Do the Charge-Transfer Complexes of 1,2,4,5-Tetracyanobenzene with Arenes Serve as a Probe for Surveying Chemical Properties Inside the Cavities of Faujasite Zeolites? Time-Resolved and Steady-State Spectroscopic Studies

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Received October 22, 1998. In Final Form: February 22, 1999

Charge-transfer (CT) complexes of 1,2,4,5-tetracyanobenzene (TCNB) with arene donor molecules were assembled within the supercages of faujasite zeolites with a two-step adsorption technique from solutions, and the transient absorption characteristics as well as the absorption and emission properties of these complexes were investigated. Several observations were made relevant to these neutral-type CT complexes which are adsorbed with a weak electronic interaction into zeolites rather than the Coulombic attraction which is predominant for the binding of CT complexes of pyridinium acceptors previously studied: (1) the peak position of the CT bands suffers an appreciable shift depending on the chemical nature of the zeolites, (2) the apparent equilibrium constant for the complex formation depends both on the chemical nature of the zeolites and on the arene donors, (3) an appreciable effect of coadsorbed water, which has stronger interaction with the zeolite frameworks than the guest species, on the complex formation is noted, and (4) the relaxation process of the excited CT complexes is significantly retarded (at least 10 times) in dehydrated zeolites compared with that in polar solutions. These points were discussed on a qualitative basis because of the complexity of the systems. The CT complexes of TCNB with arene donors were found to be sensitive to the chemical properties of zeolites while those of pyridinium acceptors with arenes have been reported to be sensitive to the physical properties such as the shape of cages as well as the size of entry apertures of zeolites.

Introduction

Zeolites have attracted much attention in photochemistry because they host various organic transformations in their cavities and channels, leading often to product distributions considerably different from those in solutions. It was pointed out that zeolites have potential use for controlling the photophysical and photochemical behaviors of organic molecules adsorbed into their cavities. Despite the fascinating features of the zeolites as a novel solid reaction medium, there still remain gaps between our understanding of photophysics within zeolites and that of the outcome of the reactions. Thus, much effort has been devoted in recent years to establishing the correlation of the mechanistic aspects of photophysical and photochemical processes occurring in zeolite-adsorbed systems with the remarkable specificity and selectivity of photochemical reactions.

Singlet- and triplet-state properties of aromatic molecules adsorbed within zeolites have been investigated, and several unique aspects of the photophysics and photochemistry of these aromatic molecules characteristic to zeolites have been revealed. For this purpose, transient absorption spectroscopic studies using a diffuse reflectance detection technique were especially useful in combination with more commonly employed emission studies. The study of charge-transfer complex (CT complexes) within zeolite-adsorbed systems can be challenged

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10.1021/la981496p CCC: $18.00 © 1999 American Chemical Society
Published on Web 04/08/1999
lenging because (1) assembling CT complexes within the zeolite cages needs some elaborate work and (2) femtosecond/picosecond time resolution is required for investigating the excited-state properties of the CT complexes. Nevertheless, it is intriguing to reveal novel properties of the guest CT complexes characteristic to the confined systems and in turn to unravel the chemical properties of the host zeolites by using CT complexes as a physical probe. For example, geometrical restrictions imposed by the cage frameworks and the electronic interaction with the specific adsorption sites are expected to have profound influence on the formation and properties of the CT complexes. Besides, in the adsorbed systems, the relaxation processes from the Franck--Condon state to a relaxed excited state can be severely restricted as can the relaxations to the ground state; that is, the charge-recombination processes are also possibly retarded due to the restricted motions of donor–acceptor pairs and the absence of solvent reorientation.

Earlier works by Yoon and co-workers demonstrated that CT complexes were assembled within zeolite supercages between aromatic donors and pyridinium acceptors (e.g. methyl viologen, MV$^+$–) by introducing various arene molecules (Ar) with low ionization energy into the zeolites in which charge-compensating cations (usually Na$^+$) were partially exchanged with the organic cations. Characteristic CT absorption bands similar to those in solutions (e.g. methyl viologen, MV$^+$–) were found to be well in accord with the Mulliken theory. Nevertheless, it is intriguing to reveal novel properties of the zeolites as an electron donor–acceptor pair in the CT complexes with those in solutions were found to proceed rather slowly in contrast to the solution in systems. This marked retardation of the back electron-transfer rate was ascribed to adsorption effects of the ionic species at the polar aluminosilicate surface and/or the effect of the electrostatic field within the zeolite supercage.

Recently, we have investigated the adsorption and photophysical properties of neutral organic compounds with strong electron-accepting nature represented by 1,2,4,5-tetrayanobenzene (TCNB) within faujasite zeolites of different electron-donating abilities. We found that TCNB molecules interact strongly with framework oxygens adjacent to Al and form the anion radical of TCNB, $\text{TCNB}^-$, on excitation of TCNB inside the cavities of NaY and CsNaY with amion-electron-donating abilities through the photoinduced electron-transfer mechanism from the zeolite framework to the singlet and triplet excited states of TCNB molecules. The result showed for the first time that the reduction potential of the zeolites is estimated to be compared with that of benzene or dioxane as observed by TCNB as a photoinduced electron-transfer probe in zeolites. Furthermore, the results indicating that TCNB molecules are adsorbed in the zeolite supercages with the CT interaction prompted us to investigate the formation and photophysical properties of CT complexes of TCNB with various aromatic donor molecules within zeolites which provide the guest species with steric and electronic perturbations.

We expect that the CT complexes of TCNB with arenes behave differently within zeolite cages from those of pyridinium ion acceptors with arene donors studied previously because the former can be adsorbed in zeolites with the weak electronic interaction while the latter are dominated by the Coulombic interaction. Thus, the TCNB complexes can be more sensitive to the chemical properties such as an electron donor–acceptor property of the host zeolites. On the other hand, the complexes of pyridinium ion acceptors may be insensitive to the chemical nature of zeolites although they were reported to be sensitive to the physical properties of the cages such as pore shapes (channel-type or cage-type) or pore and entry aperture sizes. In addition, the TCNB complexes usually emit and the excited-state properties can be investigated with emission studies, while no emission has been reported for the CT complexes of pyridinium acceptors. Accordingly, we have the advantage of pursuing the properties of the excited states of the CT complexes both with transient absorption and with emission spectroscopic methods.

