

# Modulating the Charge Recombination in DNA

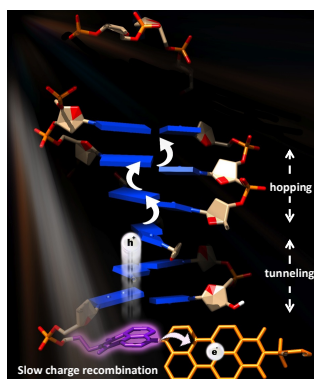
Mahesh Hariharan\*

*Indian Institute of Science Education and Research-Thiruvananthapuram,  
Maruthamala P. O., Vithura, Thiruvananthapuram, Kerala- 695 551, INDIA.*

*Corresponding author: [mahesh@iisertvm.ac.in](mailto:mahesh@iisertvm.ac.in)*

Mechanistic insight into hole transport across DNA has huge implications in the areas of oxidative damage in DNA,<sup>1</sup> DNA-based nanoelectronics<sup>2</sup> and DNA-protein crosslinking.<sup>3</sup> Slow rates of charge separation and ultrafast charge recombination have limited the use of DNA in device applications. Efficiency of charge separation in DNA can be modified by choosing suitable donor-acceptor systems to act as electron or hole acceptors and through modification of the DNA bases in the bridge. While the length dependence of DNA-mediated charge transport across adenine-tracts is found to be attenuated by back electron transfer, such back electron transfer from the reduced ligand to oxidized DNA also reduces the efficiency of DNA damage. A 10-fold increase in photoinduced DNA damage was observed using randomly distributed externally bound co-sensitizer that reduces the rate of back electron transfer. The role of counter-ions in reducing the charge recombination in DNA is also demonstrated to be vital. However, modulating the rate of back electron transfer in DNA employing sequential electron transfer has received less attention.

Our approach to modulate charge recombination in DNA employs a donor-acceptor dyad NP, consisting of naphthalimide and perylenimide connected across a single bond, end-capped on short DNA hairpins (Scheme 1). The near orthogonal arrangement of naphthalimide (N) and perylenimide (P) chromophoric units makes the dyad a combination of two independent redox centers at a short separating distance of 1.49 Å, as shown previously, with absorption maxima at 345 and 475 nm respectively.<sup>4</sup> By virtue of the significant spectral overlap and favorable dipole-dipole orientation, highly efficient photoinduced energy transfer is found to occur from the singlet excited state of naphthalimide (<sup>1</sup>N\*) to perylenimide. Excitation energy transfer results in the emission corresponding to perylenimide chromophore, when NP excited at 345 nm, similar to the direct excitation of perylenimide at 475 nm. Photoinduced electron transfer<sup>4</sup> is also observed from the singlet excited state of naphthalimide to perylenimide that results in a marginal decrease in the efficiency of energy transfer. The survival time of perylenimide radical anion upon excitation of naphthalimide vs. direct excitation of perylenimide exhibited a significant increase, ca. 37-fold upto 3 base-pair separation. The rate of charge recombination in short DNA bridges is modulated through a tandem electron transfer process employing a secondary acceptor. Details of these results will be discussed in the lecture.



Scheme 1. Representative DNA hairpin conjugate with end-capped NP dyad demonstrating sequential electron upon photoexcitation.

## References:

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