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1 **Revisiting Fluorescein and layered double hydroxide using a synergistic approach: a complete**
2 **optical study**

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6 **Abstract**

7 The luminescence of Fluorescein, an inexpensive dye, ought to be interesting for lighting
8 application devices such as commercial LEDs. However, the molecule suffers from severe instability,
9 making it inappropriate for such applications. As previously studied, fluorescein molecules may be
10 hosted in a layered double hydroxide (LDH), and the role of such an inorganic material in stabilizing
11 the dye has been underlined. However, a deep understanding of the resulting optical properties is
12 still required. Using extremely small amounts of fluorescein, it is demonstrated here that Zn₂Al
13 cation-based LDH tethering acts as a «solid solvent» for the dye, enabling its luminescence even in
14 powder form, whereas fluorescein molecules on their own emit no luminescence at all in the solid
15 state. However, aggregations of the dye occur in the interlamellar space, leading to non-radiative
16 emission. Emission and excitation spectra, as well as fluorescence decays, are studied to explain the
17 difference between the hybrid LDH-Fluorescein material and an aqueous solution of fluorescein.
18 Additionally, LDH platelets are found to help the dispersion of the intercalated fluorescein in silicone
19 to obtain a homogeneous composite film, which exhibits luminescent properties. Finally, an
20 accelerated photoaging study demonstrates that the LDH-fluorescein filler has a pro-degradant effect
21 on polymer aging under UV radiation.

22 **1. Introduction**

23 In recent years, global warming on Earth has been causing major environmental problems. To
24 respond to this growing concern, scientists orient their research towards sustainable solutions, and
25 develop processes to save energy. Almost 20 % of the electricity consumption in the world is due to
26 the lighting sector, explaining why light-emitting diodes (LED) have emerged to provide efficient and
27 sustainable products replacing common lighting devices such as incandescent bulbs. However,
28 commercial LEDs are manufactured using rare earth-based phosphors; these elements are expensive
29 and not eco-friendly due to their extraction process and their life-cycle assessment. They might be
30 replaced by organic fluorescent molecules that are cheaply available and sustainable. Even if these
31 molecules exhibit high photoluminescent quantum yields, they nevertheless suffer from a lack of
32 robustness in standard operating conditions, thus greatly limiting them as efficient phosphors in
33 marketed lighting devices.

34 Fluorescein is a very common organic dye which has met with great interest for many years in a
35 wide range of applications thanks to its biocompatibility, high molar absorptivity and excellent
36 fluorescence quantum yield [1].

37 Fluorescein is an organic molecule belonging to the xanthene family and is used as a probe in
38 medical and biological applications (optical imaging, detection of analytes...) [2-4]. Fluorescein is a
39 red powder in the solid state, emitting a strong yellow-green light in liquid solution (in water at basic
40 pH or ethanol for example) at low concentration (below 10⁻³ M) and under UV-blue excitation. At
41 higher concentrations, a quenching phenomenon appears to reduce its light emission, and the solid
42 powder does not luminesce at all. In solution, the dye can take several prototropic forms depending
43 on the pH [5]. The dianionic form is the most luminescent one, and its contribution to the dye total

44 emission exceeds the others. A shoulder on the edge of the main peak (emission of the dianionic
45 form) may be observed, indicating the presence of the monoanionic form [6]. Indeed, the
46 monoanionic form also exhibits luminescent properties but its emission is much weaker, and the
47 global emission spectra are blue-shifted with a broadening of the emission band compared to that of
48 the dianionic form.

49 The optical properties of fluorescein could also lead to an interesting future in lighting
50 applications, and particularly in the LED-based field. Indeed, fluorescein emits green-yellow radiation
51 under blue excitation ($\lambda_{\text{max exc}} = 490 \text{ nm}$) compatible with a blue LED chip to produce a modulable
52 (warm or cold) white light emission for lighting applications. Some studies [1, 7] have already
53 emphasized the potential of fluorescein to replace phosphors associated with blue LEDs in
54 commercial devices such as rare-earth based common YAG:Ce. However fluorescein, like organic
55 molecules, is very sensitive to external photonic and thermal stress, and its luminescence quickly
56 breaks down in use [8], which has so far been a limiting factor for further development.

57 To overcome this issue, one alternative is to protect the dye from quenching and instability (i.e.
58 avoiding aggregation, thermal degradation, and so on) using a solid inorganic matrix, such as for
59 example using Layered Double Hydroxides (LDH), an anion host structure. Recently, photoactive
60 molecules intercalated into LDH layers have drawn much attention for the development of
61 nanophotosensitizers for therapeutic uses [9], stimuli-responsive intelligent materials and
62 luminescent sensors [10, 11]. Some studies [12] reported the intercalation of fluorescein molecules
63 into LDH. These materials present an interest, especially for catalysis and environmental applications
64 [13-15]. Their general chemical formula is: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot nH_2O$ where M(II) is a
65 bivalent cation such as Zn^{2+} , Mg^{2+} , Fe^{2+} , etc.; M(III) is a trivalent cation such as Al^{3+} , Fe^{3+} , etc. and A^{n-} is
66 an anion. The structure is layered and therefore anisotropic, built from cations and hydroxides having
67 a net positive charge caused by the partial substitution of bivalent cations by trivalent cations. To
68 ensure electroneutrality, anions are located in the interlayer space of the LDH with the presence of
69 water molecules. Since the Fluorescein molecule is an anionic dye, it may be hosted within the LDH
70 structure. The idea here is to possibly tether and stabilize fluorescein molecules while optimizing
71 their luminescence properties. It also allows fluorescein to be isolated from the outside environment
72 (O_2 from air) to avoid any accelerated oxidation and improve the dispersion of the fluorescein in a
73 polymer to produce homogeneous composite films for LED-based devices. LDH-based fluorescent
74 and phosphorescent thin films (TFs) elaborated by layer by layer (LBL) method have been reported in
75 the literature [16-18]. Herein, we focused on self-supporting thin luminescent composite films LDH-
76 Fluorescein/silicone which have been prepared by solution casting onto a Teflon surface using an
77 Elcometer 4340 automatic film applicator. Indeed, from the point of view of the organic dye, LDH
78 inorganic filler can be viewed as an anti-aggregation and protective agent, while from the LDH side,
79 the dye appears as an organo-compatibilizing agent to better resist polymer dispersion.

80 In this paper, the synthesis and characterization of a hybrid LDH-Fluorescein (LDH-F) material are
81 presented, and its optical properties are thoroughly examined. Among the several LDH, the Zn-Al
82 host matrix was chosen for this study as it displays a higher crystallinity compared to the more usual
83 hydroxalcite Mg-Al for example, thus allowing a more accurate characterization by XRD of the hybrid
84 materials as well as the filler upon polymer dispersion. LDH was used as host matrix to prevent
85 aggregation of fluorescein dye, allowing to avoid the quenching of the luminescence and acting as a
86 protective environment. Indeed, the usual passive LDH filler becomes here a photofunctional active
87 filler. The LDH matrix creates a dilute environment for the dye that is normally observed in an
88 aqueous solution: the LDH provides the fluorescein molecules with an environment which is suitable
89 for them to luminesce well. Although, several studies [19-21] about nanohybrids LDH-Fluorescein
90 have been reported for different applications a complete understanding of the mechanisms involved
91 is scarcely reported so far. In this work, the optical properties were deeply investigated and a better
92 understanding is highlighted to unravel mechanisms responsible of the luminescence of the solid

93 powder LDH-F. Indeed, a better understanding permits here the mechanisms responsible for the
94 luminescence to be identified. It is also demonstrated from an analysis of the photostability that LDH
95 platelets stabilize the dye under potential operating conditions.

96 2. Experimental section

97 2.1. Materials

98 The two-component silicon polymer, Bluesil RTV 141 part A and part B, was supplied by Elkem.
99 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity 99.9+%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity 99.9+%) and NaOH (97%) were obtained from
100 Sigma Aldrich. The fluorescein disodium salt $\text{C}_{20}\text{H}_{10}\text{Na}_2\text{O}_5$ was purchased from Alfa Aesar.

101 2.2. Synthesis procedure of LDH hybrid materials using the 102 coprecipitation method

103 The fluorescein layered double hydroxide phase, $\text{Zn}_2\text{Al-F}$, was prepared by the coprecipitation
104 method with different fluorescein concentrations. The synthesis of $[\text{Zn}_2\text{Al}_1(\text{OH})_6]^+[\text{NO}_3^-]_{1-x}[\text{F}^{2-}]_x \cdot \text{mH}_2\text{O}$
105 was performed using fluorescein disodium salt in 50 mL of de-ionized water. 50 mL of an aqueous
106 solution of Zn^{2+} (3.4×10^{-2} M) and Al^{+3} (1.7×10^{-2} M) was added dropwise over a period of 3 hours under
107 magnetic stirring. For instance, to make the $[\text{Zn}_2\text{Al}_1(\text{OH})_6]^+[\text{NO}_3^-]_{0.999}[\text{F}^{2-}]_{0.0005} \cdot \text{mH}_2\text{O}$ sample, 5.2×10^{-1}
108 mmol of fluorescein disodium salt was used.

109 The pH was maintained at 10.5 by adding 0.25 M NaOH during the synthesis processes.
110 Coprecipitation was performed under nitrogen at 20°C. The mixture was centrifuged at 5,000 rpm for
111 5 minutes; the sedimented solid on the bottom of the flask was washed several times with de-ionized
112 water until a clear and transparent supernatant was obtained. A paste was recovered and stored at
113 5°C. A small amount was dried overnight at room temperature to obtain a powder and to determine
114 the proportion of the dry extract.

115 2.3. Elaboration of Silicone/HDL-F resin composite films

116 The LDH-F (0.05 %) powder or the similar paste was used to elaborate the polymer/hybrid
117 composite material with different loadings. The two-component silicone polymer (silicone Bluesil-
118 RTV 141 A&B) was composed of a viscous liquid, called part A, cured by a polyaddition reaction with
119 a catalyser, part B.

120 The silicone film was prepared as follows: a mixture of part A and 10 phr of part B was prepared,
121 homogenised with a mechanical mixer (Planetary Centrifugal vacuum Mixer “Thinky Mixer”) for 10
122 minutes at 500 rpm. Next, the final composite film was prepared by casting onto a Teflon surface
123 using an Elcometer 4340 automatic film applicator. The knife blade height was set at 200 μm and the
124 casting speed was 30 mm/s. This two-component silicone polymer was cured at 80°C for 2 hours. The
125 film thickness was measured using an Elcometer 456 coating thickness gauge.

