Directional Electron Transfer in Crystals of [CrCo] Dinuclear Complexes Achieved by Chirality-Assisted Preparative Method

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S *Supporting Information*

ABSTRACT: The polarization switching mechanism is used in various devices such as pyroelectric sensors and memory devices. The change in polarization mostly occurs by ion displacement. The development of materials whose polarization switches via electron transfer in order to enhance operation speed is a challenge. We devised a synthetic and crystal engineering strategy that enables the selective synthesis of a [CrCo] heterometallic dinuclear complex with a polar crystal structure, wherein polarization changes stem from intramolecular charge transfer between Co and the ligand. Polarization can be modulated both by visible-light irradiation and temperature change. The introduction of chiral ligands was paramount to the successful polarization switching in the valence tautomeric compound. Mixing Cr and Co complexes with enantiopure chiral ligands resulted in the selective formation of only pseudosymmetric [CrCo] heterometallic complexes. Furthermore, the left-handed chiral ligands preferentially interacted with their right-handed counterparts, enabling molecules to form a polar crystal structure.

The ability to synthesize crystalline polar structures is essential for functional devices such as pyroelectric sensors and ferroelectric memories.[1−5] The change in polarization induced by a temperature change and application of an electric field plays roles in these devices. A challenge in this field is the synthesis of new compounds that exhibit a polarization switch[6] via the movement of electrons,[7−11] as opposed to the more typical mechanism of ion displacement[12−14] or molecular motion.[15,16] The charge transfer process is faster than the movement of ions, potentially enabling an improvement in the switching speed of resultant devices. However, relatively few electronic ferroelectric compounds have been reported. This is because the strategies for obtaining these materials have not been developed completely. We therefore aimed to synthesize materials exhibiting polarization switching due to intramolecular charge transfer in a rational manner. The intramolecular charge transfer mechanism differs from that of typical ferroelectric and electronic ferroelectric compounds.

Our strategy to realize the polarization change originating from the intramolecular charge transfer was inspired by a previous report on the valence tautomeric $[(Co(rac\text{-}cth))_2(\mu\text{-}dhbq)]^{3+}$ dinuclear complex[17] (abbreviated as [CoCo]) from racemic cth terminal ligands (Figure 1a); cth = 5,5,7,12,12,14-hexamethyl-
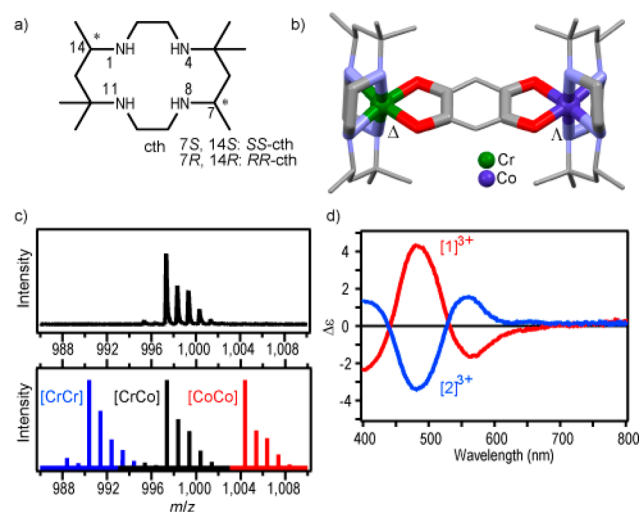

Figure 1. (a) Molecular structure of the chiral terminal ligand (cth). (b) Molecular structure of the heterometallic dinuclear complex $[1]^{3+}$ obtained by single-crystal structural analysis of $1(PF_6)_2Cl$ at 220 K. (c) Comparisons of the ESI-MS spectra of $1(PF_6)_2Cl$ obtained (top) in MeCN and the calculated (bottom) isotopic distribution patterns. (d) Circular dichroism spectra of $1(PF_6)_2Cl$ (red) and its enantiomer $2(PF_6)_2Cl$ (blue).

