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Preparation of Charge-transfer Host Complex Composed of [9,9′-Biphenanthryl]-10,10′-diol Having a Large and Widely π-Conjugated Phenanthrene Ring

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A colored supramolecular charge-transfer (CT) host complex composed of racemic *rac*-[9,9′-biphenanthryl]-10,10′-diol, having a large and widely π-conjugated phenanthrene ring, as an electron donor and 2,5-dimethyl-1,4-benzoquinone as an electron acceptor has been developed. The molecular recognition properties (guest inclusion behavior and color) of the CT complex can be tuned by using electron donor molecules with different steric bulkiness and electron-donating properties.

Although many organic host systems that can include guest molecules have been developed, it is two-component supramolecular organic host systems that have attracted considerable attention.[1] This is because the molecular recognition properties of these host systems can be tuned by changing the component molecules without additional synthesis. Recently, we focused on donor–acceptor interactions as intermolecular forces for preparing host complexes and controlling their properties and prepared supramolecular charge-transfer (CT) host systems composed of [1,1′-biaryl]-2,2′-diol, in which *rac*-1,1′-bi-2-naphthol (*rac*-**1**) acts as an electron donor and *p*-benzoquinone derivatives act as an electron acceptor.[2] Characteristically, the color of these inclusion CT complexes depend on the type of included guest molecules. The molecular recognition properties of these complexes can be tuned by using *p*-benzoquinone derivatives having different electron-accepting properties.[3]

In this study, we attempt to tune the molecular recognition properties (guest inclusion behavior and color) of CT host complexes not by changing the type of *p*-benzoquinone derivatives (electron-accepting properties), but by using [1,1′-biaryl]-2,2′-diol with different steric bulkiness and electron-donating properties. 2,2′-Biphenyldiol (**2**) and *rac*-[9,9′-biphenanthryl]-10,10′-diol (*rac*-**3**)[4] having a large and widely π-conjugated phenanthrene ring were used instead of *rac*-**1** as [1,1′-biaryl]-2,2′-diol (Chart 1). 2,5-Dimethyl-1,4-benzoquinone (2,5Me-BQ) was used an electron acceptor. For the X-ray crystallographic analysis of the obtained CT host complexes, benzene, which is the simplest aromatic molecule, was used as the guest.

In a previous study, a CT host complex **I** including guest benzene molecules was prepared by combining *rac*-**1** and 2,5Me-BQ.[3] Similarly, the inclusion of benzene molecules was attempted by crystallization from a benzene solution containing **2** (or *rac*-**3**) and 2,5Me-BQ. **2** (or *rac*-**3**) (0.04 mmol) and 2,5Me-BQ (16 mg, 0.12 mmol) molecules were dissolved in the benzene solution (4–5 mL) by heating. The obtained solutions were left to stand at room temperature. After 7–9 days, colored CT complexes **II** (6 mg) and **III** (10 mg) were obtained from the **2**/2,5Me-BQ system and the *rac*-**3**/2,5Me-BQ system, respectively. Complexes **II** and **III** were orange and madder red, respectively, in color.

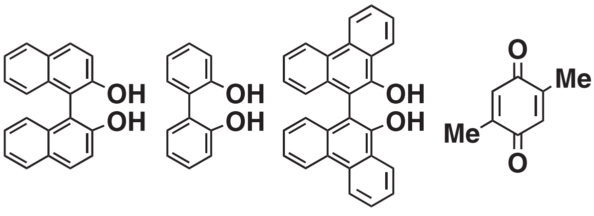

Chart 1.

In order to study their guest inclusion behavior, X-ray crystallographic analyses of complexes **II** and **III** were performed. The crystal structure of complex **II**, which is composed of **2**/2,5Me-BQ, is shown in Figure 1.[5] Although the previously reported complex **I** composed of *rac*-**1** and 2,5Me-BQ included benzene molecules as guests,[3,6] complex **II** obtained in this study included no guest benzene molecule. The X-ray analysis revealed that the stoichiometry of complex **II** is **2**:2,5Me-BQ = 1:1, and the space group is $C2/c$. This complex has a 1D hydrogen-bonded network structure composed of **2** and 2,5Me-BQ molecules (Figure 1a). The distance of the hydrogen bond (Figure 1a: indicated by red arrow A, O···O) is 2.80 Å. Moreover, the 2D layered network structure along the *b* and *c* axes is formed of the 1D hydrogen-bonded network structure due to CT interactions (3.22 Å)[7] (Figure 1a). This complex is formed by the self-assembly of the 2D layered network structure (Figure 1b: indicated by the red dotted rectangle) along the *a* axis without major interlayer interactions.[8]

The crystal structure of complex **III**, which is composed of *rac*-**3**/2,5Me-BQ, is shown in Figure 2.[5] In contrast to complex **II**, complex **III** included benzene molecules as guests. The X-ray analysis revealed that the stoichiometry of **III** is (*R*)-**3**:(*S*)-**3**:2,5Me-BQ:benzene = 1:1:2:1, and the space group is $P\bar{1}$. This complex has a 1D column-like structure composed of (*R*)-**3**, (*S*)-**3**, and 2,5Me-BQ molecules (Figure 2a). In contrast to complex **II**, 2,5Me-BQ is sandwiched between the phenanthrene rings of (*R*)-**3** and (*S*)-**3** molecules. The distance of the CT interaction between (*R*)-**3** (or (*S*)-**3**) and 2,5Me-BQ is 3.66 Å.[9] The carbonyl

