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Charge-transfer host complex with channel-like cavity using disubstituted-1,1′-bi-2-naphthol and benzylviologen

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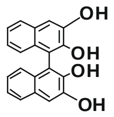
ABSTRACT

A novel charge-transfer (CT) host system is developed using CT complexes composed of *rac*-3,3′-dihydroxy-1,1′-bi-2-naphthol and 1,1′-dibenzyl-4,4′-bipyridinium dichloride. This CT host complex has a 1D channel-like cavity in which guest (MeOH and EtOH) molecules can be discharged and adsorbed. The color and DRS of the CT crystals change according to the presence of guest molecules in the host complex.

Although many organic and supramolecular organic host systems composed of two or more organic molecules have been reported,[1] there has been an increasing demand for enhancing the functionality of these host systems, in addition to the inclusion of guest molecules. Then, in such host systems, the utility of donor–acceptor interactions between host and guest has attracted the attention, and a few porous charge-transfer (CT) host compounds using this type of interaction have been reported to date.[2] Recently, we have reported the CT host complexes composed of *rac*-1,1′-bi-2-naphthol as the electron donor and *p*-benzoquinone derivatives as electron acceptors; these donor and acceptors serve as excellent visual indicators for the presence of guest (aromatic hydrocarbon) molecules.[3] These CT host complexes use the donor–acceptor interactions to construct host structure. However, these CT complexes can incorporate guest molecules but not reversibly discharge and adsorb them. Moreover, CT complexes composed of *rac*-1,1′-bi-2-naphthol as the electron donor and 1,1′-dimethyl-4,4′-bipyridinium dichloride (methyl viologen, $MVCl_2$) or 1,1′-dibenzyl-4,4′-bipyridinium dichloride (benzyl viologen, $BVCl_2$) as the electron acceptor have been reported.[4] However, we could not incorporate guest molecules into these CT complexes. An important property of these supramolecular systems is that the physical and chemical properties of the complex can be varied by simply changing the component molecules without involving any synthetic process.

In this Letter, we report the formation of novel CT host complex with channel-like cavity by using *rac*-3,3′-dihydroxy-1,1′-bi-2-naphthol (*rac*-**1**) (electron donor) and $BVCl_2$ (electron acceptor). Simple *n*-alkyl alcohols such as methanol (MeOH) and ethanol (EtOH) are used as guest molecules in order to obtain good-quality single crystals for X-ray crystallographic analysis.



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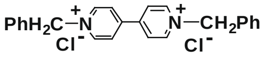

$BVCl_2$

The guest inclusion behavior of the *rac*-**1**/$BVCl_2$ host system was studied. Inclusion of MeOH (EtOH) was attempted by crystallization from a solution of *rac*-**1** and $BVCl_2$ in MeOH (EtOH) solutions.[5] As expected, colored inclusion CT complexes **I** and **II** were obtained from the MeOH and EtOH solutions, respectively. The colors of complexes **I** and **II** are almost the same (red). However, the red color of these crystals is unique to the solid state since highly concentrated solutions of these crystals are light red in color.

X-ray crystallographic analyses of these CT complexes were performed in order to investigate the guest inclusion mechanism.

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The results of the X-ray crystallographic analysis of complex **I** revealed the disordered nature of the guest MeOH molecules. The crystal structure of complex **I** with squeezed guest MeOH molecules is shown in Figure 1.[6]

