


371  
 372 **Figure 10.** LDH-DS-SRB powder in daylight before (a) and after (b) HTK-XRD analysis (220 °C then  
 373 cooled to 25 °C) and under UV radiation at 365 nm before (c) and after (d) this analysis.



374  
 375 **Figure 11.** XY CIE 1931 diagram representing the trichromatic coordinates of the LDH-DS-SRB powder  
 376 before and after HTK analysis.

377 The effect of the thermal treatment on the UV-vis absorption spectra of LDH-DS-SRB is shown in  
 378 Fig. 12 a. The main absorption band of the SRB molecule, centred at 570 nm, is still observed after  
 379 the thermal treatment at 220°C. However, the overall absorption is found after such heat treatment  
 380 to increase significantly in the 400-600 nm range. This could be explained by the formation of  
 381 absorbent residual product from the decomposition of the DS molecules from 120 to 150°C (Fig. 3 &  
 382 4). This is confirmed by the UV-vis absorption spectra of the LDH-DS powder (Fig. 12 b). The LDH-DS  
 383 powder initially presents a white colour, whereas after heat treatment at 220°C it is black, which is  
 384 consistent with the formation of carbonaceous products.



385

386 **Figure 12.** UV-visible spectra of a) LDH-DS-SRB and b) LDH-DS powders before and after HTK-XRD  
387 analysis.

388 The PL  $QY_{int}$  of the LDH-DS-SRB powders before and after thermal treatment at 220°C are  
389 reported in Table 2 for  $\lambda_{exc} = 480$  and 365 nm. The drop in optical performance is clearly shown by  
390 these PL  $QY_{int}$  values.

391

392 **Table 2.** PL  $QY_{int}$  for  $\lambda_{exc} = 480$  nm and 365 nm of LDH-DS-SRB powder before and after the HTK-XRD  
393 analysis (after cooling to 25 °C)

	Excitation wavelength	LDH-DS-SRB 25 °C	LDH-DS-SRB 220°C then cooled to 25°C
PL $QY_{int}$ (%)	$\lambda_{exc} = 480$ nm	$68.9 \pm 3.5$	$15.0 \pm 0.8$
	$\lambda_{exc} = 365$ nm	$73.1 \pm 3.7$	$4.3 \pm 0.2$

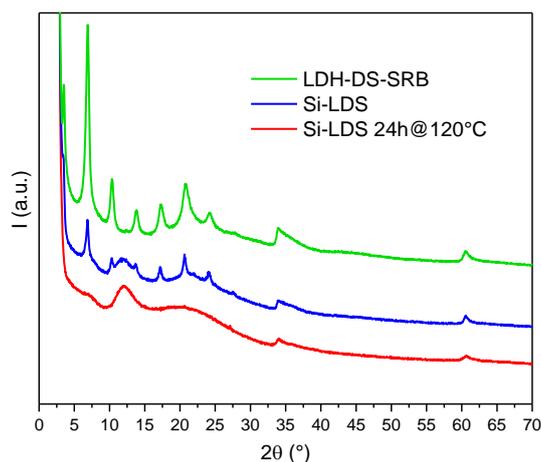
394

### 395 **3.2.2. Silicone/LDH-DS-SRB composite film (Si-LDS) behaviour under thermal stress**

396 The thermal stability of the Si-LDS composite film with the optimal formulation was further  
397 studied at 120 °C for 24 h.

#### 398 X-ray diffraction

399 XRD patterns of the Si-LDS composite film before and after the thermal treatment are presented  
400 in Fig. 13 and were compared to the pattern of the LDH-DS-SRB reference powder. First, the LDH  
401 matrix relative diffraction peaks are observed on the composite film pattern. After the thermal  
402 treatment the harmonic peaks (00 $l$ ) disappear, indicating that the dispersion of the LDH-DS-SRB  
403 powder in silicone does not improve its thermal stability in terms of structural 2D integrity.



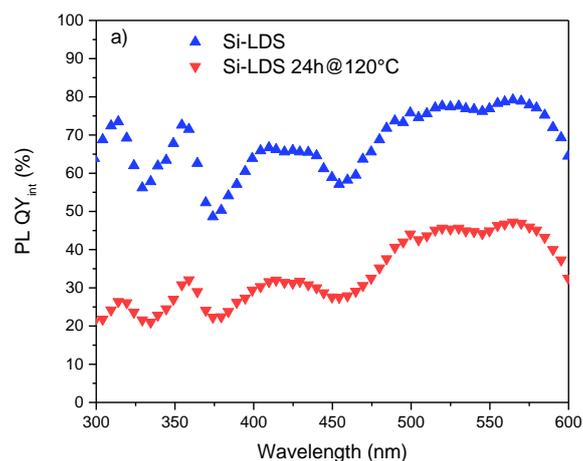
404  
 405 **Figure 13.** XRD patterns of the Si-LDS composite film before and after thermal treatment as well as  
 406 the pattern of the LDH-DS-SRB powder

