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Investigation of DNA nucleobases – thin films for potential applications in electronics and photonics

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ABSTRACT

In previous research we have demonstrated improvements in device performance with the incorporation of a deoxyribonucleic acid (DNA)-based biopolymer into organic light emitting diodes, organic thin film transistors and other organic photonic and electronic devices. Here, we investigate nucleobases, nitrogen-containing biological compounds found within DNA, ribonucleic acid (RNA), nucleotides and nucleosides, for use in a few of those previously investigated photonic and electronic devices. Used as an electron blocking layer in OLEDs, a gate insulator for graphene transistors and as a dielectric in organic-based capacitors, we have produced comparable results to those using DNA-based biopolymers.

1. INTRODUCTION

Nucleobases are nitrogen-containing biological compounds found within deoxyribonucleic acid (DNA), ribonucleic acid (RNA), nucleotides and nucleosides [1-3]. See fig. 1. The primary nucleobases, cytosine (C), guanine (G), adenine (A), thymine (T) and uracil (U) possess a few promising properties that suggest potential building blocks for new biopolymer materials for electronic and photonic applications. Their ability to form base-pairs and stack upon one another lead to the helical structures of DNA and RNA. The most common use of nucleobases has been the synthetic formulation of DNA and RNA [1-3], but more recently their use as potential photonic crystal materials [4] and gate dielectrics for organic field effect transistors (OFETs) [5, 6] has been reported. With much smaller molecular weights than DNA, nucleobases are suitable for vapor deposition, which has been demonstrated [5, 6]. They also have large reported dielectric constants comparable to that of DNA, high refractive indices [2, 3] and high temperature stabilities [7]. In addition, they have demonstrated a strong resistance to aqueous and organic solvents.

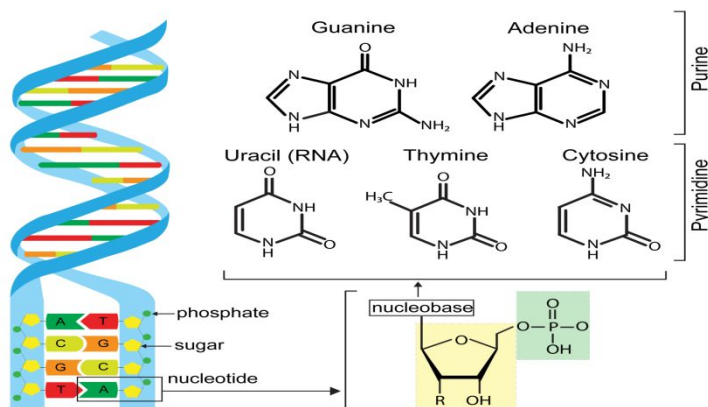


Figure 1. Nucleobases: guanine, adenine, uracil, thymine and cytosine.

Our idea to investigate nucleobases comes from recently published work of Sariciftci's group at the University of Linz [5, 6]. Vapor depositing individual and stacked layers of nucleobase gate insulators, his group demonstrated n- and p-type organic-based FETs, with low operating voltages (3-4 volts), low leakage currents, 4.5×10^3 times lower than the source-drain current, and hysteresis-free behavior [5, 6]. See figs. 2 and 3.

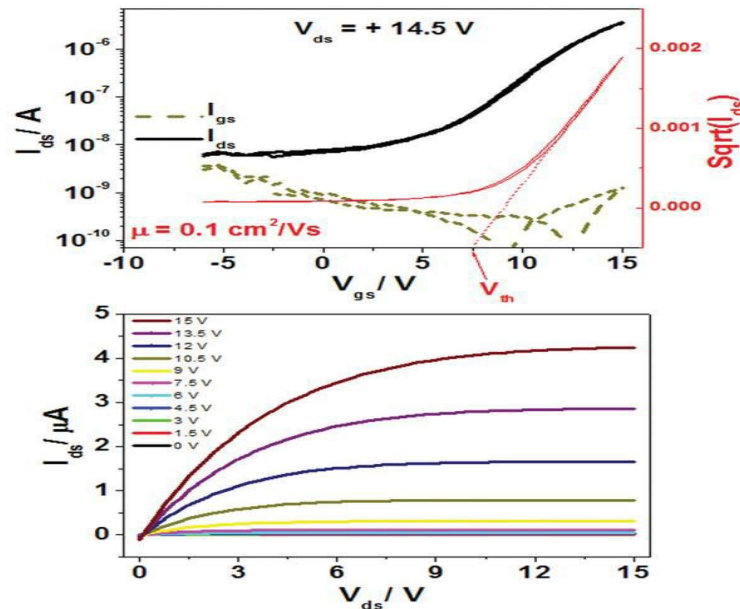


Figure 2. Transfer & output characteristics of C₆₀ OFET with 300 nm thick, “DNA-like” sequence gate dielectric, GTAGCGAGC: (G: guanine; T: thymine; A: adenine; & C: cytosine), operating voltage 15 V (due to high surface roughness), capacitance per unit area $C_{0d} = 10.2 \text{ nF cm}^2$, field-effect mobility $\mu = 0.1 \text{ cm}^2/\text{Vs}$ [5, 6].

