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Spiro-Driven Ferroelectric Coordination Polymer Exhibiting Distinct Phase Transitions Under Thermal and Pressure Stimuli

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Abstract: Controllable strategies for the design of molecular ferroelectrics have been actively pursued in recent years due to their promising applications in modern electronic devices. In this work, we present a spiro-driven approach for the design of a new class of molecular ferroelectrics. Using 2-morpholinoethanol (MEO) as a bidentate chelating ligand and the SCN^- anion as a bridging co-ligand, we obtained a neutral chain-like ferroelectric coordination polymer, $[\text{Cd}(\text{MEO})(\text{SCN})_2]$. Interestingly, it undergoes both a thermal-induced phase transition, driven by ring-conformational flipping of the spiro-like $[\text{Cd}(\text{MEO})]$ fragment, and a pressure-induced transition, triggered by significant deformation of the spring-like $[\text{Cd}(\text{SCN})_2]_\infty$ helical chain. Unlike most previously reported ferroelectric coordination polymers, which often rely on organic cationic guests, this work introduces a new avenue for designing neutral ferroelectric coordination polymers. Overall, the spiro-driven strategy provides valuable insights and a novel structural motif for the development of advanced molecular ferroelectrics.

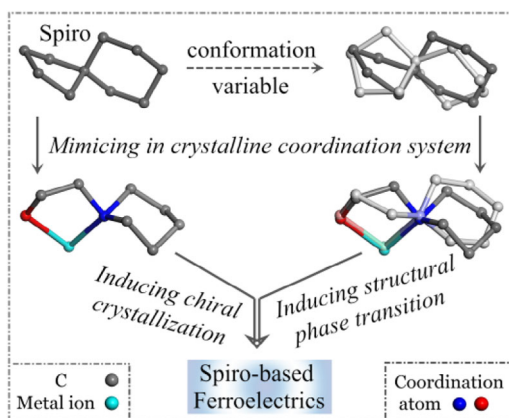
Ferroelectric materials have attracted significant attention due to their extensive applications in modern electronic devices such as memory storage, sensors, and actuators.^[1–4] In the recent years, prominent progress has been achieved in molecular-based ferroelectric materials, including single-component organic crystals,^[5–9] supramolecular complexes,^[10–15] ionic co-crystals,^[16–21] and notably the organic–inorganic hybrid perovskites.^[22–35] Compared to traditional inorganic ferroelectrics, these molecular fer-

roelectrics offer prominent advantages, such as structural diversity with flexible design, mild synthetic conditions, and lightweight for portable devices.

Ferroelectricity requires not only spontaneous polarization in a polar space group but also polarization switching under external electric field. To date, effective strategies regarding polarization switching have been adopted to afford molecular-based ferroelectrics, such as proton tautomerization of organic molecules,^[11,36,37] charge transferring in electronic donor–acceptor system,^[10,38,39] and bowl-to-bowl inversion in liquid crystals.^[40,41] Especially, Xiong et al. proposed the chemistry of molecular ferroelectrics (ferroelectrochemistry) for their design and syntheses.^[42–44] To further expand molecular ferroelectrics with desirable properties, it is pursuing to explore new design strategies. As our ongoing research into low-dimensional molecular ferroelectrics,^[45] we screen out that a spiro-like ring within a crystalline coordination system, as a mimic of the spiro compounds,^[46] may be utilized as a potential structural motif to construct molecular ferroelectrics (Scheme 1), holding the following two conjoint benefits: (1) Incorporating spiro-like unit into a crystallizable coordination polymer system, which may easily adopt an asymmetric conformation in its local environment, promotes chiral crystallization. (2) A spirocyclic structural unit with flexible ring-conformational flipping is prone to induce structural phase transitions. Therefore, the combination of these two characteristics may greatly increase the probability of forming molecular ferroelectrics.

Encouraged by the above-mentioned conception, we experimentally selected 2-morpholinoethanol (MEO) as a bidentate chelating ligand and SCN^- as a bridging ligand to form a spiro-like building block for coordination polymer construction. We yielded a 1D coordination polymer $[\text{Cd}(\text{MEO})(\text{SCN})_2]$ (**1**), which represents the first example

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- Additional supporting information can be found online in the Supporting Information section



Scheme 1. Spiro-modulated strategy for the preparation of molecular ferroelectrics in coordination system.

of spiro-driven molecular ferroelectrics. Unlike the majority of previously reported ferroelectric coordination polymers, it introduces a new avenue for designing ferroelectric coordination polymers without the reliance on organic cationic guests. More interestingly, it not only exhibits a ring-flipping-triggered phase transition with thermal stimuli but also features a chain-deformation-induced phase transition under pressure.

