JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Extending Photoinduced Charge Separation Lifetimes by Using Supramolecular Design: Guanine–Perylenediimide G-Quadruplex

Yi-Lin Wu, Kristen E. Brown, and Michael R. Wasielewski*

Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois 60208-3113, United States

S Supporting Information

ABSTRACT: We report here a potassium-induced guanine quadruplex as a supramolecular platform for controlled assembly of electron donor–acceptor systems. A monodisperse, C_4-symmetric octamer of a guanine–perylene-3,4,9,10-bis(dicarboximide) conjugate (**GPDI**) was prepared in tetrahydrofuran. The two layers of cyclic guanine tetramers have the same direction of rotation, and the PDI moiety between the layers adopts a nearly eclipsed relationship (*H*-aggregation), as revealed by small- and wide-angle X-ray scattering, NMR spectroscopy, and steady-state UV/vis absorption. Following photoexcitation of the PDI moiety in the quadruplex, charge separation occurs in τ_{CS} = 98 ± 12 ps to give $G^{+\bullet}$-$PDI^{-\bullet}$ that recombines in τ_{CR} = 1.2 ± 0.2 ns, which is >100 times longer than that in the monomeric **GPDI** dyad. The transient absorption spectrum of $G^{+\bullet}$-$PDI^{-\bullet}$ within the **GPDI** quadruplex suggests the formation of a radical anion delocalized over the neighboring PDI units, and this result is consistent with the more favorable electrochemical reduction potential for PDIs in the quadruplex relative to the monomer.

Controlled assembly of multi-chromophoric systems is essential to solar energy conversion. The well-positioned chromophores and optimized energy and electron-transfer cascades in natural photosynthetic systems result in efficient light-harvesting and long-lived charge separation (CS),[1] features which have been the inspiration for designing artificial photosynthetic systems.[2] For example, the use of spatially organized electron donor and acceptor conduits in organic photovoltaics could provide independent channels for efficient exciton and charge transport.[3] The development of easily tailorable scaffolds for multi-chromophore organization and photophysical studies of the energy- and charge-transfer dynamics in such systems can provide insight into how factors such as geometry, energetics, and environment modulate these photoconversion processes.

Supramolecular organization has been recognized as a primary strategy for assembling molecules into nanometer-sized structures for long-distance charge transport.[4] We have previously utilized the strong π–π stacking tendency of planar polyaromatic hydrocarbons to furnish self-assembled donor–acceptor (D-A) aggregates that exhibit photoinduced CS over the non-covalently associated chromophore units.[5] A fine balance between solubility and intermolecular association was struck for these systems, leading to narrowly disperse aggregates as suggested by X-ray scattering experiments. The π–π stacking abilities of D-A chromophores, especially common for those with highly symmetric core motifs, could afford a core–shell columnar aggregate with segregated charge conduits for hole and electron transport (Figure 1a).[6]

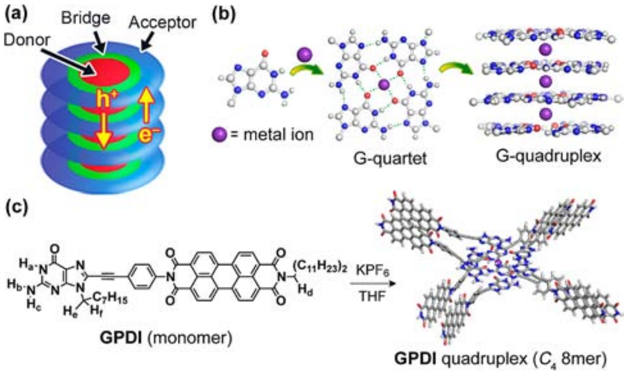

Figure 1. (a) Independent hole (h^+) and electron (e^-) transport in a core–shell columnar assembly of donor–bridge–acceptor molecules. (b) Cation-induced formation of a guanine (G)-quartet and a G-quadruplex. (c) A C_4-symmetric G-quadruplex based on the **GPDI** conjugate. Aliphatic substituents in the quadruplex are omitted for clarity.

