Supplementary Materials for

Exploring far-from-equilibrium ultrafast polarization control in ferroelectric oxides with excited-state neural network quantum molecular dynamics

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I. Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) Simulation

To study the thermalization of electronic occupation numbers upon excitation by a laser pulse, we performed RT-TDDFT simulations(27), which has recently been incorporated into our quantum molecular dynamics (QMD) software, QXMD(53, 54). RT-TDDFT simulation follows the time evolution of Kohn-Sham (KS) wave functions \( \{ \psi_{s\sigma}(r, t) \} \) at spatial position \( r \) and time \( t \):

\[
i \hbar \frac{\partial}{\partial t} \psi_{s\sigma}(r, t) = \left[ \frac{1}{2m} \left( \frac{\hbar}{\imath} \frac{\partial}{\partial r} + \frac{e}{c} A(t) \right)^2 + v_{\text{ion}}(r) + v_{\text{Hxc}}[r, t; \rho(r, t)] \right] \psi_{s\sigma}(r, t), \tag{S1}
\]

where \( \hbar \) is the Planck constant, \( c \) is the light speed, \( m \) and \( e \) are electron mass and charge, \( s \) and \( \sigma \) are KS-orbital and spin indices, \( A \) is the vector potential, \( v_{\text{ion}} \) is the ionic pseudopotential, and \( v_{\text{Hxc}} \) is the Hartree and exchange-correlation potential which is a functional of the electron density,

\[
\rho(r, t) = \sum_s f_{s\sigma} |\psi_{s\sigma}(r, t)|^2. \tag{S2}
\]

In Eq. (S2), \( f_{s\sigma} \) are the initial occupation numbers of the KS orbitals, which we assume to be the ground-state occupation. The vector potential in Eq. (S1) is a sum of external and induced terms,

\[
A(t) = A_{\text{ext}}(t) + A_{\text{ind}}(t). \tag{S3}
\]

Since experimental laser-spot sizes are typically on the order of micrometer or larger, we here consider an external laser pulse to be spatially uniform, with the form of

\[
A_{\text{ext}}(t) = -\frac{e}{\omega_{\text{ext}}} E_{\text{ext}} \sin(\omega_{\text{ext}} t) \sin^2 \left( \frac{\pi t}{\tau_{\text{ext}}} \right) \quad (0 < t < \tau_{\text{ext}}), \tag{S4}
\]

where \( \omega_{\text{ext}} \) and \( \tau_{\text{ext}} \) are the angular frequency and duration of the pulse, and \( E_{\text{ext}} \) is the peak electric field. The induced vector potential, \( A_{\text{ind}}(t) \), satisfies the equation

\[
\frac{1}{c^2} \frac{\partial^2}{\partial t^2} A_{\text{ind}}(t) = \frac{4\pi}{c} j(t), \tag{S5}
\]

where the spatially-averaged electric current is computed by an integration
\[
\mathbf{j}(t) = -\frac{e}{m}\int_{\Omega} d\mathbf{r} \left\{ \sum_{s\sigma} f_{s\sigma} \text{Re} \left[ \psi_{s\sigma}^* \left( \mathbf{r}, t \right) \frac{\hbar}{i} \nabla \psi_{s\sigma} \left( \mathbf{r}, t \right) \right] + \frac{e}{c} \mathbf{A}(t) \right\}
\]  
(S6)

over the entire simulated volume $\Omega$.

In RT-TDDFT simulation, time-dependent KS equations, Eq. (S1), for electrons are solved concurrently with Eq. (S5) for electromagnetic field. We considered an external laser pulse with a wave number of 200 nm to excite electrons above the band gap of 3.88 eV in PbTiO$_3$ (PTO)(25). It is worth noting that recent experimental studies have shown 400 nm laser pulses to be sufficient to create electron-hole pairs in PTO-based heterostructures(5, 25), but it is likely due to the band alignment at hetero-interfaces(67, 68).

Fig. S1A and S1B show time evolutions of the external vector potential for a 200 nm laser pulse and energy absorbed by the electronic system, respectively, for the case of $E_{\text{ext}} = 0.2$ a.u. and $\tau_{\text{ext}} = 6$ fs.

