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1 **Saponite-anthocyanin derivatives: The role of organo-clays in pigment**  
2 **photostability**

3

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14

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19

20           **ABSTRACT**

21           Hybrid pigments based on organo-saponite (cetyltrimethyl ammonium bromide (CTAB-  
22 Sap) and a commercial anthocyanin (ACN) dye, Crystal Red Grape, were prepared. The  
23 interactions between organic dye guest and hosts (including saponite and organo-saponite) were  
24 investigated by X-ray diffraction, transmission electron microscopy and Fourier transform  
25 infrared spectroscopy. The pigments exhibit different colors function of their host-guest  
26 interactions. The blue color of organo-clay-anthocyanin indicates the stabilization of quinoidal  
27 base form of the dye. The hybrids have good stability against visible light irradiation and basic  
28 pH conditions. These dyed materials are environmentally friendly and can be promising  
29 candidates in different application fields.

30           Keywords: organo-saponite, anthocyanin, photostability, chemical stability

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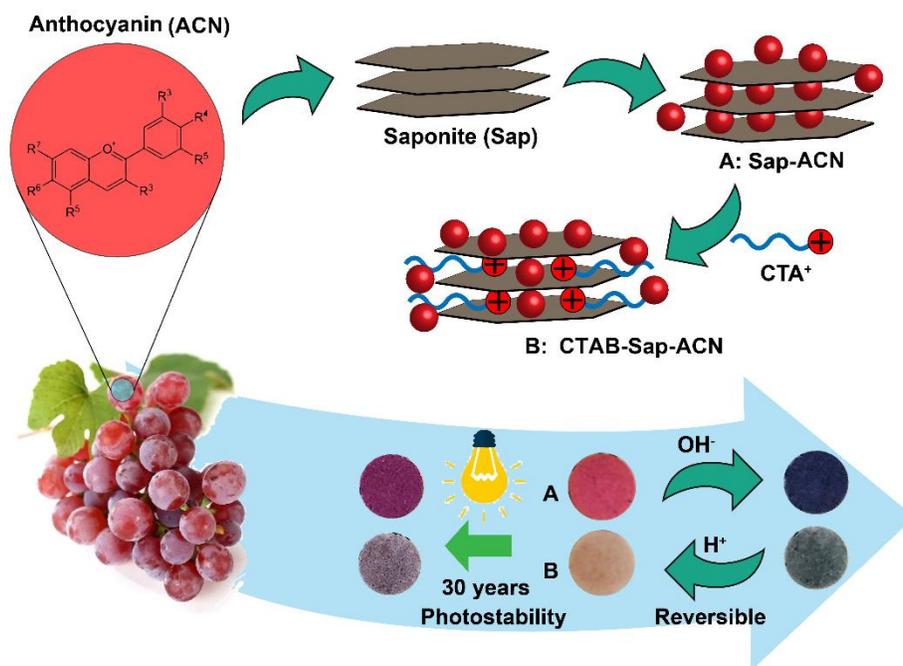
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39 GRAPHICAL ABSTRACT

40



41

42 **KEYWORDS:** Saponite, Organo-functionalization, Natural dye, hybrid pigment, Color change.

43

## 44 **1. Introduction**

45

46 The increasing awareness of consumers regarding food safety has been leading the  
47 preference for natural dyes instead of synthetic ones. Anthocyanins (ACN) have an antioxidant  
48 and free-radical scavenging properties that make them attractive as substitutes of synthetic dyes.  
49 These natural dyes have the 7-hydroxyflavylium cation chromophoric group in their structure  
50 which is responsible for most of the purple, blue and red colors of flowers and fruits (Brouillard,  
51 1982; Fang et al., 2020). In spite of their potential use in several fields, anthocyanins have  
52 limitations due to their photo- and chemical-stabilities (Torres et al., 2011; Silva et al., 2018).  
53 Anthocyanin dyes are unstable to external environmental conditions such as light, pH, oxygen,  
54 temperature (Piffaut et al., 1994).

