

Colored Supramolecular Host System Using a Charge-Transfer Complex Composed of 1,1'-Bi-2-naphthol and 2,5-Substituted 1,4-Benzoquinone

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A colored, two-component, supramolecular, host system has been developed. This supramolecular host system uses a charge-transfer (CT) complex composed of racemic (*rac*)-1,1'-bi-2-naphthol, which acts as an electron donor, and 2,5-substituted 1,4-benzoquinone, which acts as an electron acceptor. This CT host system can selectively include aromatic guest molecules into a channel-like cavity by tuning the

packing of the electron-donor and electron-acceptor molecules. Characteristically, the color and diffuse reflectance spectra (DRS) of the inclusion CT complex can be tuned by changing the type of the component 2,5-substituted 1,4-benzoquinone.

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Introduction

Although many organic host systems that can include guest molecules have been reported so far,^[1] two-component, supramolecular, organic, host systems have particularly attracted considerable attention. This is because they can easily tune the shape and properties of a cavity by merely changing the component molecules without additional synthesis.^[2] Moreover, the chemical and physical properties of supramolecular host systems can be easily changed by changing the component molecules. Recently, we have focused on the use of donor-acceptor interactions as intermolecular forces for constructing and controlling the host structure.^[3] It has been reported that racemic (*rac*) and chiral supramolecular charge-transfer (CT) complexes composed of racemic or chiral 1,1'-bi-2-naphthol (BN) derivatives as an electron-donor molecule and *p*-benzoquinone (BQ) as an electron-acceptor molecule can act as a host system.^[4] Such a BN/BQ-CT host system can selectively include third component molecules as guests. More-

over, the colors of these CT complexes depend on the included guest molecules, and therefore, these complexes can be used as a visible molecular recognition system in the solid state. The advantage of the BN/BQ-CT host system is that the crystal structure and the chemical properties of CT complexes can be easily tuned by changing the 1,1'-bi-2-naphthol moieties without additional synthesis. On the other hand, the disadvantage of using the BN/BQ-CT host system is that since BQ molecules sublime easily, it is difficult to maintain the structure of the CT host complex for a long time. To overcome this problem, recently, 2-chloro-5-methyl-1,4-benzoquinone (2Cl-5Me-BQ) was used as an electron acceptor instead of BQ, and a comparatively stable CT complex composed of *rac*-1,1'-bi-2-naphthol (*rac*-1) was developed.^[5] However, the optical properties of this CT complex, that is, the color and diffuse reflectance spectra (DRS), have not been studied. Moreover, with the exception of 2Cl-5Me-BQ, no other *rac*-1-CT host system composed of 2,5-substituted 1,4-benzoquinone (2,5-substituted BQ) has been studied.

In this paper, we report the preparation, optical and molecular recognition properties, and crystal structure of a novel CT host system composed of *rac*-1 as an electron donor and 2,5-substituted BQ as an electron acceptor. Three types of 2,5-substituted BQ, namely, 2,5-dimethyl-1,4-benzoquinone (2,5Me-BQ), 2Cl-5Me-BQ, and 2,5-dichloro-1,4-benzoquinone (2,5Cl-BQ), were used. In such a CT host system, it is expected that the chemical and physical properties are controlled by the component 2,5-substituted BQ moieties. In order to study the guest inclusion mechanism of this CT host system by X-ray crystallographic analysis, two simple aromatic molecules (benzene and toluene) have been used as guests (Figure 1).

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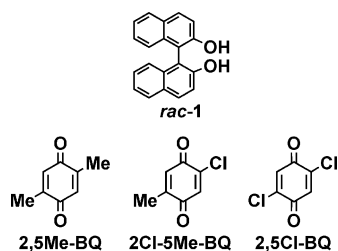
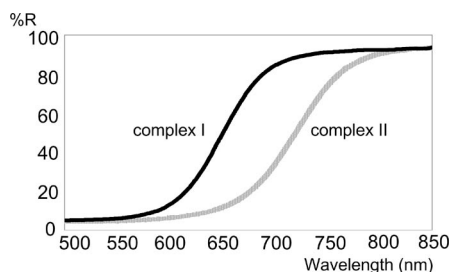


Figure 1. Component molecules.

