Strategic Synthesis of 2,6-Pyridylene-Bridged β-to-β Porphyrin Nanorings through Cross-Coupling
Song Li Kim, D.: Shinokuba, U.: Osuka, A. Cham, Eur. J. 2010, 16

Song, J.; Kim, P.; Aratani, N.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem. Eur. J.* **2010**, *16*, 3009-3012.



The bridge determines the size of the loop? Palladium-catalyzed cross-coupling of borylporphyrins led to the construction of β -pyridine-bridged porphyrin nanorings in good yields (around 55-60 %; see scheme). The photophysical study revealed that these nanorings exhibit weakly coupled chromophores and longer fluorescent lifetimes, which is an apparent advantage in the process of efficient excited energy transfer.

 Dispersion of HiPco[®] and CoMoCAT[®] Single-Walled Nanotubes (SWNTs) by Water Soluble Pyrene Derivatives - Depletion of Small Diameter SWNTs Backes, C.; Mundloch, U.; Ebel, A.; Hauke, F.; Hirsch, A. Chem. Eur. J. 2010, 16, 3314-3317.

Abstract:



Nanotube surfactant design: The dispersion of SWNTs by designed surfactants based on water-soluble pyrene derivatives is reported. Significantly, nanotubes with small diameters are depleted in the supernatant after centrifugation, presenting the foundation for future nanotube separation by selective dispersion.

 Heme Oxygenase Reveals Its Strategy for Catalyzing Three Successive Oxygenation Reactions

Matsui, T.; Unno, M.; Ikeda-Saito, M. *Acc. Chem. Res.* **2010**, *43*, 240–247. <u>Abstract:</u>



Heme oxygenase (HO) is an enzyme that catalyzes the regiospecific conversion of heme to biliverdin IX α , CO, and free iron. In mammals, HO has a variety of physiological functions, including heme catabolism, iron homeostasis, antioxidant defense, cellular signaling, and O₂ sensing. The enzyme is also found in plants (producing light-harvesting pigments) and in some pathogenic bacteria, where it acquires iron from the host heme.

The HO-catalyzed heme conversion proceeds through three successive oxygenations, a process that has attracted considerable attention because of its reaction mechanism and physiological importance. The HO reaction is unique in that all three O_2 activations are affected by the substrate itself. The first step is the regiospecific self-hydroxylation of the porphyrin α -meso carbon atom. The resulting α -meso-hydroxyheme reacts in the second step with another O_2 to yield verdoheme and CO. The third O_2 activation, by verdoheme, cleaves its porphyrin macrocycle to release biliverdin and free ferrous iron. In this Account, we provide an overview of our current understanding of the structural and biochemical properties of the complex self-oxidation reactions in HO catalysis.

The first *meso*-hydroxylation is of particular interest because of its distinct contrast with O_2 activation by cytochrome P450. Although most heme enzymes oxidize exogenous substrates by high-valent oxo intermediates, HO was proposed to utilize the Fe–OOH intermediate for the self-hydroxylation. We have succeeded in preparing and characterizing the Fe–OOH species of HO at low temperature, and an analysis of its reaction, together with mutational and crystallographic studies, reveals that protonation of Fe–OOH by a distal water molecule is critical in promoting the unique self-hydroxylation. The second oxygenation is a rapid, spontaneous auto-oxidation of the reactive α -*meso*-hydroxyheme; its mechanism remains elusive, but the HO enzyme has been shown not to play a critical role in it. Until recently, the means of the third O_2 activation had remained unclear as well, but we have recently untangled its mechanistic outline. Reaction analysis of the verdoheme–HO complex strongly suggests the Fe–OOH species as a key intermediate of the ring-opening reaction. This mechanism is very similar to that of the first *meso*-hydroxylation, including the critical roles of the distal water molecule.

A comprehensive study of the three oxygenations of HO highlights the rational design of the enzyme architecture and its catalytic mechanism. Elucidation of the last oxygenation step has enabled a kinetic analysis of the rate-determining step, making it possible to discuss the HO reaction mechanism in relation to its physiological functions.

