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Delocalized Hole Domains in Guanine-Rich DNA Oligonucleotides

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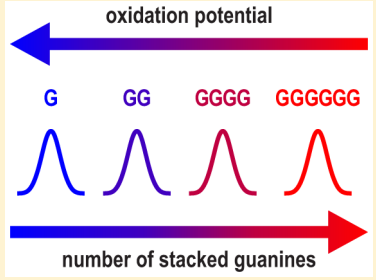
Supporting Information

ABSTRACT: Differential pulse voltammetries of guanine-rich single- and double-stranded oligonucleotides containing up to six consecutive guanines are reported. The observed progressive lowering of the first voltammetric peak potential as the number of adjacent guanines increases unambiguously points toward the establishment of delocalized hole domains; the hole stabilization energy is ca. 0.1 eV per GG step, significantly lower than that observed for AA steps.



INTRODUCTION

Since its discovery,[1] long-range hole transfer (HT) in DNA has attracted much attention because of its important implications in the field of DNA oxidative damage and for potential applications of DNA in nanoelectronics. Time-dependent spectroscopy and steady-state damage yield measurements have provided precious information for understanding the mechanism of HT in single strands and duplexes.[2−9] It is now widely accepted that long-range HT in DNA mainly proceeds via an incoherent multistep mechanism, in which a hole migrates by hopping between neighboring sites,[4,6,10,11] but the nature of such hole sites is still controversial: they could be either localized on a single base or spread over a certain number of nucleobases, especially in sequences containing two or more consecutive homobases.

The possible establishment of delocalized hole domains is a long debated issue in the field of hole transport in DNA;[7,12−14] it is particularly intriguing because a rational choice of the nucleobase sequence could allow for a fine-tuning of hole site energies, thus opening interesting routes in nanoelectronics. Some of the most stringent experimental evidence of the establishment of delocalized domains in DNA has been provided by strand cleavage experiments that have shown that sequences containing two or three consecutive guanines (G) are better hole traps than a single G.[15−20] Although theoretical computations in the gas phase predict a significant lowering of the oxidation potential for GG steps with respect to a single G,[21] modest selectivity ratios have been observed: in duplexes containing G, GG, and GGG tracts, the ratios of oxidative damage that occurred at these sites are 1.0:3.7:5.3, respectively.[19] The observed low selectivity is not necessarily evidence that the stacking interaction energy between two adjacent Gs is intrinsically small or lower than solvent polarization energy, which tends to localize charges,[13,14] but it can also be interpreted in different ways: (i) More stable GG and GGG hole sites could be less susceptible to oxidative damage than a single G. (ii) The observed reactivity ratios could be under kinetic, rather than thermodynamic, control. Indeed, Giese reported that the selectivity ratio for G versus GGG significantly increases up to 1:250 in duplexes in which the G and GGG tracts are separated by a single T:A step,[20] thus showing that the observed cleavage ratios must significantly depend on the kinetics of hole transfer.

So far, no direct experimental determinations of the hole site energies for adjacent stacked Gs have been reported. To the best of our knowledge, only thermodynamic data were obtained from time-resolved measurements in short DNA hairpins. For those systems, nonlinear fitting of time-dependent spectroscopical signals led to Gibbs free energy differences for hole transfer from a single G to GG and GGG steps of about 0.052 and 0.077 eV, respectively.[22] Here we report the results of voltammetric measurements on G-rich oligonucleotides, hexamers, and dodecamers, containing up to six consecutive Gs. Differential pulse voltammetry (DPV) measurements proved to be very effective in determining the effects of the pairing of a complementary base on the oxidation potential of guanosine and adenosine in nonprotic solvent[23,24] and, properly integrated by spectroscopic measurements, provided a reliable estimate of the oxidation potential of cytidine in the Watson−Crick complex with guanosine[25] and of the electro-

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chemical properties of adenine (A) dimers.[26] Mostly important, the ability of DPV measurements to determine the effects of π-stacking interactions on the oxidation potentials of stacked rings has been recently demonstrated by Bard and co-workers for poly(fluorenemethylene) oligomers[27] and by some of us, who recently investigated the oxidation of short single-stranded (ss) oligonucleotides containing up to four consecutive adenines, alternated with thymines and cytosines in different sequences and ratios.[28] In both studies, a progressive lowering of the oxidation potential upon increasing the number of stacked units has been observed and reasonably attributed to charge delocalization effects. As in previous works on A-rich oligonucleotides, we will start by considering short oligomers, hexamers in ss configurations, containing only G and T units, because those simple systems should not pose problems in the attribution of the voltammetric signals. We will then consider both hexamers and longer oligomers, dodecamers, in double-stranded (ds) configurations.

