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

For decades, much attention has been 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, strong visible-NIR light absorption, and high electronic conductivity. The tendency toward DA stacking in a crystal indicates that D-A conjugated molecules can form a network structure, which may manifest interesting physical properties. We are interested in the properties of a new D-A conjugated system [1-3] of ferrocenylethynylanthraquinones (FcAq's), from two viewpoints: the protonation-induced intramolecular electron transfer reaction causing valence tautomers, and the construction of D-A stacked nanoporous network structures, which have attracted much recent attention due to their high potential for applications such as selective gas adsorption, heterogeneous catalysts, and molecular recognition. In the present study, we have found that a new T-shaped FcAq compound, 1,4-bis(ferrocenylethynyl) anthraquinone (1,4-Fc_2Aq), gives a facile single crystal formation in the presence of guest solvent molecules, and undergoes an instant and reversible crystal-to-crystal transformation by heating and guest vapor treatment [4].

The crystal structures of 1,4-Fc_2Aq's obtained from various solvents were confirmed by single-crystal X-ray diffraction analysis. Most of the structures show the inclusion of the solvent as the guest molecule. The crystal structure of α-1,4-$Fc_2Aq{\cdot}CH_2Cl_2$ along the *b* axis is shown in Fig. 1(a) as an example. The crystal was obtained by recrystallization from dichloromethane-hexane at 263 K; under such conditions, a large (25 × 1 × 1 mm^3) crystal was grown within a week. α-1,4-$Fc_2Aq{\cdot}CH_2Cl_2$ has subnanopores with dimensions of 5.7 Å × 3.5 Å along the *b* axis, in which dichloromethane as guest molecules are contained with a 1,4-Fc_2Aq to dichloromethane mole ratio of 1:1. An infinite one-dimensional columnar structure is formed along the *b* axis by an alternating arrangement of π-conjugated spacers and π-π stacking interactions between Fc (D) and Aq (A) moieties (Fig. 2(b)). The Aq and Cp planes lean about 45 degrees to the *b* axis. The two kinds of complex columns are almost perpendicular to each other and are arranged alternately to construct the porous framework. Crystals with the formula 1,4-$Fc_2Aq{\cdot}X$ (X = guest molecule) were formed in various solvents. Their crystal structures are similar to the structure of α-1,4-$Fc_2Aq{\cdot}CH_2Cl_2$, but the size of the subnanopores changes according to the size of the guest molecules included.

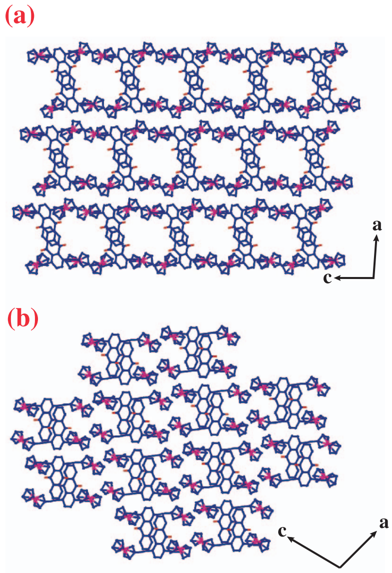

Fig. 1. Crystal structure of α -1,4-$Fc_2Aq{\cdot}CH_2Cl_2$ along the *b* axis **(a)** and that of solvent-free 1,4-Fc_2Aq along the *b* axis **(b)**. Hydrogen atoms and disordered guest molecules (CH_2Cl_2) are omitted for clarity.

The recrystallization of 1,4-Fc_2Aq from *o*-dichlorobenzene-hexane at 293 K produced crystals without pores and solvent molecules, the structure of which is shown in Fig. 2(b). In the solvent-free form, a columnar structure is maintained (Fig. 2), whereas the syn conformation of the ferrocenes in 1,4-Fc_2Aq allows for 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 that of the porous 1,4-$Fc_2Aq{\cdot}X$.

Thermal desorption of the guest molecules in 1,4-$Fc_2Aq{\cdot}X$ was examined by thermal gravimetric analysis (TGA). The TG curve indicated the desorption of guest molecules at T_{de} = 346-380 K without chemical decomposition. To clarify the crystal structure after the desorption of guest molecules, the synchrotron XRPD of a sample prepared by heating 1,4-$Fc_2Aq{\cdot}THF$ at 420 K under vacuum 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 1,4-Fc_2Aq. Thus, it is confirmed that guest desorption causes crystal-to-crystal transformation from 1,4-$Fc_2Aq{\cdot}X$ to solvent-free 1,4-Fc_2Aq.