In the present report, we describe the properties of the CT complexes consisting of TCNB with arene donors revealed with a femtosecond transient absorption technique in addition to the conventional absorption and emission spectroscopies. Also we refer to the chemical properties of the host zeolites probed with the CT complexes employed as a guest species.

### Experimental Section

1,2,4,5-Tetrayanobenzene, TCNB (Tokyo Kasei, >98%), was three times recrystallized from absolute ethanol. Naphthalene, Nap (Tokyo Kasei, zone refined), phenanthrene, Phe (Tokyo Kasei, zone refined), and anthracene, Ant (Merck, scintillation grade), were used as received. Pyrene, Py (Wako Chemicals), was purified by silica gel chromatography. 9-Methylnaphthalene (Tokyo Kasei, >98%) and other arenes were recrystallized. n-Hexane (Wako chemicals, HPLC grade) was distilled and stored over molecular sieves (Dichromehane (Wako chemicals, reagent grade) was refluxed over calcium hydride and distilled prior to use. Zeolite NaX (unit cell contents Na$^+$Al$_{48}$Si$_{48}$O$_{192}$H$_2$O) and NaY (unit cell contents Na$^+$Al$_{72}$Si$_{72}$O$_{288}$) were obtained from Tosoh (Japan). The pore volume of NaX (3.14 $\times$ 10$^{-4}$ dm$^3$-g$^{-1}$) and NaY (3.78 $\times$ 10$^{-4}$ dm$^3$-g$^{-1}$) was determined by the M–P method. Cation-exchanged zeolites were prepared via ion exchange of NaX and NaY according to the procedure described in the literature. The exchange ratio was determined by the atomic absorption analysis to be > 98% for LiX, LiY, KX, and KY, 63% for CsNaY, and 68% for CsNaX. The zeolite powder was calcined in air at 500 °C for approximately 8 h just before sample preparation.

CT complexes were assembled in zeolite cavities by the following stepwise procedure in a nitrogen-filled glovebox. First, a weighed amount of the powdered zeolite was mixed with a dichloromethane solution of the acceptor molecule, TCNB, in a stoppered vial at room temperature for 5–10 min; the sample was filtered and the solid washed twice with dichloromethane and vacuum-dried. The amounts of unadsorbed TCNB in the supernatant solution were quantified by UV–vis spectrophotometry. Then, the zeolite doped with TCNB was treated with n-hexane solutions of aromatic donor molecules. Distinctive colors developed immediately upon addition of the aromatic donors in most cases. The mixture was stirred at room temperature for a

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few minutes, filtered, washed twice with n-hexane, and vacuum-dried. The unadsorbed aromatic donor molecules in the supernatant solutions were assayed spectrophotometrically. Dissolution of TCNB adsorbed in the zeolites into n-hexane was found to be negligible. Note, however, that reversing the order of adsorption of TCNB and the aromatic species caused the dissolution of considerable amounts of aromatics into dichloromethane. The colored zeolite powder was then transferred into a Suprasil cell with a 2 mm optical path length which was evacuated at 0.1 Pa for 6 h. Complete removal of n-hexane was found to be difficult with this evacuation treatment; heating treatment under vacuum was necessary. However, the heating causes problems of possible evaporation of guest species and thermal reactions of guest molecules with the zeolites.

The ground-state reflectance spectra were measured on a Shimazu UV-3101PC double-monochromator spectrophotometer equipped with an integrating sphere coated with BaSO₄. The reference was BaSO₄ (Kodak white reflectance standard). Absorption spectra of ground-state species were obtained by using the Kubelka–Munk function. Fluorescence spectra were recorded with a Hitachi F-3010 spectrophotometer. The spectral response of the fluorometer was corrected with fluorescence standards.17 Femtosecond (fs) time-resolved transient absorption measurements were carried out by excitation with the second harmonics (390 nm, 170 fs pulse width, ~1.0 mJ cm⁻² per pulse, 10 Hz) of a regeneratively amplified output of a Ti:sapphire laser (Coherent Mira 900 & Continuum TR 70).20 White continuum light was generated by focusing the fs fundamental (780 nm) into a quartz cell containing H₂O and used as a monitor light with various optical delays. The absorption signals were averaged 150 times.

We adopted an approach by Wilkinson et al.15 in which the percentage absorption (absorption (%)) was employed to describe the transient optical absorption signal following laser excitation of guest-doped zeolites. The absorption (%) is defined as absorption (%) = R(t)/R₀ (100%) where Rₜ and R₀ denote the intensities of diffusely reflected light with and without excitation, respectively. The transient absorption (%) spectra were corrected for luminescence by subtracting a laser-only shot signal from the initial signal trace. The previous theoretical study11 assured a linear relationship between the value of absorption (%) and the amount of transient species present up to 10% in the absorption (%) values. However, the linear relationship has been experimentally confirmed at least up to 25%.11 All the measurements were carried out at ambient temperature (19–21 °C).

Results and Discussion

1. CT Complexes Are a Sensitive Probe for the Acid–Base Properties of Dehydrated Cation-Exchanged Zeolites As Observed with Steady-State Spectroscopic Studies. Figure 1 shows the absorption spectra, represented by the Kubelka–Munk units, of TCNB-doped NaY zeolite powders which were exposed to a solution of phenanthrene (Phe), anthracene (Ant), and 9-methylanthracene followed by drying in vacuo. The spectra show the appearance of a new band which is absent in the absorption spectra of zeolites doped with TCNB alone or merely arenes; the new bands are ascribed to the charge-transfer (CT) bands of TCNB and arenes in analogy with the bands observed for solutions19 of TCNB and these arenes. The great majority of the CT complexes are assumed to be formed between the molecules adsorbed inside the cavities of NaY; the reason for this assumption is given in the following.