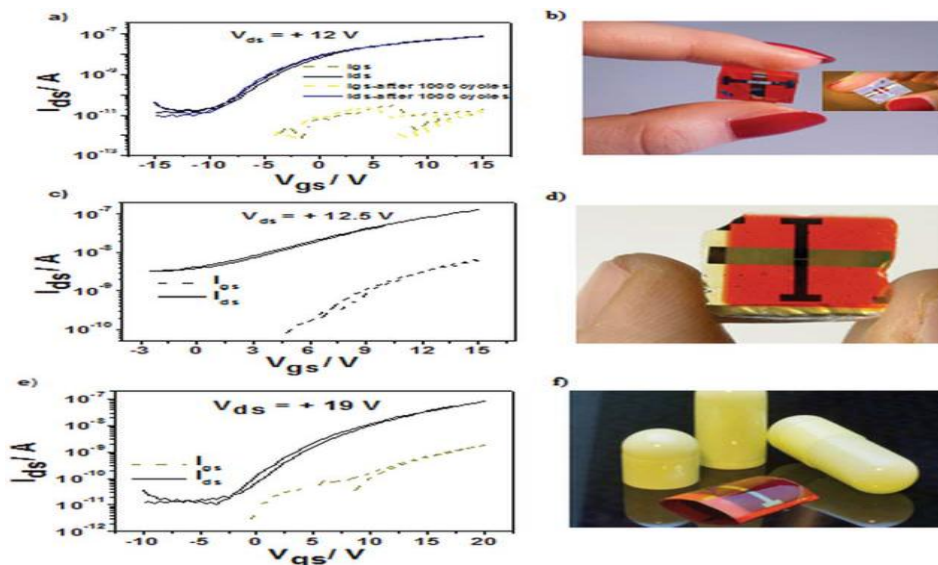


Figure 3. Transfer Characteristics of OFETs on: (a) & (b) Aurin-coated ecoflex & plain ecoflex substrates, adenine gate dielectric, perylene diimide semiconductor, $\mu = 0.01 \text{ cm}^2/\text{Vs}$, $C_{0d} = 3.1 \text{ nF cm}^2$, (c) & (d) aurin-coated caramelized glucose substrate, four alternating layers of guanine & adenine form gate dielectric, indanthrene yellow G semiconductor, $\mu = 0.012 \text{ cm}^2/\text{Vs}$, $C_{0d} = 5.6 \text{ nF cm}^2$, (e) & (f) aurin-coated hard gelatine capsule, adenine & guanine gate dielectric, perylene diimide semiconductor, $\mu = 0.02 \text{ cm}^2/\text{Vs}$, $C_{0d} = 5.1 \text{ nF cm}^2$ [5, 6].

Table 1 lists previously published properties of guanine (G), adenine (A), thymine (T), cytosine (C) and uracil (U).

Table 1. Properties of Nucleobases

	G	A	C	T	U
Refractive index^{2,3} (580 nm)	1.96	1.73	1.76	1.50	1.67
Relative dielectric constant⁵ (1 MHz)	~4.0	~3.4	~4.3	~2.0	~1.6
HOMO⁷ (eV)	5.7	6.0	6.2	6.5	6.7
LUMO⁷ (eV)	1.8	2.2	2.6	2.8	3.0
Molecular orbital gap⁷ (eV)	3.9	3.8	3.6	3.7	3.7

2. EXPERIMENTAL DETAILS AND RESULTS

We first measured the temperature stability of guanine, cytosine and adenine powder that we purchased from Sigma-Aldrich using thermogravimetric analysis (TGA) in both nitrogen and air. As can be seen from fig. 4a 4b, the temperature stability of nucleobases is quite high, 290 °C for adenine, 325 °C for cytosine and 465 °C for guanine and stable in air. This is very promising, with potential use in both inorganic and organic photonics and electronics.