Results and Discussion

First, we studied the inclusion of benzene as a guest aromatic molecule in this CT system. We attempted to include benzene by crystallization from a benzene solution containing *rac*-1 and each of the three types of 2,5-substituted BQ separately. We incubated each benzene solution at room temperature for 2–7 d. We found that when we used 2,5Me-BQ and 2Cl-5Me-BQ as electron acceptors, we obtained colored inclusion complexes **I** and **II**, respectively. Interestingly, although we prepared 10 batches of benzene solution containing *rac*-1 and 2,5Cl-BQ by the above method, we obtained small amounts of a black powder-like solid only from one batch. We did not observe such colored solids in the other nine batches. This could imply that the guest inclusion ability of this CT host system can be tuned by changing the component 2,5-substituted BQ.

Interestingly, the colors of these inclusion CT complexes dramatically changed according to the type of 2,5-substituted BQ used. The inclusion complex **I**, composed of 2,5Me-BQ, was light red. Complex **II**, composed of 2Cl-5Me-BQ, was deep red. Both crystals exhibited these colors only in the solid state. Highly concentrated solutions of these crystals were yellow in color. Moreover, the colors of these CT complexes were quite different from those of the component solids (*rac*-1: white, 2,5Me-BQ: light yellow, and 2Cl-5Me-BQ: yellow). The DRS of complexes **I** and **II** in the solid state are shown in Figure 2.

Figure 2. DRS of complexes **I** (black line) and **II** (gray line).

Expectedly, the DRS of **I** and **II** in the solid state differed. The absorption edges of **I** and **II** are located at about 550 nm and 580 nm, respectively. These results suggest that the *rac*-1/2,5-substituted BQ-CT host system can function as a visual host in the solid state. Moreover, the results show that the optical properties of this CT host system can be tuned by changing the component 2,5-substituted BQ.

In order to understand the guest inclusion mechanisms of these CT complexes and the origins of their different electronic absorptions, we attempted X-ray analyses of these CT complexes. The crystal structure of complex **I** obtained from the *rac*-1/2,5Me-BQ system is shown in Figure 3.

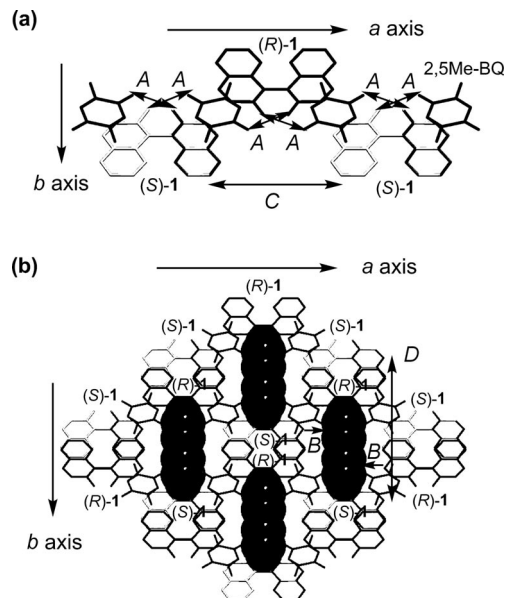


Figure 3. Crystal structure of complex **I**. (a) An extracted 1D-column-like structure is observed along the *c* axis. Arrows *A* indicate hydrogen bonds. (b) A 1D-channel-like cavity formed by the self-assembly of the 1D-column-like structure is observed along the *c* axis. Benzene is indicated by space-filling models. Arrows *B* indicate naphthalene–benzene edge-to-face interactions.

The stoichiometry of complex **I** is *(R)*-1:*(S)*-1/2,5Me-BQ/benzene (0.5:0.5:1:1), and the space group is *C2/c*. This complex has a characteristic 1D-column-like structure composed of *(R)*-1, *(S)*-1, and 2,5Me-BQ molecules (Figure 3, a); that is, 2,5Me-BQ is sandwiched between the naphthol rings of the *(R)*-1 and *(S)*-1 molecules. The CT distance between the center of 2,5Me-BQ and the center of the naphthol ring of **I** is 3.36 Å. The length of the hydrogen bond [O⋯O] between the carbonyl group of 2,5Me-BQ and the hydroxy group of **I** is 2.71 Å (Figure 3, a, indicated by arrows *A*). The torsion angles of *(R)*-1 and *(S)*-1 are identical ($\pm 98.1^\circ$). Complex **I** is formed by the self-assembly of the 1D-column-like structure along the *b* and *c* axes (Figure 3, b). Characteristically, 1D-channel-like cavities are formed along the *c* axis by the self-assembly of the 1D-column-like structures (Figure 3, b), although naphthalene–naphthalene edge-to-face interactions are not observed between these 1D-column-like structures.^[6] In these cavities, the guest benzene molecules (Figure 3, b, indicated by space-filling models) are trapped by a naphthalene–benzene edge-to-face interaction between the 4-CH of the naphthol ring in **I** and the guest benzene (Figure 3, b, indicated by arrows *B*, 2.75 Å).^[6]

