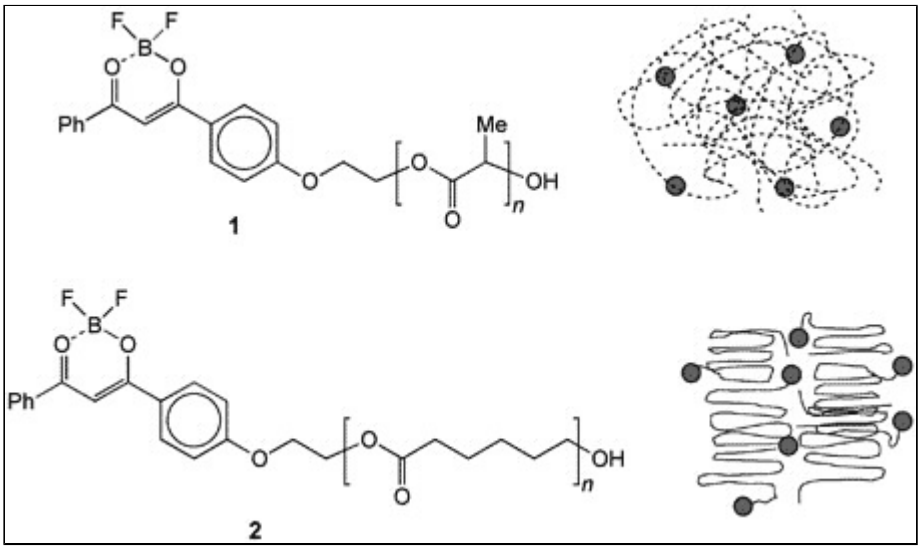
Noteworthy Chemistry

May 18, 2009

The surrounding matrix dictates the luminescent nature of an organoboron label. Luminophores often change their emission behavior with variations in conditions such as solvent, temperature, pressure, and pH. These factors form the photophysical basis for stimulus-responsive luminescence sensors. Less frequently, a luminophore changes the nature of its emission from fluorescence to phosphorescence in response to environmental variations. A team at the University of Virginia (Charlottesville) led by C. L. Fraser found a unique matrix effect that changes the light emission of an organoboron luminophore between fluorescence and phosphorescence.



In the solid state, boron-labeled polylactide **1** is fluorescent and phosphorescent, whereas its poly(ε-caprolactone) analogue (**2**) emits only fluorescent radiation. In **1**, the labels are dispersed throughout the rigid polymer matrix in which their rotations and vibrations are restricted. This allows singlet and triplet excited states to decay radiatively; the labels are therefore fluorescent and phosphorescent. In **2**, however, the labels are located in the large microcavities between the crystalline domains. The molecular motions of the labels in the microcavities annihilate their phosphorescence, and the labels are only fluorescent. (*Macromolecules* **2009,** *42,* **3162–3169**; **Ben Zhong Tang**)

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Electrochemically oxidize ethanol to carbon dioxide with ternary catalysts. EtOH would, in many ways, be a better fuel than MeOH in direct alcohol fuel cells; but current electrocatalysts have been unable to break the C–C bond. As a result, the main products of slow, inefficient EtOH electrooxidation have been MeCHO and AcOH rather than CO_2 and H_2O. M. Shao, J. Zhang, and coauthors at Brookhaven National Laboratory (Upton, NY), the University of Delaware (Newark), and Yeshiva University (New York City) have improved this technology.

The authors prepared a ternary electrocatalyst, $PtRhSnO_2/C$, that can oxidize EtOH to CO_2 and H_2O. The ternary catalyst has higher activity than commercial Pt/C and PtRu/C catalysts. The structural properties, electronic properties, and potential dependence of $PtRhSnO_2/C$ were determined by using in situ X-ray absorption near-edge structure, extended X-ray absorption fine structure, transmission electron microscopy, inductively coupled plasma, and IR reflection–absorption spectroscopy techniques.

