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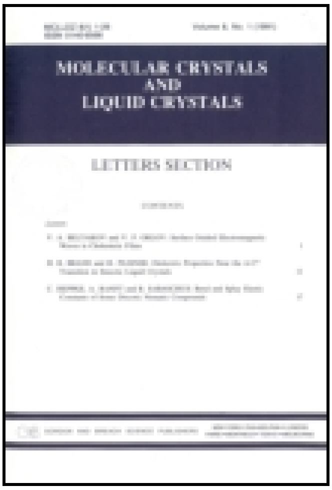

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Polymorphism of Supramolecular Charge-Transfer Complex Composed of 10,10′-dihydroxy-9,9′-biphenanthryl and p-benzoquinone

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Published online: 28 Apr 2014.

To cite this article: Kouhei Ookuma, Tomoyuki Amako, Hiyori Aoyama, Tomohiro Sato, Nobuo Tajima, Reiko Kuroda & Yoshitane Imai (2014) Polymorphism of Supramolecular Charge-Transfer Complex Composed of 10,10′-dihydroxy-9,9′-biphenanthryl and p-benzoquinone, Molecular Crystals and Liquid Crystals, 592:1, 209-217, DOI: 10.1080/15421406.2013.841558

To link to this article: http://dx.doi.org/10.1080/15421406.2013.841558

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Mol. Cryst. Liq Cryst., Vol. 592: pp. 209–217, 2014
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.841558

Polymorphism of Supramolecular Charge-Transfer Complex Composed of 10,10′-dihydroxy-9,9′-biphenanthryl and *p*-benzoquinone

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*Charge-transfer (CT) complexes were prepared using racemic (*rac*)-10,10′-dihydroxy-9,9′-biphenanthryl, which has a large and highly π-conjugated phenanthrene ring, as the electron donor and* p*-benzoquinone as the electron acceptor. This CT system showed a polymorphism.*

Keywords Benzoquinone; charge-transfer (CT) complex; 10,10′-dihydroxy-9,9′-biphenanthryl; polymorphism; supramolecule

Introduction

The properties of organic compounds in the solid state differ from those in the solution state because molecules in the solid state are densely packed and are strongly influenced by the neighboring molecules. In solid-state chemistry, polymorphism is considered to be an important property of a compound. The polymorphs of a compound, which can be produced by changing its conformation or packing structure in the solid state, generally show unique physical and chemical properties [1]. We reported that supramolecular organic complexes can be produced by using achiral 2-anthracenecarboxylic acid (or 2-naphthalenecarboxylic acid) and achiral benzylamine [2]. These complexes have two or three conformational polymorphs. Generally, it is difficult to predict whether a newly designed compound and newly combinational complex are polymorphic or not. Therefore, the development of novel molecular skeletons for functional polymorphic compounds and novel combinations of component molecules for functional polymorphic supramolecular complexes has attracted considerable attention as a bottom-up approach to solid-state polymorphic chemistry.

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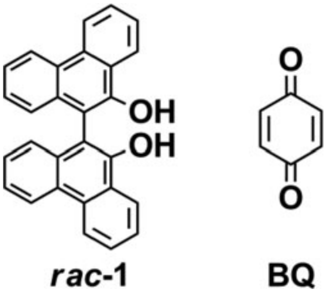

Figure 1. Component molecules.

Quinhydrone is one of the most famous charge-transfer (CT) complexes [3]. Recently, we reported that supramolecular CT complexes that are composed of racemic 1,1′-bi-2-naphthol or 10,10′-dihydroxy-9,9′-biphenanthryl (*rac*-**1**), which has a large and highly π-conjugated phenanthrene ring, as the electron-donor molecule and 2,5-dimethyl-1,4-benzoquinone (2,5Me-BQ) [or 2-chloro-5-methyl-1,4-benzoquinone (2Cl-5Me-BQ)] as the electron-acceptor molecule, can act as host systems that can include simple aromatic molecules as guests [4].

