Electronic Supplementary Information for

Well-ordered self-assembled nanostructures of block copolymer films *via* synergistic integration of chemoepitaxy and zone annealing

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Part A: Details of computational model

To probe into the directed self-assembly of block copolymers in the presence of dual field of chemical template and zone annealing, the proposed model is based on the standard Hamiltonian in framework of polymeric field-theoretic method under a mean-field approximation. As schematically illustrated in Fig. 1 of main text, the system with volume V consists of n chains of AB block copolymers confined between two hard walls. The block copolymers have a chain length N and ideal gyration radius R_g. The top wall or substrate (represented by black color) contains the chemically guiding stripes with pitch p_s and width w_s. The top wall is neutral and represented by transparent color. The free energy functional (in unit of thermal energy k_BT) is given by

$$\frac{F}{n} =-\ln Q + \int dr\left\{-\omega_A\varphi_A - \omega_B\varphi_B + \chi N\varphi_A\varphi_B + \frac{1}{2}\kappa(\varphi_A + \varphi_B - 1)^2 + V_0\varphi_s(\varphi_B - \varphi_A)\right\} \qquad \text{(S1)}$$

where φ_A and φ_B are local volume fractions of A and B blocks, respectively. The parameter χN represents the Flory-Huggins interaction parameter and κ is the Helfand-type coefficient to control the deviation of local volume fractions from the average value. The quantity Q is single-chain partition function in external potential fields ω_A and ω_B produced by the surrounding chains. The last term represents the contribution of interactions between the blocks and the chemically guiding stripes *via* a short-range potential field. The function φ_S is the surface potential field for the chemical templates and their strength is denoted by V_0.

The kinetics of phase separation of multicomponent system is described by the Cahn-Hilliard-Cook equation, where the local volume fractions $\varphi_I(\mathbf{r}, t)$ (I=A and B blocks) at position $\mathbf{r}$ and time t are chosen as order parameters. The set of quantities obey the following diffusion equations given by

$$\frac{\partial \varphi_I(r,t)}{\partial t} = \sum_{J=A,B} \int D_{IJ}(r,r')\mu_I(r')dr' + \eta_I(r,t) \tag{S2}$$

where the intrinsic chemical potentials μ_I are calculated from the functional derivative $\mu_I(\mathbf{r})\equiv\delta F[\varphi_I(\mathbf{r})]/\delta\varphi_I$. η_I are the Gaussian thermal noises satisfying the fluctuation-dissipation theorem. $D_{IJ}(r,r') = \nabla_r \cdot \Lambda_{IJ}(r,r')\nabla_{r'}$ and Λ_{IJ} are the Onsager kinetic coefficients. In order to simplify the calculation process, the local coupling approximation is utilized

$$\Lambda_{IJ}(r,r') = M_I\varphi_I\delta_{IJ}\delta(r-r') \tag{S3}$$

where M_I are the mobility coefficients of blocks. The corresponding diffusion motion described in Eq. (S2) is written as

$$\frac{\partial \varphi_I(r,t)}{\partial t} = M_I\nabla \cdot \varphi_I(r)\nabla\mu_I(r) + \eta_I(r,t) \tag{S4}$$

It should be mentioned that the connectivity and entanglement of polymer chains are neglected due to the computational expense of pair-correlation functions in the numerical implementation of Rouse or reptation dynamics.

The model of zone annealing for the template-guided block copolymers is also schematically illustrated in Fig. 1 of main text. The system is divided into α and β regions, which are determined by the spatially and temporally dependent Flory-Huggins interaction parameter $\chi(\mathbf{r},t)N$. The corresponding interaction parameters in the α and β regions are denoted by the minimum value $(\chi N)_{min}$ and the maximum value $(\chi N)_{max}$, respectively. The zone width or the width of α region is represented by the parameter w. The movement of α region in the simulations is realized as follows: The center of α region is shifted for one lattice space Δy along the y direction in each set of n_t step of discrete time Δt, and the corresponding Flory-Huggins interaction parameters $\chi(\mathbf{r}, t)N$ in the α and β regions are reset. The moving velocity of zone annealing is defined as

$$v \equiv \frac{\Delta y}{n_t \, \Delta t} = \frac{\Delta \tilde{y}}{n_t \, \Delta \tilde{t}} \tilde{v} \tag{S5}$$

where $\Delta \tilde{y}$ and $\Delta \tilde{t}$ are the dimensionless discrete space and time, respectively. The basic velocity unit is given by $\tilde{v} = R_g / \tau$, which is specified by the basic length unit R_g and time unit τ in the model.