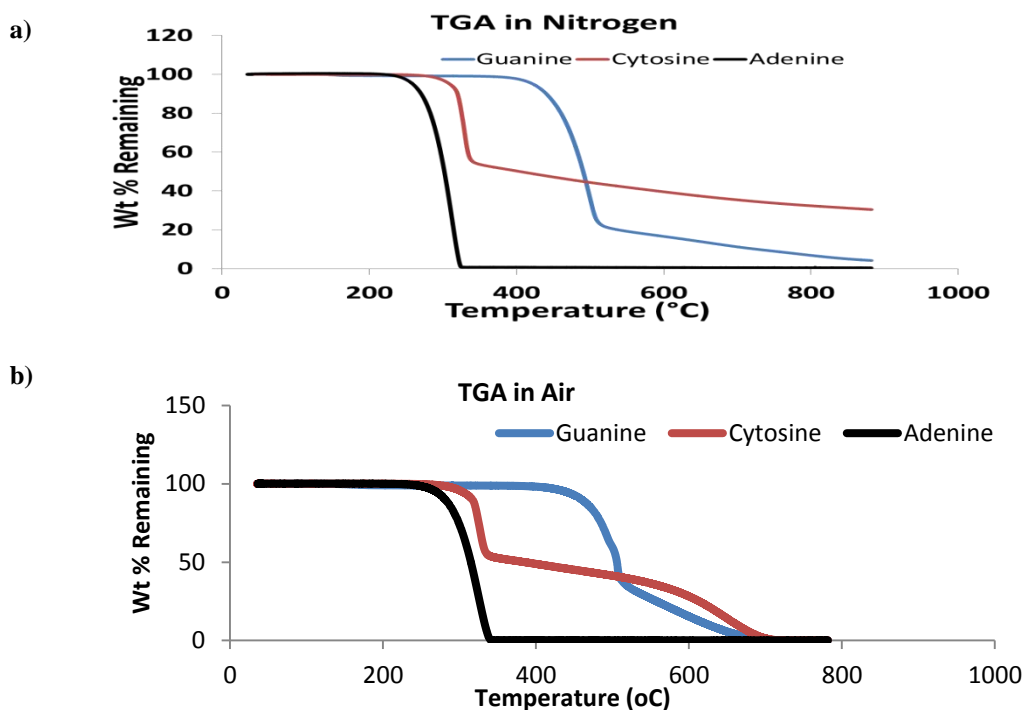


Figure 4. Thermogravimetric analysis of guanine, cytosine and adenine.

We also performed molecular beam deposition (MBD) (10^{-8} Torr, ~ 1 Å/s deposition rate), physical vapor deposition (PVD) ($\sim 4.5 \times 10^{-6}$ Torr, ~ 3 Å/s deposition rate) and plasma enhanced chemical vapor deposition PECVD) (10-12 Å/s deposition rate) on a few of the nucleobase powders. Fig. 5 illustrates the typical film quality we achieved using MBD and PVD.

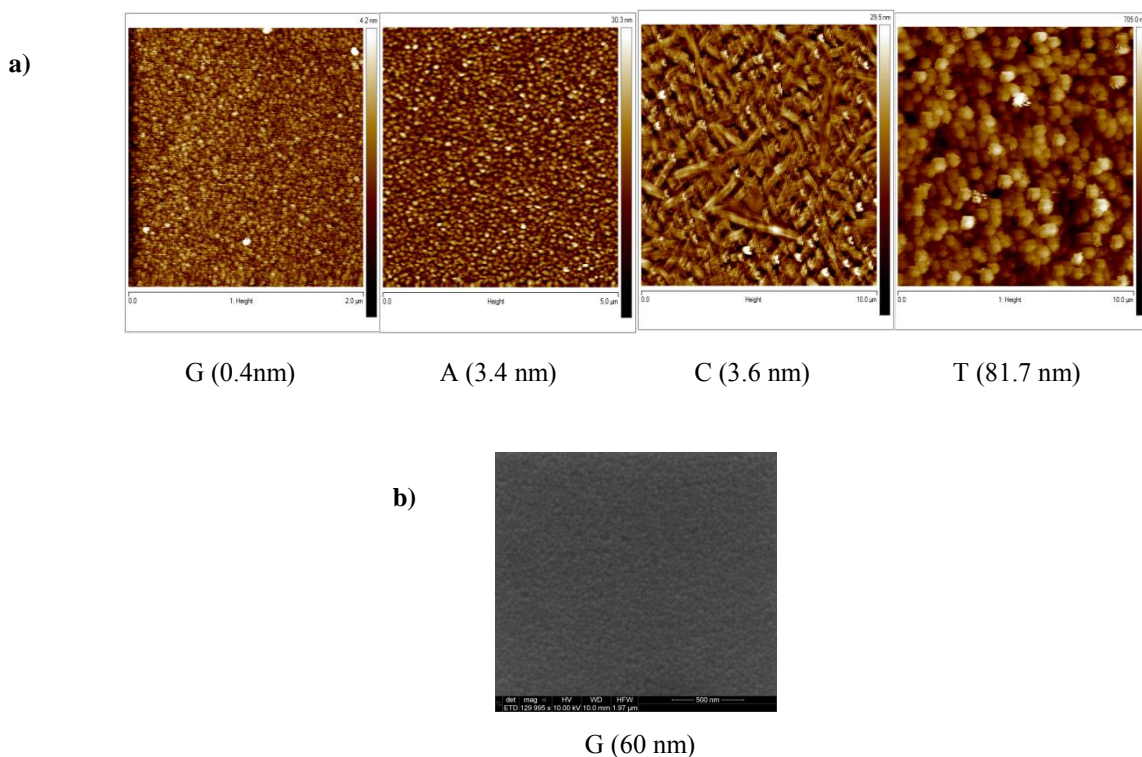


Figure 5. a) Molecular beam deposition and b) physical vapor deposition of nucleobases.

