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An isoselective and visual inclusion host system using charge-transfer complexes of 3,3′-disubstituted-1,1′-bi-2-naphthol and methylviologen

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Abstract—A charge-transfer (CT) complex, composed of *rac*-3,3′-dibromo-1,1′-bi-2-naphthol as the electron donor and 1,1′-dimethyl-4,4′-bipyridinium dichloride as the electron acceptor, is formed only by the inclusion of specific guest molecules. The color of this inclusion CT complex is sensitive to the component guest molecules.

Many supramolecular host compounds that contain guest molecules have been reported.[1] Recently, there has been increased demand to impart further functionality to these host compounds. We have been focusing on the use of donor–acceptor interactions as intermolecular forces for constructing and controlling the host structure. For supramolecular host compounds using donor–acceptor interactions, charge-transfer (CT) host complexes composed of 1,1′-bi-2-naphthol derivatives as electron donors and *p*-benzoquinone as an electron acceptor serve as excellent visual indicators for guest aromatic hydrocarbon molecules.[2] However, it is difficult to use aromatic molecules having hydroxyl groups as guest molecules because these aromatic molecules may themselves form CT complexes with *p*-benzoquinone. In addition to *p*-benzoquinone, we have also reported a CT complex with *rac*-1,1′-bi-2-naphthol (*rac*-**1a**) as an electron donor and 1,1′-dimethyl-4,4′-bipyridinium dichloride (methylviologen, $MVCl_2$) as an electron acceptor.[3] Unfortunately, this CT complex was unable to incorporate guest molecules.

In this Letter, we report the isoselective inclusion behavior and molecular recognition visualization of guest aromatic molecules having hydroxyl groups by using a CT complex composed of a *rac*-3,3′-disubstituted-1,1′-bi-2-naphthol as an electron donor and $MVCl_2$ as an electron acceptor. It is expected that this CT host system will exhibit both isoselectivity and color changes when complexed with guest molecules. Moreover, since this system is not composed of one molecule but is supramolecular and composed of two molecules, it is expected that the molecular recognition ability can easily be modified by changing the combination of the components. *rac*-3,3′-Dimethyl-1,1′-bi-2-naphthol (*rac*-**1b**) and *rac*-3,3′-dibromo-1,1′-bi-2-naphthol (*rac*-**1c**) were used as the *rac*-3,3′-disubstituted-1,1′-bi-2-naphthol derivative. For aromatic molecules with hydroxyl groups, 1,2-, 1,3-, and 1,4-benzenediol (*o*-**2**, *m*-**2**, and *p*-**2**), were studied.

The inclusion behavior of the *rac*-**1b**–$MVCl_2$ host system was first studied. The formation of a CT complex

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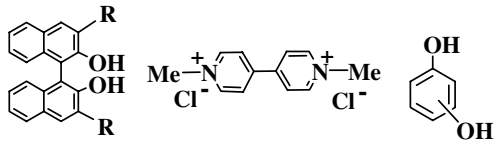

1a: R=H
1b: R=Me
1c: R=Br

$MVCl_2$ **2**

including **2** was attempted by crystallization from EtOH solution (3 mL) containing *rac*-**1b** (10.0 mg, 3.18×10^{-2} mmol), $MVCl_2$ (8.2 mg, 3.18×10^{-2} mmol) and each benzenediol derivative **2** (3.5 mg, 3.18×10^{-2} mmol). Each solution was left to stand at room temperature for a few days, but inclusion CT complexes were not obtained.

Consequently, formation of a *rac*-**1c**–$MVCl_2$ host system including guest molecules was attempted. Inclusion of each benzenediol was attempted by crystallization from EtOH solution (3 mL) containing *rac*-**1c** (10.0 mg, 2.25×10^{-2} mmol), $MVCl_2$ (5.8 mg, 2.25×10^{-2} mmol) and each benzenediol derivative **2** (2.5 mg, 2.25×10^{-2} mmol). Each solution was left to stand at room temperature for a few days. When *p*-**2** and *m*-**2** were used as guest molecules, colored inclusion crystals **I** (9.0 mg)[4] and **II** (8.6 mg)[4] were obtained, respectively. Interestingly, this host system showed isoselective inclusion ability, and CT complexes including *o*-**2** were not formed. X-ray analysis was performed to investigate the structure of these crystals (**I**), shown in Figure 1.[5]

