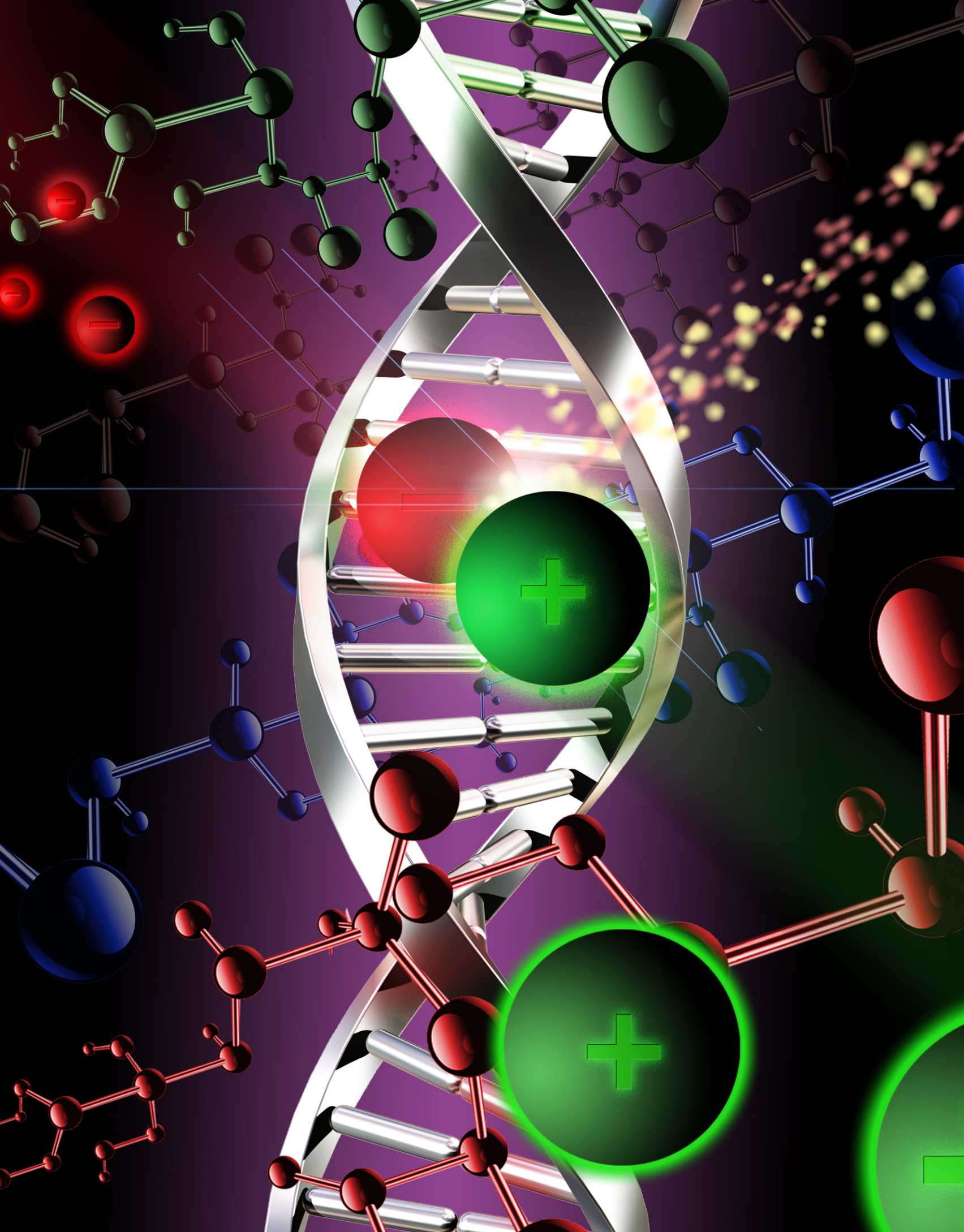
