Supplement I

Table S1. Vertical excitation energies of nucleic acid bases: energies of monomers corrected for BSSE and trimers .

		A-DNA		B-DNA	
		E ($\pi\pi$)*	E (nπ)*	E ($\pi\pi$)*	E (nπ)*
CYT	cC, Cc[a]	4.639, 4.627	4.740, 4.765	4.590, 4.608	4.764, 4.789
	cCc	4.607	4.719	4.585	4.759
	CCC	4.536, 4.590, 4.659	4.629, 4.637, 4.811	4.407, 4.513, 4.524	4.492, 4.624, 4.660
THY	tT, Tt	5.249, 5.266	4.877, 4.878	5.191, 5.222	4.848, 4.856
	tTt	5.229	4.868	5.182	4.836
	TTT	5.052, 5.191, 5.258	4.657, 4.695, 4.834	5.079, 5.087, 5.230	4.719, 4.781, 4.807
URA	uU, Uu	5.672, 5.672	4.823, 4.822	5.624, 5.631	4.801, 4.800
	uUu	5.657	4.823	5.615	4.793
	UUU	5.601, 5.672, 5.751	4.647, 4.666, 4.786	5.491, 5.532, 5.649	4.694, 4.748, 4.754
ADE	aA, Aa	5.518, 5.515	5.404, 5.391	5.491, 5.494	5.402, 5.410
	aAa	5.502	5.372	5.476	5.386
	AAA	5.242, 5.327, 5.462	5.289, 5.366, 5.384	5.342, 5.435, 5.465	5.298, 5.361, 5.365

[a]C(c) corresponds to methylated cytosine, T(t) to methylated thymine, U(u) to uracil and A(a) to methylated adenine moieties. Capital letters denote the inclusion of nuclear charges, lower case characters describe only the consideration of the basis set without any nuclear charge

Supplement II

Details of various approximations for the transition Coulomb interaction

Using the (RI)-CC2 method and cc-pVDZ basis set, we have calculated the transition dipole moments for the lowest $\pi \rightarrow \pi^*$ transitions of methylated thymine, uracil, and methylated cytosine. Placing these transition dipoles in the centres of the aromatic rings, we were able to evaluate the point dipole–dipole splitting within the DNA structure.

Another interesting approximation is the extended-dipole model,[1,2] where the charge distribution is represented by two opposite charges separated by the distance L. The magnitude and the direction of the resulting dipole moment coincide with those of the point-dipole moment. In the multipole expansion of the extended dipole, only the $2^{(2n+1)}$ multipole moments are nonzero (with n being a natural number). However, the extended dipole model is not well-founded in theory, because not only all quadrupoles, hexadecapoles, etc. but also other multipole components not parallel to the dipole direction are neglected. It has been demonstrated that the extended-dipole model may become incorrect for certain twist angles between the neighbouring moieties[3].

We have tested an alternative method and used the multipole expansion of the transition-Coulombic interaction up to $1/R^5$ (R being the interchromophore separation), including the dipole–dipole, dipole–quadrupole, quadrupole–quadrupole and dipole–octupole terms.

The comparison of the transition dipole moments calculated using the (RI)-CC2 and MRCI methods is shown in Table S2.

Table S2. The calculated squares of the transition dipole moments and the separation of the point charges (L) in the extended dipole model

	$(\lvert \boldsymbol{\mu} \rvert^2)^a$		L^b
	(RI)-CC2	MRCI[c]	
methylated thymine	1.81	2.14	4.36
uracil	1.29	1.91	4.15
methylated cytosine	0.42	0.44	2.89

[a]in atomic units, [b]in Angstroms, [c]calculated at the MCSCF/MRCI level using the aug-cc-pVDZ basis set.

The values of the calculated transition dipoles markedly depend on the theoretical method, but their correspondence with their directions is better: the difference between the (RI)-CC2 and MRCI transition-dipole-moment directions is not greater than 4°, which has encouraged us to carry out a scaling: by multiplying all MRCI multipole moments by the same factor and slightly rotating them, we achieved identical transition dipoles for the two theoretical methods. It must be emphasised that although the values of transition dipole moments calculated using the MRCI method are expected to be more reliable, it is necessary to scale them to fit the (RI)-CC2 results so that it would be possible to analyse the total electronic coupling calculated using this method.

However, the L value determined by means of the MRCI-octupole-moment component parallel to the dipole direction (see Table S2) is of the order of the

interchromophore distance. This indicates that the convergence of the multipole expansion may be slow. Therefore, the truncation of the multipole interaction after $1/R^5$ is problematic.

In order to avoid the drawbacks discussed above, we have introduced a hybrid multipole model representing a combination of the truncated-multipole and the extended-dipole model. The results of the calculations of the transition Coulombic interaction energies using the various approximate models for the X-ray geometries are given in Table S3.

Table S3. Coulombic[a] interaction energies (in eV) calculated using selected approximations for the X-ray geometries

	point dipole	truncated multipole[b]	extended dipole	hybrid multipole
A-DNA				
methyl-thymine	0.0650	0.0572	0.0528	0.0506
uracil	0.0489	0.0350	0.0392	0.0289
methyl-cytosine	0.0217	0.0248	0.0168	0.0253
B-DNA				
methyl-thymine	0.0173	0.0481	0.0346	-0.0017
uracil	0.0147	0.0249	0.0247	-0.0115
methyl-cytosine	0.0207	0.0092	0.0161	0.0095

[a]Coulombic interaction energies are calculated for homodimers. [b]truncated up to $1/R^5$, where R is the distance between the bases

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3. G. D. Scholes. *J. Phys. Chem. B,* 1999, **103**, 2543.