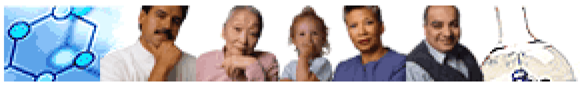

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Heart Cut

March 21, 2005

- Synthesize platinum – carbon cathodes by copyrolysis
- Organofullerenes “harvest” light efficiently
- Organized composites efficiently convert light to electricity
- A catalyst for producing polyesters at room temperature
- Simulate the dissolution and growth of zeolite β C
- Observe growth defects in zeolite β directly
- Reduction by catalytic asymmetric transfer hydrogenation
- Trimethyltin hydroxide promotes mild ester hydrolysis

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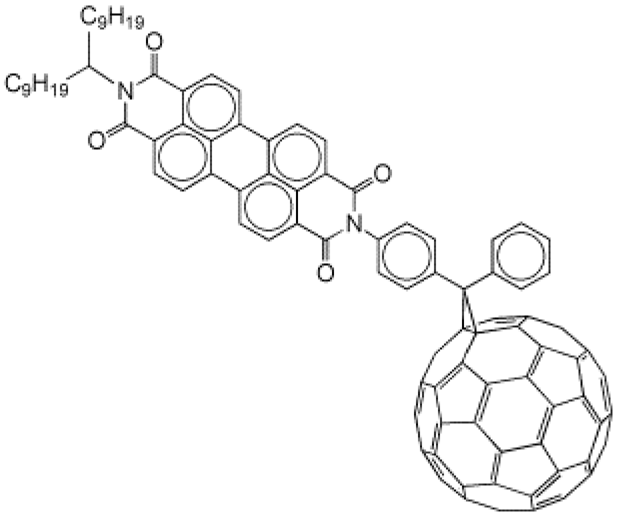
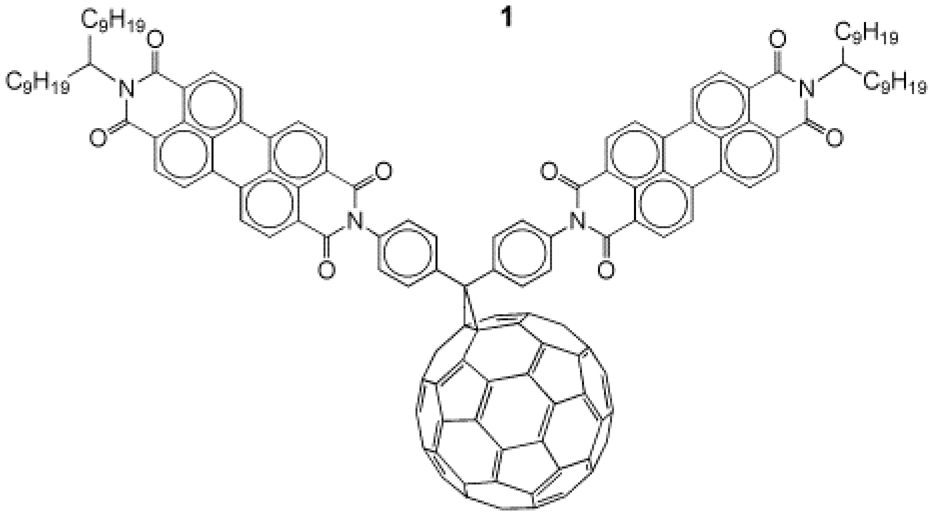
Synthesize platinum – carbon cathodes by copyrolysis. S. I. Woo and coauthors at the Korea Advanced Institute of Science and Technology and the Korea Research Institute of Chemical Technology, both in Daejon, report the synthesis of Pt – C composites by pyrolyzing platinum and carbon precursors within the pores of the mesoporous silica SBA-15. The product is composed of regularly interconnected nanocomposite arrays and can be used as methanol-tolerant cathodes in direct-methanol fuel cells.

