Designing emissive conjugated polymers with small optical gaps: a step towards organic polymeric infrared lasers

Alok Shukla\textsuperscript{1,2} and Sumit Mazumdar\textsuperscript{1}

\textsuperscript{1}Department of Physics and The Optical Sciences Center, University of Arizona, Tucson, AZ 85721
\textsuperscript{2}Cooperative Excitation Project ERATO, Japan Science and Technology Corporation (JST)

We show that chemical modification of the trans-polyacetylene structure that involves substitution of the backbone hydrogen atoms with conjugated side groups, leads to reduction of the backbone bond alternation as well as screening of the effective Coulomb interaction. Consequently the optical gap of the substituted material is smaller than the parent polyene with the same backbone length, and the excited state ordering is conducive to efficient photoluminescence. The design of organic polymeric infrared lasers, in the ideal long chain limit, thereby becomes possible.

Much of the current experimental work on conjugated polymers centers around the strong photoluminescence (PL) observed in specific materials. A complete physical understanding of the structural characteristics necessary for luminescence is clearly desirable for designing materials with emission wavelengths that can vary over a wide range. Within existing theories, light emission should be restricted to systems with optical gaps larger than that of the nonemissive polymer trans-polyacetylene (t-PA). In the present Letter we show that suitable molecular engineering can screen the many-body Coulomb interactions, thereby lifting this restriction.

The distinction between nonluminescent and luminescent conjugated polymers is related to the Coulomb correlations between the π-electrons in these systems. Excited states of these centrosymmetric systems are either one-photon allowed and of $B_u$ symmetry, or two-photon allowed and of $A_g$ symmetry. A consequence of moderate Coulomb interactions is that the the $2A_g$ excited state occurs below the $1B_u$ state in linear polyenes and t-PA.[1,2] The optically pumped $1B_u$ state here rapidly decays to the $2A_g$ instead of to the ground state. Radiative transition from the $2A_g$ to the $1A_g$ ground state is forbidden, and polyenes and t-PA are therefore nonemissive. Strong PL in the common light emitting polymers, such as the poly(paraphenylenevinylene) (PPV) and poly(pseudobenzidinevinylene) (PPV), 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.[3] 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”. Excited state orderings of the effective linear chain are understood most simply within the dimerized Hubbard model

$$H = - \sum_{i} t (1 \pm \delta) (c_{i,\sigma}^\dagger c_{i+1,\sigma} + c_{i+1,\sigma}^\dagger c_{i,\sigma}) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

where $c_{i,\sigma}^\dagger$ creates a π electron of spin σ on carbon atom $i$, $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$, $t$ is the nearest neighbor hopping matrix element, and δ is the effective bond alternation parameter. For small δ, the $2A_g$ is a spin excitation that occurs below the charge excitation $1B_u$.[2,3] For large δ, the $2A_g$ acquires charge excitation character, and occurs above the $1B_u$.[3]

The prescription for obtaining light emission within existing theories is then to increase the effective δ. Since larger δ increases $E(1B_u)$, this prescription restricts light emission from polymers whose optical gaps are necessarily larger than that of t-PA. Whether or not it should be possible to design light emitting materials with smaller optical gaps, at least theoretically, is clearly an intriguing question. The necessary conditions for this are: (i) δ same or even smaller than in linear polyenes, and (ii) an effective Hubbard correlation parameter $U_{eff}$ that is also smaller than in the polyenes, such that $E(2A_g) > E(1B_u)$, in spite of smaller δ. In the present Letter, we show how both of these can be achieved through “site-substitution”, in which individual CH groups of the parent polyene structure (as opposed to pairs of them) are modified.

Although our work is general, for clear illustration of the principle, we focus here on the recently synthesized poly(diphenylacetylene) (PDPA) (see inset Fig. 1) class of conjugated polymers.[3] The current materials have short conjugation lengths (five to seven backbone double bonds), but the observation of PL quantum efficiency > 50% in several PDPA oligomers is nevertheless counterintuitive, given their polyene backbones. The estimated conjugation lengths are large enough that in the corresponding polyenes $E(1B_u) > E(2A_g)$.[3] Since the Hubbard U is an atomic property, naively one would have expected the energy ordering in PDPA to be the same as in the corresponding polyene, and therefore weak PL. An alternate naive interpretation, viz., the relative location of the $2A_g$ in PDPA will be somewhere in between...
that of trans-stilbene (the unit cell of PDPA) and linear polyenes, is incorrect, since this interpretation implies that the absolute 1B$_a$ energy in PDPA is higher than that in the polyene with the same chain length and lower than that in trans-stilbene. However, both experimentally and theoretically (see below), the 1B$_a$ in PDPA occurs below that of the corresponding polyene. We show here that the correct interpretation involves a reduction in the effective Coulomb correlation.