Cation-induced guanine quadruplexes,[7] often found in G-rich DNA and RNA sequences, could be exploited to furnish this columnar architecture. Driven by synergistic cation–dipole, π–π, and Coulombic interactions, derivatives of guanine in the presence of metal cations form H-bonded cyclic tetramers (G-quartets), which stack into higher 8-, 16-, or 24-mers (G-quadruplexes, Figure 1b), depending on the salts and solvents of choice.[8] Recently, guanines functionalized with π-chromophores have attracted attention for making well-defined supramolecular assemblies. G-quadruplexes with porphyrins, pyrenes, oligophenylenevinylenes, oligo-thiophenes, and nitroxyl radicals have been reported,[9] but little is known about their photophysics and excited-state dynamics, especially with regard to charge separation and transport.

In addition to being a structural motif that directs G-quadruplex formation, when functionalized with electron-accepting units on the periphery, the electron-rich guanines[10] are suitable electron donors in photoinduced electron-transfer

Received: July 24, 2013
Published: August 27, 2013

dx.doi.org/10.1021/ja407648d | *J. Am. Chem. Soc.* 2013, 135, 13322–13325

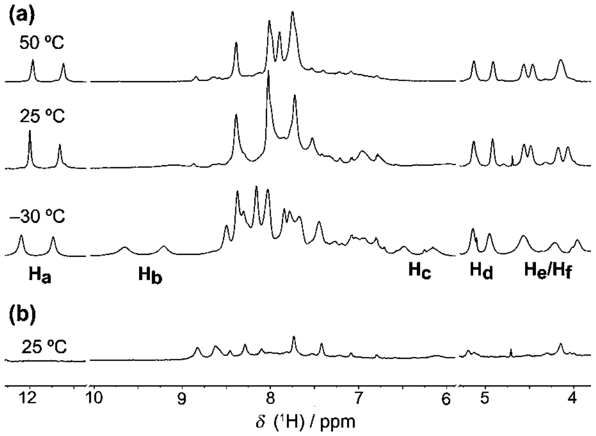

Figure 2. (a) Partial ^{1}H NMR (600 MHz, THF-d_8) spectra of a **GPDI** quadruplex solution ($c = 3 \times 10^{-3}$ M for **GPDI** + 0.25 equiv of KPF_6); temperatures are indicated at the left and the signal assignments given according to the ^{1}H-labeling in Figure 1c. (b) Partial ^{1}H NMR (600 MHz, THF-d_8, 25 °C) spectrum of a saturated solution of **GPDI** ($c < 3 \times 10^{-3}$ M).

(PET) processes, analogous to their role as hole traps in DNA charge transfer.[11] Two recent reports on PET from G-quadruplex-containing DNAs to the covalently linked thymine dimer[12a] or riboflavin[12b] suggested the promise of employing a G-quadruplex as a supramolecular electron donor in self-assembled multi-chromophoric systems. Furthermore, given that the size of G-quadruplexes can be controlled using metal ion coordination, PET rates within a monomeric D-A system can be compared directly to those in specific monodisperse $\pi-\pi$ stacked D-A aggregates.

With perylene-3,4:9,10-bis(dicarboximide) (PDI) as the peripheral electron acceptor, a structurally defined G-quadruplex based on a lipophilic guanine−PDI conjugate (**GPDI**) is presented in this work (Figure 1c). Small- and wide-angle X-ray scattering (SAXS/WAXS), UV/vis absorption, and NMR (including DOSY experiments) were utilized to examine the size and geometry of this monodisperse aggregate. Femtosecond transient absorption spectroscopy reveals a much longer-lived CS lifetime in the **GPDI** quadruplex than in the monomeric **GPDI** dyad.

Sonogashira coupling between 8-ethynylated guanine and *N*-iodophenyl PDI furnished **GPDI** in this work (see the Supporting Information (SI) for synthetic details). The molecule is monomeric in dilute tetrahydrofuran (THF) solution ($c \approx 10^{-4}-10^{-5}$ M), suggested by the relative intensities of the 0−0 and 0−1 vibronic transitions of PDI ($A_{0\text{-}0}$ and $A_{0\text{-}1}$, respectively; see also the SI).[13] Addition of potassium hexafluorophosphate to this dilute solution resulted in a slight reduction of the ratio of $A_{0\text{-}0}/A_{0\text{-}1}$, consistent with *H*-aggregation of the PDI moieties induced by K^+.