EXPERIMENTAL METHODS

Hexamers and dodecamers DG3, DC3, DG6, and DC6 have been purchased from Sigma-Aldrich and used without further purification. The 12mer oligodeoxynucleotides (ODNs), DG2 and DG4, and their respective complementary strands (DC2 and DC4) were prepared by automated synthesis following the phosphoramidite protocol at the 1 μmol scale. After standard deprotection, the crude 5′-DMTr-on ODNs were purified and detritylated on-column by reverse-phase (RP) HPLC. Further purification was carried out by HPLC, and the purified fractions were desalted by RP chromatography on Water SepPakTM-C18-cartridges. The purity of the oligonucleotides was assessed by SAX-HPLC and mass spectrometry by MALDI-TOF in the negative mode (Supporting Information).

Equimolar amounts of complementary strands were annealed in buffer solutions containing 10 mM sodium phosphate, 100 mM NaCl, and 0.1 mM EDTA, pH 7.2. The resulting duplexes were heated to 90 °C for 10 min and allowed to cool slowly to room temperature. The melting curves were determined by monitoring the absorbance of the solutions at 260 nm as a function of the temperature, using a 0.3 °C/min heating rate and the Cary 100 spectrophotometer system equipped with a temperature controller (Supporting Information).

DPV measurements were carried out by using an Autolab PGSTAT302N potentiostat, using positive feedback to compensate for ohmic drop. A standard three-electrode configuration was used, consisting of an ultratrace graphite electrode as working electrode and two Pt bars as counter-electrode and quasi-reference electrode calibrated with the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple.[29] All the electrodes were purchased from Metrohm. All samples were annealed as described above and deaerated before any measurement; fresh solutions were used for each voltammetric measurement. Ultrapure water and phosphate buffer from Aldrich was used throughout.

CD and NMR spectra were recorded using the JASCO J810 spectropolarimeter and the Bruker DRX-600 spectrometer, respectively.

RESULTS AND DISCUSSION

The DPVs of ss-5′-d(TTTGTT)-3′and ss-5′-d(TTGGTT)-3′ (ss-HG1 and ss-HG2), 2 mM in aqueous solution with 20 mM Na phosphate buffer at room temperature, are shown in Figure 1.

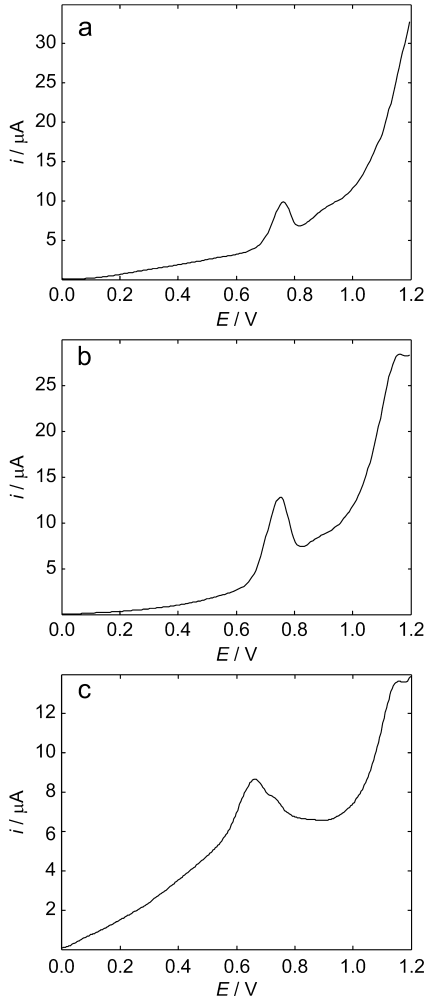

Figure 1. Differential pulse voltammetry of (a) ss-HG1 at T = 298 K, (b) ss-HG2 at T = 298 K, and (c) ss-HG2 at T = 278 K. Scan rate = 10 mV/s, step potential = 2.5 mV.

