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Disposition of Ferrocenes in β- or γ-Cyclodextrin Cavity and Consideration on the Absorption Bands of Ferrocene

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By comparing the induced circular dichroism (ICD) spectrum of 1,4,7,10,13-pentaoxa[13](1,1′)-ferrocenophane, **I**, in the presence of β-cyclodextrin (β-CDx) with that of ferrocenes (Fcs) in β-CDx or γ-CDx cavity, the disposition of Fcs in the CDxs is determined. Thus, the orientation of Fc in the Fc:β-CDx 1:1 complex and ferrocenecarboxylic acid (FcMA) in β-CDx at pH 2 is considered to be nearly parallel to the molecular axis of β-CDx, while that of Fc in the Fc:γ-CDx 1:1 complex, FcMA in β-CDx cavity at pH 9, and FcMA and ferrocenedicarboxylic acid (FcDA) in γ-CDx cavity appears to be close to normal to the molecular axis of the CDx. In addition, based on the ICD spectra, an intense band of Fcs at around 200 nm is assigned as a charge-transfer (CT) transition between the cyclopentadienyl (Cp) rings and iron(II). The advantage of using CDxs for the determination of the polarization direction of absorption bands of chromophore molecules is mentioned in comparison with previous methods.

Induced circular dichroism (ICD) studies on inclusion complexes between aromatic guest molecules and cyclodextrins (CDxs) have developed over the past decade.[1,2] In particular, concerning the ICD of CDx–chromophore 1:1 inclusion complexes, the following have been substantiated or shown[1] with high accuracy on the basis of the Kirkwood–Tinoco coupled oscillator expression.[3] (i) Electronic transitions parallel to the molecular axis of CDxs produce positive ICD, while those normal to the axis show negative ICD. (ii) The sign of the calculated rotational strength does not change by the movement of guest molecules along the X-, Y-, and Z-axis, although their magnitude is affected[1g] (the origin of the axes is set at the center of CDx and the Z-axis is parallel to the molecular axis of CDx). (iii) Rotation of the guest molecule in the X–Y plane has no influence on the calculated rotational strength, while that in the X–Z plane does have a great influence on it.[1g] Figure 1, obtained by the procedure shown in Ref. 1h, depicts this dependence of calculated rotational strength on the rotation of the electric transition moment in the X–Z plane. As can be judged from curve b in this figure, electronic transitions whose directions are within 54.44 degrees from the axis of CDxs produce positive ICD sign while those more than 54.44 degrees yield negative ICD sign. Accordingly, it is now possible to determine the polarization direction of the absorption band of chromophore molecules from the sign of the ICD spectra of the chromophore: CDx 1:1 complex. Conversely, the orientation of guest molecules trapped in CDxs cavity can be inferred from the sign of the ICD spectra, if the polarization directions of the bands of the guest molecules are known. This method is valid in particular for molecules which have clear long- and short-axes, because their orientation in CDxs is likely to be fixed. However, if relatively round or square molecules are used as guest molecules, determination of the polarization direction of bands or elucidation of the orientation of guest molecules in CDxs becomes difficult, because more than one kind of orientation may exist. Typical examples are ferrocene (Fc) and its derivatives. Ferrocene is a relatively round molecule, with H atoms displaced towards the Fe atom.[4] As indicated recently by calculation,[5] Fc can bind to β-CDx in both an axial and equatorial orientation. Since the energy difference is too small to be significant (calculated value is 0.5 kcal mol^{-1}),[5] packing forces in a crystal, solvation effects in solution, or even a slight change in Fc structure and the size of the CDxs could well determine the preferred binding mode in real systems. In fact, the disposition of ferrocenecarboxylic acid (FcMA) in β-CDx cavity is altered by dissociation of its carboxyl group,[6] and the orientation of Fc in β-CDx cavity differs markedly from that in γ-CDx cavity.[7] Despite the publication of over 20 articles on Fc derivative–CDx complexes,[5–8] the orientation of Fc in CDxs cavity has not been determined to date. This difficulty is due to

