**Multiply-Reduced Oligofluorenes:
Their Nature and Pairing with
THF-Solvated Sodium Ions**

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Multiply-Reduced Oligofluorenes: Their Nature and Pairing with THF-Solvated Sodium Ions

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Abstract

Conjugated oligofluorenes are chemically reduced up to five charges in tetrahydrofuran solvent and confirmed with clear spectroscopic evidences. Stimulated by these experimental results, we have conducted a comprehensive computational study of the electronic structure and the solvation structure of representative oligofluorene anions with a focus on the pairing between sodium ions and these multi-anions. Using density functional theory (DFT) methods and a solvation model of both explicit solvent molecules and implicit polarizable continuum, we first elucidate the structure of tightly solvated free sodium ions, and then explore the pairing of sodium ions either in contact with reduced oligofluorenes or as solvent-separated ion pairs. Computed time-dependent-DFT absorption spectra are compared with experiments to assign the dominant ion pairing structure for each multi-anion. Computed ion pair binding energies further support our assignment. The availability of different length and reducing level of oligofluorenes enables us to investigate the effects of total charge and charge density on the binding with sodium ions, and our results suggest both factors play important roles in ion pairing for small molecules. However, as the oligofluorene size grows, its charge density determines the binding strength with the sodium ion.

Introduction

Much of our information about energies for formation of electrons and holes in conjugated molecules comes from voltametric reduction and oxidation of conjugated oligomers and polymers.¹⁻³ Formation of multipolarons is almost certainly involved, but their natures are poorly understood. Recently we reported the spectra of singly and doubly reduced oligofluorenes⁴. The convergence of the near IR P_1 absorption band in longer oligomers provides unambiguous evidence to determine the polaron size, which was corroborated by density functional theory (DFT) calculations with tuned long-range correction of the exchange-correlation functional. Calculations further established the transition from bipolaron to side-by-side polarons in doubly reduced oligomers as the molecular size increases. True bipolaron character, diagnosed spectroscopically and in a computational test devised by one of us (QW) was rare. We report here that the same oligomers can be reduced up to 5 times by sodium metal in tetrahydrofuran (THF), as evidenced by their absorption spectra, and provide computational descriptions of the multipolarons formed. However, unlike singly reduced oligomers where pairing with counterions was insignificant due to the low ion concentration, multiply reduced oligomers are almost certainly stabilized by one or more counterions, so this study will compare experimental results with computed estimates in the context of ion pairing.

We will first attempt to establish the molecular structure of THF-solvated sodium ions via DFT calculations. For that, we use explicit THF molecules to represent the first solvation shell and further augment it with the polarizable continuum model for implicit solvent. The second and more challenging goal of this work is to probe different ion pair structures systematically in series of molecules with increasing size or charges. We use the electronic absorption spectra as our probe because they have clear signatures in charged conjugated polymers.⁵ Though the spectra of polarons and bipolarons have been investigated before under the influence of counter ions,⁶ they have not been studied extensively in the ion pairing context. It is well understood that ion pairs can be either in contact or solvent-separated,⁷ but how will these two different structures affect the UV-vis absorption spectra of the anions? In another words, can we use the spectrum to probe the formation of ion pairs?

Computational study of the THF-solvated sodium ion has a long history, with the early work from Jorgensen⁸ and later from Schwartz⁹⁻¹¹. Computational methods, however, have been applied to ion pairing only recently, such as in a series of studies by Fry.¹²⁻¹⁸ More recently, modeling of ion pairs in electrolytes has been used to reveal the importance of such structures in the research of electrochemical energy storage.^{19,20} While those studies are on species with fixed charges, here we have systematically studied a series of oligofluorenes (Fig. 1) of different lengths and different reduction levels. Although computation is the workhorse in this study, we rely heavily on experimental results for calibrating the method and more importantly, conjecturing a coherent physical picture of these complex systems. Experimentally, we are able to record clear optical spectra for these systems. Computationally, we not only calculated the energetic in ion pairing, but also for the first time computed the electronic spectra of various ion pairs. Together results from experiment and computation lead us to a better understanding of the factors that determine ion pair formation. In the following, we first present the experimental spectroscopy results. We then explain our computation approaches before showing the detailed

computational results for selected systems. We will conclude after some further discussion on the nature of these multiply reduced oligomers.

Figure 1. The structure of oligofluorenes, F_n , $n=2-10$

Experimental Results

Figure 2 presents spectra of the oligomers containing up to five electrons. The spectra of radical anions and dianions described before¹ are included for comparison. Shorter oligomers would accept only two electrons when reduced by sodium biphenyl (NaBip), while sometimes reduction by sodium (Na) or sodium-potassium alloy could achieve further reduction. Relative reducing strengths have been discussed by Petrov.²¹ Table S1 summarizes the degree of reduction by three methods. For F_6 the spectrum of the penta-anion, F_6^{-5} , produced by NaK reduction is shown. F_6^{-5} could not be produced by NaBip. The NIR band for F_6^{-5} is slightly broader than others, possibly due to ion pairing with K^+ , which tends to pair more strongly with anions than does Na^+ , which acts like a larger ion due to tight solvation by THF molecules.²² Ion pairing is thus clearly important in the production of multi-anions, leading us to seek a computational description, which may also clarify general features of the spectra in Fig. 2: Anions and dianions usually have distinct spectra, but multianions are often similar, displaying gradual shifts with increasing level of reduction. While anions typically have two strong absorption bands, an NIR “P₁” band and a visible, “P₂” band, the multianions behave differently as will be discussed in more detail after presentation of computations that will yield insight.