55 Therefore, biohybrid compounds that combine these biomolecules and an inorganic  
56 substrates such as clay minerals have been widely investigated to reverse these limitations by  
57 interaction/protection in the host materials (Kohno et al., 2009; Teixeira-Neto et al., 2012;  
58 Pimchan et al., 2014; Lu et al., 2019; Samuei et al., 2020).

59 This strategy is inspired by Maya Blue pigments, in which a variety of clay minerals and  
60 organic dyes have been used to prepare stable pigments (Trigueiro et al., 2018; Chen et al., 2019;  
61 Zhuang et al., 2019a; Silva et al., 2020). Concerning the ACN stabilization, montmorillonite,  
62 synthetic non-swelling mica and silica were employed by Kohno et al., 2009 to improve the  
63 stability of ACN against alkaline environment and visible light irradiation. In their study, the best  
64 results were obtained by ACN intercalation into montmorillonite. Electrostatic interactions  
65 between the intercalated dye and the montmorillonite surface were highlighted and the  
66 intercalation protected the dye from atmospheric oxygen (Kohno et al., 2009). Li et al., 2019  
67 have reported the acid/base reversible allochroic hybrid pigments prepared by incorporation of

68 ACN on sepiolite, halloysite, kaolinite and montmorillonite. Their comparative study has  
69 demonstrated the influence of the clay compositions on color properties, the nanochannels of Sep  
70 were claimed to be responsible for the optimum vivid color properties, thermal stability, and  
71 chemical corrosion resistance (Li et al., 2019b). Palygorskite was also studied to provide  
72 enhancement in ACN stability (Li et al., 2019a).

73 Functionalized clays have also attracted broad attention in the field of lake pigments since  
74 they provide better chemical and thermal stability. Recent studies have improved the clay  
75 properties by pillaring process (Trigueiro et al., 2018), organo-functionalization with  
76 aminosilane (De Queiroga et al., 2019) as well as incorporating a variety of surfactants (Wang  
77 and Wang, 2008; Baez et al., 2009; Micó-Vicent et al., 2017). In addition, our group recently  
78 reported hybrid pigments with excellent stability by incorporation of alizarin with a variety of  
79 organo-modified clays with cetyltrimethylammonium bromide (CTAB) (Silva et al., 2020),  
80 Rhodamine 640 perchlorate, sulforhodamine B and Kiton red 620 (Tangaraj et al., 2017) dyes.  
81 Despite of the wide use of modified clays to enhance the stabilities of organic dyes, no study  
82 explored the stability enhancement for anthocyanin after adsorption on modified clay.

83 This work describes the hybrid pigments formation by adsorption of anthocyanin on  
84 saponite (Sap) and an organic modified saponite with cetyltrimethylammonium bromide (CTAB-  
85 Sap). These pigments were characterized and their photo- and chemical- stabilities were  
86 evaluated.

87

## 88 **2. Materials and methods**

### 89 **2.1. Materials**

90

91 Anthocyanin (ACN) source was a Crystal Red Grape (90%, wt) donated by San Joaquin  
92 Valley Concentrates (Fresno, CA, USA). cetyltrimethylammonium bromide (CTAB) (99%, wt),  
93 citric acid (99.5 %, wt), sodium citrate (99 %, wt), sodium hydroxide (98 %, wt), hydrochloric  
94 acid, and other applied chemicals were purchased from Aldrich or Sigma-Aldrich, all with an  
95 analytical grade and used without any previous purification.

96

## 97 **2.2. CTAB-Saponite preparation procedure**

98 2 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 10 mL of 1 mol L<sup>-1</sup>  
99 HCl solution and added dropwise at room temperature to the stirred aqueous suspension of Na-  
100 Sap (previously prepared by us (Jaber and Miéché-Brendlé, 2005; Tangaraj et al., 2017). After  
101 continuous stirring the mixture at 400 rpm for 3 h, the white precipitate was collected by  
102 centrifugation, washed with water until no bromide ion could be detected by an aqueous AgNO<sub>3</sub>  
103 solution, and then dried at 60°C for 24 h.

