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# Probing Basic Properties of Zeolites with Charge-Transfer Complexes of Aromatic Donor–Acceptor Pairs Formed Inside the Cavities

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**Abstract**—Spectroscopic properties were investigated of the charge-transfer (CT) complexes of electron-accepting 1,2,4,5-tetracyano-benzene (TCNB) with arene donors assembled inside the cavities of various alkali metal-exchanged faujasite zeolites. It was found that the peak position of the CT absorption bands blue-shifted depending on the basicity of the zeolites originating from the exchanged cations. The Stokes shift, the separation between the peak energies of absorption and emission was larger in more basic zeolites and linearly correlated with the basicity. TCNB–arene CT complexes were found to be a promising candidate for probing the basicity of the zeolites. © 2000 Elsevier Science Ltd. All rights reserved.

## Introduction

There have been numerous activities in the study of chemistry within zeolites from photochemical aspects, because of fascinating features such as the remarkable specificity and selectivity of photochemical reactions carried out in zeolites.<sup>1–7</sup> As a novel solid reaction medium, zeolites have potential use for controlling photophysical and photochemical behavior of molecules adsorbed into their cavities and channels. Yet, there still remain gaps of our understanding between photophysics within zeolites and intrazeolite photochemical events. Thus much effort has been devoted in recent years to fill the gaps.

Zeolites have been known for their distinct physical and chemical properties. Although the size and shape restrictions by the cavities and channels are comprehended ubiquitously,<sup>1,2,5,8</sup> internal properties such as the electrostatic field exerted by charge-compensating cations distributed throughout the structures and electron donating/accepting properties of sites responsible for adsorption play a major role in the perturbations imposed by the zeolite hosts on the reaction pathways of guest molecules.<sup>4,6,7</sup> Thus probing these properties is essential for predicting the course of photoinduced processes of adsorbed guest species.

For this purpose, photophysical probes that can sense bulk

properties such as polarity, geometrical restrictions and molecular diffusivity inside the zeolite have been utilized. For instance, the fluorescence properties of pyrene and other organic molecules were exploited to monitor the environmental polarity inside the zeolite cavities.<sup>9–11</sup> It was suggested that the micropolarity of the supercages of NaX and NaY is considerably high and comparable to that of 50% aqueous methanol.<sup>10</sup>

This finding was postulated to be responsible for a highly efficient photoionization observed for pyrene and anthracene adsorbed in the zeolites.<sup>12,13</sup> Another example is the spectroscopic detection of guest distribution within the cage networks, i.e. fluorescence spectroscopic observation of associated dimers of aromatics, pyrene,<sup>14,15</sup> naphthalene<sup>16</sup> and anthracene<sup>17</sup> adsorbed within the confined space of zeolite cavities. Of these, naphthalene was found to form dimeric cations<sup>16,18</sup> on photoexcitation, and the enhanced association of molecules due to confinement within the small space was ascribed as being key to the observation of dimeric cations, an important intermediate in photochemistry. Furthermore, the collisional quenching reactions of long-lived triplet molecules were exploited for estimating molecular diffusivity within the cage networks.<sup>19</sup> One of the intriguing conclusions derived from the study was that, in the faujasite zeolites bearing open cage networks,<sup>20</sup> the intercage quenching mechanism operates from direct neighboring cages besides the intracage quenching process. This aspect is especially important for exploring the mechanisms of photoreactions involving triplet intermediate states. Overall, probing average properties with photophysical probes has been found to be viable in terms of simplicity and effectiveness.

*Keywords:* arenes; cyano compounds; complexation; zeolites.

