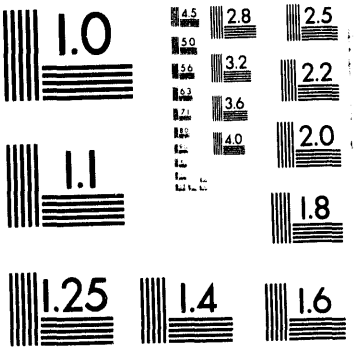
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CONJUGATED POLYMER FLUORESCENCE: INTERPLAY OF CORRELATIONS AND ALTERNATION

Conf-931108--89

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Conjugated polymers have been intensively studied in connection with high conductivity on doping, large nonlinear optical responses in their semiconducting state, and recently[1] as novel light-emitting diodes (LEDs). Many different polymers are realized in Fig. 1 on varying the substituents R, including the best characterized examples[2,3] that have centrosymmetric conjugated backbones in their idealized extended geometry. The PS and PPV families fluoresce strongly, the PT family moderately, and the PDA's or PA hardly at all. We have related [4,5] polymer fluorescence to the nature of the lowest singlet excited state, S_1, which in D_{2h} symmetry is either a dipole-allowed B_u or a two-photon allowed A_g state. Since the ground state is A_g, S_1 is either 1B or 2A and fluorescence requires E(1B) < E(2A). The idea is simply that radiationless decay wins out for the low excitation energies and many vibrational degrees of freedom of conjugated polymers unless S_1 has a strong transition dipole to the ground state.

The observed excitation energies E(1B) and E(2A) indicate that S_1 is indeed 1B in polymers that fluoresce[5]. Two-photon absorption is then detected by monitoring the 1B emission following rapid internal conversion. When 2A is below 1B, its location can be obtained from two-photon absorption, a more conclusive but also more difficult measurement, or indirectly[6] from resonances in third-harmonic generation or from electroabsorption spectra. Nonlinear optical responses of conjugated polymers also probe excited-state structure, especially the even-parity A_g states[7] with large transition moments to the ground state and to 1B. We have emphasized[8] the desirability of establishing the energy thresholds for one-photon, two-photon, triplet, and charge-carrying excitations of conjugated polymers by as many techniques as possible. Different thresholds characterize the PS, PDA, PPV, and PT families.

All the conjugated polymers in Fig. 1 are semiconductors in their pristine form, with half-filled π-electron bands arising from an even number of carbons per repeat unit and a half-filled σ-band in PS for the sp^3 orbitals along the Si-Si backbone. The divergent density of states at band edges of infinite systems implies equal excitation thresholds in this limit. The observed thresholds thus point to electron-electron (e-e) correlations and 1B is a singlet exciton. The band or Hückel limit remains the starting point, with a band gap of $4t\delta$ for alternating transfer integrals $t_\pm = t(1 \pm \delta)$. The band or single-particle gap sets the scale for e-e correlations in semiconductors. Detailed theoretical analysis[9] places the 1B/2A crossover around $U = 2t_+$ in alternating Hubbard chains and around $(U - V_1) = \sqrt{2}t_+$ in Pariser-Parr-Pople(PPP) chains with long-range Coulomb interactions.

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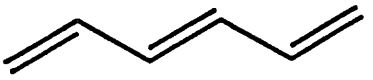
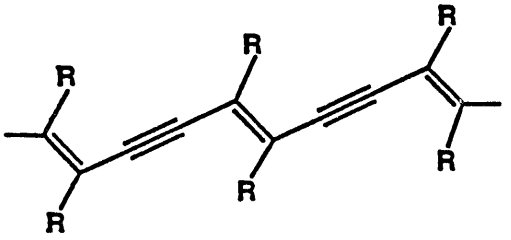
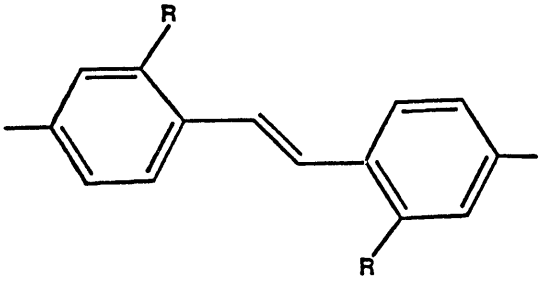