126 The preparation and the curing process for the composite films were the same as for the silicone
127 film.

128 2.4. Characterisation

129 2.4.1. X-ray diffraction

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

133 2.4.2. Elemental analyses CHNS

134 Elemental analyses of LDH powders LDH-F were performed to determine the composition of samples
135 with a Flash 2000 CHNS analyzers (Thermo Electron).

136 2.4.3. Thermogravimetric analysis

137 Thermogravimetric (TG) analysis were performed on a Setaram TGA 92 instrument with a
138 linear heating rate of 5 °C.min⁻¹ under air.

139 2.4.4. Fourier-transformed infrared spectroscopy

140 The infrared spectra were recorded using a Nicolet 5700-FTIR spectrometer with Omnic
141 software. Spectra were obtained using a summation of 32 scans and a resolution of 4 cm⁻¹. LDH and
142 fluorescein powders were studied using the KBr pellet technique.

143 In the case of silicone/LDH-F composite films, calibration of the thickness of the non-
144 photodegraded samples was performed by normalising the absorbance at 2140 cm⁻¹ in IR spectra,
145 which corresponds to a vibration band of the (Si-H) bending mode relative to the silicone. All the
146 spectra were compared with an absorbance of 0.240 at 2140cm⁻¹.

147 2.4.5. UV-Visible absorption

148 The UV-visible absorption spectra of the samples were recorded in the wavelength range of
149 200 to 800 nm with a UV-vis spectrophotometer (SP-3000 Plus) equipped with an integrating sphere
150 and UV-Probe software.

151 2.4.6. Luminescence

152 Quantum yield efficiencies were measured using a C9920-02G PL-QY integrating sphere
153 measurement system from Hamamatsu Photonics. The setup consisted of a 150 W monochromatized
154 Xe lamp, an integrating sphere (Spectralon coating, $\varnothing= 3.3$ in.) and a high-sensitivity CCD camera.
155 Excitation and blue-excited emission spectra were recorded with a Jobin-Yvon apparatus consisting
156 of a Xe lamp operating at 400 W coupled with two monochromators (Triax 550 and Triax 180) and a
157 cryogenically cooled charge-coupled device (CCD) camera (Jobin-Yvon Symphony LN2 series) for
158 emission spectra and Hamamatsu 980 photomultiplier for excitation spectra. Excitation spectra
159 were corrected for instrument response and Xe lamp intensity using sodium salicylate. The resolution
160 of the system was better than 0.1 nm in both emission and excitation configurations. Luminescence
161 decays were recorded using second-harmonic generation on a pulsed Nd:YAG OPO Ekspla NT342A
162 laser (3–5 ns pulse duration, 10 Hz, 5 cm⁻¹ line width, 0.3 mJ- 20 mJ in the UV-blue). The emitted
163 photons were detected at right angles to the excitation and analyzed via an Edinburgh FLS980
164 spectrometer (Czerny-Turner monochromator, 300 mm focal length, 1200 grooves mm⁻¹ grating and
165 minimum pass band of 0.1 nm) equipped with Hamamatsu R928P PMT (200–850 nm range).

166

167 2.4.7. Scanning electron microscopy (SEM)

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

170 2.5. Irradiation of films

171 Polymer and composite photodegradation under artificial aging conditions was performed in a
172 SEPAP 12-24 unit (ATLAS) by UV-visible light irradiation ($\lambda>300$ nm) in presence of oxygen at 60°C
173 (controlled by a Pt thermocouple). The device comprised four medium-pressure mercury lamps
174 (Novalamp RVC 400W) situated vertically at each corner of the chamber. The samples were placed

175 on a rotating carousel positioned in the centre of the chamber. Wavelengths below 300 nm were
176 filtered by the glass envelope of the lamps.

177 3. Results and discussion

178 3.1. XRD characterisation

179 3.1.1. Diffractogram results

180 Figure 1 shows the XRD patterns of LDH-fluorescein powders synthesized by coprecipitation. The
181 XRD patterns are shown as a function of the fluorescein relative input. The latter is expressed by the
182 mole ratio between fluorescein and Al^{3+} cations used during coprecipitation. Diffraction planes (00 l)
183 are the fingerprints of the layered structure of LDH [22]. For the sample with the least amount of
184 fluorescein (a), the positions of $2\theta = 10.1^\circ$ and 20.2° (i.e. 0.78 nm and 0.39 nm) are characteristic of a
185 nitrate LDH phase, and assigned to diffraction planes (003) and (006), respectively. As the amount of
186 fluorescein increases, these peaks at 10.1° and 20.2° progressively disappear, and a series of
187 harmonic peaks is shifted to a lower angle and located at 5.5° , 11° , 16.5° , and 22° for the sample with
188 the highest fluorescein content. For the intermediate contents (fig. 1b, 1c, 1d and 1e), the XRD
189 patterns overlapped and correspond to a combination of nitrate and fluorescein phases which are
190 mixed. These XRD peaks can be integrated to calculate the amount of fluorescein present in the
191 interlayer space (inset fig 1). A simple methodology based on pole concentration is used here.
192 Indeed, for sample (h), the experimental XRD pattern does not show the nitrate signal, and the ratio
193 of the integration of the first and second harmonics (003)/(006) of the fluorescein signals can be
194 calculated, resulting in a constant $R_{(003)/(006)}^{\text{Fluo}}$. For other samples for which a combination of nitrate
195 and fluorescein is observed, the (006) peak of the fluorescein signal merges with the (003) peak of
196 the nitrate signal. Using the constant $R_{(003)/(006)}^{\text{Fluo}}$ and the integration of the merged signals, the ratio
197 $(003)_{\text{Fluo}}/(003)_{\text{nitrate}}$ may be calculated for all the samples studied. These results are shown in the inset
198 in figure 1.

199 For the series of harmonic peaks, the one at $2\theta = 5.5^\circ$ leads to a basal spacing of 1.61 nm and is
200 ascribed to diffraction plane (003), such values agreeing well with the basal spacing observed for
201 fluorescein intercalated between LDH layers according to either Costantino et al. [23] or Tanaka et al.
202 [24]. Indeed, Costantino et al. showed that fluorescein can be intercalated in a Zn_2Al LDH matrix by
203 the ion-exchange method from a LDH-perchlorate in a fluorescein solution. As in the present study,
204 several concentrations of fluorescein were used, resulting in the presence of a pristine LDH phase
205 with a fluorescein LDH phase exhibiting a basal spacing of 1.65 nm. A slightly lower value of 1.58 nm
206 is observed for MgAl LDH. In this case and similarly to the present study, Tanaka et al. performed
207 fluorescein intercalation by coprecipitation and reported the setting up of two distinct fluorescein
208 phases depending on the pH of the synthesis, leading to two interlayer distances of 0.78 and 1.58
209 nm. According to Tanaka et al., guest accommodation within the interlayer domain for the former is
210 horizontal to the inorganic sheets, while it is vertical (perpendicularly tilted) for the latter.

211 Elemental analysis of powders was performed for some samples (sample a, d and h) to
212 determine the experimental fluorescein amounts remaining in the LDH powders after the synthesis.
213 Microanalyses CHNS allows to find the mass fraction of C, N and H elements contained in each
214 sample. Elemental analyses results are reported in table 1. Carbonate pollution in interlamellar space
215 is likely as XRD patterns shown and has been taken into account in the calculations. Thus, the
216 experimental formula can be easily calculated by using the experimental molecular mass M_w
217 determined with thermogravimetric analysis (see fig. S1 in the Supporting Information). For instance,
218 the experimental formula of the sample d obtained is: $\text{Zn}_2^{2+}\text{Al}^{3+}(\text{OH})_6 (\text{CO}_3^{2-})_{0.26}(\text{NO}_3^-)_{0.22}(\text{Fluo}^{2-})_{0.13}$,

219 1.5 H₂O in making assumption that the ratio Zn/Al = 2 is fixed, in this way x = 0.13 for fluorescein
220 amount whereas the theoretical value expected was x = 0.15. In the same way, experimental formula
221 for sample h is Zn₂²⁺Al³⁺(OH)₆ (CO₃²⁻)_{0.09}(NO₃⁻)_{0.06}(Fluo²⁻)_{0.38}, 2.8 H₂O whereas theoretical amount of
222 fluorescein was x = 0.5. The experimental calculations were distorted when the amount of
223 fluorescein was too weak (for the sample a) otherwise the experimental values are closed from the
224 theoretical values. Thus, the coprecipitation method for intercalation fluorescein is well effective.

225

226 3.1.2. XRD interpretation of fluorescein intercalation

227 From the above interpretations, the attribution of the former value to an intercalated fluorescein
228 LDH phase is questionable, since it corresponds to the basal spacing of the nitrate form. Tanaka et al.
229 argued that the amount of fluorescein was 16.5 % of the total interleaved anions and that the
230 amount of fluorescein adsorbed onto LDH carbonate platelets represented only 2.70 %. However, it
231 is known [25] that carbonate anions present a high affinity towards the LDH framework and that they
232 are not easily displaced unless acidic conditions or calcination are employed. Although Costantino et
233 al. also worked with different concentrations of fluorescein, only one unique basal spacing of 1.65
234 nm was observed, although the pH of the ion-exchange reaction was the same (pH = 8) as the one for
235 which Tanaka et al. observed a horizontal distribution of the fluorescein molecules with a basal
236 spacing of 0.78 nm. The interpretation of Tanaka et al. is also in discrepancy with the present results,
237 showing a unique stacked structure for a fluorescein loading of 10 %, which is comparable to some
238 extent to the Tanaka et al. experimental conditions. It is interesting to note that for the low
239 fluorescein content, the nitrate phase is observed. However, for a loading of 10 % fluorescein, a
240 carbonate phase is clearly evidenced by the saw-toothed structure around 60° and attributed to
241 diffraction peaks (110) and (103). Interestingly, carbonates anions displaced the initially interleaved
242 anions when the interlayered gap was not fully occupied by the same anions (b, c and d), making
243 some possible paths available within the interlayer space for the carbonate anions to diffuse.

244 To conclude this structural discussion, the basal spacing at 0.78 nm is characteristic of the nitrate
245 LDH phase, and does not correspond to horizontally accommodated fluorescein molecules, since the
246 space available, 0.30 nm (knowing that the thickness of the LDH cationic sheets is 0.48 nm), is too
247 small for the cumbersome guest molecule and the not strictly planar fluorescein molecule (Figure 2)
248 to be correctly lodged in the interlamellar space; this in addition to the low charge matching, which is
249 not reasonably in favour of such a horizontal accommodation.

