Stabilization of flavylum dye by incorporation into the pore of protonated zeolites

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Abstract

Flavylum dye, a model compound of natural anthocyanin, has a defect that its color

stability is very poor. We have complexed the flavylum dye with protonated zeolites and succeeded to enhance both the thermal and chemical stability of the dye. The aqueous dispersion of the flavylum/zeolite complex maintains its color even at 353 K or at pH=9, under which conditions the aqueous solution of the flavylum loses its color immediately. The stability is enhanced when the dye is incorporated into the pore of the zeolites, and a large stabilization effect is obtained by a tight adsorption with a narrow pore, as long as the dye is incorporated into the pore. Because of its enhanced color stability, the flavylum dye incorporated in the zeolite pore can be a candidate for an environmentally friendly coloring material.

Keywords: Flavylum, Anthocyanin, Stabilization, Zeolite Y, Mordenite

1. Introduction

Flavylium (FV) is a cationic dye having 2-phenylbenzopyrylium skeleton. Since the FV derivatives exhibiting yellow, magenta and cyan (the three primary colors) have been obtained by selecting proper substituents [1-5], FV can potentially be used as a coloring material. The structure of FV (2-phenylbenzopyrylium skeleton) is the same as those of the naturally occurring anthocyanin dyes. Therefore the impact of FV on the environment is expected to be rather small compared with other synthetic dyes.

---Scheme 1---

However, the stability of FV is known to be poor; FV easily undergoes transformation to a colorless 2-hydroxychalcone under slightly basic or heated conditions [1, 5-9]. The reaction route is shown in Scheme 1 [10]. At the beginning FV is hydrated by the attack of water or hydroxyl ion to give a colorless hemiacetal. The hemiacetal undergoes isomerization to become *cis* 2-hydroxychalcone. Finally the *cis* 2-hydroxychalcone isomerizes into more stable *trans* 2-hydroxychalcone. These 2-hydroxychalcones also show no color (or pale yellow).

If the stability of FV can be enhanced, we expectedly use FV as an environmentally friendly coloring material. The strategy of the enhancement of the stability can be mentioned as follows: (1) giving acidic condition to prevent hydration of FV, (2) presenting steric hindrance from the attack of water or hydroxyl ion, (3) removing free space to inhibit FV to undergo the reaction to 2-hydroxychalcone.

We have previously reported that FV is stabilized by incorporation of FV between the layers of the clay pretreated with mineral acid [11]. The dye is stabilized by the static electric field and acidic nature in the interlayer, as well as the protection against various attacks from external environment.

Zeolite is another example of the inorganic host that can exhibit acidity and incorporate some organic molecules [12-14]. For example, the research group of Calzaferri has investigated in detail the incorporation of several organic dyes into the pore of zeolite L and the change in the properties of the incorporated dyes [15-18]. In general, zeolite is a microporous crystalline aluminosilicate, and some kind of the zeolite has a micropore whose size is roughly the same as those of organic molecules [19]. In the pore exists an exchangeable cation, and proton-exchanged zeolite is known

to exhibit strong acidity and used as an acid catalyst. Considering this, we can expect that FV incorporated in the proton-exchanged zeolite is protected against the attack from external environment, prohibited to undergo the conversion to the 2-hydroxychalcone in the narrow pore, and stabilized by the acidity of the protonated zeolite.

In this study, we have tried to incorporate the flavylum dye into the pore of the zeolite. Two types of zeolites, zeolite Y and mordenite, have been used because they have different pore structure and simultaneously their pore size is different from each other [20]. Zeolite Y has a large pore with diameter of 1.3 nm, called “supercage”, which is connected to each other by four 12-membered ring channels with diameter of 0.74 nm, resulting in the 3-dimensional pore network. On the other hand, mordenite has a 1-D linear pore with a strained 12-membered ring channel whose diameter is 0.65 to 0.70 nm. Hence, the pore size of mordenite is smaller than that of zeolite Y. We have used proton-exchanged zeolites, H-Y and H-mordenite, since the protonated zeolites exhibit solid acidity and are expected to show stronger stabilization effect on FV. We have checked the enhancement of thermal and chemical stability of FV brought about

by the complexation with the zeolites. We have compared the stability of the samples with FV adsorbed inside or outside the pore, using several FV derivatives of different molecular size.

