Kinetic Simulations:

The formation of Mo Blue structures can be simulated using a kinetic Monte Carlo approach [ref Gillespie]. This technique represents all reactions as either uni-molecular (in the case of degradation A -> B+ C) or bimolecular ( A +B -> C). The formation of structures is therefore modelled in a step wise fashion, based on the possible combination of building blocks and intermediates. Structures and intermediates form as the products of bimolecular reactions between building blocks and other intermediates. The propensity of those reactions depends on the concentration of reactants, temperature, the reduced mass of the reactants, the reaction volume, and a bimolecular rate constant, which is a parameter of the model. We assume that all molecules (besides Mo1) can degrade into component parts. Degradation is modeled with unimolecular reactions and therefore the propensity depends only on the concentration of the molecules and a unimolecular rate constant, another parameter of the model. In all the simulations described here we initialized the system with 1E6 Mo1 molecules.

The difference between building blocks, structures, and intermediates is their relative stability. For simplicity we assume that building blocks are one hundred times more stable than intermediates, and that completed structures are a further one hundred times more stable than building blocks. For the model we use Mo1, two different Mo2 species, and Mo6, as building blocks, which have a degradation rate constant of 0.01. The following structures form in the model: Mo36, Mo132 (Ball), Mo154 (wheel), and have a degradation rate constant of 1e-5. Intermediates degrade rapidly with a degradation rate constant of 1.0. The effect of templating is also included in this model. Templates host intermediate compounds and act to enhance the net rate of bimolecular reactions with those intermediates. This enhancement may be due to several different effects, for example, stabilizing the reactants and overcoming electrostatic repulsion. For simplicity this is included in the model by increasing the reactant rate constant of bimolecular reactions by a factor of 10.0 when one of the reactants is bound to a template. This model also distinguishes between the rate constant associated with the formation of edge bonded dimers (reduced) and corner bonded dimers. A schematic representation of this model is shown in figure XX, which black lines represent mass flow, and blue lines represent the effect of templates.

To characterize the formation of Mo Blue structures, simulations were run using different sets of bimolecular rate constants. We first modeled the system by inhibiting templates and setting the rate constant to 1.0 for all bimolecular reactions, such that the only differences in propensities were due to the differences in the reduced mass and the relative abundances of molecules. In this setting the only structure which formed was Mo36. We next included the effect of templating for the formation of Mo6 (templated by the Mo36) and the formation of Mo154 (also templated by Mo36). We found that including the effect of templating did not ensure the formation of Mo154 or Mo132. While intermediate compounds between the Mo36 and the Mo154 or Mo132 formed readily, those intermediates always degraded before forming complete structures, resulting in many “frustrated attempts”. This limitation cannot be easily overcome by increasing the stability of all intermediates, which only serves to preferentially increase the abundance of smaller mass intermediates, effectively trapping building blocks `down-stream.’

To overcome the frustrated formation of larger structures without fine-tuning the model, an additional feature was included. We assumed that the rate constant for bimolecular reactions between intermediates increased for molecules which are closer to being completed structures. This could, for example, represent the fact that a nearly complete structure serves to coordinate building blocks, pulling them into gaps in the structure. We implemented this using a linear function in the number of building blocks in the molecule with a slope of 1000.0. This means that reactions which convert an intermediate to a complete structure have a rate constant which is 1000. higher than reactions between building blocks, and reactions which produce an intermediate half way to a complete structure have a rate constant which is 500.0 higher. Including this feature in the model results in the robust formation of larger structures over a large range of parameters, without fine-tuning individual rate constants.

By incorporating these features, the model recovers many of the dynamical characteristics of the experimental system. For example, the formation of the Mo132 structure is sensitive to the relative rates of dimerization. As the rate of edge bonded dimer formation increases the net yield of the Mo132 in simulations, increases until the formation of pentagonal units is affected at which point the yield falls quickly to zero, which is observed by the progressive reduction of the solution in the physical experiments. Our model also recovers essential features of the formation of Mo154, namely the autocatalytic nature of the Mo36 template. In typical simulations the abundance of Mo154 remains 0 for a time followed by a brief period of exponential growth due and subsequent saturation. This feature is also seen in experimental data when the solution is not seeded with Mo36.

Our model also allows us to explore the dynamical consequences of different assumptions surrounding the formation of Mo Blue structures. For example, it is possible that Mo36 templates the formation Mo6 building blocks [ref]. Unfortunately, due to the time scales associated with the formation it is difficult to test this assumption experimentally. Using our model, we can explore the consequences of including or excluding this dynamical feature. Interestingly, we find that if we suppress the templating effect of Mo36 on Mo6, the Mo132 structure becomes much less likely to form over a large range of parameters. The increased production Mo6 due to templating is required to compensate for the reduced production of corner bonded dimers required for Mo6 synthesis. 