IPS-2000

Overview Lecture

Photoinduced Electron Transfer and Charge Transport in Biopolymers

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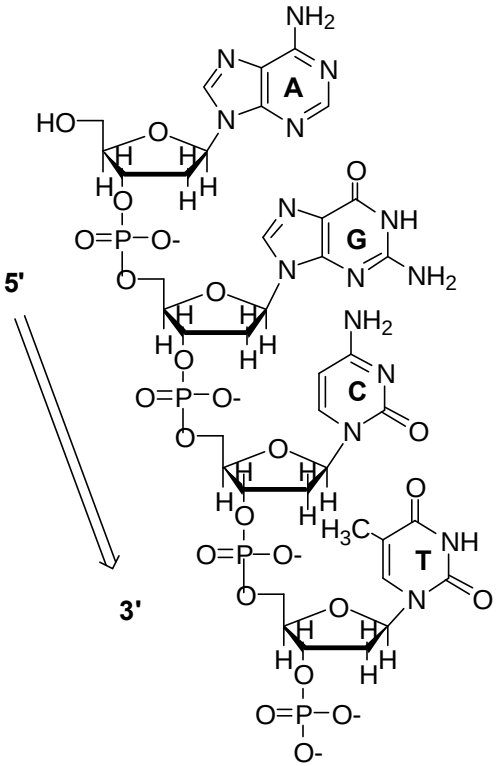
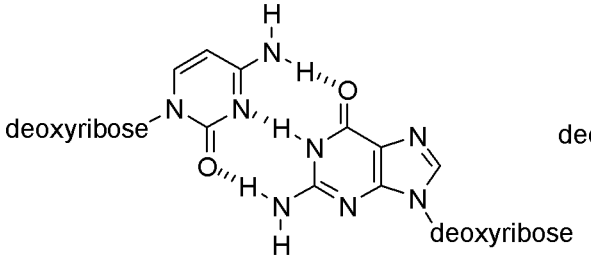
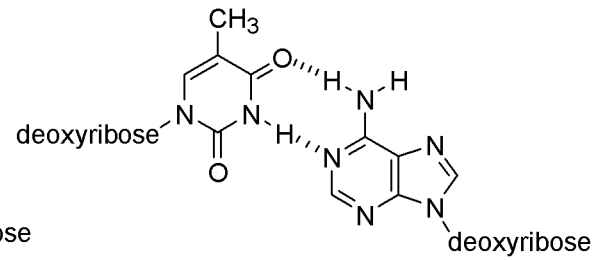

5'
3'
A
G
C
T


deoxyribose
deoxyribose


deoxyribose
deoxyribose

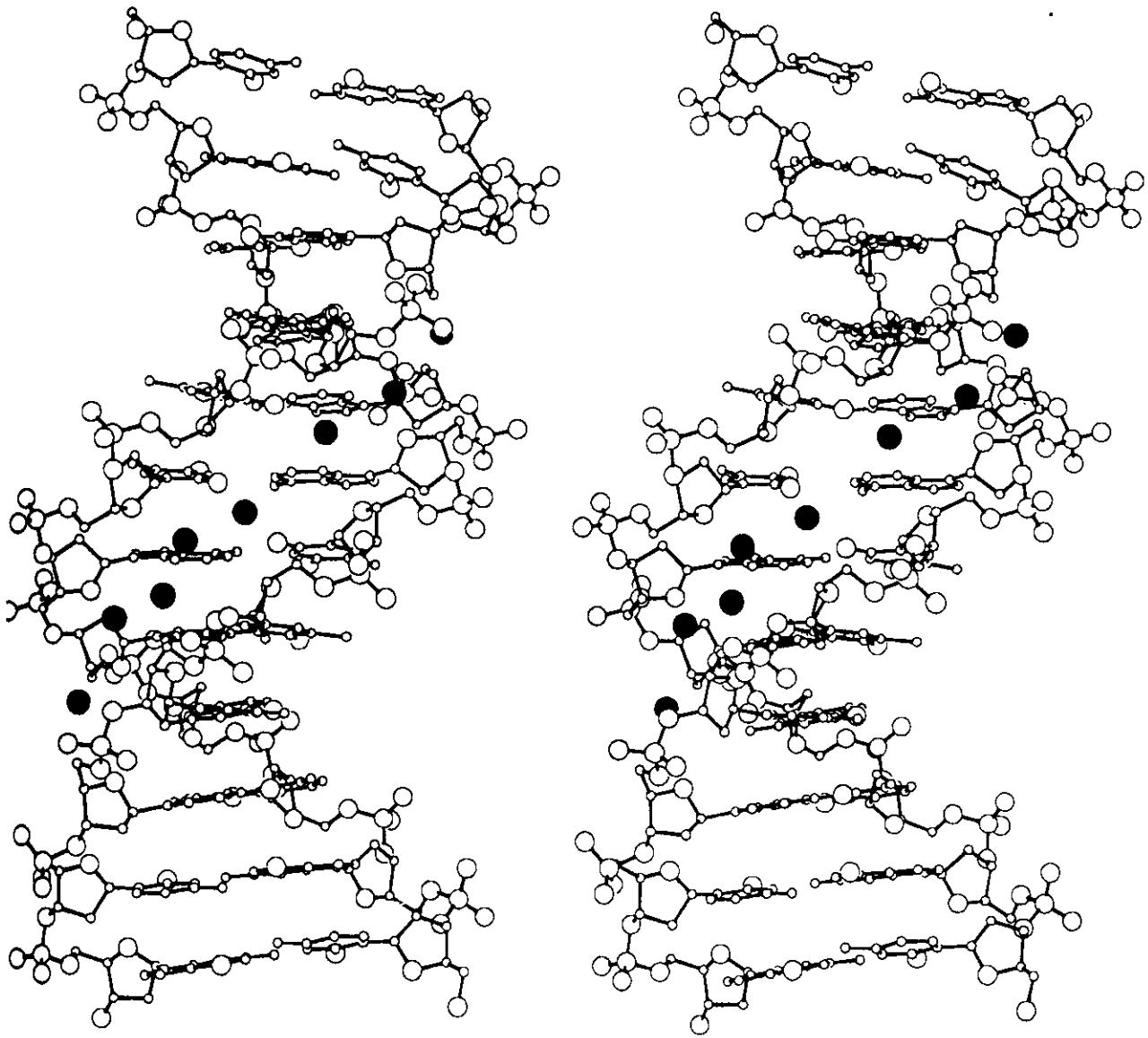


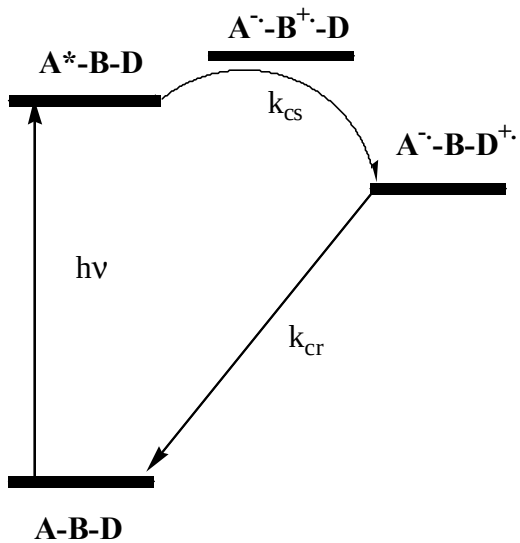
Figure 4-14. The crystal structure of the dodecamer d(CGCGAATTCGCG). This is stereoscopic ball-and-stick representation with water molecules in the minor groove shown as black circles.

Why study electron transfer processes in DNA??

