

## Charge Recombination in DNA Hairpins Controlled by Counterions

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The slow charge recombination in DNA hairpins of various lengths<sup>1</sup> is investigated. The distance dependence for the charge recombination rate between stilbene donor (Sd<sup>+</sup>) and stilbene acceptor (Sa<sup>-</sup>) linkers (see Figure 1) separated by AT bridges of various lengths has the double exponential form

$$k(r) = k_0(\exp(-\beta_1 r) + C \exp(-\beta_2 r)),$$

$$\beta_1 = 0.97 \text{ \AA}^{-1}, \beta_2 = 0.42 \text{ \AA}^{-1}, C = 8.70 \times 10^{-5}, k_0 \approx 10^{11} \text{ s}^{-1} \quad (1)$$

We suggest that this puzzling dependence is associated with two tunneling channels distinguished by the presence or absence of a Cl<sup>-</sup> counterion bound to an Sd<sup>+</sup> linker. When Cl<sup>-</sup> is associated with Sd<sup>+</sup>, the energy of the positive charge is lower compared to Sd<sup>+</sup> without a counterion (see Figure 2). Therefore, the potential barrier for charge recombination is higher in the presence of Cl<sup>-</sup> bound to Sd<sup>+</sup>, and the recombination is characterized by the larger tunneling exponent  $\beta_1$  than the tunneling exponent  $\beta_2$  in the absence of a counterion (see eq 1 and Figure 2, cases A and B). The constant  $C$  expresses the probability that a counterion is not associated, which is small because of the large binding energy, which we estimated as  $\Delta \approx 0.41$  eV. Experiment-based estimates of binding parameters agree within reasonable expectations. We suggest a control

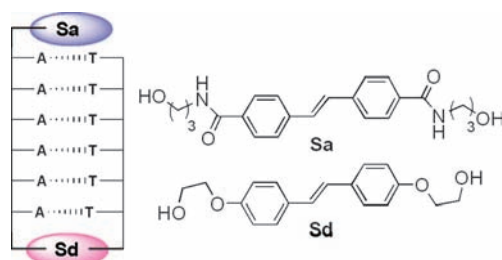


Figure 1. Structures of a hairpin having six AT base pairs and the stilbene linkers.

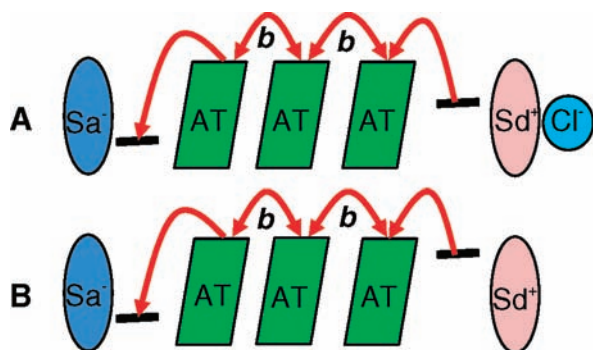


Figure 2. Stilbene capped hairpin; charge recombination channels.

experiment where the Cl<sup>-</sup> ion is replaced by other halogen ions. This replacement enables control of the charge recombination rate modifying it in either direction by orders of magnitude (see Table 1).

Table 1. Approximate Parameters of Recombination Rates Controlled by Different Counterions (See Eq 1,  $\beta_2 = 0.42 \text{ \AA}^{-1}$ )

X	$\Delta_x$ (eV)	$\beta_1$ ( $\text{\AA}^{-1}$ )	C	$k_r$ ( $\text{s}^{-1}$ )
F	0.56	1.14	$2.71 \times 10^{-7}$	0.3
Cl	0.41	1.03	$8.02 \times 10^{-5}$	88
Br	0.38	1.01	$2.68 \times 10^{-4}$	293
I	0.34	0.97	$1.31 \times 10^{-3}$	1436