Figure 2. Optical spectra of oligofluorenes, F_n , $n=2-10$, reduced by sodium biphenyl to make anions, F_n^{m-} , in THF solution. Up to 5 electrons were added per oligomer molecule; spectra are labeled by the degree of reduction, m . Small absorption bands at 3.0 eV in the most reduced spectra for F_5 , F_6 and F_9 are due to biphenyl anions.

Computational Methods

All calculations are done using Gaussian 09 (Rev. D.01)²³ with the default Polarizable Continuum Model (PCM)²⁴ to simulate the solvent reaction field. To be consistent with our previous work,⁴ we used the same tuned long-range corrected PBE functional²⁵ with the range parameter being 0.1 bohr⁻¹, which we refer to as $\omega(0.1)$ PBE. This choice is motivated by the polaron localization test in conjugated polyfluorenes. Specifically, $\omega(0.1)$ PBE successfully reproduces the length saturation (convergence) phenomenon for the P_1 band observed, while B3LYP was shown unable to localize the charge in conjugated polymers.²⁶ Vertical excitations are calculated using time-dependent DFT (TDDFT) with the default linear response, non-equilibrium solvation.²⁷ The 6-31G(d) basis set is used throughout. Though anions are known to require more diffuse basis function in gas phase, the PCM reaction field stabilizes anions, and all anions we studied have a negative HOMO eigenvalue even with the modest basis set size we used. Additionally, we have verified that all electron affinities are negative; i.e. adding an extra

electron always ends in a lower total PCM energy. For instance, in the most extreme case of F_4^- , its energy is lower than F_4^{-3} by 0.14 eV, assuming the free electron's energy is zero.

We choose the multiplicity to be either 1 or 2 for systems with even or odd number of electrons. All calculations use unrestricted Kohn-Sham, which means the α and β spins can have different spatial orbitals, even for singlets. When there is a difference, the single determinant formed from these orbitals is not an eigenfunction of the total spin operator S^2 , i.e. spin contaminated. In our previous work, we introduced the spin contamination as an approximate and convenient diagnostic tool for polaron pair overlap⁴. This $\langle S^2 \rangle$ -diagnostic works because Coulomb repulsion tends to push the orbitals occupied by the extra electrons to be spatially non-overlapping. Assuming that all orbitals for α and β spins have identical spatial components except for those occupied by the extra electrons, it can be shown that $\langle S^2 \rangle$ increases from 0 to 1 as these orbitals overlap less and less until they become disjoint,²⁸ at which point it is suggested side-by-side polarons are formed.^{29,30} Using Eq. 2.271 in Page 107 of Reference³¹, we can further show that for three extra electrons, the $\langle S^2 \rangle$ will range from 0.75 (one unpaired electron and the other two share the same orbital) to 1.75 (all three electrons occupy non-overlapping orbitals). Similarly for four extra electrons, the $\langle S^2 \rangle$ will range from 0.0 (closed-shell, no unpaired electrons) to 2.0 (all four extra electrons occupy non-overlapping orbitals). We emphasize here that the $\langle S^2 \rangle$ -diagnostic is designed for the special cases of multi-anions, and should be used with caution for other systems. It also should be noted that the $\langle S^2 \rangle$ of the Kohn-Sham non-interacting system, as reported by default in all unrestricted calculations and used in this work, is not the same as density functional based $\langle S^2 \rangle$.³²⁻³⁴

While the functional we use is unconventional, we do not expect it to alter the qualitative results for the solvated sodium ions because the interactions between Na^+ and solvent molecules are predominantly electrostatics and Pauli repulsion, not chemical bonds. Because these interactions have no strong directional preference, there exist multiple stable structures for a given complex. Therefore, sampling these configurations becomes a larger issue when the molecular size increases and more ions are treated explicitly. What we have presented should be viewed as representative structures, especially for loosely bound complexes. Our discussion will mostly focus on qualitative differences among ion pair structures.

On some occasions, the binding energy of a complex is examined. Unless specified, all energies are calculated at optimized geometries with PCM, and the binding energy is calculated unambiguously as the PCM energy difference between the complex and the sum of its parts. It should be noted that the default PCM energy does not contain the solute-solvent dispersion or repulsion interaction energies. Nor is the cavitation energy included. Therefore the calculated binding energy may not match experimental findings (see discussion later). But we are more interested in the trend demonstrated by these binding energies than their absolute values. For the particular molecules studied here, another reason for not attaching too much meaning to the absolute binding energies is that we have replaced all hexyl side chains with hydrogen atoms in our models to save computation cost. This replacement is not expected to affect the electronic structure of the polymer; however, it certainly can significantly alter the solvation energy.

Because we use explicit solvent molecules within the implicit PCM that is designed to capture free energy changes,²⁴ it is important to make sure the explicit solvent molecules are indeed

strongly bound to the solute.³⁵ For Na⁺, we will gauge the coordinating strength of THF molecules by the Na-O distance (infra vide) and will remove THF molecules from the explicit model when this distance becomes large. We do not consider any explicit solvent molecules for the anions because they are not expected to bind.