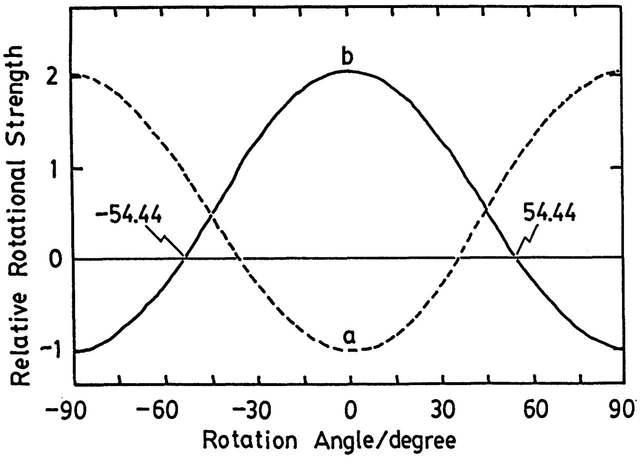

Fig. 1. The dependence of the calculated rotational strength of a CDx–chromophore complex on the rotation angle in the X–Z plane. Curves a and b are the transitions normal and parallel to the molecular axis of CDxs, respectively.

the uncertainty of the assignment of the electronic absorption band of Fc and its derivatives.[9] By preparing a Fc derivative which can bind to CDxs cavity in only one binding mode, we can infer the orientation of other Fc derivatives in CDx cavity by comparing their ICD spectra. In addition, it may be possible to conjecture the polarization direction of UV bands of Fc derivatives. For these reasons we have prepared compound **I** (Fig. 2 inset) and measured its ICD spectra in the presence of β-CDx. For this molecule, only an equatorial inclusion is possible because of size limitations. As will be shown below, the orientation of other Fc derivatives in β- or γ-CDxs was conjectured based on the ICD spectrum of **I** in β-CDx.

Experimental

Measurements. UV-visible absorption and ICD spectra were recorded at 20 °C on a Shimadzu UV-250 spectrophotometer and JASCO J400X spectrodichrometer, respectively. Cells of pathlength 0.5, 1, 2, 5, 10, and 20 mm were used.

Materials. Fc, FcMA, and 1,1′-ferrocenedicarboxylic acid (FcDA) were commercially available reagents and were recrystallized from ethyl acetate, hexane, and ethanol, respectively. β-CDx and γ-CDx were donated by Japan Maize Product Co., and recrystallized from water. Fc-β-CDx and Fc-γ-CDx 1 : 1 complexes were prepared accodrding to the method reported in the literature.[7,8f)] Anal. For Fc-β-CDx complex, Found: C, 45.96; H, 6.49; Fe, 4.0%. Calcd for $C_{52}H_{80}O_{35}Fe \cdot 1.5H_2O$: C, 46.26; H, 6.35; Fe, 4.14%. For Fc-γ-CDx complex, Found: C, 45.57; H, 6.45; Fe, 3.5%. Calcd for $C_{58}H_{90}O_{40}Fe \cdot 2H_2O$: C, 45.85; H, 6.24; Fe, 3.68%. Compound **I** was synthesized from 1,1′-ferrocenediol and 1,11-dichloro-3,6,9-trioxaundecane according to the literature.[10)] Anal. Found: C, 57.23; H, 6.37; Fe, 14.6%. Calcd for $C_{18}H_{24}O_5Fe$: C, 57.46; H, 6.43; Fe, 14.84%. Mp 59.5—60 °C (lit, 59—61 °C).[10a)]

Results

Figure 2 shows the UV-visible absorption and ICD spectra of **I** in the presence of β-CDx in ethylene glycol. The shape of the absorption spectrum is similar to that of Fc (Fig. 3), indicating that the attached crown unit does not significantly affect the electronic structure of the Fc chromophore. Corresponding to the absorption peaks at approximately 430 and 220 nm, a negative and positive ICD peak appeared, respectively. Continuous variation experiments for the determination of complex stoichiometry were not carried out through Figs. 2 to 5,