The crystal structure of complex **II** obtained from the *rac*-1/2Cl-5Me-BQ system is shown in Figure 4.

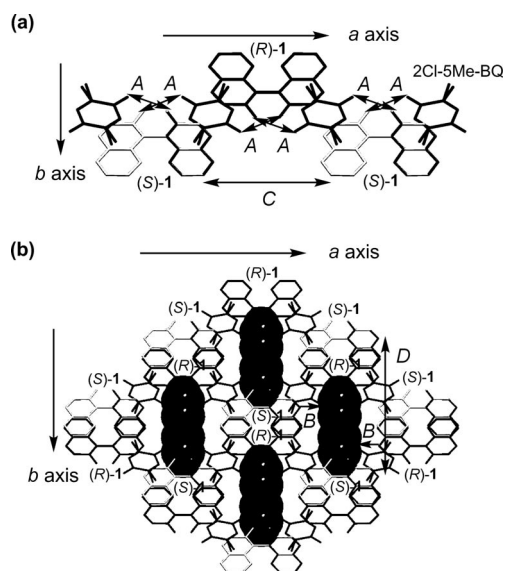


Figure 4. Crystal structure of complex II. (a) An extracted 1D-column-like structure is observed along the *c* axis. Arrows *A* indicate hydrogen bonds. (b) A 1D-channel-like cavity formed by the self-assembly of the 1D-column-like structure is observed along the *c* axis. Benzene is indicated by space-filling models. Arrows *B* indicate naphthalene–benzene edge-to-face interactions.

The stoichiometry of complex II is (R)-1:(S)-1/2Cl-5Me-BQ/benzene (0.5:0.5:1:1), and the space group is $C2/c$. In this complex, although 2Cl-5Me-BQ is disordered, (R)-1 and (S)-1 molecules form a 1D-column-like structure with 2Cl-5Me-BQ by a CT interaction along the *a* axis, which is similar to complex I (Figure 4, a). The distance of the CT interaction between (R)-1 [or (S)-1] and 2Cl-5Me-BQ is 3.55 Å.^[7] Both the carbonyl groups of 2Cl-5Me-BQ form identical hydrogen bonds with the hydroxy groups of a naphthol moiety (Figure 4, a, indicated by arrows *A*, O···O 2.73 Å). The torsion angles of (R)-1 and (S)-1 are also identical ($\pm 97.9^\circ$). 1D-channel-like cavities are formed along the *b* and *c* axes without naphthalene–naphthalene edge-to-face interactions (Figure 4, b).^[6] In these cavities, the guest benzene molecules (Figure 4, b, indicated by a space-filling model) are trapped by a naphthalene–benzene edge-to-face interaction between the 4-CH of the naphthol ring in I and the guest benzene (Figure 4, b, indicated by arrows *B*, 2.75 Å), as is the case in complex I.^[6]

The electron affinities of 2,5Me-BQ, 2Cl-5Me-BQ, and 2,5Cl-BQ are –1.32, –1.65, and –2.01 eV, respectively.^[8] Generally, it is well-known that a strong electron acceptor with a small substituent easily forms a CT complex. On the other hand, a molecule with a large and bulky substituent easily forms a cavity for guest inclusion in the solid state. In this case, 2,5Cl-BQ is the strongest electron acceptor among the three types of 2,5-substituted BQ, and it has the smallest substituent (chloride) among them. However, in the *rac*-1/2,5Cl-BQ system, the formation of the CT complex and the inclusion of the guest benzene were difficult. This indicates that the steric effect of the two substituents

of BQ derivatives is more important than the electron-acceptor strengths of BQ derivatives with regard to the formation of the *rac*-1/2,5-substituted BQ-CT complex.