Computational Results

Structure of the solvated sodium ion

The structure of solvated sodium ion in THF has been well studied computationally. Though earlier Monte Carlo simulation suggests a coordination number between 5 and 6,⁸ later work suggest it to be dominantly 4 with possible 3 and 5 coordinated structures.¹⁰ We have located an optimized geometry for each n of 3, 4, 5 and 6. Table 1 compares their average coordination energy and the distances between Na and O of the coordinating molecules. The average coordination energy is defined as $E_{c,av} = (E[Na^+(THF)_n] - E[Na^+] - n * E[THF])/n$. Also presented is the average Mulliken charge on each THF molecule ($q_{THF,av}$).

Table 1. Comparisons of Na⁺(THF)_n (n=3,4,5,6)

n ^a	3	4	5	6
E _{c,av} (eV)	-0.437	-0.443	-0.423	-0.390
q _{THF,av}	0.136	0.141	0.130	0.116
r _{Na-O} (Å)	2.31, 2.32, 2.32	2.30, 2.31, 2.32, 2.33	2.37, 2.38, 2.40, 2.40, 2.41	2.39, 2.40, 2.40, 2.40, 2.41, 4.31

^a n is the number of THF molecules coordinated to Na⁺; E_{c,av} is the average coordination energy per THF molecule (see text), q_{THF,av} is the average charge on each coordinating THF and r_{Na-O} is the distance from Na to O for each THF.

Our results show that for a THF molecule to contribute to the coordination of Na ion, its O atom is about 2.3-2.4 Å away from the ion. Therefore, it can be concluded that Na⁺(THF)₆ does not form a stable structure because one of the Na-O distances is 4.31 Å. For n=5, while a stable structure is formed without any one particular THF molecule left out, the Na-O distances are clearly all longer than those for n=4, while the Na-O distances are similar between n=3 and 4. Therefore, n=3 is under-coordinated; n=5 is less favorable than n=4. This is further supported by the fact that the average coordination energy and the average THF charge both peak when n=4. The most stable THF solvated structure of Na ion has 4 coordinated THF molecules.

The Bjerrum treatment of ion pairing

If we use the Bjerrum approach for ion pairing⁷, cations and anions will not pair when their distance is larger than $q = z_i z_j e^2 / 2 \epsilon k_B T$. At room temperature (T=293K), for z_i=1, z_j=-1 and $\epsilon_r=7.4257$, q=3.84 nm. In our experiments, the concentration of the F_n oligomers is 50-200 uM, the lower oligomer concentrations were used for longer oligomers, which means each anion has a volume of about 10⁴ cubic nanometers. So the average distance between anions is about 20 nm. If the cation is of the same concentration, the average cation-anion distance is then about 10 nm, much greater than the Bjerrum distance. Therefore most anions should be free.

When the anions turn to dianions, the cation concentration has to double. That leads to 20% decrease of average distances to about 8 nm. At the same time, the doubling of anion charges, z_i, brings the Bjerrum distance to be the comparable 7.68 nm. Therefore ion pairing is expected.

The above estimation ignores the molecular size. One can imagine that for longer molecules like F_8 , which can stretch 7 nm, this estimation breaks down. In fact, as we will show in this work, the pairing of counter ions depends on both the total charge and the charge density of a molecular ion.

Pairing of $Na^+(THF)_n$ with F_2 dianion

We first consider an ion pair between F_2 dianion and $Na^+(THF)_4$. The size and shape of the F_2 molecule warrants a question of where the counterion will be attached. If only electrostatic force is considered, we would expect the cation to sit at the center of F_2^{2-} . Geometry optimization starting from such a configuration does lead to a stable structure (verified by the frequency calculation), where the counterion sits in the middle of F_2 , i.e. on top of the central C-C bond. ($F_2^{2-}Na^+(THF)_4$, Fig. 3 left) The sodium ion is 4.28 Å away from the F_2 molecular plane, while the THF molecule on the opposite side has a Na-O distance of 2.41 Å, slightly larger than the other three Na-O distances, which are 2.34, 2.36 and 2.38 Å, respectively. These Na-O distances are similar to those in 5-THF-coordinated Na^+ complex, i.e. longer than the 4-coordinated one. Therefore this structure is best viewed as a solvent-separated ion pair (SSIP) because the sodium ion is still 4-coordinated in a way similar to that in its most stable free ion structure. There exist other SSIP structures where Na^+ has a similar solvation shell and a similar distance from the molecular plane. We have identified two such structures where the cation-complex moves off the center of and becomes slightly closer to the molecular plane. Details of these structures can be found in SI, which we label as SSIP 2 and SSIP 3, while the previous one is SSIP 1. The number index also corresponds to decreasing distance from the F_2 dianion plane. In all these SSIP structures, the F_2 dianion electronic structure is qualitatively similar, in contrast to the contact ion pair (CIP) that will be discussed next.

Figure 3. The ion pairs formed between F_2 dianion and the tetrakis- or tris-THF solvated sodium ion.

