Electron Conduits

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Electron Hopping among Cofacially Stacked Perylenediimides Assembled by Using DNA Hairpins**

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The self-assembly of redox-active molecules into ordered arrays capable of rapid, long-distance charge transport is important for the development of functional nanomaterials for organic electronics. In this regard, DNA shows great promise as a structural scaffold for the helical arrangement of chromophores and other (semi)conducting materials.[1–3] Base substitutions and modifications, sugar modifications, and noncovalent interactions have all been used for the construction of such DNA-based structures. Perylenediimides (PDIs), which have the advantages of strong absorptivity, high fluorescence quantum yields, high photochemical and thermal stability, strong hydrophobic π–π stacking interactions, and semiconducting properties, have been incorporated in a variety of structures.[4–16] Recently, Wagner and Wagenknecht[10] reported the preparation of a PDI derivative, **P** (Figure 1), which is readily incorporated into an oligonucleotide and serves as a base-pair surrogate when located opposite an abasic site in a duplex structure. The incorporation of **P** in opposite complementary oligonucleotides has been shown to result in the formation of stable duplexes in which the **P** units are located in a zipperlike fashion within the hydrophobic interior of the resulting duplex.[5,17] The stacking of **P** units within the duplex resulted in an excimer-like state following photoexcitation.[16]

We report herein the results of our investigation of intramolecular electron hopping within a series of synthetic DNA hairpins **1**–**4** (Figure 1). These hairpins possess compact 3′-CCA loop regions connecting poly(T)–poly(A) stems containing a single **P** moiety located opposite an abasic site (**1**), two **P** moieties located opposite abasic sites and attached either to the same strand (in **2s**) or to opposite strands (in **2o**), or three or four **P** moieties positioned adjacent to one another but on opposite strands in a zipperlike fashion (in **3** and **4**). The EPR spectra of the singly reduced duplexes were consistent with electron hopping between two sites in both dimers (the hairpins containing two **P** moieties) and the trimer **3**, and among three sites in the tetramer **4**. Herein, we discuss the origin and implications of partial electron sharing.

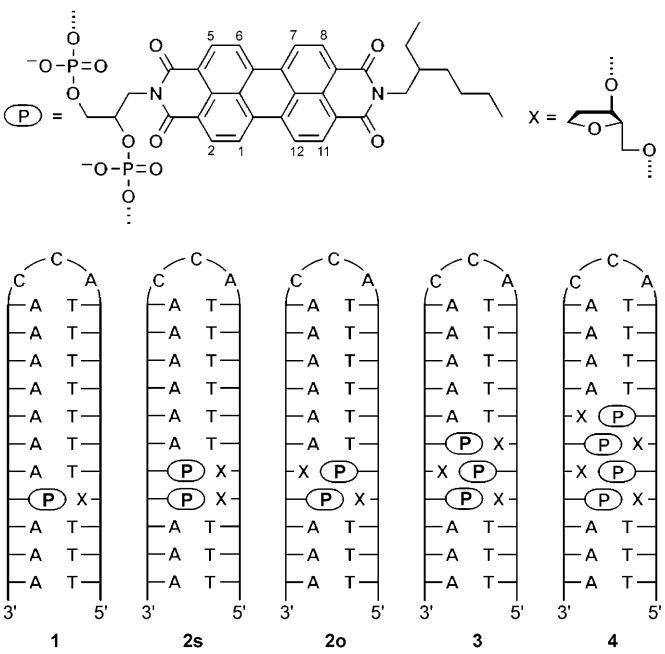

Figure 1. DNA hairpin structures.

Oligonucleotides containing **P** were synthesized by the method of Wagner and Wagenknecht;[10] the CCA linker in hairpins **1**–**4** has been employed previously in the synthesis of stable minihairpins.[13,17,18] The characterization of **1**–**4**, including mass spectrometry and circular dichroism (CD), is described in the Supporting Information.

An intensity reversal was observed in the UV/Vis absorption spectra for the 0→0 and 0→1 transitions in **2**–**4** with respect to those of **1** (Figure 2). This result indicates that the π-stacked **P** chromophores are exciton-coupled.[19–21] Moreover, the $A^{0\rightarrow0}/A^{0\rightarrow1}$ ratio for the vibronic bands decreased as the number of **P** units increased, and there was a notable difference between dimers **2s** and **2o**, presumably as a result of the conformational changes imposed by the attachment of the two **P** units to either one strand or opposite strands within the duplex. Upon the partial chemical reduction of **P** with sodium dithionite, peaks corresponding to the radical anion appeared at 727, 815, and 980 nm, whereas the vibronic progression in the visible region decreased in intensity (see Figure S1 in the Supporting Information). The

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degree of reduction was maintained well under 50, 33, and 25% for the dimers, trimer, and tetramer, respectively, to ensure that each duplex contained a single $\mathbf{P}^{\bullet-}$ unit.