Part B: Acceleration ratio of parallel algorithm

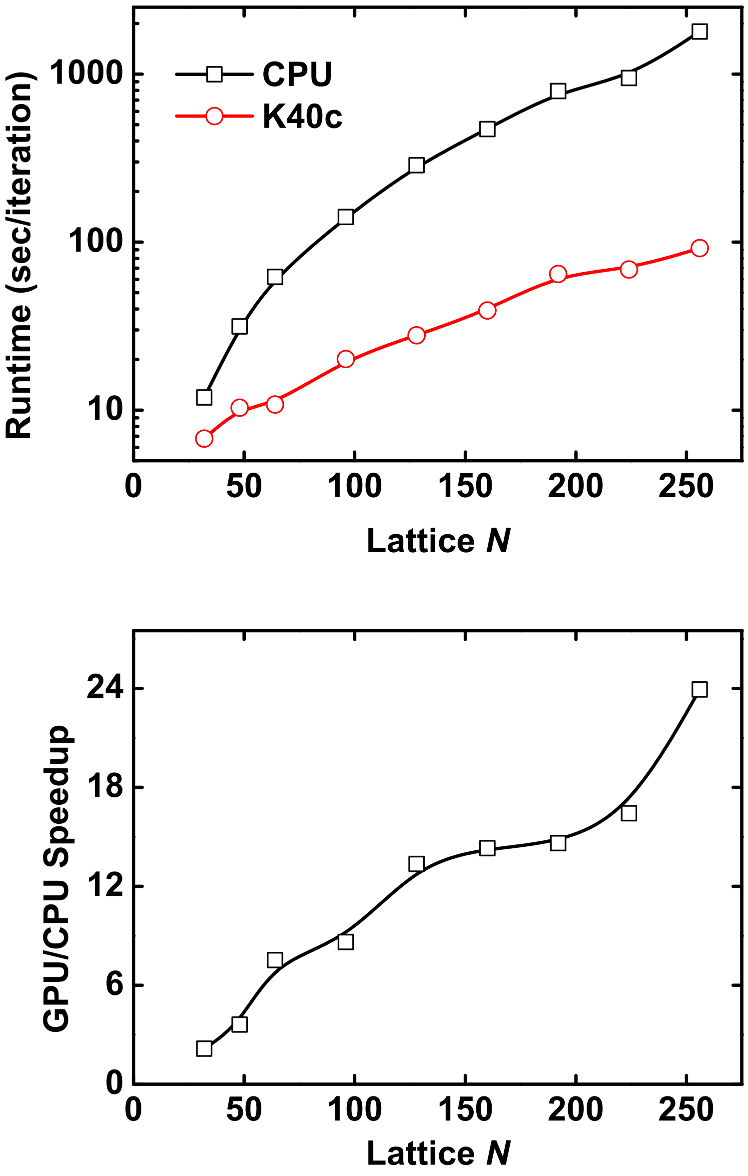

Fig. S1 (a) Absolute timings in seconds per time step (includes the calculation of propagators and the determination of potential fields) in a cubic box with lattice size N×N×48. (b) Relative speedup of GPU over a single CPU. All timings are averaged over ten runs with each simulation containing 20 time steps. The simulations use the single precision architecture.

