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Complexation behaviour of a CT complex composed of 9,10-bis(3,5-dihydroxyphenyl)anthracene and viologen derivatives

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A chiral charge-transfer (CT) complex was formed using achiral 9,10-bis(3,5-dihydroxyphenyl)anthracene (BDHA) as an electron donor and achiral 1,1′-dimethyl-4,4′-bipyridinium dichloride ($MVCl_2$) as an electron acceptor. This chiral CT complex can include *n*-alkyl alcohol molecules as guests. On the other hand, when 1,1′-diphenyl-4,4′-bipyridinium dichloride and 1,1′-dibenzyl-4,4′-bipyridinium dichloride were used as electron acceptors, achiral CT complexes without guests were formed. It was found that the chiral crystallisation of the BDHA/$MVCl_2$–CT host system was caused by steric and electric intermolecular interactions between host component molecules BDHA and $MVCl_2$ during crystallisation.

Keywords: 9,10-bis(3,5-dihydroxyphenyl)anthracene; charge-transfer complex; chiral; spontaneous resolution; viologen

1. Introduction

The properties of organic compounds in the solid state are different from those in the solution state because molecules in the solid state are densely packed and strongly influenced by neighbouring molecules. To date, several solid-state chiral supramolecular organic host compounds for chiral molecular recognition and enantioselective reactions have been reported (*1*). Recently, the demand for modulating the size and shape of the chiral cavity of such chiral host systems in order to correspond to various guest molecules has been increased. Therefore, supramolecular organic host systems composed of two or three types of organic molecules have been developed (*2*). If a solid-state host system is composed of two or more types of organic molecules, the chemical and physical properties of the host system may be easily controlled by changing the component molecules without additional synthesis steps. Although a lot of charge-transfer (CT) complexes have been reported to date (*3*), we have focused on utilising donor–acceptor interactions as intermolecular forces for preparing and controlling a supramolecular host structure (*4*). Furthermore, we have developed a coloured chiral CT host system that can include alcohol molecules as guests, using chiral 1,1′-bi-2-naphthol and 1,1′-dibenzyl-4,4′-bipyridinium dichloride ($BVCl_2$, benzylviologen) as an electron donor and acceptor, respectively (*5*). In this manner, typical chiral functional organic materials are prepared using chiral molecules. However, most chiral molecules are not easily available and are more expensive than achiral molecules. Therefore, if chiral CT host systems can be prepared from achiral component molecules, they can be proved to be useful from practical and economic viewpoints. Recently, the preparation of a chiral CT complex using achiral 9,10-bis(3,5-dihydroxyphenyl) anthracene (BDHA), which is one of the most important component organic molecules used for preparing supramolecular complexes (*6*), as an electron donor and achiral 1,1′-dimethyl-4,4′-bipyridinium dichloride ($MVCl_2$, methylviologen) as an electron acceptor has been reported (*7*). This BDHA/$MVCl_2$–CT complex has a chiral cavity in spite of being prepared from achiral component molecules and can include *n*-alkyl alcohols as guests. On the other hand, when 1,1′-diphenyl-4,4′-bipyridinium dichloride ($PVCl_2$, phenylviologen) and $BVCl_2$ were used as electron acceptors, achiral CT complexes without guests were formed. However, in this system, the detailed structural analyses of the obtained CT complexes by X-ray crystallographic analyses were unsatisfactory. Therefore, the complexation behaviour of the BDHA/$MVCl_2$–CT system has not been explained in detail.

In this paper, we describe the complexation behaviour and crystal structure of a CT complex composed of achiral BDHA and viologen derivatives, evaluated using X-ray crystallographic analysis. Three types of viologen derivatives – $MVCl_2$, $PVCl_2$ and $BVCl_2$ – were used. Generally,

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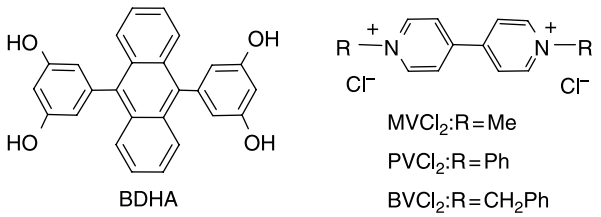

Scheme 1. Component electron donor and acceptor.

it is difficult to predict the structure of supramolecular complexes prepared using new component molecules. Therefore, this study is a significant step towards the advancement in the design of novel two-component chiral supramolecular host systems (Scheme 1).

2. Results and discussion

In the BDHA/$MVCl_2$–CT system, the inclusion of three simple types of *n*-alkyl alcohols – ethanol (EtOH), *n*-propanol (*n*-PrOH) and *n*-butanol (*n*-BuOH) – as guest molecules was studied. The guest molecules were included in the BDHA/$MVCl_2$–CT system by means of crystallisation from these guest solutions. A mixture of BDHA and $MVCl_2$ was dissolved in the three guest solutions and left to stand at room temperature. After 5–10 days, orange-coloured CT complexes including each guest molecule [**I** obtained from the EtOH solution (7 mg), **II** obtained from the *n*-PrOH solution (7 mg) and **III** obtained from the *n*-BuOH solution (8 mg)][1] were obtained by crystallisation from each guest solution (see Section 3). The colours of these CT complexes were quite different from those of the component solids (BDHA, white solid; $MVCl_2$, light yellow solid).