Comparing the channel-like cavity of inclusion complex I with that of inclusion complex II, we found that the size of the channel-like cavity depends on the type of 2,5-substituted BQ (2,5Me-BQ and 2Cl-5Me-BQ) used; that is, as the 2,5-substituted BQ changes from 2,5Me-BQ to 2Cl-5Me-BQ, the distances between the binaphthol molecules along the 1D column (*C*, Figures 3, a and 4, a) and the distances between the 1D columns (*D*, Figures 3, b and 4, b) become slightly shorter (from 11.25 to 11.23 Å and from 12.80 to 12.75 Å, respectively).

Moreover, as shown in Figure 2, the different colors of complexes I and II originate from the different absorption edges of these crystals. Complex II has a longer wavelength absorption than that of complex I. This order is the same as the electron-acceptor strength of 2,5-substituted BQ. In other words, because the BQ derivative of complex II (2Cl-5Me-BQ) is a stronger electron acceptor than that of the BQ derivative of complex I (2,5Me-BQ), the absorption wavelength of complex II is longer than that of complex I.

Next, we studied the inclusion of toluene as the guest molecule. As in the case with benzene, we attempted to include toluene by crystallization from a toluene solution containing *rac*-1 and each of the three types of 2,5-substituted BQ separately. We incubated each solution at room temperature. In contrast to the inclusion of benzene, after 5–7 d, we obtained colored inclusion complexes from all the systems; that is, complex III from the *rac*-1/2,5Me-BQ system, complex IV from the *rac*-1/2Cl-5Me-BQ system, and complex V from the *rac*-1/2,5Cl-BQ system. Thus, we can conclude that this CT host system has selective inclusion ability. In the *rac*-1/2,5Cl-BQ system, the formation of CT complex from benzene solution was difficult. In order to study the complexation behavior in solution, we measured the UV/Vis spectra of *rac*-1, 2,5Cl-BQ, and the mixture of *rac*-1 and 2,5Cl-BQ in benzene and toluene solutions, respectively (see Supporting Information). As a result, in neither solutions did we observe the formations of CT complexes. This also shows that the formation and the characteristics of these CT complexes are peculiar to the solid state.

Expectedly, for this guest molecule as well, the colors of the inclusion CT complexes changed according to the type of 2,5-substituted BQ used. The inclusion complex III, composed of 2,5Me-BQ, was light red. The colors of complex IV, composed of 2Cl-5Me-BQ, and complex V, composed of 2,5Cl-BQ, were deep red and dark blue, respectively. The DRS of complexes III–V in the solid state are shown in Figure 5.

The DRS of complexes III–V in the solid state differed. The absorption edges of III–V are located at ca. 550 nm, 590 nm, and 670 nm, respectively. These results also suggest that this *rac*-1/2,5-substituted BQ-CT host system can function as a visual host in the solid state, and the optical properties of CT host complexes can be easily tuned by changing the 2,5-substituted BQ moieties.

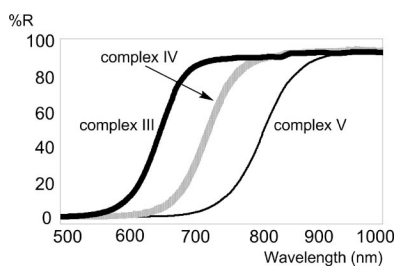


Figure 5. DRS of complexes **III** (black line), **IV** (gray line), and **V** (narrow black line).

