Supporting Information

Selective Cooperative Self-Assembly between an Organic Semiconductor and Native Adatoms on Cu(110)

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Motivation for Agent-Based Kinetic Monte Carlo Simulations

An agent-based simulation using a Kinetic Monte Carlo (KMC) algorithm was developed to simulate the growth of Cu-TiOPc nanoribbons. The KMC method is a simple yet powerful approach to simulate the dynamical evolution of absorbate systems.[1] Taking an agent-based[2] approach allows us to simplify an *n*-body system into *n* one-body systems, dramatically enhancing computational efficiency. As an example, consider *n* Cu adatoms located randomly at lattice sites on an fcc (110) surface. In typical KMC simulations, the state of the system is defined by the equilibrium positions of all *n* adatoms. Therefore, moving one adatom to a new equilibrium position constitutes a transition between states of the entire system. As the trajectory of the system depends on the rate constants to every state the system enters, finding transitions between states is computationally intensive when considering all possible final states formed by every possible combination of concerted movements for all *n* adatoms, even when taking the symmetry of the surface into account. In contrast, in an agent-based KMC simulation, we consider a limited set of transitions available to individual agents (atoms or molecules), dictated by their immediate environment, and propagate the trajectory of each agent independently. Similar agent-based models have already been discussed in the literature.[3]

Simulation Details

The physical assumptions underlying our model are: *(i)* Adatoms bind to adatom islands OR adatoms are anchored by a molecule; *(ii)* a nucleation event occurs when a molecule overtakes an adatom; *(iii)* adatoms and molecules do not interact through long-range pair interactions; and *(iv)* the mobility of adatoms and molecules far exceeds the mobility of adatom clusters.[4] The "world" in our AB-KMC model is defined as a network of lattice sites with rectangular

symmetry and periodic boundary conditions. Agents are restricted to positions that coincide with lattice sites. We consider two species of agents, TiOPc "O-down" molecules and Cu adatoms, each separated into two *breeds*: One breed each for *stationary* agents, i.e. adatoms incorporated into islands or molecules anchoring at adatoms and step edges, and one breed each for *mobile* or diffusive agents. The set of transitions available to each agent depends on the breed of the agent, but may include: diffusion to adjacent lattice sites in the four cardinal directions on the (110) surface, attachment and detachment from islands (adatoms), nucleation and detachment from adatoms and step edges (molecules). We explicitly exclude double occupation of lattice sites by identical species (two adatoms or two molecules).

The rate constants for each possible transition constitute the basis of the parameter space which is systematically swept during a simulation experiment. We first form a set of basis transitions, assigning each transition a rate constant. We then compile a repository of subsets that include only the transitions available to an agent in a certain environment. As an example, an isolated adatom more than one lattice position away from an island has five possible transitions: Moving in each of the four cardinal directions and anchoring with a molecule. Adatoms within one lattice position of an island have additional possible transitions that include incorporating into an island with different rates for incorporating from different surface directions. We will refer to agents in unique environments as A_e^b where b is the breed of the agent and e is the environment of the agent. In order to determine the set of transitions available to a given agent, the agent polls its immediate surroundings to identify its specific environment. In polling nearest neighbor positions, typically a radius is employed. The rectangular lattice allows for easy discrimination between neighbors at distances corresponding to different surface directions. From here, only transitions available to agents in that environment are considered for that agent. The agent then

draws a random number that corresponds to one specific transition, in the same way as is done in KMC (see ref 1 for details on the KMC method).

As transition rates are limited by the "frame" rate inherent to agent-based simulations (arbitrary time "ticks" or iterations through the program loop), we incorporate a "system time" for each frame by drawing an exponentially distributed random time t_{frame} from a distribution $p(t) = k_{tot} \exp(-k_{tot}t)$ defined by agent set A_e^b with the fastest escape time from its present state. The fastest escape time is associated with the agent set A_e^b with the greatest k_{tot} where $k_{tot} = \sum_i k_i$ and i designates each possible, unique transition. Each individual agent also draws an exponentially distributed random time $t_{transition}$ from the distribution characterized by k_{tot} for the agent set A_e^b to which the agent belongs. The time drawn by each agent is then compared to the "system time" for that frame. If $t_{transition} < t_{frame}$, the agent makes the transition mentioned in the preceding paragraph. If $t_{transition} > t_{frame}$, no transition occurs in that frame and this may be considered an unsuccessful attempt.

