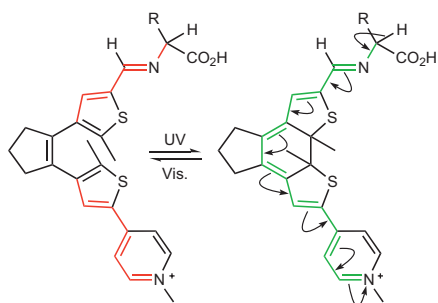


PHOTOCHEMICAL SWITCHES

Control of a cofactor

Angew. Chem. Int. Ed. **51**, 5431–5434 (2012)



Using an external stimulus to switch on and off the function of biomolecules such as enzymes is useful both in biomedical research and in the development of new therapies. The use of light as the stimulus is particularly attractive because it can be applied rapidly and in a spatially and temporally controlled manner. Modifying large, complex molecules such as enzymes can be difficult, and some researchers have moved towards producing light-regulated enzyme inhibitors.

Now, Danielle Wilson and Neil Branda from Simon Fraser University in Canada have developed an approach that involves preparing a photochemically controlled cofactor mimic. Some enzymatic cofactors are small organic molecules that are more easily amenable to the necessary modifications to make them responsive to a photostimulus. In addition, the same cofactor can be involved in many different enzymatic processes. This approach thus has the potential to be much more widely applicable.

Vitamin B₆ (pyridoxal 5' phosphate) is the cofactor that Wilson and Branda have chosen to mimic; it is involved in a range of enzymatic reactions and is also known to act as a catalyst alone. The key feature of the displayed activity is the through-bond electronic connection of an electron-withdrawing pyridinium with an aldehyde. In one example of its activity, the aldehyde forms a Schiff base (or imine) with an amino acid.

The electronic connection with the pyridinium enhances the acidity of the amino acid's α -hydrogen and facilitates racemization. To create their mimic, Wilson and Branda prepared a molecule in which

the well-known dithienylethene photoswitch separates the aldehyde and the pyridinium.

In the inactive form of the catalyst the aldehyde and pyridinium are 'insulated' from one another. Irradiation with UV light induces a ring-closing electrocyclic reaction that 'connects' the two groups. The ring-closed form of the catalyst was shown to catalyse the racemization of L-alanine. Irradiation with visible light causes ring opening and returns the catalyst to the inactive state, which is a poor catalyst for racemization. SD

ELECTROCATALYSIS

Lead lends a hand

J. Am. Chem. Soc. **134**, 8655–8661 (2012)

Platinum is a king among catalysts and it, along with its alloys, provides the benchmark for many reactions in the electrocatalysis community. One important use for platinum is in fuel cells, in which it can be employed to both oxidize the fuel of choice and reduce oxygen. Researchers have tried various methods to improve the properties of platinum-based catalysts and now a team led by Sanjeev Mukerjee from Northeastern University have shown how a

METAL-ORGANIC FRAMEWORKS

The big indoors

The free space inside metal-organic frameworks (MOFs) can be used to store small molecules, with much research effort devoted to gases such as carbon dioxide (for sequestration) and hydrogen (for energy-related applications). The sizes of the pores inside a MOF depend on a number of factors, including the nature of the building blocks, the way they connect together into a network, and whether these networks interpenetrate.

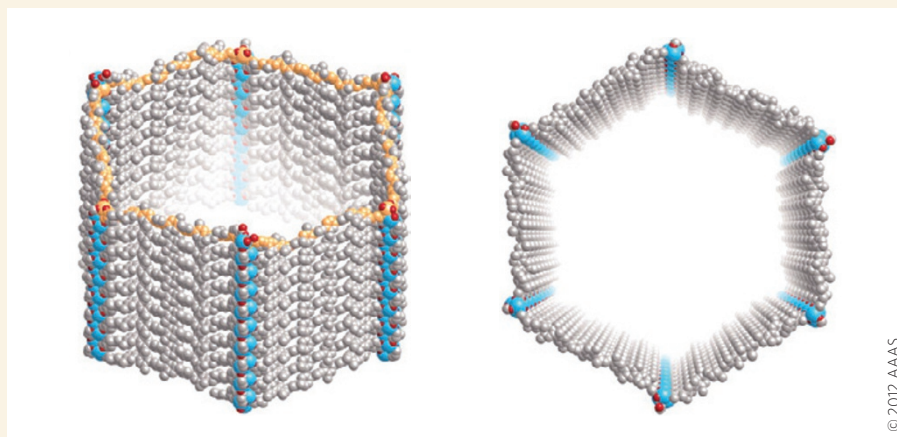
One way to increase the pore size, and thereby enable MOFs to trap larger guest molecules, is to increase the length of the organic linkers between the metal-based nodes. This is not a guaranteed strategy for success, however, because making the organic linker longer can lead to interpenetrated frameworks or structures that are quite fragile and prone to collapse.

Now, Omar Yaghi at the University of California Berkeley and a team of co-workers from around the globe have succeeded in making a series of robust MOFs in which the length of the organic linker is systematically increased from 7 to 50 Å. The starting point for the team was a well-known MOF in which

small metal clusters are linked into hexagonal sheets by single phenyl rings, each adorned with two carboxyl and two hydroxyl groups.

By increasing the number of phenyl rings in the linkers, MOFs with the same basic structure — but with much larger hexagonal channels — could be made. The longest linker comprised 11 phenyl groups connected in a row, and solubilizing hexyl chains were added at intervals along the backbone.

Science **336**, 1018–1023 (2012)



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The resulting MOF has a pore aperture measuring 98 Å (pictured) — the largest for any crystalline material reported so far.

The pore sizes found in this series of MOFs enable very large molecules to enter the void spaces found within. The MOF made from a linker with seven phenyl groups could accommodate myoglobin and the one built from a nine-phenyl linker could host green fluorescent protein. SC