To study the inclusion mechanism of this BDHA/$MVCl_2$–CT host system, the crystal structures of **I**, shown in Figure 1, were investigated by X-ray crystallographic analysis (*7*). Although all the component molecules used in this experiment are achiral, the CT complex is a chiral crystal. The stoichiometry of **I** is BDHA:$MVCl_2$:EtOH = 1:1:1, and the space group is $P2_12_12$. The molecules of BDHA are connected by chloride ions

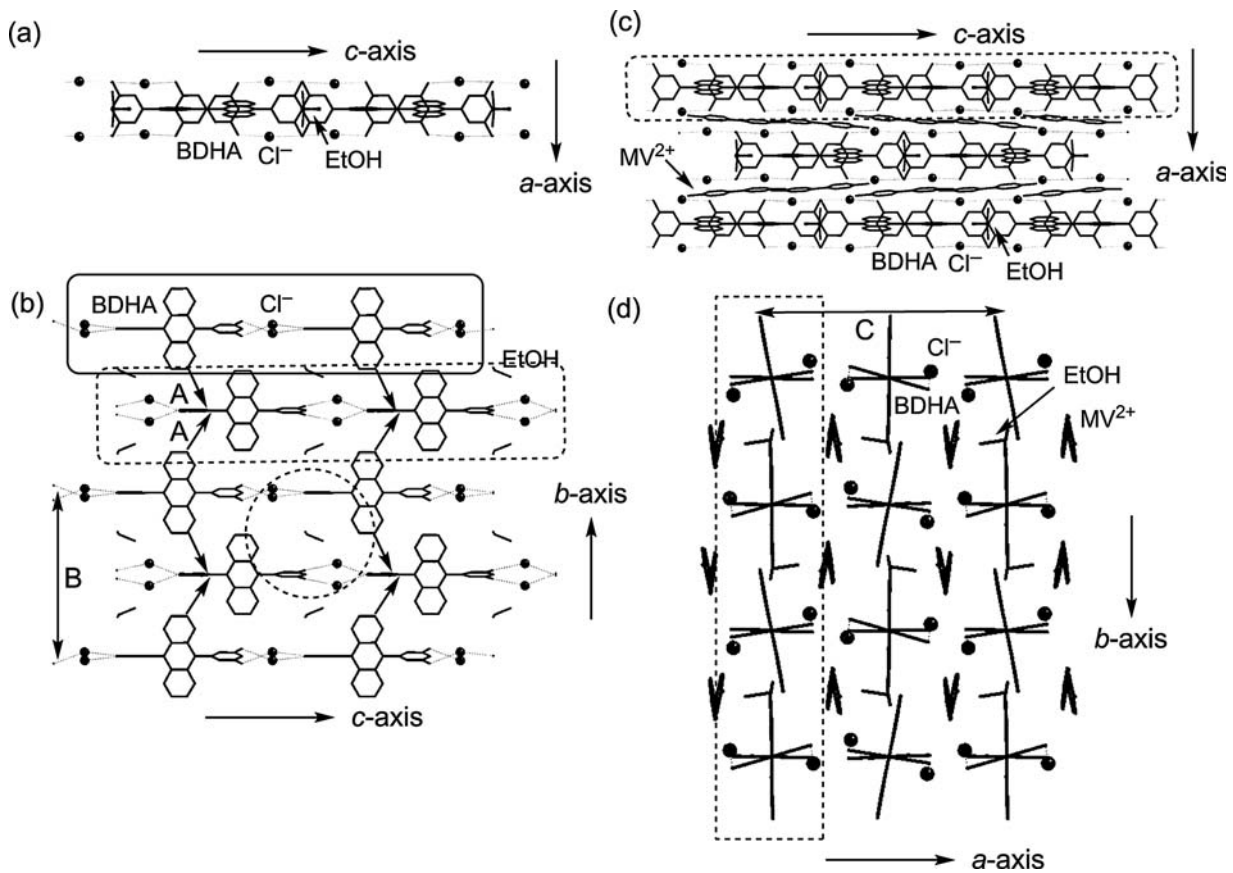

Figure 1. Crystal structures of **I**. Cl^- are represented as balls. (a) Extracted 2D layered structure unit observed along the *b*-axis. (b) Extracted 2D layered structure unit observed along the *a*-axis. MV^{2+} is squeezed. The solid and dotted rectangles denote the 1D structure unit. The dotted circle shows a chiral cavity. Arrows A denote anthracene–benzene edge-to-face interactions. (c) Packing diagram observed along the *b*-axis. The dotted rectangle denotes a 2D layered structure unit. (d) Packing diagram observed along the *c*-axis. The dotted rectangle denotes a 2D layered structure unit.

(Cl^-; balls, Figure 1) through hydrogen bonds. Two types of 1D structure units are formed along the *c*-axis (Figure 1(a)). One is composed of molecules of BDHA wherein the torsion angles between benzene and anthracene rings are 87.9° and 107.5° (solid rectangles, Figure 1(b)). The other is composed of molecules of BDHA wherein the torsion angles between benzene and anthracene rings are 92.6° and 106.4° (dotted rectangles, Figure 1(b)). Moreover, a two-dimensional (2D) layered network structure is formed along the *b*- and *c*-axes by the self-assembly of these two types of 1D structure units through anthracene–benzene edge-to-face interactions (arrows A, Figure 1(b), 2.95 Å).[2] Disordered guest EtOH molecules are included in the chiral cavity (dotted circle, Figure 1(b)) formed by the self-assembly of these 1D structure units in the 2D layered network structure (Figure 1(b)). In this case, a hydrogen bond and a CH–π interaction between EtOH and the host component molecule are not observed.[2] Methylviologen ions (MV^{2+}) connect the 2D layered network structures (dotted rectangle, Figure 1(c),(d)) by CT interactions along the *a*-axis and form the chiral crystal (Figure 1(c),(d)). The distances between the centre of the six-member ring of MV^{2+} and the centre of the nearest six-member ring of BDHA are 3.62 and 3.89 Å.