While most of the **GPDI** remains monomeric in dilute THF solution with added K^+ (according to X-ray scattering and transient absorption spectroscopy; data not shown), homogeneous and monodisperse G-quadruplexes were found in a solution of millimolar concentration ($c_{\mathbf{GPDI}} = 3 \times 10^{-3}$ M in THF-d_8, with 0.25 equiv of KPF_6). Two sets of amido (H_a), amino (H_b and H_c), and N^9-methylene (H_e and H_f) guanine proton signals of equal intensities were observed in the temperature range from −30 to 50 °C by ^{1}H NMR spectroscopy (Figure 2a). This pattern is consistent with C_4-symmetric 8-mers or D_4-symmetric 16-mers[8,14] and suggests the strong association

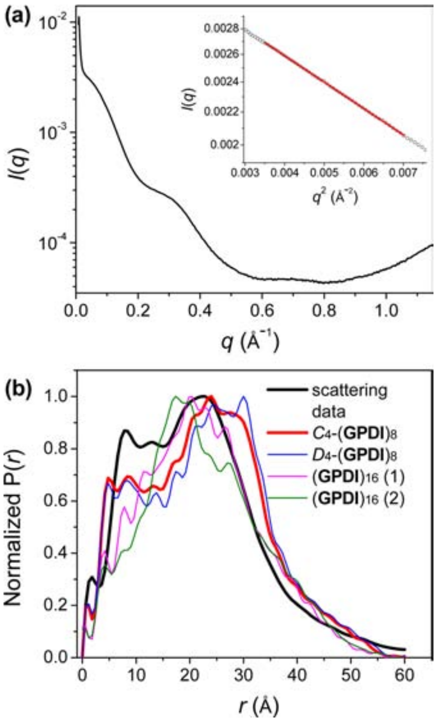

Figure 3. (a) SAXS/WAXS data of **GPDI** (3×10^{-3} M + 0.25 equiv of KPF_6) in THF. Inset shows the Guinier fit of the SAXS data; radius of gyration $R_g = 15.13 \pm 0.01$ Å. (b) Comparison of the pair distribution functions generated from the scattering data with those from the structural models.

of the **GPDI** quadruplex. In contrast, only unresolved signals were observed from the saturated solution in the absence of K^+ ($c < 3 \times 10^{-3}$ M in THF-d_8; Figure 2b). Diffusion-ordered NMR spectroscopy (DOSY) experiments (Bruker *dstebpgp3s* pulse program,[15] 600 MHz, 25 °C; SI) revealed the diffusion coefficient of this G-quadruplex ($D_{(\mathbf{GPDI})_n}$) to be 14 ± 1 times smaller than D_{TMS} (TMS = tetramethylsilane), indicating the presence of a supramolecular species. Using these data, the estimated hydrodynamic radius (R_h) is $R_{(\mathbf{GPDI})_n} = R_{TMS}[D_{TMS}/D_{(\mathbf{GPDI})_n}] \approx 29$ Å ($R_{TMS} = 2.1$ Å).[8]

SAXS/WAXS experiments on the **GPDI** quadruplex,[16] in conjunction with modeling by molecular mechanics[17] (MMFF94s for the K^+-free geometries first, followed by UFF for the K^+-included full structures), provide the supramolecular structure at a resolution of a few angstroms. Figure 3a shows a plot of the logarithm of the scattering intensity $[I(q)]$ vs the modulus of the scattering vector ($q = (4\pi \sin \theta)/\lambda$, where λ is the X-ray wavelength and 2θ the scattering angle). Guinier analysis[18] at the low q region (0.059−0.083 Å^{-1}) gives the radius of gyration $R_g = 15.13 \pm 0.01$ Å of the aggregates (Figure 3a, inset). The smaller value for R_g relative to R_h is partly due to the low scattering contrast between the solvent and the flexible alkyl chains on the periphery of the G-quadruplex, and is consistent with the size of the **GPDI** aromatic unit in each cyclic G-quartet according to modeling (see the SI).