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The method of inspecting site-specific information such as the extent of electron donating/accepting abilities at the individual adsorption sites in the zeolite cages seems to be under developing also thanks to the photophysical probes. Broader spectral envelopes of fluorescence from anthracene or pyrene observed in the zeolites with small alkali metal cations was ascribed to the cation- $\pi$  interaction between the charge-compensating cations and the aromatic species.<sup>15,17</sup> The observation suggests that the adsorption sites of electron-donating aromatics is associated with the cationic sites serving as electron accepting centers within the zeolites. Contrastingly, it was suggested that 1,2,4,5-tetracyanobenzene (TCNB), a strong electron acceptor, is adsorbed at the electron donating sites, presumably at framework oxygens by the charge-transfer (CT) interaction on the basis of ground-state absorption spectra, fluorescence spectra and lifetimes, and transient absorption spectra indicating the formation of radical anions of TCNB (TCNB<sup>-</sup>).<sup>21</sup> Similarly, methylviologen dication (MV<sup>2+</sup>) also known for its strong electron accepting nature was incorporated into the zeolites through a cation exchange and the spectroscopic and photophysical properties were investigated.<sup>22,23</sup> The MV<sup>2+</sup> cation that gives rise to MV<sup>+</sup> on photoexcitation afforded appreciable changes in the ground state absorption band in UV region depending on the electron donor nature of the cation-exchanged zeolites.<sup>23,24</sup> Both TCNB and MV<sup>2+</sup> are found to be a good candidate for a photophysical probe capable of detecting electron-donating ability of the zeolite framework. Thus qualitatively speaking, photophysical probes bearing electron donor-acceptor nature is useful for obtaining site-specific information. However, the probes investigated so far seem to be unsatisfactory for quantitatively estimating donor-acceptor abilities of the adsorption sites because of only minor spectral changes.

Charge-transfer (CT) complexes consisting of electron donors and acceptors have been assembled inside the zeolite cavities and channels originally aimed at investigating the effect of size and shape segregation on the complex formation by the rigid frameworks.<sup>25–31</sup> Very recently we have found that the CT complexes of TCNB and anthracene fabricated in various cation-exchanged X and Y zeolites afforded unusual blue shift of the peak position of the CT absorption band as large as ca. 60 nm.<sup>32</sup> Almost simultaneously, Yoon and co-workers reported<sup>24</sup> a similar blue shift of the CT absorption band observed for the complexes of MV<sup>2+</sup> with a few arene donors in various types of zeolites. It was pointed out that the CT complexes have potential use for probing chemical properties of intrazeolite adsorption sites in terms of the positions of their absorption bands that are strongly dependent on the site-specific electron donor nature of the host material.

This paper describes the exploratory study of the spectroscopic properties of CT complexes of TCNB with various arene donors fabricated inside the cavities of faujasite zeolites with different alkali metal cations. Examination was made for the relationship of the Stokes shift of CT absorption and emission with the electron donor property of the zeolites, in addition to that of CT peak energy with the electron donating property. At the same time, comparison with the absorption spectroscopic characteristics of MV<sup>2+</sup>-arene CT complexes by Yoon and co-workers<sup>24</sup> was made.

Both advantageous and disadvantageous features of TCNB-arene CT complexes over MV<sup>2+</sup>-arene CT complexes were discussed.

## Experimental

Zeolites NaX (FAU (Si/Al=1.26), Lot No CKP-3345) and NaY (FAU (Si/Al=2.75), Lot No. 3001) were obtained from Tosoh. Cation-exchanged zeolites were prepared via ion exchange of NaX and NaY according to the procedure described in the literature.<sup>33,34</sup> The exchange ratio was determined by the atomic absorption analysis and listed in Table 1. 1,2,4,5-Tetracyanobenzene (TCNB) and other aromatics were from the same sources as those described previously.<sup>32</sup>