Similarly, the crystal structures of **II** and **III** (*7*), shown in Figures 2 and 3, respectively, were investigated by X-ray crystallographic analyses. Thus far, the crystal structures of complex **II** including *n*-PrOH molecules as guests have not been investigated. In this study, complex **II** was found to be a chiral crystal similar to complexes **I** and **III**. The stoichiometries of complexes **II** and **III** are BDHA:$MVCl_2$:*n*-PrOH (or *n*-BuOH) = 1:1:1, and the space groups are the same $C222_1$. The crystal structures of **II** and **III** are similar to those of **I**. These complexes, similar to complex **I**, had a 1D structure unit that was composed of molecules of BDHA and Cl^- (balls, Figures 2 and 3) and that was formed along the *b*-axis (Figures 2(a) and 3(a)). This 1D structure unit was composed of one type of molecules of BDHA which is different from complex **I**. In complex **II**, the torsion angles between the benzene and anthracene rings of BDHA were 72.3° and 89.6°.

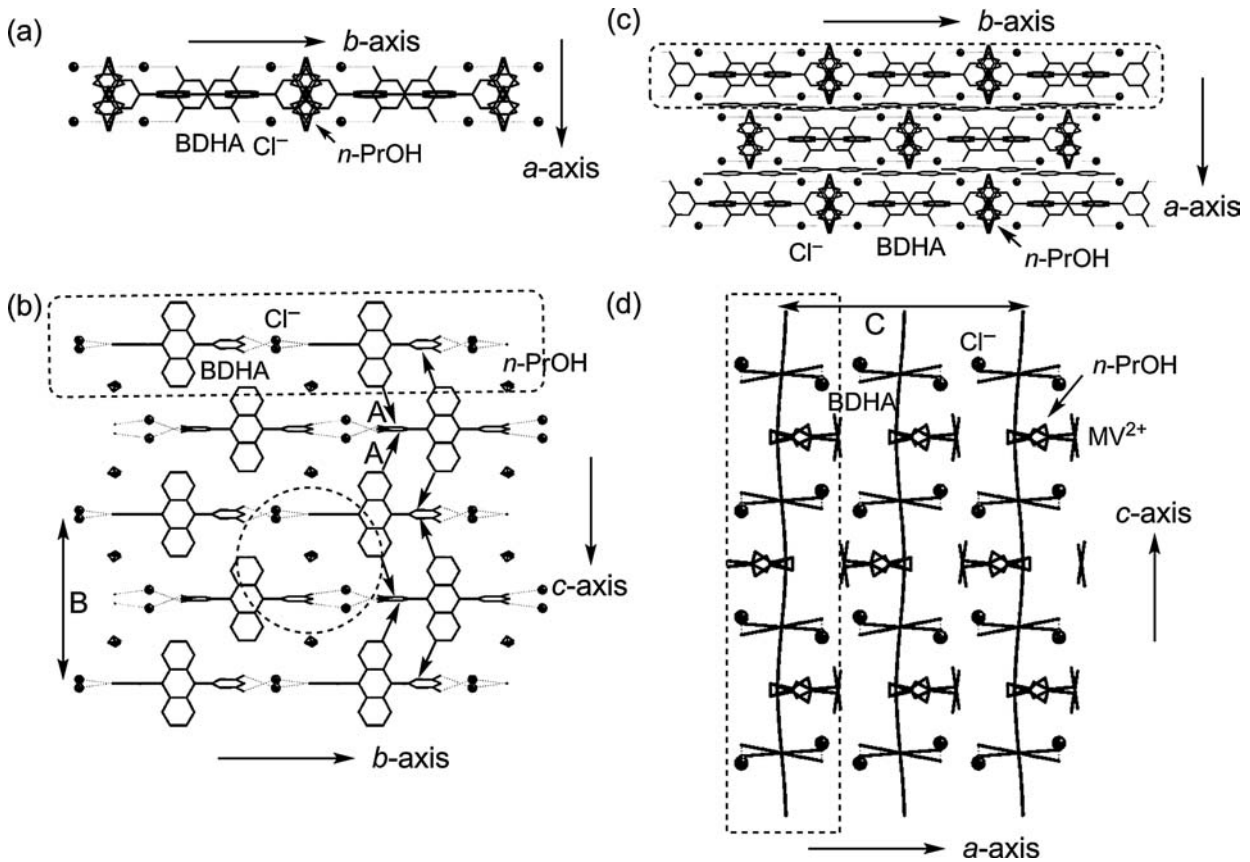

Figure 2. Crystal structures of **II**. Cl^- are represented as balls. (a) Extracted 2D layered structure unit observed along the *c*-axis. (b) Extracted 2D layered structure unit observed along the *a*-axis. MV^{2+} is squeezed. The dotted rectangle and circle denote a 1D structure unit and a chiral cavity, respectively. Arrows A denote anthracene–benzene edge-to-face interactions. (c) Packing diagram observed along the *c*-axis. The dotted rectangle denotes a 2D layered structure unit. (d) Packing diagram observed along the *b*-axis. The dotted rectangle denotes a 2D layered structure unit.

