DYNAMICS OF PHOTOINDUCED CHARGE TRANSFER IN PERYLENEDIIMIDE-DNA CONJUGATES

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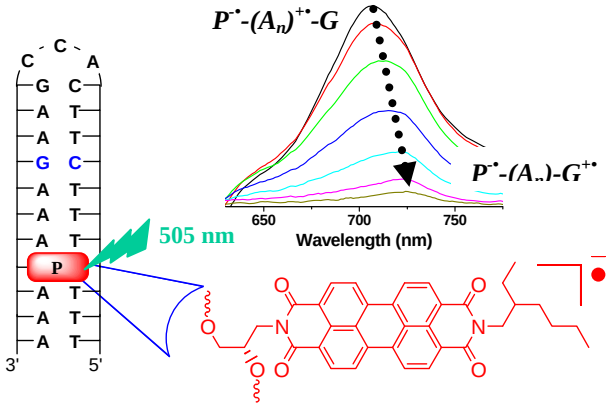
INTRODUCTION

For the last decade, our group has been involved in the study of DNA molecular photonics. We have reported the absolute rate constant for charge separation and charge recombination in a series of stable synthetic B-form DNA hairpins capped with chromophores (1). Recently, our group has shown that a synthetic DNA hairpin structures capped with perylenediimide chromophores (Pdi) form dimeric hairpin structures in aqueous buffer as a consequence of Pdi-Pdi association (2). Perylene-3,4:9,10-bis(dicarboximide) and its derivatives have attracted significant interest as active materials for light harvesting (3), photovoltaics (4), and studies of basic photoinduced charge and energy transfer processes (5) mainly due to its photochemical and thermal stability.

EXPERIMENTAL

Perylenediimide chromophore (P) was incorporated into short DNA hairpins as a base pair surrogate (6) to prevent the self-aggregation of P that is typical when it is used as the hairpin linker. The photoinduced charge transfer and spin dynamics of these hairpins were studied using femtosecond transient absorption.



RESULTS

P is a sufficiently powerful photooxidant to quantitatively inject holes into adjacent adenine (A) and guanine (G) nucleobases. Charge transfer dynamics observed following hole injection from P into the A-tract of the DNA hairpins are consistent with formation of a polaron involving an estimated 3-4 A bases. Trapping of the $(A_{3\text{-}4})^{+\bullet}$ polaron by a G base at the opposite end of the A-tract from P is only competitive with charge recombination of the polaron and $P^{-\bullet}$ at short P-G distances. Our data suggest that hole injection and transport in these hairpins is completely dominated by polaron generation and movement to a trap site rather than by superexchange. On the other hand, the barrier for charge injection from $G^{+\bullet}$ back onto the A-T base pairs is strongly activated, so that charge recombination from G most likely proceeds by a superexchange mechanism.

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