250 3.2. Luminescence properties

251 3.2.1. Emission spectra interpretation

252 Fluorescein powder does not exhibit luminescence properties; while in aqueous media the
253 fluorescein dye is characterized by a bright yellow-green emission under blue excitation (fig. 3a) [5,
254 26, 27]. As shown in Fig 3b and c, a yellow green emission is recorded for HDL/fluorescein powder
255 upon excitation at 450 nm, which is the wavelength corresponding to the emission of a commercial
256 blue LED for a potential further association.

257 Fluorescence emission studies were undertaken using an excitation wavelength of 450 nm
258 (corresponding to the emission of a commercial blue LED). The emission spectra of LDH-fluorescein
259 (0.05 %, 1.25 % and 35%) powders are shown in fig. 3c. For comparison, the emission spectrum of
260 fluorescein in aqueous solution (10⁻⁷ M, pH 10) has been added (fig. 3a). As the amount of fluorescein
261 in the LDH phase increases, fluorescence intensity decreases and the spectra show a gradual red shift
262 (fig. 3c). A high concentration of fluorescein in the LDH phase leads to a luminescence quenching

263 phenomenon (as seen in fig. 3c). The emission spectrum of the 0.05% LDH-Fluorescein sample shows
264 a predominant peak at 520 nm with a shoulder at 556 nm. A similar trend in the emission spectrum is
265 observed for fluorescein in diluted solution (fig. 3a). As described by De et al. [26, 28] the main
266 emission is ascribed to the dianion while the shoulder contains several contributions, arising from the
267 emission of some species due to a neutral form of the dye or some dye aggregates. The
268 deconvolution of the broad emission band by Gaussian functions (fig. 3a and b) defines three
269 contributions, both for the fluorescein in solution and for the LDH-F powder. However, as shown in
270 table 2, the position and the intensity of each contribution are slightly different for the two samples,
271 which can be explained by a change in the environment of the fluorescein dye. Each contribution
272 could be ascribed to three different fluorescent species. Thus, based on previous work, we can
273 consider that fluorescein luminesces through three forms which can be attributed, for the aqueous
274 solution, to the dianionic form as well as the monoanionic and the neutral forms [28]. In this case,
275 the dianionic form is the most luminescent form (red curve/solid line in fig. 3a), whereas the
276 monoanionic form (green curve/dashed line in fig. 3a) and the neutral form (blue curve/dash-dot
277 line) are red-shifted with a lower intensity. For the LDH-F sample, the green (dashed line)
278 contribution intensity becomes higher than the red one (solid line) indicating that the monoanionic
279 population is higher than the dianionic population. This result can be explained by introducing the
280 concept of "aggregates". Aggregation depends on many parameters, such as the structure of the
281 monomer but also the nature of the solvent (if the environment is liquid), temperature, pH values
282 and ionic strength. According to the Kasha and El-Bayoumi report [29], several absorption peaks are
283 observed in a solution containing aggregates. A monomer molecule has a singlet excited state, while
284 a dimer will have two levels: one with lower energy than the monomer singlet excited state and one
285 at higher energy, according to the molecular exciton model. Figure 4 illustrates the mechanism
286 resulting from the aggregation of two single fluorescein molecules. Depending on the orientation of
287 the molecules in the aggregate, one of these levels will be a permitted absorption transition, which
288 will be forbidden for the others. For a dye such as fluorescein, which belongs to the xanthene family,
289 aggregation is due to conjugated rings through the π -stacking effect. When dipoles of each molecule
290 are arranged in a parallel manner (fig. 4a), only the transition to the higher energy level is allowed,
291 and hence the electronic absorption transition in the dimer will be blue-shifted in comparison to the
292 monomer [30]. For aggregates in which the monomers are arranged in a head-to-tail manner (fig.
293 4b), only a transition to the lowest split level is permitted. As a result, the emission spectrum is red-
294 shifted with respect to the monomer. As mentioned by S. Das et al., the head to tail arrangement
295 cannot be observed in LDH-F. Based on these results, the different contributions of the emission
296 spectrum in figure 3b can be detailed as follows: the main emission peak can be assigned to the
297 dianionic form (monomer), while the peak at the shorter wavelength can be attributed to the
298 dianionic dimer arranged in a parallel manner, and the peak at the higher wavelength (590 nm)
299 corresponds to the monoanionic monomer.

300 To examine the fluorescein environment close to LDH platelets, the excitation spectra were
301 recorded and studied.

302 3.2.2. Excitation spectra

303 The excitation spectra of the LDH-F sample were recorded by monitoring three emission
304 wavelengths (fig. 5). It appears that the excitation spectra depend strongly on the monitored
305 emission wavelength. In any case, the excitation bands were located in the range lying between 375
306 and 530 nm and exhibited three contributions corresponding to the different arrangements of the
307 fluorescein dye. As previously stated, we can easily attribute the band close to 490 nm to the
308 dianionic form, and the shoulder around 475 nm to the monoanionic form of the fluorescein. The
309 broad band located at 400 nm can be ascribed to another fluorescein form. Indeed, according to

310 Sjoback et al. [31] this excitation band may arise from dimers constituted of two aggregated
311 monomers in parallel stacking. This assumption is in agreement with the findings of Kasha and El
312 Bayoumi, who expected a blue-shifted band [21]. We also could not exclude the possibility that part
313 of the fluorescein was adsorbed onto the surface of the LDH layers. To attempt to discard or retain
314 this possibility, the excitation spectra of calcinated LDH-nitrate and LDH-carbonate with adsorbed
315 fluorescein were recorded (fig. 5b and c, respectively). These samples were prepared from calcinated
316 LDH-nitrate and LDH-carbonate dispersed in fluorescein solution (10^{-6} M). In these conditions, the
317 fluorescein dye was only adsorbed at the surface of the oxide obtained by the calcination of the LDH
318 or of the layers in the case of the LDH-carbonate. In the absence of any intercalation, the same
319 behaviour was observed, meaning that the environment between intercalated and adsorbed
320 fluorescein molecules in the LDH (fig. 5a) is similar. Stacking onto the platelets is surmised at this
321 stage.

322 3.2.3. Luminescence Decays

323 All the excitation spectra shown in Fig.5 clearly exhibit three broad contributions peaking at
324 around 400, 450 and 490 nm. The intensities of these bands differ from one sample to another, but
325 remain quite constant in position when the monitored emission is modified. Selective excitation is
326 difficult to elucidate, since the three contributions are close in position and overlapping. Considering
327 the sample of interest (Fig.5a), the excitation at around 490 nm seems to be the most useful for an
328 analysis of the dynamic processes. This position fits the absorption maximum observed for
329 fluorescein in the xanthenes major form in solution, as reported by Zhang et al. [32], which is around
330 496 nm. It is attributed to the $^1S_0 \rightarrow ^1S_1$ absorption transition. The time decay of the fluorescein in
331 solution is reported to be around 3-4 ns and must be measured using a high-frequency laser with ~ps
332 pulse duration. These possibilities are not available with our measurement apparatus.

333 Despite this, luminescence decays can be recorded for the LDH-F sample, indicating that the
334 LDH host modifies the decay time of the fluorescein since the time range of luminescence decays
335 extends to the ms range, as observed in fig 6. To record the luminescence decays, three wavelengths
336 were considered, one in the middle of the broad emission band at 535 nm and the two others on the
337 high and low edge energy sides at 485 and 605 nm.

338 The deconvolution method was used to fit the decays by double exponential form, one in the
339 rise and the second in the tail of the decays using the function $I(t) = A - B \cdot \exp(-t/\tau_1) + C \cdot \exp(-t/\tau_2)$, where
340 A corresponds to the contribution of the noise and B and C are respectively the contributions of the
341 rise and the long decay with the τ_1 and τ_2 time constants. The reliability of the fits is higher than 96%,
342 the A contribution to the overall luminescence decays is less than $\sim 4 \cdot 10^{-3}$ % and can be considered
343 as negligible. The derived τ_1 and τ_2 values are reported in table 3. All decays have the same shape and
344 show no dependence on either emission or excitation wavelengths. We can state that the recorded
345 luminescence, due to the long luminescence decay time, is inherently phosphorescent, arising from
346 the triplet state of the fluorescein. Such consideration has been reported by D-J. Loughnot et al. [33]
347 which have estimated that absorption-emission-decaying $^1S_0 \leftrightarrow ^1S_1$ processes occur during the laser
348 pulse when its duration is larger than the photoionization process. However, the transition emission
349 arising from the 3T_1 state should be accompanied by a red shift for the emission. To the best of our
350 knowledge, only one paper reports the position of the $^3T_1 \rightarrow ^1S_0$ transition in the case of fluorescein,
351 which lies at around 625 nm. Our measurements of the luminescence emissions show clearly that no
352 such notable shift was observed between fluorescein in solution and that in LDH-F. Moreover, the
353 luminescence decays of the fluorescein in solution exhibit the same shape than that of fluorescein
354 intercalated in LDH.

355 Considering the decay results, the rise is always similar at around 700 ns. The nature of this
356 rise was the subject of further experiments, notably by checking Time Resolved Spectroscopy. The
357 long decay time constant is around 700 ns. The two values are similar, indicating that that the species
358 present in the LDH-F are probably thermalized in terms of energy levels and exhibit mutual energy
359 transfer. The increase in fluorescence lifetime in LDH-F compared to the reported results concerning
360 fluorescein in solution is an indication that the photoluminescence quantum yield is reduced.

361 3.2.4. Absolute photoluminescence quantum yields

362 The absolute photoluminescence quantum yields (PL QY_{ab}) of LDH-F powder and paste samples
363 with varying amounts of fluorescein (between 0.05% to 35% of the occupied interlamellar space)
364 were recorded upon excitation in the 250-500 nm range, as shown in fig. 7. For all the samples
365 (fig. 7a for powders and 7b for pastes), the PL QY_{ab} evolution as a function of the excitation
366 wavelength, leads to the same profiles. The absolute quantum yield of the fluorescein in water-based
367 solution of 10⁻⁴ mol. concentration, upon 450 nm excitation, is of about 65%. The emission spectrum
368 of LDH-F (fig. 3b) is the same as the emission spectrum of fluorescein in solution (fig. 3a) under such
369 excitation, indicating that the intercalation doesn't modify the main electronic structure of the
370 emitting species. For the LDH-F the LDH layers to some extent confine the fluorescein molecules on
371 the basis of host-guest interactions (such as ionic interactions), and the anionic state, molecular
372 configuration and microenvironment of interlayer fluorescein may be totally different from the
373 fluorescein solution.

