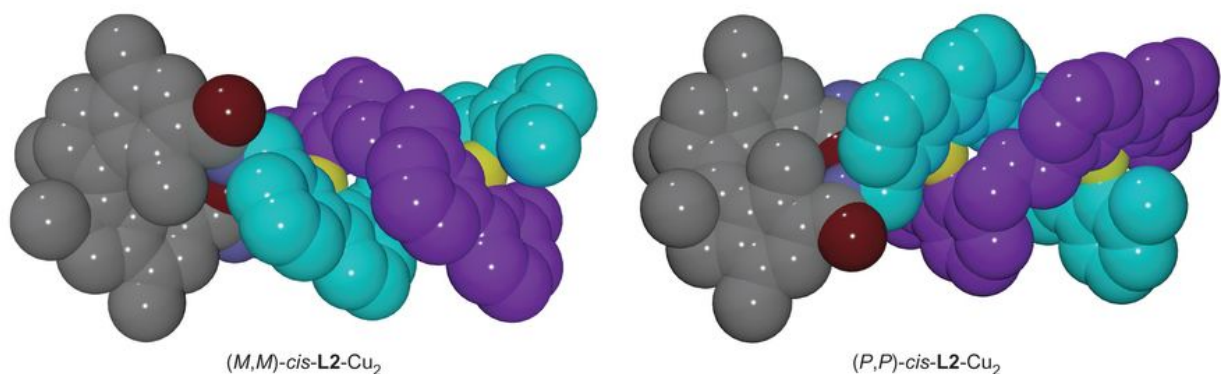


Rotary molecular motor controls self-assembly and handedness of double-stranded helicates

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Optimized structures of (M,M)-cis-L2-Cu₂ and (P,P)-cis-L2-Cu₂. Credit: (c) *Nature Chemistry* (2016) doi:10.1038/nchem.2668

(Phys.org)—A group of researchers from the University of Groningen in the Netherlands have developed a way to change the handedness of a double-stranded metal helicate by photo and thermal stimulation by attaching bipyridine subunits to a unidirectional molecular rotary motor. Their work appears in *Nature Chemistry*.

DNA has served as a model molecule for chemists wanting to create information-carrying macromolecules. One unique feature of DNA is that its [helix](#) is found in nature as a right-handed helix. Researchers are

interested in making synthetic helical structures that can reversibly switch handedness for various functions.

In the current research, Depeng Zhao, Thomas van Leeuwen, Jinling Cheng, and Ben L. Feringa use as their model helical structure metal-coordinated bipyridine. Research by Lehn et al. (*Proc. Natl. Acad. Sci. USA* vol. 84, pp. 2565-2569, May 1987) explored the self-assembly capabilities of bipyridine units coordinated to two or three Cu(I) metals, and reported their ability to self-assemble into a double helix. Based on this research, Zhao, et al. attached bipyridine units to a molecular [rotary motor](#) via an amide bond.

Upon addition of 2.1 equivalents of Cu(I), oligomers formed. Then, upon irradiation at lower temperatures, the rotary motor changes orientation, and the oligomers self-assemble into a metal helicate. The molecular rotary motor cycles through four isomers, two of which are stable and two of which are less stable. The isomers move from the more stable to the less stable conformations after irradiation with 312nm of light at low temperature. Boosting the temperature converts the less stable to the more stable [isomer](#).

Half of the molecular motor rotates with respect to the other half, leading to the shorthand identifiers: (P,P)-trans-1, which is stable, (M,M)-cis-1, which is less stable, (P,P)-cis-1, which is stable, and (M,M)-trans-1, which is less stable. When the bipyridine-based helix is attached to the motor, it is the cis isomers that dictate the handedness of the helix. (M,M)-cis-1 induces a (P')-double metal-helicate, or right-handed helix, while (P,P)-cis-1 induces a (M')-double metal-helicate, or left-handed helix.

Zhao, et al. also looked at subunits made from two bipyridine subunits on each strand of the motor, and found that they were able to self-assemble to metal helicates and to left-handed in the same way as the

single bipyridine units. Thermodynamic and half-life studies showed very similar results to the single bipyridine units. As before, switching between the (M,M)-cis-1 isomer and the (P,P)-cis-1 isomer changed the handedness of the [double helix](#).

Finally, Zhao, et al. used NMR and circular dichroism studies to determine the enantiomeric excess of the handedness of the double helices. Analyses indicated a >90:10 preference for the (P,P)-cis isomer of the longer metal helix over the (M,M)-cis isomer after heating the (M,M)-cis isomer.

This research shows that rotary molecular motor with bipyridine subunits attached via an amide bond is able to cycle through self-assembly from oligomer to metal-bound double helicates of varying length, as well as reversing the handedness of the helix. This research provides a springboard for designing dynamic molecular systems.

More information: Depeng Zhao et al. Dynamic control of chirality and self-assembly of double-stranded helicates with light, *Nature Chemistry* (2016). [DOI: 10.1038/nchem.2668](https://doi.org/10.1038/nchem.2668)

Abstract

Helicity switching in biological and artificial systems is a fundamental process that allows for the dynamic control of structures and their functions. In contrast to chemical approaches to responsive behaviour in helicates, the use of light as an external stimulus offers unique opportunities to invert the chirality of helical structures in a non-invasive manner with high spatiotemporal precision. Here, we report that unidirectional rotary motors with connecting oligobipyridyl ligands, which can dynamically change their chirality upon irradiation, assemble into metal helicates that are responsive to light. The motor function controls the self-assembly process as well as the helical chirality, allowing switching between oligomers and double-stranded helicates

with distinct handedness. The unidirectionality of the light-induced motion governs the sequence of programmable steps, enabling the highly regulated self-assembly of fully responsive helical structures. This discovery paves the way for the future development of new chirality-dependent photoresponsive systems including smart materials, enantioselective catalysts and light-driven molecular machines.

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