 Biocatalytic Strategies for the Asymmetric Synthesis of α-Hydroxy Ketones Hoyos, P.; Sinisterra, J.-V.; Molinari, F.; Alcántara, A. R.; Domínguez de María, P. Acc. 3 Chem. Res. 2010, 43, 288–299.
<u>Abstract:</u>



The development of efficient syntheses for enantiomerically enriched α -hydroxy ketones is an important research focus in the pharmaceutical industry. For example, α -hydroxy ketones are found in antidepressants, in selective inhibitors of amyloid- β protein production (used in the treatment of Alzheimer's), in farnesyl transferase inhibitors (Kurasoin A and B), and in antitumor antibiotics (Olivomycin A and Chromomycin A3). Moreover, α -hydroxy ketones are of particular value as fine chemicals because of their utility as building blocks for the production of larger molecules. They can also be used in preparing many other important structures, such as amino alcohols, diols, and so forth. Several purely chemical synthetic approaches have been proposed to afford these compounds, together with some organocatalytic strategies (thiazolium-based carboligations, proline α -hydroxylations, and so forth). However, many of these chemical approaches are not straightforward, lack selectivity, or are economically unattractive because of the large number of chemical steps required (usually combined with low enantioselectivities).

In this Account, we describe three different biocatalytic approaches that have been developed to efficiently produce α -hydroxy ketones:

(i) The use of thiamine diphosphate-dependent lyases (ThDP-lyases) to catalyze the umpolung carboligation of aldehydes. Enantiopure α -hydroxy ketones are formed from inexpensive aldehydes with this method. Some lyases with a broad substrate spectrum have been successfully characterized. Furthermore, the use of biphasic media with recombinant whole cells overexpressing lyases leads to productivities of ~80–100 g/L with high enantiomeric excesses (up to >99%).

(ii) The use of hydrolases to produce α -hydroxy ketones by means of (in situ) dynamic kinetic resolutions (DKRs). Lipases are able to successfully resolve racemates, and many outstanding examples have been reported. However, this approach leads to a maximum theoretical yield of 50%. As a means of overcoming this problem, these traditional lipase-catalyzed kinetic resolutions are combined with racemization of remnant substrate, which can be done in situ or in separate compartments. Examples showing high conversions (>90%) and enantiomeric excesses (>99%) are described.

(iii) Whole-cell redox processes, catalyzed by several microorganisms, either by means of free enzymes (applying a cofactor regeneration system) or by whole cells. Through the use of redox machineries, different strategies can lead to high yields and enantiomeric excesses. Some enantiopure α -hydroxy ketones can be formed by reductions of diketones and by selective

oxidations of vicinal diols. Likewise, some redox processes involving sugar chemistry (involving α -hydroxy ketones) have been developed on the industrial scale. Finally, the redox whole-cell 4 concept allows racemizations (and deracemizations) as well.

These three strategies provide a useful and environmentally friendly synthetic toolbox. Likewise, the field represents an illustrative example of how biocatalysis can assist practical synthetic processes, and how problems derived from the integration of natural tools in synthetic pathways can be efficiently tackled to afford high yields and enantioselectivities.

Quick Access to Diverse Polymerizable Molecules (a Monomer Library) by Catalytic [2 + 2 + 2] Cycloaddition Reactions of Functionalized Alkynes

Watanabe, J.; Sugiyama, Y.; Nomura, A.; Azumatei, S.; Goswami, A.; Saino, N.; Okamoto, S. *Macromolecules* **2010**, *43*, 2213–2218. Abstract:



