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Chain Length Dependence of Energies of Electron and Triplet Polarons in Oligofluorenes

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Abstract

Bimolecular equilibria measured the one-electron reduction potentials and triplet free energies (ΔG°_T) of oligo(9,9-dihexyl)fluorenes and a polymer with lengths of $n=1-10$ and 57 repeat units. Accurate one-electron potentials can be measured electrochemically only for the shorter oligomers. Starting at $n=1$ the free energies change rapidly with increasing length and become constant for lengths longer than the delocalization length. Both the reduction potentials and triplet energies can be understood as the sum of a free energy for a fixed polaron and a positional entropy. The positional entropy increases gradually with length beyond the delocalization length due the possible occupation sites of the charge or the triplet exciton. The results reinforce the view that charges and triplet excitons in conjugated chains exist as polarons and find that positional entropy can replace a popular empirical model of the energetics.

Introduction

The natures of charges and excited states in conjugated oligomers and polymers can determine performance of those molecules in molecular electronics,¹ organic light-emitting

diodes,²⁻³ or organic solar cells.⁴ The redox potentials and excited state energies determined as functions of length for conjugated oligomers provide insight to understand the electron and energy transfer in the conjugated polymers. Charges and excitons do not span the entire lengths of long, conjugated molecules, but to delocalize partly to form polarons.^{5-8, 9, 10-11} As a consequence, we might expect their energies to become constant once the length of the oligomer exceeds the delocalization length of the polaron, and to be identical to those for long polymers. But the redox potentials in such as the oligofluorene⁷ and oligothiophene^{5,8} have been found to change slowly at lengths longer than the delocalization length of the polaron. A linear relation between these redox potentials and $1/n$ has roots related to particles in a 1D boxes has been widely used.^{5, 7-8, 12-19} We propose here an alternate picture, in which the energy of the polaron becomes constant for chain lengths greater than the delocalization length (n_d) while the free energy continues to change slowly due to the positional entropy arising because the polaron can reside at varied positions along the chain.

Entropy in three dimensions may be an important driver of charge separation in organic photovoltaic cells. It may explain, in substantial part, the mystery of how photo-generated electrons and holes escape from each other in these low-dielectric media.²⁰⁻²² Here in the simpler one-dimensional case we test the role of entropy on redox potentials described above through measurements of the reduction potentials and the triplet free energies ΔG°_T of oligo(9,9-dihexyl)fluorene with repeat-unit lengths of 1-10 and 57. Both were determined by bimolecular electron transfer ET or triplet energy transfer (TT) equilibria in solution. It is crucial that this method is capable of measuring *one-electron* reduction potentials for molecules such as F_n ($n=1-10,57$), which are not readily measured by electrochemical techniques for lengths longer than 7.⁷ The results are consistent with the simple picture that the redox potentials and ΔG°_T are sums of the electronic energies and entropic energies from positional entropy. This simple picture can be applied to oligomers, polymers and possibly to their solid films.

Experiments

Samples were prepared under an argon atmosphere in purified THF, toluene, or *p*-xylene and placed in airtight quartz cells with 5 or 20 mm path lengths. THF was purified by a commercial THF purifier (Solvent Purification System, VAC Inc.). Toluene and *p*-xylene were passed through a silica gel column to remove water and impurities. Chemicals were used as received without further purification. Syntheses of oligo(9,9-dihexyl)fluorenes, F_n ($n=1-10,57$), were described previously.²³ For pulse radiolysis, <50 ps, 9 MeV electron pulse was provided by Laser Electron Accelerator Facility²⁴ at Brookhaven National Laboratory. The probe light source is a Xenon arc lamp. The probe wavelengths are selected by optical interference filters with 10 nm band width. The optical detector is a silicon photodiode (EG&G FND-100, 2 ns response time). The signals were collected with LeCroy 8620A, 640Zi, or HRO 66Zi digitizing oscilloscopes.

Results

Electron Transfer Equilibria These experiments used mixtures of a donor (D) and an acceptor (A) in THF solution. D is usually a fluorene oligomer or polymer and A is a molecule with a known redox potential; all will be listed in tables below. Because we seek equilibria the labels D and A are convenient, but interchanging the labels would have no effect. Pulse radiolysis creates solvated electrons which rapidly attach to the solutes. The radiation chemistry in THF is described in Section S1 of the supporting information (SI). In addition to homogeneous electrons the solutes also capture geminate electrons, those inside the Onsager radius,²⁵ to create geminate anions. Geminate anions decay rapidly by recombination with solvated protons created by the THF radical cations²⁶ (Reaction R5 of the SI). Those geminate decays are seen in the first ~100 ns in Figure 1, which gives an example of data used to determine equilibrium constants, K_{eq} . After ~100 ns most anions are homogeneous anions, which recombine much more slowly with solvated protons. Because ionizing radiation ionizes solvent almost exclusively, the yield of ions does not depend on the solute concentration, which are dilute (the samples are >>99% solvent). Thus for each of the three traces in Figure 1 the concentration of anions is the same so K_{eq} is readily evaluated utilizing geminate or homogeneous anions. In practice we evaluated K_{eq} at times >>100 ns where almost all anions are homogeneous. Because the solute concentrations are high enough to capture almost all homogeneous electrons, the concentration of anions is nearly constant from sample to sample. The concentration of the D is typically much greater than that of the A, so most solvated electrons created by pulse radiolysis will attach to the D and then transfer to A, $D^{\bullet-} + A \rightleftharpoons D + A^{\bullet-}$.

The equilibrium constants (K_{eq}), reduction potentials ($E^0(M^{0/-})$), and bimolecular electron transfer rate constants (k_{ET}) were determined from sets of data like those in Figure 1. In this example, trans-stilbene (ES) is the D and F_8 is the A. The experiments determined the ratio of the extinction coefficients between the $ES^{\bullet-}$ and $F_8^{\bullet-}$ at the 710 nm absorption maximum of $ES^{\bullet-}$. Because the concentration of anions is the same in each trace, the ratio of extinction coefficients at 710 nm was readily obtained from the ratio of the ES and F_8 traces. Extinction coefficient ratios found here were consistent with those from Pederson and Zaikowski.^{9, 27} $K_{eq} = [D][A^{\bullet-}]/[D^{\bullet-}][A]$ was determined for mixtures of ES and F_8 from kinetic traces using the ratio of absorbances of $ES^{\bullet-}$, $F_8^{\bullet-}$ at 710 nm and the determined ratio of extinction coefficients. We calculated the free energy change for the electron transfer reaction $\Delta G^\circ = -RT\ln(K_{eq})$. Because $\Delta G^\circ = E^0(F_8^{0/-}) - E^0(M^{0/-})$, $E^0(F_8^{0/-})$ was obtained using $E^0(M^{0/-})$, the known reduction potential for the reference molecule, in this case ES. k_{ET} is determined by observing the slow decays of the $ES^{\bullet-}$ with different F_8 concentrations.