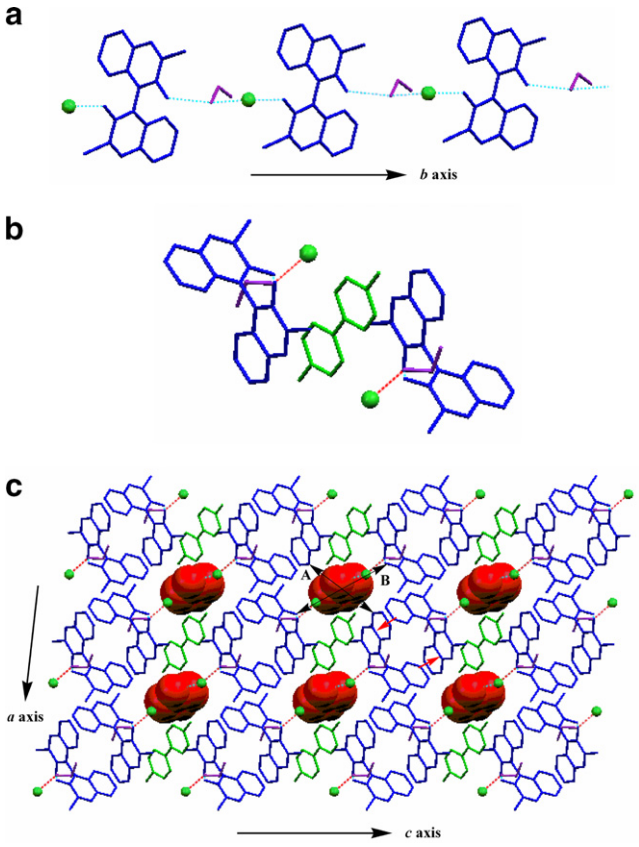

Figure 1. (a) 1D-structure unit, which is parallel to the *b* axis in crystal **I**. (b) 1D-layered structure observed along the *b* axis. (c) One-dimensional cavity formed by self-assembly of the 1D-layered structure observed along the *b* axis.

The stoichiometry of crystal (**I**) is (*R*)-**1c**–(*S*)-**1c**–$MVCl_2$–EtOH–*p*-**2** = 1:1:1:2:1 and the space group is $P\bar{1}$. (*R*)-**1c** (or (*S*)-**1c**, shown in blue in Fig. 1) is connected by a hydrogen bond through EtOH (shown in purple in Fig. 1) and a chloride ion (green ball in Fig. 1) and forms a 1D-structure unit along the *b* axis (Fig. 1a). Moreover, a 1D-layered structure unit is formed by CT interactions between two 1D-structure units and the MV^{2+} (1,1′-dimethyl-4,4′-bipyridinium) ions (green molecule in Fig. 1b). Characteristically, one-dimensional cavities are formed along the *b* axis by self-assembly of this 1D-layered structure (Fig. 1c). These cavities are maintained by naphthalene–naphthalene edge-to-face interactions (Fig. 1c, indicated in red arrows, 2.86 Å) between the 7-CH of the naphthol ring in **1c** and the naphthol ring of another **1c**. In these cavities, guests *p*-**2** (Fig. 1c, indicated in red spacefill view) are one-dimensionally trapped by a hydrogen bond to a chloride ion. Characteristically, in this system, the CT complex could not be obtained by crystallization in the absence of *p*-**2**.

The structure of crystal (**II**) is shown in Figure 2.[6]

The stoichiometry of crystal **II** is the same as that of **I**, that is, (*R*)-**1c**–(*S*)-**1c**–$MVCl_2$–EtOH–*m*-**2** = 1:1:1:2:1, with the same space group of $P\bar{1}$. Crystal **II** also has a