In order to study their guest inclusion mechanisms and the origins of their different electronic absorptions, we performed X-ray crystallographic analyses of complexes **III–V**. The crystal structure of complex **III**, which is composed of *rac*-1/2,5Me-BQ, is shown in Figure 6. The X-ray analysis revealed that the stoichiometry of **III** is identical to that of **I**, that is, (*R*)-1:(*S*)-1/2,5Me-BQ/toluene (0.5:0.5:1:1), and the space group is *Cc*. This complex also has a 1D-column-like structure composed of (*R*)-1, (*S*)-1, and 2,5Me-BQ molecules, as is the case with **I** (Figure 6, a). The distance of the CT interaction between (*R*)-1 [or (*S*)-1] and 2,5Me-BQ is 3.41 Å.^[7] The carbonyl groups of 2,5Me-BQ form hydrogen bonds with the hydroxy groups of a naphthol moiety. However, although the torsion angles of (*R*)-1 and (*S*)-1 are identical ($\pm 97.7^\circ$), the carbonyl groups of 2,5Me-BQ form hydrogen bonds of a slightly different length with the hydroxy groups of a naphthol moiety (Figure 6, a, indicated by arrows *A* and *A'*, O...O are 2.71 and 2.72 Å, respectively). In this complex, 1D-channel-like cavities are formed along the *c* axis by the self-assembly of the 1D-column-like structures without naphthalene–naphthalene edge-to-face interactions (Figure 6, b), as observed in the case of **I**.^[6] Toluene guest molecules (Figure 6, b, indicated by a space-filling model) are trapped in these cavities, although the toluene molecules are disordered and naphthalene–benzene edge-to-face interactions are not observed.^[6] Comparing complexes **I** (including benzene) and **III** (including toluene), we found that although the packing style of the shared 1D-column-like structure in both complexes is similar, the distances between the binaphthol molecules along the 1D-column [*C*, Figures 3, a and 6, a] and between the 1D-columns [*D*, Figures 3, b and 6, b] increases from 11.25 Å for complex **I** to 11.45 Å for complex **III** and from 12.80 Å for complex **I** to 12.98 Å for complex **III**, respectively.

The crystal structure of complex **IV**, which is composed of *rac*-1/2Cl-5Me-BQ, is shown in Figure 7. The X-ray analysis revealed that the stoichiometry of **IV** is identical to that of **III**, that is, (*R*)-1:(*S*)-1/2Cl-5Me-BQ/toluene (0.5:0.5:1:1), and the space group is *Cc*. This complex also has a characteristic 1D-column-like structure composed of (*R*)-1, (*S*)-1, and 2Cl-5Me-BQ molecules, as is the case in **III** (Figure 7, a). The distance of the CT interaction between (*R*)-1 [or (*S*)-1] and 2Cl-5Me-BQ is 3.60 Å.^[7] In this case as well, although the torsion angles of (*R*)-1 and (*S*)-1 are identical ($\pm 97.3^\circ$), the carbonyl groups of 2Cl-5Me-BQ

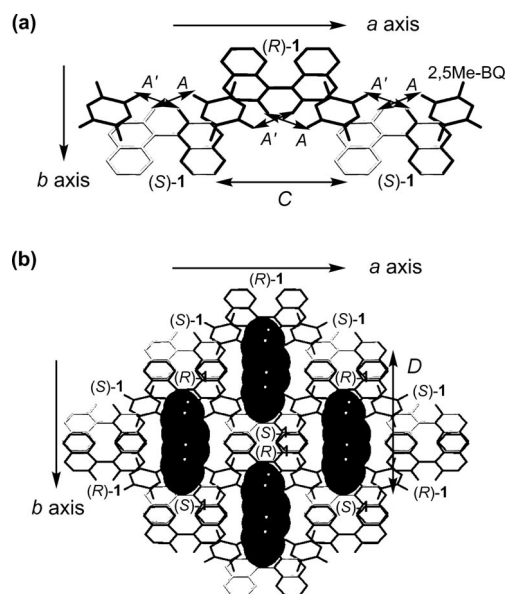


Figure 6. Crystal structure of complex **III**. (a) An extracted 1D-column-like structure is observed along the *c* axis. Arrows *A* and *A'* indicate hydrogen bonds. (b) A 1D-channel-like cavity formed by the self-assembly of the 1D-column-like structure is observed along the *c* axis. Toluene is indicated by space-filling models.

form hydrogen bonds of a slightly different length with the hydroxy groups of a naphthol moiety (Figure 7a, indicated by arrows *A* and *A'*, O...O are 2.63 and 2.66 Å, respectively). Further, 1D-channel-like cavities are formed along the *c* axis without naphthalene–naphthalene edge-to-face interactions (Figure 7, b).^[6] Disordered toluene guest molecules (Figure 7, b, indicated by a space-filling model) are trapped in these cavities by two kinds of naphthalene–benzene edge-to-face interactions: (a) one between the 4-CH of the naphthol ring and the benzene ring of toluene and (b) one between the 14-CH of the naphthol ring and the benzene ring of toluene (Figure 7, b, indicated by arrows *B* and *B'*, 2.75 and 2.74 Å, respectively).^[6] In the *rac*-1/2Cl-5Me-BQ-CT system, as the aromatic guest changes from benzene to toluene, although the packing style of the shared 1D-column-like structure is similar in **II** and **IV**, the distances between the binaphthol molecules along the 1D-column in complex **IV** (*C*, Figures 4, a and 7, a) decrease from 11.23 to 10.28 Å while the distances between the 1D-columns (*D*, Figures 4, b and 7, b) increase from 12.75 to 12.88 Å. Although this variation is different from that of the *rac*-1/2,5Me-BQ system, this shows that this CT host system includes guest aromatic molecules by tuning the 1D-column-like structure and its packing.