![Fig. S1. Vector potential and absorbed energy.](image)

Time evolutions of the external vector potential due to a 200 nm laser pulse (A) and energy absorbed by the electronic system (B).

The absorbed energy in Fig. S1B generates non-equilibrium electron occupation numbers, which are subsequently thermalized toward the equilibrium Fermi-Dirac distribution due to electron-electron interaction. Fig. S2 shows the occupation number of each KS orbital for both spins,
\[ f_s(t) = \sum_{s\sigma} |\int d\mathbf{r} \psi_{s\sigma}^*(\mathbf{r}, 0) \psi_{s\sigma}^p(\mathbf{r}, t)|^2 f_{s\sigma}, \]  

(S7)

as a function of the KS energy at times \( t = 0.7 \) fs and 2.4 fs. At \( t = 0.7 \) fs, we see a sharp peak (shaded red) corresponding to photo-excited electrons, along with a dip (blue shade) corresponding to holes, which are superimposed on top of a step-function-like Fermi-Dirac distribution. At \( t = 2.4 \) fs, these sharp features are absorbed into broadened Fermi-Dirac distribution. These results signify rapid thermalization of electronic occupation numbers toward thermalized Fermi-Dirac distribution within femtoseconds, thus justifying the use of Fermi-occupation quantum molecular dynamics (FOQMD) simulations in the main text.

**Fig. S2. Electronic thermalization.** Occupation numbers of KS orbitals as a function of KS energies at time \( t = 0.7 \) fs (A) and 2.4 fs (B).

The number of excited electrons from the valence band to the conduction band can be estimated by summing \( f_s(t) \) over initially unoccupied orbitals \( s \). We have simulated 200 nm laser pulses with duration 2 fs for various values of electric field. Fig. S3 shows the fraction of valence electrons that are excited to the conduction band as a function of the corresponding laser fluence. With a fluence of 0.15 J/cm\(^2\), 5% of the valence electrons were promoted to the conduction band,
which corresponds to the FOQMD simulations in the main text. We should note that this estimate is for a perfect PTO crystal without defect or trap states. In actual experiments, much lower fluence would be required to achieve the same excitation level due to these factors.

Fig. S3. Excitation as a function of fluence. Fraction of valence electrons that are excited as a function of laser fluence.

II. Non-Adiabatic Quantum Molecular Dynamics (NAQMD) Simulation Based on Surface Hopping

We also quantified the effects of non-adiabatic coupling between electrons and phonons using NAQMD simulation(28, 55) based on surface-hopping(69, 70). Details of the NAQMD algorithm are provided in Ref. 54. Fig. S4 shows time evolutions of polarization, fractional excited electron participation (fep), and fractional hole participation (fhp) on given unit-cell within a 4×4×4 PTO supercell with 5 carriers excited (neh = 0.48%). The fep and fhp are computed as the contribution of the atoms in a given unit cell to the excited state electron and hole wave-function respectively using Mulliken analysis(71). Scattering of carriers with phonons will drive the localization of the excited electron and hole pairs from different lattice sites. When the electrons and holes are more concentrated on the given lattice site, the unit-cell polarization will trend towards to zero, but when the carriers scatter and de-localize from the unit-cell the polarization will rebound, resulting in large fluctuating unit-cell dipoles. Electron-electron scattering modeled by RT-TDDFT at high laser fluences suggests a more uniform scattering of carriers than that
described by surface hopping. This results in more uniform charge transfer from O to Ti that can be well approximated with FOQMO. As the number of excited carriers is increased in the surface-hopping based approach, more lattice sites will be occupied with excited carriers and the results will better match those of FOQMD as more lattice sites will become occupied with excited state carriers. To better model both electronic and phonon scattering at the experimental pump-probe time scales, a unified approach combining Ehrenfest dynamics based on RT-TDDFT and surface-hopping dynamics may shed light in this area, which will be focus of future works (72).