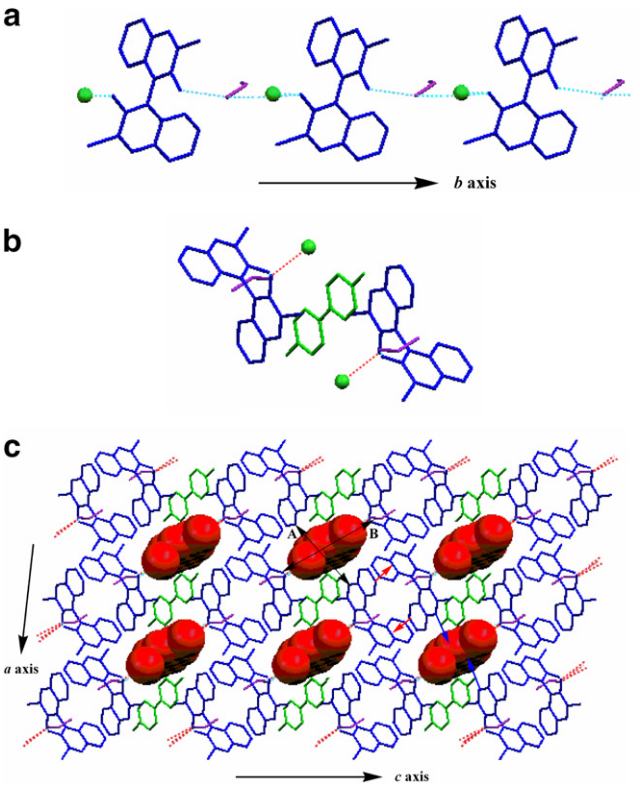

Figure 2. (a) 1D-structure unit, which is parallel to the *b* axis in crystal **II**. (b) 1D-layered structure observed along the *b* axis. (c) One-dimensional cavity formed by self-assembly of the 1D-layered structure observed along the *b* axis.

common 1D-structure unit of (*R*)-**1c** (or (*S*)-**1c**) and a 1D-layered structure formed by CT interactions between two 1D-structure units and the MV^{2+} ions (Fig. 2a and b). One-dimensional cavities are formed along the *b* axis by self-assembly of these 1D-layered structures by the same naphthalene–naphthalene edge-to-face interactions (Fig. 2c, indicated in red arrows, 2.82 Å) as in crystal **I** (Fig. 2c). In these one-dimensional cavities, *m*-**2** (Fig. 2, indicated in red spacefill view) is included. One *m*-**2** molecule sits very close to a center of symmetry, which generates another one of a different orientation. These two orientations are related to the positional disorder found with the chlorine atom. In Figure 2, only one of two *m*-**2** orientations is shown. The *m*-**2** molecule is trapped by two interactions: (1) a naphthalene–benzene edge-to-face interaction (Fig. 2, indicated in blue arrows, 2.91 Å) between the 4-CH of the naphthol ring in **1c** and the benzene ring of *m*-**2**, and (2) a hydrogen bond with the chloride ion.

In complexes **I** and **II**, the packing styles of the 1D-layered structure, as well as each 1D-layered structure, are common. As the guest changes from *p*-**2** to *m*-**2**, although the distance between the 1D-layered structure along the *a* axis (**A**, Figs. 1c and 2c) is almost same (8.12 and 8.17 Å, respectively), the distance along the *c* axis (**B**, Figs. 1c and 2c) increases from 9.18 to 9.44 Å, respectively. Thus, by slightly changing the packing style of the 1D-layered structure, this CT host system can regioselectively accommodate these alcohols. This host system, however, does not accommodate *o*-**2**. To determine the reason for this, the inclusion behaviors of phenol, *o*-fluorophenol and *o*-cresol were studied. It was found that only phenol was included. This result suggests that *o*-**2** is excluded by steric repulsions between the 1D-structure unit and the two hydroxyl groups of *o*-**2**.

Moreover, the guest inclusion behavior of this CT host system under coexistence of *p*-**2** and *m*-**2** as guest molecules was studied.[7] Both crystals **I** and **II** were obtained, but crystal **I**, which included *p*-**2**, was the major product (63%/37% = crystal **I**/**II**). Although selective formation of CT crystals with a substituted aromatic hydrocarbon as the donor molecule had been reported previously, it was believed that molecular recognition of aromatic molecules with hydroxyl groups using CT host systems is rare.[8] We now show that this is not the case.

Interestingly, the color of this CT host system changes according to the included guest molecule, that is, inclusion crystals **I** containing *p*-**2** were red in color, whereas inclusion crystals **II** containing *m*-**2** were orange. The diffuse reflectance spectra (DRS) of complexes **I** and **II** are shown in Figure 3.

The solid-state DRS of crystals **I** and **II** are substantially different from each other, with absorption edges located at ca. 490 and 380 nm, respectively. The colors of these complexes are unique to the solid state, as highly concentrated solutions of these crystals exhibit a light yellow color. This suggests that the *rac*-**1c**–$MVCl_2$ host system can be used not only as a isoselective inclusion host complex but also as a visual indicator for molecular recognition.

