Reversible Change in Optical Properties of Chromophores in Zeolites by Interaction with Alkali Metal Cations

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Reversible color changes of chromophores in cationic zeolites were investigated in order to elucidate the effect of cations and chromophores on the color change. We prepared a series of alkali metal cation exchanged zeolite Y and mordenite accommodating *N*,*N*-dimethyl-*p*-nitroaniline (DMpNA) molecules. The UV−vis absorption spectra showed an extraordinarily large red shift of the $\pi-\pi^*$ bands of DMpNA in the dehydrated form. The degree of the red shift is larger as the size of the cation decreases. ^{13}C MAS NMR spectra showed sites and dynamic behavior of DMpNA. The color change behavior was also examined for *p*-nitroaniline and *N*-methyl-*p*-nitroaniline in NaY. Large red shifts of the $\pi-\pi^*$ bands were again observed in the dehydrated form, and the degree of the band shift was correlated well with the scale of susceptibility of the chromophores to the solvent polarity. These results indicated that the color change behavior depended on the combination of cationic zeolites and guest chromophores.

Introduction

Porous materials accommodating functional organic molecules have attracted increasing attention in recent years since the porous hosts are advantageous for dispersing and stabilizing chromophores in the micropores.[1−4] The functions of the hybrid compounds are varied by unique host−guest interactions such as hydrogen bonding, ion pairs, hydrophobic interaction, and cation−guest interaction. Therefore, detailed understanding of the host−guest interaction is important to construct functional materials tailor-made at a molecular level.

The interactions between cationic zeolites and chromophores have been studied extensively since cations in zeolite are one of important factors in controlling the properties of the guest molecules in the micropores. In general, cations play a role of compensating the negative charges in the framework and sensitively governing the donor strength of the zeolite framework.[5−9] It has been reported that the donor strength of the framework affects the absorption band of chromophores of strong electron acceptors such as methyl viologen.[10−16] On the other hand, direct interaction between cations and aromatic molecules has been studied considerably by using neutral aromatic molecules such as benzene, anthracene, and naphthalene.[17−31] It has been reported that photophysical properties of molecules depend on the kinds of cations and the presence of adsorbed water. Furthermore, NMR analysis has revealed that dynamics of molecules are affected by cations.[21,29] These results have indicated the presence of a cation−π interaction.[32]

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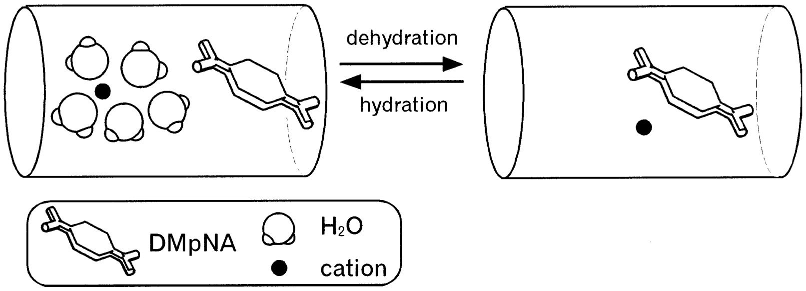
Scheme 1. Mechanism of the Reversible Color Change



Recently, we have found a reversible color change caused by the interaction of a neutral chromophore, *N,N*-dimethyl-*p*-nitroaniline (DMpNA), with alkali metal cations in the micropores of Na^+ type mordenite (NaMOR).[33] The mechanism of the reversible color change is depicted in Scheme 1. In the hydrated form, DMpNA molecules are far from Na^+ because of the presence of H_2O around Na^+. The weak interaction with Na^+ provides the typical $\pi-\pi^*$ band similar to that of crystalline DMpNA. On the other hand, when the amount of water molecules is reduced by heat treatment, DMpNA molecules can be present in the neighborhood of Na^+. The strong interaction with Na^+ provides an extraordinarily large red shift of the absorption band by 85 nm. Dehydration and hydration induce the reversible color change of the compounds.

