Effect of Oligomer Length on Vibrational Coupling and Energy Relaxation in Double-Stranded DNA

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Supporting Information

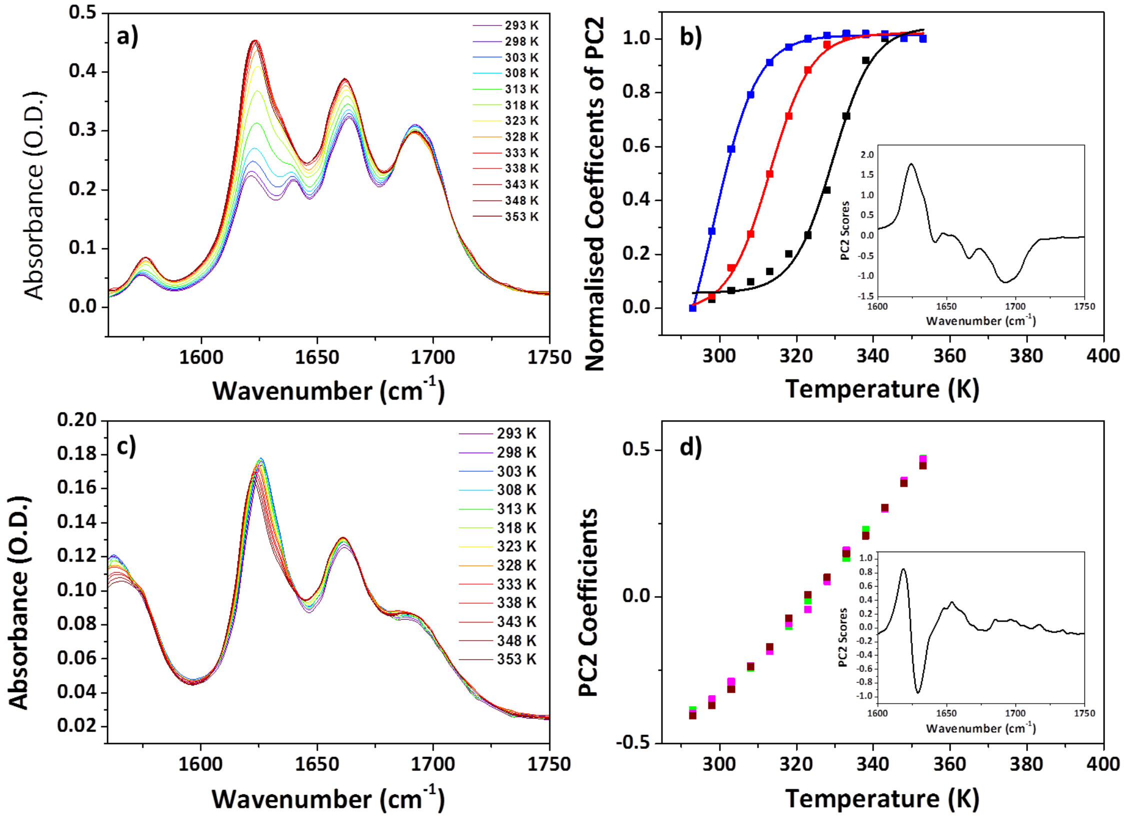

Figure S1. *a) Representative IR spectra (n = 10) as a function of temperature in the base region of the IR spectrum. b) Melting curves obtained from PCA analysis of base region IR absorption spectra. Solid lines show the results of fitting to Boltzmann sigmoidal functions for n = 15 (black), n = 10 (red) and n = 6 (blue) sequences. c) Representative IR spectra (n = 4) as a function of temperature in the base region of the IR spectrum. d) Melting curves obtained from PCA analysis for n = 4 (green), n = 2 (pink) n = 1 (brown) sequences. Insets to b) and d) show the spectral density of the temperature-dependent PC2 contributions referred to in the text. It should be noted that PCA returns coefficients that are of a comparable order for the two different processes observed for the n > 6 and n < 6 sequences. However the variance in the n ≥ 6 spectra (b) represented by PC2 (2-3%) is notably larger than the variance in the n ≤ 6 spectra (d) represented by PC2 (<1%).*