104

## 105 **2.3. Hybrid pigments preparation procedure**

106

107 1 g of Na-Sap or CTAB-Sap were dispersed in 100 mL of anthocyanin (ACN sample  
108 donated by San Joaquin Valley Concentrates (Fresno, CA, USA)) citric acid buffer solution at  
109 pH 3 (the ACN concentration was 100 mg L<sup>-1</sup>) and was stirred at 400 rpm for 1 h. The samples  
110 were then centrifuged and dried at 50°C overnight. The hybrid pigments samples are named  
111 Sap/ACN and CTAB-Sap/ACN.

112

## 113 **2.4. Characterizations**

114

115 X-ray diffraction were recorded using D8 Advance Bruker-AXS Powder X-ray  
116 diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Infrared analyzes were performed on Agilent  
117 Cary 630 FTIR spectrometer using an Agilent diamond Attenuated Total Reflectance (ATR)  
118 technique mode. Thermogravimetric analyses were carried out using a TA Instrument SDT Q600  
119 analyzer. The heating rate was of  $5^\circ\text{C min}^{-1}$  from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$ , air flow of  $10 \text{ mL} \cdot \text{min}^{-1}$ , and  
120 using alumina pan. TEM study of the samples was performed on a JEOL 2010 microscope, 200  
121 kV LaB6 coupled Orius camera, from Gatan Company.

122

## 123 **2.5. Chemical stability and photostability**

124

125 Exposure of the hybrid pigments to basic and acidic conditions in a desiccator containing  
126 aqueous  $\text{NH}_4\text{OH}$  or  $\text{HCl}$  to saturate the atmosphere with  $\text{HCl}$  or  $\text{NH}_3$  vapors was carried out,  
127 sequentially and repeatedly (Ogawa et al., 2017).

128 The pigments were exposure to white light irradiation for 192 h, using a LED lamp set to  
129 provide 100 Klux of illumination intensity, in which this time is equivalent to approximately 32  
130 years of exposure in ambient light conditions (Zhuang et al., 2019a, 2019b). The pressed  
131 pigments (into pellets) were placed in a desiccator filled with air or nitrogen. The absorbance,  
132 reflectance and CIE (Commission Internationale de L'Eclairage) parameters were obtained from  
133 an Ocean Optics Halogen and Deuterium Light Source HL-2000-FHSA device as incident light  
134 beam and ocean optics USB4000 detector for acquisition. Ocean Optics QP400-1-UV-VIS  
135 fiberglass was used to link these devices.

136 The diffuse reflectance (R) converted into equivalent absorption coefficient F(R) using  
137 Kubelka–Munk equation (Eq. (1)) (Silva et al., 2018).

138

139 
$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

140

141 The “Commission Internationale of l’Eclairage” CIE 1976 color space system was applied

142 to evaluate the color of the pigments. Measurements were done on pressed pellets samples as

143 function of  $L^*$ ,  $a^*$  and  $b^*$  coordinates. The parameter Lightness ( $L^*$ ) represents the brightness (+)

144 or darkness (-) of the color, i.e., more positive  $L^*$  values refer to whiter while more negative  $L^*$

145 values represent darker. While, the values of  $a^*$  and  $b^*$  indicate the color details:  $+a^*$  is the red

146 direction,  $-a^*$  the green direction,  $+b^*$  the yellow direction, and  $-b^*$  the blue direction (Zhuang et

147 al., 2019b). The differences of colors between unexposed and exposed samples were calculated

148 by  $\sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)}$  equation.

