DOI: 10.1002/ange.200600933

Guest-Induced Instant and Reversible Crystal-to-Crystal Transformation of 1,4-Bis(ferrocenylethynyl)anthraquinone**

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For decades, much attention has focused on crystallization from a mixture of electron-donor (D) and -acceptor (A) molecules, forming D- and/or A-stacked column structures that exhibit unique physical properties such as ferromagnetism,[1] strong absorption of Vis/NIR light,[2] and high electronic conductivity.[3] The tendency toward DA stacking in the crystal indicates that D–A conjugated molecules can form network structures which may manifest interesting physical properties. We are interested in the chemistry of a new class of D–A conjugated systems, namely, ferrocenylethynylanthraquinones (FcAq), from two viewpoints: protonation-induced intramolecular electron transfer resulting in valence tautomers,[4] and the construction of D–A stacked nanoporous network structures, which have attracted much recent attention because of great potential for applications such as selective gas adsorption,[5–7] heterogeneous catalysts,[8,9] and molecular recognition.[10,11] In the present study, we found that the new T-shaped FcAq compound 1,4-bis(ferrocenylethynyl)anthraquinone (1,4-Fc_2Aq (**1**); Figure 1 a) in the presence of guest solvent molecules forms single crystals, which show instant and reversible crystal-to-crystal transformation on heating or treatment with guest vapors. Recently, several reversible crystal-to-crystal transformations have been reported,[5,12] among which examples accompanying a significant conformational change are few.[13,14] The present study demonstrates an instant and reversible trans-

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[**] The synchrotron radiation experiments were performed at BL02B2 in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal nos. 2005A0454-Nb1b-np, 2005B0466, 2006A1595). This work was supported by Grants-in-Aid for Scientific Research (nos. 16047204 (area 434) and 17205007), and by a grant from The 21st Century COE Program for Frontiers in Fundamental Chemistry from MEXT, and CREST, Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

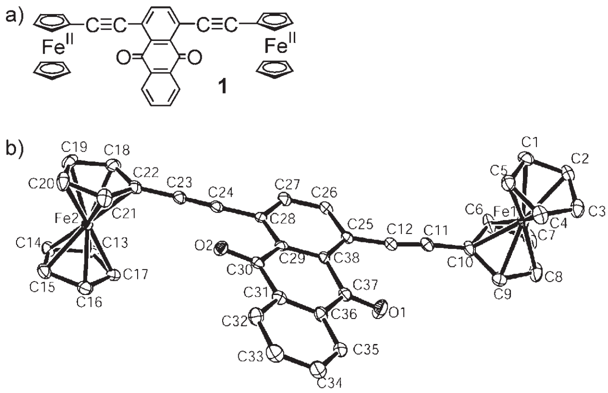

Figure 1. a) Chemical structure of 1,4-Fc$_2$Aq (**1**); b) ORTEP plot of a 1,4-Fc$_2$Aq molecule in a crystal of α-**1**·CH$_2$Cl$_2$. Hydrogen atoms and disordered guest molecules are omitted for clarity.

formation despite a very large conformational change in the D–A stacked structure, which can be monitored by variable-temperature synchrotron X-ray powder diffraction (VT-XRPD).

We synthesized 1,4-Fc$_2$Aq (**1**) by Sonogashira cross-coupling of 1,4-dibromoanthraquinone with 1-ethynylferrocene in 33% yield. Crystals of **1** obtained from various solvents were analyzed by single-crystal X-ray diffraction. An ORTEP diagram of a 1,4-Fc$_2$Aq molecule in a crystal of α-**1**·CH$_2$Cl$_2$ is shown in Figure 1b.[15] In most of the structures, inclusion of solvent as guest molecule is observed. The crystal structure of α-**1**·CH$_2$Cl$_2$ along the *b* axis is shown in Figure 2a as an example. The crystal was obtained by recrystallization from dichloromethane/hexane at 263 K; under these conditions, a large crystal (25 × 1 × 1 mm) grew within a week (Figure 2d). α-**1**·CH$_2$Cl$_2$ has subnanopores with dimensions of 5.7 × 3.5 Å[16] along the *b* axis in which dichloromethane guest molecules are contained with a **1**/CH$_2$Cl$_2$ molar ratio of 1:1. An infinite one-dimensional columnar structure is formed along the *b* axis by an alternating arrangement of a π-conjugated spacer and a π–π stacking interaction between Fc (D) and Aq (A) moieties (Figure 3a). The shortest distance between a cyclopentadienyl (Cp) plane of Fc and an Aq plane is 3.44 Å. The Aq and Cp planes form angles of about 45° with the *b* axis. Two kinds of complex columns are almost perpendicular to each other and are arranged alternately to construct the porous framework. Crystallographic data of single crystals with the composition **1**·X (X = guest molecule) obtained by recrystallization from different solvents are summarized in the Supporting Information.[15] Their crystal structures are similar to that of α-**1**·CH$_2$Cl$_2$, but the size of the subnanopores changes according to the size of the included guest molecules. Two types of crystals (α and β phases in Figure 2a and b; see the Supporting Information) were obtained when X was dichloromethane, chloroform, or carbon tetrachloride. The guest molecules in these structures are extremely disordered. The α phase has a shorter plane-to-plane distance between Fc and Aq but a larger dihedral angle ϕ between the Cp ring of ferrocene and the Aq plane (C25–C29, and C38) than the β phase (see the Supporting Information). Because of the balance between these two factors, that is, the shorter distance stabilizing the α phase and the large ϕ destabilizing it, both α and β phases may exist under the same conditions. Only one type of structure was formed when X was a larger guest molecule such as THF, trichloroethylene, or hexane.