In this paper, we describe a novel polymorphic CT system composed of *rac*-**1** as the electron donor and *p*-benzoquinone (BQ) as the electron acceptor [Fig. 1]. The formation, and optical and structural properties of the polymorphic CT complexes were examined. We believe that the results of this study will be useful for the design of a novel supramolecular CT complex that has polymorphic properties.

Experimental

General Methods

Rac-**1** was synthesized according to a previously described method [5]. BQ and biphenyl were purchased from Tokyo Kasei Kogyo Co. Benzene, naphthalene, and crystallization solvents were purchased from Wako Pure Chemical Industry.

Formation of CT Complex by Crystallization from Solution

BQ (8 mg, 0.074 mmol) and *rac*-**1** (10 mg, 0.026 mmol) were dissolved by heating in the various solvents (4 mL). Each solution was then allowed to stand at room temperature. The colored crystals that precipitated from the solutions after 4–5 days were collected.

X-Ray Crystallographic Study of Crystals

X-ray diffraction data for single crystals were collected using *BRUKER APEX*. The crystal structures were solved by the direct method [6] and refined by full-matrix least-squares using *SHELXL97* [6]. The diagrams were prepared using *PLATON* [7]. Absorption corrections were performed using *SADABS* [8]. Nonhydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. These data can be obtained free of

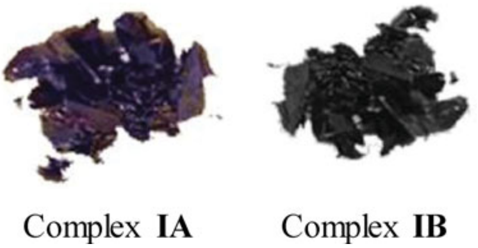

Figure 2. Photographs of the CT complexes **IA** and **IB**. (The reader is referred to the web version of this article.).

charge via 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).

Measurement of X-Ray Powder Diffraction (XRPD) Spectra of Crystals

X-ray powder diffraction (XRPD) patterns were recorded on a *Rigaku MiniFlex II* using graphite-monocromated CuKα radiation (30 kV, 15 mA). The spectra were measured at room temperature between 3° and 35° in the 2θ scan mode with steps 0.02° in 2θ and 40°/min.

Measurement of Diffuse Reflectance Spectra (DRS) of CT Complexes

Diffuse reflectance spectra (DRS) of CT complexes were measured with a *HITACHI U-4000 Spectrometer*.

Results and Discussion

Formation of the CT complexes was performed by crystallization from a diethylether/hexane (v/v = 1/1) solution containing *rac*-**1** and BQ. Subsequently, the diethylether/hexane solution was left to stand at room temperature for 4–5 days. When the diethylether/hexane solvent mixture was evaporated, two types of crystals (minor crystal **IA** and major crystal **IB**) formed. These two crystals were composed of only *rac*-**1** and BQ, and they did not contain any other molecules such as those of the crystallization solvent. Both crystals were black purple in the solid state [Fig. 2]. However, highly concentrated diethylether/hexane solutions of these complexes were yellow. Moreover, the colors of these CT complexes were quite different from those of the component solids (*rac*-**1** and BQ were light yellow).

X-ray crystallographic analyses were performed to study the structures of these crystals. Crystal **IA** was analyzed first. Its structures are shown in Fig. 3. And its crystal data and structure refinement details are shown in Table 1.

X-ray analysis revealed that the stoichiometry of **I** is (*R*)-**1**/(*S*)-**1**/BQ = 1:1:2 and that its space group is $P2_1/c$. This complex has a 1D column-like structure that is composed of (*R*)-**1**, (*S*)-**1**, and BQ molecules [Figs. 3(a) and (b)]. BQ is sandwiched between the phenanthrene rings of the (*R*)-**1** and (*S*)-**1** molecules. The distance of the CT interaction between (*R*)-**1** [or (*S*)-**1**] and BQ is 3.38 and 3.56 Å [9]. The carbonyl groups of BQ form hydrogen bonds with the hydroxyl groups of the phenanthrol moiety. Although the