The DPV of ss-HG1 (Figure 1a) shows a single anodic wave at ca. 0.76 V versus $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, used as external standard, which can be attributed to the oxidation of G. The DPV of ss-HG2 (Figure 1b) shows two peaks, the first one occurring at the same potential as that of ss-HG1, the other at about 1.16 V. The absence of any significant lowering of the oxidation potential of the strand containing two consecutive Gs can be attributed either to the intrinsic smallness of the stacking interaction energy between G units or to the fact that the considered single strands are not highly structured in solution as it instead occurs for those containing adjacent A units.[28] By decreasing the temperature to 278 K, the first anodic wave of ss-HG2 shifts at lower potential (Figure 1c), exhibiting a broader anodic wave at 0.66 V with a pronounced shoulder at 0.75 V, close to the peak potential observed at 298 K. Those results suggest that at lower temperature an appreciable fraction of ss-HG2 assumes a more structured conformation that is characterized by stronger stacking interactions between the two adjacent G bases. The difference between the peak potentials of ss-HG1 and ss-HG2 at 278 K is ca. 0.1 V, which is in reasonable

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agreement with the estimate obtained by time-resolved spectroscopical measurements in short DNA hairpins.[30]

Because of the conformational problems posed by ss-HG2 and the propensity of G-rich single strands to form quadruplex architectures,[31−33] oligomers containing three or more consecutive Gs have been analyzed only in the presence of an equimolar concentration of their complementary strands. The following sequences have been considered: 5′-d(TTGGTT)-3′ (ds-HG2), 5′-d(TGGGGT)-3′ (ds-HG4), and 5′-d(GGGGGG)-3′ (ds-HG6). The formation of duplexes has been checked by CD absorption spectra and melting point analyses, except for ds-HG2, the system with the lowest melting temperature, for which ^{1}H NMR spectra at different temperatures have also been recorded. The CD and UV spectra of all the oligonucleotides are reported in the Supporting Information. As concerns HG2 in the presence of its complementary strand, the ^{1}H NMR spectrum at $T \approx 273$ K shows the characteristic signal at 12.6 ppm, attributed to the formation of the double helix,[34] which as expected disappears at 298 K (Supporting Information). For HG4 and HG6 with equimolar concentration of their complementary strands, melting point analyses indicate the formation of double helix configurations at room temperature, which has also been confirmed by CD spectra. The CD spectrum of 5′-d(TGGGGT)-3′, recorded in the presence of its complementary strand, exhibits a positive signal at about 276 nm and two negative ones at 237 and 212 nm, all typical of double helix coiled DNA. The same also holds for the CD spectrum of HG6 and its complementary strand in an equimolar concentration, which also shows the characteristic features of duplex B-form DNA (Supporting Information).[35] By contrast, the CD spectrum of ss HG4 suggests the presence of quadruplex structures in sodium phosphate buffer at room temperature.[35]

The DPV of ds-HG2 at T = 278 K (Figure 2a) shows two peaks at 0.65 and 1.05 V, which can be attributed to oxidation of GG and of A, respectively, whereas the pronounced shoulder at 0.82 V can be assigned to the oxidation of the ending AA step.[28]

The first anodic wave of ds-HG4 peaks at 0.56 V (Figure 2b). A second peak appears at 0.85 V, and the signal of A oxidation is still at 1.05 V. We assign the first peak of Figure 2b to the oxidation of four π-stacked Gs. Of note is that the observed oxidation potentials are clearly not compatible with the formation of quadruplex structures, inasmuch as oxidation of quadruplexes are shifted at higher potentials than those of ss poly-G sequences.[33]

The DPV of ds-HG6 is shown in Figure 2c; the first anodic wave occurs at 0.47 V, about 0.3 V below the oxidation of a single G. The voltammogram of ds-HG6 also shows a second anodic wave at 0.75 V, whereas the peak of A oxidation, observed at 1.05 V in both ds-HG2 and ds-HG4, disappears, confirming previous assignments.