When the Na^+ is pushed even closer to the molecular plane, geometry optimizations lead to a stable structure where the sodium is only 2.42 Å away from the conjugated plane. However, the THF molecule opposite the plane is now pushed away with a Na-O distance of 5.04 Å ($\text{F}_2^{2-}\text{Na}^+(\text{THF})_{3+1}$, Fig. 3 center). This THF is better viewed as non-coordinated and therefore should be part of the continuum model. We thus also considered the ion pair formed between F_2 dianion and $\text{Na}^+(\text{THF})_3$ (Fig. 3 right). The optimized geometry has the same short distance between the sodium ion and the benzene plane, and this structure is better viewed as a contact ion pair (CIP). Further evidence comes from the Mulliken charge distribution on F_2 and the $\text{Na}(\text{THF})_n$ complex, as shown in Table 2. $\text{F}_2^{2-}\text{Na}^+(\text{THF})_{3+1}$ clearly has the same charge distribution with the CIP $\text{F}_2^{2-}\text{Na}^+(\text{THF})_3$, supporting the idea of assigning the farthest THF molecule to the continuum, not part of the first solvation shell.

We note that charge transfer has led to less than a unit charge on the cation, with the Na in the CIP $\text{F}_2^{2-}\text{Na}^+(\text{THF})_3$ having even less charge than in the SSIP $\text{F}_2^{2-}\text{Na}^+(\text{THF})_4$. Furthermore, the distances between the sodium atom and the oxygen atoms in coordinated THF molecules increase with decreasing charge on the cation (Table 2). The charge transfer is probably because highly charged F_2^{2-} does not bind its electrons strongly, in contrast to $\text{Na}^+(\text{THF})_4\text{Cl}^-$ where computational results show no charge transfer between the anion and cation. Nonetheless, it is interesting to note that the desolvation of Na^+ is enhanced when it is in close contact with a high charge density surface.

Table 2. Mulliken charge distribution and Na-O distances for structures in Figure 3.

	$\text{F}_2^{2-}\text{Na}^+(\text{THF})_4$	$\text{F}_2^{2-}\text{Na}^+(\text{THF})_{3+1}$	$\text{F}_2^{2-}\text{Na}^+(\text{THF})_3$
$q_{\text{F}_2}^a$	-1.79 (-0.89/-0.90)	-1.60 (-0.78/-0.82)	-1.61 (-0.77/-0.84)
$q_{\text{Na}(\text{THF})_n}$	0.79	0.60	0.61
$r_{\text{Na-O}} (\text{Å})$	2.34, 2.36, 2.38, 2.41	2.35, 2.40, 2.41, 5.04	2.41, 2.41, 2.42

^a Numbers in parentheses are the charge on each fluorene unit.

Having considered the difference in the cation between SSIP and CIP, we now turn to the electronic structure of F_2^{2-} . Earlier investigation¹ found F_2^{2-} to be a classic bipolaron, comprising a closed-shell singlet ($\langle S^2 \rangle = 0.0$) in which the two added electrons occupy identical orbitals and the P_1 and P_2 bands merge into a single absorption. Pairing with a counterion has not changed the bipolaron nature of F_2 dianion. That is to say, the closed-shell Kohn-Sham solution is stable with respect to the relaxation of spin restriction. However, the proximity of the counterion has an effect on the computed absorption spectrum. Using TDDFT, we have computed the absorption spectra for various F_2 dianions (Fig. 4). We have focused on the spectral energy range of up to 2 eV, where distinguished peaks are observed experimentally and therefore provide possible signals to decide the solvated ion structures. Besides the highest peak, the computed spectrum for the free dianion contains a clear second peak near 2 eV. The absence of such a distinct peak in experiment leads us to conclude that an unpaired dianion is probably not observed. When a counterion is paired, the height of the second peak becomes lower. The height decreases further as the counterion comes closer to the F_2 dianion plane as from SSIP 1 to SSIP 3. Because the CIP removes the second peak more completely than the SSIPs, and thus provides a better match to the experiment, we further conclude that the dominant structure for the F_2^{2-} is a contact ion pair. The dominance of CIP in F_2 dianion is further supported by energetics that will be presented below. We will also examine the nature of these absorption peaks in the **Discussion**.

Figure 4. Computed spectra for the dianions of F_2 compared with experimental spectra from Figure 2. The TDDFT computations use a broadening factor of 0.1 eV and assuming Lorentzian band shape, these spectra are simulated following the procedures on Gaussian 09 web site.³⁶

Selected energetics in ion pairing comparison

Before we present results of $Na^+(THF)_n$ pairing with other anionic species, we introduce two calculated quantities that will be used to study the ion pairing trends. Both quantities are energies, and we emphasize that their relative values are likely to be more reliable than their absolute magnitudes.

The first quantity is the energy change in the conversion from SSIP to CIP, defined as

where F_n^{-m} represents an F_n anion with charge $-m$, and the energy change is represented by $E_{SSIP \rightarrow CIP}$. When $E_{SSIP \rightarrow CIP}$ is negative the CIP is more stable.

The second quantity is the binding strength of the SSIP, defined as the energy difference in the following:

and the energy change is labeled E_b^{SSIP} . The binding energies are always negative, reflecting the favorable Coulombic attraction. In Table 3, we compare these two quantities for the anions that will be discussed in detail in the following subsections.

Table 3. The energy change from SSIP to CIP, $E_{SSIP \rightarrow CIP}$, defined by Eq. 1 and the binding strength of SSIP as defined by Eq. 2.

