Electronic Supplementary Information (ESI)

Electronic Coupling Between Base Pair Dimers of LNA:DNA Oligomers

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Formalism used in the manuscript

For convenience of the reader, we summarize below the essentials of the FCD method .[1]

Within the framework of the FCD method,[1] the following formula is used for calculation of the coupling matrix elements between the donor and the acceptor state:

$$H_{DA} = \frac{(E_2 - E_1)|\Delta q_{12}|}{\sqrt{(\Delta q_1 - \Delta q_2)^2 + 4\Delta q_{12}^2}}, \qquad \text{(S1)}$$

where Δq_1 and Δq_2 are the donor-acceptor charge differences in the corresponding adiabatic states within a two-state model, Δq_{12} is the off-diagonal term, and E_2-E_1 is the adiabatic splitting between donor and acceptor states. E_2-E_1 is estimated within Koopmans' approximation as the difference between the two highest occupied molecular orbitals (HOMO and HOMO-1) in the closed-shell neutral base-pair dimer. The dimer wavefunctions are calculated with RHF/6-31G*. Fragment charge differences (Δq_{mn}) are based on Mulliken-type fragment charges (q_{mn}):

$$q_{mn}(F) = \frac{1}{2}\left[\sum_{i\in F} C_{i,HOMO+1-m} \sum_{j=1}^{M} C_{j,HOMO+1-n} S_{ij} + \sum_{i\in F} C_{i,HOMO+1-n} \sum_{j=1}^{M} C_{j,HOMO+1-m} S_{ij}\right] \qquad (S2)$$

$$\Delta q_{mn} = q_{mn}(D) - q_{mn}(A) \qquad (S3)$$

F – D or A; m,n – 1,2; M – index for basis-set atomic orbitals; C_i and C_j – coefficients of the corresponding molecular orbitals, and S_{ij} – overlap integrals.

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1 A. A. Voityuk and N. Rösch, *J. Chem. Phys.*, 2002, **117**, 5607-5616.

Table S1: Average values $\left\langle H_{DA}^{2} \right\rangle$ (with standard deviations) of the FCD coupling elements, calculated for dimer **5-6** in **DNA-DNA** and **5_1LNA-DNA** from batches of different size, i.e. consisting of snapshots extracted at different time intervals. Time steps in ps, energies in eV^2.

Duplex	Time step	Structures in batch	$\left\langle H_{DA}^{2} \right\rangle$
5_1LNA-DNA	20	500	0.0095±0.0115
	14	714	0.0093±0.0109
	10	1000	0.0094±0.0113
	8	1250	0.0093±0.0111
	6	1666	0.0089±0.0105
	4	2500	0.0093±0.0110
	2	5000	0.0092±0.0109
DNA-DNA	20	500	0.0084±0.0111
	14	714	0.0087±0.0114
	10	1000	0.0084±0.0114
	8	1250	0.0081±0.0110
	6	1666	0.0084±0.0113
	4	2500	0.0083±0.0111
	2	5000	0.0083±0.0113

Table S2: p-values yielded by the double-sided t-tests on the difference between the calculated average H_{DA}^{2} values for pairs of identical dimers in different duplexes.

