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Tetrahedron Letters 47 (2006) 3603–3606
Tetrahedron Letters

Formation of chiral charge-transfer complex with axially chiral 1,1′-bi-2-naphthol and viologen derivatives

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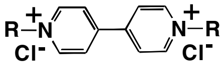
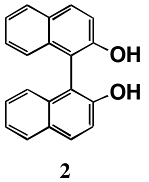
Received 1 February 2006; revised 24 February 2006; accepted 2 March 2006
Available online 5 April 2006

Abstract—By using three types of viologen derivatives, we synthesized chiral charge-transfer (CT) complexes with an axially chiral 1,1′-bi-2-naphthol molecule and successfully controlled the crystal structure and inclusion ability of the third component by changing the viologens.

The donor–acceptor interactions in a complex that leads to charge-transfer (CT) absorption have been attracting attention with regard to their photo and electronic properties.[1] In the field of supramolecular chemistry, donor–acceptor interactions have also received considerable attention as an intermolecular force for constructing and controlling a network structure.[2] Especially, 1,1′-bi-2-naphthalene derivatives are most important chiral sources for deriving various chiral supramolecular complexes. Recently, we reported the crystallization behavior of supramolecular CT complexes with chiral- or racemic(*rac*)-1,1′-bi-2-naphthol derivatives as an electron-donor molecule and *p*-benzoquinone as an electron-acceptor molecule.[3] However, when a chiral 1,1′-bi-2-naphthol molecule without a substituent was used, crystallization of a chiral CT complex with *p*-benzoquinone molecule was not observed. Moreover, although 7,7,8,8,-tetracyanoquinodimethane (TCNQ), tetracyanobenzene (TCNB) molecules and other benzoquinone derivatives were tried as an electron-acceptor molecule, crystallization of a chiral CT complex could not be observed with chiral 1,1′-bi-2-naphthol molecule. In this letter, we report the crystallization of chiral CT complexes by using viologen derivatives (**1a**–**c**) and chiral 1,1′-bi-2-naphthol molecule ((*R*)-**2**). Viologens are diquaternary salts of 4,4′-bipyridine and act as electron-acceptor molecules.[4] In this system, **1a**–**c** molecules are used as electron-acceptors and as a stereo-control unit, and the chiral (*R*)-**2** molecule acts as an electron-donor and a chiral source unit.



1a: R=Me, 1b: R=CH$_2$Ph, 1c: R=Ph



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The complexation behavior of 1,1′-dimethyl-4,4′-bipyridinium dichloride (MVCl$_2$, **1a**) and chiral (*R*)-**2** molecules was studied. 6.5 mg of **1a** and 10.0 mg of (*R*)-**2** were dissolved in an ethanol(EtOH) solution (4 ml) with heating and left to stand at room temperature. After a few days, many crystals (**I**) (9.7 mg) were produced. From the analysis, these crystals contained **1a** and

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Keywords: Chiral; CT complex; 1,1′-Bi-2-naphthol; Viologen.

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0040-4039/$ - see front matter
doi:10.1016/j.tetlet.2006.03.108

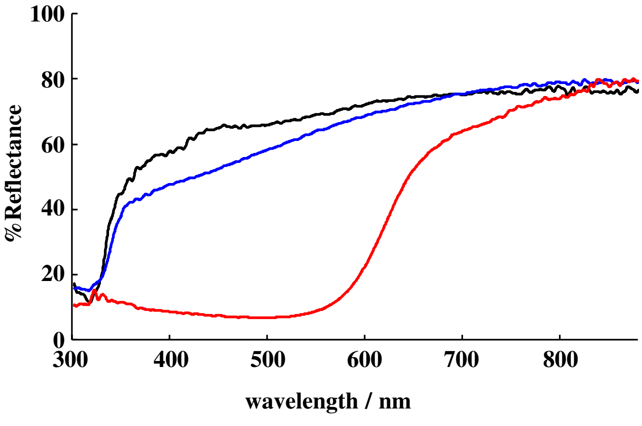

Figure 1. Diffuse reflectance spectrum of **1a** (blue), (*R*)-**2** (black) and complex **I** (red).