The [2 + 2 + 2] cycloaddition reactions of 1,6-diynes and alkynes with a functional group(s), such as epoxide, oxetane, ester, alcohol, phenol, amine, borate, styrene, and methacrylate, catalyzed by a dipimp/CoCl₂·6H₂O/Zn reagent [dipimp: 2-(2,6-diisopropylphenyl)-iminomethyl-pyridine] yielded a variety of polymerizable molecules (monomers) having a 2,3-dihydro-1*H*-indene core structure. Similarly, the [2 + 2 + 2] cycloaddition reactions of 1,6-diynes and nitriles with a functional group(s) catalyzed by a dppe/CoCl₂·6H₂O/Zn reagent [dppe: 1,2-bis(diphenylphosphino)ethane] gave a variety of polymerizable molecules (monomers) with a 6,7-dihydro-5*H*-cyclopenta[*c*]pyridine core structure. Among the resulting monomers, 5-phenyl-1,3-dihydrospiro[indene-2,3'-oxetane] prepared from 3,3-di(prop-2-ynyl)oxetane and phenylacetylene was representatively polymerized in the presence of BF₃ catalyst. A cationic random copolymerization of one of 1,3-dihydrospiro[indene-2,3'-oxetane] derivatives with 3-ethyl-3-(phenoxymethyl)oxetane and radical random copolymerization of diethyl 5-(4-vinylphenyl)-1*H*-indene-2,2(3*H*)-dicarboxylate with styrene have also been demonstrated.

 Self-Assembly in Solution of a Reversible Comb-Shaped Supramolecular Polymer Pensec, S.; Nouvel, N.; Guilleman, A.; Creton, C.; Boué, F.; Bouteiller, L. *Macromolecules* 2010, 43, 2529–2534.





We report a single-step synthesis of a polyisobutene with a bis-urea moiety in the middle of the chain. In low polarity solvents, this polymer self-assembles by hydrogen bonding to form a comb-shaped polymer with a central hydrogen bonded backbone and polyisobutene arms. The comb backbone can be reversibly broken, and consequently, its length can be tuned by changing the solvent, the concentration, or the temperature. Moreover, we demonstrate that the bulkiness of the arms has a strong influence on both the self-assembly pattern and the length of the backbone. Finally, the number of polyisobutene arms can be controlled by simply mixing with a low-molar-mass bis-urea. This system thus combines a tunable structure and a dynamic backbone in solution. It is worth investigating its self-healing properties in bulk.

 Actuator Prototype: Capture and Release of a Self-Entangled [1]Rotaxane Xue, Z.; Mayer, M. F. J. Am. Chem. Soc. 2010, 132, 3274–3276. Abstract:



A conformationally dynamic chain compound that rapidly and reversibly samples both selfentangled and disentangled conformations, yet favors disentangled conformations, and an exclusively self-entangled [1]rotaxane were separately prepared and characterized. The conformationally dynamic state and the conformationally locked state were shown to reversibly and controllably interconvert under appropriate conditions, with an accompanying observable change in size that was calculated to approximate a 35% contraction in length upon capture of the self-entangled state.

• Synthesis of a Molecular Charm Bracelet via Click Cyclization and Olefin Metathesis Clipping

Clark, P. G.; Guidry, E. N.; Chan, W. Y.; Steinmetz, W. E.; Grubbs, R. H. J. Am. Chem. Soc. 2010, 132, 3405–3412.

Abstract:



We describe the synthesis of a polycatenated cyclic polymer, a structure that resembles a molecular charm bracelet. Ruthenium-catalyzed ring-opening metathesis polymerization of an amino-containing cyclic olefin monomer in the presence of a chain transfer agent generated an α, ω -diazide functionalized polyamine. Cyclization of the resulting linear polyamine using pseudo-high-dilution copper-catalyzed click cyclization produced a cyclic polymer in 19% yield. The click reaction was then further employed to remove linear contaminants from the cyclic

polymer using azide- and alkyne-functionalized scavenging resins, and the purified cyclic polymer product was characterized by gel permeation chromatography, 1H NMR spectroscopy, 6 and IR spectroscopy. Polymer hydrogenation and conversion to the corresponding polyammonium species enabled coordination and interlocking of diolefin polyether fragments around the cyclic polymer backbone using ruthenium-catalyzed ring-closing olefin metathesis to afford a molecular charm bracelet structure. This charm bracelet complex was characterized by 1H NMR spectroscopy, and the catenated nature of the small rings was confirmed using two-dimensional diffusion-ordered NMR spectroscopy.