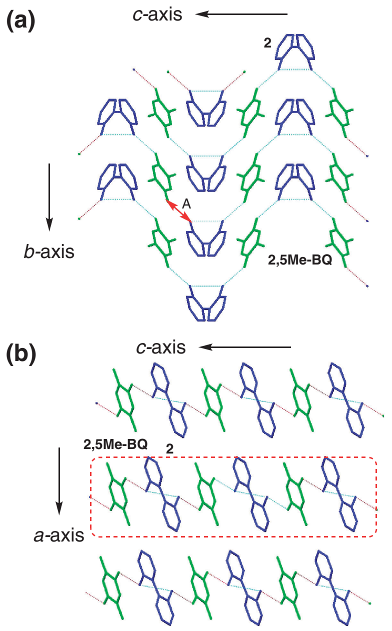

Figure 1. Crystal structure of complex **II**. (a) 2D layered network structure observed along *a* axis. Red arrow A indicates a hydrogen bond. (b) Packing structure comprising 2D layered network structure observed along *b* axis. The red dotted rectangle indicates the 2D layered network structure. **2** and 2,5Me-BQ molecules are indicated in blue and green, respectively.

groups of 2,5Me-BQ form hydrogen bonds with the hydroxy groups of a phenanthrol moiety. Although the torsion angles of (*R*)-**3** and (*S*)-**3** are identical (±77.8°), the carbonyl groups of 2,5Me-BQ form hydrogen bonds of slightly different lengths with the hydroxy groups of a phenanthrol moiety (Figure 2a: indicated by red arrows A and blue arrows A′, O···O are 2.71 and 2.77 Å, respectively). In addition, CH–π interactions between the methyl group of 2,5Me-BQ and the phenanthrene ring of **3** maintain this 1D column-like structure (Figure 2a: indicated by black arrows B and C, 2.69 and 2.74 Å, respectively).[8] In complex **III**, 1D channel-like cavities are formed along the *a* axis by the self-assembly of the 1D column-like structures without major intercolumnar interactions (Figure 2b).[8] Benzene guest molecules (Figure 2b: indicated by red spacefill view) are trapped in these cavities due to the phenanthrene–benzene edge-to-face interaction between 5-CH of the phenanthryl ring and the benzene (Figure 2b: indicated by black arrows D, 2.92 Å).[8]

These results suggest that a π-conjugated aryl ring larger than the naphthalene ring is effective for guest inclusion in the obtained CT host systems. This is the first example of preparation of a CT host complex composed of 9,9′-biphenanthryl-10,10′-diol, having a large and widely π-conjugated phenanthrene ring, and benzoquinone derivatives. In addition, this host complex may function as a visual host complex. In this CT host system, since [1,1′-biaryl]-2,2′-diol changes from *rac*-**1** to *rac*-**3**, the pattern of the 1D column-like structure is similar in complexes **I** and **III**; however, the distance between biarylalcohols along the 1D column-like structure in the complexes increase from 19.20 Å for complex **I**[3,6] to 19.55 Å for complex **III**.

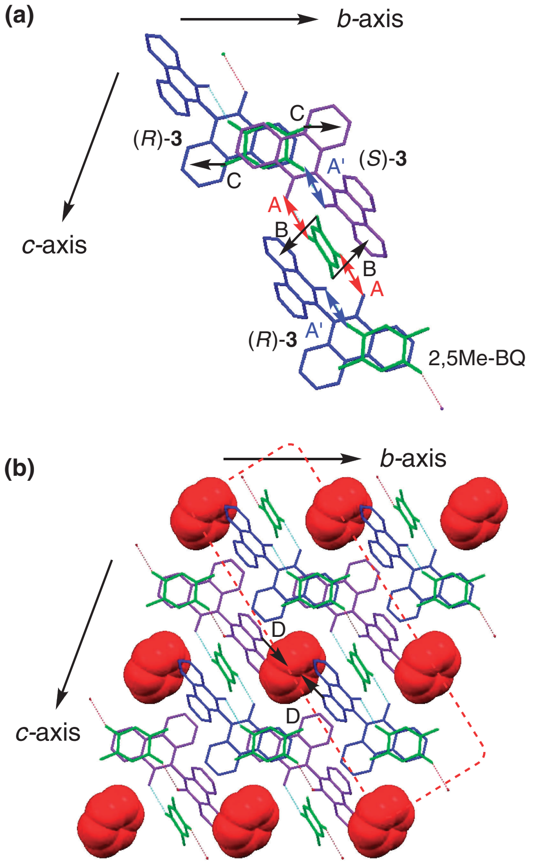

Figure 2. Crystal structure of complex **III**. (a) 1D column-like structure observed along *a* axis. Red arrows A and blue arrows A′ indicate hydrogen bonds. Black arrows B and C indicate CH–π interactions. (b) Packing structure comprising 1D column-like structure observed along *a* axis. Benzene is indicated by red spacefill view. Black arrows D indicate phenanthrene–benzene edge-to-face interactions. The red dotted rectangle shows the 1D column-like structure. (*R*)-**3**, (*S*)-**3**, and 2,5Me-BQ molecules are indicated in blue, purple, and green, respectively.

