ORGANIC
LETTERS

2006
Vol. 8, No. 14
2941−2944

Visualization of Molecular Recognition: A Novel System Based on Charge-Transfer Complexes Composed of 1,1′-Bi-2-naphthol Derivatives and *p*-Benzoquinone

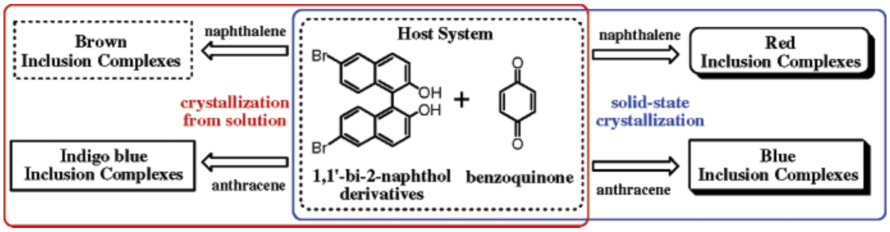
Yoshitane Imai,[†,§] Nobuo Tajima,[†] Tomohiro Sato,[†] and Reiko Kuroda*,[†,‡]

*JST ERATO-SORST Kuroda Chiromorphology Team, 4-7-6, Komaba,
Meguro-ku, Tokyo, 153-0041, Japan, and Department of Life Sciences,
Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1,
Komaba, Meguro-ku, Tokyo, 153-8902, Japan*

ckuroda@mail.ecc.u-tokyo.ac.jp

Received April 10, 2006

ABSTRACT



Charge-transfer (CT) complexes composed of 1,1′-bi-2-naphthol derivatives as an electron donor and *p*-benzoquinone as an acceptor serve as an excellent host system for visual molecular recognition. This is because they form inclusion crystals with guest aromatic compounds which display remarkably different colors depending on the structure of the component molecules and on the method of crystallization (i.e., solution crystallization or solid cogrinding of component crystals).

In the field of chemistry, the development of a simple molecular recognition system, particularly, a visual molecular recognition system, is an important issue. Thus, extensive studies have been carried out and several indicators have been developed. However, these indicators are mostly composed of one molecule.[1] If the indicator is supramolecular and composed of two or more molecules, the molecular recognition ability can be easily modified by changing the combination of the components. Recently, we have reported charge-transfer (CT) complexation between 1,1′-bi-2-naphthol (BN) derivatives as an electron donor and *p*-benzoquinone (BQ) as an acceptor.[2] All these CT complexes display strong colors in the visible region. We have further found that these CT complexes include other aromatic guest molecules to form three-component inclusion crystals.[2b] The color of a CT complex is generally sensitive to the distances between the electron donor and acceptor molecules.[3] Thus,

---

[†] ERATO-SORST Kuroda Chiromorphology Team.

[‡] The University of Tokyo.

[§] Current address: Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashi−Osaka 577−8502, Japan.

(1) For reviews, see: (a) Takagi, M.; Nakamura, H. *J. Coord. Chem.* **1986**, *15*, 53. (b) Takagi, K.; Ueno, K. *Top. Curr. Chem.* **1984**, *121*, 39. (c) Löhr, H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65.

(2) (a) Toda, F.; Senzaki, M.; Kuroda, R. *Chem. Commun.* **2002**, 1788. (b) Kuroda, R.; Imai, Y.; Sato, T. *Chirality* **2001**, *13*, 588. (c) Imai, Y.; Tajima, N.; Sato, T.; Kuroda, R. *Chirality* **2002**, *14*, 604. (d) Kuroda, R.; Imai, Y.; Tajima, N. *Chem. Commun.* **2002**, 2848. (e) Braga, D.; Grepioni, F. *Angew. Chem. Int. Ed.* **2004**, *43*, 4002; *Chem. Commun.* **2005**, 3635.