Adenine had a surface roughness of 3.4 nm. Thymine had a surface roughness 10X-25X higher than adenine depending on film thickness. The thicker the thymine film, the higher the surface roughness. The surface roughness of guanine was not done in time for this publication, however, from fig. 5b) the surface roughness appears to be qualitatively similar to that of adenine, defect free and featureless.

Results of the PECVD deposition are not included. Even though we were able to deposit the nucleobases, there was contamination in the chamber from other materials being deposited, so this will need to be redone at a later date before any conclusions can be drawn.

We performed x-ray photoelectron spectroscopy (XPS) on the guanine film produced by PVD of the guanine powder and compared it to XPS performed on guanine crystals by S. Ptasinska, A. Stypczynska, T. Nixon, N. Mason, D. Klyachko & L. Sanche, "X-Ray Induced Damage in DNA Monitored by X-Ray Photoelectron Spectroscopy, *Journal of Chemical Physics*, **129**, 065102, (2008). As can be seen in fig. 6, the crystal structure for both materials is very similar suggesting that vapor deposition is a viable deposition process for nucleobases.

Fig. 7 contains plots of the absorption spectra of several nucleobases deposited using MBD as well as DNA-cetyltrimethylammonium chloride (CTMA), for comparison. As can be seen, adenine, thymine and uracil are similar to DNA-CTMA. Guanine and cytosine are very different, but similar to each other. Taking measurements at longer wavelengths we found that all the nucleobases were relatively flat with >95% transmission over the range of 400-900 nm, which is similar to that for DNA-CTMA.

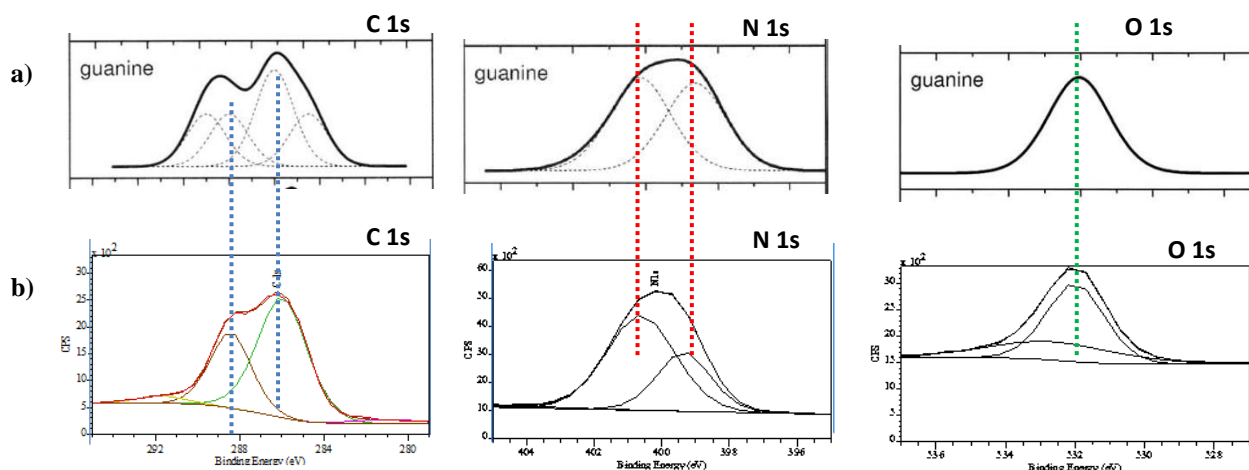


Figure 6. X-ray photoelectron spectroscopy of guanine a) guanine crystal measured by S. Ptasinska, A. Stypczynska, T. Nixon, N. Mason, D. Klyachko & L. Sanche, "X-Ray Induced Damage in DNA Monitored by X-Ray Photoelectron Spectroscopy, *Journal of Chemical Physics*, **129**, 065102, (2008) and b) physical vapor deposited guanine powder.