The above results are further supported by the DPV measurements of ds dodecamers containing up to six consecutive guanines: 5′-d(CGTAT GG TATCG)-3′ (ds-DG2), 5′-d(CGTAT GGG TACG)-3′ (ds-DG3), 5′-d(CGAT GGGG TACG)-3′ (ds-DG4), and 5′-d(CGT GGGGGG TGC)-3′ (ds-DG6). The melting temperatures of those dodecamers are significantly above room temperature: 44.5, 49.2, 54.1, and 61.0 °C, for ds-DG2, ds-DG3, ds-DG4, and ds-DG6, respectively (Supporting Information). The ^{1}H NMR spectra of ds-DG2 and ds-DG4 show in both cases only the signals attributed to the formation of the double helices, ruling out the formation of quadruplexes (Supporting Information).[34] The DPVs of ds dodecamers recorded at room temperature are reported in Figure 3. The first anodic waves of ds-DG2, ds-DG3, ds-DG4, and ds-D6 are peaked at 0.66, 0.61, 0.57, and 0.48 V versus $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, respectively, in very good agreement with those of the hexamers.

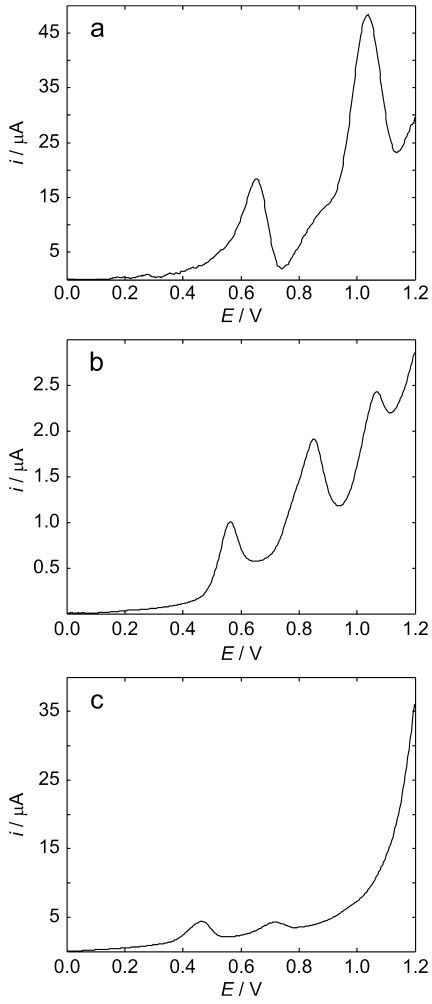

Figure 2. Differential pulse voltammetry at T = 278 K of (a) ds-HG2, (b) ds-HG4, and (c) ds-HG6. Scan rate = 10 mV/s, step potential = 2.5 mV.

CONCLUSIONS

The observed lowering of the oxidation potential upon increasing the number of consecutive Gs in the oligomer sequence is clear-cut experimental evidence of the establishment of delocalized hole domains in G-rich oligonucleotides. The shift of the oxidation potential amounts to ca. 0.1 V for each GG step, significantly lower than that observed and also predicted by computations in ss A-rich oligonucleotides.[28,36,37] However, a direct comparison between the two sets of data could be misleading, inasmuch as single strands are much more flexible than duplexes and could favor the formation of stronger stacking interactions. The existence of delocalized domains is a very important issue not only for understanding mechanistic aspects of long-range HT[6,7,12,38] but also for other applications. Indeed, we have shown that by increasing the number of adjacent Gs in the strand the hole site energies can be lowered up to ∼0.3 V; thus use of consecutive guanines together with