Compound **1** was synthesized from a volatile solution of mixed $\text{Cd}(\text{NO}_3)_2$, MEO, and NH_4SCN in water/acetone (Supporting Information for details). The thermo-gravimetric analysis (TGA) shows that it is stable up to $\sim 160^\circ\text{C}$ (Figure S1). Differential scanning calorimetry (DSC) curves of **1** show a pair of endothermic/exothermic peaks at heating/cooling runs, suggesting that it undergoes a reversible structural phase transition at $T_{\text{C-heating}}/T_{\text{C-cooling}}$ of $10.7/9.9^\circ\text{C}$

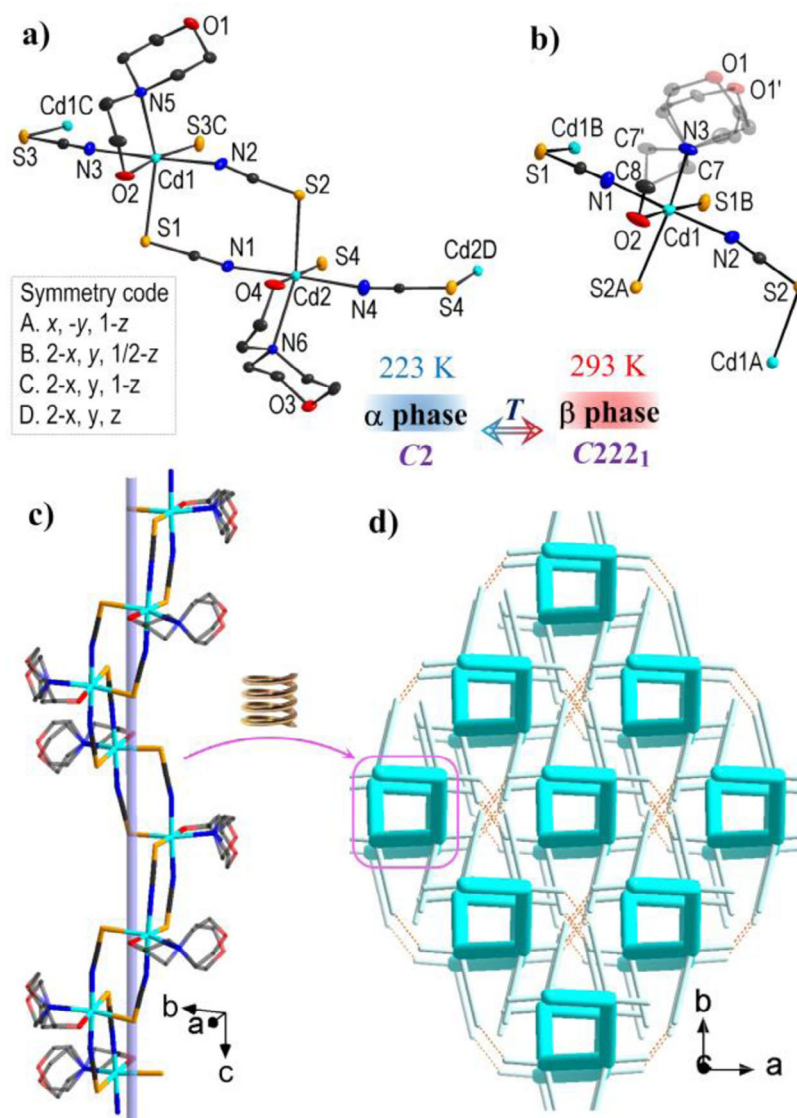


Figure 1. ORTEP representation for the selected unit of **1α** a) and **1β** b). For clarity, all H atoms have been omitted. Disordered atoms in **1β** are shaded in transparent. c) 1D helical chain structure of **1β**. d) Topological diagram for the 3D stacking of the chains in **1β**, interconnected by hydrogen bonding interactions (dotted lines).

