Visible blue light induces copper-catalyzed C-N cross-couplings

February 12 2016, by Bob Yirka

(Phys.org)—A small team of researchers at California Institute of Technology has found a way to use visible blue light to induce copper-catalyzed C-N cross-couplings. In their paper published in the journal *Science*, the team describes the technique and why they believe the work may lead to bigger things. Michael Greaney with the University of Manchester offers a Perspectives piece on the work done by the team in the same journal issue outlining the process and explaining why the use of visible light to effect photochemical transformations has become so important in recent years.

One of the main parts of chemical research lies in discovering what happens when different chemicals come into contact with other chemicals—the reactions that occur can lead to the development of new products or a better understanding of how things work in the natural world. In recent years, chemists have begun to explore more fully the types of reactions that can occur when chemicals or substances are exposed to different kinds of light. Initially, such work focused more heavily on ultraviolet photochemistry, but as Greaney notes, such work requires specialized equipment—because of that, many chemists have begun to move their focus to using visible light to effect photochemical transformations. In this new effort, the researchers used the light from a blue LED to cause a C-N coupling to occur.

The researchers were focused on a class of biologically active molecules that contain chiral (asymmetric) carbon centers—in this case nitrogen-containing carbon centers. They were looking to solve one of the

problems of working with such molecules (their tendency to block or inhibit subsequent reactions), by combining base-metal catalysis, asymmetric synthesis and visible-light photoredox catalysis. Taking a cue from other research involving visible light, the team applied the light from a simple blue LED. They also noted that other experiments had involved noble metal complexes, which do the job well, but cost a lot—so they decided to go instead with copper salt. They found that the blue light was able to start the photoreduction of a substrate to form an alkyl radical via electron transfer. The result was the formation of a C-N bond.

The work done by the team is another step forward in finding simpler and cheaper ways to instigate reactions that can result in products such as those used in the pharmaceutical and materials industry.

More information: Asymmetric copper-catalyzed C-N cross-couplings induced by visible light, *Science* 12 Feb 2016: Vol. 351, Issue 6274, pp. 681-684, DOI: 10.1126/science.aad8313 , http://science.sciencemag.org/content/351/6274/681

Abstract

Despite a well-developed and growing body of work in copper catalysis, the potential of copper to serve as a photocatalyst remains underexplored. Here we describe a photoinduced copper-catalyzed method for coupling readily available racemic tertiary alkyl chloride electrophiles with amines to generate fully substituted stereocenters with high enantioselectivity. The reaction proceeds at –40°C under excitation by a blue light-emitting diode and benefits from the use of a single, Earth-abundant transition metal acting as both the photocatalyst and the source of asymmetric induction. An enantioconvergent mechanism transforms the racemic starting material into a single product enantiomer.