In the present study, we have investigated the reversible color change of DMpNA molecules in zeolites possessing various kinds of alkali metal cations in order to elucidate the effect of the monovalent cations on the color change. Zeolite Y and mordenite have been selected as cationic zeolites. Zeolite Y consists of an interconnected three-dimensional network of supercages with a diameter of about 1.3 nm. Each supercage is connected tetrahedrally to four other supercages through the 12-membered ring openings with a diameter of 0.74 nm. Mordenite has straight channels which consist of 12-membered rings with a channel size of 0.70×0.65 nm^2. Furthermore, reversible color changes of *p*-nitroaniline (pNA) and *N*-methyl-*p*-nitroaniline (NMpNA) in zeolite Y have been investigated in order to obtain deeper understanding of the color change mechanism.

Experimental Section

Materials. The starting host materials were NaY and NaMOR, which were reference catalysts distributed by The Catalysis Society of Japan, coded JRC-Z-Y5.6 ($Na_{51}Al_{51}Si_{141}O_{384}$) and JRC-Z-M20 ($Na_{4.8}Al_{4.3}Si_{44}O_{96}$), respectively. DMpNA was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). *para*-Nitroaniline and NMpNA were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Zeolites with various kinds of alkali metal cations were prepared by ion exchange. NaY and NaMOR were treated three times with an aqueous solution of alkali chloride and subsequently washed with deionized water until the silver ion test for chloride ions resulted in no response. Exchange ratios of Na^+ to other cations estimated by ^{23}Na solid-state NMR were 82%, 100%, 75%, and 73% for LiY, KY, RbY, and CsY, and 93%, 100%, 100%, and 100% for LiMOR, KMOR, RbMOR, and CsMOR, respectively.

Chromophores were incorporated into zeolites as follows. Zeolites were dehydrated by evacuation at 473 K for 3 h before use. A weighted amount of a chromophore was introduced into the dehydrated zeolites. The introduced amounts of chromophores were four molecules per unit cell of zeolite Y and one molecule for mordenite. The sample tube was sealed in vacuo and heated at 443 K for 24 h. After the heating, the sample was exposed to an ambient atmosphere to prepare a hydrated form. Dehydrated samples were obtained after heating the hydrated ones at 393 K in air.

Thermogravimetric (TG) curves of all samples consisted of two steps of mass losses; the former was mainly due to desorption of water molecules, and the latter was due to the loss of chromophores. The amounts of adsorbed water were estimated based on the TG analysis and the introduced amount of chromophores. The amounts of water in DMpNA/zeolite were 24.5, 23.0, 19.8, 15.4 and 14.0 mass % for LiY, NaY, KY, RbY, and CsY, and 10.0, 8.2, 5.8, 4.4, and 3.7 mass % for LiMOR, NaMOR, KMOR, RbMOR, and CsMOR, respectively. Those of NMpNA/NaY and pNA/NaY were 21.1 and 21.8 mass %, respectively. These results indicated that all the hydrated samples contained considerable amounts of water molecules.

Analysis. TG analysis was performed by using Rigaku Thermo plus TG 8120 under a flow of air. The heating rate was 10 K min^{-1}. UV−vis diffuse reflectance spectra were measured by Shimadzu UV-3100PC equipped with an integral sphere unit, whose spectral resolution was 7.5 nm. The samples were diluted with MgO powders to concentrations of 10 mass %. The sample and MgO powder were mixed in a mortar, and the mixture was put into a sample holder with a sample thickness of 0.5 mm. MgO powder was used as a reference. The reflectance spectra were converted into spectra similar to conventional absorption spectra, using a Kubelka−Munk function.

The measurements of ^{13}C cross polarization (CP)/magic angle spinning (MAS) NMR spectra were performed by Bruker ASX 400. Larmor frequency and the contact time were set at 100.61 MHz and 1 ms, respectively. The samples were packed into a 7-mm rotor, and spinning rates were set at 3.5 kHz to prevent overlap between isotropic peaks and spinning sidebands. Spectra were obtained using 5000−15000 scans with a recycle delay time of 15 s. Chemical shifts were expressed with respect to neat tetramethylsilane. Analysis of spinning sidebands was carried out according to a method based on Herzfeld et al.[34] and Fenzke et al.[35]

^{23}Na MAS NMR spectra were measured by ASX 400 in order to estimate the exchange ratio of Na^+ to other cations by quantitating residual Na^+. Larmor frequency was 105.84 MHz. The samples were packed into a 4-mm rotor, and spinning rates were set at 5 kHz. Spectra were measured by the ordinary single pulse sequence with high power ^1H decoupling. The flip angle of the pulse was set at $\pi/8$ for solution.[36] The spectra of the hydrated NaY sample had two components with different line widths. The sharper component had a nutation frequency similar to NaCl, indicating that this component

