EMN OPEN ACCESS WEEK
Energy Materials Nanotechnology
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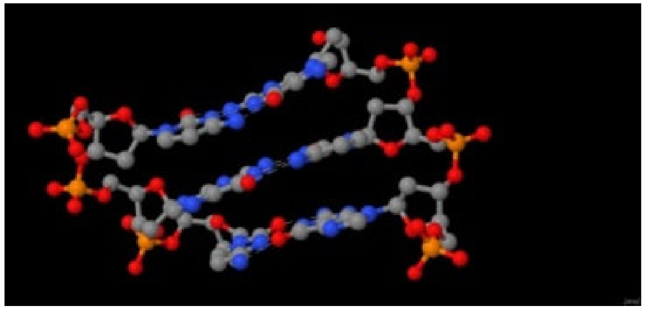

Systematic study of carrier transfer in DNA polymers

monomer = a DNA base-pair

carrier = electron (through LUMOs) or hole (through HOMOs)

monomers, dimers, trimers, tetramers, polymers

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Aim:

easily determine spatiotemporal evolution of electrons or holes along a *N* base-pair DNA segment

Important for:

nanotechnology (molecular wires, nanocircuits)

biology (carcinogenesis, mutagenesis, damage, repair)

monomer = a DNA base-pair

systematic study of carrier transfer along

all possible dimers, all possible trimers, and

characteristic polymers, including segments taken from experiments

Physical quantities defined:

Periodic cases (period T):

maximum transfer percentage p ,   pure maximum transfer rate p/T

All cases (charge transfer distance d):

pure mean transfer rate $k = \dfrac{\left\langle \left| A_N(t) \right|^2 \right\rangle}{t_{Nmean}}$,   speed $u = k\,d$

Introduction to DNA

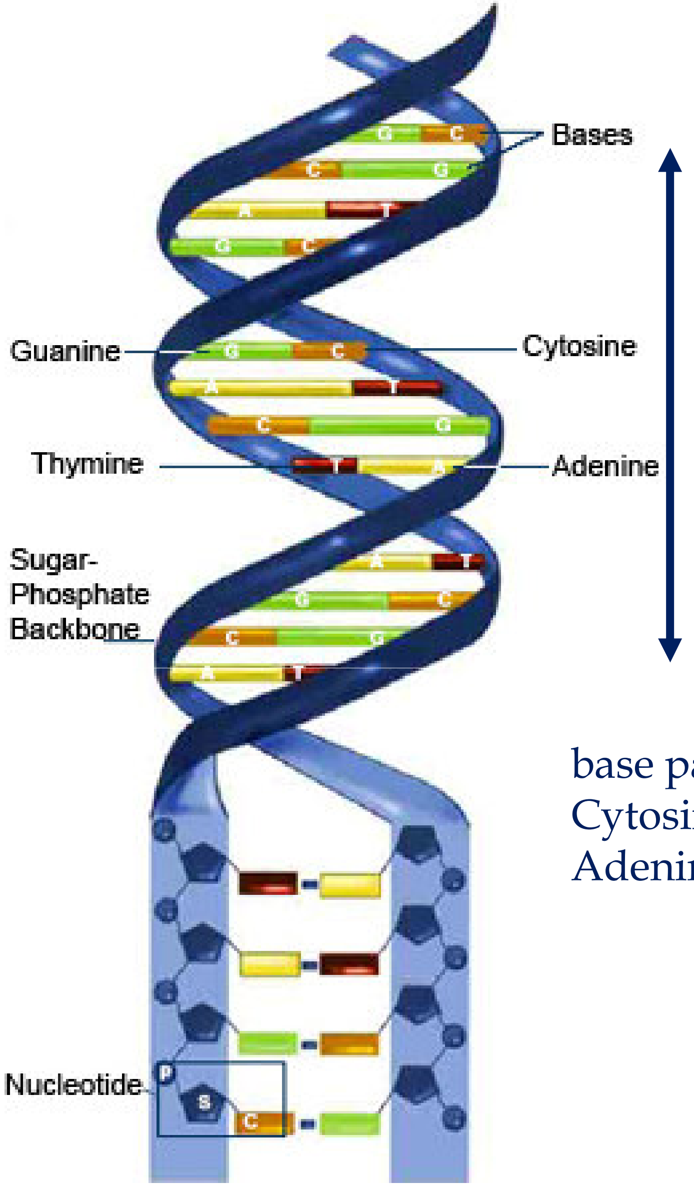
Charge transfer in DNA

Results for dimers

Results for trimers

Greater sequences

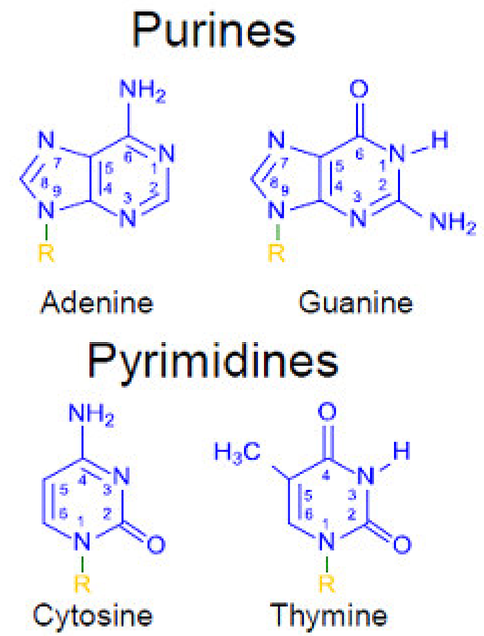
Introduction to DNA



base pair separation
~ 3.4 Å

helix step ~ 34 Å

base pairs:
Cytosine <3 H bonds> Guanine
Adenine <2 H bonds> Thymine



Charge transfer in DNA

From Schrödinger equation to a Tight-Binding System of Differential Equations

Description at the base-pair level

Starting from the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\Psi_{H/L}^{DNA}}{\partial t} = \hat{H}^{DNA}\Psi_{H/L}^{DNA}$$

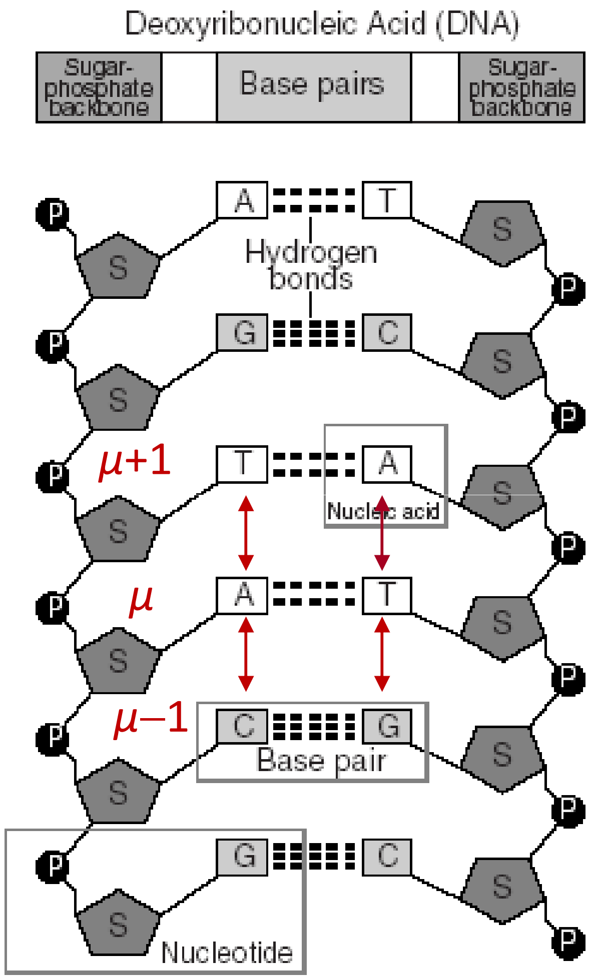
We analyze the DNA wavefunction into the bp wavefunctions:

$$\Psi_{H/L}^{DNA}(\mathbf{r},t) = \sum_{\mu} A_{\mu}(t)\,\Psi_{H/L}^{bp(\mu)}(\mathbf{r})$$