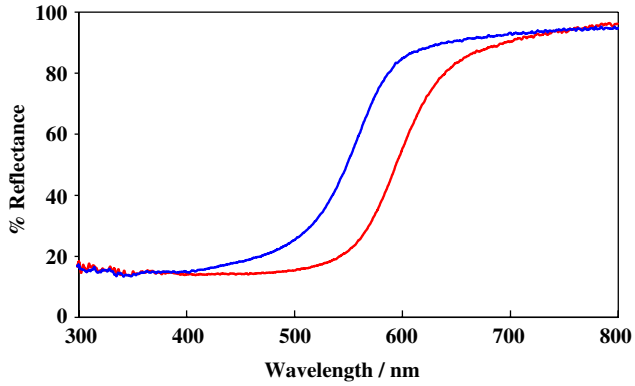

Figure 3. Diffuse reflectance spectra of crystal **I** (red line) and crystal **II** (blue line).

To understand the origins of the different electronic absorptions of crystals **I** and **II**, the excited states of the CT chromophores in their X-ray structures were examined theoretically using the ZINDO method.[9,10] The calculated chromophores are molecular clusters consisting of a viologen ion (MV^{2+}), two binaphthol molecules (**1c**), two guest molecules (*m*-**2** or *p*-**2**), and two counter anions (Fig. 4), where the Br atoms and the Cl atoms in the original X-ray structures have been replaced with F atoms to calculate the excited states by the ZINDO method.

The calculated least energy excited states of these molecular clusters are listed in Table 1. The cluster from crystal **I** has smaller excitation energies than that from crystal **II**, corresponding to the DRS of these two crystals. The data suggest that the absorptions at the lowest energy side, which differentiate the color of the two crystals, come from the electronic transitions from **1c** to MV^{2+} (excitations to S1 and S2) and those from **2** to MV^{2+} (excitations to S3 and S4). It may be noteworthy that the CT interactions within the host molecules ($MVCl_2$ and **1c**), as well as the interaction of the host molecules with the guests (*p*-**2** and *m*-**2**), contribute to the guest-dependent crystal color.

The smaller excitation energies in cluster **I** versus cluster **II** are thought to be related to the relative locations of the counter anions Cl^- to the molecules, because the arrangement of the molecules are fairly similar in the two clusters with the exception of Cl^- (see Fig. 4). In fact, the excitation energies of the two clusters become close when the counter anions are removed, that is, 1.92 and 1.92 eV (cluster **I**) and 1.86 and 1.87 eV (cluster **II**) for the first two states. Most likely, the larger $Cl^-\cdots MV^{2+}$ distance destabilizes the ground state more than the excited states (where $Cl^-\cdots MV^+$), giving the smaller excitation energies. The excitation energy difference between the two crystals is remarkable in S3 and S4 compared with the other excited states. This would reflect the ionization properties (electron donation strengths) of *p*-**2** and *m*-**2**: the ionization energies of

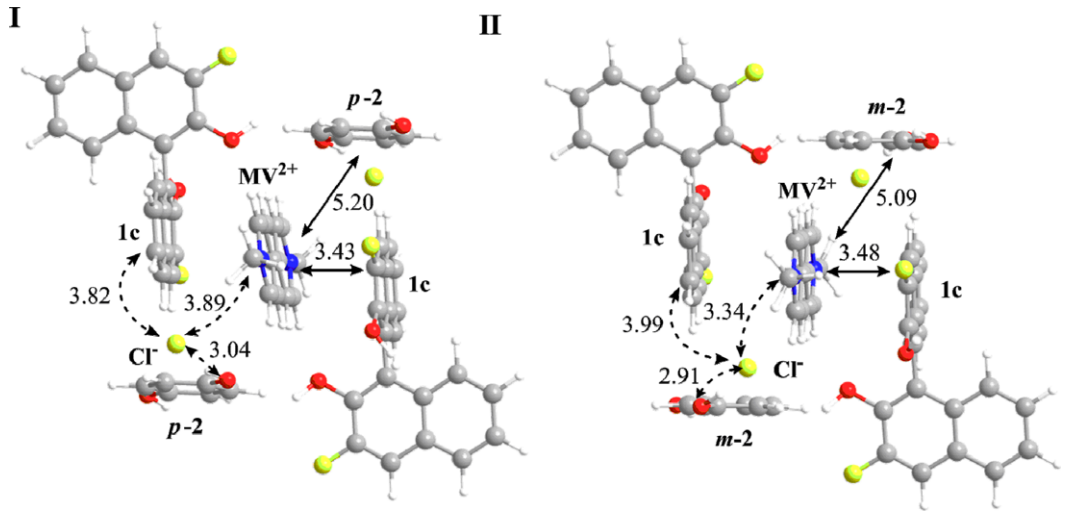

Figure 4. The chromophores from the X-ray structures of crystals **I** and **II**. The Cl and Br atoms in the original X-ray structures are replaced by F atoms for the ZINDO[10] calculations. The atomic coordinates of the F atoms on **1c** are optimized by the PM3 method[11] to correct the C–F bond length. The distances given are the center–plane distances for $MV^{2+}\cdots$**1c**, the center–center distances for $MV^{2+}\cdots$**2**, and the smallest interatomic (non-hydrogen) distances for $Cl^{-}\cdots MV^{2+}$, $Cl^{-}\cdots$**1c**, and $Cl^{-}\cdots$**2**, in Å.