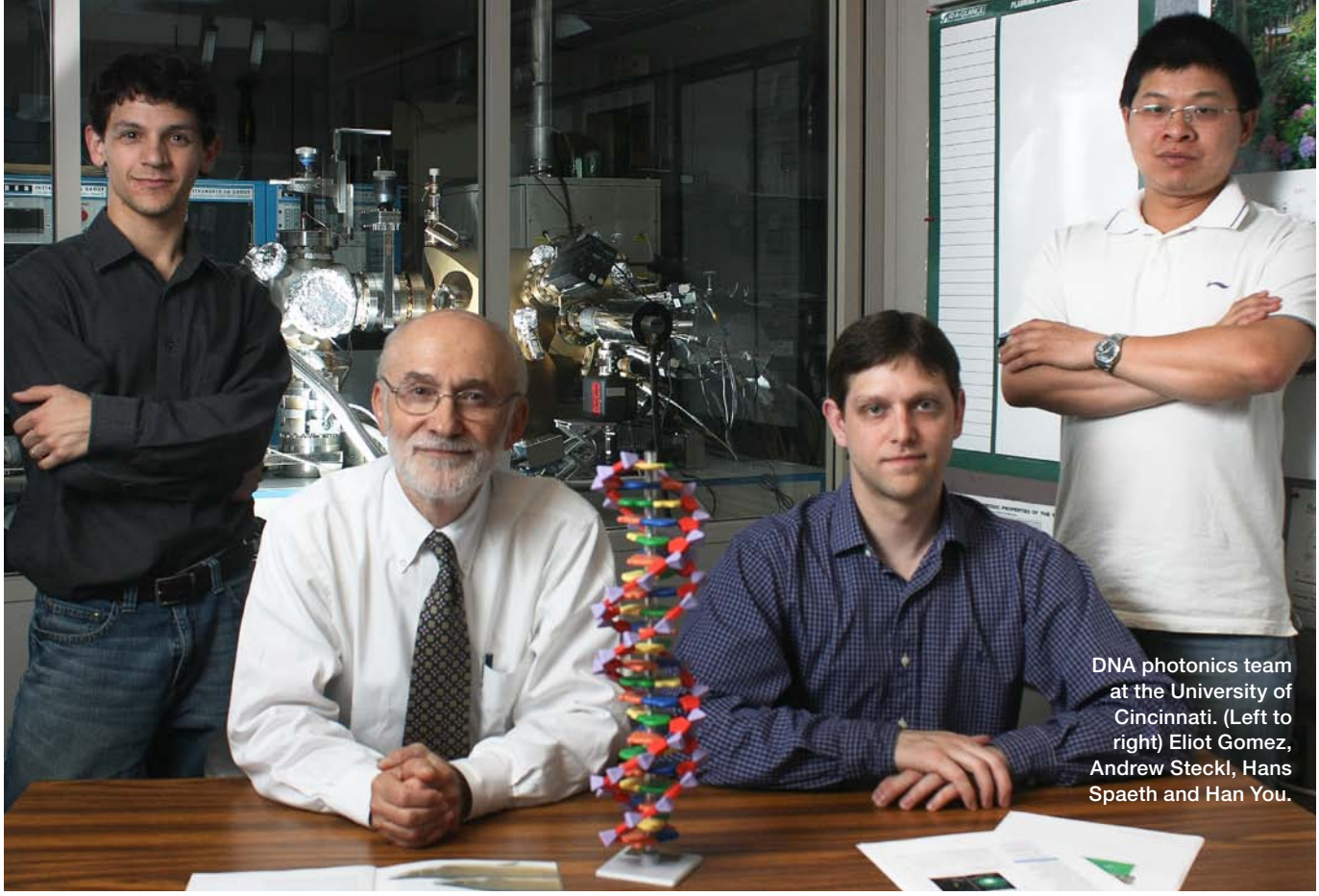