The EPR spectra of $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ at 290 K (Figure 3) exhibited Gaussian line shapes and were inhomogeneously broadened into single unresolved lines owing to the large number of electron–nuclear hyperfine interactions within each molecule, except for the spectrum of $\mathbf{1}^{\bullet-}$, in which some of the hyperfine lines were observed. Whereas the spectrum of $\mathbf{1}^{\bullet-}$ was similar to that of other PDI radical anions,[22–24] with an overall peak-to-peak width of 4.4 G, the EPR linewidths, ΔH, of the dimers, trimer, and tetramer were narrower than that of the monomer (Table 1). All radical anions had a measured g factor of 2.0026 ± 0.0001, which is typical for organic aromatic molecules.

The number of sites over which the unpaired electron is shared, either by hopping or delocalization, can be estimated from the narrowing of Gaussian EPR lines on the basis of Equation (1):[25]

$$\Delta H_N = \left(1/\sqrt{N_S}\right)\Delta H_M \quad (1)$$

which relates the linewidth of the monomer, ΔH_M, to the observed linewidth ΔH_N when an unpaired spin is shared over N_S molecular sites. The $\Delta H_M/\Delta H_N$ ratios are reported in Table 1 along with the number of sites N_S over which the charge is shared on the EPR timescale according to Equation (1). This timescale is determined by the hyperfine coupling constants (hfccs) between the unpaired electron spin and the proton nuclear spins of **P** (a_H), such that for typical values of a_H, the charge hopping rate between **P** moieties must exceed about $10^7\ s^{-1}$ for complete EPR line narrowing to be observed. The unpaired spin is fully shared between the two **P** molecules in dimers $\mathbf{2s}^{\bullet-}$ and $\mathbf{2o}^{\bullet-}$. However, the spin is only shared between two **P** moieties in $\mathbf{3}^{\bullet-}$ and among three **P** moieties in $\mathbf{4}^{\bullet-}$.

The number of sites over which a radical ion in a multisite redox system hops or is delocalized can also be determined by second-moment analysis of the EPR lineshape by using a different form of Equation (1):[25,26]

$$\langle \Delta\omega_N^2 \rangle = \frac{1}{N_S}\langle \Delta\omega_M^2 \rangle \quad (2)$$

according to which the second moment of an EPR line for an unpaired spin delocalized over N_S molecular sites, $\langle \Delta\omega_N^2 \rangle$, is proportional to $1/N_S$ times the second moment of the EPR line for the monomer $\mathbf{1}^{\bullet-}$, $\langle \Delta\omega_M^2 \rangle$. The second moments (Table 1) were calculated from the measured first-derivative signals by using Equation (3):

$$\langle \Delta\omega^2 \rangle = \frac{\int_{-\infty}^{\infty} (\omega - \omega_{center})^2 f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} \quad (3)$$

in which ω_{center} is the magnetic field at the center of the band and $f(\omega)$ is the experimentally measured spectrum. The values of N_S determined by using Equation (2) were in agreement with those obtained from Equation (1): $\mathbf{2s}^{\bullet-}$ and $\mathbf{2o}^{\bullet-}$ clearly showed charge sharing between the two **P** moieties, an intermediate value indicative of partial electron sharing between two **P** moieties was found for $\mathbf{3}^{\bullet-}$, and $\mathbf{4}^{\bullet-}$ demonstrated electron sharing among three **P** moieties.

Table 1: EPR data, calculated second moments, and N_S values derived from Equations (1) and (2) for $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$.

Molecule	ΔH [G]	$\Delta H_M/\Delta H_N$	N_S[a]	$\langle \Delta\omega^2 \rangle$	N_S[b]	a_H (1-H, 6-H, 7-H, 12-H) [MHz]	a_H (2-H, 5-H, 8-H, 11-H) [MHz]
$\mathbf{1}^{\bullet-}$	4.4	—	—	4.7	—	4.2	2.8
$\mathbf{2s}^{\bullet-}$	3.0	1.5	2	2.4	2.0	2.9, 2.0	1.5, 1.2
$\mathbf{2o}^{\bullet-}$	3.1	1.4	2	2.5	1.9	2.1	1.3
$\mathbf{3}^{\bullet-}$	3.3	1.3	2	3.0	1.6	3.2, 2.5	1.5
$\mathbf{4}^{\bullet-}$	2.7	1.6	3	1.5	3.1	1.8, 1.5	0.9

[a] Determined from Equation (1) and rounded to the nearest whole number. [b] Determined from Equation (2).