- “oxidative stress” ⇒ strand cleavage ⇒ mutagenesis ⇒ cell death
- damage by high energy ionizing radiation
- photorepair of T-T dimers - undoing the damage caused by light
- molecular electronics
- scientific curiosity
  - o mechanisms of charge transfer in a π-stacked systems
  - o dynamics of charge separation, charge recombination and charge transport
  - o mechanism and selectivity of strand cleavage

Two Possible Mechanisms for Charge Transfer in DNA

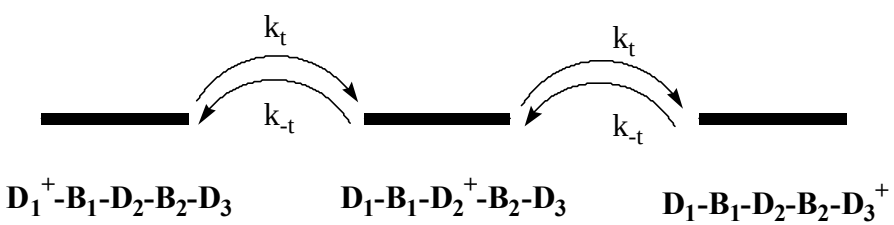
(a) Bridge-Mediated Superexchange



$$k_{cs} = k_o e^{-bR}$$

$$b = 0.1\text{-}1.4$$

(b) Hole Hopping



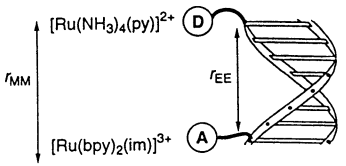
$$k_{hop} = k_o N^{-n}$$

$$n = 1 - 2$$

Three Different Types Of DNA Electron Transfer Experiments

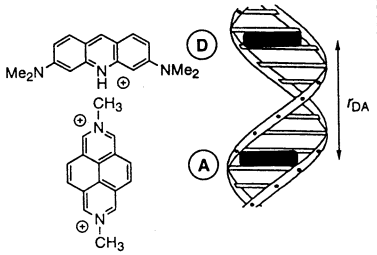
- $k_{et} = A\exp(-\beta r)$

Meade, T. J.; Kayyem, J. F. *Angew. Chem. Int. Edn. Engl.* **1995**, *34*, 352



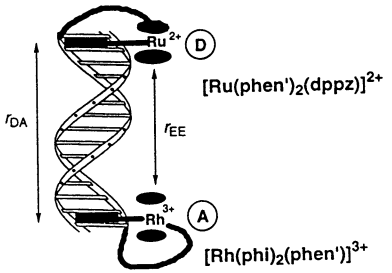
- 8–mer; covalently linked non-intercalating transition metal donor and acceptor
- $\Delta G^o = -0.70$ eV
- $k_{et} = 1.6 \times 10^6\ s^{-1}$
- $r = 21$ Å (MM); 13 Å (EE)
- **DNA is protein–like**

Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1992** *114*, 3656



- organic donor and acceptor randomly intercalated
- $\Delta G^o = -0.67$ eV
- $k_{et} = 1.3 \times 10^7\ s^{-1}$
- $r = 17$ Å (DA)
- $\beta = 0.9$ Å^{-1}
- **DNA is protein–like**

Barton, J. K. *et al.* *Science* **1993**, *262*, 1025



- 15-mer; covalently linked intercalating transition metal donor and acceptor
- $\Delta G^o = -0.75$ eV
- $k_{et} \geq 3.0 \times 10^9\ s^{-1}$
- $r = 41$ Å (DA); 26 Å (EE)
- $\beta < 0.2$ Å^{-1}
- **DNA is a molecular wire?**

DNA ET rates 1 2.0 24/6/98 6:58 AM

Hole Hopping

k_{rel} = 1.0 — CAACCC 5' / *GTTGGG 3'

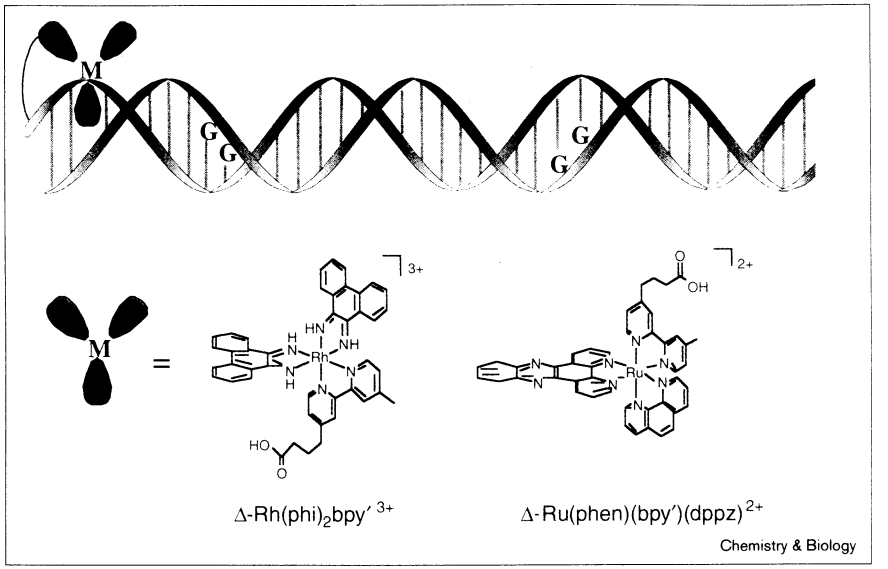
0.31 — CAACAACCC 5' / *GTTGTTGGG 3'

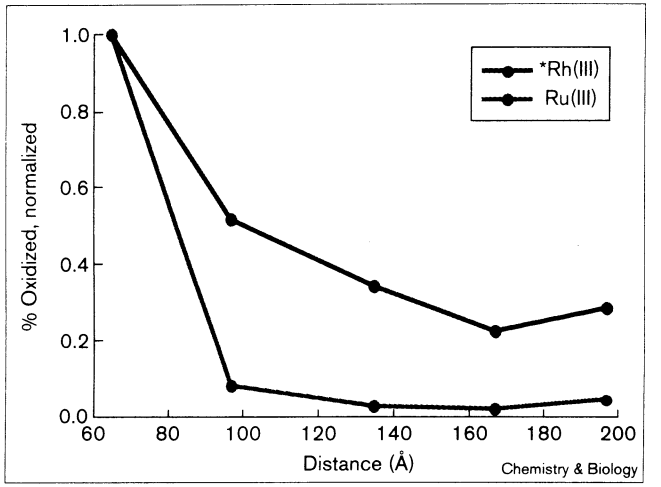
0.22 — CAACAACAACCC 5' / *GTTGTTGTTGGG 3'

0.10 — CAACAACAACAACCC 5' / *GTTGTTGTTGTTGGG 3'

0.26 — CTGCAGACTGAGCTGACCC 5' / * GACGTCTGACTCGACTGGG 3'

