

Progress of DNA photonics

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ABSTRACT

In this paper we present our current research in developing non-conductive, optically transparent electromagnetic interference (EMI) or radio frequency (RF) shielding. It uses metallic nanopowders blended with deoxyribonucleic acid (DNA) based host materials. Recent results of this DNA-based EMI shielding demonstrate 18-27dB over a frequency range of 18 - 6 GHz, respectively, with an electrical resistivity measuring $> 20M\Omega$ for a 20 μm dielectric spacing. These films were optical transparent in the visible wavelength range.

1.0 INTRODUCTION

Deoxyribonucleic Acid (DNA) has been used, and continues to be used, as an optical and electrical material for various applications including organic light emitting diodes, organic thin film transistors, polymer electro-optic modulators, polymer lasers, varactors and capacitors. This research has been reported in previously published works [1-21], as well as at this year's Nanobiosystems: Processing, Characterization and Applications Conference [21-25]. Therefore, this paper focuses on previously unreported work developing DNA-based non-conductive, optically transparent electromagnetic interference (EMI) or radio frequency (RF) shielding. As the speeds of micro-electronic devices and systems continue to increase, radio frequency radiation, or EMI, in and around these devices and systems, will limit their performance and operation. These devices not only create EMI but can also be affected by EMI.

Types of EMI shielding include reflection, absorption and multiple-reflection.

Reflection EMI shielding is the most common type for microelectronic applications. For this type of shielding a conductive surface reflects radiation. It consists of metal sheets or conductive coatings that surround the device. This requires a nonconductive, or dielectric insulating material, coating on top of the microelectronic device, to prevent shorting, followed by the conductive metal layer [26]. The conductive layer must also make contact with a common ground. Reflective EMI shielding is a multiple step process, is difficult to ground, has a low thermal conductivity due to the dielectric insulating layer, does not affect EMI between conductive wires on the micro-electronic circuit and is costly.

Absorption EMI shielding absorbs the EMI where electric dipoles, such as barium titanate (BaTiO_3) or magnetic dipoles, such as iron oxide (Fe_3O_4) interact with the electric field. For this type of shielding the EMI absorbing material must be nonconductive, have a large dielectric constant, have a large thermal conductivity, be film formable, spreadable and have a low curing temperature. It has the potential to be lower cost.

Multiple-Reflection EMI shielding is a modified type of reflection EMI where metal nanoparticles or nanopowders are blended with the dielectric insulating material. It would need to be either nonconductive or would require an additional dielectric insulating layer and ground. So it would have similar characteristics to that of reflection EMI, however, it may not have the same level of shielding if nonconductive, since the amount of metal fillers would need to be small.

DNA was considered for this research because to its high dielectric constant of ~ 8 , compatibility with conductive nanoparticles and nanopowders and film forming properties.

2.0 EXPERIMENTAL

For this work the DNA was first blended with the surfactant hexadecyltrimethyl ammonium chloride (CTMA) to render it water insoluble, soluble in alcohol solvents. All the DNA-CTMA samples were made using DNA with lower molecular weight (MW) that was processed using a high power ultrasonic system to break the large DNA molecules into smaller ones. For comparison Fig. 1 shows two bottles of DNA-CTMA solutions, which were made using the DNA with larger/smaller MW. The bottle on the left is high MW DNA-CTMA in butanol and the bottle on the right is low MW DNA-CTMA in butanol. The high MW DNA blend appears darker in color than the low MW DNA blend. We also compared the viscosity of both MW DNA blends and found that the viscosity of the high MW DNA blend is much lower, given that both the high and low MW DNA blends have the same DNA-CTMA weight ratio to solvent. In addition, we found that it was more difficult to dissolve the high MW DNA-CTMA blend and that it takes a much longer time to completely dissolve it in solvent. After the large MW DNA-CTMA blend is completely dissolved, the solution is not always even. There were also thicker portions of DNA-CTMA in the solution. This in turn caused unwanted uneven distribution of the metal nanopowders in the solution when mixed with the DNA-CTMA solution.