(*R*)-**2** molecules. The color of these crystals was deep red and quite different from those of the component solids. The diffuse reflectance spectrum of **1a**, **2** and complex **I** were measured and are shown in Figure 1.[3c] The spectra of complex **I** suggests that the CT complexes were formed. X-ray analysis was performed in order to investigate the inclusion style of these molecules. The structure of these crystals (**I**) is shown in Figure 2.[5] The stoichiometry of the inclusion crystal is **1a**/(*R*)-**2**/H_2O = 1:2:1. The (*R*)-**2** molecule (blue molecule in Fig. 2) is connected by a hydrogen bond of a water molecule (purple ball in Fig. 2), which is included in ethanol and a chloride anion (green ball in Fig. 2) along the *a*-axis and forms a single unit (Fig. 2a). When the packing diagram of the crystal is observed along the *a*-axis, this unit forms a hydrogen-bonded wavy layered structure (Fig. 2b). The entire structure of this crystal is a layered structure stacked along the *b*-axis. The folds of the adjacent wavy layers face each other, and a vacant space is generated between them. This space functions as a channel-like cavity that extends one-dimensionally along the direction of the *a*-axis. In this cavity, the MV^{2+} (1,1′-dimethyl-4,4′-bipyridinium) cations are trapped. Interestingly, the MV^{2+} cations (green molecule in Fig. 2) are arranged one-dimensionally along the running direction of the cavity. The distance between the molecular centers of the adjacent MV^{2+} cations is 9.6 Å. These MV^{2+} cations are sandwiched between two (*R*)-**2** molecules.

A *rac*-**2** molecule was used instead of the chiral (*R*)-**2** molecule. The crystallization of the two compounds from an ethanol solution produced deep red crystals. From the X-ray analysis, these crystals were identical to the chiral crystal **I**. The HPLC analyses of these crystals (CHIRALPAK AD (Daicel), MeOH, 1.0 ml/min, 25 °C, 254 nm) also suggested that one crystal is composed of an enantiomerically pure chiral **1a** molecule. Interestingly, the *rac*-**2** molecule was enantioselectively divided by the formation of a CT complex with the **1a** molecule. In other words, this crystallization process of **1a** and *rac*-**2** molecules is a system of spontaneous resolution. Hence, this chiral crystal **I** can be easily obtained from the *rac*-**2** molecule. At the same time, a small amount of different orange crystals (**II**) was obtained.[6] From the analysis, these crystals contained both (*R*)-**2** and (*S*)-**2** molecules. However, from the X-ray analysis, the space group is $P2_1$, and the stoichiometry is **1a**/(*R*)-**2**/(*S*)-**2**/H_2O = 1:1:1:2. The structure of this chiral crystal is shown in Figure 3. When the packing diagram of this crystal is observed along the *a*-axis (Fig. 3), the (*R*)-**2** (blue molecule in Fig. 3) and (*S*)-**2** (orange molecule in Fig. 3) molecules have a supramolecular hydrogen-bonded 3D network through the water molecules (purple ball in Fig. 3), which are included in ethanol and chloride anions (green ball in Fig. 3). The MV^{2+} cations are arranged two-dimensionally along the *a*- and *b*-axis into the 3D-network structure.

Next, the structural change due to the steric effect of a viologen cation was investigated. Two types of viologen molecules, that is, 1,1′-dibenzyl-4,4′-bipyridinium

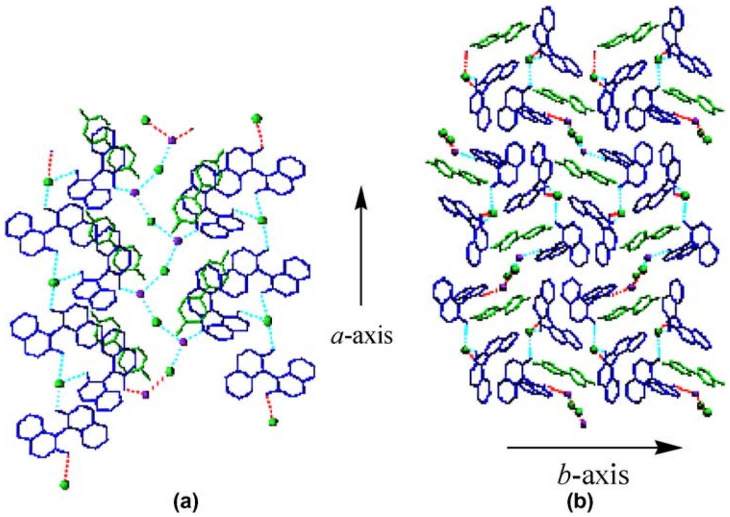

Figure 2. (a) Hydrogen-bonded wavy layered structure of a single unit that is parallel to the *a*-axis in **1a**·(*R*)-**2**·H_2O (**I**). (b) Packing structure observed along the *a*-axis.