Anion	F_2^{-1}	F_2^{-2}	F_3^{-2}	F_4^{-2}	F_4^{-3}	F_4^{-4}	F_8^{-4}
$E_{SSIP \rightarrow CIP}$ (eV)	0.166	-0.045	0.024	0.144	0.039	-0.013	0.048
E_b^{SSIP} (eV)	-0.53	-0.90	-0.70	-0.68	-0.92	-1.13	-0.75

Measurements of dissociation free energies of Na^+ to monoanions by Slates and Swarc³⁷ may be compared to our computed results for F_2^{-1} . The anion studied by Slates that is closest in size to F_2^{-1} is tetracene⁻, for which the binding energy is 0.285 eV ($K_d=1.5 \times 10^{-5}$ M), which is considerably smaller than the value for F_2^{-1} in Table 3. This may indicate that the computed estimates, which do not include entropies of association, overestimate the binding of Na^+ to the anions. Again the relative values are likely to be more meaningful than their absolute values.

The relative values predict much stronger binding of Na^+ to F_2^{-2} than to F_2^{-1} , as would be expected from Coulomb's law in which the potential at each distance scales with the charge, z . From the results of Slates (tetracene⁻, Na^+) would be expected to be mostly dissociated at concentrations below ($K_d=1.5 \times 10^{-5}$ M), but based on the trends in Table 2 the dianion would be associated with one Na^+ down to concentrations near 10^{-10} M. Thus dianions would always be associated with one counterion in the μ M and nM concentration regions. We suggest that this would be true for any ion with a net charge of -2, so F_5^{-5} would associate with three Na^+ ions to concentrations below ~ 1 nM. Values of $E_{SSIP \rightarrow CIP}$ in Table 3 are positive, meaning that contact ion pairs are disfavored, except for F_2^{-2} and F_4^{-4} .

Pairing of $Na^+(THF)_n$ with F_3 and F_4 dianion

In our earlier study where counterions were not included in computations, we have shown that the F_3 and F_4 dianion presents a transition from bipolarons to pairs of side-by-side polarons due to the increased space for charge distribution. For these dianions the computed results found that $\langle S^2 \rangle = 0$ for F_2^{-2} , meaning the two extra electrons share the same spatial orbital, i.e. a bipolaron. But for dianions of F_3 and F_4 , $\langle S^2 \rangle$ is 0.69 and 0.95, respectively, meaning the two extra electrons become spatially non-overlapping. ($\langle S^2 \rangle = 1$ would imply the two polarons are completely separate.) The observed spectra of F_3^{-2} and F_4^{-2} , unlike that of F_2^{-2} , depart from the single band typical of a bipolaron.

Here we include counterions in the computations. We have identified both CIP and SSIP structures for Na^+ with F_3^{-2} and F_4^{-2} and calculated their absorption spectra in the low energy range. Comparison to experimental spectra suggests that the SSIP is the dominant structure, in contrast to the CIP that Na^+ forms with F_2^{-2} . This conclusion is first supported by the relative stability of CIP and SSIP as calculated by the energy difference of the SSIP to CIP conversion. (Table 3) Under our calculation conditions, this energy is -0.045 eV for F_2^{-2} but +0.024 eV for F_3^{-2} , meaning a decrease of 0.07 eV in the driving force. This result can be attributed to the fact that F_3^{-2} has a lower charge density than F_2^{-2} due to partial separation of the bipolaron into two polarons. We emphasize that this separation is partial (see our earlier study⁴ and Figure 6 below). We next compare the TDDFT spectra with experiments as shown in Fig. 5 (left). Here we see that the computed free ion and the SSIP spectra have structures that match the experimental spectrum better than the CIP does. Combined with the binding energy results, we tentatively assign the SSIP to be the dominant structure in F_3^{-2} , different from the CIP for F_2^{-2} due to decreased charge density. This point is made clearer when F_4^{-2} is considered because of

its more complete polaron separation. As result, even though the overall charge is -2, the charge density on F_4^{-2} is closer to that in F_2^- than F_2^{-2} . We have identified optimized CIP and SSIP structures for F_4^{-2} . Their TDDFT spectra are shown in the right panel of Fig. 5. Comparing to experiment, we can again exclude the formation of CIPs. While formation of SSIPs remains a possibility, the spectra of bare F_4^{-2} , which has no small peaks above 1.5 eV, actually matches the experiment even better. Therefore it is possible that F_4^{-2} does not form ion pairs at the $\sim 100 \mu\text{M}$ concentrations used in these experiments. F_4^{-2} may behave like F_2^- because they have the same charge density. Another conclusion is that since the structure seen in the computed spectra is due to different *electronic* transitions, not to vibronic bands, the structure in the experimental spectra should be assigned to distinct electronic transitions.

Figure 5. Computed spectra of F_3 and F_4 dianions compared to experimental spectra from Figure 2.