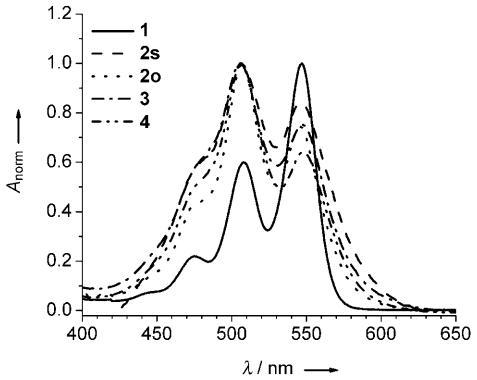

Figure 2. Normalized UV/Vis absorption spectra of neutral compounds **1**–**4**.

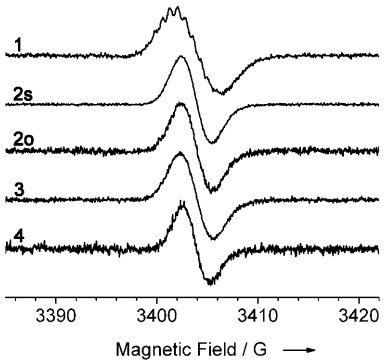

Figure 3. CW EPR spectra of $\mathbf{1}^{\bullet-}$, $\mathbf{2s}^{\bullet-}$, $\mathbf{2o}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, and $\mathbf{4}^{\bullet-}$ (produced by the monoreduction of **1**–**4** with sodium dithionite in TE buffer at 290 K). The microwave power was 0.6 mW with a modulation amplitude of 0.2 G ($\mathbf{1}^{\bullet-}$) or 0.5 G ($\mathbf{2s}^{\bullet-}$, $\mathbf{2o}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, $\mathbf{4}^{\bullet-}$) at 25 kHz.

Isotropic hfccs for $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ were obtained by electron–nuclear double resonance (ENDOR) spectroscopy (Figure 4, Table 1) in liquid TE buffer (composed of 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) and ethylenediaminetetraacetic acid) by using the resonance condition $\nu^{\pm}_{\mathrm{ENDOR}} = |\nu_n \pm {}^{\alpha_H}/_2|$, in which $\nu^{\pm}_{\mathrm{ENDOR}}$ is the ENDOR transition frequency and ν_n is the proton Larmor frequency.[27] The ENDOR spectrum of $\mathbf{1}^{\bullet-}$ exhibits two well-defined line pairs with hfccs of 4.2 MHz (1-H, 6-H, 7-H, 12-H) and 2.8 MHz (2-H, 5-H, 8-H, 11-H). The spectrum is consistent with previously assigned spectra of $PDI^{\bullet-}$ with an unsubstituted perylene core.[23,24] The ENDOR spectrum of $\mathbf{2o}^{\bullet-}$ also has two paired lines, but with splittings of 2.1 and 1.3 MHz, which are just slightly larger than half those observed for the monomer. Thus, electron hopping between the **P** moieties must occur at a rate higher than $10^7\ s^{-1}$. Dimer $\mathbf{2s}^{\bullet-}$ also has hfccs not much larger than those of the monomer, but its spectrum is more complex, with each proton resonance further split. This additional splitting is a common ENDOR spectral feature when $PDI^{\bullet-}$ is asymmetric,[28] and is consistent with the asymmetric environment of the adjacent **P** moieties in **2s**. The ENDOR spectrum of $\mathbf{3}^{\bullet-}$ does not exhibit a reduction in the magnitude of the hfccs by a factor of three relative to $\mathbf{1}^{\bullet-}$. Rather, the spectrum of $\mathbf{3}^{\bullet-}$ has an overall spectral width that is narrower than that observed for the monomer, but broader than that observed in the spectra of the dimers, with indistinct spectral features. This spectrum is in accord with the aforementioned EPR analysis of $\mathbf{3}^{\bullet-}$. The overall spectral width of the ENDOR spectrum of $\mathbf{4}^{\bullet-}$ is 1.8 MHz, clearly narrower than that observed for the dimers, and best fit by dividing the hfccs of the monomer spectrum by three. EPR and ENDOR spectra measured from 275–310 K, in the liquid temperature range and below the DNA melting points, did not exhibit any substantial broadening or other changes with respect to the spectra reported at 290 K.