2. Experimental

Flavylium dyes used in this study were previously synthesized in this laboratory according to the literature [3, 10, 21], by the aldol condensation reaction of the corresponding 2-hydroxybenzaldehydes and acetophenones [22]. The structure and molecular size of each FV are summarized in Scheme 1. It has been known that the absorption band of FV shifts to longer wavelength when FV has an electron-donating substituents at the 4'- or 7-position (R_1 or R_2 in Scheme 1). FVY has less electron-donating methoxy group and shows yellow color. FVM shows magenta color since it has more electron-donating dimethylamino group than methoxy group. FVC and FVC2 have two amino groups at 4'- and 7-position, and exhibit cyan color. FVC2 also has a phenyl group at 4-position (R_3 in Scheme 1); it has been reported that the

substituents at 4-position has little effect on the color of flavylum [5].

Zeolites used in this study were supplied from the Catalyst Society of Japan. As protonated zeolite Y and mordenite, JRC-Z-HY5.3 (Si/Al=2.88, ion exchange ratio 92%) and JRC-Z-HM20 (Si/Al=9.47, ion exchange ratio 99%) were used respectively. They were supplied as a protonated form and used without further protonation. In the following, they were denoted as HY and HM, respectively.

The complexation of FV and zeolites was carried out as follows. Firstly, a methanolic solution of FV was prepared. Unless otherwise noted, the concentration of the solution was 1 mmol/dm³. The solution was mixed with 1 g of each zeolite powder and kept in the dark under room temperature for 24 h. The sediment was separated from the solution by filtration and dried at room temperature in the air. The samples thus obtained were denoted as FV/HY or FV/HM.

UV-Vis spectra of FV solutions were recorded using Hitachi U-3000 spectrophotometer in the transmission mode. The concentration of each solution was adjusted for the absorbance to be 1.0. The spectra of FV/zeolite dispersions and FV/zeolite powder samples were recorded using JASCO V-550 spectrophotometer

equipped with ISV-469 integration-sphere attachment. The spectra of the dispersions were measured in a diffuse-transmittance mode, whereas those of the powder samples were measured in a diffuse-reflectance mode. The dispersions were prepared by mixing 2 mg of FV/zeolite and 4 cm³ of deionized water in a cell made of polystyrene, followed by sonication for 5 minutes. To avoid settlement of the particle during the measurement, the dispersions were mixed vigorously just before collecting the spectra. In this method, sufficient reproducibility of the diffuse-transmittance spectra was obtained.

3. Results and discussion

3.1. Absorption spectra of FV/zeolite complexes

In order to get information about the state of FV adsorbed on the zeolites, we measured the UV-Vis absorption spectra of respective FV/zeolite samples, and compared them with those of the corresponding FV solutions

---Figure 1---

Figure 1(a) represents the diffuse reflectance UV-Vis spectra of FVY/HY and FVY/HM powders, as well as the absorption spectrum of FVY aqueous solution. The absorption maximum of FVY/HY and FVY/HM samples was seen at 448 nm and 452 nm, respectively, while that of FVY aqueous solution was at 436 nm. The red shift of 12 to 16 nm is due to the effect of the electrostatic interaction between the cationic dye and the zeolite pore [5, 23]. As the pore size of HM is smaller than that of HY, FV is closer to the sidewall of the zeolite pore of HM than HY. Therefore the effect of the zeolite pore on the cationic dye is stronger in HM than in HY, resulting in the slightly larger red shift of the peak in HM.

Figure 1(b) represents the spectra of FVM/HY, FVM/HM and FVM aqueous solution. The monomer peak of FVM was observed at 532 nm in the aqueous solution [24]. FVM/HY showed a broad absorption band with peaks at both longer (around 570 nm) and shorter (around 514 nm) wavelengths in addition to the monomer peak. When FVM was complexed with HM, the spectrum showed the maximum peak at 532 nm which was the same as that of the solution. In addition, FVM/HM showed another peak at 570 nm. This peak at 570 nm was observed more clearly than in FVM/HY.

As described above, the interaction between the adsorbed dye and the zeolite pore causes the red shift on the absorption peak. Therefore the peak observed at 570 nm should be assigned to the FVM influenced by the zeolite pore. On the other hand, the peak observed at shorter wavelength of 514 nm in FVM/HY is tentatively assigned to aggregates of FVM, because there is a general tendency for FV to form H-aggregate and exhibit blue shift of the absorption peak [3, 25]. As the FVM molecules are condensed by the adsorption into the supercage of HY, there exists strong interaction between the FVM molecules themselves, resulting in the formation of the aggregates in the supercage of HY. The aggregate was scarcely seen in FVM/HM since there is no room to form aggregates in the linear pore of HM, just as zeolite L [13, 26].

