

along with the demonstration of good performance of the devices, opens the way to further exploration of these methods for organic laser production.

AMANDA GIERMANN

### Poly(3,3'-dialkyl-terthiophene) OTFTs Stable under Ambient Atmospheric Conditions

Organic thin-film transistors (OTFTs) have the advantages of low-cost solution fabrication and excellent flexibility, which enable their application in devices such as flexible displays and electronic paper. However, most solution-processed organic semiconductor materials used in OTFTs either have poor structural order from solution or their performance is degraded by atmospheric oxygen doping. Recently, a group of scientists from Xerox Research Center of Canada demonstrated that poly(3,3'-dialkyl-terthiophene)s have sufficient air stability to enable solution fabrication of functionally useful OTFTs under ambient conditions.

As reported in the January 25 issue of *Chemistry of Materials* (p. 221; DOI: 10.1021/cm048678r), B.S. Ong and co-

workers synthesized poly(3,3'-di-*n*-octylterthiophene) by a controlled FeCl<sub>3</sub>-mediated polymerization in chlorobenzene. While most solution-processed semiconductors used in OTFTs need high-temperature *in situ* reactions or postdeposition thermal annealing, the material the research team designed, poly(3,3'-di-*n*-octylterthiophene), could be processed at room temperature and showed higher field-effect transistor (FET) mobility without thermal treatment. Through the study of poly(3,3'-di-*n*-octylterthiophene), the researchers demonstrated the profound influence of side-chain regiochemistry on molecular ordering behavior and the subsequent impact on field-effect characteristics.

Using poly(3,3'-di-*n*-octylterthiophene) as the channel material, the researchers then fabricated and characterized their OTFT devices at room temperature and in open air. These 20–50-nm-thick devices (90 μm or 190 μm channel length, channel width of 1 mm or 5 mm), fabricated on a 100-nm-thick thermal oxide on an *n*-doped silicon wafer, showed near-ideal FET behavior and greater ambient stability

compared with other organic semiconductors. The researchers said that the excellent self-organization ability in thin films from solution at room temperature without thermal assistance and its stability in air may render poly(3,3'-dialkyl-terthiophene) an ideal channel semiconductor for low-cost OTFTs. This technology could ultimately lead to inexpensive large-area devices like flat-panel and flexible displays and low-end microelectronics such as rf identification tags.

TAO XU

### Low-Density Sublimed *p*-tert-butylcalix[4]arene Demonstrates Ability for Methane Storage at Room Temperature

Calixarenes are complex organic compounds formed by phenolic molecules arranged in open structures capable of encapsulating different ions or molecules. One form of these compounds is calix[4]arene, which can stably entrap vapor or gas molecules, releasing them only after heat decomposes its structure. As *p*-tert-butylcalix[4]arene, it can selectively adsorb CO<sub>2</sub> from a mixture with H<sub>2</sub>.



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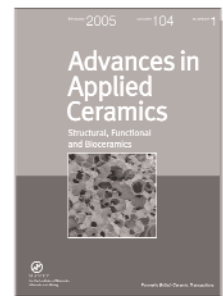
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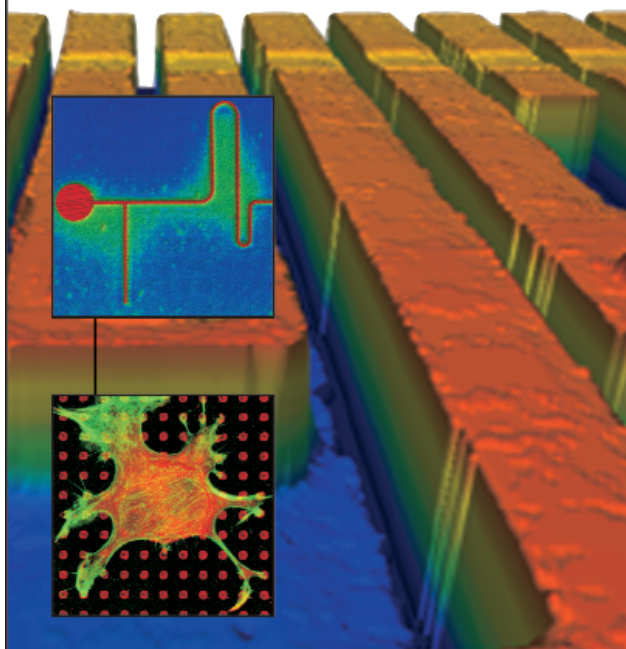
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Using this form of the compound, J.L. Atwood and colleagues from the University of Missouri—Columbia together with L.B. Barbour from the University of Stellenbosch, South Africa, have demonstrated its ability to absorb methane at standard conditions of temperature and pressure, as they explained in the January issue of *Chemistry Communications* (p. 51; DOI: 10.1039/b416752j).

