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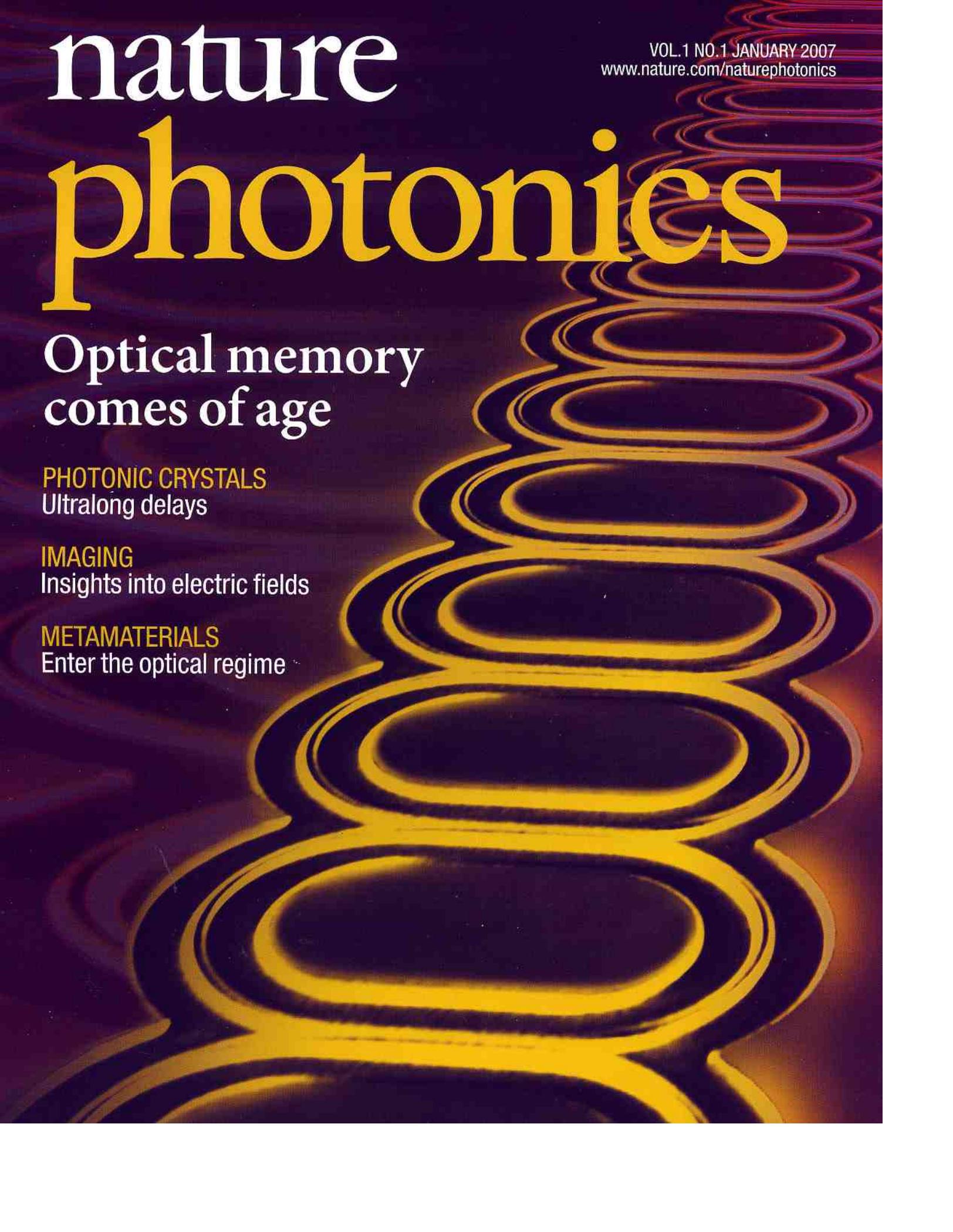
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DNA – a new material for photonics?