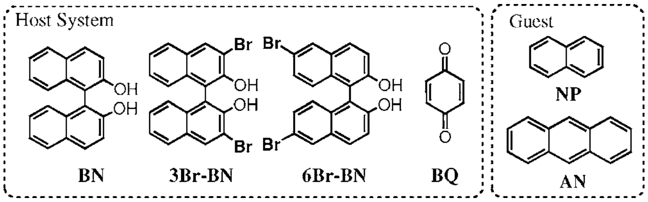
(3) Tanaka, J.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 739. Prochorow, J. *J. Chem. Phys.* **1965**, *43*, 3394. Prochorow, J.; Tramer, A. *J. Chem. Phys.* **1966**, *44*, 4545. Offen, H. W.; Studebaker, J. F. *J. Chem. Phys.* **1967**, *47*, 253.

10.1021/ol060862q CCC: $33.50

if the color of the CT crystals changes substantially by the inclusion of the guest molecules, the system may serve as a visual indicator of molecular recognition.

Generally, adduct crystals are formed by crystallization from solution. However, solid-state crystallization by simple mixing/grinding of component crystals under a solvent-free condition also generates adduct crystals, and this has attracted interest because of its unique chemistry.[2] The aforementioned CT complexes are good examples.[2b] Interestingly, we have found that racemic BN−BQ CT crystals obtained in the solid phase are different from those obtained from solution.[2d] Thus, the mechanism for complexation may vary depending on the crystallization method.

In this paper, we report a visual molecular recognition system that uses the CT complexes of racemic 1,1′-bi-2-naphthol derivatives (BN, 6,6′-dibromo-1,1′-bi-2-naphthol (6BrBN), or 3,3′-dibromo-1,1′-bi-2-naphthol (3BrBN)) and BQ as the host systems. Two aromatic compounds (naphthalene (NP) and anthracene (AN)) were used as the guest molecule, and the inclusion behavior was studied both in solution and in the solid state.



Inclusion of guest molecules (NP or AN) into the BN−BQ host system was attempted in solution by adding either NP or AN to the ether/hexane solution of BN and BQ. The solutions were left to stand at room temperature. In both cases, after 1 day, several indigo blue crystals were obtained and they were found to contain NP (crystal **I**) or AN (crystal **II**). The solid-state reflection spectra of crystals **I** and **II** are similar to each other as expected from the crystal colors. Thus, the color of the BN−BQ system is insensitive to the type of guest molecule included, and hence, the system cannot be used as a visible molecular recognition tool.

By changing the component molecule of this system, we altered the molecular recognition ability. In the 6BrBN−BQ system where 6BrBN, instead of BN, was used as an electron donor, inclusion of guest molecules (NP or AN) was attempted by crystallization from solution. After 1 day, several CT crystals including the guest molecules were produced. Interestingly, the inclusion crystals containing NP (**III**) were brown in color, whereas those containing AN (**IV**) were indigo blue. The solid-state reflection spectra of crystals **III** and **IV** were substantially different from each other with the absorption edge located at ca. 620 and 720 nm, respectively (Figure 1). The colors of these complexes are unique to the solid state, as the highly concentrated solutions of these inclusion crystals exhibited a similar deep orange color.

The results indicate that the 6BrBN−BQ system can be used as a visual indicator of molecular recognition. X-ray analysis was performed to investigate the inclusion mechanism of the guest molecules. The structures of crystals **I**−**IV** are compared in Figure 2. The stoichiometries of these crystals are identical: BN (or 6BrBN)/BQ/guest molecule = 2:1:2, with the same space group of $P\bar{1}$.

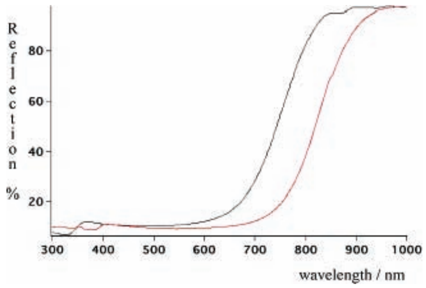


Figure 1. Reflection spectra of crystal **III** (black line) and crystal **IV** (red line).