Part C: Morphological evolution of quenching block copolymers

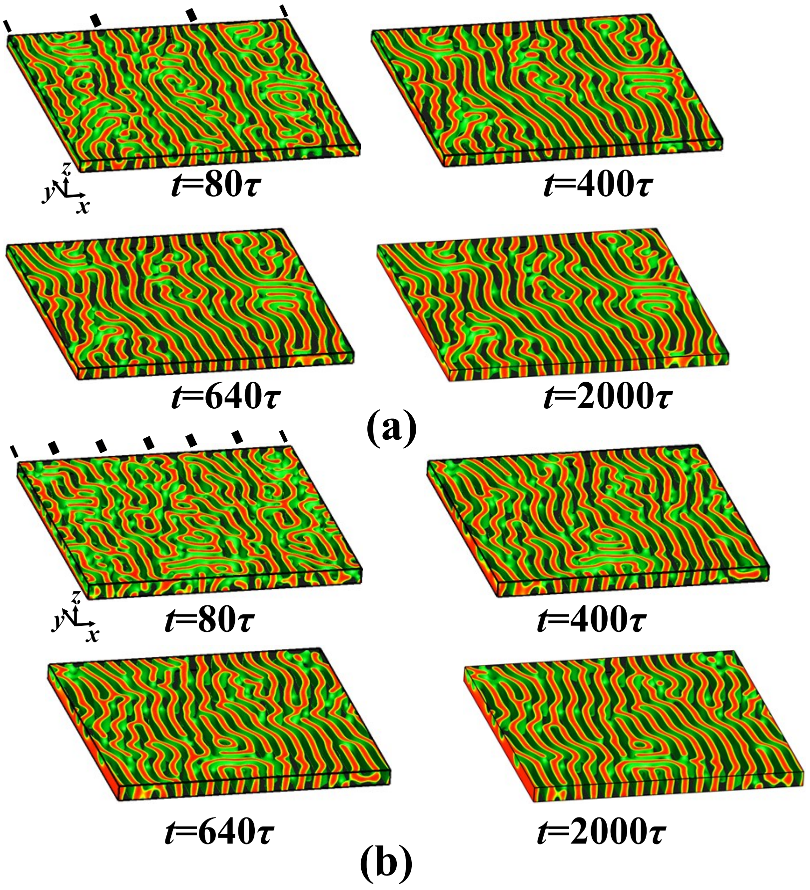

Fig. S2 Morphological evolution of self-assembled nanostructures registered by chemical template in the quenching simulation. (a) Film thickness L_z=0.75L_0 and stripe pitch p_s=6L_0. (b) Film thickness L_z=1.00L_0 and stripe pitch p_s=3L_0. The simulation times are indicated below the images. Here and in all the morphologies of self-assembled nanostructures below, the A-rich domains and the substrates are represented by the red and black colors, respectively. The interfaces between the A- and B-rich domains are shown in green. The top wall and the B-rich domains are transparent for the sake of visualization. The solid lines on images of self-assembled nanostructures at t=80τ highlight the positions of guiding stripes.

Part D: Three-dimensional view of self-assembled nanostructures

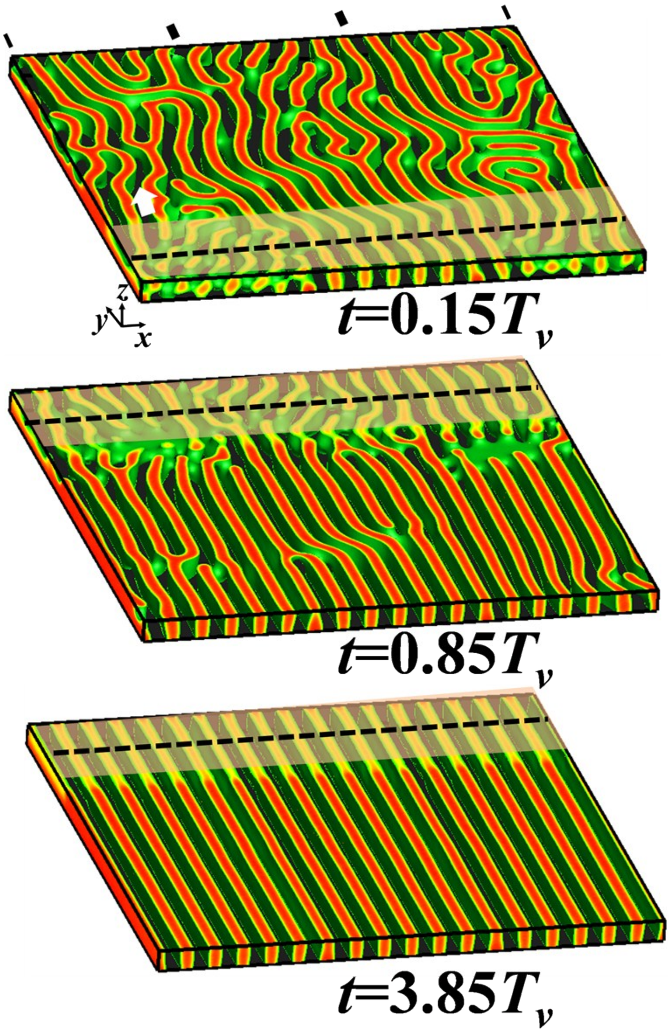

Fig. S3 Three-dimensional view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing. The zone width and the moving velocity are respectively w=5.0L_0 and v=0.06$\tilde{v}$ (corresponding to the case of Fig. 2c in the main text).