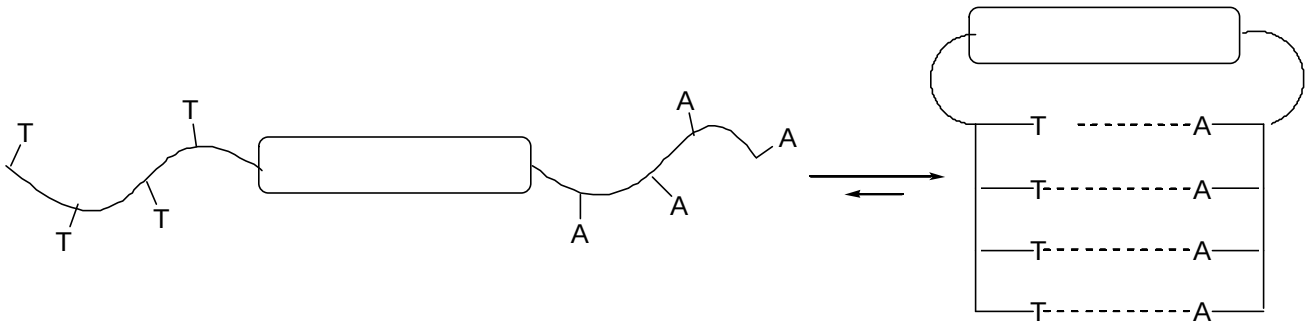
Giese et al. Angew. Chem. 1999

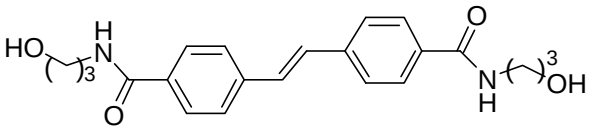




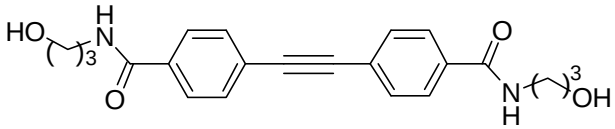
Barton et al. Chem. & Biol. 1999

Hairpin-Forming Bis(oligonucleotide) Conjugates

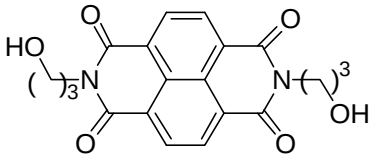




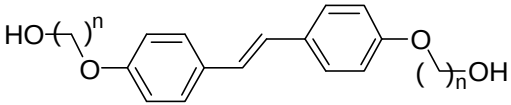
SA Letsinger and Wu, JACS 1995



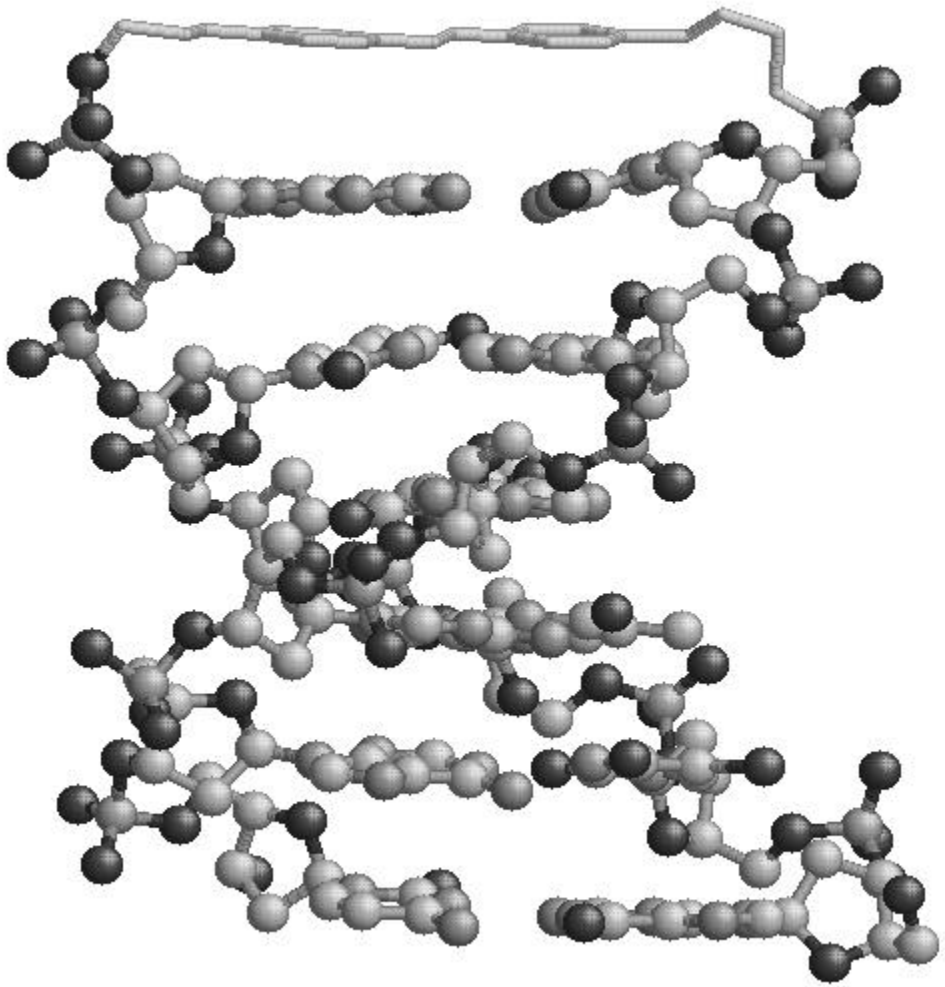
DPA Lewis and Wasielewski, JACS 1999



NDI Lewis and Wu, unpublished



SE Lewis and Liu, JACS 1999

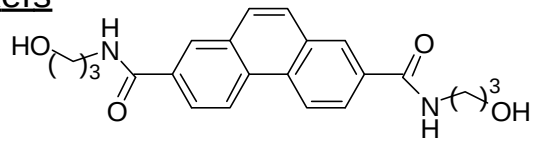


Crystal Structure of a Stilbene-Linked DNA Hairpin
JACS, **1999**, *121*, 9905.

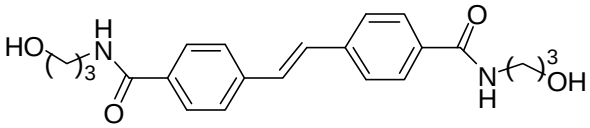
Electron Transfer Energetics

$\Delta G = E_S + E_{rdn}(A) - E_{ox}(D) + C$ (Weller)

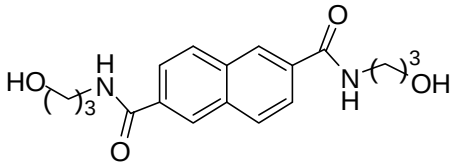
acceptor linkers



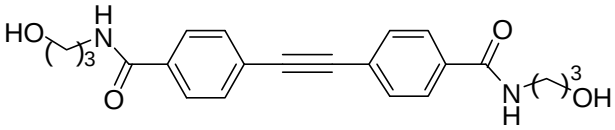
PA, E_S = 3.35 eV, E_{rdn} = - 2.16 V, E_{rdn}* = 1.19



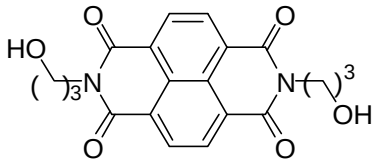
SA, E_S = 3.35 eV, E_{rdn} = - 1.99 V, E_{rdn}* = 1.44



