

1 Abstract

2 Because of its non-toxicity, naturally occurring anthocyanin has a potential for the
3 utilization as a harmless coloring material. Its color instability under alkaline condition
4 or light irradiation limits its practical use. Anthocyanin can be stabilized by the
5 intercalation into montmorillonite. The anthocyanin-montmorillonite maintains the
6 original color at basic condition of even pH 11. The intercalated anthocyanin also
7 exhibits enhanced stability against visible light irradiation compared with the
8 anthocyanin simply adsorbed on the external surface of the mineral particles. The
9 stability enhancement is attributed to the electrostatic host-guest interaction and to steric
10 protection from the attack of atmospheric oxygen. The intercalated complex can be a
11 candidate of an environmentally friendly coloring material.

12

13 Keywords: anthocyanin; montmorillonite; colorant

1 **1. Introduction**

2 Anthocyanins are found in many flower petals and fruits (Goto and Kondo, 1991).
3 Their non-toxicity is suitable for the utilization of food dyeing. However, their color
4 durability is not satisfactory for practical use. They are easily discolored on exposure to
5 light (Bakowska et al., 2003; Torskangerpoll and Andersen, 2004) or slightly basic
6 conditions (Brouillard and Delaporte, 1977; Brouillard and Dubois, 1977). As shown in
7 Scheme 1, flavylium form **1** of the anthocyanin is converted to quinonoidal base **2** in
8 mild alkaline conditions, and finally to non-colored chalcone **4** via carbinol pseudobase
9 form **3**. All these conversions are accompanied by a marked color change. The problem
10 about the stability is very serious and prevents the wide use of the anthocyanin as a
11 colorant other than for food dyeing.

12 ---Scheme 1---

13 On the other hand, incorporation of organic dyes into inorganic host materials is
14 widely investigated in recent days (Gomez-Romero and Sanchez, 2005; Takagi et al.,
15 2006a, 2006b), and there have been many reports concerning the enhancement of the
16 stability of organic dyes by complexation with inorganic host materials such as clays

1 (Bujdák et al., 2002; Endo et al., 1989; Saito et al., 2005; Shichi and Takagi, 2000) or
2 zeolites (Calzaferri, 1998; Hölderich et al., 2000; Hoppe et al., 1994; Ramamurthy,
3 2000; Telbiz et al., 2001). We have reported that a synthetic cationic flavylum dye can
4 be stabilized by intercalation into montmorillonite K10 (Kohno et al., 2007) or
5 incorporation into the pores of zeolites (Kohno et al., 2008). The flavylum dye has the
6 same core structure as anthocyanins (2-phenylbenzopyrylium), and is considered as a
7 model compound of anthocyanins (Iacobucci and Sweeny, 1983; Ito et al., 2002; Jurd,
8 1969; Mazza and Brouillard, 1987).

9 In this study, we report the stabilization of a naturally occurring anthocyanin by
10 intercalation into montmorillonite. The anthocyanin assumes the cationic flavylum
11 form under an acidic condition, and is expected to be intercalated by the ion exchange
12 reaction. Therefore, the complexation of the anthocyanin with clay minerals may be a
13 key technology for the development of an environmentally friendly coloring material.

14 Lima et al. (2007) have reported the adsorption of anthocyanin on several inorganic
15 hosts including clay minerals. In their study, montmorillonite has been confirmed to
16 adsorb anthocyanin, but the effect of the stabilization by adsorption has not been

1 investigated in detail, and the adsorption condition has not been fully optimized for
2 intercalation. In the present study, we try to confirm the enhancement of the stability of
3 the anthocyanin by intercalation of the anthocyanin. As described above, we have
4 already found that the model compound, flavylum dye, is stabilized by the adsorption
5 between the layers of montmorillonite (Kohno et al., 2007). We show in this study that
6 intercalated anthocyanin was sufficiently stabilized against an alkaline environment or
7 visible light irradiation.