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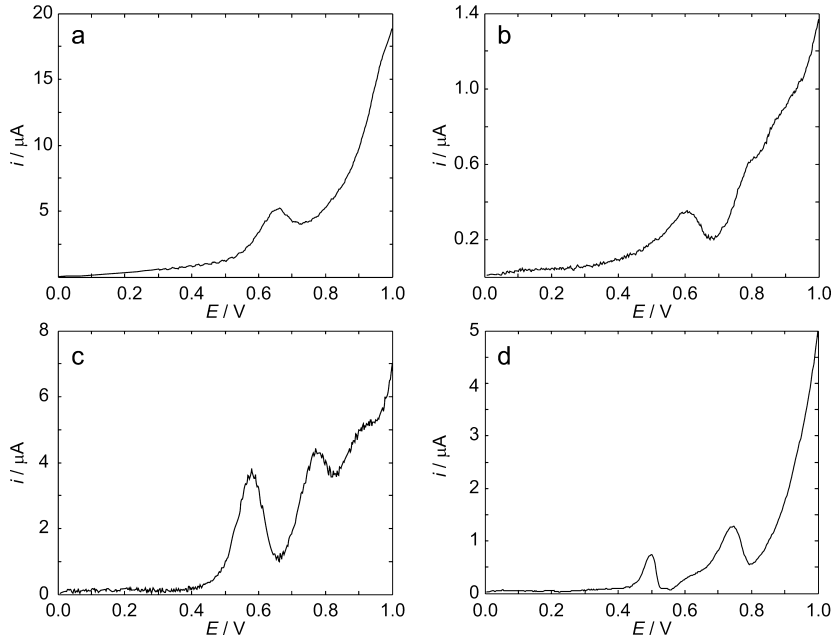

Figure 3. Differential pulse voltammetry of (a) ds-DG2, (b) ds-DG3, (c) ds-DG4, and (d) ds-DG6. Scan rate = 10 mV/s, step potential = 2.5 mV.

the use of modified nucleobases with the same self-assembly properties,[39] could allow for fine-tailoring of DNA electric properties, opening interesting routes in nanoelectronics.[40]

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of nucleotides (Table S1), TOF spectra (Figures S1 and S2), SAX-HPLC chromatograms (Figures S3 and S4), melting point experiments (Figures S5–S10), ^{1}H NMR spectra (Figures S11–S13), and CD spectra (Figures S14–S20). This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. Long-Range Photoinduced Electron Transfer through a DNA Helix. *Science* **1993**, *262*, 1025–1029.

(2) Schuster, G. B. Long-Range Charge Transfer in DNA: Transient Structural Distortions Control the Distance Dependence. *Acc. Chem. Res.* **2000**, *33*, 253–260.

(3) Giese, B. Long Distance Charge Transport in DNA: The Hopping Mechanism. *Acc. Chem. Res.* **2000**, *33*, 631–636.

(4) Lewis, F. D.; Zhu, H.; Daublain, P.; Fiebig, T.; Raytchev, M.; Wang, Q.; Shafirovich, V. Crossover from Superexchange to Hopping as the Mechanism for Photoinduced Charge Transfer in DNA Hairpin Conjugates. *J. Am. Chem. Soc.* **2006**, *128*, 791–800.

(5) Cadet, J.; Douki, T.; Ravanat, J. L. Oxidatively Generated Damage to the Guanine Moiety of DNA: Mechanistic Aspects and Formation in Cells. *Acc. Chem. Res.* **2008**, *41*, 1075–1083.

(6) Kanvah, S.; Joseph, J.; Schuster, G. B.; Barnett, R. N.; Cleveland, C. L.; Landman, U. Oxidation of DNA: Damage to Nucleobases. *Acc. Chem. Res.* **2009**, *43*, 280–287.

(7) Genereux, J. C.; Barton, J. K. Mechanisms for DNA Charge Transport. *Chem. Rev.* **2010**, *110*, 1642–1662.

(8) Kawai, K.; Majima, T. Hole Transfer Kinetics of DNA. *Acc. Chem. Res.* **2013**, *46*, 2616–2625.

(9) Rokhlenko, Y.; Cadet, J.; Geacintov, N. E.; Shafirovich, V. Mechanistic Aspects of Hydration of Guanine Radical Cations in DNA. *J. Am. Chem. Soc.* **2014**, *136*, 5956–5962.