407 Optical properties

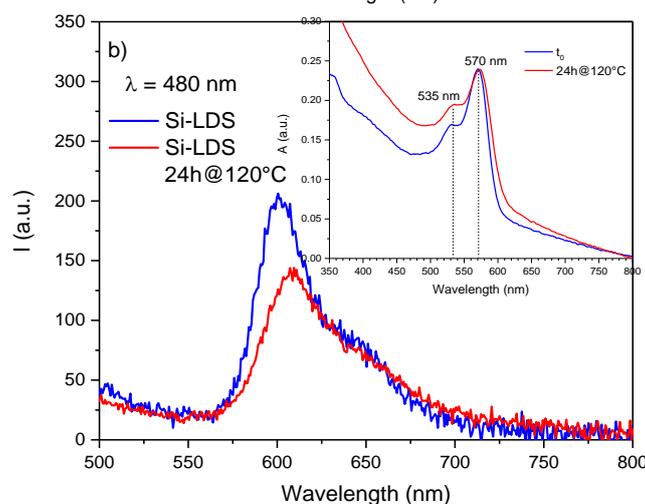
408 The PL  $QY_{int}$  of the composite film were recorded as a function of the excitation wavelengths  
 409 before and after the thermal treatment in an oven at 120 °C for 24 hours, and are shown for each  
 410 sample in Fig. 14 a. After the thermal treatment, the PL  $QY_{int}$  decreases significantly in the studied  
 411 spectral range of 300-600 nm.

412 The emission spectrum of the composite film is shifted after the thermal treatment towards  
 413 higher wavelengths (Fig. 14 b). This is the result of the aggregation of SRB molecules, as already  
 414 observed with the LDH-DS-SRB reference powder (Fig. 6). The UV-Vis emission spectra also support  
 415 these findings, with a significant broadening and an increase in absorption over the 550-350 nm  
 416 range for the sample heat-treated at 120°C. Finally, for this thermal treatment, the PL  $QY_{int}$  of the Si-  
 417 LDS composite film and of the LDH-DS-SRB powder (Fig. 5), exhibit the same change in their spectral  
 418 features. However, the PL  $QY_{int}$  values recorded for the film are lower than for powder. This is in part  
 419 explained by the dilution effect provided by the silicone matrix.

420 A film composed exclusively of silicone was also produced; it underwent the same 24-hour heat  
 421 treatment at 120°C as the Si-LDS film. Recording the UV-Vis and infrared spectra led to the  
 422 conclusion that the silicone does not undergo any modification after this treatment. The decrease in  
 423 optical performance after the heat treatment at 120°C is thus explained, as for the powder, by an  
 424 aggregation phenomenon generated by temperature.



425



426

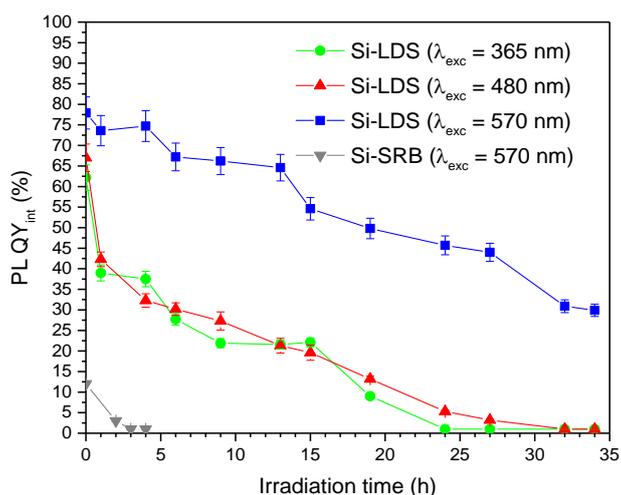
427 **Figure 14.** a) Variation in PL  $QY_{int}$  as a function of the excitation wavelength for the Si-LDS composite film before and after thermal treatment. b) Emission spectra ( $\lambda_{exc} = 480$  nm), and UV-visible spectra (inset) of the composite film before and after thermal treatment.

### 430 3.3. Composite film: durability under photonic and thermal stresses

#### 431 3.3.1. Accelerated photo-aging in a SEPAP 12/24 unit

432 The photo-aging of the Si-LDS composite film was studied using a SEPAP 12/24 unit. In order to  
 433 have a reference, a second Si-SRB composite film was produced by dispersing 0.05 %wt. pure SRB in  
 434 the silicone matrix. Thus, the amounts of SRB in both films are comparable.