Electronic excitation of DNA using various optical methods is important for investigating DNA structure and biological function.<sup>2</sup> It also plays a fundamental role in a variety of DNA applications in nanotechnology which have been extensively considered during the past decade.<sup>3–6</sup> Stilbene capped DNA hairpins (see Figure 1), where the first time-resolved observation of charge transfer in DNA was made,<sup>7</sup> are used very successfully for the investigation of DNA electronic excitations and their kinetics. It is remarkable that hairpins having Sa and Sd linkers connected by poly-A poly-T bridges (Figure 1) can possess extremely long recombination times for the charge separated state  $\text{Sa}^- \cdot \text{Sd}^+$  created after Sa photoexcitation. Increasing the number of AT pairs forming the bridge from  $n = 1$  to  $n = 7$  reduces the charge recombination rate by 8 orders of magnitude.<sup>1</sup> This interesting property of stilbene capped DNA hairpins has potential for a variety of applications involving charge separation such as solar cells.<sup>8</sup>

Therefore, it is important to understand mechanisms of charge recombination in DNA hairpins and investigate possible ways to control this process. This requires understanding the distance dependence of the charge transfer rate, eq 1. We suggest that this dependence is related to the Cl<sup>-</sup> counterion, which is either paired (Figure 2A) or not (Figure 2B) to an Sd<sup>+</sup> group. If the counterion is present with the probability close to unity, the charge recombination rate depends on the distance as  $\exp(-\beta_1 r)$ . If Cl<sup>-</sup> is not attached, the charge recombination rate depends on the distance as  $\exp(-\beta_2 r)$  and the probability of this configuration is  $C \ll 1$ . Two different exponents are due to different energies of Sd<sup>+</sup> in the absence or presence of a counterion.

A Hückel model is used to describe charge tunneling from Sd to Sa linkers.<sup>9,10</sup> This model should be reasonably relevant in the tunneling regime despite polaron formation and possible environmental fluctuations which can reduce the energy barrier. We can then determine the electron overlap integral  $b$  for the polaron. We assume that the thermal equilibrium of the counterion and the Sd<sup>+</sup> ion is established before recombination begins. This is justified by the large diffusion rate of counterions in water:  $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (see ref 11 and the Supporting Information).

According to our model, the factor  $C$  in eq 1 stands for the probability that counterion  $\text{Cl}^-$  is not bound to the  $\text{Sd}^+$  group. This probability can be expressed as

$$C = \Omega \exp(-\Delta/(k_{\text{B}}T)) \quad (2)$$

Here  $\Delta$  is the ion binding energy in aqueous solution, and the prefactor  $\Omega$  is the relative phase volume of unbound states compared to bound states for the  $\text{Cl}^-$  ion. The product  $k_{\text{B}}T = 0.026$  eV is the thermal energy at room temperature. Experiments<sup>1</sup> were performed in a 0.1 M aqueous solution of NaCl. The prefactor  $\Omega$  can be estimated as the ratio of water molecules per chloride ion, so that  $\Omega \approx 556$ . The error of this estimate is assumed to be less than an order of magnitude so we can consider  $10^2 < \Omega < 10^3$ . Lower and upper boundaries for  $\Omega$  will be used to estimate the accuracy of our estimate of the binding energy  $\Delta$ . Solving eq 2 with the probability  $C$  taken from experimental data<sup>1</sup> (see eq 1), one finds

$$0.36 \text{ eV} < \Delta < 0.42 \text{ eV} \quad (3)$$

This estimate is within the range of typical counterion binding energies.<sup>12,13</sup>

In the next step, a relationship is derived between energies  $E_1$  and  $E_2$  of the  $\text{Sd}^+$  linker in the presence or absence of  $\text{Cl}^-$ , respectively, and corresponding tunneling exponents  $\beta_1$  and  $\beta_2$  in eq 1. The energy of an isolated  $(\text{AT})^+$  is set to zero. The energy  $E_1$  taken in the presence of  $\text{Cl}^-$  is less than the energy  $E_2$  taken in the absence of  $\text{Cl}^-$  by its binding energy (eq 3) so we have

$$E_2 = E_1 + \Delta \quad (4)$$

One can establish a clear relationship between energy and the tunneling exponent. This relationship involves the electron transfer integral  $b$  responsible for charge tunneling between adjacent AT base pairs, shown in Figure 2. It can be written as<sup>9</sup>

$$2b \cosh(\beta_{1,2}a/2) = E_{1,2} \quad (5)$$

where  $a = 3.4$  Å is the distance between adjacent base pairs.

