Supporting information

Formation of a charge transfer complex within a hydrophobic cavity in DNA

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General.

DNA oligonucleotides modified with deoxyribospacers (**dS**) or propyl linkers were prepared using a DNA synthesizer (ABI-3400) on a 1 μmol scale, and phosphoroamidite reagents and dSpacer CE phosphoramidite were obtained from Glen Research. The synthesized oligodeoxynucleotides were purified and characterized according to the general procedure. The naphthaldiimide with dimethyl amino groups (**NDI**) and dialkoxynaphthalene (**DAN**) were synthesized according to previous reports.[1,2] All reagents and solvents used for the organic synthesis and measurements are commercially available and were used as received.

Preparation and spectroscopic characterization of charge transfer complex in DNA

All sample solutions were prepared in a 20 mM Na phosphate buffer containing 100 mM NaCl adjusted to pH 7.0 and annealed prior to use. Temperature of the buffer solution containing double-stranded DNA was kept for 10 min at 80 ºC, and then gradually cooled to room temperature. After the addition of an aliquot of a highly concentrated **NDI** solution (1 mM) to the desired concentration, sample solutions were incubated for a few minutes until the absorbance became constant. The stock solution containing **DAN** (10 mM) was then added to the mixed solution of **NDI** and **DNA** to create a charge transfer complex. The UV/Vis absorption or circular dichroism (CD) spectra were obtained using a U-3000 (Hitachi) and a 62A-DS (Shimazu), respectively. Thermal denaturing experiments were carried out using a Bechman Coulter DU800 apparatus under the following conditions: 2.5 μM DNA, 2.5 μM **NDI** and 25 μM **DAN** in 20 mM Na phosphate buffer (pH 7.0), and a temperature gradient of 0.5 ºC/min in the temperature range of 10–80 ºC. The melting temperatures (T_m) of DNA were determined from the maximum of the first derivative of the melting curve at 260 nm.

Circular dichroism (CD) spectra of DNA with a **NDI**/**DAN** complex.

The CD spectra were examined for the complex formed in **S0** and **S2** (Figure S1). Both the **NDI**/**S0** and **NDI**/**S1** complexes gave a CD spectrum with a positive Cotton effect at around 280 nm and negative effect at 250 nm, showing that the B-type structure of DNA was maintained irrespective of the presence of the **dS**/**dS** pairs and **NDI**. **NDI**/**S0** showed a positive induced CD in the visible region and negative CD of less than 400 nm, which originated from the intercalated NDI.[3] Compared to **NDI**/**S0**, **NDI/S2** showed a much smaller induced CD signal, indicating the different local environment nearby **NDI** bound to the cavity within the DNA. The addition of **DAN** to the complex of **NDI**/**S2** resulted in a decrease in the CD bands, while no noticeable change was observed for **NDI**/**S0**. These comparisons of the CD bands between **S0** and **S2** support the formation of the CT complex between **NDI** and **DAN** in the cavity within the DNA.

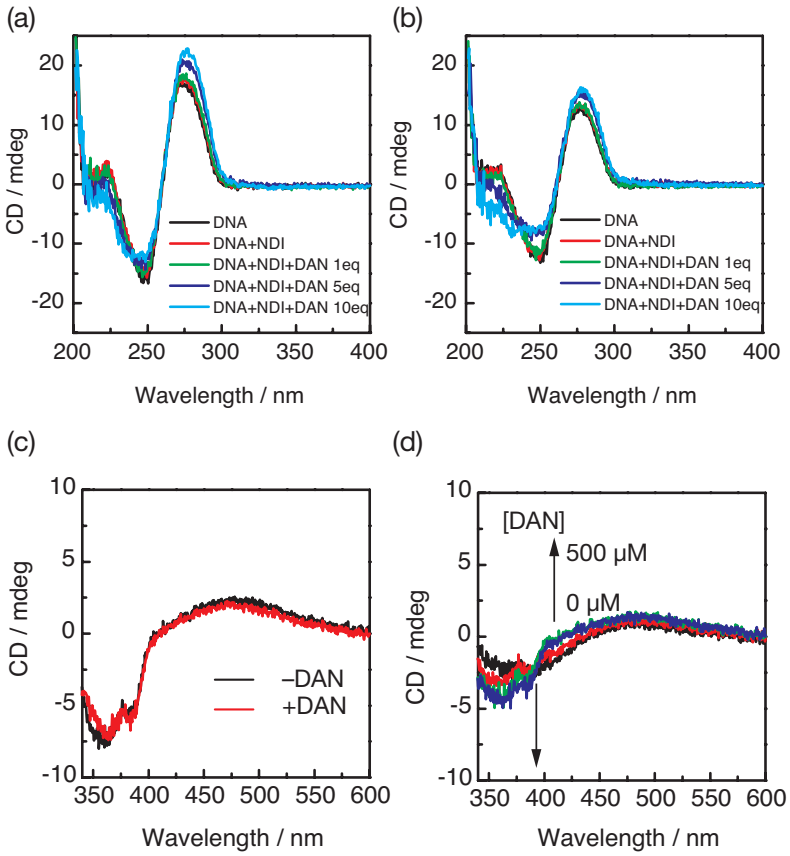

Figure S1. CD spectra of (a, c) **S0** and (b, d) **S2** after the addition of **NDI** and **DAN** (black: only DNA, red: DNA/**NDI**, green: 1 eq., blue: 5 eq, light blue:10 eq) in 20 mM Na phosphate buffer solution (pH 7.0) with 100 mM NaCl.

1. T. Takada, K. Kawai, X. Cai, A. Sugimoto, M. Fujitsuka, and T. Majima, *J. Am. Chem. Soc.*, 2004, **126**, 1125–1129.
2. A. Das and S. Ghosh, *Chem. Eur. J.*, 2010, **16**, 13622–13628.
3. S. F. Yen, E. J. Gabbay, and W. D. Wilson, *Biochemistry*, 1982, **21**, 2070–2076.