First, the loading level of guest aromatic molecules attainable is critically dependent upon the host pore size—

\[ \text{hv}_{\text{CT}} (eV) = 1.00 \times \text{I}_D (eV) - 4.87 \]

with a coefficient of determination \( R^2 = 0.945 \). It is known that \( \text{hv}_{\text{CT}} \) is approximated by

\[ \text{hv}_{\text{CT}} = \text{I}_D - \frac{E_A}{4 \pi \varepsilon_0} \frac{e^2}{R_{DA}} \]

in which \( \text{I}_D \) is the ionization energy of the donor, \( E_A \) is the electron affinity of the acceptor, and \( 4 \pi \varepsilon_0 R_{DA} \) is the Coulombic attraction energy between the donor and the acceptor at a nuclear separation of Rda. If we employ the value of \( E_A = 1.6 \times 10^{-20} \) known for TCNB in the gas phase,
the Coulombic term in NaY is estimated as 3.27 eV, which is compared with the value reported in CH2Cl2 solution (3.30–3.45 eV). The peak positions of the CT bands in NaY are located at similar wavelengths to those reported previously in CH2Cl2 solution while they are located at slightly shorter wavelengths (higher energies) than those in the crystalline state. The peak positions of [MV2+, Ar] complexes with various donors in MV2+-exchanged Y-type zeolite have been reported to appear at similar wavelengths to those in acetonitrile solution. Note that MV2+ has a similar reduction potential in value to that of TCNB in solution. Thus, spectroscopically speaking, the CT complexes of arene donors assembled inside the zeolite supercages have a resemblance to those in solutions regardless of the type of the acceptor, cationic or neutral.

In contrast to the nonluminescent nature of the CT complexes of MV2+ and other pyridinium acceptors, CT complexes of TCNB usually give CT fluorescence, and we actually observed emission on excitation of the CT bands in the zeolite-adsorbed systems. Figure 2 represents the corrected fluorescence spectra for a number of CT complexes in NaY recorded at room temperature along with the corresponding absorption spectra. The energy levels of the CT state estimated from the peak energy of the emission were found to be similar to those in solution systems.

Our observation firmly established that the CT complexes consisting of the neutral donor-acceptor pairs formed inside the cavities of faujasite zeolites follow the behavior generally observed in solutions. While the general pictures of these CT complexes are basically similar to those of MV2+ and pyridinium acceptors, observations were made which are characteristic of the complexes of TCNB in zeolites and thus significantly different from those for cationic acceptors: (1) CT peak energies afford a noticeable shift depending on the chemical properties of the zeolites, and (2) the equilibrium constant of CT complex formation is dependent on the nature of the host zeolites and on the donor arene molecules. These observations are discussed in the following.

The peak energy of a particular CT complex is found to depend on the charge-compensating cations in Y-type zeolites and also on the Si/Al ratio of the zeolites. Such an observation is typically shown in Figure 3A for a TCNB-Ant pair in various dehydrated zeolites. The excitation energy (hνCT) of CT complexes, which is envisaged as the energy required for transferring one electron from the HOMO (highest occupied molecular orbital) of

Figure 2. Absorption (---) and corrected emission (---) spectra of CT complexes: (A) TCNB-naphthalene; (B) TCNB-phenanthrene; (C) TCNB-anthracene adsorbed in NaY zeolite.
the donor to the LUMO (lowest unoccupied molecular orbital) of the acceptor, can be approximated by eq 1. For the present TCNB-Ant pair $I_D = 7.41 \text{ eV}^{20}$ and $E_A = 1.60 \text{ eV}^{20}$ were reported in the gas phase. These values can be subject to change in the environment of zeolite cavities in which guest molecules are supposed to experience the electrostatic field and the interaction with various adsorption sites.

Let us consider first the origin of the shift of $h_{\text{CT}}$ (the shift of the peak wavelength of CT bands) observed in the faujasite zeolites of differing composition. Our explanation is based on the assumption that the local interaction of donor and/or acceptor molecules which constitute CT complexes with adsorption sites within zeolites is more decisive rather than the effect of average electric field or polarity inside the supercage networks.

The absorption peak wavelength of the CT bands is plotted against the mean charge on oxygens in the zeolite framework and shown in Figure 3B. Note that the mean oxygen charge, estimated according to the traditional procedure, is a measure of the basic strength or the electron-donating ability of the zeolites, since the electron-donating sites in zeolites are considered to be located at the framework oxygens adjacent to Al. It is known that the electron-donating ability (the basic strength) of the zeolites increases with decreasing Si/Al ratio and for zeolites with larger alkali metal cations. As illustrated in Figure 3B, the basic nature of the zeolites has a fairly good correlation with the peak position of the CT bands: they experience a larger hypsochromic shift in the zeolites with stronger basic sites despite the fact that spectral bandwidth is scarcely affected by the host zeolite. The basic sites are expected to interact with TCNB, which is a strong electron acceptor. Thus, according to the simple molecular orbital picture, the basicity of the zeolites affects the peak position of the CT band by destabilizing the energy level of the LUMO in the acceptor molecule, TCNB. The larger destabilization energy of the LUMO in TCNB estimated in the zeolites with stronger basic sites due to the stronger interaction explains the observed hypsochromic shift in the zeolites with stronger electron donor sites.

Zeolites have amphoteric nature, and their acid strength can also be altered by the change in the composition. Generally speaking, the composition of zeolites influences the acid strength in the reverse order of the basic strength; that is, the acid strength of zeolites (the electron-accepting ability) increases with increasing Si/Al ratio and for zeolites with smaller alkali metal cations. The electronegativity of the zeolites calculated according to the Sanderson's equalization principle has been used as a good measure for the acid strength in various dehydrated zeolites. Here the electronegativity estimated from the composition of the zeolite is considered to represent the overall electron-accepting ability of the zeolites although the acid sites are known to be located in specific sites, such as the cationic sites (Lewis acid sites). As shown in Figure 3C, a fairly good correlation can also be found for the CT peak wavelength versus the electronegativity of the zeolites. It turns out, however, that the correlation between the acidity of the zeolite and the CT peak position is the reverse. The acidity of the zeolite should affect the HOMO level of anthracene, which acts as an electron donor: the larger the electron-accepting ability of the zeolite, the larger the stabilization energy of the HOMO level of anthracene due to stronger interaction between anthracene and the acid sites, giving rise to a hypsochromic shift of the CT peak wavelength in highly acidic zeolites. This deduction contradicts the present observation. Accordingly, the acidic nature of the zeolite is suggested to play only a minor role in the CT peak position dependent on the composition of the zeolites.

