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Spotlights on Recent *JACS* Publications

SINGLE-STEP SYNTHESIS OF NONCLASSICAL NANOTUBE END-CAPS

Their unique physical properties and potential applications have fueled a phenomenal amount of research directed toward carbon nanotubes, and in particular their use in energy storage, microelectronics, and biomedical devices. The biggest limitation is the challenge of producing this nanomaterial in perfect uniformity. One strategy to overcome this problem is to use carbon nanotube end-caps—usually curved polycyclic aromatic hydrocarbons—as potential seeds for the controlled growth of carbon nanotubes. However, current methods for end-cap synthesis involve many steps and are very costly. Now, Marcin Stępień and co-workers report a solution-based synthesis of heteroaromatic nanotube end-caps in a single step (DOI: 10.1021/ja511951x).

The researchers combine a self-templated method with an intramolecular nickel-mediated homocoupling reaction to construct a new carbon nanoring from dibromo starting materials. The method represents a new strategy for concise preparation of complex aromatic structures from simple starting materials and, when coupled with a cap removal process, can be a powerful size-selective route to hoop-shaped molecules. It may be used to construct 3D π-conjugated porous structures, which are of great interest as prospective receptors and materials for organic electronics.

Lingling Chen, Ph.D.

SELF-ASSEMBLING CARBOHYDRATES TRAP CANCER CELLS IN A CAGE

Ricardo Pires, Rein Ulijn, and colleagues have designed a carbohydrate-based molecule that can surround and strangle bone cancer cells by self-assembling into a tangled web of nanofibers (DOI: 10.1021/ja5111893). The molecule spares healthy cells because its assembly is triggered by an enzyme that is overexpressed on cancer cells.

In nature, many of the body's cells are enmeshed in a complex web of biomolecules that provides structure for tissues, facilitates intercellular communication, and traps nutrients. Here, the researchers seek a carbohydrate-based molecule that would self-assemble into simpler yet structurally diverse versions of this matrix.

To test the molecule's cancer-killing prowess, the researchers add it to cultures of bone cancer cells as well as to normal cartilage cells, which have only about 5% of the alkaline phosphatase activity observed in the cancerous ones. After 7 h, about 95% of the bone cancer cells have died, while only 15% of the cartilage cells die.

Scanning electron microscope images of the cells reveal a cage-like hydrogel on the surface of the bone cancer cells. Although the mechanism of cell death remains unknown, the authors suspect the nanofiber cage suffocates the cancer cells, allowing neither nutrients in nor waste products out.

Erika Gebel Berg , *adapted from Chemical & Engineering News with permission.*

ROLE OF PHOSPHODIANION-GATED CONFORMATIONAL CHANGES REVEALED

The enzymes orotidine monophosphate decarboxylase (OMPDC), triosephosphate isomerase (TIM), and L-glycerol phosphate dehydrogenase (GPDH) have almost nothing in common, save that their substrates are phosphodianions. Here, John Richard and colleagues investigate the enzymology of these three proteins to work out their overarching molecular mechanisms (DOI: 10.1021/ja5123842).

The team collects kinetic data on yeast OMPDC, yeast TIM, and human liver GPDH using substrate molecules that have been split to separate the reacting moiety from the dianion. They then supply a series of oxydianions (HPO_3^{2-}, FPO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, and $HOPO_3^{2-}$) at different concentrations, as well as inhibitors, and record the kinetic results.

The data suggest these three enzymes operate via an induced fit mechanism where the oxydianions bind to an inactive "open" enzyme configuration, inducing a conformational shift to a high-energy "closed" configuration that organizes the catalytic side chains into their reactive state.

The authors suggest that "the formal contribution to catalysis (if any) of coupling protein and reaction coordinate motions is of incidental importance compared to the large transition state stabilization obtained from strong protein−ligand interactions".

Jeffrey M. Perkel

UNVEILING STEREOSELECTIVITY IN *CIS*–*TRANS* ISOMERIZATION OF CHIRAL FULLEROIDS

The chemical reactivity of fullerenes largely depends on their angularly strained molecular surfaces, which provide an unusual platform for exploring novel reactions. Although common transformations of fullerene derivatives, such as rearrangements and cycloadditions, have been extensively studied, the stereochemical aspect of these reactions remains to be addressed.

By preparing a series of chiral [60]-, [70]-, and H_2O@[60]-fulleropyrrolidines, Sílvia Osuna, Salvatore Filippone, Miquel Solà, Nazario Martín, and co-workers systematically investigate the *cis*–*trans* isomerization of five-membered cyclic pyrrolidinyl groups on the fullerene surface (DOI: 10.1021/ja5108854). While the pyrrolidinyl groups in all three types of fulleroids isomerize with high enantiospecificity, the reaction of H_2O@C_{60} pyrrolidines proceeds at faster rates, which is attributed to the stabilization of intermediate carbanions by hydrogen bonding with trapped water molecules.

Through a thorough analysis of substituents, fullerene surfaces, and especially the enhancing factor of endohedral water, the researchers are able to depict a detailed mechanistic scenario for the stereospecific isomerization of chiral fulleropyrrolidines. Moreover, this study opens a new avenue to gain stereochemical control over fullerene functionalization.

Xin Su, Ph.D.

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