Fig. S4. NAQMD simulation of PTO. (A) PTO unit cell with O types labeled. Spheres with black, silver and red colors represent Pb, Ti and O atoms, respectively. (B) Polarization dynamics for given unit cell. (C) Excited electron participation dynamics on Ti atom in given unit cell. (D) Hole participation dynamics on O atoms in given unit-cell with coloring given by O atom type as labeled in (a). The O1(green) and O2(magenta) curves are overlapping.

III. Mulliken Charge and Bond-Overlap Population Analysis
We also examined the effects of far-from-equilibrium optical excitation on charge and bond dynamics in the crystal using Mulliken analysis (71). Fig. S5 shows time evolution of the oxygen charges divided into oxygen atoms located perpendicular to the polarization axis $O_\perp$ and those parallel to polarization axis $O_\parallel$ relative to Ti atom, with the shading representing the standard deviation. Fig. S5A for the ground state shows the existence of two distinct oxygen charges depending on the oxygen position with respect to the polarization axis. In the excited state within the iso-thermal iso-baric (NPT) ensemble, the charge is initially uniformly more positive across all oxygen atoms as charge is transferred from O to Ti upon optical excitation as shown in Fig. S5B. As the structure transforms to a cubic non-polar phase the two types of oxygen atoms become identically charged. If the lattice is not allowed to relax and dynamics are performed in the iso-thermal iso-volume (NVT) ensemble, the O charge still becomes more positive, but the two types of O atoms still remain distinctively charged. The charge dynamics are more frustrated with a large standard deviation as the lattice is being optically strained.

**Fig. S5. Oxygen charge dynamics.** (A) O charge dynamics in the ground state within NVT ensemble. (B) and (C) O charge dynamics in the excited state within NPT and NVT ensembles, respectively. Shading represents standard deviation.
We also performed Mulliken bond-overlap population analysis to understand the bond dynamics under optical excitation (Fig. S6). Figs. S6A and S6B illustrate how optical excitation weakens both Pb-O and Ti-O bonds. However, the relative Pb-O overlap in comparison to the Ti-O overlap increases, indicating an increase in relative strength of the Pb-O interaction. This is consistent with the notion that tilting in ABO$_3$ perovskites is often thought to result from a necessity of stabilizing short A-O interactions.

**IV. Ground State Versus Excited State Polar Displacement Dynamics at 300K**

Fig. S7 shows the difference between the ground-state and excited-state Ti polar displacements $\langle D_z \rangle$. $\langle D_z \rangle$ was computed as the average difference of the Ti atoms from the centroid of the TiO$_6$ octahedra. In a centrosymmetric non-polar structure, Ti atoms will be located at the center of TiO$_6$ octahedra, while in the polar structure they are displaced. Fig. S7A illustrates that the PTO crystal remains polar at room temperature as expected. Fig. S7B illustrates the loss of polarization under illumination.
V. Lattice Dynamics Under Excitation

We also examined the dynamics of the lattice constants under excitation in the NPT-MD simulation. Fig. S8A illustrates the dynamics of the ratios between the different axes. At the end of the simulation the ratio between all three lattice constants oscillate around 1.0 illustrating a phase change to cubic structure. Fig. S8B illustrates the contraction of the lattice under excitation. This consistent with the observed activation of the A1 TO1 and E TO2 modes which have been previously been associated with the negative thermal expansion of PTO(39).

Fig. S8. Lattice evolution under excitation in NPT ensemble. (A) Evolution of the lattice constant ratios. (B) Evolution of the average unit-cell volume for the 4x4x4 supercell. Contraction of the lattice is consistent with the observed activation of the A1 TO1 and E TO2 modes.
VI. Photoinduced Octahedral Tilts:

Tilting in perovskites is often characterized using the glazer notation \((73)\), where tilting is described with \(a^l b^m c^n\), where \(a, b, c\) refer to their respective crystallographic axes and \(l, m, n = 0, +, -\) for no tilt, in-phased tilt, and out-of-phase tilt. Upon photoexcitation, phonon eigenvector analysis reveals \(a' a^0 c^0\) and \(a^+ a^0 c^0\) tilting instabilities from \(\text{M+R}\) phonon motions, with videos of the motions provided in supplementary videos S1 and S2. Collective excitations of the A and E TO phonon modes then drive the PTO structure to a cubic non-polar structure, which resulted in in-phase tilting about the original \(c\) axis\((a^0 a^0 c^\pm)\). This resulted in cubic structure with two planes with in-phase tilting and one plane with out-of-phase tilting. For the large-scale excited-state neural network quantum molecular dynamics (XS-NNQMD) simulation, we focused on the tilting about the \(c\) axis as this was where the frustration is seen. As the modification of the potential-energy surface by photoexcitation is uniform, all tilts about the \(c\) axis acquire the same in-phase symmetry; however, their parity with respect to the original un-titled lattice can be different, which creates a double-well potential as illustrated in Fig. S9A. Even though these parities belong to the same symmetry group, different parity domains can become frustrated if they meet at a boundary that is not commensurate to the periodicity of tilt and form a tilt domain wall as illustrated in Fig. S9B.

![Fig S9. Photo-induced octahedral tilting.](image_url)
VII. Neural Network Quantum Molecular Dynamics (NNQMD) Training and Validation

NNQMD(74) consists of a multi-layered perceptron (MLP) with two hidden layers and twenty nodes in each layer with modified hyperbolic tangent as the activation function. We employ the energy model with the symmetric functions proposed by Behler and Parrinello(65, 66).

\[
G_l^{\text{rad}} = \sum_j e^{-\eta(R_{ij}-R_S)^2} \cdot f_c(R_{ij})
\]

(S8)

\[
G_l^{\text{ang}} = 2^{1-\xi} \sum_{j,k \neq i} (1 + \lambda \cos \vartheta_{ijk})^\xi e^{-\eta(R_{ij}^2+R_{jk}^2-R_{ik}^2)} \cdot f_c(R_{ij}) \cdot f_c(R_{jk}) \cdot f_c(R_{ik})
\]

(S9)

\[
f_c(R_{ij}) = 0.5 \ast \cos \left( \frac{\pi R_{ij}}{R_c} \right) \text{ if } R_{ij} \leq R_c, \text{ else } 0
\]

(S10)

Equations (S8) and (S9) are the radial and angular symmetric functions of \( i \)-th atom as a function of \( R_{ij} \), the interatomic distance between \( i \)-th and \( j \)-th atoms. Hyperparameters \( \eta, R_S, \xi, \) and \( \lambda \) are used to capture the atomic local environment. The cutoff function \( f_c(R_{ij}) \) in (S10) smoothly truncates the symmetric functions at the cutoff distance \( R_c \). We found that \( G^{\text{rad}} \) with \( \eta = \{0.5, 1.0, 3.0\} \) and \( R_s = \{1.0, 2.0, 3.0, 4.0\} \) (Å) provides sufficient accuracy and computational efficiency for Pb, Ti and O atoms.

The loss function includes mean square error (MSE) of the system energy as well as the atomic forces to improves the model fidelity and robustness.

\[
L = \frac{p_E}{2} \frac{1}{N_t} \sum_{l=1}^{N_t} \left( E_{l}^{\text{MD}} - E_{l}^{\text{NN}} \right)^2 + \frac{p_F}{2} \frac{1}{N_t} \sum_{l=1}^{N_t} \frac{1}{3N_{\text{atom}}} \sum_{i=1}^{N_{\text{atom}}} \left( F_{l,i}^{\text{MD}} - F_{l,i}^{\text{NN}} \right)^2
\]

(S11)

The loss function \( L \) consists of the root mean square errors (RMSE) of system energy \( E \) and atomic forces \( F_i \) between NNQMD prediction and ground truth QMD trajectory(75). Here, \( N_t \) is \( I \)-th frame of training dataset, \( N_{\text{atoms}} \) is the number of atoms in the frame. The atomic force is obtained by the derivative of the system energy with respect to their coordinates. The adjustable parameter \( p_E \) and \( p_F \) work may be used to guide the model training process. We use equal weight for the energy and force loss functions and the Limited memory Broyden–Fletcher–Goldfarb–Shanno for Bound constrained optimization (L-BFGS-B) method to minimize the loss function.