The stoichiometry of complex **I**, as determined by X-ray crystallography and ^{1}H NMR, is (*R*)-**1**:(*S*)-**1**:BVCl$_2$:MeOH:H$_2$O = 0.5:0.5:1:1:1, and this complex belongs to the space group $P\bar{1}$. The (*R*)- and (*S*)-**1** molecules are connected by hydrogen bonding between the water molecules and Cl$^-$ to afford a 2D-layered structural unit (Fig. 1a and b). The BV^{2+} ions included in the structural unit contribute to the maintenance of this layered unit. The distance between the centers of the six-membered BV^{2+} ring and the nearest six-membered **1** ring is 3.56 Å. In these 2D-layered structural units, benzene–benzene edge-to-face interactions (2.90 Å, indicated by solid arrows *A* in Fig. 1a), which are caused by the benzyl groups of the BV^{2+} ions, are observed.[7] Interestingly, 1D channel-like cavities (Fig. 1c, indicated by a solid circle) are formed along the *a*-axis by the self-assembly of these 2D-layered structural units (Fig. 1c, indicated by a dotted circle). These 1D channel-like cavities are maintained by two types of benzene–naphthalene edge-to-face interactions (2.88 and 2.96 Å, indicated by solid arrows *B* and *C* in Fig. 1c, respectively) between the benzene ring of BV^{2+} and the naphthalene ring of **1**.[7] Although the guest MeOH molecules are disordered and squeezed (Fig. 1c) in these 1D channel-like cavities, they are one-dimensionally trapped.

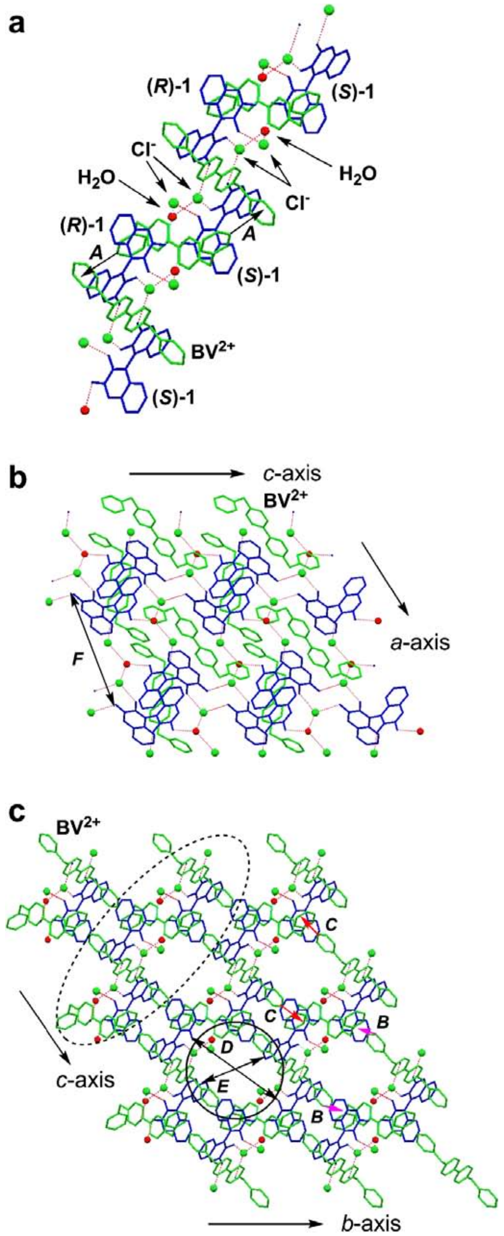

Figure 1. Crystal structure of complex **I**. (a) Extracted 2D-layered structural unit observed along the *a*-axis. Solid arrows *A* show benzene–benzene edge-to-face interactions. (b) Extracted 2D-layered structural unit observed along the *b*-axis. (c) Channel-like cavity formed by self-assembly of the 2D-layered structural unit observed along the *a*-axis. Dotted circle shows a 2D-layered structural unit. Solid circle shows a channel-like cavity. Solid arrows *B* and *C* show benzene–naphthalene edge-to-face interactions. Guest MeOH molecules are squeezed.

X-ray crystallographic analysis of complex **II**, which includes EtOH molecules, was attempted. In this complex too, the guest EtOH molecules are disordered, as revealed during X-ray crystallographic analysis. The stoichiometry of complex **II**, as determined by X-ray crystallography and ^{1}H NMR, is (*R*)-**1**:(*S*)-**1**:BVCl$_2$:EtOH:H$_2$O = 0.5:0.5:1:1:1, and this complex belongs to space group $P\bar{1}$. The crystal structures **I** and **II** are identical. The crystal structure of complex **II** with the squeezed guest EtOH molecules is shown in Figure Electric Supporting Information (ESI)-1.[8] As same as complex **I**, guest EtOH molecules are trapped into 1D channel-like cavities, although they are squeezed, as shown in Figure ESI-1c. These crystal structures **I** and **II** are identical, however, the distances of intermolecular interactions in complexes **I** and **II** are slightly different (Table 1).