Part E: Block copolymers at film thickness L_z=1.25L_0

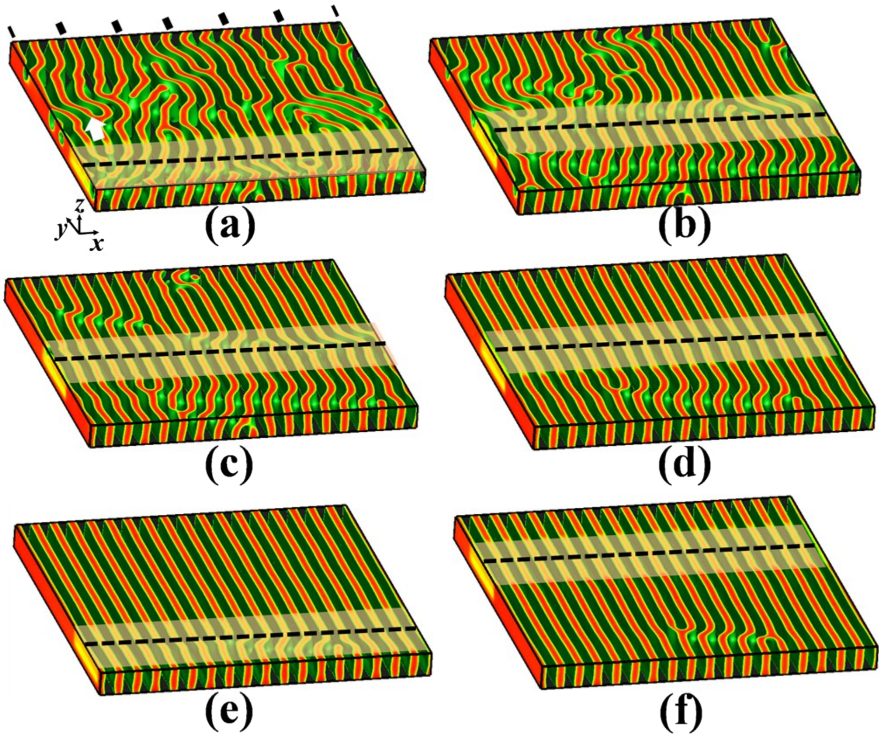

Fig. S4 Three-dimensional view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing at film thickness L_z=1.25L_0. The simulation time is (a) t=0.17T_v, (b) t=1.38T_v, (c) t=2.43T_v, (d) t=3.47T_v, (e) t=4.17T_v and (f) t=5.70T_v, where the period T_v of zone annealing has a value of 480τ. The zone width and the moving velocity are set as w=5.0L_0 and v=0.15$\tilde{v}$, respectively.

Part F: Bottom view of self-assembled nanostructures

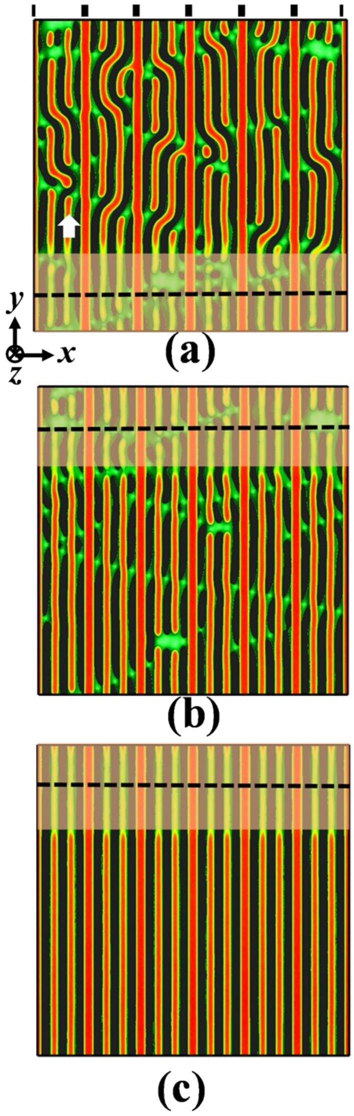

Fig. S5 Bottom view of morphological evolution of self-assembled nanostructures programmed by dual field of chemical template and zone annealing at film thickness $L_z=1.00L_0$. The simulation time is (a) $t=0.15T_v$, (b) $t=0.85T_v$ and (c) $t=4.0T_v$, where the period T_v of zone annealing has a value of 480τ. The zone width and the moving velocity are set as $w=5.0L_0$ and $v=0.15\tilde{v}$, respectively.