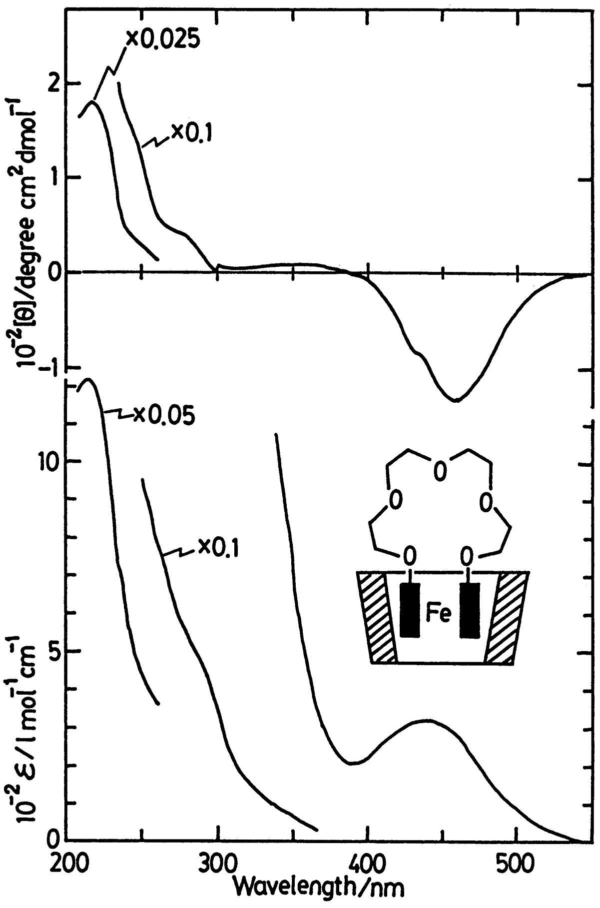

Fig. 2. ICD (top) and UV-visible (bottom) spectra of **I** in the presence of β-CDx in ethylene glycol. [**I**]/M=9.98×10^{-4} and [β-CDx]/M=0.020.

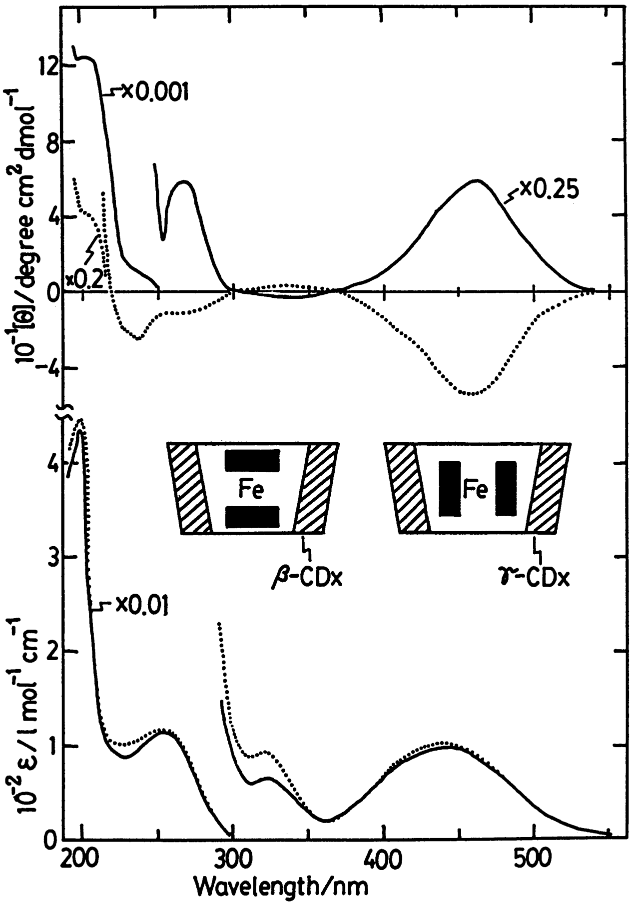

Fig. 3. ICD (top) and UV-visible (bottom) spectra of Fc-β-CDx (solid lines) and Fc-γ-CDx (dotted lines) in ethylene glycol. [Fc-β-CDx]/M=[Fc-γ-CDx]/M=0.001.

since 1 : 1 complex formation between β- or γ-CDx and Fcs has been established by many studies.[5—8]

Figure 3 shows spectra of Fc-β-CDx and Fc-γ-CDx 1 : 1 complexes in ethylene glycol. In the absorption spectra, peaks appear at around 200, 250—260, 330 and 440 nm. ICD spectra of Fc-β-CDx and Fc-γ-CDx complexes are interesting in that their signals are opposite over a wide range of wavelengths.[8p,r] Except at 300—370 nm, Fc-β-CDx complex produced positive ICD peaks or shoulders associated with each absorption peak, while Fc-γ-CDx complex showed negative ICD over a wide range of wavelengths. Note, however, that both complexes produced a positive ICD signal corresponding to the transition at approximately 200 nm.