9 **2. Experimental**

10 **2.1 Materials**

11 We used montmorillonite, a synthetic non-swelling mica and silica. Kunipia F
12 montmorillonite (designated as KF) was supplied from the Clay Science Society of
13 Japan (JCSS-3101) and was used as received. The synthetic non-swelling mica
14 (designated as NSM) was supplied from Wako Chemical Co. and used as received.
15 Silica (designated as SIO) was supplied from Catalysis Society of Japan (JRC-SIO-9A).

16 KF is a purified natural montmorillonite. The cation exchange capacity of KF was

1 1.15 meq/g. NSM does not show cation exchange because the K^+ ions are strongly
2 bound in the interlayer space.

3 As an anthocyanin dye, we used commercially available powdered Grape Color
4 BC-120 supplied from Kiriya Chemical Co., extracted from grape skins. The
5 anthocyanin BC-120 was purified as described in the literature (Baublis et al., 1994)
6 using an adsorption column XAD-7. The dye was dissolved in a 5 % aqueous solution
7 of formic acid, and passed through the XAD-7 column for three times. The eluate was
8 concentrated, and mixed with an excess amount of diethyl ether to precipitate the
9 purified dye. The precipitate was air-dried at room temperature. Thus purified
10 anthocyanin was denoted as AN. AN was analyzed by HPLC using Mightysil as
11 packing material, with an aqueous solution of acetic acid and acetonitrile as eluent. The
12 purity and the composition of AN was determined by UV and ESI-MS (Table 1). AN
13 was found to be a mixture of five anthocyanins, and the main component was
14 malvidin-3-glucoside. The composition was in agreement with other studies concerning
15 the analysis of the anthocyanins extracted from grape skins (Baublis et al., 1994;
16 Kammerer et al., 2005; Vivar-Quintana et al., 2002).

1 ---Table 1---

2

3 **2.2 Adsorption of AN**

4 A given amount of AN was dissolved in 2 ml of methanol, and 100 ml of the 5 %
5 aqueous formic acid solution was added. The pH of the solution was 2.5. Anthocyanins
6 are reported to be stable for about 15 days at pH 1 to 3 (Cabrita et al., 2000). The
7 solution was mixed with 1 g of KF and kept in the dark. After 24 h, the resulting
8 sediment was separated from the solution by filtration, dried at 353 K, and powdered
9 (sample AN/KF). The same procedure was used for AN and NSM (AN/NSM). Unless
10 otherwise noted, the amount of AN in AN/KF and AN/NSM was 10 mg per 1 g of the
11 host materials.

12 AN was not adsorbed on SIO by simply mixing the AN solution with SIO.
13 Therefore, AN was loaded on the surface of SIO by evaporating the solvent of the
14 mixture of the AN solution and SIO. AN powder of 30 mg was mixed with 1 g of SIO
15 in a mortar, and then 1 ml of the 5 % aqueous formic acid solution was dropped to the
16 mixture. To evaporate the solvent, the paste was kept in the dark at room temperature in

1 the air for 24 h. After drying, the solid was powdered (AN/SIO).

2

3 **2.3 Measurements**

4 XRD patterns were measured with the Rigaku MiniFlex X-ray diffractometer
5 (CuK α , step angle and scan speed 0.05° and 2°/min, 15 mA, 30 kV).

6 UV-Vis spectra were collected with the JASCO V-550 spectrophotometer. To
7 measure diffuse-reflectance spectra, the ISV-469 integrating sphere was equipped to the
8 spectrometer.

9 To investigate the durability of the sample against alkaline environment, the pH of
10 the AN solution and the AN/KF dispersion was adjusted to 11 by adding a small
11 amount of 1 M aqueous NaOH. Immediately after the pH was raised, the spectral
12 changes of both samples were recorded.

