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Investigation of Local Piezo- and Ferroelectric Properties in a Single-Ion Zn/Dy Molecular Complex

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In this work, the piezoelectric and ferroelectric properties in Zn/Dy single-ion molecular complex have been studied by local piezoresponse force microscopy and switching spectroscopy. It is demonstrated that the chosen strategy for the synthesis of integrated magnetoelectric molecular systems makes it possible to grow molecular single crystals in the polar group. Switching of the intrinsic domain structure in Zn/Dy single crystal at a bias voltage of $+15\,\mathrm{V}$ and the possibility of changing the induced domain structure at a bias voltage of $-20\,\mathrm{V}$ were demonstrated. The effective piezoelectric coefficient d_{33} was attained of about 14 pm/V at a bias voltage of 50 V.

Keywords: Integrated magnetoelectric molecular systems, magnetoelectric interaction, single-ion molecular chiral complex, piezoresponse force microscopy (PFM).

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Integrated molecular systems are materials with active optical, magnetic, and piezoelectric properties [1–3]. In certain cases, these properties interact, giving rise to magnetooptical, electrooptical, and magnetoelectric effects [3–5]. Magnetoelectric (ME) materials are systems with spontaneous electric polarization, which can be switched by an applied magnetic field, and magnetization that can be switched by an applied electric field [6]. A room-temperature magnetoelectric effect is a rather rare phenomenon, since magnetic and electric subsystems need to be closely coupled for it to be observable [6,7]. The concept of such interactions is based on chemical bonding between ions of transition metals at sites A and B of the ABO_3 perovskite structure. Specifically, ME materials synthesized with the perovskite structure are being used to construct magnetically switchable ferroelectrics, wherein data stored in an electric cell are controlled by an applied magnetic field [7]. However, the implementation of magnetically controlled polarization with the use of weak magnetic fields at room temperature still remains a complex and relevant problem of research into novel ME materials [6–9].

Drawing on the molecular chemistry concept, we have recently demonstrated [10] integrated magnetoelectric molecular systems manifesting the direct magnetoelectric effect at room temperature. The present work is a continuation of our research into the development of integrated magnetoelectric molecular systems based on a single-ion $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ chiral molecular complex that exhibits strong luminescent, optical, and magnetic properties [11–13]. The approach to synthesis of molecular ME systems with enhanced coupling relies on the association of a lanthanide ion, which affects the magnetic moment and the order of polar anisotropy, and chiral ligands, which promote the assembly of the crystal structure into polar ferroelectric spatial groups. We used high-purity neutral tetradentate ligands with Schiff bases: 1,2-cyclohexanediamine, N1,N2-bis(2-pyridinylmethylene)-, $(1S, 2S)$ and 1,2-cyclohexanediamine, N1,N2-bis(2-pyridinylmethylene)-, $(1R, 2R)$, which are denoted as S, S-2 and R, R-1 in the inset of Fig. 1. Dysprosium Dy^{3+} served as a lanthanide ion. It has one of the highest room-temperature values of magnetic moment $(\sim 10.65\,\mu_\mathrm{B})$, exhibits strong magnetic anisotropy, and is thus commonly used in the development of single-molecule ion magnets [12,13].

It turned out to be impossible in our previous studies of $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ single crystal to establish a correlation between ferroelectric polarization and the crystal structure via macroscopic Sawyer—Tower measurements of the polarization properties [12]. This result can be explained the fact that the electric field required to polarize the crystal is fairly strong $(\sim 1\,\mathrm{MV/m})$; the contribution of leakage currents became significant, which made it impossible to examine polarization components in $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ single crystal. In this study, we used a method of local measurements for piezo- and ferroelectric properties, so called piezoresponse force microscopy (PFM) in order to overcome the drawbacks of macroscopic measurements. The PFM method is known as a highly efficient approach to the examination of piezo- and ferroelectric properties and local topography with a high spatial resolution in inorganic and organic materials [14]. The measured PFM signal features vertical (E_OOP) and lateral (E_IP) piezoresponse components, and each of them is characterized by amplitude and phase elements (Fig. 1). An Ntegra Prima (NT-MDT) scanning probe microscope