Duplex 1	Duplex 2	Dimer	p-value	Duplex 1	Duplex 2	Dimer	p-value
DNA-DNA	**2_1LNA-DNA**	**1-2**	6.6×10^{-2}	**DNA-DNA**	**3LNA-DNA**	**1-2**	2.2×10^{-2}
		2-3	4.0×10^{-5}			**2-3**	$<1\times10^{-5}$
		3-4	$<1\times10^{-5}$			**3-4**	$<1\times10^{-5}$
		4-5	4.1×10^{-3}			**4-5**	$<1\times10^{-5}$
		5-6	4.1×10^{-2}			**5-6**	1.0×10^{-5}
		6-7	4.2×10^{-1}			**6-7**	$<1\times10^{-5}$
		7-8	3.6×10^{-2}			**7-8**	4.1×10^{-2}
		8-9	1.2×10^{-3}			**8-9**	$<1\times10^{-5}$
DNA-DNA	**5_1LNA-DNA**	**1-2**	4.9×10^{-1}	**DNA-DNA**	**9LNA-DNA**	**1-2**	$<1\times10^{-5}$
		2-3	1.8×10^{-2}			**2-3**	$<1\times10^{-5}$
		3-4	$<1\times10^{-5}$			**3-4**	$<1\times10^{-5}$
		4-5	2.1×10^{-3}			**4-5**	$<1\times10^{-5}$
		5-6	1.1×10^{-1}			**5-6**	$<1\times10^{-5}$
		6-7	6.5×10^{-2}			**6-7**	$<1\times10^{-5}$
		7-8	9.5×10^{-1}			**7-8**	$<1\times10^{-5}$
		8-9	5.0×10^{-4}			**8-9**	$<1\times10^{-5}$
DNA-DNA	**7_1LNA-DNA**	**1-2**	6.4×10^{-1}	**3LNA-DNA**	**9LNA-DNA**	**1-2**	$<1\times10^{-5}$
		2-3	5.7×10^{-2}			**2-3**	$<1\times10^{-5}$
		3-4	3.3×10^{-2}			**3-4**	$<1\times10^{-5}$
		4-5	1.1×10^{-1}			**4-5**	$<1\times10^{-5}$
		5-6	1.2×10^{-2}			**5-6**	$<1\times10^{-5}$
		6-7	6.0×10^{-1}			**6-7**	$<1\times10^{-5}$
		7-8	$<1\times10^{-5}$			**7-8**	$<1\times10^{-5}$
		8-9	$<1\times10^{-5}$			**8-9**	$<1\times10^{-5}$