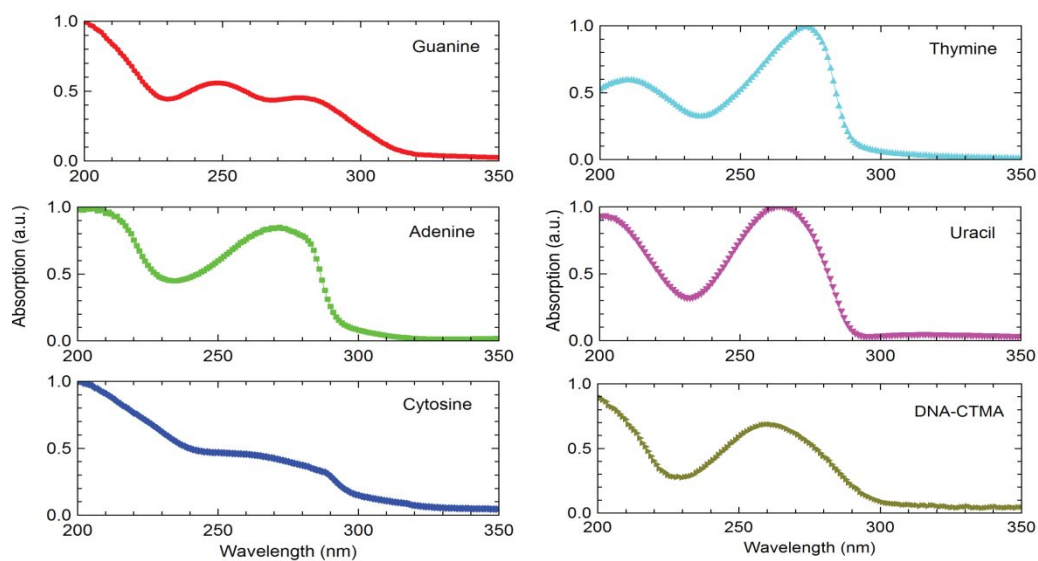
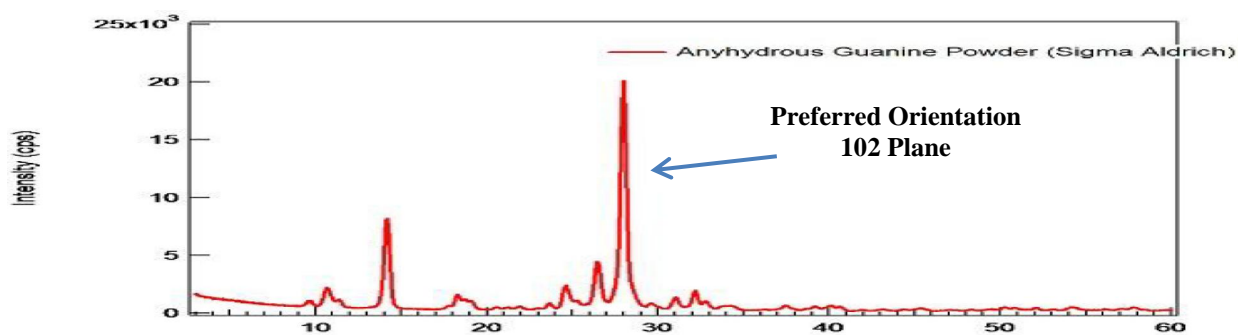


Figure 7. Absorption spectra of molecular beam deposited nucleobases.

X-ray diffraction (XRD) performed on the guanine powder used for this experiment was very similar to the theoretical x-ray diffraction pattern calculated for anhydrous guanine (A. Levy-Lior, B. Pokroy, B. Levavi-Sivan, L. Leiserowitz, S. Weiner and L. Addadi, "Biogenic Guanine Crystals from the Skin of Fish May Be Designed to Enhance Light Reflectance", *Crystal Growth and Design*, **8**(2), 507–511, (2008). See fig. 8. XRD was also performed on PVD guanine powder on a SiO₂/Si substrate and as can be seen in fig. 9, it has the same preferred 102 plane orientation, only less ordered.

a)



b)

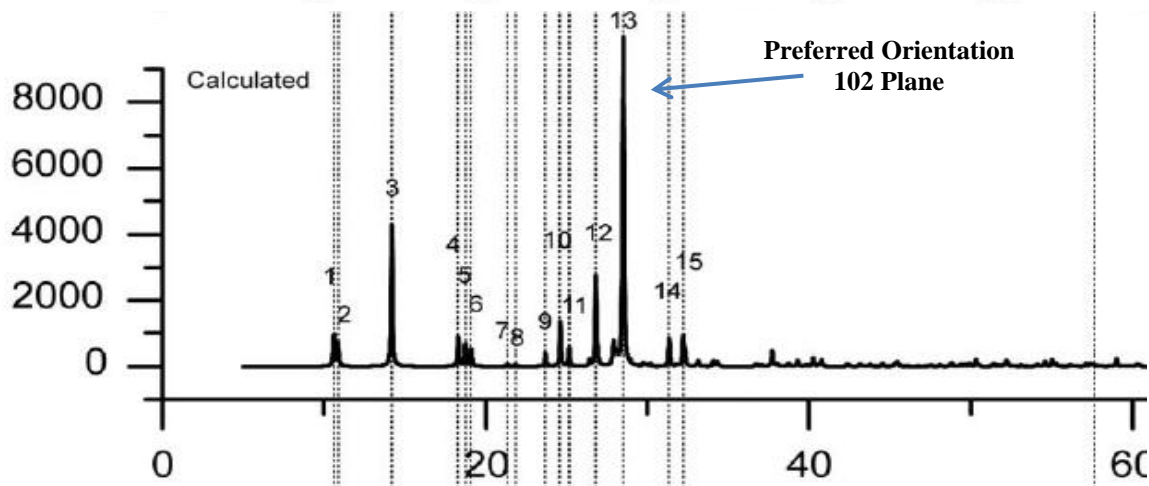


Figure 8. a) Measured and b) theoretical x-ray diffraction pattern of anhydrous guanine.