$|A_{\mu}(t)|^2$ probability to find the carrier at base-pair μ

we find that the time evolution of the coefficients $A_{\mu}(t)$ obeys the following system of equations:

$$i\hbar\frac{dA_{\mu}}{dt} = E_{H/L}^{bp(\mu)}A_{\mu} + t_{H/L}^{bp(\mu,\mu-1)}A_{\mu-1} + t_{H/L}^{bp(\mu,\mu+1)}A_{\mu+1}$$



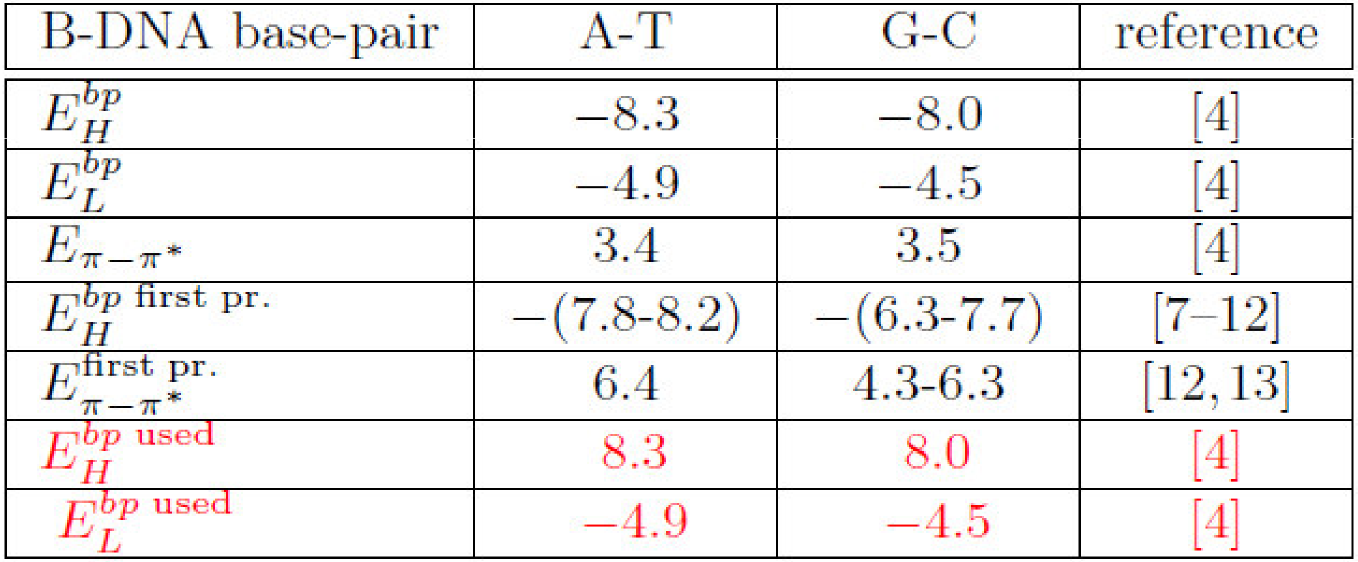
$E_{H/L}^{bp}$: on-site energies of the two possible base-pairs

$t_{H/L}^{bp}$: hopping parameters for all possible combinations of successive base-pairs

HOMO and LUMO on-site energies of the base-pairs

- Calculated by various authors
- Used for the solution of the tight-binding system of equations

$$i\hbar\frac{dA_\lambda}{dt} = \boxed{E^{bp(\lambda)}_{H/L}} A_\lambda + t^{bp(\lambda;\lambda-1)}_{H/L} A_{\lambda-1} + t^{bp(\lambda;\lambda+1)}_{H/L} A_{\lambda+1}$$



B-DNA base-pair	A-T	G-C	reference
E^{bp}_H	-8.3	-8.0	[4]
E^{bp}_L	-4.9	-4.5	[4]
$E_{\pi-\pi^*}$	3.4	3.5	[4]
$E^{bp\text{ first pr.}}_H$	$-$(7.8-8.2)	$-$(6.3-7.7)	[7–12]
$E^{\text{first pr.}}_{\pi-\pi^*}$	6.4	4.3-6.3	[12, 13]
$E^{bp\text{ used}}_H$	8.3	8.0	[4]
$E^{bp\text{ used}}_L$	-4.9	-4.5	[4]

All energies in eV

Hopping parameters between successive base-pairs

- Calculated by various authors
- Used for the solution of the tight-binding system of equations

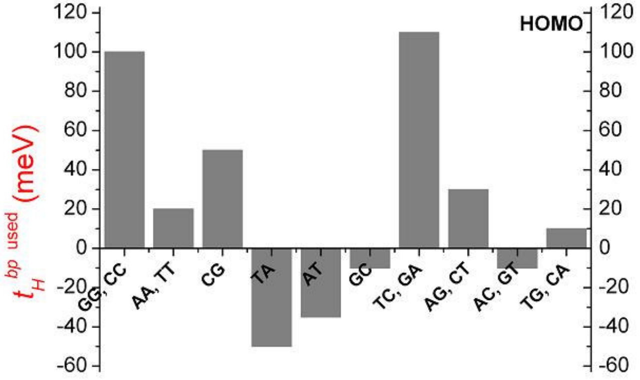
$$i\hbar\frac{dA_\lambda}{dt} = \boxed{E_{H/L}^{bp(\lambda)}}A_\lambda + \boxed{t_{H/L}^{bp(\lambda;\lambda-1)}}A_{\lambda-1} + \boxed{t_{H/L}^{bp(\lambda;\lambda+1)}}A_{\lambda+1}$$

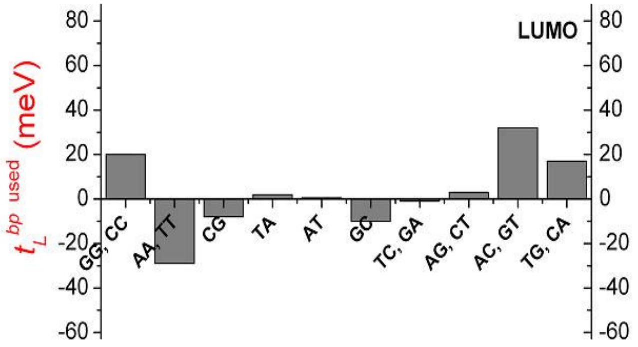
- Successive base-pairs ⇔ denoted by *YX*

$$\left\{\begin{array}{llcl} & 5' & & 3' \\ \lambda & Y & - & Y_{compl} \\ \lambda' & X & - & X_{compl} \\ & 3' & & 5'\ . \end{array}\right.$$