The authors found that most of the 1 – 5 nm platinum clusters are studded inside the composite nanorods and do not block the openings of the mesopores. In contrast, the conventional impregnation method leads to randomly dispersed irregular platinum clusters with sizes >8 – 10 nm. The findings demonstrate that the aggregation and movement of metal precursors are hindered by polymerizing or carbonizing the carbon precursors, resulting in the formation of ultrafine platinum clusters despite the 900 ° C pyrolysis temperature. This strategy can be extended to preparing other porous metal – carbon nanocomposites. (*Adv. Mater.* **2005**, *17*, 446 – 451; George Xiu Song Zhao) Go to top

Organofullerenes “harvest” light efficiently. R. Gómez, J. L. Segura*, and N. Martín* of the Universidad Complutense de Madrid synthesized C_{60} fullerenes that incorporate perylenebisimide dyes. These structures function as light harvesters and electron acceptors, leading to their potential use in photovoltaic devices. The fullerene – perylene dyad (**1**) and triad (**2**) were synthesized. The preparation was based on initially forming the amino- or diamino-substituted [6,6]-closed diphenylmethanofullerenes. These intermediates were then condensed with an anhydride-functionalized perylene using $Zn(OAc)_2$ catalyst to form **1** and **2**.



1



2

The long alkyl chains attached to the perylene units are crucial to the success of this method. They provide enhanced solubility to the structures, allowing their full electrochemical and spectroscopic characterization. The redox potentials of **1** and **2** are similar to those of other fullerene derivatives that exhibit very high open-circuit voltages in photovoltaic devices. This feature, together with their strong absorption throughout the visible spectrum, makes **1** and **2** suitable candidates for fashioning devices such as solar cells. (*Org. Lett*. **2005**, *7*, 717–720; W. Jerry Patterson) Go to top

Organized composite nanoclusters efficiently convert light to electricity. The development of efficient solar cells will benefit society because they convert solar energy, a no-cost light source, to much needed electrical power. An attractive strategy for developing such cells is mimicking photosynthesis, the natural energy conversion process. However, the photovoltaic devices developed so far have only limited degrees of self-organization, whereas the components in the natural system are highly organized into quaternary protein structures.

An international team led by H. Imahori at Kyoto University, Japan, P. V. Kamat at the University of Notre Dame, IN, D. Kim at Yonsei University, Korea, and S. Fukuzumi at Osaka University, Japan, and including coauthors at Seoul National University, Korea, constructed hierarchically organized solar cells with nanocluster components ordered at up to the quaternary level. Porphyrinalkanethiol, fullerene, and gold nanoparticle were used as the primary building blocks for self-organization at these levels:

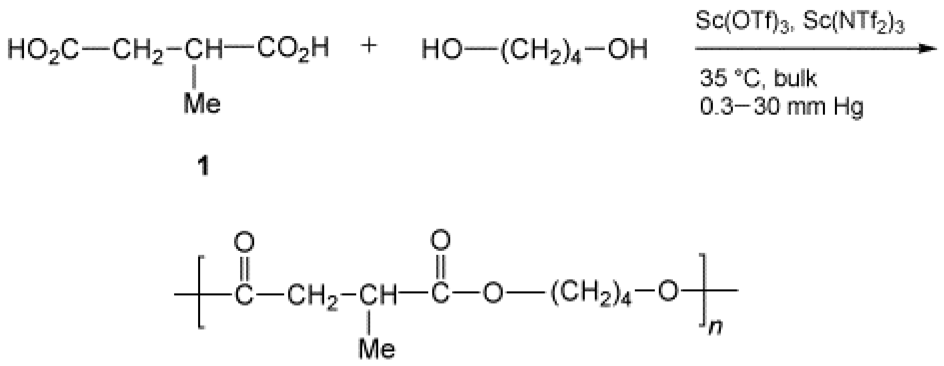
- Secondary organization: The porphyrinalkanethiol molecules self-assemble with the gold nanoparticles via metal–thiol bonds to give monolayer-protected gold nanoparticles.
- Tertiary organization: The peripheral porphyrin molecules form complexes with fullerene molecules by donor–acceptor interactions.
- Quaternary organization: The complexes are finally clustered into higher order structures using MeCN–toluene as the solvent.

The self-organized clusters are then assembled as 3-D arrays onto nanostructured tin oxide films by an electrophoretic deposition method to provide nanocomposite electrodes.

The films of the composite nanoclusters exhibit broad photocurrent action spectra (up to 1 μm) and incident photon-to-photocurrent efficiencies as high as 54%. The power conversion efficiency of the nanocomposite electrodes approaches 1.5%, 45 times greater than that of the nonorganized reference system. Such a remarkable enhancement of photovoltaic performance and the broader photoresponse in the visible and infrared spectra relative to the reference system demonstrate that quaternary organization of composite nanoclusters provides a novel entry for developing efficient organic solar cells. (*J. Am. Chem. Soc*. **2005**, *127*, 1216–1228; Ben Zhong Tang) Go to top

This catalyst lets you produce polyesters at room temperature. Polyesters are generally synthesized with the help of Lewis-acid catalysts such as SbO_3, tetraalkyl titanates, and various tin complexes. Typical polymerization temperatures with these catalysts range from 120 to 300 °C and of course depend strongly on the melting point of the target polymer.

