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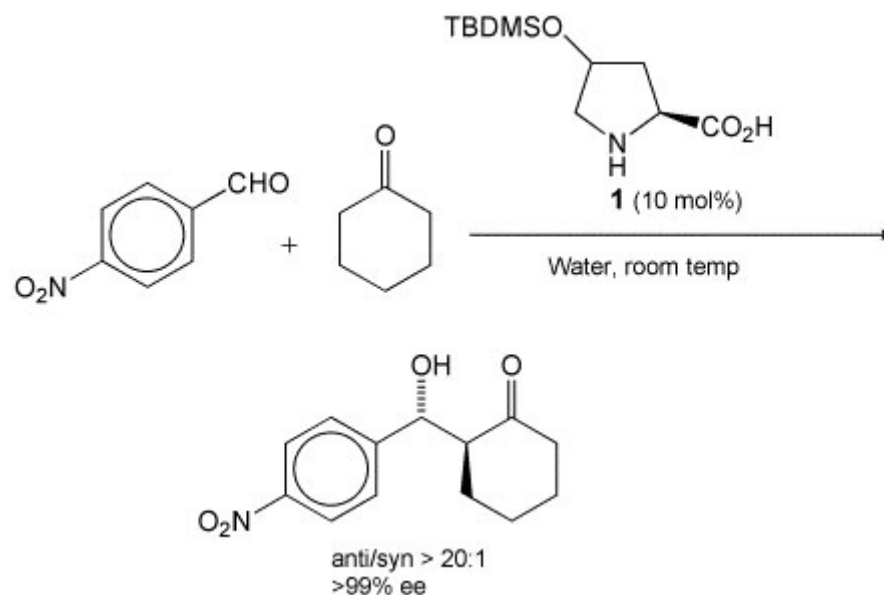
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- [Direct aldol reactions in water have high enantioselectivity](#)
- [Comonomer ratio affects cloud point of polymer solutions](#)
- [Here is a new direct laser-writing technique](#)
- [Metal - organic materials for separating hydrocarbons](#)
- [Faintly luminescent discs self-assemble into emissive helices](#)
- [Reduce side reactions in pyridine - sulfur trioxide oxidations](#)
- [This synthesis of polyynes also provides functionalization](#)
- [Control the morphologies of 2-D ordered arrays](#)

[Patent Watch](#)
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Carry out direct aldol reactions in water with high enantioselectivity. The aldol condensation is an important method for creating the β -hydroxycarbonyl structural unit in many natural products and drugs. Currently, only enzymes and antibodies with very high molecular weights catalyze the direct aldol reaction in water with high enantioselectivity. Y. Hayashi and co-workers at the Tokyo University of Science report, however, that 4-*tert*-butyldimethylsiloxy (TBDMOS) derivative **1** of commercially available *trans*-4-hydroxyproline catalyzes this process with remarkable efficiency. They carried out the aldol reaction of cyclohexanone and benzaldehyde in water at room temperature, yielding the anti aldol product with excellent diastereoselectivity in nearly optically pure form.

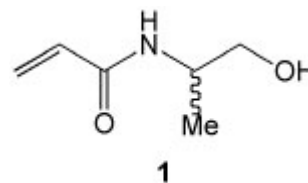


The authors also found that triisopropylsilyl- and *tert*-butyldiphenylsilyl-protected prolines were excellent catalysts. In all cases, the anti isomer was obtained in good yield and in almost optically pure form. The reaction was general with respect to the aldehyde, giving excellent results with reactive, electron-deficient, and neutral aldehydes. High enantiomeric excesses were obtained for electron-rich aldehydes, although the yields were only moderate. Neither proline nor hydroxyproline promoted the reaction in water, showing that the siloxy group on **1** is clearly essential for the success of this reaction.

The catalyst loading of **1** could be reduced to 1 mol% in the aldol reaction without compromising enantioselectivity. The authors observed that **1** is the first organic catalyst that promotes the aldol condensation in water, a process that has until now been solely in the realm of enzyme chemistry. (*Angew. Chem., Int. Ed.* **2006**, *45*, 958 – 961; [W. Jerry Patterson](#)) [Go to top](#)

Ratio of comonomers affects the cloud point of these polymer solutions. T. Aoyagi* and co-workers at Kagoshima University (Japan) have designed a thermoresponsive copolymer with a high hydroxyl group content.

