

Selective dihydroxylation of 1 with OsO4 and N-methylmorpholine-N-oxide gave the diol 2. Subsequent

ÕН 5 Dess-Martin periodinane oxidation yielded the hydroxy ketone **3**. Oxidation of **3** with *m*-chloroperbenzoic acid provided the epoxide **4**. Finally, **4** was treated with  $Me_3CISi - NaI$  to promote the tandem transannular cyclization and ring contraction leading to the target structure **5**.

This synthetic strategy should provide a new approach to nine-membered carbocycles with potentially useful biological properties. (*Angew. Chem., Int. Ed.* **2005**, *44*, <u>319 – 322</u>; <u>W. Jerry Patterson</u>) Go to top

**Polyelectrolyte coatings provide precise control over the photonic bandgap of photonic crystals.** I. Manners and co-workers at the University of Toronto and the Polytechnical University of Valencia (Spain) describe the optical properties of conventional photonic crystals from self-assembled monodisperse colloidal spheres. Using current processes, if the stop band of a photonic crystal is not exactly at a required wavelength, a new photonic crystal has to be made after estimating and performing appropriate adjustments. In this paper, high-quality photonic crystal films are first fabricated and then coated iteratively with layers of water-soluble polyelectrolytes. The coating process produces nanometer-scale shifts in the photonic stop band. In addition, the curvature and the geometry of the confining space strongly affect the deposition of polymer electrolytes on colloidal sphere surfaces. (*Langmuir* **2005**, *21*, 499 – 503; George Xiu Song Zhao) Go to top.

**Make perovskite hybrids by intercalating metal halides with ammonium halides.** Inorganic and organic materials enjoy their own advantageous characteristics, but also suffer their own limitations. For example, inorganic materials are stable but difficult to process, whereas organic materials are readily processable but less robust. Hybridization of inorganic and organic components offers the potential of combining the best parts of the two classes of materials, as well as generating new properties from molecularly melding the two kinds of building blocks. M. Rikukawa and coauthors at Sophia University, Tokyo, and Japan Science and Technology Agency, Saitama, have recently succeeded in making ultrathin films of two-dimensional layered perovskite hybrids by a simple intercalation process.



Alkyldiammonium dihalides (XNH<sub>3</sub>RNH<sub>3</sub>X, **1**), such as 1,12-dodecanediammonium dibromide [X = Br, R =  $(CH_2)_{12}$ ], are used to prepare self-assembled organic thin films by conventional spin-coating technique. Immersing the organic films into solutions of metal halides such as lead bromide (PbBr<sub>2</sub>) enables intercalation of the inorganic species into the organic framework, giving the layered perovskite hybrids (NH<sub>3</sub>RNH<sub>3</sub>)PbX<sub>4</sub> (**2**). The intercalated hybrid films exhibit a characteristic exciton peak at 400 nm and emit a strong, sharp photoluminescence at 404 nm, even at room temperature. This indicates that the intercalation readily offers quantum well structures, in which the excitons are confined in the semiconducting inorganic layers sandwiched with organic barrier layers. (*Chem. Commun.* **2005**, <u>378 – 380; Ben Zhong Tang.) Go to top</u>

**Silica particles accelerate epoxy resin curing.** Y.-L. Liu and S.-H. Li of Chung Yuan Christian University (Taoyuan, Taiwan) report that nanoscale silica particles can act as fillers in particles and serve as reactants as well. In the preparation of cured epoxy resins, silica particles can accelerate the

curing reaction, presumably acting as multifunctional silanol monomers. The authors found that this curing was significantly enhanced by adding magnesium chloride, which they suggest serves as a catalyst for silanol – epoxide reactions, lowering the activation energy by 25 kJ/mol. Other metal salts evaluated in this study did not show such catalysis. (*J. Appl. Polym. Sci.*, **2005**, *9*5, <u>1237-1245</u>; <u>David A. Schiraldi</u>) Go to top

**This polymer-supported ligand is very efficient for aldehyde alkylation.** Spanish researchers M. A. Pericàs and coauthors at the Institute of Chemical Research of Catalonia, Tarragona, the University of Barcelona, and the University of Zaragoza-CSIC, found that supported enantiopure amino alcohols could be prepared in two steps, starting from commercially available, enantiomerically pure (*S*)-triphenylethylene oxide. Piperazine anchored Merrifield resin to the chiral ligand, giving a 97% yield of the desired supported ligand (1).



The efficiency of **1** was assessed in the ethylation of several aromatic aldehydes that had substitution in all three ring positions and electron-donating and -withdrawing groups in the ortho position. All substrates were completely converted (>99%), and the alcohol products were obtained with 94 - 95% ee by using a ligand loading as low as 2 mol%. When aliphatic aldehydes were used, percentages of conversions and ee' s were somewhat lower.