Absorption and ICD spectra of FcMA in the presence of β-CDx or γ-CDx at pH 2 and 9 are shown in Fig. 4. The general features of the absorption spectra are similar to the spectrum of Fc (Fig. 3) but some differences occur, suggesting that the carboxyl group affects the Fc chromophore to some extent. In the presence of β-CDx at pH 9, i.e. where the carboxyl group is dissociated, the sign of the ICD spectrum is negative, except at <220 nm. On the other hand, it is positive in all regions when it is not dissociated (pH 2). The wavelengths of the absorption maxima and ICD peaks or troughs are in relatively good agreement. In the presence of γ-CDx, ICD was negative except at ca. 290—380 nm. Three troughs were observed at ca. 200—220, 270, and 470—480 nm at both pH 2 and 9.

Figure 5 shows the spectra of FcDA in the presence of β-CDx or γ-CDx at pH 2 and 9. The shape and intensity of the absorption spectrum change with dissociation of the carboxyl groups. However, the shape of the absorption spectra of FcDA is roughly similar to that of Fc without substituent groups (Fig. 3). An absorption band at around 220—230 nm is a band which lie on the tail of the higher transition band, since the absorption coefficient increases dramatically in the wavelength shorter than 200 nm (not shown). The ICD spectra in the presence of β-CDx are complex at

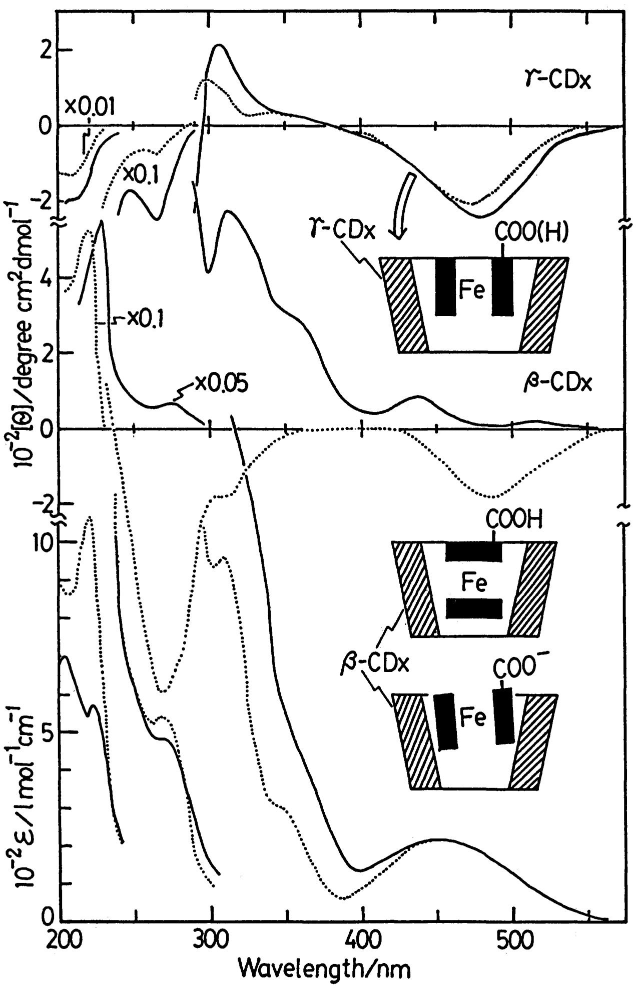

Fig. 4. ICD (middle and top) and UV-visible (bottom) spectra of FcMA in the presence of β-CDx (middle and bottom) or γ-CDx (top) at pH 2 (solid lines) and 9 (dotted lines). [β-CDx]/M=[γ-CDx]/M=0.010 and [FcMA]/M=0.001.