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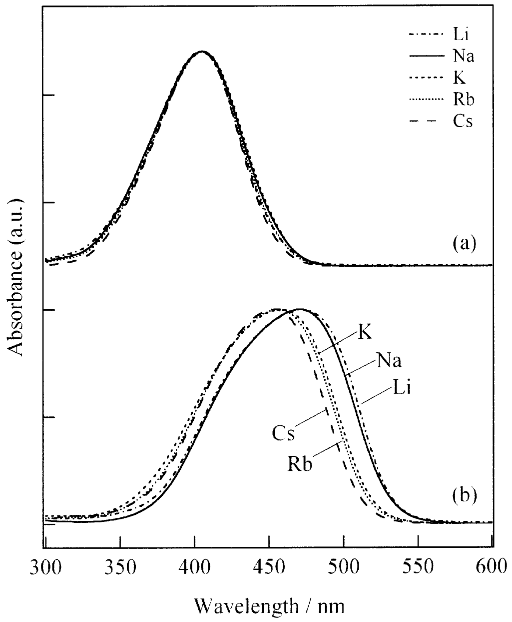

Figure 1. UV−vis absorption spectra of DMpNA in (a) hydrated and (b) dehydrated zeolite Y. The spectra were measured by a diffuse reflectance method and converted with a Kubelka−Munk function. Intensities are normalized.

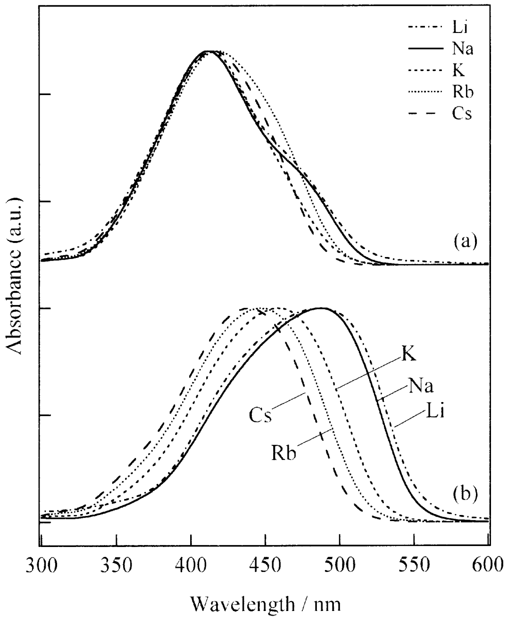

Figure 2. UV−vis absorption spectra of DMpNA in (a) hydrated and (b) dehydrated mordenite. The spectra were measured by a diffuse reflectance method and converted with a Kubelka−Munk function. Intensities are normalized.

contained both central and satellite transitions. On the other hand, the broader component showed the higher nutation frequency, demonstrating that this component contained only the central transition ($m = +^1/_2 \leftrightarrow -^1/_2$). Therefore, the intensity of the sharp signal was corrected by multiplying a factor of $^4/_{10}$.[37,38]

Results and Discussion

Effects of Cations on the Reversible Color Change. Cation dependence of the absorption band positions of DMpNA is investigated by using zeolite Y and mordenite as host materials. Figure 1 shows absorption spectra of DMpNA in zeolite Y with various kinds of cations. The fully hydrated samples show a $\pi-\pi^*$ transition band at 405 nm (white-yellow), which is similar to that of crystalline DMpNA (yellow). The band positions are independent of the kinds of cations in the hydrated form. This is reasonable because DMpNA molecules are far from the cations due to the presence of H_2O around the cations. In marked contrast, the intensity at 405 nm decreases, and new absorption bands appear in the longer wavelength region in the dehydrated form. The color of the sample is changed to orange by dehydration. The band positions depend on the kinds of cations; the degree of the red shift is larger as the size of the alkali metal cation decreases. The absorption bands are asymmetric and have shoulders in the shorter wavelength, suggesting that some DMpNA molecules cannot interact with cations sufficiently due to incomplete dehydration or a limited space of the confined pore.