13 To investigate the light endurance of AN/KF, AN/NSM and AN/SIO, visible light
14 was irradiated to the samples under ambient temperature and pressure. The color fading
15 was measured by the decrease of the absorption in the diffuse reflectance spectra. A 100
16 W halogen lamp (Schott Megalight 100) equipped with a 30 cm length flexible light

1 guide was used as a visible light source. The powder samples were loaded in a plastic
2 cell covered with a thin glass, and placed at the position of 2 cm from the aperture of the
3 light guide. In this condition, the increase in the temperature of the sample under
4 irradiation was only within 7 K, so that the influence of the temperature on the stability
5 could be neglected. When the sample was irradiated under N₂ atmosphere, the sample
6 cell was packed in a gas barrier film filled with nitrogen.

8 **3. Results and discussion**

9 **3.1 Intercalation of anthocyanin**

10 Fig. 1 represents the XRD patterns of AN/KF samples with different amounts of AN.
11 The basal spacing increased with increasing amount of adsorbed AN, indicating that AN
12 was intercalated. The basal reflection of NSM remained unchanged, indicating that AN
13 was not intercalated.

14 ---Figure 1---

15 Fig. 1(b) illustrates the variation of the basal reflection d_{001} with the amount of AN
16 added. Thus, the interlayer spacing at the full adsorption of AN (plateau value, 1.56 nm)

1 was 0.6 nm (subtracting the thickness of 0.96 nm from the basal spacing) (Endo et al.,
2 1988). Considering that the anthocyanin has a planar flavylum skeleton with a glucose
3 moiety, and that the sugar moiety of the anthocyanin is thought to be positioned
4 perpendicular to the flavylum skeleton (Borkowski et al., 2005), this interlayer distance
5 roughly corresponds to the molecular thickness of AN. In addition, the hydrophilic
6 sugar moiety may adsorb water molecules in the interlayer space. A planar molecule
7 such as xanthene dye showed the tendency to be adsorbed parallel to the silicate layer
8 (Endo et al., 1988; Endo and Shimada, 1991). Similarly, the planar flavylum skeleton
9 of AN is expected to have an affinity to the internal surface of KF. Not only the cationic
10 polysaccharide chitosan (Darder et al., 2005) but also non-ionic starch (Wilhelm et al.,
11 2003) was intercalated. Thus, a sugar moiety should also have affinity to the interlayer
12 space. We concluded that AN was adsorbed between the layers of KF with the
13 flavylum skeleton parallel to the clay mineral layer.

14

15 **3.2 Spectral change of anthocyanin**

16

---Figure 2---

1 The acidic aqueous solution of AN showed an absorption peak at 523 nm (Fig. 2).
2 Considering that the components of AN were 3-glucoside of five aglycons (malvidin,
3 peonidin, petunidin, delphinidin and cyanidin), this result agrees well with the previous
4 report (Cabrita et al., 2000; Vivar-Quintana et al., 2002).

5 The peak of AN was significantly shifted from 523 nm to 540 nm. Such a red shift
6 has been observed for cationic dyes such as rhodamine 590 (Endo et al., 1988), thionine
7 (Sunwar and Bose, 1990), or cyanine (Ogawa et al., 1996) intercalated into
8 montmorillonite or saponite. The reason is the electrostatic interaction between the clay
9 layer and the dye. The spectral shift observed for AN/KF indicated that the electrostatic
10 interaction of AN with the silicate layers is important.

11 AN/NSM also showed a peak at 540 nm. This red shift also indicated electrostatic
12 interaction between AN and the external surface of NSM.

13 AN/SIO showed an absorption peak at 520 nm, as the AN solution. Thus, the
14 electrostatic interaction was rather weak.

15 In addition, the red shift may be caused by the coplanarization in the structure of
16 anthocyanin. Since the flavylum skeleton of the anthocyanin is thought to be strongly

1 adsorbed parallel to the clay mineral layer, it is expected that the orientation of the
2 flavylum skeleton is forced to be more planar than in a solution. Therefore, the
3 coplanarization of the benzopyrylium ring and phenyl group of the anthocyanin can also
4 result in the red shift of the 523-nm peak. The observed spectral change might reflect
5 the sum of these effects.