Base-pair sequence	t_H^{bp} [9]	$\lvert t_H^{bp}\rvert$ [19]	t_H^{bp} [8]	t_H^{bp} [20]	t_H^{bp} [21]	t_H^{bp} [22]	t_H^{bp} used	t_L^{bp} [9]	t_L^{bp} [8]	t_L^{bp} used
AA, TT	−8	26	−25	8-17	19(19)	22	20	−29	35	−29
AT	20	55			47(74)	37	−35	0.5		0.5
AG, CT	−5	25	−50		35(51)	43	30	3	35	3
AC, GT	2	26			25(38)	20	−10	32		32
TA	47	50			32(68)	52	−50	2		2
TG, CA	−4	27			11(11)	25	10	17		17
TC, GA	−79	122	−160		71(108)	60	110	−1	35	−1
GG, CC	−62	93	−140	75	72(101)	63	100	20	35	20
GC	1	22			20(32)	22	−10	−10		−10
CG	−44	78			51(84)	74	50	−8		−8

All hopping parameters in meV





General solution of the tight-binding system of equations

To solve the system:

$$i\hbar\frac{dA_\lambda}{dt} = E_{H/L}^{bp(\lambda)}A_\lambda + t_{H/L}^{bp(\lambda;\lambda-1)}A_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}A_{\lambda+1}$$

we define the vector matrix $\boldsymbol{x}(t) = \begin{bmatrix} A_1(t) \\ A_2(t) \\ \vdots \\ A_N(t) \end{bmatrix}$

Therefore:

$$\dot{\boldsymbol{x}}(t) = \widetilde{\boldsymbol{A}}\boldsymbol{x}(t), \qquad \widetilde{\boldsymbol{A}} = -\frac{i}{\hbar}\begin{bmatrix} E_{H/L}^{bp(1)} & t_{H/L}^{bp(1;2)} & 0 & \cdots & 0 & 0 & 0 \\ t_{H/L}^{bp(2;1)} & E_{H/L}^{bp(2)} & t_{H/L}^{bp(2;3)} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & t_{H/L}^{bp(N-1;N-2)} & E_{H/L}^{bp(N-1)} & t_{H/L}^{bp(N-1;N)} \\ 0 & 0 & 0 & \cdots & 0 & t_{H/L}^{bp(N;N-1)} & E_{H/L}^{bp(N)} \end{bmatrix}$$

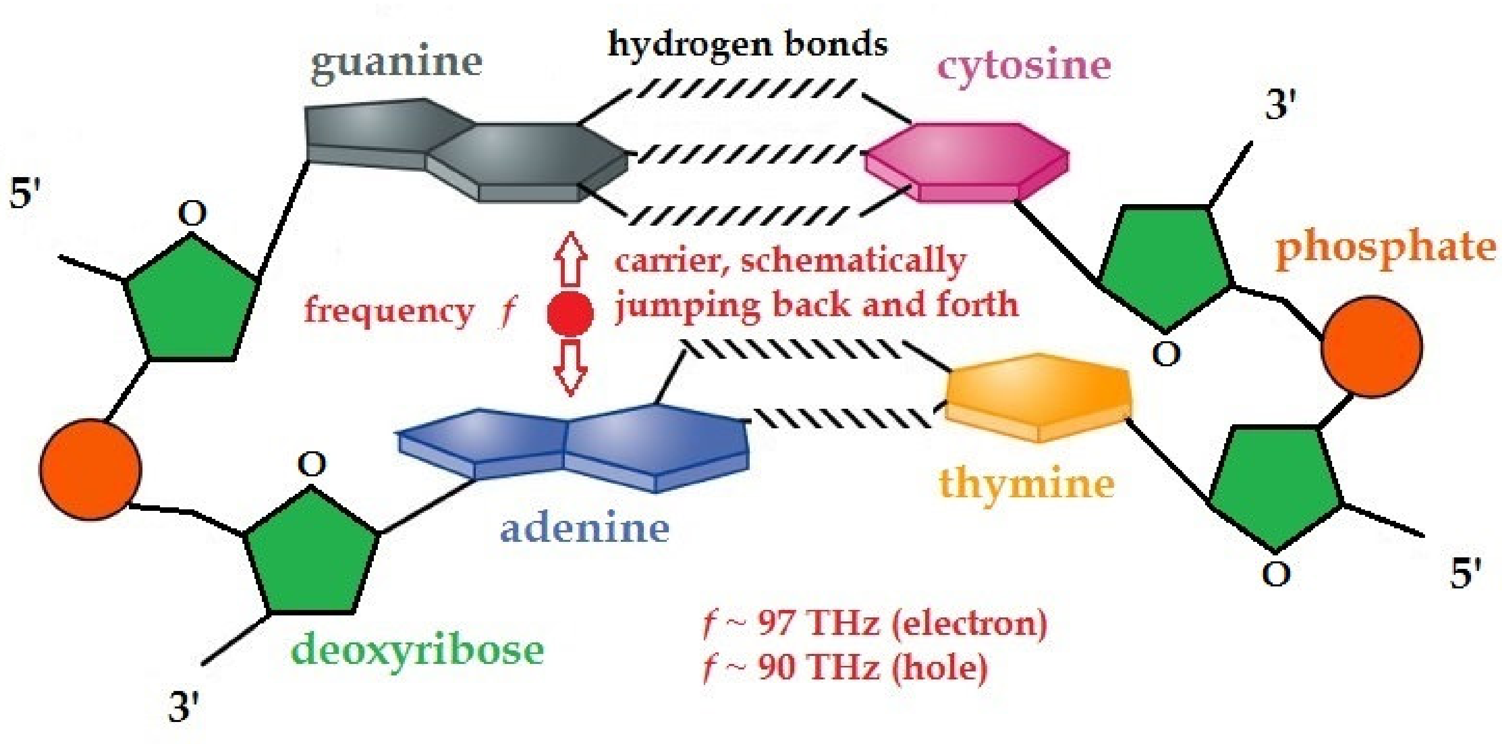
eigenvalue method, the general solution is:

$$\boldsymbol{x}(t) = \sum_{k=1}^{N} c_k \boldsymbol{v}_{\boldsymbol{k}} e^{-\frac{i}{\hbar}\lambda_k t}$$

$\boldsymbol{\upsilon}_k$: normalized (linearly independent) eigenvectors

λ_k: eigenvalues.