Profiles of the absorption bands are reproduced well repeatedly by the dehydration−hydration treatments. Furthermore, the color change takes place rapidly. When the dehydrated sample with the orange color is exposed to a humid atmosphere, the color changes to yellow in a few seconds. These reversible behaviors indicate that every sample obeys the mechanism in Scheme 1 without decomposition of DMpNA molecules.

Absorption spectra of DMpNA in mordenite are shown in Figure 2. In the hydrated form, the $\pi-\pi^*$ bands are observed around 415 nm. Compared with zeolite Y in Figure 1, the bandwidths of all samples are broader, and shoulders are observed at about 480 nm for the samples of NaMOR and LiMOR, suggesting that DMpNA molecules are influenced by the cations even in the hydrated form. In the dehydrated form, new absorption bands appear in the longer wavelength region, and reversibility of the color change between the hydrated and dehydrated forms is confirmed in every sample. The cation-dependent progressive shift is similar to that of zeolite Y. However, the magnitude of the shift is more noticeable in mordenite than in zeolite Y.

In order to evaluate the cation dependence of the band position, we use a parameter λ_{half}, which is a wavelength at a half-height and at the longer wavelength side. The parameter λ_{half} is used instead of λ_{max} to extract the relative band position dependent on the cation because the value of λ_{max} may be affected by the shoulder in the shorter wavelength. Figure 3 shows λ_{half} as a function of an ionic radius, r.[39] The λ_{half} value has a good linear relationship with r. Since the ionic radius of the monovalent cation is intimately related with the polarizing ability, the linear relationship implies that the band position is correlated with the polarizing ability of cations. The cations with the higher polarizing ability induce the larger red shift. The correlation is roughly formulated as $\lambda_{\mathrm{half}} = 531-243r$ for zeolite Y and $\lambda_{\mathrm{half}} = 578-551r$ for mordenite. For small cations such as Li^+ and Na^+, the values of λ_{half} are in the order mordenite > zeolite Y, indicating that the polarizing effect of

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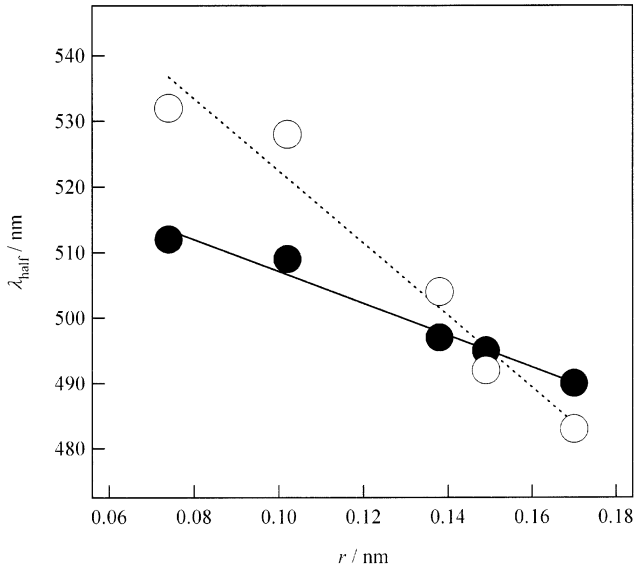

Figure 3. Relationship between a band position, λ_{half}, and an ionic radius, r. The λ_{half} is defined as the wavelength at the half-height of a band in the longer wavelength side. Solid circles and a solid line indicate the results of zeolite Y, and open circles and a dashed line are of mordenite. Lines are drawn with least-squares fits.

cations works better in mordenite. On the other hand, the values of λ_{half} become smaller in mordenite than in zeolite Y for the large cations such as Rb^+ and Cs^+. Consequently, the slope is significantly larger for mordenite than for zeolite Y.