In addition, as the guest molecules are changed from MeOH to EtOH, the distance along the *c*-axis (*D*, Figs. 1c and ESI-1c) increases from 12.48 to 12.59 Å. On the other hand, the distance along the *b*-axis (*E*, Figs. 1c and ESI-1c) decreases from 12.66 Å for complex **I** to 12.45 Å for complex **II**. Moreover, in these 2D-layered structures, as the guest molecules are changed from MeOH to EtOH, the intermolecular distance between the component **1** molecules along the *a*-axis (*F*, Figs. 1b and ESI-1b) decreases from 13.19 to 13.07 Å. These results show that by modifying the structure and packing style of the 2D-layered structural units, guest alcohols are incorporated into the 1D channel-like cavities of the *rac*-**1**/BVCl$_2$-host system.

Since the guest molecules are trapped in the 1D channel-like cavity, volatile guest molecules such as MeOH and EtOH may discharge into the atmosphere from the inclusion cavity. In order to study the discharge and adsorption of guest molecules in this CT host system, X-ray powder diffraction (XRPD) patterns of complex **I**, which includes MeOH, are recorded under air or MeOH vapor conditions (Fig. 2).

MeOH molecules were released from complex **I** when it was allowed to stand in air for a week. Subsequent to the ^{1}H NMR analysis, which confirmed the noninclusion of MeOH molecules in complex **I**, XRPD analysis of this complex was carried out, which revealed the formation of a novel complex **I-1** (Fig. 2b). Exposure of complex **I-1** to MeOH vapors resulted in the formation of complex **I-2**, whose XRPD pattern was similar to that of complex **I** (Fig. 2c).

This host system is composed of a CT complex; therefore, the color and DRS of this complex are expected to change reversibly with the presence of guest molecules. The change in the DRS of this complex is examined (Fig. 3).

Table 1
The distances of intermolecular interactions in complexes **I** and **II**

	BV^{2+}···**1**[a] (Å)	*A* (Å)	*B* (Å)	*C* (Å)
Complex **I**	3.56	2.90	2.88	2.96
Complex **II**	3.57	2.84	2.93	2.86

[a] The distance between the centers of the six-membered BV^{2+} ring and the nearest six-membered **1** ring.

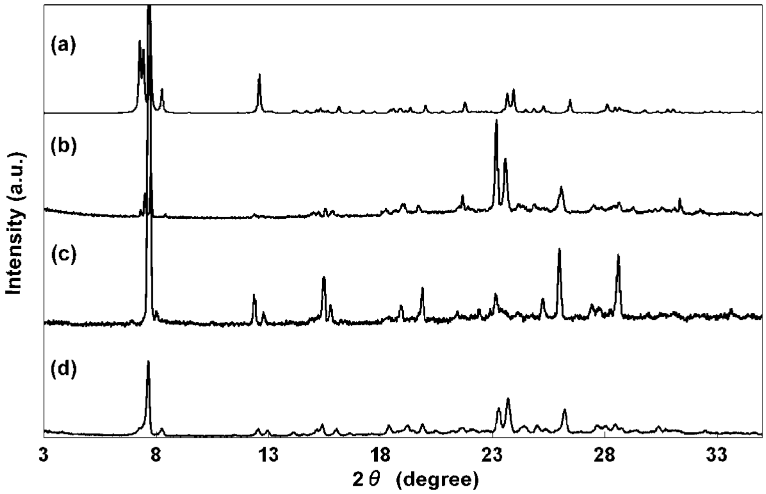

Figure 2. Change in XRPD patterns obtained for complex **I**. (a) Calculated pattern of crystal **I**. (b) XRPD pattern for complex **I**. (c) XRPD pattern for complex **I-1** obtained in air. (d) XRPD pattern for complex **I-2** obtained under MeOH vapor atmosphere.