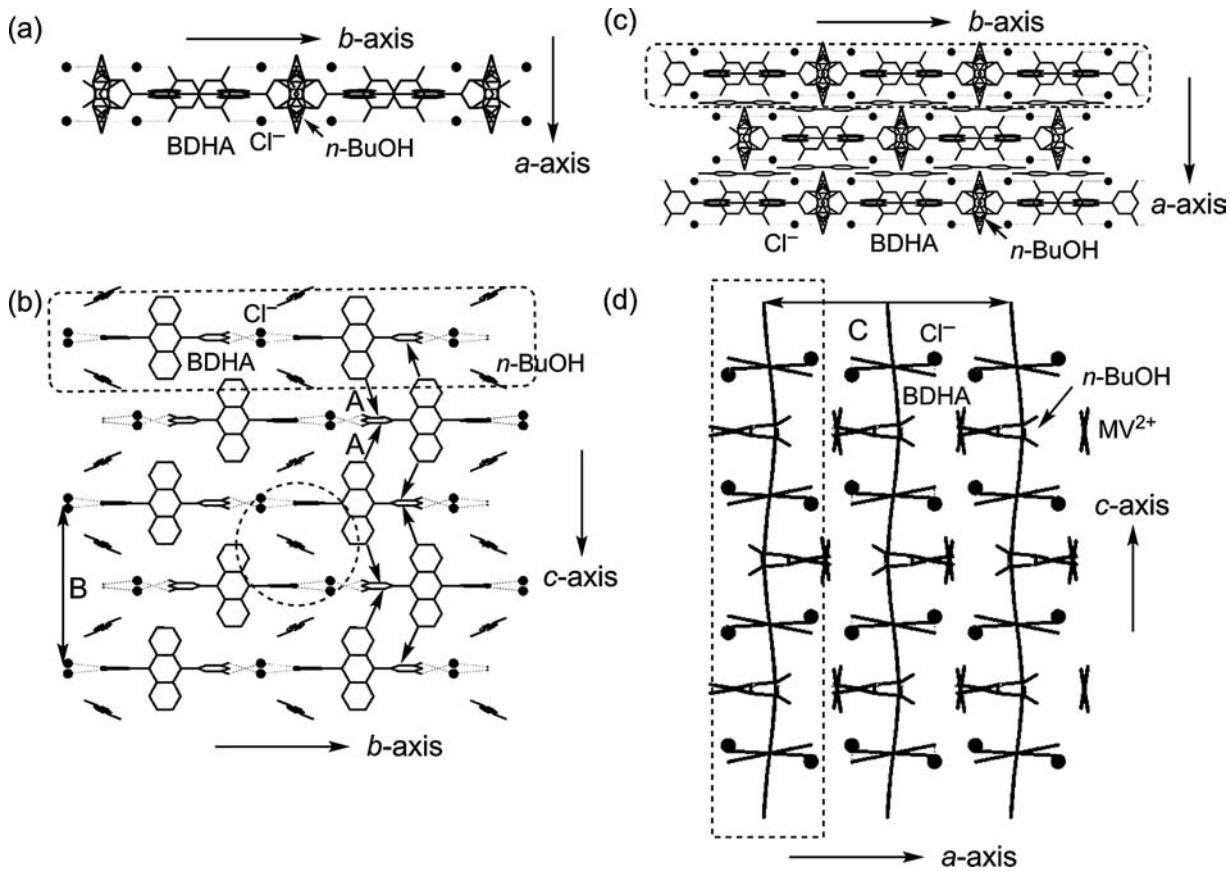

Figure 3. Crystal structures of **III**. Cl^- are represented as balls. (a) Extracted 2D layered structure unit observed along the *c*-axis. (b) Extracted 2D layered structure unit observed along the *a*-axis. MV^{2+} is squeezed. The dotted rectangle and circle denote a 1D structure unit and a chiral cavity, respectively. Arrows A denote anthracene–benzene edge-to-face interactions. (c) Packing diagram observed along the *c*-axis. The dotted rectangle denotes a 2D layered structure unit. (d) Packing diagram observed along the *b*-axis. The dotted rectangle denotes a 2D layered structure unit.

On the other hand, in complex **III**, the torsion angles between the benzene and anthracene rings of BDHA were 93.1° and 109.3°. In both these complexes, the self-assembly of these 1D structure units (dotted rectangle, Figures 2(b) and 3(b)) due to anthracene–benzene edge-to-face interactions (arrows A, Figures 2(b) and 3(b), 2.98 Å for complexes **II** and **III**) results in the formation of a 2D layered network structure along the *b*- and *c*-axes (Figures 2(b) and 3(b)). Although the guest *n*-PrOH and *n*-BuOH molecules are disordered in both the complexes, they are included in the chiral cavity (dotted circle, Figures 2(b) and 3(b)) formed by the self-assembly of these 1D structure units in the 2D layered network structure due to the absence of a hydrogen bond and a CH–π interaction between the guest *n*-alcohol and host component molecules.[2] MV^{2+} (Figures 2(c),(d) and 3(c),(d)) connect these 2D layered network structures (dotted rectangle, Figures 2(c),(d) and 3(c),(d)) by CT interactions along the *a*-axis and form a chiral crystal (Figures 2(c),(d), 3(c),(d)). The distances between the centre of the six-member ring of MV^{2+} and the centre of the nearest six-member ring of BDHA in complexes **II** and **III** are almost the same, i.e. 3.73 and 3.72 Å, respectively.