Difference in the cation dependence between zeolite Y and mordenite is interpreted on the basis of the size of the micropores. As for zeolite Y, the $\pi-\pi^*$ bands of DMpNA are influenced simply by the polarizing ability of cations because the supercage of zeolite Y affords a sufficient space for DMpNA molecules even if the large cations of Cs^+ coexist. On the other hand, the $\pi-\pi^*$ bands of DMpNA in the micropore of mordenite are influenced by both the confined pore space and the polarizing ability of cations. The pore size of mordenite is 0.70 × 0.65 nm^2,[40] the ion radii are 0.10 nm for Na^+ and 0.17 nm for Cs^+(VI coordinated),[39] and the size of DMpNA is roughly estimated to be 0.34 nm (thickness of the benzene ring) × 0.67 nm (the width of the benzene ring). The larger band shift in mordenite than in zeolite Y observed in the case of the smaller cations might be caused by negative charges of framework oxygen atoms around DMpNA molecules in the confined micropores as well as an intimate interaction of DMpNA molecules with cations. However, for the larger cations, the micropore may be too small for DMpNA and the cation to take an effective cation–chromophore interaction. The insufficient cation–chromophore interaction may result in the smaller band shift than expected.

^{13}C CP/MAS NMR Spectra. ^{13}C CP/MAS NMR spectra have been measured for DMpNA molecules in zeolite Y and mordenite possessing Na^+ and Cs^+ in order to construct a microscopic view of the guest molecules. Figure 4 shows ^{13}C NMR spectra of DMpNA in NaY and CsY. Spectra of the hydrated form show resolved isotropic signals and their spinning sidebands due to DMpNA molecules. There are no noticeable differences between the hydrated DMpNA/NaY and DMpNA/CsY. The chemical shifts of isotropic signals are similar to those of crystalline DMpNA (spectrum is not shown). However, signals of the aromatic carbons **2** and **3** have broad shoulder peaks, indicating that all DMpNA molecules are not adsorbed on a single site. On the basis of the intensities of the spinning sidebands, it is found that the DMpNA molecules are in a rigid state because profiles of the spinning sidebands are similar to that of DMpNA in a crystalline form.

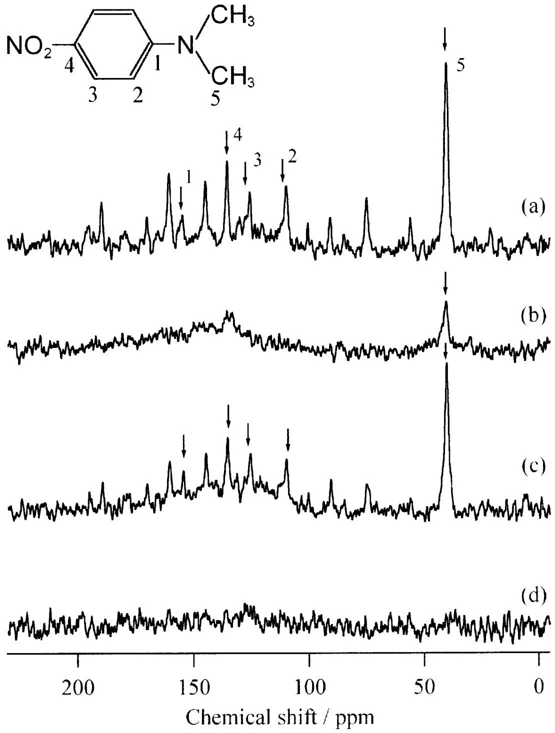

Figure 4. ^{13}C CP/MAS NMR spectra of DMpNA in (a, b) NaY and (c, d) CsY. Spectra a and c are for the hydrated form, and b and d are for the dehydrated form. The arrows on the peaks indicate the positions of the isotropic signals, and the numbers represent the assignments.

On the other hand, the intensities of the signals reduce significantly in the dehydrated forms. The most probable reason is motion of a DMpNA molecule with a correlation time of the order of 50 kHz, which is comparable to the strength of the ^{1}H decoupling field.[41] A motion of the order of 50 kHz makes the ^{1}H decoupling ineffective. The supercage affords a sufficient space for a DMpNA molecule to rotate isotropically.

Figure 5 shows ^{13}C CP/MAS NMR spectra of DMpNA in NaMOR and CsMOR. In the spectra of hydrated DMpNA/NaMOR (Figure 5a), signals of the aromatic carbons **1**, **2**, and **3** do not consist of a single component, indicating that DMpNA molecules are not adsorbed on a single site. On the other hand, the signals of hydrated DMpNA/CsMOR are broader than those of hydrated DMpNA/NaMOR. It is suggested that the large size of Cs^+ influences adsorbed sites of DMpNA molecules.