Mechanical Reconfiguration of Stereoisomers
Wiggins, K. M.; Hudnall, T. W.; Shen, Q.; Kryger, M. J.; Moore, J. S.; Bielawski, C. W. J. Am. Chem. Soc. 2010, 132, 3256–3257.
Abstract:



Poly(methyl acrylate) of varying molecular weight was grown from the enantiopure ditopic initiator (*R*)- or (*S*)-1,1'-binaphthyl-2,2'-bis-(2-bromoisobutyrate). Subjecting CH₃CN solutions of high-molecular-weight derivatives ($M_N > 25$ kDa) to sonication at 0 °C resulted in >95% racemization after 24 h, as determined by circular dichroism; no appreciable racemization was observed in low-molecular-weight derivatives. Control experiments excluded the possibility of a thermal racemization mechanism.

Tuning the Charge-Transport Parameters of Perylene Diimide Single Crystals via End and/or Core Functionalization: A Density Functional Theory Investigation Ruiz Delgado, M. C.; Kim, E.-G.; da Silva Filho, D. A.; Bredas, J.-L. J. Am. Chem. Soc. 2010, 132, 3375–3387.
<u>Abstract:</u>



Perylene tetracarboxylic diimide (PTCDI) derivatives stand out as one of the most investigated families of air-stable *n*-type organic semiconductors for organic thin-film transistors. Here, we use density functional theory to illustrate how it is possible to control the charge-transport parameters of PTCDIs as a function of the type, number, and positions of the substituents. Specifically, two strategies of functionalization related to core and end substitutions are investigated. While end-substituted PTCDIs present the same functional molecular backbone, their molecular packing in the crystal significantly varies; as a consequence, this series of derivatives constitutes an ideal test bed to evaluate the models that describe charge-transport

in organic semiconductors. Our results indicate that large bandwidths along with small effective masses can be obtained with the insertion of appropriate substituents on the 7 nitrogens, in particular halogenated aromatic groups.

 CO₂ Binding by Dynamic Combinatorial Chemistry: An Environmental Selection Leclaire, J.; Husson, G.; Devaux, N.; Delorme, V.; Charles, L.; Ziarelli, F.; Desbois, P.; Chaumonnot, A.; Jacquin, M.; Fotiadu, F.; Buono, G. *J. Am. Chem. Soc.* 2010, *132*, 3582–3593.
<u>Abstract:</u>

We now report that a dynamic combinatorial selection approach can quantitatively provide, from trivial building blocks, an architecturally complex organic material, in which carbon dioxide is reversibly but covalently incorporated as a guest with a mass content of 20%. Solidstate analyses combined with covalent disconnection and quantization of the liberated components allowed identification of a three-component monomeric unit repeated within a range of assembled oligomeric adducts whose repartition and binding capacity can be finely tuned through the starting stoichiometries. The self-assembly of these architectures occurs through the simultaneous creation of more than 25 covalent bonds per molecular entity. It appears that the thermodynamic selection is directed by the packing efficiency of these adducts, explaining the spectacular building block discrimination between homologues differing by one carbon unit. This selectivity, combined with the reversible nature of the system, provided pure molecular building blocks after a simple chemical disconnection, promoting CO_2 as a green auxiliary to purify polyaldehyde or polyamine from mixtures of homologous structures. Moreover, the gas template could be expelled as a pure compound under thermodynamic control. This cooperative desorption process yielded back the initial libraries of high molecular diversity with a promising reduction of the energetic costs of capture and recycling.

 Significance of Hydrophilic Characters of Organic Dyes in Visible-Light Hydrogen Generation Based on TiO₂
Lee, S.-H.; Park, Y.; Wee, K.-R.; Son, H.-J.; Cho, D. W.; Pac, C.; Choi, W.; Kang, S. O. Org. Lett. 2010, 12, 460–463.
<u>Abstract:</u>



A series of dyes were synthesized to examine the roles of the hydrophilic characteristics of R in sensitized hydrogen generation by dye-grafted Pt/TiO_2 under visible light irradiation. The hydrogen-generation efficiencies and optimum amounts of the dyes grafted to Pt/TiO_2 were affected substantially by the hydrophilic and steric effects of R; moderately hydrophilic DEO1 and DEO2 showed higher sensitization activity at a lower loading than hydrophobic D-H.