When aqueous poly(*N*-isopropylacrylamide) solutions are heated to >31 ° C, the polymer turns from hydrophilic to hydrophobic; and an emulsion, or “cloud”, forms. To modify this polymer, the authors synthesized a structurally similar monomer, *N*-(1-hydroxy-2-propyl)acrylamide (**1**), and randomly copolymerized it in various ratios with the original monomer.



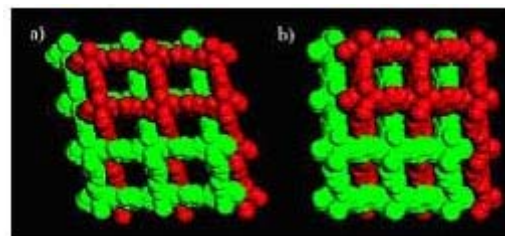
The cloud points of solutions of the resulting series of copolymers were temperature-responsive, shifting to higher temperature with increasing hydrophilic **1** content. This effect was unresponsive to pH changes.

The phase transition temperature could also be easily adjusted by adding NaCl to the solutions: It decreased with increasing NaCl concentration. Furthermore, copolymers that contained high levels of **1** formed monodisperse coacervate droplets above the cloud point. Because of the hydroxyl group in the side chain, the droplets could immobilize peptide and protein molecules, creating potential applications in bioseparation and purification. (*Biomacromolecules* **2006**, 7, 545–549; [Sally Peng Li](#)) [Go to top](#)

Here is a new direct laser-writing technique. G. A. Ozin, G. von Freymann, and coauthors at the University of Toronto, the Helmholtz-Gemeinschaft Karlsruhe Research Center (Germany), and the University of Karlsruhe created direct laser-written (DLW) 3-D photonic crystals with a photonic band gap (PBG) made from high-index As₂S₃ glasses. These materials are amorphous semiconductors with high transparency throughout the IR and near-IR spectral regions. The crystals' index of refraction (*n*) lies between 2.45 and 2.53, sufficient to open a PBG.

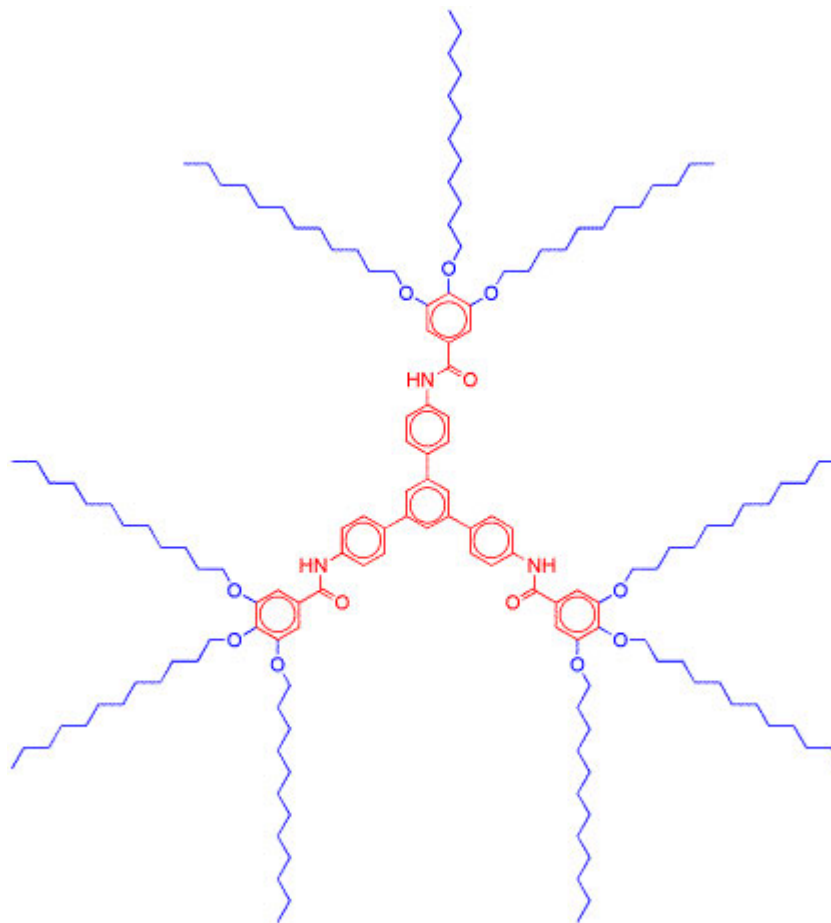
Further modifications of the writing parameters could lead to a complete gap approaching a gap/midgap ratio of 9%. Even larger PBGs may be achieved if higher refractive index chalcogenide glasses, such as As₂Se₃ (*n* = 2.78) or As – Se – Te composites (*n* as high as 3.2), behave similarly under photoexposure and compensation is made for higher order spherical aberrations. When combined with the inherent ability of DLW to produce functional defects such as waveguides and resonators, this approach might be a powerful alternative to established production techniques. (*Adv. Mater.* **2006**, 18, 265 – 269; [George Xiu Song Zhao](#)) [Go to top](#)