In the dehydrated form, signals and their spinning sidebands are detected, which is in contrast to the case

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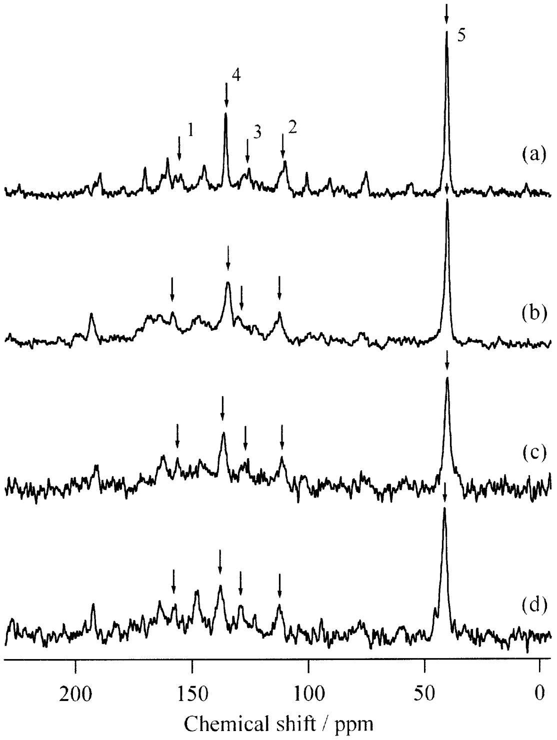

Figure 5. ^{13}C CP/MAS NMR spectra of DMpNA in (a, b) NaMOR and (c, d) CsMOR. Spectra a and c are for the hydrated form and b and d are for the dehydrated form. The arrows on the peaks indicate the positions of the isotropic signals, and the numbers represent the assignments.

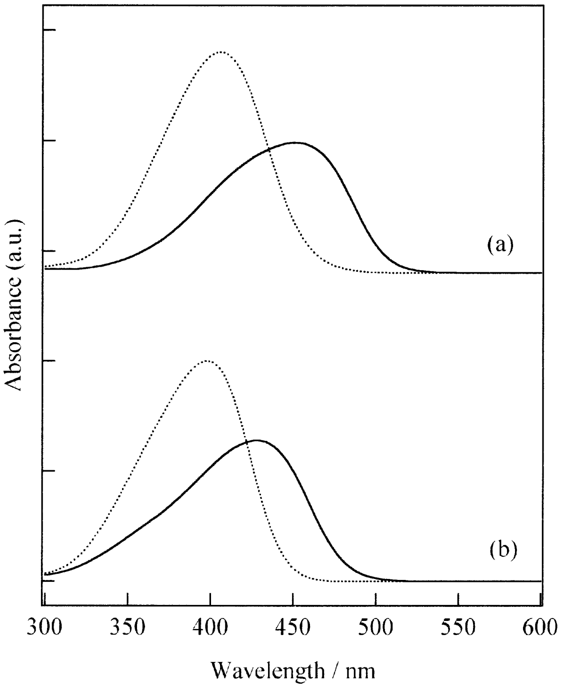

Figure 6. UV–vis absorption spectra of (a) NMpNA and (b) pNA in NaY. Solid and dashed lines are for the dehydrated and hydrated samples, respectively. The spectra were measured by a diffuse reflectance method and converted with a Kubelka–Munk function.

Table 1. Positions of Absorption Bands (λ_{max}/nm) of Chromophores in Various Environments

		NaY			Solvent[a]		
	crystal	hyd[b]	dehyd[b]	Δ_{NaY}[c]	CH[d]	DMSO	Δ_{sol}[c]
DMpNA	402	405	472	67	355.9	405.4	49.5
NMpNA	408	406	450	44	340.5	384.5	44.0
pNA	383	397	427	30	321.5	357.6	36.1

[a] The band positions in unit of nanometers are calculated by using the values in ref 43. [b] Hyd and dehyd correspond to hydrated and dehydrated forms, respectively. [c] Δ_{NaY} and Δ_{sol} are λ_{max}(dehyd) − λ_{max}(hyd) and λ_{max}(DMSO) − λ_{max}(CH), respectively. [d] CH stands for cyclohexane.