DNA photonics team at the University of Cincinnati. (Left to right) Eliot Gomez, Andrew Steckl, Hans Spaeth and Han You.

E. Gomez, UC NanoLab

DNA as an Optical Material

A.J. Steckl, H. Spaeth, H. You, E. Gomez and J. Grote

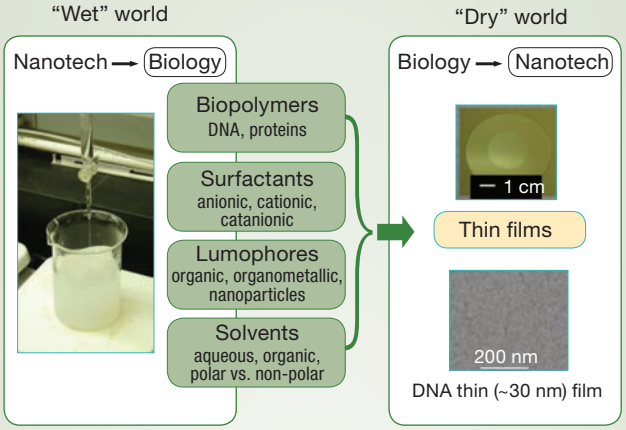
DNA, the beautifully symmetrical "molecule of life," carries the core genetic blueprint for every living organism. Now, through the emerging field of DNA photonics, it also has the potential to serve as an inexpensive, renewable resource in the development of optical waveguides, organic LEDs and laser structures.

Most of us have at least a superficial knowledge of what deoxyribonucleic acid (DNA) is and how it determines our genetic makeup through its sequence of base pairs. However, many do not realize just how much DNA organisms have: In humans, for example, the total length of the DNA in the chromosomes of a cell is of the same order as the length of a human being (about 1.5 to 2 m). This very long and very "skinny" molecule (roughly 2 nm in diameter) is compressed into a tight ball within the nucleus of each cell (around 1 μm in diameter). Compacted DNA, along with some protein, floats in a watery solution.

The abundance of DNA begs the question of how this resource might be used to advance science and technology—including optical science. The first intersection between DNA and photonics occurred as fluorescent molecules, or "labels," were attached to specific bases in order to determine the base pair sequence. Today, through the use of capillary electrophoresis and photonics techniques, scientists routinely perform DNA sequencing and analysis in the laboratory.

John Newhart

[Making the wet-to-dry transition with DNA]



In the natural world and in many biotech applications DNA is surrounded by a watery soup. For optical and electronic applications, DNA must be converted into a solid thin film. This "wet-to-dry" transformation is a complex process that involves many stages: extracting and purifying DNA from natural sources forming fibrous powder, precipitating it from aqueous solution by making it react with surfactants, and forming thin films from organic solvent solutions.

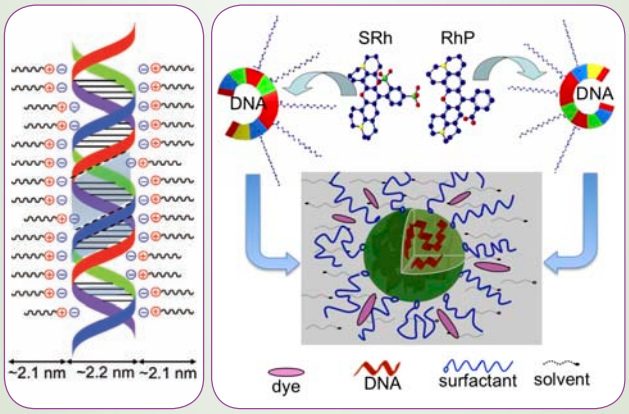
[DNA with surfactant/dye]

Cetyltrimethylammonium Chloride: $H_3C(CH_2)_{15}(CH_3)_3N^+Cl^-$

Sulforhodamine: $C_{31}H_{30}N_2O_7S_2 - Na^+$

Rhodamine perchlorate: $C_{32}H_{30}N_2O_3 - (ClO_4)^-$

Typical surfactants contain an ammonium head ion; cationic and anionic dyes from the rhodamine family are excellent emitters.



(Left) Natural DNA-Na salt in aqueous solution is transformed into DNA-surfactant salt, which is insoluble in water but soluble in organic solvents. (Right) Dye molecules interacting with DNA-surfactant complex.

Source: H. You et al. Langmuir **25** (19), 11698 (2009).

The DNA polymer in solid-state thin-film form has a unique combination of optical and electronic properties—which have formed the basis of the new field of DNA photonics. This burgeoning area explores how DNA can be used to improve photonic devices such as organic LEDs, lasers or lab-on-a-chip devices. In addition to photonics applications, researchers are also combining DNA with light-emitting materials to investigate new diagnostic and drug-delivery techniques in the biomedical field.

For most biomedical applications, generally little DNA is needed—in the realm of micrograms; however, expensive synthetic DNA must be used in order to ensure a common standard. On the other hand, for nanotechnology applications, researchers typically need milligrams to grams of DNA, and a natural DNA source is more appropriate. Currently available sources of natural DNA include fish sperm (e.g., from salmon or herring) and calf thymus. The DNA photonics teams at the University of Cincinnati's NanoLab and the Air Force Research Lab have mostly used salmon DNA.

