The Optical Signature of Charges in Conjugated Polymers

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ABSTRACT: Electrical charge flowing through organic semiconductors drives many of today’s mobile phone displays and television screens, suggesting an internally consistent model of charge-carrier properties in these materials to have manifested. In conjugated polymers, charges give rise to additional absorption of light at wavelengths longer than those absorbed by the electrically neutral species. These characteristic absorption bands are universally being related to the emergence of localized energy levels shifted into the forbidden gap of organic semiconductors due to local relaxation of the molecular geometry. However, the traditional view on these energy levels and their occupation is incompatible with expected changes in electron removal and addition energies upon charging molecules. Here, I demonstrate that local Coulomb repulsion, as captured by nonempirically optimized electronic-structure calculations, restores compatibility and suggests a different origin of the charge-induced optical transitions. These results challenge a widely accepted and long-established picture, but an improved understanding of charge carriers in molecular materials promises a more targeted development of organic and hybrid organic/inorganic (opto-)electronic devices.

INTRODUCTION

The transport of charge carriers through light-emitting organic semiconductors is one of the fundamental processes enabling the current evolution of display technology. Since the discovery of metallic conduction in doped polyacetylene,1 the presence of charges in \( \pi \)-conjugated and aromatic polymers has been inferred from the emergence of distinct features in their near-infrared/visible absorption spectrum.2,3 These features have historically been assigned to one-electron transitions involving single-particle energy levels situated within the band gap of the electrically neutral polymer.4,5 In the more common case of nondegenerate ground-state systems, these intragap states are thought to arise from local, adiabatic lattice relaxation around excess charges, and the envisioned self-localized electrons or holes are habitually referred to as polarons.3–5 The picture illustrating the charge-induced energy levels, and the associated optical transitions, has pervaded pertinent scientific literature over the past three decades,3–8 it is featured in topical textbooks,9,10 and it is invoked to interpret spectroscopic data to the present day.7,8 Here, I argue that the occupation of the charge-induced intragap states in this picture entails implausible consequences for electron removal and addition energies. On the basis of state-of-the-art first-principles calculations, I then demonstrate that local Coulomb repulsion dictates a different occupation scheme. With only a minor increase in complexity, this revised picture lifts undesirable inconsistencies and suggests a different origin for the ubiquitously observed optical signature of charges in conjugated polymers. I expect the present work to lead to new insights into the nature and transport of charge carriers in organic semiconductors—central to understanding and improving organic as well as hybrid organic/inorganic (opto-)electronic devices—both through the critical re-examination of past results and through the informed design of new experiments.

RESULTS AND DISCUSSION

The process by which polarons are widely perceived to form in conjugated polymers with nondegenerate ground states is schematically depicted in Figure 1. By adding an electron to the bottom of the conduction band, an energy corresponding to the vertical electron affinity of the neutral system, \( \text{EA}^0 \), is gained (Figure 1a). Subsequently, the nuclei around the added electron are envisioned to adiabatically rearrange so as to stabilize the excess charge—now spatially confined to a polymer segment of finite length—in energy. The resulting, singly occupied energy level below the conduction-band edge is accompanied by a comparably localized, but doubly occupied, energy level that relaxes upward in energy from the valence-band edge owing to the local lattice distortion. This local distortion, together with the charge that both causes it and is trapped by it, is then termed a negative polaron. In full analogy, a positive polaron is understood to form by investing the vertical ionization energy of the neutral polymer, \( \text{IE}^0 \), to remove an electron from the top of the valence band (Figure 1b). Again, the nuclei around the excess charge—now a hole—are then thought to adiabatically rearrange so as to localize it and to stabilize it in energy, which is represented by a singly occupied energy level above the valence-band edge, accompanied by a comparably localized but empty energy level, which relaxes downward from the conduction-band edge of the neutral polymer into its fundamental gap.
The picture just described obviously portrays a static, zero-Kelvin situation, and it could be criticized for treating the nuclear degrees of freedom as a classical deformation potential rather than as quantized vibrations at finite temperature. That it (spuriously) implies the breaking of translational symmetry in idealized one-dimensionally periodic systems might be acceptable because some degree of disorder is inherent to realistic polymers and, with it, the possibility for localized electronic states. Less accepted, however, are the implications of the established polaron picture for the electron addition and removal energies of singly charged polymer chains.

The fact that, in the anion case, the horizontal line representing the upper, singly occupied intragap state is drawn as long as that representing the lower, doubly occupied state implies that also the former can accept a second electron (Figure 1c). This, however, entails that the vertical electron affinity of the anion, EA\(^{-}\), that is, the second electron affinity of the neutral polymer, is always larger than EA\(^{0}\), its first electron affinity. Likewise, in the cation case, the arrow on the horizontal line representing the lower, singly occupied intragap state suggests that the vertical ionization energy of the cation, IE\(^{+}\), that is, the second ionization energy of the neutral polymer, is always smaller than IE\(^{0}\), its first ionization energy (Figure 1d).