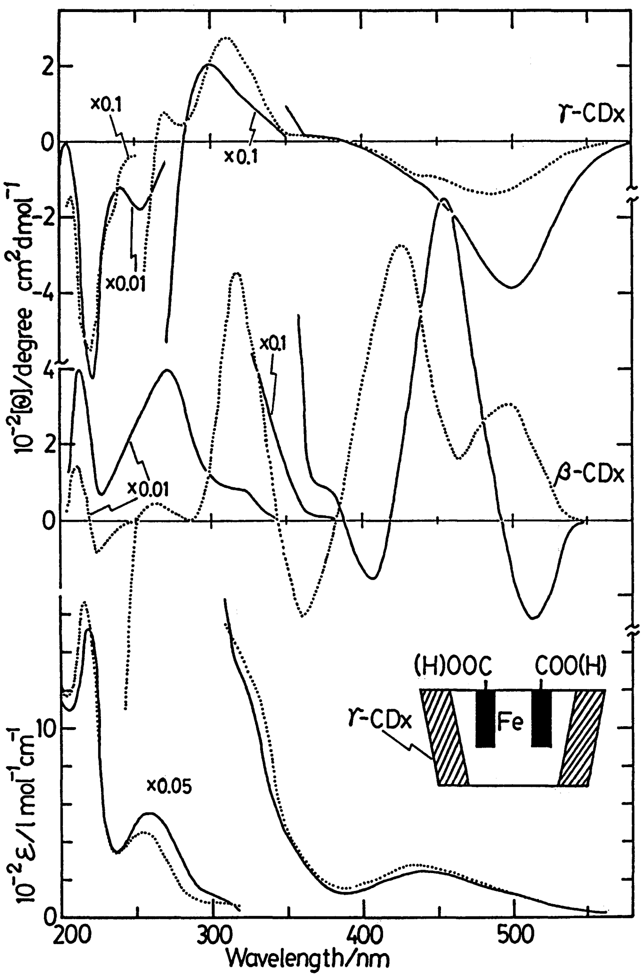

Fig. 5. ICD (middle and top) and UV-visible (bottom) spectra of FcDA in the presence of β-CDx (middle and bottom) or γ-CDx (top) at pH 2 (solid lines) and 9 (dotted lines). [β-CDx]/M=[γ-CDx]/M=0.010 and [FcDA]/M=0.001.

both pH 2 and 9, although the ICD pattern in the region <370 nm at pH 2 is relatively similar to that of FcMA at pH 2. Corresponding to an absorption maximum at around 220 nm, a positive ICD peak was observed at both pH 2 and 9. In contrast, ICD spectra in the presence of γ-CDx is relatively simple, showing negative signs in a wide range of wavelengths. The shape of the ICD curves is similar to each other at both pH 2 and 9, and resembles that of FcMA in the presence of γ-CDx (Fig. 4).