To demonstrate how our simulations are capable of reproducing the experimentally observed nanostructures, we include the results of a simulation based on literature values. Using an Arrhenius framework and theoretical activation energies, we can estimate the ratio of rate constants ($\eta = \frac{k_{Cu,ads}^{1\bar{1}0}}{k_{Cu,ads}^{001}}$) between the two competing rate-limiting processes that are most responsible for nanostructure elongation, i.e. attachment along $[1\bar{1}0]$ and along $[001]$. The ratio of attempt frequencies can be crudely estimated by treating each potential well (isolated adatom on surface and adatom attached to nucleated Cu island) in the harmonic limit and estimating the ratio of vibrational frequencies from theoretical activation energies and the known lattice spacing. This results in attempt frequencies that lie within 15% of each other. With

approximately identical attempt frequencies and an activation energy difference obtained from effective medium theory (≈ 450 meV),[5] at 463 K we find that $\eta \approx 75000$.

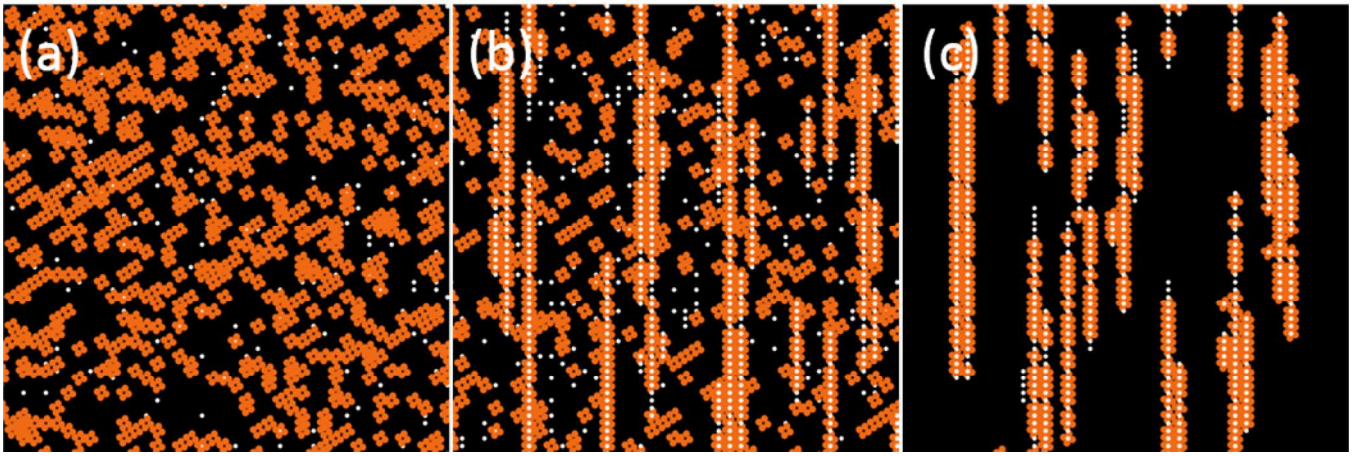

Figure S1 Sample images from AB-KMC simulations. a) Initial conditions. b) Complete simulated STM image after 8000 iterations. c) Repeat of (b), with unanchored species removed for improved clarity.