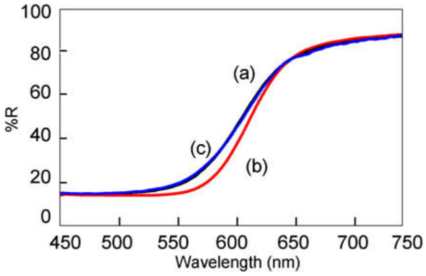

Figure 3. Change in DRS of complex **I**. (a) Complex **I** (black line). (b) Complex **I-1** obtained after discharge of MeOH (red line). (c) Complex **I-2** obtained after readsorption of guest MeOH molecules (blue line).

As before, the guest MeOH molecules are discharged from this complex when it is allowed to stand in air for a week, and its DRS are measured (complex **I-1** in Fig. 3b). The absorption edge of the resultant changes to 550 nm, and a bathochromic shift (by 40 nm) is observed. The color of this complex changes from red to deep red. This complex is exposed to MeOH vapors, and the DRS are measured again (complex **I-2** in Fig. 3c). The peak pattern in the obtained DRS is similar to that in the DRS of the original complex **I**. At the same time, the color of this complex changes from deep red to red.

Moreover, the discharge and adsorption behaviors of complex **II**, which includes EtOH molecules, were similar to those of complex **I**, as revealed by XRPD analyses (Fig. 4).

When complex **II** was allowed to stand in air for a week, the EtOH molecules were released, resulting in the formation of a novel complex **II-1** (Fig. 4b). Complex **II-1** was exposed to EtOH vapors, and the resulting complex was subjected to XRPD analysis. The XRPD pattern of complex **II-2** was similar to that obtained for complex **II** (Fig. 4c).

Similar to the case of complex **I**, the change in the DRS of complex **II** was examined (Fig. 5).

When guest EtOH molecules were discharged from complex **II**, the absorption edge changed to 550 nm, and a bathochromic shift (by 40 nm) was observed (complex **II-1** in Fig. 5b). Complex **II-1** was then exposed to EtOH vapors, and the DRS of the resulting compound were recorded. The peak patterns in the obtained DRS were similar to those in the original DRS (as complex **II-2** in Fig. 5c). In this case too, the color of the complex underwent a reversible change [red color for complex **II** (and **II-2**) and deep

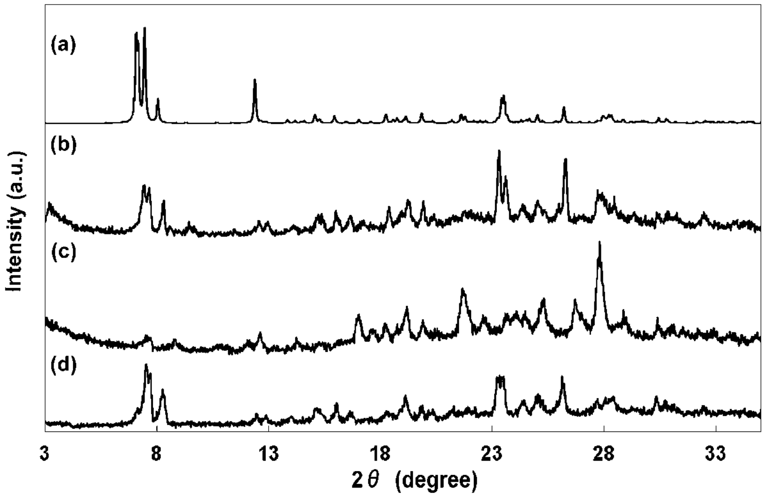

Figure 4. Change in XRPD pattern obtained for complex **II**. (a) Calculated pattern of crystal **II**. (b) XRPD pattern for complex **II**. (c) XRPD pattern for complex **II-1** obtained in air. (d) XRPD pattern for complex **II-2** obtained under EtOH vapor atmosphere.