6

7 **3.3 Durability against alkaline environment**

8 Fig. 3 represents the spectral change of AN solution and AN/KF dispersion when
9 the pH of the sample was rapidly raised to 11 by adding NaOH. The peak of the AN
10 solution shifted to 594 nm immediately after the pH was raised, and was gradually
11 weakened and almost disappeared within 2 hours. The observed red shift to 594 nm in
12 the spectrum was assigned due to the conversion of AN to the quinonoid base (Cabrita
13 et al., 2000; Figueiredo et al., 1996; Mazza and Brouillard, 1987) (Scheme 1). The
14 quinonoid base was finally degraded and faded by the attack of hydroxyl groups in the
15 alkaline solution. On the contrary, the spectrum of the AN/KF dispersion was
16 unchanged even at elevated pH (Fig. 3b). In addition, the AN/KF dispersion showed no

1 fading under the alkaline condition at pH = 11 during 2 hours. Thus, complexation of
2 AN with KF enhanced the stability against an alkaline environment.

3 ---Figure 3---

4

5 **3.4 Durability against irradiation**

6 The samples AN/KF, AN/NSM and AN/SIO were kept under visible light
7 irradiation from a 100 W halogen lamp, and the spectral changes caused by the
8 irradiation were traced. During light irradiation, the shape and λ_{\max} of the spectra was
9 unchanged in every sample, only the absorption decreased (Fig. 4), indicating photo
10 degradation. Side reactions such as photoisomerization did not occur.

11 In Fig. 4 the change in the absorption at λ_{\max} under visible light irradiation was
12 expressed by the time dependence of the ratio A/A_0 (A = absorption at time t , A_0 =
13 absorption at time $t = 0$). Photostability of AN/KF was much higher than that of
14 AN/SIO. Thus, the photostability of AN/NSM was between AN/KF and AN/SIO. This
15 might be due to the non-swelling character of NSM. When AN/NSM was irradiated
16 under nitrogen atmosphere (*i.e.*, without oxygen) (Fig. 4, B), AN/NSM was stable. A/A_0

1 for AN/NSM after 400 min irradiation under N₂ was 0.91, which was the same level as
2 that of AN/KF.

3 ---Figure 4---

4

5 **3.5 Stability enhancement**

6 The stability of AN against an alkaline environment or visible light irradiation was
7 enhanced by complexation with clay minerals.

8 The absorption peak of AN/SIO was observed at almost the same wavelength as that
9 of AN solution, but AN/KF and AN/NSM showed a red-shift (Fig. 2). Various cationic
10 dyes intercalated into clay minerals showed a red shift caused by the electrostatic
11 interaction between the dye and the clay mineral layer (Endo et al., 1988; Ogawa et al.,
12 1996; Sunwar and Bose, 1990). Stabilization of various cationic dyes by electrostatic
13 interaction with zeolites (Calzaferri, 1998; Komori and Hayashi, 2003; Wöhrle et al.,
14 1995) or clay minerals (Bujdák et al., 2002) has been reported. Anthocyanin is
15 stabilized in plant petals by copigmentation with water-soluble organic compounds such
16 as rutin (Alluis et al., 2000; Bakowska et al., 2003). The copigmentation causes a red

1 shift in the spectrum of anthocyanin due to π - π interaction (Alluis et al., 2000). The
2 acylated anthocyanin, such as red cabbage dye, has a phenyl moiety such as coumaric
3 acid, and the intramolecular π - π interaction with the residue stabilizes the anthocyanin
4 effectively (Dyrby et al., 2001). The stabilized dyes showed a considerable spectral shift
5 caused by the electrostatic interaction.