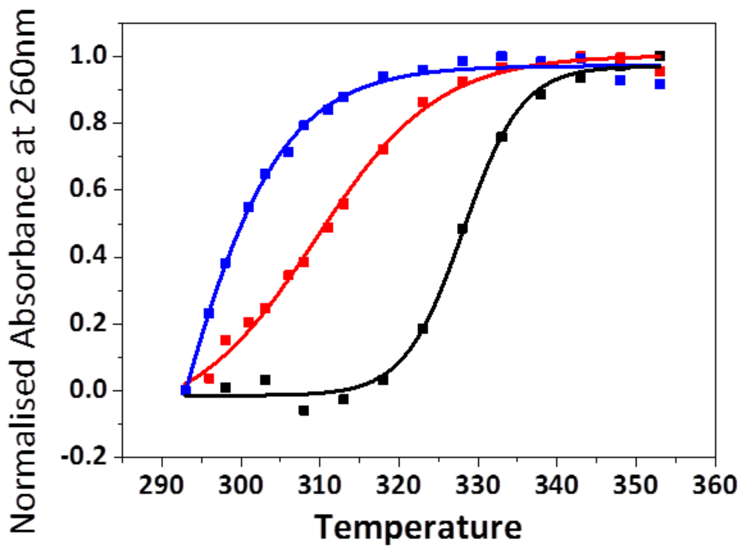

Figure S2. *– Normalised UV-Visible melting curves obtained for n = 15 (black), n = 10 (red) and n = 6 (blue) oligomers. Solid lines show the results of fitting the data to Boltzmann sigmoidal functions to extract the melting temperature (T_m) for each sequence. T_m values obtained were 328 ± 2 K, 309 ± 2 K and 290 ± 5 K for the n = 15, n = 10 and n = 6 sequences respectively. Due to the high concentrations required for IR measurements, UV-Visible experiments were performed at half the concentration of the respective IR samples (Table 1). Consequently, T_m values obtained from UV-Vis measurements are slightly lower than those obtained from the IR absorption analysis. No sigmoidal melting behavior was observed for n ≤ 4.*