 Triphenylamine-Based Dyes Bearing Functionalized 3,4-Propylenedioxythiophene Linkers with Enhanced Performance for Dye-Sensitized Solar Cells Liang, Y.; Peng, B.; Liang, J.; Tao, Z.; Chen, J. Org. Lett. 2010, 12, 1204–1207. <u>Abstract:</u>



Introduction of modified 3,4-propylenedioxythiophene units into triphenylamine-based dyes is found to enhance light capturing, suppress dye aggregation, and remarkably retard charge recombination in dye-sensitized solar cells. Open circuit voltages of the as-synthesized dyes (~ 800 mV) are much higher than that with a thiophene congener (720 mV) under similar conditions as a result of self-passivation benefiting from their three-dimensional branched structures.

 Annulation of Tetrathiafulvalene to the Bay Region of Perylenediimide Jaggi, M.; Blum, C.; Marti, B. S.; Liu, S.-X.; Leutwyler, S.; Decurtins, S. Org. Lett. 2010, 12, 1344–1347.

Abstract:



A tetrathiafulvalene donor has been annulated to the bay region of perylenediimide affording a new π -conjugated molecular dyad. Various electronic excited charge-transfer states are

generated in different oxidation states, leading to almost full absorption in the visible to near-IR region with a high extinction coefficient.

 Fast Assembly of Cyanine Dyes into Aggregates onto [6,6]-Phenyl C61-Butyric Acid Methyl Ester Surfaces from Organic Solvents Heier, J.; Steiger, R.; Nuesch, F.; Hany, R. Langmuir 2010, 26, 3955-3961.
<u>Abstract:</u>



Supramolecular agglomerates of organic colorants based on noncovalent interactions are promising candidates for the development of sensors, optoelectronics, lighting, or photovoltaics. However, their fast and defect-free fabrication on large scales using low-cost technologies has proven elusive so far. Here, we introduce a so far unreported mechanism to induce molecular order in cyanine dyes within minutes from organic solvents by self-assembly. Spin coating blends of a cyanine dye and a soluble fullerene derivative ([6,6]-phenylC61-butyric acid methyl ester (PCBM)) from apolar, aprotic solvents leads to phase-separated structures on the micrometer scale. With this superordinated phase structure, adjustment of dye aggregation is possible, leading to novel optical properties of the film emerging from dye self-assembly on the nanometer scale. In the primary process, semiporous PCBM domains act as nucleation sites for H-aggregates. H-aggregates can then be reconstructed into J-aggregates by dissolving PCBM from the film. Unexpectedly, the method even works for sterically hindered cyanine dyes that are known for their reduced tendency to aggregate. Additionally, selective removal of H-aggregates leaves a template ofPCBMnanocrystals, onto which cyanine dye monomers readsorb from solution, forming H-aggregates of similar quality.

• Cyclodextrin Supramolecular Complex as a Water-Soluble Ratiometric Sensor for Ferric Ion Sensing

Xu, M.; Wu, S.; Zeng, F.; Yu, C. *Langmuir* **2010**, *26*, 4529-4534. <u>Abstract:</u>



Heightened concern for human health and environmental protection has stimulated active research on the potential impact of transition-metal ions and their toxic effects, thus it is very demanding to design transition-metal ion detection methods that are cost-effective, rapid, facile, and applicable to the environmental and biological milieus. In this study, we demonstrated an alternative strategy for constructing a water-soluble FRET-based ratiometric

sensor for ferric ion detection by forming a supramolecular β -cyclodextrin/dye complex. This water-soluble FRET system consists of a dansyl-linked β -cyclodextrin (β -CD-DNS) and a spirolactam rhodamine-linked adamantane (AD-SRhB). The dansyl moiety serves as the donor, and the spirolactam-rhodamine B derivative (SRhB) was chosen as a sensitive, selective chemosensor for Fe(III) ions and a very efficient ring-opening reaction induced by Fe(III) generates the long-wavelength rhodamine B fluorophore that can act as the energy acceptor. Moreover, the adamantyl (AD) group, which is known for its capability to form stable host-guest inclusion complexes with β -CD derivatives, was covalently linked to the spirolactam rhodamine, thus the adamantyl moiety of the ion-recognition element can be anchored inside the CD cavity. In this way, the donor-acceptor separation can be kept within the critical F⁰ rster distance; accordingly, energy transfer can take place from the donor (dansyl) to the acceptor (rhodamine derivative/Fe(III) complex), and thus ratiometric detection for Fe(III) in an aqueous medium can be fulfilled. This FRET-based supramolecular sensor can be readily formed via an inclusion process using the donor part and the acceptor part, hence this strategy could afford a robust approach for constructing a wide range of FRET-based water-soluble sensing systems simply by assembling a specifically predesigned donor-linked CD and acceptorlinked adamantine.