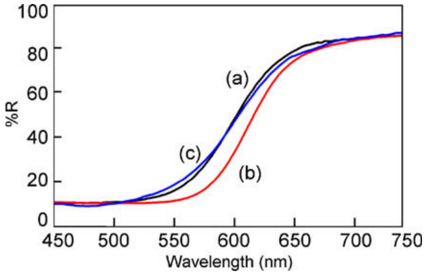

Figure 5. Change in DRS of complex **II**. (a) Complex **II** (black line). (b) Complex **II-1** obtained after discharge of EtOH (red line). (c) Complex **II-2** obtained after readsorption of guest EtOH molecules (blue line).

red color for complex **II-1**]. These results suggest that the CT host system used in this study facilitates reversible discharge and adsorption of guest molecules; this is because the 1D channel-like cavities are prevented from collapsing by benzene–benzene edge-to-face interactions between 2D-layered structural units. Moreover, although this CT host system cannot be used as molecular recognition system between MeOH and EtOH molecules since the colors and DRS of complexes **I** and **II** are similar, this CT host system can reversibly change the color and DRS of the complex according to the presence of these alcohol molecules.

In conclusion, we have developed a novel host system using CT complex composed of *rac*-**1** and $BVCl_2$. A 1D channel-like cavity is successfully formed in this *rac*-**1**/$BVCl_2$-CT host complex. MeOH and EtOH molecules as guests can be discharged and adsorbed into this 1D channel-like cavity, and the color and DRS of the complex reversibly change with the presence of the guest alcohol molecules. It is expected that this study is useful for the design of novel solid-state molecular sensing system exhibiting color change.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.090.

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5. *Rac*-**1** (10 mg, 3.14×10^{-2} mmol) and $BVCl_2$ (13 mg, 3.19×10^{-2} mmol) were dissolved in the corresponding *n*-alkyl alcohol solutions (2 mL) with heating. Each solution was allowed to stand at room temperature. After 5–7 days, the respective colored crystals [**I** from MeOH including *rac*-**1**/$BVCl_2$ (10 mg), and **II** from EtOH including *rac*-**1**/$BVCl_2$ (11 mg)] were deposited and collected. The weight of each type of crystal is the total crop of the crystals obtained in a single batch.
6. *Crystallographic data for* **I**: $C_{20}H_{10}O_4 \cdot C_{24}H_{22}N_2Cl_2 \cdot O$, $M = 741.63$, triclinic, space group $P\bar{1}$, $a = 13.1869(10)$, $b = 13.3725(10)$, $c = 13.8836(10)$ Å, $\alpha = 64.5000(10)°$, $\beta = 70.5130(10)°$, $\gamma = 88.3520(10)°$, $V = 2064.1(3)$ Å^3, $Z = 2$, $Dc = 1.193$ g cm^{-3}, μ(Mo Kα) = 0.202 mm^{-1}, 18,017 reflections measured, 9179 unique, final $R(F^2) = 0.0883$ using 7400 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.1012, $T = 115(2)$ K. CCDC 724938.
7. It is determined by PLATON geometry calculation.
8. *Crystallographic data for* **II**: $C_{20}H_{14}O_4 \cdot C_{24}H_{22}N_2Cl_2 \cdot H_2O$, $M = 745.66$, triclinic, space group $P\bar{1}$, $a = 13.0660(11)$, $b = 13.4247(12)$, $c = 14.0340(12)$ Å, $\alpha = 63.9590(10)°$, $\beta = 70.5750(10)°$, $\gamma = 88.110(2)°$, $V = 2067.2(3)$ Å^3, $Z = 2$, $Dc = 1.198$ gcm^{-3}, μ(Mo Kα) = 0.202 mm^{-1}, 18,122 reflections measured, 9193 unique, final $R(F^2) = 0.0776$ using 5519 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.1257, $T = 130(2)$ K. CCDC 724939. Crystallographic 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).