

## CHEMISTRY

### Radical Ring

Charge transport in conjugated  $\pi$ -bonded carbon frameworks is central to the operation of organic photovoltaic systems. Multiple studies have therefore probed the role of charge delocalization in facilitating this process. Kayahara *et al.* examined a simple model system, [8]cycloparaphenylene, in which eight phenyl rings are bound to one another at the para positions to form a loop. Applying one equivalent of nitrosyl hexafluoroantimonate as an oxidant stripped one electron from the compound, whereas five equivalents cleanly stripped two. Spectroscopic analyses by electron spin resonance (for the radical monocation) and nuclear magnetic resonance (for the dication) were consistent with complete spin and charge delocalization throughout the loop. Both salts were also relatively stable under a nitrogen atmosphere. The dication was characterized by x-ray crystallography and manifested a belt geometry, with a coplanar arrangement of all the constituent phenyl rings normal to the loop plane. — JSY

*Angew. Chem. Int. Ed.* 52, 10.1002/anie.201306881 (2013).

## CANCER

### Resistance, Gene by Gene

About half of melanoma patients harbor an identical tumor-specific mutation in the *BRAF* gene, which encodes a protein kinase that helps drive cell growth. One of the most exciting recent advances in clinical cancer research was the discovery that this subgroup of patients respond—sometimes dramatically—to a new class of drugs targeting the MAPK pathway through which *BRAF* signals. Unfortunately, in most patients the melanoma recurs within a year because the tumor cells develop drug resistance. Understanding the mechanisms by which resistance arises is essential for optimizing the clinical benefits of these drugs.

Johannessen *et al.* used a highly systematic approach to identify candidate genes and signaling networks that contribute to resistance. After exploiting a technology that allowed them to activate each of nearly 16,000 genes individually in human melanoma cell lines containing mutant *BRAF*, the authors then treated the panel of cells with the drugs and monitored which cells showed altered drug sensitivity. Among the unexpected “hits” revealed by this assay were

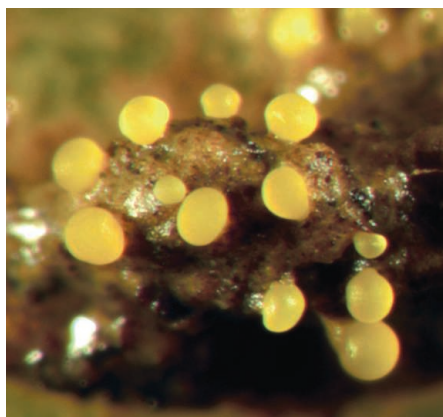
a cyclic AMP signaling network and a group of transcription factors important in melanocyte development, each suggesting potential new strategies for overcoming resistance. — PAK

*Nature* 10.1038/nature12688 (2013).

## CELL BIOLOGY

### Playing Kissy with the Relatives

Our understanding of how bacteria actually respond to their natural environment is sparse. Individual cells of several groups of bacteria co-



operate to form multicellular fruiting bodies, but how do they select with whom to cooperate and avoid freeloaders or predators? Pathak *et al.* have discovered that when they cooperate, cells of the social bacterium *Myxococcus xanthus* exchange large quantities of membrane material. First, however, these cells want to know with whom they are getting intimate. It turns out that a polymorphic surface receptor, TraA, encodes a spectrum of receptors that can spot degree of relatedness via degree of affinity for the cognate Tra pair on other cells encountered. If close relatives are rare in the environment, this mechanism allows a less-related cell in the neighborhood to be selected as a stopgap that will cooperate enough to allow some form of multicellular reproductive structure to be built. — CA

*PLOS Genet.* 9, 10.1371/journal.pgen.1003891 (2013).

## MOLECULAR BIOLOGY

### Bridging the Genome

Alternative splicing is one means by which the genome is able to generate functional diversity through the differential expression of transcripts, but the regulation and process of how transcripts become alternatively spliced are not well understood. Lovci *et al.* examined the Rbfox family of RNA-binding proteins with cross-linking immunoprecipitation and sequencing (CLIP-seq) and demonstrated that binding sites are conserved within mammalian genomes and that Rbfox clusters tended to be within distal introns (more than 500 nucleotides away from annotated exons). These clusters were determined to be associated with alternatively spliced exons, with downstream clusters correlating with inclusion of an exon and upstream clusters correlating with the exclusion of the exon. Mutation of Rbfox binding sites in vitro demonstrated that these proteins function in alternative splicing and that conserved RNAs with specific secondary structures bridge the exons that are alternatively spliced. On the basis of these results, the authors propose that a distal binding site of Rbfox proteins is brought into the vicinity of the exon via an RNA bridge. — LMZ

*Nat. Struct. Mol. Biol.* 10.1038/nsmb.2699 (2013).