149

### 150 3. Results and Discussion

151

152 The XRD pattern of the sodium saponite (Fig. 1A) showed the (001) reflection at  $7.66^\circ$

153 ( $2\theta$ ), corresponding to the basal spacing of 1.16 nm. After organic modification with CTAB, the

154 basal spacing increased to 1.62 nm in CTAB-Sap. This phenomenon indicates that  $CTA^+$  cations

155 successfully intercalated into the interlayer space of Sap by cation exchange with  $Na^+$ . The

156 difference between the Sap layer thickness (0.96 nm) and the basal spacing of CTAB-Sap (1.62

157 nm) was 0.66 nm, which is consistent with a monolayer arrangement of the organic molecules

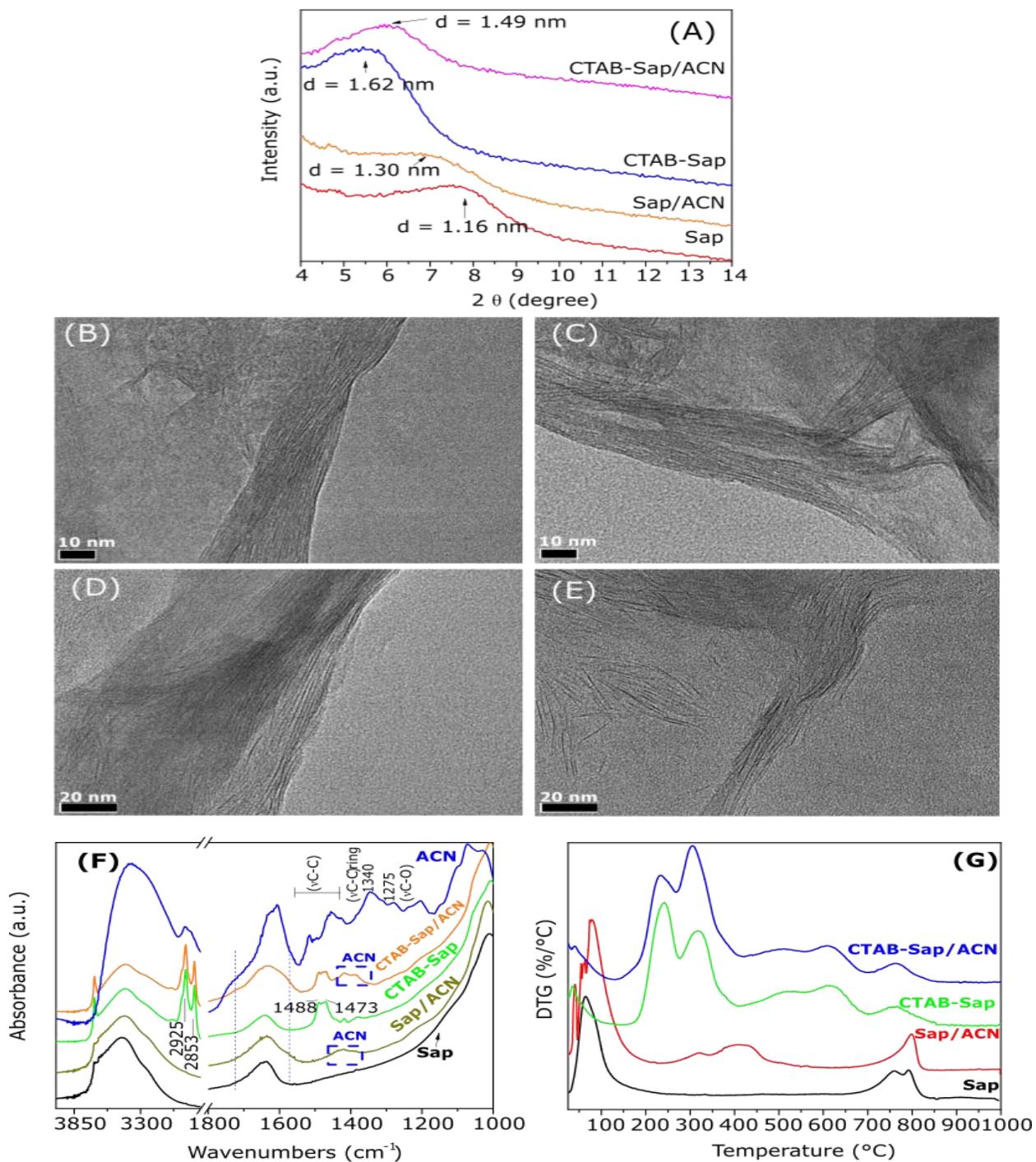
158 considering the dimensions of  $CTA^+$  cations (at about 0.51 nm) (Marçal et al., 2015).