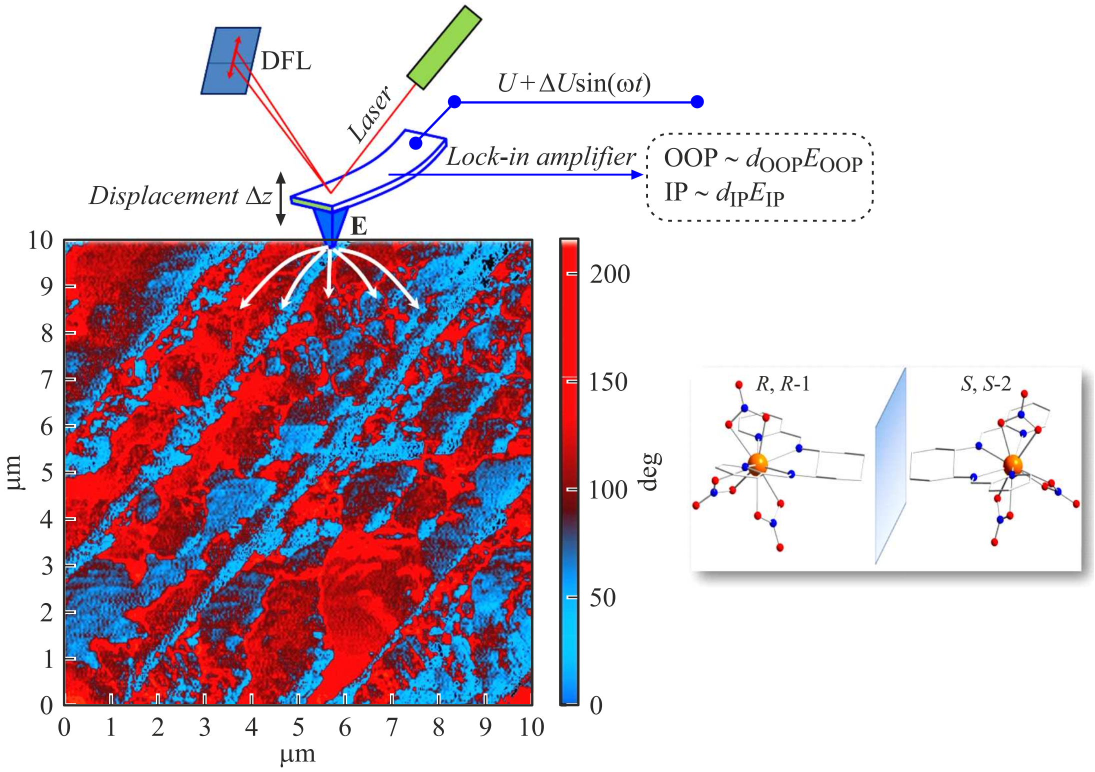

Figure 1. Scheme of the piezoresponse force microscopy experiment and image of the local topography scan superimposed onto phase element E_{OOP} for the $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ single crystal. Alternating independent complexes *R*, *R*-1/*S*, *S*-2 are shown in the inset. The scan parameters were as follows: contact-mode piezoresponse force microscopy (contact force: 2 DFL), the frequency of applied ac voltage was 50 kHz, and amplitude was 10 V.

operated in the contact PFM mode was used. The switching spectroscopy technique (SS-PFM) was applied in order to obtain local hysteresis loops [14]. ElectriMulti75-G (Budget Sensors) cantilevers with a Cr/Pt coating, a resonance frequency on the order of 70 kHz, and a force constant on the order of 3 N/m were used in PFM and SS-PFM measurements, which were performed at an alternating voltage frequency of 50 kHz and a voltage amplitude of 10 V under controlled conditions (25°C and a humidity of $\sim 40\%$). The calibration of PFM scans was carried out on a Si substrate in accordance with the procedure described in [14].