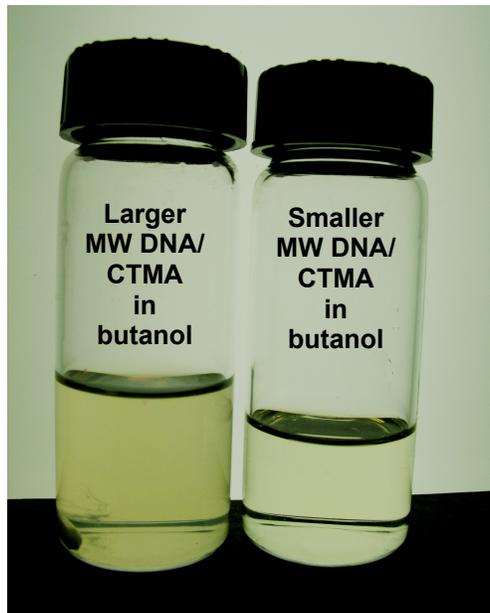


Figure 1. Comparison of DNA-CTMA solutions made using larger and smaller MW DNA.

The filler materials we used were silver (Ag), silver-coated aluminum (Al+Ag), iron (Fe), Nickel (Ni), graphite, brass and copper (Cu) powders which we blended with the DNA/CTMA butanol solution and then spread-coated onto glass plates to make the EMI shield samples. Ag nanopowder was the most expensive at \$25/g and graphite nanopowder was the least expensive at \$0.25/g. Table 1 listed these samples together with some polymethylmethacrylate (PMMA) based, gold film, conductive paint and anti-static plastic films for comparison. All DESM samples were tested for their surface conductivities. As designed, most samples are non-conductive and some conductive samples were intentionally fabricated. The samples formulated are listed in Table 1. Fig. 2 is a photograph of an actual Ag-DNA-CTMA sample.

The test setup for the samples was a testing cell containing an RF transmitter and receiver with a frequency range of 4-20 GHz. See Fig 3.

We also measured the thermal coefficient of DNA and DNA-CTMA using a femtosecond laser pump-probe. Prior to the experiment 100 nm thick layer of Al was deposited on the film.

Table 1

Samples	Fillers	DNA Concentration	Filler Concentration	Surface Conductivity
S1	Graphite #1	~ 10 wt%	10 wt%	No
S2	Graphite #2	~ 10 wt%	10 wt%	Yes
S3	Dopers	~ 10 wt%	20 wt%	No
S4	Ni	~ 10 wt%	20 wt%	No
S5	Ag + Brass	~ 10 wt%	Ag: 5.3 wt%, Brass: 7.8 wt%	No
S6	Ag + Cu	~ 10 wt%	Ag: 5 wt%, Cu: 5 wt%	No
S7	Ag + Ag-Al*	~ 10 wt%	Ag: 5 wt%, Ag-Al*: 5 wt%	Yes
S8	Ag + Fe	~ 10 wt%	Ag: 5.3 wt%, Fe: 6.5 wt%	No
S9	Ag + Graphite #1	~ 10 wt%	Ag:5 wt%, Graphite: 5.7 wt%	No
S10	Ag + "Mumetal" **	~ 10 wt%	Ag: 5 wt%, Mumetal: 5 wt%	Yes
S11	"Mumetal" **	~ 10 wt%	Mumetal **: 10 wt%	No
S12	Ni	~ 10 wt%	Ni: 10 wt%	No
S13	Ag	~12 wt%	10 wt%	No
S14	Ag	~8 wt%	10 wt%	Yes
S15	Ag	N/A PMMA Host	10 wt%	No

* Ag-Al: Silver coated aluminum; **"Mumetal": Fe: 15%, Ni: 75%, Cu 10%



Figure 2. Ag + DNA-CTMA EMI shield sample.