Finally, the crystal structure obtained by the X-ray analysis of complex **V**, which is composed of *rac*-1/2,5Cl-BQ, is shown in Figure 8. The stoichiometry of complex **V** is (*R*)-1:(*S*)-1/2,5Cl-BQ/toluene (0.5:0.5:1:1), and the space group is *Cc*. This complex also has a characteristic 1D-column-like structure composed of (*R*)-1, (*S*)-1, and 2,5Cl-BQ molecules, similar to complexes **I–IV** (Figure 8, a). The distance of the CT interaction between (*R*)-1 [or (*S*)-1] and 2,5Cl-BQ is 3.34 Å.^[7] Although the torsion angles of (*R*)-1

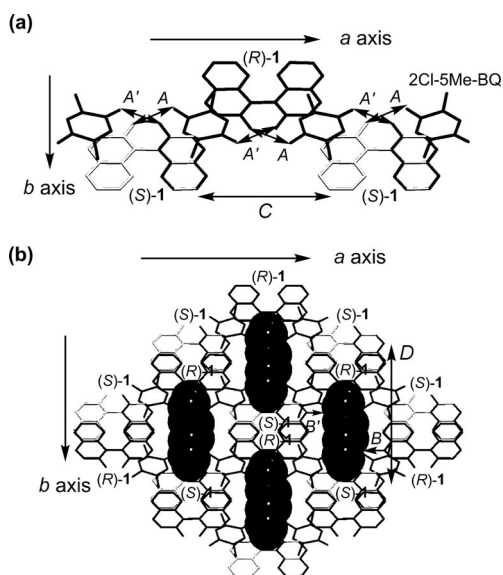


Figure 7. Crystal structure of complex IV. (a) An extracted 1D-column-like structure is observed along the *c* axis. Arrows *A* and *A'* indicate hydrogen bonds. (b) A 1D-channel-like cavity formed by the self-assembly of the 1D-column-like structure is observed along the *c* axis. Toluene is indicated by space-filling models. Arrows *B* and *B'* indicate naphthalene–benzene edge-to-face interactions.

and *(S)-1* are identical ($\pm 96.6^\circ$), the carbonyl groups of 2,5Cl-BQ form hydrogen bonds with the hydroxy groups of a naphthol moiety (Figure 8, a, indicated by arrows *A* and *A'*, $O\cdots O$ are 2.74 and 2.72 Å, respectively). In this complex, 1D-channel-like cavities are formed along the *c* axis without naphthalene–naphthalene edge-to-face interactions.

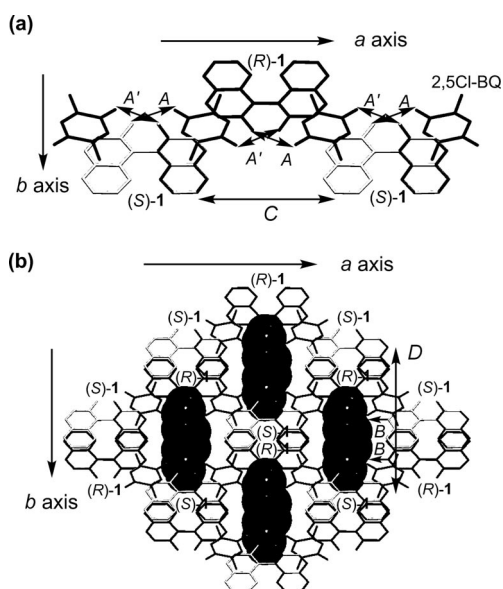


Figure 8. Crystal structure of complex V. (a) An extracted 1D-column-like structure is observed along the *c* axis. Arrows *A* and *A'* indicate hydrogen bonds. (b) A 1D-channel-like cavity formed by the self-assembly of the 1D-column-like structure is observed along the *c* axis. Toluene is indicated by space-filling models. Arrow *B* indicates naphthalene–benzene edge-to-face interactions.