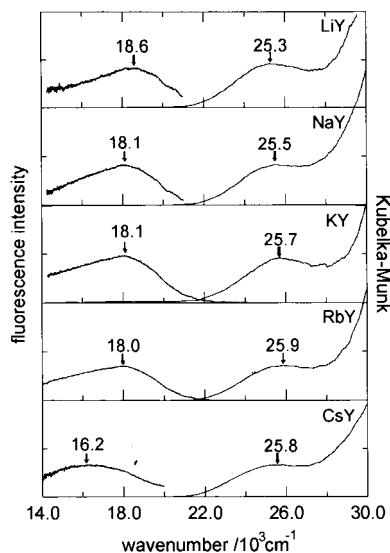
CT complexes were assembled in zeolite cavities by the following stepwise procedure in a nitrogen-filled glovebox. First, weighed amount of the dehydrated (at 500°C for ca. 8 h in air) zeolite powder was stirred with a dichloromethane solution of the acceptor molecule, TCNB in a stoppered vial at room temperature for 5–10 min; the sample was filtered and the solid washed twice with dichloromethane and vacuum dried. The amount of unadsorbed TCNB in the supernatant solution was 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. The mixture was stirred at room temperature for a few minutes, filtered, and washed twice with *n*-hexane and vacuum dried. The unadsorbed aromatic donor molecules in the supernatant solutions were assayed spectrophotometrically. Dissolution of TCNB molecules adsorbed in the zeolites into *n*-hexane was found to be negligible. The colored zeolite powder was then transferred into a Suprasil cell with a 2 mm optical path length and evacuated at 0.4 Pa for 6 h (at ca.100°C).

The adsorption isotherm study of aromatic guest species in various zeolites showed that the maximum loading levels were largely dependent on the relationship of the size of supercage openings with the diameter of guest molecules; this strongly suggests the formation of complexes inside the supercages. Typical loading levels of guest species were  $5 \times 10^{-5}$  mol g<sup>-1</sup> both for TCNB and arenes. This loading corresponds to average supercage occupancy of ca. 0.08. Hence, we assumed that the CT complexes were composed of a 1:1 ratio of donor and acceptor.

The ground-state reflectance spectra were measured on a Shimadzu UV-3101PC double-monochromator

**Table 1.** Exchange ratio of corresponding alkali metal ions, chemical composition, electronegativity ( $S_z$ ) and mean charge on oxygen ( $\delta_o$ ) of alkali metal-exchanged faujasite zeolites employed in this study

Zeolite	Exchange ratio (%)	Unit cell composition	$S_z$	$\delta_o$
LiY	70	Li <sub>36</sub> Na <sub>15</sub> Al <sub>51</sub> Si <sub>141</sub> O <sub>384</sub>	2.64	-0.254
NaY		Na <sub>51</sub> Al <sub>51</sub> Si <sub>141</sub> O <sub>384</sub>	2.61	-0.262
KY	98	K <sub>50</sub> NaAl <sub>51</sub> Si <sub>141</sub> O <sub>384</sub>	2.57	-0.272
RbY	63	Rb <sub>32</sub> Na <sub>19</sub> Al <sub>51</sub> Si <sub>141</sub> O <sub>384</sub>	2.54	-0.279
CsY	60	Cs <sub>30</sub> Na <sub>21</sub> Al <sub>51</sub> Si <sub>141</sub> O <sub>384</sub>	2.49	-0.292
NaX		Na <sub>85</sub> Al <sub>85</sub> Si <sub>107</sub> O <sub>384</sub>	2.39	-0.317
CsX	68	Cs <sub>58</sub> Na <sub>27</sub> Al <sub>85</sub> Si <sub>107</sub> O <sub>384</sub>	2.20	-0.365

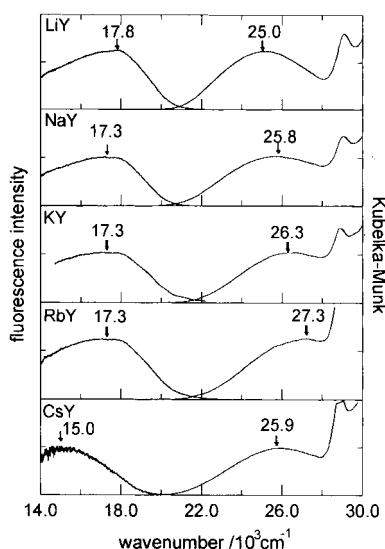


**Figure 1.** Absorption and corrected emission spectra of TCNB–naphthalene CT complexes in alkali metal ion-exchanged zeolite Y.