Platinum in the catalyst provides the sites for dehydrogenating EtOH. Water molecules strongly adsorb on SnO_2, providing OH species to oxidize dissociated CO at the rhodium sites. The formation of $Ru–CH_2CH_2O$ on the catalyst surface facilitates the direct breaking of the C–C bond as a result of changes in the electronic structure of rhodium. (*Nat. Mater.* **2009,** *8,* **325–330**; **George Xiu Song Zhao**)

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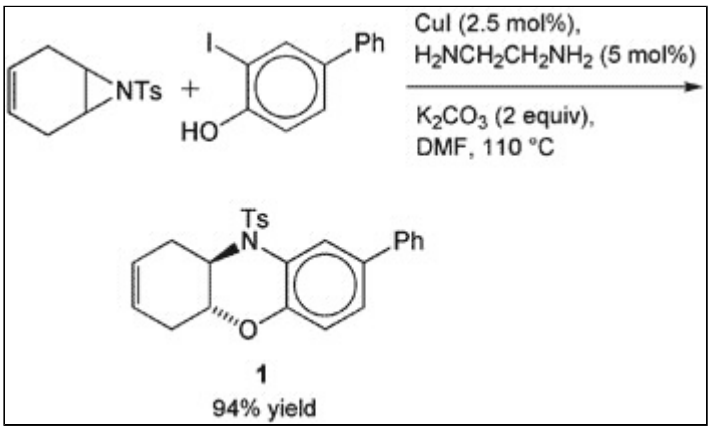
Here's a highly efficient synthesis of benzoxazines. Researchers have found that the 1,4-benzoxazine scaffold is a key feature in a variety of biologically active compounds, including serotonin antagonists, antioxidants, potassium channel activators, vasodilators, and calcium antagonists. R. K. Rao, A. B. Naidu, and G. Sekar* at the Indian Institute of Technology Madras (Chennai) note that multistep syntheses are available for this heterocyclic structure, but its value drives the need for more efficient routes.

The authors report the first single-step synthesis of the 1,4-benzoxazine skeleton from readily available aziridines and *o*-iodophenols via a domino-type aziridine ring opening followed by intramolecular copper-catalyzed cyclization of the aryl iodide coreactant. K_2CO_3 serves as a mild base to deprotonate the iodophenol reactant to form the necessary phenoxide anion. Ts is *p*-toluenesulfonyl.



The procedure also uses the simple, inexpensive ligand ethylenediamine to provide high yields of the all-trans product **1**. The study encompasses 15 pairs of reactants; the 80–99% product yields for 14 of the 15 pairs demonstrate the high efficiency of the reaction.

One of the remarkable features of this method is the formation of the all-trans isomer of the 1,4-benzoxazine ring. The authors suggest a mechanism in which the aziridine is initially opened by an S_N2 reaction with the phenoxide anion to give a trans intermediate. Coordination of the nitrogen substituent with the copper complex is followed by oxidative addition to give the 1,4-trans heterocycle that contains the complex in the form of a seven-membered ring intermediate. Reductive elimination then ejects the complex to liberate the 1,4-benzoxazine product with the desired trans configuration. (*Org. Lett.* **2009**, *11*, **1923–1926**; **W. Jerry Patterson**)

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Fresh, clean equipment hinders crystallization. J. A. Ragan and co-workers at Pfizer (Groton, CT; Sandwich, UK; and County Cork, Ireland) developed a direct crystallization of CP-945,598-01, a CB_1 antagonist for treating obesity. The authors diluted crude reaction mixture dissolved in *N*-methylpyrrolidinone with H_2O–THF and then slowly added water to induce crystallization. In the lab, with equipment and fume hoods that had been used several times for making CP-945,598-01, this process worked well.