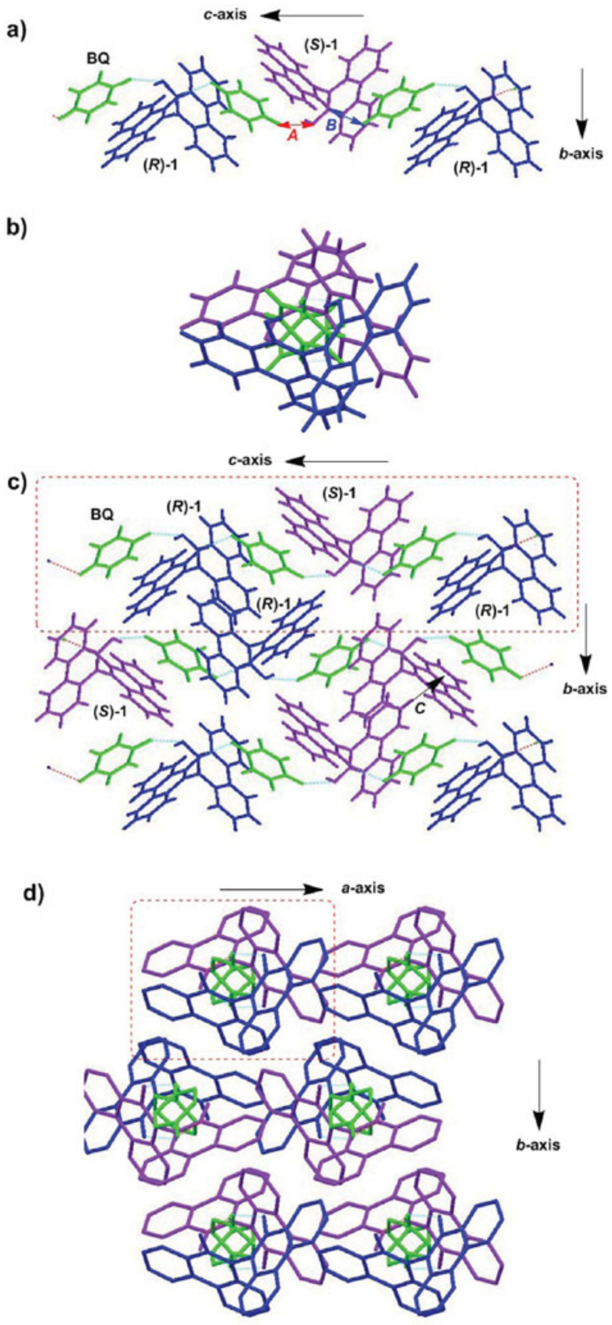

Figure 3. Crystal structures of the complex **IA**. (a) Extracted 1D column-like structure observed along the *a*-axis. The red arrow *A* and blue arrow *B* indicate hydrogen bonds. (b) The structure viewed along the *c*-axis. (c) The packing structure comprising 1D column-like structures observed along the *a*-axis. The black arrow *C* indicates CH–π interaction. (d) The structure viewed along the *c*-axis. (*R*)-**1**, (*S*)-**1**, and BQ molecules are indicated in blue, purple, and green, respectively. The red dotted rectangles show a 1D column-like structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1. Crystal data and structure refinement details

	IA	IB
Formula	$C_{34}H_{22}O_4$	$C_{34}H_{22}O_4$
Formula weight	494.52	494.52
Temperature	103(2) K	103(2) K
Radiation	Mo(Kα)0.71073 Å	Mo(Kα)0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions	$a = 9.0619(18)$ Å	$a = 9.5311(19)$ Å
	$b = 13.510(3)$ Å	$b = 10.283(2)$ Å
	$c = 19.905(4)$ Å	$c = 12.416(3)$ Å
	$\alpha = 90.00°$	$\alpha = 86.82(3)°$
	$\beta = 91.90(3)°$	$\beta = 77.39(3)°$
	$\gamma = 90.00°$	$\gamma = 86.85(3)°$
Volume (Å^3)	2435.6(8)	1184.6(4)
Z, density (g/cm^3)	4, 1.349	2, 1.386
μ(mm^{-1})	0.088	0.090
F (0 0 0)	1032	516
Crystal size(mm)	0.70 × 0.40 × 0.30	0.30 × 0.20 × 0.10
Theta range	2.99−27.45	3.02−27.48
Reflection collected/unique	22,661/5525	11,511/5373
Data/parameters	5525/345	5373/345
S (on F^2)	1.074	1.054
R [$I > 2.0\sigma(I)$]/R [all data]	0.0407/0.0614	0.0769/0.1544
wR [$I > 2.0\sigma(I)$]/wR [all data]yydapdata] data] data]	0.0948/0.1065	0.2075/0.2900
CCDC	915,523	915,524