Figure 1. An example of transient absorption at the 710 nm absorption maximum for trans-stilbene anion, $ES^{\bullet-}$, to measure K_{eq} for the electron transfer reaction $ES^{\bullet-} + F_8 \rightleftharpoons ES + F_8^{\bullet-}$ in THF. Decays in the first 100 ns are due to geminate recombination (see text). The kinetic trace for F_8 without stilbene (ES) has been corrected for a small contribution from F_8 triplets. In mixtures, absorption from $ES^{\bullet-}$ decays to a final absorption higher than in 1 mM F_8 alone as equilibrium is established.

To measure the $E^0(F_1^{0/-})$ we used phenanthrene as the reference, and determined K_{eq} from data collected at the 650 nm, absorption maximum of $F_1^{\bullet-}$.²⁸ *Trans*-stilbene (ES) was the reference molecule for $E^0(F_n^{0/-}, n=2-9)$; 1-methylpyrene (MePy) was the reference molecule for $E^0(F_n^{0/-}, n=10,57)$. The K_{eq} were determined from data collected at the absorption maxima of $ES^{\bullet-}$ and $MePy^{\bullet-}$. A potential complication comes from small yields of triplets created by pulse radiolysis. The contributions of triplets was noticed because the time-dependence of their decay is different than that of anions. We quantified their presence by taking spectra and making use of their known extinction coefficients.²⁹⁻³¹ When these triplets absorb at the wavelengths where the anions are measured, they can introduce an error. In samples containing ES, F_n triplets were rapidly removed by triplet energy transfer to ES, which has a lower triplet energy, $\Delta G^\circ_T = 2.137$ eV,³² compared to those for oligofluorenes (see Table 2). This transfer forms ES triplets which do not absorb at 710 nm and which have a very short lifetime (~ 100 ns).³³ In samples without ES, we measured the concentrations of $^3F_n^*$ at their maximum absorption and applied the corrections to the 710 nm data based on measured extinction coefficients of the $^3F_n^*$ at the two wavelengths. The measured K_{eq} and $E^0(F_n^{0/-}, n=1-10,57)$ are given in Table 1.

Table 1. Reduction potentials $E^0(M^{0/-})$, bimolecular electron transfer rate constants k_{ET} , and equilibrium constants K_{eq} for the electron transfer reactions of F_n ($n=1-10,57$).

Name	$E^0(F_n^{0/-})$ vs. $Fc^{0/+}$ (V)	Reactions	$[D]/[A]$ (mM)	k_{ET} ($M^{-1}s^{-1}$) ^b	K_{eq} ^b
F_1	$-3.098(\pm 0.014)^a$	$F_1^{\bullet-} + Phe \rightleftharpoons F_1 + Phe^{\bullet-}$	100/0.062-0.52	1.6×10^{10}	2548(± 1080)
F_2	$-2.818(\pm 0.016)^a$	$Phe^{\bullet-} + F_2 \rightleftharpoons Phe + F_2^{\bullet-}$	20/0.244-1.111	1.4×10^{10}	22(± 8)

		$F_2^{\bullet-} + ES \rightleftharpoons F_2 + ES^{\bullet-}$	30/0.07-0.6	1.0×10^{10}	39(± 11)
F ₃	$-2.642(\pm 0.005)^a$	$ES^{\bullet-} + F_3 \rightleftharpoons ES + F_3^{\bullet-}$	20/0.1-1.85	6.3×10^9	24(± 4)
F ₄	$-2.594(\pm 0.003)^a$	$ES^{\bullet-} + F_4 \rightleftharpoons ES + F_4^{\bullet-}$	20/0.04-0.41	8.6×10^9	161(± 20)
F ₅	$-2.583(\pm 0.008)^a$	$ES^{\bullet-} + F_5 \rightleftharpoons ES + F_5^{\bullet-}$	50/0.2-1.48	9.7×10^9	225(± 71)
F ₆	$-2.572(\pm 0.007)^a$	$ES^{\bullet-} + F_6 \rightleftharpoons ES + F_6^{\bullet-}$	50/0.1-0.74	1.3×10^{10}	366(± 99)
F ₇	$-2.557(\pm 0.006)^a$	$ES^{\bullet-} + F_7 \rightleftharpoons ES + F_7^{\bullet-}$	50/0.1-0.84	2.0×10^{10}	656(± 163)
F ₈	$-2.542(\pm 0.007)^a$	$ES^{\bullet-} + F_8 \rightleftharpoons ES + F_8^{\bullet-}$	50/0.1-0.84	2.2×10^{10}	1191(± 273)
F ₉	$-2.535(\pm 0.010)^a$	$ES^{\bullet-} + F_9 \rightleftharpoons ES + F_9^{\bullet-}$	50/0.05-0.366	3.9×10^{10}	1581(± 525)
F ₁₀	$-2.513(\pm 0.002)^a$	$MePy^{\bullet-} + F_{10} \rightleftharpoons MePy + F_{10}^{\bullet-}$	0.2-7.8/1	1.95×10^{10}	48(± 5)
F ₅₇	$-2.476(\pm 0.002)^d$	$MePy^{\bullet-} + F_{57} \rightleftharpoons MePy + F_{57}^{\bullet-}$	15/0.027-0.12	1.22×10^{11}	202(± 16)
^c MePy	$-2.612(\pm 0.005)^a$	$ES^{\bullet-} + MePy \rightleftharpoons ES + MePy^{\bullet-}$	50/0.83-5.83	1.01×10^{10}	81(± 14)

^aThe reduction potential of *trans*-stilbene, $E^0(ES^{0/-}) = -2.724$ V vs. $Fc^{0/+}$ served as the reference. This value is based on $E^0(ES^{0/-}) - E^0(AC^{0/-}) = -0.22$ V ³⁴ and $E^0(AC^{0/-}) = -2.504$ V vs. $Fc^{0/+}$ in THF (AC=anthracene).³⁵

^b k_{ET} and K_{eq} for electron transfer from $D^{\bullet-}$ to A are the root-mean-square values from 5 different $[D]/[A]$ ratios.