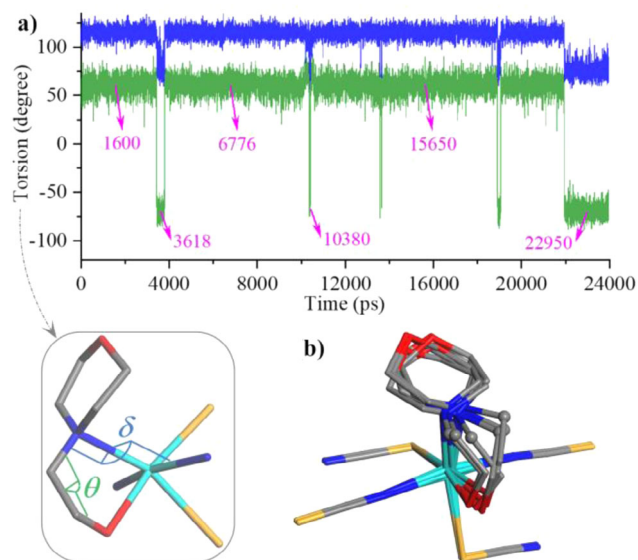


Figure 2. a) Evolution of torsions $\theta_{\text{N}-\text{C}-\text{O}}$ and $\delta_{\text{C}-\text{N}-\text{Cd}-\text{N}}$ in **1 β** over an NVT dynamic simulation process at 500 K. b) Six evolutionary snapshots labeled in a) are overlapped, showing the dynamic ring flipping over the simulation process. The flipping C7 is highlighted in ball.

(Figure S2). For convenience, we label the phases below and above T_{C} as α and β , respectively.

Single-crystal X-ray diffraction reveals that **1 α** and **1 β** crystallize in the noncentrosymmetric space groups $C2$ and $C222_1$, respectively (Table S1). The noncentrosymmetric characteristic of both phases is confirmed by the variable-temperature SHG (second-harmonic generation) test, where the SHG signal varied a little after the phase transition (Figure S3a). Compound **1** is a chain-like coordination polymer. In **1 β** , the asymmetric unit comprises one unique Cd^{2+} ion, one MEO ligand, and two crystallographically independent SCN^- anions. The Cd1 ion is a six-coordinate with two S and two N from four SCN^- ligands as well as one N and one hydroxyl O of a MEO ligand, in a distorted octahedral geometry (Figure 1b and Table S3). While both SCN^- ions function as an end-to-end bidentate bridging ligand, the MEO molecule behaves as a terminal bidentate chelating ligand. For the MEO molecule, one remarkable characteristic is that it displays two-fold disorder. The interconnection of the Cd^{2+} ions via the bridging SCN^- ligands leads to a 1D helical chain $[\text{Cd}(\text{SCN})_2]_{\infty}$ along the c -axis (Figure 1c), where the adjacent Cd^{2+} ions are doubly bridged by a pair of the SCN^- anions. Furthermore, these chains are stacked along the ab -plane by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding interactions between adjacent chains, in a crisscross pattern (Figure 1d and Table S4). Remarkably, the MEO molecule exhibits two-fold disorder, leading **1 β** to crystallize in the noncentrosymmetric $C222_1$ space group.

After the transition from β to α , a symmetry breaking occurs, and the asymmetric unit of **1 α** comprises two unique Cd^{2+} ion, four independent SCN^- ligands, and two MEO ligands (Figure 1a). Similar to **1 β** , the Cd1/Cd2 ions in **1 α** also feature a distorted octahedron $[\text{Cd}(\text{S}_2\text{N}_3\text{O}_1)]$, albeit

with slight differences in the detailed geometry (Table S3). All four SCN^- ions also function as a bidentate bridging ligand. Accordingly, a 1D chain running along the c -axis is formed, identical in topology to **1 β** . It is noteworthy that the disordered MEO molecules in **1 β** become ordered in **1 α** upon cooling.

The driving force for $\alpha \rightarrow \beta$ can be primarily ascribed to the order-disorder of the spirocyclic-like $[\text{Cd}(\text{MEO})]$ fragment. The energy difference between the DFT-based optimized structures for the two disordered states in **1 β** (C7- and C7'-containing MEO, respectively), calculated by the DMol3 module of Materials Studio,^[47] is about 0.19 eV per unit cell, indicating that these two different conformations are thermodynamically inequivalent in the crystal. Such finding can be further confirmed by the in situ variable-temperature single-crystal X-ray diffraction of **1 β** , which shows that the refined ratio of the two disordered states steadily decreases with increasing temperature (from 80:20 at 293 K to 69:31 at 293 K, Figure S4), which strongly suggests that the disorder is inherently dynamic and that the switching between the two disordered states is asymmetric.