However, when the process was transferred to kilo-lab scale with scrupulously clean equipment, crystallization

did not occur until the water addition and cool-down were complete; and even then the crystallization required seeding. This caused a rapid, uncontrolled crystallization and very slow filtration. The authors corrected the problem by seeding earlier in the process to avoid supersaturation. (*Org. Process Res. Dev.* **2009,** *13,* **186–197**; **Will Watson**)

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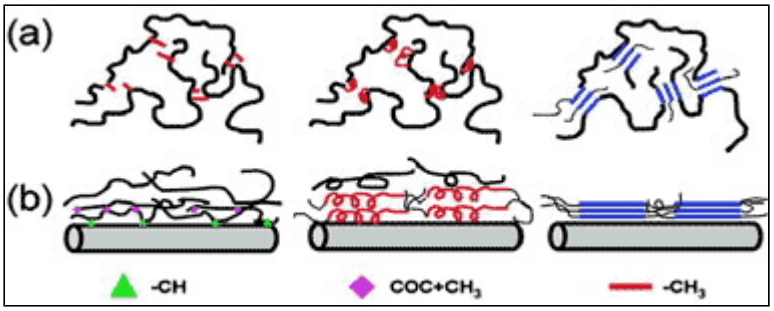
Carbon nanotubes influence poly(L-lactide) crystallization. Z.-M. Li and coauthors at Sichuan University (Chengdu, China), Ludong University (Yantai, China), and the University of Science and Technology of China (Hefei) explored the crystallization behavior of poly(L-lactide) (PLLA) nucleated by pure or carboxyl-functionalized carbon nanotubes (CNTs).

Under isothermal crystallization conditions at 124 °C, the authors used time-resolved Fourier transform IR spectroscopy to characterize the crystallization of PLLA and PLLA–CNT nanocomposites. By examining the intensity of the characteristic PLLA crystallization band at 921 cm^{-1} as a function of time, they found that PLLA nanocomposites have faster crystallization kinetics than PLLA alone, and the PLLA in the PLLA–pure CNT nanocomposites crystallizes faster than the PLLA in the carboxylated PLLA–CNT nanocomposites.



The authors also showed that the differences in crystallization behavior are the result of variations in the initial nucleation processes, which are dominated by interchain conformational changes. Whereas the early-stage crystallization of PLLA is controlled by interchain methyl group interactions that produce 1456 cm^{-1} IR bands (a in the figure), crystallization of PLLA in the nanocomposites is dominated by a combination of carbonyl and methyl group interchain interactions at 1210 cm^{-1} (b). The authors believe that the adsorption phenomena (CH–π interactions) of the PLLA chains onto the CNT surfaces dictate PLLA conformation that leads to PLLA nucleation and crystal growth, which explains the reduction in PLLA nucleation for the carboxylated CNTs. (*Macromolecules* **2009,** *42,* **3215–3218**; **LaShanda Korley**)

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Make novel 3-D structures by using strategic assembly, binding interactions, and processing. J. Huskens and colleagues at the University of Twente (The Netherlands) have generated ordered, stable 3-D structures by using these techniques:

- ordering by synergistic convective nanoparticle assembly;
- binding by supramolecular host–guest interactions; and
- transfer printing.

The authors assembled host polystyrene particles functionalized with β-cyclodextrin (CD) onto a patterned surface of CD self-assembled monolayers. This functionalized particle assembly was then infiltrated with guest adamantyl-terminated poly(propyleneimine) generation 5 dendrimers. They demonstrated that noncovalent interactions are essential for forming well-ordered, robust particle arrays as hexagonally close-packed crystals.

The authors extended this ordering–binding method to elastomeric poly(dimethylsiloxane) stamps that were subsequently transferred to CD-functionalized substrates of various sizes and shapes under humid conditions with high precision. The integrity of the crystal packing (90% yield) of the 3-D arrays and the host functionality was retained after transfer printing. The authors note that multiple guest molecules can be incorporated simultaneously into the host particle structure. Without the addition of the guest dendrimers, defined features with less-than-ideal packing of particle monolayers are obtained during the transfer process.