ANDREW J. STECKL

Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030, USA
e-mail: a.steckl@uc.edu

Scientists have recently discovered that DNA — ‘the molecule of life’ — is an exciting new material for fabricating photonic devices with enhanced properties.

In the past decade there has been an intensive effort to develop photonic devices based on organic materials. Research has been inspired by the wealth of materials on offer and the potential for cost-effective mass production. An excellent case in point is the organic LED¹ (OLED), which is at the heart of the display technology now breaking into the consumer electronics market and replacing the small LCDs found in music players, cameras and mobile phones.

From the rich world of organic materials, biomaterials are of particular interest as they often have unusual properties that are not easily replicated in conventional organic or inorganic materials. Furthermore, natural biomaterials are a renewable resource and are inherently biodegradable.

Arguably the most important and famous biomaterial known to man is DNA, the polymeric molecule that carries the genetic code in all living organisms. It is, therefore, not surprising that the nascent field of DNA photonics, which explores the potential for constructing photonic devices from ‘the molecule of life’, is attracting the interest of the wider scientific community.

The DNA molecular structure (the famous double helix) consists of two intertwined spirals of sugar and phosphate molecules linked by hydrogen-bonded base pairs. The width of the double helix is about two nanometres and the length of the DNA molecule depends on the number of base pairs (about a third of a nanometre per base pair). Synthesizing or manipulating DNA molecules by physical and chemical means can lead to

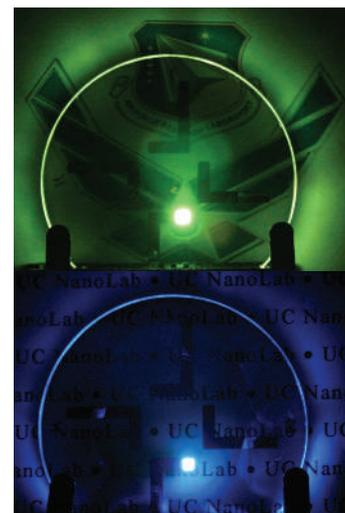
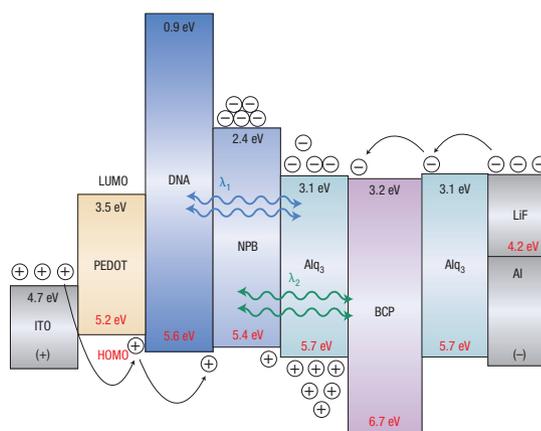


Figure 1 BioLEDs, which use DNA to help boost light emission¹⁵. Shown are the energy-level diagrams for both blue-emitting (NPB) and green-emitting (Alq3) BioLEDs, with photographs of both devices in operation. Hole and electron injection from PEDOT and LiF layers respectively, and transport through the layers of the device, are indicated schematically. λ_1 and λ_2 indicate blue and green emission, respectively. ITO is indium tin oxide, PEDOT is poly(3,4-ethylenedioxythiophene), NPB is (N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)benzidine), Alq₃ is tris(8-hydroxyquinoline) aluminium and BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

a variety of structures² at the nanoscale. Potential applications include assembly of molecular electronic devices³, nanoscale robotics⁴, DNA-based computation⁵, for example. Synthetic DNA is also the material of choice for fundamental studies⁶ of electronic processes resulting from the interaction of DNA molecules with light.

Although the cost of synthetic DNA continues to decrease, it is still a barrier to many applications that require a significant amount of material. For this and other reasons, the research on DNA photonics has used predominantly natural DNA, mainly from salmon sperm, which is normally a waste product of the salmon-fishing industry.

