Electronic Supplementary Material for Isotope Effects in Colloidal Molecules

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I. SAMPLE PREPARATION PROTOCOL

We used the following protocol to construct sample chambers for the self-assembly of 2D colloidal molecules.

1. Prepare one small (22 mm × 22 mm) and one large (24 mm × 60 mm) glass coverslip (VWR Micro Cover Glasses, No. 1) by rinsing with deionized water and drying with high-purity compressed nitrogen.

2. Plasma clean the large coverslip for 2 minutes in a PDC-32G Plasma Cleaner/Sterilizer (Harrick Plasma) with the RF Level set to High. Plasma cleaning greatly reduces sticking between particles and the coverslip. Only the large coverslip needs to be plasma cleaned because it will form the bottom of the sample chamber and, thus, be the surface on which the 2D self-assembly occurs. We found that using coverslips instead of glass slides was essential for preventing unwanted particle sticking.

3. To assemble the sample chamber, center the small coverslip on the large coverslip and separate them with two narrow (approximately 3-mm-wide) strips of 35-µm-thick Mylar® A film (wiped clean with isopropanol) parallel to the long edges of the large coverslip. With the two coverslips clamped together (e.g., with binder clips), use UV-curing Norland Optical Adhesive 61 and a UV lamp to seal the two edges of the small coverslip parallel to the spacers. We find that sealing the four corners and then removing the clips before sealing the two edges works well.

4. Use a pipette to dispense well-dispersed colloidal suspension near one of the two unsealed edges of the small coverslip and let capillary action fill the sample chamber.

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5. Use Devcon 5 Minute® Epoxy to seal the two unsealed edges of the small coverslip and to go over the two previously sealed edges for extra protection against evaporation.

6. Keep the sample chamber oriented such that the large coverslip forms the bottom of the chamber. In this transparent chamber, self-assembly can be directly observed with an inverted microscope.

We thank Jerome Fung for teaching us how to make this style of sample chamber.

II. IMAGE PROCESSING

Our custom image processing routine identifies isomers after the individual particles have been located with Trackpy[1]. Here, we describe our post-processing routine on the data used in this study.

The first step is to identify which of the 115,825 found particles are polystyrene, which are silica, and which are false positives. To do this, we plot the sizes of the particles returned by Trackpy (that is, the radii of the bright spots shown in Figure 2 of the manuscript, which are not the true particle radii) versus the particles' intensity maxima in the raw images. By plotting the data in this way, we see three distinct regions corresponding to silica particles, (27%), polystyrene particles (40%), and false positives (33%) (Figure S1). By eye, we choose lines with slopes of 0.033 pixels/intensity value to delineate the three regions (Figure S1). We checked the lines' ability to discriminate particle types by examining the complete set of micrographs annotated with the determined particle types. We saw that more than 99% of the particles identified as silica or polystyrene were identified correctly. The main failure mode was silica particles that were either erroneously discarded as false positives or never located in the first place. Around 15% of small molecules contained more particles than were identified by the algorithm. Less than 1% of molecules had fewer particles than the algorithm determined. Wecorrected misidentifications in our list of molecules manually.

Next, we use proximity to group the individual particles into molecules. We calculate the distances between all possible pairs of particles in an image and, for each particle, we make a list of the other particles within a "molecule-sized" search radius, which we set to 3.5 µm. This distance is sufficiently large to encompass all rigid and almost all non-rigid configurations of molecules with up to five 1-µm-diameter particles. We then use these sets of nearby particles to assign each particle to a molecule, which we label numerically. The list of each particle's associated molecule is then converted to a list of molecules including information about which particles are members of each molecule. This method of grouping particles into molecules has two failure modes. First, two small molecules will get grouped together if they lie entirely within the same search radius. We check for and manually correct such occurrences by looking at the micrographs annotated with the algorithmic results. Second, the search radius can truncate large molecules or encapsulate pieces of multiple nearby molecules. Such occurrences are flagged by our algorithm, and the particles in these molecules are removed from further analyses (19% of the polystyrene and silica particles). We then eliminate 6% of the remaining particles

