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Comment on "Molecular Beam Deposition of DNA Nanometer Films"

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A paper published earlier in *Nano Letters*[1] reports the deposition of very thin electron-blocking films for organic light-emitting devices (OLEDs) derived from salmon DNA that has been modified by substituting long-chain quaternary ammonium ions for the sodium ions to provide a material soluble in organic media. The pertinent information given in the paper is as follows: molecular weight of the DNA, 146 000, initially 8 MDa but "adjusted by mechanical or acoustic shearing to reduce its resistivity"; evaporation cell temperature, 155−170 °C; rate of evaporation, 0.2−0.3 nm/s. Film thicknesses were 10−80 nm, although a thicker film of 250 nm was examined for surface characterization

The chemical nature of the deposited material is open to important questions. The paper reports that the electronic spectrum resembles that of the initial DNA, although there are differences that are not explained further.

It is quite unlikely that a polymer with such high molecular weight would have a significant vapor pressure in the temperature range used. This is, in fact, acknowledged in the introduction to the paper, but the authors believe that "several types of complexed DNA" can be evaporated. There is no further explanation of the mysterious complexing effect, and invoking it fails to convince the author of this comment based on his five decades of experience in organic and polymer chemistry.

Thermal decomposition to smaller molecules is an obvious thought. The authors cite a thermogravimetric analysis scan that shows decomposition beginning at 225 °C as evidence that the DNA is stable at the temperature of the evaporation cell. In fact, the raw plot in the Supporting Information shows significant decomposition well below 225 °C. Further, thermogravimetric analysis scans are normally done at a ramp rate of 10−20 °C/min. The time that the deposition source (unknown size or content quantity) takes to get to high temperature and how much time has elapsed before deposition begins are not given. Nevertheless, the time required for film deposition would allow thermal decomposition to occur, evaporating low molecular weight material. Decomposed material would be expected to contain the same nucleic acid bases as the starting material, and thus the resemblance (not identity) of the electronic optical spectrum is not definitive evidence. In fact, the paper reports that the deposited material is of lower molecular weight. Fluorescence observed when Picogreen dye is infused into the film is not solid evidence for the nature of the deposit. This dye is said to emit only when intercalated into DNA. While that can be accepted, the observation of fluorescence does not prove anything about the nature of the deposited material.

The deposited films have a much lower electrical resistance than solution deposited material (10^5 vs 10^{10} Ω cm). While it appears that no study of electronic versus ionic conductivity was made, this result is a sure sign of chemical change caused by heating. Changes in morphology are far less likely to account for the difference. Thus, it is clear that thermal change has occurred during deposition and that the chemical composition of the deposit is quite unknown. We are simply invoking Occam's razor.

The paper also reports results using DNA that has been modified by reaction with "a europium pigment", identified only as a "complex" in the Supporting Information. While the chemistry of this change is unknown, the product is said to be more sensitive to thermal degradation. The oxidation state of the Eu ion is unknown, but it could be an effective catalyst for chemical change in DNA at the temperatures used.

There are much more important questions to raise. The authors describe a BiOLED that is said to have improved performance that is due to the use of an evaporated DNA film as an electron-blocking layer. Many materials have been studied for this application in an extensively researched field. Why would biologically derived materials of unknown composition have advantages in electronics compared to the better understood synthetic polymers studied? What characteristics of nucleic acid bases make them attractive for such applications? Could this methodology be used in any way other than to prepare a single, very small device?

Research into electronic properties of biological materials is by no means a new field. Proteins were thought to have interesting electrical behavior in the1940s and 1950s, and in his declining years Albert Szent Gyorgi promoted the area (1970s). The more recent, much hyped, view of DNA as an electronic wire has been abandoned after studies showed that holes can move only a few base pairs away from the initial site. Electrons are known to be readily trapped in many organic materials, although mechanism details are not generally established.

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If biological materials are to be accepted as relevant to electronic devices other than in sensors, it is time that logical reasoning be given as to why they are attractive.

The main points in this Comment were communicated to Professor Steckl well before submission for publication but no response was received.

References

(1) Hagen, J. A.; Li, W.-X.; Spaeth, H.; Grote, J. G.; Steckl, A. J. *Nano Lett.* **2007**, *7*, 133.

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