^c1-methylpyrene

^d $E^0(MePy^{0/-}) = -2.600$ V vs. $Fc^{0/+}$ as the reference. This value was measured by the bimolecular equilibria method with *trans*-stilbene as the reference. Like others in the table this measurement was in THF without electrolyte. Thus all the measurements from F₃-pF₅₇ used the same reference, although the phenanthrene reference for F₁ and F₂ used a measurement in THF with electrolyte.

Triplet Absorption Spectra. Pulse radiolysis in non-polar solvents is one of the best ways to produce triplets.³⁶ The radiation chemistry in toluene and *p*-xylene is described in Section S1 of the SI. Figure 2 shows the triplet absorption spectra from pulse radiolysis of F_n ($n=2-6$) in toluene containing 100 mM of biphenyl. The triplet bands shift to longer wavelength until $n=5$. In aromatic solvents (Ar) such as toluene and *p*-xylene, large yields of the $^3Ar^{\bullet}$ and $^1Ar^{\bullet}$ are created by pulse radiolysis via the excitation, charge recombination, and intersystem crossing reactions (SI Reactions R6-R9). While the solvent triplet and singlet excited states are both short-lived (<20 ns), they were both rapidly transferred to biphenyl, which has a long-lived triplet state $\tau = 130$ μs ,³⁷ a high triplet free energy $\Delta G^{\circ}_T = 3.01$ eV,³⁸ and a high triplet yield $\Phi_T = 0.84$,³⁹ so nearly all excited states become biphenyl triplets, which then transfer almost quantitatively to the oligofluorenes or polyfluorene.

Figure 2. The triplet absorption spectra from pulse radiolysis of F_n ($n=2-6$) in toluene with 100 mM of biphenyl.

Triplet Transfer Equilibria With the methods above and 100 mM of the triplet energy donors, naphthalene or biphenyl, we could measure the equilibrium constants $K_{eq} = [D][^3A^*]/[^3D^*][A]$ for triplet energy transfer $^3D^* + A \rightleftharpoons D + ^3A^*$ in a manner analogous to that described above for electron transfer. The lifetime of naphthalene triplet is 175 μs ,⁴⁰ $\Delta G^\circ_T = 2.64$ eV,⁴¹ and $\Phi_T = 0.75$,³⁹ so either naphthalene or biphenyl serves equally well. Figure 2 shows that the triplet absorption spectrum of F_3 is well-separated from those of other oligofluorenes, so triplet transfer to or from F_3 can readily be observed to obtain the K_{eq} and bimolecular triplet transfer rate constant (k_{TT}). Figure 3 shows an example of triplet transfer from $^3F_3^*$ to pF₅₇ to obtain the K_{eq} and k_{TT} . Similar data was used in other reactions. Figure S4 in SI plots spectra for one such reaction. The ΔG°_T of F_n ($n=2,4,5,7,10,57$) with $\Delta G^\circ_T = 2.276$ eV⁴² of FA as the reference are reported in Table 2.

Figure 3. The equilibrium constant (K_{eq}) of the reaction, $^3F_3^* + pF_{57} \rightleftharpoons F_3 + ^3F_{57}^*$, was determined from the kinetic traces of F_3 (5 mM), pF₅₇ (27 μM) and mixtures having $[F_3]/[pF_{57}]$ ratios of 151, 83, 56 and 42 in *p*-xylene with 100 mM of biphenyl at the 650 nm maximum of $^3F_3^*$.

Table 2. Triplet free energy change, ΔG°_T , for forming the lowest triplet excited state, the bimolecular triplet excitation transfer rate constants (k_{TT}), and equilibrium constants (K_{eq}) of triplet energy transfer reactions for F_n ($n=2,4,5,7,10,57$).

Name	ΔG°_T (eV)	Reactions	[D]/[A] (mM)	k_{TT} ($M^{-1}s^{-1}$) ^a	K_{eq} ^a
F ₁	2.94 ¹⁷				
F ₂	2.411 ^d	$^3F_2^* + F_3 \rightleftharpoons F_2 + ^3F_3^*$	20/1	2.2×10^8	41.14 ^b
F ₃	2.316(± 0.004) ^d	$^3F_3^* + FA \rightleftharpoons F_3 + ^3FA^*$	1/0.04-0.20	8.69×10^8	4.78(± 0.71) ^c
F ₄	2.288 ^d	$^3F_3^* + F_4 \rightleftharpoons F_3 + ^3F_4^*$	8.5/0.85	1.2×10^8	2.93 ^b
F ₅	2.263 ^d	$^3F_3^* + F_5 \rightleftharpoons F_3 + ^3F_5^*$	8.85/1.93	1.5×10^8	8.07 ^b
F ₇	2.237(± 0.009) ^d	$^3F_3^* + F_7 \rightleftharpoons F_3 + ^3F_7^*$	0.26/0.06-0.55	4.05×10^8	21.6(± 4) ^c
F ₁₀	2.228(± 0.014) ^d	$^3F_3^* + F_{10} \rightleftharpoons F_3 + ^3F_{10}^*$	0.65/0.05-0.44	4.10×10^8	31(± 10) ^c
F ₅₇	2.178(± 0.024) ^d	$^3F_3^* + F_{57} \rightleftharpoons F_3 + ^3F_{57}^*$	5/0.03-0.11	2.35×10^9	220 ^{c,e}

^a k_{TT} and K_{eq} for triplet energy transfer from D to A. Uncertainties on k_{EXT} are $\pm 20\%$.

^bMeasured in toluene with 100 mM of naphthalene (see text). Uncertainties are $\pm 30\%$

^cMeasured in *p*-xylene with 100 mM of biphenyl (see text) and a root-mean-square values from 5 different [D]/[A] ratios.

