



The ability to hold a reaction in limbo to then start and stop it at will with an external stimulus is highly sought after. Light — being easy to control — is the ideal trigger and has the capacity to afford spatiotemporal control over a reaction. Potential applications for such a technology are many and varied, from the patterning of functional materials, to *in vivo* monitoring of biochemical reactions. Writing in the *Journal of the American Chemical Society*, Kyle Ruhl and Tomislav Rovis demonstrate, through investigations of light-gated, cobalt-catalysed [2 + 2 + 2] cycloadditions, just how powerful such a method can be.

Metal-catalysed cycloadditions are among the few direct methods to build arene rings from scratch. The convergent nature of cycloadditions is particularly attractive for the synthesis of functional materials. “We’ve had a long-standing interest in metal-catalysed cycloadditions, and while earlier work focused mostly on rhodium, cobalt is attractive from a sustainability standpoint and for its potential to interface with photoredox catalysis,” says Rovis.

Catalysis of [2 + 2 + 2] cycloadditions using cobalt carbonyls is well known; heat- or light-induced dissociation of a carbonyl ligand accelerates the reaction. A purely light-controlled cycloaddition, which can be switched completely on or off using only light, has proven more elusive. Ruhl and Rovis had initially planned to develop a simple reaction — the reduction of a Co(II) precatalyst to an active Co(0) species by photoactivated Ir(III) — such that light is only necessary for initiating the reaction. To their delight (and surprise), they discovered that the cycloaddition not only needs light to start it, but also needs it all the time to proceed. Indeed, theirs is a truly light-gated reaction, in which Co(0) must continually be regenerated. How this happens is not entirely clear, but it is proposed that the iridium catalyst fulfills two roles. It was initially expected that Ir(II) would reduce the Co(II) precatalyst to an active Co(0) species. The Ir(III) product, upon excitation, would then be converted back to the Ir(II) species by a sacrificial amine reductant. “After initial activation, the cobalt catalyst would cycle between

Co(0) and Co(II) with no further light being needed for the reaction,” explains Rovis.

The first of these steps — the reduction of Co(II) — fits the observed reactivity, but Ruhl and Rovis now suggest that photoexcited Ir(III) is reduced by a Co(II) species rather than the amine. Such a mechanism, in which cobalt exists in every oxidation state from 0 to +III, would account for the observed light-gated reactivity. “The need to maintain light irradiation for the reaction to proceed is stunning and, as it turns out, deeply enabling,” says Rovis.

To illustrate the utility of their reaction, Ruhl and Rovis prepared patterned polydimethylsiloxane (PDMS) surfaces. The PDMS was initially functionalized with a diyne and then treated with a solution containing an alkyne-appended fluorophore, in addition to the cobalt precatalyst and iridium photocatalyst. Irradiating the system with a blue light-emitting diode through a photomask, and then removing excess reagents, affords a surface patterned with excellent spatial resolution. The extent of patterning correlates directly with light exposure; when irradiation is performed using a greyscale mask, the surface is patterned to an intermediate degree.

Ruhl and Rovis plan to pursue new applications for the light-gated reaction they have discovered, but are also particularly interested in the reaction mechanism. “We have an on-going effort to gain a better understanding of how the photoredox catalyst enables and disables the reaction,” says Rovis. “We hope this will enable us to extend the reaction scope of the present catalyst system, as well as developing more efficient systems and even new reactions.”

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