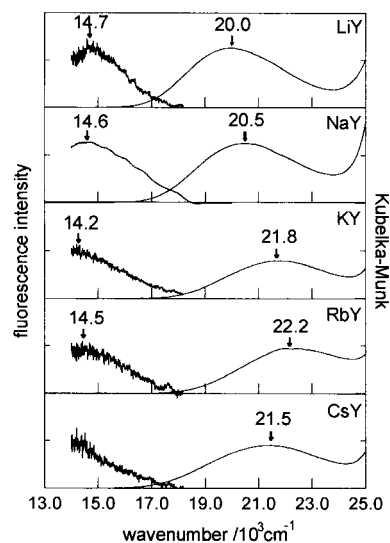
spectrophotometer equipped with an integrating sphere coated with BaSO<sub>4</sub>. The reference was BaSO<sub>4</sub> (Kodak white reflectance standard). Absorption spectra of ground state species were obtained by using the Kubelka–Munk function. Fluorescence spectra were recorded on a Hitachi F-3010 spectrofluorometer in the front surface geometry. Appropriate optical filters were employed in the measurements. The spectral response of the fluorometer was corrected with fluorescence standards.<sup>35</sup> At least three independent samples were prepared for the determination of the peak positions of absorption and fluorescence spectra, and averaged values were employed. All the measurements were carried out at ambient temperature (21–23°C).

## Results and Discussion

Figs. 1–3 show the absorption and fluorescence spectra



**Figure 2.** Absorption and corrected emission spectra of TCNB–phenanthrene CT complexes in alkali metal ion-exchanged zeolite Y.



**Figure 3.** Absorption and corrected emission spectra of TCNB–anthracene CT complexes in alkali metal ion-exchanged zeolite Y.

(corrected) of TCNB–naphthalene (Nap), TCNB–phenanthrene (Phe) and TCNB–anthracene (Ant) complexes prepared in various alkali metal exchanged zeolite Y, whereas Fig. 4 represents the absorption spectra of TCNB-9-methylanthracene (9-Me). Note that the fluorescence from TCNB-9-Me complexes was too weak to be measured. We also investigated TCNB–pyrene (Py), TCNB-1-methylnaphthalene (1-MeNap) and TCNB-1-methoxynaphthalene (1-MeONap) complexes whose spectra were not given. The shapes of both absorption and emission spectra were basically similar to those observed in solutions: the mirror-image absorption–fluorescence relationship prevailed.<sup>36</sup> Inspection of the spectra shows the unequivocal tendency of a blue shift of the absorption peaks and a larger Stokes shift on going from Li<sup>+</sup> to Cs<sup>+</sup> in the series of Y zeolites. Note that the Stokes shift is defined by the energy separation between the absorption and emission peaks despite the fact that the spectra of CT complexes generally have a broad envelope and a very large bandwidth.<sup>36</sup> It turned out that the present observations are unusual and unique to zeolites as will be described.

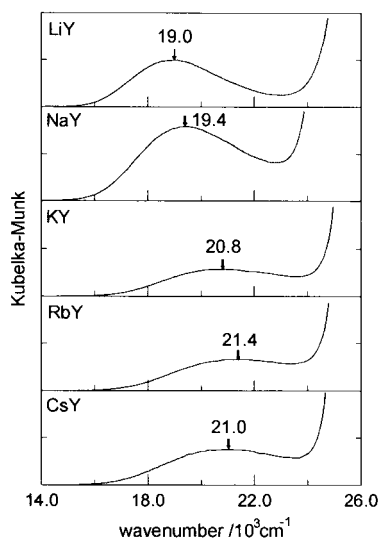
A few factors need to be taken into account for the interpretation of the effect brought about by the cation exchange. First, acid/base properties or electron donor–acceptor abilities can be altered. It is generally accepted that the electron-donating ability of the donor sites, presumably framework oxygens adjacent to Al atoms, is greater for the zeolites with larger alkali metal ions for a given Si/Al ratio whilst the electron-accepting ability is in reverse order.<sup>37</sup> Note also that the donor ability increases with decreasing Si/Al ratio and the accepting ability increases with increasing Si/Al ratio. Second, the electrostatic field strength inside the cavities can be modified.<sup>6</sup> The effect of the electrostatic field is akin to that of solvent polarity and the field inside the cavities of zeolites is considered to be sufficiently high in general. Still, the field is dependent both on cation size and on Si/Al ratio. Namely, the small Li<sup>+</sup> induces a stronger field in its proximity than the larger Cs<sup>+</sup> ion. Third, the size of pores and that of entry apertures