The atomic pair-distance distribution function (PDF) based on the experimental $I(q)$ at $q = 0-1.15$ Å^{-1} and PDFs based on the C_4-$(\mathbf{GPDI})_8$, D_4-$(\mathbf{GPDI})_8$, and two $(\mathbf{GPDI})_{16}$ structural models were constructed by GNOM[19] and are overlaid in Figure 3b for comparison (see the SI for the geometries of these G-quadruplexes). The PDF from the scattering data shows the highest probability density around 22 Å and slightly lower probability between 8 and 13 Å. Additionally, a spike at 1.7 Å and some residual probability from 40 to 60 Å were noticed. All these features were qualitatively captured by the PDFs of the two $(\mathbf{GPDI})_8$ isomers, whereas the larger quadruplexes $(\mathbf{GPDI})_{16}$ share a similar, skewed and bell-shaped PDFs peaking around 18 Å. In another words, the shape of the PDF is more sensitive to the number of G-quartets as opposed to the relative rotation direction of each G-quartet layer; the bell-shaped profiles for the two 16-mers reflect more spherical geometries overall. The D_4-symmetric 8-mer, however, is ruled out on the basis of the observed ^{1}H NMR pattern (see above). Therefore, the **GPDI** aggregates in the presence of KPF_6 in THF are best described as C_4-symmetric 8-mers $[C_4\text{-}(\mathbf{GPDI})_8]$, based on both the NMR and SAXS/WAXS studies.

Examining the **GPDI** solutions in the absence or presence of K^+ enables comparisons to be made between the properties of the monomer and the G-quadruplex. The kinetics of photo-induced CS were measured using femtosecond transient absorption spectroscopy[20] (SI). The monomeric sample was excited with 525 nm, 0.5 μJ, ~60 fs pulses, ensuring selective excitation of PDI. The G-quadruplex was excited with 470 nm pulses to avoid laser scatter and allow observation of the positive feature at 520 nm. Additionally, the per-pulse energy was limited to 80 nJ to mitigate singlet−singlet annihilation, a common occurrence in multi-chromophore arrays. Excitation of the monomeric **GPDI** solution in THF resulted in instrument-limited ground-state bleaching at 487 and 525 nm, stimulated emission at 573 nm, and a positive feature corresponding to the PDI excited-state absorption at 705 nm (Figure 4a). The kinetics of these transient features were fit with a monoexponential decay function convoluted with a Gaussian instrument response function of 200 fs. A decay time constant of $\tau = 13 \pm 1$ ps was obtained at all the wavelengths mentioned above, suggesting that charge recombination (CR) for monomeric **GPDI** is faster than the forward CS (i.e., inverted kinetics; $\tau_{CR} \ll \tau_{CS} \approx 13$ ps).

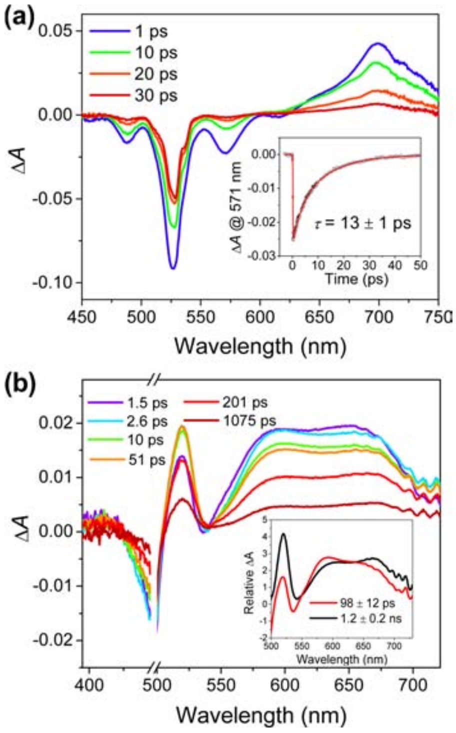

Figure 4. Femtosecond time-resolved absorption spectra of (a) monomeric **GPDI** ($c \approx 10^{-5}$ M) and (b) **GPDI** quadruplex (3×10^{-3} M + 0.25 equiv of KPF_6) in THF. Insets: (a) kinetic fit at 571 nm of **GPDI** and (b) principal kinetic components and decay-associated spectra of **GPDI**-quadruplex.

