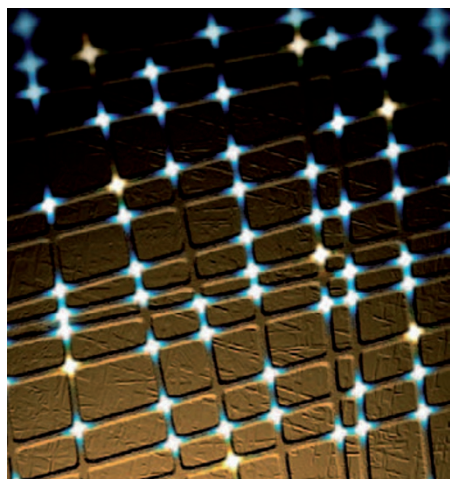


CHEMICAL SENSING

Attoreactor arrays

Angew. Chem. Int. Ed. <http://doi.org/c5ddsw> (2012)



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The ability to detect trace quantities of chemical entities is important in a wide variety of applications ranging from environmental monitoring to medical diagnostics. One approach to chemical sensing is to use sensor arrays that are capable of detecting — and distinguishing between — multiple analytes. Now, Pavel

Anzenbacher Jr and co-workers from Bowling Green State University in Ohio have made porous mats from polymer nanofibres that are able to identify metal cations in a qualitative and quantitative manner.

Anzenbacher and colleagues overlapped roughly perpendicular polymer nanofibres and formed junctions between them by exposing them to heat or a solvent. In these ‘attoreactor’ junctions, an oligoamine embedded in one nanofibre reacts with a fluorophore precursor impregnated in the other to form fluorescent probe molecules. By using large numbers of fibres embedded with different reagents (one of three different fluorophore precursors or one of three oligoamines of differing lengths), the Ohio team produced high-density arrays of attoreactors containing different fluorescent probes. When the arrays are exposed to different metal ions, the fluorescence of the probe molecules is either amplified or quenched to varying degrees.

Rather than reading out the response from each individual attoreactor, the fluorescence of the mat is recorded as a whole, and statistical methods can be used to determine the accuracy of the array in discriminating between the various analytes — with the ten different metal ions used in this study, 100% accuracy was observed. SC

ATMOSPHERIC CHEMISTRY

Important intermediates

Science **335**, 204–207 (2012)

The reactions of atmospheric ozone are of great importance to our understanding of the complex network of chemistry above and around us. The ozonolysis of alkenes, oxidizing them across the C=C double bonds and splitting them apart, is known to occur through a ‘Criegee intermediate’: a carbonyl oxide biradical species, R₂COO. Direct measurements of the reaction kinetics of gas-phase Criegee intermediates have been difficult to obtain, however, and until now researchers have had to make do with indirect measurements of the products of ozonolysis reactions, which are difficult to interpret.

Now, Craig Taatjes at Sandia National Laboratories and colleagues have directly measured the kinetics of several important reactions involving the elusive Criegee intermediate by making use of the reaction of O₂ with the CH₂I radical (created through the photolysis of CH₂I₂). One of the products of this reaction is the Criegee radical CH₂OO, the concentration of which decays through various subsequent reactions. Taatjes and colleagues measured this decay by generating time-resolved mass spectra

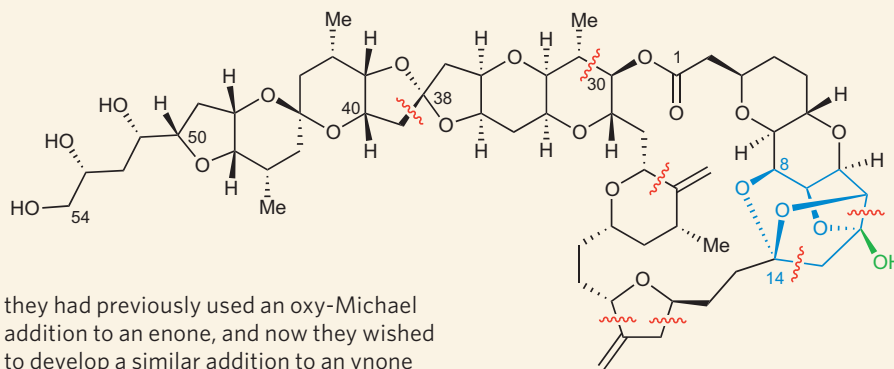
NATURAL PRODUCT SYNTHESIS

The halichondrin C campaign

J. Am. Chem. Soc. **134**, 893–896 (2012)

Halichondrin C (pictured) is a polyether macrolide whose isolation from a marine sponge was first described in the mid-1980s. Thanks to the work of Yoshito Kishi and co-workers from Harvard University, it has now succumbed to total synthesis. The total synthesis of another family member — halichondrin B, which lacks the hydroxyl group highlighted in green — was reported by Kishi and co-workers almost 20 years ago. Biological testing showed that the right-hand side of the molecule was most important for its anticancer properties — knowledge that eventually led to the development of the drug Halaven (Erbulin) which is used to treat metastatic breast cancer.

The key to the synthesis of these molecules was always the construction of the C8–C14 polycycle, highlighted in blue. Kishi and co-workers planned to use a method analogous to that used in their halichondrin B synthesis. Specifically,



they had previously used an oxy-Michael addition to an enone, and now they wished to develop a similar addition to an ynone — a strategy that, if successful, might be suited to the synthesis of halichondrin A as well. The ynone Michael addition worked but was followed by a second, unplanned, oxy-Michael addition to the resulting enone. The researchers were, however, able to convert this to the polycycle found in halichondrin C using a Lewis-acid-mediated isomerization. SD

Kishi and co-workers used some of the building blocks developed in their previous work (C14–C38 and C39–C54), but improved the synthesis along the way. They were able to use a chromium/nickel-mediated coupling to form no fewer than seven C–C bonds of the target (disconnections shown in red). SD