Results for dimers

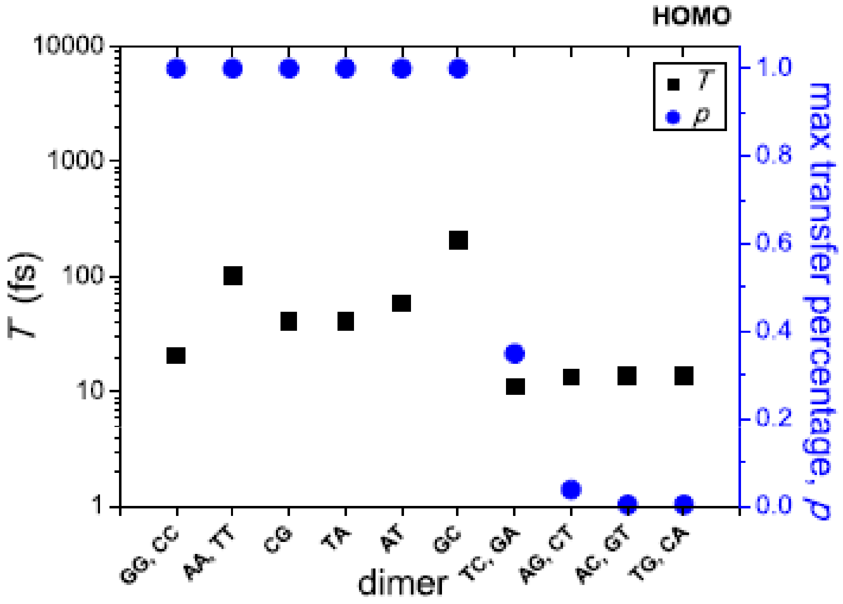


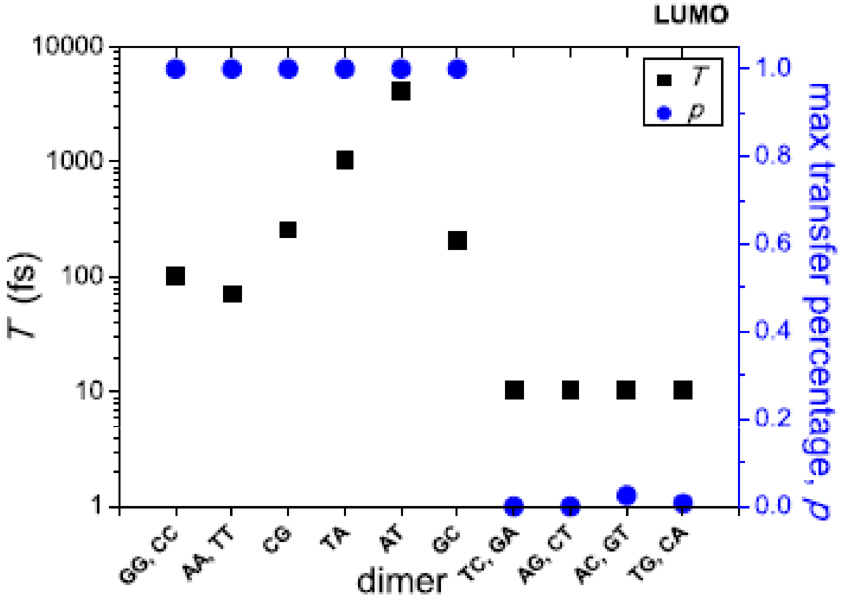
10 unique dimers, 6 made of identical monomers

periodic carrier transfer in all cases

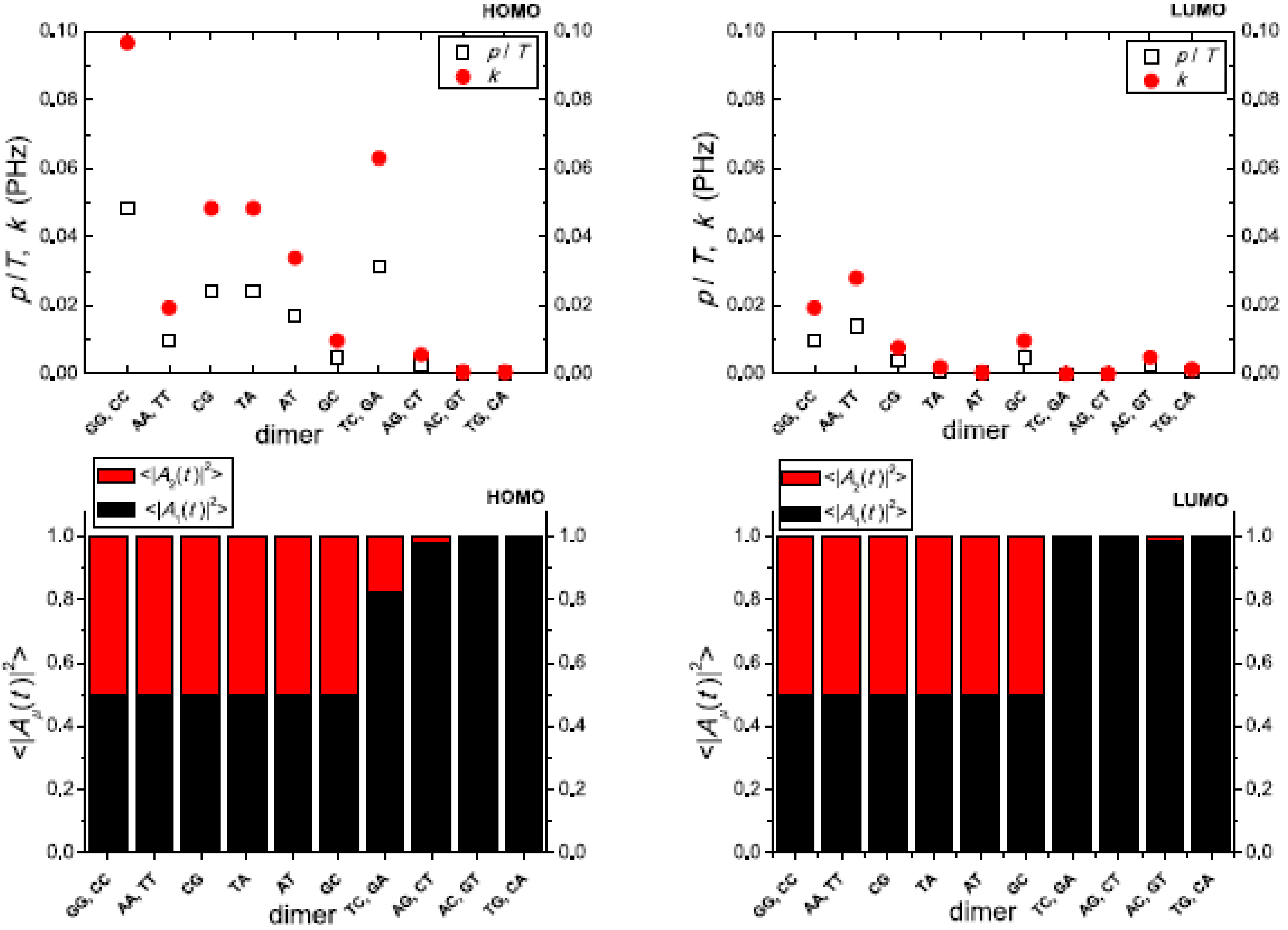
(equations, details . . . in our articles)

