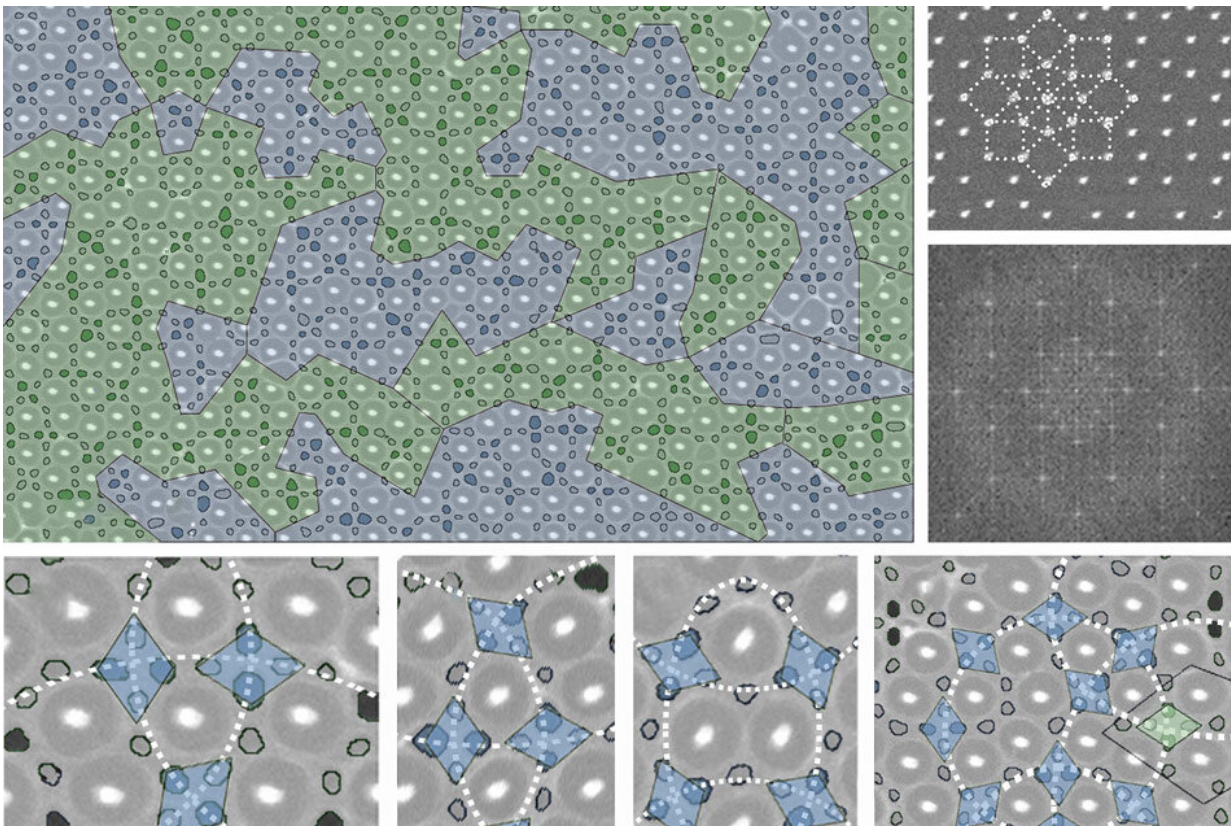


# Self-assembling materials can form patterns that might be useful in optical devices

July 5 2019, by David L. Chandler



Scanning electron microscope images of the crystal structure of the block copolymer material, illustrating their unusual quasicrystal symmetries. Regions with different symmetry properties are highlighted in different colors, and examples of the different patterns, which resemble some ancient tiling patterns, are shown in the accompanying diagrams. Credit: Massachusetts Institute of Technology

Self-assembling materials called block copolymers, which are known to form a variety of predictable, regular patterns, can now be made into much more complex patterns that may open up new areas of materials design, a team of MIT researchers say.

The new findings appear in the journal *Nature Communications*, in a paper by postdoc Yi Ding, professors of materials science and engineering Alfredo Alexander-Katz and Caroline Ross, and three others.

"This is a discovery that was in some sense fortuitous," says Alexander-Katz. "Everyone thought this was not possible," he says, describing the team's discovery of a phenomenon that allows the polymers to self-assemble in patterns that deviate from regular symmetrical arrays.

Self-assembling [block copolymers](#) are materials whose chain-like molecules, which are initially disordered, will spontaneously arrange themselves into periodic structures. Researchers had found that if there was a repeating pattern of lines or pillars created on a substrate, and then a thin film of the block copolymer was formed on that surface, the patterns from the substrate would be duplicated in the self-assembled material. But this method could only produce simple patterns such as grids of dots or lines.

In the new method, there are two different, mismatched patterns. One is from a set of posts or lines etched on a substrate material, and the other is an inherent pattern that is created by the self-assembling copolymer. For example, there may be a rectangular pattern on the substrate and a hexagonal grid that the copolymer forms by itself. One would expect the resulting block copolymer arrangement to be poorly ordered, but that's not what the team found. Instead, "it was forming something much more unexpected and complicated," Ross says.

There turned out to be a subtle but complex kind of order—interlocking areas that formed slightly different but regular patterns, of a type similar to quasicrystals, which don't quite repeat the way normal crystals do. In this case, the patterns do repeat, but over longer distances than in ordinary crystals. "We're taking advantage of molecular processes to create these patterns on the surface" with the block copolymer material, Ross says.

This potentially opens the door to new ways of making devices with tailored characteristics for [optical systems](#) or for "plasmonic devices" in which electromagnetic radiation resonates with electrons in precisely tuned ways, the researchers say. Such devices require very exact positioning and symmetry of patterns with nanoscale dimensions, something this new method can achieve.

Katherine Mizrahi Rodriguez, who worked on the project as an undergraduate, explains that the team prepared many of these block copolymer samples and studied them under a scanning electron microscope. Yi Ding, who worked on this for his doctoral thesis, "started looking over and over to see if any interesting patterns came up," she says. "That's when all of these new findings sort of evolved."

The resulting odd patterns are "a result of the frustration between the [pattern](#) the polymer would like to form, and the template," explains Alexander-Katz. That frustration leads to a breaking of the original symmetries and the creation of new subregions with different kinds of symmetries within them, he says. "That's the solution nature comes up with. Trying to fit in the relationship between these two patterns, it comes up with a third thing that breaks the patterns of both of them." They describe the new patterns as a "superlattice."

Having created these novel structures, the team went on to develop models to explain the process. Co-author Karim Gadelrab Ph.D. '19,

says, "The modeling work showed that the emergent patterns are in fact thermodynamically stable, and revealed the conditions under which the new patterns would form."

Ding says "We understand the system fully in terms of the thermodynamics," and the self-assembling process "allows us to create fine patterns and to access some new symmetries that are otherwise hard to fabricate."

He says this removes some existing limitations in the design of optical and plasmonic materials, and thus "creates a new path" for [materials](#) design.

So far, the work the team has done has been confined to two-dimensional surfaces, but in ongoing work they are hoping to extend the process into the third dimension, says Ross. "Three dimensional fabrication would be a game changer," she says. Current fabrication techniques for microdevices build them up one layer at a time, she says, but "if you can build up entire objects in 3-D in one go," that would potentially make the process much more efficient.

**More information:** Yi Ding et al. Emergent symmetries in block copolymer epitaxy, *Nature Communications* (2019). [DOI: 10.1038/s41467-019-10896-5](https://doi.org/10.1038/s41467-019-10896-5)

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