Excitation of $(\mathbf{GPDI})_8$ gives rise to a broad absorption at 550−700 nm (Figure 4b), which consists of two principal components revealed by global fitting and singular value decomposition. The shorter-time component of $\tau_{CS} = 98 \pm 12$ ps is associated with the decay of the excimer-like state of PDI that leads to CS. The second feature, which decays in $\tau_{CR} = 1.2 \pm 0.2$ ns, is slightly red-shifted and characteristic of a PDI radical anion shared (and stabilized) by interaction with neighboring PDIs.[5b,21] Comparison between **GPDI** and $(\mathbf{GPDI})_8$ clearly demonstrates the influence of self-assembly on the increased lifetime of the charge-separated state ($G^{+\bullet}$-$PDI^{-\bullet}$) in the G-quadruplex.

The distinctly different excited-state dynamics of the **GPDI** monomer and quadruplex could in part be attributed to the better hole-trapping ability of the G-quartet unit. It was suggested by Choi et al. that the photogenerated radical cation could delocalize over the H-bonded G-quartets;[12b] however, we were unable to observe oxidation waves less positive than the THF-imposed limit of ~1.2 V vs SCE in our electrochemical measurements, which prevented us from testing this hypothesis.[22] Instead, the first reduction of $(\mathbf{GPDI})_8$ quadruplex was found to occur about 100 mV more positive compared to the monomer.

Using cyclic voltammetry (0.1 M $n\mathrm{Bu_4NPF_6}$ in THF), the reduction of monomeric **GPDI** to the monoanion and dianion states occurs at −0.5 and −0.8 V vs SCE, respectively. For $(\mathbf{GPDI})_8$ quadruplex, two reversible reduction waves were observed at −0.41 and −0.52 V in the scan window from 0 to −0.7 V (−0.38 and −0.50 V by differential pulse voltammetry). Scanning beyond this range reveals reduction waves at −0.91 and −1.68 V, and on reversal, re-oxidation waves appear at −1.67 and −1.33 V (SI).[23] The first two reversible waves can be tentatively attributed to one-electron reductions of two different sets of PDIs and the latter irreversible waves, possibly involving dissociation of the G-quadruplex (due to electrostatic repulsion), to the further reduction of the monoanions of the PDI moieties.

Although information about the oxidation potential of the **GPDI** quadruplex cannot be provided in our current study, the greater ease with which the **GPDI** quadruplex is reduced relative to the monomer suggests a difference in the thermodynamic driving force for photoinduced CS and CR between the monomer and G-quadruplex of **GPDI**. Such a change is likely caused by the stabilization of hole and electron by the neighboring chromophore units in G-quadruplexes, consistent with the broad transient absorption of $PDI^{-\bullet}$ observed by femtosecond transient absorption and the reduced ionization potential of stacked guanines suggested by Cauët[24a] and Saito and co-workers.[24b]

The extended CS lifetime in the **GPDI** quadruplex following photoexcitation demonstrates that the easily functionalizable scaffold of G-quadruplexes provides an interesting and potentially useful platform for organization of D-A chromophores. Photophysical and electrochemical measurements suggest that charge delocalization or hopping occurs in the non-covalently linked aggregate, implying possible applications for organic photovoltaics. The detailed mechanism of delocalization or hopping for each charge carrier through the π-stack, within the quartet layer, or both, is especially interesting and will be investigated on quadruplexes of guanine-based triad chromophores, where nano- to microsecond CS lifetimes are expected, allowing for time-resolved EPR measurements. These studies should also provide information on the role of guanine $\pi-\pi$ stacks in DNA charge transport or in cathodic protection of genes.