torsion angles of (*R*)-**1** and (*S*)-**1** are identical (±81.3°), the carbonyl groups of BQ form hydrogen bonds of slightly different lengths with the hydroxyl groups of the phenanthrol moiety [In Fig. 3(a), for the hydrogen bonds indicated by the red arrow *A* and blue arrow *B*, O···O distances are 2.7311(16) and 2.8006(16) Å, respectively]. This CT complex is formed by the self-assembly of 1D column-like structures [Figs. 3(c) and (d), indicated by the red dotted rectangle] along the *b*-axis via phenanthrene–phenanthrene edge-to-face interaction [Fig. 3(c), 3.6501(18) Å, indicated by black arrow *C*] [10]. On the other hand, major intercolumnar interactions along the *a*-axis were not observed [Figs. 3(c) and (d)] [10].

The crystal structures of **IB** are shown in Fig. 4. And its crystal data and structure refinement details are shown in Table 1.

X-ray analysis revealed that the stoichiometry of **IB** is identical to that of **IA**, that is, (*R*)-**1**/(*S*)-**1**:**2**/BQ = 1:1:2, and that its space group is *P*-1. Although this complex also has a 1D column-like structure composed of **1** and BQ, this 1D column-like structure is organized differently from that of **IA** [Figs. 4(a) and (b)]. That is, BQ is stacked with one phenanthrene ring of **1**. In contrast to complex **IA**, the 1D column-like structure is composed of the same chiral bisphenanthrol molecule (*R*)-**1** [or (*S*)-**1**] having the same absolute conformation. The distance of the CT interaction between (*R*)-**1** [or (*S*)-**1**] and BQ

