

Spotlights on Recent JACS Publications

■ SYNTHETIC PORPHYRIN DISRUPTS LOCAL AROMATICITY OF NAPHTHALENE

A conventional porphyrin is a fully conjugated macrocycle of four pyrroles separated by carbon atoms called meso carbons. In order to study molecules with unique aromaticity or metal coordination abilities, scientists may use synthetic porphyrins, made by modifying known porphyrins or by directly replacing one of the pyrrole rings with new building blocks during synthesis. Such porphyrin analogues are in demand, and their syntheses can present significant challenges.

Dong-Gyu Cho, Hiroyuki Furuta, and their colleagues report the synthesis of a new porphyrin, meso-fused carbaporphyrin, using 2-(naphthalen-1-yl)thiophene to replace two of the pyrroles and one meso-carbon (DOI: [10.1021/jacs.6b01063](https://doi.org/10.1021/jacs.6b01063)). By design, the naphthalene ring is in the same plane as the rest of porphyrin.

¹H NMR spectroscopy shows that the global aromaticity of the porphyrin macrocycle clearly disrupts the 10π local aromaticity of the naphthalene ring. This observation is the first time that a large conjugated system has been shown to disrupt local aromaticity larger than 6π electrons. The authors conclude that this synthetic approach and the resulting unique aromaticity “could be applied to understand other π -conjugation pathways and obtain new macrocycles”.

Melissae Fellet, Ph.D.

■ A NEW VIEW OF CONDENSED-PHASE REACTIVE INTERMEDIATES

In their recent Perspective, Carpenter, Harvey, and Orr-Ewing give an overview of the latest developments in experimental and computational methods for studying reactive intermediates in solution (DOI: [10.1021/jacs.6b01761](https://doi.org/10.1021/jacs.6b01761)). The behavior of reactive intermediates in condensed phases is less well understood than in the gas phase, in part because their transient existence may not permit them to reach equilibrium with their surroundings.

Until recently, reactive intermediates have typically not been directly observable, and so interpretation of their behavior has depended on fitting theoretical models to indirect observations. The authors highlight limitations of these models by presenting findings from newly developed experimental techniques, which do not allow direct detection of reactive intermediates. Experimental data about energy exchange between transient intermediates and the solvent, and about solvent reorganization during a reaction, are becoming available. Time scales for both phenomena are often revealed to be significantly longer than most models had assumed. Simulations that correctly model the energy flow come to similar conclusions, and show results in much better accord with experiment.

Experiments that can directly image interactions between reactive intermediates and surrounding solvent are on the horizon. Meanwhile, improved solvent models will be required, especially to describe short-time nonequilibrium interactions of reacting solutes with the surrounding solvent.

Xin Su, Ph.D.

■ RADICAL BONDING OPENS WINDOW TO MOLECULAR ELECTRONICS

Miniaturizing computers well beyond today's capabilities will require building not with small materials, or even nanomaterials, but with molecules. Molecular electronic devices promise miniaturization, high speed, and low power usage, but fabrication and stability remain significant hurdles. The key to making practical devices may lie in a better understanding of intrinsic material properties. In particular, electronically stabilized phenalenyl radicals are attractive candidates with great research interest, but these are notoriously difficult to create and study.

Here Miklos Kertesz, Takashi Kubo, and their colleagues present the first in-depth examination of a phenalenyl radical derivative with fluxional—or rapidly changing—electron arrangement and bonding (DOI: [10.1021/jacs.6b01791](https://doi.org/10.1021/jacs.6b01791)). Theoretical and experimental investigations reveal competing, nearly energy equivalent electron bonding configurations, which lead to continuous bond dissociation and re-formation.

Much work has focused on understanding the basis for the unusual behavior observed in these materials, but until now researchers have not been able to expose and measure the relative preferences of competing bonding pathways. This work helps to break through a fundamental barrier to the practical use of these materials as components in devices that require unusual electronic, optical, and magnetic properties.

Jenny Morber, Ph.D.

■ MOLECULAR ROTORS FORM WIGGLY CRYSTALS

Scientists envision molecular machines that repair cells, transport tiny cargo, and store information, among other tasks, and building the parts is the first step toward this goal. To develop rotating components for molecular machines, a team led by Miguel Garcia-Garibay and K. N. Houk has designed and synthesized a single-molecule rotor modeled on gyroscopes (DOI: [10.1021/jacs.6b01398](https://doi.org/10.1021/jacs.6b01398)). This molecule is larger than previously designed rotors, and a step forward toward the size range of biomolecular machines, such as the rotary enzyme responsible for the synthesis of ATP. The new molecular rotor is shaped like a dumbbell, with two highly branched arms ending in aromatic fingers reaching out from an aromatic core.

The researchers crystallize the molecule and characterize it with X-ray diffraction and solid-state ²H NMR experiments, finding an unusual, loosely packed structure. Normally, crystals and their constituent molecules are fairly static. Yet, the molecular rotor forms amphidynamic crystals, which are both ordered and mobile. The crystal's low-density environment gives each aromatic group in the molecular rotor the elbow room for fast rotation about its axis. The novel crystal properties are important for the development of molecular machines, which need to strike the right balance between order and motion.

Erika Gebel Berg, Ph.D.

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