Non-planar push–pull chromophores
Kato, S. I.; Diederich, F. Chem. Commun. 2010, 46, 1994 – 2006.
<u>Abstract:</u>



The development of a unique class of non-planar push–pull chromophores by means of [2+2] cycloaddition, followed by cycloreversion, of electron-deficient olefins, such as tetracyanoethene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ), as well as dicyanovinyl (DCV) and tricyanovinyl (TCV) derivatives, to donor-substituted alkynes is explored in this feature article. This high-yielding, click-chemistry-type transformation with acetylenic dendrimers affords dendritic electron sinks capable of multiple electron uptake within a narrow potential range. An [AB]-type oligomer with a dendralene backbone was synthesised by a one-pot, multi-component cascade reaction of polyyne oligomers with TCNE and tetrathiafulvalene (TTF). In most cases, the resulting chromophores feature intense intramolecular charge-transfer bands extending far into the near infrared region and some of them display high third-order optical nonlinearities. Despite substitution with strong donors, the electron-withdrawing moieties in the new chromophores remain potent acceptors and a number of them display positive first reduction potentials (vs. the ferrocenium/ferrocene (Fc^+/Fc) couple in CH_2Cl_2), which rival those of parent TCNE, TCNQ and F_4 -TCNQ. The non-planarity of the chromophores strongly

enhances their physical properties when compared to planar push-pull analogues. They feature high solubility, thermal stability and sublimability, which enables formation of amorphous, high-optical-quality thin films by vapour phase deposition and makes them - interesting as advanced functional materials for novel opto-electronic devices.

• Multiport logic operations triggered by protonation—a trisphenanthroline as a 3-input AND–NOR–OR circuit

Abstract:

Schmittel, M.; Mal, P.; De los Rios, A. Chem. Commun. 2010, 46, 2031 – 2033.

A linear bisphenanthroline (two binding sites) is set up to operate as a XNOR gate and a linear trisphenanthroline (three binding sites) as a molecular 3-input AND–NOR–OR logic circuit, both with H⁺ as input signal and luminescence as output signal.

 Catalytic Carbene Insertion into C-H Bonds Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. Chem. Rev. 2010, 110, 704–724. <u>Abstract:</u>

$$\begin{array}{ccc} XY & H-CR_{3} \\ \hline R_{2}CXY & \overbrace{carbene}{generation}}^{XY} & [R_{2}\dot{C}] & \overbrace{C-H}^{H} & R_{2}C-CR_{3} \\ \hline generation & insertion \end{array}$$

From its earliest observation as an unusual reaction only a half century ago,1 the insertion of a carbene into a carbon-hydrogen bond has attracted considerable interest because of its potential in forming carbon-carbon bonds (Figure 1). Thermally or photochemically generated carbenes, initially considered to be unselective in insertion reactions,2–4 have been studied in sufficient detail to distinguish virtually unselective (:CH2) to modestly selective (:CCl2 and PhCCl) carbenes;4,5 however, few of these reactions have shown potential for synthetically meaningful transformations. How to modify the reactivity of the carbene while still maintaining its reactivity toward carbon-hydrogen insertion was the challenge confronting those desiring to take advantage of what is an efficient and atom-economical transformation. Carbene generation can occur from diazoalkanes photochemically and thermally or, as was initially reported in 1958 (eq 1),6 by the use of a transition metal. Copper and copper compounds were initially employed, but few examples were reported that portrayed generality or synthetic utility except for intramolecular reactions in geometrically rigid systems.