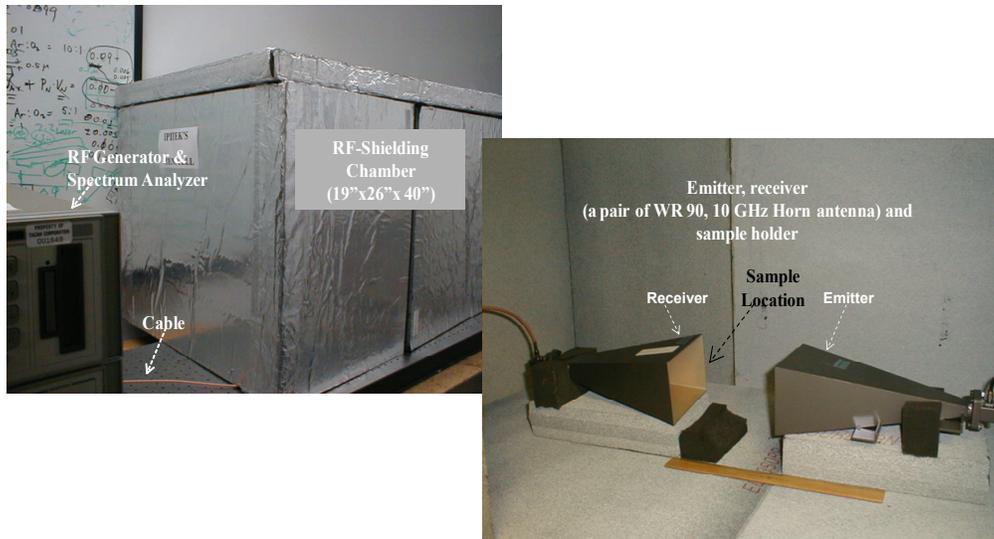


Figure 3. Test sample characterization setup.

3.0 RESULTS

We performed EMI shielding tests, for the samples listed in Table 1. Table 2 lists the surface conductivity and the RF shielding measured for DNA-CTMA+Ag and PMMA+Ag. At lower DNA ratios the DNA-CTMA+Ag, or at higher concentrations of Ag the material becomes conductive.

Sample#	DNA Ratio	Ag Ratio	S-Resistivity*	RF Shielding (10 GHz)
DNA-CTMA+Ag	12 wt%	10 wt%	> 30 MΩ/sq	21 dB
DNA-CTMA+Ag	8 wt%	10wt%	> 0.32 Ω/sq	20.5 dB
PMMA+Ag	N/A	10 wt%	> 30 MΩ/sq	18 dB

Fig. 4 is a plot of the RF shielding effectiveness nonconductive DNA-CTMA+Ag sample compared with PMMA+Ag for various concentrations of Ag.