The results of PFM studies for the $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ single crystal are presented in Fig. 1. The image of the local topography scan superimposed onto phase element E_{OOP} reveals the presence of a domain structure (*R*, *R*-1/*S*, *S*-2 complexes) identical to the one examined in [10] for a $\mathrm{Zn}^{2+}/\mathrm{Yb}^{3+}$ single crystal.

The application of a „square-in-square“ PFM pattern [15], where squares differ in the sign and amplitude of the applied bias voltage (Fig. 2, *a*), is one of the methods for verifying the local switching of ferroelectric polarization in a sample. Figure 2 demonstrates the results of this procedure applied to the $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ sample. The signals of vertical (Fig. 2, *b*) and lateral (Fig. 2, *c*) PFM components demonstrate that the intrinsic domain structure of the sample may be altered by a applying a bias voltage of +15 V and then switched by a higher bias voltage of −20 V (repolarization). The obtained result shows that the $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ sample was grown in the polar phase and exhibits ferroelectric properties. Examining the force-distance curves in the initial and repolarized regions (see the inset in Fig. 2), one finds a substantial change in the force magnitude away from the contact (adhesion force) and in the area between the force curves of cantilever approach and retraction (work of adhesion, which is represented as a shaded area in the inset). The adhesion force variation is indicative of surface changes: the surface deforms due to the redistribution of ions in a strong electric field applied for an extended period of time (Vegard law), thus inducing a noncoherent component of a nonswitchable part of residual polarization (screening surface potential). The change in work of adhesion is also indicative of the presence of a surface electrostatic potential that causes the cantilever to stick to the sample surface. It was demonstrated in earlier studies with a $\mathrm{Zn}^{2+}/\mathrm{Dy}^{3+}$ sample [12] that the surface electrostatic potential produces a depolarizing field that screens the field applied in PFM measurements.

Local hysteresis loops were measured by SS-PFM in the initial (points *1* and *5* in Fig. 3, *a*), polarized (+15 V, points *2* and *4*), and repolarized (−20 V, point *3*) regions. It follows from the results of analysis of local hysteresis

