Journal of Molecular Structure 982 (2010) 45–49

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Solid-state thermochromism observed in charge-transfer complex composed of binaphthol and viologen

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ARTICLE INFO

Article history:
Received 17 June 2010
Received in revised form 28 July 2010
Accepted 28 July 2010
Available online 3 August 2010

Keywords:
1,1′-Bi-2-naphthol
Charge-transfer complex
Crystal-engineering
Thermochromism
Viologen

ABSTRACT

Charge-transfer complexes composed of 1,1′-bi-2-naphthol as an electron donor and viologen derivatives as electron acceptors exhibit thermochromic properties in the solid state without dramatical isomerization of the component molecules such as proton transfer.

1. Introduction

The intriguing phenomenon of thermochromism has recently become a subject of interest owing to its possible application to the development of imaging and sensing materials [1]. Although a variety of thermochromic systems have been reported, most show thermochromic properties only in the solution state; few systems show thermochromic functions in the solid state. Moreover, the thermochromic properties of almost all these systems are due to dramatical isomerization of the component molecules such as proton transfer [2]. The donor–acceptor interactions in a complex that lead to charge-transfer (CT) absorption confer these materials with interesting photoactive and electronic properties that have attracted much attention among researchers [3]. It is well known that the color of a CT complex in the solid state mainly depends on the packing type of the donor and acceptor molecules [4]. Hence, if the packing type is sufficiently controlled in the solid state, CT complexes should show thermochromic properties without dramatical isomerization of the component molecules such as proton transfer. One such complex has already been reported [5], although the report does not include structural analysis.

We recently reported the complexation behaviors of supramolecular CT complexes containing 1,1′-bi-2-naphthol derivatives as electron donors and various 4,4′-bipyridinium dication salts (usually called viologens) as electron acceptors [6]. In this paper, we report a simple thermochromic system, based on variations in intermolecular interactions between 1,1′-bi-2-naphthol and viologens, in which dramatical isomerization of the component molecules such as proton transfer does not take place. In this system, the 1,1′-bi-2-naphthol (BN) molecule is used as an electron donor, and 1,1′-dimethyl-4,4′-bipyridinium dichloride (methylviologen, $MVCl_2$) or 1,1′-dibenzyl-4,4′-bipyridinium dichloride (benzylviologen, $BVCl_2$) is used as an electron acceptor (Fig. 1).

2. Experimental

2.1. General methods

All reagents were used directly as obtained commercially. Component molecules *rac*-**1**, $MVCl_2$, and $BVCl_2$ were purchased from Tokyo Kasei Kogyo Co., Ltd. Crystallization solvent was purchased from Wako Pure Chemical Industry.

2.2. Formation of complexes ***I*** and ***II***

(*R*)-**1** (11 mg, 3.8×10^{-2} mmol) [or *Rac*-**1** (11 mg, 3.8×10^{-2} mmol)] and $MVCl_2$ (10 mg, 3.9×10^{-2} mmol) [or $BVCl_2$ (16 mg,

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doi:10.1016/j.molstruc.2010.07.048

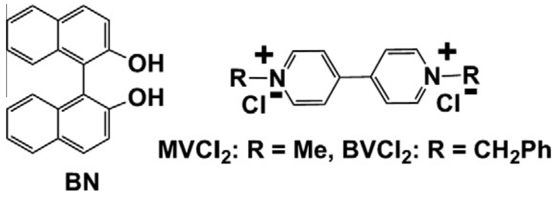

Fig. 1. Structures of BN, $MVCl_2$, and $BVCl_2$.

3.9×10^{-2} mmol)] were dissolved in an ethanol (EtOH) solution (3 mL) with heating, respectively. Each solution was allowed to stand at room temperature. After 5–7 days, the color crystals [**I** from (*R*)-**1**/$MVCl_2$ system (11 mg) and **II** from *rac*-**1**/$BVCl_2$ system (15 mg)] were deposited and collected. The weight of crystal is the total crop of the crystals obtained in a single batch.

2.3. X-ray crystallographic study of crystal

X-ray diffraction data for single crystals were collected using a *BRUKER APEX* instrument. The crystal structures were solved by the direct methods [7] and refined by full-matrix least-squares using *SHELXL97* [7]. The diagrams were prepared using *PLATON* [8]. Absorption corrections were performed using *SADABS* [9]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. Crystallographic data and details of measurements are summarized in Table 1. The CSD reference number of complexes **I** and **II** is 620,900 and 620,901, respectively. Crystallographic data can be obtained free of charge via http://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).

3. Results and discussion

It has been reported that when racemic (*rac*)-BN and $MVCl_2$ molecules crystallize from ethanol (EtOH) solution, a chiral CT complex composed of (*R*)-BN [or (*S*)-BN] and $MVCl_2$ is observed by spontaneous resolution [6a]. Therefore, chiral CT complex **I** composed of (*R*)-BN and $MVCl_2$ and complex **II** composed of *rac*-BN and $BVCl_2$ were used.