^dUsed the $\Delta G^\circ_T = 2.276 \text{ eV}^{42}$ of fluoranthene (FA), determined by an equilibrium method, as the reference (see text).

^e F_3 and pF_{57} triplets decayed at different rates creating larger uncertainties, $K_{eq}=220$ (+200,-100).

Computed Anion and Triplet Energies. Table 3 presents the standard free energy changes and enthalpies for the anions and triplets of F_n ($n=1-10$) computed by the long-range-corrected ω PBE/6-31G(d) ($\omega=0.1 \text{ bohr}^{-1}$) with the SMD solvation model⁴³ for THF. Earlier work found that ω PBE with $\omega=0.1 \text{ bohr}^{-1}$ successfully described excitation energies and delocalization lengths in F_n neutrals and radical anions.⁹ Here we add additional data on anion free energies (redox potentials) and ΔG°_T . In computing the triplets we found that optimization under symmetry constraints resulted in slightly higher triplet energies for $^3F_n^*$ for $n = \text{odd}$ than for $n = \text{even}$ (see Table S2); these energies are the computed electronic energy differences between the optimized ground and lowest triplet-excited states. The optimized structures found in the computations on triplets contained two nearly-coplanar repeat units. F_n with odd n , like F_3 , cannot have symmetric structures with two nearly coplanar fluorenes, and a larger dihedral for the third. The calculations for both anions and triplets were therefore performed with symmetry disabled.

Computed estimations of the standard free energy for the anion or triplet formation were obtained from frequency calculations performed by Gaussian 09 D.1;⁴⁴ these standard free energies do

not include the “positional entropy”, described below in the discussion section. The enthalpies and free energies for forming anions and triplets change rapidly with increasing oligomer length, but more slowly after F_4 (anions) or F_3 (triplets). Computed molecular orbitals of the F_{10} anion and triplet shown in Figure 4 suggest that the delocalization lengths, n_d , are near 4 repeat-units for the anion and 3 for the triplet. Because computations describe polarons that do not change length for oligomers longer than n_d , a reasonable hypothesis is that these computed internal entropies would also become constant for $n > n_d$. We hoped the calculations would test this hypothesis. The computed vibrational entropies (ΔS_{vib}) for oligomers longer than the n_d (Table S3 of the SI) instead changed irregularly with the length, and calculations sometimes failed to converge, indicating some computational problem even though the frequency analyses found no imaginary vibration frequencies. The computed results therefore did not support the hypothesis, but neither did they find any trend to refute it. They did find that the computed internal vibrational entropy changes were smaller than the positional entropies. To compute the free energies for the oligomers longer than the n_d , we therefore took the formation enthalpy, and averages of entropic contributions to the formation free energy from the successful calculations (see Table S3). These averages were $T\Delta S_{\text{vib}}=38\pm33$ meV for forming an anion and $T\Delta S_{\text{vib}}=57\pm9$ meV for forming a triplet; the uncertainties are standard deviations.

Table 3. For $F_n(n=1-8,10,57)$, the computed standard free energy changes, ΔG_{calc} and enthalpies ΔH_{calc} of the anions and triplets by the long-range corrected $\omega\text{PBE}/6-31\text{G(d)}$ ($\omega=0.1$ bohr⁻¹) with the SMD⁴³ solvation model for THF with symmetry disabled. For anions $\Delta H_{\text{calc}}=\Delta H(F_n^{\bullet-})-\Delta H(F_n)$, and $\Delta H_{\text{calc}}=\Delta H(^3F_n^{\bullet})-\Delta G^\circ(F_n)$ for triplets; $\Delta G_{\text{calc}}=\Delta H_{\text{calc}}-T\Delta S$ (see Table S3 for the details).

Name	Anion		Triplet	
	ΔG_{calc} (eV)	ΔH_{calc} (eV)	ΔG_{calc} (eV)	ΔH_{calc} (eV)
F_1	-1.187	-1.135	2.815	2.897
F_2	-1.647	-1.622	2.382	2.439
F_3	-1.784	-1.733	2.305	2.374
F_4	-1.816	-1.778	2.263	2.345
F_5	-1.852	-1.787	2.275	2.361
F_6	-1.843	-1.787	2.265	2.347
F_7	-1.851	-1.794	2.256	2.338
F_8	-1.857	-1.801		
F_9			2.262	2.336
F_{10}	-1.852	-1.796	2.260	2.341
F_{57}	-1.851 ^a	-1.795 ^a	2.265 ^a	2.347 ^a

^a For pF₅₇ we report the root-mean-square values from F_n (n=6-8,10) for anions and F_n (n=4-7,9,10) for triplets.

(a)

(b)

Figure 4. The highest occupied molecular orbitals (HOMO's) of F₁₀ (a) anion and (b) triplet computed by the long-range corrected ω PBE($\omega=0.1$ Bohr⁻¹)/6-31G(d) with the SMD⁴³ solvation model for THF and symmetry disabled. The HOMO's suggest 4 and 3 repeat-unit long of polaron delocalization lengths for the anion and triplet.

Discussion

Reduction Potentials. Figure 5a plots the measured $E^0(\text{F}_n^{0/-}, n=1-10, 57)$ which become less negative (easier reduction) as n increases. Similarly Chi⁷ found that the oxidation potentials of F_n (n=2-7) become less positive (easier oxidation) as n increases and predicted that the $E^0(\text{F}_n^{0/-})$ would become less negative with increasing n mirroring the behavior of the oxidation potentials. Elandalousi¹² reported similar observations on the oxidation potentials of oligothiénylenevinylenes. A comparison of potentials reported here for reduction with those reported by Chi⁷ for oxidation of F_n shown in Figure S5 of the SI supports the mirror image behavior predicted by Chi,⁷ which may be due to the symmetric bonding and anti-bonding molecular orbitals of conjugated oligomers predicted by the molecular orbital theory and similar solvation energies of the anions and cations.