To gain further insight into the molecular dynamics (MD) of the spirocyclic $[\text{Cd}(\text{MEO})]$ fragment, an NVT dynamic simulation was performed based on the optimized structure of one relatively stable disordered state in **1 β** (C7-containing MEO). The tracking of MEO-related torsions θ/δ (Figure 2) clearly demonstrates that θ and δ can synergistically switch back and forth between two states (ca. 55° and -70° for θ while ca. 113° and 77° for δ), with the former being the relatively stable state. This result coincides well with the above-mentioned two thermodynamically inequivalent disordered states of the $[\text{Cd}(\text{MEO})]$ fragment. More importantly, the result uncovers that the ganged switching of θ/δ stems from the restricted small-amplitude rotation around the Cd–N bond. In other words, the conformational change of the $[\text{Cd}(\text{MEO})]$ fragment (particularly the flipping between C7 and C7') is mainly caused by the restricted rotation of the MEO ligand around the Cd–N bond. Such directed and constrained motion of the organic component in **1**, resulting from its direct integration into the inorganic chain, is significantly different from the random and unrestricted motion of discrete organic cations in 1D hybrid perovskites.

Notably, the structure of **1** can also be described as a helical chain formed by the connection of eight-membered $[\text{Cd}_2(\text{SCN})_2]$ ring units via the Cd^{2+} ions at both ends of the ring, with paired $[\text{Cd}(\text{MEO})]$ fragments alternately anchoring on both sides of the chain (Figure 1c). From a mechanical perspective, this helical chain resembles a spring, potentially exhibiting deformability and torsional flexibility under external pressure. Thus, we further performed variable-pressure single-crystal structure analysis of **1**. Five main findings are uncovered: (1) The MEO rings on both sides of the chain transit from dynamic disorder at ambient pressure to ordered under pressure above 0.29 GPa (Figure 3a). (2) At ~ 3.5 GPa, a new first-order phase transition was observed, accompanied by a volume collapse of $\sim 1.5\%$, which resulted in the formation of the γ phase crystallizing in $P2_1$ (Figures 3b and S5; Table S2). The acentric nature of **1** under compression is further verified by the variable-pressure