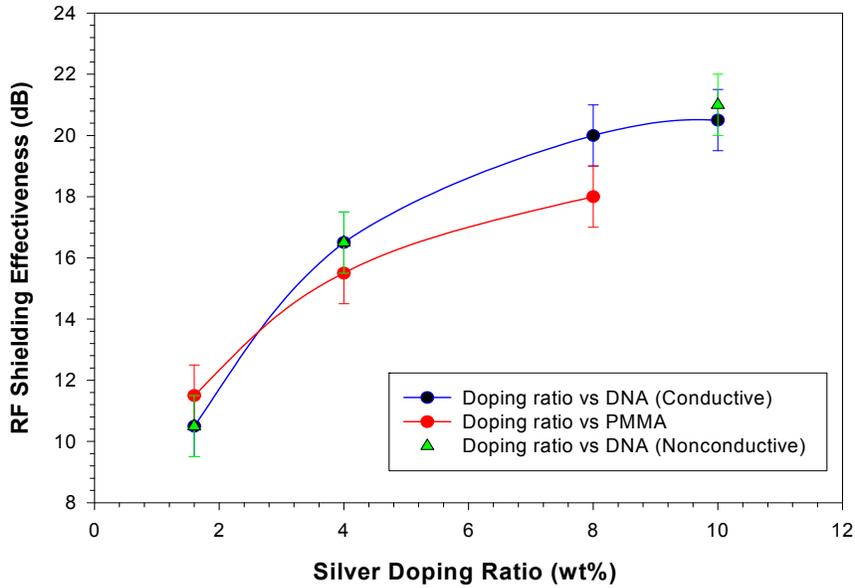


Figure 4. RF shielding effectiveness versus Ag doping ratio for both DNA-CTMA+Ag and PMMA+Ag.

From Table 2 and Fig. 4 nonconductive DNA-CTMA+Ag provides 50% better EMI shielding at 10 GHz than PMMA+Ag.

Table 3 compares nonconductive DNA-CTMA+Ag with current shielding such as Desco Statshield, Parker Chomerics conductive paint and gold plated glass plates. From Table 3 nonconductive DNA-CTMA+Ag provides 60%-70% better EMI shielding than current conductive shielding.

All measurements were conducted at room temperature.

Sample	Thickness	Maker	S-Resistivity*	RF Shielding (10 GHz)
Nonconductive DNA-Silver	~ 40 μm	IPITEK	> 30 $\text{M}\Omega/\text{sq}$	21 dB
Statshield Plastic Bag	~ 76 μm	Desco	> 30 $\text{M}\Omega/\text{sq}$	16 dB
Gold-Coated Glass Plate	0.6 μm	IPITEK	~ 0.3 Ω/sq	17 dB
Conductive Paint coated	~ 60 μm	Parker Chromerics	~ 0.3 Ω/sq	16.5 dB

Fig. 5 is a plot of Effective EMI shielding versus frequency for the samples 1-12 listed in Table 1.