In zeolites, the polarity which represents the electrostatic field originating from the minus charge on Al atoms embedded in the framework and from charge-compensating cations distributed in the cage network is generally high and spans a narrow range with respect to chemical composition. The polarity in NaX and NaY zeolites was suggested to be similar to that of an aqueous methanol solution. In general, the polarity is considered to be higher in zeolites with a smaller size of charge-compensating cations because of their larger charge density giving rise to the stronger electrostatic field within the cages. It has been known that the absorption maxima of CT complexes between neutral species usually show no dependence on solvent polarity. The CT absorptions are expected to be similar in zeolites and in solutions unless some specific orbital interactions occur, as is apparently observed here.

According to the previous work by Yoon and co-workers in zeolite Y, the CT complexes of cyanopyridinium acceptors with arene donors are expected to undergo interaction with the acid sites of the zeolite through the coordination of nonbonding electrons of N-atoms to the electron-accepting center of the zeolite, resulting in an increased electron-accepting nature of the cyanopyridinium acceptors. This effect gave an explanation for the red-shifted CT bands in NaY relative to those in other channel-type zeolites in which the interaction of cyanopyridinium acceptors with the acid sites cannot be expected due to narrow pore diameters. An explanation similar to that of Yoon and co-workers is not applicable in the present case because we must expect a blue-shift in a more acidic zeolite, which contradicts the experimental results. We assume that in our systems the $\pi$-orbitals of TCNB interact with the basic sites of the zeolites.

Consequently, the major cause of the large peak shift of the CT bands in the TCNB-Ant system is ascribed to the magnitude of the interaction between TCNB and the zeolites. We expect that the great majority of the TCNB-Ant complexes are formed within the zeolite cavities between TCNB, which bears a strong interaction with the basic sites in the zeolite walls, and anthracene, which has only a weak interaction with the zeolites. The present observation of CT peak energy depending on the chemical nature of the zeolite is unique to the CT complexes with TCNB as an acceptor. The CT complexes of MV and pyridinium acceptors can be insensitive to the change in the chemical properties or the basicity of the zeolites resulting from the change in composition because the cationic acceptors are expected to be fixed with the Coulombic interaction in a similar environment regardless of the composition of the faujasite.

Now we will go into the discussion of the second subject, the equilibrium constant of CT complex formation. The

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Table 1. Apparent Equilibrium Constant ($K_{eq}$) of Complex Formation with TCNB for Anthracene (Ant), Phenanthrene (Phe), and Naphthalene (Nap) in Dehydrated NaX and/or NaY Zeolite Determined with a Modified Scott Plot (E: Relative Absorption Coefficient of CT Complex)

<table>
<thead>
<tr>
<th>donor</th>
<th>Ant</th>
<th>Ant</th>
<th>Phe</th>
<th>Nap</th>
</tr>
</thead>
<tbody>
<tr>
<td>zeolite</td>
<td>NaX</td>
<td>NaY</td>
<td>NaY</td>
<td>NaY</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>17</td>
<td>0.79</td>
<td>3.8</td>
<td>0.18</td>
</tr>
<tr>
<td>$E$</td>
<td>0.031</td>
<td>0.032</td>
<td>0.027</td>
<td>0.026</td>
</tr>
</tbody>
</table>

bound to the strong acid sites such as the cationic sites than in NaX; this renders the chance of CT complex formation less favorable. Much larger CT band intensity was recorded also for TCNB–Ant and TCNB–Phe complexes in NaX than in NaY at similar concentrations ([number of guests]/[total pore volume]) of both the donor and the acceptor. Thus, the idea that the CT complex formation is more favored in NaX than in NaY seems widely applicable.

Previously, Alvaro and co-workers\(^{29}\) reported the observation of the CT complexes between MV\(^{2+}\) and anthracene or 1,4-dimethoxybenzene within the cavities of a series of zeolite Y containing different alkali metal ions. They observed that for the same uptake of donor the intensity of the complex absorption is always higher for zeolites with larger alkali metal ions. They interpreted that a reduction in the free volume ($V_f$) available inside the zeolite supercage in the presence of large metal ions favors complex formation. However, our observation is different because the value of $K_{eq}$ in NaX is profoundly larger even if the effect of the free volume ($V_f$/NaX)/$V_f$/NaY = 0.829) is taken into consideration. This result suggests that the chemical properties of the zeolites are decisively associated with the equilibrium constant of CT complex formation.

Table 1 also shows that the value of $K_{eq}$ in NaY is strongly dependent on the donor molecule: $K_{eq}$(TCNB–Phe) > $K_{eq}$(TCNB–Ant) > $K_{eq}$(TCNB–Nap). We assume a picture in which donor molecules distribute themselves into the zeolite cavities where TCNB molecules are adsorbed. The adsorbed molecules, donor molecules, and TCNB molecules alike are either in the bound state or in the mobile state. Thus, for the donor molecules in the bound state the question is whether they should take the acid sites in zeolites or TCNB as a partner of complexation. A simple explanation is not possible for the trend observed for the values of $K_{eq}$ dependent on the guest donor molecule. It does not follow the order expected from the $I_2$ values of the donors. We will come back to the problem of the association constant later when we discuss the effect of coadsorbed water on CT complex formation in zeolites.

