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A Charge-Transfer Complex of 10,10′-Dihydroxy-9,9′-biphenanthryl and Methylviologen as a Visual Inclusion Host System

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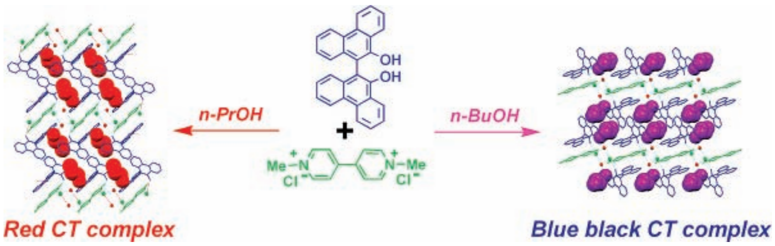
ABSTRACT



A charge-transfer (CT) complex, composed of 10,10′-dihydroxy-9,9′-biphenanthryl as the electron donor and 1,1′-dimethyl-4,4′-bipyridinium dichloride as the electron acceptor, is formed only by the inclusion of guest molecules. The color of this inclusion CT complex is sensitive to the component guest molecules.

Many solid-state organic host systems that contain guest molecules have been reported.[1] However, they are mostly composed of a single organic molecule. If a solid-state host system is composed of two or more organic molecules, the property of molecular recognition may be easily controlled by changing the component molecules without additional synthesis, and the target guest molecules may also be extended.[2] Recently, there has been increased demand to impart further functionality to these host systems. We have been focusing on the use of donor−acceptor interactions as intermolecular forces for forming and controlling the func-

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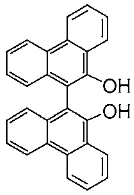
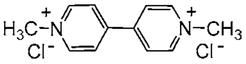
tional host system. For example, charge-transfer (CT) host systems composed of 1,1′-bi-2-naphthol or 6,6′-(or 3,3′-)-disubstituted-1,1′-bi-2-naphthol as electron donors and *p*-benzoquinone or 1,1′-dimethyl-4,4′-bipyridinium dichloride (methylviologen, $MVCl_2$) as electron acceptors serve as excellent visual indicators for guest aromatic molecules.[3] However, these CT complexes were unable to recognize alkyl or alkyl alcohol molecules as guests.

One of the key properties of these supramolecular complexes is the ability to easily tune physical and chemical properties by changing the component molecules. In this paper, we report a novel visual inclusion host system composed of *rac*-10,10′-dihydroxy-9,9′-biphenanthryl (*rac*-**1**) as the electron donor and $MVCl_2$ as the electron acceptor. It is expected that this CT host system will exhibit both a different guest inclusion ability and different color changes with the included guest molecules compared to reported CT host systems composed of 1,1′-bi-2-naphthol derivatives since **1** has a larger and wider π-conjugated phenanthrene ring compared to the naphthalene ring of the 1,1′-bi-2-naphthol derivatives. As guest molecules, three *n*-alkyl alcohols [ethanol (EtOH), *n*-propanol (*n*-PrOH), and *n*-butanol (*n*-BuOH)] with different chain lengths were used to study the influence of the size of the included guest molecule on this system.



***rac*-1**



$MVCl_2$

***rac*-1** was synthesized by the previously reported method.[4] The guest inclusion behavior of the *rac*-**1**−$MVCl_2$ host system was then studied. Inclusion of each *n*-alkyl alcohol was attempted by crystallization from each *n*-alkyl alcohol solution (2 mL) containing *rac*-**1** (10.0 mg, 2.58×10^{-2} mmol) and $MVCl_2$ (6.7 mg, 2.58×10^{-2} mmol). Each solution was left to stand at room temperature for a few days. From EtOH, *n*-PrOH, and *n*-BuOH solutions, colored inclusion crystals **I** (8.3 mg), **II** (9.7 mg), and **III** (8.7 mg) were obtained, respectively.[5]

As anticipated, the color of this inclusion crystal changes according to the included guest molecule; i.e., inclusion crystals **I** and **II** containing EtOH and *n*-PrOH were similarly red in color, whereas inclusion crystals **III** containing *n*-BuOH were blue-black. The diffuse reflectance spectra (DRS) of complexes **I**−**III** are shown in Figure 1.[6]

The solid-state DRS of crystals **I**−**III** are substantially different from each other, especially complexes **I** (or **II**) and **III**, with absorption edges located at ca. 510, 510, and 620 nm, respectively. Interestingly, the colors of these crystals are unique to the solid state, as highly concentrated solutions of these crystals exhibit a light yellow color. These results suggest that this *rac*-**1**−$MVCl_2$ host system can function as a visual indicator host system or indicator host system using DRS for molecular recognition in the solid state.