Creating DNA thin films

While DNA is normally found in solution in organisms, it must be transformed into a thin film with robust properties in order to be used as a device material. This "wet" to "dry" transformation is quite complex, as it involves the interaction of the DNA molecules with different solvents, surfactants, and—for many optical applications—fluorescent molecules. To construct DNA-based "devices," one must treat the natural water-soluble DNA-Na^+ salt with surfactants, producing DNA compounds that are insoluble in water but soluble in organic solvents.

This treatment enables the formation of high-quality DNA-surfactant solid-state thin films, which can be used to fabricate multi-layer device structures, including optical waveguides, laser structures, organic light emitting diodes (OLEDs) and organic field-effect transistors.

Properties of DNA thin films

Somewhat surprisingly, the material properties of DNA-surfactant films can be catalogued in a similar way as those of other materials used in optical devices—by their transmission spectrum, optical loss, refractive index, dielectric constant, electrical conductivity, dielectric breakdown field, etc. (vs. the actual content of the genetic code that is often studied in biology).

Characterization of thin films of DNA-cetyltrimethylammonium (DNA-CTMA), the organic soluble formed by precipitating DNA in water with cetyltrimethylammonium chloride (CTAC) or other surfactants, has shown excellent optical transparency in the visible range, while displaying a signature DNA double peak at 230 nm and 260 nm. The index of refraction of thin DNA-CTMA films decreased from about 1.54 to 1.48 as the wavelength increased from 300 nm to 1,600 nm. The resistivity of DNA was shown to decrease six

The use of DNA combined with light-emitting materials is opening new diagnostic and drug-delivery possibilities in the biomedical field.

orders of magnitude (from 10^{15} Ω-cm to 10^{9} Ω-cm) as molecular weight was reduced from 8 MDa to 165 kDa (equivalent to 250 base pairs).

DNA-based lasing

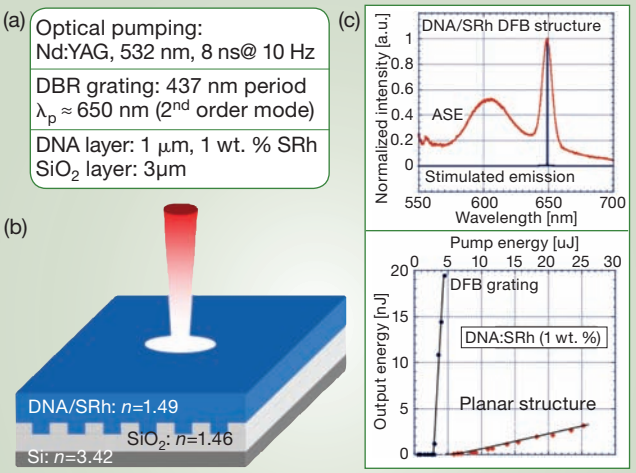
Solid-state polymer-based lasers are a fertile subject for research. Replacing the relatively expensive inorganic host of conventional solid-state lasers with a biopolymer such as DNA could result in significant cost reduction. This could also make flexible operation possible as well as the integration of lasers with other organic devices into an optical chip. Furthermore, compared with conventional liquid dye lasers, solid-state polymer lasers are much easier and safer to operate. A critical characteristic of the host material is high transparency at wavelengths of the pump laser and dye emission.

The incorporation of fluorescent dye molecules into the DNA-surfactant structure is a complex process. It has been reported that certain dye molecules can be attached directly to major or minor grooves of the DNA spiral or inserted between base pairs, resulting in so-called DNA-specific dyes that exhibit a marked increase in fluorescent signal with DNA concentration in solution.

For the DNA-surfactant complex that is used in optical devices, our recent study indicates that the DNA double helix serves as a template for the interaction between dye and surfactant molecules. This finding also explains the large concentration of dye molecules that can be incorporated in the DNA-surfactant complex while still preserving the DNA structure.

