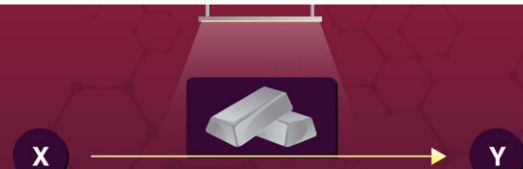


An improved, visible light-harvesting catalyst to speed up reactions


March 30 2023

Synthesizing Novel Visible-Light-Driven Catalysts



X → **Y**

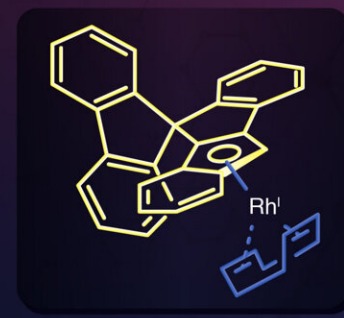
Visible-light-driven single transition metal catalysts are ideal as they perform both light absorption and chemical transformation



However, they are limited by their radical mechanisms or substrate dependence due to their low light-harvesting abilities

Novel single transition metal catalyst




Spiro-fluorene-indenoidenyl-Rh(I) complex (SFI-Rh(I))



π -extended

Small slippage parameters with Rh

Coordinatively saturated by 1,5-cyclooctadiene (cod) ligand

-  Reduced substrate dependence
-  High visible light-harvesting ability
-  High stability against protonation

The SFI-Rh(I) catalysts are versatile and overcome several limitations of previously reported catalysts

Design, synthesis, and visible-light-induced non-radical reactions of dual-functional Rh catalysts
Nagashima et al. (2023) | *Nature Synthesis*

Credit: Tokyo Tech

Photocatalysis is the use of light to accelerate the rate of a reaction in the presence of a photocatalyst. The catalyst plays a crucial role in this process—it absorbs the light being shined onto it and makes it available in ways that can help accelerate the chemical reaction and also enhance it. These catalysts are used for a variety of light-dependent reactions ranging from the production of paper to the conversion of carbon dioxide to fuel.

Given these applications, the development of ideal photocatalysts is important. An ideal photocatalyst is one that uses a single transition metal that performs both visible light absorption and chemical transformation. Currently, visible light-driven single transition metal catalysts are limited to only one mechanism of operation, known as the radical mechanism, or have a low light-harvesting ability, making them heavily dependent on certain substrates. Thus, there is a need for an ideal single transition metal catalyst that solves these problems.

A team of researchers from Tokyo Institute of Technology (Tokyo Tech), led by Assistant Professor Yuki Nagashima, have reported a novel visible light-driven single transition metal catalyst that solves these issues. Their findings are published in *Nature Synthesis*. Dr. Nagashima explains, "We envisioned unprecedented rhodium (Rh)-based photocatalysts—spiro-fluorene-indenoindenyl (SFI)-Rh(I) complexes—that combine high light harvesting abilities with broad applicability."

The team found that extending the molecules around the central Rh atom—called the ligand—is necessary to increase the light harvesting abilities of these complexes, but also makes them less stable. Thus, the

team designed SFI-Rh(I) complexes using a non-fused extension strategy, extending the molecules around the ligand without compromising the stability of the resultant catalyst.

In fact, their extension strategy made the catalyst stable against protonation and helped in increasing its light-harvesting ability, thus reducing its substrate dependence. The catalyst was also designed to be able to perform using multiple mechanisms, beyond the radical mechanism used by previous catalysts.

"The careful design of our catalyst enabled it to have many advantages compared to previously described catalysts, while making it suitable for complex reactions. The SFI-Rh(I) complexes can easily extend the scope of typical Rh-catalyzed reactions using [blue light](#) LED irradiation at room temperature. This opens many avenues for future applications of these catalysts, as well as photocatalytic reactions in general," says Nagashima.

"We believe that this catalyst has the potential to be a versatile light-driven [catalyst](#) that can break through the ground-state limitations in various photoreactions."

More information: Yuki Nagashima, Design, synthesis and visible-light-induced non-radical reactions of dual-functional Rh catalysts, *Nature Synthesis* (2023). [DOI: 10.1038/s44160-023-00268-9](https://doi.org/10.1038/s44160-023-00268-9).
www.nature.com/articles/s44160-023-00268-9

Provided by Tokyo Institute of Technology

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