of zeolite Y. The motions of DMpNA molecules in mordenite are slower than those in dehydrated zeolite Y. In the spectra of dehydrated DMpNA/NaMOR (Figure 5b), signals due to the aromatic carbons are significantly broadened as compared with the hydrated sample (Figure 5a). It is suggested that absorbed sites of DMpNA molecules are diversified by a strong interaction with Na$^+$. In the case of dehydrated CsMOR, the change of the chemical shift is observed for the methyl group. The value of 41.3 ppm is higher than that of other samples of about 40.0 ppm. It has been reported that the ^{13}C chemical shift of a methyl group is well correlated with the size of the cage of zeolites, and that the signal shifts to a higher frequency as the size decreases.[42] Therefore, the higher frequency shift in dehydrated DMpNA/CsMOR indicates that the methyl group in DMpNA molecules is confined in a narrow space. Furthermore, a peculiar shift of the aromatic carbon **4** is observed at 138 ppm (Figure 5d), which is much higher than those of other samples (135–136 ppm). These results imply that adsorbed sites of DMpNA molecules in CsMOR are influenced strongly by both the confined narrow space and the polarizing ability of Cs$^+$.

Application to Other Chromophores. We have investigated the reversible color changes of NMpNA and pNA in NaY and compared the results with those of DMpNA. We have selected NaY as the cationic zeolite because of exhibiting a clear reversibility between the hydrated and dehydrated forms (Figure 1). Figure 6 shows absorption spectra of NMpNA and pNA in NaY. The spectra show $\pi-\pi^*$ bands of chromophores at around 400 nm in the hydrated form. After dehydration, the band positions shift to longer wavelengths at 450 and 427 nm for NMpNA and pNA, respectively. Profiles of the absorption bands are reproduced well repeatedly by the dehydration–hydration treatments, suggesting that the behaviors of these compounds obey also the mechanism in Scheme 1.

The magnitude of the red shift depends on the chromophores. The values of the band position are summarized in Table 1. The differences in the band positions between the hydrated and dehydrated forms, Δ_{NaY}'s, are 44 and 30 nm for NMpNA and pNA, respectively, and thus, they are in the order DMpNA > NMpNA > pNA.

This order can be explained by the susceptibility of a chromophore to the solvent polarity. A scale of the susceptibility, *s*, has been developed on the basis of solvatochromic studies.[43] The value of *s* reflects the magnitude of the spectral shift between two reference solvents, cyclohexane and dimethyl sulfoxide (DMSO).

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The larger value of $-s$ means that the absorption band of a chromophore is more affected by the solvent polarity. The values of $-s$ are 3.436, 3.364, and 3.138 kK (K = cm^{-1}) for DMpNA, NMpNA, and pNA, respectively.[43] The order of Δ_{NaY} in Table 1 is correlated well with the order of $-s$, suggesting that a chromophore with the larger value of $-s$ indicates the larger shift of the absorption band to the longer wavelength by interaction with cations.

Table 1 also lists absorption band positions of the chromophores in cyclohexane and DMSO and in a crystalline form. The table shows that the values of Δ_{NaY} are comparable to those of Δ_{sol}, indicating that the polarizing ability of Na$^+$ is comparable to that of DMSO. Furthermore, it is found that the absorption bands of the chromophore in dehydrated NaY appear at much longer wavelengths than those in solvents and the crystalline form, implying that the cationic zeolite gives a quite unique environment to the chromophores.

Conclusion

The UV−vis absorption spectra of DMpNA in dehydrated zeolite Y and mordenite show an extraordinarily large red shift of the $\pi-\pi^*$ bands. The magnitude of the red shift is larger as the size of the cation decreases. In the case of small cations, the band positions for mordenite appear at longer wavelengths than those for zeolite Y. ^{13}C MAS NMR spectra showed diversity of adsorption sites and dynamic behavior of DMpNA. The large red shifts of the $\pi-\pi^*$ bands are also observed for pNA and NMpNA molecules in dehydrated NaY. The magnitude of the shift is correlated well with the scale representing a susceptibility of the chromophore to the solvent polarity. These results indicate that the reversible cation−chromophore interactions are applicable to various combinations of guest chromophores and host materials, and that the absorption band positions of chromophores can be controlled by selecting cations and zeolites. This fundamental study would provide a guideline for future developments of functional materials using the interactions between cations and chromophores.

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