Heart Cut

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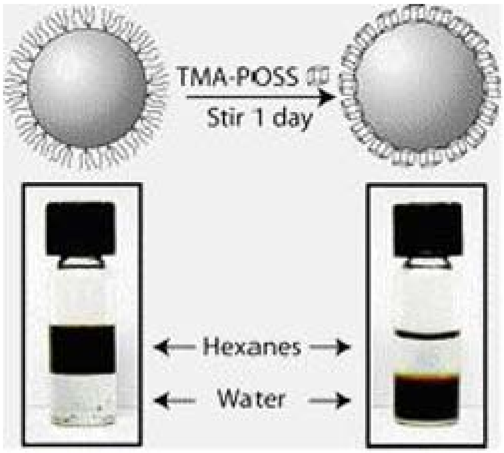
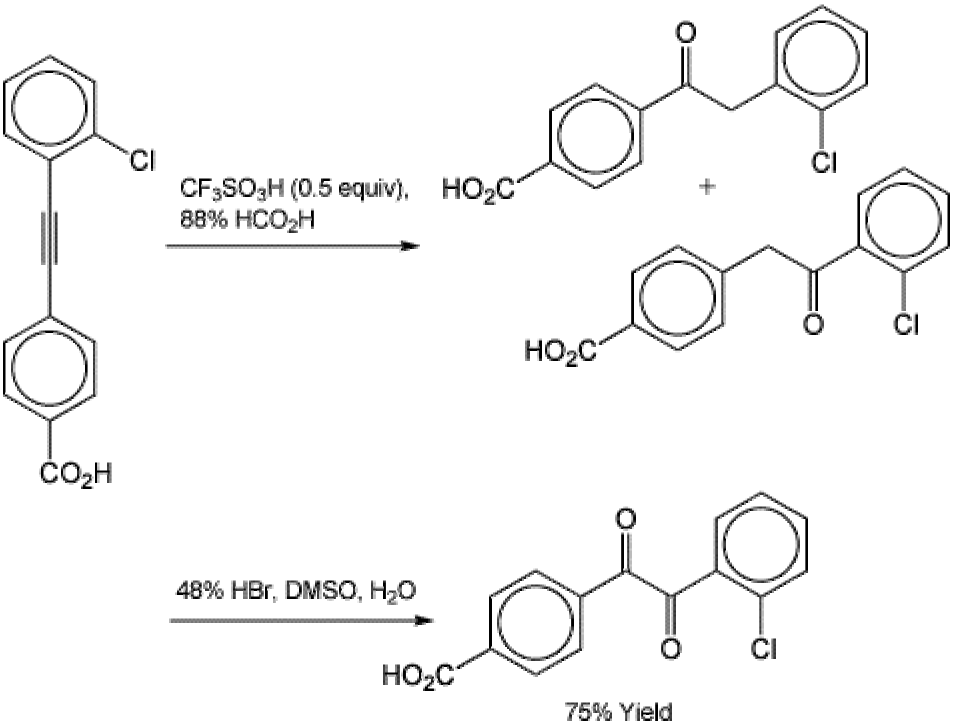
Make metal oxide particles water-soluble with nanoscale "POSS". Polyhedral oligomeric silsesquioxanes (POSS; see www.hybridplastics.com for an overview) form a family of nanoscale materials that typically couple an inorganic Si_8O_{12} cube with eight peripheral organic units. By tailoring the organic groups, it is possible to make the POSS structure compatible or even miscible with polymers and other materials. In recent years, researchers have reported property enhancements such as flame retardancy, protection against cosmic rays, improved mechanical wear, and increased use temperatures.

V. M. Rotello and co-workers at the University of Massachusetts–Amherst report that a water-soluble POSS derivative, functionalized with $–O^- N(Me)_4^+$ at each of the eight corners of the molecular cube, can be used to solubilize otherwise water-insoluble metal oxide nanoparticles. The authors produced iron oxide nanopolymers by the thermal decomposition of iron cupferron in the presence of octylamine and trioctylamine. The resulting particles, surface-modified by the long-chain amines, were soluble in hydrocarbon solvents.