A comparison of **1** with a similar homogeneous ligand gave almost identical reaction rates and activities in the formation of 1-phenylpropanol. However, **1** could be recovered and reused over five consecutive cycles without any loss in catalytic activity or enantioselectivity. (*J. Org. Chem.* **2005**, *70*,  $\frac{433-438}{2005}$ ; W. Jerry Patterson) Go to top

**Functionalizing carbon nanotubes improves their solubility and biocompatibility.** A. Bianco and co-workers at the Institute of Molecular and Cellular Biology (Strasbourg, France), the University of London, and the University of Trieste (Italy) review carbon nanotube (CNT) applications in the field of biotechnology. CNTs have been proposed as a promising carrier system for delivering drugs, antigens, and genes. The major drawback of CNTs so far has been their poor compatibility with biological systems because of their complete insolubility in various types of solvents. The authors summarize the organic functionalization of CNTs to improve their solubility and biocompatibility substantially. They demonstrate that many functional groups, such as amino acids, fluorescent probes, and bioactive peptides, can be covalently linked to CNTs through amino groups on the walls of the CNTs.

Functionalized CNTs are highly soluble in aqueous biological media and exhibit notably reduced cellular toxicity in vitro, enabling adsorption or attachment of various molecules or antigens. The CNTs can be subsequently targeted to the desired cell populations for immune recognition or a therapeutic effect, and they can pave a way to gene therapy and genetic vaccination. The authors anticipate the discovery of compounds that are more compatible with carbon nanotube technology and to facilitate more effective use of the nanotubes as delivery systems in therapeutic, preventive, and diagnostic nanomedicine applications. (*Chem. Commun.* **2005**, 571 - 577; George Xiu Song Zhao) Go to top

**One-pot synthesis produces chiral trifluoromethylamines.** Enantiomerically enriched chiral amines are of significant interest as components of biologically active compounds. According to F. Gosselin, P. D. O ' Shea, and coauthors at the Merck Frosst Centre for Therapeutic Research, Kirkland, PQ, and Merck Research Laboratories, Rahway, NJ, a simple one-pot reductive amination of trifluoromethyl ketones provides trifluoromethylated amines in high yields and high enantioselectivities.

Lithium bis(trimethylsilyl)amide was first added to the ketone substrate to yield an N-

trimethylsilylketimine (1) that underwent solvolysis with MeOH to cleave the Si – N bond and form a stable N – H imine (2) as a racemic mixture. Varying amounts of the MeOH adduct were typically observed in the mixture. Catalytic asymmetric reduction of this mixture with a oxazaborolidine catalyst and a borane reductant provided the desired trifluoromethylated amine (3) as the *R*-isomer in the form of a hydrochloride salt.



(*S*)-butyl-OAB is (*S*)-*B*-butyldiphenylpyrrolidinooxazaborolidine. Yields of **3** were in the range of 72 - 95%, depending on the aryl group on the ketone substrate. Similarly, ee values in the range of 75 - 98% were observed. (*Org. Lett.* **2005**, *7*, <u>355 - 358</u>; <u>W. Jerry Patterson</u>) Go to top

**First-principles method predicts catalysis mechanism and kinetics.** K. Honkala and co-workers at the Technical University of Denmark and Haldor Tops øe A/S (Lyngby) developed a complete first-principles description method for predicting the mechanism and kinetics of heterogeneous catalysis. Using the example of ammonia synthesis catalyzed by ruthenium nanoparticles supported on magnesium aluminum spinel, the authors calculated the potential energy of the reaction and showed that rate-limiting step is nitrogen dissociation along step sites where the active (B<sub>5</sub>) sites exist.

In consideration of the effect of local environments on the rate-limiting step, grand canonical Monte Carlo simulations were used to predict the probabilities ( $P_i$ ) of the occurrence of the different local environments to obtain the statistical rate constant of the whole reaction. Further calculation of the activity of the supported ruthenium catalyst suggests that the configuration where hydrogen is adsorbed on the upper step controls the total reaction rate. The authors suggest possible reasons for the good consistency of the model and for discrepancies between the calculated and experimental results. (*Science* **2005**, *307*, <u>555 – 558</u>; <u>George Xiu Song Zhao</u>) Go to top

What do you think of Heart Cut and Patent Watch? Let us know at hcpw@chemistry.org

Patent Watch. Heart Cut Archive Heart Cut in the <u>Chemical Innovation archive</u>. Requires subscription.

> contact us > about acs > faqs > sitemap > login

Copyright © 2005 American Chemical Society. All Rights Reserved. Terms of Use | Privacy Policy | Feedback | Au sujet de la ACS. | Acerca de la ACS.