(10) Bixon, M.; Giese, B.; Wessely, S.; Langenbacher, T.; Michel-Beyerle, M. E.; Jortner, J. Long-Range Charge Hopping in DNA. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 11713–11716.

(11) Reanaud, N.; Berlin, Y. A.; Lewis, F. D.; Ratner, M. A. Between Superexchange and Hopping: An Intermediate Charge-Transfer Mechanism in polyA-polyT DNA Hairpins. *J. Am. Chem. Soc.* **2013**, *135*, 3953–3963.

(12) Augustyn, K. E.; Genereux, J. C.; Barton, J. K. Distance-Independent DNA Charge Transport across an Adenine Tract. *Angew. Chem., Int. Ed.* **2007**, *46*, 5731–5733.

(13) Basko, D. M.; Conwell, E. M. Effect of Solvation on Hole Motion in DNA. *Phys. Rev. Lett.* **2002**, *88*, 098102.

(14) Kurnikov, L. V.; Tong, G. S. M.; Madrid, M.; Beratan, D. N. Hole Size and Energetics in Double Helical DNA: Competition between Quantum Delocalization and Solvation Localization. *J. Phys. Chem. B* **2002**, *106*, 7–10.

(15) Kovalsky, O. I.; Panyutin, I. G.; Budowsky, E. I. Sequence-Specificity of Alkali-Sensitive Lesions Induced in DNA by High-Intensity Ultraviolet Laser Radiation. *Photochem. Photobiol.* **1990**, *52*, 509–517.

(16) Saito, I.; Takayama, M.; Sugiyama, H.; Nakatani, K.; Tsuchida, A.; Yamamoto, M. Photoinduced DNA Cleavage via Electron Transfer: Demonstration That Guanine Residues Located 5′ to Guanine Are the Most Electron-Donating Sites. *J. Am. Chem. Soc.* **1995**, *117*, 6406–6407.