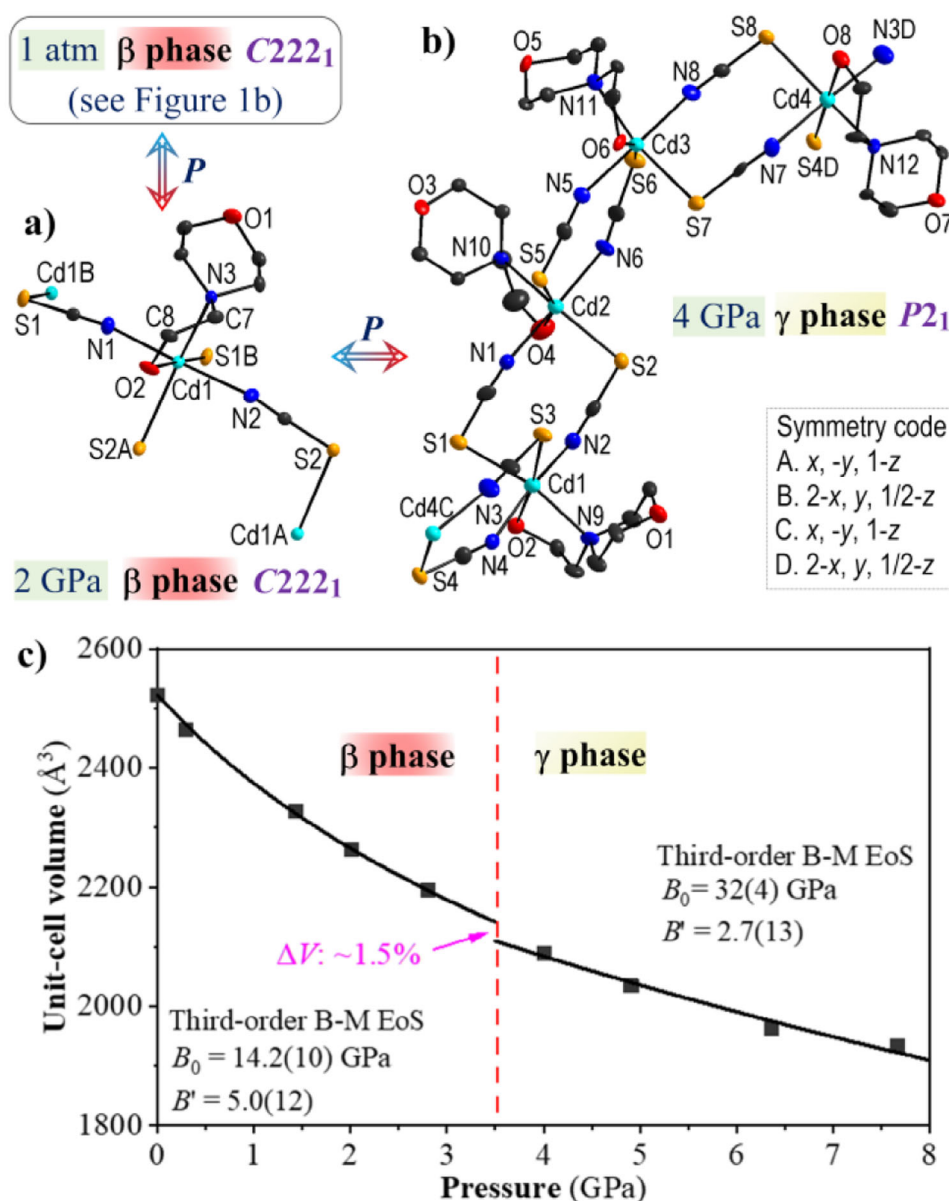


Figure 3. ORTEP representation for the selected unit of **1β** at 293 K/2 GPa a), and **1γ** at 293 K/4 GPa b). Pressure-dependent unit-cell volume of **1** at 293 K c).

SHG measurements (Figure S3b). (3) The fitted third-order Burch–Murnaghan equation of states (B–M EoS) on both phases indicates that the sample became stiffer under compression, consistent with other coordination polymers.^[48,49] (4) Between **1β** and **1γ**, not only the $[\text{Cd}_2(\text{SCN})_2]$ ring units of the main chain are compressed and deformed, but also half of the $[\text{Cd}(\text{MEO})]$ fragments anchored on the chain undergo a process of ring flipping (Figure S6). The different structural alignments of inter-chain O–H...O hydrogen bonds in β and γ phases give rise to their distinct anisotropic compressibility. Specifically, **1β** shows high incompressibility along the c -axis (the stacking direction) but greater compressibility in the ab -plane, whereas **1γ** exhibits pronounced compressibility in the bc -plane. (5) Compared to the $\beta \rightarrow \alpha$ transition, driven by the ring flipping only, the $\beta \rightarrow \gamma$ transition involves both

this flipping and the main chain deformation (Figure S7). As a result, **1γ** crystallizes in another polar group $P2_1$, where the direction of spontaneous polarization shifts from being perpendicular to the chain in **1α** to parallel to the chain in **1γ** (Figure S8). Overall, these findings highlight that, in addition to temperature, pressure is also a crucial factor influencing the crystal structure of **1**.

The phase transitions $\beta \rightarrow \alpha$ and $\beta \rightarrow \gamma$ are both theoretically ferroelectric according to the Aizu notation “222F2” (Figure S9),^[50] although α and γ phases feature different space groups and polarization directions. To investigate the ferroelectricity and the detailed confined molecular dynamics of MEO, we first conducted the dielectric spectroscopy analysis for **1** at ambient pressure (note: challenges in high-pressure characterization limited further studies for **1γ**). Upon heating,