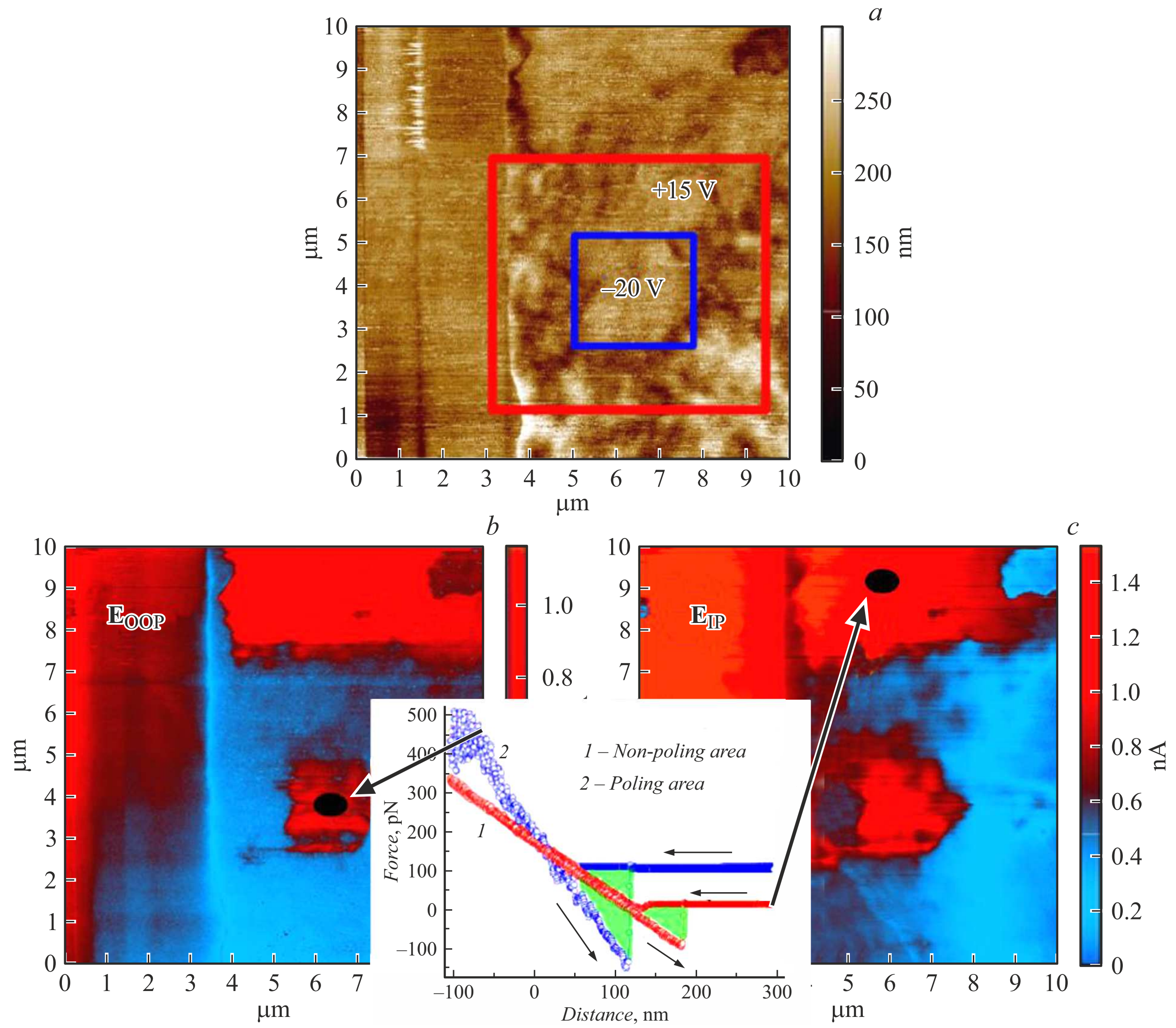

Figure 2. Results of application of a „square-in-square“ PFM pattern to the Zn^{2+}/Dy^{3+} sample: topography (*a*) and the corresponding elements of vertical (*b*) and lateral (*c*) PFM components. The results of force-distance curve spectroscopy obtained in the initial and repolarized regions are shown in the inset.

loops in Fig. 3, *b* (lower part) that the response in the same regions (points *1* and *5*, *2* and *4*) is characterized by loops of equal height. The differences in loop amplitudes measured in different regions are indicative of significant changes of the electromechanical properties in the initial, polarized, and repolarized sections. The repolarized region is the one that undergoes the greatest change. The saturation of a local hysteresis loop and the corresponding local effective piezoelectric coefficient ($\sim d_{33}$) were measured by SS-PFM in the initial (point *1* in Fig. 3, *a*) region of the sample (see the upper part of Fig. 3, *b*). The measurement results demonstrate that the local hysteresis loop area and the effective piezoelectric coefficient increase with increasing bias voltage. The maximum applied bias voltage was 50 V; the corresponding piezoelectric coefficient was $d_{33} \sim 14$ pm/V. It should be emphasized that the maximum applied electric field was around 2 GV/m, which is three orders of magnitude higher than the field strength in macroscopic measurements in [12]. Notably, the results of local piezoresponse measurements are not distorted by leakage currents, and hysteresis loops reveal switching of the domain structure, thus verifying the presence of ferroelectric properties achieved in the synthesis of a single-ion Zn^{2+}/Dy^{3+} chiral molecular complex.