tions.^[6] In these cavities, disordered toluene guest molecules (Figure 8, b, indicated by a space-filling model) are trapped by a naphthalene–benzene edge-to-face interaction between the 4-CH of the naphthol ring and the benzene ring of the guest toluene (Figure 8, b, indicated by arrows *B*, 2.77 Å).^[6]

Comparing the channel-like cavity of inclusion complexes III–V, we found that the size of the channel-like cavity depends on the type of 2,5-substituted BQ used (2,5Me-BQ, 2Cl-5Me-BQ, or 2,5Cl-BQ); that is, although the distances between the binaphthol molecules along the 1D-column (*C*, Figures 6, a, 7, a, and 8, a) are 11.45, 10.28, and 11.38 Å, respectively, the distances between the 1D-columns (*D*, Figures 6, b, 7, b, and 8, b) gradually decrease from 12.98 to 12.88 and finally to 12.81 Å.

Comparing the DRS of inclusion complexes III–V, we observed that the absorption edge shifted to longer wavelengths [from 550 nm (III) to 590 nm (IV) and finally to 670 nm (V)] as the electron affinity of the BQ-derivative became stronger [from 2,5Me-BQ (III, lowest affinity) to 2Cl-5Me-BQ (IV) and to 2,5Cl-BQ (V, highest affinity)]. The colors of the CT complexes of the three CT host systems therefore would reflect the electron-acceptor properties of 2,5-substituted BQ, as is the case in complexes I and II.

Conclusions

A supramolecular host system comprising CT complexes composed of *rac-1* as the electron donor and 2,5-substituted BQ as the electron acceptor has been developed. From X-ray crystallographic analyses, we found that the CT host system can include benzenes or toluenes as guests by tuning the 1D-column-like structure composed of *rac-1* and 2,5-substituted BQ and its packing. The color and DRS of the CT crystals formed by the inclusion of guest molecules are sensitive to the 2,5-substituted BQ moiety. Moreover, the molecular recognition ability of the CT complexes can be tuned by changing the type of 2,5-substituted BQ used. We also found that the major factor that decides the absorption of the CT host system is the electron-accepting property of the type of 2,5-substituted BQ used. This is the first systematic study on a tunable and visual CT host system that was carried out by changing an electron-acceptor component molecule. The unique abilities of the CT host system further enhance its potential applications, for example, in the design of novel visual indicators in the solid state for molecular recognition.

Experimental Section

General Methods: All reagents were used directly as obtained commercially. 2,5Me-BQ, 2Cl-5Me-BQ, and 2,5Cl-BQ were purchased from Tokyo Kasei Kogyo Co., Ltd. Component molecule *rac-1*, benzene, and toluene were purchased from Wako Pure Chemical Industry.

Formation of a CT Complex Through the Inclusion of Benzene: *rac-1* (0.04 mmol) and 2,5-substituted BQ (0.12 mmol) were dissolved in benzene (4–5 mL) through heating. Each solution was allowed

to stand at room temperature. After 2–7 d, colored crystals [**I** from *rac*-1/2,5Me-BQ system (7 mg) and **II** from *rac*-1/2Cl-5Me-BQ system (9 mg)] were found to be deposited and were subsequently collected. The weight of each type of crystal is the total crop of the crystals obtained in a single batch.

Formation of a CT Complex Including Toluene: *rac*-1 (0.04 mmol) and 2,5-substituted BQ (0.12 mmol) were dissolved in toluene (4–5 mL) with heating. Each solution was allowed to stand at room temperature. After 5–7 d, the respective colored crystals [**III** from *rac*-1/2,5Me-BQ system (7 mg), **IV** from *rac*-1/2Cl-5Me-BQ system (9 mg), and **V** from *rac*-1/2,5Cl-BQ system (8 mg)] were deposited and collected. The weight of each type of crystal is the total crop of the crystals obtained in a single batch.

Measurement of DRS of CT Complex: The DRS of the crystals were measured using a Hitachi U-4000 spectrometer.