We have fabricated distributed feedback (DFB) lasing structures on oxidized silicon substrates. This consisted of a grating etched into the SiO_2 layer over which a DNA - (cationic) surfactant-dye layer was deposited. The dye we chose was sulforhodamine (SRh), an anionic dye used extensively in dye lasers with strong red emission. The DFB grating had a period of 437 nm, which corresponded to the 2nd order emission at the SRh amplified spontaneous emission wavelength of 650 nm.

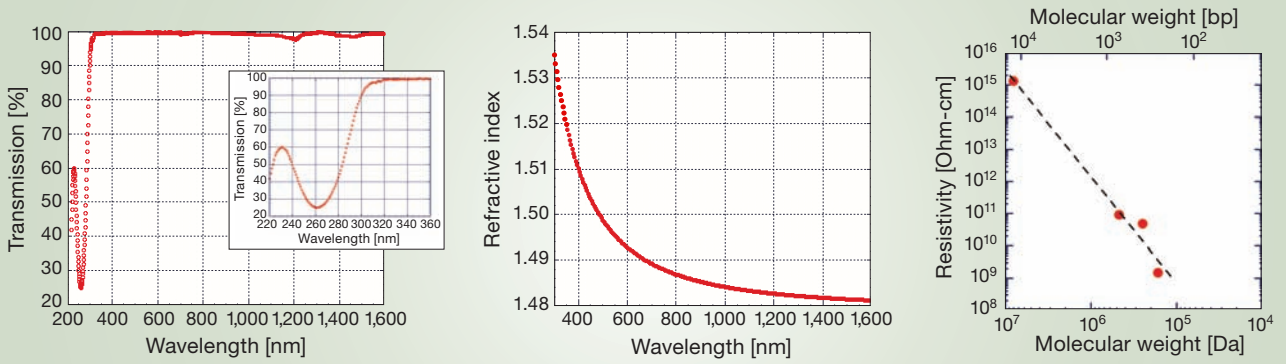
[DNA/dye distributed feedback laser]



(a) Optical pumping conditions for stimulated emission in sulforhodamine loaded DNA-surfactant complex. (b) DNA / SRh distributed feedback laser structure on SiO_2/Si grating. (c) Photoemission from DNA/SRh DFB structure: spontaneous and stimulated emission vs. wavelength (top); lasing output vs. pump energy (bottom) for grating and slab (planar) structures.

Source: Z. Yu et al. Appl. Opt. **46**, 1507 (2007).

[DNA-CTMA thin film properties]



(Left) Optical transmission for micrometer-scale films; (center) refractive index; (right) resistivity with decreasing molecular weight (obtained by DNA sonication).

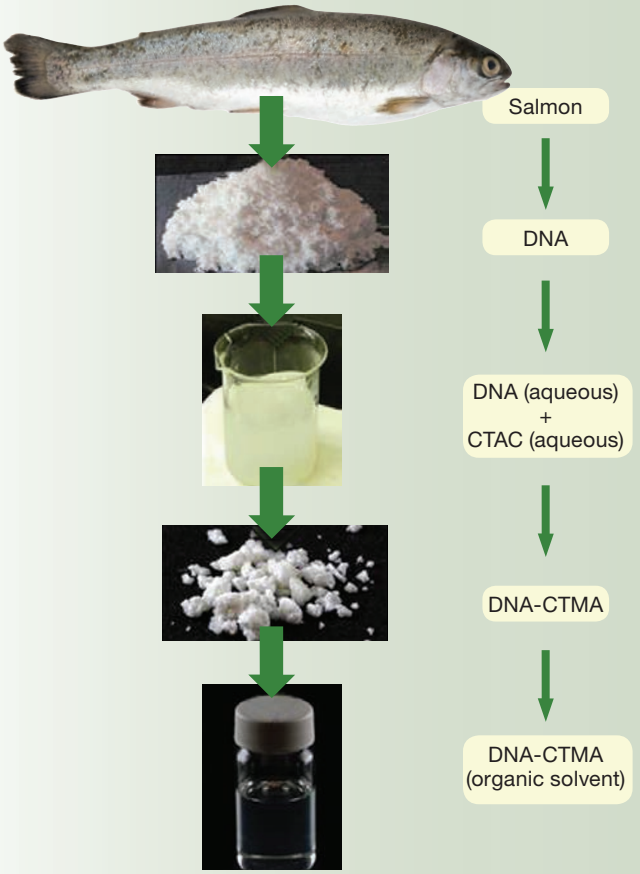
Source: A.J. Steckl et al. Proc. 26th Int'l. Display Res. Conf (Soc. for Info. Display – ISSN1083-1312/2006), p. 25 (2006), and J.A. Hagen, Ph.D. Thesis, University of Cincinnati, 2006.