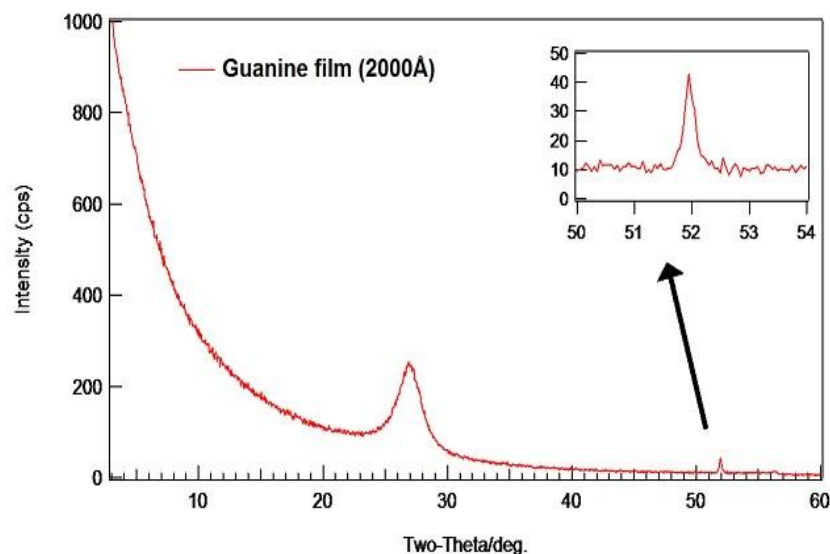


Figure 9. X-ray diffraction of physical vapor deposited guanine powder on SiO_2/Si substrate.

APPLICATIONS

After we performed the initial characterizations we used PVD to deposit a 60 nm thick layer of guanine on top of p-type monolayers of graphene to investigate the potential use of nucleobases as gate dielectrics for graphene transistors. See fig. 10 for a layout of the structures tested.

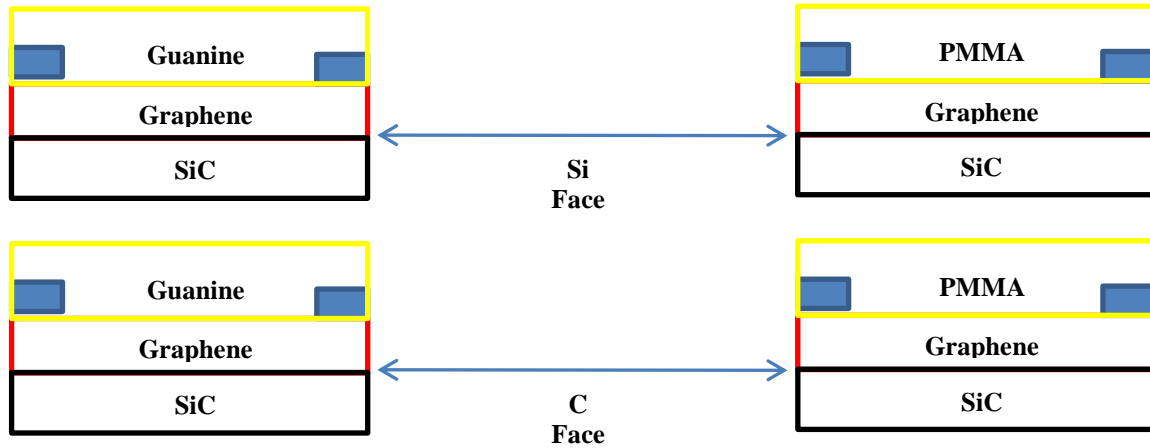


Figure 10. Layout of the guanine layer and PMMA layer on graphene.

For comparison we also spin deposited a 60 nm thick layer of polymethylmethacrylate (PMMA) on top of the p-type graphene. See fig. 10. The monolayers of graphene were grown on top of copper foil substrates using chemical vapor deposition (CVD) and then using tape were transferred onto silicon carbide (SiC) substrates on both the silicon (Si) face and the carbon (C) face of the substrates. Four monolayers of graphene were stacked on top of each other on the surface of the SiC substrates for this experiment. Hall charge carrier mobility measurements were performed on the graphene alone and then on the graphene with the guanine layer and the graphene with the PMMA layer. Table 2 highlights the results of this experiment.