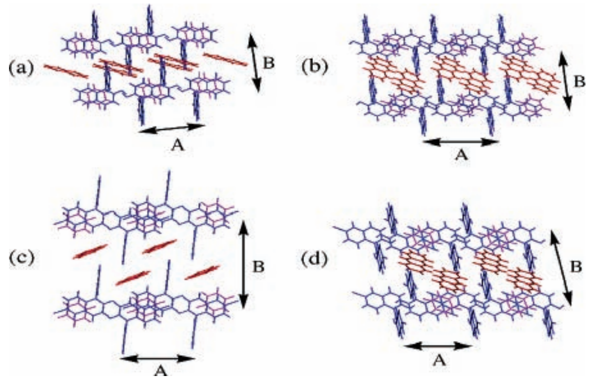


Figure 2. Crystal structures of (a) complex **I** (view down the middle of the *a*- and *b*-axes), (b) complex **II** (view down the *b*-axis), (c) complex **III** (view down the *b*-axis), and (d) complex **IV** (view down the *c*-axis). BN and 6BrBN molecules are displayed in blue, and BQ molecules are displayed in purple. NP and AN molecules are displayed in red.

The crystals **I**−**IV** are composed of a common CT unit, a triplet where a BQ molecule is sandwiched almost in parallel by two naphthol rings of two BN (or 6BrBN) molecules, and the unit structure is strengthened by the hydrogen bonds between the carbonyl O of BQ and the hydroxy groups of BNs. There are less strong interactions between the triplets as compared to within them. Thus, the guest molecules are included in the cavity created by the assembly of the common triplet units. It can be interpreted that the guest molecules themselves can change the arrangement of the CT units to allow the inclusion in the created cavity. In the BN−BQ system, as the size of the guest molecules increases from NP to AN, the distance between the neighboring CT units along the long axis of the naphthol ring (A in Figure 2a,b) increases from 9.71 Å for **I** to 9.85 Å for **II**. The corresponding distance along the short axis of the naphthol ring

(B in Figure 2a,b) also increases from 10.34 Å for **I** to 10.91 Å for **II**. In the case of the 6BrBN−BQ system, a similar relationship holds between the size of the guest molecules and the distances between the triplet CT units: A is 9.51 and 9.68 Å for **III** and **IV**, respectively (Figure 2c,d). In crystal **III** (Figure 2c), channellike cavities that extend along the crystal *b*-axis are formed and thus the NP molecules are located one-dimensionally along the axis.

It is well-known that the color of CT complexes depends on the intermolecular distance between the donor and acceptor molecules.[3] The distance between the donor (BN or 6BrBN) and the acceptor (BQ) in the CT triplet of these inclusion crystals was compared to understand the origin of the colors of these crystals. Although the reflection spectra of crystals **I** and **II** are similar, the distances between the donor and acceptor molecules (the distance between the center of BQ and the nearest naphthol plane) are substantially different (3.511 and 3.353 Å and for **I** and **II**, respectively). On the other hand, although the reflection spectra of complexes **III** and **IV** are dissimilar, the distances between the donor and acceptor molecules differ only slightly (3.389 and 3.375 Å and for **III** and **IV**, respectively).

To study the strength of the D···A interactions, the geometry of the BQ molecules in these CT complexes, i.e., the C=O, C=C, and C−C bond lengths, were examined (Table 1). They are similar to those of the neutral BQ molecule in the crystal of BQ.[5] These bond distances should differ clearly for the benzoquinone radical anion (BQ^-) and the neutral BQ, as shown by the theoretical calculations of Pou-Amerigo et al.[4] (Table 1). It is therefore suggested that the D···A complex in the inclusion crystals is a pair of electronically neutral molecules in the ground electronic state. At the same time, these results suggest that the different colors of these adduct crystals originate not only from the D···A interactions within a CT unit but also from the intermolecular interactions beyond the CT unit.

