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Spotlights on Recent *JACS* Publications

TWIST IN DONOR–ACCEPTOR DYAD EXTENDS CHARGE SEPARATION LIFETIME

Molecules that produce charges when excited by light are useful for a variety of organic electronic applications. To maximize the utility of these molecules, researchers work to keep the induced charges separate for as long as possible. Stacking the excitable molecules can extend the charge lifetime, but often the donor and acceptor parts of the molecule naturally alternate in the stack, which causes the charges to immediately recombine.

Mahesh Hariharan and his colleagues aim to minimize charge recombination by separating the donor and acceptor portions of the molecule on different spatial planes (DOI: 10.1021/jacs.5b08257). They have synthesized a naphthalimide-naphthalene dyad where the donor and acceptor units are twisted into different planes. The twisted monomers also assemble into a stacked tower. When illuminated by ultraviolet light, the charge separated state of the stack can last more than 1.2 ns, 10,000 times longer than in the monomeric dyad. This molecule could be a novel scaffold for light harvesting, molecular electronics, or new light-induced electronic applications.

Melissae Fellet, Ph.D.

ELECTRIFYING NEW MECHANISM TOWARD DIRECT H_2O_2 SYNTHESIS

Hydrogen peroxide (H_2O_2) is an environmentally friendly alternative to chlorinated oxidizers. It can be used to selectively oxidize organic molecules, bleach pulp and paper, and treat wastewater, leaving behind just H_2O and O_2 as byproducts. However, H_2O_2 cannot compete financially with these other reagents because of the costly and energy-intensive separation and concentration steps currently involved in its synthesis. Although direct synthesis that combines H_2 and O_2 would be an ideal method, uncertainty over its molecular-level mechanism has hampered rational design of new catalysts.

In a new study, Neil Wilson and David Flaherty suggest a mechanism to explain H_2O_2's direct synthesis, in which this compound forms through an unexpected electrochemical method despite the absence of an electrical potential (DOI: 10.1021/jacs.5b10669). Heterolytic H_2 and O_2 redox reactions occur simultaneously on individual palladium clusters. The authors propose that H_2O_2 forms through sequential proton–electron transfer to O_2 and OOH surface intermediates, competing with H_2O synthesis by oxygen–oxygen bond rupture within OOH surface species. This knowledge, they say, explains why the process can be skewed toward selectively generating more H_2O_2 by using larger palladium clusters and acidic solvents that can serve as proton donors and stabilize charge transition states. Such knowledge can help in tweaking the current catalysts, they say, and could lead to more efficient and cost-effective H_2O_2 production.

Christen Brownlee

CRACKING THE COMMON CORE OF COMPLEX ALKALOIDS

Sergey Pronin and co-workers develop a concise strategy for synthesis of the paxilline family of indole diterpenes, a class of diversely bioactive fungal metabolites (DOI: 10.1021/jacs.5b11129). Since 1985, the quest for their total syntheses has proven onerously challenging because of the stereochemical complexity in a common pentacyclic core shared by over 80 congeners found so far.

The terpenoid core features a *trans*-hexahydroindene unit containing vicinal quaternary stereocenters that the authors choose to address first. From a cyclopentanone-derived dialdehyde, they build the tricyclic motif through radical–polar crossover cyclization, initiated by iron-mediated chemoselective hydrogen atom transfer and followed by a radical addition to an electron-deficient alkene. Subsequent aldol reaction completes construction of the desired polycyclic fragment. To achieve high levels of stereocontrol, the authors use a transient intramolecular tether that takes advantage of the innate indole functionality of the target terpenoids.

Facile assembly of the polycyclic core can dramatically shorten the synthesis of paxilline indole diterpenes, as demonstrated by the 11-step access to (±)-emindole SB, the simplest member in the family. This elegant design will likely lend itself to the divergent synthesis of additional derivatives, unnatural analogues, and other families of terpenoid natural products.

Xin Su, Ph.D.

BEST SUPPORTING ROLE: CATALYST SUPPORT ROLE ELUCIDATED

Xavier Carrier and co-workers have identified the role of the catalyst support—the high surface area material to which a heterogeneous catalyst is affixed—for an important group of hydrotreating catalysts (DOI: 10.1021/jacs.5b10975). These hydrotreating catalysts are a group of transition metal (e.g., molybdenum) sulfide materials commonly used to remove contaminants from crude oil, but a fine control of the structure and composition of these industrially important catalysts remains a challenging task.

When synthesizing and evaluating heterogeneous catalysts to maximize their performance, researchers typically optimize many variables, such as catalyst design and composition. In this experimental and theoretical study, Carrier and colleagues have examined the role of the oxide support.

The work uses a practical, aqueous-phase surface science approach in order to show support-dependent variation in molybdenum disulfide structure. The findings reveal that controlling the support morphology may be even more important for molecular-scale design of this class of hydrotreating catalysts than previously reported synthesis methods that rely, for example, on the use of organic additives to modify the structure of molybdenum disulfide.

Dalia Yablon, Ph.D.

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