will be affected.<sup>6</sup> In faujasites, the supercage openings (about 0.74 nm in diameter for Na<sup>+</sup>) will be remarkably reduced while the free volumes of supercages decreases only by 6% with the increase in cation size from Li<sup>+</sup> to Cs<sup>+</sup>. These points will be examined with respect to the spectroscopic properties of CT complexes although the steric factor<sup>38</sup> that may not be directly relevant to the electronic properties can be ruled out. We will focus on the CT absorptions in the first place.

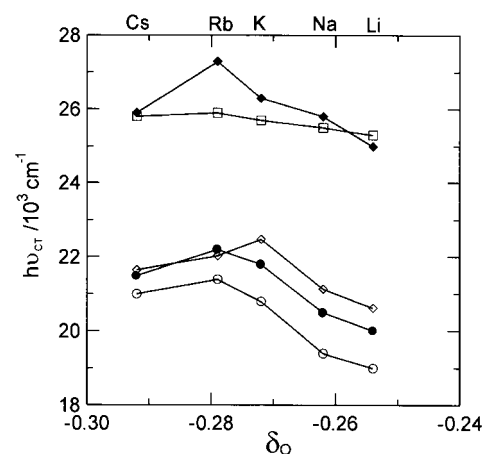
It is most likely that the electron donating property of the host zeolites is amenable for the blue shift of the CT absorption bands. Fig. 5 shows the relationship of the peak energy of CT absorptions with mean charge on oxygen ( $\delta_O$ ) calculated according to the Sanderson's electronegativity equalization principle.<sup>37,39</sup> The  $\delta_O$  has been accepted as a good measure of the electron donor ability of the zeolites on an average, although, in reality, a considerable distribution of the electron donor sites with various degree of donor ability prevails. At this moment no empirical measure for the electron donor strength such as the ionization energy of zeolites is available.

In Fig. 5, a good negative correlation is observed except for TCNB–Nap complex in which only a weak correlation is obeyed. Close inspection of Fig. 5, however, reveals that the relationship is not completely linear but levels off at a large negative value of  $\delta_O$ , namely in CsY. This problem will be discussed later.

Qualitatively speaking, the blue-shift of CT absorption is explained by the destabilization of the LUMO (lowest unoccupied molecular orbital) level of TCNB by the interaction with the electron-donating sites of the zeolites, since the excitation of CT complexes is envisaged as the transfer of a electron from the HOMO (highest occupied molecular orbital) of the donor to the LUMO of the acceptor.<sup>40,41</sup> Interaction of arene donors with the electron accepting sites seems unimportant for the electronic properties of the complexes. A similar observation has been made by Yoon and co-workers<sup>42</sup> of the visible absorption band of iodine



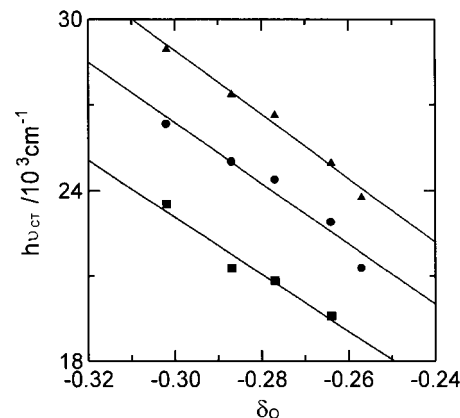
**Figure 4.** Absorption spectra of TCNB-9-methylanthracene CT complexes in alkali metal ion-exchanged zeolite Y.