Measurement of UV/Vis Spectra: The UV/Vis spectra were measured using a Shimadzu UV-2400PC spectrometer.

X-ray Crystallographic Studies

The X-ray diffraction data for single crystals were collected using a Bruker Apex instrument. The crystal structures were solved by the direct method^[9] and refined by full-matrix least-squares using SHELX97.^[10] The diagrams were drawn using PLATON.^[11] The absorption corrections were performed using SADABS.^[12] The non-hydrogen 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.

CCDC-706420 (for **I**), -679179 (for **II**), -706242 (for **III**), -696153 (for **IV**), and -706241 (for **V**) contain the crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/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].

I: $C_{20}H_{14}O_2 \cdot 0.5C_8H_8O_2 \cdot 0.5C_6H_6$, $M = 250.28$, monoclinic, space group $C2/c$, $a = 14.5266(12)$, $b = 12.7974(10)$, $c = 13.9484(11)$ Å, $\beta = 95.2280(10)^\circ$, $V = 2582.3(4)$ Å³, $Z = 8$, $D_c = 1.288$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.083$ mm⁻¹, 7905 reflections measured, 2972 unique, final $R(F^2) = 0.0430$ using 2593 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0492$, $T = 115(2)$ K.

II: $C_{20}H_{14}O_2 \cdot 0.5C_7H_5O_2Cl_1 \cdot 0.5C_6H_6$, $M = 260.49$, monoclinic, space group $C2/c$, $a = 14.5320(10)$, $b = 12.7450(10)$, $c = 13.9860(10)$ Å, $\beta = 95.267(2)^\circ$, $V = 2579.4(3)$ Å³, $Z = 8$, $D_c = 1.342$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.187$ mm⁻¹, 7872 reflections measured, 2977 unique, final $R(F^2) = 0.0491$ using 2557 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0565$, $T = 130(2)$ K.

III: $C_{20}H_{14}O_2 \cdot C_8H_8O_2 \cdot C_7H_8$, $M = 514.59$, monoclinic, space group Cc , $a = 14.4969(8)$, $b = 12.9791(7)$, $c = 14.0426(7)$ Å, $\beta = 94.2330(10)^\circ$, $V = 2635.0(2)$ Å³, $Z = 4$, $D_c = 1.297$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.084$ mm⁻¹, 11360 reflections measured, 3054 unique, final $R(F^2) = 0.0440$ using 2701 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0497$, $T = 115(2)$ K.

IV: $C_{20}H_{14}O_2 \cdot C_7H_5O_2Cl_1 \cdot C_7H_8$, $M = 535.01$, monoclinic, space group Cc , $a = 14.4557(9)$, $b = 12.8781(8)$, $c = 14.0147(9)$ Å, $\beta = 94.1710(10)^\circ$, $V = 2602.1(3)$ Å³, $Z = 4$, $D_c = 1.366$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.187$ mm⁻¹, 11259 reflections measured, 3036 unique, final $R(F^2) = 0.0420$ using 2762 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0456$, $T = 115(2)$ K.

V: $C_{20}H_{14}O_2 \cdot C_6H_2O_2Cl_2 \cdot C_7H_8$, $M = 555.42$, monoclinic, space group Cc , $a = 14.4522(9)$, $b = 12.8116(8)$, $c = 14.0348(9)$ Å, $\beta = 94.1430(10)^\circ$, $V = 2591.8(3)$ Å³, $Z = 4$, $D_c = 1.423$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.290$ mm⁻¹, 7881 reflections measured, 2969 unique, final $R(F^2) = 0.0352$ using 2686 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0394$, $T = 115(2)$ K.

$K_\alpha) = 0.290$ mm⁻¹, 7881 reflections measured, 2969 unique, final $R(F^2) = 0.0352$ using 2686 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0394$, $T = 115(2)$ K.

Theoretical Calculations of Electron Affinities of BQ Derivatives: The electron affinities of the three BQ derivatives were calculated by the hybrid density functional theory (B3LYP)^[13] with the cc-pVDZ basis set.^[14] The calculations were carried out using the GAUSSIAN 03 program.^[15]

Supporting Information (see also the footnote on the first page of this article): UV/Vis spectra of *rac*-1, 2,5Cl-BQ, and a mixture of *rac*-1 and 2,5Cl-BQ in benzene or toluene solution.

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