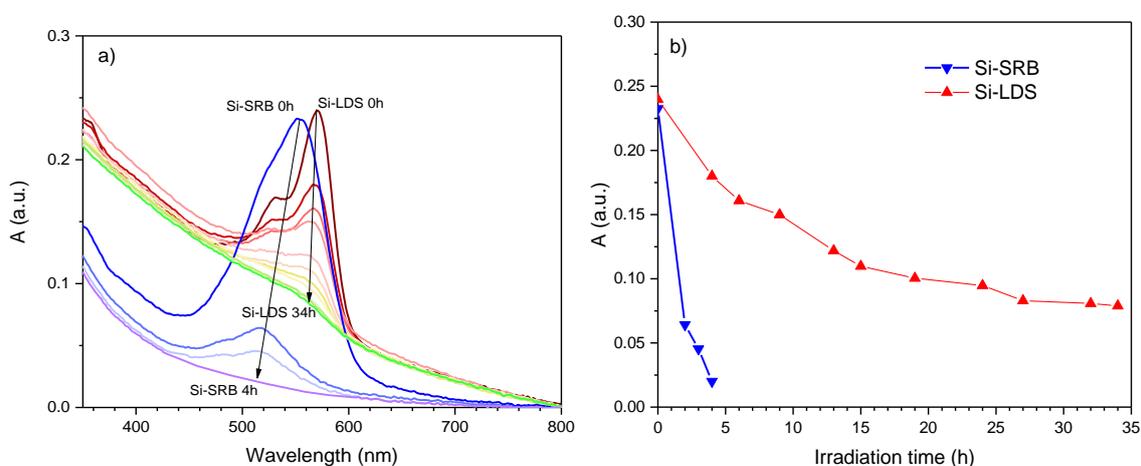
435 Fig. 15 plots PL  $QY_{int}$  as a function of irradiation time for three excitation wavelengths of interest  
 436 (365, 480 and 570 nm) for Si-LDS composite film. Only the variation in the PL  $QY_{int}$  for excitation at  
 437 570 nm is provided for the S-SRB film because its luminescence is initially very low or even non-  
 438 existent for excitations at 365 and 470 nm. At 570 nm, after only 3 hours, the Si-SRB film has entirely  
 439 lost its luminescence, whereas the luminescence of the Si-LDS film remains identical to that observed  
 440 initially, showing the benefit of the inorganic vessel for stabilizing the SRB optical properties.  
 441 Quantitatively, after 35 hours the PL  $QY_{int}$  of the Si-LDS film is still above 30 %. For excitation at 365  
 442 and 480 nm, the kinetic of luminescence extinction is close to that at 570 nm.



443

444 **Figure 15.** Variation in PL  $QY_{int}$  as a function of irradiation time in the SEPAP 12/24 unit for both Si-  
 445 SRB and Si-LDS composite films for several excitation wavelengths (365, 480 and 570 nm).

446 In order to have a better understanding of these observations, UV-vis spectra were recorded  
 447 after photo-aging. The asymmetric band relative to SRB molecules is observed for both composites  
 448 before the irradiation process starts. Maximum absorbance is the same for both composites, which  
 449 confirms the similar quantity of SRB molecules in both composites. However, the maximum is shifted  
 450 by 20 nm between the two, and can safely be explained by a higher amount of SRB aggregates in Si-  
 451 SRB than in Si-LDS.



452

453 **Figure 16.** Variation in UV-visible spectra (a) and maximum absorbance (b) for Si-SRB and Si-LDS  
 454 composites as a function of irradiation time.

455 During the irradiation process, the main absorbance band decreases for both composites (Fig.  
 456 16 a). The SRB molecules are irreversibly damaged by irradiation in the SEPAP 12/24 unit. However,  
 457 the degradation kinetic is considerably faster for the Si-SRB film (Fig. 16 b) than for Si-LDS. Indeed,  
 458 absorbance is almost extinguished after only 4 hours for the Si-SRB film, whereas a value still subsists  
 459 after 34 hours for Si-LDS. This observation matches the decrease in the PL  $QY_{int}$  described above (Fig.  
 460 15).