Discussion

From its shape and size, **I** can be trapped in β-CDx cavity only as an equatorial inclusion, as shown in the inset of Fig. 2. Based on the arguments (i) and (ii) mentioned in the introduction, the polarization direction of the band at the longest wavelength is not parallel to the β-CDx axis. Judging from Fig. 1 curve b, it is inclined by more than 54.44 degrees from the molecular axis of β-CDx. By argument (iii) and from the intensity change on rotation in the X–Z plane (Fig. 1), the Fc in Fc–γ-CDx complex (Fig. 3) appears to have a similar disposition to that of **I** in β-CDx cavity (equatorial inclusion), while that in Fc–β-CDx complex is completely different. In addition, since the positions of an ICD trough of Fc–γ-CDx complex and ICD peak of Fc–β-CDx complex coincide almost exactly at 460 nm, they seem to be almost normal to each other. Accordingly, the inclusion of Fc in Fc–β-CDx complex is considered to be close to axial. These results on the disposition of Fc in β- or γ-CDx cavity accord essentially with those obtained by NMR technique for solid samples. Namely, according to what one of the reviewers taught us, the Cp–Fe–Cp axis of Fc molecule declines from the axis of β-CDx by 6.5 degrees but by 72 degrees from that of γ-CDx.[11] Since the ICD pattern of FcMA in the presence of β-CDx at pH 9 (Fig. 4) is quite similar to that of Fc in Fc–γ-CDx complex (Fig. 3), the inclusion of FcMA by β-CDx also appears almost equatorial at pH 9. Although a clear ICD peak was not observed in the region >400 nm, the arrangement of this molecule at pH 2 appears to be close to axial in β-CDx cavity, since the ICD spectroscopic pattern of FcMA in the 200—400 nm region at this pH is similar to that of Fc–β-CDx complex (Fig. 3). The stoichiometry and inclusion type of CDx–chromophore host–guest complexes are determined by many factors. In the case of FcMA–β-CDx system, the pH value of the solution affects the type of inclusion. In alkaline solution, the carboxyl group dissociates and the resultant highly hydrophilic carboxylate anion may resist to be deeply accommodated into β-CDx cavity. As a result, an equatorial inclusion occurs, although FcMA may be deeply trapped by an axial inclusion when the carboxyl group is not dissociated in acidic solution, i.e. when it is less hydrophilic than carboxylate anion. Judging from the spectroscopic pattern of ICD, the inclusion of FcMA and FcDA in γ-CDx is similar at both pH 2 and 9, and it appears to be equatorial from the presence of a trough at ca. 380—550 nm. On the other hand, a zig-zag pattern in the wavelength longer than 380 nm (Fig. 5) indicates that the orientation of FcDA in β-CDx cavity is obscure both when the carboxyl groups are dissociated and undissociated. Because of steric hindrance by the two carboxyl groups, FcDA may be trapped in β-CDx cavity obliquely. In this respect, the results in FcDA–γ-CDx system suggest the possibility that the mutual positions of the two carboxyl groups may change on inclusion. That is, the two carboxyl groups would take many conformations to each other with respect to Cp–Fe–Cp axis in solution. Especially, there is no particular requirement that the two carboxyl groups of FcDA must stay in the same side of Fe atom in the absence of γ-CDx. And, if FcDA molecule is accommodated to γ-CDx cavity in the same conformations as it is in solution, it is conceivable from the consideration using the CPK molecular model that a zig-zag ICD pattern appears in >380 nm because of steric hindrance, although the cavity of γ-CDx is larger than that of β-CDx. However, no such pattern was observed in reality as shown in Fig. 5. Now that the Cp rings are much more hydrophobic than carboxyl groups, it would be most natural to think that the two Cp moieties are trapped in γ-CDx first, leaving the carboxyl groups behind (see the inset in Fig. 5).

The absorption peak in the longest wavelength region has been proposed to contain two components with absorption maxima at around 420—430 and 460—470 nm, and both are assigned as d-d transitions.[9] Interestingly, an ICD peak in the axial inclusion system (Fig. 3, Fc–β-CDx system) and ICD troughs in the equatorial inclusion system (Fig. 2, Fc–γ-CDx system in Fig. 3, FcMA–γ-CDx system in Fig. 4, and FcMA–β-CDx system at pH 9 in Fig. 4) always appear at around 460—470 nm. Hence, out of two components included in this band, the one to the red is deemed to have a polarization direction along the Cp–Fe–Cp axis, as has been found for crystals of Fc.[9f] This result appears to be in agreement with low temperature studies[9b] which indicate that the band is a symmetry-forbidden d-d transition containing charge-transfer (CT) character.

The ICD intensity of Fc–γ-CDx complex is much weaker than that of Fc–β-CDx complex. Two reasons are conceivable for this phenomenon. The first one is attributed to a difference in polarization direction. As shown in Fig. 1 curve b, when the transition dipole which is parallel to the molecular axis of CDx rotates by ca. 90 degrees in the X–Z plane, the calculated rotational strength lessens to ca. half of the original value, together with a change of ICD sign. Accordingly, for example, if a transition dipole at 460 nm which has its polarization direction along the Cp–Fe–Cp axis rotates 90 degrees in the X–Z plane (this corresponds to a change from an axial to an equatorial inclusion), its intensity becomes ca. one-half of the original value.

However, since the observed ICD intensity of Fc–γ-CDx complex is about 25% of that of Fc–β-CDx complex at 460 nm, another factor must be taken into account in order to explain the intensity difference between Fc–β-CDx and Fc–γ-CDx complexes. This factor is the distance between the Fc unit and CDx. The rotational strength is known to be proportional to the inverse of the cube of the distance.[12] Since the radius of β-CDx cavity (4.7—5.2 Å) is about 80% of that of γ-CDx cavity (6.0—6.4 Å),[13] the rotational strength in γ-CDx is estimated to be about half ($0.8^3 \fallingdotseq 0.5$) of that in β-CDx. Thus, the smaller ICD intensity at 460 nm in Fc–γ-CDx complex is quantitatively ($0.5 \times 0.5 = 0.25$, 25%) rationalized by taking the above two factors into account. If, however, the orientation of Fc in Fc–β-CDx complex is equatorial and that in Fc–γ-CDx complex is axial, the ICD intensity at 460 nm would be almost comparable by the same argument, although the sign of ICD is opposite to each other (negative and positive for Fc–β-CDx and Fc–γ-CDx systems, respectively). Thus the observed ICD sign and intensity relationship between Fc–β-CDx and Fc–γ-CDx systems can be interpreted reasonably only when the inclusion of Fc in Fc–β-CDx complex is axial while that of Fc–γ-CDx complex is equatorial. In this way, these considerations also lend support to our conclusion about the disposition of Fc in Fc–β-CDx and Fc–γ-CDx complexes.