The investigators constructed a system to measure gas sorption, composed of two chambers joined by modular brass components with valves for isolating and regulating pressure and electronic transducers on each chamber to measure pressure. By placing it in an insulated enclosure, the researchers were able to maintain the system at a constant temperature during testing. First, the research team placed 1.4 g of sublimed powders of *p*-*tert*-butylcalix[4]arene in one chamber (volume = 12.6 cm<sup>3</sup>) and vacuum-sealed the system, closing all valves to isolate each chamber. Then, they filled the other chamber (volume = 15.4 cm<sup>3</sup>) with methane to a pressure of 1503 Torr, and later allowed the pressure in both chambers to balance, opening the communicating valve for 1 s and then closing it. At this point, the recorded pressure in the chamber containing the *p*-*tert*-butylcalix[4]arene powders started to decrease continuously, until it reached equilibrium after 2.5 h. The corresponding pressure measured was 410 Torr, giving a molar ratio of 0.14:1 methane to calixarene.

A rigid model of the crystalline structure of *p*-*tert*-butylcalix[4]arene shows this compound as a pair of concave molecules in front of each other but slightly off, containing a 235 Å<sup>3</sup> cavity, thus forming a capsule with seemingly nonporous walls, which would prevent gas adsorption. In order to explain the occurrence of gas adsorption, the researchers analyzed the solid-state model of the *p*-*tert*-butylcalix[4]arene structure: finding that the *tert*-butyl groups of the molecule could rotate around the C(ar)-C(sp<sup>3</sup>) bond, while the aromatic and hydroxyl regions remained static. The proposed interpretation of the results is based on the existence of windows of opportunity created by the cooperative rotation of these groups, which the gas molecules use to gain entrance to the *p*-*tert*-butylcalix[4]arene cavity. This study demonstrated that methane represents the optimal occupation of available space, since the compound cavity can accommodate two molecules of the methane instead of just one for CO<sub>2</sub>. Calculations from the results demonstrated that 14% of the capsules thus formed contain two molecules of methane at 0.54 atm on average. So long as the *p*-*tert*-butylcalix[4]arene remains low density, said the researchers, its potential as a sorbant for volatile gases qualifies it as a viable gas-storage substrate.

SIARI SOSA

### Far-Field Raman Scattering Reveals Surface Plasmons of Gold Nanoparticle Arrays

Surface plasmons are collective excitations of conduction electrons that are excited by the interaction of an electromagnetic field (light) with a metal surface. When the size of the metal particles is much smaller (i.e., nanoparticles) than the characteristic wavelength of the impinging light wavelength, the surface plasmon is at the same time an excited electronic state localized on the particle surface and a local polariton mode of the electromagnetic field. In both cases, the surface plasmon is accompanied by an enhancement of the electromagnetic field, which has opened new applications in subwavelength optics and high-sensitivity spectroscopy (i.e., surface-enhanced Raman scattering, or SERS). In the February 9 issue of *NanoLetters* (p. 253; DOI: 10.1021/nl048234u), in a joint collaboration, G. Laurent (Université de Paris 7), J.R. Krenn (Karl Franzens Universität, Austria), and their colleagues have recorded images of localized surface plasmons using Raman scattering of a molecular probe (methylene blue, MB) adsorbed on regular arrays of gold nanoparticles.

SERS spectroscopy has demonstrated that only a few particles are responsible for the Raman signal of a molecular probe adsorbed on silver or gold nanoparticles deposited on a substrate. These active