A comparison of the sizes of the chiral cavities of **I**, **II** and **III** reveals that the sizes depend on the type of included guest molecule. When the guest molecule is changed from EtOH to *n*-PrOH to *n*-BuOH, the distance between the shared 1D structure units in the 2D layered network structure (arrow B, Figures 1(b)–3(b)) reduces from 14.85 to 14.81 to 14.70 Å. On the other hand, the distance between the shared 2D layered network structures (arrow C, Figures 1(d)–3(d)) increases from 13.82 to 13.89 to 14.09 Å. This shows that this chiral CT host system includes guest molecules by tuning the distance between the 1D structure units and between the 2D layered network structures.

From X-ray crystallographic analyses of these complexes, in all the chiral complexes, intermolecular interactions between the guest *n*-alcohol and the host component were not observed.[2] Moreover, the structure of the host complex in all the chiral complexes was almost

the same. These results suggest that chiral crystallisation of the BDHA/$MVCl_2$–CT host system is mainly caused by steric and electric intermolecular interactions between BDHA and $MVCl_2$ and not by intermolecular interactions between the guest *n*-alkyl alcohol and the host component.

The measured diffuse reflectance spectra (DRS) of chiral CT complexes **I**–**III** are shown in Figure 4. It is well known that the colour of a CT complex primarily depends on the intermolecular distance between the electron donor and acceptor molecules. The X-ray crystallographic analyses show that there is no remarkable difference in the distances between the electron donor and the acceptor molecules in the three complexes, which is consistent with the similar colours of the three complexes. However, the DRS of these CT complexes differ only slightly. This is because complex **I** absorbs slightly longer wavelengths than **II** and **III**. This difference might be related to the distance between the donor and acceptor molecules.

X-ray crystallographic analyses of the BDHA/$PVCl_2$–CT system and BDHA/$BVCl_2$–CT system were carried out. A procedure similar to that used for the analysis of the BDHA/$MVCl_2$–CT system was adopted. The CT complex was formed first by crystallisation from the EtOH solution containing BDHA along with one of the two types of viologen molecules at a time. Both the EtOH solutions were left to stand at room temperature for 6–8 days. As a result, coloured complexes **IV** (8 mg) from the BDHA/$PVCl_2$–CT system and **V** (11 mg) from the BDHA/$BVCl_2$–CT system were obtained (see Section 3). Complexes **IV** and **V** are brown and purple in colour, respectively; the colours of the CT complexes depend on the viologen molecules. However, the colours of these CT complexes were quite different from those of the component solids (white solid for BDHA, $BVCl_2$ and $PVCl_2$).

The crystal structure of complex **IV** is shown in Figure 5. CT complex **IV** does not include guest EtOH molecules and is not a chiral crystal. The stoichiometry of complex **IV** is BDHA:$PVCl_2$:H_2O = 1:1:1 and the space

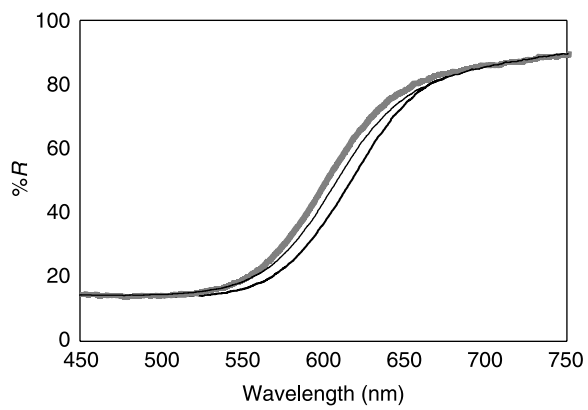

Figure 4. DRS of **I** (thick black line), **II** (grey line) and **III** (thin black line).

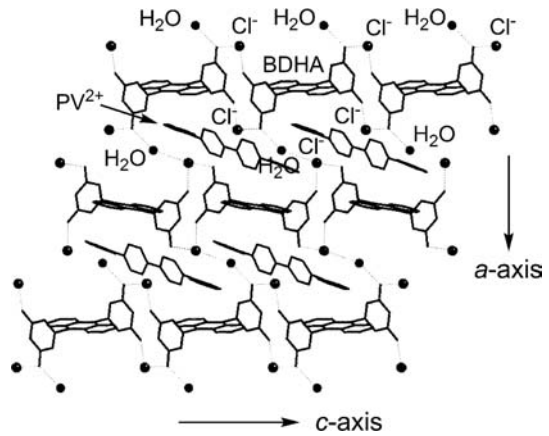

Figure 5. Crystal structure of **IV** observed along the *b*-axis. Cl^- and water molecules (H_2O) are represented as balls.

group is $P2_1/c$. The crystal structure of this complex is quite different from that of chiral complexes **I**, **II** and **III**. Characteristically, this crystal has a 3D network structure composed of BDHA connected by a hydrogen bond between a hydroxyl group of BDHA, Cl^- (balls, Figure 5) and water molecules (H_2O) (balls, Figure 5). Phenylviologen ions (PV^{2+}, Figure 5) are included in the cavity of the 3D network structure. The distance between the centre of the six-member ring of PV^{2+} and the centre of the nearest six-member ring of BDHA is 3.63 Å.