This relationship can be derived as follows. The tunneling rate through  $n$  AT pairs (cf. eq 1) is determined by the exponential tail of the positive charge wave function  $k_n \approx \psi_n^2$ . Here  $\psi_m^2$  is the probability of finding the charge at the  $m^{\text{th}}$  base pair. The wave function of charge under the barrier decreases exponentially with the base number as  $\psi_n \approx \exp(-\kappa n)$ , while the charge transfer rate decreases exponentially with the bridge length as  $\exp(-\beta a n)$ . Comparing the two exponents, we have  $\kappa = \beta a/2$ . Equation 5 results from the discrete Schrödinger equation<sup>9</sup>  $E\psi_m = -b(\psi_{m-1} + \psi_{m+1})$  if the exponential  $m$  dependence for  $\psi_m$  is assumed as above ( $\psi_m \approx \exp(-\kappa m)$ ).

Using eqs 3–5, one can evaluate the electron transfer integral and the energies of  $\text{Sd}^+$  in the absence or presence of  $\text{Cl}^-$  as  $b = 0.13 \pm 0.01$  eV,  $E_1 = 0.73 \pm 0.06$  eV, and  $E_2 = 0.34 \pm 0.03$  eV. It is remarkable that the estimate for the electron transfer integral  $b$  agrees very well with the calculations of Voityuk and co-workers.<sup>14,15</sup>

It is not quite clear to us as to why there is no observation of thermally activated recombination for  $(\text{AT})_n$  bridges up to  $n = 7$  in contrast to ref 16. A possible explanation of this behavior is edge effect, which can be crucially important for thermally activated transport. For instance, the energy of the  $\text{AT}^+$  state of an AT pair adjacent to an Sd linker can be larger than the energy of other AT pairs due to its electrostatic interaction with Sd. This difference can increase the activation energy of the first hopping step thus suppressing the hopping channel.

Another reason can be the difference of charge recombination<sup>1</sup> with charge shift reactions.<sup>15</sup> For example, the investigation of

charge recombination in DNA hairpins using naphthalimide and phenothiazine as acceptor and donor separated by various AT bridges exhibits behavior similar to that in ref 1.<sup>1</sup> Indeed, a tunneling exponent  $\beta = 0.40$  Å<sup>-1</sup> was reported for charge recombination across 4–8 AT base pairs. The small preexponential factor<sup>17</sup> ( $10^8$  s<sup>-1</sup>) compared to  $k_0$  in eq 1 can be due to the fact that charge recombination for 4–8 base pairs also occurs without associated counterions.

Our model can be verified in a number of ways. One way is to change the NaCl concentration. According to eq 1, the reduction of NaCl concentration by a factor of 10 will increase the recombination rate 10-fold for long AT bridges ( $n > 4$ ).

A more interesting experiment is to replace chloride ions with other counterions, e.g.,  $\text{F}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ . The binding energy should decrease with increasing ionic radius. Crude estimates in Table 1 were made assuming that the binding energy is inversely proportional to ionic radius. This estimate ignores the contribution of water to binding energy and thus underestimates possible changes in recombination rates for different counterions (see Table 1). We used the same values for the electron transfer integral  $b$ , energy  $E_2$  of the  $\text{Sd}^+$  state in the absence of a counterion (and, consequently, exponent  $\beta_2$ ), and the phase volume factor  $\Omega$ . The last column in Table 1 shows the recombination rate for the longest bridge of 7 AT pairs. For the smallest ion  $\text{F}^-$ , the recombination time is as long as 3.33 s.

Thus it is shown that the complicated double exponential recombination kinetics in DNA hairpins can be interpreted assuming that this process is controlled by the binding of a counterion. Key experiments are suggested to verify our theory and to control the recombination process by varying counterions.

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**Supporting Information Available:** Equation 1 for the equilibrium charge transfer rate is derived. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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