By varying the generation number of the adamantyl guest dendrimers, the authors showed that the strength of

the specific binding interaction is also crucial for creating stable polystyrene particle arrays. An understanding of the dynamics governing the observed phenomena in these functional 3-D particle structures will help in developing these systems as sensing platforms. (*ACS Appl. Mater. Interfaces* **2009,** *1,* **960–968**; **LaShanda Korley**)

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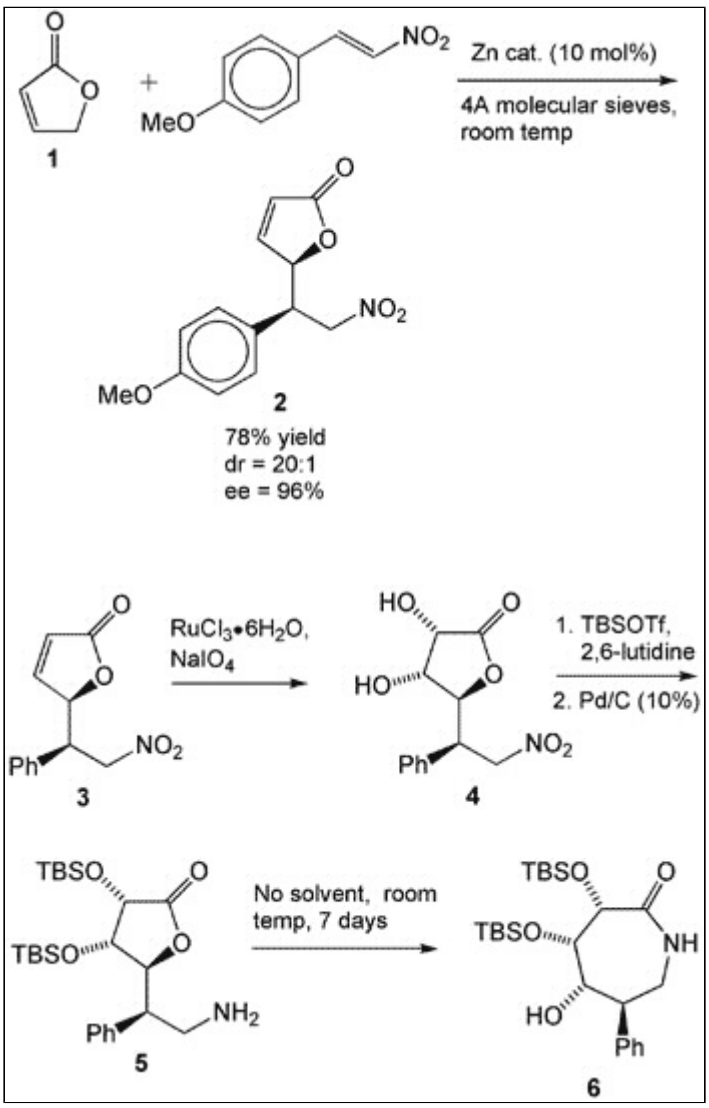

This asymmetric addition to nitroalkenes is an efficient route to Michael adducts. B. M. Trost* and J. Hitce at Stanford University (California) observed that 2(5*H*)-furanone (**1**) serves as an effective Michael donor in the asymmetric conjugate addition with nitroalkenes mediated by a zinc-based binuclear catalyst complex. Nucleophiles such as **1** typically require preactivation for use in the Michael addition; but in this study, compound **1** is used directly.

Several nitroalkenes led to γ-substituted butenolide products (e.g., **2**) with excellent diastereoselectivity and enantioselectivity and generally good yields. The authors used X-ray analysis to establish the syn stereochemistry of the products.

They also used the reaction to illustrate the formation of highly functionalized products **4**–**6** from starting furanone **3**. Oxidizing **3** in the presence of a ruthenium catalyst provides *cis*-diol **4** with complete diastereoselectivity; this reaction is remarkable for its control of four adjacent stereocenters. The hydroxyl groups are protected as *tert*-butyldimethylsilyl ethers and then reduced by using standard conditions to generate primary amine **5**; Tf is trifluoromethanesulfonyl. Compound **5** spontaneously rearranges to the seven-membered lactam **6**. The authors note that similar polyhydroxyazepanones are being studied as potential glycosidase inhibitors. (*J. Am. Chem. Soc*. **2009,** *131,* **4572–4573**; **W. Jerry Patterson**)

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