The difference $E_{SSIP \rightarrow CIP} = 0.144 \text{ eV}$ for F_4^{-2} is unusually large, even astonishing. This large preference for the SSIP can be explained by the electronic structure change of F_4^{-2} due to the proximity of a counterion. Namely, the strong repulsion in the bare dianion that leads to a side-by-side polaron pair is now mitigated by the counterion. Indeed, when we use the $\langle S^2 \rangle$ -diagnostic, we find that the SSIP $F_4^{-2}\text{Na}^+(\text{THF})_4$ has $\langle S^2 \rangle = 0.85$, already reduced from the bare (free ion) F_4^{-2} value of 0.95. In the CIP of $F_4^{-2}\text{Na}^+(\text{THF})_3$, $\langle S^2 \rangle$ is significantly smaller at 0.51, meaning the two polarons have a large overlap, thus an energy penalty. Such overlap can be visualized by the HOMOs of both α and β spins. (Fig. 6) Their significance to the spectra will be discussed in the **Discussion**.

Figure 6. The highest occupied α and β spin orbitals for F_4^{-2} in an SSIP (left) and a CIP (right) complex.

Pairing of $Na^+(THF)_n$ with F_4 trianion

With strong reducing agents it is possible to cram more than two extra electrons into F_4 and longer molecules. Experimentally, the absorption spectrum of F_4^{-3} has been established. We thus explored its ion pairing structures and associated spectra.

For $[Na^+(THF)_4]F_4^{-3}$, with its E_b^{SSIP} comparable to that of F_2^{-2} , it may lose a THF and form a CIP or it can attract another solvated Na^+ to form the complex $[Na^+(THF)_4]_2F_4^{-3}$. We first explore the latter possibility. Due to the planar structure of F_4 , the second Na^+ can be attached from the side that is the same as (*cis*-) or opposite to (*trans*-) the first Na^+ . It is expected that two cations would prefer opposite sides to avoid repulsion. Using Eq. 2 and assuming An to be $Na^+(THF)_4F_4^{-3}$ (SSIP), we find E_b^{SSIP} is -0.66 and -0.79 eV, for *cis*- and *trans*- $[Na^+(THF)_4]_2F_4^{-3}$, respectively. These energies are comparable to those for F_3^{-2} and F_4^{-2} . On the other hand, using Eq. 1, we find the driving force for $[Na^+(THF)_4]F_4^{-3}$ to form CIP is 0.039 eV, (Table 2) i.e. even more uphill than F_3^{-2} . Therefore $[Na^+(THF)_4]_2F_4^{-3}$ is likely the dominant structure in F_4 trianion solution, with the *trans*- configuration more favorable than the *cis*- configuration.

Unlike the anion and dianion, the experimental spectrum of F_4 trianion has a much broader peak, suggesting that multiple species coexist. Computed spectra of the free trianion as well as $[Na^+(THF)_4]F_4^{-3}$ (SSIP) and $[Na^+(THF)_4]_2F_4^{-3}$ (*cis*- and *trans*-2Na-SSIP) are compared to the experimental spectrum in Figure 7. While free ion and SSIP have large dominant peaks, 2Na-SSIPs have similar multiple smaller peaks, with the *trans* structure resembling the experimental spectrum most. The assignment of attaching two counterions to F_4^{-3} agrees with the conclusion from energetics and also supports the idea that dianions would always be associated with one counterion in the μM and nM concentration regions.

Figure 7. Computed spectra of F_4 trianions compared to the experimental spectrum from Figure 2.

Even longer chains F_8^{-4}

As an example of even longer chains, we will briefly mention F_8 tetraanion. Our spin-unrestricted calculation of F_8^{4-} shows that the four highest occupied orbitals, two for each spin, are spatially separated (Fig. 8), leading to $\langle S^2 \rangle = 1.85$ and suggesting a chain-of-polarons picture.

Figure 8: Highest occupied orbitals of F_8^{4-} . Starting from top: α spin HOMO-1, α spin HOMO, β spin HOMO-1, and β spin HOMO.

A computational description of pairing of solvated Na^+ to F_8^{4-} presents a big challenge because of the increased shape mismatch, where the former is closer to a sphere while the latter a stripe. Placement of the cation in the case of an ion pair can have many options. We identified one representative SSIP structure where the solvated Na^+ is right in the middle of the stripe, and one representative CIP structure, where the Na^+ is on top of the six-member ring (its preferred

binding site) closest to the F_8 molecule center. Fig. 9 is a plot of the computed spectra as compared to the experiment. While all computed spectra overestimate the height of the absorption peak, the SSIP spectrum does give a better match in the tail region (0.8-1.5 eV) with no obvious small peaks. We have also computed the binding energetics for F_8^{-4} (Table 2) and found they are similar to those of F_3^{-2} . Based on these evidences, we tentatively assign the dominant ion pair structure for F_8^{-4} to be single Na^+ SSIP. 2 Na^+ or 3 Na^+ SSIPs remain very likely, but we did not explore those structures.

Figure 9. Computed spectra of the F_8^{-4} as compared to the experimental one.

