

Symmetry Switch of Cobalt Ferrocyanide Framework by Alkaline Cation Exchange

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Abstract: We observed a reversible symmetry switch of a cobalt ferrocyanide framework by the alkaline cation exchange and resultant control of the optical properties at room temperature.

Coordination polymers, which often contain cavities or channels that can be used for the inclusion and exchange of various guest species, are attracting the current interest of the materials scientist, because it can be utilized for hydrogen storage, molecular sensors, molecular filters, and so on.^{1,2} In some cases, a strong guest–host interaction between the polymer framework and the guest species modifies the physical properties of the host framework. Among the coordination polymers, Prussian blue analogues,^{3–8} represented as $A_xM_A[M_B(CN)_6]_y \cdot zH_2O$ (M_A and M_B are transition metal ions, and A is an alkali metal ion), have a nanoporous framework together with the strong guest–host interaction. The alkaline cations (A^+) and a portion of water molecules (zeolitic waters) are accommodated in the nanopores, and the other portion of water molecules (ligand waters) occupy the vacancy of the $[M_B(CN)_6]$ site and coordinate to the M_A site.³ The magnetic and electronic properties of the host can be controlled by the alkaline cation^{6,7} and water⁸ concentration. Sato et al.^{6a} reported that substitution of K^+ for Na^+ induces a phase transition from the $Co^{II}_{hs}-Fe^{III}_{ls}$ phase to the $Co^{III}_{ls}-Fe^{II}_{ls}$ phase without altering the lattice symmetry.

If we switch the crystallographic symmetry of the host framework, we can switch more useful functionalities, such as second-harmonic generation and/or ferroelectricity. The crystal structure of the Prussian blue framework is usually a face-centered-cubic ($Fm\bar{3}m$) lattice.³ The size of the nanopores well fit the ionic radius of the larger cations, i.e., the Rb^+ ion or Cs^+ ion, but is rather too large for the smaller cations, such as the K^+ ion and Na^+ ion. In the latter case, a cooperative displacement of the cations from the center of the interstitial site may cause a macroscopic distortion of the framework or a structural phase transition (Figure 1). In this paper, we report a reversible switch of the inversion symmetry in a cobalt ferrocyanide framework by alkaline cation exchange and resultant control of second harmonic generation (SHG) at room temperature.

The target material was prepared by mixing an aqueous solution of KCl (3 mol dm^{-3}), $CoCl_2 \cdot 6H_2O$ (5 mmol dm^{-3}), and $K_4[Fe(CN)_6] \cdot 3H_2O$ (5 mmol dm^{-3}). The precipitated red powder was filtered and washed with water and then dried in air. Elemental analyses by inductively coupled plasma atomic emission spectrometry and standard microanalytical methods confirmed that the formula of the compound was $K_{1.88}Co[Fe(CN)_6]_{0.97} \cdot 3.8H_2O$ (**1**). Calcd: K, 18.08; Co, 14.50; Fe,

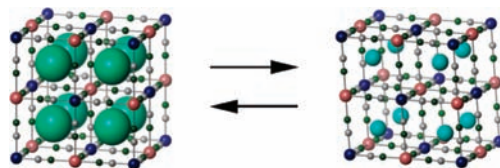


Figure 1. Schematic illustration of symmetry switch of the host framework by cation exchange.

13.33; C, 17.20; H, 1.88; N, 20.05%. Found: K, 18.24; Co, 14.78; Fe, 13.55; C, 17.02; H, 1.84; N, 19.56%. When **1** was sintered in 1 mol dm^{-3} of NaCl solution, **1** gradually turns from red to green (**2**). Again, the color recovered by sintering in 1 mol dm^{-3} of KCl solution (**3**) (Figure 2). The formula of **2** was $Na_{1.52}K_{0.04}Co[Fe(CN)_6]_{0.89} \cdot 3.9H_2O$. Calcd: Na, 9.86; K, 0.44; Co, 16.63; Fe, 14.03; C, 18.10; H, 2.22; N, 21.11%. Found: Na, 9.90; K, 0.50; Co, 16.67; Fe, 13.82; C, 18.21; H, 1.89; N, 21.11%. The formula of **3** was $Na_{0.04}K_{1.48}Co[Fe(CN)_6]_{0.88} \cdot 2.6H_2O$. Calcd: Na, 0.26; K, 16.48; Co, 16.79; Fe, 14.00; C, 18.06; H, 1.49; N, 21.07%. Found: Na, 0.19; K, 16.39; Co, 16.75; Fe, 13.50; C, 18.34; H, 1.27; N, 21.02%. The elemental analysis by ICP-AES spectrometry after respective cation exchanges revealed nearly complete cation exchange at least for 8 cycles (Figure S1).

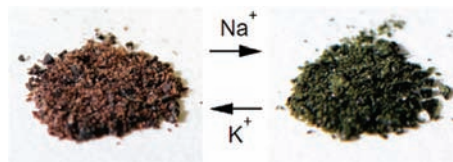


Figure 2. Cation exchange-induced color change.

