Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information

DNA hosted and aligned in aqueous interstitia of a lamellar liquid crystal – a membrane-biomacromolecule interaction model system

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DNA sequences with dye position.

(1) Cy3 – 5′-CCTGACTTGCTATGCTATCGAATGC

(2) ROX – 5′-CCTGACTTGCTATGCTATCGAATGC

(3) 5′-CCTGACTTGCTATGCTATCGAATGC

(4) Cy5 – 5′-GCATTCGATAGCATAGCAAGTCAGG

(5) FAM – 5′-GCATTCGATAGCATAGCAAGTCAGG

(6) 5′-GCATTCGATAGCATAGCAAGTCAGG

The combinations used were 1-6, 2-6, 3-4, 3-5, and 3-6

Solvent behavior of dye-DNA constructs

To establish the solution behavior of our dye-DNA constructs steady-state fluorescence anisotropy measurements in solution (no liquid crystal) was performed. The results reveal further evidence that the cyanine dyes interact more with the DNA helix than at least FAM (Figure S 2). The large increase in anisotropy observed for the DNA attached cyanine dyes as compared to the corresponding free dyes indicates that the cyanine dyes are constrained by the DNA helix. This alone cannot prove end-stacking, but it fits well with the hypothesis. Free Cy3, free Cy5 and DNA-attached ROX in turn all have significantly higher anisotropies than

DNA attached FAM. This helps to prove the point made by Sanborn *et al.* [1] that the steady-state fluorescence anisotropy can be misleading when investigating the rotational freedom of a fluorophore. Using the fluorescence lifetimes (Table S 1) measured for the samples the rotational correlation times were calculated (Table S 1). Here the samples divide in two groups with rotational correlation times in the range 0.4-0.6 ns or 2.5-3.5 ns. We ascribe the short rotational correlation times to free movement (Free Cy3, Cy5 and DNA-attached FAM) and the longer to restricted movement (DNA-attached Cy3, Cy5 and ROX). An even more complex relation is reported for DNA-attached Cy3 (sulfonated) with two rotational correlation times measured by time-resolved anisotropy [1]. Although the rotational correlation time does neither tell by which mechanism the movement is restricted nor the orientation of the dye, the rotational correlation time can be useful in evaluating the response from a DNA-attached dye.

Figures and tables

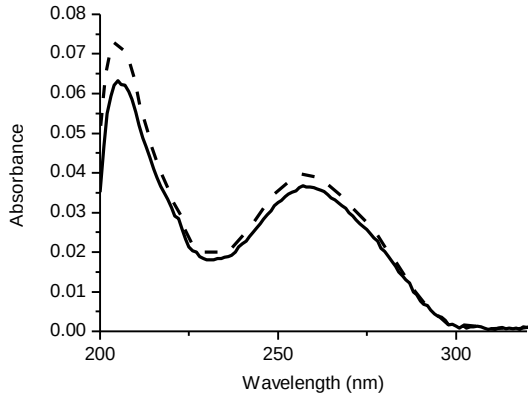

Figure S 1 Comparison of the absorption spectrum of a 25mer DNA duplex as measured in the anisotropic liquid crystal sample, and the corrected isotropic absorbance A_{iso} obtained as in equation **3** of the main text. Water layer thickness d_w = 5 nm

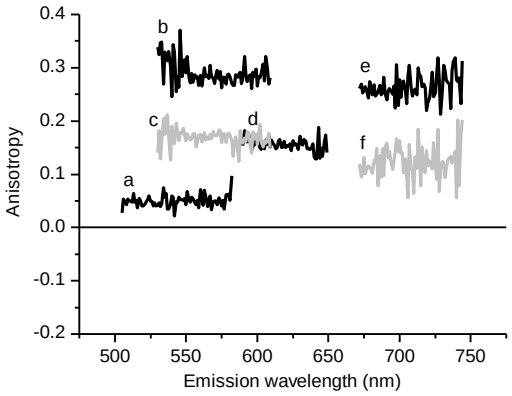

Figure S 2. Emission anisotropy of dyes both attached to DNA (black) and free (grey) in solution (90% buffer and 10% ethanol). Curves are denoted a. FAM-DNA b. Cy3-DNA c. Cy3 d. ROX-DNA e. Cy5-DNA f. Cy5.

Table S 1 Anisotropy and fluorescence lifetimes (**τ**) for indicated samples in aqueous solution (90 % buffer and 10 % EtOH)

Dye	r0	r	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	‹τ›[d] (ns)	Θ[e] (ns)
Cy3-DNA	0,386[a]	0,283	5,54	0,98	0,31	0,92	2,52
Cy5-DNA	0,39[b]	0,265	1,35	0,40	-	1,26	2,67
ROX-DNA	0,373[c]	0,155	4,95	-	-	-	3,53
FAM-DNA	0,373[c]	0,050	3,92	-	-	-	0,61
Cy3	0,386[a]	0,169	0,97	0,43	-	0,58	0,45
Cy5	0,39[b]	0,123	1,01	0,34	-	0,91	0,42

[a] From reference [1]. [b] From reference [2]. [c] From reference [3]. [d] Mean lifetime $\langle\tau\rangle = \sum_i \alpha_i\tau_i^2/\sum_i \alpha_i\tau_i$. [e] Rotational correlation time $\Theta = \tau/(r_0/r - 1)$ [4].

References

1. Sanborn, M.E., B.K. Connolly, K. Gurunathan, and M. Levitus, *Fluorescence properties and photophysics of the sulfoindocyanine Cy3 linked covalently to DNA.* J. Phys. Chem. B, 2007. **111**(37): p. 11064-11074.

2. Yasuda, R., T. Masaike, K. Adachi, H. Noji, H. Itoh, and K. Kinosita, *The ATP-waiting conformation of rotating F1-ATPase revealed by single-pair fluorescence resonance energy transfer.* Proc. Natl. Acad. Sci. U. S. A., 2003. **100**(16): p. 9314-9318.

3. Johansson, L.B.Å., *Limiting fluorescence anisotropies of perylene and xanthene derivatives.* J. Chem. Soc., Faraday Trans., 1990. **86**(12): p. 2103-2107.

4. Lakowicz, J.R., *Principles of fluorescence spectroscopy*. 3 ed. 2006, New York, NY, USA: Springer.