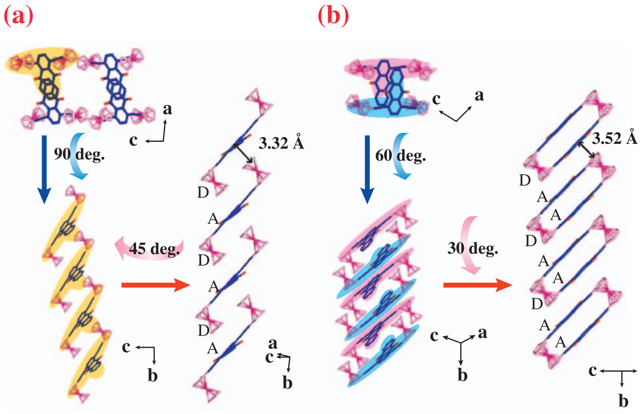

Fig. 2. One-dimensional columnar structure of 1,4-Fc$_2$Aq·X **(a)** and that of solvent-free 1,4-Fc$_2$Aq **(b)**.

The reversibility of the crystal-to-crystal transformation by guest desorption and adsorption of 1,4-Fc$_2$Aq were studied by variable-temperature XRPD (VT-XRPD) at beamline **BL02B2**. For this measurement, we prepared a vacuum-sealed cell, shown in Fig. 3(a). After the tube stood for 3 hours at room temperature, the XRPD pattern completely changed from that of solvent-free 1,4-Fc$_2$Aq to that of 1,4-Fc$_2$Aq•THF (Fig. 3(b), from i to ii). Then, THF was frozen at 90 K and the sample was heated from 300 K to 420 K, followed by maintenance of the temperature of the sample capillary, T_s, at 300 K and increasing the temperature of the THF capillary, T_g, from 90 K to 400 K. XRPD patterns were measured at every 50 K, and the X-ray exposure time was 5 min for every measurement. By heating the 1,4-Fc$_2$Aq•THF sample, THF molecules were released and the XRPD patterns of solvent-free 1,4-Fc$_2$Aq emerged. At 400 K, patterns corresponded perfectly with the pattern of solvent-free 1,4-Fc$_2$Aq (Fig. 3(b), iii). When the capillary was filled with THF vapor by increasing T_g, THF molecules were adsorbed on the host, and XRPD patterns arising from 1,4-Fc$_2$Aq•THF were observed (Fig. 3(b), iv-vii). When T_s and T_g were kept at 300 K, guest adsorption was completed within 5 min. These results indicate a rapid and reversible crystal-to-crystal transformation between 1,4-Fc$_2$Aq•THF and solvent-free 1,4-Fc$_2$Aq. In view of the conformational change required, this fast transformation is particularly remarkable. These features are derived from the crystal structure flexibility caused by the D-A interaction, which is weaker than other chemical bonds, and from the higher stability of 1,4-Fc$_2$Aq•THF compared with solvent-free 1,4-Fc$_2$Aq.

In conclusion, a D-A conjugated compound, 1,4-Fc$_2$Aq, was newly synthesized. Crystals of 1,4-Fc$_2$Aq have either a solvent-incorporated porous structure or a solvent-free nonporous one, which can be reversed instantly by the desorption and absorption of guest molecules, causing the alternation of the D-A arrangement in a one-dimensional columnar structure.

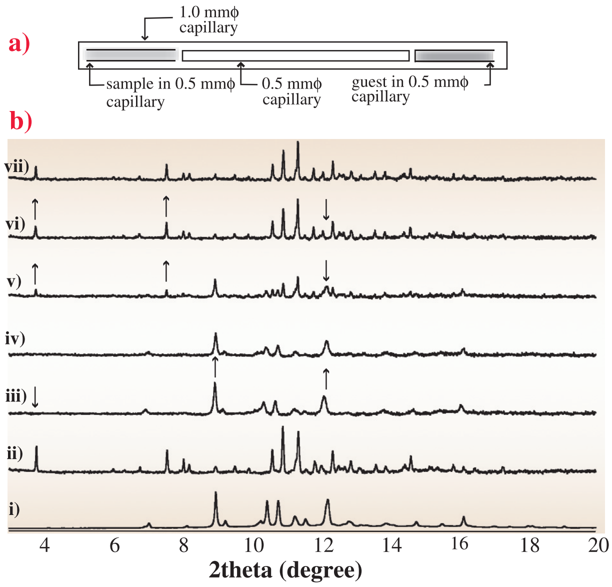

Fig. 3. **(a)** Illustration of capillary used in VT-XRPD experiment. **(b)** XRPD pattern of solvent-free 1,4-Fc$_2$Aq (i) and results of VT-XRPD measurement (ii-vii). The temperatures of the sample (T_s) and guest (T_g) are (ii) T_s = 350 K, T_g = 90 K, (iii) T_s = 400 K, T_g = 90 K, (iv) T_s = 300 K, T_g = 200 K, (v) T_s = 300 K, T_g = 300 K, (vi) T_s = 300 K, T_g 350 K, and (vii) T_s = 300 K, T_g = 400 K, respectively.

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