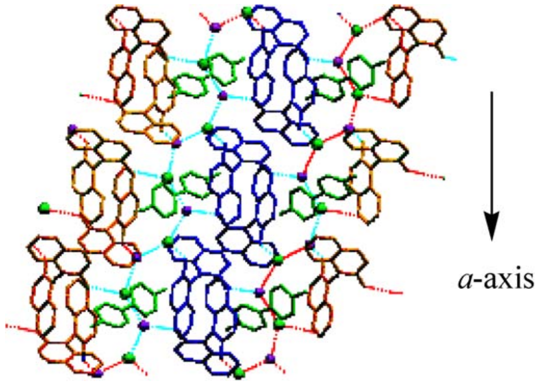

Figure 3. Crystal structure of **1a**·(*R*)-**2**·(*S*)-**2**·H_2O (**II**) observed along the *b*-axis.

dichloride ($BVCl_2$, **1b**) and 1,1′-diphenyl-4,4′-bipyridinium dichloride ($PVCl_2$, **1c**), which have bulky substituents, were used. Crystallization in two combinations (**1b**–(*R*)-**2** and **1c**–(*R*)-**2** systems) was attempted. In both cases, a lot of red crystals were obtained. From the analysis, the ethanol molecule was contained as a third component in the **1b**–(*R*)-**2** system. Then, the inclusion style of the ethanol molecule and its crystal structure were analyzed. The X-ray analysis revealed that the stoichiometry of the inclusion crystal is **1b**/(*R*)-**2**/EtOH = 1:2:1. The structure of these crystals (**III**) is shown in Figure 4.[7] This structure differs from the other structures (**I** and **II**) since a network structure is not constructed. In this crystal, two (*R*)-**2** molecules (blue molecule in Fig. 4) are connected by a hydrogen bond with a hydroxyl group through chloride anions (green ball in Fig. 4), and a dibenzylviologen cation (BV^{2+}, green molecule in Fig. 4) resides between two (*R*)-**2** molecules (Fig. 4a). Two ethanol molecules (red molecule in Fig. 4) are trapped with each chloride anion by a hydrogen bond.

When the **1c**–(*R*)-**2** system was used, colored crystals were obtained. However, these crystals were needle shaped. Hence, the structural information was not obtained from the X-ray analysis. However, these crystals are composed of **1c** and (*R*)-**2** molecules from the ^1H NMR spectrum and it is thought that a CT complex is formed.

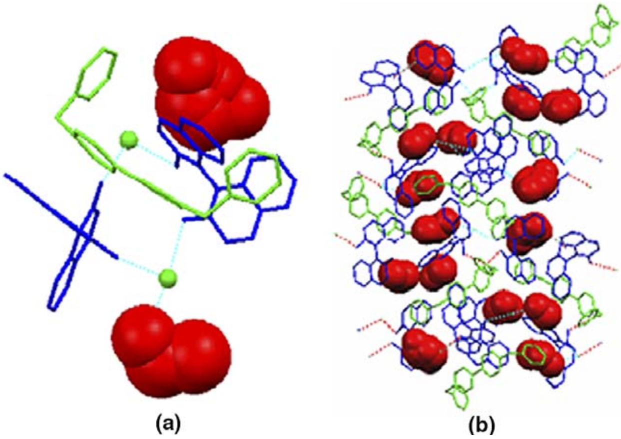

Figure 4. (a) An extracted unit structure of **1b**·(*R*)-**2**·EtOH (**III**). (b) Packing structure observed along the *a*-axis.

Next, recognition ability of **1b** and **1c** molecules to the axial chirality of *rac*-**2** molecule was studied. In both viologen derivatives, CT complexes were formed. In the case of the **1b**–*rac*-**2** system, a lot of red crystals (**IV**) were obtained. The structure of the crystals (**IV**) is shown in Figure 5.[8] A pair of (*R*)-**2** and (*S*)-**2** molecules is connected by a hydrogen bond through the chloride anions in this crystal and a unit is formed in the same manner as in complex **III**. However, it differs from complex **III**, and the BV^{2+} cation lies between (*R*)-**2** and (*S*)-**2** molecules of different units (Fig. 5a). The crystal structure of this complex is interesting; the BV^{2+} cations are closely arranged two-dimensionally along the channel-like cavities, which are parallel to both the *a*- and *b*-axis.