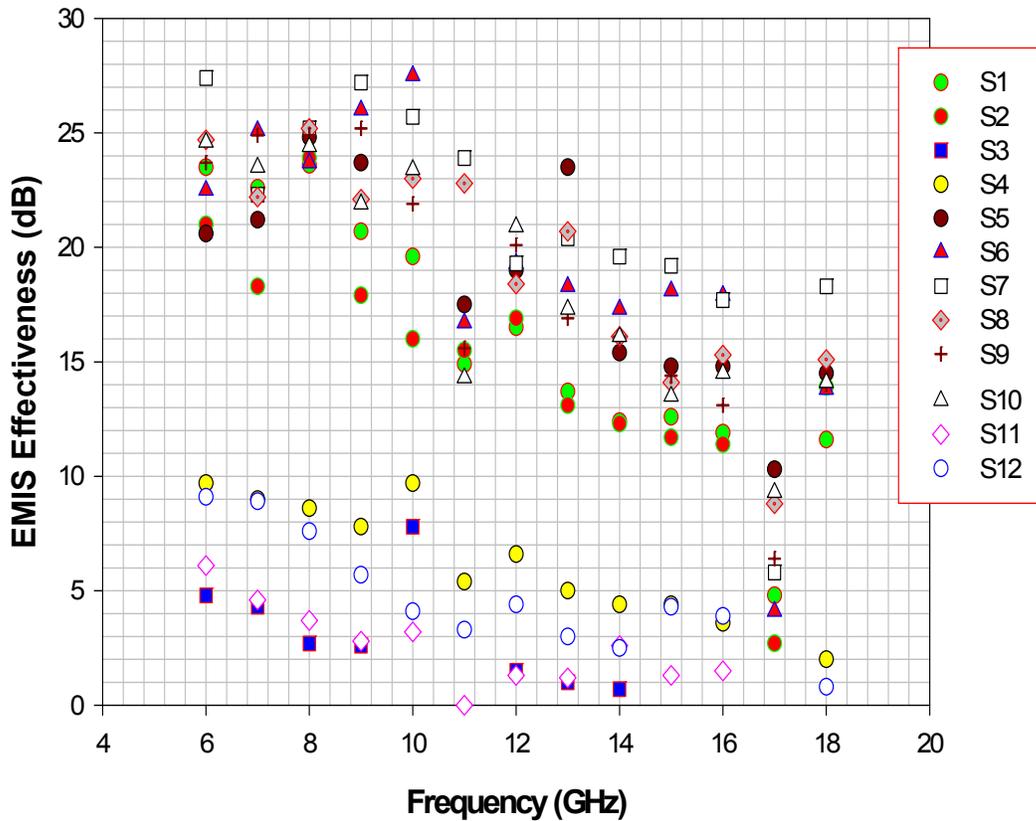


Figure 5. Plot of the EMI shielding data versus frequency.

From Fig 5 one observes that the Ag-mixture and graphite fillers provide better EMI shielding than most of the pure metal fillers except for the pure Ag nanopowder filler. However, the Ag-mixture fillers are much less expensive than pure Ag since only 5 wt% Ag was needed. Graphite fillers proved to be the least expensive filler and provided comparable EMI shielding to the more expensive fillers. Figure 6 is a plot of 10 wt% graphite.

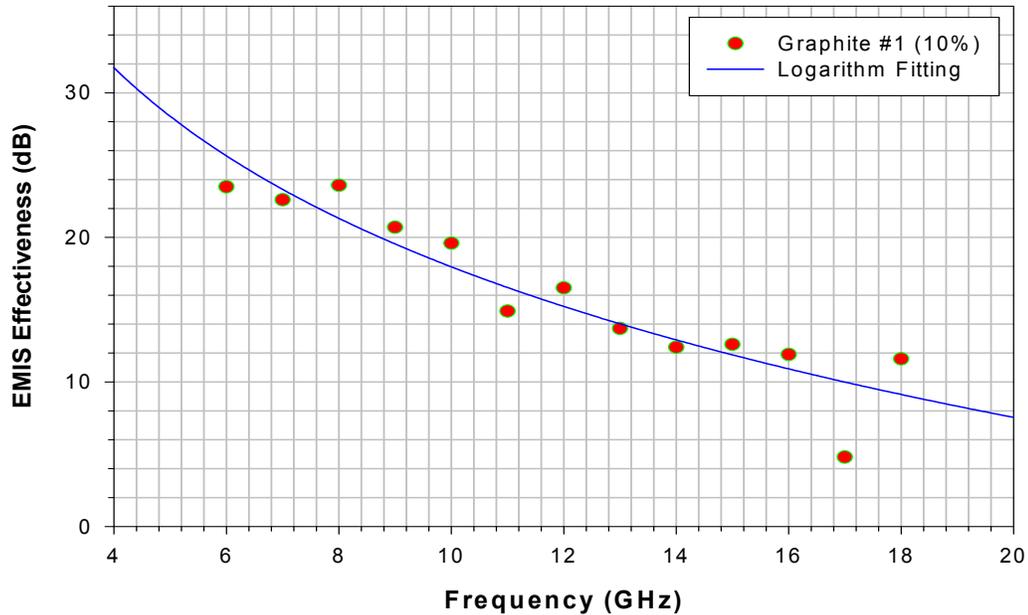


Figure 6. EMI effectiveness versus frequency for 10 wt% graphite filler in DNA-CTMA

The EMI shielding frequency responses of most samples (conductive and nonconductive) appear to decay with increased frequency, followed a logarithmic-decay pattern. This suggests that the EMIS mechanism of the DNA-CTMA-based samples may be due to reflection or scattering.

The thermal conductivity of a 1 μm thick film of DNA measured 0.82 W/mK. This is 7X higher than PMMA, which has a thermal conductivity of 0.12 W/mK. The thermal conductivity of a 1 μm thick film of DNA-CTMA measured 0.62 W/mK. This is 5X higher than PMMA. This is promising given that the DNA-based nonconductive EMI shield material will coat the microcircuit. A higher thermal conductivity will remove heat much more efficiently.