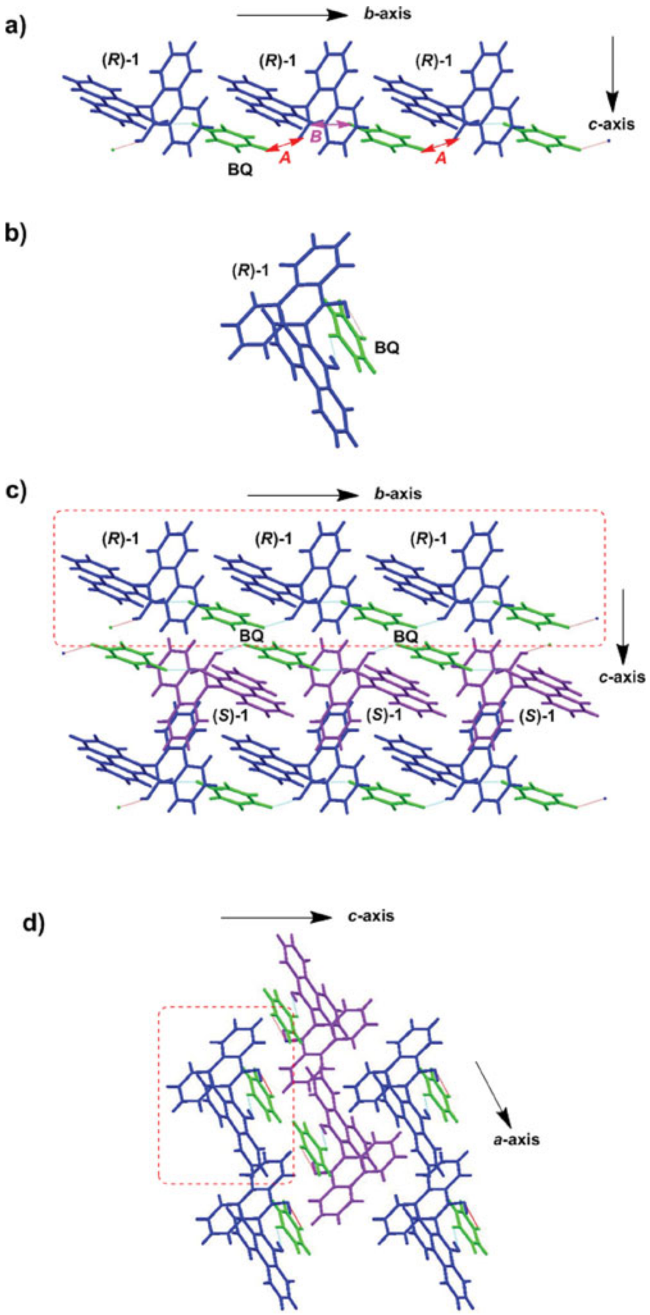

Figure 4. Crystal structures of complex **IB**. (a) Extracted 1D column-like structure observed along the *a*-axis. Red arrows *A* and purple arrow *B* indicate hydrogen bonds. (b) The structure viewed along the *b*-axis. (c) Packing structure comprising 1D column-like structures observed along the *a*-axis. (d) The structure viewed along the *b*-axis. (*R*)-**1**, (*S*)-**1**, and BQ molecules are indicated in blue, purple, and green, respectively. The red dotted rectangles show a 1D column-like structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

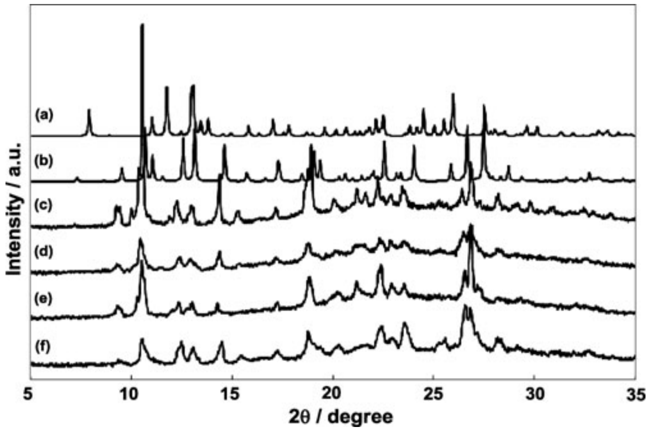

Figure 5. XRPD patterns of complexes (a) **IA** and (b) **IB**;[11] patterns of crystals obtained by crystallization from (c) diethylether, (d) hexane, (e) CH_2Cl_2, and (f) MeOH.

is 3.32 Å [9]. The torsion angles of (*R*)-**1** [or (*S*)-**1**] are identical [−83.5° (or +83.5°)]. The carbonyl groups of BQ form hydrogen bonds of slightly different lengths with the hydroxyl groups of the phenanthrol moiety [In Fig. 4(a), for the hydrogen bonds indicated by red arrow *A* and purple arrow *B*, O···O distances are 2.806(4) and 2.784(3) Å, respectively]. This CT complex is formed by the self-assembly of various 1D column-like structures having opposite chiralities [Figs. 4(c) and (d), indicated by the red dotted rectangle] along the *a*- and *c*-axes without major intercolumnar interactions [Figs. 4(c) and (d)] [10]. These results confirm that the *rac*-**1**/BQ-CT system is a polymorphic CT system.

In general, controlling the formation of polymorphs was the most difficult problem in the polymorphic system. We tried to control the polymorphic CT system first by attempting crystallization from various solvents containing *rac*-**1** and BQ. The solvents diethylether,

