Tunable electroresistance and electro-optic effects of transparent molecular ferroelectrics

Zhulei Zhang,1 Peng-Fei Li,2 Yuan-Yuan Tang,2 Andrew J. Wilson,3 Katherine Willets,3 Manfred Wuttig,4* Ren-Gen Xiong,2* Shenqiang Ren1*

Recent progress in molecular ferroelectrics (MOFEs) has been overshadowed by the lack of high-quality thin films for device integration. We report a water-based air-processable technique to prepare large-area MOFE thin films, controlled by supersaturation growth at the liquid-air interface under a temperature gradient and external water partial pressure. We used this technique to fabricate ImClO$_4$ thin films and found a large, tunable room temperature electroresistance: a 20-fold resistance variation upon polarization switching. The as-grown films are transparent and consist of a bamboo-like structure of (2,1,0) and (1,0,2) structural variants of R$_{3m}$ symmetry with a reversible polarization of 6.7 $\mu$C/cm$^2$. The resulting ferroelectric domain structure leads to a reversible electromechanical response of $d_{33} = 38.8$ pm/V. Polarization switching results in a change of the refractive index, $n$, of single domains, $\frac{dn}{dP} = 0.3$. The remarkable combination of these characteristics renders MOFEs a prime candidate material for new nanoelectronic devices. The information that we present in this work will open a new area of MOFE thin-film technologies.

INTRODUCTION

The first molecular ferroelectric (MOFE) crystal, Rochelle salt, was discovered in 1921 (1). The switchable polarization of MOFE crystals is useful in modern memory and capacitor elements (2–8), and their secondary characteristics, piezoelectricity, pyroelectricity, and electro-optic activity (9–11), have technological potential in actuators, sensors, and transducers (12–14). Whereas magnetoresistance is well known and serves as the basis of the reading mechanism of modern magnetic memories, electroresistance of MOFEs is much less known, let alone used in devices (3, 15–17). However, a way of determining their controlled deposition on arbitrary supports in the form of thin films should be found, considering that both large-area solution processability and crystal flexibility are rare themselves, lagging behind of their inorganic oxide counterparts (18).

The low symmetry of MOFEs poses difficulties because each film grain crystallite can be polarized in only one direction determined at the time of thin-film formation, which is either random or unfavorably distributed in most cases (19, 20). Hence, without appropriate control of the crystallite orientations, only a small portion of structural and electrical domains can be effectively switched. This inadequate orientation control of MOFEs has, so far, limited practical applications in molecular electronics, in drastic contrast to inorganic perovskites whose high-symmetry polarization can be electrically oriented by poling, which renders polycrystalline perovskite ceramics the most industrially valuable ferroelectric material (21, 22). Here, we present the first report on the preparation of high-quality large-area MOFE films using in-plane liquid-phase (IP-LP) growth (Fig. 1). This generally applicable approach allows precise control of film thickness, roughness, homogeneity, and crystal orientation by the solute concentration and growth environment, thereby enabling further studies to achieve orientation-controlled polarization and customizable ferroelectric properties for memory elements and sensors.