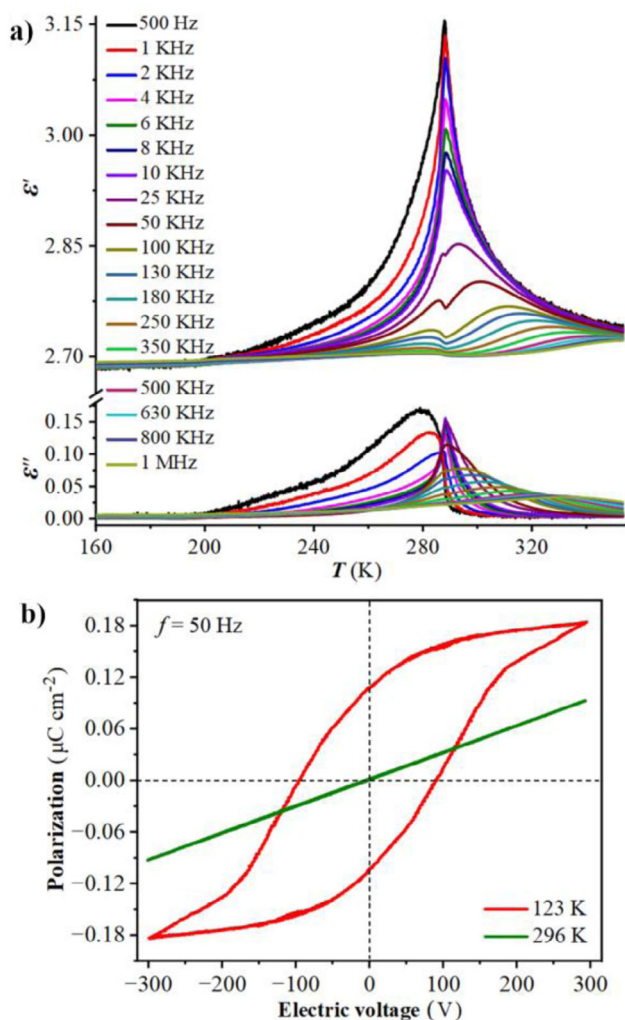


Figure 4. a) Temperature-dependent ϵ' and ϵ'' of a powder-pressed sample of **1** at various AC frequencies. b) The $P-E$ hysteresis loops for the same single crystal of **1** measured at 123 K (**1a**) and 296 K (**1b**) approximately parallel to the b -axis.

the dielectric spectroscopy of the complex permittivity ϵ^* ($\epsilon' - i\epsilon''$) was measured for **1** over a wide frequency range (Figure 4a). The recorded curves of ϵ' under low frequencies exhibit a λ -shaped dielectric anomaly near T_C , which is a typical characteristic of ferroelectric phase transition. Above T_C , dielectric relaxation is observed in the test temperature range, mainly owing to the orientation polarization of the [Cd(MEO)] fragment. We fitted the dielectric anomaly with the Curie–Weiss law, $\chi' = C_{\text{para}}/(T - T_0)$ or $C_{\text{ferro}}/(T_0' - T)$, where $\chi' = \epsilon' - 1$, C is the Curie–Weiss constant, and T_0 (T_0') is the Curie temperature (Figure S10). The $C_{\text{para}}/C_{\text{ferro}}$ ratio ranges from 0.7 to 3.03 at different frequencies (Table S6), indicating distinct frequency-dependent dipole dynamics.

The ferroelectricity of **1a** was positively confirmed by the rectangular-like $P-E$ (polarization vs. electric field) hysteresis loop in a Sawyer–Tower circuit, measured along the b -axis of sample crystal at 123 K (Figure 4b). The less ideal $P-E$ loop may result from incomplete polarization saturation, domain wall pinning, or circuit imperfections. Under ~ 233 K,

the polarization retention experiment of **1** demonstrated that the remnant polarization (P_r) remained almost unchanged throughout the 10-h testing period (Figure S11). By comparison, no hysteresis loop was observed for **1b** at 296 K. The occurrence of spontaneous polarization in **1a** can be attributed to the incomplete cancellation of the dipole moments in the upward and downward directions along the b -axis of the crystal structure (Figure S8a), whereas those in **1b** can completely offset (Figure S8b). In addition, the inter-chain hydrogen-bond interactions facilitate the dipole–dipole interaction in the lattice. The mechanism of ferroelectric phase transition can be mainly ascribed to the ring flipping within the spirocyclic-like [Cd(MEO)] fragment. Unlike most ferroelectric coordination polymers, where dipoles are correlated through interactions between guest cations, the dipoles in **1** interact directly via 1D coordination bonds and are further coupled through inter-chain hydrogen bonding between spiro units. This represents a novel instance of dipole interaction that contributes to ferroelectricity. Although the spontaneous polarization ($0.18 \mu\text{C cm}^{-2}$) is moderate (Table S7), it introduces a new polarization switching mechanism. Based on this model, we will aim at exploring other spiro-driven molecular ferroelectrics with enhanced properties.