1,4,8,11-tetraazacyclotetradecane, dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone. The [CoCo] complex prepared from *rac*-cth (1:1 mixture of *SS*-cth and *RR*-cth) formed a symmetric molecular structure (Figure S1a); the [Δ-Co(*SS*-cth)] and [Λ-Co(*RR*-cth)] moieties were bridged by the dhbq ligand. The [CoCo] dinuclear complex exhibited valence tautomerism in

the crystalline state; however, crystal structure analysis indicated that the directions of the intramolecular charge transfers are random in a crystal (Figure S1b), suggesting that crystalline polarization is absent. When the direction of the charge transfer can be controlled within the entire crystal, polarization switching can be achieved at a macroscopic level, not only at a molecular level. To this end, we attempted to synthesize crystals of heterometallic [CrCo] dinuclear complexes in which the [CrCo] complex is aligned such that the molecular-level polarization change arising from charge transfer between Co and the bridging ligand is not canceled out in the crystalline form. However, the methodologies to synthesize the heterometallic complexes and also to control the molecular orientation within crystals remain challenging despite significant efforts in crystal engineering.[18−20]

We thus devised a strategy for the selective synthesis of a heterometallic dinuclear complex possessing a molecular alignment that facilitates polarization switching; this switching originates from valence tautomerism in crystals. The key to our synthetic method is the use of chiral ligands. The chiral ligands can produce differences in stability between symmetric (*SS-RR* ligand pair) and asymmetric (*SS-SS* or *RR-RR* ligand pairs) molecular structures when dinuclear complexes are formed. The molecular structures of [CoCo] dinuclear complexes prepared with *rac*-cth ligands suggest that symmetric dinuclear complexes (*SS-RR* ligand pair) are preferentially formed over asymmetric complexes. We predict that the heterometallic [CrCo] complex, with an almost symmetrical molecular structure and pseudoinversion center (Figure 1b), will be formed using an enantiopure chromium complex and a cobalt complex with a different enantiomer. Furthermore, the crystal structure of the heterometallic [CrCo] complex is expected to be a well-ordered polar structure in the form [(*SS*-cth)CrCo(*RR*-cth)]-[(*SS*-cth)CrCo-(*RR*-cth)]-[(*SS*-cth)CrCo(*RR*-cth)] because each chiral ligand faces its counterpart resulting more stable (and denser) crystals.[21] Indeed, homometallic [CoCo] complex with *rac*-cth ligands crystallized in such a molecular packing (Figure S1b).

The enantiopure mononuclear complexes consisting of different metal ions and enantiomers of cth ligands, [CrCl$_2$(*SS*-cth)]Cl and [Co(AcO)(*RR*-cth)](PF$_6$) (Figure S2), were mixed in a methanoic solution of dhbq in an equimolar ratio. From this reaction, the heterometallic dinuclear complex of Cr and Co, [(Cr(*SS*-cth)) (Co(*RR*-cth))(μ-dhbq)](PF$_6$)$_2$Cl (**1(PF$_6$)$_2$Cl**), was obtained as dark-purple crystals (Figure 1b). The enantiomer of **1(PF$_6$)$_2$Cl**, [(Cr(*RR*-cth)) (Co(*SS*-cth))(μ-dhbq)](PF$_6$)$_2$Cl (**2(PF$_6$)$_2$Cl**), can be obtained from the same reaction using [CrCl$_2$(*RR*-cth)]Cl and [Co(AcO)(*SS*-cth)](PF$_6$) as starting materials.

The selective formation of a [CrCo] heterometallic dinuclear complex was confirmed by ESI-MS and circular dichroism (CD) analyses. The ESI-MS spectrum of **1(PF$_6$)$_2$Cl** in MeCN only exhibited the peaks of the [CrCo] dinuclear complex (m/z = 997.33 for [**1(PF$_6$)Cl**]$^+$) with an isotopic distribution. No peaks corresponding to [CrCr] or [CoCo] homometallic dinuclear complexes were detected (m/z = 990.40 and 1004.38 for [CrCr] and [CoCo], respectively), as shown in Figure 1c. Importantly, by simply mixing the corresponding mononuclear Cr and Co complexes with *rac*-cth ligands, the formation of a mixture of [CrCr], [CoCo] and [CrCo] dinuclear complexes can be achieved. (Figure S3d) The CD spectra of **1(PF$_6$)$_2$Cl** and **2(PF$_6$)$_2$Cl** in MeCN showed mirror-image relationships in the visible light region (Figure 1d). These data clearly show that the **1(PF$_6$)$_2$Cl** and **2(PF$_6$)$_2$Cl** were enantiomerically pure and retained the optical purities of the starting mononuclear