Previously, Yoon and co-workers reported that the formation of the CT complexes of pyridinium acceptors with arene donors is shape- and size-selective. They observed the trend that the intensities of the CT band for any given acceptor–donor pair are always increasing for zeolites with the larger openings of the apertures. Thus, in their systems, the physical nature of the zeolites appears to be very important for the complexation. They also concluded that the apparent complexation constants of MV\(^{2+}\) with 1,4-dimethoxybenzene, 1-methynaphthalene, and 9-methylanthracene are invariant with the type of zeolite employed (mordenite, mazzite, zeolite-L, and zeolite-Y). This result suggests that the CT complexes of MV\(^{2+}\) are insensitive to the chemical nature of the zeolites and markedly different from those of TCNB. Furthermore,

they observed the red-shift of the CT bands of [MV\textsuperscript{2+}, hexamethylbenzene] and [(diquart) DQ\textsuperscript{2+}, hexamethylbenzene] in going from zeolite-Y to mazzite and to zeolite Li in the decreasing order of pore size. Besides, the spectral envelope of the CT band of [MV\textsuperscript{2+}, 2,6-dimethoxynaphthalene] was observed to be significantly broader in the zeolites with small pore size. These results were explained by the effect of constraint, which depends on the shape and size of cages and channels, imposed by the frameworks of the zeolites. In essence, the results of the CT complexes of pyridinium acceptors studied by Yoon and co-workers suggest that the physical nature of host zeolites is crucial to the complex formation.

2. Coadsorbed Water Mostly Enhances the Formation of CT Complexes and Causes Crystallization When Introduced in Large Quantities. The CT absorption bands are significantly affected on deliberate introduction of water molecules into NaY. The dramatic change in CT absorption bands in the presence of coadsorbed water may be worth mentioning as one of the features characteristic to the zeolite-adsorbed systems. Figure 5 shows the changes in the absorption spectrum of the TCNB–naphthalene (Nap)–NaY system in going from a dehydrated sample after preparation (A) to that in the presence of 1.0 \times 10\textsuperscript{-2} mol\cdot g\textsuperscript{-1} of water (B) and to that in the presence of 2.0 \times 10\textsuperscript{-2} mol\cdot g\textsuperscript{-1} of water (C). Finally, the hydrated sample (C) was evacuated for 7 h at 0.1 Pa at room temperature, and the spectrum after this treatment is shown in Figure 5D. In the first place, the absorption intensity increases, leaving only a minor change in the peak position on initial introduction of water (A \rightarrow B). Then, an appreciable red-shift of the peak position occurred (B \rightarrow C) upon further introduction of water molecules. At this stage, the CT absorption peak initially located at 382 nm is displaced to \( \lambda_{\text{max}} = 408 \) nm, accompanied by a substantial increase in the absorption intensity. Furthermore, a similar CT absorption band to the original one is recovered after evacuation (compare the spectra in B and D). In this case, the complete recovery to the one similar to the spectrum in A was not observed due to incomplete dehydration by the evacuation treatment at room temperature. However, one should note that the effect of water is reversible, since repeated hydration and dehydration treatments always reproduced similar spectral changes. A quite similar observation was made for naphthalene derivatives: 2,6-dimethylnaphthalene, 2,6-dimethoxynaphthalene, and 2,7-dimethoxynaphthalene, with regard to the reversible effect of water on the change in the CT absorption spectra.

We consider the account of the changes in the CT absorption bands in the presence of coadsorbed water as in the following. The initial increase in the absorption band with minor changes in the peak position and the spectral shape is due to the enhanced formation of the CT complexes. Since water molecules have high affinity both for the cationic sites and for the framework oxygens, they tend to line the inner surface of the zeolites, thus weakening the direct interaction of the aromatic guest molecules with the cationic sites and also with the zeolite walls. As a result, the aromatic guest molecules are expected to gain larger mobility than those adsorbed in the dehydrated zeolites. This assumption is supported by our previous observation\textsuperscript{29} with fluorescence spectroscopy that the interaction of anthracene with the cationic sites of NaX and NaY was weakened on introduction of water and other polar molecules which have a stronger interaction with the zeolite frameworks than anthracene itself.

Under the circumstances, it is reasonable to consider that enhanced formation of the CT complexes generally takes place due to an inherent attractive interaction in the ground state, if other factors such as steric restrictions imposed by zeolite frameworks are neglected. On the contrary, dimers of aromatic species, such as pyrene or anthracene, formed in the adsorbed state within dry zeolites have been reported\textsuperscript{3,30} to dissociate on hydration presumably due to the nonattractive nature in the ground state. An alternative explanation on the basis of the reduction in the free volume in zeolites proposed previously\textsuperscript{29} seems to apply for the present enhancement of the CT bands. However, we emphasize the importance of attractive interaction between the guest species and the zeolites; since in dry zeolites, a small free volume is not directly responsible for the enhancement of the CT bands as seen in the previous section.

The effect of coadsorbed water was investigated for the CT complexes of TCNB with other arene molecules presently. In most cases, enhanced absorption intensities were observed as in the case of Nap and the derivatives. However, Phe is exceptional. Figure 6 compares the contrasting effect on the intensity of CT band observed for TCNB–Ant and TCNB–Phe systems. While the CT absorption intensity increased appreciably on introducing 1.0 \times 10\textsuperscript{-4} mol\cdot g\textsuperscript{-1} of water for TCNB–Ant in NaY, the intensity of the CT absorption band decreased remarkably for TCNB–Phe in NaY. We should note that neither the peak position nor the spectral shape of the CT band was affected by the coadsorbed water in both of the complexes. As already mentioned, coadsorbed water is considered to reduce the interaction of guest species with the zeolites, leading to the enhancement of the mobility of guest species. This effect usually brought about increased equilibrium constants in most of the cases studied presently. We cannot pinpoint the exact mechanism of the unusual reduction in the equilibrium constant for TCNB–Phe.