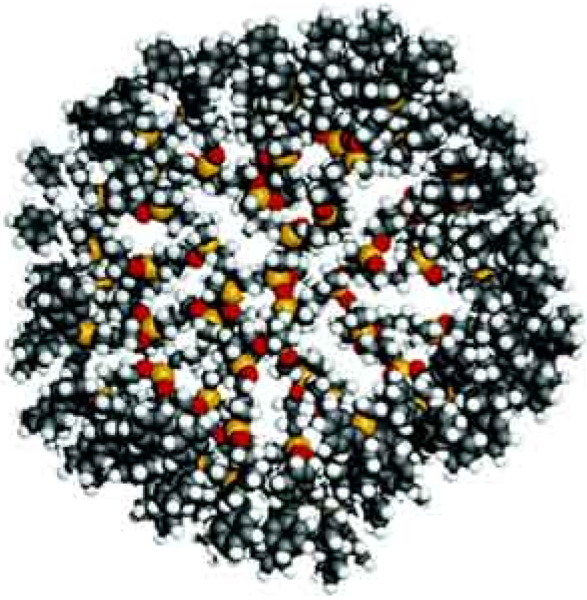
Ligand exchange by stirring a toluene solution of the nonpolar particles with aqueous $N(Me)_4^+$ POSS, as shown above, replaced the alkylamines with POSS, making the particles water-soluble. The POSS–iron oxide particles were stable under physiological temperature, salinity, and pH conditions. Their solubility in water may lead to using them for phase-transfer agents in medicine. (*Chem. Mater.* **2006,** *18,* 956–959; David A. Schiraldi) Go to top

Convert alkynes to α-diketones. X. Wan and co-workers at Eli Lilly and Company (Indianapolis, IN) were looking for a conversion that would be practical under mild reaction conditions. They also wanted to avoid stoichiometric inorganic oxidants and toxic transition metal catalysts. Their strategy was to circumvent the problems encountered with direct oxidation of alkynes to α-dicarbonyl structures via a sequence in which the alkyne was first hydrated to the monoketone, then oxidized to the diketone.
The researchers carried out the hydration step using a strong Brønsted acid, CF_3SO_3H, with commercially available 88% HCO_2H serving as water donor and solvent. Then they added DMSO (as the stoichiometric oxidant) and a catalytic amount of HBr to oxidize the intermediate to the desired dicarbonyl compound.



Product yields were in the range of 53–93%. The reaction was restricted for the most part to diarylalkynes, and it proceeded smoothly with electron-rich or electron-poor aryl substituents. The reaction tolerated free amine and carboxylic acid groups, allowing the preparation of highly functionalized molecules of potential synthetic interest. (*J. Org. Chem*. **2006,** *71*, 826–828; W. Jerry Patterson) Go to top

Cap the edges of dendrimers with luminescent silole rings. The luminescence properties of most dendritic macromolecules synthesized to date are provided by their chromophoric cores. C. Kim, J. Ko, S. O. Kang, and coauthors at Korea University (Chung-nam), Dong-A University (Pusan, South Korea), and Ewha Woman's University (Seoul) have prepared a series of new luminescent dendrimers that feature emissive silole groups on their peripheries. The researchers synthesized the silole-capped dendrimers using an eight-membered cyclotetrasiloxane as the core and allyl alcohol and $HSiMeCl_2$ as iterative building blocks. The reaction of the chloride groups of the dendrimers with 1,4-lithiotetraphenylbutadiene attached the silole rings to the peripheries. A molecular model of the fourth-generation dendrimer is shown below as an example: It contained 3 propylenoxy inner layers and 32 silole peripheral rings. Its molecular weight (M_w) was as high as 17,595, with a polydispersity index as low as 1.011, demonstrating the effectiveness of the synthesis route and the defect-free nature of the dendritic structure.

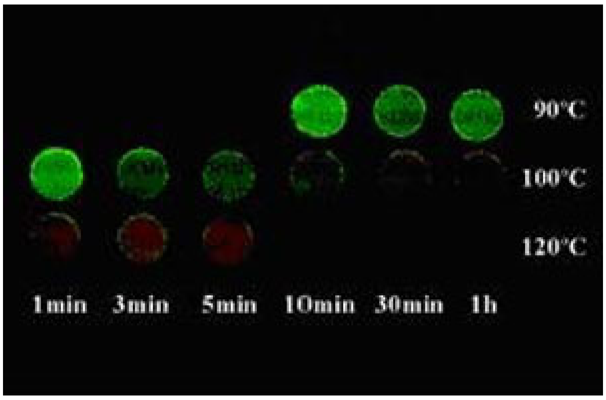


The authors also prepared dendritic siloles with vinyl inner shells and silolyl peripheral end groups. The absorption and emission features of the solutions and films of the two types of dendrimer were similar, suggesting that their dendritic nature is preserved in the solid state. (*Organometallics* **2006**, *25*, 766–774; Ben Zhong Tang) Go to top