The ferroelectric transition of **1** is further corroborated by piezoresponse force microscopy (PFM), which detects the piezoelectric signals on the sample surface. By a detailed analysis of its phase and amplitude parameters, we can indirectly infer both the polarization direction and intensity.^[51,52] As illustrated in Figure 5a, a rod-like structure with a $\sim 180^\circ$ phase difference between the interior and exterior suggests the potential presence of a bipolar domain structure within the thin film of **1**. The amplitude signal of the domain wall depicted in Figure 5b approaches zero. The independence of PFM signals from surface morphology (Figure 5c) confirms their piezoelectric origin, thereby verifying the existence of ferroelectric domains. Subsequently, we applied a DC voltage to switch the ferroelectric domains and employed an AC voltage to continuously monitor the piezoelectric signal in each state. As shown in Figure 5d, the phase–voltage curve manifests a distinct hysteresis loop, while the amplitude–voltage curve displays a characteristic butterfly shape, signifying that these ferroelectric domains experience polarization switching under the electric field. These evidences clearly demonstrate the presence of different ferroelectric domains within the thin film of **1**, capable of polarization switching under an applied electric field, thus verifying its microscopic ferroelectricity.

In summary, this study introduces a new strategy for the design of molecular ferroelectrics through the incorporation of a spiro-like structural motif into a 1D coordination polymer. The title compound, [Cd(MEO)(SCN)₂], showcases a remarkable dual-phase transition behavior, with distinct ferroelectric transitions induced by thermal or pressure stimuli. Detailed analyses employing single-crystal X-ray diffraction, DSC measurement, DFT-based structural optimization, molecular dynamics simulation, dielectric spectroscopy, the $P-E$ hysteresis loop, and PFM test have contributed significantly to a comprehensive understanding of the phase transition and ferroelectric polarization mechanism. This work underscores the potential of spiro-modulated

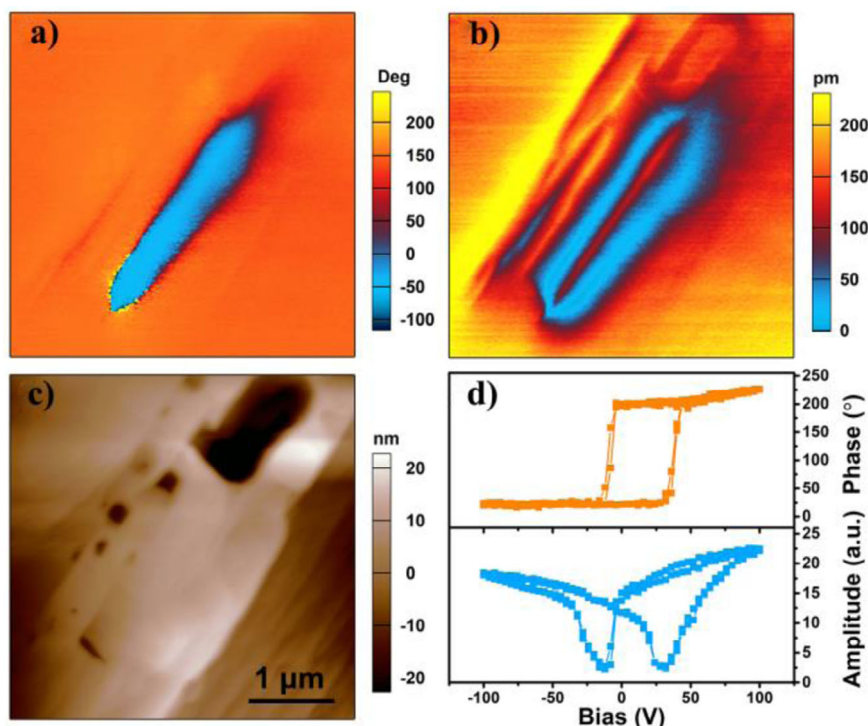


Figure 5. PFM phase a), PFM amplitude b), and corresponding topographic images on the thin film of 1 c). Local PFM hysteresis loops generated by plotting the phase and amplitude signals against the tip voltage for a specific point are shown in d).

coordination polymers as promising candidates for advanced molecular ferroelectrics.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the [Supporting Information](#) of this article.

Keywords: Coordination polymer • Ferroelectrics • Pressure-induced phase transition • Thermal-induced phase transition

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