When the **1c**–*rac*-**2** system was used, a lot of colored crystals (**V**) were obtained. The X-ray analysis revealed that (*R*)-**2** and (*S*)-**2** molecules are included in this crystal (**V**), and the stoichiometry of this crystal is **1c**/(*R*)-**2**/(*S*)-**2**/H_2O/EtOH = 0.5:0.5:0.5:1:1.[9] The characteristics of the structure differs from those of complex **III** as these crystals have a supramolecular hydrogen-bonded 3D network composed of (*R*)-**2** and (*S*)-**2** molecules (Fig. 6). The water molecule (purple ball in Fig. 6),

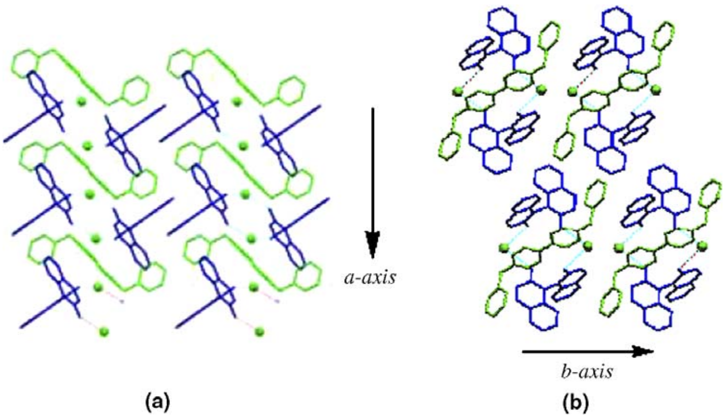

Figure 5. Crystal structure of **1b**·*rac*-**2** (**IV**). (a) Observed along the *b*-axis. (b) Observed along the *a*-axis.

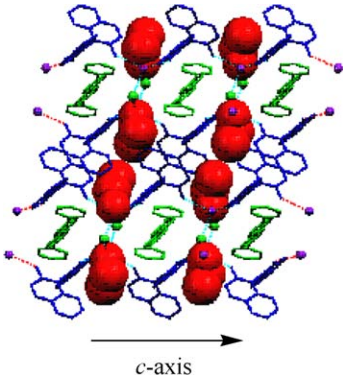

Figure 6. Crystal structure of **1c**·*rac*-**2** (**V**) observed along the *b*-axis.

which is included in ethanol and a chloride anion (green ball in Fig. 6), links the two (*R*)-**2** and (*S*)-**2** molecules through hydrogen bonds and contributes to the maintenance of the 3D-network frame. This crystal has a channel-like cavity that extends one-dimensionally along the direction of the *b*-axis. In this cavity, the PV^{2+} (1,1′-diphenyl-4,4′-bipyridinium) cations are arranged one-dimensionally along the running direction of the cavity, and the distance between the molecular centers of the adjacent PV^{2+} cations is 13.3 Å. In this channel-like cavity, the PV^{2+} cations are sandwiched between (*R*)-**2** and (*S*)-**2** molecules. The included ethanol molecule (red molecule in Fig. 6) acts as one of the composition units of the 3D-network frame.

In summary, a chiral CT complex of chiral 1,1′-bi-2-naphthol molecule ((*R*)-**2**) was successfully created by using viologen derivatives (**1a**–**c**). The *Rac*-**2** molecule was enantioselectively divided through the formation of a CT complex with the **1a** molecule. The structure of the CT-complex and the inclusion ability of the guest molecule could be tuned by changing the combination of the component molecules. Moreover, viologens undergo one-electron reduction to yield strong-colored radical cations and are also used in many electron-transfer processes.[10] So, it is expected that this type of CT complex can be used for a variety of conducting and chiral materials.