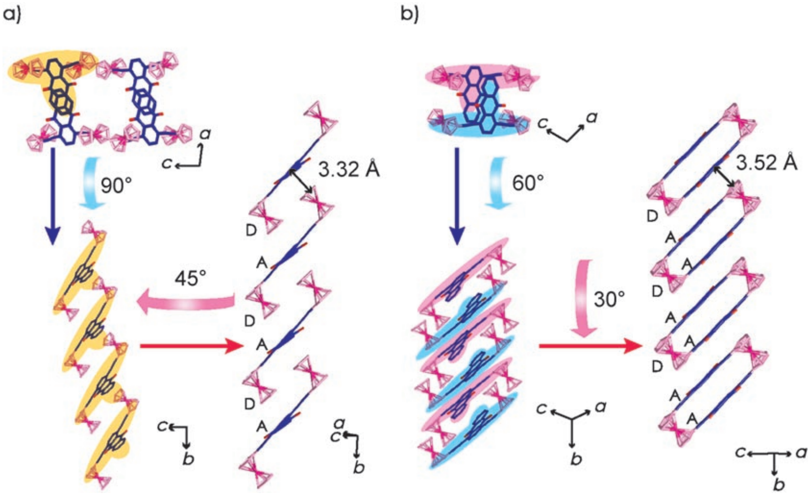

Figure 3. One-dimensional columnar structures of **1**·X (a), and solvent-free **1** (b).

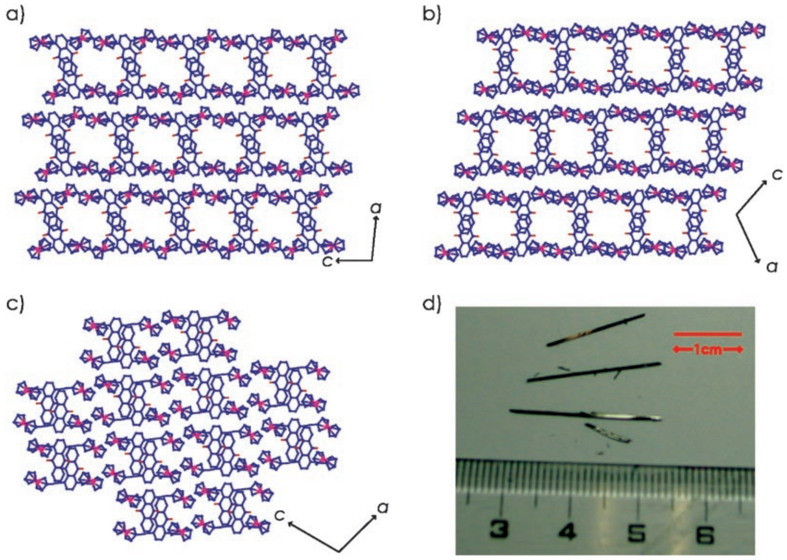

Figure 2. Crystal structures of α-**1**·CH$_2$Cl$_2$ along the *b* axis (a), β-**1**·CH$_2$Cl$_2$ along the *b* axis (b), solvent-free **1** along the *b* axis (c), and a photograph of α-**1**·CH$_2$Cl$_2$ crystals (d). Hydrogen atoms and disordered guest molecules (CH$_2$Cl$_2$) are omitted for clarity.