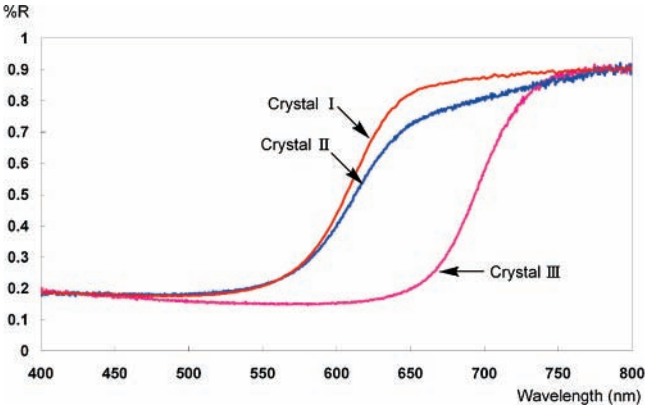


Figure 1. Diffuse reflectance spectra (DRS) of crystals **I** (red line), **II** (blue line), and **III** (purple line).

To understand the guest inclusion mechanisms and origins of the different electronic absorptions of these crystals, X-ray analyses of these complexes were attempted. The crystal structure of CT complex **III** including *n*-BuOH is shown in Figure 2.[7]

The stoichiometry of crystal **III** is (*R*)-**1**/(*S*)-**1**/$MVCl_2$/*n*-BuOH/H_2O = 0.5:0.5:0.5:1:1 and the space group is $P\bar{1}$. Characteristically, this crystal is composed of a biphenanthrol cluster formed from (*R*)- and (*S*)-**1** molecules (blue molecules in Figure 2) connected by hydrogen bonds between a hydroxyl group of **1**, two chloride ions (green balls in Figure 2), and two water molecules (red balls in Figure 2) (Figure 2a). Although guest *n*-BuOH molecules (purple molecules in Figure 2) are observed as disorder, *n*-BuOH clearly links the hydroxyl group of **1** and a water molecule through hydrogen bonds and contribute to the maintenance of the biphenanthrol cluster (Figure 2a). A channel-like cavity (red circle in Figure 2b) along the *a*-axis is formed by self-assembly of these clusters by CT interactions with methylviologen ion (MV^{2+}, green molecules in Figure 2b) (Figure 2b). Guest *n*-BuOH molecules (Figure 2b, indicated by purple spacefill view) are incorporated into the channel-like cavity. These cavities are also maintained by two types of phenanthrene−phenanthrene edge-to-face interactions (Figure 2b, red and orange arrows, 2.95 and 2.94 Å, respectively) between the 6-CH of the phenanthrene ring and another phenanthrene ring, and between the 1-CH of the phenanthrene ring and another phenanthrene ring, respectively.

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(5) This weight is the total crop of obtained crystals in one batch.

(6) Diffuse reflectance spectra of crystals were measured with a HITACHI U-4000 Spectrometer.

(7) Crystallographic data of **II**: $0.5C_{12}H_{14}N_2Cl_2{\cdot}C_{28}H_{18}O_2{\cdot}C_3H_8O{\cdot}H_2O$ $M = 593.11$, triclinic, space group $P\bar{1}$, $a = 9.2804(8)$ Å, $b = 10.1749(9)$ Å, $c = 17.6738(16)$ Å, $\alpha = 80.247(2)°$, $\beta = 77.003(2)°$, $\gamma = 64.981(2)°$, $V = 1468.3(2)$ Å^3, $Z = 2$, $D_c = 1.342$ g cm^{-3}, μ(Mo Kα) = 0.174 mm^{-1}, 13007 reflections measured, 6591 unique, final $R(F^2) = 0.0625$ using 4517 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0979, $T = 120(2)$ K.