It is the central tenet of the present work that neither of these notions, EA\(^{-}\) > EA\(^{0}\) and IE\(^{+}\) < IE\(^{0}\), is borne out in reality and that, in fact, the opposite is the case. If, indeed, a negative charge should be (self-)confined to a finite spatial region, then a second negative charge added to the same region in space will experience Coulomb repulsion, thereby lowering EA\(^{-}\). Likewise, removing a second electron from an already positively charged spatial region will cost additional energy to overcome Coulomb attraction, thereby increasing IE\(^{+}\). In spite of the fact, however, that the neglect of Coulomb interaction has been explicitly acknowledged early on, and despite its foreseen impact on the optical signature of charges in conducting polymers, the qualitative features of the underlying energy-level diagrams in Figure 1 have long stood unchallenged. Notwithstanding ongoing progress in calculating the spectral function, that is, the equivalent to the density of states (DOS) in many-electron systems that are correlated through Coulomb and electron-phonon interactions, a much simpler, still adiabatic, picture has recently been proposed for the molecular semiconductor C\(_{60}\) (ref 21). It suggests that local Coulomb interaction, already when treated at the mean-field level of theory, dramatically alters the energies and occupations of the charge-induced intragap states, observed there by (inverse) photoelectron spectroscopy. No attempt, however, has been made to assess the compatibility of this picture with the optical signature of charges in the system, and the impact of intermolecular hybridization has been disregarded entirely. While this might be permissible for C\(_{60}\), where the widths of conduction and valence bands are small compared to local Coulomb repulsion, the chemical repeat units in polymers...
are linked by covalent bonds and band widths can, therefore, be substantial. 

**Electronic Structure.** To illustrate the consequences of the competition between (mean-field) Coulomb interaction, adiabatic lattice relaxation, and the delocalization of excess charges on the energy levels of conducting-polymer ions, I performed density functional theory (DFT) calculations on the archetypical example of poly(\textit{para}-phenylene) or, rather, a 30 repeat-unit oligomer thereof (Figure 2a). Adiabatic relaxation after adding or removing an electron leads to local changes in its geometry (Figure 2b–d), which reflect the more quinoidal nature of the ionic species. The DOS around the localized charges might at first appear reminiscent of that in Figure 1, but recent advances in DFT (see Methods) allow highlighting critical differences. In the anion case (Figure 2e), a singly occupied, localized intragap state just below the conduction-band edge indeed emerges in the spin-up manifold. Its counterpart in the spin-down manifold, however, is notably absent. Consequently, no second electron can be added at this energy (cf. Figure 1c), and...
the unlikely notion of $EA^- > E A^0$ is refuted. Rather, all unoccupied levels “bulge upward” around the localized negative charge, visualizing that a second electron brought into its vicinity would be repelled and that, therefore, $EA^- < E A^0$ locally.

Results for the cation case (Figure 2f) are even more striking in that the energy level locally relaxing upward from the valence-band edge is, in fact, completely empty. It is a hole state and no electron can, therefore, be removed from it (cf. Figure 1d). Its occupied counterpart in the spin-up manifold merges into the locally downward-bulging valence band, which affirms that removing a second electron from an already positively charged spatial region costs more energy than removing it from a neutral polymer segment—not less—and that, therefore, $IE^+ > IE^0$ locally.

Qualitatively, the results in Figure 2 thus corroborate the validity of the view proposed in ref 21 also for polymers and its signature is actually visible in previous computational studies.27,28 Discrepancies to the established polaron picture, however, have not been commented there and neither have their far-reaching implications for the expected optical transitions.

**Optical Absorption.** The historical energy-level diagram (Figure 1) suggests three optical transitions to be, in principle, observable in polymer ions of either sign, all at lower energies than the onset of absorption in the neutral system.3−5 According to this view, the lowest-energy transition in the anion, labeled “P1” in Figure 3a (left), corresponds to promoting the single electron from the upper intragap level into the conduction band. Such a transition still seems plausible in the revised DOS (Figure 2e). Next in energy, the traditional picture suggests a transition promoting an electron from the lower, doubly occupied intragap level into the upper, single occupied state (Figure 3a, center). Previously argued to have appreciable oscillator strength,26,29−31 Figure 2e shows that, on the contrary, it does not even exist owing to the absence of the upper, accepting intragap state. The third, highest-energy subgap absorption is predicted to comprise two transitions in...
the historical picture. The first, from the lower, doubly occupied intragap state into the conduction band (Figure 3a, right) has been attributed vanishing oscillator strength. but it is still plausible in the revised DOS (Figure 2e). The last transition, however, from the valence band into the upper, singly occupied intragap state is no longer possible in the picture emerging from the present study, again owing to the manifest absence of the upper, accepting level (Figure 2e). For the cation case (Figure 3b) similar revisions are necessary. While, again, P1 is certainly plausible and so is a transition from the valence band into the upper, unoccupied intragap state, no electron can be promoted from the lower intragap state to anywhere because this state is empty (Figure 2f).