NA, E_S = 3.55 eV, E_{rdn} = - 2.05 V, E_{rdn}* = 1.50

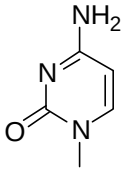


DPA, E_S = 3.76 eV, E_{rdn} = - 1.98 V, E_{rdn}* =1.78

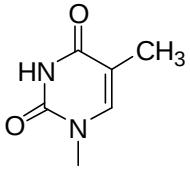


NI, E_S = 3.24 eV, E_{rdn} = - 0.55 V, E_{rdn}* = 2.69

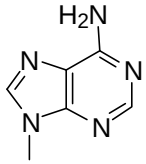
donor nucleobases



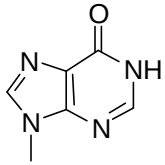
cytosine, C
E_{ox} = 1.87 V



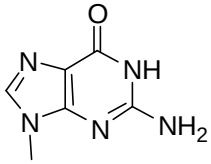
thymine, T
E_{ox} = 1.84 V



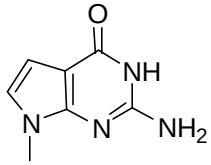
adenine, A
E_{ox} = 1.69 V



inosine, I
E_{ox} = 1.4 V

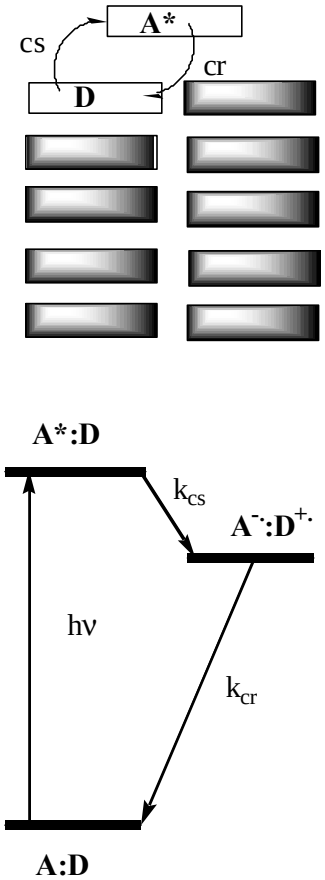


guanine, G
E_{ox} = 1.24 V

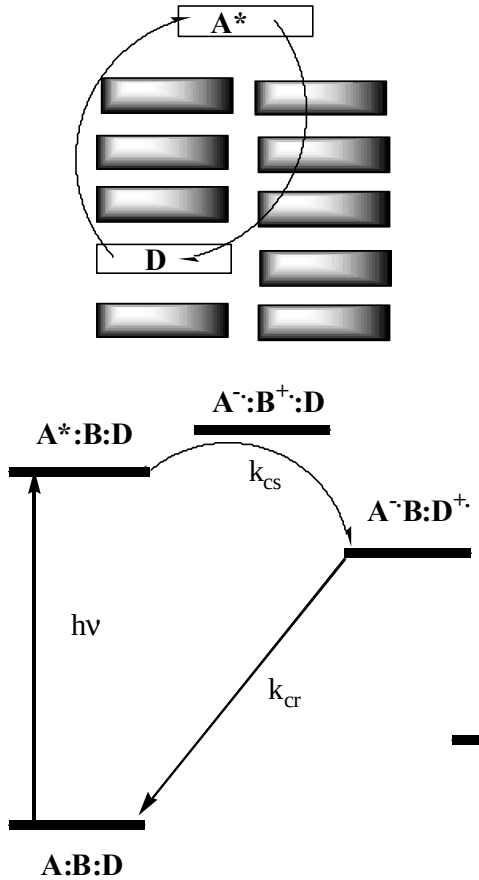


deazaguanine, Z
E_{ox} = 0.8 V

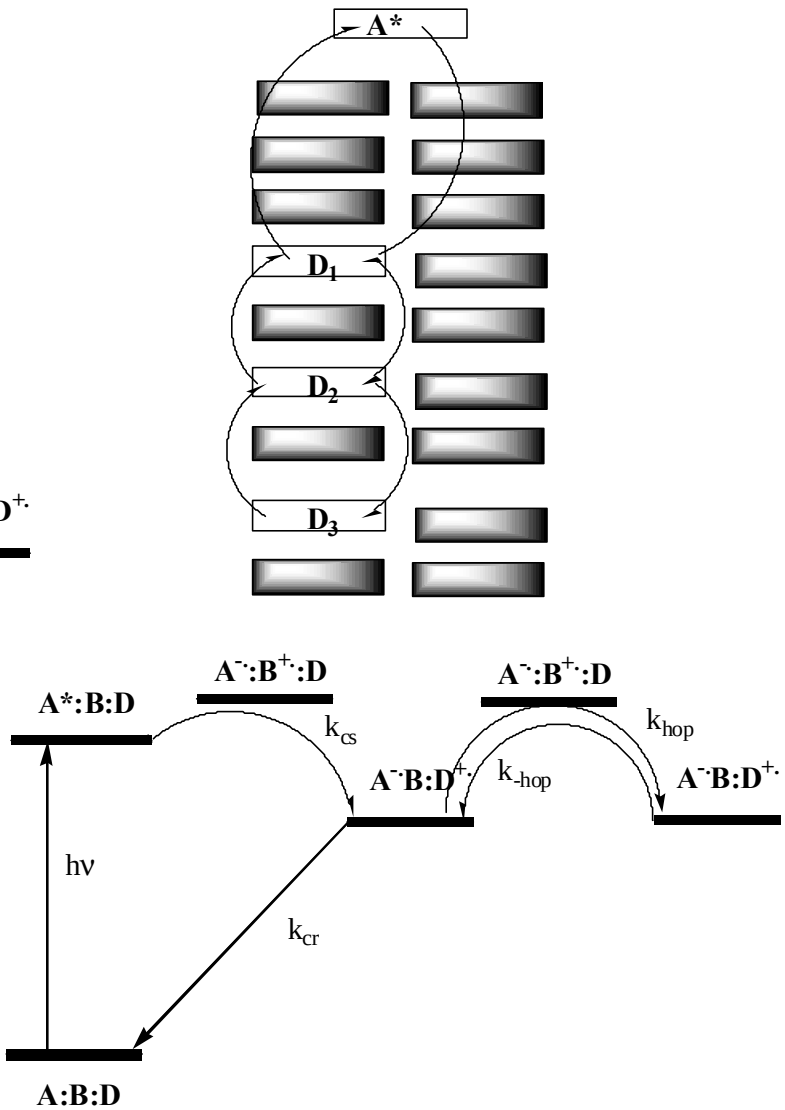
Contact Charge Transfer

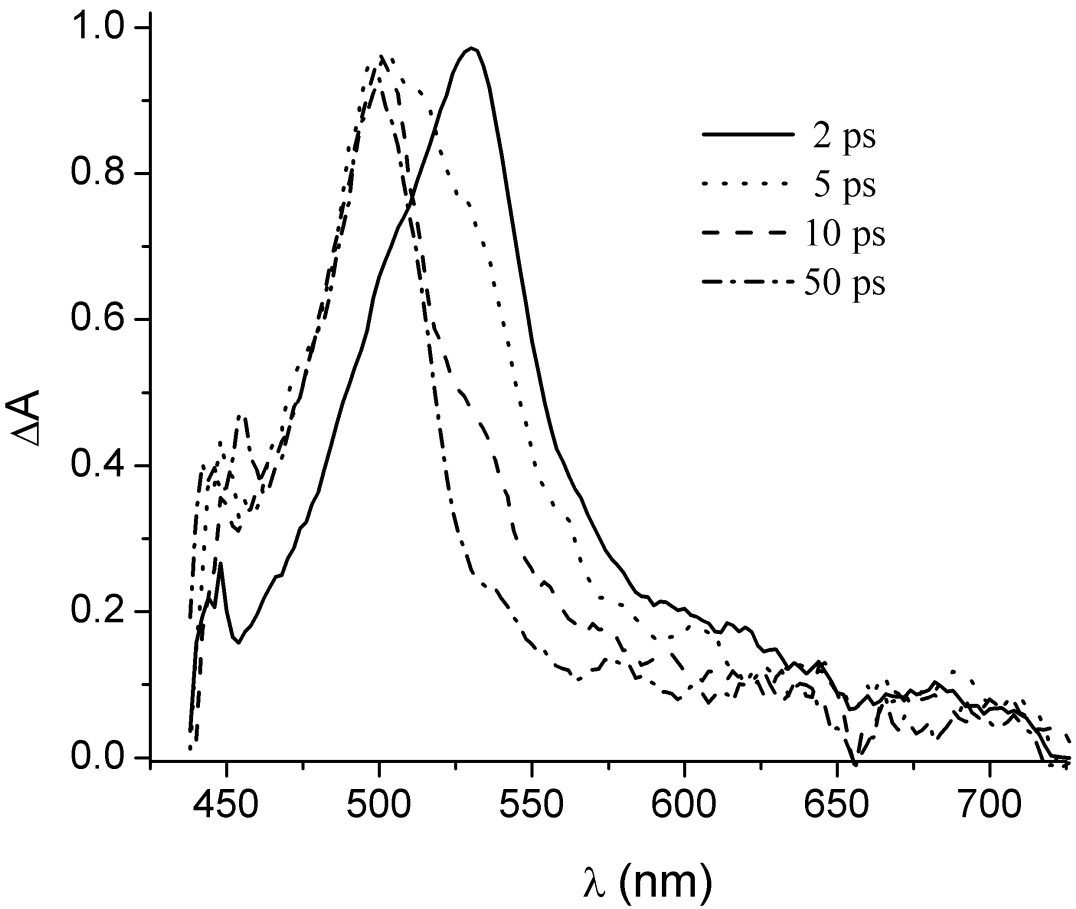


Bridge-Mediated Charge Transfer



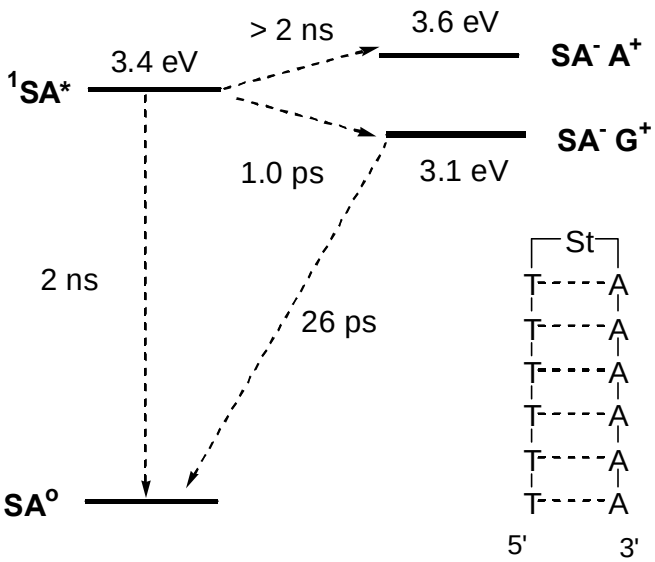
Charge Transport (Hole Hopping)

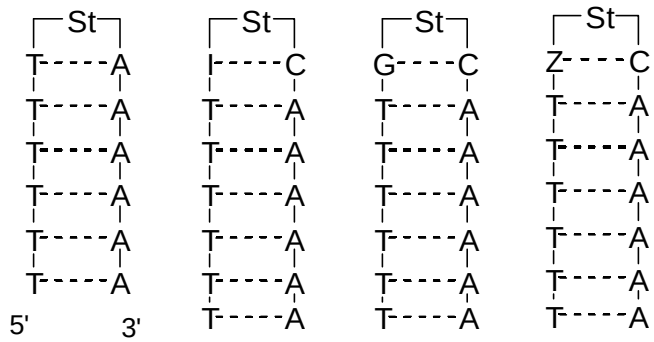




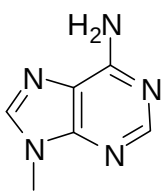
Transient absorption spectra of the T_5-DPA-A_5 hairpin obtained after a 0.2 ps 327 nm excitation pulse at indicated delay times. Spectral intensities are normalized at their maxima.