Metal – organic framework materials may be suitable for gas chromatographic separations of hydrocarbons. B. Chen, S. Dai, and coauthors at the University of Texas – Pan American (Edinburg), Oak Ridge National Laboratory (TN), the University of Michigan (Ann Arbor), and Cornell University (Ithaca, NY) report that zeolite analogues—microporous metal – organic framework materials—can be used for efficient gas chromatographic separations of alkanes. Their 4.0 x 4.0 Å pores, which are capable of discriminating between linear and branched hydrocarbons, are the key to these new materials.



$\text{Zn}(\text{NO}_3)_2$, terephthalic acid, and 4,4'-bipyridine were heated for 24 h at 90 °C to produce $\text{Zn}(\text{1,4-benzenedicarboxylate})(\text{4,4'-bipyridine})_{0.5}$. This material is stable to 300 °C and undergoes a reversible open phase – dense phase transformation (**a** and **b**, respectively, in the figure). The open-phase form has the ability to separate out larger molecules. (*Angew. Chem., Int. Ed.* **2006**, *45*, 1390 – 1394; [David A. Schiraldi](#)) [Go to top](#)

Symmetric, faintly luminescent discs self-assemble into strongly emissive helical fibers. Helical morphologies have been generated by the supramolecular self-assembly of chiral molecules, but few reports have described the helical organization of achiral molecules. R. Lu and coauthors at Jilin University (Changchun, China) and Kanagawa Academy of Science and Technology (Japan) report a system in which a group of achiral discotic molecules self-organize into helical organogels.



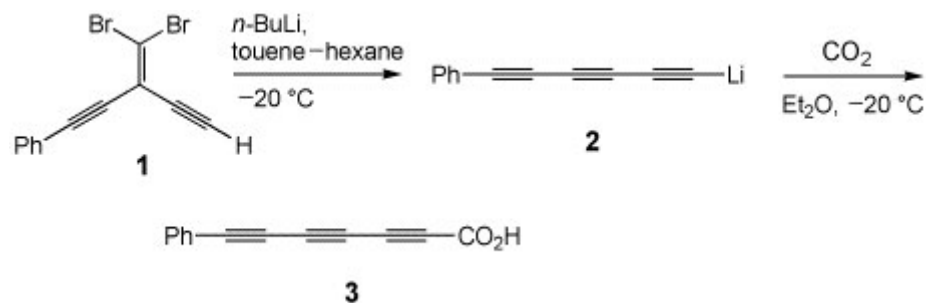
The discotic molecules consist of triarylbenzene cores and alkoxy side chains. One example, shown above, is a molecule with nine dodecyl chains. The discotic molecules form organogels in apolar aromatic, aliphatic, and chlorinated solvents. The gels' morphologies vary with the structures of the alkoxy groups.