6 However, it was not always the case that the sample showing large spectral shift was
7 superior in stability. AN/NSM showed a significant red shift but was not stabilized
8 enough against visible light irradiation in the air (Fig. 4, C). This result suggests that the
9 enhancement of stability was not brought about only by the electrostatic interaction. We
10 must consider the effect of atmospheric oxygen, since the degradation under
11 irradiation is considered in relation to the oxidation caused by the evolution of singlet
12 oxygen (Attoe and Elbe, 1981; Caine et al., 2001; Usui et al., 1965). Shown in Fig.
13 4(A)-(C) is the photostability of AN/NSM samples maintained under N₂ and in the air,
14 together with that of AN/KF in the air. While the stability of AN/NSM in the air was
15 inferior to that of AN/KF, significant enhancement of the photostability was observed
16 when the AN/NSM sample was kept under N₂ atmosphere. This result indicates that

1 blocking out oxygen brings about the stabilization under irradiation. In other words, the
2 AN molecule in the AN/KF sample is sterically protected from atmospheric oxygen by
3 the intercalation to the interlayer space of KF. The enhancement of the durability
4 against alkaline environment may also be considered due to the steric hindrance from
5 the attack of hydroxyl ion to the anthocyanin dye. Similar steric hindrance effect,
6 together with the electrostatic effect, has been proposed about the stability enhancement
7 by the copigmentation in natural anthocyanin (Dyrby et al., 2001; Mazza and Brouillard,
8 1987).

9 From these, we concluded that AN was stabilized by the electrostatic interaction and
10 the suppression of the attack of oxygen or hydroxyl ions within the narrow interlayer
11 space of montmorillonite.

12

13 **4. Conclusion**

14 The stability of natural anthocyanin toward alkaline environment and visible light
15 irradiation was greatly enhanced by intercalation into montmorillonite. The
16 enhancement of the stability was brought about both by the electrostatic interaction

1 between the intercalated dye and the montmorillonite surface and by the protection of
2 the intercalated dye from atmospheric oxygen. The intercalated and stabilized
3 anthocyanin can be a candidate of an environmentally friendly coloring material.

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- 25

1 **Fig. 1** (a) XRD patterns of AN/KF with different amounts of AN added. The amount
2 of AN was (A) none, (B) 10 mg, (C) 100 mg, (D) 200 mg, (E) 300 mg and (F) 500 mg.
3 (b) Changes in the basal spacing of KF by adsorption of AN.

4
5 **Fig. 2** Diffuse reflectance UV-Vis spectra of (A) AN/KF, (B) AN/SIO and (D)
6 AN/NSM samples, together with (C) the spectrum of the aqueous AN solution with 5 %
7 formic acid.

8
9 **Fig. 3** UV-Vis spectral change of (a) aqueous AN solution and (b) aqueous AN/KF
10 dispersion after the pH was rapidly raised to 11. The spectra were recorded at 5, 20, 30,
11 60, 90 and 120 min after adding some drops of 1 M NaOH.

12
13 **Fig. 4** Changes in the absorption at λ_{\max} of (A) AN/KF, (B) AN/NSM under N₂
14 atmosphere, (C) AN/NSM and (D) AN/SIO under visible light irradiation. The change
15 in the absorption is related to the initial absorption before irradiation.

16
17 **Scheme 1** Several forms of anthocyanin. **1**: flavylium, **2**: quinonoidal base, **3**:
18 pseudobase, **4**: chalcone.

1 Table 1 Components of AN and their ingredients

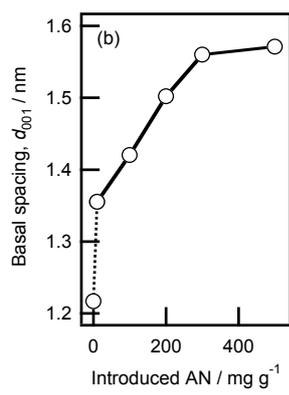
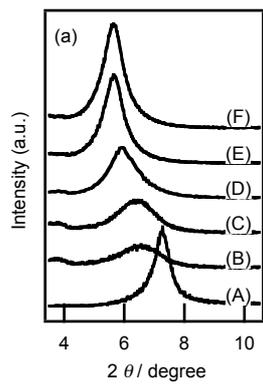
Compound name	Substituents ^a		Ingredient (%) ^b
	R ₁	R ₂	
Malvidin-3-glucoside	OMe	OMe	49
Peonidin-3-glucoside	OMe	H	20
Petunidin-3-glucoside	OMe	OH	15
Delphinidin-3-glucoside	OH	OH	13
Cyanidin-3-glucoside	OH	H	3

