

Supplementary Information

Orthogonal alignment of DNA using hexafluoroisopropanol as solvent for film castings

Materials

Sodium salt of salmon DNA was purchased from Sigma-Aldrich. Cetyltrimethylammonium (CTMA) bromide was purchased from Fisher and used as received. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and n-butanol (BuOH) were purchased from Sigma-Aldrich and Fisher, respectively, and were used as received. Glass slides and quartz slides were also purchased from Fisher. For making the base bath, potassium hydroxide pellets and isopropyl alcohol were bought from Fisher and Sigma-Aldrich, respectively. Solutions were filtered using PTFE propylene housing Whatman syringe filter (25 mm diameter, 0.45 μm pore size, Fisher).

DNA-CTMA Preparation

This modified procedure for DNA-CTMA preparation was recently published¹ and used in this study. Two grams of DNA is dissolved in deionized water with a final concentration of 4g/L. After which, the solution is filtered through a nylon filter with a 0.60 μm pore size. A separate solution of CTMA is prepared by dissolving 2 g of CTMA in deionized water at a concentration of 4 g/L. The filtered DNA solution is added drop-wise to the CTMA solution using a burette forming a white precipitate. The solution is mixed for another 4 h at room temperature.

To remove excess CTMA and NaCl from the ion exchange reaction, a combined technique that involves dialysis and Soxhlet extraction was done. The dried DNA-CTMA is dissolved in absolute grade ethanol (EtOH) at 8-10%wt, depending on the starting

molecular weight of the DNA. The solution is loaded into dialysis tubing (MWCO ~ 12 kDa) and then placed in a Soxhlet extractor. The bulk solvent for the dialysis process is 0.25L of EtOH. The dialyzed solution outside the membrane is refreshed every 15 min, made possible through the Soxhlet process, over a period of 8 h for a total of 32 rinsing cycles. Following this step is the removal of solvent using a BUCHI R 205 rotary evaporatory system. The recovered DNA-CTMA solid is dried overnight in a Teflon beaker at 50 °C under vacuum.

Substrate Preparation

Quartz slides for CD spectroscopy were cleaned in a base-bath prior to film deposition. Glass slides with gold-deposited electrodes for dielectric measurements were spun on a spin-coater at 800 rpm while being washed with the following solvents in this order: acetone, methanol and n-propanol.

DNA-CTMA Film Preparation

For UV-Vis and circular dichroism (CD) measurements, 4% (wt./wt.) solutions of DNA-CTMA were spin-coated on quartz substrates at 2000 rpm for 60 s. For dielectric measurements, the same solutions of DNA-CTMA in butanol and HFIP were drop-casted on glass slides with gold-deposited electrodes and covered with Petri dishes to allow for slow evaporation of solvents. All of the films were vacuum dried at 90 °C overnight.

UV-Vis Spectroscopy

A Varian Cary 5000 UV-Vis-NIR spectrophotometer was used to obtain the UV spectra between the wavelengths 190 to 340 nm and baseline corrected with a quartz substrate. Absorbance values should fall between 0.1 and 1 prior to getting the CD spectra. No CD signal will be detected if the absorbance values are too low or the CD detector will saturate if the absorbance values are too high.

Circular Dichroism Spectroscopy

UV-Vis measurements of films were done prior to the CD measurements and were used to normalize the CD spectra obtained. The secondary conformations of the DNA in the DNA-CTMA films were determined using a JASCO J-710 CD Spectropolarimeter. The following scan parameters were used: 190 to 340 nm collection window, 20 nm/min scanning speed, 10.0 nm bandwidth and 4 to 5 data accumulation.

X-ray Diffraction

Wide-angle X-ray diffraction (WAXD) was collected on an Xcalibur PX Ultra diffractometer (Oxford diffractometer) with a sample to Onyx CCD detector distance of 65 mm using a copper X-ray source (1.54Å, 45 kV, 45 mA). One-dimensional WAXD measurements were performed on the DNA-CTMA films with the incident X-ray beam oriented both perpendicular “face view” and parallel “edge view” to the face of the material. A Goniometer Rigaku Ultima IV was utilized to collect the small-angle X-ray scattering (SAXS) using a copper X-ray source (1.54Å, 40 kV, 44 mA). SAXS measurements were performed with the incident beam perpendicular to the film surface.

Low signal strength was due to poor sample geometry (i.e. non-planar and thin) therefore causing weak scattering to occur. A Lorentz correction was applied to all SAXS data to account for the stacked layered structure that was projected onto a one-dimensional I(q) vs. q profile, where q is the scattering vector, $q = 4\pi \sin\theta / \lambda$.²

Dielectric Measurements

The capacitance measurements were conducted using a metal-insulator-metal (MIM) test structure as described in previous publications.³ The actual area of each device was designed to be 0.1963 cm². The Capacitance-frequency (C-F) data were collected using a Keithley (model 4210-CVU 1kHz-10MHz) equipped with a Capacitance Voltage measurement unit (CVU). The dielectric constant k is obtained using the equation:

$$C = \frac{\epsilon_0 k}{d} A$$

Where ϵ_0 is the permittivity of vacuum, k is the dielectric constant, A the device area and d is the thickness of the dielectric film.

Reference

1. F. Ouchen, G. A. Sotzing, T. L. Miller, K. M. Singh, B. A. Telek, A. C. Lesko, R. Aga, E. M. Fehrman-Cory, P. P. Yaney, J. G. Grote, C. M. Bartsch and E. M. Heckman, *Applied Physics Letters*, 2012, **101**, 153702-153703.
2. N. Striebeck, in *Scattering from Polymers*, American Chemical Society, 1999, vol. 739, pp. 41-56.
3. P. P. Yaney, F. Ouchen and J. G. Grote, 2009, 74030M-74030M.