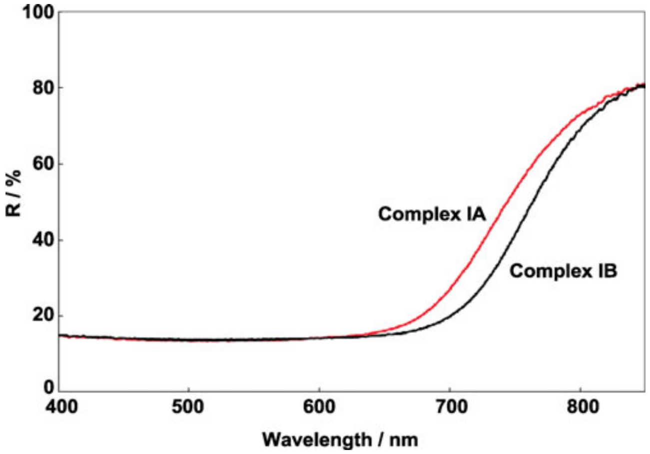

Figure 6. DRS of CT complexes **IA** (red line) and **IB** (black line). (The reader is referred to the web version of this article.).

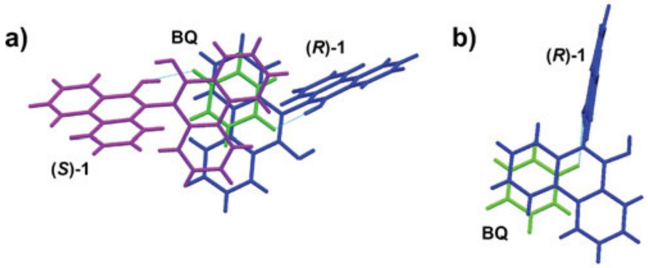

Figure 7. The local view concerning the overlap of the rings in **1** and **BQ**. (a) Complex **IA** (b) Complex **IB** (The reader is referred to the web version of this article.).

hexane, dichlorometane (CH_2Cl_2), and methanol (MeOH) were used. As in the crystallization from diethylether/hexane solvent, the solution containing *rac*-**1** and BQ was left to stand at room temperature for 4–5 days. When the solvent was evaporated, black purple crystals were obtained. The XRPD pattern of these crystals was obtained and compared against those of the complexes **IA** and **IB** [11] [Fig. 5]. All XRPD patterns (especially, $2\theta = 9 \sim 20$ degrees) of obtained crystals were similar to that of complex **IB**. That is, complex **IB** was the chief crystal type obtained in all cases. This result is corroborated by the higher density and melting points of **IB** (1.386 g·cm^{-3} and 233–234 °C, respectively) compared with those of **IA** (1.349 g·cm^{-3} and 222–223 °C, respectively). This shows that **IB** is more stable than **IA**.

A marked difference in crystal color between **IA** and **IB** was not observed. Diffuse reflectance spectroscopy (DRS) of complexes **IA** and **IB** in the solid state was also performed [Fig. 6]. In contrast to the absence of difference in visible crystal color, a difference between the DRS spectra of **IA** and **IB** was observed. The absorption edges of **IA** and **IB** are located at ca. 640 nm and 670 nm, respectively. When compared to crystal structures of **IA** and **IB**, the dramatic difference of the overlap of the rings between **1** and **BQ** was not observed (Fig. 7). However, the distance of the CT interaction between (*R*)-**1** [or (*S*)-**1**] and BQ in **IB** is shorter than that in **IA**. Therefore, it is thought that the absorption edge of **IB** is longer than that of **IA**. This shows that the CT system containing BQ may be utilized as a color-polymorphic CT system.

Conclusion

We found that the CT complexes composed of *rac*-10,10′-dihydroxy-9,9′-biphenanthryl (*rac*-**1**) as the electron donor and *p*-benzoquinone (BQ) as the electron acceptor are two polymorphs. On the basis of X-ray crystallographic analyses, these polymorphic CT complexes were found to form by the various assemblies of 1D-column-like structures composed of **1** and BQ. Interestingly, a difference between the DRS spectra of two polymorphs was observed. These unique abilities of this CT system provide information that is useful for producing a complex that exhibits novel polymorphism.

Acknowledgments

This study was supported by a Grant-in-Aid for Scientific Research (No. 24550165) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and The Ogasawara Foundation for the Promotion of Science & Engineering.

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[9] Distance between the center of BQ and the average plane of the phenanthrol 14-member ring.

[10] It is determined by PLATON geometry calculation.

[11] Simulated XRPD pattern calculated from crystal structure data.