PA



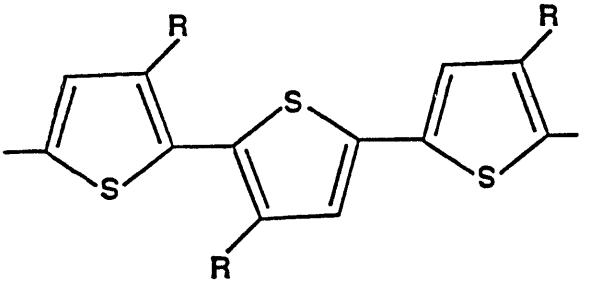
PDA

R = PTS,4BCMU,etc



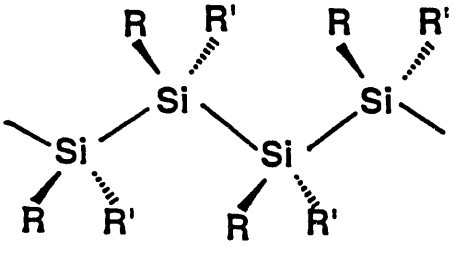
PPV

R = H, alkyl, aryl, etc



PT

R = H, alkyl, aryl, etc



PS

R = alkyl or aryl

Fig. 1. Idealized structure of conjugated polymers. Polyacetylene(PA) and polysilanes(PS) are alternating chains with $\delta \sim 0.07$ and 1/3, respectively; the effective alternation is $\delta \sim 0.15$ in polydiacetylenes(PDA) and is higher in poly-p-phenylene-vinylene (PPV) due to topology and in polythiophene(PT) due to nonconjugated S heteroatoms.

The partial single and double bonds of PA illustrate an alternating chain, as do the inter and intra-atomic transfers of PS, and alternating chains are representative of all polymers. The multiple bonds of PDA and heteroatoms of PT lead to four sites per repeat unit and thus to an effective alternation. PPV has eight sites per repeat unit, which in Hückel theory can rigorously be decomposed[4] into two states localized on each ring and an extended chain with increased $\sqrt{2}$ t at the bridgehead carbons. The gap between the valence and conduction bands is of order t even when all bond lengths are equal. The discrete eigenstates of oligomers always lead to finite E(1B) and E(2A), and the even/odd spectrum of linear systems implies E(1B) < E(2A).

The regular ($\delta = 0$) Hückel chain has no gap. Exact results for the infinite Hubbard chains[10] show E(1B) to be finite for any U > 0, while E(2A) vanishes for arbitrary U. Since the electron-hole symmetry of half-filled Hubbard models is retained for any spin-independent potential V(R), the ratio E(2A)/E(1B) vanishes[9] at $\delta = 0$ for one-dimensional metals with arbitrarily small e-e correlations. But the Hückel gap $4t\delta$ leads to E(2A)/E(1B) = 1 in Fig. 2 at U = 0 for any $\delta > 0$. As U increases, 2A becomes a spin wave at E(2A) ~ t^2/U and the one-photon gap increases as E(1B) ~ U for any δ. Spin-charge separation in strongly correlated systems is independent of δ and that may be why the importance of alternation has not been appreciated.

Polymer fluorescence illustrates an interesting interplay between correlations and alternation. We summarize below experimental and theoretical results for the location of 2A and 1B. Quite generally, the 1B/2A crossover[9] of S_1 requires intermediate correlations. Typical Hubbard models of PA have U ~ 2t and δ ~ 0.1, close to the crossover. So are PPP models that were introduced[11] for molecular π-π^* spectra. The location of E(2A) below E(1B) in finite polyenes[12] has been a paradigm of Coulomb correlations.

Both polymer and oligomer data for E(2A)/E(1B) are shown in Fig. 2, along with exact PPP results. PPP models for conjugated polymers[13] require no adjustable parameters, since molecular choices[11] have sufficed so far. We find E(2A) < E(1B) for polyenes, whose bond lengths correspond to $\delta = 0.07$. The recent addition of the N = 14 point in Fig. 2 suggests some systematic deviations from the gas-phase results[12]. The greater stabilization of 1B, an ionic state, in alkane matrices leads to higher[14] E(2A)/E(1B) but similar 1/N slope in Fig. 2. The same PPP parameters predict[4] E(1B) < E(2A) in PPV, as subsequently found[15], and account[16] for molecular one and two-photon spectra. The consequences of larger effective alternation in conjugated phenylenes is particularly striking for PPV, PA, and polyenes, where closely similar e-e correlations are expected on physical grounds.