ASSOCIATED CONTENT

Supporting Information

Experimental details including synthesis, DOSY, SAXS/WAXS, transient absorption, and electrochemistry experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

m-wasielewski@northwestern.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, DOE under grant no. DE-FG02-99ER14999. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. The authors thank L. E. Shoer and S. W. Eaton (Northwestern) for acquiring the SAXS/WAXS data, and Dr. R. M. Young (Northwestern) for his help with the fs-transient absorption experiments and for helpful discussions. Y.-L.W. is grateful for the fellowship for prospective researchers from the Swiss National Science Foundation (PBEZP2-140153).

REFERENCES

(1) (a) Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S. *Science* **2004**, *303*, 1831. (b) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517.

(2) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (c) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, *35*, 57. (d) Guldi, D. M. *J. Phys. Chem. B* **2005**, *109*, 11432.

(3) (a) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. *Science* **2012**, *335*, 1340. (b) Baumann, A.; Savenije, T. J.; Murthy, D. H. K.; Heeney, M.; Dyakonov, V.; Deibel, C. *Adv. Funct. Mater.* **2011**, *21*, 1687. (c) van Duren, J. K. J.; Yang, X. N.; Loos, J.; Bulle-Lieuwma, C. W. T.; Sieval, A. B.; Hummelen, J. C.; Janssen, R. A. J. *Adv. Funct. Mater.* **2004**, *14*, 425. (d) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533. (e) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (f) Lindner, S. M.; Hüttner, S.; Chiche, A.; Thelakkat, M.; Krausch, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3364.

(4) (a) Wasielewski, M. R. *Acc. Chem. Res.* **2009**, *42*, 1910. (b) Wasielewski, M. R. *J. Org. Chem.* **2006**, *71*, 5051. (c) Frischmann, P. D.; Mahata, K.; Würthner, F. *Chem. Soc. Rev.* **2013**, *42*, 1847−1870.

(5) (a) Bullock, J. E.; Carmieli, R.; Mickley, S. M.; Vura-Weis, J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2009**, *131*, 11919−11929. (b) Bullock, J. E.; Kelley, R. F.; Wasielewski, M. R. *PMSE Prepr.* **2007**, *96*, 805.

(6) (a) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832. (b) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491. (c) Warman, J. M.; Piris, J.; Pisula, W.; Kastler, M.; Wasserfallen, D.; Müllen, K. *J. Am. Chem. Soc.* **2005**, *127*, 14257. (d) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.

(7) (a) Davis, J. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 668. (b) Davis, J. T.; Spada, G. P. *Chem. Soc. Rev.* **2007**, *36*, 296. (c) Lena, S.; Masiero, S.; Pieraccini, S.; Spada, G. P. *Chem.—Eur. J.* **2009**, *15*, 7792.

(8) González-Rodríguez, D.; van Dongen, J. L. J.; Lutz, M.; Spek, A. L.; Schenning, A. P. H. J.; Meijer, E. W. *Nat. Chem.* **2009**, *1*, 151.

(9) (a) González-Rodríguez, D.; Janssen, P. G. A.; Martín-Rapún, R.; De Cat, I.; De Feyter, S.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2010**, *132*, 4710. (b) Graziano, C.; Masiero, S.; Pieraccini, S.; Lucarini, M.; Spada, G. P. *Org. Lett.* **2008**, *10*, 1739. (c) Martić, S.; Liu, X.; Wang, S.; Wu, G. *Chem.—Eur. J.* **2008**, *14*, 1196. (d) Masiero, S.; Gottarelli, G.; Pieraccini, S. *Chem. Commun.* **2000**, 1995. (e) Okamoto, A.; Inasaki, T.; Saito, I. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3415. (f) Spada, G. P.; Lena, S.; Masiero, S.; Pieraccini, S.; Surin, M.; Samori, P. *Adv. Mater.* **2008**, *20*, 2433.

(10) (a) Paleček, E.; Bartošík, M. *Chem. Rev.* **2012**, *112*, 3427. (b) Seidel, C. A. M.; Schulz, A.; Sauer, M. H. M. *J. Phys. Chem.* **1996**, *100*, 5541.

