

porous, size-selective, zeolite particles to polymer matrices. However, the reliability of such membranes was compromised by poor polymer/zeolite adhesion and inadequate particle dispersion. In this research study, nonporous, fumed silica particles were added to disrupt the molecular bonding in a rigid glassy polymer. Fine silica particles subtly increased the size of the free-volume voids in the polymer matrix, as revealed by positron annihilation lifetime spectroscopy (PALS). Since it is through a network of these larger voids that the penetrants are assumed to diffuse, slightly increasing their size enhanced the membrane's reverse-selectivity by further weakening the size-sieving character of the PMP and improved its permeability by enabling faster diffusion.

Critical to this method, said the researchers, was the addition of particles comparable in size to the polymer molecule; adding an equivalent volume of particles larger than 50 nm in diameter did not improve permeability since it did not uniformly alter the polymer chain packing. Transmission electron microscopy imaging of the membranes revealed well-distributed, discrete silica particles and silica aggregates within the PMP matrix, consistent with the proposed mode of enhanced transport and selectivity by molecular-scale alteration of the polymer structure.

JULIE NUCCI

Metallo-Supramolecular Cylinders Induce Intramolecular DNA Coiling

Proteins regulate the structure and function of life encoded in DNA with their ability to recognize the genetic code in a sequence-selective manner and induce structural changes in DNA. The ability to turn processing of the genetic code on or off requires a variety of molecular tools. Advancing toward this goal, researchers from the University of Warwick in Coventry, England; Universitat de Barcelona, Spain; and the University of Bergen, Norway have employed synthetic supramolecular assemblies to selectively bind to the major groove of DNA, causing the DNA to coil significantly. (DNA's surface is not a smooth cylinder but has two differently sized grooves.)

Enantiomers are molecules that are nonsuperimposable mirror images of each other. In enantio-selective binding, one enantiomer binds but not the other. As reported in the April 16 issue of the *Proceedings of the National Academy of Sciences*, teams led by University of Warwick researchers A. Rodger and M.J. Hannon employed a variety of experimental techniques to explore the

enantio-selectivity of the binding of $[\text{Fe}_2(\text{C}_{25}\text{H}_{20}\text{N}_4)_3]\text{Cl}_4$ —a cylindrical tetra cationic dimetallo triple helicate—to DNA. Rodger and Hannon previously showed that a racemic mixture (i.e., contains equal amounts of both enantiomers) of $[\text{Fe}_2\text{L}_3]\text{Cl}_4$ induced a dramatic intramolecular bending, but the resulting DNA coils contained only the M enantiomer.

Small synthetic molecules designed to achieve DNA sequence selectivity typi-

cally bind to the minor groove of DNA. Recognition is generally limited to 2–3 base pairs due to size limitations. Sequence recognition within the major groove may prove more fruitful because its size and shape vary much more with base sequence than does the minor groove, said the researchers. Indeed, they said, many biomolecules target the major groove. Rodger and Hannon believe that supramolecular chemistry provides an

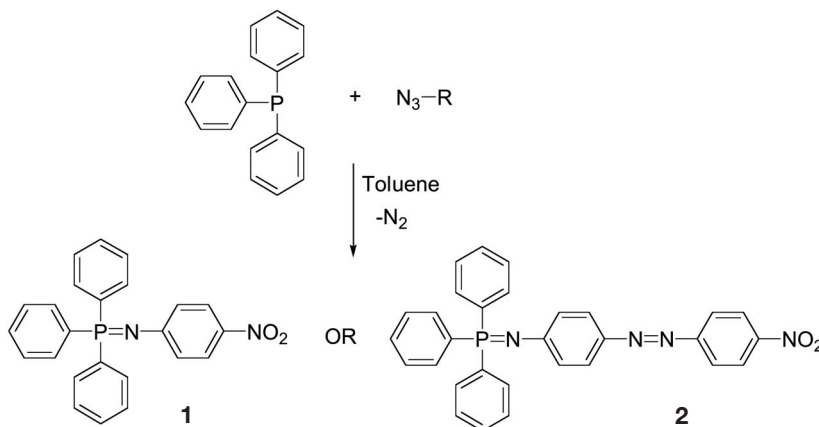
Versatile and Efficient Nonlinear Optical Material Chromophore Developed

Researchers at the University of Missouri and the Dow Chemical Company have demonstrated that azaphosphane compounds can act as electron-donor functional groups in nonlinear optical (NLO) materials. NLO materials have found applications in optical data storage, optical information processing, and optical/electro-optical switching devices. The researchers, led by Kattesh Katti, determined that the azaphosphane chromophores exhibited good NLO activity while maintaining excellent solubility in common organic solvents. The compounds also exhibited thermal stability up to 335°C. According to Katti, "the azaphosphanes will allow the design and development of novel, thermally stable NLO materials."