Figure 3 shows the X-ray powder diffraction patterns for **1–3** obtained at the BL02B2 beamline⁹ of SPring-8. The wavelength of the X-ray was 0.502 43 Å, which was calibrated by the lattice constant of standard CeO_2 powders. We performed Rietveld analysis¹⁰ to refine the lattice constant. **1** showed a usual face-centered-cubic ($Fm\bar{3}m$) structure with a lattice constant of $a = 10.057(7)$ Å. In contrast, the peak pattern of **2** was different from those of the face-centered-cubic lattice. We could index the pattern with a rhombohedral structure. The lattice constant was refined with rhombohedral structure: $a = 10.340(2)$ Å and $\alpha = 91.32^\circ$. Again, **3** showed a face-centered-cubic ($Fm\bar{3}m$) structure with lattice constant of $a = 10.082(3)$ Å. Thus, cation exchange induced a reversible structural phase transition between cubic and rhombohedral phases.¹¹

We investigated the valence states for **1** and **2** by the infrared (IR) spectra and the magnetic susceptibility. The IR spectra are shown in Figure S2. The CN stretching peaks of $[Fe^{II}(CN)_6]$ were observed at 2079.9 cm^{-1} in **1** and 2086.6 cm^{-1} in **2**. The products

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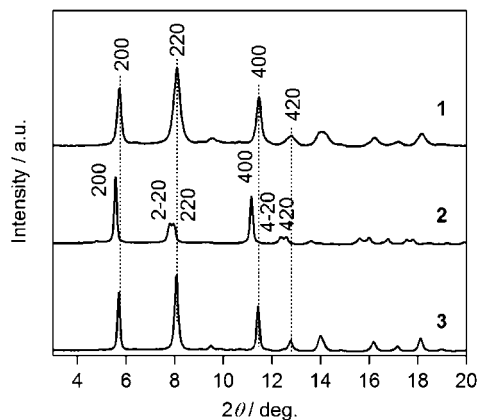


Figure 3. XRD patterns for **1** (upper), **2** (middle), and **3** (bottom). X-ray wavelength was 0.50243 Å.

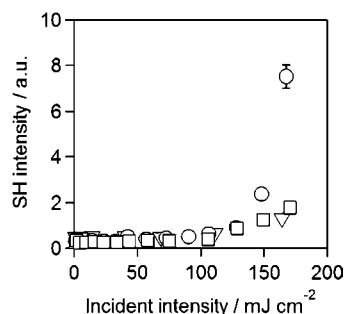


Figure 4. SH intensity versus incident light intensity of **1** (□), **2** (○), and cover glass (▽).

of magnetic susceptibility (χ_M) and temperature (T) plots are shown in Figure S3. The $\chi_M T$ value at 300 K was almost the expected spin-only values of 3.0, i.e., 3.06 (**1**) and 3.02 cm³ K mol⁻¹ (**2**). These data indicate that the valence states are the same, i.e., Co^{II}_{hs}–Fe^{II}_{ls}. Thus, the symmetry switch observed in the present system has a purely structural origin. We further investigated the diffuse reflectance spectra (Figure S4). The cation exchange alters the position of the absorption band from 520 nm (**1**) to 610 nm (**2**). The rather sharp 610 nm band in **2** can be ascribed to the d–d transition of Co^{II}_{hs}. The rhombohedral distortion of the framework can dipole-activate such a d–d transition.

We performed the SHG measurement in a transmittance mode. A detailed setup for the SHG measurements is shown in Figure S5. A Q-switched Nd:YAG laser (New wave research, Tempest 30, wavelength of 1064 nm, pulse duration of 3–5 ns, repetition rate of 30 Hz) was used as the excitation light source. The sample powders were spread over a cover glass and were sandwiched by another cover glass. The thickness of the sample powders was ca. 50 μm. The SHG light was guided to a photomultiplier tube (Hamamatsu, H6780-04) through sharp-cut filters and a band-pass filter. The temporal response of the photomultiplier was monitored with an oscilloscope (Tektronix, DPO4054). Figure 4 shows the SHG signal against the incident intensity for **1** and **2**. Before each SHG measurement, we checked the SHG signal originated in the cover glasses only (triangles in Figure 4). The small SHG signal of **1** mainly comes from the cover glasses. On the other hand, **2** shows a detectable SHG signal above 150 mJ cm⁻². We cannot determine the intensity of the SHG signal above 190 mJ cm⁻² due to significant sample deterioration. The SHG signal of **2** indicates absence of the inversion symmetry in the rhombohedral phase.¹²

Here, we propose a possible atomic arrangement, which causes the rhombohedral distortion. In **2**, the nanopore size (= 5.17 Å) is

much larger than the ionic radius (= 1.18 Å) of the Na ion. Then, the electrostatic force from the surrounding ions can cause a [111] displacement of the cation toward the [Fe(CN)₆]⁴⁻ molecule. The displacement of the cation further induces bending of the adjacent three CN⁻ groups, to gain the electrostatic energy between them. Such a trigonal distortion of the [Fe(CN)₆]⁴⁻ molecule causes the rhombohedral distortion, as observed.

In summary, we report a reversible switch of inversion symmetry in a cobalt ferrocyanide, Na_xK_yCo^{II}[Fe^{II}(CN)₆]_{(x+y+z)/4} · zH₂O, induced by alkaline cation exchange. The symmetry change switches the color, magnetic properties, and the SHG activity of the compound.

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Supporting Information Available: Reversibility of the alkaline cation exchange, IR spectra, magnetic data, diffuse reflectance measurement, and the setup for SHG measurement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) We estimated the crystalline size by Scherrer formula, and the values were around 15 nm (**1**), 30 nm (**2**), and 30 nm (**3**), respectively.
- (12) There are seven space groups in the rhombohedral lattice. Among them, four space groups, i.e., *R3*, *R3m*, *R32*, and *R3c*, have no inversion symmetry. We further observed 021 and 003 reflections in the XRD pattern, which excludes the *R3c* symmetry. Thus, the possible space groups are *R3*, *R3m*, and *R3*. Further analysis is unsuccessful due to rather broad XRD pattern.

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