374 The samples with a very small amount of fluorescein exhibit only photoluminescence
375 properties. Indeed, the amount of fluorescein must be lower than 1 % in the LDH to record a PL QY_{ab}
376 higher than 5% for either powder or paste. For both samples, the best PL QY_{ab} is reached for an
377 excitation wavelength of 490 nm, corresponding to maximum fluorescein absorption. The maximum
378 values of absolute quantum yield were measured for LDH-F (0.05 %) paste, with a value of 21.4 %. PL
379 QY_{ab} is higher for the paste sample than for the powder, and two assumptions can be suggested. The
380 first concerns the effect of water in the paste; indeed, the paste produced after centrifugation
381 contains roughly 80 wt. % of water and 20 wt. % of powder. In this case, the fluorescein molecules
382 are in an environment that is close to that of a solution, explaining why luminescence is increased.
383 The second possibility relies on the reflective index (RI). The RI of water is 1.33, against 1 for air; thus,
384 the paste which contains water will absorb more photons. Accordingly, absorption is greater for the
385 paste and its PL QY_{ab} is improved.

386 The intercalation of fluorescein in such low concentrations (0.05 %) cannot be detected from
387 XRD patterns, where only the nitrates are visible (as seen in fig. 1). Nevertheless, we can suppose,
388 based on the emission and excitation spectra that the fluorescein molecules are in close proximity to
389 the LDH, most probably adsorbed onto the LDH platelet surfaces.

390 We have demonstrated that the fluorescein dye must be present in the LDH in small
391 quantities to provide luminescence properties. Such behaviour can be explained by a concentration
392 quenching phenomenon, which is predominant when the concentration of fluorescein dye increases.
393 When the fluorescein molecules are closed, they formed aggregates by π -stacking (parallel stacking)
394 due to conjugated xanthene rings or by hydrogen bonding (head-to-tail) with carboxylic acid and
395 alcohol groups [26]. Fluorescein is well-known [28] for self-quenching its luminescence when the
396 concentration reaches a sufficiently high value to form these aggregates of monomer molecules such
397 as dimers, trimers etc. Although the monomer exhibits good luminescence properties, all the
398 aggregates led to an extinction of the optical properties due to non-radiative energy transfer
399 between the dye molecules [34]. This phenomenon increases with the dye concentration in solution,
400 and for fluorescein powder no luminescence is observed. As a conclusion, we have shown that the

401 lamellar space of the LDH host matrix can be considered as a dilution medium for the fluorescein
402 dye, and plays the same dispersing role as that of an aqueous solution.

403 3.3. Composite film LDH-F/silicone

404 3.3.1. Luminescence properties

405 The LDH-F powder presenting the best absolute quantum yield efficiency value was used in
406 this section. TEM (see fig. S2 in the Supporting Information) revealed that LDH-F powder consisted of
407 pseudo-hexagonal nanosheets stacked on top of each other. The LDH-F (0.05 %) was dispersed in a
408 silicone resin to prepare the composite films. The thickness of the composite films ranged from 100
409 to 120 μm . Composite film homogeneity as well as the random orientation dispersion of the LDH
410 platelets has been shown by SEM (see fig. S3 in the Supporting Information). In order to get a
411 composite film suitable for a commercial blue LED, the LDH/dye nanohybrids were dispersed in a
412 polymer such as silicone. The PL QY_{ab} of the composite films with variable amounts (between 10 %
413 to 60 %) of LDH-F (0.05% powder), were recorded under excitation in the 250-500 nm range, as
414 shown in fig. 8a. The best PL QY_{ab} was achieved on excitation at 490 nm for each composite film,
415 and increased gradually with the quantity of LDH-F particles in the silicon matrix. This could be
416 explained by an increase in the absorption of photons with the increase in filler loading. On the other
417 hand, when the percentage of LDH-F particles was too high (> 40 wt. %), the mixture of powder and
418 silicon became inhomogeneous and the composite films could not be hardened, due to excessive
419 quantities of nanoparticles compared to the silicone resin. Thus, the percentage of LDH-F (0.05 %)
420 particles dispersed within the silicone resin is fixed at 20 wt. % in the following. Moreover, the PL
421 QY_{ab} recorded for the homogenous composite film elaborated with a loading of LDH-F of 40 wt. % (PL
422 QY_{ab}=25%) is higher than that obtained for the powder and paste LDH-F (0.05 %) samples. The value
423 of 25% for the PL QY_{ab} remains low for general lighting LED but could be of interest for other LED
424 applications such as display and anticounterfeiting for example. We can also add that the silicone
425 matrix enables the creation of a dilution medium for the LDH-F powder, thus improving its
426 luminescent properties.

427 LDH platelets exhibit a good compatibility with the silicone matrix thereby providing a
428 homogeneous dispersion. Previous studies demonstrated an efficient dispersion of organo-modified
429 LDH within PDMS type polymer [35]. To confirm the interest of the LDH matrix in the dispersion of
430 fluorescein in the silicone matrix, a composite (silicone/fluorescein_{0.02%}) film was prepared. The
431 amount of fluorescein therein was comparable to the amount of pure fluorescein contained in the
432 composite silicone LDH-F (0.05 %) film with 20 wt. % of filler loading. This composite
433 silicone/fluorescein_{0.02%} film emits no luminescence at all, as shown in figure 8a, thus confirming the
434 action of LDH as a “solid solvent” in diluting the fluorescein, resulting in greater luminescent
435 properties for the composite films. In this 2D organized structure, the fluorescein dye is intercalated
436 in the interlayer gallery space. In this configuration, the fluorescein molecules are spaced away from
437 each other and the quenching due to the aggregation is avoided.

438

439 The emission spectrum of the composite films is similar to that recorded for the powder.
440 Indeed, as for the LDH-F (0.05 %) powder, the three contributions of fluorescein are observed (fig.
441 8b).

442 3.3.2. Photostability of LDH-F/silicone composite films

443 The photostability of the fluorescein chromophore dispersed into the composite films
444 represents one of the key parameters for potential application in LED device. To the best of our

445 knowledge, this paper is the first study of the photostability of LDH-F/silicone composite films.
446 Composite films with LDH-fluorescein and LDH-nitrate and pure silicone film were irradiated in
447 accelerated ageing conditions ($\lambda > 300$, 60°C) to study the potential effects that LDH and fluorescein
448 could have on silicone photooxidation.

449 The chemical modifications during irradiation were monitored by IR spectroscopy. Fig. 9a
450 presents the FTIR spectra of a pure silicone film (without filler) as a reference during irradiation
451 under accelerated artificial conditions. The initial spectrum is typical of a silicon polymer like PDMS.
452 The two intense bands at 2960 and 2075 cm^{-1} are relative to the (C-H) vibration mode of the silicone.
453 The region between 1800 and 2200 cm^{-1} reveals IR bands corresponding to (Si-O) and (Si-H) vibration
454 modes. The two bands near 1405 and 1445 cm^{-1} are ascribed to CH_3 symmetrical bending vibration.
455 The IR spectrum of silicone during the aging process presents a decrease in two bands, one at 2140
456 cm^{-1} relative to the (Si-H) vibration mode and one at 905 cm^{-1} (Si-O-Si). In fig. 9b and c, both IR bands
457 are shown after subtracting the spectra from the initial spectrum ($t = 0$). To distinguish the thermal
458 curing effect from the photooxidation of the silicone polymer, a post-curing experiment was
459 performed at 80°C for 264 hours on the composite films and the pure silicone film. FTIR spectra were
460 then recorded before and after post-curing. Both FTIR spectra of the pure silicon film are presented
461 in fig. 10. The IR spectrum after post-curing shows the decrease in absorbance of the two IR bands at
462 2140 cm^{-1} and 905 cm^{-1} . Thus, the modifications of these two bands are due to a post-curing
463 phenomenon and not to a photooxidation process.

464 Fig. 11a shows the spectra of a silicone/LDH-F composite film during irradiation, and Figs 11b
465 and c, present subtracted spectra. Before irradiation, the IR spectrum of the silicone/LDH-F
466 composite film shows a broad and intense band around $3500\text{--}3600\text{ cm}^{-1}$, assigned to the (O-H)
467 stretching of water molecules and hydroxyl groups from the LDH matrix. At 1605 cm^{-1} , water from
468 the LDH is observed, as well as the characteristic band at 1350 cm^{-1} of nitrate in LDH. The metal-
469 oxygen vibrations of LDH can be noticed in the region of $1000\text{--}400\text{ cm}^{-1}$. During irradiation, two IR
470 bands are modified at 2140 cm^{-1} and 905 cm^{-1} , as observed in the case of the reference silicone film.
471 Moreover, a new IR band at 1725 cm^{-1} develops upon irradiation for the silicone/LDH-F composite
472 film. This new IR band can be ascribed to photodegradation products of the polymer matrix. The
473 modification observed for the broad and intense band around 3500 cm^{-1} may be due to a change in
474 the hydration of the samples during irradiation.

475 Variations in the absorbance of the IR bands at 2140 cm^{-1} , 1725 cm^{-1} and 905 cm^{-1} during
476 irradiation were plotted as a function of time for the silicone film and both composite films,
477 silicone/HDL-F (0.05%) and silicone/LDH-N (with nitrate ions intercalated), and are shown in Fig. 12.
478 A decrease in absorbance for the two IR band at 2140 cm^{-1} and 905 cm^{-1} was observed for the three
479 films (pure silicone and the two composite films with LDH-F and LDH-N), with approximately the
480 same kinetic curves, due to a post-curing phenomenon.

481 At 1725 cm^{-1} , the same modification is observed during photoaging between the
482 silicone/LDH-F composite and the composite film with LDH-N, both adopting a similar kinetic. The
483 band at 1725 cm^{-1} in the pristine silicone film is also slightly visible (Fig. 9b). Thus, the formation of
484 this IR band in the composite film could be explained by the photodegradation of the silicone
485 polymer, where the presence of an LDH matrix (in both cases, LDH-F and LDH-N) has a pro-degradant
486 effect.

487 These results show that in accelerated aging conditions, photodegradation of the silicone
488 matrix is observed in presence of LDH, either with LDH-F or with LDH-N. This effect is not due to the
489 presence of fluorescein molecules in the composite.