 CsH Bond Activation in Transition Metal Species from a Computational Perspective Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* 2010, *110*, 749–823.
<u>Abstract:</u>



Alkanes constitute the cheapest and most abundant feedstock for organic chemicals. However, the redistribution of CsC and CsH bonds in hydrocarbons into more sophisticated value-added architectures is a highly difficult task. The bonds to be broken are thermodynamically strong and kinetically inert. Therefore, hydrocarbons are mainly used as fuels, and the energy content of the bonds is dispensed as heat. Consequently, the efficient and selective activation of CsH bonds, the elementary building block of hydrocarbons, constitutes an interesting alternative with potentially a huge economic impact.

 Bacteria Incorporation in Deep-eutectic Solvents through Freeze-Drying Gutierrez, M. C.; Ferrer, M. L.; Yuste, L.; Rojo, F.; del Monte, F. *Angew. Chem. Int. Ed.* 2010, 49, 2158–2162. Abstract:



Taking fish out of water: Freeze-drying can be used to incorporate bacteria in a deep-eutectic solvent with outstanding preservation of integrity and viability. (Intact *E. coli* are marked by arrows in the image.) These findings open interesting perspectives for the use of whole microorganisms in biocatalytic processes carried out in nonaqueous solvents.

 Inversion of Particle-Stabilized Emulsions to Form High-Internal-Phase Emulsions Sun, G.; Li, Z.; Ngai, T. Angew. Chem. Int. Ed. 2010, 49, 2163 –2166.
<u>Abstract:</u>



Two triggers: Phase inversion of a particle-stabilized oil-water system from an ordinary oil-inwater emulsion (see picture, left; green: oil, pink: water) to a water-in-oil high-internal-phase

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emulsion (right) at a fixed oil/water ratio (27:73 vol %) can be simply driven by either a change of pH value or salt concentration in a single system. Scale bars: 30 μ m.

 Supramolecular design of self-assembling nanofibers for cartilage regeneration Shah, R. N.; Shah, N. A.; Del Rosario Lim, M. M.; Hsieh, C.; Nuber, G.; Stupp, S. I. *Proc. Nat. Acad. Sci.* 2010, *107*, 3293-3298.
Abstract:



Molecular and supramolecular design of bioactive biomaterials could have a significant impact on regenerative medicine. Ideal regenerative therapies should be minimally invasive, and thus the notion of self-assembling biomaterials programmed to transform from injectable liquids to solid bioactive structures in tissue is highly attractive for clinical translation. We report here on a coassembly system of peptide amphiphile (PA) molecules designed to form nanofibers for cartilage regeneration by displaying a high density of binding epitopes to transforming growth factor β -1 (TGF β -1). Growth factor release studies showed that passive release of TGF β -1 was slower from PA gels containing the growth factor binding sites. In vitro experiments indicate these materials support the survival and promote the chondrogenic differentiation of human mesenchymal stem cells. We also show that these materials can promote regeneration of articular cartilage in a full thickness chondral defect treated with microfracture in a rabbit model with or even without the addition of exogenous growth factor. These results demonstrate the potential of a completely synthetic bioactive biomaterial as a therapy to promote cartilage regeneration.

• An expedient route to substituted furans via olefin cross-metathesis Donohoe, T. J.; Bower, J. F. *Proc. Nat. Acad. Sci.* **2010**, *107*, 3373-3376. <u>Abstract:</u>



The olefin cross-metathesis (CM) reaction is used extensively in organic chemistry and represents a powerful method for the selective synthesis of differentially substituted alkene products. Surprisingly, efforts to integrate this remarkable process into strategies for aromatic and heteroaromatic construction have not been reported. Such structures represent key elements of the majority of small molecule drug compounds; methods for the controlled preparation of highly substituted derivatives are essential to medicinal chemistry. Here we show that the olefin CM reaction, in combination with an acid cocatalyst or subsequent Heck arylation, provides a concise and flexible entry to 2,5-di- or 2,3,5-tri-substituted furans. These cascade processes portend further opportunities for the regiocontrolled preparation of other highly substituted aromatic and heteroaromatic classes.