Figure S1 shows images captured at t = 0 and after ≈ 8000 iterations. The conditions for the simulation are such that 25% of lattice sites are occupied by TiOPc, 6% of lattice sites are occupied by a constant number of *mobile* Cu adatoms, $\eta = 75000, \zeta = 30$ and molecular-mediated blocking is enabled. Figure S1b shows the result after ≈ 8000 iterations. Figure S1c shows a similar frame from a separate simulation where mobile agents have been removed for improved clarity. This is the procedure used in all simulation results in the manuscript in order to eliminate distraction and emphasize the nanostructures. Sufficiently long simulation times eventually result in the anchoring of nearly all TiOPc molecules. To reduce CPU time, we do not quite reach the limit of $t \to \infty$ since, the de-anchoring rate is quite small. Figure S2 shows a sequence of time snapshots from a single simulation, following the nanostructure growth process from initial conditions through nucleation and elongation. Unanchored molecules are darkened to

emphasize the nanostructures.

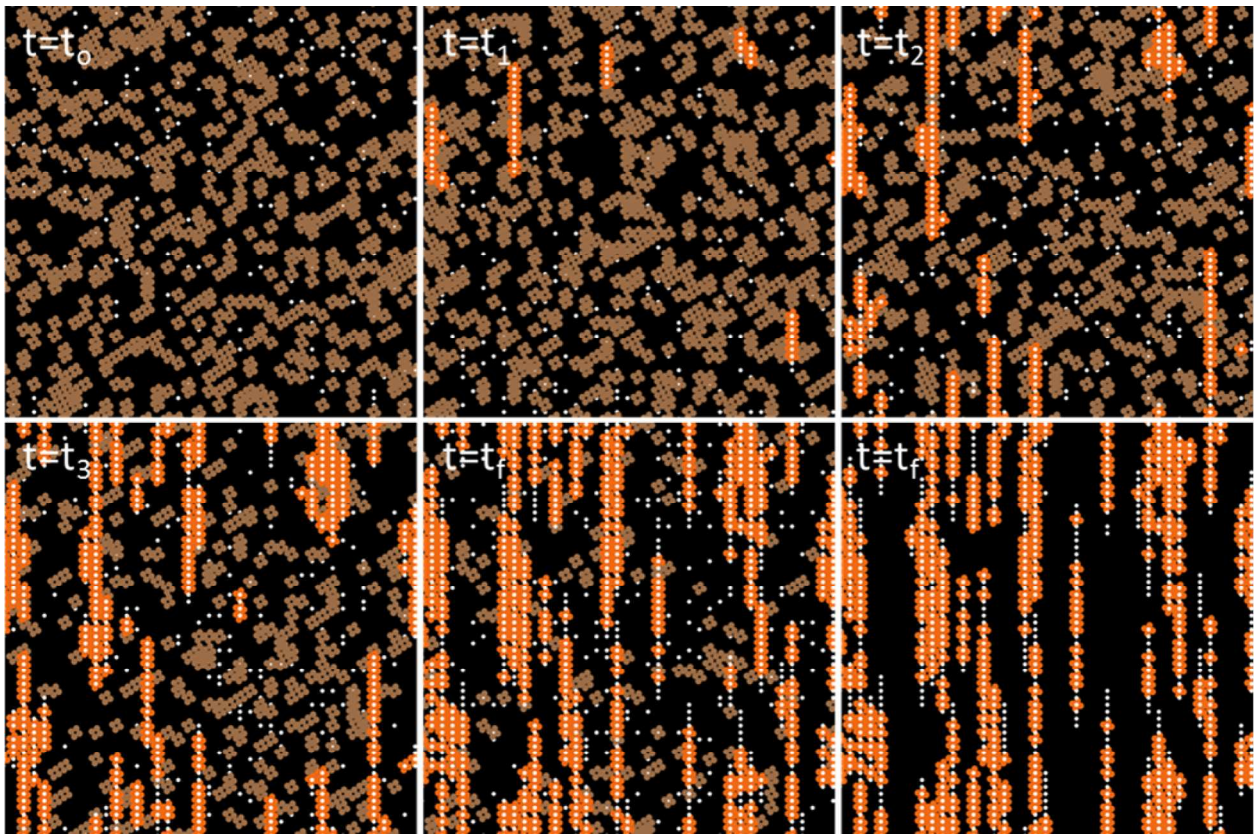

Figure S1 Evolution of thermally coarsened nanostructures. Final pane: $t=t_f$ and mobile agents removed.

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