490 4. Conclusion

491 In this study, it has been demonstrated that fluorescein molecules could be intercalated in large
492 amounts into an LDH host structure, adopting a vertical orientation. However, only extremely small
493 amounts of fluorescein in the lamellar space enable a yellow luminescent powder to be obtained.
494 Fluorescein accommodation is then not detected by XRD. Indeed, from the optical properties of the
495 LDH-F hybrid material, several emission contributions relative to different species are explained by a
496 model in which the dianionic monomer, the monoionic monomer and the dianionic dimer forms of
497 the fluorescein coexist. Thus, LDH brings a “solid solvation effect” to the fluorescein. The LDH-F
498 hybrid material can be dispersed in a polymer matrix such as silicone to yield a luminescent
499 composite film. LDH enables a homogeneous film to be produced, which was not possible with
500 fluorescein alone. From the point of view of the organic phosphor, LDH layers provide dispersion
501 avoiding quenching and migration while for LDH, the dye supplies the photoactivity.
502 The dispersion of the LDF-F filler in the silicone matrix does not affect the optical properties of the
503 hybrid material, the PLQY being even higher than for the powder. From the photoaging study, it has
504 been shown that the presence of LDH-F or LDH-N filler modifies polymer photostability during
505 irradiation, and that this is due to the presence of LDH platelets rather than being caused by the
506 fluorescein molecules. Fluorescein was used as a model to study the added-value of hybrid materials
507 based on a phosphor and an LDH host matrix. In this vein LDH host efficiently the organic phosphor.
508 These results showed the potentiality of LDH as photofunctional active filler and this approach can be
509 extended to other phosphors such as organic dyes or quantum dots.

510

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LDH sample	C (wt %)	N (wt %)	H (wt %)	Mw (g.mol ⁻¹)
a	0.84	4.6	3.0	449.84
d	0.93	10.5	3.20	334.13
h	0.21	21.4	3.8	431.43

619 Table 1 : Elemental analyses obtained from CHNS analysis and molecular mass obtained by TGA analysis of LDH samples a, d
620 and h.

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622

Emission spectra		λ_{\max} (nm)	E (cm ⁻¹)	FMWH (cm ⁻¹)
Fluorescein in water (10 ⁻⁷ M)	Red contribution (dash)	514	19437	926
	Green contribution (dot)	535	18706	1453
	Blue contribution (dash-dot)	564	17736	2239
LDH-fluorescein (0.05%) powder	Red contribution (dash)	518	19288	1083
	Green contribution (dot)	545	18358	1707
	Blue contribution (dash-dot)	582	17171	2660

623 Table 2 : Results of the emission bands deconvolution by the sum of three gaussian functions fig. 3a and b

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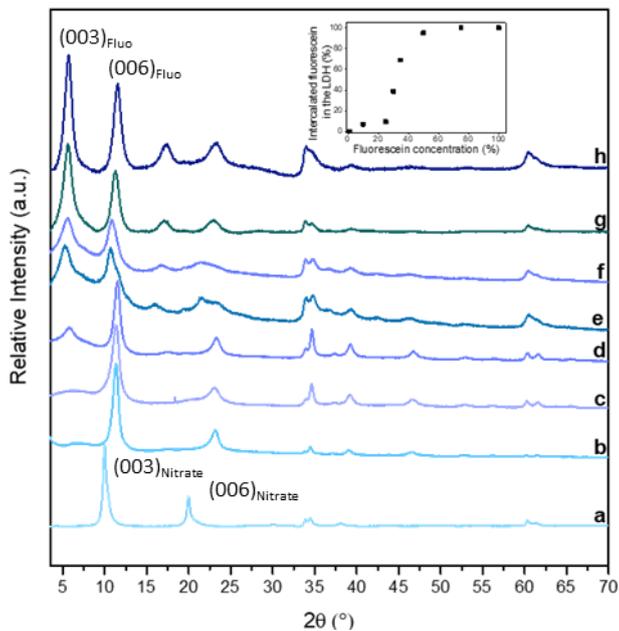
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		Time constants		Fitting goodness
		τ_1 (ns)	τ_2 (ns)	Adjusted R^2
Emission wavelengths	485 nm	706	716	0.967
	535 nm	707	723	0.992
	605 nm	674	676	0.996

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Table 3 : Time constants derived from the fitting of the experimental values of the LDH-F (0.05%) powder fluorescence lifetime decay monitored at three emission wavelengths



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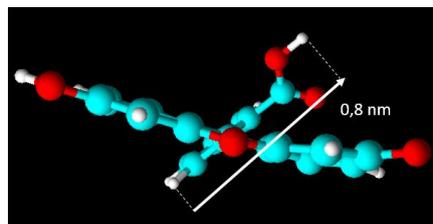
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Figure 1 : X-Ray diffractograms of LDH-Fluorescein powder samples with different concentrations of fluorescein (a, b, c, d, e, f, g and h: 0.05%, 10%, 25%, 30%, 35%, 50%, 75% and 100%). Inset: Amount of intercalated fluorescein in LDH interlayer space in function of fluorescein concentration used in the XRD samples taking a and h as end-member of the nitrate vs fluorescein LDH substitution respectively.

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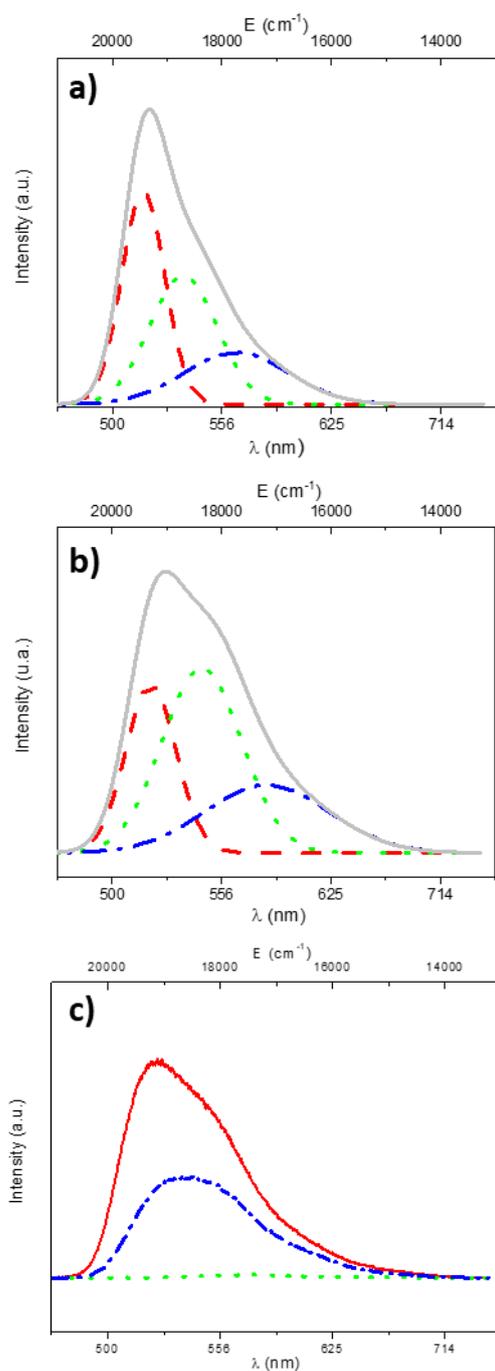


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Figure 2 : Schematic representation of fluorescein seen from the xanthen frame plan

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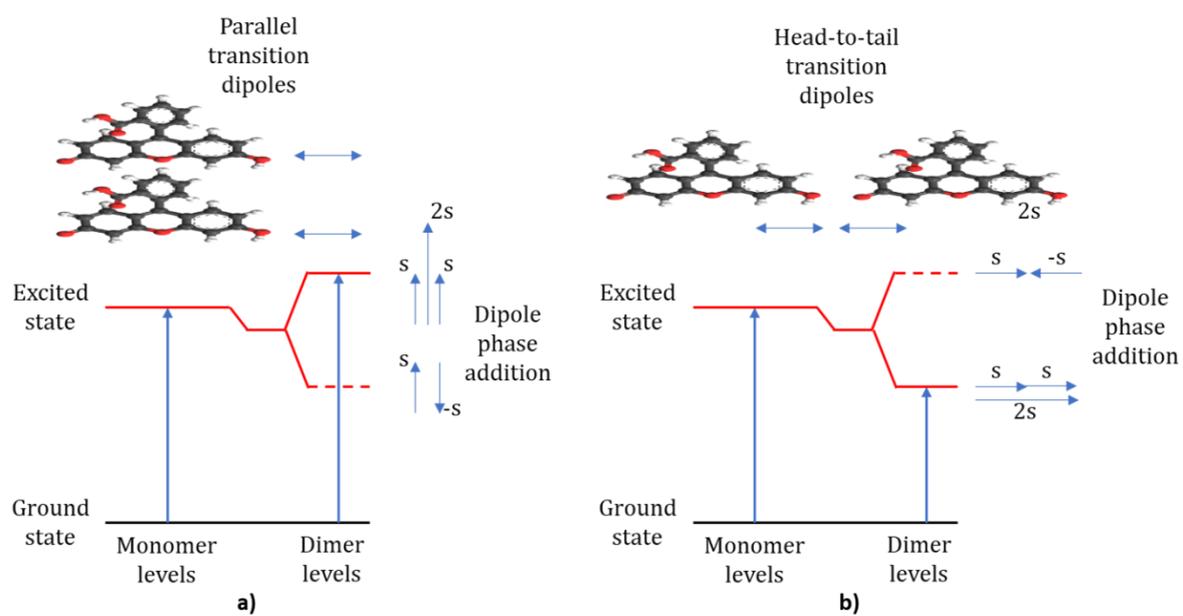
639 *Figure 3: Emission spectra at 20°C with excitation at 450 nm of: a)*
 640 *fluorescein in water (10^{-7} M) with deconvolution in three*
 641 *contributions. b) LDH-fluorescein (0.05%) powder with deconvolution*
 642 *in three contributions. c) LDH-fluorescein powder with three loadings*
 643 *of fluorescein in LDH host (0.1 % —, 1.25 % --- and 35% - - -)*