DOI: 10.1021/acs.jpcb.5b02940
J. Phys. Chem. B 2015, 119, 5462–5466

(17) Muller, J. G.; Hickerson, R. P.; Perez, R. J.; Burrows, C. J. DNA Damage from Sulfite Autoxidation Catalyzed by a Nickel(II) Peptide. *J. Am. Chem. Soc.* **1997**, *119*, 1501−1506.
(18) Yoshioka, Y.; Kitagawa, Y.; Takano, Y.; Yamaguchi, K.; Nakamura, T.; Saito, I. Experimental and Theoretical Studies on the Selectivity of GGG Triplets toward One-Electron Oxidation in B-Form DNA. *J. Am. Chem. Soc.* **1999**, *121*, 8712−8719.
(19) Hickerson, R. P.; Prat, F.; Muller, J. G.; Foote, C. S.; Burrows, C. J. Sequence and Stacking Dependence of 8-Oxoguanine Oxidation: Comparison of One-Electron vs Singlet Oxygen Mechanisms. *J. Am. Chem. Soc.* **1999**, *121*, 9423−9428.
(20) Giese, B.; Amaudrut, J.; Köhler, A.-K.; Spormann, M.; Wessely, S. Direct Observation of Hole Transfer through DNA by Hopping between Adenine Bases and by Tunneling. *Nature* **2001**, *412*, 318−320.
(21) Sugiyama, H.; Saito, I. Theoretical Studies of GG-Specific Photocleavage of DNA via Electron Transfer: Significant Lowering of Ionization Potential and 5′-Localization of HOMO of Stacked GG Bases in B-form DNA. *J. Am. Chem. Soc.* **1996**, *118*, 7063−7068.
(22) Lewis, F. D.; Liu, X.; Miller, S.; Hayes, R. T.; Wasielewski, M. R. Direct Measurement of Hole Transport Dynamics in DNA. *Nature* **2000**, *406*, 51−53.
(23) Caruso, T.; Carotenuto, M.; Vasca, E.; Peluso, A. Direct Experimental Observation of the Effect of the Base Pairing on the Oxidation Potential of Guanine. *J. Am. Chem. Soc.* **2005**, *127*, 15040−15041.
(24) Caruso, T.; Capobianco, A.; Peluso, A. The Oxidation Potential of Adenosine and Adenosine-Thymidine Base-Pair in Chloroform Solution. *J. Am. Chem. Soc.* **2007**, *129*, 15347−15353.
(25) Capobianco, A.; Carotenuto, M.; Caruso, T.; Peluso, A. The Charge-Transfer Band of an Oxidized Watson-Crick Guanosine-Cytidine Complex. *Angew. Chem., Int. Ed.* **2009**, *48*, 9526−9528.
(26) Capobianco, A.; Caruso, T.; Celentano, M.; La Rocca, M. V.; Peluso, A. Proton Transfer in Oxidized Adenosine Self-Aggregates. *J. Chem. Phys.* **2013**, *139*, 145101.
(27) Qi, H.; Chang, J.; Abdelwahed, S. H.; Thakur, K.; Rathore, R.; Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence of π-Stacked Poly(fluorenemethylene) Oligomers. Multiple, Interacting Electron Transfers. *J. Am. Chem. Soc.* **2012**, *134*, 16265−16274.
(28) Capobianco, A.; Caruso, T.; Celentano, M.; D'Ursi, A. M.; Scrima, M.; Peluso, A. Stacking Interactions between Adenines in Oxidized Oligonucleotides. *J. Phys. Chem. B* **2013**, *117*, 8947−8953.
(29) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley and Sons, Inc.: New York, 2001; pp 53−54.
(30) Lewis, F. D.; Liu, X.; Liu, J.; Hayes, R. T.; Wasielewski, M. R. Dynamics and Equilibria for Oxidation of G, GG, and GGG Sequences in DNA Hairpins. *J. Am. Chem. Soc.* **2000**, *122*, 12037−12038.
(31) Sen, D.; Gilbert, W. Formation of Parallel Four-Stranded Complexes by Guanine-Rich Motifs in DNA and its Implications for Meiosis. *Nature* **1988**, *334*, 364−366.
(32) Mergny, J. L.; De Cian, A.; Ghelab, A.; Saccà, B.; Lacroix, L. Kinetics of Tetramolecular Quadruplexes. *Nucleic Acids Res.* **2005**, *33*, 81−94.
(33) Chiorcea-Paquim, A.-M.; Santos, P. V.; Eritja, R.; Oliveira-Brett, A. M. Self-Assembled G-Quadruplex Nanostructures: AFM and Voltammetric Characterization. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9117−9124.
(34) Deng, H.; Braunlin, W. H. Duplex to Quadruplex Equilibrium of the Self-Complementary Oligonucleotide d(GGGGCCCC). *Biopolymers* **1995**, *35*, 677−681.
(35) Kypr, J.; Kejnovská, I.; Renčiuk, D.; Vorlíčková, M. Circular Dichroism and Conformational Polymorphism of DNA. *Nucleic Acids Res.* **2009**, *37*, 1713−1725.
(36) Capobianco, A.; Peluso, A. The Oxidization Potential of AA Steps in Single Strand DNA Oligomers. *RSC Adv.* **2014**, *4*, 47887−47893.
(37) Capobianco, A.; Caruso, T.; Peluso, A. Hole Delocalization over Adenine Tracts in Single Stranded DNA Oligonucleotides. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4750−4756.
(38) Borrelli, R.; Capobianco, A.; Peluso, A. Hole Hopping Rates in Single Strand Oligonucleotides. *Chem. Phys.* **2014**, *440*, 25−30.
(39) Kawai, K.; Kodera, H.; Majima, T. Long-Range Charge Transfer through DNA by Replacing Adenine with Diaminopurine. *J. Am. Chem. Soc.* **2010**, *132*, 627−630.
(40) Endres, R. G.; Cox, D. L.; Singh, R. R. P. The Quest for High-Conductance DNA. *Rev. Mod. Phys.* **2004**, *76*, 195−214.

DOI: 10.1021/acs.jpcb.5b02940
J. Phys. Chem. B 2015, 119, 5462−5466