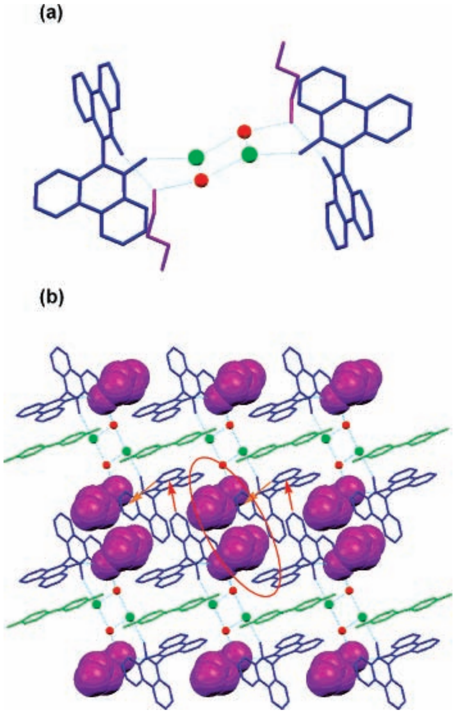

Figure 2. Crystal structure of complex **III**: (a) structure of extracted biphenanthrol cluster; (b) channel-like cavity formed by self-assembly of the biphenanthrol cluster observed along the *a*-axis. Red circles show channel-like cavities. Red and orange arrows show phenanthrene−phenanthrene edge-to-face interactions.

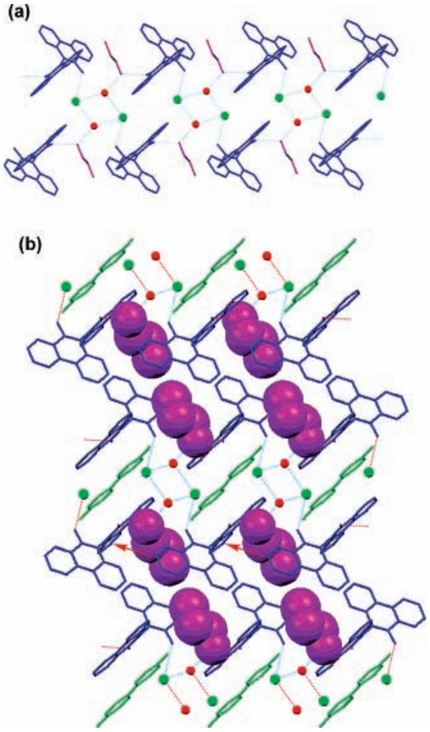

Figure 3. Crystal structure of complex **II**: (a) structure of extracted 1D-structure unit; (b) cavity formed by self-assembly of the 1D-structure unit observed along the *a*-axis. Red arrows show phenanthrene−phenanthrene edge-to-face interactions.

The structure of complex **II** including *n*-PrOH is shown in Figure 3.[8]

Although the stoichiometry of crystal **II** is the same as that of **III**, i.e., (*R*)-**1**/(*S*)-**1**/MVCl$_2$/*n*-PrOH/H$_2$O = 0.5:0.5: 0.5:1:1, with the same space group of $P\bar{1}$, the crystal structure is quite different from that of crystal **III**. (*R*)- and (*S*)-**1** (blue molecules in Figure 3) are connected by a hydrogen bond through water molecules (red balls in Figure 3) and chloride ions (green balls in Figure 3) and form a 1D-structure unit (Figure 3a). Guest *n*-PrOH molecules (purple molecules in Figure 3) link the hydroxyl group of **1** and water molecules through hydrogen bonds and contribute to the maintenance of the 1D-structure unit. Characteristically, cavities are formed by self-assembly of this 1D-structure unit through CT interactions between two 1D-structure units and the MV^{2+} ions (green molecules in Figure 3b). These cavities are also maintained by phenanthrene−phenanthrene edge-to-face interactions (Figure 3b, red arrows, 2.92 Å) between the 2-CH of the phenanthrene ring and another phenanthrene ring. In one cavity, two *n*-PrOH molecules (Figure 3b, indicated by purple spacefill view) are included.

On the other hand, since complex **I** including EtOH was not of good quality, structural information on these crystals could not be obtained from X-ray crystallographic analysis. Therefore, X-ray powder diffraction patterns of these crystals were measured and compared to those of complexes **II** and **III** (Figure 4).

The X-ray powder diffraction pattern of complex **I**, especially at low angle, is very similar to that of complex **II**. Moreover, ^{1}H NMR analysis reveals that the stoichiometry

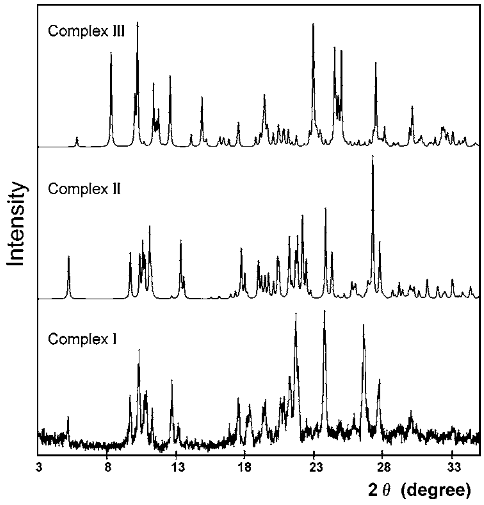

Figure 4. X-ray powder diffraction patterns of complexes **I**−**III**.

