

Mirror-image forms of corannulene molecules could lead to exciting new possibilities in nanotechnology

August 29 2014

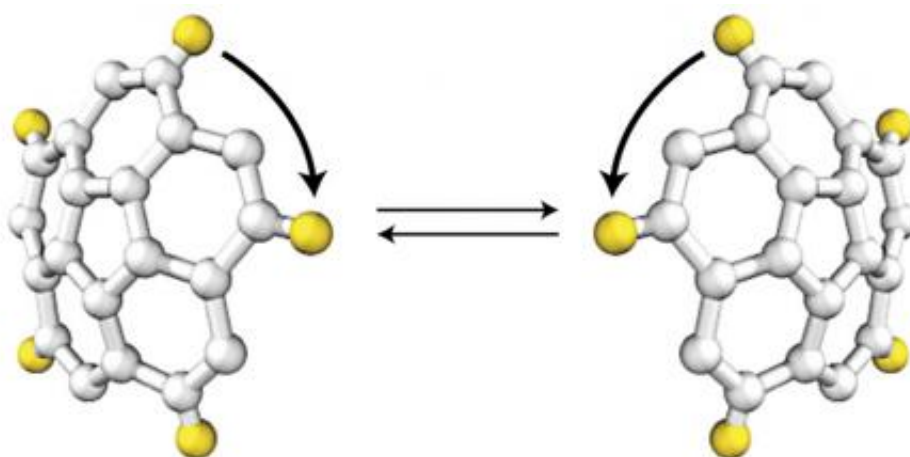


Figure 1: The inversion between asymmetric non-superimposable mirror image forms of corannulenes. The yellow spheres represent different chemical groups in clockwise or anticlockwise arrangements as seen from the convex side of the bowl. Credit: American Chemical Society

Corannulene is a bowl-shaped polycyclic aromatic hydrocarbon with a skeleton of bonded carbon atoms equivalent to a segment of the buckminsterfullerene or 'buckyball'—a soccer-ball-like structure of 60 carbon atoms. This similarity to the buckyball has led to corannulene being dubbed the 'buckybowl'. Chemists are interested in the chemical potential of corannulenes as catalysts and in nanotechnology applications, but exploring the potential of these molecules is

complicated because they invert rapidly between their mirror-image or 'chiral' forms (Fig. 1).

Daigo Miyajima and colleagues from the RIKEN Center for Emergent Matter Science, in collaboration with co-workers from the University of Tokyo and Osaka University, have now developed a molecular design strategy that allows them to 'desymmetrize' the corannulene inversion equilibrium, resulting in solutions enriched in either one of its chiral forms. The achievement marks an important step toward being able to work with and perhaps isolate the individual chiral forms to explore their possible uses. "For example, if we can desymmetrize and produce corannulene complexes with transition metals, it might be possible to develop asymmetric catalysts with unique characteristics due to the bowl-shaped structure of corannulene," explains Miyajima.

The key to biasing the inversion process was to add different chemical groups that can interact through intramolecular hydrogen bonding, whereby hydrogen atoms with a slight positive charge are attracted to other atoms with a slight negative charge. These forces of attraction within each molecule stabilize the corannulene bowl in one of its chiral versions by establishing a thermodynamic preference for the chiral form that allows all the interacting units to be hydrogen bonded at the same time.

Although a significant achievement, this desymmetrization of corannulene equilibrium is only partial. The conversion between the two forms is not stopped completely but is merely slowed down and made to favor one form over the other. The next challenge for the research team is to find modifications that can stop the conversion completely and perhaps allow just one of the stabilized bowl structures to be purified and used in the complete absence of its inverted partner.

There are numerous incentives for achieving chiral purity of

corannulenes beyond catalyst applications. "Other researchers are working on utilizing corannulenes for making carbon nanotubes," says Miyajima, "and so our research may contribute to the synthesis of chirality-selective nanotubes." As chiral asymmetry is critical for many precise chemical reactions, the selective enrichment of nanotubes favoring one chirality could open new possibilities in nanotechnology.

More information: Kang, J., Miyajima, D., Itoh, Y., Mori, T., Tanaka, H., Yamauchi, M., Inoue, Y., Harada, S. & Aida, T. "C₅-symmetric chiral corannulenes: Desymmetrization of bowl inversion equilibrium via "intramolecular" hydrogen-bonding network." *Journal of the American Chemical Society* 136, 10640–10644 (2014). [DOI: 10.1021/ja505941b](https://doi.org/10.1021/ja505941b)

Provided by RIKEN

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