1Department of Mechanical Engineering and Temple Materials Institute, Temple University, Philadelphia, PA 19122, USA. 2Ordered Matter Science Research Center, Southeast University, Nanjing 211898, P. R. China. 3Department of Chemistry, Temple University, Philadelphia, PA 19122, USA. 4Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA. *Corresponding author. Email: wuttig@umd.edu (M.W.); xiongrg@seu.edu.cn (R.-G.X.); shenqiang.ren@temple.edu (S.R.)
The ferroelectricity of ImClO₄ thin films is demonstrated by the polarization–electric field hysteresis loop (Fig. 2A). It can be attributed to the small permanent dipole moment of the slightly distorted ClO₄⁻ anion together with the contribution from the off-center displacement of the Im⁺ cation (Fig. 57) (16) and switched at kilohertz frequencies. The measured spontaneous saturation polarization of ImClO₄ thin films is as high as 6.7 μC/cm², as compared to the values 1 μC/cm² for irregularly structured bulk material (27) and 23 μC/cm² for inorganic perovskite BaTiO₃ (28). The coercive field of 5 kV/cm equals 1/10 of that of perovskite oxide ferroelectrics (29), making it an ideal candidate for molecular electronics with low-energy consumption. Piezoresponse force microscopy (PFM) (Fig. 2, B to D) confirms the ferroelectric properties of the as-grown ImClO₄ thin films. The domain boundaries, the yellow/purple-colored region, represent 180° subboundaries. We monitored polarization switching of the MOFE ImClO₄ films through their electromechanical response using PFM at a fixed tip position on the film surface as a function of a cyclic writing voltage, revealing a clear hysteresis and butterfly behavior (Fig. 2E). The distinct 180° domain switching in precise 180° intervals further corroborates a robust ferroelectric polarization in ImClO₄ thin films. Notably, the phase of the PFM response signal corresponds directly to the direction of the electric polarization of the microscopic region of the surface monitored under the tip. Thus, the hysteretic switching of the response signal phase by 180° in response to a sweeping dc voltage is attributed to the electric switching of polarization according to the direction of the electric field (Fig. 2E, top). The hysteretic 180° phase switching observed in the PFM response represents evidence of local ferroelectricity of the ImClO₄ films. The amplitude signal obtained from the PFM image (Fig. 2E, bottom) is directly correlated to the local strain of the ImClO₄ film experienced by the cantilever. Together, the hysteretic amplitude and the butterfly loops confirm the piezoelectricity of ImClO₄ films.

Our observation allows us to determine the piezoelectric voltage and piezoelectric strain constants, \( g = \frac{d E_0}{r} \) and \( x = d E \), where \( d \) is the piezoelectric charge constant and \( E_0 \) and \( E \) are the vacuum dielectric constant and the relative dielectric constant, respectively (30–34). To demonstrate the electromechanical coupling of a piezoelectric ImClO₄ film, we sandwiched the film between two electrodes and applied a periodic mechanical stress using a dynamic mechanical test system. The generated electrical output signal was recorded by measuring the current and voltage outputs. Figure 2 (F and G) shows the piezoelectric current and voltage responses of the ImClO₄ thin films. The signals reverse polarity, corresponding to the alternating compression and tension along the [1,0,2] direction. Typical peak current and voltage values are 3.2 nA and 0.073 V, respectively. The time-integrated single current peak yields a charge, \( Q \approx 3.8 \times 10^2 \) pC, generated at an applied peak load of \( F = 9.8 \) N. We can thus estimate the global piezoelectric coefficient \( d_{33} = Q/F = 38.8 \) pm/V, which is similar to the local value measured by PFM in ImClO₄ thin films. The piezoelectric charge constant measured by the polarity switching from PFM measurement and force-induced current/voltage signal confirms that the electrical signals stem from the piezoelectric ImClO₄ thin films. Figure 2 (H and I) and figs. S8 to S11 further demonstrate that the piezoelectric signal is linear in a range of 0.73 to 3.2 nA or 0.013 to 0.068 V. The electromechanical energy conversion is reversible and repeatable in more than 1000 cycles (Fig. 2I, inset), as required for devices.
A unique feature of transparent MOFE ImClO$_4$ thin films is the large electro-optic activity (35, 36), which we characterized through polarization light spectroscopy. We use a broadband polarization rotator to control the polarization direction of a beam of 488-nm laser light incident on an ImClO$_4$ film and record the resultant luminescence images from the film (Fig. 3A). The polarization-dependent luminescence is depicted in Fig. 3B. As the angle of the polarizer rotates, the intensity increases to a maximum at 0°/180° and decreases to a minimum at 90°/270° when the electric field vector of incident light, $E \to$, is parallel or antiparallel to the vector of polarization, $P \to$. The linearly polarized light of wave vector $k$, interacting with the polarization $P_{210}$, can lead to a strong light-matter interaction because of the linear electro-optic effect of transparent ferroelectric ImClO$_4$ films. The electric field–dependent transmittance of the transparent ImClO$_4$ films can also be used to investigate domain inversion or polarization switching. We find that our ImClO$_4$ films show a strong and repeatable contrast change under cyclic poling (Fig. 3, C and D). Studies of the transmission spectrum of ImClO$_4$ films from 450 to 1000 nm revealed strong contrast changes in the poled areas. Figure 3D represents a comparison of transmission spectra between three different domain states during a poling cycle: original and negatively and positively poled states. Negative saturation poling decreases the transmission with a modulation of 3%, as obtained from the integral area of transmission spectrum (350 to 1100 nm). Positive saturation poling reverts to the unmodulated state. The transmittance of ImClO$_4$ films can thus be varied by the linear electro-optic, piezoelectric, and interference effects. In an electro-optic material, such as MOFE ImClO$_4$, the refractive index increases to $n + \Delta n$ under positive poling, whereas it decreases to $n - \Delta n$ under negative poling. The linear electro-optical effect induced the modulation of the refractive index, $\Delta n \propto \varepsilon \cdot E$, where $\varepsilon$ is the electro-optic tensor. The index difference, $\Delta n$, results from the phase retardation of the transmitted beam in the ImClO$_4$ films. A second phase retardation due to the piezoelectric effect is caused by the thickness variation, $\pm \Delta d$, in the reversed domain.
because of the linear electro-optic and piezoelectric effects, which, along the [2,1,0] axis, is given by
\[
\Delta \phi = 2 \left[ \frac{2 \pi}{\lambda} \Delta n d + \frac{2 \pi}{\lambda} (n_0 - n_{ew}) \Delta d \right] = \left[ -\varepsilon n_0^3 + 2(n_0 - n_{ew}) k_3 \right] V
\]
where \( V \) is the poling voltage, \( n_0 \) is the refractive index, \( \Delta n \) is the refractive index change, \( \lambda \) is the wavelength of light, and \( \Delta d \) is the piezoelectric thickness change dependent on the constant \( k_3 \) (the ratio between the linear piezoelectric and the stiffness tensor \( n_{ew} = 1.33 \)). The equation illustrates how the thin-film interference pattern of MOFE ImClO_4 is determined by the piezoelectric and electro-optic characteristics (38–40).