4.0 SUMMARY

In summary we have blended metal and graphite nanopowders with a bio-organic material DNA-CTMA to render an effective EMI shield that is nonconductive. With these encouraging results we to look ahead and work to optimize the characteristics and determine which theory best fits the data. We also plan to measure the thermal conductivity of the various metal nanopowder blends in DNA-CTMA. With the metal nanopowders the thermal conductivity could potentially be higher.

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REFERENCES

1. J. Hagen, J. Grote, N. Ogata, J. Zetts, R. Nelson, D. Diggs, F. Hopkins, P. Yaney, L. Dalton and S. Clarson, "DNA Photonics", *SPIE Proceedings*, Eds., J. Grote and T. Kaino, **5351**, pp. 77-86, (2004)
2. J. Grote, E. Heckman, J. Hagen, P. Yaney, G. Subramanyam, S. Clarson, D. Diggs, R. Nelson, J. Zetts, F. Hopkins and N. Ogata, "Deoxyribonucleic Acid (DNA) Based Optical Materials", *SPIE Proceedings*, Eds., A. Vere, J. Grote and F. Kajzar, **5621**, pp. 16-22, (2004)
3. J. Grote, J. Hagen, J. Zetts, R. Nelson, D. Diggs, M. Stone, P. Yaney, E. Heckman, C. Zhang, W. Steier, A. Jen, L. Dalton, N. Ogata, M. Curley, S. Clarson and F. Hopkins, "Investigation of Polymers and Marine Derived DNA in Optoelectronics", *Journal of Physical Chemistry B*, **108(25)**, pp. 8589-8591, (2004)
4. J. Subramanyam, E. Heckman, J. Grote and F. Hopkins, "Microwave Dielectric Properties of DNA Based Polymers Between 10 and 30 GHz", *IEEE Microwave & Wireless Components Letters*, **15(4)**, pp. 232-234, (2005)
5. J. Grote, N. Ogata, J. Hagen, E. Heckman, P. Yaney, M. Stone, D. Diggs, R. Nelson, J. Zetts, F. Hopkins and L. Dalton, "DNA Photonics [Deoxyribonucleic Acid]", *Journal of Molecular Crystals and Liquid Crystals*, **426**, pp. 3-17, (2005)
6. G. Subramanyam, E. Heckman, J. Grote, F. Hopkins, R. Neidhard and E. Nykiel, "Microwave Dielectric Properties of Marine DNA Based Polymers", *Microwave and Optical Technology Letters*, Wiley, **46(3)**, pp. 278-282, (2005)
7. E. Heckman, P. Yaney, J. Hagen, J. Grote and F. Hopkins, "Processing Techniques for DNA: A New Biopolymer for Photonics Applications", *Applied Physics Letters*, **87**, 211115, (2005)
8. G. He, Q. Zheng, P. Prasad, J. Grote and F. Hopkins, "Toward Biological Laser: IR Two-Photon Excited Visible Lasing From a DNA-Chromophore-Surfactant Complex", *Optics Letters*, **31(3)**, pp. 359-361, (2006)
9. P. Gupta, P. Markowicz, K. Baba, J. O'Reilly, M. Samoc, P. Prasad and J. Grote, "DNA-Ormocer Nanocomposite - A New Biocomposite for Fabrication of Photonic Structures", *Applied Physics Letters*, **88**, 213109, (2006)
10. J. Hagen, W. Li, A. Steckl, J. Grote and K. Hopkins, "Enhanced Emission Efficiency in Organic Light Emitting Diodes Using Deoxyribonucleic Acid Complex as Electron Blocking Layer", *Applied Physics Letters*, **88**, 171109, (2006)
11. B. Singh, S. Sariciftci, J. Grote and F. Hopkins, "Bio Organic-Semiconductor Field-Effect Transistor (BiOFET) Based on Deoxyribonucleic Acid (DNA) Gate Dielectric", *Journal of Applied Physics*, **100**, 024514, (2006)
12. E. Heckman, J. Grote, F. Hopkins and P. Yaney, "Performance of an Electro-Optic Waveguide Modulator Fabricated Using a Deoxyribonucleic-Acid-Based Biopolymer", *Applied Physics Letters*, **89**, 181116, (2006)
13. Z. Yu, J. Hagen, Y. Zhou, D. Klotzkin, J. Grote and A. Steckl, "Photoluminescence and Stimulated Emission from Deoxyribonucleic Acid Thin Films Doped with Sulforhodamine", *Applied Optics*, **46(9)**, pp. 1507-1513, (2006)
14. J. Hagen, W-X Li, H. Spaeth, J. Grote and A. Steckl, "Molecular Beam Deposition of DNA Nanometer Films", *Nano Letters*, **7(1)**, pp. 133-137, (2007)
15. D. Zang and J. Grote, "Photoelectrical Effect and Current-Voltage Characteristics in DNA-Metal Schottky Barriers", *SPIE Proceedings*, Eds., J. Grote, F. Kajzar and N. Kim, **6470**, pp. 0A1-0A10, (2007)