DNA processing

DNA's journey from salmon cells into a processable organic solution begins with the harvesting of the fish's waste milt and roe sacs. (Unlike meat and eggs, these elements are not used for cuisine.) From these, DNA is extracted and the proteins are removed. This material is then freeze-dried for use in bio-optoelectronic devices.

If optical scientists need to modify the molecular weight of a DNA sample for a specific application, they can dissolve it in water and sonicate it to break the molecular chains into smaller fragments. However, because natural DNA salts are soluble in water but insoluble in organic solvents, it is difficult to process into thin films. In order to remedy this, one must bind the DNA-Na salt to surfactant molecules (such as cetyltrimethylammonium chloride - CTAC) through ion exchange.

The resulting DNA-CTMA (cetyltrimethylammonium) complex precipitates from the aqueous mixture and can be captured via filtration. It is thoroughly rinsed to remove excess surfactant and then vacuum dried in low heat. The resulting material is a white powder, which is now soluble in organic solvents, forming a visually transparent solution that may be easily spin-coated onto a substrate. From there, it can be characterized and ultimately serve as a layer in an optoelectronic device.



DNA's journey from fishing industry byproduct to processable DNA-CTMA in organic solution.

Note: CTAC is the chloride salt of CTMA (cetyltrimethylammonium).

Lasing was obtained by pumping with a frequency-doubled Nd:YAG laser at 532 nm.

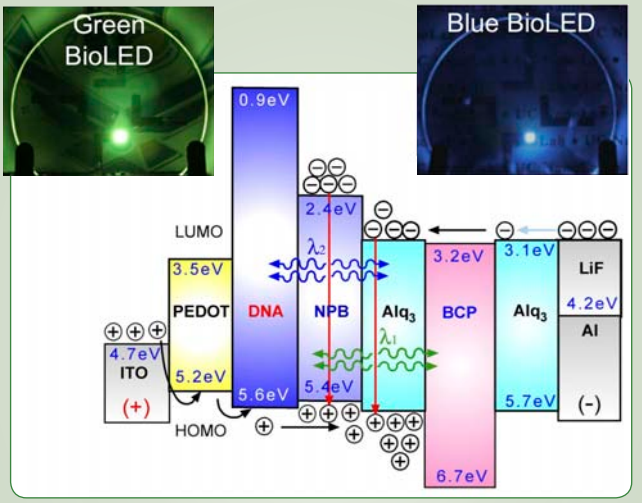
The lasing threshold was 3 μJ, which corresponded to roughly 30 μJ/cm^2 or 4 kW/cm^2. The emission linewidth decreased from 30 nm in the amplified spontaneous emission mode to less than 0.4 nm (instrument limited) in the lasing mode. The slope efficiency of the lasing was roughly 1.2 percent. Both the threshold and the slope efficiency was about twice that obtained with other polymer hosts, indicating the promise of DNA as a host material for dye-based polymer lasers.

DNA-based organic light emitting diodes

OLEDs use semiconducting organic materials (either small molecules or polymers) instead of conventional inorganic semiconductors. The advantages of OLEDs include their potential to be produced at low cost (through roll-to-roll processing), their application to large-area light panels, and their use as flexible substrates.

DNA in the form of thin solid-state films has been used as an integral element in various types of OLEDs. The thin films that form OLEDs have various specific purposes, including metal electrodes, charge injection and transport (separately for electrons and holes), lumophore-containing emitting layers, etc. OLEDs that use fluorescent emitting materials and incorporate DNA thin films have resulted in order-of-magnitude increases in brightness and efficiency. These improvements in performance were the result of introducing a DNA layer into the OLED structure, where it serves as an electron blocking layer (EBL).

[DNA in fluorescent OLEDs]



DNA-surfactant thin films incorporated into fluorescent OLEDS. (Top) Green- and blue-emitting BiOLEDs (bottom) HOMO/LUMO energy levels in OLED structure showing the electron blocking function of the DNA layer; electroluminescence occurs in either the AlQ_3 (green) or NPB layer (blue) layers.