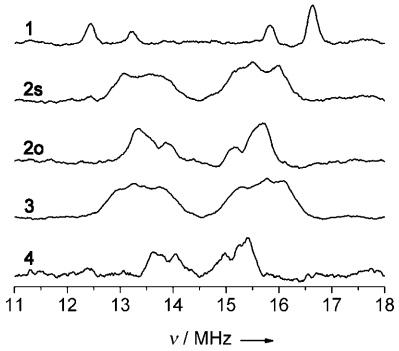

Figure 4. ^{1}H ENDOR spectra of $\mathbf{1}^{\bullet-}$, $\mathbf{2s}^{\bullet-}$, $\mathbf{2o}^{\bullet-}$, $\mathbf{3}^{\bullet-}$, and $\mathbf{4}^{\bullet-}$ (produced by the monoreduction of **1**–**4** with sodium dithionite in TE buffer at 290 K). The microwave power was 20–62 mW, and the radio-frequency power was 240–400 W with frequency modulation at 100 kHz.

Line narrowing in continuous wave (CW) EPR spectra as a result of electron hopping has previously been observed for very large cofacial PDI aggregates.[22,23] In this study we were able to examine the effects of electron hopping in a cofacial PDI system as the oligomer length increased incrementally. When the number of **P** moieties in the hairpins was increased from two to three, hopping was still only observed between no more than two **P** moieties. The rate of charge hopping is frequently limited by counterion movement,[27] but in this case the motion of Na^+ should be rapid. The limited range of charge hopping could result from insufficient similarity of the reduction potentials (LUMO energies) of the three **P** moieties in $\mathbf{3}^{\bullet-}$ to enable thermally activated electron hopping among all three **P** moieties at room temperature.[28,29] In the next-larger system, $\mathbf{4}^{\bullet-}$, electron hopping at a rate above $10^7\ s^{-1}$ was only observed among three of the four **P** moieties. Again, the fact that not all **P** units were involved in electron hopping could be due to a difference in the LUMO energies of the **P** moieties of the tetramer stack. Alternatively, the natural 36° twist between **P** conjugates in B-form DNA,[5] that is, imperfect **P** stacking, could limit the degree of π-orbital overlap between the stacked **P** moieties and thus limit the extent of electron hopping to only two to three **P** moieties. It is also possible that the degree of charge sharing in these systems reflects the extent of charge delocalization in a polaron formed by two to three **P** units. This idea is consistent with the observation that even in non-DNA PDI systems with a much longer aggregation length, CW EPR line narrowing has previously been observed only down to about 2.3 G, the equivalent of three to four PDI units.[22,23] However, the UV/Vis spectra of $\mathbf{2}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ are all very similar to that of $\mathbf{1}^{\bullet-}$ (see Figure S1 in the Supporting Information), so that it is unlikely that the electron is delocalized on the electronic-transition timescale as would be expected for a polaron.

In summary, electron hopping occurs among two to three π-stacked **P** moieties held together in a zipperlike fashion by a B-DNA hairpin scaffold with rates above $10^7\ s^{-1}$, as indicated by EPR and ENDOR spectroscopy. The observed number of sites that the electron visits is similar to that observed in crystalline or self-assembled PDIs that also have a π–π stacking interchromophoric distance of approximately 3.4 Å,[23,24] and may be limited by structural variation between sites. Our results demonstrate the potential of synthetic DNA scaffolds, readily obtainable by using automated synthesis techniques, to promote large-scale ordering and charge transport through the use of redox-active organic molecules with a demonstrated potential for application in organic electronic devices.

Experimental Section

P was prepared by a previously reported method.[10] The synthesis of **2s**, **2o**, **3**, and **4** followed that of **1**.[13] Conjugates were purified by HPLC and characterized by MALDI-TOF mass spectrometry and CD (see the Supporting Information). UV/Vis spectra of reduced species were measured through 1.4 mm I.D. quartz tubes at room temperature. EPR and ENDOR spectra were acquired with a Bruker Elexsys E580 spectrometer (see the Supporting Information).