complexes. Heterometallic dinuclear molecules, [(Cr(*SS*-cth)) (Co(*RR*-cth))(μ-dhbq)]$^{3+}$, [**1**]$^{3+}$, are stable in solution and participate in anion-exchange reactions; this compound's Cl$^−$ anion can be replaced with PF$_6^−$ by treating **1(PF$_6$)$_2$Cl** with AgPF$_6$ in MeCN/H$_2$O to yield **1(PF$_6$)$_3$** as reddish brown crystals.

Single-crystal analysis revealed that both **1(PF$_6$)$_3$** and **1(PF$_6$)$_2$Cl** were polar in structure. **1(PF$_6$)$_3$** crystallized in the polar space group $P2_1$ at 200 K (Figures S4 and S5, Table S1). Structural analysis revealed that the discrete cationic molecules of [**1**]$^{3+}$ comprised [Δ-Cr(*SS*-cth)] and [Λ-Co(*RR*-cth)] moieties bridged by a dhbq ligand. The bond lengths around the Cr ions (Cr-O, 1.93 and 1.94 Å; Cr-N, 2.05-2.11 Å) and the Co ions (Co-O, 1.86, 1.86 Å; Co-N, 1.98-2.00 Å) suggest that the valence states of the metals were Cr^{3+} and Co^{3+} at 200 K. (Table S2). Although the [**1**]$^{3+}$ molecule appeared to possess a mirror symmetric structure as in the case of the homometallic [CoCo] complex, [**1**]$^{3+}$ lost i symmetry due to its metal-centered chirality with different metal ions. It is important to note that the Cr-to-Co orientation in each [Cr-dhbq-Co] is almost entirely aligned in the same direction along the b-axis in the structure of [(*SS*-cth)CrCo(*RR*-cth)]-[(*SS*-cth)CrCo(*RR*-cth)]-[(*SS*-cth)CrCo-(*RR*-cth)] throughout the crystal. Figure 2a shows the orientation
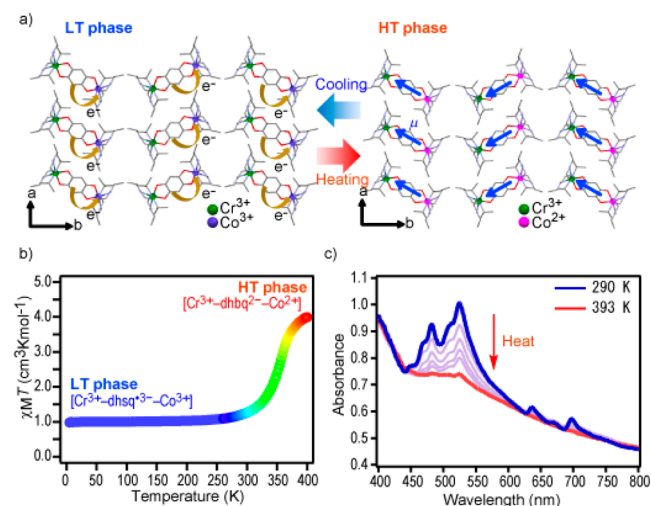

Figure 2. (a) Molecular packing of **1(PF$_6$)$_3$** along c-axis. Upon heating, charge transfer from dhsq$^{•3−}$ to Co^{3+} is induced. Blue arrows in the HT phase indicate a dipole moment calculated by DFT (see text). (b) Temperature dependence of magnetic susceptibilities displayed as plot of $\chi_M T$ vs T. (c) Temperature dependence of absorption spectra of **1(PF$_6$)$_3$** in visible region over heating from 290 K (blue) to 393 K (red).