Recrystallization of **1** from *o*-dichlorobenzene/hexane at 263 K afforded crystals containing *o*-dichlorobenzene and hexane guests in an ordered arrangement (see the Supporting Information). In contrast, when **1** was recrystallized at 293 K from *o*-dichlorobenzene/hexane, crystals without pores and solvent molecules were obtained (Figure 2c).[15] In the solvent-free form, a columnar structure is maintained (Figure 3b), whereas the *syn* conformation of the ferrocene moieties in **1** allows the formation of pairs of adjacent molecules in the crystal and the pattern of the stacking arrangement changes from D–A to D–A–A compared with the porous **1**·X form.

Thermal desorption of the guest molecules in **1**·X was examined by thermogravimetric analysis (TGA). The TG curve indicated desorption of guest molecules at $T_{de} = 346$–380 K without chemical decomposition. The T_{de} values do not correlate with the boiling points of the guest molecules (e.g., the most volatile dichloromethane had high T_{de}), that is, the host–guest interaction affects T_{de} significantly.

To clarify the crystal structure after desorption of guest molecules, the synchrotron X-ray powder diffraction (XRPD) pattern of a sample prepared by heating **1**·THF at 420 K under vacuum for 12 h was measured, and the cell parameters of the sample were determined by the Rietveld method. The XRPD-derived cell parameters were consistent with those of solvent-free **1** (see the Supporting Information). The XRPD patterns of samples of **1**·CH_2Cl_2 from which guests had been desorbed thermally were also the same as those of solvent-free **1**. Thus, it is confirmed that guest desorption causes crystal-to-crystal transformation from **1**·X to solvent-free **1**.

Reversibility of the crystal-to-crystal transformation on guest desorption and adsorption by **1** was studied by variable-temperature XRPD (VT-XRPD). For this measurement, we prepared a vacuum-sealed 1-mm-diameter glass capillary containing a 0.5-mm-diameter capillary filled with frozen THF and a 0.5-mm-diameter capillary packed with powdered solvent-free **1** (Figure 4a). After 3 h at room temperature, the XRPD pattern had completely changed from that of solvent-free **1** to that of **1**·THF (Figure 4b, A→B). Then, THF was frozen at 90 K and the sample was heated from 300 to 400 K. Subsequently, the temperature of the sample capillary T_s was maintained at 300 K, and the temperature of the THF capillary T_g was increased from 90 to 400 K. XRPD patterns were measured at every 50 K with an X-ray exposure time of 5 min for each measurement. On heating a sample of **1**·THF, THF molecules were released, the XRPD pattern of solvent-free **1** emerged, and, at 400 K, the pattern corresponded completely to that of solvent-free **1** (Figure 4b, C). When the capillary was filled with THF vapor by increasing T_g, THF molecules were adsorbed by the host, and XRPD patterns arising from **1**·THF were observed (Figure 4b, D–G). When T_s and T_g were kept at 300 K, guest adsorption was complete within 5 min (see the Supporting Information).

These results indicate rapid and reversible crystal-to-crystal transformation between **1**·THF and solvent-free **1**. In view of the conformational change required, the fast transformation is particularly remarkable.[14] These features are derived from the flexibility of the crystal structure as a result of the D–A interaction, which is weaker than other chemical bonds, and from the higher stability of **1**·THF compared with solvent-free **1** ($\Delta G = -32\ \mathrm{kJ\,mol^{-1}}$[17]). Diffuse reflectance UV/Vis spectra of **1**·THF and solvent-free **1** indicated appearance of a CT band that is not present in the spectrum of **1** in solution and a red shift of the CT band for **1**·THF ($\lambda_{max} = 619$ nm) from that of solvent-free **1** ($\lambda_{max} = 601$ nm; see the Supporting Information). This result suggests stronger D–A interaction in **1**·X, which is consistent with the one-dimensional columnar D–A structure and the shorter Cp–Aq distance compared with that in solvent-free **1**.