The chosen approach to synthesis of integrated magnetoelectric molecular systems made it possible to grow a single-ion Zn/Dy molecular single crystal. Local piezoresponse force microscopy revealed switching of the intrinsic domain structure in the Zn/Dy sample at a bias voltage of +15 V and the possibility of changing the induced domain structure at a bias voltage of −20 V. Effective local piezoelectric

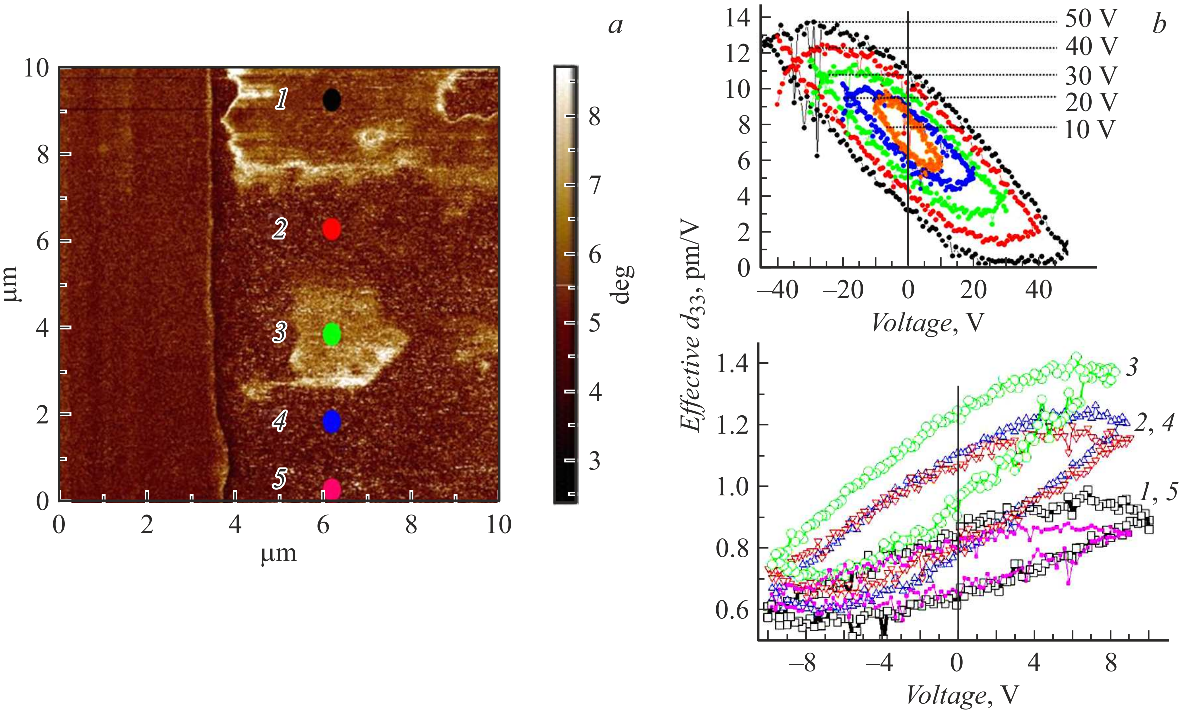

Figure 3. Image of the local topography scan superimposed onto phase element E_{OOP} (*a*) and positioning of the probe for measurement of local hysteresis loops (*b*). The results of measurement of local hysteresis loops under a varying bias voltage are presented in the upper part of panel *b*. The lower part of panel *b* shows the results of measurement of local hysteresis loops with the probe positioned in the initial (points *1* and *5*), polarized (+15 V) (points *2* and *4*), and repolarized (−20 V) (point *3*) regions. The scan parameters were as follows: contact-mode piezoresponse force microscopy (pressing force: 2 DFL), the frequency of applied ac voltage was 50 kHz, and amplitude was 10 V.

coefficient d_{33} was found to be as high as 14 pm/V at a bias voltage of 50 V.

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Conflict of interest

The authors declare that they have no conflict of interest.

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