MOFE thin films that are electrically switchable at room temperature can facilitate organic memory elements (41–43). As shown in Fig. 4A, conducting AFM and related PFM images performed on ImClO_4 films reveal a distinct local resistance contrast between the upward and downward polarization domains. When an electric poling field (writing voltage) is applied on the ImClO_4 film, the polarization is directed parallel to the electric field direction, and the potential barrier encountered by the electrons is reduced, leading to an increased circuit current and a reduced electroresistance, termed ON state (Fig. 4B, left). When the electric field is switched, the dipole direction is reversed, and the increased average height of the potential barrier leads to a reduced current and an increased electroresistance, termed OFF state (Fig. 4B, right). Therefore, we applied a positive/reverse writing field larger than the coercivity to polarize the dipoles in the same direction. Simultaneously, we applied a reading field smaller than the coercivity to investigate the resistive switching of MOFE ImClO_4 thin films. Figure 4C shows the continuous, nonlinear, and symmetric current-voltage (I-V) curves for the ON and OFF states, with a small reading field corresponding to a voltage between −0.5 and 0.5 V. The pronounced 2400% difference of the I-V curves indicates the electroresistance of the ImClO_4 film. The current ratio of the ON and the OFF states (Fig. 4D) further confirms the polarization-modulated electroresistance of the ImClO_4 film, in which an average OFF/ON ratio of about 20 has been achieved. Figure 4E presents the retention performance of MOFE ImClO_4 thin films at \( V_{\text{read}} = 0.2 \) V for the ON and OFF states, which exhibit resistances of \( 1.5 \times 10^7 \) and \( 7.2 \times 10^6 \) ohms, respectively. There is no significant deterioration both in the ON and OFF states, indicating good information retention of ImClO_4 thin films. The inset of Fig. 4E shows near-identical I-V curves before and after a 5-hour retention time in both ON and OFF states, suggesting very small switching fatigue of the ImClO_4 films. The switching performance of ImClO_4 films is further tested by repeatedly switching the ferroelectric barrier with positive and reverse poling (writing). Again, polarization switching–induced electroresistance with good reproducibility is achieved and shown in
The ON/OFF resistance ratio of about 20 is maintained in more than 30 write/read cycles. Future nonvolatile resistive memory elements based on molecular ImClO4 films with high electroresistance and fatigue resistance comparable to ferroelectric polymers thus appear possible.