The second large red-shift of the CT absorption bands in Figure 5 (B \rightarrow C) observed on addition of a large amount

of water is due to the formation of crystals, that is, CT crystals of TCNB–Nap. The red-shifted absorption band is quite reminiscent of that of TCNB–Nap crystals reported previously.19b,21b Our previous study30 observed the formation of crystals of Ant and biphenyl adsorbed in NaY on introduction of water to an amount as large as 60–90% of the maximum amount attainable for adsorption. Phe has also been found to come out from the zeolite as a crystal previously on hydration.31 The crystal formation of Ant dependent on the hydration level was found to be reversible; in other words, the Ant crystals once formed in the hydrated zeolite disintegrate to molecules to be adsorbed on the surface of the zeolites on dehydration by pumping out of water. The behavior of the CT complexes of Nap and the derivatives on hydration with a large amount of water and dehydration with evacuation exactly coincides with that of Ant. For the CT crystals of TCNB with arenes in NaY we obtained the Mulliken relationship $h\nu_{CT} (eV) = 0.91 \pm 0.430 (R^2 = 0.942)$. Remember that Hubig and co-workers19b obtained $h\nu_{CT} (eV) = 0.87 \pm 0.402$ for the authentic CT crystals consisting of TCNB with arenes similar to those employed presently; the agreement of the two sets of data is acceptable within experimental error. Thus, we believe that the formation of the CT crystals is unequivocal evidence in the present cases.

To sum up, our present investigation revealed that the intentional introduction of water generally enhances the intensity of the CT bands of TCNB with arenes in the first place except for the TCNB–Phe pair and produces crystals when introduced in large quantities. Previously, Yoon and co-workers studied29 the effect of coadsorbed water on the CT complexes of pyridinium acceptors in various zeolites. In most cases, they observed a bathochromic shift of the CT bands in channel-type zeolites, zeolite L, mordenite, and mazzite, but not in large-pore zeolite Y. Also, they observed a hypsochromic shift for the CT bands of cyano-substituted pyridinium acceptors in zeolite Y. The former (the bathochromic shift) was explained by an increase in intrazeolitic pressure, leading to a decreased interpanar separation of the CT complexes, and the latter (the hypsochromic shift) by the prevention of interaction of nonbonding electrons of N atoms with the electron-accepting center in the zeolite frameworks by water molecules. We only employed faujasite zeolites presently, and we did not see any indication of the pressure effect. As was described in the previous section, we observed the spectral shift, the trend of which is opposite to that observed by Yoon and co-workers.

We finally give only a few words about the effect of water on the CT emission. In the hydrated samples, we note that the emission on excitation with the CT bands is too weak to be seen on the fluorometer probably because of the enhanced decay rates of the CT excited states, as will be described in the following section. Therefore, we put aside the pursuit of the CT emission spectra in hydrated zeolites.

3. The Decay Rates of the Transient Absorption Are Notably Slow in Dehydrated NaY but Increase Approximately an Order of Magnitude in Hydrated NaY. Figure 7 compares the transient absorption spectra in the absence and in the presence of $1.0 \times 10^{-2}$ mol-g $^{-1}$ of water upon photoexcitation of the TCNB–Nap CT complex assembled within the NaY zeolite, and Figure 8, those of the TCNB–Phe complex. The transient absorption signals evolved within the temporal response of the spectroscopic system (a few picoseconds) and decayed without being accompanied by any appreciable spectral change. These transient spectra bear resemblance to those consisting of the composite absorptions which are more or less similar to the superposition of the spectra of the cation radicals of the donors and the anion radicals of TCNB (TCNB$^-$). For example, Nap$^+$ is known32,33 to absorb at 680 nm with a vibrational structure, and TCNB$^-$ at 470 nm.22,32,34 Likewise, the spectra in Figure 8 are similar to those consisting of TCNB$^-$ and Phe$^+$.32 It is thus reasonable to consider that the decay of the transient absorption is due to the charge recombination (CR) process of the excited CT state to the ground state, since the time


Figure 8. Transient absorption spectra of the TCNB–phenanthrene CT complex at various delays. Delays in dehydrated NaY: 10 ps, 500 ps, 1 ns, 2 ns, 4 ns, and 6 ns from the top. Delays in $1.0 \times 10^{-2}$ mol·g$^{-1}$ hydrated NaY: 10 ps, 50 ps, 250 ps, and 800 ps from the top.

Figure 9. Time-dependent decays of transient absorption in dehydrated NaY. (A) TCNB–napththalene: (○) at 457 nm (TCNB$^-$); (●) at 682 nm (Nap$^+$). (B) TCNB–phenanthrene: (○) at 460 nm (TCNB$^-$). (C) TCNB–pyrene: (○) at 452 nm (TCNB$^-$ and Py$^+$). (D) TCNB–anthracene: (●) at 740 nm (Ant$^+$).

Figure 10. Time-dependent decays of transient absorption in $1.0 \times 10^{-2}$ mol·g$^{-1}$ hydrated NaY. (A) TCNB–napththalene: (○) at 460 nm (TCNB$^-$); (●) at 685 nm (Nap$^+$). (B) TCNB–phenanthrene: (○) at 460 nm (TCNB$^-$). (C) TCNB–anthracene: (●) at 735 nm (Ant$^+$).

course of the decay is similar at the peak wavelengths of both species, Nap$^+$ and TCNB$^-$, for instance. Previously, the observation has been made of the formation of the excited CT states and the subsequent CR processes on excitation of the CT complexes of TCNB with arenes in solutions and in the crystalline state as well as a heterogeneous medium such as a silica gel-adsorbed system.

A careful scrutiny of the transient absorption spectra and their decay kinetics in the dehydrated zeolite system revealed that they are considerably different from the observation in solution and other systems. In addition, the controlled amount of water affects greatly both the spectral shape and the decay kinetics of the transient absorption. Figure 9 illustrates the decay curves of the absorption intensities at peak wavelengths in dehydrated NaY, and Figure 10, those in $1.0 \times 10^{-2}$ mol·g$^{-1}$ hydrated NaY, on excitation with the fs laser pulse. Figure 9 includes the CR decays in TCNB–Py and TCNB–Ant systems, and Figure 10, the decay in the TCNB–Ant system. Two points should be noted regarding the transient spectra and the CR decays characteristic of the CT complexes in NaY zeolite: (1) in dehydrated NaY, the transient spectra are appreciably broader (the spectra of Nap$^+$ in Figure 7A and those of TCNB$^-$ in Figure BA) than those observed in solutions and the decay rates of the CR process are remarkably slow compared with those in other media; (2) in hydrated NaY, the transient spectra are as sharp as those observed in solution at sufficient delays and the CR decay rates are as fast as those in solution.