Nearest Neighbor Charge Transfer Dynamics

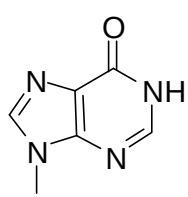




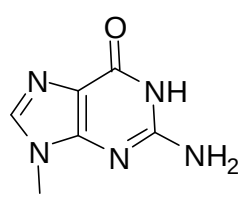
	T_6-A_6	1I:C	1G:C	1Z:C
τ_{cs}, ps	> 2,000	18	1.0	<0.2
τ_{cr}, ps		284	26	14



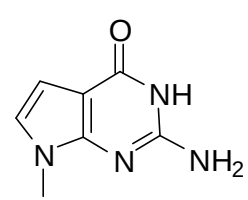
adenine, A
E_{ox} = 1.69 V



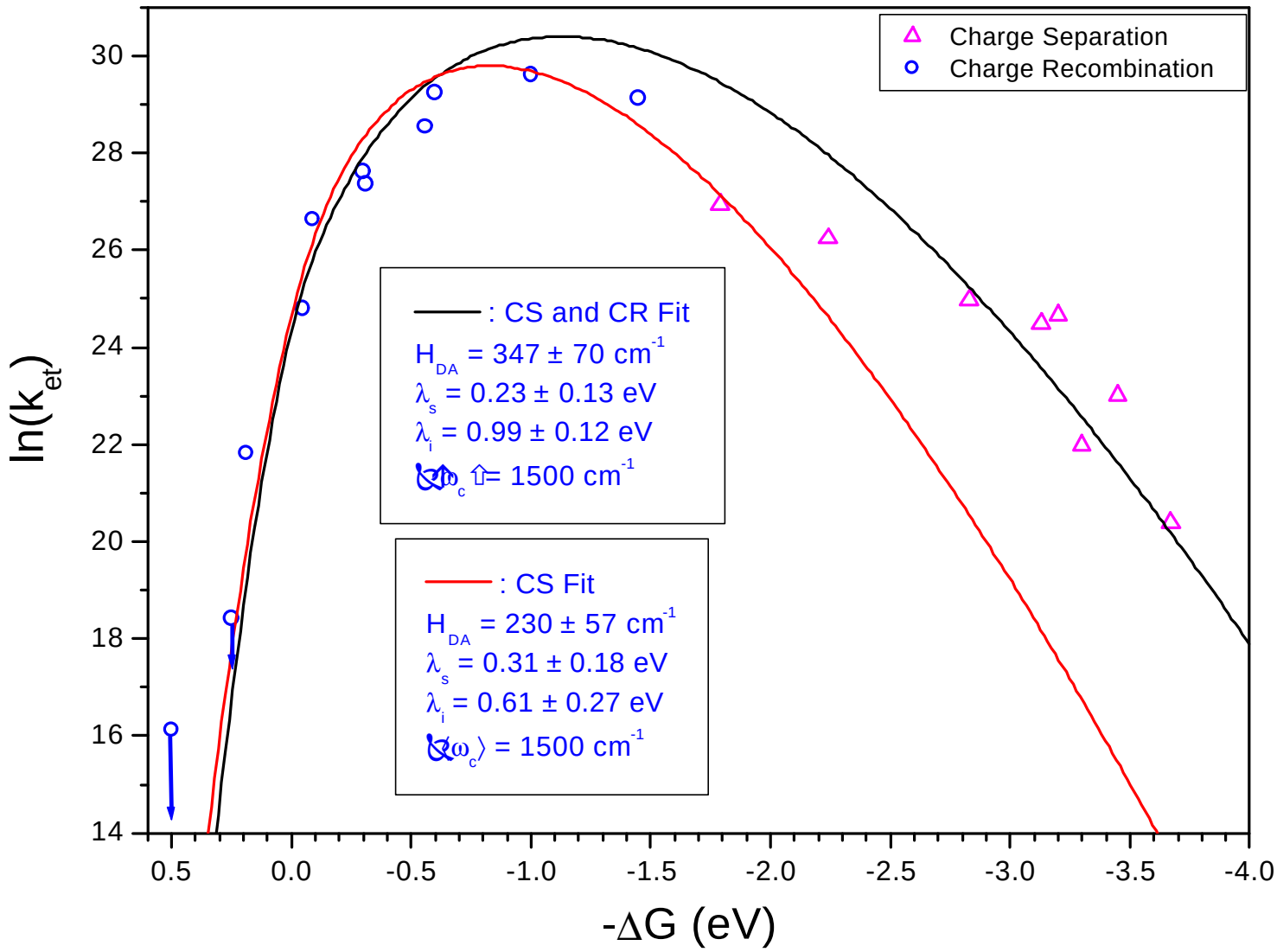
inosine, I
E_{ox} = 1.4 V



guanine, G
E_{ox} = 1.24 V

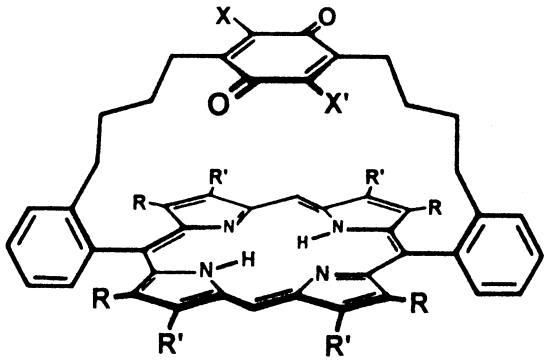


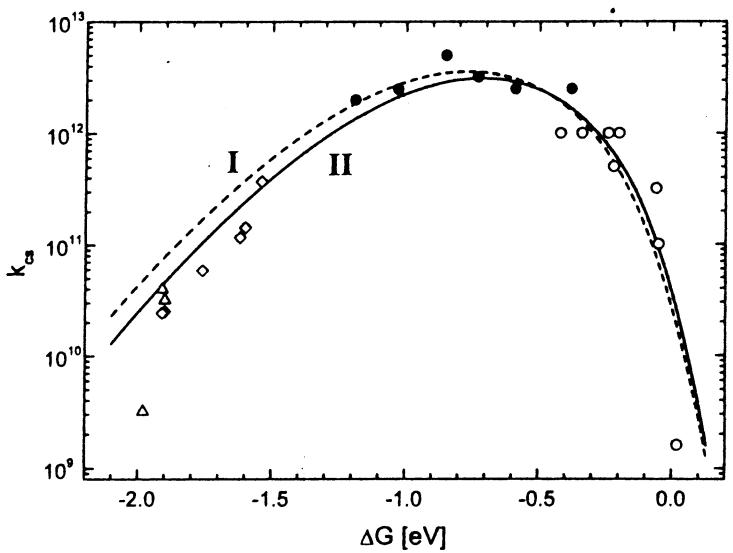
deazaguanine, Z
E_{ox} = 0.8 V


Charge Separation
Charge Recombination
: CS and CR Fit
H_DA = 347 ± 70 cm^-1
λ_s = 0.23 ± 0.13 eV
λ_i = 0.99 ± 0.12 eV
⟨ħω_c⟩ = 1500 cm^-1
: CS Fit
H_DA = 230 ± 57 cm^-1
λ_s = 0.31 ± 0.18 eV
λ_i = 0.61 ± 0.27 eV
⟨ħω_c⟩ = 1500 cm^-1
ln(k_et)
-ΔG (eV)
30
28
26
24
22
20
18
16
14
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0

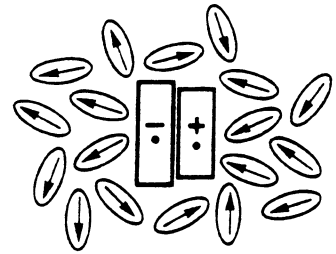
Driving-Force Dependence of Electron Transfer Dynamics in Cofacial Donor-Acceptor Systems

Staab and Michel-Beyerle
Ber. Bunsenges Phys. Chem. *1996*
$\lambda_s = 0.27$ eV, $\lambda_i = 0.53$ eV, $H_{DA} = 133$ cm^{-1}