of [Cr-dhbq-Co] molecules in the **1(PF$_6$)$_3$** crystal. The molecular packing is similar to that in the homometallic [CoCo] complex, [(Co(*rac*-cth))$_2$(μ-dhbq)](PF$_6$)$_3$. Therefore, the crystal structure of **1(PF$_6$)$_3$** can be regarded as the one in which chromium ions regioselectively replace one of the cobalt ions of the [CoCo] complex. **1(PF$_6$)$_2$Cl** also crystallized in the polar space group $P2_1$ (Figures S6 and S7, Tables S1 and S2). The crystal exhibited a one-dimensional structure of [(*SS*-cth)CrCo(*RR*-cth)]-[(*SS*-cth)CrCo(*RR*-cth)]-[(*SS*-cth)CrCo(*RR*-cth)] in which the valences of the metals were Cr^{3+} and Co^{3+} at 100 K. However, in contrast to **1(PF$_6$)$_3$**, the chains were aligned such that the orientation of the neighboring chain was nearly opposite throughout the crystal, even though **1(PF$_6$)$_2$Cl** had a polar structure.

Next, we investigated the magnetic properties of $1(\mathbf{PF_6})_3$ to determine the valences and spin states of the metal centers (Figures 2b and S8). The $\chi_M T$ product was 0.99 cm^3 K mol^{-1} at 5 K and remained almost constant upon heating up to 250 K. The $\chi_M T$ value gradually increased with further heating and reached 3.99 cm^3 K mol^{-1} at 400 K. The $\chi_M T$ value at 400 K is in good agreement with the value expected for the sum of the magnetically isolated metal centers of Cr^{3+} ($S = 3/2$) and high spin Co^{2+} ($S = 3/2$) in an octahedrally coordination environment.[22] The transition temperature ($T_{1/2}$) was determined to be $T_{1/2} = $ ca. 360 K. The transition behavior between the high-temperature (HT) and low-temperature (LT) phases is considered to be valence tautomerism in which electron transfer occurs between the metal ion and the redox-active dhbq ligand.[23−25] Crystal structure analysis at 420 K revealed that the bond lengths around the Co ions (Co-O, 2.10 and 2.11 Å; Co-N, 2.09-2.12 Å) were longer than those at 200 K, and the Co ion was considered to be high-spin Co^{2+} in the HT phase (Table S2). We then determined the electronic states to be [Cr^{3+}-dhbq^{2-}-Co^{2+}] and [Cr^{3+}-dhsq$^{\bullet3-}$-Co^{3+}] for the HT and LT phases, respectively (dhsq = deprotonated dihydroxysemiquinone). $1(\mathbf{PF_6})_2\mathbf{Cl}$ underwent a charge transfer phase transition with hysteresis at 175 and 140 K on heating and cooling, respectively (Figure S9). The presence of hysteresis indicates that the change in polarization had bistable character within the hysteresis loop.

The variable temperature IR and UV−vis absorption spectra of $1(\mathbf{PF_6})_3$ and $1(\mathbf{PF_6})_2\mathbf{Cl}$ support the occurrence of the thermally induced charge transfer (Figures 2c and S10). The UV−vis absorption spectra of $1(\mathbf{PF_6})_3$ at 290 K showed clear peaks at approximately 480 and 525 nm, corresponding to ligand-to-metal charge transfer (LMCT) from dhsq$^{\bullet3-}$ to Co^{3+}.[17,26] The intensity of these peaks decreases up to 393 K. The temperature-dependent spectra indicate valence tautomeric transition from LT to HT phase and agree well with the magnetic measurement results.

To elucidate further the electronic structures of the HT [Cr^{3+}-dhbq^{2-}-Co^{2+}] and LT [Cr^{3+}-dhsq$^{\bullet3-}$-Co^{3+}] phases, DFT calculations were conducted using the results of the crystal structure analysis (Figures 3 and S11). The DFT results showed
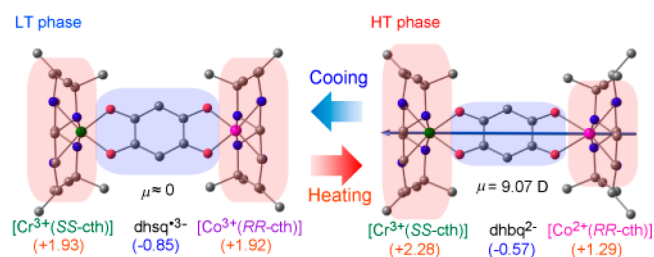
Figure 3. Optimized structure of $[\mathbf{1}]^{3+}$ in LT phase (left) and HT phase (right). Numbers in parentheses are sums of Mulliken charges of atoms for each moiety. Blue arrow indicates direction of computed dipole moment of 9.07 D in HT phase.