Discussion

The proximity of a counterion can significantly affect the electronic structure of a multianionic conjugated oligomer, as demonstrated with F_4 dianion where a larger spatial overlap of the two polarons is present in the CIP than in SSIP. Understandably, the counterion can also have significant impact on the absorption spectrum. For that we take a look at the transitions for the F_2 dianions, whose spectra were plotted in Fig. 4. In Table 4, we compare the main TDDFT absorption features for the free ion and the CIP and plot the natural transition orbitals³⁸ (NTO). The NTO yields a picture of where the electron(s) come from (the “hole” created) and where they go to, even in transitions involving multiple configurations. For the free ion, there are two distinct peaks, which correspond to the third and fourth transition in F_2^{-2} TDDFT spectra. When a CIP is formed, there are four transitions with significant strength. But one of them (**S4**, 0.8951) is much stronger than the others, which results in the single peak spectrum shape seen in Fig. 4. From the NTO’s in Table 4 we see that the spectrum of CIP contains transitions to NTO’s having substantial densities of Na atoms. The NTO’s thus explain differences between the spectra for contact and solvent-separated ion pairs. To confirm that the spectral change with ion pair formation is not an artifact of the exchange-correlation functional, we also performed TDDFT calculations with the B3LYP functional at the same geometries for the F_2^{-2} free ion and

$\text{Na}^+(\text{THF})_3\text{F}_2^{-2}$ CIP. We find the same results. For the F_2^{-2} free ion, the TD-B3LYP spectrum has two strongly absorbing (oscillator strength in parentheses) states at 1.76 eV (1.4013) and 2.02 eV (0.8273). For the CIP, there are four absorbing states: 1.70 eV (0.1151), 1.81 eV (1.0008), 1.86 eV (0.1607) and 2.02 eV (0.6233).

Table 4. Comparison of the transitions that contribute to the absorption spectra of F_2^{-2} free ion and $\text{Na}^+(\text{THF})_3\text{F}_2^{-2}$ contact ion pair (CIP). The number in parentheses is the oscillator strength. Only transitions with oscillator strengths greater than 0.1 are shown. All natural transition orbitals (NTO) have an eigenvalue of 1.

Transition	NTO/hole	NTO/electron
F_2^{-2} free ion		
S3 1.69 eV (1.2772)
S4 1.93 eV (0.7997)
CIP: $\text{Na}^+(\text{THF})_3\text{F}_2^{-2}$		
S3 1.71 eV (0.2932)
S4 1.76 eV (0.8951)
S5 1.87 eV (0.3164)

When comparing computed spectra to experimental ones, we have focused on spectral features rather than the absolute heights because TDDFT calculations can be less reliable for oscillator strengths. Fortunately computed spectra of CIPs and SSIPs usually have distinct features, which enabled us to assign experimental structures in such cases as F_2 , F_3 and F_4 dianions, and tentatively for F_8^{-4} . Such success also suggests that those experimental observed features used in assignment are of pure electronic origin.

It is reassuring to see that our assignments based on spectra features are consistent with the trends in computed binding energies. These trends also provide further insight on how the binding strength depends on the total charge and the charge density on a planar molecule. For this purpose, we also included the binding energies for F_2^- and F_4^{-4} in Table 2, even though their spectra are not studied here. Comparing the binding of one sodium cation, E_b^{SSIP} , for systems with the same total charges but different sizes, i.e. F_2^{-2} (0.90 eV) and F_4^{-2} (0.68 eV), or F_4^{-4} (1.13 eV) and F_8^{-4} (0.75 eV), we can clearly see that decreasing charge density reduces the binding energy. On the other hand, although F_2^- , F_4^{-2} and F_8^{-4} have similar charge densities, the binding energy increases with the total charge, i.e. from 0.53 to 0.68 and then 0.75 eV. However, the increase is leveling off, which is understandable because major contribution to the binding of the cation comes from the anion charges on the molecular part close to the cation. It should also be pointed out that when more than two ions are involved, details of the ionic complex structure is also a significant factor. This fact is demonstrated by the example that even though $Na^+(THF)_4F_4^{3-}$ has the same total charge as F_4^{-2} , E_b^{SSIP} for F_4^{-2} lies between those for *cis*- and *trans*- $[Na^+(THF)_4]_2F_4^{-3}$.

It appears that an oligomer with multiple spatially non-overlapping charges has nearly the same first peak position in the absorption spectra as the singly charged oligomer, even while the height increases with the number of charges. Experimentally this phenomenon is most evident for F_6 and longer oligomers. Computationally we exemplify this finding with F_8 , where the energy (strength) for the first excitation is 0.5268 eV (1.7243) for the anion and 0.5611 eV (5.1897) for the tetra-anion. To gain some insight, we take a look at the NTOs for the first excitation of the F_8^{-4} SSIP complex. Figure 10 plots the dominant NTO pair, which contributes 96% to the transition. It is thus clear that even though the four charges in F_8^{-4} are spread out spatially, the excitation is local, meaning that the “electron” and “hole” NTO’s occupy almost the same region in the chain: the transition is not a charge transfer type that moves charge along the chain. While the transition is local, it involves more than one of the polarons seen in Figure 8, giving it larger spatial extent. The result is that the transition is not too different from what would be expected in F_8^- .

Figure 10. Calculated natural transition orbitals for the first excitation of the F_8^{-4} SSIP complex.

What we term the mainly non-overlapping charges in Figure 8 suggests a way to understand the nature of multiply reduced species. Reduced species formed in longer (F_5 - F_{10}) oligomers with 1-5 charges have roughly similar spectra in Figure 2. For the multiply-reduced species the spectra gradually shift from the P_1 and P_2 bands in the singly-reduced cases. Computed results for F_8^{-4} (Figure 10) let us explain these in terms of multiple, mainly non-overlapping charges, which gradually increase their overlaps at higher charge densities causing attenuation of the P_2 bands. Earlier results on dianions¹ showed that F_{10}^{-2} consisted of two side-by-side polarons with very little overlap. As charge density increased in dianions of shorter oligomers the charges partly overlapped, $\langle S^2 \rangle$ decreased, and the P_2 bands were suppressed and shifted blue. These behaviors are seen in the multianions of longer oligomers.