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[8] Crystallographic data of **III**: $0.5C_{12}H_{14}N_2Cl_2 \cdot C_{28}H_{18}O_2 \cdot C_4H_9O \cdot H_2O$ $M = 607.14$, triclinic, space group $P\bar{1}$, $a = 9.3019(6)$ Å, $b = 11.4319(7)$ Å, $c = 15.3935(10)$ Å, $\alpha = 87.3230(10)°$, $\beta = 85.2890(10)°$, $\gamma = 69.6400(10)°$, $V = 1529.18(17)$ Å^3, $Z = 2$, $D_c = 1.319$ g cm^{-3}, μ(Mo Kα) = 0.168 mm^{-1}, 13607 reflections measured, 6871 unique, final $R(F^2) = 0.0535$ using 5563 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0661, $T = 200(2)$ K.

of complex **I** is **1**/MVCl$_2$/EtOH = 1:1:1, although accurate information on included water molecules was not obtained. These results suggest that complex **I** shares a 1D-structure unit, as in complex **II**, and the packing structure is also similar to that of complex **II**. That is, it is thought that this CT complex **I** includes guest EtOH molecules by slightly changing the packing style of complex **II**.

The DRS in Figure 1 show that the different absorptions of crystals **I**−**III** result from the CT absorption bands around the absorption edge. To understand the structural differences corresponding to these spectra, the intermolecular distances in the X-ray structures have been examined (Table 1).

Table 1. Distances of the Nearest Molecule Pairs in Crystals **II** and **III** (in Å)[a]

	MV$^{2+}\cdots$MV^{2+}	MV$^{2+}\cdots$Cl$^-$	MV$^{2+}\cdots$**1**	**1**$\cdots$Cl$^-$	**1**$\cdots$**1**
II	5.54 (C$\cdots$C)	3.62 (C$\cdots$Cl)	3.17 (C$\cdots$O)	3.10 (O$\cdots$Cl)	3.33 (C$\cdots$C)
	6.67 (C$\cdots$C)	3.56 (C$\cdots$Cl)	3.37 (C$\cdots$C)	3.79 (C$\cdots$Cl)	3.59 (C$\cdots$O)
III	3.96 (C$\cdots$C)	3.64 (C$\cdots$Cl)	3.03 (C$\cdots$O)	3.11 (O$\cdots$Cl)	3.49 (C$\cdots$C)
	6.38 (C$\cdots$C)	3.67 (C$\cdots$Cl)	3.21 (C$\cdots$C)	4.06 (C$\cdots$Cl)	3.58 (C$\cdots$O)

[a] The distance between the nearest intermolecular atom pair (non-hydrogen) is given.

The data indicates that the major difference between crystals **II** and **III** is in the distance of the nearest MV$^{2+}\cdots$MV^{2+} pair. The distances for the other molecule pairs are not so markedly different, although the global packings of molecules in these crystals are quite different as described above. The smaller MV$^{2+}\cdots$MV^{2+} distance in **III** than in **II** can account for the presence of smaller energy absorptions in the former crystal than in the latter crystal (see DRS). (One of the MV cations is mono-positive (MV$^+$) in the lowest energy CT excited states of both the crystals, since an electron moves from **1** to MV^{2+} by the corresponding CT electronic transitions. Thus, the smaller MV$\cdots$MV distance means the smaller excitation energies, since the excited states have an MV$^+\cdots$MV^{2+} interaction in place of an MV$^{2+}\cdots$MV^{2+} interaction in the ground state.) This is most likely be one of the factors that impart the different colors for crystals **II** and **III**.

In conclusion, we have developed a novel visual inclusion host system using CT complexes composed of *rac*-**1** and MVCl$_2$. This CT host system can include an *n*-alkyl alcohol as guest. Moreover, the color of this inclusion crystal is sensitive to the structure of the included alcohol. This further enriches the functionality of this CT host system, and it may prove useful as sensitive visual indicator of molecular recognition.

Supporting Information Available: Crystallographic reports (CIF) of complexes **II** and **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

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