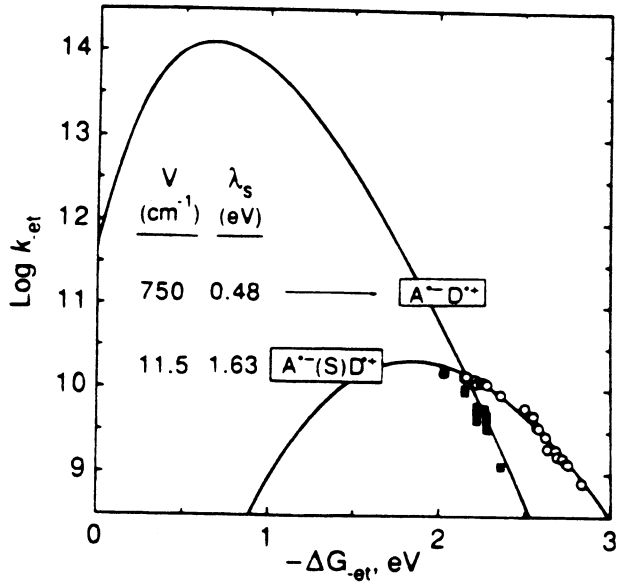


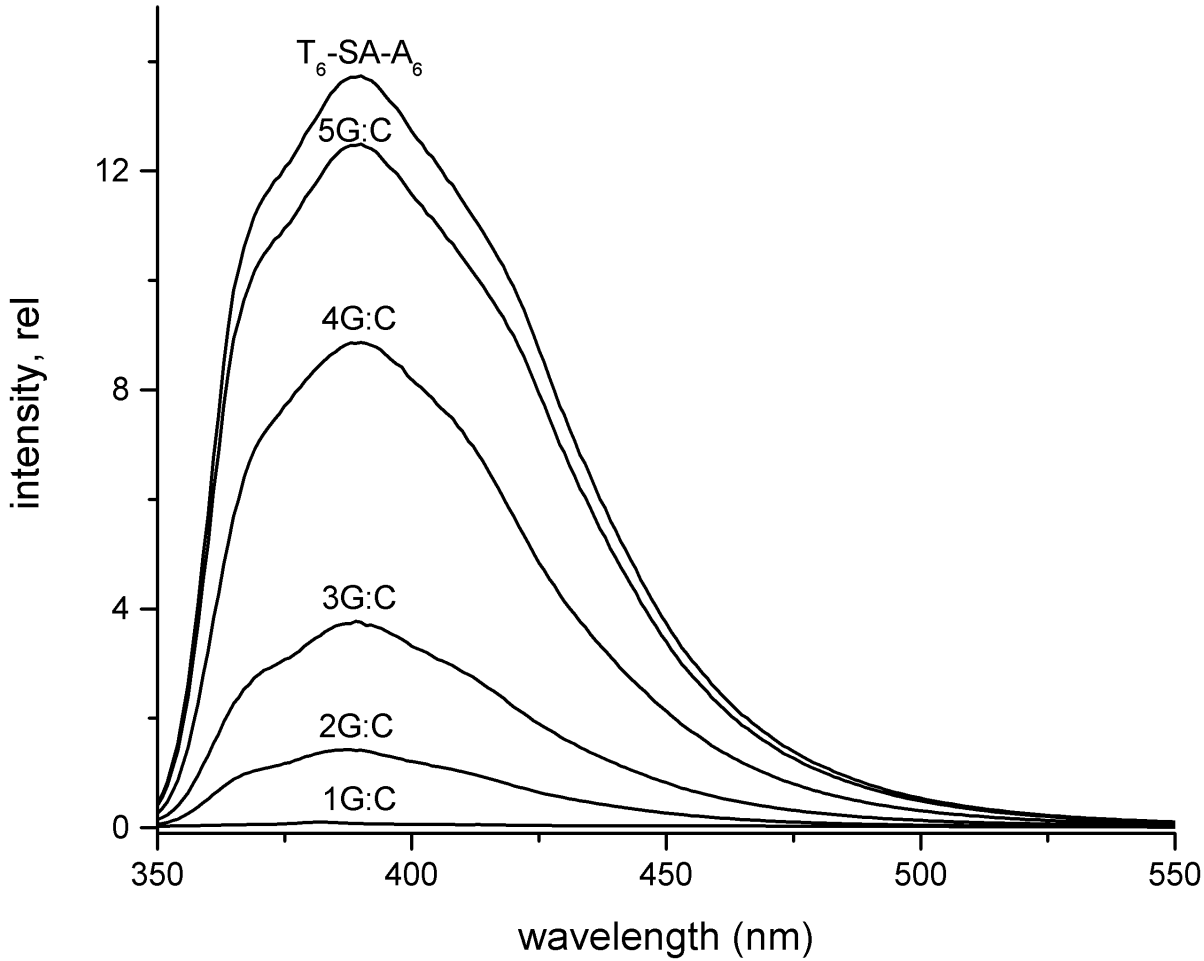


Gould and Farid
Acc. Chem. Res. *1996*
$\lambda_s = 0.48$ eV, [$\lambda_i = 0.25$ eV], $H_{DA} = 750$ cm^{-1}



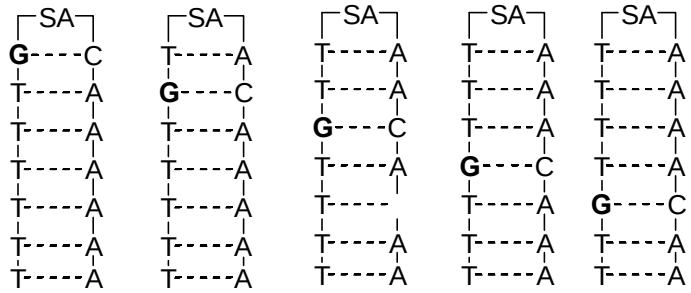
Contact Radical-Ion Pair (CRIP)



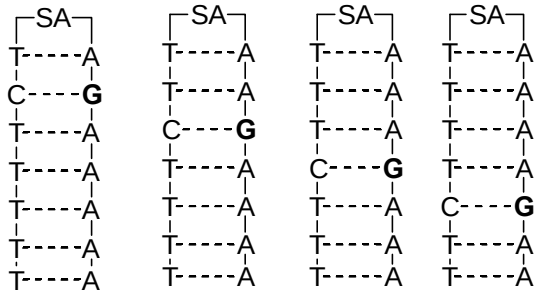


Fluorescence spectra of the T_6-SA-A_6 and the SA-linked nGC hairpins

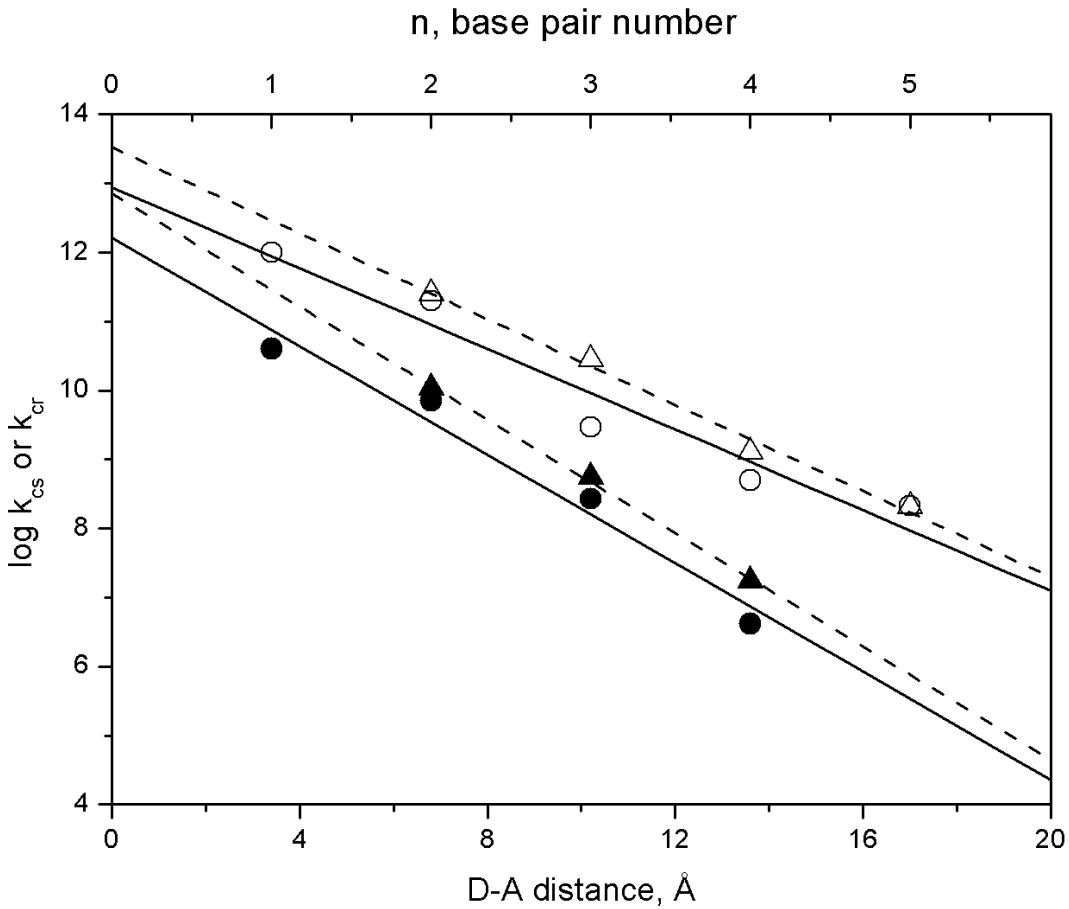
Chart 6. Decay Times of SA-Linked nG:C and nC:G Hairpins