Here is a new method for synthesizing substituted pyrazoles. A. Ohigashi*, K. Temmaru, and N. Hashimoto of Astellas Pharma Inc. (Osaka, Japan) converted 3-cyanopyridine to 4-(3-aminopropyl)-5-amino-1-methylpyrazole in two steps. First, the starting material was reduced with $NaBH_4$ to give the cyanoenamine 1,4,5,6-tetrahydropyridine-3-carbonitrile. The subsequent reaction with NH_2NHMe in the presence of 1 equiv of concd HCl gave a 90:10 mixture of regioisomers in favor of the desired compound. Higher acid loadings or alternative acids such as H_2SO_4 gave a less favorable regioisomeric ratio. (*Org. Process Res. Dev.* **2006,** *10,* 159–162; Will Watson) Go to top

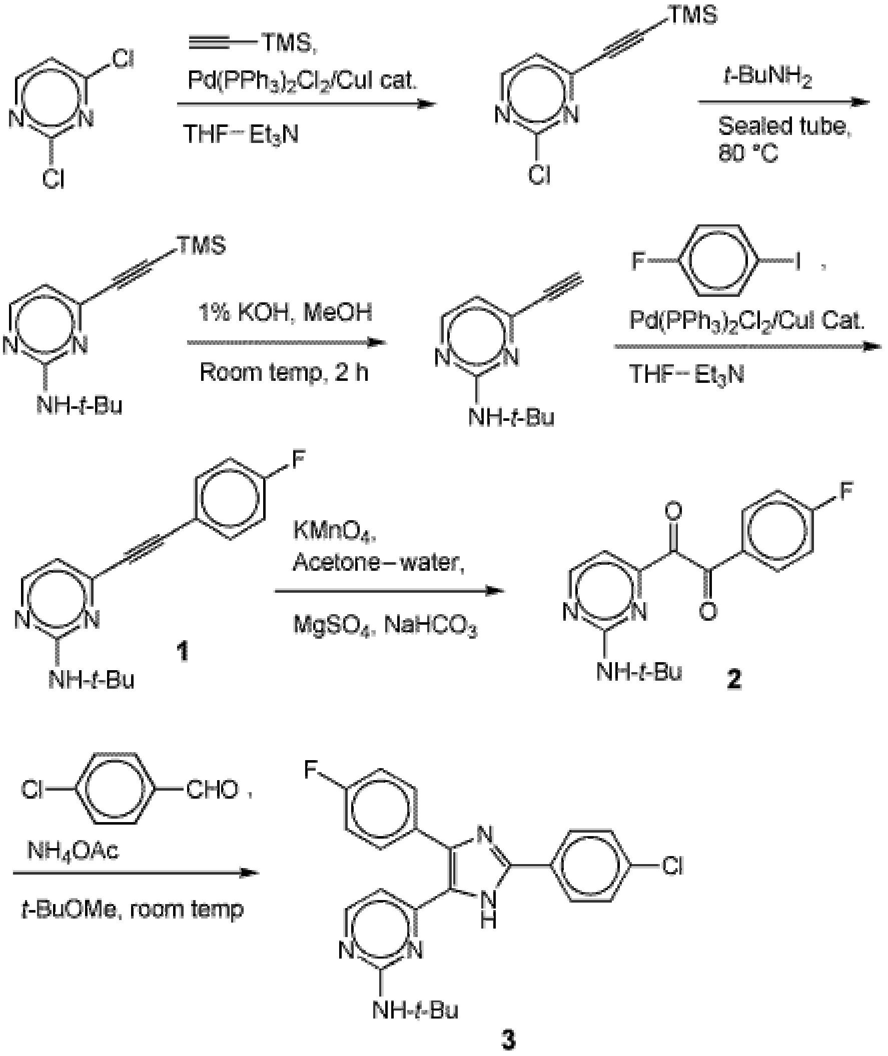
Dye-doped polymers can be used as temperature or deformation sensors. M. Kinami, B. R. Crenshaw, and C. Weder* of Case Western Reserve University (Cleveland, OH) report that distributing excimer-forming photoluminescent dyes within polymer matrices can produce films that change color upon heating or deformation. Dyes such as 1,4-bis(α-cyanooctadecyloxystyryl)benzene were chosen for blending into poly(ethylene terephthalate) and its copolymers because they can be distributed within the matrix despite their limited solubility.

When the dye–polymer blends are heated to above the polymer’s *T*g, they tend to aggregate. Mechanical deformation of the films similarly changes the distances between dye molecules. Changing the degree of dye molecule aggregation alters the excimer emissions, causing as much as a 138-nm shift in the wavelength of the visible light produced by UV irradiation, as shown below.