Based on the knowledge obtained above, we are now able to resolve a question which has been disputed for a long time,[9] i.e. the assignment of an intense band of Fcs at around 200nm. Two opinions exist concerning the assignment of this band. Some[9a] groups have assigned this band as a π–π^* transition of the Cp rings, while others[9b,c] have interpreted this as a CT transition between the Cp rings and iron(II). As shown in Figs. 2 and 3, Fcs produce a positive ICD peak corresponding to this band when they are included by CDxs as both an axial and equatorial inclusion. If this band is a π–π^* transition, the sign of the ICD should be positive for an equatorial inclusion and negative for an axial inclusion based on the arguments (i)—(iii) above (note that an equatorial inclusion of Fc is equivalent to an axial inclusion of the Cp rings). Thus, the results do not agree with assignment as a "pure" π–π^* transition. Can, then, the observed ICD be reasonably interpreted as a CT transition? As depicted in Fig. 1, transitions whose polarization directions are within 54.44 degrees from the molecular axis of CDxs produce positive ICD whenever Fc is in the CDx cavity (criterion (ii)). On the other hand, the d_{xz} and d_{yz} orbitals of iron decline theoretically 45 degrees from the Cp–Fe–Cp axis of Fc. Hence, whether or not Fcs are included in CDxs cavity by an axial or equatorial inclusion, these orbitals are still declining 45 degrees from the molecular axis of CDxs. This means that if these orbitals are used in CT between the Cp rings and iron, then the sign of the ICD signal becomes positive. In this way, an intense band of Fcs at around 200 nm is reasonably assigned to a CT transition. Although negative ICD is observed at ca. 220—230 nm in FcDA–γ-CDx system, this may be due to the strong electron-withdrawing effect of the carboxyl groups attached to the Cp rings.

Previous reports[9] also discuss the polarization direction of other bands. Using crystals of Fc,[9f] the bands at ca. 260 and 320 nm are proposed to possess polarization along the Z (Cp–Fe–Cp) axis mixed with some polarization along the X or Y axis. Figures 2 and 3 indicate that the present results do not contradict this proposal concerning the 260 nm band, since the sign of ICD of this band is the same as that of the 440 nm band which is polarized along the Z (Cp–Fe–Cp) axis. The sign of ICD between 300 and 370 nm suggests that the band at ca. 320 nm is polarized more strongly along the X or Y direction rather than the Z direction. Otherwise, negative ICD is not produced in this region.

Conclusion

The proposed orientations of Fcs in CDxs are presented in each Figure. Based on the ICD spectra of **I** in β-CDx cavity, the orientations of Fcs in CDxs cavity are determined, and an answer is given for the assignment of a band of Fc which has been in dispute. We would like to stress here the importance of using CDxs for determination of the polarization direction of bands of aromatic compounds. In order to determine the polarization direction of the electronic absorption of non-crystalline compounds experimentally, measurements of dichroic spectra in stretched polymer sheet,[14] and of ICD in mesophases have been of great use.[15] However, there are limitations to these methods. Firstly, since the most essential factor is the alignment of solute molecules, it is difficult to apply these methods to relatively round or square molecules. Round molecules are, of course, not easily studied even in CDx systems. However, as shown in this paper, the orientation of round guest molecules in CDxs cavity can be regulated by modifying their structure. ICD spectra of such guest-oriented inclusion complexes then enable the polarization direction to be determined. Secondly, due to the absorption of polymers or mesophases, only a few polymers can be used for bands lying shorter than ca. 220 nm. In this respect, the CDx system appears to be superior, since water and alcohols are generally used. If water is used, this method is applicable to bands as short as ca. 190 nm.

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