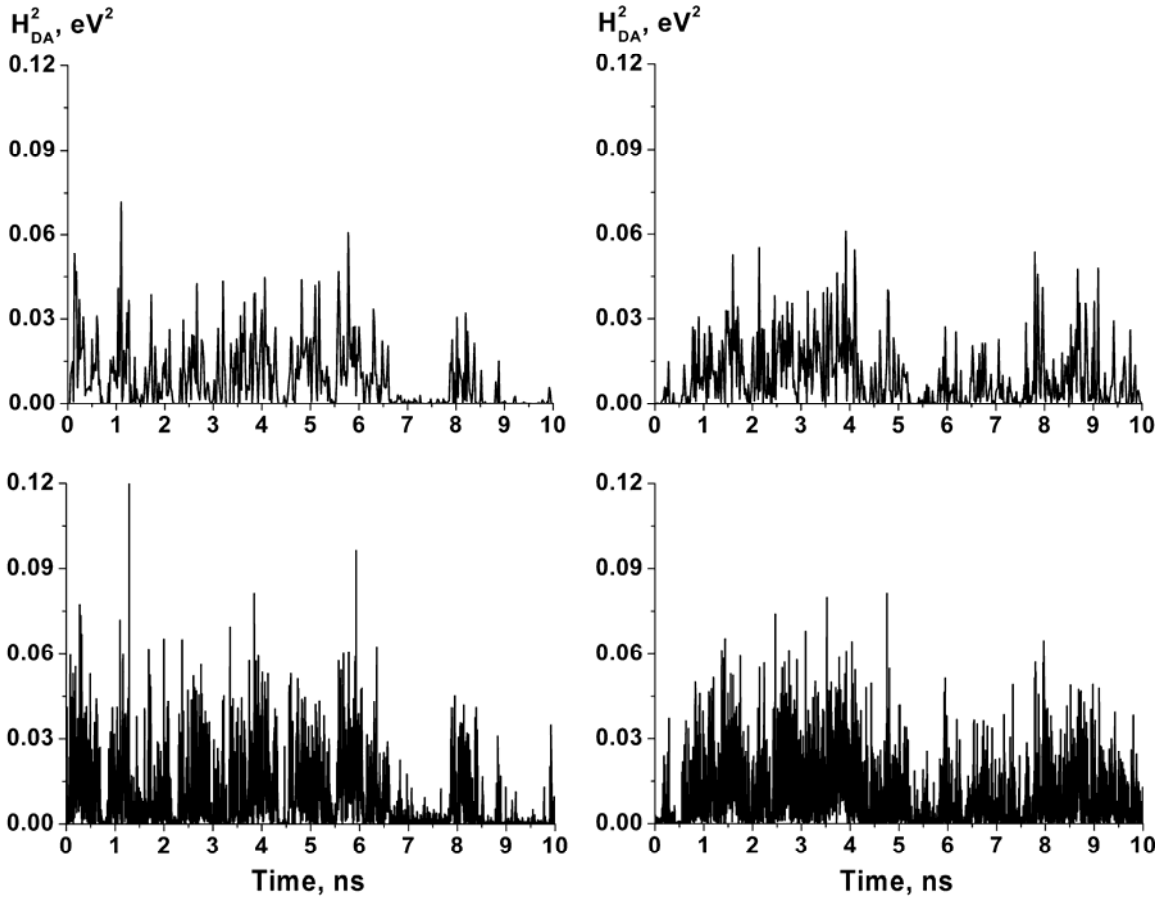

Figure S1: Trajectory evolution of H_{DA}^{2} calculated for dimer **5-6** in **DNA-DNA** (left panels) and **5_1LNA-DNA** (right panels) within snapshot sets of 500 (top panels) and 5000 (bottom panels) structures.