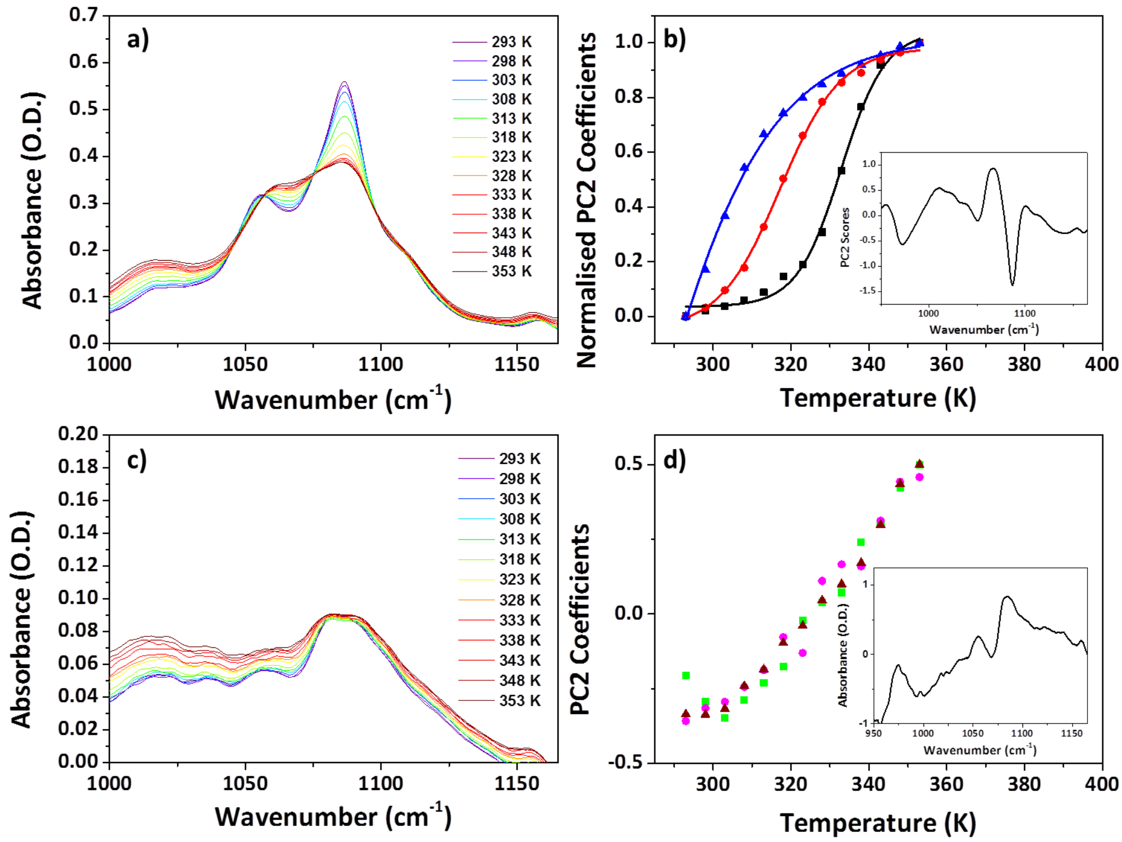

Figure S3. *a) IR absorption spectra (n = 6) and b) melting curves obtained from PCA analysis of IR absorption spectra obtained in the backbone region of the spectrum. Solid lines in b) show the results of fitting the data to a Boltzmann sigmoidal function for n = 15 (black), n = 10 (red) and n = 6 (blue) sequences. c) IR absorption spectra (n = 4) and d) melting curves obtained from PCA analysis for n = 4 (green), n = 2 (pink) n = 1 (brown) sequences. Insets to b) and d) show spectral density distributions of the temperature-dependent PC2 contributions referred to in the text.*

Excited Base Mode	Average Dynamics (fs)							
	L_2 T_r	L_2 T_d	P_2 T_r	P_2 T_d	Rib_2 T_r	Rib_2 T_d	Rib_1 T_r	Rib_1 T_d
AT_{2S}	620 ±300	>5000	490 ± 100	6200 ± 1600	530 ± 100	430 ± 30	-	1180 ± 200
AT_{4S}	850 ± 130	>5000	490 ± 140	3760 ± 1000	440 ± 50	600 ± 30	-	1160 ± 100
AT_R	-	>5000	-	-	420 ± 60	1050 ± 200	-	1630 ± 70

Table S1. *Summary of the vibrational relaxation dynamics (both rising, T_r, and decaying, T_d) obtained for the backbone vibrational modes for the DNA sequences at 293 K. The long decay (T_d) observed for the kinetics of the L_2 off-diagonal features did not fit well to an exponential. However a fixed 5000 fs exponential decay function reproduced the data well and indicates that the timescale of this decay is at least of the order of 5000 fs. The rise times (T_r) presented for the P_2 off-diagonal is the rise observed for the negative features (blue arrow Fig.7.) while the decay times (T_d) are the decays of the narrow positive features (red arrow Fig.7.). T_r presented for the Rib_2 off-diagonal is the rise observed for the negative features while the decay times (T_d) are the decays of the positive features. T_d values presented for the Rib_1 mode are the decays of the positive features (orange arrow Fig.7.).*

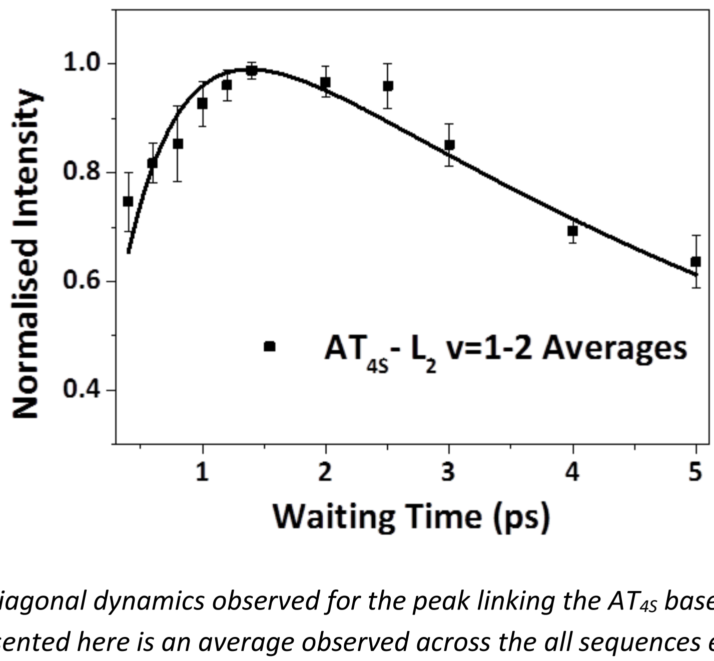

Figure S4. *Off-diagonal dynamics observed for the peak linking the AT_{4S} base modes to the L_2 mode. The trace presented here is an average observed across the all sequences except n = 1 at 293 K.*