Figure 1(c) represents the spectra of FVC/HY, FVC/HM and FVC aqueous solution. The aqueous solution of FVC showed a maximum peak at 594 nm, which was assigned to a monomer peak [3, 27]. FVC/HY exhibited a strong absorption peak at 560 nm, in addition to a maximum peak at 590 nm that is almost the same wavelength as that of the solution. We think that the absorption observed at 560 nm suggests the existence of the aggregates of FVC, as seen in the case of FVM/HY. On the other hand, FVC was

scarcely adsorbed on HM, and the absorption of FVC/HM sample was very weak, as can be found in the right axis of Figure 1(c). The peak of FVC/HM was slightly blue shifted from that of the solution, suggesting the formation of the aggregates. The molecular size of FVC is larger than FVY and FVM because the FVC molecule has a rather large diethylamino group as well as a dimethylamino group. Therefore, we can imagine that the difference in the molecular size influences the adsorption behavior. In some cases the slight difference of the molecular size greatly influences the adsorption properties. For example, Calzaferri has reported that thionine (with amino group) can be incorporated in the linear pore of zeolite L, while slightly large methylene blue (with dimethylamino group) or ethylene blue (with diethylamino group) cannot be incorporated in the pore but adsorbed on the external surface to form aggregates [15]. Considering this, we concluded that FVC cannot be incorporated in the pore of HM, which is smaller than that of HY, but is adsorbed on the external surface of HM, and may form aggregates.

Figure 1(d) represents the spectra of FVC2/HY, FVC2/HM and FVC2 aqueous solution. FVC2 is the molecule having a bulky phenyl group at 4-position (see Scheme

1). The aqueous solution of FVC2 exhibited an absorption peak at 587 nm. FVC2/HY showed very weak absorption compared to other FV/HY complexes. It can be said that FVC2 molecules cannot be incorporated into the supercage of HY because FVC2 has a bulky phenyl substituent. Similarly, very small amount of FVC2 was adsorbed on HM. The wavelength and the shape of the absorption band of FVC2/HY and FVC2/HM were almost the same as those of the aqueous solution, indicating that the FVC2 molecule exists on the external surface of the zeolites as a monomer form rather than aggregates. In the literature [3], it can be seen that the aggregation of FVC2 was less favorable than FVC, perhaps because the conformation of the phenyl group at 4-position in FVC2 is tilted from the molecular plane.

3.2. Enhancement of FV stability

3.2.1. Thermal stability

We confirmed the enhancement of the thermal stability of FV/zeolites, by maintaining the samples in water at 353 K and comparing the fading rate to that of the aqueous

solutions.

---Figure 2---

The spectral changes of FVY aqueous solution, FVY/HY and FVY/HM kept at 353 K are shown in Figure 2. As shown in Figure 2(a), when the aqueous solution of FVY was maintained at 353 K for 30 minutes, the color of the solution was perfectly faded and lost. Simultaneous growth of the peak at around 350 nm was observed, indicating the formation of the corresponding 2-hydroxychalcone [7, 28]. Therefore, the FVY was found to be converted to the 2-hydroxychalcone derivative in the solution maintained at 353 K, which was in agreement with the previous studies [1, 11, 29, 30]. As shown in Figure 2(b), the FVY/HY dispersion also lost its color when maintained at 353 K for 30 minutes. However, the stability seemed to be enhanced to some extent, as a shoulder peak at 436 nm was still observed after 30 minutes of heating. The FVY/HY sample also showed the growth of the peak at around 350 nm, indicating the occurrence of the conversion from FVY to the 2-hydroxychalcone in the supercage of HY. On the other hand, FVY/HM exhibited almost no change in the spectrum even after 30 minutes of heating, as shown in Figure 2(c). It is possible to think that FVY may be stabilized in

the pore of HM because the acidity of HM is slightly stronger than HY [31]. In addition, the fact that the pore size of HM is smaller than HY seems to contribute to the enhancement of the stability. It is reported that the restriction of the molecular motion of some phenyl derivatives is stronger in the linear pore of zeolite L than in the large supercage of zeolite Y [32]. Because the pore size of HM is smaller than zeolite L, such a restriction should be effective on the molecule incorporated into the pore of HM. Considering this, the molecular motion of FVY may be restricted in the pore of HM, and the conversion from FVY to the 2-hydroxychalcone may be suppressed, resulting in the enhancement of the color stability. This point will be discussed in detail later.