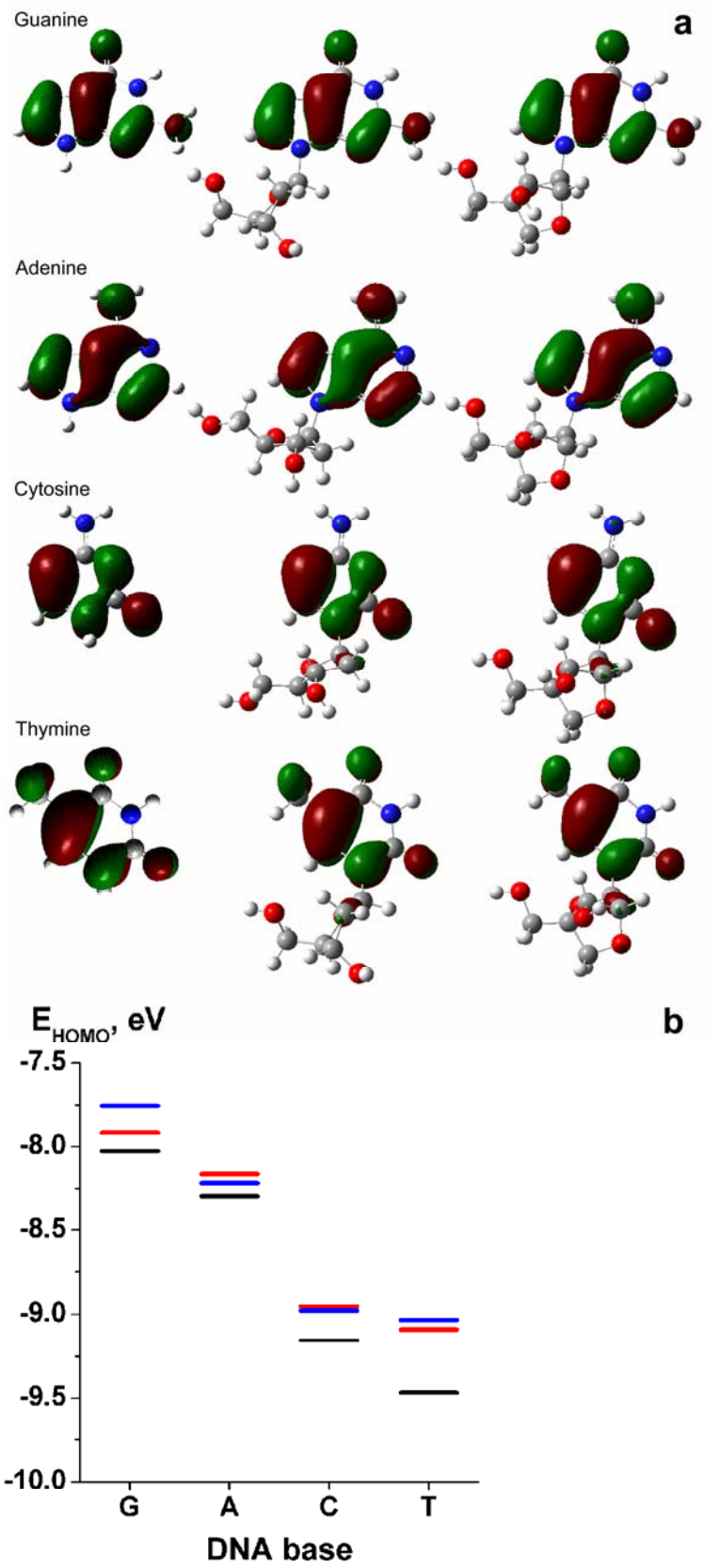

Figure S2: (a) Highest occupied molecular orbitals (HOMOs) of DNA bases without sugar (left panels), with DNA sugar (middle panels) and with LNA sugar (right panels); (b) energy diagram of HOMOs of DNA bases without sugar (black), with DNA sugar (blue) and with LNA sugar (red).