A. Takasu and co-workers at the Nagoya Institute of Technology, Japan, report that strong Lewis acid complexes, such as scandium trifluoromethanesulfonate [$Sc(OTf)_3$] and scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$], can be used to produce low-melting aliphatic polyesters at temperatures as low as 35 ºC. The authors ran the reactions under vacuum to remove condensation byproducts. They polycondensed methylsuccinic acid (1) and 1,4-butanediol to make polymers with M_n>10,000.

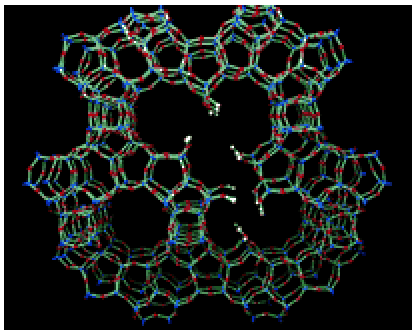


Under the same conditions, Brønsted acids produced polymers with M_n ~3000 and uncatalyzed polycondensations produced oligomers with molecular weights <500. Room-temperature polymerization will not be possible for high-melting commercial polymers such as poly(ethylene terephthalate), but this work might suggest opportunities for improving current commercial catalysts and could be very useful in producing laboratory-scale polymers that contain thermally sensitive functional groups. (*Macromolecules* **2005**, *38*, 1048－1050; David A. Schiraldi) Go to top

Simulate the dissolution and growth of zeolite β C. To understand how zeolites form on the atomic scale, M. E. Chiu of the University of Cambridge, UK, B. Slater* of the Royal Institution of Great Britain, London, and J. D. Gale of the Curtin University of Technology, Perth, Australia, investigated the layered assembly of monomers of zeolite β C by using atomistic computer simulation techniques. They explored the enthalpy changes associated with the dissolution and assembly of monomers to assess whether growth can proceed exclusively by monomer addition or whether oligomers are required to build the crystals.

The authors found that many and possibly all of the stages of growth are thermally accessible, and that oligomers may play a key role in accelerating the rate-determining stages of growth. However, they could not definitively assign the roles of the primary and secondary building units because additional data regarding the distribution of oligomers in solution and their sensitivities to extraframework cations, pH, and other parameters were needed. (*Angew. Chem., Int. Ed.* **2005**, *44*, 1213－1217; George Xiu Song Zhao) Go to top

Here is a technique for observing growth defects in zeolite β directly. Zeolite β is constructed by the random intergrowth of two end-member structures, polytypes A and B. P. A. Wright and coauthors at the University of St. Andrews, Fife, UK, and the Institute of Catalysis and Petroleum Chemistry, CSIC, Madrid, directly observed the disordered layer stacking sequence by using high-resolution transmission electron microscopy (HRTEM). The defects are illustrated in the model shown below.



