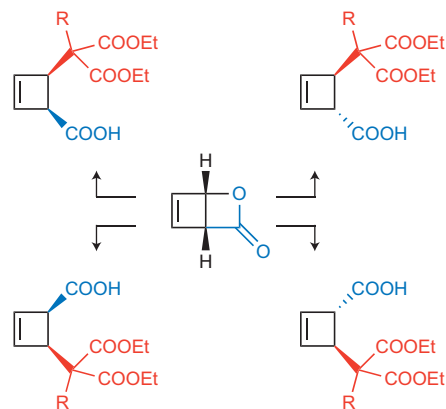


ASYMMETRIC CATALYSIS

Access all isomers

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201106321> (2011)



Synthetic routes to enantiopure compounds often rely on resolution methods — removing the unwanted enantiomer — which limit the theoretical yield to 50%. In contrast, deracemization processes convert a mixture of enantiomers to a single enantiomer of product. There are several different classes of deracemization processes, but all of

them rely on the transformations of a single stereocentre and thus provide access to only two possible products. Now, Nuno Maulide and co-workers from the Max-Planck-Institut für Kohlenforschung in Mülheim, Germany, have developed methodology that converts a racemic cyclobutene–lactone into any one of four diastereomeric disubstituted cyclobutene products. The conversion is highly selective and controlled by the choice of chiral ligand.

The methodology relies on a palladium-catalysed allylic alkylation (the Tsuji–Trost reaction) with a soft nucleophile. The expected mechanistic course of this type of reaction would be nucleophilic attack of the palladium catalyst on the lactone from the face opposite the carboxylate leaving group, resulting in ring opening and formation of π -allyl palladium species. In a second step, a soft nucleophile would be expected to attack the π -allyl from the face opposite the palladium. Such a double inversion leads to the *cis*-substituted product, and Maulide and co-workers could indeed make either enantiomer of this product using a chiral phosphoramidite ligand.

Using a phosphine–oxazoline ligand, however, resulted in the *trans*-product — again in highly selective fashion. Maulide

and co-workers identified four possible scenarios that might lead to this outcome, and ultimately conclude that it is the result of an unusual attack of palladium from the same face as the carboxylate leaving group in the first step of the reaction. SD

DYE-SENSITIZED SOLAR CELLS

Improving efficiency

Science **334**, 629–634 (2011)

The Sun bathes the Earth in enough energy to cover current global energy consumption around 8,000 times over, and with dwindling resources and environmental concerns, there is a great need for cheap and efficient methods for turning light into electricity. One system in particular, the dye-sensitized solar cell (DSC), has received much attention. DSCs have several components, which must all work together to convert incident light into a current. These include a photoexcitable dye, which transfers one of its electrons to a titania semiconductor during operation, and a redox mediator, which enables the dye to regenerate by supplying a replacement electron.

Conventionally the mediator is a triiodide/iodide (I_3^-/I^-) redox couple, but

MICROFLUIDICS

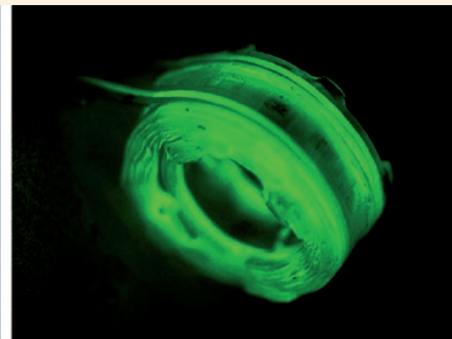
Bent into shape

Many microfluidic systems have been developed, but they are typically made in block-like geometries, rather than curved ones that would resemble the vascularized three-dimensional systems found in nature. David Gracias and co-workers from Johns Hopkins University in Baltimore have now prepared microfluidic networks that reversibly curve into complex structures.

The assembly relies on SU-8, a polymer that can be photo-patterned: UV irradiation, followed by a heating step, induces crosslinking. Non-irradiated regions remain free from crosslinks and are subsequently removed by an organic solvent. Through carefully controlled irradiation, the researchers created a gradient of crosslinking across the thickness of a planar SU-8 film. Once the solvent is removed, the less crosslinked side of the hydrophobic film undergoes a larger contraction than the highly crosslinked one, spontaneously bending the film. This process is reversible and reproducible, through successive de- and re-solvation



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with the original solvent. The curving can be precisely controlled by the UV exposure, film morphology and heating conditions, which enabled the researchers to assemble various differently curving segments into complex three-dimensional architectures.

These SU-8 films served as support layers for the organization of hollow channels of polydimethylsiloxane (PDMS) into three-dimensional bent geometries. Both materials are widely used

in microfluidics, making the resulting SU-8/PDMS networks well suited to fluid transportation. The transport of a green and a red dye (fluorescein and Rhodamine B, respectively) through a dual-channel cylindrical device was clearly observed by fluorescence. Furthermore, the devices are biologically inert and remain curved in cell culture media, which means they are promising for bio-applications. AP

Nature Commun. **2**, 527 (2011)