Table 2 Hall mobility measurements of guanine/graphene and PMMA/graphene layers on SiC substrates

SiC Substrate Side	Mobility Prior to Dielectric Deposition (cm ² /Vs)	Mobility Post Dielectric Deposition (cm ² /Vs)	Charge Carrier Concentration (cm ³)	Resistivity (Ω-cm)	Type	Dielectric Material
Si face	980	1000	3.8×10^{13}	1.64×10^2	P	Guanine
C face	920	900	2.7×10^{13}	2.48×10^2	P	Guanine
Si face	955	720	2.9×10^{13}	2.2×10^2	P	PMMA
C face	735	730	4.1×10^{13}	2.0×10^2	P	PMMA

As can be seen in Table 2, there was no reduction in charge carrier mobility on either the Si or the C face when using guanine, where there was a 33% reduction in charge carrier mobility on the Si face when using PMMA. Though these initial results are encouraging, additional experiments need to be performed to confirm these results. Additional benefits for using nucleobases for gate dielectrics include higher temperature stability and resistance to aqueous and organic solvents and humidity, compared to PMMA and other polymers.

For the next application we then used PVD to deposit a 60 nm thick guanine layer on both sides of a DNA-CTMA-sol-

gel capacitor dielectric layer, sandwiched between an ITO and aluminum electrode. See fig. 11b. Compare this with our standard capacitor layout in fig. 11a.

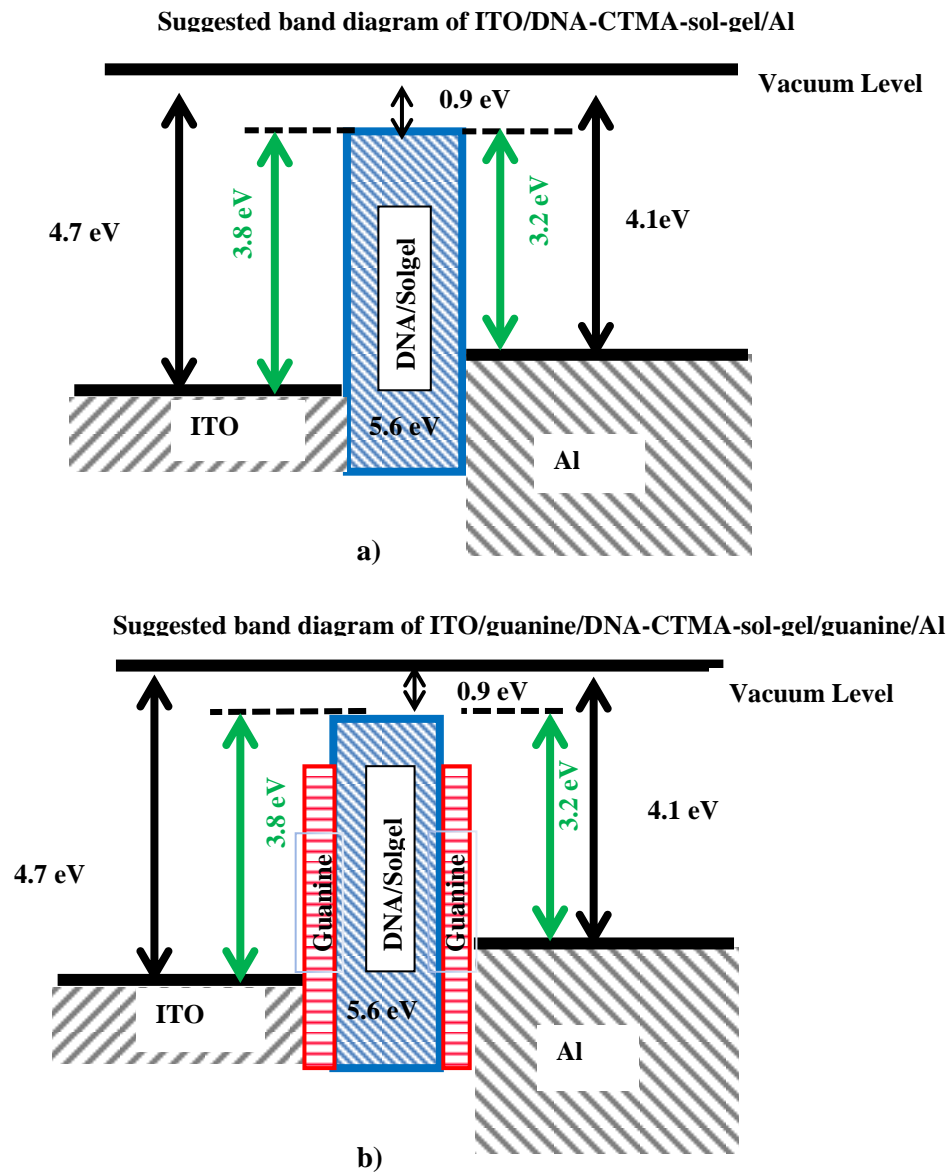


Figure 11. Layout of a) ITO/DNA-CTMA -sol-gel/Al capacitor structure and b) layered ITO/guanine/DNA-CTMA-sol-gel/guanine/Al capacitor structure.