16. Y. Ner, J. Grote, J. Stuart and G. Sotzing, "Enhanced Fluorescence in Electrospun Dye Doped DNA Nanofibers", *Soft Matter*, **4** (b717581g), pp1-7 (2008)
17. K. Sarma, S. Dodd, C. Chanley, J. Roush, S. Sariciftci, R. Naik and J. Grote, "Biopolymer-based Gate Dielectric Layer for Organic Field Effect Transistors", *SPIE Proceedings*, **7118**, 71180L, (2008)
18. F. Ouchen, S. Kim, G. Subramanyam, P. Yaney, L. Dai, R. Naik and J. Grote, "Semiconductive Properties of DNA-Based Materials", *SPIE Proceedings*, **7118**, 71180M, (2008)
19. Q. Sun, L. Dai, J. Grote and R. Naik, "Multi-Structured and Multilayer White Polymer Light-Emitting Diodes Using a Deoxyribonucleic Acid Complex as Hole-Transporting Layer/Electron-Blocking Layer", *Applied Physics Letters*, **92**, 251108, (2008)
20. R. A. Norwood, C. T. DeRose, R. Himmelhuber, N. Peyghambarian, J. Wang, L. Li, F. Ouchen, and J. G. Grote, "Dielectric and Electrical Properties of Sol-Gel/DNA Blends", *SPIE Proceedings*, **7403**, 74030A
21. Y. Ner, J. Grote, J. Stuart and G. Sotzing, "White Luminance from Multi-Dye Doped Electrospun DNA Nanofibers via Fluorescence Resonance Energy Transfer", *Angewandte Chemie*, **48**, 1-6, (2009)
22. J. Yoshida, "Device Manufacturing Processes of DNA-CTMA Based Photonic Devices", *SPIE Proceedings*, Eds., N. Kobayashi, F. Ouchen and I. Rau, **7765**, TBP, (2010)
23. N. Ogata, "Progress of DNA Bionics and Other Applications", *SPIE Proceedings*, Eds., N. Kobayashi, F. Ouchen and I. Rau, **7765**, TBP, (2010)
24. F. Ouchen and J. Grote, "DNA-PEDOT Based Field Effect Transistors", *SPIE Proceedings*, Eds., N. Kobayashi, F. Ouchen and I. Rau, **7765**, TBP, (2010)
25. R. Norwood, J. Thomas, N. Peyghambarian, J. Wang, J. Grote and F. Ouchen, "Hybrid DNA Materials for Energy Storage and Optical Information", *SPIE Proceedings*, Eds., N. Kobayashi, F. Ouchen and I. Rau, **7765**, TBP, (2010)
26. R. Joshi, "Method of and Apparatus for Providing an RF Shield on Electronic component," US patent application, 20090032300 (2009)