Narcissistic, Integrative, and Kinetic Self-Sorting within a System of Coordination Cages

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ABSTRACT: Many useful principles of self-assembly have been elucidated through studies of systems where multiple components combine to create a single structure. More complex systems, where multiple product structures self-assemble in parallel from a shared set of precursors, are also of great interest, as biological systems exhibit this behavior. The greater complexity of such systems leads to an increased likelihood that discrete species will not be formed, however. Here we show how the kinetics of self-assembly govern the formation of multiple metal–organic architectures from a mixture of five building blocks, preventing the formation of a discrete structure of intermediate size. By varying ligand symmetry, denticity, and orientation, we explore how five distinct polyhedra—a tetrahedron, an octahedron, a cube, a cuboctahedron, and a triangular prism—assemble in concert around CoII template ions. The underlying rules dictating the organization of assemblies into specific shapes are deciphered, explaining the formation of only three discrete entities when five could form in principle.

Molecules may follow complex pathways during self-assembly processes that generate multiple products. Understanding the self-sorting processes that occur within these pathways may allow us to decipher how simple prebiotic chemicals developed into life, and also how to design synthetic chemical systems that may be of practical use.

When different molecules self-assemble, one of three outcomes may result: social sorting, narcissistic sorting, or integrative self-sorting, during which all components are assimilated into a single product. Other sorting modes have recently been discovered, including biased sor...
also observed by ESI-MS (Figure S17). Product 7 incorporates three residues of B and two of A, and we infer it to have a similar trigonal-prismatic framework to structurally characterized 6 (Figure 2b).

The combination of amines A and B with 2-formylphenanthroline P2 (Figure 3b, pathway (iv)) resulted in a mixture of products that gave a complex NMR spectrum (Figure S21) that did not display peaks corresponding to any isolated discrete product. Multiple different products may thus form, integrating both A and B, without a strong thermodynamic preference for any single outcome. The lack of narcissistic sorting of octahedron 2 and cuboctahedron 4 may also contribute to the lack of observation of the former species in the five-component sorting experiment described below.

When all five building blocks (A, B, CoII, P1, and P2) were combined in the correct ratio so as to allow an equimolar mixture of cages 1:2:3:4 to form, octahedron 2 was not observed to form (Figure 3b, pathway (v)). Instead, tetrahedron 1, cube 3, and cuboctahedron 4 were the only species observed by both 1H NMR (Figure 4) and ESI-MS.
Monitored over 3 days of heating, 2 was not observed to form at any time (Figure S25).

In contrast with reported systems, the mixtures of products obtained in the system of Figure 3b, pathway (v) is not determined uniquely by the stoichiometry of subcomponents employed. A subset of only two or three of the four cages (1, 2, 3, 4) will be able to consume all of a balanced set of building blocks, i.e., where the total number of aldehyde groups is equal to the total number of amine groups, and where all CoII is coordinatively saturated. Thus, the selectivity observed when all subcomponents are present together (Figure 3b, pathway (v)) must be a result of further factors acting upon the system.

The rates of formation of the four cages were gauged, as shown in Figure 5. At regular intervals during self-assembly at 60 °C, we extracted aliquots and measured the degree of completion of assembly by UV−vis spectroscopy (SI Section 4). For all cages, we monitored the evolution of MLCT transitions (which often overlapped with ligand π → π* transitions, and porphyrin Soret bands in the cases of 3 and 4) as a function of time. A plateau in the intensity of the absorbance marked complete formation of the cage, which was then verified by 1H NMR spectroscopy. As the assembly kinetics of these structures are complex, we fitted our data to a simple exponential rate equation, enabling a comparison of assembly half-lives between cages.

The data of Figure 5 show clear differences between the rates of formation of the four structures. Tetrahedron 1 forms most rapidly, followed by octahedron 2, cube 3, and cuboctahedron 4. This sequence reflects the increasing structural complexity of these assemblies.

These rate differences (Figure 5) shed light upon the selectivity exhibited by the system of Figure 3b, pathway (v), as shown in Figure 6. As tetrahedron 1 forms most rapidly, it consumes all of the A and most of the P1 from the initial mixture. The remaining P1 must react with B to form cube 3, leaving additional B to react with the P2 to form cuboctahedron 4. Structures 3 and 4 may form in either order, as the system becomes deterministic following the conversion of all A into 1, with only one fate possible for each of the remaining subcomponents. The relative rates of 3 and 4 formation (Figure 5) suggest that 3 will be formed ahead of 4, however.

The first structure to form, tetrahedron 1, thus sets the scene for the system’s subsequent self-assembly by preferentially consuming all of A that octahedron 2 would have otherwise required. This system appears quite sensitive to subtle effects,
given the relatively small (less than a factor of 2) difference between the formation times of the competing structures 1 and 2. Notably, 2 was never observed when different reactant stoichiometries were employed during the reaction described in Figure 3b, pathway (v) (Figures S26–S28).

Host–guest binding can influence the kinetics of cage formation.40,41 This study thus lays the foundations to direct the self-assembly of systems of cages that share building blocks through the addition of guests, and other “cofactors” whose influence on one component of the system may propagate through its entirety, amplifying certain structures and suppressing others. In systems where cages are serving useful functions, such as catalysis52,43 or cargo transport,44,45 such an understanding may allow the development of these functions to be programmed in a complex way from a simple set of input stimuli.

■ ASSOCIATED CONTENT

*SUPPORTING INFORMATION*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02444.

Syntheses of cages, sorting experiments, crystallographic details (PDF)
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Notes
The authors declare no competing financial interest.

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