The mainly non-overlapping charges in Figures 8 raise the question: Do bipolarons play a role when many electrons are injected into a chain? Bipolarons were once thought to be the main form that charges took in chemically doped conjugated chains. While F_2^{-2} was confirmed to be a bipolaron, do bipolarons occur in longer structures? A principal factor leading to bipolaron formation is charge density, which is one electron per repeat unit in F_2^{-2} . By this measure, F_4^{-4} might have two bipolarons. The observed spectrum for F_4^{-4} does have just one clear peak, like that for F_2^{-2} , but it occurs at ~ 0.5 eV higher energy and is broader, with a high-energy tail. Computationally, we found F_4^{-4} to be closed-shell, i.e. with no polarons, even in the presence of counterions. The doubly occupied orbitals of HOMO and HOMO-1, i.e. those for the 4 charges, can be viewed as the symmetric and anti-symmetric combinations of the HOMO of the bipolaronic F_2^{-2} (shown in the SI Section S2.3), which is consistent with the idea of F_4^{-4} having two bipolarons from charge density consideration. Table S1, which summarizes levels of reduction achieved with three reducing agents, shows that the experiments succeeded to produce this high level of reduction only in F_2^{-2} and F_4^{-4} , but in a few cases the reduction level came close. The prediction⁵ that bipolarons possess a single absorption band between the P_1 and P_2 bands of polarons has served as diagnostic criterion for bipolaron formation. To test this theory, we extended the TDDFT calculations for F_3 anion and dianions beyond the P_2 region. Earlier we found F_3^{-2} free ion has partially separated polarons ($\langle S^2 \rangle = 0.69$). This separation is reduced when F_3^{-2} is paired with a counterion, leading to $\langle S^2 \rangle = 0.55$ in SSIP and $\langle S^2 \rangle = 0.29$ in CIP. In fact, in the CIP the separation is so small, we can force a bipolaron formation (i.e. spin restricted

calculation, $\langle S^2 \rangle = 0.00$) and raise its energy by a mere 11 meV. TDDFT spectra of all these different F_3^{-2} structures are compared in Fig. 11. Interestingly, there is a clear correlation between the height of the second peak and the presence of a bipolaron, to the point that the second peak disappears in a complete bipolaron, which confirms the theoretical prediction. Therefore, if a single band between P_1 and P_2 is the criterion for bipolaron formation, F_3^{-2} , F_4^{-3} , F_4^{-4} , F_5^{-4} , F_6^{-4} , F_6^{-5} might contain bipolarons.

Figure 11. Simulated spectra for F_3 anion and dianion. The dianions with different bipolaron components are shown using the $\langle S^2 \rangle$ (in parentheses) as indicator.

Conclusions

For high degrees of reduction that can occur in conjugated oligomers, like those that may occur in electrochemical measurements,¹⁻³ comparison of computations with experiment can provide insight into the nature of the charged species. For the present case where formation of multi-anions is accompanied by pairing with multiple Na^+ ions, we developed a description of the ion pairing. This description found the difference between contact (or “tight”) and “loose” or solvent-separated (SSIP) ion pairs to be more subtle than depictions available in the past, as indicated in Fig. 2 where the SSIP does not place a THF molecule directly between the anion and a paired Na^+ . Thus this work may be a new, possibly improved, understanding of the differences between these two species.

This description yielded computed TDDFT spectra that matched observed spectra reasonably well and allowed interpretation of experiments to learn what type of ion pairing occurred. The computed spectra also provided strong evidence that structure comprised of two or three peaks and shoulders in shorter oligomers, can be due to multiple *electronic* peaks, not to vibronic structure. The computational description predicted that in some cases SSIPs were more stable, while in others, usually with higher charge density (electrons/repeat unit) CIPs were more

stable, and we obtained estimates of energy differences. Comparison with experimental dissociation constants suggested that the computed binding energies may be too high. While there are no specific tests, relative trends appeared plausible and may be more useful than absolute numeric values for binding of counter ions.

Multiply reduced species in long oligomers appear to be principally non-overlapping (“side-by-side”) polarons, which gradually overlap more as the density of charges increases. When the charge density reaches one extra electron per monomer, such as in F_2^{-2} and F_4^{-4} , there are only bipolarons. For lower charge densities, the proximity of counterions may enhance the local charge density and increase the polaron overlap, as demonstrated in F_4^{-2} . On the other hand, higher charge density on the oligomer also draws the counterion closer than lower charge density, i.e. to form CIP instead of SSIP, which also enhances the desolvation of the sodium ion. In future work, we will investigate the implication of these results to the interaction between ions and carbon electrodes.

Supporting Information

Details of the experimental methods, i.e. our approaches to chemical reductions, pulse radiolysis, and spectroscopy, and additional computational results, including the G09 keyword for the DFT method used in this work, coordinates for selected F_2 dianion SSIP and CIP structures, and comparison of HOMOs between F_2^{-2} and F_4^{-4} , can be found in the Supporting Information.

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