The supramolecular assembly is driven mainly by intermolecular hydrogen bonding and π - π interactions. Helix formation is the result of cooperative chiral induction in the packing process of the aryl cores and the alkoxy chains. The discotic molecules show unusual aggregation-induced emission enhancement: Their solutions are weakly luminescent, but their gels are highly emissive. (*Chem. Eur. J.* **2006**, *12*, Early View [DOI: 10.1002/chem.200501058]; [Ben Zhong Tang](#)) [Go to top](#)

A simple modification reduces side reactions in pyridine – sulfur trioxide oxidation reactions. Commercial sources of the pyridine – SO_3 complex often contain pyridine – H_2SO_4 1:1 and 2:1 salts. L. Chen and co-workers at Pfizer Chemical Research and Development (San Diego) showed that the 1:1 salt can significantly increase the formation of impurities during Swern-type oxidations, whereas the less acidic 2:1 salt does not. This finding led to a simple fix—adding additional pyridine to convert all of the 1:1 salt to the 2:1 salt before carrying out the oxidation. (*Org. Process Res. Dev.* **2006**, *10*, 163 – 164; [Will Watson](#)) [Go to top](#)

A one-pot synthesis of polyynes also provides terminal functionalization. Y. Morisaki, T. Luu, and R. R. Tykwinski* at the University of Alberta (Edmonton) have developed a one-pot method for synthesizing di- and triynes based on the in situ formation of a lithium acetylide intermediate (**2**) directly from a *gem*-dibromoolefin (**1**). The synthesis of **2** leads to two routes for functionalizing the polyynes.

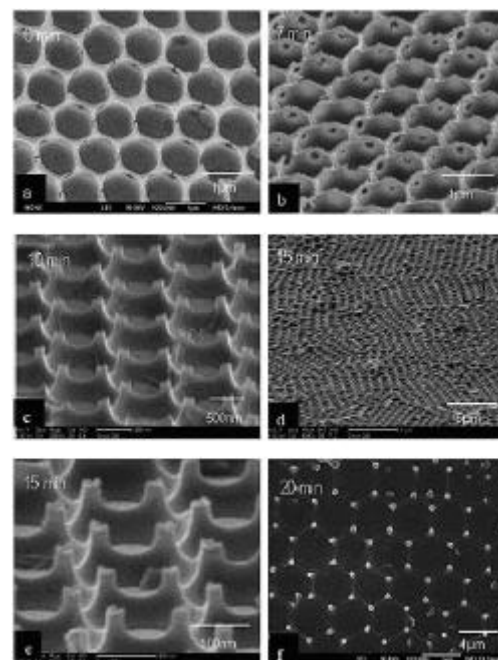
In the first route (illustrated), **2** is trapped in situ with an electrophile, yielding the terminally functionalized polyyne **3**. In the second, transmetalation of **2** provides a zinc- or tin acetylide, ultimately leading to aryl- or ketone-functionalized polyynes via cross-coupling reactions.



This method was applied to a series of electrophiles to provide terminally functionalized diynes and triynes in good yields. This overall process eliminates the need for terminal polyynes as precursors, and it still provides functional derivatives that are difficult to prepare in a stepwise process. This is important because the kinetic stability of terminal alkynes decreases dramatically as the number of conjugated $\text{C}\equiv\text{C}$ bonds increases. (*Org. Lett.* 2006, *8*, 689 – 692; [W. Jerry Patterson](#)) [Go to top](#)

Control the morphologies of 2-D ordered arrays by the heating-induced deformation of 2-D colloidal monolayers. W. Cai and co-workers at the Chinese Academy of Sciences (Anhui) present a new strategy of solution dipping sintered monolayer

colloidal templates to make morphology-controlled 2-D ordered arrays. The authors control the sintering time to deform the colloidal-monolayer templates to various extents. Increasing the heating time of the templates produces, in order, spherical-pore arrays, honeycomb-shaped arrays, nanopillar arrays, and regular networks, as shown in the figure.



The unit size in the arrays is adjustable by changing the diameter of the polystyrene spheres in the templates. Moreover, this strategy should apply to many materials beyond the Fe_2O_3 and SiO_2 described in this article. Such morphology-controlled arrays may have practical applications in waveguide ring lasers, energy storage or conversion, gas sensors, catalysts, field emission, and biomedical devices. (*J. Mater. Chem.* **2006**, *16*, 609 – 612; [George Xiu Song Zhao](#)) [Go to top](#)

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