that $[\mathbf{1}]^{3+}$ in the HT phase had a permanent electric dipole moment of 9.07 D in the direction from the Co atom to the Cr atom. In the LT phase, the permanent electric dipole moment was almost zero (0.06 D). These results can be attributed to the asymmetric Mulliken charge population in the HT phase and the almost symmetric one in the LT phase. Because $[\mathbf{1}]^{3+}$ is aligned in the crystal, this molecular-level transition corresponds to a nonpolar-to-polar transformation at the crystal level, although, the LT phase is not completely nonpolar. $1(\mathbf{PF_6})_3$ should have a much larger change in crystal polarity compared to $1(\mathbf{PF_6})_2\mathbf{Cl}$

because each [Cr-dhbq-Co] moiety is oriented in the same direction within the entire crystal in $1(\mathbf{PF_6})_3$. The nonpolar-to-polar transformation behavior in $1(\mathbf{PF_6})_3$ is depicted in Figure 2a.

An important characteristic of the [CrCo] complex is that the change in its polarization is induced by intramolecular charge transfer, not ion displacement.[7,27] Intramolecular charge transfer induces a significant change in the electronic transition within the molecule and in the magnetic properties.[28−31] Therefore, charge transfer involving a change in polarization can be clearly detected by changes in the absorption spectra and magnetization measurements (Figures 2, S9 and S10); these properties are not observed in compounds exhibiting ion displacement. Another important characteristic of the [CrCo] complex is that the polarization can be controlled by light irradiation. The excitation of a LMCT band in Co valence tautomeric complexes was reported to induce transient charge transfer between the ligand and metal center.[17,32] To produce the excited states, TD-DFT calculations were carried out using the ground-state geometry of $[\mathbf{1}]^{3+}$. Occupied (ψ_o) and virtual (ψ_v) orbitals define the transition. The changes in the electron densities for the first and second excited states are shown as the electron density difference maps (EDDMs) in Figure 4. The two excited triplet energies are
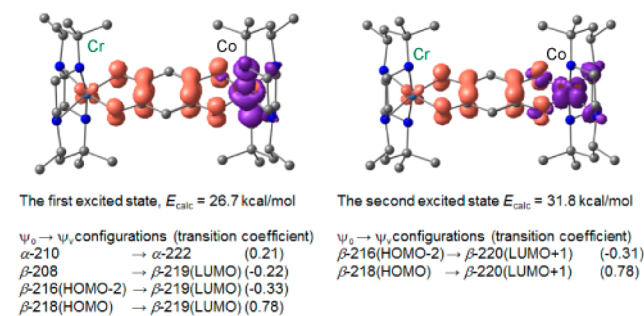
The first excited state, $E_{calc} = 26.7$ kcal/mol

$\psi_o \rightarrow \psi_v$ configurations (transition coefficient)		
α-210	$\rightarrow \alpha$-222	(0.21)
β-208	$\rightarrow \beta$-219(LUMO)	(-0.22)
β-216(HOMO-2)	$\rightarrow \beta$-219(LUMO)	(-0.33)
β-218(HOMO)	$\rightarrow \beta$-219(LUMO)	(0.78)

The second excited state $E_{calc} = 31.8$ kcal/mol

$\psi_o \rightarrow \psi_v$ configurations (transition coefficient)	
β-216(HOMO-2) $\rightarrow \beta$-220(LUMO+1)	(-0.31)
β-218(HOMO) $\rightarrow \beta$-220(LUMO+1)	(0.78)

Figure 4. EDDMs of first excited triplet state (left) and second excited triplet state (right) of AF triplet state (LT phase). Red indicates decrease in charge transfer; purple indicates increase.

