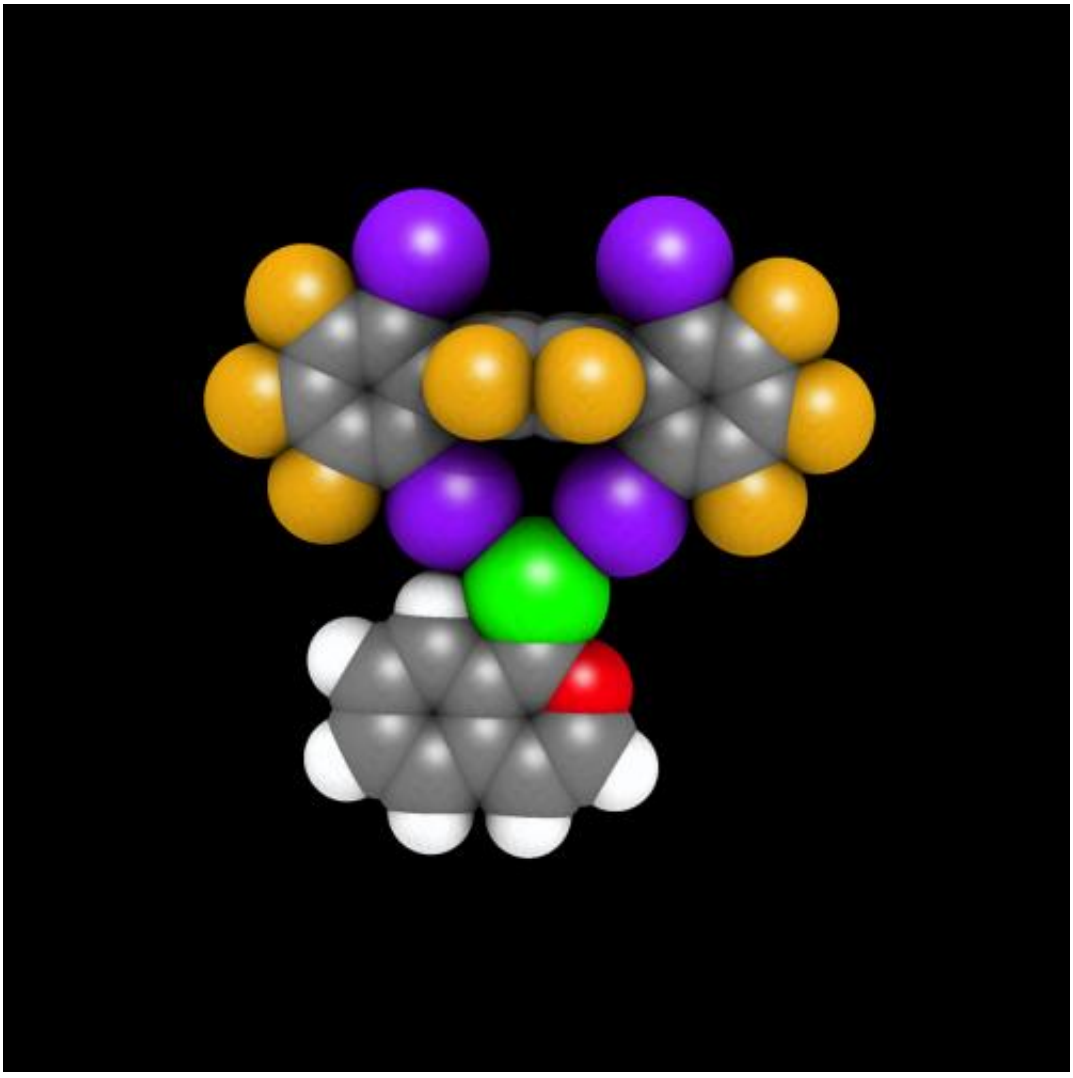
New catalyst class uses halogen bridges for environmentally friendlier production

September 12 2013



Halogen bridges of two iodine atoms (blue) loosen the chlorine (green)-carbon (gray) bond, helping to replace the chlorine with another building block. Credit: Stefan Huber / TUM

Catalysts are essential for the chemical industry because they accelerate reactions and increase their yields. However, many of today's catalysts are based on expensive and environmentally harmful metals. Stefan Huber and Florian Kniep from the Chair of Organic Chemistry at the Technische Universitaet Muenchen have now presented an alternative: Non-toxic compounds, so-called halogen bridge donors, can serve as organic catalysts. Evonik Industries AG awarded Florian Kniep their research prize for his work.

Ninety percent of all chemical products require catalysts in the course of their manufacture. They accelerate reactions and reduce the energy needed. Catalysts participate in reactions, but are not consumed. As a result one catalyst molecule can convert millions of substrate molecules, which explains the great economic value of catalysts.

Unfortunately, catalysts for organic reactions – for example, in plastics manufacturing – are often based on expensive and toxic heavy or transition metal compounds. Organic nonmetal catalysts pose a good alternative here.

Many such organocatalysts have so far been based on the Lewis acid/base principle: Strong positively polarized hydrogen atoms, so-called Lewis acids, interact via weak hydrogen bridge compounds with negatively polarized substrates, so-called Lewis bases.

Now a team of scientists headed by Stefan Huber, research group head at the Institute of Organic Chemistry at the Technische Universitaet Muenchen (TUM) and Florian Kniep, a doctoral candidate at the Institute of Organic Chemistry, is introducing a new type of organocatalyst: A so-called halogen bridge donor, which bonds to the substrate via a halogen atom, for instance an iodine atom.

The presence of one or more iodine atoms gives the halogen bridge-

based catalyst special properties that open up new avenues for application. According to a well-known chemical rule, so-called hard Lewis acids, which display low polarizability, interact best with similarly hard Lewis bases. This is the case for hydrogen bridge-based catalysts.

It works exactly the same the other way around: easily polarizable soft Lewis acids react best with soft Lewis bases. The new halogen bridge donors are precisely such soft Lewis acids, which makes them excellent catalysts for soft Lewis base substrates – an area that hydrogen bridge donors barely covered until now.

"In the long run we expect that halogen bridge-based organocatalysts and hydrogen bridge donors will complement each other," says Florian Kniep. "Besides, halogen bridges could prove to be useful for future enantioselective applications, where only one of two possible molecules is formed."

End of July Florian Kniep was awarded the research prize of Evonik Industries AG for his excellent work in the field of organocatalysis.

More information: Florian Kniep, Stefan H. Jungbauer, Qi Zhang, Sebastian M. Walter, Severin Schindler, Ingo Schnapperelle, Eberhardt Herdtweck und Stefan M. Huber: Organocatalysis by Neutral Multidentate Halogen-Bond Donors, *Angewandte Chemie* Int. Ed. 2013, 52, 7028-7032, DOI: 10.1002/anie.201301351

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Provided by Technical University Munich