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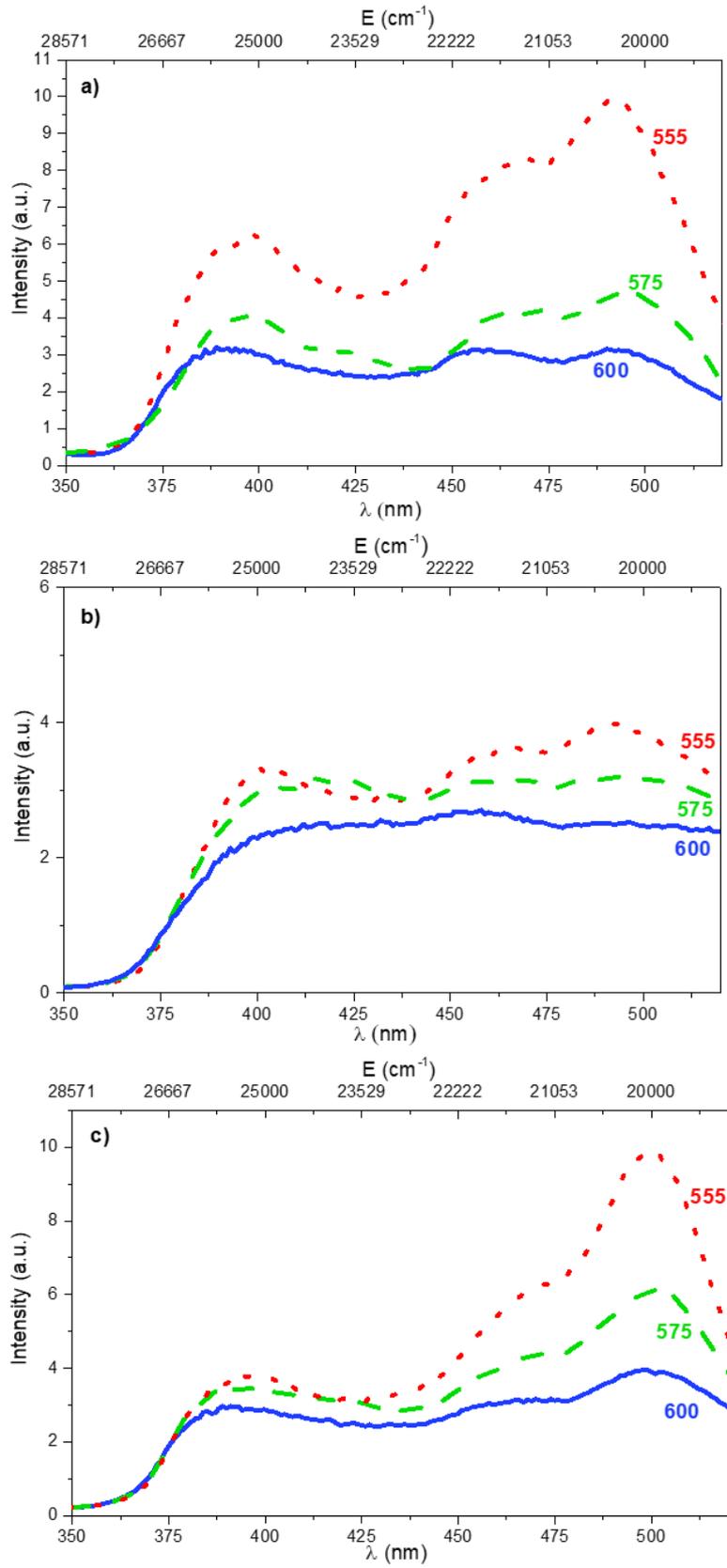
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649 *Figure 4 : Exciton band energy diagram for a molecular dimer with parallel (a) and head-to-tail (b) transition dipoles*



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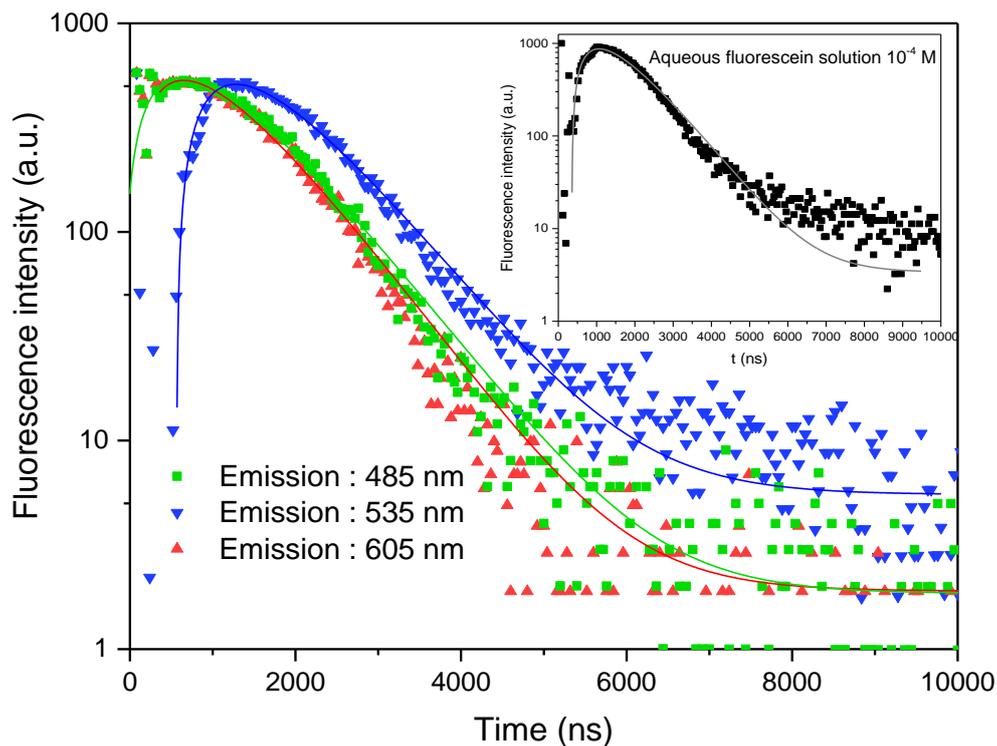
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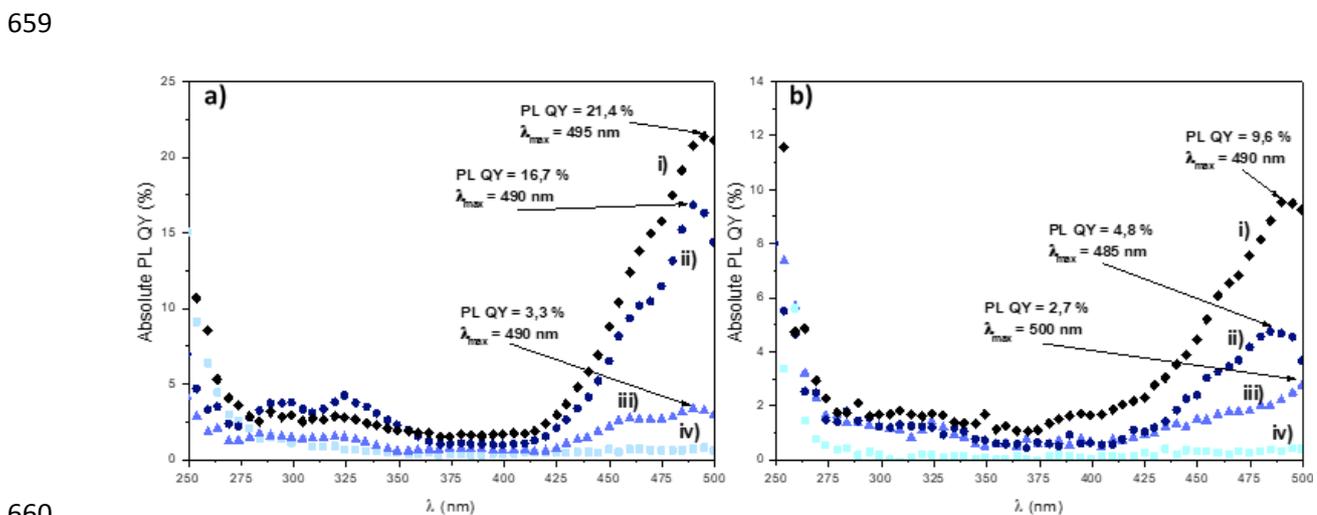
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Figure 5 : Fluorescence excitation spectra monitoring at several wavelengths emission (555, 575 and 600) of: a) LDH-fluorescein (0,05%) powder b) calcinated LDH-nitrate with fluorescein adsorption c) LDH-carbonate with adsorbed fluorescein



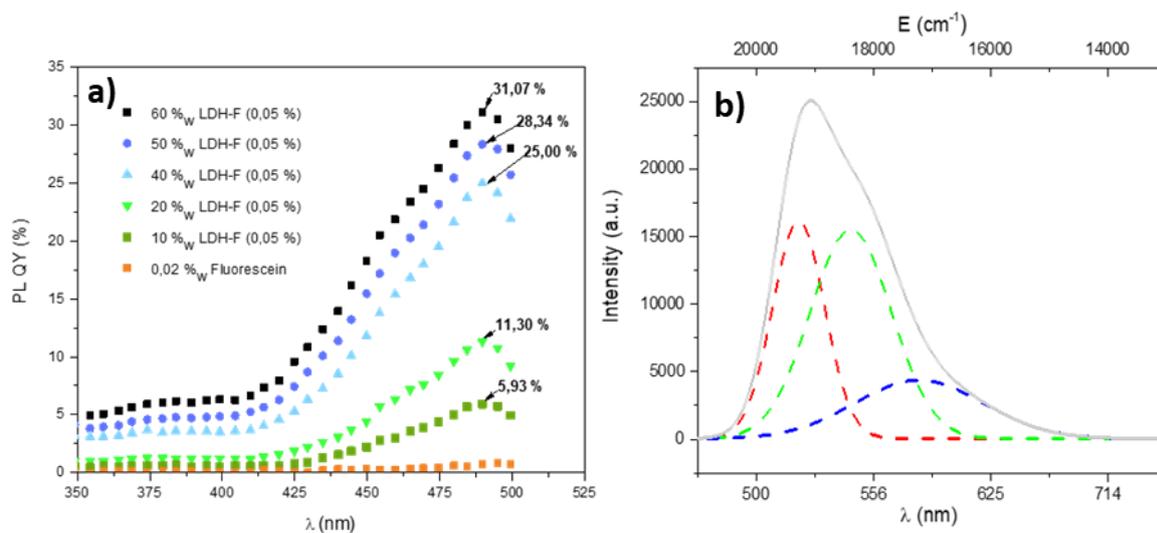
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 656 *Figure 6: Fluorescence lifetime decay of the powder LDH-F (0.05%) monitored at different emission wavelengths and with an*
 657 *excitation wavelength fixed at 492 nm. Inset: fluorescence lifetime decay of aqueous fluorescein solution (10^{-4} M) with*
 658 *excitation wavelength fixed at 450 nm and emission wavelength at 520 nm.*