The broad spectral bandwidth in dehydrated zeolites suggests the presence of significant electronic interactions between the donor and the acceptor in the excited CT state. Accordingly, the excited state carries only a partial charge-transfer nature presumably due to the fixed geometry of the complexes under the influence of the host zeolite. It has been shown that profoundly broad spectra are observed for the TCNB–toluene CT complex in toluene at 170 K and in the PMMA matrix, where configurational rearrangement of the CT complexes from the Frac–Condon excited state to a stable excited state is severely prohibited. In solution at room temperature, a transient spectral change was observed for the TCNB–toluene CT complex within a few picoseconds from a broad to a narrow shape, suggesting a feasible geometrical relaxation within the excited CT state. Also, Asahi and co-workers observed a transient spectrum which is similar to that of the anion radical of pyromellitic dianhydride (PMDA), PMDA$^-$, but markedly broad and red-shifted in the crystalline system consisting of PMDA with benzene derivatives; consideration was given to ascribe these spectra to the insufficient CT nature in the excited state. They suggested that a structural change to a stable configuration in the excited CT state is severely restricted in the crystal; this renders the CT nature in the excited state to a lesser extent. We expect that in the adsorbed state in the dry zeolite CT complexes experience a limited degree of freedom with respect to the structural change, considering their broad transient spectra. In hydrated systems, on the other hand, the observed sharp spectra

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adsorbed systems. For instance, Miyasaka and co-workers have shown that the decay rate obtained except for the TCNB system is also in accord with the decay kinetics of the transient absorption, as will be described.

The experimental decay curves are analyzed with single- and double-exponential functions. We rule out the possibility of the involvement of the second-order annihilation process because the CT complexes are expected to be compartmentalized within the cages at such low concentrations relative to those of the cages (for NaY, the supercage ≈ 6.3 × 10^4 mol·g⁻¹), and we employed the laser intensities as low as to minimize the annihilation. The solid curves in Figures 9 and 10 show the fitted curves; the parameters used for the fitting are given in Table 2. We should note that the slow decay component observed for TCNB-Py and TCNB-Ant systems originates from the direct excitation of the arenes Py and Ant because of the limitation of the excitation wavelength at 390 nm. Nevertheless, we still observe a non-single-exponential decay for TCNB-Nap while we note a nearly single-exponential decay for TCNB-Phe in the dry NaY. The difference may stem from the heterogeneity of the adsorption interaction with the host zeolite, depending on the donor of the CT complex. On the other hand, in the hydrated NaY, almost single-exponential decays with at least one order of magnitude larger decay constants are obtained except for the TCNB-Ant system, in which the excitation still involves anthracene itself.

For the CR decay of excited CT complexes, the following relationship has been shown to apply for the decay rate constant k_CR versus the energy gap −ΔG:

$$\ln(k_{CR}) = \alpha - \beta(-\Delta G)$$

in homogeneous solutions. CT crystals, and silica gel-adsorbed systems. For instance, Miyasaka and co-workers showed that a similar energy gap dependence of k_CR is observed for CT complexes consisting of TCNB or TCNE with arenes in a porous vycal glass (silica)-adsorbed system to that in a polar solvent, that is CH3CN. On the basis of this result, they suggested that the high-frequency quantum modes in the ion pair predominately in the CR process rather than the solvent dynamic motions. Asahi and co-workers have shown that in CT crystals of pyromellitic dianhydride (PMDA) with electron-donating benzene derivatives the same linear relationship is observable with an approximately 3 times larger / value than that in solution. They ascribed a possible cause of the large / value to the rigidity of donor–acceptor pairs, leading to limited structural changes in the excited state in crystals and to the lattice vibrational mode coupled with the CR process.

Regarding our result for the energy gap dependent rate constants, the values of k_CR versus −ΔG are plotted in Figure 11 along with the results by Miyasaka and co-workers and Asahi and co-workers. The values of / were estimated from the peak energies of absorption and emission spectra according to the traditional method and given in Table 3. For the double-exponential decays, the major component was employed in Figure 11. Due to the influence of water as well as from that of the zeolite surface. Besides, the polarity may not increase dramatically on addition of water, as discussed in section 2 of the Results and Discussion.

### Table 2. Values of k_CR for CT Complexes of TCNB with Various Donors, including Naphthalene (Nap), Phenanthrene (Phe), Pyrene (Py), and Anthracene (Ant), in Dehydrated and 1.0 × 10⁻² mol·g⁻¹ Hydrated NaY

<table>
<thead>
<tr>
<th>donor</th>
<th>k_CR/dehydrated NaY</th>
<th>k_CR/hydrated NaY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nap</td>
<td>4.9 × 10^3 (57%)</td>
<td>2.7 × 10^3 (&gt;95%)</td>
</tr>
<tr>
<td>Phe</td>
<td>1.8 × 10^3 (95%)</td>
<td>1.9 × 10^3 (&gt;95%)</td>
</tr>
<tr>
<td>Py</td>
<td>1.0 × 10^3 (83%)</td>
<td>1.4 × 10^3 (67%)</td>
</tr>
<tr>
<td>Ant</td>
<td>1.5 × 10^6 (69%)</td>
<td>9.5 × 10^5 (31%)</td>
</tr>
</tbody>
</table>

*The decay curves were analyzed with a double-exponential function, and the value inside parentheses shows the percentage of fast and slow components.