Table 1. Calculated singlet excited states of clusters **I** and **II**[a]

	I			II		
	E[b] (eV)	f[b]	Character[c]	E[b] (eV)	f[b]	Character[c]
S1	2.29	0.0000	**1c**→MV^{2+}	2.47	0.0000	**1c**→MV^{2+}
S2	2.30	0.0273	**1c**→MV^{2+}	2.50	0.0127	**1c**→MV^{2+}
S3	2.35	0.0079	***p*-2**→MV^{2+}	2.97	0.0046	***m*-2**→MV^{2+}
S4	2.36	0.0000	***p*-2**→MV^{2+}	2.97	0.0000	***m*-2**→MV^{+}
S5	2.84	0.0226	**1c**→MV^{2+}	3.17	0.0126	**1c**→MV^{2+}
S6	2.98	0.0000	**1c**→MV^{2+}	3.18	0.0000	**1c**→MV^{2+}
S7	3.04	0.0004	**1c**→MV^{2+}	3.21	0.0141	**1c**→MV^{2+}
S8	3.05	0.0000	**1c**→MV^{2+}	3.30	0.0000	**1c**→MV^{2+}

[a] Calculated by the ZINDO method.
[b] Excitation energies (E) and oscillator strength (f).
[c] Electronic transition from the ground state is given.

***p*-2** and ***m*-2** (with the X-ray geometry) are calculated as 8.08 and 8.27 eV, respectively, by the ZINDO method.

In conclusion, we have developed a molecular recognition system using CT host complexes composed of *rac*-**1c** and $MVCl_2$. This CT host system isoselectively includes an aromatic molecule having a hydroxyl group. Moreover, the color of this inclusion crystal is sensitive to the structure of the guest molecules. This further enriches the functionality of these host CT systems, and they may prove useful as isoselective host systems and sensitive visual indicators of molecular recognition.

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4. This weight is the total crop of obtained crystals in one batch.
5. Crystallographic data of **I**: $0.5C_{12}H_{14}N_2Cl_2{\cdot}0.5C_6H_6O_2{\cdot}C_{20}H_{12}O_2Br_2C_2H_6O$, $M = 673.82$, triclinic, space group $P\bar{1}$, $a = 10.4014(6)$ Å, $b = 10.8798(6)$ Å, $c = 13.6206(8)$ Å, $\alpha = 105.8690(10)°$, $\beta = 92.0130(10)°$, $\gamma = 110.3700(10)°$ $V = 1375.33(14)$ Å^3, $Z = 2$, $D_c = 1.632$ g cm^{-3}, μ(Mo Kα) = 3.083 mm^{-1}, 12220 reflections measured, 6177 unique, final $R(F^2) = 0.0342$ using 5332 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0405, $T = 200(2)$ K. CCDC 644048.
6. Crystallographic data of **II**: $0.5C_{12}H_{14}N_2Cl_2{\cdot}0.5C_6H_6O_2{\cdot}C_{20}H_{12}O_2Br_2{\cdot}C_2H_6O$, $M = 673.82$, triclinic, space group $P\bar{1}$, $a = 10.4370(14)$ Å, $b = 10.7106(15)$ Å, $c = 13.7403(19)$ Å, $\alpha = 104.967(2)°$, $\beta = 91.731(2)°$, $\gamma = 112.771(2)°$, $V = 1353.5(3)$ Å^3, $Z = 2$, $D_c = 1.653$ g cm^{-3}, μ(Mo Kα) = 3.133 mm^{-1}, 11740 reflections measured, 6016 unique, final $R(F^2) = 0.0662$ using 4928 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0803, $T = 100(2)$ K. CCDC 644049. 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).
7. *rac*-**1c** (10.0 mg, 2.25×10^{-2} mmol), $MVCl_2$ (5.8 mg, 2.25×10^{-2} mmol), *p*-**2** (2.5 mg, 2.25×10^{-2} mmol), and *m*-**2** (2.5 mg, 2.25×10^{-2} mmol) were dissolved in EtOH (3 mL). After a few days, colored crystals were deposited and collected.
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