References and notes

1. (a) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: London, 1969; (b) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948; (c) Kuwata-Gonokami, M.; Peyghambarian, N.; Meissner, K.; Fluegel, B.; Sato, Y.; Ema, K.; Shimano, R.; Mazumdar, S.; Guo, F.; Tokihiro, T.; Ezaki, H.; Hanamura, E. *Nature* **1994**, *367*, 47; (d) Koshihara, S.; Takahashi, Y.; Sakai, H.; Tokura, Y.; Luty, T. *J. Phys. Chem. B* **1999**, *103*, 2592; (e) Magueres, P. L.; Hubig, S. M.; Lindeman, S. V.; Veya, P.; Kochi, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 10073.
2. Lehn, J. M. *Supramolecular Chemistry*; Wiley-VCH, 1995.
3. (a) Kuroda, R.; Imai, Y.; Sato, T. *Chirality* **2001**, *13*, 588; (b) Toda, F.; Senzaki, M.; Kuroda, R. *Chem. Commun.* **2002**, 1788; (c) Imai, Y.; Tajima, N.; Sato, T.; Kuroda, R. *Chirality* **2002**, *14*, 604; (d) Kuroda, R.; Imai, Y.; Tajima, N. *Chem. Commun.* **2002**, 2848.
4. (a) Monk, P. M. S. *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4′-Bipyridine*; John Wiley & Sons: Chichester, 1988, and references cited therein; (b) Jaschinski, B.; Blachnik, R.; Reuter, H. *Z. Naturforch., B; Chem. Sci.* **1998**, *53*, 565; (c) Hunig, S.; Metzenthin, T.; Peters, K.; von Schutz, J.-U.; von Schnering, H. G. *Eur. J. Org. Chem.* **1998**, 1653; (d) Yoshikawa, H.; Nishikiori, S. *Chem. Lett.* **2000**, 142; (e) Yoshikawa, H.; Nishikiori, S.; Suwinaka, K.; Luboradzki, R.; Lipkowski, J. *Chem. Commun.* **2001**, 1398; (f) Kidowaki, M.; Tamaoki, N. *Chem. Commun.* **2003**, 290.
5. Crystallographic data of **I**: $C_{12}H_{14}N_2Cl_2{\cdot}2C_{20}H_{14}O_2{\cdot}H_2O$, $M = 847.79$, orthorhombic, space group $P2_12_12_1$, $a = 9.5651(7)$, $b = 14.2837(10)$, $c = 30.290(2)$ Å, $V = 4138.3(5)$ Å^3, $Z = 4$, $D_c = 1.361$ g cm^{-3}, μ(Mo Kα) = 0.211 mm^{-1}, 25,431 reflections measured, 9445 unique, final $R(F^2) = 0.0491$ using 8372 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0581, $T = 120(2)$ K. CCDC 288419.
6. Crystallographic data of **II**: $C_{12}H_{14}N_2Cl_2{\cdot}2C_{20}H_{14}O_2{\cdot}2H_2O$, $M = 865.81$, monoclinic, space group $P2_1$, $a = 18.8914(17)$, $b = 11.0326(9)$, $c = 21.5092(19)$ Å, $\beta = 108.8250(10)$, $V = 4243.2(6)$ Å^3, $Z = 4$, $D_c = 1.389$ g cm^{-3}, μ(Mo Kα) = 0.214 mm^{-1}, 26,049 reflections measured, 17,717 unique, final $R(F^2) = 0.0562$ using 15,278 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0666, $T = 120(2)$ K. CCDC 288420.
7. Crystallographic data of **III**: $C_{24}H_{22}N_2Cl_2{\cdot}2C_{20}H_{14}O_2{\cdot}2C_2H_6O$, $M = 1074.10$, orthorhombic, space group $P2_12_12_1$, $a = 13.4711(11)$, $b = 22.4703(18)$, $c = 36.832(3)$ Å, $V = 11148.9(15)$ Å^3, $Z = 8$, $D_c = 1.280$ g cm^{-3}, μ(Mo Kα) = 0.173 mm^{-1}, 71,434 reflections measured, 26,306 unique, final $R(F^2) = 0.0817$ using 20,271 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.1069, $T = 120(2)$ K. CCDC 288423.
8. Crystallographic data of **IV**: $0.5C_{24}H_{22}N_2Cl_2{\cdot}C_{20}H_{14}O_2$, $M = 490.98$, triclinic, space group $P\bar{1}$, $a = 8.6204(4)$, $b = 10.3908(5)$, $c = 14.7884(6)$ Å, $\alpha = 72.3600(10)$, $\beta = 81.6840(10)$, $\gamma = 78.1620(10)$, $V = 1230.67(10)$ Å^3, $Z = 2$, $D_c = 1.325$ g cm^{-3}, μ(Mo Kα) = 0.186 mm^{-1}, 11,189 reflections measured, 5698 unique, final $R(F^2) = 0.0423$ using 5272 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0457, $T = 120(2)$ K. CCDC 288421.
9. Crystallographic data of **V**: $0.5C_{22}H_{18}N_2Cl_2{\cdot}C_{20}H_{14}O_2{\cdot}H_2O{\cdot}C_2H_6O$, $M = 541.04$, monoclinic, space group $P2_1/c$, $a = 12.7009(9)$, $b = 13.2681(9)$, $c = 16.9145(12)$ Å, $\beta = 101.4370(10)$, $V = 2793.8(3)$ Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, μ(Mo Kα) = 0.176 mm^{-1}, 17,504 reflections measured, 6557 unique, final $R(F^2) = 0.0446$ using 5832 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0495, $T = 120(2)$ K. CCDC 288422.
10. Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49; Tsukahara, K. *Trends Inorg. Chem.* **1991**, *2*, 17.