Training Data Generation

We performed QMD simulations of PTO crystal to generate training set for the ground- and excited-state NNQMD. The training dataset consists of \( 3 \times 3 \times 3 \) and \( 4 \times 4 \times 4 \) unit cells and each system is thermalized at 300 K using NVT ensemble. A plane-wave basis was used with a cutoff energy of 410 eV for the wave functions and 3,400 eV cutoff for the charge density. Vanderbilt style ultra-soft pseudopotentials (USPPs) were used, and local density approximation (LDA) was used for the exchange-correlation. Only the gamma-point was sampled from the Brillouin zone.
Atomic trajectories were obtained using the velocity-Verlet algorithm at time step of 10 a.u. (1.209 fs). In total, 500 frames of QMD trajectory were used. 95% of the total frames were used as training set and 5% frames were so for test. QMD simulations were carried out using the highly parallelized plane-wave based QXMD software (56).

**Training and Validation of Ground-State NNQMD Model**

Fig. S10 shows the training and test performance for the ground state NNQMD model. Table S1 summarizes RMSE and correlation coefficient between model prediction and ground truth the after 500 epochs.

![Fig. S10. Ground state NNQMD training.](image)

**Table S1. Ground-state NNQMD Model Training Performance and Correlation Coefficient.**

|                  | RMSE          | Correlation Coefficient |
|------------------|---------------|-------------------------|
|                  | Energy (meV)  | Force (eV/Å)            | Energy (%)      | Force (%)     |
| Train            | 9.399         | 0.1501                  | 99.87           | 99.07         |
| Test             | 10.08         | 0.1544                  | 99.87           | 98.97         |

We validate the NNQMD model prediction using pair distribution function $g(r)$ and bond angle distribution. Fig. S11 presents $g(r)$ obtained by the ground-state QMD and NNQMD simulations. The off-center Ti position in the O octahedron appears as tiny splits in $g(r)$ that are captured by NNQMD. Fig. S12 shows the bond angle distributions between QMD and NNQMD. Again, the peak position, height, and width agree well between QMD and NNQMD results. Note that NNQMD also reproduces the peaks at 102.4°, 87.3°, and 77.6° in the O-Ti-O angle indicate the offset Ti atoms arising from the asymmetry of the PTO unit cell in the $c$-axis. Overall, the fine structures of PTO tetragonal crystal including their peak position, height, and width are well reproduced by NNQMD model.
**Fig. S11 Comparison of NNQMD and QMD radial distribution functions.** Radial distribution functions $g(r)$ of ground-state QMD (black) and its NNQMD model (red). Both systems are thermalized at 300 K with NVT ensemble. Overall, QMD and NNQMD show excellent agreements in their peak position, height and width of $g(r)$. Fine structures in the Pb-Ti, Ti-Ti, and Ti-O $g(r)$ signify the off-center position of Ti atom in the tetragonal unit cell.

**Fig. S12 Comparison of NNQMD and QMD bond angle distributions.** Bond angle distribution functions of ground state QMD (black) and its NNQMD model (red). O-Pb-O, O-Ti-O and O-O-O angles distribution are shown with bond cutoff distance of 3 Å.

**Training and Validation of Excited-state NNQMD Model**

Fig. S13 shows the training and test performance for the excited-state NNQMD model, and Table S2 summarizes RMSE and correlation coefficient between model prediction and the ground truth after 500 epochs. Here, the same set of feature vector and hyperparameters are used in the ground-state model. We have obtained well-converged RMSE and high correlations for the system energy and atomic forces for the excited state NNQMD model.
Fig. S13 Excited State NNQMD training. Training (black) and test (red) performance for the excited-state NNQMD model. (a) RMSEs of the system energy (A) and aggregated atomic force (B).