We consider the Pariser-Parr-Pople Hamiltonian for PDPA, supplemented by the Su-Schrieffer-Heeger (SSH) electron-phonon (e-ph) coupling [4]

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

\[
H_1 = -\sum_{(k,k'),M} (t_0 - \alpha \Delta_k M) B_{k,k';M,M+1} + \frac{1}{2} K \sum_{k,M} \Delta_k^2 M, \tag{2a}
\]

\[
H_2 = -t_0 \sum_{(\mu,\nu),M} B_{\mu,\nu;M,M}, \tag{2b}
\]

\[
H_3 = -t_\perp \sum_{M} B_{k,\mu;M,M}, \tag{2c}
\]

\[
H_{ee} = U \sum_{i,M} n_{i,M}^+ n_{i,M} + \frac{1}{2} \sum_{i \neq j,M,N} V_{i,j,M,N}(n_{i,M} - 1)(n_{j,N} - 1), \tag{2d}
\]

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, etc. $B_{k,k';M,M+1}$ describes the phonon oscillations 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. Within Eq. (2) this affects only $V_{i,j,M,N}$ and $t_\perp$.

In the following we first show that bond alternation in PDPA is smaller than that in t-PA, thereby proving that the observed PL is not due to enhanced bond alternation. We then present a single configuration interaction (SCI) theory of the 1B$_a$ that provides the mechanism of the reduction of $U_{ee}$. Finally, we present many-body calculations of excited state orderings, and of a pair correlation function that directly demonstrates reduced $U_{ee}$ in PDPA.

We compare the bond-alternations in t-PA and PDPA for $H_{ee} = 0$ within Eq. (2) and postpone the justification of ignoring $H_{ee}$. We have chosen $t_0 = 2.4$ eV, $\alpha = 4.1$ eV/A and $K = 21$ eV/A$^2$. It is difficult to estimate $t_\perp$, but it is smaller than the usual “single” bond. In Fig. 5 we show our calculated bond alternation $u_0$ [$u_0 = (-1)^n u_0$ in Eq. (2)] for perfectly dimerized PDPA periodic rings with chain lengths of N backbone carbon atoms, for $t_\perp = 0, 1.4$ eV and 2.0 eV. The calculated $u_0$ decreases rapidly with increasing $t_\perp$.

An a posteriori justification of the neglect of $H_{ee}$ in the above calculations can now be given. In previous studies of Coulomb effects on bond alternation in the infinite polyene [9], it was shown that for all parametrizations of the Pariser-Parr-Pople Hamiltonian bond alternation is enhanced compared to the SSH prediction. More importantly, these parameters belong in a regime where further increasing of Coulomb interactions enhances the bond alternation even more. Since we show below that the effective correlations in PDPA are smaller than that in t-PA, inclusion of $H_{ee}$ would lead to even smaller bond alternation in PDPA than in t-PA.

A preliminary understanding of the many-body effects in PDPA can be obtained by a detailed examination of the 1B$_a$ state alone. We calculate the transition dipole couplings between the ground state and the 1B$_a$, for the five double-bond oligomer. Our calculations are for both zero and nonzero $H_{ee}$. We chose rigid bond alternation $\alpha u_0/t_0 = \delta = 0.07$, the same as in linear polyenes. The Coulomb parameters were chosen from the Ohno relationship [11],

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

where $U = 11.13$ eV and $R_{i,j,M,N}$ is the separation in A. between carbon atoms $i$ on unit M and $j$ on unit N. The backbone polyene bond lengths are assumed to be 1.45 and 1.35 A. in length, as in t-PA, and all phenyl bond lengths are taken to be 1.4 A. The bond between the backbone atoms and the phenyl groups is taken to be a true single bond with length 1.54 A. 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 nonzero $H_{ee}$ calculations were done within the single configuration interaction (SCI) approximation, which is known to give a reasonable description of the 1B$_a$. We define the backbone axis as the x-axis and the transverse direction as the y-axis. The results of our calculations of transition dipole couplings $\mu_x$ and $\mu_y$ along x- and y-directions are summarized in Table I for several $t_\perp$. We have included in Table I the calculated results for an artificial trans-stilbene monomer in which the hopping integral between the ethylenic linkage and the phenyl groups is 1.4 eV (the y-axis corresponds to the long molecular axis of trans-stilbene).
The PDPA transition dipole couplings in Table I have significant y-contribution. For all $t_{\perp}$, $H_{ee}$ strongly decreases $\mu_x$, a well-known result in the case of linear polyenes: the transition dipole moment is a direct measure of the particle-hole separation in the 1B$_u$, and since $H_{ee}$ leads to particle-hole confinement and exciton formation, the reduction in $\mu_x$ is expected. More interesting conclusions emerge upon comparisons of the different $t_{\perp}$ cases. For nonzero $H_{ee}$, the particle-hole confinement in the x-direction is significantly enhanced by $t_{\perp}$, as indicated by the strong reduction in $\mu_x$ as $t_{\perp}$ is increased from zero. Simultaneously, there is an effective “deconfinement” in the y-direction, as evidenced by the increase in $\mu_y$. This deconfinement is large enough that $\mu_y$ is larger for the interacting Hamiltonian than for the noninteracting model for all nonzero $t_{\perp}$, indicating that the confinement along the x-axis and the deconfinement along the y-axis are synergic. The synergic nature of the deconfinement is further confirmed upon comparison with the transition dipole moments of the trans-stilbene monomer: $H_{ee}$ suppresses $\mu_x$ in the isolated monomer, but enhances it in PDPA. Physically, as the exciton is squeezed along the x-direction, it spreads out in the y-direction.