DISCUSSION

In summary, we show in this study that films of the MOFE ImClO4 have all the characteristics desirable in a candidate material for nanoelectronic devices. Films of ImClO4, fabricated using a novel technique—controlled supersaturation growth at the liquid-air interface under temperature gradient and external water partial pressure—are transparent and consist of a bamboo-like structure of (2,1,0) and (1,0,2) variants of R3m symmetry. The ImClO4 thin films show the Curie temperature of 373.6 K and a room temperature reversibly switchable polarization of 6.7 μC/cm², as well as a reversible electromechanical response, d33 = 38.8 pm/V. Polarization switching results in a 30% change of the refractive index of single domains. Foremost, the electroresistance of the films changes reversibly by a factor of 20 upon polarization switching without fatigue. The ImClO4 MOFE thin film that we describe here thus represents an attractive multifunctional material that will germinate a new generation of molecular electronic sensing, actuation, data, and energy storage devices.

MATERIALS AND METHODS

Synthesis of ImClO4 molecular film by an IP-LP growth with controlled water evaporation rate

A near-supersaturated ImClO4 solution (~700 mg/ml at 363 K) on an ITO-patterned glass substrate was used to synthesize the ImClO4 thin films. We started the synthesis by transferring supersaturated ImClO4...
solution onto the substrate preheated at 363 K. The higher super- 
saturation at the surface leads to surface nucleation of the ImClO$_4$ film. Because of the high surface tension and high spreading ability, the film 
nucleus floats on the solution surface, stabilized by the hydrogen 
bonding between water and imidazolium molecules. The evaporation-
induced lower temperature of the surface creates a thermal gradient be-
tween the surface and the bottom of the solution, resulting in Marangoni 
flow of [Im$^+$] and [ClO$_4^-$] from the bottom to the surface, leading to IP-LP 
epitaxy of the film on the surface of the solution.

An external water vapor flow with a different water partial pressure, 
controlled by nitrogen gas from a second heated water container, kept at 
a different temperature was used to set an artificial nonequilibrium partial 
pressure of water above the solution, thereby controlling the growth 
rate and uniformity of the ImClO$_4$ crystallized film. The partial pres-
sure of water, ranging from 10.2% at 328 K to 58.1% at 363 K, was 
maintained with a pressure sensor. This arrangement maintained a 
steady-state film growth of controllable thickness and quality. In general, 
higher growth rates promoted thicker films, whereas lower growth rate 
induced a lower surface roughness. After removing the bottom solution 
by super absorptive materials, the smooth film can be readily transferred 
to a device, which was further vacuum-treated for more than 2 hours 
before subsequent use. For this study, we adopted large-area continuous 
films synthesized by rapid growth.

**Morphology and structure characteristics**

Real-time measurements of optical images were recorded by an Olympus 
BX51 microscope and were computer-processed. Scanning electron 
microscopy images were taken via FEI Quanta 450 FEG. X-ray diffraction 
analysis was carried out using a Rigaku charge-coupled device diffractometer 
with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection, 
cell refinement, and data reduction were performed using Rigaku 
CrystalClear software. The crystal structures were refined by the full-
matrix method using the SHELXL97 software package.

**Characteristics of ferroelectric properties**

Room temperature polarization hysteresis loops were obtained by 
Radiant Precision Premier LC II, in air at measurement frequencies 
of 5, 10, and 20 kHz. PFM was conducted using Asylum Research 
Radiant Precision Premier LC II, in air at measurement frequencies 
Characteristics of ferroelectric properties 
matrix method using the SHELXL97 software package.

**Fabrication of resistance switching devices**

We prepared ITO/ImClO$_4$/100-nm Ag sandwiches to determine the resistance of the ImClO$_4$ films. The ~400-nm ImClO$_4$ film was 
transferred onto the ITO-prepatterned glass substrate and annealed 
in a vacuum oven for 2 hours, and then a 100-nm Ag film was deposited 
on to the molecular film through a shadow mask to serve as the top 
electrode. The dimension of the electrically active area was 0.1 cm $\times$ 
0.1 cm. All sandwiches were characterized in a darkened glove box. 
An external voltage of 2 V from an Agilent 8114A 001 pulse generator, 
producing a field of 50 KV/cm, was applied to the electrodes to deter-
mine resistance switching characteristics using a Keithley 4200A-SCS 
multimeter.