461 In conclusion, the LDH host matrix makes it possible to elaborate a homogeneous composite  
 462 luminescent film, but also to significantly increase SRB stability under stresses (thermal and

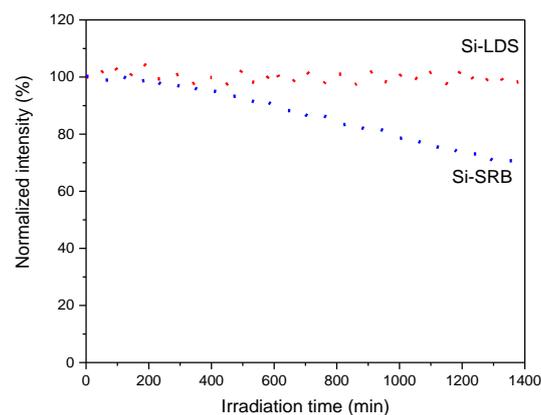
463 photonic). The conditions in the SEPAP 12/24 unit were very drastic ( $\lambda > 300$  nm and  $T = 60$  °C) and  
464 are not well representative of the photo-aging of composites associated with commercial blue LEDs.  
465 Nevertheless, these experiments provide information on the stability of the Si-LDS film under UV LED  
466 excitation. In the following section, the behaviour of these composites is studied in direct association  
467 with a commercial blue LED.

### 468 3.3.2. Aging under blue LED

469 In order to assess the stability of the Si-LDS composite film in operating conditions close to  
470 those encountered in LED devices, the Si-LDS film and the Si-SRB composite film were irradiated by a  
471 powerful blue LED (460 nm, power:  $2480 \text{ W/m}^2$ ) for 1400 minutes at  $80^\circ\text{C}$  in a black chamber. A  
472 spectrophotometer recorded the emission spectra every 20 minutes for 24 hours.

473 The variation in the integrated areas of the emission spectra as a function of irradiation time is  
474 illustrated in Fig.17.

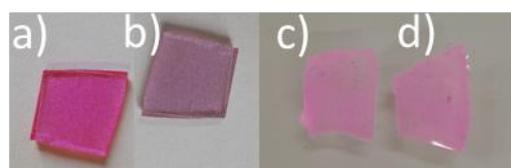
475 The Si-LDS composite film, using the LDH hosting the SRB molecules, is not affected at all by the  
476 stresses, and photoluminescence intensity is stable. On the contrary, the intensity of Si-SRB  
477 decreases significantly with irradiation time. A loss of 32 % was observed at the end of the first 24  
478 hours. The beneficial effect of the LDH matrix is thus clearly demonstrated in such real conditions of  
479 use, and confirms that this Si-LDS film is fully compatible with a blue LED device.



480

481 **Figure 17.** Variation in normalized photoluminescence intensity with respect to irradiation time for  
482 the Si-LDS and Si-SRB composite films heated to  $80^\circ\text{C}$  and irradiated by a commercial blue LED (460  
483 nm,  $2480 \text{ W.m}^{-2}$ ).

484 Photographs of both composite films, Si-SRB and Si-SDS, are presented in Fig.18 before and after  
485 the 24 h irradiation process. The colour fading of Si-SRB reveals the degradation of the SRB  
486 molecules. The aspect of Si-LDS is not modified by photo-aging; the role of LDH is well highlighted  
487 here again.



488

489 **Figure 18.** Photographs of Si-SRB and Si-LDS composite films before (a) and c), respectively)  
490 and after (b) and d), respectively) aging under photonic (blue LED) and thermal (80°C) stresses.

#### 491 **4. Conclusions**

492 This study emphasises the ability of a LDH host structure to protect the SRB luminescent dye  
493 against various stresses. The LDH interior, filled with spacer, impedes SRB intermolecular interaction.  
494 This effect is found to be more pronounced for tightly-packed interlayer space obtained from a  
495 mono-functional co-intercalate such as DS than from TP. In the latter case, SRB molecules are freer to  
496 diffuse and thus to quench the optical properties. It is pointed out that the hybrid LDH-DS-SRB and  
497 the associated composite film exhibit a suitable orange - red emission under blue LED excitation.

498 The progressive loss in the optical properties of the LDH-DS-SRB hybrid powder after a  
499 treatment at 120 °C is explained by a breakdown of the LDH stacking structure, as confirmed by XRD  
500 analysis in temperature. This structural disruptive effect modifies the environment of the SRB  
501 molecules, most probably provoking their partial aggregations and thus leading to non-radiative  
502 energy transfers. Satisfactorily, a significant photoluminescence quantum yield is still observed after  
503 the thermal treatment.

504 Similarly, the LDH-DS-SRB/silicone composite film exhibits luminescence after thermal exposure,  
505 and this is also the case after being exposed to severe photo-aging conditions. Interestingly, the  
506 emission of the composite film when irradiated by a commercial blue LED at 80 °C to reproduce “real  
507 conditions of use” is completely stable after 24 hours. These results highlight the stability provided  
508 by the LDH host structure for dyes, and the potential of LDH-DS-SRB for commercial lighting  
509 applications based on a blue LED.

#### 510 **CONFLICTS OF INTEREST**

511 There is no conflict to declare.

#### 512 **FORMATTING OF FUNDING SOURCES**

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