159 After loading with anthocyanin, the (001) reflection of Sap/ACN was broader, however, no

160 significant change was observed in the  $d_{(001)}$  values of CTAB-Sap/ACN suggesting a surface (or

161 edge) loading

162 TEM micrographs showed layers with alternate dark and bright fringes allowing the  
163 measurement of interplanar distances. For Na-Sap, an interlayer distance of  $1.19\pm 0.11$  nm was  
164 obtained (Figure 1B). In CTAB-Sap, the interlayer distance increased to  $1.57\pm 0.19$  nm (Figure  
165 1C). After loading with anthocyanin molecules, the  $d_{(001)}$  spacing were  $1.39\pm 0.19$ ,  $1.49\pm 0.20$  nm  
166 for Sap/An, CTAB-Sap/ACN, respectively (Figure 1 D and E) and some exfoliated layers were  
167 observed corroborating with the enlargement of the (001) reflection observed in XRD. .  
168



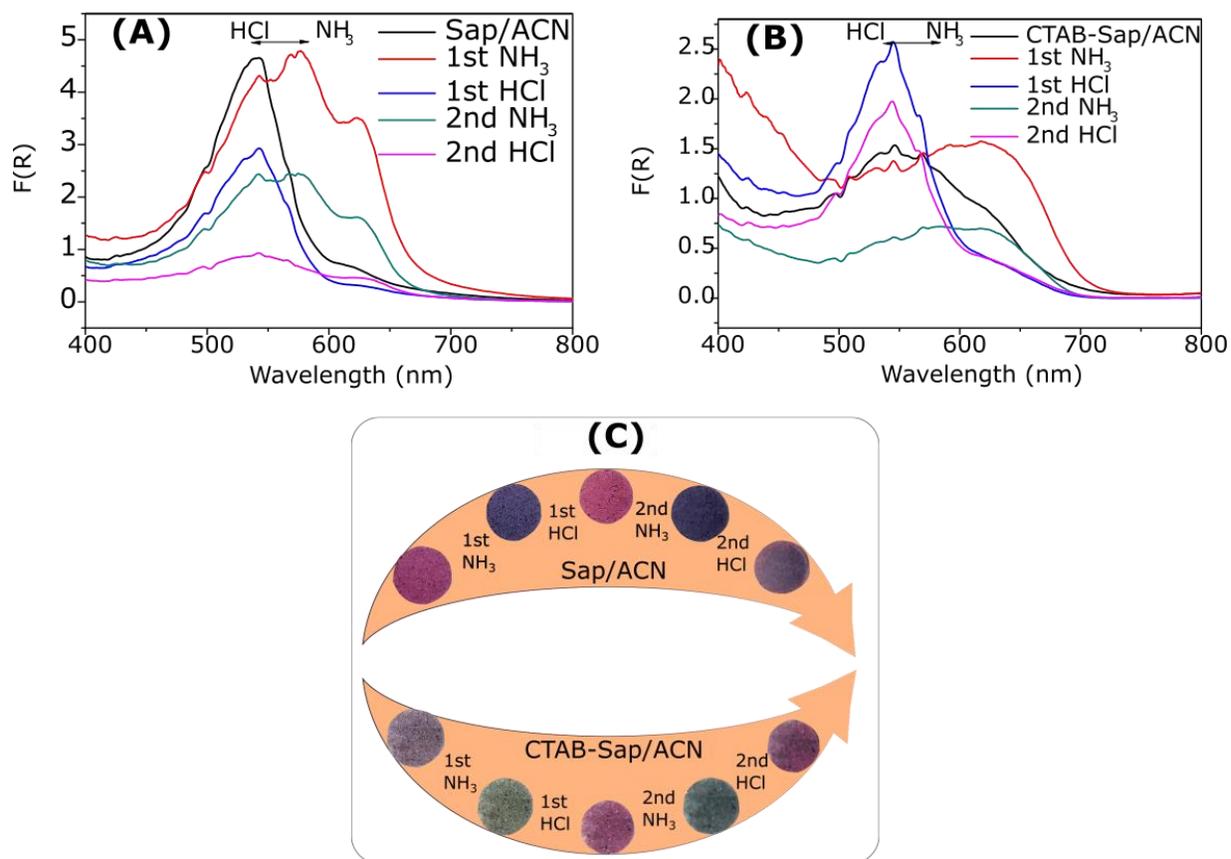
169  
 170 **Figure 1.** (A) XRD patterns of Sap, Sap/ACN, CTAB-Sap and CTAB-Sap/ACN; TEM images  
 171 of (B) Sap, (C) Sap/ACN, (D) CTAB-Sap and (E) CTAB-Sap/ACN; (F) FTIR spectra of Sap,  
 172 Sap/ACN, CTAB-Sap, CTAB-Sap/ACN and (G) DTG curve of Sap, Sap/ACN, CTAB-Sap and  
 173 CTAB-Sap/ACN.