The deconfinement along the transverse direction is a signature of reduced Coulomb effects in PDPA. In any mapping of the excited states of PDPA to that of an effective linear chain, a composite site is to be constructed from each carbon atom on the polyene backbone and the carbon atoms of the phenyl group. For moderate $U$ the particle and the hole correspond to a double occupancy and a vacancy in the 1/2-filled band, which in PDPA are delocalized over the phenyl segments. The synergic deconfinement then indicates that (i) the on-site repulsion $U_{eff}$ on a composite site of an effective linear chain is of the form $U - W_{\perp}$, and (ii) $W_{\perp}$ is large.

We confirm this conjecture by direct evaluations of $E(2A_g)$ and $E(1B_u)$. Electron correlation calculations considerably more sophisticated than the SCI are required for the determination of the energy of the highly correlated 2A$_g$ state. Such calculations are not possible for the PDPA oligomer with five double bonds. We therefore compare the PDPA oligomer with four backbone carbons and butadiene within the rigid band approximation for Eq. (2). Such a calculation is representative, since any reduction in $U_{eff}$ occurs at every composite site of longer oligomers. Even for this short oligomer with twenty eight carbon atoms, however, it is not possible to perform full CI (FCI) calculations retaining all the orbitals. Instead of making further questionable approximations we perform three different FCI calculations, retaining only a limited set of molecular orbitals (MOs) in each case. The three calculations, taken together, provide an unambiguous picture.

In Figs. 3 we have shown the bonding MOs of the PDPA oligomer with four backbone carbons, for $\delta = 0$, and for $t_{\perp} = 0$ and 1.4 eV. For nonzero $t_{\perp}$ there is considerable mixing between the backbone and phenyl MOs, but nevertheless, it is possible to identify the two chain-derived MOs from the large separations of their one-electron energies from those of the benzene-derived MOs, as well as from their large contributions to the electron densities on the backbone carbon atoms (1.34 and 1.12). There exist only three other bonding MOs whose contributions to the backbone carbon electron densities (0.30, 0.50 and 0.54) are substantial. Our first set of FCI calculations (hereafter set 1) involve all ten bonding and antibonding MOs with strong chain components. A second set (set 2) were done with the two chain-derived bonding MOs and the four highest delocalized benzene-derived bonding MOs (only two of which contribute to chain carbon electron densities), and the corresponding six antibonding MOs. Set 3 calculations involved the two chain-like MOs and the four localized benzene MOs, and the corresponding antibonding MOs.

The results of our calculations for Ohno parameters are shown in Table I where we have included the exact results for butadiene. Only for $\delta = 0$ within set 1 is the 2A$_g$ in PDPA below the 1B$_u$, while for all other cases $E(2A_g) > E(1B_u)$, in contrast to butadiene, where $E(2A_g)$ is substantially smaller than $E(1B_u)$. We emphasize that the MOs retained within sets 1, 2 and 3, with the exclusion of the chain-derived MOs, are mutually exclusive. Therefore, in the absence of peculiar and unexpected interference effects, standard CI concepts predict that a complete calculation performed with all the MOs would also find the 2A$_g$ above the 1B$_u$. Although it may be argued that in the longer PDPA oligomers the relative $E(2A_g)$ is smaller, we emphasize that the calculations in Table I are for a rather small $t_{\perp}$ (1.4 eV), and the realistic $t_{\perp}$ can be larger, enhancing $E(2A_g)$. The cosine dependence of hopping integrals on the rotational angle that is often assumed predicts $t_{\perp} = 1.9$ eV for a rotational angle of 30°. The trend indicated in Table I is valid for all chain lengths and $\delta$.