Periodic carrier transfer in base-pair dimers

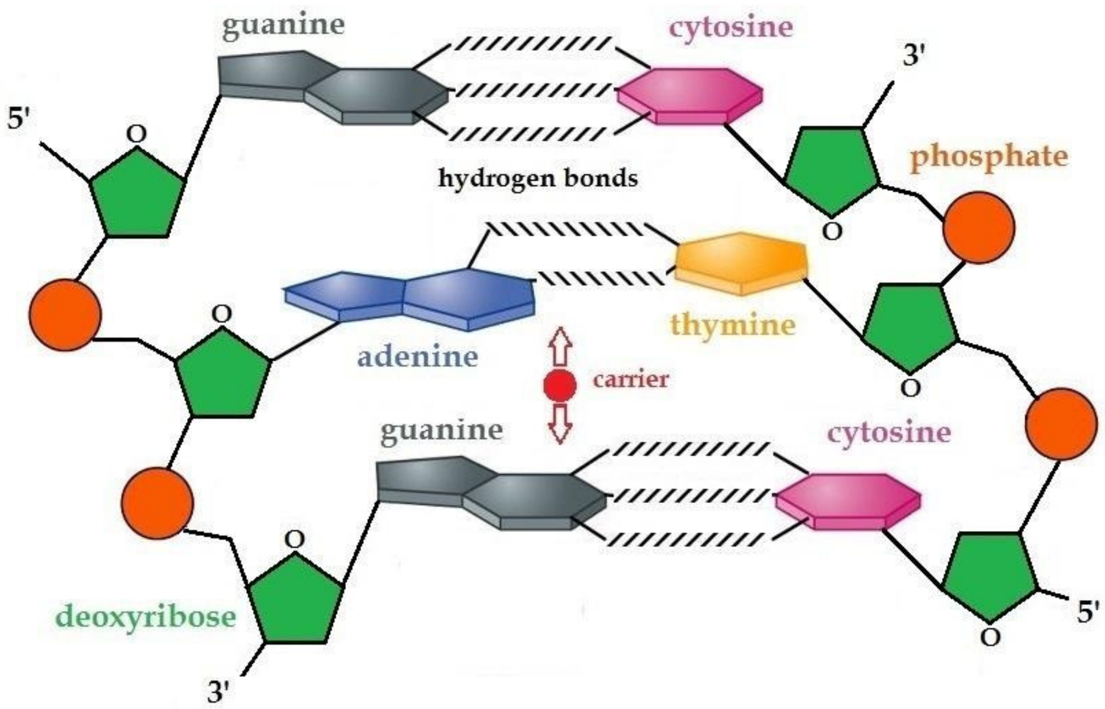




Periodic carrier transfer in base-pair dimers



Results for trimers



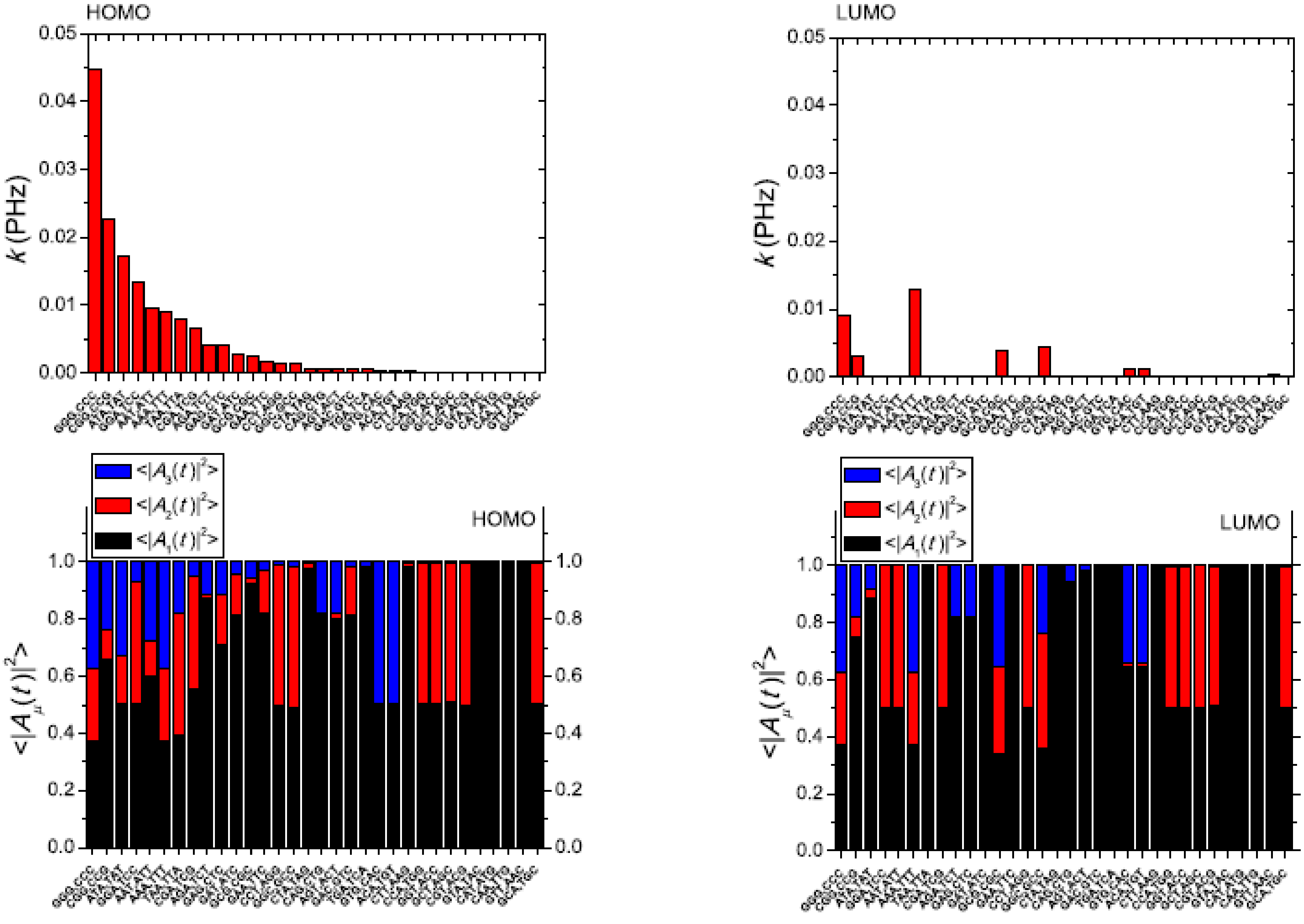
32 unique trimers, 8 made of identical monomers