174 The FTIR spectra are depicted in Fig.1. For Sap, the sharp and weak band at  $3677\text{ cm}^{-1}$  and  
175 the one between  $3000\text{-}3600\text{ cm}^{-1}$  correspond to the stretching vibration of structural  $\text{-OH}$  group  
176 and adsorbed water, respectively. The band at  $1633\text{ cm}^{-1}$  is attributed to the bending vibration of  
177  $\text{-OH}$ . The band at  $980\text{ cm}^{-1}$  was assigned to the Si-O-Si stretching (Tao et al., 2016; Fatimah et  
178 al., 2019). Several new bands at  $2925$ ,  $2853$ ,  $1488$  and  $1473\text{ cm}^{-1}$ , which were assigned to the  
179 characteristic vibrations of CTAB alkyl chain, emerged in the FTIR spectrum of CTAB-Sap,  
180 demonstrating the presence of organic molecules. Concerning the Sap/ACN and CTAB-  
181 Sap/ACN samples, the contributions of OH and C=O modes brought from loaded ACN as well  
182 as the new hydrogen bond formed in the hybrid pigments make the bands at the regions between  
183  $3000\text{-}3760\text{-cm}^{-1}$  and  $1550\text{-}1760\text{ cm}^{-1}$  broader than the respective precursor. The signals in the  
184 region between  $1350\text{-}1470\text{ cm}^{-1}$  are attributed to the contribution of  $\nu(\text{C-C})$  in aromatic ring of  
185 anthocyanin loaded.

186 In Figure 1G, the first step of mass loss (8%) at  $25\text{-}238^\circ\text{C}$  for Na-SAP was assigned to the  
187 dehydration of surface and interlayer water. The second event at  $640\text{-}859^\circ\text{C}$  is due to  
188 dehydroxylation of Sap with a mass loss of 3% (Tangaraj et al., 2017; Zhang et al., 2017). The  
189 DTG curve of Sap/ACN shows an additional mass loss of 7% in the region  $210\text{-}623^\circ\text{C}$  attributed  
190 to the degradation of the incorporated anthocyanin. The mass loss in the second event of CTAB-  
191 Sap sample before the ACN adsorption was 30%. After dye loading, the organic mass loss  
192 increases to 32% for CTAB-Sap/ACN sample.