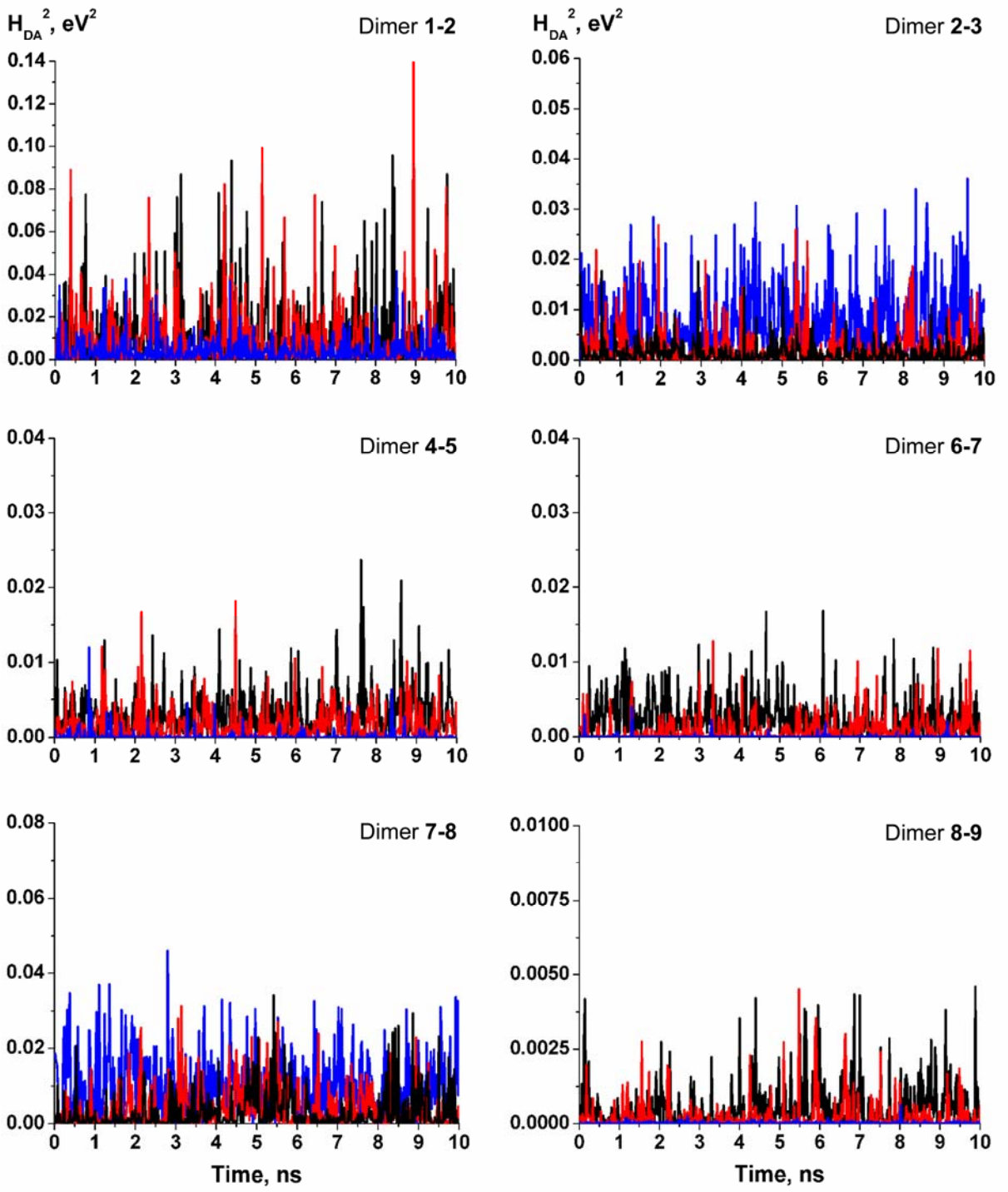

Figure S3: Squared values of the electronic coupling elements calculated for each snapshot of dimers **1-2** and **2-3** (top panels), **4-5** and **6-7** (middle panels), and **7-8** and **8-9** (bottom panels) from **DNA-DNA** (blue), **3LNA-DNA** (red) and **9LNA-DNA** (black).

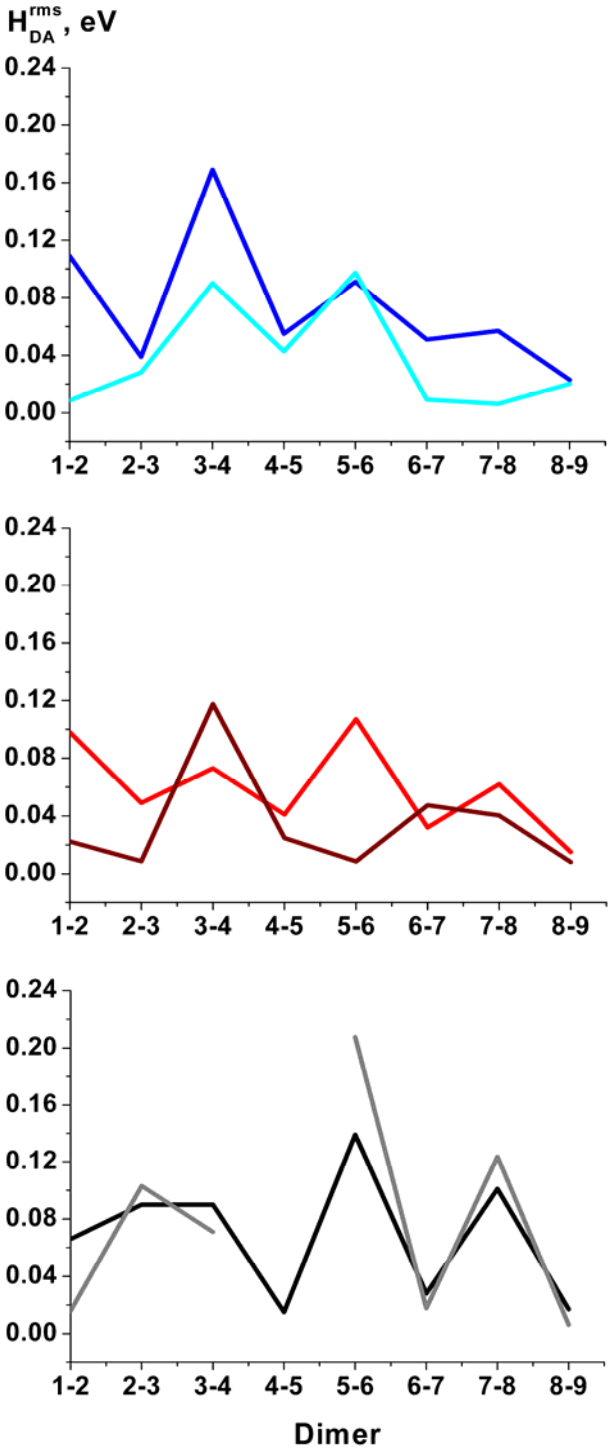

Figure S4: Comparison of rms values of coupling elements H_{DA} between dimers, from MD trajectory snapshots, with coupling elements of the corresponding average structures. Color code: **DNA-DNA** (MD) – blue, **DNA-DNA** (average) – cyan, **3LNA-DNA** (MD) – red, **3LNA-DNA** (average) – brown, **9LNA-DNA** (MD) – black, **9LNA-DNA** (average) – grey.