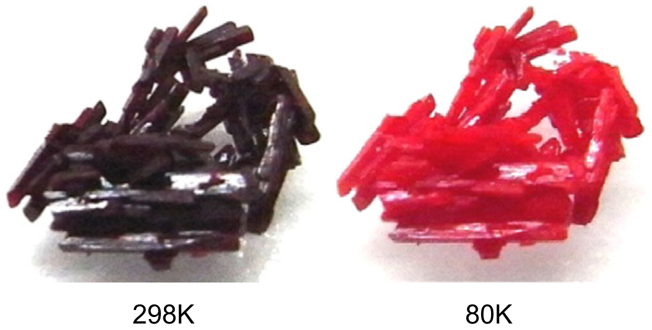

Fig. 2. Photographs of complex **I** at 298 and 80 K.

Table 1
Crystal data and structure refinement details.

	Complex **I**	Complex **II**
Formula	$C_{52}H_{44}Cl_2N_2O_5$	$C_{32}H_{25}$ $ClNO_2$
Formula weight	847.79	490.98
Temperature	295(2) K	295(2) K
Radiation	Mo(Kα) 0.71073 Å	Mo(Kα) 0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	*P*-1
Unit cell dimensions	$a = 9.5959(8)$ Å	$a = 8.6986(7)$ Å
	$b = 14.5664(13)$ Å	$b = 10.4103(9)$ Å
	$c = 30.489(3)$ Å	$c = 14.9923(13)$ Å
	$\alpha = 90.00°$	$\alpha = 72.1400(10)°$
	$\beta = 90.00°$	$\beta = 81.1900(10)°$
	$\gamma = 90.00°$	$\gamma = 77.9460(10)°$
Volume (Å^3)	4261.6(6)	1257.91(18)
Z, density (g/cm^3)	4, 1.321	2, 1.296
μ (mm^{-1})	0.205	0.182
F (0 0 0)	1776	514
Crystal size (mm)	0.60 × 0.40 × 0.20	0.40 × 0.30 × 0.15
Theta range	1.55–27.86	1.43–27.89
Reflection collected/unique	26,157/9625	10,976/5586
Data/parameters	96,257/560	5586/327
S (on F^2)	1.005	1.068
R [$I > 2.0\sigma(I)$]/R [all data]	0.0465/0.0738	0.0556/0.0701
wR [$I > 2.0\sigma(I)$]/wR [all data]	0.1046/0.1153	0.1345/0.1435
CCDC	620,900	620,901

At 298 K, complex **I** is deep red[1], but as the temperature decreases, the color gradually lightens, becoming light red at 80 K (Fig. 2). When raising and lowering the temperature several times, the color change is reversible. This result suggests that complex **I** has reversible thermochromism.

X-ray analyses of complex **I** were carried out at 295 and 120 K to study the correlation between the thermochromic properties and crystal structure. The crystal structure at 295 K is shown in Fig. 3.

Comparison of the crystal structures at 295 and 120 K, the latter of which was reported previously [6a], shows that the packing type of the complex is the same at each temperature. Each (*R*)-BN molecule (blue molecules in Fig. 3) is connected to its neighbors by hydrogen bonds via water molecules (red balls) and chloride anions (green balls) along the *a*-axis to form one unit (Fig. 3a). When the packing structure of the crystal is observed along the *a*-axis, these units form a hydrogen-bonded wavy layered structure (Fig. 3b). The overall structure of the crystal is layered and stacked along the *b*-axis. The folds of the adjacent wavy layers face each other, generating a vacant space between that functions as a channel-like cavity extending one-dimensionally along the direction of the *a*-axis. The MV^{2+} cations (green molecules in Fig. 3) are arranged one-dimensionally along the direction of the cavity, with each MV^{2+} cation sandwiched between two (*R*)-BN molecules. When comparing the crystal structures at 295 and 120 K, no phase transition of the crystal is observed. Moreover, since the packing type of the complex is the same at each temperature and the color gradually lightens until 80 K, it is thought that no phase transition of the crystal is happened even at 80 K. On the other hand, the cell constants differ. The changes in cell constants of complex **I** between 295 and 120 K are presented in Table 2.

When the temperature decreases from 295 to 120 K, the lengths of the unit cell decrease. Although the changes in the *b*- and *c*-axis lengths are relatively large, the change in the *a*-axis length is small. This result is further evidence of the suggested crystal structure; while the wavy layer can easily move within the complex, movement along the *a*-axis is difficult because this is the direction of the hydrogen-bonded network. Moreover, as the cell volume decreases, changes in intermolecular distances are observed. The change in separation of two nearest molecules of complex **I** between 295 and 120 K is presented in Table 3 and Fig. 4.

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[1] For interpretation of color in Figs. 2–7, the reader is referred to the web version of this article.