Going beyond the single-particle picture just discussed, which suggests at most two out of three optical transitions to survive the revision of the underlying DOS, I performed time-dependent DFT (TDDFT) calculations on the neutral and ionic oligomers to capture the intrinsically excitonic nature of excited states in such systems. Figure 3c,d clearly shows that, indeed, two broad, subgap absorption features (P1 and, at higher energies, “P2”), are to be expected. Both are composed of a multitude of individual transitions, each of which is by itself a linear combination of many single-electron excitations from an occupied into an unoccupied energy level. Analysis of the expansion coefficients leads to the cartoons in Figure 3e,f, which I suggest should replace the historical picture of charge-induced energy levels and optical transitions in conjugated polymers: In the anion case, feature P1 is composed of transitions that all start from the upper, single occupied intragap level and that end first at the conduction-band edge and then in successively higher-lying unoccupied states. In the cation, the corresponding transitions all end in the lower, unoccupied intragap level and they start first from the valence-band edge and then from successively lower-lying occupied states. The transitions contributing to feature P2 in the anion case start in the lower, doubly occupied intragap state (and lower-lying occupied levels) and end at the conduction-band edge (and higher-lying unoccupied levels). In the cation, they start from the valence-band edge (and lower-lying occupied levels) and end in the upper, empty intragap state (and higher-lying unoccupied levels).

**CONCLUSIONS**

It is possible that even this revised picture, which is still adiabatic, still breaks translational symmetry, and treats Coulomb interaction only at the mean-field level, will eventually be further refined in the future. The minimum physics required for doing so, however, would seem to be captured only by a fully quantized, two-band Holstein-Peierls-Hubbard model, possibly extended to capture the intrinsically excitonic nature of excited states in such systems. Figure 3c,d clearly shows that, indeed, two broad, subgap absorption features (P1 and, at higher energies, “P2”), are to be expected. Both are composed of a multitude of individual transitions, each of which is by itself a linear combination of many single-electron excitations from an occupied into an unoccupied energy level. Analysis of the expansion coefficients leads to the cartoons in Figure 3e,f, which I suggest should replace the historical picture of charge-induced energy levels and optical transitions in conjugated polymers: In the anion case, feature P1 is composed of transitions that all start from the upper, single occupied intragap level and that end first at the conduction-band edge and then in successively higher-lying unoccupied states. In the cation, the corresponding transitions all end in the lower, unoccupied intragap level and they start first from the valence-band edge and then from successively lower-lying occupied states. The transitions contributing to feature P2 in the anion case start in the lower, doubly occupied intragap state (and lower-lying occupied levels) and end at the conduction-band edge (and higher-lying unoccupied levels). In the cation, they start from the valence-band edge (and lower-lying occupied levels) and end in the upper, empty intragap state (and higher-lying unoccupied levels).
absorption spectra so obtained (that is, lists of transition energies and corresponding oscillator strengths) were broadened by a Gaussian peak-shape function with a full width at half-maximum of 0.2 eV.

To assess the possibility of bipolaron formation, which—in the historical picture—corresponds to the coalescence of two spin-antiparallel excess charges of the same sign onto the same (locally geometry-relaxed) polymer segment, also calculations on diions were attempted. Adhering to the bipolaron picture of spin-less charge carriers, these calculations were restricted to a singlet and, therefore, conducted in a closed-shell manner. Relaxing the atomic positions (with those of the radical ions as starting guesses) led to an additional stabilization of 0.20 and 0.16 eV for the dianion and dication, respectively, but the centrally localized geometry distortion—clearly visible in Figure 2d—disappeared. More importantly, the total energy of two isolated, noninteracting radical anions was still lower by 1.20 eV than the total energy of one neutral and one dianionic oligomer, and the total energy of two radical cations was lower by 1.14 eV than that of one neutral and one dicaticonic oligomer, suggesting Coulomb repulsion between two like charges on the same chain to significantly outweigh the energy gained through additional lattice relaxation. This is also manifest in the fact that the spin-restricted, closed-shell wave functions of the diions exhibit external instabilities toward spin-unrestricted solutions. Indeed, reoptimization as triplets lowers the energies of the dianion and the dication by 0.67 and 0.66 eV, respectively. In the absence of charge-stabilizing counterions,25 the formation of bipolarons in the traditional sense is, therefore, unlikely on isolated strands of poly(para-phenylene) in a vacuum.

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Notes

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