Figure 5. Plots of (a) the measured (■) and computed (○) reduction potentials $E^0(F_n^{0/-})$ vs. the length of the oligomer in the repeat units (n). The computed $E^0(F_n^{0/-}) = -(\Delta G_{\text{calc}} - \Delta G_{\text{calc}}(Fc) - T\Delta S_p^0)/e$. Here ΔG_{calc} is the computed formation free energy for the anion in THF as in Table 3, $\Delta G_{\text{calc}}(Fc)$ is the similarly computed free energy change for reduction of Fc^+ in THF, and ΔS_p^0 is the positional entropy calculated by Eq. 1 with the delocalization length $n_d = 4.3$ repeat units. (b) The contributions of ΔG_{calc} (green) and positional entropy ($T\Delta S_p^0$; $T = 298$ K, purple) of F_n ($n = 1-8, 10, 57$) vs. n . The ΔS_p^0 of F_n ($n = 1-4$) are assumed to be zero (see text).

Figure 5a shows a rapid change of the measured $E^0(F_n^{0/-}, n=1-4)$ and a slower change of the measured $E^0(F_n^{0/-}, n=5-10)$. The offset of the measured (left) and computed (right) vertical axes indicates an error of -0.33 V in the absolute estimates of the computed energetics that will be discussed below. Figure 5b shows that the measured potentials can be explained by a simple picture in which the standard free energy changes (ΔG^0) of anion is the sum of the computed standard free energy change (ΔG_{calc}) and a free energy change from positional entropy ($T\Delta S_p^0$), where T is temperature. The ΔG_{calc} , estimated by the DFT computations, are the free energy differences between the neutral molecules and their anions. From measurements of absorption spectra of $F_n^{\bullet-}$ ($n=2-10$), Zaikowski⁹ concluded that the n_d of the electron was 4.3 repeat units. With increasing n , the ΔG_{calc} changes rapidly until $n = n_d$ and then remains almost constant. For long oligomers with $n > n_d$, if we assume that the charge can move freely along oligomer, then a positional entropy (ΔS_p^0) will arise from the number of the possible positions of the charge along the oligomer.^{9, 45} In a similar spirit we used a simple permutation to calculate the ΔS_p^0 treating

the charge as a having a length of $n_d = 4.3$ repeat units⁹ and the oligomers as a chain with a finite length in n repeat units (eq 1).

$$\Delta S_p^0 = k_B \ln(n - n_d + 1) \quad (1),$$

The $T\Delta S_p^0$ for $F_n^{0/-}$, $n=5-10$, from eq 1, are given in Table 4 and plotted in Figure 5b. In F_n ($n=1-4$), the delocalization length is confined by the length of the oligomer, n . ΔS_p^0 is assumed to be zero because there is only one possible position for the charge. The computed reduction potentials in Figure 4a, which are the sums of ΔG_{calc} and $T\Delta S_p^0$ from eq 1 are in good accord with the measured reduction potentials. The ΔG_{calc} of anions in Table 1 are the computed free energy changes for forming anions in THF from electrons in vacuum. To compare with the experimental data we computed the reduction potential of ferrocenium (Fc^{*+}) from the free energy difference between Fc and Fc^{*+} in THF. This computed ($\omega\text{PBE}/6-31\text{G(d)}$, $\omega=0.1$) value, -4.743 V, provides an estimate for $E^0(\text{Fc}^{0/+})$ in THF vs. e^- in vacuum. This computed estimate is ~ 0.50 V less negative than the electrochemical estimate, $E^0(\text{Fc}^{0/+}) = -5.245$ V vs. e^- in vacuum, based on $E^0(\text{Fc}^{0/+}) = 0.545$ V vs. SCE in THF⁴⁶⁻⁴⁷ and -4.7 eV for the Fermi level of the SCE in aqueous solution vs. e^- in vacuum.⁴⁸ Computed estimates for $E^0(F_n^{0/-}$, $n=1-8,10,57$) were plotted on the right axis of Figure 5a vs. the computed $E^0(\text{Fc}^{0/+})$.

The computed values of $E^0(F_n^{0/-}$, $n=2-8,10,57$) are an excellent match to the length-dependence of the experimental values, but are ~ 0.33 V more negative as indicated by the offset of the right vertical axis. The ~ 0.33 V difference may arise from errors in computations of the ΔG_{calc} and from errors in computations of the reference potential $E^0(\text{Fc}^{0/+})$. Both were computed with long-range corrected ωPBE ($\omega=0.1$ bohr⁻¹). While this long-range corrected functional was found to be effective for delocalized state, self-interaction errors may make it less accurate for smaller molecules like ferrocene. We have also not accounted for a difference that will arise because the experimental values were based on equilibria in the absence of electrolyte, while the reference reduction potentials were from electrochemical measurements in the presence of electrolyte. The results show that the length-dependence of $E^0(F_n^{0/-}$, $n=1-10,57$) can be described well as the sum of the ΔG_{calc} and position-entropic energy, but the goal of an accurate prediction of the absolute potentials remains only roughly fulfilled. This simple picture of the $E^0(F_n^{0/-})$ described here includes positional entropy in addition to internal entropy changes estimated by the frequency calculation. Because the implicit continuum model such as SMD model⁴³ ignores the microscopic solute-solvent interaction,⁴⁹ the solvation entropy may not be predicted accurately.

Table 4. Contributions of positional-entropic energies ($T\Delta S_p^0$) to the reduction potentials in the F_n ($n=5-10,57$), and to the lowest triplet free energies in F_n ($n=4-10,57$).

Name	Anion (F_n^{*-})	Triplet ($^3F_n^*$)
	^a $T\Delta S_p^0$ (meV)	^b $T\Delta S_p^0$ (meV)
F_4		18

F ₅	14	28
F ₆	26	36
F ₇	34	41
F ₈	40	46
F ₉	45	50
F ₁₀	49	53
F ₅₇	102	103

^aT=298 K. The ΔS_p^0 is calculated by Equation 1 (see text) with the charge delocalization length $n_d=4.3$ repeat units.⁹

^bT=298 K. The ΔS_p^0 is calculated by Equation 1 (see text) with the triplet delocalization length $n_d=3.0$ repeat units.