---Figure 3---

Figure 3 indicates the thermal stability of FVM samples. On heating the FVM solution, the absorption of FVM at 532 nm decreased, while the absorption at 400 nm due to the corresponding 2-hydroxychalcone increased [5, 21]. Judging from this, FVM was converted to the 2-hydroxychalcone by hydration in the solution at 353 K. On the other hand, both FVM/HY and FVM/HM dispersions showed almost no spectral change when they were kept at 353 K for 30 minutes. Considering that the color of FVY/HY

was lost when kept at 353 K for 30 minutes, it can be said that the stability of FVM/HY is higher than that of FVY/HY. Since FVM has diethylamino group that shows larger electron-donating effect than methoxy group of FVY, the stability of the FVM molecule itself is superior to FVY [5, 21, 24, 33]. Therefore, the stability of FVM/HY against hydration is higher than that of FVY/HY. As the stability of FVM was relatively high, the difference in the stabilization effect between HY and HM was not clearly observed.

---Figure 4---

The spectral changes of FVC aqueous solution and FVC/HY dispersion when maintained at 353 K are shown in Figure 4. As described above, the amount of FVC adsorbed on HM was very small, and we could not measure the correct spectrum of the FVC/HM dispersion. After the FVC solution was kept at 353 K for 60 minutes, the absorption of FVC decreased to about 60 %, while the absorption of FVC in FVC/HY dispersion did not change so drastically. Only 10 % of the absorption was missing by heating the FVC/HY dispersion for 60 minutes. Therefore, we concluded that FVC was stabilized in the supercage of HY, as FVY and FVM were. In the FVC aqueous solution, the increase of the absorption due to the 2-hydroxychalcone was observed at around 430

nm along with the decrease of FVC. However, no absorption of the 2-hydroxychalcone was observed when the FVC/HY dispersion was heated. Because the molecular size of FVC is larger than FVY or FVM, the free space may not be enough for FVC to undergo isomerization reaction to 2-hydroxychalcone in the supercage of HY. Therefore, FVC may not be converted to the 2-hydroxychalcone but remained as a hemiacetal form, showing no absorption peak in the wavelength range over 350 nm.

3.2.2. Chemical stability

We investigated the durability of the FV/zeolite samples against alkali by adding an NaOH aqueous solution to the FV/zeolite dispersions. The durability of FV/zeolites was compared to that of FV aqueous solutions.

---Figure 5---

Figure 5(a) depicts the time course of the absorption of FVY samples after the pH of the solutions or dispersions was rapidly raised to about 9 by adding NaOH solution. The absorption of the FVY aqueous solution at 436 nm drastically decreased within 1 minute and the color was perfectly lost. Since the growth of the absorption at around

350 nm due to the 2-hydroxychalcone during the fading process was not observed, FVY was not converted to the 2-hydroxychalcone but remained as a hemiacetal form at this pH [7]. This is due to the weak basicity of the solution: the conversion of FVY to 2-hydroxychalcone was observed at higher pH. On the other hand, FVY/HY dispersion also lost its color when the pH was raised, but the retention ratio of the absorption was quite higher than the FVY aqueous solution. FVY/HM dispersion showed no decrease of the absorption in the given alkaline environment. From these results, we can conclude that incorporation of FVY into the zeolite pore enhanced the durability of FVY against the alkaline environment. It is noteworthy that the enhancement of the stability was remarkable when FVY was incorporated in the pore of HM rather than in the supercage of HY. This is in agreement with the result obtained in the experiment confirming the thermal stability, as described above.

The durability of FVM samples against the alkaline environment was shown in Figure 5(b). While the aqueous solution of FVM exhibited significant loss of its absorption within 5 minutes after adding NaOH, the dispersions of FVM/HY and FVM/HM did not show any change in their color and absorption under the same environment as the

solution. As discussed in the previous section, the difference in the stabilization effect between FVM/HY and FVM/HM was not so clear as FVY, because the stability of FVM was enough high.

