Photophysics of phenyl-substituted polyacetylenes, theory

Alok Shukla\textsuperscript{a,}\textsuperscript{*}, Haranath Ghosh\textsuperscript{b}, Sumit Mazumdar\textsuperscript{b}

\textsuperscript{a}Cooperative Excitation Project ERATO, Japan Science and Technology Corporation (JST) and Physics Department, Indian Institute of Technology, Powai, Mumbai 400076, India
\textsuperscript{b}Department of Physics and The Optical Sciences Center, University of Arizona, Tucson, AZ 85721, USA

Abstract

We present a theoretical study of the electronic structures of poly-phenylacetylene (PPA) and poly-diphenylacetylene (PDPA). Strong photoluminescence (PL) in PDPA’s is a consequence of the occurrence of the 2A\textsubscript{g} two-photon state above the optical 1B\textsubscript{u}, in spite of the polyene backbone. This reversed energy ordering (as compared to linear polyenes and trans-polyacetylene, t-PA) is a signature of reduced effective electron correlations in PPA and PDPA. The optical gaps of the substituted materials are smaller than polyenes of the same chain length.

Keywords: Poly-diphenylacetylene (PDPA); Photoluminescence (PL); Two-photon; trans-Stilbene

1. introduction

Linear polyenes, t-PA and polydiacetylenes are weakly emissive, as the 2A\textsubscript{g} state in these systems occurs below the optical 1B\textsubscript{u}. The optically pumped 1B\textsubscript{u} decays to the 2A\textsubscript{g} in ultrafast times, and radiative transition to the 1A\textsubscript{g} ground state from the 2A\textsubscript{g} ground state is forbidden. Strong PL in the common light emitting polymers, such as PPV and PPP, implies a reversed excited state ordering $E(2A_g) > E(1B_u)$ (where $E(\ldots)$ is the energy of the state), which is understood within the effective linear chain models for these systems \cite{1}. Within this theory, the lowest excitations of the above class of materials can be mapped into those of polyene-like chains with large effective bond alternations. For example, replacement of all (alternate) double bonds of polyacetylene with phenyl groups gives PPP (PPV), a chemical modification that we hereafter refer to as “bond substitution”. Enhanced effective bond alternation raises the energy of the 2A\textsubscript{g} \cite{1} with respect to the 1B\textsubscript{u}, and PPP and PPV are therefore emissive. Note that enhanced bond alternation also raises the energy of the 1B\textsubscript{u}, and therefore it appears that strong PL can be a characteristic only of materials whose optical gaps are larger than that of t-PA.

Here we show that this restriction does not apply to materials obtained by “site substitution”, viz., substitution of the hydrogen atoms of polyenes with conjugated side groups. PPA’s and PDPA’s are examples of such materials. The recent demonstrations of strong PL (quantum efficiency $\sim 50\%$) in many PDPA’s, and even in some poly-alkylphenylacetylenes (PAPA’s), \cite{2–6} are counterintuitive, in view of the polyene backbones in these materials (Fig. 1). The current materials have relatively short conjugation lengths (five to seven backbone double bonds [4]), but nevertheless, the 2A\textsubscript{g} in polyenes with the same lengths occur below the 1B\textsubscript{u}. One naive interpretation could be that the effective bond alternations in the PPA’s or PDPA’s are larger than those in linear polyenes of the same chain lengths. We show below that this is incorrect. A second naive interpretation could be that the optical properties of PDPA’s are intermediate between that of linear polyenes and trans-stilbene (the unit cell of PDPA). This view is incorrect, as it implies that the optical gap in PDPA is larger than that of polyenes and smaller than that of trans-stilbene. We show that the optical gaps in PPA’s and PDPA’s are smaller than those in corresponding polyenes. The correct interpretation involves a confinement–deconfinement effect; as Coulomb interactions confine the exciton on the backbone chain, there is a deconfinement effect in the transverse direction, i.e. delocalization of the particle–hole pair of the optically excited state into the phenyl groups. The effective electron correlation thereby decreases, and the 2A\textsubscript{g} occurs above the 1B\textsubscript{u} in PDPA. This screening effect in PPA is obviously smaller, since phenyl groups now occur on only alternate backbone carbon atoms, and we find here that the 2A\textsubscript{g} is nearly degenerate with the 1B\textsubscript{u}. Relatively small chemical modifications now determine the actual energy ordering, which
is why light emission in PAPA’s depends strongly on the size of the alkyl group. A brief presentation of this work has been made elsewhere [7]. Here we present new results based on the one-electron band structure, emphasizing that the photophysics is a combined effect of the peculiarity of the band structure and electron correlation effects.