193 The hybrid pigments were exposed to HCl or  $\text{NH}_3$  saturated atmosphere. The results upon  
194 exposure to acidic and basic vapors were monitored by visible absorption spectroscopy and also  
195 by visual changes in their photographs, these results are present in Figure 2.

196



197  
 198 **Figure 2.** Spectra changes after each step of sequential exposure to acidic and basic atmosphere  
 199 for (A) Sap/ACN; (B) CTAB-Sap/ACN. (C) Digital photographs of the color changes of hybrid  
 200 pigments upon exposure.

201 Colors changes from red to blue after exposure to basic atmosphere (NH<sub>3</sub> from aqueous  
 202 NH<sub>4</sub>OH) were observed in the Sap/ACN. The process is reversible, as shown in Figure 2C. The  
 203 exposure time to change the color was about 10 min. Similar results were obtained in the  
 204 literature.

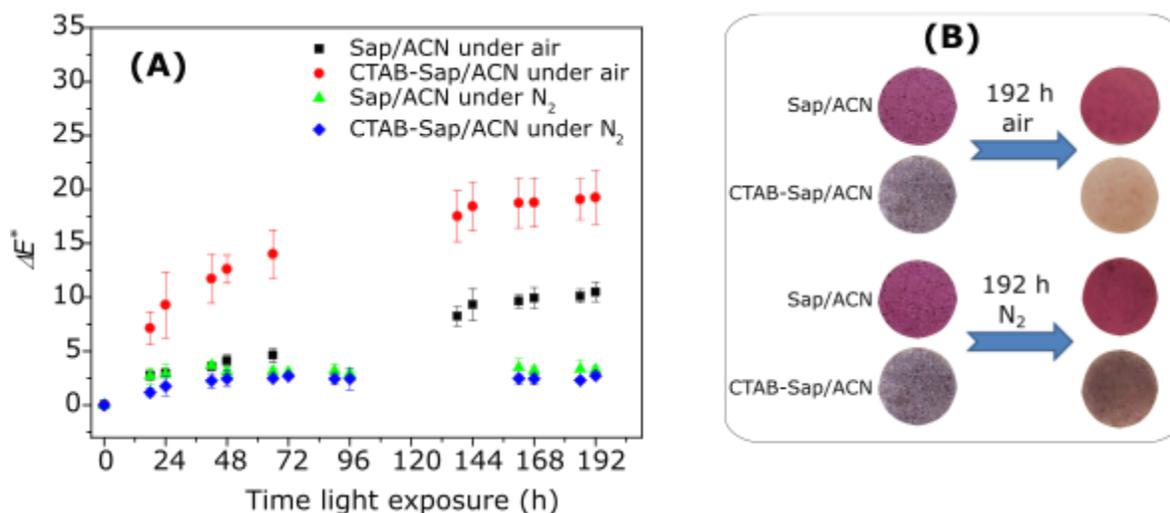
205 In Figure 2A, the absorption band has a redshift after exposure to basic atmosphere, and  
 206 return to the same wavenumber, after exposure to basic atmosphere. After several cycles; the  
 207 same observations on the spectra were noticed. The color change was reversible and repeatable

208 for at least two cycles. The color changes are still observed after the second cycle of exposure,  
209 although strong acid and base conditions degraded the pigments.

210 The contribution of quinoidal base in the anthocyanin molecule in CTAB-Sap/ACN was  
211 more pronounced than in the other hybrid and explains its initial blue color. After the first  
212 exposure to basic vapor, the right shift observed in Figure 3B is due to the conversion of  
213 remaining flavylium cations to quinoidal base, which causes a change only in nuance of blue  
214 (Figure 2C). Hybrids being exposed to basic conditions were again submitted to acidic  
215 environment, the color of CTAB-Sap/ACN change to red and their spectra were similar to the  
216 Sap/ACN, indicating that the anthocyanin molecules became flavylium cation form. The  
217 behavior of color change in the following cycles was also similar to the Sap/ACN (Ogawa et al.,  
218 2017; Silva et al., 2018; Eskandarabadi et al., 2019; Koosha and Hamed, 2019). The decreases  
219 in relative absorbance after the end of four cycles are 80.4% and 73.8% for Sap/ACN, CTAB-  
220 Sap/ACN, indicating a slightly better chemical stability for CTAB-Sap/ACN.