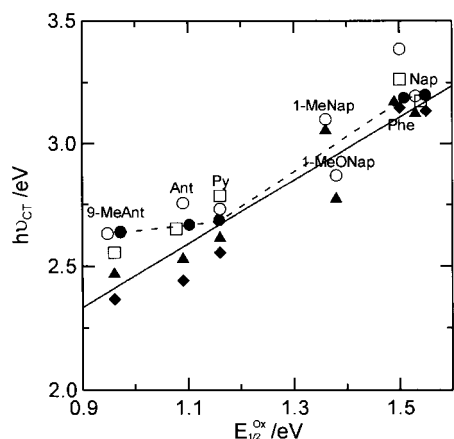
**Figure 5.** Relationship between the peak energy of CT absorption and mean charge on oxygen,  $\delta_O$  calculated according to the Sanderson's electronegativity equalization principle. Key:  $\square$ , TCNB–naphthalene;  $\blacklozenge$ , TCNB–phenanthrene;  $\diamond$ , TCNB–pyrene;  $\bullet$ , TCNB–anthracene;  $\circ$ , TCNB–9-methylanthracene.

occluded in zeolites. They observed a large blue shift dependent on the basicity of zeolite originating from the exchanged cations and Si/Al ratio. The results were explained on the basis of Mulliken theory<sup>40,41</sup> as due primarily to an increased LUMO level ( $\sigma^*$ ) of iodine by the interaction with the electron-donating sites. Very recently, Yoon and co-workers<sup>24</sup> have reported that a larger blue shift is observable for MV<sup>2+</sup>-arene CT complexes assembled in various zeolites with different alkali metal cations in going from Li<sup>+</sup> to Cs<sup>+</sup>. The present results of TCNB–arene CT complexes are relevant to those by Yoon and co-workers.<sup>24</sup> Thus the blue shift of CT absorptions in basic zeolites is a general phenomenon characteristic to zeolites. However, an appreciable difference is noted for the spectroscopic nature between TCNB–arene and MV<sup>2+</sup>-arene systems.

Fig. 6 shows a negative linear relationship of the CT peak energy with  $\delta_O$  for MV<sup>2+</sup>-arene complexes investigated by



**Figure 6.** Negative linear relationship of the peak energy of CT absorption with mean charge on oxygen,  $\delta_O$  in cation-exchanged zeolite Y. Key:  $\blacktriangle$ , MV<sup>2+</sup>-pentamethylbenzene (PMB);  $\bullet$ , MV<sup>2+</sup>-1-methoxynaphthalene (MeONap);  $\blacksquare$ , MV<sup>2+</sup>-anthracene (Ant). Data were extracted from a paper by Yoon and co-workers.<sup>24</sup>



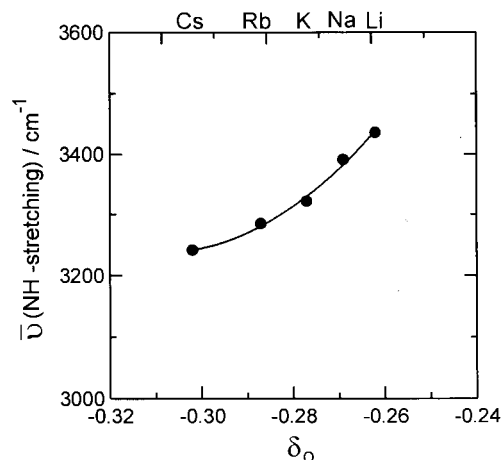
**Figure 7.** Mulliken plot of the peak energy of CT absorption vs. the oxidation potential of donor arenes for TCNB–arene complexes in alkali metal cation-exchanged zeolites. Solid line represents a linear relationship in NaY zeolite while dashed curve represents a nonlinear relationship in CsY. The point of TCNB–Nap complexes was excluded from the solid line.

Yoon and co-workers.<sup>24</sup> It is noteworthy that no saturation behavior is observed in cation-exchanged zeolite Y. This is highly in contrast to our observation of TCNB–arene complexes (Fig. 5).