2. Model Hamiltonian

We study the materials under consideration using the Pariser–Parr–Pople model Hamiltonian, supplemented by the Su–Schrieffer–Heeger (SSH) electron–phonon coupling along the polyene backbone

\[ H = H_1 + H_2 + H_3 + H_{ee}, \]  

\[ H_1 = -\sum_{\langle k,k'\rangle,M} (t_0 - \alpha \Delta_{k,M}) B_{k,k',M,M+1} + \frac{1}{2} K \sum_{k,M} \Delta_{k,M}^2, \]  

\[ H_2 = -t_0 \sum_{\langle \nu,\nu'\rangle,M} B_{\nu,\nu',M,M}, \]  

\[ H_3 = -t_1 \sum _{M} B_{k,y,M,M}, \]  

\[ H_{ee} = U \sum_{M} n_{i,M} n_{i',M} + \frac{V}{2} \sum_{i,j,M,N} V_{i,j,M,N} (n_{i,M} - 1)(n_{j,N} - 1). \]  

In the above, \( k, k' \) are carbon atoms on the polyene backbone, \( \mu, \nu \) are carbon atoms belonging to the phenyl groups, \( M \) is a unit consisting of a phenyl group and a polyene carbon, \( \langle \cdots \rangle \) implies nearest neighbors, and \( B_{i,j,M,M'} = \sum_{\sigma} c_{i,M,\sigma}^\dagger c_{j,M',\sigma} + h.c. \). The number operators \( n_{i,M,\sigma} = c_{i,M,\sigma}^\dagger c_{i,M,\sigma} \) and \( n_{i,M} = \sum_{\sigma} n_{i,M,\sigma} \). \( H_1 \) and \( H_2 \) describe the electron hoppings within the polyene backbone and the phenyl rings, respectively, and \( H_3 \) is the hopping between them. In \( H_1 \), \( \alpha \) is the e–ph coupling constant, \( K \) the spring constant, and \( \Delta_{k,M} = (u_{k+1,M+1} - u_{k,M}) \), where \( u_{k,M} \) is the displacement of the chain carbon atom of the \( M \)th unit from equilibrium. \( H_{ee} \) is the e–e interaction, with \( i \) and \( M \) including now all atoms. Steric interactions imply considerable phenyl group rotation in PDPA, which implies a reduction in \( t_\perp \) and changes in \( V_{i,j,M,N} \).

3. Band structure

The one-electron band structures of PPA and PDPA, with zero bond alternation along the t-PA backbone, are presented in Fig. 2 for the specific case of \( t_0 = 2.4 \text{ eV} \) and \( t_\perp = 1.4 \text{ eV} \). The qualitative natures of the bands are similar for other values of \( t_\perp \). The band structures of PPA and PDPA differ from simple superposition of the bands of isolated t-PA and benzene molecules because of the non-zero transverse \( t_\perp \), which leads to hybridization between the isolated t-PA and benzene energy levels. The HOMOs (LUMOs) of each benzene molecule are doubly degenerate. One member of each degenerate pair is delocalized over the entire phenyl group, while the other is localized, with zero electron densities on the carbon atom of the phenyl group that is bonded to the chain carbon, and on the carbon atom in para position relative to this. Hybridization involves only the delocalized members of each degenerate pair, as well as the outermost delocalized MO of each benzene. The quantity \( \rho_c = \sum_{\mu} c_{\mu,F}^\dagger c_{\mu,F} \) where \( k_F \) is the Fermi momentum and \( c_{\mu,F} \) is the coefficient of the \( i \)th backbone chain atom in the one-electron expansion of the band at the Fermi level, is then a useful measure of the extent of the hybridization at \( k_F \). The behavior of \( \rho_c \) as a function of \( t_\perp \) is presented in Fig. 3.