As described in the June 17 issue of *Chemistry of Materials*, the researchers synthesized two azaphosphane compounds having a P=N donor group and a NO_2 acceptor group that are separated by one (Compound 1) or three (Compound 2) conjugated double bonds (see Scheme). The air-stable product compounds were characterized by nuclear magnetic resonance spectroscopy and mass spectrometry. The NLO activities of the two chromophores were measured by the electric-field second-harmonic technique using 1579-nm light. This technique yields the NLO activity as a product of the dipole moments (μ) and the hyperpolarizability (β) of the azaphosphane molecules. Compounds 1 and 2 exhibited $\mu\beta$ values of 3.1×10^{-46} and 11×10^{-46} esu, respectively. The larger $\mu\beta$ value corresponds to a larger change in the molecular dipole moment upon irradiation which leads to a higher NLO activity. The researchers attribute this larger NLO activity of Compound 2 to increased conjugation length, which improves donor-acceptor interactions. While these $\mu\beta$ values are not as high as those reported for thiophene-based chromophores, Compounds 1 and 2 exhibit excellent solubility in organic solvents that decreases for molecules with large dipole moments. High solubility will allow the azaphosphanes to be used with a large number of polymer hosts in the manufacture of NLO materials.

Also important for applications in NLO materials is the thermal stability of the chromophore. The thermal stability of the azaphosphanes was studied by thermogravimetric analysis and differential scanning calorimetry. Compound 1 was stable to above 282°C, while Compound 2 was stable to 335°C, much higher than thiophene-based chromophores. The researchers attribute the high thermal stabilities to the inherent stability of P–N compounds.

GREG KHITROV



Scheme. Synthesis of azaphosphanes. Reprinted with permission from *Chem. Mater.*, June 17, 2002, 14. Copyright 2002 American Chemical Society.

excellent method for designing the large synthetic arrays necessary to bridge the gap between small-molecule and macro-molecule DNA-recognition motifs.

Absorption, nuclear magnetic circular dichroism, and flow linear dichroism spectra showed that while both the M and P enantiomers of $[\text{Fe}_2\text{L}_3]^{4+}$ bind strongly to DNA, their binding modes and structural effects are very different; the first binding mode of the M enantiomer is along the major groove, and the P enantiomer most likely binds in the minor groove, according to the researchers. Molecular-level images obtained with atomic force microscopy are consistent with these binding modes and provided visual evidence of the induced DNA bending/coiling. The M enantiomer kinks and coils DNA substantially more than the P enantiomer, whose effect was significant but much less dramatic. The coiling had little effect on the local structure of the base-base interactions, a characteristic in common with molecules that serve to package DNA into chromosomes.

In current studies, Rodger and Hannon are derivitizing the M-enantiomer backbone in order to optimize the hydrogen-bonding and steric effects in the major groove. Rodger and Hannon anticipate that tuning sequence selectivity into the backbone of the M enantiomer will enable them to target specific sequences to be coiled.

STEVEN TROHALAKI

Extraordinary Magnetoresistance of InSb Allows Fabrication of a Read-Head Sensor without Magnetic Noise

Read-head sensors are one of the main devices for data recording and storage in hard-disk drives. These sensors are commercially manufactured from magnetic materials with properties such as giant magnetoresistance (GMR) or tunneling magnetoresistance (TMR), and therefore are subject to magnetic noise. As a consequence, the use of read heads based on GMR and TMR is limited to areal densities of the order of 100 Gb/in.². However, the extraordinary magnetoresistance (EMR) exhibited by nonmagnetic narrow-gap semiconductors such as InSb is free of magnetic noise and represents an alternative for a new class of read-head sensors that are compatible with large capacity storage.

A group of scientists from the NEC Research Institute in Princeton, N.J., the NEC Fundamental Research Laboratories in Japan, and the University of Oklahoma joined efforts under the guidance of NEC Institute's Stuart Solin to take advantage of the EMR properties of InSb to fabricate a mesoscopic read-head sensor, as they explained in the May 27 issue of *Applied Physics Letters*.