Table S2. Excited state NNQMD Model Training Performance and Correlation Coefficient.

|                | RMSE       |                         |                   |                   |                   |
|----------------|------------|-------------------------|-------------------|-------------------|-------------------|
|                | Energy (meV) | Force (eV/Å)        | Energy (%)        | Force (%)         |                   |
| Train          | 4.203      |                         | 97.46             |                   |                   |
| Test           | 3.591      |                         | 97.01             |                   |                   |

Fig. S14 Comparison of excited state NNQMD and QMD radial distribution functions. Radial distribution functions \(g(r)\) of excited-state QMD (black) and its NNQMD model (red) up to 6 (Å) cutoff distance. The systems are thermalized at 300 K using NVT ensemble. Overall, QMD and NNQMD show excellent agreements in their peak position, height and width of \(g(r)\). Due to the photo-induced structural change, the fine structures originated from the tetragonality of PTO crystal disappeared.
Fig. S15. Comparison of Excited State NNQMD and QMD bond angle distributions. Bond angle distribution functions of ground state QMD (black) and its NNQMD model (red). O-Pb-O, O-Ti-O and O-O-O angles distribution are shown with bond cutoff distance of 3Å.

The excited-state NNQMD model is validated by comparing the pair distribution function $g(r)$ and bond angle distribution against ground truth QMD result. We obtain excellent agreement in $g(r)$ and bond angle between QMD and NNQMD (Figs. S14 and S15). Due to the photo-induced FE reduction in PTO crystal, the signatures of the off-center Ti atom position disappear in both $g(r)$ and bond angle distributions. Emergent structural features due to the octahedral rotation, such as the split in the O-O-O peak around 120 degree, are successfully reproduced by NNQMD model.

VIII. Polar Vortex Simulation using NNQMD

Fig. S16. Emergent polar vortex in NNQMD Simulation. (A) PTO crystal with circular anti-polar domain. Dotted-line indicate the anti-polar domain boundary. (B-D) Emergent polar vortex pattern in PTO system with the radius of 8, 12, and 16 Å respectively.

With the ground state NNQMD model, we have studied the formation of polar vortex pattern in the PTO crystal. Fig. S16 presents the induced polarization pattern around the peripheral of a circular domain with opposite polarization in the $c$-axis. The observed polar vortex is akin to
Bloch-type skyrmion\(^7\) and is consistent with phase-field model simulation\(^{76}\). The system contains PTO unit cell replicated 12\(\times\)12\(\times\)2 times with periodic boundary condition in the three directions. Total number of atoms are 288 Pb, 288 Ti and 864 O respectively. The anti-polarization within the circular domain is introduced by displacing Ti atoms by 0.6 (Å) along the c-axis, then subsequently thermalized at 10K using NVT ensemble. We have examined three different radii \(r = 8, 12, \) and 16 Å. After the relaxation phase, stable polar vortex was formed except for the smallest radius of 8 Å.

IX. FOQMD Simulation of Light-induced Lattice Frustration

To examine the effects of tilting frustration on the polarization dynamics we preformed FOQMD simulations at low temperature (10 K) on a 3\(\times\)3\(\times\)3 PTO supercell. As an even number of unit cells are required to completely accommodate the Ti-O\(_6\) rotation, the 3\(\times\)3\(\times\)3 supercell system is expected to respond differently to the light-induced oxygen rotation, as the rotations are artificially frustrated by the non-commensurate supercell. Fig. S16A shows the low temperature polarization dynamics for the frustrated 3\(\times\)3\(\times\)3 PTO crystal, while Fig. S16B shows the dynamics for a 4\(\times\)4\(\times\)4 supercell. At low temperature in the 3\(\times\)3\(\times\)3 supercell, the polarization is preserved in the crystal as result of the rotations being frustrated. Time evolution of the lattice constants for the low temperature systems are also plotted in Figs. S17A and S17B for 3\(\times\)3\(\times\)3 and 4\(\times\)4\(\times\)4 supercells, respectively. In the frustrated system with 3\(\times\)3\(\times\)3 supercell, the lattice remains tetragonal and polar. In the non-frustrated system on the other hand, the lattice transformed to cubic structure and the polarization becomes negligible after 600 ps.
X. Size Dependence of Domain Boundary Dynamics