## ARCHAEOLOGY

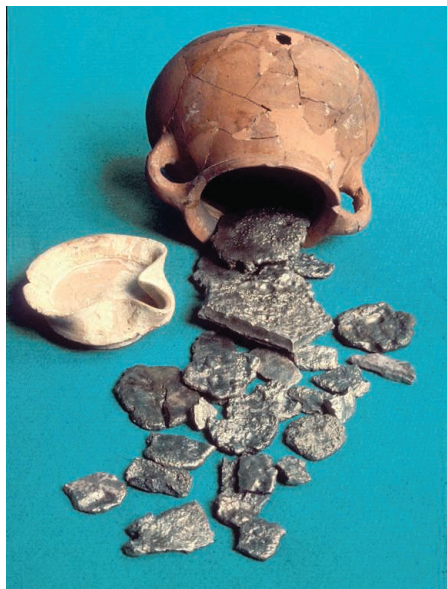
### King Solomon's Silver

Isotope analysis of archaeological materials can play critical roles in both dating of the artifacts and identification of their origin. Thompson and Skaggs use the lead isotope ratios in silver from

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silver hoards to investigate trade patterns during a Mediterranean "Dark Age" between 1200 and 800 BCE precipitated by the collapse of palace-based economies in the Near East. Lead isotope analysis of 48 precoinage silver artifacts from what was southern Phoenicia [the region between the Yarkon River and Akko (Acre) in present-day Israel] and dated from 1200 to 800 BCE shows that they have isotope ratios similar to those of galena (the mineral form of lead sulfide) and other lead ores from southern and



southwestern Sardinia, and the Iberian Peninsula. These analyses tentatively identify regions in the western Mediterranean as contributing mineral resources to Phoenician precolonial silver trade and production. The results correlate with ancient documentary sources indicating Phoenician precolonial silver trade with Sardinia and Spain and suggest that the Phoenician precolonial expansion into the west may have involved the acquisition of silver. Thompson and Skaggs further support suggestions that the legendary Tarshish region, a possible source of King Solomon's silver, may have been a refinery town, possibly Nora, on Sardinia. — GR

*Internet Archaeol.* **35**, 10.111141/ia.35.6 (2013).

## CHEMISTRY

### Pressuring CO<sub>2</sub> to React

One sustainable approach for converting CO<sub>2</sub> from large-scale industrial production processes into chemicals and fuels is by reacting it with hydrogen generated from solar or wind energy. The catalytic hydrogenation of CO<sub>2</sub> into methanol offers a potential route for conversion, but most commercial catalysts, which use copper

and zinc oxide supported on alumina and operate at pressures of 50 to 100 atm, have low single-pass conversions and require product separation and reactant recycling. Bansode and Urakawa, noting that high pressures thermodynamically favor the methanol product, studied this reaction on such catalysts at higher pressures. They could boost single-pass conversions to >95% at 355 atm and 260°C and at high H<sub>2</sub> partial pressures (H<sub>2</sub>/CO<sub>2</sub> ratios > 10:1). These conditions should suppress formation of CO as a final product, but the increasing conversion for methanol as temperature was increased to 260°C suggests that the reaction proceeds initially through reduction to CO. This reaction is endothermic and competes with exothermic methanol synthesis. They also show that addition of a solid acid catalyst, H-ZSM-5, as a physical mixture led to the single-pass production of dimethyl ether with selectivities of >80%; when this catalyst was added in a second series reactor, light alkanes or propylene could be produced as well. — PDS

*J. Catal.* **309**, 66 (2014).

## CLIMATE SCIENCE

### Forward into the Past

It has been well established that high concentrations of atmospheric CO<sub>2</sub> caused by anthropogenic emissions will persist for thousands of years after those emissions cease and that the consequences for climate will last even longer than that. Suggestions have been made that CO<sub>2</sub> could be removed from the atmosphere artificially in order to speed global climate recovery, but what can be expected from such a capture scheme? MacDougall uses a climate model of intermediate complexity, employing scenarios of CO<sub>2</sub> removal that move from the more idealized schemes used in past studies toward more realistic ones, in order to continue refining our understanding of what would be the effects of such an undertaking. He finds that by assuming a moderate value of climate sensitivity and that CO<sub>2</sub> is removed from the atmosphere as fast as it was added once emissions cease, surface air temperatures like those of preindustrial times can be approached by the year 3000 CE in all but the most extreme emission scenarios. Other components of the climate system, such as mass of the polar ice sheets, and sea level, will take longer to recover, however. So, even if we dial back atmospheric CO<sub>2</sub> concentrations by massive geoengineering, we will be living with the effects of fossil fuel burning for many hundreds of years, at the least. — HJS

*Geophys. Res. Lett.* **40**, 5480 (2013).

## Pressuring CO<sub>2</sub> to React

Phil Szuromi

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