CT complex **V** obtained from the BDHA/$BVCl_2$ system also does not include any guest molecule. The crystal structures of complex **V** are shown in Figure 6. The

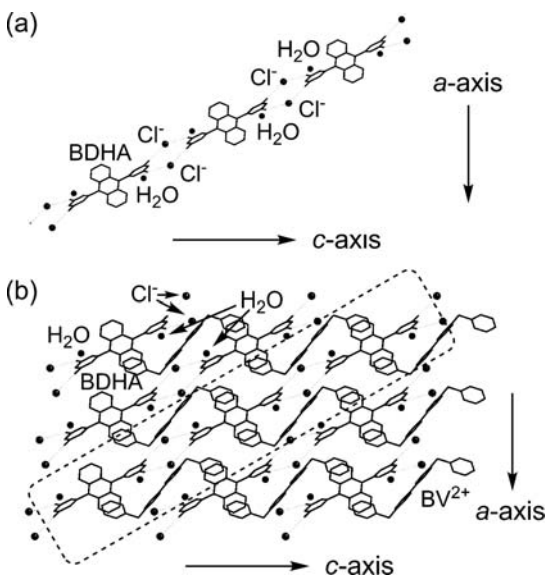

Figure 6. Crystal structures of complex **V**. Cl^- and H_2O are represented as balls. (a) Extracted 1D structure unit observed along the *b*-axis. (b) Packing diagram observed along the *b*-axis. The dotted rectangle denotes a 1D structure unit.

stoichiometry of complex **V** is BDHA:$BVCl_2$:H_2O = 1:1:1 and the space group is $P\bar{1}$. Although complex **V** is also not a chiral crystal, its crystal structure is different from that of complex **IV**. As opposed to complex **IV**, this crystal has a 1D structure unit composed of BDHA and Cl^- (balls, Figure 6(a)). In this 1D network structure, host component molecules BDHA are connected through a hydrogen bond between Cl^-. Water molecules (H_2O, balls, Figure 6) are linked to the hydroxyl group of BDHA by hydrogen bonds. Benzylviologen ions (BV^{2+}, Figure 6) maintain the complex by CT interactions with the 1D structure units (dotted rectangle, Figure 6(b)). The distance between the centre of the six-member ring of BV^{2+} and the centre of the nearest six-member ring of BDHA is 3.85 Å. From X-ray crystallographic analyses, it is inferred that since flexible benzyl groups of BV^{2+} are treated as guest molecules, EtOH molecules are not included as guests in the CT complex.

3. Experimental

3.1 General methods

All reagents were used directly as obtained commercially. Component molecules BDHA and three types of viologen derivatives were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Guest solutions were purchased from Wako Pure Chemical Industry (Osaka, Japan).

3.2 Formation of the supramolecular CT host complex

BDHA (10 mg, 0.025 mmol) and each of the three types of viologen molecules (0.025 mmol) were dissolved in guest *n*-alkyl alcohols (3–5 ml). After 5–10 days, coloured crystals were deposited and collected. The total weight of all the crystals obtained in a batch is 7–11 mg.

3.3 X-ray crystallographic study of the CT complex

X-ray diffraction data for single crystals were collected using BRUKER APEX. The crystal structures were solved by the direct method (*8*) and refined by full-matrix least-squares using SHELX97 (*9*). The diagrams were prepared using PLATON (*10*). Absorption corrections were performed using SADABS (*11*). Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. Crystallographic data for **I**: $C_{26}H_{18}O_4{\cdot}C_{12}H_{14}N_2Cl_2{\cdot}C_2H_6O$, $M = 697.62$, orthorhombic, space group $P2_12_12$, $a = 13.8192(12)$, $b = 14.8487(13)$, $c = 17.0490(15)$ Å, $V = 3498.4(5)$ Å^3, $Z = 4$, $D_c = 1.325$ g cm^{-3}, μ(Mo Kα) = 0.233 mm^{-1}, 21,881 reflections measured, 4558 unique, final $R(F^2) = 0.0581$ using 4348 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0604, $T = 130(2)$ K. CCDC 714754. Crystallographic data for **II**: $C_{26}H_{18}O_4{\cdot}C_{12}H_{14}N_2Cl_2{\cdot}C_3H_8O$, $M = 711.65$, orthorhombic, space group $C222_1$, $a = 13.8881(8)$, $b = 17.1239(10)$, $c = 14.8079(9)$ Å, $V = 3521.6(4)$ Å^3, $Z = 4$, $D_c = 1.3423(2)$ g cm^{-3}, μ(Mo Kα) = 0.233 mm^{-1}, 10,925 reflections measured, 4019 unique, final $R(F^2) = 0.0487$ using 3857 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0508, $T = 115(2)$ K. CCDC 727912. Crystallographic data for **III**: $0.5C_{26}H_{18}O_4{\cdot}0.5C_{12}H_{14}N_2Cl_2{\cdot}0.5C_4H_{10}O$, $M = 362.84$, orthorhombic, space group $C222_1$, $a = 14.0895(12)$, $b = 17.1652(14)$, $c = 14.6979(12)$ Å, $V = 3554.7(5)$ Å^3, $Z = 8$, $D_c = 1.356$ g cm^{-3}, μ(Mo Kα) = 0.233 mm^{-1}, 15,435 reflections measured, 2337 unique, final $R(F^2) = 0.0503$ using 2109 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0582, $T = 105(2)$ K. CCDC 714755. Crystallographic data for **IV**: $C_{26}H_{18}O_4{\cdot}C_{22}H_{18}N_2Cl_2{\cdot}H_2O$, $M = 793.70$, monoclinic, space group $P2_1/c$, $a = 21.1059(12)$, $b = 9.0081(5)$, $c = 21.2583(12)$ Å, $\beta = 111.3530(10)°$, $V = 3764.3(4)$ Å^3, $Z = 4$, $D_c = 1.4005(1)$ g cm^{-3}, μ(Mo Kα) = 0.227 mm^{-1}, 22,752 reflections measured, 8643 unique, final $R(F^2) = 0.0605$ using 6788 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0797, $T = 115(2)$ K. CCDC 727913. Crystallographic data for **V**: $C_{26}H_{18}O_4{\cdot}C_{24}H_{22}N_2Cl_2{\cdot}H_2O$, $M = 819.74$, triclinic, space group $P\bar{1}$, $a = 8.4425(10)$, $b = 9.4073(11)$, $c = 13.7738(16)$ Å, $\alpha = 91.467(2)°$, $\beta = 97.475(2)°$, $\gamma = 109.264(2)°$, $V = 1021.2(2)$ Å^3, $Z = 1$, $D_c = 1.3330(3)$ g cm^{-3}, μ(Mo Kα) = 0.211 mm^{-1}, 6475 reflections measured, 4525 unique, final $R(F^2) = 0.0536$ using 3574 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0704, $T = 115(2)$ K. CCDC 727914. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336-033; deposit@ccdc.cam.ac.uk).