26.7 and 31.8 kcal/mol relative to the AF triplet ground state. These EDDMs are consistent with two LMCT transitions from the dhbq ligand to the 3d orbital of Co^{III}.

Complex $[\mathbf{1}]^{3+}$ with a [Cr^{3+}-dhsq$^{\bullet3-}$-Co^{3+}] redox state exhibited an absorption band around 500 nm assigned to LMCT (Figure 2c). When $1(\mathbf{PF6})_2\mathbf{Cl}$ was cooled to cryogenic temperature (7 K) to slow the relaxation rate from the photoinduced metastable state, the IR spectrum measured upon visible-light irradiation revealed a difference corresponding to the transformation from [Cr^{3+}-dhsq$^{\bullet3-}$-Co^{3+}] to [Cr^{3+}-dhbq^{2-}-Co^{2+}] (Figure S11). The magnetic properties of the material after irradiation indicated the photoinduced metastable state reverted to the original [Cr^{3+}-dhsq$^{\bullet3-}$-Co^{3+}] state at ca. 90 K (Figure S9). When the IR spectrum of $1(\mathbf{PF_6})_3$ was measured at 7 K after visible-light irradiation, only a small change was observed, indicating the major component of the photoinduced [Cr^{3+}-dhbq^{2-}-Co^{2+}] state quickly relaxes back to the ground state under light-irradiation. This is consistent with the expectation a higher thermal valence tautomeric phase-transition temperature corresponds to a lower relaxation temperature from the photoinduced metastable state.[33] These experimental results are consistent with the idea the absorption in the visible region is due to ligand-to-metal charge transfer, and the polarization in $[\mathbf{1}]^{3+}$ can be transiently modulated by visible light.

Note that the polarization switching mechanism in the synthesized [CrCo] complex differs from that typically found in electronic ferroelectric and ferroelectric compounds. The change in polarization originates from the charge transfer phase transition within the polar crystals, not the ferroelectric phase transition. Furthermore, the [CrCo] complex shows different properties compared with ferroelectric and electronic ferroelectric compounds. We observed an enhanced polarization in the HT phase of the [CrCo] compound whereas polar structures usually form an LT phase in general ferroelectric compounds. This charge transfer involves a shift in the redox and spin states between high-spin Co^{2+} and low-spin Co^{3+}. The entropy gain in the HT phase arises from the contributions of spin and vibration.[6,34,35] Therefore, an enhanced polar structure with an entropically favorable [Cr^{3+}-dhbq^{2-}-Co^{2+}] state is realized in the HT phase. Furthermore, polarization switching in ferroelectric compounds usually decreases as compound size decreases; this is not the case for the [CrCo] heterometallic dinuclear complex because the change in polarization results from intramolecular charge transfer in the dinuclear complex, which is essentially a single molecular event, although intermolecular interactions do play a role.

We realized directional charge transfer in the polar crystalline [CrCo] complex. In polar crystals, polarization switching usually occurs with ion displacement or with a change in orientation. However, in our compound, polarization switching occurred with intramolecular charge transfer, which was accompanied by significant changes in the magnetization and absorption spectra. Furthermore, charge transfer is induced by the excitation of the LMCT band in the visible region, meaning that polarization in the [CrCo] complex can be modulated by visible light. A [CrCo] dinuclear complex exhibiting this electronic polarization switching was prepared using our chirality-assisted synthetic method; the use of enantiopure mononuclear complexes with different metal ions as starting materials enabled the formation of well-designed and high-purity heterometallic complexes in one-pot syntheses. The use of chiral ligands was also essential to form directional molecular orientations in the [CrCo] crystal. This method has potential to prepare heterometallic clusters and polymers for use as functional materials (e.g., heterometallic catalysts)[36,37] and develop further polar crystalline materials.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05089.

Experimental details, and crystal structure data for **1(PF$_6$)$_2$Cl** at 100 K (CIF), at 220 K (CIF) and for **1(PF$_6$)$_3$** at 200 K (CIF), at 420 K (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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