From the dependence of reduction potentials on oligomer length we can obtain information about n_d . In Table 4 we see that $T\Delta S_p^0$ for an increase of the oligomer length by one repeat unit changes $E^0(F_n^{0/-})$ by less 12 meV, which is about half of $k_B T$ (26 meV) at T=298 K. Therefore when the observed change on adding one unit in $\Delta E^0(F_n^{0/-})$ is substantially greater than 12 meV, we may conclude that it contains electronic contributions from the energy of the polaron. Conversely when $\Delta E^0(F_n^{0/-}) < 12$ meV it is entirely due to positional entropy, and there is no longer a contribution from the ΔG_{calc} . From Table 4 that $E^0(F_3^{0/-}) - E^0(F_4^{0/-}) = -48$ meV, and $E^0(F_5^{0/-}) - E^0(F_4^{0/-}) = -11$ meV, these signal that a possible n_d of the electron in the oligofluorene is between 4 and 5 repeat units, consistent with $n_d = 4.3$ repeat units from the depletion of neutral absorption in $F_n^{\bullet-}$ ($n=2-10$) in THF.⁹

Here eq 1 computes positional entropies under the arbitrary assumption that a change in length of one repeat unit produces a distinct state. If some other value, such a half a repeat unit, is used, the result changes by a small additive factor; while the length-dependence remains almost unchanged. A general procedure to determine the delocalization length from redox potentials or similar data on a series of oligomers is to find the point at which the change of potential upon shortening by one unit is greater than that predicted by eq 1, in this case 12 meV. When n_d is an integral number of repeat units lengthening by $\Delta n_d = 1$ gives a change of 18 meV, regardless of n_d , so once a change of oligomer length by one repeat unit yields a change >18 meV, then the oligomer is shorter than n_d .

Chain Entropy vs Empirical Models: Contrasting Predictions. Empirical relationships are frequently used for describing oligomer properties as a function of $1/n$ (2a)^{5, 7-8, 12, 50} and similarly e^{-n} (2b)^{19, 51-53}:

$$E_n = a + b/n \quad (2a)$$

$$E_n = E_\infty + (E_1 - E_\infty) e^{-a(n-1)} \quad (2b)$$

They can roughly describe the $E^0(F_n^{0/-})$ data as shown in Figure S5 of the SI, as well as triplet energies discussed below (Fig. S6, SI). The empirical models of eq 2 were developed for short oligomers, so they might not be expected to work well at long lengths where they predict little change. Those predictions are not physically sensible as we can see with a simple example. Here we consider a reaction in which an electron (or hole or exciton) is confined to one molecule, M. Addition of a second M molecule lets the electron be located on either of the two, decreasing its free energy by $k_B \ln(2) = 18$ meV. Now if the molecule, call it M_{100} , is a 100 unit long polymer the free energy of the electron in M_{100} decreases by 116 meV due to positional entropy according to eq 1. For a 200 unit long polymer M_{200} the decrease is by 134 meV, so the free energy change for electron transfer from $M_{100}^{\bullet-}$ to M_{200} is 18 meV. We would expect that the free energy change for placing the electron on M_{200} would be almost the same as for placing it on two M_{100} molecules. Indeed this is so. The free energy change for placing the electron on two M_{100} molecules is $-(116 \text{ meV} + k_B \ln(2)) = -133$ meV, which is very close to that value, -134 meV for placing it on M_{200} . The prediction of eq 1 is physically reasonable.

Predictions of the empirical models, eq 2, on the other hand, are not reasonable. Eq 2a predicts differences in polaron free energies for addition of an electron to M_{100} and M_{200} to be far less than 1 meV, although it should be close to 18 meV. This is true for all values of parameters considered⁵³ and is also true for eq 2a. This simple example thus shows that eq 1 makes thermodynamic sense, while eqs 2a and 2b do not.

Triplet Free Energies. Relative ΔG°_T for of F_n ($n=2,4,5,7,10,57$) were measured from equilibria. The absolute values rely on the *free* energy change for formation of the triplet state of fluoranthene, based on an analysis of equilibria among triplets of many molecules that obtained free energies.⁴² Therefore reported ΔG°_T in the present data are free energy changes for triplet formation. Figure 6a shows that as n increases, the ΔG°_T of F_n ($n=1-3$) sharply decrease with increasing n ; the ΔG°_T of F_n ($n=3-5,7,10$) decrease more slowly, qualitatively similar to the anions. Computed triplet energies matched well to those from experiment without the shift needed for the anions, so Figure 6a has just one vertical axis. The repeat-unit-length dependence of the ΔG°_T based on phosphorescence spectral shifts has been described by using the empirical relationship in eqn. 2b.⁵³ Similar fits using empirical functions of current measurements are shown in Figure S6 of the SI. We also estimate n_d of the triplet from the n dependence of $\Delta G^\circ_T(F_n)$ in a way analogous to that used above for anions. In Table 2, the triplet free energy difference between F_2 and F_3 , $\Delta\Delta G^\circ_T(F_2-F_3)=95$ meV, is clearly too large to arise solely from positional entropy. $\Delta\Delta G^\circ_T(F_3-F_4)=28$ meV and $\Delta\Delta G^\circ_T(F_4-F_5)=25$ meV both appear too large to be due to positional entropy only, but by an amount close to uncertainty of the measurements. We conclude that the triplet delocalization length is between 3 and 5 repeat units: determination of n_d for triplets is unsatisfyingly uncertain. Similarly imprecise determinations have been reported based on comparisons of the length-dependence of spectral shifts between fluorescence and phosphorescence,⁵³ as well as computations.⁵² We note that use of spectral shifts does not capture free energies due to positional entropy. While the picture introduced here describes the observations well in terms of a rigid polaron of fixed length, this simple picture is not exact.

Dihedral angles fluctuate thermally, producing fluctuations in polaron lengths for both anions and triplets: polarons “breathe” as dihedrals fluctuate. The vague determination of the delocalization length for triplets may signal that the triplet spreads and contracts by large amounts as dihedral angles undergo thermal fluctuations, producing fluctuation in the length of the triplet. The average length of the triplet may near three repeat units, but may fluctuate to lengths greater than four units because the triplet length is more sensitive to dihedral angles than is the anion. This hypothesis is supported by the finding, first reported by Jansson⁵² that optimized structures of triplets contain one dihedral angle close to zero. A similar analysis is presented in Figure S7.