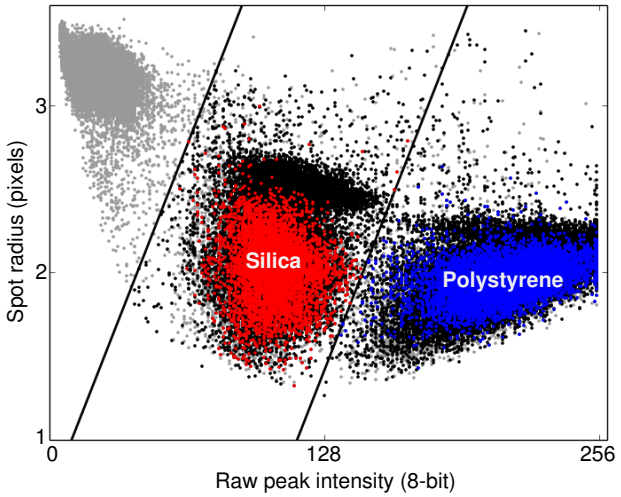

FIG. S1. Automatically distinguishing silica and polystyrene particles. A scatter plot of particle attributes reveals found "particles" of three types: silica particles (center), polystyrene particles (lower right), and false positives (upper left). The red and blue points are the particles in rigid 4- and 5-particle molecules. The clusters of black points directly above the colored regions are single particles of each isotope that are not bound to any other particles.

on the basis that the center of mass of each of their molecules is located less than 20 pixels (2.3 µm) from the edge of an image. We do this to avoid analyzing molecules that are truncated by an edge.

To identify rigid molecules from the set of all molecules, we analyze the interparticle distances. To classify pairs of particles as bound or unbound we set a cutoff distance of 1.18 μm, about 15% larger than the distance between two bonded particles. Molecules with interparticle distances slightly larger than a particle diameter are likely to have been in the neighboring rigid state just after or just prior to the instants their images were captured. Our cutoff distance effectively rounds molecules with slight bond breaks to their nearest rigid molecules and also allows for some polydispersity among the particles.

Finally, we determine each rigid 4- and 5-particle molecule's configuration in terms of the set of possible isomers. We use a modified adjacency matrix that encodes the locations of different isotopes within a molecule. In previous studies on homogeneous molecules,[2–4] we used adjacency matrices to distinguish between molecules of different geometries. The standard adjacency matrix is populated with binary values, indicating whether the particles are separated (0) or bound (1). Here, to keep track of the different types of bonds, we use a 1 for an S-S bond, a 2 for an P-S bond, and a 3 for a P-P bond (Figure S2). To obtain an isomer identification from the adjacency matrix, we perform a column sum and sort the resulting one-dimensional list from low to high. This method yields a list that uniquely identifies each 4- and 5-particle isomer composed of 1 or 2 isotopes (note that enantiomers are grouped together). This approach to identifying isomers is not a general solution

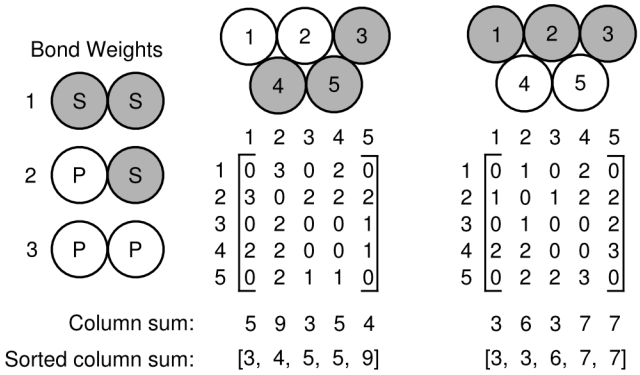

FIG. S2. Modified adjacency matrix for colloidal molecules with two species. These two 5-particle molecules have identical compositions and identical numbers of bonds of each type (S-S, P-S, P-P), yet are distinct isomers. A modified adjacency matrix with 1's, 2's, and 3's indicating different bond types is converted to a sorted column sum that is a unique identifier for all rigid one- and two-species isomers with fewer than 6 particles, regardless of the order in which the particles are numbered.

to labeling networks constructed from two types of nodes, but it is sufficient for our small molecules. We do not examine molecules with 6 or more particles because they have multiple rigid states and require a much larger data set to investigate their many isomers.

III. INTERACTIVE VISUALIZATION OF CONTROLLABLE SELECTIVITY

The interactive visualization accessible at http://people.seas.harvard.edu/~vnm/isotopes/clusters.html uses our model to allow users to modify two sticky parameters and explore the possibilities for selective placement of dopants.

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