FINDING FLUORIDE VIA ELECTRON TRANSFER

With the help of an unusual anion-π orbital interaction, scientists have created a chemical sensor that changes color in the presence of fluoride (J. Am. Chem. Soc., DOI: 10.1021/ja107382x). The sensor molecule could be used to detect fluoride in drinking water and consumer products, as well as in bone and muscle tissue for the early detection of fluoride-related diseases. The new sensor, developed by Florida State University’s Sourav Saha and Samit Guha, makes use of a π-electron-deficient naphthalene diimide (NDI) receptor. Strong interactions between fluoride’s lone pair of electrons and NDF’s π-orbitals lead to an unprecedented F⁻ to NDI electron-transfer event, which produces an orange NDI radical anion. Additional fluoride reduces the sensor to a pink NDI dianion. The sensor is specific for fluoride and remains colorless in the presence of other anions, such as chloride or iodide. “The selectivity and reusability of NDI-based sensors distinguish them from existing fluoride sensors,” Saha notes. By tethering two NDI moieties together in overlapping positions with intramolecularly hydrogen-bonded folded polyamide linkers, Saha and Guha were able to push the sensor’s sensitivity into the nanomolar range.—BH

METAL-METHANE INSERTION MILESTONE

Researchers at the University of Arizona led by Lucy M. Ziury have captured the first detailed structure of a molecule formed by insertion of a transition metal into a C–H bond of methane (J. Am. Chem. Soc., DOI: 10.1021/ja106121w). The achievement gives new insight into the mechanisms of catalytic C–C and C–H bond activations that are important in organic synthesis. Scientists have previously tried multiple approaches for obtaining a structural snapshot of metal-methane insertion complexes. These efforts have been limited until now to photochemical reactions in low-temperature inert-gas matrices or gas-phase molecular beam experiments, which can help researchers tell that metal insertion has taken place but can’t provide exact structural details about the insertion products. Ziury and coworkers produced HZNCH₃ in the gas phase by reacting Zn(CH₃)₂ with H₂ and CH₄ in an electric discharge or by reacting zinc vapor with CH₄ in an electric discharge. The researchers determined HZNCH₃’s precise structure by examining zinc, carbon, and hydrogen isotopic variations in high-resolution rotational spectra recorded using a combination of microwave spectroscopy techniques. They found that HZNCH₃ is relatively stable, has covalent H-Zn and Zn-C bonds, and likely forms by direct Zn insertion into a C–H bond rather than first forming ZnH or ZnCH₃ species.—SR

WATER INFLUENCES AMYLOID AND PRION AGGREGATION RATES

When aggregation occurs in aqueous solution between amyloid or prion peptides—which are associated with protein-misfolding diseases—a dry interface between the biomolecules forms in two different ways, suggesting how aggregation rates might differ substantially (Proc. Natl. Acad. Sci. USA, DOI: 10.1073/pnas.1008616107). Theoretical models of aggregate formation created by Govardhan Reddy and Devandraj (Dave) Thirumalai of the University of Maryland and John E. Straub of Boston University show that when amyloid β peptide aggregates, fibril formation and expulsion of water from between the joining peptides occur virtually simultaneously. But when the more polar peptides from the yeast prion Sup35 aggregate, long-lived strings of water molecules called “water wires” form in the interface and have to be squeezed out for the dry interface to form, a process that takes additional time. Because of the different dewetting time-

KINASE’S OSCILLATORY BEHAVIOR CONTROLS CELL SIGNALING

A key protein kinase enzyme participates in unusual oscillatory behavior that represents a new mechanism of signal transmission in cells. Andre Levchenko, Jin Zhang, and coworkers at Johns Hopkins University School of Medicine monitored signaling activity with fluorescence and used mechanistic modeling to show that protein kinase A, which helps regulate insulin secretion, calcium influx, and other important cellular processes, forms an oscillatory signaling circuit with cyclic adenosine monophosphate and Ca⁺⁺ in insulin-secreting cells (Nat. Chem. Biol., DOI: 10.1038/nchembio.478). The circuit integrates diverse input signals by transducing them into different oscillatory frequencies and amplitudes, resulting in changes in cellular function. The study shows “that oscillatory patterns of activation allow protein kinase A to exercise effective spatially localized signaling control scales of the amyloid and prion processes, “we surmise that amyloid fibrils can form nearly 1,000 times faster than prion fibrils,” the researchers write. The study elucidates “the role of water in amyloid fibril assembly and also points the way toward studying water in quasi-one-dimensional confinement,” comments theoretical biophysicist Gerhard Hummer of the National Institutes of Health.—S8