Triplet absorption (TA) spectra in Figure 2, on the other hand, continue to change with n until at least $n=6$. This observation does not conflict with the idea that the triplet delocalization length is near 3 repeat units, as noted by Jansson⁵² and coworkers, who found similar changes in computed TA spectra,⁵² consistent with experimental determinations by Wasserberg in 80K MTHF glasses.⁵³ The positions of the TA bands are determined by differences between the energies of triplet ground and excited states (T_1 and T_n). The data in Figure 2 thus show that the delocalization length of the T_n state is at least $n=6$, but the delocalization length of the T_1 state could be much shorter. Determination of delocalization length for the lowest, T_1 , state should be based on properties of this state, as are the energies in Figure 4.

Still, as for the anions the dependence on n for the triplets is also described well by the sum of the ΔG_{calc} and $T\Delta S_p^0$ in Figure 6a. Here, ΔS_p^0 is calculated by eq. 1 with $n_d = 3.0$ repeat units; $T\Delta S_p^0$ in the ΔG°_T of F_n ($n=4-10,57$) are given in Table 4. Figure 6b shows the plots of the ΔG_{calc} and $T\Delta S_p^0$ versus n . As for anions, ΔS_p^0 is zero for $n < n_d$.

Figure 6. Free energies changes (ΔG°_T) vs. oligomer or polymer length n for formation of triplets from ground states: (a) measured (red) and computed (blue), ΔG°_T , for F_n ($n=1-7,9,10,57$); (b) the computed triplet free energy (ΔG_{calc} , green) and positional-entropic energy ($T\Delta S_p^\circ$; $T=298$ K, purple) of F_n ($n=1-10$) vs. n . The computed ΔG°_T is $\Delta G_{\text{calc}} - T\Delta S_p^\circ$ eV. ΔS_p° is from eq 1 with the triplet delocalization length $n_d = 3.0$ repeat units. The ΔS_p° of F_n ($n=1-3$) are assumed to be zero (see text).

Rate Constants for Electron and Triplet Transfer. Rate constants for bimolecular triplet transfer usually utilized F_3 due to its strong, but distinct spectrum. Except for transfer to pF_{57} these rate constants were all below $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. For example triplet transfer from ${}^3F_3^*$ to F_{10} , with $\Delta G^0 = 88 \text{ meV}$ proceeded with a rate constant of $4.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. By contrast several rate constants for electron transfer were $> 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. The slow rates for triplet transfer are remarkable. They may arise because electronic coupling for triplet excitation transfer is smaller than that for electron transfer or because reorganization energies are larger for triplet transfer. One source of reorganization energy is the large change in one dihedral angle noted in Figure S7 of the SI.

Summary and Recommendations

For oligofluorenes with repeat unit lengths (n) less than the delocalization length, n_d , ΔG^0 for forming anions or triplets decreases rapidly with increasing n . For $n > n_d$, the observed free

energy change decreases much more slowly in a way similar earlier reports of length dependence in varied oligomers. The present paper describes a definite origin for the changing free energies in longer oligomers and polymers. The changes with length are in accord with a picture in which for $n > n_d$ the energy of the electron or triplet polaron is constant, but “positional entropy” arising from different positions of the electron or triplet polaron in the chain slowly decreases the free energy change. A smaller internal entropy change also accompanies the creation of each polaron. A simple picture of the length-dependences accounts for the experimental measurements and is an alternative to widely-used empirical relations.^{5, 51} The delocalization length of the electron polaron is 4-5 repeat units in agreement with previous reports.⁹ There is some ambiguity about the length of the triplet exciton which lies between 3 and 5 repeat units. This simple picture, which includes an electron or triplet polaron of fixed length, is readily expressed in a quantitative model. While it is oversimplified because it does not include fluctuations of polaron length, it works well enough that departures from it are close to experimental uncertainties. The predictions of long-range corrected ω PBE computations on electrons and triplet oligofluorenes are in accord with this length range. The polaron delocalization lengths found here use the redox potential, a ground state property, or the energy of the lowest triplet to obtain lengths of the polarons in their lowest electronic states. These lengths are consistent with previous reports.

Positional entropy explains the chemical physics behind the evolution of free energy changes past the delocalization length for conjugated polymers. Such insight is missing and possibly misleading in empirical $1/n$ or e^{-n} descriptions commonly employed for spectral and energetic data. Positional entropies can be substantial, >100 meV for example for F_{57} , as shown in Table 4, or 158 meV for a 500 unit polymer. When measurements on a series of oligomers are available the positional entropy also provides a new and more rigorous method compared to inspecting plots vs $1/n$ to determine delocalization lengths for polarons. A general procedure to determine the delocalization length from redox potentials or similar data on a series of oligomers is to find the point at which the change of potential upon shortening by one unit is greater than that predicted by eq 1. This change is 12 meV or somewhat smaller if n_d is not an integer. The empirical descriptions, eqs 2 have no clear meaning, but provide good descriptions for oligomers having lengths less than n_d .

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

1. Radiation Chemistry in THF, toluene, and *p*-xylene.
2. Tables for computed electronic energies with the symmetry constraints for forming the triplets, and the computed free energies, enthalpies, and entropies without symmetry constraints for forming the anions and triplets.

- Figures showing spectral evolution between triplets from which ΔG°_T is determined, comparison of F_n oxidation and reduction potentials with empirical fits, and a plot showing the commonly used empirical $1/n$ relationship for triplet energy with oligomer length.
- Computed dihedral angles for triplet oligomers F_n , $n = 3-7, 10$.

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TOC Graphic

Supporting Information For:

Chain Length Dependence of Energies of Electron and Triplet Polarons in Oligofluorenes

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Section S1: Radiation Chemistry for making anions and triplets

Anions in Tetrahydrofuran (THF) With the concentration of the donor (D) much greater than that of the acceptor (A), the radiation chemistry in THF(=RH) solution are:

where RH_2^+ is the solvated proton and e_s^- is the solvated electron. The formation of the solvated protons are fast (< 1 ps),¹ so very little solute will be oxidized by $\text{RH}^{\bullet+}$. Reaction R4 involves encounters of $\text{D}^{\bullet-}$ with A and reaction and the reverse, which are not dependent on reactions of R5a and R5b so once decay due to R5a and R5b is accounted for, equilibria can be determined independently. Because of $[\text{D}] \gg [\text{A}]$, most solvated electrons will kinetically attach to the D and then the electrons transfer (ET) to A (Reaction R4). In THF, the anions are annihilated by the proton transfer reaction (Reaction R5).