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 661 *Figure 7: Absolute quantum yield depending on the wavelength with different amounts of fluorescein (i :0.05 %, ii: 0.1 %, iii:*
 662 *1.25 %, iv: 10 for paste samples (a) and powder samples (b)*

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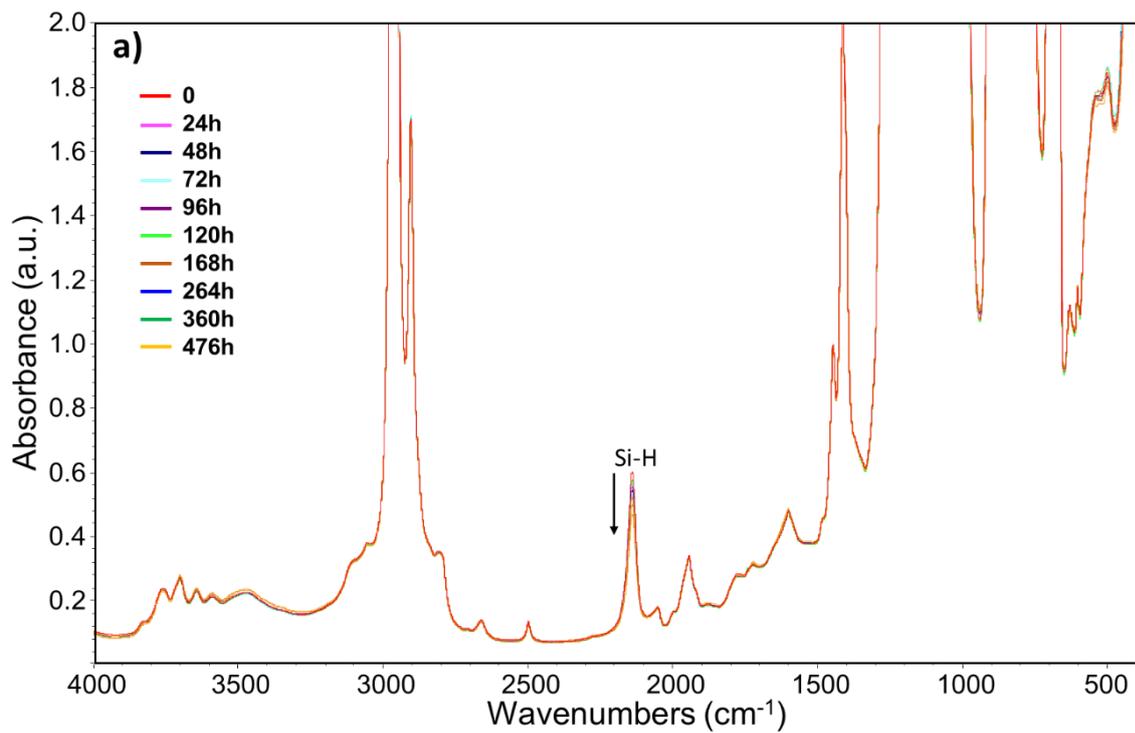


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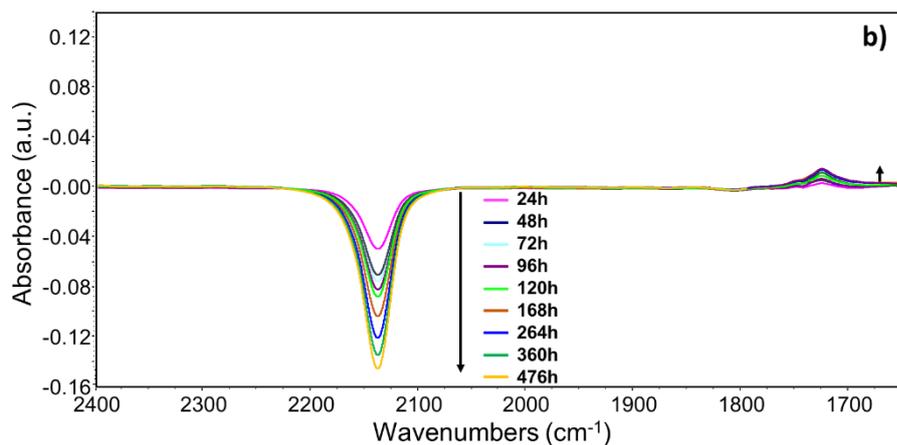
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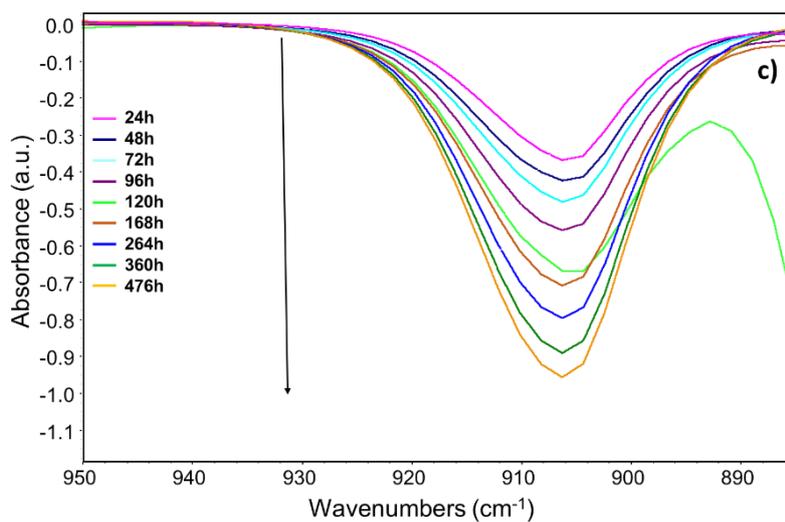
Figure 8 : Absolute PL QY of composite films silicone/LDH-F (0,5 %) for several loadings of LDH powder (a). Emission spectrum of a composite film silicone/LDH-F (0,05 %) 80:20 with $\lambda_{exc}=450$ nm (b).



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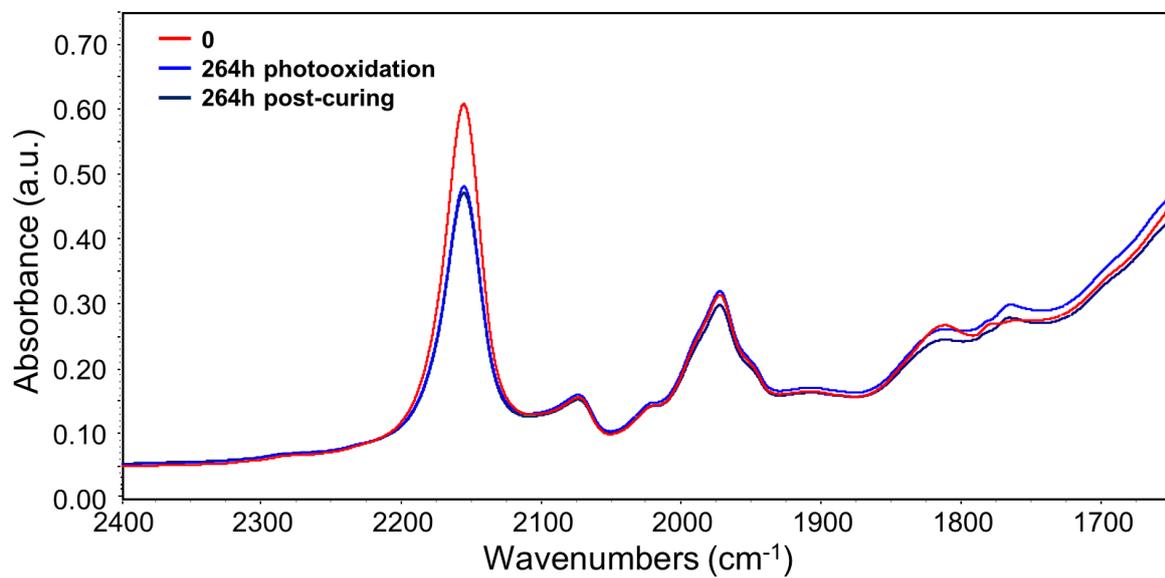
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Figure 9 : FTIR spectra during photooxidation at $\lambda > 300 \text{ nm}$, 60°C , of a pristine silicone film : a) between 400 and 4000 cm^{-1} b) between 1650 and 2400 cm^{-1} (after subtraction of the initial spectrum) and c) between 885 and 950 cm^{-1} (after subtraction of the initial spectrum).



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Figure 10 : FTIR spectra of a pristine silicone film (between 1600 and 2400 cm^{-1}), after 264h of photooxidation $\lambda > 300 \text{ nm}$, 60°C and after post-curing treatment in oven at 80°C.