3.4 Measurement of DRS of the CT complex

DRS of crystals were measured with a HITACHI U-4000 spectrometer.

4. Conclusion

A CT host system composed of achiral BDHA and $MVCl_2$ molecules was prepared. This CT host system has a chiral cavity in spite of being prepared from achiral component molecules and can include *n*-alkyl alcohols as guest molecules by tuning the packing of the shared 1D structure units composed of BDHA and Cl^- and of the 2D layered network structures. The crystal structures of BDHA/$MVCl_2$, BDHA/$PVCl_2$ and BDHA/$BVCl_2$–CT systems were analysed using X-ray crystallographic analyses. It was found that chiral crystallisation of the BDHA/$MVCl_2$–CT host system was caused by steric and electric intermolecular interactions between host component molecules BDHA and $MVCl_2$ during crystallisation. These results further

improve the abilities of the chiral CT host system and may be useful for the design of novel host systems for asymmetric reactions and molecular recognition.

Acknowledgements

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Notes

1. The weight of crystal is the total weight of obtained crystals in one batch.
2. It is determined by PLATON geometry calculation.

References

(1) (a) Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Eds.; *Inclusion Compounds*; Academic Press: New York, 1984; Vols. 1–3. (b) Walba, D.M.; Clark, N.A.; Razavi, H.A.; Parmar, D.S. In *Inclusion Phenomenon and Molecular Recognition*; Atwood, J.L., Ed.; Plenum Press: New York, 1990. (c) Lehn, J.-M., Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Vogtle, F., Eds.; *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vols. 1–11. (d) Atwood, J.L., Steed, J.W., Eds.; *Encyclopedia of Supramolecular Chemistry*; Mercel Dekker: New York, 2004. (e) Toda, F., Bishop, R., Eds.; *Perspectives in Supramolecular Chemistry*; John Wiley & Sons: Chichester, 2004; Vol. 8. and reference cited therein.

(2) (a) Sada, K.; Shiomi, N.; Miyata, M. *J. Am. Chem. Soc.* **1998**, *120*, 10543–10544. (b) Nakano, K.; Hishikawa, Y.; Sada, K.; Miyata, M.; Hanabusa, K. *Chem. Lett.* **2000**, 1170–1171. (c) Kobayashi, Y.; Kodama, K.; Saigo, K. *Org. Lett.* **2004**, *6*, 2941–2944. (d) Imai, Y.; Sato, T.; Kuroda, R. *Chem. Commun.* **2005**, 3289–3291. (e) Kodama, K.; Kobayashi, Y.; Saigo, K. *Chem.-Eur. J.* **2007**, *13*, 2144–2152. (f) Imai, Y.; Kawaguchi, K.; Asai, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *CrystEngComm.* **2007**, *9*, 467–470. (g) Kodama, K.; Kobayashi, Y.; Saigo, K. *Cryst. Growth Des.* **2007**, *7*, 935–939. (h) Imai, Y.; Murata, K.; Kawaguchi, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Org. Lett.* **2007**, *9*, 3457–3460. (i) Imai, Y.; Murata, K.; Kawaguchi, K.; Sato, T.; Tajima, N.; Kuroda, R.; Matsubara, Y. *Chem.-Asian. J.* **2008**, *3*, 625–629. (j) Imai, Y.; Murata, K.; Matsuno, H.; Sato, T.; Kuroda, R.; Matsubara, Y. *CrystEngComm*. **2008**, *10*, 947–950. (k) Imai, Y.; Nagasaki, K.; Murata, K.; Kawaguchi, K.; Harada, T.; Nakano, Y.; Sato, T.; Fujiki, M.; Kuroda, R.; Matsubara, Y. *CrystEngComm.* **2008**, *10*, 951–953 and references cited therein.