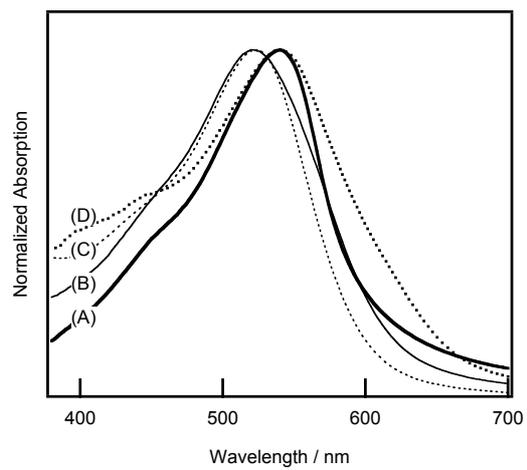
2 ^a For positions of R₁ and R₂, see Scheme 1. ^b Total amount of anthocyanin in AN was
 3 estimated to be 14 %.

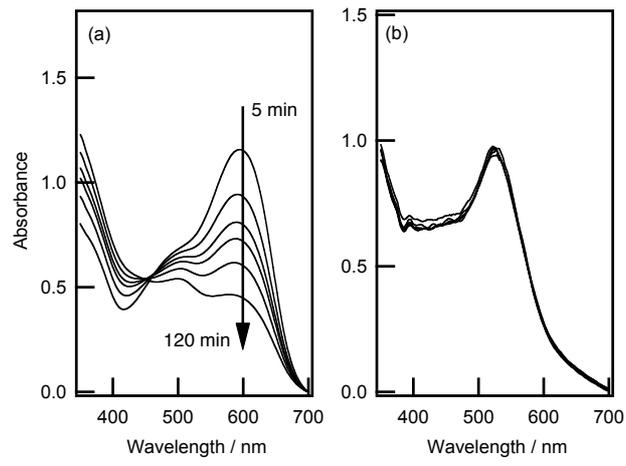
4

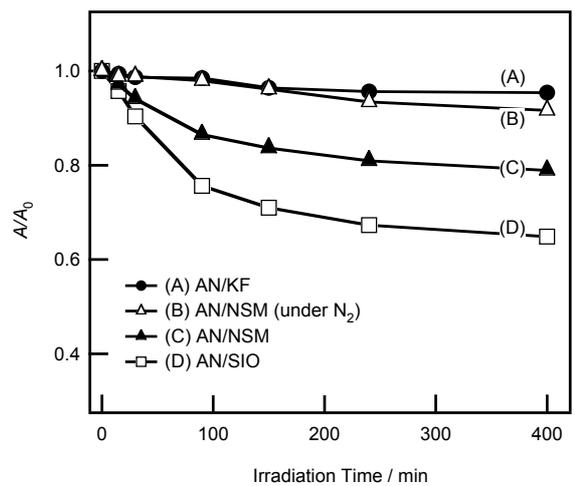
5

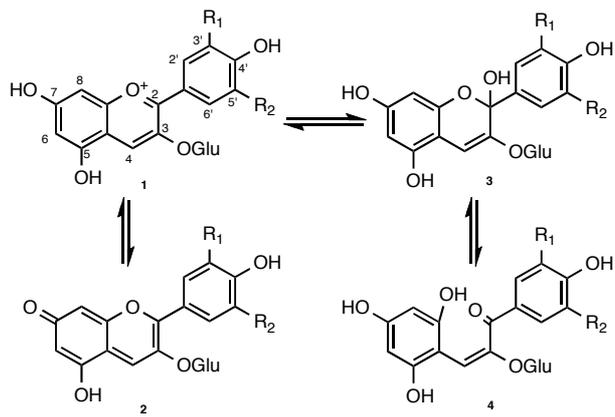
6











Scheme 1

Several form of anthocyanin (1: flavylium, 2: quinonoidal base, 3: pseudobase, 4: chalcone)