Part G: Temporal evolution of order parameters at film thickness L_z=1.50L_0

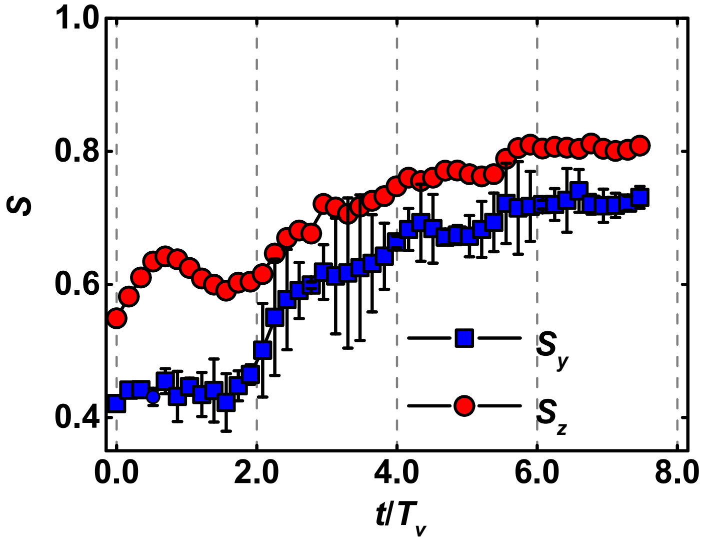

Fig. S6 Temporal evolution of order parameters S_y and S_z of lamellar nanostructures programmed by dual field of chemical templates and zone annealing at film thickness L_z=1.50L_0. Other parameter settings of simulations are the same as those in Figure 7 of main text.

Part H: Steady order parameters at film thickness L_z=1.50L_0

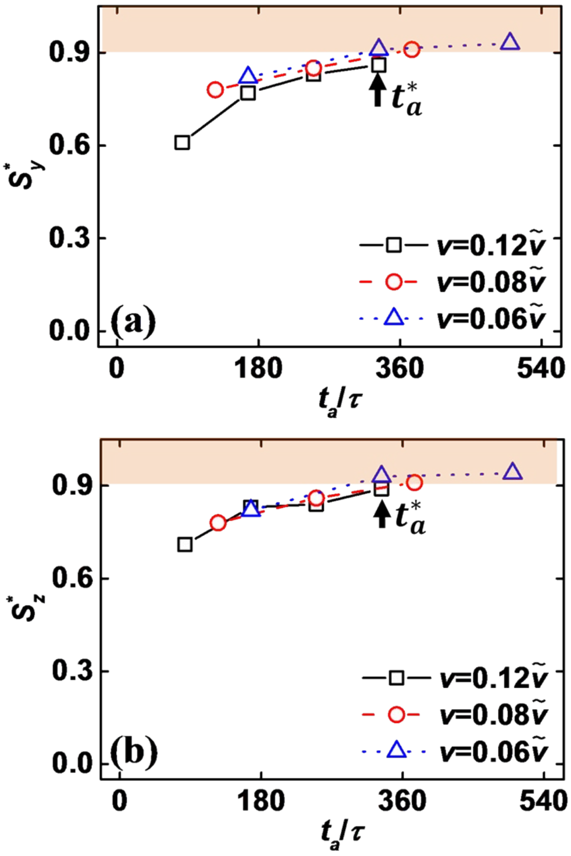

Fig. S7 Steady order parameters S_y^* and S_z^* of lamellar nanostructures as a function of the effective annealing time t_a under various moving velocities v. The shaded area highlights the fact that the steady order parameters are larger than 0.9, corresponding to the case of well-ordered nanostructures. The film thickness is set as L_z=1.50L_0. The zone width is changed from w=2.5L_0 to 10.0L_0.