(3) (a) Desiraju, G.R.; Curtin, D.Y.; Paul, I.C. *J. Org. Chem.* **1977**, *42*, 4071–4075. (b) Chiang, C.C.; DeCamp, W.H.; Curtin, D.Y.; Paul, I.C.; Shifrin, S.; Weiss, U. *J. Am. Chem. Soc.* **1978**, *100*, 6195–6201. (c) Patil, A.O.; Curtin, D.Y.; Paul, I.C. *J. Am. Chem. Soc.* **1984**, *106*, 348–353. (d) Miller, J.S.; Epstein, A.J. *Angew. Chem.* **1987**, *99*, 332–339. (e) Miller, S.J.; Epstein, J.A.; Reiff, M.W. *Chem. Rev.* **1988**, *88*, 201–220. (f) Paul, I.C.; Curtin, D.Y. *Acta. Cryst.* **1994**, *C50*, 78–81. (g) Kako, M.; Nakadaira, Y. *Coordinat. Chem. Rev.* **1998**, *176*, 87–112. (h) Rhodes, T.A.; Farid, S.; Goodman, J.L.; Gould, I.R.; Young, R.H. *J. Am. Chem. Soc.* **1999**, *121*, 5340–5341. (i) Enoki, T.; Miyazaki, A. *Chem. Rev.* **2004**, *104*, 5449–5477. (j) Girlando, A.; Painellia, A.; Bewick, S.A.; Soos, Z.G. *Synthetic. Metals* **2004**, *141*, 129–138. (k) Horiuchi, S.; Kumai, R.; Okimoto, Y.; Tokura, Y. *Chem. Phys.* **2006**, *325*, 78–91. (l) Ho, K.Y.; Kim, E.; Hwang, I.; Kim, K. *Chem. Comm.* **2007**, 1305–1315. (m) Kumar, J.; Singh, R.K.; Kumar, V.; Rastogi, R.C.; Singh, R.; *Diamond Relat. Mater.* **2007**, *16*, 446–453.

(4) (a) Kuroda, R.; Imai, Y.; Sato, T. *Chirality* **2001**, *13*, 588–594. (b) Imai, Y.; Tajima, N.; Sato, T.; Kuroda, R. *Chirality* **2002**, *14*, 604–609. (c) Imai, Y.; Tajima, N.; Sato, T.; Kuroda, R. *Org. Lett.* **2006**, *8*, 2941–2944. (d) Imai, Y.; Kamon, K.; Kinuta, T.; Tajima, N.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron Lett.* **2007**, *48*, 6321–6325. (e) Imai, Y.; Kido, S.; Kamon, K.; Kinuta, T.; Tajima, N.; Sato, T.; Kuroda, R.; Matsubara, Y. *Org. Lett.* **2007**, *9*, 5047–5050. (f) Imai, Y.; Kamon, K.; Kido, S.; Sato, T.; Tajima, N.; Kuroda, R.; Matsubara, Y. *Eur. J. Org. Chem.* **2008**, 4784–4789. (g) Imai, Y.; Kamon, K.; Kinuta, T.; Sato, T.; Tajima, N.; Kuroda, R.; Matsubara, Y. *Eur. J. Org. Chem.* **2009**, 2519–2525.

(5) Imai, Y.; Kamon, K.; Kinuta, T.; Tajima, N.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron* **2007**, *63*, 11928–11932.

(6) (a) Kobayashi, K.; Endo, K.; Aoyama, Y.; Masuda, H. *Tetrahedron Lett.* **1993**, *34*, 7929–7932. (b) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341–8352. (c) Aoyama, Y.; Endo, K.; Anzai, T.; Yamaguchi, Y.; Sawaki, T.; Kobayashi, K.; Kanehisa, N.; Hashimoto, H.; Kai, Y.; Masuda, H. *J. Am. Chem. Soc.* **1996**, *118*, 5562–5571. (d) Dewa, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8933–8940. (e) Dewa, T.; Saiki, T.; Imai, Y.; Endo, K.; Aoyama, Y. *Bull. Chem. Soc. Jpn* **2000**, *73*, 2123–2127. (f) Dewa, T.; Saiki, T.; Aoyama, Y. *J. Am. Chem. Soc.* **2001**, *123*, 502–503. (g) Sun, J.; Wang, L.; Yu, X.; Zhang, X. *Eur. Polym. J.* **2005**, *41*, 1219–1224. (h) Sun, J.; Wang, L.; Gao, J.; Wang, Z. *J. Colloid Interf. Sci.* **2005**, *287*, 207–212. (i) Kometani, Y.; Matsui, K. *J. Lumin.* **2007**, 122–123, 259–261. (j) Li, X.; Zhen, L.; Fan, Y.; Fan, X.; Zeng, Q. *Int. J. Mol. Sci.* **2007**, *8*, 241–256. (k) Akimoto, K.; Suzuki, H.; Kondo, Y.; Endo, K.; Akiba, U.; Aoyama, Y.; Hamada, F. *Tetrahedron* **2007**, *63*, 6887–6894.

(7) Imai, Y.; Kinuta, T.; Kamon, K.; Tajima, N.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron* **2009**, *65*, 3740–3744.

(8) Sheldrick, G.M. SHELX97. *Program for the Solution of Crystal Structures*; University of Goettingen: Germany, 1997.

(9) Sheldrick, G.M. SHELX97. *Program for the Refinement of Crystal Structures*; University of Goettingen: Germany, 1997.

(10) Spek, A.L. PLATON, *Molecular Geometry and Graphics Program*; University of Utrecht: The Netherlands, 1999.

(11) Sheldrick, G.M. SADABS. *Program for Empirical Absorption Correction of Area Detector Data*; University of Gottingen: Germany, 1996.