Table 1 Typical thin-film properties for surfactant-modified DNA–CTMA.

DNA thin-film property	Value	Comments and references
Thermal stability limit	200–250 °C	Thermogravimetric measurement ^{9,19}
Optical transmission: $\lambda = 300\text{--}1,600\text{ nm}$	~100%	Absolute peak at 260 nm (DNA bases) ⁷
Optical loss (dB cm ⁻¹ at given λ)	0.05 (800 nm), 0.05 (1,300 nm), 0.2 (1,550 nm)	For a very thick film (>100 μm); ref. 20
Index of refraction (at given λ)	1.535 (350 nm) to 1.48 (1,600 nm)	For film thickness: 2–3 μm ; ref. 20
Dielectric constant (low frequency)	~7.8	For film thickness: 200 nm; ref. 14
Dielectric constant (high frequency)	~4.5 (15 GHz) to ~3 (25 GHz)	For film thickness: 2–3 μm ; ref. 13
Electrical resistivity ($\Omega\text{ cm}$)	10^{15} (8–10 MDa) to $\sim 10^9$ (~150 kDa)	For film thickness: 2–3 μm ; ref. 20

DNA THIN-FILMS

DNA photonic devices can be split into two categories — wet devices and solid-state devices. The wet category contains primarily optofluidic devices, where the DNA molecules are present in either an aqueous or organic-solvent solution and are transported in a fluid under the influence of electric fields or fluid flow.

In contrast, solid-state devices are based on thin films of DNA. DNA films are produced by solution methods^{7,8} at present, where a reaction between the DNA and a cationic surfactant (such as cetyltrimethyl ammonium — CTMA) produces a DNA–lipid complex that is insoluble in water but soluble in alcohols.

This technique allows casting or spin coating of DNA thin-films, which do not dissolve other organic layers on contact and can thus be integrated into organic devices. Some of the important properties of such DNA–CTMA thin-films for photonic and

electronic applications are summarized in Table 1. In addition, a dry process using ultrahigh vacuum molecular beam deposition has recently been reported⁹ to produce nanometre-scale films with very controllable properties.

The characteristics of DNA–CTMA films can be controlled¹⁰ by adjusting the DNA molecular weight and the concentration of the reagents. Reducing the starting DNA molecular weight has been shown to significantly decrease the electrical resistivity of the DNA film, which can be very useful for optimizing device operation. Furthermore, the DNA–CTMA complex is thermally stable up to 200–250 °C, which gives some flexibility in device fabrication.

The resulting optical properties of these DNA films are excellent, with very high transmission throughout the visible and near-infrared regions. Optical losses as low as 0.05 dB cm⁻¹ at 800 nm and 1,300 nm, and 0.2 dB cm⁻¹ at 1,550 nm

have been reported¹¹. This very low optical attenuation makes DNA films promising candidates for applications as polymer waveguides, for example. In addition, combining DNA–CTMA films with polymers that have large nonlinear optical coefficients can result in improved poling efficiency¹² when creating nonlinear optical devices.

Research has shown that DNA–CTMA films also have useful electronic properties. Characterization at microwave frequencies¹³ has yielded low dielectric-loss values, ranging from 0.11 dB at 10 GHz to 0.5 dB at 30 GHz, and a loss tangent of less than 0.1. At low frequencies, DNA–CTMA films have been used as the gate insulator in organic field-effect transistors (OFETs) with great success, enabling drain current to be modulated by over three orders of magnitude¹⁴ by means of a gate voltage span of just 10 V. This research indicates that DNA films may also hold much promise for applications in microwave photonics and bio-electronics.