periodic carrier transfer for trimers of identical monomers

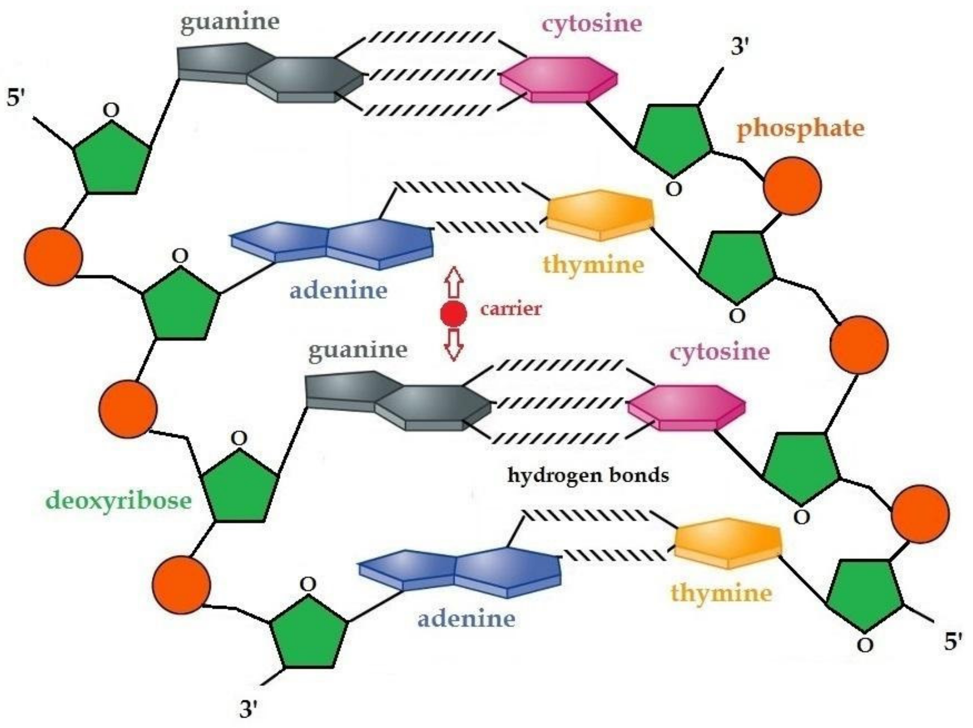
for trimers of different monomers the carrier movement may be non periodic

(equations, details . . . in our articles)

Pure mean transfer rate *k* & $<|A_\mu(t)|^2>$ for all possible trimers. Initially, we place the carrier in monomer 1.



Greater sequences, polymers



e.g. there are 136 unique tetramers, 20 made of identical monomers

increasing the number of monomers above 3
periodicity is (generally) lost

(equations, details . . . in our articles)

Polymers

pure mean transfer rate, *k*

Exponential fit	$k = k_0 \exp(-\beta d)$	inverse decay length β
Power-law fit	$k = k_0' N^{-\eta}$	*exponent* η

Computed values

$\beta \approx 0.2 - 2$ Å^{-1}, k_0 usually 10^{-2}-10^{-1} PHz, generally 10^{-4}-10 PHz

$\eta \approx 1.7$-17, k_0' usually 10^{-2}-10^{-1} PHz, generally 10^{-4}-10^{3} PHz