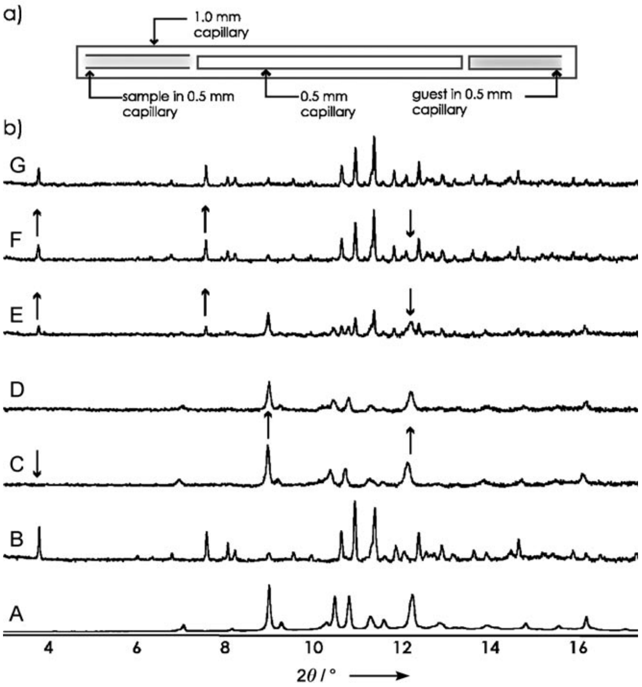

Figure 4. a) Illustration of the capillary used in VT-XRPD experiment. b) XRPD pattern of solvent-free **1** (A) and results of VT-XRPD measurements (B–G). Temperatures of sample (T_s) and guest (T_g) were B: $T_s = 350$, $T_g = 90$ K; C: $T_s = 400$, $T_g = 90$ K; D: $T_s = 300$, $T_g = 200$ K; E: $T_s = 300$, $T_g = 300$ K; F: $T_s = 300$, T_g 350 K; and G: $T_s = 300$, $T_g = 400$ K.

In conclusion, the new D–A conjugated compound 1,4-Fc_2Aq (**1**) has been synthesized. Crystals of **1** have either a solvent-incorporating porous structure or a solvent-free non-porous structure, which can be instantly and reversibly interconverted by desorption and adsorption of guest molecules, with alternation of D–A and D–A–A arrangements in the one-dimensional columnar structure. A preliminary study has shown that **1** exhibits protonation-induced intramolecular electron transfer. We are currently investigating the combination of physical property changes resulting from the interaction with acid molecules and the crystal structural transformation.

Experimental Section

1: 1,4-Dibromoanthraquinone (2.42 g, 6.6 mmol) and 1-ethynylferrocene (2.831 g, 13.5 mol) were dispersed in triethylamine (120 mL) and stirred. CuI (136 mg, 0.72 mmol) and $[PdCl_2(PPh_3)_2]$ (482 mg, 0.69 mmol) were added. The suspension was heated to reflux for 3 h. The color of the reaction mixture turned from orange to dark red.

The solvent was removed under vacuum. The residue was dissolved in 100 mL of dichloromethane, washed with water, and then dried over anhydrous Na$_2$SO$_4$. The filtrate was subjected to chromatography on an alumina column (activity II–III, 6×20 cm) with dichloromethane/hexane (1:3→1:1). The third brown band was collected. The product was recrystallized from dichloromethane/hexane, and black crystals were collected. Yield: 1.3442 g (32.6 %). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.34$ (t, 4H, $J = 1.8$ Hz; Cp), 4.35 (s, 10H; Cp), 4.67 (t, 4H, $J = 1.8$ Hz; Cp), 7.78 (m, 2H; Ph), 7.81 (s, 2H; Ph), 8.34 ppm (s, 2H; Ph). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 65.4$ (Cp), 70.2 (Cp), 70.8 (Cp), 72.4 (Cp), 86.9 (C≡C), 98.1 (C≡C), 123.9 (Aq), 127.4 (Aq), 134,1 (Aq), 134.8 (Aq), 139.0 (Aq), 182.4 ppm (C=O). MS (ESI-TOF-MS): m/z 623.9541; calcd: 624.29 [M^+].

X-ray diffraction measurements: The crystals were mounted in a loop. Data was collected with a Rigaku AFC8 diffractometer with the Rigaku Mercury CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). An empirical absorption correction using equivalent reflections and Lorentzian polarization were performed with the program Crystal Clear 1.3.5. The structure was solved with the program SHELXS-97[18] and refined against F^2 using SHELXL-97[19] Selected crystallographic data and experimental details are listed in the Supporting Information.

The in situ synchrotron powder diffraction experiment on THF adsorption was performed on a large Debye–Scherrer camera installed at SPring-8 BL02B2 with an imaging plate as detector. The wavelength of the incident X-rays was 1.001 Å. VT-XRPD measurements were performed with a nitrogen gas-flow system.

Received: March 9, 2006
Revised: May 10, 2006

Keywords: donor–acceptor systems · host–guest systems · metallocenes · microporous materials · X-ray diffraction

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[15] CCDC-600337–CCDC-600347 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[16] The size was determined by considering van der Waals radii of constituent atoms.

[17] Estimated from the DSC measurement.

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