Finally, we substantiate our argument for a reduced $U_{eff}$ in PDPA from calculations of the ground state pair correlation function $g = (1/N)\sum_i\langle n_i, n_{i+1} \rangle$ ($N$ total number of sites) Larger $g$ implies smaller $U_{eff}$ (for the half-filled band, $g = 0.25$ at $U = 0$, while $g = 0.47$ for $U \to \infty$). In order to demonstrate that the reduced $U_{eff}$ is due to deconfinement of the double occupancy, and not due to the additional inter-site Coulomb interactions in PDPA, these calculations were done for $V_{i,j,M,N} = 0$. The pair-correlation functions were calculated from the relationship $g = (1/N)\langle 0 \parallel H \parallel 0 \rangle / \langle 0 \parallel U \parallel 0 \rangle$. For $U = 2t_0$, $g = 0.152$ for butadiene and 0.18 for benzene, while for PDPA this quantity is 0.237 within the set 1 calculation and 0.207 within set 2 (set 3 would give even larger $g$, from the results of Table I), suggesting that the exact $g$ for PDPA is in between 0.207 and 0.237. Larger $g$ in PDPA than that of both the constituents is due to the synergic nature
of the deconfinement discussed above.

Smaller $\delta$ and $U_{\text{eff}}$ in PDPA, compared to t-PA, necessarily implies smaller optical gap. Within one-electron theory, and with SSH parameters, the optical gap in PDPA in the long chain limit is 0.9 (0.56) eV for $t_{\perp} = 1.4$ (2.0) eV, compared to 1.4 eV for t-PA. For nonzero $H_{ce}$, we have calculated E(1B$_{u}$) within SCI for linear polyenes and PDPA oligomers up to eight double bonds, with fixed $\delta$. For all chain lengths the PDPA optical gap is smaller than the polyene with the same number of carbon atoms. For example, at five (seven) double bonds, our calculated gap for the polyene is 3.8 (3.4) eV, close to the experimental value. The calculated gap in PDPA with five (seven) double bonds and $t_{\perp} = 1.4$ eV is 3.2 (2.9) eV. With self-consistent (and therefore smaller) $\delta$, the gap in PDPA will get even smaller. Moreover, within our theory, poly(1-alkyl,2-phenylacetylene) (PAPA) with conjugated side groups on only alternate backbone carbons will have larger $\delta$ and $U_{\text{eff}}$. Significantly, optical gaps in PAPA oligomers are uniformly larger than those in PDPA. The reduction in $U_{\text{eff}}$ found here will occur in any system modified by site-substitution (or suitable combination of site and bond-substitution). While the current PDPA oligomers emit in the visible due to short conjugation lengths, it is then possible conceptually to have conjugated polymers emitting in the infrared. The synthetic challenge would be to obtain polyene derivatives which have conjugated side groups but which still possess long rigid segments.

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TABLE I. The $x$ and $y$ components of $1A_g \rightarrow 1B_u$ transition dipole moments $\mu_x$ and $\mu_y$ (in Å), as a function of $t_\perp$, for a PDPA oligomer with five double bonds. The results for an artificial trans-stilbene molecule (see text), oriented as in the inset of Fig. 1 are included for comparison.

| $t_\perp$ | $H_{ee} = 0$ | $H_{ee} \neq 0$ (SCI) |
|----------|---------------|------------------------|
|          | $\mu_x$  | $\mu_y$  | $\mu_x$  | $\mu_y$  |
| 0.0      | 2.25     | 0.35     | 1.74     | 0.50     |
| 0.2      | 2.25     | 0.37     | 1.43     | 0.80     |
| 1.4      | 2.17     | 0.98     | 1.39     | 1.08     |
| “trans-stilbene” | 0.34     | 1.08     | 0.19     | 0.59     |

TABLE II. Correlated $2A_g$ and $1B_u$ energies for PDPA with four backbone carbons and butadiene. Sets 1, 2 and 3 refer to three different calculations (see text).

| System     | State | Energy Gaps (eV) |
|------------|-------|------------------|
| PDPA       | $2A_g$ | $\delta = 0.0$ | $\delta = 0.07$ |
|            |       | Set 1 | Set 2 | Set 3 | Set 1 | Set 2 | Set 3 |
|            | $1B_u$ | 4.49  | 4.13  | 4.30  | 4.81  | 4.46  | 4.72  |
| butadiene  | $2A_g$ | 4.66  | 5.35  |       |       |       |       |
|            | $1B_u$ | 5.49  | 5.80  |       |       |       |       |