The activation of chemical reactions by visible light has attracted much interest over recent years. There are two key reasons for this: 1) visible light has been recognized as an abundant source of energy and is therefore in line with current interests of developing sustainable chemistry, and 2) visible-light activation provides a convenient tool for triggering single-electron transfer (redox chemistry) under mild conditions, thereby allowing exploitation of the useful reactivity of odd-electron species such as radical ions and radicals.

The group of Professor Eric Meggers at Philipps-Universität Marburg (Germany) has recently introduced a novel class of visible-light-activated asymmetric catalysts \((\text{Nature} \ 2014, \ 515, \ 100; \ \text{Chem. Eur. J.} \ 2015, \ 21, \ 7355)\). In this ‘2-in-1’ design, a single and structurally surprisingly simple catalyst serves simultaneously as a photosensitizer and asymmetric chiral Lewis acid catalyst.

Haohua Huo, the first author on this new publication, said: “At the onset of the current study, we were seeking a useful application to demonstrate the merit of our asymmetric photoredox catalyst design and this culminated in the development of an enantioselective, catalytic trichloromethylation through visible-light-activated photoredox catalysis.” Their study was also inspired by elegant work from the Zakarian lab, which developed a diastereoselective redox-mediated haloalkyl radical addition to metal enolates (e.g. \(\text{J. Am. Chem. Soc.} \ 2010, \ 132, \ 1482\)).

Concerning the reaction mechanism, Professor Meggers explained: “The proposed mechanism involves the framed key intermediate iridium(III) enolate complex (Scheme), which is supposed to act as the chiral reaction partner for the electron-deficient trichloromethyl radical and, simultaneously, as the active photosensitizer.” Thus, according to Professor Meggers, the active photosensitizer is generated by coordination of the deprotonated substrate to the catalyst. This in situ assembly of the active photosensitizer is supported by a number of investigations, such as cyclovoltammetry and luminescence-quenching experiments. Professor Meggers continued: “This process can be classified as an electron-transfer-catalyzed reaction. It is overall redox-neutral. The role of an electron as a catalyst has been discussed recently by Studer and Curran (\(\text{Nat. Chem.} \ 2014, \ 6, \ 765\)).”

Professor Meggers remarked: “The use of light produces a complete switch in the reaction mechanism! When executed in the dark, a bromination product is formed, but in the presence of light only the trichloromethylation occurs.” A typical reaction setup is shown in the Figure, just to demonstrate that the equipment is available in every lab.

The enantioselectivities of this process are very high, in several cases ≥ 99%. The group found this to be intriguing, considering that the reaction proceeds through intermediate reactive trichloromethyl radicals. Furthermore, it demonstrates that the catalyst, in which the chirality is exclusively based on metal centrochirality, is configurationally absolutely stable.
Scheme: Plausible mechanism for a combined photoredox and asymmetric catalysis with a chiral iridium Lewis acid photoredox sensitizer; light source: 20 W compact fluorescent lamp (CFL)
under the reaction conditions, something the group was not sure about at the onset of this project.

Professor Meggers concluded: “Looking from the viewpoint of the catalyst, we find it fascinating that the metal center serves multiple functions at the same time: it constitutes the exclusive center of chirality (only achiral ligands!), the catalytically active Lewis acid center, and additionally functions as the key component of the photosensitizer.”

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Eric Meggers was born and raised in Bonn (Germany). He received his Diploma in chemistry from the University of Bonn (Germany) in 1995 and a Ph.D. from the University of Basel (Switzerland) in 1999, under the guidance of Professor Bernd Giese. After postdoctoral research with Professor Peter G. Schultz at the Scripps Research Institute (La Jolla, USA), he became in 2002 an Assistant Professor in the Department of Chemistry at the University of Pennsylvania (USA). Since 2007, Eric Meggers has been Professor at the Department of Chemistry of the University of Marburg (Germany) and currently holds a secondary appointment as Professor at the College of Chemistry and Chemical Engineering of Xiamen University (P. R. of China). His research program currently focuses on aspects of metal-centered stereochemistry for applications in the life sciences and asymmetric catalysis.