EMR appears as a consequence of a magnetic-field-induced deflection of current around a patterned metallic inhomogeneity present in or on the boundary of a semiconductor. A narrow-gap semiconductor with high-mobility carriers such as InSb shows this property in films thicker than 1 μm . Read-head sensors require thinner films of ≤ 100 nm. Since carrier mobility in InSb decreases dramatically for thicknesses below 1 μm , this group of scientists designed a quantum-well structure to fabricate a mesoscopic sensor within the targeted thickness with a high mobility of 2.3 m²/V s at 300 K.

The fabrication of this device was accomplished using a shadow-mask electron-beam lithography technique. A 30-nm layer of Si_3N_4 was first deposited over the substrate, where gold strips for wiring defined an 80- μm -square area. In the corners of this square, a pattern of four 30 nm \times 3 μm strips was delineated after a second 30-nm layer of calixarene, a new type of high-resolution resist developed by NEC, was deposited. A mesa containing the quantum well was then reactive-ion-etched using a mixture of $\text{CH}_4 + \text{H}_2$, ensuring that the mesa walls were almost vertical. This process allowed the achievement of a structure below 100 nm with high alignment accuracy (± 10 nm). A suspended Ge stencil mask allowed the preparation of gold leads and a gold shunt to allow electrical contact.

Measurements at 300 K of the field-dependence of the observed effective resistance show a quasi-parabolic trend similar to that of macroscopic EMR plate structures. The observed maximum current sensitivity was 147 Ω/T , and the EMR had an optimized value of 6% at a bias field of 0.27 T when the applied signal field was 0.05 T. The EMR at zero bias was 2%, and is lower than the 500% obtained from macroscopic plates with higher mobility and much less leakage current bypassing the mesa. The observed resistance was 1253 Ω , and is controlled by the conductance of the shunt and the dopant level of the quantum well. Therefore, the researchers were able to fabricate an EMR read-head sensor using the e-beam lithography technique. The conservatively calculated areal density of the sensor, based on geometry considerations, is 116 Gb/in.². At this level, estimations of the signal-to-noise ratio at 200 MHz give 41 dB, which is larger than estimations for a hypothetical 100 Gb/in.² TMR device at similar conditions, 34 dB. By reducing the mesa width and voltage lead spacing by factors of 2 and 3 respectively, the research group expects to optimize the performance of such a device in the future to reach areal densities of the order of 1 Tb/in.².

SIARI S. SOSA

Annular Dark-Field Scanning Transmission Electron Microscopy Captures Sb-Related Clusters in Silicon

The electrical properties of a semiconductor can be controlled through the addition of dopant atoms to the material. However, at high dopant concentrations, the linear relationship of increased electrical activity with dopant concentration starts to break down. As silicon-based electronic devices continue to become smaller, higher charge carrier concentrations are required to maintain device performance. It therefore becomes important to understand exactly how dopant atoms become electrically inactive. To study how this happens, researchers at Bell Laboratories and Agere Systems have used atomically resolved, annular dark-field scanning transmission electron microscopy (ADF-STEM) to study antimony (Sb) dopant atoms in crystalline silicon (Si) in samples with $\sim 30\%$ of dopants electrically inactive.

The researchers reported in the April 25 issue of *Nature* that they were able to distinguish between Sb and Si atoms with ADF-STEM technique because the image intensity of each species is proportional to the atomic number of the element raised to the 1.7 power ($Z^{1.7}$). Thus, one Sb atom appeared approximately nine times as intense as one Si atom in the images, they said. The research group found that the intensity and distribution of Sb in the samples was well described by a binomial distribution, suggesting that Sb substitution in Si sites is random.

From the images, the research team concluded that the deactivating dopant cluster in the Si crystals contained only two Sb atoms. Paired defects outnumbered four atom clusters by 50:1. Since ADF-STEM images view structures in projection, the experiments do not allow for determining whether the primary pair defect contains a vacancy, or is of the donor pair type.

While single heavy atoms on surfaces have been visualized previously, "this is the first time individual impurity atoms have been imaged inside a crystal at atomic resolution," said David Muller of Bell Laboratories. "Because we are viewing the atoms in their undisturbed bulklike states, we can identify bulk-defect complexes."

The key to this work lies in the TEM sample preparation, according to Muller and co-workers. Instead of using ion milling, which leaves a damaged layer a few nanometers thick, the researchers use chemical-mechanical polishing. Then an etch is used to remove any oxide. The researchers reported, "Random variations in thickness must be less than the contrast of one Sb atom, and the surfaces must be free from native amorphous SiO_2 layers and damaged bulk Si layers amorphized during thinning."

CHRISTOPHER MATRANGA