Figure 5(c) represents the durability of the FVC aqueous solution and the FVC/HY dispersion against the alkaline environment. When the pH was raised with NaOH, the absorption of the aqueous solution decreased and turned pale, although the rate of fading was significantly lower than the FVY or FVM solutions. The difference in the fading rate of respective FV derivatives comes from the difference in the stability of FV molecules themselves. On the other hand, the FVC/HY dispersion showed no color change during the experiment. Therefore, the stability of FVC/HY is superior to that of the FVC aqueous solution.

From these results, we concluded that the incorporation of FV in the zeolite enhanced the stability of FV against alkaline environment, as well as the thermal stability. In other words, the chemical stability of FV is enhanced by the adsorption on the zeolites.

3.3. Factors of the stability enhancement

Now we compare the stability of FVY incorporated in HY and HM here. As shown in Figure 2 and Figure 5(a), the enhancement of both the thermal and chemical stability of FVY/HM was superior to FVY/HY. We can propose two reasons for this result: the difference in the acidity inside the pore, and the difference in the pore size between HY and HM. Indeed the acidity of HM is stronger than HY, but the difference is not so significant [31]. Therefore the difference in the acidity should not be the main reason for the difference in the stability. On the other hand, the pore size of HM is smaller than the supercage of HY, so that the adsorption of FVY molecule may be a tight one in FVY/HM. It is thought that the stabilization effect may be strong when the FVY molecule exists close to the sidewall of zeolites. Since the pore size of HM fits the FVY molecule tightly, as shown in Scheme 2, the FVY molecule in HM is more stabilized than in HY.

---Scheme 2---

---Figure 6---

However, the FV/HM does not always show more enhanced stability than FV/HY.

Figure 6 illustrates the change in the UV-Vis spectra of FVC/HY and FVC/HM samples kept at 423 K in the air. As shown in Figure 6(a), the peak of FVC/HY observed at 590 nm significantly shifted to 502 nm. The peak observed at 502 nm is tentatively assigned to the absorption of protonated FVC, since the acid site inside the supercage of HY works effectively by dehydration [15]. This assignment is further supported by the fact that the red shift of the absorption peak was observed even by heating at 373 K, but by exposing to the air at room temperature, the wavelength and the absorbance of the peak were restored to 590 nm and almost 80 %, respectively. Therefore we judged that the peak shift did not mean the decomposition of FVC. Although the peak at 502 nm was gradually decreased along with the continuous heating, the absorption of FVC still remained even after 210 minutes of heating. On the other hand, when FVC/HM was heated at 423 K for 30 minutes, the absorption of FVC perfectly disappeared. The peak was not restored even after exposing to the air at room temperature. These results indicate that FVC was decomposed by heating FVC/HM at 423 K for 30 minutes. Therefore, the stability of FVC/HY is superior to that of FVC/HM. It should be noted that the amount of adsorbed FVC was very small in FVC/HM compared to that in

FVC/HY. The poor adsorption suggests that FVC is not incorporated in the pore of HM but adsorbed only on the external surface of HM. This is because the pore size of HM is not enough for the incorporation of the relatively large FVC molecule, as discussed above. On the contrary, the FVC molecule is incorporated in the supercage of HY, as is suggested by the strong color (*i.e.*, large amount of adsorption) of FVC/HY. Considering these, it can be concluded that the FVC molecule adsorbed on the external surface was not stabilized sufficiently, so that the color of FVC/HM was more quickly disappeared at 423 K than FVC/HY.

---Figure 7---

Next, we compared the stability of FVC and FVC2 in alkaline environment. Figure 7(a) and (b) illustrates the spectral changes of FVC and FVC2 aqueous solutions after the pH was raised to about 9. Since the degree of the change in the spectrum of FVC2 solution was smaller than in the FVC solution, the fastness of FVC2 against alkali was superior to that of FVC. This result is in agreement with the previous report that the flavylum substituted at 4-position shows resistance against hydrolysis to 2-hydroxychalcone [5, 34]. However, when the dispersions of FVC/HY and FVC2/HY

were kept in the alkaline environment, the stability of FVC/HY was superior to that of FVC2/HY. As shown in Figure 7 (c) and (d), the color of FVC/HY dispersion was maintained for 60 minutes after the pH was raised to 12, whereas the color of FVC2/HY perfectly disappeared within 5 minutes after the pH was raised. Thus, in the form of FV/HY, FVC2 is less stable than FVC, although the fundamental stability of FVC2 is superior to FVC. This result derives from the difference in the molecular size of FVC and FVC2. FVC molecule can be incorporated in the supercage of HY, whereas 4-phenyl substituted FVC2 is too large to be incorporated even in HY.