### Table 3. Peak Energies of Absorption (hν_max/) and Emission (hν_max/), Energy Gap (−ΔG), and Recombination Energy (/) for CT Complexes of TCNB with the Donors Naphthalene (Nap), Phenanthrene (Phe), Pyrene (Py), and Anthracene (Ant) Adsorbed in Dehydrated NaY Zeolite

<table>
<thead>
<tr>
<th>donor</th>
<th>hν_max/ (10^3 cm⁻¹)</th>
<th>hν_max/ (10^13 cm⁻¹)</th>
<th>−ΔG/eV</th>
<th>/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nap</td>
<td>25.8</td>
<td>17.2</td>
<td>2.67</td>
<td>0.53</td>
</tr>
<tr>
<td>Phe</td>
<td>25.8</td>
<td>17.1</td>
<td>2.66</td>
<td>0.54</td>
</tr>
<tr>
<td>Py</td>
<td>21.3</td>
<td>14.9</td>
<td>2.12</td>
<td>0.40</td>
</tr>
<tr>
<td>Ant</td>
<td>20.5</td>
<td>15.0</td>
<td>2.20</td>
<td>0.34</td>
</tr>
</tbody>
</table>

(36) One of the reviewers indicated the different view on the origin of the broad transient spectra as being due to the complexes being adsorbed at different sites. Nonexponential decays of the transient absorption can be explained by the same assumption according to the reviewer. Our interpretation stands of the previous studies of the band shapes of the CT complexes in various media. We share the same view for the nonexponential decays; however, we do not have enough evidence for the transient spectral shift depending on the adsorption sites.


(39) One of the reviewers suggested that the increase in the decay rate of excited CT complexes upon addition of water can be explained by the change in polarity inside the zeolite. We assume that the CT complexes adsorbed on zeolites behave differently from those in solution. Hydration of the complexes is unlikely because they crystallize when deprived of the adsorption sites in the zeolites by the water molecules in quantities to fill the entire pore volume. We assume that the CT complexes liberated from the interaction with the immediate surface of the zeolite reside in the free volume within the cage in the presence of a relatively small amount of water and thus relatively free from the influence of water as well as from that of the zeolite surface. Besides, the polarity may not increase dramatically on addition of water, as discussed in section 2 of the Results and Discussion.
the limitation of the zeolite-adsorbed system, the number of our data points is small. For example, molecules with large electron-donating ability such as perylene cannot be accommodated within NaY because of the large molecular size compared with the diameter of the entry aperture. Neither can a stronger electron acceptor than TCNB such as tetracyanoethylene (TCNE) be employed due to a thermal reduction in NaY zeolite by the reaction with the basic sites. Due to these limitations, we reserve detailed discussion of the energy gap dependence of $k_{CR}$ in NaY.

Our minimal conclusion is that the rate of the CR process is significantly slow in dehydrated NaY: at least 10 times slower than that in homogeneous solution. The restriction of the geometrical change in the excited CT state of the adsorbed complexes in NaY seems responsible for the marked retardation of the CR rate, since the possible liberation of the CT complexes from the zeolite walls by introducing water molecules into the cavities caused the recovery of the CR rate to values similar to those in solution (see Figure 11).

**Summary**

We have demonstrated that the charge-transfer (CT) complexes of 1,2,4,5-tetracyanobenzene (TCNB) with aromatic donors as photophysical and photochemical probes are prepared within the supercage networks of faujasite zeolites. While pioneering works by Yoon and co-workers have shown that the CT complexes of cationic organic acceptors (pyridinium ions) with arene donors were formed within zeolites and investigated the photophysical and photochemical properties of these complexes, we observed a few remarkable properties unique to the neutral-type CT complexes in which both the donor and acceptor molecules are adsorbed in zeolites with non-Coulombic interactions.

The peak position of the CT bands suffers an appreciable shift depending on the chemical properties originating from the cation exchange of the zeolite in which the complexes are formed. For example, a larger blue-shift was observed in more basic zeolites. Thus, the CT complexes can probe inside the cavities of intact zeolites. In contrast, the CT bands of the complexes of pyridinium acceptors were insensitive to the acid—basic nature of the zeolites. From a certain point of view, the pyridinium ion exchanged zeolites are no longer an intact host material for usual adsorption purposes but are regarded as functionalized materials which acquired the extreme chemical nature.

The apparent equilibrium constant ($K_{eq}$) of CT complex formation depends on the chemical properties of zeolites and also on aromatic donor molecules. For instance, the value of $K_{eq}$ for the TCNB-anthracene pair is larger in NaX than in NaY. In this case, the correlation between the value of $K_{eq}$ and the free volume within the cage networks is very small and the chemical nature of the zeolite is predominant for the CT complex formation. On the other hand, the CT complexes of pyridinium acceptors have been found to be formed in a size- and shape-selective manner and thus to be sensitive to the physical properties of zeolites, such as pore or channel diameter.

An appreciable effect of coadsorbed water is observed; in most cases the water enhances the complex formation within the zeolites. This result was explained by the expelling effect of the water on the CT complexes adsorbed on the dry zeolite surface. Namely, an increased mobility of the guest species is caused by the liberation of adsorption interaction with the zeolite walls by the action of water molecules which have strong interaction with the zeolites and thus are preferentially adsorbed directly on the zeolite surfaces. The present result is in marked contrast with those for the CT complexes of pyridinium acceptors, for which a physical effect such as a pressure effect of water was observed.

The photoexcitation of the CT complexes in NaY zeolite with a fs laser pulse gives rise to the excited CT state, which deactivates to the ground state through the charge-recombination (CR) process. This CR process is found to proceed very slowly in dehydrated NaY but is accelerated in the hydrated zeolite where the CR process are similar to those observed in solution. The restricted conformational change in the excited CT complexes in the adsorbed state is considered to be responsible for the slow decay kinetics. The present result showed that the effect of zeolite on the kinetics is not only limited to the back electron transfer of ion pairs formed on excitation of the CT complexes of pyridinium acceptors but also applicable more generally to the relaxation process of excited CT complexes within zeolites.

Accordingly, we provided new data to utilize CT complexes as a probe for investigating zeolites. The results demonstrated that the properties of the host zeolites sensed by the CT probes are rather site specific and more or less a reflection of the chemical or acid—base properties of the adsorption sites. This type of information is significantly different from that obtained from usual fluorescence probes which explore bulk or average properties, for example polarity or free volume.

**Acknowledgment.** We wish to thank one of the reviewers for informative comments leading to an important improvement of the report. Financial support by the Japanese Ministry of Education, Science, Sports and Culture through a grant-in-aid (#10640502) is gratefully acknowledged.

LA981496P