

Switching between liquid and gel

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Twisted nanostructures are an important biological motif—just think of the DNA double helix or proteins with helical sections important to their function. Researchers are anxious to produce artificial helices, which could be useful in nanotechnological applications. Korean researchers have now successfully created a molecular system that can even form helices “on demand”, turning the initially liquid solution into a gel.

A team at Yonsei University in Seoul, Korea, headed by Myongsoo Lee, have developed a special type of molecule as the basic building block for their helices. This involves a base consisting of three aromatic rings which is bent like a boomerang. The central ring has a long, branched side-chain hanging from it. When a silver salt is added to a solution of these molecules, complexes form between the molecules and the positively charged silver ions; the “boomerangs” really get a hold on the silver ions. If the negatively charged counterion in the silver salt is boron tetrafluoride (BF_4^-), the complexes pile up into long, twisted columns. The BF_4^- ions fit exactly into the cavity that remains inside the “belly” of the helices and stabilize them. This results in a surprise: The liquid turns into a jelly-like mass.

How does this happen? It turns out that the helices aggregate into regular bundles of fibers, which get tangled up with each other to form an interwoven, three-dimensional network. The liquid remains trapped inside this fibrous framework; this forms a gel, a kind of intermediate between a liquid and a solid. If a fluoride salt is then added to the gel, it liquefies. This is a result of the enormous attraction of the fluoride ions (F^-) for the silver ions, which are lured out of their complexes. The

fibrous aggregates collapse back into individual molecules. This effect is reversible if the fluoride ions are trapped by the addition of other salts.

If salts containing the $\text{C}_2\text{F}_5\text{CO}_2^-$ ion are added to the gel, it also liquefies. Electron microscopy images show that in this case, the phenomenon has a different cause. The complexes do not fall apart into individual molecules, but form a different structure instead. Instead of interwoven helical columns, they form individual zigzagging bands. The reason for this change in structure is the difference in size of the anions: $\text{C}_2\text{F}_5\text{CO}_2^-$ is bigger than BF_4^- and thus does not fit into the cavity inside the helices, which are thus not stabilized. The result of all this is the birth of a new type of “intelligent” nanomaterial whose properties can be switched solely by the choice of counterion.

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