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[1] T. Carell, C. Behrens, J. Gierlich, *Org. Biomol. Chem.* **2003**, *1*, 2221 – 2228.
[2] R. Varghese, H.-A. Wagenknecht, *Chem. Commun.* **2009**, 2615 – 2624.
[3] J. Wengel, *Org. Biomol. Chem.* **2004**, *2*, 277 – 280.
[4] M. A. Abdalla, J. Bayer, J. O. Rädler, K. Müllen, *Angew. Chem.* **2004**, *116*, 4057 – 4060; *Angew. Chem. Int. Ed.* **2004**, *43*, 3967 – 3970.
[5] D. Baumstark, H.-A. Wagenknecht, *Chem. Eur. J.* **2008**, *14*, 6640 – 6645.
[6] S. Bevers, T. P. O'Dea, L. W. McLaughlin, *J. Am. Chem. Soc.* **1998**, *120*, 11004 – 11005.
[7] S. Bevers, S. Schutte, L. W. McLaughlin, *J. Am. Chem. Soc.* **2000**, *122*, 5905 – 5915.
[8] N. Bouquin, V. L. Malinovskii, R. Haner, *Chem. Commun.* **2008**, 1974 – 1976.
[9] N. Rahe, C. Rinn, T. Carell, *Chem. Commun.* **2003**, 2120 – 2121.
[10] C. Wagner, H.-A. Wagenknecht, *Org. Lett.* **2006**, *8*, 4191 – 4194.
[11] W. Wang, W. Wan, H. H. Zhou, S. Q. Niu, A. D. Q. Li, *J. Am. Chem. Soc.* **2003**, *125*, 5248 – 5249.
[12] Y. Zheng, H. Long, G. C. Schatz, F. D. Lewis, *Chem. Commun.* **2005**, 4795 – 4797; Y. Zheng, H. Long, G. C. Schatz, F. D. Lewis, *Chem. Commun.* **2006**, 3830 – 3832.
[13] T. A. Zeidan, R. Carmieli, R. F. Kelley, T. M. Wilson, F. D. Lewis, M. R. Wasielewski, *J. Am. Chem. Soc.* **2008**, *130*, 13945 – 13955; M. Hariharan, Y. Zheng, H. Long, T. A. Zeidan, G. C. Schatz, J. Vura-Weis, M. R. Wasielewski, X. B. Zuo, D. M. Tiede, F. D. Lewis, *J. Am. Chem. Soc.* **2009**, *131*, 5920 – 5929.
[14] B. A. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 15259 – 15278.
[15] F. Würthner, *Chem. Commun.* **2004**, 1564 – 1579.
[16] D. Baumstark, H.-A. Wagenknecht, *Angew. Chem.* **2008**, *120*, 2652 – 2654; *Angew. Chem. Int. Ed.* **2008**, *47*, 2612 – 2614.
[17] F. D. Lewis, L. G. Zhang, X. Y. Liu, X. B. Zuo, D. M. Tiede, H. Long, G. C. Schatz, *J. Am. Chem. Soc.* **2005**, *127*, 14445 – 14453.
[18] S. Yoshizawa, G. Kawai, K. Watanabe, K. Miura, I. Hirao, *Biochemistry* **1997**, *36*, 4761 – 4767.
[19] J. M. Giaimo, J. V. Lockard, L. E. Sinks, A. M. Scott, T. M. Wilson, M. R. Wasielewski, *J. Phys. Chem. A* **2008**, *112*, 2322 – 2330.
[20] M. Kasha, H. R. Rawles, M. L. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371 – 392.
[21] A. D. Q. Li, W. Wang, L. Q. Wang, *Chem. Eur. J.* **2003**, *9*, 4594 – 4601.
[22] Y. K. Che, A. Datar, X. M. Yang, T. Naddo, J. C. Zhao, L. Zang, *J. Am. Chem. Soc.* **2007**, *129*, 6354 – 6355.
[23] S. G. Chen, H. M. Branz, S. S. Eaton, P. C. Taylor, R. A. Cormier, B. A. Gregg, *J. Phys. Chem. B* **2004**, *108*, 17329 – 17336.
[24] V. A. Ryabinin, V. F. Starichenko, G. N. Vorozhtsov, S. M. Shein, *J. Struct. Chem.* **1979**, *19*, 821 – 823.
[25] J. R. Norris, R. A. Uphaus, H. L. Crespi, J. Katz, *Proc. Natl. Acad. Sci. USA* **1971**, *68*, 625 – 628.
[26] G. Vincow, P. M. Johnson, *J. Chem. Phys.* **1963**, *39*, 1143 – 1153.
[27] H. Kurreck, B. Kirste, W. Lubitz, *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*, VCH, Weinheim, **1988**.
[28] T. M. Wilson, M. J. Tauber, M. R. Wasielewski, *J. Am. Chem. Soc.* **2009**, *131*, 8952 – 8957.
[29] U. Müller, M. Baumgarten, *J. Am. Chem. Soc.* **1995**, *117*, 5840 – 5850.