	1G:C	2G:C	3G:C	4G:C	5G:C
τ_{cs}, ps	1.0	5.1	120	990	1,400
τ_{cr}, ns	0.026	0.14	3.8	240	

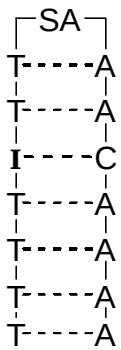


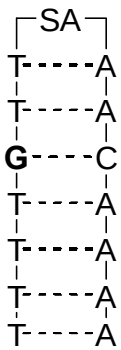
	2C:G	3C:G	4C:G	5C:G
τ_{cs}, ps	3.9	31	460	1,400
τ_{cr}, ns	0.094	1.9	57	

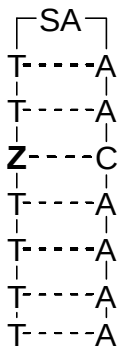


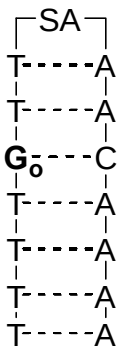
Distance dependence of the rate constants for charge separation (open symbols) and charge recombination (filled symbols) for SA-linked hairpin families (Chart 6) in which guanine is either in the polyT arm (e.g. 3G:C, , , solid lines) or in the polyA arm (e.g. 3C:G, Δ, , dashed lines).

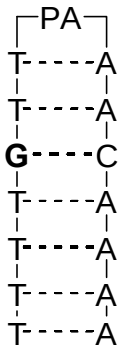
Dynamics of Bridge-Mediated Charge Separation and Charge Recombination



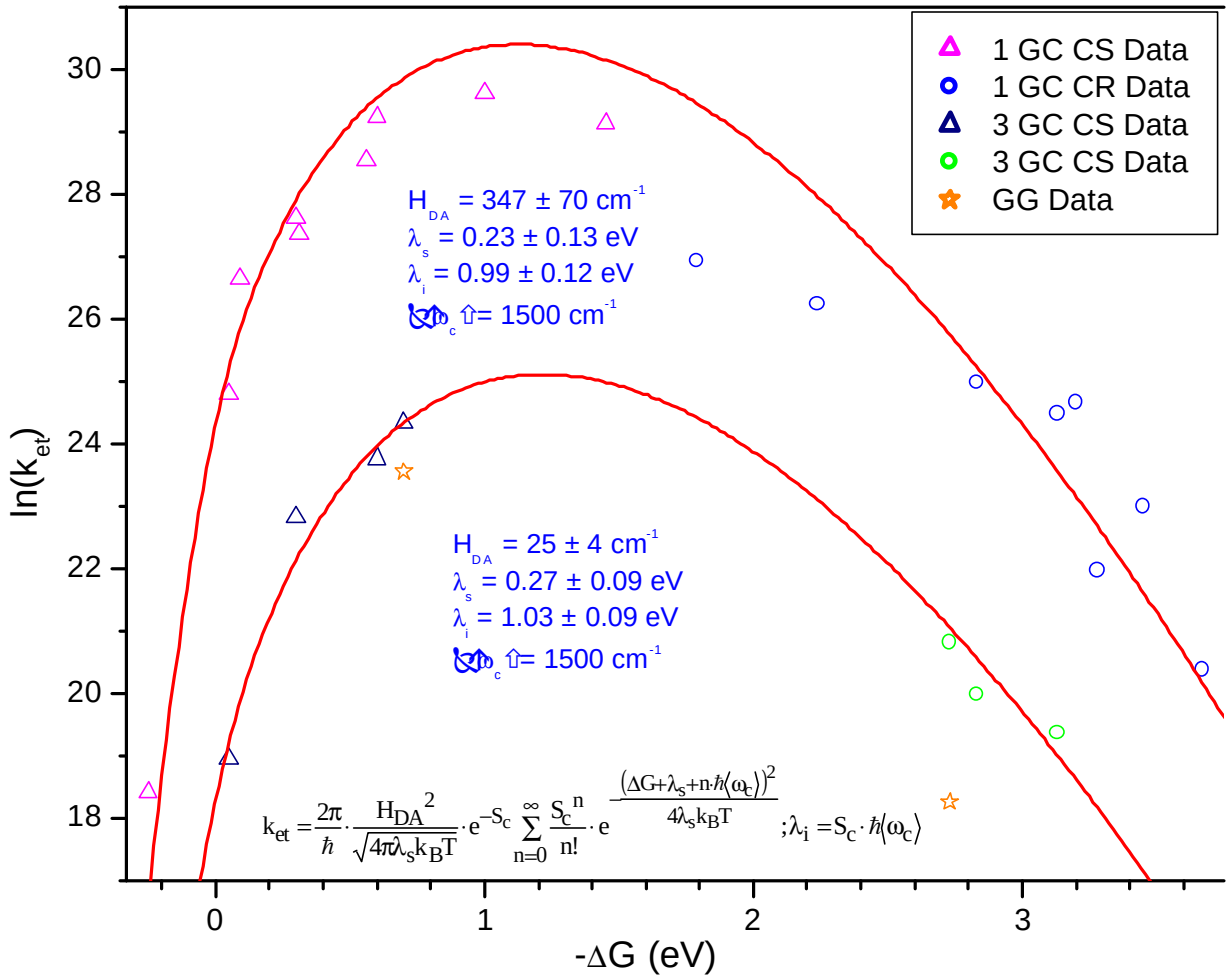








$-\Delta G_{cs}$, eV	0.04	0.20	0.49	0.59	-0.05
$10^9\ k_{cs}$, s^{-1}	0.17	0.83	21	37	0.03
$-\Delta G_{cr}$, eV	3.28	3.13	2.83	2.73	
$10^9\ k_{cr}$, s^{-1}	0.11	0.26	0.48	1.1	


1 GC CS Data
1 GC CR Data
3 GC CS Data
3 GC CS Data
GG Data
H_DA = 347 ± 70 cm^-1
λ_s = 0.23 ± 0.13 eV
λ_i = 0.99 ± 0.12 eV
ħω_c = 1500 cm^-1
H_DA = 25 ± 4 cm^-1
λ_s = 0.27 ± 0.09 eV
λ_i = 1.03 ± 0.09 eV
ħω_c = 1500 cm^-1
$k_{et} = \frac{2\pi}{\hbar} \cdot \frac{H_{DA}^2}{\sqrt{4\pi\lambda_s k_B T}} \cdot e^{-S_c} \sum_{n=0}^{\infty} \frac{S_c^n}{n!} \cdot e^{-\frac{(\Delta G+\lambda_s+n\cdot\hbar\langle\omega_c\rangle)^2}{4\lambda_s k_B T}}$; $\lambda_i = S_c \cdot \hbar\langle\omega_c\rangle$
ln(k_et)
-ΔG (eV)
30
28
26
24
22
20
18
0
1
2
3

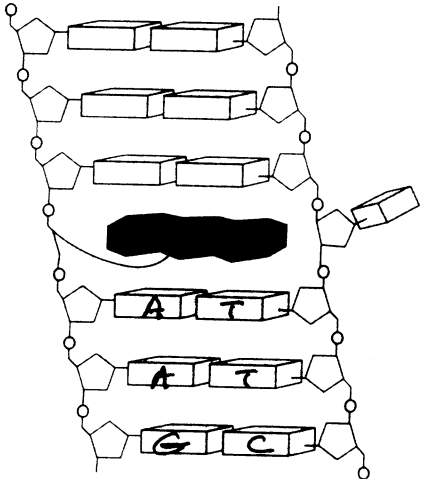
Values of β for $(A:T)_n$ Bridges

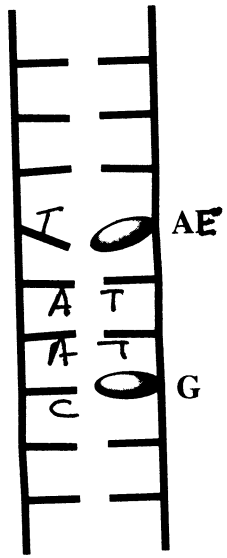
3'-CGATTATATTATGGG **N_m** GCA ATTATAATACGCTGCACGCA-^{32}P

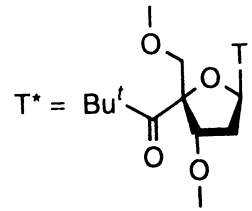
5'-GCTAATATAATACCC **N_n** CGT*TAATATTATGCGACGTGCGT-3'