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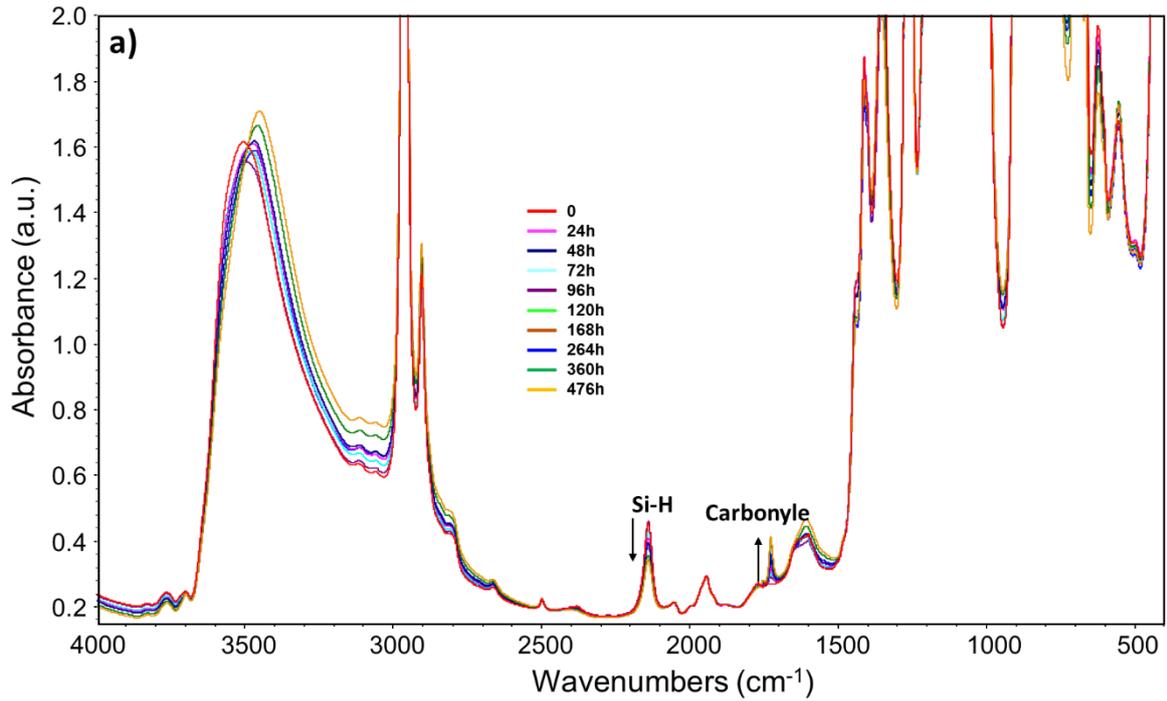
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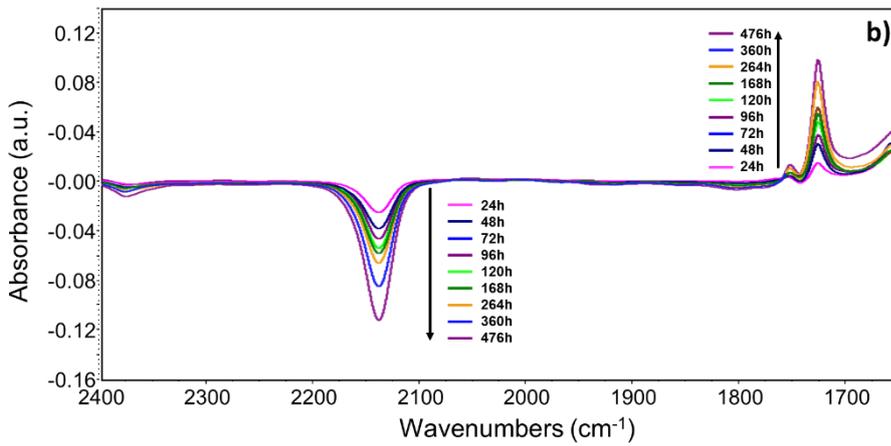
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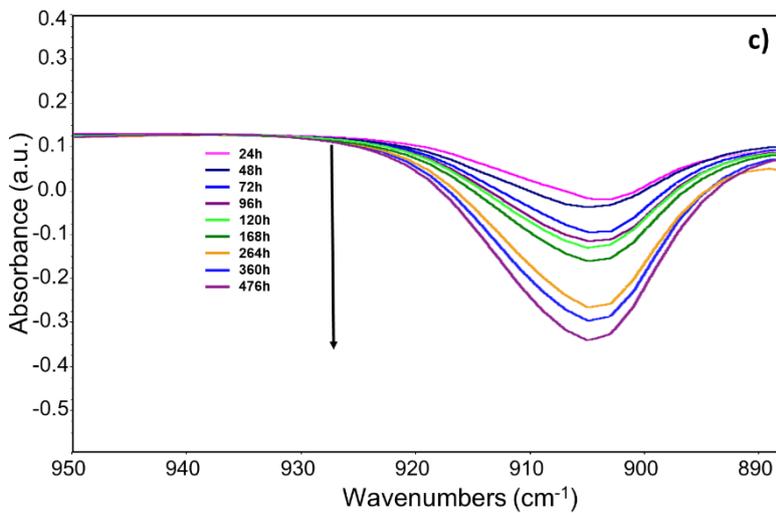
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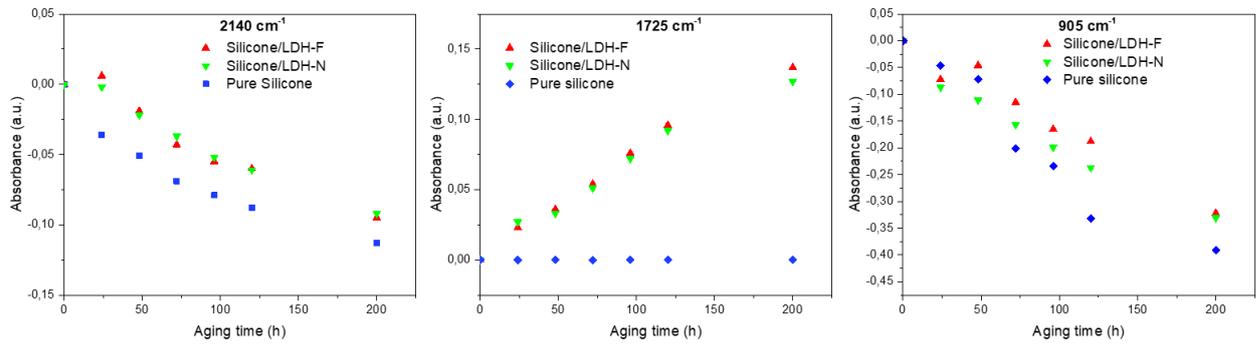
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Figure 11: FTIR spectra during photooxidation at $\lambda > 300$ nm, 60°C , of a composite film silicone/LDH-F (0.05%) (with 20 %w of LDH-F) : a) between 400 and 4000 cm^{-1} b) between 1650 and 2400 cm^{-1} (after subtraction of the initial spectrum) and c) between 885 and 950 cm^{-1} (after subtraction of the initial spectrum).

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692 *Figure 12: Variations of absorbance at 2140, 1725 and 905 cm⁻¹ as a function of irradiation time for the composite film*
693 *silicone/LDH-F (0.05%), the composite film silicone/LDH-N and the pristine silicone film*

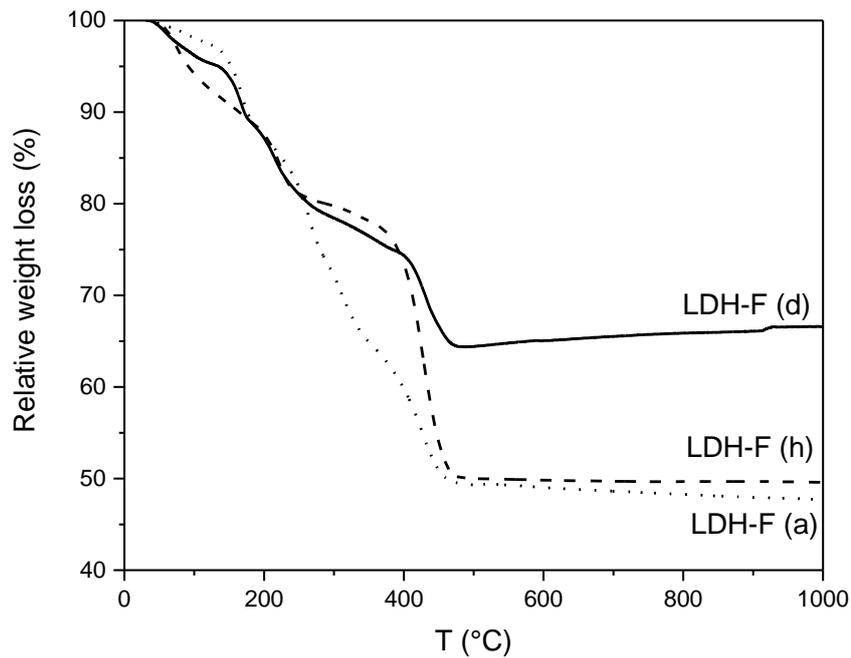
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696 Supporting Information

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701 **Figure S1: TGA of LDH-F powders under air (sample a, d and h)**

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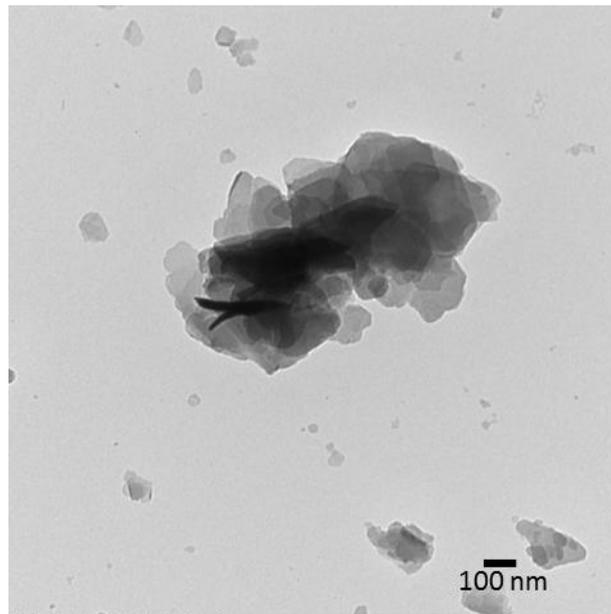
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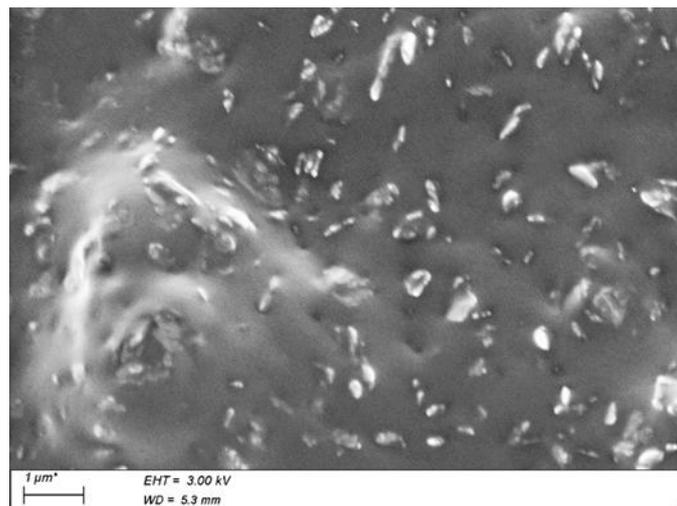
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Figure S2: TEM image of LDH-F powder



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Figure S3: SEM image of Silicone/LDH-F composite film