Table 1. Bond Distances of BQ and BQ^- (Å) in Crystals

crystal	C=O	C=C	C−C
BQ[a]	1.223	1.334	1.477
BQ[b]	1.210	1.343	1.479
BQ^- [b]	1.246	1.369	1.443
I	1.234	1.333	1.476
II	1.233	1.330	1.471
III	1.230	1.340	1.473
IV	1.238	1.339	1.469

[a] Crystal structure.[5] [b] Theoretical calculation.[4]

Inclusion of guest molecules (NP or AN) was attempted for the 3BrBN−BQ system as well. When NP was used as the guest, red crystals (**V**) were obtained. On the other hand, in the case of AN, no color change was observed and the X-ray powder diffraction pattern showed no signs of new crystal formation. Single-crystal X-ray analysis of complex **V** was performed to investigate the inclusion mechanism. The structure is shown in Figure 3. The stoichiometry of these crystals is 3BrBN/BQ/NP = 2:1:2 with the space group of *C*2/*c*. One CT unit is composed of two 3BrBN and one BQ molecules, as in crystals **I**−**IV**. The guest NP molecule is tightly encapsulated in the cavity which is enclosed with four CT units. There is no channellike or open cavity as found in the BN−BQ or 6BrBN−BQ system, and hence, the CT units cannot adjust their relative orientation to accommodate various guest molecules. This may be the reason that AN, which is bigger than NP, was not included in the host system.

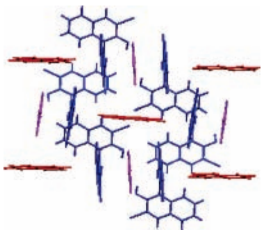


Figure 3. Crystal structure of complex **V** observed along the *a*-axis. 3BrBN and BQ molecules are displayed in blue and purple, respectively. NP molecules are displayed in red.

The visual molecular recognition ability was further investigated for the solid-phase crystallization. When crystals of BN and BQ were coground with NP crystals in an agate mortar, the color of the powder changed to indigo blue (Figure 4). After grinding, the X-ray powder diffraction pattern was recorded; the peaks corresponding to the BN, BQ, and NP crystals disappeared, and a set of new peaks appeared. The new crystal was found to be identical to the inclusion crystal (**I**) obtained from solution (Supporting Information, Figure S1). On the other hand, as we have previously reported, when AN was used as a third component, reddish purple inclusion crystals (**VI**, Figure 4) were

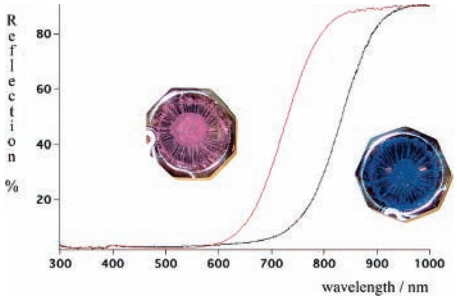


Figure 4. Reflection spectra of *rac*-BN−BQ crystals including NP (blue crystal **I** (black line)) or AN (reddish purple crystal **VI** (red line)) as a guest, which were obtained in the solid cogrinding.

---

(4) Pou-Amerigo, R.; Serrano-Andress, L.; Merchan, M.; Orti, E.; Forsberg, N. *J. Am. Chem. Soc.* **2000**, *122*, 6067.

(5) Bolhuis, v. F.; Kiers, C. T. *Acta Crystallogr., Sect. B* **1978**, *34*, 1015.

obtained by solid-state crystallization and they were different from the indigo blue crystals (**II**) obtained from solution.[6] The reflection spectra confirm the visual color difference (Figure 4). Thus, the BN−BQ host system is sensitive to the structure of the guest compound if the inclusion crystals are formed in the solid state.

Solid-state crystallization was performed for the 6BrBN−BQ system as well. When 6BrBN and BQ crystals were ground with either NP or AN in an agate mortar, the color of the powder changed to either red (**VII**) or blue (**VIII**) (Figure 5). Interestingly, these colors are different from the colors of the respective inclusion complexes obtained from solution, **III** and **IV**. The reflection spectra of complexes **VII** and **VIII** are different from each other with the absorption edge at almost 500 and 650 nm, respectively (Figure 5). In crystal **VIII**, a small peak is additionally observed at 380 nm. Thus, the 6BrBN−BQ host displays a wide spectrum of colors.