Source: J. A. Hagen et al. Appl. Phys. Lett. **88**, 171109 (2006).

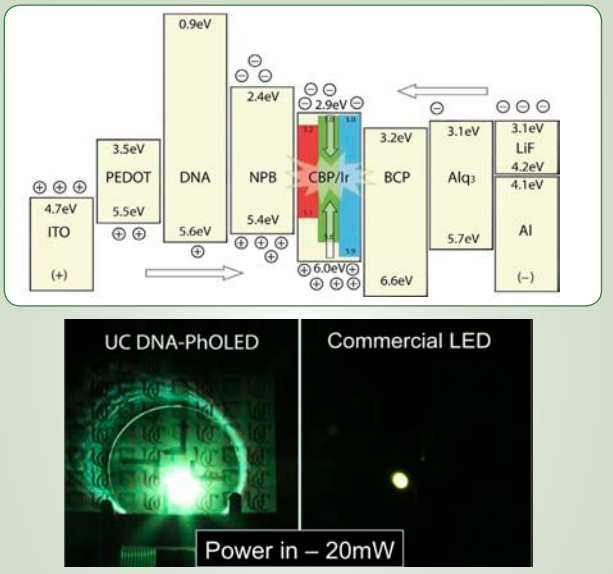
Organic materials such as DNA are an attractive possibility for LEDs and many other applications because they are natural, renewable and easily biodegradable.

Based on the approximate values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the DNA layer and those of adjacent organic layers, we have found that a DNA layer acts as a very efficient EBL while not hindering the transport of holes. Therefore, DNA can enhance the probability of exciton formation and eventual photon emission. The improvement in OLED emission with DNA incorporation has been observed for several fluorescent materials with different HOMO/LUMO levels, including AlQ_3 (green emission) and NPB (blue emission).

OLEDs that utilize phosphorescent emitting materials can take advantage of excitons in singlet states (which are responsible for light emission in fluorescent materials) and excitons in triplet states. As one might expect from the name "triplet," there are three times more triplet states available than singlet states. Thus, phosphorescent OLEDs (or PhOLEDs) display much higher brightness and efficiency than fluorescent OLEDs.

Recently, we have investigated PhOLEDs that incorporate DNA layers and have obtained nearly ideal performance: maximum brightness of nearly 100,000 cd/m^2 at 13 V (632 mA/cm^2); maximum current efficiency of nearly 90 cd/A, and luminous efficiency of 55 lm/W at 5 V (0.11 mA/cm^2). Assuming Lambertian emission, the measured luminous efficiency converts to approximately 100 percent internal quantum efficiency. This performance is comparable to the best inorganic semiconductor LEDs.

[DNA in phosphorescent OLEDs]



DNA-surfactant thin films incorporated in phosphorescent OLEDs: (top) HOMO/LUMO energy levels in the OLED structure show the DNA electron blocking layer and the CBP emitting layer containing Ir(ppy)$_3$ phosphorescent molecules; (bottom) electroluminescence from DNA PhOLED compared to commercial inorganic green LED both biased at 20 mW.

Future prospects

Light-emitting devices based on organic materials clearly have a bright future. Their brightness and efficiency are comparable to their inorganic counterparts. Their Achilles heel has been their limited lifetime, but that has rapidly improved. Because they can be produced in large quantities at reduced cost, OLEDs are accelerating the development of related commercial applications.

Organic materials such as DNA are an attractive possibility for LEDs and many other applications because they are natural, renewable and easily biodegradable. As the photonic and electronic industries strive to become more "green," these raw materials may play an important role in creating a sustainable future.

Among biomaterials, DNA, the "molecule of life," is quite a robust polymer with many useful electronic and photonic properties, including good temperature stability, mechanical robustness, and a wide HOMO/LUMO energy gap. In addition, preliminary results indicate that OLEDs that incorporate DNA layers have longer operating lifetimes than devices without DNA. The natural DNA that is used in device applications is quite abundant and relatively inexpensive. It is important to search for other natural polymers that can replace the remaining inorganic and synthetic organic materials used in optical devices—and to continue to learn about how we can shape the properties of DNA for device use and expand its applications. Perhaps in the future DNA could earn a new nickname: "molecule of light."

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