(11) (a) Genereux, J. C.; Barton, J. K. *Chem. Rev.* **2010**, *110*, 1642. (b) Lewis, F. D.; Liu, X.; Liu, J.; Hayes, R. T.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12037. (c) Conwell, E. M.; Bloch, S. M. *J. Phys. Chem. B* **2006**, *110*, 5801. (d) Zeidan, T. A.; Carmieli, R.; Kelley, R. F.; Wilson, T. M.; Lewis, F. D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 13945. (e) Lewis, F. D.; Thazhathveetil, A. K.; Zeidan, T. A.; Vura-Weis, J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2010**, *132*, 444.

(12) (a) Chinnapen, D. J.-F.; Sen, D. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 65. (b) Choi, J.; Park, J.; Tanaka, A.; Park, M. J.; Jang, Y. J.; Fujitsuka, M.; Kim, S. K.; Majima, T. *Angew. Chem., Int. Ed.* **2012**, *52*, 1134.

(13) Spano, F. C. *Acc. Chem. Res.* **2010**, *43*, 429.

(14) Masiero, S.; Trotta, R.; Pieraccini, S.; De Tito, S.; Perone, R.; Randazzo, A.; Spada, G. P. *Org. Biomol. Chem.* **2010**, *8*, 2683.

(15) (a) Jerschow, A.; Müller, N. *J. Magn. Reson.* **1997**, *125*, 372. (b) Jerschow, A.; Müller, N. *J. Magn. Reson.* **1998**, *132*, 13.

(16) (a) Mariani, P.; Spinozzi, F.; Federiconi, F.; Amenitsch, H.; Spindler, L.; Drevensek-Olenik, I. *J. Phys. Chem. B* **2009**, *113*, 7934–. (b) Mariani, P.; Spinozzi, F.; Federiconi, F.; Ortore, M. G.; Amenitsch, H.; Spindler, L.; Drevensek-Olenik, I. *J. Nucleic Acids* **2010**, *2010*, 472478. (c) Gonnelli, A.; Ortore, M. G.; Baldassarri, E. J.; Spada, G. P.; Pieraccini, S.; Perone, R. C.; Funari, S. S.; Mariani, P. *J. Phys. Chem. B* **2013**, *117*, 1095.

(17) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. *J. Cheminf.* **2012**, *4*, 17.

(18) Guinier, A.; Fournet, G. *Small-angle scattering of X-rays*; Wiley: New York, 1955.

(19) Svergun, D. I. *J. Appl. Crystallogr.* **1992**, *25*, 495−503.

(20) Brown, K. E.; Veldkamp, B. S.; Co, D. T.; Wasielewski, M. R. *J. Phys. Chem. Lett.* **2012**, *3*, 2362.

(21) (a) van der Boom, T.; Hayes, R. T.; Zhao, Y.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 9582. (b) Tauber, M. J.; Kelley, R. F.; Giaimo, J. M.; Rybtchinski, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 1782. (c) Rybtchinski, B.; Sinks, L. E.; Wasielewski, M. R. *J. Phys. Chem. A* **2004**, *108*, 7497.

(22) A recent electrochemistry study on G-rich oligodeoxynucleotides showed that the K^+-free oligonucleotides are more easily oxidized than the K^+-added samples. However, the large quantity of Na^+ in the buffer solutions could trigger the formation of G-quadruplexes in both samples and thus complicate the comparison. See: Chiorcea-Paquim, A.-M.; Santos, P. V.; Eritja, R.; Oliveira-Brett, A. M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9117.

(23) One (or more) of these high-energy events might be related to the reduction of guanine units. See also ref 10a.

(24) (a) Cauët, E. *J. Biomol. Struct. Dyn.* **2011**, *29*, 557. (b) Yoshioka, Y.; Kitagawa, Y.; Takano, Y.; Yamaguchi, K.; Nakamura, T.; Saito, I. *J. Am. Chem. Soc.* **1999**, *121*, 8712.