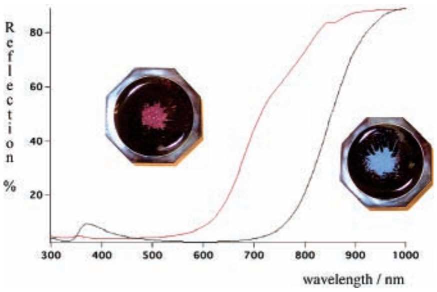


Figure 5. Reflection spectra of 6BrBN−BQ crystals including NP (red crystal **VII** (red line)) or AN (blue crystal **VIII** (black line)) as a guest.

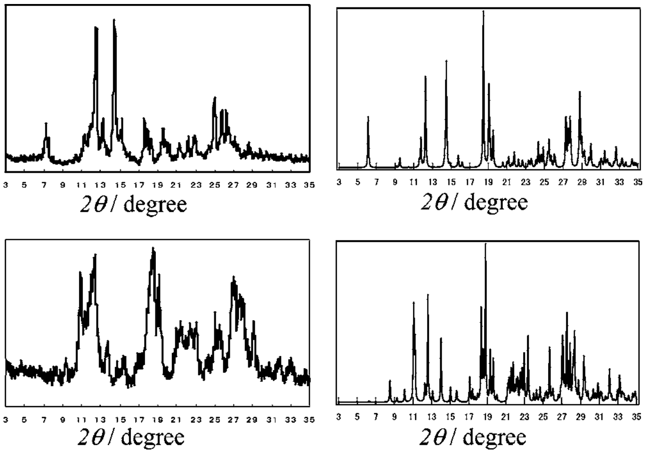


Figure 6. X-ray powder diffraction patterns of crystals (a) **VII**, (b) **III**, (c) **VIII**, and (d) **IV**.

The X-ray diffraction patterns revealed the formation of new inclusion crystals (**VII** and **VIII**), and they are clearly different from those of crystals **III** and **IV** (Figure 6). The stoichiometry was established to be 6BrBN/BQ/guest = 1:1:0.5 (Supporting Information, Figure S2) in both crystals, a different value from **III** and **IV**.

The 3BrBN−BQ system was examined in the same manner. When NP was used as a guest molecule, the color of the powder changed to red (Figure 7a). Analysis of the X-ray powder diffraction pattern has shown that the newly formed adduct crystallines in the solid state are identical to the inclusion crystal (**V**) obtained from solution. When AN was used, no color change (Figure 7b) and no new set of peaks in the X-ray powder diffraction pattern (data not shown) were observed, indicating the absence of adduct crystal formation as in solution crystallization.

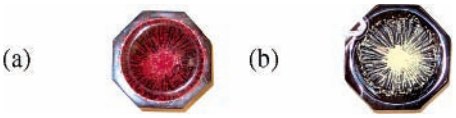


Figure 7. (a) Inclusion CT complex (**V**) formed by cogrinding of crystals of 3BrBN, BQ, and NP, and (b) no CT complex formation by cogrinding of crystals of 3BrBN, BQ, and AN.

In conclusion, we could successfully visualize molecular recognition using the CT host complexes composed of BN derivatives and BQ. They form inclusion crystals with various aromatic compounds, and the color of these crystals is highly sensitive to the structure of the component molecules. Crystallization of the inclusion compounds occurs both in solution and in the solid phase, and three out of five cases produced different crystals of different stoichiometry/structure and hence different color for the two crystallization phases. This further enriches the ability of the host CT systems, and they may prove useful as a sensitive visual indicator of molecular recognition/interactions.

Supporting Information Available: X-ray powder diffraction patterns for **I**, **VII**, and **VIII**, as well as crystallographic reports (CIF) of complexes **I**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL060862Q

---

(6) Cheung, E. Y.-G.; Kitchin, S. J.; Harris, K. D. M.; Imai, Y.; Tajima, N.; Kuroda, R. *J. Am. Chem. Soc.* **2003**, *125*, 14658.