The PS calculations[17] in Fig. 2 are based on E(1B) of permethylated oligomers and both E(2A) and E(1A) for polymers. Poly(di-n-hexylsilane), PDHS, is a crystalline polymer with the all-trans structure of Fig. 1, while poly(methylphenylsilane), PMPS, is an amorphous photoconductor. Each has[8] E(2A) > E(1B). The same t = -2.40 eV is used, but with larger $\delta = 1/3$, and U = 9.04 eV for the larger Si orbital is some 20% less than for C. The E(2A)/E(1B) ratio now increases slightly with N, as can be understood[9] in terms of weakly coupled dimers with singlet excitons of B_u symmetry at k = 0. Simple band theory also precludes *positive* deviations of E(2A)/E(1B) from unity.

The PDA triple bonds increase δ to ~0.15 and lead to E(2A) slightly below E(1B), in agreement with both oligomer[18] and polymer results in Fig. 2. The direct measurement[19] of E(2A) in optical quality PDA-4BCMU films has recently been extended[20] to PDA-PTS crystals whose well-resolved E(1B) = 2.00 eV and threshold

for photoconduction allows sharper tests of theoretical models. The 6T result in Fig. 2 is for the six-ring PT oligomer[21]. The nonconjugated S atoms induce a charge-density-wave ground state whose modeling[22] for interacting π-electrons leads to an electrostatic site energy ε. We find E(2A) > E(1B) for an ε = 1.8 eV, consistent with quantum chemical calculations of the ground-state charge distribution. Thus heteroatoms in PT and the PPV topology both increase the effective alternation, with an adjustable parameter in PPP theory for PT and none for PPV.

