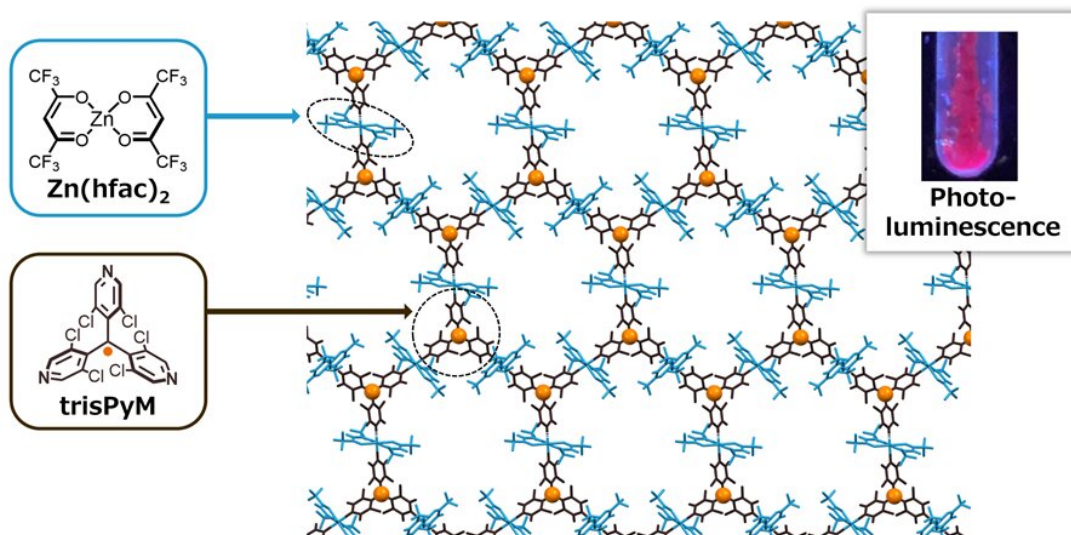


A novel recipe for air-stable and highly-crystalline radical-based coordination polymer

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A 2D honeycomb lattice structure of a radical-based coordination polymer, trisZn, constructed from trisPyM and $\text{Zn}(\text{hfac})_2$. Photoluminescence from trisZn is shown. Credit: NINS/IMS

Coordination polymers (CPs) composed of organic radicals have been the focus of much research attention in recent years due to their potential application to a wide variety of next-generation electronics,

from more flexible devices to spintronics information storage technology. However, CPs often exhibit limited stability and poor crystallinity. Researchers from Japan's Institute for Molecular Science (IMS), National Institute of Natural Sciences (NINS), have developed a novel recipe that not only produces a stable material, but offers a variety of other useful attributes.

Their findings appear in the journal *Journal of the American Chemical Society* on March 15.

Materials with unpaired electrons on 2D honeycomb lattices have attracted much attention as [potential candidates](#) for future electronic, spintronic and photonic device applications. An organic [radical](#) based coordination polymer (CP) is one candidate of such materials, and has a structure containing [metal atoms](#) at the center of the repeating sequence of organic radicals. Several radical-based CPs with honeycomb lattice structures have been prepared so far, but in-depth investigation of their functions and materials development are often hindered due to their instability and poor-crystallinity.

Radicals are an atoms or molecules an unpaired electron in the outer shell. This lack of pairing with another electron makes it extremely reactive with other substances, so radicals tend to be very short-lived. There are, however, some radicals that are long-lived, even in everyday temperature and pressure conditions. These stable radicals demonstrate electrical, magnetic and photoemission properties, similar to features of inorganic materials such as metals, oxides and chalcogenides.

"Stable, highly crystalline, radical-based CPs with honeycomb lattice structures have a great potential to expand the utility of this class of materials in future applicatiосn. But even though such materials are in principle possible, the design and synthesis have been pretty elusive," said Tetsuro Kusamoto of IMS at NINS.

The IMS team has produced a recipe for CPs that are long-lived under ambient conditions. It uses an entirely new, triangular-shaped organic radical, tris(3,5-dichloro-4-pyridyl)methyl radical, or trisPyM. This radical is not just stable, but also exhibits photoluminescence in solution and solid states. In addition, combining trisPyM with a zinc-containing molecule, $\text{Zn}^{\text{II}}(\text{hexafluoroacetylacetonato})_2$, producing what they call trisZn, the researchers developed a stable, crystalline and photoluminescent radical-based CP with a 2D honeycomb lattice structure.

"TrisZn is just a proof of concept of our recipe, and a plenty of radical-based CPs can in principle be produced by simply employing different metal ions or metal complex units. I hope some of these materials find real-world applications or exhibit unprecedented phenomena that advance materials science." Tetsuro said.

More information: Shun Kimura et al, An Open-shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice and Triangular Organic Radical, *Journal of the American Chemical Society* (2021). [DOI: 10.1021/jacs.0c13310](https://doi.org/10.1021/jacs.0c13310)

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