& probability to find the carrier at a particular monomer $<|A_i(t)|^2>$

Polymers transfer rates

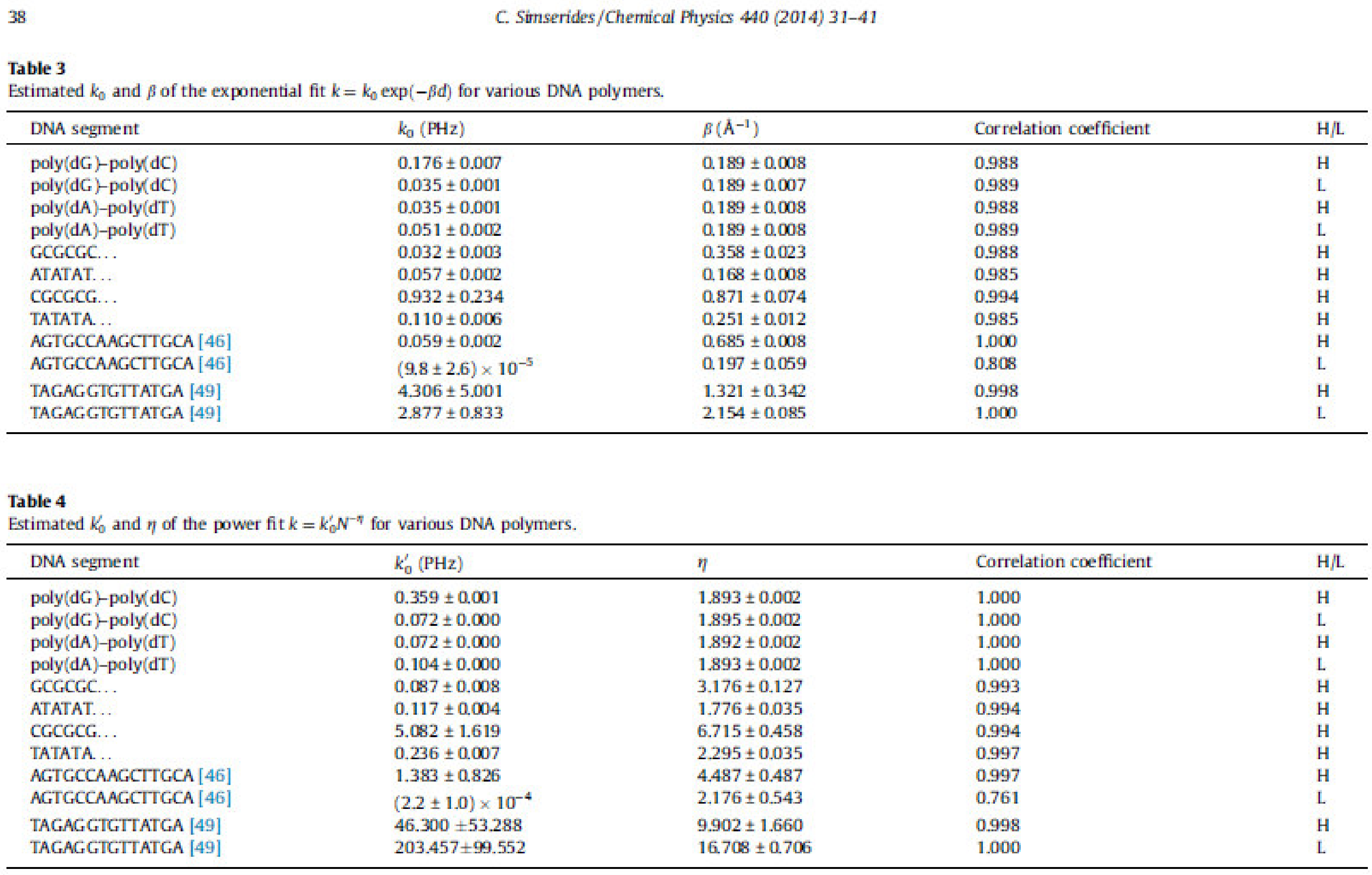


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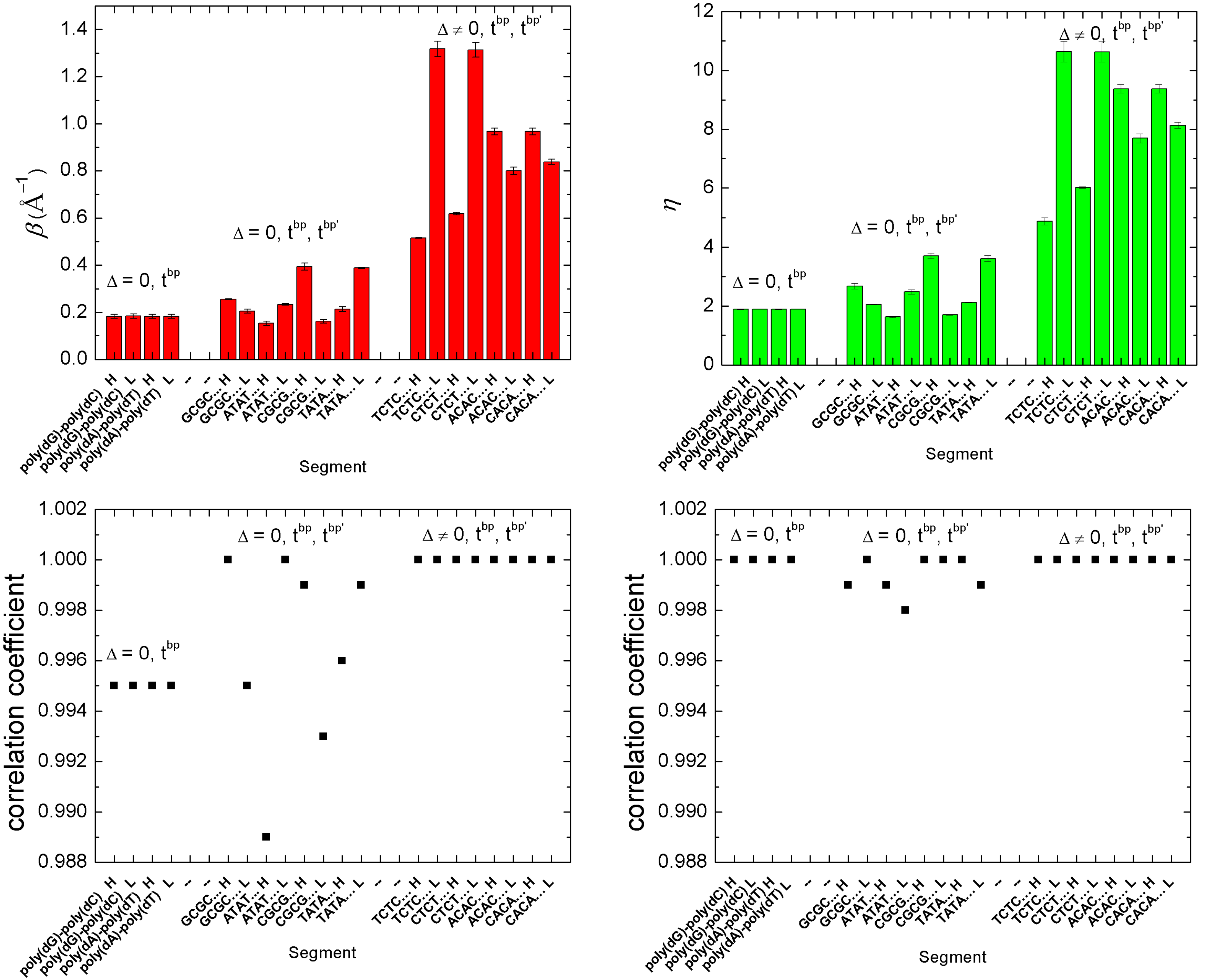
Table 3
Estimated k_0 and β of the exponential fit $k = k_0 \exp(-\beta d)$ for various DNA polymers.

DNA segment	k_0 (PHz)	β ($Å^{-1}$)	Correlation coefficient	H/L
poly(dG)–poly(dC)	0.176 ± 0.007	0.189 ± 0.008	0.988	H
poly(dG)–poly(dC)	0.035 ± 0.001	0.189 ± 0.007	0.989	L
poly(dA)–poly(dT)	0.035 ± 0.001	0.189 ± 0.008	0.988	H
poly(dA)–poly(dT)	0.051 ± 0.002	0.189 ± 0.008	0.989	L
GCGCGC...	0.032 ± 0.003	0.358 ± 0.023	0.988	H
ATATAT...	0.057 ± 0.002	0.168 ± 0.008	0.985	H
CGCGCG...	0.932 ± 0.234	0.871 ± 0.074	0.994	H
TATATA...	0.110 ± 0.006	0.251 ± 0.012	0.985	H
AGTGCCAAGCTTGCA [46]	0.059 ± 0.002	0.685 ± 0.008	1.000	H
AGTGCCAAGCTTGCA [46]	$(9.8 \pm 2.6) \times 10^{-5}$	0.197 ± 0.059	0.808	L
TAGAGGTGTTATGA [49]	4.306 ± 5.001	1.321 ± 0.342	0.998	H
TAGAGGTGTTATGA [49]	2.877 ± 0.833	2.154 ± 0.085	1.000	L

Table 4
Estimated k'_0 and η of the power fit $k = k'_0 N^{-\eta}$ for various DNA polymers.

DNA segment	k'_0 (PHz)	η	Correlation coefficient	H/L
poly(dG)–poly(dC)	0.359 ± 0.001	1.893 ± 0.002	1.000	H
poly(dG)–poly(dC)	0.072 ± 0.000	1.895 ± 0.002	1.000	L
poly(dA)–poly(dT)	0.072 ± 0.000	1.892 ± 0.002	1.000	H
poly(dA)–poly(dT)	0.104 ± 0.000	1.893 ± 0.002	1.000	L
GCGCGC...	0.087 ± 0.008	3.176 ± 0.127	0.993	H
ATATAT...	0.117 ± 0.004	1.776 ± 0.035	0.994	H
CGCGCG...	5.082 ± 1.619	6.715 ± 0.458	0.994	H
TATATA...	0.236 ± 0.007	2.295 ± 0.035	0.997	H
AGTGCCAAGCTTGCA [46]	1.383 ± 0.826	4.487 ± 0.487	0.997	H
AGTGCCAAGCTTGCA [46]	$(2.2 \pm 1.0) \times 10^{-4}$	2.176 ± 0.543	0.761	L
TAGAGGTGTTATGA [49]	46.300 ±53.288	9.902 ± 1.660	0.998	H
TAGAGGTGTTATGA [49]	203.457±99.552	16.708 ± 0.706	1.000	L


β (Å⁻¹)
η
correlation coefficient
Segment
Δ = 0, t^bp
Δ = 0, t^bp, t^bp'
Δ ≠ 0, t^bp, t^bp'
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
2
4
6
8
10
12
0.988
0.990
0.992
0.994
0.996
0.998
1.000
1.002
poly(dG)-poly(dC) H
poly(dG)-poly(dC) L
poly(dA)-poly(dT) H
poly(dA)-poly(dT) L
GCGC... H
GCGC... L
ATAT... H
ATAT... L
CGCG... H
CGCG... L
TATA... H
TATA... L
TCTC... H
TCTC... L
CTCT... H
CTCT... L
ACAC... H
ACAC... L
CACA... H
CACA... L

poly(dG)-
poly(dC)