We achieved electric field breakdowns 20% higher, with fewer number of failures, for the layered capacitor structures with guanine. This translates to a 35% higher energy density. See Table 3. More experiments are planned to validate these findings and to investigate these structures more thoroughly.

Table 3. Dielectric constants and electric field strengths of DNA-CTMA-sol-gel and guanine/DNA-CTMA-sol-gel/guanine capacitor structures.

Device	Dielectric Constant ϵ (1 kHz)	Electric Field Strength E (V/cm)	Calculated Volumetric Energy Density ($\epsilon\epsilon_0 E^2/2, \text{J/cc}$)*
DNA-CTMA-Sol-Gel	4.94	312×10^4	2.20
Sol-Gel	5.03	294×10^4	1.92
Polystyrene	2.6	248×10^4	0.71
Guanine-DNA-CTMA-Sol-Gel-Guanine Multilayer	5.02	375×10^4	2.97

For our final application we used adenine as an electron blocking layer (EBL) in a phosphorescent-type OLED. Figure 12 illustrates the OLED structure we tested using adenine as the EBL layer and an iridium-based lumophore for the emitting layer. We compared results to the baseline structure, without the EBL.

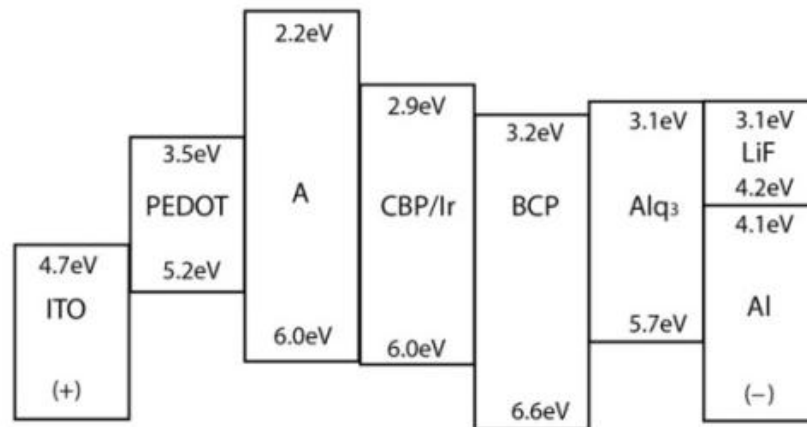


Figure 12. OLED structure.

The adenine was deposited using MBD. The thickness of the adenine layer measured 20 nm.

Fig. 13 contains plots of the results. As can be seen in fig. 13, preliminary results indicate that the OLED structure with the adenine EBL has a higher luminous efficiency than the baseline OLED. The peak efficiency measured 70 cd/A, compared to 34 cd/A for the baseline OLED. OLED structures using the other nucleobases are planned and will be compared to our previous BioLEDs with DNA-CTMA EBLs.

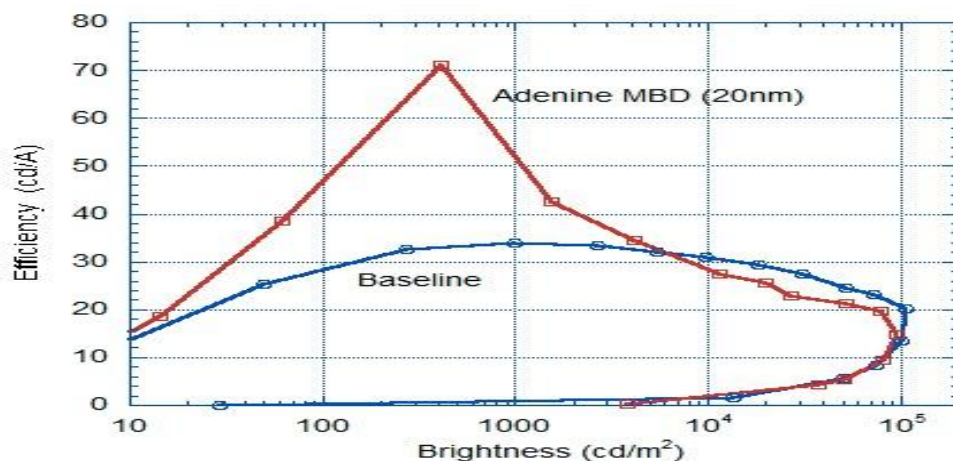


Figure 13. Luminous efficiency of baseline OLED versus OLED with adenine EBL.

4. CONCLUSIONS

We have presented here, our preliminary characteristics of nucleobases and encouraging results for a few photonic and electronic applications. In addition to the experimental results, nucleobases have much higher temperature stabilities, are resistant to aqueous and organic solvents, are resistant to humidity and are 10X lower in cost than DNA-CTMA. Much more work is needed.

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