From these results, it can be concluded that the stabilization effect of FV cannot be obtained unless FV is not incorporated in the pore of zeolites. At the same time, the stabilization effect is larger when the pore size is as small as possible to bring about tight adsorption of the FV molecule.

4. Conclusion

We found that the complexation of the flavylum dye with the zeolites brought about

the enhancement of the thermal and chemical stability of the dye. The stability was enhanced when the dye was incorporated into the pore of the zeolites. A larger stabilization effect was obtained by a better fit with a pore of small size, as long as the dye was incorporated into the pore. Because of its enhanced stability, the flavylum dye incorporated in the zeolite pore can be a candidate for an environmentally friendly coloring material.

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Figure captions

Figure 1 Diffuse-reflectance UV-Vis spectra of (a) FVY, (b) FVM, (c) FVC and (d) FVC2 samples incorporated in zeolites; line a (solid line): FV/HY, line b (dashed line): FV/HM. The spectrum of FV aqueous solution is also shown as line c (dotted line). The left axis of each figure indicates the absorption (Kubelka-Munk function of the reflectance) of the complex between HY and each FV, while the right axis indicates the absorption of the complex between HM and each FV.

Figure 2 UV-Vis Spectral changes of (a) FVY aqueous solution, (b) FVY/HY dispersion and (c) FVY/HM dispersion maintained at 353 K. The spectra were recorded at 0, 1, 5, 10, 15 and 30 min.

Figure 3 UV-Vis Spectral changes of (a) FVM aqueous solution, (b) FVM/HY dispersion and (c) FVM/HM dispersion maintained at 353 K. The spectra were recorded at 0, 1, 5, 10, 15 and 30 min.

Figure 4 UV-Vis Spectral changes of (a) FVC aqueous solution and (b) FVC/HY

dispersion maintained at 353 K. The spectra were recorded at 0, 1, 5, 10, 15, 30 and 60 min.

Figure 5 Time course of the absorption of (a) FVY, (b) FVM and (c) FVC samples after the pH was rapidly raised to ca. 9. Close circles indicate FV/HM dispersions, whereas open circles and squares indicate FV/HY dispersions and FV aqueous solutions, respectively. The ordinate values are shown as the ratio to the initial absorbance at $\sim\lambda_{\max}$ of each sample (FVY/HM: 454 nm; FVY/HY: 446 nm; FVY solution: 436 nm; FVM/HM: 534 nm; FVM/HY: 512 nm; FVM solution: 532 nm; FVC/HY: 564 nm; FVC solution: 594 nm). The pH was raised by adding 1 drop of 0.01 M NaOH_{aq} to 4 ml of FV dispersions or solutions.

Figure 6 Changes in the diffuse-reflectance UV-Vis spectra of (a) FVC/HY and (b) FVC/HM samples maintained at 423 K in the air.

Figure 7 (a, b) UV-Vis spectral changes of (a) FVC and (b) FVC2 aqueous solutions

after the pH was rapidly raised to ca. 9. The pH was raised by adding 1 drop of 0.01 M NaOHaq to 4 ml of FV solutions. (c, d) UV-Vis spectral changes of (c) FVC/HY and (d) FVC2/HY dispersions after the pH was rapidly raised to ca. 12. The pH was raised by mixing 2 ml of 0.07 M NaOHaq to 2 ml of FV/HY dispersions.

Figure 1

Figure 1

"Stabilization of flavylum dye ... "

by Yoshiumi Kohno

Figure 2

Figure 2

"Stabilization of flavylum dye ... "
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Figure 3

Figure 3
"Stabilization of flavylum dye ... "
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Figure 4

Figure 4
"Stabilization of flavylum dye ... "
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Figure 5

Figure 5

"Stabilization of flavylum dye ... "
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Figure 6

Figure 6

"Stabilization of flavylum dye ... "
by Yoshiumi Kohno

Figure 7

Figure 7

"Stabilization of flavylum dye ... "
by Yoshiumi Kohno

Scheme 1

"Stabilization of flavylium dye ... "
by Yoshiumi Kohno

Scheme 2

Scheme 2

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