To see the difference between the two systems more clearly, examination of Mulliken plot is appropriate. Anomaly of CT absorptions of TCNB–arene complexes in CsY is apparent when the CT peak energy ( $h\nu_{CT}$ ) was plotted vs. the ionization energy ( $IE_D$ ) or oxidation potential ( $E_{1/2}^{ox}$ ) of donors according to Mulliken's theory:<sup>40,41</sup>

$$h\nu_{CT} = IE_D - EA_A + C \quad (1)$$

where  $EA_A$  represents electron affinity of acceptors and  $C$ , a constant. In Fig. 7 is depicted the Mulliken plot for TCNB–arene complexes in the alkali metal-exchanged zeolites under investigation. As typically shown for NaY system, a linear relationship is held for four arenes excluding Nap in the same zeolite host with a similar slope apart from the CsY system. This result suggests that the CT complexes of



**Figure 8.** NH-stretching wavenumber of pyrrole adsorbed in cation-exchanged zeolite Y vs. mean charge on oxygen ( $\delta_O$ ). Data were extracted from a paper by Kaliaguine and co-workers.<sup>43</sup>

TCNB with arenes except for Nap behave similarly in most of the zeolites with those in solutions or in crystalline state.

Contrastingly, excellent linear relationship can be held for the Mulliken plots (not shown) of  $MV^{2+}$ -arene complexes in the zeolites including CsY. Several factors might be responsible for the difference between the two systems. First of all, there is no guarantee for the linear relationship to be held between the  $\delta_O$  scale and the electron donor strength of zeolites. For example a saturation behavior was observed for the plot of a NH-stretching wavenumber of pyrrole vs.  $\delta_O$  in going from  $Li^+$  to  $Cs^+$  as shown in Fig. 8. Pyrrole that is assumed to interact mainly with the basic sites of zeolites through the hydrogen bonding between the NH group and the framework oxygen has been frequently used as a reliable probe for evaluating the basic strength of zeolites.<sup>43</sup> Thus the saturation phenomena do not necessarily mean unfavorable interaction of the probes with the zeolites.

Second, saturation in the plot of the CT peak energy vs.  $\delta_O$  can be observed even for  $MV^{2+}$ -arene complexes if the data points in a series of cation-exchanged X zeolites are included in the same plot. Although Yoon and co-workers treated the CT-absorption data in the X zeolites separately from those in Y zeolites because of a different Si/Al ratio, they should be handled simultaneously if the basicity scale,  $\delta_O$  is truly a reliable measure. The saturation behavior for large values of  $\delta_O$  is more appreciably observed for the CT complexes of TCNB. We confirmed the absence of further blue shift for TCNB–arene complexes incorporated in zeolites with much greater basic strength. For example, the peak wavenumber was  $21\,700\text{ cm}^{-1}$  in NaX and  $22\,100\text{ cm}^{-1}$  in CsX for TCNB–anthracene pairs. Presumably, the onset of the saturation comes slower for  $MV^{2+}$ -arene complexes because of slightly stronger electron accepting nature of  $MV^{2+}$  than that of TCNB.<sup>44</sup>

Third, one should be careful about the possibility that the cation exchange with the  $MV^{2+}$  may affect the distribution of positive charge, and consequently the microenvironment within the zeolites although the amount of exchange with  $MV^{2+}$  was minimal according to Yoon and co-workers.<sup>24</sup> This effect, on the other hand, cannot be anticipated for the neutral acceptor. This difference can also be the cause of the contrasting spectroscopic properties of the CT complexes with the different acceptors.

It is pertinent to note that the effect of medium polarity on the spectral shift of CT bands should be minor. Our general understanding is that the absorption maxima of CT complex between neutral species usually show no dependence on solvent polarity since the increase in solvent reorganization energy on going to more polar solvents is compensated by a corresponding decrease in excited state energy, leading to an almost constant vertical excitation energy. Indeed, as shown in Table 2, the data from the literature<sup>45–48</sup> suggest that the positions of CT absorption bands are not affected by solvent, nor by a state such as in solution or crystalline. It is noteworthy that the CT peak positions are similar in LiY zeolite, a medium of the highest polarity to those in other media. Hence we can conclude that in the zeolites with