Edge Group = first and last monomer

Middle Group = rest monomers

total probability
at Edge Group & Middle Group

probability
at each member of Groups

pure mean transfer rate
***k*(*d*)**

speed
$u = k\,d$

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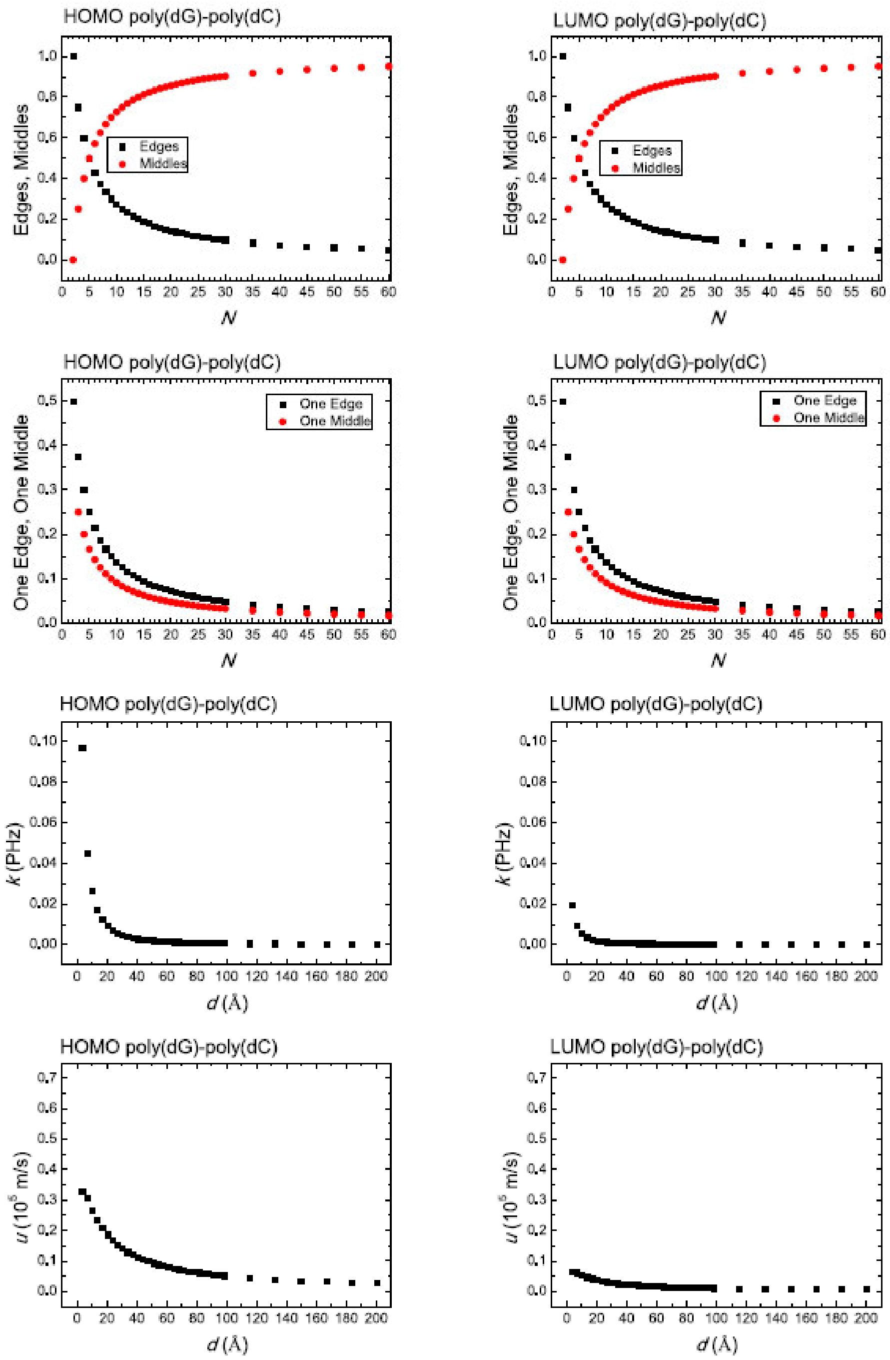
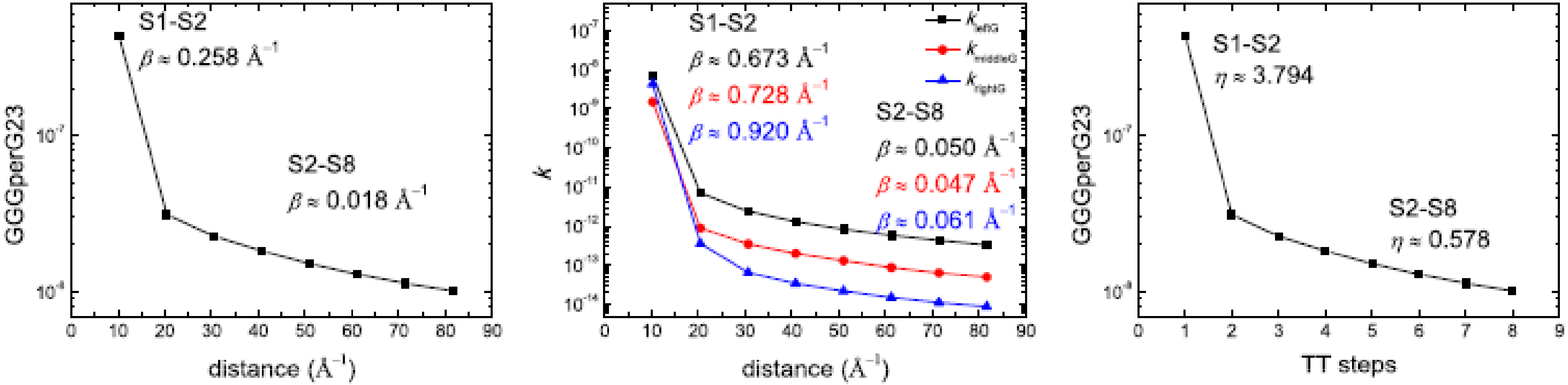


e.g. comparison with the experiment
[48] B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, M.E. Michel-Beyerle, Angew. Chem. Int. Ed. 38 (1999) 996



Hole transfer in ACGCACGTCGCATAATATTACG [bridge] GGGTATTATATTACGC.
The [bridge] is made up of TT dimers separated by G monomers.

Conclusions

A handy method to examine the charge transfer in DNA segments.

. . . illustrates the extent a specific DNA segment can serve as a medium for charge transfer.

The temporal and spatial evolution of electrons or holes along a N base-pair DNA segment can be determined, solving a system of N coupled differential equations.

As input one needs the relevant ***on-site energies*** of the base-pairs and the ***hopping parameters*** between successive base-pairs.

The method can be applied to any DNA segment.

Conclusions

The method has been applied here (either for electrons or holes) to

all possible dimers,
all possible trimers,
various polymers,
experimentally relevant segments

The results were compared with results obtained by other workers.

Useful physical quantities defined & calculated

maximum transfer percentage	p	(periodic cases)
pure maximum transfer rate	p/T	(periodic cases)
pure mean transfer rate	k	(all cases)
speed of charge transfer	$u = kd$	(all cases)

where d is the charge transfer distance.

The end

Thank you !

Related Work

[1] C. Simserides, Chemical Physics **440** (2014) 31

[2] K. Lambropoulos, K. Kaklamanis, G. Georgiadis, C. Simserides, Annalen der Physik (Berlin) **526** (2014) 249

[3] L.G.D. Hawke, G. Kalosakas, C. Simserides, Eur. Phys. J. E **32** (2010) 291; ibid.**34** (2011) 118