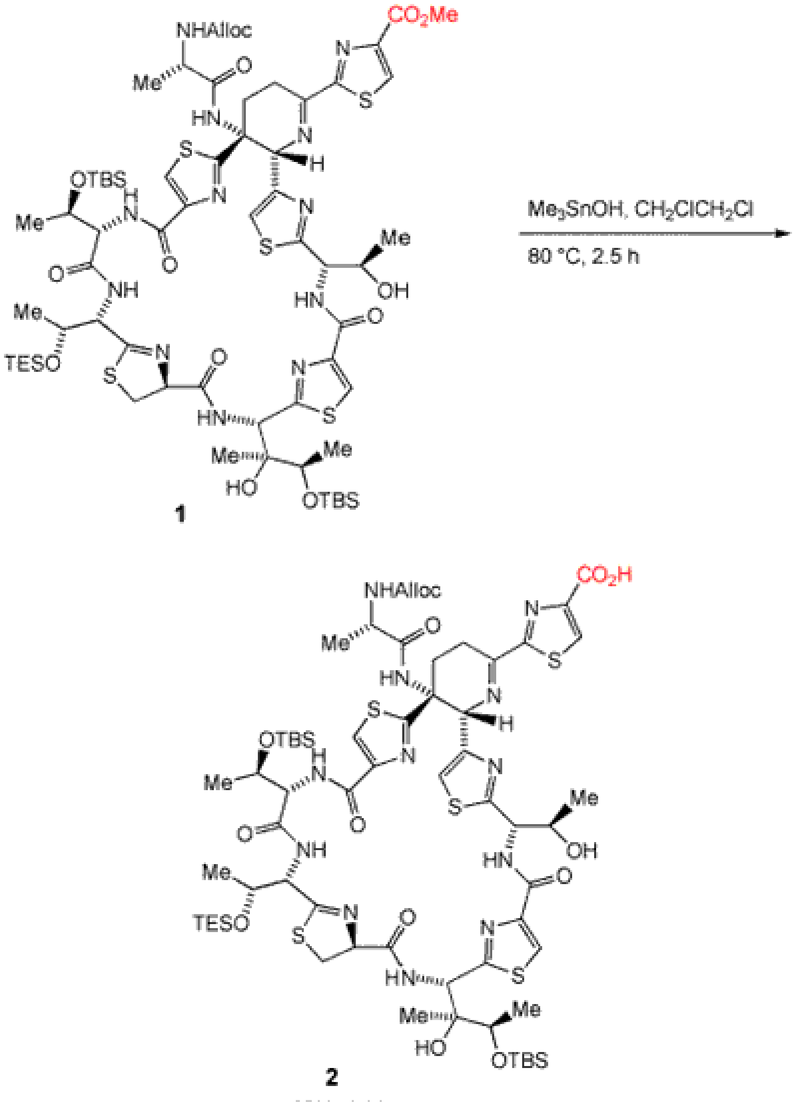
The authors found that the defects occur where nanodomains of polytypes A and B with different stacking directions meet. The HRTEM evidence for these defects sheds light on the layer-by-layer crystallization mechanism of zeolite β, in which crystal growth may nucleate at different parts of the same layer with different stacking vectors. The technique also reveals the presence of silanol hydroxyl groups at the surfaces of defects and pores. (*J. Am. Chem. Soc.* **2005**, *127*, 494－495; George Xiu Song Zhao) Go to top

Produce chiral 1-aryl-2-imidazol-1-ylethanols by catalytic asymmetric transfer hydrogenation. I. C. Lennon and J. A. Ramsden* of Dow Chemical (UK) studied the reduction of imidazolylacetophenones and pinpointed the optimum reaction conditions. The catalyst of choice was [(*R,R*)-TsDPEN]Ru(cymene) Cl (TsDPEN is *N*-*p*-toluenesulfonyl-2,3-diphenylethylenediamine). The reaction can be carried out over a reasonably wide temperature range (25－70 ° C), although more impurities form at higher temperatures.

Typically, if the hydrogenation is carried out in CH_2Cl_2 at 40 ° C with $Et_3N－HCO_2H$ as the reductant, a substrate/catalyst ratio of 1000:1 can be used, and the desired product is produced in 97% yield and 91% ee. Under the same conditions, but with a lower substrate/catalyst ratio (200:1), ee increases to 97%. (*Org. Process Res. Dev.* **2005**, *9*, 110－112; Will Watson) Go to top

Trimethyltin hydroxide promotes mild ester hydrolysis. K. C. Nicolaou and co-workers at the Scripps Research Institute, San Diego, and the University of California, San Diego, were searching for very mild esterification catalysts for their synthesis of the structurally complex thiopeptide antibiotic thiostrepton. The intermediates leading to this drug were too fragile to tolerate standard ester hydrolysis conditions.

The reagent trimethyltin hydroxide (Me_3SnOH) proved to be a solution to this problem, and in several cases resulted in quantitative conversions of the intermediate esters to the corresponding carboxylic acids. The densely functionalized macrocyclic ester intermediate **1** was hydrolyzed to corresponding acid **2** in 100% yield, illustrating the mildness of the technique.



1

2

100% yield

The reaction was tested on 19 substrates and was compatible with a variety of protecting groups, including tributylsilyl, triethylsilyl, *tert*-butoxycarbonyl, 9-fluorenylmethoxycarbonyl (Fmoc), and allyloxycarbonyl. The Fmoc group was of particular interest because other methods did not allow it to survive hydrolysis intact. Also, substrates sensitive to epimerization were stable during this reaction.

The easy isolation of the acid products complemented this new method. Generally, the workup involved washing the organic layer with aqueous $KHSO_4$ or 5% HCl. This procedure usually produced a virtually pure sample of product due to the high solubility of Me_3SnOH in water. (*Angew. Chem., Int. Ed.* **2005**, *44*, 1378－1382; W. Jerry Patterson) Go to top

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