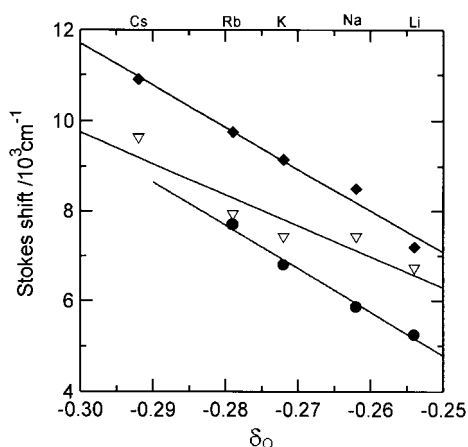
**Table 2.** Absorption peak energy ( $\text{cm}^{-1}$ ) of TCNB–arene CT complexes with different donors in various media

Donor	$\text{C}_6\text{H}_6$ <sup>45</sup>	$\text{CHCl}_3$ <sup>46</sup>	Crystal <sup>47,48</sup>	LiY
Naphthalene	25 100	25 000	25 000	25 300
Phenanthrene	24 900	25 000	23 800	25 400
Pyrene	20 700	20 100		20 600
Anthracene	20 100	19 700	19 600	19 700

sufficiently basic nature CT bands are remarkably blue-shifted with respect to the peak positions observed in solutions.

One of the advantageous features of TCNB–arene complexes over  $\text{MV}^{2+}$ -arene complexes are that the former emits while the latter does not. We observed the CT fluorescence, the peak position of which in LiY or NaY is similar to that in solution. For example, the peak position reported in benzene<sup>45</sup> is  $18\,100\text{ cm}^{-1}$  for TCNB–Nap,  $17\,900\text{ cm}^{-1}$  for TCNB–Phe and  $15\,000\text{ cm}^{-1}$  for TCNB–Ant. Thus we can explore fluorescence spectroscopic properties of TCNB–arene complexes adsorbed in zeolites. For this purpose, the Stokes shift of the fluorescence was plotted vs.  $\delta_{\text{O}}$  for TCNB–Nap, TCNB–Phe and TCNB–Ant complexes, and depicted in Fig. 9.

A good linear correlation was obtained in this plot. The Stokes shift is a measure of the structural rearrangement in the Frank–Condon excited state of the complexes, i.e. a larger Stokes shift is usually expected for the complex which undergoes a larger rearrangement to form the geometry in the lowest (fluorescent) excited state. In solution, our general understanding is that a larger Stokes shift is observed for CT complexes in the solvent with higher polarity because of a larger stabilization of the excited CT-state in polar media.<sup>45,49</sup> In zeolites, the situation is completely different. The blue shift of the absorption band is a major factor contributing to the increase in the Stokes shift dependent on the zeolite host except for CsY. In CsY, strikingly small blue shift of the absorption peak is compensated by a large red shift of the fluorescence peak, leading to the large Stokes shift observed.

**Figure 9.** Negative linear relationship between the Stokes shift and mean charge on oxygen,  $\delta_{\text{O}}$  for TCNB–phenanthrene ( $\blacklozenge$ ), TCNB–naphthalene ( $\nabla$ ) and TCNB–anthracene ( $\bullet$ ) CT complexes.

In summary, we observed unusual blue shift of the absorption band of a few TCNB–arene CT complexes in alkali metal cation-exchanged faujasite zeolites. The basic nature was ascribed to be responsible for the observation. Unexpected saturation of the blue shift against the basicity scale,  $\delta_{\text{O}}$  was observed for the CT band in CsY and X-type zeolites, both of which are supposed to carry a larger basicity. This behavior is highly contrasting with the CT band of  $\text{MV}^{2+}$ -arene complexes that were reported<sup>24</sup> to have a simple linear correlation with  $\delta_{\text{O}}$  in cation exchanged Y zeolites. Despite the saturation phenomenon of CT absorption bands, a linear correlation was found between the Stokes shift of TCNB–arene complexes and the basicity scale,  $\delta_{\text{O}}$ . Mechanistic detail is under investigation.

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