Triplets in Toluene and *p*-Xylene In aromatic solvents (Ar) such as toluene and *p*-xylene with that the concentration of the donor (D) greater than that of the acceptor (A), the radiation chemistry is:

Here $^1\text{Ar}^*$ and $^3\text{Ar}^*$ are the singlet and triplet excited solvent molecules; $^3\text{A}^*$ and $^3\text{D}^*$ are the triplet excited states of A and D. The electron pulse can excite Ar directly to form $^1\text{Ar}^*$ and $^3\text{Ar}^*$. The ionization of the solvent is rapidly (< 2 ns) followed by charge recombination (Reaction S8) that leads to $^1\text{Ar}^*$ and $^3\text{Ar}^*$. The $^1\text{Ar}^*$ convert into $^3\text{Ar}^*$ via the intersystem crossing (Reaction S9). Due to the concentration gradient $[\text{D}] > [\text{A}]$, the D will capture the triplet energy first (Reaction R10) and then the triplet energy will transfer to A (Reaction R11).

Table S2: Computed electronic formation energies for F_n (n=1-10) triplets by long-range corrected ω PBE/3-21G ($\omega = 0.07 \text{ bohr}^{-1}$) with the symmetry constraints, and the PCM solvation model for THF. These energies are the computed electronic energy differences between the ground and lowest triplet excited states.

Name	Triplets
F ₁	3.09876
F ₂	2.60391
F ₃	2.58195
F ₄	2.53106
F ₅	2.56752
F ₆	2.52923
F ₇	2.56716
F ₈	2.52885
F ₉	2.56755
F ₁₀	2.52815

Table S3 Computed free energies (ΔG^0), enthalpies (ΔH^0), and vibration-entropic energies ($T\Delta S_{\text{vib}}$; T = 298 K) for forming F_n (n=1-8,10) anions, and F_n (n=1-7,10) triplets by long-range corrected ω PBE/6-31G(d) ($\omega = 0.1 \text{ bohr}^{-1}$) with the SMD solvation model in THF, and without the symmetry constraints. These contributions are internal to the polarons and do NOT include the larger contributions from positional entropies.

	^a Anions			^b Triplets		
	ΔG^0 (eV)	ΔH^0 (eV)	$T\Delta S_{\text{vib}}$ (eV)	ΔG^0 (eV)	ΔH^0 (eV)	$T\Delta S_{\text{vib}}$ (eV)
F ₁	-1.187	-1.135	0.033	2.815	2.897	0.057
F ₂	-1.680	-1.622	0.058	2.382	2.439	0.028
F ₃	-1.784	-1.733	0.038	2.305	2.374	0.042
F ₄	-1.816	-1.778	0.022	2.258	2.345	0.057
F ₅	-1.852	-1.787	0.047	2.262	2.361	0.071
F ₆	-1.802	-1.787	-0.003	2.273	2.347	0.056
F ₇	-1.877	-1.794	0.064	2.257	2.338	0.053
F ₈	-1.842	-1.801	0.041			
F ₉				2.233	2.336	0.075
F ₁₀	-1.829	-1.796	-0.002	2.252	2.341	0.048

^aFor forming the anions at T= 298 K, the electron-entropic energies are 18 meV, and both the rotation and translation entropic energies are ~1 meV.

^bFor forming the triplets at T= 298 K, the electron-entropic energies are 28 meV, and both the rotation and translation entropic energies are ~1 meV.

Figure S4. Spectral evolution showing triplet transfer between F_3 and F_5 . Figure In toluene with 40 mM of naphthalene, triplet spectra from pulse radiolysis of a mixture sample of F_3 and F_5 . As time goes by, the F_3 triplets gradually transfer to F_5 to reach equilibria, allowing determination of ΔG°_T from K_{eq} .

Figure S5. A plot of the reduction potentials of F_n ($n=1-10,57$) vs. the length in the repeat units (data from Figure 5) compared with the empirical functions Eq 2a (blue line) and 2b (green line). These empirical functions for the oligomers are fair, but not as good as the description based on positional entropy given in the main manuscript. Eq 2a is almost as good but eq 2b fails to predict the substantial change for pF_{57} . The empirical fits are $E^0(F_n^{0/-}) = -2.46 - 0.65(1/n)$ (Eq. 2a, blue line), and $E^0(F_n^{0/-}) = -2.256 - (-3.098 + 2.256)\exp[-0.693(n-1)]$ (Eq. 2b, green line).

Figure S6. The lowest triplet energy (ΔG_T^0) of F_n ($n=2,5,7,10,57$) vs. the length in the repeat units (n) (data from Figure 6) compared with Eq. 2.; $\Delta G_T^0 = 2.12 + 0.73(1/n)$ eV (Eq. 2a, blue line), and $\Delta G_T^0 = 2.234 + (2.9 - 2.234)\exp[-1.191(n-1)]$ eV (Eq. 2b, green line). The parameter 2.9 eV is the reported triplet energy of F_1 . The other two parameters were adjusted for best fit. Eq 2a can approximately describe the length dependence, but is slightly inferior to that given by the positional entropy model seen in figure 6. Again Eq 2b fails to predict the noticeable change between F_{10} and pF_{57} .

Figure S7: Dihedral Angles in the Lowest Triplet Excited State. Dihedral angles between adjacent fluorene repeat units in DFT optimized structures of the triplet ground states of the oligofluorenes ($n=3-7,10$) are shown in (a). The dihedral angle closest to the center of the triplet is labeled as DA 0. Plots of the dependence of dihedral angles (DA) are shown in (b), with red lines mark the position of each dihedral angle. Values of DA 0 are $\phi \sim 1-10^\circ$, and those of DA ± 1 and larger are $\phi \sim 28-33^\circ$. The dihedral angle differences between DA 0 and DA ± 1 cause a 40-50 meV⁴ energy barrier to the triplet exciton transport along the polyfluorene.

We see that in long oligomers three dihedral angles are perturbed from the ~ 36 degrees typical of ground states. One, near the center of the triplet exciton is close to 0 degrees, while two others are around 30 degrees. These changes are consistent with the depiction in Figure b in which the triplet exciton is approximately 3 units long, consistent with the conclusions from measurements of triplet free energies.

References

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