**Fabrication of piezoelectric and pyroelectric devices**

After the ImClO$_4$ film was transferred onto the ITO-patterned glass 
substrate and dried in vacuum, a 100-nm silver film was deposited on 
top of the film through a shadow mask to serve as the top electrode. 
After soldering signal wires to the silver electrodes, the assembly was 
sealed in a 4-mm-thick polydimethylsiloxane (PDMS) matrix to assure 
structural stability for the piezoelectric tests. All devices used in this 
study were poled by an applied voltage of 5 V. The piezoelectric device 
was driven by a dynamic mechanical test system (ElectroForce 3200, 
Bose). A Keithley 4200A-SCS instrument recorded the current and 
open circuit voltage characteristics as a function of the varying stress. 
The impedance used to measure voltage is 1 megohm. A thermoelectric 
element was used to change the temperature of the device, monitored 
by a sensor on top of the device. The voltage and current outputs were 
recorded as for the piezoelectric measurements. All devices were char-
acterized in a glove box.

**Optical measurement**

For the angle-dependent fluorescence measurement, a thin film was 
mounted on an Olympus IX73 inverted microscope. Fluorescence 
was excited with a 488-nm laser and collected with a Princeton 
Instruments ACTON SpectraPro 2500i/Spec-10 spectrometer using a 
20× objective. A linear polarizer in the detection path served to select 
defined polarization vectors. Pulses of ±2 V were applied to the device 
from an Agilent 8114A 001 pulse generator to switch the polarization. 
The optical contrast images before and after poling of molecular films 
were captured by an Olympus BX51 microscope. The transmission 
spectra of different polarization states were determined by a spectrom-
eter that detected the variations of the collimated light over the entire 
electrode.

Note that the Im molecule and the perchlorate ion may both cause 
irritation to eyes and skin. Therefore, it is better to wear fitting goggles, 
protective gloves, and clothes when performing the experiments.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ 
content/full/3/8/e1701008/DC1

fig. S1. Optical images of ImClO$_4$ molecular crystals synthesized by spin coating an ImClO$_4$ 
solution (700 mg/ml) on an ITO-prepatterned glass substrate at 3000 rpm, at different 
magnifications.

fig. S2. Optical images of ImClO$_4$ molecular crystals synthesized by drop-casting ImClO$_4$ 
solution on ITO glass substrate at a concentration of 700 mg/ml at different magnifications.

fig. S3. Optical images of ImClO$_4$ molecular films synthesized by IP-LP growth on ITO glass 
substrate at a concentration of 700 mg/ml at different magnifications.

fig. S4. Optical images of ImClO$_4$ molecular films synthesized by IP-LP growth on ITO glass 
substrate at a water partial pressure of 35.5%.

fig. S5. Optical images of ImClO$_4$ molecular films synthesized by IP-LP growth on ITO glass 
substrate at a water partial pressure of 45.1%.

fig. S6. Morphology and elements distribution analysis of ImClO$_4$ molecular films at a water 
partial pressure of 35.5%.

fig. S7. Morphology and elements distribution analysis of ImClO$_4$ molecular films at a water 
partial pressure of 45.1%.

fig. S8. Piezoelectric voltage response of the Ag/ImClO$_4$/Ag sandwiches to external stresses 
from 2.4, 4.1, and 6.7 to 9.8 N, which generate the proportional voltages shown in the right-
hand side.

fig. S9. Evolution of the piezoelectric current outputs at different applied stresses from 2.4, 4.1, 
and 6.7 to 9.8 N on the ImClO$_4$ film.

fig. S10. Evolution of the piezoelectric voltage outputs with decreasing magnitude of the 
applied stress on the ImClO$_4$ film from 2.4, 4.1, and 6.7 to 9.8 N, which generate the proportional voltages shown in the right-
hand side.

fig. S11. Piezoelectric voltage as a function of the frequency resulting from applied forces,

**REFERENCES AND NOTES**

J. Li, R.-G. Xiong, Disopropylammonium bromide is a high-temperature molecular 


42. J. F. Scott, Ferroelectric Memories (Springer Science and Business Media, 2013), vol. 3.
Tunable electroresistance and electro-optic effects of transparent molecular ferroelectrics

Zhuolei Zhang, Peng-Fei Li, Yuan-Yuan Tang, Andrew J. Wilson, Katherine Willets, Manfred Wuttig, Ren-Gen Xiong and Shenqiang Ren

Sci Adv 3 (8), e1701008.
DOI: 10.1126/sciadv.1701008