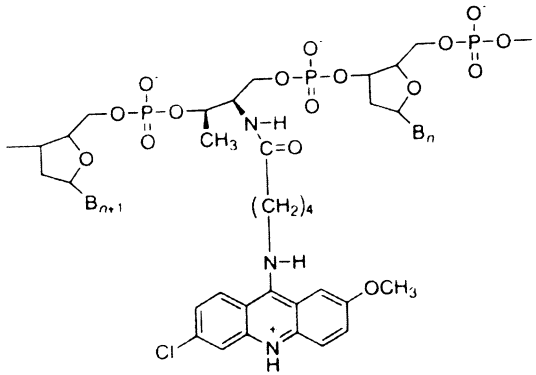
1

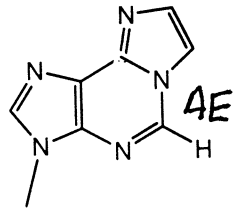
1	N_m / N_n
a	T / A
b	TA / AT
c	TTA / AAT
d	TATA / ATAT

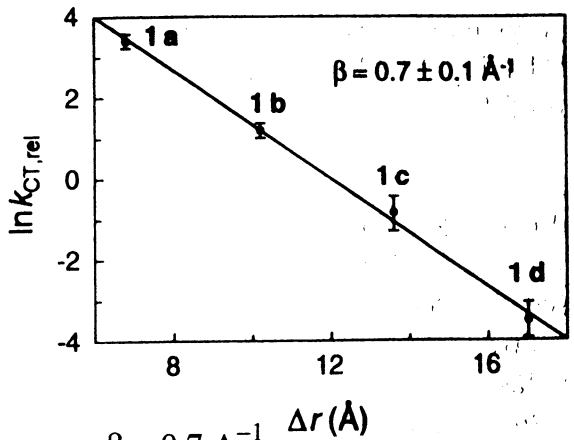












$\beta = 1.4\ A^{-1}$

Takaka, Angew. Chem. 1998

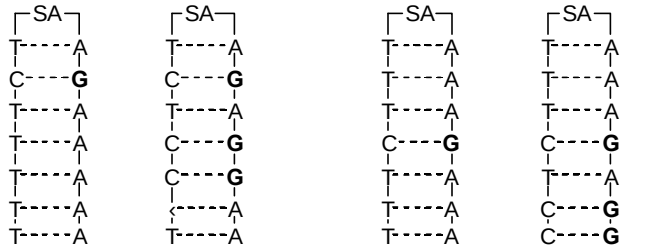
$\beta = 1.0\ A^{-1}$

Barton, Science 1999

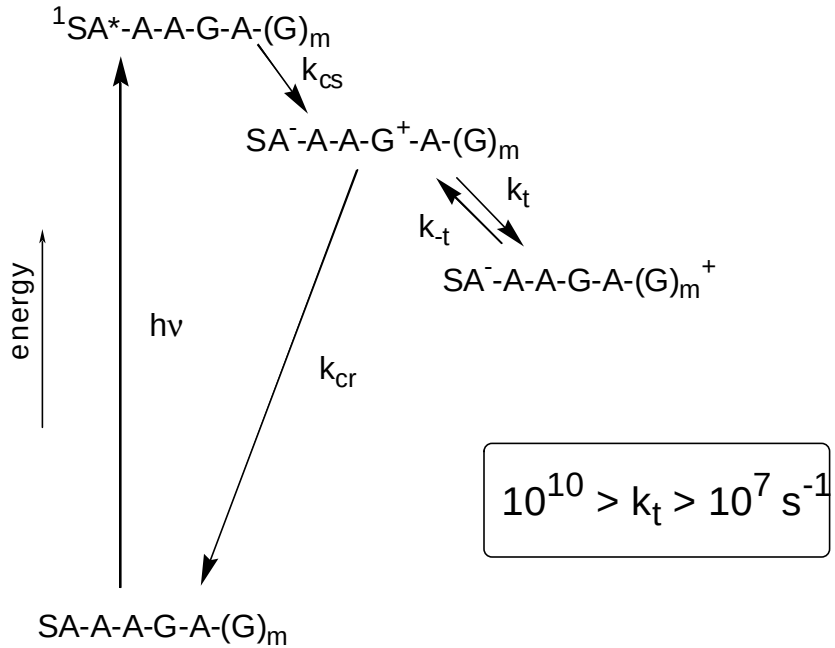
$\beta = 0.7\ A^{-1}$

Giese, JACS 1998

Decay Times for Hairpins with Hole Transport Sequences



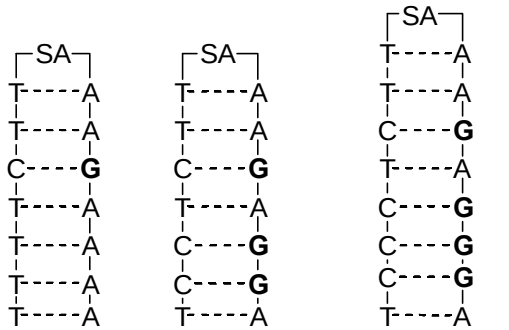
	2C:G	2,4,5C:G	4C:G	4,6,7C:G
τ_{cs}, ps	3.9	3.9	460	610
τ_{cr}, ns	0.094	0.10	57	220



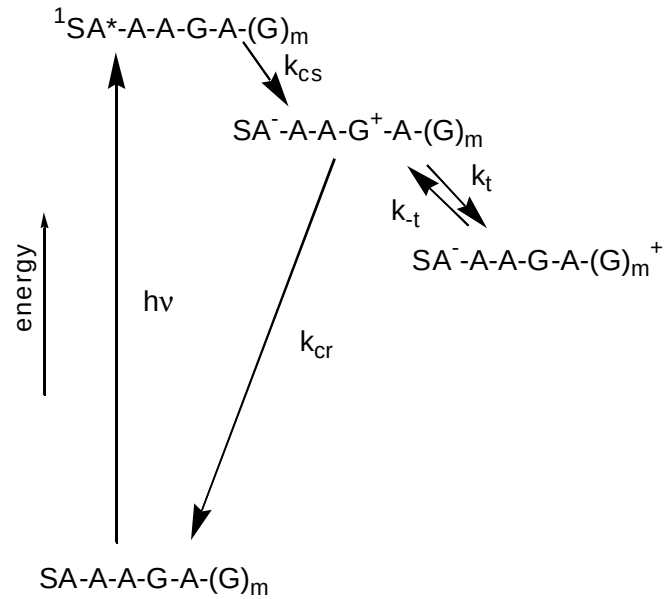
$$10^{10} > k_t > 10^7\ s^{-1}$$

Nature, **2000**, *406*, 51-53.

Hole Transport Dynamics and Equilibria



	3C:G	3,5,6C:G	3,5,6,7C:G
τ_s, ps	31	15	22
τ_a, ns	1.9	1.5, 170	0.92, 295



$$G^{+\cdot} + GG \underset{7.5 \times 10^6}{\overset{5.6 \times 10^7}{\rightleftharpoons}} G + GG^{+\cdot} \qquad K_{ht} = 7.7 \pm 1,\ \Delta G_{ht} = -0.052 \pm 0.006$$

$$G^{+\cdot} + GGG \underset{4.3 \times 10^6}{\overset{8.7 \times 10^7}{\rightleftharpoons}} G + GGG^{+\cdot} \qquad K_{ht} = 20 \pm 1,\ \Delta G_{ht} = -0.077 \pm 0.005$$

Strand Cleavage Selectivity: GGG > GG > G

Burrows and Foote, *JACS*, 1999

sequence	G	GG	GGG
k_{cl}, rel.	1.0	3.7	5.3
$[G_n^+]$, rel	1.0	7.7	20
$k_{cl}/[G_n^+]$	1.0	0.48	0.27

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