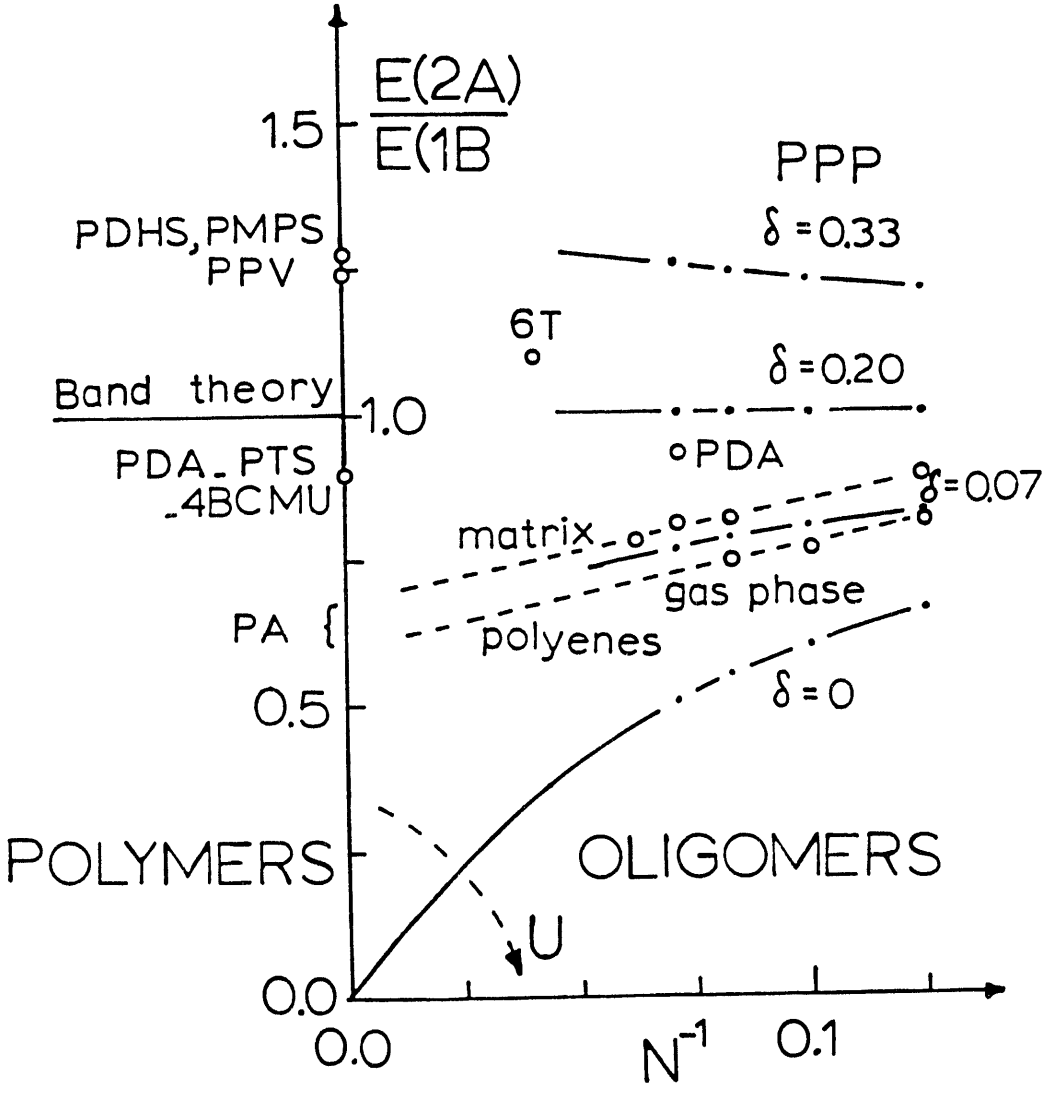


Fig. 2. Ratio E(2A) / E(1B) of the two-photon and one-photon gaps of conjugated polymers and N-site oligomers discussed in the text. Experimental results are shown as open circles, exact PPP calculations at alternation δ as closed circles. Electron-hole symmetry fixes the δ = 0 value of infinite alternating chains; increasing U >> t leads to E(2A) / E(1B) ~ $(t/U)^2$ for spin and charge excitations.

The PA geometry and bandwidth were retained for the $\delta = 0.20$ points in Fig. 2, with E(2A)/E(1B) ~ 1 in oligomers up to 14 sites. The slight 2% rise between N = 8 and 14 suggests that the polymer crossover is a bit lower for these correlations. The weak N-dependence at the S_1 crossover has already been noted[9]. Indeed, the prominent one-photon gap E(1B) is a convenient internal standard[6] for multiphoton spectra of amorphous samples with unspecified backbone geometries. The more rapid convergence with N at large δ has long been exploited in terms of exchange or hopping between dimers. Regular ($\delta = 0$) chains are clearly the most difficult to extrapolate. The $\delta = 0$ points in Fig. 2 are for polyenes with bond lengths $R_0 = 1.40$ A, bond angles of $2\pi/3$, t = -2.40 eV and the standard PPP potential. The ratio E(2A)/E(1B) now decreases with 1/N and its small value in the polymer is fully consistent with the symmetry result of a vanishing two-photon gap in infinite chains.

These experimental and theoretical results show a 1B/2A crossover to occur with increasing e-e correlations in any centrosymmetric chain with an insulating ground state. Although the correlation strength is the natural variable in theoretical studies, systematic variations of U or V(R) are difficult or impossible experimentally. Similar e-e correlations, on the other hand, are indicated for conjugated hydrocarbons and polymers by their identical bond lengths and angles. Moreover, the data base provided by molecular excitations largely fixes Coulomb correlations in semi-conductors, where shielding is not an issue. The π-conjugated polymers in Fig. 1 thus present a variety of band gaps at constant correlations, and single-particle gaps can accurately be related to the structure. Quite remarkably, the exact PPP results in Fig. 2 for the 1B/2A crossover of conjugated polymers are based previous molecular $t_{\pm}$ and V(R) values. Stronger correlations shift the 1B/2A crossover to larger δ, out of the range realized physically, or suppress it altogether. The nature of S_1 thus depends sensitively on both correlations and alternation.

Acknowledgments: We thank S. Ramasesha for stimulating discussion and the National Science Foundation for support through DMR-9300163. Work at Sandia was supported through the Department of Energy under DE-AC04-76DP00789. DSG is grateful to the Brazilian Agency FAPESP for financial support.

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