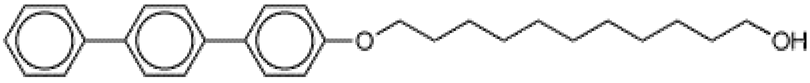
Thus, the nature of the groups bonded to the chromophore (which determines dye solubility and therefore the ability of dye molecules to diffuse) and the stress–strain properties and *T*g of the matrix polymer can be used to tune the observed effects. Applications for this technology include temperature-monitoring films that report warming of refrigerated foods as well as antitampering seals for foods and pharmaceuticals. (*Chem. Mater.* **2006,** *18,* 946–955; David A. Schiraldi) Go to top

Functionalizing 2,4-dichloropyrimidine efficiently provides 4,5-disubstituted imidazoles. Several companies are pursuing derivatives of 4-aryl-5-pyrimidinylimidazole for use as possible anti-inflammatory drugs. X. Deng and N. S. Mani* at Johnson & Johnson (San Diego) have developed a concise six-step reaction sequence to this important scaffold that compares favorably with existing methods.

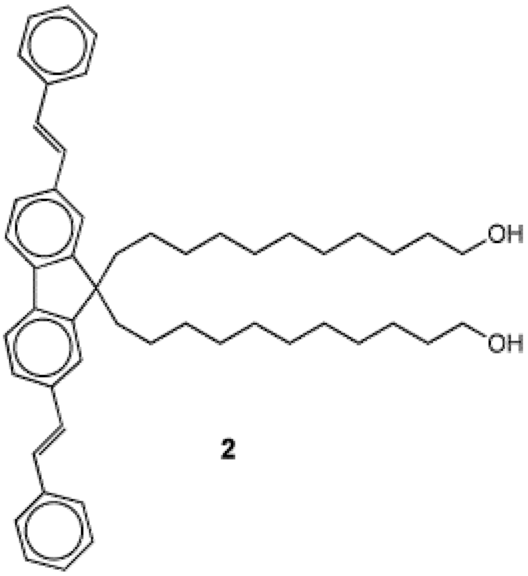


The authors’ strategy involved the sequential substitution of the 4- and 2-chloro groups in the starting compound by regioselective Sonogashira coupling to give alkyne **1**. Oxidizing the alkyne group by very finely powdered $KMnO_4$ gave the diketone intermediate **2**. Finally, cyclocondensation of **2** with an aldehyde gave the target pyrimidinyl-substituted imidazole **3** in good overall yield. The method appears to provide ready access to a variety of structurally related 1,2-diketone and imidazole analogues. (*Org. Lett.* **2006,** *8,* 269–272; W. Jerry Patterson) Go to top

More highly ordered aggregates luminesce more efficiently. When chromophoric molecules are packed in an orderly fashion, the resulting crystalline aggregates exhibit high charge mobilities. Unfortunately, however, crystal formation often weakens or completely quenches the luminescence of the chromophores. Therefore, researchers are seeking other types of ordered chromophoric molecules that can emit efficiently. C. J. Bhongale and C.-S. Hsu* of the National Chiao-Tung University of Taiwan (Hsinchu) have synthesized such a molecular system.



1



2

The researchers synthesized the chromophoric amphiphiles **1** and **2**, which are emissive in dilute solution. Their solid films are, as expected, only weakly luminescent because of the well-known quenching effect of chromophoric aggregation. Surprisingly, however, their self-assembled hybrid nanocomposites with silica emit efficiently, with the fluorescence quantum yields as much as ~6-fold higher than those of their film counterparts. The crystalline aggregates in the amphiphile–silica nanocomposites show promise as charge-transporting and light-emitting materials for the manufacture of efficient electroluminescent devices. (*Angew. Chem., Int. Ed.* **2006,** *45,* 1404–1408; Ben Zhong Tang) Go to top

Helical liquid crystals self-assemble from achiral building blocks. Z. D. Cheng and coauthors at the University of Akron (OH) and the City University of New York (Staten Island) prepared a series of derivatives of 4'-hydroxy-4-biphenylcarboxylic acid in which a six-carbon aryl ether–terminated flexible chain is attached to the phenolic oxygen atom. The aryl group was phenyl, *m*-hydroxyphenyl, *p*-hydroxyphenyl, or *m*-methoxyphenyl. These molecules form carboxylic acid hydrogen-bonded dimers that serve as building blocks for liquid crystals. Despite the absence of chirality or fixed-bent (banana) geometries in these molecules, the carboxylic acid dimers self-assemble into helical supramolecular structures. Computer simulations indicate that the dimers exist in twisted conformations–axial chiral conformers of individual head-to-head dimers–that create the supramolecular helices. Right- and left-handed helices can be formed from the same starting materials. This work sheds additional light on the fundamental nature of liquid crystals, which are currently being used in many applications. (*Chem. Mater.* **2006,** *18,* 680–690; David A. Schiraldi) Go to top