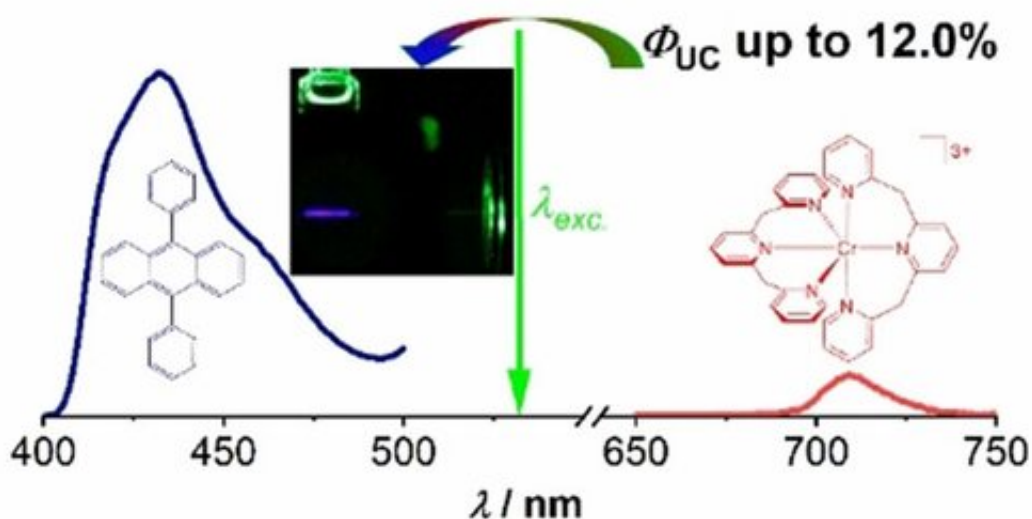


A novel path for sustainable photon upconversion with non-precious metals

June 3 2022



The molecular ruby [Cr(bpmp)₂]³⁺ with an earth-abundant chromium(III) central ion sensitizes green-to-blue triplet-triplet annihilation upconversion with 9,10-diphenylanthracene as the annihilator. The process involves a near-unity energy transfer efficiency via an underexplored reaction pathway, an anti-Stokes shift of 0.54 eV, and a maximum upconversion quantum yield of 12.0 %. Credit: *Angewandte Chemie International Edition* (2022). DOI: 10.1002/anie.202202238

Sustainable chemical applications need to be able to employ renewable energy sources, renewable raw materials, and earth-abundant elements. However, to date many techniques have only been possible with the use of expensive precious metals or rare earth metals, the extraction of which can have serious environmental impacts. A team of researchers

including Professor Katja Heinze and Professor Christoph Kerzig of Johannes Gutenberg University Mainz (JGU) as well as Dr. Ute Resch-Genger of the German Bundesanstalt für Materialforschung und -prüfung (BAM) has now achieved a breakthrough in the use of chromium, an abundant base metal which Heinze's group has been investigating for some time.

The new findings show that chromium compounds, also called molecular rubies, can substitute expensive precious metals in photon upconversion. Photon upconversion (UC) is a process in which the sequential absorption of two photons of lower energy leads to the emission of one photon of higher energy. This higher energy photon can in principle be employed to expand the use of low-energy sunlight in solar cells or [photochemical reactions](#) which otherwise require UV light for activation. The use of molecular rubies can thus help to reduce the impact of environmentally damaging processes such as mining of precious metals or [rare earth elements](#) and to expand photochemistry to more sustainable processes.

Chromium compounds as a promising alternative

Most photochemical and photophysical applications such as phosphorescent organic light-emitting diodes, dye-sensitized [solar cells](#), or light-driven chemical reactions use precious metals such as gold, platinum, ruthenium, iridium, or [rare earth metals](#). However, precious metals are expensive because they are scarce while rare earth elements are only mined in a few countries, in China in particular. Furthermore, their extraction often involves considerable consumption of water, energy, and chemicals. In some cases, such as gold mining, highly toxic substances such as cyanide or mercury are employed.

On the other hand, resources of the metal chromium, which gets its name from the ancient Greek word for color, are 10,000 times more

plentiful in the Earth's crust than those of platinum and 100,000 times greater than those of iridium, meaning that it is available in sufficient quantities. "Unfortunately, the photophysical properties of abundant metals like chromium or iron are just not good enough to be useful in technological applications, especially when it comes to the lifetimes and energies of their electronically excited states," explained Professor Katja Heinze of JGU's Department of Chemistry. A significant progress in this regard has been made only in the last few years, with Heinze's team being one of the main contributors. They were also involved in the development of so-called molecular rubies. These are soluble molecular compounds which possess exceptionally good excited state characteristics. Molecular rubies have already been used as molecular optical thermometers and pressure sensors.

Direct observation of the energy transfer processes thanks to new large-scale laser device

The team of scientists from Mainz and Berlin has now achieved yet another breakthrough. "In the process, we observed a novel mechanism and understood the high efficiency of the new chromium compounds in detail," said Professor Christoph Kerzig. The scientists managed to directly observe the unusual energy transfer pathway using a laser setup recently installed in the Kerzig group. This so-called laser flash photolysis technique allowed them to detect all intermediates that are important for the upconversion mechanisms. Furthermore, quantitative laser experiments established the absence of inherent energy loss channels and side reactions, which lays the grounds for efficient applications of this underexplored way to transfer and convert solar energy with chromium compounds.

Consequently, scientists may be able to develop new light-driven reactions using the common [metal chromium](#) in the future instead of

using the rare, more costly ruthenium and iridium compounds, which today are still the most frequently used. "Together with our partners at BAM in Berlin and other universities we will continue to push on with our efforts to develop a more sustainable photochemistry," said Professor Katja Heinze.

The group's results have been published in *Angewandte Chemie*.

More information: Cui Wang et al, Efficient Triplet-Triplet Annihilation Upconversion Sensitized by a Chromium(III) Complex via an Underexplored Energy Transfer Mechanism, *Angewandte Chemie International Edition* (2022). [DOI: 10.1002/anie.202202238](https://doi.org/10.1002/anie.202202238)

Provided by Universitaet Mainz

Citation: A novel path for sustainable photon upconversion with non-precious metals (2022, June 3) retrieved 10 July 2024 from <https://phys.org/news/2022-06-path-sustainable-photon-upconversion-non-precious.html>

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