221 The colors of solid hybrid pigments were evaluated before and after light exposure during  
222 192 h (32 years of exposure in a museum). Measurements of  $L^*a^*b^*$  parameters were carried out  
223 at different light irradiation time (Figure 3).

224



225  
 226 **Figure 3.** (A) Photo-ageing of pigments and (B) digital photographs of color change  
 227 observations over 192 h of light exposure in air and nitrogen atmosphere.

228 In solution, the color of ACN changes from red in acid conditions to blue in neutral to  
 229 weak alkaline conditions. However, the difference in color presented by the hybrids results from  
 230 the different interactions between the host and the guest since the effect of pH on the color was  
 231 controlled with the citric acid buffer solution. The color for Sap/ACN is probably due to the  
 232 intercalation of ACN molecule in the interlayer space of Sap, which stabilizes the red color of  
 233 flavylum cations. While adsorption in the CTAB-Sap/ACN sample probably induced  
 234 stabilization of the ACN quinoidal base, leading to a blue color for the hybrid.

235 The  $\Delta E^*$  value (Figure 3A) is related to total color difference and is indicative of the light  
 236 stability of the pigments. Under air, the  $\Delta E^*$  values of the pigments increased gradually with the  
 237 increase of the ageing time. Finally, the values reached  $10.5 \pm 0.9$  for Sap/ACN and  $19.3 \pm 2.5$  for  
 238 CTAB-Sap/ACN after 192 h of light exposure. Lower  $\Delta E^*$  variation in Sap/ACN is probably due  
 239 to the protection of the dye in the interlayer space of the saponite, creating an oxygen hindering  
 240 and stabilizing the pigments under irradiation. In nitrogen atmosphere,  $\Delta E^*$  values were lower  
 241 after 192 h of light exposure, the  $\Delta E^*$  values were  $2.7 \pm 0.2$  and  $3.3 \pm 0.2$  for CTAB-Sap/ACN and

242 Sap/ACN, respectively. In addition, when compared the photostability in air with the  
243 photostability in nitrogen, the most significant differences were observed for CTAB-Sap/ACN,  
244 which corroborate with the greater exposure of ACN molecules to oxygen attack on air  
245 atmosphere for these hybrids.

246

#### 247 **4. Conclusion**

248

249 It is known that the quinoidal base form of anthocyanin is less stable than the flavylum  
250 one and it occurs in neutral to basic conditions. The stabilization of quinoidal base form was  
251 brought by the intermolecular interactions in CTAB-Sap/ACN, since the synthesis of the hybrids  
252 were performed at pH 3. In the Sap/ACN pigment, a cation exchange mechanism leads to the  
253 intercalation of the flavylum cation of the natural dye. The enhanced stability against visible  
254 light irradiation and basic environmental conditions was brought by the intercalation and/or the  
255 intermolecular interaction between the dye and the respective host materials. The intercalation of  
256 the dye molecules into the interlayer space of saponite in Sap/ACN sample provide more  
257 protection against reactive oxygen species. Reversibility in color upon exposure to acidic and  
258 basic atmosphere is an evidence for a possible application of the obtained pigments as a sensor to  
259 atmospheric acidity, which can be exploited in several cycles if applied in less extreme pH  
260 conditions. These dyed materials are environmentally friendly and can be promising candidates  
261 in different application fields.

262

#### 263 **Declaration of Competing Interest.**

264 The authors declare that they have no known competing financial interests or personal  
265 relationships that could have appeared to influence the work reported in this paper

266

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