To investigate size dependence of the dynamics of photo-induced polar stripes and TiO$_6$ tilt domains, we have performed a series of XS-NNQMD simulations using three different system sizes that consist of single PTO crystal and are thermalized at 150K. The system dimensions and the total number of atoms are summarized in Table S3. Fig. S18A shows the nucleation of photo-induced polar domains after 2.5 ps of XS-NNQMD simulation in system 1. Atoms are color-coded by their order parameter based on the TiO$_6$ tilt angle. At 7.5 ps, the domains that have the same order parameter coalesce and grow into larger domains, at the same time, domains with different order parameters are well separated by the polar stripes; see Fig. S18b. Similarly, Fig. S18C and Fig. S18D shows the domain nucleation and growth for the larger system 2 at 2.5 ps and 7.5 ps. By increasing the system size, we observe increasing heterogeneity in the domain nucleation and increase in domain size. For the largest system 3, we see a saturation in the domain size resulting in a large number nano-domains emerging on the multi-micrometer scale as illustrated in Fig. S18, E and Fig. S18F, which again shows the domain structures at 2.5 ps and 7.5 ps, respectively. A zoom in on domain structures for system 3 illustrated in Fig. S18G shows the substructures of
polar stripes can extend over 100 nm spatial extent. This spatial extent was quantified through computation of the structure factor for the non-rotated polarized unit-cells:

\[ S(Q) = 1 + \rho_{\text{defect}} \int d^3 r \, e^{iQ \cdot r} g_{T_{\text{defect}}-T_{\text{defect}}} (r) \]  

(S12)

where \( \rho_{\text{defect}} \) is the density of Ti atoms composing the polar stripes and \( g_{T_{\text{defect}}-T_{\text{defect}}} (r) \) is the radial distribution function for the Ti atoms composing the polar stripes, which is illustrated in Fig. S18h. Due to the small system size, system 1 is unable to accurately capture small \( Q \) region of \( S(Q) \) corresponding to the large ~10-100 nm nano-domains that were only seen in system 3. For system 3 in this region a shoulder curve similar to that of polymers is seen in the \( S(Q) \) curve due to the string like nature of polar defects.

| Table S3: Total Number of Atoms and System Dimensions of XS-NNQMD simulation |
|-------------------------------------------------|
| Number of Atoms | System Dimensions (Å³) |
|-----------------|------------------------|
| System 1        | 1,737,280              |
|                 | 998.9 × 749.2 × 12.5   |
| System 2        | 2,949,120              |
|                 | 1997.8 × 1498.4 × 12.5 |
| System 3        | 1,045,954,560          |
|                 | 37958.7 × 27969.5 × 12.5 |
Fig. S18. Size-dependence of domain boundary dynamics. (A) and (B) show the domain dynamics for system 1 at 2.5 ps and 7.5 ps respectively. Unit-cells are color-coded by the order parameters based on the tilt angle of TiO$_6$ cage. The original PTO structure with zero tilt angle is shown blue. Red and green show positive and negative tilt angles due to the light-induced symmetry breaking described in the main text. (C) and (D) show the domain dynamics for system 2 and (E) and (F) show the dynamics system 3 again at 2.5 ps and 7.5 ps. (G) shows a zoom in on the domain structures of system 3. (H) shows the computed structure factor $S(Q)$ at small Q for system 1 and system 3. System 1 is unable to capture the small Q region of $S(Q)$ due to inadequate system size.

XI. Supplementary Video Description
Video S1: R-point phonon motion (MP4).
Video S2: M-point phonon motion (MP4).
Video S3: Excited-state QMD trajectory with polarization vectors (MOV).
Video S4: Excited-state NNQMD trajectory with unit-cell colored by polarization for large bulk crystal (MOV).
Video S5: Excited-state NNQMD trajectory with unit-cell colored by polarization for Bloch skyrimion nano-domains (MOV).
Video S6: Excited-state NNQMD trajectory with unit-cell colored by octahedral tilt orientation for large bulk crystal (MOV).
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