The Peierls bond-alternation in the present case is a strictly one-dimensional phenomenon, and from Fig. 3, the decreasing chain character at \( k_F \) implies strong reduction...
in the extent of bond alternation with increasing \( t_{\perp} \) in PPA and PDPA. Explicit calculations of the self-consistent bond alternations within the one-electron version of Eq. (1) show that the bond-alternation goes as \( t_{\text{PA}} \gg \text{PPA} \gg \text{PDPA} \) [7,8]. PL in PDPA is not due to enhanced bond alternation.

The band structures of the bond dimerized systems are essentially similar, except near \( k_F \), where a gap opens up between the chain-derived valence and conduction bands upon dimerization. A quantity analogous to \( \rho_c \) can be calculated for each individual band level. For the chain-derived bands, chain character decreases with increasing energy separation from the Fermi energy. In discrete systems, this implies that the chain character of the HOMO \(-1\) (LUMO \(+1\)) level is smaller than that of the HOMO (LUMO).

4. Optical absorption

The reduction in the effective \( H_{ee} \) in PPA and PDPA can be understood from the study of the absorption to the 1B\textsubscript{u}. The linear optical absorption of PDPA was studied both within the single-particle (Hückel), as well as Coulomb-correlated picture, employing the singles-configuration-interaction (SCI) method. The Coulomb parameters were chosen from the Ohno relationship,

\[
V_{i,j,M,N} = \frac{U}{(1 + 0.6117R_{ij,M,N}^2)^{1/2}},
\]

where \( U = 11.13 \text{ eV} \) and \( R_{ij,M,N} \) is the separation in Å between carbon atoms \( i \) on unit \( M \) and \( j \) on unit \( N \). We define the polyene backbone as the \( x \)-axis, and the transverse direction in the plane as the \( y \)-axis. Along the backbone, we chose rigid bond alternation \( z_{0j}/z_0 = \delta = 0.07 \), the same as in linear polyenes. The backbone polyene bond lengths were assumed to be 1.45 and 1.35 Å, in length, as in t-PA, and all phenyl bond lengths are taken to be 1.4 Å. The bond between the backbone atoms and the phenyl groups is taken to be a true single bond with length 1.54 Å. We considered both parallel and antiparallel ordered rotations of neighboring phenyl groups, with rotation angles of 30°. The difference in the dipole moments for these two cases was insignificant. The components of 1A\textsubscript{g} \( \rightarrow \) 1B\textsubscript{u} transition dipole moments for a PDPA oligomer with five chain double bonds, as functions of \( t_{\perp} \), are presented in Table 1. The results for an artificial trans-stilbene monomer with \( t_{\perp} = 1.4 \text{ eV} \) are also included. Considering that the transition dipole moment is a direct measure of the particle–hole separation in the 1B\textsubscript{u} exciton, the following trends emerge from the data in Table 1 [7]: (a) For all \( t_{\perp} \), \( H_{ee} \) strongly confines the exciton in the \( x \)-direction, (b) for non-zero \( H_{ee} \), the particle–hole confinement in the \( y \)-direction is significantly enhanced by \( t_{\perp} \), as indicated by the strong reduction in \( \mu_y \) as \( t_{\perp} \) is increased from zero (c) there is an effective “deconfinement” of the exciton in the \( y \)-direction (for each \( t_{\perp} \), \( \mu_y \) is larger with non-zero \( H_{ee} \)), which is synergic with its confinement along the \( x \)-direction. The synergic nature of the deconfinement in PDPA is confirmed by comparing it to the transition dipole moments of the trans-stilbene monomer, \( H_{ee} \) suppresses both \( \mu_x \) and \( \mu_y \) in the isolated monomer. Since the particle within the Coulomb correlated model consists of a doubly occupied site, its deconfinement in the transverse direction implies that the effective Hubbard parameter in PDPA is reduced by the transverse bandwidth [7]. A \( k \)-space explanation is obtained from the band structure non-zero \( H_{ee} \) mixes in HOMO \(-1\) \( \rightarrow \) LUMO \(+1\) transition to the exciton wavefunction, which has a larger \( y \)-character than the HOMO \( \rightarrow \) LUMO transition, implying again a deconfinement along \( y \).