In order to study the stability of this host system, CT host complex **III**, which includes benzene, was allowed to stand under air atmosphere. After 30 min and 10 days, X-ray powder diffraction (XRPD) patterns of this complex were recorded and compared to simulated X-ray powder pattern of crystal **III** calculated from crystal structure data (Figure. ESI-2).[6] As a result, these XRPD patterns are similar. Moreover, ^{1}H NMR analyses of these complexes show **3**:2,5Me-BQ:benzene = 2:2:1. These results suggest that this CT host complex is stable under air atmosphere at least for 10 days.

Interestingly, the CT complex **III** including benzene exhibits a madder red color only in the solid state. A highly concentrated solution of this complex is yellow in color. Moreover, the color of the obtained CT complexes is quite different from that of the component solids (*rac*-**3** and 2,5Me-BQ: light yellow).

Expectedly, the color of host complexes **I** and **III** depends on the type of [1,1′-biaryl]-2,2′-diol used. Although the guest molecule is same (benzene), complex **I**, composed of *rac*-**1**, is light red, and complex **III**, composed of *rac*-**3**, is madder red (Figure 3).

Complex **I** Complex **III**

Figure 3. Photographs of CT complexes **I** and **III**.

In order to study the change in the color of the CT host systems, the ionization energy of *rac*-**1** and *rac*-**3** was calculated by using the hybrid density functional theory (B3LYP)[10] with the cc-pVDZ basis set.[11] The calculations were carried out using the Gaussian 03 program.[12] The ionization energies of *rac*-**1** and *rac*-**3** are 6.95 and 6.73 eV, respectively. This shows that the electron-donating property of [1,1′-biaryl]-2,2′-diol becomes stronger from *rac*-**1** to *rac*-**3**. On the other hand, as [1,1′-biaryl]-2,2′-diol changes from *rac*-**1** to *rac*-**3**, the distance of the CT interaction between [1,1′-biaryl]-2,2′-diol and 2,5Me-BQ in the complexes also increases from 3.36 to 3.66 Å. This shows that the CT interactions between donor and acceptor molecules become weaker from complex **I** to complex **III**. The difference in the colors of the inclusion CT complexes **I** and **III** is mainly caused by these two contradictory influences.

In conclusion, a supramolecular CT host system composed of *rac*-[9,9′-biphenanthryl]-10,10′-diol, having a large and widely π-conjugated phenanthrene ring, as the electron donor and 2,5Me-BQ as the electron acceptor has been developed. The molecular recognition properties (guest inclusion behavior and color) of the obtained CT host complex can be tuned by using electron donor molecules with different steric bulkiness and electron-donating properties. This study shows the potential application of novel visual host systems having a π-conjugated moiety in the solid state for molecular recognition.

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5 The X-ray diffraction data for single crystals were collected using Bruker Apex. The crystal structures were solved by the direct method[13] and refined by full-matrix least-squares using SHELX97.[13] The diagrams were drawn using PLATON.[14] The absorption corrections were performed using SADABS.[15] The nonhydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included in the models at their calculated positions in the riding-model approximation. Crystallographic data of **II**: $0.5C_{12}H_{10}O_2 \cdot 0.5C_8H_8O_2$, $M_r = 161.17$, Monoclinic, space group $C2/c$, $a = 16.839(4)$, $b = 5.8321(15)$, $c = 15.896(4)$ Å, $\beta = 94.042(5)°$, $V = 1557.3(7)$ Å^3, $Z = 8$, $D_{calcd} = 1.375$ g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha) = 0.095$ mm^{-1}, 4256 reflections measured, 1766 unique, final $R(F^2) = 0.0639$ using 1309 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0905, $T = 115(2)$ K. CCDC 754620. Crystallographic data of **III**: $C_{28}H_{18}O_2 \cdot C_8H_8O_2 \cdot 0.5C_6H_6$, $M_r = 561.62$, Triclinic, space group $P\bar{1}$, $a = 10.7984(18)$, $b = 11.0571(19)$, $c = 12.696(2)$ Å, $\alpha = 106.224(3)$, $\beta = 90.705(3)$, $\gamma = 103.874(3)°$, $V = 1408.0(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.325$ g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha) = 0.085$ mm^{-1}, 12177 reflections measured, 6205 unique, final $R(F^2) = 0.0582$ using 5084 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0722, $T = 115(2)$ K. CCDC 754621. 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, CB2 1EZ, U.K.; fax: +44 1223 336033; deposit@ccdc.cam.ac.uk).

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Distance between the center of 2,5Me-BQ and the average plane of the phenol 6-member ring.

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