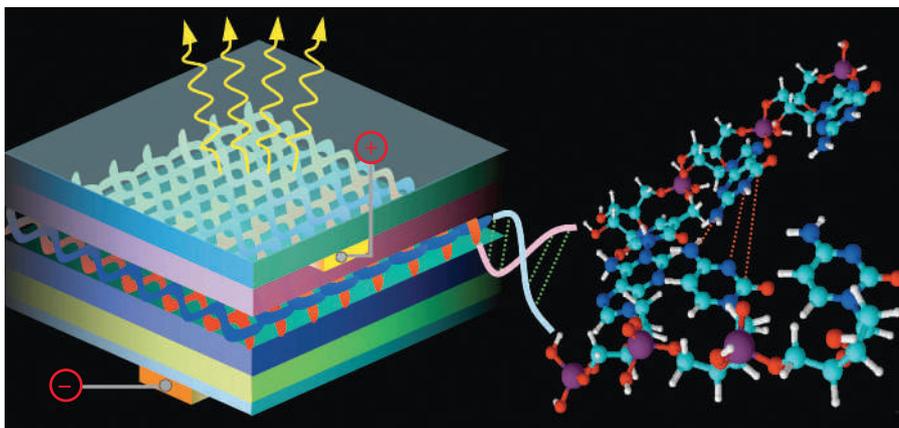
ENHANCED EMISSION

Lastly and perhaps most importantly, is the role that DNA can play in enhancing light emission. Incorporating DNA into OLEDs as an electron-blocking layer (EBL) has been reported¹⁵ to result in BioLEDs that are as much as ten times more efficient and thirty times brighter than their OLED counterparts.

Enhanced efficiency using DNA–CTMA nanometre-thick films as EBL material has been demonstrated in both green- and blue-emitting devices (Fig. 1). The resulting green and blue BioLEDs showed a maximum luminous efficiency of about 8 and 1 cd A⁻¹, respectively. Typical turn-on and operating voltages for these devices were about 4–5 V and about 10–25 V, respectively. The green BioLED achieved the highest luminance of about 21,000 cd m⁻², whereas the blue BioLED showed a maximum luminance of about 1,500 cd m⁻².

In addition, by adding lumophores (which display colour owing to specific light emission) or chromophores (which display colour through selected absorption or reflection of ambient light) to DNA molecules it is possible to create an exciting new range of optically active materials.

Lumophores can be attached to DNA at several locations: intercalated between base pairs, or bound to the minor or major grooves of the double helix. Lumophore intercalation is known to result in a very sensitive signature in the presence of DNA molecules in solution¹⁶. Lumophore intercalation is particularly important as it has been reported¹⁷ that DNA films can



An artist's view of DNA being incorporated into an OLED structure (drawing by W. Li).

act as a far better host for lumophores than conventional polymer hosts, resulting in much higher luminescence.

For example, DNA–CTMA thin-films doped with the luminescent dye sulphorhodamine (SRh) have been reported¹⁸ to exhibit a photoluminescence intensity more than an order of magnitude higher than that of SRh in poly(methyl methacrylate), which is a popular polymer host. Other lumophores have also been reported^{17,19} to luminesce very efficiently in DNA thin-films.

Although the mechanisms are not yet completely understood, it is speculated that excited molecules, which are intercalated between base pairs in the DNA structure, are essentially shielded from non-radiative relaxation centres in the host material, thus opening the door to efficient photon emission. Another possible explanation is related to the tight spatial fit between intercalated molecules and the base-pair structure, which may prevent the conformational relaxation of

excited lumophores and thereby enhance the process of radiative relaxation.

It is clear that the unique structure of DNA results in many optical and electronic properties that are extremely interesting for photonic applications. Indeed, it is possible to contemplate 'all-DNA' devices in which all (or most) of the layers are fabricated from DNA customized for specific purposes. Much research on the basic optical mechanisms in lumophore-doped DNA and demonstrating their full potential in devices remains to be done. It is hoped that this article will stimulate an increased level of interest in the photonic community towards this extraordinarily fascinating material.

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