The behavior of the lowest absorption in PPA is similar to that of PDPA, with, however, a smaller reduction in the effective Hubbard \( U \). The energies of the optical transitions are discussed for many different chain lengths elsewhere [8]. In all cases, the optical gaps in PPA (PDPA) oligomers are smaller than those of polyenes (PPA oligomers) of the same length.

5. Two-photon states

We performed large scale multireference singles and doubles configuration interaction (MRSDCI) calculations

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**Fig. 3.** The contribution by the backbone chain atoms to the wavefunction at \( k_F \) as a function of \( t_{\perp} \) for PPA and PDPA.

**Table 1**

<table>
<thead>
<tr>
<th>( t_{\perp} )</th>
<th>( H_{ee} = 0 )</th>
<th>( H_{ee} \neq 0 ) (SCI)</th>
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<tr>
<td>( \mu_x )</td>
<td>( \mu_y )</td>
<td>( \mu_x )</td>
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*The results for an artificial trans-stilbene molecule (see text), oriented along the \( y \) axis, are included for comparison.*
on oligomers of PPA and PDPA, both without ($\delta = 0$) and with bond alternation ($\delta = 0.07$) to determine the relative ordering of the 2$A_g$ and 1$B_u$ states. The details of the calculation, along with the convergence behavior of different states, will be presented elsewhere \cite{8}. Our final MRSDCI results for oligomers of PPA and PDPA containing 6 backbone carbon atoms are summarized in Table 2.

From Table 2, the following trends emerge. For the PDPA oligomer, the 2$A_g$ and 1$B_u$ states are almost degenerate for $\delta = 0$. However, for $\delta = 0.07$, the 1$B_u$ state is significantly below the 2$A_g$. This, clearly, is in agreement with the efficient PL observed in PDPA. For PPA, without bond alternation, the 2$A_g$ is significantly lower in energy compared to 1$B_u$, while, with bond alternation, the two states are nearly degenerate, indicating an energy ordering in agreement with weak PL observed in the system. The 2$A_g$ energies of both PPA and PDPA oligomers, when compared to that of the six-site polyene, appear to be relatively unchanged. However, the 1$B_u$ of PPA and PDPA are significantly lower. The dominant effect of phenyl substitution is therefore lowering of the 1$B_u$ energy. As compared to PPA, the lowering of 1$B_u$ is stronger in PDPA, making it a more efficient emitter of light.

6. Conclusions

Site-substitution reduces both the effective bond alternation and the effective correlations. Such systems have smaller optical gaps than corresponding polyenes but are still emissive. Current PDPA’s have finite conjugation lengths \cite{4}. Synthesis of novel long-chain site-substituted emissive materials with optical gaps smaller than $t$-PA is currently being pursued.

Acknowledgements

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References


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<th>System</th>
<th>State</th>
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<tr>
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*Exact results for the six-site polyene are also included. $N_{ref}$ is the number of reference configurations necessary for energy convergence.*